Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

A catalyst-free cross-coupling of isocyanates and triarylboranes for secondary amide synthesis

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1. General methods

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware by using Schlenk line techniques with a four-port dual-bank manifold under a nitrogen atmosphere. Anhydrous solvents such as 1,2-dichloroethane, benzotrifluoride, chlorobenzene, chloroform, 1,1,2,2-tetrachloroethane, and 1,1,2-trichloroethane were purchased in a septum-sealed bottle with 4 Å molecular sieve beads. Triarylboranes including triphenylborane, tris(4-methylphenyl)borane, tris(2-methylphenyl) borane, tris(4-fluorophenyl)borane, tris(3,5-dimethylphenyl)borane, tri-1-naphthalenylborane, tributylborane and tribenzylborane, as well as all isocyanates used are commercial available, which were purchased from Energy-Chemical, Aladdin, J&K Scientific, Macklin, Adamas, Bidepharm, Heowns, Chemieliva, etc without further purification. Other triarylboranes were freshly prepared according to the literature reports.[1] Diphenylborinic acid was prepared according to the known procedure.[2]

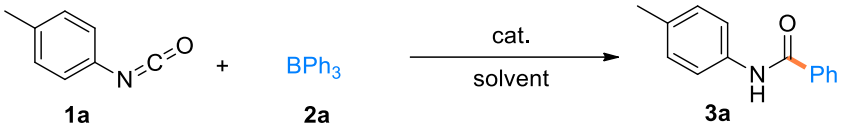
Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating on a hot plate. Flash chromatography was performed using NUOTAI silica gel (200 – 300 mesh) with distilled solvents. Columns were typically packed as slurry and equilibrated with petroleum ether prior to use.

Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on a Bruker Advance 400 MHz and JEOL 400 MHz spectrometers. Chemical shifts for ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (*J* = 7.264, singlet), methanol-d_4 (*J* = 3.310, quintet), and dimethylsulfoxide-d_6 (*J* = 2.500, quintet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); td (triplet of doublets); qd (quartet of doublets); m (multiplet), etc. The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ = 0.0) and relative to the signal of chloroform-*d* (δ = 77.16, triplet), methanol-d_4 (*J* = 49.00, septet), and dimethylsulfoxide-d_6 (*J* = 39.52, septet). To clarify the complete

signal assignments, "× number" indicates the multiple carbons due to the superposition of chemical shifts.

High resolution mass spectral analysis (HRMS) was performed on Water Q-TOF Premier mass spectrometer (Thermo Electron Corporation).

Table S1 Reaction optimization[a]

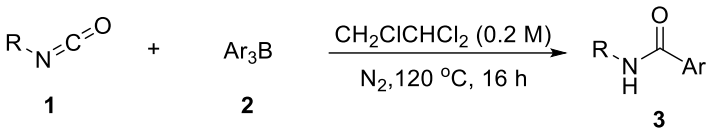


1a **2a** **3a**

Entry	Catalyst	Solvent	*t* (°C)	Time (h)	Yield (%)[b]
1	$Ni(cod)_2$, KO^{t}Bu	CH_2ClCH_2Cl	120	24	20
2	KO^{t}Bu	CH_2ClCH_2Cl	120	24	21
3	None	CH_2ClCH_2Cl	120	24	53
4	None	$PhCF_3$	120	24	47
5	None	PhCl	120	24	24
6	None	$CHCl_3$	120	24	51
7	None	$CHCl_2CHCl_2$	120	24	51
8	None	$CH_2ClCHCl_2$	120	24	76
9	None	$CH_2ClCHCl_2$	120	16	84
10	None	$CH_2ClCHCl_2$	120	12	71
11	None	$CH_2ClCHCl_2$	110	16	72
12	None	$CH_2ClCHCl_2$	130	16	69
13[c]	**None**	**$CH_2ClCHCl_2$**	**120**	**16**	**83**
14[d]	None	$CH_2ClCHCl_2$	120	16	76
15[c,e]	None	$CH_2ClCHCl_2$	120	16	73

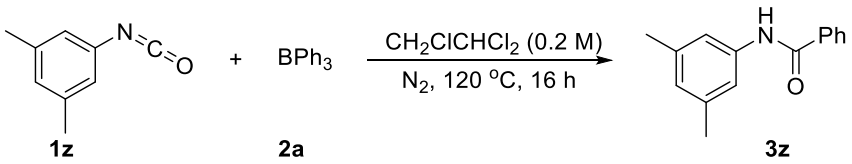
[a] Unless other specified, reactions were conducted with **1a** (0.3 mmol), **2a** (0.36 mmol), and solvent (2.0 mL) under N_2 for 24 h. [b] Isolated yields. [c]1.5 mL solvent was used. [d]1.0 mL solvent was used. [e]The reaction was performed under air. cod = 1,5-cyclooctadiene. n.d. = not detected.

2. General procedure for the synthesis of the products 3a−3ah



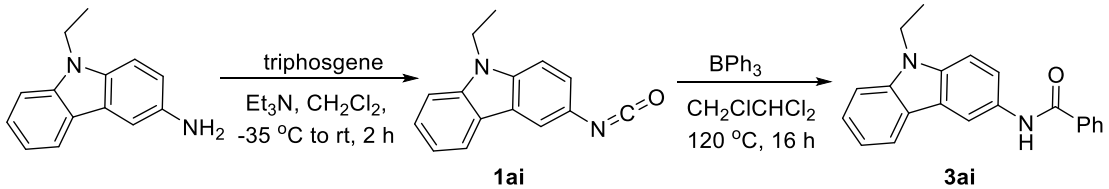
A 10 mL screw-capped Schlenk tube equipped with a stir bar was charged with isocyanate **1** (0.30 mmol, 1.0 equiv.), triarylborane **2** (0.36 mmol, 1.2 equiv.) and 1,1,2-trichloroethane (1.5 mL). The mixture was stirred at 120 °C in oil bath for 16 h under N_2 atmosphere. After full conversion, the reaction mixture was cooled down to room temperature, quenched with sat. aq. $NaHCO_3$ (10 mL), and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with sat. NaCl, dried over Na_2SO_4 and concentrated under vacuum. The resultant residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the corresponding amide **3a−3ah**.

3. Scale-up synthesis of the product 3z



A 100 mL screw-capped Schlenk tube equipped with a stir bar was charged with 3,5-dimethylphenyl isocyanate **1z** (0.88 g, 6.0 mmol, 1.0 equiv.), triphenylborane **2a** (1.74 g, 7.2 mmol, 1.2 equiv.), and 1,1,2-trichloroethane (30 mL). The mixture was stirred at 120 °C in oil bath for 16 h under N_2 atmosphere. After full conversion, the reaction mixture was cooled down to room temperature, quenched with sat. aq. $NaHCO_3$ (50 mL), and then extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with sat. NaCl, dried over Na_2SO_4 and concentrated under vacuum. The resultant residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 – 12:1) to give **3z** (1.07 g, 4.75 mmol, 79%).

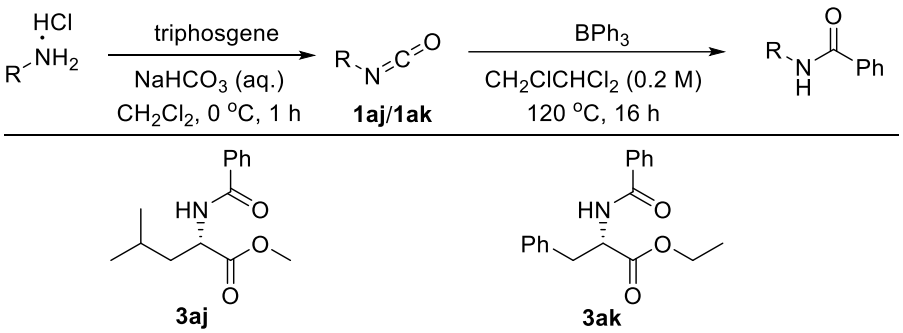
4. Sequential modular synthesis of the products 3ai−3ak[3,4]



To a stirred CH_2Cl_2 (1 mL) solution of triphosgene (0.1 mmol, 29.7 mg, 0.33 equiv.) was added

a CH_2Cl_2 (0.5 mL) solution of 3-amino-9-ethylcarbazole (0.3 mmol, 63.1 mg, 1.0 equiv.) dropwise. After 30 min, the solution was cooled to -35 °C. Et_3N (0.1 mL) was added dropwise. The mixture was warmed to room temperature slowly and stirred for 2 h. The mixture was concentrated under vacuum to give the isocyanate **1ai**, which was used in the next step immediately.

A 10 mL screw-capped Schlenk tube was charged with the above isocyanate **1ai**, triphenylborane (0.36 mmol, 87.2 mg, 1.2 equiv.), and 1,1,2-trichloroethane (1.5 mL). The mixture was stirred at 120 °C in oil bath for 16 h under N_2 atmosphere. After that, the reaction mixture was cooled down to room temperature, quenched with sat. aq. $NaHCO_3$ (10 mL), and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with sat. NaCl, dried over Na_2SO_4 and concentrated under vacuum. The resultant residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 – 10:1) to give the desired product **3ai** (73.2 mg, 0.233 mmol, 78% over two steps).



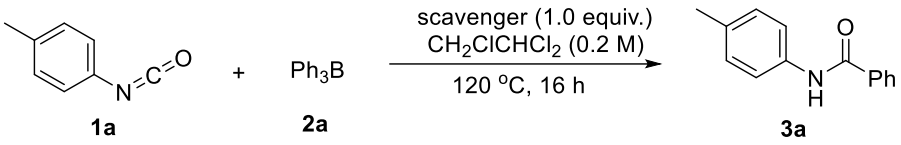
A 10 mL round-bottom flask was charged with amino acid ester hydrochloride (0.3 mmol, 1.0 equiv.), sat. aq. $NaHCO_3$ (1.2 mL) and CH_2Cl_2 (1.2 mL). The solution was stirred at 0 °C for 20 min. Whereafter, triphosgene (0.1 mmol, 29.7 mg, 0.33 equiv.) was added into the solution. The mixture was stirred at 0 °C for 1 h. After that, the reaction mixture was warmed to room temperature and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with sat. NaCl, dried over Na_2SO_4 and concentrated under vacuum to give the isocyanate **1aj** or **1ak**, which was used in the next step immediately.

A 10 mL screw-capped Schlenk tube equipped with a stir bar was charged with the above isocyanate **1aj** or **1ak**, triphenylborane (0.36 mmol, 87.2 mg, 1.2 equiv.), and 1,1,2-trichloroethane (1.5 mL). The mixture was stirred at 120 °C in oil bath for 16 h under N_2 atmosphere. After that, the reaction mixture was cooled down to room temperature, quenched with sat. aq. $NaHCO_3$ (10 mL), and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with sat.

NaCl, dried over Na_2SO_4 and concentrated under vacuum. The resultant residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the product **3aj** (33.1 mg, 0.133 mmol, 44% over two steps) or **3ak** (35.4 mg, 0.119, 40% over two steps).

5. Mechanistic exploration experiments

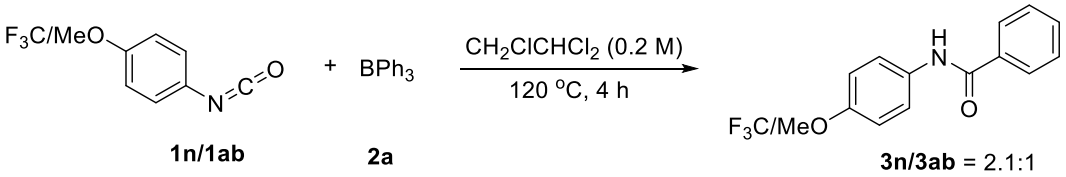
5.1 Radical trapping experiments



Entry	Scavenger	Yield of **3a** (%)
1	TEMPO	37
2	BHT	78
3	1,1-diphenylethylene	76

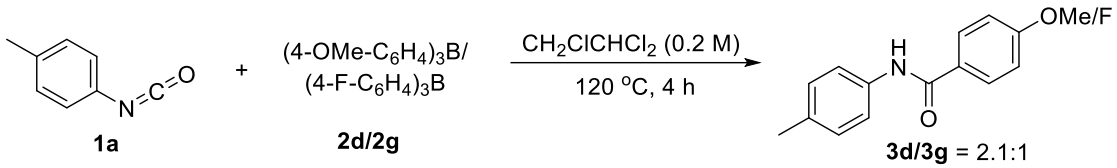
An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with 4-methylphenyl isocyanate **1a** (40.3 mg, 0.30 mmol, 1.0 equiv.), triphenylborane **2a** (87.2 mg, 0.36 mmol, 1.2 equiv.), and radical scavenger (1.0 equiv.): TEMPO (0.3 mmol, 46.9 mg), BHT (0.3 mmol, 66.1 mg) or 1,1-diphenylethylene (0.3 mmol, 54.5 mg), and 1,1,2-trichloroethane (1.5 mL). The mixture was stirred at 120 °C for 16 h under N_2 atmosphere. After cooling to room temperature, the mixture was quenched with sat. aq. $NaHCO_3$ (10 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. NaCl (10 mL), dried over Na_2SO_4, and concentrated under vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 – 12:1) to give the product **3a** (with TEMPO, **3a**: 23.2 mg, 37%; with BHT, **3a**: 49.2 mg, 78%; with 1,1-diphenylethylene, **3a**: 47.9 mg, 76%).

5.2 Competition experiments



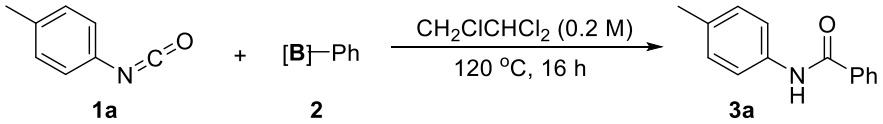
An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with 4-(trifluoromethyl)phenyl isocyanate **1n** (45.7 mg, 0.30 mmol, 1.0 equiv.), 4-methoxyphenyl isocyanate **1ab** (56.7 mg 0.30 mmol, 1.0 equiv.), triphenylborane **2a** (72.6 mg, 0.30 mmol, 1.0

equiv.), and 1,1,2-trichloroethane (1.5 mL). The mixture was stirred at 120 °C for 4 h under N_2 atmosphere. After cooling to room temperature, the mixture was quenched with sat. aq. $NaHCO_3$ (10 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. NaCl, dried over Na_2SO_4, and concentrated under vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 – 6:1) to give the product **3n** (46.6 mg, 0.176 mmol, 59%) and **3ab** (19.4 mg, 0.085 mmol, 28%). The ratio of **3n** and **3ab** was determined to be 2.1:1.



An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with 4-methylphenyl isocyanate **1a** (40.3 mg, 0.30 mmol, 1.0 equiv.), tris(4-methoxyphenyl)borane **2d** (99.6 mg, 0.30 mmol,1.0 equiv.), tris(4-fluorophenyl)borane **2g** (88.8 mg, 0.30 mmol, 1.0 equiv.) and 1,1,2-trichloroethane (1.5 mL). The mixture was stirred at 120 °C for 4 h under N_2 atmosphere. After cooling to room temperature, the mixture was quenched with sat. aq. $NaHCO_3$ (10 mL). The layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were rinsed with sat. NaCl, dried over Na_2SO_4, and concentrated under vacuo. The resultant residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 – 6:1) to give the product **3d** (19.3 mg, 0.080 mmol, 27%) and **3g** (8.7 mg, 0.038 mmol, 13%). The ratio of **3d** and **3g** was determined to be 2.1:1.

5.3 Control experiments



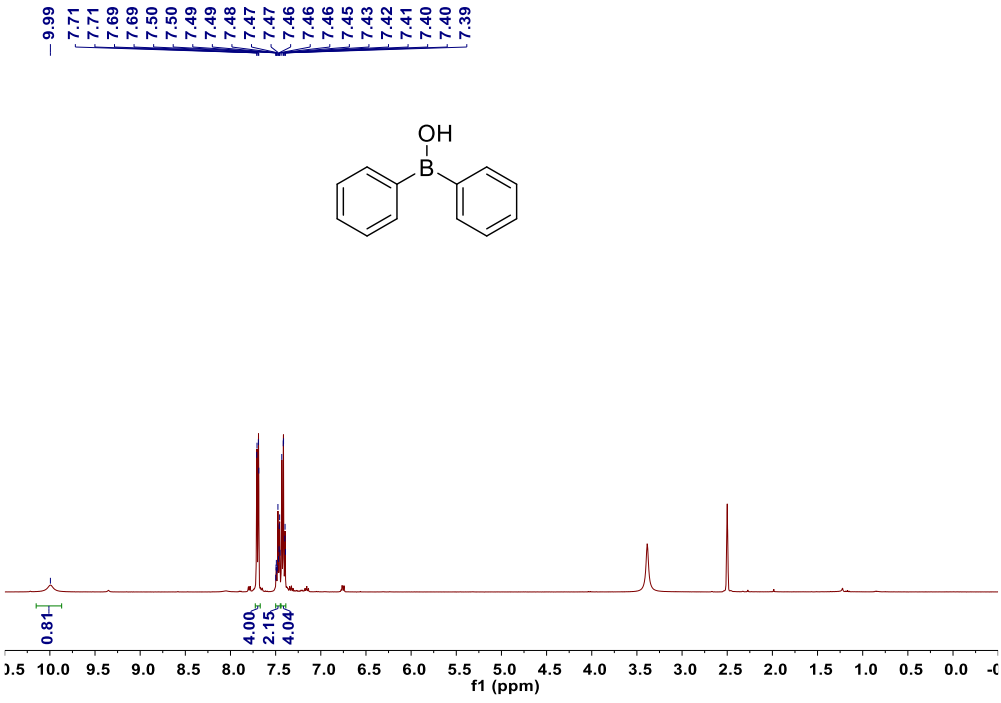
Entry	[B]—Ph	x (equiv.)	Yield of **3a** (%)
1	Ph_3B	0.34	30
2	Ph_3B	0.67	57
3	$NaBPh_4$	1.2	52
4	Ph_2BOH	1.2	7
5	$PhB(OH)_2$	1.2	0

A 10 mL screw-capped Schlenk tube equipped with a stir bar was charged with 4-methylphenyl isocyanate **1a** (0.30 mmol, 1.0 equiv.), specific borane (x equiv.), and 1,1,2-trichloroethane (1.5 mL).

The mixture was stirred at 120 °C in oil bath for 16 h under N_2 atmosphere. After that, the reaction mixture was cooled down to room temperature, quenched with sat. aq. $NaHCO_3$ (10 mL), and then extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with sat. NaCl, dried over Na_2SO_4 and concentrated under vacuum. The resultant residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1 – 12:1) to give the product **3a** (with 0.34 equiv. Ph_3B, **3a**: 19.0 mg, 30%; with 0.67 equiv. Ph_3B, **3a**: 36.2 mg, 57%; with 1.2 equiv. $NaBPh_4$, **3a**: 33.2 mg, 52%; with 1.2 equiv. Ph_2BOH, **3a**: 4.5 mg, 7%; with 1.2 equiv. $PhB(OH)_2$, **3a**: 0%).

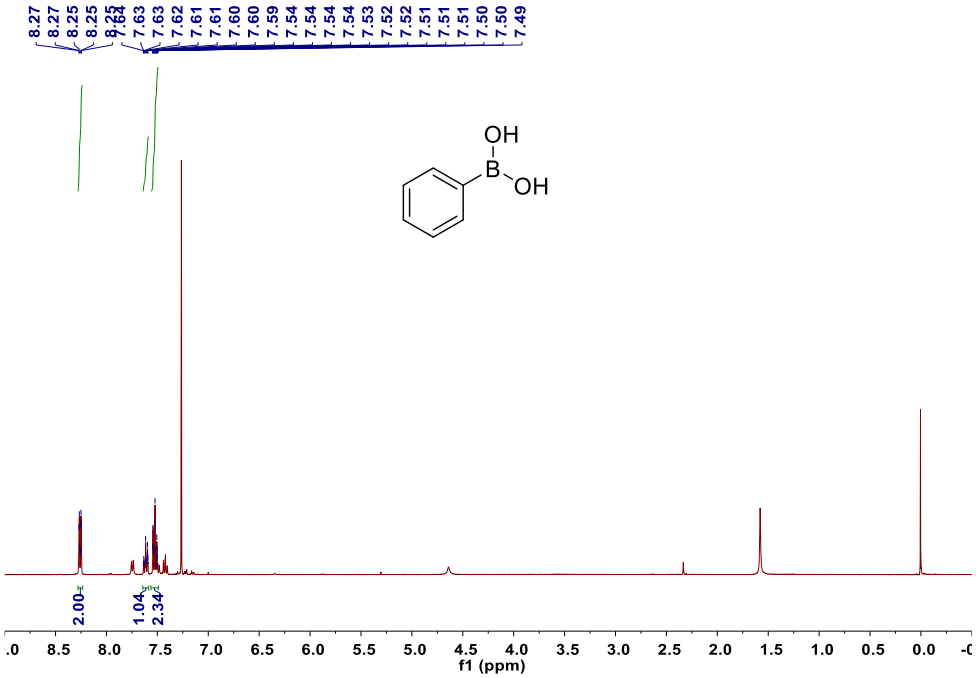
Note: Under the standard reaction conditions, both diphenylborinic acid and phenylboronic acid could be isolated by flash column chromatography (petroleum ether/ethyl acetate). ^1H NMR data and spectra of two compounds are provided below.

Ph_2BOH: **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.99 (brs, 1H), 7.70 (dd, J = 7.6, 1.5 Hz, 4H), 7.50 – 7.45 (m, 2H), 7.44 – 7.38 (m, 4H). The data of diphenylborinic acid is consistent with the literature report.[5]



^{1}H NMR spectrum for diphenylborinic acid (DMSO-d_6)

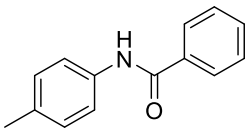
PhB(OH)$_2$: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.33 – 8.19 (m, 2H), 7.65 – 7.57 (m, 1H), 7.55 – 7.49 (m, 2H). The data of phenylboronic acid is consistent with the literature report.[6]



^{1}H NMR spectrum for phenylboronic acid ($CDCl_3$)

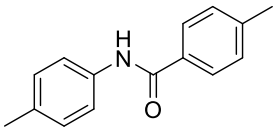
6. NMR data of the products

_N_-(_p_-Tolyl)benzamide (3a)[7]



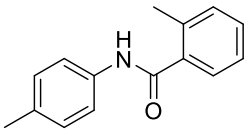
The title compound was prepared according to the general procedure and isolated as a white solid (52.7 mg, 0.249 mmol, 83%). M.p.: 155.8 – 157.4 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (brs, 1H), 7.86 – 7.84 (m, 2H), 7.54 – 7.50 (m, 3H), 7.46 – 7.42 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 135.5, 135.1, 134.3, 131.8, 129.6 × 2, 128.8 × 2, 127.1 × 2, 120.5 × 2, 21.0. **HRMS** (ESI): m/z calculated for $C_{14}H_{14}NO$ $[M + H]^+$: 212.1070; Found: 212.1068.

4-Methyl-_N_-(_p_-tolyl)benzamide (3b)[7]



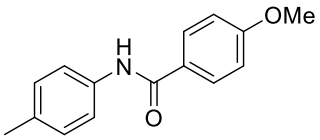
The title compound was prepared according to the general procedure and isolated as a white solid (41.9 mg, 0.186 mmol, 62%). M.p.: 165.4 – 166.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (brs, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 142.1, 135.6, 134.0, 132.2, 129.5 × 2, 129.3 × 2, 127.2 × 2, 120.6 × 2, 21.5, 21.0. **HRMS** (ESI) m/z calculated for $C_{15}H_{16}NO$ $[M + H]^+$: 226.1226; Found: 226.1228.

2-Methyl-_N_-(_p_-tolyl)benzamide (3c)[7]



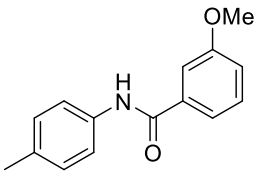
The title compound was prepared according to the general procedure and isolated as a white solid (45.2 mg, 0.201 mmol, 67%). M.p.: 145.4 – 146.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (brs, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.1, 136.7, 136.5, 135.6, 134.3, 131.3, 130.3, 129.7 ×2, 126.7, 126.0 ×2, 120.1, 21.0, 19.9. **HRMS** (ESI) m/z calculated for $C_{15}H_{16}NO$ $[M + H]^+$: 226.1226; Found: 226.1228.

4-Methoxy-_N_-(_p_-tolyl)benzamide (3d)[7]



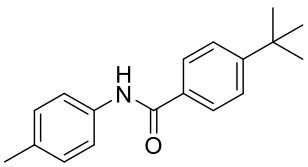
The title compound was prepared according to the general procedure and isolated as a yellow solid (56.3 mg, 0.233 mmol, 78%). M.p.: 147.0 – 147.8 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (brs, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.5, 162.4, 135.6, 134.0, 129.6 × 2, 129.0 × 2, 127.2, 120.5 × 2, 113.9 × 2, 55.5, 21.0. **HRMS** (ESI) m/z calculated for $C_{15}H_{16}NO_2$ $[M + H]^+$: 242.1176; Found: 242.1178.

3-Methoxy-*N*-(*p*-tolyl)benzamide (3e)[8]



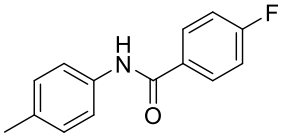
The title compound was prepared according to the general procedure and isolated as a brown solid (51.2 mg, 0.212 mmol, 71%). M.p.: 122.5 – 125.7 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (brs, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.38 – 7.36 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.08 – 7.05 (m, 1H), 3.85 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 160.0, 136.7, 135.4, 134.4, 129.8 ×2, 129.7 ×2, 120.4, 118.8, 118.1, 112.5, 55.6, 21.0. **HRMS** (ESI) m/z calculated for $C_{15}H_{16}NO_2$ $[M + H]^+$: 242.1176; Found: 242.1186.

4-(*tert*-Butyl)-*N*-(*p*-tolyl)benzamide (3f)[8]



The title compound was prepared according to the general procedure and isolated as a white solid (51.3 mg, 0.192 mmol, 64%). M.p.: 125.6 – 127.9 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 3H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 155.4, 135.6, 134.2, 132.3, 129.7 ×2, 127.0 × 2, 125.8 ×2, 120.3 ×2, 35.1, 31.3 ×3, 21.0. **HRMS** (ESI) m/z calculated for $C_{18}H_{22}NO$ $[M + H]^+$: 268.1696; Found: 268.1700.

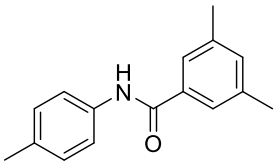
4-Fluoro-*N*-(*p*-tolyl)benzamide (3g)[8]



The title compound was prepared according to the general procedure and isolated as a white solid (39.9 mg, 0.174 mmol, 58%). M.p.: 174.0 – 174.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 – 7.85 (m, 3H),

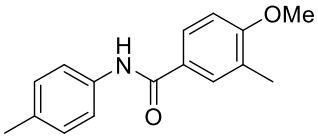
7.49 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.11 (m, 4H), 2.34 (s, 3H). **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -107.56. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.0 (d, *J* = 253.1 Hz), 164.8, 135.3, 134.5, 131.3 (d, *J* = 3.3 Hz), 129.7 × 2, 129.6 (d, *J* = 9.0 Hz) × 2, 120.6 × 2, 115.9 (d, *J* = 21.9 Hz) × 2, 21.0. **HRMS** (ESI) m/z calculated for $C_{14}H_{13}FNO$ $[M + H]^+$: 230.0976; Found: 230.0983.

3,5-Dimethyl-*N*-(*p*-tolyl)benzamide (3h)[9]



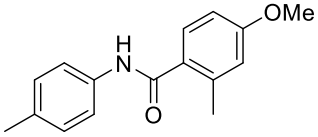
The title compound was prepared according to the general procedure and isolated as a yellow solid (44.5 mg, 0.186 mmol, 62%). M.p.: 123.9 – 125.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (brs, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 1.5 Hz, 2H), 7.18 – 7.16 (m, 3H), 2.38 (s, 6H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.2, 138.6 × 2, 135.6, 135.2, 134.2, 133.4, 129.7 × 2, 124.9 × 2, 120.3 × 2, 21.4 × 2, 21.0. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}NO$ $[M + H]^+$: 240.1383; Found: 240.1389.

4-Methoxy-3-methyl-*N*-(*p*-tolyl)benzamide (3i)



The title compound was prepared according to the general procedure and isolated as a yellow solid (51.8 mg, 0.203 mmol, 68%). M.p.: 124.5 – 125.2 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.63 (m, 3H), 7.57 – 7.48 (m, 2H), 7.23 – 7.12 (m, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.5, 160.7, 135.7, 134.0, 129.7 × 2, 129.6, 127.1, 126.8, 126.5, 120.3 × 2, 109.6, 55.6, 21.0, 16.5. **IR** (KBr): *v* 3282, 2972, 1646, 1592, 1568, 1519, 1393, 1047, 868, 508 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}NO_2$ $[M + H]^+$: 256.1332; Found: 256.1334.

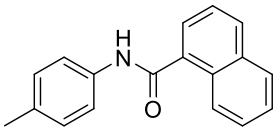
4-Methoxy-2-methyl-*N*-(*p*-tolyl)benzamide (3j)



The title compound was prepared according to the general procedure and isolated as a white solid (49.1 mg, 0.192 mmol, 64%). M.p.: 161.4 – 163.5 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 – 7.45 (m, 3H), 7.39 (brs, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.79 – 6.75 (m, 2H), 3.84 (s, 3H), 2.52 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 159.9, 139.1, 136.3, 134.0, 129.6 × 2,

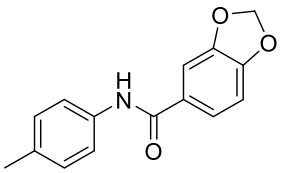
129.0, 127.5, 120.8, 117.3, 111.8 × 2, 56.1, 21.0, 20.5. **IR** (KBr): *v* 3279, 2972, 1732, 1644, 1607, 1520, 1398, 1263, 824, 506 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}NO_2$ $[M + H]^+$: 256.1332; Found: 256.1337.

_N_-(_p_-Tolyl)-1-naphthamide (3k)[10]



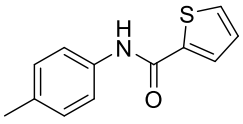
The title compound was prepared according to the general procedure and isolated as a yellow solid (47.9 mg, 0.183 mmol, 61%). M.p.: 192.8 – 194.2 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.36 – 8.34 (m, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.74 (brs, 1H), 7.70 (d, *J* = 7.0 Hz, 1H), 7.58 – 7.54 (m, 4H), 7.49 – 7.45 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.6, 135.6, 134.7, 134.4, 133.8, 131.0, 130.2, 129.7 ×2, 128.5 ×2, 127.4, 126.7, 125.4, 125.2, 124.8, 120.2, 21.1. HRMS (ESI) m/z calculated for $C_{18}H_{16}NO$ $[M + H]^+$: 262.1226; Found: 262.1216.

_N_-(_p_-Tolyl)benzo[_d_][1,3]dioxole-5-carboxamide (3l)[10]



The title compound was prepared according to the general procedure and isolated as a yellow solid (61.4 mg, 0.241 mmol, 80%). M.p.: 137.2 – 139.2 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (brs, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.34 (m, 1H), 7.20 – 7.13 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.05 (s, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.1, 150.7, 148.2, 135.4, 134.2, 129.7 × 2, 129.3, 121.8, 120.4 × 2, 108.2, 107.8, 101.9, 21.0. HRMS (ESI) m/z calculated for $C_{15}H_{14}NO_3$ $[M + H]^+$: 256.0968; Found: 256.0972.

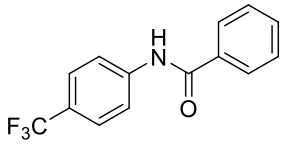
_N_-(_p_-Tolyl)thiophene-2-carboxamide (3m)[10]



The title compound was prepared according to the general procedure and isolated as a yellow solid (53.4 mg, 0.246 mmol, 82%). M.p.: 203.8 – 205.3 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (brs, 1H), 7.62 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.53 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.20 – 7.15 (m, 2H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.2, 139.6, 135.1, 134.4,

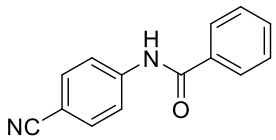
130.7, 129.6 × 2, 128.5, 127.9, 120.6 × 2, 21.0. **HRMS** (ESI) m/z calculated for $C_{12}H_{12}NOS$ $[M + H]^+$: 218.0634; Found: 218.0641.

***N*-(4-(Trifluoromethyl)phenyl)benzamide (3n)[7]**



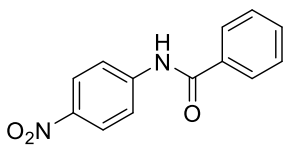
The title compound was prepared according to the general procedure and isolated as a white solid (59.2 mg, 0.223 mmol, 74%). M.p.: 206.6 – 208.2 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.59 (brs, 1H), 8.03 (d, J = 8.5 Hz, 2H), 7.98 (d, J = 7.1 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.57 – 7.53 (m, 2H). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -60.24. **^{13}C NMR** (101 MHz, DMSO-d_6) δ 166.1, 142.9 (q, J = 1.5 Hz), 134.5, 132.0, 128.5 × 2, 127.8 × 2, 126.0 × 2 (q, J = 4.0 Hz), 124.4 (q, J = 271.3 Hz), 123.6 (q, J = 32.0 Hz), 120.1 × 2. HRMS (ESI) m/z calculated for $C_{14}H_{11}F_3NO$ $[M + H]^+$: 266.0787; Found: 266.0788.

***N*-(4-Cyanophenyl)benzamide (3o)[7]**



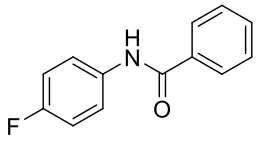
The title compound was prepared according to the general procedure and isolated as a white solid (42.1 mg, 0.189 mmol, 63%). M.p.: 171.8 – 173.4 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.23 (brs, 1H), 7.87 (d, J = 7.6 Hz, 2H), 7.81 (d, J = 8.8 Hz, 2H), 7.64 – 7.57 (m, 3H), 7.49 (t, J = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.1, 142.2, 134.2, 133.4 × 2, 132.6, 129.1 × 2, 127.3 × 2, 120.1 × 2, 119.0, 107.4. **HRMS** (ESI) m/z calculated for $C_{14}H_{11}N_2O$ $[M + H]^+$: 223.0866; Found: 223.0869.

***N*-(4-Nitrophenyl)benzamide (3p)[11]**



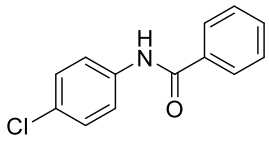
The title compound was prepared according to the general procedure and isolated as a yellow solid (54.8 mg, 0.226 mmol, 75%). M.p.: 199.8 –200.9 °C. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.28 (d, J = 9.1 Hz, 2H), 8.08 (brs, 1H), 7.91 – 7.89 (m, 2H), 7.86 (d, J = 9.2 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.56 – 7.52 (m, 2H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 169.0, 146.4, 144.8, 135.8, 133.4, 129.7 × 2, 128.8 × 2, 125.7 × 2, 121.3 × 2. **HRMS** (ESI) m/z calculated for $C_{13}H_{11}N_2O_3$ $[M + H]^+$: 243.0764; Found: 243.0762.

***N*-(4-Fluorophenyl)benzamide (3q)[11]**



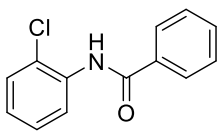
The title compound was prepared according to the general procedure and isolated as a white solid (40.7 mg, 0.189 mmol, 63%). M.p.: 184.5 – 187.3 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.82 (brs, 1H), 7.62 – 7.55 (m, 3H), 7.52 – 7.48 (m, 2H), 7.07 (t, *J* = 8.6 Hz, 2H). **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -117.48. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 159.7 (d, *J* = 243.9 Hz), 134.9, 134.0 (d, *J* = 3.1 Hz), 132.1, 129.0 × 2, 127.1 × 2, 122.3 × 2 (d, *J* = 8.2 Hz), 115.9 × 2 (d, *J* = 22.6 Hz). **HRMS** (ESI) m/z calculated for $C_{13}H_{11}FNO$ $[M + H]^+$: 216.0819; Found: 216.0828.

***N*-(4-Chlorophenyl)benzamide (3r)[7]**



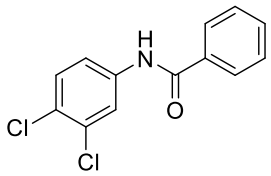
The title compound was prepared according to the general procedure and isolated as a white solid (50.3 mg, 0.217 mmol, 72%). M.p.: 188.2 – 190.7 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.38 (brs, 1H), 7.96 – 7.93 (m, 2H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.56 – 7.51 (m, 2H), 7.41 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.7, 138.2, 134.7, 131.7, 128.5 × 2, 128.4 × 2, 127.7 × 2, 127.3, 121.8 × 2. **HRMS** (ESI) m/z calculated for $C_{13}H_{11}{}^{35}ClNO$ $[M + H]^+$: 232.0524; Found: 232.0531; $C_{13}H_{11}{}^{37}ClNO$ $[M + H]^+$: 234.0494; Found: 234.0502.

***N*-(2-Chlorophenyl)benzamide (3s)[11]**



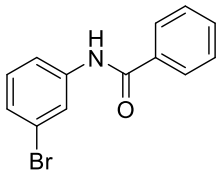
The title compound was prepared according to the general procedure and isolated as a white solid (62.6 mg, 0.270 mmol, 90%). M.p.: 120.2 – 122.8 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.58 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.46 (brs, 1H), 7.94 – 7.92 (m, 2H), 7.61 – 7.57 (m, 1H), 7.55 – 7.51 (m, 2H), 7.44 – 7.41 (m, 1H), 7.37 – 7.32 (m, 1H), 7.11 – 7.07 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.4, 134.9, 134.8, 132.3, 129.2, 129.1 × 2, 128.0, 127.2 × 2, 124.9, 123.2, 121.6. **HRMS** (ESI) m/z calculated for $C_{13}H_{11}{}^{35}ClNO$ $[M + H]^+$: 232.0524; Found: 232.0529; $C_{13}H_{11}{}^{37}ClNO$ $[M + H]^+$: 234.0494; Found: 234.0495.

***N*-(3,4-Dichlorophenyl)benzamide (3t)[12]**



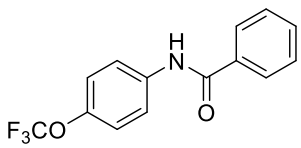
The title compound was prepared according to the general procedure and isolated as a white solid (53.1 mg, 0.200 mmol, 67%). M.p.: 148.6 – 149.3 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.88 – 7.87 (m, 1H), 7.84 – 7.82 (m, 2H), 7.58 – 7.55 (m, 1H), 7.48 – 7.44 (m, 3H), 7.38 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 137.5, 134.3, 133.0, 132.4, 130.7, 129.0 ×2, 127.9, 127.2 × 2, 122.1, 119.6. **HRMS** (ESI) m/z calculated for $C_{13}H_{10}{}^{35}Cl_2NO$ $[M + H]^+$: 266.0134; Found: 266.0138; $C_{13}H_{10}{}^{37}Cl_2NO$ $[M + H]^+$: 268.0104; Found: 268.0105.

***N*-(3-Bromophenyl)benzamide (3u)[13]**



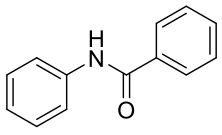
The title compound was prepared according to the general procedure and isolated as a white solid (57.3 mg, 0.208 mmol, 69%). M.p.: 138.7 – 140.1 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (brs, 1H), 7.88 (t, *J* = 2.0 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.55 – 7.50 (m, 2H), 7.44 – 7.40 (m, 2H), 7.26 – 7.24 (m, 1H), 7.17 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.1, 139.3, 134.5, 132.2, 130.4, 128.9 ×2, 127.6, 127.2 ×2, 123.4, 122.7, 119.0. **HRMS** (ESI) m/z calculated for $C_{13}H_{11}{}^{79}BrNO$ $[M + H]^+$: 276.0019; Found: 276.0018; $C_{13}H_{11}{}^{81}BrNO$ $[M + H]^+$: 277.9998; Found: 277.9994.

***N*-(4-(Trifluoromethoxy)phenyl)benzamide (3v)[14]**



The title compound was prepared according to the general procedure and isolated as a white solid (64.8 mg, 0.230 mmol, 77%). M.p.: 187.2 – 190.0 °C. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 7.94 – 7.92 (m, 2H), 7.81 (d, *J* = 9.1 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.53 – 7.49 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H). **^{19}F NMR** (376 MHz, Methanol-d_4) δ -59.62. **^{13}C NMR** (101 MHz, Methanol-d_4) δ 168.9, 146.7 (q, *J* = 2.1 Hz), 139.1, 136.0, 133.0, 129.7 ×2, 128.7 ×2, 123.4 ×2, 122.6 ×2, 122.0 (q, *J* = 254.7 Hz). **HRMS** (ESI) m/z calculated for $C_{14}H_{11}F_3NO_2$ $[M + H]^+$: 282.0736; Found: 282.0740.

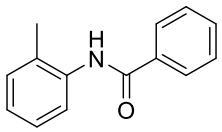
***N*-Phenylbenzamide (3w)[7]**



The title compound was prepared according to the general procedure and isolated as a white solid (42.0 mg, 0.213 mmol, 71%). M.p.: 161.6 – 162.4 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 – 7.83 (m, 3H), 7.70 – 7.61 (m,

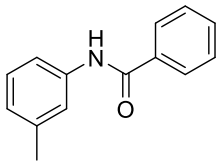
2H), 7.58 – 7.53 (m, 1H), 7.50 – 7.46 (m, 2H), 7.40 – 7.36 (m, 2H), 7.16 (td, *J* = 7.5, 1.1 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 138.0, 135.1, 132.0, 129.2 × 2, 128.9 × 2, 127.2 × 2, 124.7, 120.3 × 2. **HRMS** (ESI) m/z calculated for $C_{13}H_{12}NO$ $[M + H]^+$: 198.0913; Found: 198.0914.

***N*-(*o*-Tolyl)benzamide (3x)[7]**



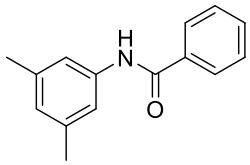
The title compound was prepared according to the general procedure and isolated as a white solid (37.6 mg, 0.178 mmol, 59%). M.p.: 145.2 – 146.5 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.89 (brs, 1H), 8.00 – 7.98 (m, 2H), 7.61 – 7.51 (m, 3H), 7.36 – 7.34 (m, 1H), 7.29 – 7.27 (m, 1H), 7.24 – 7.15 (m, 2H), 2.24 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.3, 136.4, 134.5, 133.7, 131.5, 130.3, 128.4 ×2, 127.6 ×2, 126.6, 126.0 ×2, 17.9. **HRMS** (ESI) m/z calculated for $C_{14}H_{14}NO$ $[M + H]^+$: 212.1070; Found: 212.1069.

***N*-(*m*-Tolyl)benzamide (3y)[7]**



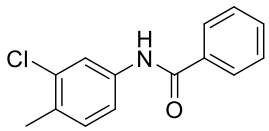
The title compound was prepared according to the general procedure and isolated as a yellow solid (44.3 mg, 0.210 mmol, 70%). M.p.: 124.9 – 125.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (brs, 1H), 7.86 – 7.83 (m, 2H), 7.54 – 7.50 (m, 2H), 7.47 – 7.40 (m, 3H), 7.25 – 7.21 (m, 1H), 6.95 (dd, *J* = 7.6, 1.4 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 139.1, 138.0, 135.2, 131.9, 129.0, 128.9 ×2, 127.1 ×2, 125.5, 121.0, 117.4, 21.6. **HRMS** (ESI) m/z calculated for $C_{14}H_{14}NO$ $[M + H]^+$: 212.1070; Found: 212.1068.

***N*-(3,5-Dimethylphenyl)benzamide (3z)[15]**



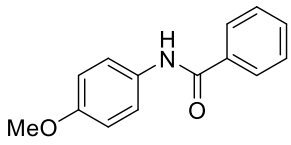
The title compound was prepared according to the general procedure and isolated as a yellow solid (50.9 mg, 0.226 mmol, 75%). M.p.: 141.3 – 143.0 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 11.1 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.53 – 7.49 (m, 1H), 7.46 – 7.41 (m, 2H), 7.29 (s, 2H), 6.79 (brs, 1H), 2.30 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 138.8, 137.9, 135.1, 131.8 ×2, 128.8 ×2, 127.1×2, 126.4, 118.2 ×2, 21.4 ×2. **HRMS** (ESI) m/z calculated for $C_{15}H_{16}NO$ $[M + H]^+$: 226.1226; Found: 226.1231.

***N*-(3-Chloro-4-methylphenyl)benzamide (3aa)[16]**



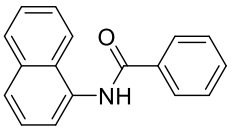
The title compound was prepared according to the general procedure and isolated as a yellow solid (53.4 mg, 0.217 mmol, 72%). M.p.: 124.4 – 125.9 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (brs, 1H), 7.85 – 7.82 (m, 2H), 7.72 (d, *J* = 2.3 Hz, 1H), 7.55 – 7.51(m, 1H), 7.47 – 7.39 (m, 3H), 7.17 (d, *J* = 8.2 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 136.8, 134.7, 134.6, 132.3, 132.1, 131.1, 128.9 ×2, 127.2 ×2, 121.1, 118.8, 19.6. **HRMS** (ESI) m/z calculated for $C_{14}H_{13}{}^{35}ClNO$ [M + H]$^+$: 246.0680; Found: 246.0686; $C_{14}H_{13}{}^{37}ClNO$ [M + H]$^+$: 248.0651; Found: 248.0658.

***N*-(4-Methoxyphenyl)benzamide (3ab)[7]**



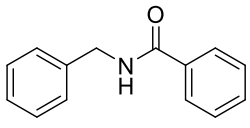
The title compound was prepared according to the general procedure and isolated as a yellow solid (41.5 mg, 0.183 mmol, 61%). M.p.: 149.0 – 151.1 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.81 (brs, 1H), 7.55 – 7.52 (m, 3H), 7.49 –7.45 (m, 2H), 6.92 – 6.89 (m, 2H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.7, 135.1, 131.8, 131.1, 128.8 ×2, 127.1 ×2, 122.3, 114.3 × 4, 55.6. **HRMS** (ESI) m/z calculated for $C_{14}H_{14}NO_2$ [M + H]$^+$: 228.1019; Found: 228.1027.

***N*-(Naphthalen-1-yl)benzamide (3ac)[7]**



The title compound was prepared according to the general procedure and isolated as a yellow solid (39.9 mg, 0.161 mmol, 54%). M.p.: 160.0 – 161.5 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 (brs, 1H), 8.07 (d, *J* = 7.4 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 2H), 7.92 (t, *J* = 5.7 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.52 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.4, 135.0, 134.3, 132.5, 132.1, 129.0 ×2, 129.0, 127.6, 127.3 ×2, 126.6, 126.3, 126.2, 125.9, 121.4, 120.8. **HRMS** (ESI) m/z calculated for $C_{17}H_{14}NO$ [M + H]$^+$: 248.1070; Found: 248.1078.

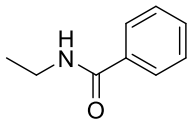
***N*-Benzylbenzamide (3ad)[11]**



The title compound was prepared according to the general procedure and isolated as a white solid (38.6 mg, 0.183 mmol, 61%). M.p.: 120.2 – 121.2 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 8.4, 1.4 Hz, 2H),

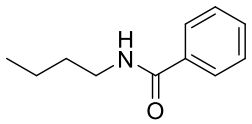
7.42 – 7.40 (m, 1H), 7.33 (td, *J* = 7.4, 1.4 Hz, 2H), 7.27 – 7.25 (m, 4H), 7.23 – 7.19 (m, 1H), 6.60 (brs, 1H), 4.55 (dd, *J* = 5.7, 1.8 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 138.3, 134.4, 131.6, 128.8 × 2, 128.6 × 2, 127.9 × 2, 127.6, 127.1 × 2, 44.1. **HRMS** (ESI) m/z calculated for $C_{14}H_{14}NO$ $[M + H]^+$: 212.1070; Found: 212.1073.

_N_-Ethylbenzamide (3ae)[11]



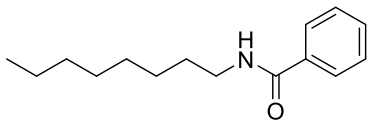
The title compound was prepared according to the general procedure and isolated as a white solid (24.5 mg, 0.164 mmol, 55%). M.p.: 119.9 – 120.2 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.75 (m, 2H), 7.51 – 7.47 (m, 1H), 7.44 – 7.38 (m, 2H), 6.22 (brs, 1H), 3.50 (qd, *J* = 7.3, 5.6 Hz, 2H), 1.25 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.7, 134.9, 131.5, 128.7× 2, 126.9 × 2, 35.1, 15.0. **HRMS** (ESI) m/z calculated for $C_9H_{12}NO$ $[M + H]^+$: 150.0913; Found: 150.0913.

_N_-Butylbenzamide (3af)[17]



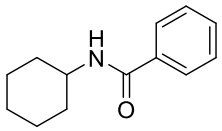
The title compound was prepared according to the general procedure and isolated as a yellow oil (28.2 mg, 0.159 mmol, 53%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.40 (m, 3H), 6.20 (brs, 1H), 3.46 (q, *J* = 6.8 Hz, 2H), 1.62 – 1.58 (m, 2H), 1.44 – 1.41 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.7, 135.0, 131.4, 128.7 × 2, 126.9 × 2, 39.9, 31.9, 20.3, 13.9. **HRMS** (ESI) m/z: calculated for $C_{11}H_{16}NO$ $[M + H]^+$: 178.1226; Found: 178.1229.

_N_-Octylbenzamide (3ag)[17]



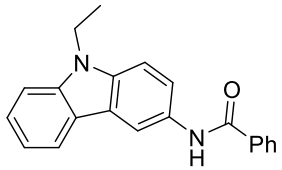
The title compound was prepared according to the general procedure and isolated as a white solid (41.2 mg, 0.177 mmol, 59%). M.p.: 119.8 – 119.9 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.75 (m, 2H), 7.51 – 7.46 (m, 1H), 7.44 – 7.39 (m, 2H), 6.23 (brs, 1H), 3.44 (td, *J* = 7.3, 5.7 Hz, 2H), 1.64 – 1.59 (m, 2H), 1.33 – 1.26 (m, 10H), 0.90 – 0.86 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.7, 134.9, 131.4, 128.6 × 2, 127.0 × 2, 40.2, 31.9, 29.8, 29.4, 29.3, 27.1, 22.7, 14.2. **HRMS** (ESI) m/z calculated for $C_{15}H_{24}NO$ $[M + H]^+$: 234.1852; Found: 234.1854.

_N_-Cyclohexylbenzamide (3ah)[18]



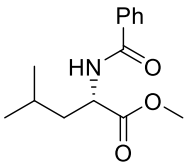
The title compound was prepared according to the general procedure and isolated as a white solid (32.3 mg, 0.159 mmol, 53%). M.p.: 137.8 – 139.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 – 7.74 (m, 2H), 7.51 – 7.47 (m, 1H), 7.45 – 7.40 (m, 2H), 5.96 (brs, 1H), 4.03 – 3.94 (m, 1H), 2.06 – 2.02 (m, 2H), 1.79 – 1.72 (m, 2H), 1.69 – 1.64 (m, 1H), 1.49 – 1.38 (m, 2H), 1.29 – 1.19 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.8, 135.3, 131.4, 128.7 × 2, 126.9 × 2, 48.8, 33.4 × 2, 25.7 × 2, 25.1. **HRMS** (ESI) m/z calculated for $C_{13}H_{18}NO$ $[M + H]^+$: 204.1383; Found: 204.1382.

_N_-(9-Ethyl-9H-carbazol-3-yl)benzamide (3ai)[19]



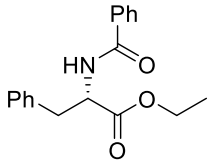
The title compound was prepared according to the typical procedure and isolated as a yellow oil (73.2 mg, 0.233 mmol, 78%). M.p.: 184.8 – 185.8 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.44 (brs, 1H), 8.12 (s, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 7.3 Hz, 2H), 7.63 (d, J = 8.4 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.40 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 8.9 Hz,1H), 7.21 (t, J = 7.4 Hz, 1H), 4.33 (q, J = 7.3 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 140.5, 137.5, 135.3, 131.7, 129.8, 128.8 × 2, 127.2 × 2, 126.0, 123.1, 122.9, 120.8, 119.9, 118.9, 113.3, 108.7 × 2, 37.7, 13.9. **HRMS** (ESI) m/z calculated for $C_{21}H_{19}N_2O$ $[M + H]^+$: 315.1492; Found: 315.1498.

Methyl benzoyl-*L*-leucinate (3aj)[20]



The title compound was prepared according to the typical procedure and isolated as a yellow oil (33.1 mg, 0.133 mmol, 44%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.43 (m, 1H), 6.54 (d, J = 8.3 Hz, 1H), 4.90 – 4.84 (m, 1H), 3.77 (s, 3H), 1.79 – 1.67 (m, 3H), 1.01 – 0.97 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.9, 167.2, 134.0, 131.9, 128.8 × 2, 127.2 × 2, 52.6, 51.2, 42.0, 25.1, 23.0, 22.2. **HRMS** (ESI) m/z calculated for $C_{14}H_{20}NO_3$ $[M + H]^+$: 250.1438; Found: 250.1437.

Ethyl benzoyl-*L*-phenylalaninate (3ak)[21]



The title compound was prepared according to the typical procedure and isolated as a yellow oil (35.4 mg, 0.119 mmol, 40%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.72 (m, 2H), 7.53 – 7.49 (m, 1H), 7.45 – 7.41 (m, 2H), 7.32 – 7.25 (m, 2H), 7.16 – 7.14 (m, 2H), 6.64 (d, J = 7.6 Hz, 1H), 5.10 – 5.05 (m, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.32 – 3.22 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.7, 166.9, 136.0, 134.0, 131.9, 129.5 × 2, 128.7 × 4, 127.3, 127.1 × 2, 61.8, 53.6, 38.0, 14.3. **HRMS** (ESI) m/z calculated for $C_{18}H_{20}NO_3$ $[M + H]^+$: 298.1438; Found: 298.1440.

7. DFT calculations for the reaction mechanism

DFT calculations were performed to gain insight into the mechanisms of the catalyst-free cross-coupling of isocyanates and triarylboranes.

Computational details

All theoretical calculations were carried out using density functional theory with the Gaussian 16 program package,[22] and the structures were illustrated by CYLview (**Figure S1**).[23] The calculations were carried out for all molecules using the B3LYP functional[24-26] and 6-31G**[27] basis set with Grimme's D3 dispersion corrections and Becke-Johnson damping.[28] The effect of solvation in 1,1,2-trichloroethane were accounted for implicitly using the SMD polarizable continuum model.[29] Intrinsic reaction coordinate (IRC)[30] calculations were conducted to verify the critical reaction steps. The energetic results were then improved by the single-point calculations at the B3LYP+D3BJ/6-311++G**[31,32]/SMD. For comparison, the performances of several popular DFT functionals (e.g., B3LYP, BP86,[33,34] M06-2X[35]), and basis sets (6-31G**, 6-311++G**, def2-SVP,[36] def2-TZVPP[37]) were studied (see Table S2), implying that our method used in this study is reliable.

Table S2. Computed free energy barriers of transition states (in kcal/mol) using different levels of theories.

Method	△△‡G(**TS1**)
B3LYP+D3BJ/6-311++G**/SMD//B3LYP+D3BJ/6-31G**/SMD	23.1
B3LYP+D3BJ/def2-TZVPP/SMD//B3LYP+D3BJ/def2-SVP/SMD	25.8
M06-2X+D3/6-311++G**/SMD// M06-2X+D3/6-31G**/SMD	21.5
M06-2X+D3/def2-TZVPP/SMD// M06-2X+D3/def2-SVP/SMD	23.8
BP86+D3BJ/def2-TZVPP/SMD//BP86+D3BJ/def2-SVP/SMD	16.2

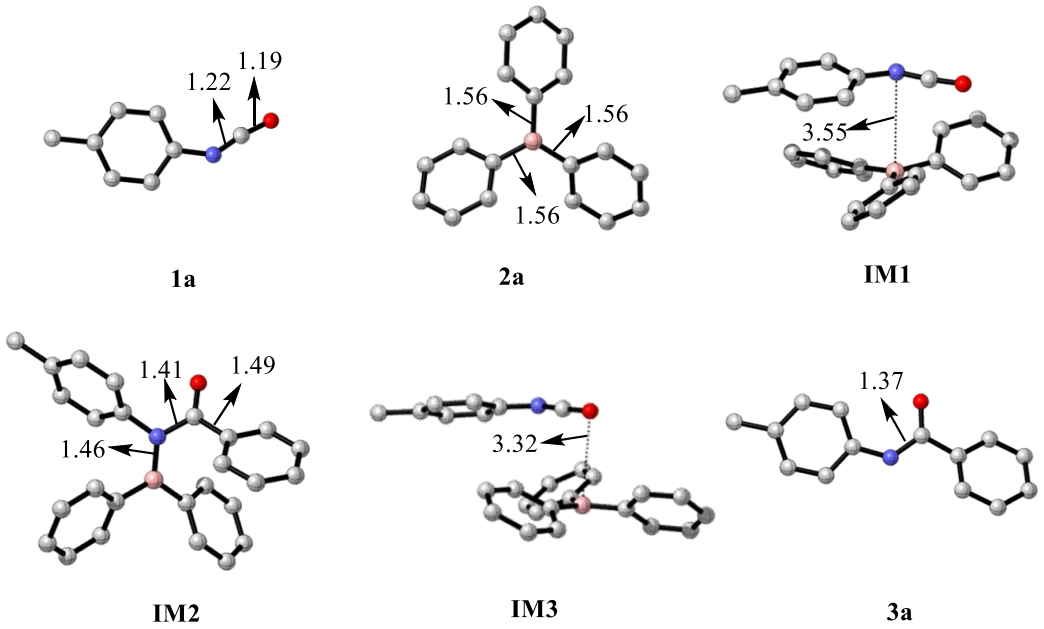


Figure S1. Computed structures of **1a**, **2a**, **IM1**, **IM2**, **IM3**, **3a**, Part of the hydrogen atoms are omitted for clarity, selected bond distance is given in Å (color code, C: grey, N: blue, O: red, H: white, B: pink).

1a

Gibbs Free Energy = -439.1123207

N	0.2092	-2.63978	-0.34139
C	1.002466	-3.52237	-0.62533
O	1.897827	-4.26698	-0.87872
C	-1.17831	-2.47521	-0.21291
C	-1.66898	-1.20895	0.153035
C	-2.07806	-3.53923	-0.4366
C	-3.04962	-1.01292	0.291306
H	-0.96389	-0.3914	0.328009
C	-3.45195	-3.32346	-0.29351
H	-1.69153	-4.52397	-0.71799
C	-3.96629	-2.05961	0.070242
H	-3.42269	-0.02391	0.578759
H	-4.14306	-4.15582	-0.46735
C	-5.45532	-1.83908	0.19723
H	-5.93682	-1.78924	-0.79682
H	-5.93976	-2.66388	0.747443
H	-5.67974	-0.89663	0.722186

2a

Gibbs Free Energy = -719.86755

B	-0.52682	-2.674	0.000023
C	1.036393	-2.6709	-0.0016
C	1.772825	-3.67728	-0.6616
C	1.770181	-1.66155	0.656814
C	3.1666	-3.67041	-0.67714
H	1.240632	-4.46841	-1.1809
C	3.164004	-1.66275	0.669267
H	1.235931	-0.87257	1.177258
C	3.865591	-2.66515	-0.00471
H	3.708465	-4.44891	-1.20646
H	3.703864	-0.88205	1.197401
H	4.951887	-2.66295	-0.0059
C	-1.31116	-1.3218	0.014774
C	-2.55611	-1.20115	0.667664
C	-0.80383	-0.17072	-0.62428
C	-3.25217	0.006237	0.694479
H	-2.97545	-2.06628	1.172151
C	-1.50656	1.033097	-0.6253
H	0.150393	-0.22806	-1.13904
C	-2.73073	1.125401	0.041144

H	-4.20129	0.075394	1.218158
H	-1.10017	1.899723	-1.13879
H	-3.276	2.064834	0.051101
C	-1.30576	-4.02931	-0.01315
C	-2.55177	-4.15475	-0.66311
C	-0.79229	-5.17851	0.624372
C	-3.24304	-5.36491	-0.68861
H	-2.97577	-3.29117	-1.16636
C	-1.49017	-6.38514	0.626696
H	0.162927	-5.11744	1.136857
C	-2.71553	-6.48216	-0.03687
H	-4.19313	-5.43775	-1.21003
H	-1.07906	-7.25028	1.138941
H	-3.25706	-7.42377	-0.04582

IM1

Gibbs Free Energy = -1158.975603

B	-2.32189	-1.9472	-1.9693
C	-1.91083	-2.99568	-0.88489
C	-0.97607	-4.01456	-1.1682
C	-2.45389	-2.96771	0.416859
C	-0.59935	-4.95044	-0.20671
H	-0.5299	-4.06346	-2.15655
C	-2.09694	-3.91089	1.37922
H	-3.18295	-2.20644	0.668397
C	-1.16548	-4.90409	1.069628
H	0.131284	-5.71644	-0.45024
H	-2.54162	-3.87123	2.369064
H	-0.88009	-5.63671	1.819229
C	-2.74761	-0.50139	-1.54705
C	-3.6832	0.238635	-2.30148
C	-2.22534	0.116163	-0.39148
C	-4.09767	1.510568	-1.91089
H	-4.09806	-0.19394	-3.20526
C	-2.61584	1.397938	-0.00596
H	-1.49227	-0.41507	0.207364
C	-3.56193	2.094841	-0.76055
H	-4.83144	2.048738	-2.50408
H	-2.18733	1.852183	0.882829
H	-3.87653	3.089234	-0.45692
C	-2.30012	-2.33861	-3.48275
C	-1.99339	-1.39276	-4.48354
C	-2.6018	-3.64962	-3.90761
C	-1.98469	-1.73483	-5.83461
H	-1.75	-0.37519	-4.19393
C	-2.62183	-3.99366	-5.25779
H	-2.853	-4.3997	-3.16533
C	-2.30935	-3.03589	-6.22534
H	-1.73621	-0.98806	-6.58309
H	-2.88083	-5.0052	-5.55704
H	-2.31917	-3.30173	-7.2785
N	-5.76601	-3.02427	-3.6293
C	-5.69666	-2.11902	-4.421
O	-5.64555	-1.33089	-5.29974
C	-5.75766	-3.26428	-2.25241
C	-5.98865	-2.23833	-1.32733
C	-5.51316	-4.56563	-1.80373
C	-5.9739	-2.5255	0.033971
H	-6.16689	-1.22788	-1.67787
C	-5.49541	-4.83235	-0.43759
H	-5.33011	-5.35107	-2.52872
C	-5.72962	-3.82285	0.504481
H	-6.14386	-1.72174	0.744892
H	-5.2881	-5.84267	-0.09694
C	-5.72197	-4.12393	1.980615
H	-6.72154	-4.41172	2.330459
H	-5.04485	-4.95048	2.213051
H	-5.41333	-3.25124	2.563575

TS1

Gibbs Free Energy = -1158.943045

B	-2.93889	-1.8858	-1.89246
C	-1.92066	-2.36189	-0.73069
C	-0.67574	-2.95077	-1.00978
C	-2.25219	-2.20868	0.630148
C	0.197697	-3.35004	0.004921
H	-0.38361	-3.11444	-2.0419
C	-1.38932	-2.60253	1.653264
H	-3.21252	-1.7782	0.902398
C	-0.15399	-3.17508	1.343545
H	1.151176	-3.80404	-0.25209
H	-1.68332	-2.46882	2.690939
H	0.521058	-3.48698	2.13543
C	-3.06535	-0.19676	-2.01701
C	-3.51524	0.39232	-3.23306

C	-2.52194	0.68119	-1.03968	C	1.145263	-0.63196	2.276991
C	-3.47047	1.763769	-3.43976	C	3.370377	-2.20935	1.706488
H	-3.92178	-0.25418	-4.00447	H	2.819962	-1.97406	-0.35489
C	-2.46763	2.052028	-1.24557	C	1.953213	-1.09095	3.313992
H	-2.15133	0.264171	-0.10928	H	0.275089	-0.02708	2.511875
C	-2.94968	2.594956	-2.44271	C	3.066007	-1.88801	3.03035
H	-3.83429	2.190558	-4.36906	H	4.232756	-2.83005	1.481295
H	-2.05166	2.704065	-0.48385	H	1.715472	-0.83498	4.342395
H	-2.91399	3.668934	-2.6004	H	3.692135	-2.25561	3.838231
C	-2.72112	-2.52678	-3.35082	C	-0.94381	2.069359	-1.08533
C	-1.57339	-2.1904	-4.09562	C	-1.34182	2.74855	-2.24361
C	-3.63682	-3.3977	-3.96253	C	0.032797	2.632127	-0.25305
C	-1.33616	-2.71446	-5.36568	C	-0.74202	3.95641	-2.58678
H	-0.85678	-1.48826	-3.67607	H	-2.10777	2.308895	-2.87309
C	-3.41307	-3.92719	-5.23739	C	0.618552	3.851486	-0.58849
H	-4.54965	-3.67035	-3.44281	H	0.325273	2.12633	0.661089
C	-2.25787	-3.59246	-5.9429	C	0.239938	4.509637	-1.75968
H	-0.4382	-2.43324	-5.90953	H	-1.03769	4.468132	-3.49739
H	-4.14486	-4.59883	-5.6786	H	1.369829	4.286135	0.06337
H	-2.08028	-4.00169	-6.93338	H	0.705181	5.453724	-2.02642
N	-4.44699	-2.04845	-1.36732	C	1.191834	-0.05743	-1.63079
C	-4.8184	-0.81322	-1.27938	C	2.492847	0.461181	-1.76801
O	-5.64218	-0.01864	-0.97412	C	0.472708	-0.33928	-2.80816
C	-5.20946	-3.15032	-0.88228	C	3.04265	0.714321	-3.02335
C	-6.53957	-3.01364	-0.47703	H	3.071499	0.685938	-0.87701
C	-4.58273	-4.4003	-0.81713	C	1.024049	-0.11015	-4.06746
C	-7.23255	-4.12946	-0.00948	H	-0.53113	-0.74868	-2.7356
H	-7.03425	-2.05046	-0.52595	C	2.309188	0.425435	-4.17691
C	-5.29259	-5.50089	-0.3497	H	4.041549	1.132908	-3.1051
H	-3.55056	-4.50304	-1.12725	H	0.453294	-0.34358	-4.96154
C	-6.62767	-5.38918	0.064634	H	2.738399	0.615088	-5.15649
H	-8.26673	-4.01431	0.302128	N	-0.86604	-0.16216	-0.0326
H	-4.79685	-6.46663	-0.30378	C	-1.62861	0.78731	-0.74327
C	-7.37732	-6.59159	0.577738	O	-2.81023	0.607151	-1.00855
H	-7.36083	-7.41029	-0.15034	C	-1.6099	-1.07927	0.785838
H	-6.926	-6.97491	1.500434	C	-2.47538	-0.60456	1.777606
H	-8.42172	-6.349	0.790915	C	-1.4436	-2.45351	0.621259
				C	-3.15217	-1.5009	2.596529
IM2				H	-2.60591	0.464744	1.908174
Gibbs Free Energy = -1159.010212				C	-2.11733	-3.34515	1.45706
				H	-0.78223	-2.8238	-0.1557
B	0.565165	-0.36241	-0.23331	C	-2.98249	-2.88769	2.455634
C	1.434404	-0.93417	0.931003	H	-3.81806	-1.12045	3.36665
C	2.56892	-1.72655	0.671973	H	-1.97111	-4.41336	1.323818

C	-3.72301	-3.84603	3.353022	O	1.510135	1.980396	1.4249
H	-3.41618	-4.87954	3.171635	C	-0.44648	-0.69082	2.86963
H	-3.5441	-3.61957	4.410136	C	0.557029	-1.64681	3.080981
H	-4.80572	-3.784	3.191273	C	-1.78708	-1.03345	3.057711
				C	0.206477	-2.93599	3.467846
IM3				H	1.596441	-1.37535	2.928211
Gibbs Free Energy = -1158.975056				C	-2.11899	-2.33009	3.44555
				H	-2.5541	-0.28917	2.877311
B	0.32696	0.890331	-1.48047	C	-1.13457	-3.30271	3.658006
C	0.840315	2.217539	-2.12749	H	0.98978	-3.67286	3.623864
C	-0.02815	3.053726	-2.85916	H	-3.16479	-2.59125	3.580415
C	2.181443	2.634452	-1.99799	C	-1.49626	-4.69824	4.097286
C	0.420674	4.234194	-3.44976	H	-0.90789	-5.45004	3.561324
H	-1.06866	2.7649	-2.97416	H	-1.29988	-4.83861	5.167516
C	2.631333	3.827434	-2.56114	H	-2.55576	-4.90736	3.926221
H	2.873443	2.021132	-1.42966				
C	1.752197	4.626733	-3.29595	**TS2**			
H	-0.26603	4.851666	-4.02175	Gibbs Free Energy = -1158.913464			
H	3.665451	4.133628	-2.43152				
H	2.102771	5.551913	-3.74449	B	-3.76829	1.555979	1.686063
C	-1.12009	0.832729	-0.89006	C	-3.24336	3.051493	1.507267
C	-1.8876	-0.35065	-0.90271	C	-3.70303	3.862333	0.45545
C	-1.69937	1.970409	-0.28944	C	-2.25168	3.583917	2.346559
C	-3.16622	-0.39726	-0.35023	C	-3.18916	5.142438	0.240258
H	-1.47732	-1.24443	-1.3623	H	-4.48429	3.488734	-0.20262
C	-2.96597	1.925052	0.290392	C	-1.73674	4.86625	2.146234
H	-1.13341	2.896194	-0.25702	H	-1.87942	2.986416	3.174652
C	-3.70536	0.740414	0.255522	C	-2.20255	5.64989	1.088482
H	-3.73915	-1.31937	-0.38263	H	-3.56245	5.746144	-0.58266
H	-3.37932	2.810811	0.763979	H	-0.97312	5.254658	2.8149
H	-4.69715	0.703807	0.697208	H	-1.80451	6.648105	0.929765
C	1.257687	-0.36385	-1.41107	C	-5.42281	1.39793	1.62646
C	2.287376	-0.57312	-2.35302	C	-6.0596	0.286283	1.003534
C	1.112663	-1.33147	-0.39417	C	-6.25786	2.476789	2.041639
C	3.122616	-1.68718	-2.28705	C	-7.43562	0.222696	0.878606
H	2.425512	0.144948	-3.15527	H	-5.44407	-0.53625	0.654244
C	1.958004	-2.43558	-0.30607	C	-7.63931	2.413114	1.921735
H	0.329339	-1.21258	0.344271	H	-5.79458	3.348375	2.493588
C	2.964446	-2.61805	-1.25719	C	-8.22672	1.280744	1.352229
H	3.89934	-1.82892	-3.03303	H	-7.9072	-0.63985	0.418579
H	1.827871	-3.15248	0.499401	H	-8.25953	3.233045	2.269032
H	3.62113	-3.4814	-1.19829	H	-9.30772	1.221956	1.264992
N	-0.14093	0.609465	2.457087	C	-2.97491	0.424166	0.880779
C	0.739554	1.241632	1.931659	C	-2.53289	0.661533	-0.43264

C	-2.72753	-0.85122	1.418148	H	3.326387	-0.31791	0.474243
C	-1.88411	-0.32354	-1.17792	C	2.948041	-2.99755	2.524473
H	-2.69236	1.640085	-0.8775	H	1.110239	-4.08964	2.810754
C	-2.07372	-1.84301	0.683436	H	4.616775	-1.71971	2.044684
H	-3.04427	-1.07625	2.432794	H	3.516583	-3.61667	3.212629
C	-1.65141	-1.5832	-0.62112	C	1.248907	0.368235	-1.39074
H	-1.55403	-0.10718	-2.19049	C	0.660069	1.596792	-1.74757
H	-1.8937	-2.8173	1.13004	C	2.383318	-0.04432	-2.11446
H	-1.14271	-2.35169	-1.19621	C	1.183073	2.384957	-2.77184
N	-5.74057	0.291855	4.107843	H	-0.21399	1.951276	-1.20486
C	-4.87873	0.813858	3.411954	C	2.903131	0.730129	-3.15178
O	-3.67589	1.17931	3.284782	H	2.856748	-0.9902	-1.86881
C	-5.59849	-0.38914	5.335819	C	2.306413	1.949647	-3.4787
C	-4.35676	-0.55838	5.967859	H	0.718108	3.334779	-3.01964
C	-6.75285	-0.91172	5.924601	H	3.773195	0.385725	-3.70329
C	-4.28859	-1.24606	7.174634	H	2.714582	2.558273	-4.28038
H	-3.45824	-0.1496	5.517889	O	-0.72883	-0.53535	-0.06181
C	-6.667	-1.59614	7.135251	H	-1.20573	-0.03429	-0.73956
H	-7.70625	-0.77319	5.425561				
C	-5.43764	-1.77824	7.780306	**3a**			
H	-3.32389	-1.37144	7.659088	Gibbs Free Energy = -671.3860386			
H	-7.57077	-1.99613	7.58617				
C	-5.33934	-2.53658	9.078945	C	-1.00351	2.227066	-0.97432
H	-4.87645	-3.51946	8.927405	C	-1.57168	3.120689	-1.89212
H	-4.72155	-2.00055	9.807139	C	0.379501	2.265723	-0.74522
H	-6.32559	-2.69903	9.521917	C	-0.7694	4.019365	-2.58985
				H	-2.64456	3.094575	-2.04692
H_2O				C	1.180256	3.172542	-1.43867
Gibbs Free Energy = -76.46416249				H	0.83749	1.616674	-0.00469
				C	0.609352	4.045957	-2.36581
O	-0.79718	-0.20389	0	H	-1.21794	4.700481	-3.30644
H	0.168678	-0.14992	0	H	2.248429	3.202004	-1.24754
H	-1.06875	0.724623	0	H	1.235191	4.749727	-2.90606
				N	-1.36043	0.143768	0.211128
Ph_2BOH				C	-1.93497	1.29681	-0.25382
Gibbs Free Energy = -564.1051826				O	-3.12851	1.570585	-0.11598
				C	-1.9468	-0.89824	0.955017
B	0.627514	-0.51062	-0.24842	C	-3.27863	-0.89637	1.392287
C	1.471392	-1.39197	0.731609	C	-1.12524	-1.98984	1.279082
C	0.86836	-2.46418	1.417678	C	-3.75887	-1.97552	2.134787
C	2.834916	-1.14514	0.977253	H	-3.91862	-0.06111	1.150057
C	1.594528	-3.26299	2.298714	C	-1.62468	-3.05526	2.017966
H	-0.1848	-2.67047	1.250338	H	-0.08894	-1.99296	0.951173
C	3.566901	-1.93337	1.865843	C	-2.95501	-3.07287	2.460836

H	-4.79314	-1.95792	2.468401
H	-0.96832	-3.88772	2.257533
C	-3.49929	-4.24441	3.237837
H	-3.75021	-5.08069	2.572942
H	-2.76834	-4.61856	3.962087
H	-4.40925	-3.97383	3.780985
H	-0.40098	-0.023	-0.05985

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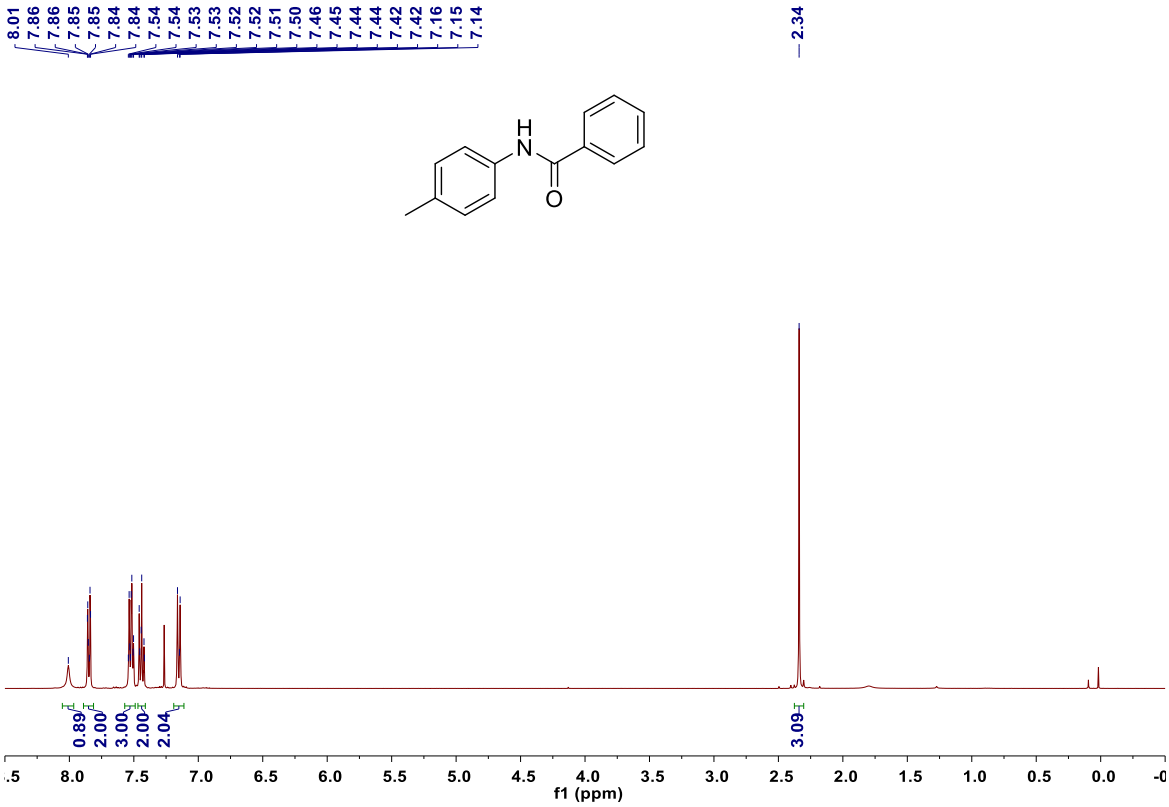
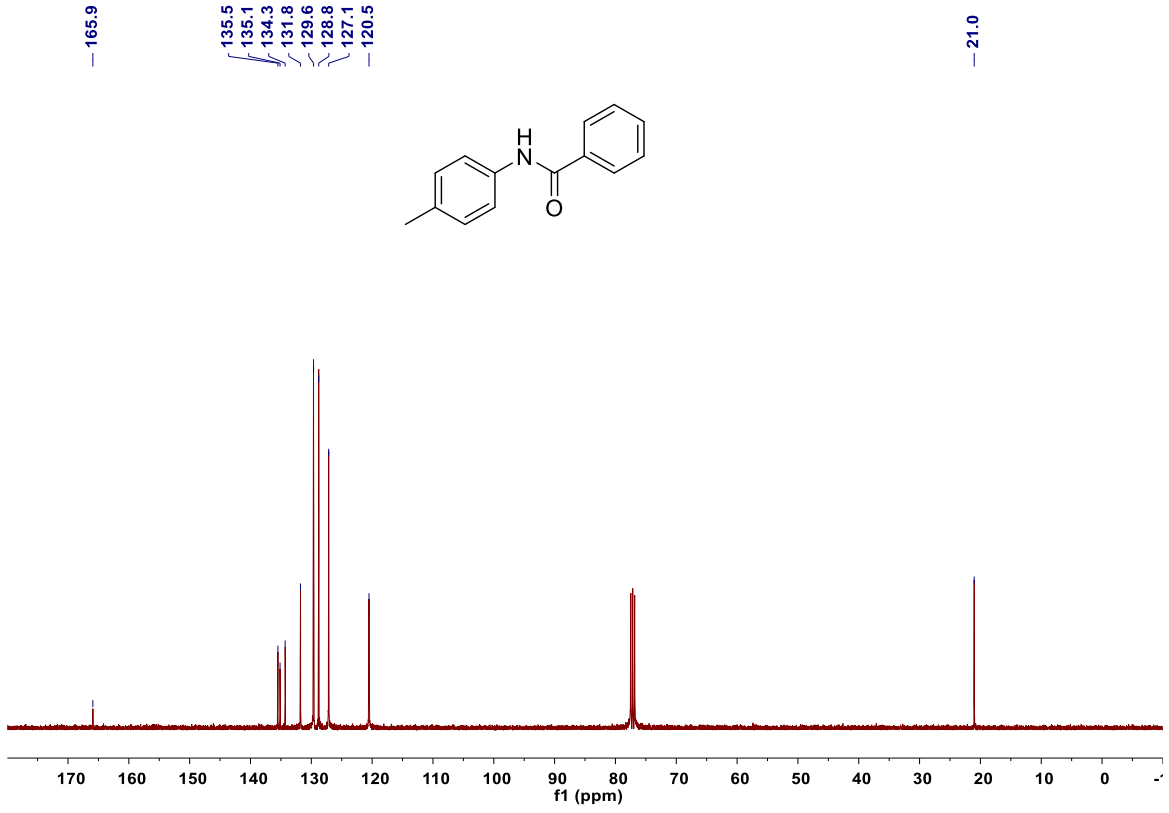
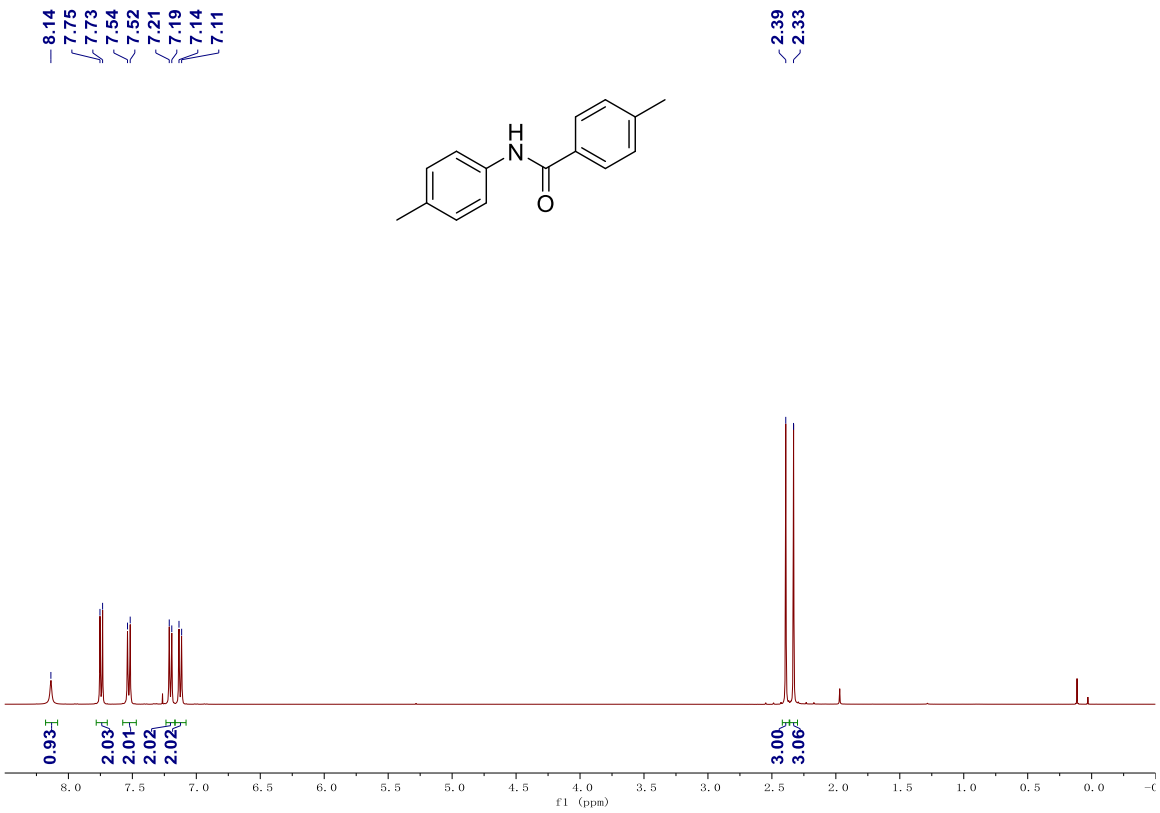
9. NMR spectra of the products



^{1}H NMR spectrum for compound **3a** ($CDCl_3$)



^{13}C NMR spectrum for compound **3a** ($CDCl_3$)



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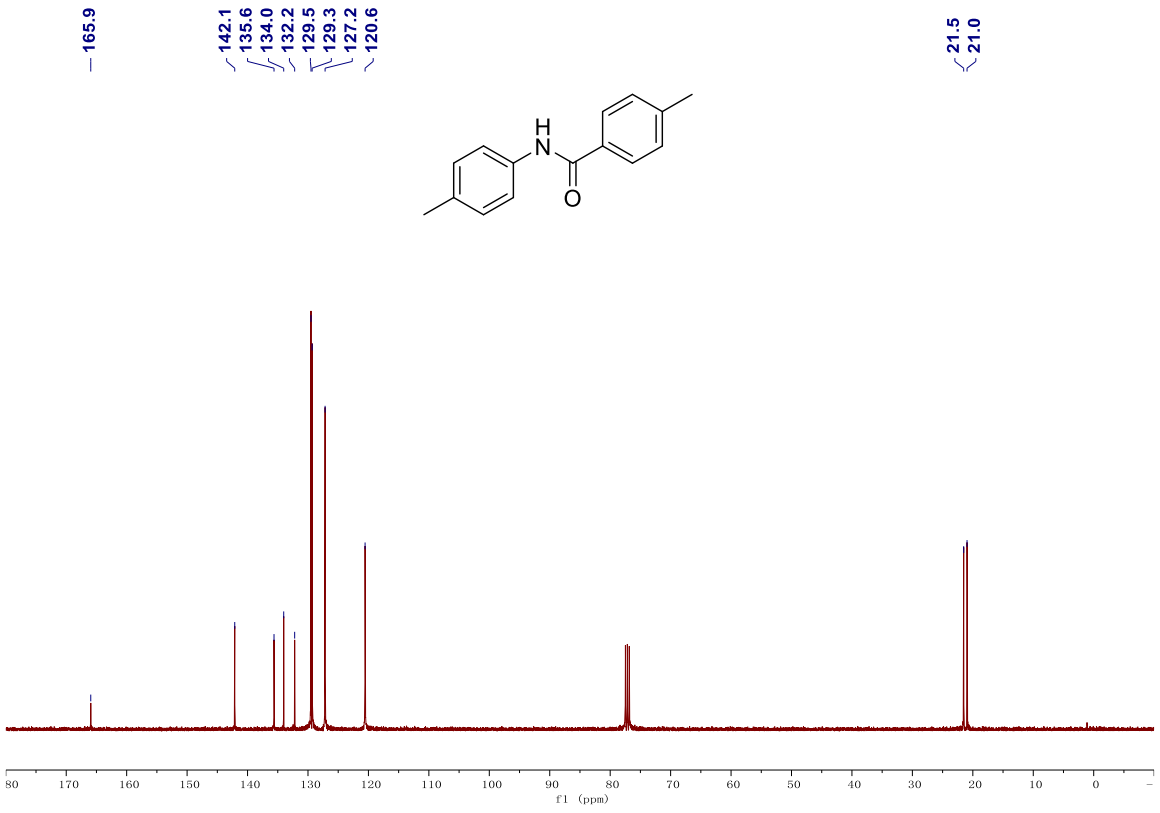
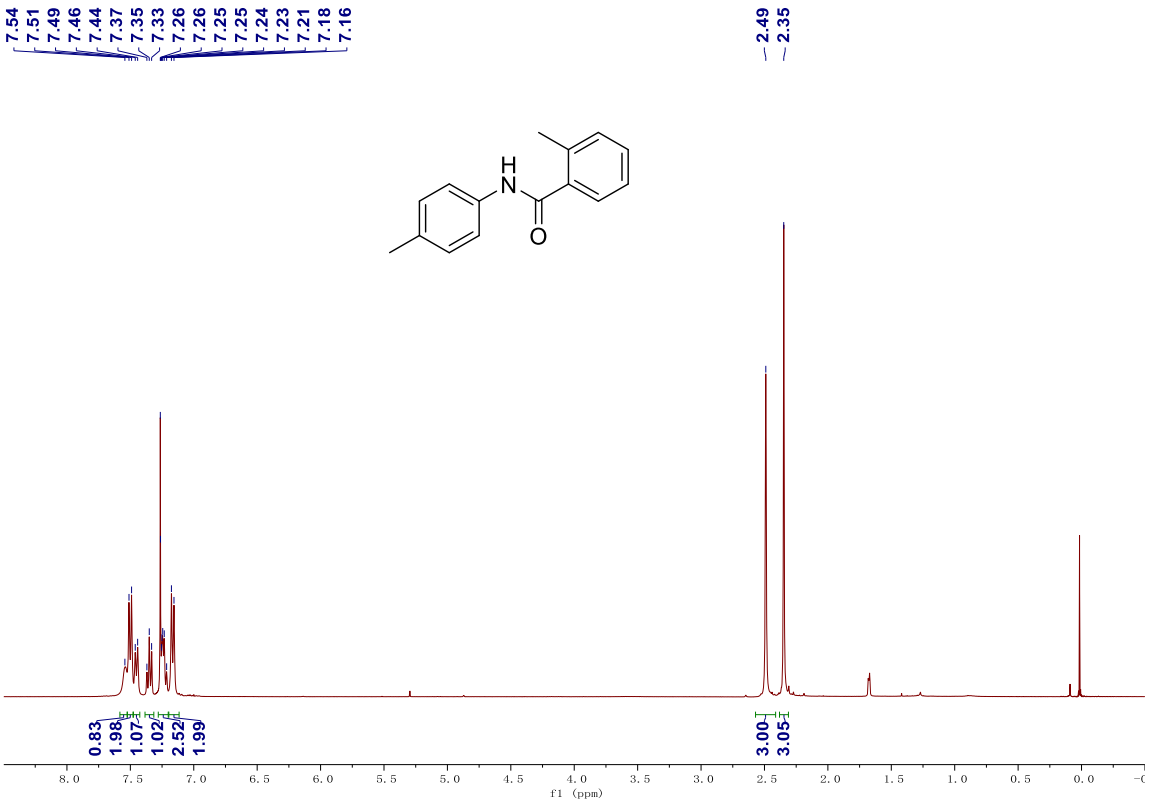
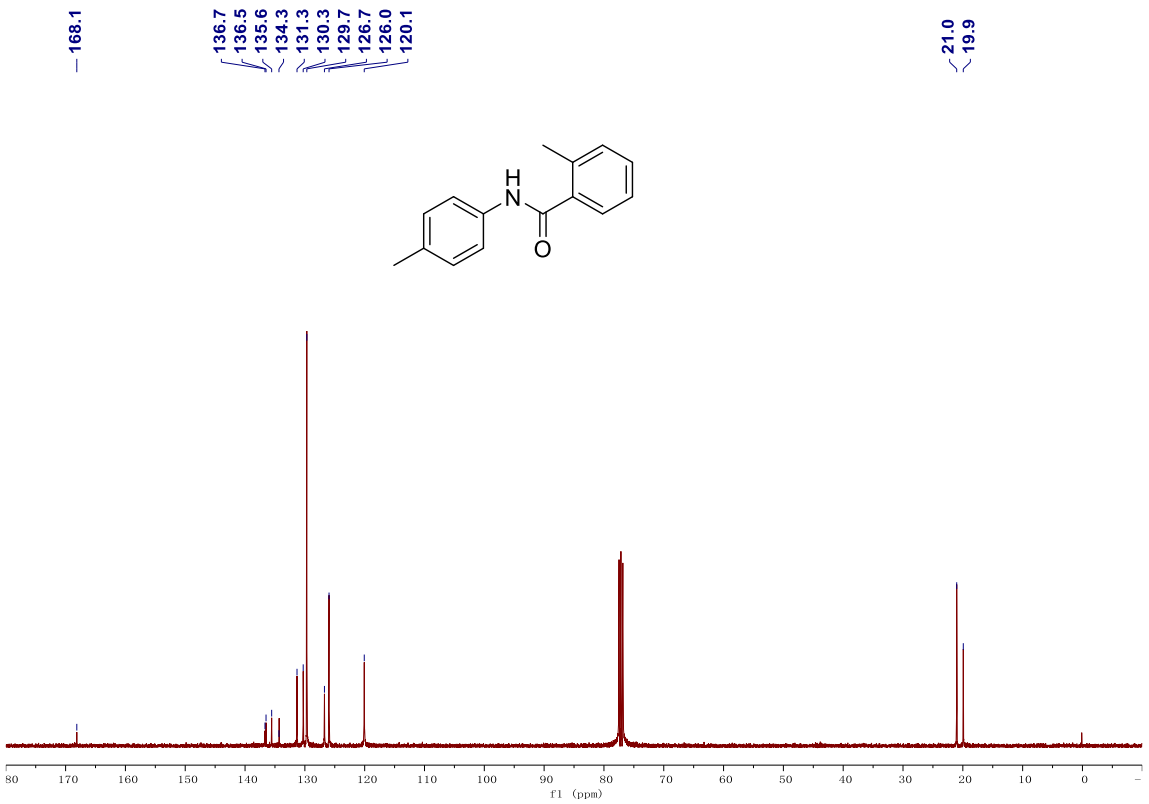


^{13}C NMR spectrum for compound **3b** ($CDCl_3$)



^{1}H NMR spectrum for compound **3c** ($CDCl_3$)



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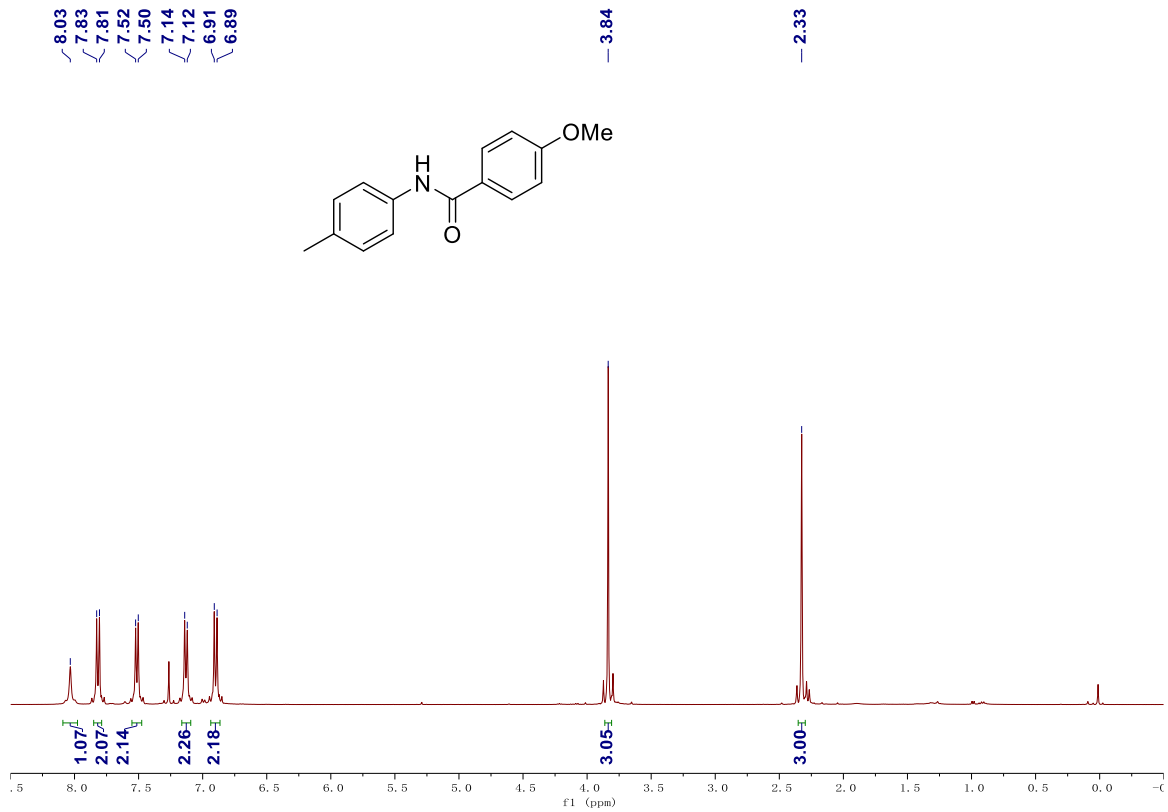

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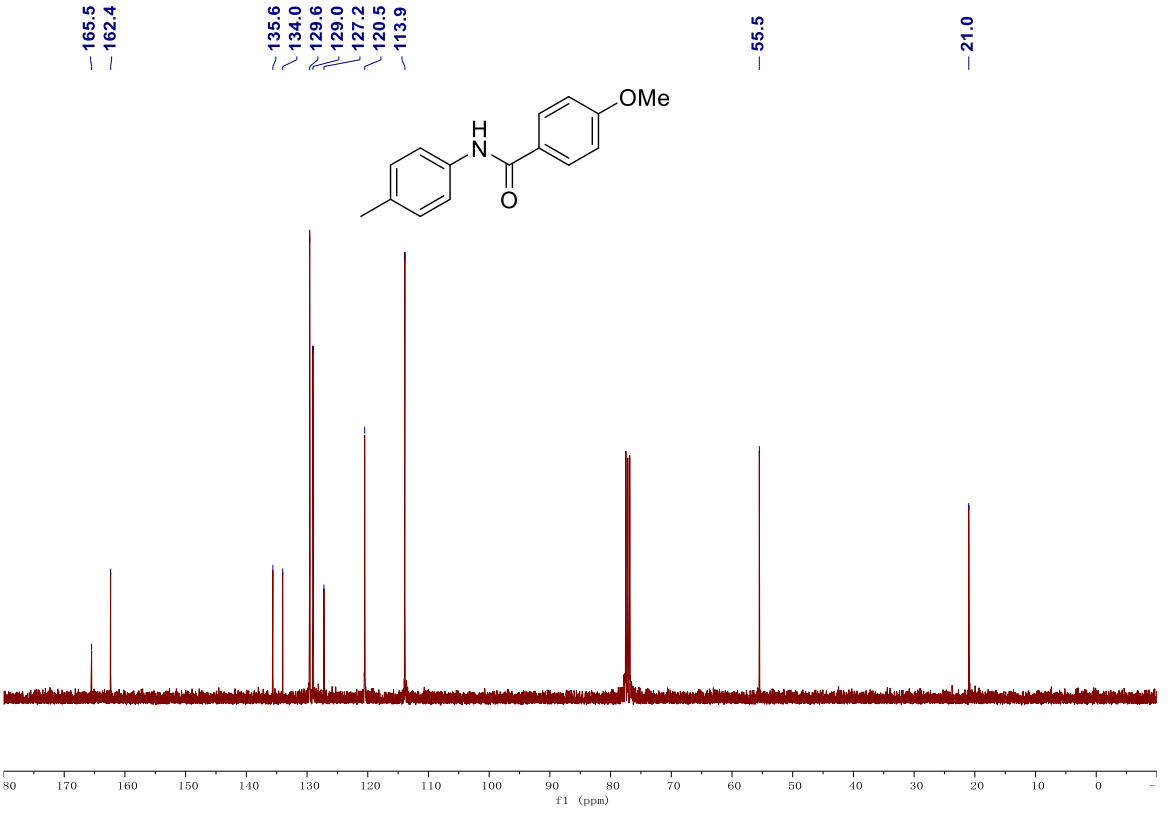

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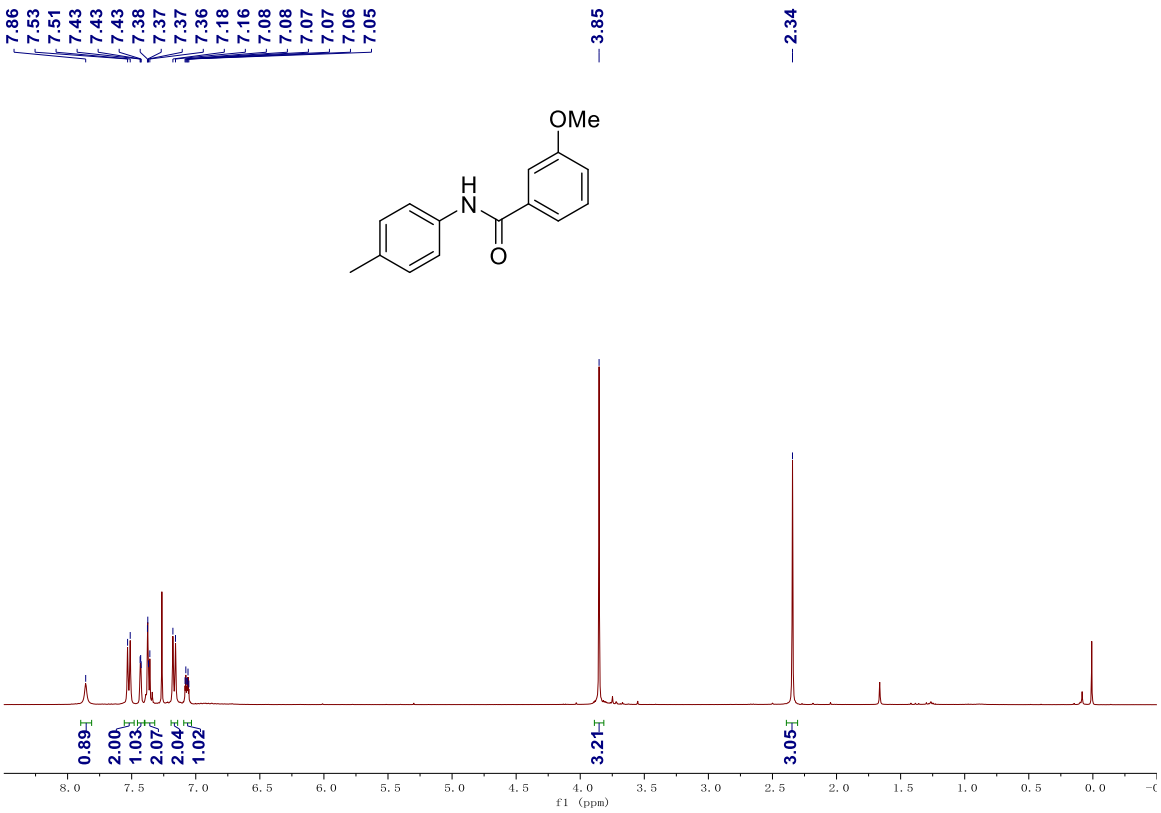

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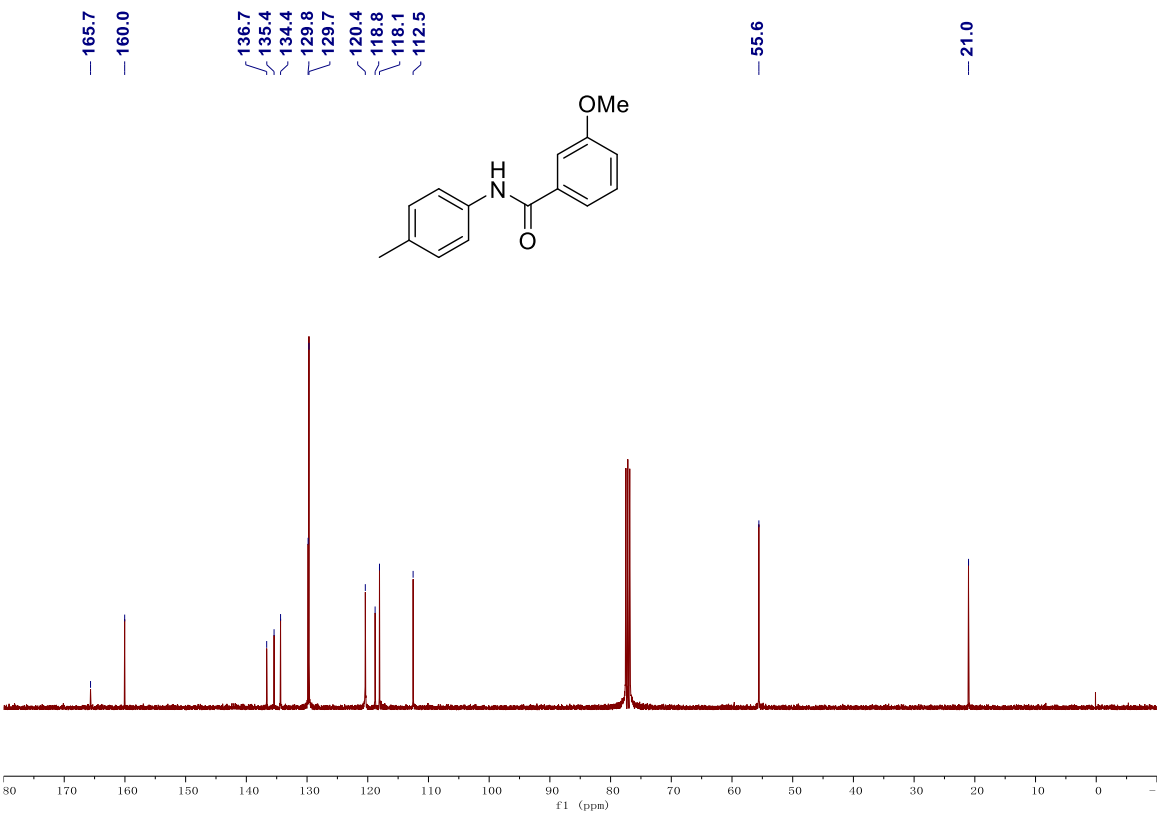

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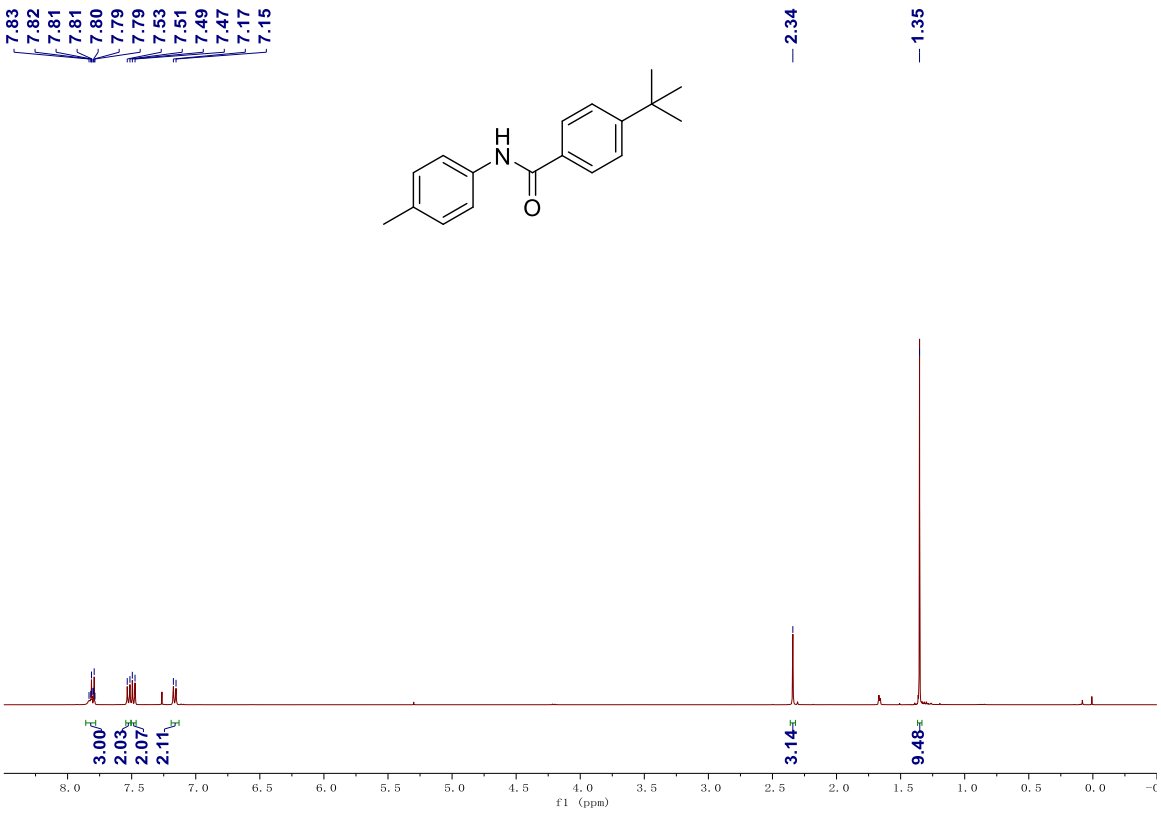

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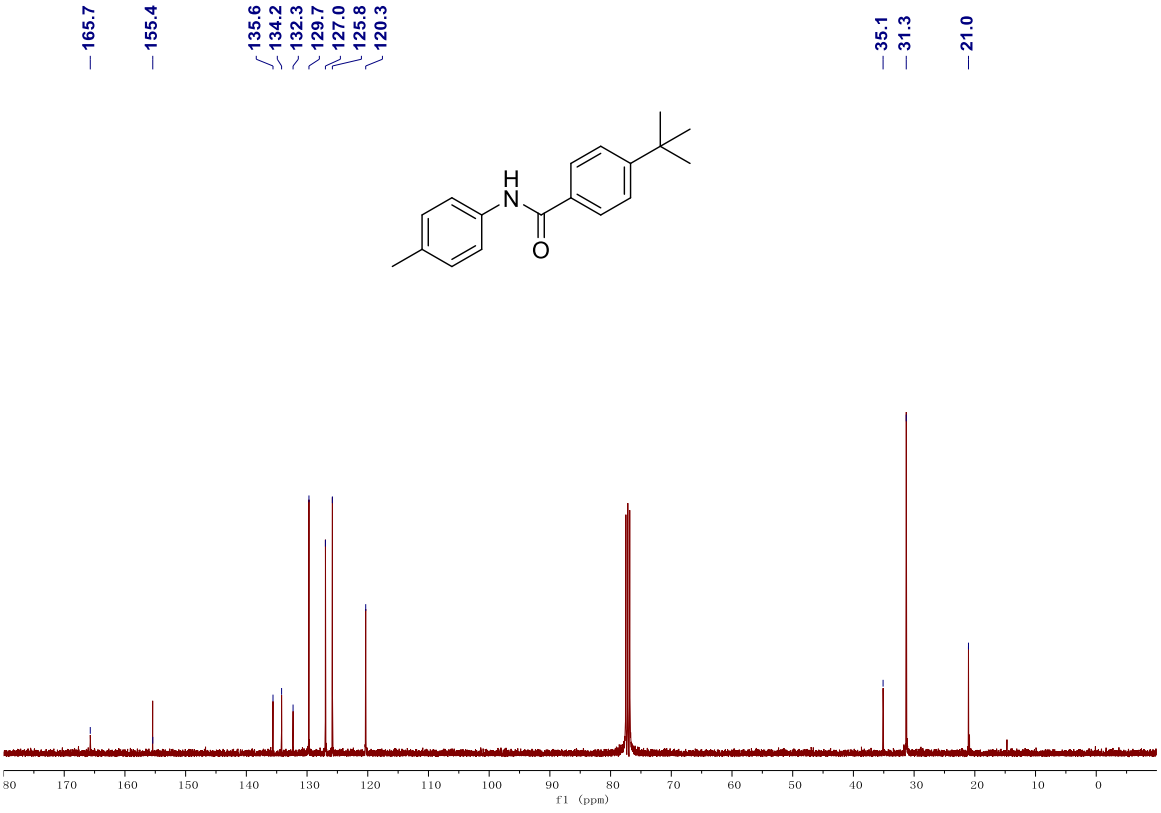

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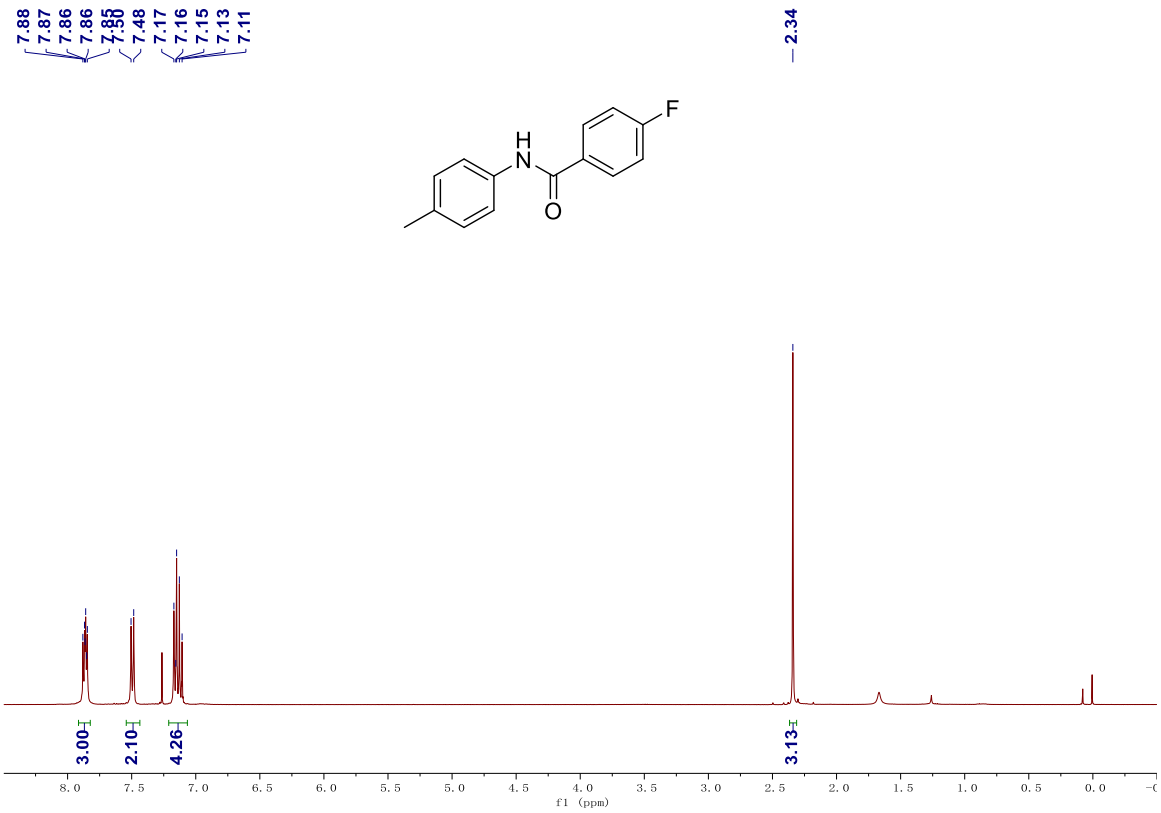

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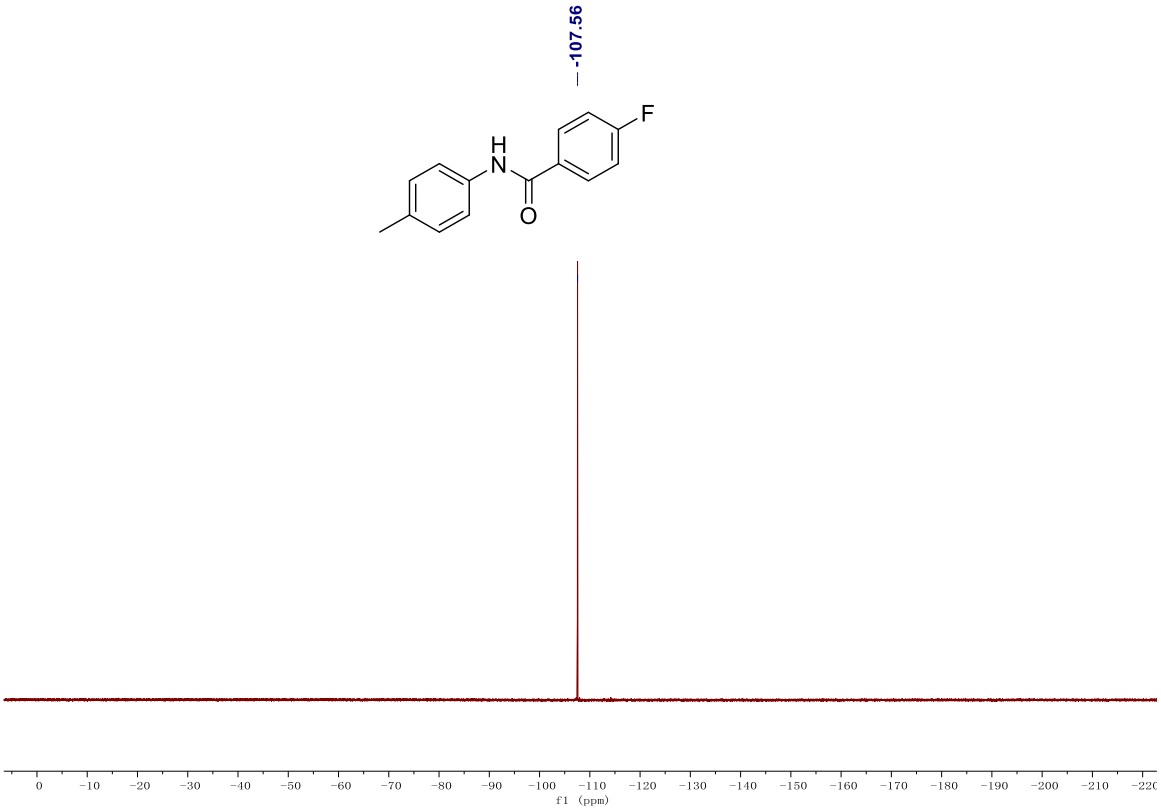
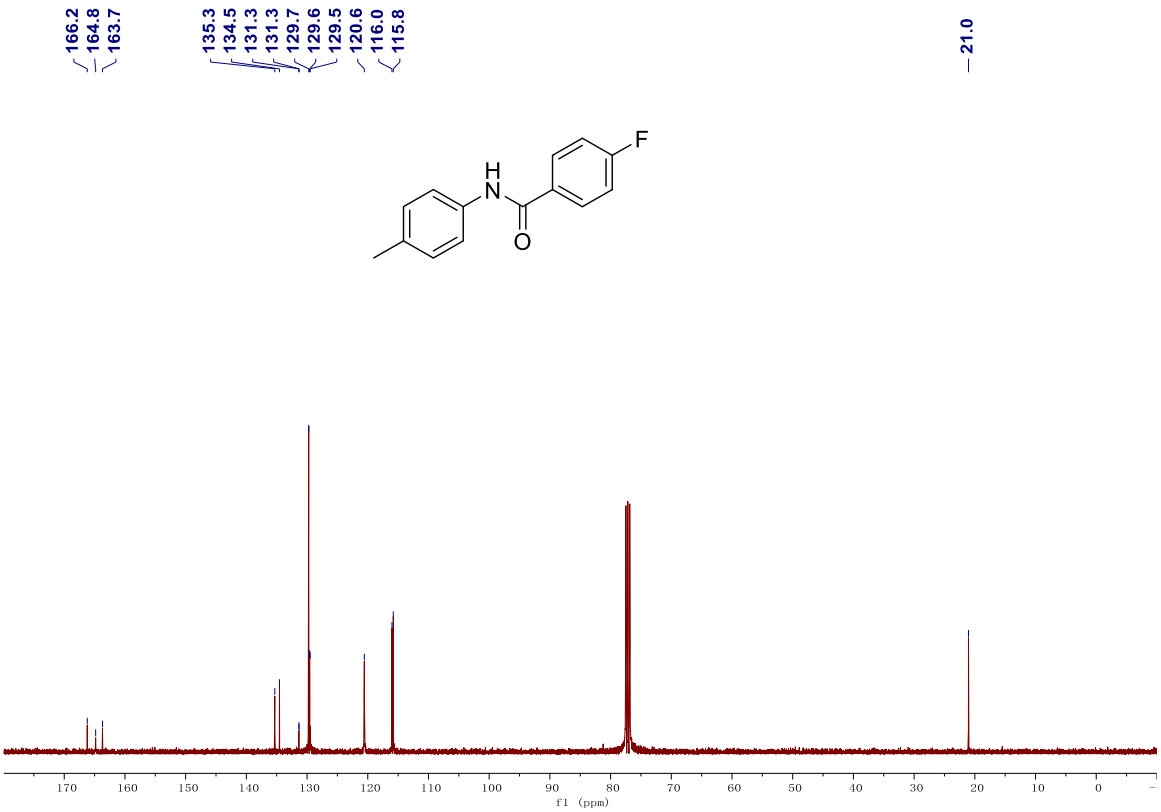


^{19}F NMR spectrum for compound **3g** ($CDCl_3$)



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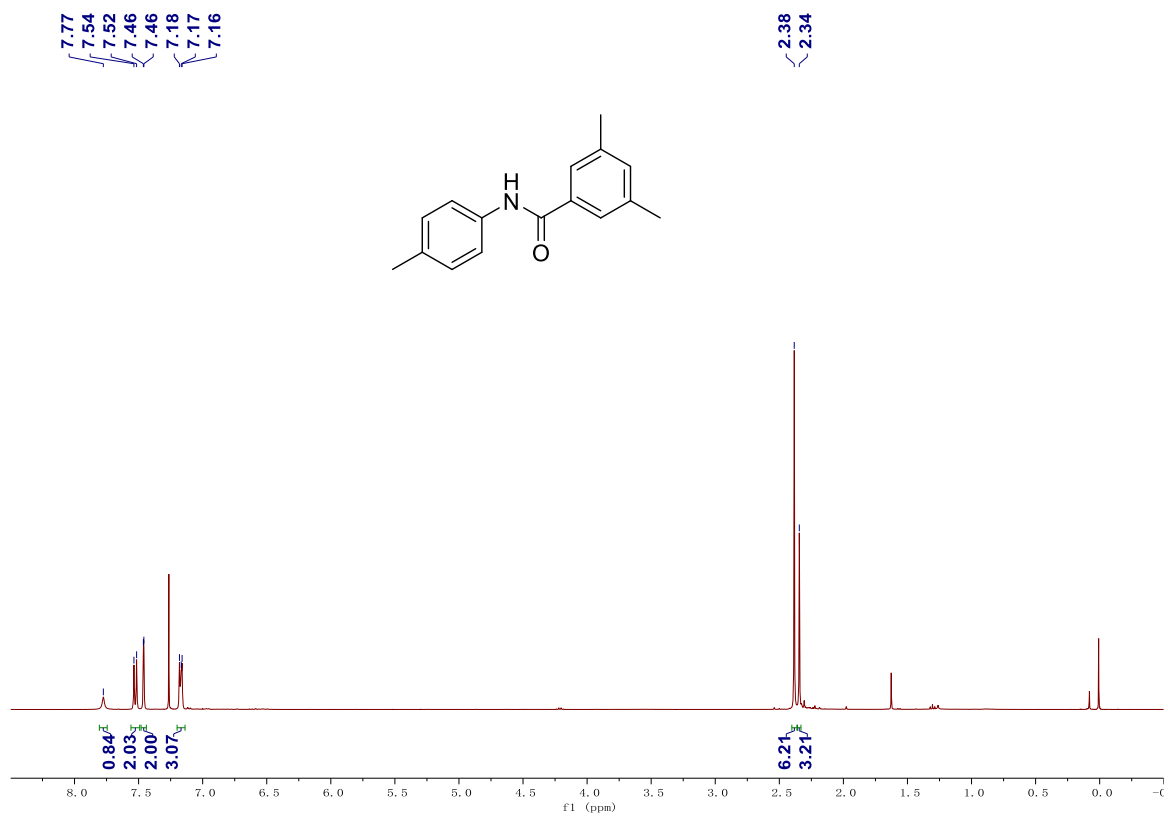

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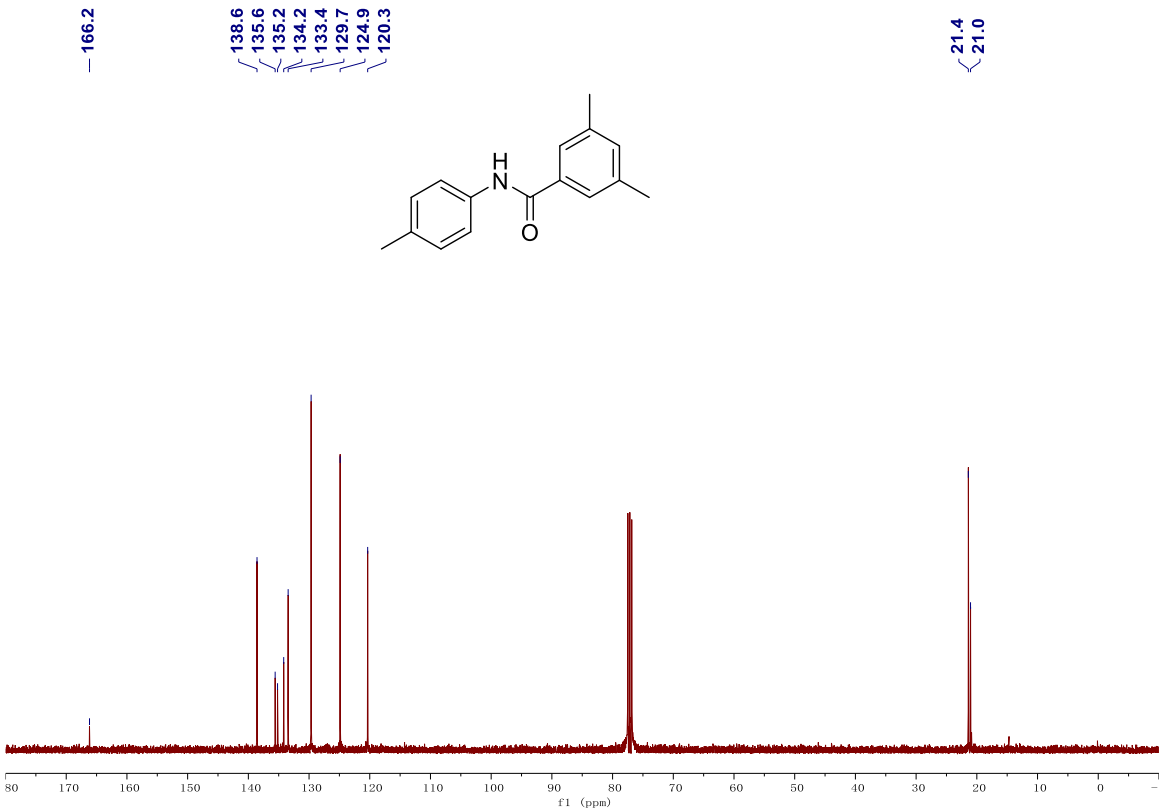

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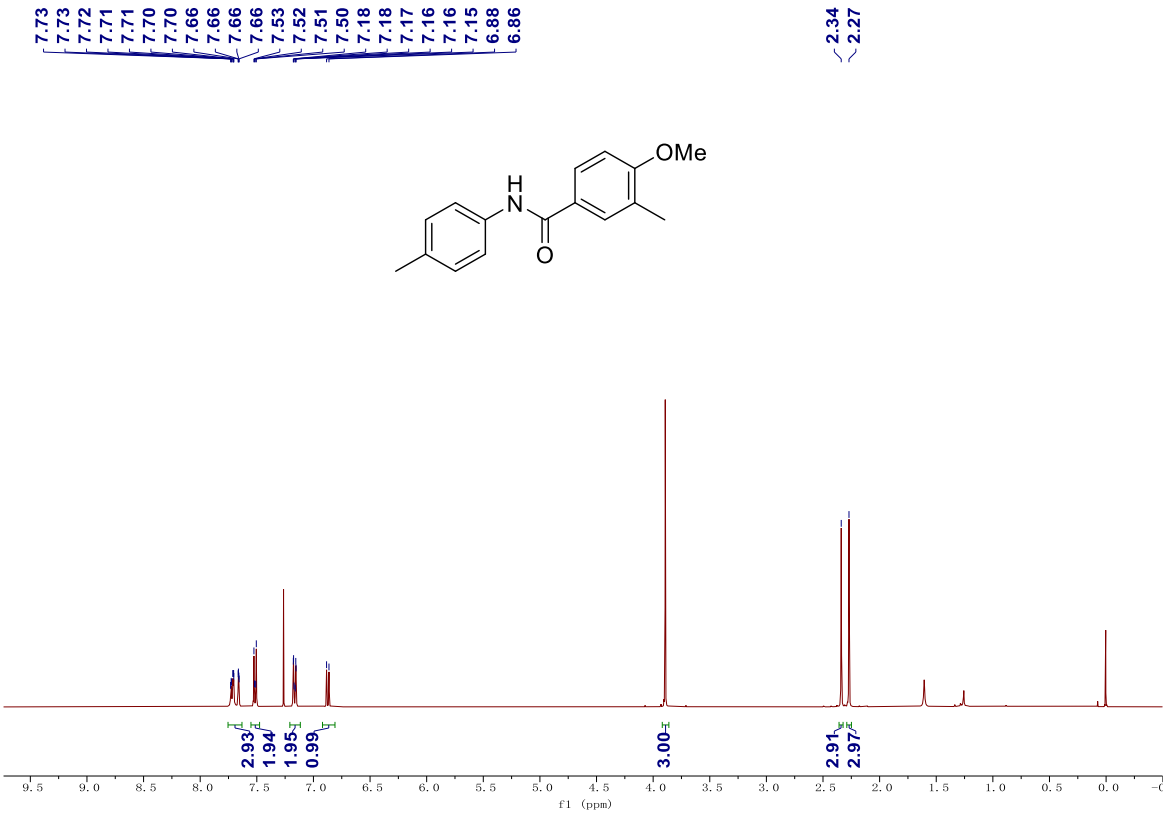

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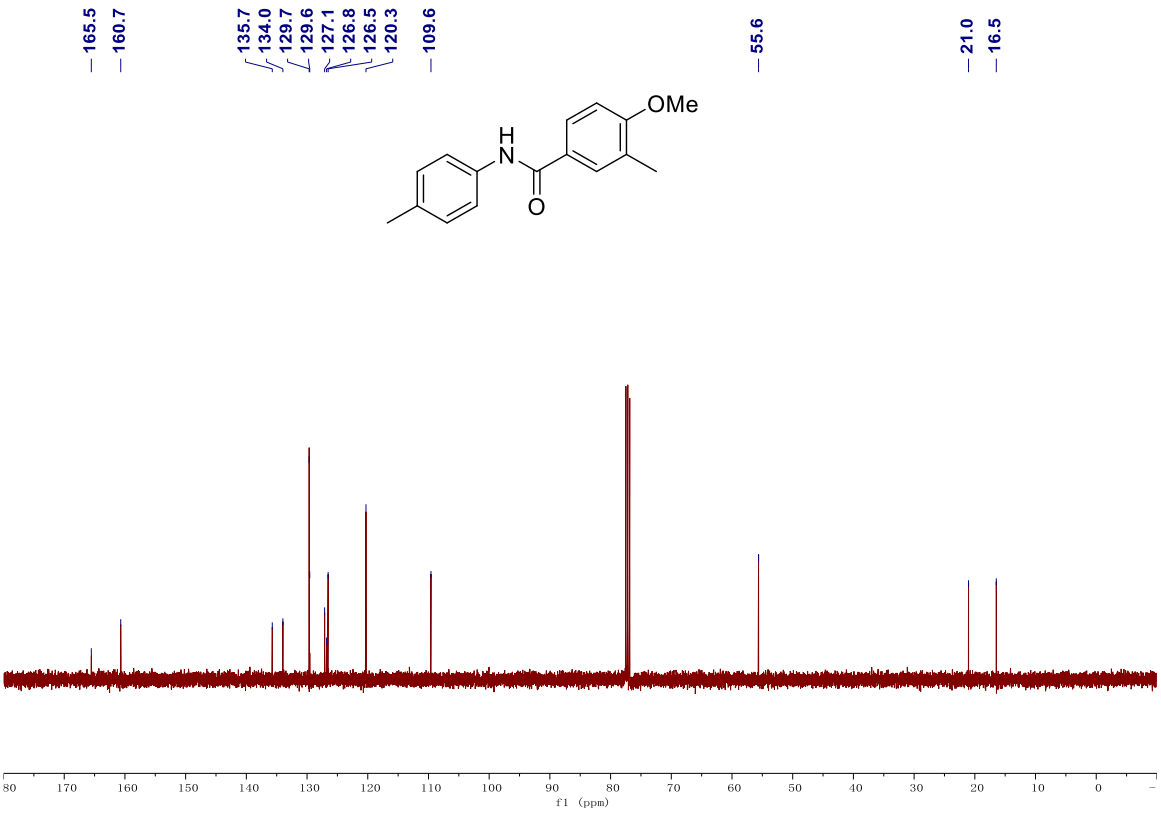

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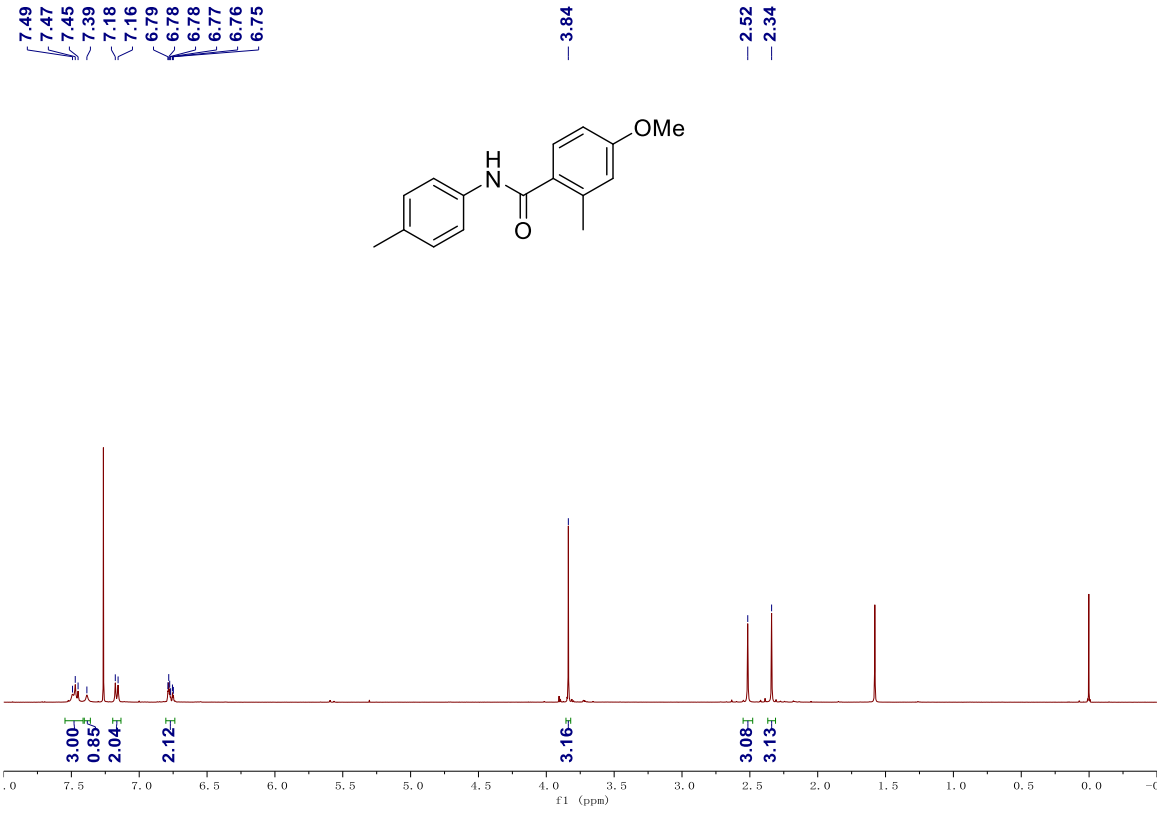

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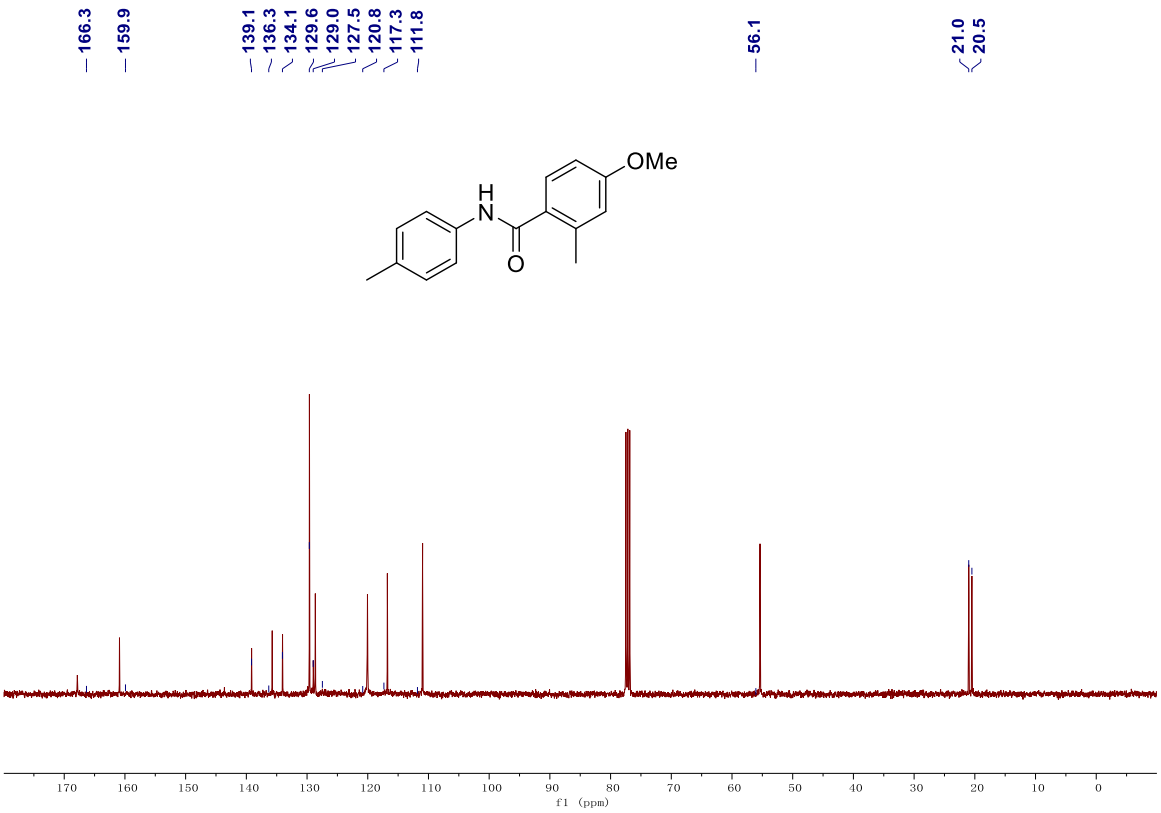

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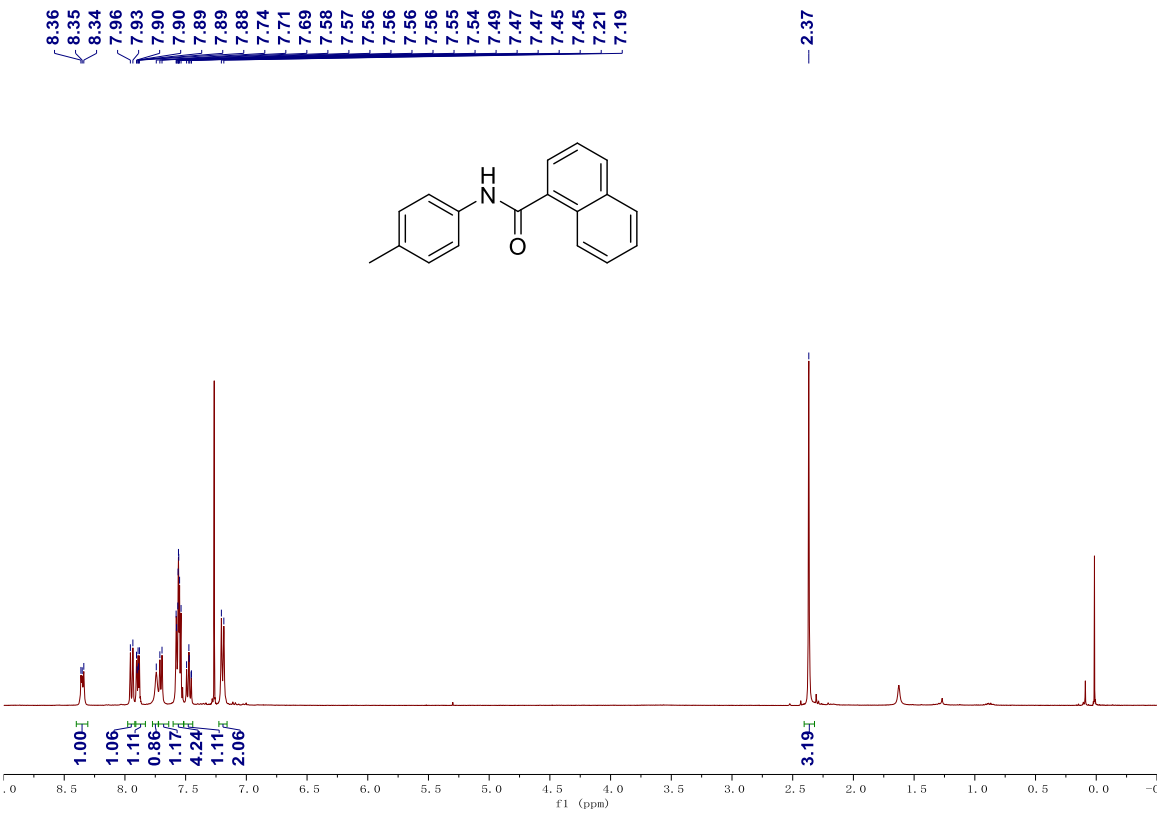

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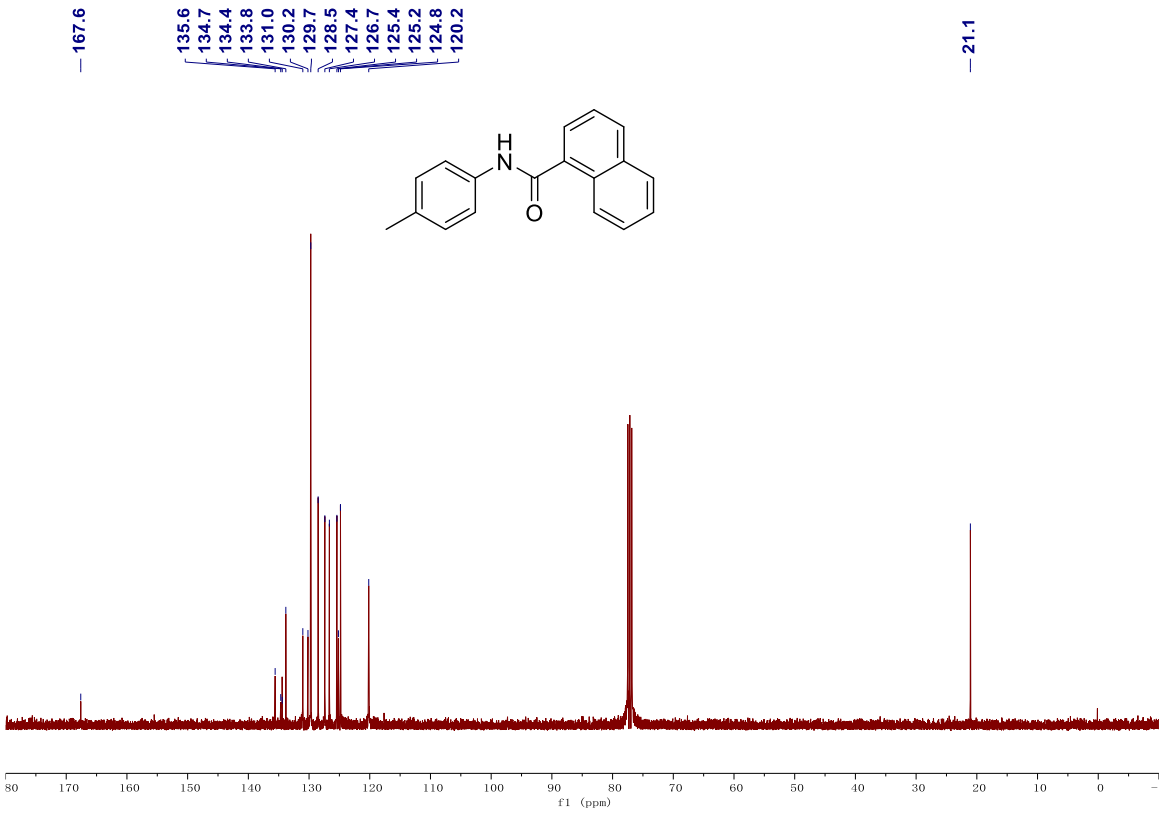

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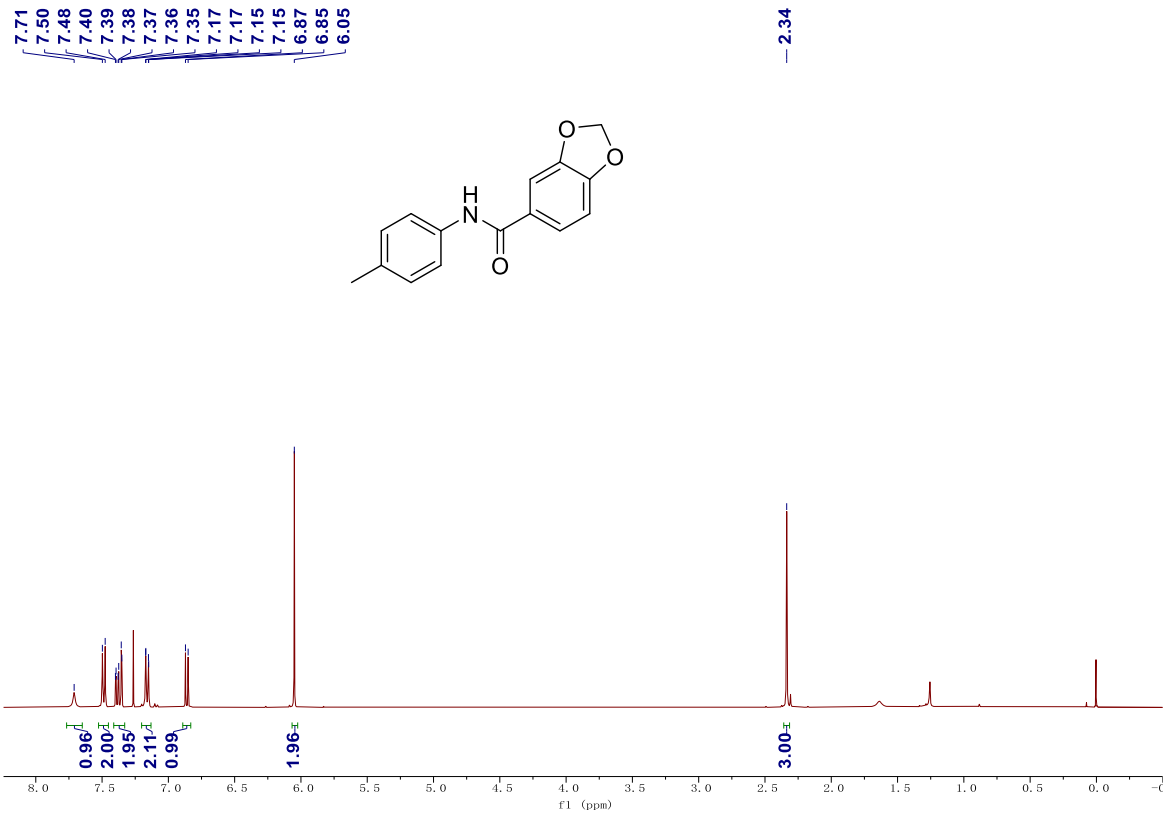

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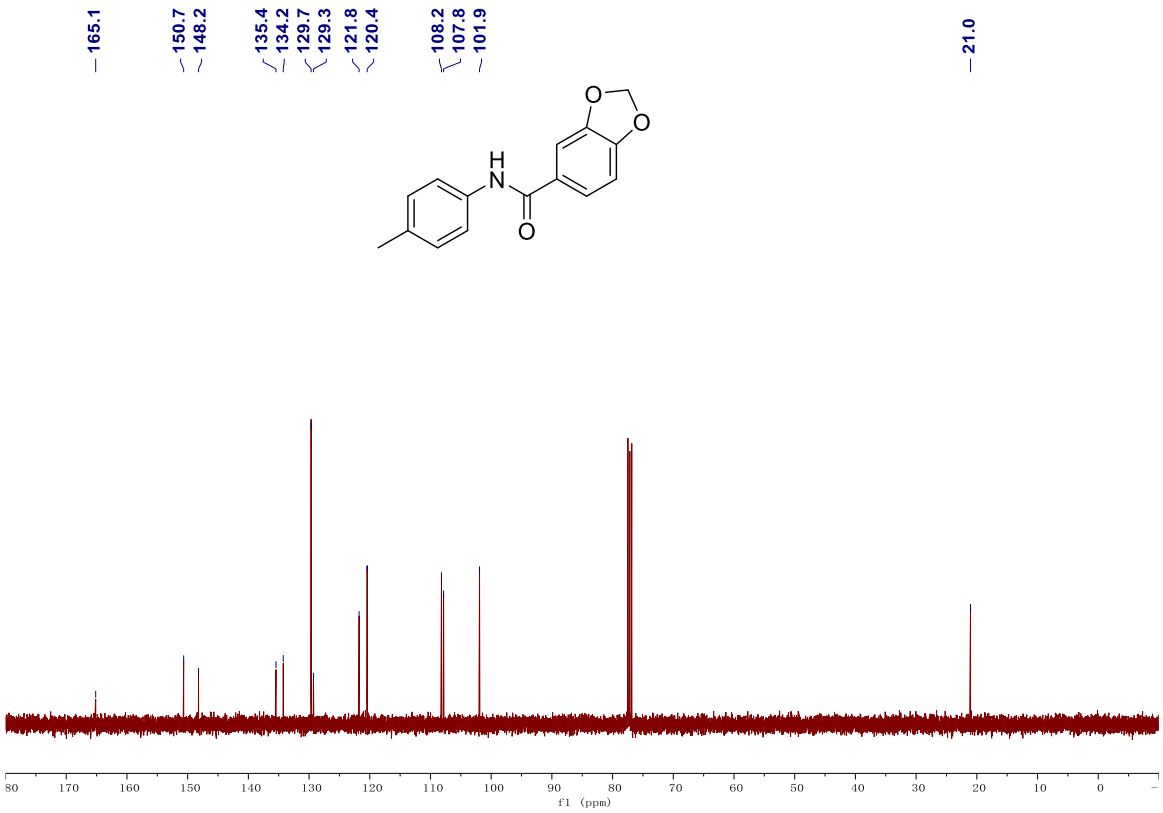

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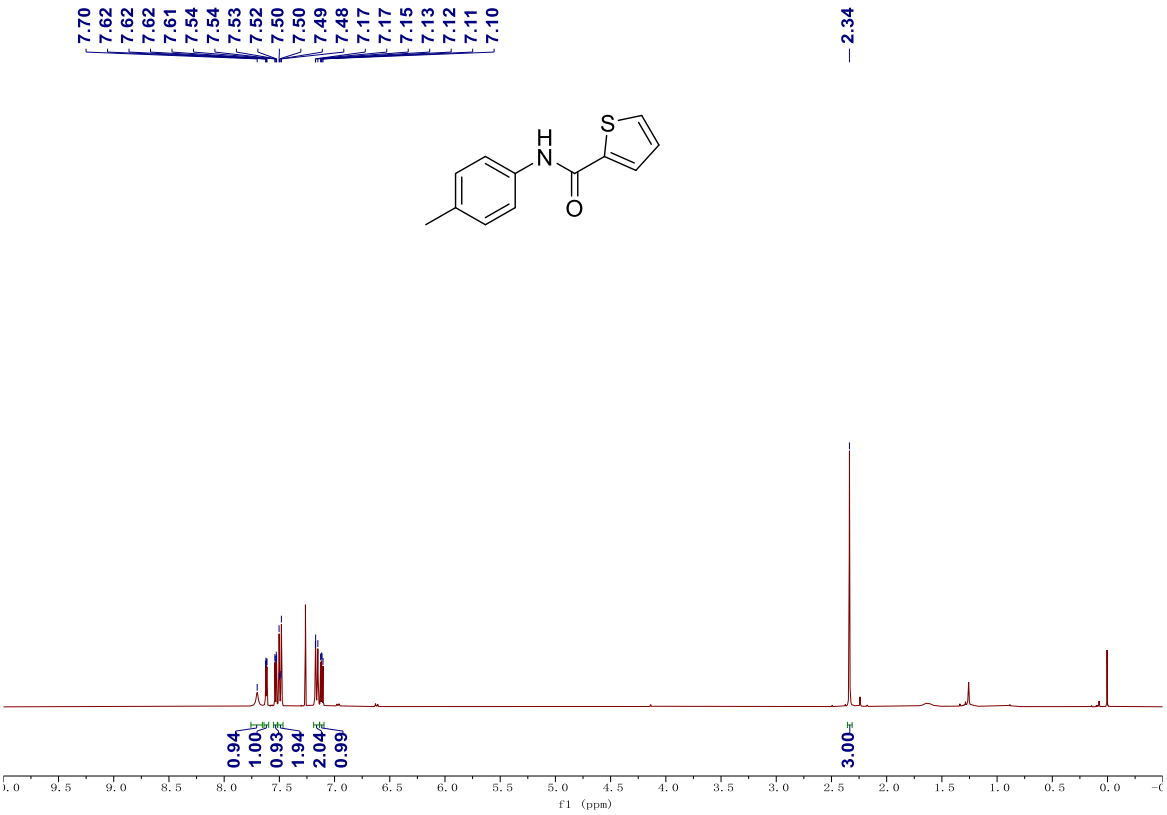

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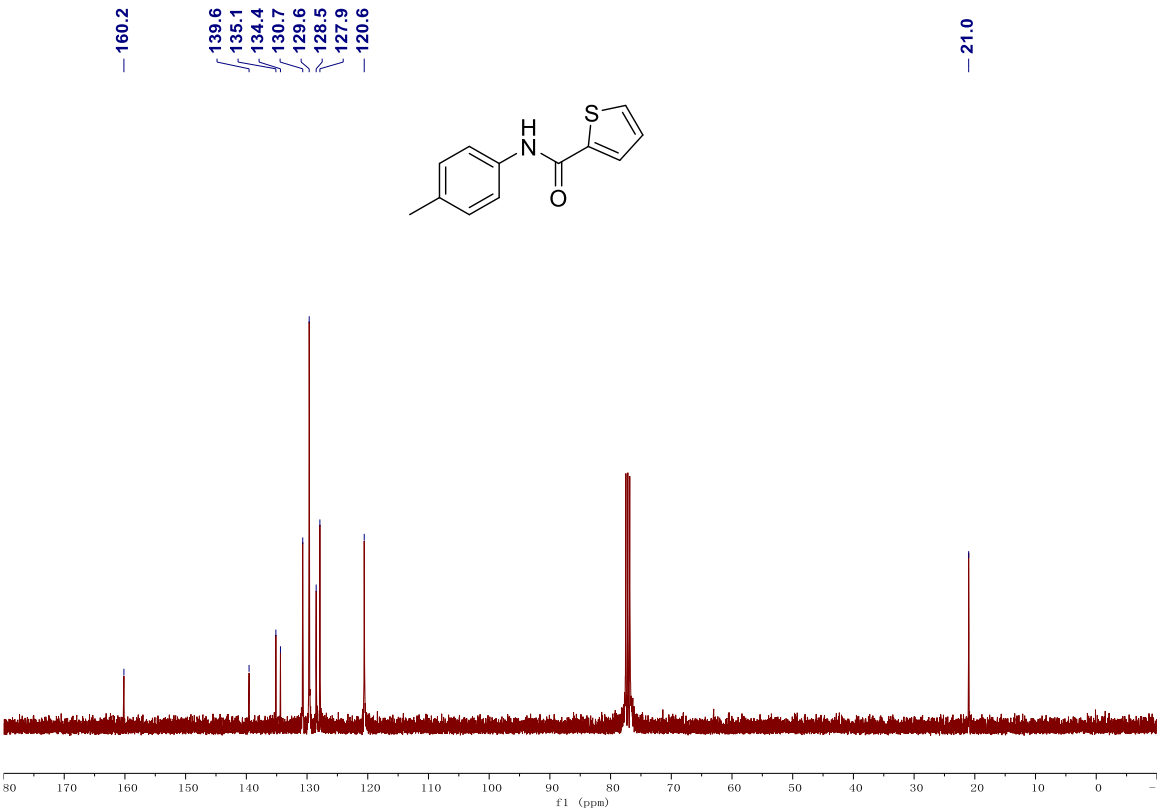

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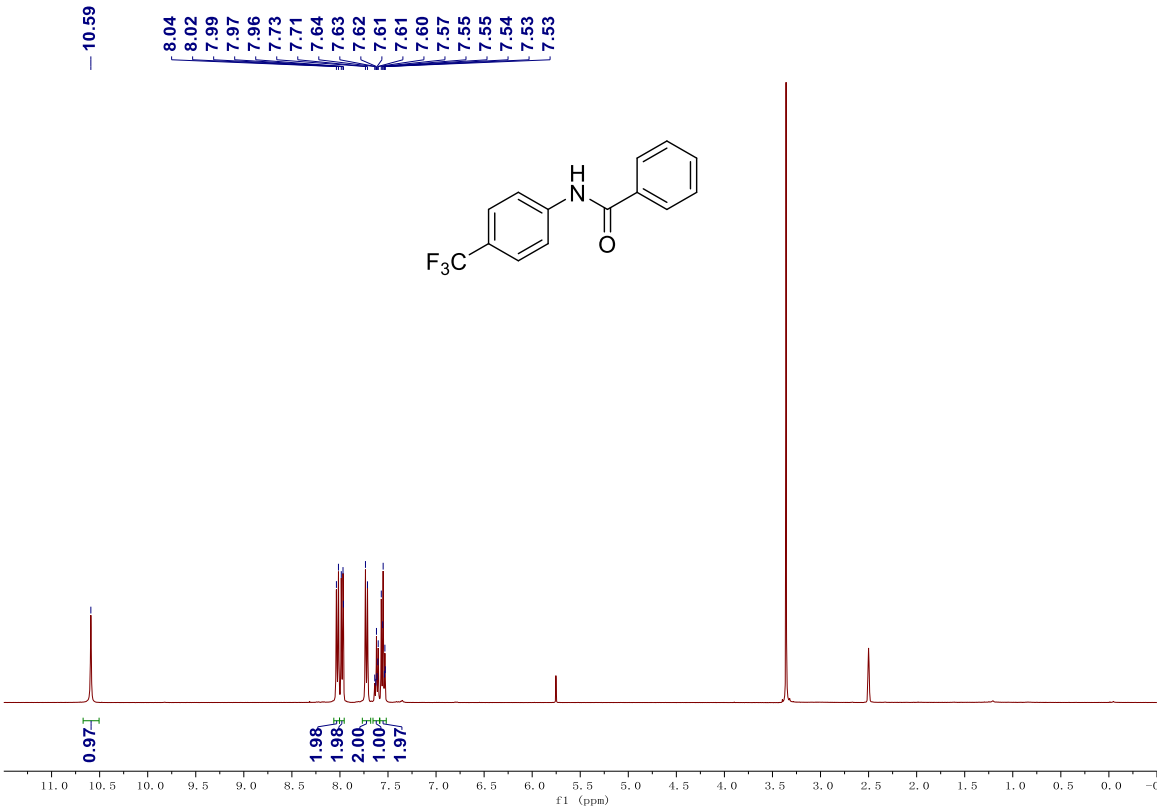

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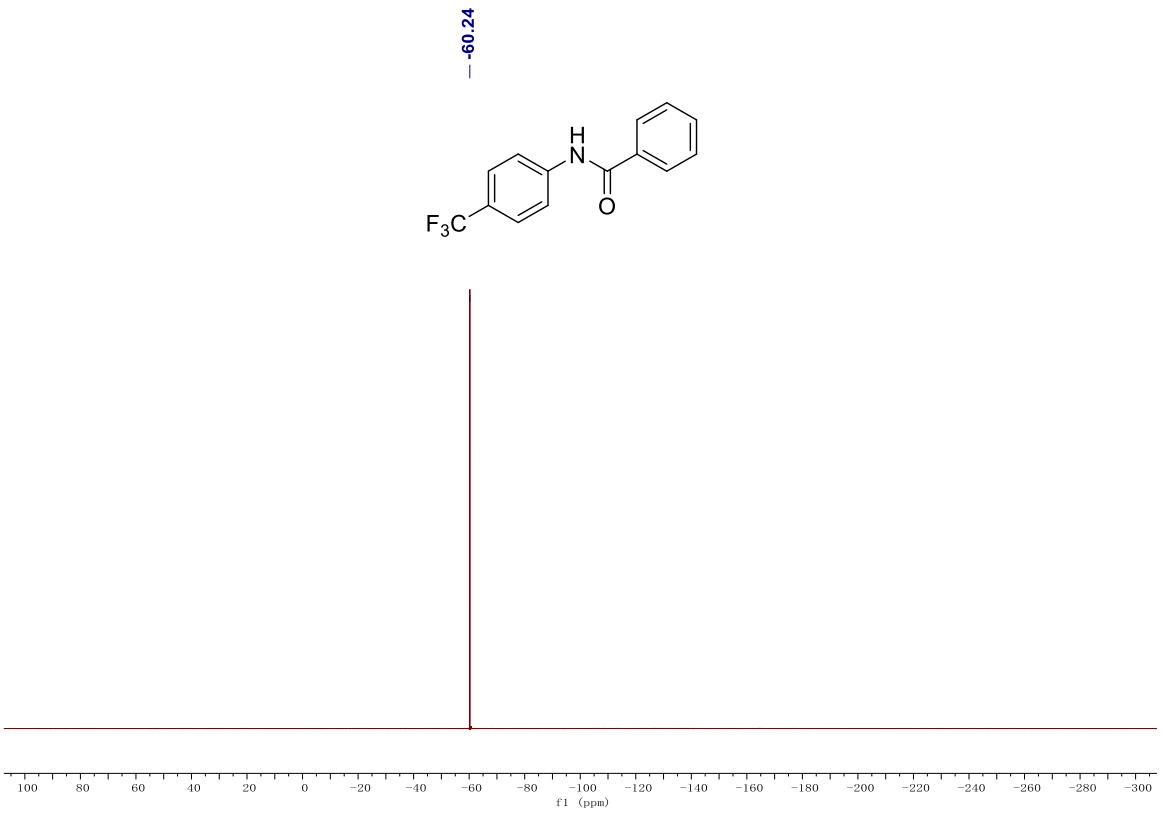
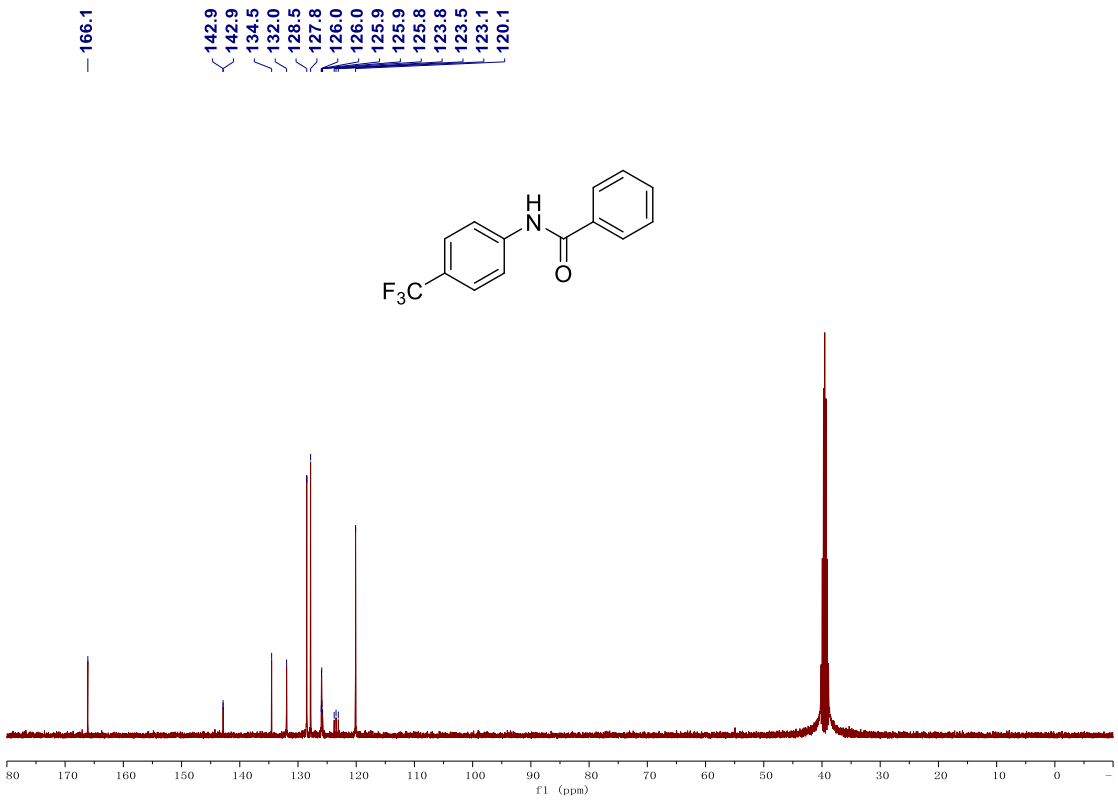


^{19}F NMR spectrum for compound **3n** (DMSO-d_6)



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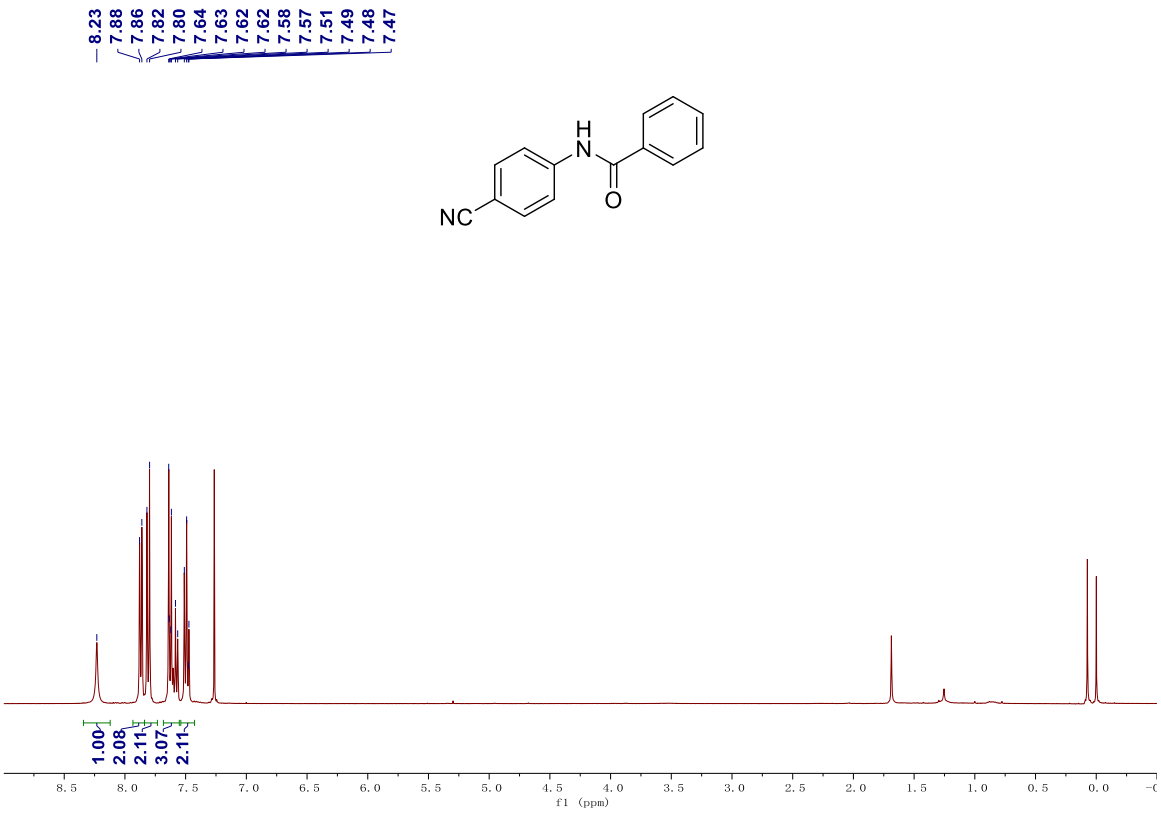

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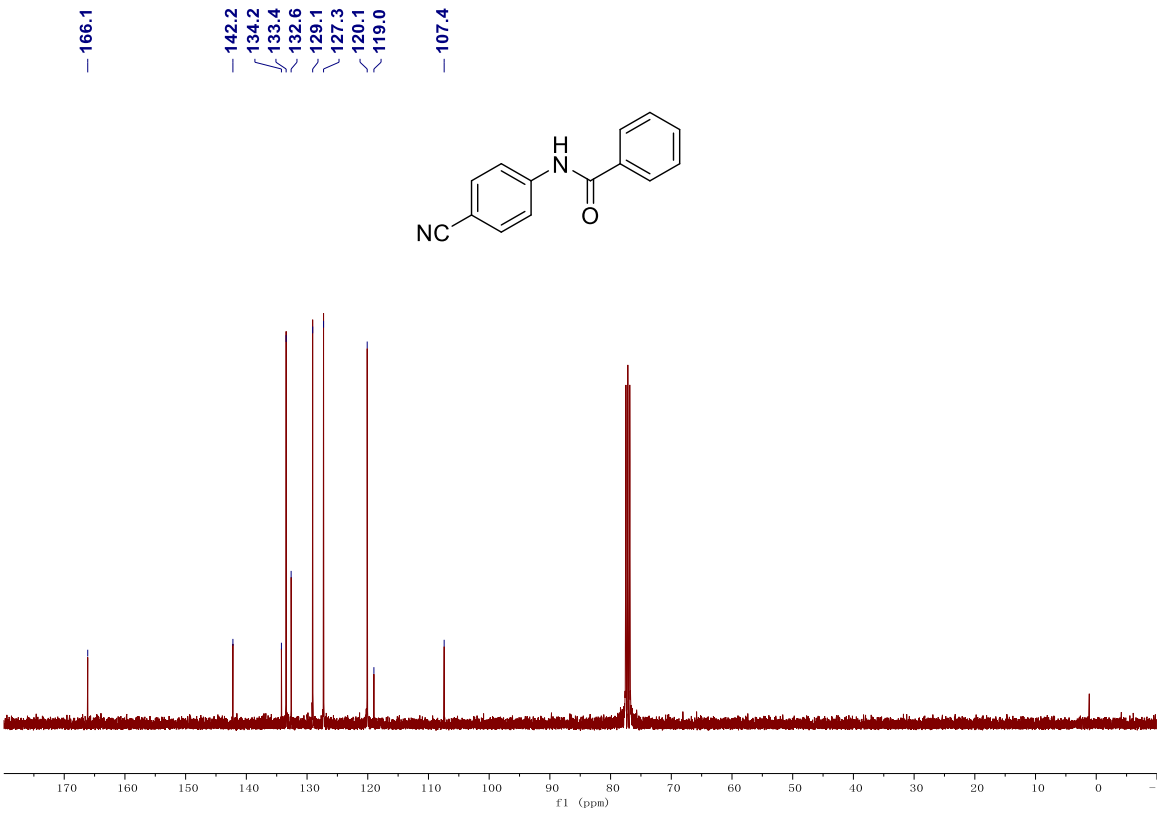

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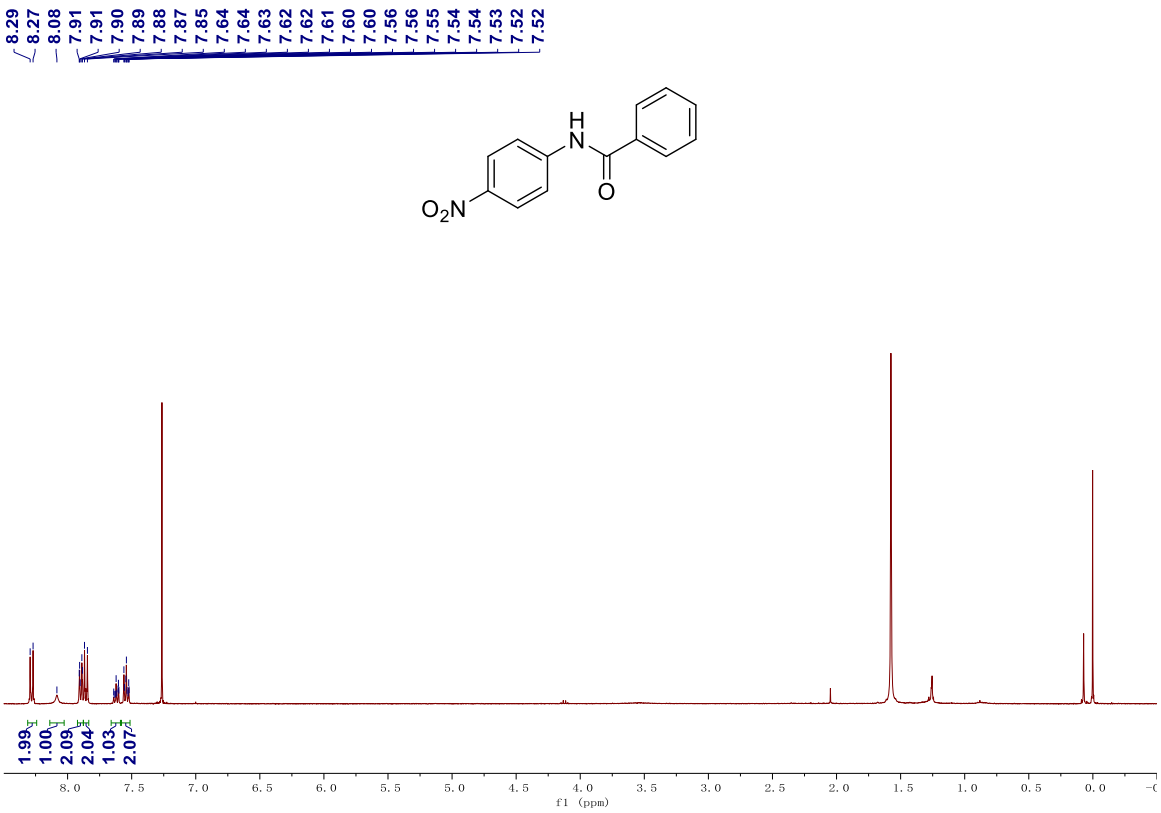

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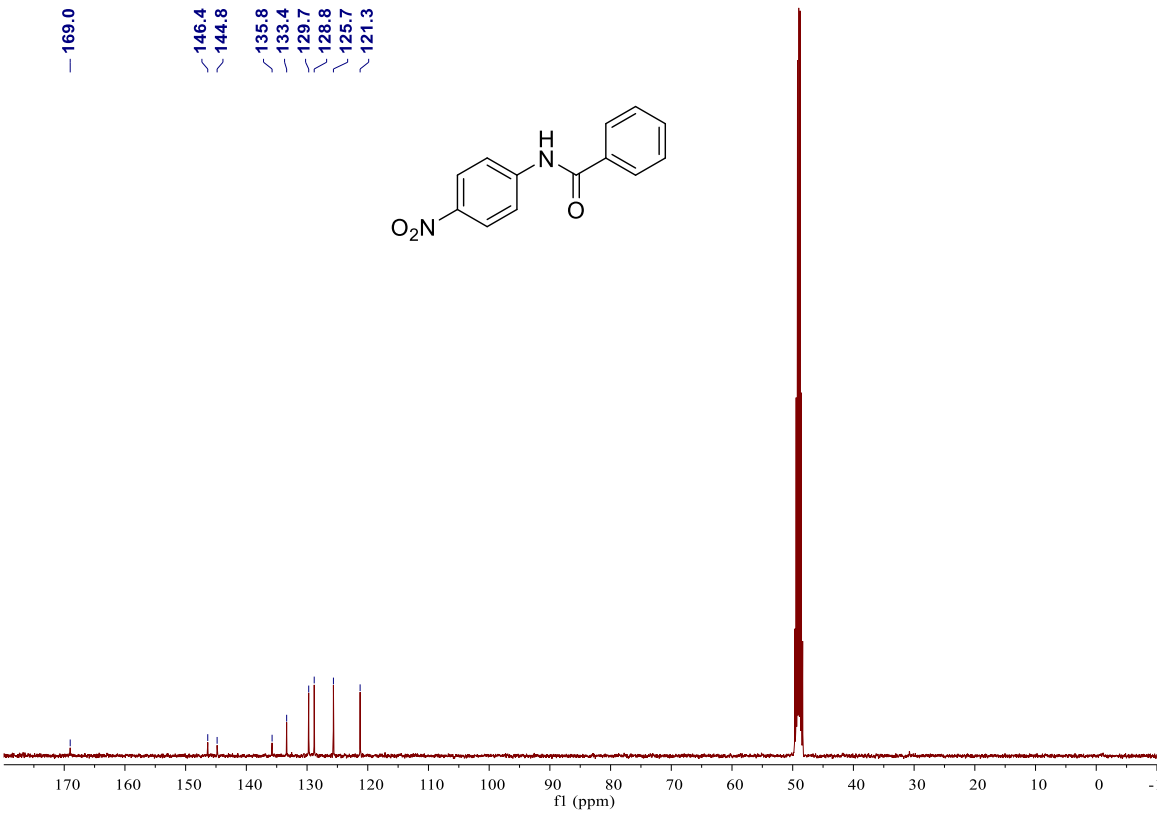

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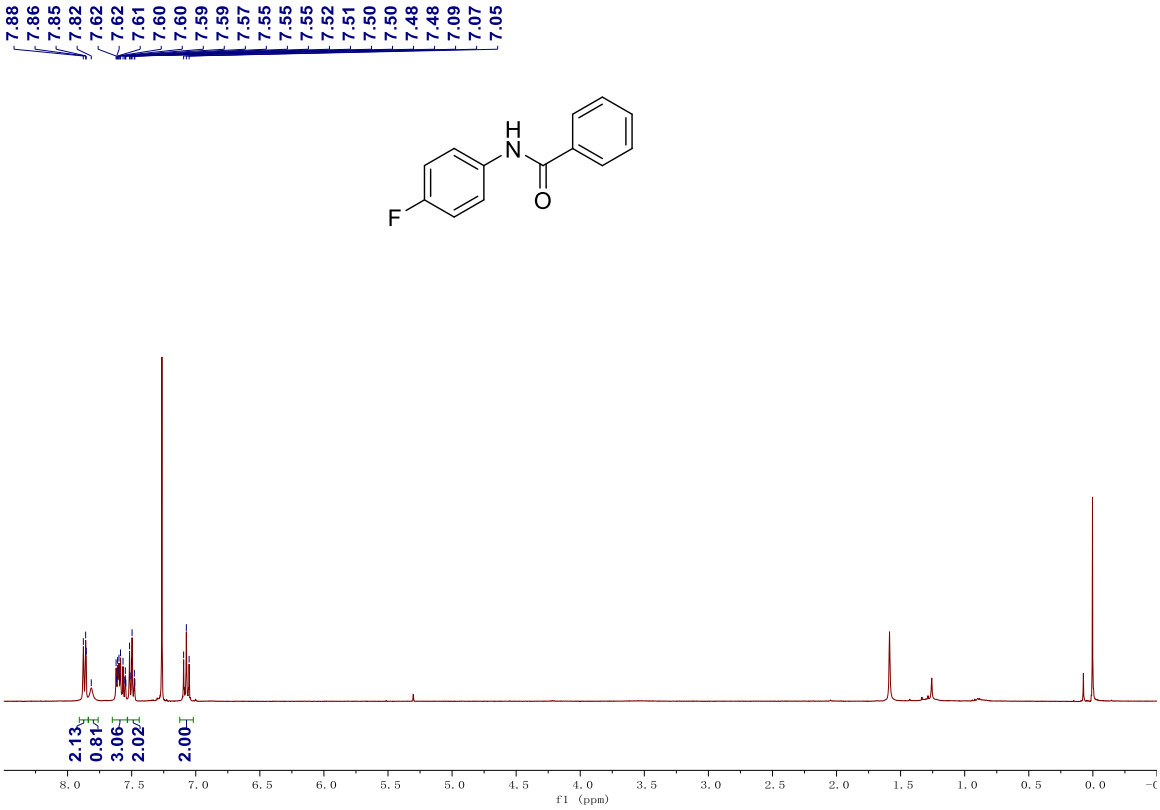

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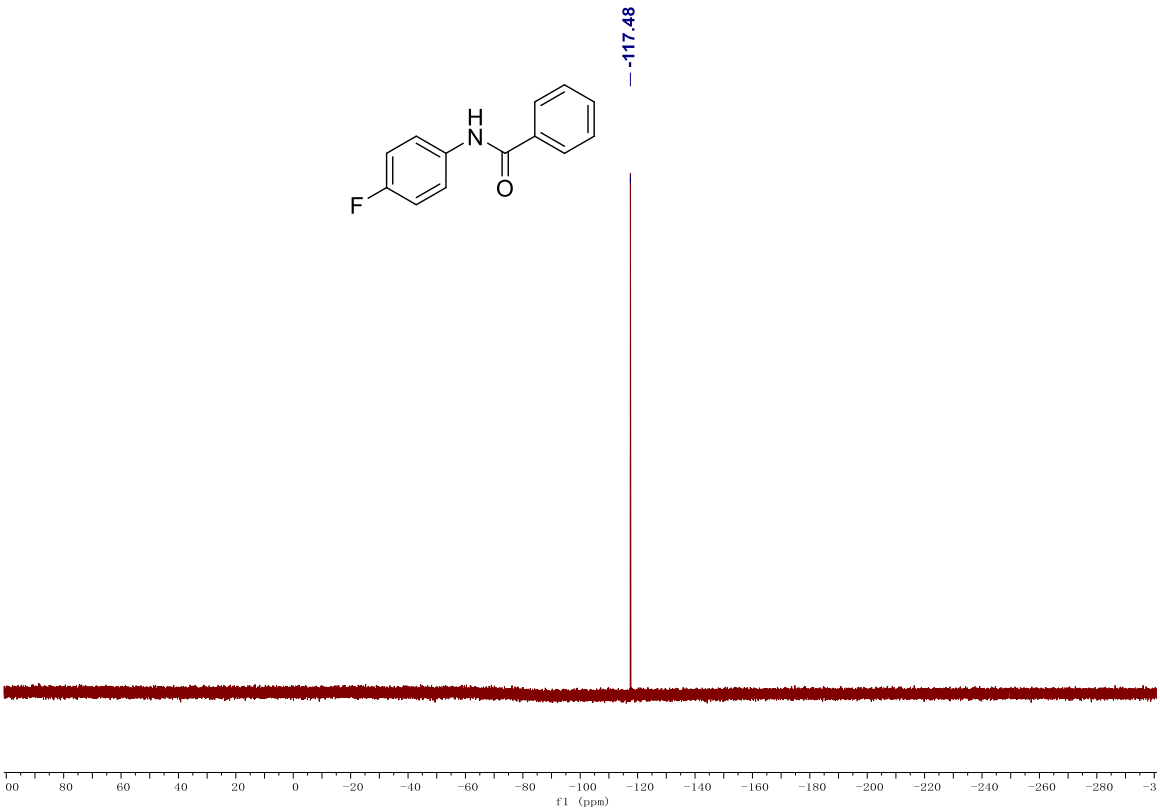

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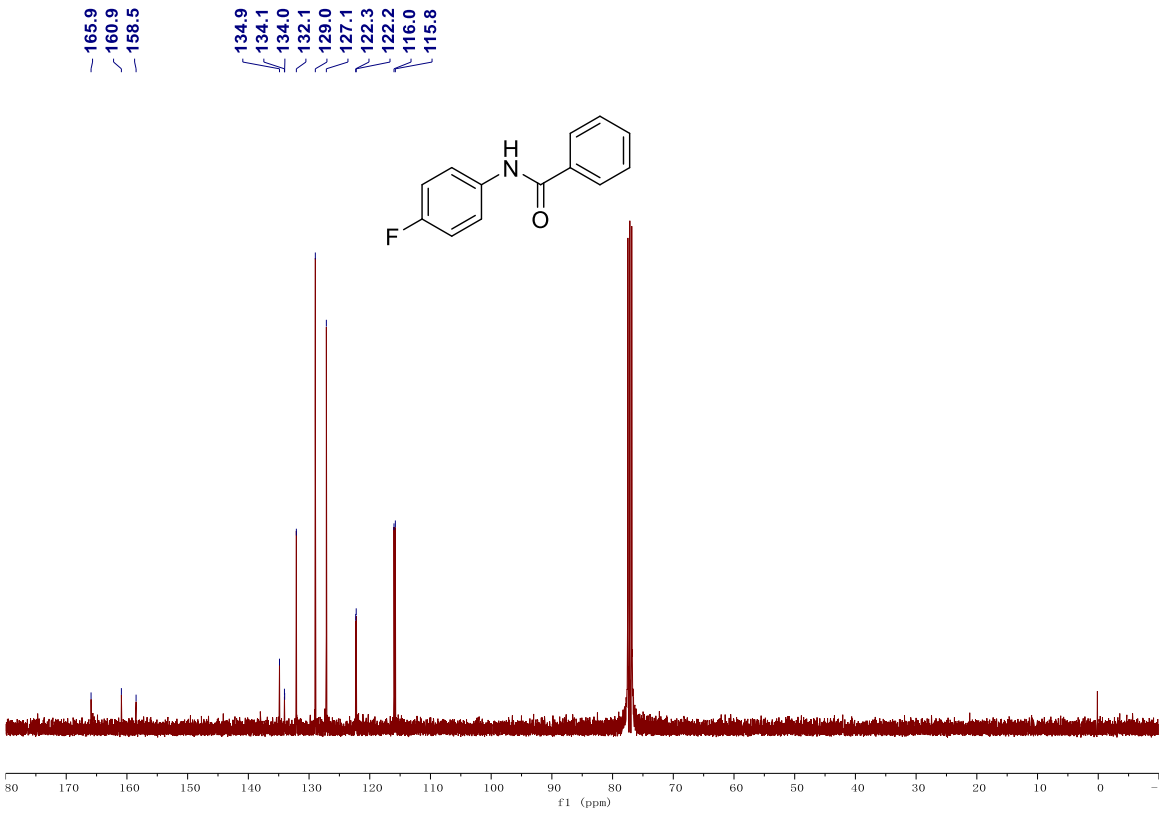

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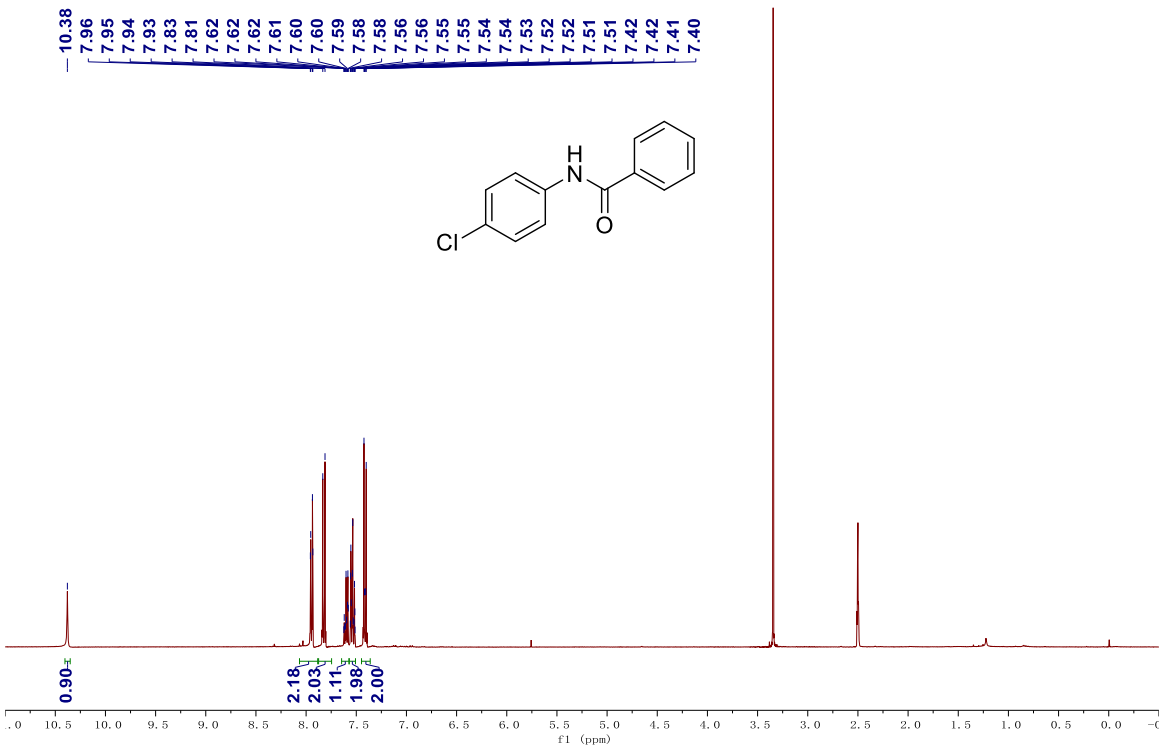

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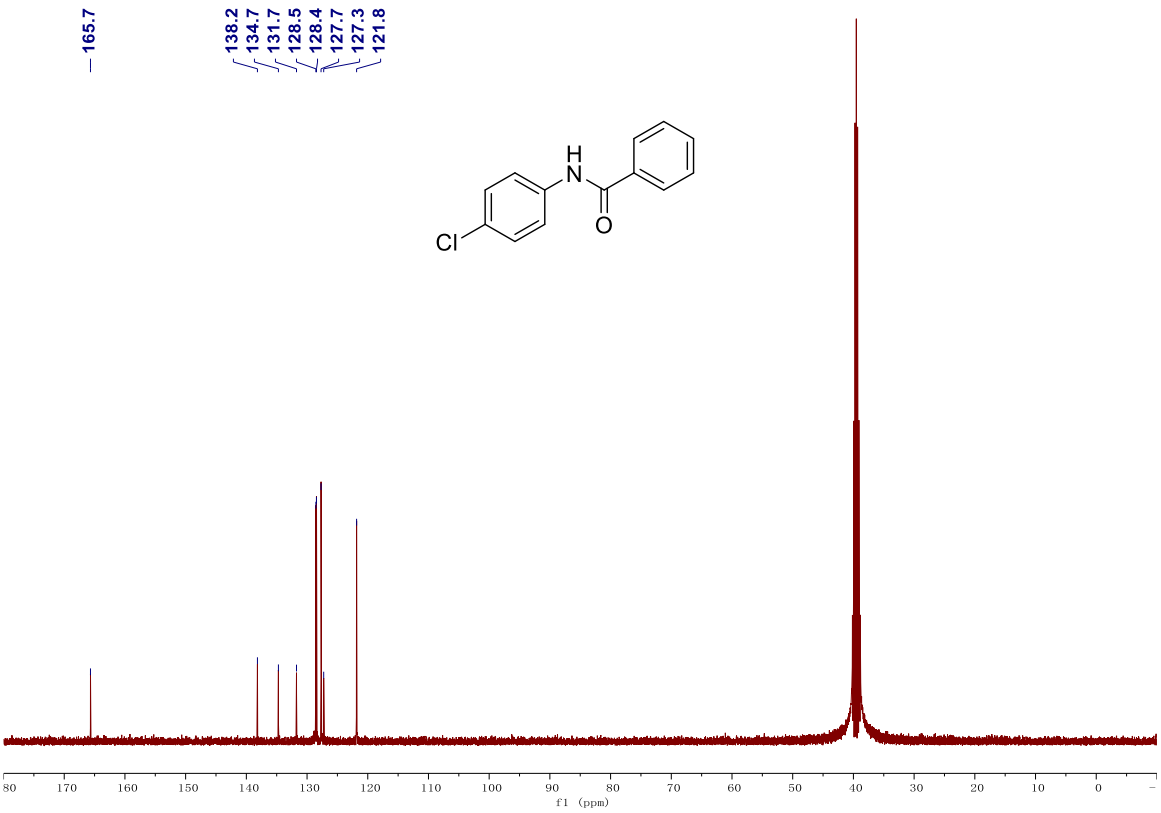

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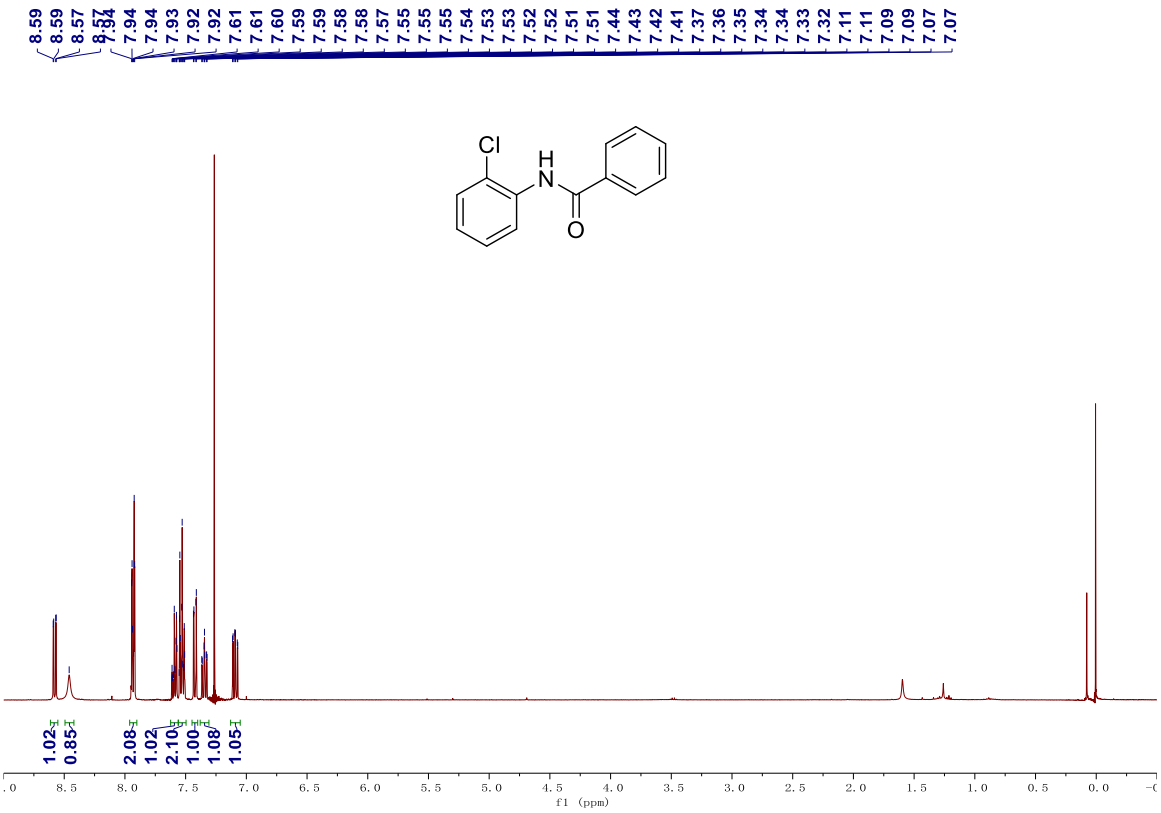

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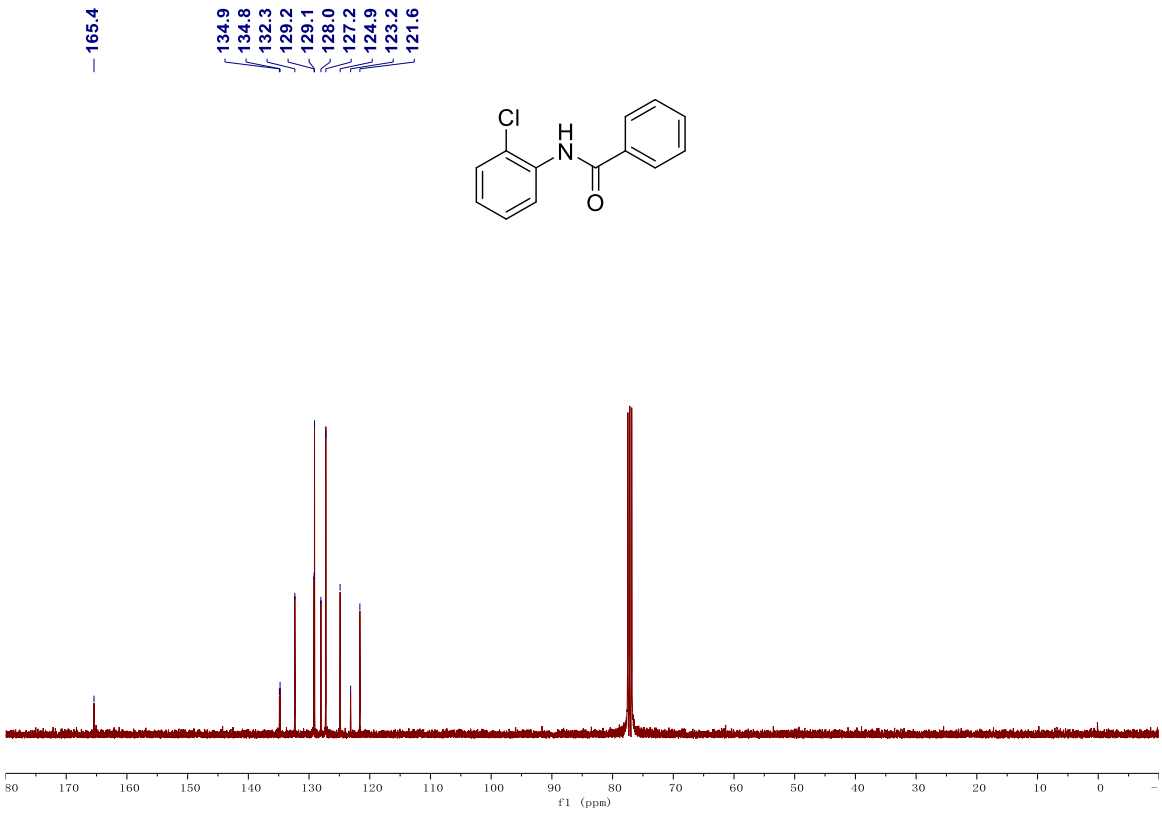

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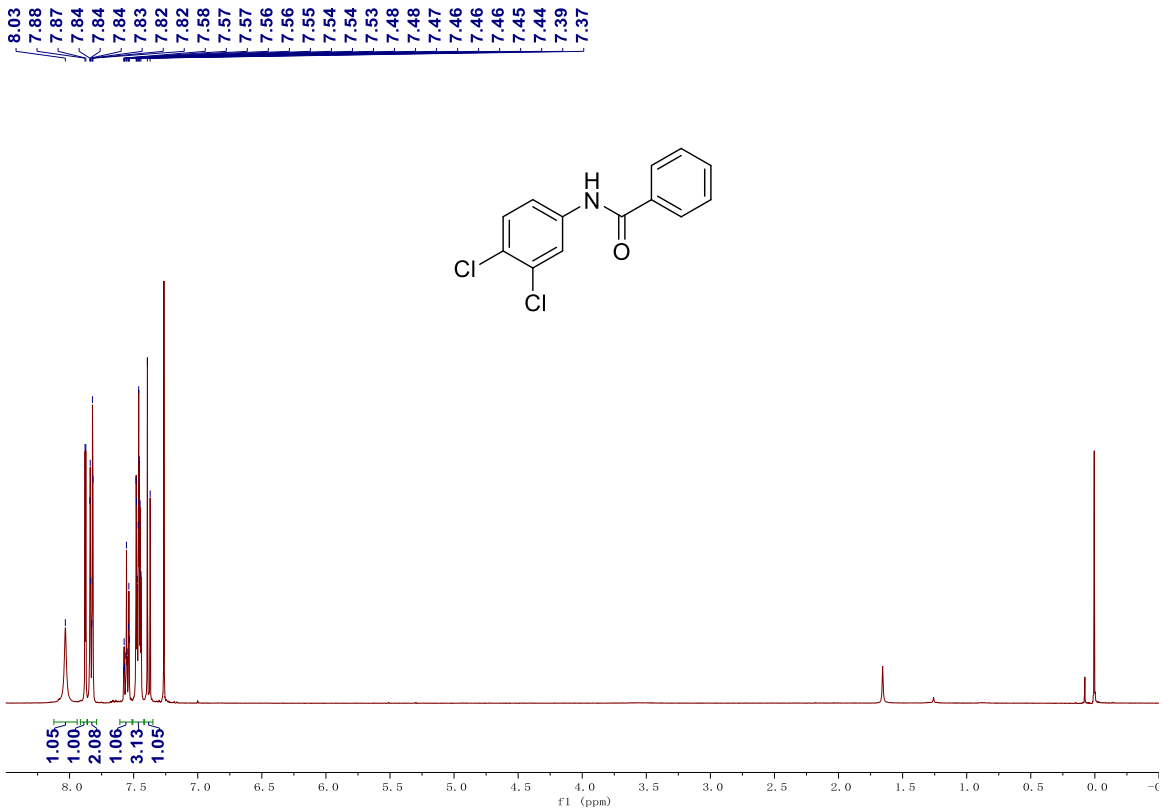

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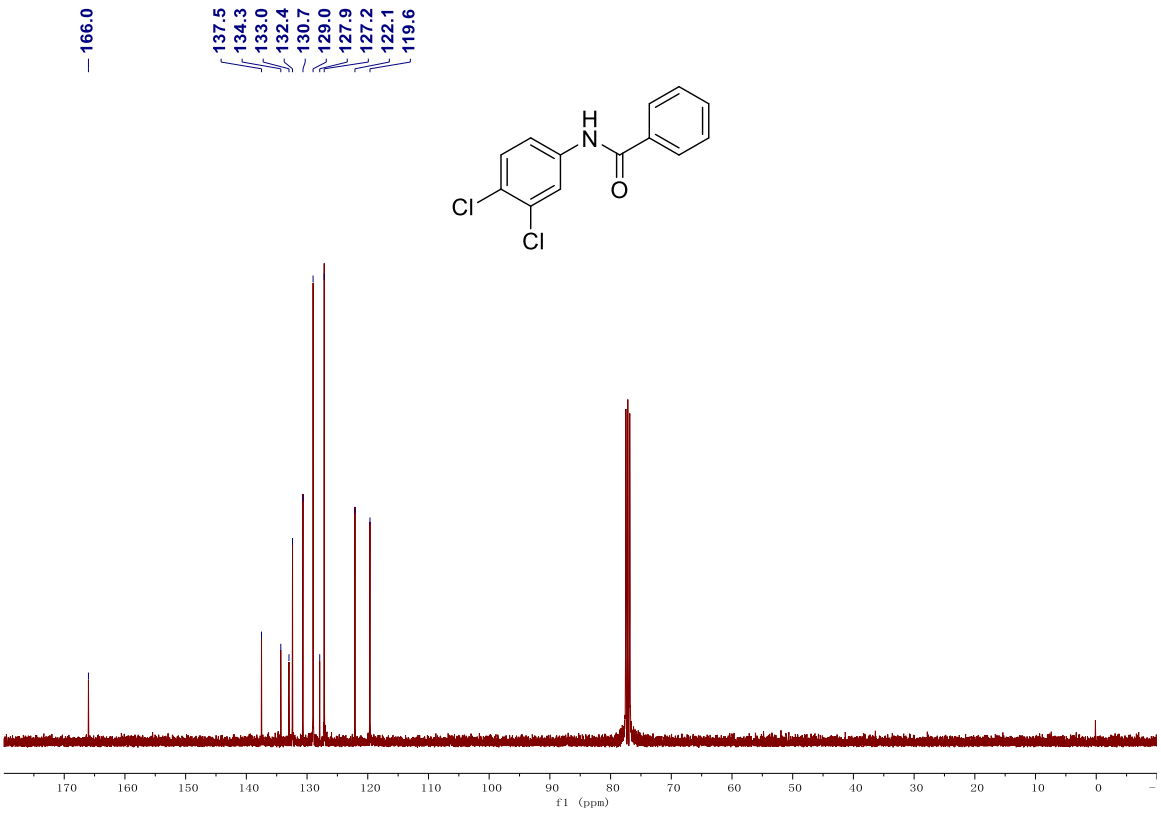

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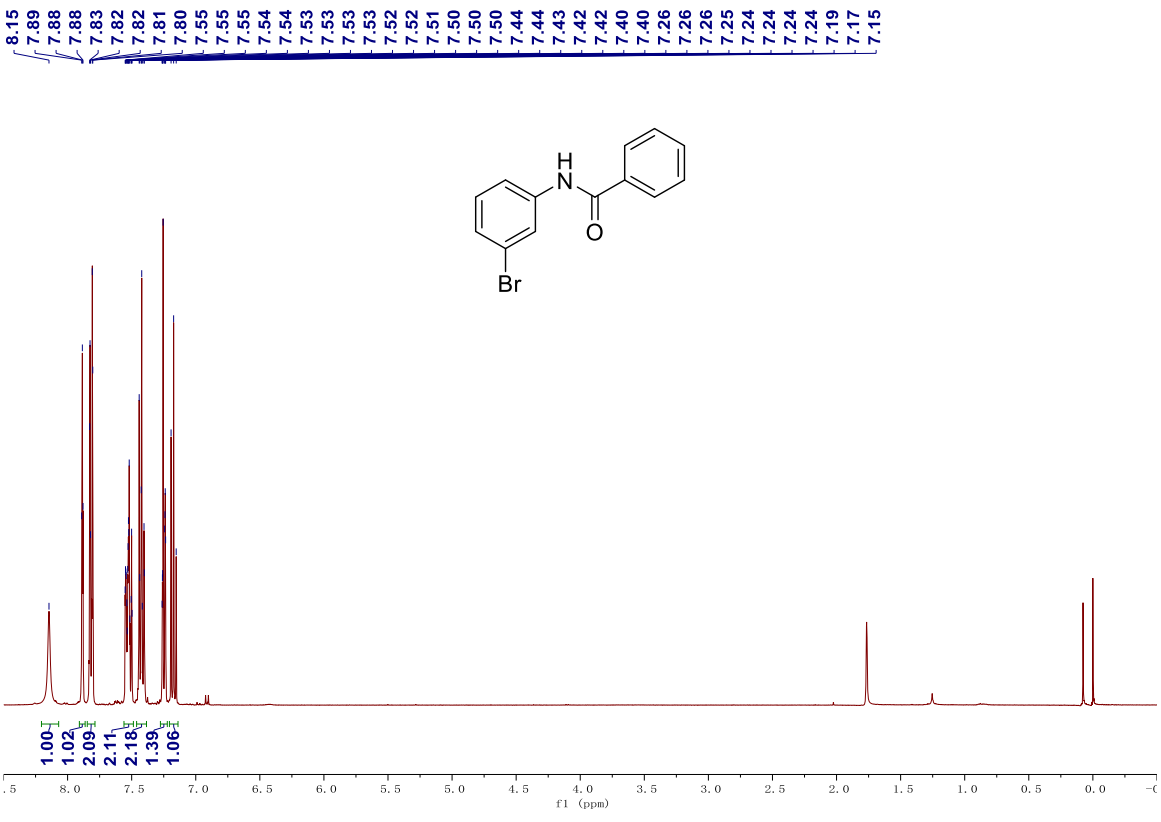

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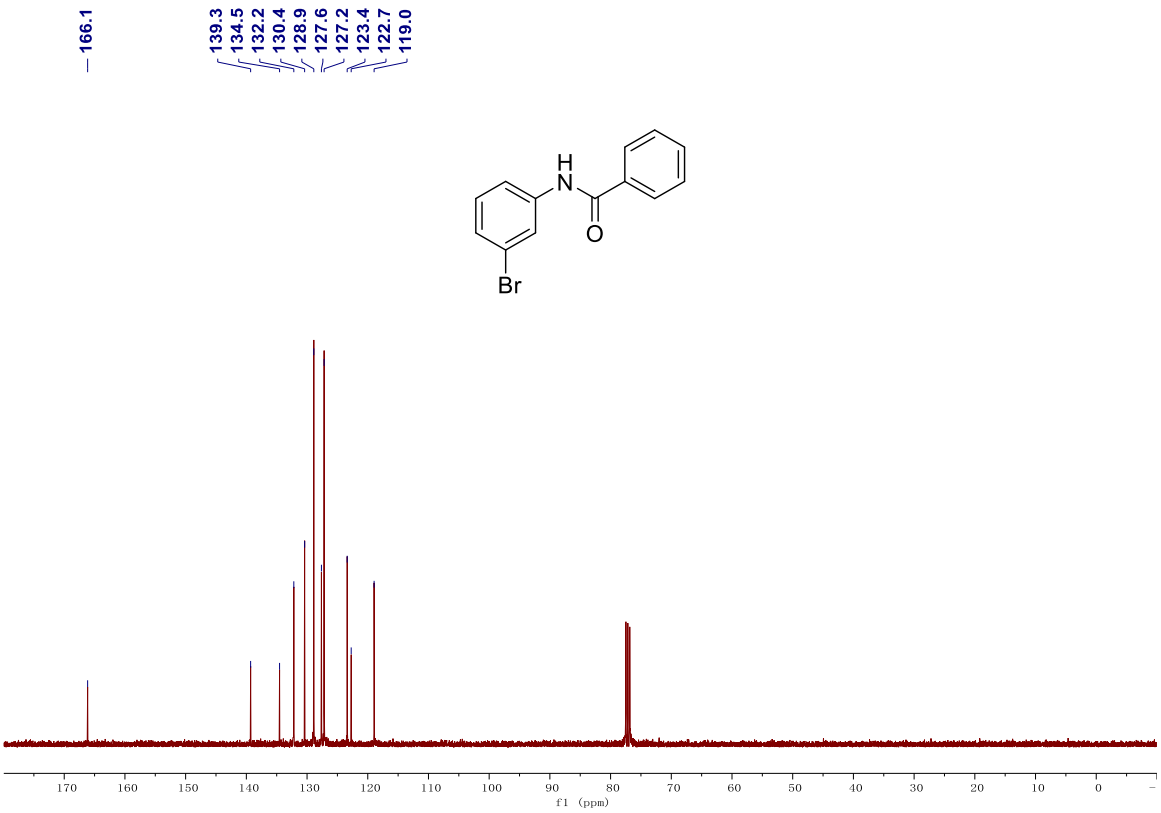

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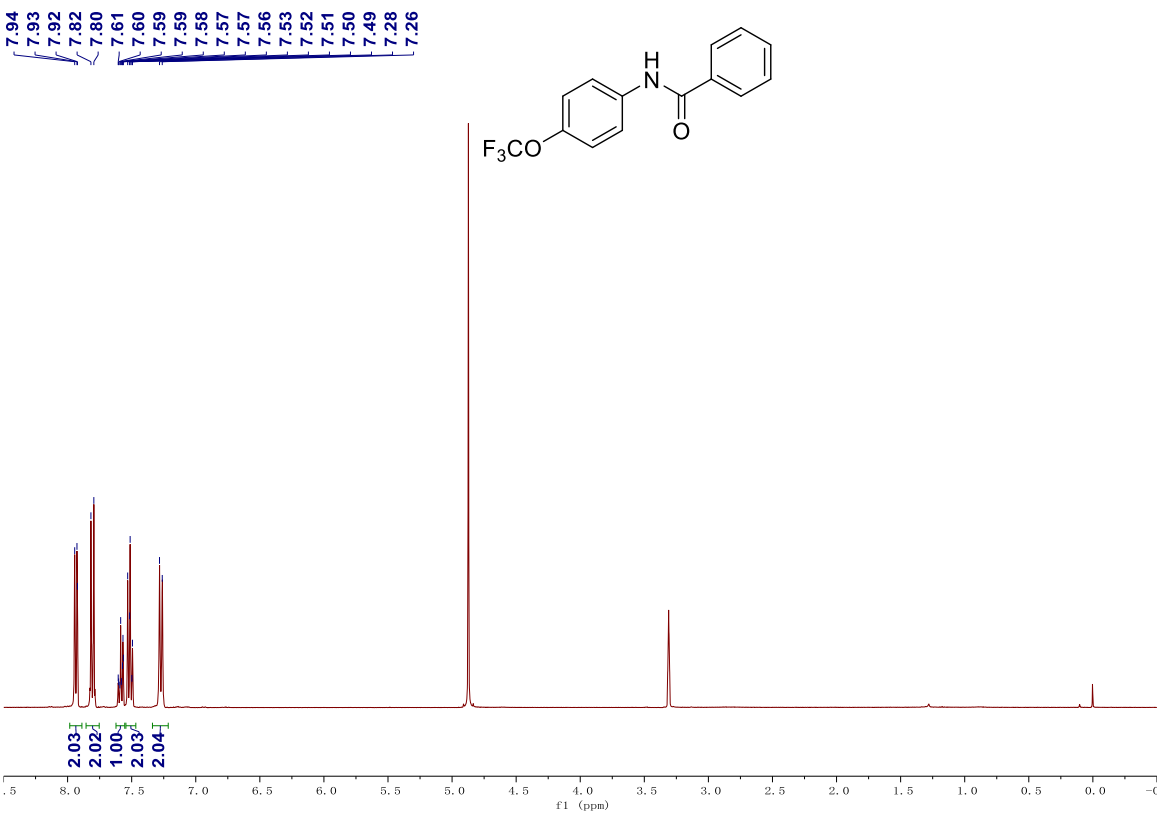

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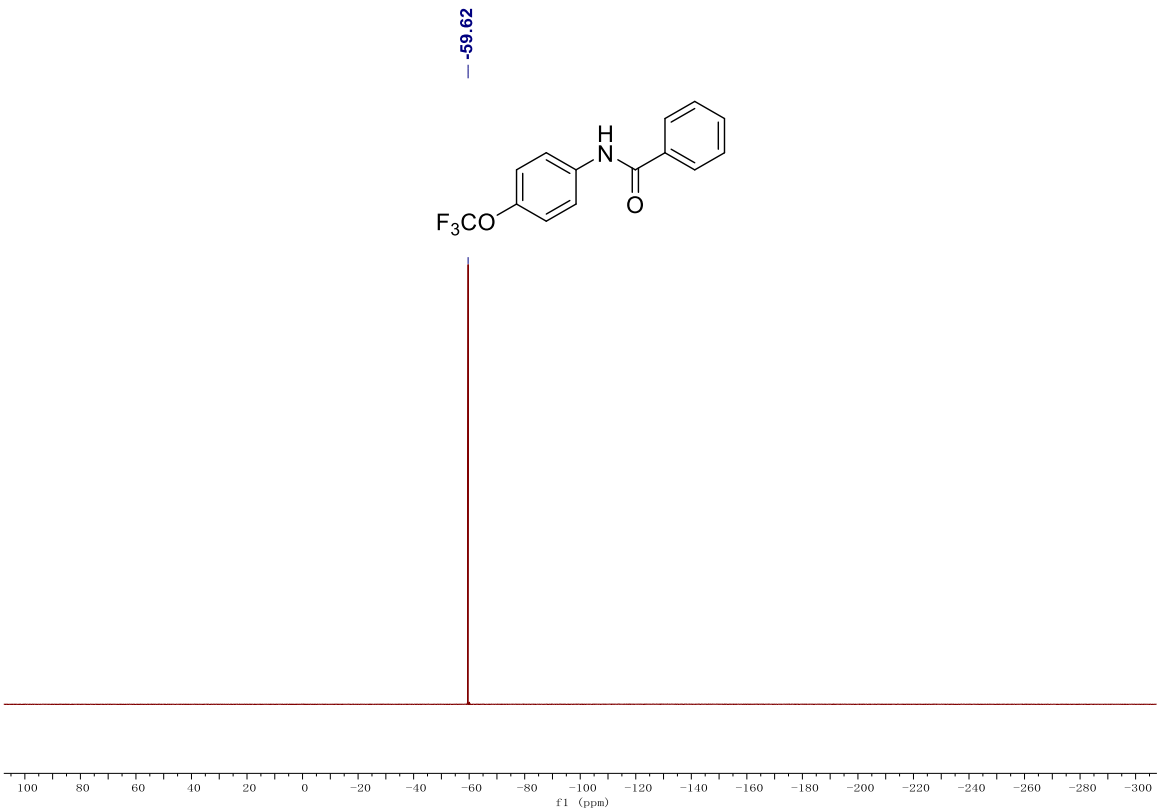

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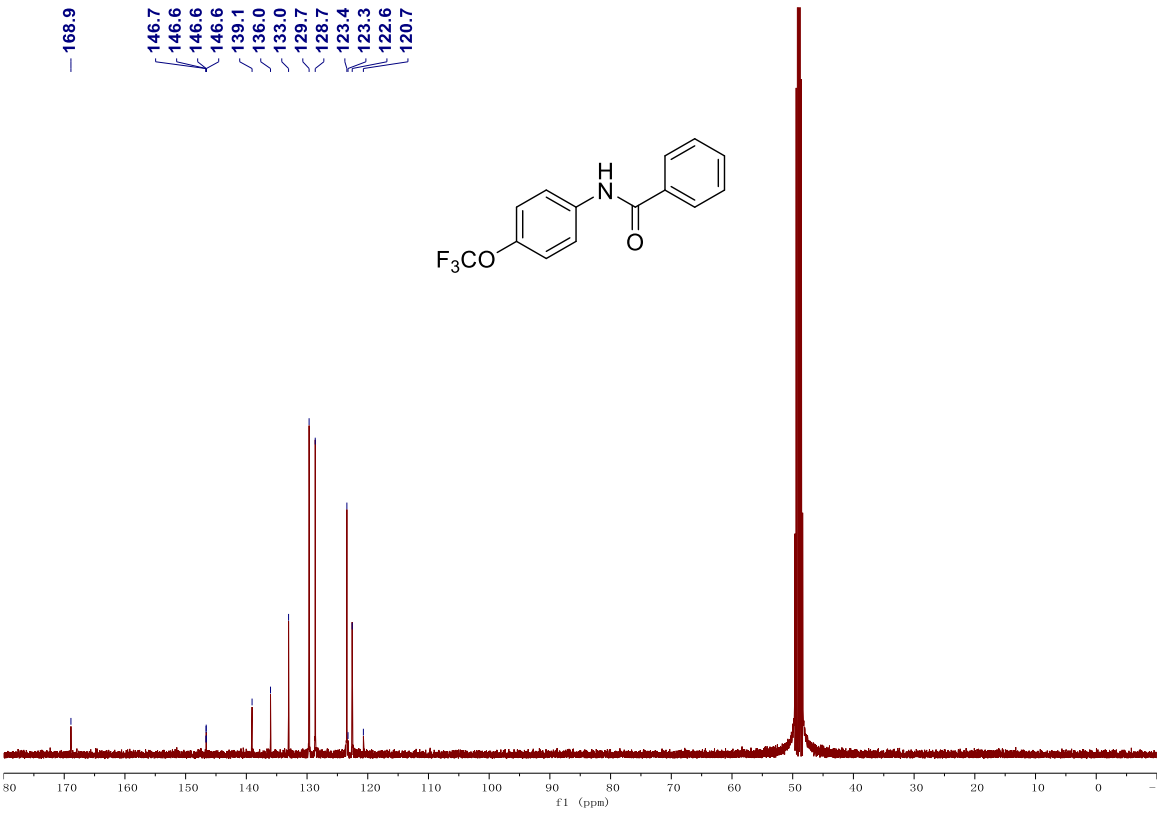
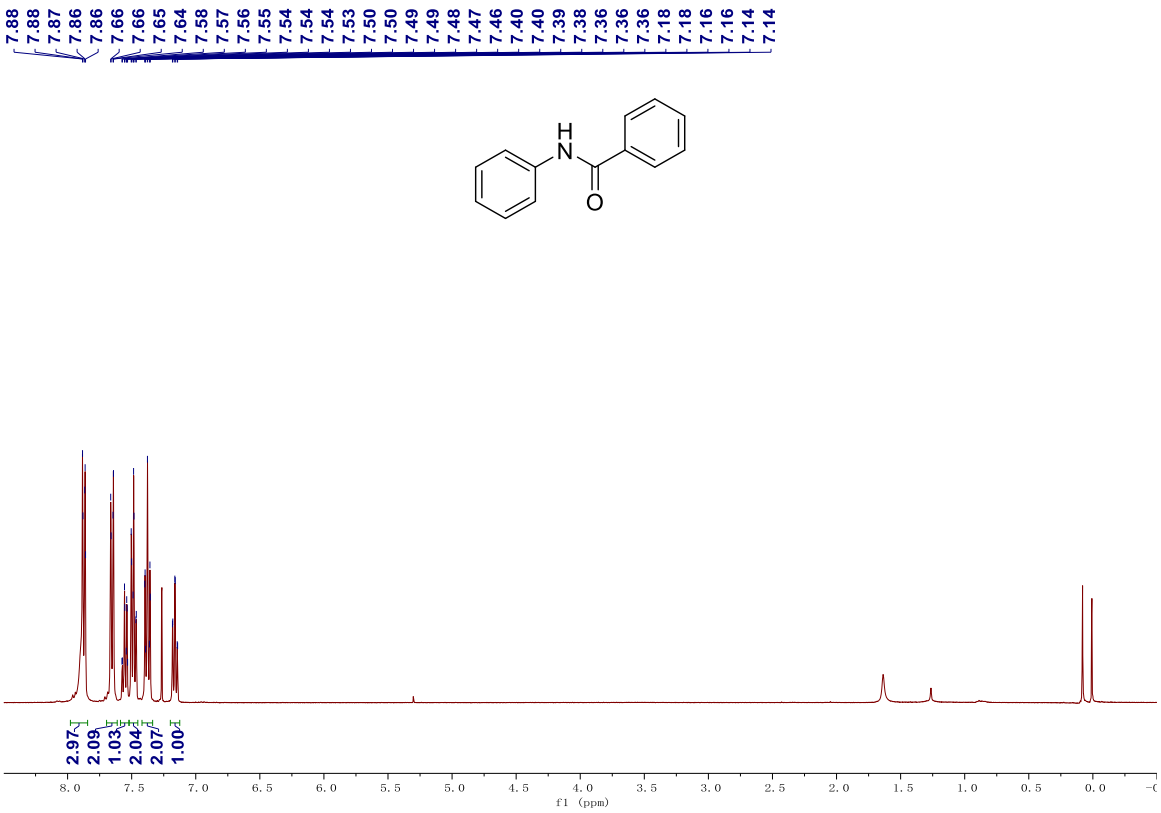
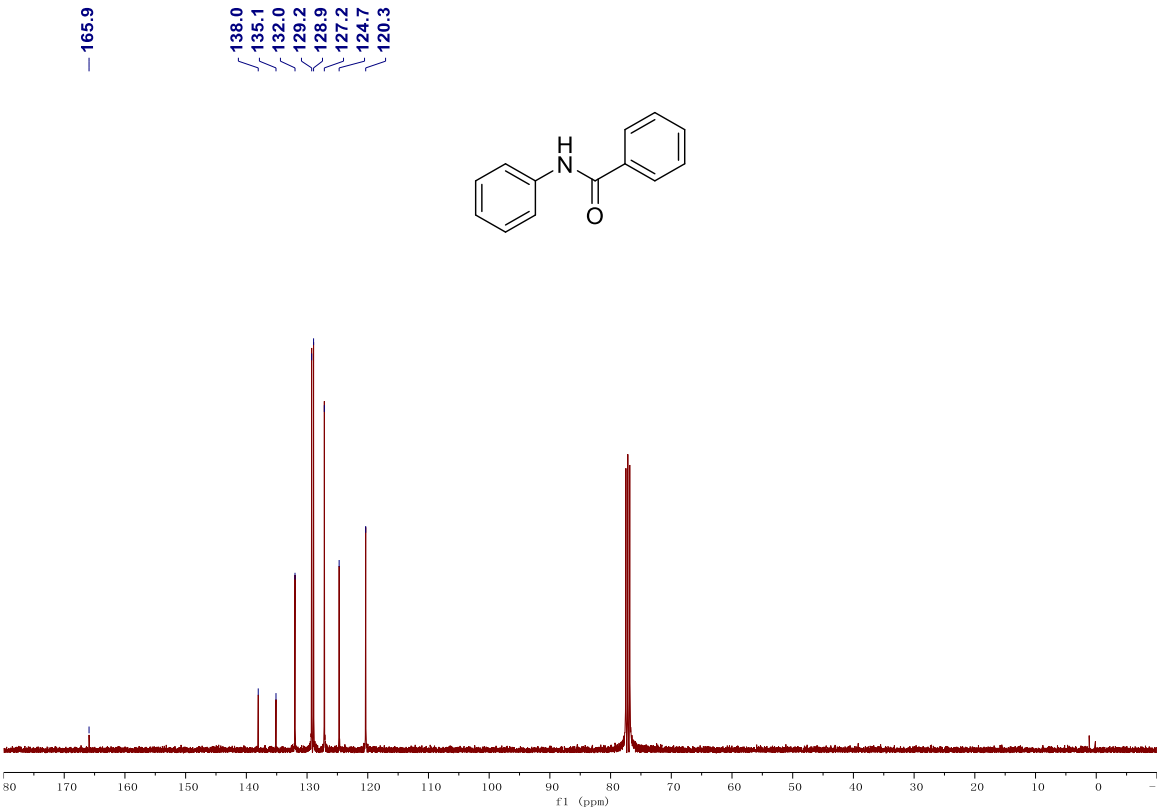


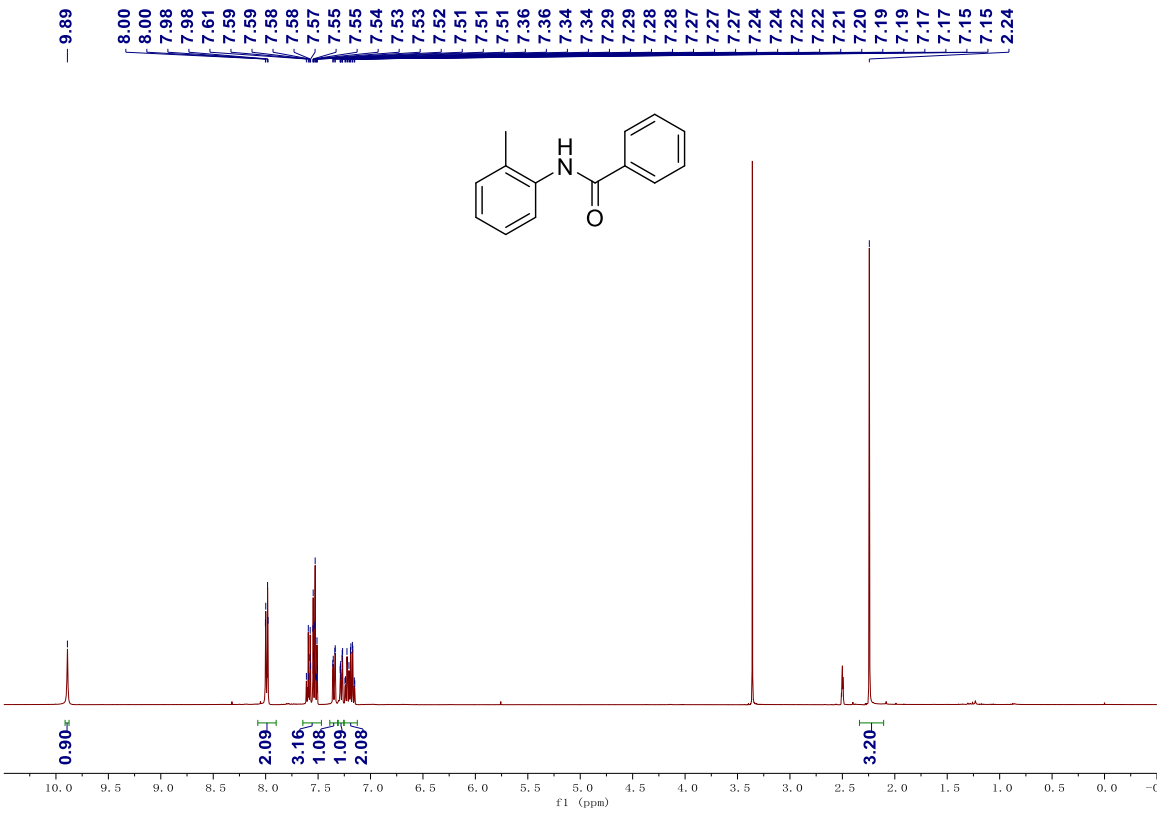
^{13}C NMR spectrum for compound **3v** (CD_3OD)



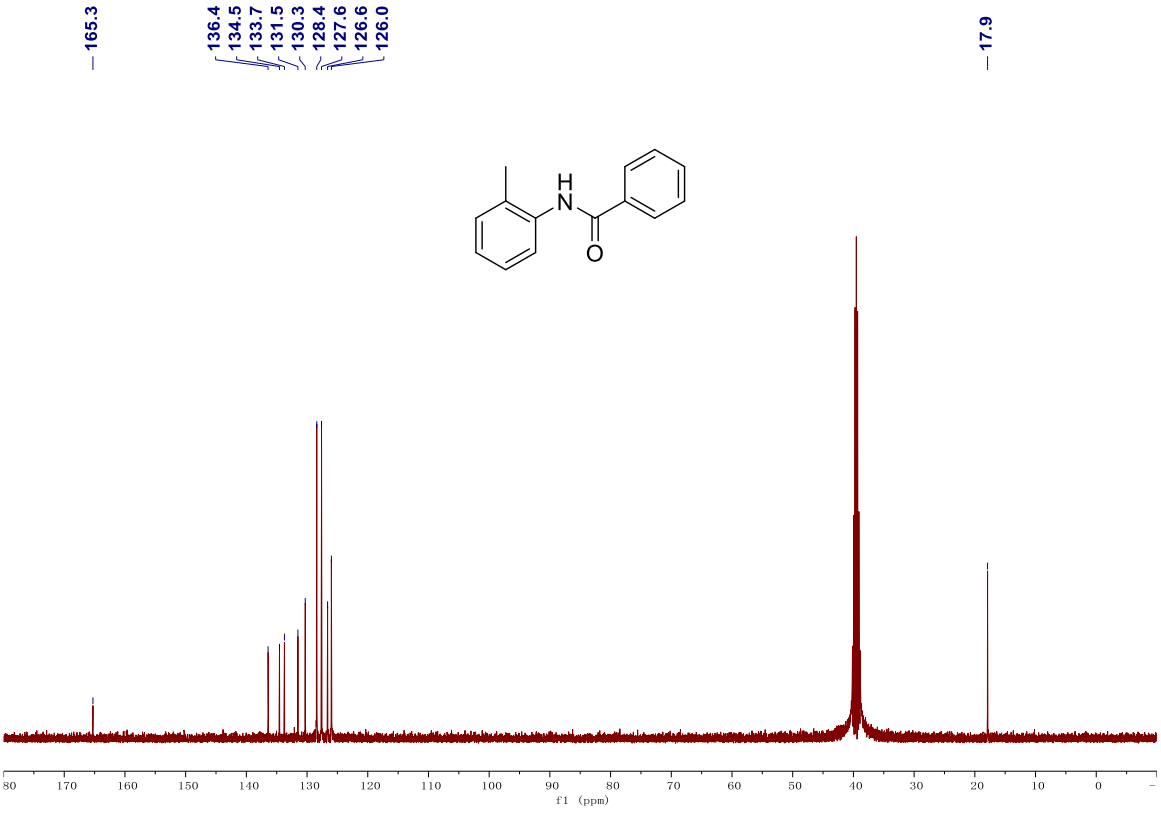
^{1}H NMR spectrum for compound **3w** ($CDCl_3$)



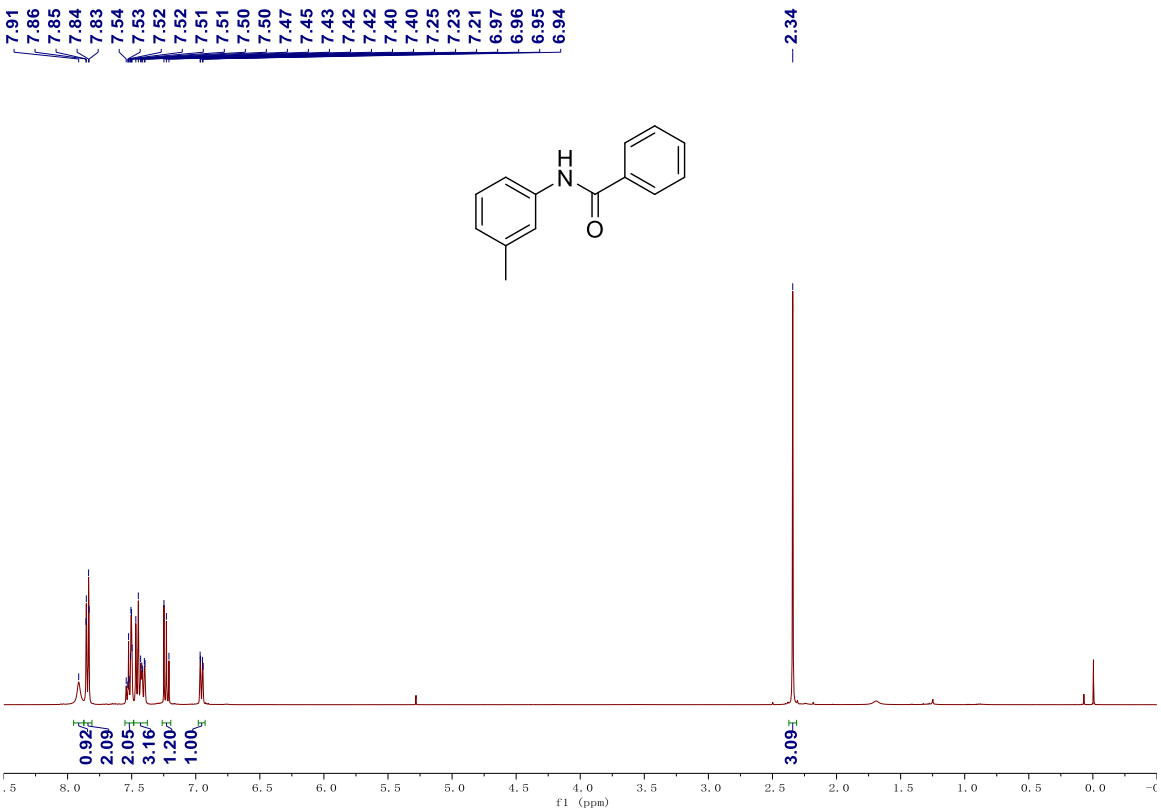
^{13}C NMR spectrum for compound **3w** ($CDCl_3$)



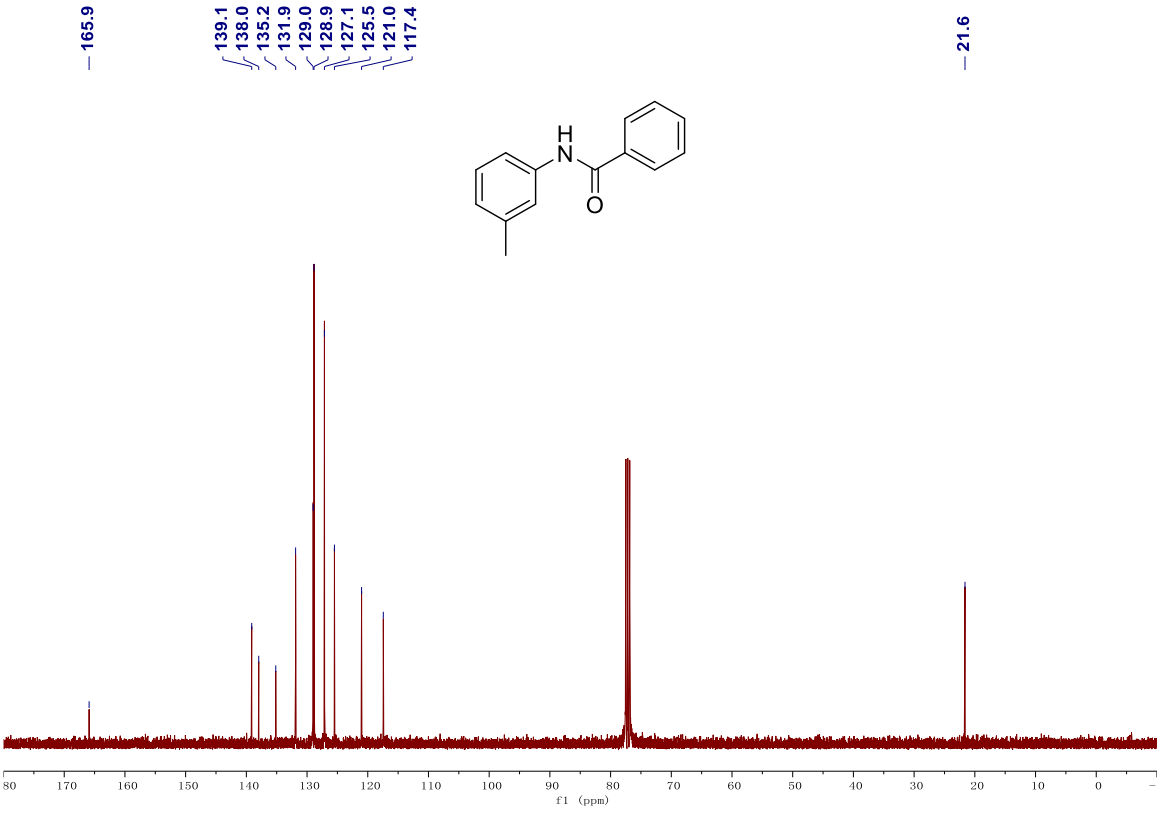
^{1}H NMR spectrum for compound **3x** (DMSO-d_6)



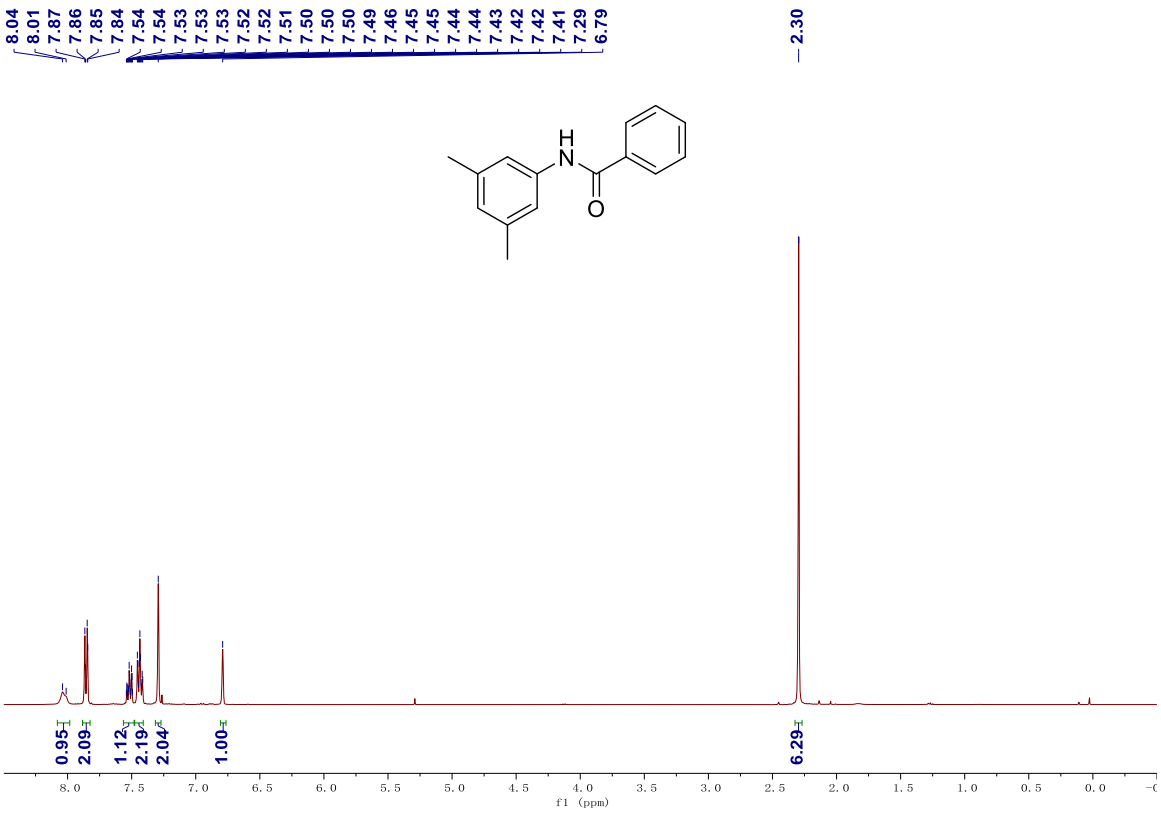
^{13}C NMR spectrum for compound **3x** (DMSO-d_6)



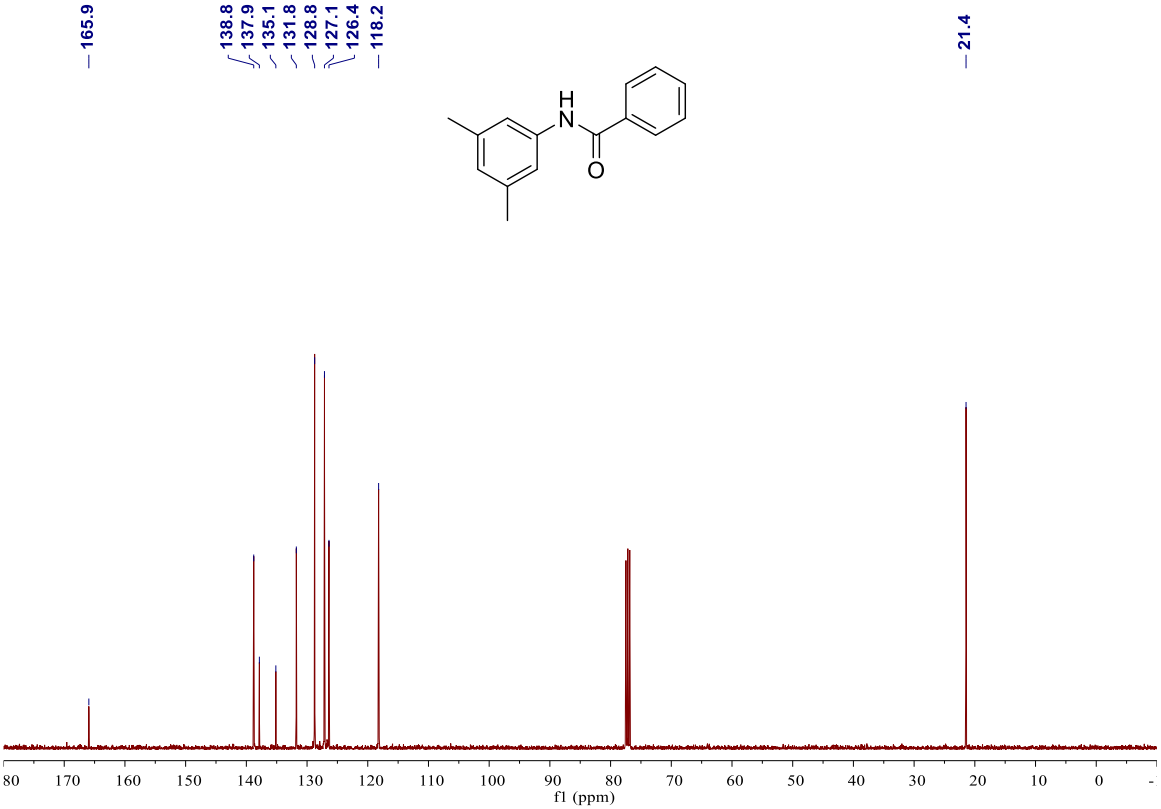
^{1}H NMR spectrum for compound **3y** ($CDCl_3$)



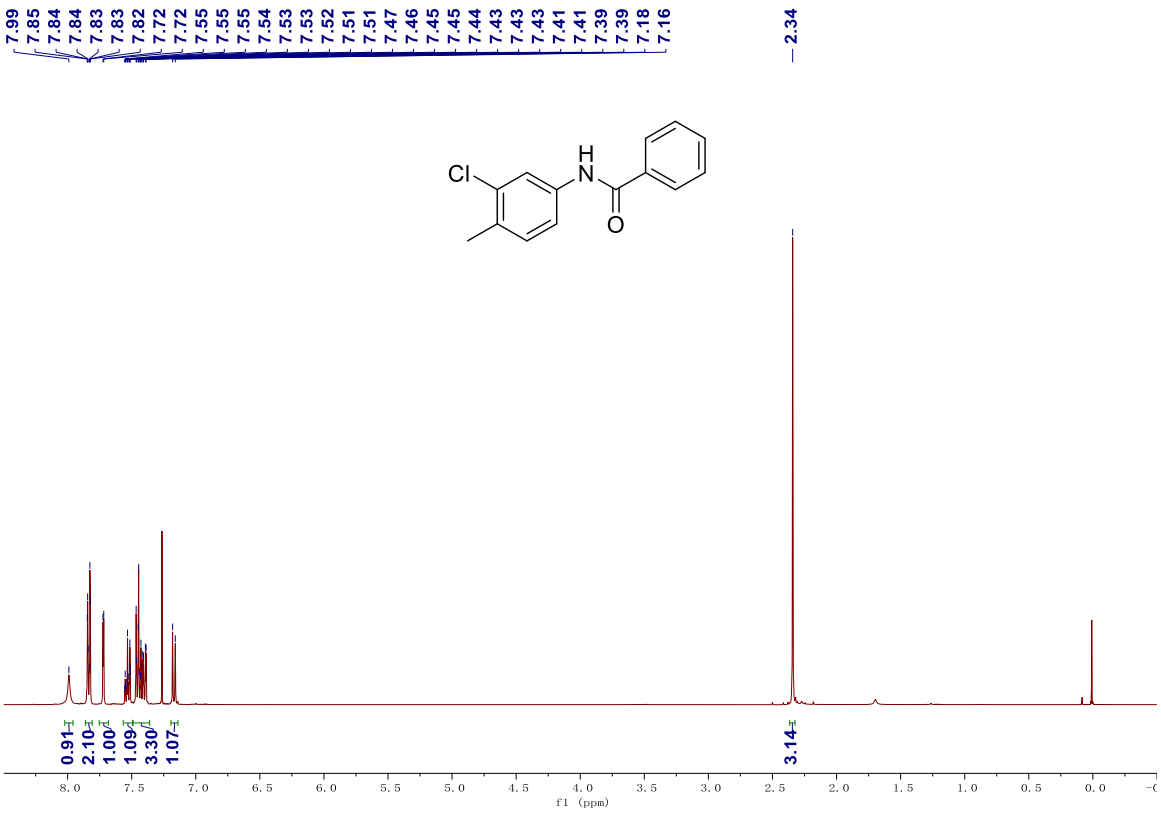
^{13}C NMR spectrum for compound **3y** ($CDCl_3$)



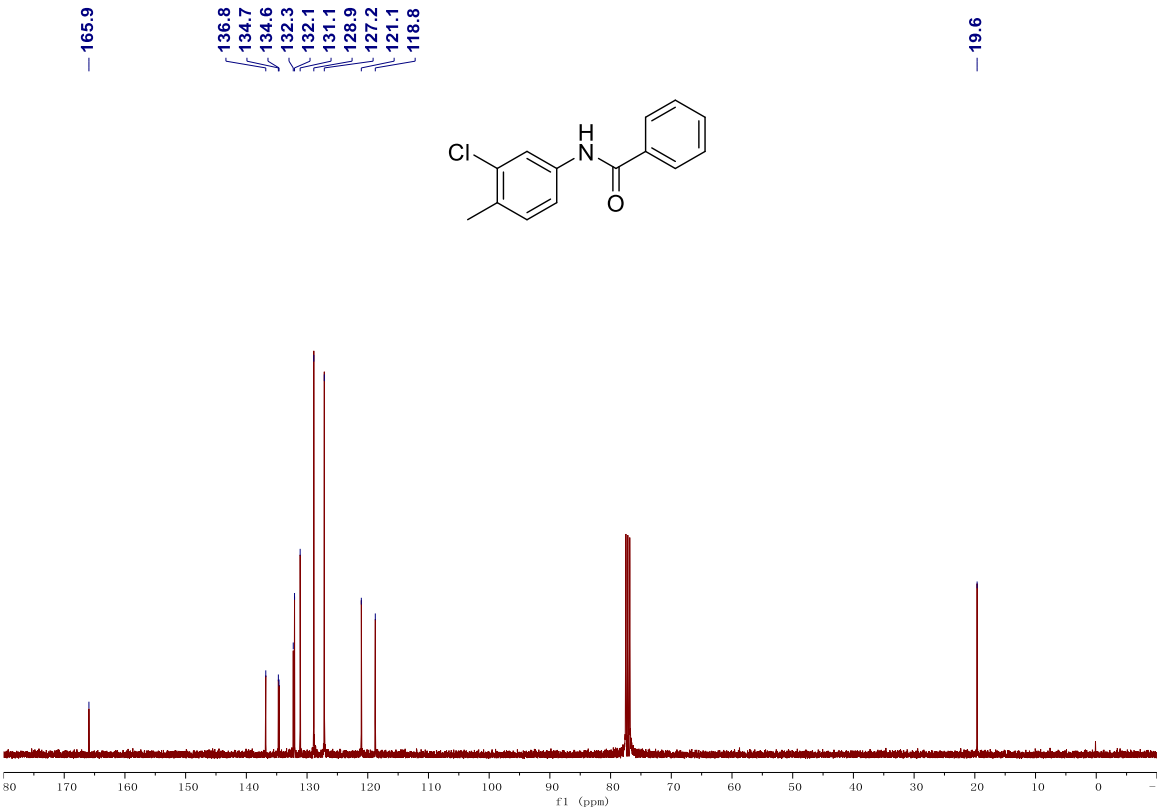
^{1}H NMR spectrum for compound **3z** ($CDCl_3$)



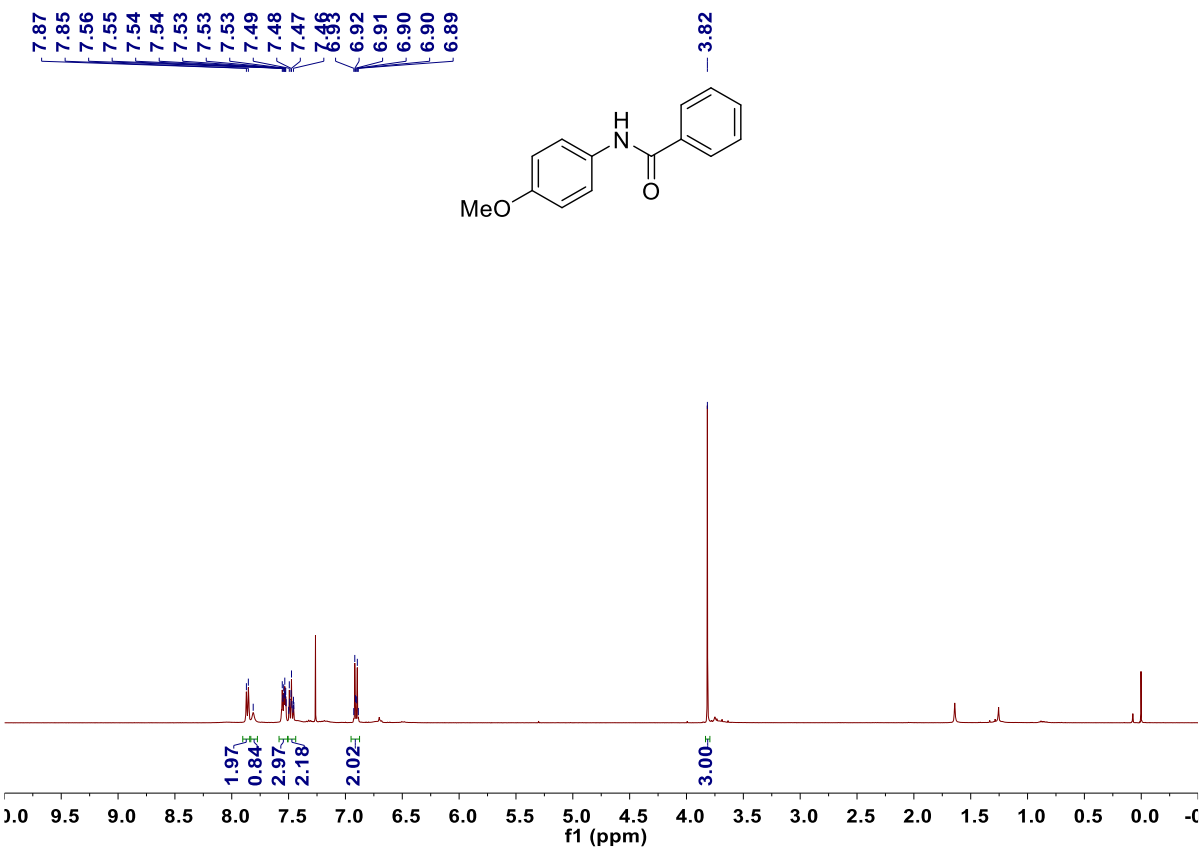
^{13}C NMR spectrum for compound **3z** ($CDCl_3$)



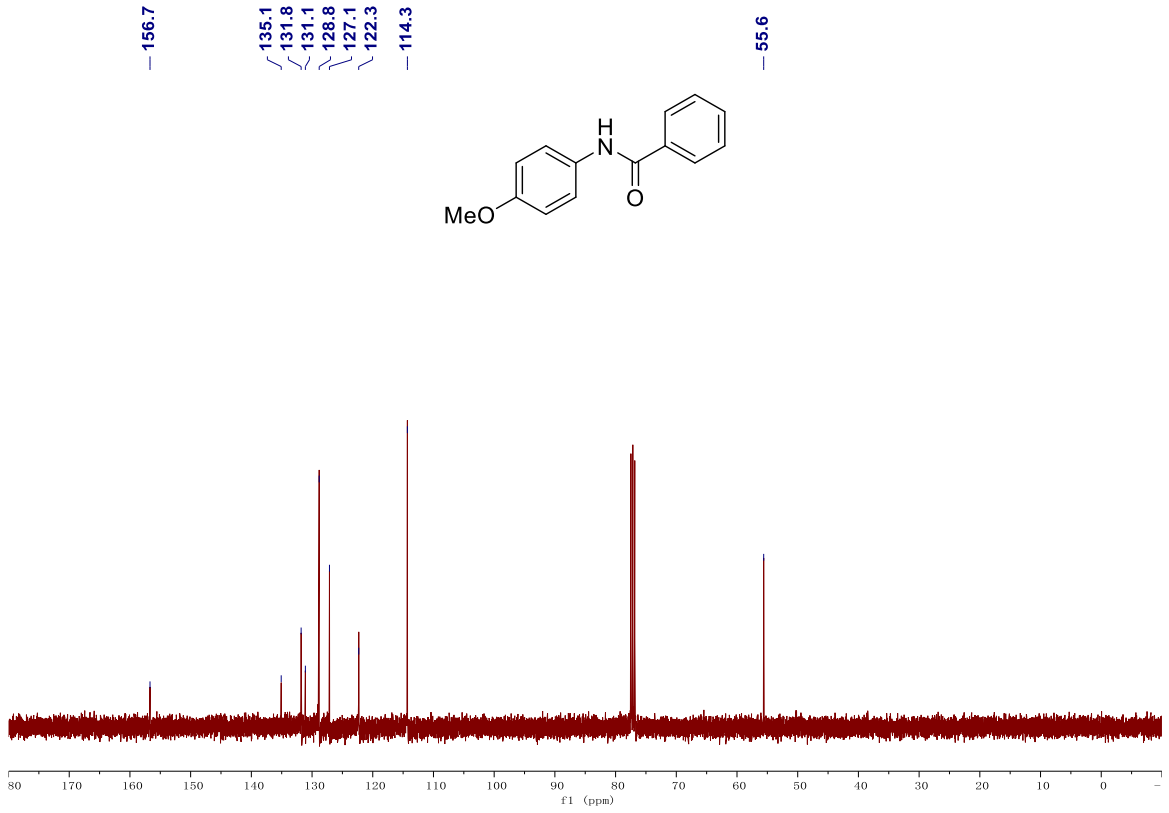
^{1}H NMR spectrum for compound **3aa** ($CDCl_3$)



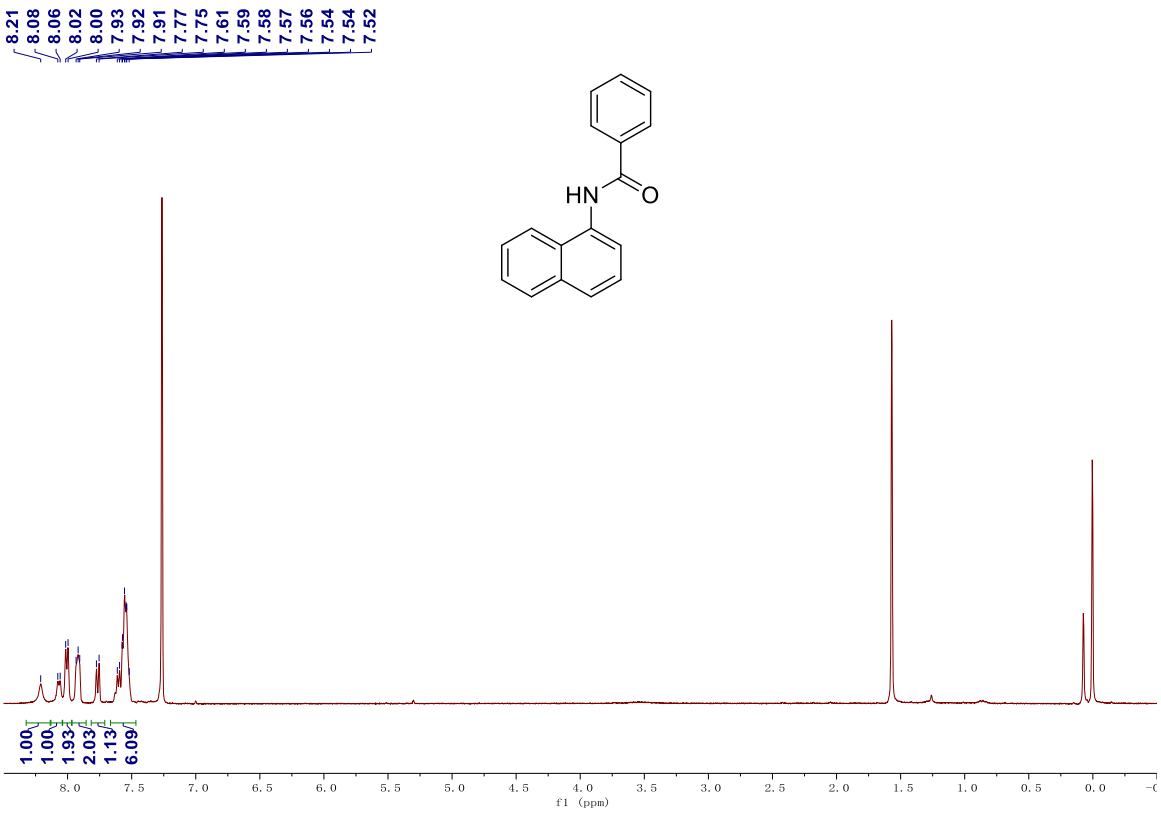
^{13}C NMR spectrum for compound **3aa** ($CDCl_3$)



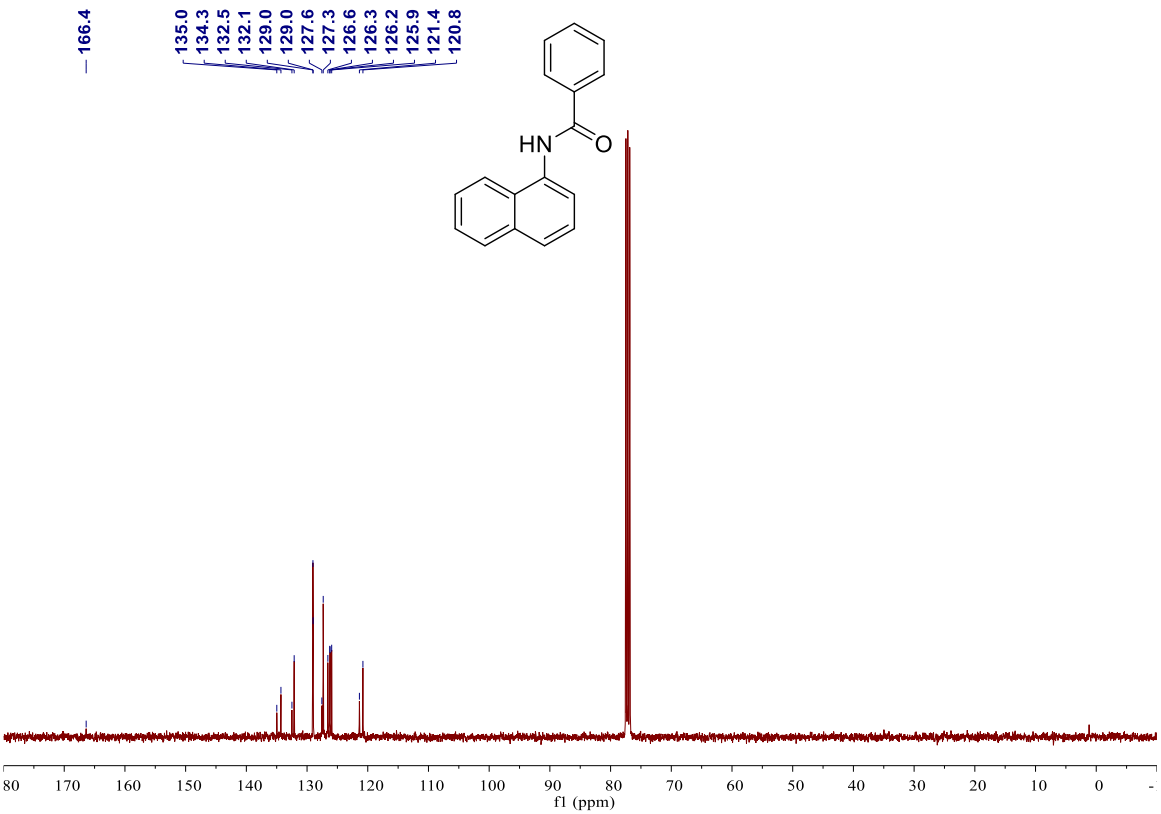
^{1}H NMR spectrum for compound **3ab** ($CDCl_3$)



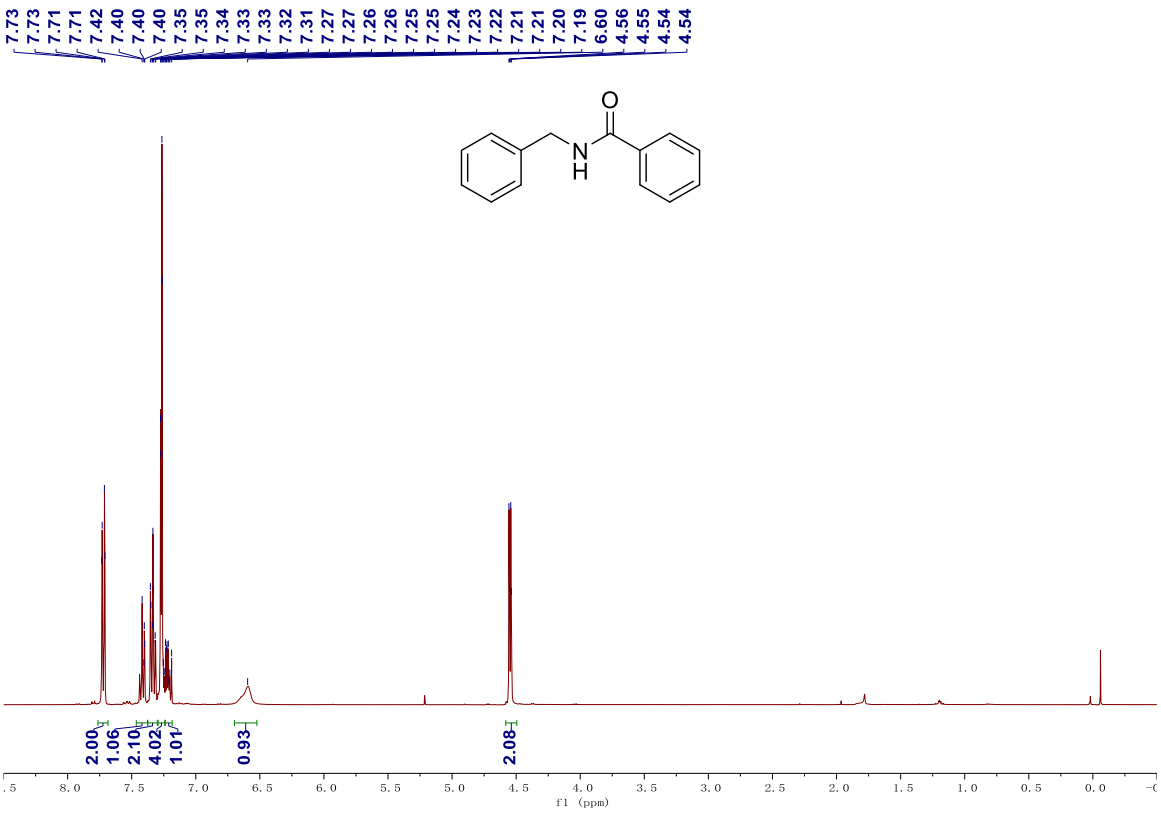
^{13}C NMR spectrum for compound **3ab** ($CDCl_3$)



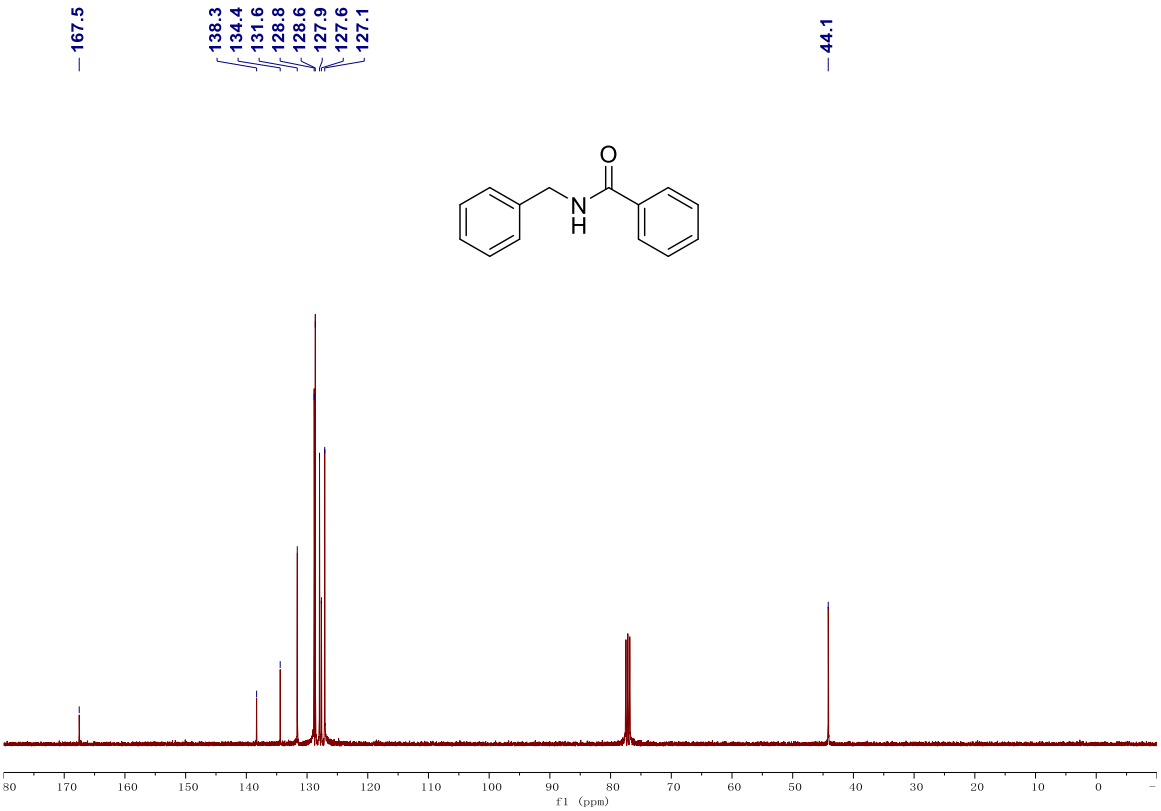
^{1}H NMR spectrum for compound **3ac** ($CDCl_3$)



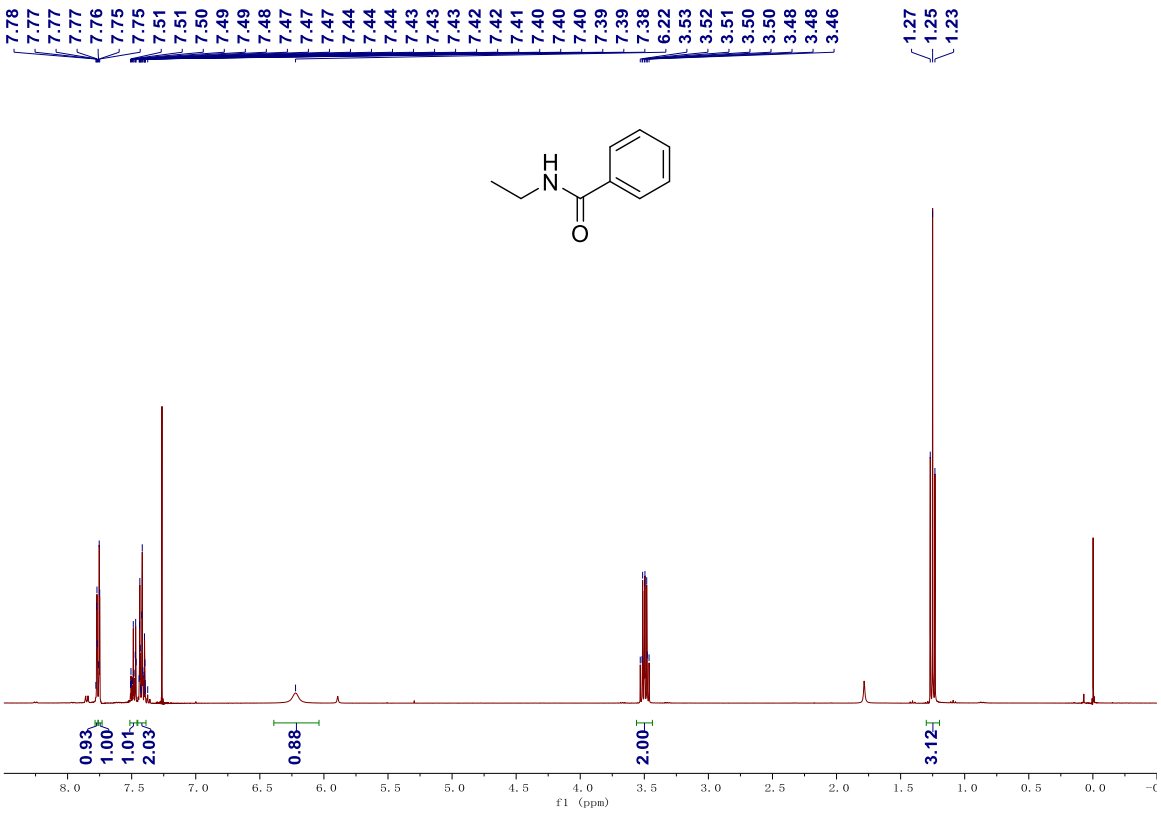
^{13}C NMR spectrum for compound **3ac** ($CDCl_3$)



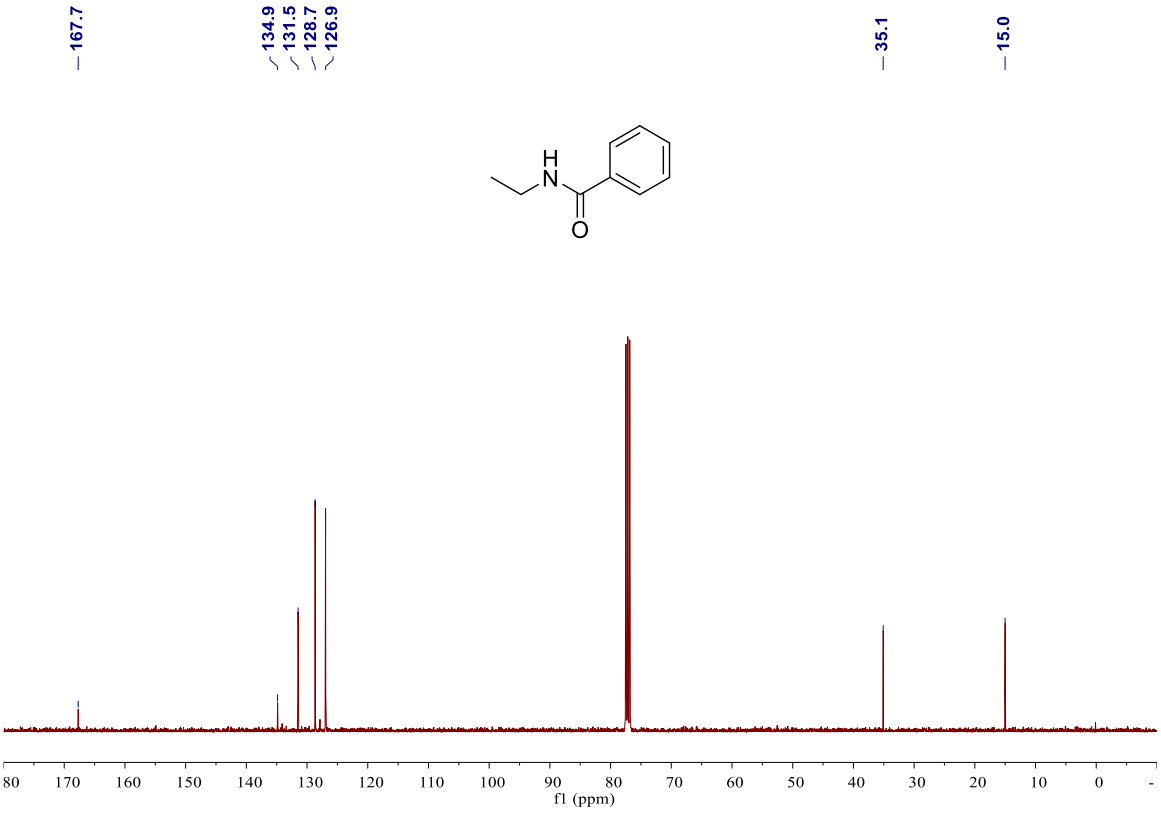
^{1}H NMR spectrum for compound **3ad** ($CDCl_3$)



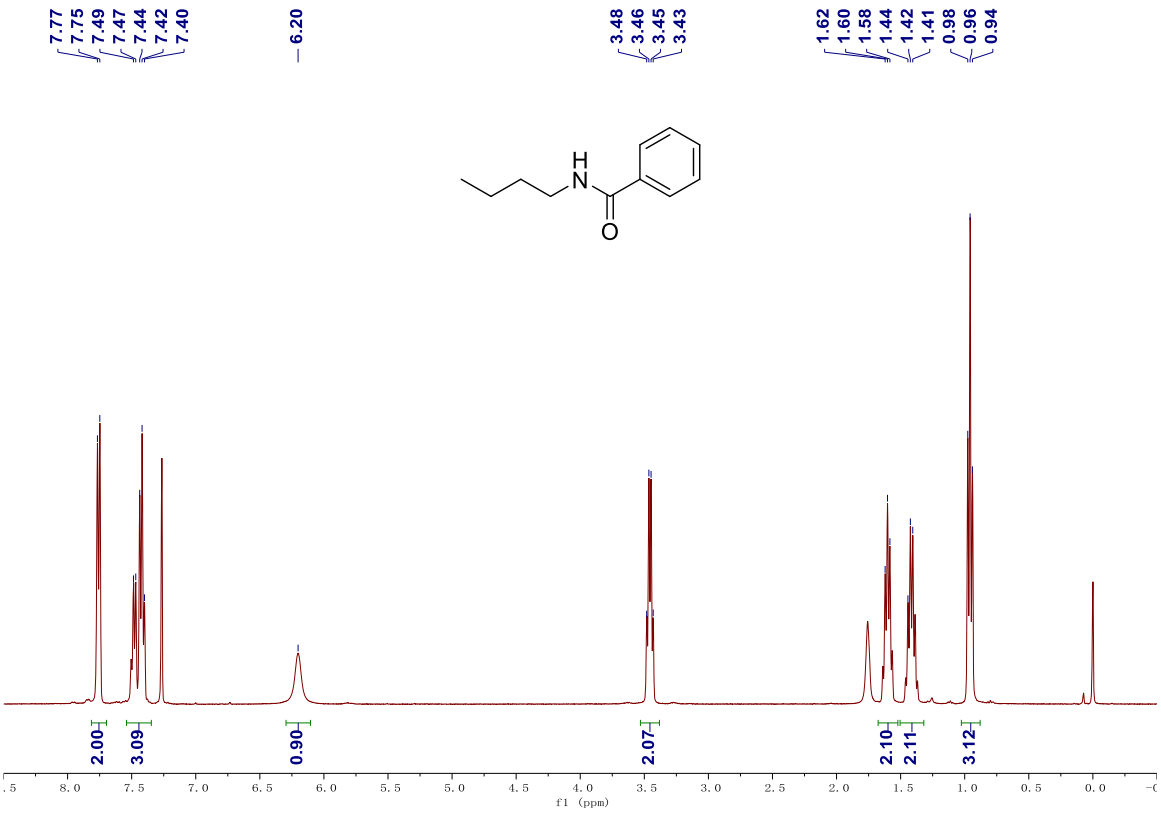
^{13}C NMR spectrum for compound **3ad** ($CDCl_3$)



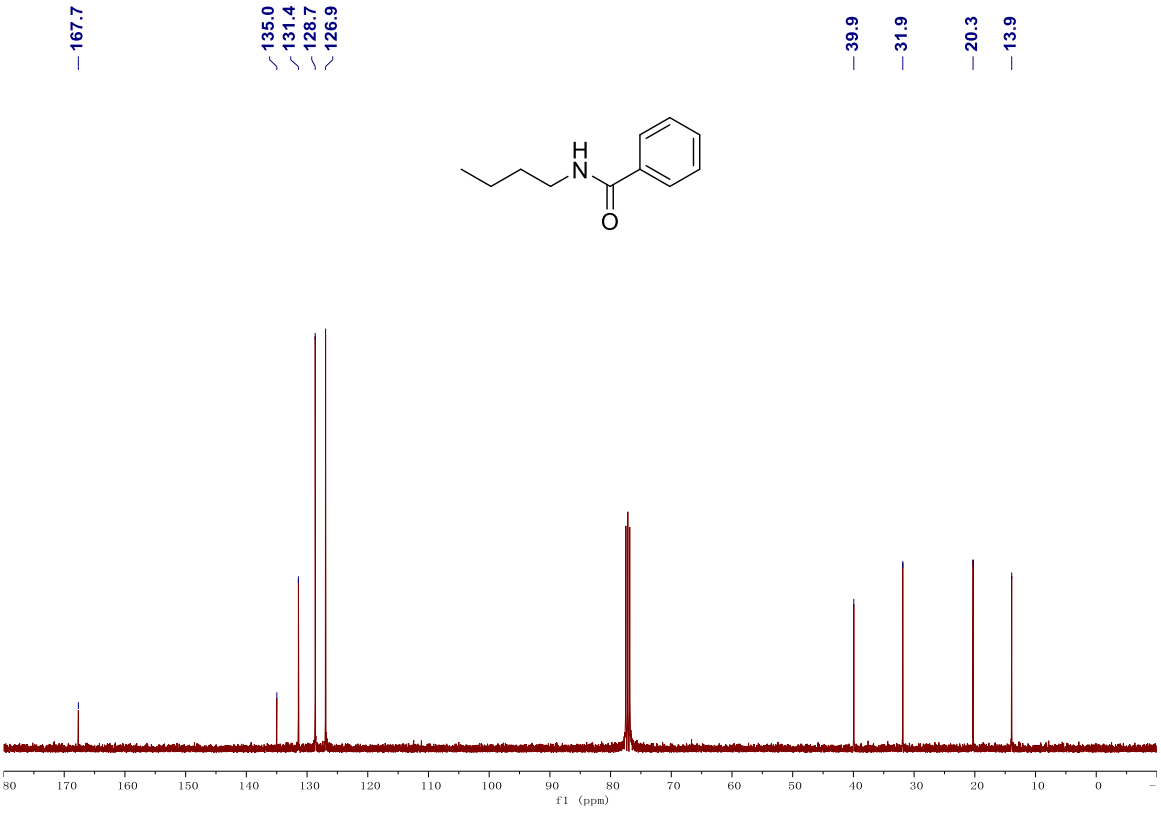
^{1}H NMR spectrum for compound **3ae** ($CDCl_3$)



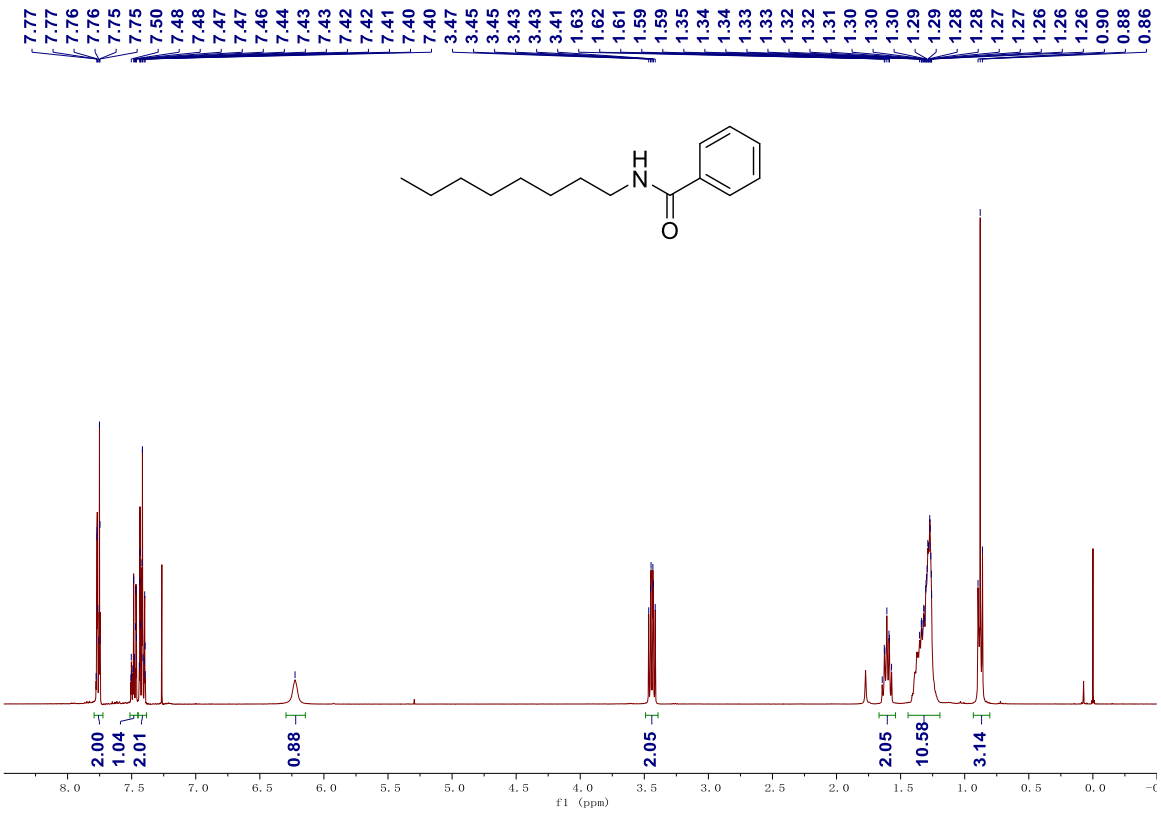
^{13}C NMR spectrum for compound **3ae** ($CDCl_3$)



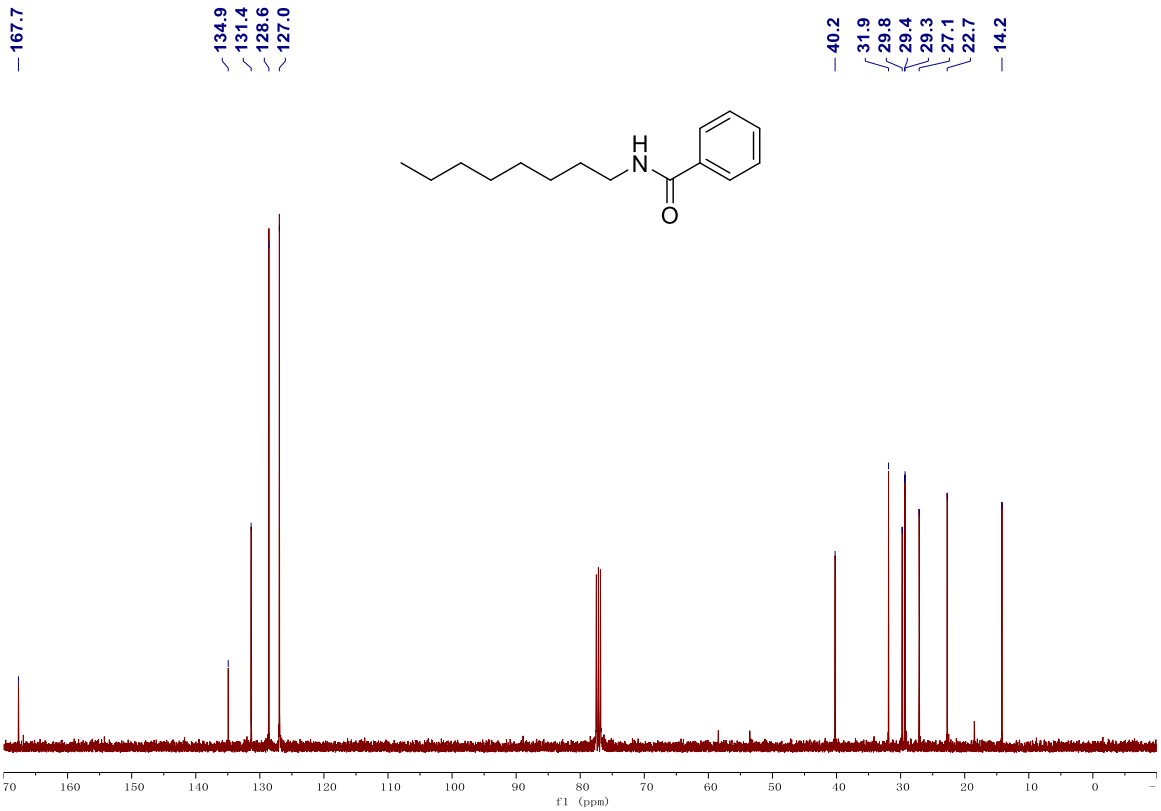
^{1}H NMR spectrum for compound **3af** ($CDCl_3$)



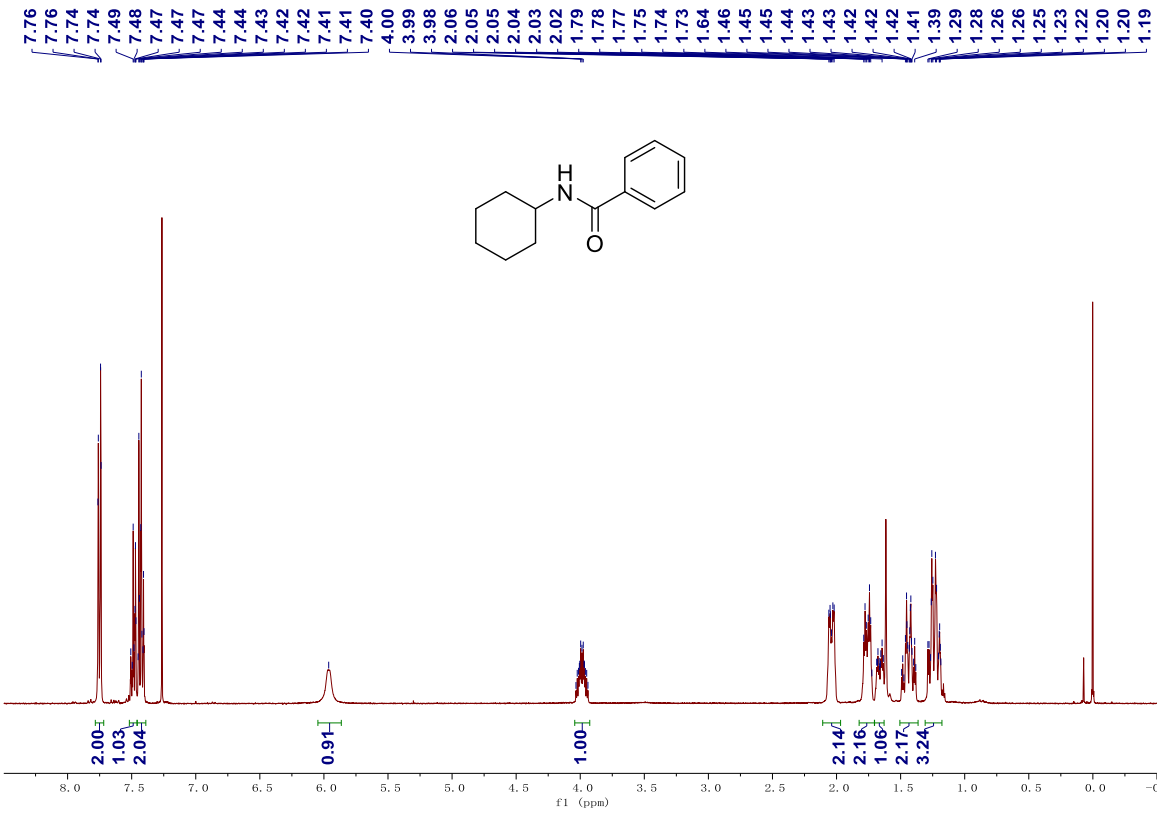
^{13}C NMR spectrum for compound **3af** ($CDCl_3$)



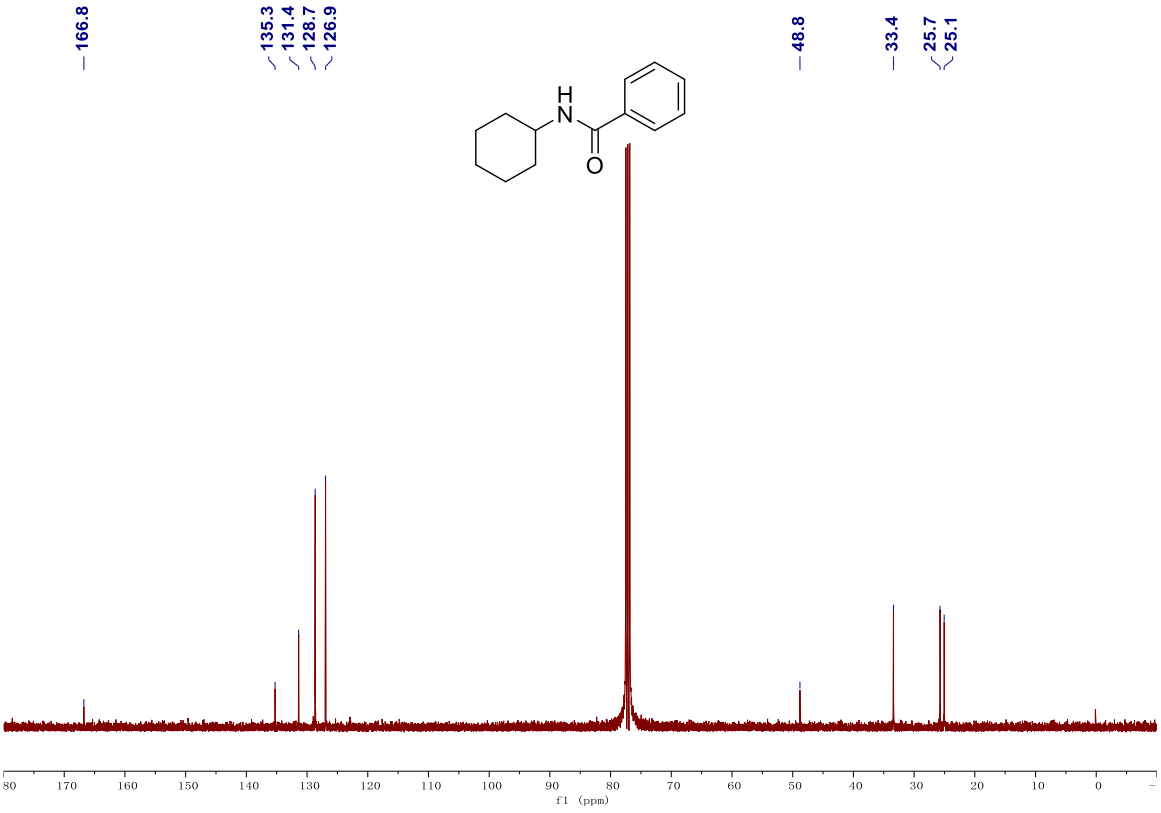
^{1}H NMR spectrum for compound **3ag** ($CDCl_3$)



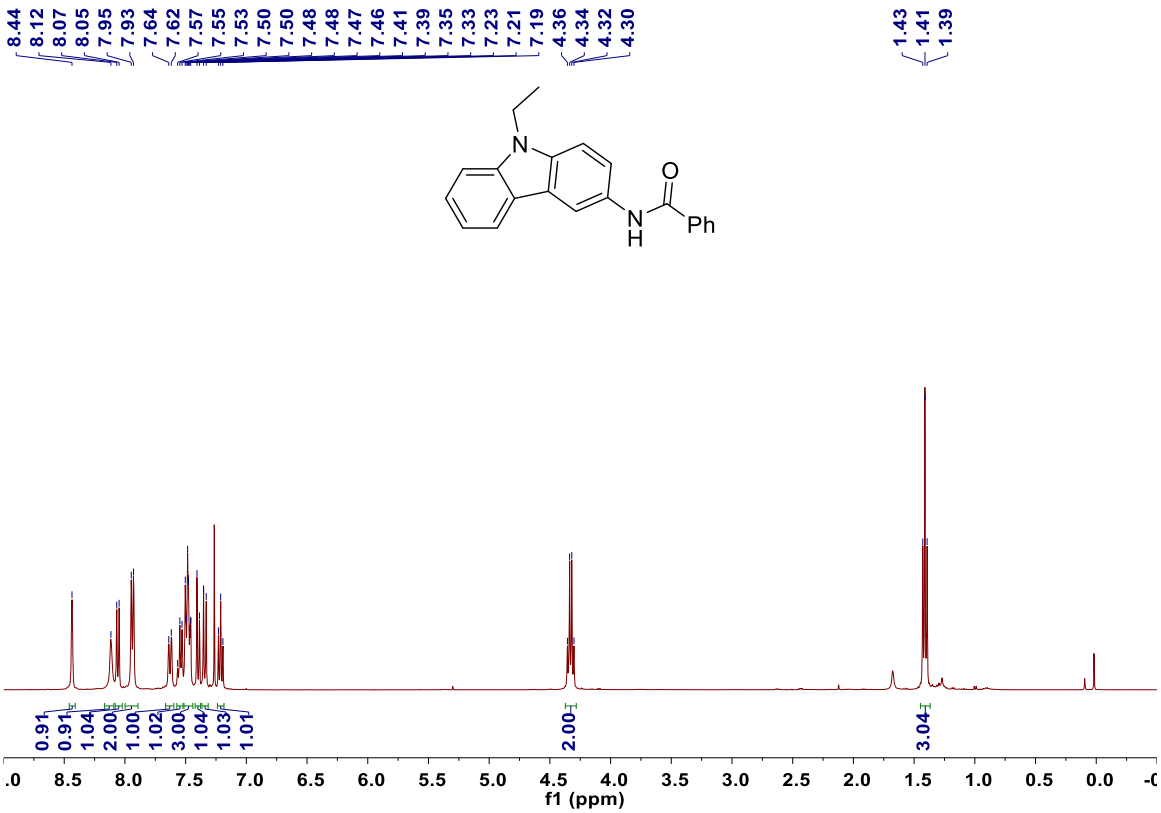
^{13}C NMR spectrum for compound **3ag** ($CDCl_3$)



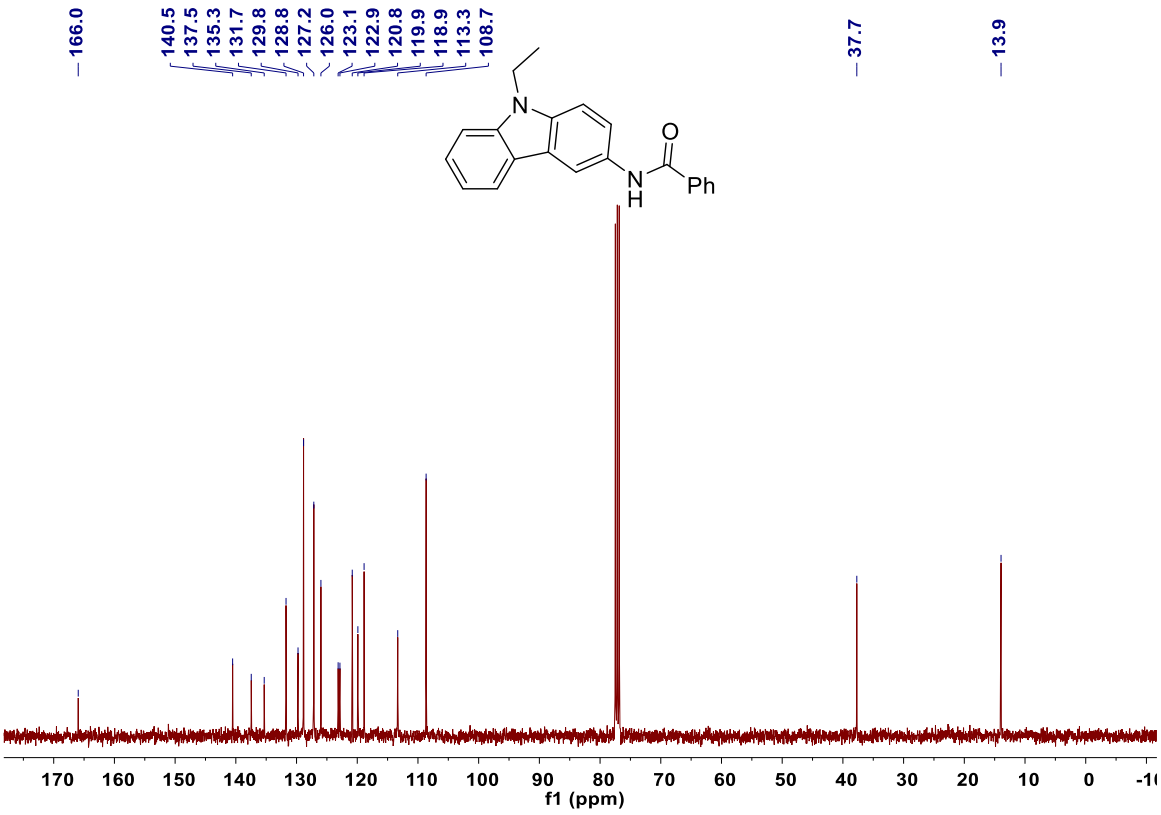
^{1}H NMR spectrum for compound **3ah** ($CDCl_3$)



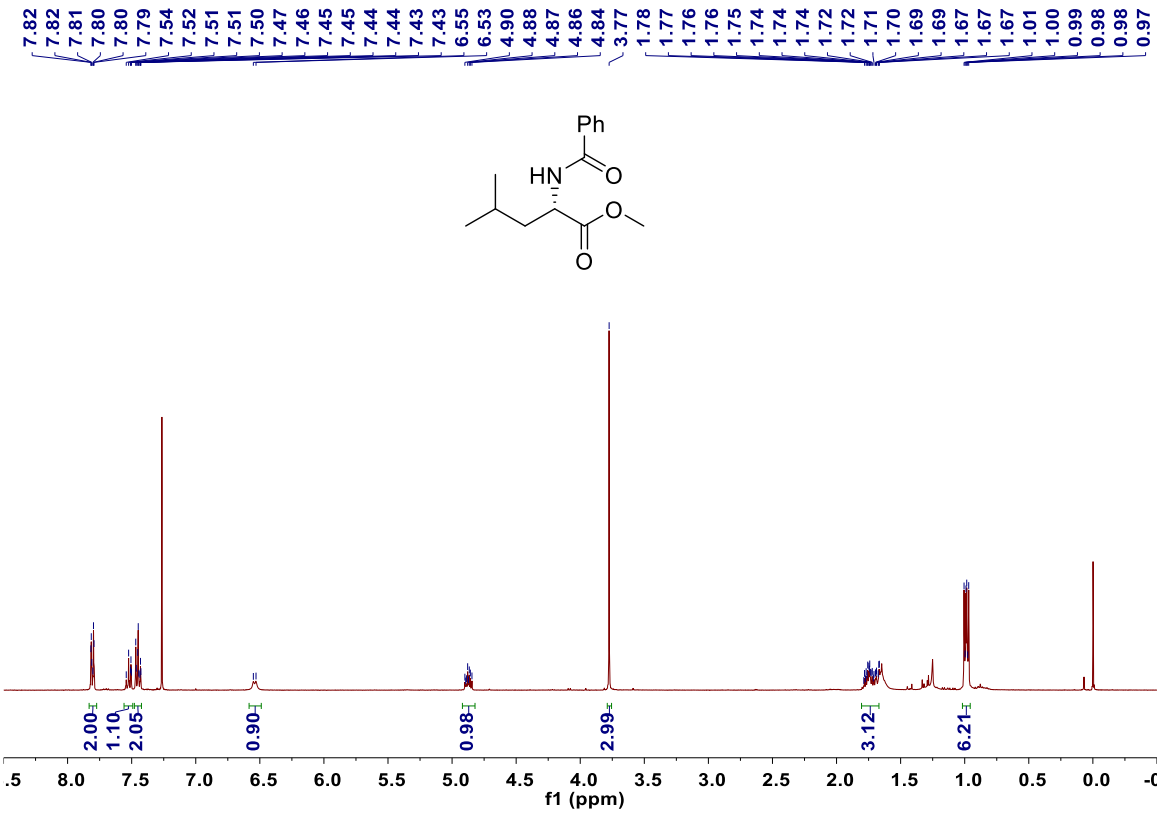
^{13}C NMR spectrum for compound **3ah** ($CDCl_3$)



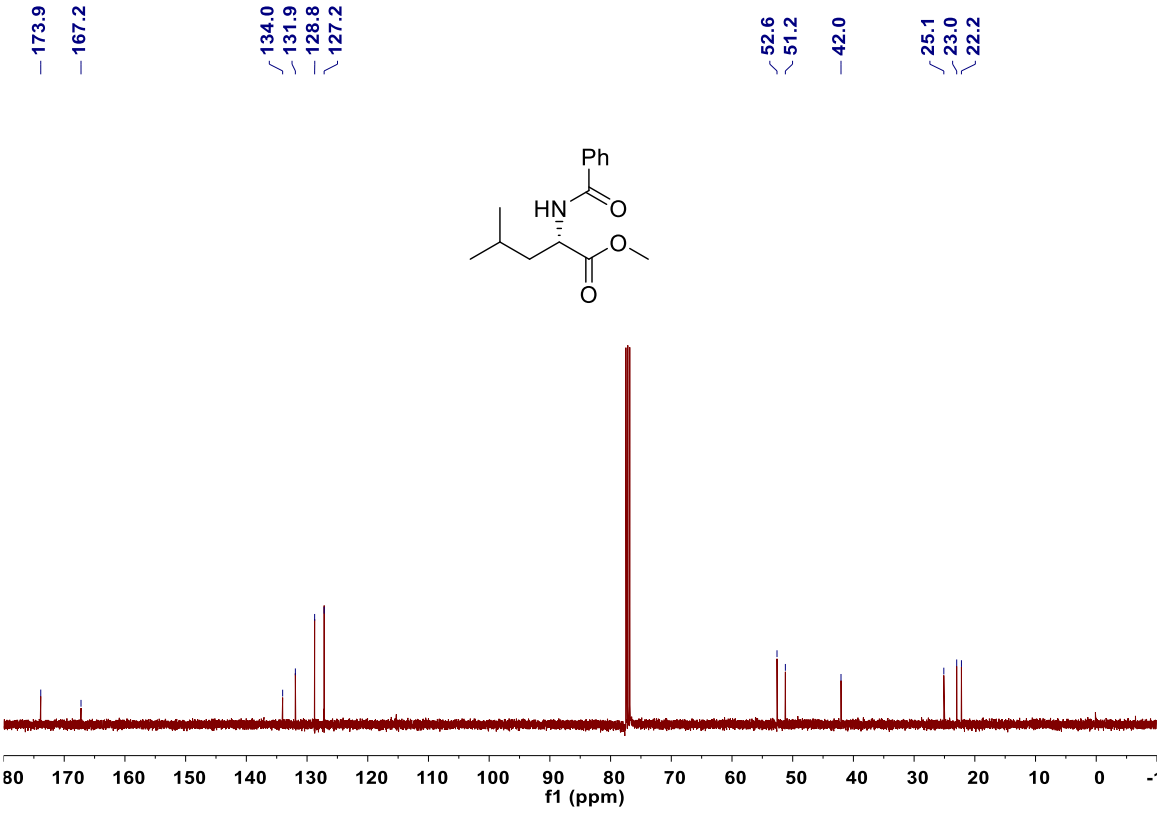
^{1}H NMR spectrum for compound **3ai** ($CDCl_3$)



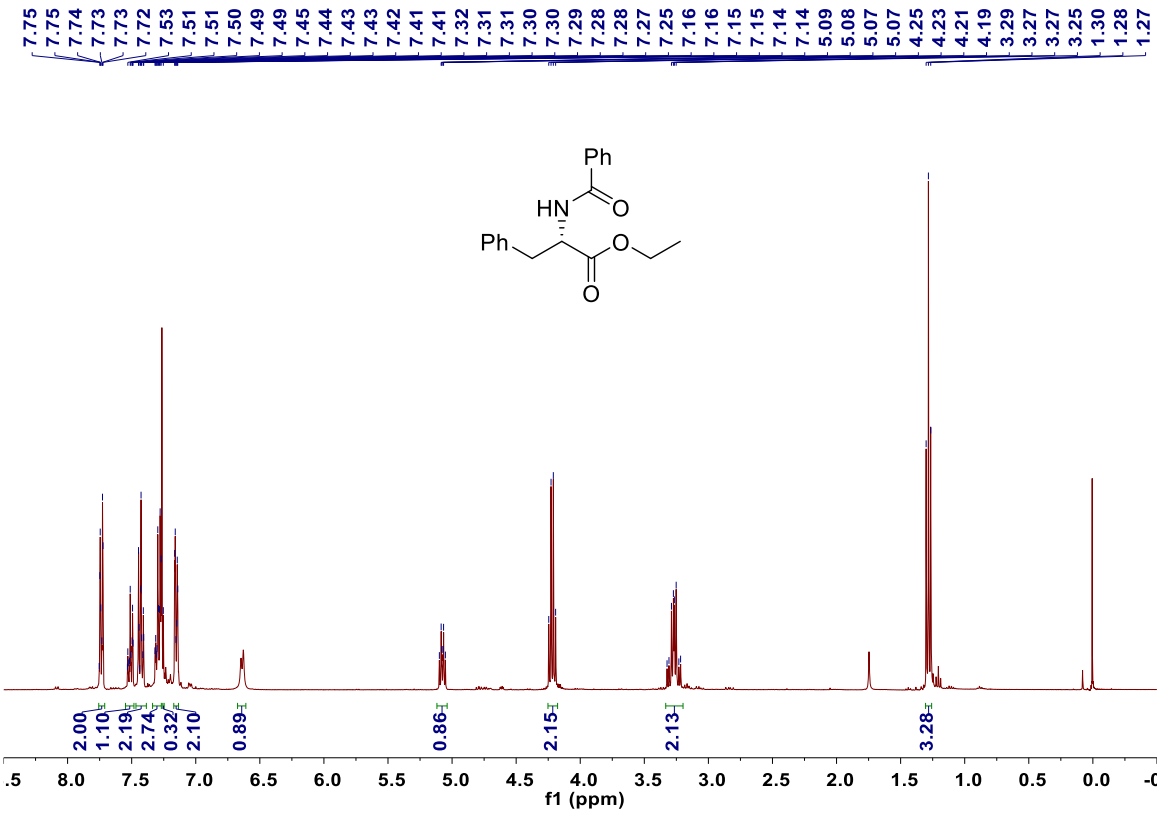
^{13}C NMR spectrum for compound **3ai** ($CDCl_3$)



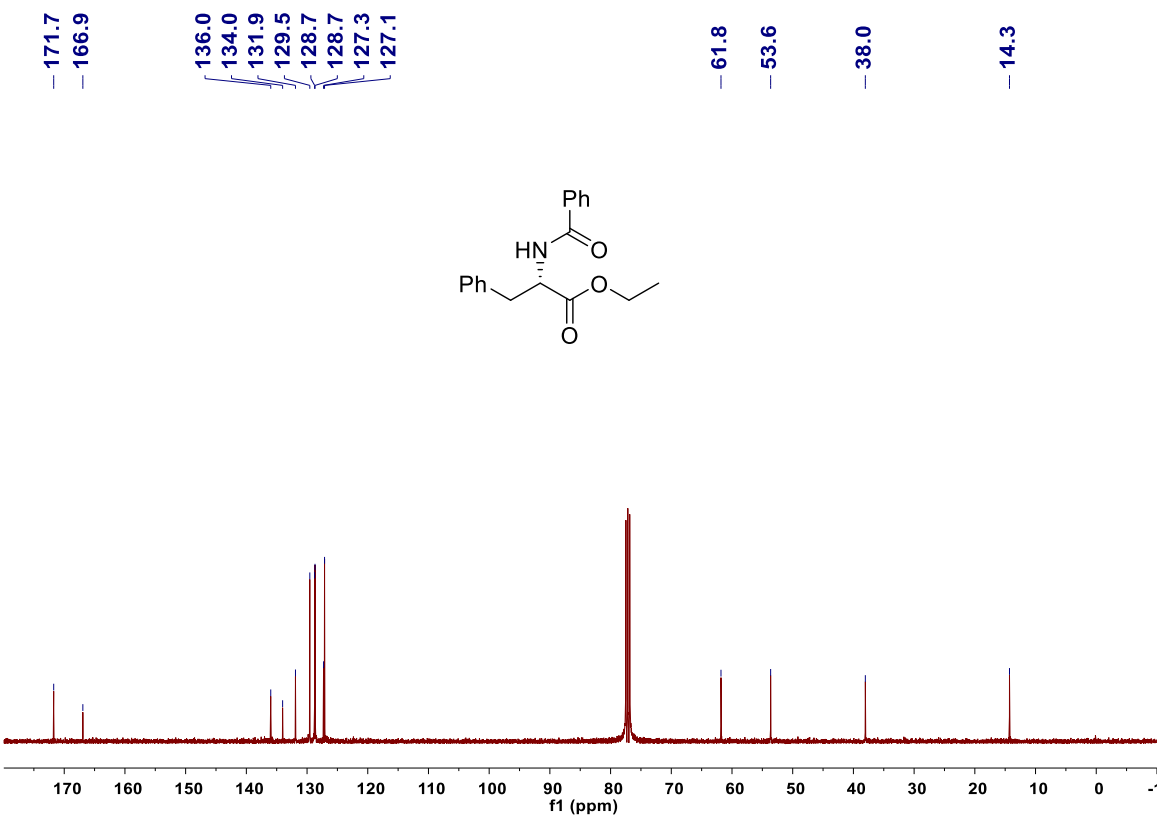
^{1}H NMR spectrum for compound **3aj** ($CDCl_3$)



^{13}C NMR spectrum for compound **3aj** ($CDCl_3$)



^{1}H NMR spectrum for compound **3ak** ($CDCl_3$)



^{13}C NMR spectrum for compound **3ak** ($CDCl_3$)