Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis and characterization of rare earth/lithium complexes stabilized by ethylenediamine-bridged bis(phenolate) ligands and their activity in catalyzing amidation reactions

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Contents

1. General procedures.

Moisture and air-sensitive materials were performed under a purified argon atmosphere using standard Schlenk techniques. The solvents were freshly distilled from sodium/benzophenone ketyl under argon prior to use. RE[N($SiMe_3$)$_2$]$_3$(μ-Cl)Li(THF)$_3$ (RE = Y, Nd, Yb) were prepared following literature procedures.[1] The phenolate ligand precursors (L^1H_2 and L^2H_2) were synthesized according to the reported methods.[2] Liquid substrates were dried over calcium hydride and distilled under reduced pressure before use. Solid substrates were predried before use. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. NMR spectra were recorded with BrukerAV-400NMR and Bruker AV-600NMR spectrometer.

Flash column chromatography was carried out using 200-300 mesh silica gel. GC analyses were performed on a Varian instrument (CP-3800) equipped with a capillary column AT. OV-101 and FID detector. The uncorrected melting points were measured using the INESA WRR machine. High-resolution mass spectra were obtained on a Bruker ESI-QTOF LC/MS instrument (source: ESI; mass analyzer type: TOF). IR spectra were recorded on a Bruker Platinum-ATR spectrometer (Model: ALPHA) operating at 4000–400 cm^{-1}. A Bruker at 293 K D8 Venture diffractometer (Mo Kα radiation 0.71073 Å) was used to determine complexes' solid-state structures. The Bruker APEX program did data reduction. The structures were refined and solved by a least-squares technique based on F^2 using the SHELXL program.

2. Synthesis of ligand precursors.

***N,N'*- Di-*tert*-butyl -*N,N'*-bis(2-hydroxy-3,5-di-methylbenzyl)ethylenediamine L^1H_2:**[2]

Formalin (9.74 g, 120 mmol) was heated at 135 °C for 10 min, and then a mixture of 2,4-di-methylphenol (14.66 g, 120 mmol), and *N,N'*-di-*tert*-butylethylenediamine (10.33 g, 60 mmol) in methanol (100 mL) was added. The mixture was heated under reflux overnight. After cooled to room temperature, the product was isolated through filtration. Washing with cold methanol (50 mL), gave the pure product as white precipitate. Yield: 13.20 g, 29.9 mmol, 50%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ 10.69 (s, 2H, O*H*), 6.80 (s, 2H, Ar-*H*), 6.54 (s, 2H, Ar-*H*), 3.57 (s, 4H, ArCH_2), 2.38 (s, 4H, NCH_2CH_2N), 2.18 (s, 6H, Ar(CH_3)$_2$), 2.16 (s, 6H, Ar(CH_3)$_2$), 0.84 (s, 18H, C(CH_3)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 153.7, 130.3, 127.8, 126.6, 124.5, 122.7 (Ar-*C*), 55.6 (N*C*(CH_3)$_3$), 54.3 (NCH_2*C*H_2N), 51.5 (Ar*C*H_2N), 26.0 (C(*C*H_3)$_3$), 20.4, 15.6 (*C*H_3).

***N,N'*- Dicyclohexyl -*N,N'*-bis(2-hydroxy-3,5-di-methylbenzyl)ethylenediamine L^2H_2:**[2]

L^2H_2 was synthesized in analogy to L^1H_2 from *N,N'*-dicyclohexylethylenediamine (13.46g, 60 mmol). Yield: 16.20 g, 32.9 mmol, 55%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 10.89 (s, 2H, O*H*), 6.87 (s, 2H, Ar-*H*), 6.62 (s, 2H, Ar-*H*), 3.73 (s, 4H, ArCH_2), 2.57 (s, 4H, NCH_2CH_2N), 2.47 (t, *J* = 9.5 Hz, 2H, NC*H*$(CH_2)_5$), 2.23 (s, 6H, Ar(CH_3)$_2$), 2.21 (s, 6H, Ar(CH_3)$_2$), 1.75 (d, *J* = 10.7 Hz, 8H, CH(CH_2)$_4$), 1.61 (d, *J* = 12.1 Hz, 2H, CH(CH_2)), 1.11 (hept, *J* = 12.4 Hz, 10H, CH(CH_2)$_5$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 °C) δ 153.8, 130.4, 127.6, 126.7, 124.5, 121.5 (Ar-*C*), 60.1 (N*C*H), 55.5 (Ar*C*H_2N), 49.2 (NCH_2*C*H_2N), 28.0, 26.0, 25.1 (CH(*C*H_2)$_5$), 20.5, 15.6 (*C*H_3).

3. Synthesis of rare-earth/lithium complexes.

Synthesis of complexes 1a-3a: A toluene solution (10 mL) of L^1H_2 (1.32 g, 3 mmol) was added dropwise to a toluene solution (10 mL) of RE[N(SiMe_3)$_2$]$_3$(μ-Cl)Li(THF)$_3$ [RE = Y, Nd, Yb] (3 mmol) at room temperature and the mixture was heated at 95 °C for 24 h. After cooling down to room temperature, the volatiles were removed under reduced pressure, and the residue was washed with hexane (3 × 0.5 mL). The solid was dissolved in toluene (9 mL), and the solution was kept at 0 °C for 24 hours to give crystals. Complex **1a**: isolated as white crystals, 0.82 g, 0.96 mmol, 32% yield. Complex **2a**: isolated as blue crystals, 0.80 g, 0.88 mmol, 29% yield. Complex **3a**: isolated as yellow crystals, 0.74 g, 0.78 mmol, 26% yield.

Synthesis of complexes 1b and 2b: From the above-described reaction, the insoluble toluene part was collected and dissolved in THF (2 mL) and toluene (0.5 mL). Crystals were obtained after standing at 0 °C for several days. Complex **1b**: isolated as white crystals, 0.12 g, 0.12 mmol, 8% yield. Complex **2b**: isolated as blue crystals, 0.06 g, 0.06 mmol, 4% yield.

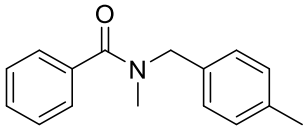
Synthesis of complexes 4a and 5a: Complexes **4a** and **5a** were synthesized following the procedure of complex **1a** from L^2H_2 (1.48 g, 3 mmol). Complex **4a**: isolated as white crystals, 1.07 g, 1.18 mmol, 39% yield. Complex **5a**: isolated as blue crystals, 1.00 g, 1.04 mmol, 35% yield.

4. Synthesis of amides (8aa as an example).

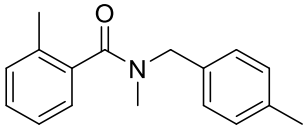
A THF (0.8 mL) solution of complex **4a** (36.3 mg, 0.04 mmol) and *N*,4-dimethylbenzylamine (147 μL, 1.00 mmol) was mixed and stirred at room temperature for 30 min. Benzaldehyde (305 μL, 3.00 mmol) was then added, and the resulting mixture was stirred for 3 hours. The reaction

was quenched with water (3 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layer was collected and dried with Na_2SO_4 and crude product was purified using ethyl acetate/ petroleum ether (1:7) as eluent by column chromatography.

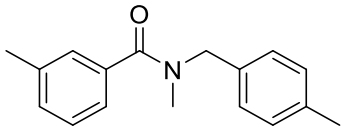
Characterization data of compounds 8aa-8aw:



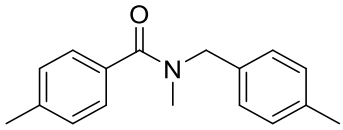
***N*-methyl-*N*-(4-methylbenzyl)benzamide** (**8aa**). Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (236 mg, 0.99 mmol, 99% yield).
^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.47 (s, 4H, Ar-*H*), 7.18 (d, *J* = 8.0 Hz, 5H, Ar-*H*), 4.73 (s, 2H, NC*H*$_2$Ar), 3.03 (s, 3H, NC*H*$_3$), 2.35 (s, 3H, ArC*H*$_3$); stereoisomer 2: 7.42 – 7.33 (m, 7H, Ar-*H*), 7.07 (s, 2H, Ar-*H*), 4.47 (s, 2H, NC*H*$_2$Ar), 2.84 (s, 3H, NC*H*$_3$), 2.35 (s, 3H, ArC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 172.3, 171.6 (Ar*C*O), 137.2, 137.1, 136.2, 134.0, 133.5, 129.7, 129.5, 128.4, 128.2, 127.0, 126.9, 126.8, 126.8 (Ar-*C*), 54.9, 50.5 (N*C*H$_2$Ar), 36.9, 33.1(N*C*H$_3$), 21.1(Ar*C*H$_3$). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{17}NONa$ 262.1208; Found 262.1203.



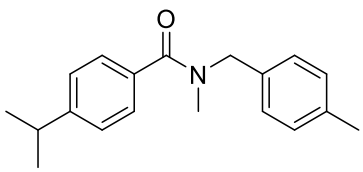
***N*,2-dimethyl-*N*-(4-methylbenzyl)benzamide (8ba)**. Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (172 mg, 0.68 mmol, 68% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.26 (t, *J* = 7.6 Hz, 3H, Ar-*H*), 7.21 – 7.15 (m, 4H, Ar-*H*), 7.12 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 4.74 (s, 2H, NC*H*$_2$Ar), 3.03 (s, 2H, NC*H*$_3$), 2.35 (s, 3H, ArC*H*$_3$), 2.32 (s, 3H, ArC*H*$_3$); stereoisomer 2: δ 7.26 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.21 – 7.15 (m, 3H, Ar-*H*), 7.12 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 7.00 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 4.31 (s, 2H, NC*H*$_2$Ar), 2.68 (s, 3H, NC*H*$_3$), 2.34 (s, 3H, ArC*H*$_3$), 2.30 (s, 3H, ArC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 171.90, 171.46 (Ar*C*O), 137.2, 136.7, 134.4, 134.1, 133.9, 130.5, 130.4, 129.4, 129.4, 128.9, 128.7, 128.4, 127.1, 126.0, 125.9, 125.9, 125.8 (Ar-*C*), 54.2, 49.8 (N*C*H$_2$Ar), 35.7, 32.2 (N*C*H$_3$), 21.2, 21.1, 19.2, 18.9 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{19}NONa$ 276.1364; Found 276.1361.



***N*,3-dimethyl-*N*-(4-methylbenzyl)benzamide (8ca).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (202 mg, 0.80 mmol, 80% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.27 (d, *J* = 17.3 Hz, 4H, Ar-*H*), 7.17 (d, *J* = 8.6 Hz, 3H, Ar-*H*), 7.06 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 4.47 (s, 2H, NC*H*$_2$Ar), 2.84 (s, 3H, NC*H*$_3$), 2.34 (s, 6H, ArC*H*$_3$); stereoisomer 2**:** 7.27 (d, *J* = 17.3 Hz, 4H, Ar-*H*), 7.17 (d, *J* = 8.6 Hz, 3H, Ar-*H*), 7.06 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 4.72 (s, 2H, NC*H*$_2$Ar), 3.01 (s, 3H, NC*H*$_3$), 2.34 (s, 6H, ArC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 172.4, 171.6 (Ar*C*O), 138.2, 137.2, 137.0, 136.4, 134.1, 133.6, 130.3, 129.5, 129.4, 128.2, 127.5, 126.8, 123.9, 123.7 (Ar-*C*), 54.9, 50.4 (N*C*H$_2$Ar), 36.8, 32.9 (N*C*H$_3$), 21.3, 21.1 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{20}NONa$ 276.1364; Found 276.1342.

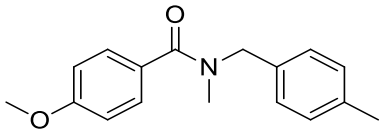


***N*,4-dimethyl-*N*-(4-methylbenzyl)benzamide (8da).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (215 mg, 0.85 mmol, 85% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.38 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.28 – 7.07 (m, 6H, Ar-*H*), 4.49 (s, 2H, NC*H*$_2$Ar), 2.86 (s, 3H, NC*H*$_3$), 2.34 (s, 6H, ArC*H*$_3$); stereoisomer 2: 7.38 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.28 – 7.07 (m, 6H, Ar-*H*), 4.71 (s, 2H, NC*H*$_2$Ar), 3.01 (s, 3H, NC*H*$_3$), 2.34 (s, 6H, ArC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 171.4, 170.6 (Ar*C*O), 138.6, 136.1, 133.1, 132.7, 132.3, 128.4, 127.9, 127.2, 125.9, 125.7 (Ar-*C*), 53.9, 49.5 (N*C*H$_2$Ar), 35.9, 32.0 (N*C*H$_3$), 20.3, 20.0 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{20}NONa$ 276.1364; Found 276.1342.

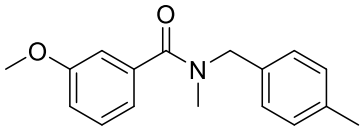


4-isopropyl-*N*-methyl-*N*-(4-methylbenzyl)benzamide (8ea). Purified by column chromatography (ethyl acetate: petroleum ether = 1:15). Isolated as colorless oil (228 mg, 0.81 mmol, 81% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.41 (s, 2H, Ar-*H*),

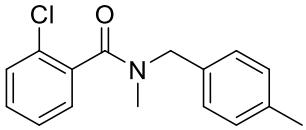
7.29 – 7.02 (m, 6H, Ar-*H*), 4.70 (s, 2H, NCH_2Ar), 2.98 (s, 3H, NCH_3), 2.29 (s, 3H, ArCH_3), 1.25 (d, *J* = 20.2 Hz, 6H, CH(CH_3)$_2$); stereoisomer 2: 7.41 (s, 2H, Ar-*H*), 7.29 – 7.02 (m, 6H, Ar-*H*), 4.48 (s, 2H, NCH_2Ar), 2.86 (s, 5H, NCH_3+C*H*(CH$_3$)$_2$), 2.29 (s, 3H, ArCH_3), 1.20 (d, *J* = 20.2 Hz, 6H, CH(CH_3)$_2$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 172.4, 171.6 (Ar*C*O), 150.5, 137.1, 134.2, 133.8, 129.4, 128.2, 127.2, 127.1, 126.7, 126.4 (Ar-*C*), 54.9, 50.5 (N*C*H$_2$Ar), 36.9, 34.0 (N*C*H$_3$), 33.1 *C*H(CH$_3$)$_2$), 23.9 CH(*C*H$_3$)$_2$), 21.1 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{23}NONa$ 304.1677; Found 304.1667.



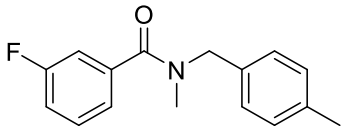
4-methoxy-*N*-methyl-*N*-(4-methylbenzyl)benzamide (8fa). Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (210 mg, 0.78 mmol, 78% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.43 – 7.26 (m, 2H, Ar-*H*), 7.06 (d, *J* = 7.3 Hz, 4H, Ar-*H*), 6.78 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 4.47 (br-s, 2H, NCH_2Ar), 3.70 (s, 3H, NCH_3), 2.85 (s, 3H, ArOCH_3), 2.24 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 170.8, 170.47 (Ar*C*O), 159.6, 136.1, 132.9, 128.4, 127.9, 127.3, 112.6 (Ar-*C*), 54.2 (ArO*C*H$_3$), 49.73 (N*C*H$_2$Ar), 28.6 (N*C*H$_3$), 20.0 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{19}NONa$ 292.1313; Found 292.1326.



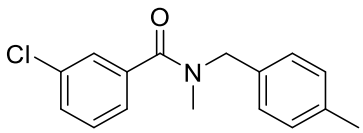
3-methoxy-*N*-methyl-*N*-(4-methylbenzyl)benzamide (8ga). Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (199 mg, 0.74 mmol, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.32 (s, 1H, Ar-*H*), 7.05 (d, *J* = 6.7 Hz, 7H, Ar-*H*), 4.54 (s, 2H, NCH_2Ar), 3.68 (s, 3H, NCH_3), 2.83 (s, 3H, ArOCH_3), 2.23 (s, 3H, ArCH_3); stereoisomer 2: 7.34 (s, 2H, Ar-*H*), 6.77 (d, *J* = 8.4 Hz, 3H, Ar-*H*), 4.44 (s 1H, NCH_2Ar), 3.67 (s, 2H, NCH_3), 2.83 (s, 2H, ArOCH_3), 2.22 (s, 2H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 171.4, 170.3 (Ar*C*O), 159.6, 136.1, 128.4, 127.4, 127.3, 112.6 (Ar-*C*), 54.3 (ArO*C*H$_3$), 54.2 (N*C*H$_2$Ar), 32.2 (N*C*H$_3$), 20.0 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{19}NONa$ 292.1313; Found 292.1304.



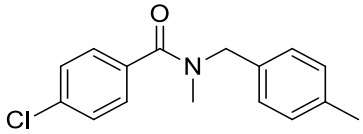
2-chloro-*N*-methyl-*N*-(4-methylbenzyl)benzamide (8ha). Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as white crystals (192 mg, 0.70 mmol, 70% yield): **m.p.** 94-95 ℃: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC) δ stereoisomer 1: 7.27 – 7.20 (m, 3H, Ar-*H*), 7.14 (m, 3H, Ar-*H*), 7.02 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 4.74 (s, 1H, NCH_2Ar), 4.48 (s, 1H, NCH_2Ar), 2.57 (s, 3H, NCH_3), 2.19 (s, 3H, ArCH_3); stereoisomer 2: 7.14 (m, 3H, Ar-*H*), 6.98 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 6.90 (d, *J* = 8.1 Hz, 1H, Ar-*H*), 4.24 (d, *J* = 15.3 Hz, 1H, NCH_2Ar), 4.11 (d, *J* = 15.4 Hz, 1H, NCH_2Ar), 2.88 (s, 2H, NCH_3), 2.17 (s, 2H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ºC) δ 168.5, 168.7 (Ar*C*O), 137.2, 136.4, 133.6, 132.9, 130.2, 130.1, 129.7, 129.6, 129.5, 129.4, 128.3, 128.0, 127.8, 127.3, 127.2 (Ar-*C*), 54.1, 50.0 (N*C*H_2Ar), 35.3, 32.2 (N*C*H_3), 21.12, 21.1 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{16}ClNONa$ 296.0818; Found 296.0815.



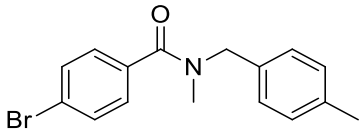
3-fluoro-*N*-methyl-*N*-(4-methylbenzyl)benzamide (8ia). Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (229 mg, 0.89 mmol, 89% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ºC) δ stereoisomer 1: 7.17 (s, 1H, Ar-*H*), 7.07 (dd, *J* = 9.2, 5.4 Hz, 4H, Ar-*H*), 7.00 (d, *J* = 8.0 Hz, 3H, Ar-*H*), 4.52 (s, 2H, NCH_2Ar), 2.83 (s, 3H, NCH_3), 2.17 (s, 3H, ArCH_3); stereoisomer 2: 7.00 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.88 (q, *J* = 6.2, 4.5 Hz, 5H, Ar-*H*), 6.72 (t, *J* = 9.8 Hz, 1H, Ar-*H*), 4.28 (s, 2H, NCH_2Ar), 2.66 (s, 3H, NCH_3), 2.17 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ºC) δ 169.7, 169.0 (Ar*C*O), 163.1, 160.2 (d, *J* = 48 Hz, Ar-*C*), 137.3, 137.2, 137.1 (t, *J* = 9 Hz, Ar-*C*), 136.4, 136.3 (d, *J* = 18 Hz, Ar-*C*), 132.6, 132.0 (d, *J* = 59 Hz, Ar-*C*), 129.3, 129.2 (d, *J* = 6.0 Hz, Ar-*C*),128.7, 128.6 (s, Ar-*C*), 128.5, 128.4 (d, *J* = 13 Hz, Ar-*C*), 127.2, 125.6 (s, Ar-*C*), 121.6, 121.4 (d, *J* = 19 Hz, Ar-*C*), 120.9 (s, Ar-*C*), 115.7, 115.5 (d, *J* = 21 Hz, Ar-*C*), 113.3-112.3 (m, Ar-*C*), 53.8, 49.5 (N*C*H_2Ar), 35.7, 32.1 (N*C*H_3), 20.0 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{16}FNONa$ 280.1114; Found 280.1114.



3-chloro-*N*-methyl-*N*-(4-methylbenzyl)benzamide (8ja). Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (233 mg, 0.85 mmol, 85% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.46 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.41 – 7.36 (m, 3H, Ar-*H*), 7.26 (s, 1H, Ar-*H*), 7.20 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.05 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 4.72 (s, 2H, NCH_2Ar), 3.03 (s, 3H, NCH_3), 2.38 (s, 3H, ArCH_3); stereoisomer 2: 7.35 – 7.32 (m, 3H, Ar-*H*), 7.26 (s, 1H, Ar-*H*), 7.20 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.05 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 4.47 (s, 2H, NCH_2Ar), 2.86 (s, 3H, NCH_3), 2.38 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 170.7, 170.0 (Ar*C*O), 138.1, 134.5, 133.1, 129.8, 129.7, 129.6, 129.5, 128.3, 127.2, 126.7, 125.1, 124.8 (Ar-*C*), 54.9, 50.6 (N*C*H_2Ar), 36.8, 33.2 (N*C*H_3), 21.1(Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{16}ClNONa$ 296.0818; Found 296.0798.

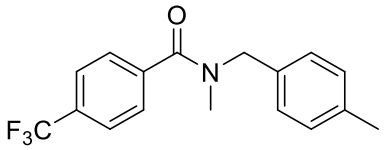


4-chloro-*N*-methyl-*N*-(4-methylbenzyl)benzamide (8ka). Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (260 mg, 0.95 mmol, 95% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.40 (s, 3H, Ar-*H*), 7.30 (dd, *J* = 6.7, 1.6 Hz, 3H, Ar-*H*), 7.06 (s, 2H, Ar-*H*), 4.71 (s, 2H, NCH_2Ar), 3.03 (s, 3H, NCH_3), 2.37 (s, 3H, ArCH_3); stereoisomer 2: 7.40 (s, 3H, Ar-*H*), 7.19 (d, *J* = 7.7 Hz, 5H, Ar-*H*), 4.47 (s, 2H, NCH_2Ar), 2.86 (s, 3H, NCH_3), 2.37 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 170.5 (Ar*C*O), 135.7, 129.5, 128.7, 128.6, 128.2, 126.6 (Ar-*C*), 54.9, 50.7 (N*C*H_2Ar), 36.9, 33.4 (N*C*H_3), 21.1 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{16}ClNONa$ 296.0818; Found 296.0798.

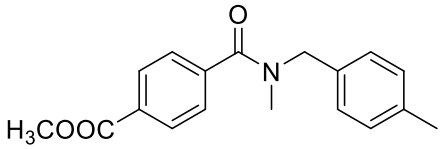


4-bromo-*N*-methyl-*N*-(4-methylbenzyl)benzamide (8la). Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (276 mg, 0.87 mmol, 87% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.49 – 7.41 (m, 2H, Ar-*H*), 7.36 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.27 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.13 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 6.99 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 4.64 (s, 2H, NCH_2Ar), 2.96 (s, 3H, NCH_3), 2.31 (s, 3H, ArCH_3); stereoisomer 2: 7.49 – 7.41 (m, 2H, Ar-*H*), 7.36 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.27 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.13 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 6.99 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 4.40 (s, 2H, NCH_2Ar), 2.79 (s, 3H, NCH_3), 2.31 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 171.3, 170.6 (Ar*C*O), 137.4, 134.9, 133.6,

131.7, 131.4, 129.6, 129.5, 129.5, 128.7, 128.6, 128.5, 128.3, 126.1, 124.0 (Ar-*C*), 54.9, 50.7 (N*C*H_2Ar), 36.9, 33.3 (N*C*H_3), 21.2 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{16}BrNONa$ 340.0313; Found 340.0305.

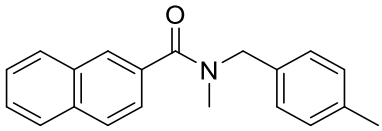


***N*-methyl-*N*-(4-methylbenzyl)-4-(trifluoromethyl)benzamide (8ma).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:3). Isolated as yellow oil (227 mg, 0.74 mmol, 74% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.67 (d, *J* = 15.5 Hz, 2H, Ar-*H*), 7.59 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.28 (t, *J* = 3.6 Hz, 1H, Ar-*H*), 7.20 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.06 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 4.75 (s, 2H, NC*H*$_2$Ar), 3.07 (s, 3H, NC*H*$_3$), 2.38 (s, 3H, ArC*H*$_3$); stereoisomer 2: 7.67 (d, *J* = 15.5 Hz, 2H, Ar-*H*), 7.59 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.28 (t, *J* = 3.6 Hz, 2H, Ar-*H*), 7.20 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.06 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 4.45 (s, 2H, NC*H*$_2$Ar), 2.85 (s, 3H, NC*H*$_3$), 2.38 (s, 3H, ArC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 170.8, 170.1 (Ar*C*O), 137.6, 137.4 (d, *J* = 18 Hz, Ar-*C*), 133.6, 133.0, 131.7 (s Ar-*C*), 129.7, 129.5 (d, *J* = 18 Hz, Ar-*C*), 128.3(s Ar-*C*), 127.4, 127.2 (d, *J* = 14 Hz, Ar-*C*), 126.6, 125.5, 122.4 (s Ar-*C*), 54.8, 50.6 (N*C*H$_2$Ar), 36.7, 33.2 (N*C*H$_3$), 21.1 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{16}F_3NONa$ 330.1082; Found 330.1079.

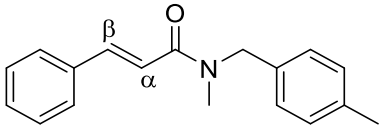


Methyl 4-(methyl(4-methylbenzyl)carbamoyl)benzoate (8na). Purified by column chromatography (ethyl acetate: petroleum ether = 1:10). Isolated as yellowish oil (226 mg, 0.76mmol, 76% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.97 (dd, *J* = 13.8, 7.8 Hz, 2H, Ar-*H*), 7.42 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 7.18 – 7.03 (m, 3H, Ar-*H*), 6.94 (d, *J* = 7.0 Hz, 1H, Ar-*H*), 4.63 (s, 2H, NC*H*$_2$Ar), 3.83 (s, 3H, COOC*H*$_3$), 2.95 (s, 3H, NC*H*$_3$), 2.26 (s, 3H, ArC*H*$_3$); stereoisomer 2: 7.97 (dd, *J* = 13.8, 7.8 Hz, 2H, Ar-*H*), 7.42 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 7.18 – 7.03 (m, 3H, Ar-*H*), 6.94 (d, *J* = 7.0 Hz, 1H, Ar-*H*), 4.33 (s, 2H, NC*H*$_2$Ar), 3.82 (s, 3H, COOC*H*$_3$), 2.73 (s, 3H, NC*H*$_3$), 2.26 (s, 3H, ArC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 166.3 (Ar*C*O), 137.5, 131.0, 129.8, 129.6, 129.4, 128.3, 126.9, 126.8, 126.6 (Ar-*C*), 54.8 (N*C*H$_2$Ar), 52.3

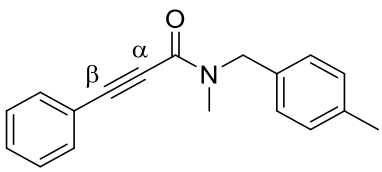
(COO*C*H$_3$), 50.5 (N*C*H$_2$Ar), 36.7, 33.1 (N*C*H$_3$), 21.1 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{18}H_{19}NO_3Na$ 320.1263; Found 320.1255.



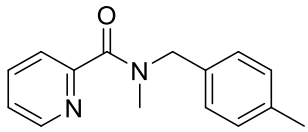
***N*-methyl-*N*-(4-methylbenzyl)-2-naphthamide (8oa).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:3). Isolated as white solid (231 mg, 0.80 mmol, 80% yield): **m.p.** 105-106 ℃: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: δ 8.02 (s, 1H, Ar-*H*), 7.88 (s, 3H, Ar-*H*), 7.61 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.56 – 7.49 (m, 2H, Ar-*H*), 7.40 – 7.31 (m, 1H, Ar-*H*), 7.27 – 7.08 (m, 3H, Ar-*H*), 4.82 (s, 2H, NC*H*$_2$Ar), 3.12 (s, 3H, NC*H*$_3$), 2.39 (s, 3H, ArC*H*$_3$); stereoisomer 2: ^{1}H NMR δ 8.02 (s, 1H, Ar-*H*), 7.88 (s, 3H, Ar-*H*), 7.61 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.56 – 7.49 (m, 2H, Ar-*H*), 7.40 – 7.31 (m, 1H, Ar-*H*), 7.27 – 7.08 (m, 3H, Ar-*H*), 4.55 (s, 2H, NC*H*$_2$Ar), 2.92 (s, 3H, NC*H*$_3$), 2.39 (s, 3H, ArC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 171.1, 170.4 (Ar*C*O), 136.1, 132.9, 132.5, 131.6, 128.4, 127.3, 127.2, 126.7, 125.9, 125.6, 125.5, 123.2 (Ar-*C*), 53.9, 49.5 (N*C*H$_2$Ar), 35.8, 32.1 (N*C*H$_3$), 20.0 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{20}H_{19}NONa$ 312,1364; Found 312.1338.



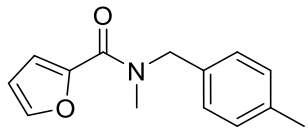
***N*-methyl-*N*-(4-methylbenzyl)cinnamamide (8pa).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:3). Isolated as brown oil (133 mg, 0.50 mmol, 50% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.67 (dd, *J* = 15.0, 3.0 Hz, 1H, C$^{\alpha}$*H*), 7.44 (d, *J* = 6.6 Hz, 1H, Ar-*H*), 7.36 (d, *J* = 4.3 Hz, 1H, Ar-*H*), 7.27 – 7.21 (m, 3H, Ar-*H*), 7.11 – 7.01 (m, 4H, Ar-*H*), 6.85 – 6.76 (m, 1H, C$^{\beta}$*H*), 4.55 (d, *J* = 14.5 Hz, 2H, NC*H*$_2$Ar), 2.95 (d, *J* = 3.3 Hz, 3H, NC*H*$_3$), 2.24 (d, *J* = 3.8 Hz, 3H, ArC*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 167.2, 166.7 (Ar*C*O), 143.1, 142.9, 137.5, 137.1, 135.4, 135.3, 134.3, 133.7, 129.7, 129.3, 128.8, 128.8, 128.2, 127.9, 126.5, 117.4 (Ar-*C*), 53.3, 51.0 (N*C*H$_2$Ar), 34.9, 34.4 (N*C*H$_3$), 21.1 (Ar*C*H$_3$). **HRMS** (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{18}H_{19}NONa$ 288.1364; Found 288.1346.



***N*-methyl-*N*-(4-methylbenzyl)-3-phenylpropiolamide (8qa).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:1). Isolated as dark brown oil (197 mg, 0.75 mmol, 75% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.56 (dd, *J* = 12.9, 7.1 Hz, 2H, Ar-*H*), 7.40 (m, 3H, Ar-*H*), 7.26 – 7.17 (m, 4H, Ar-*H*), 4.85 (s, 2H, NCH_2Ar), 2.95 (s, 3H, NCH_3), 2.38 (s, 3H, ArCH_3); stereoisomer 2: 7.56 (dd, *J* = 12.9, 7.1 Hz, 2H, Ar-*H*), 7.40 (m, 4H, Ar-*H*), 7.26 – 7.17 (m, 3H, Ar-*H*), 4.65 (s, 1H, NCH_2Ar), 3.20 (s, 2H, NCH_3), 2.37 (s, 2H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 153.8, 153.7 (Ar*C*O), 136.7, 132.1, 131.4, 131.3, 129.0, 128.9, 128.5, 128.3, 127.5, 127.2, 126.5 (Ar-*C*), 89.2 (C^{α}), 80.7 (C^{β}), 53.7, 48.6 (N*C*H_2Ar), 34.7, 30.8 (N*C*H_3), 20.1 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{17}NONa$ 286.1208; Found 286.1187.

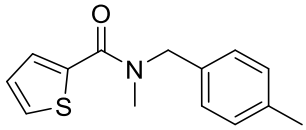


***N*-methyl-*N*-(4-methylbenzyl)picolinamide (8ta).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:1). Isolated as colorless crystals (185 mg, 0.77 mmol, 77% yield): **m.p.** 42-43 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 8.55 – 8.48 (m, 1H, Ar-*H*), 7.70 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.61 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.27 – 7.21 (m, 2H, Ar-*H*), 7.13 – 7.04 (m, 3H, Ar-*H*), 4.69 (s, 2H, NCH_2Ar), 2.96 (s, 3H, NCH_3), 2.27 (s, 3H, ArCH_3); stereoisomer 2: 8.55 – 8.48 (m, 1H, Ar-*H*), 7.70 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.61 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.27 – 7.21 (m, 2H, Ar-*H*), 7.13 – 7.04 (m, 3H, Ar-*H*), 4.57 (s, 2H, NCH_2Ar), 2.90 (s, 3H, NCH_3), 2.26 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 168.2, 167.8 (Ar*C*O), 153.6, 153.5 (N*C*CO), 147.3, 147.2 (N*C*H), 136.2, 135.9, 135.8, 132.7, 132.6, 128.3, 128.2, 127.2, 126.3, 123.3, 122.5, 122.4 (Ar-*C*), 53.3, 49.8 (N*C*H_2Ar), 35.3, 32.1 (N*C*H_3), 20.1, 20.0 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{16}N_2ONa$ 263.1160; Found 263.1157.

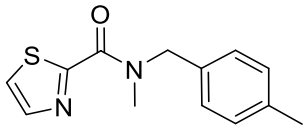


***N*-methyl-*N*-(4-methylbenzyl)furan-2-carboxamide (8ua).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:1). Isolated as yellow oil (144 mg, 0.63 mmol, 63% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.48 (s, 1H, Ar-*H*), 7.19 (d, *J* = 16.9 Hz, 4H, Ar-*H*), 7.02 (s, 1H, Ar-*H*), 6.46 (s, 1H, Ar-*H*), 4.74 (s, 2H, NCH_2Ar), 3.16 (s, 3H, NCH_3), 2.35 (s, 3H, ArCH_3); stereoisomer 2: 7.48 (s, 1H, Ar-*H*), 7.19 (d, *J* = 16.9

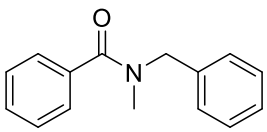
Hz, 4H, Ar-*H*), 7.02 (s, 1H, Ar-*H*), 6.46 (s, 1H, Ar-*H*), 4.74 (s, 2H, NCH_2Ar), 3.04 (s, 3H, NCH_3), 2.35 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 160.4 (Ar*C*O), 147.9 (O*C*CO), 143.9 (O*C*H), 137.2, 133.8, 129.4, 128.2, 126.9, 116.2, 111.2 (Ar-*C*), 53.9, 51.5 (N*C*H_2Ar), 35.7 (N*C*H_3), 21.1 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{15}NO_2Na$ 252.1000; Found 252.1003.



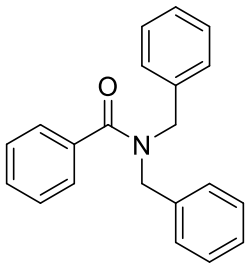
***N*-methyl-*N*-(4-methylbenzyl)thiophene-2-carboxamide (8va).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:5). Isolated as green oil (150 mg, 0.61 mmol, 61% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.37 – 7.33 (m, 1H, Ar-*H*), 7.23 (s, 1H, Ar-*H*), 7.09 (s, 4H, Ar-*H*), 6.94 – 6.86 (m, 1H, Ar-*H*), 4.64 (s, 2H, NCH_2Ar), 3.01 (s, 3H, NCH_3), 2.27 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 164.7 (Ar*C*O), 137.9 (S*C*CO), 137.31 (S*C*H), 133.71, 129.55, 129.10, 126.83, 125.3 (Ar-*C*), 59.9 (N*C*H_2Ar), 37.8 (N*C*H_3), 21.1 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{15}NOSNa$ 268.0772; Found 268.0760.



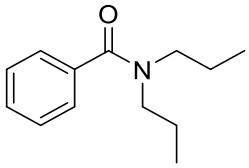
***N*-methyl-*N*-(4-methylbenzyl)thiazole-2-carboxamide (8wa).** Purified by column chromatography (ethyl acetate: petroleum ether = 1:5). Isolated as green oil (160 mg, 0.65 mmol, 65% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) stereoisomer 1: 7.89 (d, *J* = 13.2 Hz, 1H, Ar-*H*), 7.55 (s, 1H, Ar-*H*), 7.27 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.17 (d, *J* = 3.6 Hz, 3H, Ar-*H*), 5.38 (s, 2H, NCH_2Ar), 3.52 (s, 3H, NCH_3), 2.36 (s, 3H, ArCH_3); stereoisomer 2: 7.89 (d, *J* = 13.2 Hz, 1H, Ar-*H*), 7.55 (s, 1H, Ar-*H*), 7.27 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 7.17 (d, *J* = 3.6 Hz, 3H, Ar-*H*), 4.75 (s, 2H, NCH_2Ar), 3.06 (s, 3H, NCH_3), 2.36 (s, 3H, ArCH_3). **^{13}C NMR** (101 MHz, $CDCl_3$, 25 ^{o}C) δ 165.3 (Ar*C*O), 160.9 (SN*C*CO), 143.4, 143.3 (N*C*H), 137.3, 133.9, 133.5, 129.4, 128.3, 127.5 (Ar-*C*), 124.0 (S*C*H), 53.6, 52.5 (N*C*H_2Ar), 36.3, 34.6 (N*C*H_3), 21.1 (Ar*C*H_3). **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_{14}N_2OSNa$ 269.0725; Found 269.0719.



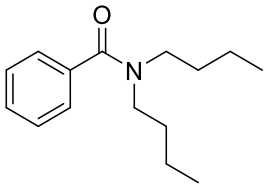
***N*-benzyl-*N*-methylbenzamide (8ab).**[3] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (205 mg, 0.91 mmol, 91% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ stereoisomer 1: 7.39 – 6.90 (m, 5H, Ar-*H*), 7.25 – 6.94 (m, 5H, Ar-*H*), 4.61 (d, *J* = 20.0 Hz, 2H, NCH_2Ar), 2.87 (d, *J* = 22.8 Hz, 3H, NCH_3); stereoisomer 2: 7.25 – 6.94 (m, 10H, Ar-*H*), 4.34 (d, *J* = 24.0 Hz, 2H, NCH_2Ar), 2.68 (d, *J* = 28.5 Hz, 3H, NCH_3).



***N*,*N*-dibenzylbenzamide (8ac).**[4] Purified by column chromatography (ethyl acetate: petroleum ether = 1:15). Isolated as white solid (232 mg, 0.77 mmol, 77% yield): **m.p.** 102-103 ℃: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.43 – 7.38 (m, 2H, Ar-*H*), 7.30 – 7.24 (m, 7H, Ar-*H*), 7.21 (d, *J* = 6.8 Hz, 4H, Ar-*H*), 7.04 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 4.62 (s, 2H, ArCH_2N), 4.31 (s, 2H, ArCH_2N).

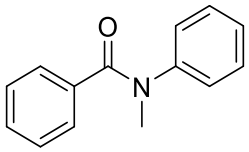


***N*,*N*-dipropylbenzamide (8ad^{nPr}).**[5] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (119 mg, 0.58 mmol, 58% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C) δ 7.31 – 7.29 (m, 2H, Ar-*H*), 7.26 (dt, *J* = 6.7, 2.1 Hz, 3H, Ar-*H*), 3.37 (d, *J* = 7.8 Hz, 2H, NCH_2), 3.08 (t, *J* = 7.7 Hz, 2H, NCH_2), 1.62 (d, *J* = 14.3 Hz, 2H, CH_3CH_2), 1.44 (q, *J* = 7.7 Hz, 2H, CH_3CH_2), 0.89 (d, *J* = 6.7 Hz, 3H, CH_3CH_2), 0.65 (t, *J* = 7.5 Hz, 3H, CH_3CH_2).

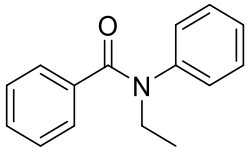


***N*,*N*-dibutylbenzamide (8ad^{nBu}).**[6] Purified by column chromatography (ethyl acetate: petroleum ether = 1:10). Isolated as colorless oil (140 mg, 0.60 mmol, 60% yield): **^{1}H NMR** (400 MHz,

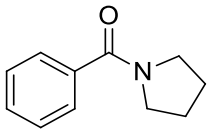
$CDCl_3$, 25 °C) δ 7.35 – 7.20 (m, 5H, Ar-*H*), 3.41 (t, *J* = 7.6 Hz, 2H, NCH_2), 3.11 (t, *J* = 7.5 Hz, 2H, NCH_2), 1.64 – 1.50 (m, 2H, NCH_2CH_2), 1.47 – 1.27 (m, 4H, CH_3CH_2), 1.11 – 0.97 (m, 2H, NCH_2CH_2), 0.90 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 0.70 (t, *J* = 7.5 Hz, 3H, CH_2CH_3).



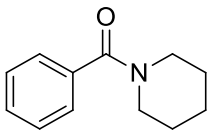
***N*-methyl-*N*-phenylbenzamide (8ae).**[7] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (152 mg, 0.72 mmol, 72% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.22 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 7.13 (d, *J* = 7.9 Hz, 3H, Ar-*H*), 7.10 – 7.02 (m, 3H, Ar-*H*), 6.95 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 3.42 (s, 3H, NCH_3).



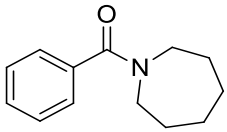
***N*-ethyl-*N*-phenylbenzamide (8af).**[7] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (135 mg, 0.60 mmol, 60% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.22 (d, *J* = 6.9 Hz, 2H Ar-*H*), 7.14 (m, 3H, Ar-*H*), 7.07 (t, *J* = 7.3 Hz, 3H, Ar-*H*), 6.98 – 6.92 (m, 2H, Ar-*H*), 3.91 (q, *J* = 7.1 Hz, 2H, NCH_2), 1.15 (t, *J* = 7.1 Hz, 3H, CH_2CH_3).



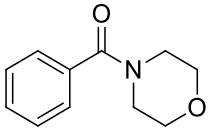
Phenyl(pyrrolidin-1-yl)methanone (8ag).[3] Purified by column chromatography (ethyl acetate: petroleum ether = 1:5). Isolated as yellowish oil (158 mg, 0.90 mmol, 90% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.46 – 7.35 (m, 2H, Ar-*H*), 7.28 (s, 3H, Ar-*H*), 3.52 (t, *J* = 7.0 Hz, 2H, NCH_2), 3.29 (t, *J* = 6.3 Hz, 2H, NCH_2), 1.82 (p, *J* = 6.8 Hz, 2H, CH_2CH_2), 1.73 (p, *J* = 6.7 Hz, 2H, CH_2CH_2).



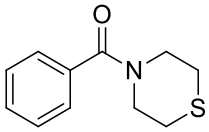
Phenyl(piperidin-1-yl)methanone (8ah).[3] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (174 mg, 0.92 mmol, 92% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.28 (s, 5H, Ar-*H*), 3.60 (s, 2H, NCH_2), 3.23 (s, 2H, NCH_2), 1.64 – 1.30 (m, 6H, CH_2CH_2).



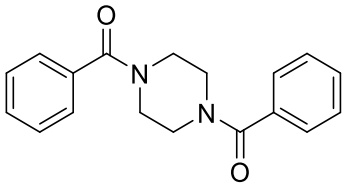
Azepan-1-yl(phenyl)methanone (8ai).[8] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as greenish oil (169 mg, 0.83 mmol, 83% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.38 – 7.30 (m, 5H, Ar-*H*), 3.65 (q, *J* = 5.2 Hz, 2H, NCH_2), 3.33 (q, *J* = 5.2 Hz, 2H, CH_2CH_2), 1.80 (p, *J* = 5.8 Hz, 2H, CH_2CH_2), 1.58 (d, *J* = 16.3 Hz, 6H, CH_2CH_2).



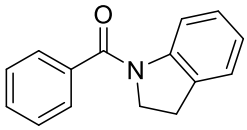
Morpholino(phenyl)methanone (8aj).[3] Purified by column chromatography (ethyl acetate: petroleum ether = 1:5). Isolated as colorless crystals (183 mg, 0.96 mmol, 96% yield): **m.p.** 42-43 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.34 (s, 5H, Ar-*H*), 3.92 – 3.24 (m, 8H, CH_2).



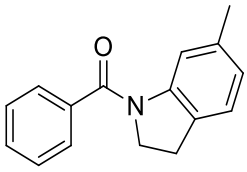
Phenyl(thiomorpholino)methanone (8ak).[9] Purified by column chromatography (ethyl acetate: petroleum ether = 1:5). Isolated as colorless oil (182 mg, 0.88 mmol, 88% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.38 – 7.33 (m, 3H, Ar-*H*), 7.30 (dd, *J* = 6.8, 3.1 Hz, 2H, Ar-*H*), 3.95 (s, 2H, NCH_2), 3.61 (s, 2H, NCH_2), 2.64 (s, 2H, SCH_2), 2.52 (s, 2H, SCH_2).



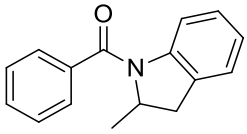
Piperazine-1,4-diylbis(phenylmethanone) (8al).[10] Purified by column chromatography (ethyl acetate: petroleum ether = 1:1). Isolated as white solid (277 mg, 0.94 mmol, 94% yield): **m.p.** 201-203 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.41 (s, 10H, Ar-*H*), 3.73 (d, *J* = 24.7 Hz, 4H, NCH_2), 3.54 (d, *J* = 22.4 Hz, 4H, NCH_2).



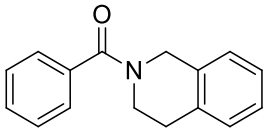
Indolin-1-yl(phenyl)methanone (8am).[10] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (199 mg, 0.89 mmol,89 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC) δ 7.57 (d, *J* = 9.3 Hz, 3H, Ar-*H*), 7.47 (q, *J* = 7.3, 6.4 Hz, 3H, Ar-*H*), 7.23 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.04 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 4.08 (s, 2H, NCH_2), 3.11 (t, *J* = 8.3 Hz, 2H, ArCH_2).



(6-methylindolin-1-yl)(phenyl)methanone (8an).[10] Purified by column chromatography (ethyl acetate: petroleum ether = 1:15). Isolated as colorless oil (232 mg, 0.98 mmol, 98% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC) δ 7.64 – 7.25 (m, 6H, Ar-*H*), 7.05 (s, 2H, Ar-*H*), 4.05 (s, 2H, NCH_2), 3.08 (q, *J* = 7.3 Hz, 2H, ArCH_2), 2.33 (s, 3H, ArCH_3).

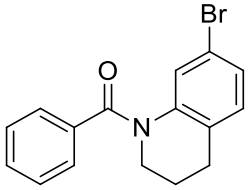


(2-methylindolin-1-yl)(phenyl)methanone (8ao).[10] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (164 mg, 0.69 mmol, 69% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC) δ 7.63 – 7.34 (m, 5H, Ar-*H*), 7.19 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 6.98 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 4.72 (s, 1H, ArCH_2), 3.39 (m, 1H, C*H*CH_3), 2.61 (d, *J* = 16.4 Hz, 1H, ArCH_2), 1.29 – 1.14 (m, 3H, CHCH_3).

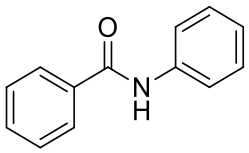


(3,4-dihydroisoquinolin-2(1H)-yl)(phenyl)methanone (8ap).[6] Purified by column chromatography (ethyl acetate: petroleum ether = 1:5). Isolated as yellow oil (171 mg, 0.72 mmol, 72% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC) δ 7.41 – 7.29 (m, 5H, Ar-*H*), 7.08 (dt, *J* =

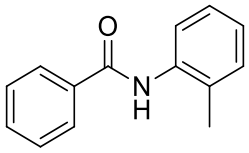
14.0, 7.6 Hz, 4H, Ar-*H*), 4.81 (s, 1H, NCH_2), 4.50 (s, 1H, NCH_2), 3.91 (s, 1H, ArCH_2), 3.55 (s, 1H, ArCH_2), 2.83 (d, *J* = 35.0 Hz, 2H, NCH_2).



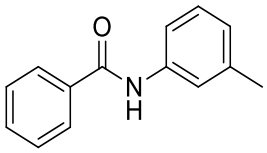
(7-bromo-3,4-dihydroquinolin-1(2H)-yl)(phenyl)methanone (8aq).[6] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as yellowish solid (253 mg, 0.80 mmol, 80% yield): **m.p.** 108-109 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.24 (dd, *J* = 25.2, 7.7 Hz, 6H, Ar-*H*), 6.90 (d, *J* = 8.6 Hz, 1H, Ar-*H*), 6.57 (d, *J* = 8.7 Hz, 1H, Ar-*H*), 3.77 (t, *J* = 6.2 Hz, 2H, NCH_2), 2.72 (t, *J* = 6.5 Hz, 2H, ArCH_2), 1.93 (p, *J* = 6.5 Hz, 2H, NCH_2CH_2).



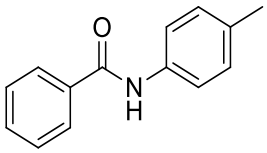
***N*-phenylbenzamide (8ar).**[11] Purified by column chromatography (ethyl acetate: petroleum ether = 1:15). Isolated as white solid (164 mg, 0.83 mmol, 83% yield): **m.p.** 167-168 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.77 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.56 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.44 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.36 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.27 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.06 (t, *J* = 7.4 Hz, 1H, Ar-*H*).



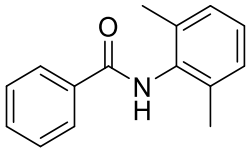
***N*-(*o*-tolyl)benzamide (8ar^{oMe}).**[11] Purified by column chromatography (ethyl acetate: petroleum ether = 1:15). Isolated as white solid (137 mg, 0.65 mmol, 65% yield): **m.p.** 147-148 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.98 – 7.88 (m, 3H, Ar-*H*), 7.58 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 7.51 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 7.31 – 7.24 (m, 2H, Ar-*H*), 7.15 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 2.35 (s, 3H, ArCH_3).



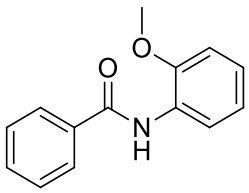
***N*-(*m*-tolyl)benzamide (8ar^{mMe}).**[11] Purified by column chromatography (ethyl acetate: petroleum ether = 1:6). Isolated as white solid (152 mg, 0.72 mmol, 72% yield): **m.p.** 114-115 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.87 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.54 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.49 – 7.43 (m, 3H, Ar-*H*), 7.25 (t, *J* = 8.1 Hz, 1H, Ar-*H*), 7.14 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.72 (dd, *J* = 8.2, 2.3 Hz, 1H, Ar-*H*), 3.82 (s, 3H, ArCH_3).



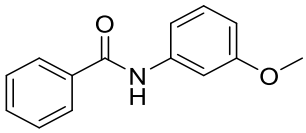
***N*-(*p*-tolyl)benzamide (8ar^{pMe}).**[11] Purified by column chromatography (ethyl acetate: petroleum ether = 1:10). Isolated as brown crystals (163 mg, 0.77 mmol, 77% yield): **m.p.** 161-162 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.72 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.46 – 7.35 (m, 3H, Ar-*H*), 7.29 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.01 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 2.22 (s, 3H, ArCH_3).



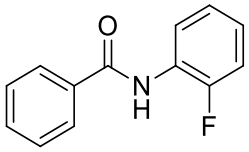
***N*-(2,6-dimethylphenyl)benzamide (8ar^{oMe2}).**[12] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as greenish oil (95 mg, 0.42 mmol, 42% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.96 (dd, *J* = 7.2, 2.0 Hz, 2H, Ar-*H*), 7.54 (d, *J* = 7.0 Hz, 3H, Ar-*H*), 7.11 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.00 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 2.19 (s, 6H, ArCH_3).



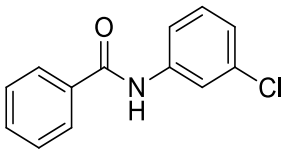
***N*-(2-methoxyphenyl)benzamide (8ar$^{o(OMe)}$).**[13] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as green oil (132 mg, 0.58 mmol, 58% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 8.60 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.96 – 7.90 (m, 2H, Ar-*H*), 7.60 – 7.48 (m, 3H, Ar-*H*), 7.14 – 7.02 (m, 2H, Ar-*H*), 6.93 (d, *J* = 9.5 Hz, 1H, Ar-*H*), 3.93 (s, 3H, ArOCH_3).



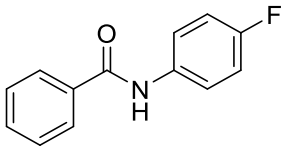
***N*-(3-methoxyphenyl)benzamide (8ar$^{m(OMe)}$).**[14] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as yellow solid (136 mg, 0.60 mmol, 60% yield): **m.p.** 113-114 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.84 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.47 (d, *J* = 13.8 Hz, 2H, Ar-*H*), 7.38 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.21 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 6.70 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 3.76 (s, 3H, ArOCH_3).



***N*-(2-fluorophenyl)benzamide (8ar^{oF}).**[15] Purified by column chromatography (ethyl acetate: petroleum ether = 1:15). Isolated as white solid (144 mg, 0.67 mmol, 67% yield): **m.p.** 114-115 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 8.46 (t, *J* = 8.3 Hz, 1H, Ar-*H*), 7.91 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.62 – 7.44 (m, 3H, Ar-*H*), 7.24 – 7.05 (m, 3H, Ar-*H*).

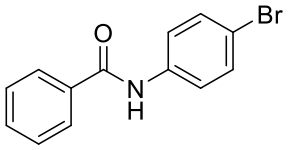


***N*-(3-chlorophenyl)benzamide (8ar^{mCl}).**[16] Purified by column chromatography (ethyl acetate: petroleum ether = 1:7). Isolated as colorless oil (157 mg, 0.68 mmol, 68% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.81 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.77 (s, 1H, Ar-*H*), 7.49 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.38 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.21 (t, *J* = 8.1 Hz, 1H, Ar-*H*), 7.10 (d, *J* = 8.1 Hz, 1H, Ar-*H*).

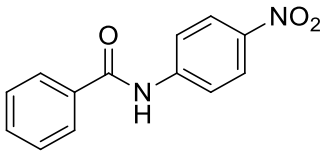


***N*-(4-fluorophenyl)benzamide (8ar^{pF}).**[11] Purified by column chromatography (ethyl acetate: petroleum ether = 1:2). Isolated as light brown solid (168 mg, 0.78 mmol, 78% yield): **m.p.** 178-

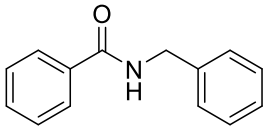
179 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.89 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.62 (dd, *J* = 8.8, 4.7 Hz, 2H, Ar-*H*), 7.51 (t, *J* = 6.5 Hz, 3H, Ar-*H*), 7.09 (t, *J* = 8.6 Hz, 2H, Ar-*H*).



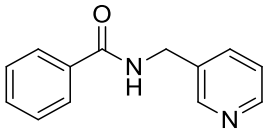
***N*-(4-bromophenyl)benzamide (8ar^{pBr}).**[11] Purified by column chromatography (ethyl acetate: petroleum ether = 1:2). Isolated as white solid (174 mg, 0.63 mmol, 63% yield): **m.p.** 197-198 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.80 – 7.76 (m, 2H, Ar-*H*), 7.48 (d, *J* = 8.6 Hz, 3H, Ar-*H*), 7.44 – 7.39 (m, 4H, Ar-*H*).



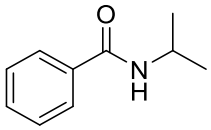
***N*-(4-nitrophenyl)benzamide (8ar^{pNO2}).**[11] Purified by column chromatography (ethyl acetate: petroleum ether = 1:10). Isolated as yellow solid (148 mg, 0.61 mmol, 61% yield): **m.p.** 206-208 °C: **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 8.30 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.90 (dd, *J* = 16.2, 8.3 Hz, 4H, Ar-*H*), 7.64 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.56 (t, *J* = 7.5 Hz, 2H, Ar-*H*).



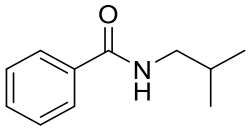
***N*-benzylbenzamide (8as).**[11] Purified by column chromatography (ethyl acetate: petroleum ether = 1:15). Isolated as colorless oil (135 mg, 0.64 mmol, 64% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 7.82 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.50 (t, *J* = 7.3 Hz, 1H, Ar-*H*), 7.41 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.38 – 7.27 (m, 5H, Ar-*H*), 4.62 (d, *J* = 8.0 Hz, 2H, NHCH_2).



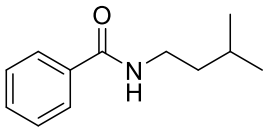
***N*-(pyridin-3-ylmethyl)benzamide (8at).**[13] Purified by column chromatography in ethyl acetate. Isolated as colorless oil (125 mg, 0.59 mmol, 59% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 8.45 – 8.34 (m, 2H, Ar-*H*), 7.79 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.59 (m, 1H, Ar-*H*), 7.42 (m, 1H, Ar-*H*), 7.32 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 7.20 – 7.10 (m, 1H, Ar-*H*), 4.51 (d, *J* = 5.6 Hz, 2H, NHCH_2).



***N*-isopropylbenzamide (8au).**[17] Purified by column chromatography (ethyl acetate: petroleum ether = 1:10). Isolated as colorless oil (103 mg, 0.63 mmol, 63% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC) δ 7.68 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.36 (dt, *J* = 28.1, 7.1 Hz, 3H, Ar-*H*), 4.20 (hept, *J* = 6.7 Hz, 1H, NHC*H*), 1.18 (d, *J* = 6.6 Hz, 6H, CHCH_3).

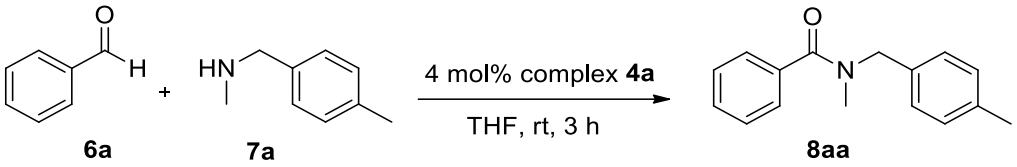


***N*-isobutylbenzamide (8av).**[17] Purified by column chromatography (ethyl acetate: petroleum ether= 1:10). Isolated as colorless oil (119mg, 0.67 mmol, 67% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC) δ 7.78 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.48 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 7.42 (t, *J* = 7.4 Hz, 2H, Ar-*H*), 3.28 (t, *J* = 6.5 Hz, 2H, NHCH_2), 1.91 (dt, *J* = 13.5, 6.7 Hz, 1H, C*H*CH_3), 0.98 (d, *J* = 6.7 Hz, 6H, CHCH_3).



***N*-isopentylbenzamide (8aw).**[18] Purified by column chromatography (ethyl acetate: petroleum ether = 1:15). Isolated as colorless oil (132 mg, 0.69 mmol, 69% yield): **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC) δ 7.79 – 7.75 (m, 2H, Ar-*H*), 7.51 – 7.45 (m, 1H, Ar-*H*), 7.44 – 7.38 (m, 2H, Ar-*H*), 3.49 – 3.43 (m, 2H, NHCH_2), 1.69 (dq, *J* = 13.3, 6.7 Hz, 1H, C*H*CH_3), 1.55 – 1.47 (m, 2H, CHCH_2), 0.95 (d, *J* = 6.6 Hz, 6H, CHCH_3).

Table S1. Solvent screening for the amidation reaction[a].



6a **7a** **8aa**

Entry	Solvent	Yield(%)[b]
1	THF	99
2	Toluene	74

3	DCM	40
4	DMSO	42
5	DME	34
6	Et_2O	54
7	*n*-hexane	75
8	1,4-dioxane	83
9	CH_3CN	71
10	Solvent-free	34

[a]Reaction conditions: aldehyde (**6a**, 3 mmol), amine (**7a**, 1 mmol), complex (4 mol%), solvent (0.8 mL), room temperature, 3 hours. [b]Yields were determined using *n*-hexadecane as an internal standard by GC analysis.

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5. Reaction rate profile for amidation reaction.

General procedure to determine the dependence of reaction rate on time:

A THF (0.8 mL) solution of complex **4a** (36.3 mg, 0.04 mmol), *N*,4-dimethylbenzylamine (147 μL, 1.00 mmol), and *n*-hexadecane (30 μL, 1 mmol) was mixed and stirred at room temperature for 30 min. Benzaldehyde (305 μL, 3.00 mmol) was then added, and the resulting mixture was kept on stirring. 100 μL of the reaction mixture was taken out after 30, 60, 90, 120, 150, 160, 170, and 180 minute reaction, which was quenched with water (2 mL) and extracted with ethyl acetate (3 × 3 mL). The organic layers were collected and evaporated, and the samples (dissolved in ethyl acetate) were assessed by GC analysis.

Table S2. Results of yield *vs.* time for the amidation reaction[a]

Entry	1	2	3	4	5	6	7	8
Time(min)	30	60	90	120	150	160	170	180
Yield%[b]	19	36	50	69	88	93	97	99

[a]Reaction conditions: benzaldehyde (305 μL, 3 mmol), *N*,4-dimethyl benzylamine (147 μL, 1 mmol), complex **4a (**36.3 mg, 4 mol%), solvent (THF, 0.8 mL), room temperature. [b]Yields were determined using *n*-hexadecane as an internal standard by GC analysis.

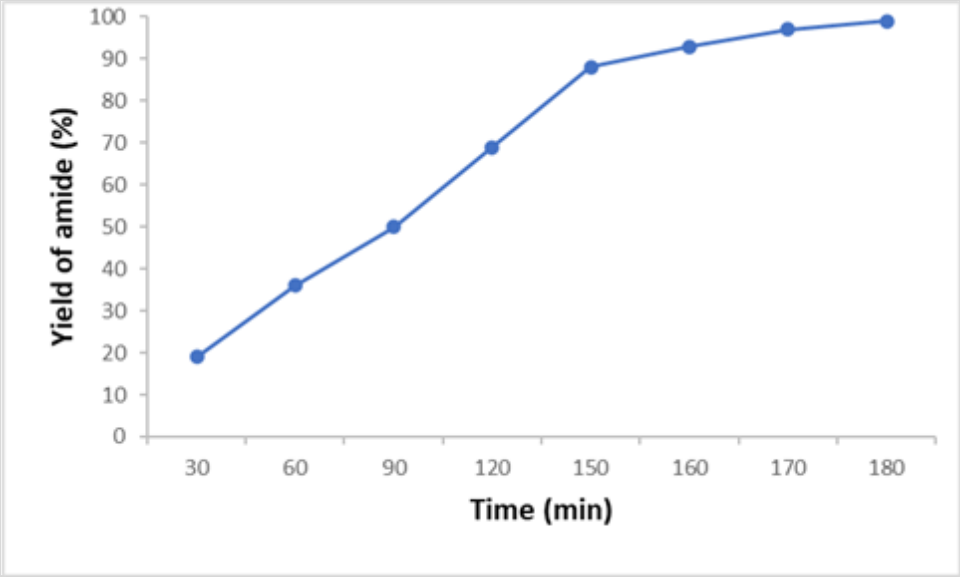


Fig. S1. Reaction profile of yield *vs.* time for the amidation reaction

6. Crystallographic data of complexes.

Table S3. Crystallographic data of complexes **1a-3a**:

Compound	**1a**	**2a**	**3a· 0.5(C_7H_8)**
Empirical formula	$C_{40}H_{78}LiN_4O_2Si_4Y$	$C_{40}H_{78}LiN_4O_2Si_4Nd$	$C_{43.5}H_{82}LiN_4O_2Si_4Yb$
Formula weight	855.27	910.60	985.47
Temperature/K	293(2)	296.15	119.98
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	13.910(3)	13.9562(7)	13.883
b/Å	15.955(3)	15.9734(8)	15.842
c/Å	23.692(4)	23.9218(12)	23.674
α/°	90	90	90
β/°	102.163(5)	102.626(2)	102.11
γ/°	90	90	90
Volume/$Å^3$	5140.1(16)	5203.9(5)	5090.7
Z	4	4	4
ρ_{calc} g/cm^3	1.105	1.230	1.286
μ/mm^{-1}	1.260	1.126	1.967
F(000)	1840.0	2040.0	2064.0
Crystal size/mm^3	0.4 × 0.3 × 0.3	0.5 × 0.4 × 0.3	0.6 × 0.5 × 0.4
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.84 to 51.36	4.80 to 55.06	3.52 to 52.74
Index ranges	$-16 \le h \le 15$, $-16 \le k \le 19$, $-27 \le l \le 28$	$-17 \le h \le 18$, $-20 \le k \le 20$, $-31 \le l \le 31$	$-17 \le h \le 13$, $-19 \le k \le 19$, $-29 \le l \le 29$
Reflections collected	27207	70042	79326
Independent reflections	9570 [R_{int} = 0.0844, R_{sigma} = 0.1060]	11980 [R_{int} = 0.0606, R_{sigma} = 0.0510]	10400 [R_{int} = 0.0531, R_{sigma} = 0.0309]
Data/restraints/parameters	9570/0/491	11980/4/508	10400/3/507
Goodness-of-fit on F^2	1.013	1.018	1.220

Final R indexes [I>=2σ (I)]	R_1 = 0.0521, wR_2 = 0.1026	R_1 = 0.0346, wR_2 = 0.0692	R_1 = 0.0229, wR_2 = 0.0603
Final R indexes [all data]	R_1 = 0.1087, wR_2 = 0.1190	R_1 = 0.0617, wR_2 = 0.0770	R_1 = 0.0309, wR_2 = 0.0770

Table S4. Crystallographic data of complexes **4a** and **5a**:

Compound	**4a**	**5a. 0.5(C_7H_8)**
Empirical formula	$C_{44}H_{82}LiN_4O_2Si_4Y$	$C_{47.5}H_{84}LiN_4O_2Si_4Nd$
Formula weight	907.34	1006.72
Temperature/K	150.0	296.15
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	12.2861(8)	12.118(2)
b/Å	12.8406(9)	24.770(5)
c/Å	17.9613(11)	18.258(3)
α/°	88.666(2)	90
β/°	87.092(2)	95.962(5)
γ/°	71.124(2)	90
Volume/$Å^3$	2677.7(3)	5450.5(17)
Z	2	4
ρ_{calc} g/cm^3	1.125	1.227
μ/mm^{-1}	1.213	1.078
F(000)	976.0	2128.0
Crystal size/mm^3	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.50 to 55.17	4.48 to 55.04
Index ranges	$-15 \le h \le 15$, $-16 \le k \le 16$, $-23 \le l \le 23$	$-15 \le h \le 15$, $-32 \le k \le 32$, $-23 \le l \le 23$
Reflections collected	97127	142600
Independent reflections	12180 [R_{int} = 0.0672, R_{sigma} = 0.0421]	12497 [R_{int} = 0.1488, R_{sigma} = 0.0904]

Data/restraints/parameters	12180/2/521	12497/7/521
Goodness-of-fit on F^2	1.039	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0923	R_1 = 0.0494, wR_2 = 0.0848
Final R indexes [all data]	R_1 = 0.0517, wR_2 = 0.0986	R_1 = 0.1015, wR_2 = 0.0975

7. Crystal structures of complexes.

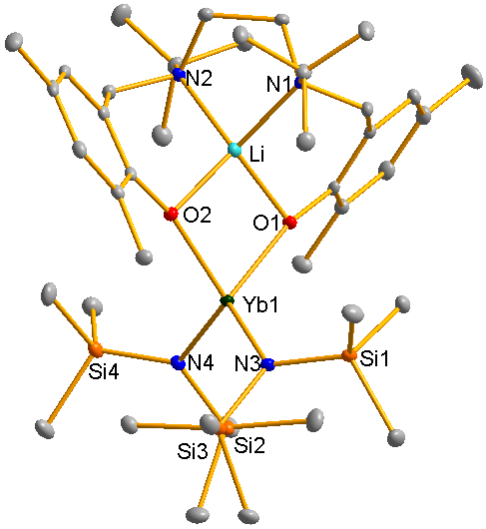


Fig. S2. Solid state structure of complex **3a**·0.5 toluene, with ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Symmetry operator: [1]1-X,1-Y,1-Z. Selected bond distances (Å) and bond angles (°): Yb1-O1 2.142(2), Yb1-O2 2.143(2), Yb1-N3 2.209(2), Yb1-N4 2.207(2), Li1-N1 2.073(6), Li1-N2 2.058(5), Li1-O1 1.938(5), Li1-O2 1.941(6); O1-Yb-O2 80.85(8), O1-Yb1-N3 118.89(8), O1-Yb1-N4 112.62(8), O2-Yb1-N3 114.63(8), O2-Yb1-N4 115.83(8), Li-O1-Yb1 93.84(17).

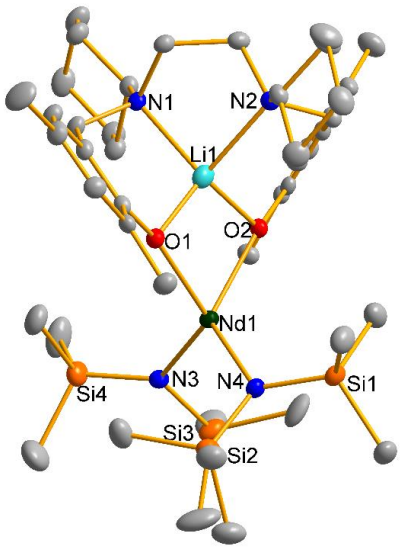


Fig. S3. Solid state structure of complex **5a**·0.5 toluene, with ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Symmetry operator: [1]-X,1-Y,2-Z. Selected bond distances (Å) and bond angles (°): Nd1-O1 2.281(2), Nd1-O2 2.284(2), Nd1-N3 2.329(3), Nd1-N4 2.319(3), Li1-O1 1.802(7), Li1-O2 1.932(7), Li1-N1 2.108(7), Li1-N2 2.144(7); O1-Nd1-O2 79.43(9), O1-Nd1-N3 122.14(10), O1-Nd1-N4 106.6(1), O2-Nd1-N3 110.05(10), O2-Nd1-N4 124.78(10), Li1-O1-Nd1 90.5(2), Li1-O2-Nd1 87.4(2).

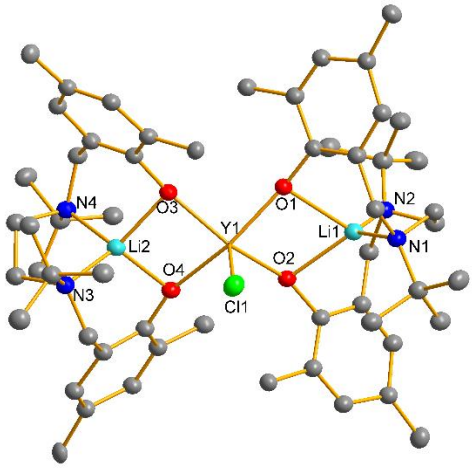


Fig. S4. Solid state structure of complex **1b**, with ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry operator: [1]1-X,1-Y,2-Z. Selected bond distances (Å) and bond angles (°): Y1-Cl1 2.484(7), Y1-O1 2.088(1), Y1-O2 2.123(2), Y1-O3 2.116(2), Y1-O4 2.142(1), Li1-O1 1.35(4), Li1-O2 1.21(4), Li2-O3 2.05(4), Li2-O4 1.90(4),

Li1-N1 1.82(4), Li1-N2 1.72(5); O2-Y1-Cl1 100.8(5), O2-Y1-O4 92.4(6), O2-Y1-O1 82.9(6), O3-Y1-Cl1 103.3(5), O3-Y1-O2 150.0(6), O3-Y1-O4 81.9(6), O4-Y1-Cl1 100.0(5), O4-Y1-O1 159.2(6).

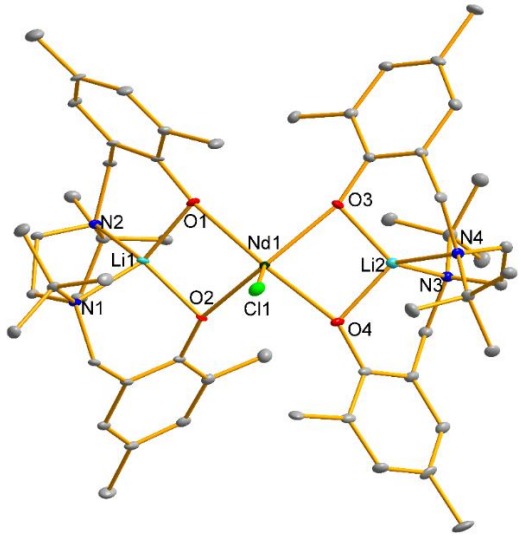
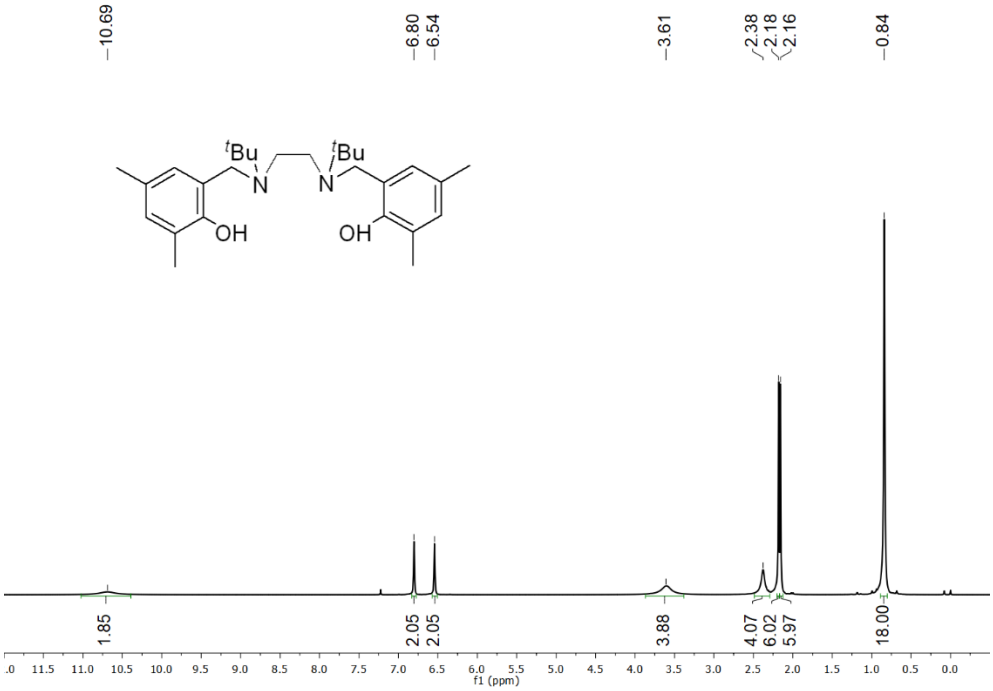
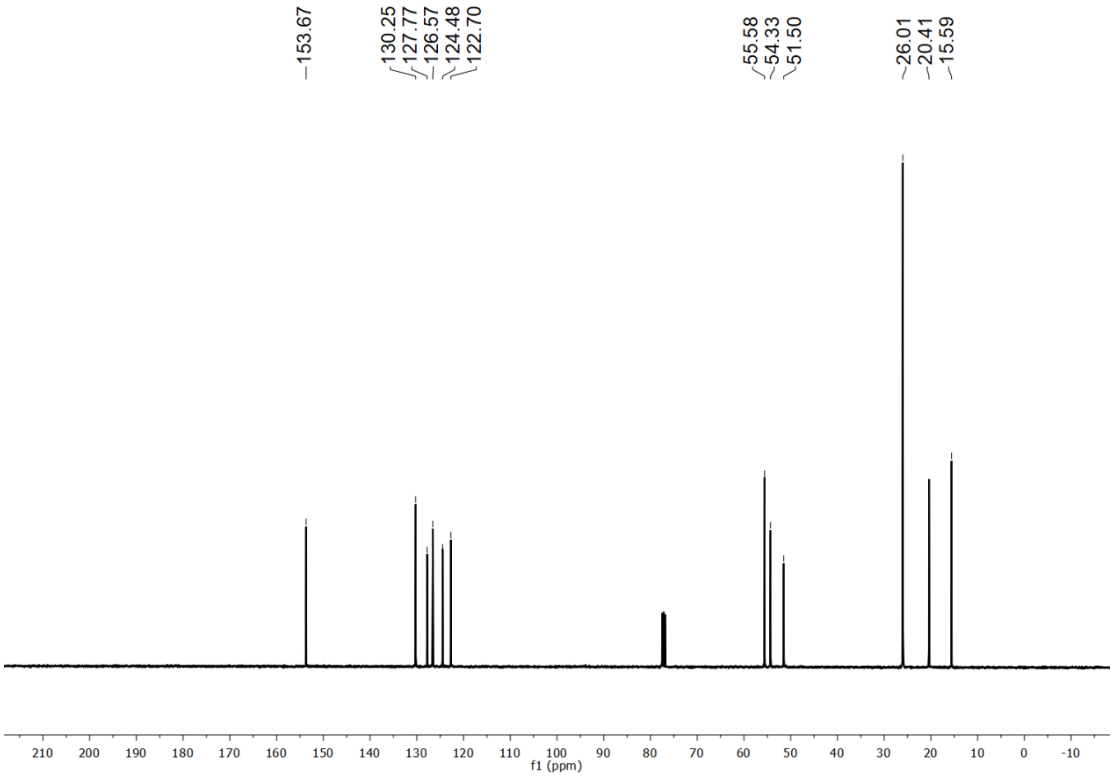


Fig. S5. Solid state structure of complex **2b**, with ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry operator: [1]2-X,1-Y,1-Z. Selected bond distances (Å) and bond angles (°): Nd1-O1 2.315(4), Nd1-O3 2.264(4), Nd1-O4 2.301(4), Li1-O1 1.95(1), Li1-O2 1.927(10), Li2-O3 1.942(11), Li2-O4 1.909(11), Li1-N1 2.066(11), Li1-N2 2.056(11), Li2-N3 2.070(11), Li2-N4 2.064(11); O2-Nd1-O1 75.53(14), O2-Nd1-O3 142.41(16), O2-Nd1-O4 90.57(14), O2-Nd1-Cl1 110.51(12), O3-Nd1-Cl1 106.82(12), O3-Nd1-O1 97.33(14), O3-Nd1-O4 76.08(15), O1-Nd1-Cl1 107.69(11), O4-Nd1-Cl1 104.26(11).

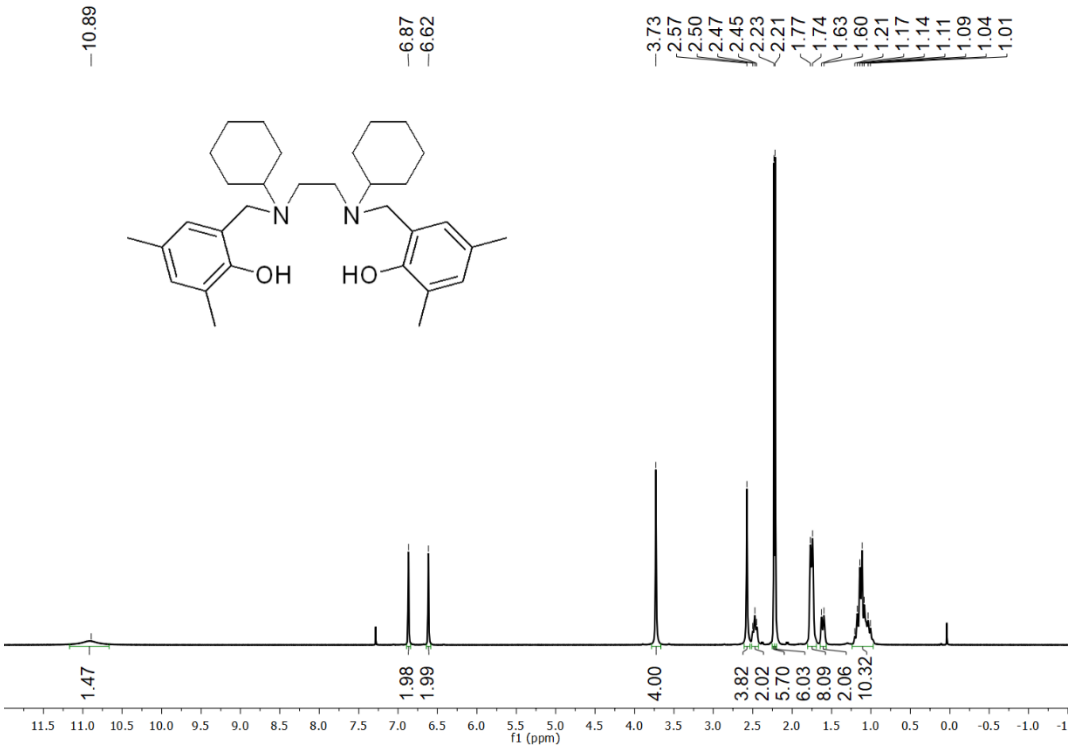
8. NMR spectra of ligand precursors and complexes.



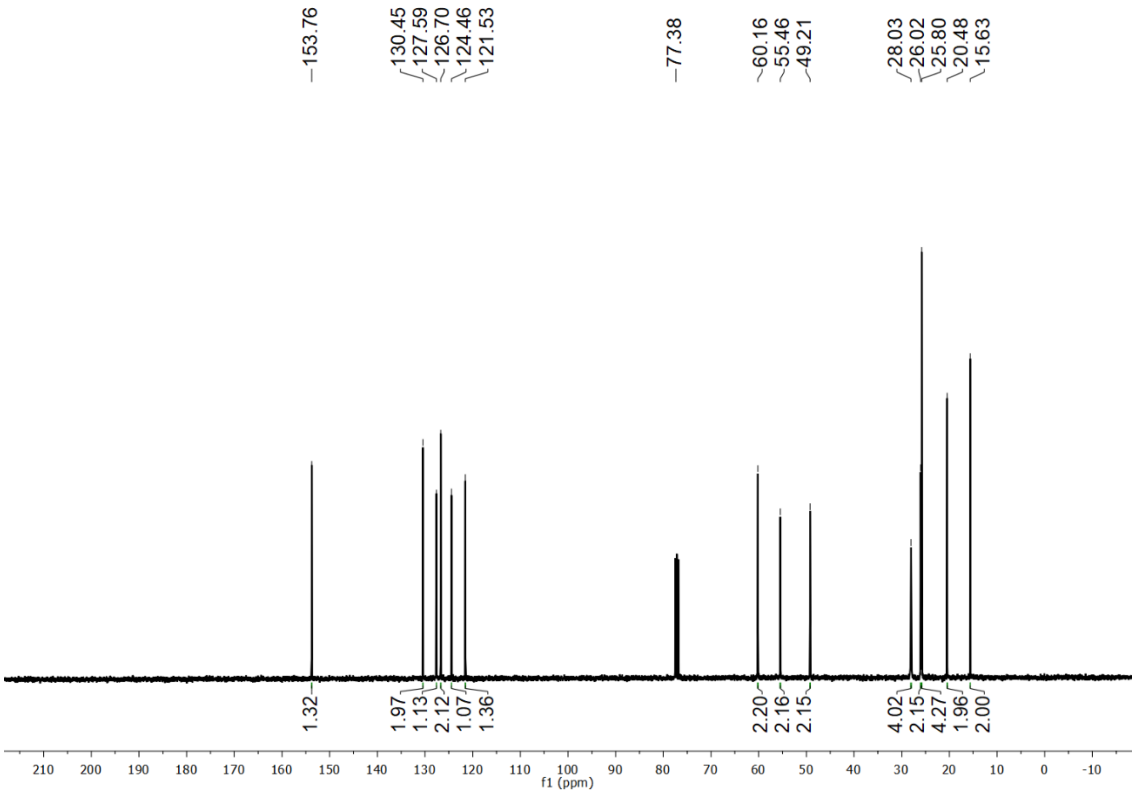
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of $L^{1}H_2$



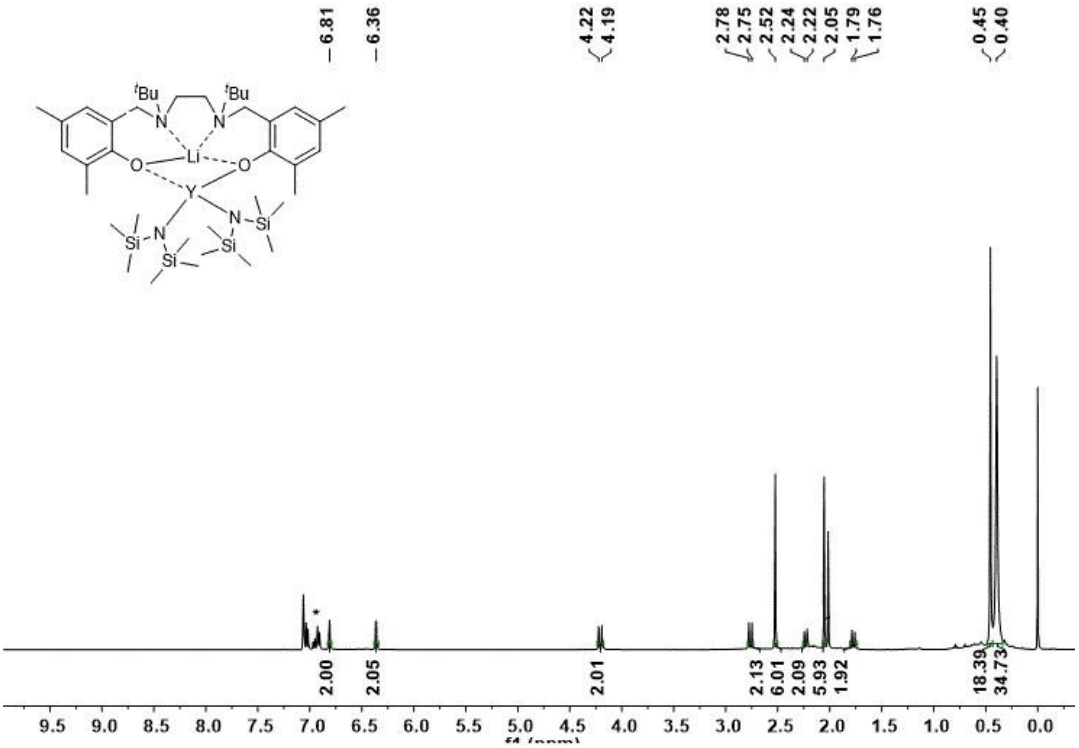
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of $L^{1}H_2$



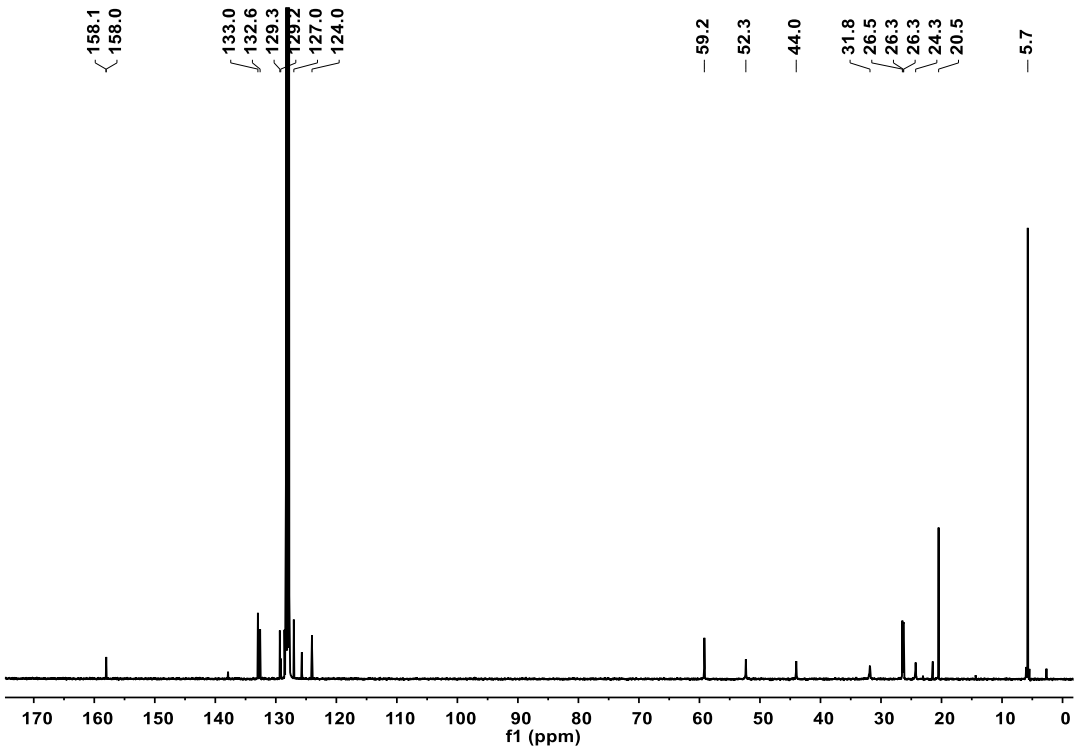
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of L^2H_2



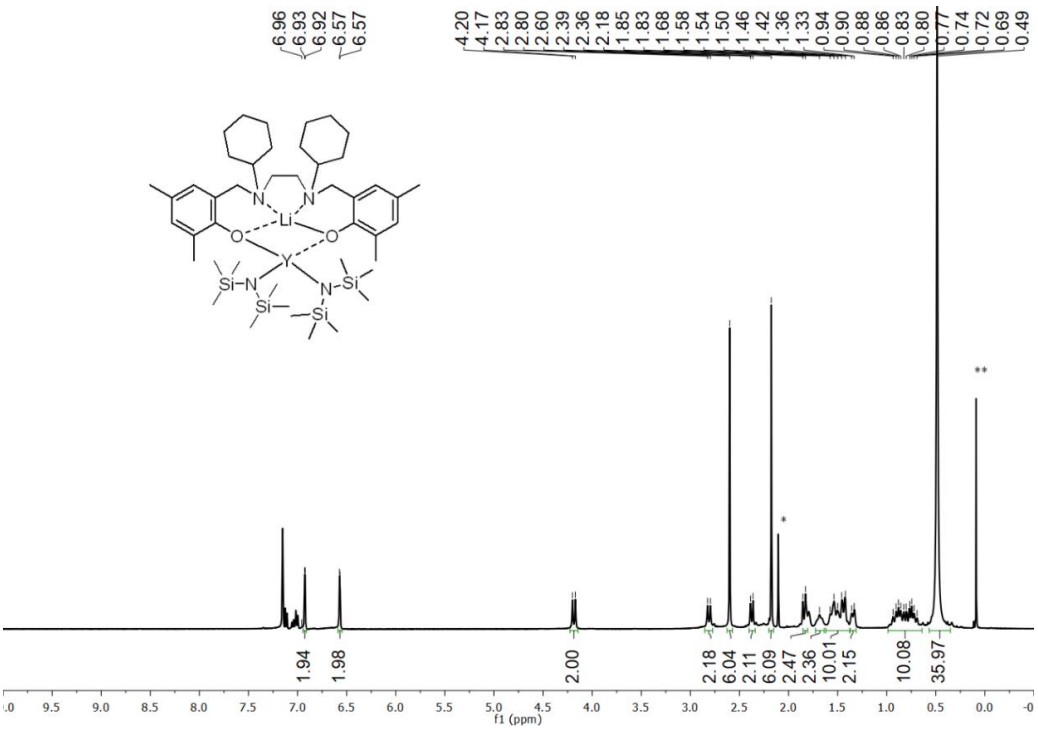
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of L^2H_2



^{1}H NMR spectrum (400 MHz, C_6D_6, 25 ^{o}C) of complex **1a**

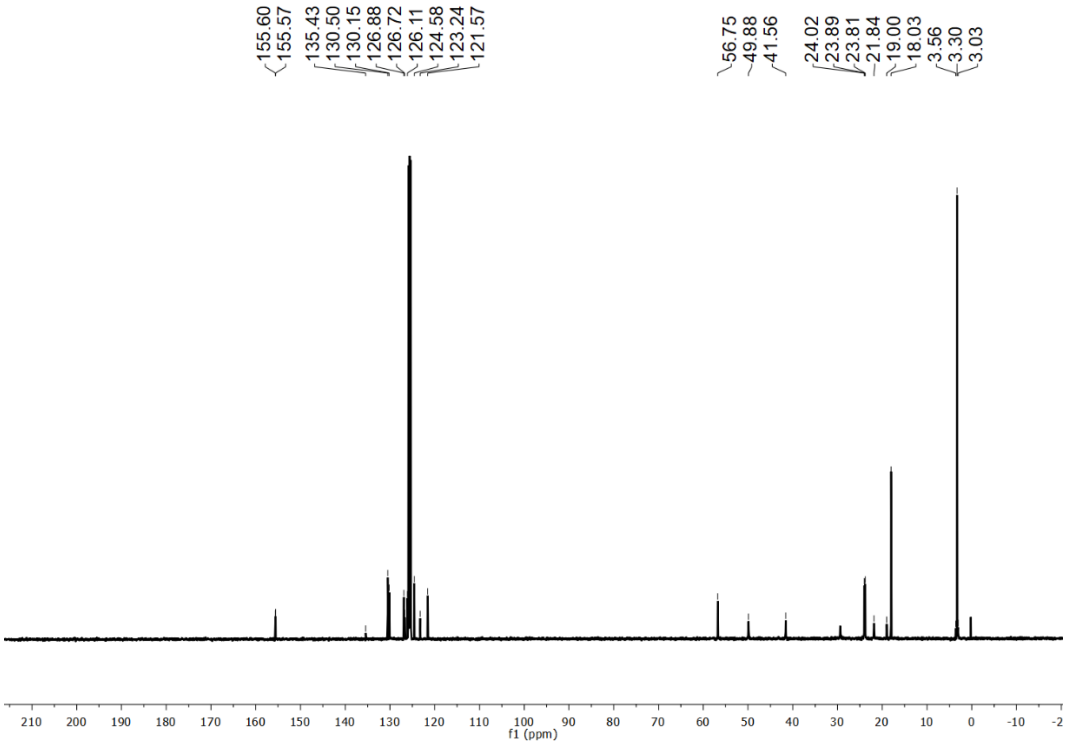


^{13}C NMR spectrum (101 MHz, C_6D_6, 25 ^{o}C) of complex **1a**

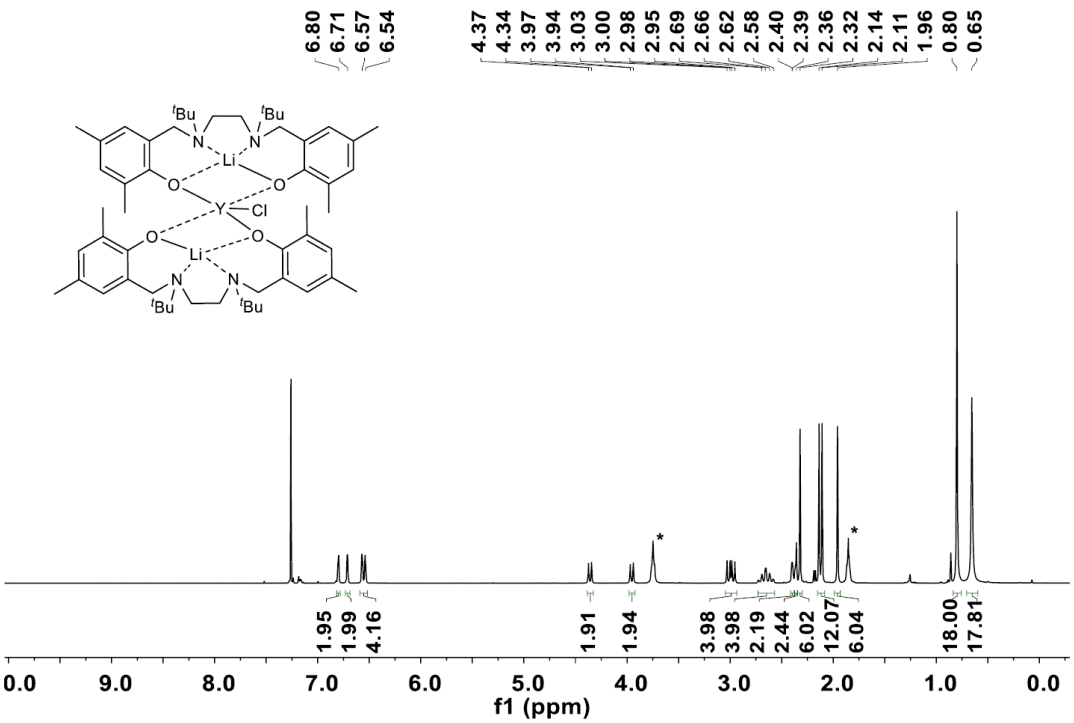


^{1}H NMR spectrum (400 MHz, C_6D_6, 25 ºC) of complex **4a**

(*= toluene; **= free $HN(SiMe_3)_2$)



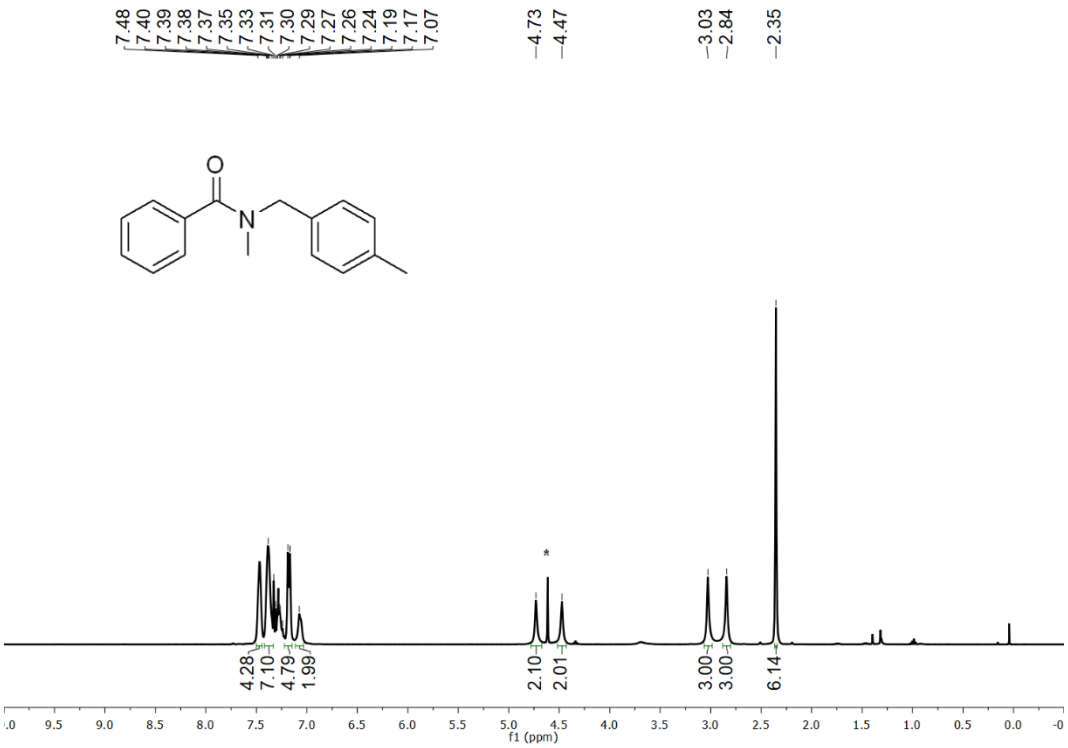
^{13}C NMR spectrum (101 MHz, C_6D_6, 25 ºC) of complex **4a**



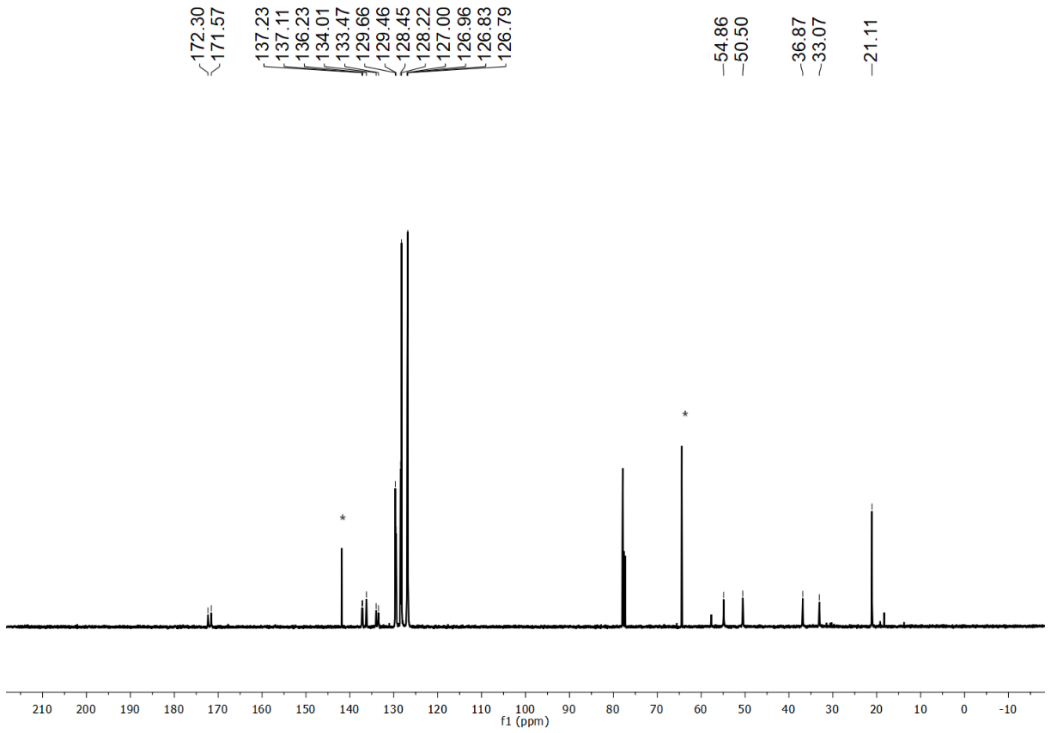
^{1}H NMR spectrum (400 MHz, C_6D_6, 25 ^{o}C) of complex **1b**

(*= toluene)

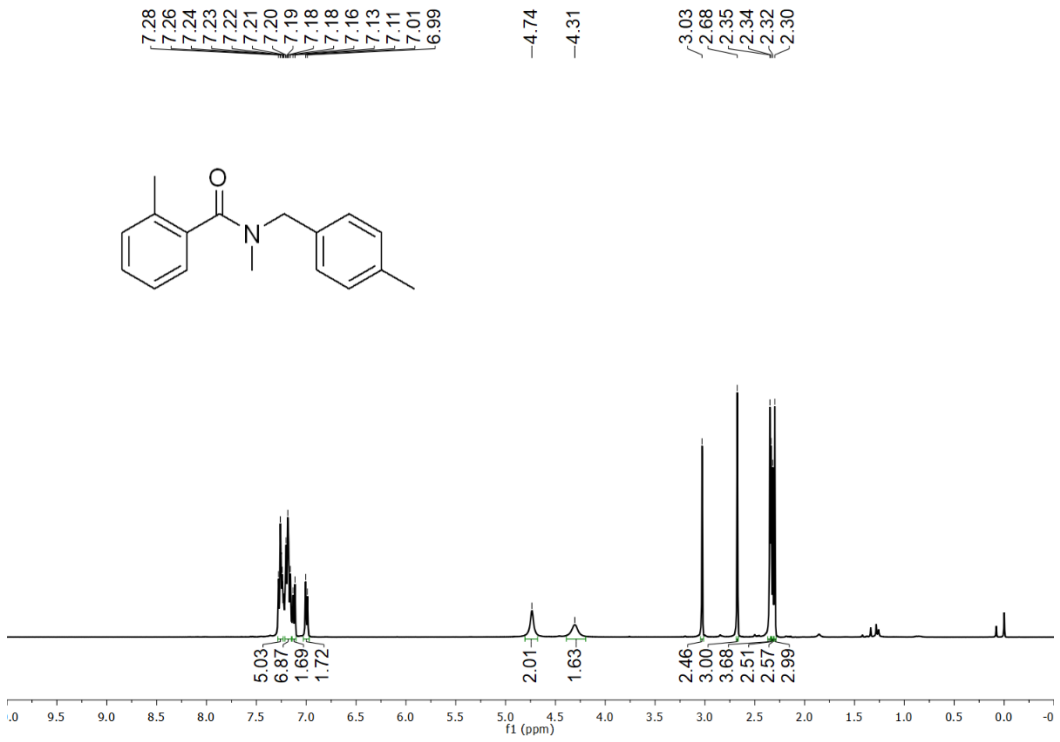
9. NMR spectra of amides.



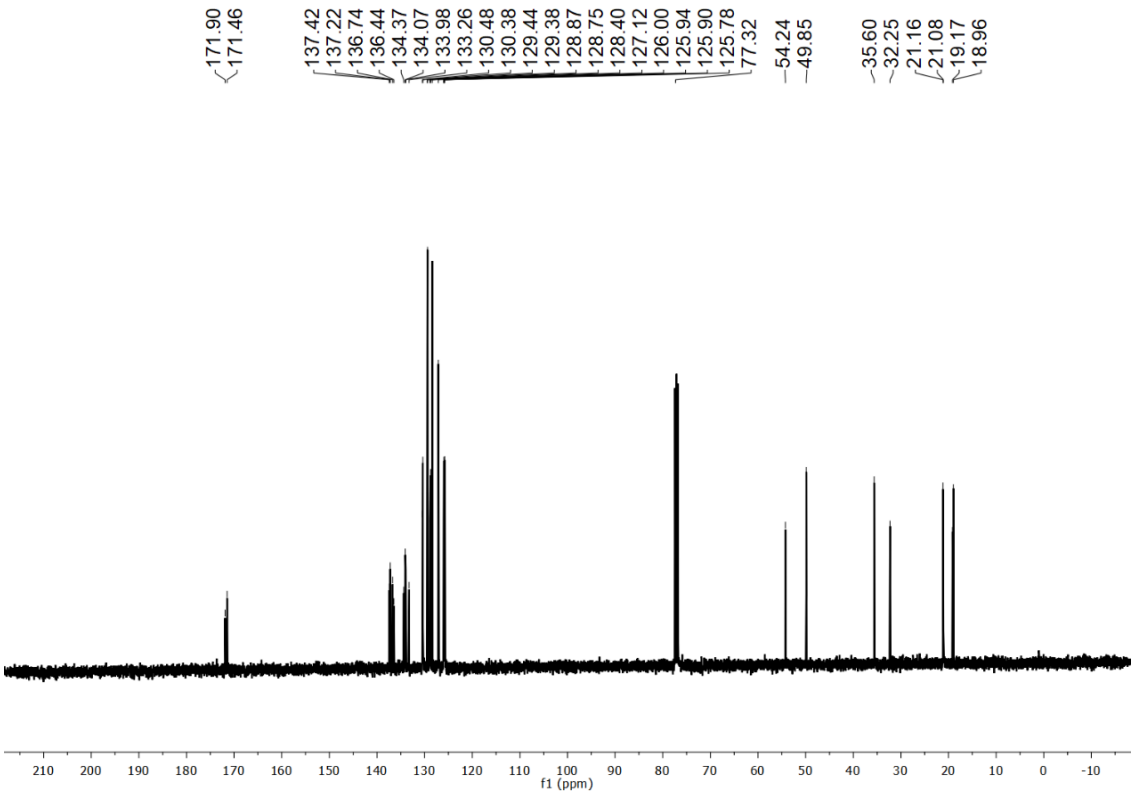
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8aa** (*= benzyl alcohol)



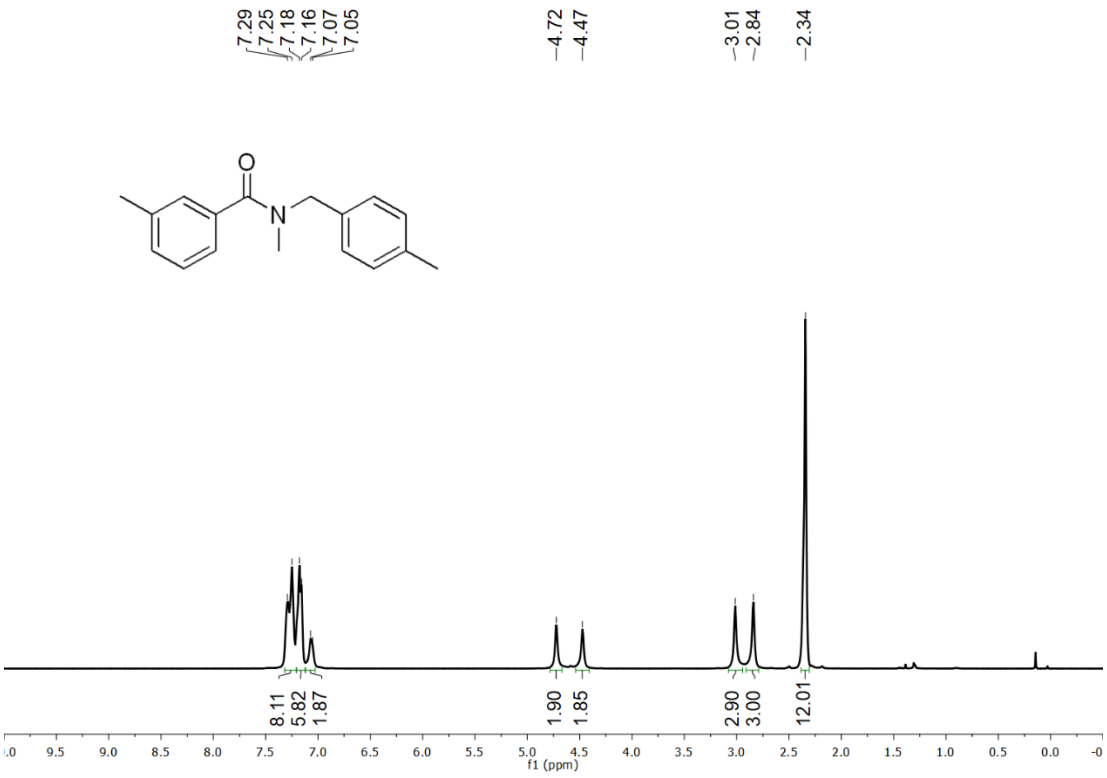
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8aa** (*= benzyl alcohol)



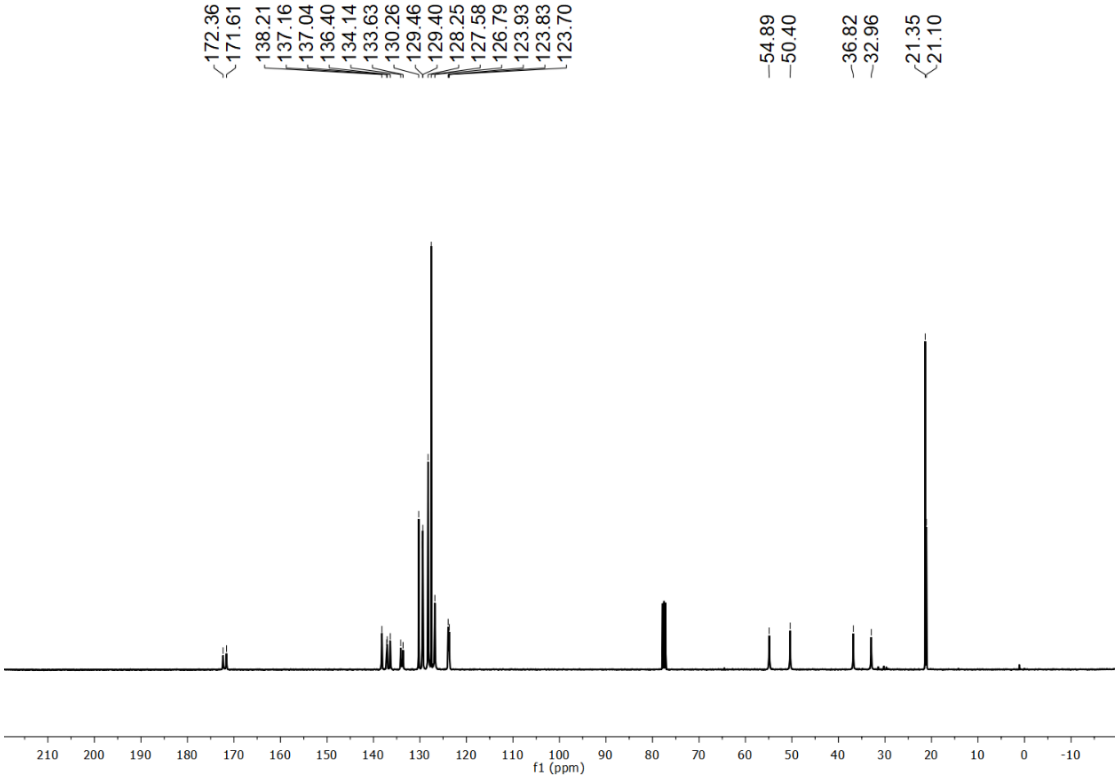
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ba**



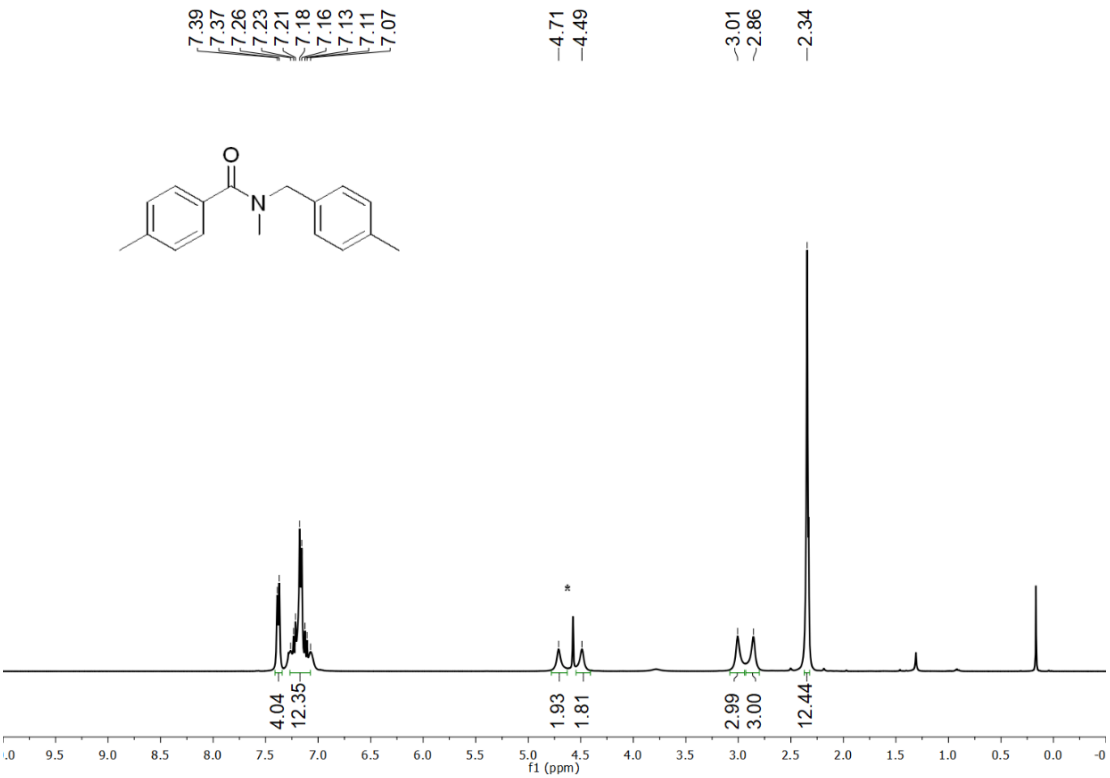
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ba**



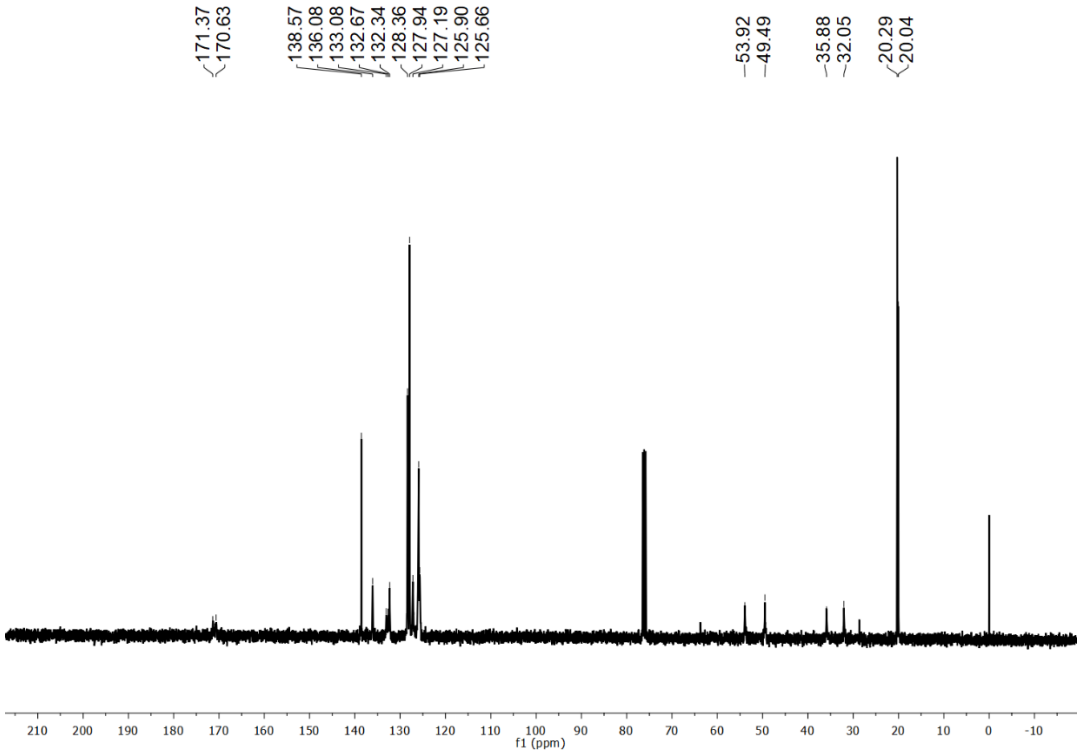
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ca**



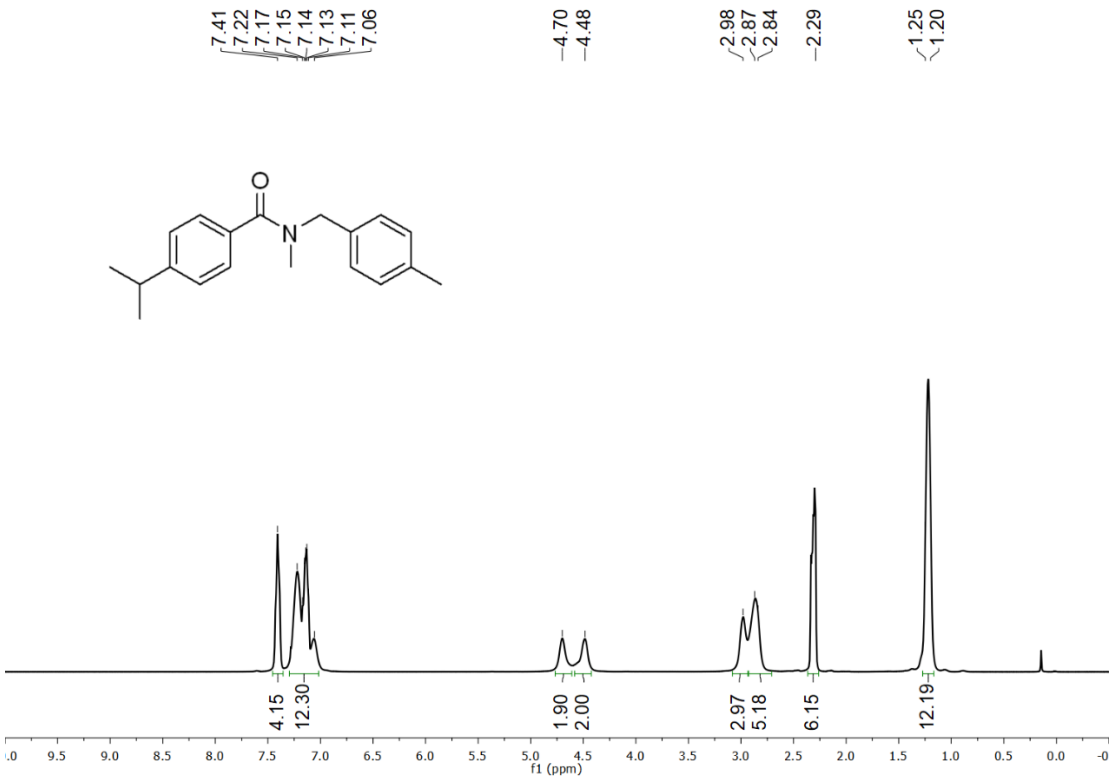
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ca**



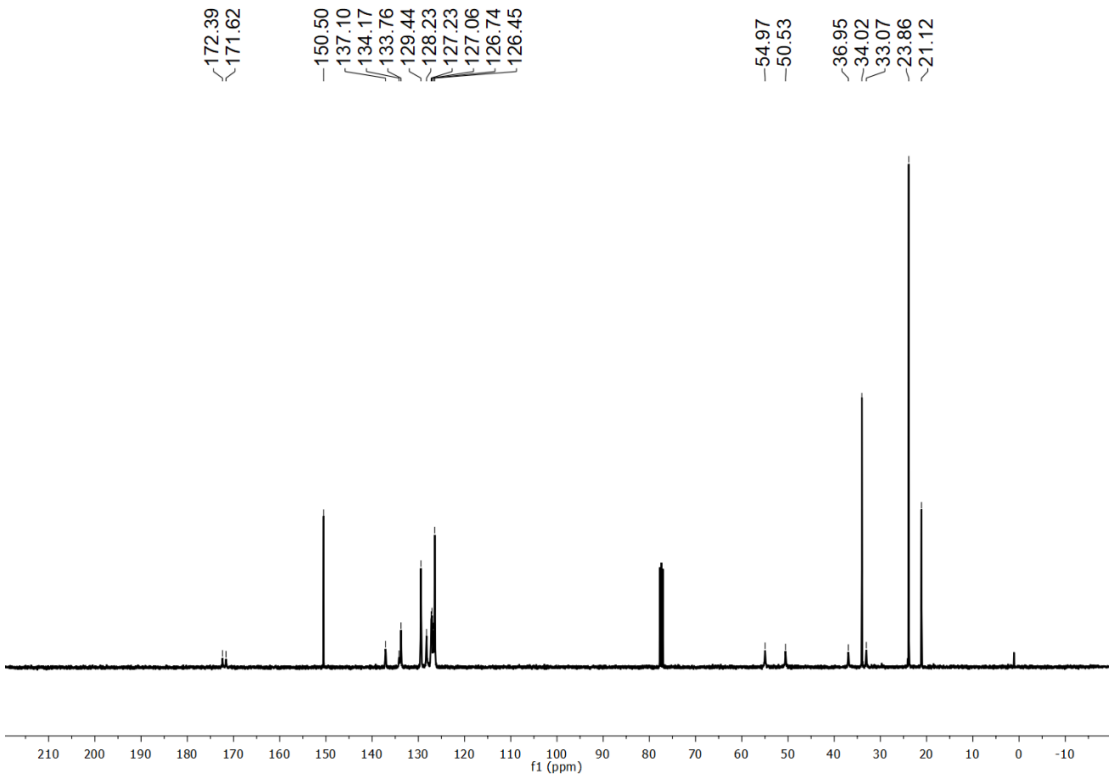
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8da** (*= benzyl alcohol)



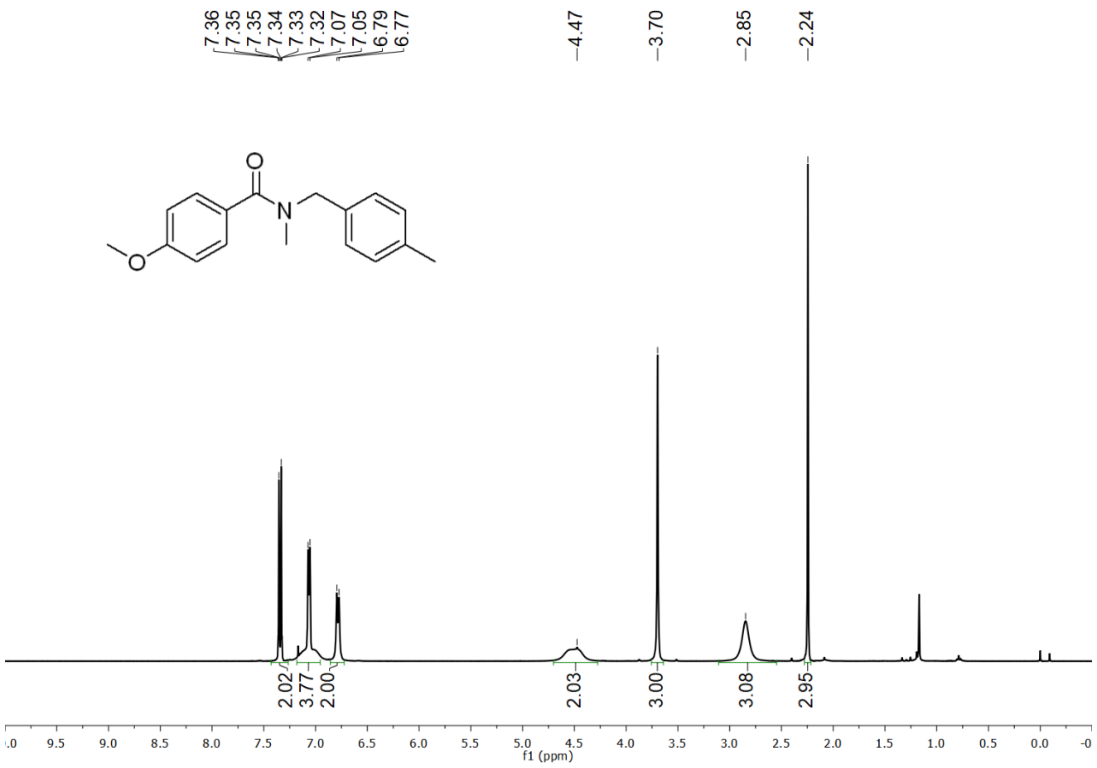
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8da**



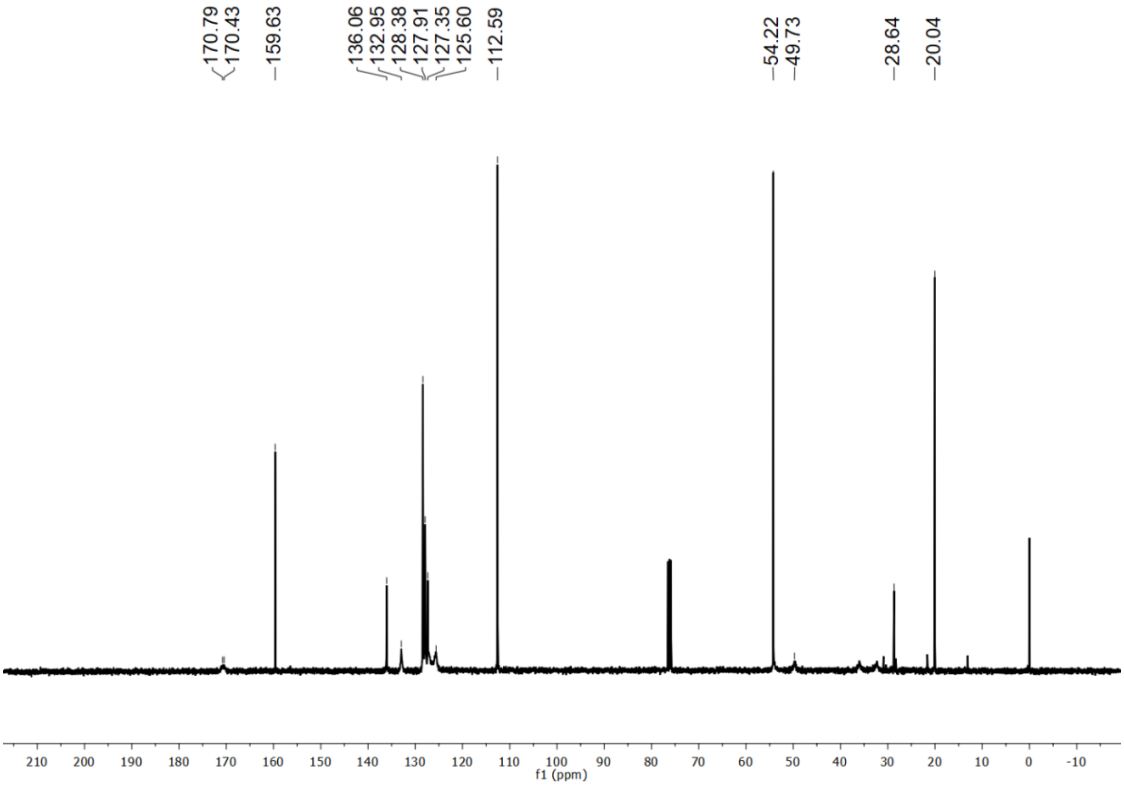
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ea**



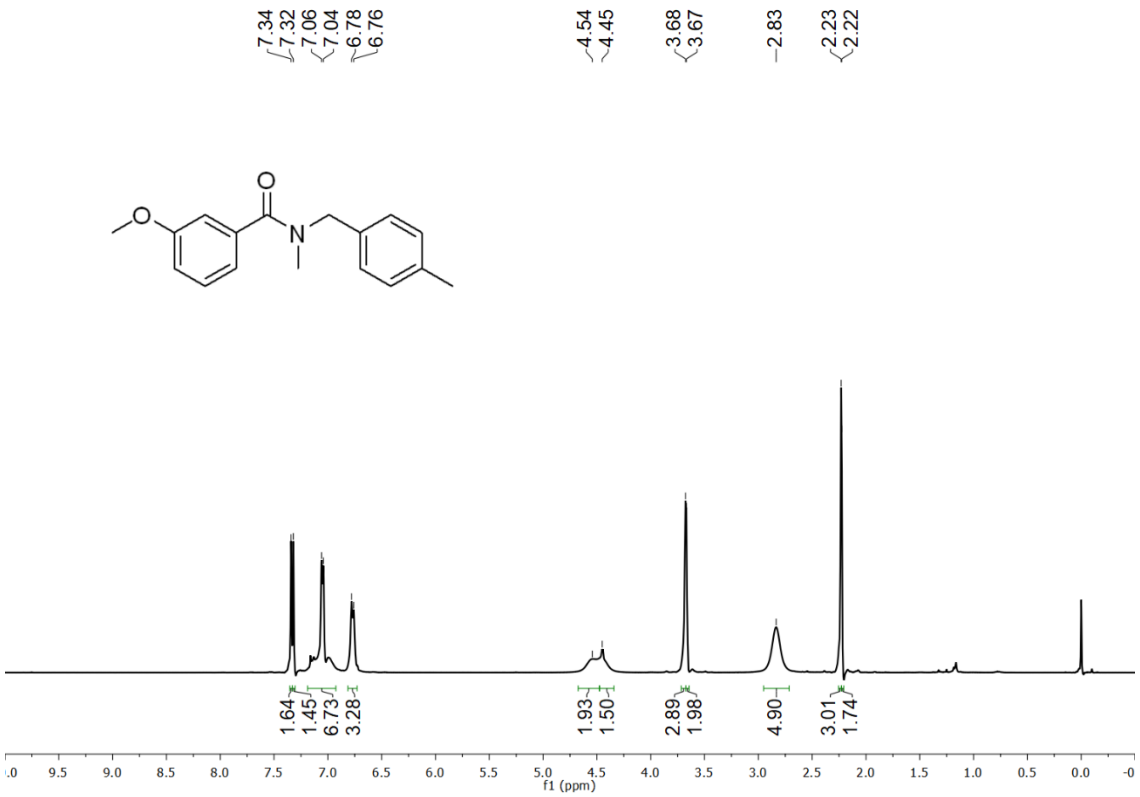
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ea**



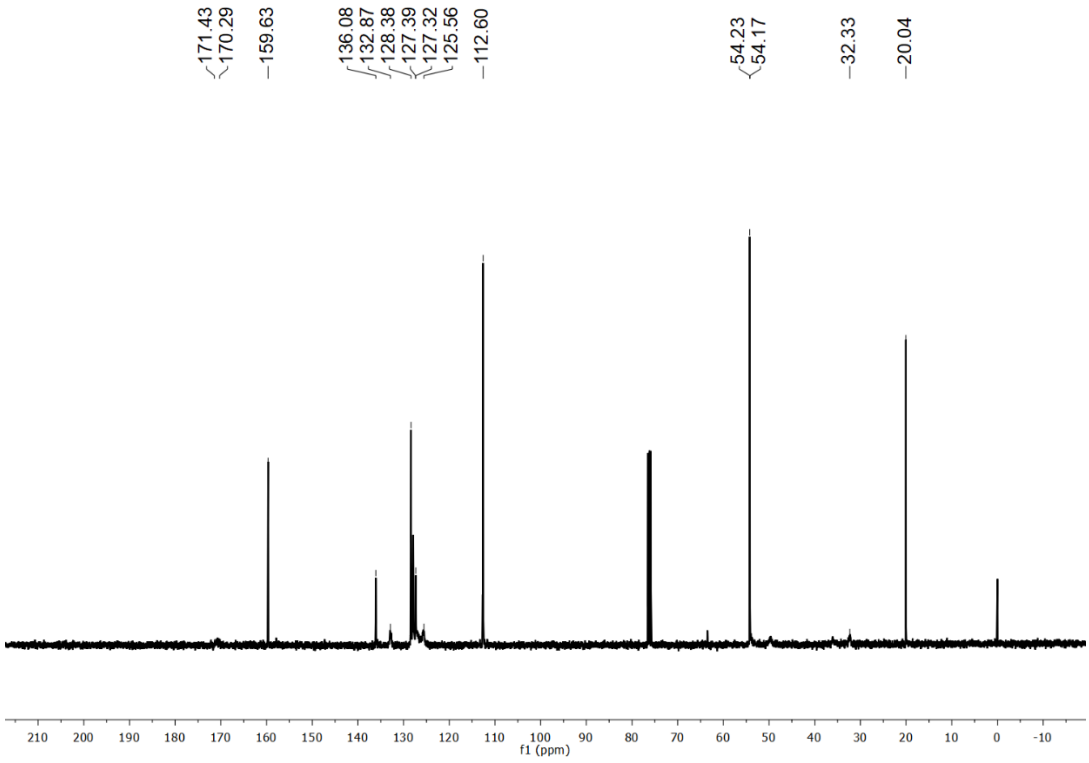
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8fa**



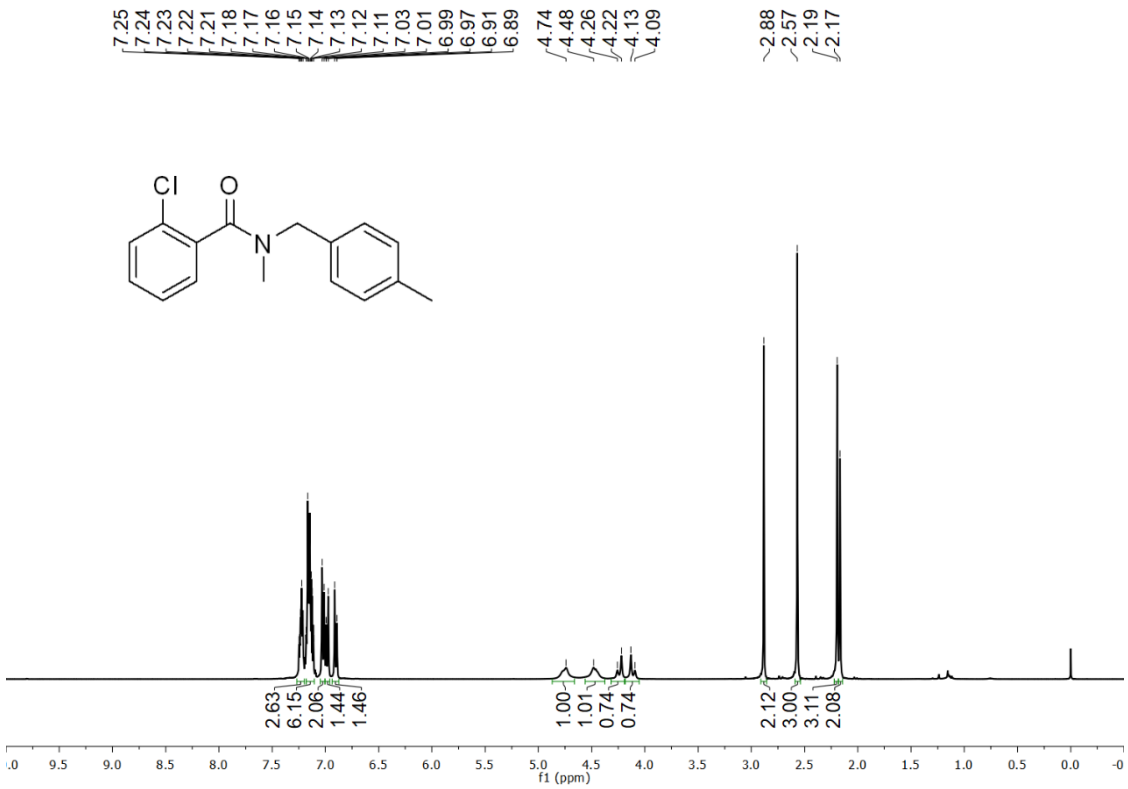
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8fa**



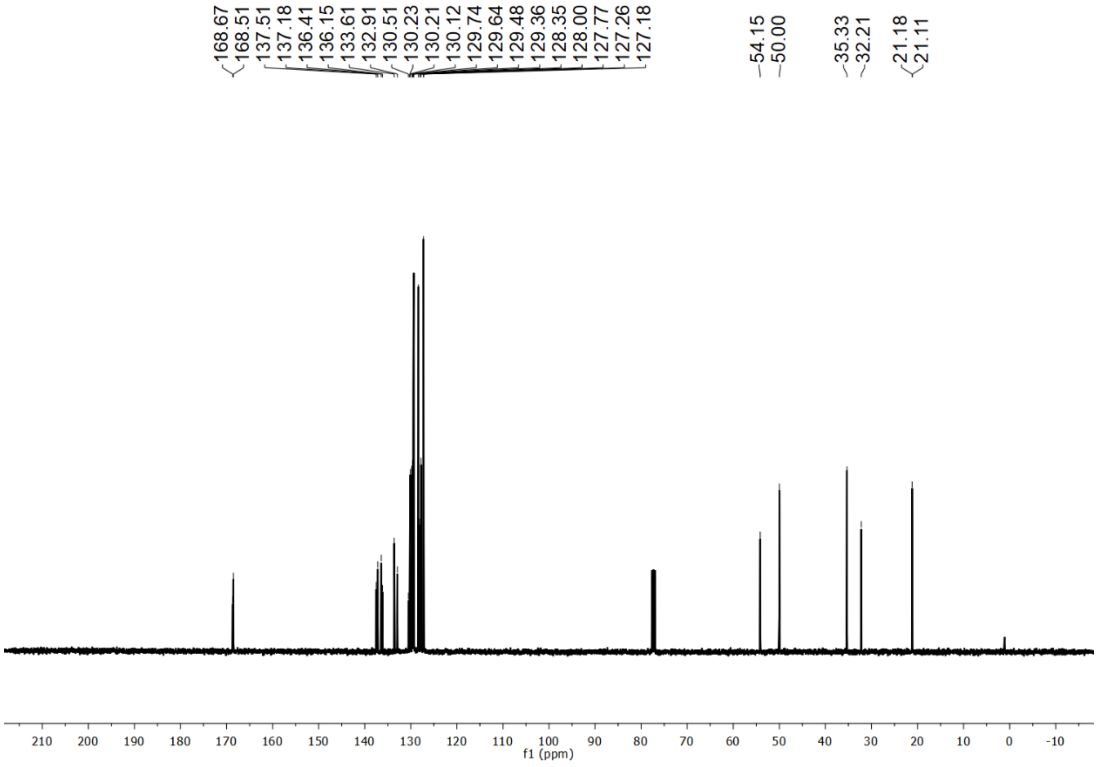
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ga**



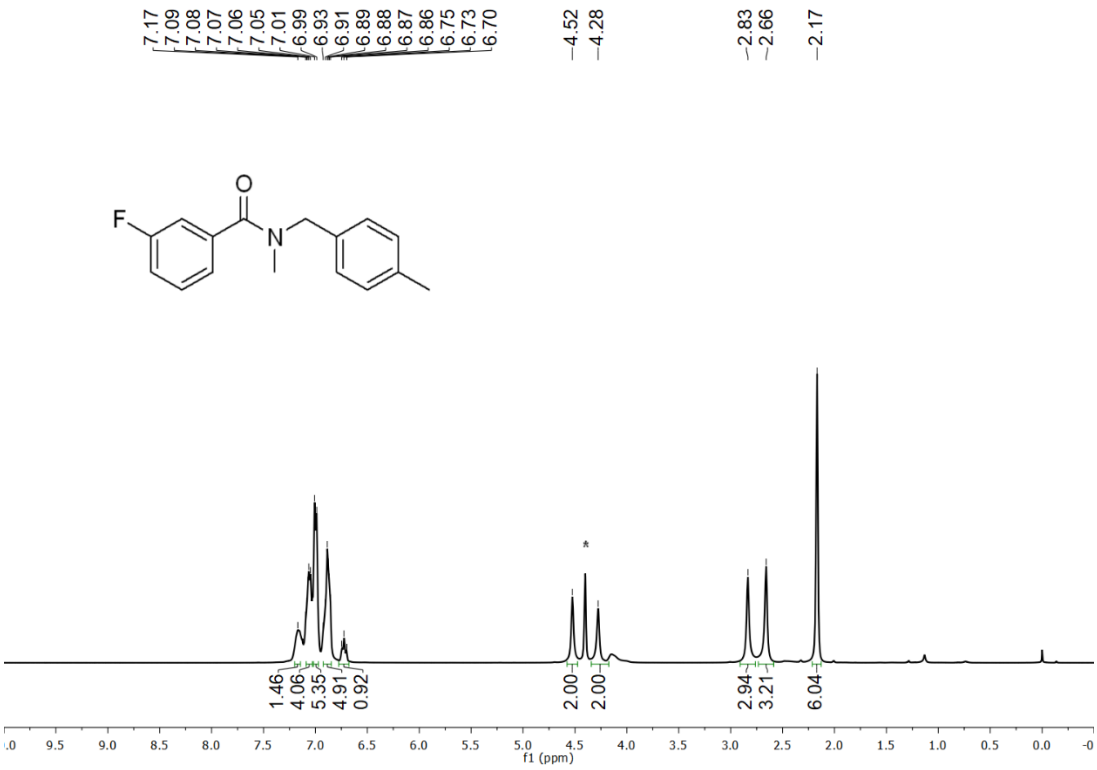
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ga**



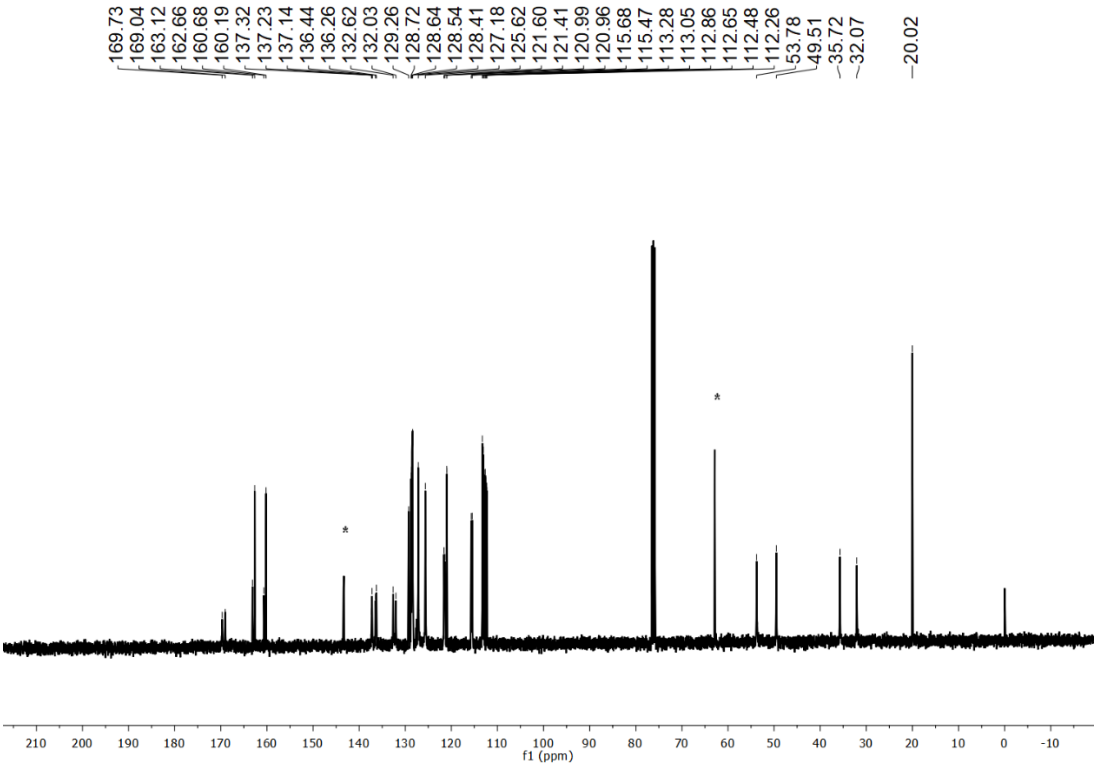
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ha**



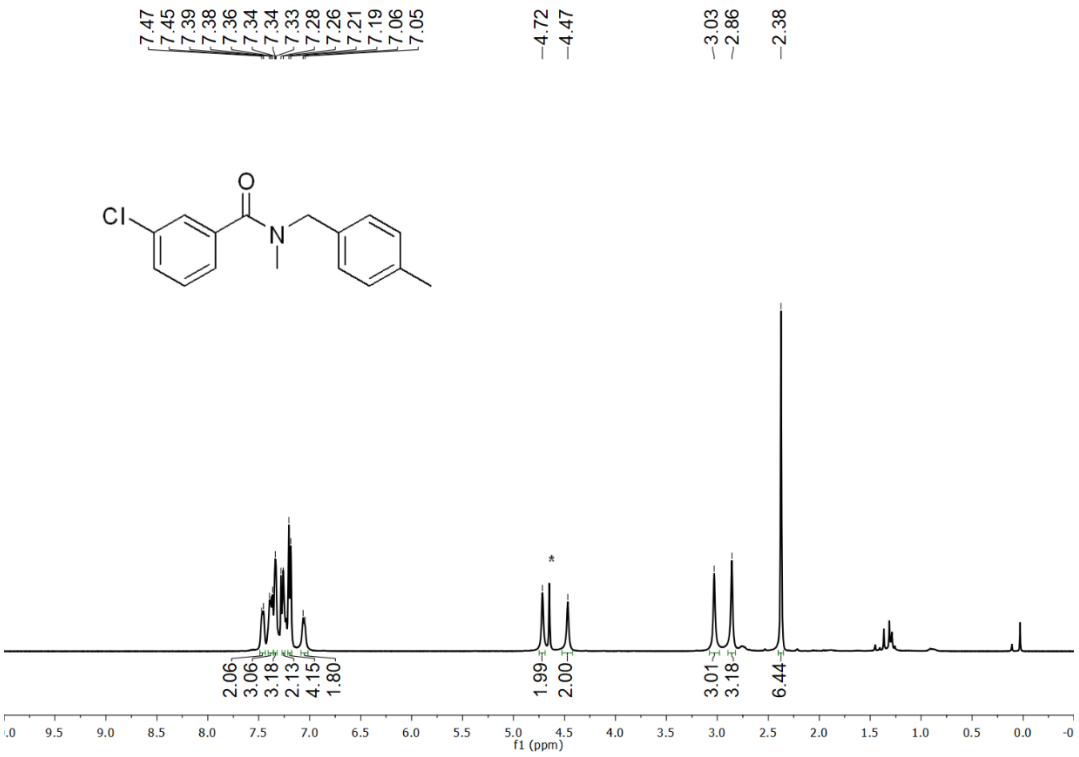
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ha**



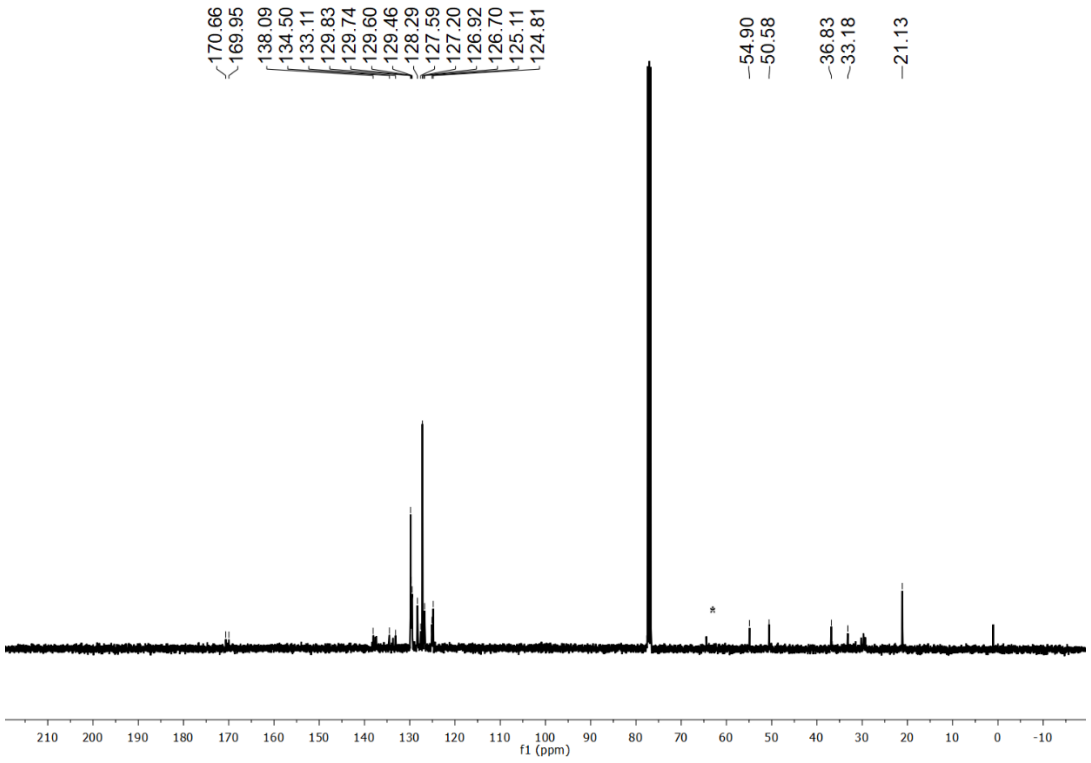
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ia** (*= benzyl alcohol)



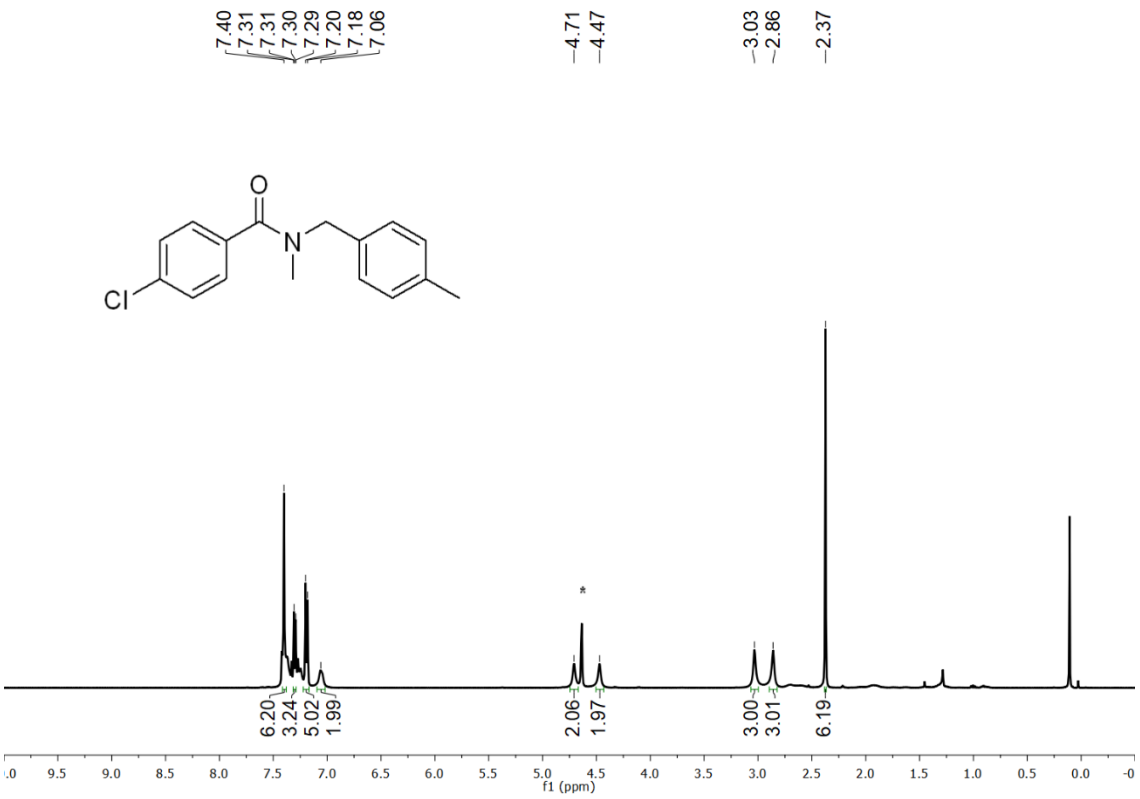
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ia** (*= benzyl alcohol)



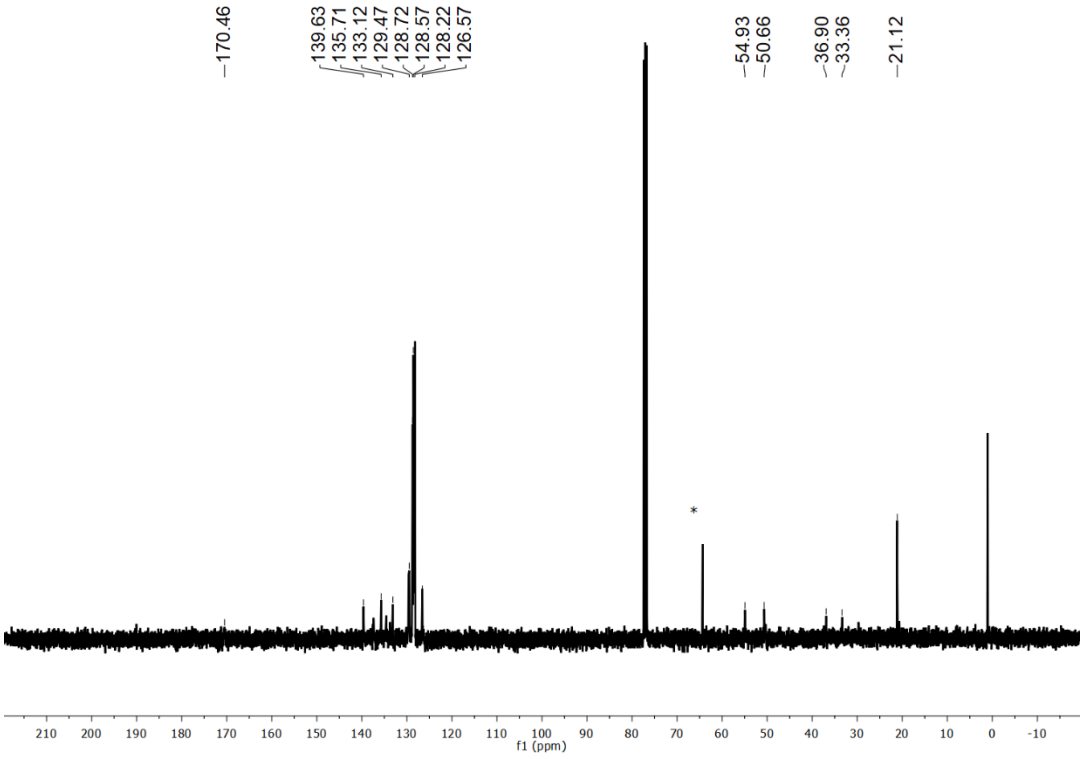
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ja** (*= benzyl alcohol)



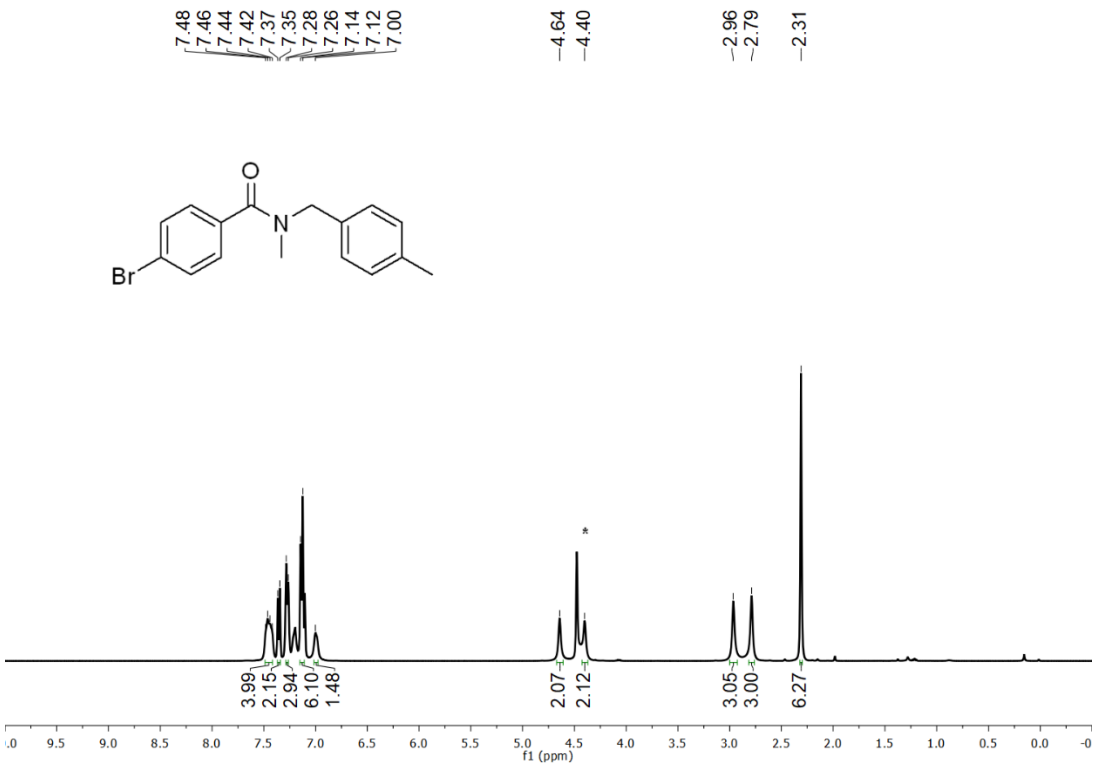
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ja** (*= benzyl alcohol)



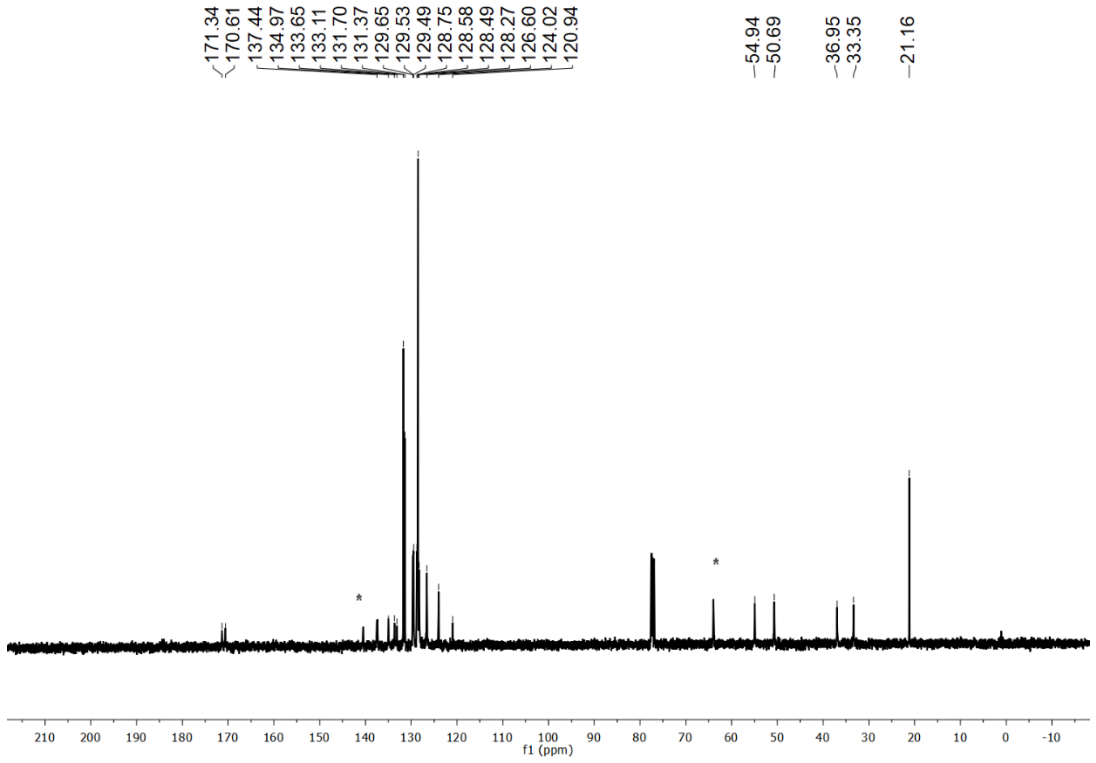
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ka** (*= benzyl alcohol)



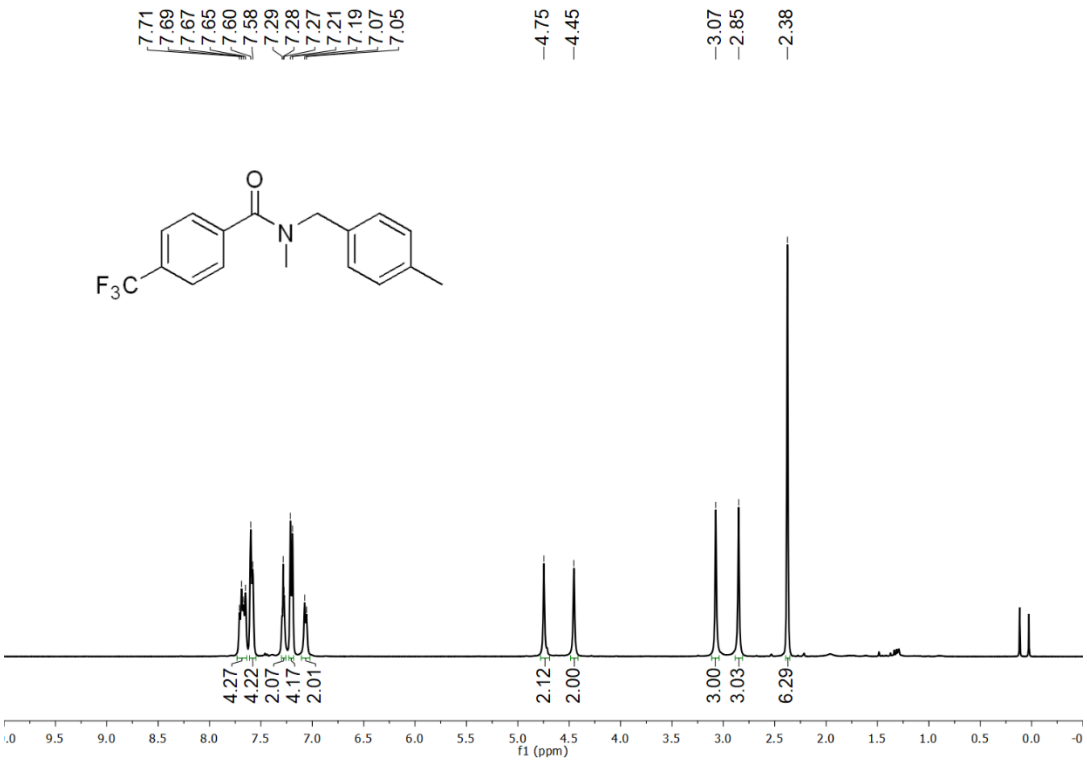
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ka** (*= benzyl alcohol)



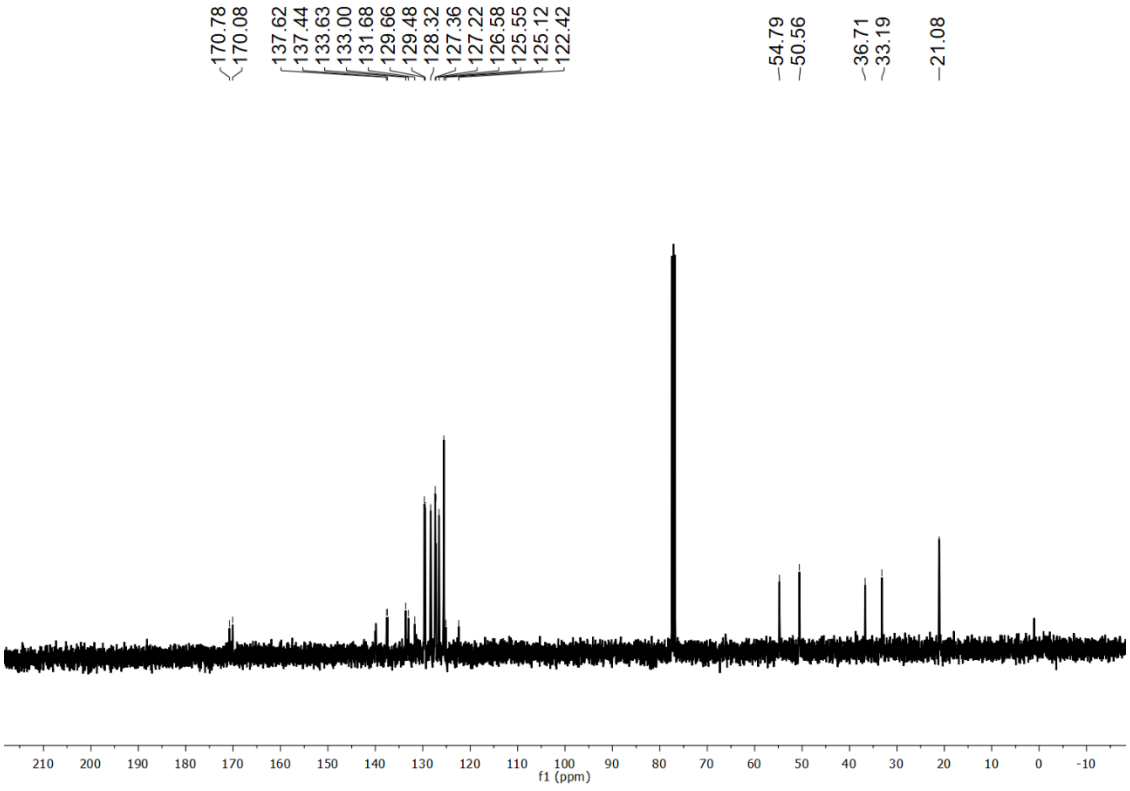
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8la** (*= benzyl alcohol)



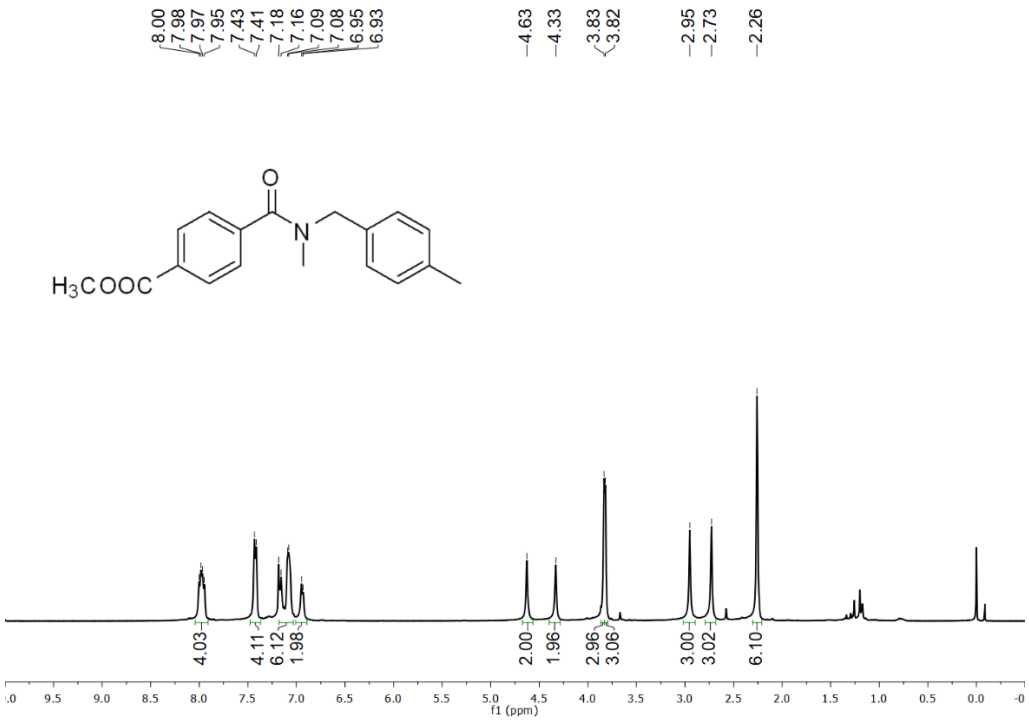
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8la** (*= benzyl alcohol)



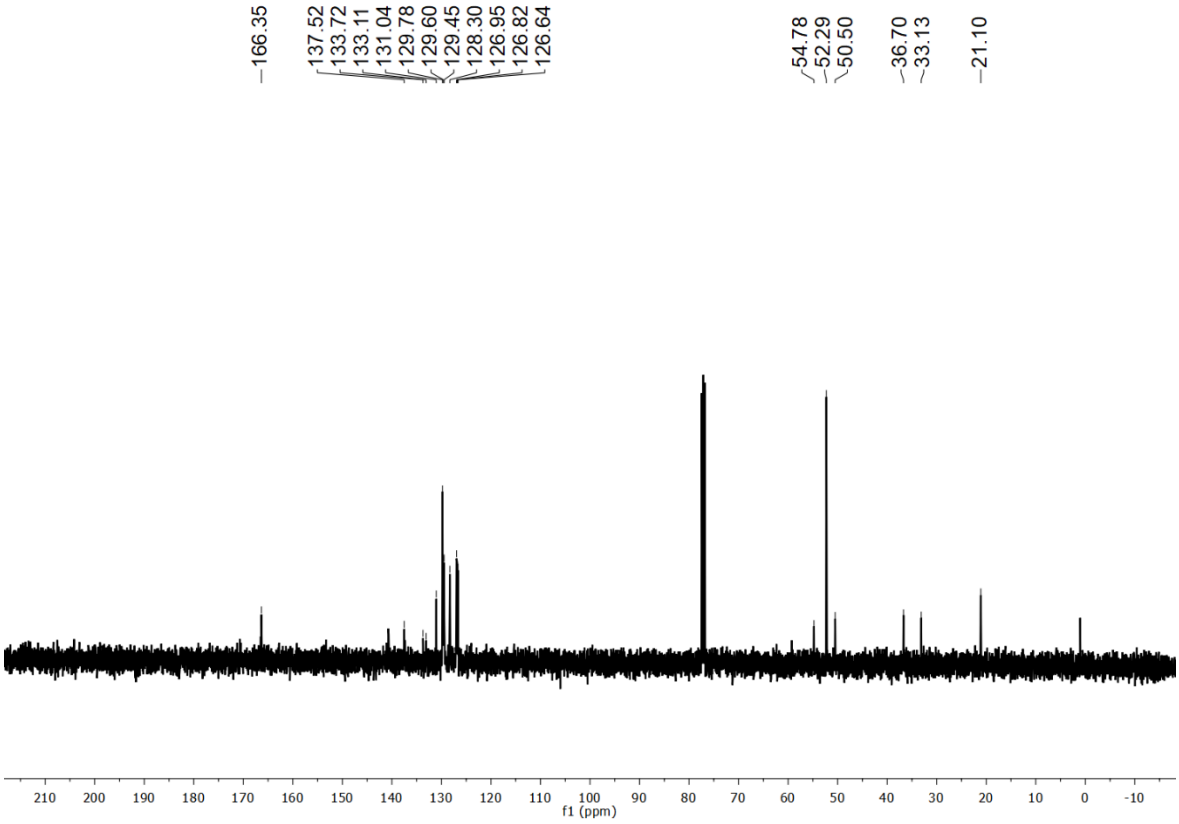
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ma**



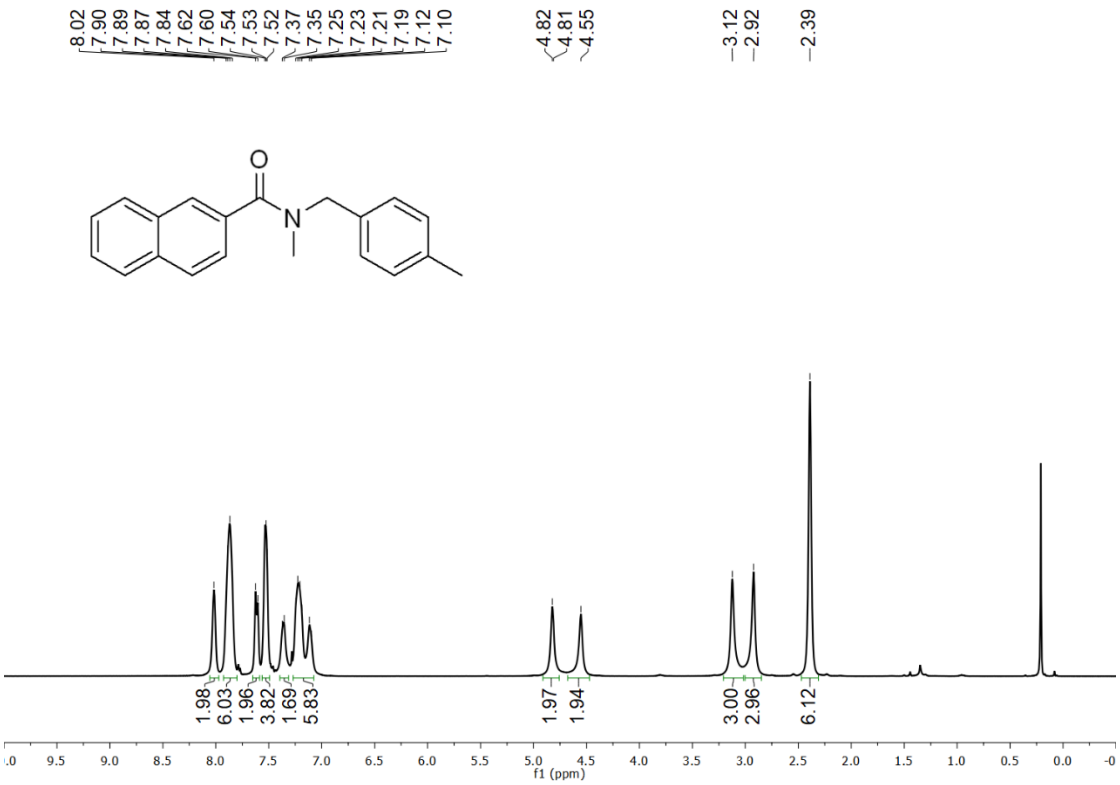
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ma**



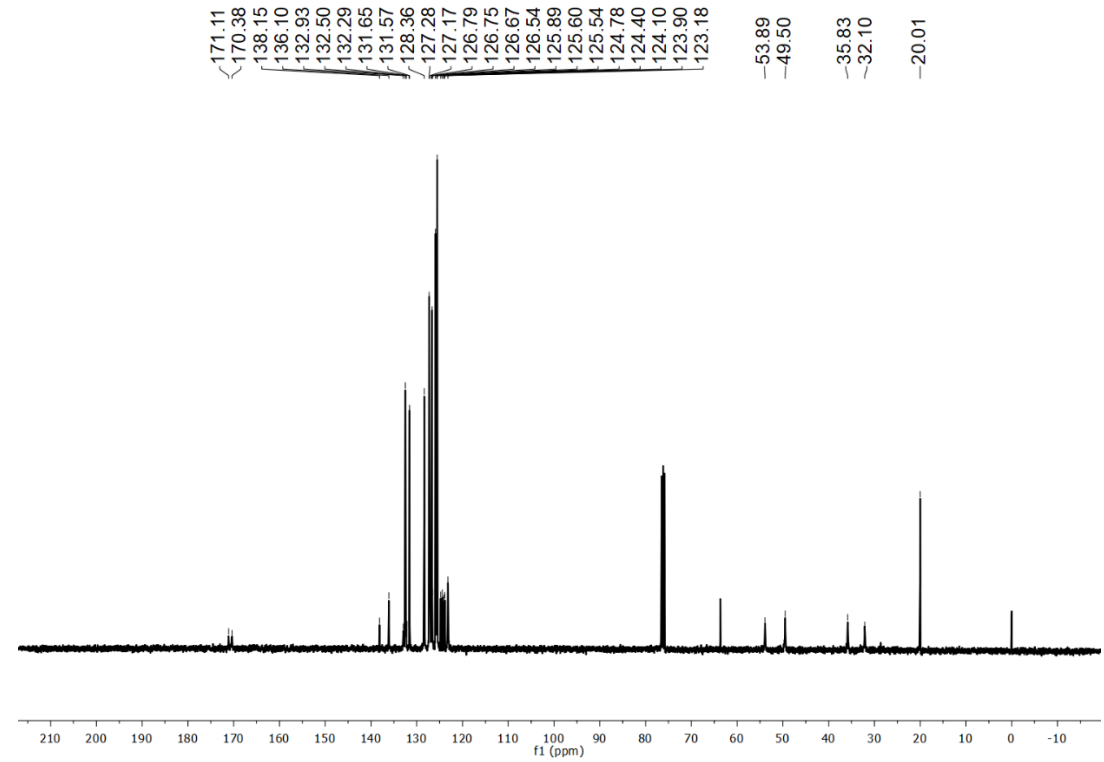
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8na**



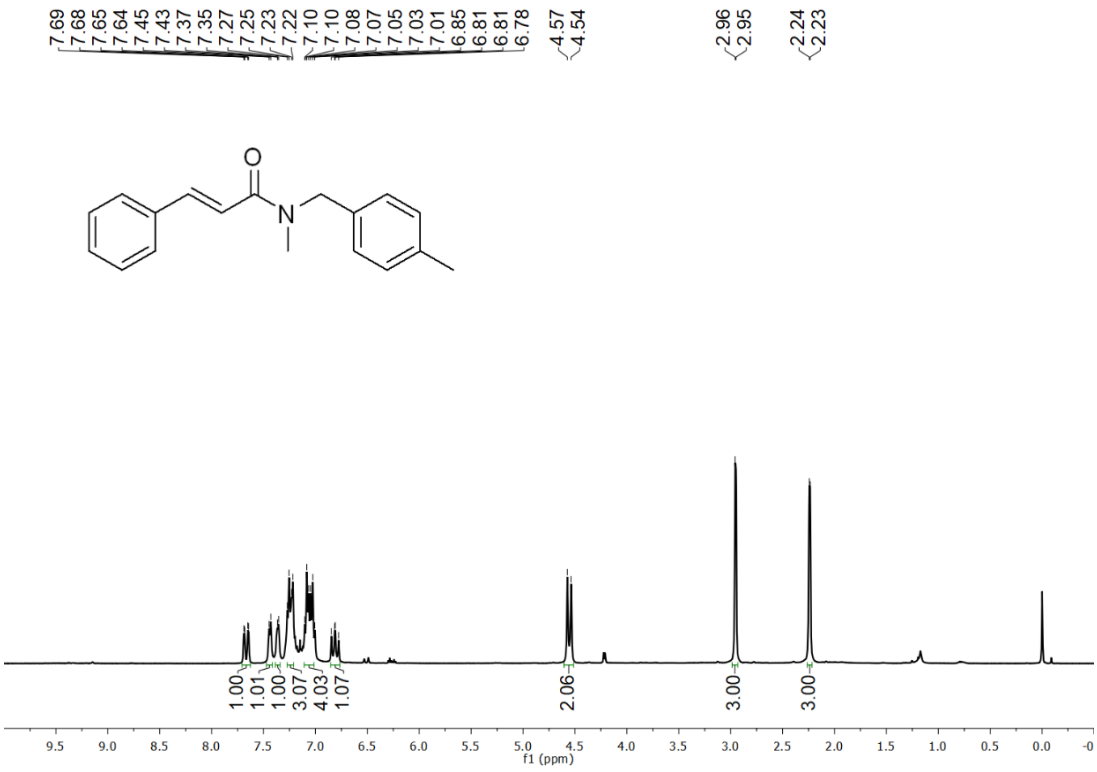
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8na**



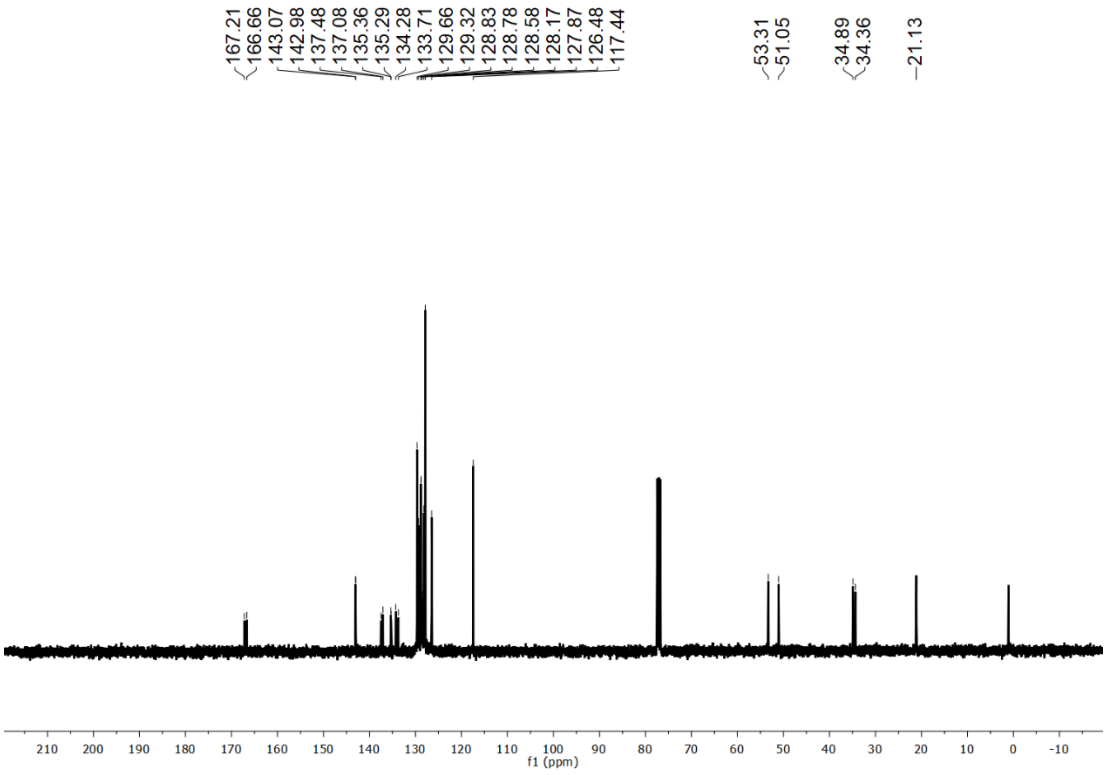
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8oa**



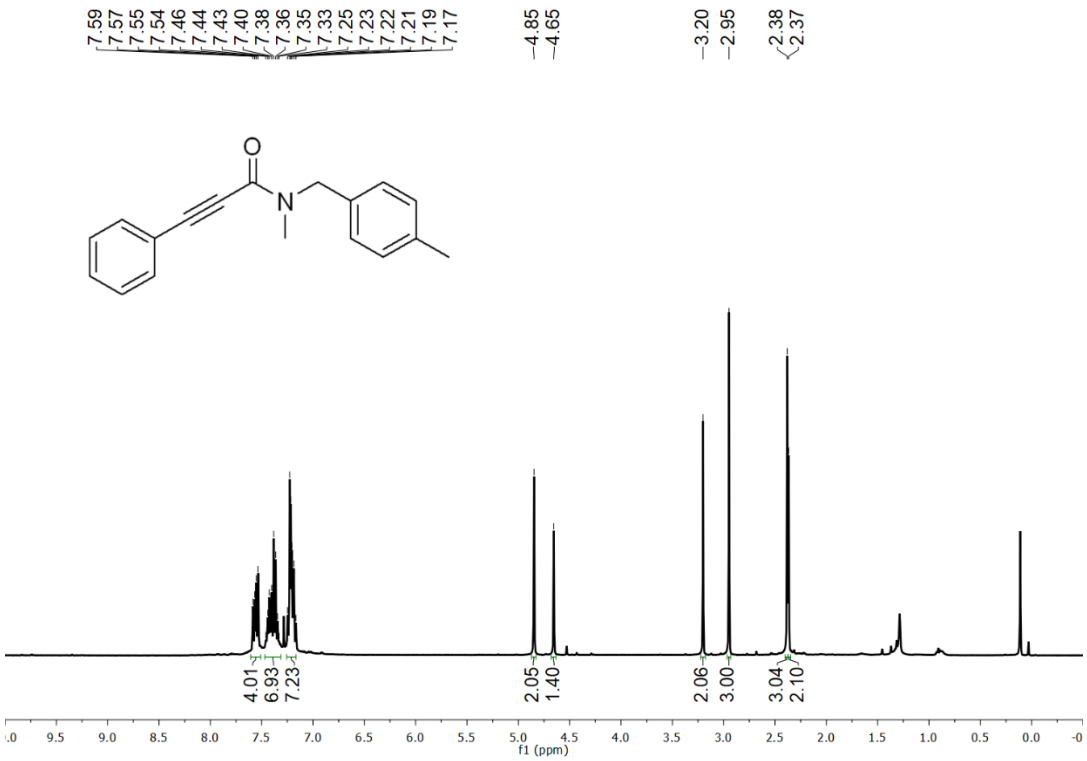
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8oa**



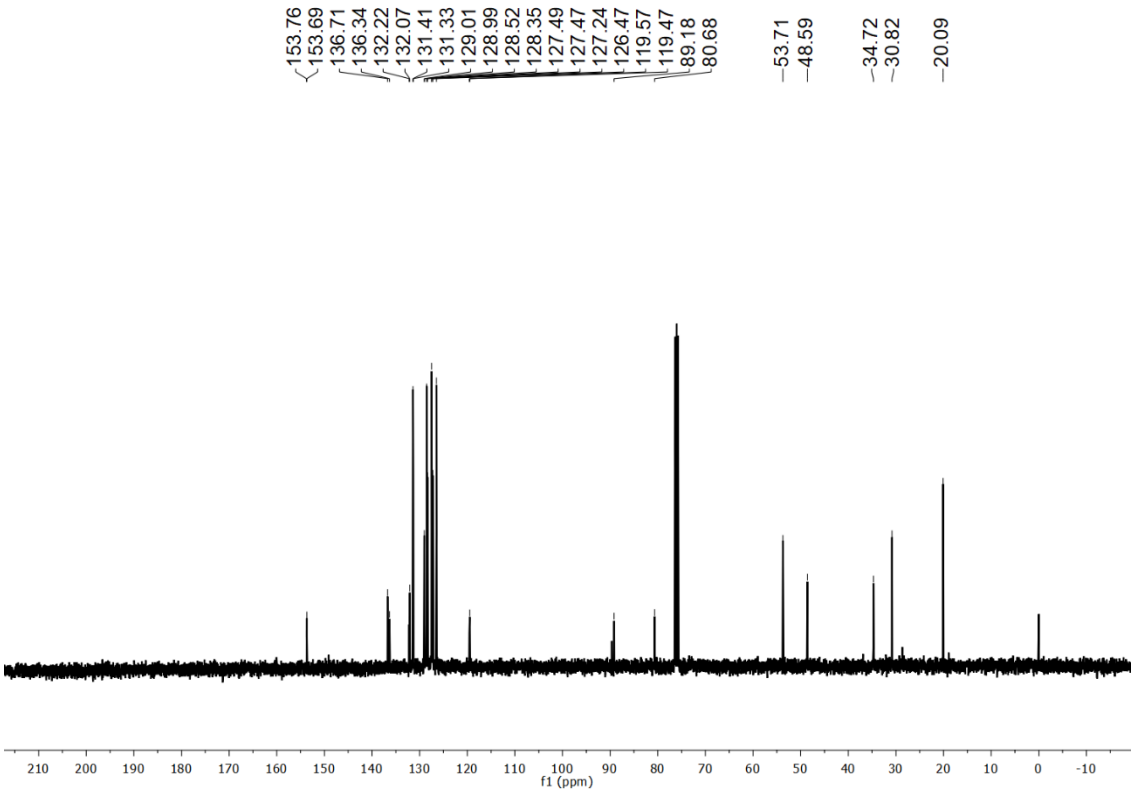
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8pa**



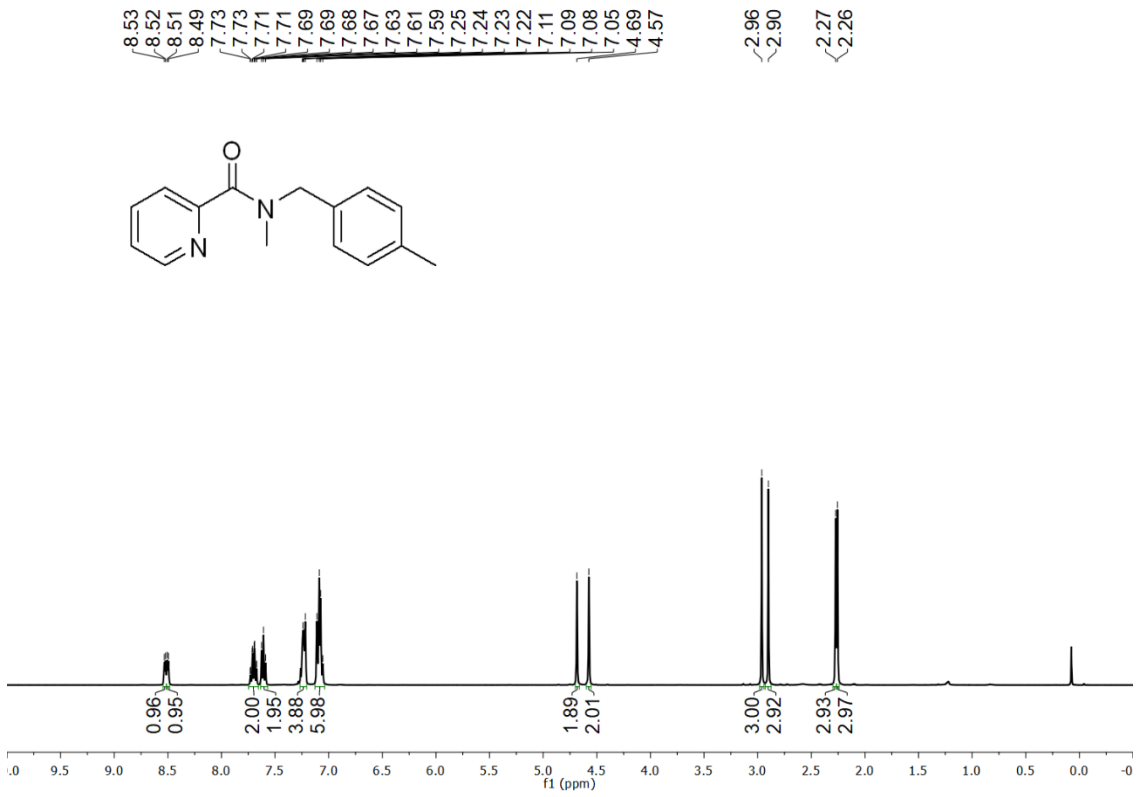
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8pa**



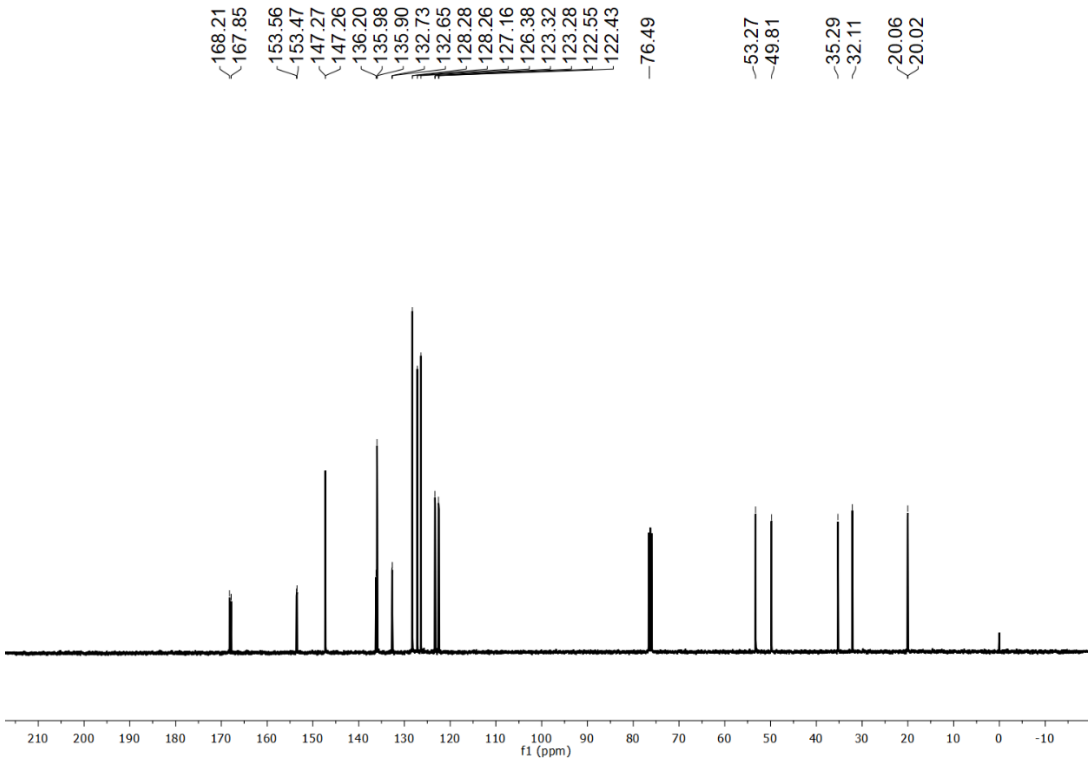
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8qa**



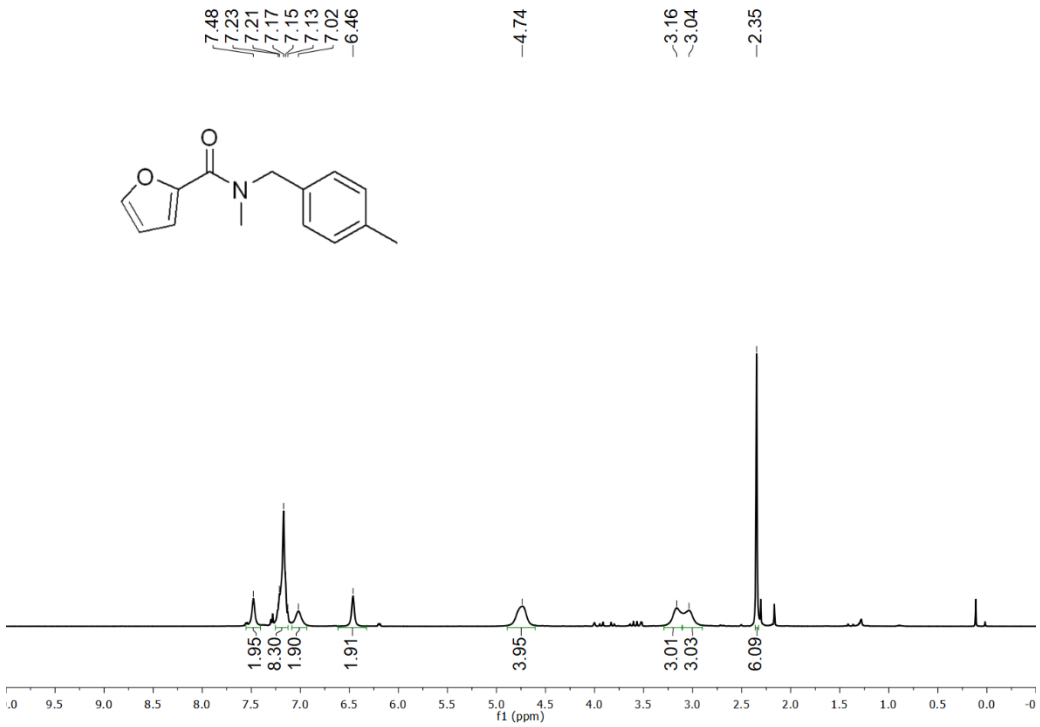
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8qa**



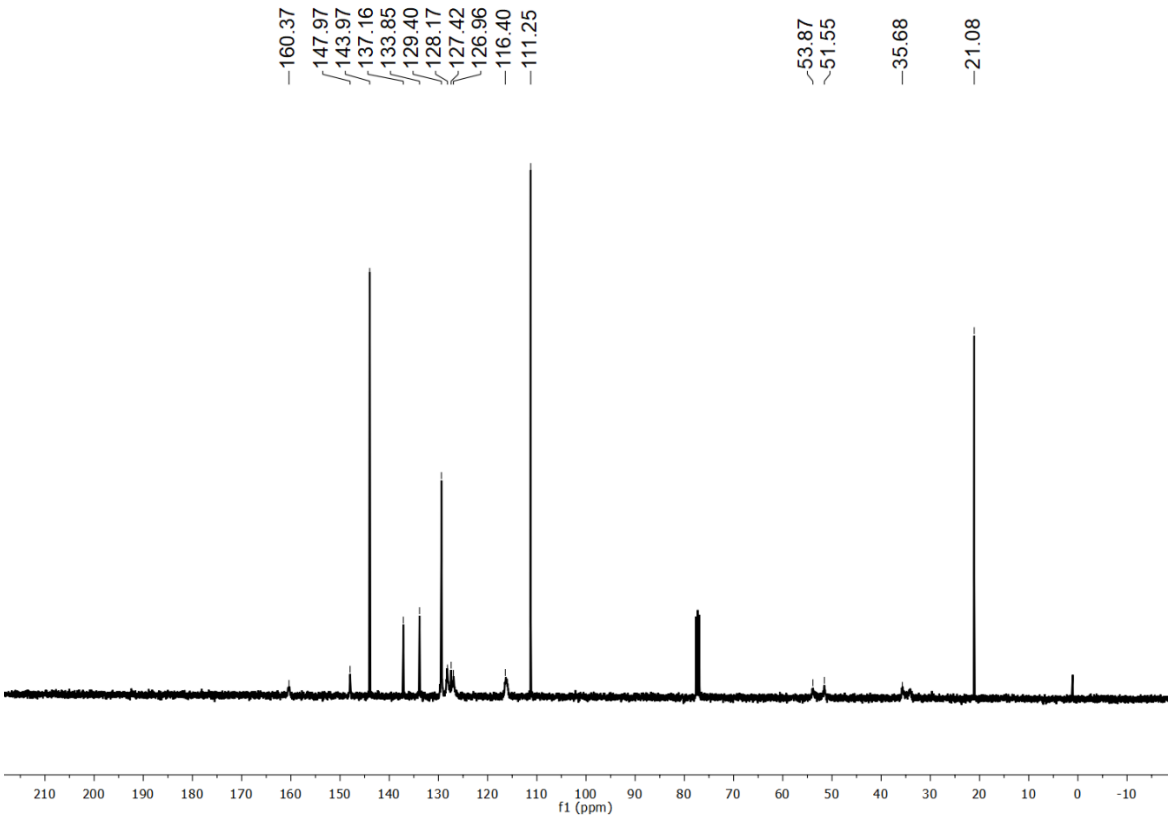
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ta**



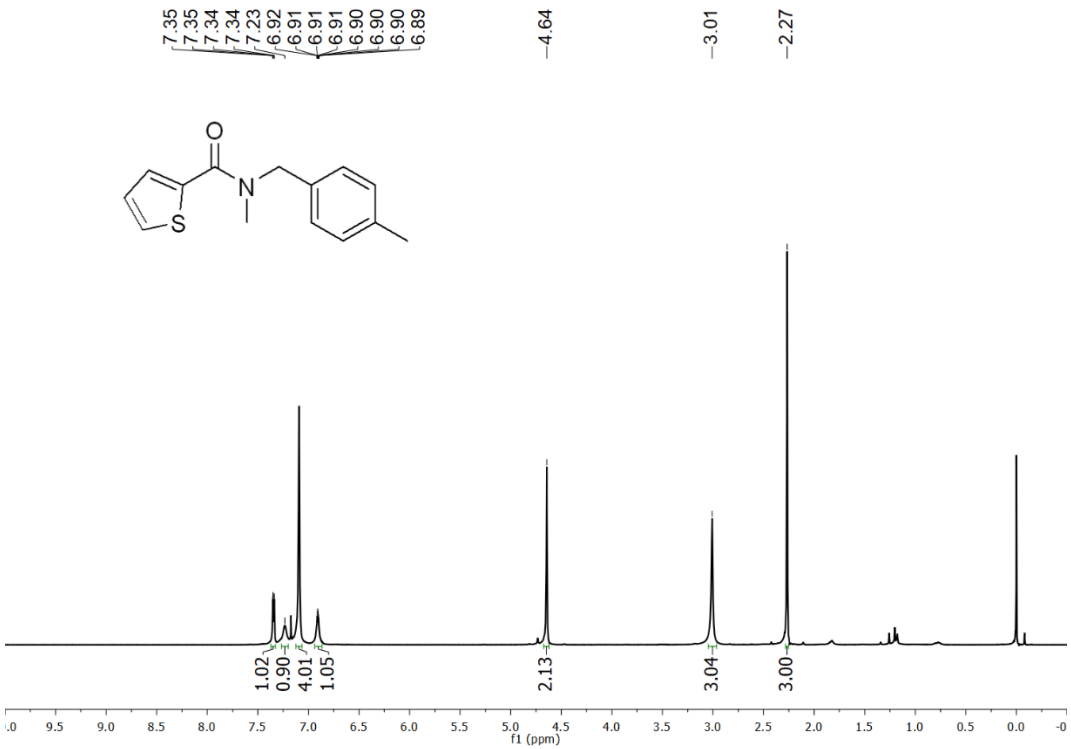
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ta**



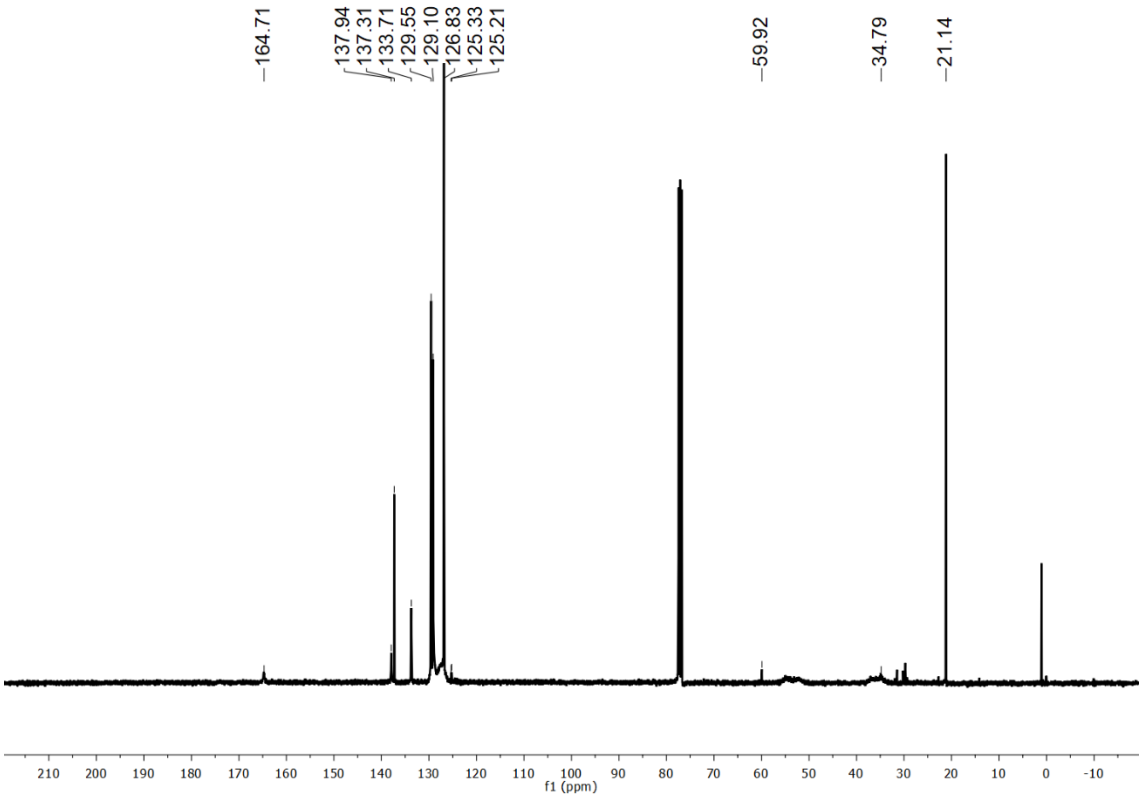
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ua**



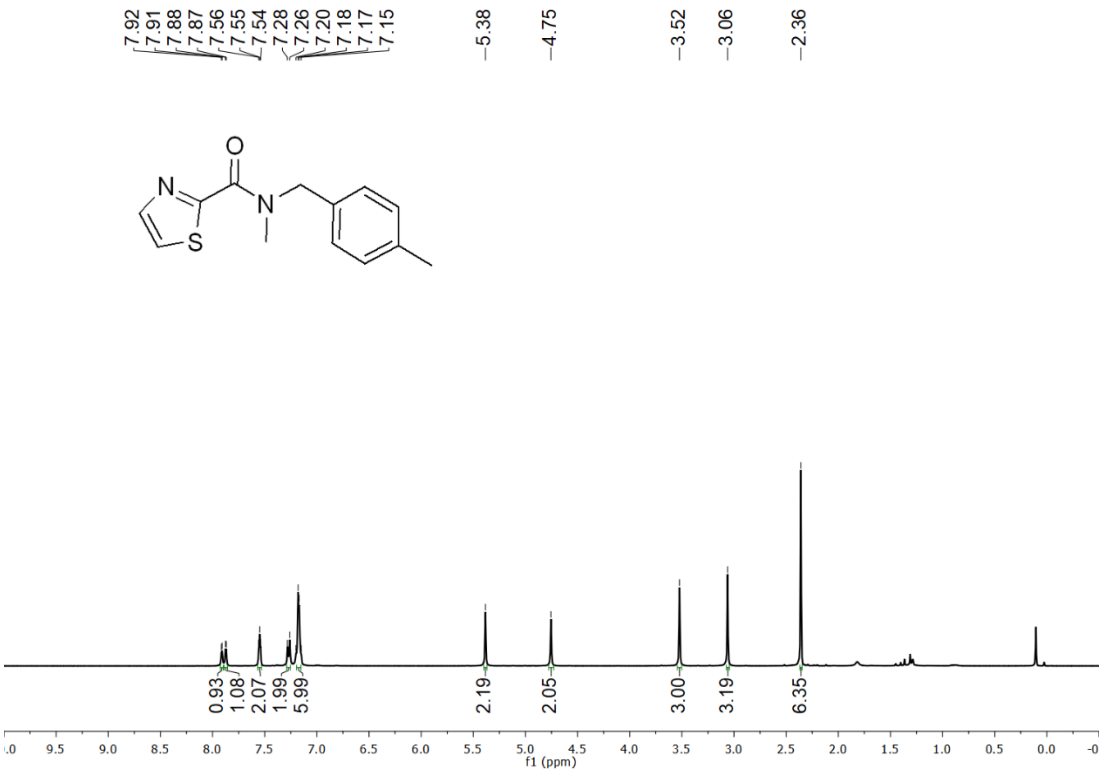
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8ua**



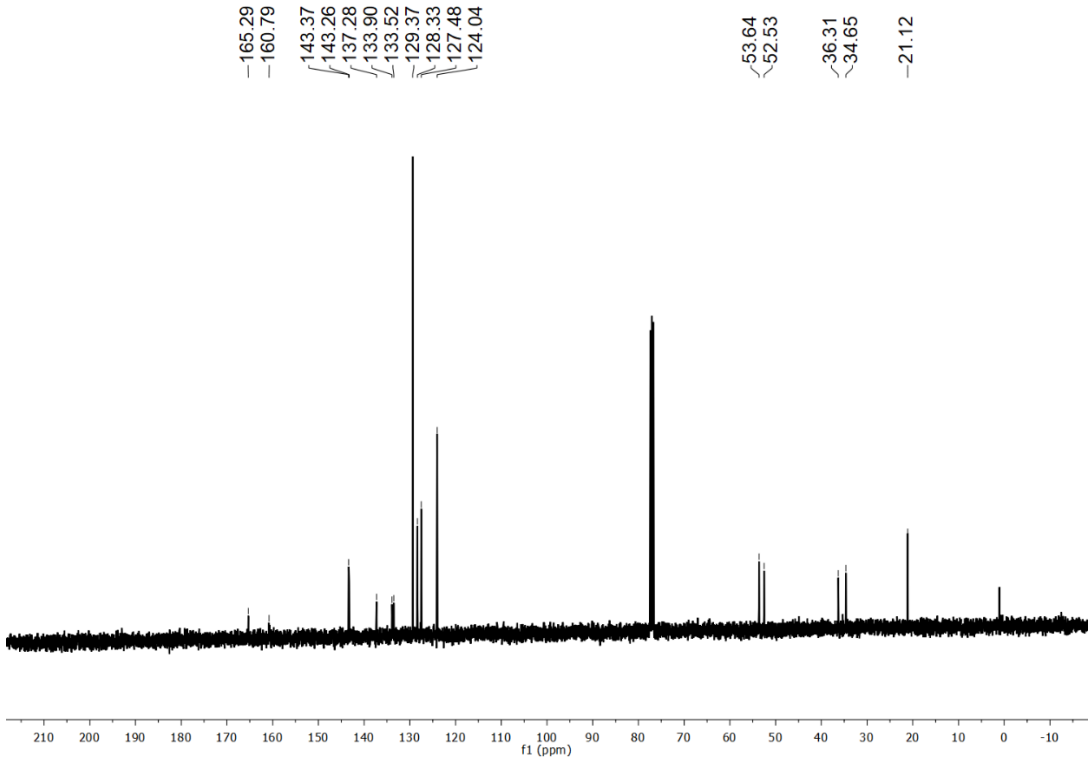
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8va**



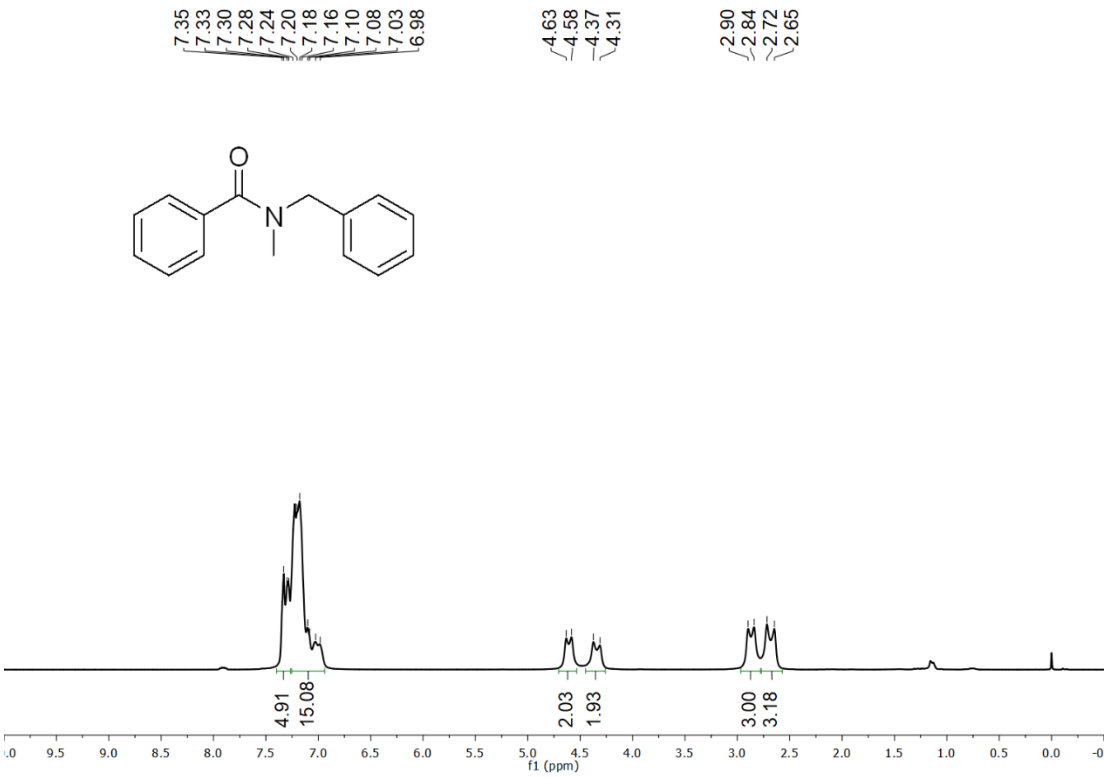
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8va**



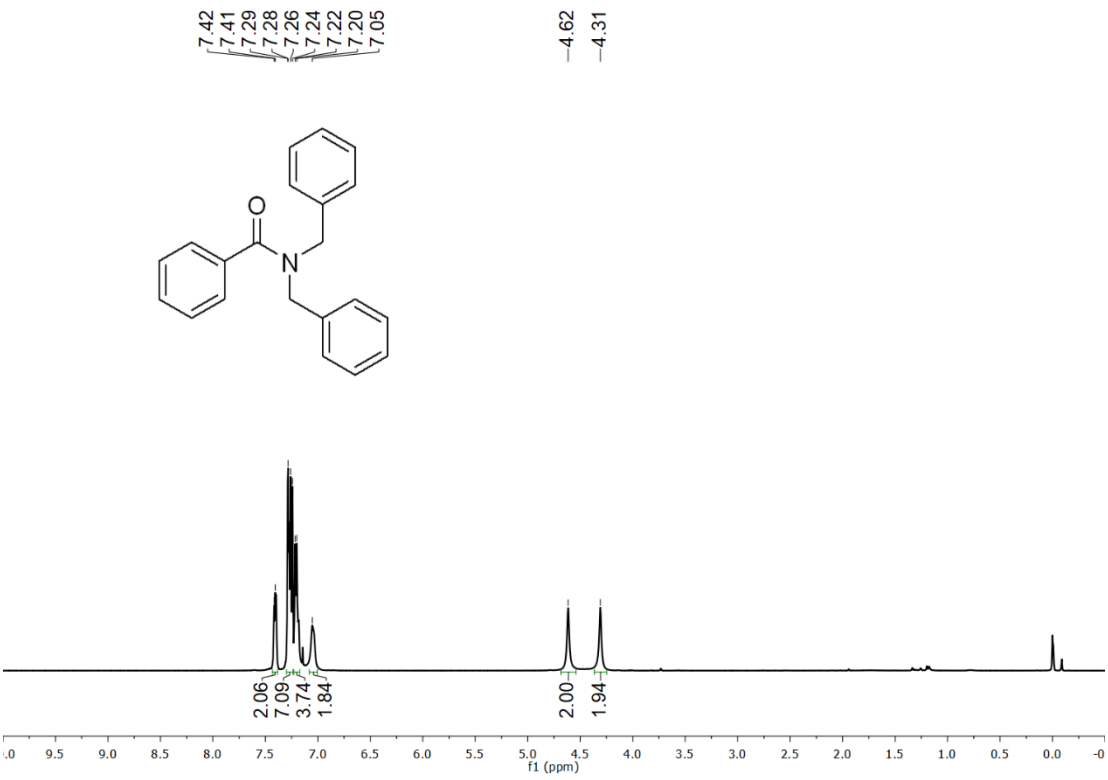
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8wa**



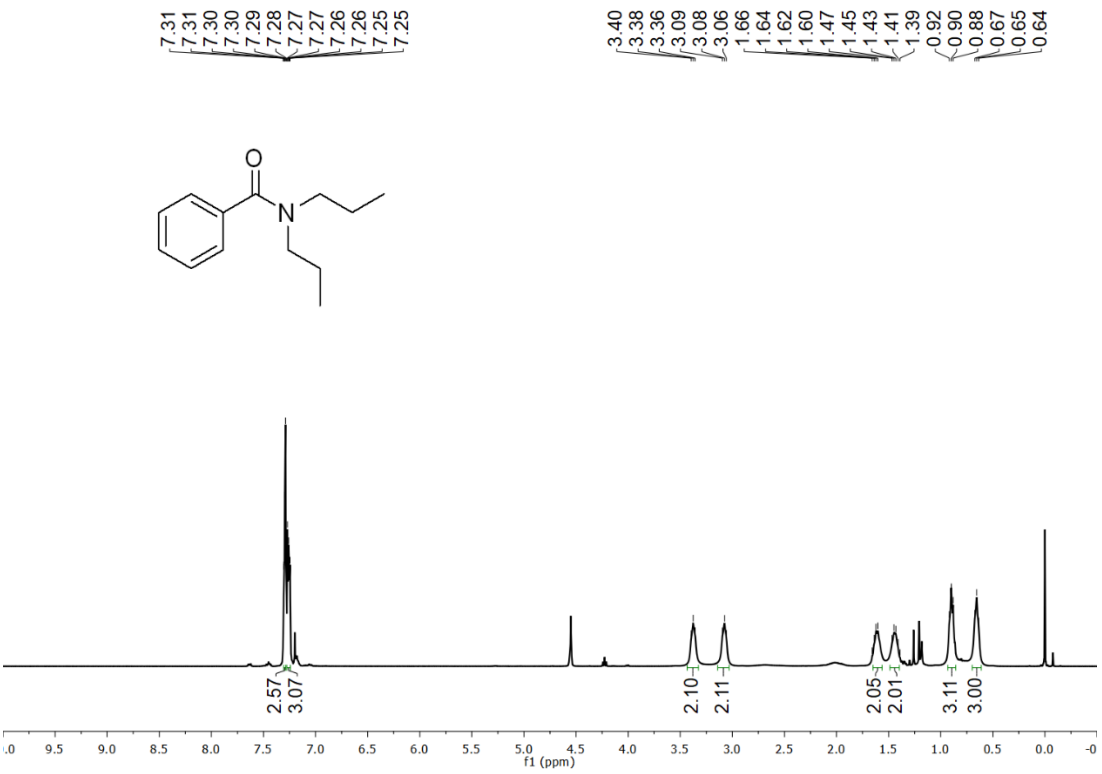
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25 ^{o}C) of **8wa**



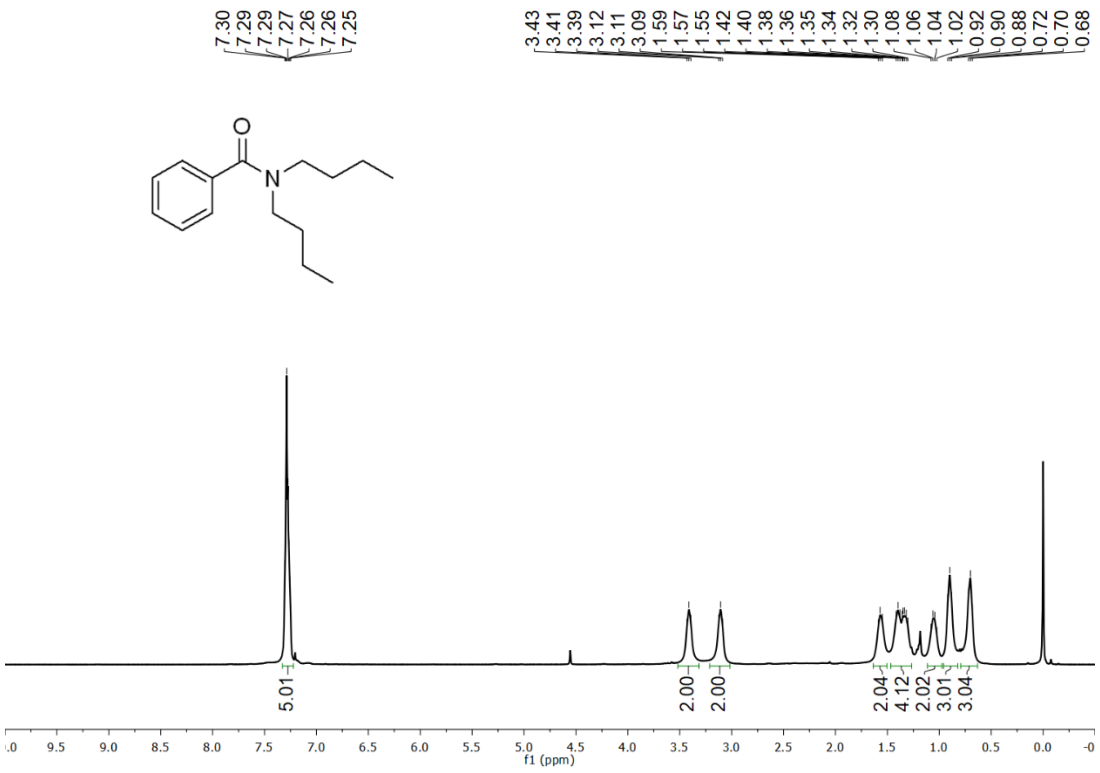
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ab**



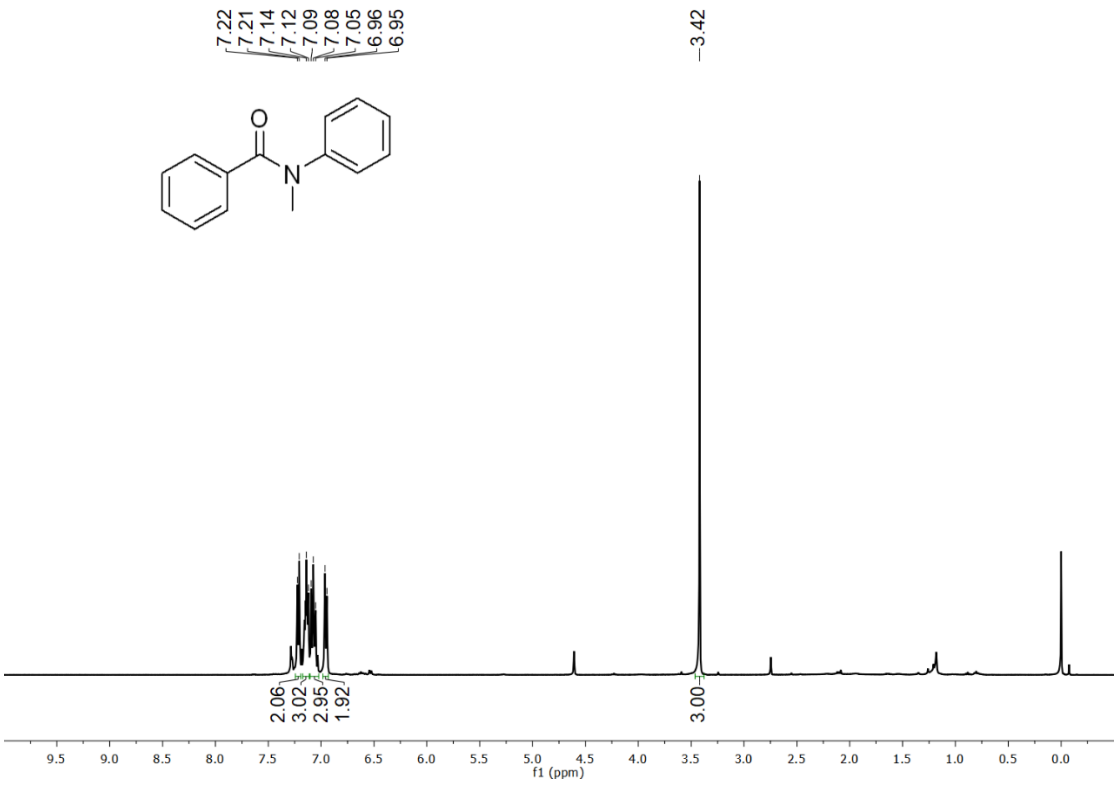
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ac**



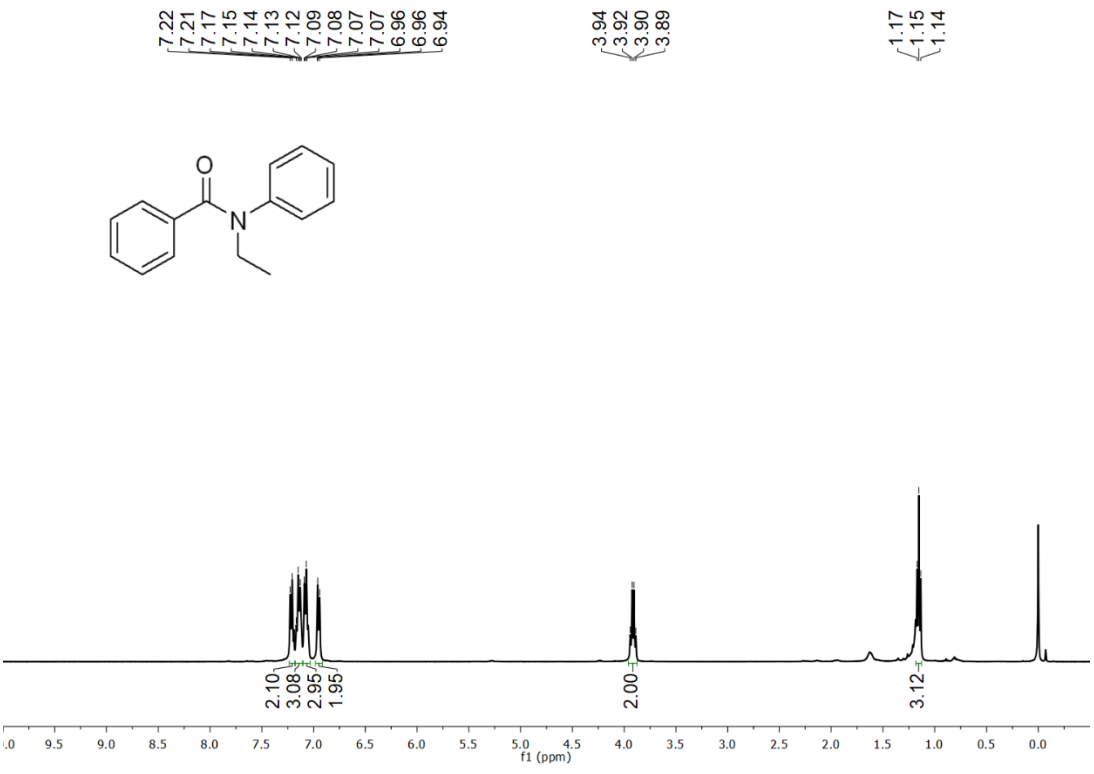
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ad^{nPr}**



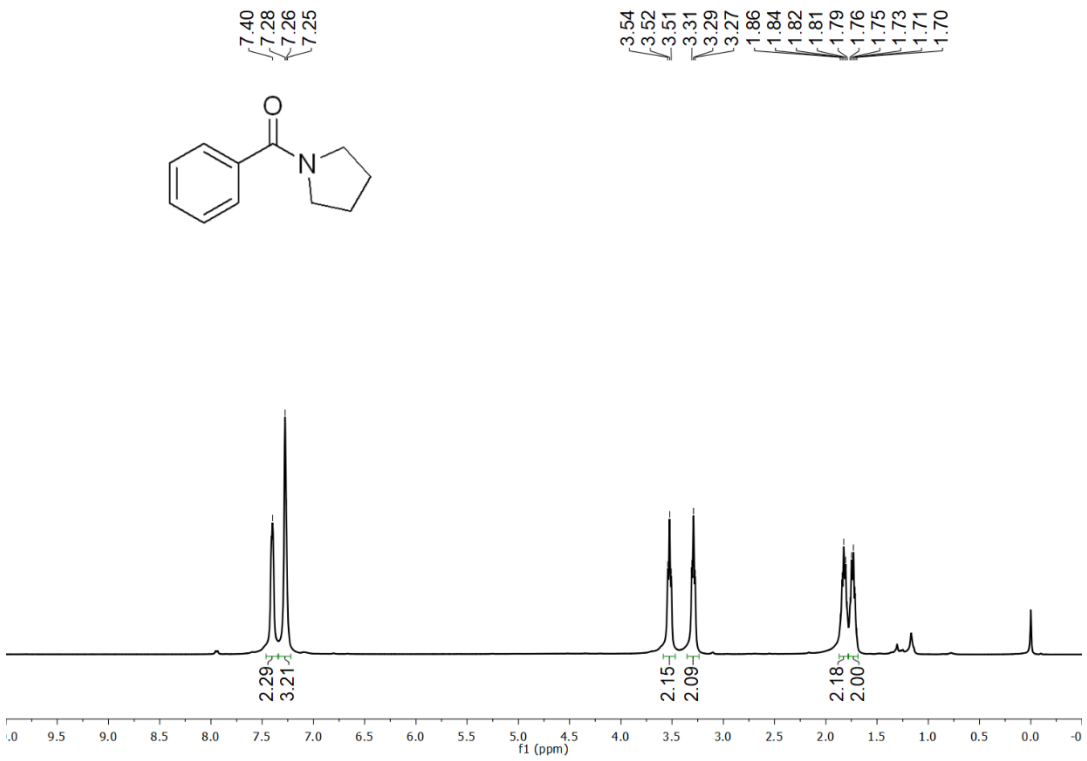
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ad^{nBu}**



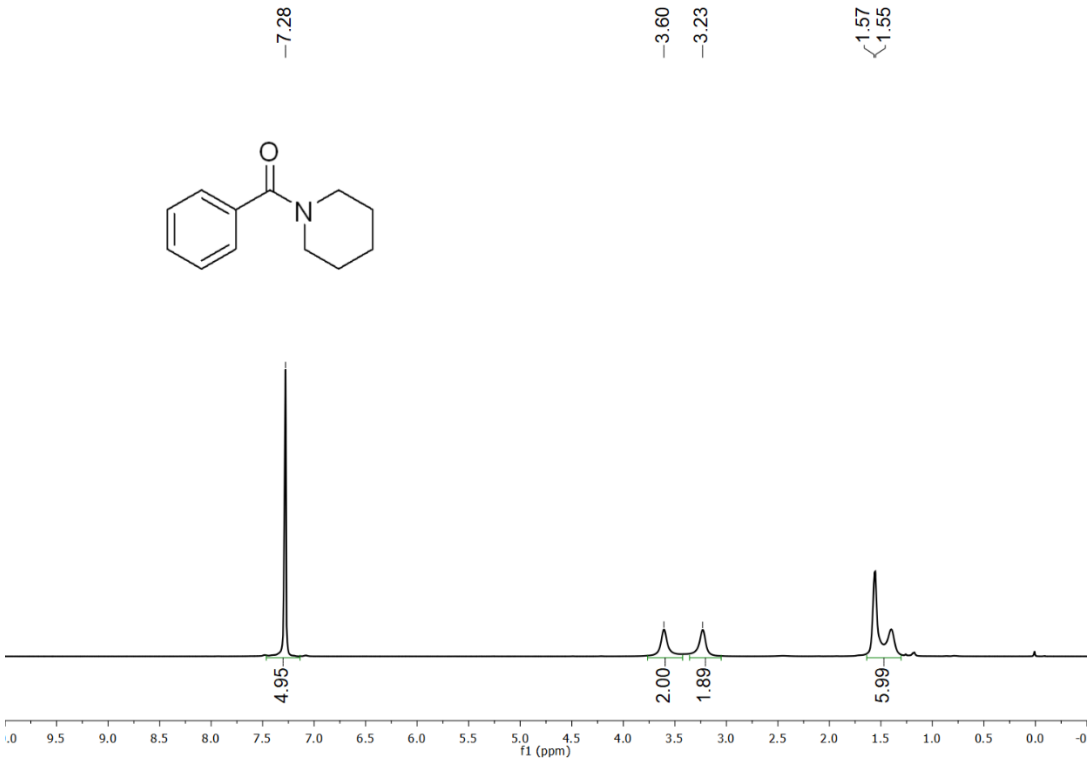
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^oC) of **8ae**



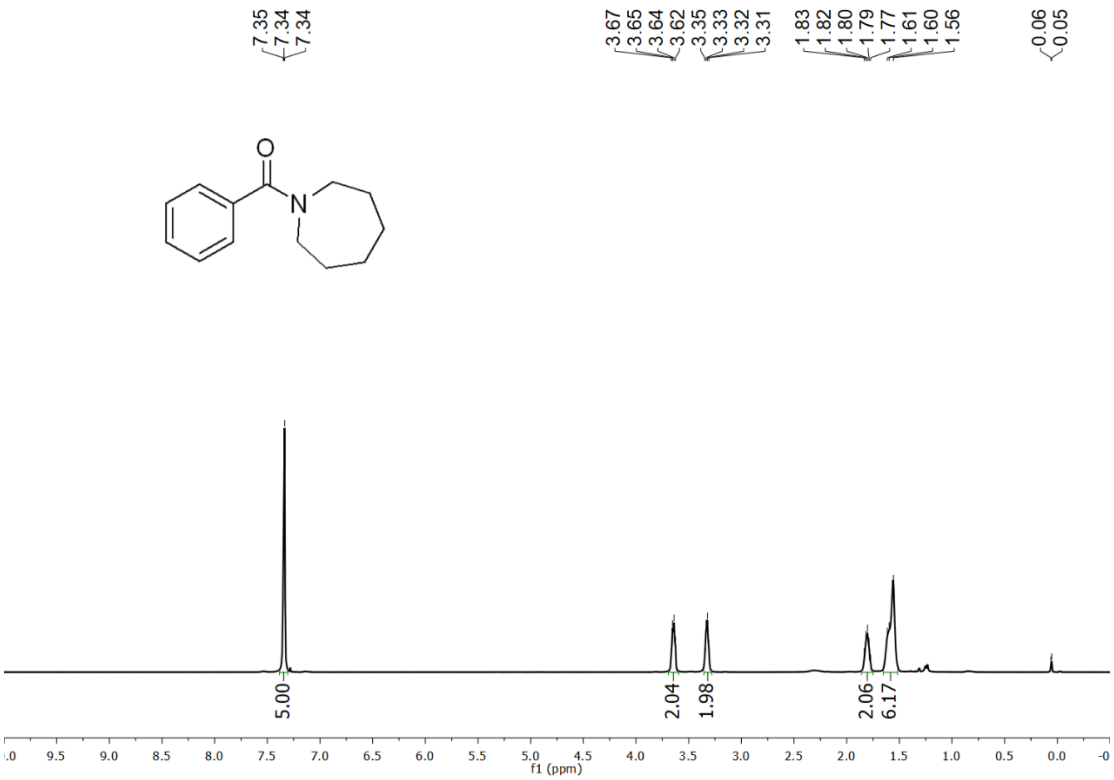
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^oC) of **8af**



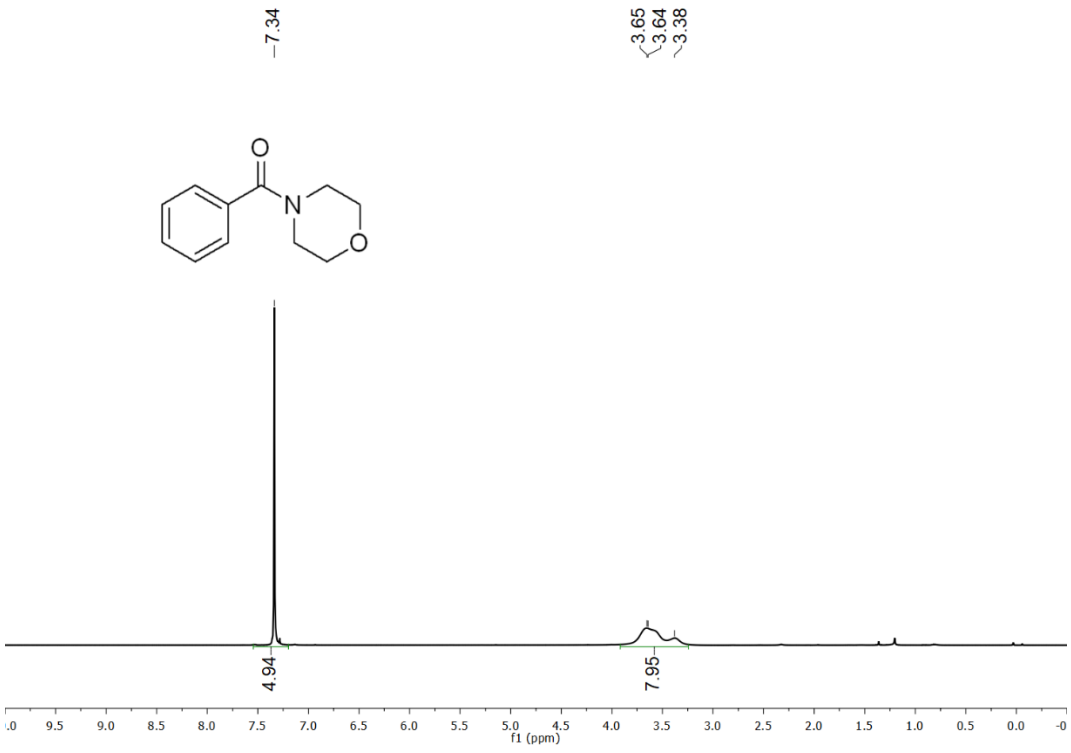
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ag**



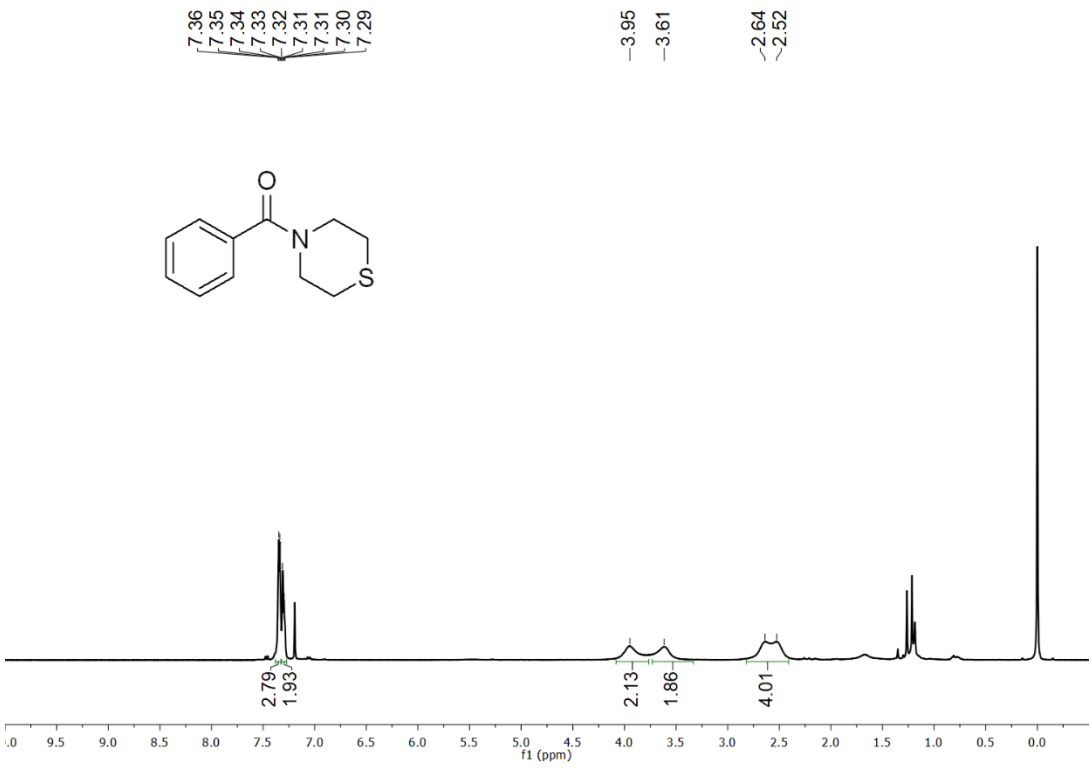
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ah**



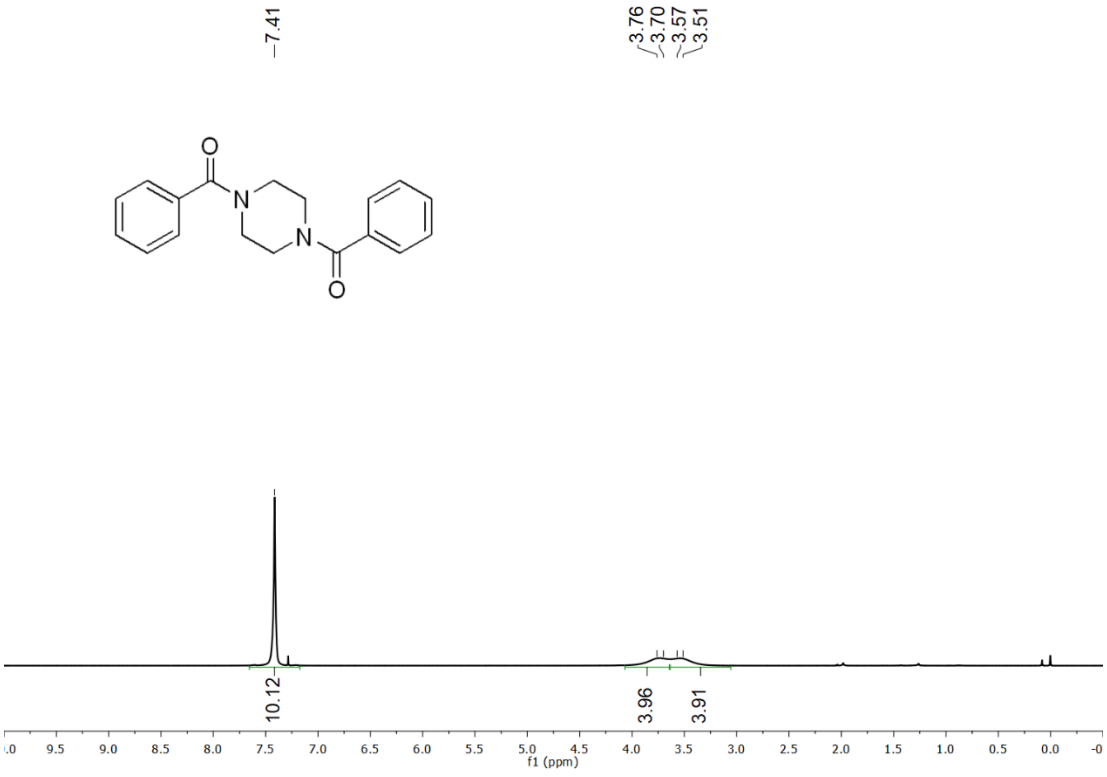
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ai**



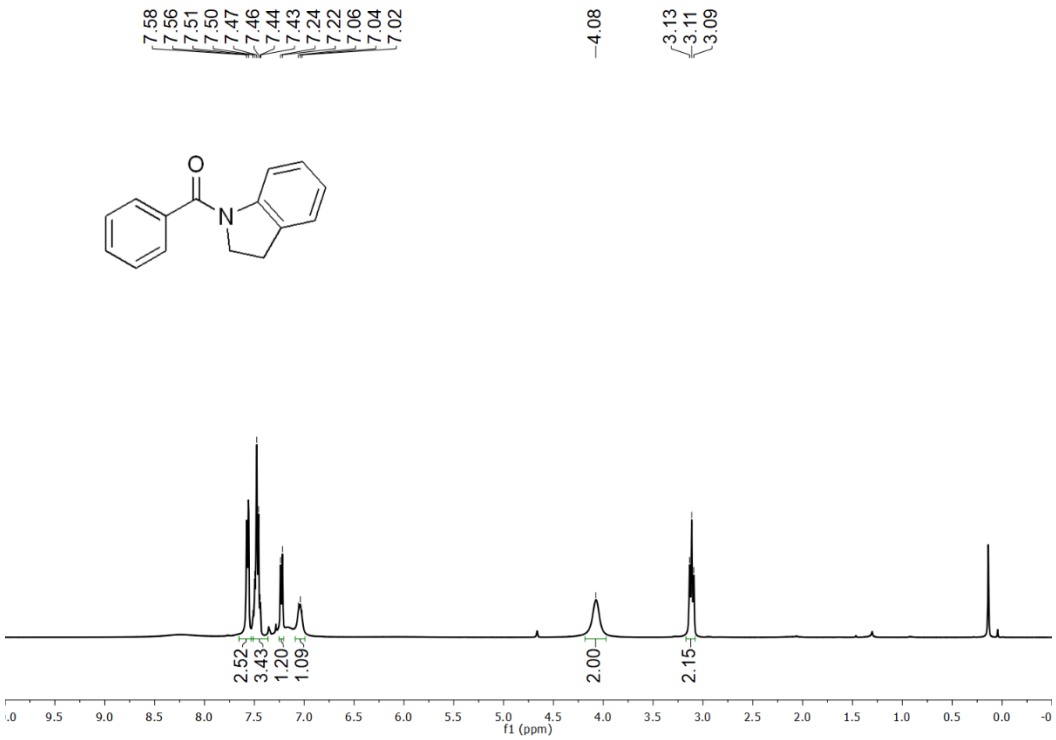
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8aj**



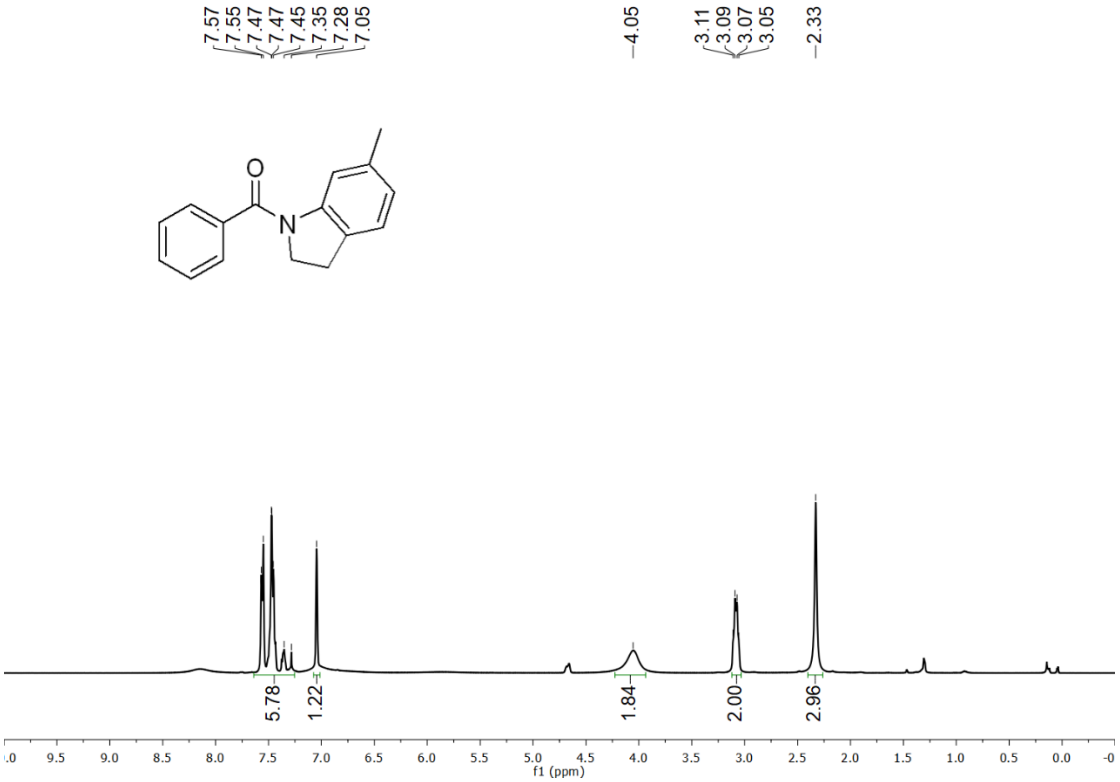
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ak**



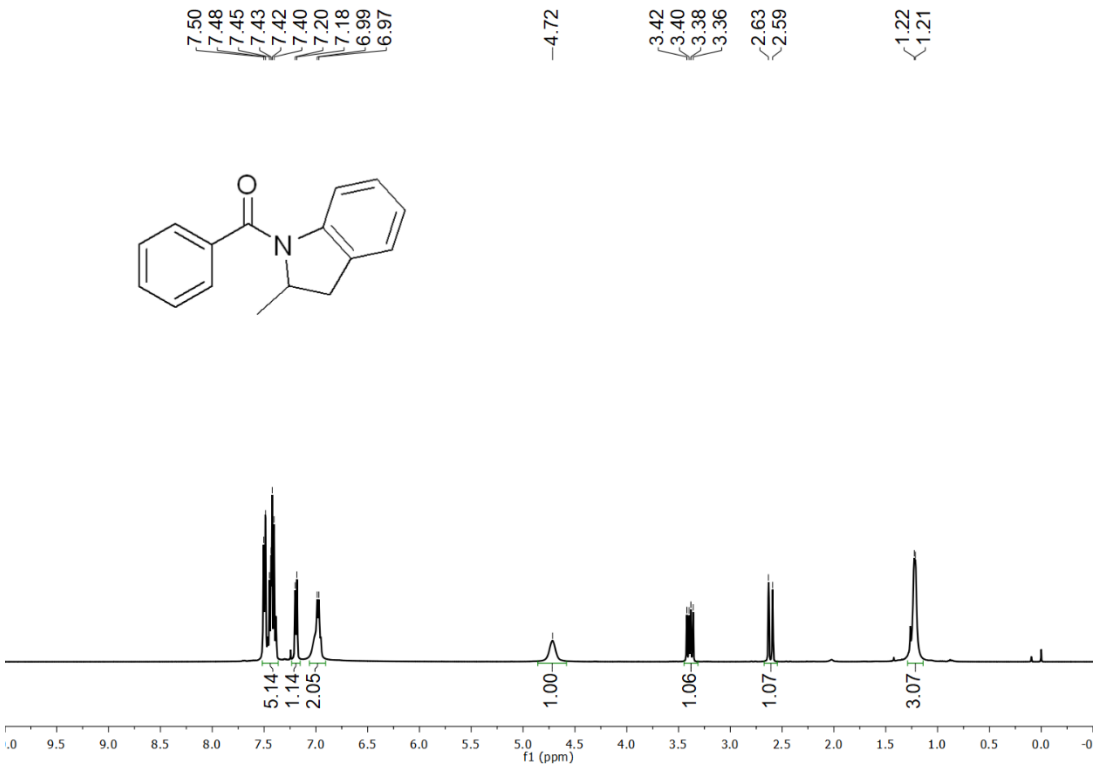
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8al**



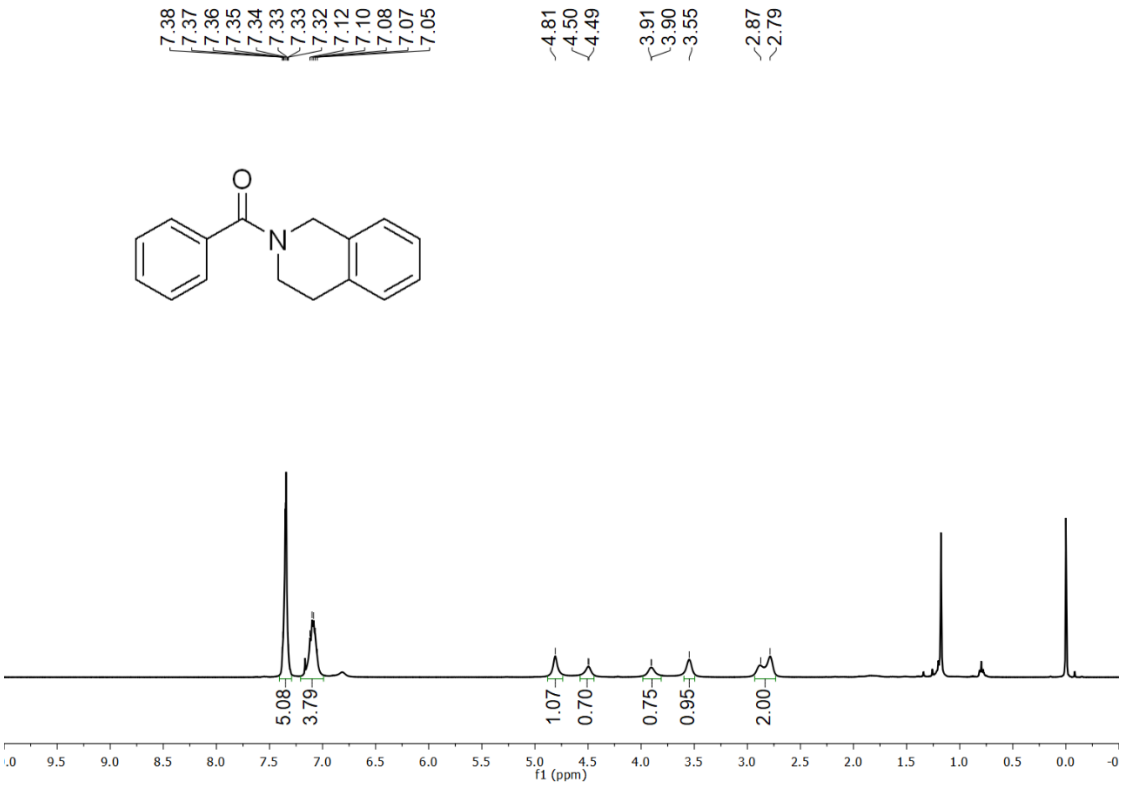
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8am**



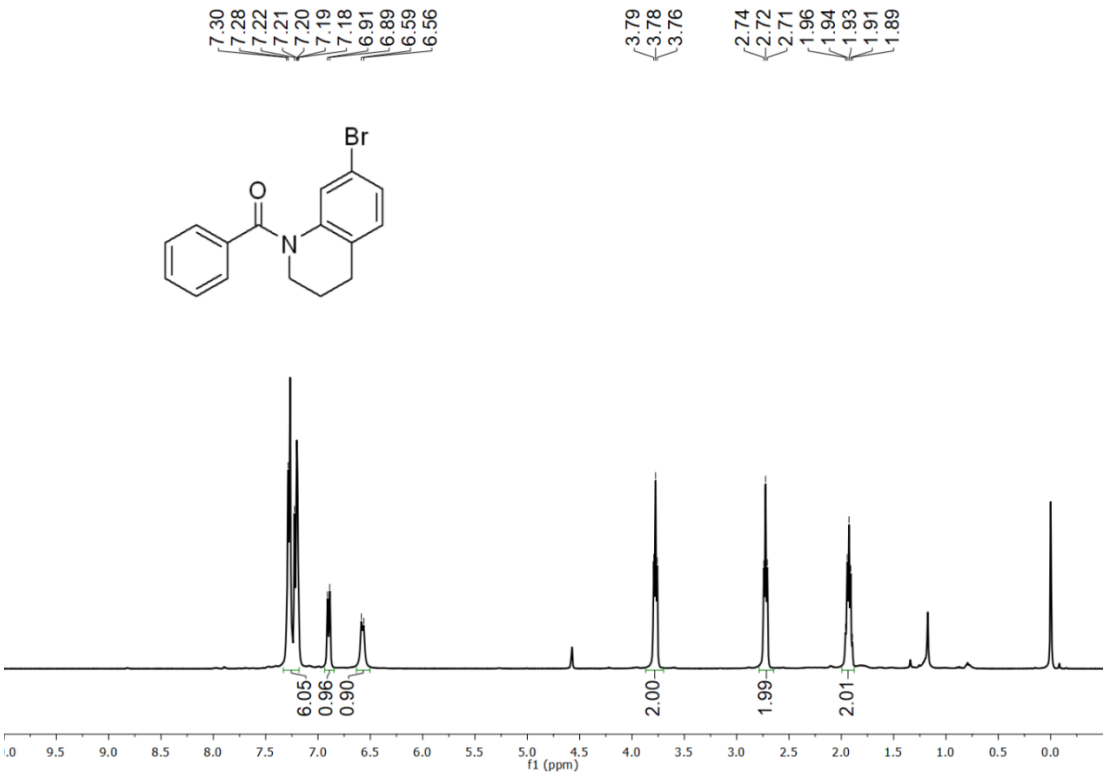
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8an**



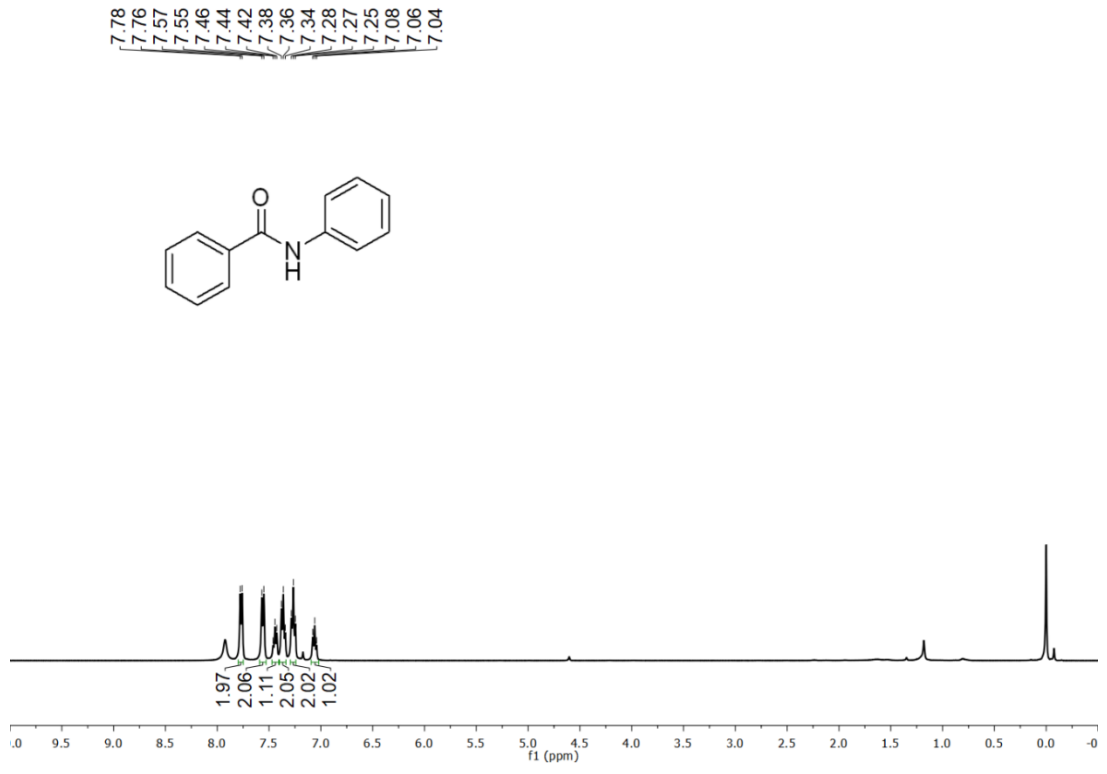
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ao**



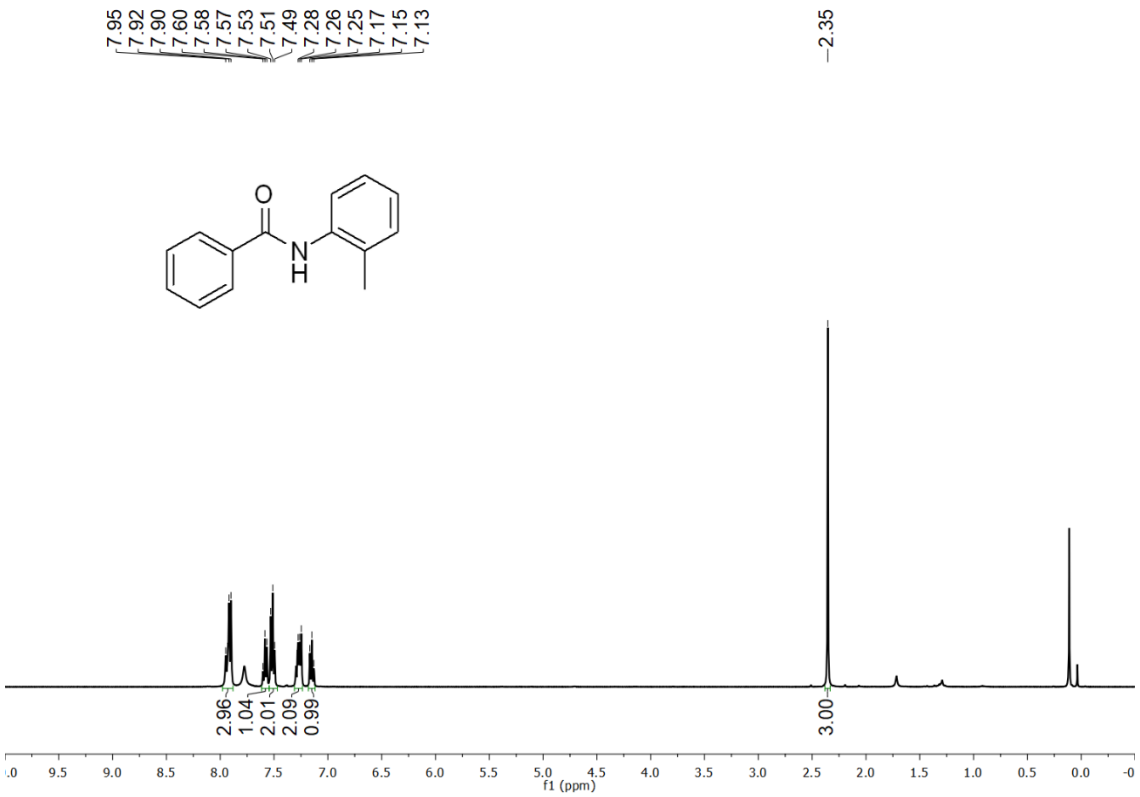
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ap**



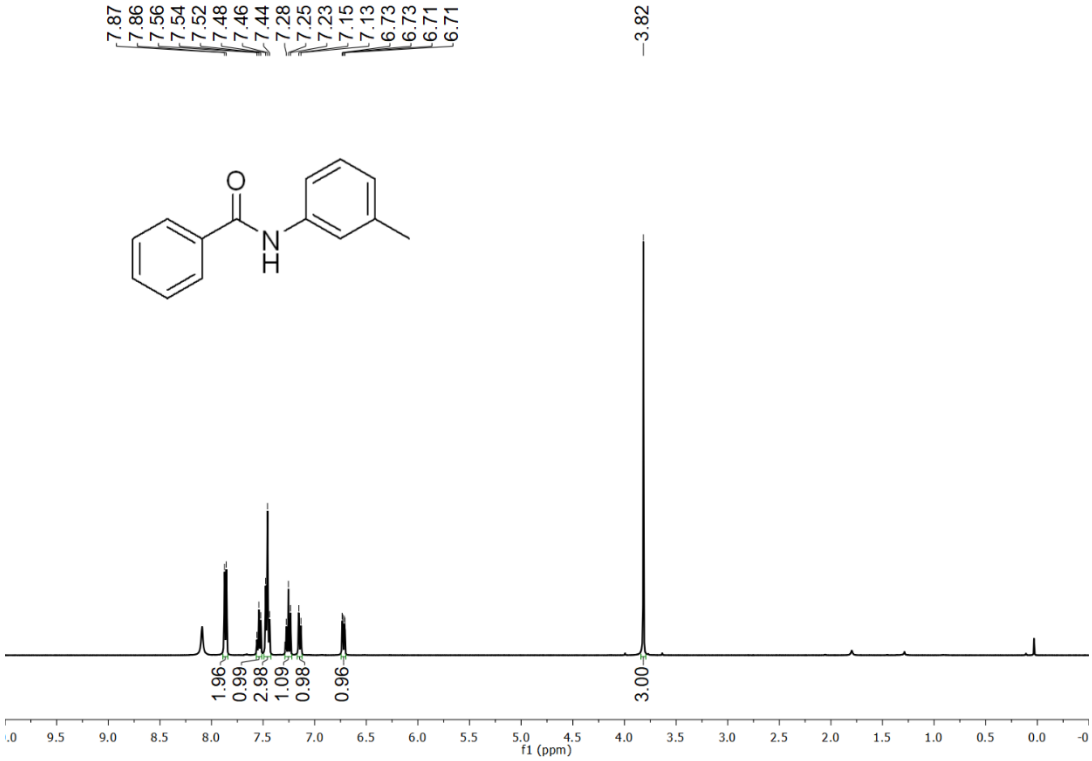
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^oC) of **8aq**



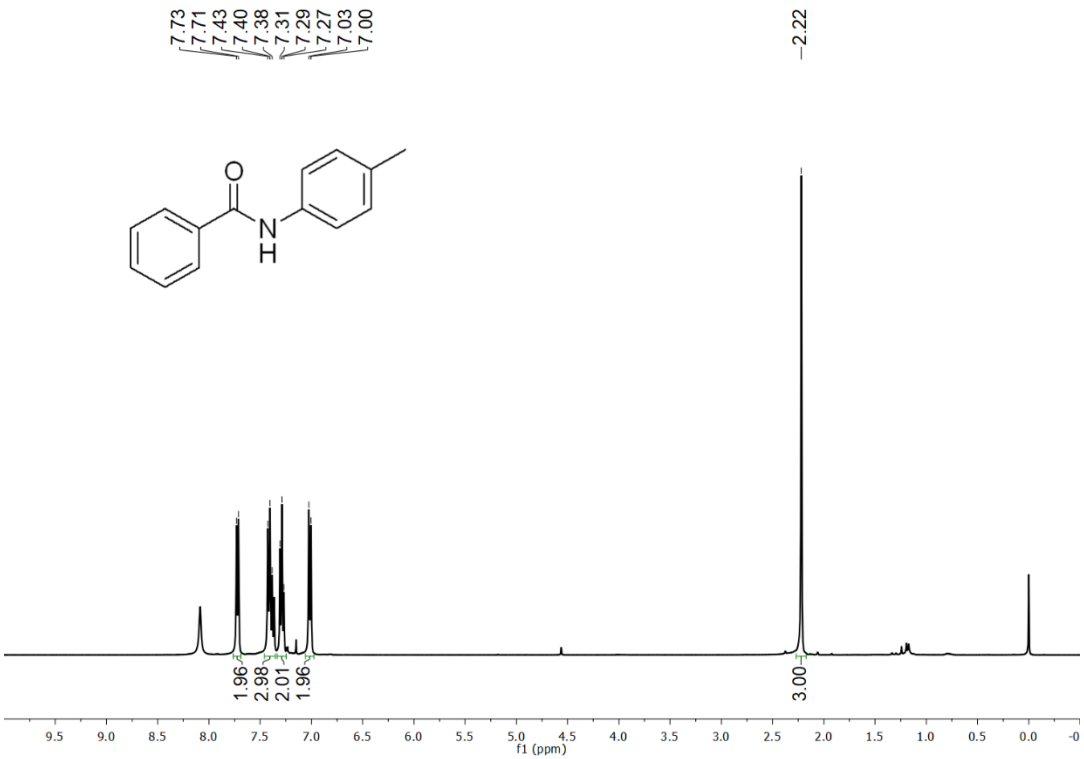
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^oC) of **8ar**



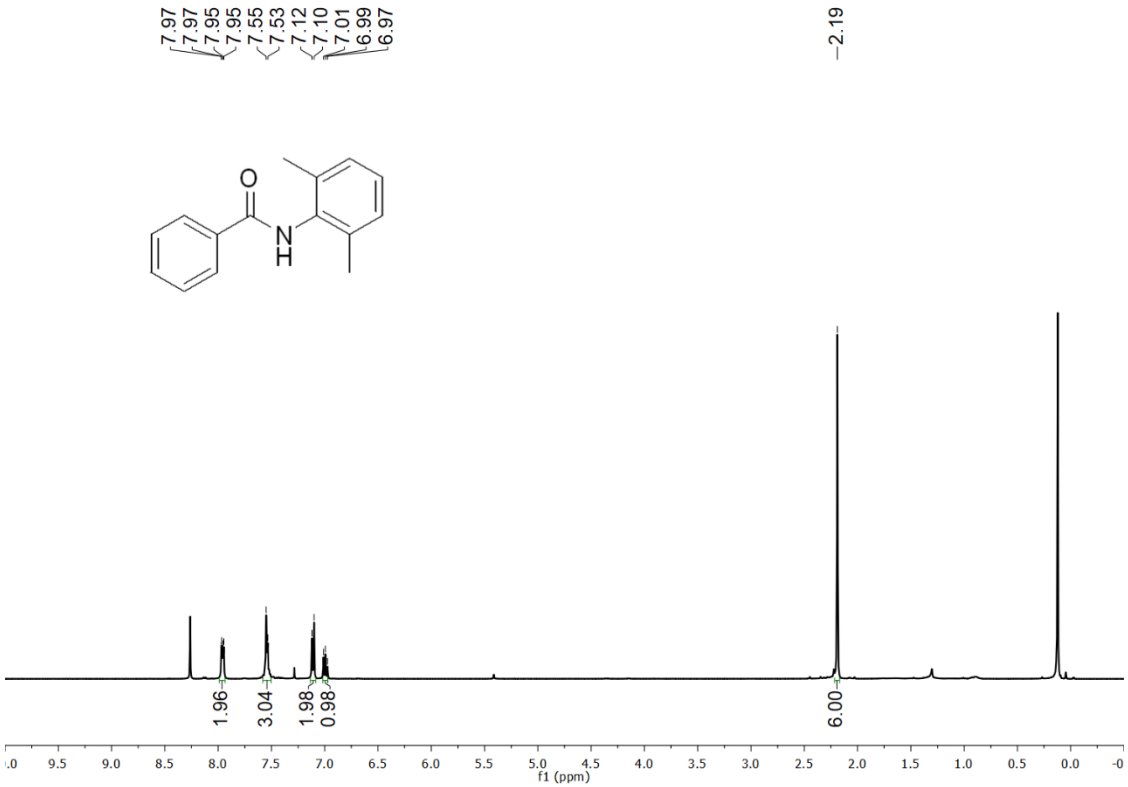
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar^{oMe}**



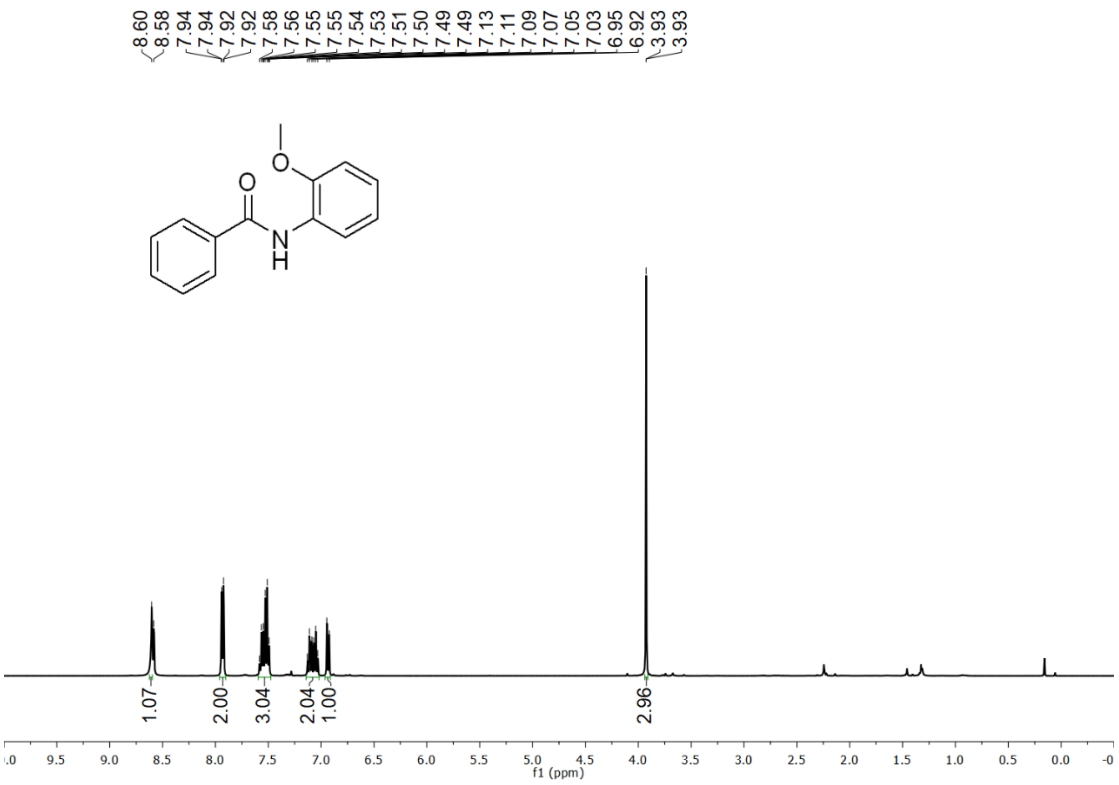
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar^{mMe}**



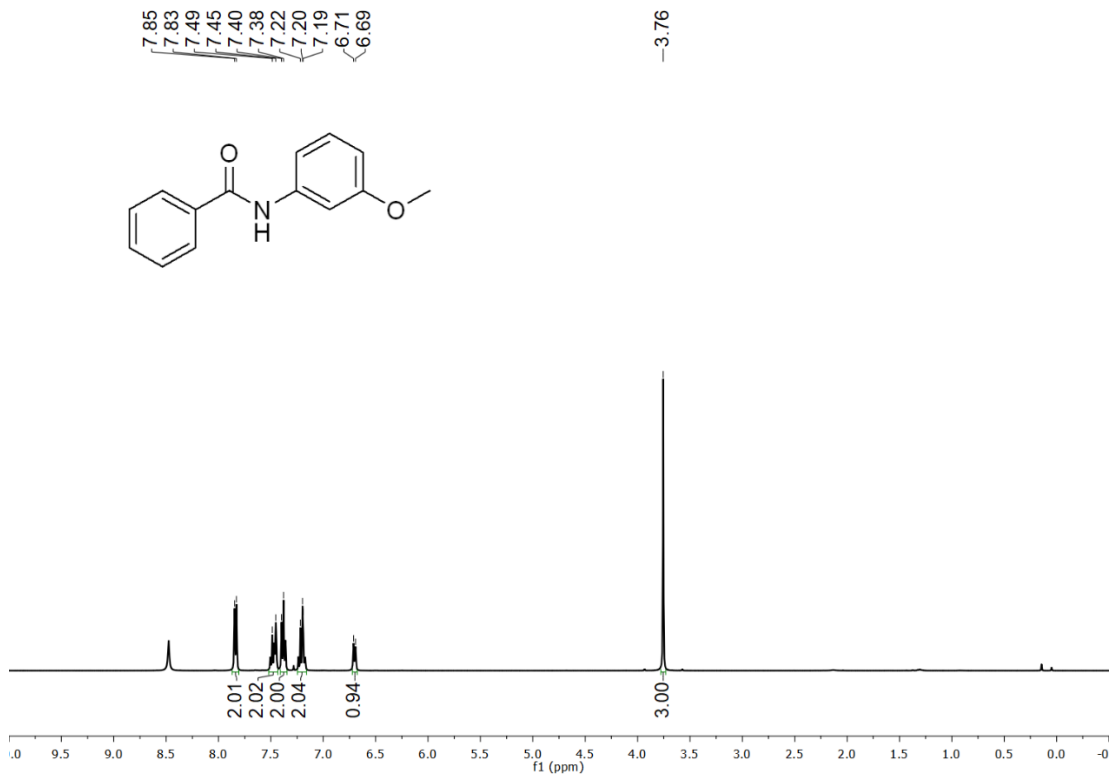
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar^{pMe}**



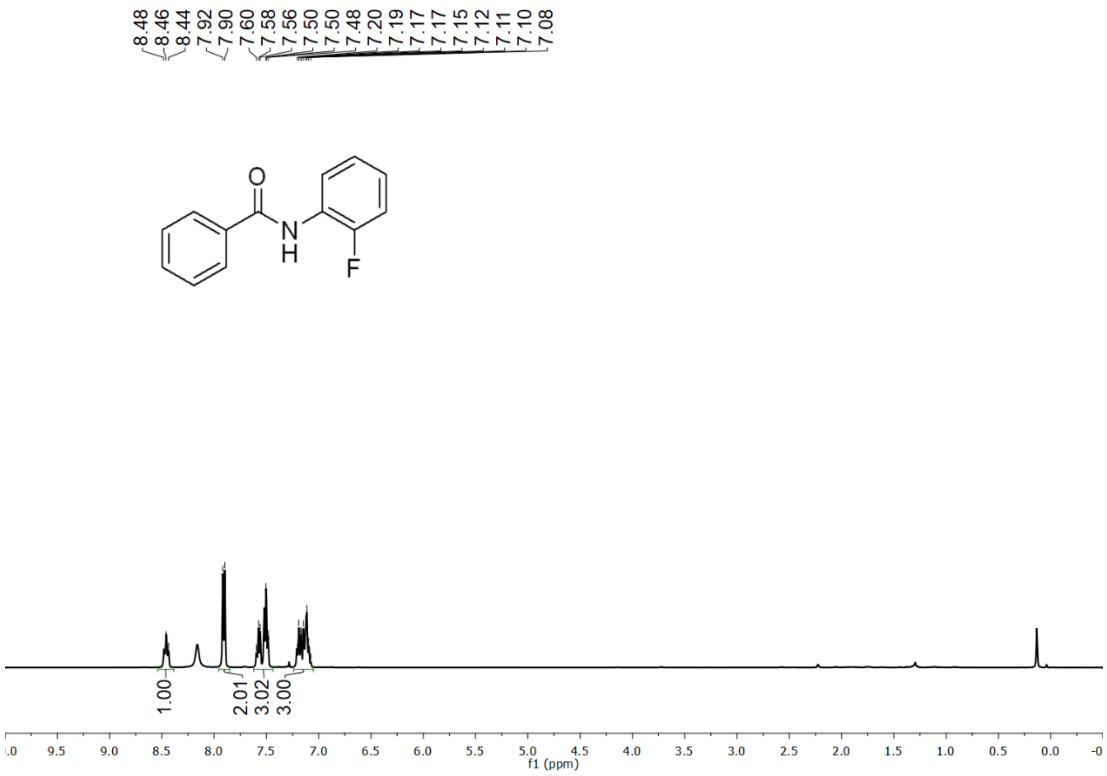
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar^{oMe2}**



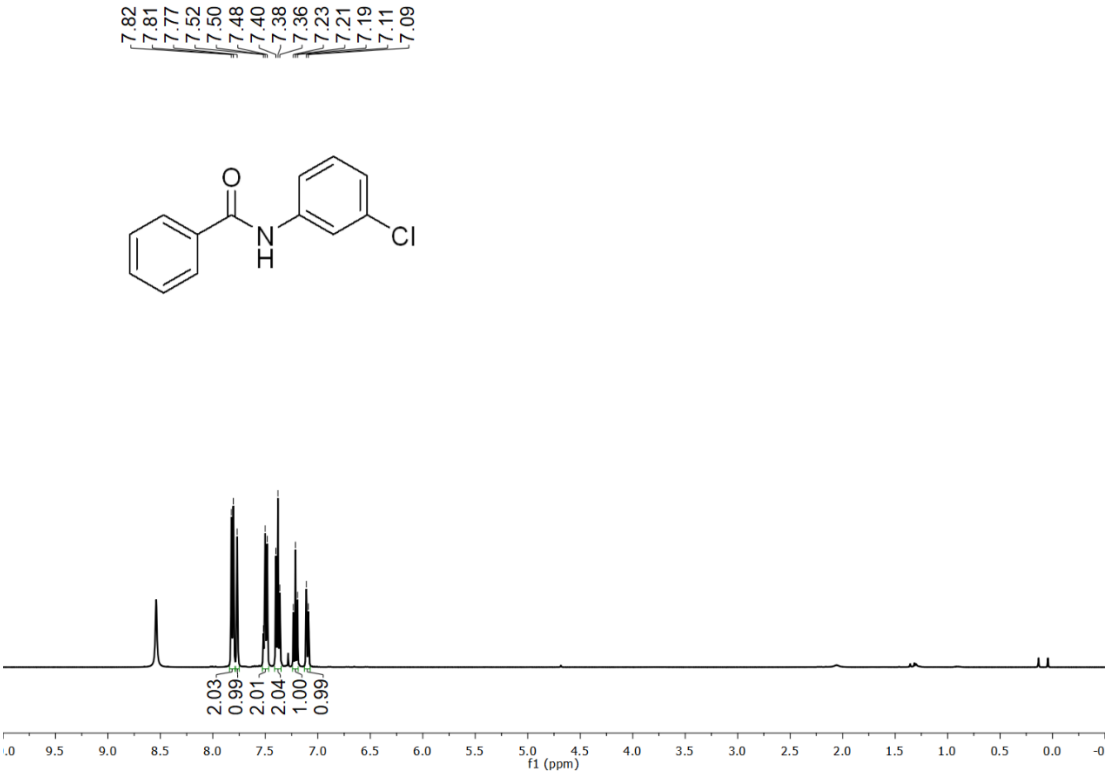
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar$^{o(OMe)}$**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar$^{m(OMe)}$**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar^{oF}**



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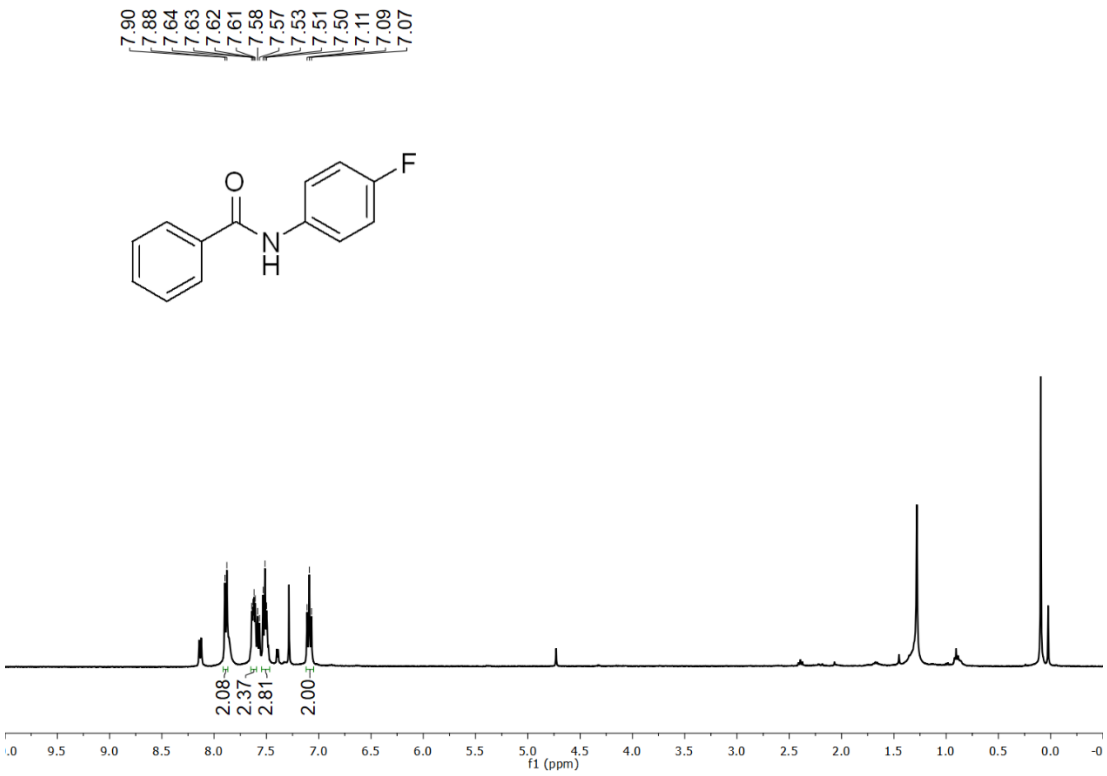
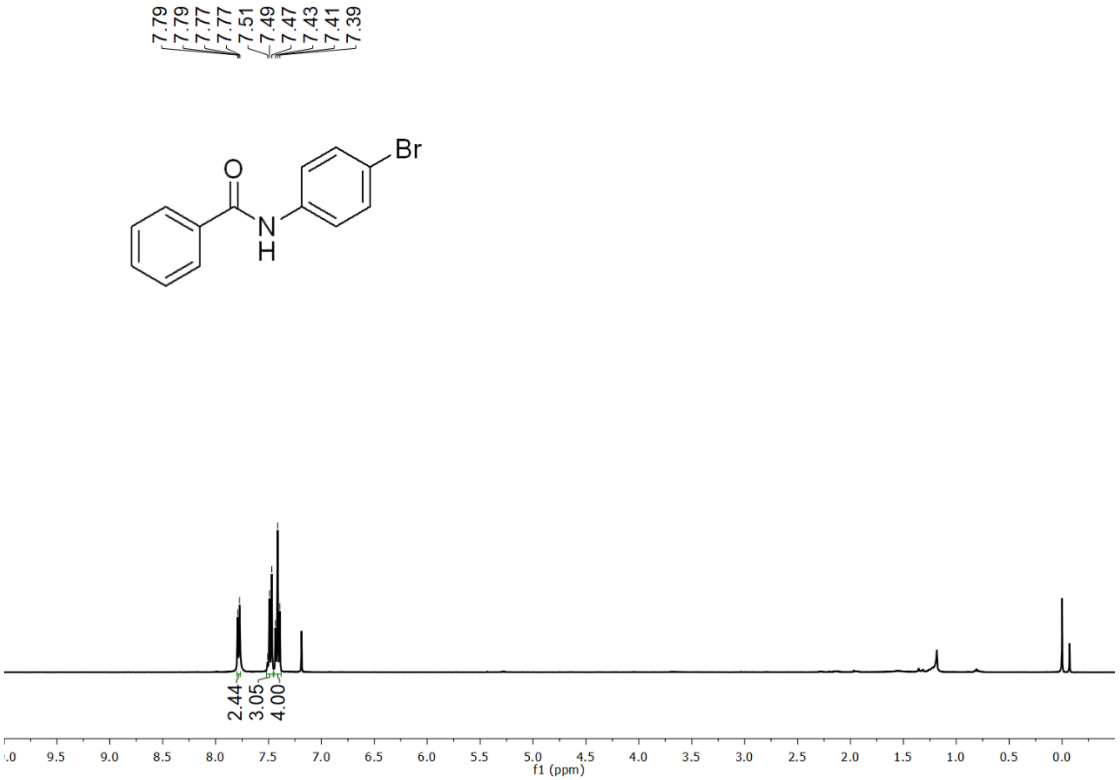
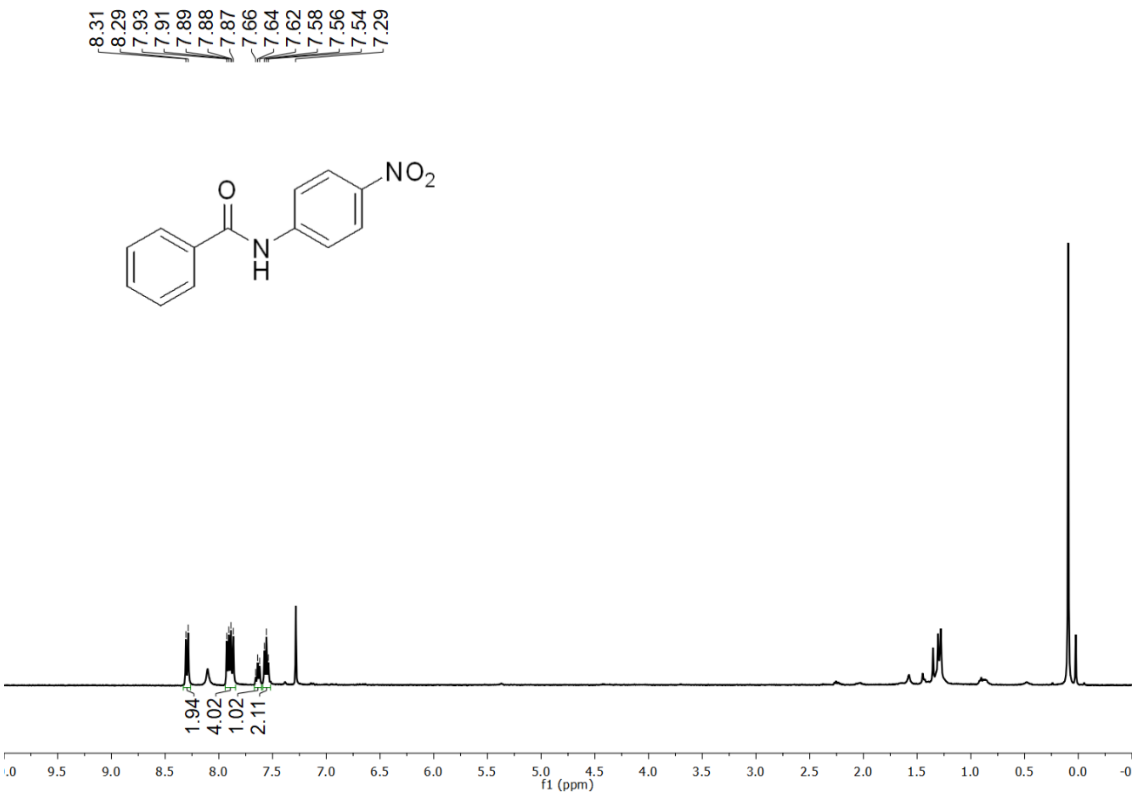


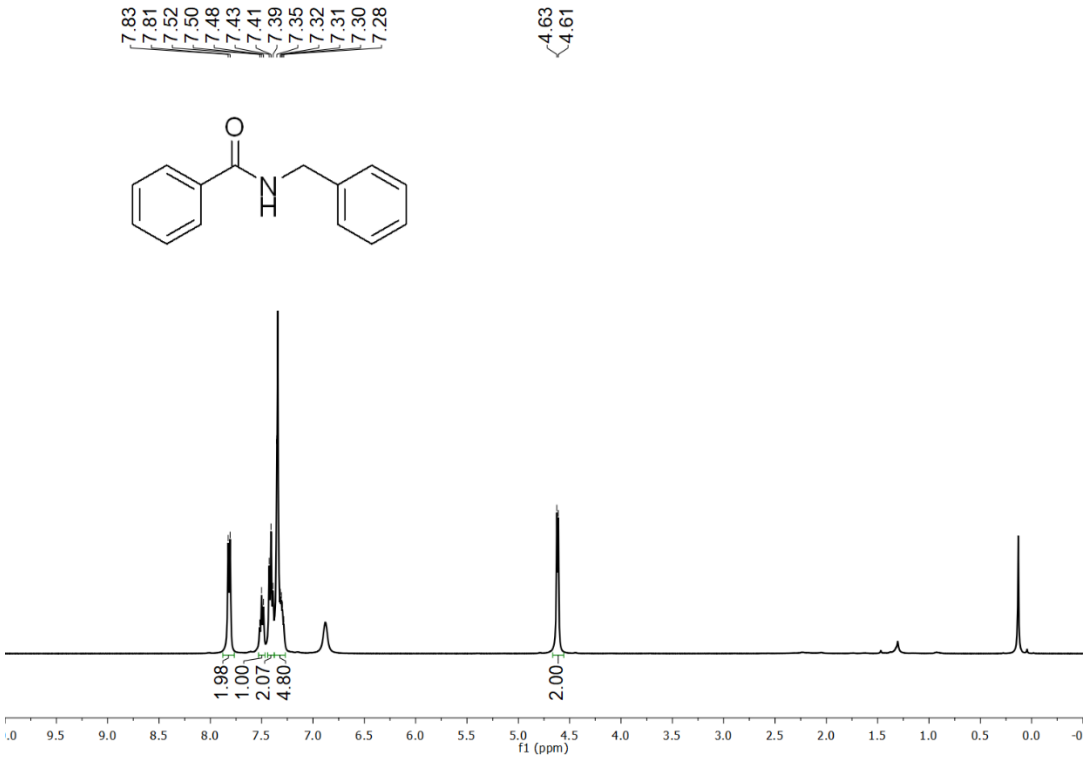
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar^{pF}**



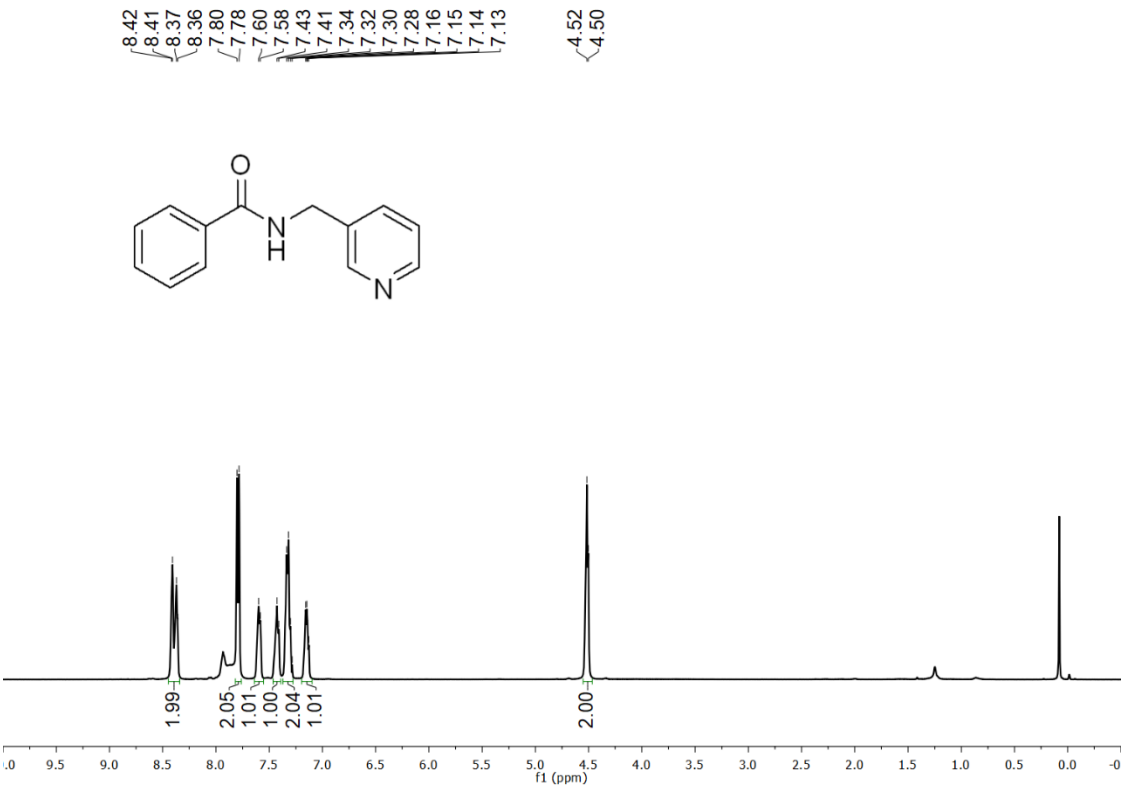
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar^{pBr}**



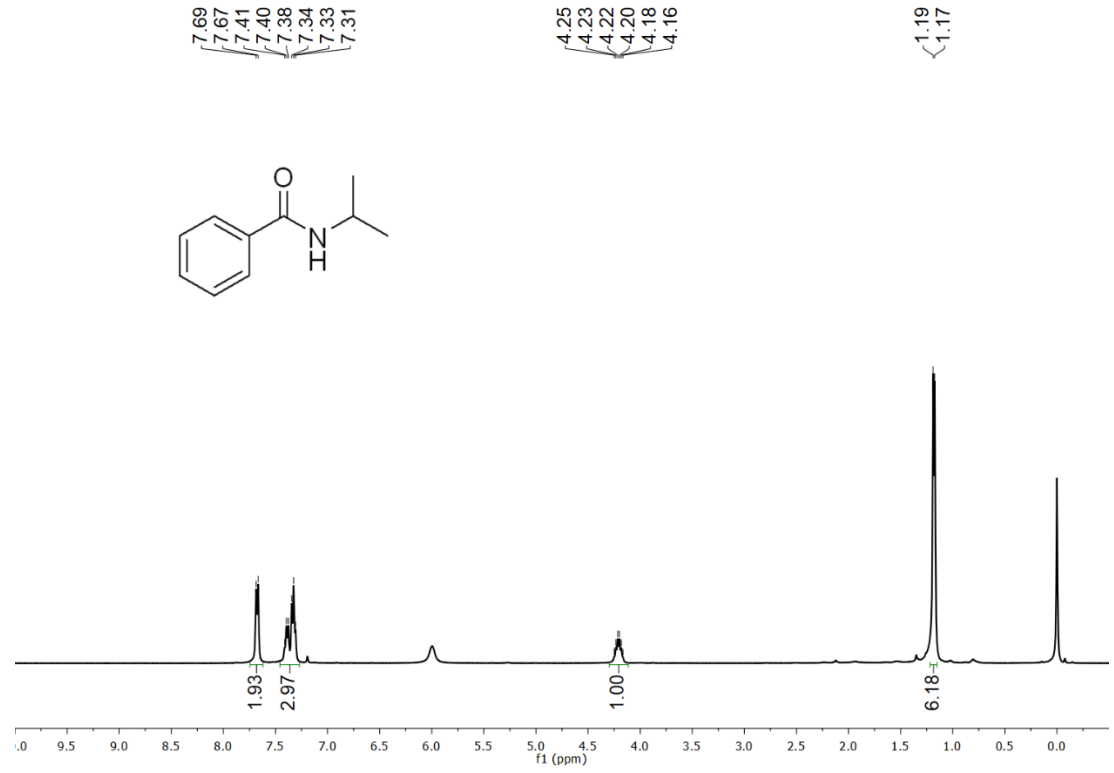
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8ar^{pNO2}**



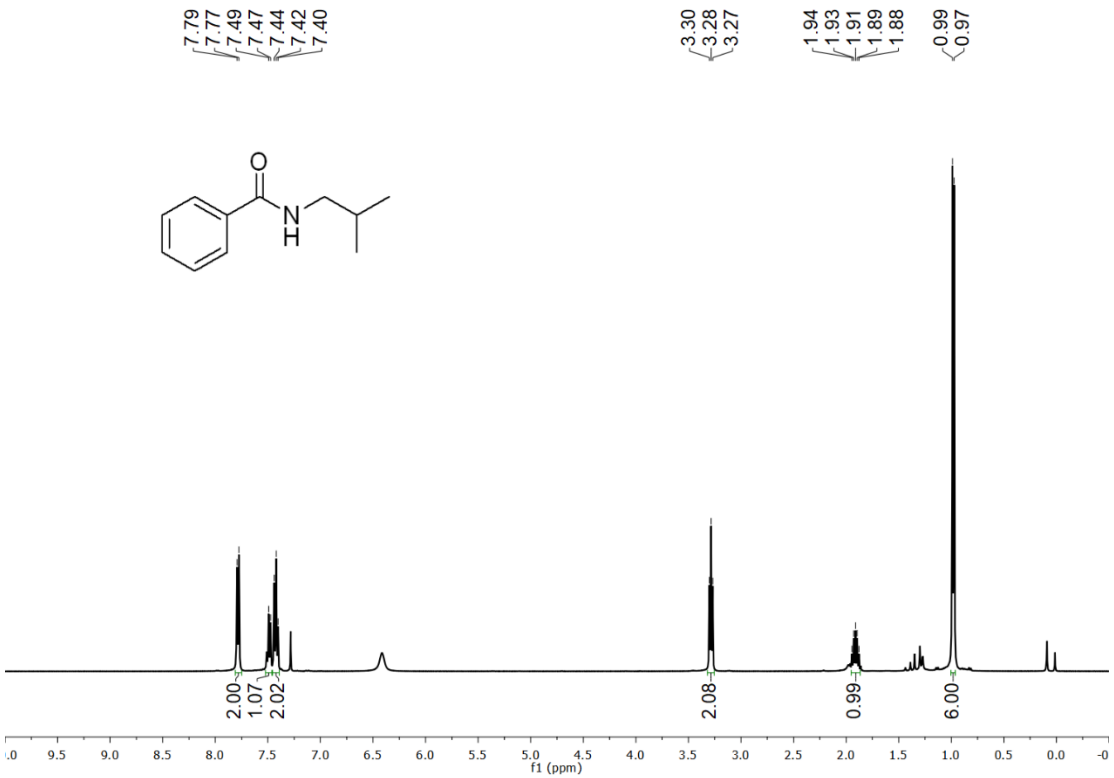
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8as**



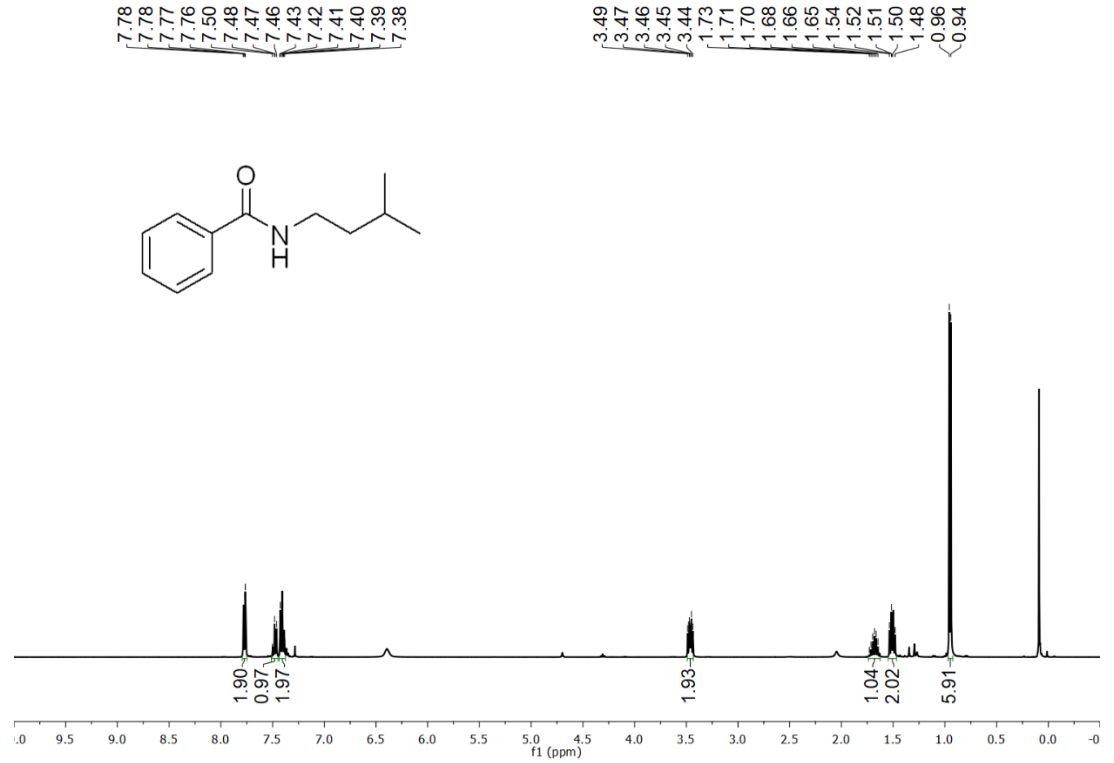
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8at**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8au**

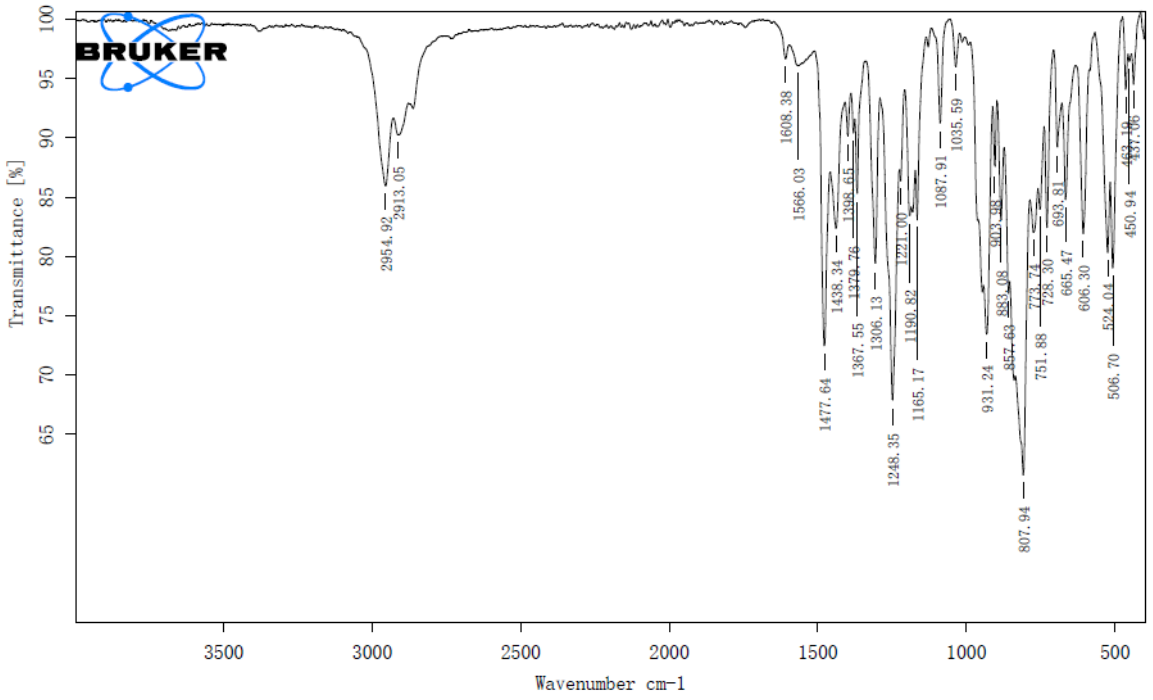


^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8av**

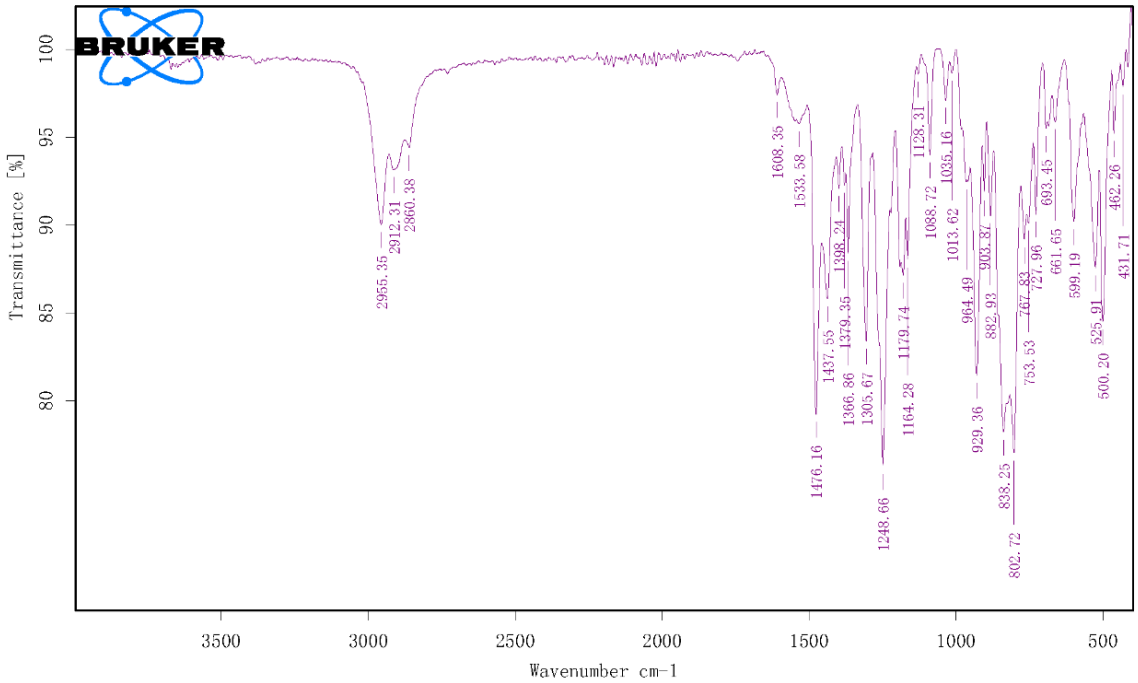


^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 ^{o}C) of **8aw**

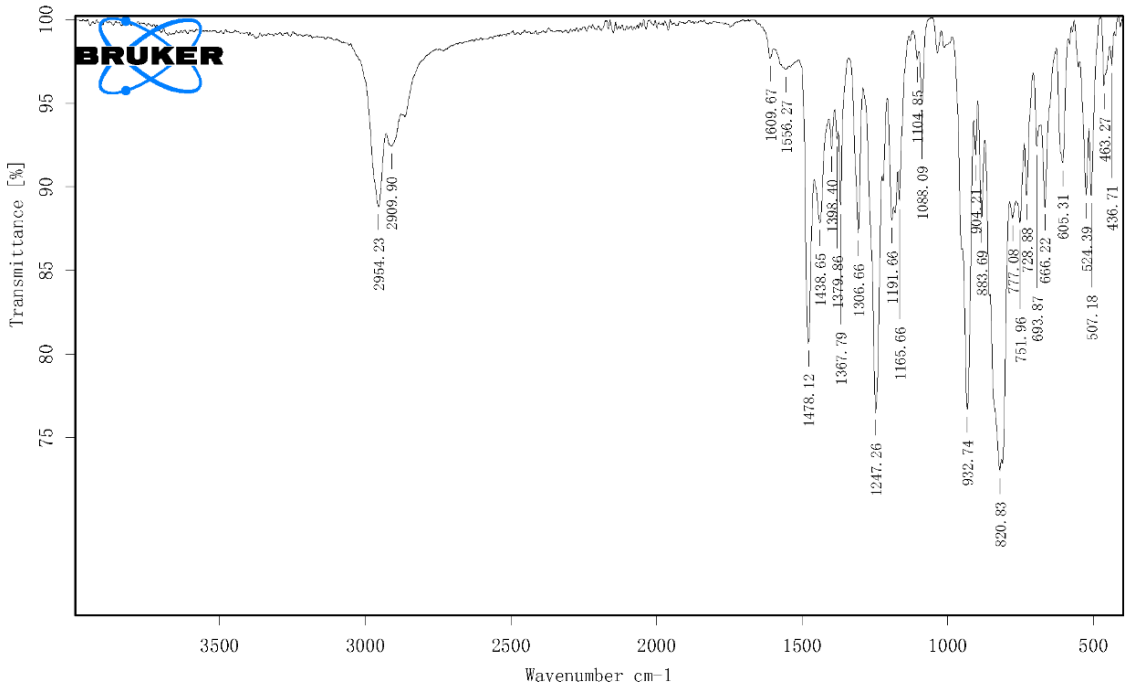
10. IR spectra of complexes.



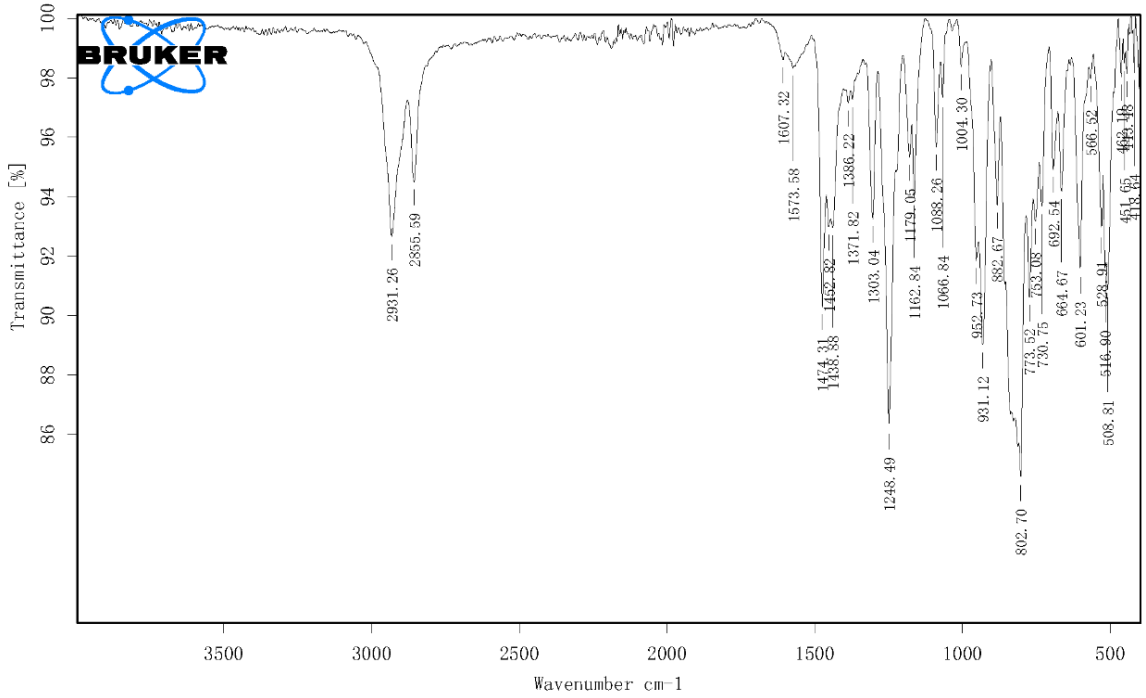
IR spectrum of complex **1a**



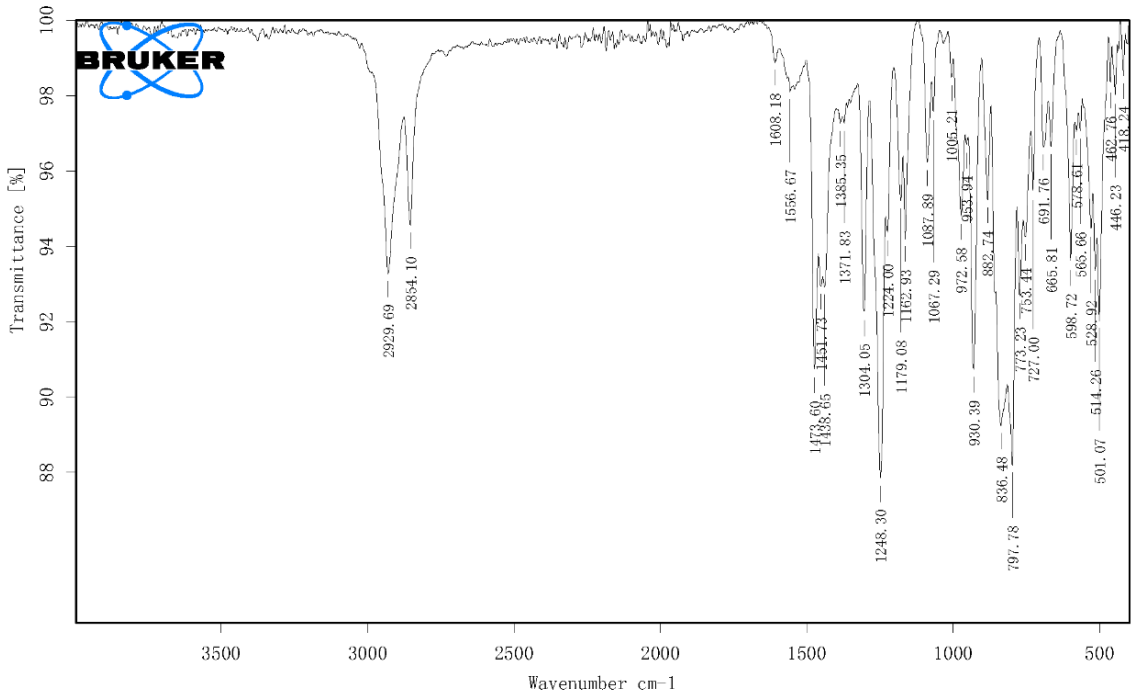
IR spectrum of complex **2a**



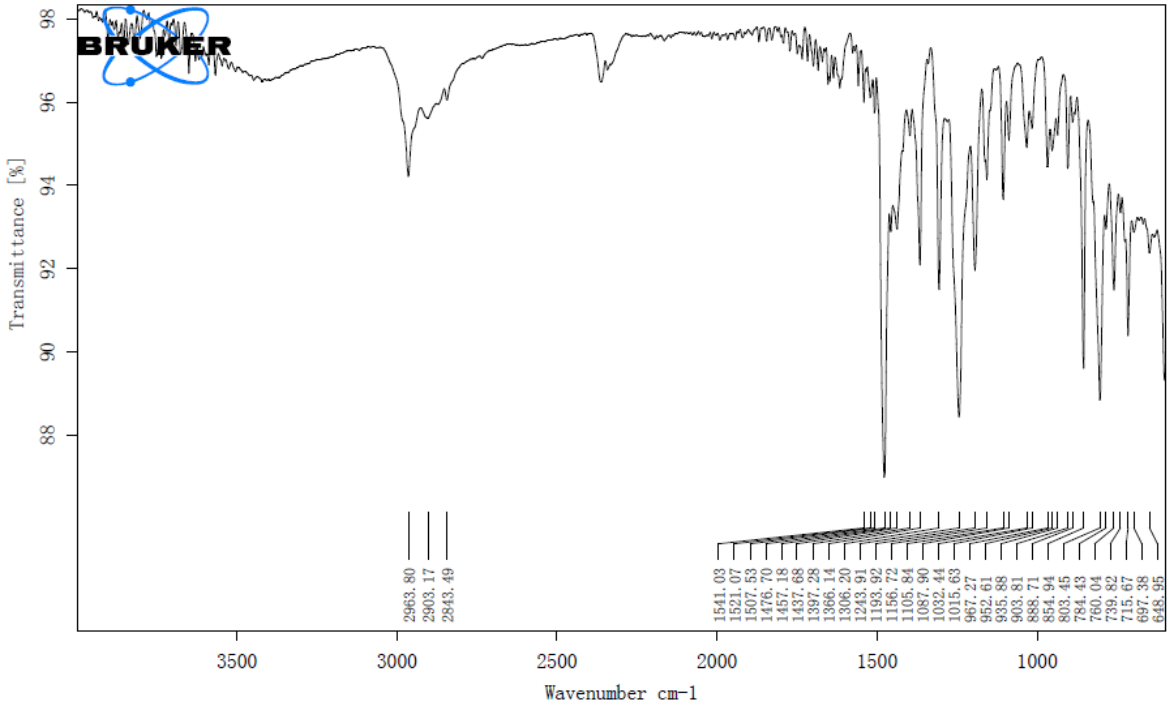
IR spectrum of complex **3a**



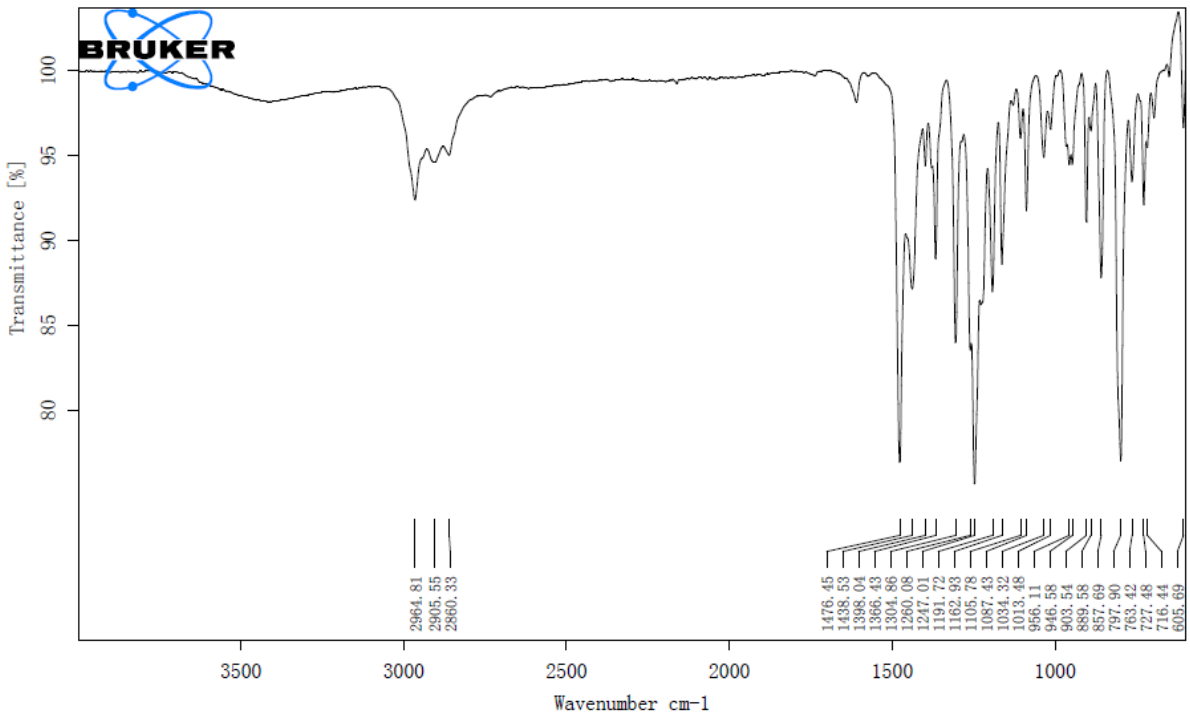
IR spectrum of complex **4a**



IR spectrum of complex **5a**



IR spectrum of complex **1b**



IR spectrum of complex **2b**

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