# *Supporting Information*

## Reductive Transamidation of Tertiary Amides with Nitroarenes Enabled by Magnesium and Chlorosilane

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## Content

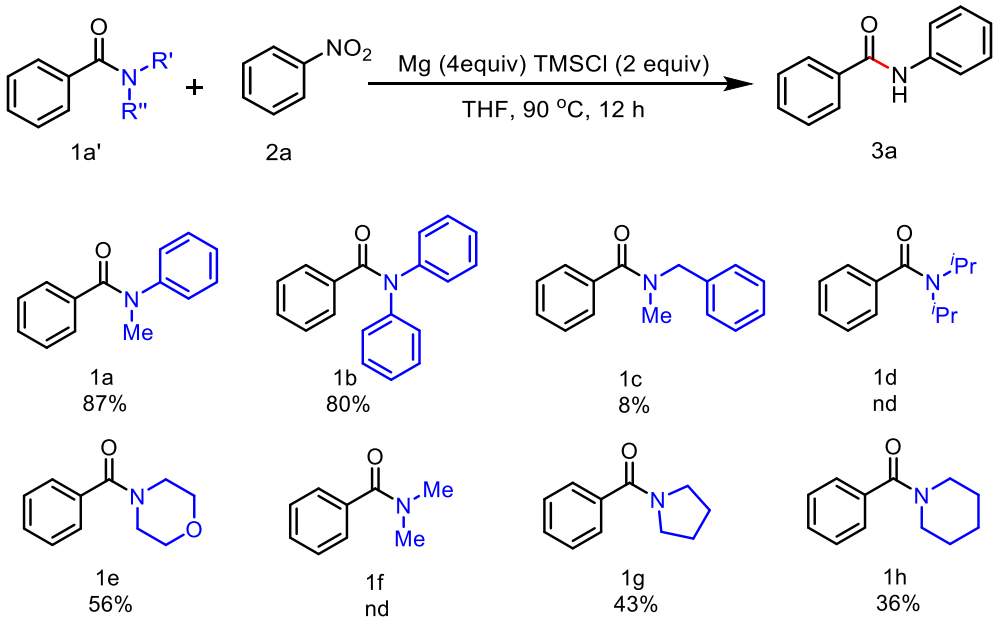
## 1. General Information

**General.** All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still.[1] NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. $^{1}$H NMR spectra were recorded at 400 MHz in $CDCl_3$ or DMSO-$d_6$ were referenced internally to tetramethylsilane as an internal standard, $^{13}$C NMR spectra were recorded at 100 MHz and $^{19}$F NMR spectra were recorded at 376 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on an Agilent Technologies 7890B GC–system, equipped with FID detector and a J&W GC column (0.32 mm × 30 m × 0.25 μm). The methods used start with the injection temperature $T_0$; after holding this temperature for 3 min, the column was heated to temperature $T_1$ (ramp). (GC Method: $T_0$ = 50 °C, T1 = 280 °C, ramp = 15 °C/min). GC–MS spectra were recorded on an Agilent Technologies 7890B GC–system with an Agilent 5977B MSD and a HP–5MS column (0.25 mm × 30 m × 0.25 $\mu$m). The major signals were quoted in m/z with the relative intensity in parentheses.

**Materials.** Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, and other commercial suppliers and used as received. Solvents were dried over sodium (for THF) by refluxing for overnight and freshly distilled prior to use. Mg (99.99%) was purchased from Aldrich Inc. and used as received.

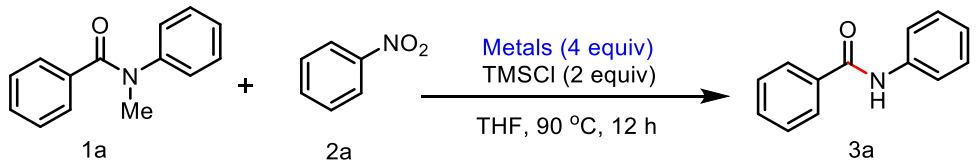
## 2. Optimization of Reaction Parameters

***Table S1.*** **Studying the Effect of *N*-Substituents of Tertiary Amides on the Reductive Transamidation[a,b]**




[a]Reaction conditions: **1a'** (0.2 mmol), **2a** (0.4 mmol), Mg (0.8 mmol) and TMSCl (0.4 mmol), THF (1 mL), 90 °C, 12 h. [b]The yields are determined by GC analysis using *n*-tridecane as internal standard.

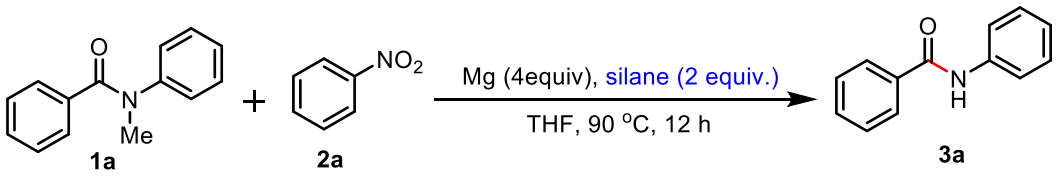
**Table *S2*. Studying the Effect of Metallic Reductants on the Transamidation[a]**




| entry | metal | yield (%) [b] |
|---|---|---|
| 1 | Cu | nd |
| 2 | Zn | nd |
| 3 | Na | nd |
| 4 | Mn | nd |
| 5 | Fe | nd |
| 6 | Mg | 87 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), metal (0.8 mmol) and TMSCl (0.4 mmol), THF (1 mL), 90 °C, 12 h. [b]The yields are determined by GC analysis using *n*-tridecane as internal standard. NR = Not detected.

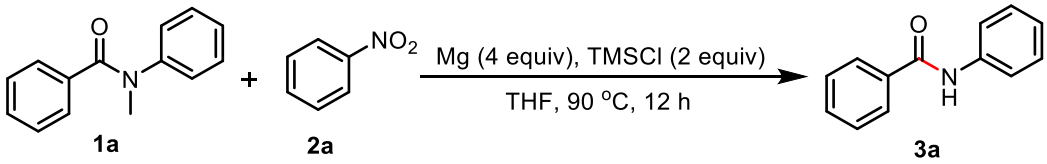
**Table *S3*. Studying the Effect of Silane Additive on the Reductive Transamidation[a]**




| entry | silane additive | yield (%) [b] |
|---|---|---|
| 1 | TMSBr | 72 |
| 2 | TMSCl | 87 |
| 3 | TMSCN | nd |
| 4 | TIPSCl | <5 |
| 5 | $Me_2SiHCl$ | 64 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Mg (0.8 mmol), silane (0.4 mmol), THF (1 mL), 90 °C, 12 h. [b]The yields are determined by GC analysis using *n*-tridecane as internal standard.

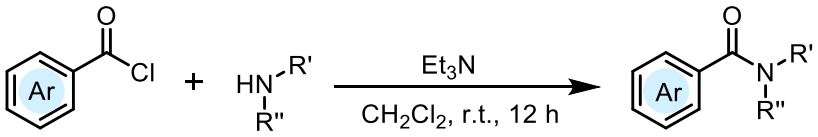
**Table *S4*. Optimization of Reaction Parameters[a]**




| entry | variation from "standard conditions" | yield (%)[b] |
|---|---|---|
| 1 | no variations | 86 |
| 2 | 80 °C instead of 90 °C | 36 |
| 3 | 120 °C instead of 90 °C | 80 |
| 4 | 24 h instead of 12 h | 84 |
| 5 | 8 h instead of 12 h | 59 |

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Mg (0.8 mmol), TMSCl (0.4 mmol), THF (1 mL), 90 °C, 12 h. [b]The yields are determined by GC analysis using *n*-tridecane as internal standard.

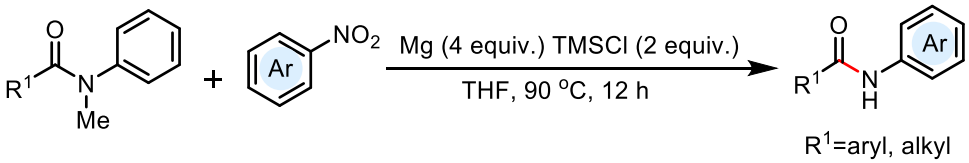
### 3. General Procedure for the Synthesis of Tertiary Amides



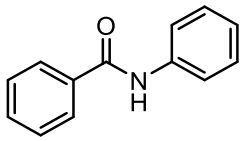

*N*-methyl-*N*-phenylbenzamide derivatives were prepared by modifying the reported procedure[1]. A 500 mL round bottom flask with a magnetic stir bar was charged with

*N,N*-diphenyl amine (1.2 equiv), $Et_3N$ (1.5 equiv), and anhydrous DCM (50 mL) and the mixture was cool down at 0 ºC. The appropriate acid chloride (1 equiv) was added dropwise under nitrogen atmosphere, and the mixture was warmed to room temperature. After stirring for overnight, DCM (50 mL) was added and the mixture was transferred to a separatory funnel. The organic layer was washed with 1 M HCl (aq) (3 × 100 mL) and NaCl (aq) (1 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$, and the volatiles was removed under vacuum. The crude product was purified by column chromatography.

**4. General Procedure for the Mg-Promoted Reductive Transamidation**



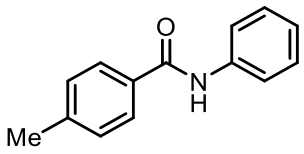

A dried Schlenk tube was sequentially charged with magnesium (4 equiv, 0.8 mmol, 20 mg), tertiary amide (1 equiv, 0.2 mmol), nitroarene (2 equiv, 0.4 mmol), freshly distilled THF (1 mL) and TMSCl (2 equiv, 0.4 mmol, 50 $\mu$L) under atmosphere of nitrogen. After stirring at 90 ºC for 12 h, the mixture was quenched by saturated $NH_4Cl$ solution (3 mL) and then neutralized with saturated $NaHCO_3$ solution (6 mL). The crude product was extracted with ethyl acetate (EtOAc, 10 mL). The aqueous fraction was further washed with EtOAc (3 × 10 mL). The combined organic fractions phases were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum. The residue was purified by preparative thin-layer chromatography (TLC) using a solvent mixture (petroleum ether, EtOAc, $CH_2Cl_2$) as an eluent to afford the desired secondary amide product.




**3a: *N*-phenylbenzamide**

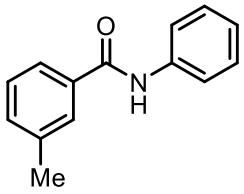
Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/20) as an eluent to

give **3a** (34 mg, 87% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.58–7.51 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.9, 138.1, 135.1, 132.0, 129.2, 128.9, 127.2, 124.7, 120.4. Spectroscopic data are in accordance with those described in the literature.[2]



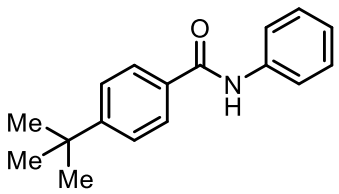

**3b: 4-methyl-*N*-phenylbenzamide**

Following the general procedure, 4-dimethyl-*N*-phenylbenzamide (45 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3b** (30 mg, 72% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H),2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 142.4, 138.2, 132.2, 129.5, 129.1, 127.2, 124.5, 120.4, 21.6. Spectroscopic data are in accordance with those described in the literature.[3]



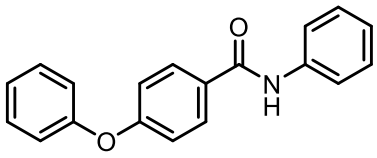

**3c: 3-methyl-*N*-phenylbenzamide**

Following the general procedure, 3-dimethyl-*N*-phenylbenzamide (45 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3c** (25 mg, 58% yield) as a white solid; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 10.20 (s, 1H), 7.79 (s, 1H), 7.78 – 7.77 (m, 2H), 7.75 (d, *J* = 6.0 Hz, 1H), 7.41 (d, J = 7.0 Hz, 2H), 7.38–7.32 (m, 2H), 7.10 (t, J = 7.4 Hz, 1H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 165.7, 139.2, 137.7, 135.0, 132.1, 128.6, 128.1, 124.8, 123.6, 120.3, 21.0. Spectroscopic data are in accordance with those described in the literature.[3]



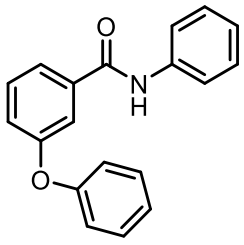
**3d: 4-(*tert*-butyl)-*N*-phenylbenzamide**

Following the general procedure, 4-(*tert*-butyl)-*N*-methyl-*N*-phenylbenzamide (53 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3d** (32 mg, 64% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.81 (d, $J$ = 8.5 Hz, 2H), 7.65 (d, $J$ = 7.6 Hz, 2H), 7.48 (d, $J$ = 8.5 Hz, 2H), 7.36 (t, $J$ = 7.9 Hz, 2H), 7.14 (t, $J$ = 7.4 Hz, 1H), 1.35 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 155.5, 138.2, 132.2, 129.2, 127.1, 125.8, 124.5, 120.4, 35.1, 31.3. Spectroscopic data are in accordance with those described in the literature.[3]



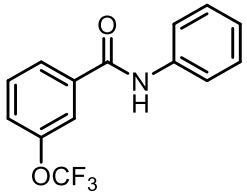
**3e: 4-phenoxy-*N*-phenylbenzamide**

Following the general procedure, *N*-methyl-4-phenoxy-N-phenylbenzamide (61 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3e** (39 mg, 67% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.87 – 7.81 (m, 2H), 7.65 (d, $J$ = 1.1 Hz, 1H), 7.63 – 7.61 (m, 1H), 7.43–7.30 (m, 4H), 7.19 (t, $J$ = 7.4 Hz, 1H), 7.13 (t, $J$ = 7.4 Hz, 1H), 7.08–7.03 (m, 2H), 7.00 (d, $J$ = 8.8 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.4, 160.9, 155.9, 138.1, 130.1, 129.3, 129.2, 129.1, 124.6, 124.5, 120.5, 112.0, 117.9. HRMS ($ESI^+$): calcd for $C_{19}H_{16}NO_2$ $[M+H]^+$ 290.1176, found 290.1175.



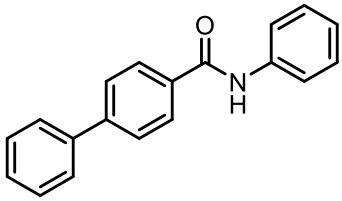
**3f: 3-phenoxy-*N*-phenylbenzamide**

Following the general procedure, *N*-methyl-3-phenoxy-N-phenylbenzamide (61 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3f** (30 mg, 51% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.50 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.39–7.31 (m, 4H), 7.19–7.12 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.3, 158.1, 156.6, 137.9, 137.0, 130.3, 130.1, 129.2, 124.8, 124.1, 122.0, 121.5, 120.4, 119.4, 117.4. HRMS ($ESI^+$): calcd for $C_{19}H_{16}NO_2$ $[M+H]^+$ 290.1176, found 290.1175.




**3g: *N*-phenyl-3-(trifluoromethoxy)benzamide**

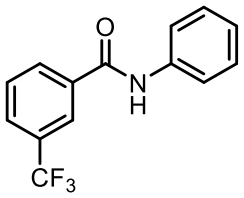
Following the general procedure, *N*-methyl-*N*-phenyl-3-(trifluoromethoxy) benzamide (59 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3g** (35 mg, 63% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.79–7.72 (m, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.42–7.34 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.4, 149.7, 137.6, 137.2, 130.4, 129.3, 125.2, 125.1, 124.3, 120.6, 120.5 (q, *J* = 256.3 Hz), 120.2.$^{19}$F NMR (376 MHz, $CDCl_3$) δ –57.81. HRMS ($ESI^+$): calcd for $C_{14}H_{11}F_3NO_2$ $[M+H]^+$ 282.0737, found 282.0734.




**3h: *N*-phenyl-[1,1'-biphenyl]-4-carboxamide**

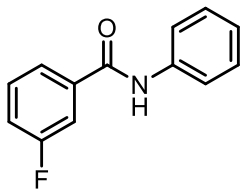
Following the general procedure, *N*-methyl-N-phenyl-[1,1'-biphenyl]-4-carboxamide (57 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3h** (33 mg, 61% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$)

δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.85 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 1H), 7.65 (d, *J* = 5.5 Hz, 2H), 7.63 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.3, 139.0, 137.7, 133.8, 129.9, 129.1, 128.3, 127.0, 126.95, 126.8, 124.1, 119.7. Spectroscopic data are in accordance with those described in the literature.[3]




**3i: *N*-phenyl-3-(trifluoromethyl)benzamide**

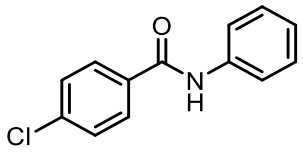
Following the general procedure, *N*-methyl-*N*-phenyl-3-(trifluoromethyl)benzamide (56 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3l** (35 mg, 66% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.65–7.55 (m, 3H), 7.40–7.32 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.7, 137.6, 135.9, 131.4 (q, *J* = 32.9 Hz), 130.5, 129.5, 129.3, 128.5 (q, *J* = 3.5 Hz), 125.2, 124.2 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 271.0 Hz), 120.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ –62.73. HRMS ($ESI^+$): calcd for $C_{14}H_{11}F_3NO$ $[M+H]^+$ 266.0787, found 266.0788.




**3j: 3-fluoro-*N*-phenylbenzamide**

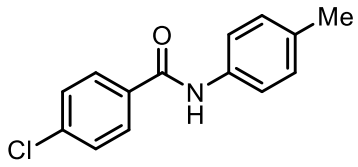
Following the general procedure, 3-fluoro-*N*-methyl-*N*-phenylbenzamide (46 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3i** (31 mg, 72% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 3H), 7.58 (d, *J* = 9.2 Hz, 1H), 7.49–7.42 (m, 1H), 7.41–7.34 (m, 2H), 7.27–7.21 (m, 1H), 7.17 (t, *J* = 7.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 288.5 Hz), 161.8, 137.7, 137.4 (d, *J* = 6.9 Hz), 130.6 (d, *J* = 7.9

Hz), 129.3, 125.0, 122.6 (d, $J$ = 2.9 Hz), 120.5, 119.0 (d, $J$ = 21.4 Hz), 114.7 (d, $J$ = 23.1 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -111.27. HRMS ($ESI^+$): calcd for $C_{13}H_{11}FNO$ $[M+H]^+$ 216.0819, found 216.0820.



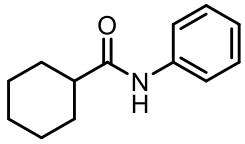

**3k: 4-chloro-*N*-phenylbenzamide**

Following the general procedure, 4-chloro-*N*-methyl-*N*-phenylbenzamide (49 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3j** (33 mg, 72% yield) as a white solid; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.30 (s, 1H), 7.99 (d, $J$ = 8.5 Hz, 2H), 7.76 (d, $J$ = 8.5 Hz, 2H), 7.61 (d, $J$ = 7.0 Hz, 2H), 7.36 (t, $J$ = 7.9 Hz, 2H), 7.11 (t, $J$ = 14.8 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 164.4, 139.0, 136.4, 133.7, 129.6, 128.6, 128.5, 123.8, 120.4. Spectroscopic data are in accordance with those described in the literature.[3]



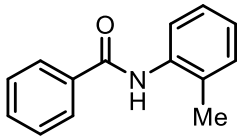

**3l: 4-chloro-*N*-(*p*-tolyl) benzamide**

Following the general procedure, 4-chloro-*N*-methyl-*N*-phenylbenzamide (49 mg, 0.2 mmol) reacted with 1-methyl-4-nitrobenzene (55 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3k** (43 mg, 87% yield) as a white solid; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.22 (s, 1H), 7.97 (d, $J$ = 8.6 Hz, 2H), 7.64 (d, $J$ = 8.4 Hz, 2H), 7.59 (d, $J$ = 8.5 Hz, 2H), 7.15 (d, $J$ = 8.4 Hz, 2H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 164.2, 136.4, 136.3, 133.7, 132.8, 129.6, 129.0, 128.5, 120.5, 20.5. HRMS ($ESI^+$): calcd for $C_{13}H_{11}FNO$ $[M+H]^+$ 246.0680, found 246.0678.



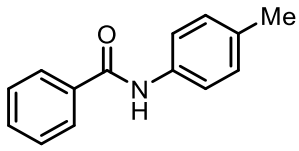
**3m: *N*-phenylcyclohexanecarboxamide**

Following the general procedure, *N*-methyl-*N*-phenylcyclohexanecarboxamide (43 mg, 0.2 mmol) reacted with nitrobenzene (49 mg, 0.4 mmol) using EtOAc/PE (1/20) as an eluent to give **3m** (18 mg, 45% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 3H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.24 (t, *J* = 11.7 Hz, 1H), 1.93 (d, *J* = 13.0 Hz, 2H), 1.82 (d, *J* = 9.7 Hz, 2H), 1.69 (s, 1H), 1.53 (d, *J* = 12.5 Hz, 2H), 1.26 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 174.8, 138.3, 129.0, 124.1, 120.0, 46.6, 29.8, 25.8. HRMS ($ESI^+$): calcd for $C_{13}H_{11}FNO$ $[M+H]^+$ 204.1383, found 204.1383.



**3n: *N*-(*o*-tolyl) benzamide**

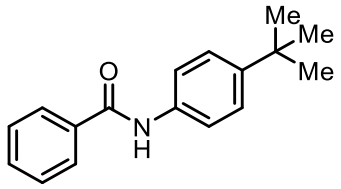
Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-methyl-2-nitrobenzene (55 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3n** (34 mg, 80% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 3H), 7.76 (s, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.18 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.8, 135.9, 135.1, 131.9, 130.7, 129.6, 128.9, 127.2, 127.0, 125.5, 123.4, 17.9. Spectroscopic data are in accordance with those described in the literature.[3]



**3o: *N*-(*p*-tolyl) benzamide**

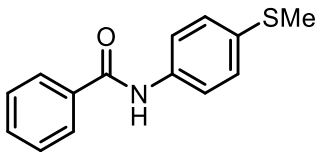
Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-methyl-4-nitrobenzene (55 mg, 0.4 mmol) using EtOAc/PE (1/10) as an

eluent to give **3o** (25 mg, 58% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87 – 7.80 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 3H), 7.45 (t, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.9, 135.5, 135.2, 134.3, 131.8, 129.7, 128.8, 127.1, 120.5, 21.0. Spectroscopic data are in accordance with those described in the literature.[3]



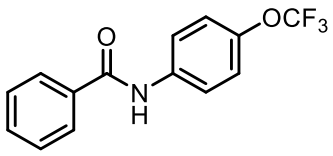

**3p: *N*-(4-(*tert*-butyl) phenyl) benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-(*tert*-butyl)-4-nitrobenzene (72 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3p** (34 mg, 67% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 1.33 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 147.6, 135.5, 135.2, 131.8, 128.8, 127.2, 126.0, 120.3, 34.5, 31.5. HRMS (ESI$^+$): calcd for $C_{13}H_{11}FNO$ $[M+H]^+$ 254.1539, found 254.1540.



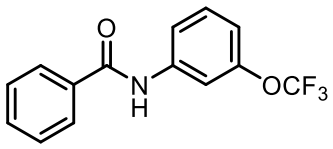

**3q: *N*-(4-(methylthio) phenyl) benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with methyl(4-nitrophenyl)sulfane (68 mg, 0.24 mmol) using EtOAc/PE (1/10) as an eluent to give **3q** (30 mg, 62% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.80 (s, 1H), 7.57 (dd, *J* = 15.4, 7.9 Hz, 3H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 2.49 (s, 3H). $^{13}$C NMR (100 MHz, DMSO) δ 165.4, 136.6, 134.9, 132.3, 131.6, 128.4, 127.6, 126.9, 121.0, 15.5. Spectroscopic data are in accordance with those described in the literature.[3]



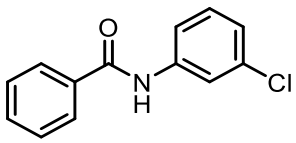
**3r: *N*-(4-(trifluoromethoxy)phenyl)benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-nitro-4-(trifluoromethoxy) benzene (83 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3r** (35 mg, 62% yield) as a white solid; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 10.43 (s, 1H), 7.98 – 7.94 (m, 2H), 7.90 (d, $J$ = 9.1 Hz, 2H), 7.60 (d, $J$ = 7.2 Hz, 1H), 7.54 (t, $J$ = 7.3 Hz, 2H), 7.37 (d, $J$ = 8.3 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 165.8, 143.9, 138.4, 134.7, 131.8, 128.4, 127.7, 121.7, 120.2 (q, $J$ = 253.0 Hz). $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ –57.08. HRMS (ESI$^+$): calcd for $C_{13}H_{11}FNO$ $[M+H]^+$ 282.0736, found 282.0734.



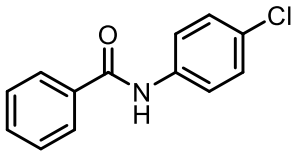
**3s: *N*-(3-(trifluoromethoxy)phenyl) benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-nitro-3-(trifluoromethoxy) benzene (83 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3s** (35 mg, 63% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.86 (d, $J$ = 7.4 Hz, 2H), 7.70 (s, 1H), 7.56 (t, $J$ = 7.4 Hz, 1H), 7.49 (q, $J$ = 8.4, 7.3 Hz, 3H), 7.37 (t, $J$ = 8.2 Hz, 1H), 7.01 (d, $J$ = 8.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 149.8, 139.5, 134.6, 132.3, 130.2, 129.0, 127.2, 120.6 (q, $J$ = 255.9 Hz), 118.3, 116.8, 113.1. $^{19}$F NMR (376 MHz, $CDCl_3$) δ –57.74. HRMS (ESI$^+$): calcd for $C_{13}H_{11}FNO$ $[M+H]^+$ 282.0736, found 282.0734.



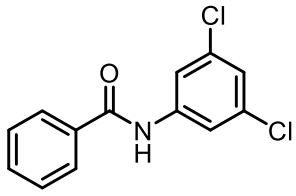
**3t: *N*-(3-chlorophenyl) benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-chloro-3-nitrobenzene (63 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3t** (43 mg, 92% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.82 (d, *J* = 7.1 Hz, 2H), 7.75 (s, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.20 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 139.2, 134.8, 134.6, 132.2, 130.1, 128.9, 127.2, 124.7, 120.6, 118.4. Spectroscopic data are in accordance with those described in the literature.[4]




**3u: *N*-(4-chlorophenyl) benzamide**

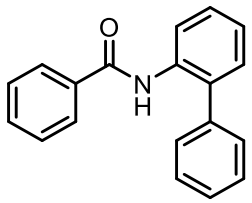
Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-chloro-4-nitrobenzene (63 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3u** (25 mg, 55% yield) as a white solid; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.39 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 165.7, 138.2, 134.7, 131.7, 128.5, 128.4, 127.7, 127.3, 121.9. Spectroscopic data are in accordance with those described in the literature.[4]




**3v: *N*-(3,5-dichlorophenyl) benzamide**

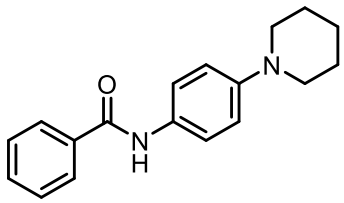
Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1,3-dichloro-5-nitrobenzene (77 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3v** (32 mg, 60% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 1.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 1.8 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ

166.1, 139.9, 135.4, 134.2, 132.5, 129.0, 127.2, 124.6, 118.6. HRMS ($ESI^+$): calcd for $C_{13}H_{10}Cl_2NO$ $[M+H]^+$ 266.0134, found 266.0133.



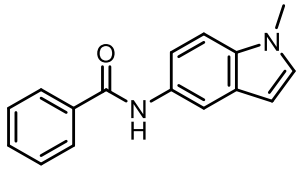
**3w: *N*-([1,1'-biphenyl]-2-yl) benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 2-nitro-1,1'-biphenyl (80 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3w** (24 mg, 44% yield) as a white solid; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.2 Hz, 1H), 8.02 (s, 1H), 7.63–7.59 (m, 2H), 7.51 (d, *J* = 7.0 Hz, 2H), 7.47–7.42 (m, 5H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 5.9 Hz, 1H), 7.26–7.20 (m, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.1, 138.2, 135.1, 134.9, 132.5, 131.9, 130.1, 129.5, 129.4, 128.9, 128.7, 128.3, 126.9, 124.5, 121.3. HRMS ($ESI^+$): calcd for $C_{19}H_{16}NO$ $[M+H]^+$ 274.1226, found 274.1127.



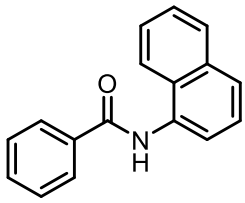
**3x: *N*-(4-(piperidin-1-yl)phenyl)benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-(4-nitrophenyl)piperidine (83 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3x** (39 mg, 69% yield) as a white solid; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.1 Hz, 2H), 7.69 (s, 1H), 7.52–7.46 (m, 5H), 6.96 (d, 2H), 3.17–3.10 (m, 4H), 1.72 (p, *J* = 5.7 Hz, 4H), 1.57 (p, *J* = 6.3 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.7, 149.7, 135.3, 131.7, 123.0, 128.8, 127.1, 121.8, 117.2, 51.2, 26.0, 24.4. HRMS ($ESI^+$): calcd for $C_{18}H_{21}N_2O$ $[M+H]^+$ 281.1649, found 281.1649.



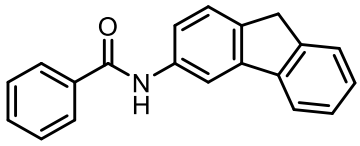
**3y: *N*-(1-methyl-1*H*-indol-5-yl) benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-methyl-4-nitro-1*H*-indole (70 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3y** (30 mg, 60% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.90 (d, *J* = 7.1 Hz, 3H), 7.53 (d, *J* = 7.1 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 6.47 (d, *J* = 3.0 Hz, 1H), 3.79 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.9, 135.6, 134.5, 131.6, 130.3, 129.9, 128.8, 128.7, 127.1, 116.2, 113.2, 109.5, 101.3, 33.1. HRMS ($ESI^+$): calcd for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1179, found 251.1178.



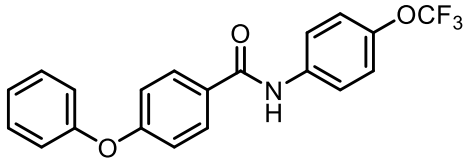
**3z: *N*-(naphthalen-1-yl) benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 1-nitronaphthalene (69 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3z** (21 mg, 42% yield) as a white solid; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 10.54 (s, 1H), 8.20 (d, *J* = 7.3 Hz, 2H), 8.11–8.03 (m, 1H), 8.03–7.97 (m, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.67–7.54 (m, 6H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 166.3, 134.5, 133.9, 133.8, 131.7, 129.3, 128.5, 128.1, 127.9, 126.3, 126.1, 126.0, 125.6, 124.0, 123.4. HRMS ($ESI^+$): calcd for $C_{17}H_{14}NO$ $[M+H]^+$ 248.1070, found 248.1068.



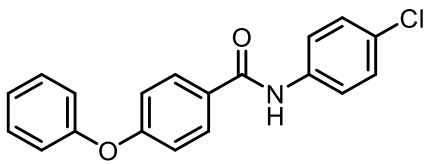
**3aa: *N*-(9*H*-fluoren-3-yl) benzamide**

Following the general procedure, *N*-methyl-*N*-phenylbenzamide (42 mg, 0.2 mmol) reacted with 3-nitro-9*H*-fluorene (84 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3aa** (43 mg, 76% yield) as a white solid; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.95 (s, 1H), 7.93–7.88 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.57–7.46 (m, 5H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 3.92 (s, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 165.6, 143.6, 142.9, 141.0, 138.2, 136.8, 135.1, 131.6, 128.4, 127.7, 126.8, 126.2, 125.1, 120.0, 119.6, 119.2, 117.2, 36.6. HRMS (ESI$^+$): calcd for $C_{20}H_{16}NO$ $[M+H]^+$ 286.1226, found 286.1227.




**3ab: 4-phenoxy-*N*-(4-(trifluoromethoxy)phenyl) benzamide**

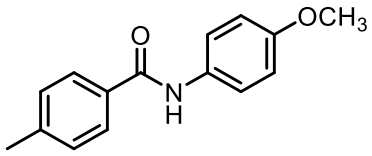
Following the general procedure, *N*-methyl-4-phenoxy-*N*-phenylbenzamide (68 mg, 0.2 mmol) reacted with 1-nitro-4-(trifluoromethoxy)benzene (83 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3ab** (55 mg, 74% yield) as a white solid; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 10.37 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 9.1 Hz, 2H), 7.50–7.43 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.11 (m, *J* = 8.2, 4.6 Hz, 4H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 164.9, 156.0, 155.5, 143.8, 138.5, 130.3, 130.0, 129.2, 124.4, 121.7, 121.5, 118.9, 118.5 (q, *J* = 212.1 Hz). $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ –57.01. HRMS (ESI$^+$): calcd for $C_{20}H_{15}F_3NO_3$ $[M+H]^+$ 374.0999, found 374.0999.




**3ac: *N*-(4-chlorophenyl)-4-phenoxybenzamide**

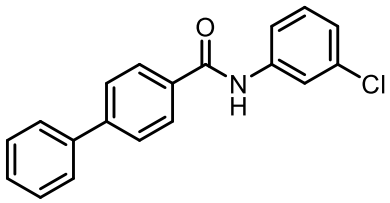
Following the general procedure, *N*-methyl-4-phenoxy-*N*-phenylbenzamide (68 mg, 0.2 mmol) reacted with 1-chloro-4-nitrobenzene (63 mg, 0.4 mmol) using EtOAc/PE

(1/10) as an eluent to give **3ac** (26 mg, 40% yield) as a white solid; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.33 (s, 1H), 8.01 (d, $J$ = 8.9 Hz, 2H), 7.83 (d, $J$ = 8.9 Hz, 2H), 7.51–7.44 (m, 2H), 7.42 (d, $J$ = 8.9 Hz, 2H), 7.25 (t, $J$ = 7.4 Hz, 1H), 7.14 (s, 1H), 7.12 (d, $J$ = 2.1 Hz, 2H), 7.10 (s, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 164.8, 159.9, 155.5, 138.2, 130.3, 130.0, 129.2, 128.5, 127.2, 124.4, 121.8, 119.6, 117.4. HRMS (ESI$^+$): calcd for $C_{19}H_{15}ClNO_2$ $[M+H]^+$ 324.0786, found 324.0783.




**3ad: *N*-(4-methoxyphenyl)-4-methylbenzamide**

Following the general procedure, 4-dimethyl-*N*-phenylbenzamide (45 mg, 0.2 mmol) reacted with 1-methoxy-4-nitrobenzene (61 mg, 0.4 mmol) using EtOAc/PE (1/10) as an eluent to give **3ad** (20 mg, 42% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, $J$ = 8.1 Hz, 3H), 7.53 (d, $J$ = 8.9 Hz, 2H), 7.27 (d, $J$ = 6.7 Hz, 2H), 6.90 (d, $J$ = 9.0 Hz, 2H), 3.81 (s, 3H), 2.42 (s, 3H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.8, 156.6, 142.3, 132.3, 131.3, 129.5, 127.1, 122.3, 114.3, 55.6, 21.6. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.1176, found 242.1176.



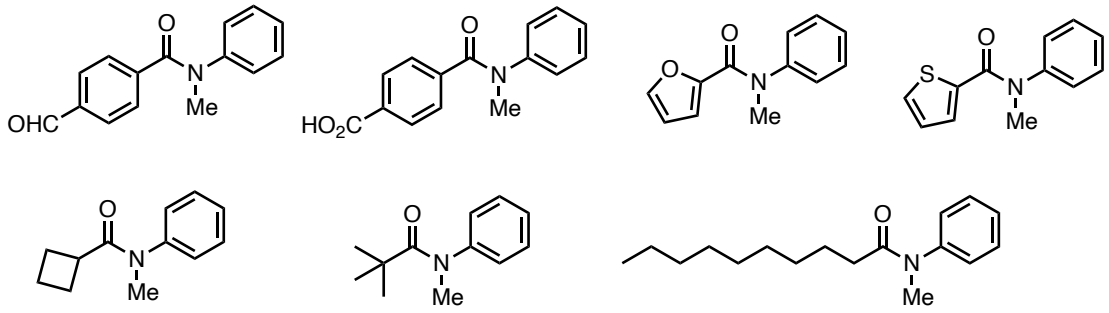

**3ae: *N*-(3-chlorophenyl)-[1,1'-biphenyl]-4-carboxamide**

Following the general procedure, *N*-methyl-*N*-phenyl-[1,1'-biphenyl]-4-carboxamide (57 mg, 0.2 mmol) reacted with 1-chloro-4-nitrobenzene (72 mg, 0.4 mmol) using EtOAc/PE (1/5) as an eluent to give **3ae** (31 mg, 50% yield) as a white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, $J$ = 6.1 Hz, 2H), 7.68 (dd, $J$ = 18.5, 5.9 Hz, 4H), 7.58 (s, 1H), 7.54–7.37 (m, 3H), 7.06 (t, $J$ = 6.0 Hz, 1H), 6.73 (dd, $J$ = 5.9, 1.5 Hz, 1H), 6.67 (t, $J$ = 1.6 Hz, 1H), 6.54 (dd, $J$ = 6.1, 1.7 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7,

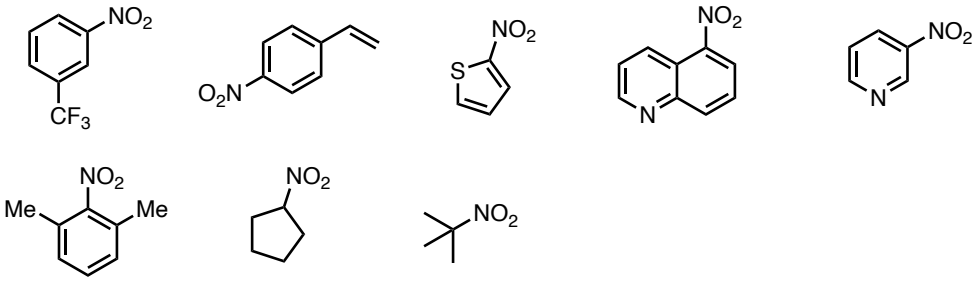
147.7, 142.6, 140.4, 135.2, 134.8, 130.8, 130.3, 129.0, 127.8, 127.3, 127.2, 118.5, 115.0, 113.2. HRMS (ESI+): calcd for $C_{19}H_{15}ClNO$ $[M+H]^+$ 308.0837, found 308.0835.

***Scheme S1. Illustrated Inefficient Substrates in the Mg-Promoted Transamidation***

***The inefficient amides in the transamidation:***

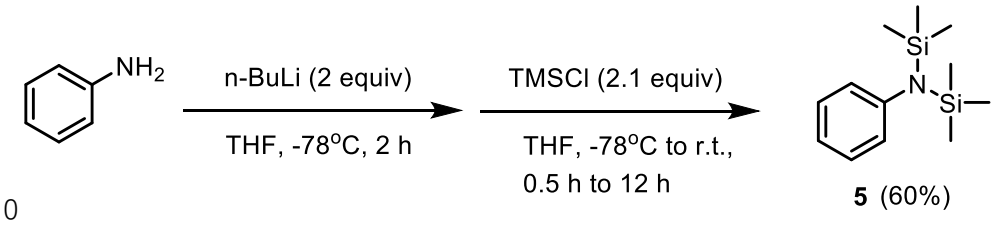


***The inefficient nitro compounds in the transamidation:***



## 5. Mechanistic Studies

***Synthesis of the possible intermediate 5***

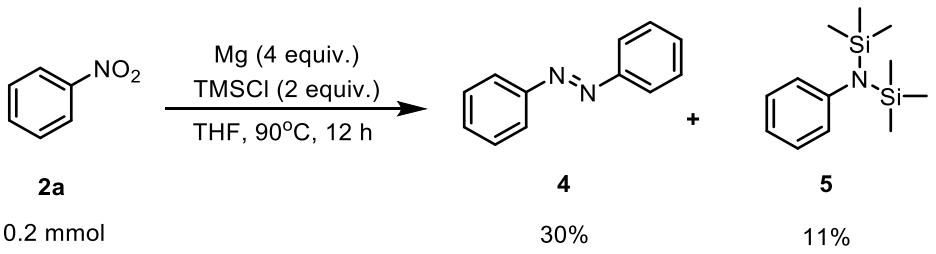



0

Compound **5** was prepared by the reported procedure.[5] Aniline (9.1 mL, 100 mmol) was dissolved in 100 mL THF and the colorless solution was cooled to –78 °C. During the addition of *n*-butyllithium (80 mL, 200 mmol) within 60 min, the reaction mixture became a colorless suspension. After stirring the suspension for additional two hours at –78 °C, trimethylsilylchloride (26.7 mL, 210 mmol) was added within 30 min. After the addition of chlorotrimethylsilane, the mixture was allowed to warm up overnight.

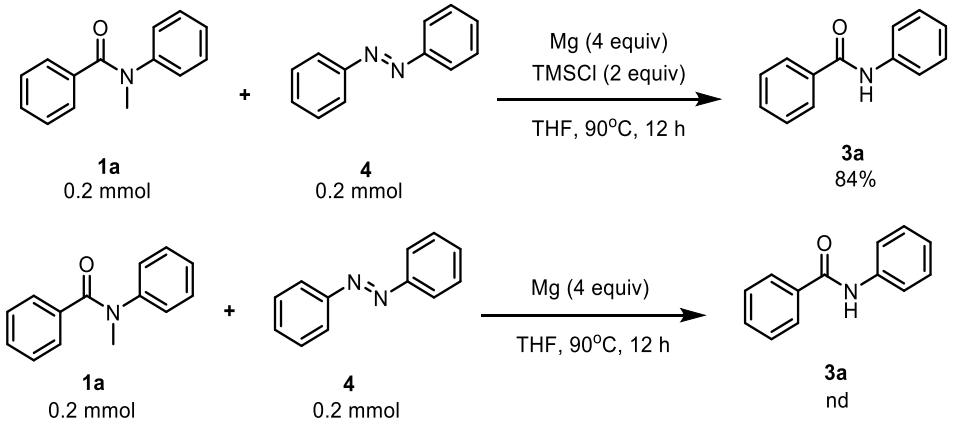
The product **5** was obtained as a colorless liquid (14.2 g, 74%). $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 7.27–7.19 (m, 2H), 7.08–7.03 (m, 1H), 6.87 (d, $J$ = 7.1 Hz, 2H), 0.03 (s, 18H). $^{13}$C (100 MHz, DMSO-$d_6$) δ 147.3, 129.6, 128.6, 123.6, 2.0.

***Reduction of nitrobenzene with Mg/TMSCl***



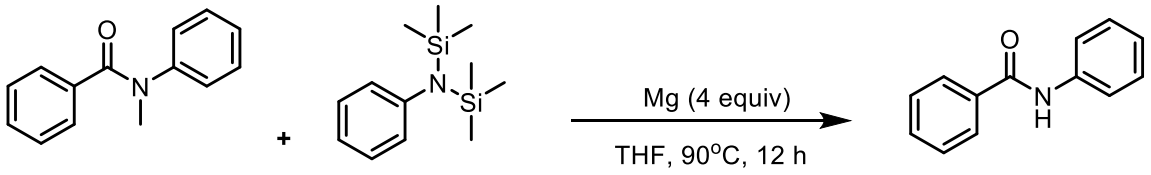

A dried Schlenk tube was charged with magnesium (4 equiv, 0.8 mmol, 20 mg), **2a** (1 equiv, 0.2 mmol), THF (1 mL) and TMSCl (0.4 mmol, 50 $\mu$L) under atmosphere of nitrogen. After stirring at 90 °C for 12 h, the mixture was quenched by saturated $NH_4Cl$ solution (3 mL) and neutralized with saturated $NaHCO_3$ solution (6 mL). The crude product was extracted with ethyl acetate (EtOAc, 10 mL), and the combined organic fractions phases were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum. The yield of compounds **4** and **5** were determined by GC analysis. Compound **4**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.99–7.90 (m, 4H), 7.57–7.45 (m, 6H).$^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.8, 131.1, 129.2, 123.0.

***The Amidation with the Intermediate 4 or 5***




A dried Schlenk tube was charged with magnesium (4 equiv, 0.8 mmol., 20 mg), **1a** (1 equiv, 0.2 mmol, 42 mg), **4** (1 equiv, 0.2 mmol, 36 mg), THF (1 mL) and TMSCl (0.4 mmol, 50 $\mu$L) under atmosphere of nitrogen, and the reaction mixture was stirred at 90

°C for 12 h. The amide **3a** was formed in 84% GC yield. In the absence of TMSCl, the reaction with Mg cannot form the amide compound **3a**.




**1a** **5** **3a**

0.2 mmol 0.4 mmol 31%

A dried Schlenk tube was charged with magnesium (4 equiv, 0.8 mmol, 20 mg), **1a** (1 equiv, 0.2 mmol, 42 mg), **5** (2 equiv, 0.4 mmol, 95 mg) and THF (1 mL) under atmosphere of nitrogen. After stirring at 90 °C for 12 h, the amide **3a** was formed in 31% GC yield.

## 6. References


1. G. Pelletier, W. S. Bechara and A. B. Charette, *J. Am. Chem. Soc*., 2010, **132**, 12817.
2. C. W. Cheung, J. Ma, and X, Hu *J. Am. Chem. Soc*., 2018, **140 (22)**, 6789-6792
3. D. Yang, T. Shin, H. Kim and S. Lee, *Org. Biomol. Chem.*, 2020,**18**, 6053-6057
4. C. Chen, L. Ling, M. Luo and X. Zeng, *Bull. Chem. Soc. Jpn.*, 2021, **94**, 762-766
5. C. Keck, C. Maichle-Moessmer and H. F. Bettinger, *Chem. Commun.*, 2019, **55**, 7470-7473.

## 7. $^{1}H$, $^{13}C$ and $^{19}F$ NMR spectra

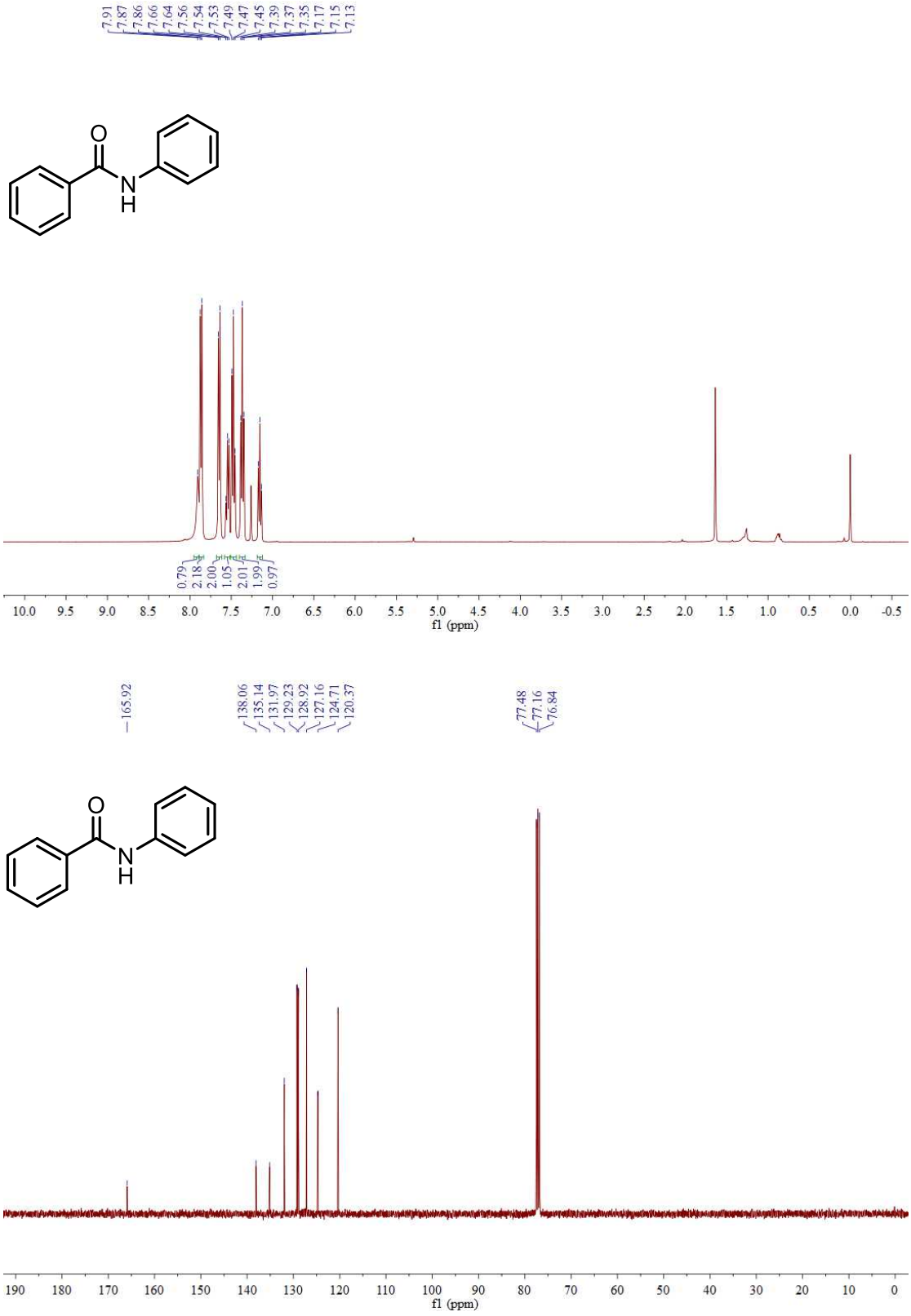



***Figure S1.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3a**

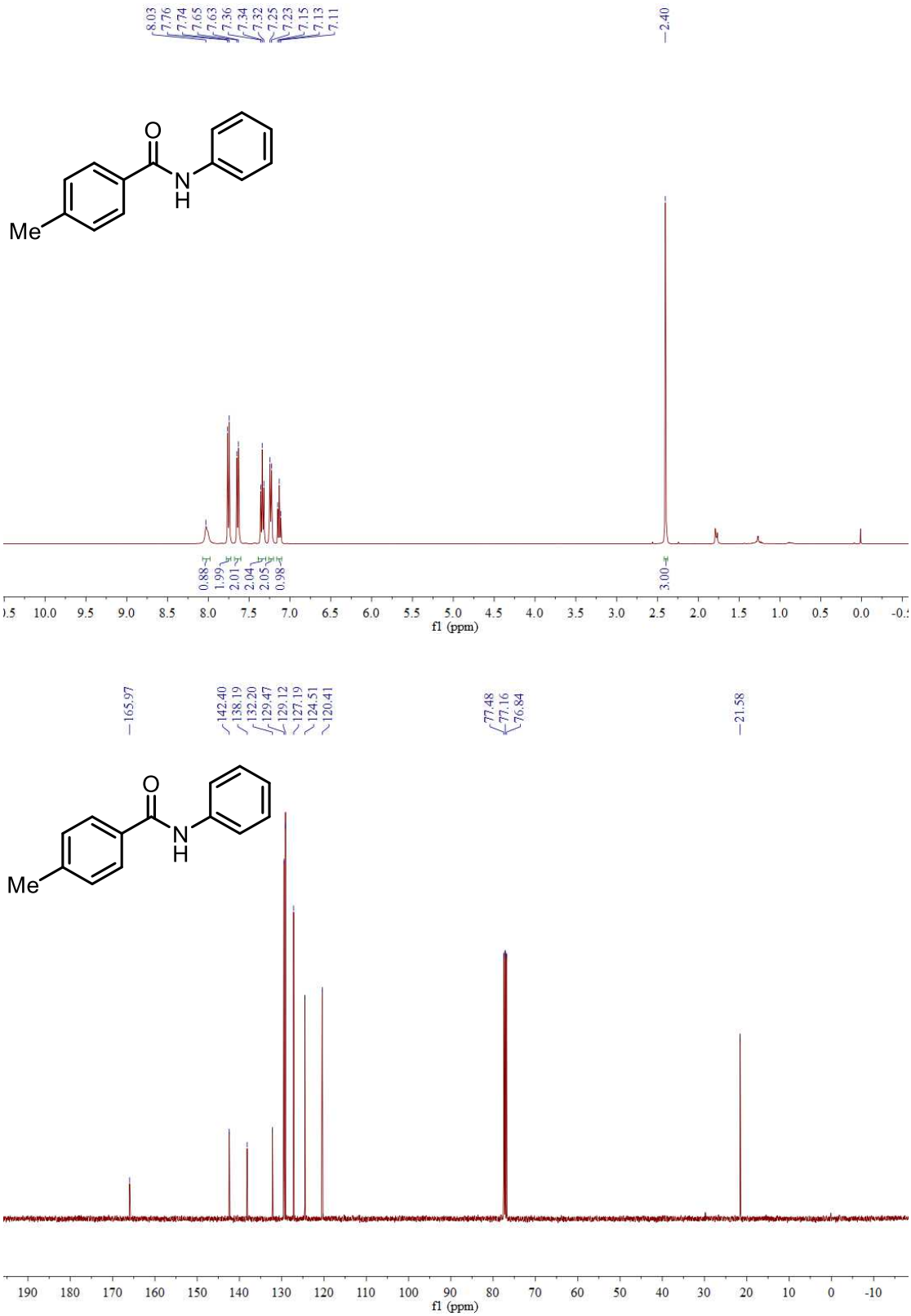



***Figure S2.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3b**

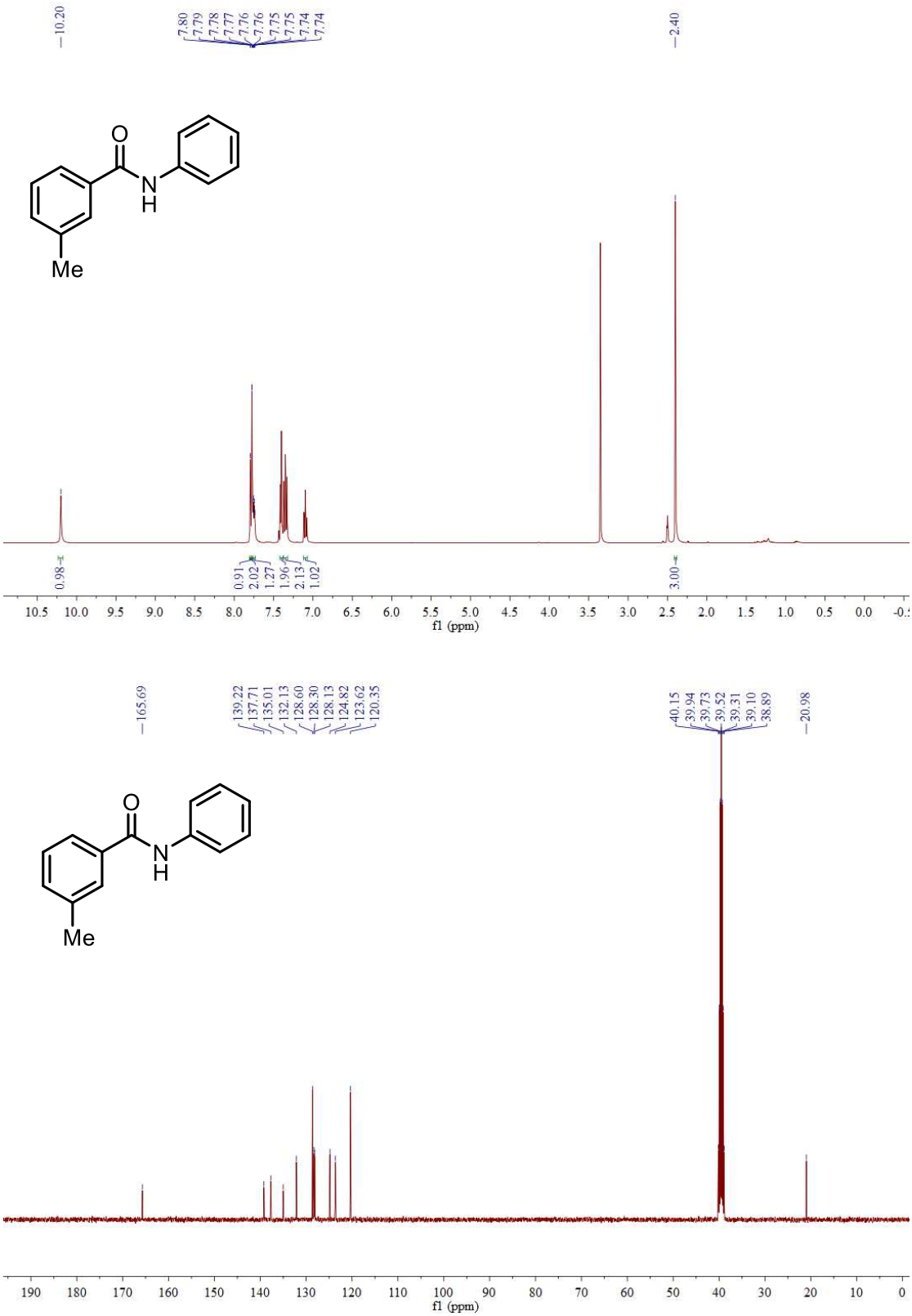



***Figure S3.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3c**

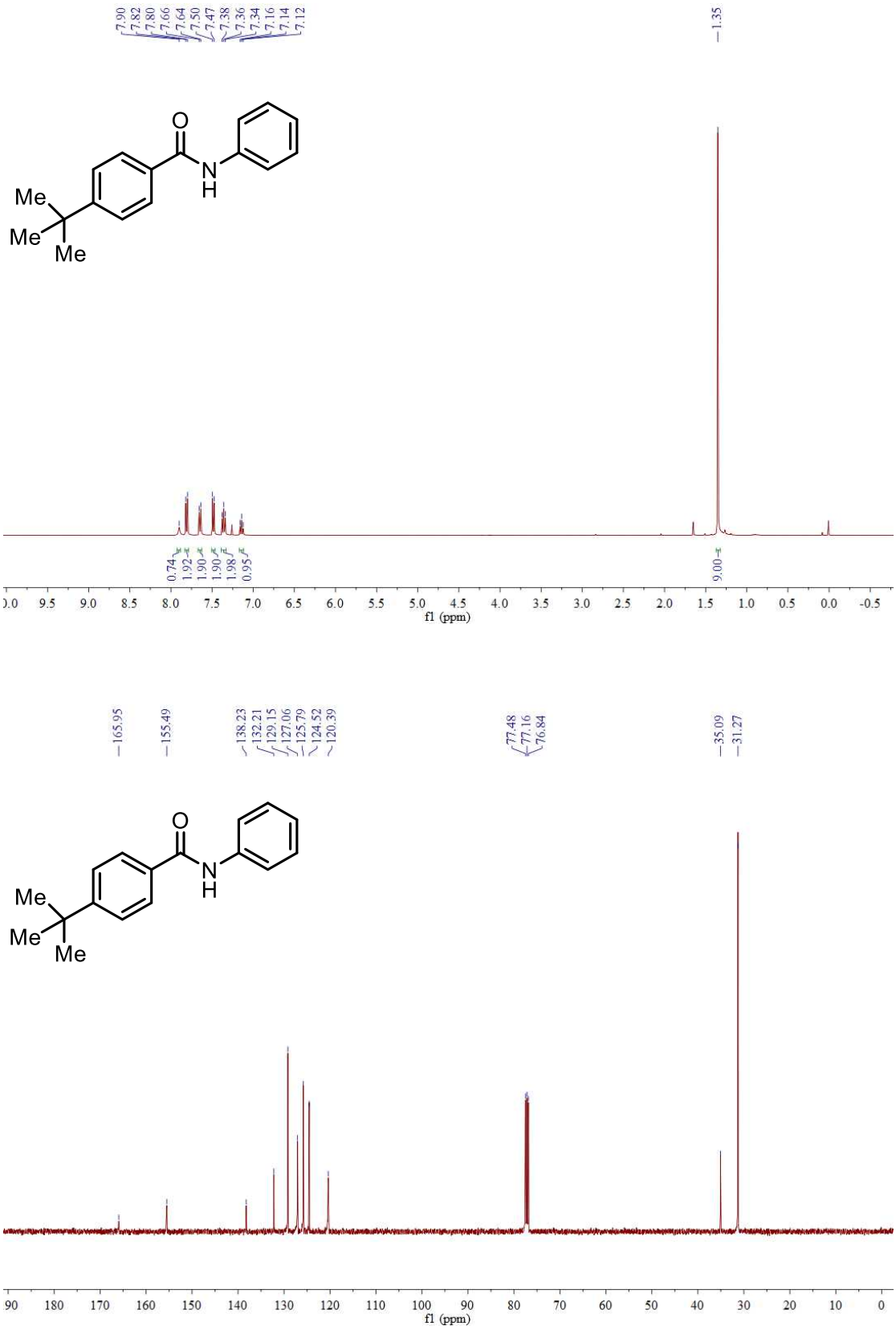



***Figure S4.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3d**

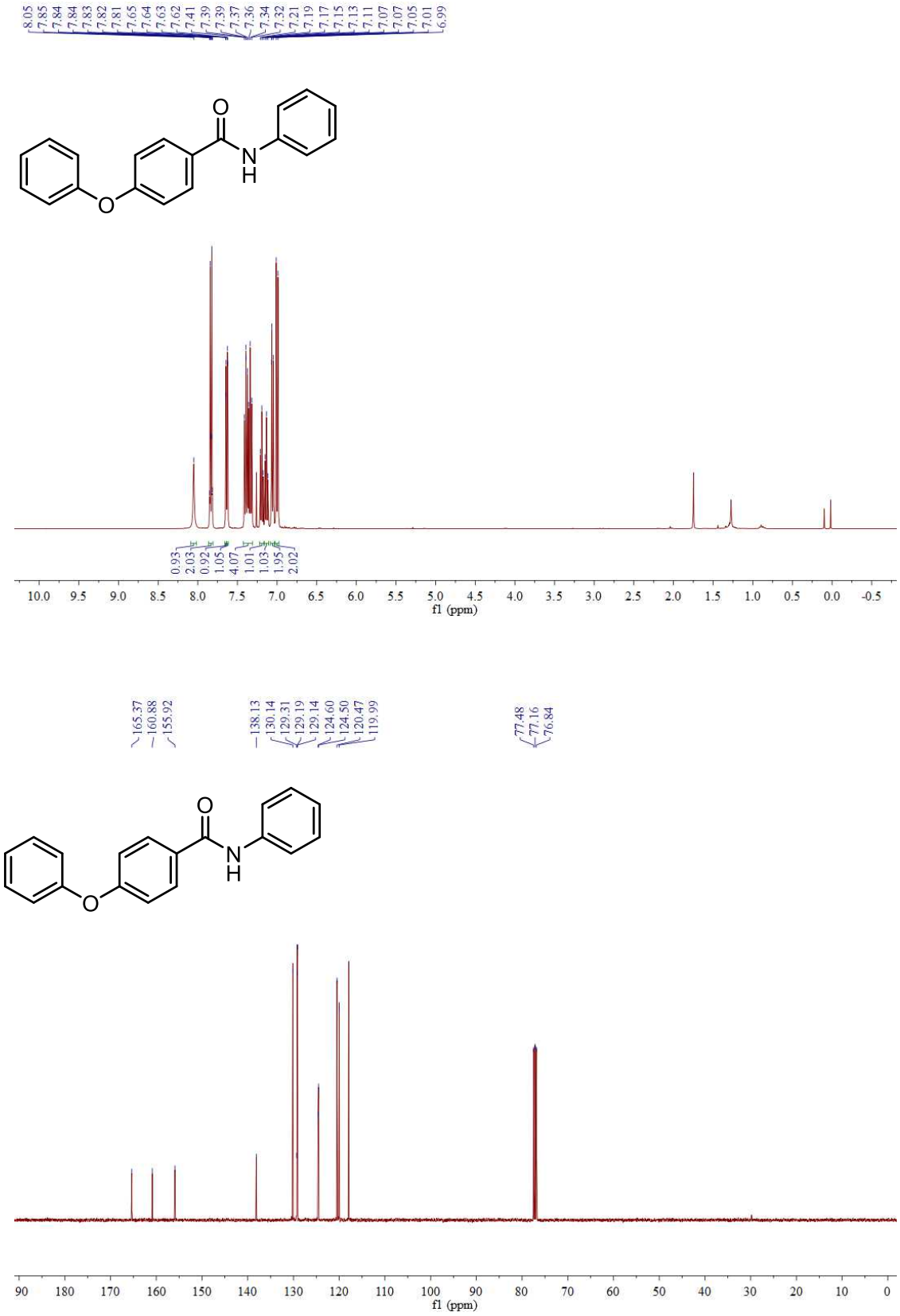



***Figure S5.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3e**

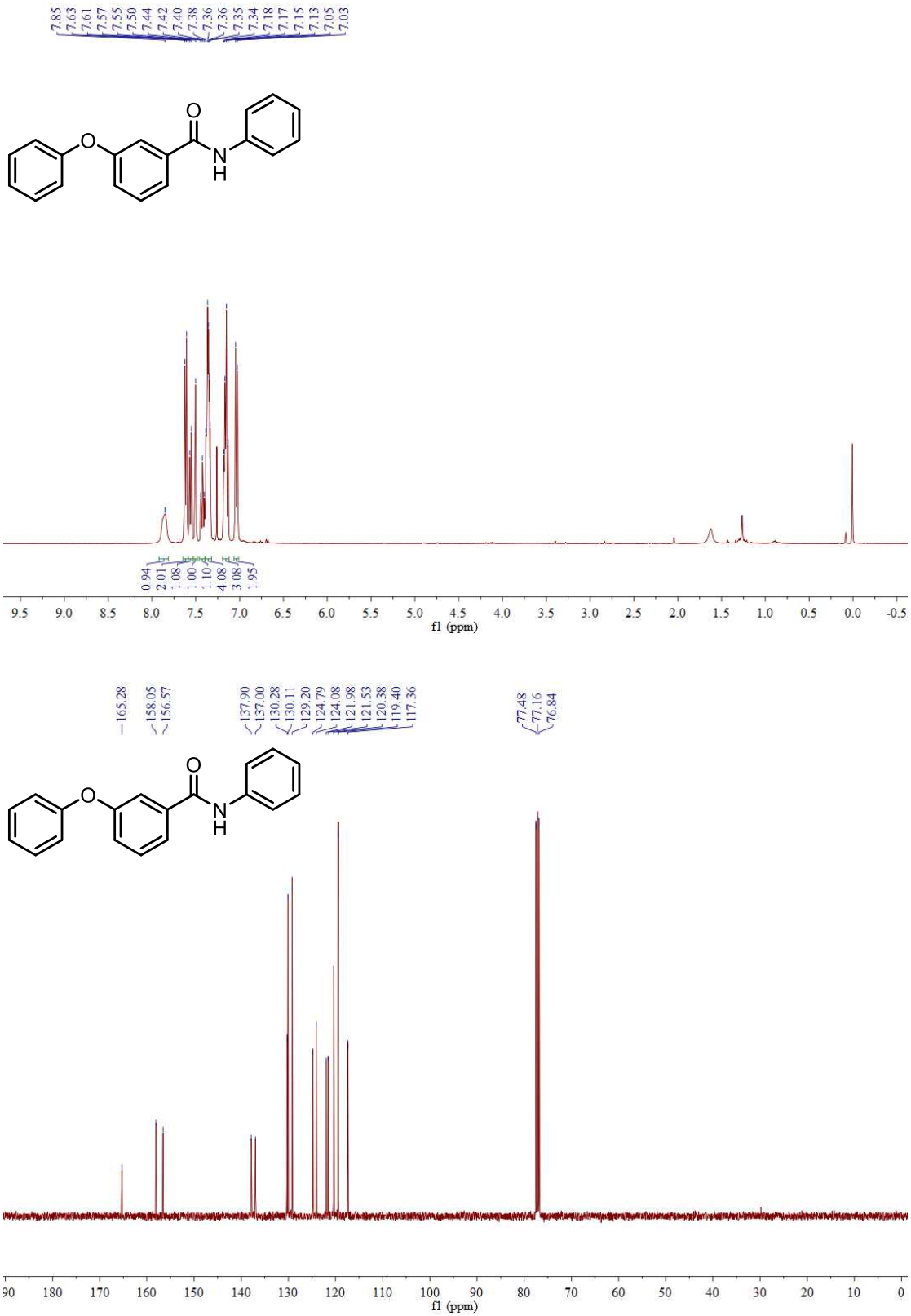
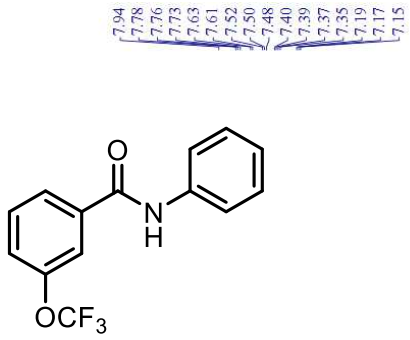
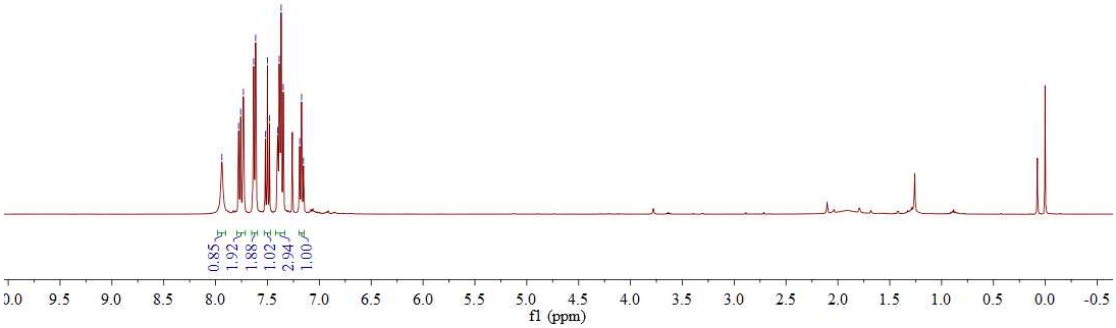
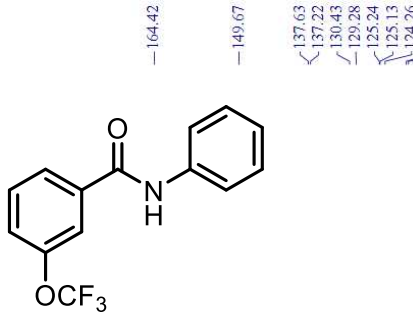
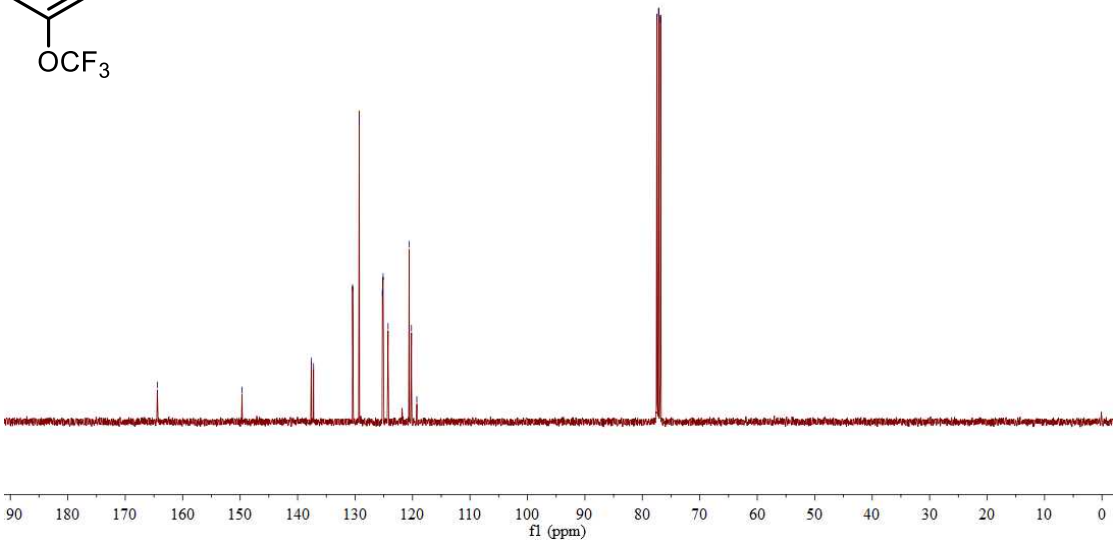



***Figure S6.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3f**


7.94
7.78
7.76
7.73
7.63
7.61
7.52
7.50
7.48
7.40
7.39
7.37
7.35
7.19
7.17
7.15
O
N
H
OCF3


0.85
1.92
1.88
1.02
2.94
1.00
f1 (ppm)


164.42
149.67
137.63
137.22
130.43
129.28
125.24
125.13
124.26
120.59
120.18
119.25
77.48
77.16
76.84
O
N
H
OCF3


f1 (ppm)

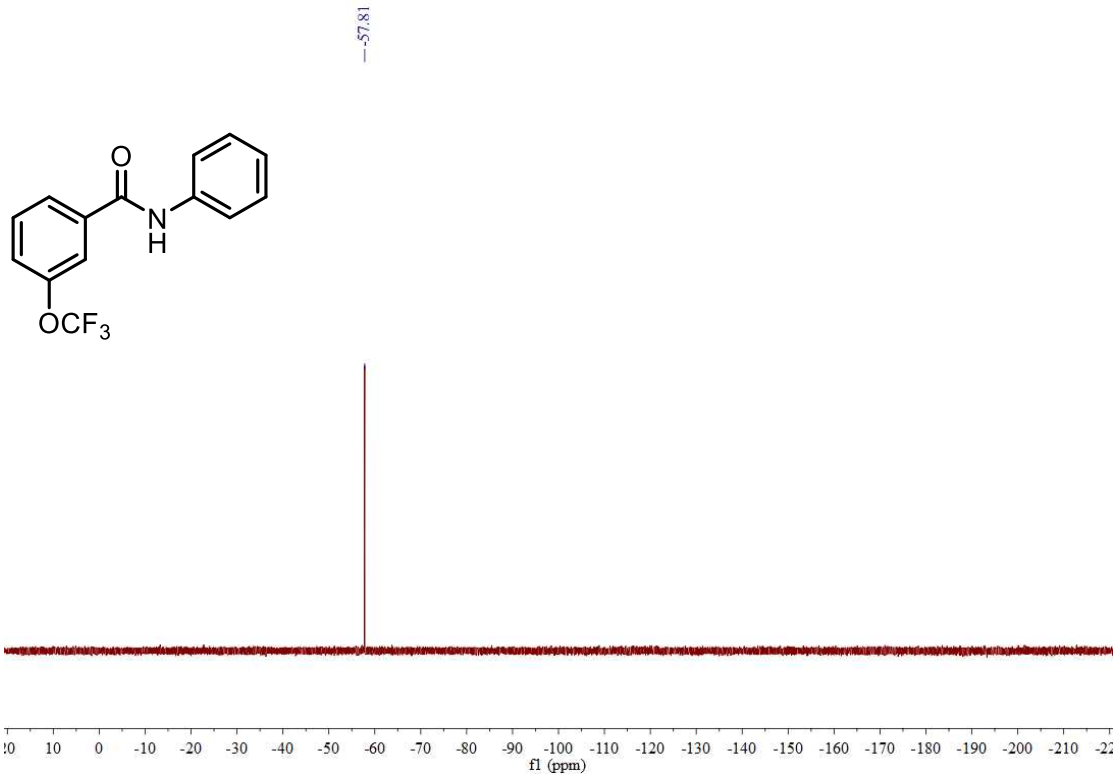
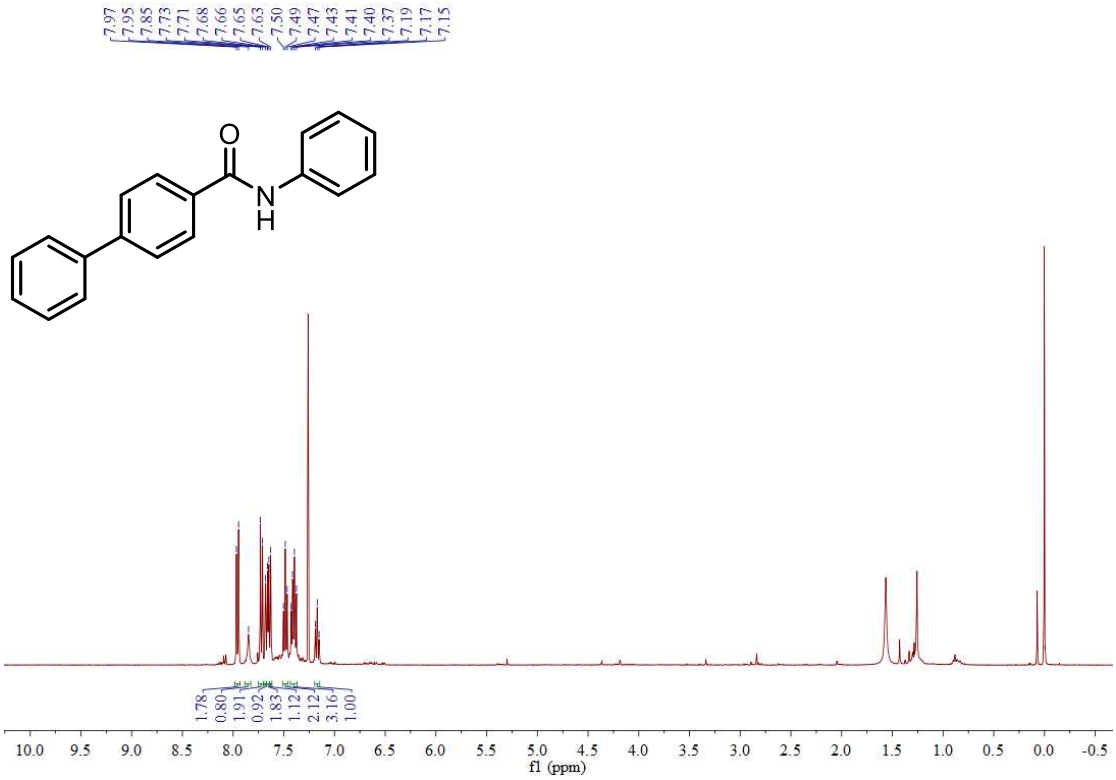



***Figure S7.*** $^{1}H$, $^{13}C$ and $^{19}F$ NMR Spectra for compound **3g**



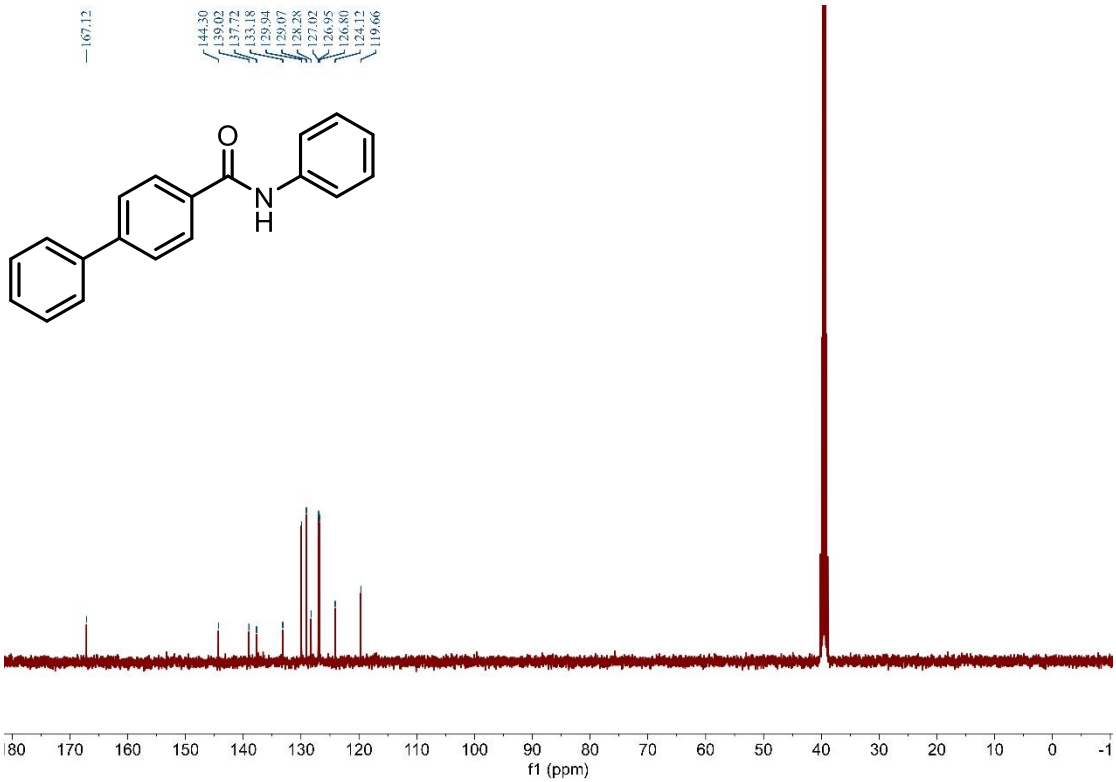
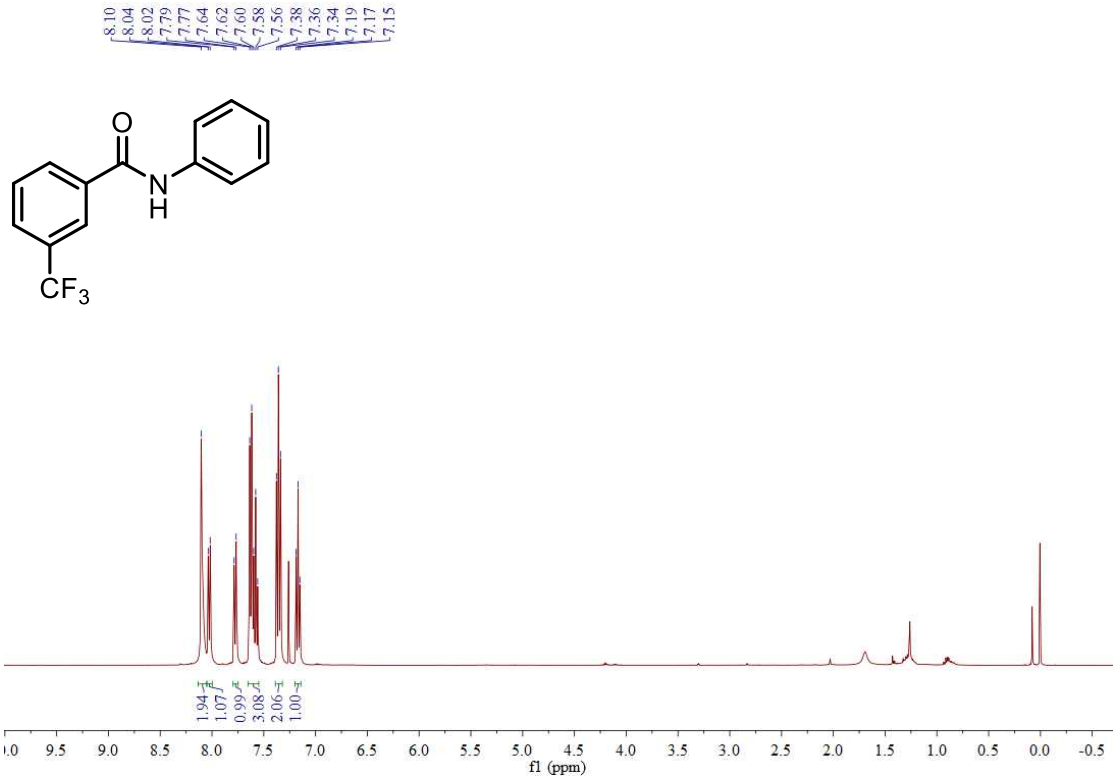



***Figure S8.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3h**



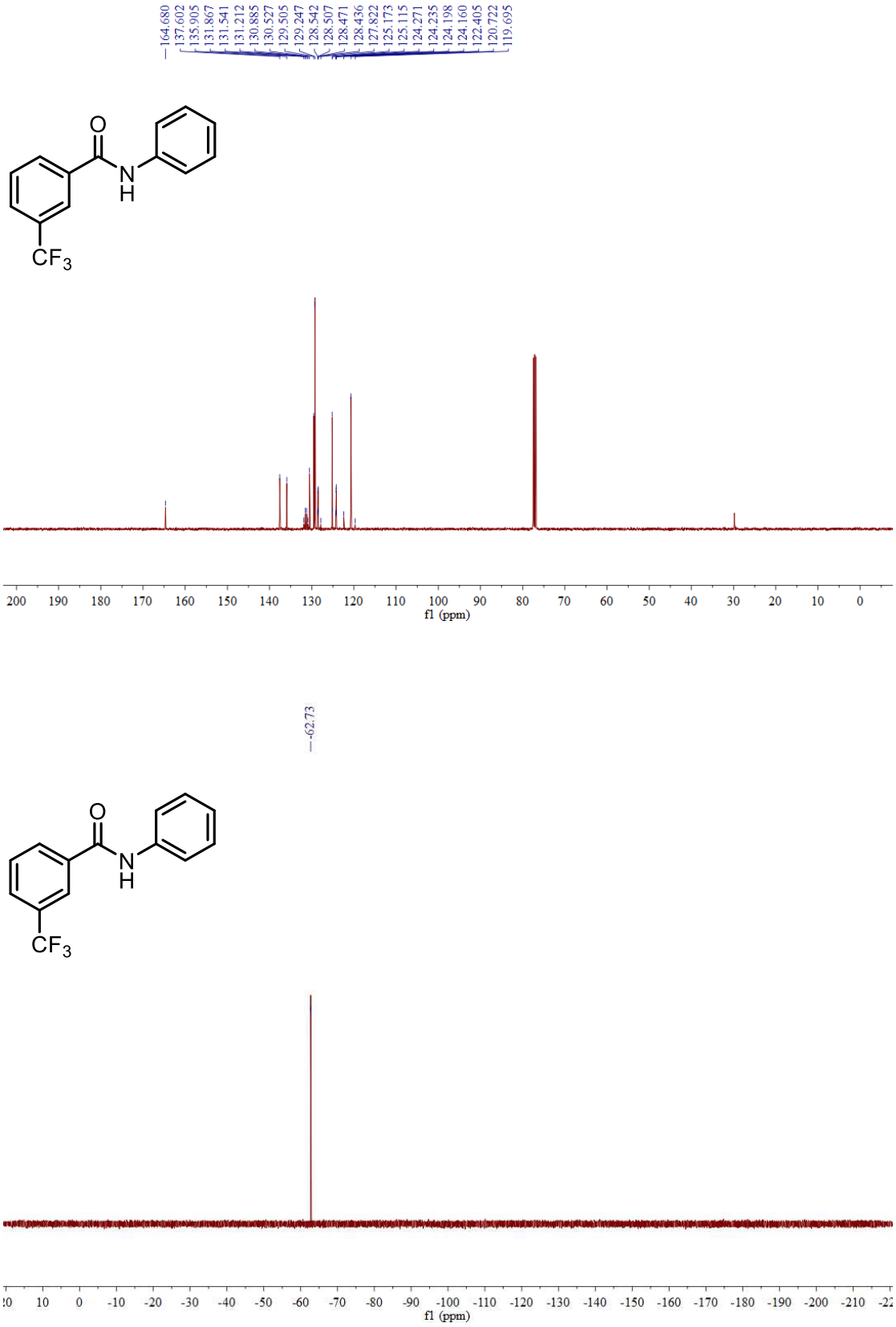
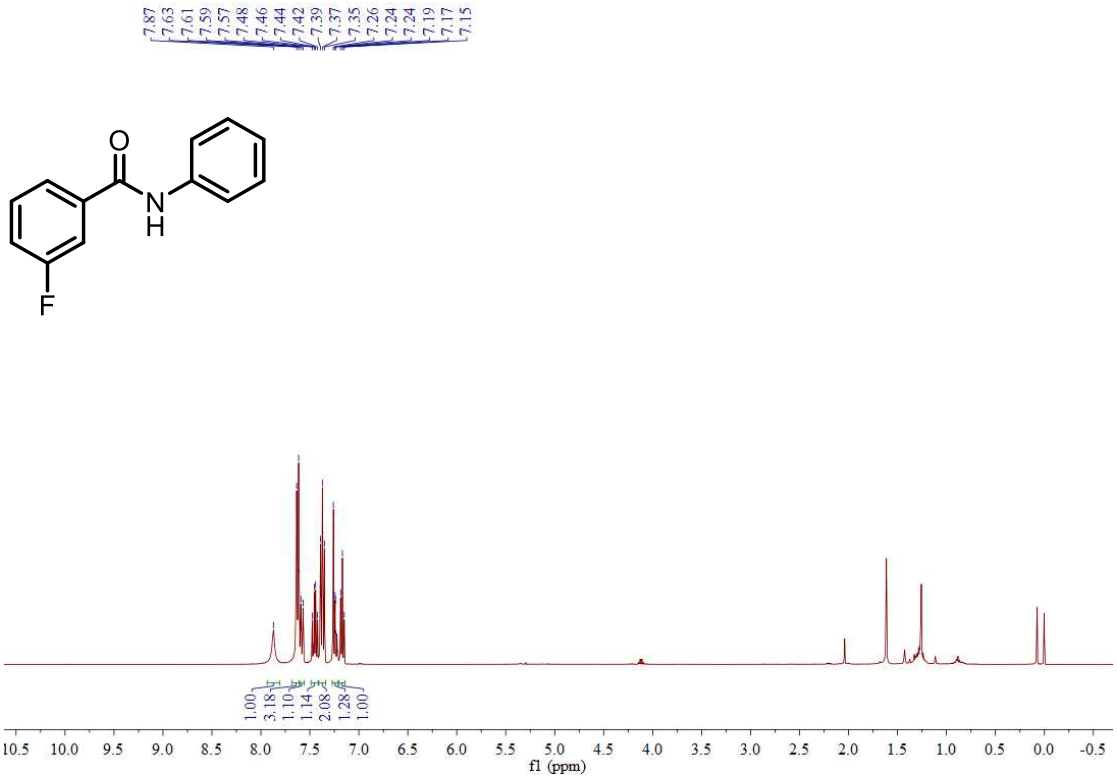
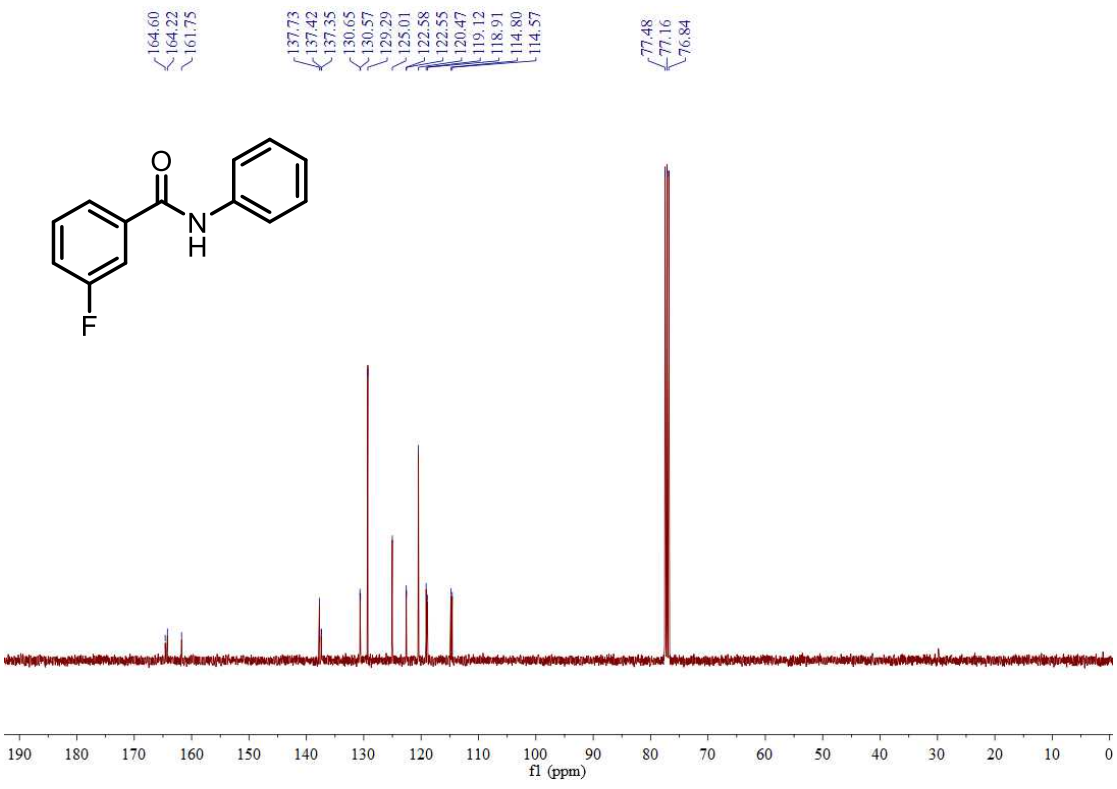



***Figure S9.*** $^{1}H$, $^{13}C$ and $^{19}F$ NMR Spectra for compound **3i**


7.87
7.63
7.61
7.59
7.57
7.48
7.46
7.44
7.42
7.39
7.37
7.35
7.26
7.24
7.19
7.17
7.15
O
N
H
F
1.00
3.18
1.10
1.14
2.08
1.28
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.60
164.22
161.75
137.73
137.42
137.35
130.65
130.57
129.29
125.01
122.58
122.55
120.47
119.12
118.91
114.80
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H
F
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f1 (ppm)

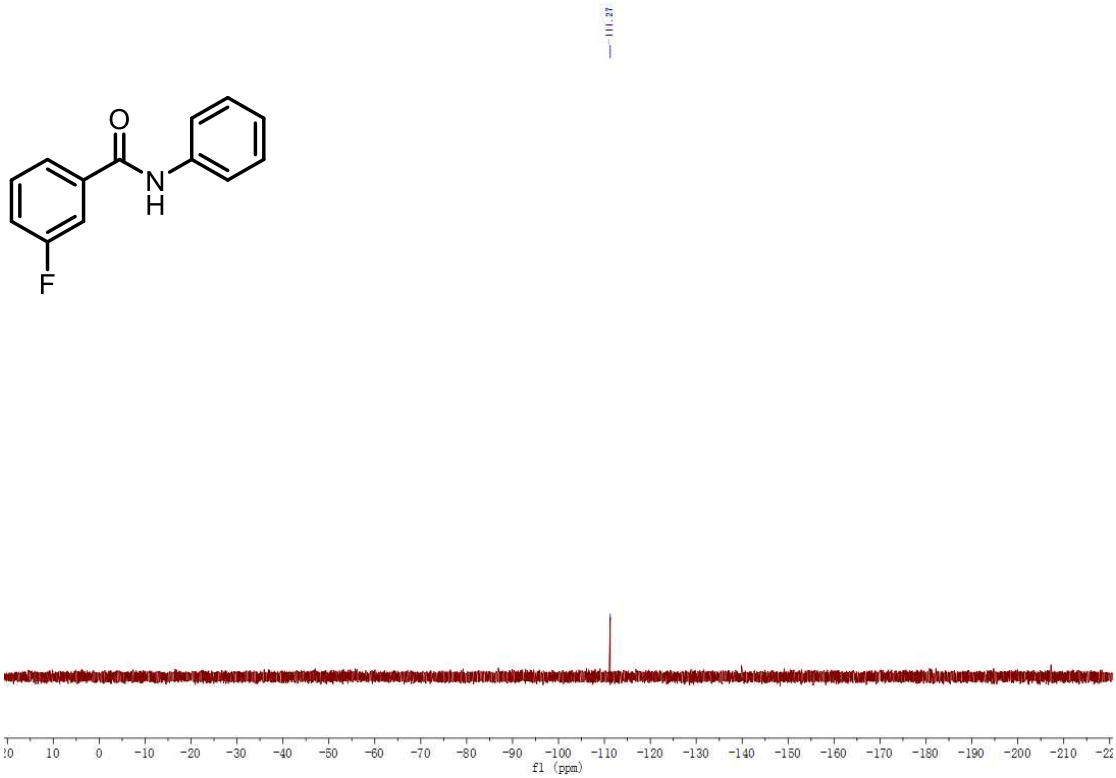
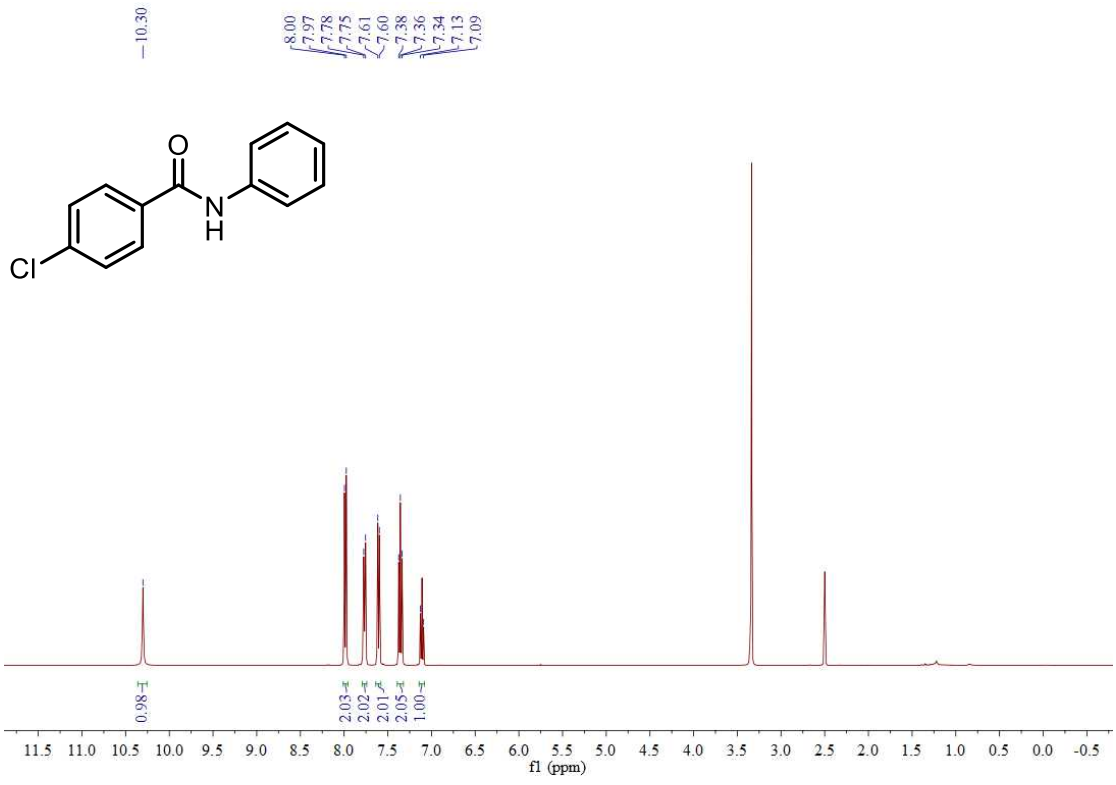



***Figure S10.*** $^{1}H$, $^{13}C$ and $^{19}F$ NMR Spectra for compound **3j**



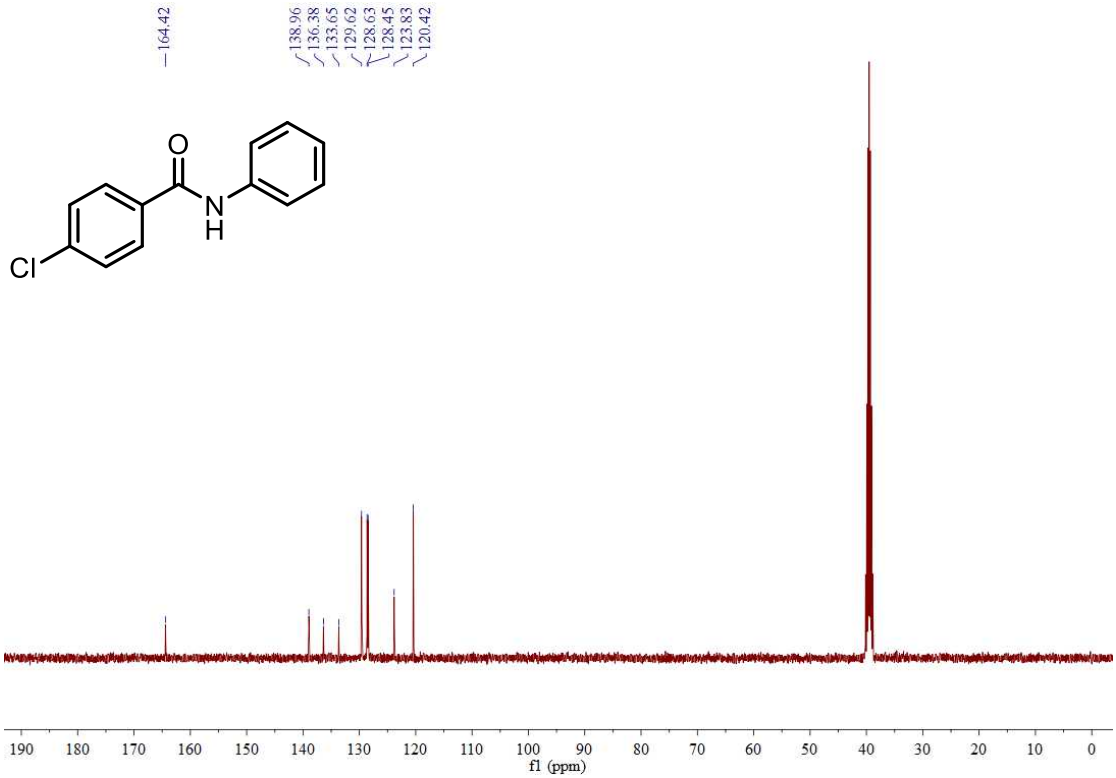
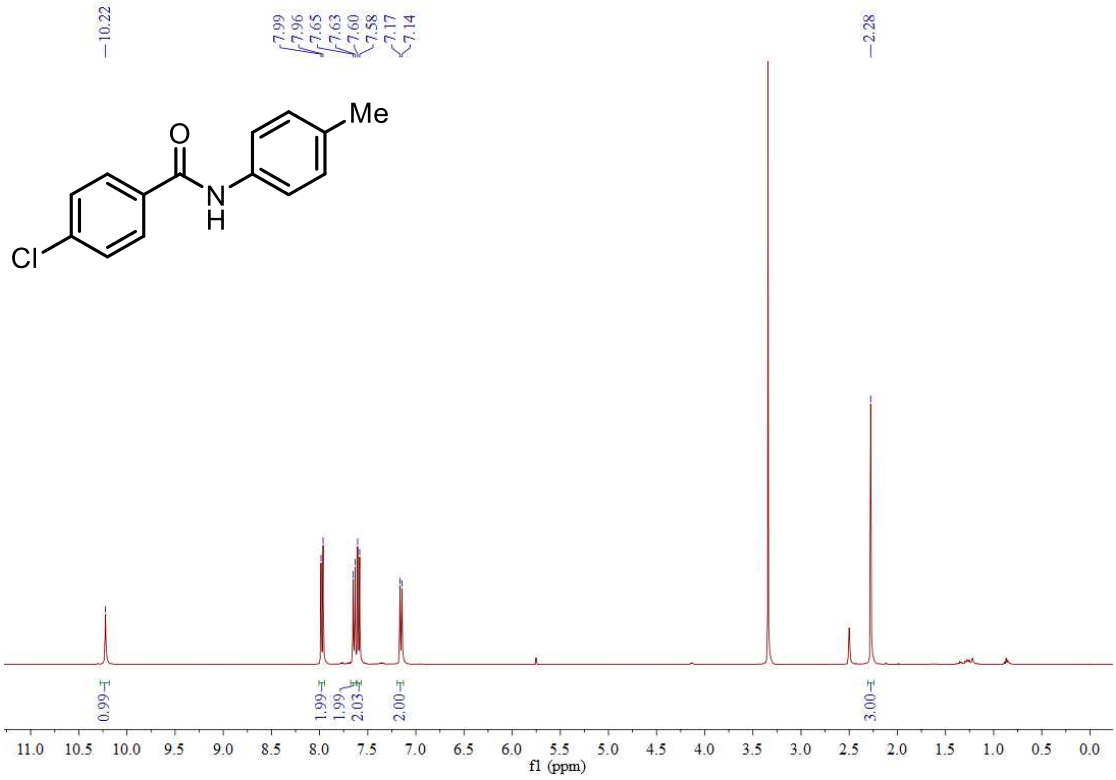



***Figure S11.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3k**



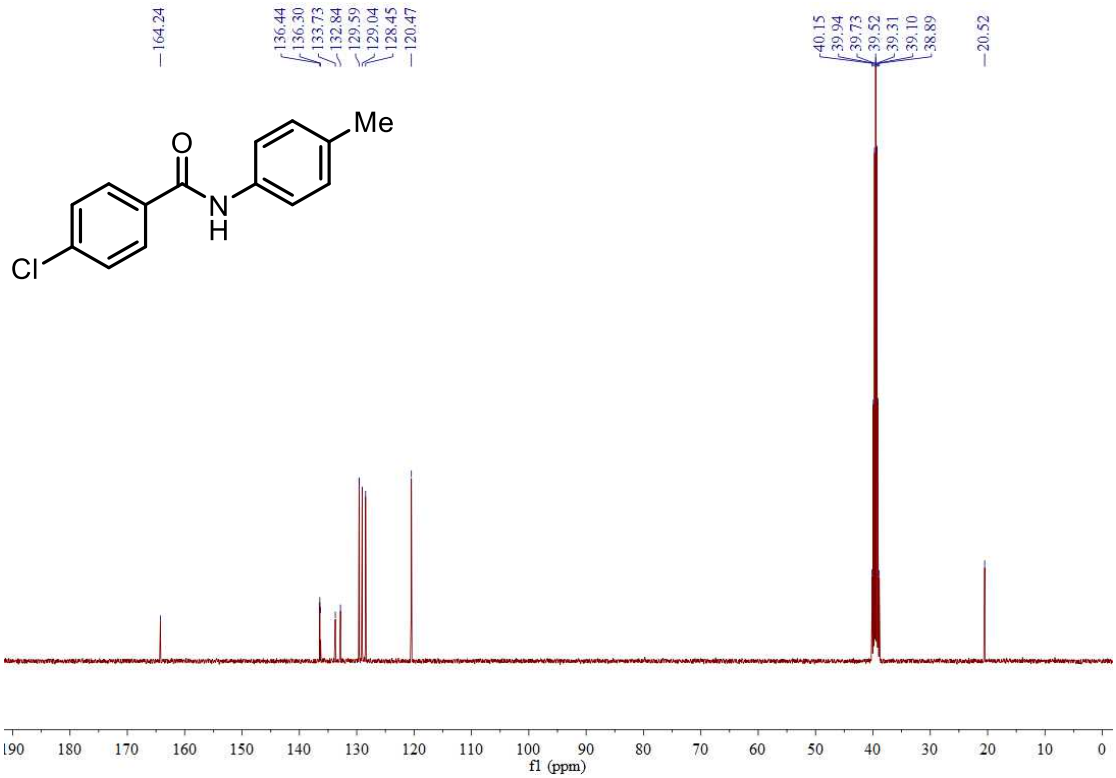
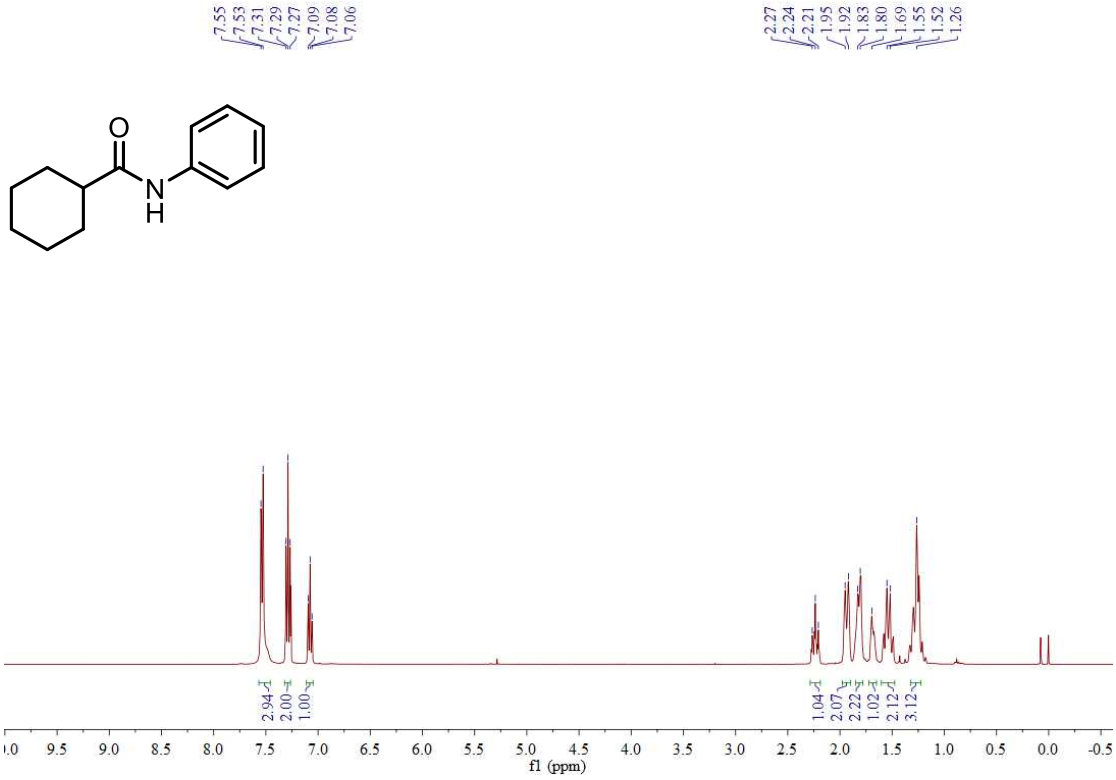



***Figure S12.*** $^{1}$H and $^{13}$C NMR Spectra for compound **3l**



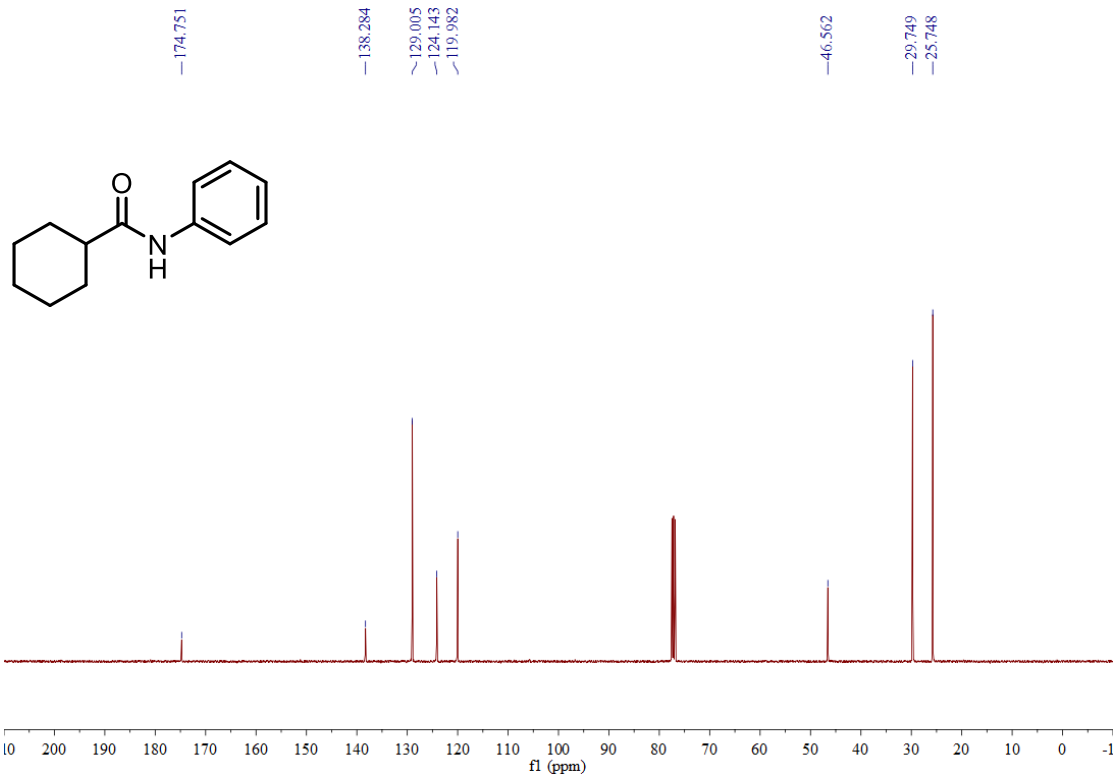
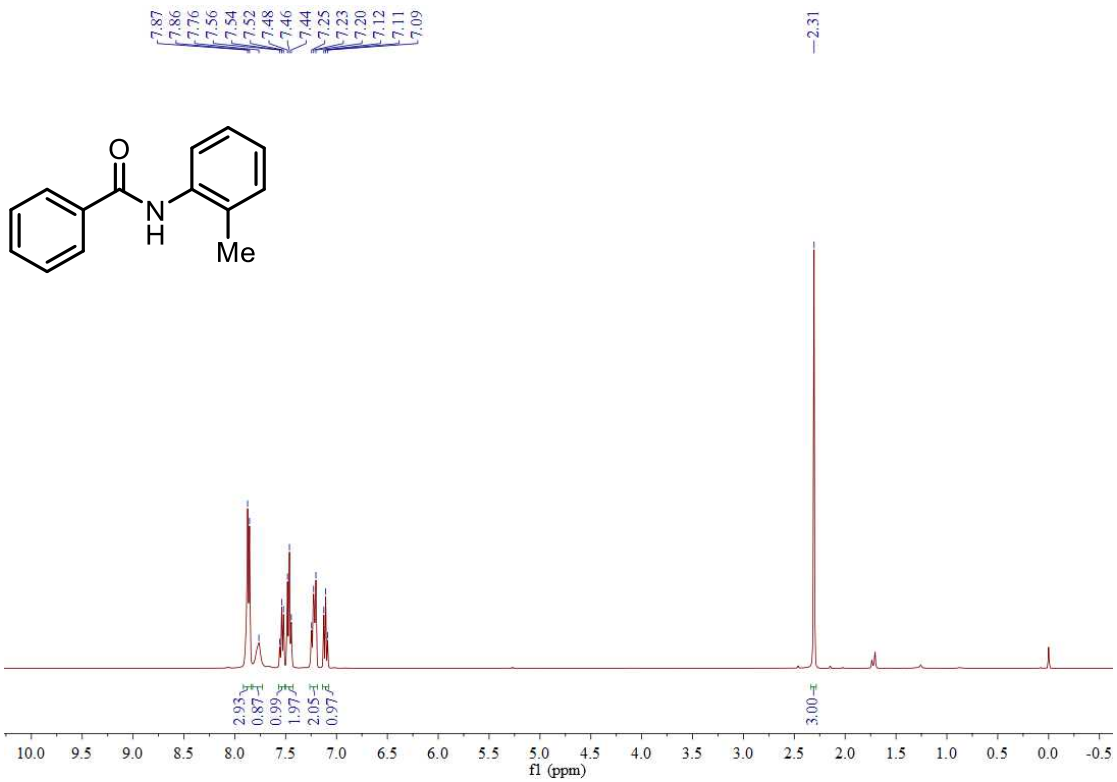



***Figure S13.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3m**



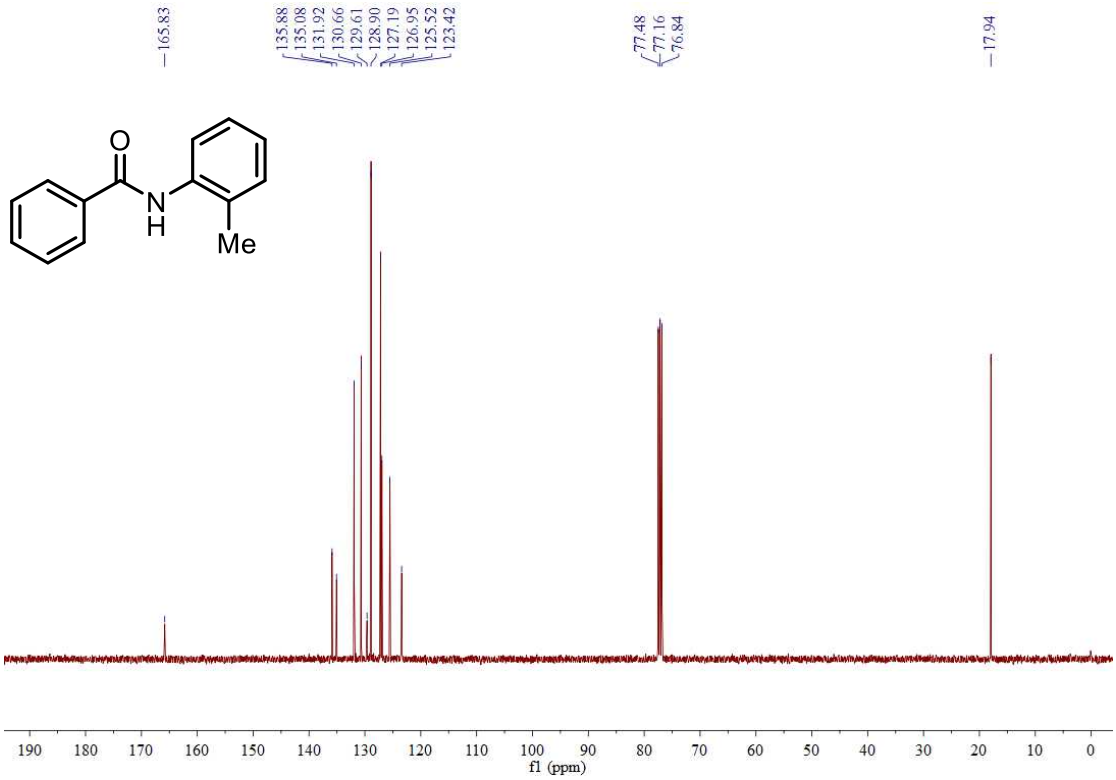
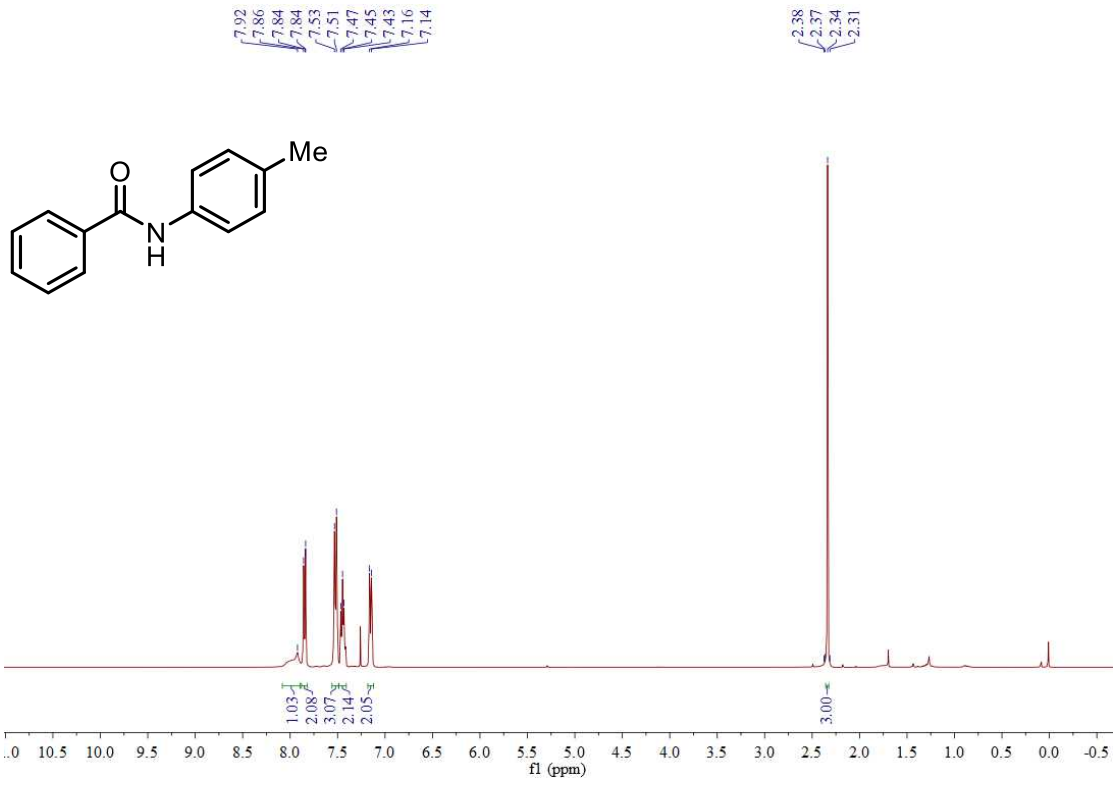



***Figure S14.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3n**



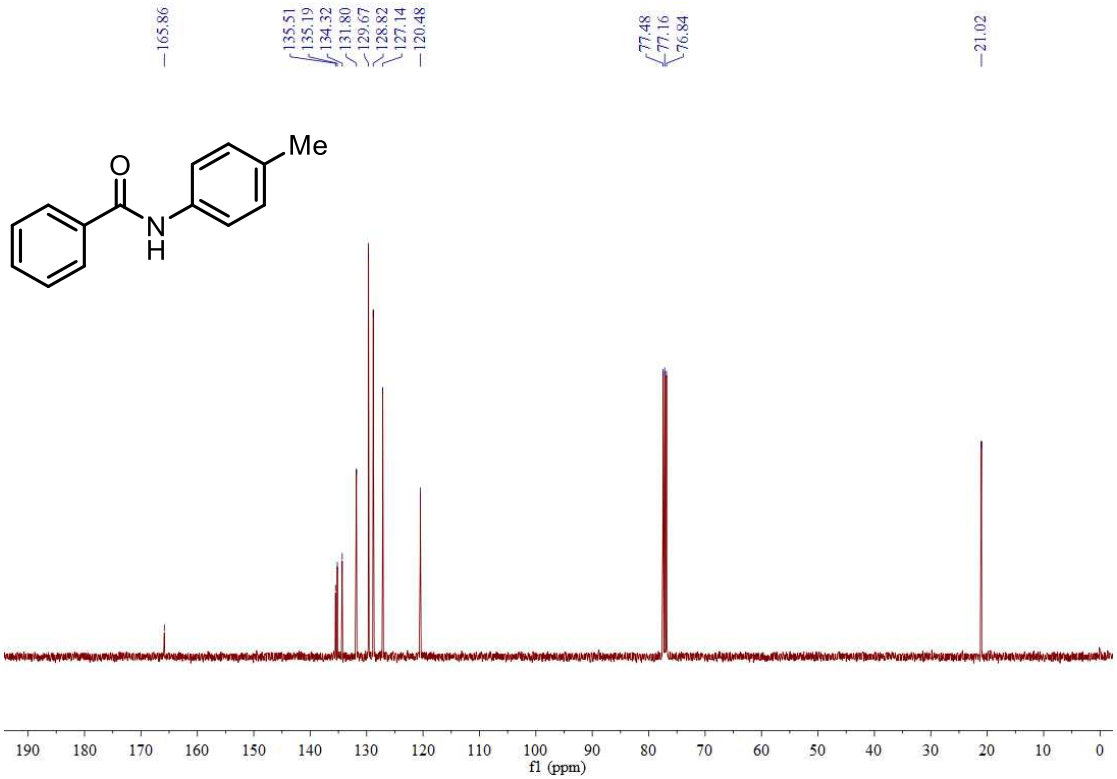
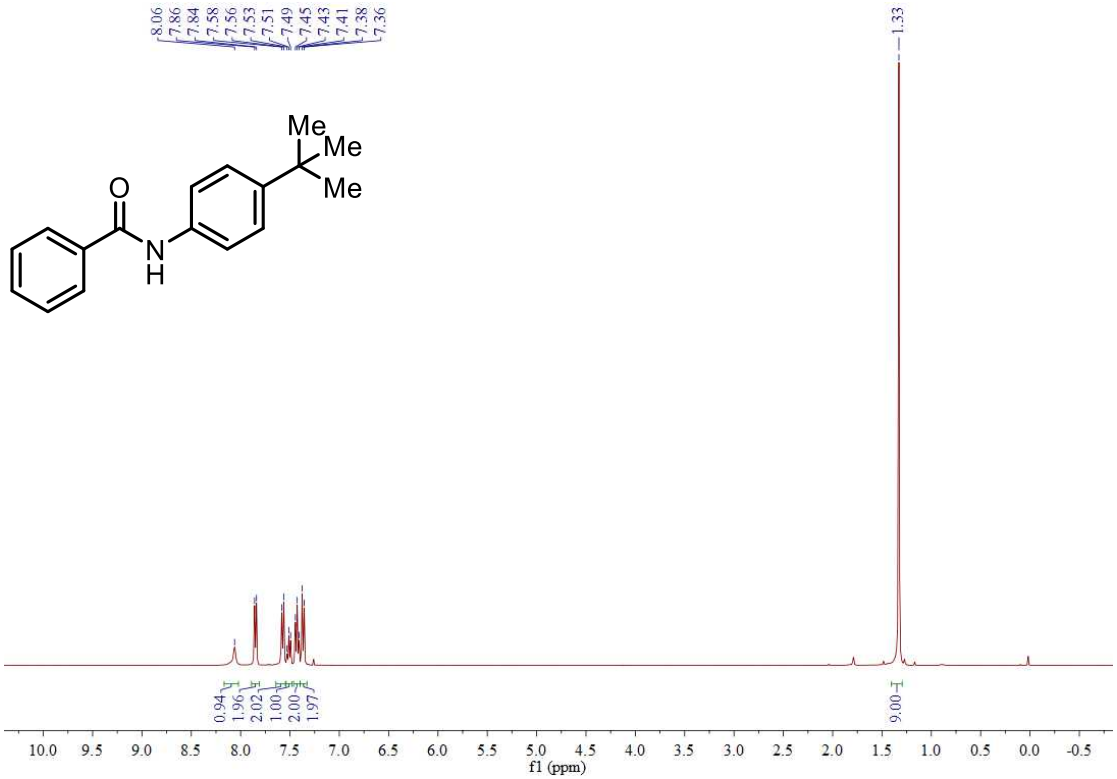



***Figure S15.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3o**



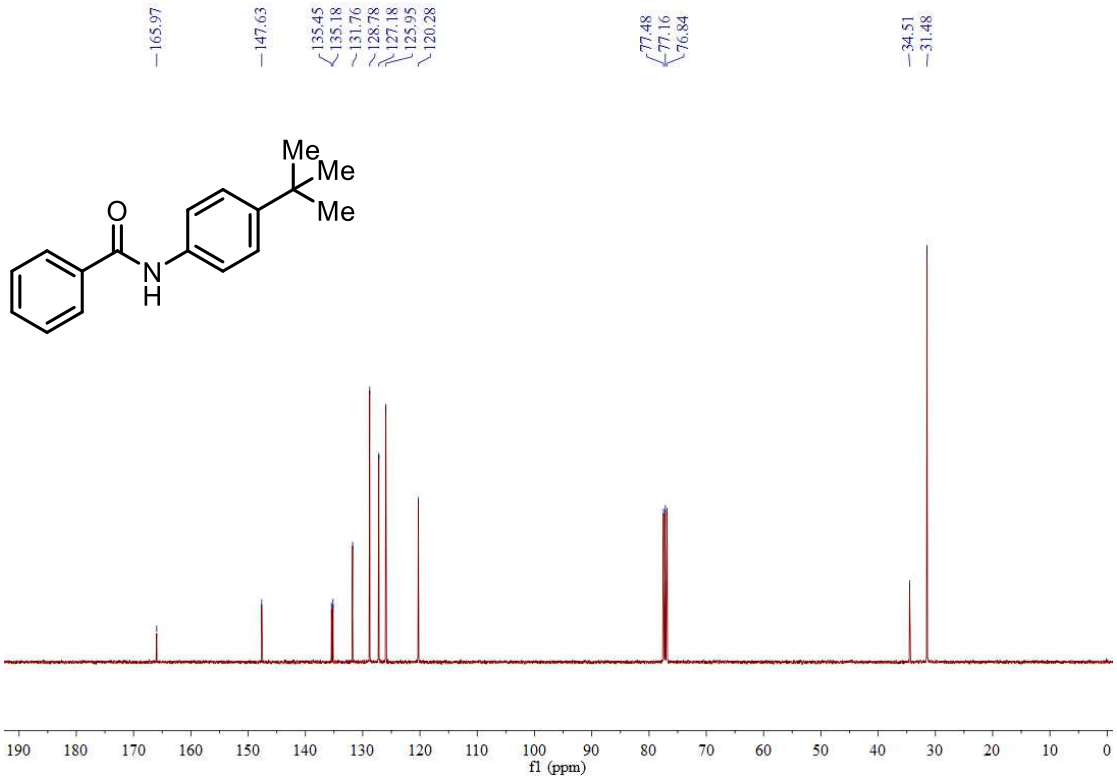
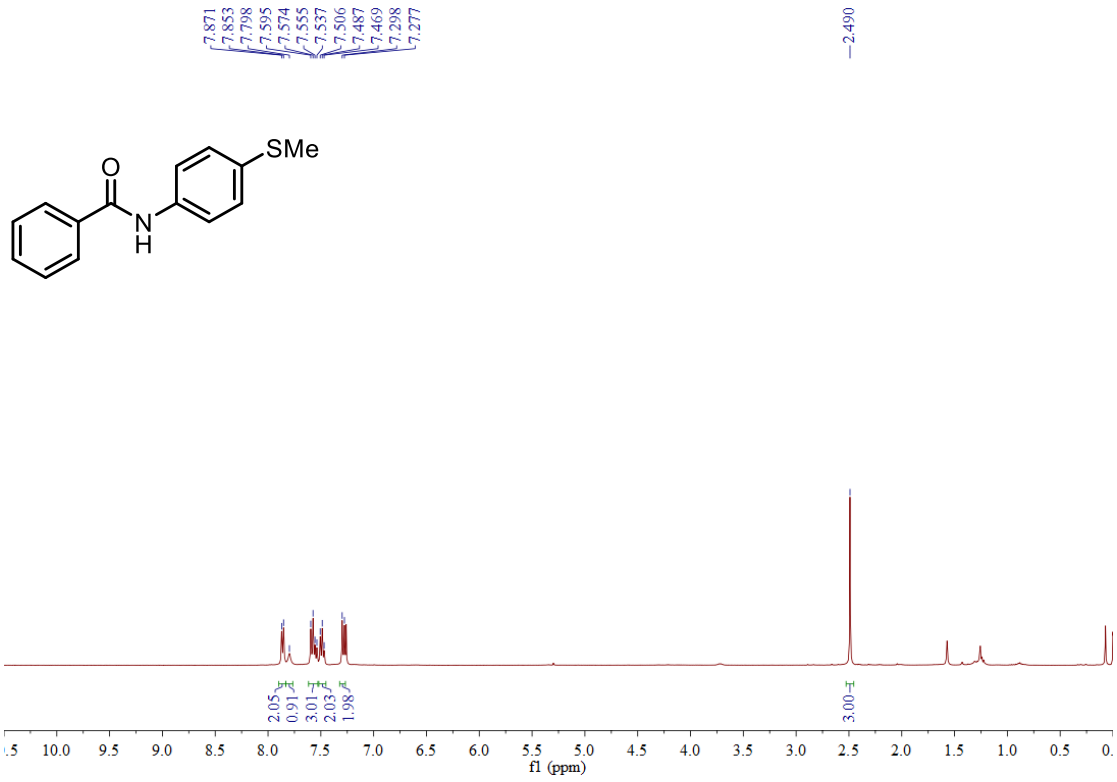



***Figure S16.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3p**



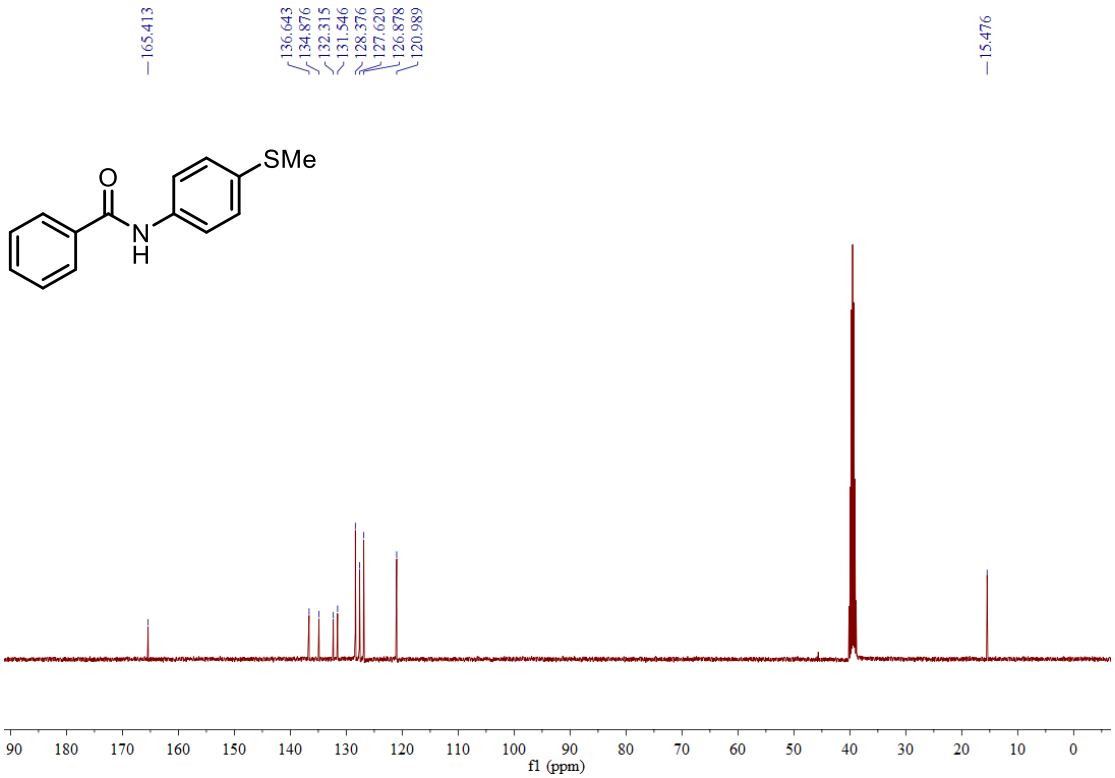
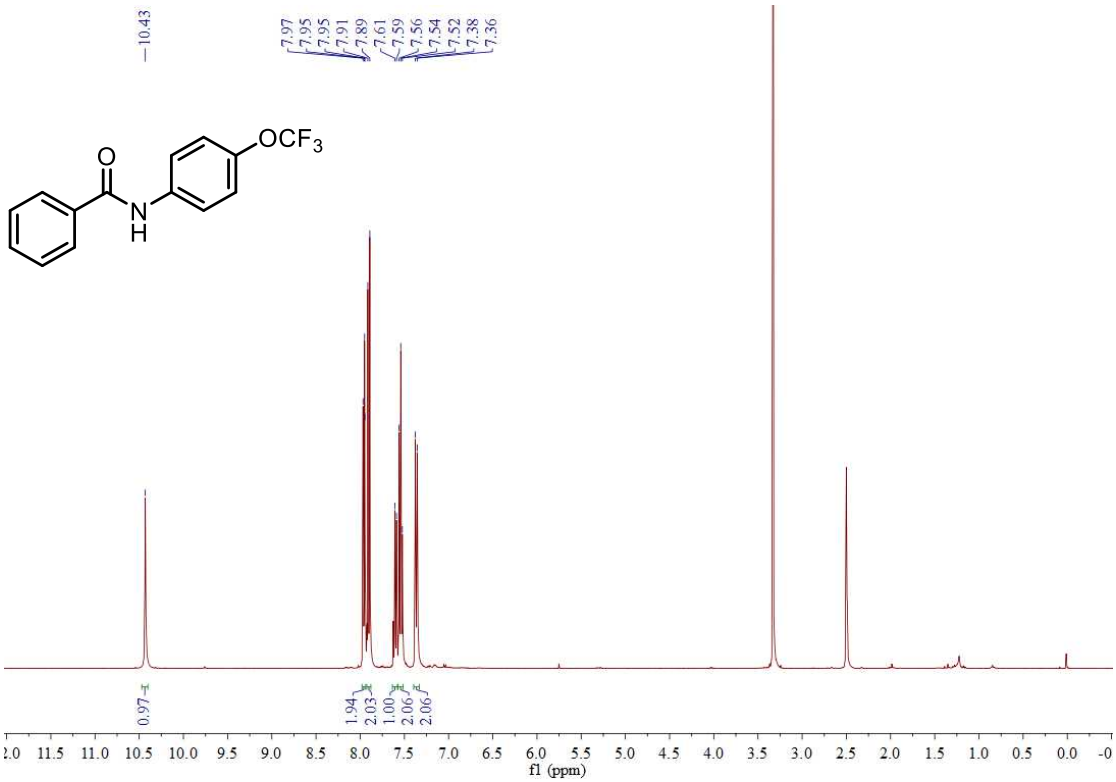



***Figure S17.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3q**



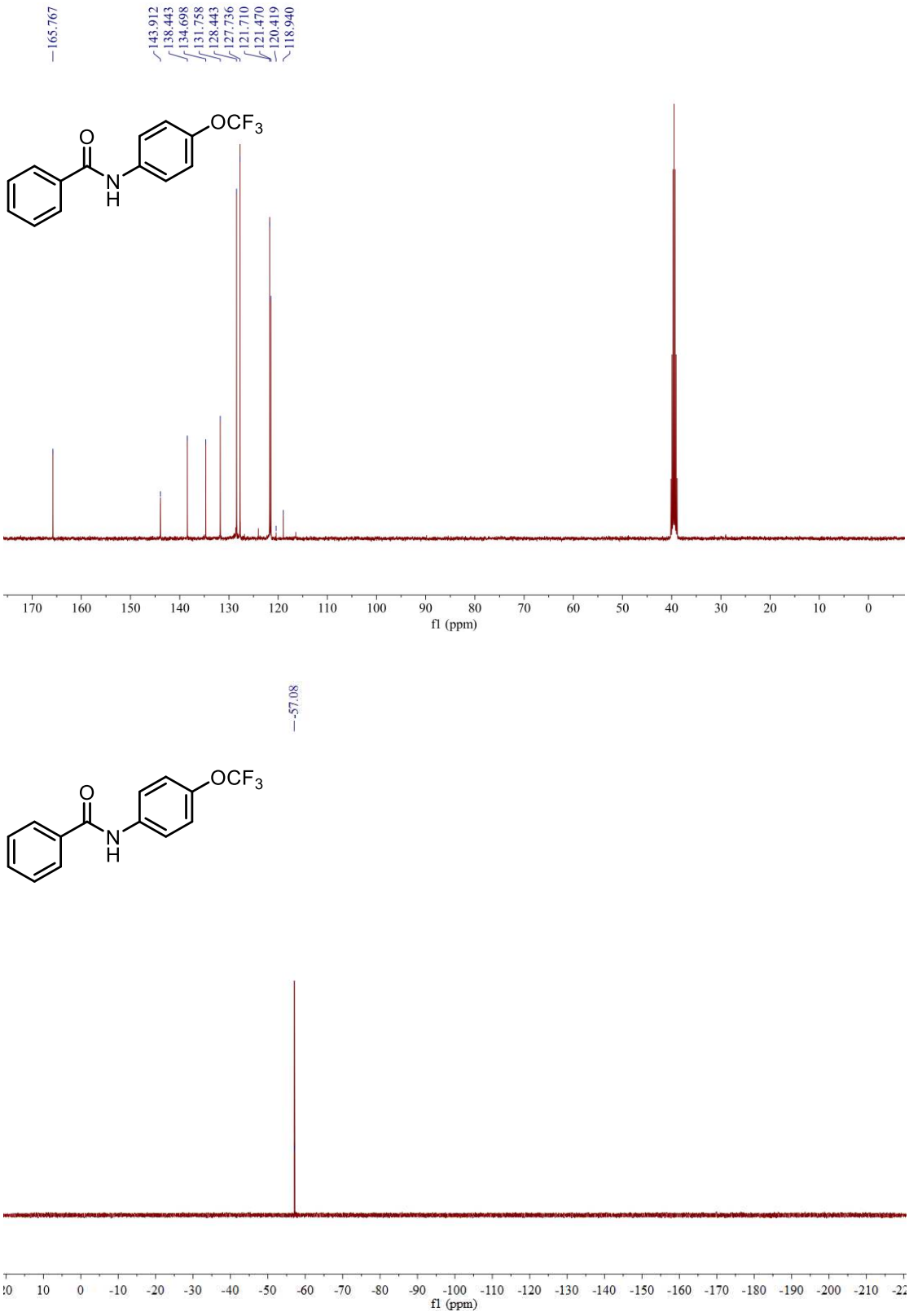
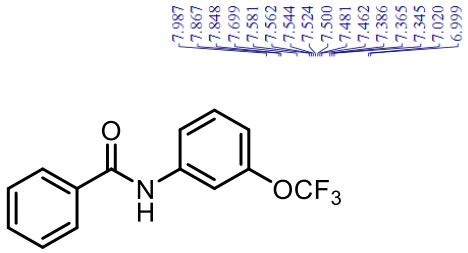
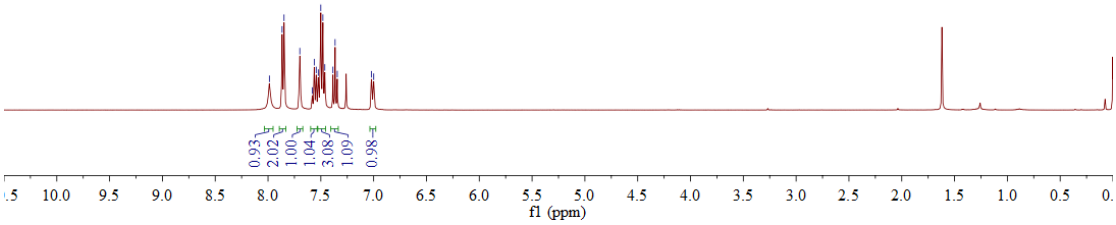
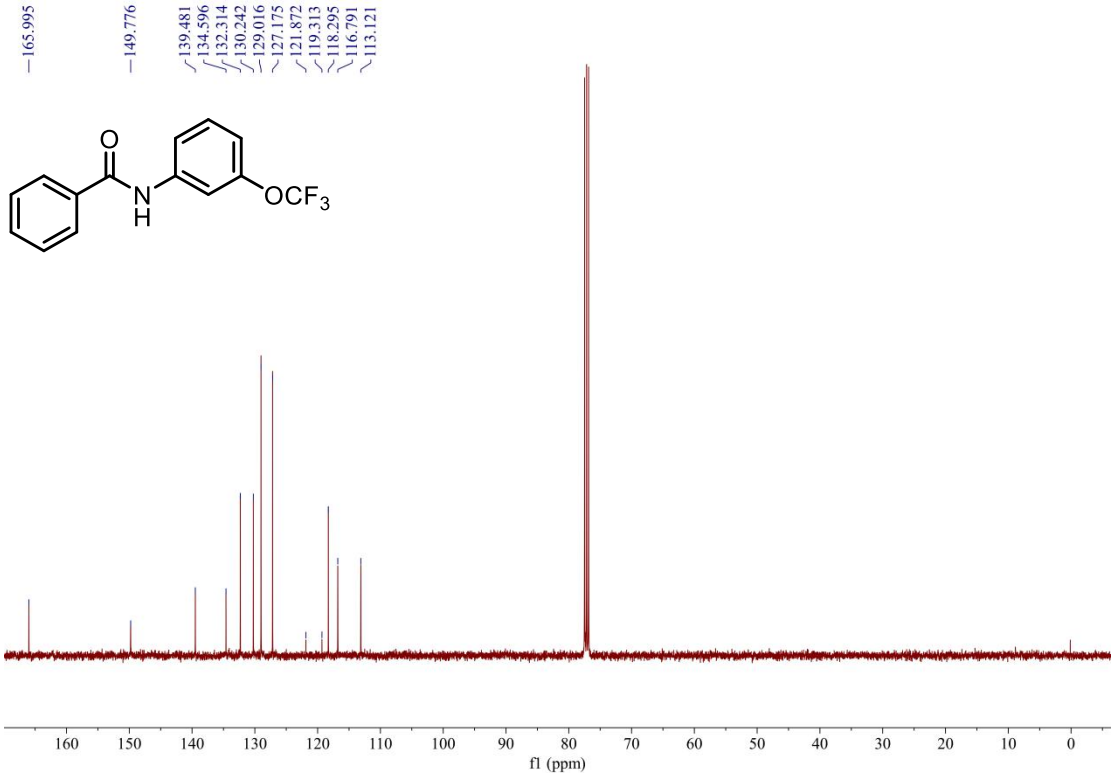



***Figure S18.*** $^{1}H$, $^{13}C$ and $^{19}F$ NMR Spectra for compound **3r**


7.987
7.867
7.848
7.699
7.581
7.562
7.544
7.524
7.500
7.481
7.462
7.386
7.365
7.345
7.020
6.999
O
N
H
OCF3


0.93
2.02
1.00
1.04
3.08
1.09
0.98
f1 (ppm)


165.995
149.776
139.481
134.596
132.314
130.242
129.016
127.175
121.872
119.313
118.295
116.791
113.121
O
N
H
OCF3
f1 (ppm)

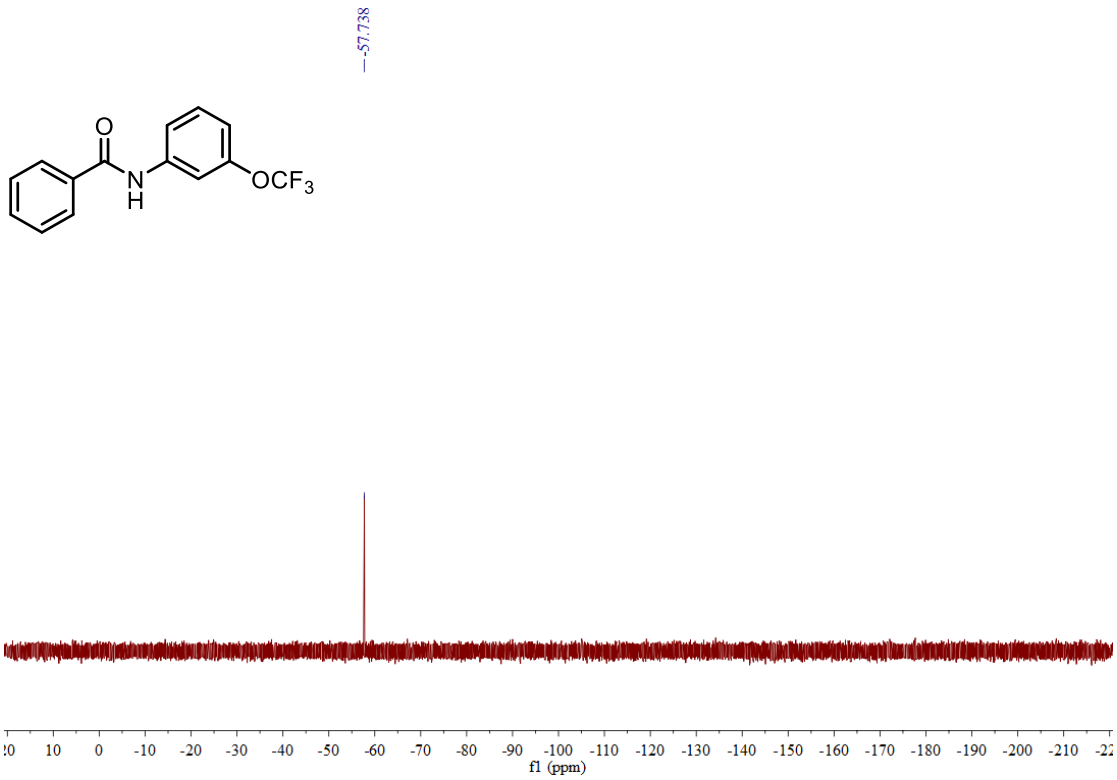
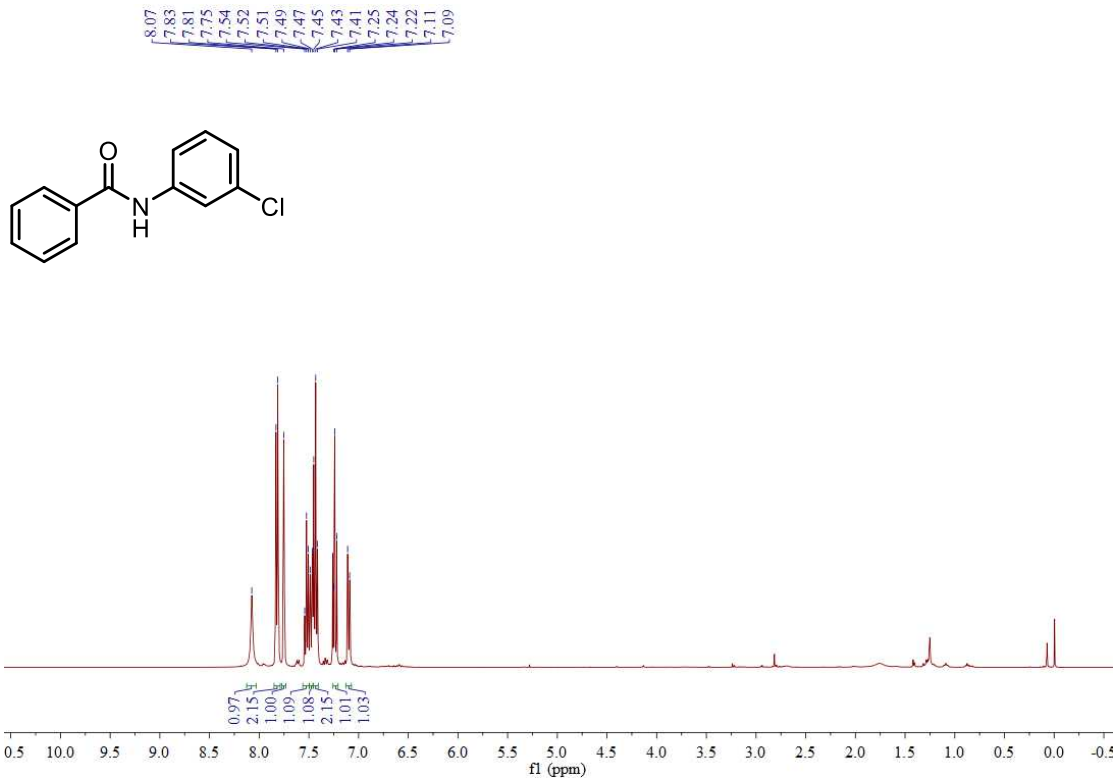



***Figure S19.*** $^{1}H$, $^{13}C$ and $^{19}F$ NMR Spectra for compound **3s**



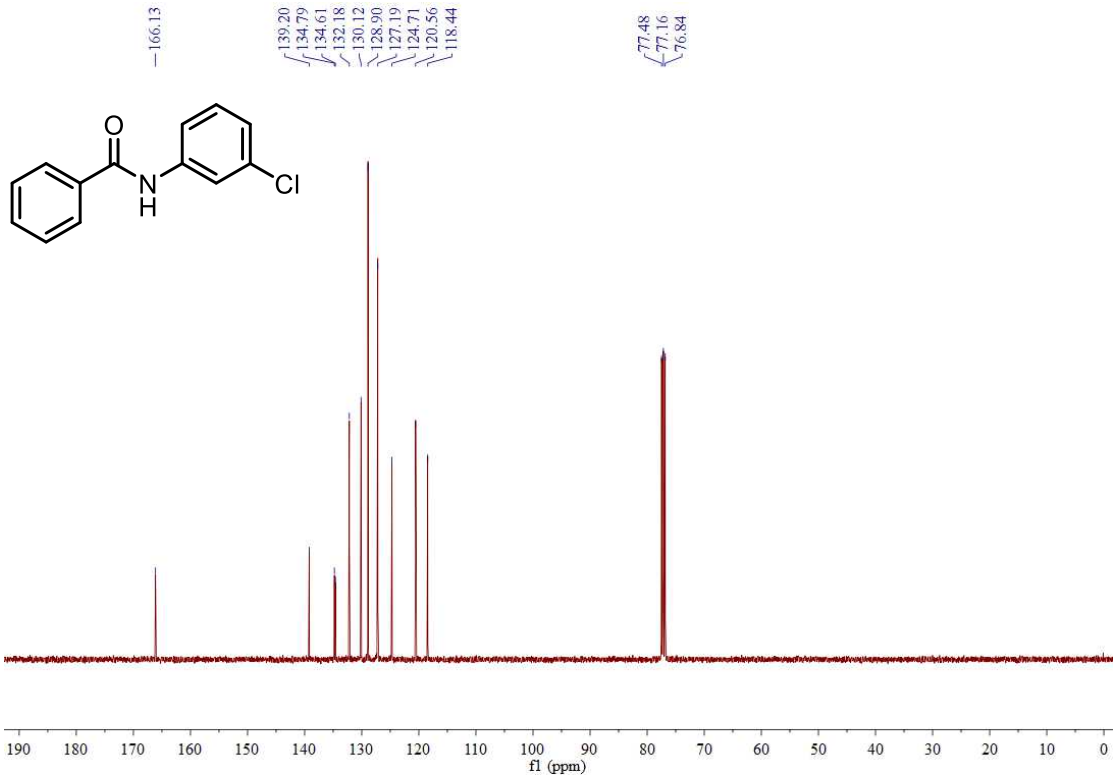
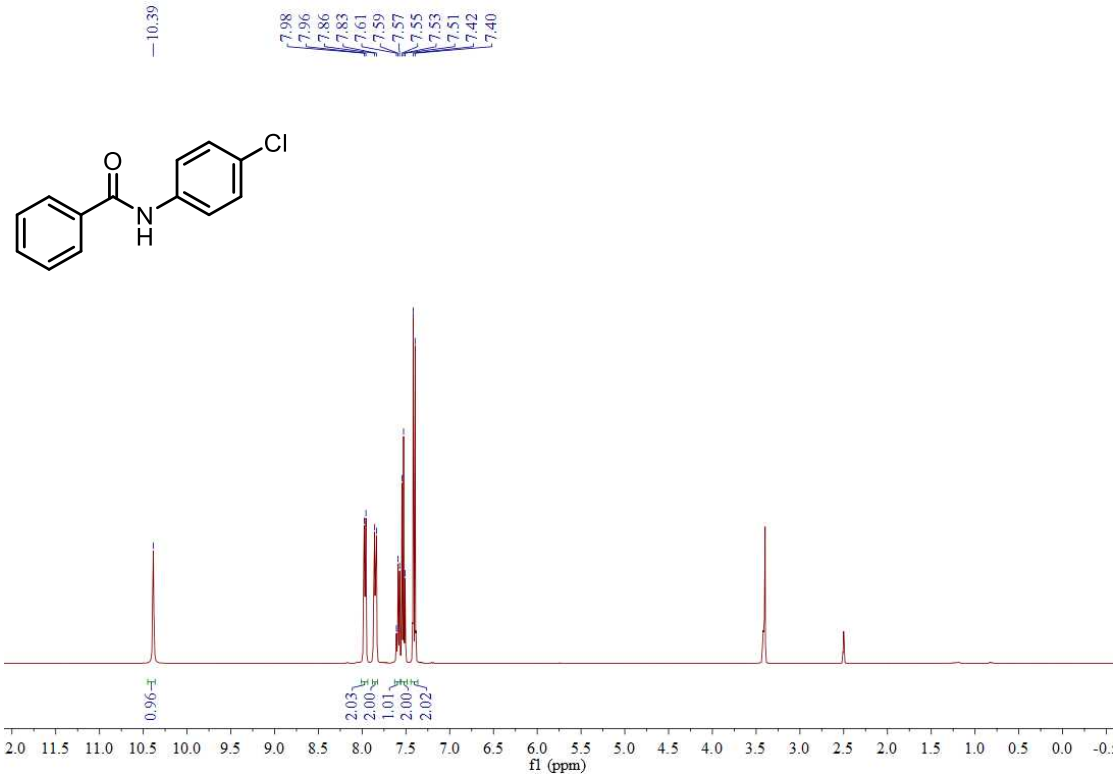



***Figure S21.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3t**



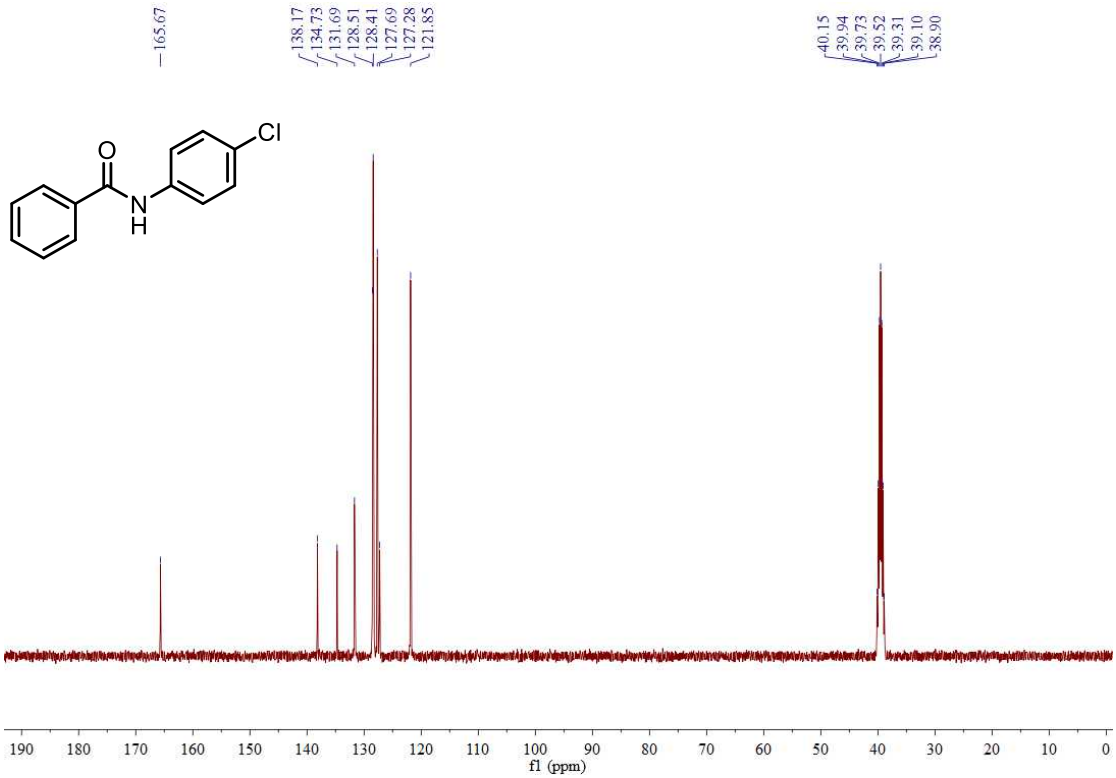
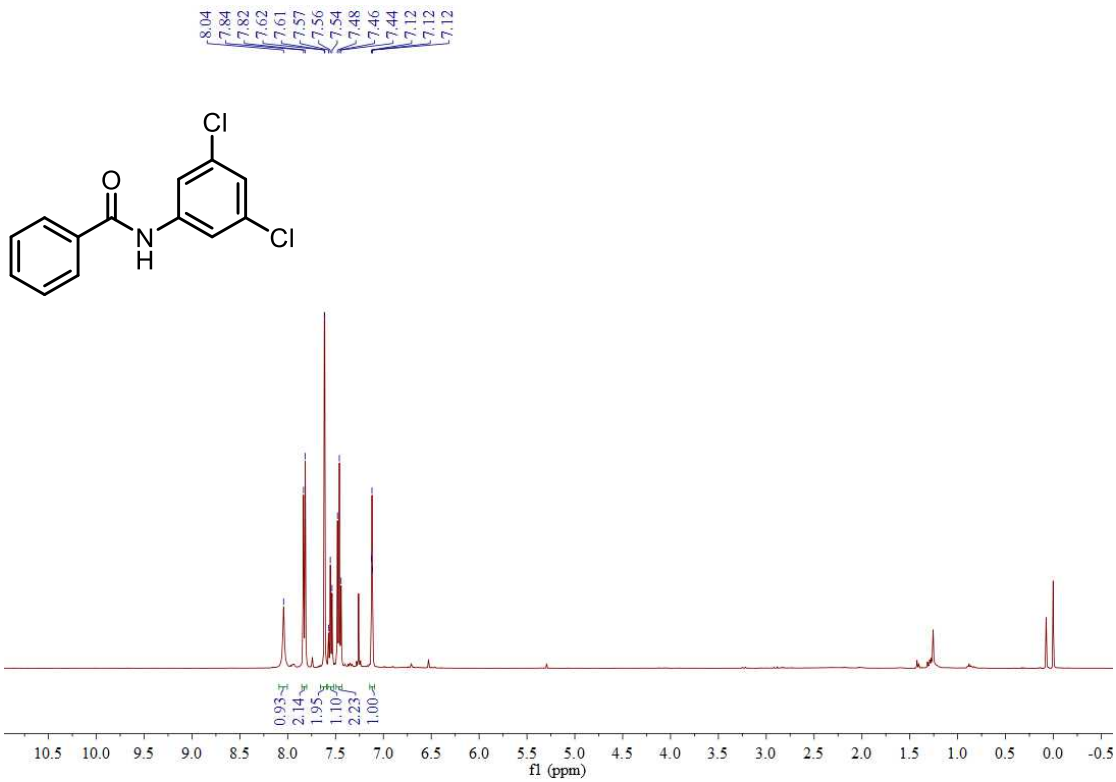



***Figure S22.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3u**



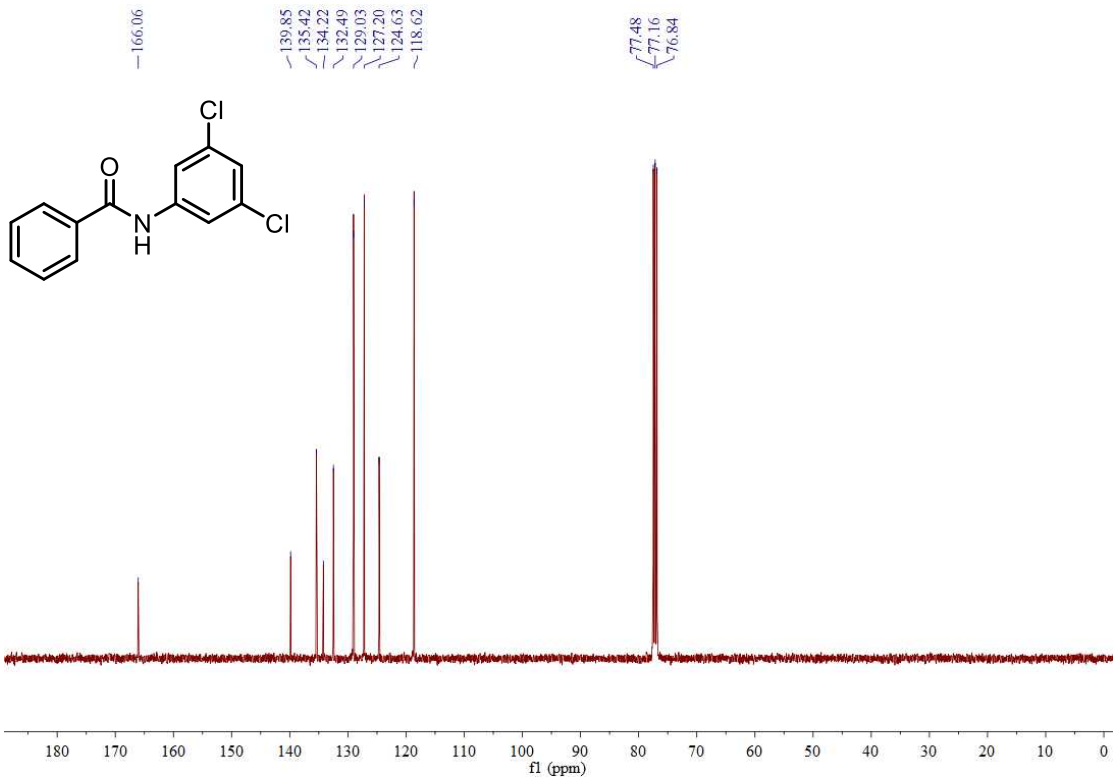
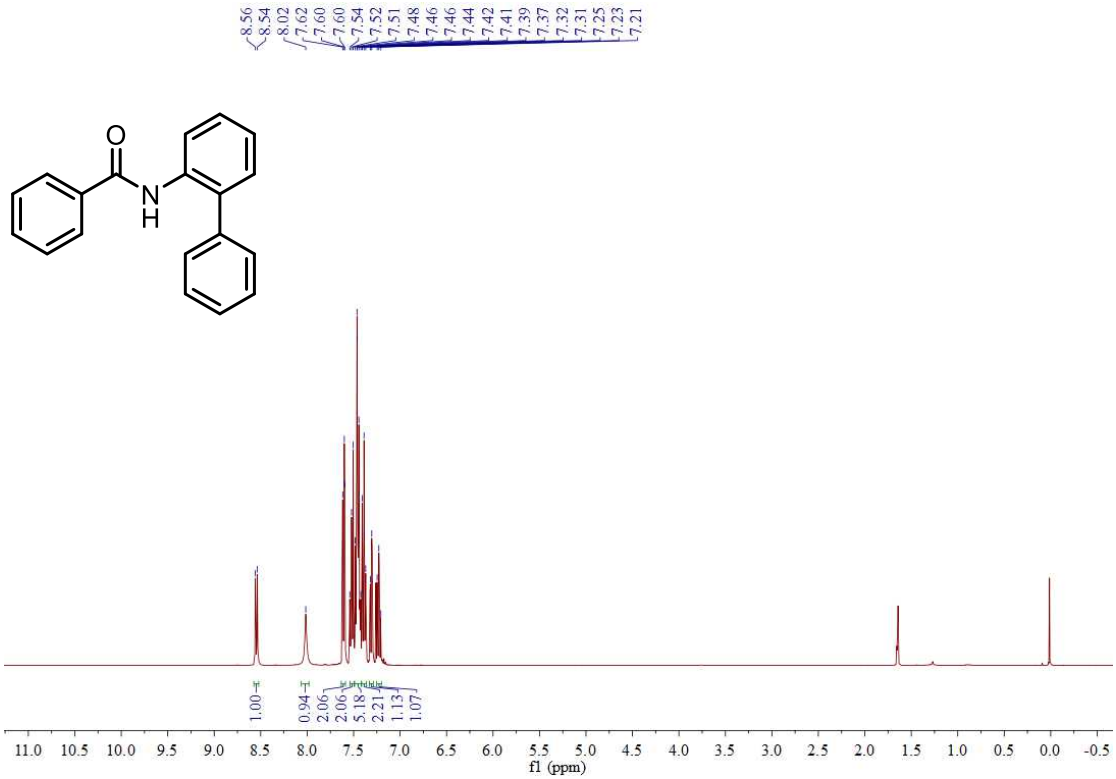



***Figure S23.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3v**



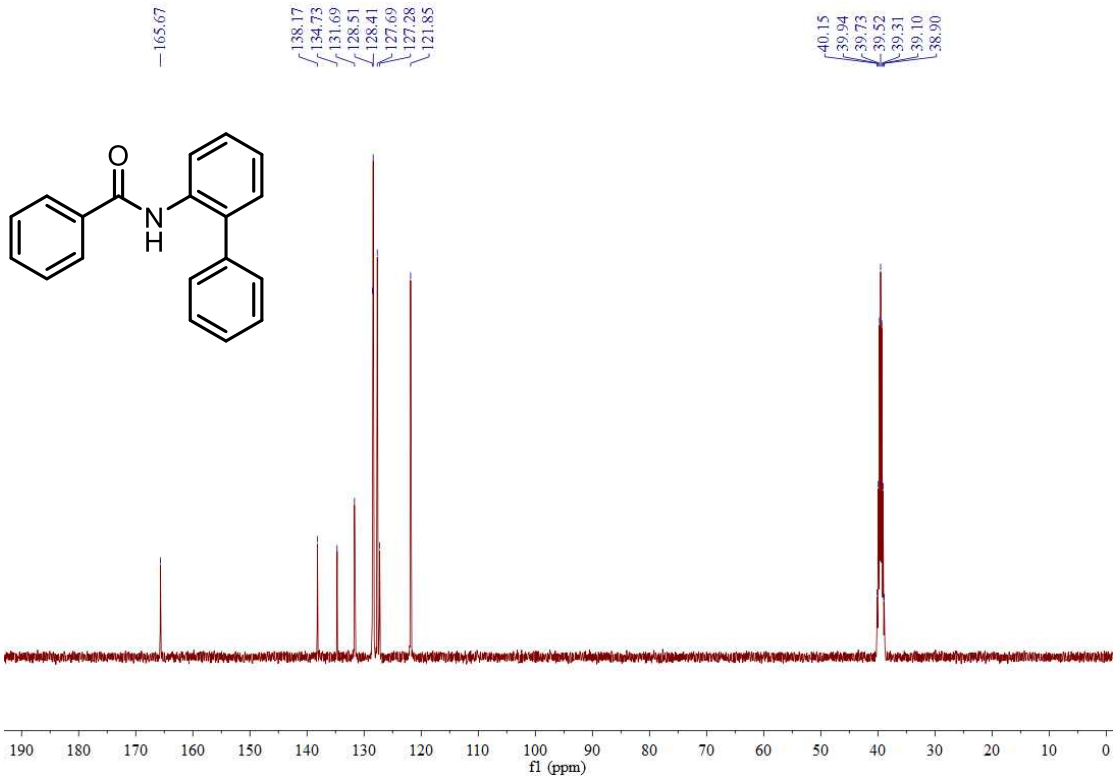
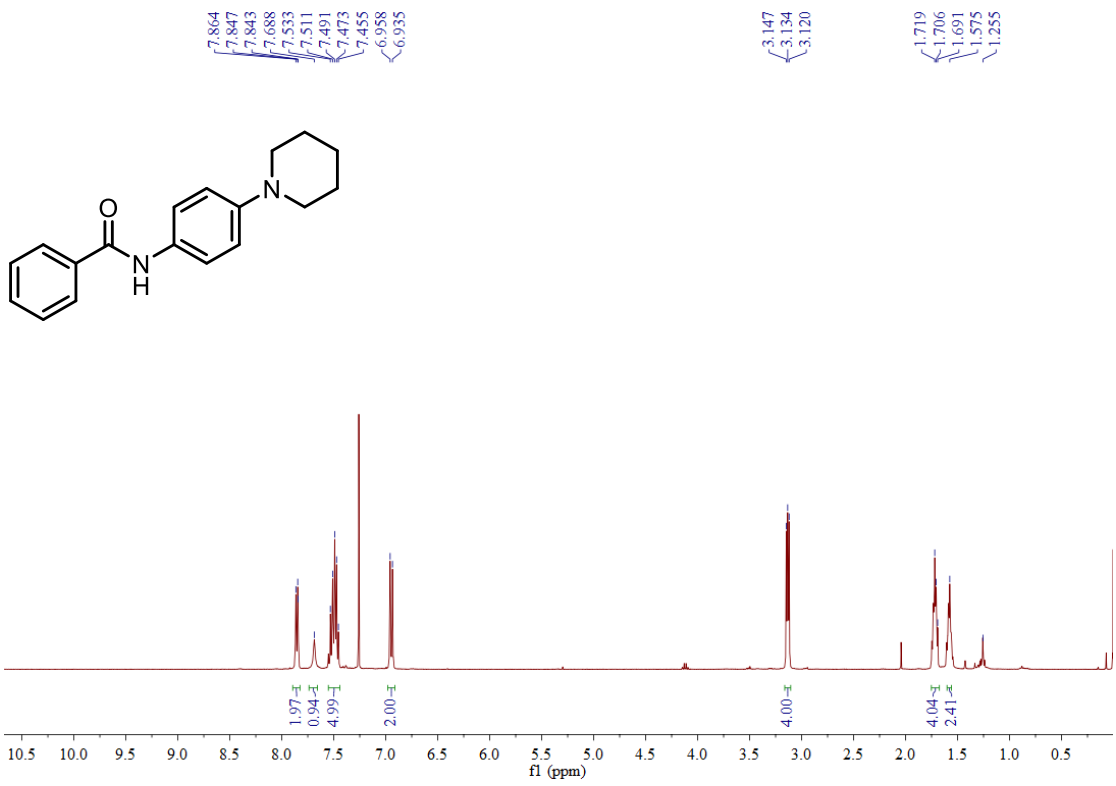



***Figure S23.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3w**



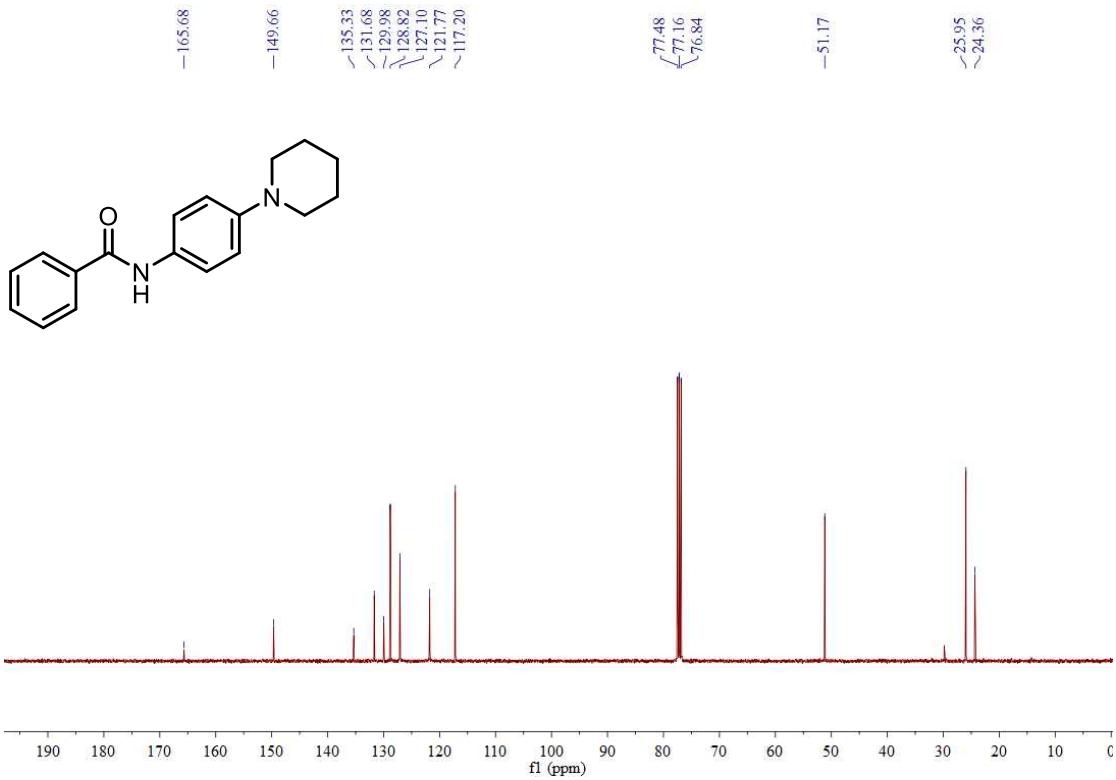
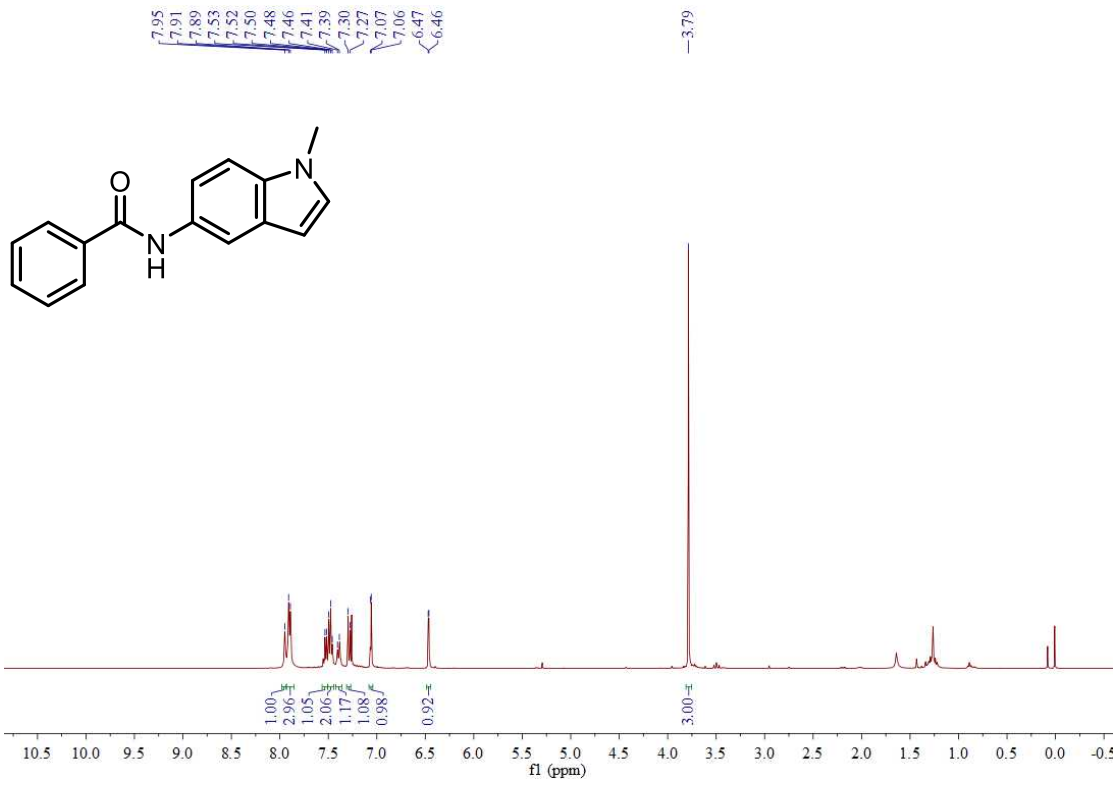



***Figure S24.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3x**



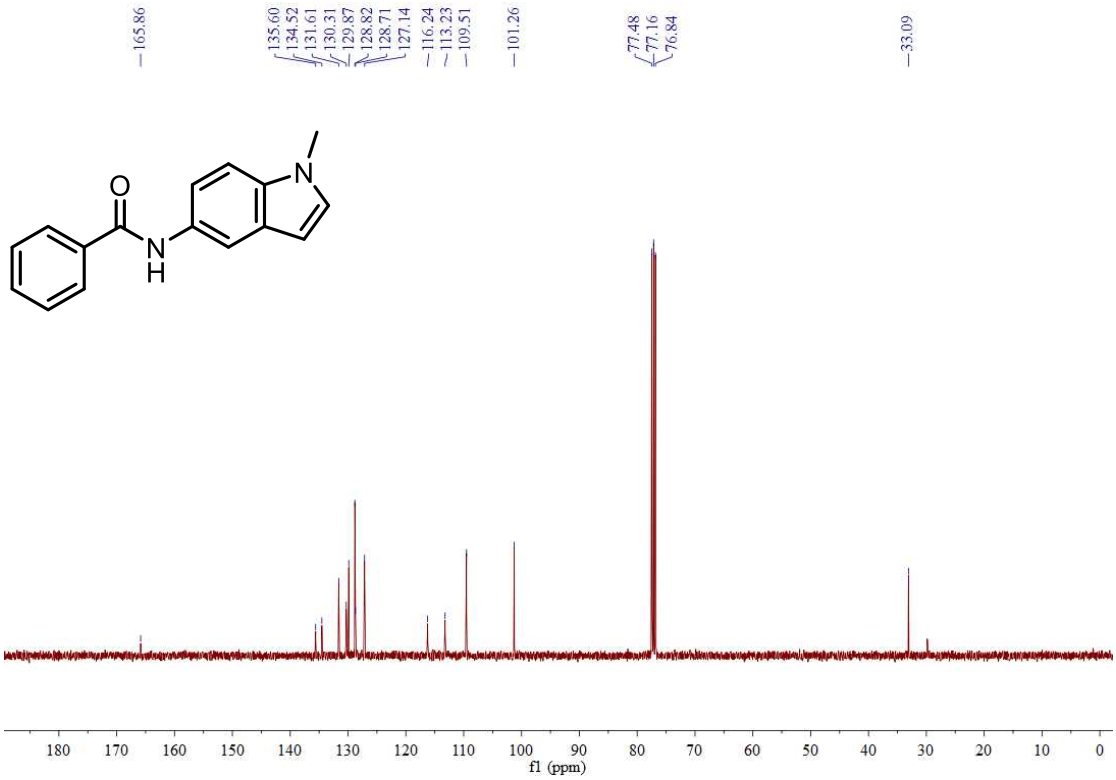
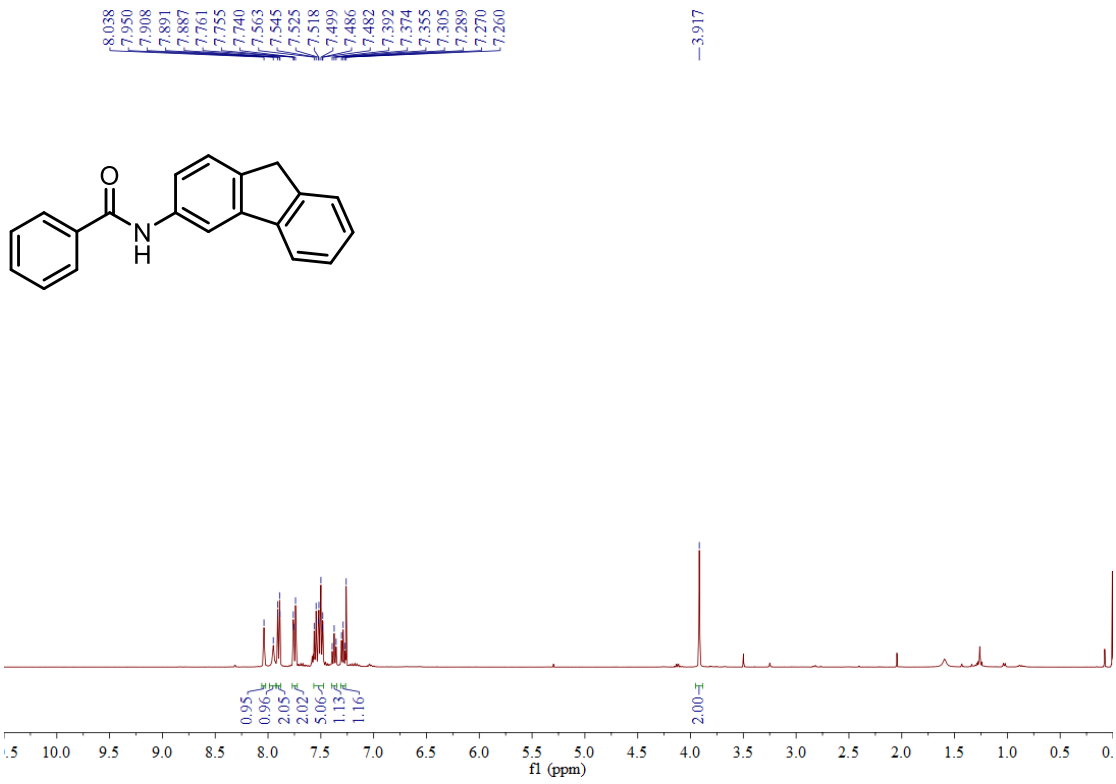



***Figure S25.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3y**



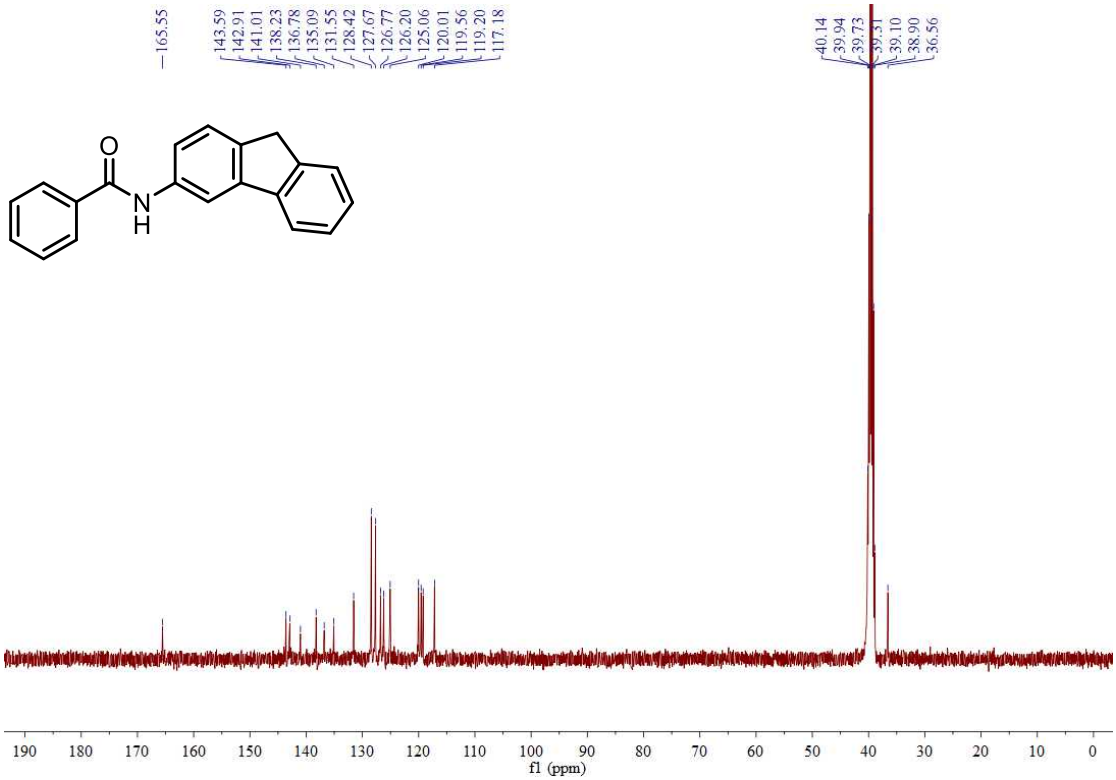
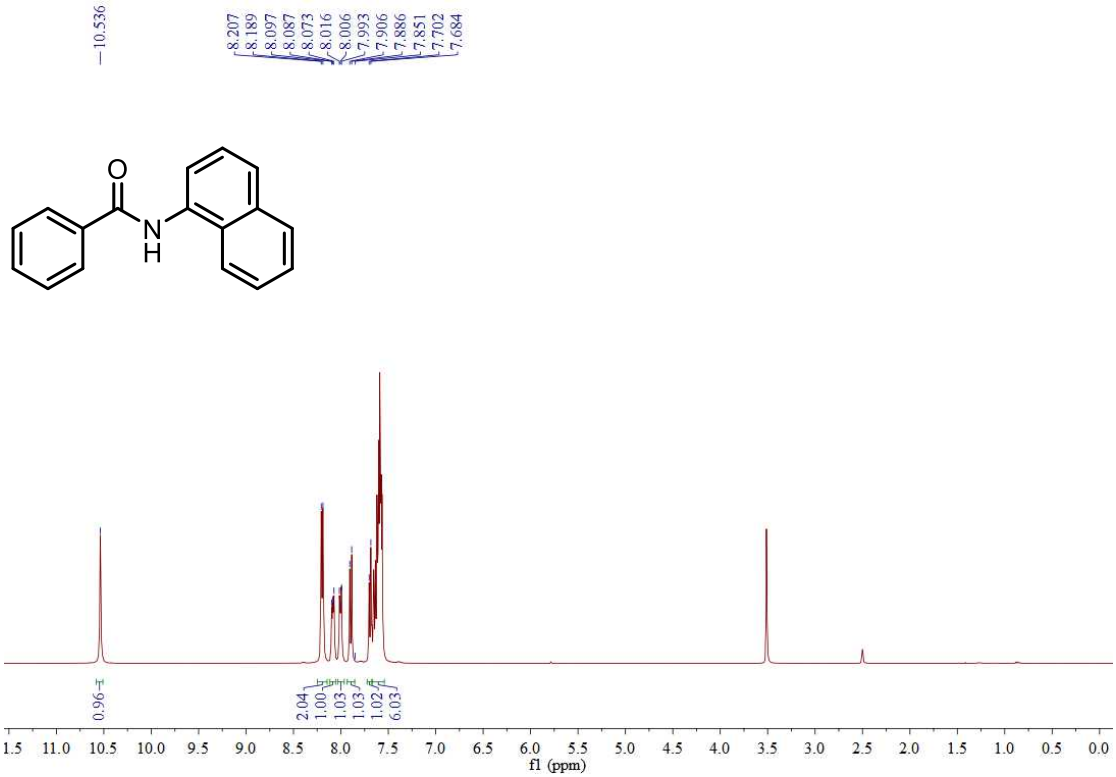



***Figure S26.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3z**



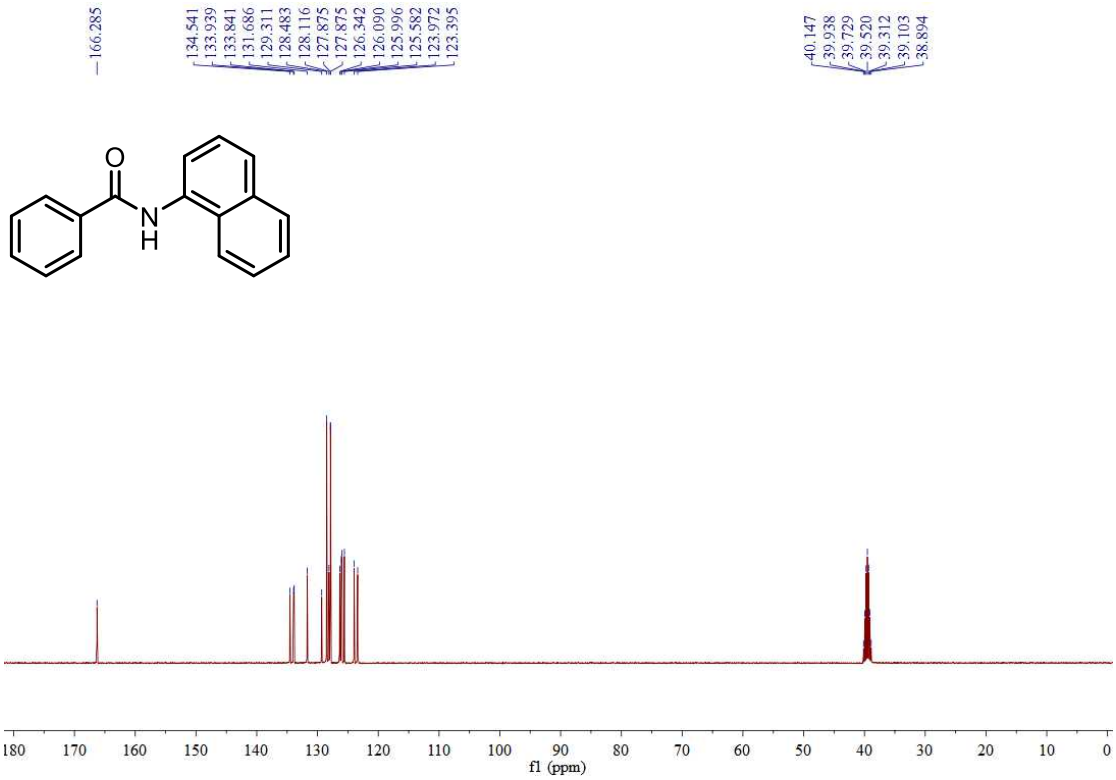
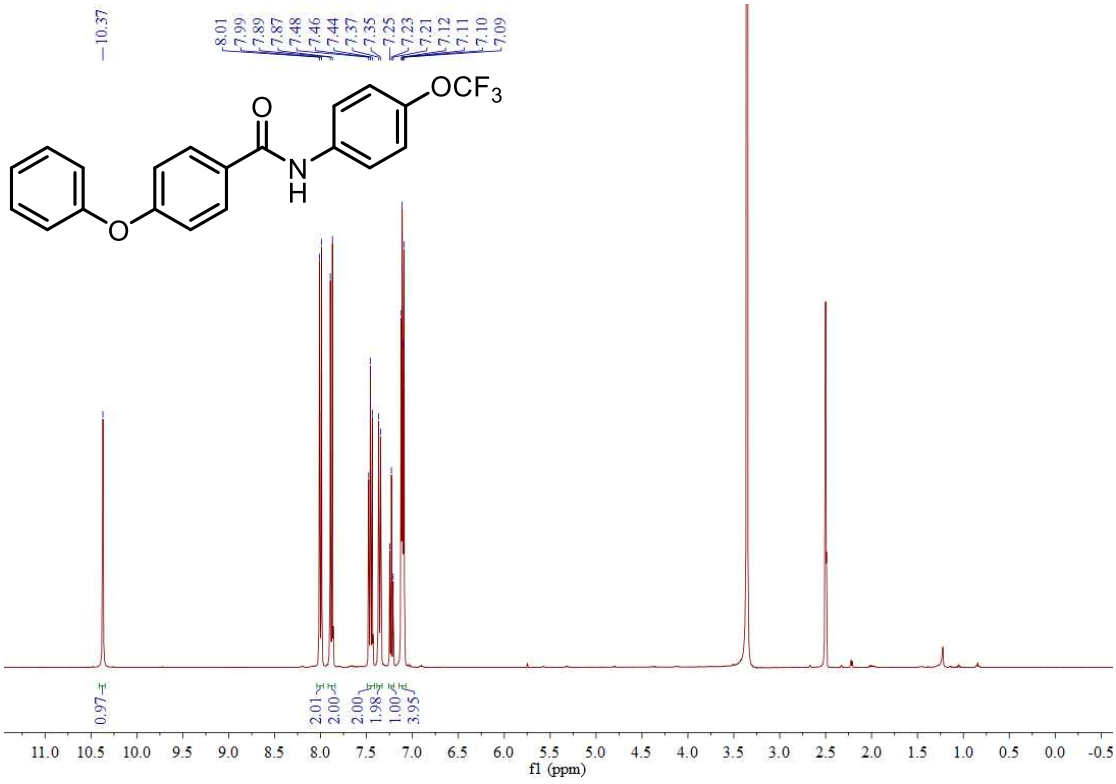
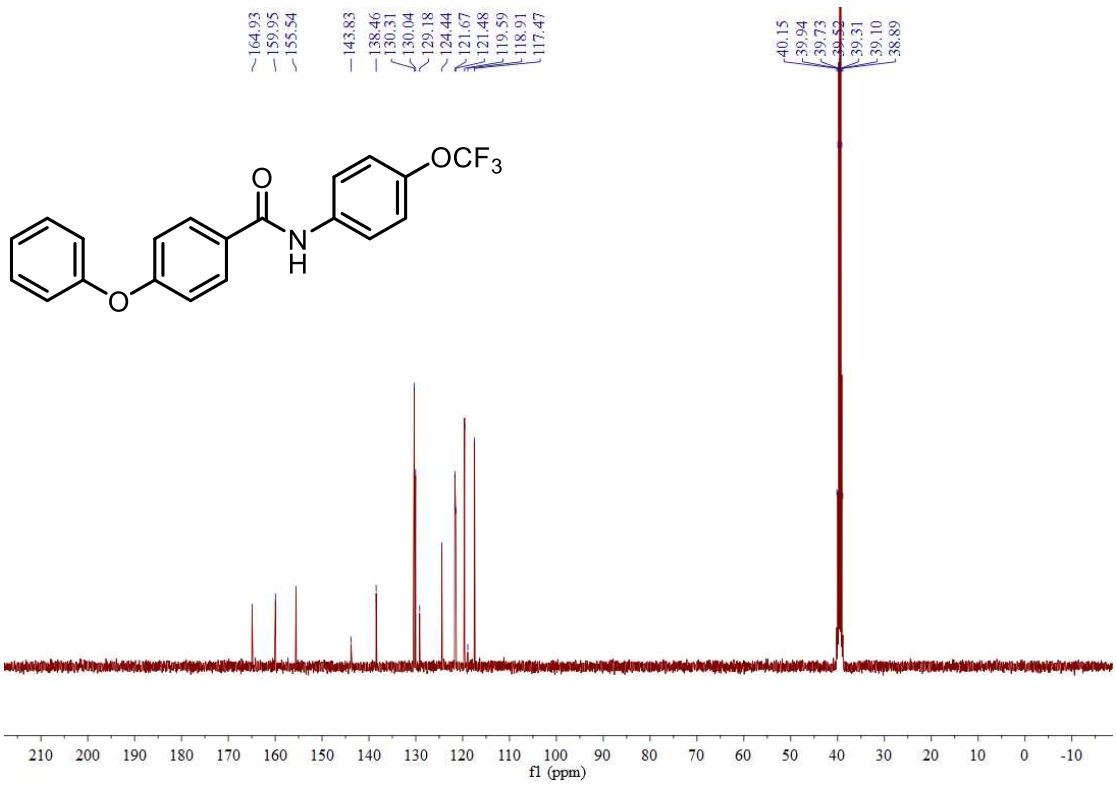



***Figure S27.*** $^{1}H$ and $^{13}C$ NMR Spectra for compound **3aa**





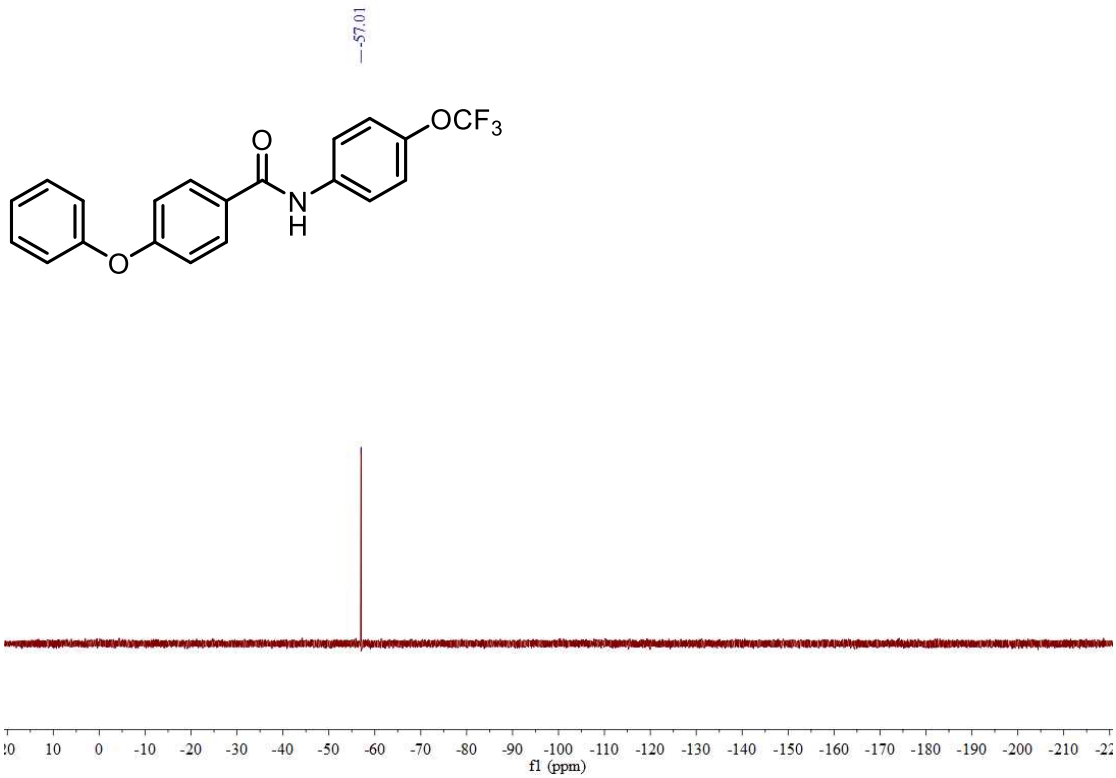




***Figure S28.*** $^{1}H$, $^{13}C$ and $^{19}F$ NMR Spectra for compound **3ab**

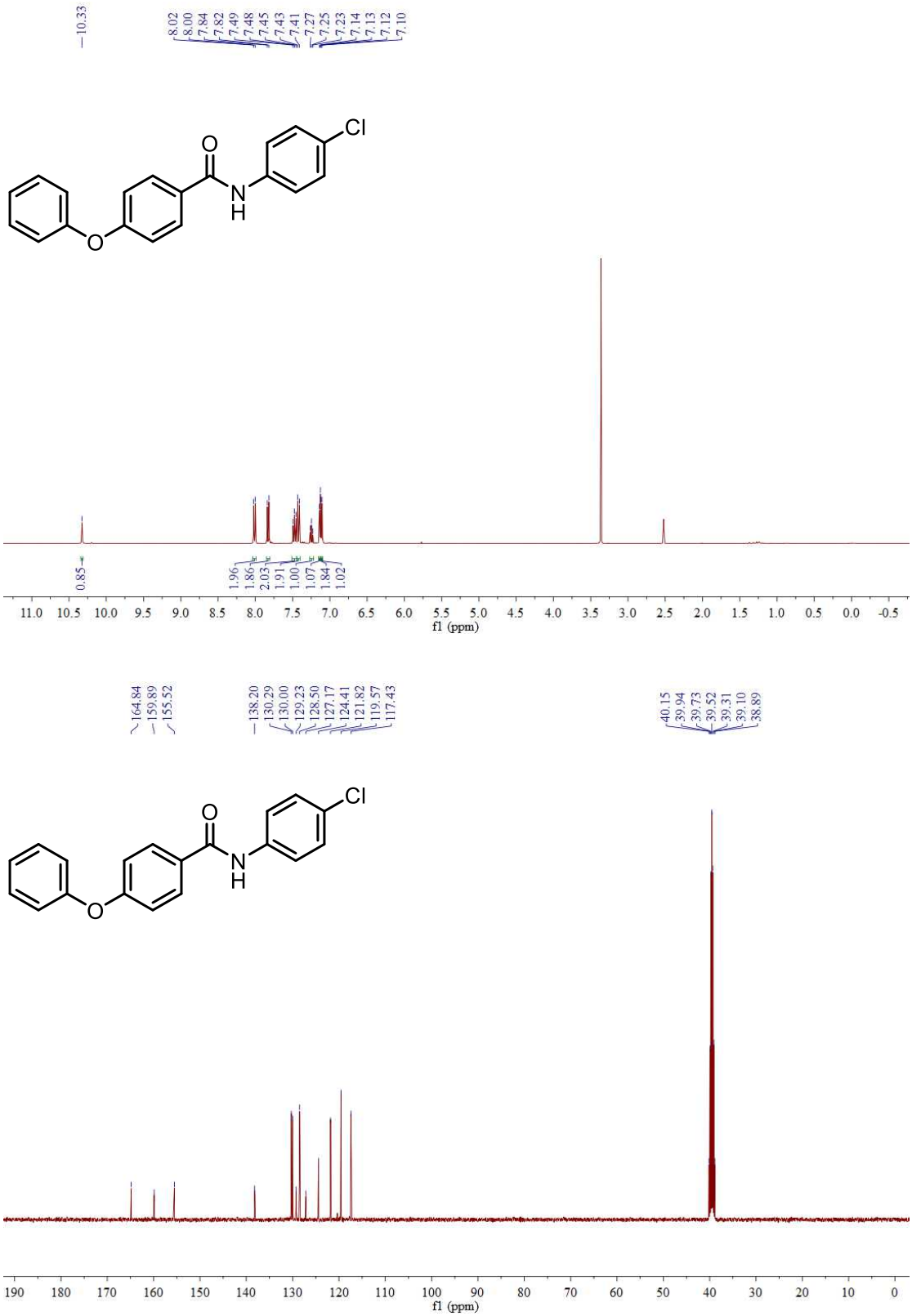



***Figure S29.*** $^{1}$H and $^{13}$C NMR Spectra for compound **3ac**

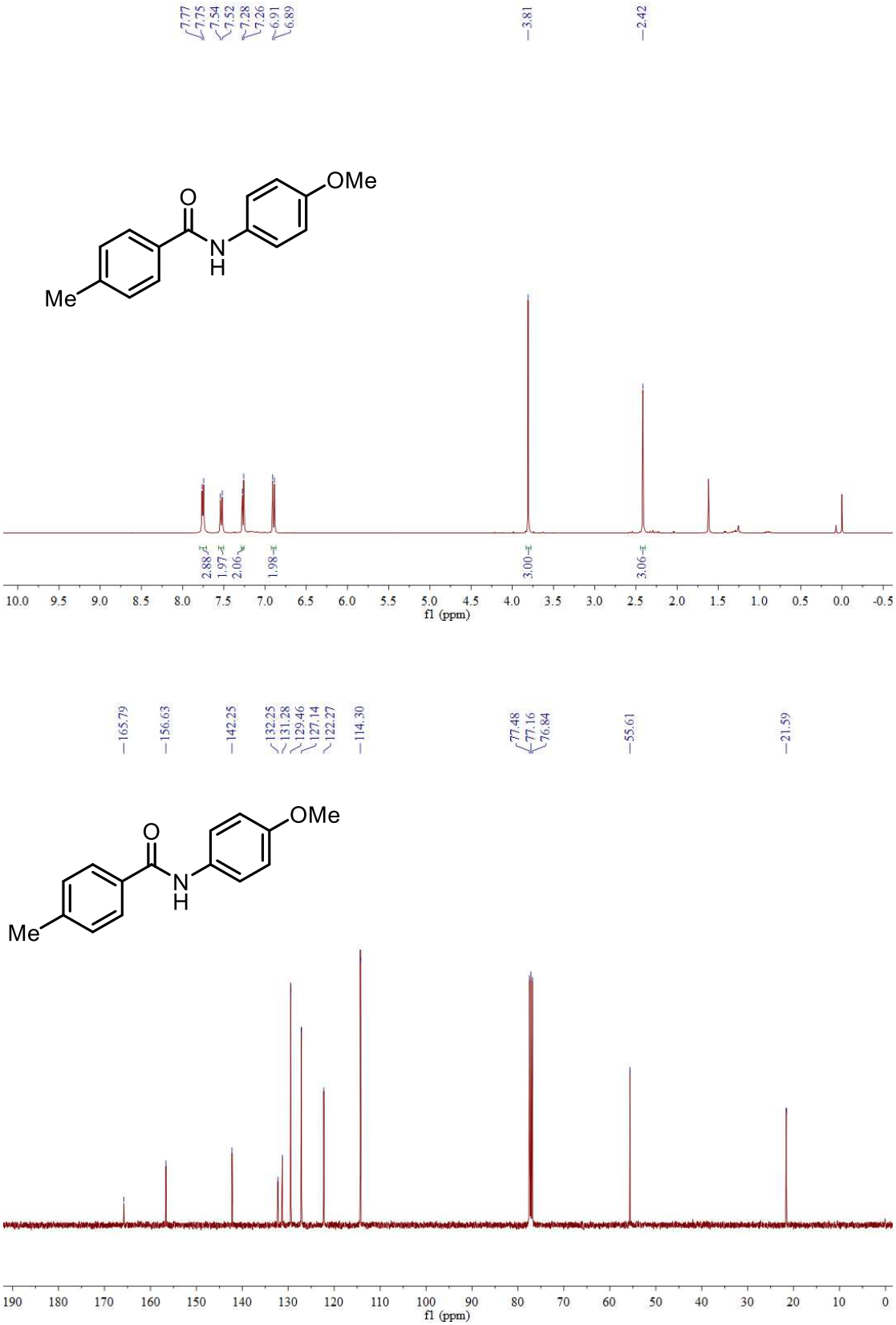
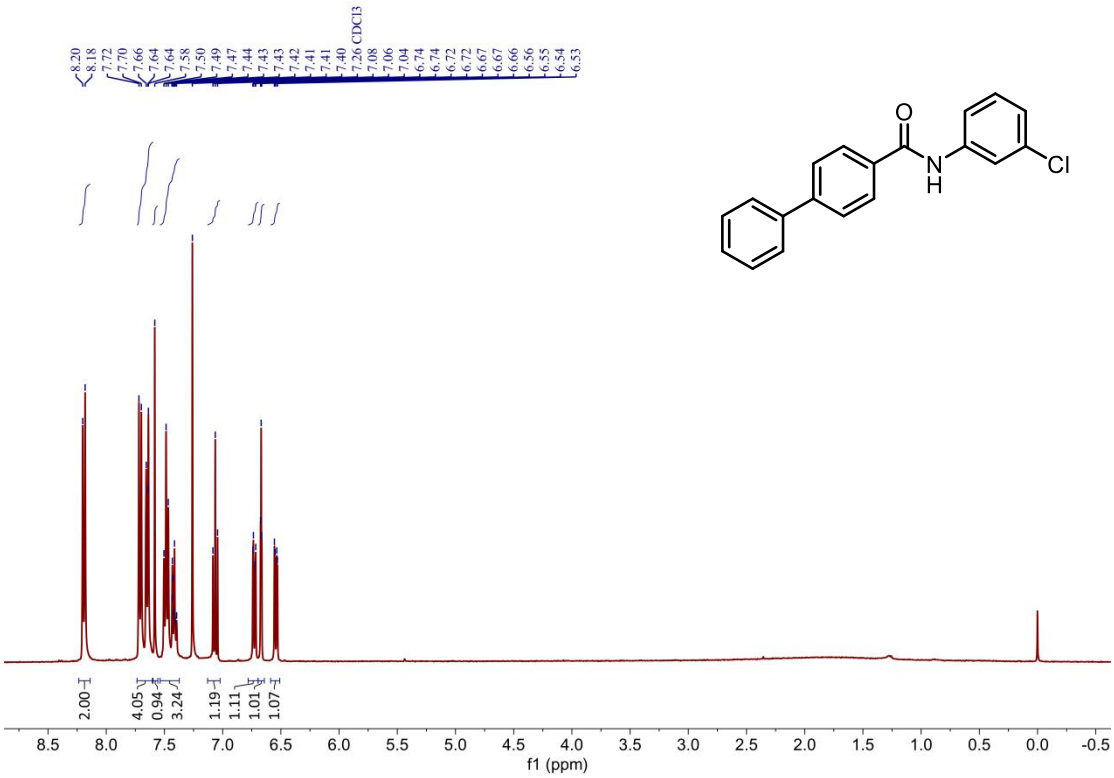



***Figure S31.*** $^{1}$H and $^{13}$C NMR Spectra for compound **3ad**



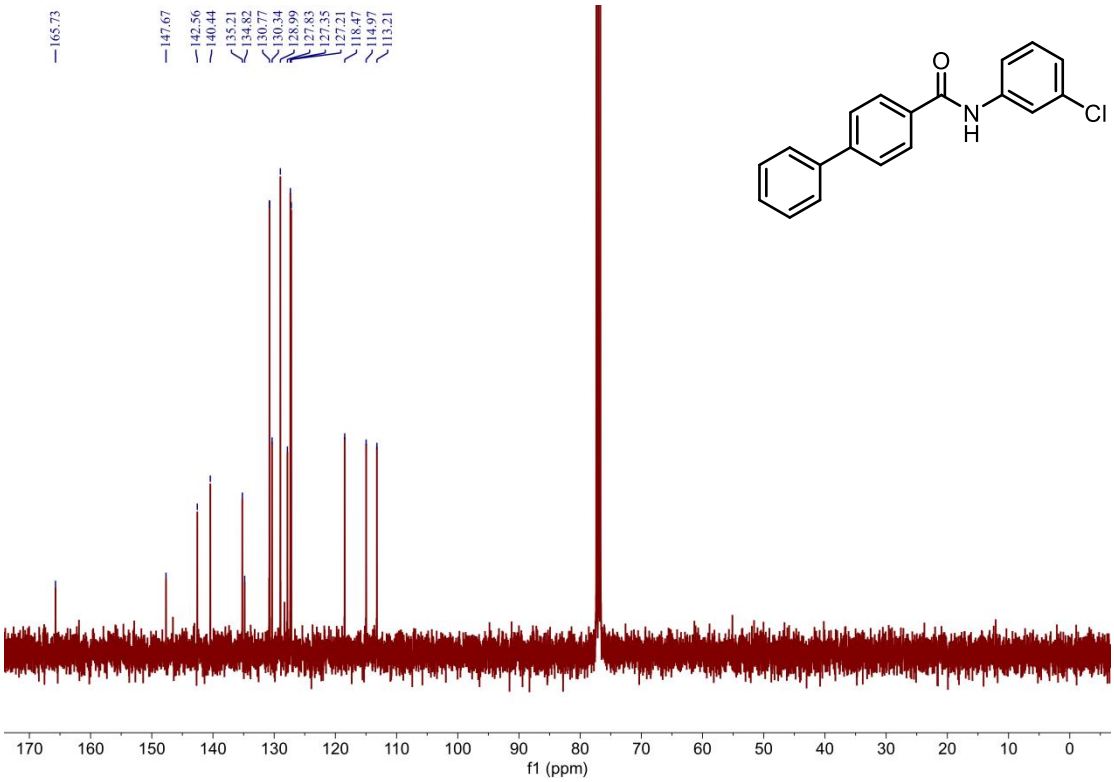




***Figure S30.*** $^{1}$H and $^{13}$C NMR Spectra for compound **3ae**

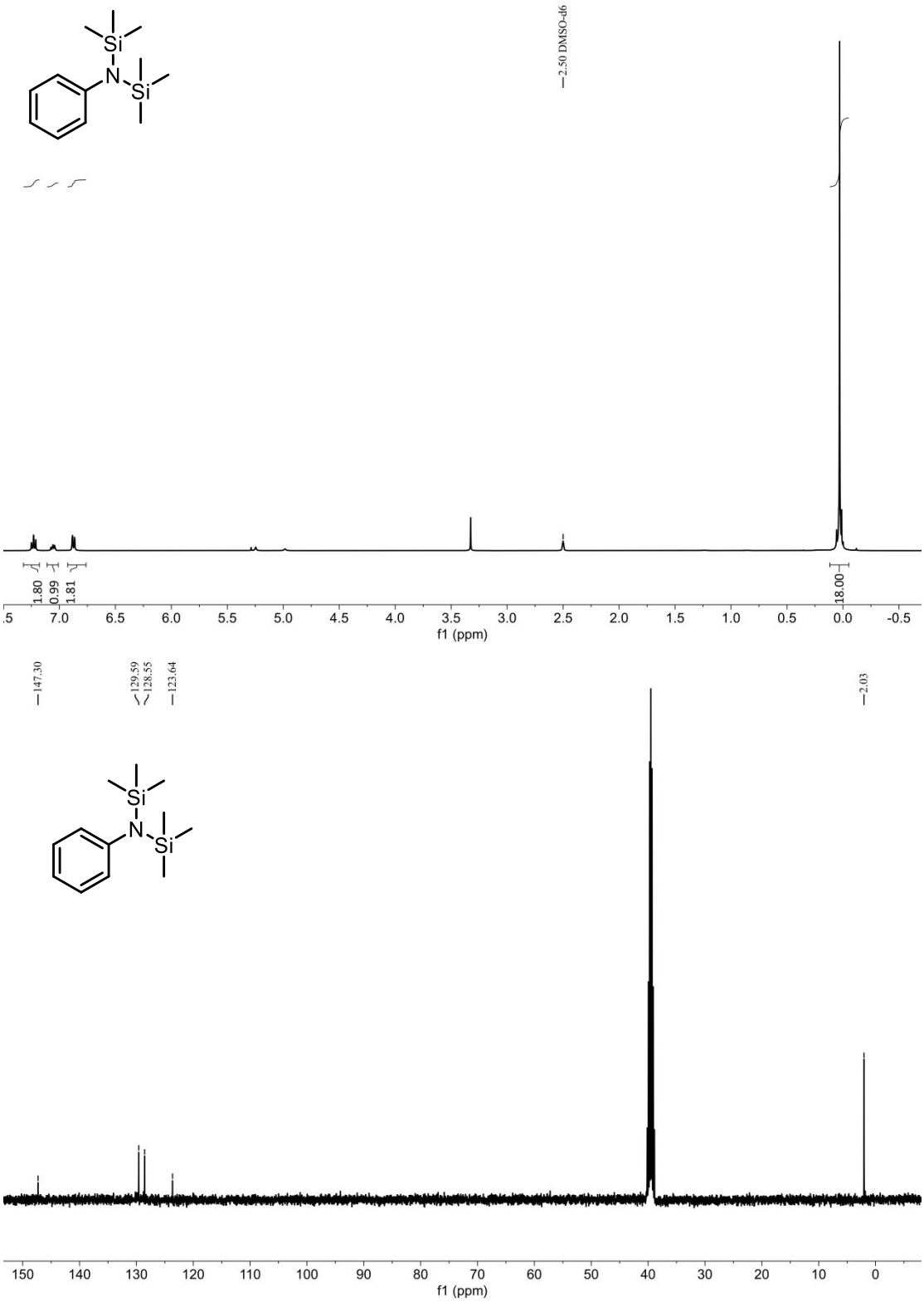
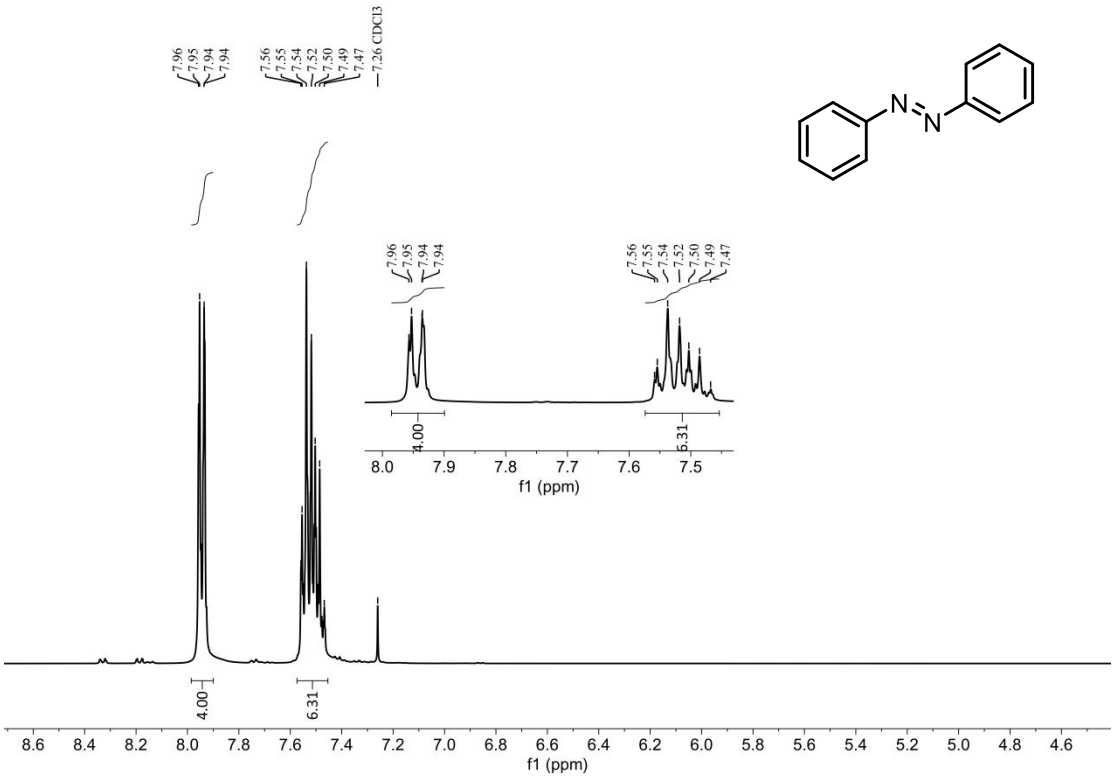



***Figure S32.*** $^{1}$H and $^{13}$C NMR Spectra for compound **5**



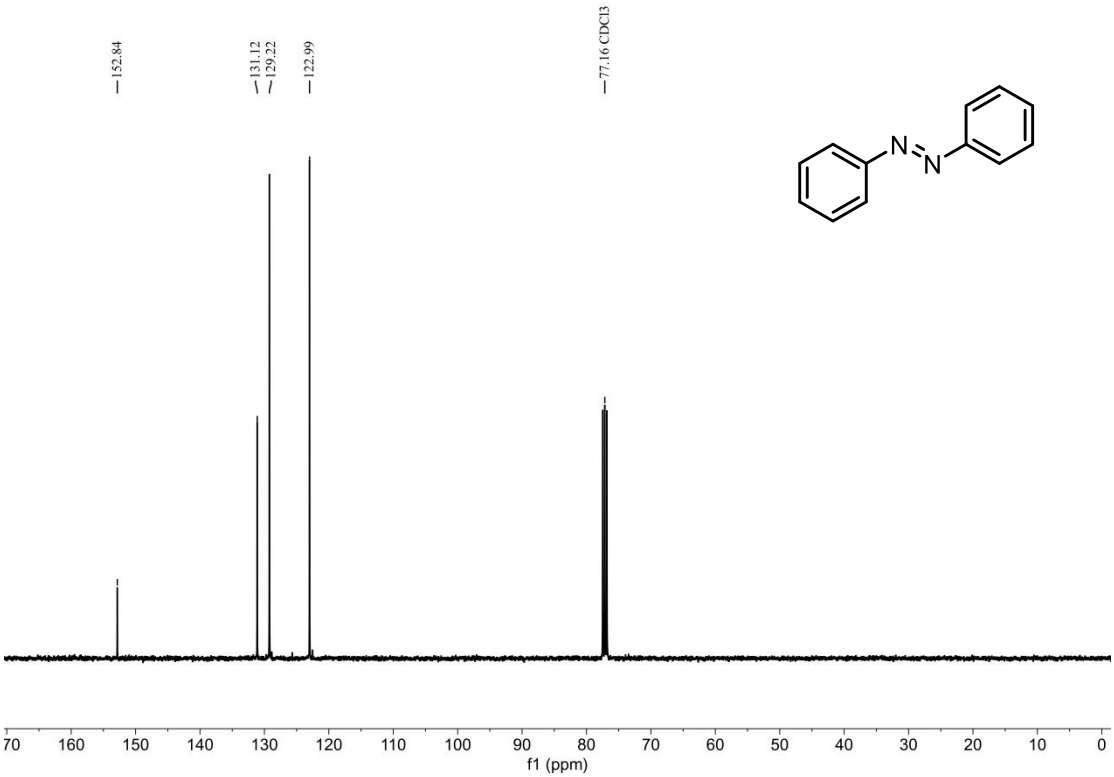




***Figure S33.*** $^{1}$H and $^{13}$C NMR Spectra for compound **4**