Supporting Information

Amine-Functionalized Cobalt-NHC Catalysis for the Adaptive Synthesis of Versatile Anthranilates

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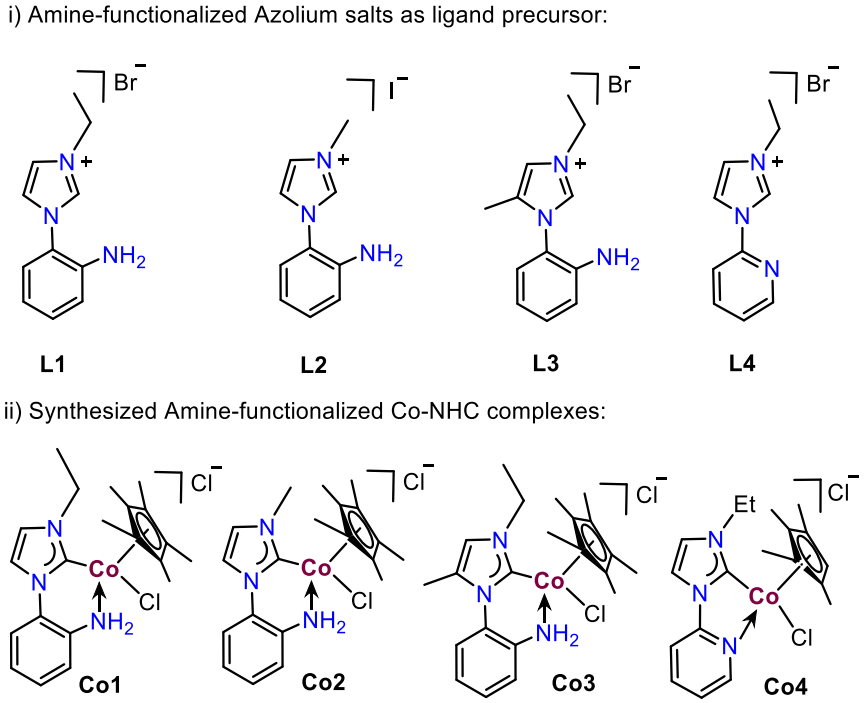
General experimental details:

All experiments with metal complexes were performed using oven-dried glassware under an inert atmosphere using either standard Schlenk line or Glove box techniques. All solvents used for the synthesis were distilled, degassed by standard methods, and stored under an inert atmosphere over 4 Å molecular sieves. All the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded using Bruker 400 and 500 MHz FT-NMR spectrometers, referenced internally to the residual solvent signals. ESI-MS spectra were measured using an Agilent 6545A Q-TOF Mass spectrometer. Starting materials e.g. cobalt precursor, $[Co(Cp^*)Cl_2]_2$, and ligands **L1-4** were synthesized according to the literature procedures.[1] All other chemicals were procured from commercial sources and used as received.

Structures of ligands and cobalt catalysts used in this study:



Scheme S1: Structures of ligands **L1-4** and cobalt catalysts **Co1-4**.

Procedures for the synthesis of ligands and catalysts:

The ligands **L1-4** and cobalt catalysts **Co1-4** were synthesized following the procedures detailed in our earlier work.[1]

^{1}H and ^{13}C NMR of the complexes (Co1-2, 4):[1]

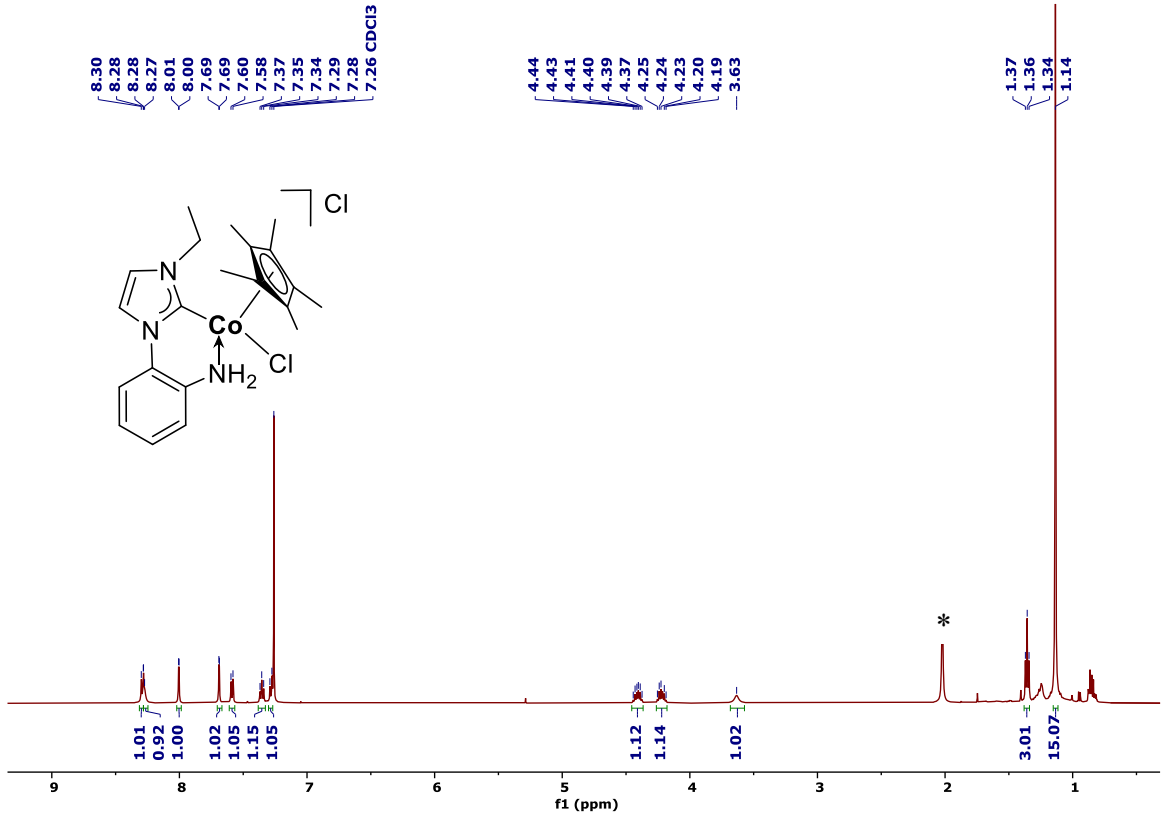


Figure S1. ^{1}H NMR spectrum of **Co1** in $CDCl_3$. * indicates the solvent impurity of H_2O in $CDCl_3$.

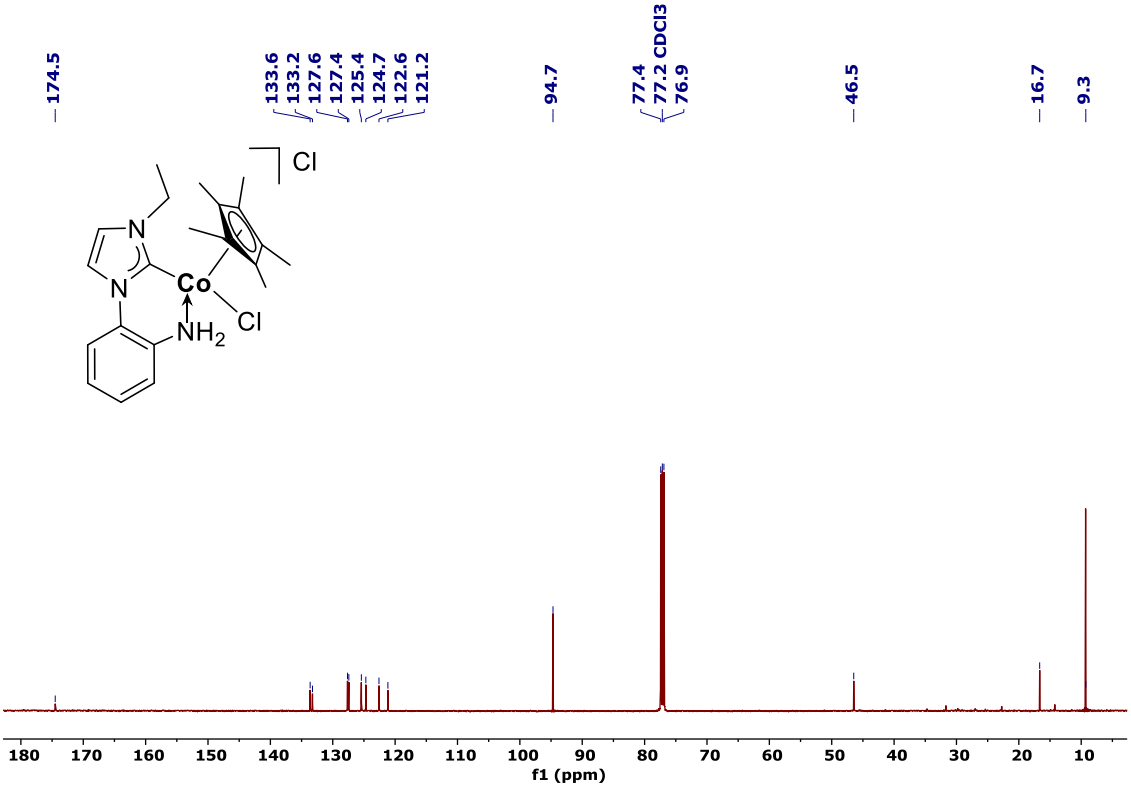


Figure S2. ^{13}C{^{1}H} NMR spectrum of **Co1** in $CDCl_3$.

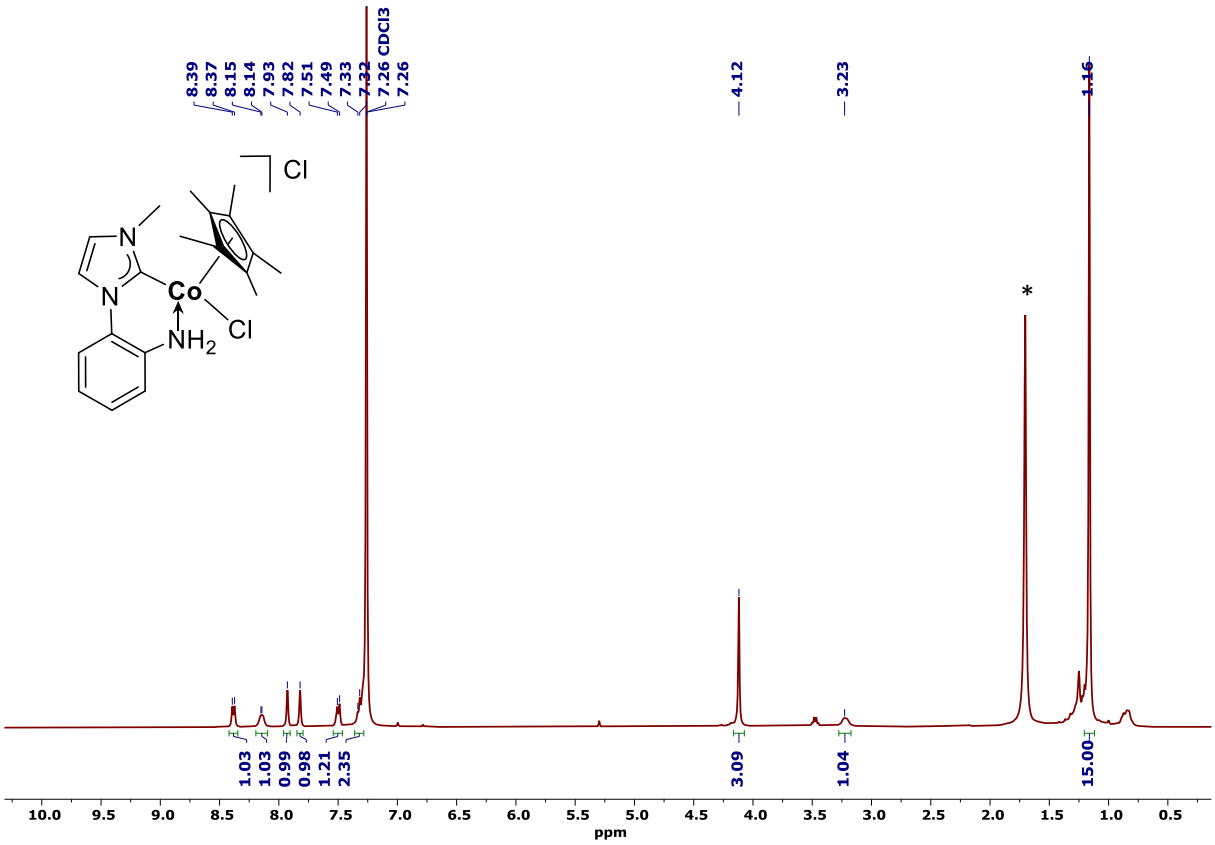


Figure S3. ^{1}H NMR spectrum of **Co2** in $CDCl_3$. * indicates the solvent impurity of H_2O in $CDCl_3$.

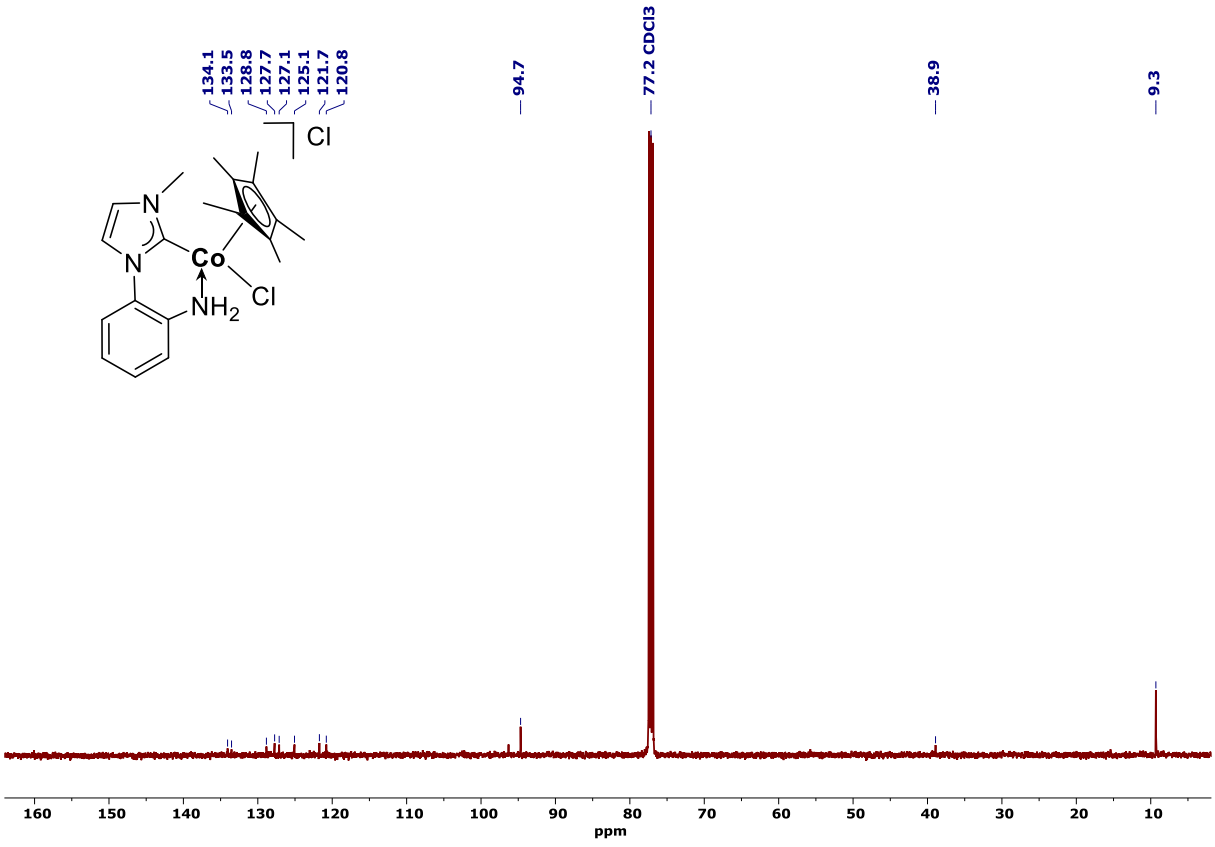


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **Co2** in $CDCl_3$.

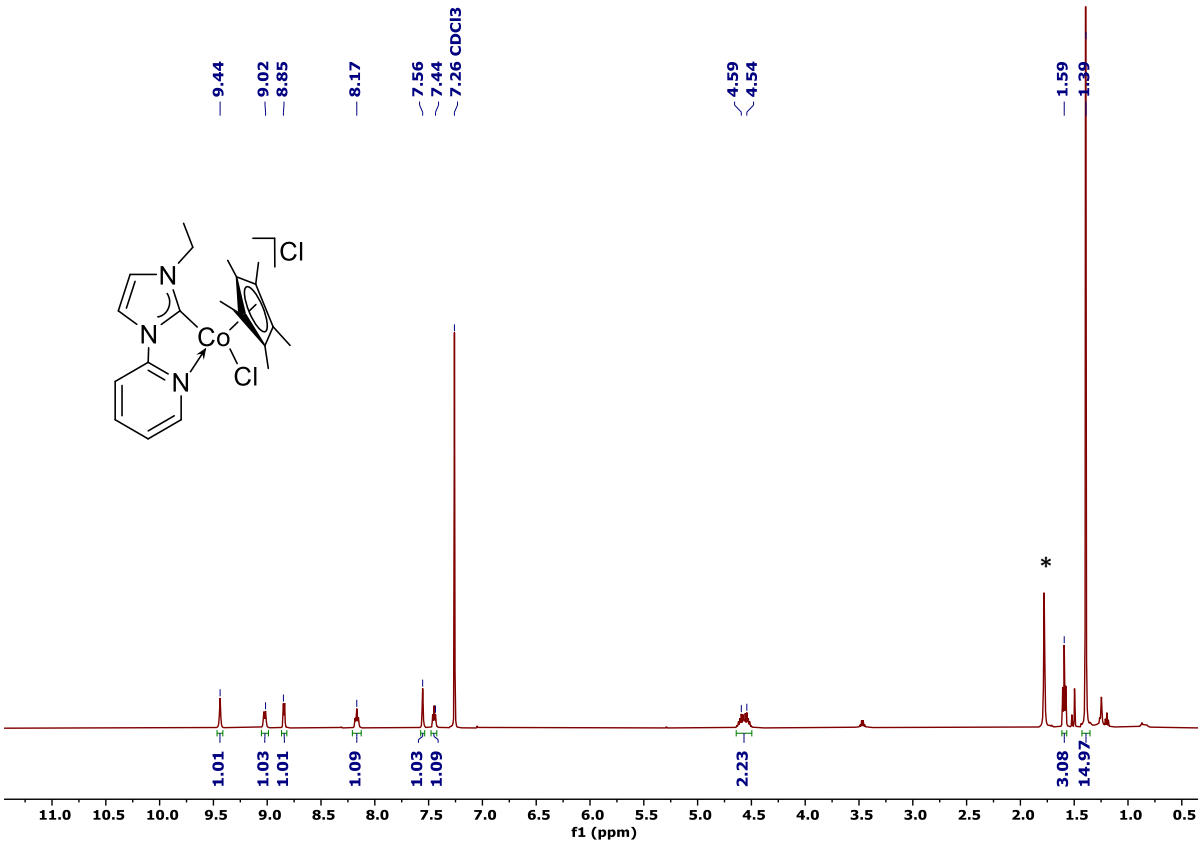


Figure S5. ^{1}H NMR spectrum of **Co4** in $CDCl_3$. * indicates the solvent impurity of H_2O in $CDCl_3$.

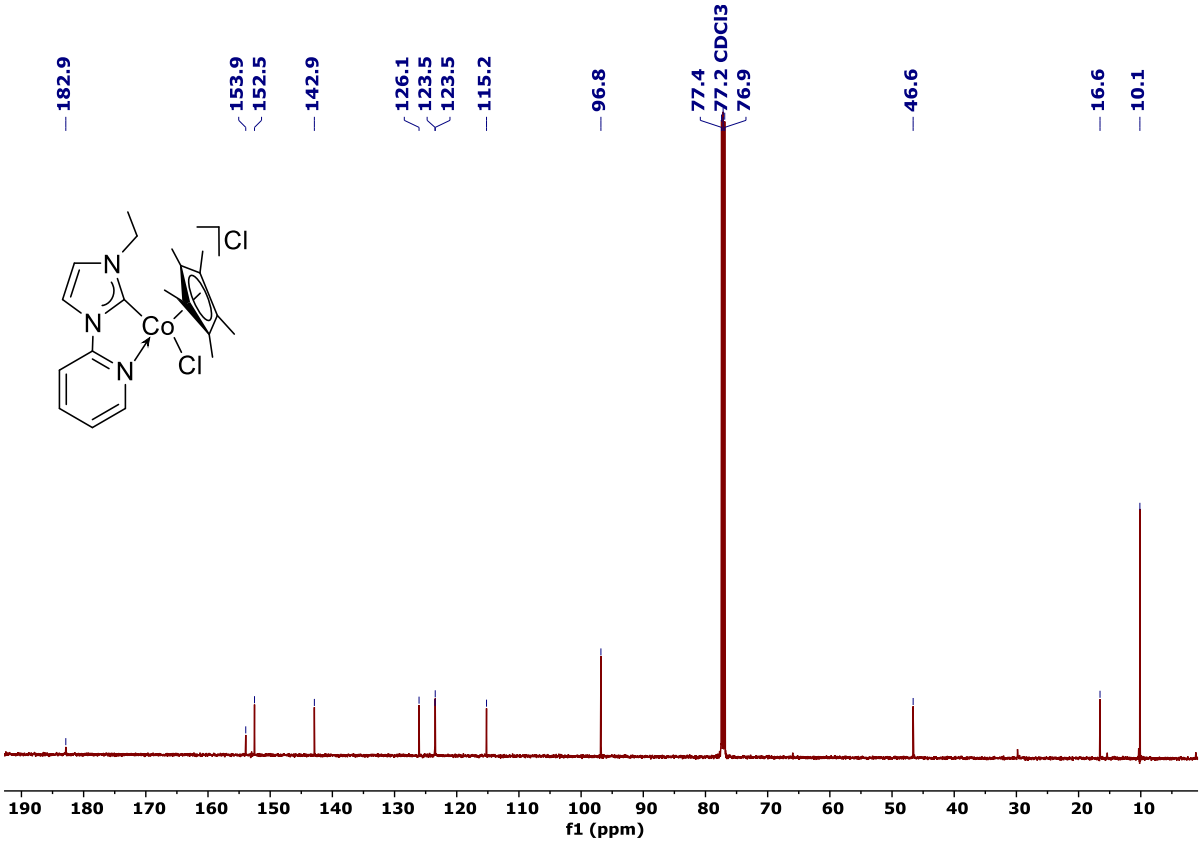
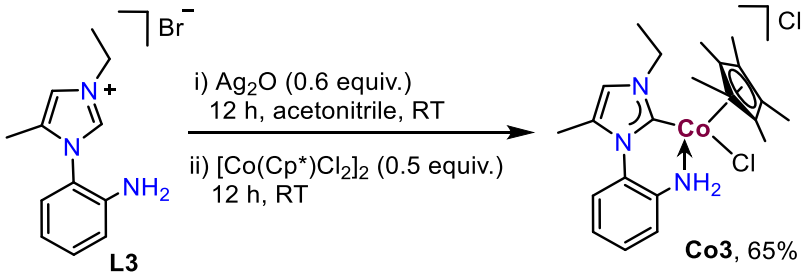


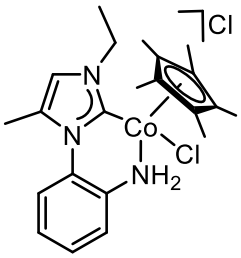
Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **Co4** in $CDCl_3$.

Procedure for the synthesis of complex Co3: The ligand **L3** (0.50 mmol) and Ag_2O (0.30 mmol) were taken in a Schlenk tube followed by the addition of acetonitrile. The reaction mixture was then stirred under the exclusion of light at room temperature. After 12 h of reaction, metal precursor $[Co(Cp^*)Cl_2]_2$ (0.25 equiv.) was added and again stirred for 12 h at RT. The crude reaction mixture was first filtered through a small pad of celite, which was followed by purification *via* column chromatography using DCM/methanol as eluent to obtain the complex **Co3** as a reddish-pink solid in 65% yield.



Scheme S2: Synthesis of complex **Co3**.

Complex Co3: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, Ph-*H,* 1H), 8.23 (d, J = 11.7 Hz, NH_2-*H*, 1H), 7.75 (s, Im-*H*, 1H), 7.55 (d, J = 8.1 Hz, Ph-*H,* 1H), 7.36–7.29 (m, Ph-*H*, 2H), 4.46– 4.42 (m, Et-CH_2-*H,* 1H), 4.24–4.19 (m, Et-CH_2-*H*, 1H), 3.66 (d, J = 12.1 Hz, NH_2-*H*, 1H), 2.48 (s, Im-CH_3, 3H), 1.29 (t, J = 7.3 Hz, Et-CH_3, 3H), 1.13 (s, *Cp**, 15H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 174.1 (Im-*N*-*C*-*N*), 134.8 (Im-*C*), 133.3 (Ph-*C*), 133.1 (Ph-*C*), 127.5 (Ph-*C*), 127.4 (Ph-*C*), 124.9 Im-*C*, 120.8 (Ph-*C*), 120.1 (Ph-*C*), 94.7 (*Cp*)*, 45.0 (Et-CH_2), 16.3 (Im-CH_3), 10.7 (Et-CH_3), 9.3 (*Cp*)* ppm. MS (ESI, positive ions): *m/z* 430.1484 (calcd for [M-Cl]+: *m/z* 430.1460).



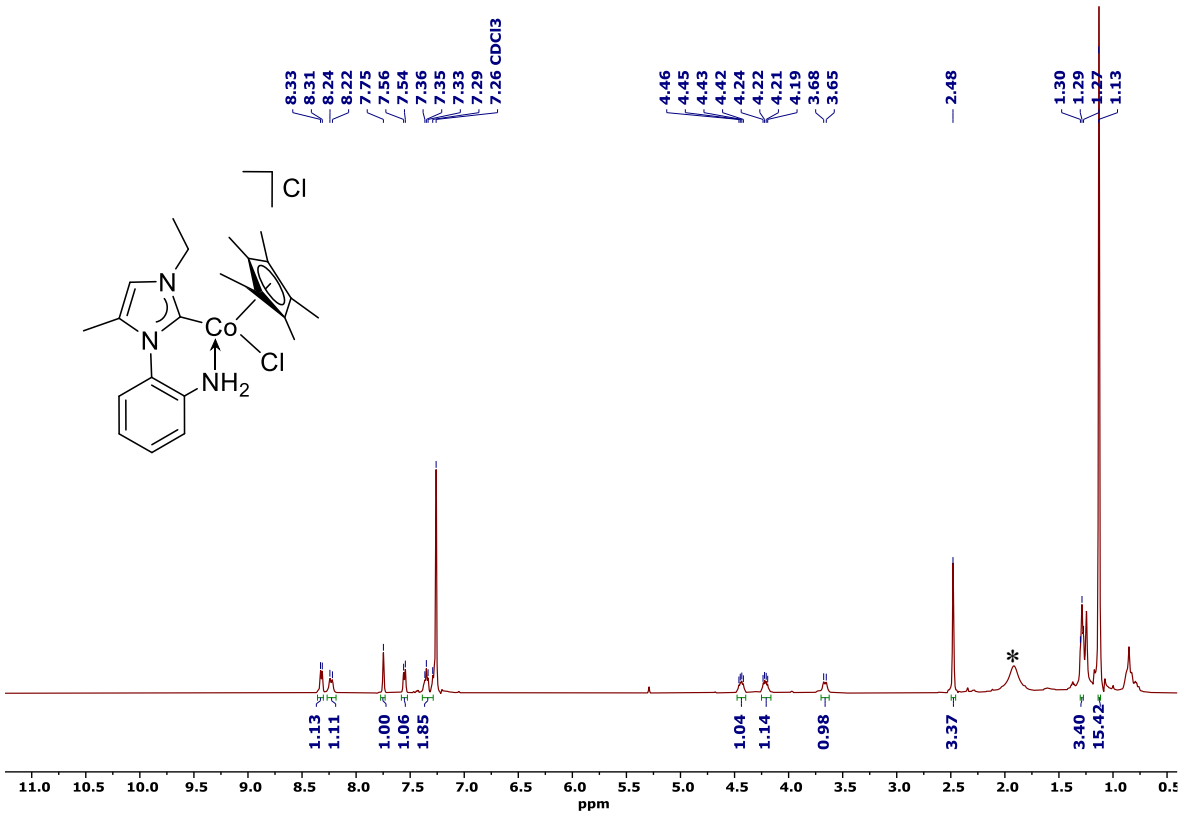


Figure S7. ^{1}H NMR spectrum of **Co3** in $CDCl_3$. * Indicates the impurity of H_2O in $CDCl_3$

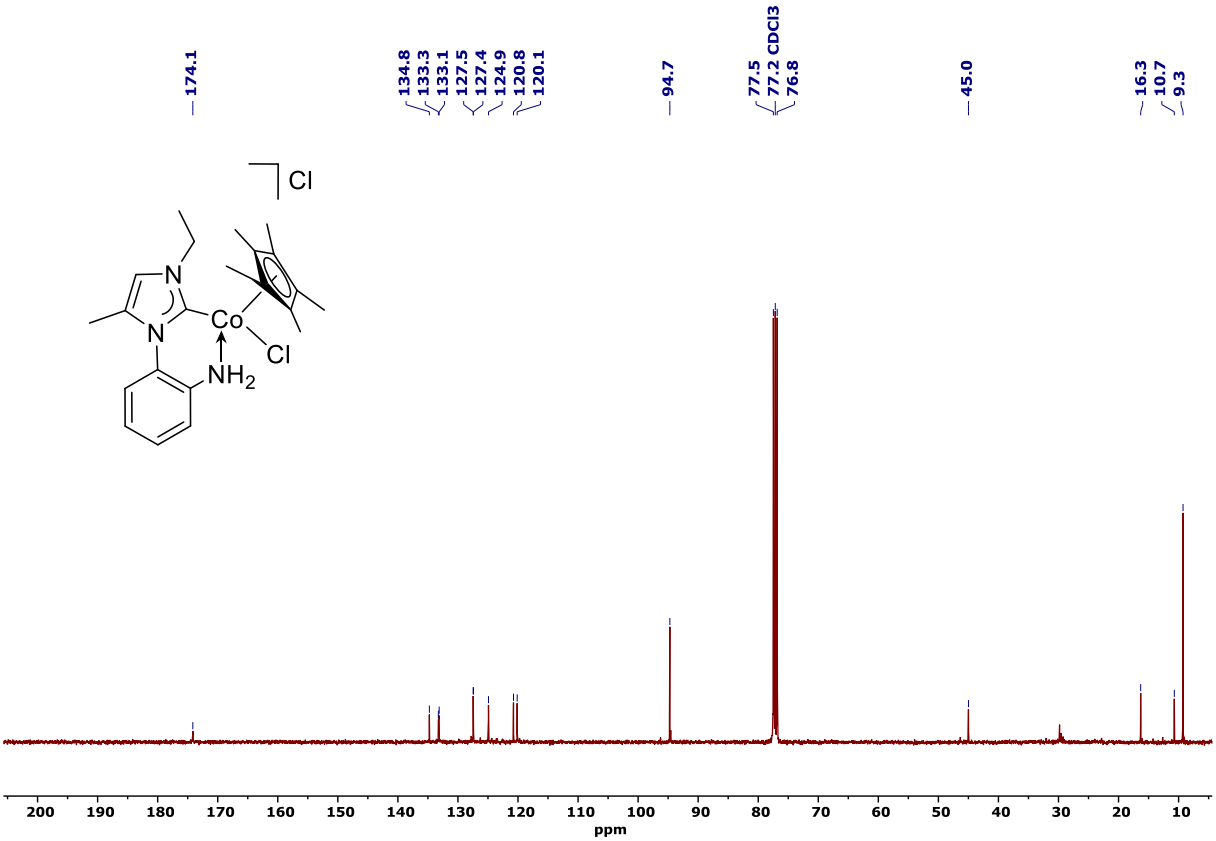


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **Co3** in $CDCl_3$.

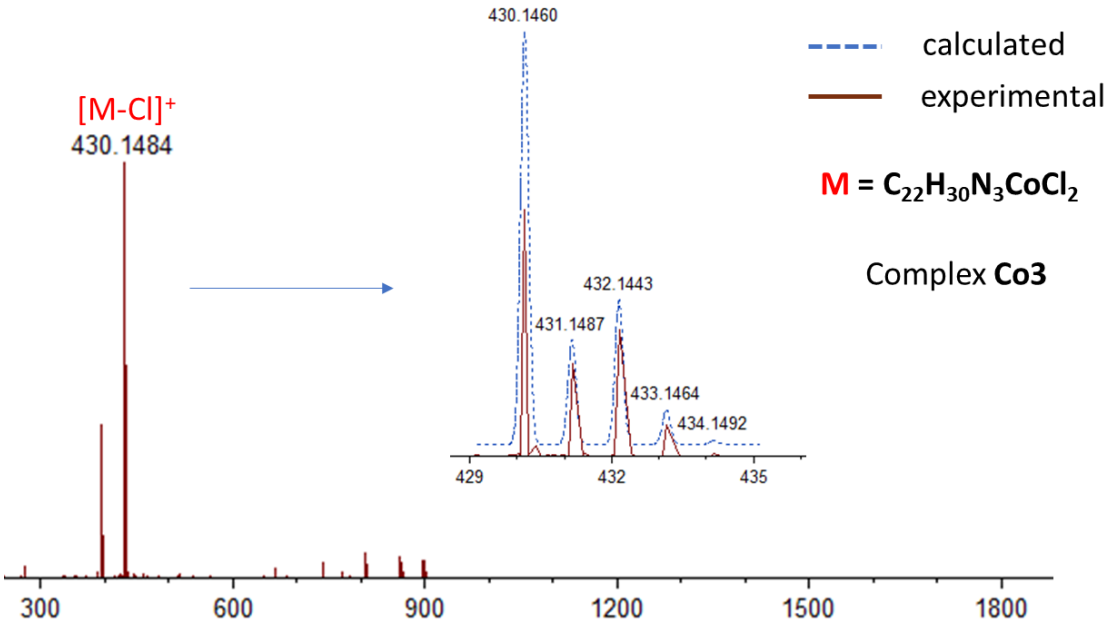


Figure S9. ESI-MS (positive ions) spectrum of the complex **Co3.**

Single crystal X-ray Crystallography

Single crystal X-ray diffraction data for **Co3** was collected on a Bruker AXS D8 VENTURE diffractometer equipped with a PHOTON-II detector. The compound was measured using MoKα radiation (λ = 0.71073 Å). Crystals were selected using a polarizing optical microscope and then mounted on a crystal-mounting loop using Paraton oil. The mounted crystal was then placed on a goniometer head and the crystal was centered with the help of a video microscope. The automatic cell determination routine, with 24/36 frames (10 sec exposure time per frame) at two/three different orientations of the detector, respectively was employed to collect reflections for the unit cell determination. The collected reflections were indexed using inbuilt APEX software[2a] to obtain unit cell parameters. Further, intensity data for structure determination were collected through an optimized strategy, which gave an average 4-fold redundancy for the reflections. The program Bruker-SAINT[2b] was then used for integrating the frames and multi-scan absorption correction was applied using the program SADABS.[2c] The structure was solved by SHELXT[2d] and refined by full-matrix least squares techniques on F^2 using SHELXL[2e] computer program incorporated in WinGX[2f] system. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were fixed at chemically meaningful positions and riding model refinement was applied. The graphical representations

were performed using the program Mercury.[2g] The crystal data (CCDC No. 2454397) and refinement details are summarized in Table S1.

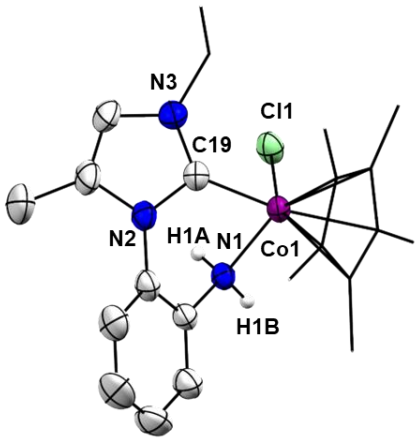


Figure S10. Molecular structure of the complex **Co3** with ellipsoids at 50% probability level, all hydrogen atoms except the NH_2 protons and the chloride counter ion along with one solvent $CHCl_3$ molecule are omitted for clarity and the *N*-ethyl/Cp* are shown in the capped stick model. Selected bond distances (Å) and bond angles (deg.): Co1-C19 1.948(4), Co1-N1 1.998(4), C19-Co1-N1 85.17(18).

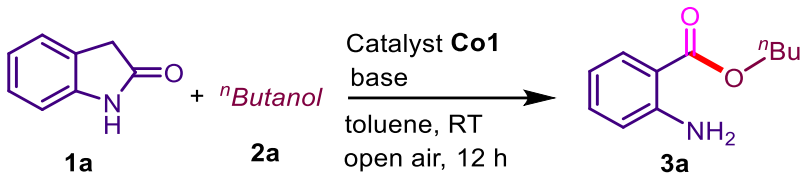
Table S1. Crystallographic data for the complex **Co3**

Compound	**Co3**
CCDC No.	2454397
Empirical formula	$C_{23}H_{31}Cl_5CoN_3$
Formula weight	585.69
Temperature	298(2) K
Crystal system	Triclinic
Space group	*P -1*
a (Å)	10.4020(9)
b (Å)	11.3998(10)
c (Å)	13.1581(12)
α (°)	81.842(4)
β (°)	67.913(3)
γ (°)	72.096(3)
V ($Å^3$)	1375.2(2)

Z	2
D calc (Mg/m^3)	1.414
F (000)	604
μ (mm^{-1})	1.126
θ Range (°)	2.477 to 25.500
Crystal size (mm^3)	0.461 x 0.221 x 0.161 mm3
No. of total reflns collected	56826
No. of unique reflns [$I > 2\sigma(I)$]	5102
Data/restraints/ parameters	5102 / 60 / 332
Goodness-of-fit on F^2	1.175
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0705, wR2 = 0.1954
R indices (all data)	R1 = 0.0855, wR2 = 0.2243

Optimization of the reaction conditions for aminophenone:

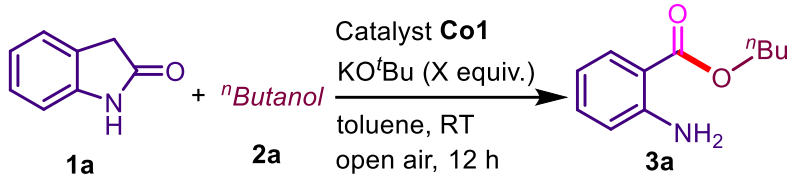
Table S2. Screening of base[a]



entry	base	3a (%)[b]
1	LiO^{t}Bu	52
2	NaO^{t}Bu	47
3	KO^{t}Bu	74
4	Cs_2CO_3	trace
5	CsOH	65

[a]**Reaction conditions**: oxindole **1a** (0.25 mmol), alcohol **2a** (0.50 mmol), base (0.075 mmol), catalyst **Co1** (2 mol%) in solvent (1 mL), RT for 12 h under open air. [b]Isolated yields.

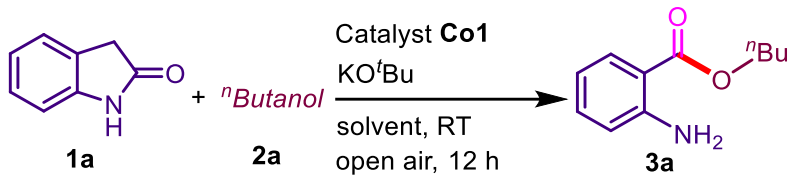
Table S3. Screening of base equivalence[a]



entry	base equiv.	3a (%)[b]
1	0.6	44
2	0.3	74
3	0.1	30

[a]**Reaction conditions**: oxindole **1a** (0.25 mmol), alcohol **2a** (0.50 mmol), KO^{t}Bu (X equiv.), **Co1** (2 mol%) in solvent (1 mL), RT for 12 h under open air. [b]Isolated yields.

Table S4. Screening of solvent[a]



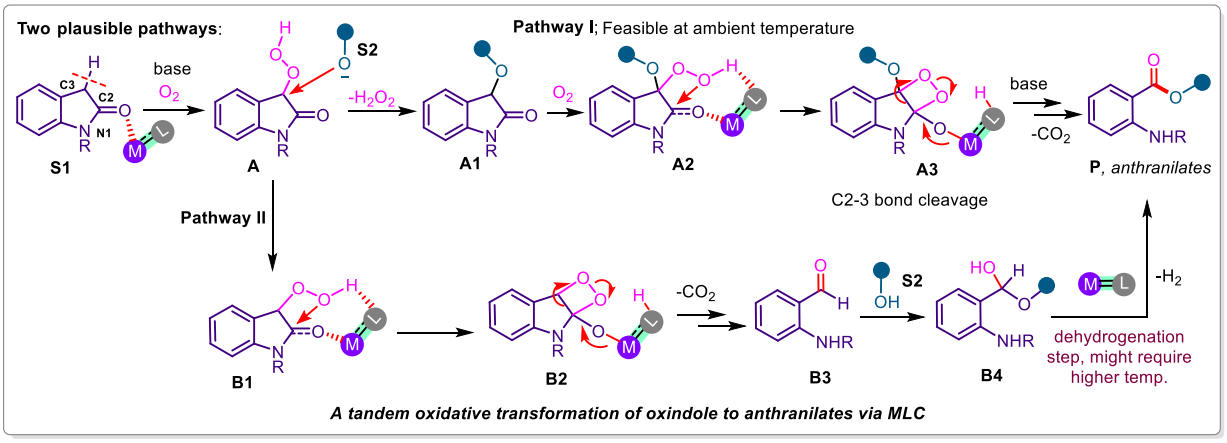
entry	solvent	3a (%)[b]
1	toluene	74
2	THF	41
3	CH_3CN	24
4	1,4-dioxane	38

[a]**Reaction conditions**: oxindole **1a** (0.25 mmol), alcohol **2a** (0.50 mmol), KO^{t}Bu (0.075 mmol), catalyst **Co1** (2 mol%) in solvent, RT for 12 h under open air. [b]Isolated yield.

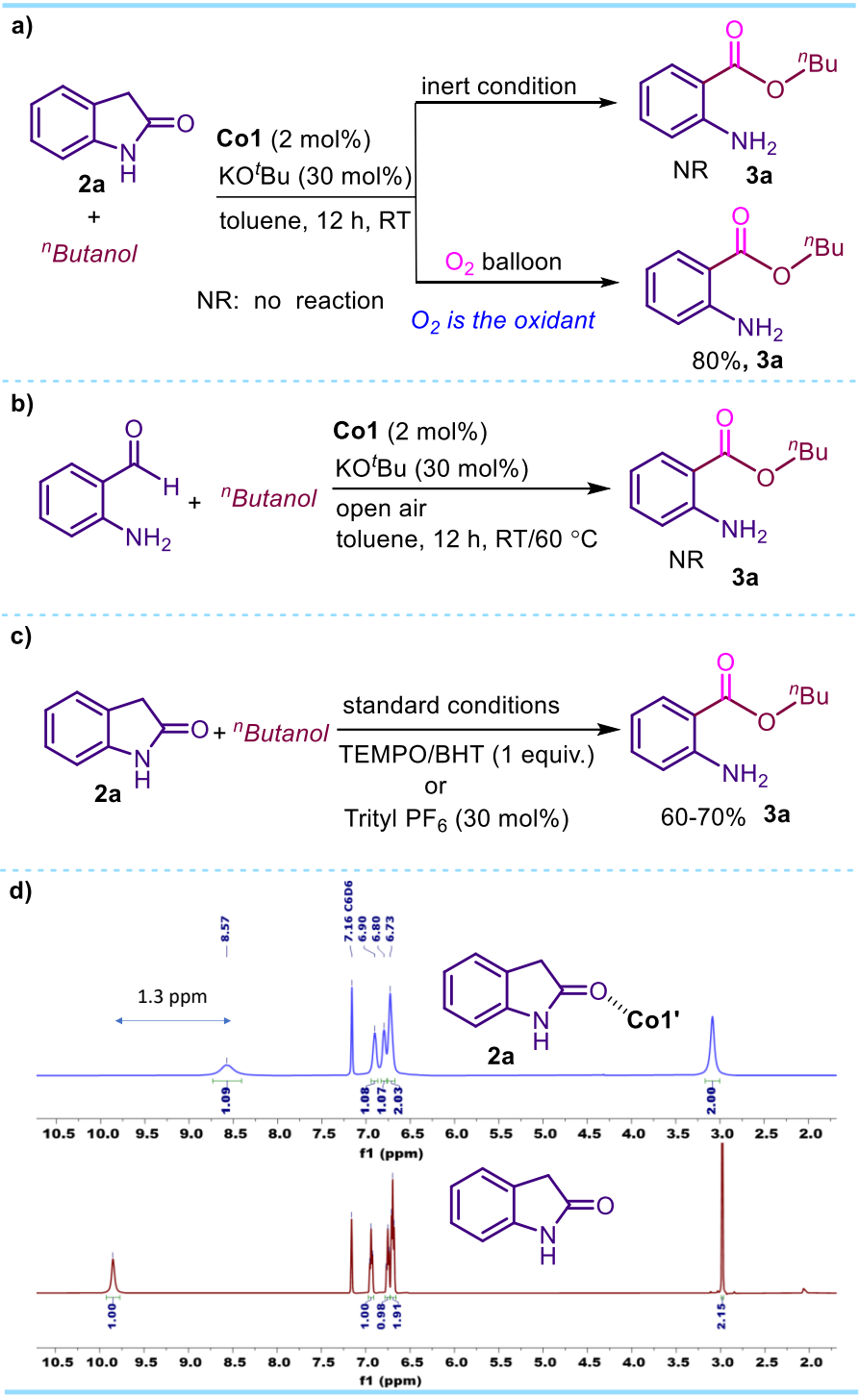
General procedure for the synthesis of Anthranilate derivatives (3/5/7):

A reaction tube was charged with catalyst **Co1** (0.005 mmol, 2 mol%), KO^{t}Bu (0.075 mmol, 30 mol%), oxindole **1** (0.25 mmol), and alcohol **2**/**4**/**6** (0.5 mmol) in toluene (1-2 mL). Then the reaction mixture was stirred at room temperature for 12 h in open air. The final product was isolated using column chromatography with ethyl acetate and hexane (1:49) as eluent.

Mechanistic proposal:



Scheme S3: Plausible pathways for the present one-pot tandem transformations.



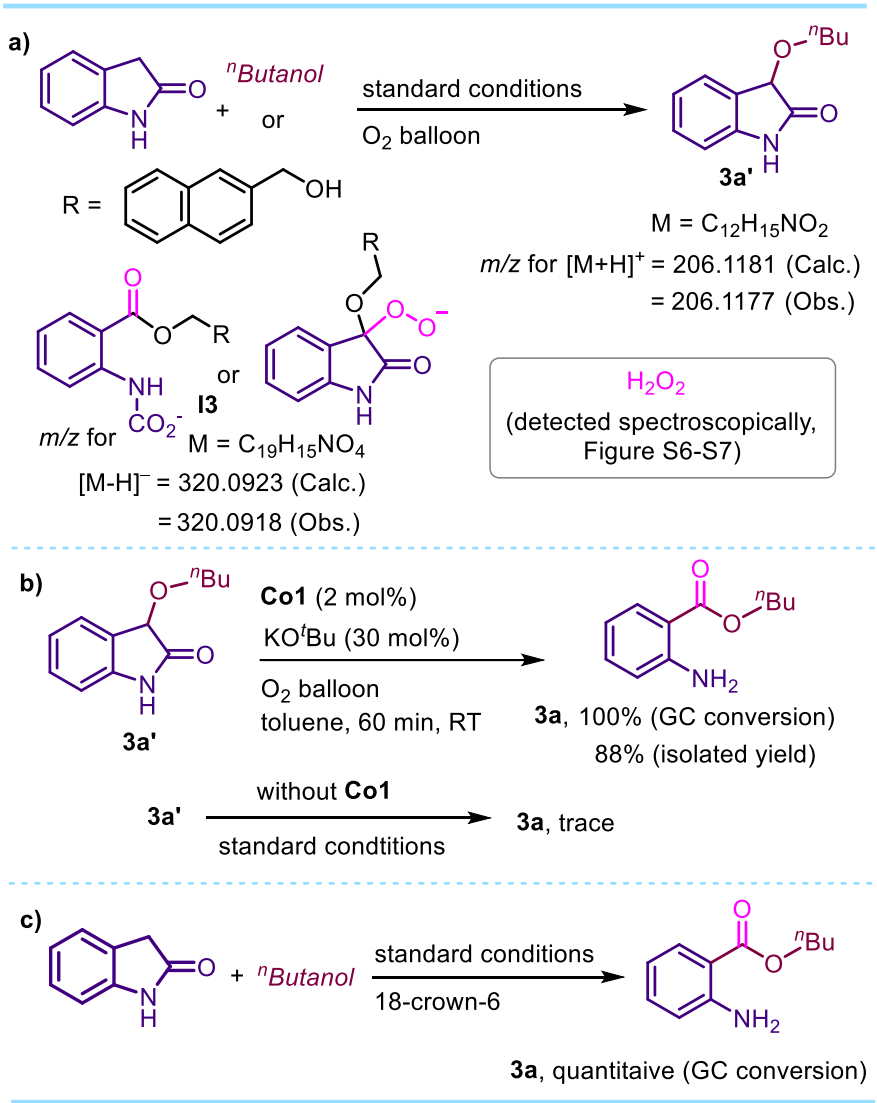
Scheme S4: Control experiments.

Reaction in presence of molecular oxygen:

A reaction tube was charged with 2 mol% **Co1** catalyst, 30 mol% KO^{t}Bu, oxindole **1a** (0.25 mmol), and ^{n}butanol **2a** (0.5 mmol) in toluene. The reaction mixture was stirred at room temperature under an oxygen balloon atmosphere instead of open air for 12 hours, resulting in the formation of product **3a** with an 80% yield.

Radical scavenger and hydride quencher experiment: A reaction tube was charged with catalyst **Co1** (2 mol%), KO^{t}Bu (30 mol%), oxindole **1** (0.25 mmol), ^{n}butanol **2** (0.5 mmol), and TEMPO/BHT (1 equiv.) or Trityl PF_6 (30 mol%) in toluene. Then the reaction mixture was stirred at room temperature for 12 h in open air. Desired product **3a** was obtained in 60-70% yields.

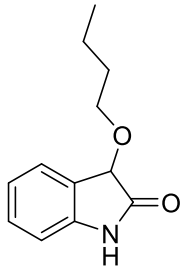
In-situ ^{1}H NMR studies: A J Young® NMR tube was charged with **Co1** (0.002 mmol), base (0.03 mmol) in C_6D_6, then sonicated for 10 minutes to generate **Co1'** in situ. Oxindole **1a** (0.1 mmol) was subsequently added, followed by 5-10 minutes of sonication. The reaction mixture was then monitored by ^{1}H NMR.



Scheme S5: Detection of catalytic intermediates.

Synthesis of 3-butoxyindolin-2-one (Compound-3a'):[3]

In a Schlenk tube, oxindole (1.0 mmol) was taken in ^{n}butanol (3 mL). Phenyliodinebis(trifluoroacetate) (PIFA) (2 mmol) was added, and the reaction mixture was stirred at room temperature for 40 min. After the reaction was completed, the reaction mixture was diluted with water, and the product was extracted with ethyl acetate, dried with $MgSO_4$, and the solvent was evaporated under vacuo. After extraction, the pure product was isolated as a yellow liquid after column chromatography with ethyl acetate and hexane as eluents (133 mg, 0.65 mmol, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.37-7.34 (m, 1H), 7.27-7.23 (m, 1H), 7.07-7.03 (m, 1H), 6.90 (d, J = 8.4 Hz, 1H), 4.94 (s, 1H), 3.76-3.70 (m, 1H), 3.63-3.57 (m, 1H), 1.66 – 1.59 (m, 2H), 1.45-1.36 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.7, 141.6, 129.9, 125.9, 125.6, 123.0, 110.6, 76.5, 68.6, 32.0, 19.3, 13.9 ppm.



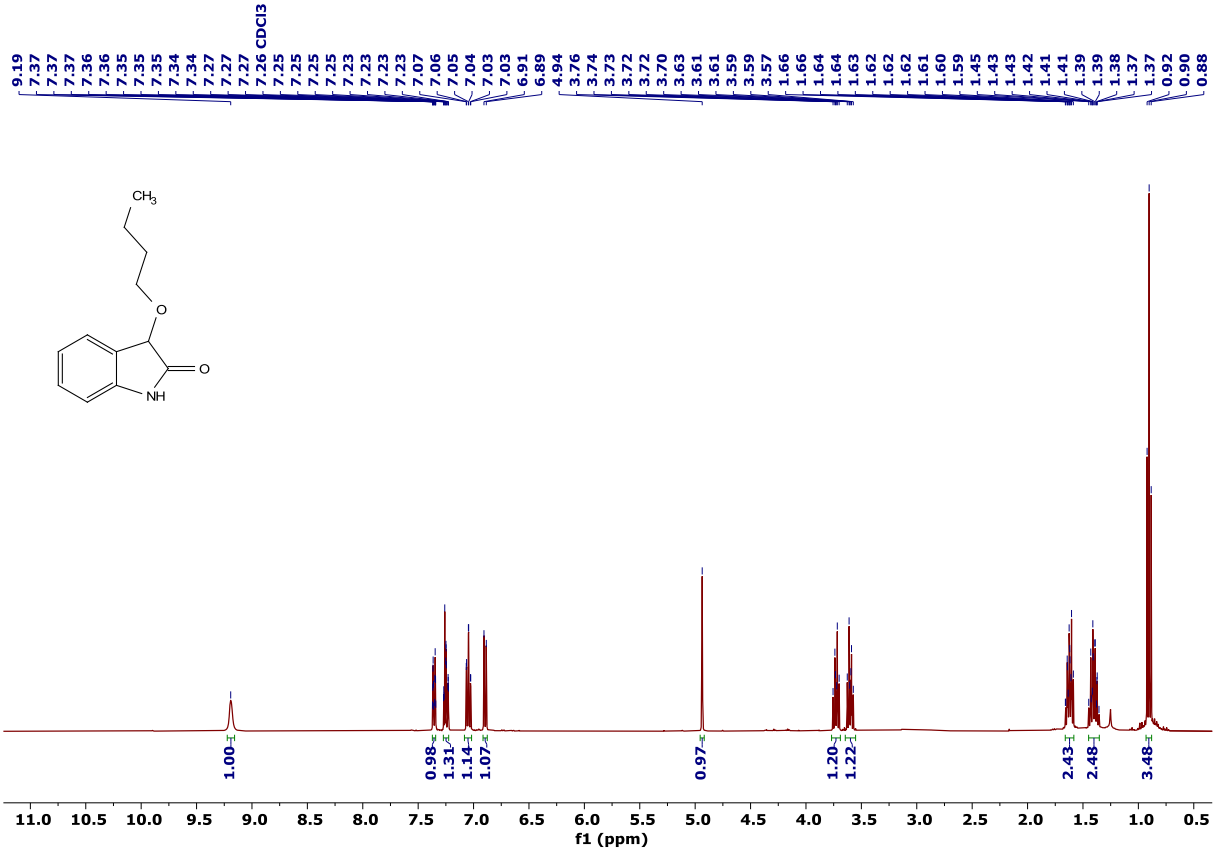


Figure S11. ^{1}H NMR spectrum of **3a'** in $CDCl_3$.

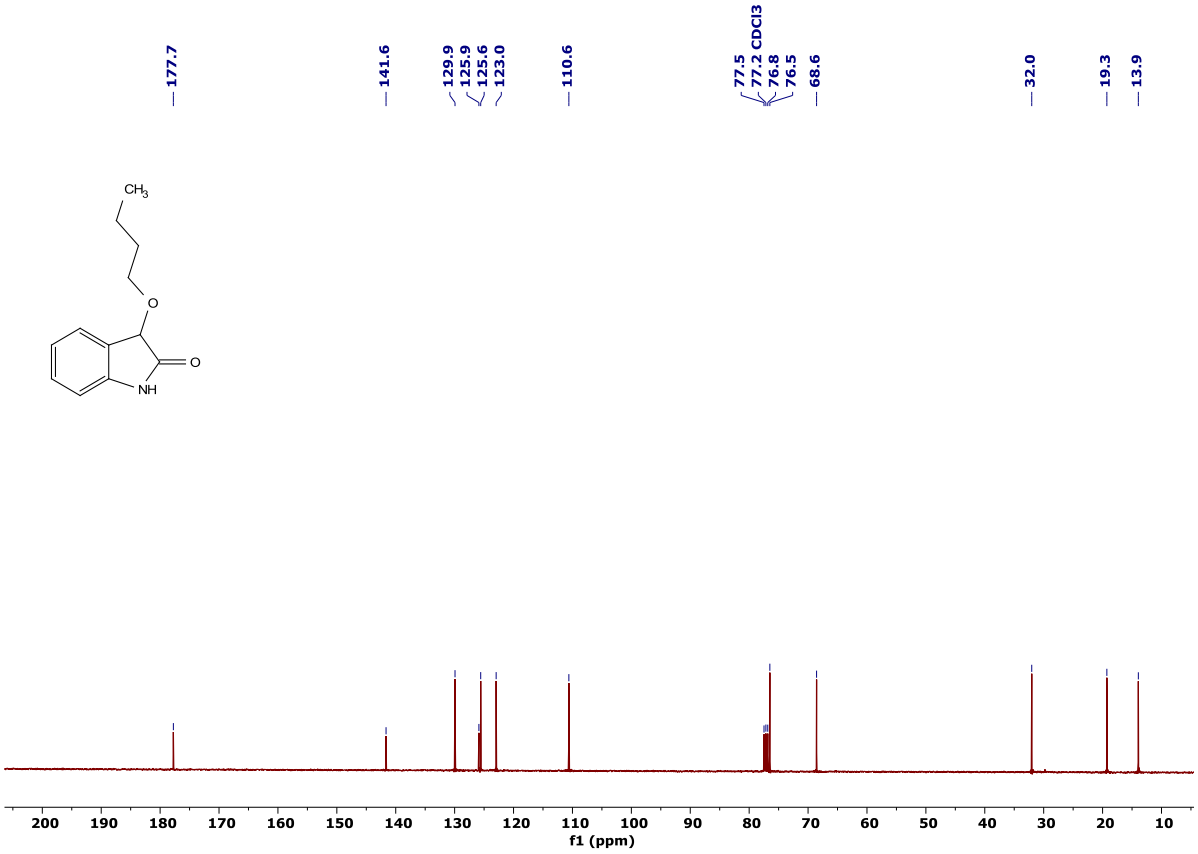


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **3a'** in $CDCl_3$.

Detection of hydrogen peroxide during the formation of anthranilate.[11]

A Schlenk tube was charged with catalyst **1a** (0.12 mmol), KO^{t}Bu (1.8 mmol), oxindole (6 mol), and benzyl alcohol (12 mmol), and the reaction was carried out under an oxygen environment using O_2 balloon for 4 h at RT. After that, distilled water (4 mL) was added to the reaction mixture, and the resultant solution was extracted with dichloromethane. The aqueous layer was separated and acidified with a few drops of aqueous H_2SO_4. To this solution, 10% KI solution and a few drops of 3% ammonium molybdate solution were added. The formation of H_2O_2 was detected spectrophotometrically by the appearance of a characteristic absorption band for I_3^- at 350 nm (Figure S6), which advocate the generation of H_2O_2 in our present catalytic protocol for anthranilate synthesis.

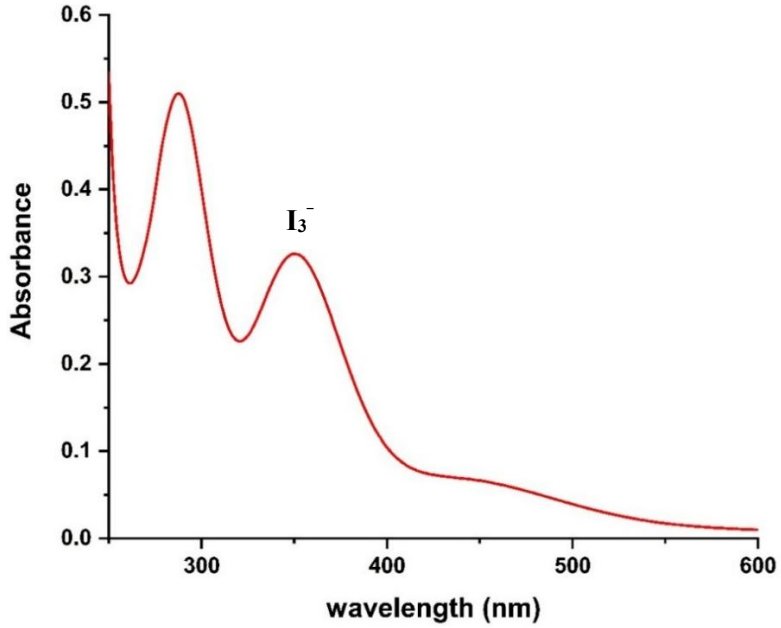


Figure S13. Detection of H_2O_2. Absorption spectra corresponding to the formation of I_3^- in presence of H_2O_2.[4]

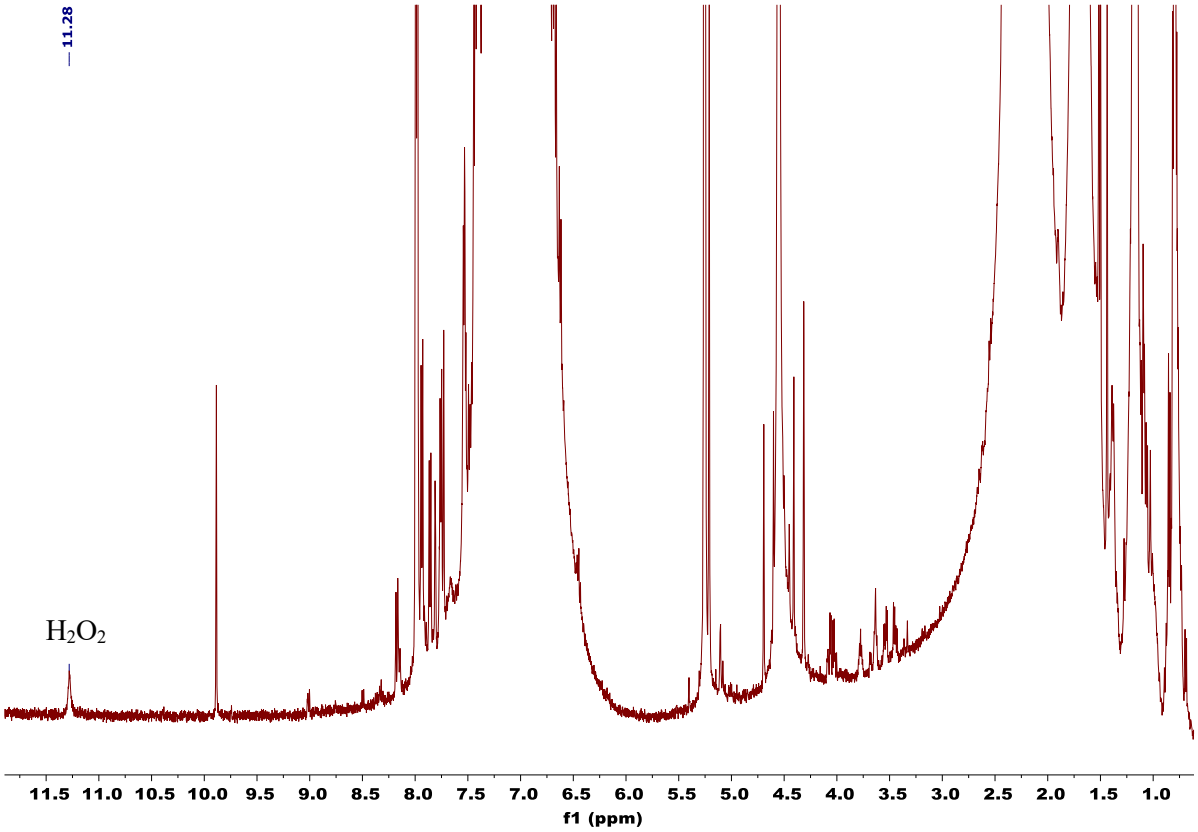
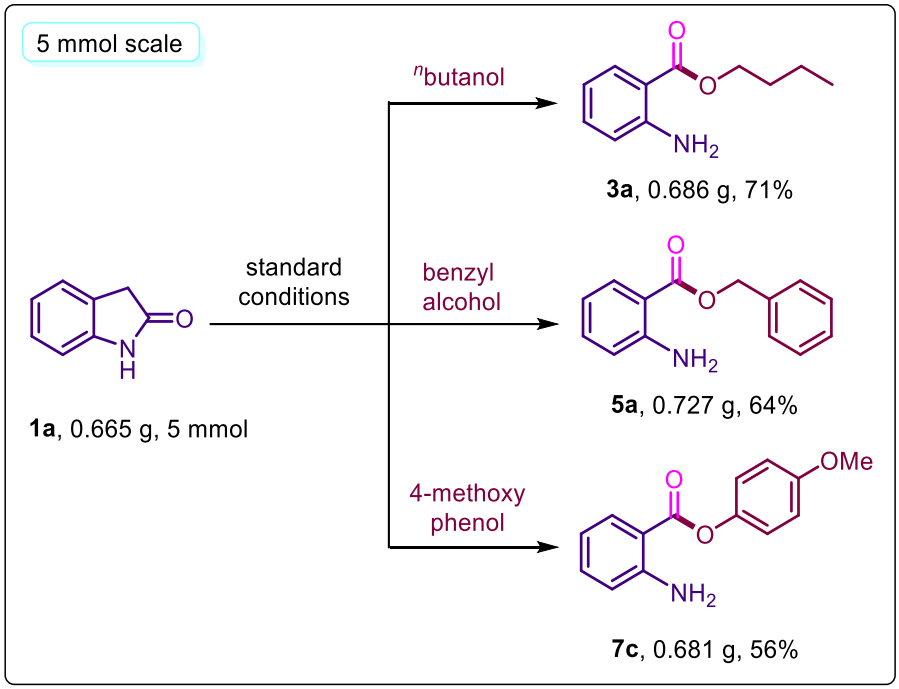


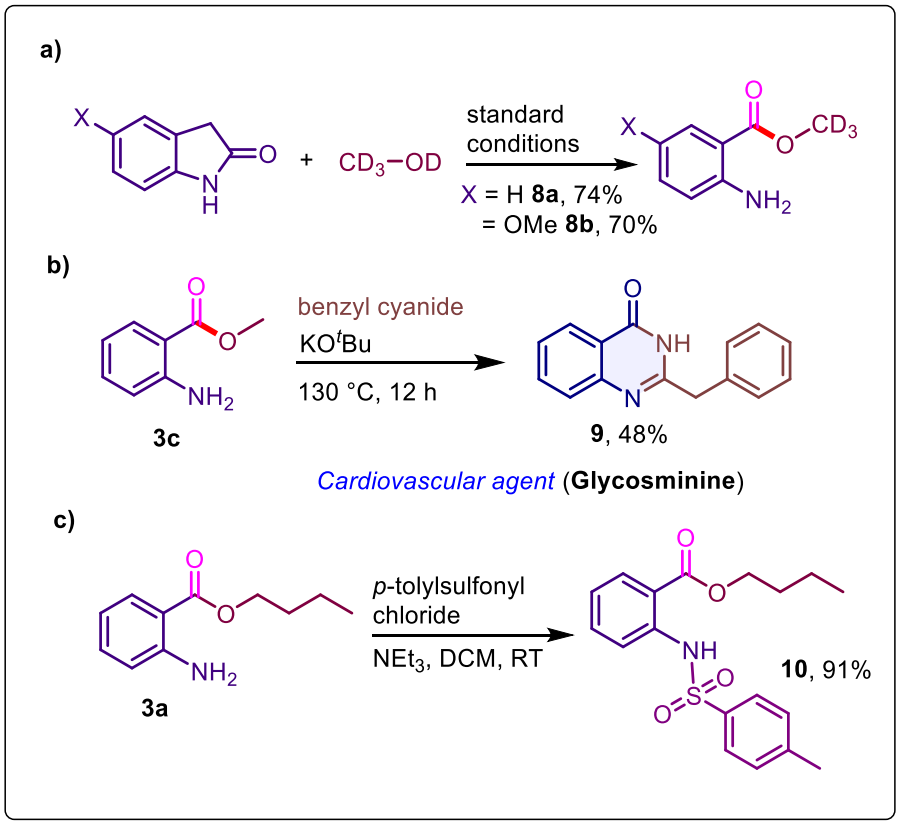
Figure S14. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the reaction mixture showing the formation of H_2O_2.[5]

Large Scale synthesis:



Scheme S6: Large scale synthesis (5 mmol scale).

Post-modification of the isolated products:



Scheme S7: Post-modifications and deuterium compounds.

Synthesis of methyl-d_3 2-aminobenzoate derivatives (8a-b):

Methyl-d_3 2-aminobenzoate (Compound-8a): Following the general procedure of the anthranilate synthesis, the titled compound **8a** was synthesized using methanol-d_3 and isolated as a yellow liquid (29 mg, 0.18 mmol, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 6.57 (t, J = 9.1 Hz, 2H), 5.63 (*br*, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 150.6, 134.2, 131.4, 116.8, 116.4, 110.9 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_8H_7D_3NO_2$ 155.0946; Found 155.0908.

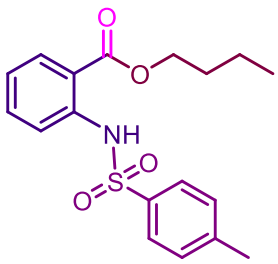
Methyl-d_3 2-amino-5-methoxybenzoate (Compound-8b): Following the general procedure of the anthranilate synthesis, the titled compound **8b** was synthesized using methanol-d_3 and isolated as a yellow liquid (32 mg, 0.17 mmol, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 1H), 6.94 (d, J = 11.6 Hz, 1H), 6.63 (d, J = 11.0 Hz, 1H), 5.42 (*br*, 2H), 3.76 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.4, 150.7, 145.2, 123.4, 118.4, 113.3, 110.9, 56.0 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_9H_9D_3NO_3$ 185.1052; Found 185.1016.

Preparation of 2-benzylquinazolin-4(3H)-one (Compound-9):

A Schlenk tube was charged **3c** (0.3 mmol), benzyl cyanide (1.8 mmol), and KO^{t}Bu (0.9 mmol) at 130 ºC for 12 h. After completion of the reaction, the compound was extracted with ethyl acetate following a water workup. Pure product **9** was isolated *via* silica gel column chromatography using ethyl acetate and hexane as eluents as a white solid (33 mg, 0.14 mmol, 48% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.42 (s, 1H), 8.06 (d, J = 6.5 Hz, 1H), 7.77 (t, J = 7.7 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.38 (d, J = 7.1 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 3.93 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 161.9, 156.0, 148.9, 136.6, 134.4, 128.9, 128.5, 127.0, 126.8, 126.3, 125.7, 120.8, 40.8 ppm.

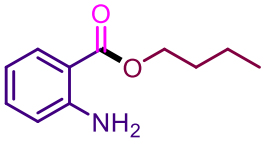
Preparation of butyl 2-((4-methylphenyl)sulfonamido)benzoate (Compound-10):

A Schlenk tube was charged with **3a** (0.2 mmol), *p*-toluenesulfonyl chloride (1.1 equiv.), and few drops of NEt_3 in DCM. Then the reaction mixture was stirred at RT for 4 h. After completion of the reaction, the pure product **10** was isolated as a colorless liquid *via* silica gel column chromatography using ethyl acetate and hexane as eluents (63 mg, 0.18 mmol, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.74-7.67 (m, 3H), 7.44 (t, J = 8.7 Hz, 1H), 7.21 (d, J = 8.3 Hz, 2H), 7.02 (t, J = 7.1 Hz, 1H), 4.27 (t, J = 6.6 Hz, 2H), 2.36 (s, 3H), 1.46-1.41 (m, 2H), 1.12 (t, J = 7.1 Hz, 1H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.9, 143.8, 140.6, 136.6, 134.3, 131.1, 129.6, 127.3, 122.8, 119.2, 116.3, 42.0, 30.5, 21.5, 19.2, 13.7 ppm.

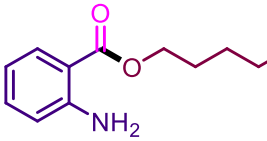


Characterization data of the isolated compounds:

Butyl 2-aminobenzoate (Compound-3a): Following the general procedure, the titled compound was isolated as a yellow liquid (36 mg, 0.18 mmol, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.9, 1.7 Hz, 1H), 7.17 (d, J = 1.7 Hz, 1H), 6.57 (t, J = 9.1 Hz, 2H), 5.64 (*br*, 2H), 4.20 (t, J = 6.6 Hz, 2H), 1.70-1.64 (m, 2H), 1.43-1.37 (m, 2H), 0.90 (t, J = 7.4 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.4, 150.6, 134.1, 131.3, 116.8, 116.4, 111.3, 64.3, 30.9, 19.5, 13.9 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{16}NO_2$ 194.1181; Found 194.1181.



Hexyl 2-aminobenzoate (Compound-3b): Following the general procedure, the titled compound was isolated as a yellow liquid (39 mg, 0.17 mmol, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.0, 1.8 Hz, 1H), 7.28 – 7.27 (m, 1H), 6.69-6.64 (dd, J = 14.8, 7.0 Hz, 2H), 4.27 (t, J = 6.7 Hz, 2H), 1.78 – 1.72 (m, 2H), 1.47 – 1.41 (m, 2H), 1.36 – 1.32 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.4, 150.3, 134.1, 131.3, 117.0, 116.6, 111.5, 64.7, 31.6, 28.8, 25.9, 22.7, 14.2 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{20}NO_2$ 222.1494; Found 222.1495.



Methyl 2-aminobenzoate (Compound-3c): Following the general procedure, the titled compound was isolated as a colorless liquid (31 mg, 0.20 mmol, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 1H), 7.31-7.28 (m, 1H), 6.73-6.67 (m, 2H), 3.88 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 149.7,

134.3, 131.4, 117.3, 117.1, 111.5, 51.7 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_8H_{10}NO_2$ 152.0712; Found 152.0704.

Ethyl 2-aminobenzoate (Compound-3d): Following the general procedure, the titled compound was isolated as a yellow liquid (32 mg, 0.19 mmol, 78% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 7.8, 1.4 Hz, 1H), 7.29-7.26 (m, 1H), 6.69-6.63 (m, 2H), 4.37 – 4.29 (m, 2H), 1.38 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.3, 150.3, 134.1, 131.4, 116.9, 116.5, 111.4, 60.5, 14.5 ppm.

Propyl 2-aminobenzoate (Compound-3e): Following the general procedure, the titled compound was isolated as a yellow liquid (34 mg, 0.18 mmol, 75% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 1H), 7.28 (s, 1H), 6.69-6.64 (m, 2H), 4.24 (t, J = 7.2 Hz, 2H), 1.82-1.76 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.3, 150.3, 134.1, 131.3, 117.0, 116.6, 111.5, 66.1, 22.3, 10.7 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{14}NO_2$ 180.1025; Found 180.1023.

Isobutyl 2-aminobenzoate (Compound-3f): Following the general procedure, the titled compound was isolated as a yellow liquid (29 mg, 0.15 mmol, 60% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 1H), 7.32 – 7.27 (m, 1H), 6.77-6.69 (m, 2H), 4.06 (dd, J = 6.6, 2.8 Hz, 2H), 2.13-2.04 (m, 1H), 1.03 (d, J = 2.9 Hz, 3H), 1.01 (d, J = 2.9 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.2, 149.3, 134.2, 131.3, 117.5, 117.3, 112.1, 70.7, 28.0, 19.4 ppm.

Isopentyl 2-aminobenzoate (Compound-3g): Following the general procedure, the titled compound was isolated as a yellow liquid (34 mg, 0.16 mmol, 65% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.1, 1.7 Hz, 1H), 7.30-7.27 (m, 1H), 6.73-6.66 (m, 2H), 4.31 (t, J = 6.8 Hz, 2H), 1.83-1.77 (m, 1H), 1.66 (q, J = 6.8 Hz, 2H), 0.97 (d, J = 6.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.3, 149.8, 134.1, 131.3, 117.2, 116.9, 111.7, 63.2, 37.6, 25.4, 22.7 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{18}NO_2$ 208.1338; Found 208.1337.

Cinnamyl 2-aminobenzoate (Compound-3h): Following the general procedure, the titled compound was isolated as a yellow liquid (45 mg, 0.17 mmol, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.8 Hz, 1H), 7.43 (d, J = 9.6 Hz, 2H), 7.35 – 7.26 (m, 4H), 6.76-6.65 (m, 3H), 6.45-6.37 (m, 1H), 4.95 (d, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 150.5, 136.4, 134.3, 134.1, 131.4, 128.7, 128.2, 126.8, 123.7, 116.9, 116.6, 111.0, 65.0 ppm.

3,7-dimethyloct-6-en-1-yl 2-aminobenzoate (Compound-3i): Following the general procedure, the titled compound was isolated as a yellow liquid (51 mg, 0.18 mmol, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 1H), 7.30-7.27 (m, 1H), 6.70-6.65 (m, 2H), 5.12-5.08 (m, 1H), 4.36-4.27 (m, 2H), 2.06-1.96 (m, 2H), 1.84-1.76 (m, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.58-1.53 (m, 2H), 1.44-1.37 (m, 1H), 1.24-1.20 (m, 1H), 0.97 (d, J = 6.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.3, 150.1, 134.1, 131.5, 131.3, 124.7, 117.1, 116.7, 111.5, 63.0, 37.1, 35.7, 29.7, 25.8, 25.5, 19.6, 17.8 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{26}NO_2$ 276.1964; Found 276.1970.

(Z)-octadec-9-en-1-yl 2-aminobenzoate (Compound-3j): Following the general procedure, the titled compound was isolated as a yellow liquid (64 mg, 0.16 mmol, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.9, 1.8 Hz, 1H), 7.27 (s, 1H), 6.67-6.63 (m, 2H), 5.36-5.34 (m, 2H), 4.26 (t, J = 6.7 Hz, 2H), 2.04-1.99 (m, 3H), 1.78-1.72 (m, 2H), 1.35-1.30 (m, 10H), 1.26 (d, J = 5.3 Hz, 13H), 0.88 (t, J = 7.4 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.4, 150.5, 134.1, 131.3, 130.1, 129.9, 116.8, 116.4, 111.3, 64.6, 32.1, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.4, 28.9, 27.4, 27.3, 26.2, 22.8, 14.3 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{42}NO_2$ 388.3216; Found 388.3220.

Phenethyl 2-aminobenzoate (Compound-3k): Following the general procedure, the titled compound was isolated as a yellow liquid (43 mg, 0.17 mmol, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.1, 1.7 Hz, 1H), 7.31-7.28 (m, 5H), 7.24 (d, J = 7.0 Hz, 1H), 6.71-6.65 (m, 2H), 4.50 (t, J = 7.0 Hz, 2H), 3.07 (t, J = 7.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.1,

149.9, 138.1, 134.2, 131.4, 129.1, 128.7, 126.7, 117.2, 116.9, 111.5, 65.1, 35.4 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}NO_2$ 242.1181; Found 242.1186.

3-oxobutyl 2-aminobenzoate (Compound-3l): Following the general procedure, the titled compound was isolated as a yellow liquid (28 mg, 0.13 mmol, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 9.8 Hz, 1H), 7.25-7.23 (m, 1H), 6.64 (t, J = 8.2 Hz, 2H), 6.21 (*br*, 2H), 3.27 (t, J = 6.5 Hz, 2H), 2.83 (t, J = 6.3 Hz, 2H), 2.26 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 207.9, 200.5, 150.4, 134.5, 131.2, 117.9, 117.4, 116.0, 37.4, 33.1, 30.3 ppm.

2-(tert-butoxycarbonyl)amino)ethyl 2-aminobenzoate (Compound-3m): Following the general procedure, the titled compound was isolated as a yellow liquid (35 mg, 0.12 mmol, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 8.1, 1.7 Hz, 1H), 7.28-7.26 (m, 1H), 6.69-6.63 (m, 2H), 4.90 (*br*, 1H), 4.32 (t, J = 5.3 Hz, 2H), 3.52-3.50 (m, 2H), 1.44 (s, 9H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.0, 156.0, 150.4, 134.4, 131.4, 117.0, 116.6, 110.7, 79.7, 63.8, 39.9, 28.5 ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{20}N_2O_4Na$ 303.1321; Found 303.1327.

5-hydroxypentyl 2-aminobenzoate (Compound-3n): Following the general procedure, the titled compound was isolated as a yellow liquid (32 mg, 0.14 mmol, 58% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.1, 1.7 Hz, 1H), 7.27 (d, J = 5.4 Hz, 1H), 6.69-6.64 (m, 2H), 4.28 (t, J = 6.6 Hz, 2H), 3.67 (t, J = 6.4 Hz, 2H), 1.82-1.75 (m, 2H), 1.66-1.60 (m, 2H), 1.56-1.51 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.3, 150.1, 134.2, 131.3, 117.1, 116.7, 111.4, 64.4, 62.8, 32.4, 28.7, 22.5 ppm.

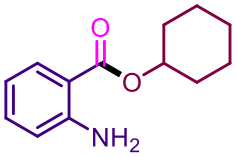
3-methoxypropyl 2-aminobenzoate (Compound-3o): Following the general procedure, the titled compound was isolated as a yellow liquid (40 mg, 0.19 mmol, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.9 Hz, 1H), 7.25 (s, 1H), 6.66-6.63 (m, 2H), 5.72 (*br*, 2H), 4.36 (t, J = 6.4 Hz, 2H), 3.53 (t, J = 6.3 Hz, 2H), 3.36 (s, 3H), 2.05-2.00 (m, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.2, 150.6, 134.2, 131.3, 116.8, 116.4, 111.1, 69.5, 61.7, 58.9, 29.3 ppm.

(tetrahydrofuran-2-yl)methyl 2-aminobenzoate (Compound-3p): Following the general procedure, the titled compound was isolated as a yellow liquid (35 mg, 0.15 mmol, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.1, 1.7 Hz, 1H), 7.28-7.26 (m, 1H), 6.69-6.63 (m, 2H), 4.36-4.31 (m, 1H), 4.26-4.21 (m, 2H), 3.95-3.90 (m, 1H), 3.85-3.80 (m, 1H), 2.10-2.03 (m, 1H), 1.99-1.90 (m, 2H), 1.77-1.69 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 150.2, 134.3, 131.5, 117.0, 116.7, 111.1, 76.8, 68.7, 66.4, 28.3, 25.9 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{16}NO_3$ 222.1130; Found 222.1133.

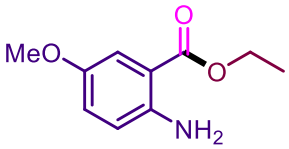
(tetrahydro-2H-pyran-4-yl)methyl 2-aminobenzoate (Compound-3q): Following the general procedure, the titled compound was isolated as a yellow liquid (38 mg, 0.16 mmol, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.1, 1.6 Hz, 1H), 7.32-7.27 (m, 1H), 6.76-6.68 (m, 2H), 4.15 (d, J = 6.5 Hz, 2H), 4.03-3.99 (m, 2H), 3.46-3.40 (m, 2H), 2.08-2.00 (m, 1H), 1.74-1.68 (m, 2H), 1.53-1.45 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 149.5, 134.3, 131.2, 117.5, 117.3, 111.7, 68.7, 67.7, 34.9, 29.8 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{18}NO_3$ 236.1287; Found 236.1290.

3-(methyl(phenyl)amino)propyl 2-aminobenzoate (Compound-3r): Following the general procedure, the titled compound was isolated as a yellow liquid (41 mg, 0.14 mmol, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.3, 1.6 Hz, 1H), 7.30-7.27 (m, 1H), 7.22-7.20 (m, 2H), 6.76-6.64 (m, 5H), 5.70 (*br*, 2H), 4.34 (t, J = 6.3 Hz, 2H), 3.51 (t, J = 6.8 Hz, 2H), 2.97 (s, 3H), 2.09-2.02 (m, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.2, 150.7, 149.3, 134.3, 131.2, 129.4, 116.9, 116.5, 116.5, 112.4, 110.9, 62.3, 49.7, 38.7, 26.4 ppm.

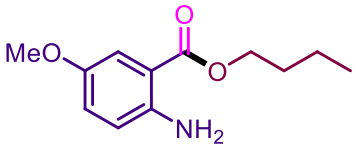
2-(thiophen-2-yl)ethyl 2-aminobenzoate (Compound-3s): Following the general procedure, the titled compound was isolated as a yellow liquid (43 mg, 0.17 mmol, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.3, 1.7 Hz, 1H), 7.18-7.16 (m, 1H), 6.97-6.91 (m, 3H), 6.67-6.63 (m, 2H), 5.69 (*br*, 2H), 4.50 (t, J = 6.6 Hz, 2H), 3.29 (t, J = 6.1 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 150.7, 140.3, 134.3, 131.5, 127.0, 125.7, 124.2, 116.8, 116.5, 110.9, 64.7, 29.6 ppm.

cyclohexyl 2-aminobenzoate (Compound-3t): Following the general procedure, the titled compound was isolated as a yellow liquid (28 mg, 0.12 mmol, 51% yield). 

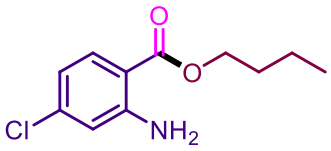
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.0, 1.6 Hz, 1H), 7.31-7.27 (m, 1H), 6.78-6.70 (m, 2H), 5.03-4.97 (m, 1H), 1.96-1.90 (m, 2H), 1.83-1.75 (m, 2H), 1.64-1.54 (m, 4H), 1.50-1.43 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6, 149.0, 134.1, 131.4, 117.6, 117.5, 112.7, 72.7, 31.8, 25.6, 23.8 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{18}NO_2$ 220.1338; Found 220.1337.

Ethyl 2-amino-5-methoxybenzoate (Compound-3u): Following the general procedure, the titled compound was isolated as a yellow liquid (38 mg, 0.19 mmol, 78% yield). 

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 3.0 Hz, 1H), 6.94 (dd, J = 8.9, 3.1 Hz, 1H), 6.63 (d, J = 8.9 Hz, 1H), 5.41 (*br*, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.0, 150.7, 145.2, 123.0, 118.3, 113.7, 111.3, 60.6, 56.1, 14.5 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{14}NO_3$ 196.0974; Found 196.0983.

butyl 2-amino-5-methoxybenzoate (Compound-3v): Following the general procedure, the titled compound was isolated as a white solid (45 mg, 0.2 mmol, 80% yield). 

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 3.1 Hz, 1H), 6.95 (dd, J = 8.9, 3.1 Hz, 1H), 6.68 (d, J = 8.9 Hz, 1H), 4.29 (t, J = 6.6 Hz, 2H), 3.76 (s, 3H), 1.77-1.72 (m, 2H), 1.51-1.44 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.0, 151.0, 144.4, 122.8, 118.7, 113.9, 111.8, 64.6, 56.0, 30.9, 19.5, 13.9 ppm.

butyl 2-amino-4-chlorobenzoate (Compound-3w): Following the general procedure, the titled compound was isolated as a yellow liquid (42 mg, 0.18 mmol, 73% yield). 

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.5 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.62 (dd, J = 8.6, 2.1 Hz, 1H), 4.27 (t, J = 6.6 Hz, 2H), 1.76-1.70 (m, 2H), 1.50-1.43 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.7, 150.9, 140.1, 132.7, 117.1, 116.3, 110.0, 64.6, 30.9, 19.4, 13.9 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{15}NO_2Cl$ 228.0791; Found 228.0793.

3-methoxypropyl 2-amino-5-methoxybenzoate (Compound-3x): Following the general procedure, the titled compound was isolated as a white solid (49 mg, 0.2 mmol, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 1H), 6.95 (d, J = 9.0 Hz, 1H), 6.68 (d, J = 11.9 Hz, 1H), 4.37 (t, J = 7.6 Hz, 2H), 3.76 (s, 3H), 3.53 (t, J = 7.7 Hz, 2H), 3.36 (s, 3H), 2.06-2.00 (m, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.8, 151.0, 144.5, 122.9, 118.7, 113.9, 111.6, 69.5, 61.9, 58.9, 56.1, 29.2 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{18}NO_4$ 240.1236; Found 240.1241.

3-methoxypropyl 2-amino-4-chlorobenzoate (Compound-3y): Following the general procedure, the titled compound was isolated as a yellow liquid (46 mg, 0.18 mmol, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.6 Hz, 1H), 6.67 (d, J = 2.0 Hz, 1H), 6.60 (dd, J = 8.6, 2.1 Hz, 1H), 4.36 (t, J = 6.4 Hz, 2H), 3.52 (t, J = 6.3 Hz, 2H), 3.35 (s, 3H), 2.05-1.98 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.6, 151.2, 140.1, 132.7, 116.9, 116.2, 109.7, 69.4, 62.0, 58.9, 29.2 ppm.

butyl 2-(phenylamino)benzoate (Compound-3z): Following the general procedure, the titled compound was isolated as a yellow liquid (32 mg, 0.12 mmol, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (*br*, 1H), 7.98 (dd, J = 8.1, 1.7 Hz, 1H), 7.36-7.27 (m, 5H), 7.24-7.23 (m, 1H), 7.10-7.06 (m, 1H), 6.75-6.71 (m, 1H), 4.31 (t, J = 6.6 Hz, 2H), 1.81-1.73 (m, 2H), 1.54-1.47 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 148.1, 141.0, 134.1, 131.7, 129.5, 123.6, 122.6, 117.2, 114.2, 112.4, 64.7, 30.9, 19.5, 13.9 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{20}NO_2$ 270.1494; Found 270.1499.

benzyl 2-aminobenzoate (Compound-5a): Following the general procedure, the titled compound was isolated as a yellow liquid (41 mg, 0.18 mmol, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.1, 1.6 Hz, 1H), 7.46-7.34 (m, 5H), 7.31-7.28 (m, 1H), 6.74-6.66 (m, 2H), 5.33 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 149.9, 136.4, 134.4, 131.5, 128.7, 128.3, 128.1, 117.3, 117.0, 111.3, 66.3 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}NO_2$ 228.1025; Found 228.1029.

4-Methylbenzyl 2-aminobenzoate (Compound-5b): Following the general procedure, the titled compound was isolated as a yellow liquid (46 mg, 0.19 mmol, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.1, 1.7 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.26-7.23 (m, 1H), 7.19 (d, J = 7.8 Hz, 2H), 6.67-6.60 (m, 2H), 5.71 (*br*, 2H), 5.28 (s, 2H), 2.37 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 150.7, 138.1, 134.3, 133.4, 131.5, 129.4, 128.3, 116.8, 116.4, 66.1, 21.3 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}NO_2$ 242.1181; Found 242.1182.

4-isopropylbenzyl 2-aminobenzoate (Compound-5c): Following the general procedure, the titled compound was isolated as a yellow liquid (52 mg, 0.19 mmol, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.1, 1.8 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.27-7.24 (m, 3H), 6.67-6.61 (m, 2H), 5.73 (*br*, 2H), 5.30 (s, 2H), 2.98-2.88 (m, 1H), 1.27 (d, J = 6.9 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 150.7, 149.1, 134.3, 133.8, 131.5, 128.3, 126.8, 126.8, 116.8, 116.4, 111.0, 66.1, 34.0, 24.1 ppm.

3-methoxybenzyl 2-aminobenzoate (Compound-5d): Following the general procedure, the titled compound was isolated as a yellow liquid (47 mg, 0.18 mmol, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 9.5 Hz, 1H), 7.30 (t, J = 7.8 Hz, 2H), 7.02 (d, J = 7.5 Hz, 1H), 6.98 (s, 1H), 6.88 (d, J = 5.6 Hz, 1H), 6.67-6.62 (m, 2H), 5.30 (s, 2H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 159.9, 150.7, 138.0, 134.4, 131.5, 129.8, 120.3, 116.8, 116.5, 113.7, 113.6, 110.8, 66.0, 55.4 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}NO_3$ 258.1130; Found 258.1129.

3-Phenoxybenzyl 2-aminobenzoate (Compound-5e): Following the general procedure, the titled compound was isolated as a yellow liquid (60 mg, 0.18 mmol, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.0, 1.6 Hz, 1H), 7.38-7.32 (m, 3H), 7.30-7.26 (m, 1H), 7.19-7.10 (m, 3H), 7.05-7.03 (m, 2H), 6.96 (dd, J = 8.3, 2.5 Hz, 1H), 6.68-6.62 (m, 2H), 5.72 (*br*, 2H), 5.29 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.9, 157.7, 157.1, 150.8, 138.5, 134.4, 131.4, 130.0, 129.9, 123.6, 122.6, 119.3, 118.3, 118.2, 116.8, 116.5, 110.7, 65.6 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{18}NO_3$ 320.1287; Found 320.1302.

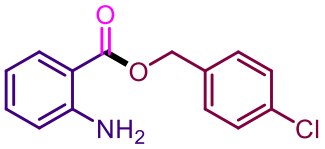
3,4-Dimethoxybenzyl 2-aminobenzoate (Compound-5f): Following the general procedure, the titled compound was isolated as a yellow liquid (48 mg, 0.16 mmol, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 6.1 Hz, 1H), 7.01 (d, J = 9.9 Hz, 1H), 6.97 (s, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.67 – 6.60 (m, 2H), 5.73 (*br*, 2H), 5.26 (s, 2H), 3.91-3.88 (m, 6H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.1, 150.7, 149.2, 134.3, 131.4, 128.9, 121.2, 116.8, 116.4, 111.8, 111.2, 66.3, 56.1 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{18}NO_4$ 288.1236; Found 288.1250.

3,4,5-trimethoxybenzyl 2-aminobenzoate (Compound-5g): Following the general procedure, the titled compound was isolated as a yellow liquid (53 mg, 0.16 mmol, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.1, 1.6 Hz, 1H), 7.29-7.27 (m, 1H), 6.68-6.62 (m, 4H), 5.24 (s, 2H), 3.87 (s, 6H), 3.85 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 153.5, 150.8, 138.1, 134.4, 132.0, 131.4, 116.9, 116.5, 110.8, 105.5, 66.4, 61.0, 56.3 ppm.

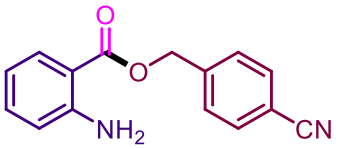
3-fluorobenzyl 2-aminobenzoate (Compound-5h): Following the general procedure, the titled compound was isolated as a yellow liquid (43 mg, 0.17 mmol, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.3, 1.9 Hz, 1H), 7.37-7.28 (m, 2H), 7.22-7.20 (m, 1H), 7.17-7.14 (m, 1H), 7.05-7.00 (m, 1H), 6.68-6.64 (m, 2H), 5.74 (br, 2H), 5.32 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 164.3, 161.8, 150.8, 139.0, 139.0, 134.5, 131.4, 131.4, 130.3, 130.2, 123.4, 123.4, 116.9, 116.5, 115.2, 115.0, 114.9, 114.7, 110.5, 65.2 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.8 ppm. . HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{13}NO_2F$ 246.0930; Found 246.0939.

3-chlorobenzyl 2-aminobenzoate (Compound-5i): Following the general procedure, the titled compound was isolated as a yellow liquid (47 mg, 0.18 mmol, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.0, 1.8 Hz, 1H), 7.38 (s, 1H), 7.26-7.21 (m, 3H), 7.22-7.21 (m, 1H), 6.65-6.59 (m, 2H), 5.24 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 150.5, 140.1, 138.5, 134.5, 131.4, 130.0, 128.4, 128.1, 126.1, 117.0, 116.7, 110.6, 65.2 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{13}NO_2Cl$ 262.0635; Found 262.0637.

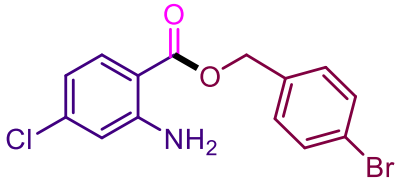
4-chlorobenzyl 2-aminobenzoate (Compound-5j): Following the general procedure, the titled compound was isolated as a yellow liquid (46 mg, 0.17 mmol, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 10.2 Hz, 1H), 7.28 (s, 1H), 7.24 (s, 1H), 7.19-7.15 (m, 2H), 6.58-6.53 (m, 3H), 5.18 (s, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.9, 150.7, 135.0, 134.5, 134.1, 131.4, 129.5, 128.9, 116.9, 116.5, 110.6, 65.3 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{13}NO_2Cl$ 262.0635; Found 262.0635.



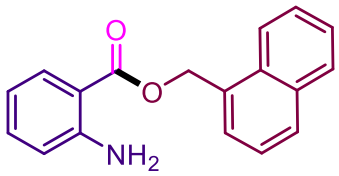
4-cyanobenzyl 2-aminobenzoate (Compound-5k): Following the general procedure, the titled compound was isolated as a yellow liquid (44 mg, 0.17 mmol, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.29 (t, J = 7.7 Hz, 1H), 6.69-6.64 (m, 2H), 5.36 (s, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 151.0, 141.9, 134.7, 132.6, 131.2, 128.2, 118.7, 116.9, 116.5, 112.0, 110.1, 64.9 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}N_2O_2$ 253.0977; Found 253.0980.



4-bromobenzyl 2-amino-4-chlorobenzoate (Compound-5l): Following the general procedure, the titled compound was isolated as a yellow liquid (58 mg, 0.17 mmol, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 2.1 Hz, 1H), 6.59 (dd, J = 8.6, 2.1 Hz, 1H), 5.81 (*br*, 2H), 5.25 (s, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.3, 151.5, 140.5, 135.2, 132.7, 131.9, 129.9, 122.4, 116.9, 116.1, 109.1, 65.6 ppm.



Naphthalen-1-ylmethyl 2-aminobenzoate (Compound-5m): Following the general procedure, the titled compound was isolated as a yellow liquid (42 mg, 0.15 mmol, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.2 Hz, 1H), 7.92-7.85 (m, 3H), 7.63 (d, J = 6.9 Hz, 1H), 7.59-7.53 (m, 2H), 7.50-7.46 (m, 1H), 7.25-7.23 (m, 1H), 6.66 (d, J = 11.1 Hz, 1H), 6.59 (t, J = 7.6 Hz, 1H), 5.78 (s, 2H), 5.74 (*br*, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.1, 150.8, 134.4, 133.9, 131.9, 131.5, 129.4, 128.9, 127.4, 126.7, 126.1, 125.4, 123.8, 116.8, 116.5, 110.8, 64.6 ppm.



Naphthalen-2-ylmethyl 2-aminobenzoate (Compound-5n): Following the general procedure, the titled compound was isolated as a yellow liquid (53 mg, 0.19 mmol, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.1, 1.7 Hz, 1H), 7.91-7.83 (m, 4H), 7.55 (dd, J = 8.4, 1.8 Hz, 1H), 7.52-7.47 (m, 2H), 7.30-7.27 (m, 1H), 6.69-6.61 (m, 2H), 5.74 (*br*, 2H), 5.49 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.9, 150.6, 134.2, 133.8, 131.4, 128.4, 128.0, 127.7, 127.1, 126.3, 126.2, 125.8, 116.7, 116.3, 66.2 ppm.

[1,1'-biphenyl]-4-ylmethyl 2-aminobenzoate (Compound-5o): Following the general procedure, the titled compound was isolated as a yellow liquid (57 mg, 0.19 mmol, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.1, 1.6 Hz, 1H), 7.63 -7.58 (m, 4H), 7.52 (d, J = 8.5 Hz, 2H), 7.48-7.42 (m, 2H), 7.39 – 7.33 (m, 1H), 7.29 (dd, J = 7.7, 2.3 Hz, 1H), 6.69 -6.62 (m, 2H), 5.74 (*br*, 2H), 5.37 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.1, 150.8, 141.3, 140.9, 135.5, 134.4, 131.5, 128.9, 128.6, 127.6, 127.5, 127.3, 116.8, 116.5, 110.8, 65.9 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{18}NO_2$ 304.1338; Found 304.1352.

Benzo[d][1,3]dioxol-5-ylmethyl 2-aminobenzoate (Compound-5p): Following the general procedure, the titled compound was isolated as a yellow liquid (45 mg, 0.16 mmol, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 8.0, 1.8 Hz, 1H), 7.25-7.24 (m, 1H), 6.94-6.90 (m, 2H), 6.80 (d, J = 7.9 Hz, 1H), 6.66-6.61 (m, 2H), 5.96 (s, 2H), 5.71 (*br*, 2H), 5.22 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.0, 150.7, 148.0, 147.7, 134.3, 131.5, 130.2, 122.1, 116.8, 116.4, 110.9, 109.0, 108.4, 101.3, 66.1 ppm.

Pyridin-2-ylmethyl 2-aminobenzoate (Compound-5q): Following the general procedure, the titled compound was isolated as a yellow liquid (39 mg, 0.17 mmol, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 6.4 Hz, 1H), 7.97 (dd, J = 7.9, 1.6 Hz, 1H), 7.76-7.72 (m, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.30-7.28 (m, 1H), 7.25 (s, 1H), 6.68-6.63 (m, 2H), 5.47 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.7, 156.3, 150.9, 149.1, 137.4, 134.6, 131.4, 123.0, 121.8, 116.9, 116.5, 110.4, 66.3 ppm.

Thiophen-2-ylmethyl 2-aminobenzoate (Compound-5r): Following the general procedure, the titled compound was isolated as a yellow liquid (38 mg, 0.16 mmol, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 6.5 Hz, 1H), 7.24 (s, 1H), 7.16 (d, J = 3.9 Hz, 1H), 7.01 (t, J = 4.3 Hz, 1H), 6.66-6.61 (m, 2H), 5.71 (*br*, 2H), 5.47 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 150.8, 138.5, 134.4, 131.5, 128.0, 126.9, 126.8, 116.8 116.5, 110.7, 60.6 ppm.

Furan-2-ylmethyl 2-aminobenzoate (Compound-5s): Following the general procedure, the titled compound was isolated as a yellow liquid (39 mg, 0.17 mmol, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.1, 1.7 Hz, 1H), 7.44 (dd, J = 1.9, 0.9 Hz, 1H), 7.28-7.26 (m, 1H), 6.68-6.61 (m, 2H), 6.46 (d, J = 3.3 Hz, 1H), 6.39-6.37 (m, 1H), 5.27 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 150.5, 149.9, 143.3, 134.4, 131.6, 116.9, 116.6, 110.7, 110.7, 58.1, 29.8 ppm.

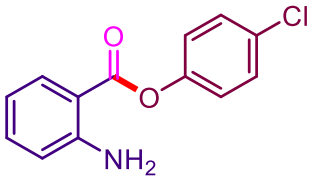
Phenyl 2-aminobenzoate (Compound-7a): Following the general procedure, the titled compound was isolated as a yellow liquid (32 mg, 0.15 mmol, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.0, 2.1 Hz, 1H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 1H), 7.30-7.26 (m, 1H), 7.22-7.17 (m, 2H), 6.76-6.69 (m, 2H), 5.77 (*br*, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.0, 151.4, 151.0, 135.0, 131.7, 129.6, 125.9, 122.1, 116.9, 116.5, 109.8 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{12}NO_2$ 214.0868; Found 214.0877.

4-(tert-butyl)phenyl 2-aminobenzoate (Compound-7b): Following the general procedure, the titled compound was isolated as a yellow liquid (42 mg, 0.15 mmol, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 7.8, 2.1 Hz, 1H), 7.46-7.44 (m, 2H), 7.36-7.32 (m, 1H), 7.14-7.10 (m, 2H), 6.75-6.69 (m, 2H), 5.78 (*br*, 2H), 1.35 (s, 9H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.2, 151.4, 148.7, 148.6, 134.9, 131.7, 126.5, 121.4, 116.9, 116.5, 110.0, 34.6, 31.6 ppm.

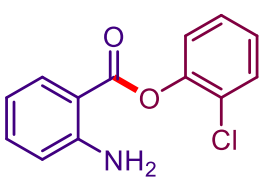
4-Methoxyphenyl 2-aminobenzoate (Compound-7c): Following the general procedure, the titled compound was isolated as a yellow liquid (40 mg, 0.16 mmol, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.5, 1.6 Hz, 1H), 7.35-7.31 (m, 1H), 7.10 (d, J = 9.1 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 6.74-6.69 (m, 2H), 5.76 (*br*, 2H), 3.82 (s, 3H)

ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 157.4, 151.3, 144.4, 134.9, 131.7, 122.9, 116.9, 116.5, 114.7, 109.9, 55.8 ppm.

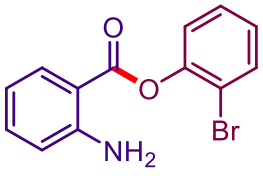
4-Chlorophenyl 2-aminobenzoate (Compound-7d): Following the general procedure, the titled compound was isolated as a yellow liquid (33 mg, 0.13 mmol, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.4, 1.6 Hz, 1H), 7.41-7.37 (m, 2H), 7.37-7.32 (m, 1H), 7.15-7.12 (m, 2H), 6.74-6.70 (m, 2H), 5.76 (*br*, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 166.7, 151.5, 149.5, 141.7, 135.2, 131.7, 129.6, 123.5, 117.0, 116.3, 109.4 ppm.



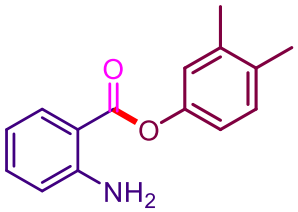
2-Chlorophenyl 2-aminobenzoate (Compound-7e): Following the general procedure, the titled compound was isolated as a yellow liquid (28 mg, 0.11 mmol, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.1, 1.9 Hz, 1H), 7.49 (dd, J = 7.9, 1.6 Hz, 1H), 7.39-7.30 (m, 2H), 7.27 (d, J = 1.4 Hz, 1H), 7.25-7.21 (m, 1H), 6.76-6.70 (m, 2H), 5.75 (*br*, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.9, 151.5, 147.3, 135.3, 132.0, 130.5, 127.9, 127.5, 127.1, 124.3, 116.9, 116.7, 109.2 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{11}ClNO_2$ 248.0478; Found 248.0488.



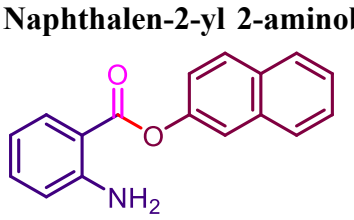
2-Bromophenyl 2-aminobenzoate (Compound-7f): Following the general procedure, the titled compound was isolated as a yellow liquid (29 mg, 0.1mmol, 40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.43-7.34 (m, 3H), 7.16 (m, 1H), 6.73 (m, 2H), 5.75 (*br*, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.9, 151.5, 148.5, 135.3, 133.5, 132.0, 129.6, 128.6, 127.4, 124.3, 122.2, 116.9, 116.7, 109.3 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for C13H11NO2 291.9973; Found 291.9986.



3,4-Dimethylphenyl 2-aminobenzoate (Compound-7g): Following the general procedure, the titled compound was isolated as a yellow liquid (36 mg, 0.15 mmol, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 9.9 Hz, 1H), 7.36-7.30 (m, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.97 (t, J = 2.6 Hz, 1H), 6.92 (dd, J = 8.1, 2.6 Hz, 1H), 6.74-6.68 (m, 2H), 5.76 (*br*, 2H), 2.28 (d, J = 5.5 Hz, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 151.3, 148.8, 138.1, 134.8, 134.2, 131.7, 130.5, 123.0, 119.2, 116.9, 116.5, 110.0, 20.0, 19.3 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{16}NO_2$ 242.1181; Found 242.1190.



Naphthalen-2-yl 2-aminobenzoate (Compound-7h): Following the general procedure, the titled compound was isolated as a yellow liquid (36 mg, 0.13 mmol, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, J = 8.1, 1.5 Hz, 1H), 7.93-7.82 (m, 3H), 7.66 (d, J = 2.4 Hz, 1H), 7.50 (pd, J = 6.9, 1.6 Hz, 2H), 7.39 – 7.33 (m, 2H), 6.77-6.71 (m, 2H), 5.80 (*br*, 2H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.1, 151.4, 148.6, 135.1, 134.0, 131.8, 131.6, 129.6, 127.9, 127.8, 126.7, 125.8, 121.7, 119.1, 116.9, 116.6, 109.7 ppm. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{14}NO_2$ 264.1025; Found 264.1033.



^{1}H and ^{13}C{^{1}H} NMR spectra of the isolated compounds from catalytic reactions

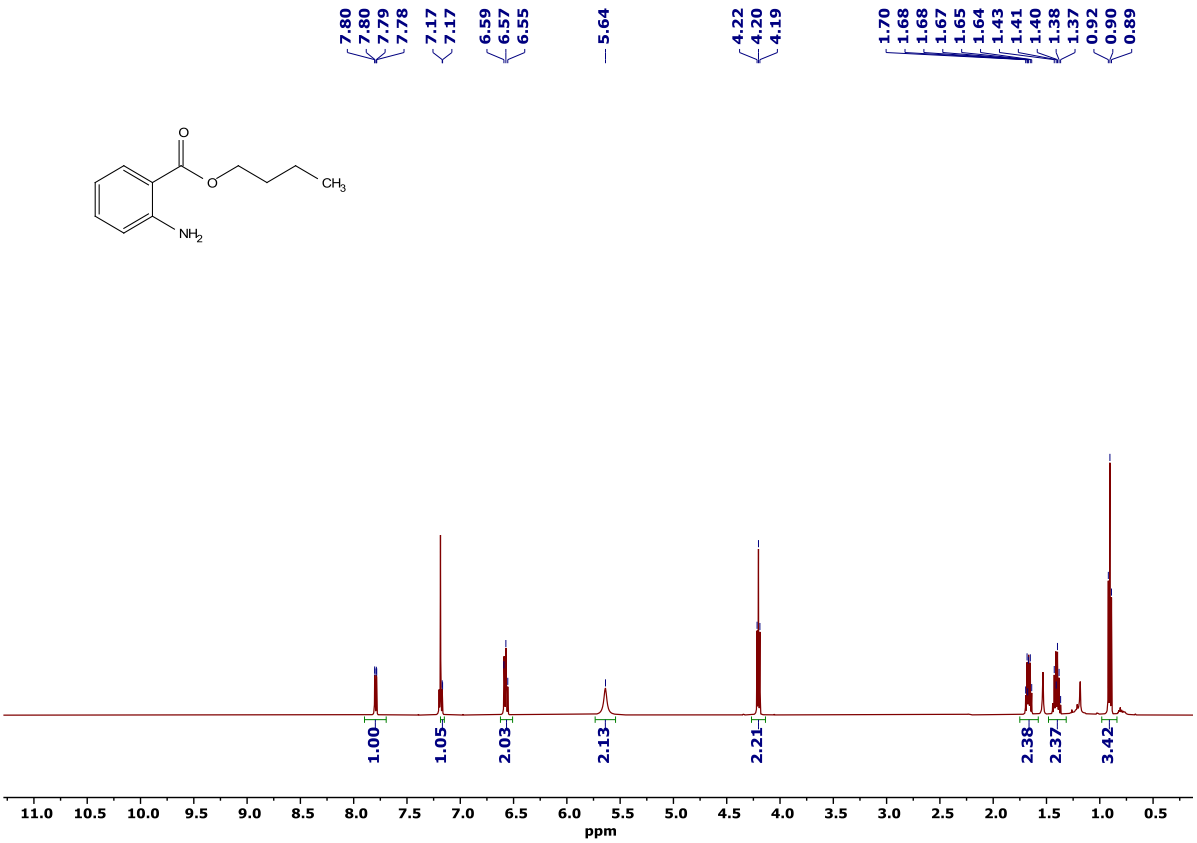


Figure S15. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

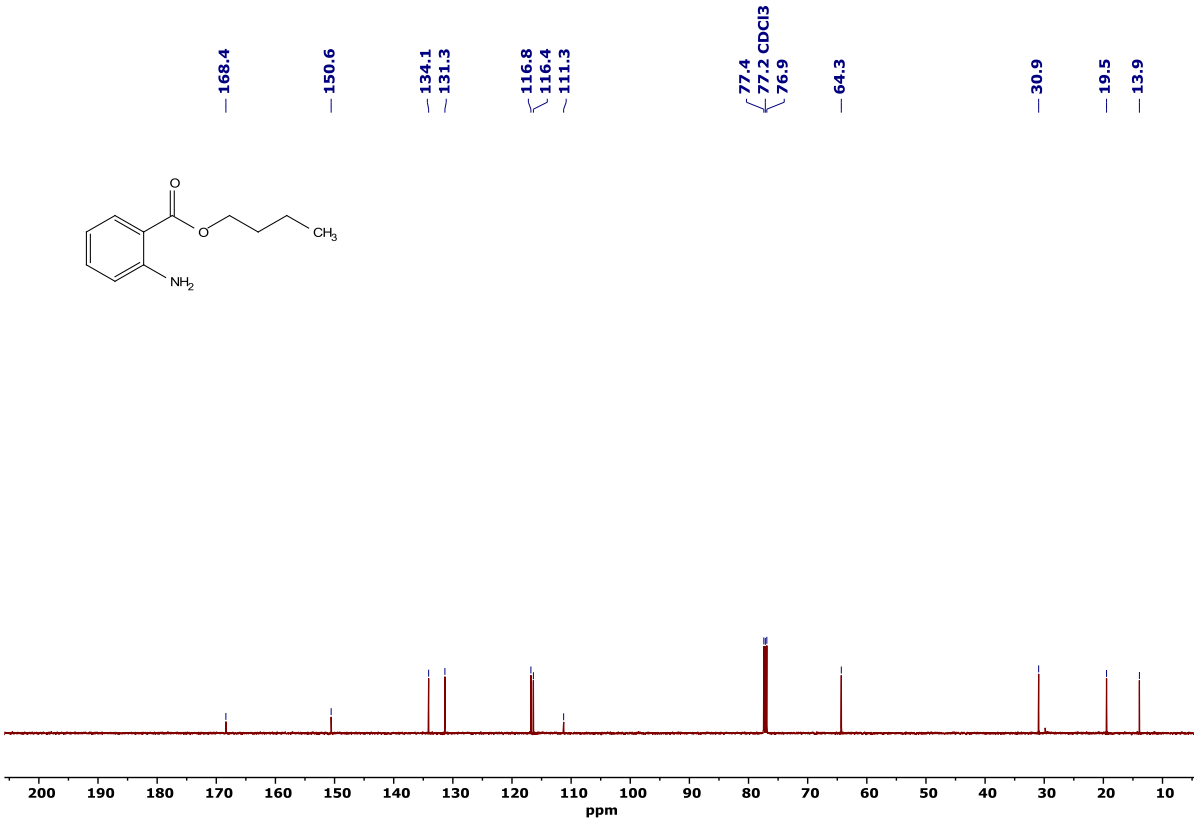


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$.

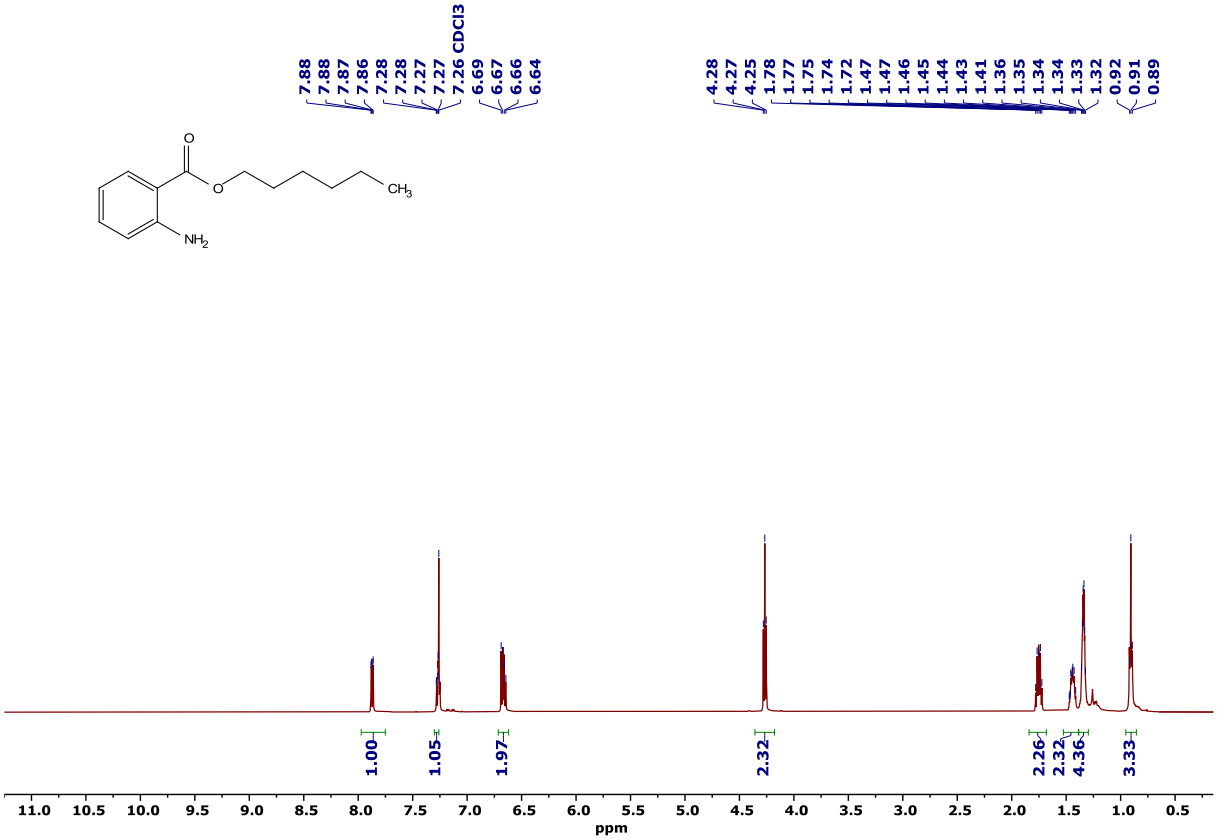


Figure S17. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

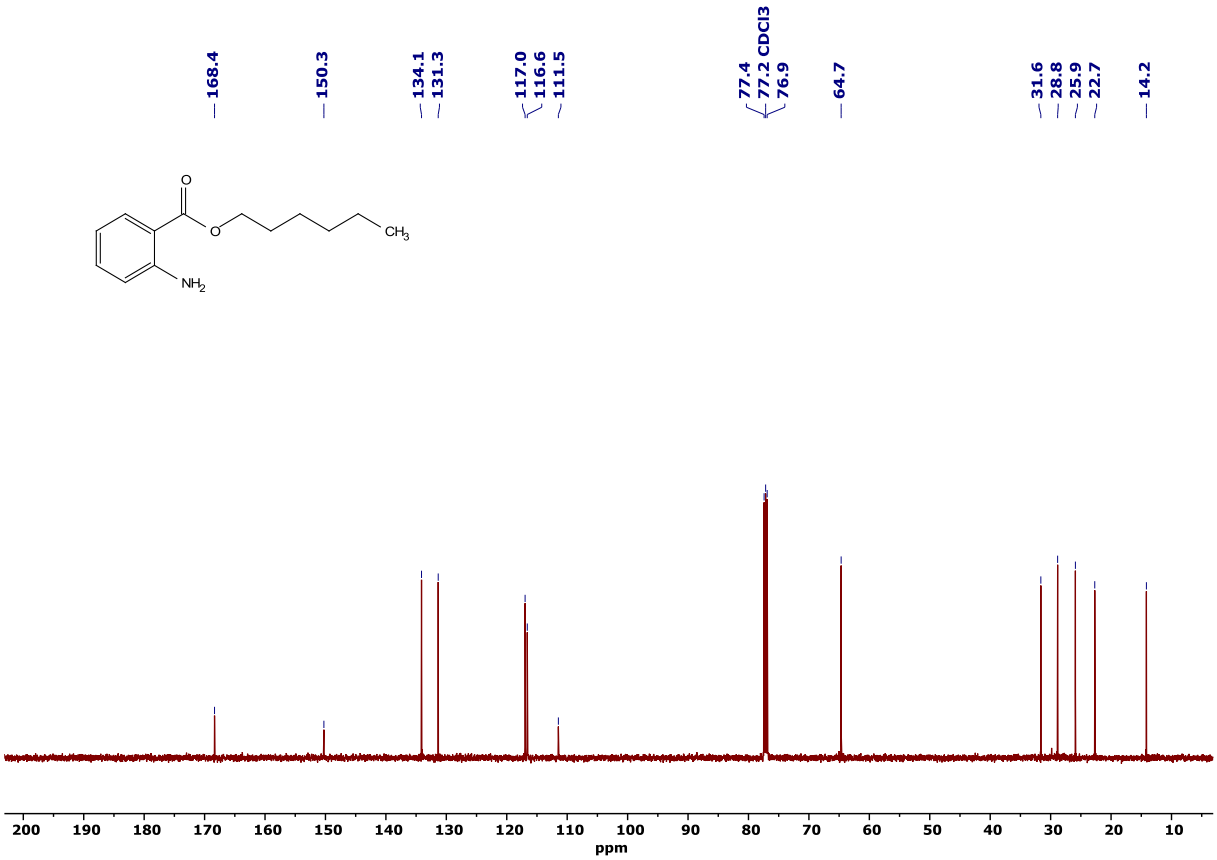


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$.

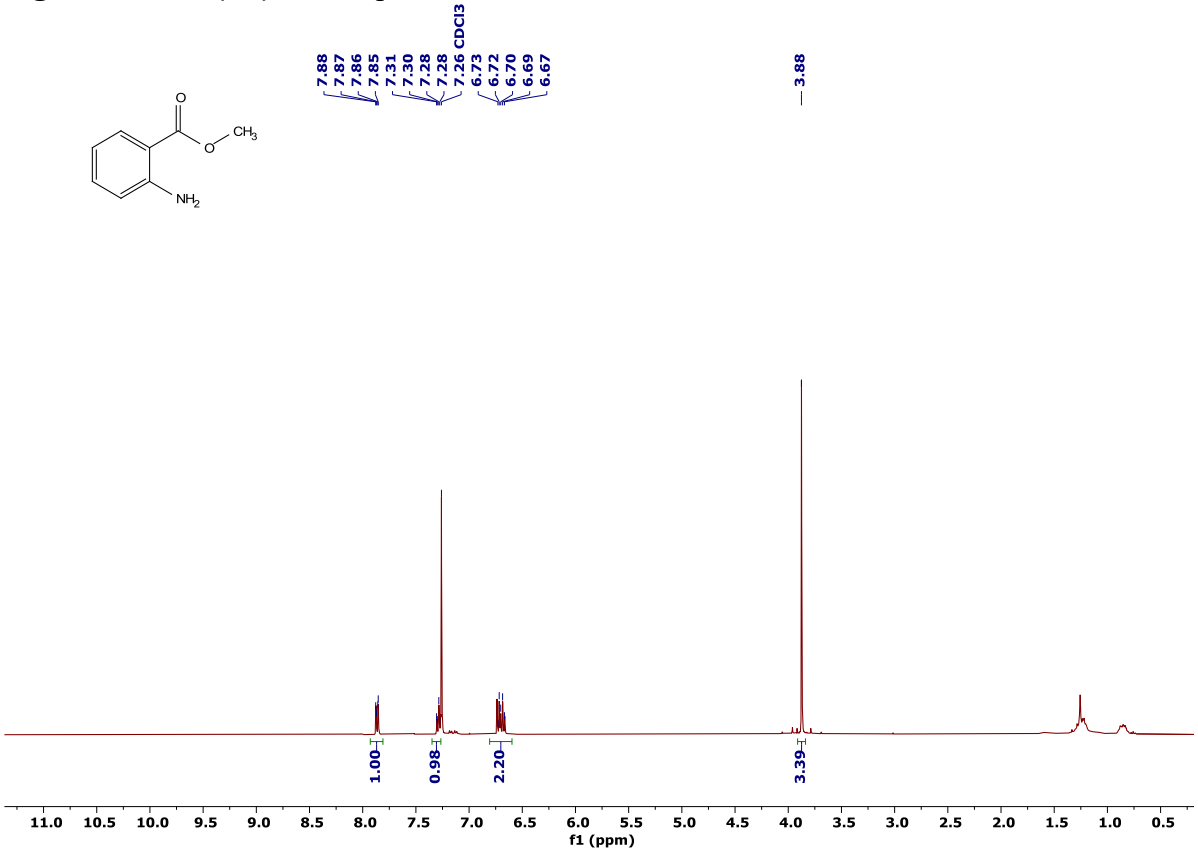


Figure S19. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

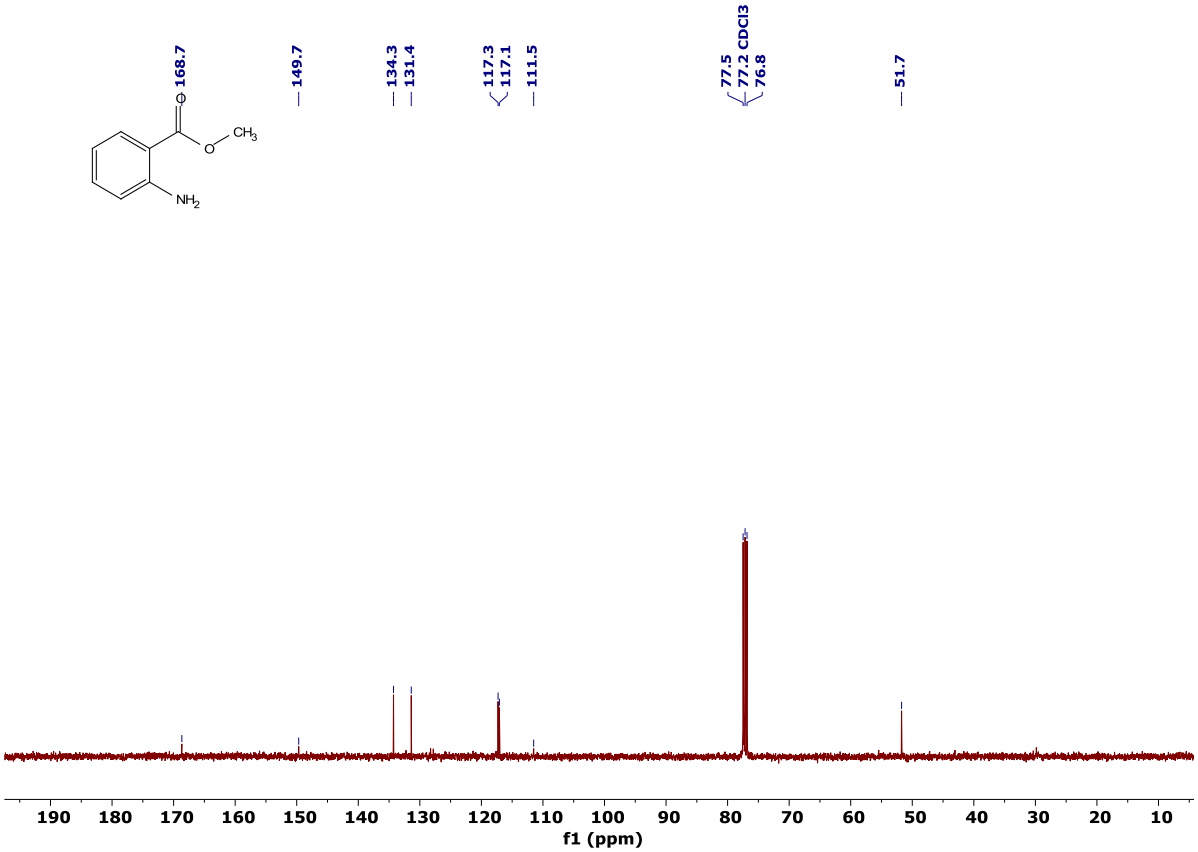


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **3c** in $CDCl_3$.

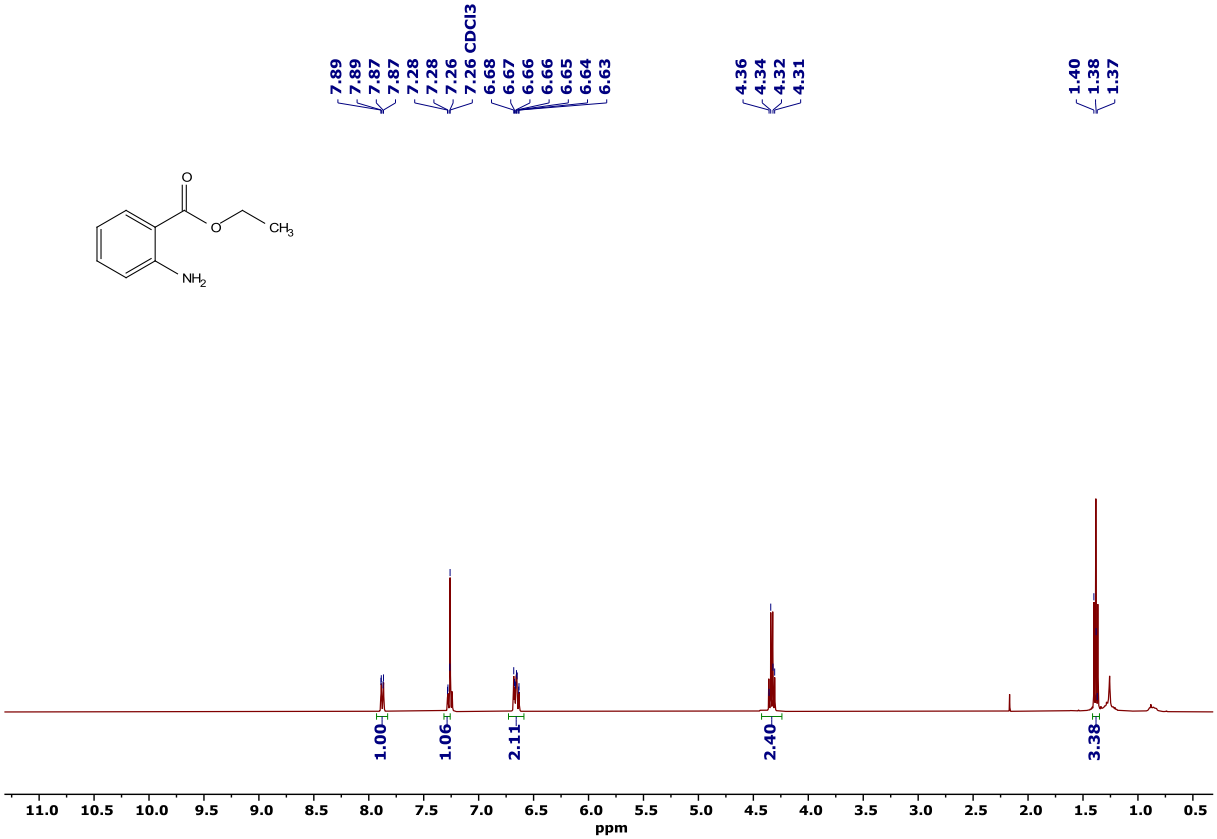


Figure S21. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

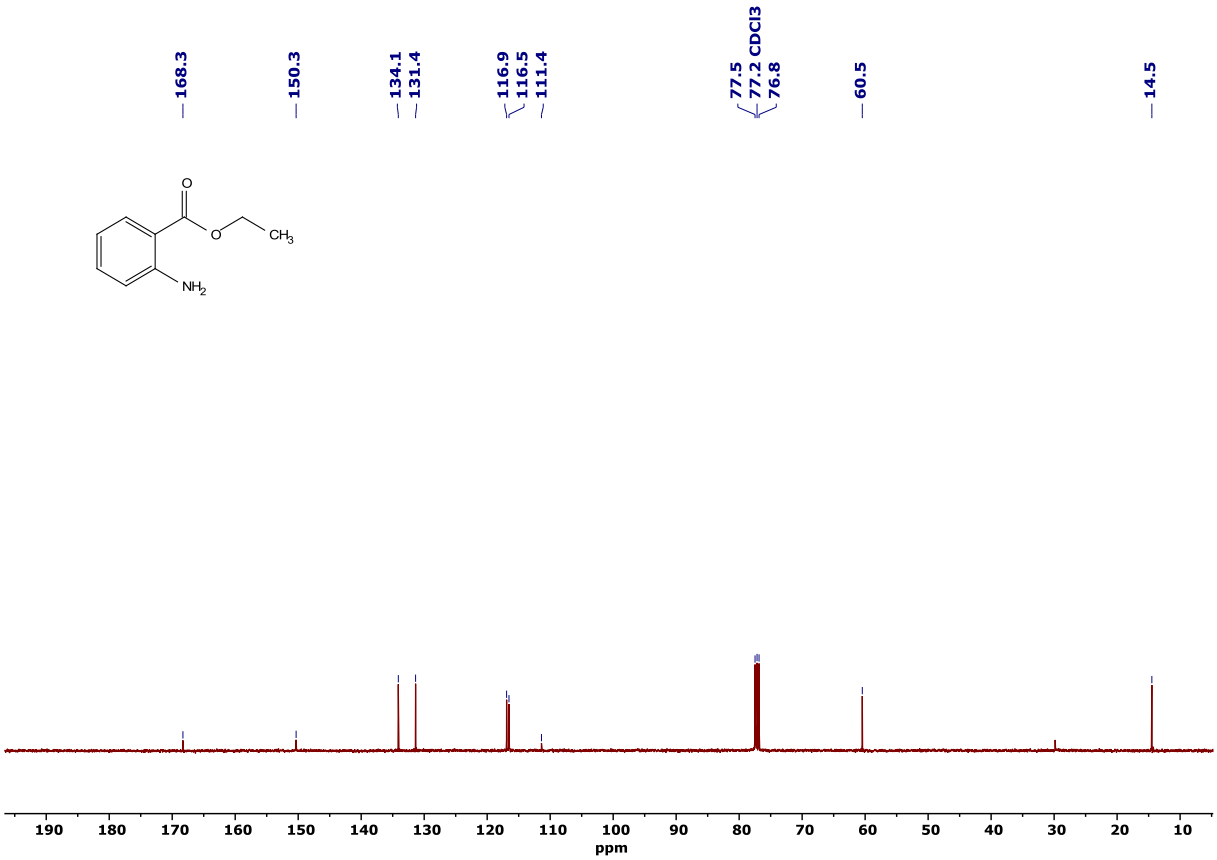


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **3d** in $CDCl_3$.

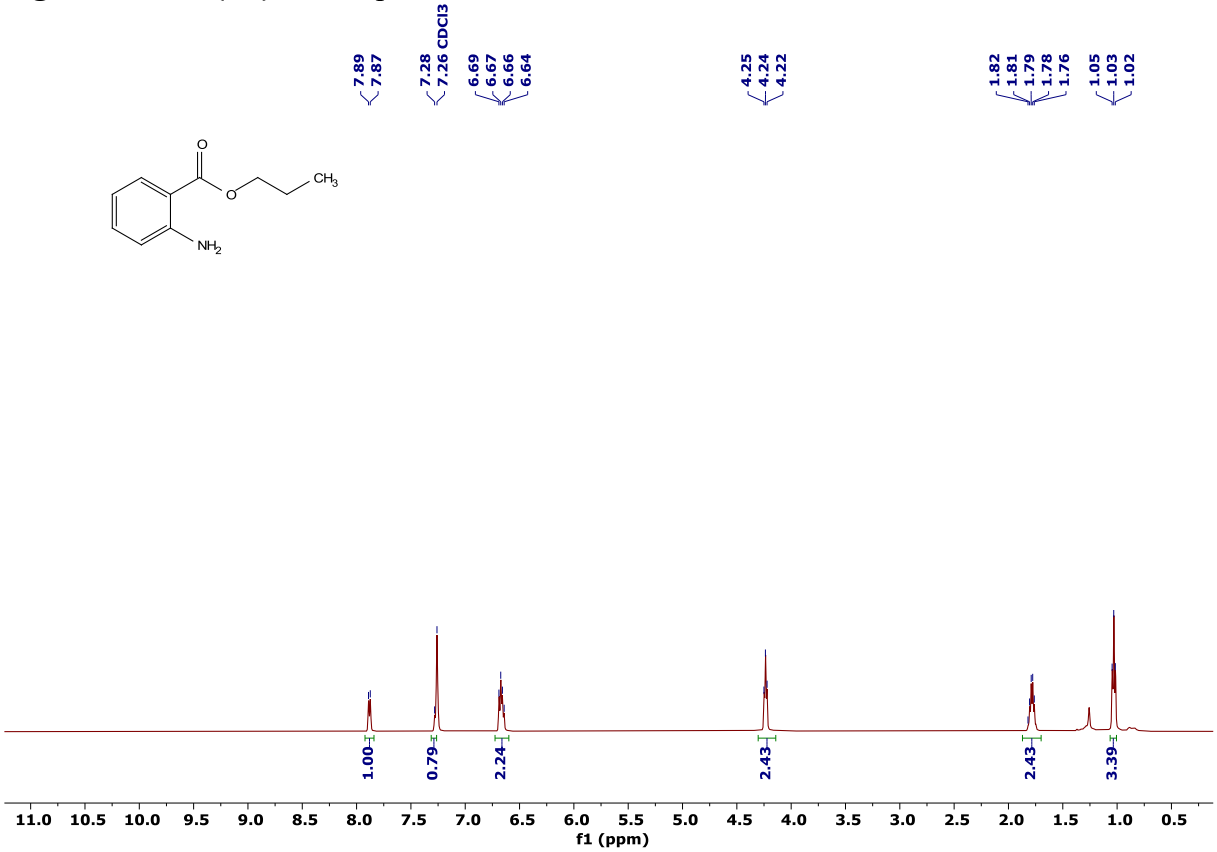


Figure S23. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

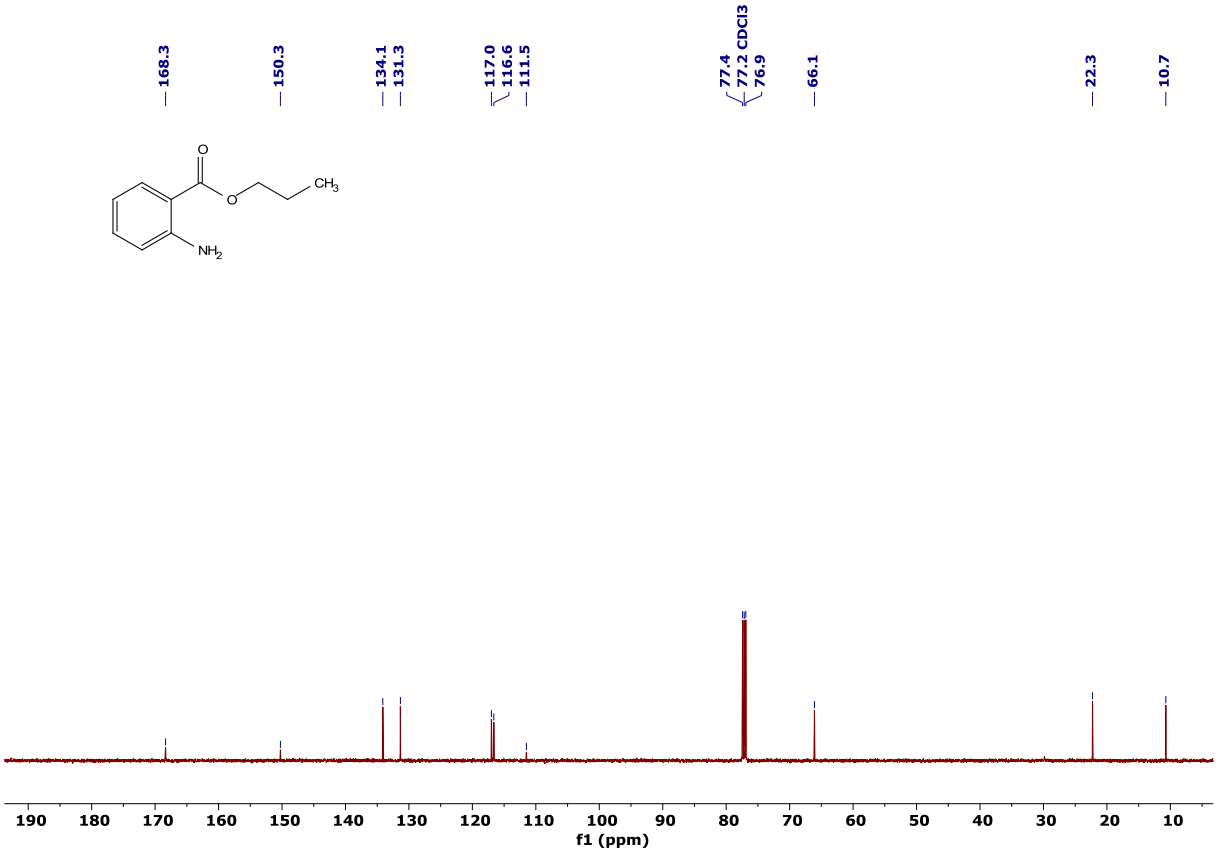


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **3e** in $CDCl_3$.

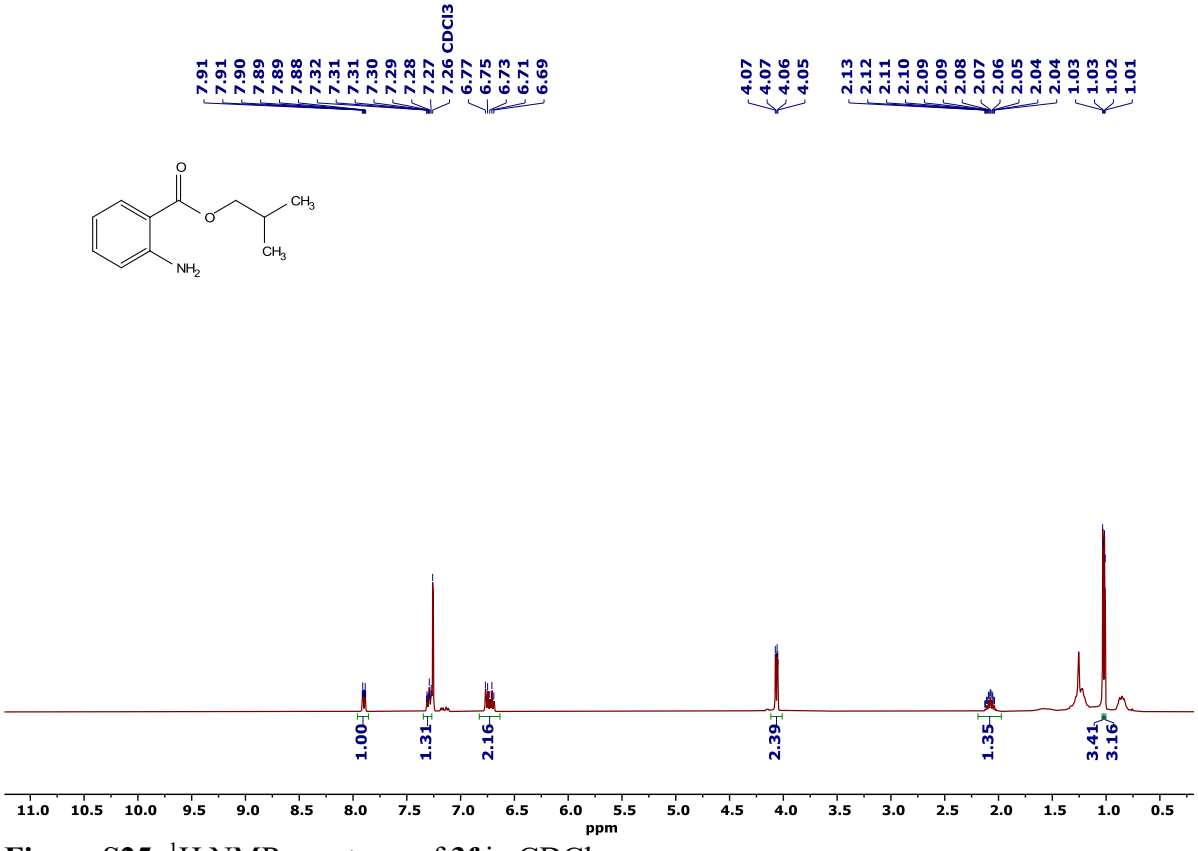


Figure S25. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

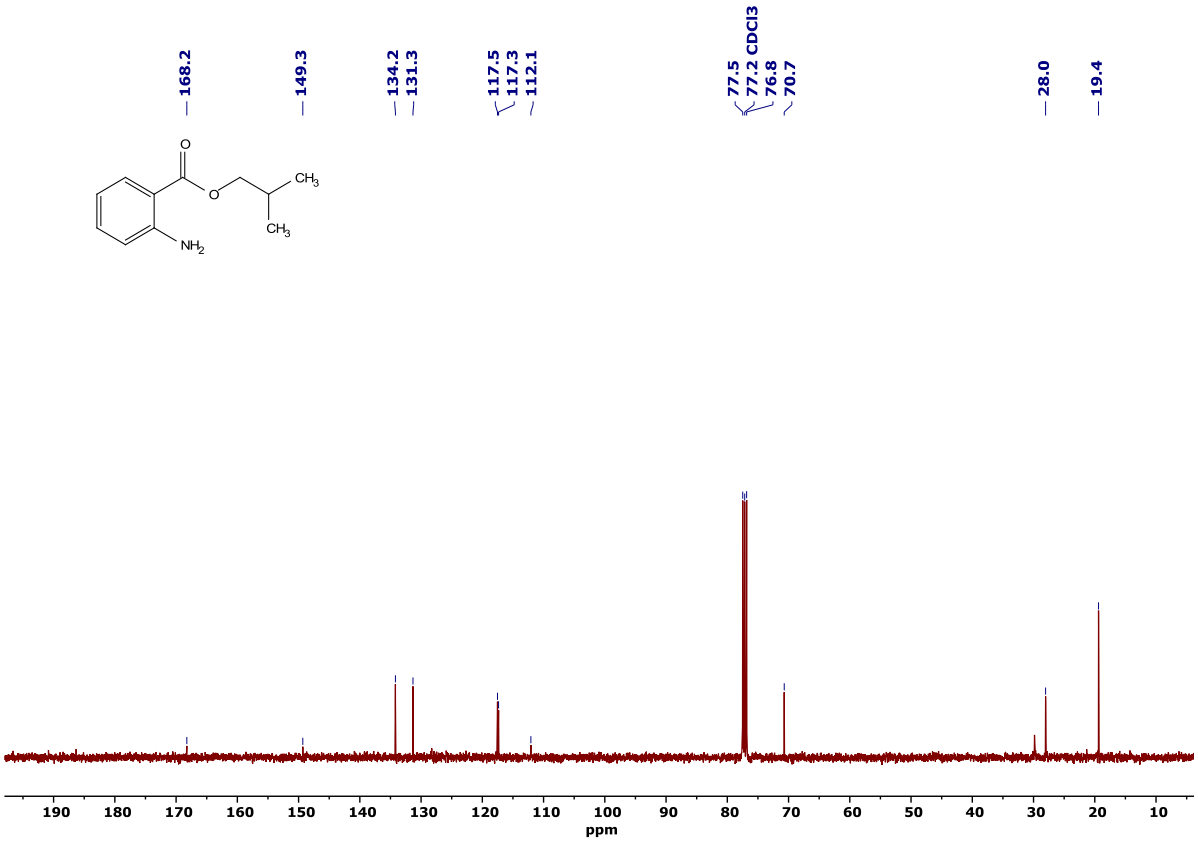


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **3f** in $CDCl_3$.

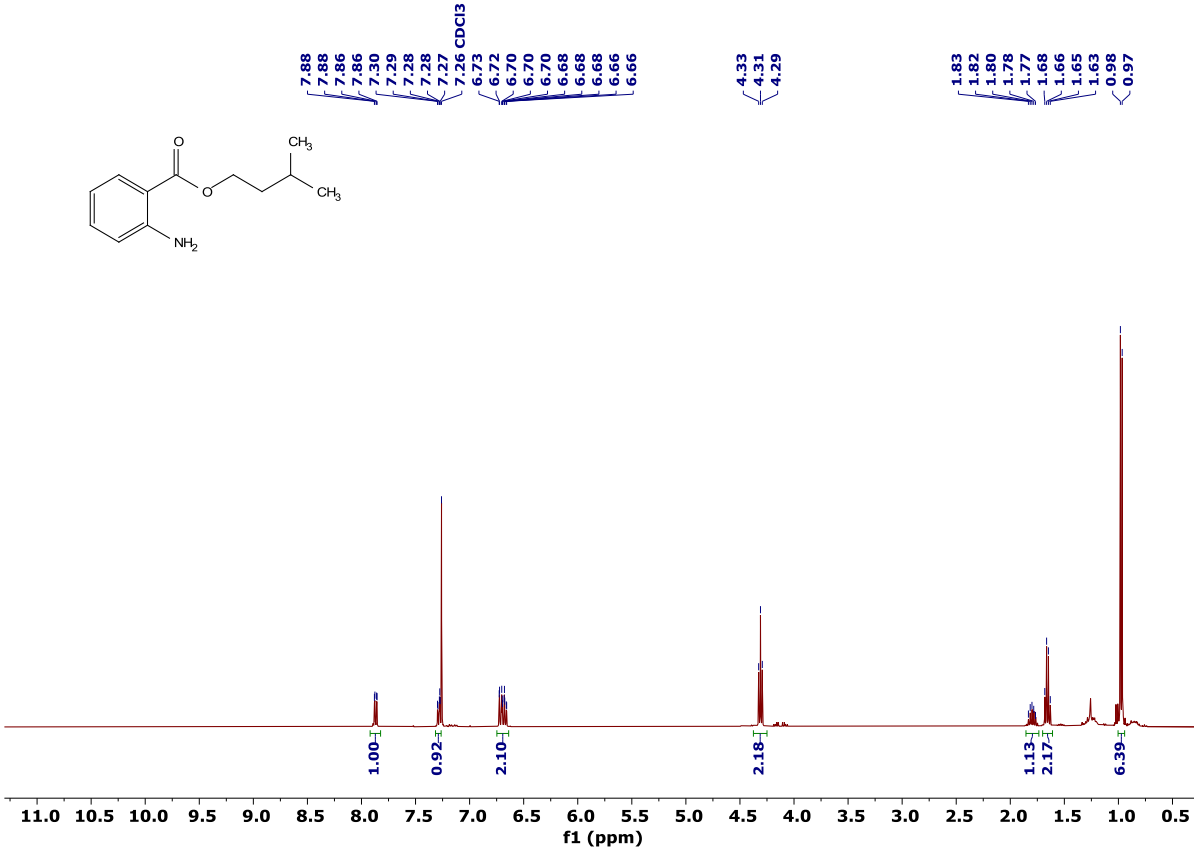


Figure S27. ^{1}H NMR spectrum of **3g** in $CDCl_3$.

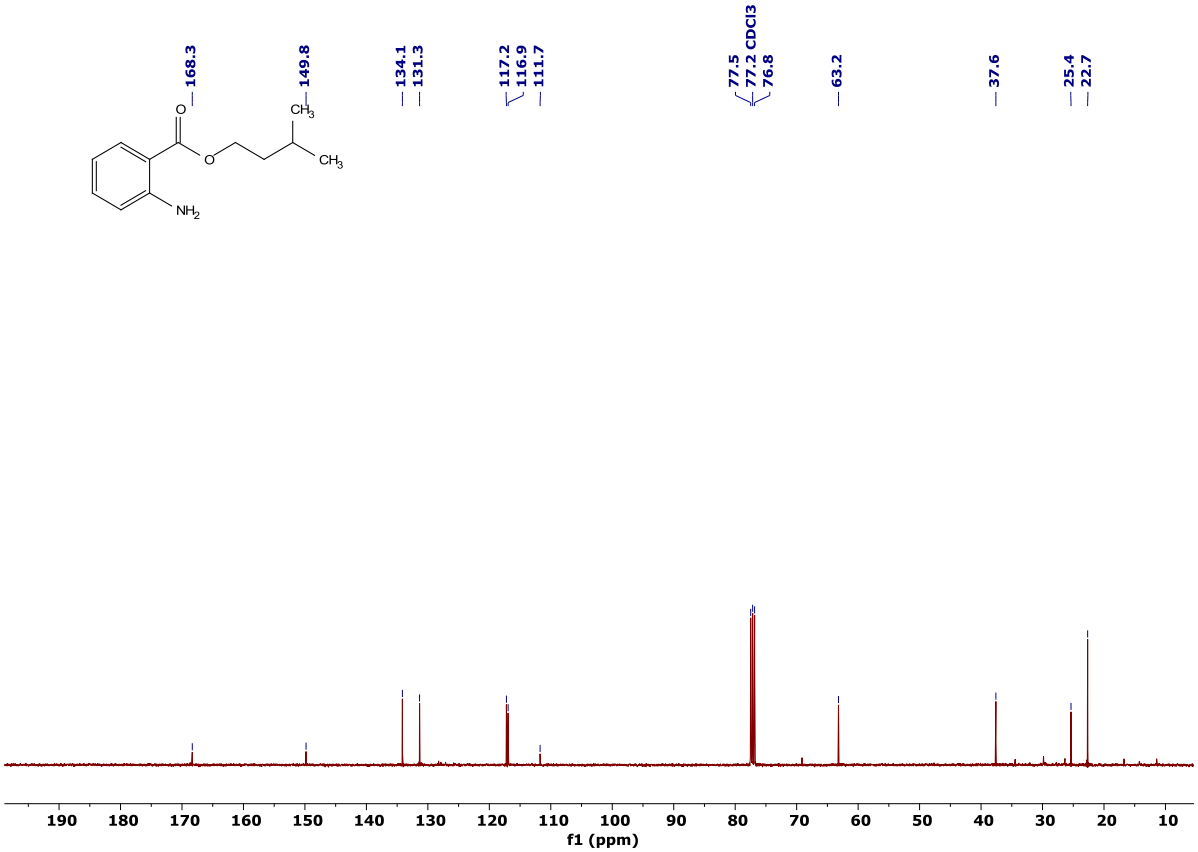


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **3g** in $CDCl_3$.

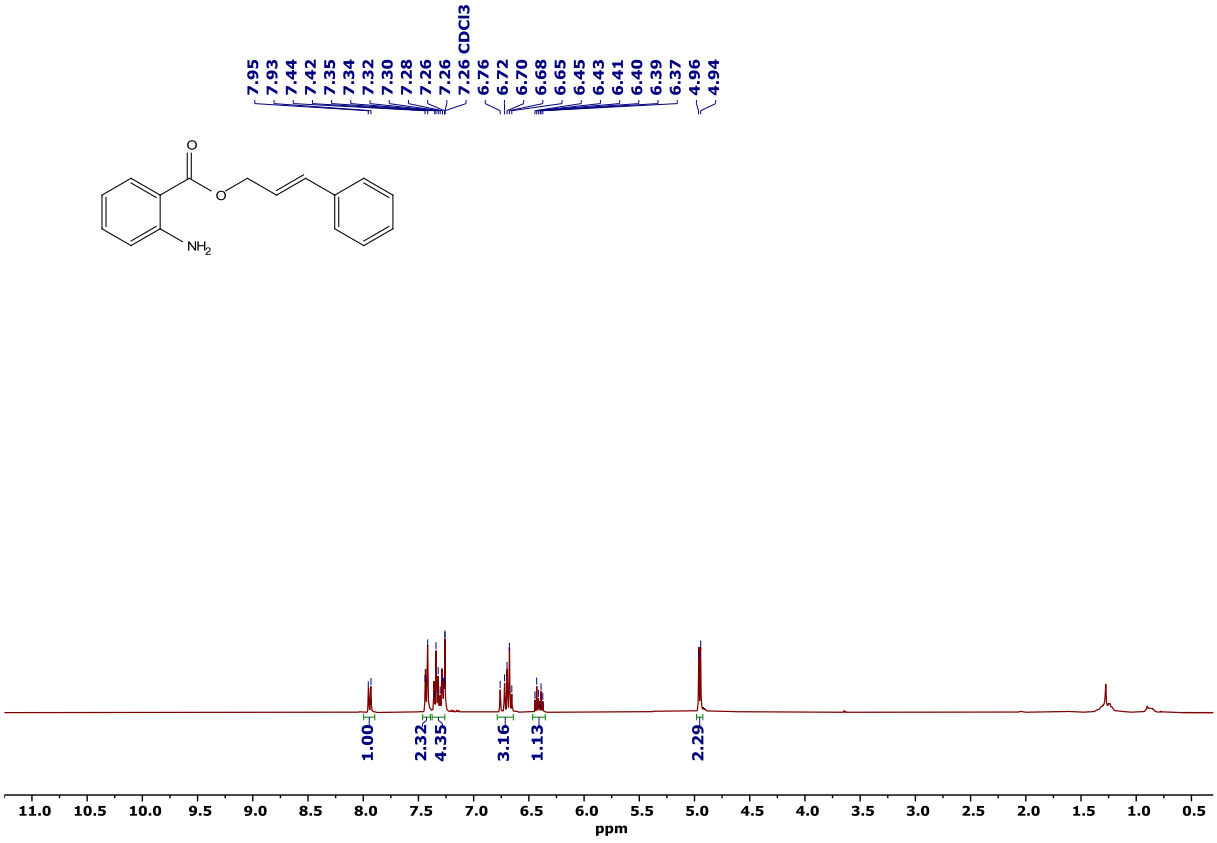


Figure S29. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

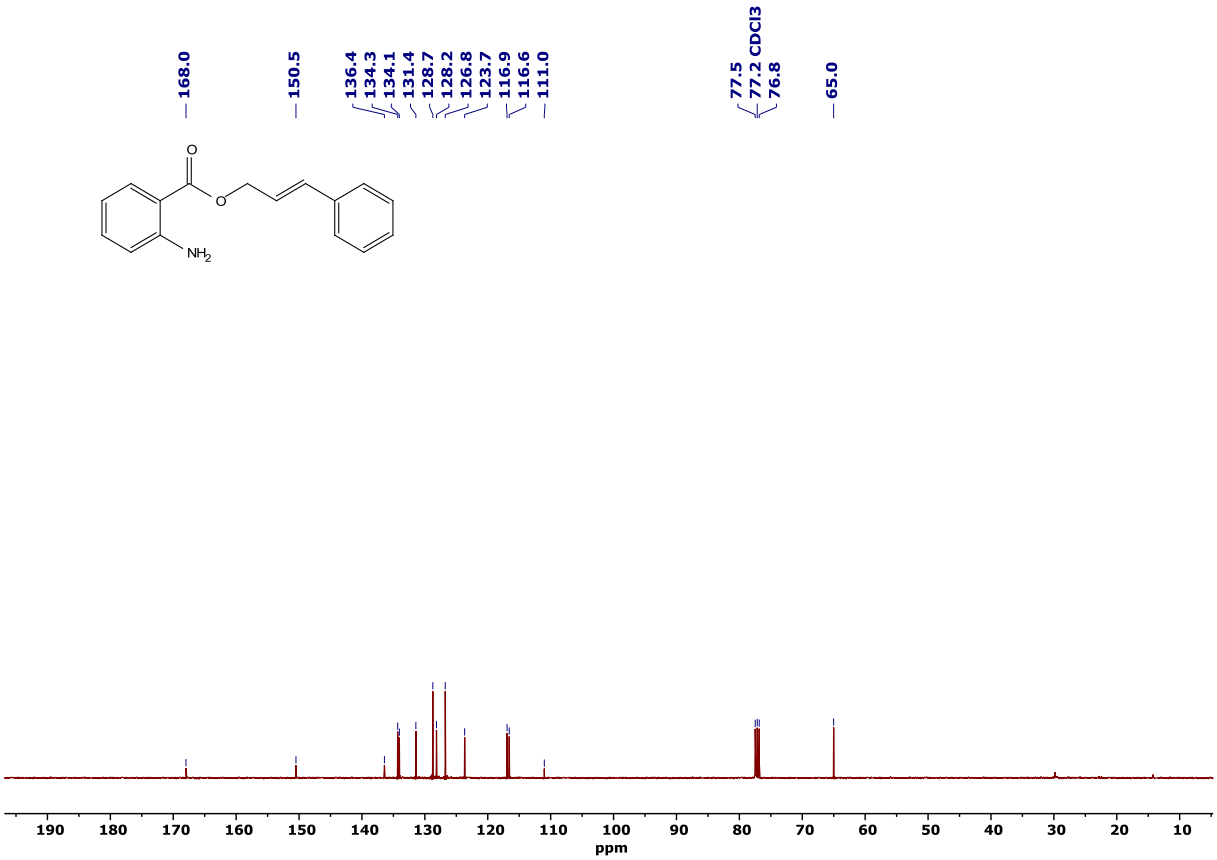


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **3h** in $CDCl_3$.

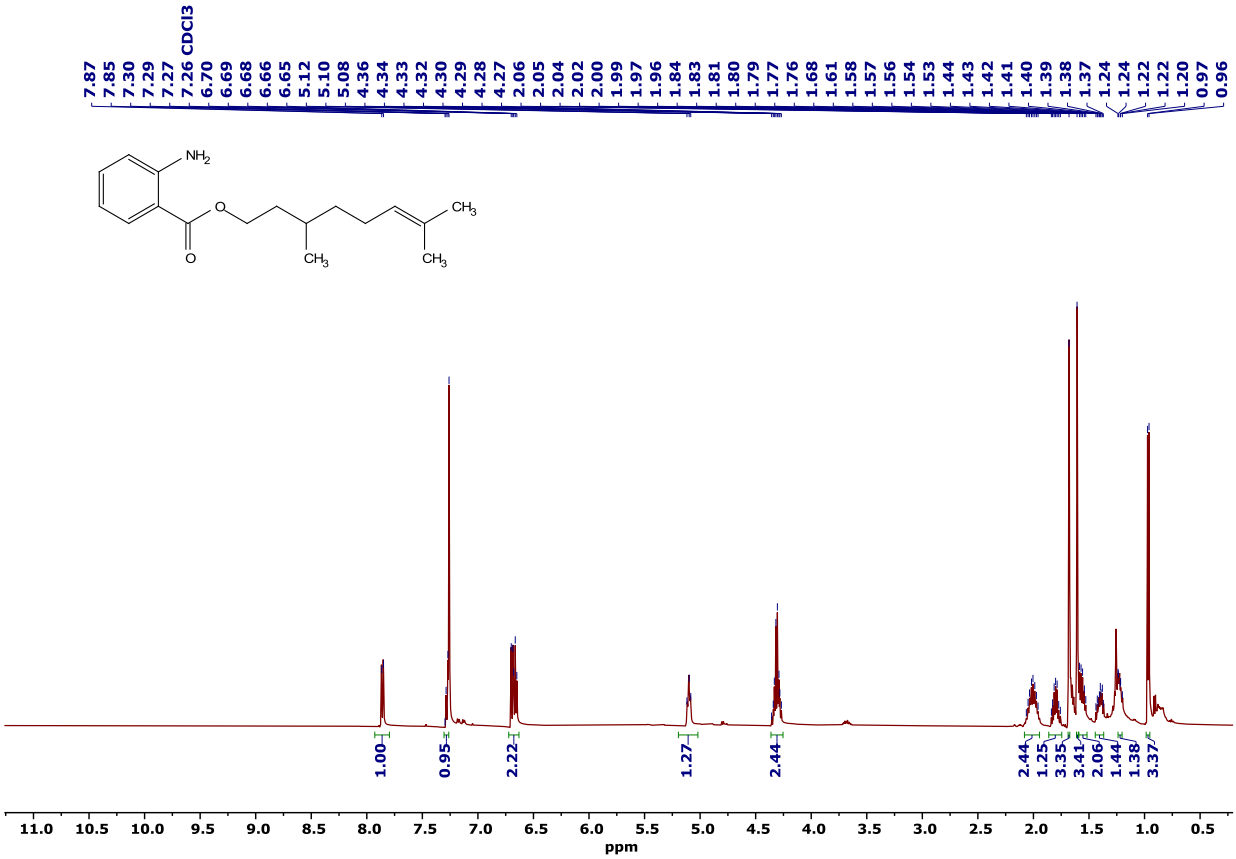


Figure S31. ^{1}H NMR spectrum of **3i** in $CDCl_3$.

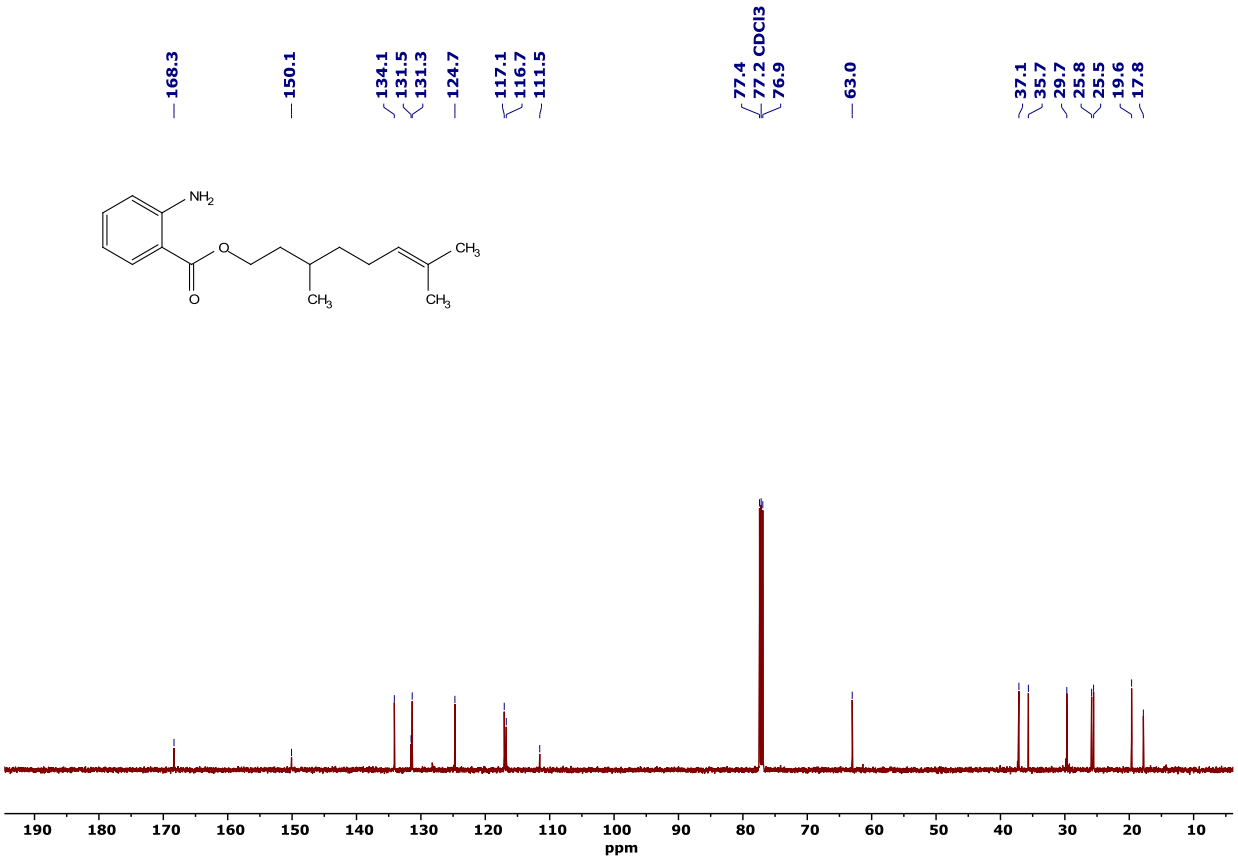


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **3i** in $CDCl_3$.

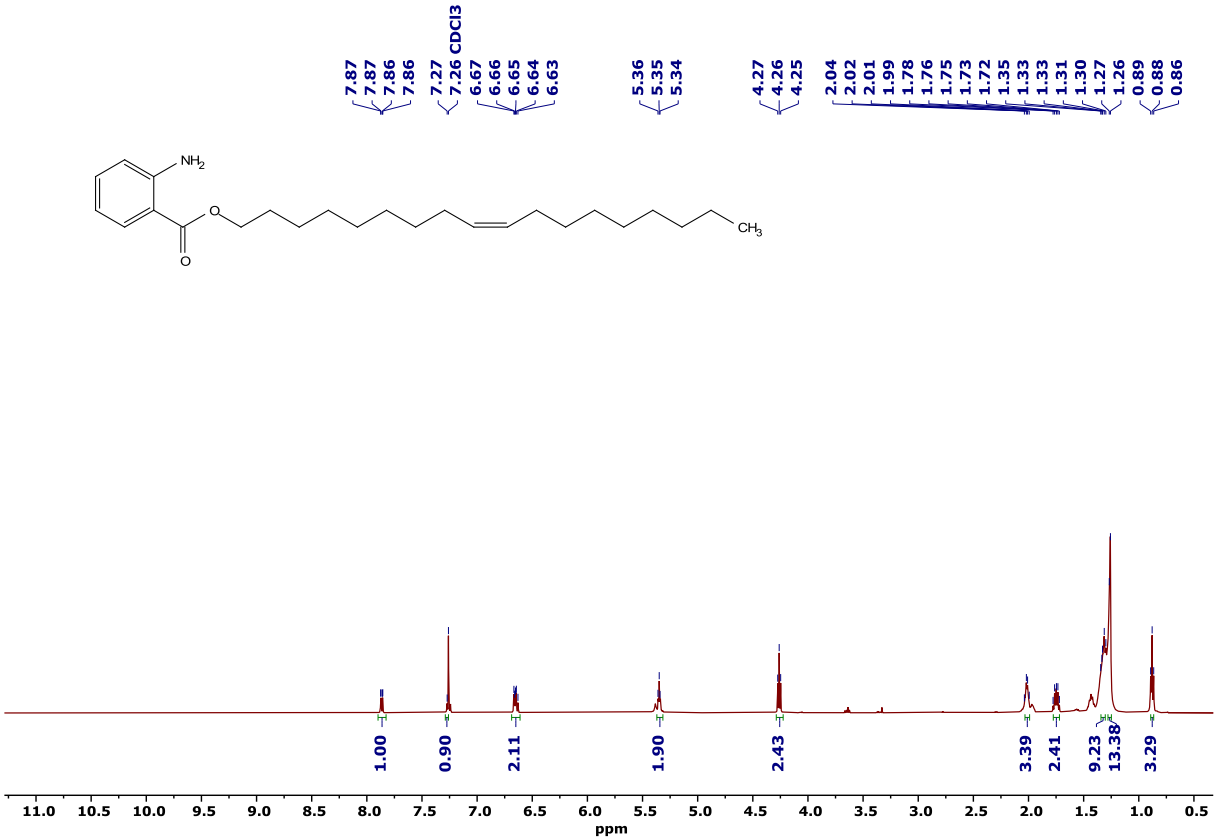


Figure S33. ^{1}H NMR spectrum of **3j** in $CDCl_3$.

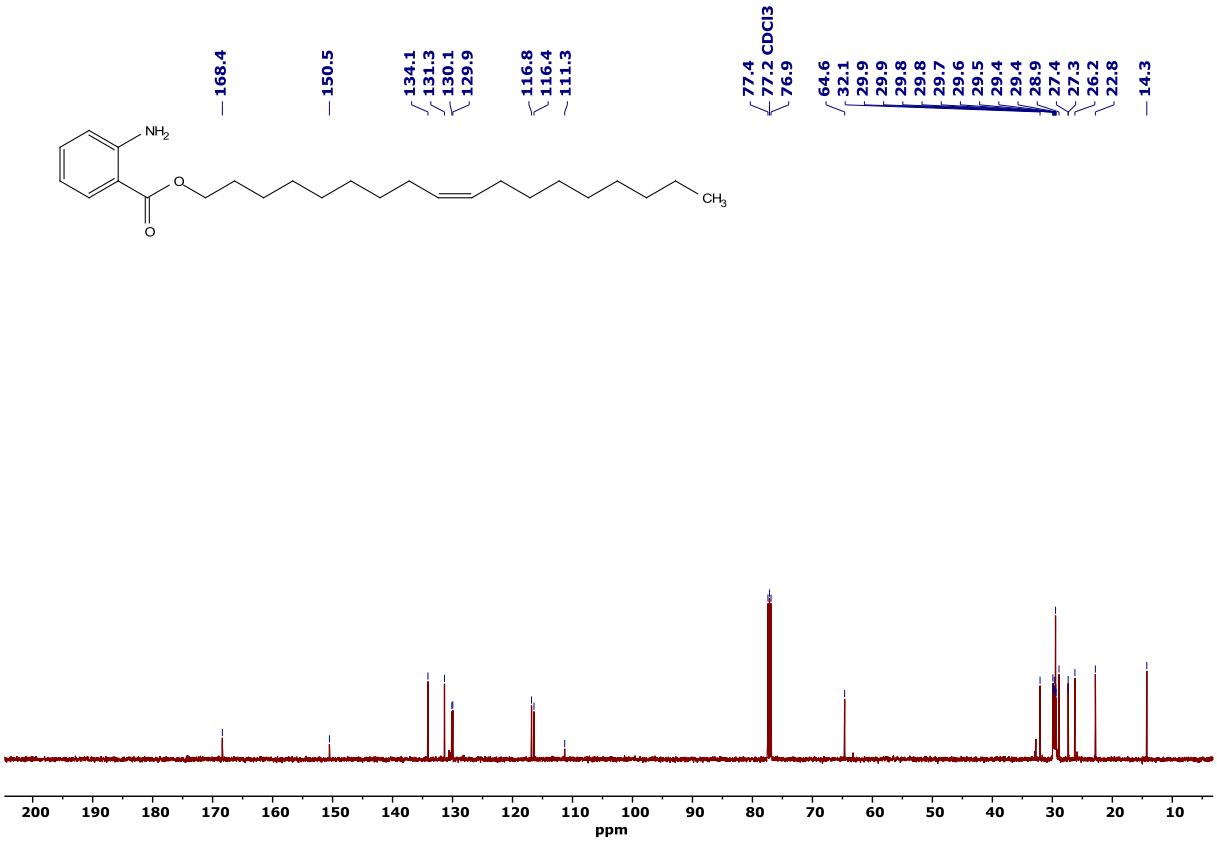


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **3j** in $CDCl_3$.

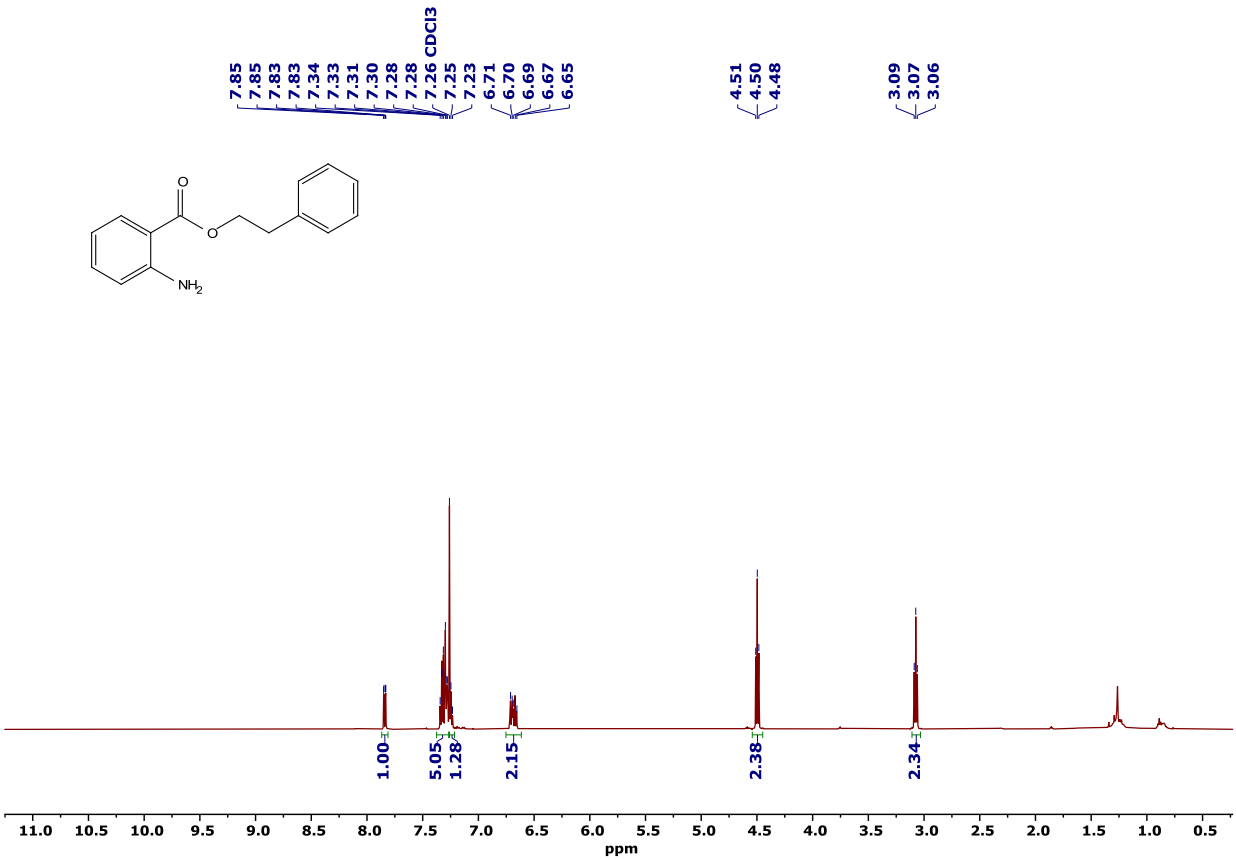


Figure S35. ^{1}H NMR spectrum of **3k** in $CDCl_3$.

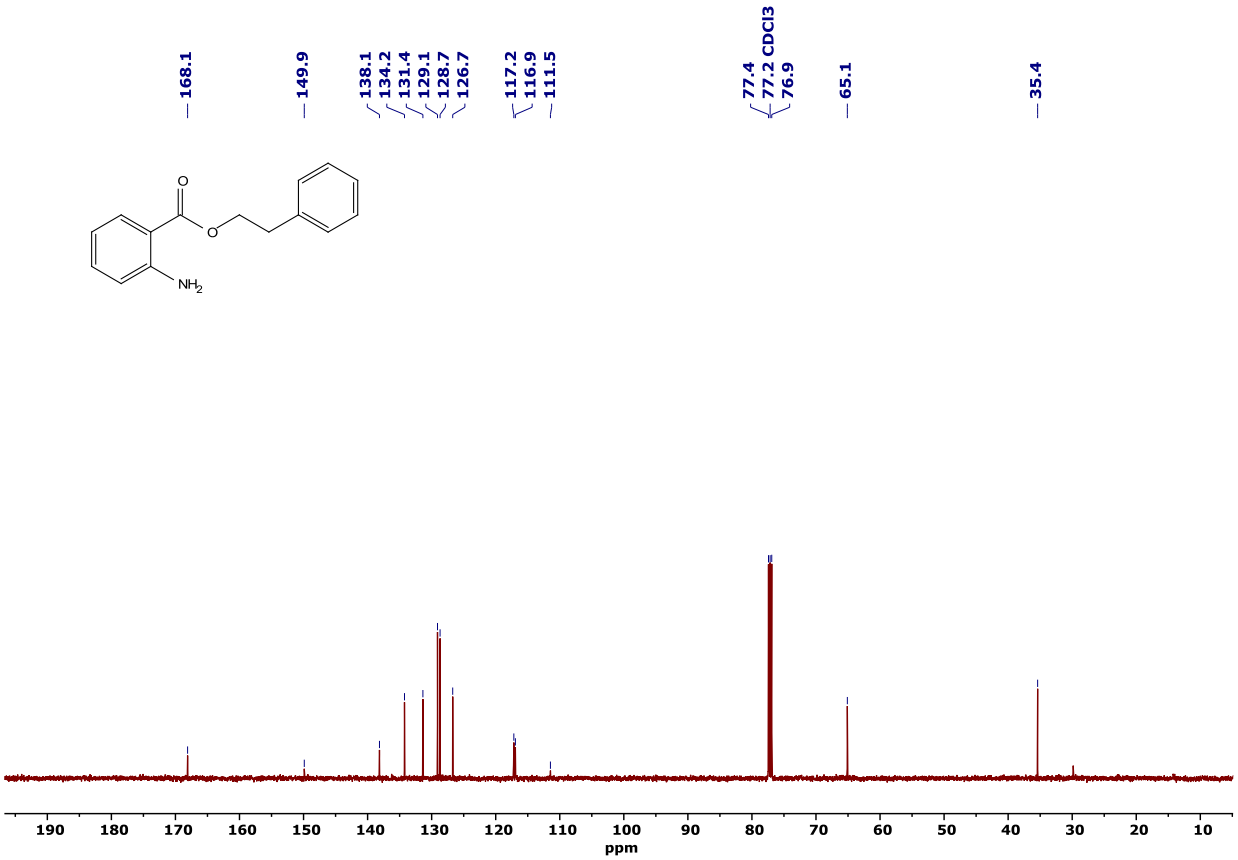


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **3k** in $CDCl_3$.

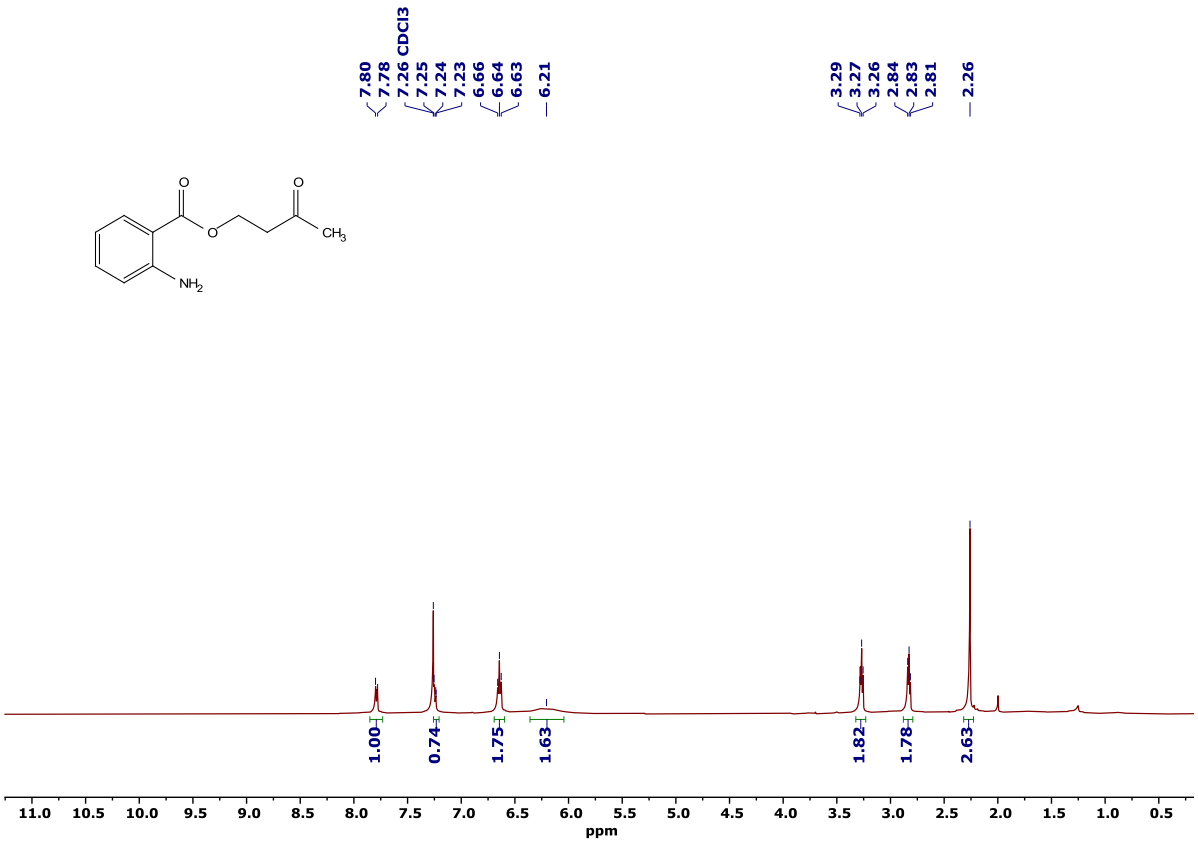


Figure S37. ^{1}H NMR spectrum of **3l** in $CDCl_3$.

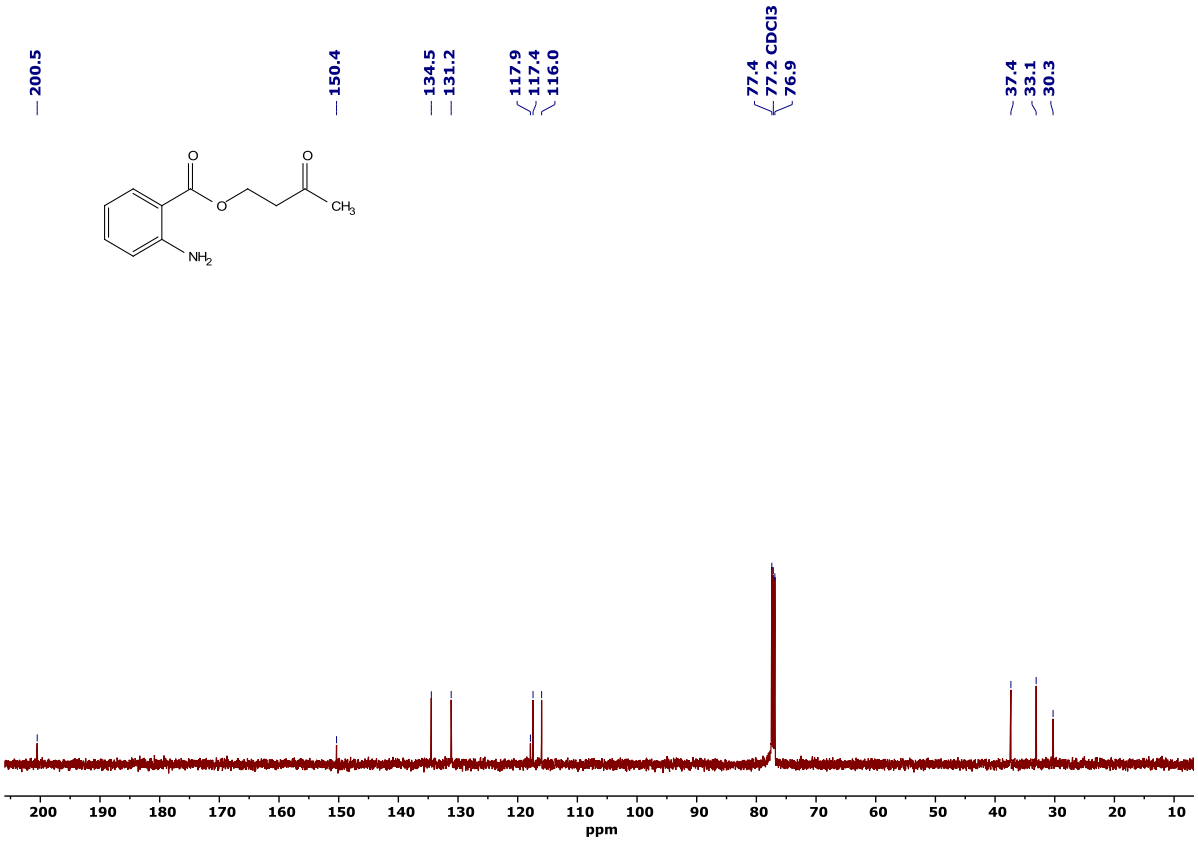


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **3l** in $CDCl_3$.

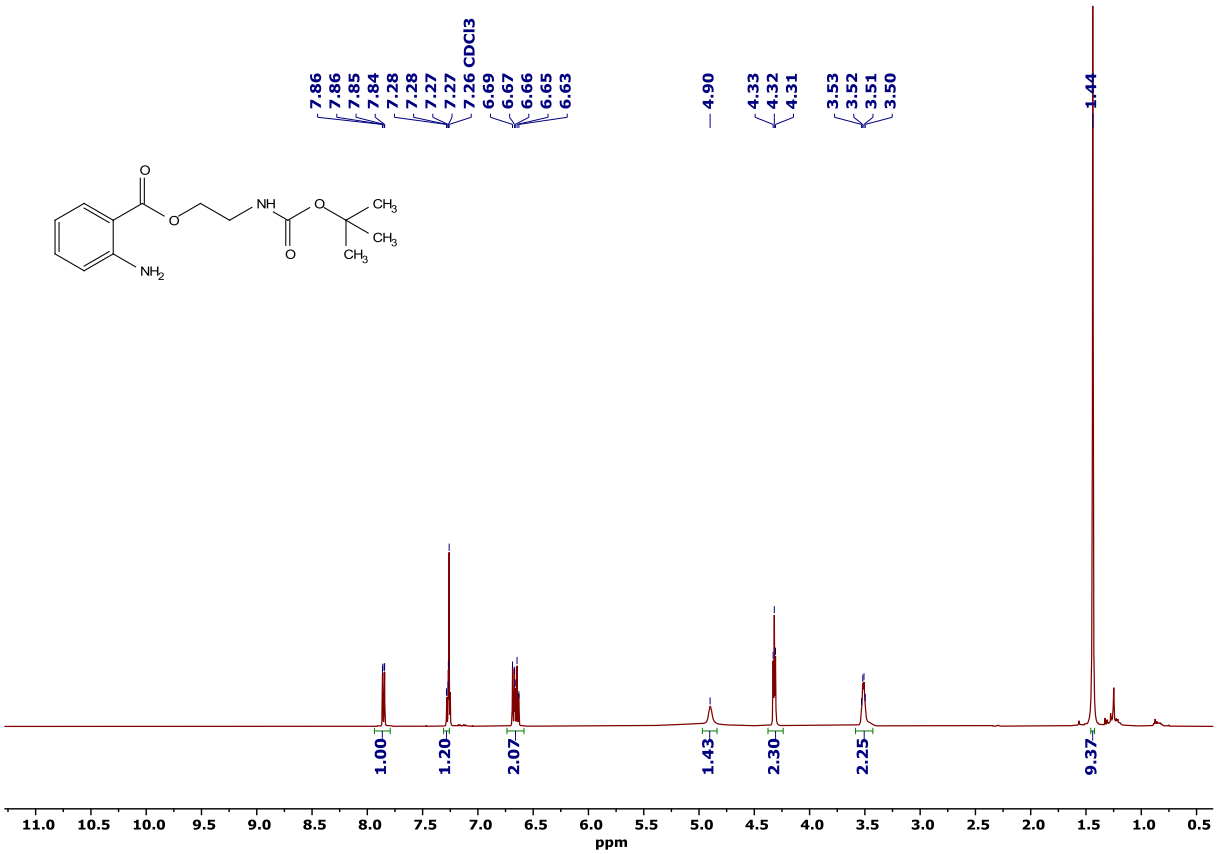


Figure S39. ^{1}H NMR spectrum of **3m** in $CDCl_3$.

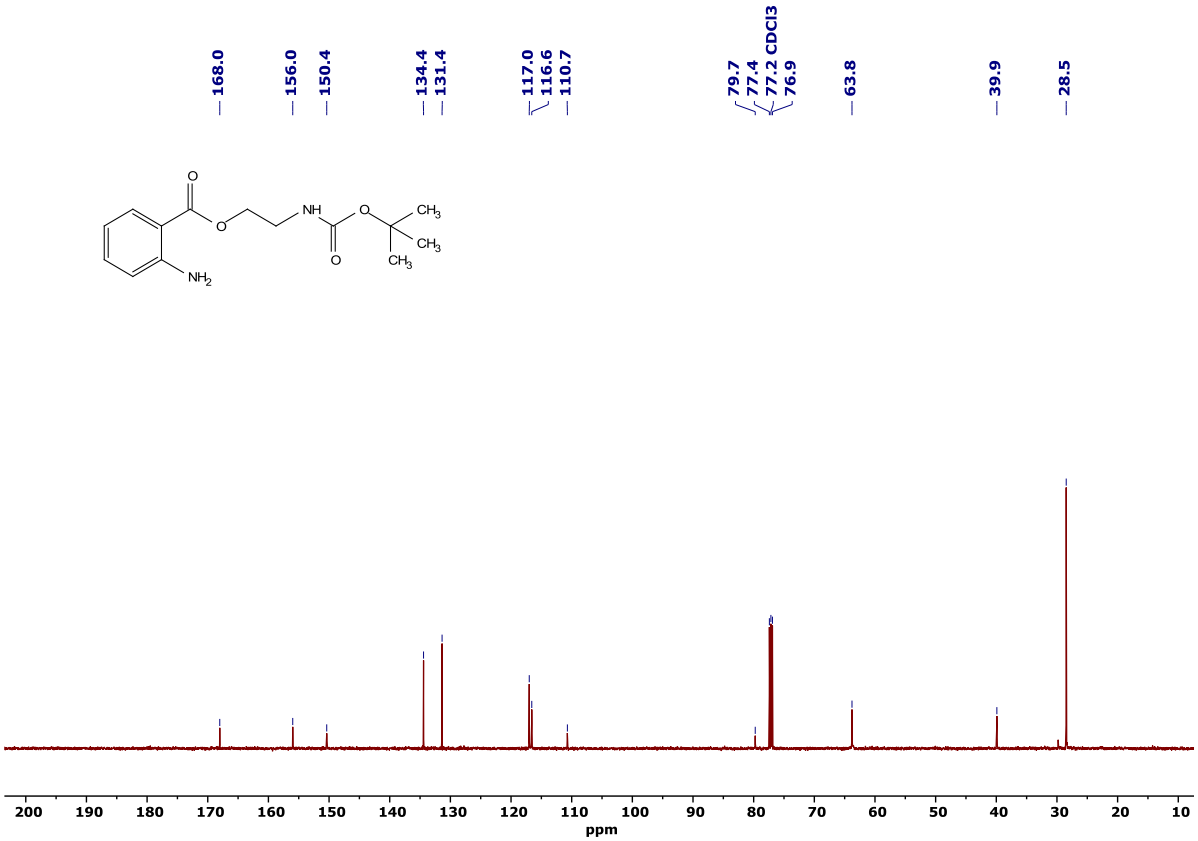


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **3m** in $CDCl_3$.

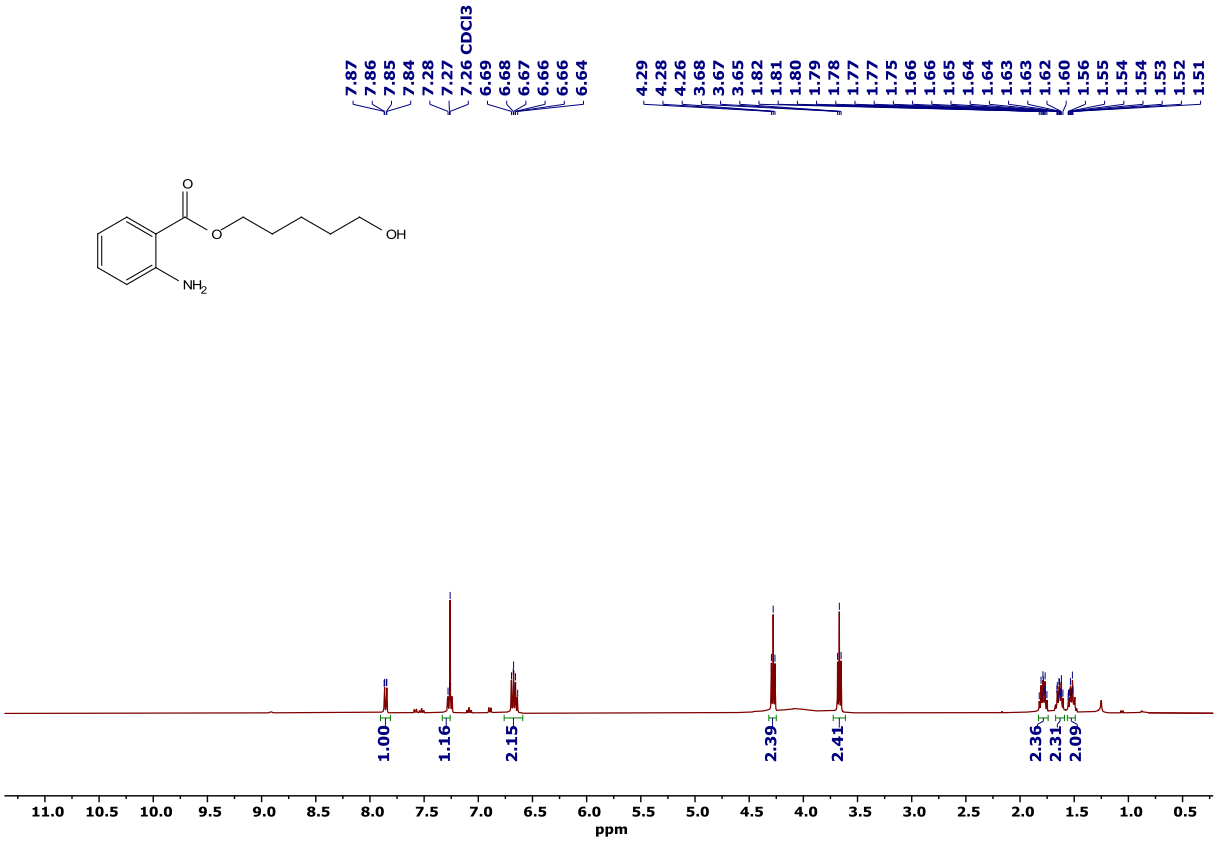


Figure S41. ^{1}H NMR spectrum of **3n** in $CDCl_3$.

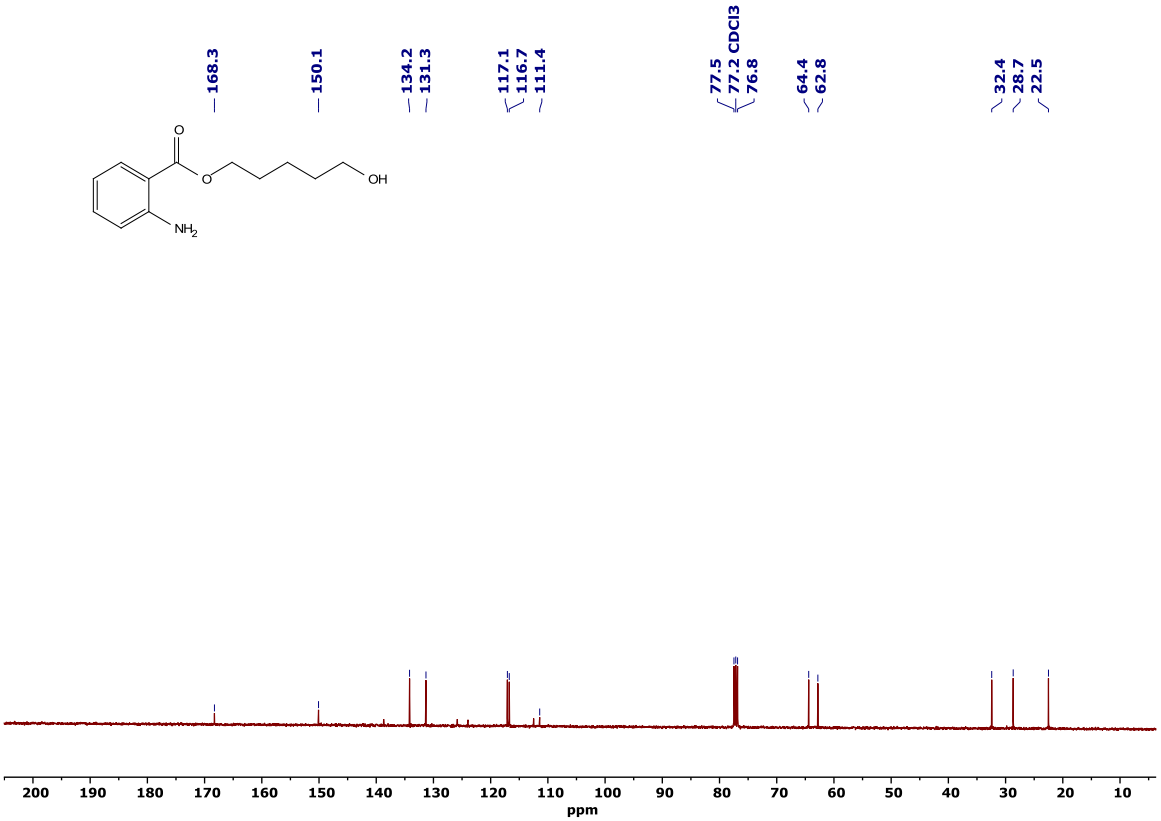


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of **3n** in $CDCl_3$.

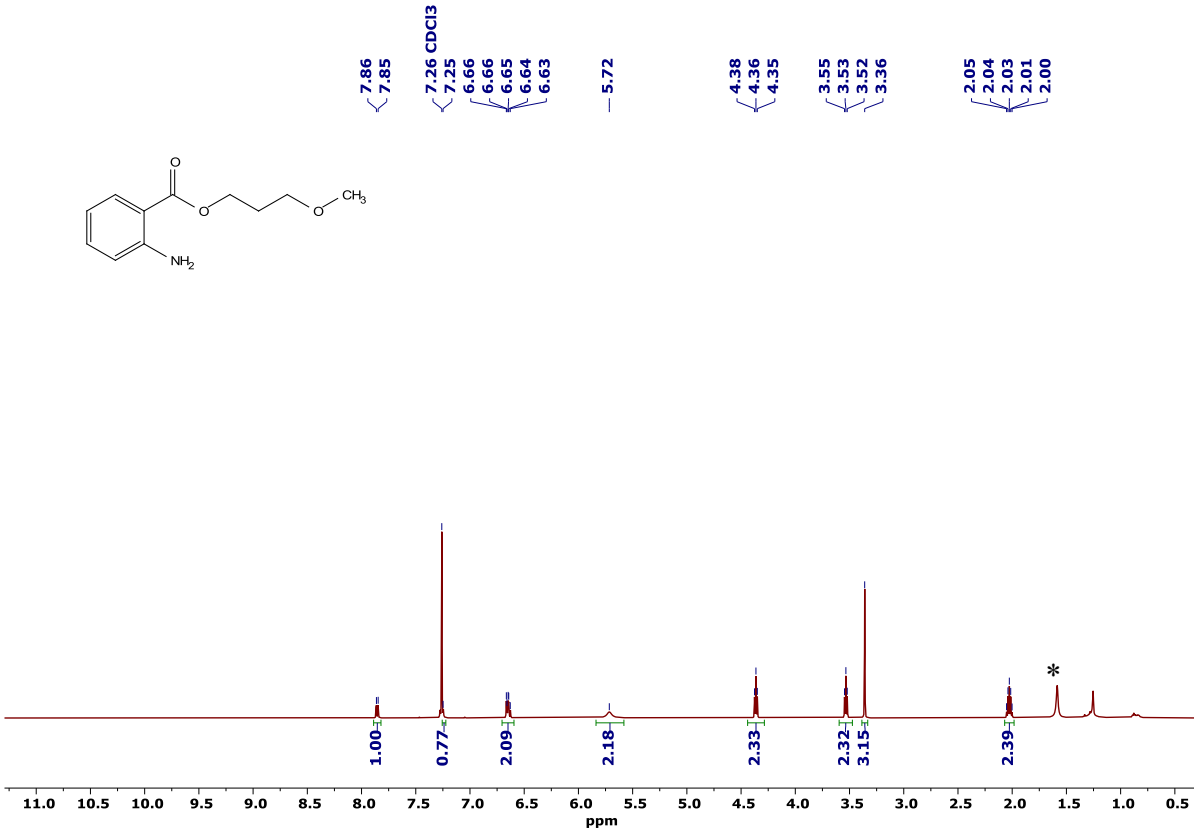


Figure S43. ^{1}H NMR spectrum of **3o** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

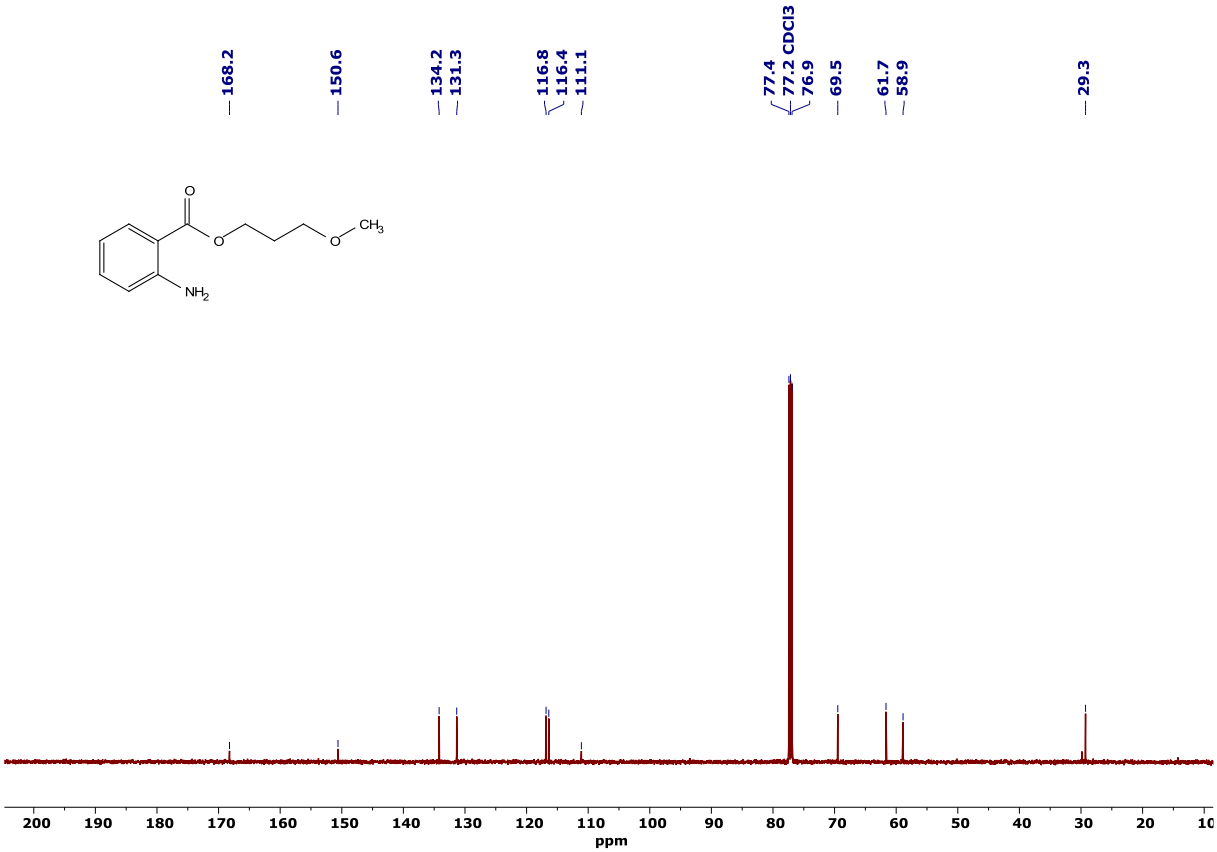


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of **3o** in $CDCl_3$.

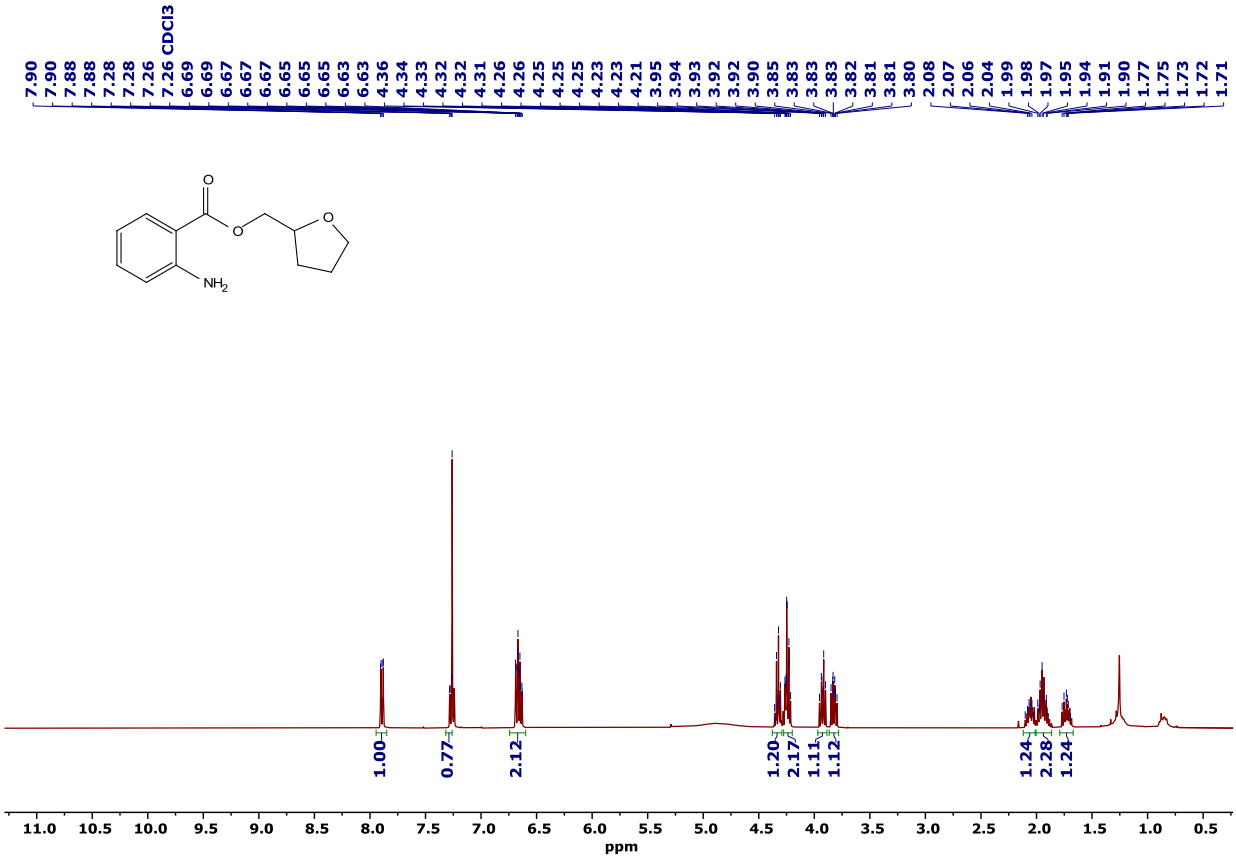


Figure S45. ^{1}H NMR spectrum of **3p** in $CDCl_3$.

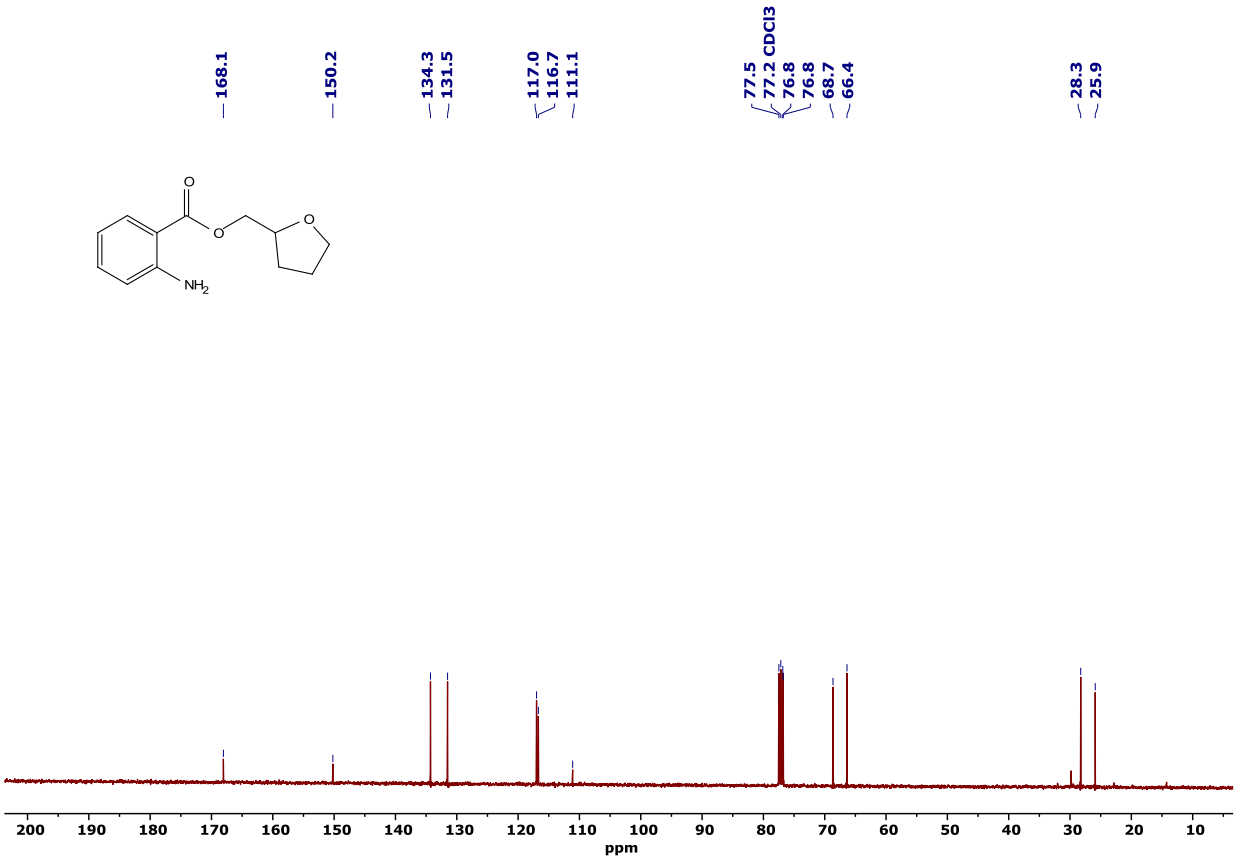


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **3p** in $CDCl_3$.

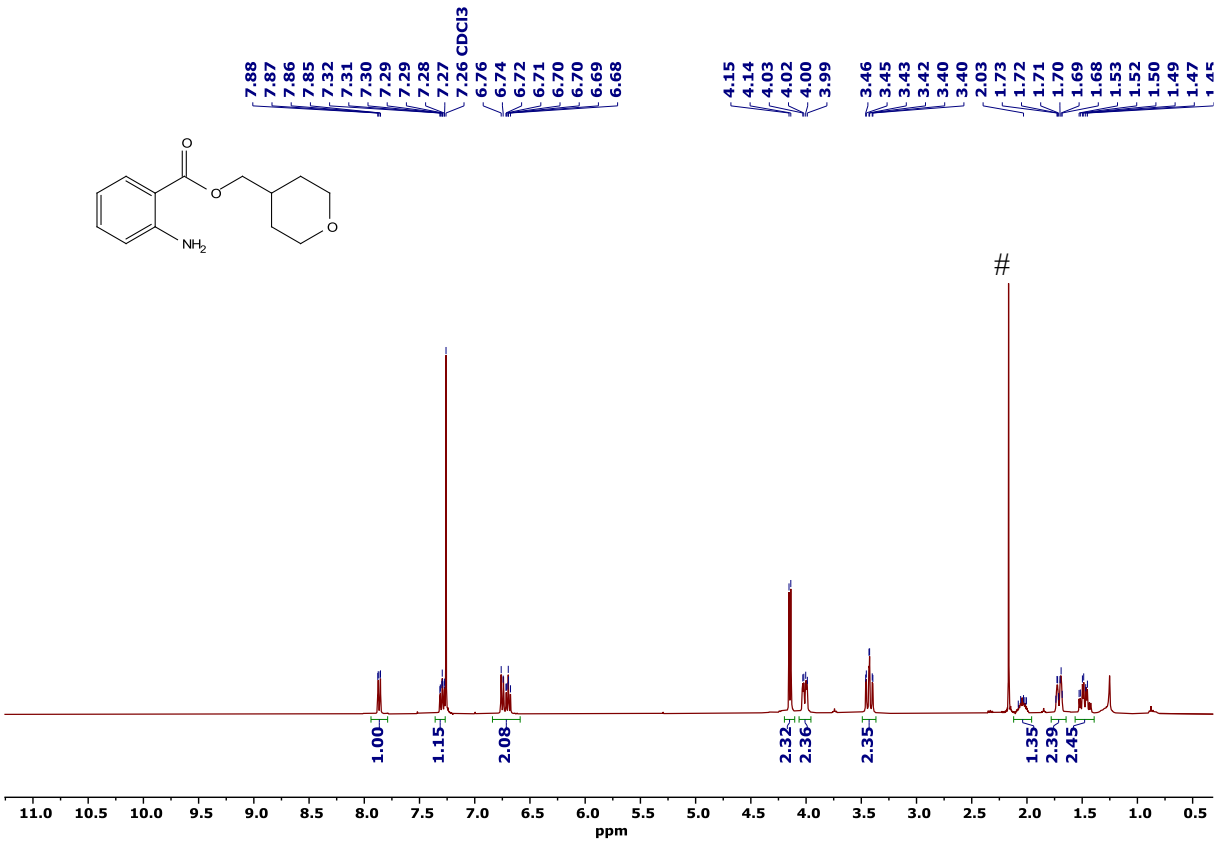


Figure S47. ^{1}H NMR spectrum of **3q** in $CDCl_3$. # indicates acetone.

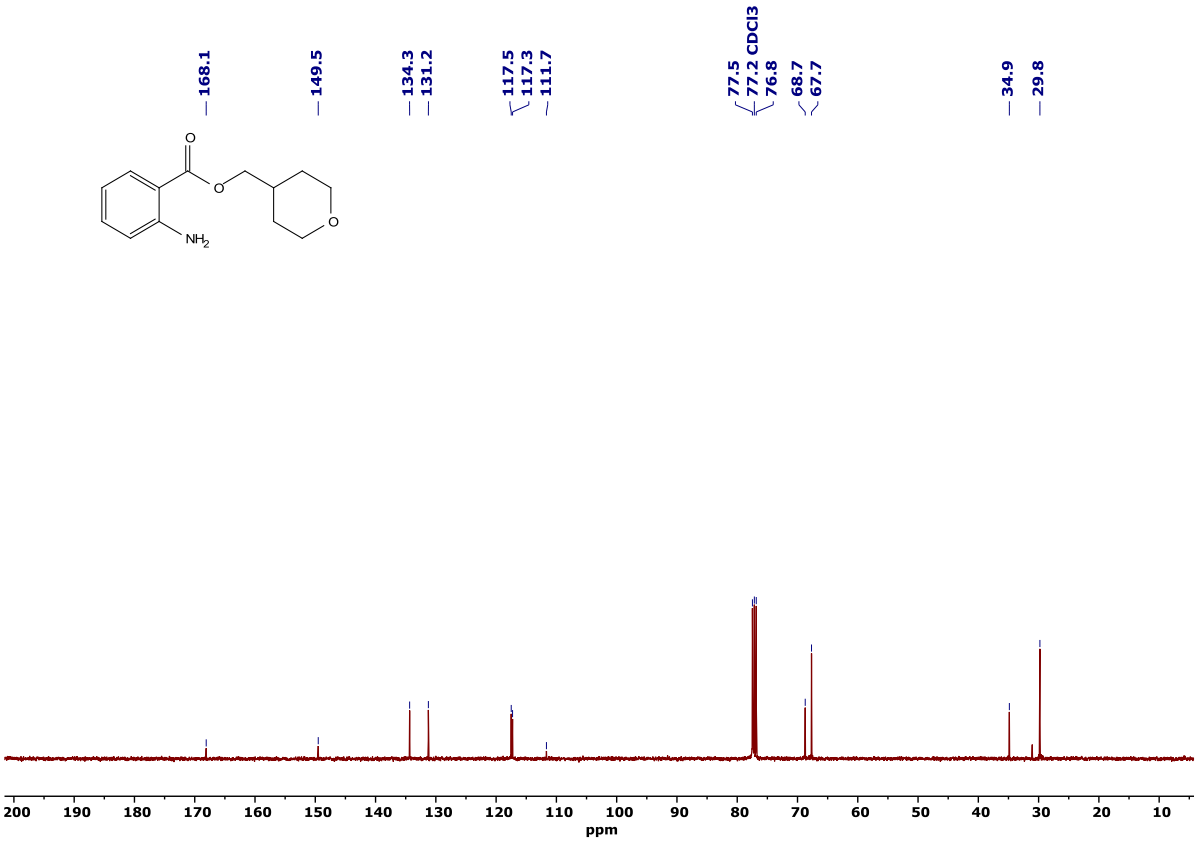


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of **3q** in $CDCl_3$.

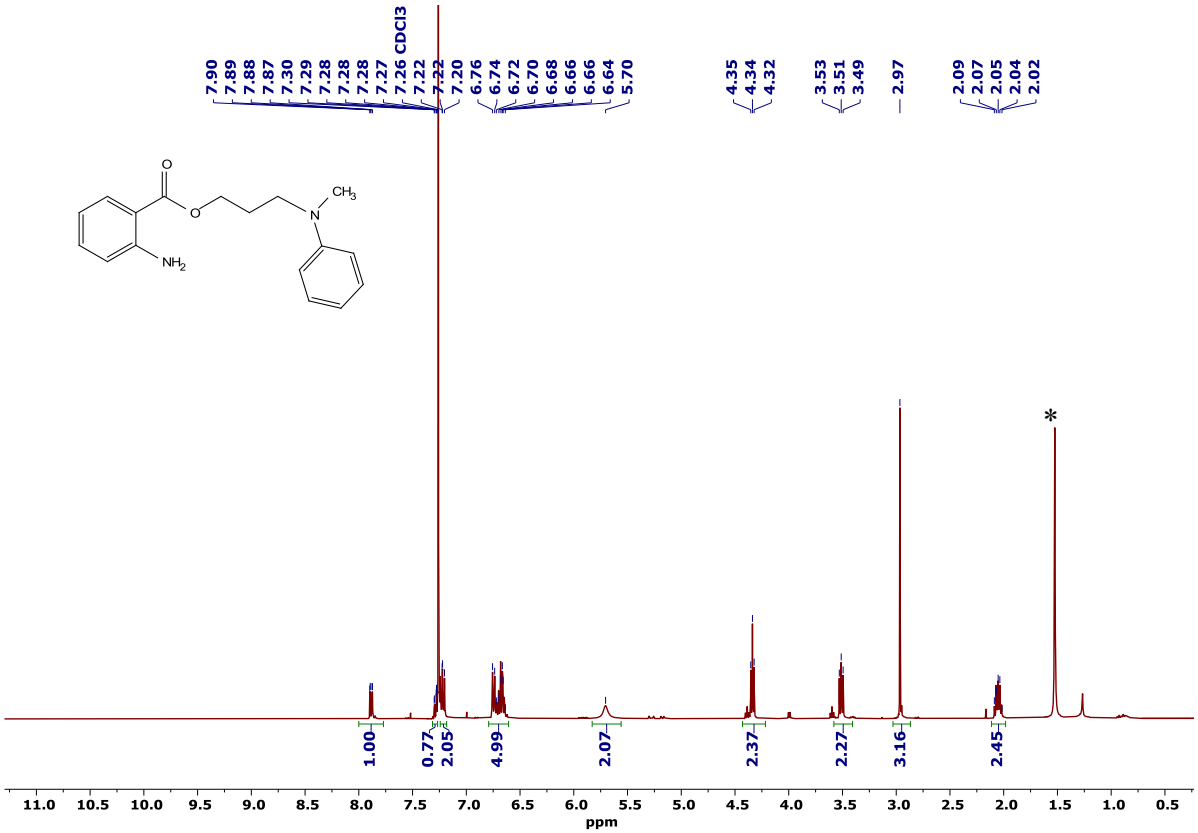


Figure S49. ^{1}H NMR spectrum of **3r** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

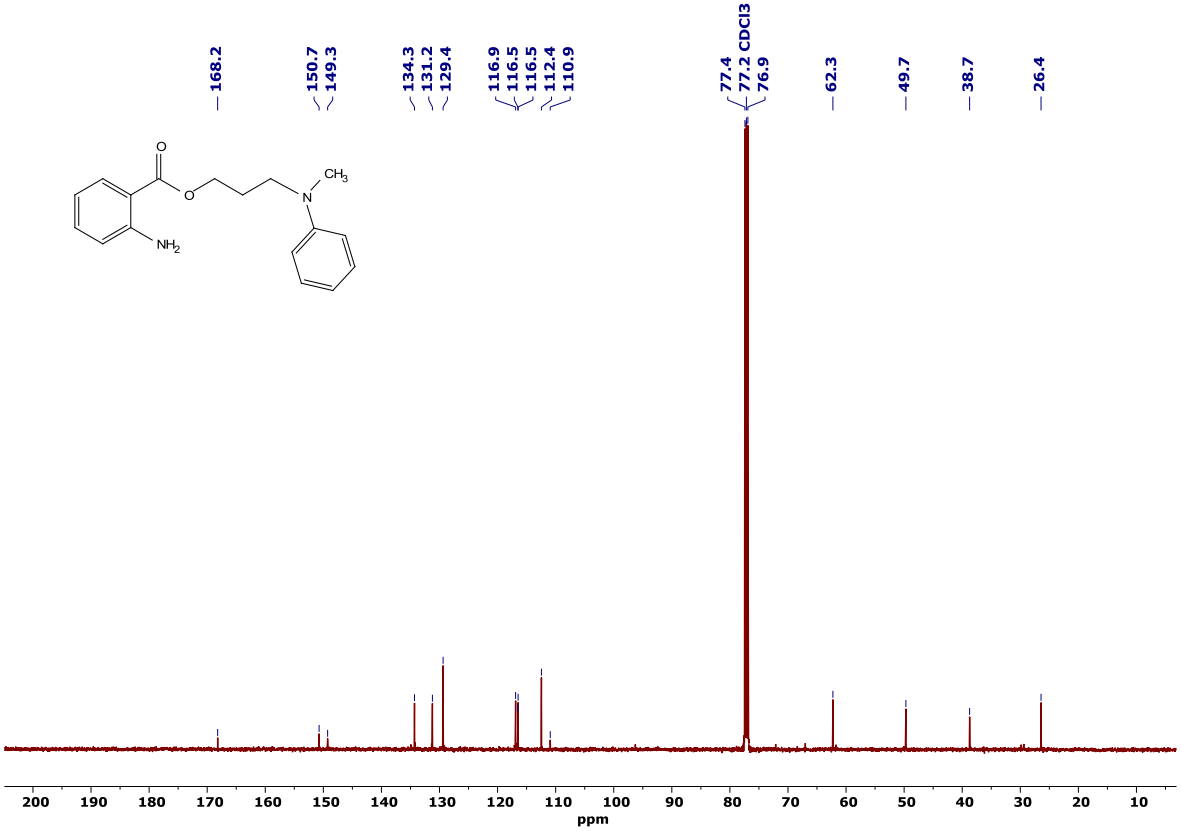


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of **3r** in $CDCl_3$.

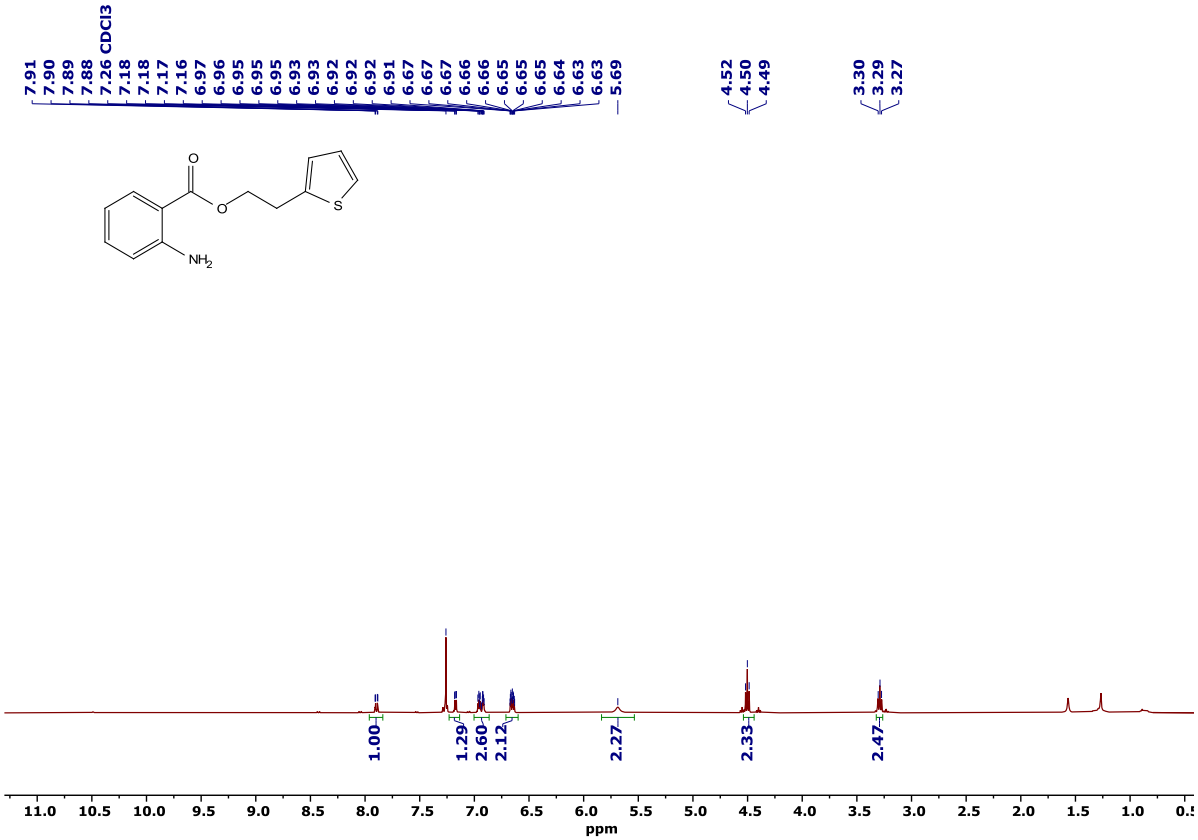


Figure S51. ^{1}H NMR spectrum of **3s** in $CDCl_3$.

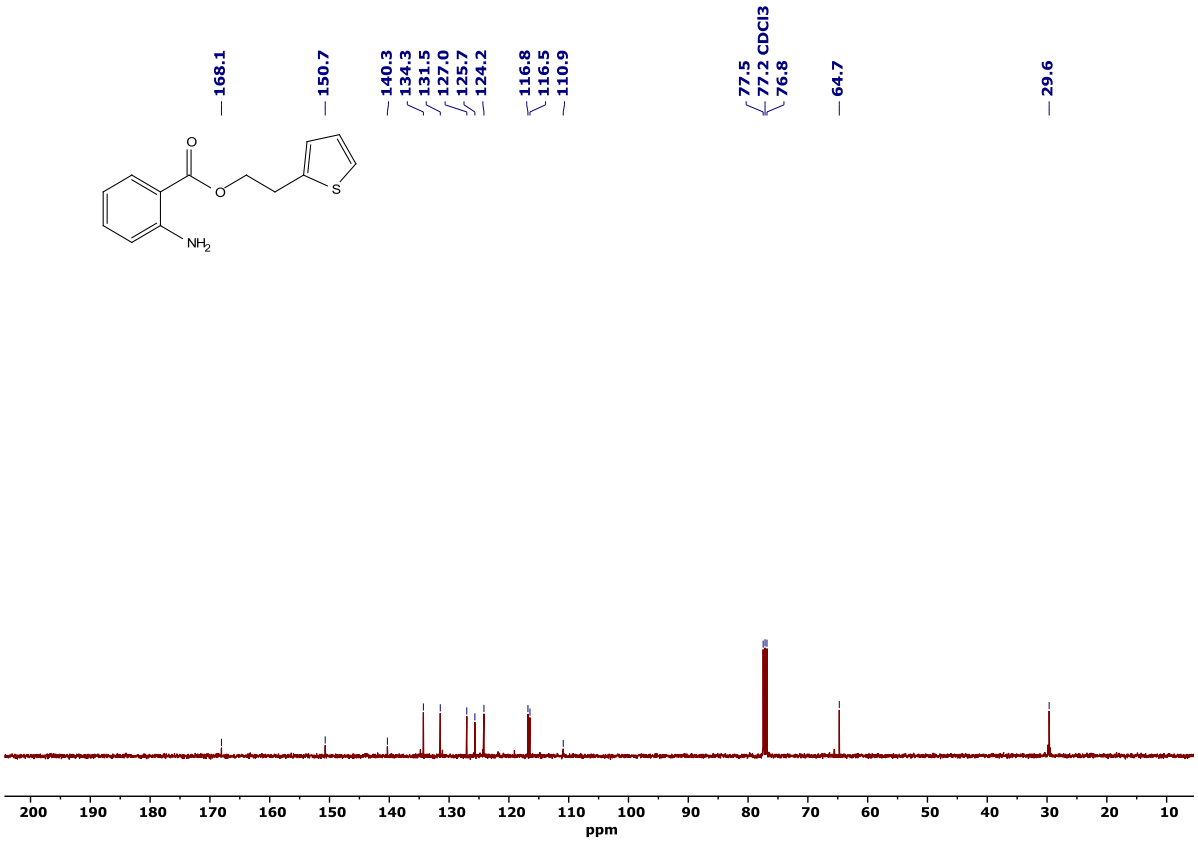


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **3s** in $CDCl_3$.

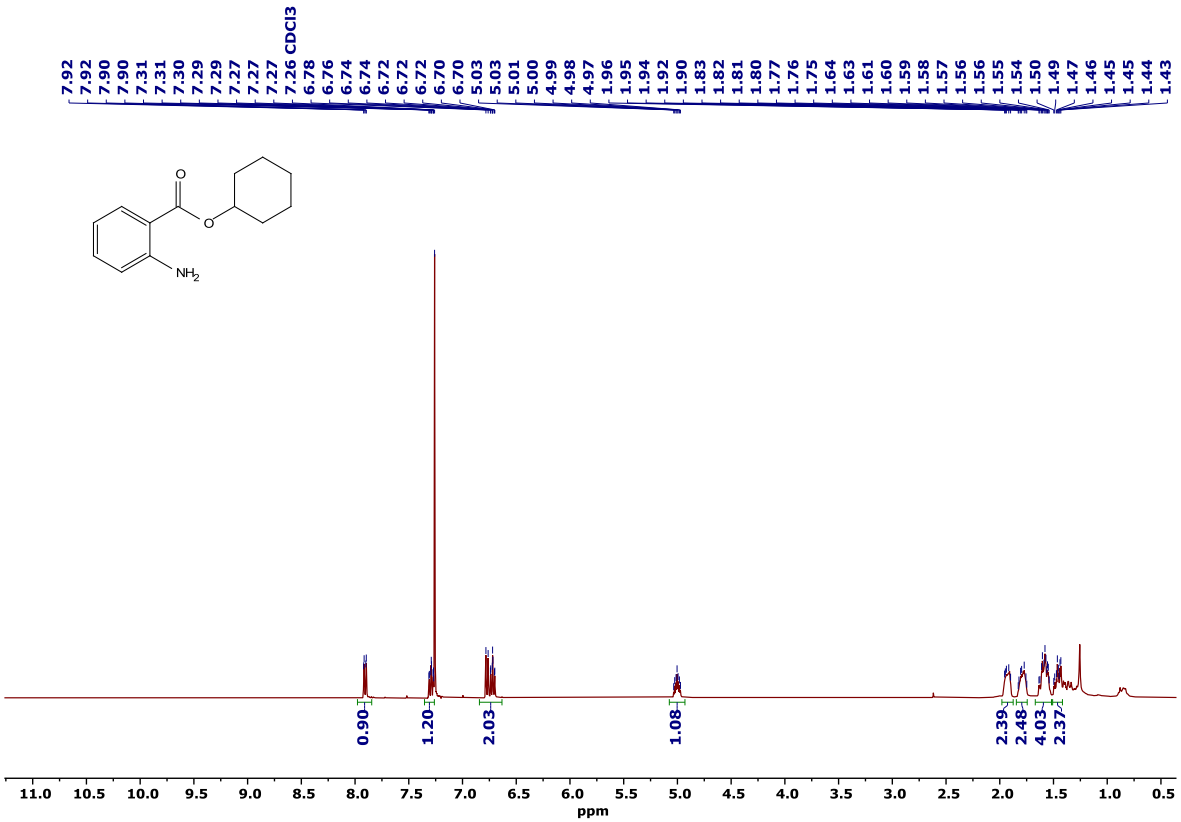


Figure S53. ^{1}H NMR spectrum of **3t** in $CDCl_3$.

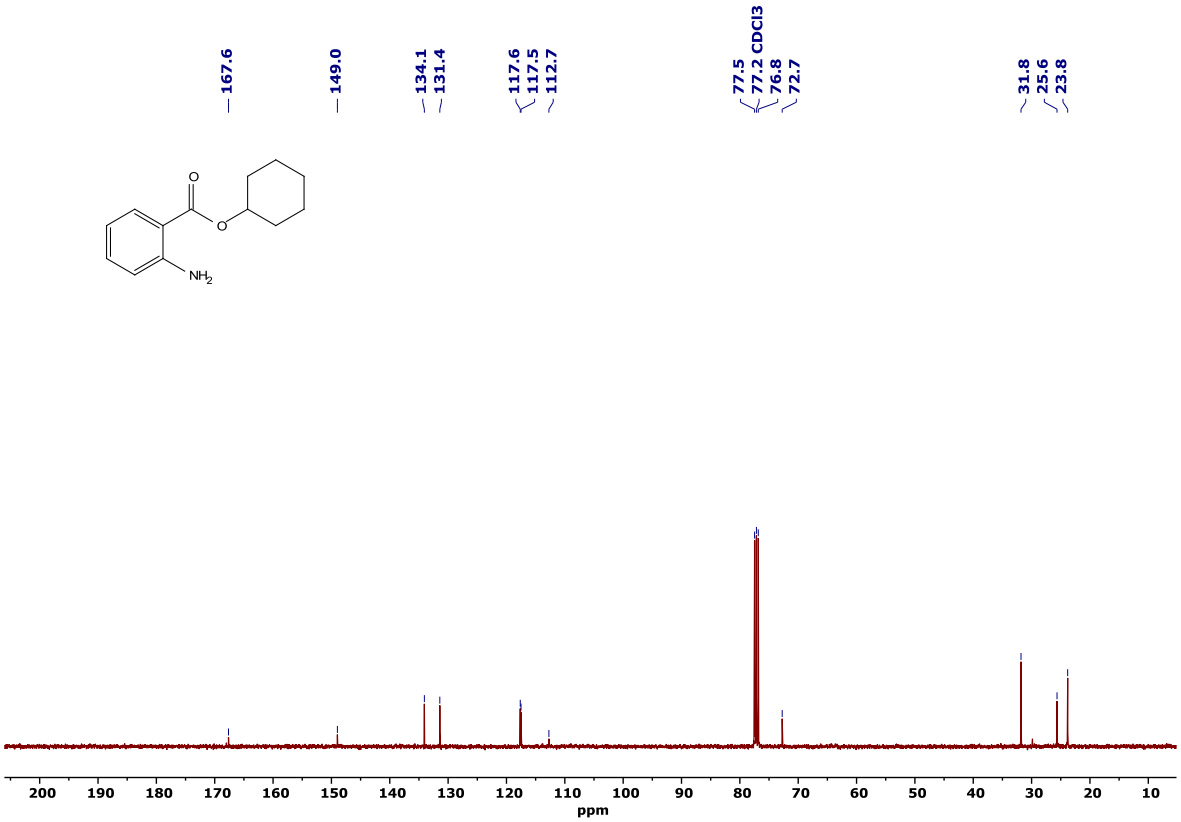


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of **3t** in $CDCl_3$.

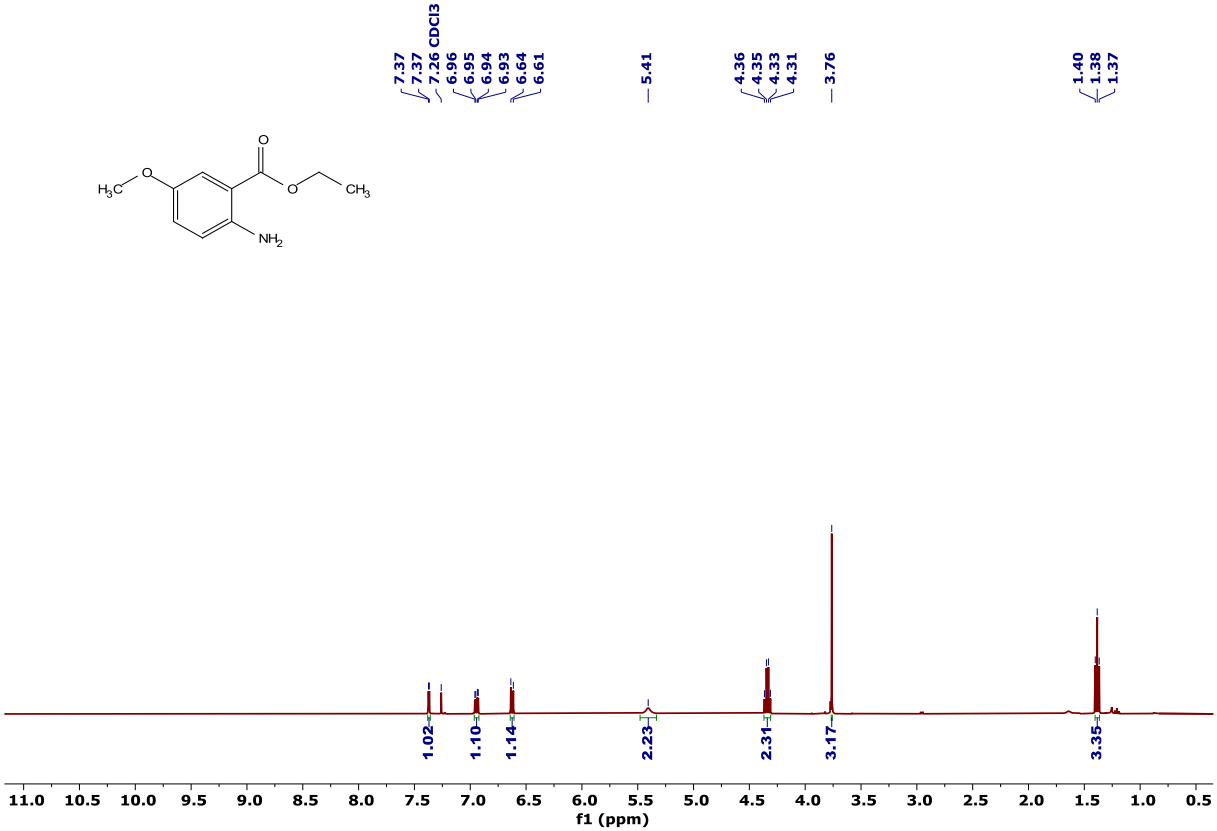


Figure S55. ^{1}H NMR spectrum of **3u** in $CDCl_3$.

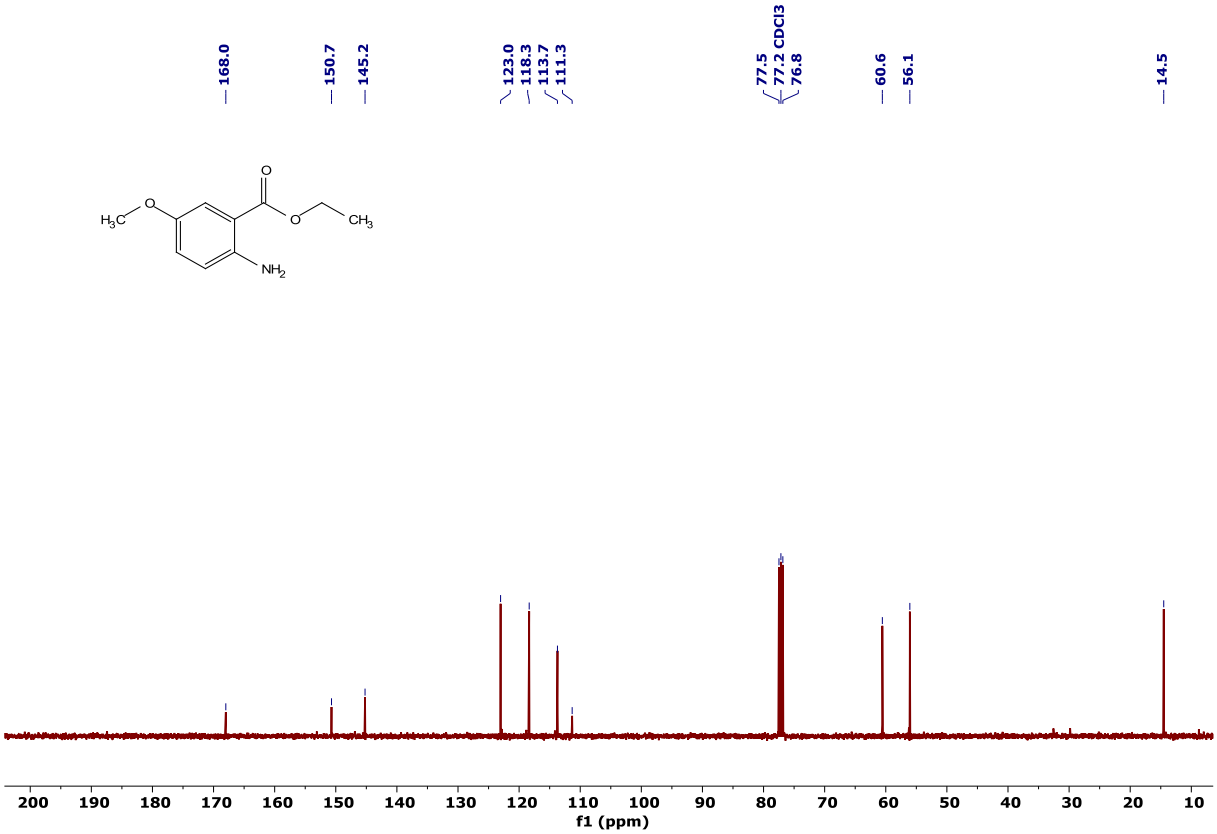


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **3u** in $CDCl_3$.

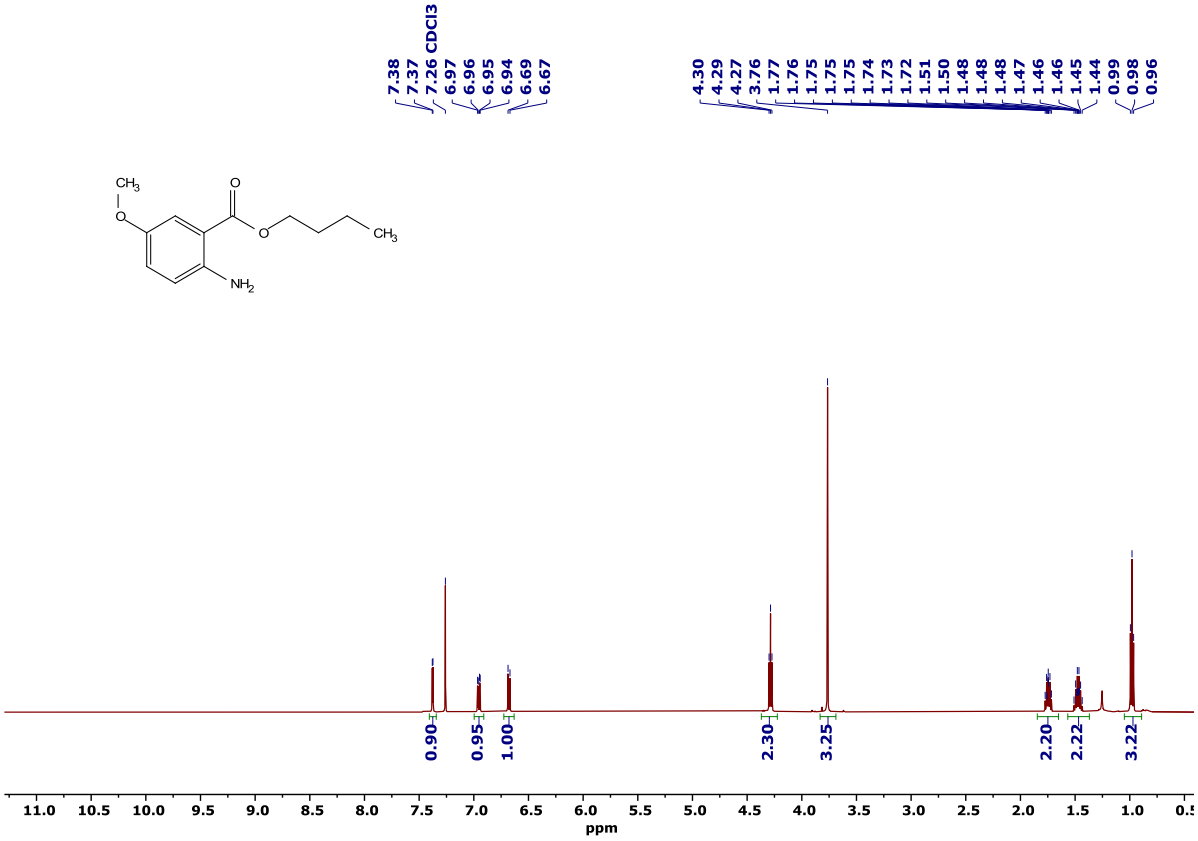


Figure S57. ^{1}H NMR spectrum of **3v** in $CDCl_3$.

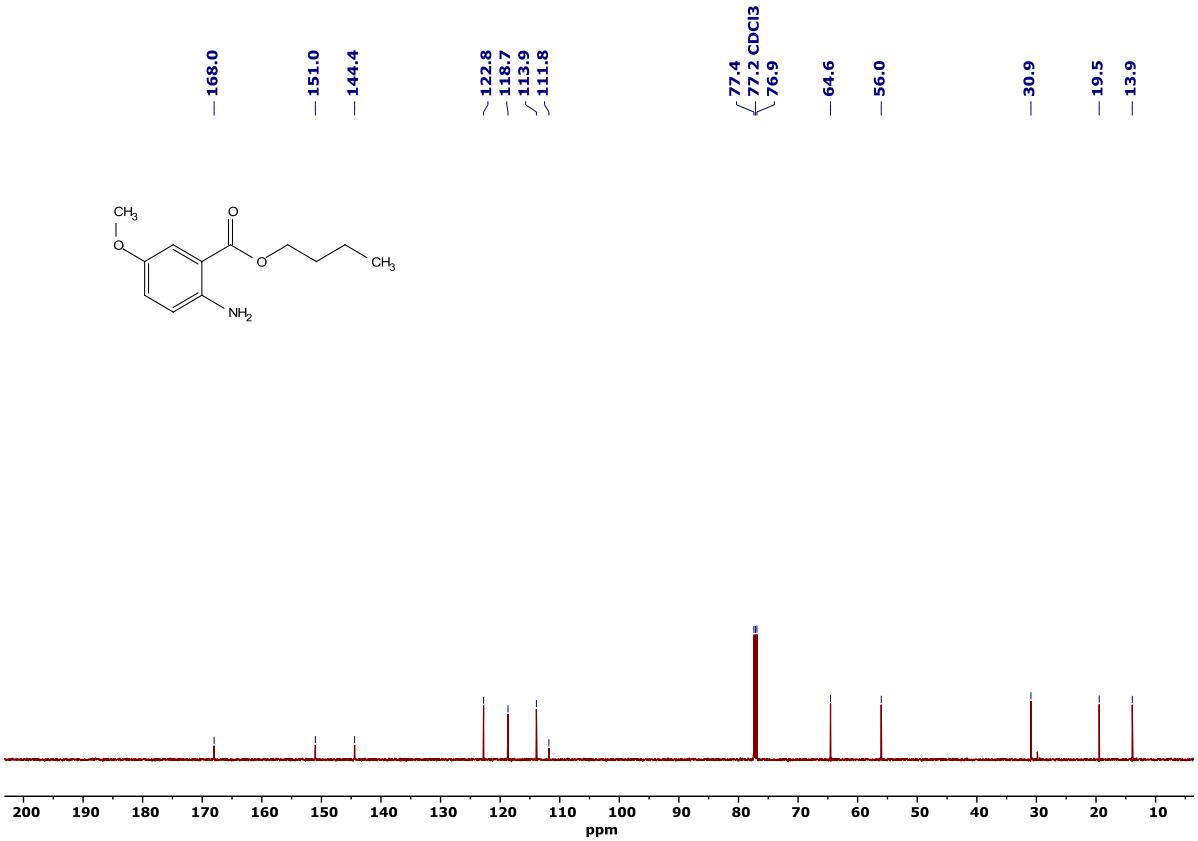


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of **3v** in $CDCl_3$.

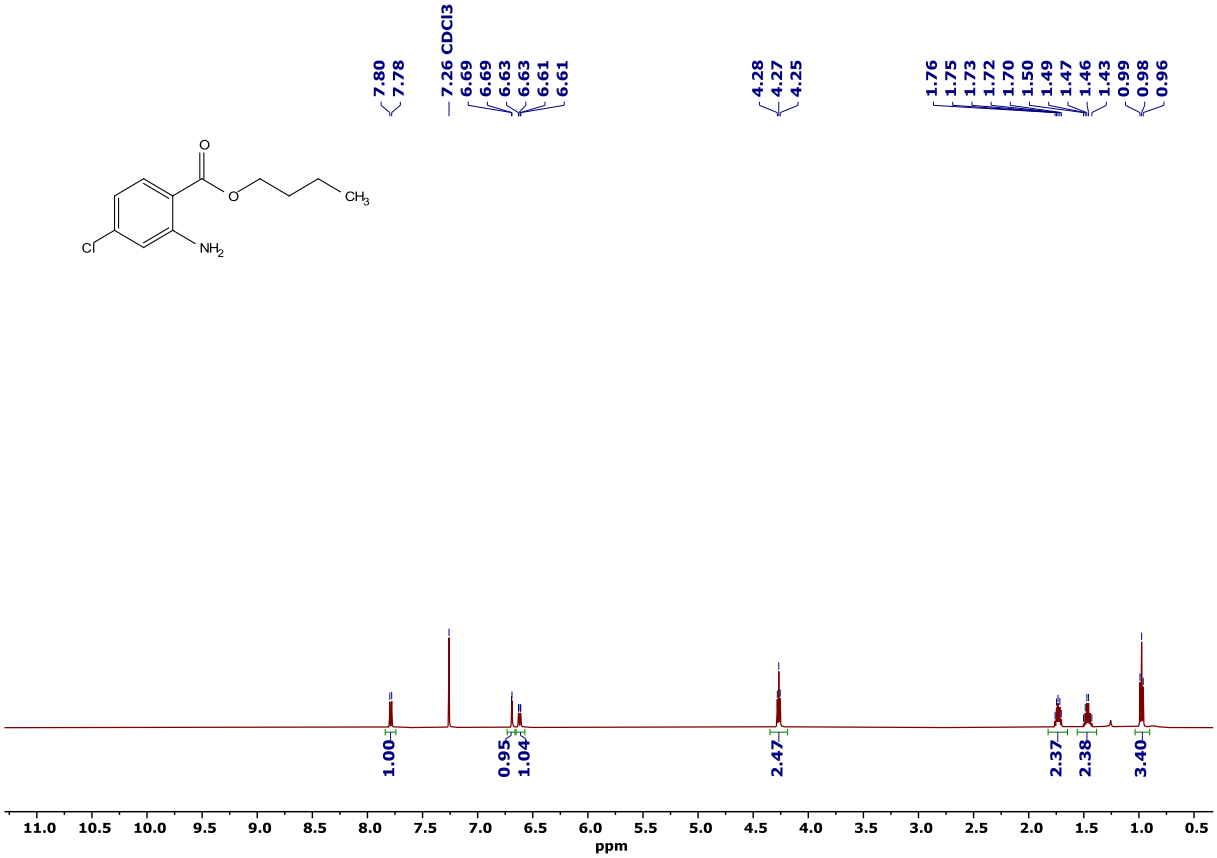


Figure S59. ^{1}H NMR spectrum of **3w** in $CDCl_3$.

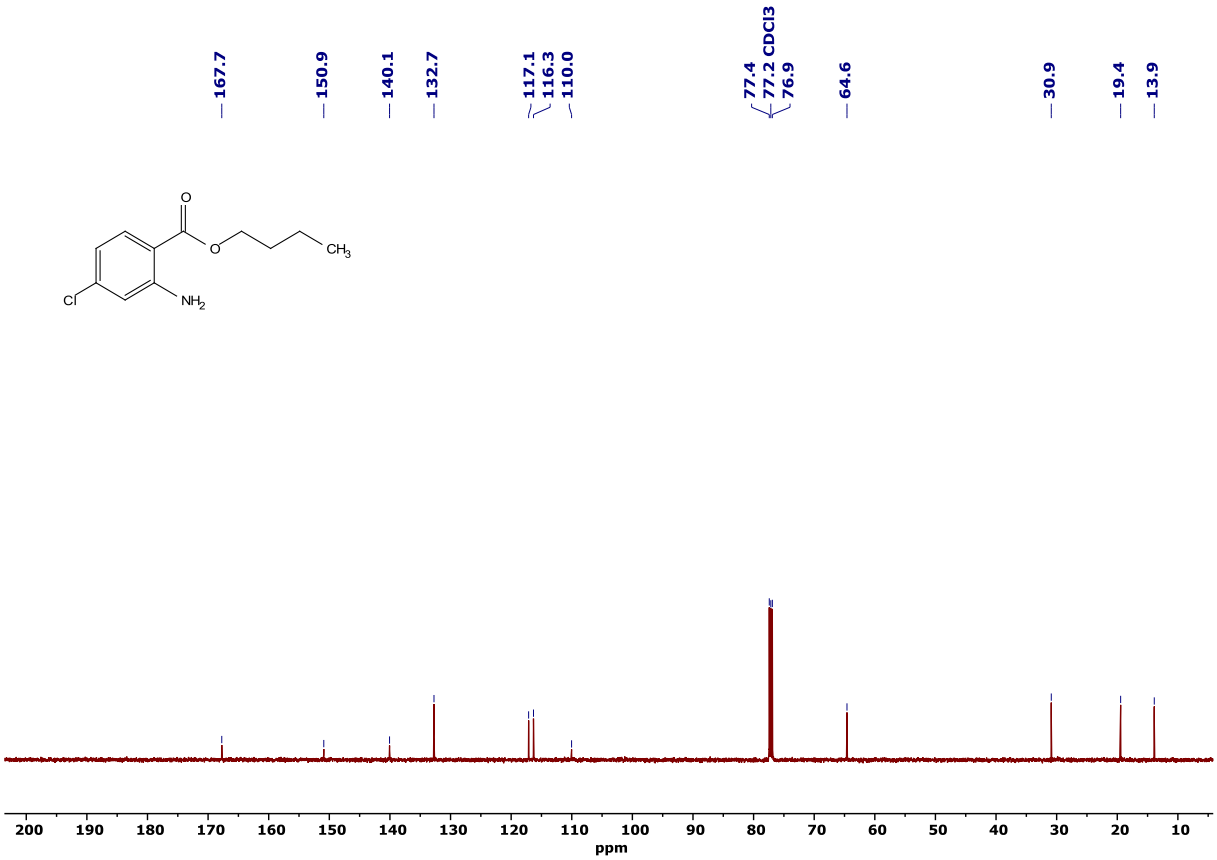


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of **3w** in $CDCl_3$.

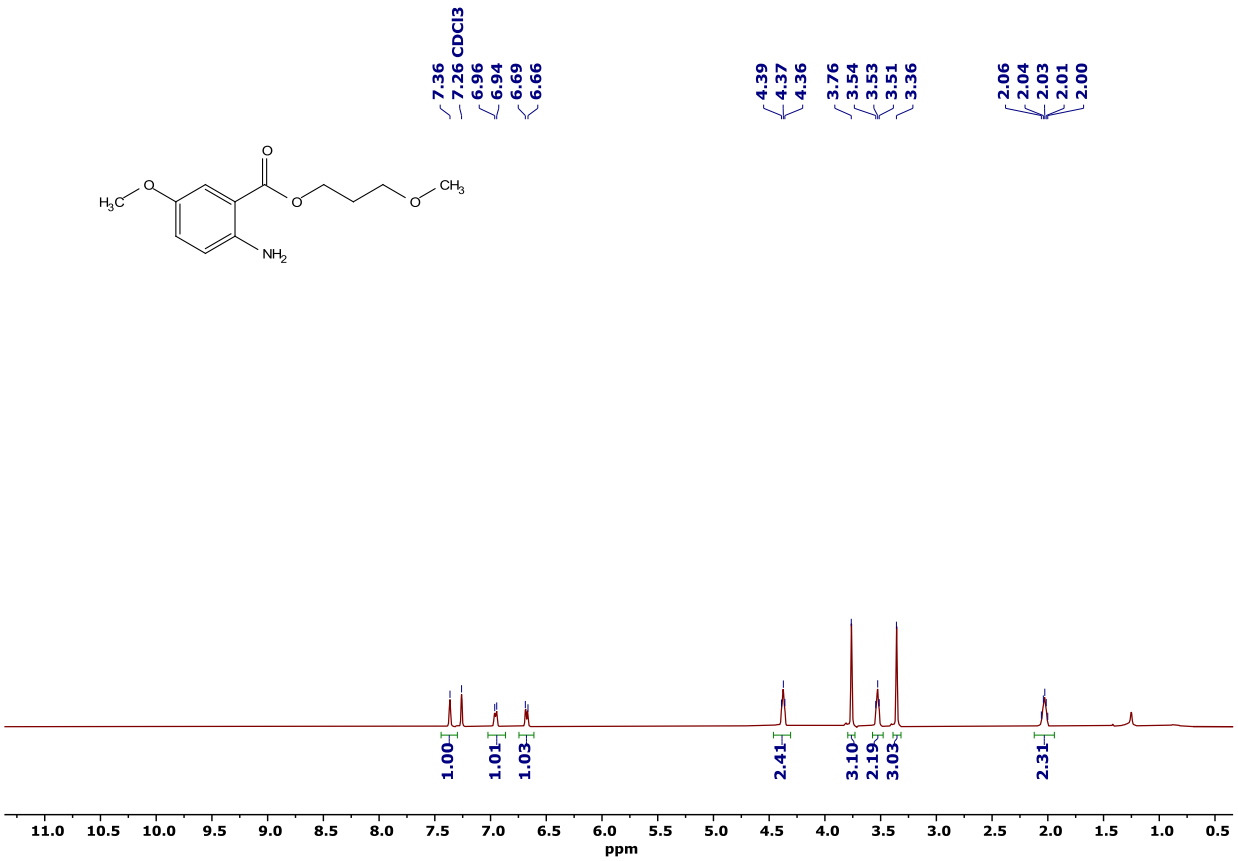


Figure S61. ^{1}H NMR spectrum of **3x** in $CDCl_3$.

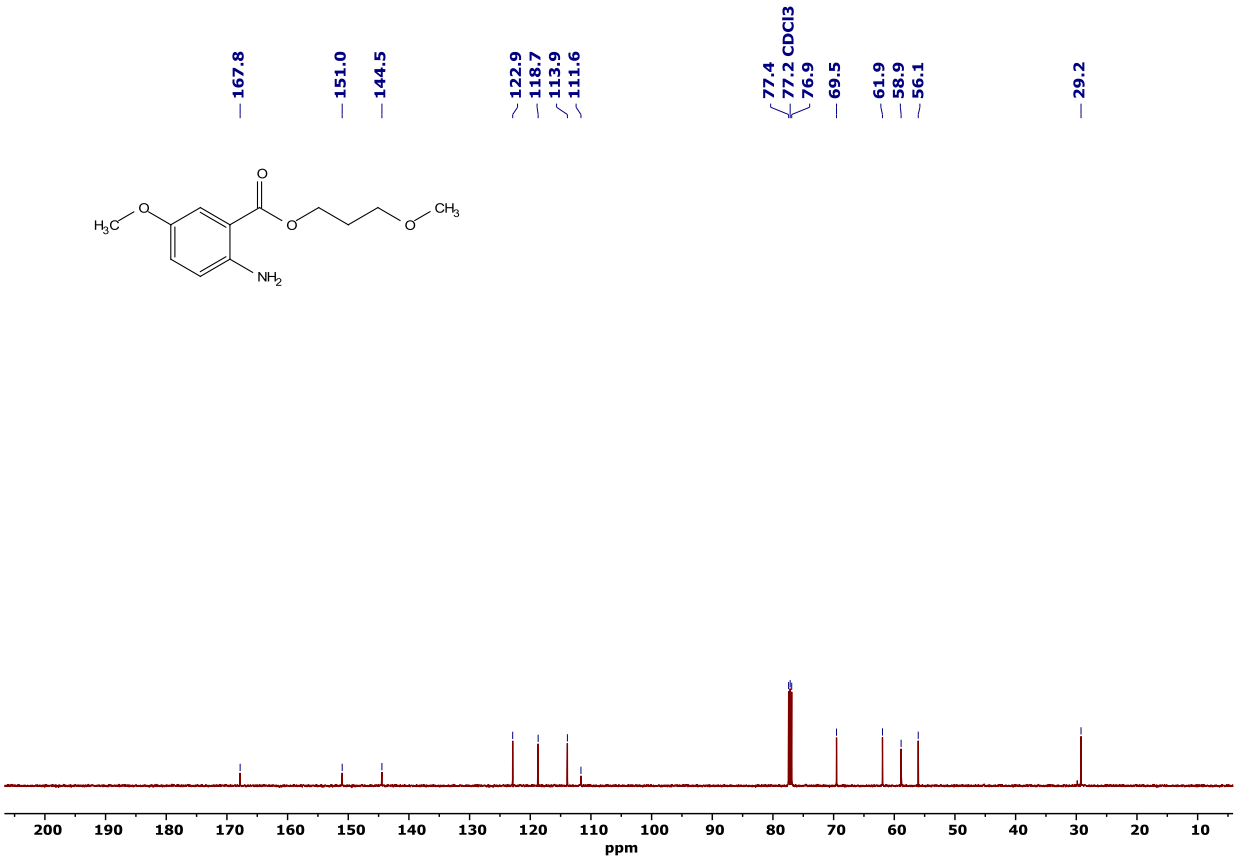


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of **3x** in $CDCl_3$.

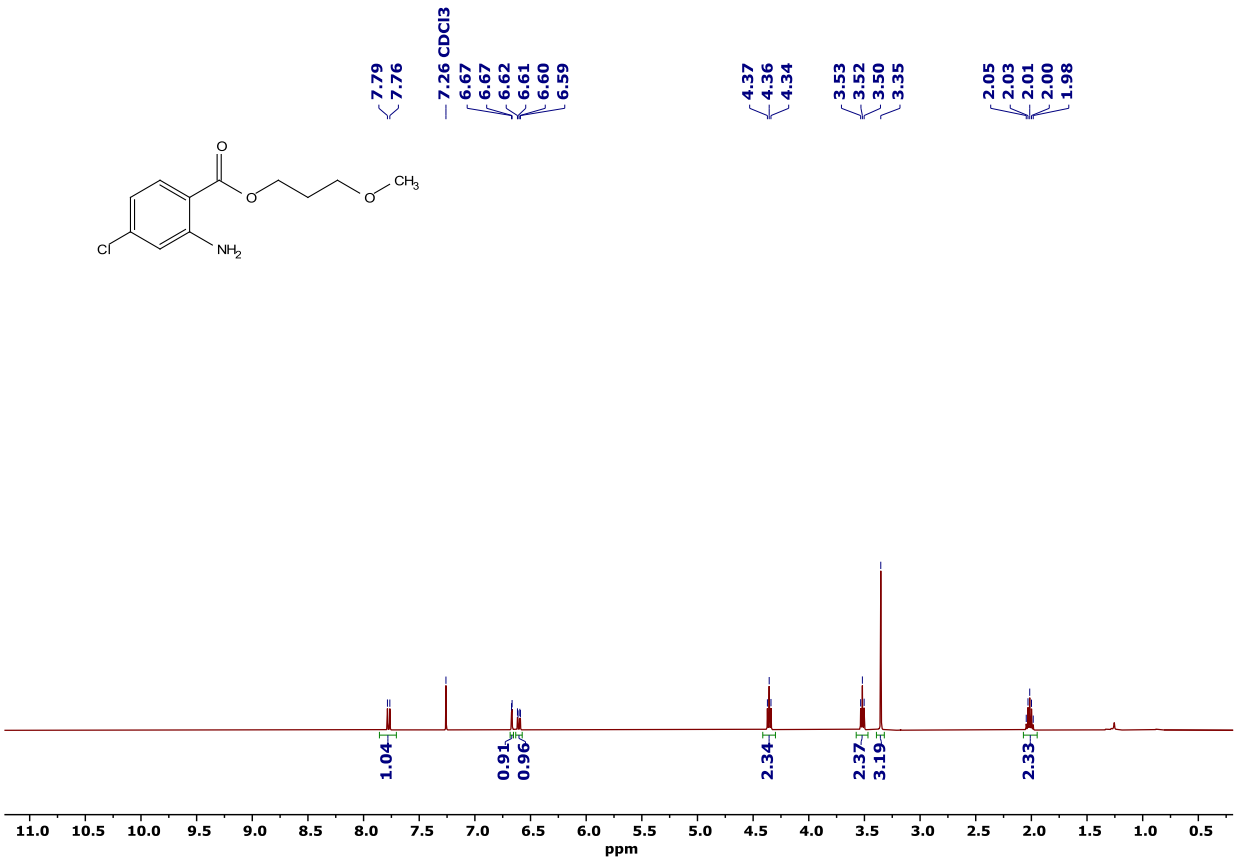


Figure S63. ^{1}H NMR spectrum of **3y** in $CDCl_3$.

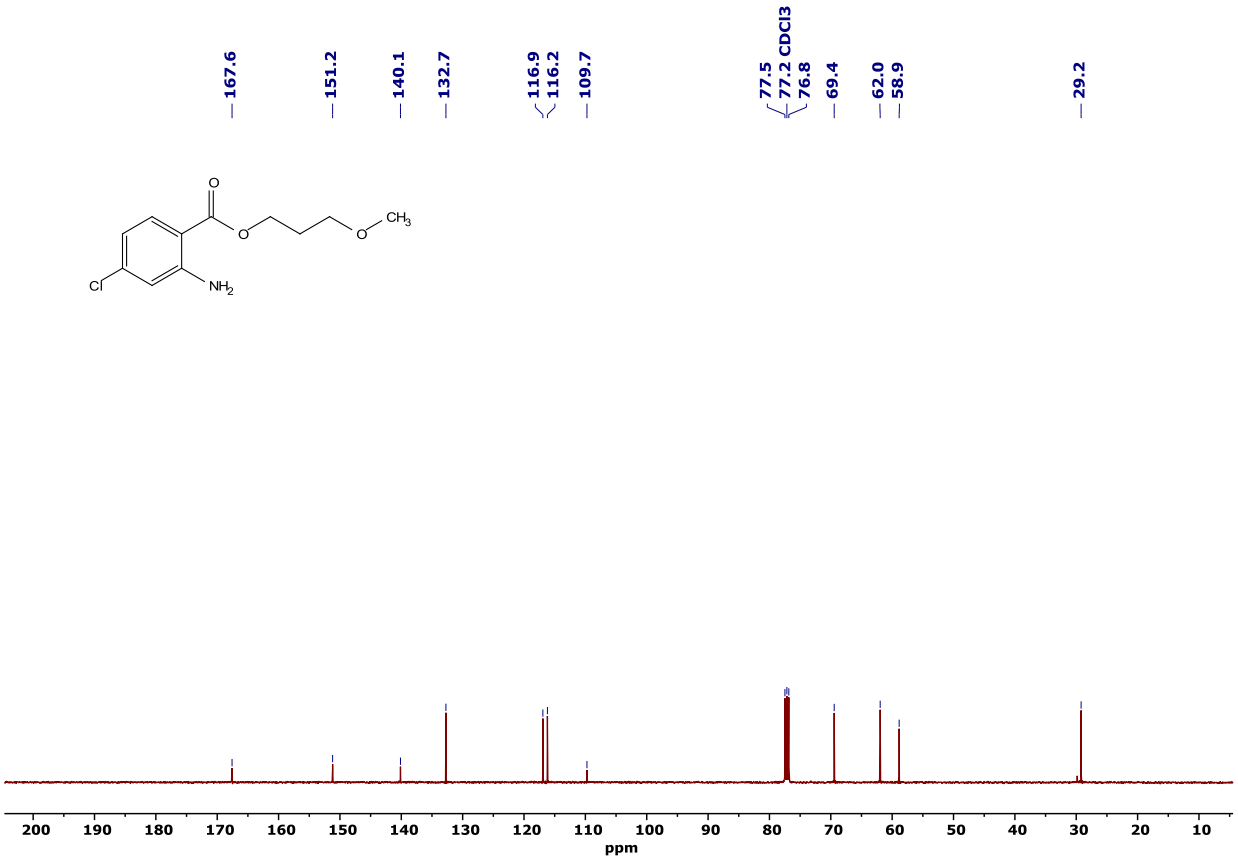


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of **3y** in $CDCl_3$.

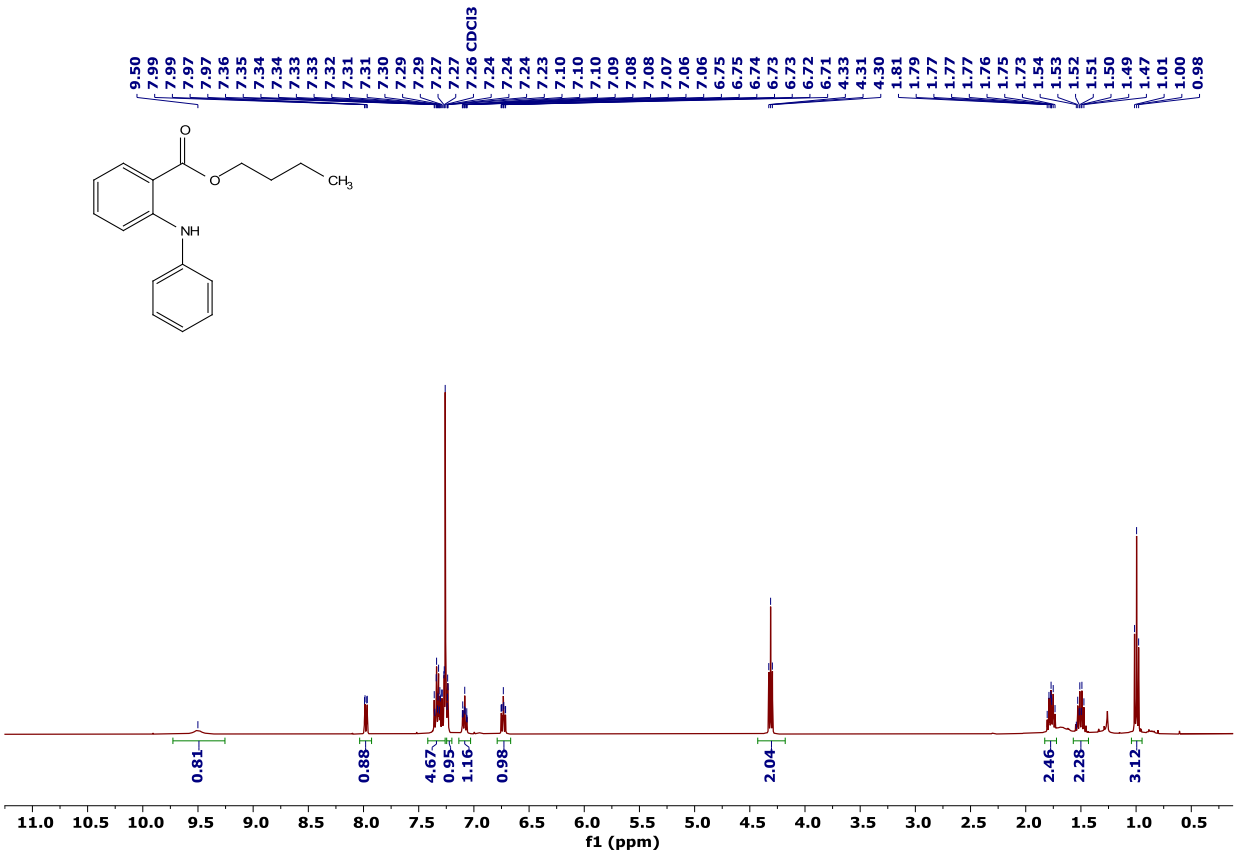


Figure S65. ^{1}H NMR spectrum of **3z** in $CDCl_3$.

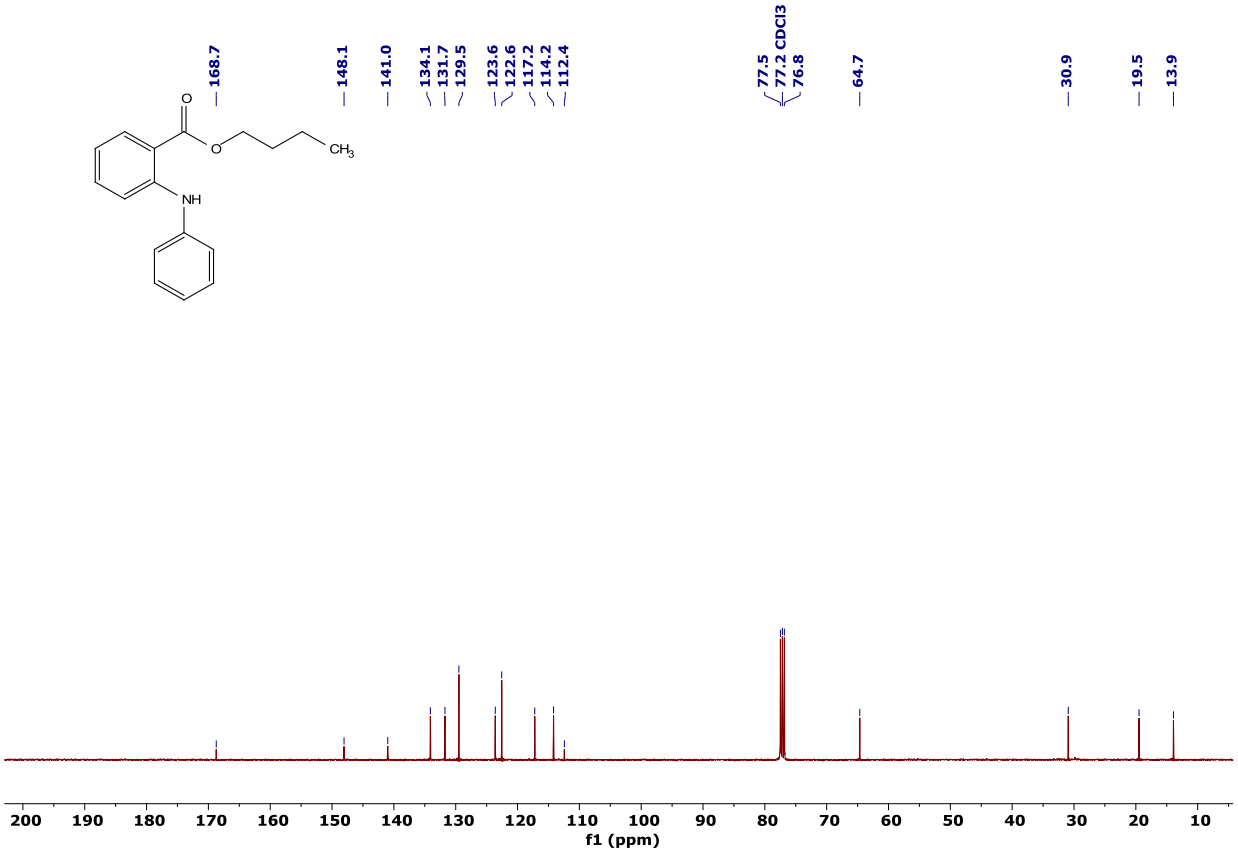


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of **3z** in $CDCl_3$.

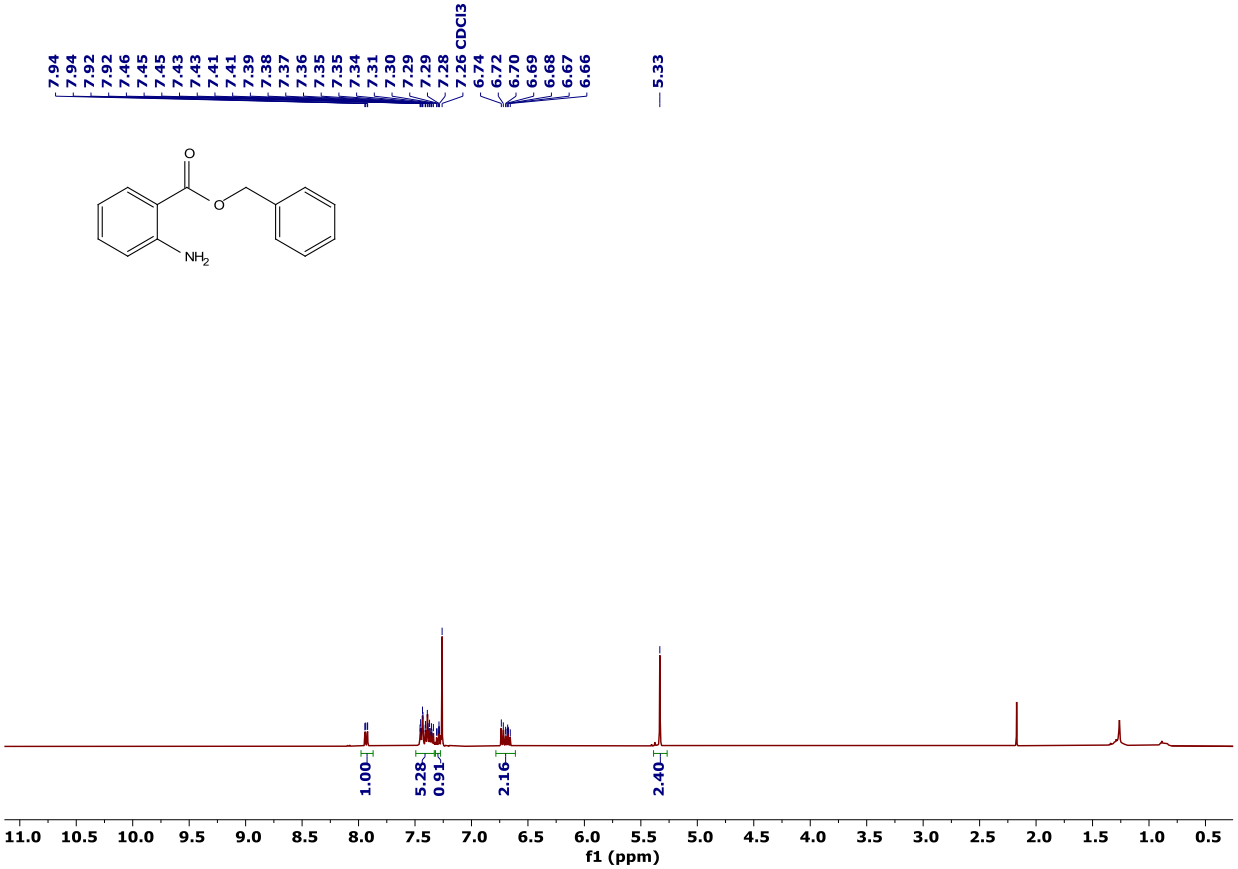


Figure S67. ^{1}H NMR spectrum of **5a** in $CDCl_3$.

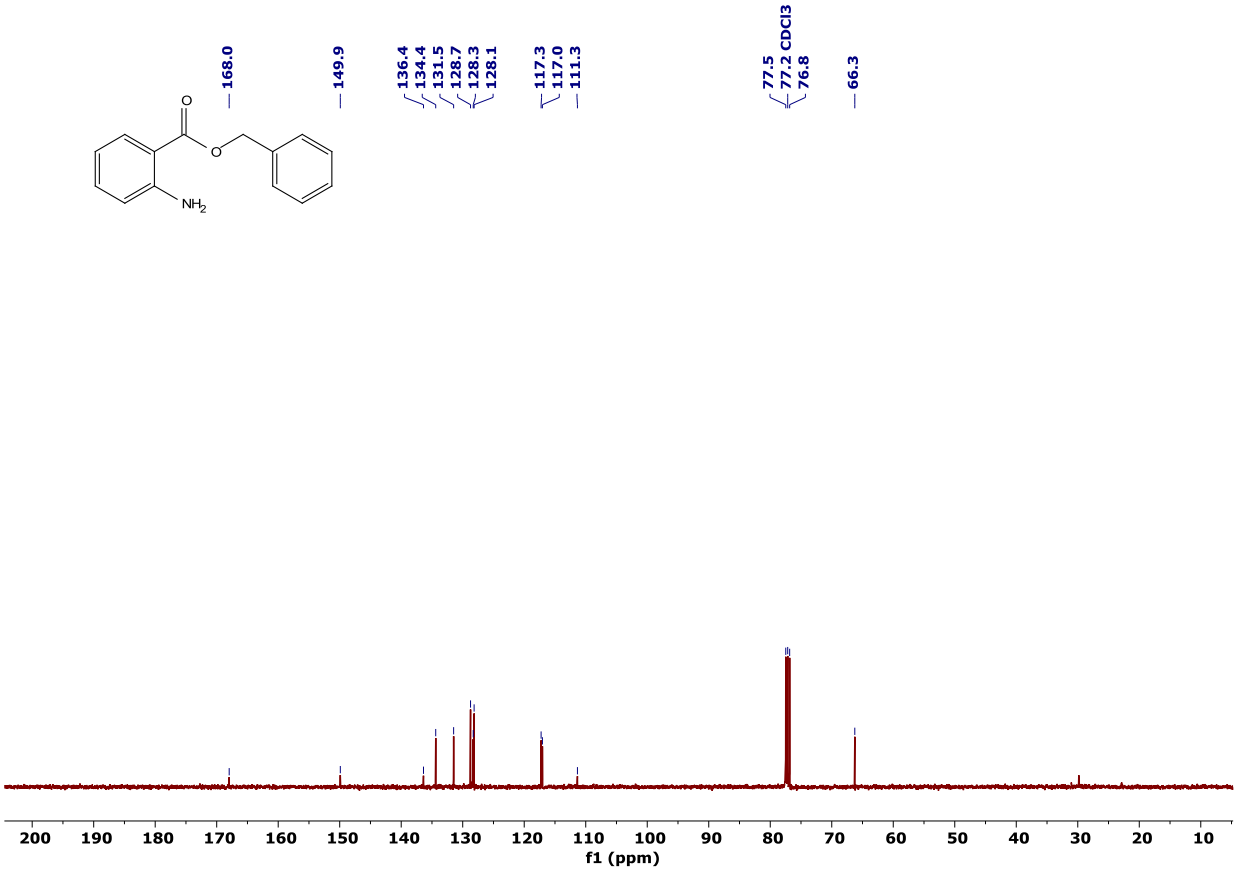


Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$.

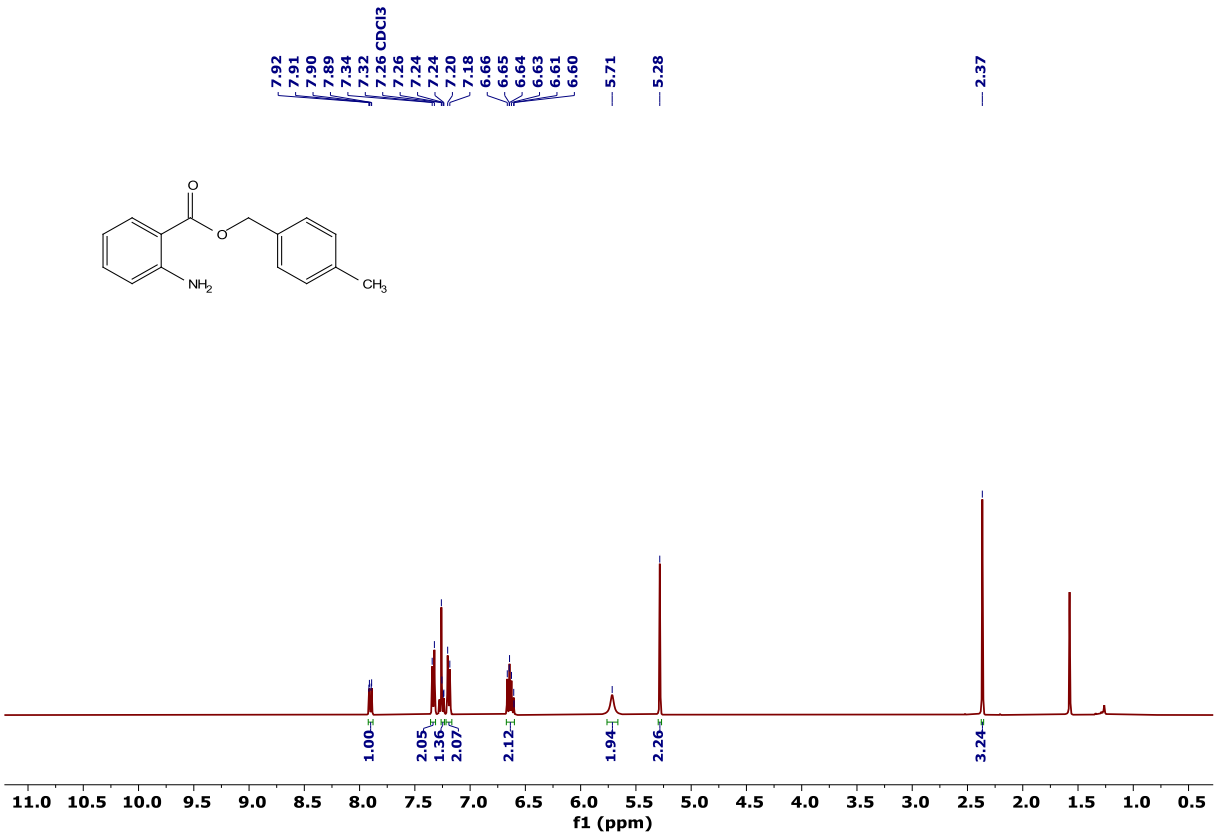


Figure S69. ^{1}H NMR spectrum of **5b** in $CDCl_3$.

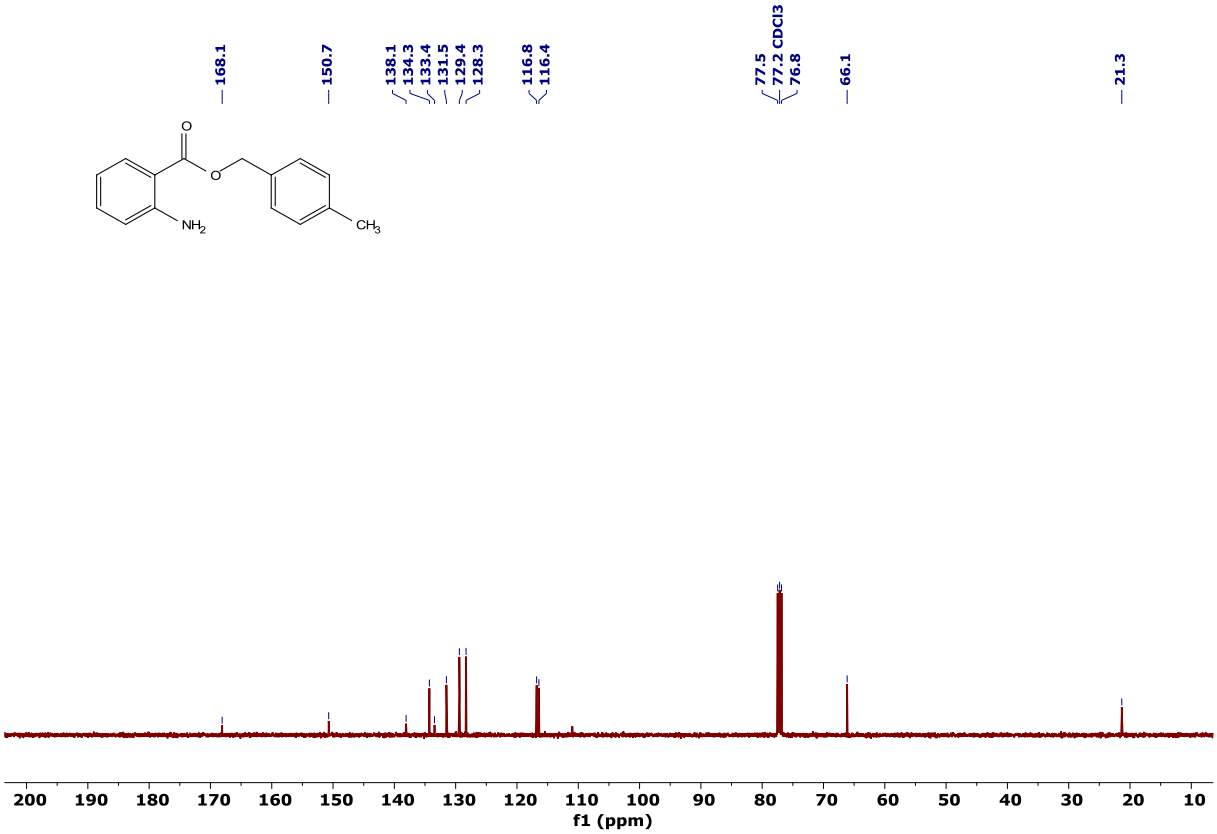


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in $CDCl_3$.

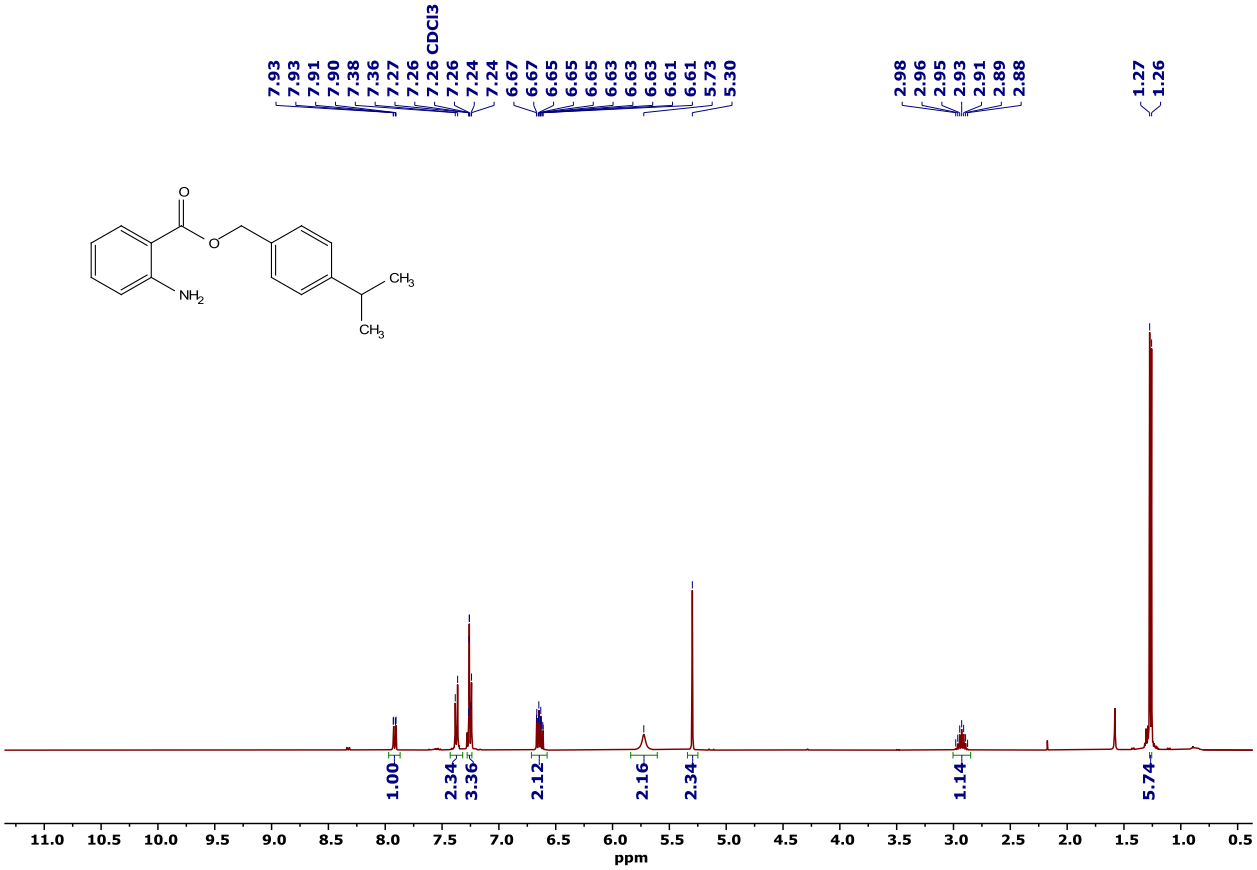


Figure S71. ^{1}H NMR spectrum of **5c** in $CDCl_3$.

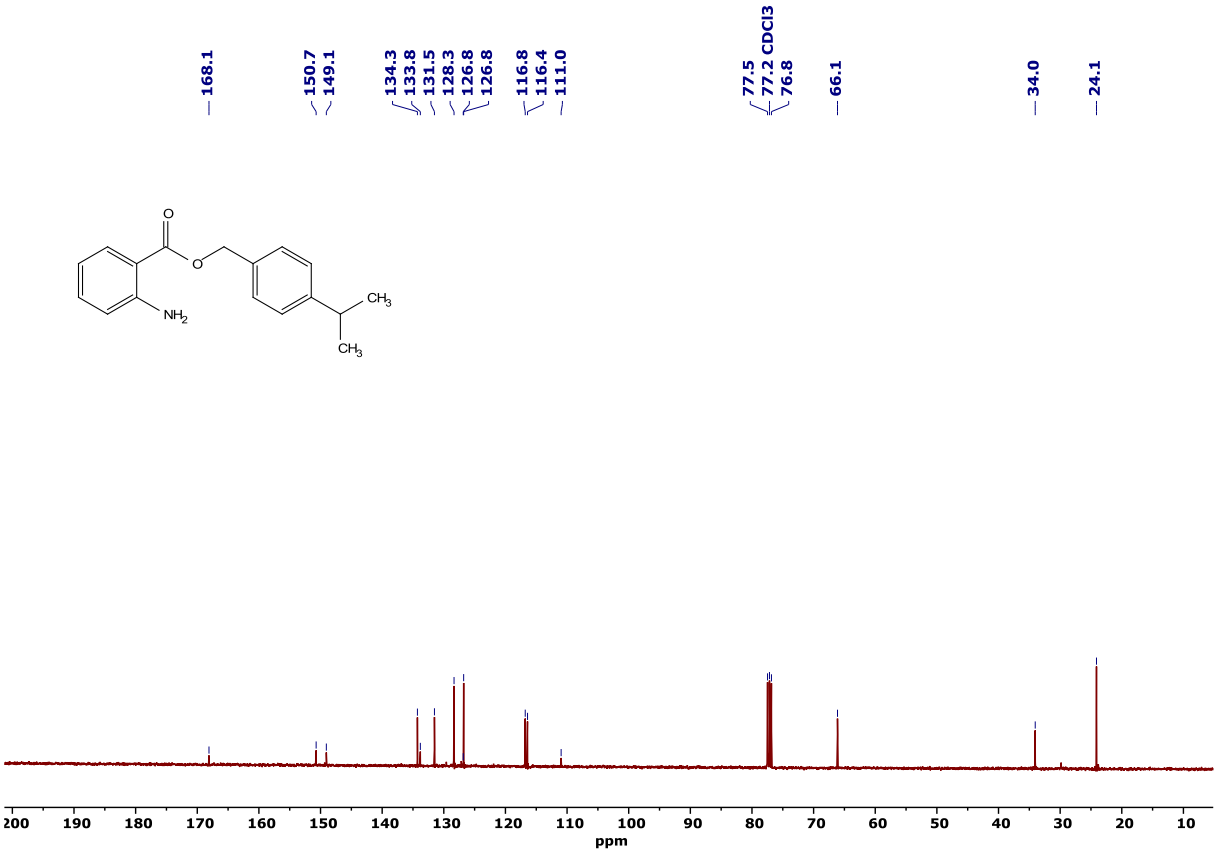


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum of **5c** in $CDCl_3$.

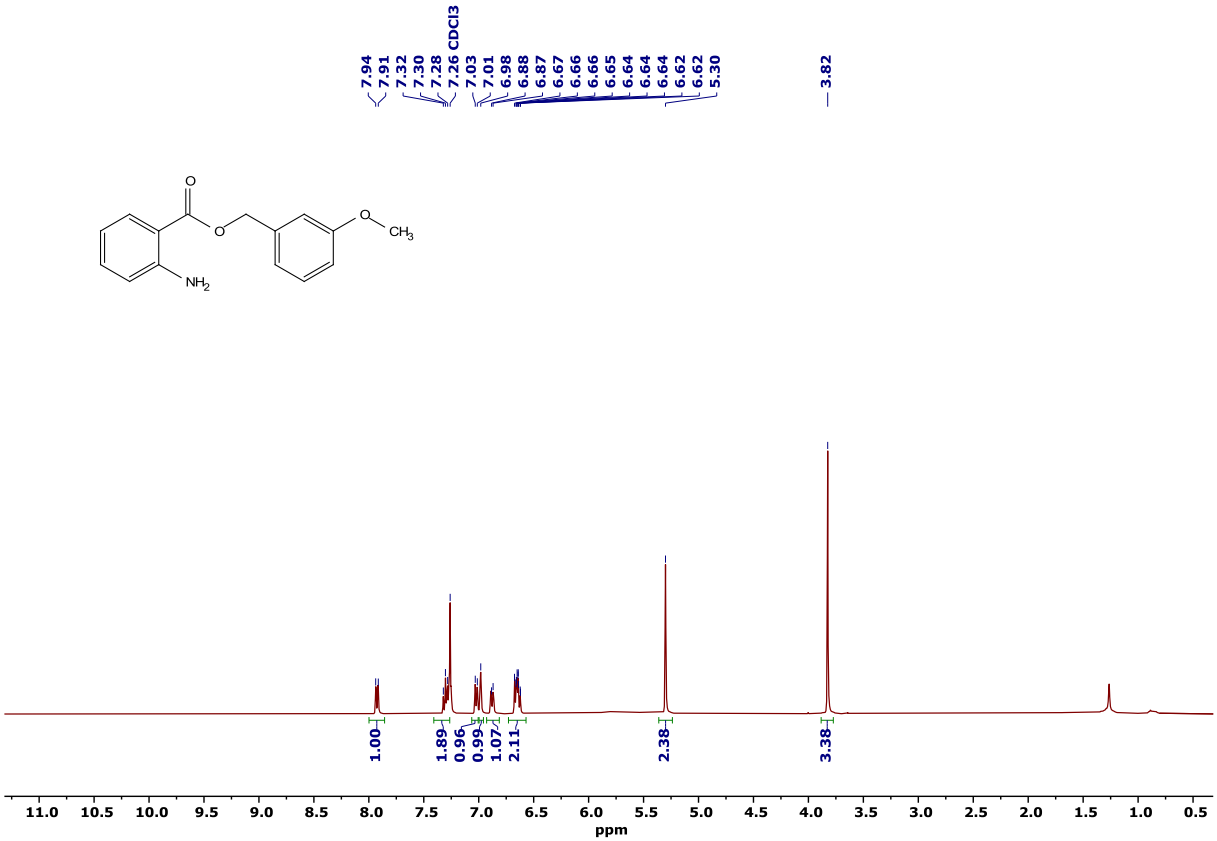


Figure S73. ^{1}H NMR spectrum of **5d** in $CDCl_3$.

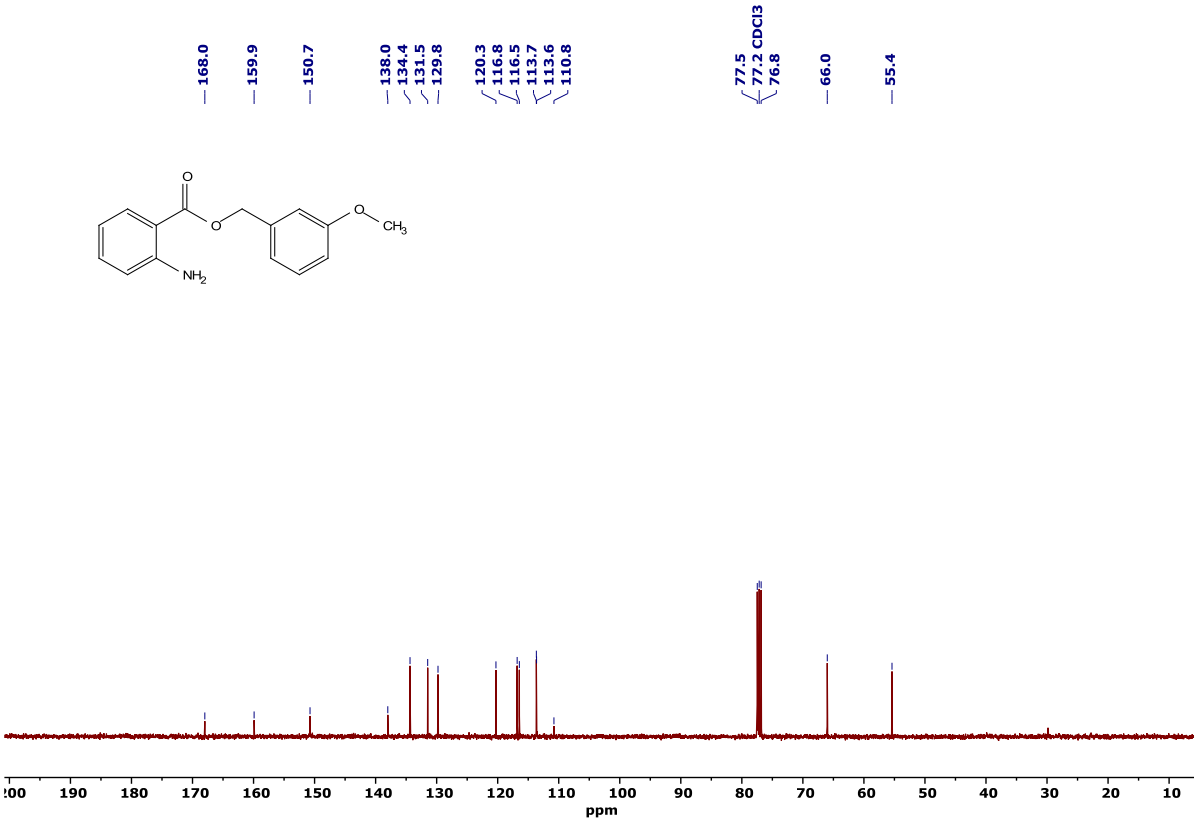


Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum of **5d** in $CDCl_3$.

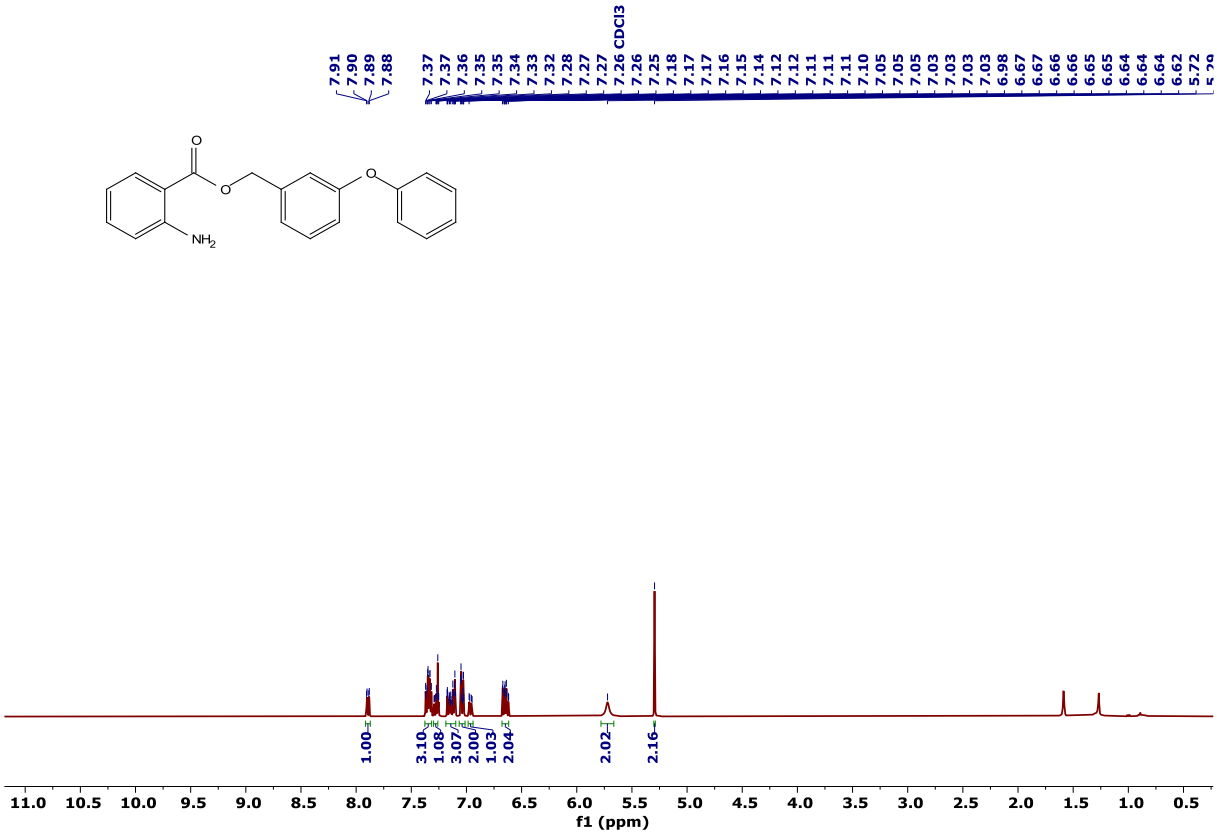


Figure S75. ^{1}H NMR spectrum of **5e** in $CDCl_3$.

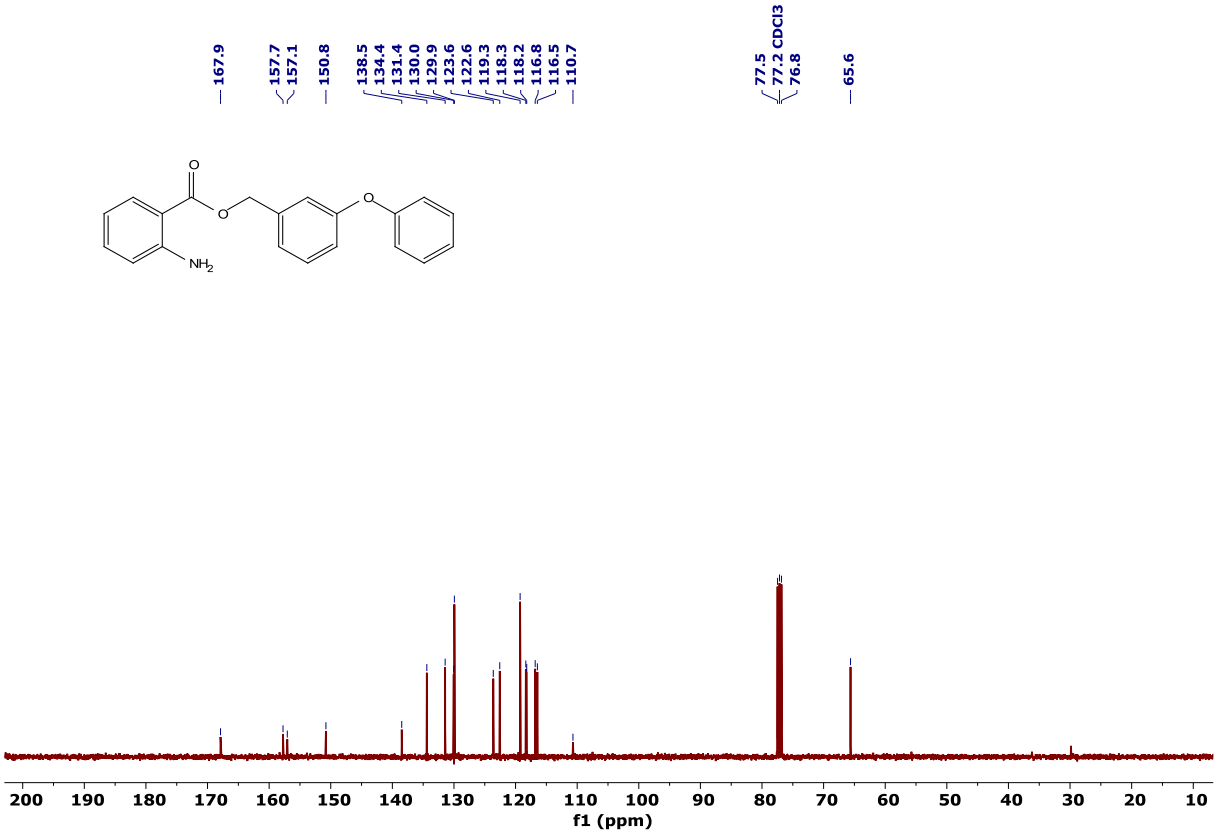


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of **5e** in $CDCl_3$.

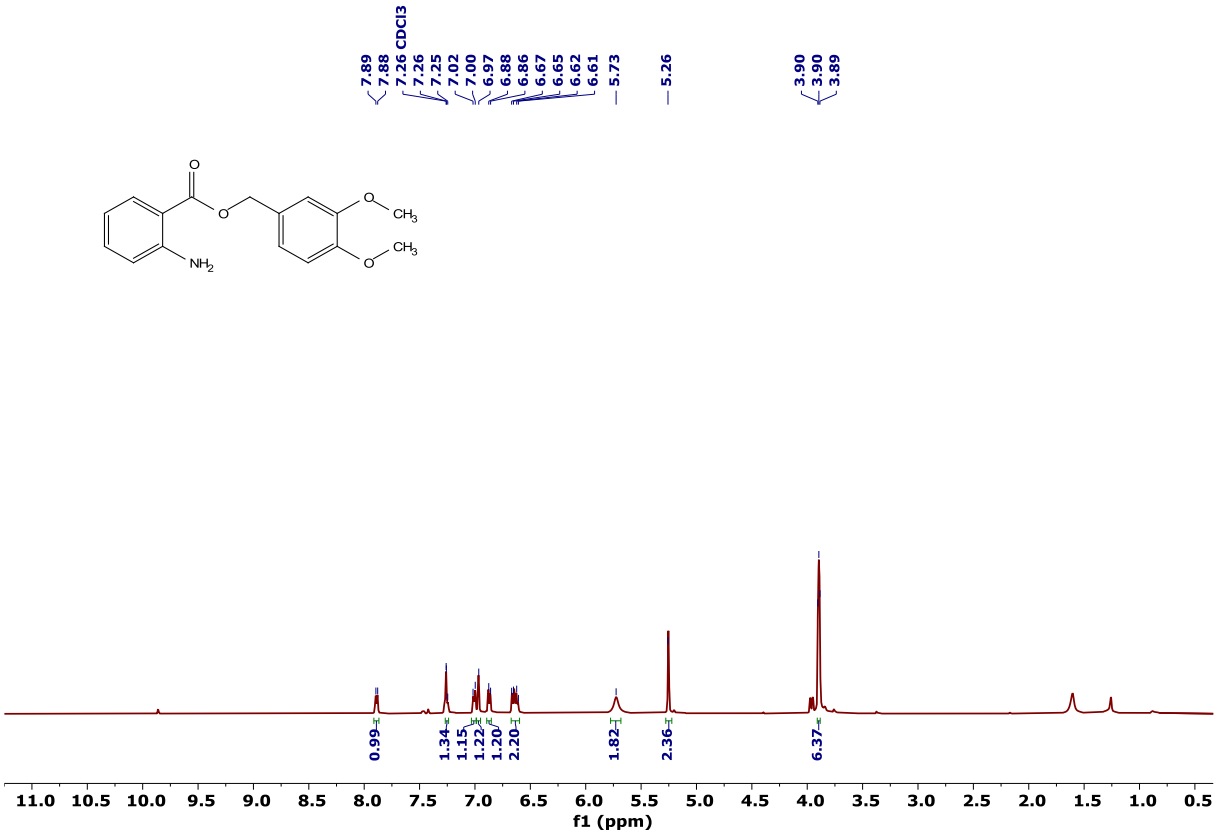


Figure S77. ^{1}H NMR spectrum of **5f** in $CDCl_3$.

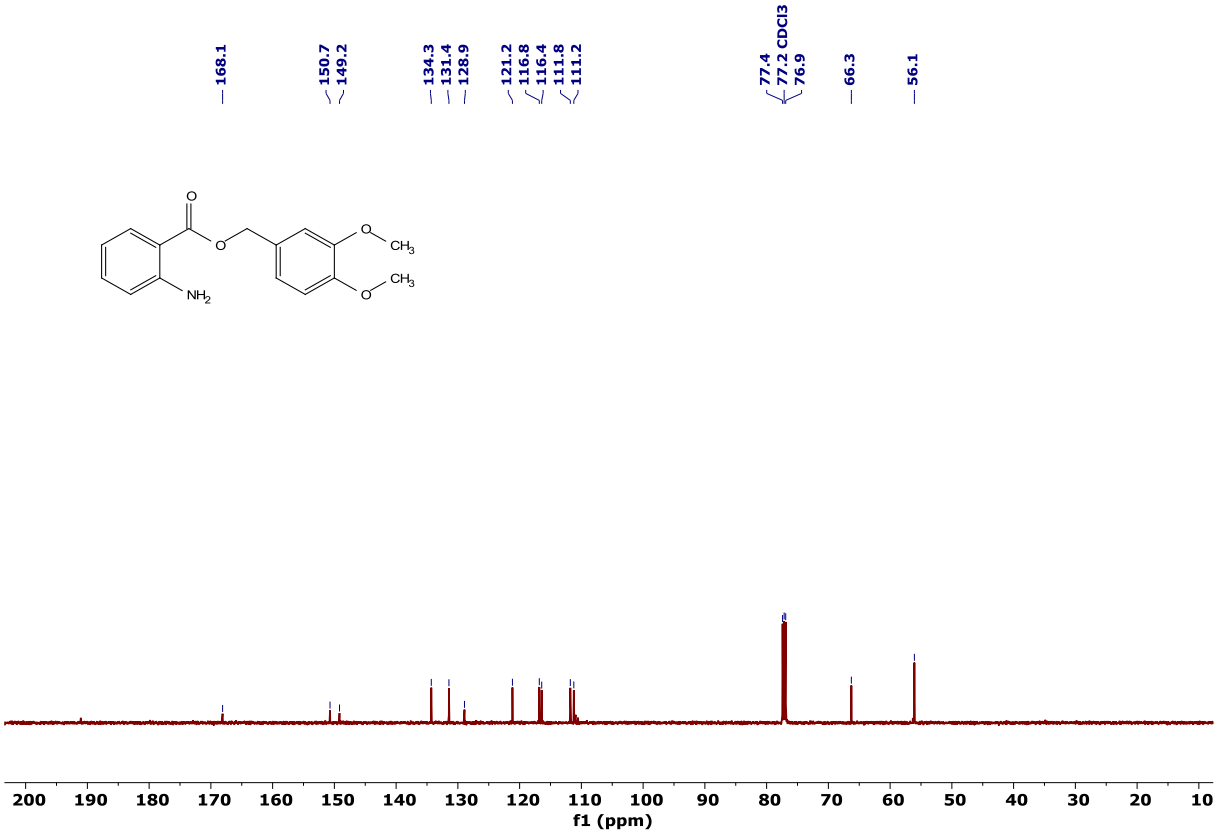


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum of **85** in $CDCl_3$.

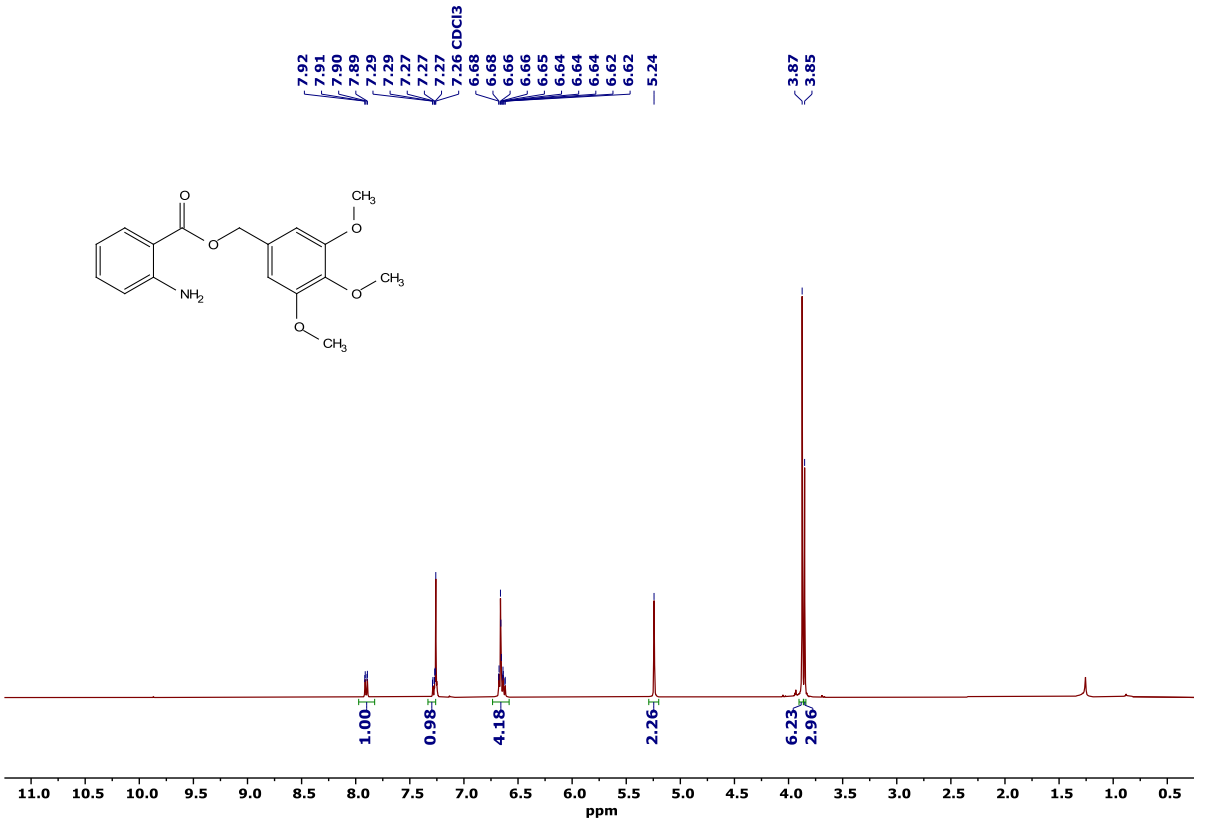


Figure S79. ^{1}H NMR spectrum of **5g** in $CDCl_3$.

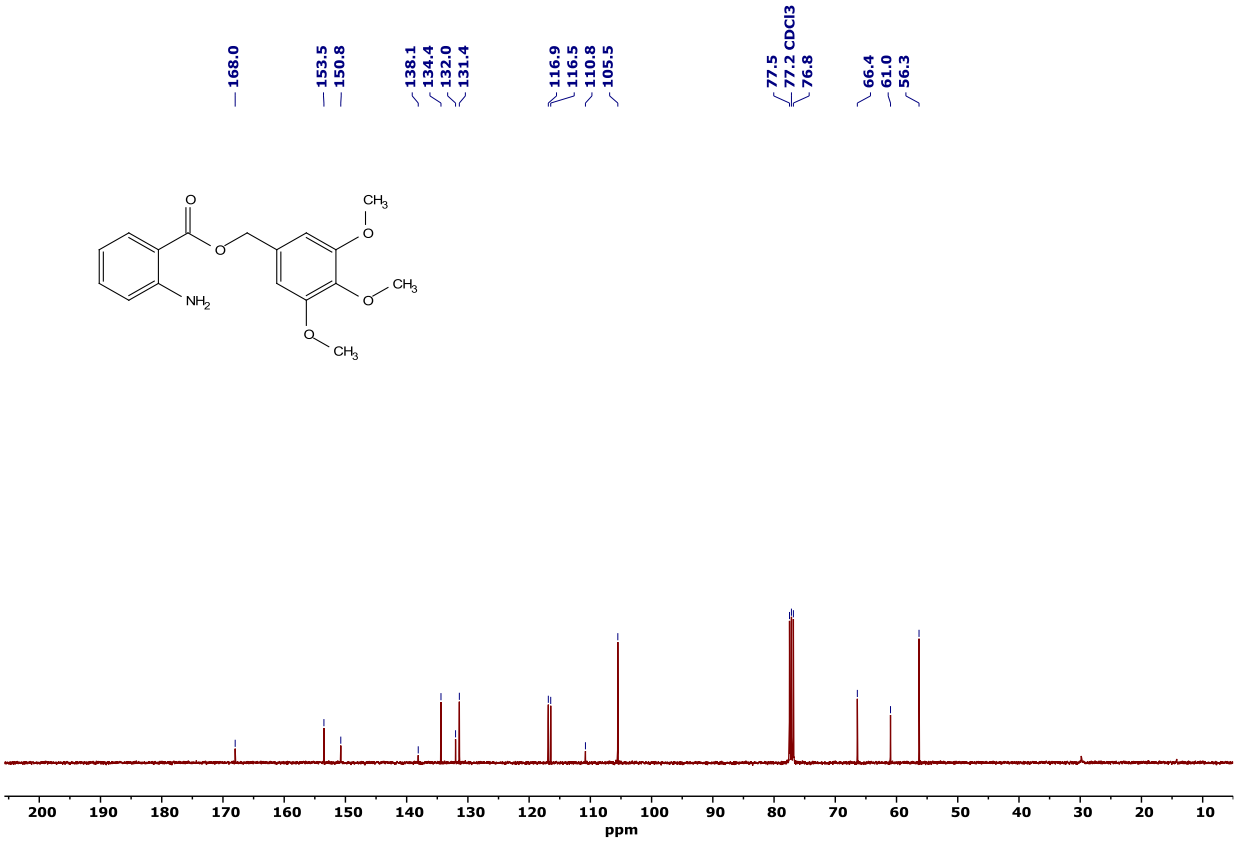


Figure S80. $^{13}C\{^{1}H\}$ NMR spectrum of **5g** in $CDCl_3$.

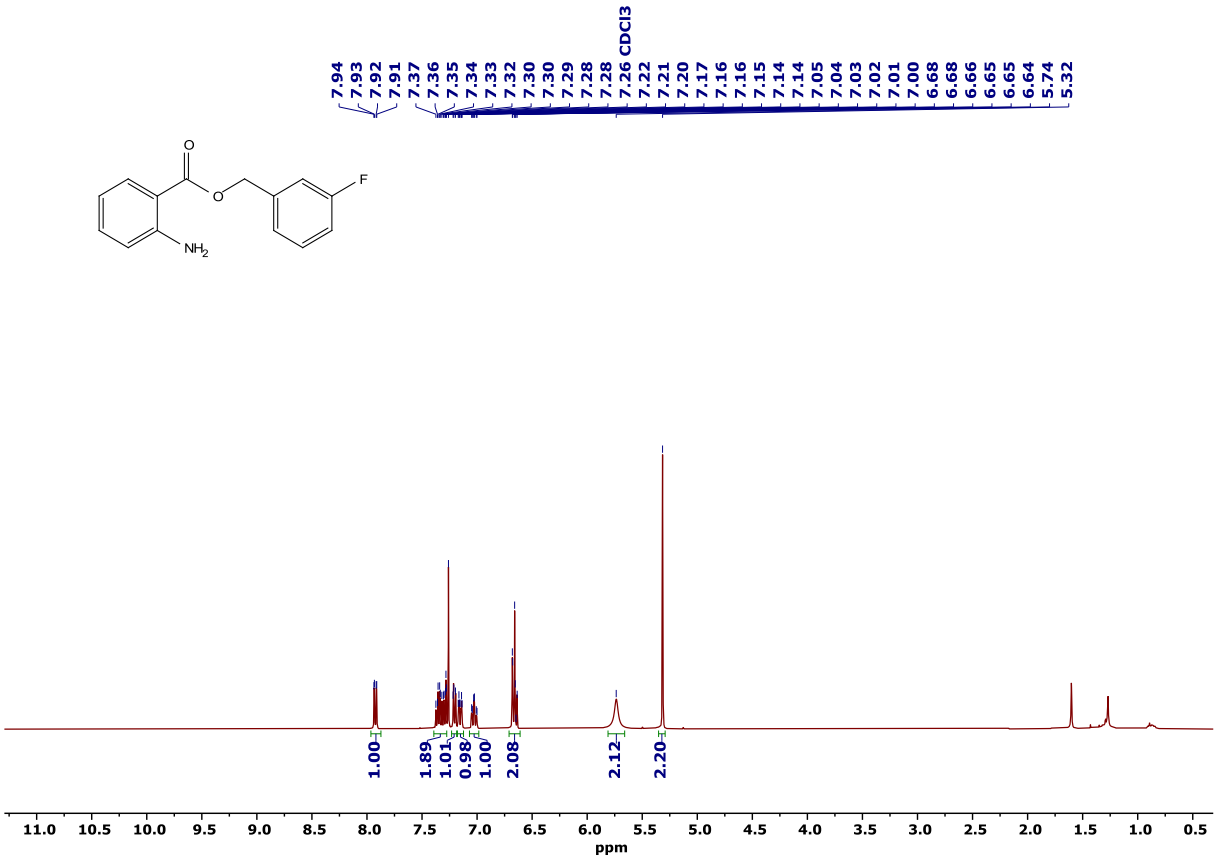


Figure S81. ^{1}H NMR spectrum of **5h** in $CDCl_3$.

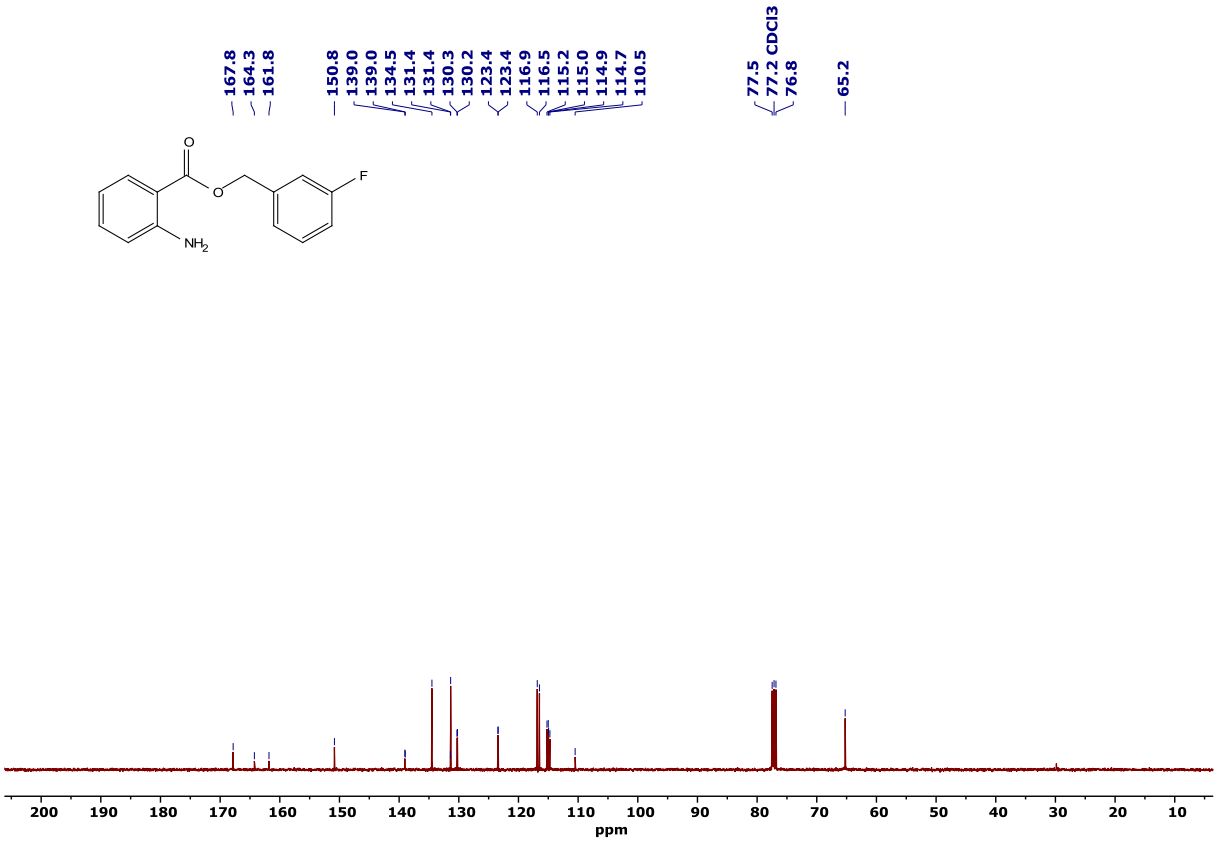


Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum of **5h** in $CDCl_3$.

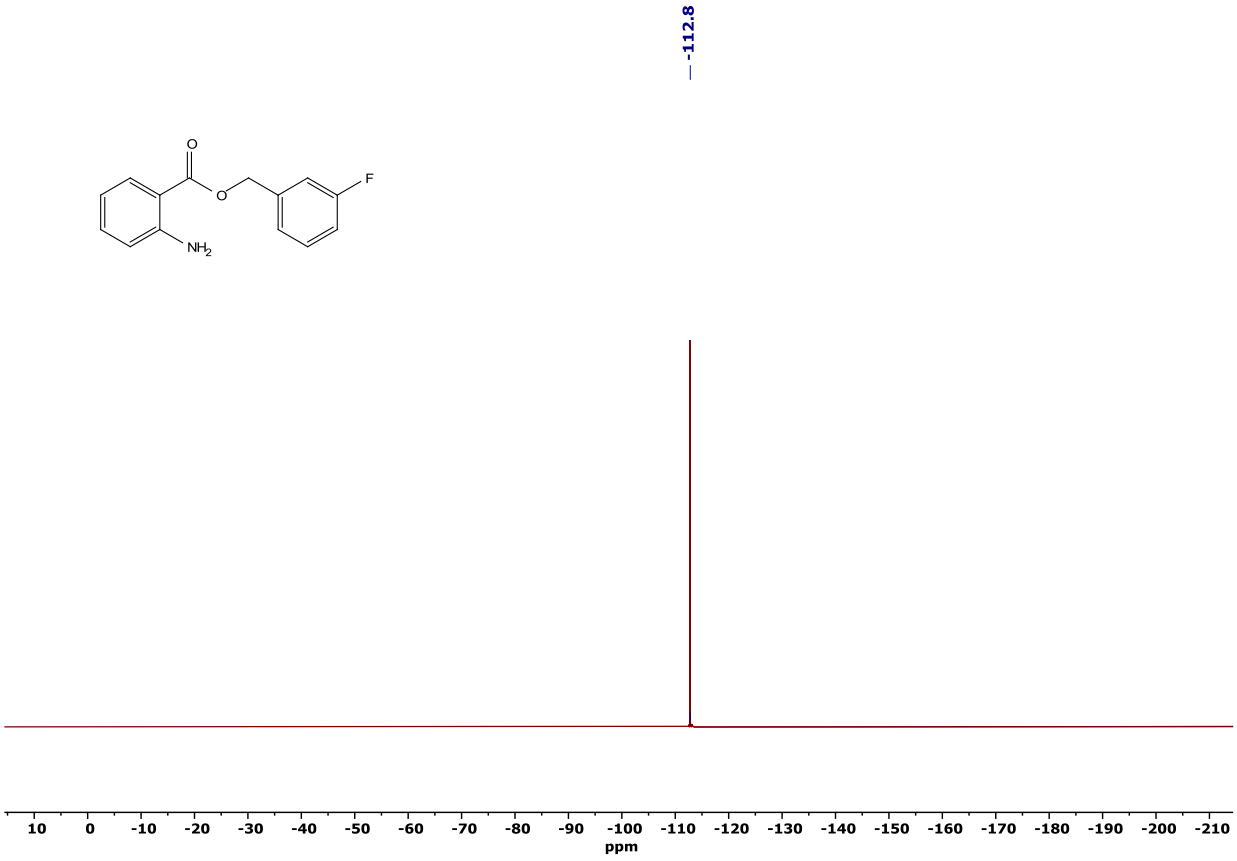


Figure S83. ^{19}F NMR spectrum of **5h** in $CDCl_3$.

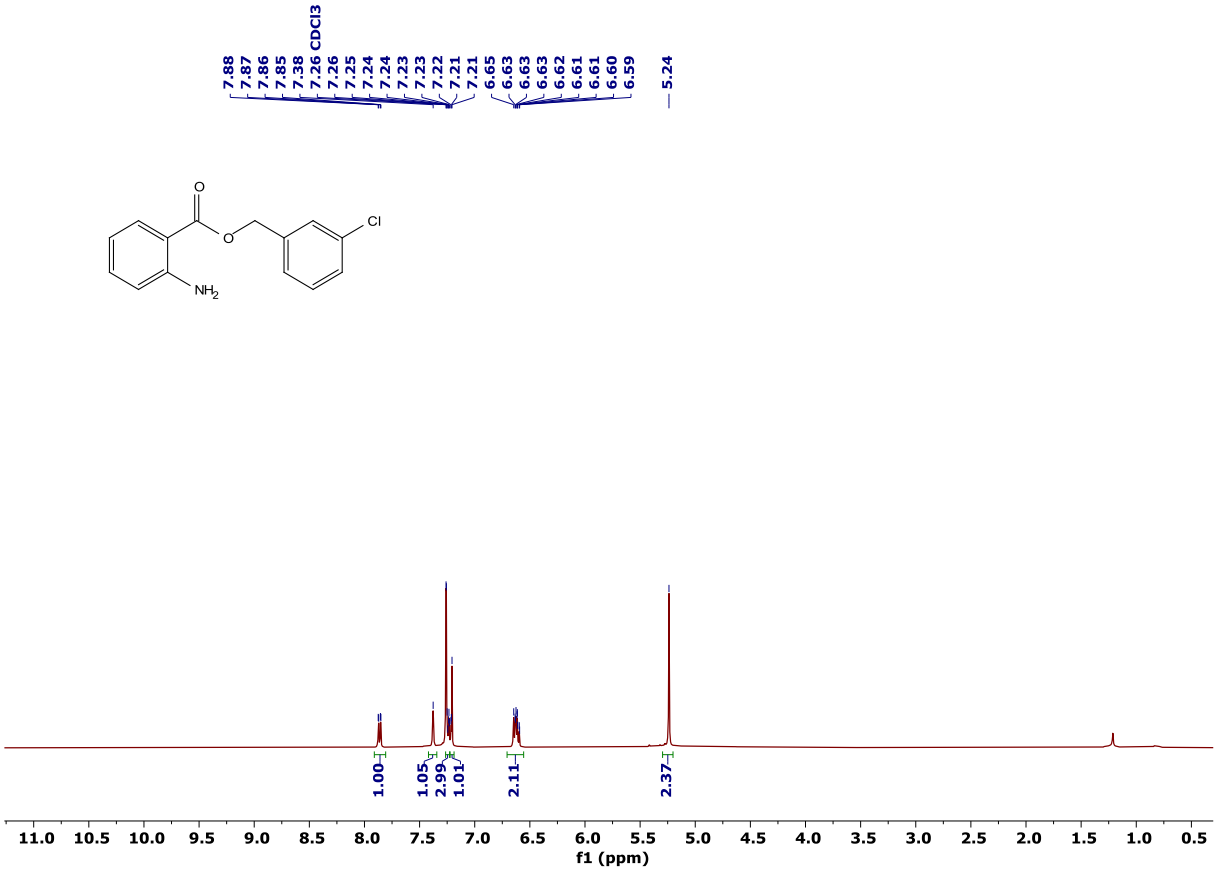


Figure S84. ^{1}H NMR spectrum of **5i** in $CDCl_3$.

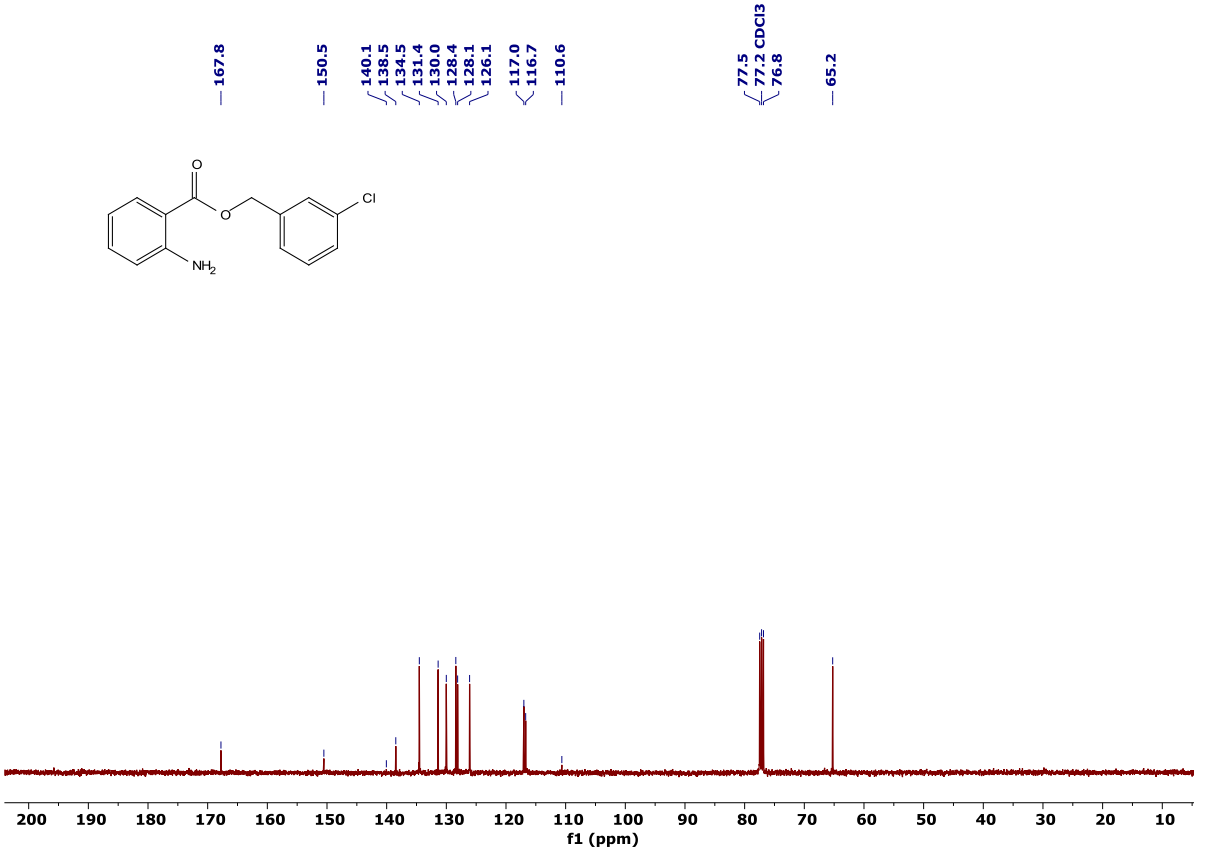


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of **5i** in $CDCl_3$.

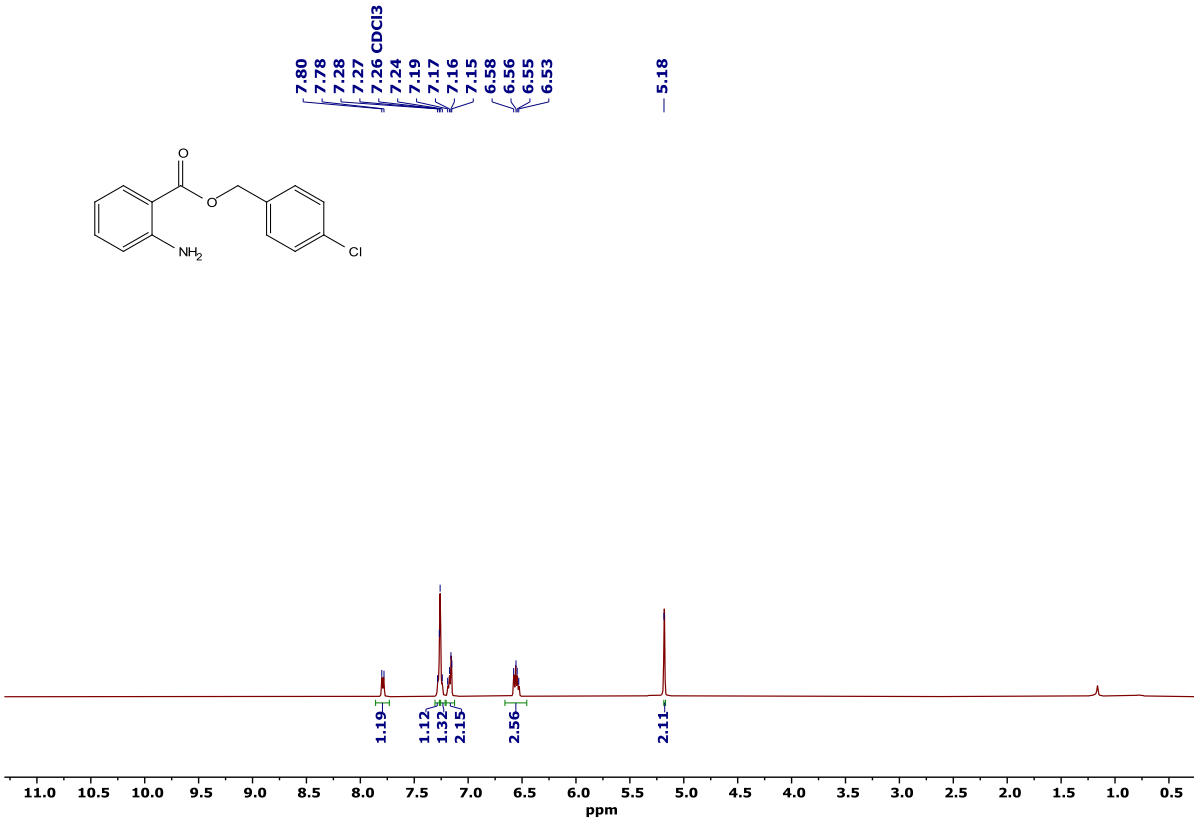


Figure S86. ^{1}H NMR spectrum of **5j** in $CDCl_3$.

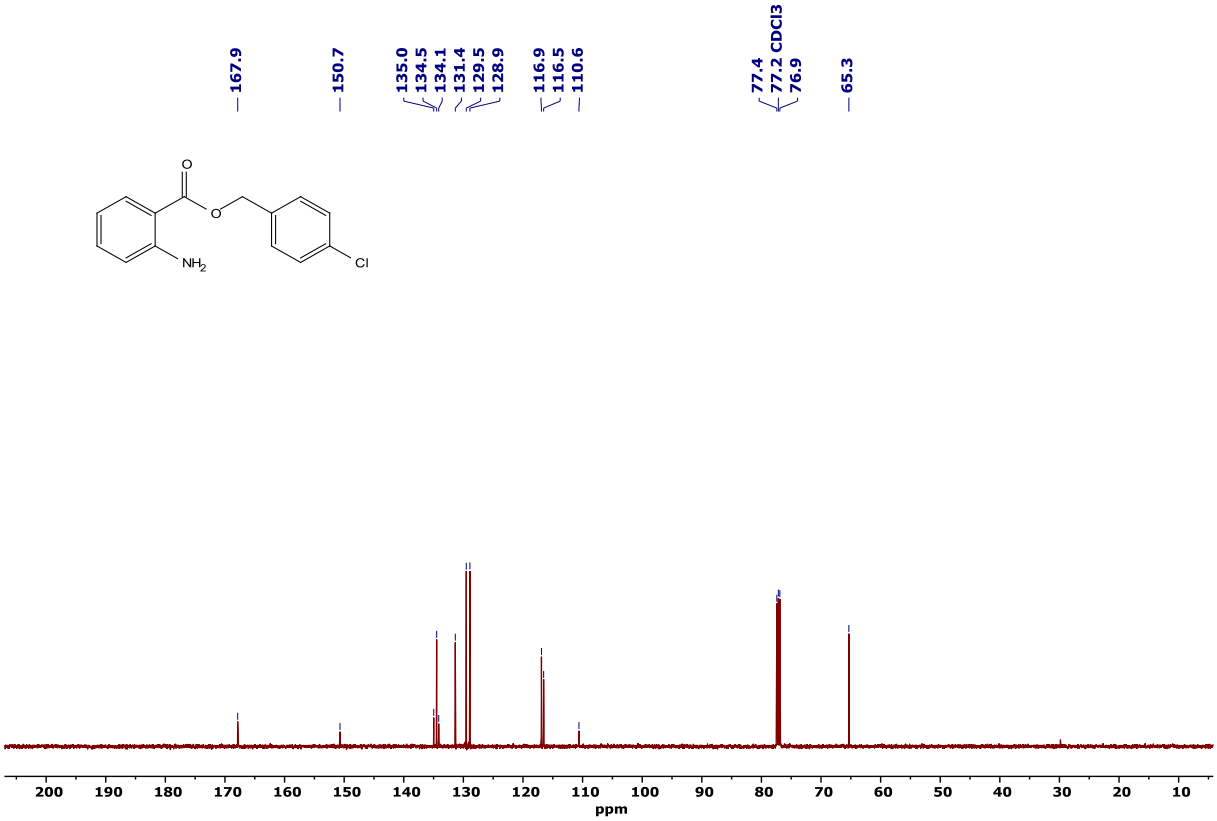


Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum of **5j** in $CDCl_3$.

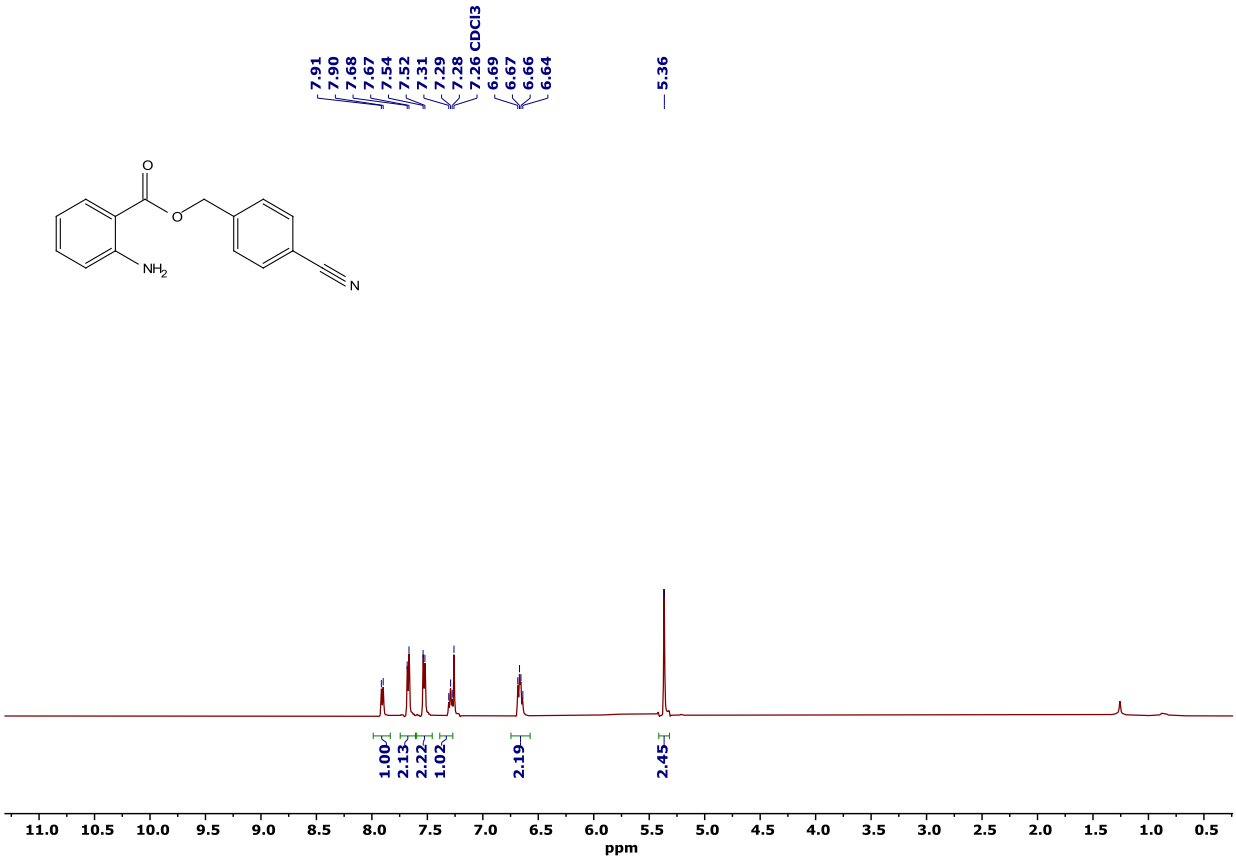


Figure S88. ^{1}H NMR spectrum of **5k** in $CDCl_3$.

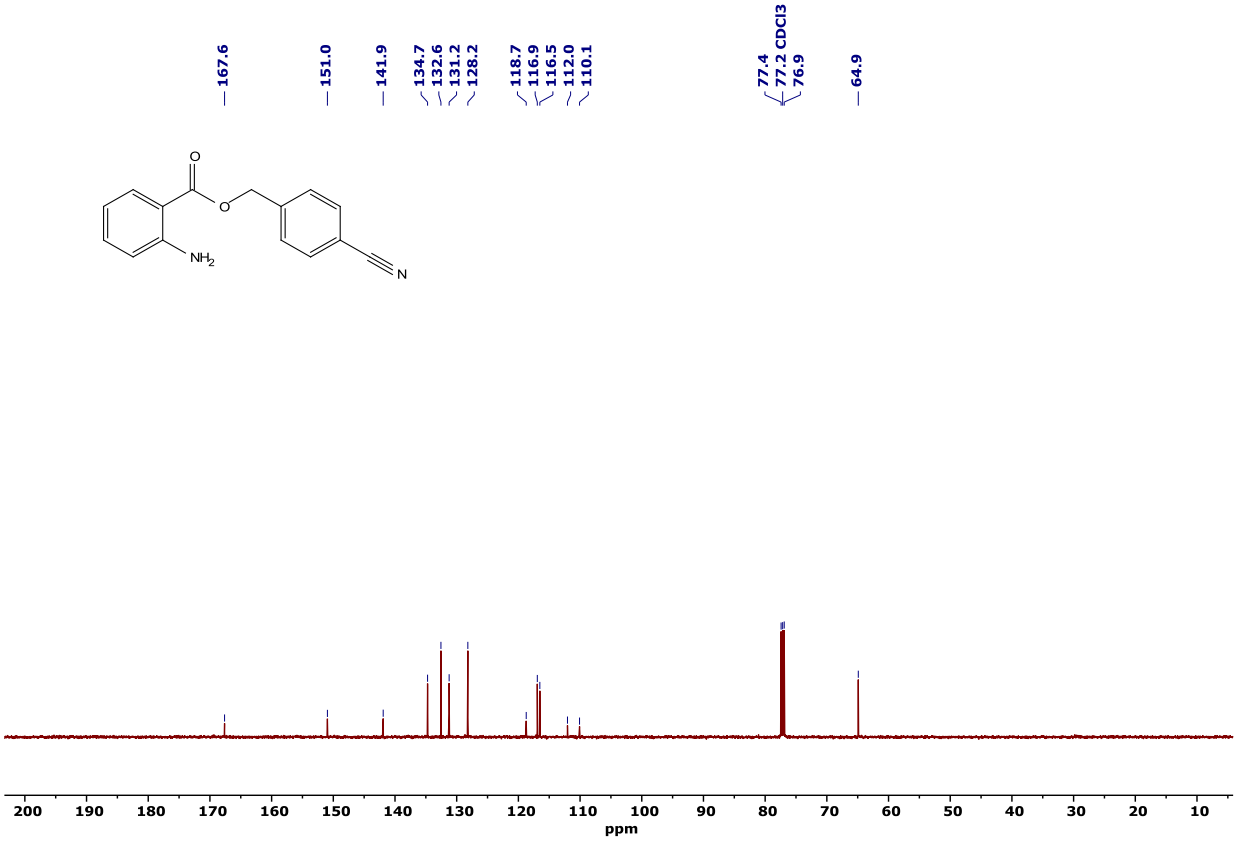


Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum of **5k** in $CDCl_3$.

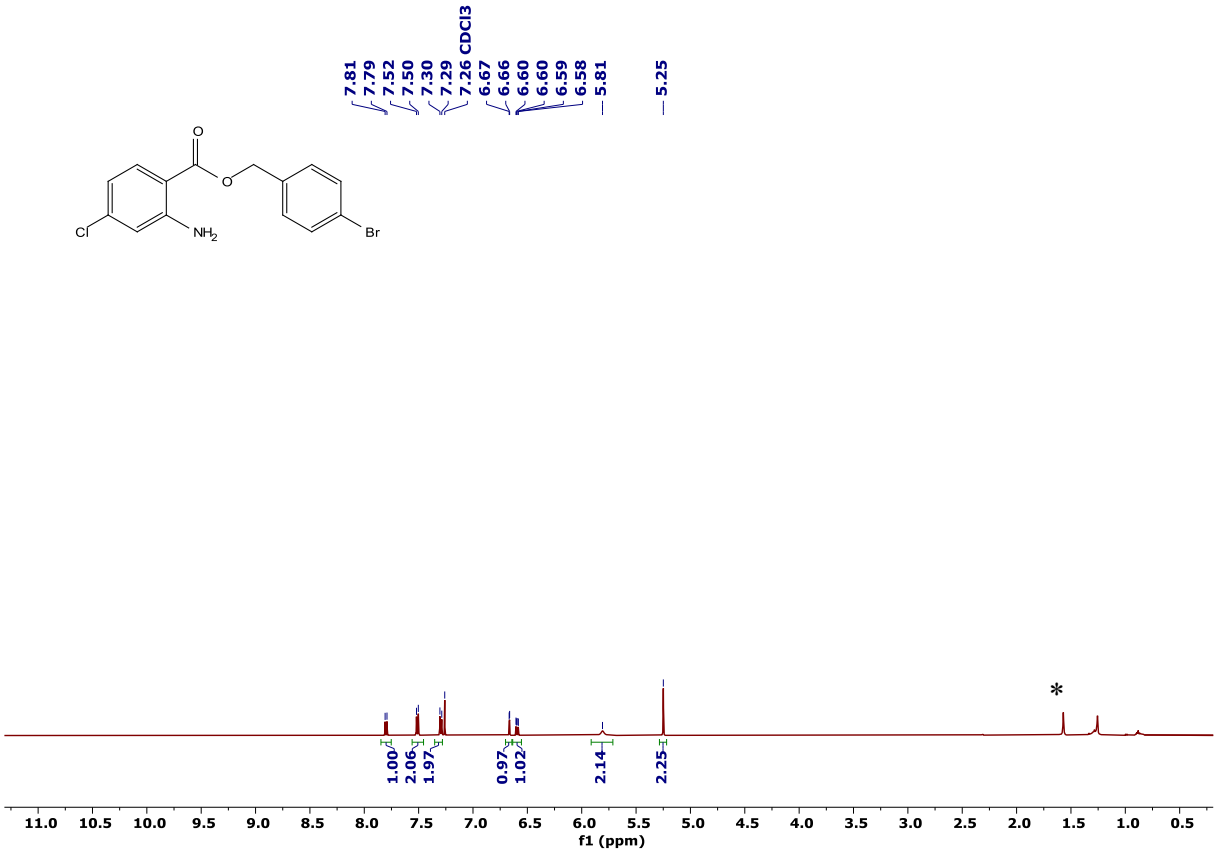


Figure S90. ^{1}H NMR spectrum of **5l** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

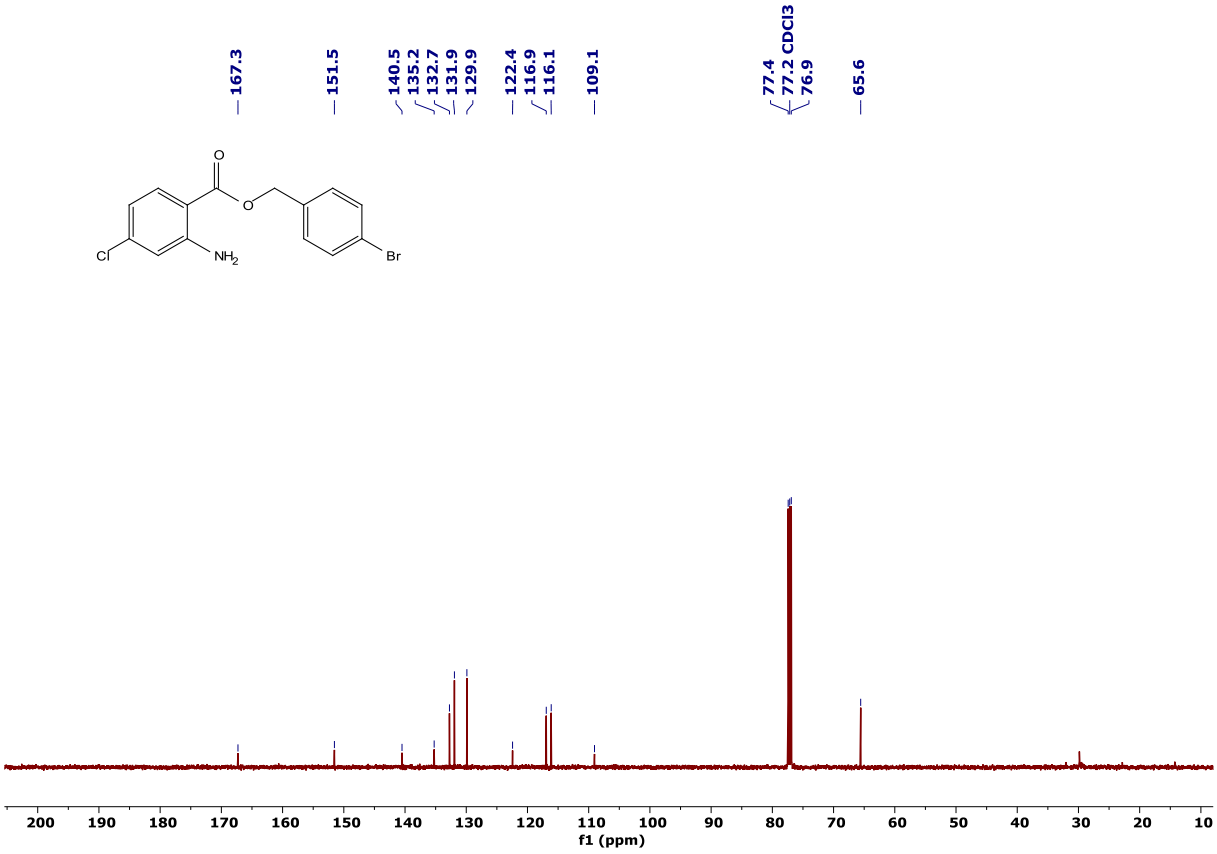


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of **5l** in $CDCl_3$.

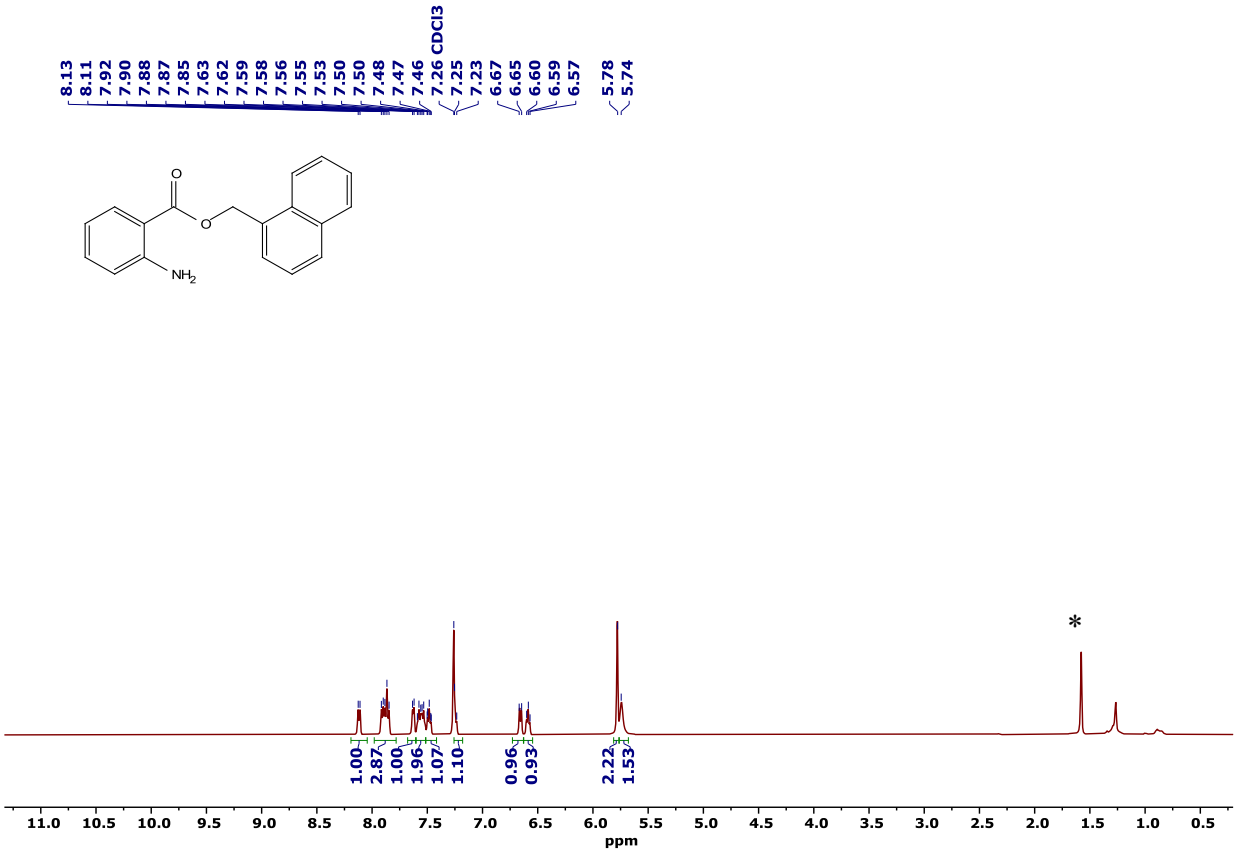


Figure S92. ^{1}H NMR spectrum of **5m** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

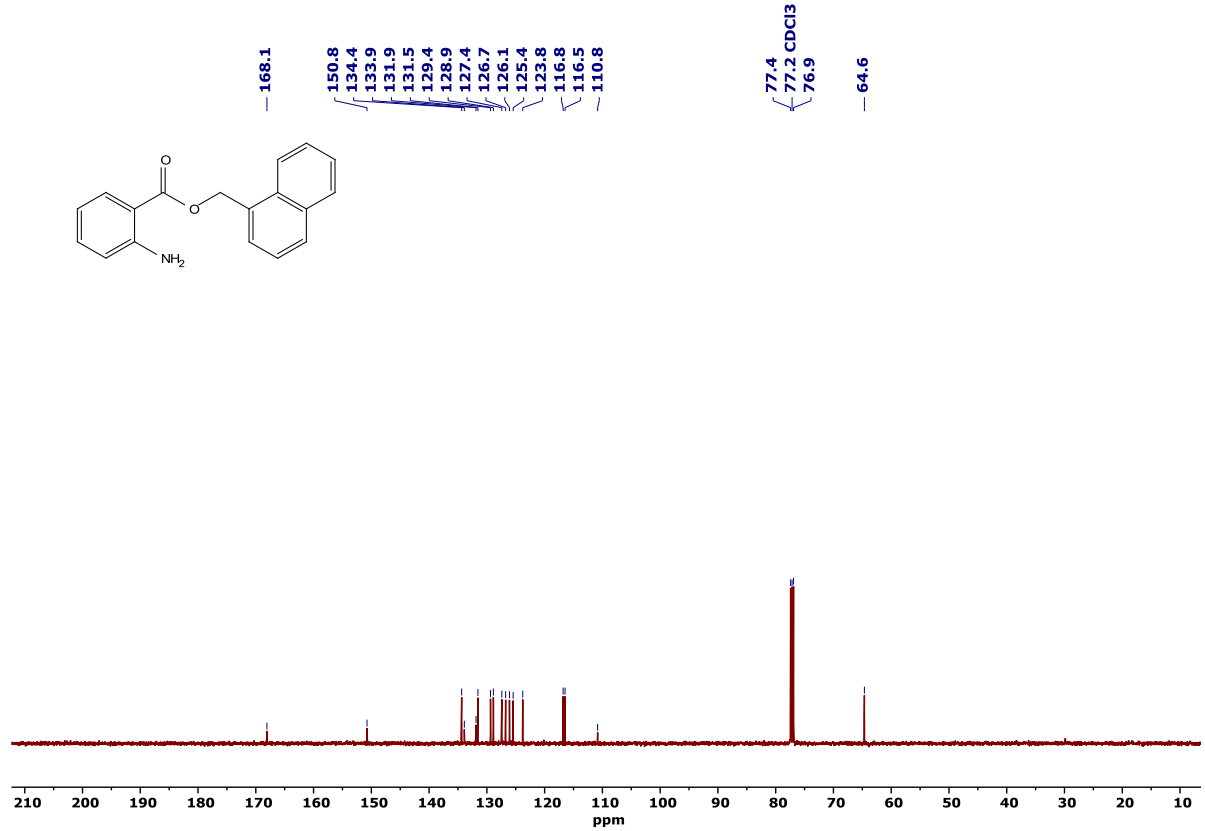


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of **5m** in $CDCl_3$.

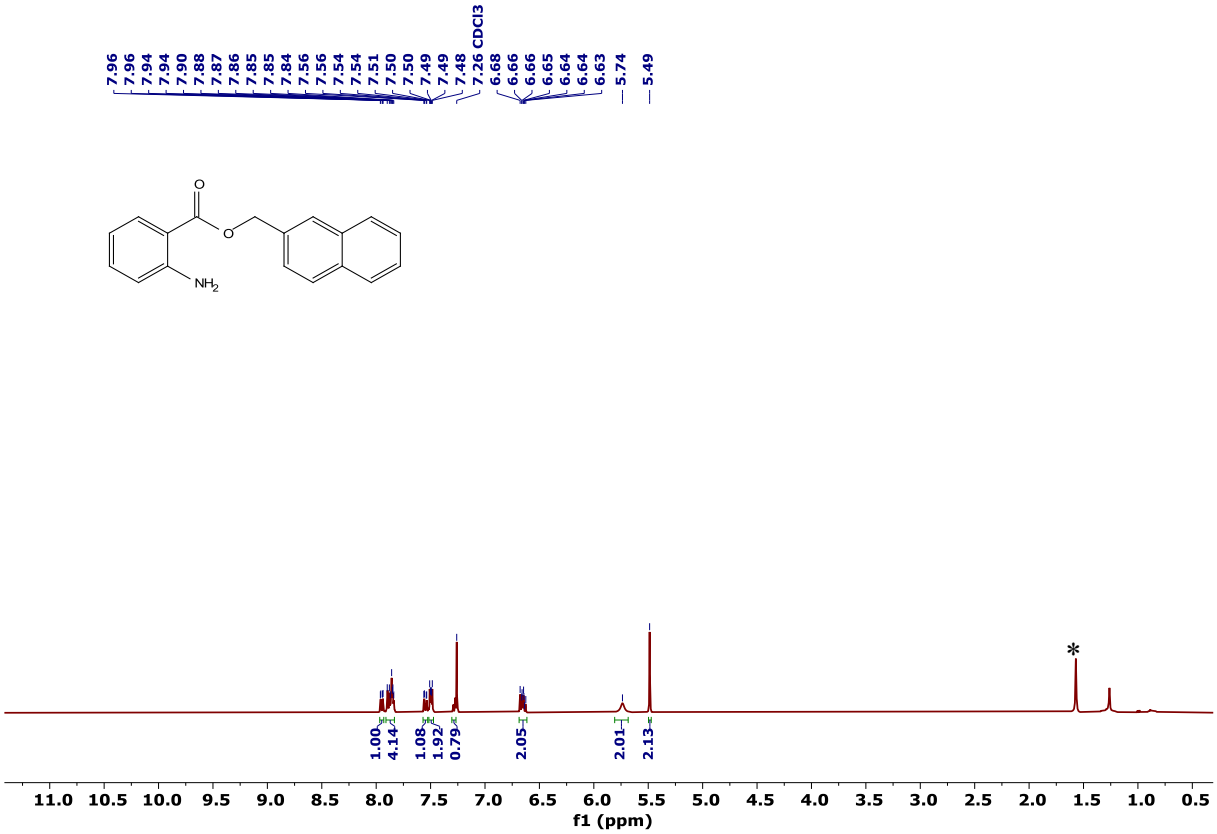


Figure S94. ^{1}H NMR spectrum of **5n** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

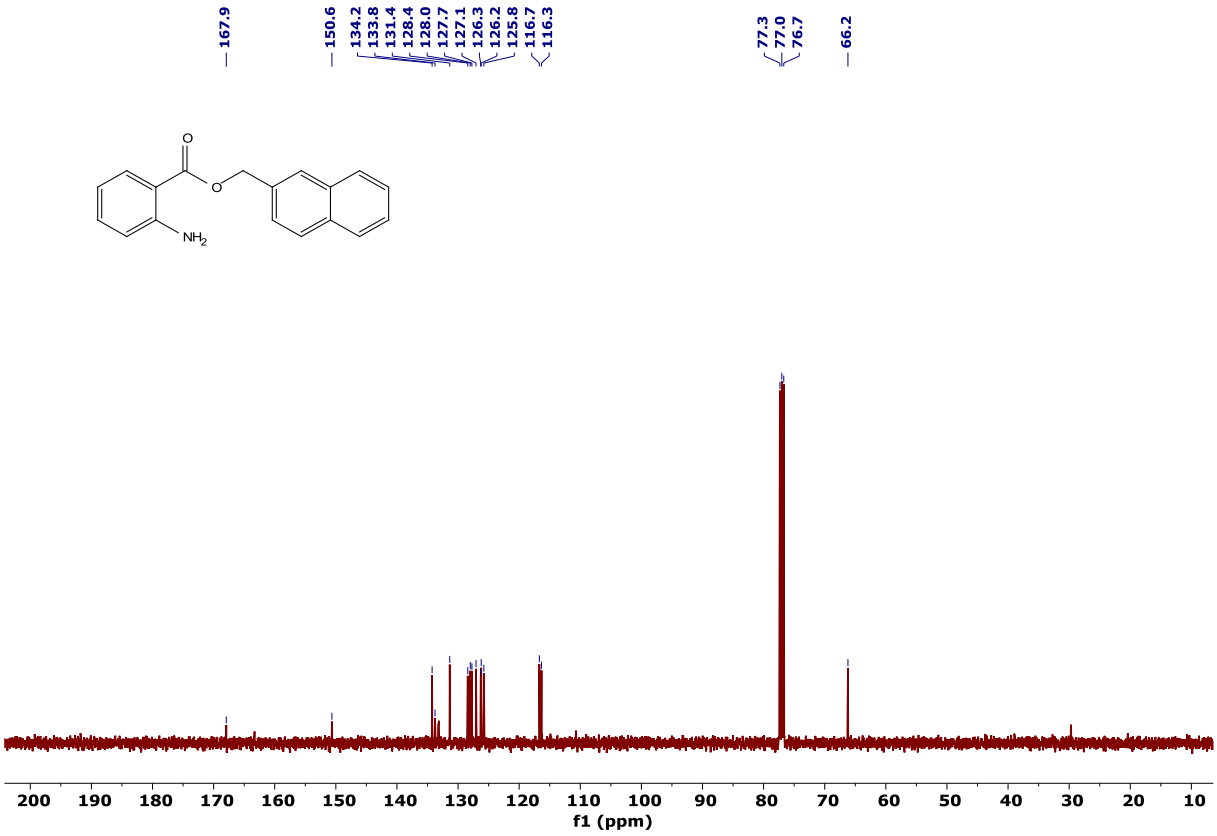


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum of **5n** in $CDCl_3$.

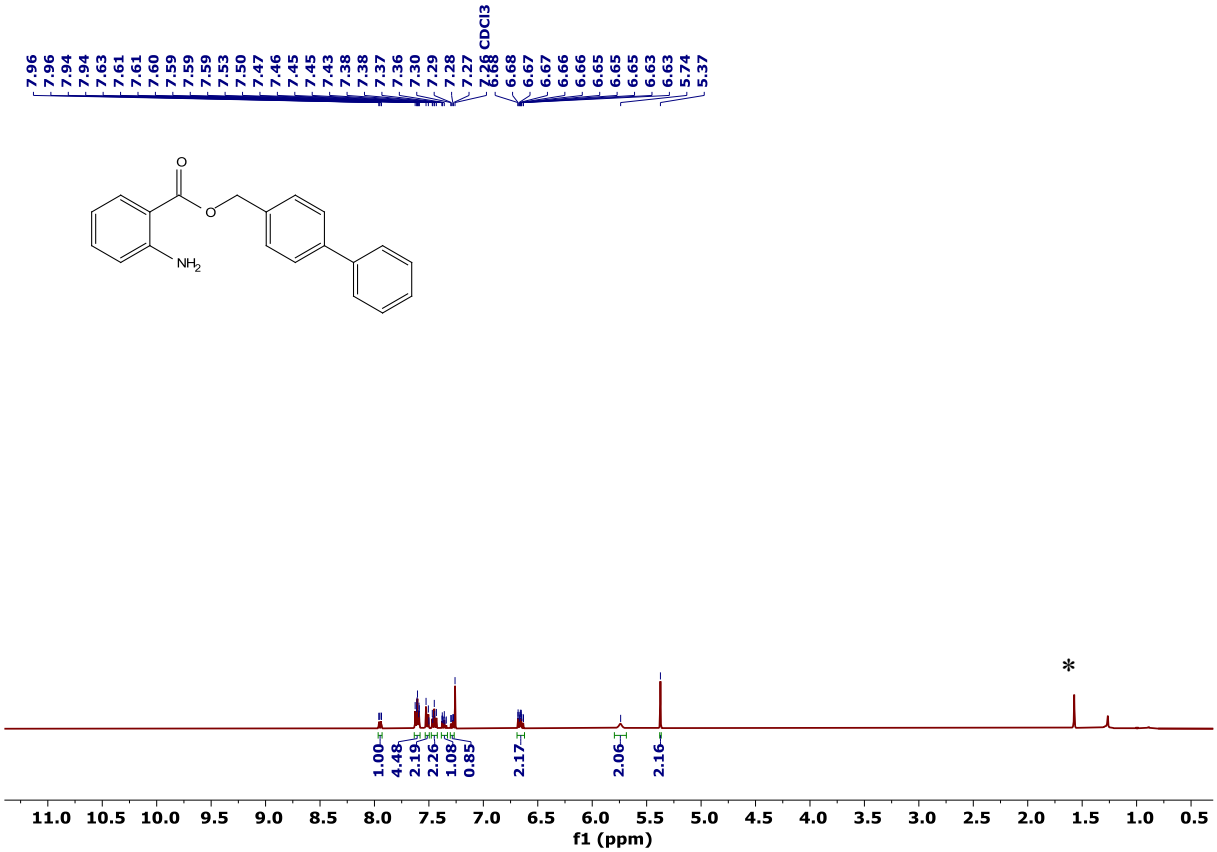


Figure S96. ^{1}H NMR spectrum of **5o** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

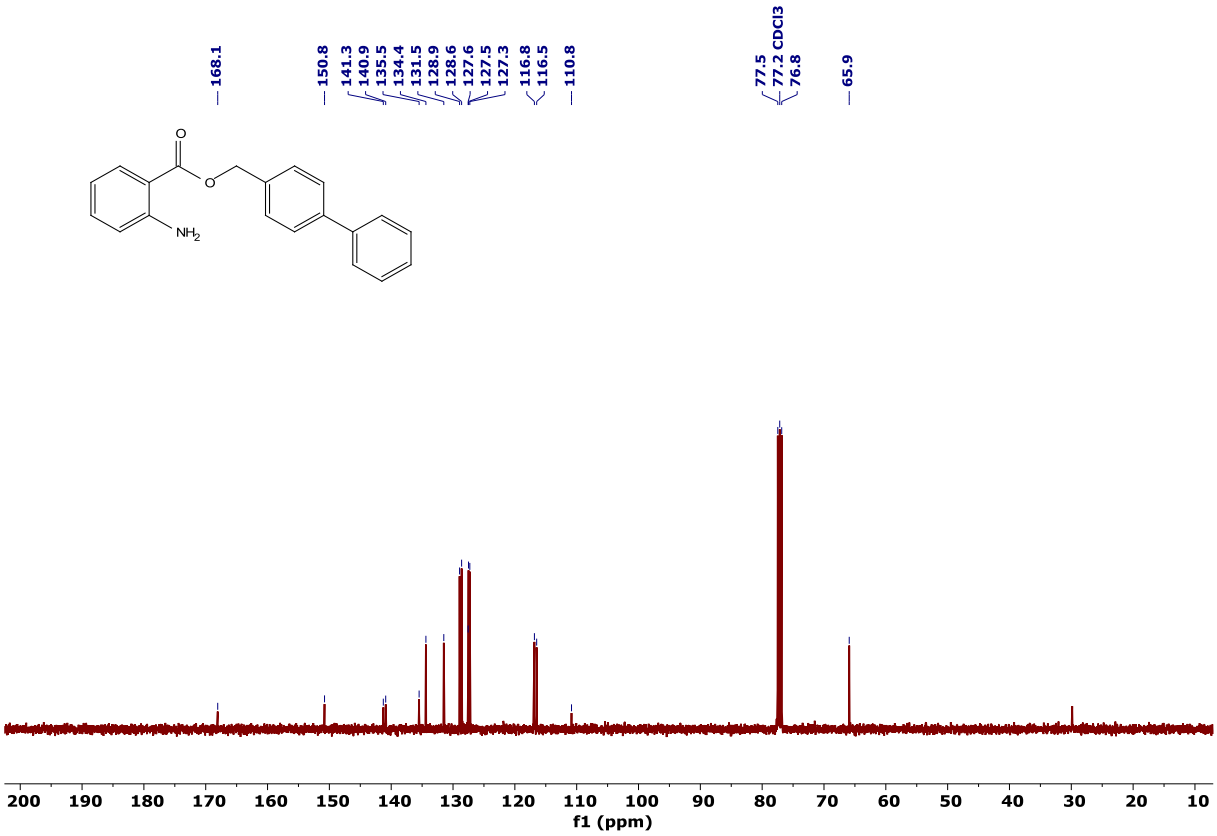


Figure S97. $^{13}C\{^{1}H\}$ NMR spectrum of **5o** in $CDCl_3$.

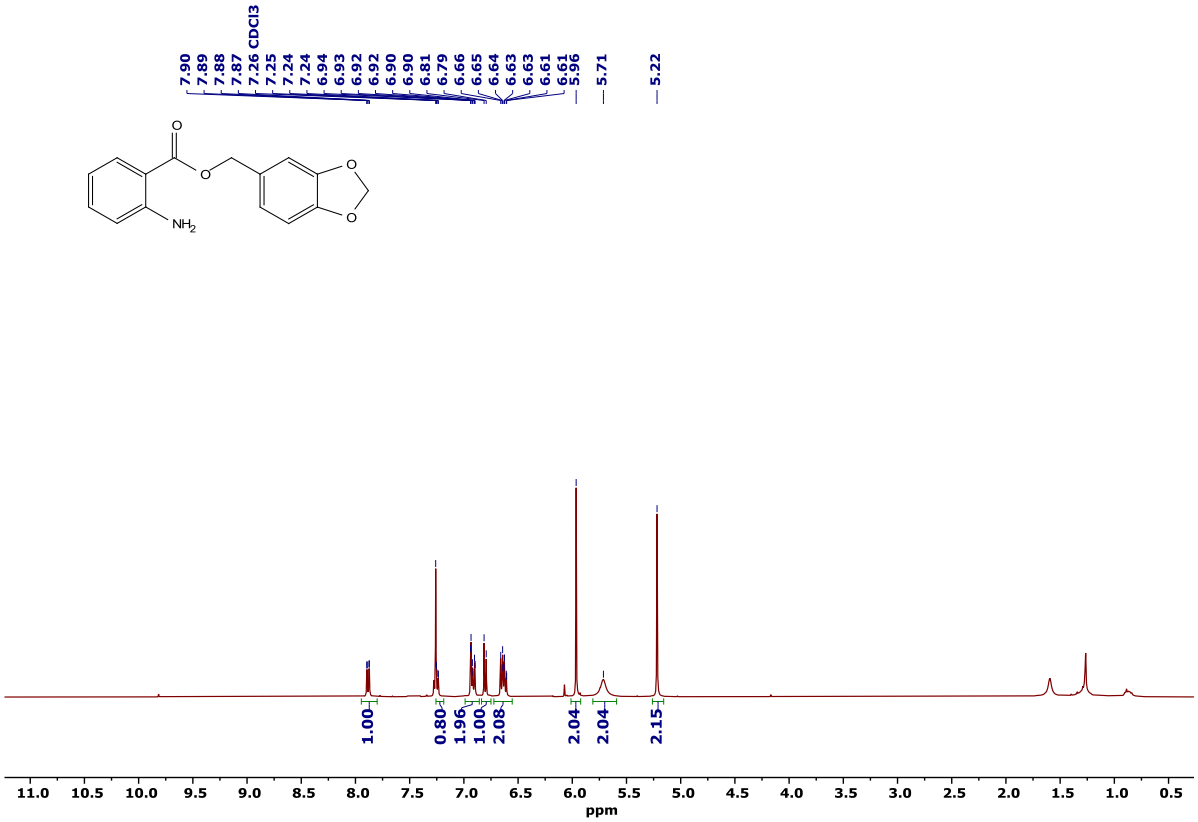


Figure S98. ^{1}H NMR spectrum of **5p** in $CDCl_3$.

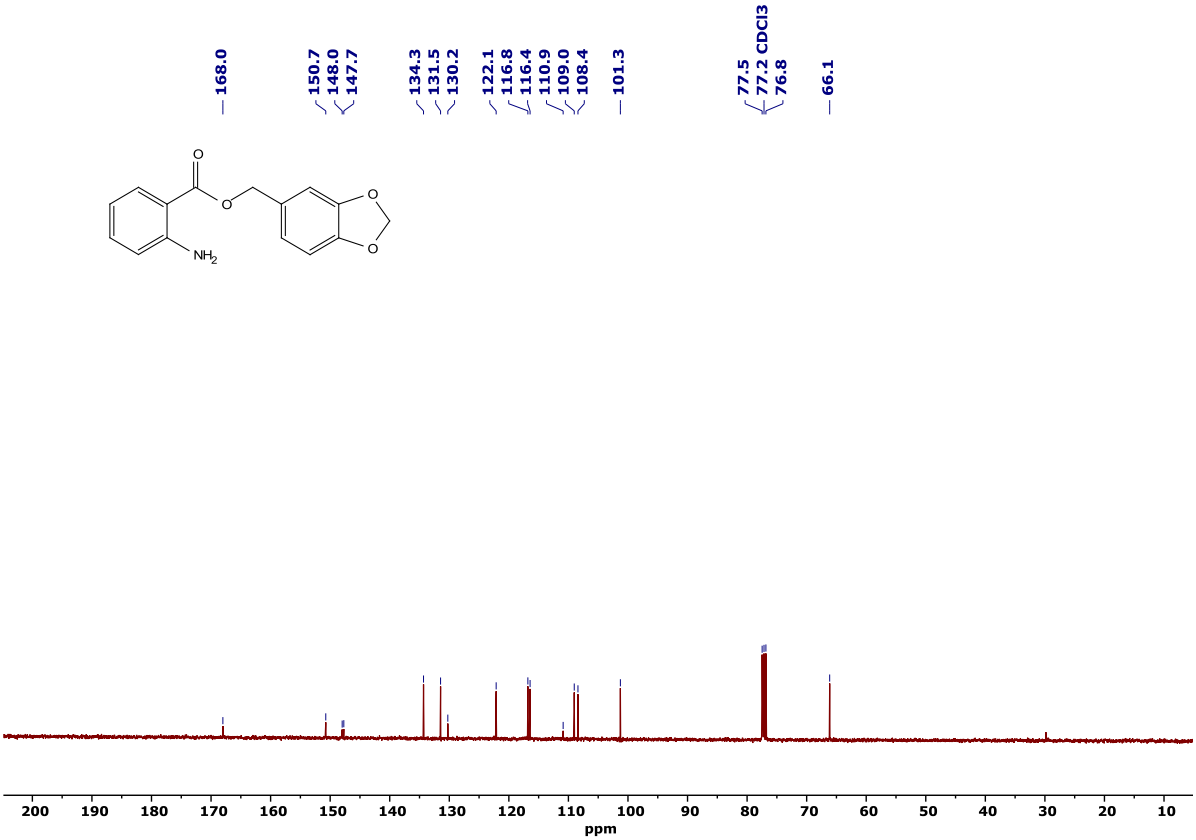


Figure S99. $^{13}C\{^{1}H\}$ NMR spectrum of **5p** in $CDCl_3$.

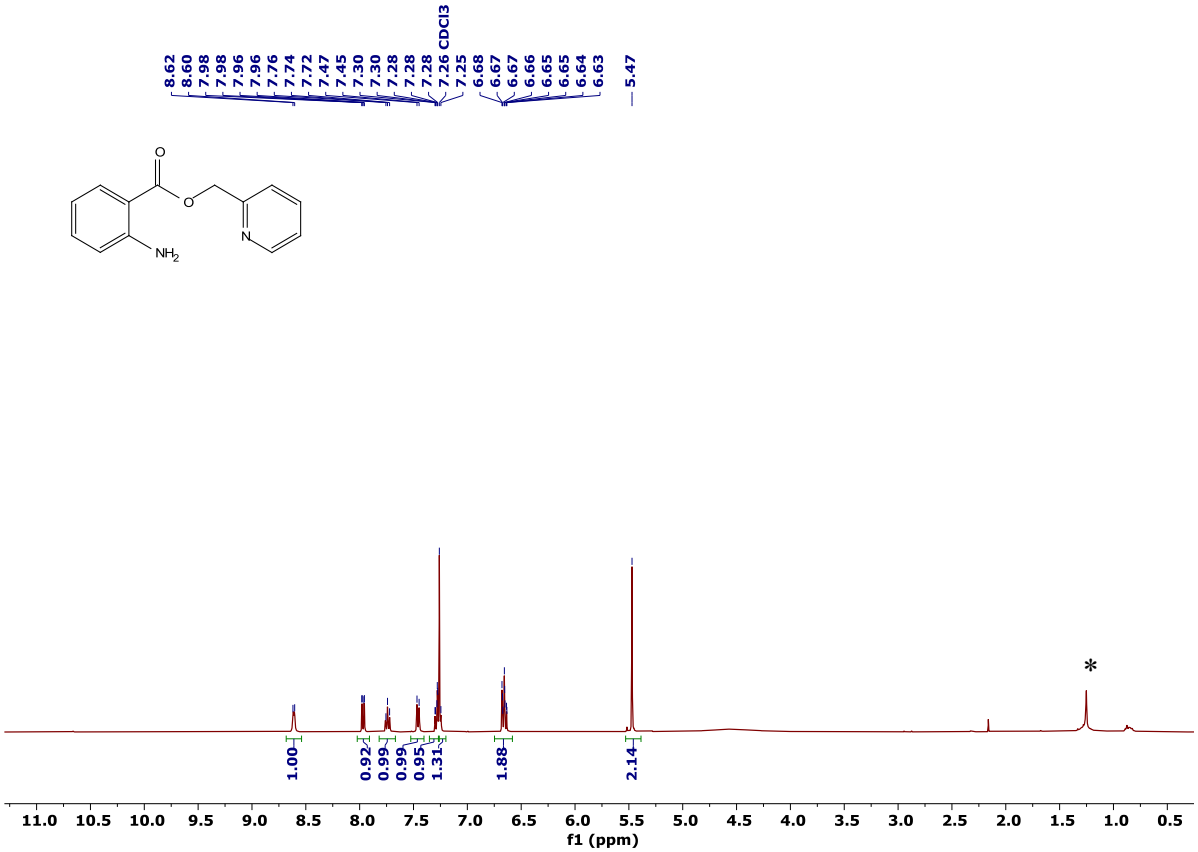


Figure S100. ^{1}H NMR spectrum of **5q** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

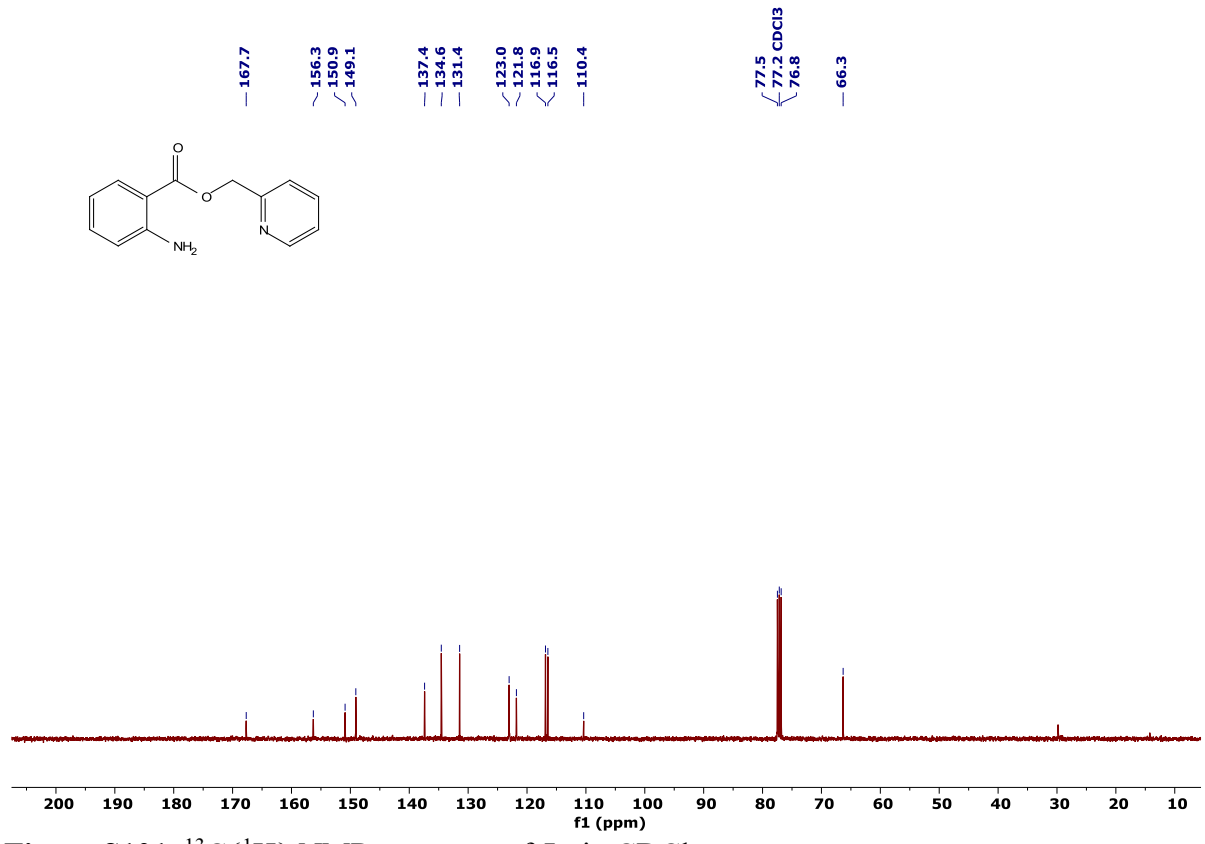


Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum of **5q** in $CDCl_3$.

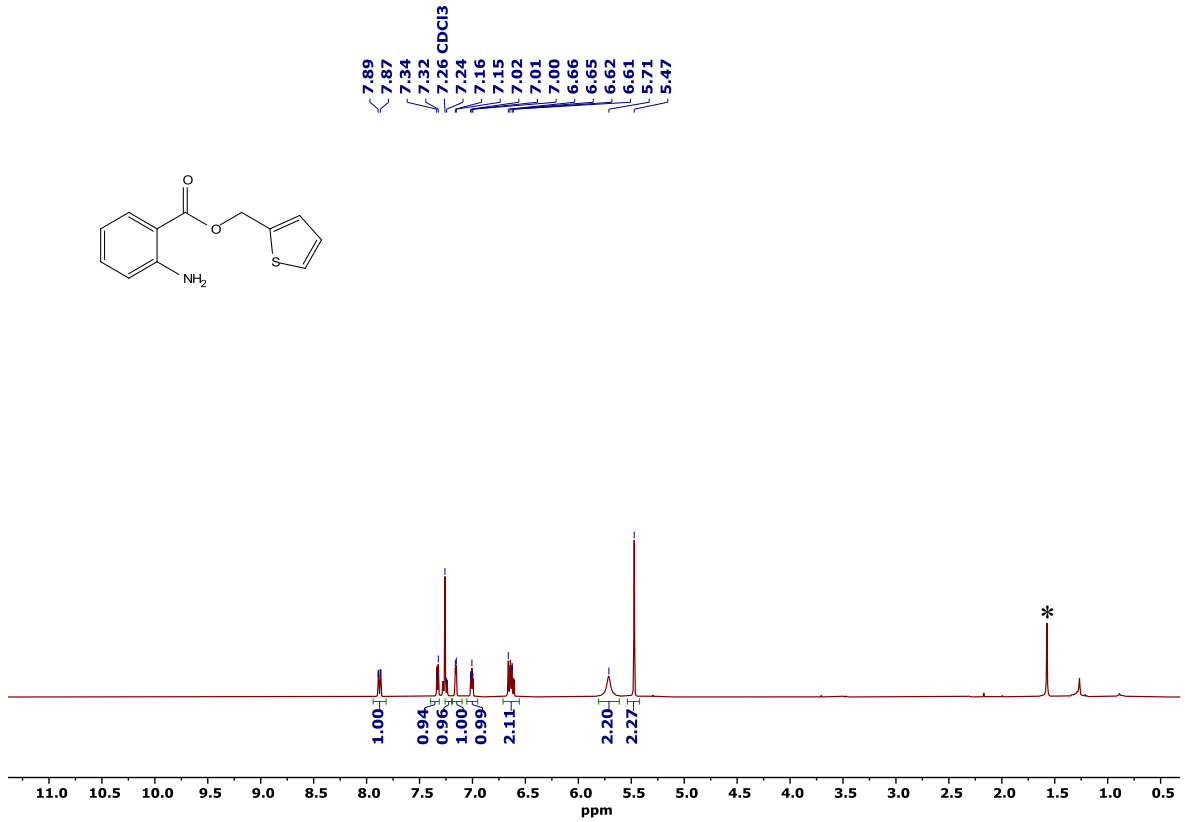


Figure S102. ^{1}H NMR spectrum of **5r** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

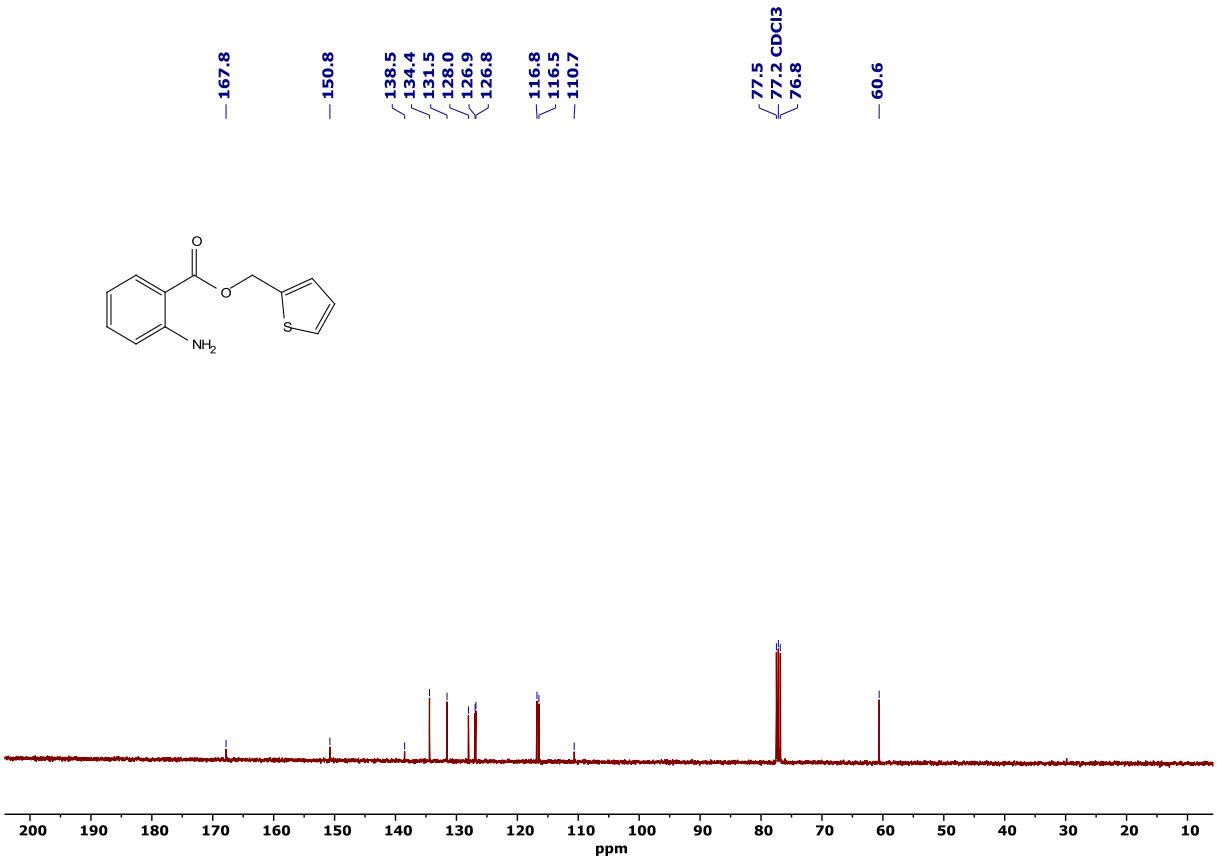


Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum of **5r** in $CDCl_3$.

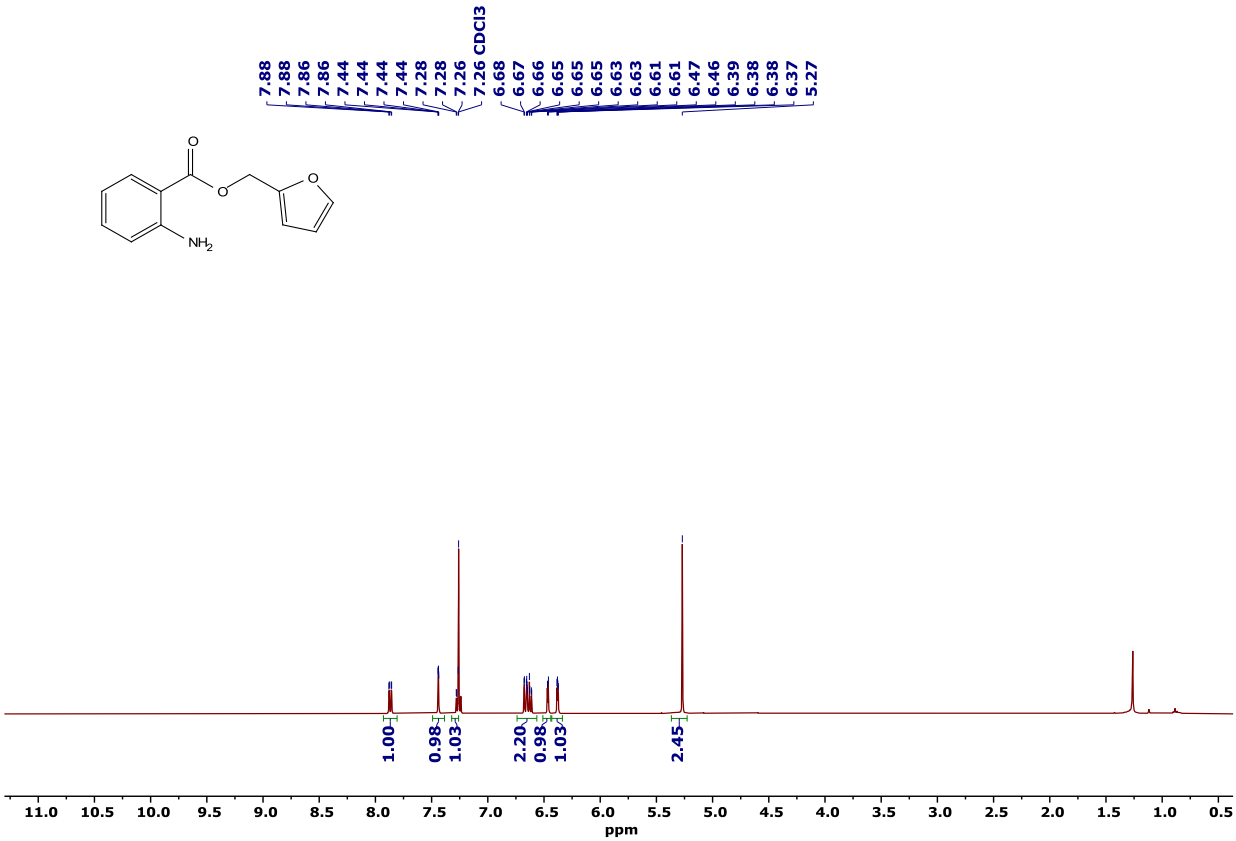


Figure S104. ^{1}H NMR spectrum of **5s** in $CDCl_3$.

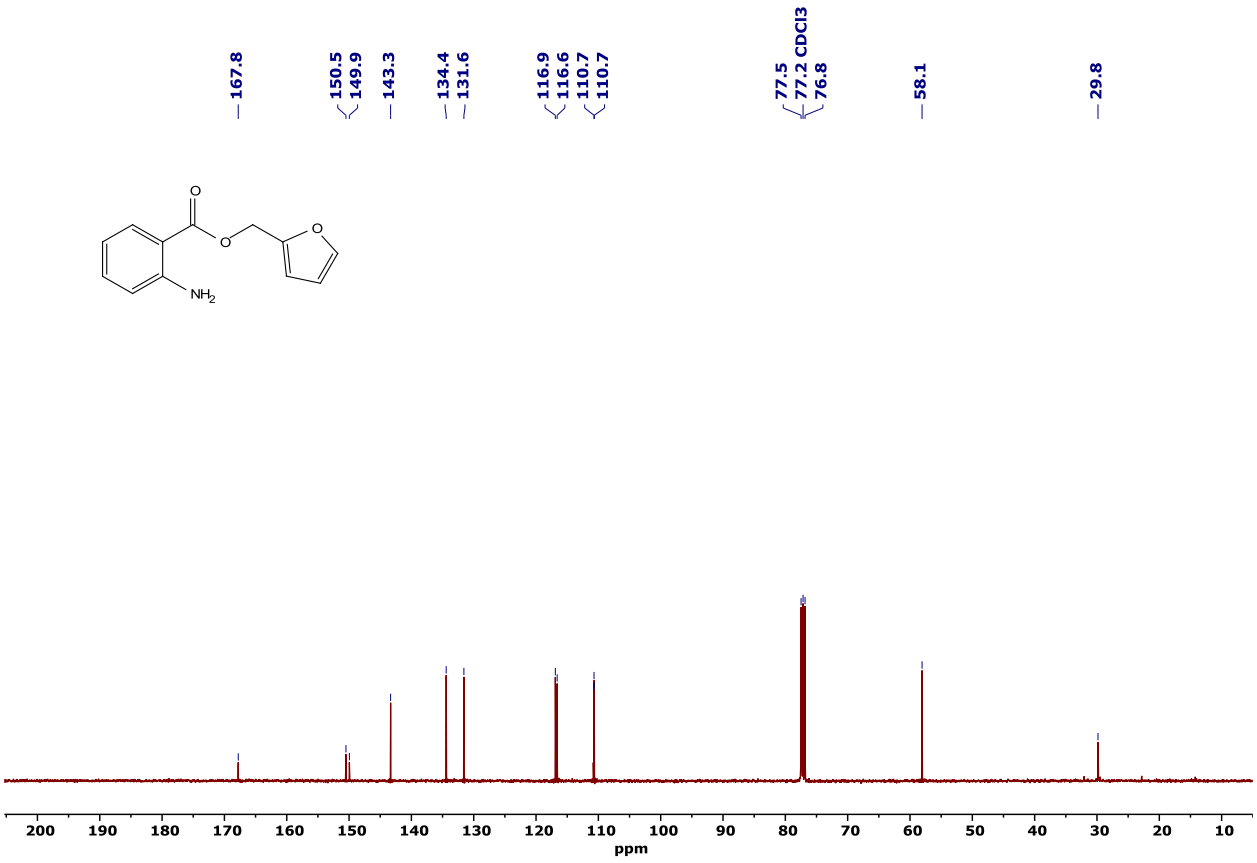


Figure S105. $^{13}C\{^{1}H\}$ NMR spectrum of **5s** in $CDCl_3$.

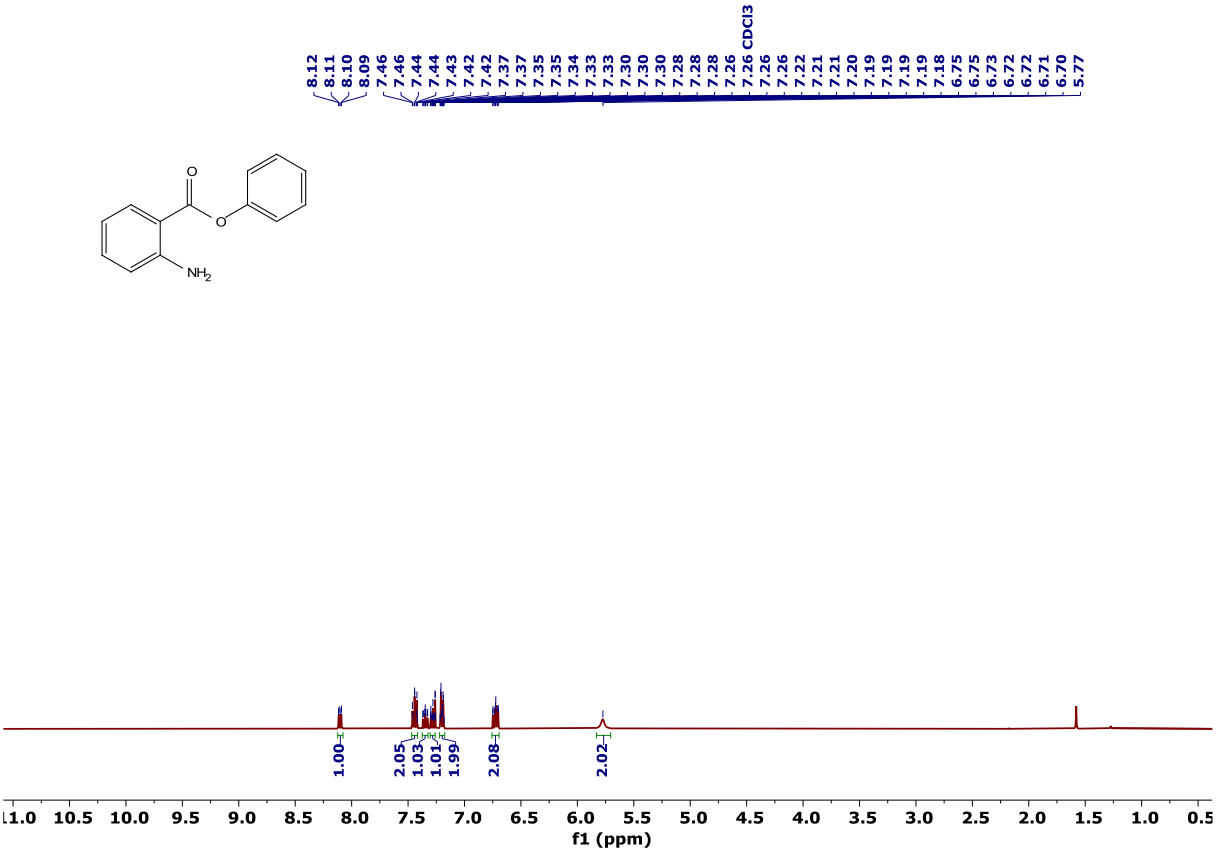


Figure S106. ^{1}H NMR spectrum of **7a** in $CDCl_3$.

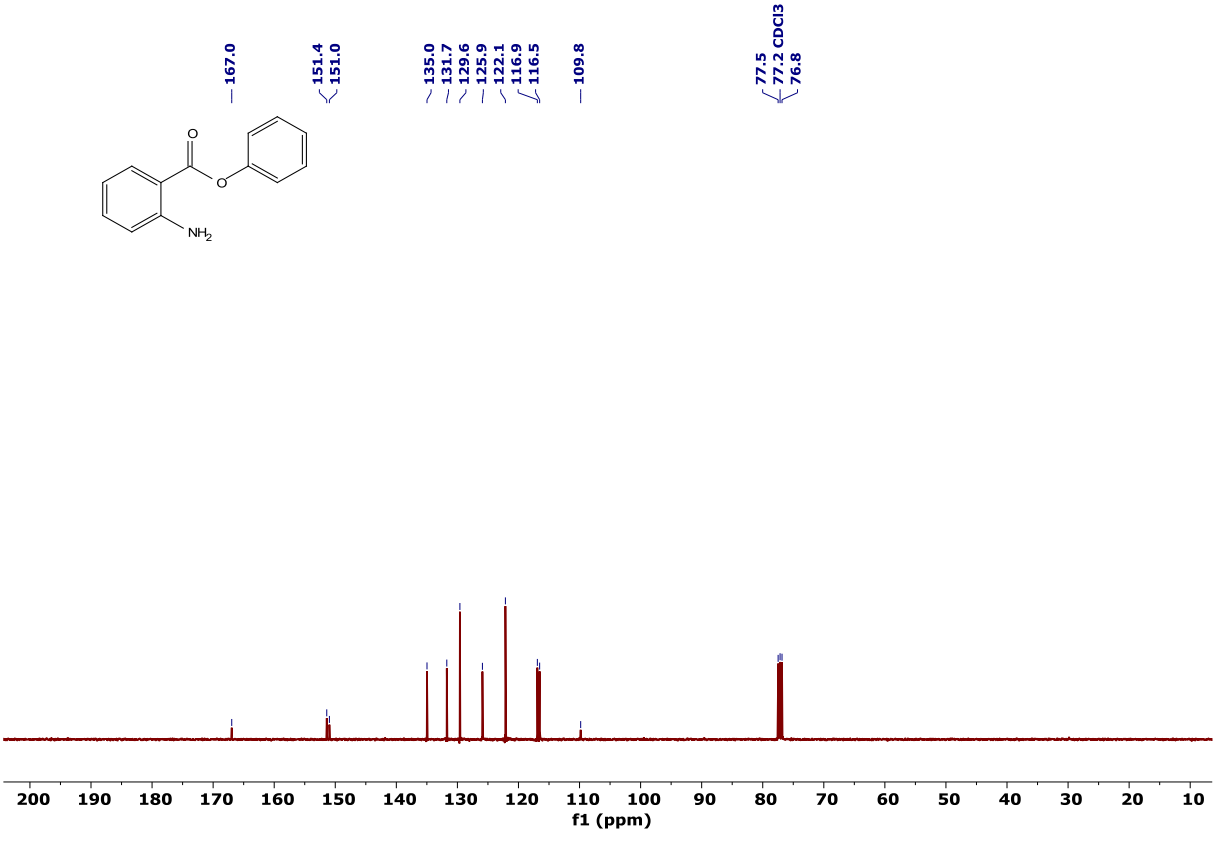


Figure S107. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** in $CDCl_3$.

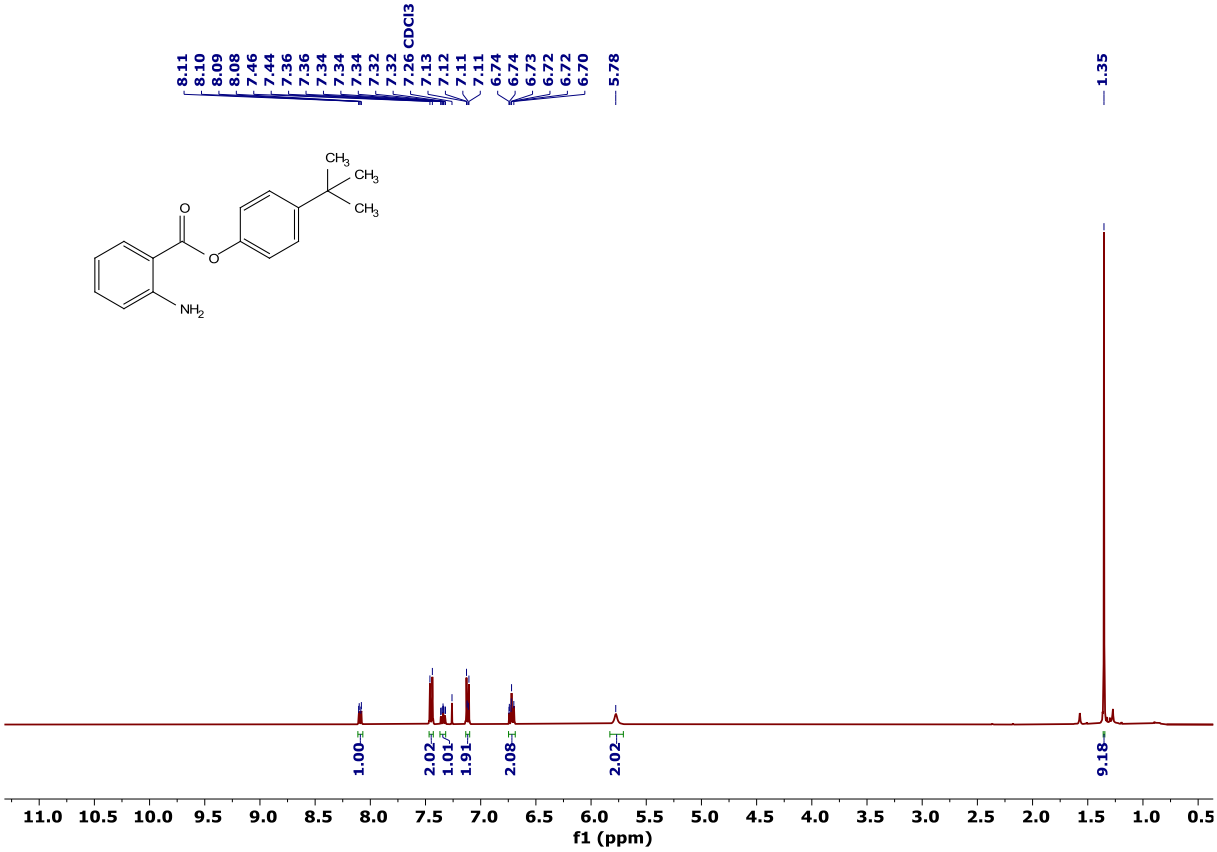


Figure S108. ^{1}H NMR spectrum of **7b** in $CDCl_3$.

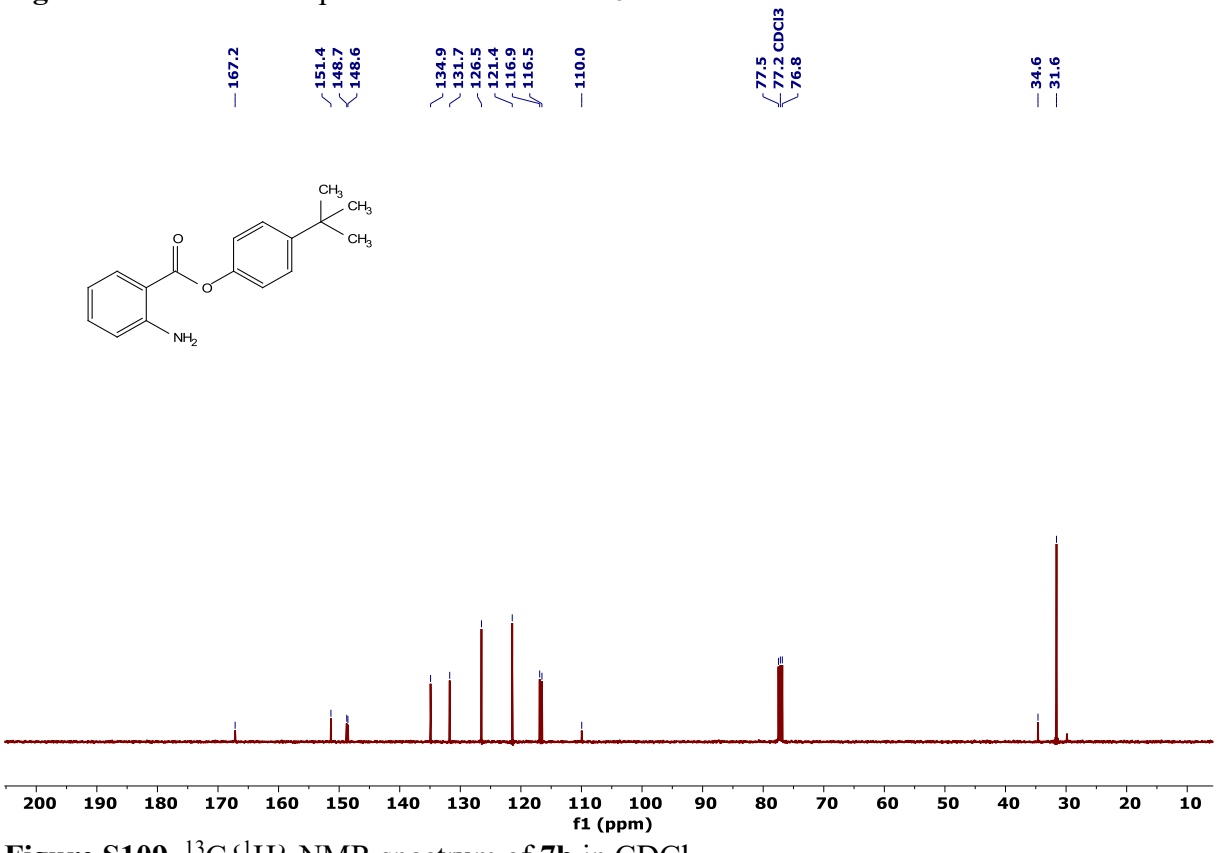


Figure S109. $^{13}C\{^{1}H\}$ NMR spectrum of **7b** in $CDCl_3$.

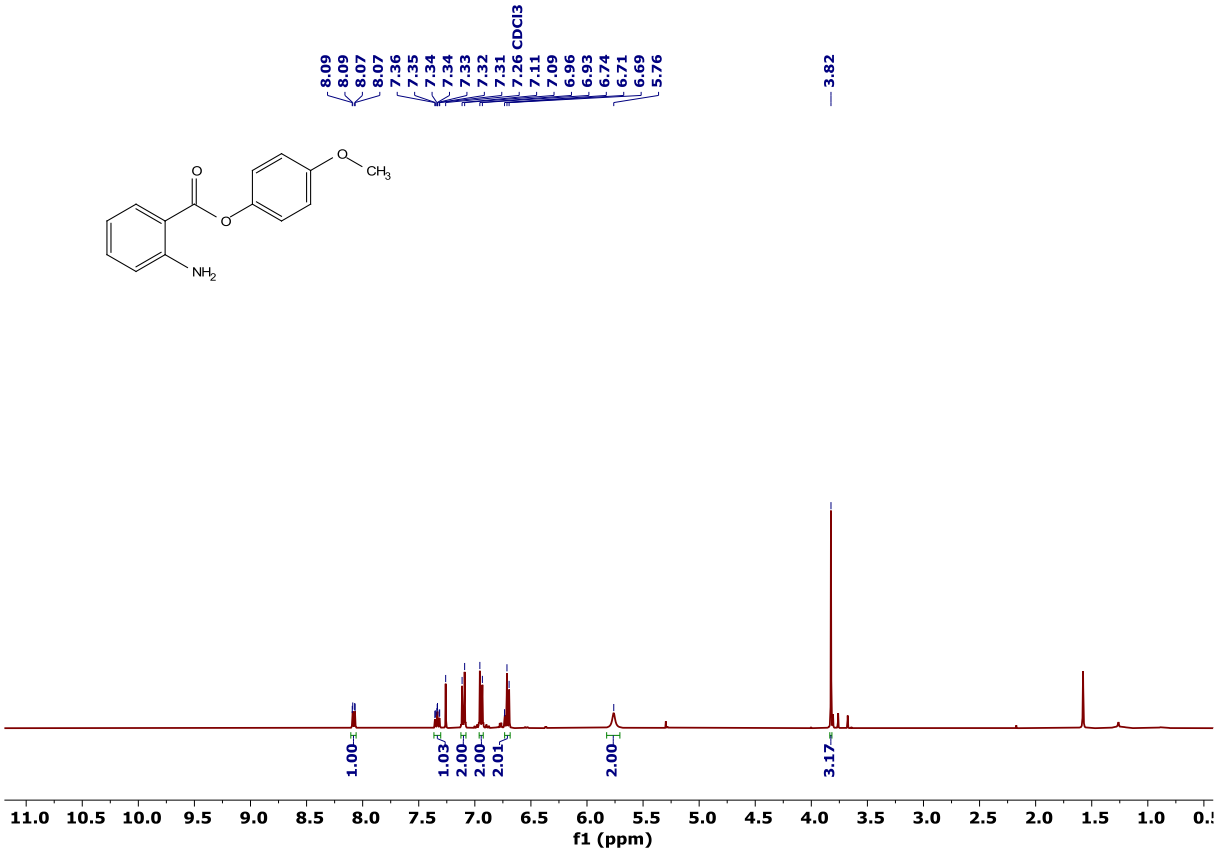


Figure S110. ^{1}H NMR spectrum of **7c** in $CDCl_3$.

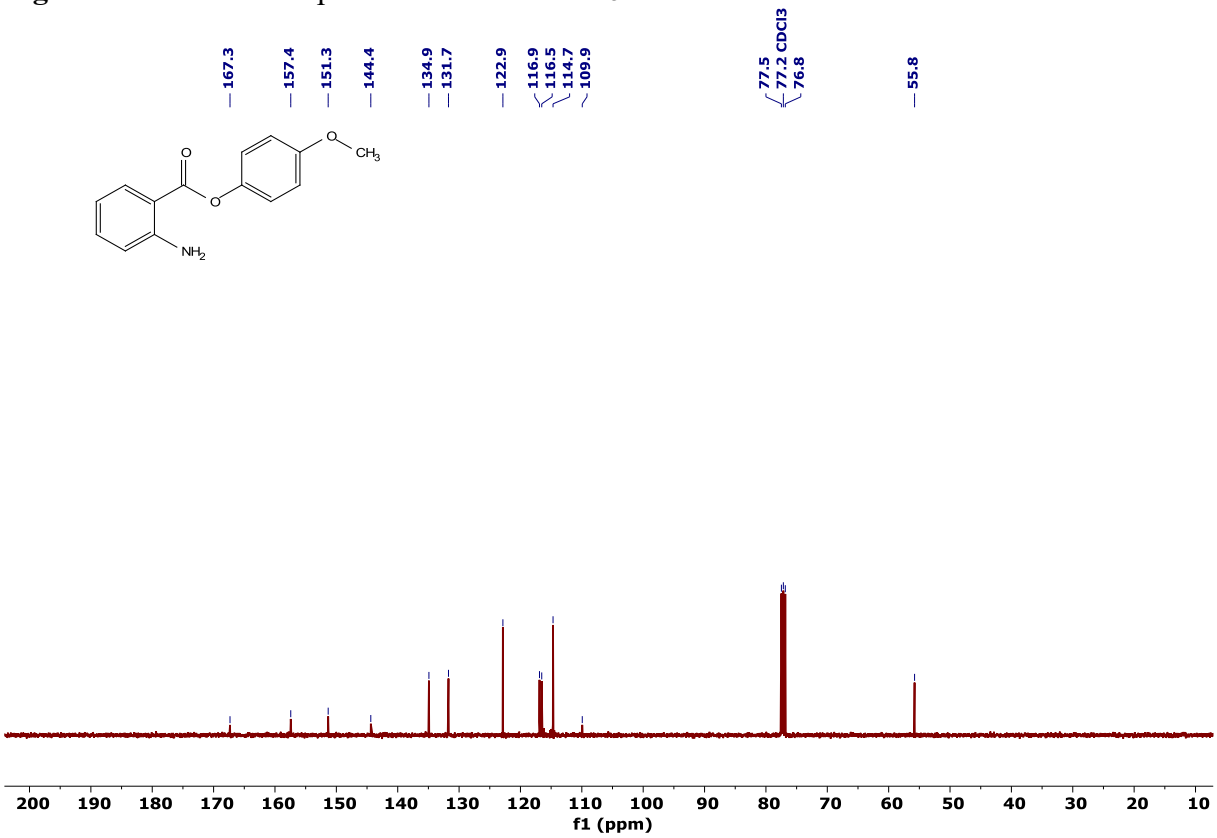


Figure S111. $^{13}C\{^{1}H\}$ NMR spectrum of **7c** in $CDCl_3$.

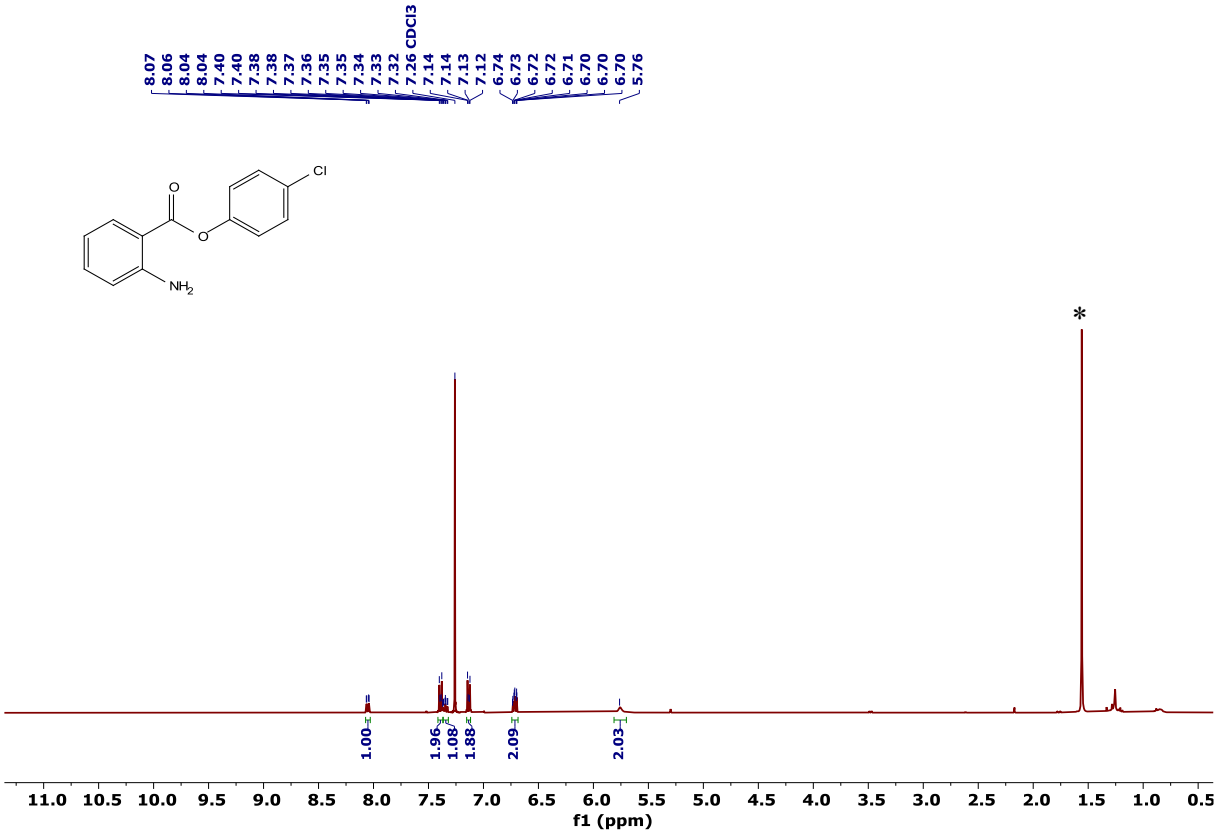


Figure S112. ^{1}H NMR spectrum of **7d** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

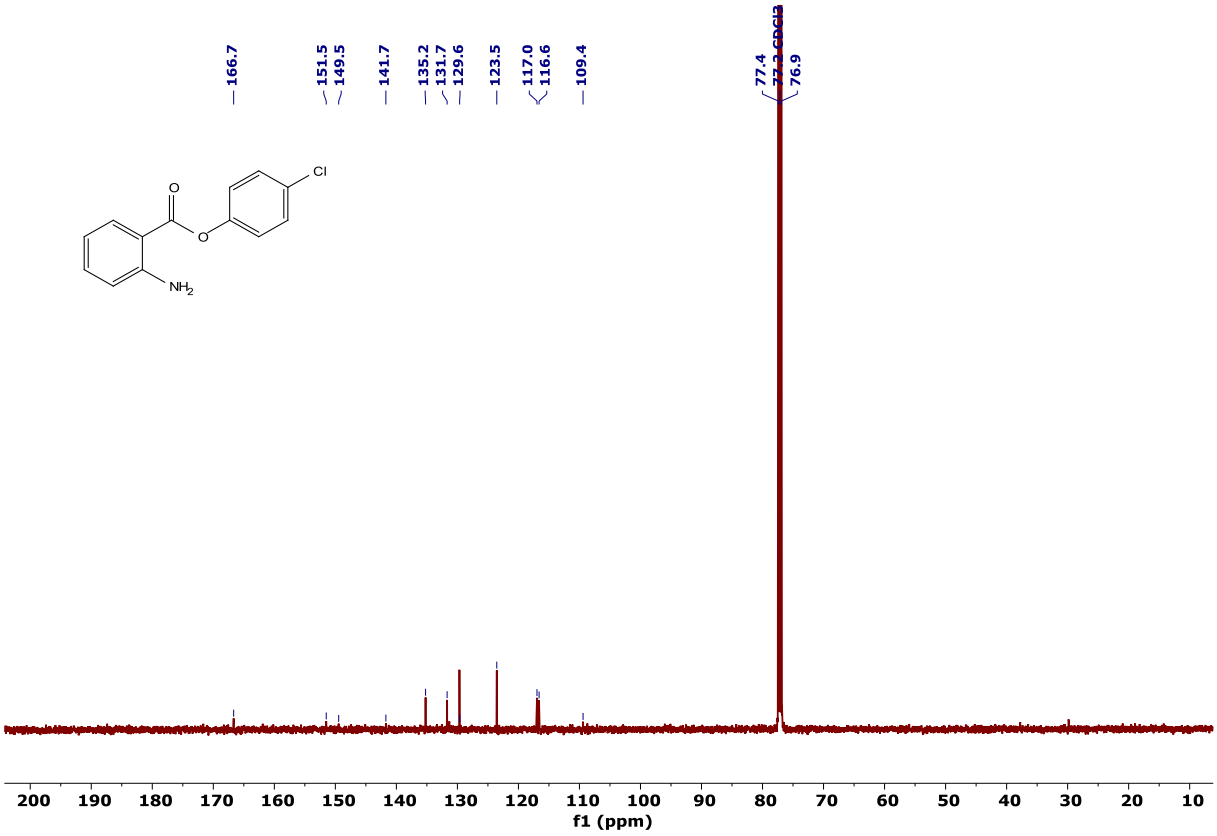


Figure S113. $^{13}C\{^{1}H\}$ NMR spectrum of **7d** in $CDCl_3$.

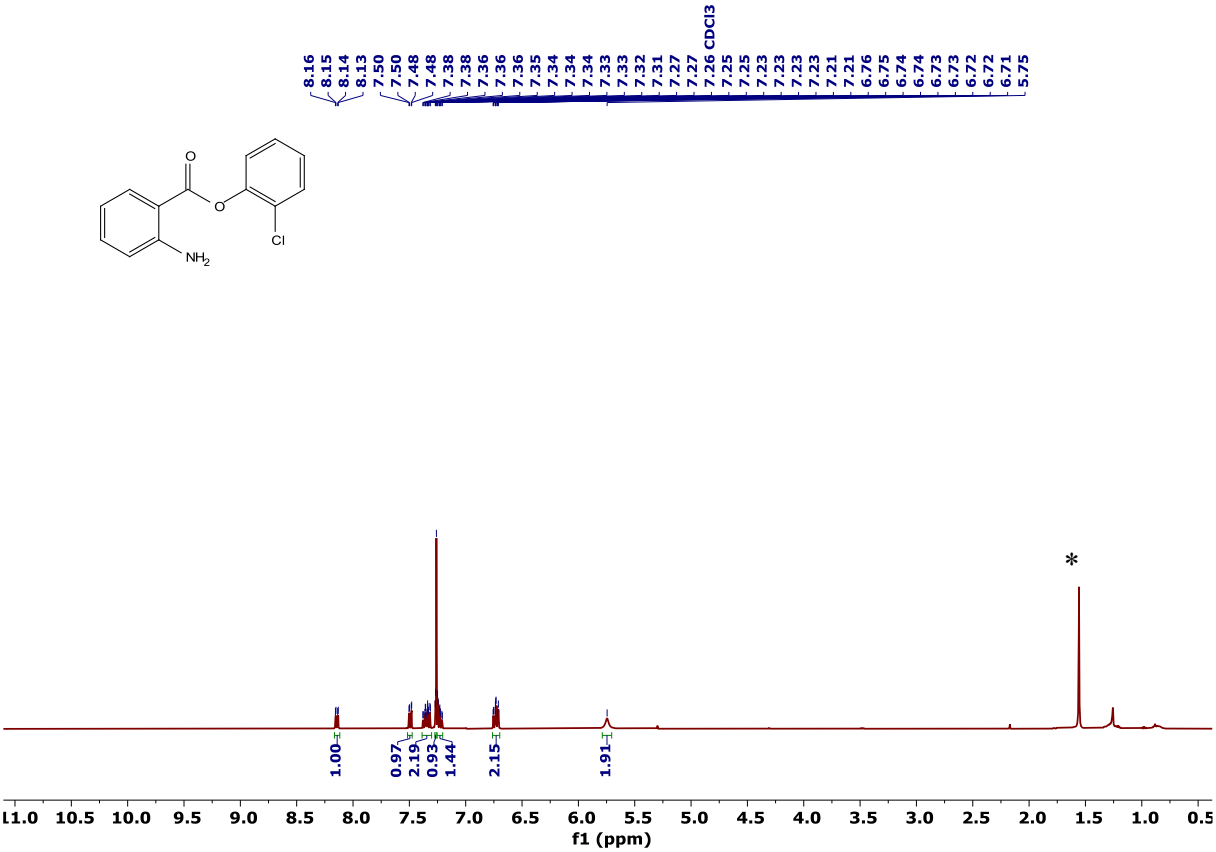


Figure S114. ^{1}H NMR spectrum of **7e** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

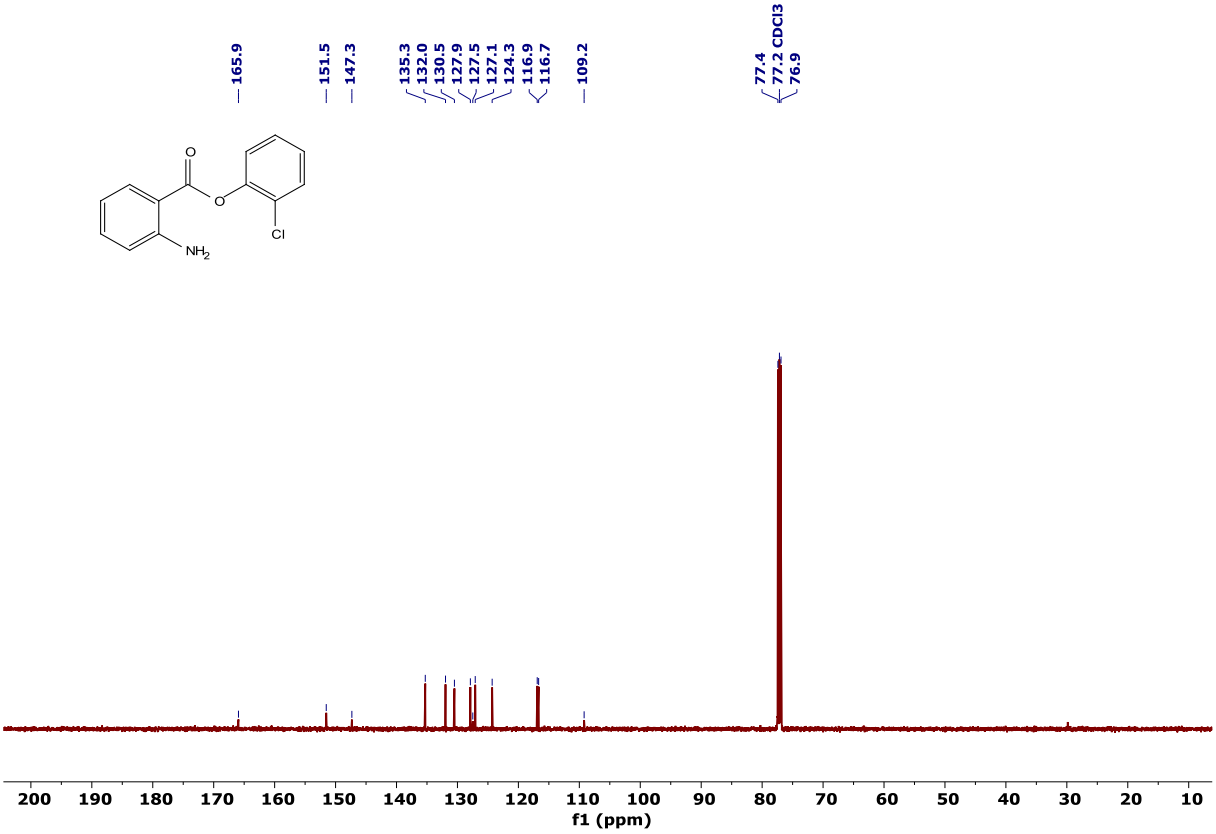


Figure S115. $^{13}C\{^{1}H\}$ NMR spectrum of **7e** in $CDCl_3$.

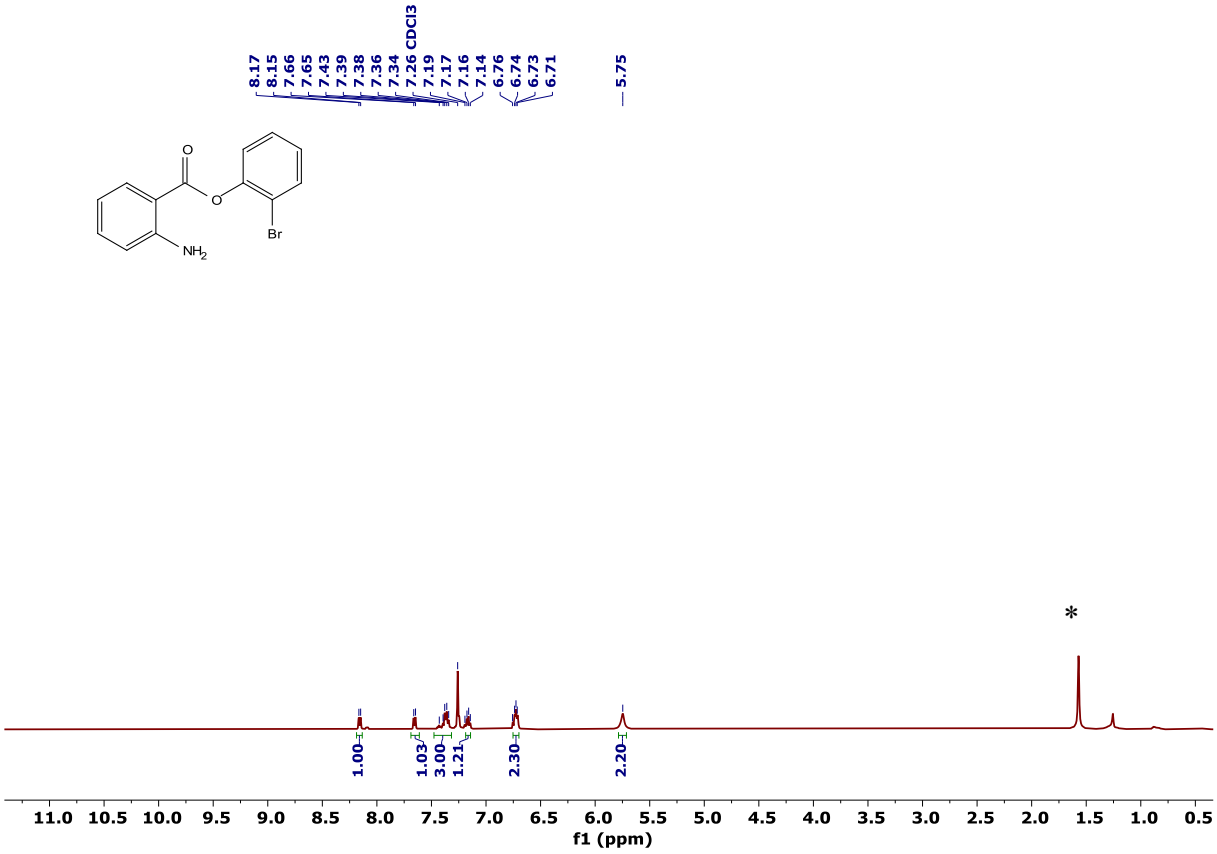


Figure S116. ^{1}H NMR spectrum of **7f** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

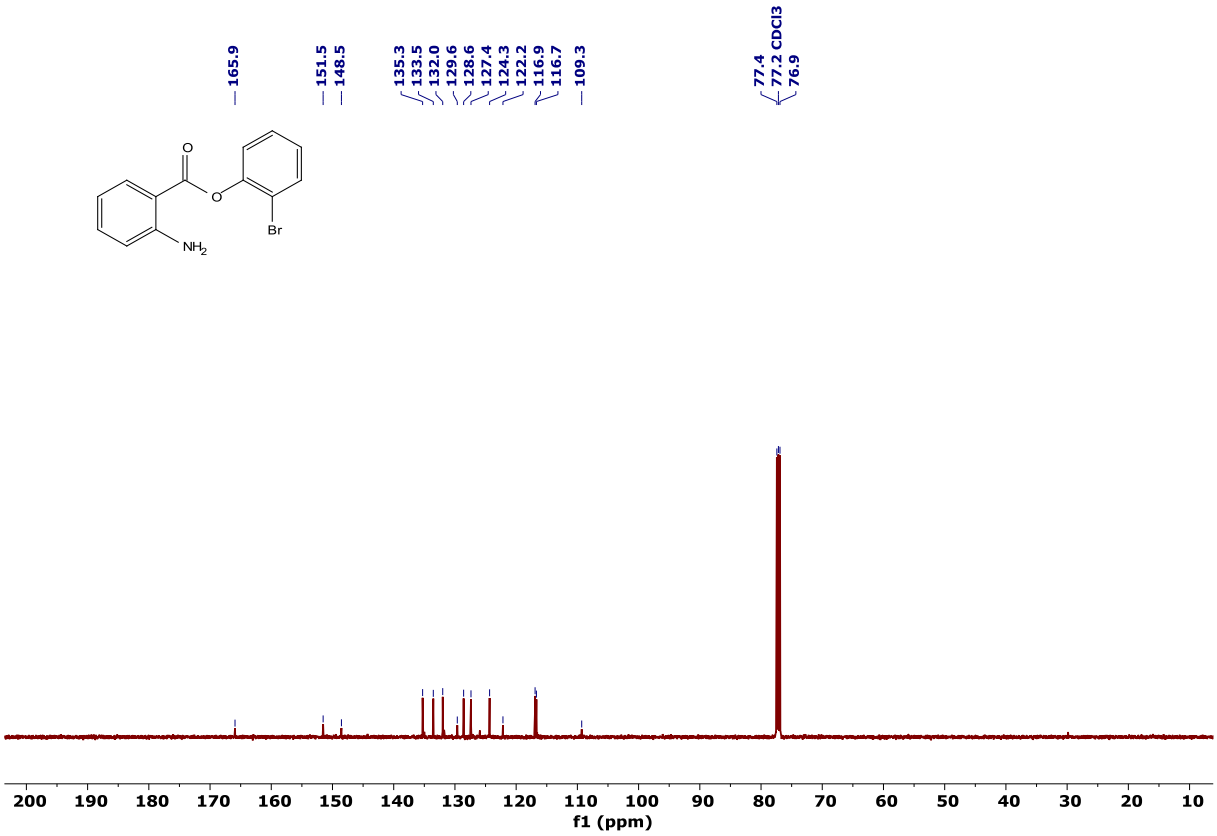


Figure S117. $^{13}C\{^{1}H\}$ NMR spectrum of **7f** in $CDCl_3$.

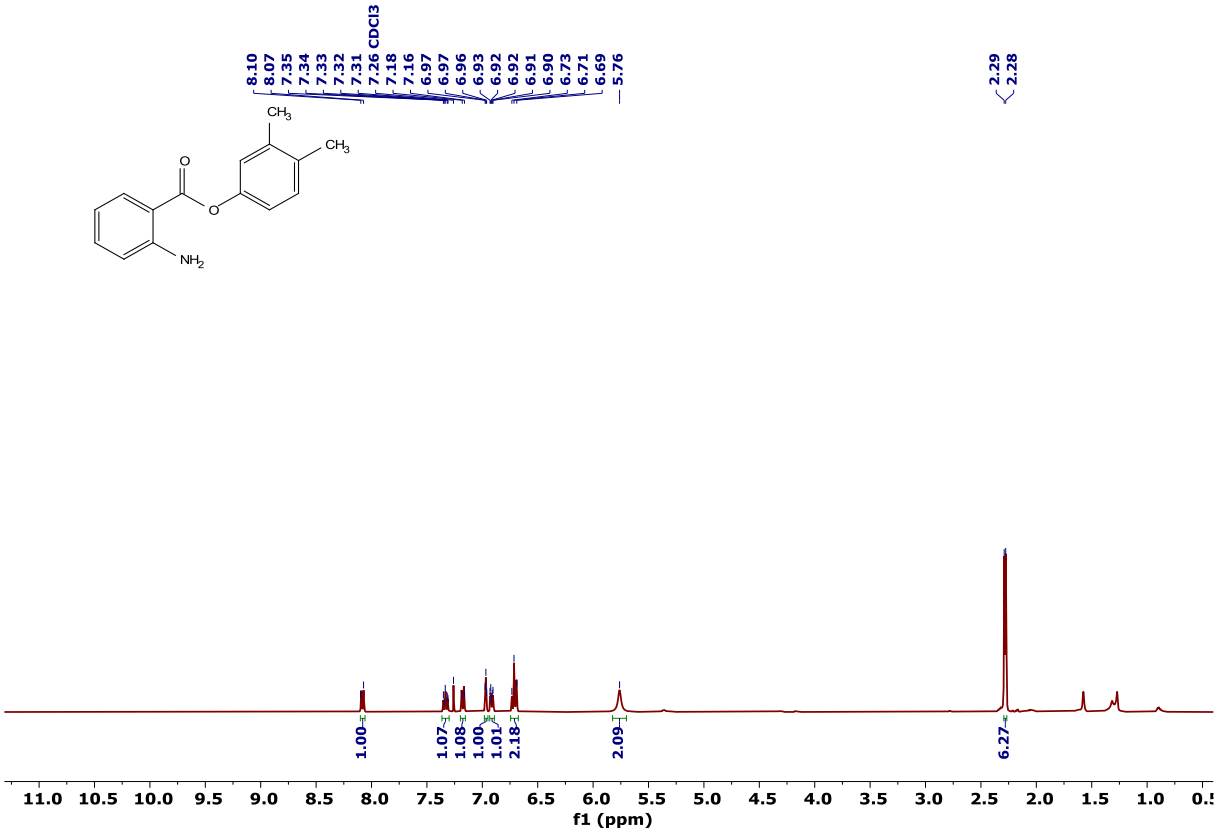


Figure S118. ^{1}H NMR spectrum of **7g** in $CDCl_3$.

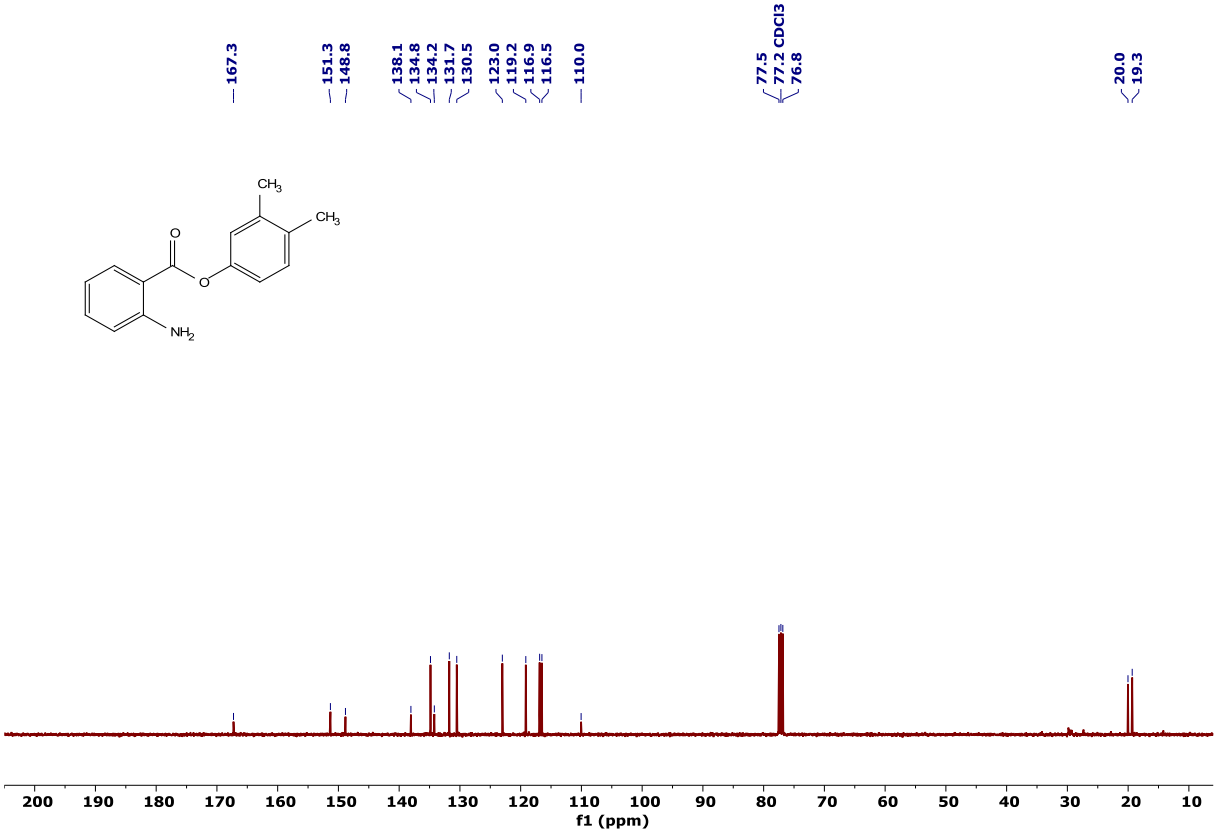


Figure S119. $^{13}C\{^{1}H\}$ NMR spectrum of **7g** in $CDCl_3$.

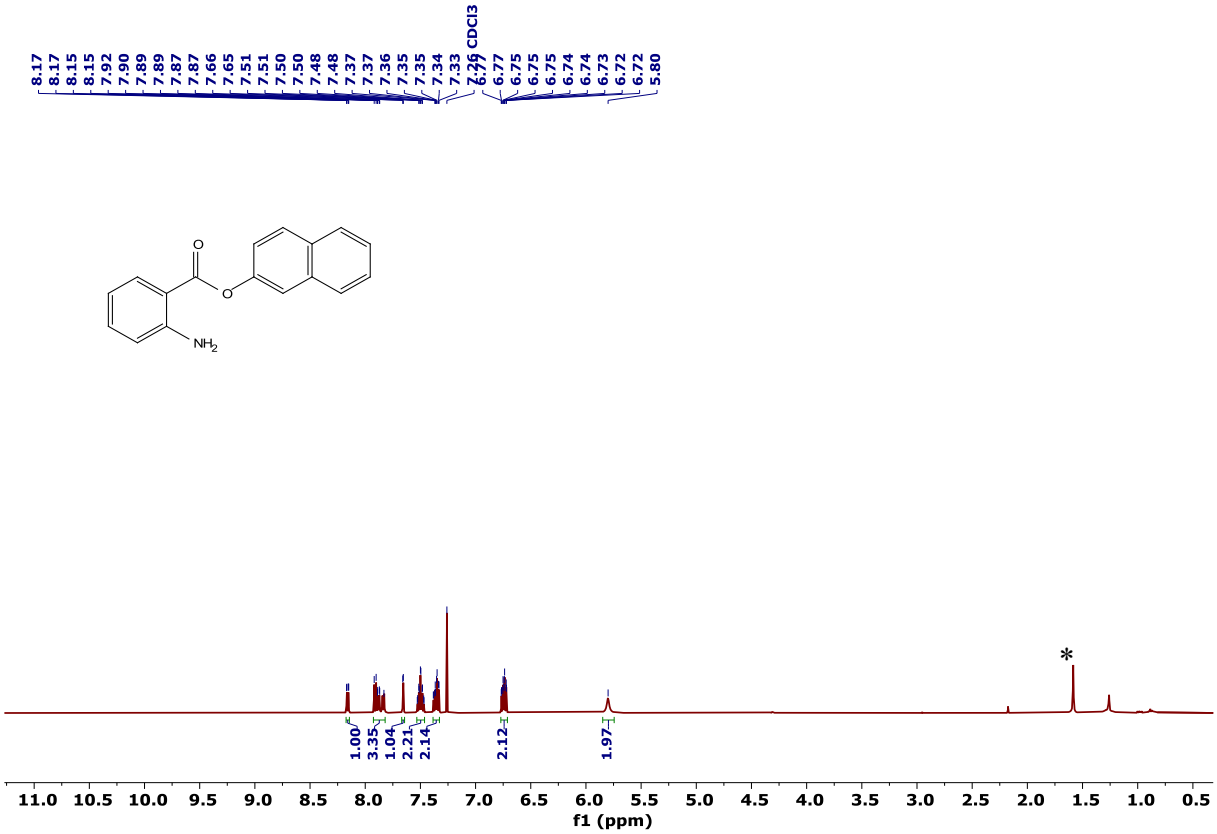


Figure S120. ^{1}H NMR spectrum of **7h** in $CDCl_3$. * Indicates the solvent impurity of H_2O in $CDCl_3$.

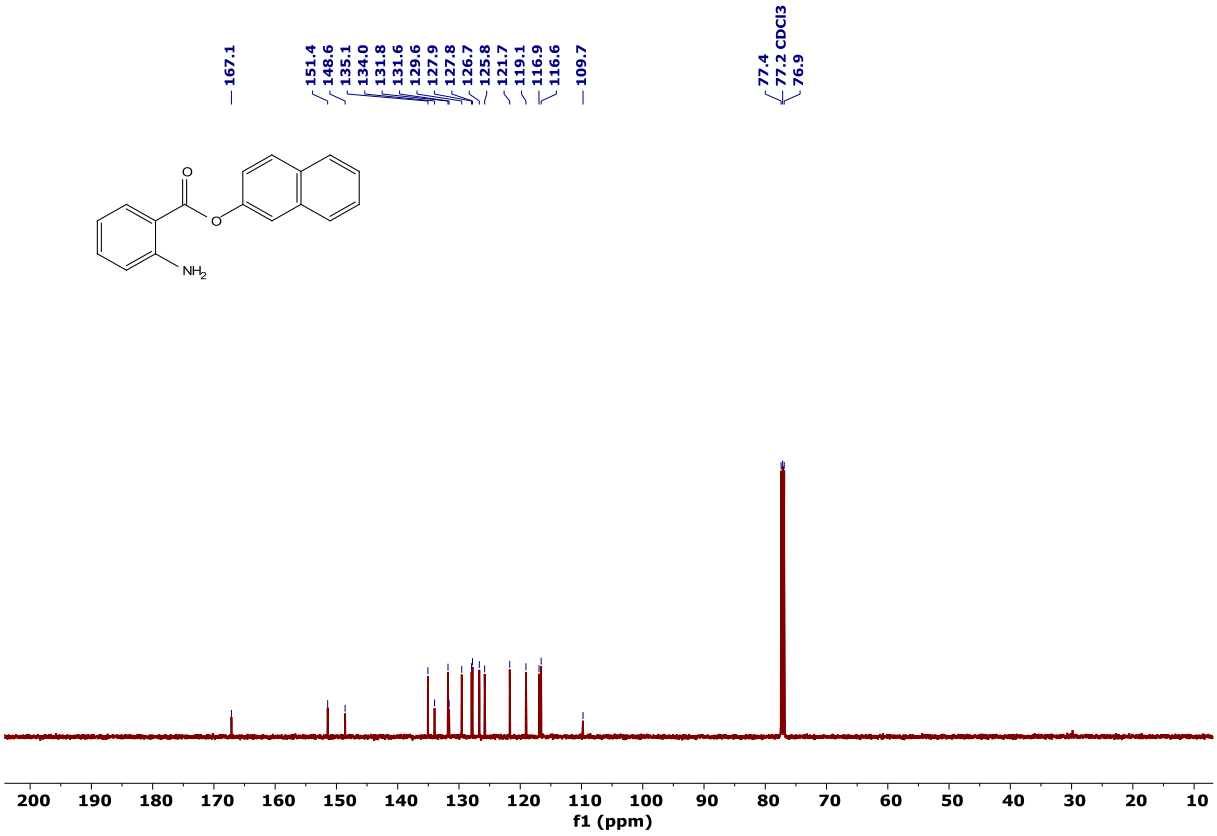


Figure S121. $^{13}C\{^{1}H\}$ NMR spectrum of **7h** in $CDCl_3$.

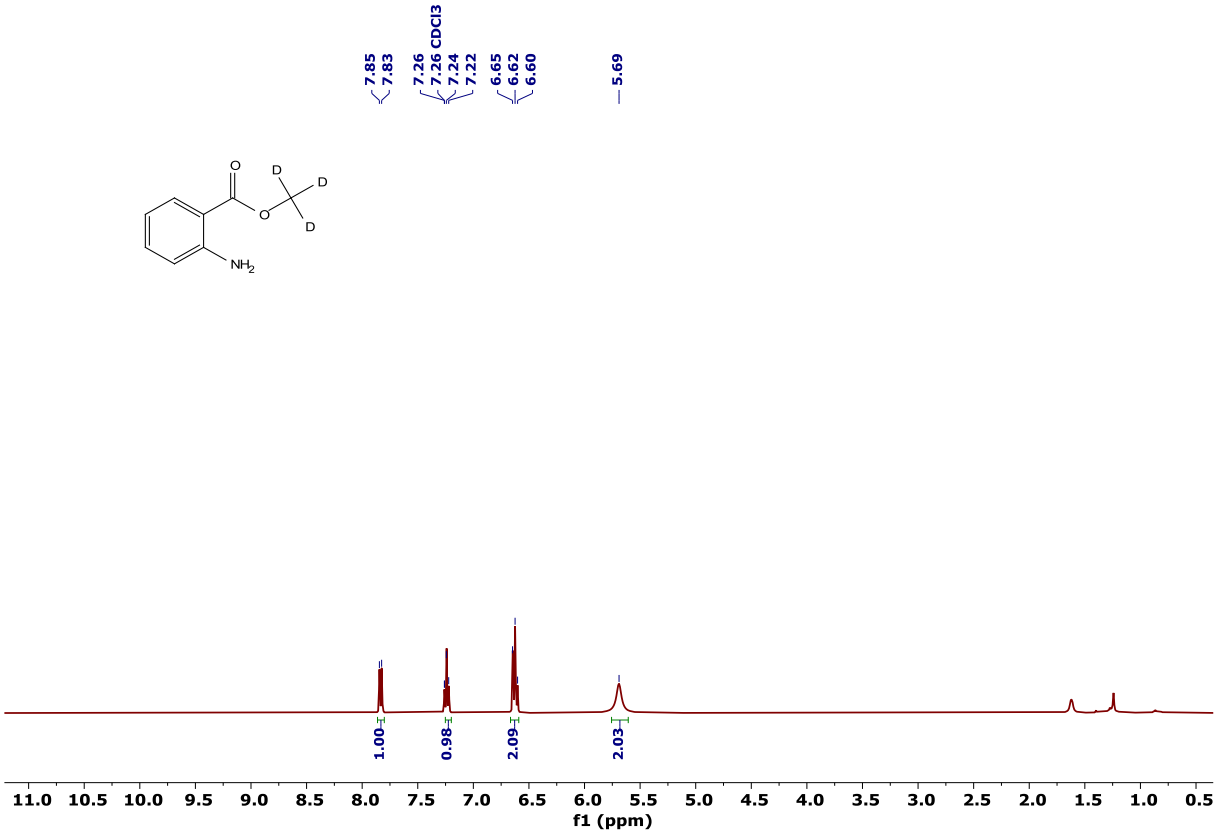


Figure S122. ^{1}H NMR spectrum of **8a** in $CDCl_3$.

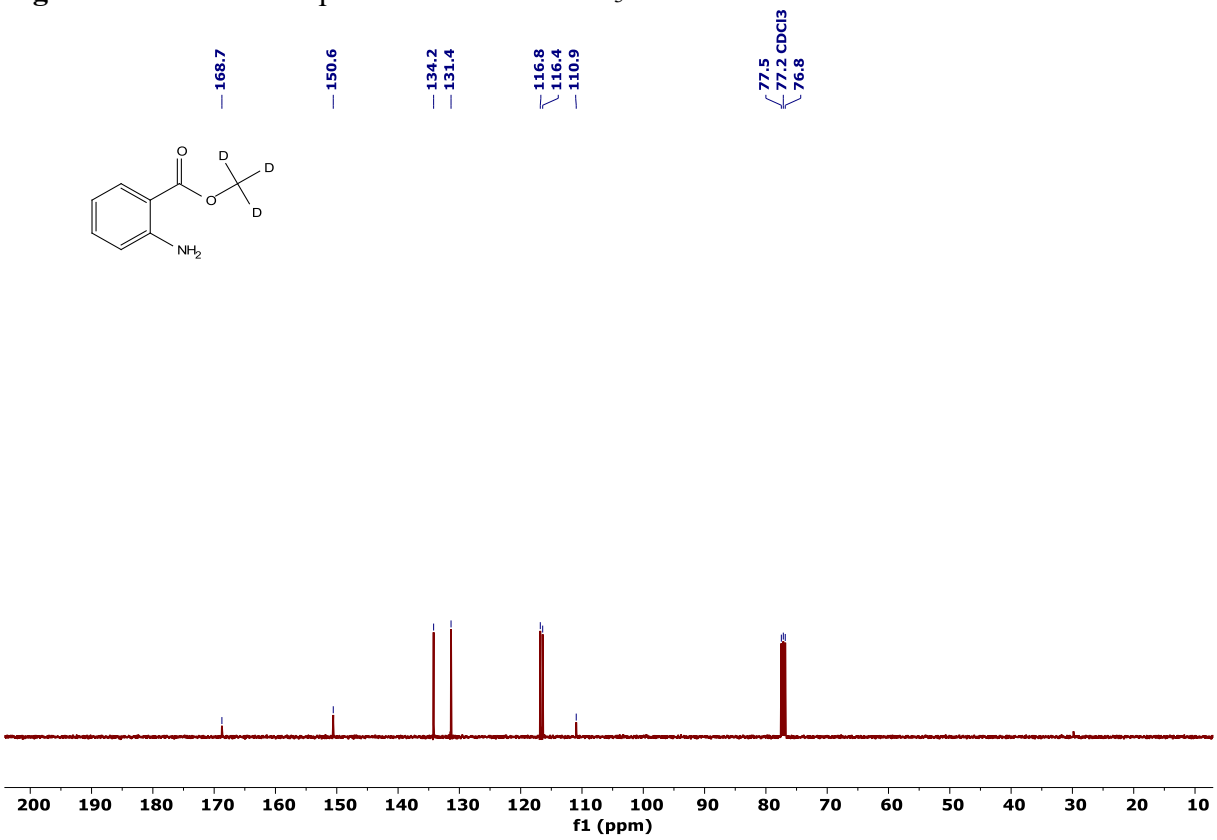


Figure S123. $^{13}C\{^{1}H\}$ NMR spectrum of **8a** in $CDCl_3$.

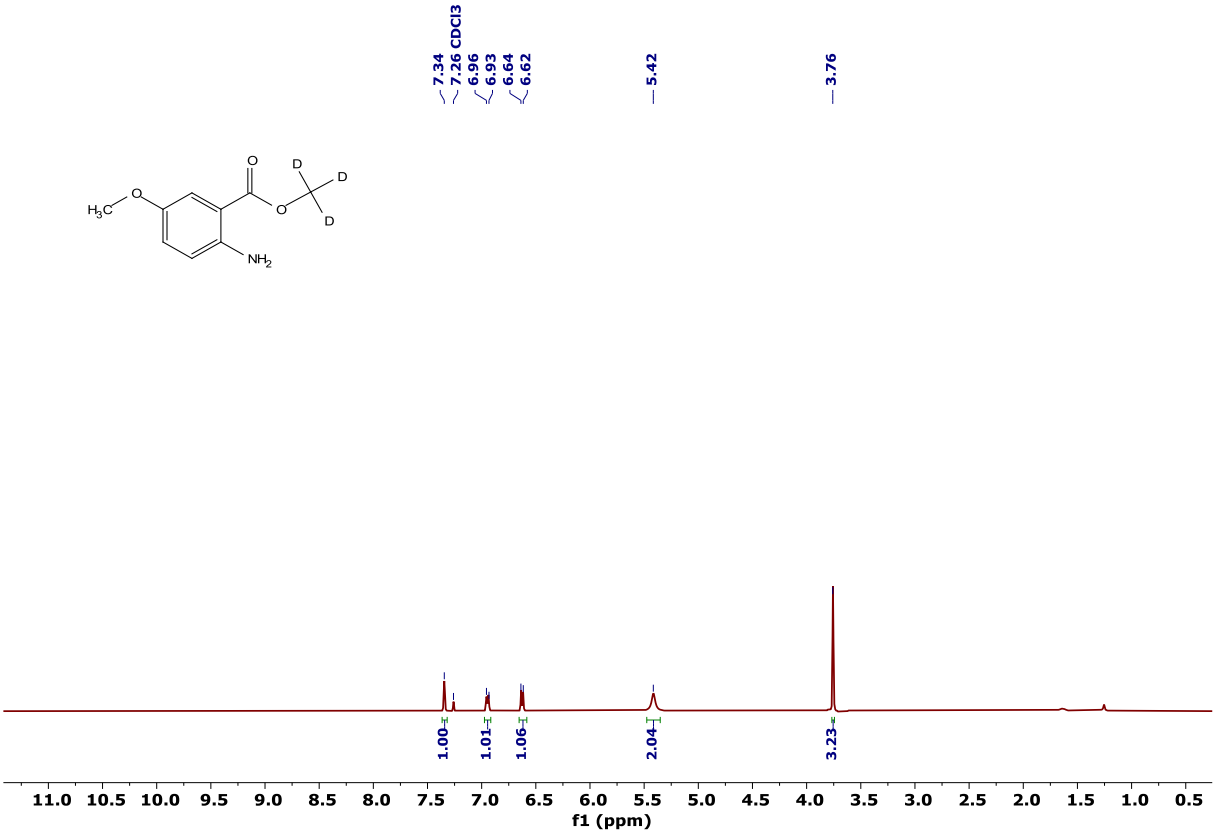


Figure S124. ^{1}H NMR spectrum of **8b** in $CDCl_3$.

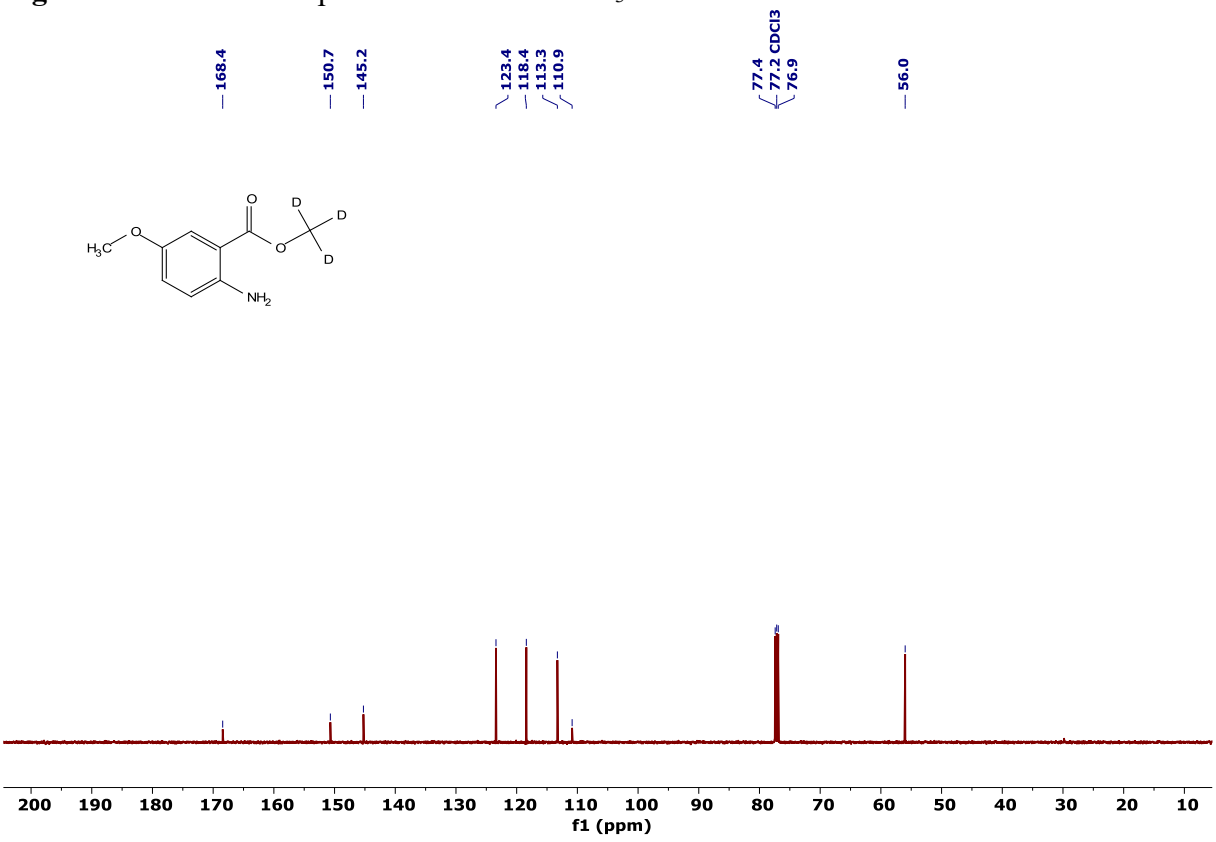


Figure S125. $^{13}C\{^{1}H\}$ NMR spectrum of **8b** in $CDCl_3$.

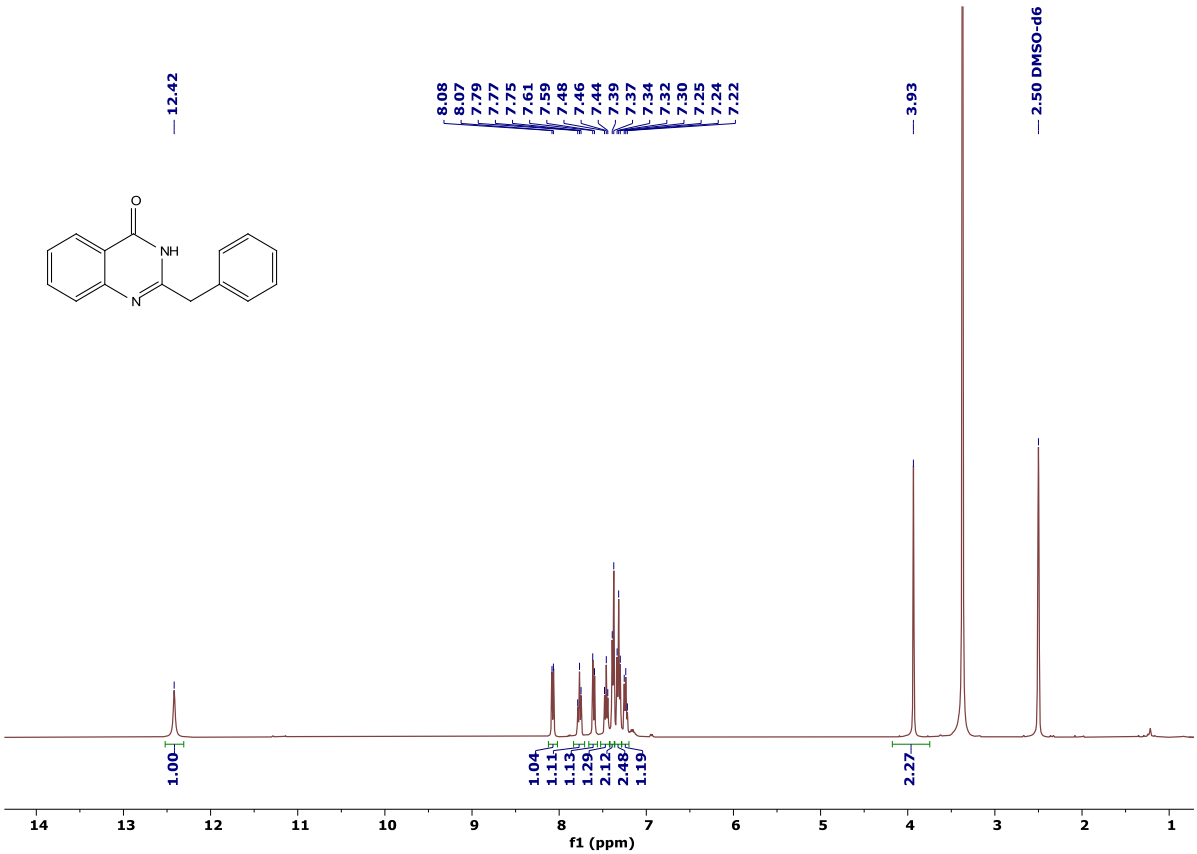


Figure S126. ^{1}H NMR spectrum of **9** in DMSO-d_6.

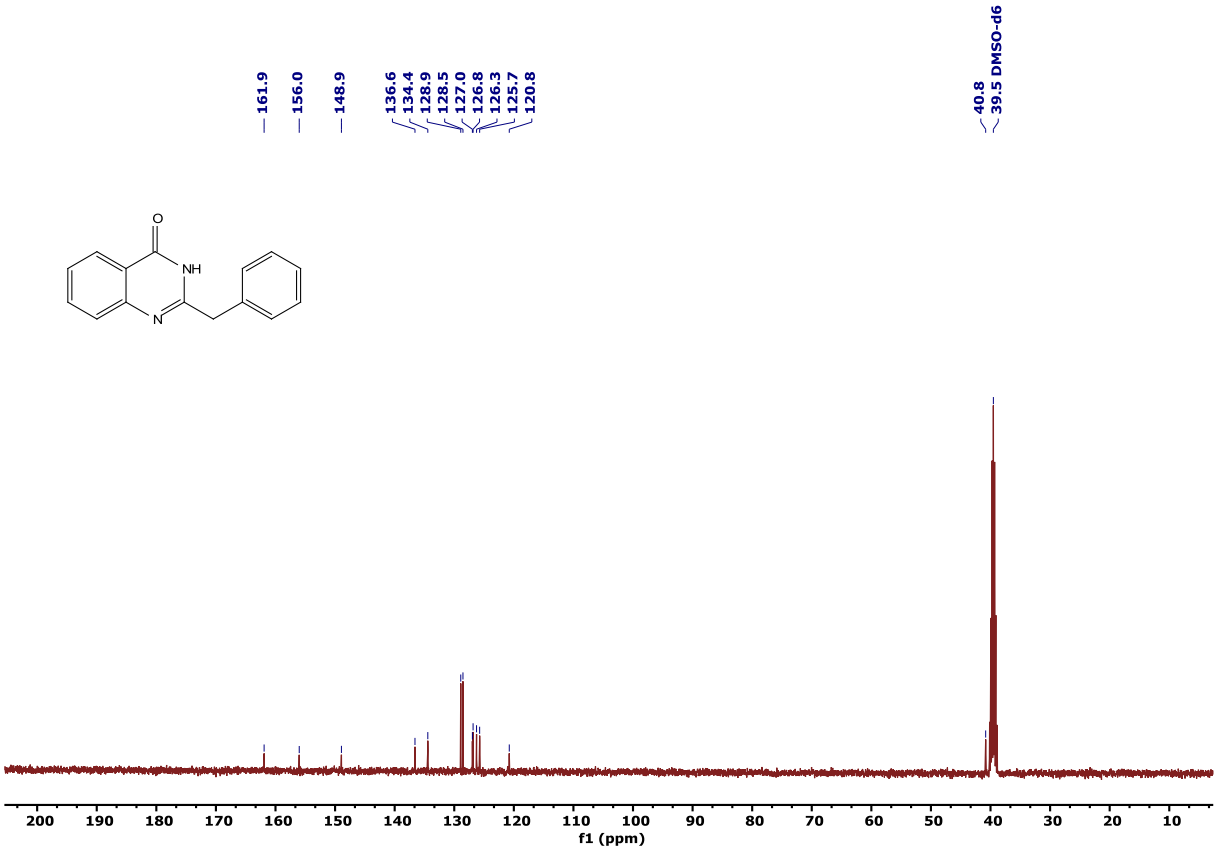


Figure S127. ^{13}C{^{1}H} NMR spectrum of **9** in DMSO-d_6.

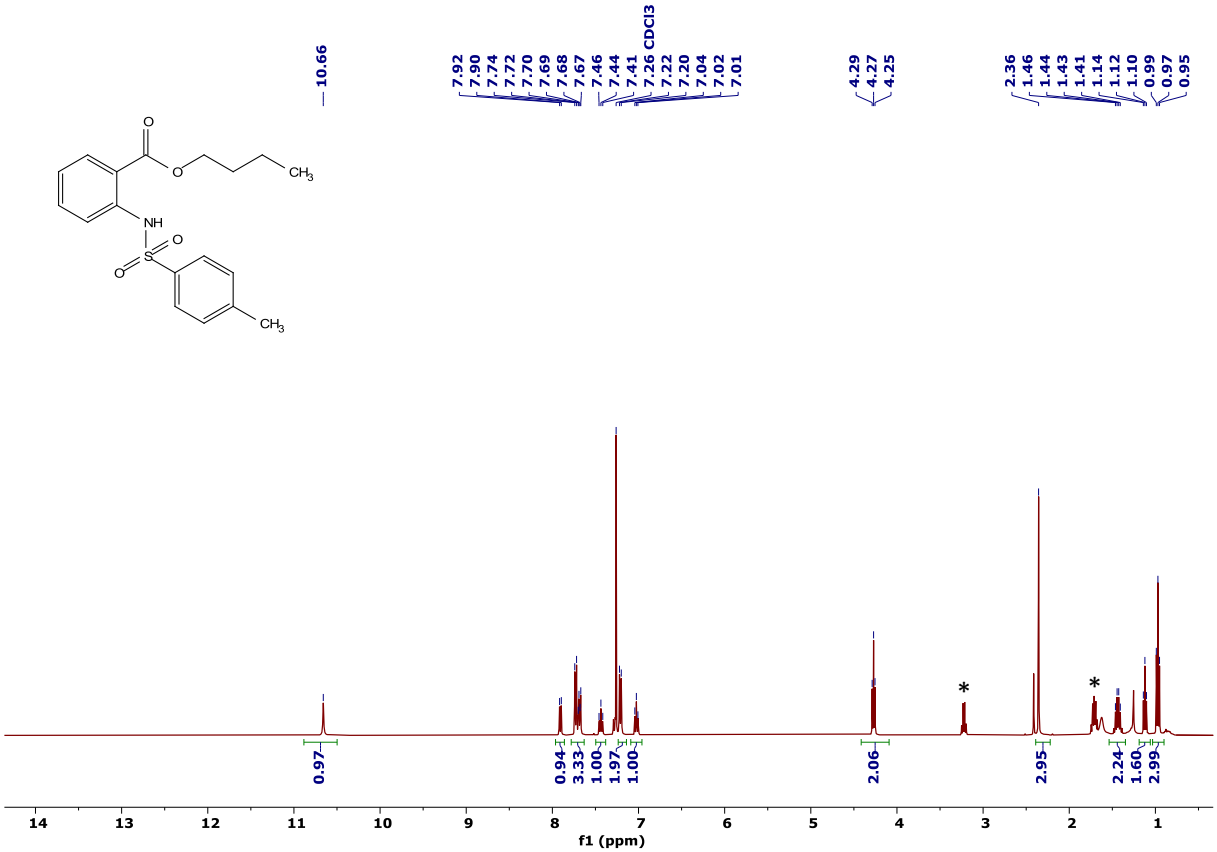


Figure S128. ^{1}H NMR spectrum of **10** in $CDCl_3$. * Indicates solvent impurity of diethyl ether.

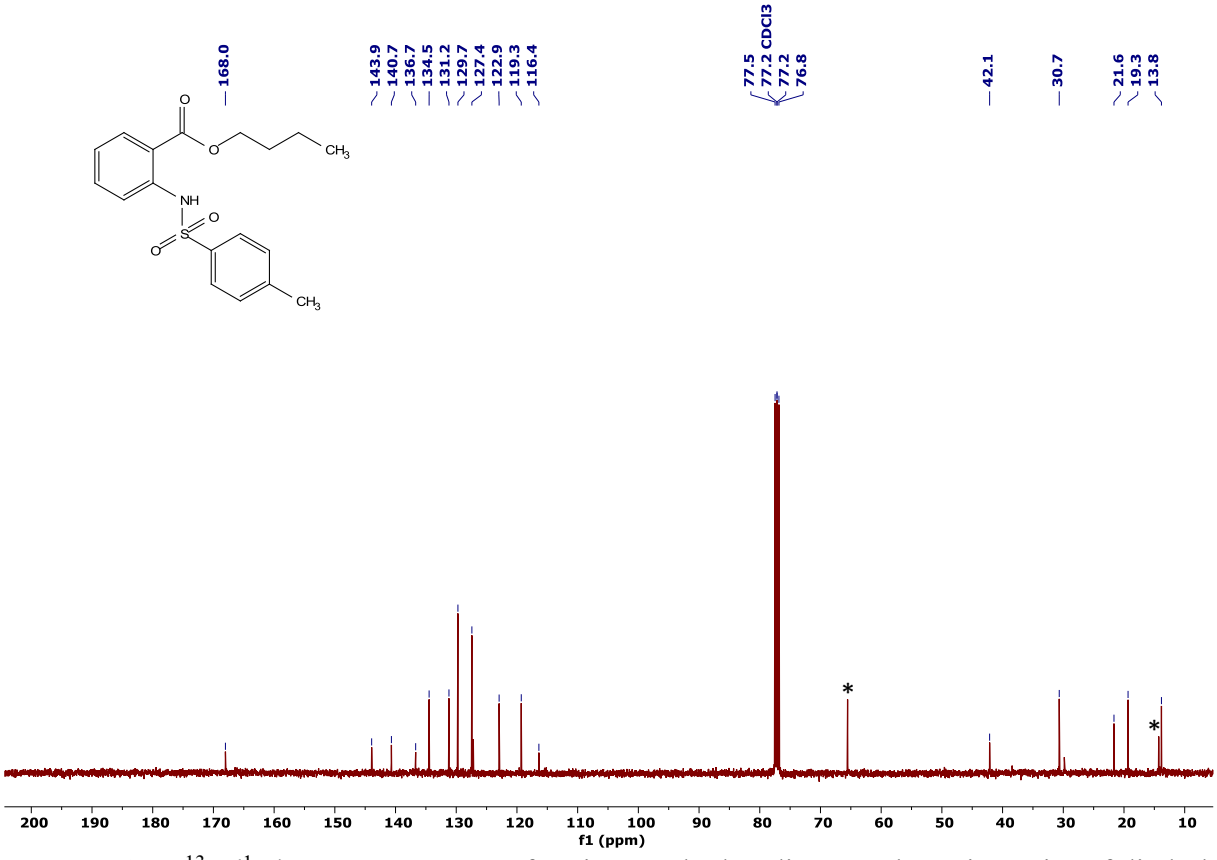


Figure S129. $^{13}C\{^{1}H\}$ NMR spectrum of **10** in $CDCl_3$. * Indicates solvent impurity of diethyl ether.

Computational studies:

Gaussian 16 software, revision B.01 program was used to carry out all the theoretical studies.[6] DFT calculations were performed with M06 functional. Metals (Co) were treated with SDD (Stuttgart-Dresden)[7] basis set with an effective core potential, while the other atoms were treated using 6-31G**,[8] a double- ζ Pople type basis set. We conducted the frequency analysis to identify the intermediates (no imaginary frequencies). The reported energies include the thermal corrections (corresponding to 298 K).

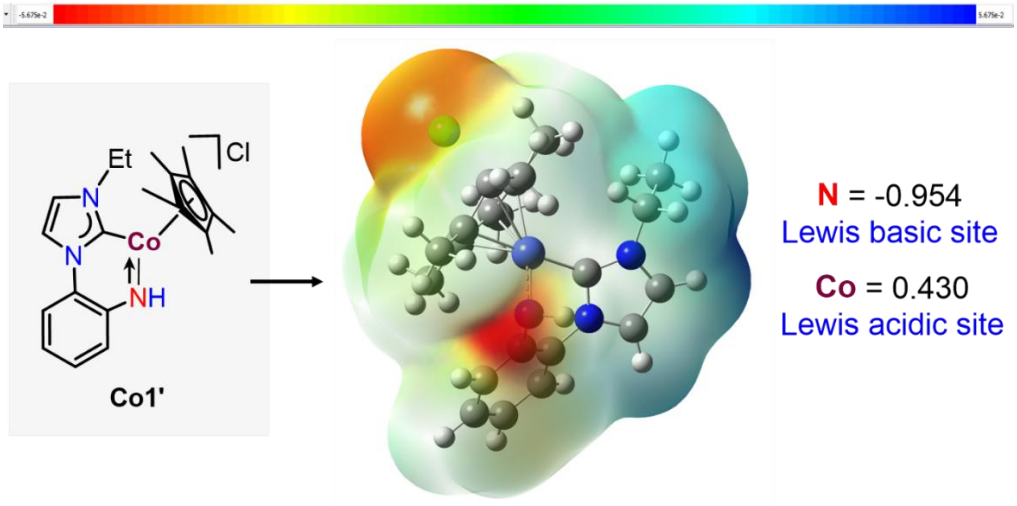
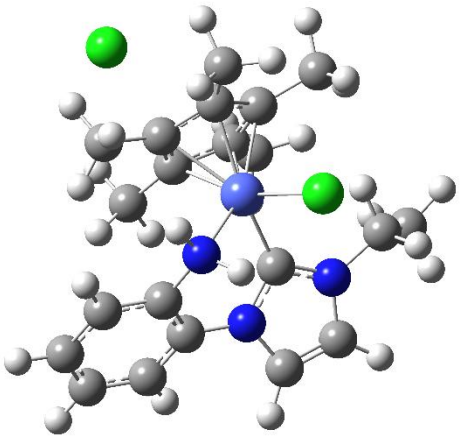


Figure S130: Electrostatic potential (ESP) mapping on the surface of total electron density at an isosurface value of 0.0004 units for the complex **Co1'** at -0.05308 to +0.05308 units. The red and blue region correspond to the negative (high e^- density) and positive part (low e^- density) of the electrostatic potential, respectively.

Cartesian coordinates of all the optimized geometries:

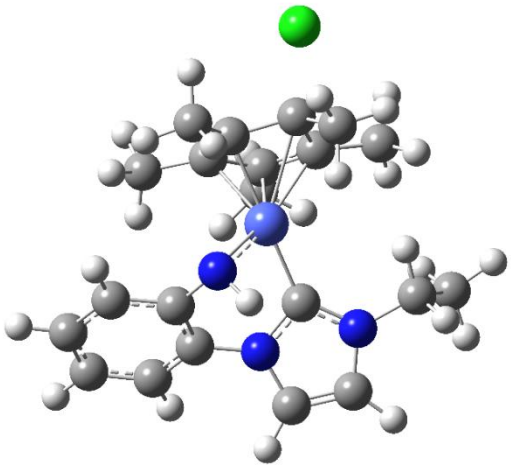


Complex Co1

Charge = 0 Multiplicity = 1

C	6.7914	3.1401	4.2113
C	5.5769	3.8854	4.3787
C	4.7328	3.5919	3.2858
C	5.3786	2.6012	2.4791
C	6.6764	2.3777	3.033
C	7.7431	1.5681	2.3709
H	8.1244	2.0706	1.6475
H	7.3618	0.7546	2.0296
H	8.4274	1.356	3.0086
C	7.9929	3.2224	5.106
H	8.6449	2.5747	4.8261
H	7.7308	3.0405	6.0109
H	8.3719	4.1014	5.0523
C	5.2868	4.8429	5.4919
H	5.7389	4.5544	6.2882
H	4.3403	4.8687	5.6543
H	5.5941	5.719	5.2491
C	3.4084	4.2258	3.0061
H	3.5439	5.0729	2.5766
H	2.9354	4.3566	3.8317
H	2.8948	3.6547	2.4309
C	4.9017	2.0684	1.1669
H	3.9419	2.0914	1.1413
H	5.2025	1.1629	1.0608
H	5.2537	2.6082	0.455
C	2.6185	0.8236	3.5123
C	1.4391	1.3402	3.0137
H	1.0267	2.0547	3.4444
C	0.8677	0.7976	1.8762
H	0.0812	1.1566	1.5324
C	1.4611	-0.2709	1.2551

H	1.0677	-0.6365	0.4959
C	2.6274	-0.808	1.7382
H	3.0205	-1.5346	1.31
C	3.2185	-0.261	2.8708
C	4.8137	-2.1231	3.309
H	4.3401	-2.8156	2.9064
C	5.978	-2.2192	3.9467
H	6.4692	-2.9991	4.0784
C	5.3833	-0.0506	4.0301
C	7.5302	-0.6509	5.1711
H	7.4012	-0.9731	6.076
H	7.6488	0.3111	5.2133
C	8.7876	-1.2794	4.596
H	8.7557	-2.2302	4.7225
H	9.5573	-0.9221	5.0446
H	8.8436	-1.0832	3.6579
Cl	5.4775	1.5865	6.6187
Co	5.1818	1.8278	4.3748
N	3.254	1.3963	4.6631
N	4.4457	-0.7889	3.3651
N	6.3294	-0.9511	4.3777
H	3.2875	0.7673	5.2811
H	2.7739	2.1695	4.9718
Cl	7.1291	12.2051	6.9625



Complex Co1'

Charge = 0 Multiplicity = 1

C	6.7914	3.1401	4.2113
C	5.5769	3.8854	4.3787
C	4.7328	3.5919	3.2858
C	5.3786	2.6012	2.4791
C	6.6764	2.3777	3.033
C	7.7431	1.5681	2.3709
H	8.1244	2.0706	1.6475
H	7.3618	0.7546	2.0296
H	8.4274	1.356	3.0086
C	7.9929	3.2224	5.106
H	8.6449	2.5747	4.8261
H	7.7308	3.0405	6.0109
H	8.3719	4.1014	5.0523
C	5.2868	4.8429	5.4919
H	5.7389	4.5544	6.2882
H	4.3403	4.8687	5.6543
H	5.5941	5.719	5.2491
C	3.4084	4.2258	3.0061
H	3.5439	5.0729	2.5766
H	2.9354	4.3566	3.8317
H	2.8948	3.6547	2.4309

C	4.9017	2.0684	1.1669
H	3.9419	2.0914	1.1413
H	5.2025	1.1629	1.0608
H	5.2537	2.6082	0.455
C	2.6185	0.8236	3.5123
C	1.4391	1.3402	3.0137
H	1.0267	2.0547	3.4444
C	0.8677	0.7976	1.8762
H	0.0812	1.1566	1.5324
C	1.4611	-0.2709	1.2551
H	1.0677	-0.6365	0.4959
C	2.6274	-0.808	1.7382
H	3.0205	-1.5346	1.31
C	3.2185	-0.261	2.8708
C	4.8137	-2.1231	3.309
H	4.3401	-2.8156	2.9064
C	5.978	-2.2192	3.9467
H	6.4692	-2.9991	4.0784
C	5.3833	-0.0506	4.0301
C	7.5302	-0.6509	5.1711
H	7.4012	-0.9731	6.076
H	7.6488	0.3111	5.2133
C	8.7876	-1.2794	4.596
H	8.7557	-2.2302	4.7225
H	9.5573	-0.9221	5.0446
H	8.8436	-1.0832	3.6579
Co	5.1818	1.8278	4.3748
N	3.254	1.3963	4.6631
N	4.4457	-0.7889	3.3651
N	6.3294	-0.9511	4.3777
H	3.2875	0.7673	5.2811
Cl	7.1291	12.2051	6.9625

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