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Exploring *N*-Centered Umpolung Reactivity in Photoredox-Catalyzed Amidation with *α*-Iminoester

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Supporting Information

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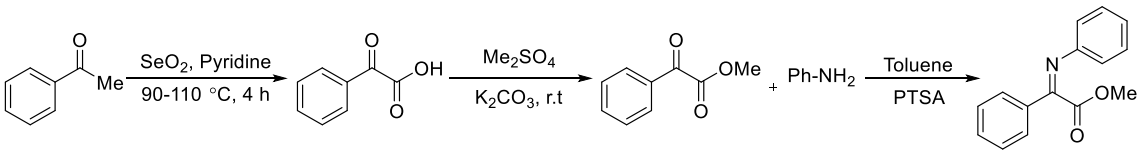
1. General information

Main Reactions were performed in oven-dried vial under argon condition with magnetic stirrer and 456 nm Kessil light as the source of light. Solvents and liquid chemicals were transferred by using syringes and micropipette. Commercially available technical grade solvents were dried as per standard procedure for reaction solvent and simply distilled for extraction or chromatography (ethyl acetate, hexane and dichloromethane) prior to use. Chemicals and catalysts were purchased from Sigma-Aldrich, Alfa-Aesar, TCI, GLR Innovations, BLDpharm and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) performed on silica gel 60 F254 plates from Merck. Flash column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from Merck using the indicated solvents. ^{1}H, ^{13}C, and ^{19}F NMR spectra recorded in $CDCl_3$ unless otherwise stated on JEOL JNM ECS–400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: δ = 7.26 ppm for ^{1}H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR. Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. All the HRMS data were recorded on XEVO G2–XS QTOF.

2. Preparation of starting materials

Starting Arylglyoxylic acids were synthesized from corresponding acetophenone following standard protocol.[1] For esterification the following standard protocol was used.[2] For the Iminoester, a known protocol was used.[3,4] *N*-Benzoyl *α*-imino esters (2w) prepared by following the literature procedure.[5] *N*-Sulfonyl *α*-imino esters (2x) prepared by following the literature procedure.[6] Aniline, acetophenone, were purchased directly from Sigma-Aldrich and BLDpharm.



2.1 General procedure 1 (GP-1)

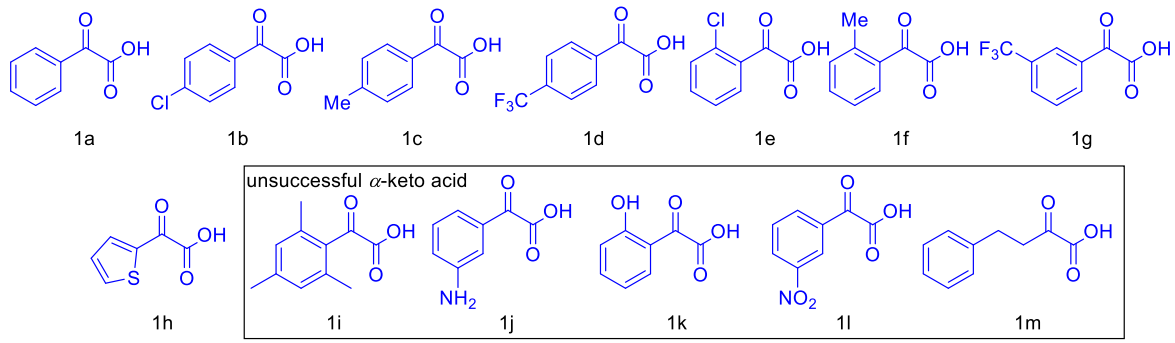
An oven dried sealed tube was charged with Selenium Dioxide (1.5 equiv), substituted aryl ketone (1 equiv), pyridine (2 M) was added to it. This mixture was heated to about 120ºC for 4 hours forming substituted 2-Oxo-2-phenylacetic acid.

The acid formed from the above step was esterified by treating with dimethyl sulphate (DMS) in presence of K_2CO_3 taking DMSO as solvent. A 100 ml round bottom flask was charged with acid (1 equiv), K_2CO_3 (1.4 equiv). dimethyl sulphoxide (5 ml) was added to make a solution. This resulting solution was stirred with dropwise addition of Dimethyl sulfate (1.2 equiv.) After the addition was complete the mixture was allowed to stir for 4 h at room temperature to generate the corresponding ester. Subsequently, work-up was performed by transferring the reaction mixture to a separating funnel mixed with ethyl acetate. The resulting organic layer was washed 3 times with dilute K_2CO_3 solution and once with brine. After drying with Na_2SO_4 and evaporating under reduced pressure the corresponding ester of the acid was obtained in significant yield.

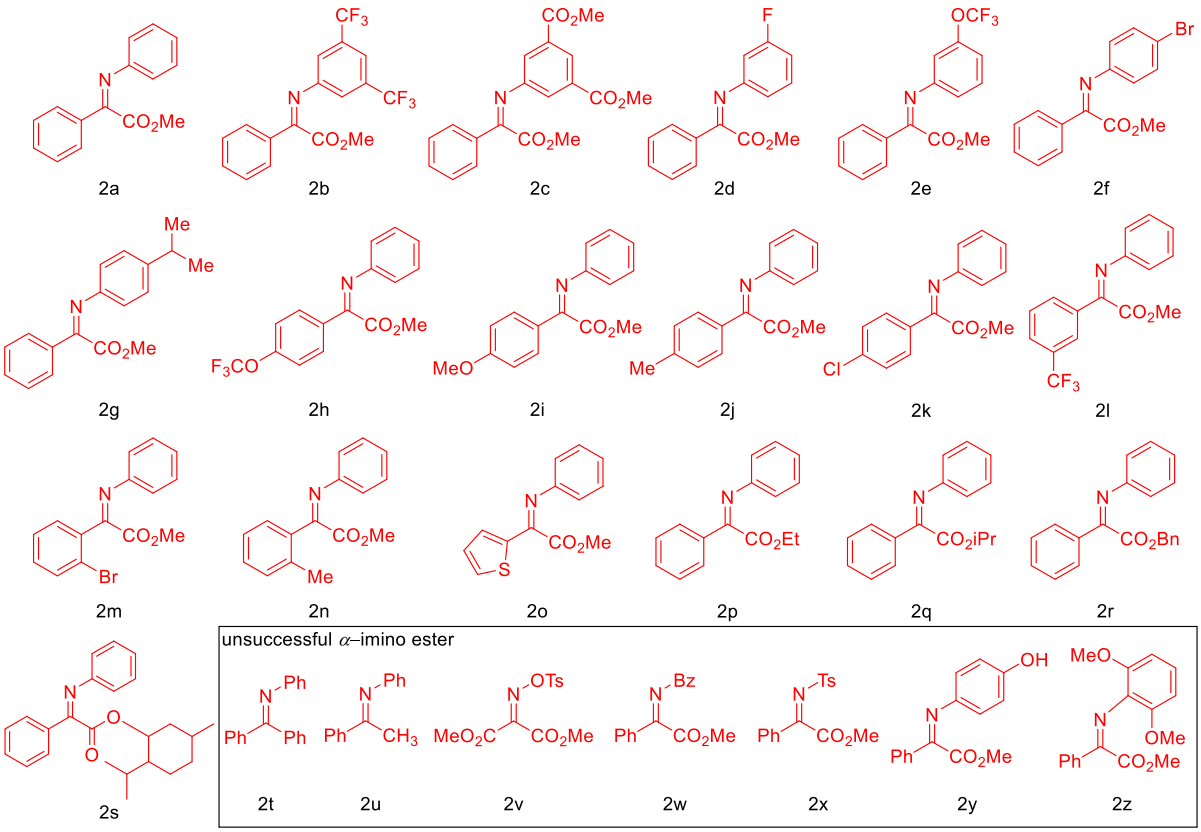
The ester thus formed was treated with aniline (2 equiv), *p*-Toluenesulfonic Acid (0.07 equiv), Toluene (2 M), and refluxed at 120ºC. Molecular sieves were also added to absorb any water formed during the reaction. Iminoester formed, was quickly filtered using sintered funnel with DCM (30 mL) and the organic layer was collected and evaporated under reduced pressure. The product of high analytical purity was achieved through column chromatography on silica gel.

3. List of starting materials

3.1 List of successful and unsuccessful *α*–keto acid for amidation

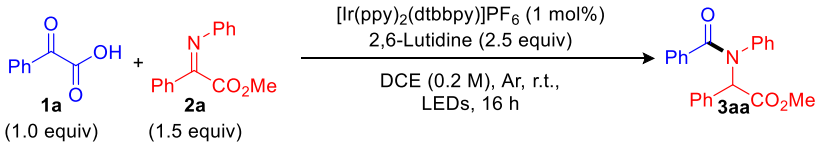


3.2 List of successful and unsuccessful *α*–imino ester for amidation



4. Optimization of reaction conditions

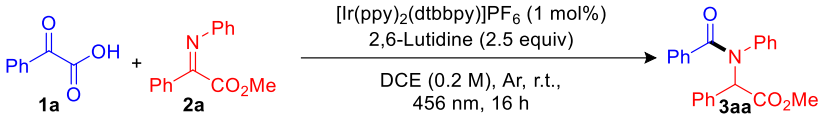
Table S1. Optimization of Light



Entry	Light Source	% Yield[a]
1	455 nm (Yarev)	30
2	450 nm (Hepatochem)	30
3	456 nm (Kessil)	41(40)[b]
4	427 nm (Kessil)	28

[a] Reaction scale 0.1 mmol, yields reported are the NMR yield using with 1,3,5–trimethoxybenzene as internal standard. [b] isolated yield

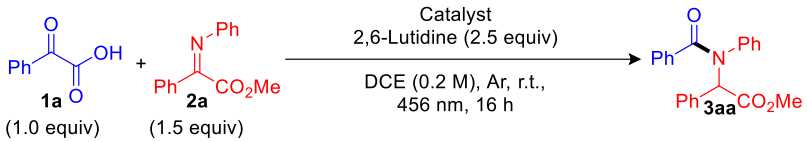
Table S2. Optimization of equivalence



Entry	Acid (equiv)	Imine (equiv)	% Yield[a]
1	1	1.5	41(40)[b]
2	1	2	24
3	1	1	18
4	2	1	28
5	1	2.5	33

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard. [b] isolated yield.

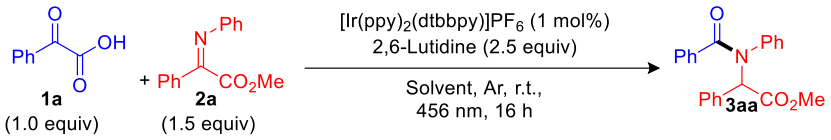
Table S3. Screening of catalyst and catalyst loading



Entry	Catalyst	Catalyst loading (mol %)	% Yield[a]
1	$[Ir(ppy)_2(dtbbpy)]PF_6$	1	41(40)[b]
2	$[Ir(ppy)_2(dtbbpy)]PF_6$	2	27
3	4CzIPN	2	11
4	4CzIPN	5	13
5	*fac*-$Ir(ppy)_3$	1	2
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	2	35
7	Eosin Y	5	0
8	$Ru(bpy)_3(PF_6)$	2	0
9	Mes-Acr^+	10	8

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard. [b] isolated yield.

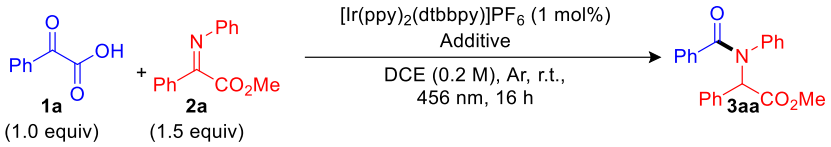
Table S4. Screening of solvent



Entry	Solvent (M)	% Yield[a]
1	DCE (0.1)	21
2	DCE (0.2)	41(40)[b]
3	DCE (0.4)	11
4	1,4-Dioxane (0.2)	18
5	DMSO (0.2)	0
6	CH_3CN (0.2)	2
7	DME (0.2)	0
8	CH_3COCH_3 (0.2)	22
9	THF (0.2)	21
10	DMF (0.2)	0
11	EtOAc (0.2)	0
12	EtOH (0.2)	0
13	HFIP (0.2)	0
14	Toluene (0.2)	0
15	DCM (0.2)	24
16	1,2-DFB (0.2)	18
17	1,2-DCB (0.2)	12
18	Chloroform (0.2)	0
19	TFE (0.2)	0

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard. [b] isolated yield. Solvent in Molarity (M).

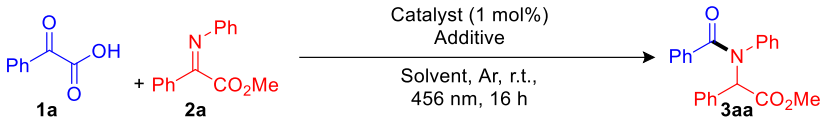
Table S5. Screening of additive and additive loading



Entry	Additive	Additive Loading (equiv)	% Yield[a]
1	2,6-Lutidine	0.5	18
2	2,6-Lutidine	1	9
3	2,6-Lutidine	1.5	20
4	2,6-Lutidine	2	19
5	2,6-Lutidine	2.5	41(40)[b]
6	K_2CO_3	2.5	8
7	K_2HPO_4	2.5	0
8	Na_2HPO_4	2.5	6
9	Cs_2CO_3	2.5	5
10	DBU	2.5	0
11	DIPEA	2.5	0
12	Pyridine	2.5	0
13	DMAP	2.5	0
14	NaOAc	2.5	0
15	TMP	2.5	0
16	PMP	2.5	0
17	Diisopropylamine	2.5	0
18	Et_3N	2.5	0
19	$NaNO_2$	2.5	0
20	NaOH	2.5	0
21	DABCO	2.5	0
22	Li_2CO_3	2.5	10
23	Morpholine	2.5	0

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard. [b] isolated yield.

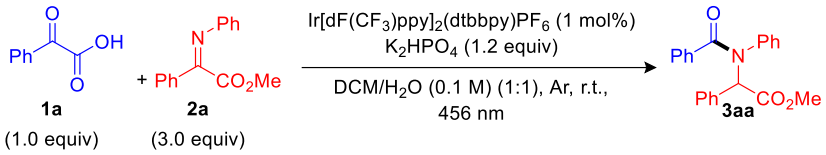
Table S6. Miscellaneous optimization



Entry	Solvent	Additive (equiv)	Catalyst (1 mol%)	1a:2a (equiv)	% Yield[a]
1	DCE (0.2 M)	2,6-Lutidine (2.5)	$[Ir(ppy)_2(dtbbpy)]PF_6$	1:1.5	41(40)[b]
2	DCE (0.2 M)	2,6-Lutidine (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:1.5	35
3	DCE (0.2 M)	K_2HPO_4 (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:1.5	10
4	DCE (0.1 M)	K_2HPO_4 (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:1.5	17
5	DCE/H_2O (0.1 M) (4:1)	K_2HPO_4 (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:1.5	30
6	DCE/H_2O (0.1 M) (2:1)	K_2HPO_4 (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:1.5	40
7	DCE/H_2O (0.1 M) (1:1)	K_2HPO_4 (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:1.5	42
8	DCE/H_2O (0.1 M) (1:1)	K_2HPO_4 (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:2.5	45
9	DCE/H_2O (0.1 M) (1:1)	K_2HPO_4 (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:3	60
10	DCM/H_2O (0.1 M) (1:1)	K_2HPO_4 (2.5)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:3	62
11	DCM/H_2O (0.1 M) (1:1)	K_2HPO_4 (2.0)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:3	65
12	DCM/H_2O (0.1 M) (1:1)	K_2HPO_4 (1.2)	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1:3	67

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard. [b] isolated yield. Solvent in Molarity (M).

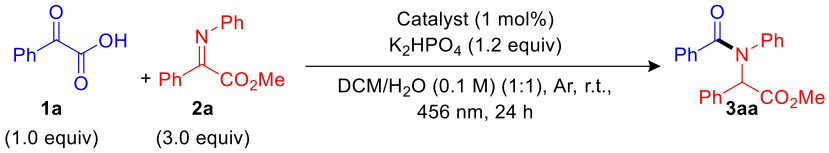
Table S7. Screening of reaction time



Entry	Time (h)	% Yield[a]
1	16	67
2	24	73
3	48	80
4	72	90 (87)[b]

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard. [b] isolated yield. Time in hour (h).

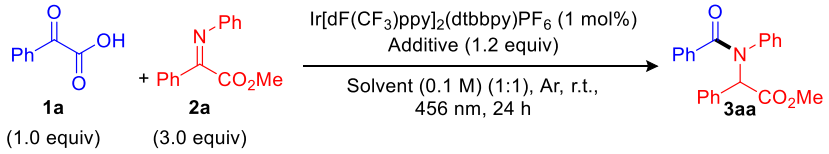
Table S8. Screening of catalyst



Entry	Catalyst	% Yield[a]
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	73
2	$[Ir(ppy)_2(dtbbpy)]PF_6$	0
3	Eosin Y	0
4	4CzIPN	0
5	*fac*-$Ir(ppy)_3$	0

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard.

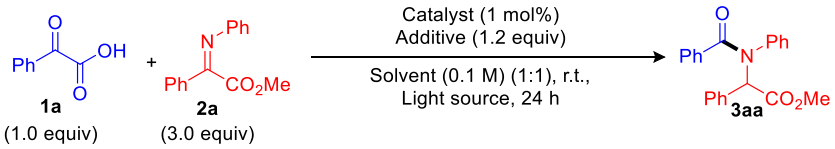
Table S9. Screening of solvent and Additive



Entry	Additive	Solvent	% Yield[a]
1	K_2HPO_4	DCM/H_2O	73
2	K_2HPO_4	DCE/H_2O	60
3	K_2HPO_4	ACN/H_2O	0
4	2,6-Lutidine	DCM/H_2O	20

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard. [b] isolated yield. Solvent in Molarity (M)

Table S10. Control experiment

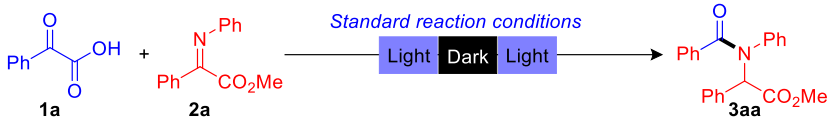


Entry	Catalyst	Solvent	Light (nm)	Additive	% Yield[a]
1	–	DCM/H_2O	456	K_2HPO_4	0
2	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	DCM/H_2O	456	–	0
3	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	DCM/H_2O	–	K_2HPO_4	0
4	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	DCM	456	K_2HPO_4	15
5	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	DCE	456	K_2HPO_4	17
6	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	H_2O	456	K_2HPO_4	27
7	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	Open air	456	K_2HPO_4	56[c]
8	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	O_2	456	K_2HPO_4	0

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard. [b] isolated yield. [c] reaction time 72 h

5. Mechanistic studies

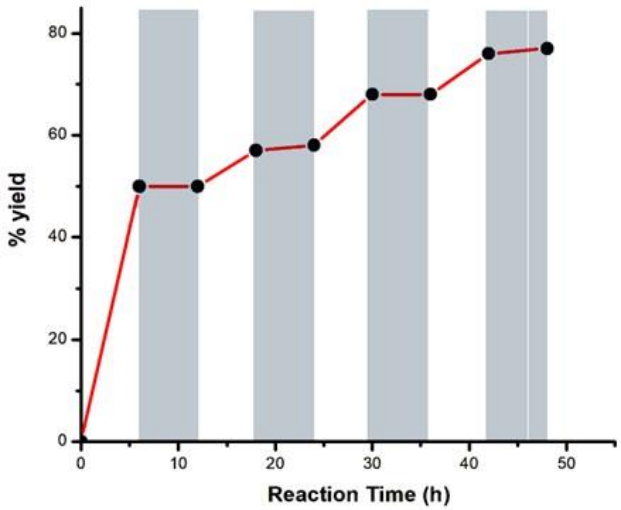
5.1 Light-Dark experiment



2-oxo-2-phenylacetic acid **(1a)** (15 mg, 0.1 mmol, 1.0 equiv), (Z)-2-(2-methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium **(2a)** (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv., 0.12 mmol), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.2 mg, 0.001 mmol, 1 mol%) were added in a pre-dried 15 mL glass vial under argon atmosphere. 1 ml DCM/H_2O (1:1) (0.1 M) was added and the reaction mixture was exposed to a 36-watt Kessil blue LED lamp emitting light at 456 nm. Following each 6-hour period, the reaction alternated between being placed in light and darkness. The progress of the reaction was checked using TLC and correspondingly NMR yield was determined using 1,3,5 trimethoxy benzene as standard.

Entry	Time (h)	Light Source	% Yield[a]
1	6	on	50
2	12	off	50
3	18	on	57
4	24	off	58
5	30	on	68
6	36	off	68
7	42	on	77
8	48	off	78

[a] Reaction scale 0.1 mmol, Yields reported are the NMR yield using with 1,3,5-trimethoxybenzene as internal standard.



5.2 Determination of Quantum yield:

(A) Determination of light intensity of Blue LED:

The determination of photon flux was performed by the use of standard ferrioxalate actinometry.[7,8] A 0.15 M solution of ferrioxalate was prepared by the addition of 737 mg of potassium ferrioxalate hydrate in 10 ml of 0.05 M H_2SO_4. Thereafter, a solution of phenanthroline was made by adding 25 mg of phenanthroline and 5.63 g of sodium acetate in 25 mL of 0.5 M H_2SO_4. Both solutions were kept in a dark environment. Next, for the determination of photon flux, 1.0 mL of the ferrioxalate solution Both a cuvette and irradiated for 60.0 seconds at λ = 456 nm placing 8 cm away from 36 W Kessil blue LED lamp. After irradiation, 0.175 mL of the phenanthroline solution was added to the cuvette. The solution was left for 1 h to permit the ferrous ions to completely coordinate to the phenanthroline. The solution gave an absorbance at 510 nm which was recorded. The same was prepared but this time without irradiation and its absorbance was determined at 510 nm. Conversion was calculated using eq. **1**

$$\text{mol of } Fe^{2+} = \frac{\nu.\Delta A}{\varepsilon.\, l} \quad \ldots\ldots\ldots\ldots\ldots\ldots \mathbf{1}$$

Where v stands for total volume (0.001175 L) of the solution after addition of the 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}).

$$\text{mol of } Fe^{2+} = \frac{0.001175L.(0.712-0.123)}{1\,cm.\,11100\;L.cm^{-1}.mol^{-1}}$$

$$= 6.238 \times 10^{-8}$$

The photon flux can be calculated using eq **2**.

$$\text{Photon Flux} = \frac{mol\;Fe^{2+}}{\Phi.\,t.\,f} \quad \ldots\ldots\ldots\ldots\ldots\ldots \mathbf{2}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 456 nm), t is the time (60 s), and f is the fraction of light absorbed at λ = 456 nm, f = 1.000 –10^{-A}.

Calculated f = $1.000-10^{-A} = 1.000-10^{-0.712} = 0.806$

$$\text{Photon Flux} = \frac{6.238\times10^{-8}\;mol}{1.01\times 60\text{s}\times 0.806}$$

$$= 1.27\times10^{-9}\;Einstein.\,S^{-1}$$

(B) Quantum yield calculation 1:

An oven-dried glass vial was charged with a magnetic stir bar, 2-Oxo-2-phenylacetic acid **(1a)** (15 mg, 0.1 mmol, 1.0 equiv), (Z)-2-(2-methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium **(2a)** (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv. , 0.12 mmol), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 catalyst (1.2 mg, 0.001 mmol, 0.01 equiv), DCM/H_2O (1:1) (0.1 M) were added to the mixture under argon atmosphere. The vial was maintained for 6 h at room temperature under 456 nm blue LED with constant stirring for 6 h. The reaction mixture containing DCM was evaporated at reduced pressure and thereafter work up of the reaction mixture was performed using ethyl acetate, and the resulting organic phases was allowed to evaporate under reduced pressure. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (5–10%) solution of petroleum ether and ethyl acetate as the elution solvents. The product (**3aa**) was confirmed by NMR. The product recorded a yield of 50% (4.99×10^{-5} mol).

The Quantum yield was calculated as follows:

$$\phi = \frac{mol\;product}{flux.\,t.\,f}$$

Where, flux is the photon flux determined by ferrioxalate actinometry (1.27 × 10^{-9} Einstein/s), t is the time (21600 s), and f (> 0.999) is the fraction of light absorbed by Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 at 456 nm under the reaction condition mentioned above.

$$\phi = \frac{4.99 \times 10^{-5}}{1.27 \times 10^{-9} \times 21600 \times 1}$$

$$= 1.819$$

(C) Quantum yield calculation 2:

An oven-dried glass vial was charged with a magnetic stir bar, 2-Oxo-2-phenylacetic acid **(1a)** (15 mg, 0.1 mmol, 1.0 equiv), (methyl (E)-2-(phenylimino)-2-(thiophen-2-yl)acetate (**2o**) (74 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv. , 0.12 mmol), Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 catalyst (1.2 mg, 0.001 mmol, 0.01 equiv), DCM/H_2O (1:1) (0.1 M) were added to the mixture under argon atmosphere. The vial was maintained for 6 h at room temperature under 456 nm blue LED with constant stirring for 6 h. The reaction mixture containing DCM was evaporated at reduced pressure and thereafter work up of the reaction mixture was performed using ethyl acetate, and the resulting organic phases was allowed to evaporate under reduced pressure. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (5–10%) solution of petroleum ether and ethyl acetate as the elution solvents. The product (**3ao**) was confirmed by NMR. The product recorded a yield of 58% (5.6×10^{-5} mol).

The Quantum yield was calculated as follows:

$$\phi = \frac{mol\ product}{flux.\ t.\ f}$$

Where, flux is the photon flux determined by ferrioxalate actinometry (1.27 × 10^{-9} Einstein/s), t is the time (21600 s), and f (> 0.999) is the fraction of light absorbed by Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 at 456 nm under the reaction condition mentioned above.

$$\phi = \frac{5.6 \times 10^{-5}}{1.27 \times 10^{-9} \times 21600 \times 1}$$

$$= 2.0$$

(D) Quantum yield calculation 3:

An oven-dried glass vial was charged with a magnetic stir bar, 2-(2-chlorophenyl)-2-oxoacetic acid (**1e**) (18 mg, 0.1 mmol, 1.0 equiv), (Z)-2-(2-methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium **(2a)** (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv. , 0.12 mmol), Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 catalyst (1.2 mg, 0.001 mmol, 0.01 equiv), DCM/H_2O (1:1) (0.1 M) were added to the mixture under argon atmosphere. The vial was maintained for 6 h at room temperature under 456 nm blue LED with constant stirring for 6 h. The reaction mixture containing DCM was evaporated at reduced pressure and thereafter work up of the reaction mixture was performed using ethyl acetate, and the resulting organic phases was allowed to evaporate under reduced pressure. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (5–10%) solution of petroleum ether and ethyl acetate as the elution solvents. The product (**3ea**) was confirmed by NMR. The product recorded a yield of 29% (2.8×10^{-5} mol).

The Quantum yield was calculated as follows:

$$\phi = \frac{mol\ product}{flux.\ t.\ f}$$

Where, flux is the photon flux determined by ferrioxalate actinometry (1.27×10^{-9} Einstein/s), t is the time (21600 s), and f (> 0.999) is the fraction of light absorbed by Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 at 456 nm under the reaction condition mentioned above.

$$\phi = \frac{2.8 \times 10^{-5}}{1.27 \times 10^{-9} \times 21600 \times 1}$$

$$= 1.0$$

5.3 Luminescence Quenching experiments:

(A) Preparation of the stock solution:

A 0.01 mM solution of catalyst Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 was prepared by dissolving 2.8 mg of catalyst in 500 µL of DCM/H2O. This freshly prepared solutions were used for the measurement of spectroscopic data. The required amount (10 µL) was taken using a micropipette from the mother solution as an aliquot and it was diluted further by dissolving in 1 mL of DCM/H_2O (1:1) placed in the cuvette. In a similar way 1 mL 0.01 mM solution of 2-oxo-2-Phenyl acetic acid **(1a)**, (Z)-2-(2-

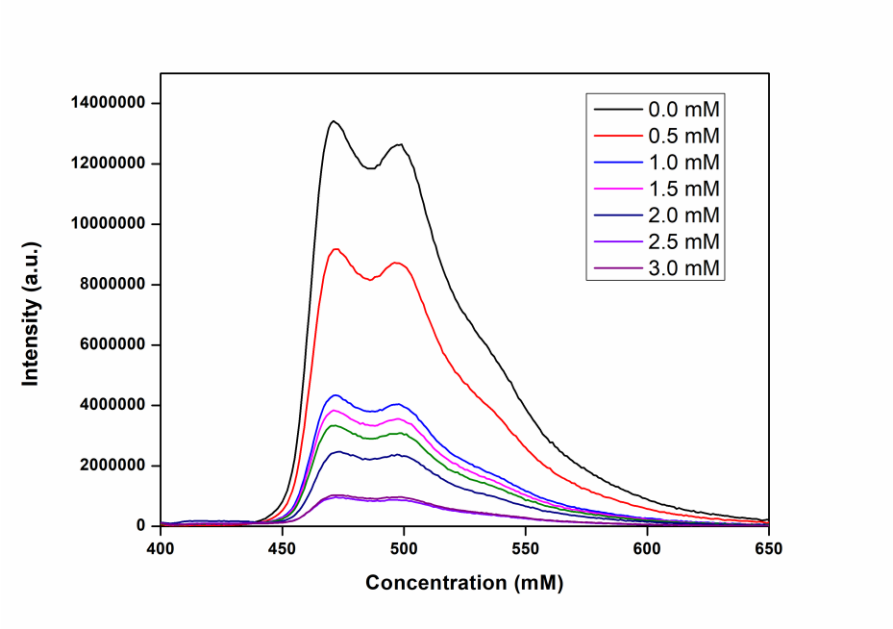
methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium **(2a)** and K_2HPO_4 were prepared by dissolving the required amount of each substrate in DCM/H_2O. These freshly prepared solutions were used for the quenching experiment.

(B) Quenching studies:

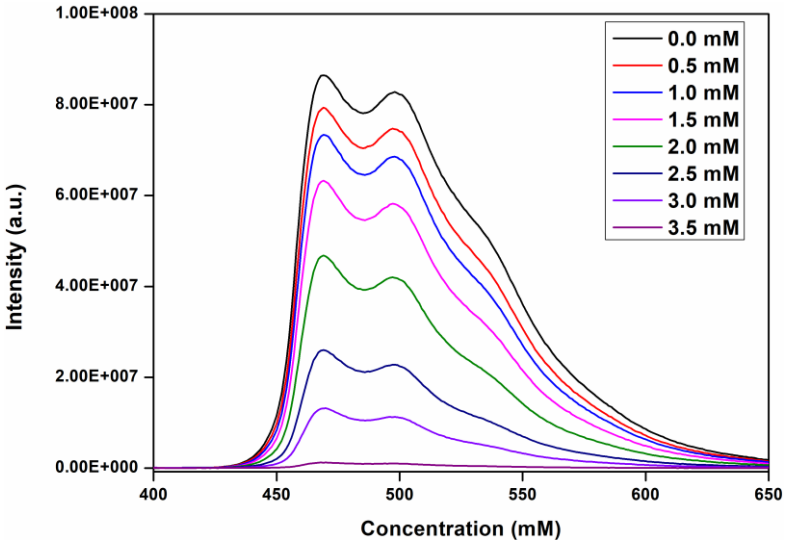
The fluorescence emission spectra of the photocatalyst Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 were examined in the presence of various reaction components. (**1a** and K_2HPO_4, **2a**), aiming to understand its emission properties and any effects from surrounding substrates. For these quenching studies a HITACHI f-7000 Scientific Spectrofluorometer with a 10.0 mm quartz cuvette was utilized to capture emission intensities. The catalyst, Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 was excited at 350 nm after degassing the sample solution (0.01 mM in DCM/H_2O) for 15 minutes. Emission peaks were consistently observed at 475 nm, while substrates **(1a)** and K_2HPO_4 and **(2a)** showed no emission within that range. Upon adding varying concentrations of **(1a)** and K_2HPO_4 to the catalyst solution, a notable decrease in emission intensity occurred, indicating its role as a redox-active quencher. **(2a)** also quench the catalyst. Stern-Volmer plots were generated for different concentrations of **(1a)** to delve into its behaviour. In contrast, **(2a)** exhibited relatively minimal quenching effects on the catalyst's emission spectra. Stern-Volmer plots were employed across all scenarios to offer a thorough analysis.

(C) Luminescence spectra:

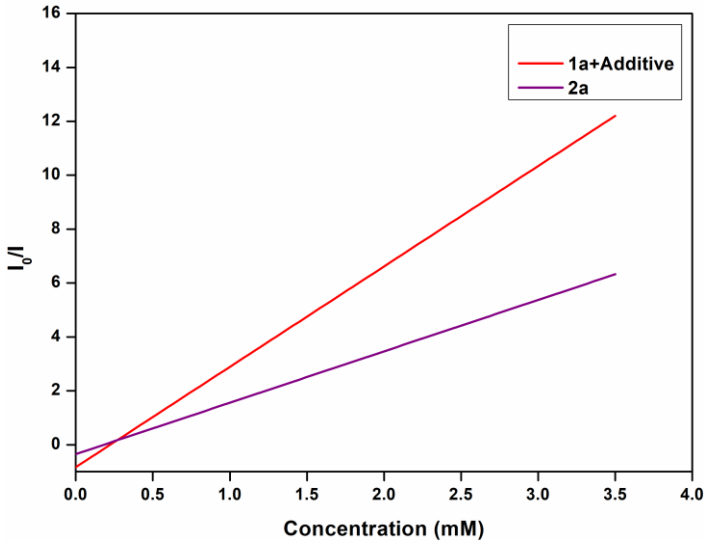
Luminescence spectra of Ir[dF(CF$_3$)ppy$_2$(dtbpy)]PF$_6$ (0.01 mM) as a function of concentration of 1a and K$_2$HPO$_4$ in DCM/H$_2$O with Excitation at 475 nm.



Luminescence spectra of Ir[dF(CF$_3$)ppy$_2$(dtbpy)]PF$_6$ (0.01 mM) as a function of concentration of 2a in DCM/H$_2$O with Excitation at 475 nm.



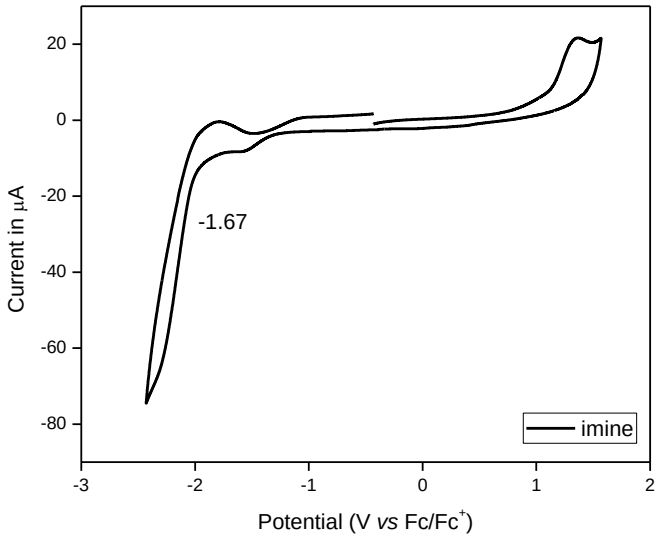
Combined Stern-Volmer plots of 1a and K_2HPO_4 and 2a



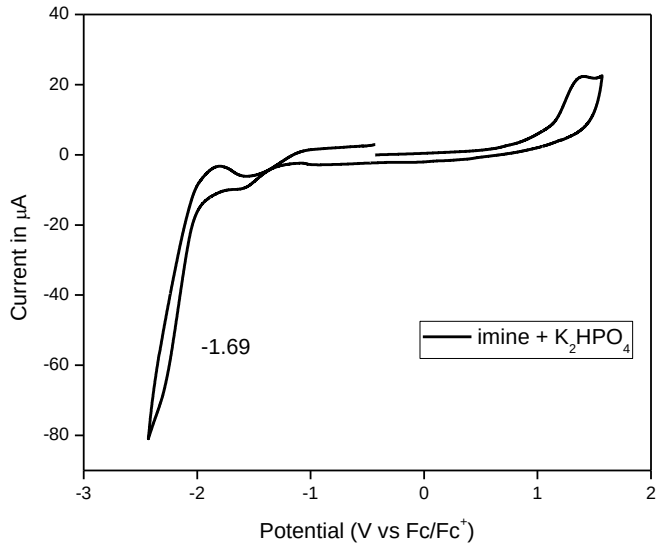
5.4 Cyclic Voltammetry experiments:

Cyclic voltammograms were recorded for (a) **2a**, (b) **2a** and K_2HPO_4 (1:1), (c) **2a** and water (1:1), (d) **1a**, (e) **1a** and K_2HPO_4. This electrochemical cell contains a glassy carbon (disc shaped with 3-mm diameter) as working electrode, Pt wire as counter electrode, and Ag wire as pseudo-reference electrode. The glassy carbon working electrode was polished with 1.0 micron *α*-alumina polishing powder using a figure eight motion. Electrolyte solution (0.1 M) was prepared from DCM and tetra-nbutylammonium hexafluorophosphate (Bu_4NPF_6). The DCM was degassed by nitrogen gas sparging for 10 minutes prior to measurements. The potential was externally calibrated against the ferrocene/ferrocenium couple (0.43 V) for imine (a, b, c). When the cyclic voltammetry (CV) value of the imine is referenced to the saturated calomel electrode, it is approximately $E_{1/2}^{red}$ =-1.24 V vs SCE. For keto acid + K_2HPO_4 this value is E_{peak}^{red} = +1.08 V *vs*. SCE in DCM

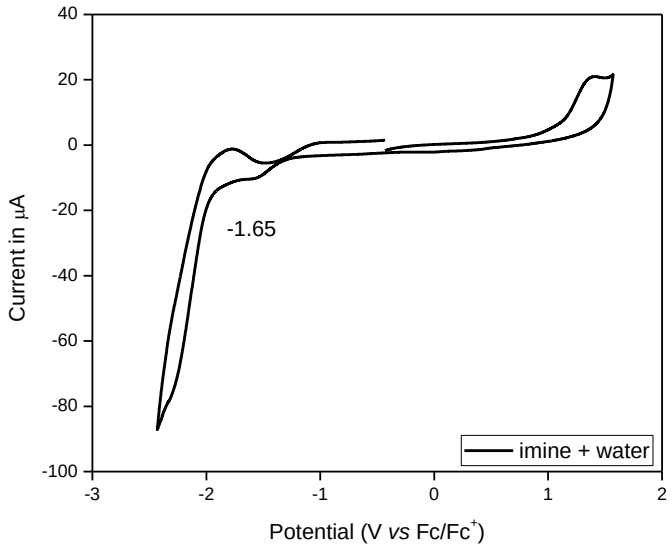
(a) Cyclic Voltammogram of imine (2a)



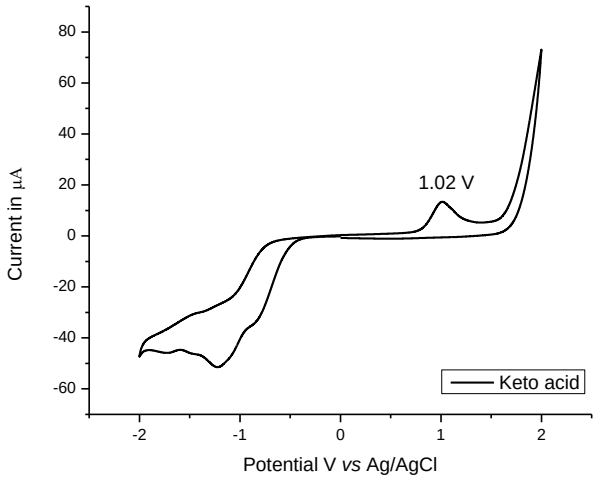
(b) Cyclic Voltammogram of imine (2a) in the presence of K_2HPO_4 (1:1)



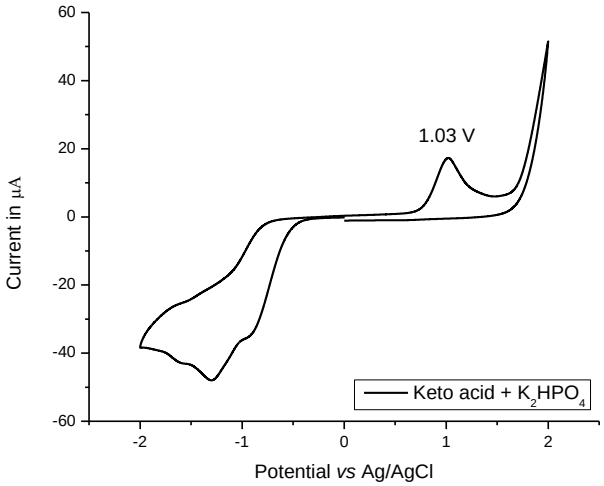
(c) Cyclic Voltammogram of imine (2a) in the presence of H_2O (1:1)



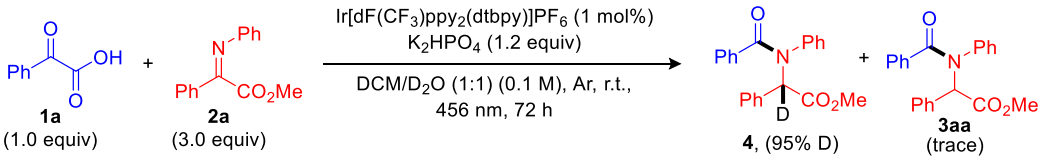
(d) Cyclic Voltammogram of Acid (1a)



(e) Cyclic Voltammogram of Acid (1a) in the presence of K_2HPO_4 (1:1)



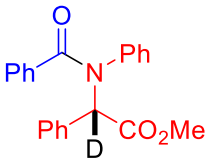
5.5 Deuterium labelling experiment:



2-oxo-2-phenylacetic acid **(1a)** (15 mg, 0.1 mmol, 1.0 equiv), (Z)-2-(2-methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium **(2a)** (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv. , 0.12mmol), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.2 mg, 0.001 mmol, 0.01 equiv) were added in a pre-dried 15 mL glass vial under argon atmosphere. To find the source of the proton in our product we replaced our previously used solvent DCM/H_2O (0.1 M) with DCM/D_2O (0.1 M). The reaction mixture was exposed to a 36-watt Kessil blue LED lamp emitting light at 456 nm for 72 h only to witness deuteration in our product. There was 85% isolated yield and 95% deuterium incorporation confirmed from ^{1}H NMR Spectroscopy.

5.5.1 Experimental details for the Deuterated compound:

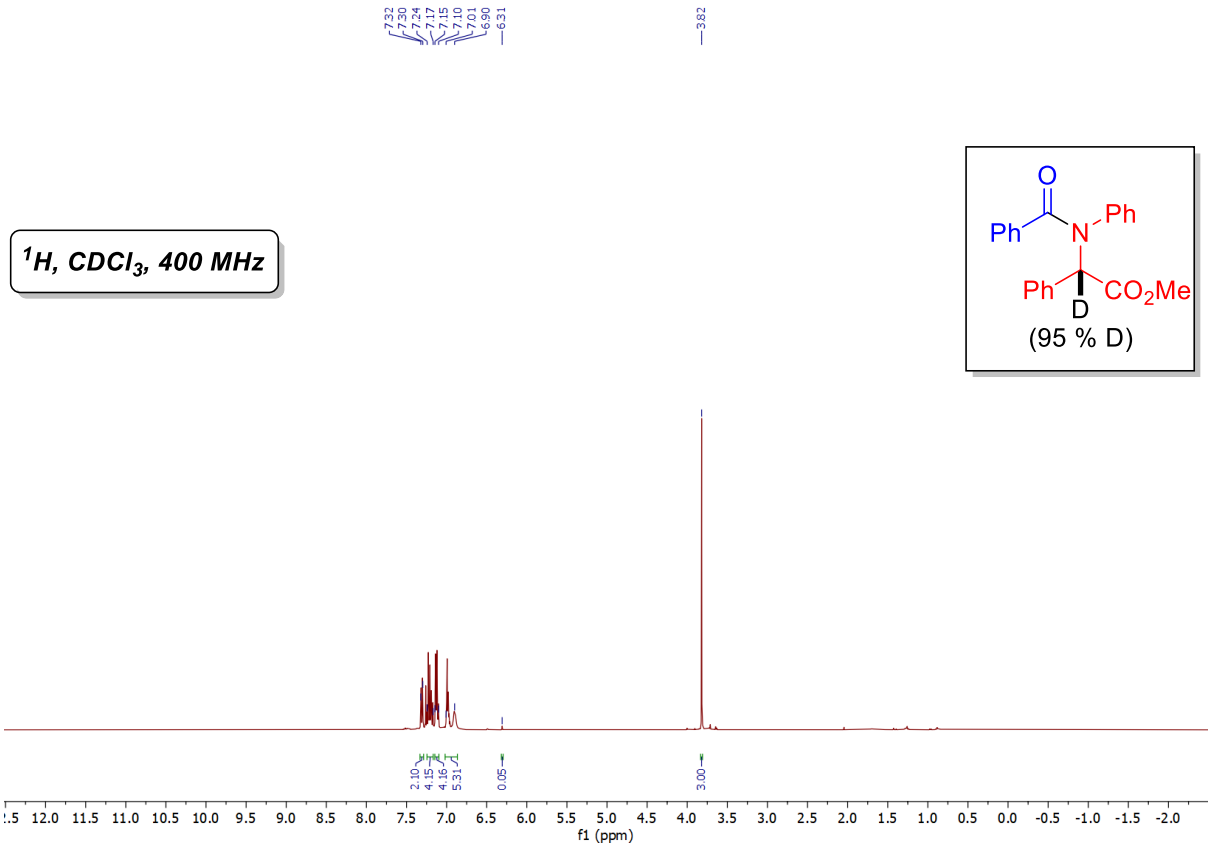
(methyl (S)-2-phenyl-2-(N-phenylbenzamido)acetate-d) (4)



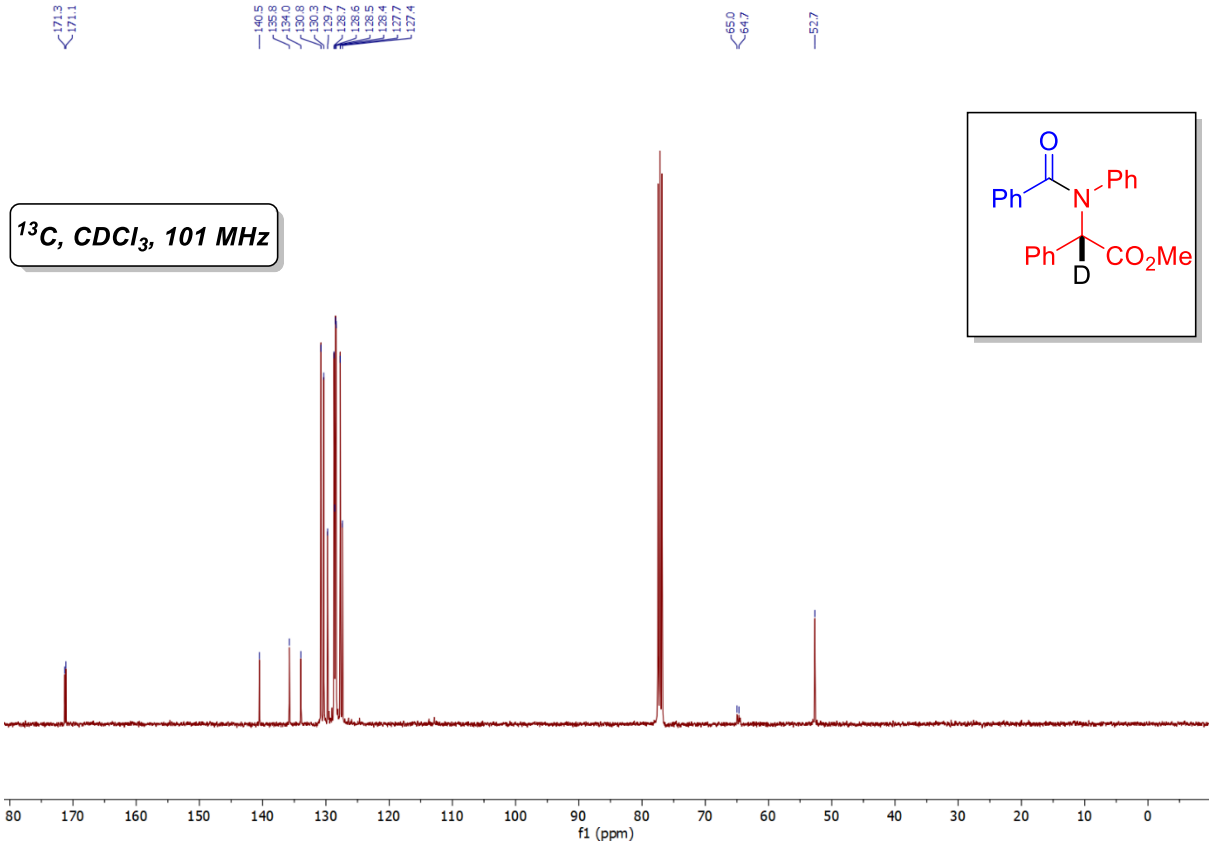
$C_{22}H_{18}DNO_3$
M W: 346.4041

HRMS (ESI)**:** m/z [$(M+H)^+$] Calculated for $[C_{22}H_{19}DNO_3]^+$: 347.1500; Found 347.1366.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.30 (m, 2H), 7.24–7.17 (m, 4H), 7.15–7.10 (m, 4H), 7.01–6.90 (m, 5H), 6.31 (s, 0.05H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 171.1, 140.5, 135.8, 134.0, 130.8, 130.3, 129.7, 128.7, 128.6, 128.5, 128.4, 127.7, 127.4, 64.84 (d, *J* = 31.6 Hz), 52.7.

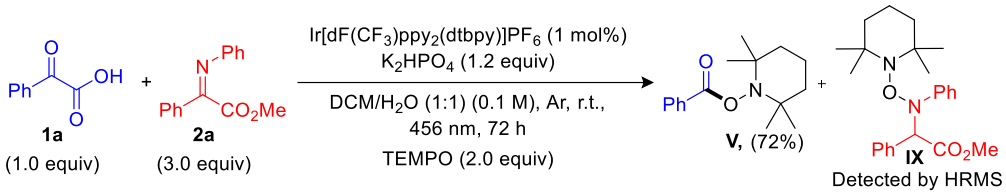


^{1}H, CDCl$_3$, 400 MHz



^{13}C, CDCl$_3$, 101 MHz

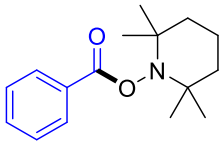
5.6 Radical trap experiment:



Following standard procedure, 2-oxo-2-phenylacetic acid **(1a)** (15 mg, 0.1 mmol, 1.0 equiv), (Z)-2-(2-methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium **(2a)** (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv. , 0.12 mmol), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.2 mg, 0.001 mmol, 1 mol%), TEMPO (31.75 mg, 2 equiv., 0.2 mmol) were added in a pre-dried 5 mL glass vial under argon atmosphere. DCM/H_2O (1:1) (0.1 M) was added and the reaction mixture was exposed to a 36-watt Kessil blue LED lamp emitting light at 456 nm for 72 h. No product **(3aa)** was observed. **(V)** was isolated (19 mg, 72%).

5.6.1 Experimental details for the TEMPO adduct:

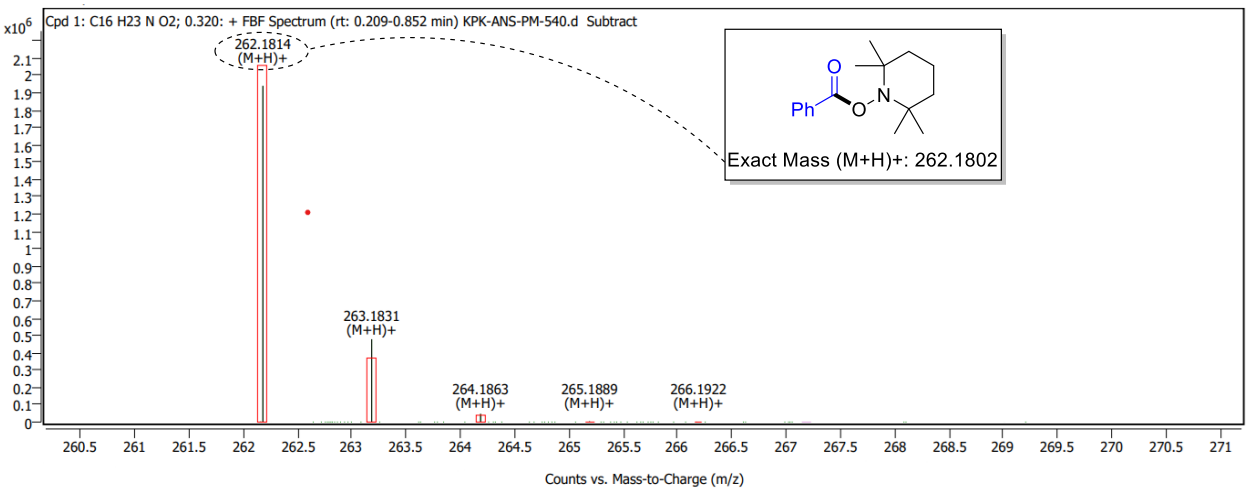
2,2,6,6-tetramethylpiperidin-1-yl benzoate (V)

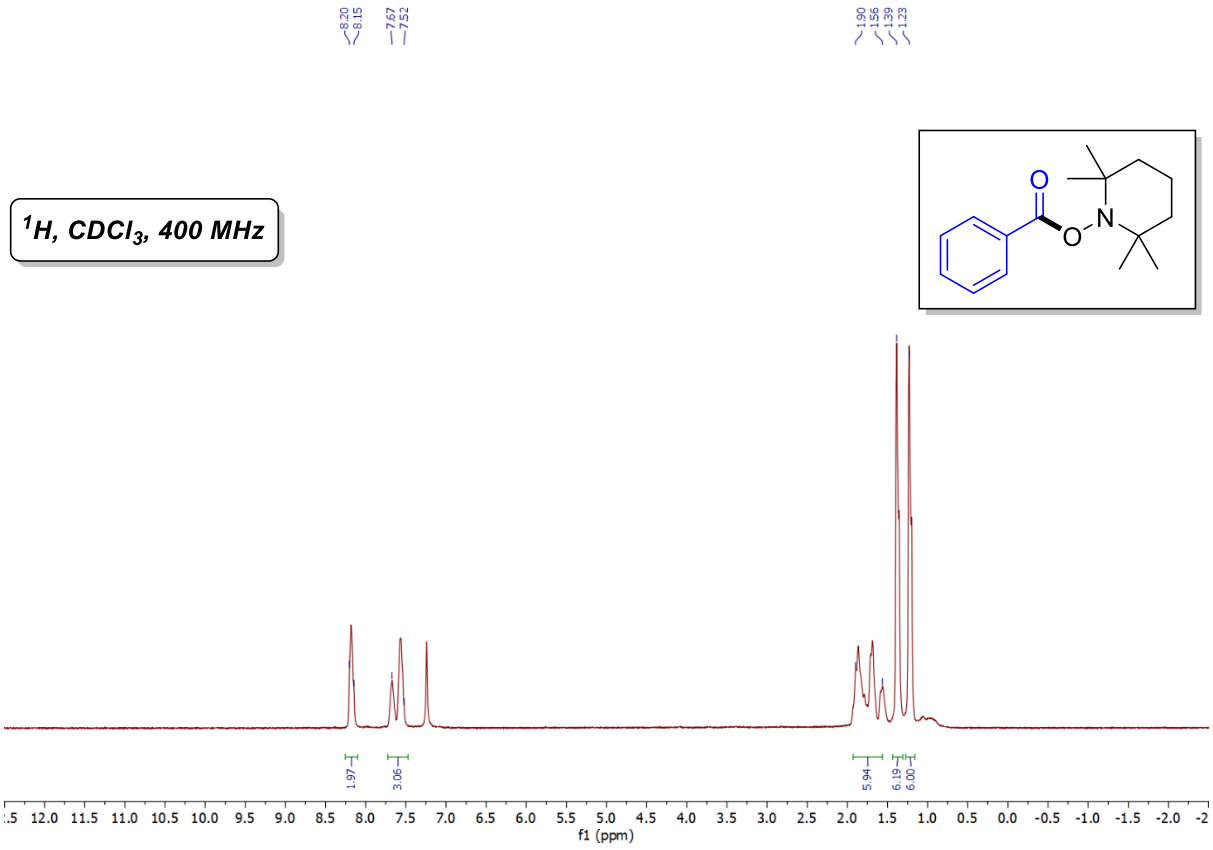


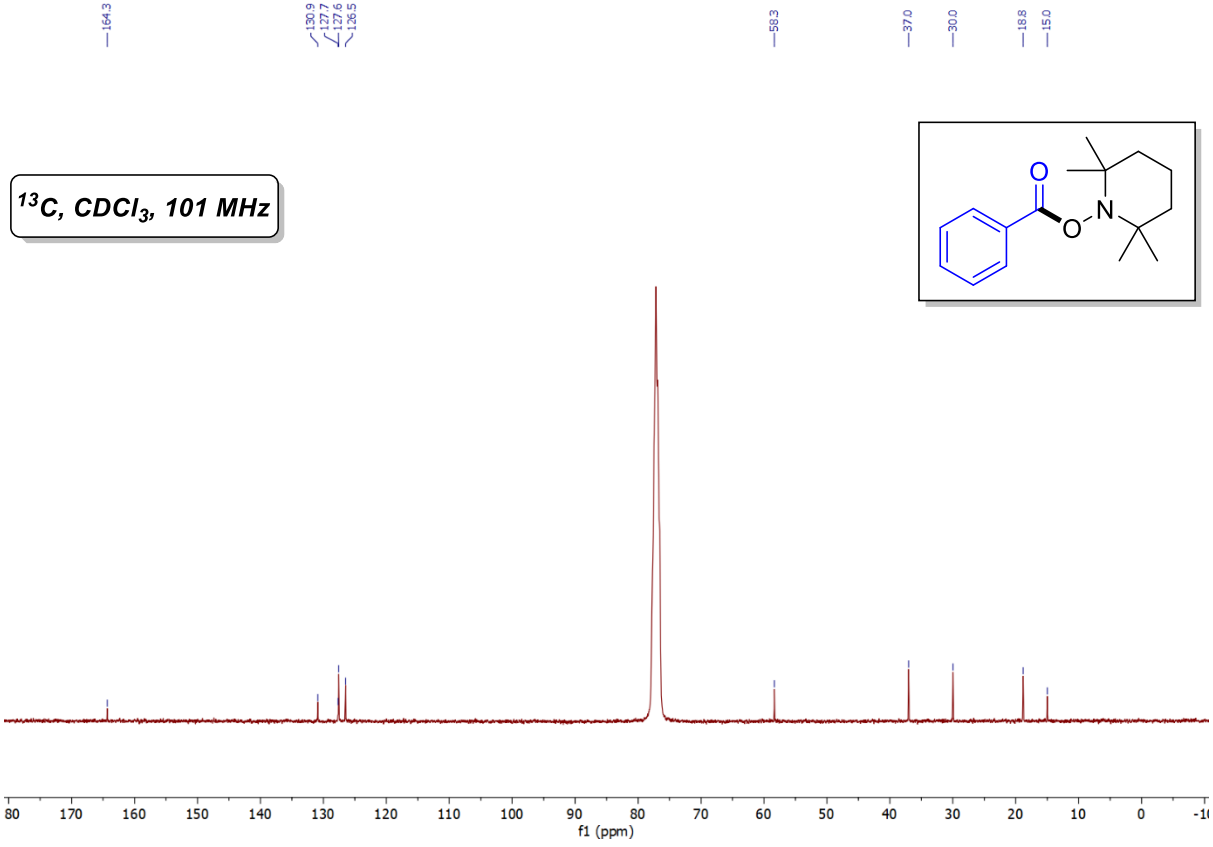
$C_{16}H_{23}NO_2$
M W: 261.3650 g/mol

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{22}H_{19}BrNO_3]^+$: 262.1802; Found 262.1814.

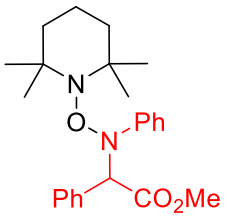
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–8.15 (m, 2H), 7.67–7.52 (m, 3H), 1.90–1.56 (m, 6H), 1.39 (s, 6H), 1.23 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.3, 130.9, 127.7, 127.6, 126.5, 58.3, 37.0, 30.0, 18.8, 15.0.




8.20
8.15
7.67
7.52
1.90
1.56
1.39
1.23
^{1}H, CDCl$_3$, 400 MHz
O
N
O
1.97
3.06
5.94
6.19
6.00
f1 (ppm)

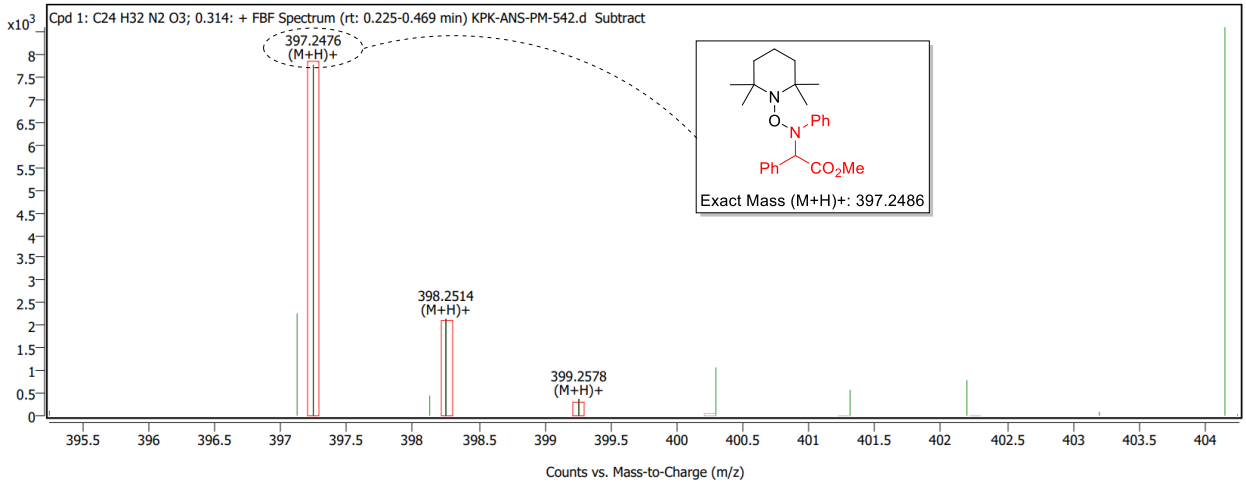

164.3
130.9
127.7
127.6
126.5
58.3
37.0
30.0
18.8
15.0
^{13}C, CDCl$_3$, 101 MHz
O
N
O
f1 (ppm)

methyl 2-phenyl-2-(phenyl((2,2,6,6-tetramethylpiperidin-1-yl)oxy)amino)acetate (IX)

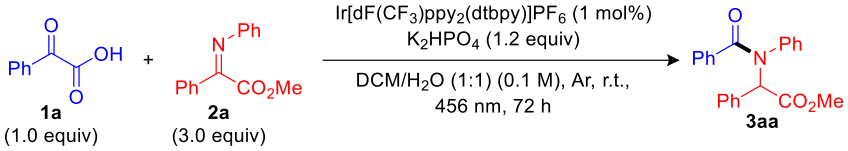


$C_{24}H_{32}N_2O_3$
M W: 396.5310 g/mol

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{24}H_{33}N_2O_3]^+$: 397.2486; Found 397.2476.



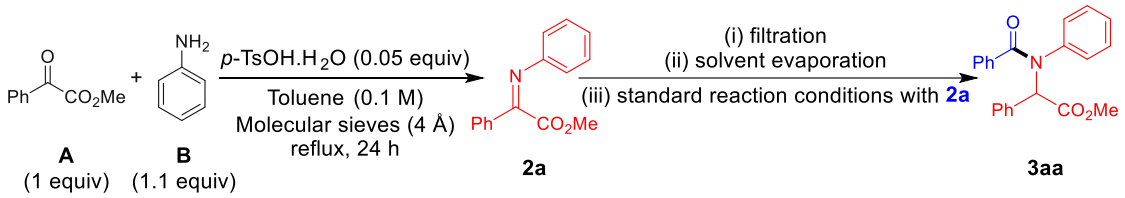
6. 1 mmol scale Synthesis:



An oven-dried 40 ml glass vial was charged with a magnetic stirring bar, 2-Oxo-2-phenylacetic acid **(1a)** (150 mg, 1 mmol, 1.0 equiv.), (Z)-2-(2-methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium **(2a)** (717 mg, 3 mmol, 3.0 equiv.), K_2HPO_4 (208 mg, 1.2mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 catalyst (11.21 mg, 0.01mmol, 0.01 equiv.), 10 ml DCM/H_2O (0.1 M) (1:1) were added under argon atmosphere. The vial was maintained for 72 h at room temperature under 456 nm blue LED with constant stirring. The reaction mixture containing DCM was evaporated at reduced pressure and thereafter work up of the reaction mixture was performed using ethyl acetate, and the resulting organic phases was allowed to evaporate under reduced pressure. The product of high analytical purity was achieved through column

chromatography on silica gel, employing petroleum ether and ethyl acetate as the elution solvents. The product was confirmed by NMR. The product **(3aa)** recorded a yield of (240 mg, 70%).

7. One-pot sequential synthesis



An oven-dried glass vial was prepared with a magnetic stir bar, compound **A** (0.3 mmol, 1.0 equiv), compound **B** (0.33 mmol, 1.1 equiv), and *p*-TsOH·H_2O (0.015 mmol, 0.05 equiv). 3 ml Toluene (0.1 M) was added to the vial, and the reaction mixture was heated to reflux for 24 hours. After refluxing, the mixture was filtered through Celite using a G-4 sintered funnel, and the solvent was evaporated. The crude material obtained was subjected to a high vacuum. This material was then taken into a glove box and exposed to our standard reaction conditions. The vial was maintained for 72 h at room temperature under 456 nm blue LED with constant stirring. The reaction mixture containing DCM was evaporated at reduced pressure and thereafter work up of the reaction mixture was performed using ethyl acetate, and the resulting organic phases was allowed to evaporate under reduced pressure. The product of high analytical purity was achieved through column chromatography on silica gel, employing petroleum ether and ethyl acetate as the elution solvents. The product was confirmed by NMR. The product **(3aa)** recorded a yield of (26 mg, 75%).

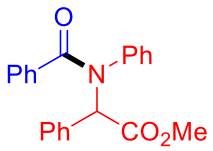
8. General procedure for the Photoredox-Catalyzed Amidation of *α*-keto acid with *α*-Iminoester (GP-2)

An oven-dried glass vial was charged with a magnetic stir bar, Aryl glyoxylic acid **(1a)** (1.0 equiv), (Z)-2-(2-methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium **(2a)** (3.0 equiv), K_2HPO_4 (1.2 equiv.), Ir[dF(CF_3)ppy_2(dtbpy)]PF_6 catalyst (1 mol%), 1ml DCM/H_2O (1:1) (0.1 M) were added to the mixture under argon atmosphere. The vial was maintained for 72 h at room temperature under 456 nm blue LED with constant stirring. The reaction mixture containing DCM was evaporated at reduced pressure and thereafter work up of the reaction mixture was performed using ethyl acetate,

and the resulting organic phases was allowed to evaporate under reduced pressure. The product of high analytical purity was achieved through column chromatography on silica gel, employing a (5–10%) solution of petroleum ether and ethyl acetate as the elution solvents. The light-yellow color product was confirmed by NMR.

9. Experimental details for the synthesized compounds obtained from GP–2

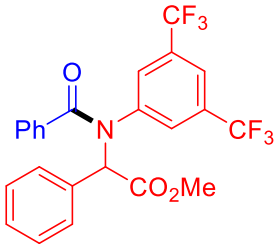
methyl 2-phenyl-2-(N-phenylbenzamido)acetate (3aa)



$C_{22}H_{19}NO_3$
M W: 345.3980 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-2-(2-methoxy-2-oxo-1-(phenylimino)ethyl)benzene-1-ylium (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv, 0.12 mmol), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3aa**) was obtained as light-yellow liquid, recording a yield of 90% (31 mg).
HRMS (ESI)**:** m/z [(M+H)$^+$] Calculated for [$C_{22}H_{19}NO_3$]$^+$: 346.1438; Found 346.1436.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.29 (m, 2H), 7.23–7.18 (m, 4H), 7.14–7.11 (m, 4H), 7.01–6.89 (m, 5H), 6.31 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 171.1, 140.5, 135.7, 134.0, 130.7, 130.3, 129.7, 128.7, 128.6, 128.5, 128.4, 127.7, 127.4, 65.0, 52.7.

methyl 2-(N-(3,5-bis(trifluoromethyl)phenyl)benzamido)-2-phenylacetate (3ab)



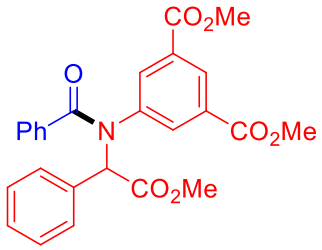
$C_{24}H_{17}F_6NO_3$
M W: 481.3944 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), methyl (Z)-2-((3,5-bis(trifluoromethyl)phenyl)imino)-2-phenylacetate (112.5 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv, 0.12 mmol), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ab**) was obtained as light-yellow liquid, recording a yield of 55% (26 mg).

HRMS (ESI)**:** m/z $[(M+H)^+]$ Calculated for $[C_{24}H_{28}F_6NO_3]^+$: 482.1185; Found 482.1189.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.30–7.22 (m, 7H), 7.19–7.15 (m, 3H), 7.05–7.02 (m, 2H), 6.48 (s, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 171.0, 141.8, 134.7, 133.0, 131.5, 131.4 (q, *J* = 40.4 Hz), 130.5, 130.2, 129.5, 129.1, 128.5, 128.3, 122.6 (q, *J* = 272.7 Hz), 120.8, 64.1, 52.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.13.

dimethyl 5-(N-(2-methoxy-2-oxo-1-phenylethyl)benzamido)isophthalate (3ac)



$C_{26}H_{23}NO_7$
M. W.: 461.4700 g/mol

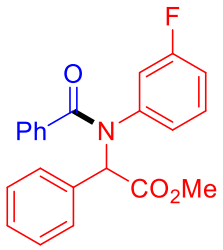
Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-dimethyl 5-((2-methoxy-2-oxo-1-phenylethylidene)amino)isophthalate (138.43 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ac**) was obtained as light-yellow liquid, recording a yield of 85% (39 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{26}H_{24}NO_7]^+$: 462.1547; Found 462.1555.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (t, *J* = 1.6 Hz, 1H), 7.30–7.26 (m, 3H), 7.24–7.17 (m, 5H), 7.15–7.11 (m, 2H), 7.09–7.07 (m, 2H), 6.40 (s, 1H), 3.84 (s, 3H), 3.83 (s,

6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 171.0, 165.3, 141.0, 136.1, 135.0, 133.3, 130.7, 130.3, 130.2, 129.4, 129.1, 128.9, 128.7, 128.1, 64.5, 52.8, 52.6.

methyl 2-(N-(3-fluorophenyl)benzamido)-2-phenylacetate (3ad)



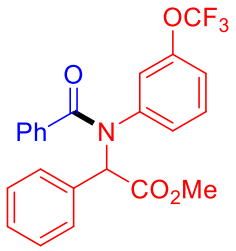
$C_{22}H_{18}FNO_3$
M. W.: 363.3884 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-((3-fluorophenyl)imino)-2-phenylacetate (109.01 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 1.2 equiv, 0.12 mmol), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ad**) was obtained as light-yellow liquid, recording a yield of 70% (25 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{22}H_{19}FNO_3]^+$: 364.1343; Found 364.1358.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.31 (m, 2H), 7.25–7.20 (m, 4H), 7.17–7.10 (m, 4H), 6.95–6.89 (m, 1H), 6.74–6.66 (m, 3H), 6.34 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 171.0, 162.0 (d, *J* = 253 Hz), 141.8 (d, *J* = 10 Hz), 135.4, 133.6, 130.2, 130.0,129.3, 129.2, 128.8, 128.6, 128.5, 127.9, 126.8 (d, *J* = 10 Hz), 118.1 (d, *J* = 20 Hz), 114.5 (d, *J* = 20 Hz), 64.7, 52.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.17.

methyl 2-phenyl-2-(N-(3-(trifluoromethoxy)phenyl)benzamido)acetate (3ae)



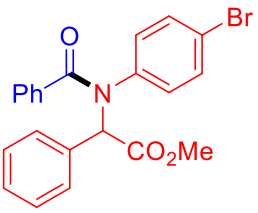
$C_{23}H_{18}F_3NO_4$
M. W.: 429.3952 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-phenyl-2-((3-(trifluoromethoxy)phenyl)imino)acetate (128.81 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ae**) was obtained as light-yellow liquid, recording a yield of 80% (34 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{19}F_3NO_4]^+$: 430.1261; Found 430.1265.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.27 (m, 2H), 7.25–7.19 (m, 4H), 7.16–7.13 (m, 2H), 7.12–7.07 (m, 2H), 6.98 (t, *J* = 8.1 Hz, 1H), 6.88–6.79 (m, 3H), 6.40 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 171.1, 148.6, 141.6, 135.4, 133.4, 130.2, 130.0, 129.7, 129.2, 128.9, 128.7, 128.4, 127.9, 124.1, 120.8 (q, *J* = 262.6 Hz), 120.2, 64.4, 52.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.09.

methyl 2-(N-(4-bromophenyl)benzamido)-2-phenylacetate (3af)



$C_{22}H_{18}BrNO_3$
M. W.: 424.2940 g/mol

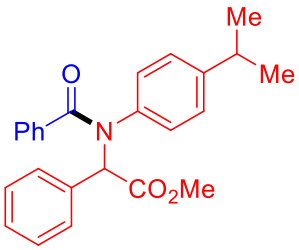
Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-((4-bromophenyl)imino)-2-phenylacetate (127.27 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of

petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3af**) was obtained as light-yellow liquid, recording a yield of 75% (31.8 mg).

HRMS (ESI)**:** m/z [(M+H)$^+$] Calculated for [$C_{22}H_{19}BrNO_3$]$^+$: 424.0543; Found 424.0540.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.25–7.21 (m, 4H), 7.18–7.13 (m, 2H), 7.11–7.07 (m, 4H), 6.74 (d, *J* = 8.1 Hz, 2H), 6.34 (s, 1H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 171.1, 139.5, 135.4, 133.6, 132.5, 131.5, 130.3, 130.0, 128.9, 128.7, 128.0, 121.4, 116.8, 64.5, 52.7.

methyl 2-(N-(4-isopropylphenyl)benzamido)-2-phenylacetate (3ag)



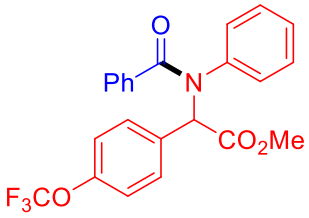
$C_{25}H_{25}NO_3$
M W: 387.4790 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-((4-isopropylphenyl)imino)-2-phenylacetate (116.24 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ag**) was obtained as light-yellow liquid, recording a yield of 60% (23 mg).

HRMS (ESI)**:** m/z [M+H]$^+$ Calculated for [$C_{25}H_{26}NO_3$]$^+$: 388.1907; Found 388.1912.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.30 (m, 2H), 7.23–7.17 (m, 4H), 7.14–7.10 (m, 4H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.23 (s, 1H), 3.81 (s, 3H), 2.74–2.66 (m, 1H), 1.08 (d, *J* = 1.3 Hz, 3H), 1.07 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 171.1, 148.2, 138.3, 135.8, 134.2, 130.3, 129.7, 128.8, 128.5, 128.4, 127.7, 126.7, 126.3, 65.3, 52.6, 33.6, 23.9, 23.9.

methyl 2-(N-phenylbenzamido)-2-(4-(trifluoromethoxy)phenyl)acetate (3ah)



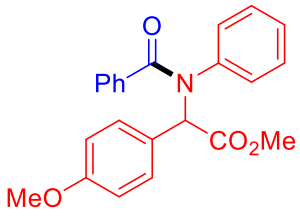
$C_{23}H_{18}F_3NO_4$
M. W.: 429.3952 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), methyl (Z)-2-(phenylimino)-2-(4-(trifluoromethoxy)phenyl)acetate (97 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ah**) was obtained as light-yellow liquid, recording a yield of 75% (32 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{19}F_3NO_4]^+$: 430.1261; Found 430.1265.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.30 (m, 2H), 7.23–7.18 (m, 3H), 7.15–7.11 (m, 2H), 7.08–7.00 (m, 5H), 6.91 (d, *J* = 7.3 Hz, 2H), 6.20 (s, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 170.5, 149.3, 140.8, 135.4, 132.9, 131.8, 130.3, 129.9, 128.7 (2C), 127.8, 127.6, 120.8, 120.4 (q, *J* = 257.4 Hz), 64.7, 52.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.21.

methyl 2-(4-methoxyphenyl)-2-(N-phenylbenzamido)acetate (3ai)



$C_{23}H_{21}NO_4$
M. W.: 375.4240 g/mol

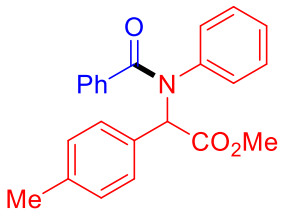
Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-(4-methoxyphenyl)-2-(phenylimino)acetate (112.62 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired

product through column chromatography on silica gel. The product (**3ai**) was obtained as light-yellow liquid, recording a yield of 88% (33 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{22}NO_4]^+$: 376.1543; Found 376.1548.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.19–7.16 (m, 1H), 7.14–7.10 (m, 2H), 7.04–6.98 (m, 5H), 6.91–6.89 (m, 2H), 6.74–6.71 (m, 2H), 6.24 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 171.3, 159.7, 140.5, 135.9, 131.6, 130.9, 129.7, 128.7,128.4, 127.7, 127.4, 126.0, 113.9, 64.0, 55.3, 52.7.

methyl 2-(N-phenylbenzamido)-2-(p-tolyl)acetate (3aj)



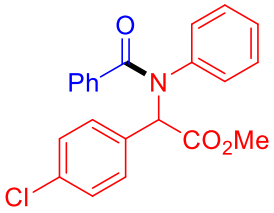
$C_{23}H_{21}NO_3$
M. W.: 359.4250 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-(phenylimino)-2-(p-tolyl)acetate (107.82 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3aj**) was obtained as light-yellow liquid, recording a yield of 78% (28 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{22}NO_3]^+$: 360.1594; Found 360.1601.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.29 (m, 2H), 7.20–7.16 (m, 1H), 7.13–7.09 (m, 2H), 7.01–6.97 (m, 7H), 6.91 (s, 2H), 6.27 (s, 1H), 3.80 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2 (2C), 140.6, 138.4, 135.9, 130.9, 130.8, 130.2, 129.6, 129.2, 128.7, 128.3, 127.7, 127.3, 64.7, 52.6, 21.3.

methyl 2-(4-chlorophenyl)-2-(N-phenylbenzamido)acetate (3ak)



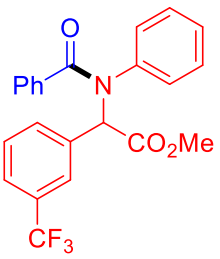
$C_{22}H_{18}ClNO_3$
M. W.: 379.8400 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-(4-chlorophenyl)-2-(phenylimino)acetate (113.95 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ak**) was obtained as light-yellow liquid, recording a yield of 75% (28 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{22}H_{19}ClNO_3]^+$: 380.1048; Found 380.1054.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dt, *J* = 6.9, 1.6 Hz, 2H), 7.22–7.17 (m, 3H), 7.14–7.09 (m, 4H), 7.05–7.01 (m, 3H), 6.95–6.89 (m, 2H), 6.19 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 170.5, 140.7, 135.4, 134.6, 132.7, 131.6, 130.4, 130.2, 129.8, 128.7 (2C), 127.7, 127.6, 64.6, 52.8.

methyl 2-(N-phenylbenzamido)-2-(3-(trifluoromethyl)phenyl)acetate (3al)



$C_{23}H_{18}F_3NO_3$
M. W.: 413.3962 g/mol

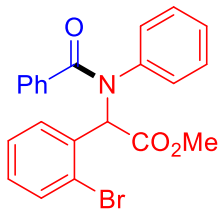
Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), methyl (Z)-2-(phenylimino)-2-(3-(trifluoromethyl)phenyl)acetate (92 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the

purification of the desired product through column chromatography on silica gel. The product (**3al**) was obtained as light-yellow liquid, recording a yield of 89% (37 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{19}F_3NO_3]^+$: 414.1312; Found 414.1322.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 1H), 7.41–7.31 (m, 5H), 7.23–7.18 (m, 1H), 7.16–7.11 (m, 2H), 7.07–7.01 (m, 3H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.27 (s, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 170.2, 140.7, 135.3, 135.2, 133.6, 130.8 (q, *J* = 30 Hz), 130.2, 130.0, 129.0, 128.8, 128.7, 127.8, 127.7, 127.1 (q, *J* = 3.9 Hz), 125.3 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 273 Hz), 64.9, 52.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.67.

methyl 2-(2-bromophenyl)-2-(N-phenylbenzamido)acetate (3am)



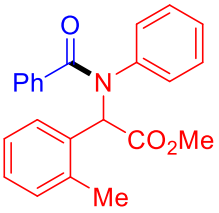
$C_{22}H_{18}BrNO_3$
M. W.: 424.2940 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-(2-bromophenyl)-2-(phenylimino)acetate (127.28 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3am**) was obtained as light-yellow liquid, recording a yield of 83% (35 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{22}H_{18}BrNO_3]^+$: 424.0543; Found 424.1420.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.34–7.32 (m, 2H), 7.21–7.16 (m, 1H), 7.14–7.10 (m, 2H), 7.08–7.04 (m, 2H), 7.00–6.94 (m, 5H), 6.86 (dd, *J* = 7.5, 1.9 Hz, 1H), 6.76 (s, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 170.9, 140.1, 135.8, 134.0, 133.1, 131.6, 130.5, 130.2, 129.7, 128.6, 128.4, 127.7, 127.6, 127.4, 126.2, 64.3, 52.8.

methyl 2-(N-phenylbenzamido)-2-(o-tolyl)acetate (3an)



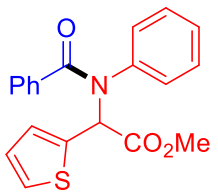
$C_{23}H_{21}NO_3$
M. W.: 359.4250 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-(phenylimino)-2-(o-tolyl)acetate (107.82 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3an**) was obtained as light-yellow liquid, recording a yield of 87% (31 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{22}NO_3]^+$: 360.1594, Found 360.1601.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.30 (m, 2H), 7.21–7.10 (m, 5H), 6.96–6.85 (m, 6H), 6.72 (s, 1H), 6.67 (dd, *J* = 7.8, 1.3 Hz, 1H), 3.82 (s, 3H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 171.5, 139.8, 137.7, 135.9, 132.4, 130.6, 130.6, 130.1, 129.6, 128.8, 128.6, 128.1, 127.7, 127.3, 125.9, 60.9, 52.5, 19.5.

methyl 2-(N-phenylbenzamido)-2-(thiophen-2-yl)acetate (3ao)



$C_{20}H_{17}NO_3S$
M. W.: 351.4200 g/mol

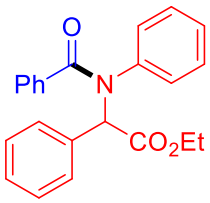
Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (E)-methyl 2-(phenylimino)-2-(thiophen-2-yl)acetate (105.42 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired

product through column chromatography on silica gel. The product (**3ao**) was obtained as light-yellow liquid, recording a yield of 92% (32 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{20}H_{18}NO_3S]^+$: 352.1002, Found 352.1005.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.31 (m, 2H), 7.27 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.24–7.19 (m, 1H), 7.15–7.10 (m, 5H), 7.05–7.01 (m, 2H), 6.91–6.87 (m, 2H), 6.25 (s, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 170.0, 141.6, 136.1, 135.3, 130.0, 129.6, 129.5 (2C), 128.9, 127.8, 127.6, 127.4, 126.4, 61.5, 53.0.

ethyl 2-phenyl-2-(N-phenylbenzamido)acetate (3ap)



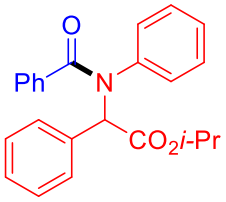
$C_{23}H_{21}NO_3$
M. W.: 359.4250 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 1 mmol, 1.0 equiv), (Z)-ethyl 2-phenyl-2-(phenylimino)acetate (107.82 mg, 3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ap**) was obtained as light-yellow liquid, recording a yield of 50% (18 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{22}NO_3]^+$: 360.1594; Found 360.1601.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 6.7, 2.0 Hz, 2H), 7.18 (dd, *J* = 14.0, 7.1 Hz, 4H), 7.13–7.08 (m, 4H), 6.91 (dt, *J* = 5.9, 3.1 Hz, 3H), 6.89 (d, *J* = 6.8 Hz, 2H), 6.26 (s, 1H), 4.33–4.24 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 170.6, 140.6, 135.9, 134.1, 130.7, 130.3, 129.7, 128.6, 128.5, 128.4, 128.3, 127.7, 127.3, 65.1, 61.7, 14.3.

isopropyl 2-phenyl-2-(N-phenylbenzamido)acetate (3aq)



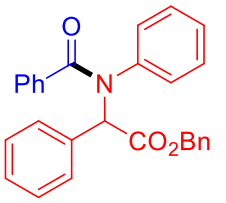
$C_{24}H_{23}NO_3$
M. W.: 373.4520 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-isopropyl 2-phenyl-2-(phenylimino)acetate (112.03 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3aq**) was obtained as light-yellow liquid, recording a yield of 85% (32 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{24}H_{24}NO_3]^+$: 374.1751; Found 374.1755.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 7.1, 2.0 Hz, 2H), 7.19 (dd, *J* = 12.2, 6.6 Hz, 4H), 7.16–7.11 (m, 4H), 7.00–6.96 (m, 3H), 6.90 (d, *J* = 4.7 Hz, 2H), 6.24 (s, 1H), 5.19 (h, *J* = 6.3 Hz, 1H), 1.33 (d, *J* = 6.4 Hz, 3H), 1.23 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 170.0, 140.8, 136.0, 134.3, 130.7, 130.3, 129.6, 128.6, 128.4, 128.3, 127.7, 127.2, 120.3, 69.3, 65.3, 22.0, 21.7.

benzyl 2-phenyl-2-(N-phenylbenzamido)acetate (3ar)



$C_{28}H_{23}NO_3$
M. W.: 421.4960 g/mol

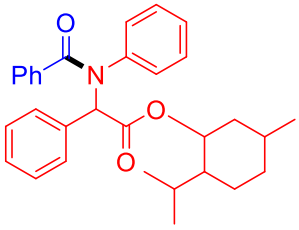
Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-benzyl 2-phenyl-2-(phenylimino)acetate (126.44 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product

through column chromatography on silica gel. The product (**3ar**) was obtained as light-yellow liquid, recording a yield of 86% (36 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{28}H_{24}NO_3]^+$: 422.1751; Found 422.1755.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 6H), 7.28 (s, 1H), 7.22–7.17 (m, 4H), 7.14–7.10 (m, 4H), 6.99–6.94 (m, 3H), 6.98 (d, *J* = 6.7 Hz, 2H), 6.32 (s, 1H), 5.30 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 170.4, 140.7, 135.8, 135.7, 133.9, 130.6, 130.4, 129.7, 128.7, 128.6, 128.5, 128.4 (3C), 128.3, 127.7, 127.3, 67.3, 65.3.

2-isopropyl-5-methylcyclohexyl 2-phenyl-2-(N-phenylbenzamido)acetate (3as)



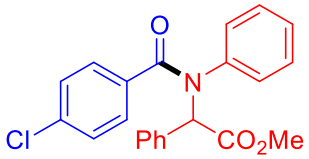
$C_{31}H_{35}NO_3$
M. W.: 469.6250 g/mol

Prepared according to the **GP-2**, using 2-Oxo-2-phenylacetic acid (15 mg, 0.1 mmol, 1.0 equiv), (Z)-2-isopropyl-5-methylcyclohexyl 2-phenyl-2-(phenylimino)acetate (140 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3as**) was obtained as light-yellow liquid, recording a yield of 83% (39 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{31}H_{35}NO_3]^+$: 470.2690; Found 470.2695.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.21–7.15 (m, 4H), 7.13–7.09 (m, 4H), 6.97 (dd, *J* = 5.2, 2.1 Hz, 3H), 6.90 (s, 2H), 6.24 (s, 1H), 4.81–4.75 (m, 1H), 2.27–2.21 (m, 1H), 1.69–1.49 (m, 5H), 1.39–1.32 (m, 1H), 1.15–1.04 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.70 (d, *J* = 7.1 Hz, 3H), 0.62 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 170.4, 140.6, 136.0, 134.1, 131.0, 130.6, 129.6, 128.7, 128.4, 128.3, 128.2, 127.7, 127.2, 76.0, 65.3, 47.1, 40.9, 34.4, 31.6, 25.8, 23.3, 22.1, 20.7, 16.0.

methyl 2-(4-chloro-N-phenylbenzamido)-2-phenylacetate (3ba)



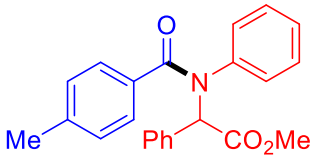
$C_{22}H_{18}ClNO_3$
M. W.: 379.8400 g/mol

Prepared according to the **GP-2**, using 2-(4-chlorophenyl)-2-oxoacetic acid (18.4 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-phenyl-2-(phenylimino)acetate (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ba**) was obtained as light-yellow liquid, recording a yield of 77% (29 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{22}H_{19}ClNO_3]^+$: 380.1048; Found 380.1053.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.17 (m, 5H), 7.12–7.08 (m, 4H), 7.03–6.98 (m, 3H), 6.89 (d, *J* = 3.5 Hz, 2H), 6.29 (s, 1H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 170.1, 140.2, 135.8, 134.1, 133.7, 130.7, 130.3, 130.2, 128.6, 128.5, 128.5, 128.0, 127.6, 65.0, 52.6.

methyl 2-(4-methyl-N-phenylbenzamido)-2-phenylacetate (3ca)



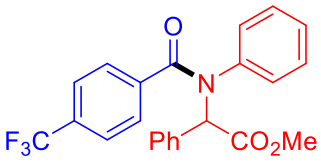
$C_{23}H_{21}NO_3$
M. W.: 359.4250 g/mol

Prepared according to the **GP-2**, using 2-oxo-2-(p-tolyl)acetic acid (16.4 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-phenyl-2-(phenylimino)acetate (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ca**) was obtained as light-yellow liquid, recording a yield of 95% (34 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{22}NO_3]^+$ 360.1594; Found 360.1596.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.18 (m, 5H), 7.15–7.11 (m, 2H), 7.02–6.98 (m, 3H), 6.91 (t, *J* = 7.4 Hz, 4H), 6.28 (s, 1H), 3.81 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.2, 171.1, 140.8, 140.0, 134.1, 132.7, 130.7, 130.3, 128.9, 128.5, 128.4, 128.4, 127.2, 127.2, 65.1, 52.6, 21.4.

methyl 2-phenyl-2-(N-phenyl-4-(trifluoromethyl)benzamido)acetate (3da)



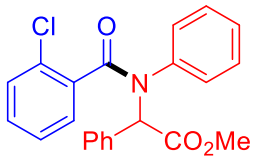
$C_{23}H_{18}F_3NO_3$
M. W.: 413.3962 g/mol

Prepared according to the **GP-2**, using 2-oxo-2-(4-(trifluoromethyl)phenyl)acetic acid (21.8 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-phenyl-2-(phenylimino)acetate (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), $Ir[dF(CF_3)ppy_2(dtbpy)]PF_6$ (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3da**) was obtained as light-yellow liquid, recording a yield of 85% (35 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{19}F_3NO_3]^+$: 414.1312; Found 414.1318.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.24–7.18 (m, 3H), 7.12–7.09 (m, 2H), 7.03–6.88 (m, 5H), 6.83–6.78 (m, 2H), 6.28 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.5, 171.1, 141.8, 134.8, 133.1, 131.6, 131.5 (q, *J* = 30.3 Hz), 130.5, 130.2, 129.5, 129.2, 128.5, 128.4, 122.6 (q, *J* = 272.7 Hz), 120.9, 64.2, 53.0.**^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.87.

methyl 2-(2-chloro-N-phenylbenzamido)-2-phenylacetate (3ea)



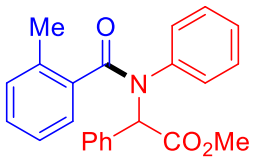
$C_{22}H_{18}ClNO_3$
M. W.: 379.8400 g/mol

Prepared according to the **GP-2**, using 2-(2-chlorophenyl)-2-oxoacetic acid (18.4 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-phenyl-2-(phenylimino)acetate (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ea**) was obtained as light-yellow liquid, recording a yield of 50% (19 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{22}H_{19}ClNO_3]^+$: 380.1048; Found 380.1052.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.18 (m, 3H), 7.16 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.12–7.10 (m, 2H), 7.06–6.99 (m, 4H), 6.94 (q, *J* = 4.4 Hz, 3H), 6.44 (s, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 168.8, 138.9, 136.2, 133.7, 130.4, 130.3, 129.8, 129.4, 128.8, 128.5, 128.3, 128.0, 126.1, 115.5, 112.9, 64.0, 52.7.

methyl 2-(2-methyl-N-phenylbenzamido)-2-phenylacetate (3fa)



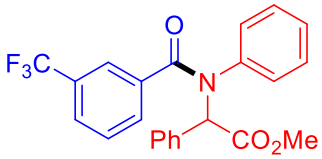
$C_{23}H_{21}NO_3$
M. W.: 359.4250 g/mol

Prepared according to the **GP-2**, using 2-oxo-2-(o-tolyl)acetic acid (16.4 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-phenyl-2-(phenylimino)acetate (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3fa**) was obtained as light-yellow liquid, recording a yield of 85% (30.5 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{22}NO_3]^+$: 360.1594; Found 360.1601.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.17 (m, 3H), 7.12–7.09 (m, 2H), 7.03–6.98 (m, 3H), 6.94–6.87 (m, 6H), 6.39 (s, 1H), 3.84 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 171.2, 139.6, 136.2, 135.0, 134.0, 130.4, 130.3, 130.1, 128.6, 128.6, 128.5, 128.2, 127.6, 127.3, 124.8, 64.2, 52.7, 19.6.

methyl 2-phenyl-2-(N-phenyl-3-(trifluoromethyl)benzamido)acetate (3ga)



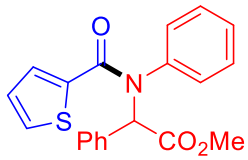
$C_{23}H_{18}F_3NO_3$
M. W.: 413.3962 g/mol

Prepared according to the **GP-2**, using 2-oxo-2-(3-(trifluoromethyl)phenyl)acetic acid (21.8 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-phenyl-2-(phenylimino)acetate (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product through column chromatography on silica gel. The product (**3ga**) was obtained as light-yellow liquid, recording a yield of 88% (36 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{23}H_{19}F_3NO_3]^+$: 414.1312; Found 414.1316.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.49–7.42 (dd, *J* = 18.5, 7.8 Hz, 2H), 7.25–7.18 (m, 5H), 7.12–7.09 (m, 2H), 7.02–6.97 (m, 3H), 6.89 (s, 1H), 6.30 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 169.7, 139.8, 136.5, 133.5, 131.9, 130.8, 130.4, 128.8, 128.6, 128.6, 128.3, 127.8, 127.4, 126.4 (q, *J* = 4.0 Hz), 125.8 (q, *J* = 4.2 Hz), 123.6 (q, *J* = 273 Hz), 65.0, 52.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.85.

methyl 2-phenyl-2-(N-phenylthiophene-2-carboxamido)acetate (3ha)



$C_{20}H_{17}NO_3S$
M. W.: 351.4200 g/mol

Prepared according to the **GP-2**, using 2-oxo-2-(thiophen-2-yl)acetic acid (15.6 mg, 0.1 mmol, 1.0 equiv), (Z)-methyl 2-phenyl-2-(phenylimino)acetate (72 mg, 0.3 mmol, 3.0 equiv), K_2HPO_4 (21 mg, 0.12 mmol, 1.2 equiv), Ir[dF(CF_3)ppy$_2$(dtbpy)]PF_6 (1.1 mg, 0.001 mmol, 0.01 equiv) and DCM:H_2O (1:1) (0.1 M). A (10/1 v/v) of petroleum ether/ethyl acetate was used as eluent for the purification of the desired product

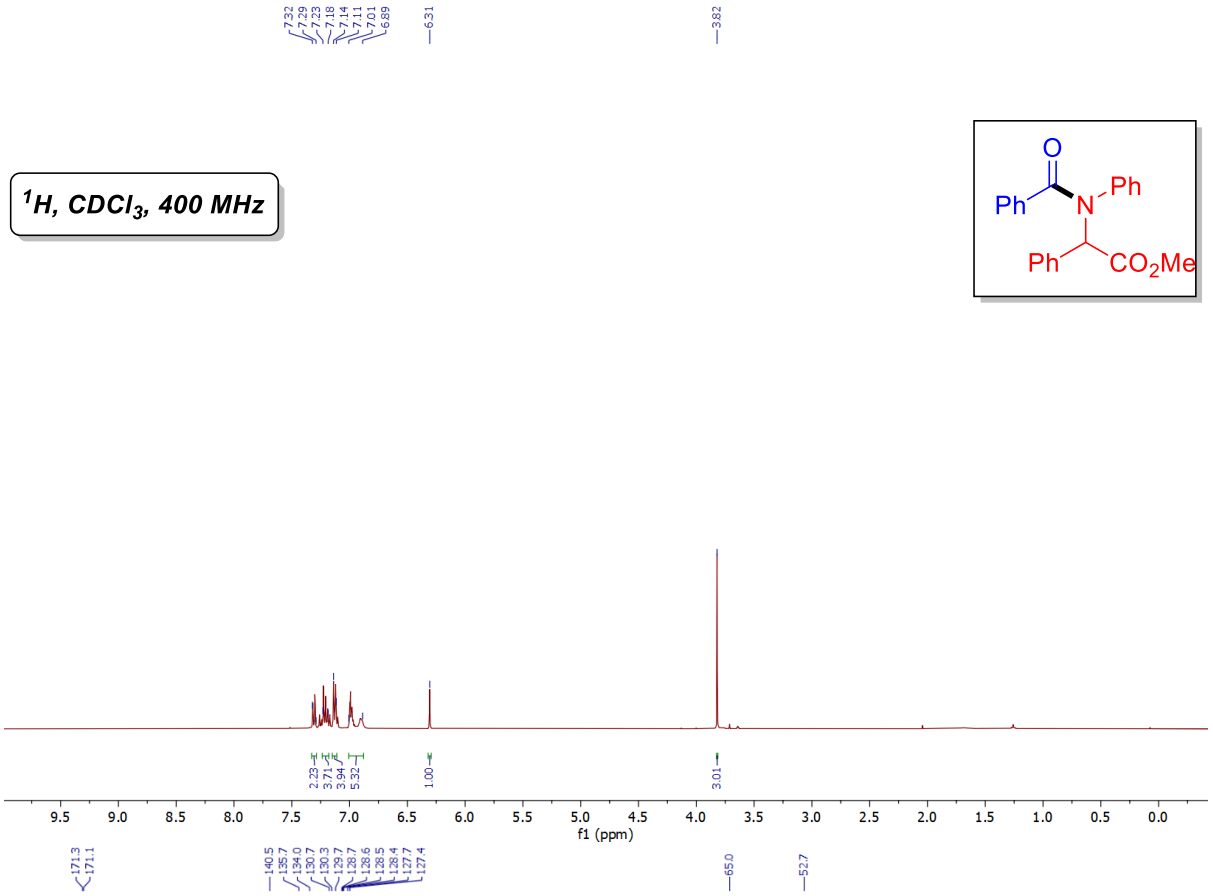
through column chromatography on silica gel. The product (**3ha**) was obtained as light-yellow liquid, recording a yield of 86% (30 mg).

HRMS (ESI)**:** m/z $[M+H]^+$ Calculated for $[C_{20}H_{18}NO_3S]^+$: 352.1002; Found 352.1008.

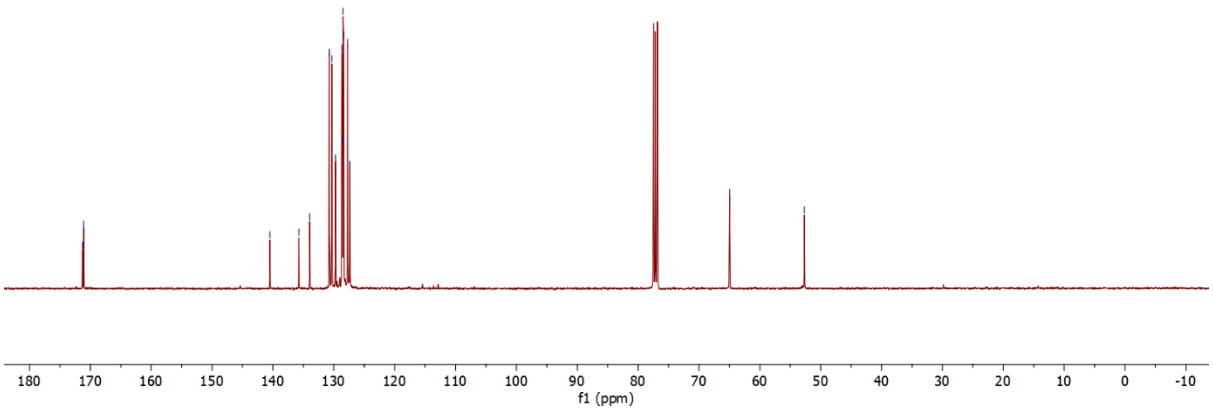
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.28–7.26 (m, 1H), 7.23–7.20 (m, 1H), 7.15–7.10 (m, 5H), 7.05–7.01 (m, 2H), 6.91–6.87 (m, 2H), 6.25 (s, 1H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 170.0, 141.6, 136.1, 135.3, 130.0, 129.6, 129.5, 128.9(2C), 127.8, 127.6, 127.4, 126.4, 61.5, 53.0.

10. Experimental NMR data

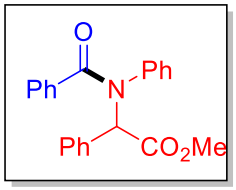
methyl 2-phenyl-2-(N-phenylbenzamido)acetate (3aa)



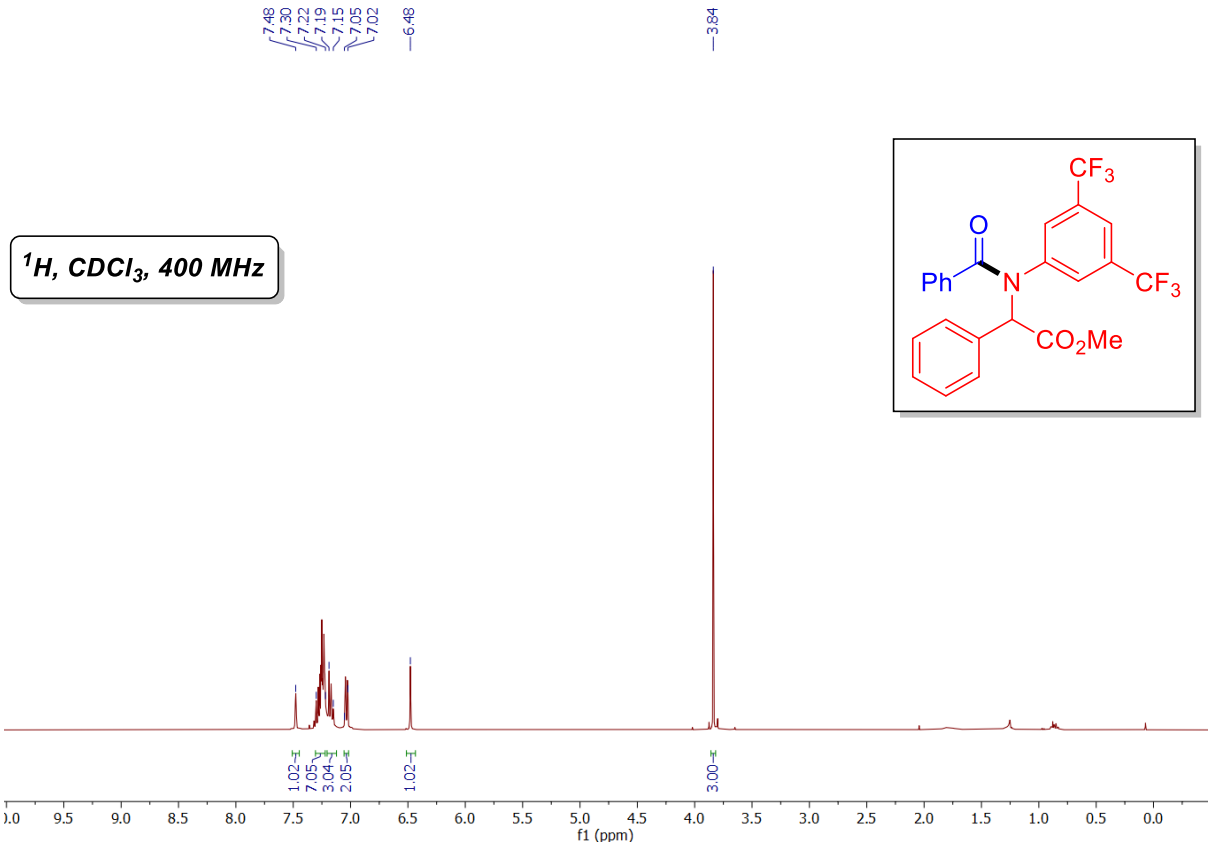
^{1}H, $CDCl_3$, 400 MHz



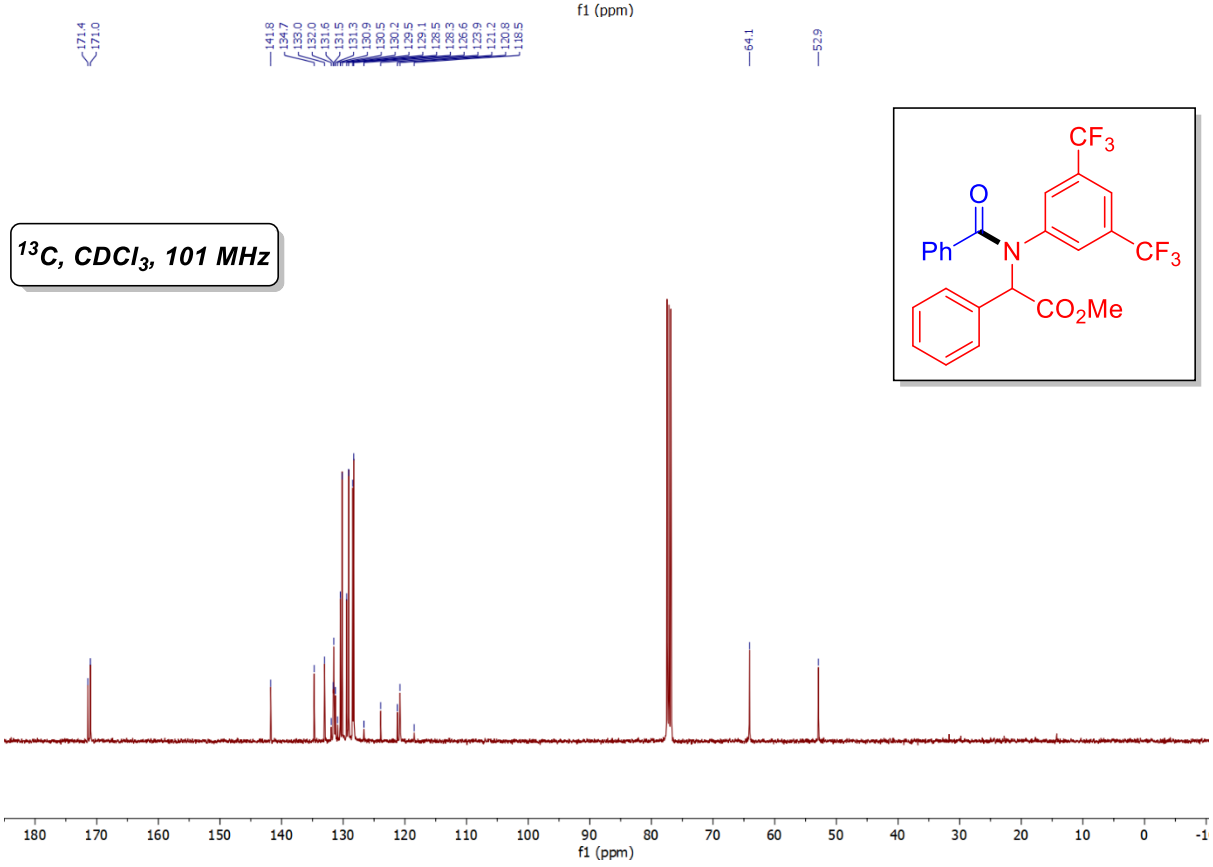
^{13}C, $CDCl_3$, 101 MHz



methyl 2-(N-(3,5-bis(trifluoromethyl)phenyl)benzamido)-2-phenylacetate (3ab)

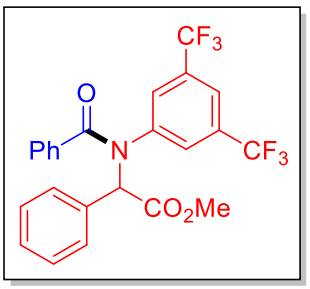


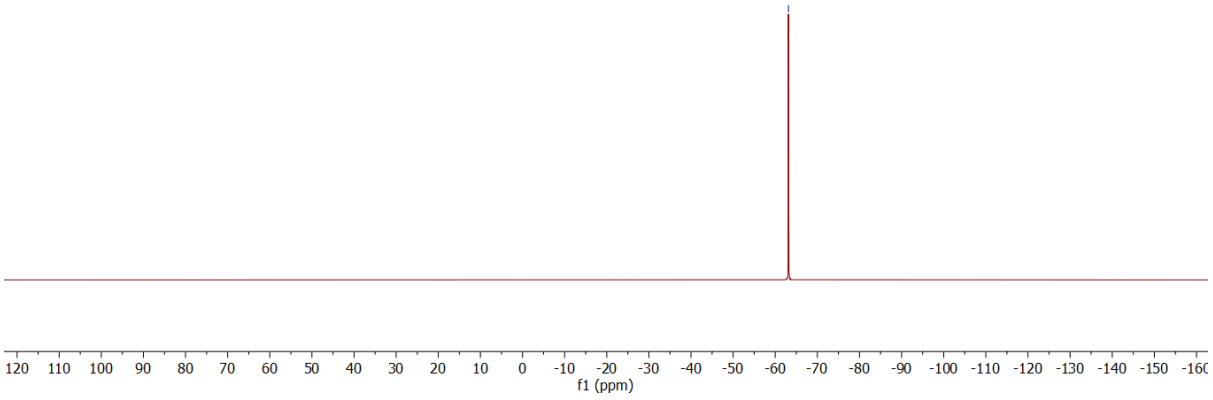
^{1}H, CDCl$_3$, 400 MHz



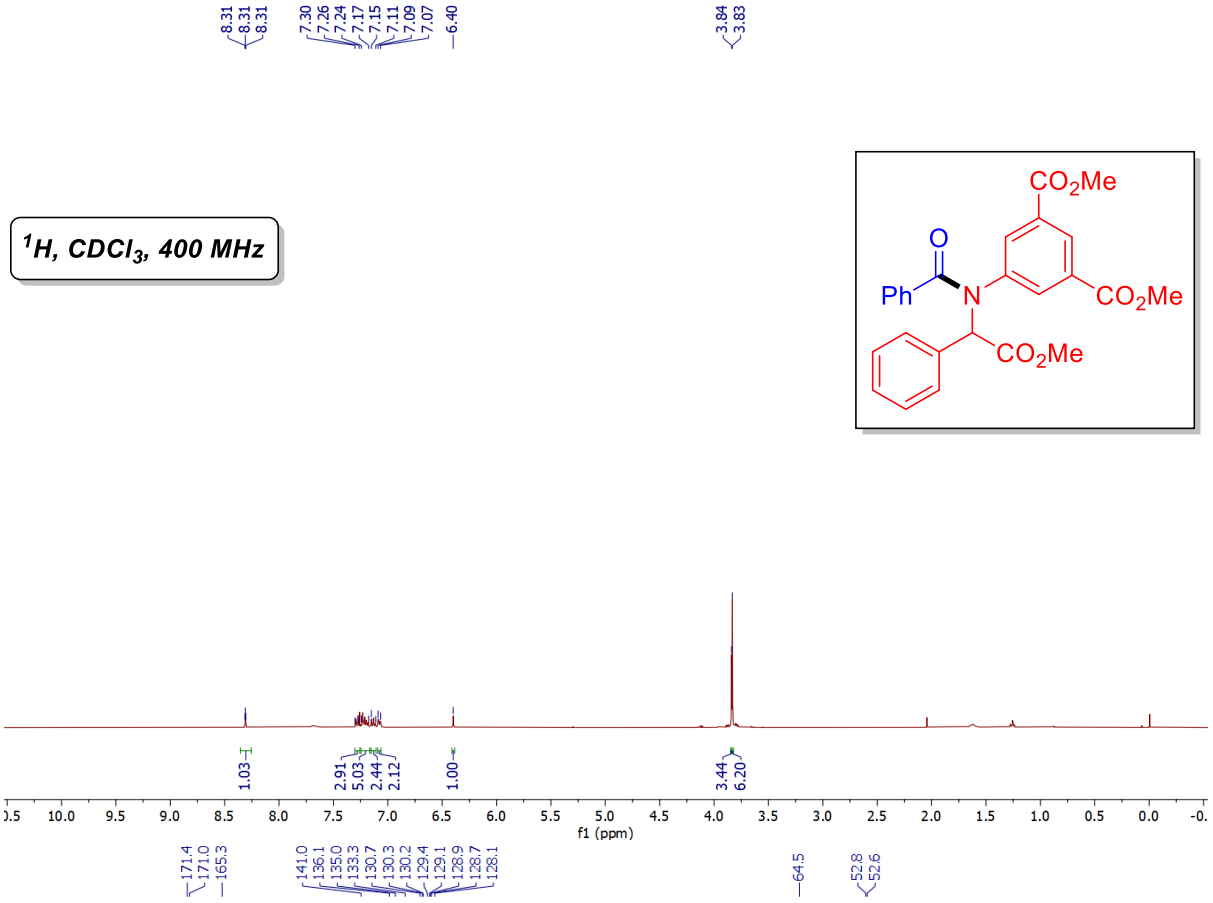
^{13}C, CDCl$_3$, 101 MHz

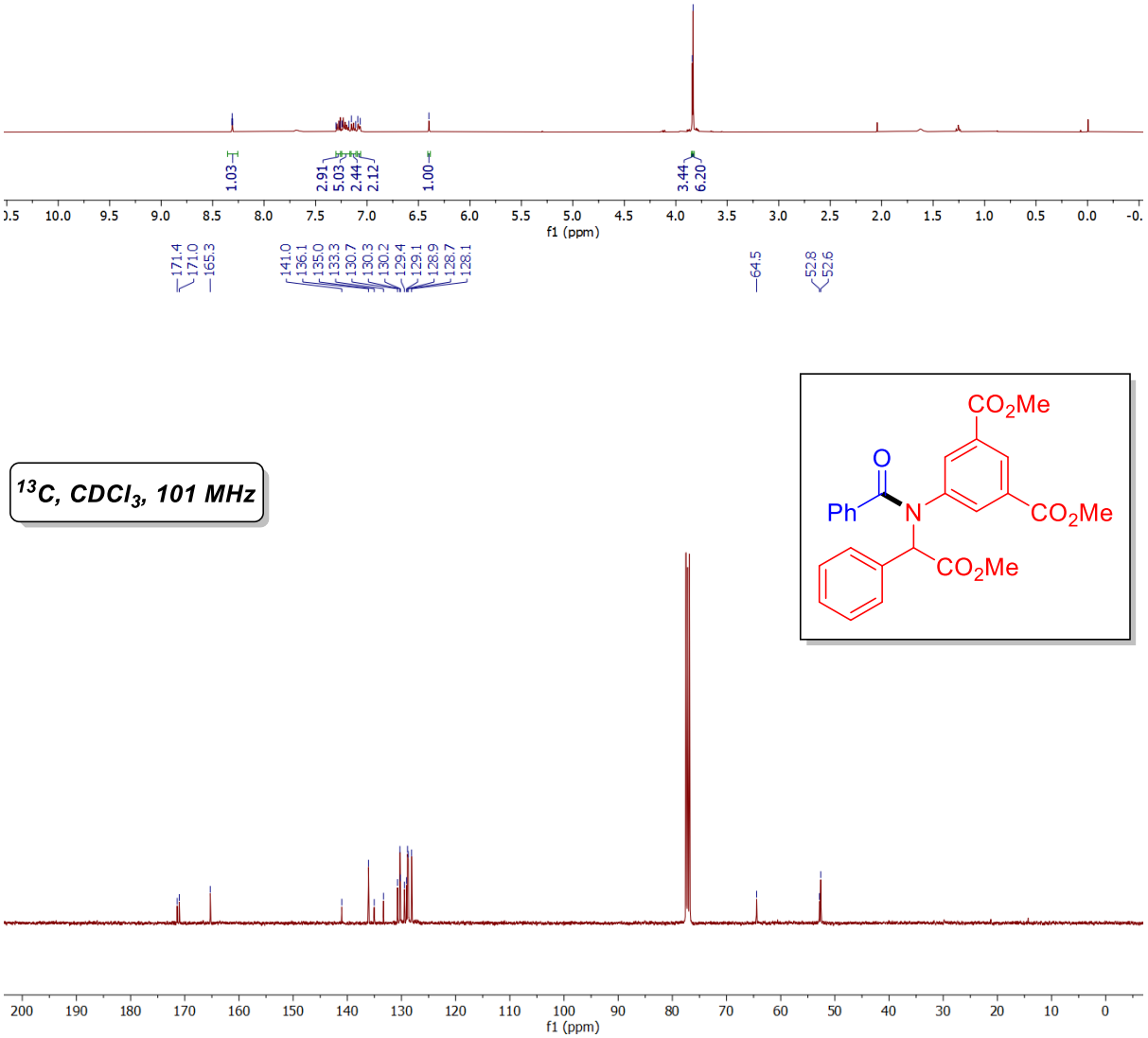
^{19}F, $CDCl_3$, 376 MHz





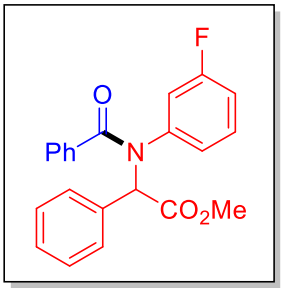
dimethyl 5-(N-(2-methoxy-2-oxo-1-phenylethyl)benzamido)isophthalate (3ac)

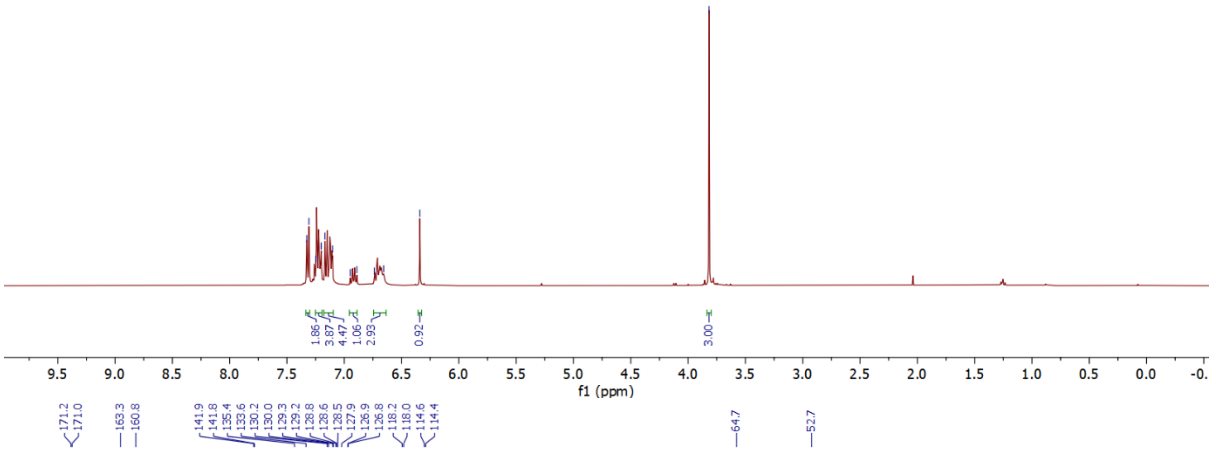




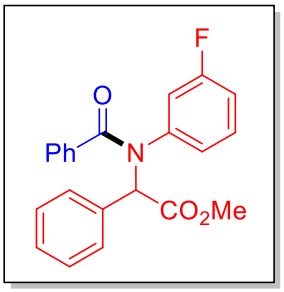
methyl 2-(N-(3-fluorophenyl)benzamido)-2-phenylacetate (3ad)

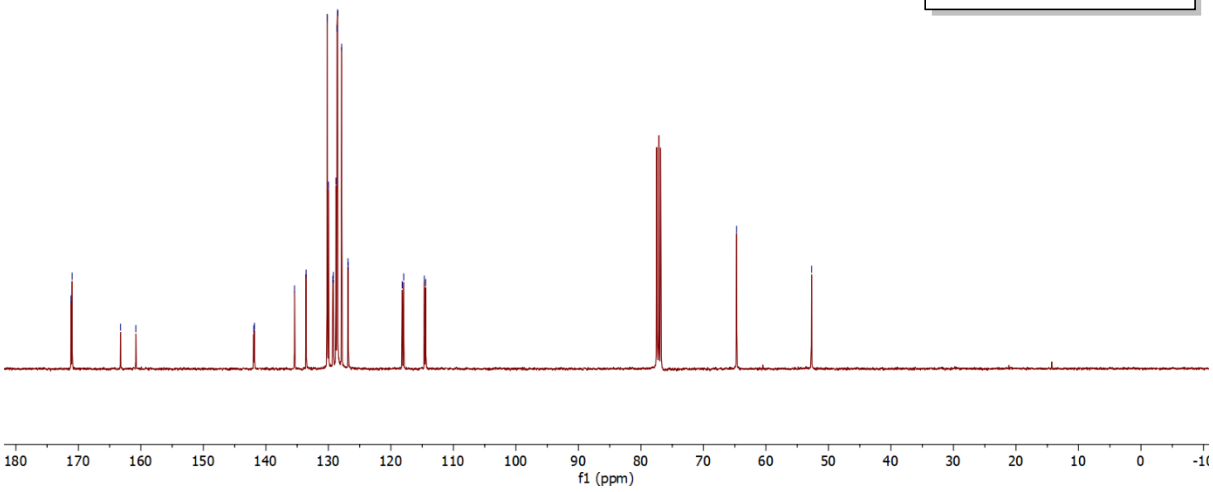
^{1}H, $CDCl_3$, 400 MHz



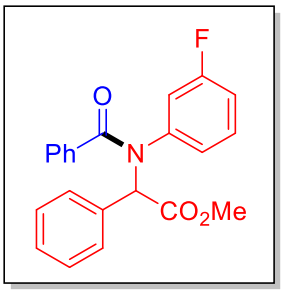


^{13}C, $CDCl_3$, 101 MHz



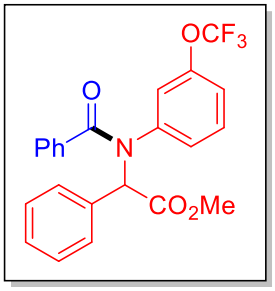


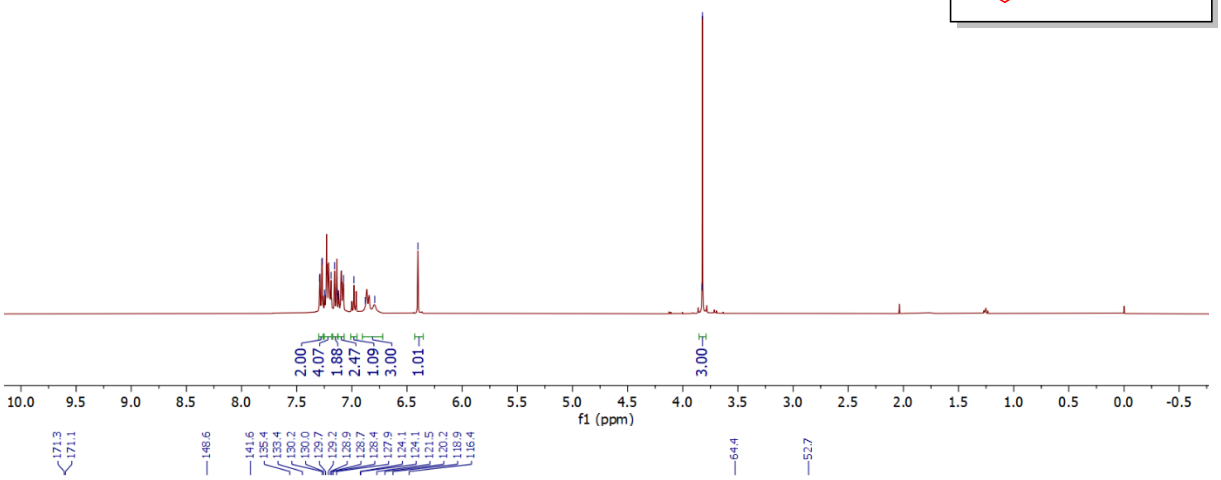
^{19}F, $CDCl_3$, 376 MHz



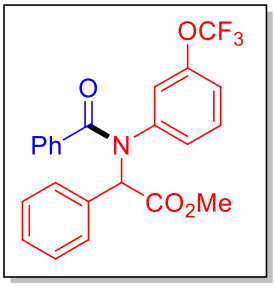
methyl 2-phenyl-2-(N-(3-(trifluoromethoxy)phenyl)benzamido)acetate (3ae)

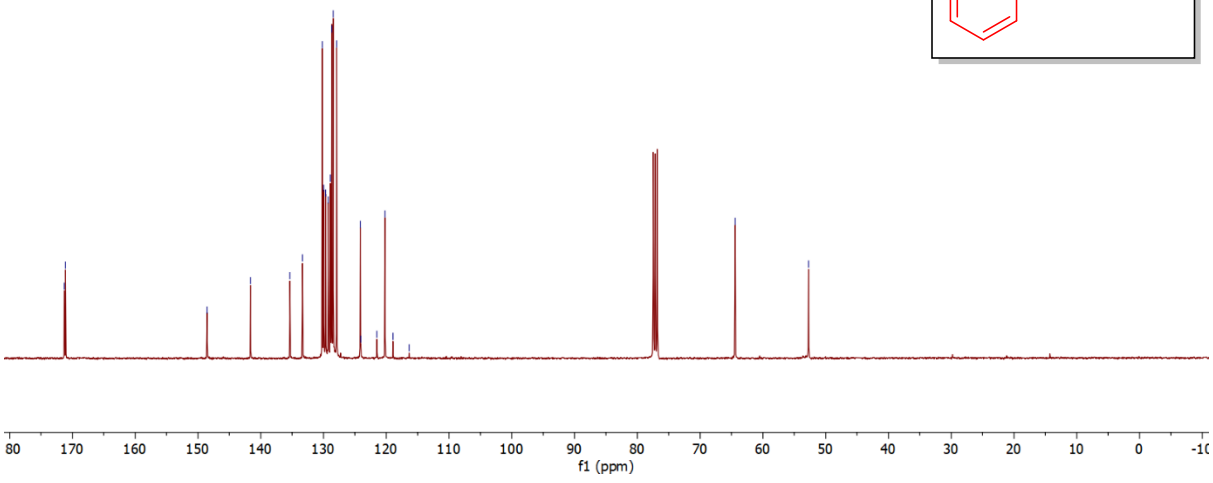
^{1}H, CDCl$_3$, 400 MHz



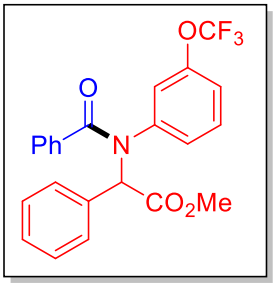


^{13}C, CDCl$_3$, 101 MHz

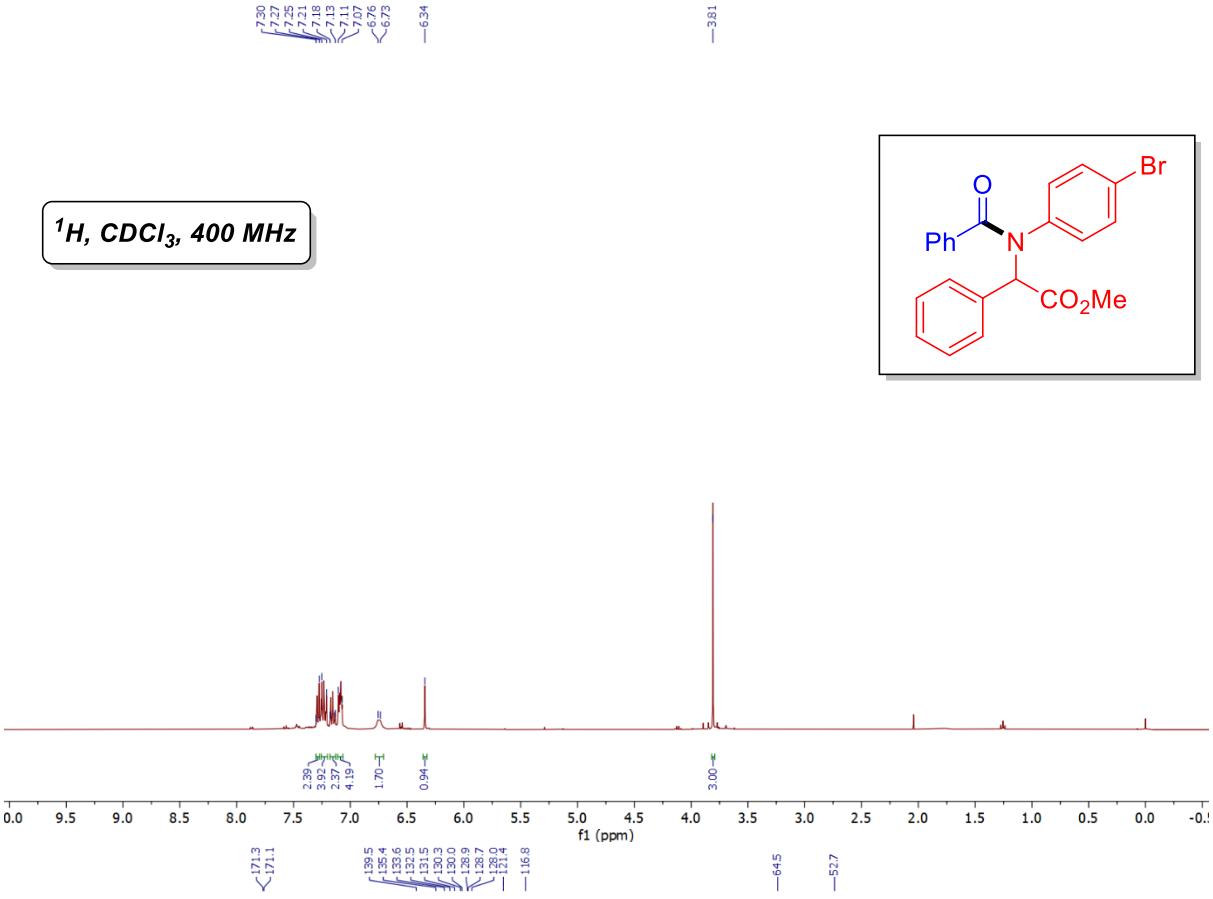




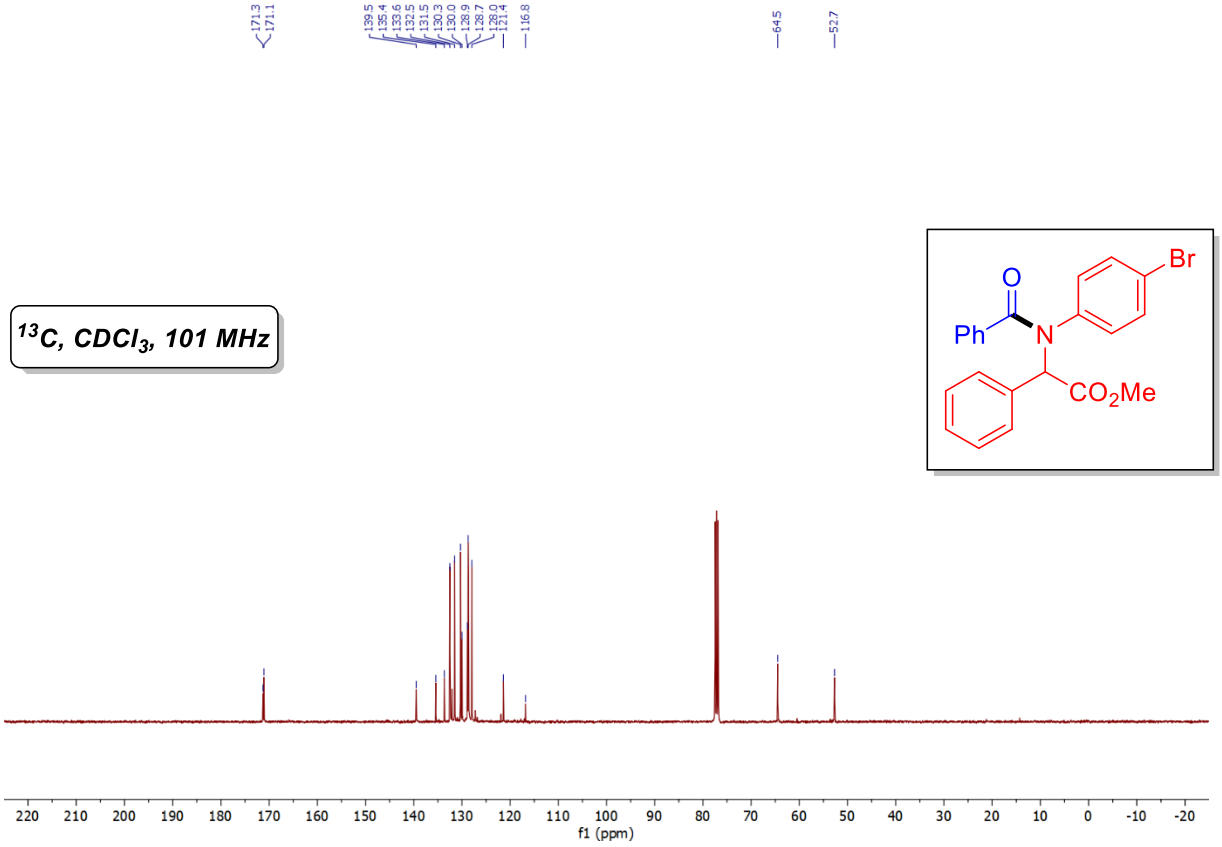
^{19}F, $CDCl_3$, 376 MHz



methyl 2-(N-(4-bromophenyl)benzamido)-2-phenylacetate (3af)

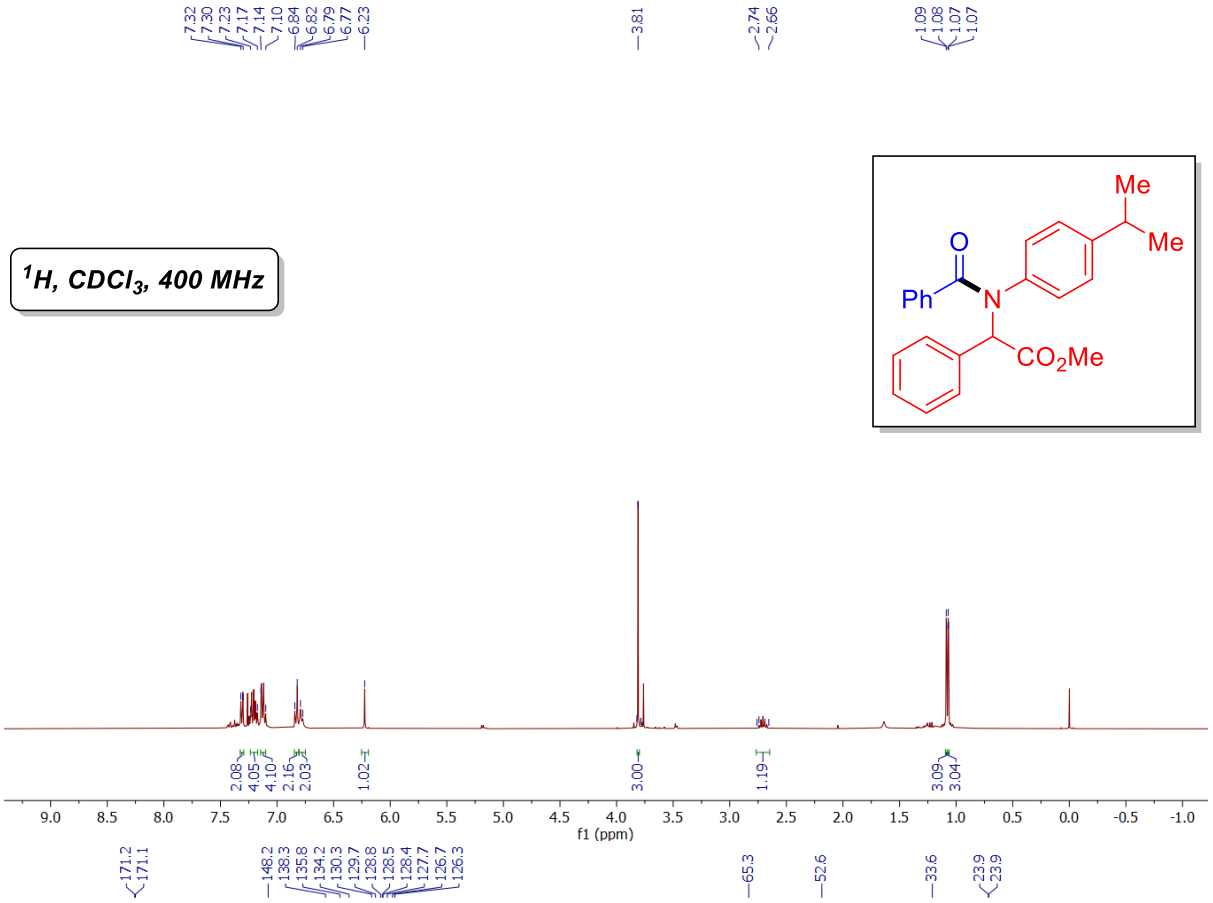


^{1}H, CDCl$_3$, 400 MHz



^{13}C, CDCl$_3$, 101 MHz

methyl 2-(N-(4-isopropylphenyl)benzamido)-2-phenylacetate (3ag)

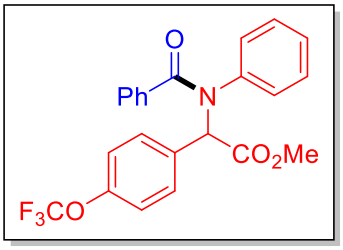


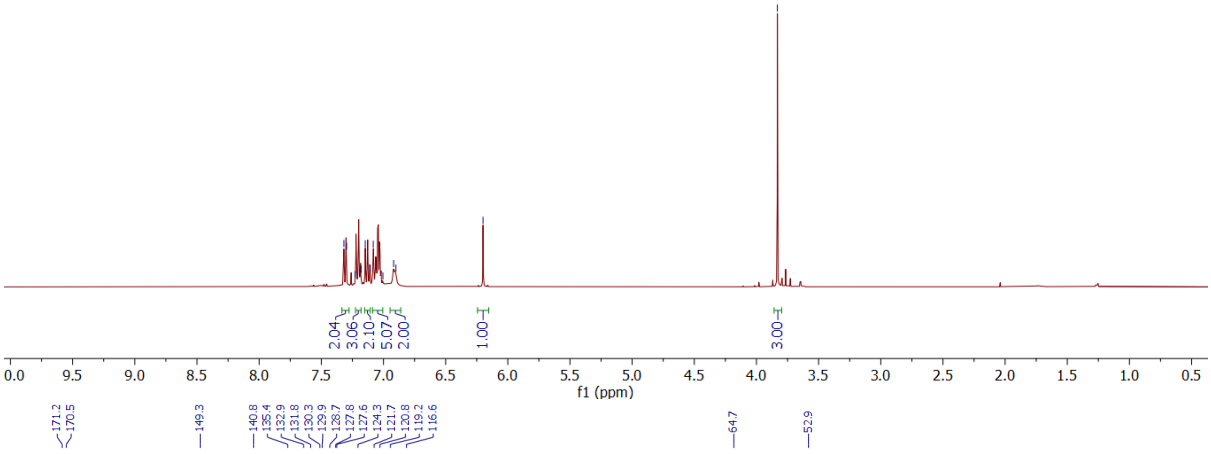
^{1}H, $CDCl_3$, 400 MHz

^{13}C, $CDCl_3$, 101 MHz

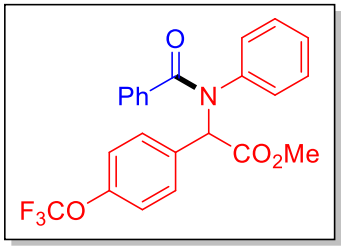
methyl 2-(N-phenylbenzamido)-2-(4-(trifluoromethoxy)phenyl)acetate (3ah)

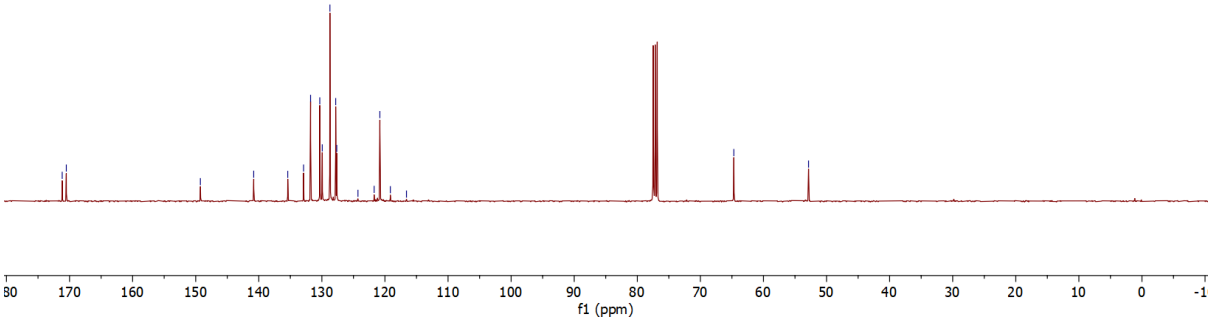
^{1}H, CDCl$_3$, 400 MHz

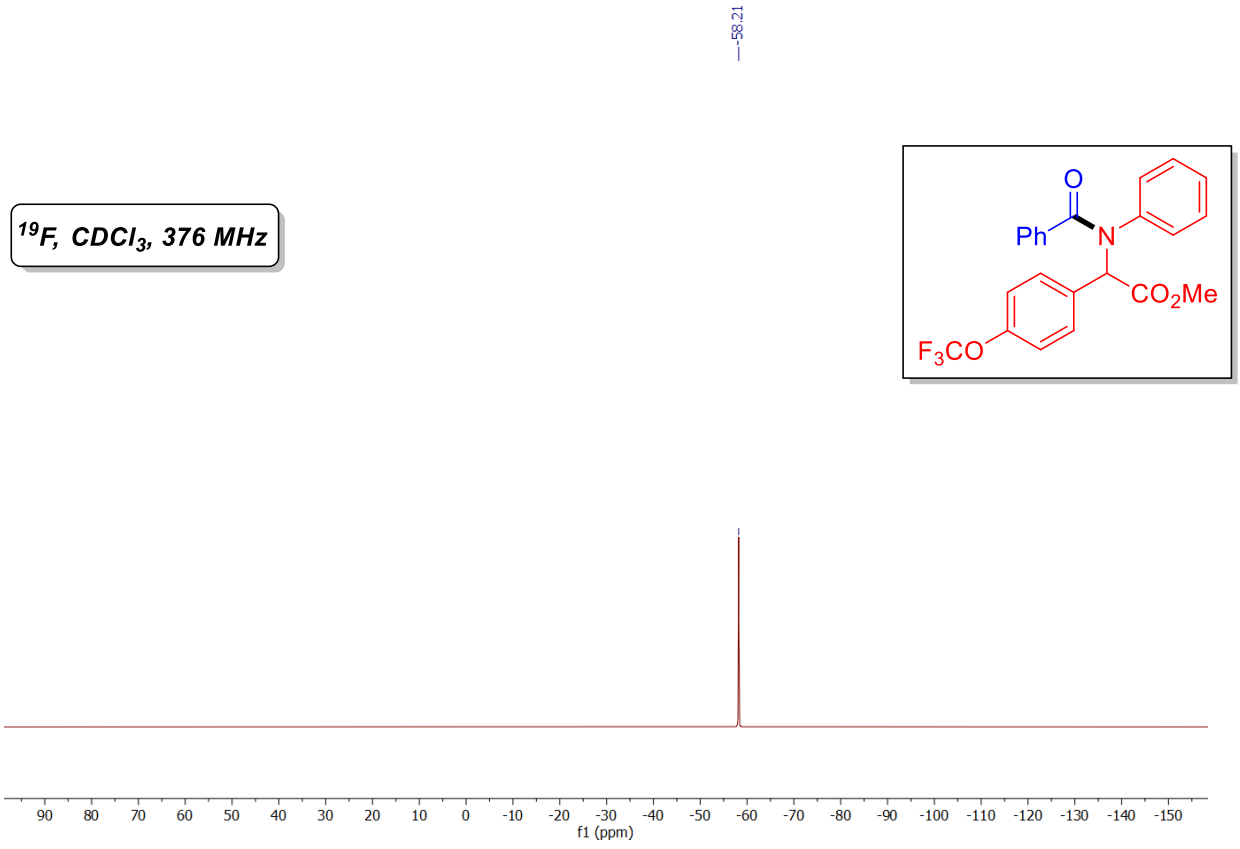




^{13}C, CDCl$_3$, 101 MHz

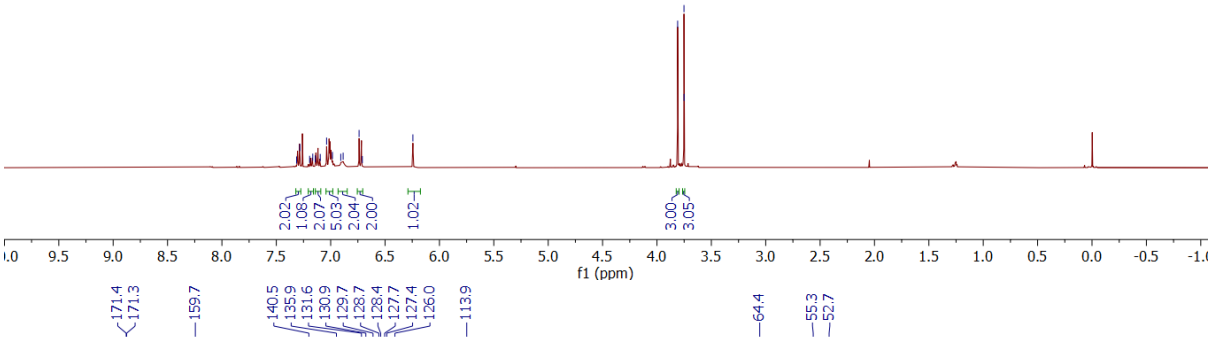




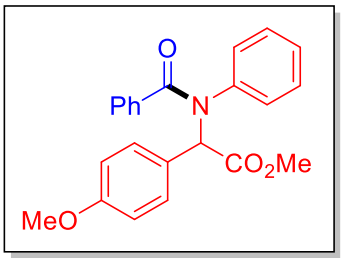

-58.21
^{19}F, $CDCl_3$, 376 MHz
O
Ph
N
CO_2Me
F_3CO
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

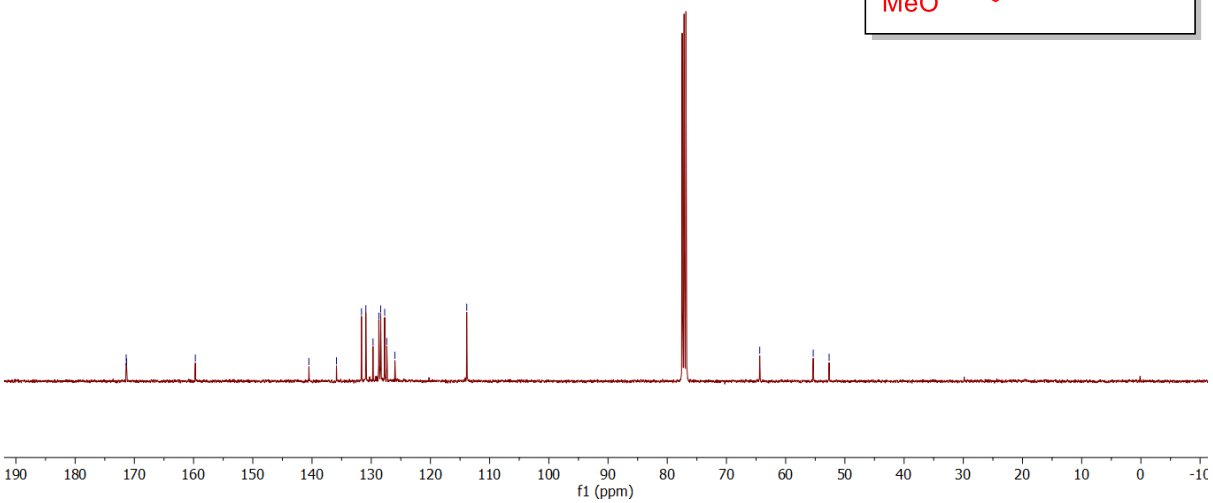
methyl 2-(4-methoxyphenyl)-2-(N-phenylbenzamido)acetate (3ai)

^{1}H, $CDCl_3$, 400 MHz

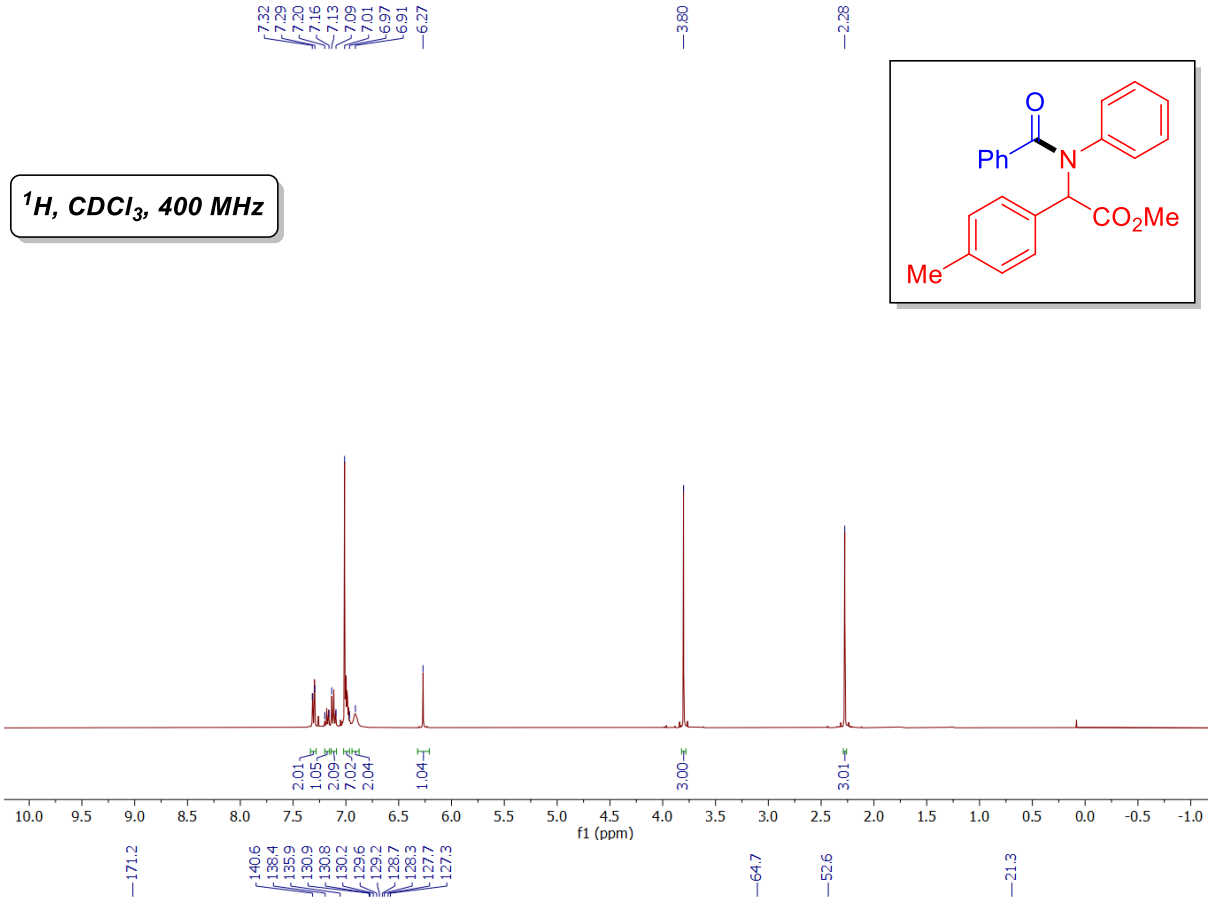


^{13}C, $CDCl_3$, 101 MHz

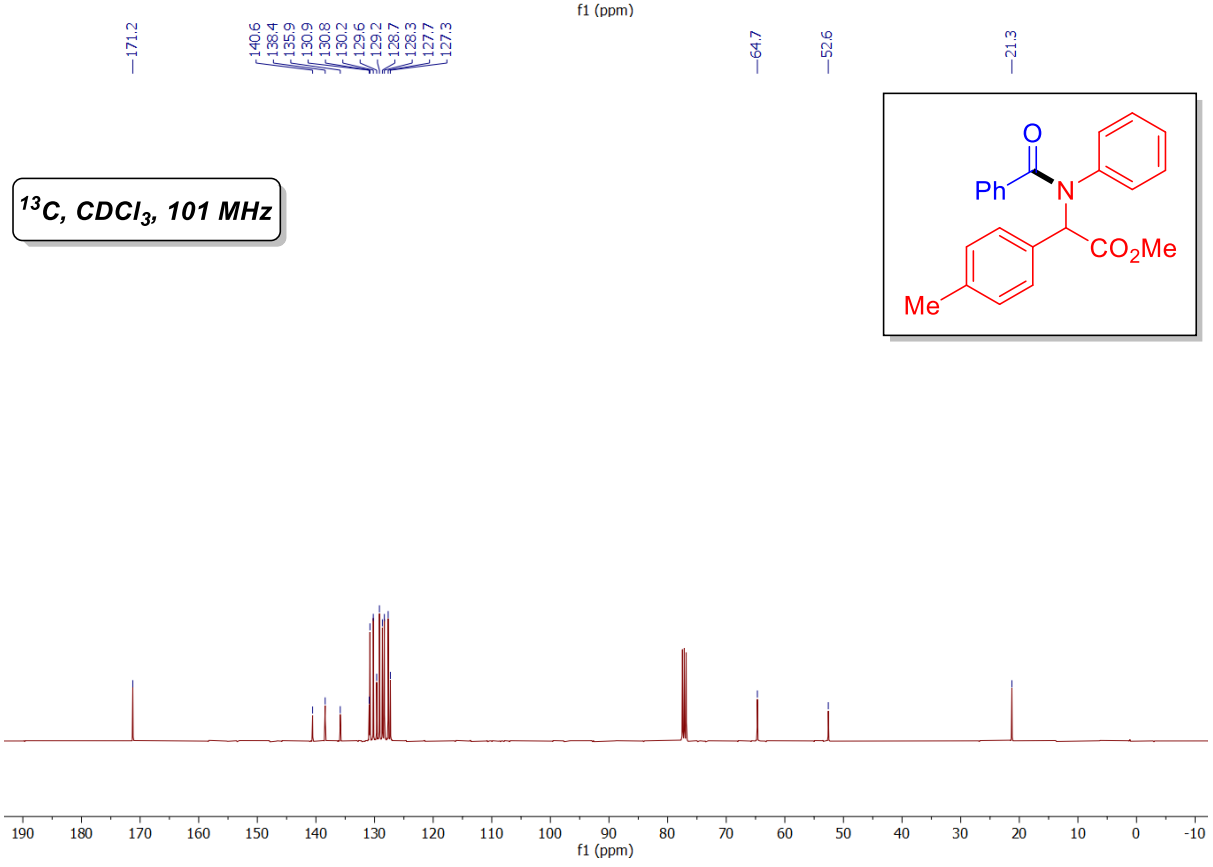




methyl 2-(N-phenylbenzamido)-2-(p-tolyl)acetate (3aj)

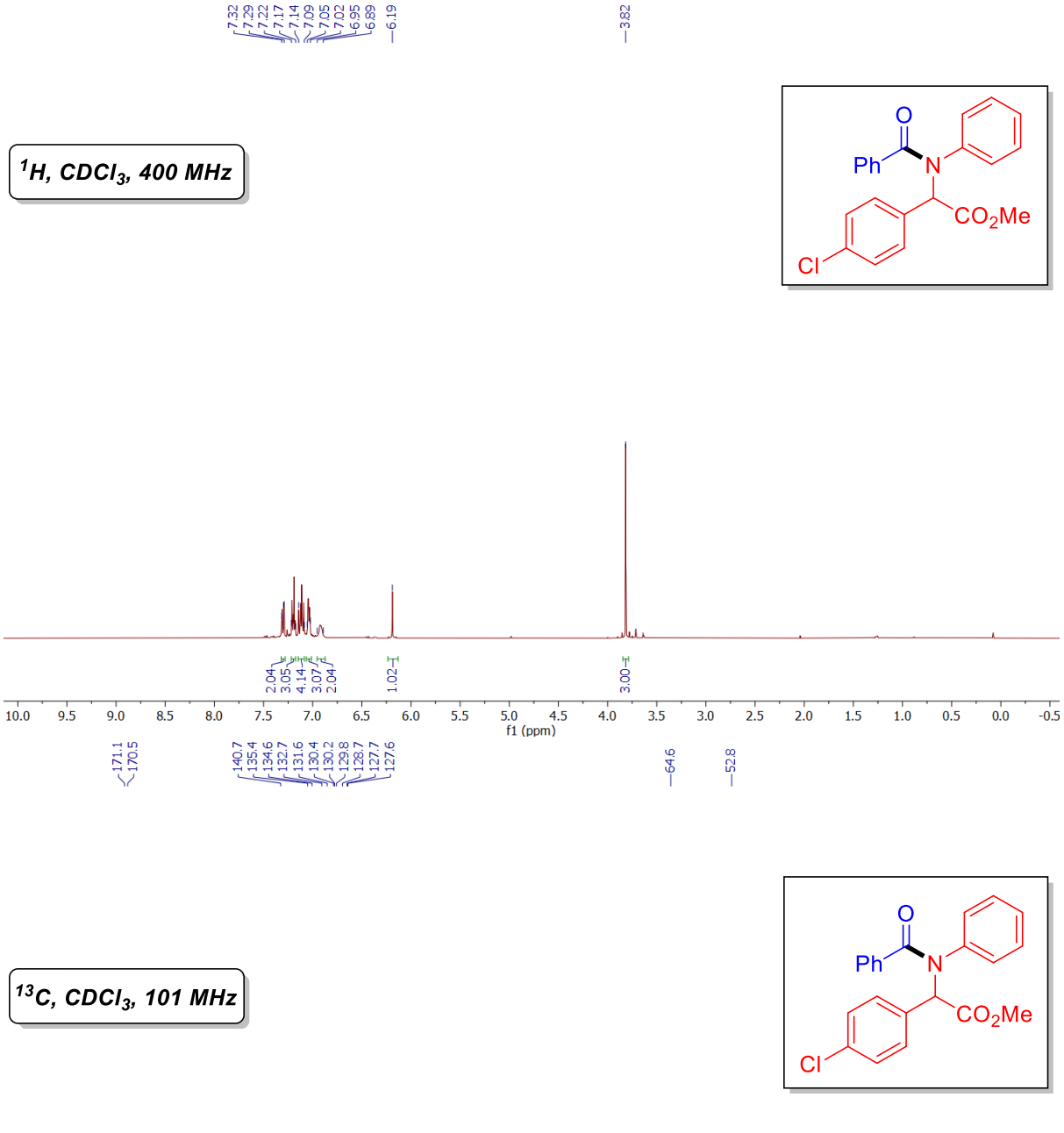


^{1}H, CDCl$_3$, 400 MHz



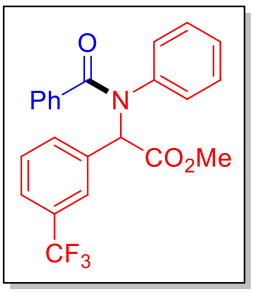
^{13}C, CDCl$_3$, 101 MHz

methyl 2-(4-chlorophenyl)-2-(N-phenylbenzamido)acetate (3ak)

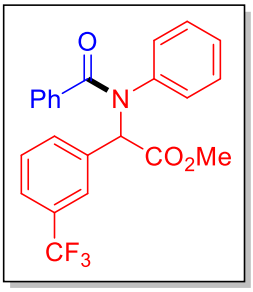


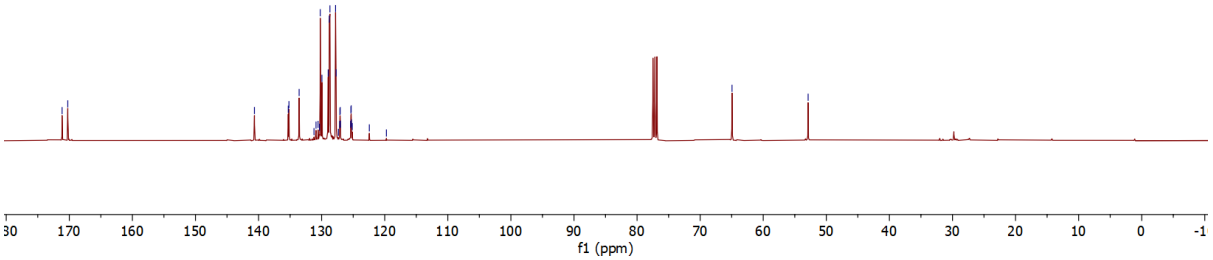
methyl 2-(N-phenylbenzamido)-2-(3-(trifluoromethyl)phenyl)acetate (3al)

^{1}H, $CDCl_3$, 400 MHz

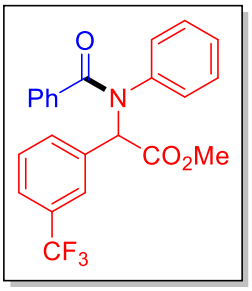


^{13}C, $CDCl_3$, 101 MHz



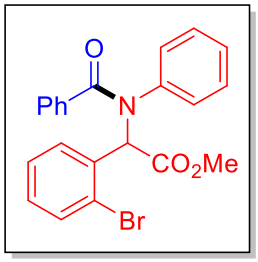


^{19}F, $CDCl_3$, 376 MHz

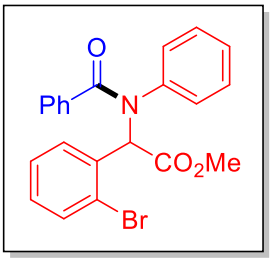


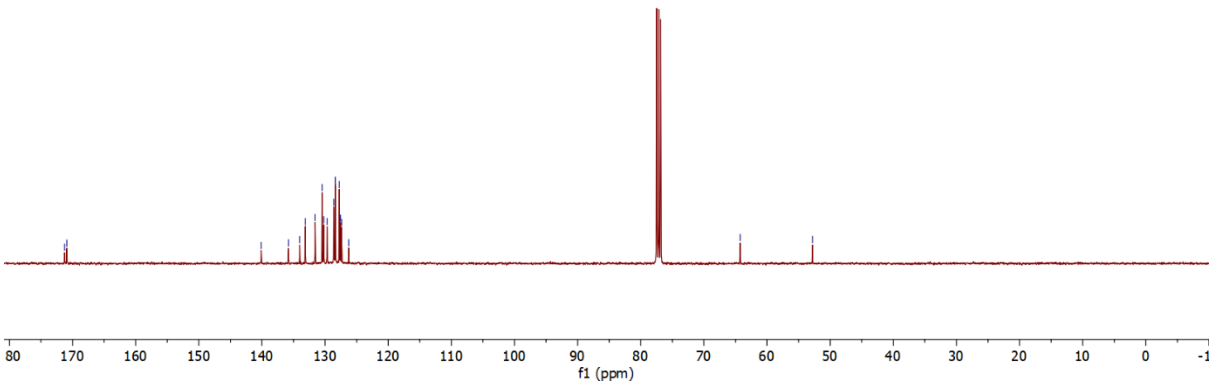
methyl 2-(2-bromophenyl)-2-(N-phenylbenzamido)acetate (3am)

^{1}H, CDCl$_3$, 400 MHz



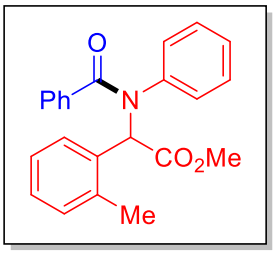
^{13}C, CDCl$_3$, 101 MHz

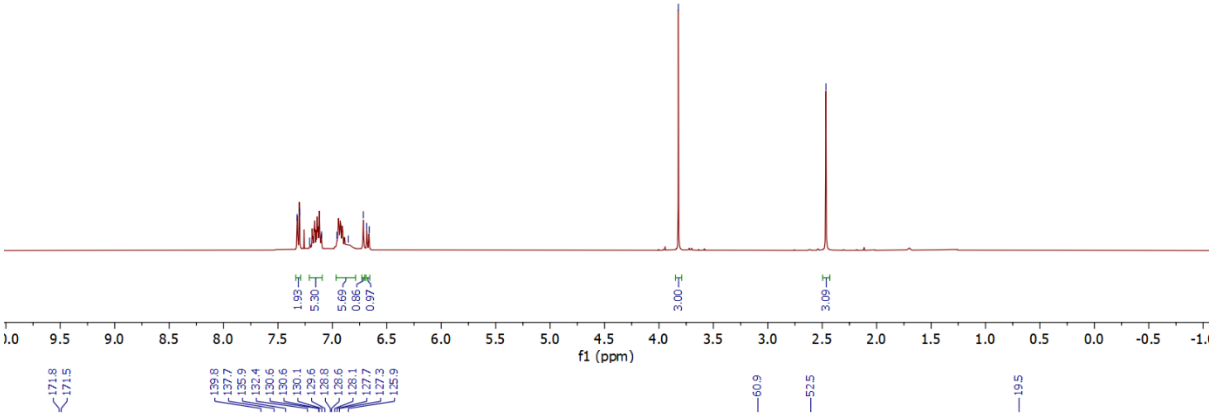




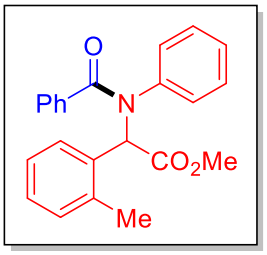
methyl 2-(N-phenylbenzamido)-2-(o-tolyl)acetate (3an)

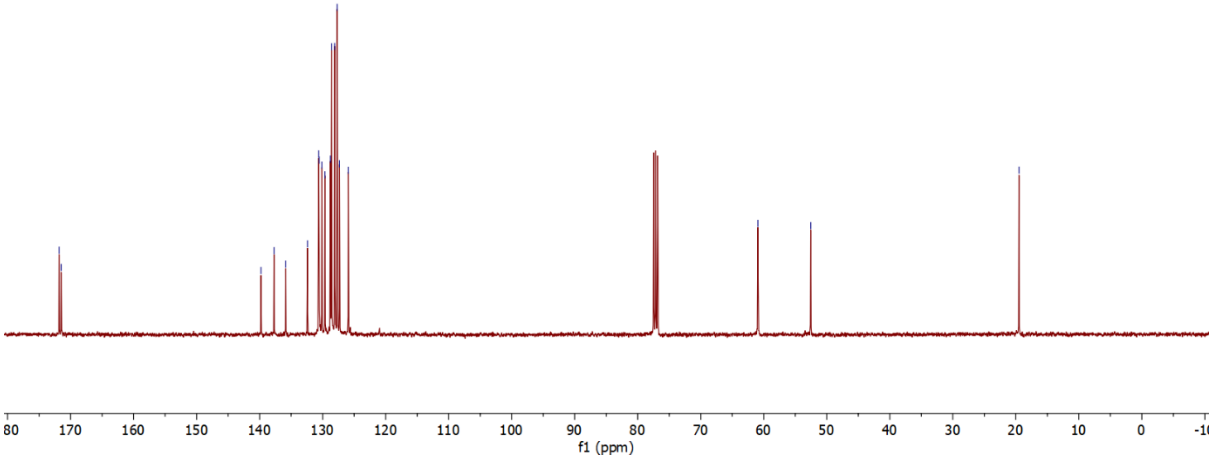
^{1}H, CDCl$_3$, 400 MHz



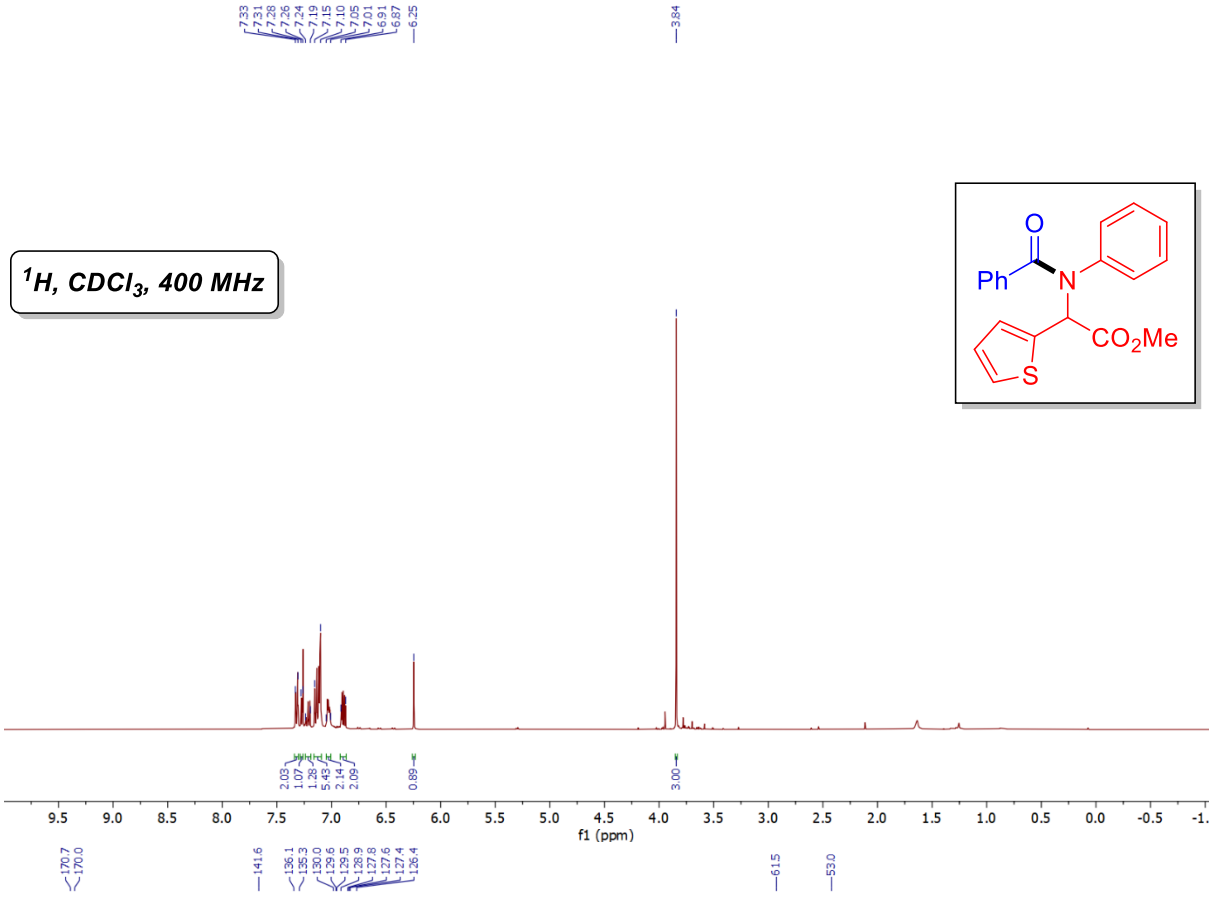


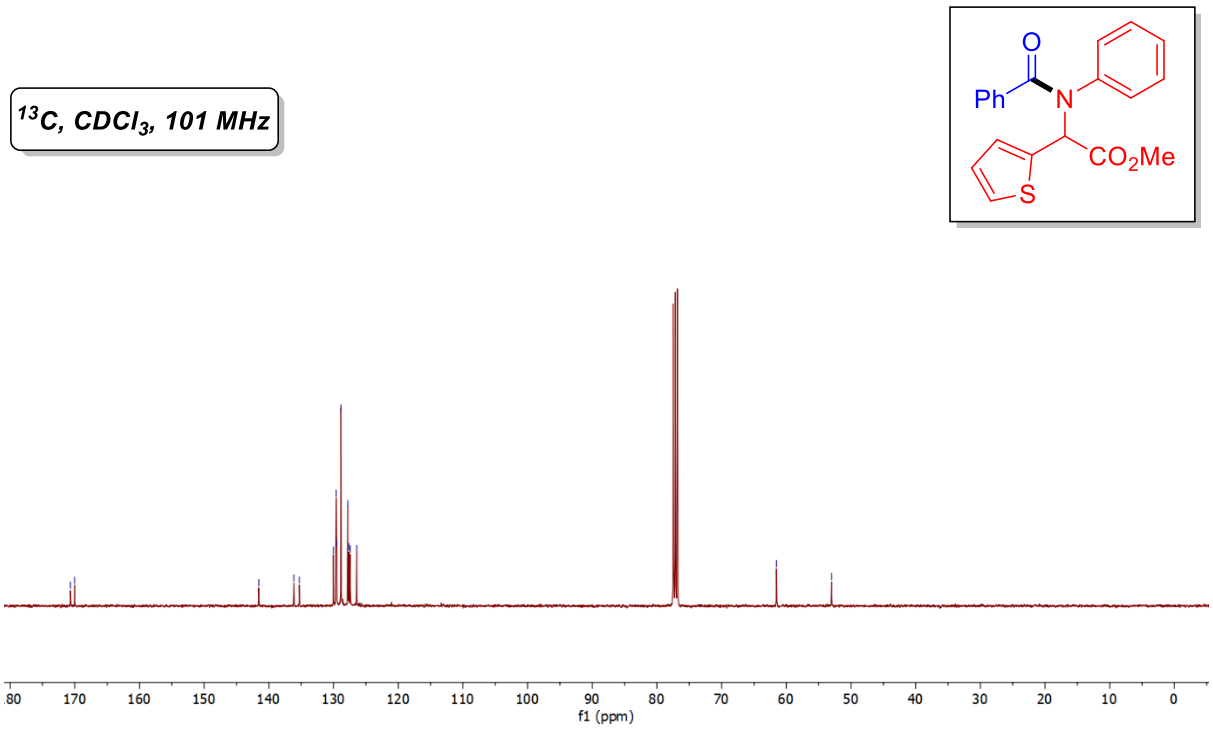
^{13}C, CDCl$_3$, 101 MHz



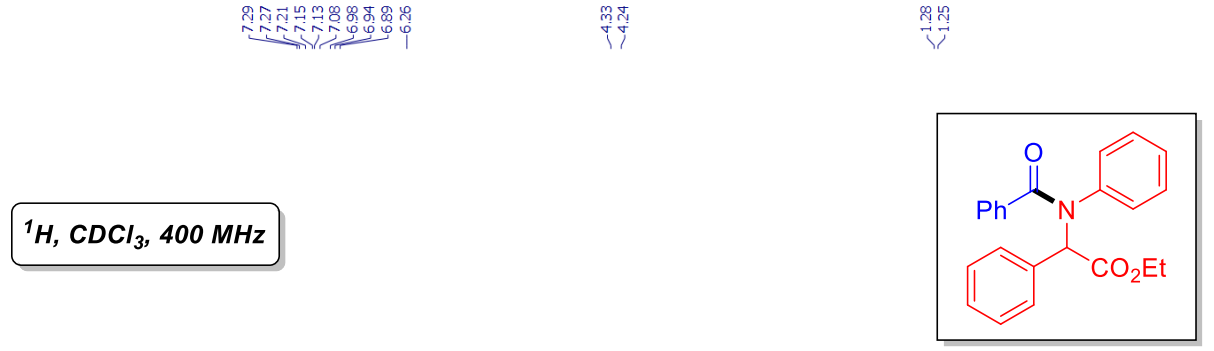


methyl 2-(N-phenylbenzamido)-2-(thiophen-2-yl)acetate (3ao)

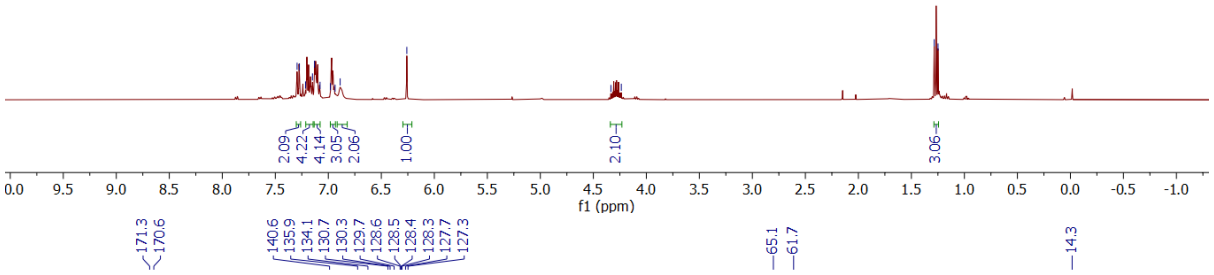




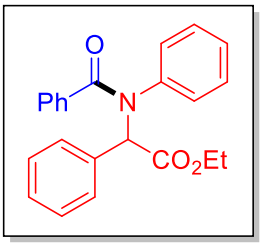
ethyl 2-phenyl-2-(N-phenylbenzamido)acetate (3ap)

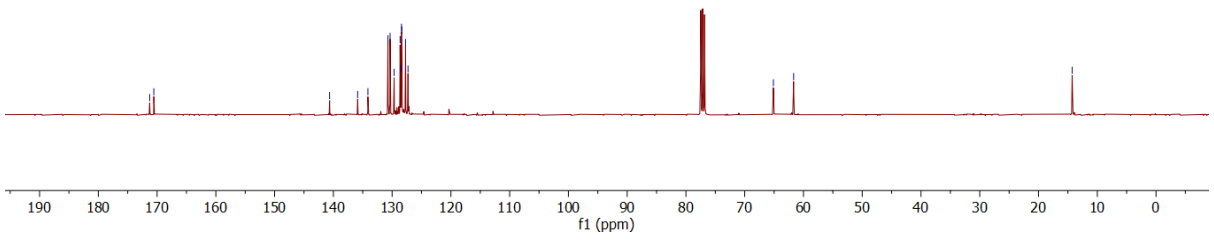


^{1}H, CDCl$_3$, 400 MHz



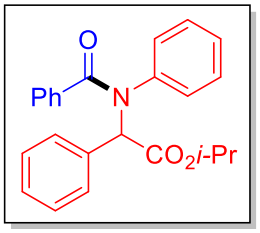
^{13}C, CDCl$_3$, 101 MHz

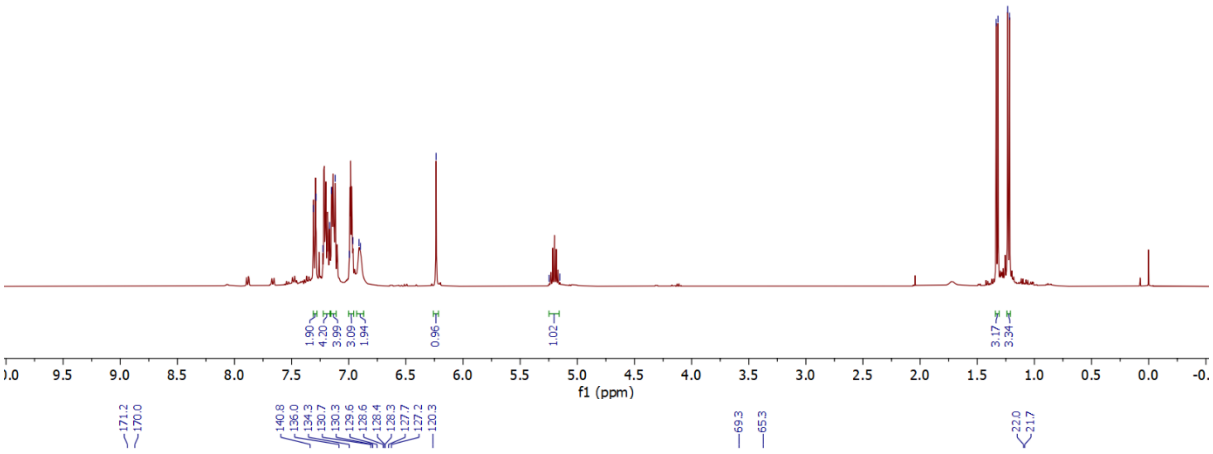




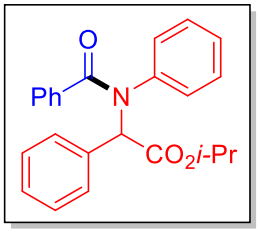
isopropyl 2-phenyl-2-(N-phenylbenzamido)acetate (3aq)

^{1}H, $CDCl_3$, 400 MHz



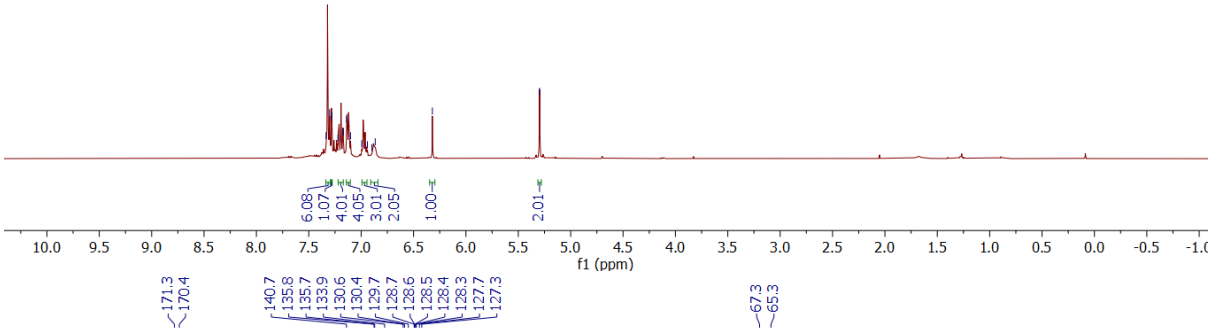


^{13}C, $CDCl_3$, 101 MHz

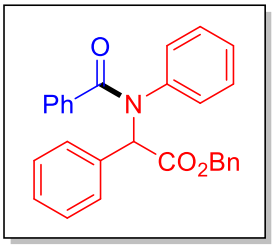


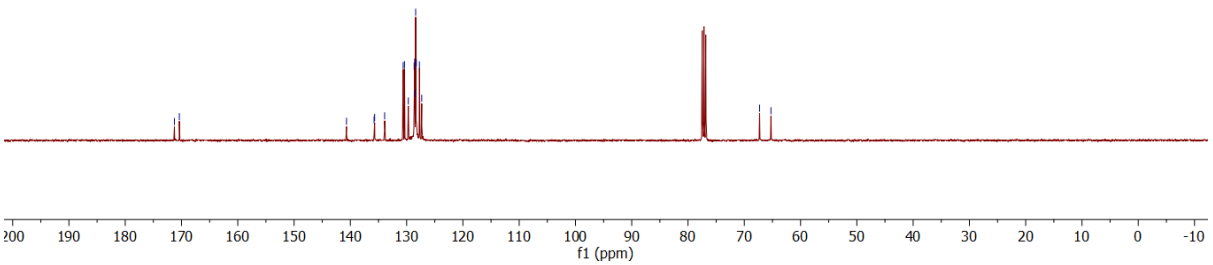
benzyl 2-phenyl-2-(N-phenylbenzamido)acetate (3ar)

^{1}H, CDCl$_3$, 400 MHz



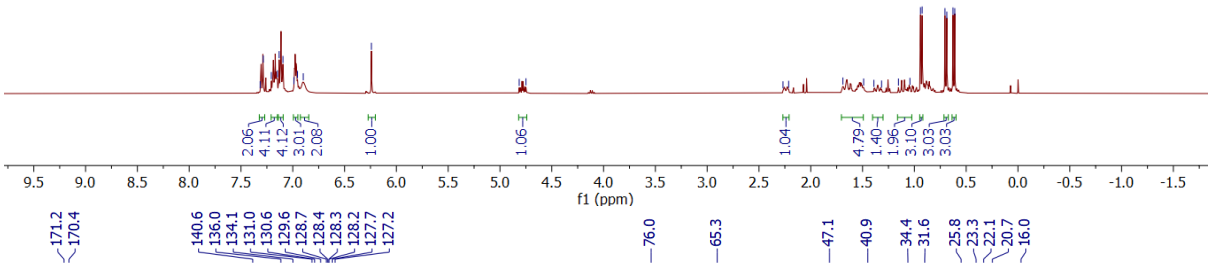
^{13}C, CDCl$_3$, 101 MHz



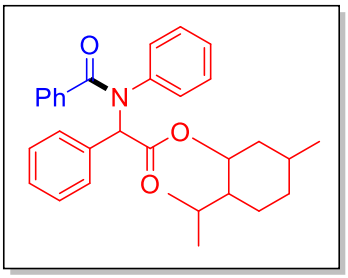


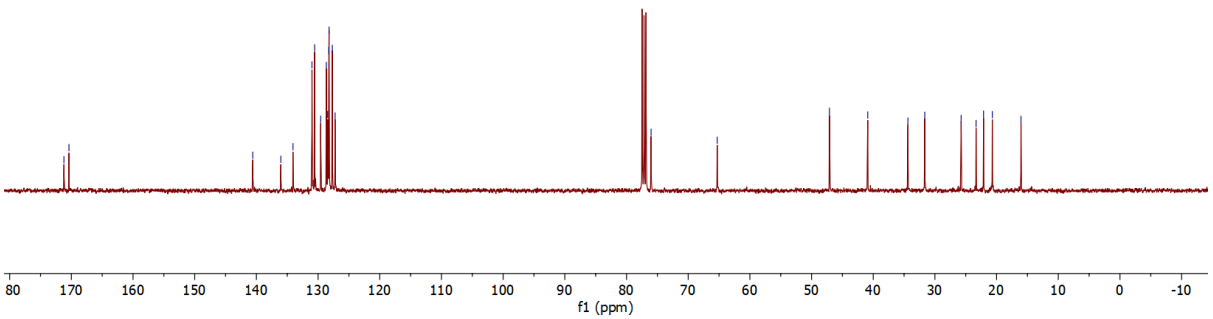
2-isopropyl-5-methylcyclohexyl 2-phenyl-2-(N-phenylbenzamido)acetate (3as)

^{1}H, $CDCl_3$, 400 MHz



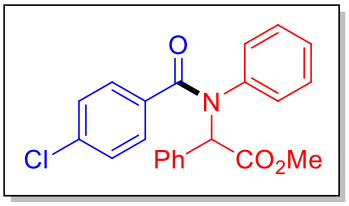
^{13}C, $CDCl_3$, 101 MHz

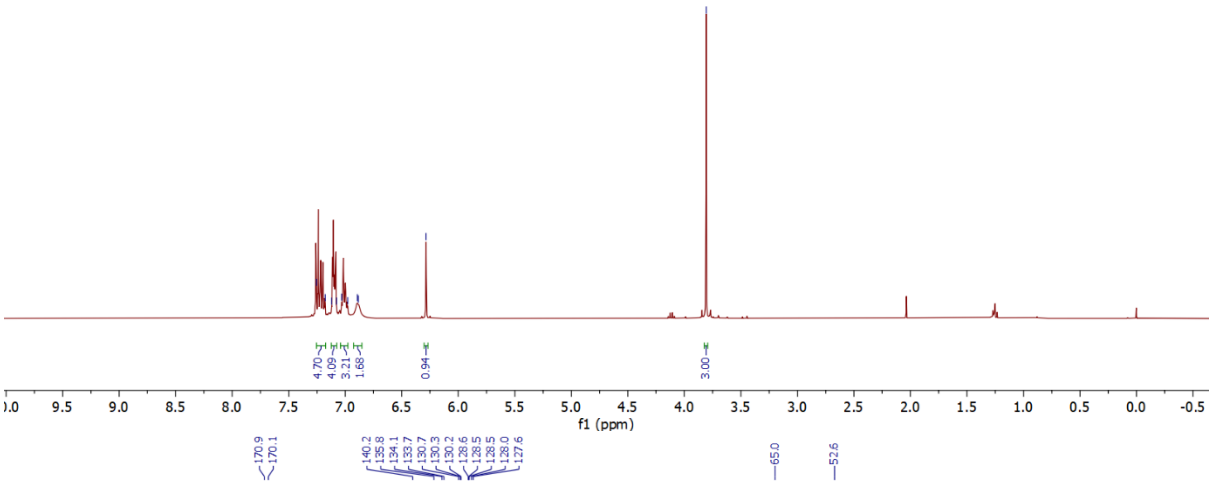




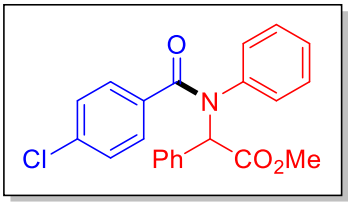
methyl 2-(4-chloro-N-phenylbenzamido)-2-phenylacetate (3ba)

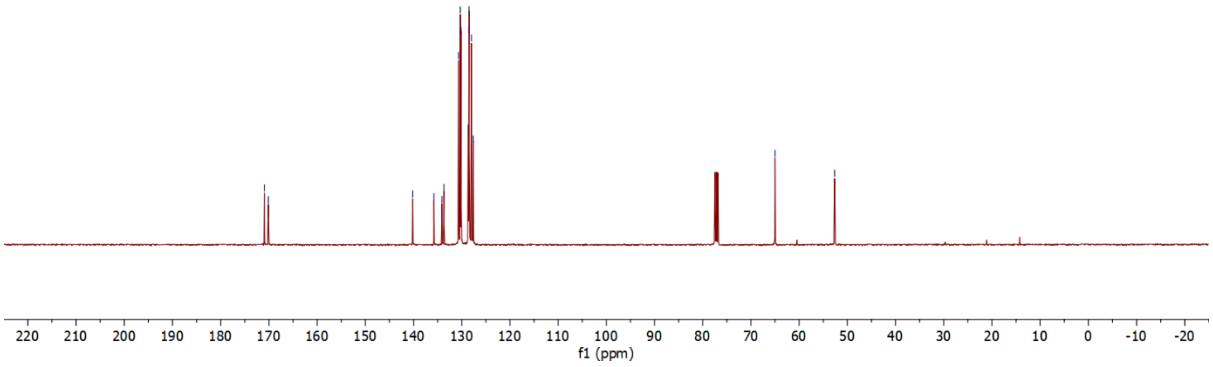
^{1}H, CDCl$_3$, 400 MHz





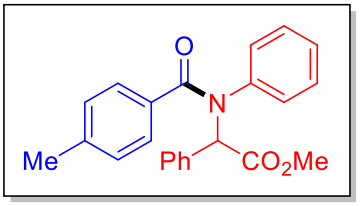
^{13}C, CDCl$_3$, 101 MHz

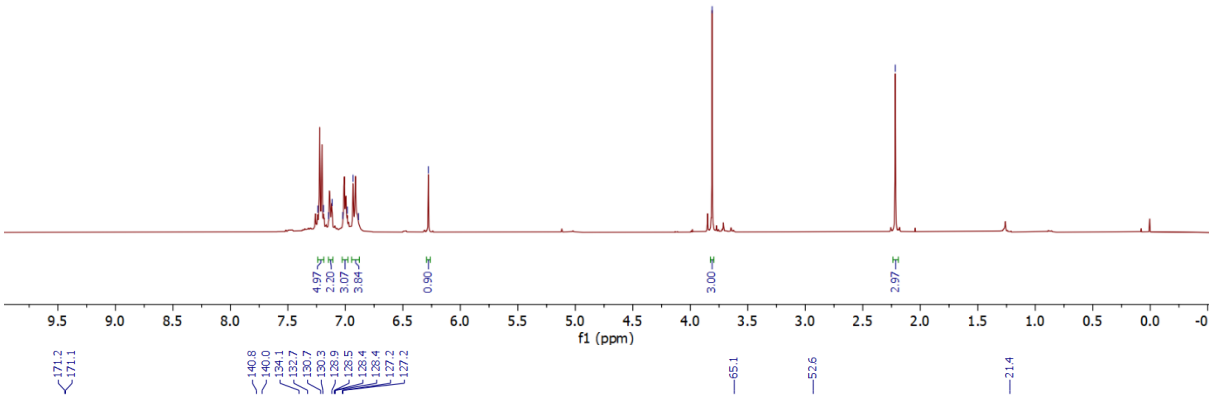




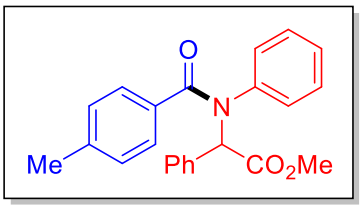
methyl 2-(4-methyl-N-phenylbenzamido)-2-phenylacetate (3ca)

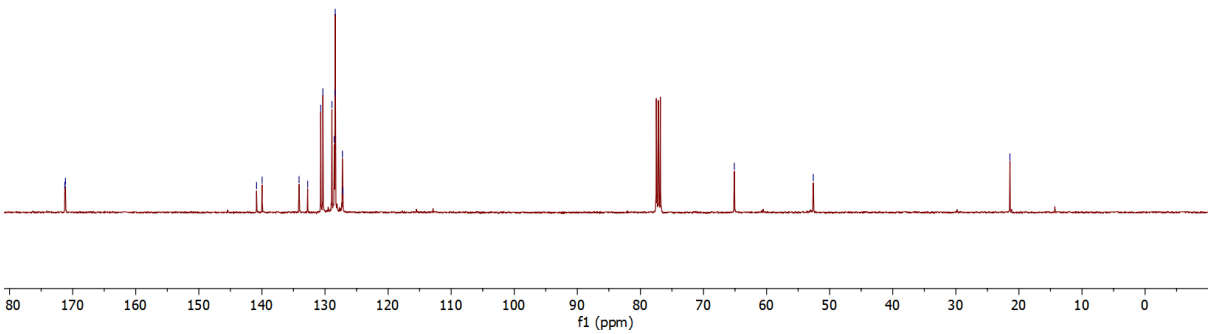
^{1}H, CDCl$_3$, 400 MHz





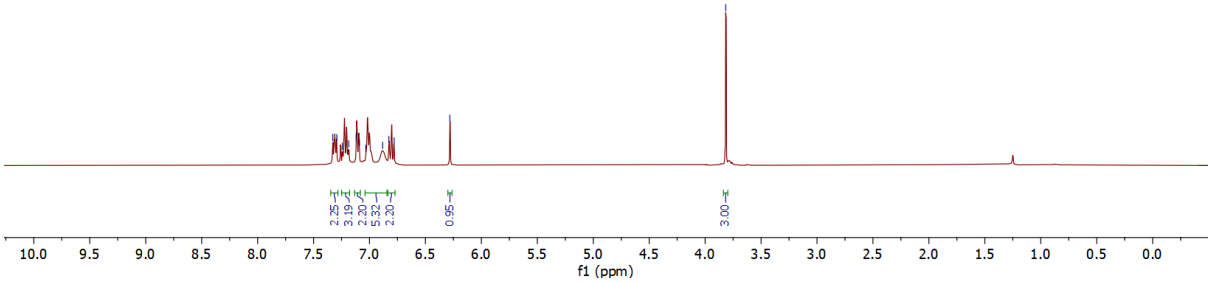
^{13}C, CDCl$_3$, 101 MHz

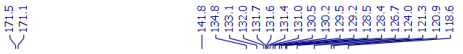


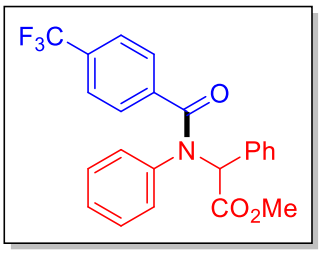


methyl 2-phenyl-2-(N-phenyl-4-(trifluoromethyl)benzamido)acetate (3da)

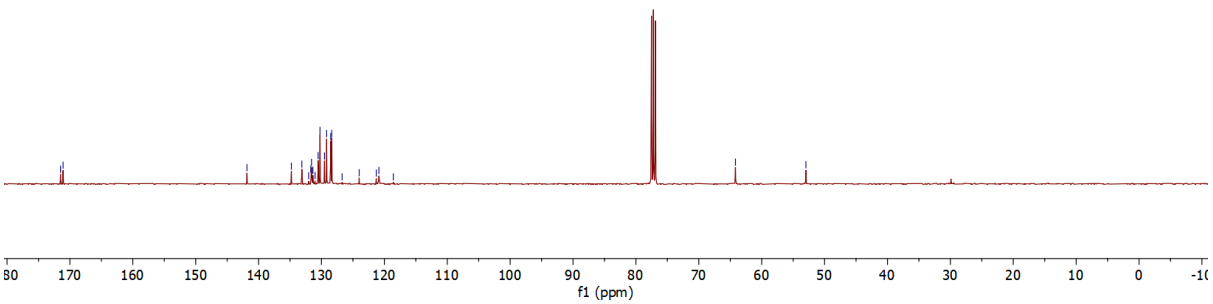
^{1}H, CDCl$_3$, 400 MHz

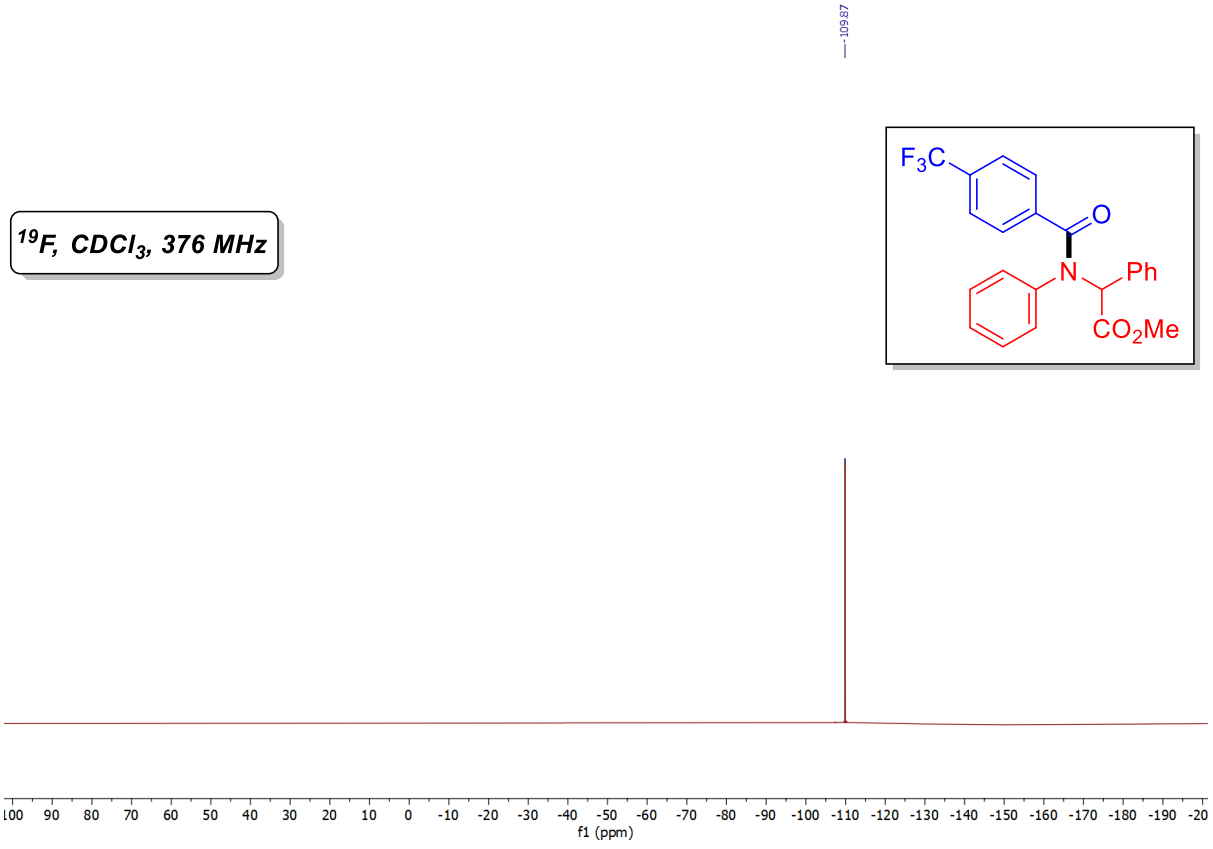




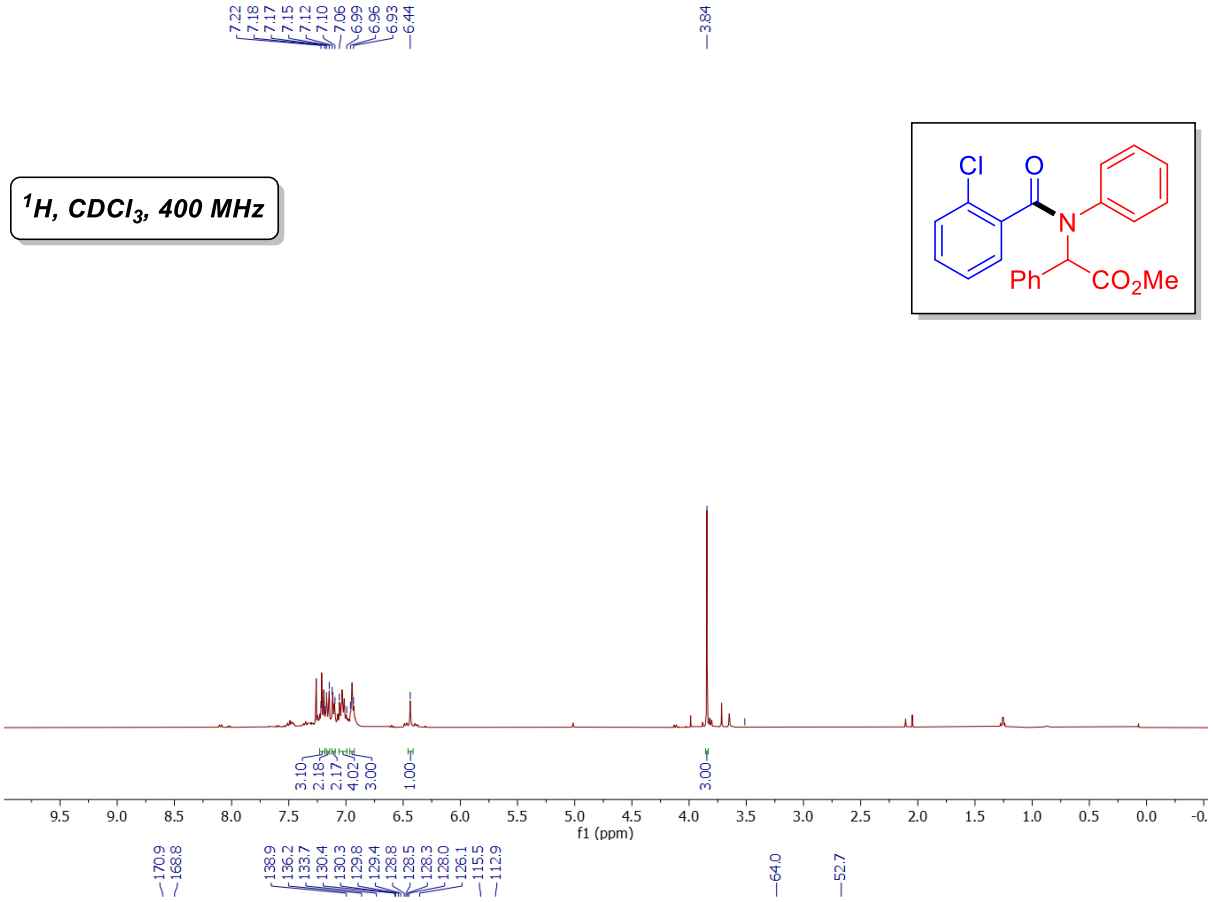


^{13}C, CDCl$_3$, 101 MHz

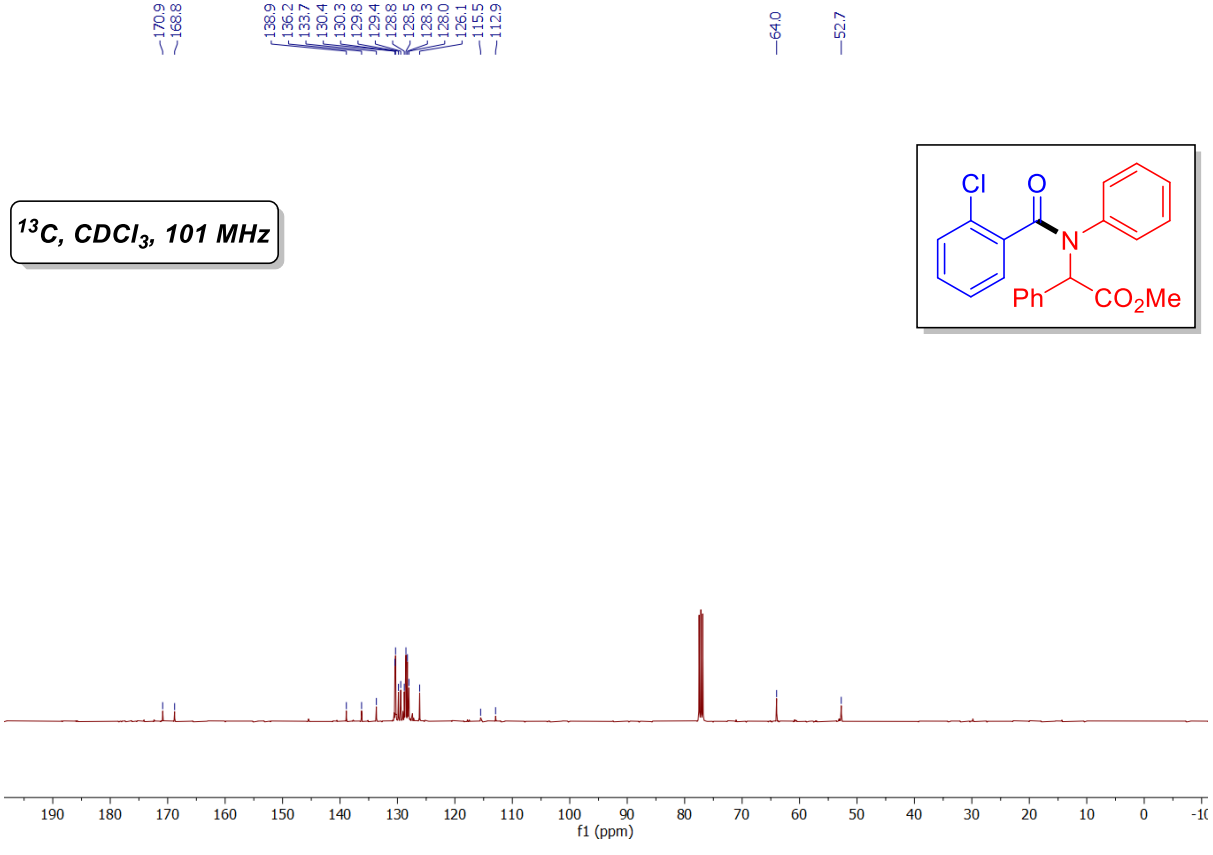



-109.87
^{19}F, $CDCl_3$, 376 MHz
F_3C
O
N
Ph
CO_2Me
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

methyl 2-(2-chloro-N-phenylbenzamido)-2-phenylacetate (3ea)



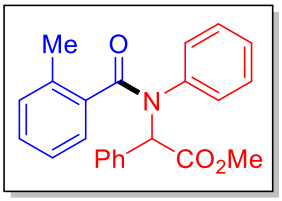
^{1}H, CDCl$_3$, 400 MHz

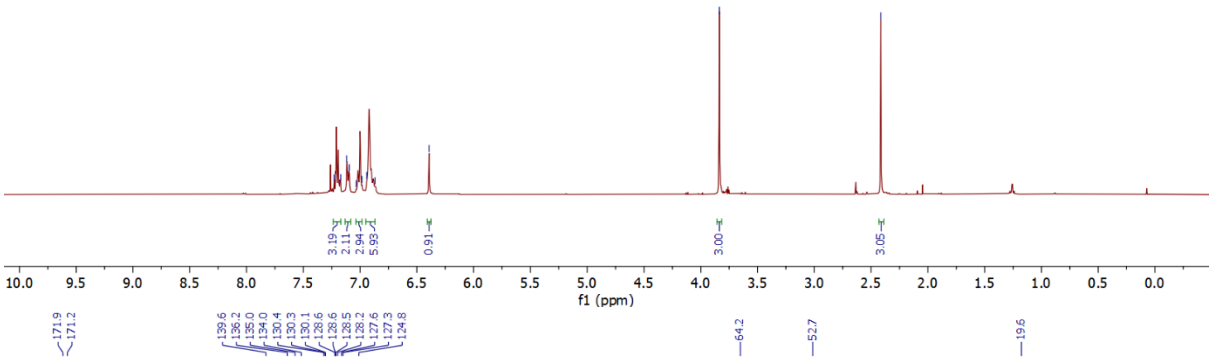


^{13}C, CDCl$_3$, 101 MHz

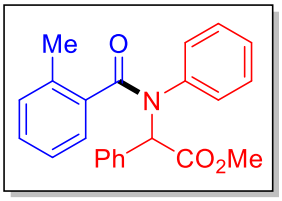
methyl 2-(2-methyl-N-phenylbenzamido)-2-phenylacetate (3fa)

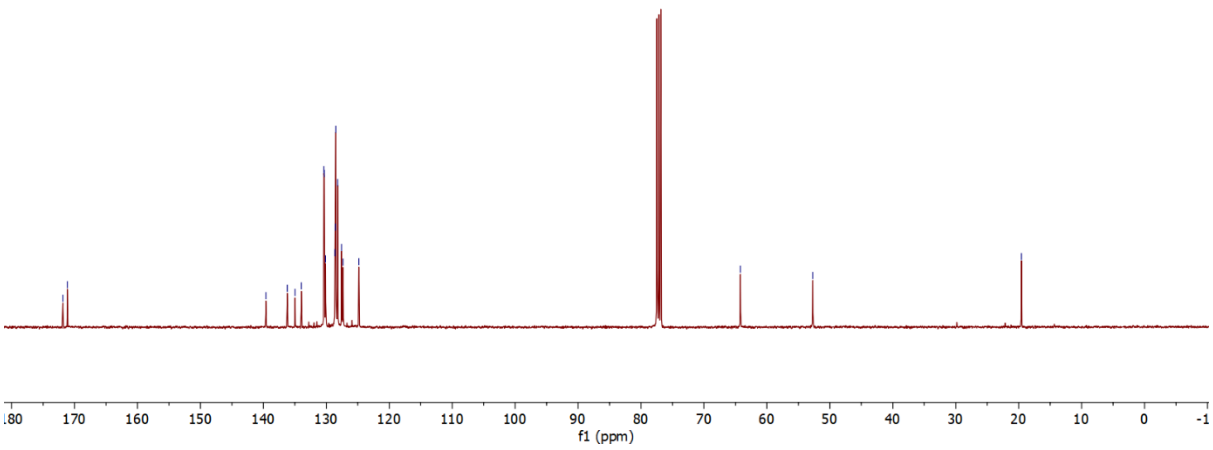
^{1}H, CDCl$_3$, 400 MHz





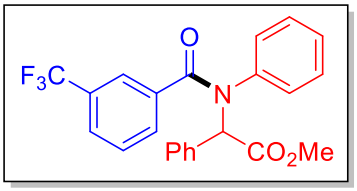
^{13}C, CDCl$_3$, 101 MHz

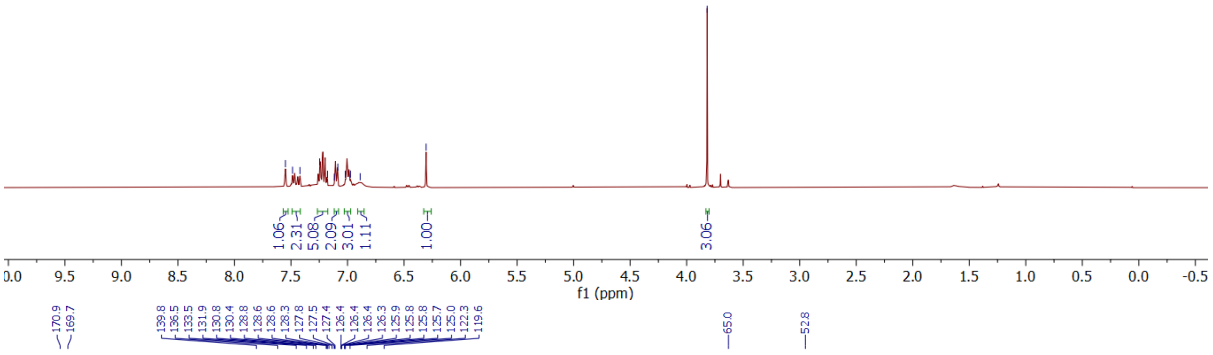




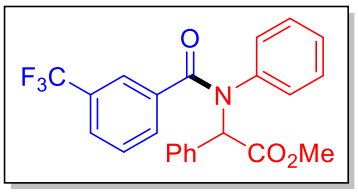
methyl 2-phenyl-2-(N-phenyl-3-(trifluoromethyl)benzamido)acetate (3ga)

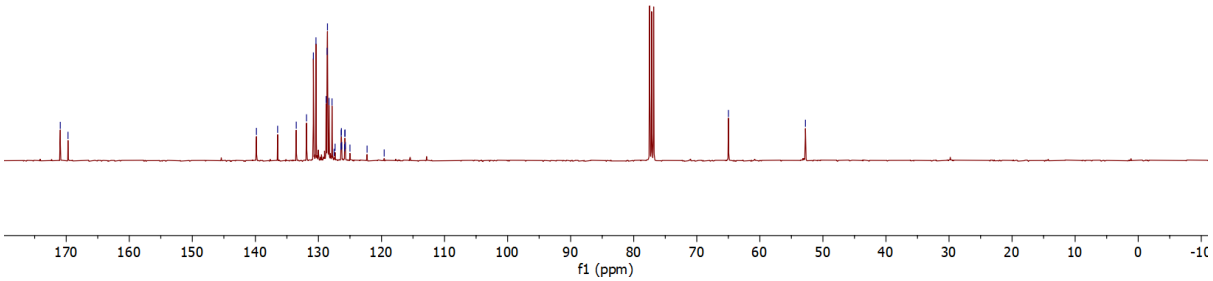
^{1}H, $CDCl_3$, 400 MHz



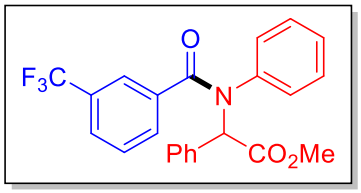


^{13}C, $CDCl_3$, 101 MHz



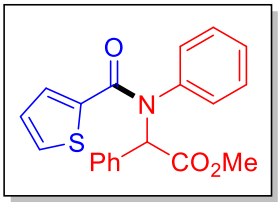


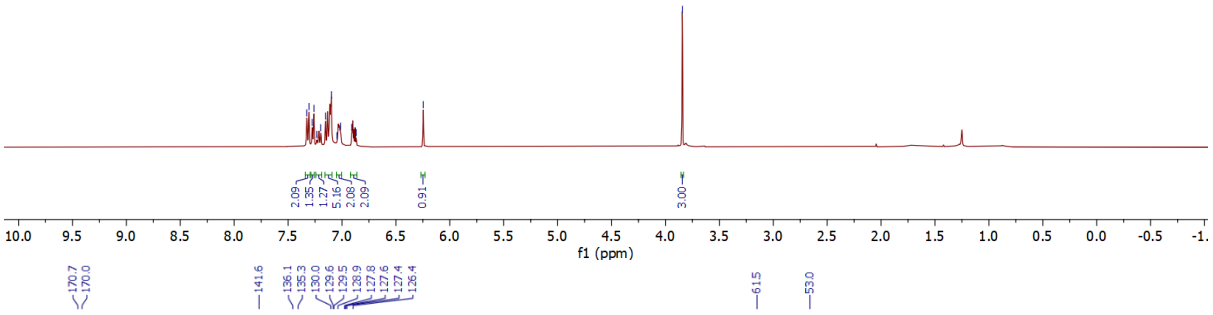
^{19}F, $CDCl_3$, 376 MHz



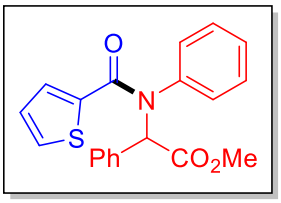
methyl 2-phenyl-2-(N-phenylthiophene-2-carboxamido)acetate (3ha)

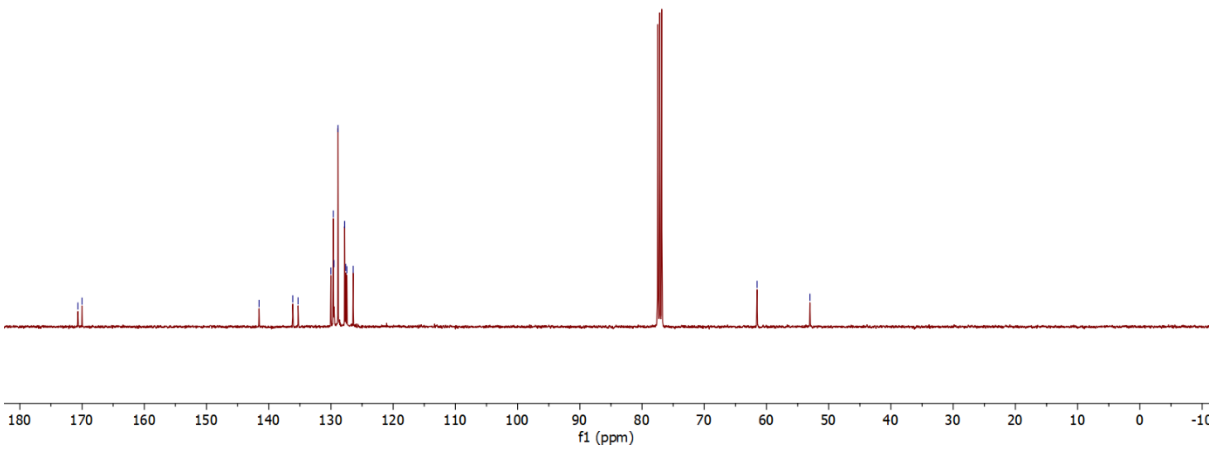
^{1}H, CDCl$_3$, 400 MHz





^{13}C, CDCl$_3$, 101 MHz





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