Electronic Supplementary Information for

Development of boronic acid catalyst for direct amidation of aromatic carboxylic acids using fluorescent-based screening

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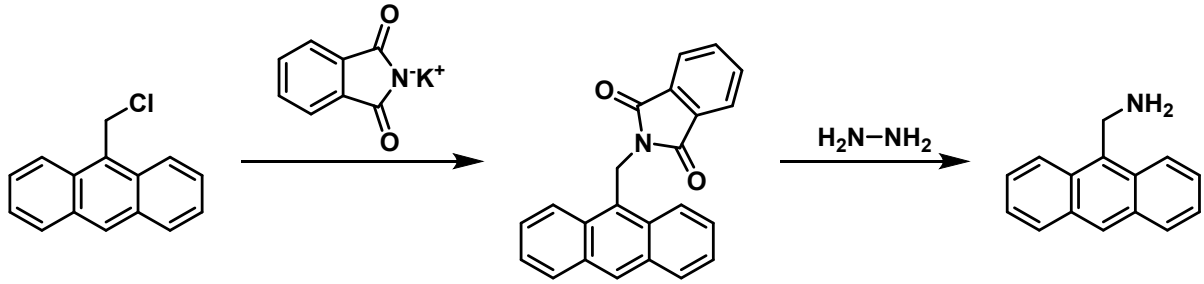
1. General information

All chemical reagents were purchased from commercial suppliers, including Sigma-Aldrich, Alfa Aesar, Tokyo Chemical Industry, Combi-Blocks, Duksan Pure Chemicals, Daejung Chemicals & Metals, and Samchun Pure Chemical, and were used as received without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL 400 MHz NMR spectrometer (JEOL, Tokyo, Japan). Fluorescence spectra were acquired using an Agilent Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Santa Clara, CA, USA).

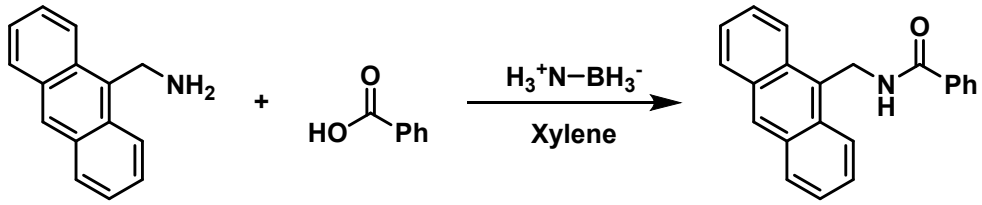
2. Synthesis and characterization of fluorescent probe and amidation product

2.1. Synthesis of anthracen-9-ylmethanamine[1, 2]



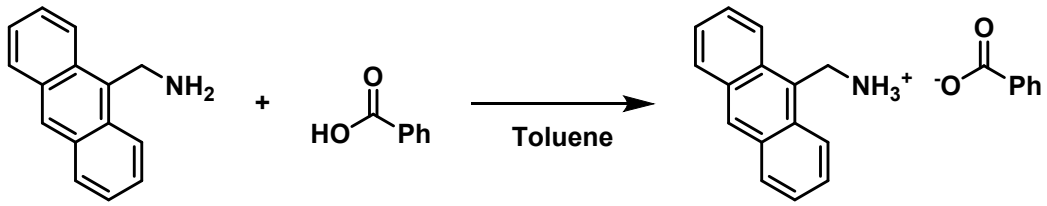
9-(Chloromethyl)anthracene (2.27 g, 10.0 mmol) was dissolved in *N,N*-dimethylformamide (20 mL), followed by the addition of potassium phthalimide (1.85 g, 10.0 mmol). The mixture was stirred at 60°C for 2 h, then cooled to room temperature. Subsequently, hydrazine hydrate (3.89 mL, 80.0 mmol) was added gradually, and the mixture was stirred at 60°C for another 2 h. The resultant mixture was filtered through Celite and washed with ethyl acetate (80 mL). The filtrate underwent washing with water (20 mL) and brine (20 mL), followed by drying of the organic layer over Na_2SO_4. The solvent was then evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 20/1) to yield anthracen-9-ylmethanamine (1.03 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34–8.41 (m, 3H), 8.03 (dt, *J* = 8.4, 0.7 Hz, 2H), 7.46–7.58 (m, 4H), 4.84 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.79, 129.43, 129.41, 127.02, 126.25, 125.08, 123.83, 38.33.

2.2. Synthesis of *N*-(anthracen-9-ylmethyl)benzamide (1)[3]



Anthracen-9-ylmethanamine (0.10 g, 0.50 mmol) was dissolved in xylene (2 mL), to which benzoic acid (0.067 g, 0.55 mmol) and ammonia-borane (1.5 mg, 0.05 mmol) were added. The suspension was refluxed for 6 h, and the solvent was then removed under reduced pressure. The residue was dissolved in ethyl acetate (4 mL) and washed twice with cold 3 M NaOH aqueous solution (2 × 3 mL) and once with brine (1 × 4 mL). After drying the organic layer over Na_2SO_4, the solvent was removed under reduced pressure. Finally, the residue was purified using column chromatography (SiO_2, EtOAc/hexane = 1/5) to obtain *N*-(anthracen-9-ylmethyl)benzamide (**1**, 0.142 g, 91%). ^{1}H NMR (400 MHz, $CHCl_3$) δ 8.51 (s, 1H), 8.37 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.70–7.72 (m, 2H), 7.57–7.61 (m, 2H), 7.49–7.53 (m, 2H), 7.42–7.47 (m, 1H), 7.34–7.38 (m, 2H), 6.25 (s, 1H), 5.65 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.52, 134.23, 131.68, 130.63, 129.40, 128.67, 128.47, 127.51, 127.34, 127.12, 126.99, 125.40, 123.92, 36.90.

2.3. Synthesis of anthracen-9-ylmethanaminium benzoate (2)



Anthracen-9-ylmethanamine (1.03 g, 4.96 mmol) was dissolved in toluene (50 mL), and benzoic acid (0.61 g, 5.0 mmol) was added. The mixture was stirred at room temperature overnight, after which the precipitated product was filtered and washed with toluene, yielding anthracen-9-ylmethanaminium benzoate (**2**, 1.56 g, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (s, 1H), 8.45 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.2 Hz, 2H), 7.92–7.94 (m, 2H), 7.50–7.62 (m, 5H), 7.41–7.46 (m, 2H), 4.82 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.61, 131.09, 131.03, 130.83, 129.68, 129.14, 128.92, 127.95, 127.49, 126.29, 125.25, 124.45, 35.76.

3. Fluorescence emission behavior

3.1. Fluorescent spectra of probe and amidation product

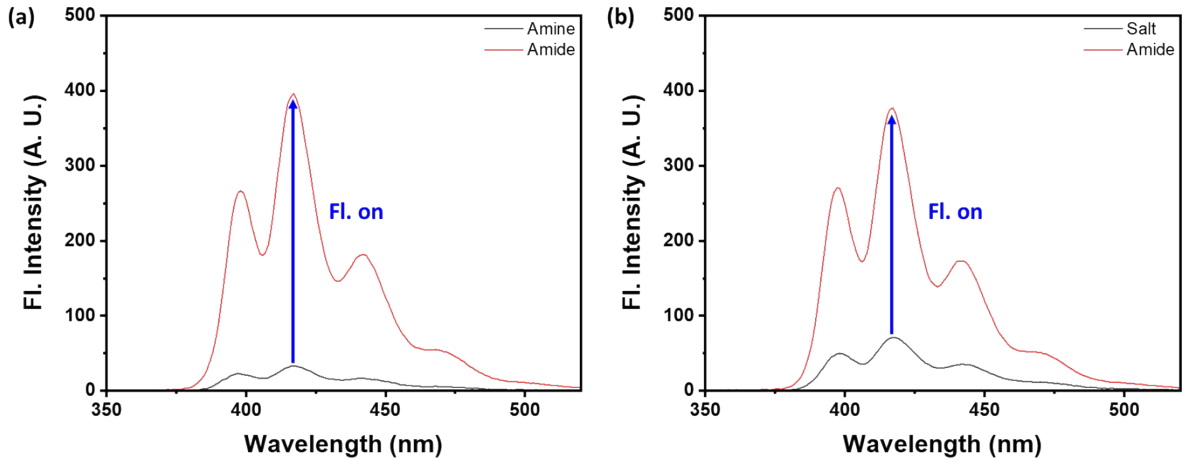


Figure S1. Fluorescent spectra of probe (black) and amidation product (*N*-(anthracen-9-ylmethyl)benzamide, **1**, red). (a) Anthracen-9-ylmethanamine as a fluorescent probe. (b) Anthracen-9-ylmethanaminium benzoate (**2**) as a fluorescent probe. The concentrations of amine, salt, and amide were 100 μM each in DMSO. Excitation light at 258 nm was irradiated, and fluorescence spectra were recorded over the 350–520 nm range. (Excitation/emission slit width: 5 nm/5 nm, PMT: 400 V)

3.2. Fluorescence calibration curve for fluorescent-based screening

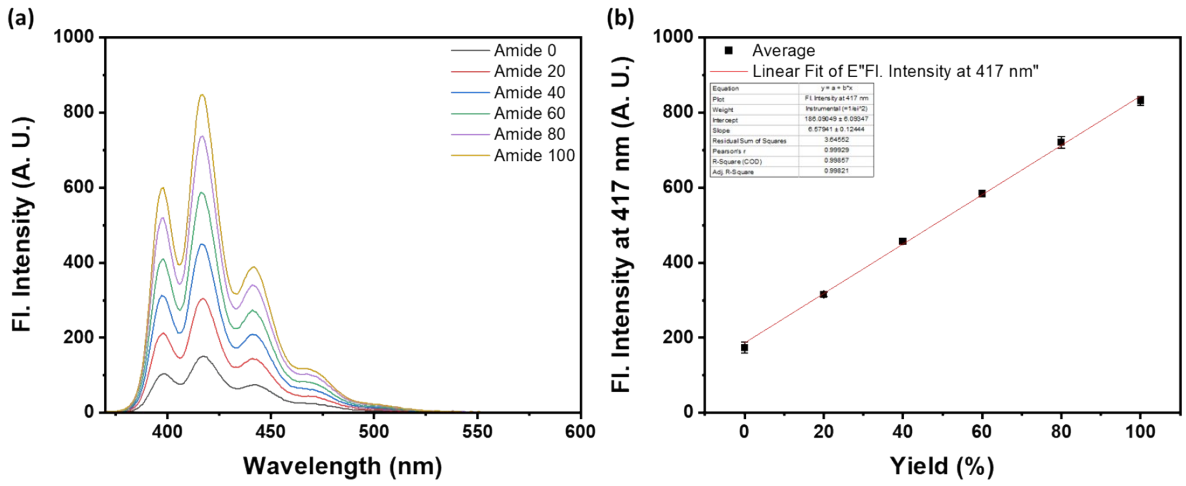


Figure S2. (a) Fluorescent spectra of mixed solutions of anthracen-9-ylmethanaminium benzoate (**2**) and *N*-(anthracen-9-ylmethyl)benzamide (**1**) depending on the progress of the amidation reaction. The sum of concentration of **1** and **2** was 100 μM in xylene/DMSO (1/999, v/v). Excitation

light at 369 nm was irradiated, and fluorescence spectra were recorded over the 370–600 nm range. (Excitation/emission slit width: 5 nm/5 nm, PMT: 450 V) (b) Plot of fluorescence intensity at 417 nm versus various mixing ratio of anthracen-9-ylmethanaminium benzoate (**2**) and *N*-(anthracen-9-ylmethyl)benzamide (**1**) depending on the progress of the amidation (average of 3 repeated measurements). The yield of the reaction is calculated as (F. $I._{417\ nm}$-186.09049)/6.57941 (%).

3.3. Fluorescence interference by arylboronic acid derivative catalysts

To evaluate whether the boronic acid derivative catalysts assessed in this screening interfere with fluorescence measurements, the fluorescence of mixtures containing the salt probe and catalysts, as well as the amide product and catalyst were measured. While it cannot be conclusively stated that all boronic acids do not interfere with the fluorescence measurements, it was confirmed that the boronic acid derivative catalysts used in this experiment did not interfere much with fluorescence.

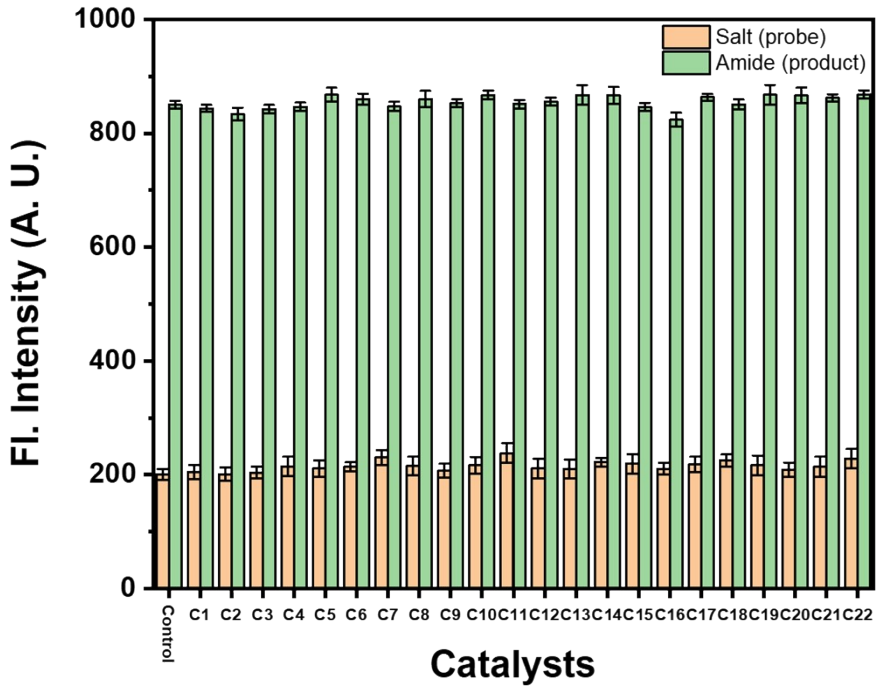


Figure S3. Fluorescence measurement of mixed solutions of anthracen-9-ylmethanaminium benzoate salt (**2**) or *N*-(anthracen-9-ylmethyl)benzamide (**1**) with arylboronic acid derivative catalysts. The concentrations of salt, amide, and boronic acid derivative catalysts were 100 μM in xylene/DMSO (1/999, v/v). Control samples do not contain any catalyst. Excitation light at 369 nm was irradiated, and the fluorescence intensities at 417 nm were plotted. (Excitation/emission slit width: 5 nm/5 nm, PMT 450 V)

3.4. Fluorescence emission behavior of probe and product

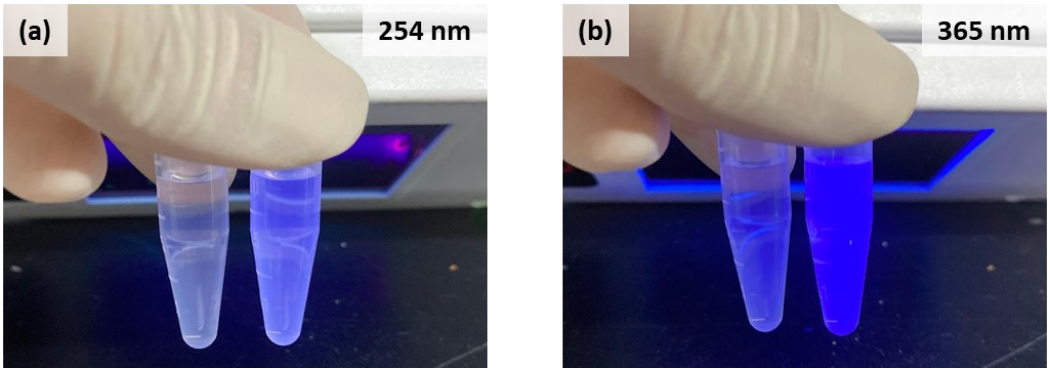


Figure S4. Fluorescence turn-on property between anthracen-9-ylmethanaminium benzoate (**2**, left tube) and *N*-(anthracen-9-ylmethyl)benzamide (**1**, right tube). Excitation light at 254 nm (a) and 365 nm (b) irradiated by hand UV. Probe (**2**) and the amidation product (**1**) were dissolved in DMSO (0.1 mM) each.

4. Procedure for fluorescence-based screening of amidation

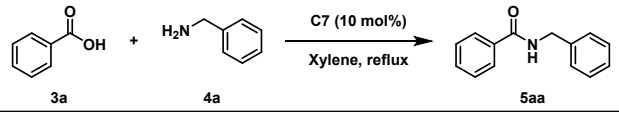
In 5 mL volume vials, anthracen-9-ylmethanaminium benzoate (**2**, 16.5 mg, 50 μmol) and boronic acid derivative catalysts (50 μmol) were dissolved in xylenes (mixture of isomers, 99.0%, 0.5 mL). These reaction mixtures were stirred at 130 °C for 4 h in a heating block. After the reactions, 2 mL of DMSO was added, and the mixtures were diluted 1/200 with DMSO for analysis by fluorescence spectrophotometry. Final concentration of the fluorescence probe (based on the amount of used aminium benzoate salt **2**) was 100 μM in xylene/DMSO (1/999, v/v) for the fluorescence measurement. Excitation light at 369 nm was irradiated, and fluorescence spectra were recorded over the 370–740 nm range. (excitation/emission slit width: 5 nm/5 nm, PMT: 450 V)

5. Reaction condition optimization – dehydration method

The direct amidation reaction of aromatic carboxylic acid using the hit catalyst **C7** revealed that the removal of by-product water is crucial. Using a Dean-Stark apparatus to remove water resulted in a high yield of 91% of **5aa** (entry 1). Under the same reaction conditions, replacing the Dean-Stark apparatus with the combination of simple reflux condenser and molecular sieves as the desiccant resulted in a high yield of 91% for **5aa** (entry 2). To eliminate errors due to the degree of molecular sieve activation, and ensure reproducible and effective water removal, while also

simplifying the work-up process, we used the Dean-Stark apparatus instead of molecular sieves in subsequent substrate scope experiments.

Table S1. Dehydration method test[a]



3a 4a 5aa

Entry	Conditions	Yield[b] (%)
1	Dean-Stark apparatus	91
2	Simple reflux condenser, with 4Å molecular sieves[c]	91

[a]Reaction conditions: 0.55 mmol of benzoic acid, 0.50 mmol of benzylamine, and 0.05 mmol of 2-hydroxyphenylboronic acid as catalyst in xylene 5 mL, refluxed for 6 h. [b]Isolated yield. [c]1 g of powdered activated 4Å molecular sieves

6. Putative mechanism for aromatic direct amidation with catalyst C7

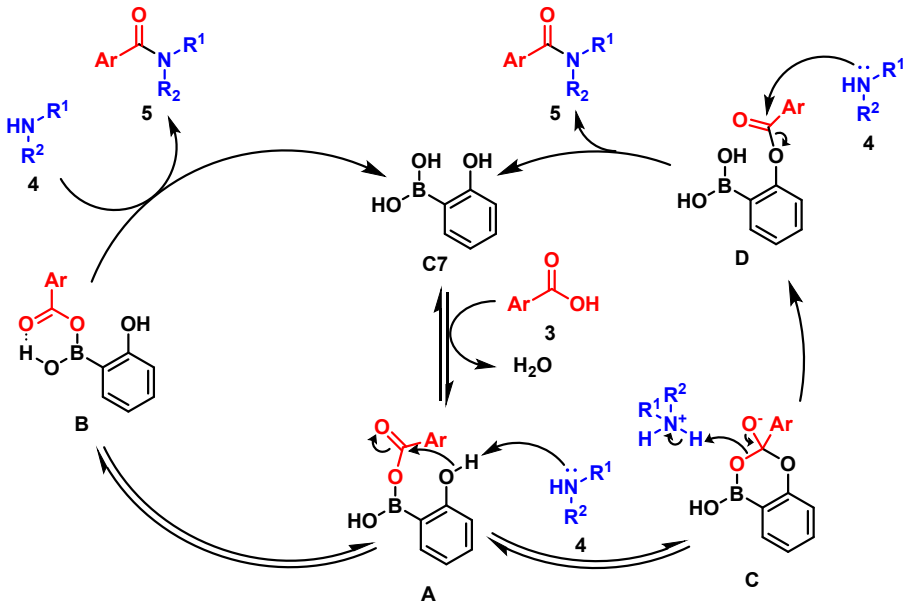


Figure S5. Putative mechanism for aromatic direct amidation with catalyst C7.

Herein, we proposed putative mechanism for catalytic direct amidation by 2-hydroxyphenylboronic acid (**C7**). Firstly, the widely accepted intermediate **A** is formed through a dehydration between the boronic acid (**C7**) and the aromatic carboxylic acid (**3**).[4] When intermediate **B** is formed through intramolecular hydrogen bonding, the electrophilic activation of the carboxylate group occurs due to boron conjugation and the hydrogen bonding.[5] Then, intermediate **B** is easily

attacked by the amine (**4**), leading to the formation of the amide product (**5**). Alternatively, similar to recent report that a six-membered ring structure can be formed by the nucleophilic attack of sulfur at the *ortho*-position of boron,[6] the hydroxyl group in intermediate **A** may nucleophilic attack the carbonyl group, resulting in the formation of a six-membered ring structure **C**. After transforming into intermediate **D**, this intermediate is then attacked by the amine (**4**), leading to the formation of the amide (**5**). Given the potential for catalysis through these two pathways, catalyst C7, which incorporates a hydroxyl group at the *ortho*-position, would have shown high catalytic activity.

7. Substrate scope

7.1. General procedure for amidation of aromatic carboxylic acids with amines

For the amidation reactions, aromatic carboxylic acids (0.55 mmol) and 2-hydroxyphenylboronic acid (6.9 mg, 0.05 mmol) were dissolved in xylenes (mixture of isomers, 99.0%, 5 mL), and amines (0.50 mmol) were subsequently added. These mixtures were refluxed for 6 h using a Dean-Stark apparatus to remove water. After completing the reaction, the solvent was evaporated under reduced pressure, and the remaining residue was purified by column chromatography using silica gel (SiO_2) with eluents of EtOAc/hexane, EtOAc/CH_2Cl_2, or CH_2Cl_2, depending on the specific requirements of the purification process.

7.2. Characterization of amide products

N-Benzylbenzamide (5aa)

Ethyl acetate/hexane (1/5, v/v) as an eluent. White solid (96.6 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.81 (m, 2H), 7.28–7.53 (m, 8H), 6.38 (s, 1H), 4.66 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.53, 138.33, 134.43, 131.60, 128.82, 128.63, 127.94, 127.62, 127.09, 44.13.

N-Benzyl-4-methoxybenzamide (5ba)

Ethyl acetate/dichloromethane (1/20, v/v) as an eluent. White solid (88.4 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.78 (m, 2H), 7.27–7.36 (m, 5H), 6.90–6.94 (m, 2H), 6.30 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.03, 162.25, 138.55, 128.91, 128.78, 127.93, 127.55, 126.70, 113.79, 55.47, 44.07.

N-Benzyl-4-methylbenzamide (5ca)

Ethyl acetate/hexane (1/5, v/v) as an eluent. White solid (95.3 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.71 (m, 2H), 7.33–7.36 (m, 4H), 7.27–7.32 (m, 1H), 7.22–7.24 (m, 2H), 6.34 (s, 1H), 4.65 (d, *J* = 5.6 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.42, 142.02, 138.50, 131.68, 129.32, 128.84, 127.99, 127.63, 127.10, 44.15, 21.53.

N-Benzyl-4-fluorobenzamide (5da)

Dichloromethane as an eluent. White solid (101.1 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.83 (m, 2H), 7.29–7.39 (m, 5H), 7.08–7.14 (m, 2H), 6.33 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52, 166.06, 163.55, 138.20, 130.61, 130.58, 129.50, 129.41, 128.86, 127.93, 127.70, 115.76, 115.54, 44.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.96.

N-Benzyl-4-chlorobenzamide (5ea)

Dichloromethane as an eluent. White solid (108.4 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.75 (m, 2H), 7.29–7.42 (m, 7H), 6.38 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.45, 138.05, 137.90, 132.81, 128.94, 128.55, 128.04, 127.83, 44.32.

***N*-Benzyl-4-trifluoromethylbenzamide (5fa)**

Ethyl acetate/hexane (1/5, v/v) as an eluent. White solid (125.0 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.30–7.40 (m, 5H), 6.44 (s, 1H), 4.66 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.22, 137.83, 137.74, 129.01, 128.08, 127.97, 127.59, 125.83, 125.80, 125.76, 125.72, 77.48, 77.16, 76.84, 44.44. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.84.

***N*-Benzyl-4-nitrobenzamide (5ga)**

Ethyl acetate/hexane (1/3, v/v) as an eluent. Yellow solid (115.3 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–8.30 (m, 2H), 7.93–7.97 (m, 2H), 7.30–7.41 (m, 5H), 6.43 (s, 1H), 4.67 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.51, 149.68, 140.00, 137.55, 129.02, 128.32, 128.04, 128.03, 123.92, 44.53.

***N*-Benzyl-3-methylbenzamide (5ha)**

Ethyl acetate/dichloromethane (1/100, v/v) as an eluent. White solid (99.0 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.55–7.59 (m, 1H), 7.28–7.37 (m, 7H), 6.39 (s, 1H), 4.65 (d, *J* = 5.7 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.70, 138.48, 138.39, 134.42, 132.33, 128.81, 128.51, 127.95, 127.84, 127.60, 124.04, 44.11, 21.42.

***N*-Benzyl-2-methylbenzamide (5ia)**

Ethyl acetate/dichloromethane (1/50, v/v) as an eluent. White solid (93.7 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.39 (m, 7H), 7.17–7.24 (m, 2H), 6.04 (s, 1H), 4.63 (d, *J* = 5.8 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.03, 138.30, 136.31, 136.24, 131.11, 130.00, 128.85, 127.90, 127.65, 126.76, 125.79, 43.93, 19.93.

***N*-Benzyl-2-naphthamide (5ja)**

Ethyl acetate/dichloromethane (1/100, v/v) as an eluent. White solid (115.1 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.84–7.92 (m, 4H), 7.51–7.59 (m, 2H), 7.30–7.42 (m, 5H), 6.57 (s, 1H), 4.72 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.58, 138.35, 134.83, 132.68, 131.66, 129.01, 128.87, 128.54, 128.04, 127.82, 127.74, 127.69, 127.59, 126.83, 123.73, 44.30.

***N*-Benzylthiophene-3-carboxamide (5ka)**

Ethyl acetate/dichloromethane (1/100, v/v) as an eluent. White solid (94.7 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.28–7.40 (m, 7H), 6.26 (s, 1H), 4.62 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.16, 138.33, 137.36, 128.78, 128.52, 127.91, 127.59, 126.52, 126.24, 43.81.

***N*-(Cyclohexylmethyl)benzamide (5ab)**

Ethyl acetate/hexane (1/5, v/v) as an eluent. White solid (105.1 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.78 (m, 2H), 7.41–7.52 (m, 3H), 6.15 (s, 1H), 3.31 (t, *J* = 6.4 Hz, 2H), 1.57–1.81 (m, 6H), 0.95–1.31 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.71, 134.99, 131.33, 128.57, 126.97, 46.31, 38.10, 31.00, 26.48, 25.91.

***N*-Cyclohexylbenzamide (5ac)**

Ethyl acetate/dichloromethane (1/50, v/v) as an eluent. White solid (99.9 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.76 (m, 2H), 7.40–7.51 (m, 3H), 5.95 (s, 1H), 3.94–4.03 (m, 1H), 2.01–2.07 (m, 2H), 1.72–1.79 (m, 2H), 1.62–1.69 (m, 1H), 1.38–1.49 (m, 2H), 1.19–1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 135.16, 131.26, 128.53, 126.95, 48.77, 33.26, 25.63, 25.02.

Phenyl(piperidin-1-yl)methanone (5ad)

Ethyl acetate/hexane (1/3, v/v) as an eluent. Colorless oil (62.6 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.42 (m, 5H), 3.71 (s, 2H), 3.33 (t, *J* = 5.1 Hz, 2H), 1.67 (s, 4H), 1.51 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.46, 136.53, 129.46, 128.50, 128.35, 126.88, 48.85, 43.24, 26.64, 25.71, 24.68.

***N*-phenylbenzamide (5ae)**

Dichloromethane as an eluent. White solid (36.1 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.89 (m, 2H), 7.79 (s, 1H), 7.63–7.66 (m, 2H), 7.54–7.58 (m, 1H), 7.47–7.52 (m, 2H), 7.36–7.41 (m, 2H), 7.14–7.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.86, 138.09, 135.20, 131.98, 129.25, 128.95, 127.16, 124.73, 120.36.

***N*'-phenylbenzohydrazide (5af)**

Ethyl acetate/dichloromethane (1/50, v/v) as an eluent. White solid (56.5 mg, 53% yield). ^{1}H NMR (400 MHz, DMSO-d6) δ 10.36 (s, 1H), 7.90–7.93 (m, 3H), 7.48–7.60 (m, 3H), 7.13–7.18 (m, 2H), 6.78 (m, 2H), 6.70–6.74 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d6) δ 166.32, 149.53, 133.03, 131.64, 128.75, 128.49, 127.29, 118.63, 112.32.

_N'_-benzoylbenzohydrazide (5ag)

Ethyl acetate/dichloromethane (1/30, v/v) as an eluent. White solid (28.6 mg, 24% yield). ^{1}H NMR (400 MHz, DMSO-d6) δ 10.50 (s, 2H), 7.92–7.94 (m, 4H), 7.51–7.63 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d6) δ 165.86, 132.58, 131.89, 128.54, 127.47.

_N_-(4-aminobenzyl)benzamide (5ah)

Ethyl acetate/dichloromethane (1/5, v/v) as an eluent. Yellow solid (105.1 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.79 (m, 2H), 7.47–7.51 (m, 1H), 7.40–7.44 (m, 2H), 7.14–7.17 (m, 2H), 6.65–6.69 (m, 2H), 6.25 (s, 1H), 4.52 (d, J = 5.4 Hz, 2H), 3.68 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.34, 146.12, 134.67, 131.54, 129.44, 128.66, 128.00, 127.04, 115.38, 43.97.

_N_-(4-benzamidobenzyl)benzamide (5ah')

Ethyl acetate/dichloromethane (1/5, v/v) as an eluent. Yellow solid (7.4 mg, 4% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.89 (m, 3H), 7.78–7.81 (m, 2H), 7.61–7.64 (m, 2H), 7.42–7.58 (m, 6H), 7.35–7.38 (m, 2H), 6.44 (s, 1H), 4.64 (d, J = 5.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.52, 165.88, 137.51, 134.95, 134.55, 134.48, 132.11, 131.76, 128.98, 128.90, 128.78, 127.17, 127.10, 120.75, 43.85.

8. NMR spectra

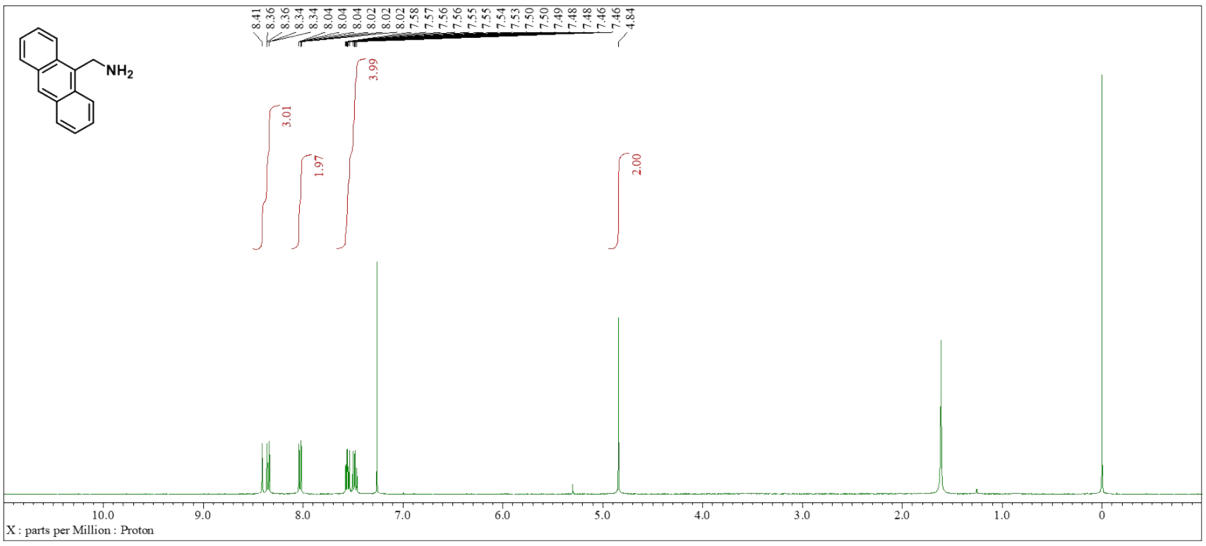


Figure S6. ^{1}H NMR of anthracen-9-ylmethanamine

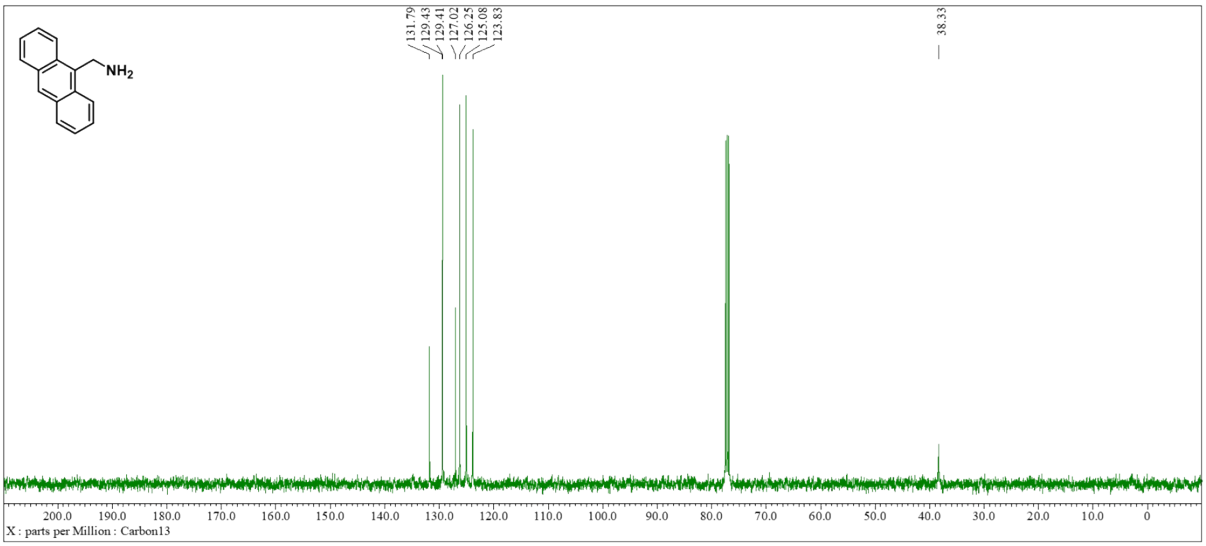


Figure S7. ^{13}C NMR of anthracen-9-ylmethanamine

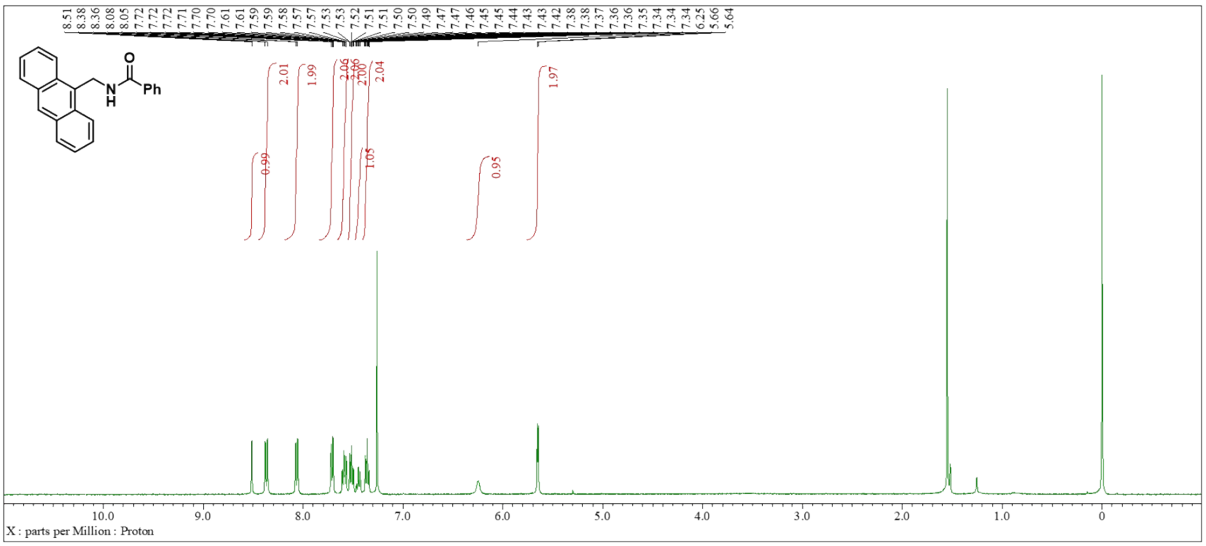


Figure S8. ^{1}H NMR of *N*-(anthracen-9-ylmethyl)benzamide (**1**)

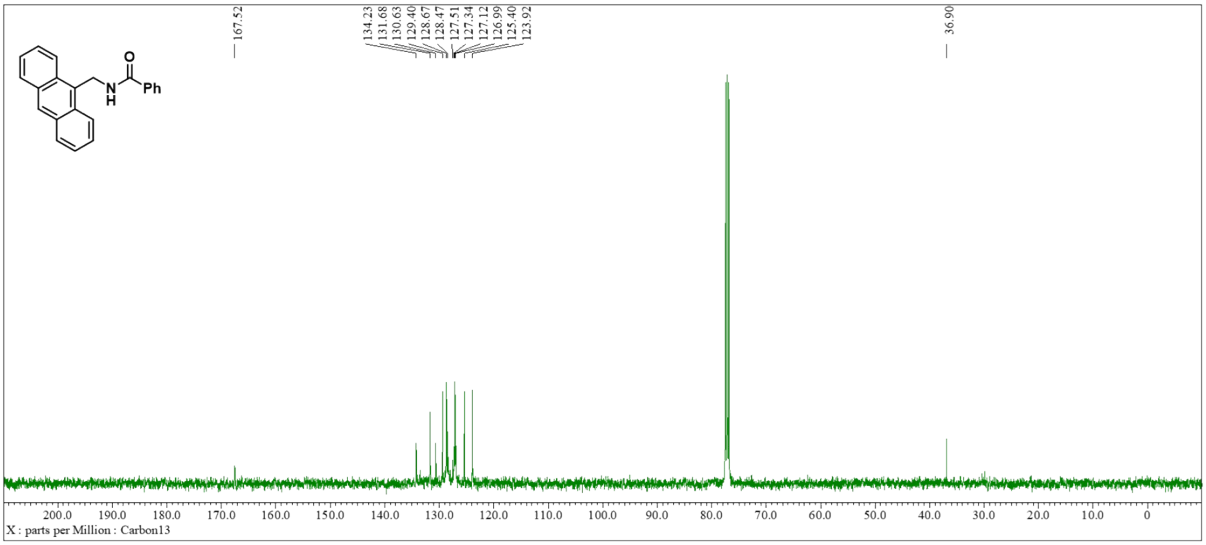


Figure S9. ^{13}C NMR of *N*-(anthracen-9-ylmethyl)benzamide (**1**)

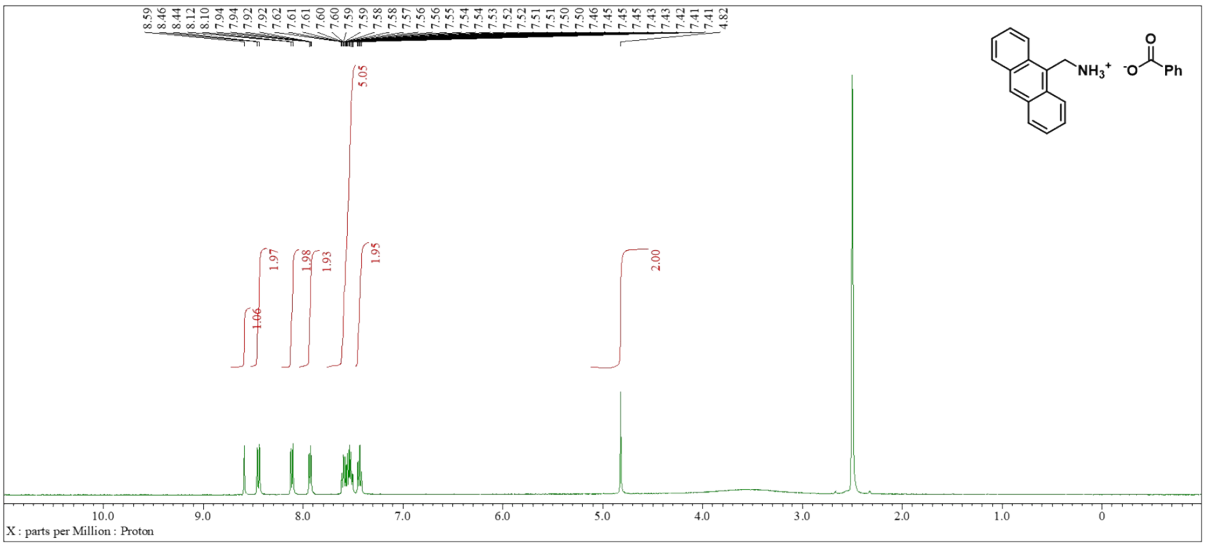


Figure S10. ^{1}H NMR of anthracen-9-ylmethanaminium benzoate (**2**)

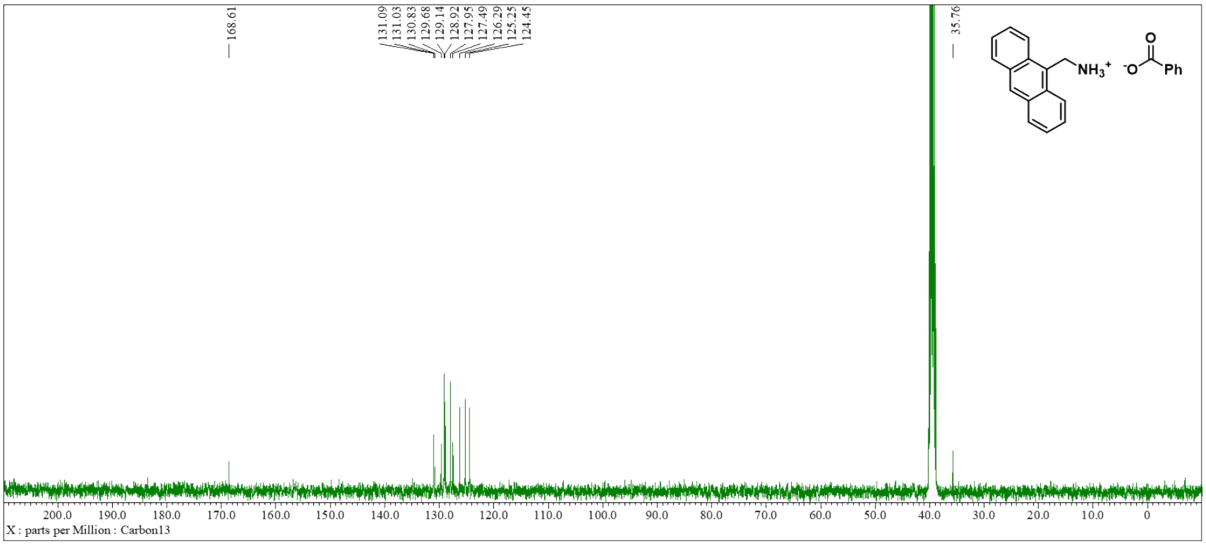


Figure S11. ^{13}C NMR of anthracen-9-ylmethanaminium benzoate (**2**)

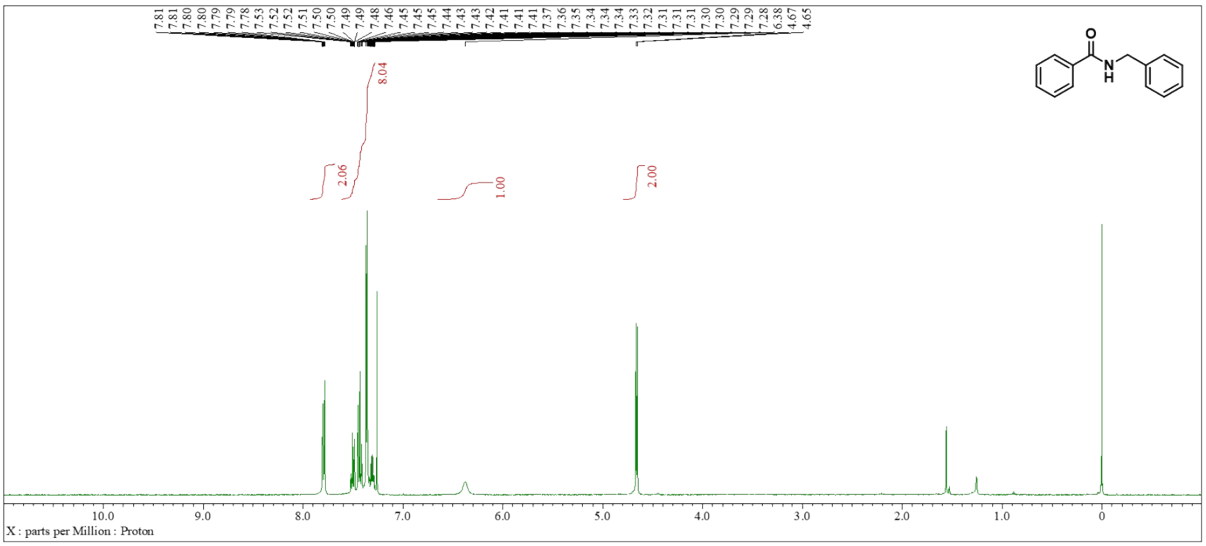


Figure S12. ^{1}H NMR of *N*-Benzylbenzamide (**5aa**)

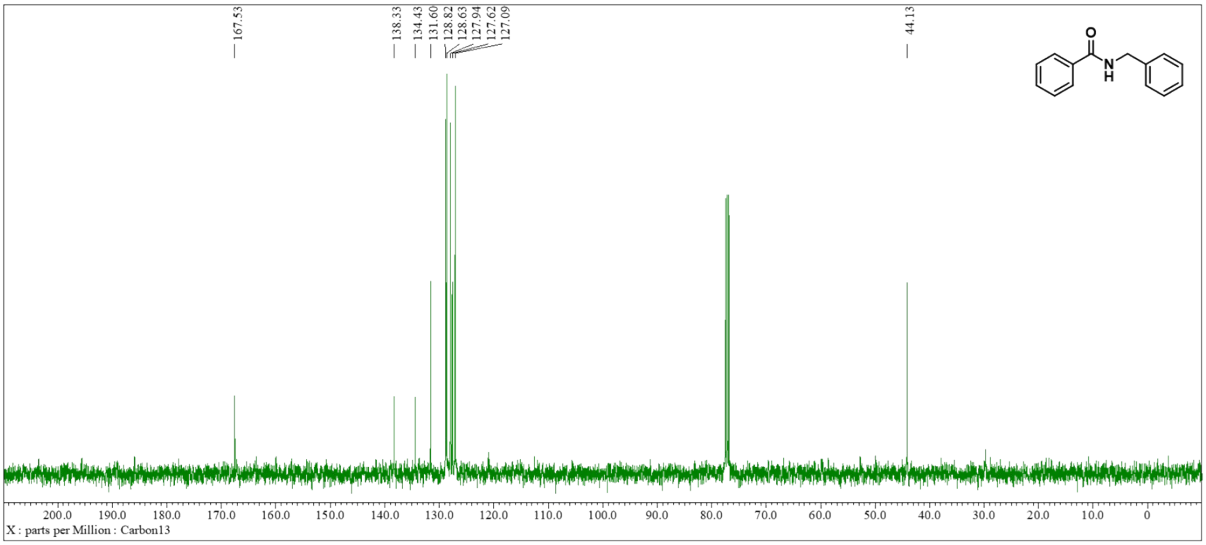


Figure S13. ^{13}C NMR of *N*-Benzylbenzamide (**5aa**)

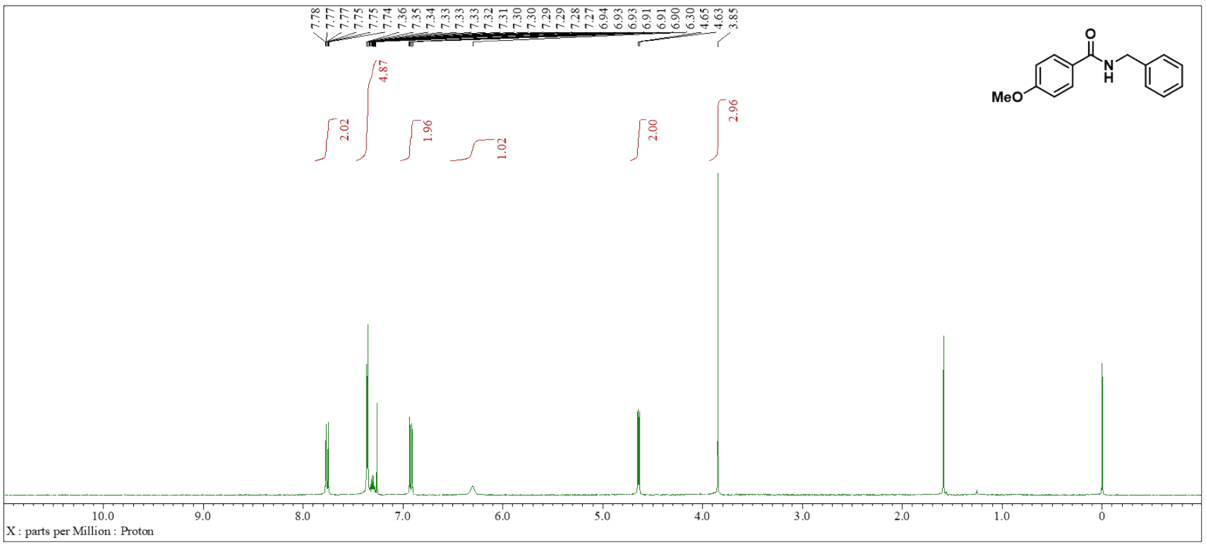


Figure S14. ^{1}H NMR of *N*-Benzyl-4-methoxybenzamide (**5ba**)

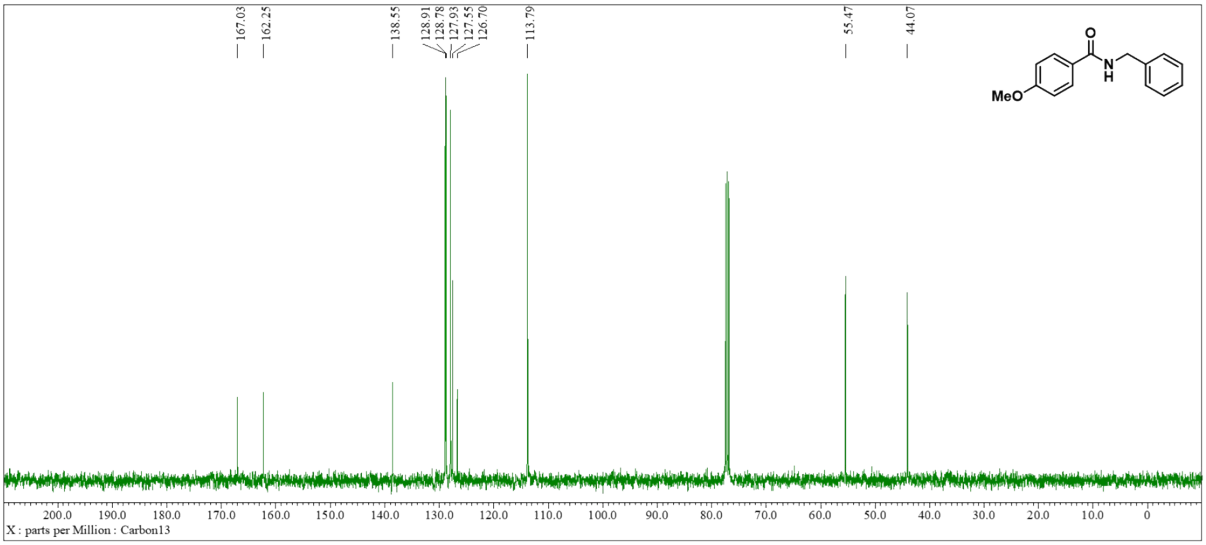


Figure S15. ^{13}C NMR of *N*-Benzyl-4-methoxybenzamide (**5ba**)

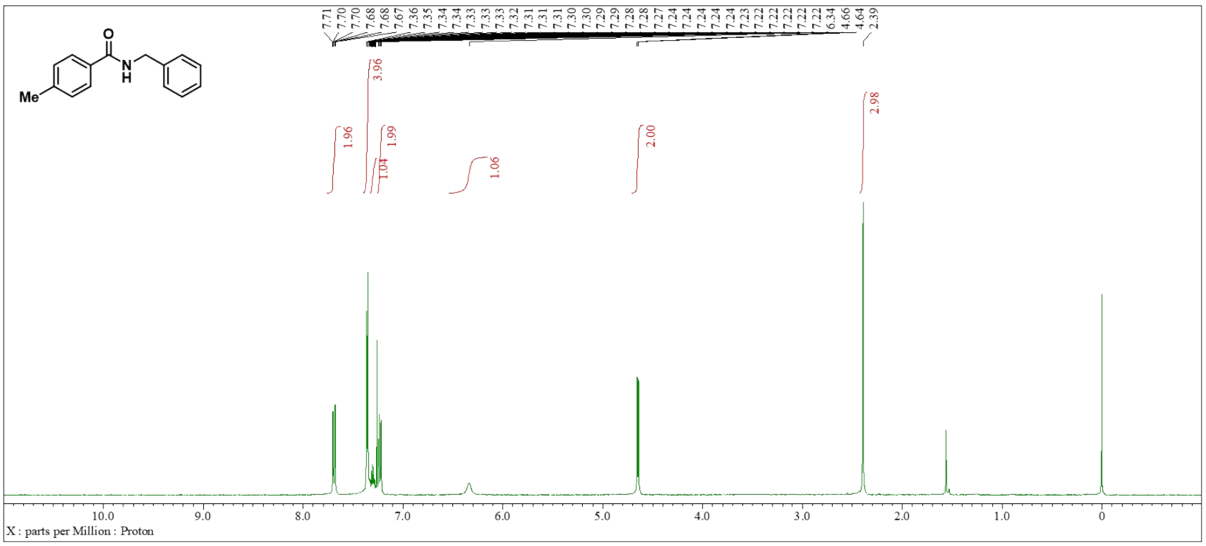


Figure S16. ^{1}H NMR of *N*-Benzyl-4-methylbenzamide (**5ca**)

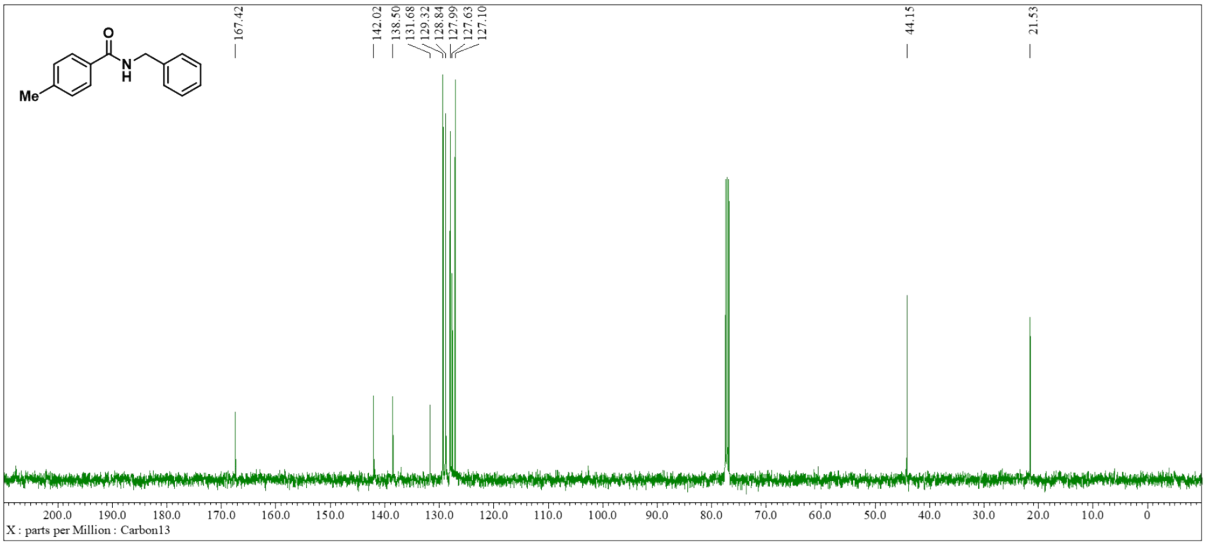


Figure S17. ^{13}C NMR of *N*-Benzyl-4-methylbenzamide (**5ca**)

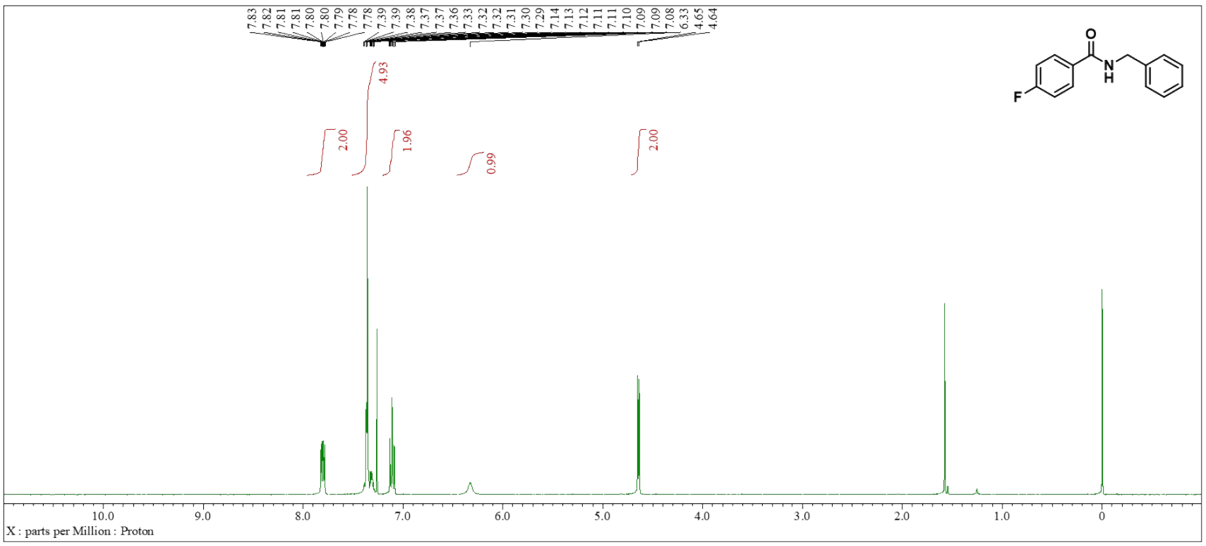


Figure S18. ^{1}H NMR of *N*-Benzyl-4-fluorobenzamide (**5da**)

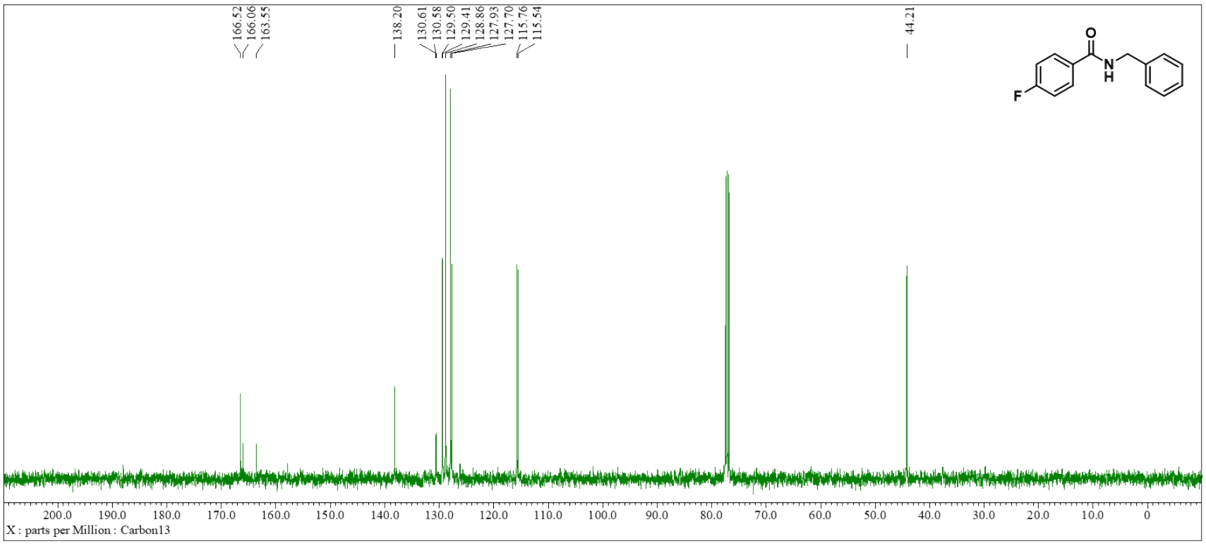


Figure S19. ^{13}C NMR of *N*-Benzyl-4-fluorobenzamide (**5da**)

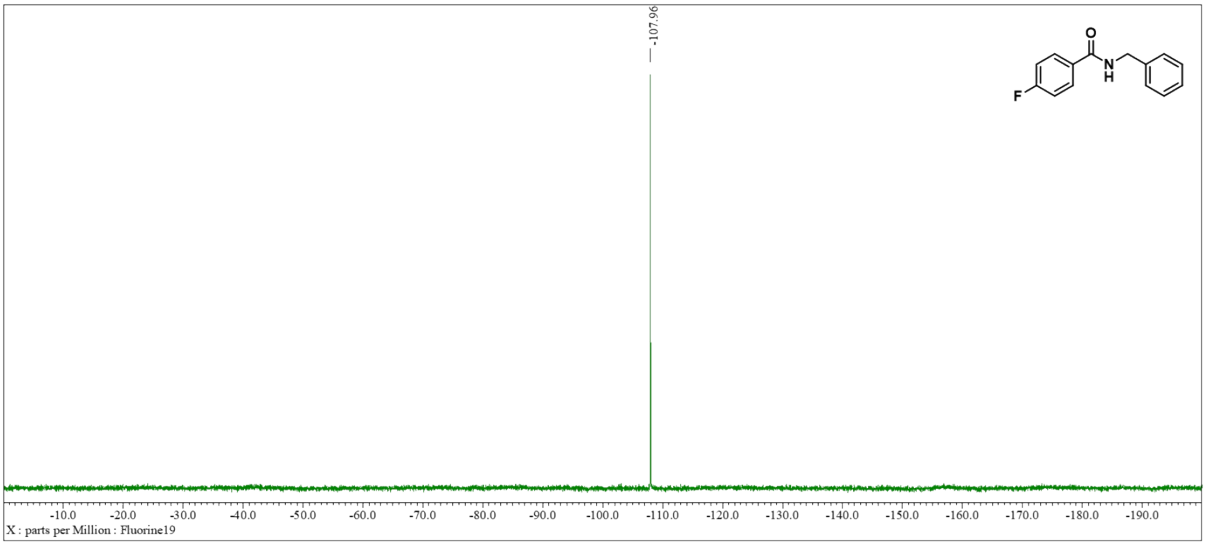


Figure S20. ^{19}F NMR of *N*-Benzyl-4-fluorobenzamide (**5da**)

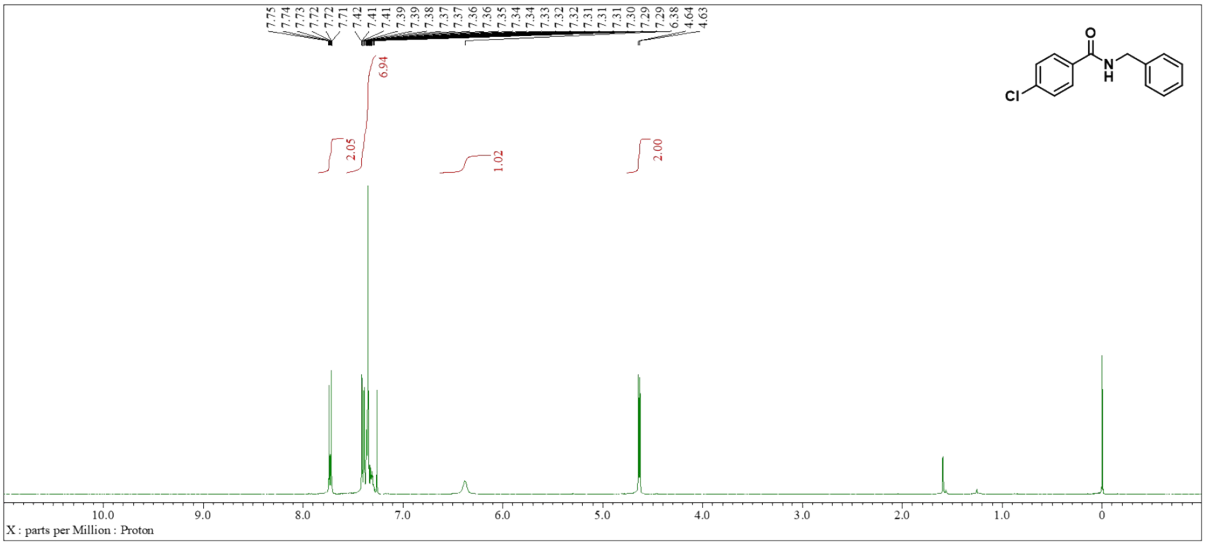


Figure S21. ^{1}H NMR of *N*-Benzyl-4-chlorobenzamide (**5ea**)

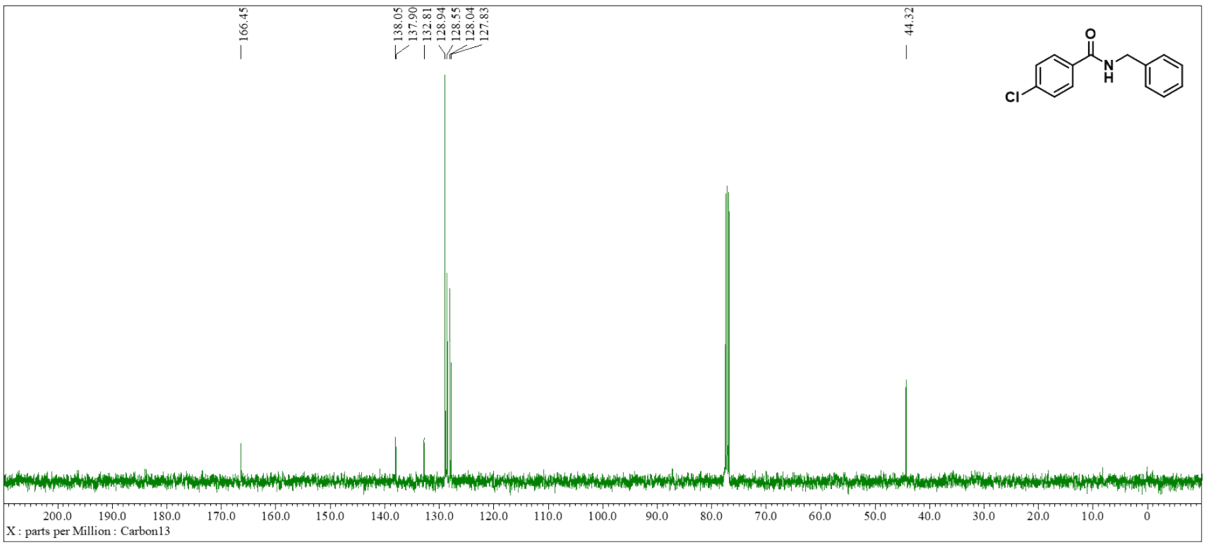


Figure S22. ^{13}C NMR of *N*-Benzyl-4-chlorobenzamide (**5ea**)

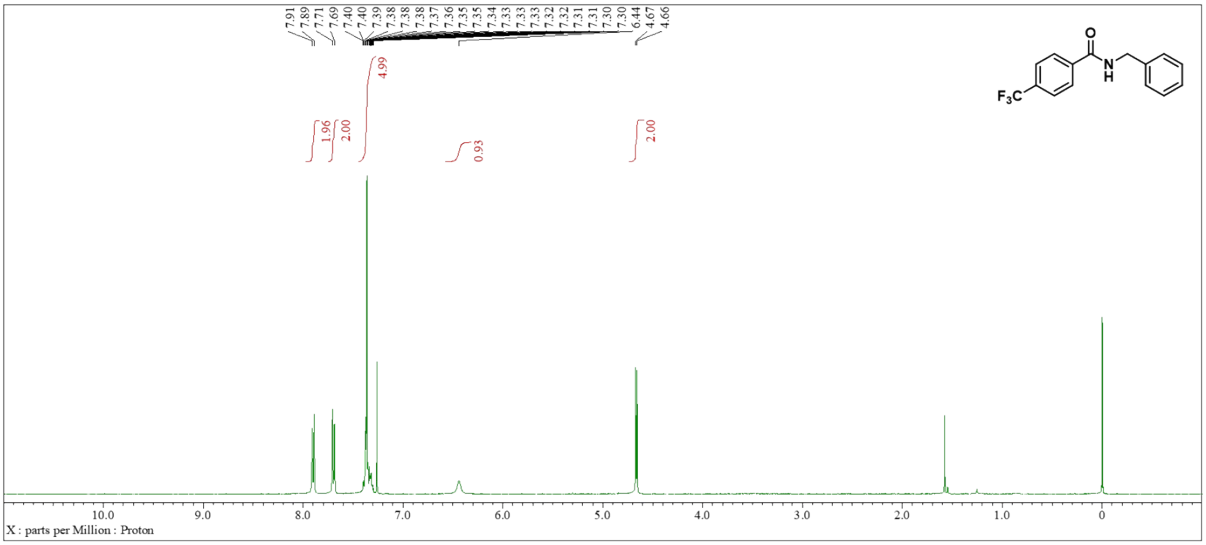


Figure S23. ^{1}H NMR of *N*-Benzyl-4-trifluoromethylbenzamide (**5fa**)

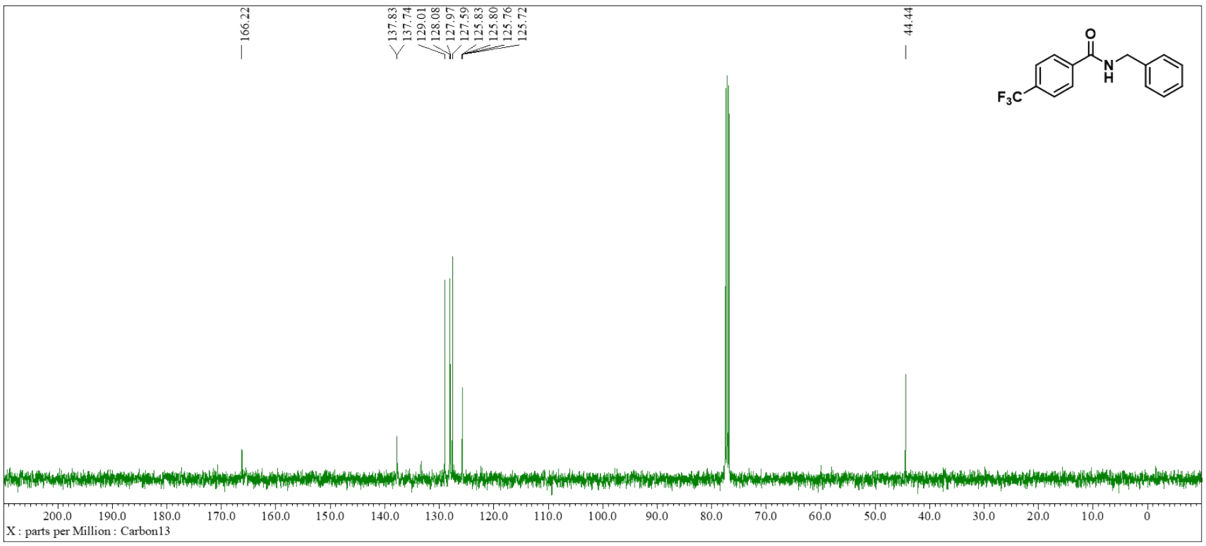


Figure S24. ^{13}C NMR of *N*-Benzyl-4-trifluoromethylbenzamide (**5fa**)

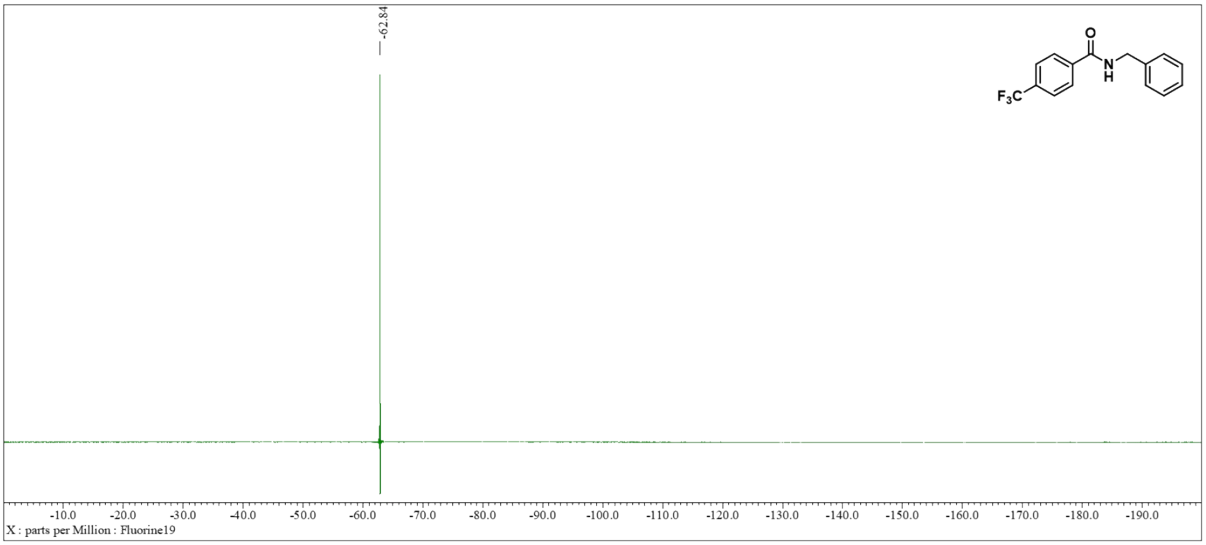


Figure S25. ^{19}F NMR of *N*-Benzyl-4-trifluoromethylbenzamide (**5fa**)

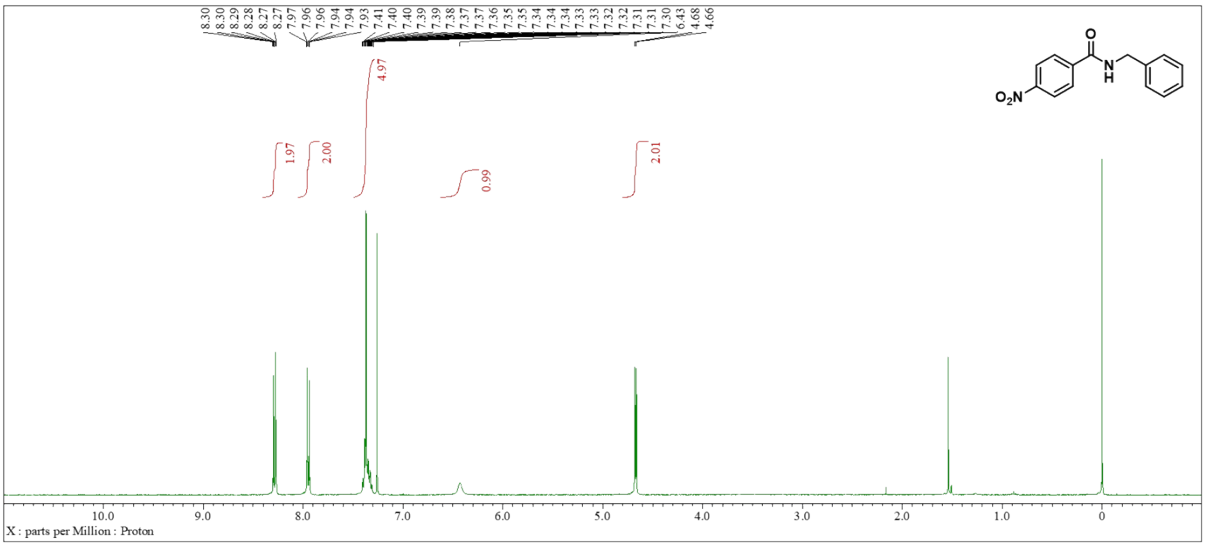


Figure S26. ^{1}H NMR of *N*-Benzyl-4-nitrobenzamide (**5ga**)

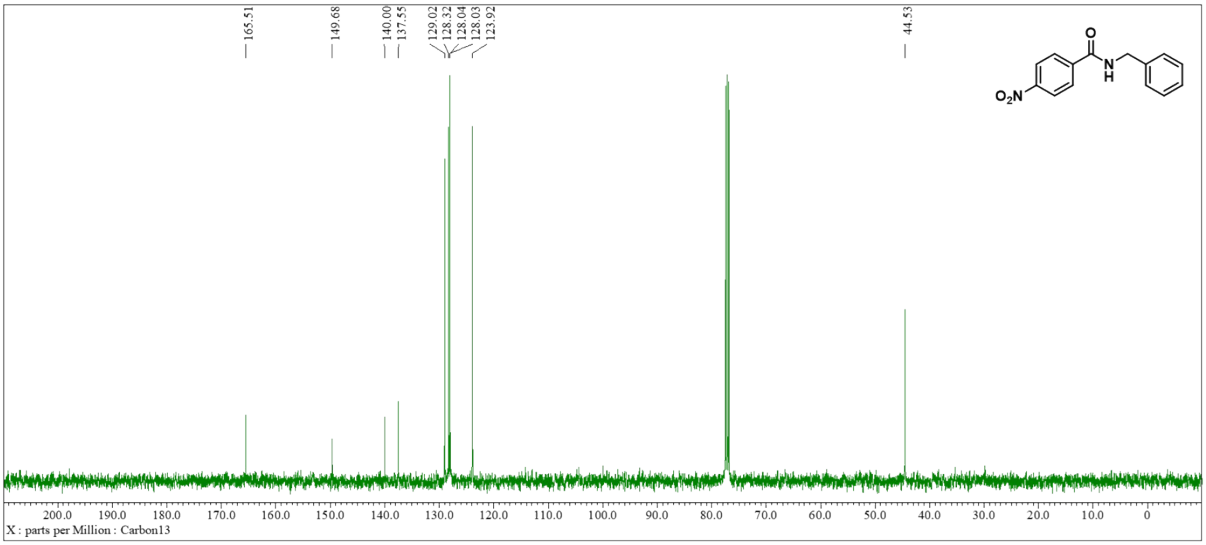


Figure S27. ^{13}C NMR of *N*-Benzyl-4-nitrobenzamide (**5ga**)

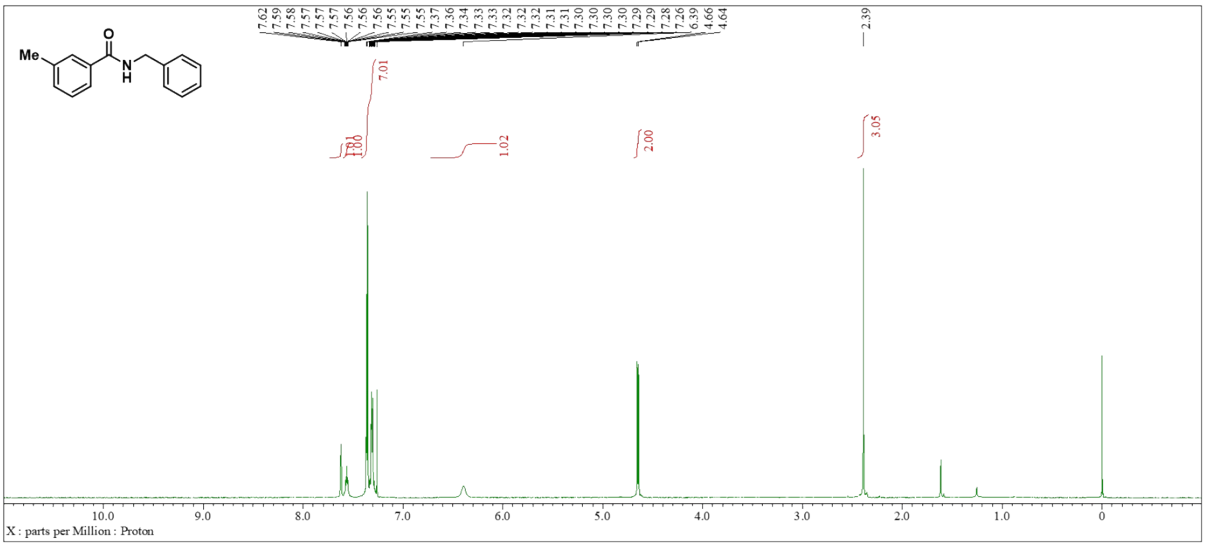


Figure S28. ^{1}H NMR of *N*-Benzyl-3-methylbenzamide (**5ha**)

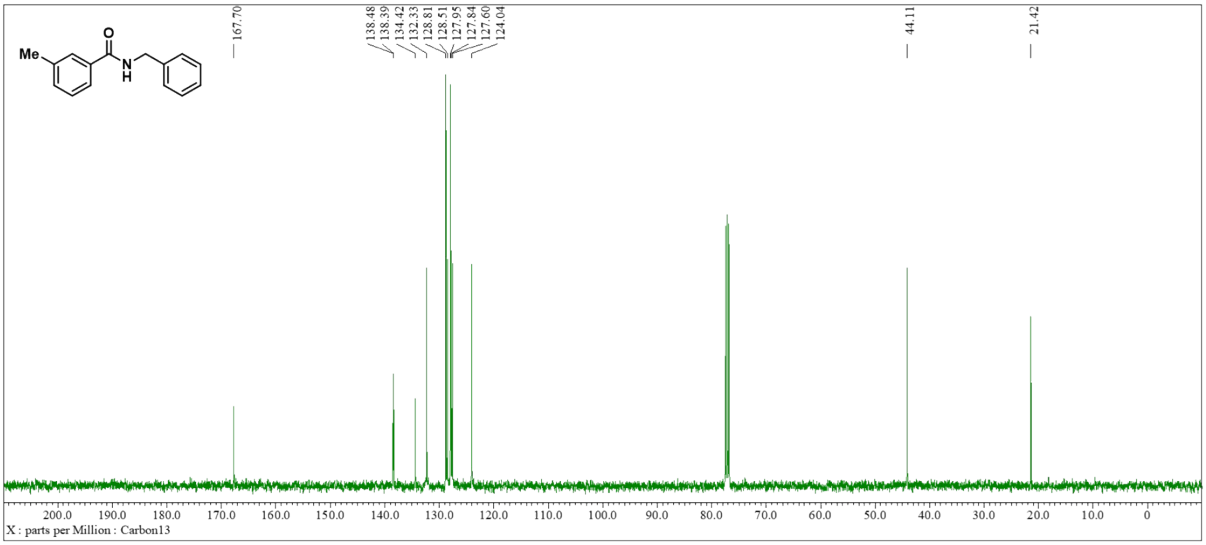


Figure S29. ^{13}C NMR of *N*-Benzyl-3-methylbenzamide (**5ha**)

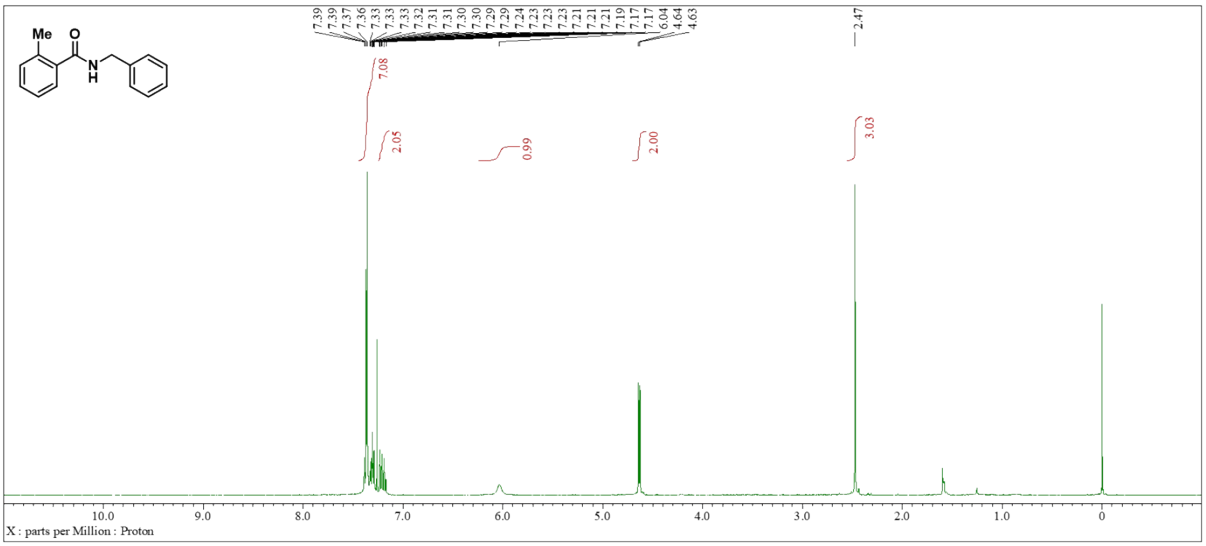


Figure S30. ^{1}H NMR of *N*-Benzyl-2-methylbenzamide (**5ia**)

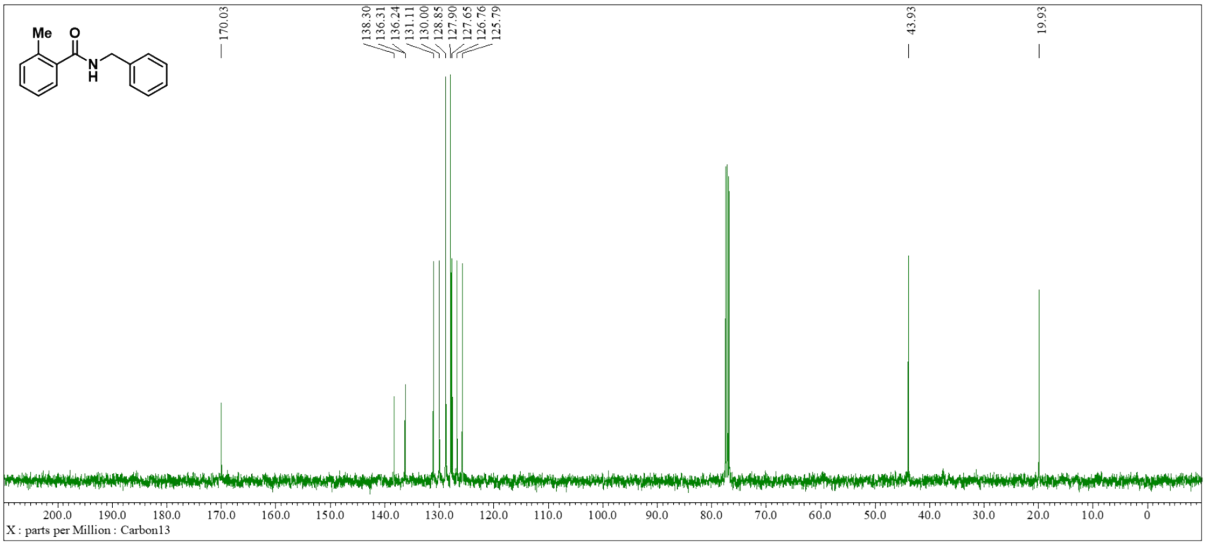


Figure S31. ^{13}C NMR of *N*-Benzyl-2-methylbenzamide (**5ia**)

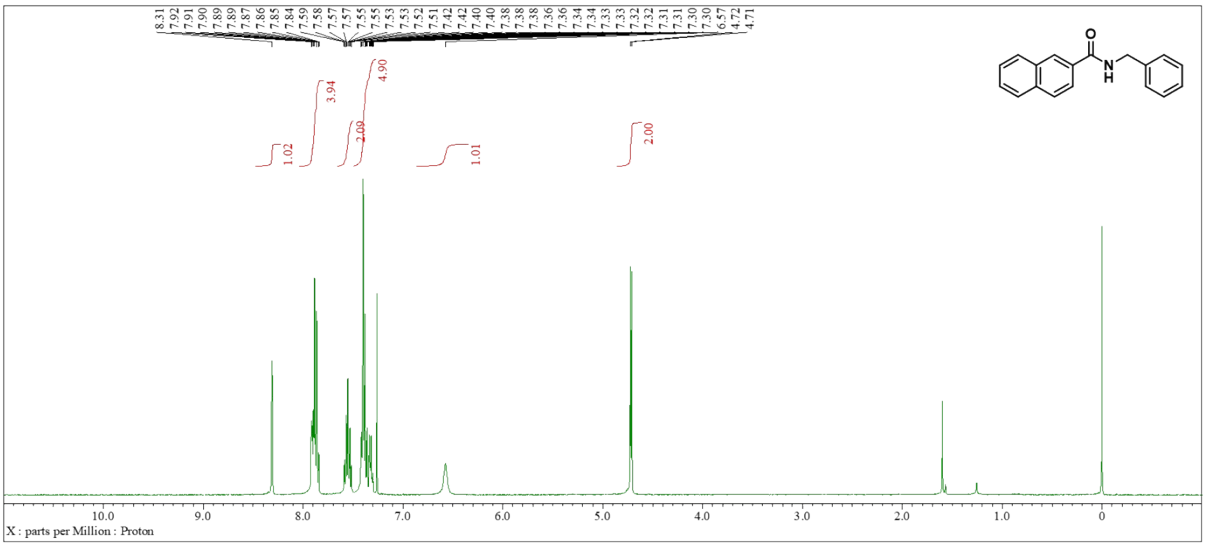


Figure S32. ^{1}H NMR of *N*-Benzyl-2-naphthamide (**5ja**)

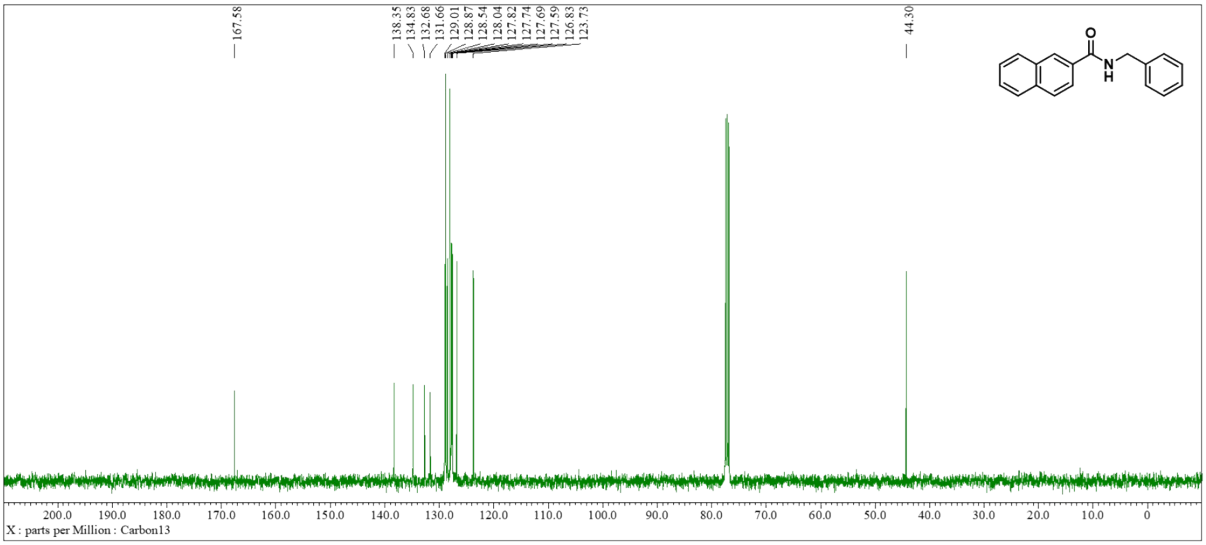


Figure S33. ^{13}C NMR of *N*-Benzyl-2-naphthamide (**5ja**)

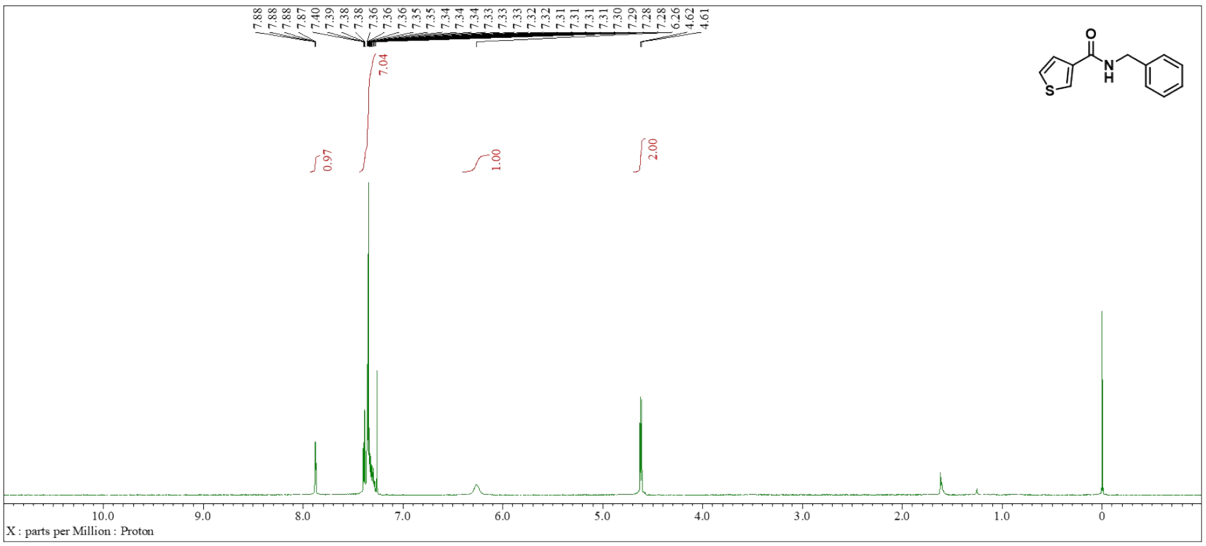


Figure S34. ^{1}H NMR of *N*-Benzylthiophene-3-carboxamide (**5ka**)

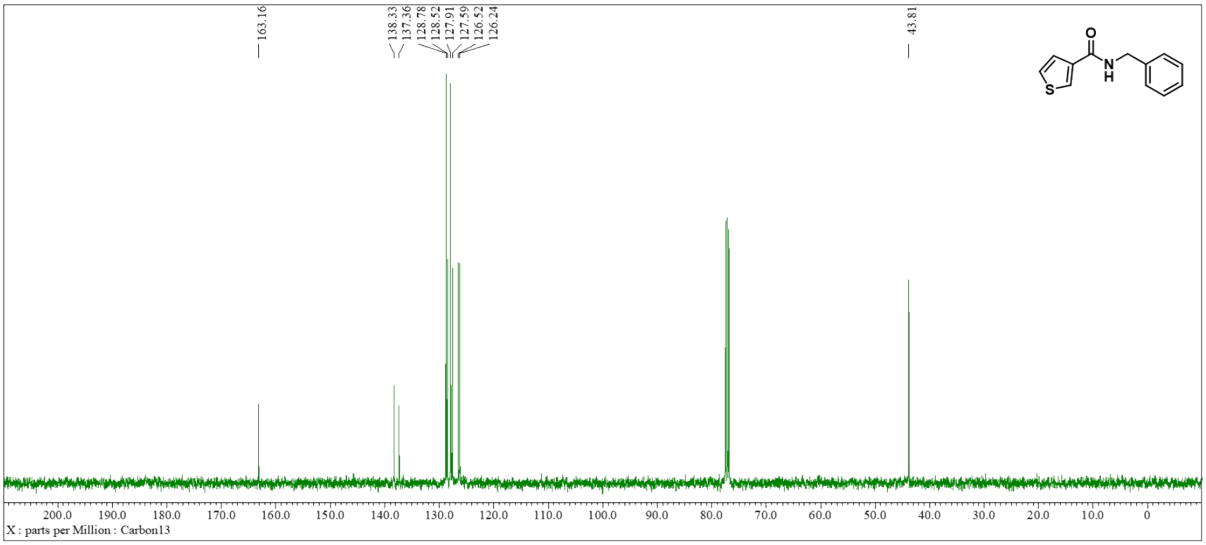


Figure S35. ^{13}C NMR of *N*-Benzylthiophene-3-carboxamide (**5ka**)

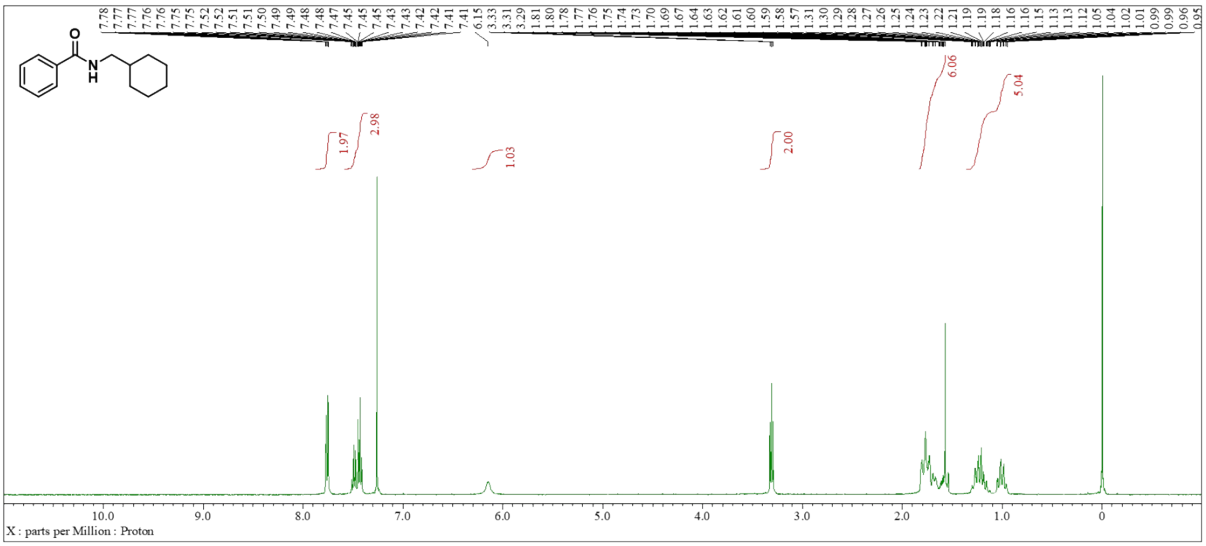


Figure S36. ^{1}H NMR of *N*-(Cyclohexylmethyl)benzamide (**5ab**)

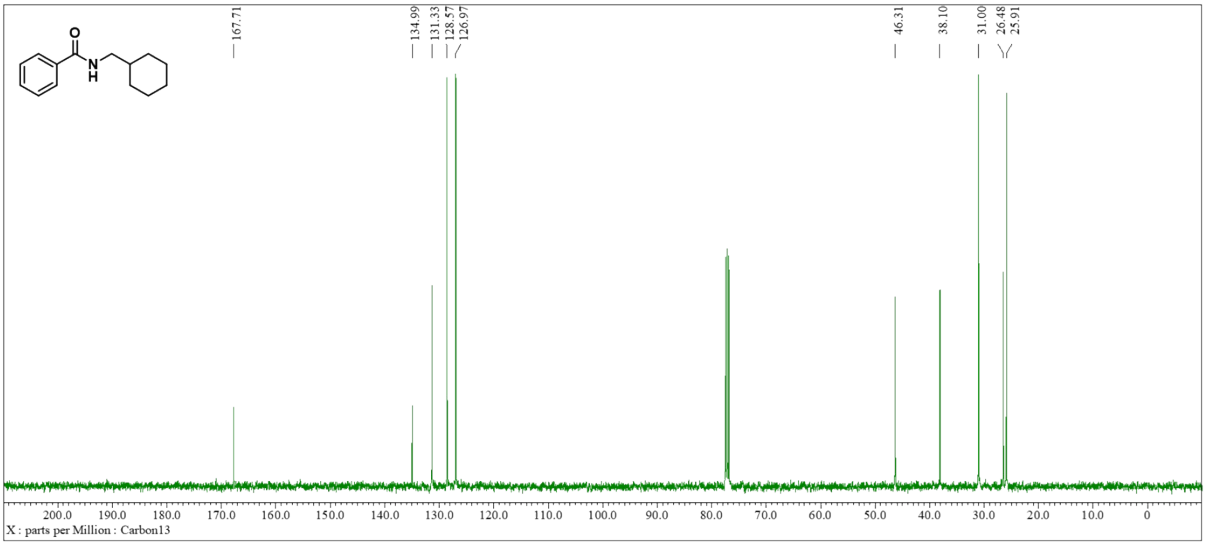


Figure S37. ^{13}C NMR of *N*-(Cyclohexylmethyl)benzamide (**5ab**)

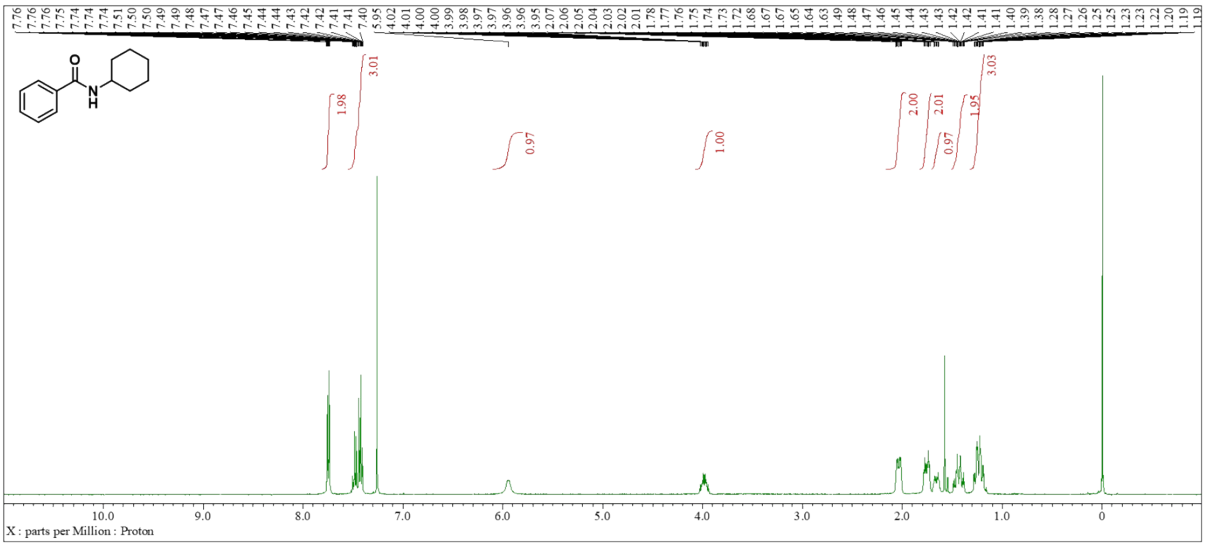


Figure S38. ^{1}H NMR of *N*-Cyclohexylbenzamide (**5ac**)

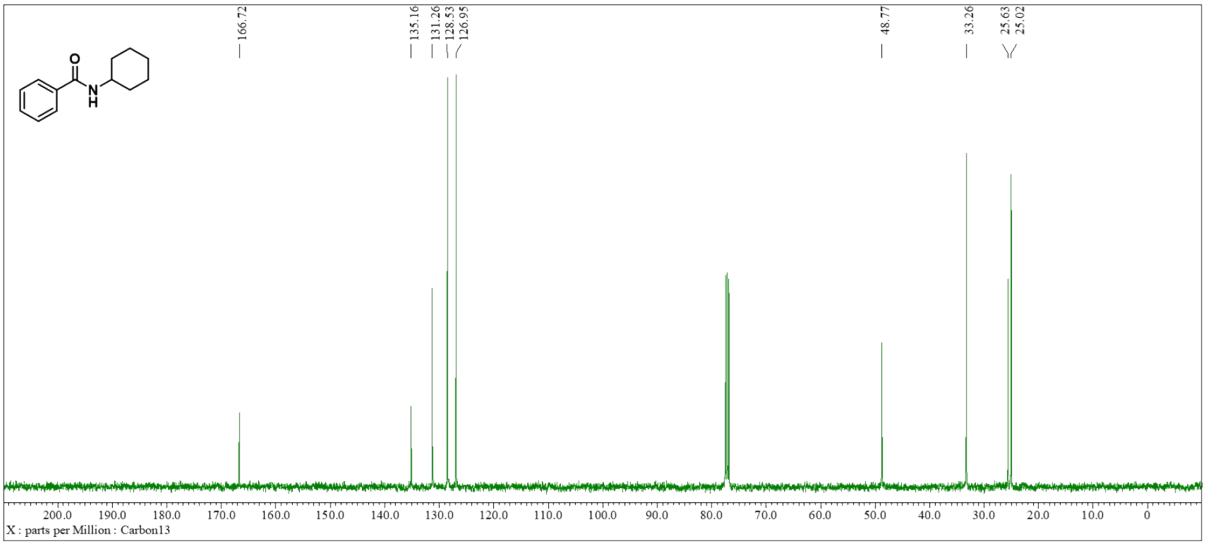


Figure S39. ^{13}C NMR of *N*-Cyclohexylbenzamide (**5ac**)

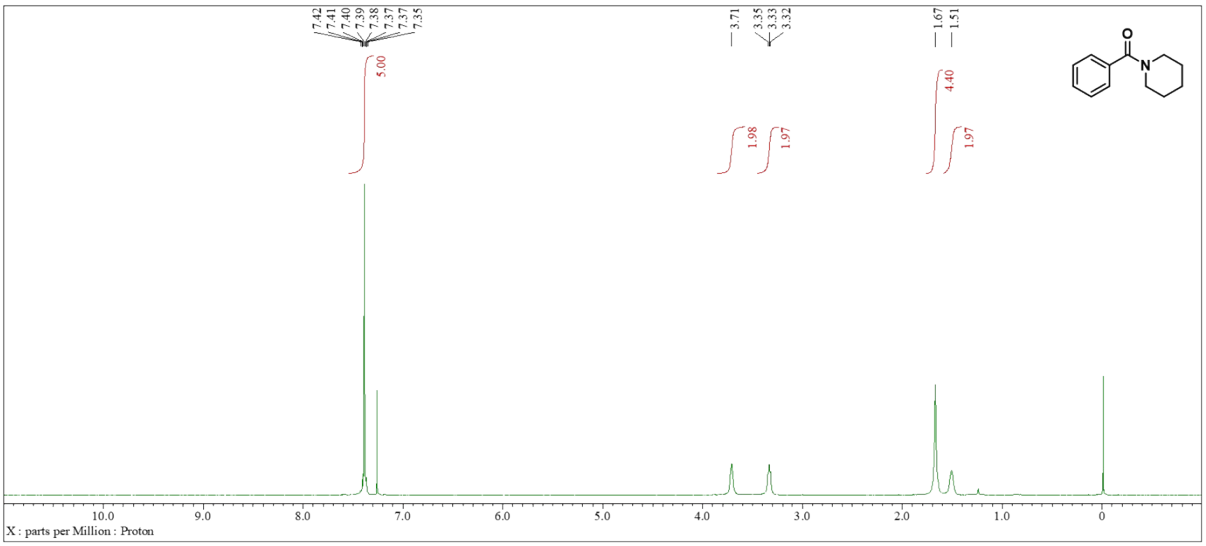


Figure S40. ^{1}H NMR of Phenyl(piperidin-1-yl)methanone (**5ad**)

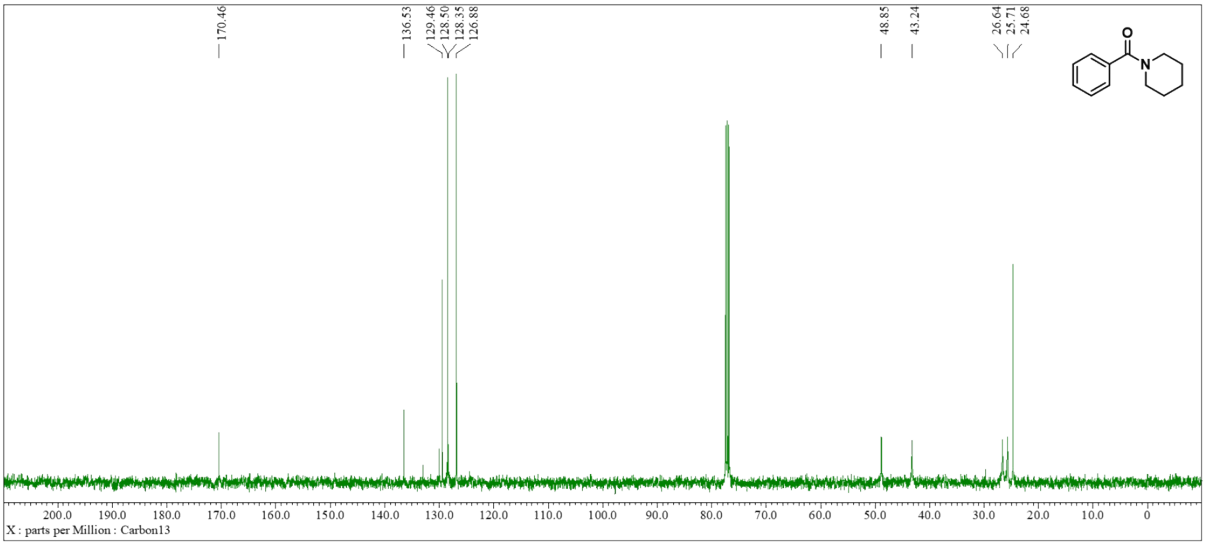


Figure S41. ^{13}C NMR of Phenyl(piperidin-1-yl)methanone (**5ad**)

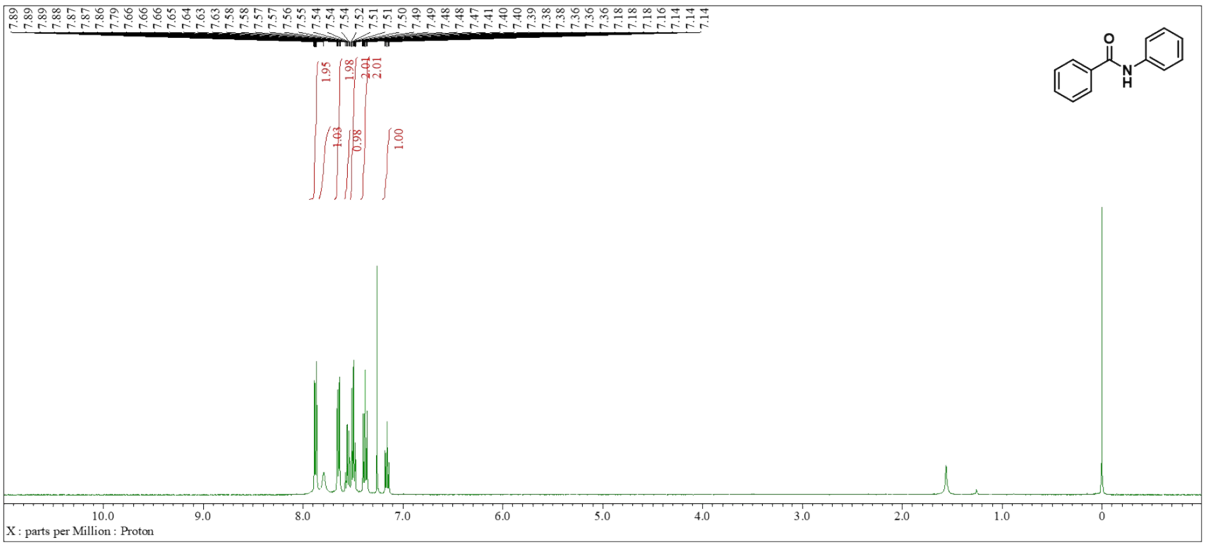


Figure S42. ^{1}H NMR of *N*-phenylbenzamide (**5ae**)

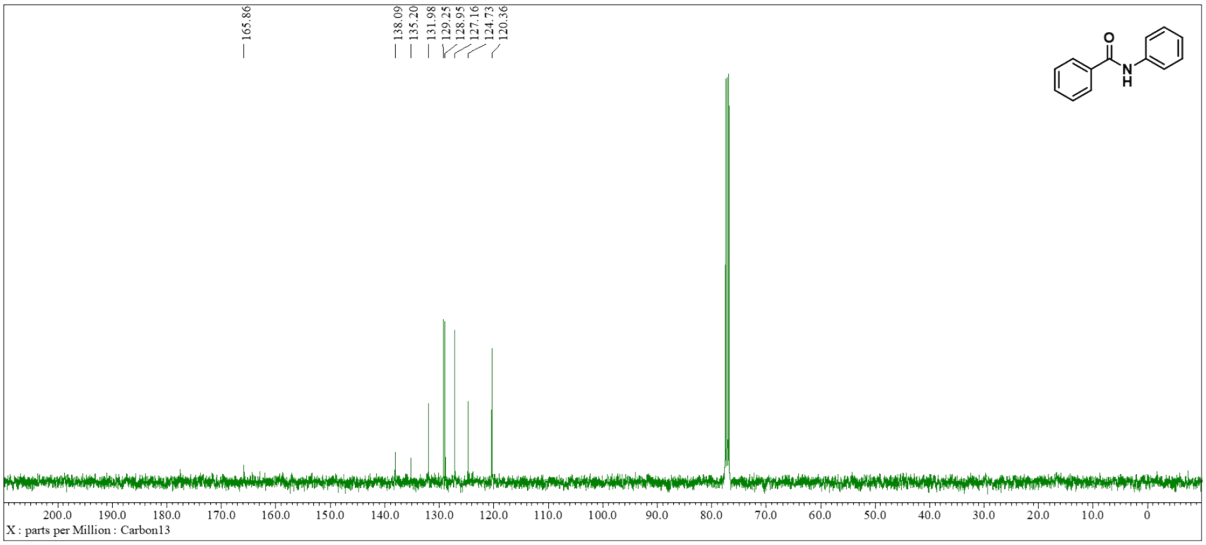


Figure S43. ^{13}C NMR of *N*-phenylbenzamide (**5ae**)

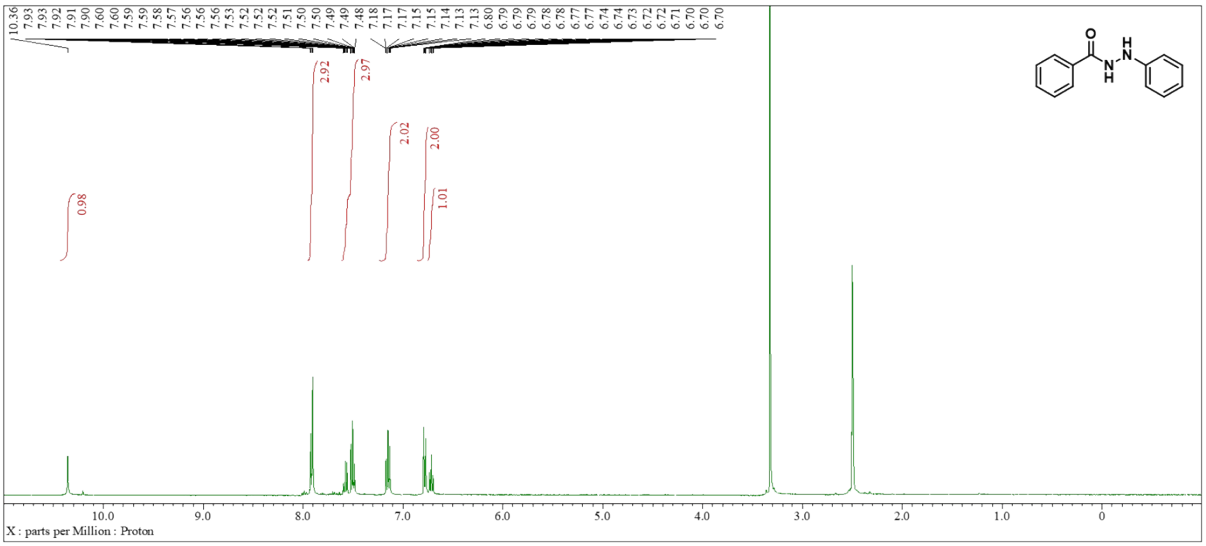


Figure S44. ^{1}H NMR of *N*′-phenylbenzohydrazide (**5af**)

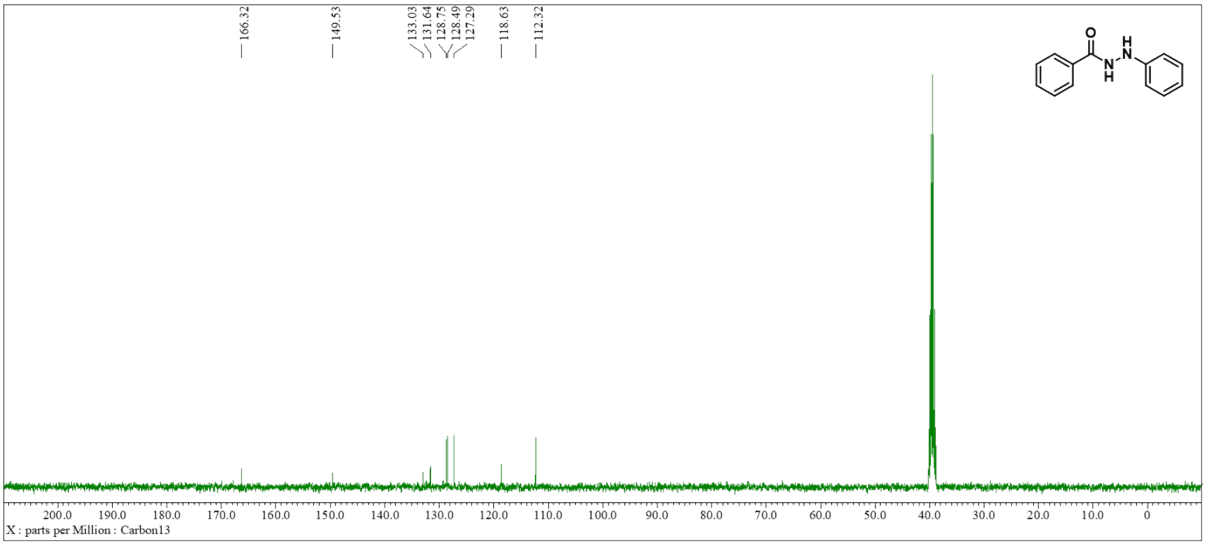


Figure S45. ^{13}C NMR of *N*′-phenylbenzohydrazide (**5af**)

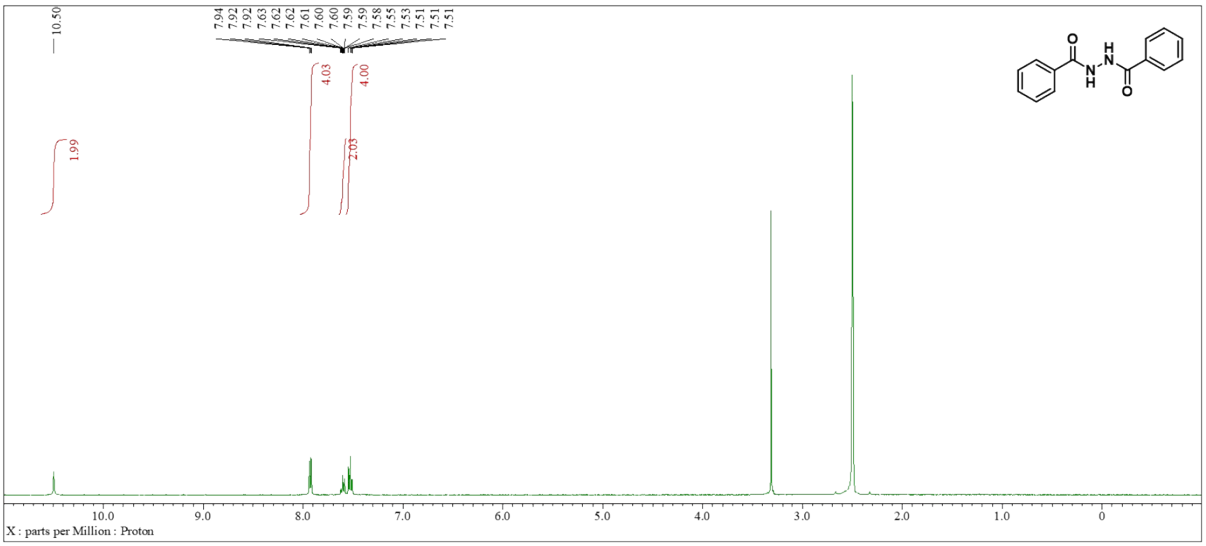


Figure S46. ^{1}H NMR of *N*′-benzoylbenzohydrazide (**5ag**)

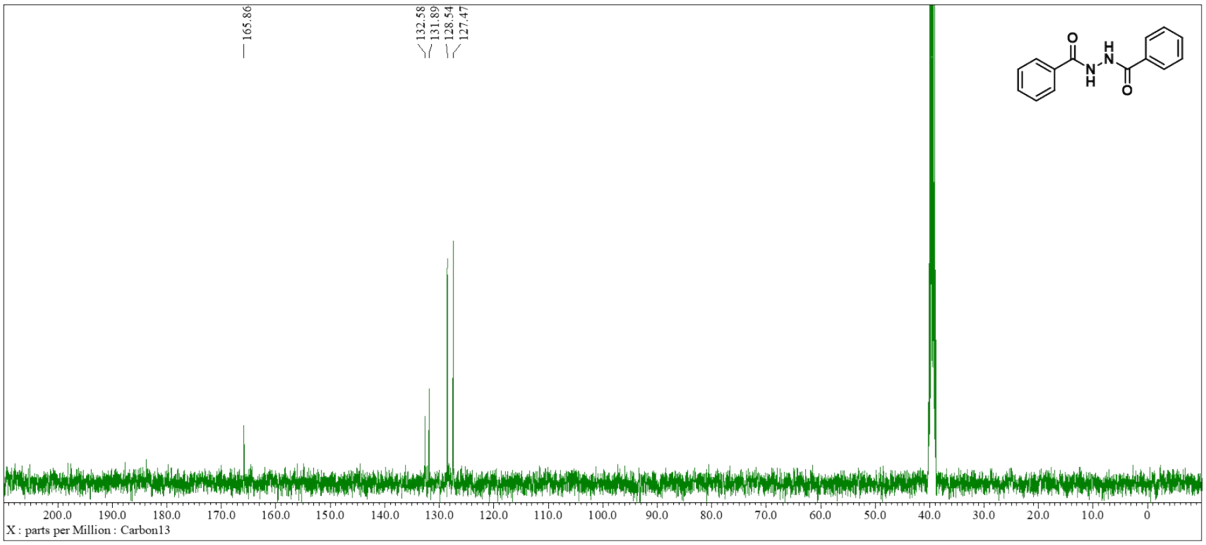


Figure S47. ^{13}C NMR of *N*′-benzoylbenzohydrazide (**5ag**)

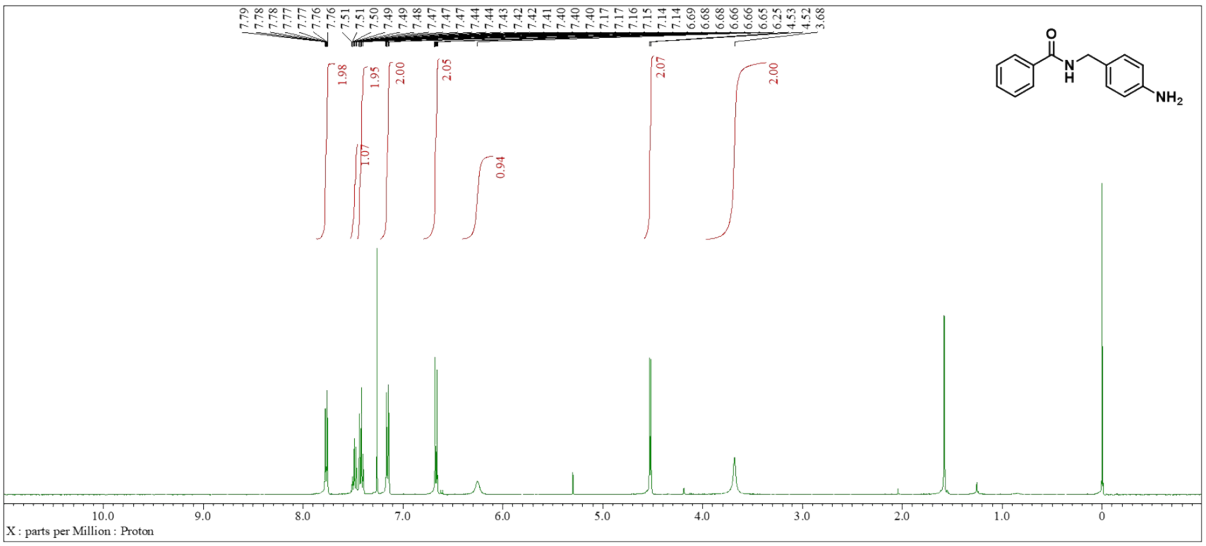


Figure S48. ^{1}H NMR of *N*-(4-aminobenzyl)benzamide (**5ah**)

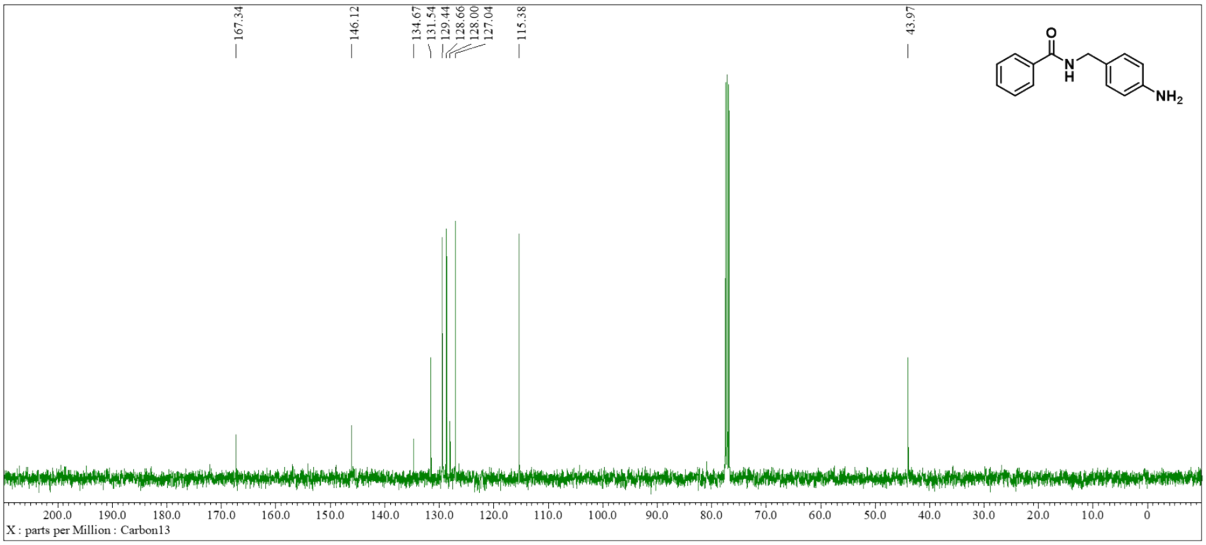


Figure S49. ^{13}C NMR of *N*-(4-aminobenzyl)benzamide (**5ah**)

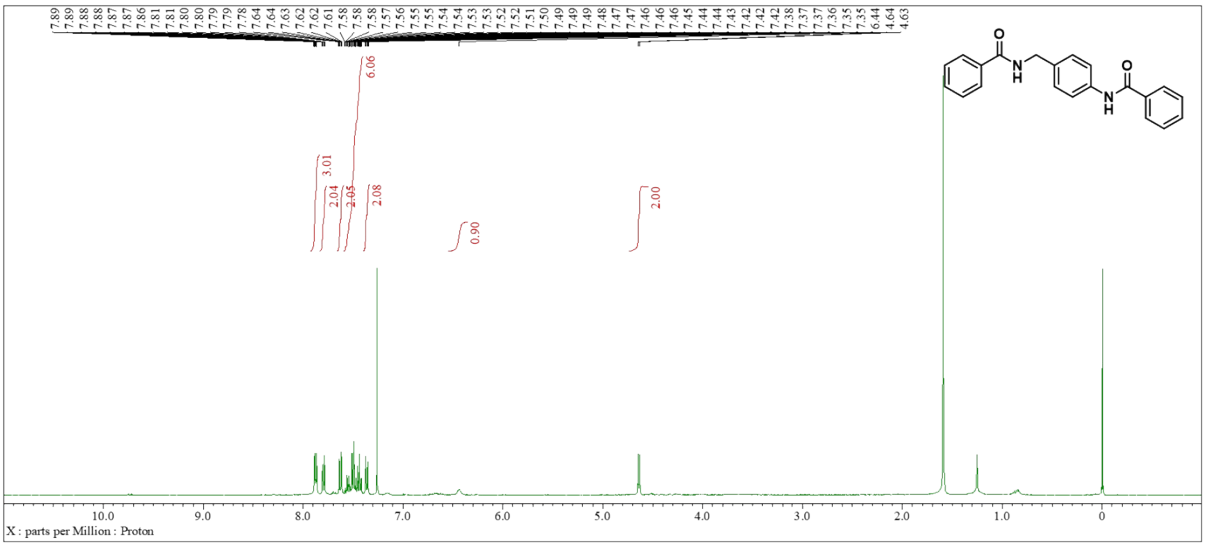


Figure S50. ^{1}H NMR of *N*-(4-benzamidobenzyl)benzamide (**5ah'**)

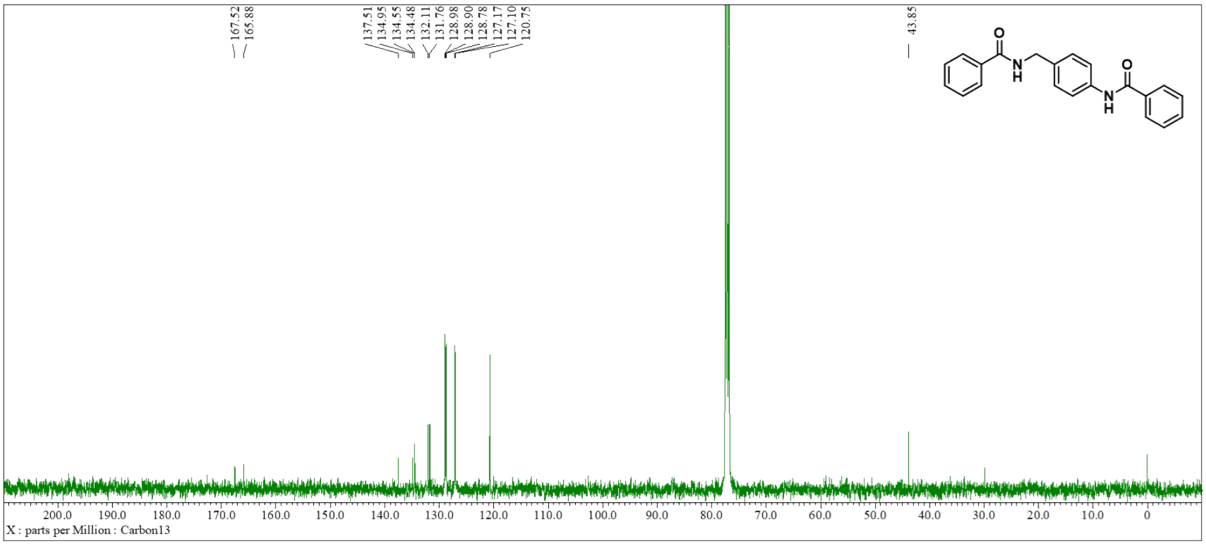


Figure S51. ^{13}C NMR of *N*-(4-benzamidobenzyl)benzamide (**5ah'**)

9. References

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2. X. Guo and O. S. Wenger, *Angew. Chem. Int. Ed.*, 2018, **57**, 2469-2473.
3. P. V. Ramachandran and H. J. Hamann, *Org. Lett.*, 2021, **23**, 2938-2942.
4. K. Ishihara, S. Ohara and H. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4196-4197.
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