Supporting Information

Ortho-C−O Arylation of Aromatic Amides with Grignard Reagents

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1.Materials and Methods

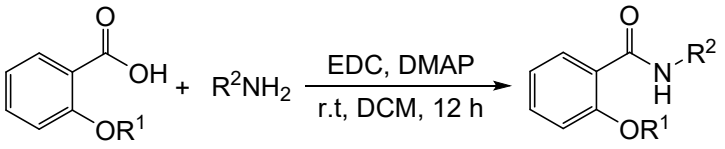
General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still. NMR spectra were measured on a Bruker AV-400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz or 500 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz or 125 MHz and referenced to the solvent resonance. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source.

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

2.Procedures for the Preparation of Substituted Benzamides[1]

General procedure A:

In a dried flask, substituted amine (1.0 equiv), 2-oxo-substituted benzoic acid (1.2 equiv), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 2.0 equiv) and 4-Dimethylaminopyridine (DMAP, 2.0 equiv) were dissolved in DCM. The resulting solution was stirring at room temperature for 12 h. After the reaction completed, added the DCM and the resulting mixture was washed with H_2O. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was then purified by flash chromatography on silica gel to give the substituted benzamides.

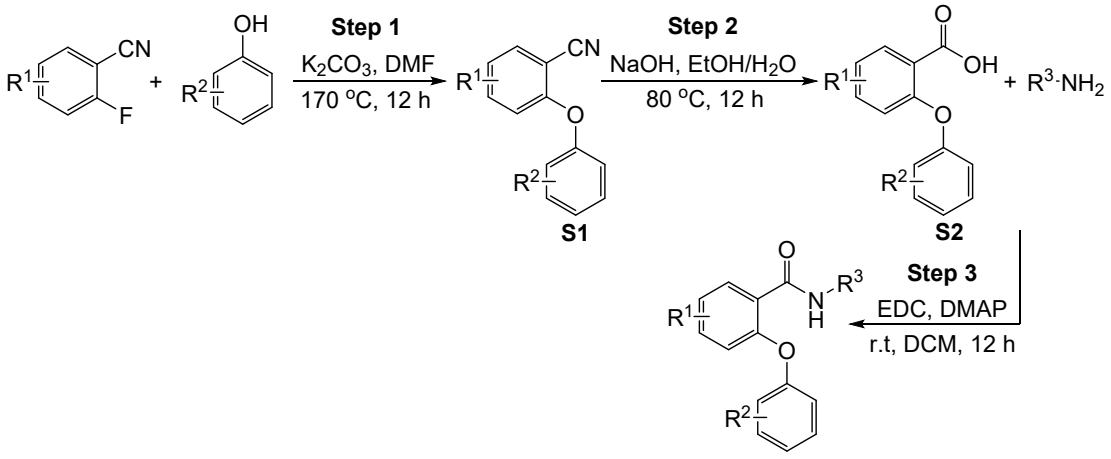


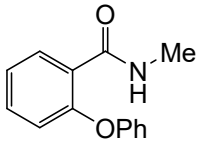
General procedure B:

Step 1: A mixture of phenol (1.2 equiv), 2-fluorobenzonitrile (1.0 equiv) and K_2CO_3 (3.0 equiv) in DMF (0.2 M) was stirred at 170 °C under Ar atmosphere for 12 h. Then the reaction mixture was cooled to room temperature and the insoluble soild was removed by filtration, washed with EtOAc. Then water was added to the liquid mixture. The organic layer was separated and the aqueous layer was extracted by EtOAc for three times. The combined organic extracts were washed with 5% NaOH, H_2O, brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product **S1** which was used without any further purification.

Step 2: A mixture of NaOH (7.5 equiv), H_2O/EtOH (1:1, 0.2 M) and the crude product **S1** (1.0 equiv) was stirred under reflux for 12 h. After cooling to room temperature, water was added and the mixture was extracted with EtOAc. Then the aqueous phase was acidified with HCl (1.0 M) and extracted with EtOAc for three times. The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatographyto afford compound **S2**.

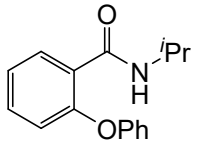
Step 3: substituted benzamides was prepared from the corresponding substituted amine and 2-oxo-substituted benzoic acid according to the **general procedure A**.





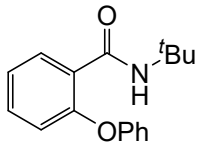
***N*-methyl-2-phenoxybenzamide (1a)**

R_f (5:1 hexanes-EtOAc) 0.41. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, J = 7.9, 1.7 Hz, 1H), 7.67 (s, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.33 (td, J = 8.4, 1.8 Hz, 1H), 7.18 (dt, J = 14.9, 7.3 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 6.78 (d, J = 8.2 Hz, 1H), 2.97 (d, J = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 155.6, 155.3, 132.4, 132.1, 130.1, 124.7, 123.7, 123.4, 119.8, 117.9, 26.6. HRMS (ESI^+): calcd for $C_{14}H_{14}NO_2$ $[M+H]^+$ 228.10245, found 228.10263. Spectroscopic data are in accordance with those described in the literature[2]



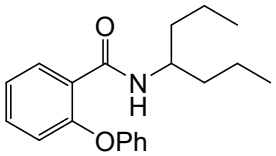
***N*-isopropyl-2-phenoxybenzamide (1b)**

R_f (6:1 hexanes-EtOAc) 0.37. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, J = 7.9, 1.8 Hz, 1H), 7.41 (s, 1H), 7.38 – 7.34 (m, 3H), 7.23 – 7.19 (m, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 8.2 Hz, 1H), 4.28 – 4.18 (m, 1H), 1.14 (d, J = 6.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 155.9, 154.6, 132.4, 132.1, 130.0, 125.0, 124.2, 124.0, 119.1, 118.6, 41.5, 22.6. HRMS (ESI^+): calcd for $C_{16}H_{18}NO_2$ $[M+H]^+$ 256.13375, found 256.13329. Spectroscopic data are in accordance with those described in the literature.[2]



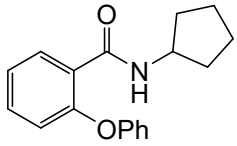
_N_-(tert-butyl)-2-phenoxybenzamide (1c)

R_f (8:1 hexanes-EtOAc) 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 7.9, 1.8 Hz, 1H), 7.50 (s, 1H), 7.41 – 7.33 (m, 3H), 7.23 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.1 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 156.2, 154.1, 132.3, 131.9, 130.1, 126.2, 124.3, 124.0, 119.5, 118.2, 51.2, 28.7. HRMS (ESI$^+$): calcd for $C_{17}H_{20}NO_2$ $[M+H]^+$ 270.14940, found 270.14952. Spectroscopic data are in accordance with those described in the literature.[2]



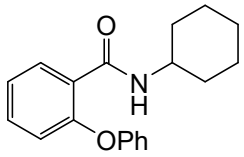
_N_-(heptan-4-yl)-2-phenoxybenzamide (1d)

R_f (8:1 hexanes-EtOAc) 0.46. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, J = 7.9, 1.7 Hz, 1H), 7.42 – 7.29 (m, 4H), 7.23 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.2 Hz, 1H), 4.13 (d, J = 8.4 Hz, 1H), 1.50 – 1.42 (m, 2H), 1.36 – 1.23 (m, 6H), 0.82 (t, J = 7.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 156.1, 154.4, 132.4, 132.2, 130.0, 125.3, 124.2, 124.1, 119.4, 118.4, 49.1, 37.4, 19.0, 14.0. HRMS (ESI$^+$): calcd for $C_{20}H_{26}NO_2$ $[M+H]^+$ 312.19635, found 312.19671.



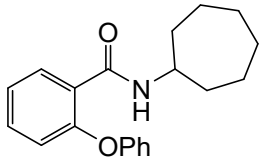
_N_-cyclopentyl-2-phenoxybenzamide (1e)

R_f (6:1 hexanes-EtOAc) 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 7.8, 1.6 Hz, 1H), 7.59 (s, 1H), 7.35 (t, J = 7.9 Hz, 3H), 7.17 (dt, J = 19.3, 7.5 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.2 Hz, 1H), 4.42 – 4.30 (m, 1H), 2.00 – 1.89 (m, 2H), 1.62 – 1.51 (m, 4H), 1.44 – 1.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.8, 154.5, 132.3, 132.0, 130.0, 124.8, 124.1, 123.9, 119.0, 118.4, 51.3, 33.0, 23.5. HRMS (ESI$^+$): calcd for $C_{18}H_{20}NO_2$ $[M+H]^+$ 282.14940, found 282.14987. Spectroscopic data are in accordance with those described in the literature.[2]



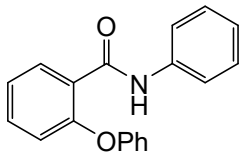
***N*-cyclohexyl-2-phenoxybenzamide (1f)**

R_f (8:1 hexanes-EtOAc) 0.37.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.54 (s, 1H), 7.35 (t, *J* = 8.1 Hz, 3H), 7.17 (dt, *J* = 23.8, 7.6 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.01 – 3.92 (m, 1H), 1.91 – 1.85 (m, 2H), 1.64 – 1.58 (m, 2H), 1.56 – 1.51 (m, 1H), 1.38 – 1.32 (m, 2H), 1.21 – 1.12 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 155.8, 154.6, 132.3, 132.0, 130.0, 125.0, 124.1, 123.9, 119.0, 118.6, 48.0, 32.6, 25.5, 24.4. HRMS (ESI^+): calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.16505, found 296.16513. Spectroscopic data are in accordance with those described in the literature.[2]



***N*-cycloheptyl-2-phenoxybenzamide (1g)**

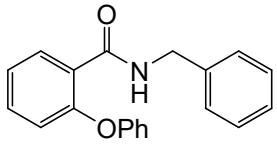
R_f (8:1 hexanes-EtOAc) 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.63 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 3H), 7.22 – 7.12 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.23 – 4.08 (m, 1H), 1.89 (t, *J* = 10.3 Hz, 2H), 1.59 – 1.42 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 155.8, 154.6, 132.3, 132.0, 130.0, 124.9, 124.1, 123.9, 118.9, 118.6, 50.3, 34.6, 27.8, 23.9. HRMS (ESI^+): calcd for $C_{20}H_{24}NO_2$ $[M+H]^+$ 310.18070, found 310.18087. Spectroscopic data are in accordance with those described in the literature.[2]



2-phenoxy-*N*-phenylbenzamide (1h)

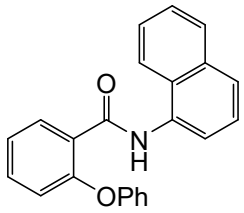
R_f (10:1 hexanes-EtOAc) 0.43. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.36 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 3H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.25 (dt, *J* = 18.8, 7.4 Hz, 2H), 7.12 (dd, *J* = 13.9, 7.6 Hz, 3H), 6.91 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 155.3, 155.2, 138.1, 133.1, 132.4, 130.3, 128.9, 124.9, 124.3, 124.1, 123.9, 120.3, 119.4, 118.4. HRMS (ESI^+): calcd for $C_{19}H_{16}NO_2$ $[M+H]^+$ 290.11810, found 290.11887. Spectroscopic data are in accordance

with those described in the literature.[2]



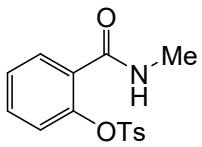
***N*-benzyl-2-phenoxybenzamide (1i)**

R_f (6:1 hexanes-EtOAc) 0.32. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, J = 7.9, 1.8 Hz, 1H), 7.99 (s, 1H), 7.36 – 7.30 (m, 3H), 7.24 – 7.13 (m, 7H), 6.95 (dd, J = 8.6, 0.9 Hz, 2H), 6.82 (dd, J = 8.2, 0.8 Hz, 1H), 4.62 (d, J = 5.7 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 155.4, 155.0, 138.2, 132.5, 132.1, 130.0, 128.4, 127.2, 127.0, 124.3, 124.1, 123.4, 119.0, 118.5, 43.6. HRMS (ESI^+): calcd for $C_{20}H_{18}NO_2$ $[M+H]^+$ 304.13375, found 304.13367.



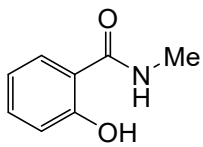
***N*-(naphthalen-1-yl)-2-phenoxybenzamide (1j)**

R_f (8:1 hexanes-EtOAc) 0.29. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.42 (dd, J = 7.9, 1.5 Hz, 1H), 8.35 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 7.38 (td, J = 7.9, 2.2 Hz, 4H), 7.30 (dd, J = 11.3, 3.9 Hz, 1H), 7.25 – 7.15 (m, 4H), 6.90 (d, J = 8.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 155.4, 155.1, 133.9, 133.1, 132.9, 132.5, 130.2, 128.6, 126.4, 126.0, 125.8, 125.6, 124.9, 124.0, 123.8, 120.3, 119.6, 118.2. HRMS (ESI^+): calcd for $C_{23}H_{18}NO_2$ $[M+H]^+$ 340.13375, found 340.13420.



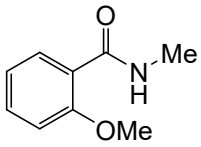
2-(methyl carbamoyl) phenyl 4-methylbenzenesulfonat (1k)

R_f (1:1 hexanes-EtOAc) 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, J = 7.7, 1.8 Hz, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.35 – 7.30 (m, 3H), 7.19 (dd, J = 8.2, 0.9 Hz, 1H), 6.57 (s, 1H), 2.85 (d, J = 4.8 Hz, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 146.2, 146.1, 131.9, 131.6, 131.4, 129.9, 128.7, 128.4, 127.4, 123.0, 26.7, 21.7. HRMS (ESI^+): calcd for $C_{15}H_{16}NO_4S$ $[M+H]^+$ 306.08000, found 306.08037.



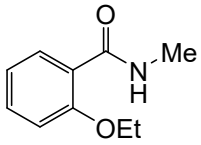
2-hydroxy-*N*-methylbenzamide (1l)

R_f (3:1 hexanes-EtOAc) 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 6.97 (d, J = 8.3 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.51 (s, 1H), 2.99 (d, J = 4.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 161.0, 134.0, 125.6, 118.7, 118.2, 114.3, 26.3. HRMS (ESI$^+$): calcd for $C_8H_{10}NO_2$ $[M+H]^+$ 152.07115, found 152.07146. Spectroscopic data are in accordance with those described in the literature.[3]



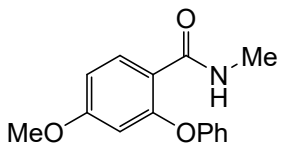
2-methoxy-*N*-methylbenzamide (1m)

R_f (2:1 hexanes-EtOAc) 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, J = 7.8, 1.4 Hz, 1H), 7.82 (s, 1H), 7.43 – 7.39 (m, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H), 2.99 (d, J = 4.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 157.0, 132.2, 131.5, 121.0, 120.6, 110.9, 55.4, 26.1. HRMS (ESI$^+$): calcd for $C_9H_{12}NO_2$ $[M+H]^+$ 166.08680, found 166.08654. Spectroscopic data are in accordance with those described in the literature.[4]



2-ethoxy-*N*-methylbenzamide (1n)

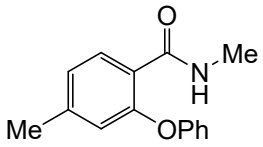
R_f (2:1 hexanes-EtOAc) 0.27. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dd, J = 7.8, 1.8 Hz, 1H), 7.96 (s, 1H), 7.37 (td, J = 8.4, 1.8 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.91 (d, J = 8.3 Hz, 1H), 4.15 (q, J = 7.0 Hz, 2H), 2.98 (d, J = 4.8 Hz, 3H), 1.48 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 156.7, 132. 4, 132.1, 121.5, 121.0, 112.2, 64.53, 26.3, 14.7. HRMS (ESI$^+$): calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$ 180.10245, found 180.10271. Spectroscopic data are in accordance with those described in the literature.[5]



4-methoxy-*N*-methyl-2-phenoxybenzamide (1o)

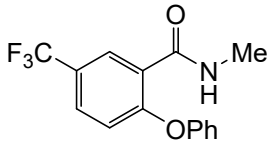
R_f (3:1 hexanes-EtOAc) 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 1H),

7.59 (s, 1H), 7.42 – 7.39 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.08 (dd, J = 8.5, 0.9 Hz, 2H), 6.71 (dd, J = 8.9, 2.4 Hz, 1H), 6.26 (d, J = 2.4 Hz, 1H), 3.72 (s, 3H), 2.97 (d, J = 4.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 162.9, 157.1, 155.0, 133.7, 130.2, 125.0, 120.1, 116.3, 108.5, 103.8, 55.5, 26.6. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_3$ $[M+H]^+$ 258.11302, found 258.11354.



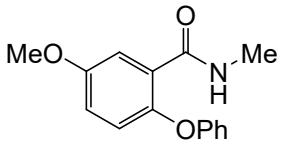
_N_,4-dimethyl-2-phenoxybenzamide (1p)

R_f (3:1 hexanes-EtOAc) 0.33. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.42 – 7.36 (m, 2H), 7.22 – 7.17 (m, 1H), 7.07 – 7.02 (m, 2H), 6.99 (dd, J = 8.0, 0.8 Hz, 1H), 6.58 (s, 1H), 2.97 (d, J = 4.8 Hz, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 155.5, 143.5, 132.1, 130.1, 124.6, 124.5, 121.1, 119.9, 118.5, 26.7, 21.3. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.11810, found 242.11833.



_N_-methyl-2-phenoxy-5-(trifluoromethyl) benzamide (1q)

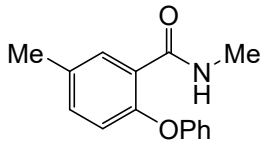
R_f (3:1 hexanes-EtOAc) 0.39. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 2.2 Hz, 1H), 7.68 (s, 1H), 7.56 (dd, J = 8.7, 2.3 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.30 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 7.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 1H), 3.04 (d, J = 4.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 158.4, 154.2, 130.5, 130.1 (q, J = 3.75 Hz), 129.3 (q, J = 3.75 Hz), 125.9, 125.5 (q, J = 32.5 Hz), 123.7 (q, J = 272.5 Hz), 123.5, 120.6, 117.2, 26.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.1. HRMS (ESI$^+$): calcd for $C_{15}H_{13}F_3NO_2$ $[M+H]^+$ 296.08984, found 296.08953.



5-methoxy-_N_-methyl-2-phenoxybenzamide (1r)

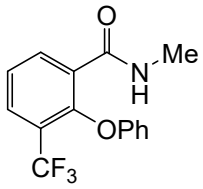
R_f (3:1 hexanes-EtOAc) 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 3.2 Hz, 1H), 7.67 (s, 1H), 7.38 – 7.33 (m, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.93 (dd, J = 8.9, 3.3 Hz, 1H), 6.80 (d, J = 8.9 Hz, 1H), 3.85 (s, 3H), 2.96 (d, J = 4.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 156.6, 155.8, 148.6, 130.0, 125.1, 124.0,

120.8, 119.7, 118.7, 114.7, 55.8, 26.8. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_3$ $[M+H]^+$ 258.11302, found 258.11325.



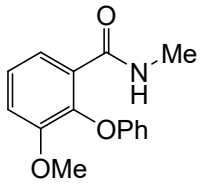
_N_,5-dimethyl-2-phenoxybenzamide (1s)

R_f (3:1 hexanes-EtOAc) 0.50. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 2.6 Hz, 1H), 7.56 (s, 1H), 7.35 (dd, J = 13.5, 5.0 Hz, 3H), 7.16 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 7.9 Hz, 2H), 6.59 (d, J = 8.8 Hz, 1H), 2.92 (d, J = 4.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 154.9, 154.8, 135.2, 134.8, 130.3, 125.2, 125.2, 119.9, 119.6, 116.2, 26.8. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.11810, found 242.11867.



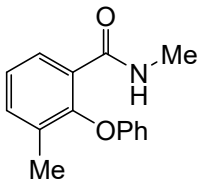
_N_-methyl-2-phenoxy-3-(trifluoromethyl)benzamide (1t)

R_f (3:1 hexanes-EtOAc) 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.39 (s, 1H), 7.20 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 6.9 Hz, 1H), 6.69 (d, J = 8.4 Hz, 3H), 2.68 – 2.62 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 158.0, 149.6, 135.5, 130.6, 130.1 (q, J = 5.0 Hz), 129.8, 125.8, 125.1 (q, J = 32.5 Hz), 123.1, 122.8 (q, J = 272.5 Hz), 115.0, 26.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.1. HRMS (ESI$^+$): calcd for $C_{15}H_{13}F_3NO_2$ $[M+H]^+$ 296.08984, found 296.08993.



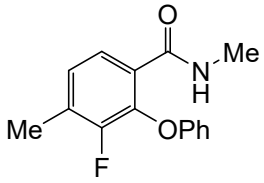
3-methoxy-_N_-methyl-2-phenoxybenzamide (1u)

R_f (3:1 hexanes-EtOAc) 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 1H), 7.20 (dt, J = 7.1, 4.8 Hz, 4H), 7.02 (d, J = 8.1 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 8.2 Hz, 2H), 3.64 (s, 3H), 2.83 – 2.78 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 157.5, 152.3, 141.4, 129.6, 128.4, 125.8, 123.0, 122.7, 115.6, 115.2, 56.2, 26.7. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_3$ $[M+H]^+$ 258.11302, found 258.11394.



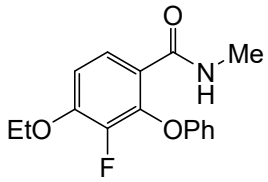
_N_,3-dimethyl-2-phenoxybenzamide (1v)

R_f (3:1 hexanes-EtOAc) 0.44. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.08 (m, 4H), 6.89 (d, J = 7.5 Hz, 1H), 6.66 (d, J = 8.6 Hz, 2H), 2.70 (d, J = 4.9 Hz, 3H), 1.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 156.8, 149.9, 134.4, 134.3, 131.9, 129.7, 129.3, 127.9, 125.4, 125.4, 122.4, 122.3, 114.9, 26.4, 16.2. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.11810, found 242.11823.



3-fluoro-_N_,4-dimethyl-2-phenoxybenzamide (1w)

R_f (3:1 hexanes-EtOAc) 0.36. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, J = 8.2, 1.0 Hz, 1H), 7.23 (t, J = 7.9 Hz, 3H), 7.08 – 6.99 (m, 2H), 6.84 (d, J = 8.2 Hz, 2H), 2.82 (d, J = 4.9 Hz, 3H), 2.21 (d, J = 2.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 157.2, 153.4 (d, J = 247.5 Hz), 140.5 (d, J = 12.5 Hz), 130.4 (d, J = 15.0 Hz), 129.9, 127.4 (d, J = 5.0 Hz), 126.2, 125.9 (d, J = 3.8 Hz), 123.4, 115.6, 26.7, 14.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -131.5. HRMS (ESI$^+$): calcd for $C_{15}H_{15}FNO_2$ $[M+H]^+$ 260.10868, found 260.10844.

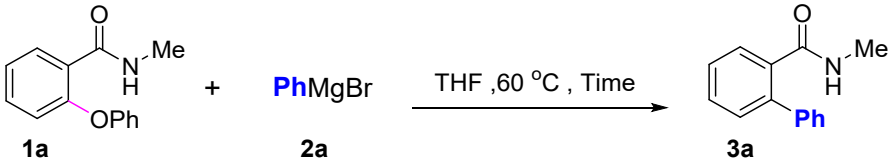


4-ethoxy-3-fluoro-_N_-methyl-2-phenoxybenzamide (1x)

R_f (2:1 hexanes-EtOAc) 0.37.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J = 9.0, 1.6 Hz, 1H), 7.22 (dd, J = 18.1, 10.1 Hz, 3H), 7.02 (d, J = 7.3 Hz, 1H), 6.85 (dd, J = 16.0, 8.2 Hz, 3H), 4.08 (d, J = 7.0 Hz, 2H), 2.82 (d, J = 4.8 Hz, 3H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 157.0, 150.9 (d, J = 8.8 Hz), 144.9 (d, J = 248.8 Hz), 141.8 (d, J = 11.3 Hz), 129.9, 126.4 (d, J = 3.8 Hz), 123.6, 119.9, 115.7, 110.2, 65.1, 26.7, 14.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -148.4. HRMS (ESI$^+$): calcd for $C_{16}H_{17}FNO_3$ $[M+H]^+$ 290.11925, found 290.11976.

3. Optimizing Reaction Parameters

Table S1. Investigation of the Effect of Time on the *Ortho*-C−O Arylation of Aromatic Amides with Grignard Reagents through Meyers Reaction[a]

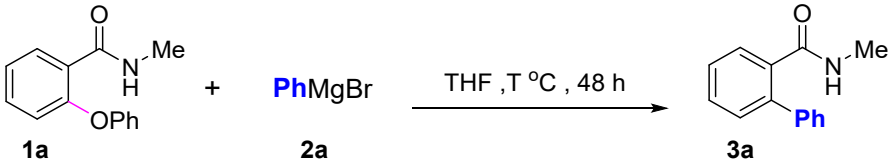


1a **2a** **3a**

Entry	Time	3a(%) [b]
1	24	42
2	48	55
3	72	55

[a]Conditions: **1a** (0.2 mmol), PhMgBr (0.8 mmol), and THF (1.0 mL), under Ar atmosphere at 60 °C for x h. [b]Isolated yield are shown.

Table S2. Investigation of the Effect of Temperature on the *Ortho*-C−O Arylation of Aromatic Amides with Grignard Reagents through Meyers Reaction[a]

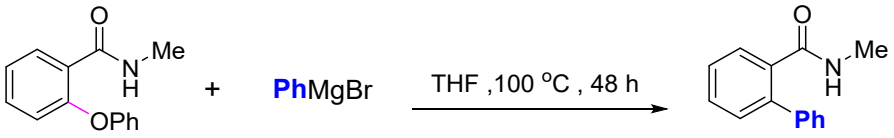


1a **2a** **3a**

Entry	T °C	3a(%) [b]
1	rt	25
2	60	55
3	70	62
4	80	70
5	90	83
6	100	92

[a]Conditions: **1a** (0.2 mmol), PhMgBr (0.8 mmol), and THF (1.0 mL), under Ar atmosphere at T °C for 48 h. [b]Isolated yield are shown.

Table S3. Investigation of the Effect of the Amount of PhMgBr on the *Ortho*-C−O Arylation of Aromatic Amides with Grignard Reagents through Meyers Reaction[a]



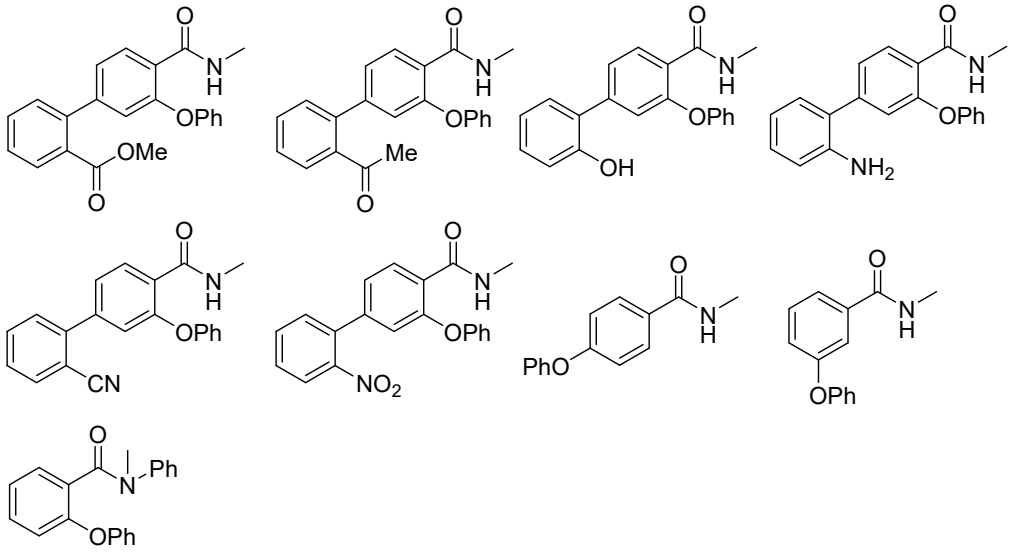
1a **2a (x equiv)** **3a**

Entry	x	3a(%) [b]
1	1.2	nd
2	2	50
3	3	69
4	3.5	76
5	4	92

[a]Conditions: **1** (0.2 mmol), PhMgBr (x equiv), and THF (1.0 mL), under Ar atmosphere at 100 ℃ for 48 h. [b]Isolated yield are shown.

Table S4. Inefficient benzamides and grignard reagents on the *Ortho*-C−O Arylation of Aromatic Amides with Grignard Reagents through Meyers Reaction[a]

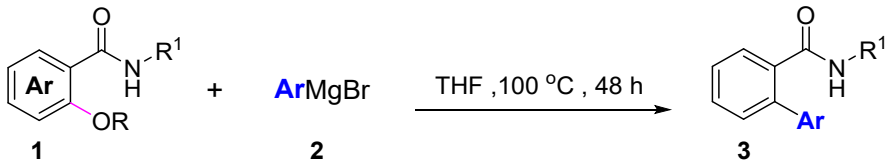
Inefficient benzamides and grignard reagents on the Ortho-C−O Arylation of Aromatic Amides with Grignard Reagents through Meyers Reaction



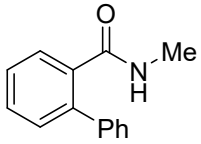
C_6F_5MgBr **3,5-$(CF_3)_2$PhMgBr** **4-OCF_3PhMgBr** **1-NPMgBr**

2,6-$(Me)_2$PhMgBr **9-PhenMgBr** **2-ThienylMgBr** **BnMgBr ...**

4. General Procedure for the *Ortho*-C−O Arylation of Aromatic Amides with Grignard Reagents through Meyers Reaction

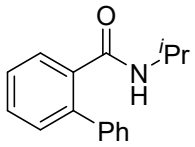


A dried Schlenk tube were placed aryl ethers 1 (0.4 mmol), phenylmagnesium bromide 2 (1.6 mmol) and freshly distilled THF (2.0 mL) under Ar atmosphere reacted at 100 °C for 48 h. The resulting mixture was quenched by an aqueous solution of NH_4Cl and extraction with ethyl acetate (3 x 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel chromatography to give the desired product 3.



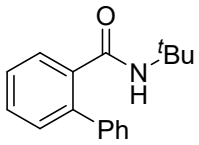
***N*-methyl-[1,1'-biphenyl]-2-carboxamide (3a)**

R_f (4:1 hexanes-EtOAc) 0.35. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.40 – 7.34 (m, 7H), 5.32 (s, 1H), 2.64 (d, J = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 140.1, 139.3, 135.7, 130.0, 123.0, 128.7, 128.5, 128.5, 127.6, 127.5, 26.5. HRMS (ESI$^+$): calcd for $C_{14}H_{14}NO$ $[M+H]^+$ 212.10754, found 212.10852. Spectroscopic data are in accordance with those described in the literature.[6]



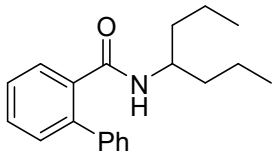
***N*-isopropyl-[1,1'-biphenyl]-2-carboxamide (3b)**

R_f (6:1 hexanes-EtOAc) 0.25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 7.6, 1.3 Hz, 1H), 7.46 (dd, J = 7.5, 1.4 Hz, 1H), 7.43 – 7.37 (m, 6H), 7.35 (dd, J = 7.6, 1.1 Hz, 1H), 4.95 (d, J = 6.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 0.83 (d, J = 6.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 140.3, 139.4, 136.0, 130.0, 129.9, 128.8, 128.8, 128.7, 127.7, 127.6, 41.5, 22.1. HRMS (ESI$^+$): calcd for $C_{16}H_{18}NO$ $[M+H]^+$ 240.13884, found 240.13749.



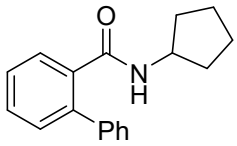
***N*-(*tert*-butyl)-[1,1'-biphenyl]-2-carboxamide (3c)**

R_f (6:1 hexanes-EtOAc) 0.33. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, J = 7.6, 1.2 Hz, 1H), 7.46 – 7.39 (m, 7H), 7.33 (dd, J = 7.5, 1.1 Hz, 1H), 4.99 (s, 1H), 1.10 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 130.0, 129.8, 129.0, 128.9, 128.6, 127.7, 127.6, 51.3, 28.2. HRMS (ESI$^+$): calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.15449, found 254.15724. Spectroscopic data are in accordance with those described in the literature.[6]



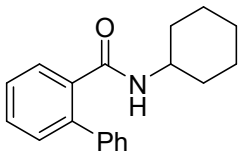
***N*-(heptan-4-yl)-[1,1'-biphenyl]-2-carboxamide (3d)**

R_f (6:1 hexanes-EtOAc) 0.44. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 7.6, 1.2 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.43 – 7.37 (m, 6H), 7.34 (dd, J = 7.5, 1.0 Hz, 1H), 4.97 (d, J = 8.7 Hz, 1H), 3.92 – 3.86 (m, 1H), 1.25 – 1.16 (m, 4H), 1.07 – 1.02 (m, 4H), 0.78 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 139.3, 130.2, 129.7, 128.8, 128.7, 128.6, 127.7, 127.5, 49.1, 36.8, 29.7, 18.7, 14.0. HRMS (ESI$^+$): calcd for $C_{20}H_{26}NO$ $[M+H]^+$ 296.20144, found 296.20357.



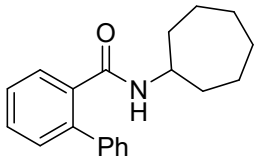
***N*-cyclopentyl-[1,1'-biphenyl]-2-carboxamide (3e)**

R_f (6:1 hexanes-EtOAc) 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.43 – 7.38 (m, 6H), 7.34 (d, J = 7.5 Hz, 1H), 5.08 (d, J = 6.0 Hz, 1H), 4.16 (d, J = 6.9 Hz, 1H), 1.72 (dd, J = 13.0, 5.5 Hz, 2H), 1.43 (dd, J = 9.8, 5.4 Hz, 2H), 1.30 (dd, J = 9.4, 5.7 Hz, 2H), 0.97 (dd, J = 12.4, 6.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 140.4, 139.4, 135.9, 130.0, 129.9, 128.9, 128.7, 128.6, 127.8, 127.6, 51.3, 32.5, 23.4. HRMS (ESI$^+$): calcd for $C_{18}H_{20}NO$ $[M+H]^+$ 266.15449, found 266.15502.



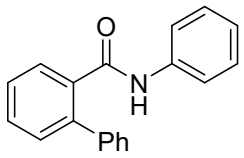
***N*-cyclohexyl-[1,1'-biphenyl]-2-carboxamide (3f)**

R_f (6:1 hexanes-EtOAc) 0.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 – 7.33 (m, 8H), 5.04 (d, *J* = 7.5 Hz, 1H), 3.73 (ddd, *J* = 10.3, 4.0, 2.1 Hz, 1H), 1.61 (dd, *J* = 8.6, 3.9 Hz, 2H), 1.49 (d, *J* = 9.6 Hz, 3H), 1.28 – 1.19 (m, 3H), 0.72 (td, *J* = 13.2, 3.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 140.3, 139.4, 136.1, 130.1, 129.9, 128.9, 128.8, 128.6, 127.7, 127.6, 48.2, 32.4, 25.4, 24.5. HRMS (ESI$^+$): calcd for $C_{19}H_{22}NO$ $[M+H]^+$ 280.17014, found 280.17202.



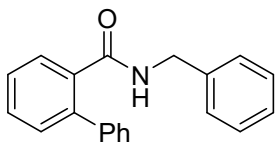
***N*-cycloheptyl-[1,1'-biphenyl]-2-carboxamide (3g)**

R_f (6:1 hexanes-EtOAc) 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.37 (m, 6H), 7.34 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.11 (d, *J* = 7.5 Hz, 1H), 3.91 (dd, *J* = 13.1, 4.4 Hz, 1H), 1.65 – 1.60 (m, 2H), 1.53 – 1.46 (m, 2H), 1.37 – 1.31 (m, 6H), 1.03 (dd, *J* = 10.3, 5.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 140.4, 139.3, 136.2, 130.1, 129.9, 128.9, 128.8, 128.6, 127.7, 127.6, 50.4, 34.3, 28.1, 23.7. HRMS (ESI$^+$): calcd for $C_{20}H_{24}NO$ $[M+H]^+$ 294.18579, found 294.18631.



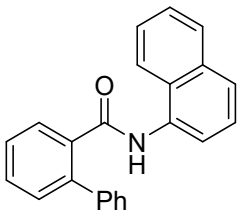
***N*-phenyl-[1,1'-biphenyl]-2-carboxamide (3h)**

R_f (6:1 hexanes-EtOAc) 0.42. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 1H), 7.55 (td, *J* = 7.5, 1.1 Hz, 1H), 7.51 – 7.40 (m, 7H), 7.23 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.90 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 139.9, 139.5, 137.5, 135.2, 130.7, 130.3, 129.6, 129.0, 128.8, 128.8, 128.1, 127.9, 124.4, 119.9. HRMS (ESI$^+$): calcd for $C_{19}H_{16}NO$ $[M+H]^+$ 274.12319, found 274.12357. Spectroscopic data are in accordance with those described in the literature.[6]



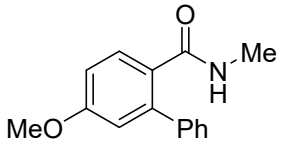
***N*-benzyl-[1,1'-biphenyl]-2-carboxamide (3i)**

R_f (5:1 hexanes-EtOAc) 0.28. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.6, 1.3 Hz, 1H), 7.39 – 7.24 (m, 8H), 7.13 – 7.07 (m, 3H), 6.78 (dd, J = 6.4, 3.0 Hz, 2H), 5.46 (s, 1H), 4.22 (d, J = 5.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 140.1, 139.4, 137.4, 135.5, 130.2, 130.1, 128.8, 128.7, 128.6, 128.5, 127.7, 127.5, 127.3, 44.1. HRMS (ESI^+): calcd for $C_{20}H_{18}NO$ $[M+H]^+$ 288.13884, found 288.13876. Spectroscopic data are in accordance with those described in the literature.[6]



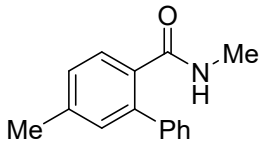
_N_-(naphthalen-1-yl)-[1,1'-biphenyl]-2-carboxamide (3j)

R_f (6:1 hexanes-EtOAc) 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (t, J = 7.1 Hz, 2H), 7.77 (d, J = 8.2 Hz, 1H), 7.66 – 7.55 (m, 4H), 7.54 – 7.35 (m, 8H), 7.24 – 7.19 (m, 1H), 6.62 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 140.1, 139.2, 135.9, 133.8, 132.1, 130.6, 130.6, 129.7, 129.1, 128.4, 128.2, 127.9, 126.6, 125.8, 125.7, 125.6, 125.4, 120.1, 119.9. HRMS (ESI^+): calcd for $C_{23}H_{18}NO$ $[M+H]^+$ 324.13884, found 324.13826. Spectroscopic data are in accordance with those described in the literature.[6]



5-methoxy-_N_-methyl-[1,1'-biphenyl]-2-carboxamide (3k)

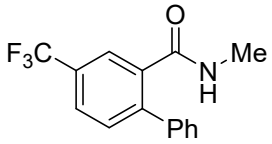
R_f (1:1 hexanes-EtOAc) 0.61. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 1H), 7.44 – 7.34 (m, 5H), 6.91 (dd, J = 8.6, 2.5 Hz, 1H), 6.83 (d, J = 2.5 Hz, 1H), 5.16 (s, 1H), 3.84 (s, 3H), 2.63 (d, J = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 160.7, 141.3, 140.3, 131.0, 128.6, 127.9, 115.4, 113.0, 55.4, 26.6. HRMS (ESI^+): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.11810, found 242.11135. Spectroscopic data are in accordance with those described in the literature.[7]



_N_,5-dimethyl-[1,1'-biphenyl]-2-carboxamide (3l)

R_f (2:1 hexanes-EtOAc) 0.32. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 1H), 7.43 – 7.34 (m, 5H), 7.22 (d, J = 7.9 Hz, 1H), 7.17 (s, 1H), 5.13 (s, 1H), 2.66 (d, J = 4.9

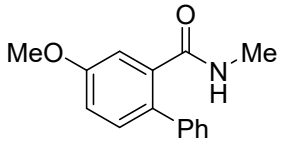
Hz, 3H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 140.5, 140.1, 139.5, 132.0, 130.9, 129.0, 128.6, 128.5, 128.3, 127.7, 26.8, 21.3. HRMS (ESI^+): calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.12319, found 226.12587. Spectroscopic data are in accordance with those described in the literature.[7]



_N_-methyl-4-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (3m)

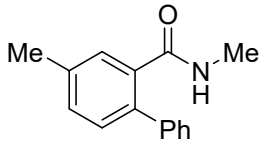
R_f (3:1 hexanes-EtOAc) 0.42. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.72 (dd, J = 8.0, 1.3 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.49 – 7.40 (m, 5H), 5.23 (s, 1H), 2.70 (d, J = 4.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 142.8, 138.7, 136.3, 130.7, 128.7, 128.4, 126.5, 125.8, 125.7, 125.7, 124.8, 122.6, 26.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6. HRMS (ESI^+): calcd for $C_{15}H_{13}F_3NO$ $[M+H]^+$ 280.09492, found 280.09486.



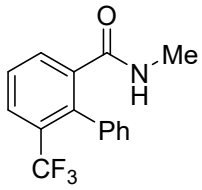
4-methoxy-_N_-methyl-[1,1'-biphenyl]-2-carboxamide (3n)

R_f (1:1 hexanes-EtOAc) 0.38. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 6H), 7.25 (d, J = 2.7 Hz, 1H), 7.02 (dd, J = 8.5, 2.8 Hz, 1H), 5.16 (s, 1H), 3.87 (s, 3H), 2.67 (d, J = 5.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 159.0, 139.9, 136.6, 131.8, 131.4, 128.7, 128.6, 127.4, 116.9, 113.2, 55.5, 26.7. HRMS (ESI^+): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.11810, found 242.11175.



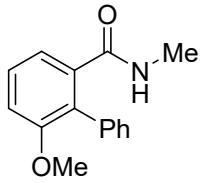
_N_,4-dimethyl-[1,1'-biphenyl]-2-carboxamide (3o)

R_f (3:1 hexanes-EtOAc) 0.35. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.34 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 7.20 (dd, J = 4.8, 1.8 Hz, 2H), 5.11 (s, 1H), 2.59 (d, J = 5.0 Hz, 3H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 140.1, 137.5, 136.4, 135.5, 130.9, 130.1, 129.4, 128.6, 128.5, 127.5, 26.6, 21.0. HRMS (ESI^+): calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.12319, found 226.12254. Spectroscopic data are in accordance with those described in the literature.[6]



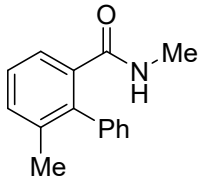
_N_-methyl-6-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (3p)

R_f (2:1 hexanes-EtOAc) 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 11.1, 7.9 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.32 – 7.26 (m, 2H), 5.12 (s, 1H), 2.53 (d, J = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 138.9, 138.0, 136.4, 131.7, 129.4 (q, J = 30.0 Hz), 129.1, 128.4, 128.1, 127.9, 127.5 (q, J = 5.0 Hz), 123.5 (q, J = 227.5 Hz), 26.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -56.9. HRMS (ESI$^+$): calcd for $C_{15}H_{13}F_3NO$ $[M+H]^+$ 280.09492, found 280.09477.



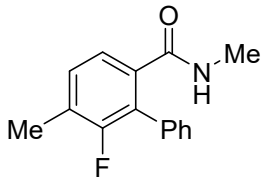
6-methoxy-_N_-methyl-[1,1'-biphenyl]-2-carboxamide (3q)

R_f (4:1 hexanes-EtOAc) 0.39. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 1H), 7.44 – 7.34 (m, 5H), 6.91 (dd, J = 8.6, 2.5 Hz, 1H), 6.83 (d, J = 2.5 Hz, 1H), 5.16 (s, 1H), 3.84 (s, 3H), 2.63 (d, J = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 157.4, 152.3, 141.3, 129.6, 128.4, 125.9, 123.0 122.7, 115.6, 115.1, 56.2, 26.7. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.11810, found 242.11074.



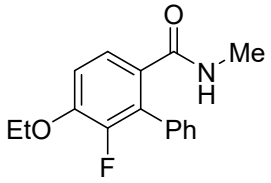
_N_,6-dimethyl-[1,1'-biphenyl]-2-carboxamide (3r)

R_f (3:1 hexanes-EtOAc) 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 1H), 7.34 (t, J = 7.4 Hz, 2H), 7.29 – 7.20 (m, 3H), 7.14 (d, J = 7.1 Hz, 2H), 5.16 (s, 1H), 2.46 (d, J = 4.9 Hz, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 139.4, 138.7, 136.6, 136.4, 131.7, 128.9, 128.5, 127.5, 125.9, 26.5, 20.7. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.12319, found 226.12261.



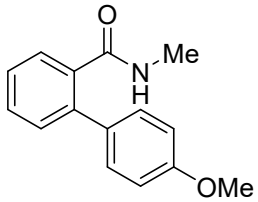
6-fluoro-*N*,5-dimethyl-[1,1'-biphenyl]-2-carboxamide (3s)

R_f (2:1 hexanes-EtOAc) 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 6H), 7.17 (t, *J* = 7.7 Hz, 1H), 5.02 (s, 1H), 2.53 (d, *J* = 4.9 Hz, 3H), 2.26 (d, *J* = 2.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 157.7 (d, *J* = 243.8 Hz), 135.4 (d, *J* = 2.5 Hz), 133.6, 130.6 (d, *J* = 5.0 Hz), 129.6, 128.5, 128.2, 127.5 (d, *J* = 18.8 Hz), 126.7 (d, *J* = 17.5 Hz), 124.0, 26.6, 14.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.9. HRMS (ESI^+): calcd for $C_{15}H_{15}FNO$ $[M+H]^+$ 244.11377, found 244.11362.



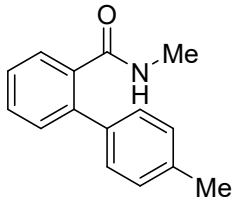
5-ethoxy-6-fluoro-*N*-methyl-[1,1'-biphenyl]-2-carboxamide (3t)

R_f (1:1 hexanes-EtOAc) 0.52. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 1H), 7.46 – 7.35 (m, 5H), 7.02 – 6.96 (m, 1H), 5.05 (s, 1H), 4.20 – 4.14 (m, 2H), 2.58 (dd, *J* = 4.8, 2.9 Hz, 3H), 1.50 – 1.44 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 149.0 (d, *J* = 245.0 Hz), 148.8 (d, *J* = 12.5 Hz), 133.2, 129.6, 128.6, 128.5 (d, *J* = 10.0 Hz), 128.4, 128.1 (d, *J* = 13.8 Hz), 125.1, 125.1 (d, *J* = 8.8 Hz), 113.0, 64.9, 26.6, 14.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -136.5. HRMS (ESI^+): calcd for $C_{16}H_{17}NO_2$ $[M+H]^+$ 274.12433, found 274.12456.



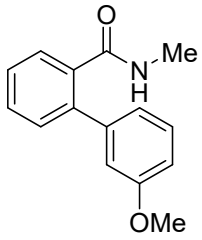
4'-methoxy-*N*-methyl-[1,1'-biphenyl]-2-carboxamide (3u)

R_f (2:1 hexanes-EtOAc) 0.37. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 1H), 7.44 – 7.34 (m, 5H), 6.91 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.83 (d, *J* = 2.5 Hz, 1H), 5.16 (s, 1H), 3.84 (s, 3H), 2.63 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 159.3, 138.9, 135.5, 132.4, 130.1, 129.8, 128.8, 127.2, 114.0, 55.3, 26.7. HRMS (ESI^+): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.11810, found 242.11795.



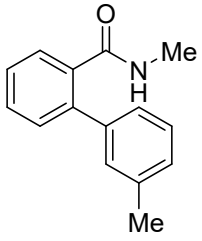
***N*,4'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3v)**

R_f (3:1 hexanes-EtOAc) 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 5.24 (s, 1H), 2.69 (d, *J* = 4.9 Hz, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 139.3, 137.5, 137.2, 135.5, 130.1, 129.3, 128.8, 128.5, 127.4, 26.7, 21.2. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.12319, found 226.12335. Spectroscopic data are in accordance with those described in the literature.[8]



3'-methoxy-*N*-methyl-[1,1'-biphenyl]-2-carboxamide (3w)

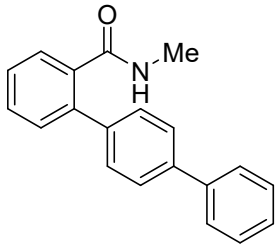
R_f (2:1 hexanes-EtOAc) 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.45 (td, *J* = 7.5, 1.3 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 6.92 (ddd, *J* = 13.5, 10.1, 4.7 Hz, 3H), 5.34 (s, 1H), 3.81 (s, 3H), 2.67 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 159.6, 141.6, 139.2, 135.7, 130.0, 129.6, 128.8, 127.6, 121.0, 113.9, 113.5, 55.3, 26.6. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.11810, found 242.11824.



***N*,3'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3x)**

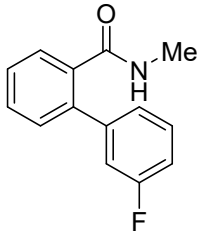
R_f (2:1 hexanes-EtOAc) 0.35. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 17.9, 8.2 Hz, 3H), 5.23 (s, 1H), 2.67 (d, *J* = 4.9 Hz, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 140.1, 139.4, 138.3, 135.6, 130.1, 130.0, 129.3, 128.8, 128.5, 128.4, 127.5, 125.7, 26.6, 21.4. HRMS (ESI$^+$): calcd for $C_{15}H_{16}NO$ $[M+H]^+$

226.12319, found 226.12327. Spectroscopic data are in accordance with those described in the literature.[9]



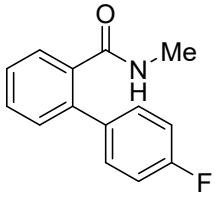
_N_-methyl-[1,1':4',1''-terphenyl]-2-carboxamide (3y)

R_f (2:1 hexanes-EtOAc) 0.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dt, J = 14.6, 8.0 Hz, 5H), 7.51 – 7.36 (m, 8H), 5.35 (d, J = 4.1 Hz, 1H), 2.71 (d, J = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 140.4, 140.3, 139.0, 138.8, 135.7, 130.1, 129.0, 128.8, 127.6, 127.5, 127.2, 127.0, 26.7. HRMS (ESI$^+$): calcd for $C_{20}H_{18}NO$ $[M+H]^+$ 288.13884, found 288.13876.



3'-fluoro-_N_-methyl-[1,1'-biphenyl]-2-carboxamide (3z)

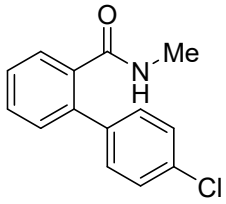
R_f (2:1 hexanes-EtOAc) 0.29. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.6, 1.1 Hz, 1H), 7.49 – 7.35 (m, 4H), 7.20 – 7.04 (m, 3H), 5.28 (s, 1H), 2.73 (d, J = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 162.7 (d, J = 245.0 Hz), 142.4 (d, J = 8.8 Hz), 138.1, 135.9, 130.2, 130.1, 130.0, 128.7, 128.1, 124.4 (d, J = 2.5 Hz), 115.5 (d, J = 21.3 Hz), 114.6 (d, J = 20.0 Hz), 26.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.7. HRMS (ESI$^+$): calcd for $C_{14}H_{13}FNO$ $[M+H]^+$ 230.09812, found 230.09835.



4'-fluoro-_N_-methyl-[1,1'-biphenyl]-2-carboxamide (3aa)

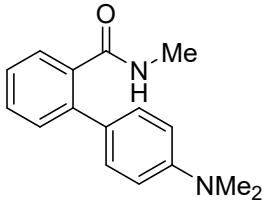
R_f (2:1 hexanes-EtOAc) 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.6, 1.1 Hz, 1H), 7.49 – 7.33 (m, 5H), 7.15 – 7.07 (m, 2H), 5.28 (s, 1H), 2.71 (d, J = 4.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 162.5 (d, J = 246.3 Hz), 138.3, 136.1 (d, J = 3.8 Hz), 135.9, 130.3, 130.2 (d, J = 11.3 Hz), 130.1, 128.6, 127.7, 115.5 (d, J = 21.3 Hz),

26.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.5. HRMS (ESI^+): calcd for $C_{14}H_{13}FNO$ $[M+H]^+$ 230.09812, found 230.09835. Spectroscopic data are in accordance with those described in the literature.[10]



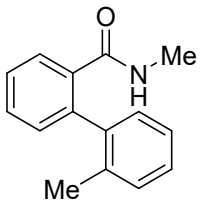
4'-chloro-*N*-methyl-[1,1'-biphenyl]-2-carboxamide (3ab)

R_f (2:1 hexanes-EtOAc) 0.27. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.5, 1.1 Hz, 1H), 7.51 – 7.34 (m, 5H), 7.22 – 7.03 (m, 3H), 5.26 (s, 1H), 2.73 (dd, J = 4.9, 3.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 163.7, 162.0, 142.4=, 138.1, 135.9, 130.2, 130.09, 130.0, 129.9, 128.8, 128.7, 128.1, 124.4, 115.6, 115.4, 114.7, 114.6, 26.7. HRMS (ESI^+): calcd for $C_{14}H_{13}ClNO$ $[M+H]^+$ 246.06857, found 246.06879.



4'-(dimethylamino)-*N*-methyl-[1,1'-biphenyl]-2-carboxamide (3ac)

R_f (1:1 hexanes-EtOAc) 0.38. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 1H), 7.44 – 7.40 (m, 1H), 7.35 – 7.27 (m, 4H), 6.78 – 6.74 (m, 2H), 5.32 (d, J = 3.0 Hz, 1H), 2.99 (s, 6H), 2.71 (d, J = 4.9 Hz, 3H).^{13}C NMR (125MHz, $CDCl_3$) δ 170.7 150.0, 139.4, 135.0, 130.0, 129.5, 129.0, 127.6, 126.6, 112.3, 40.4, 26.7. HRMS (ESI^+): calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 255.14974, found 255.14738.



***N*,2'-dimethyl-[1,1'-biphenyl]-2-carboxamide (3ad)**

R_f (2:1 hexanes-EtOAc) 0.31. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.6, 1.4 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.25 – 7.19 (m, 3H), 7.15 – 7.10 (m, 2H), 5.16 (s, 1H), 2.55 (d, J = 4.9 Hz, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 140.2, 139.1, 136.1, 134.8, 130.4, 130.3, 129.3, 129.1, 128.2, 127.7, 126.2, 26.7, 20.0. HRMS (ESI^+): calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.12319, found 226.12397. Spectroscopic data are in accordance with those described in the literature.[8]

5. Supplementary References

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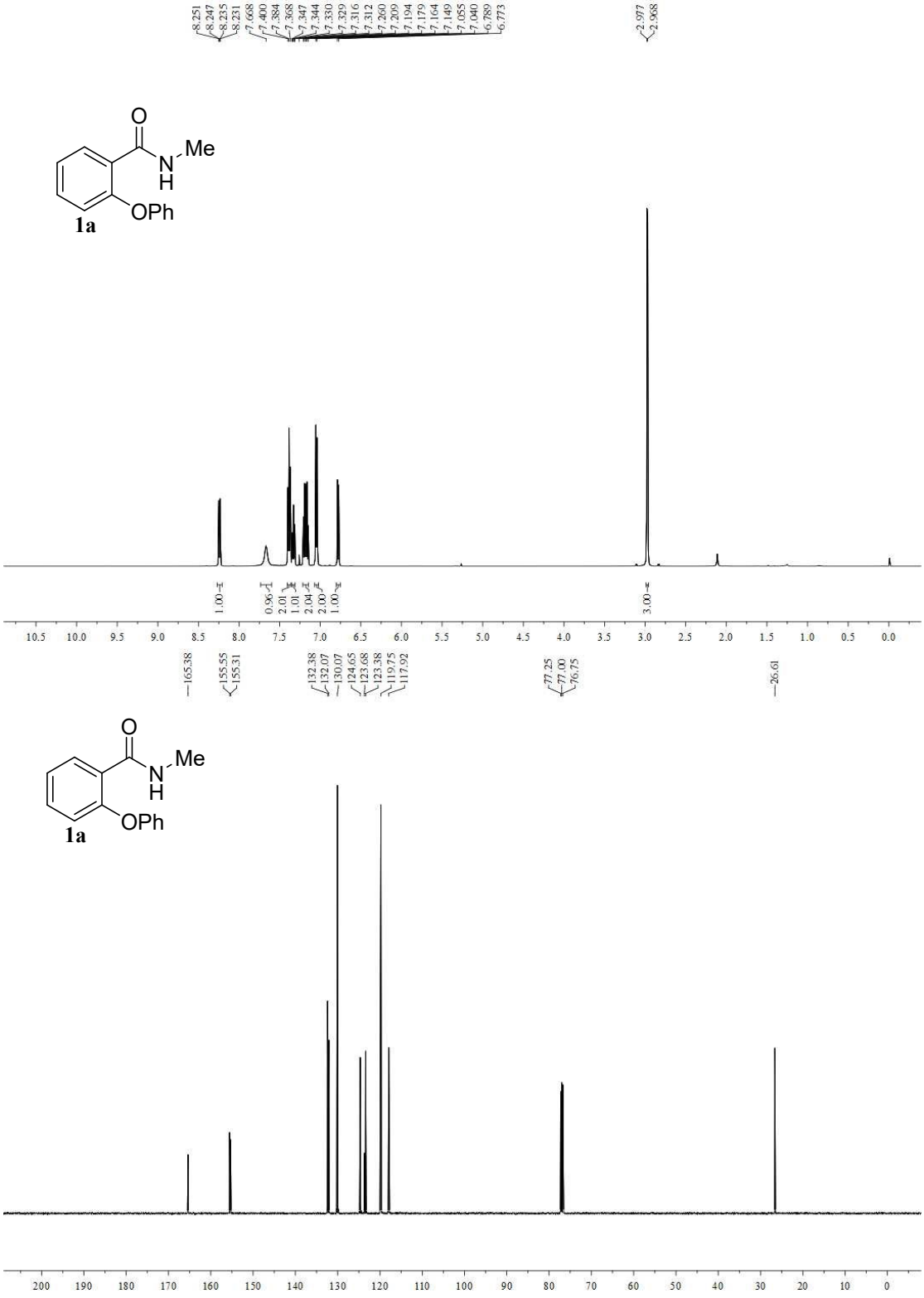
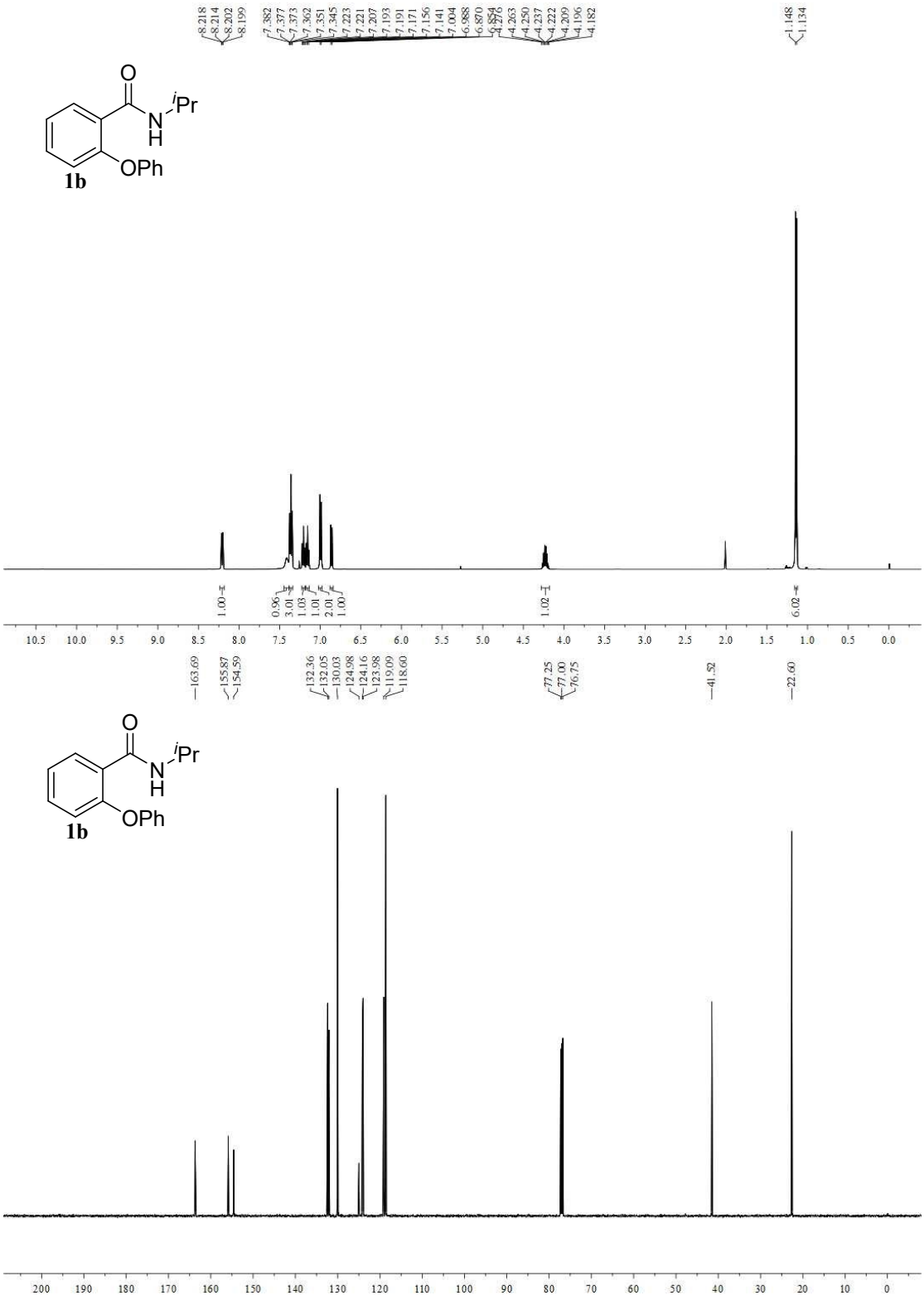
10. Shin, K.; Park, S.-W.; Chang, S., Cp*Ir(III)-Catalyzed Mild and Broad C−H Arylation of Arenes and Alkenes with Aryldiazonium Salts Leading to the External Oxidant-Free Approach. *Journal of the American Chemical Society* **2015,** *137* (26), 8584-8592.

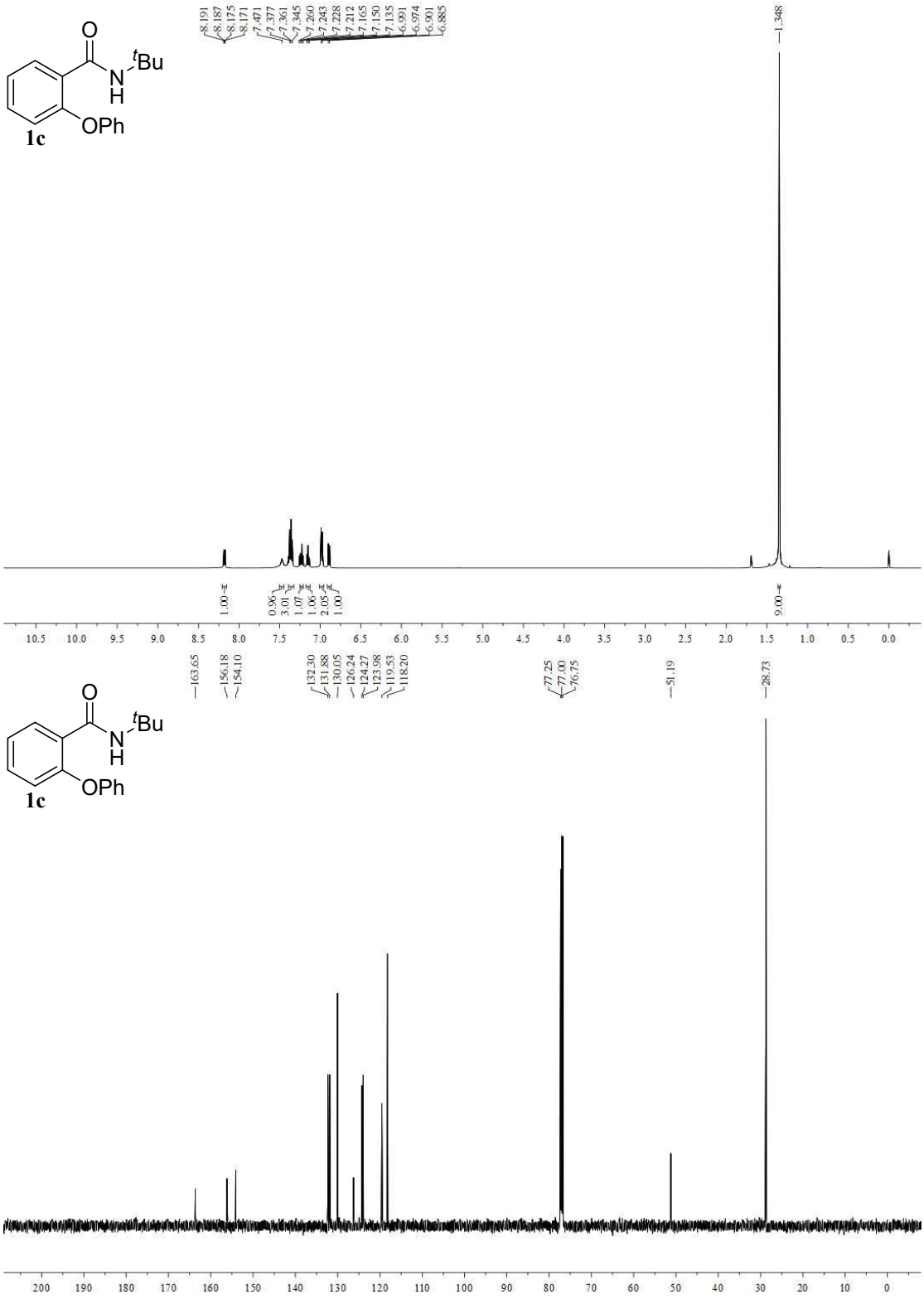
6.^{1}H, ^{13}C and ^{19}F NMR Spectra



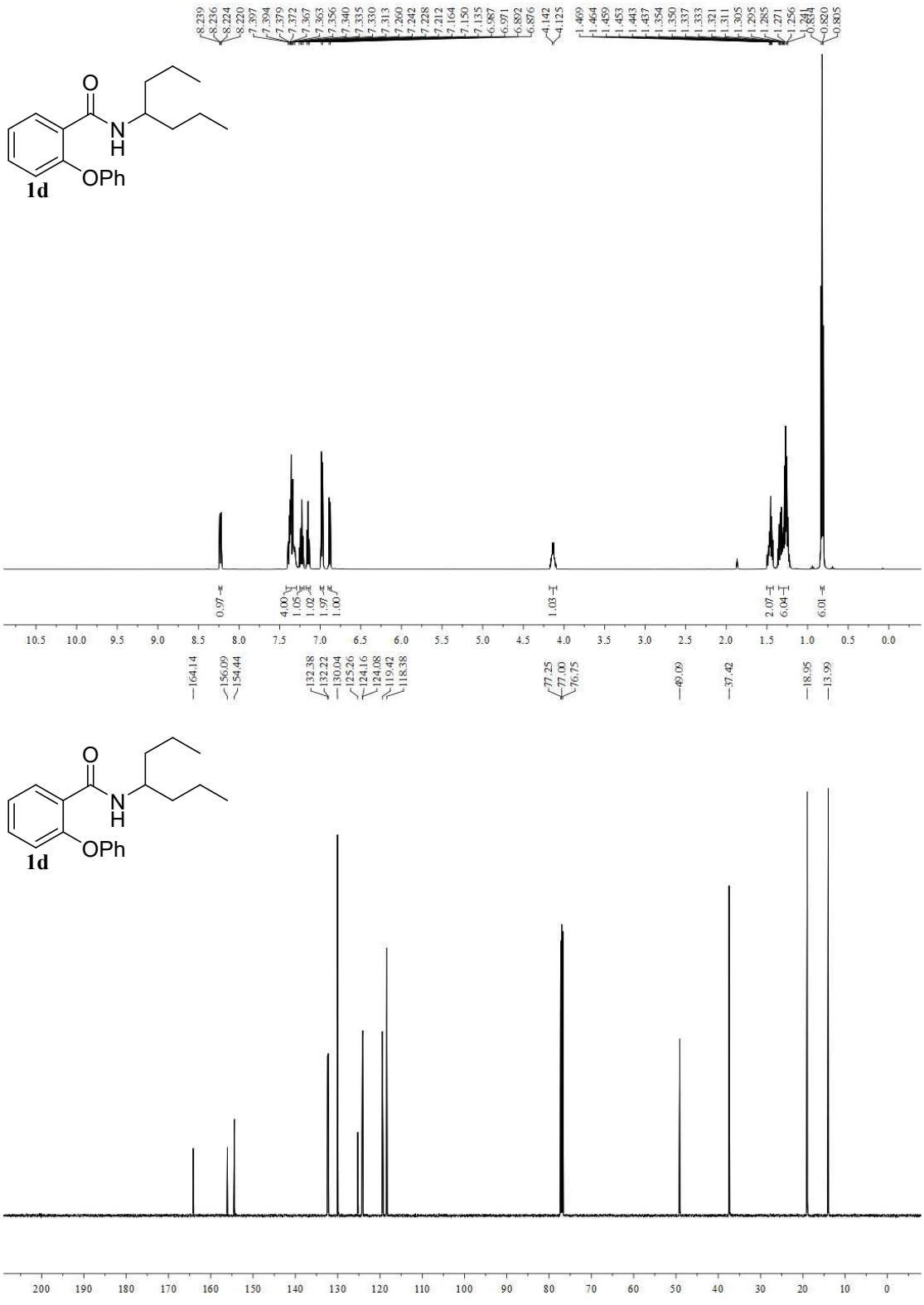
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1a



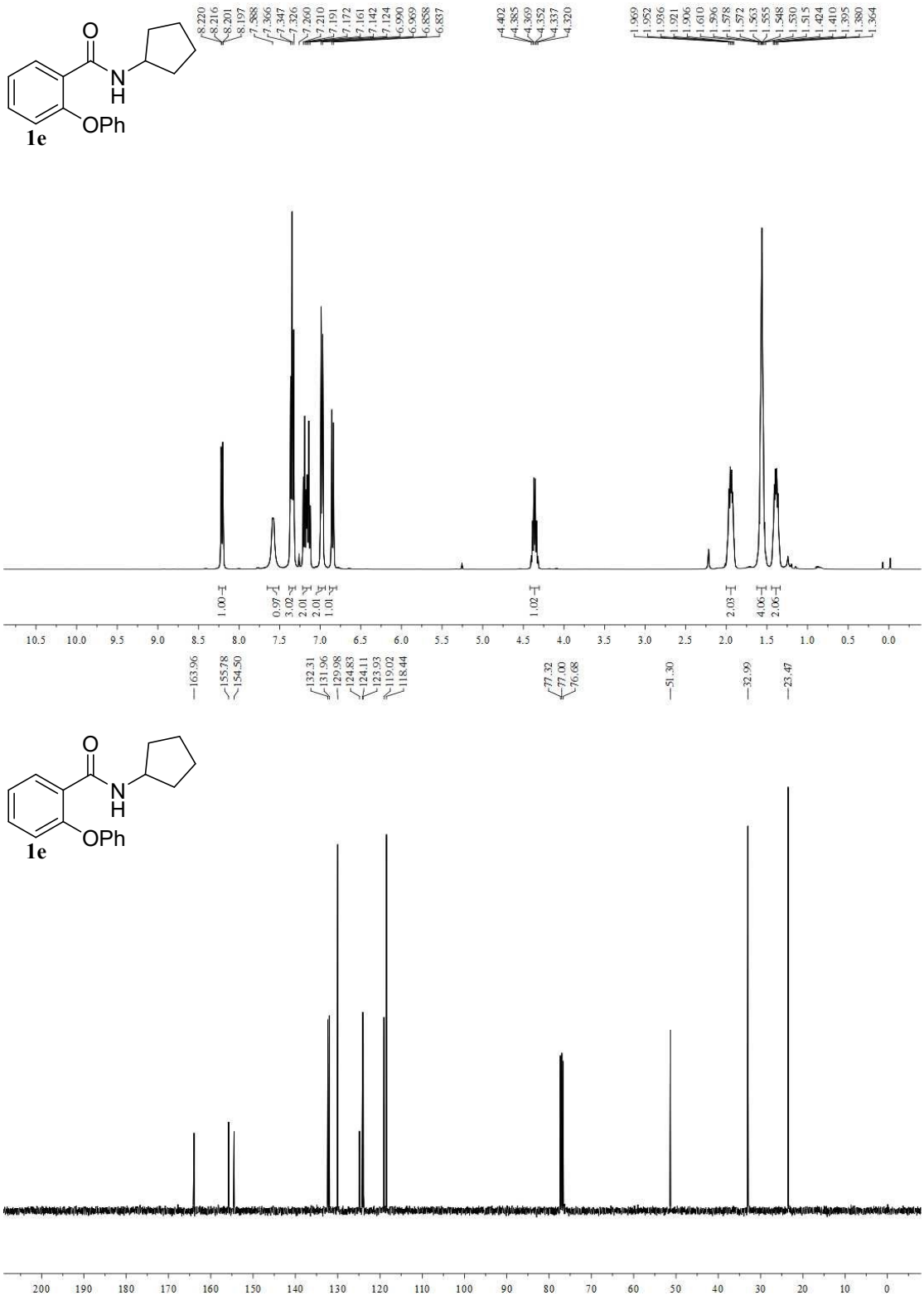
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1b



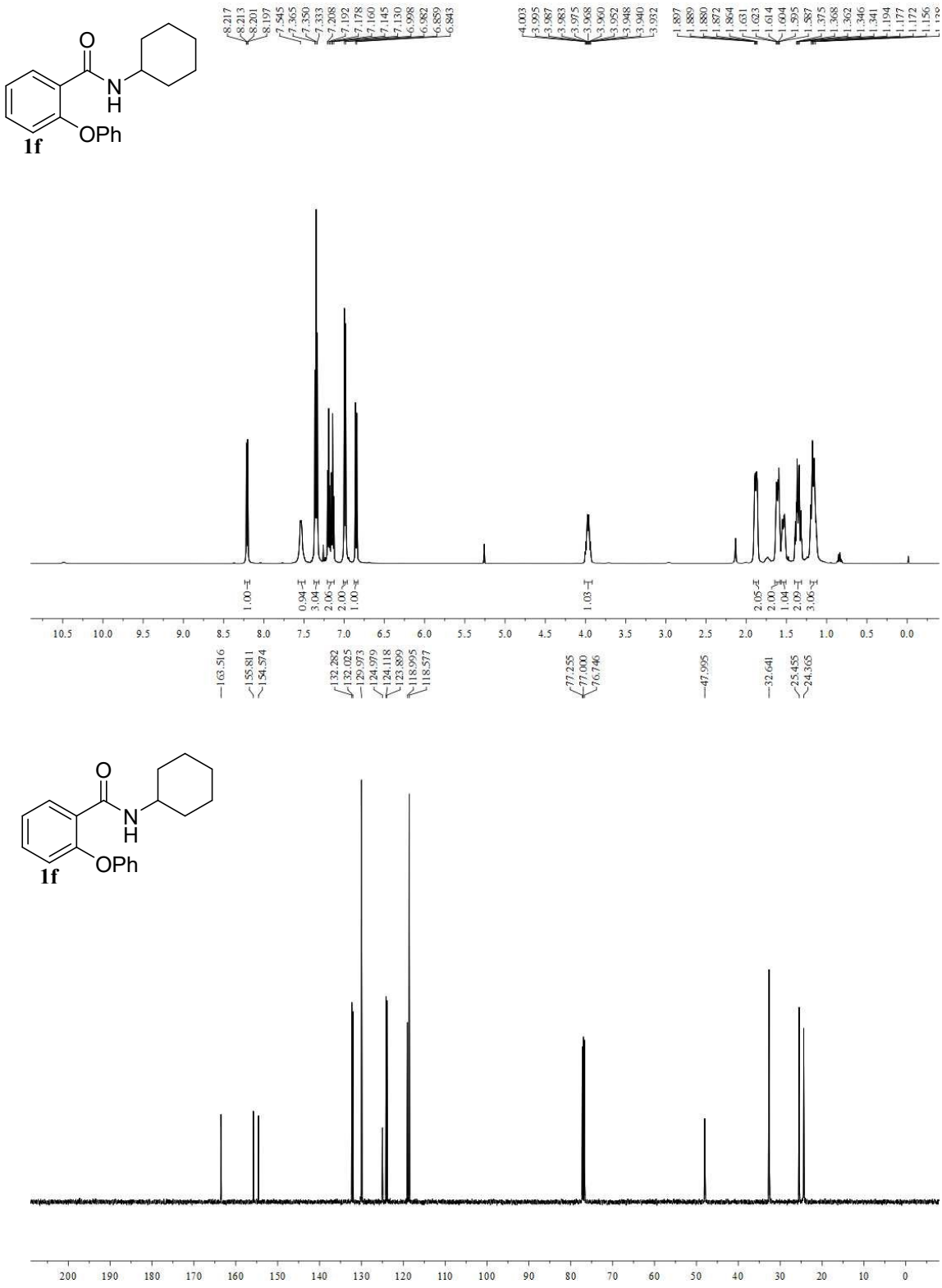
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1c



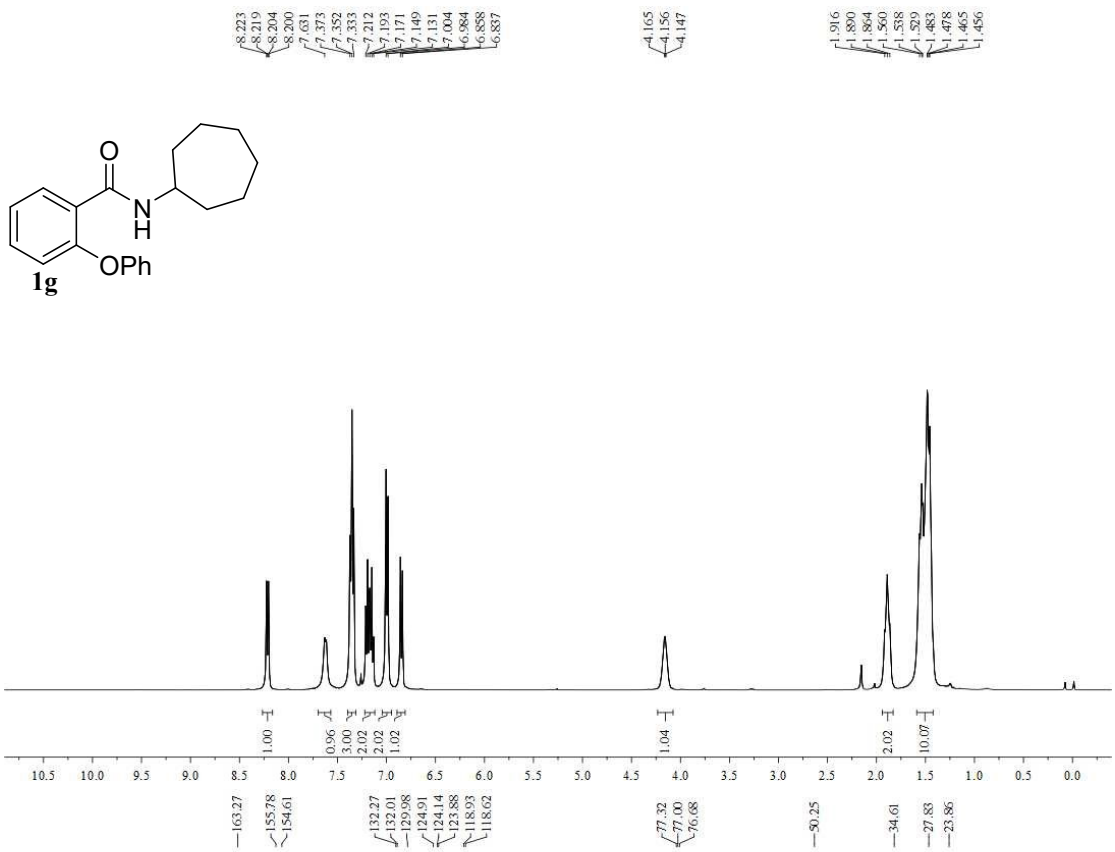
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1d



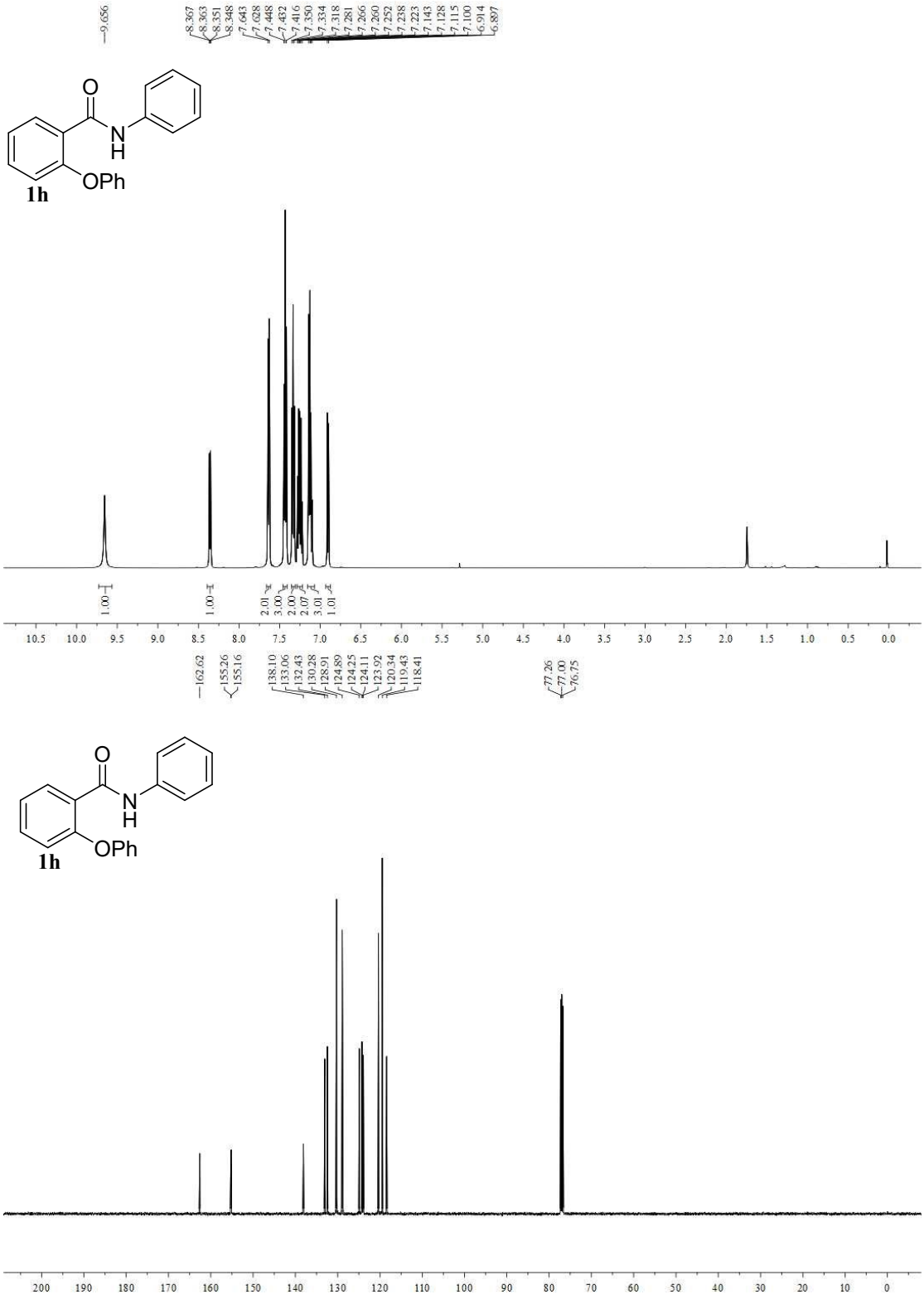
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1e



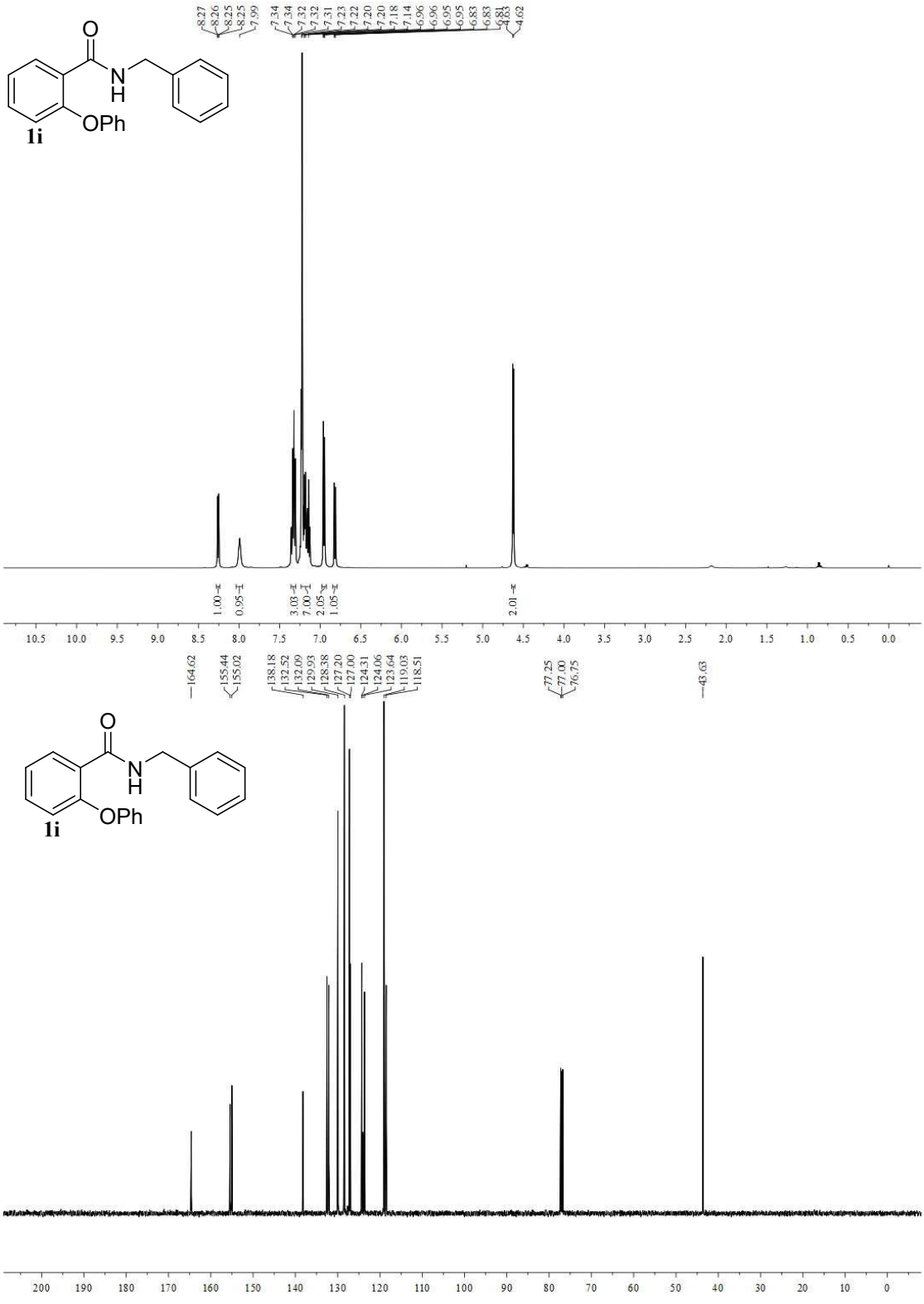
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1f



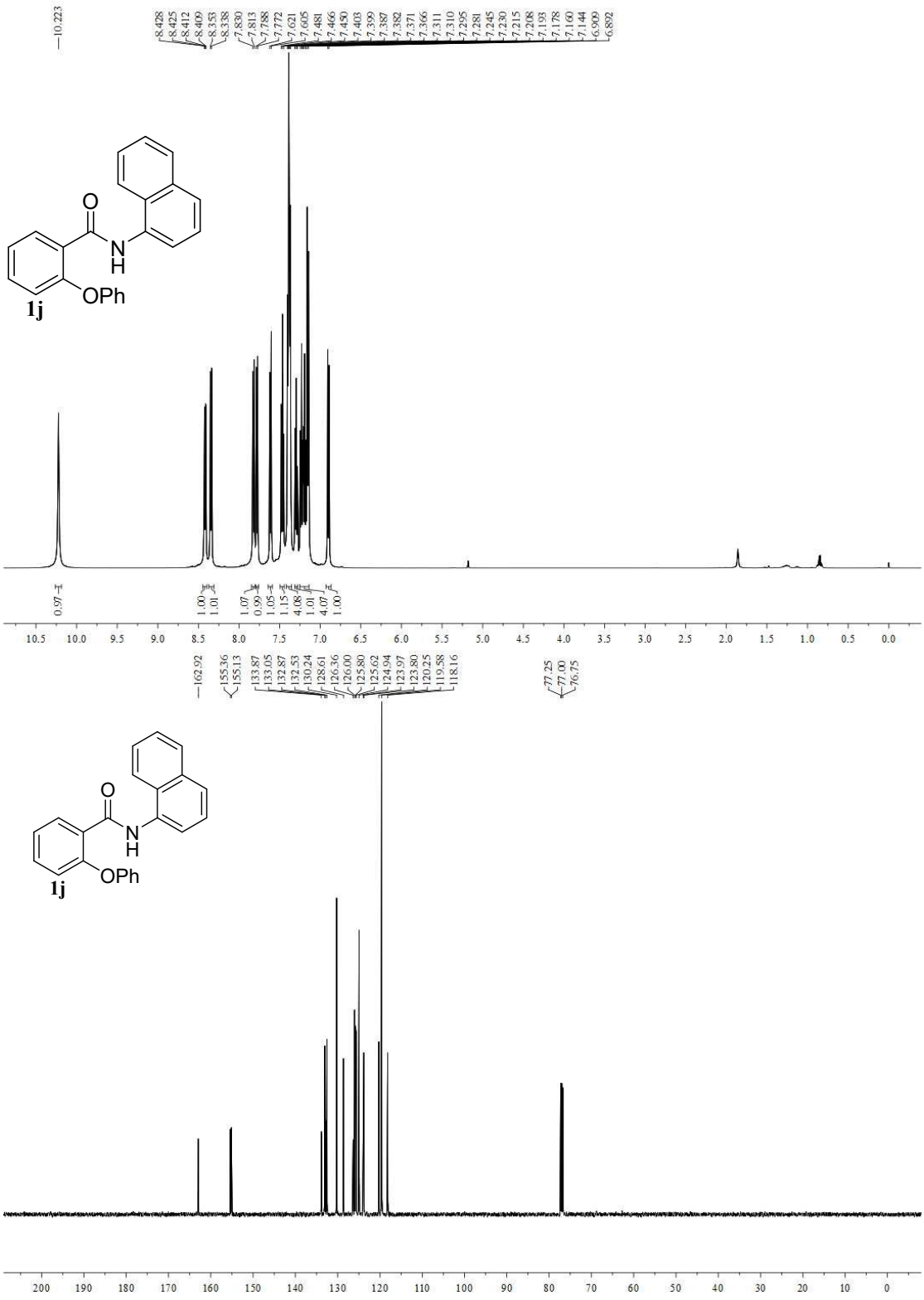
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1g



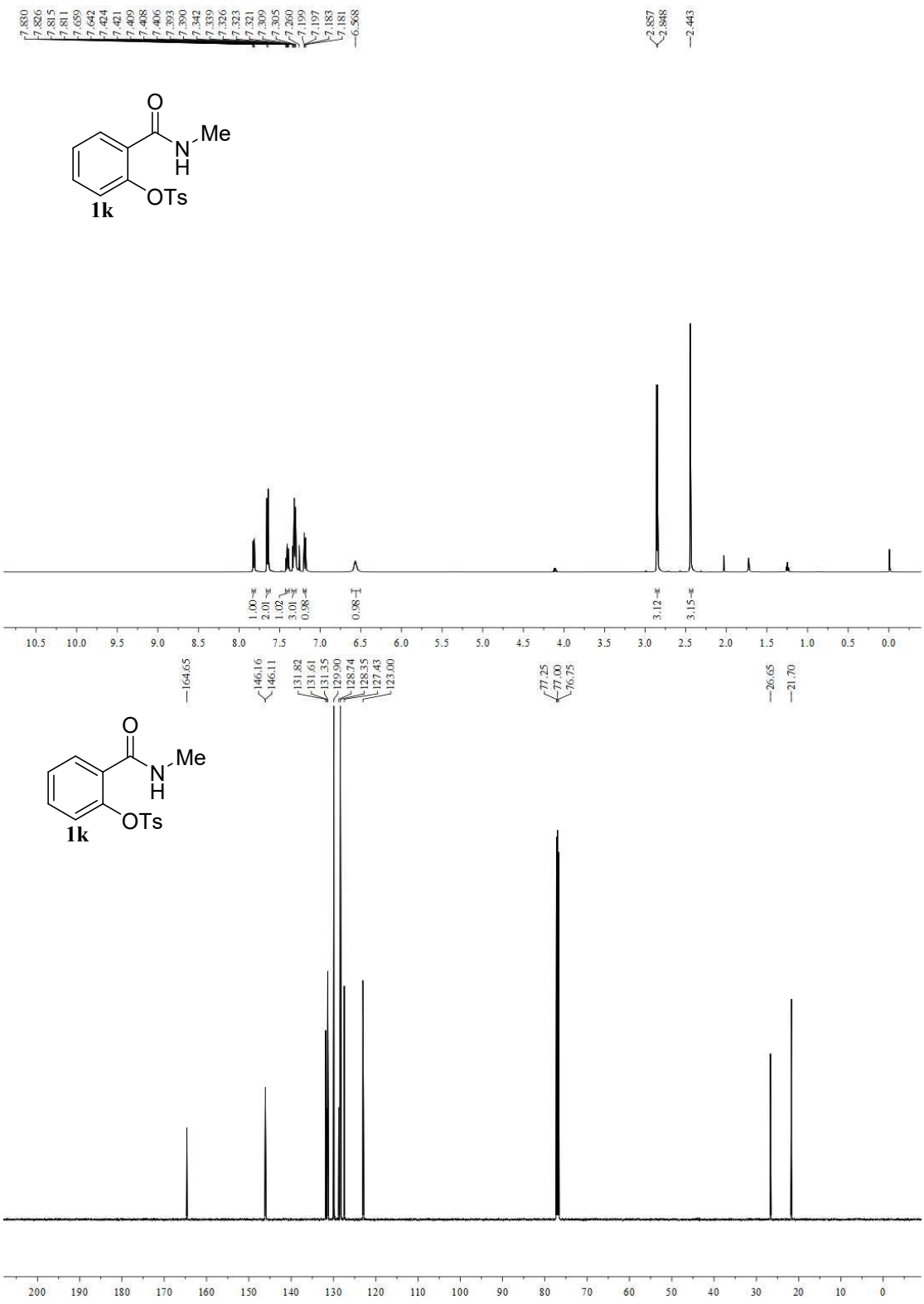
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1h



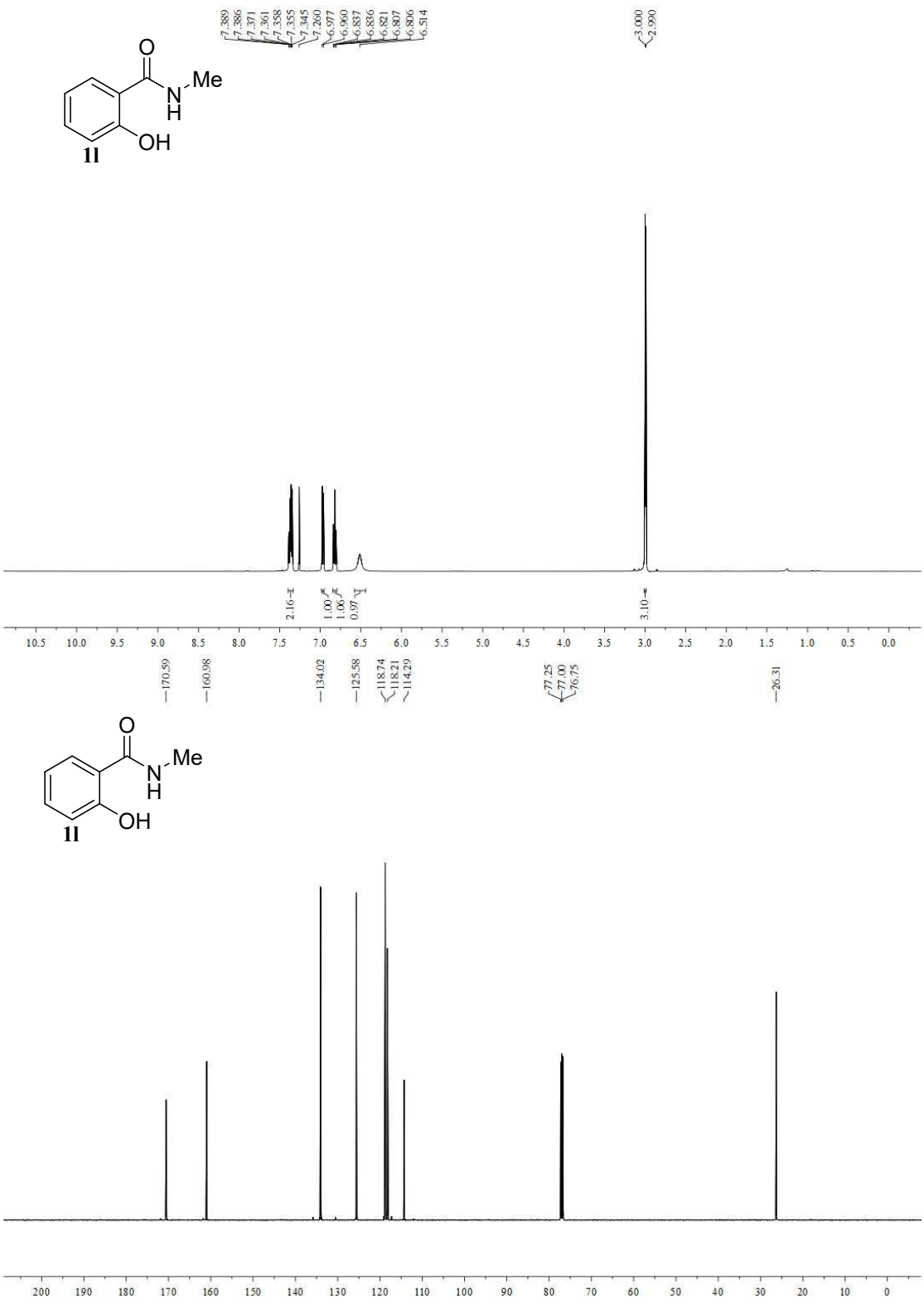
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1i



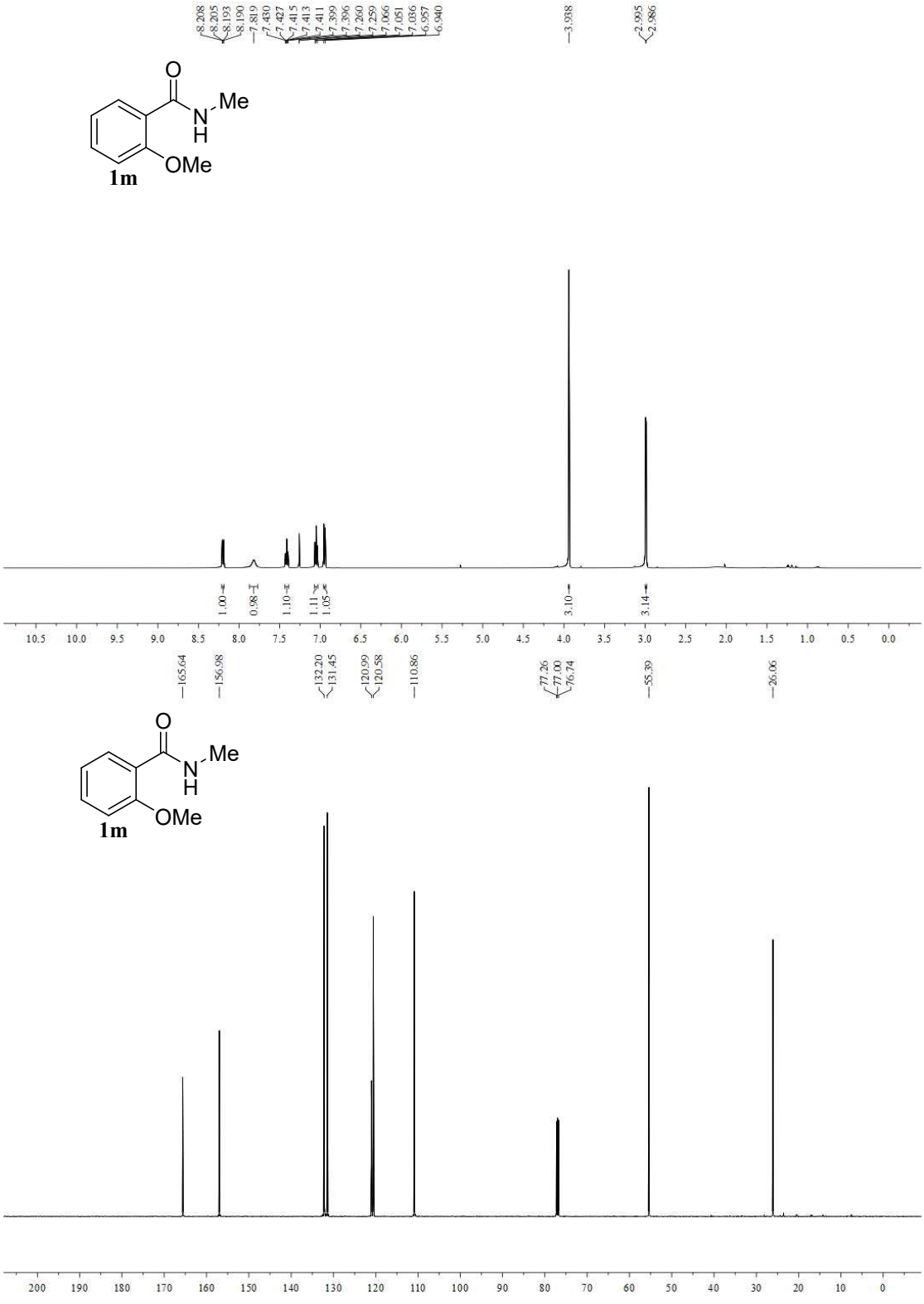
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1j



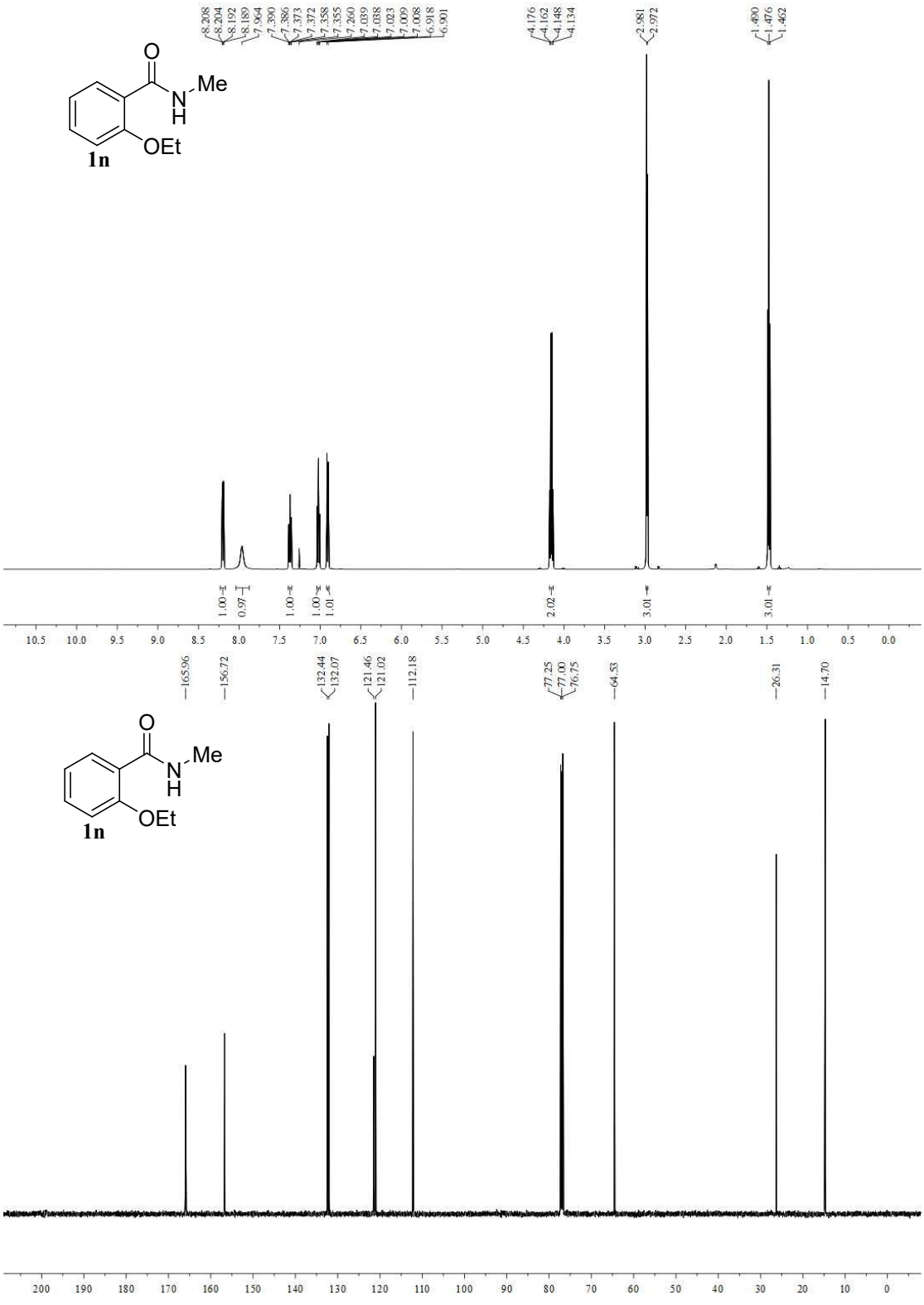
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1k



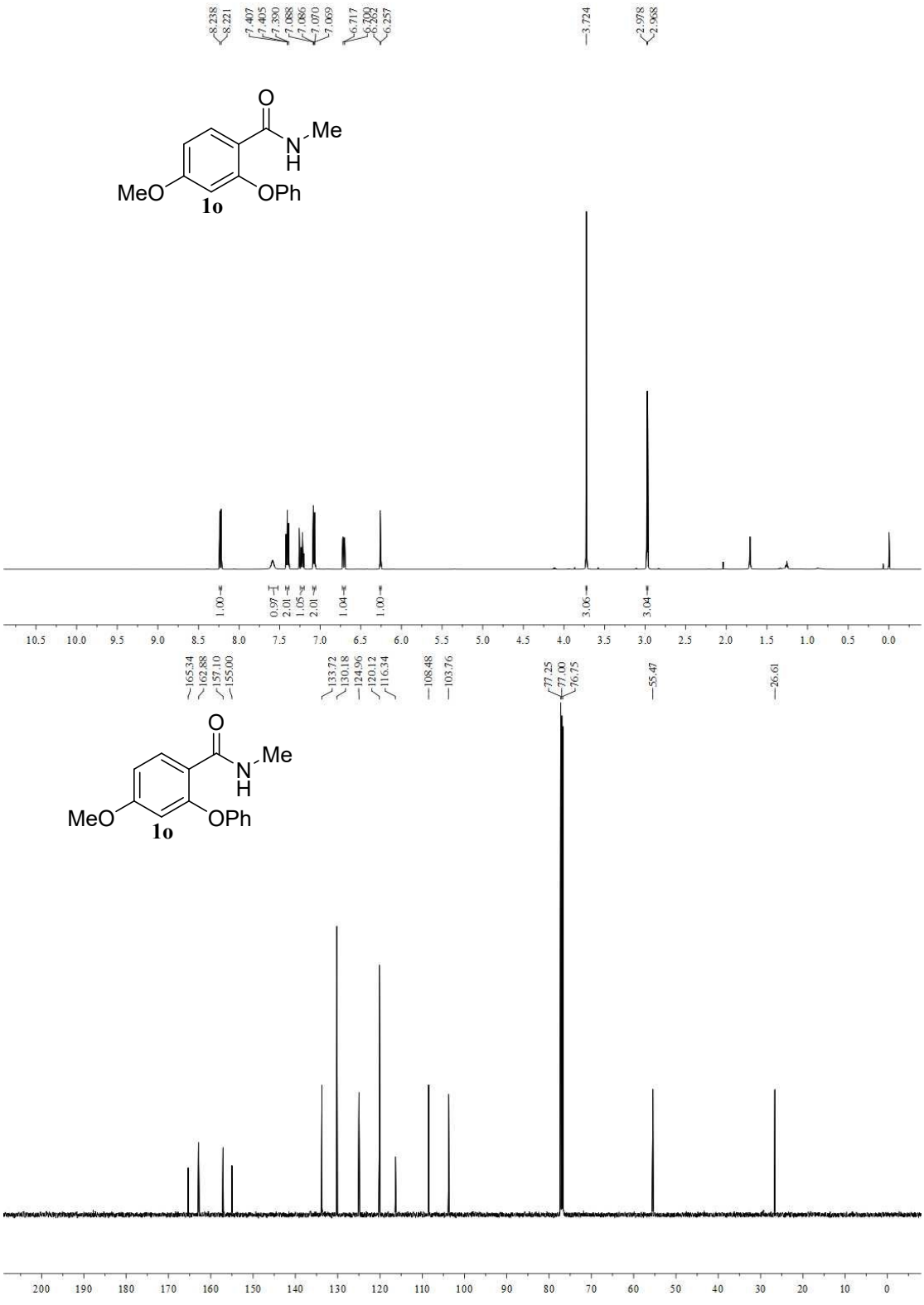
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1l



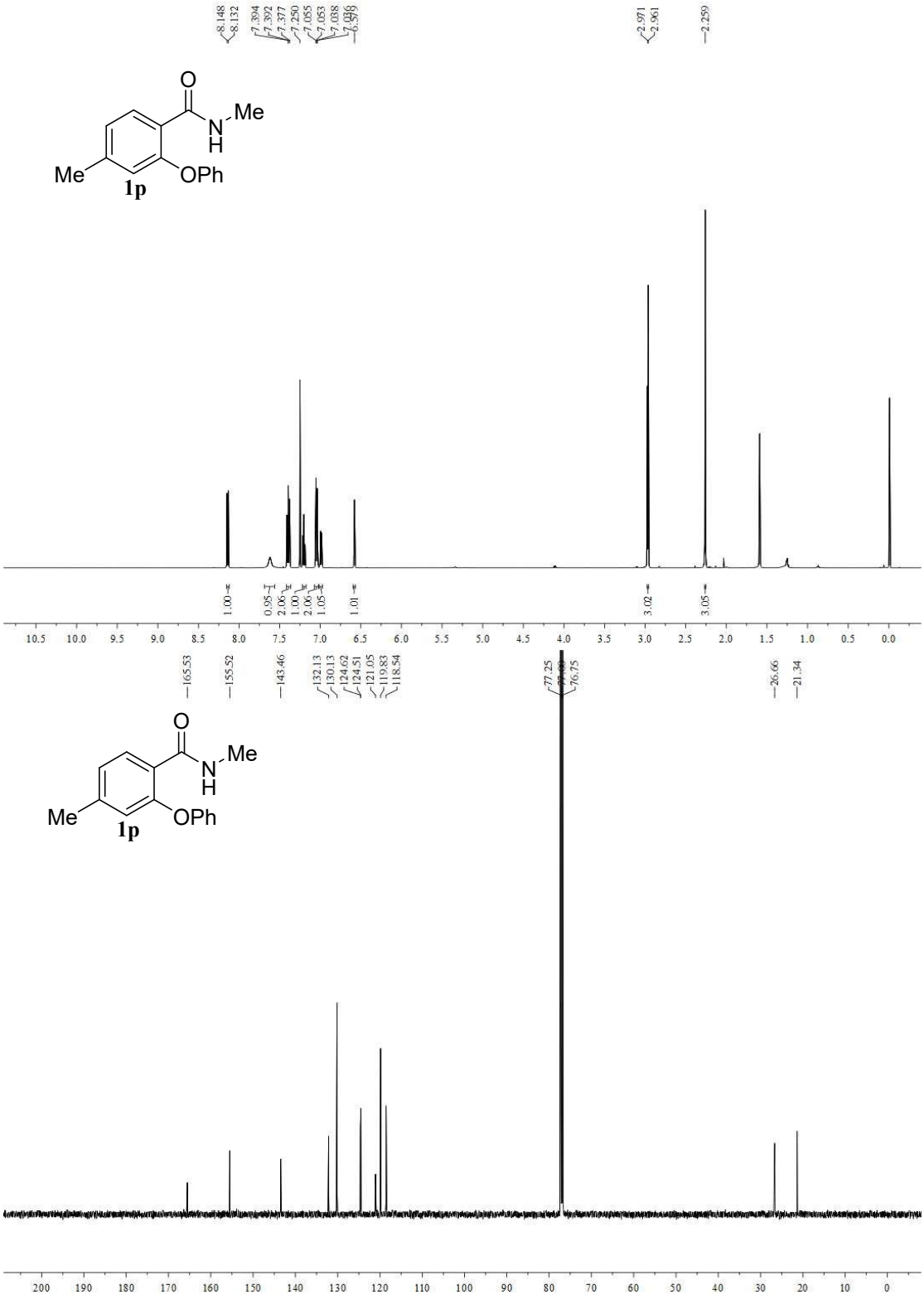
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1m



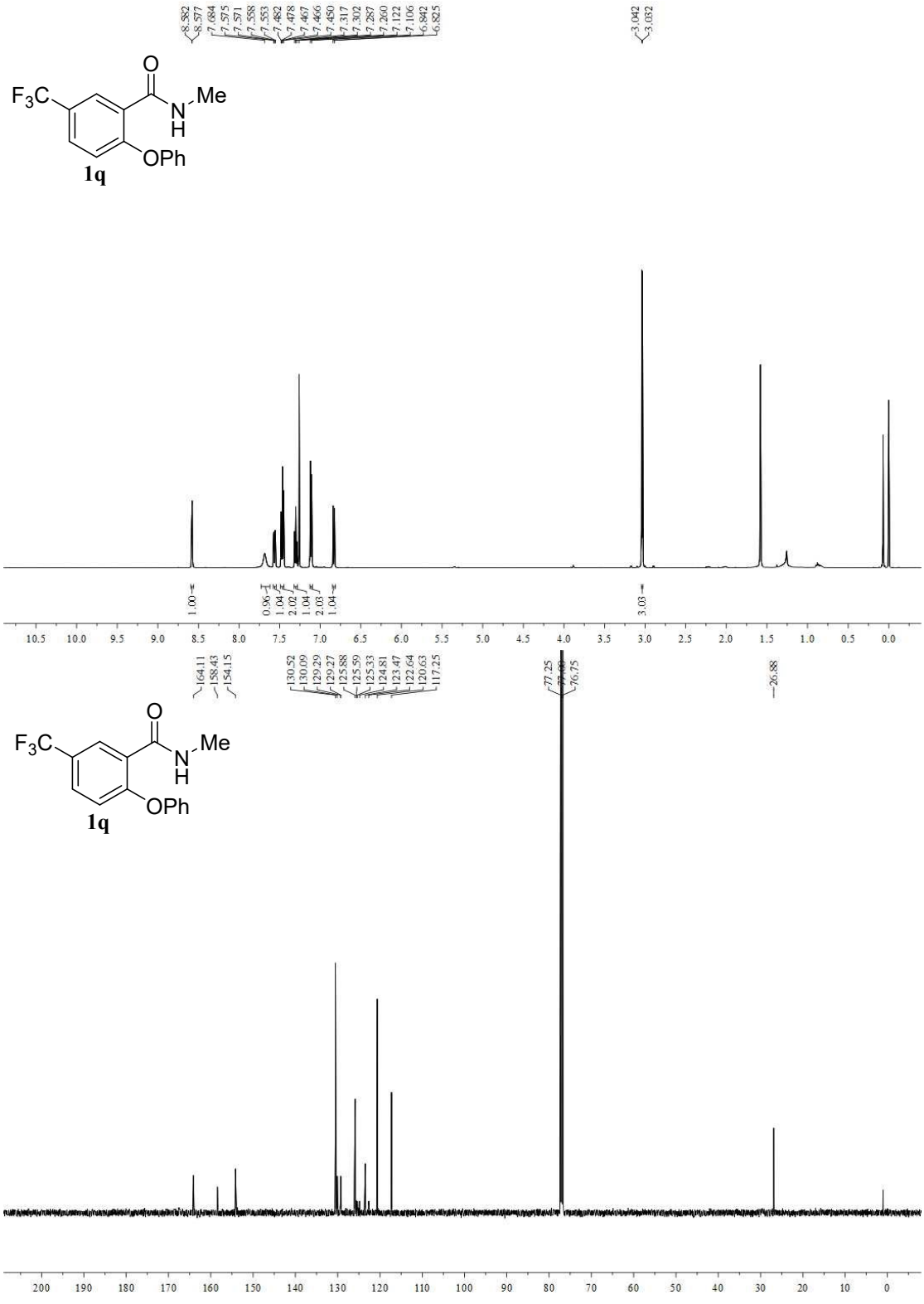
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1n



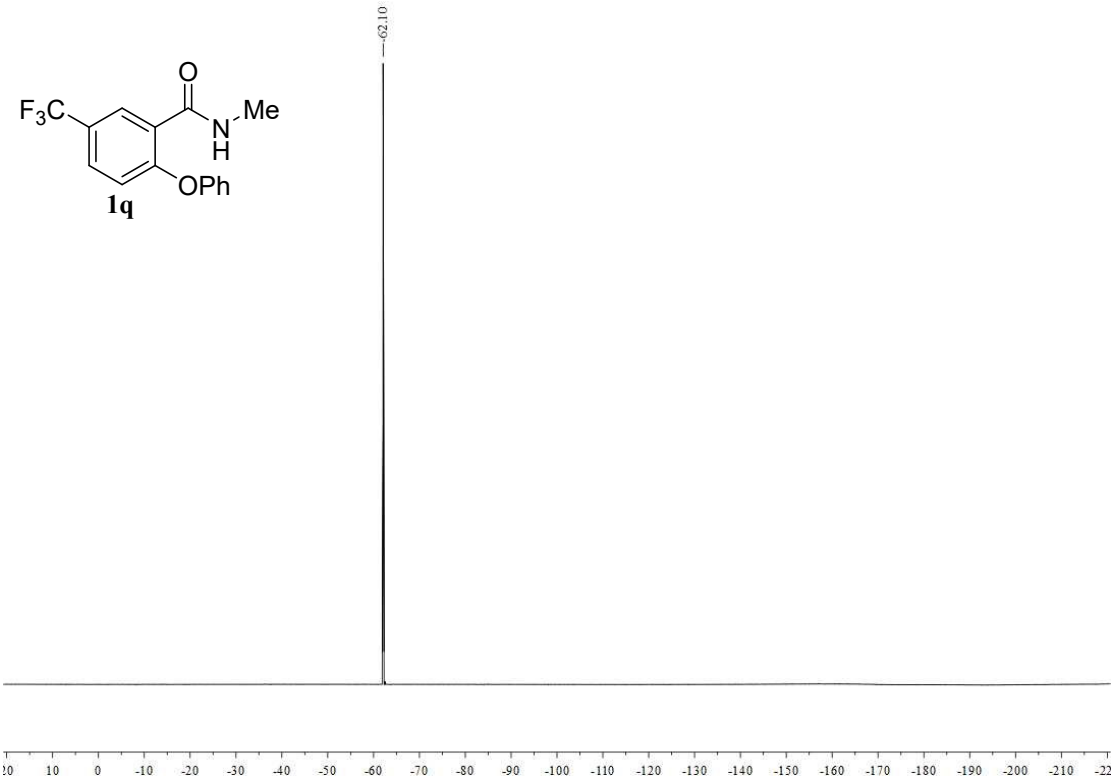
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1o



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1p

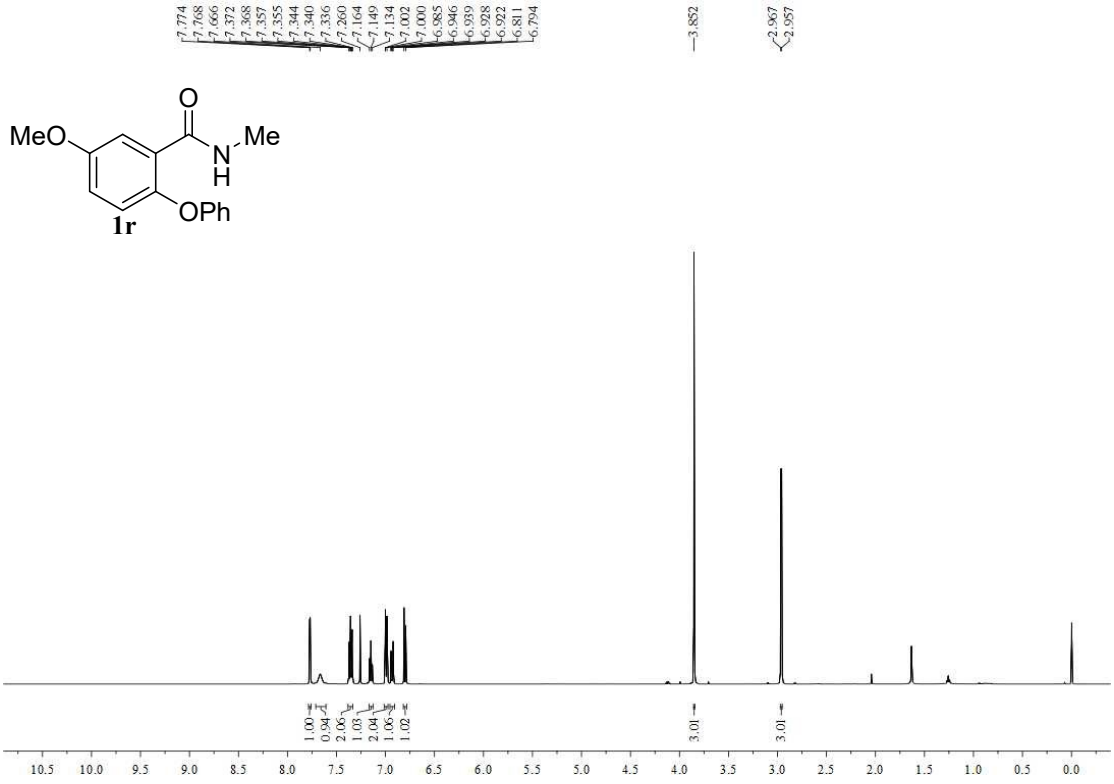


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1q

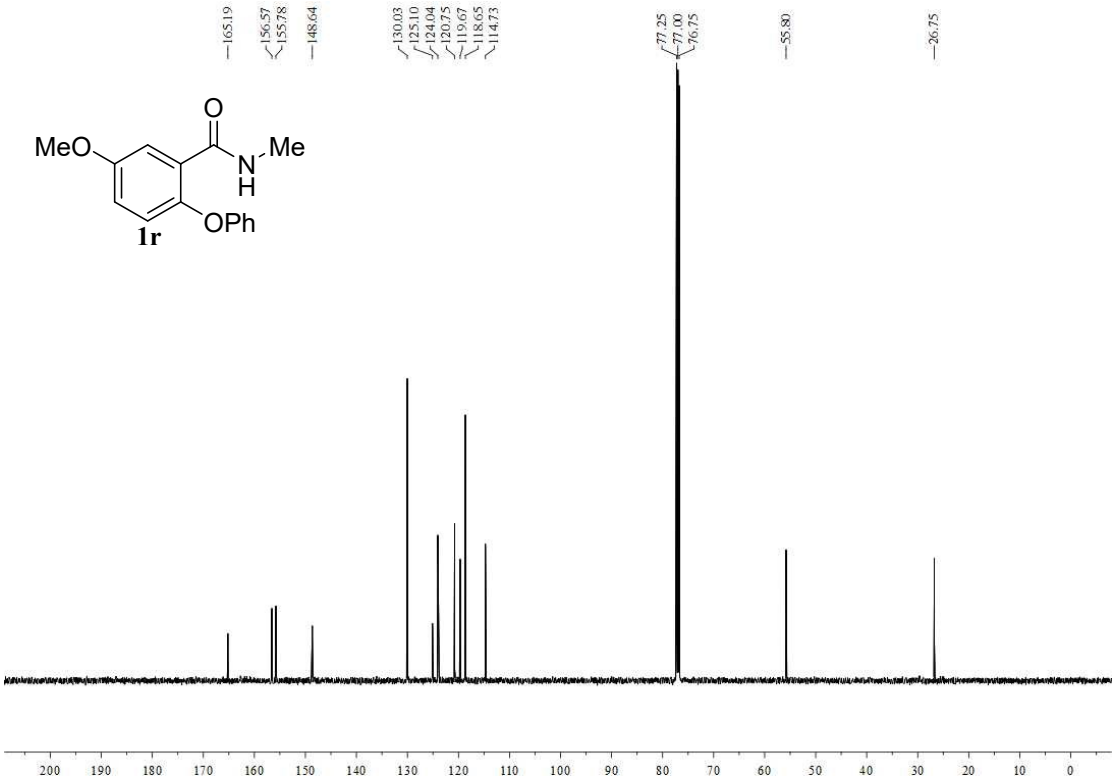


1q

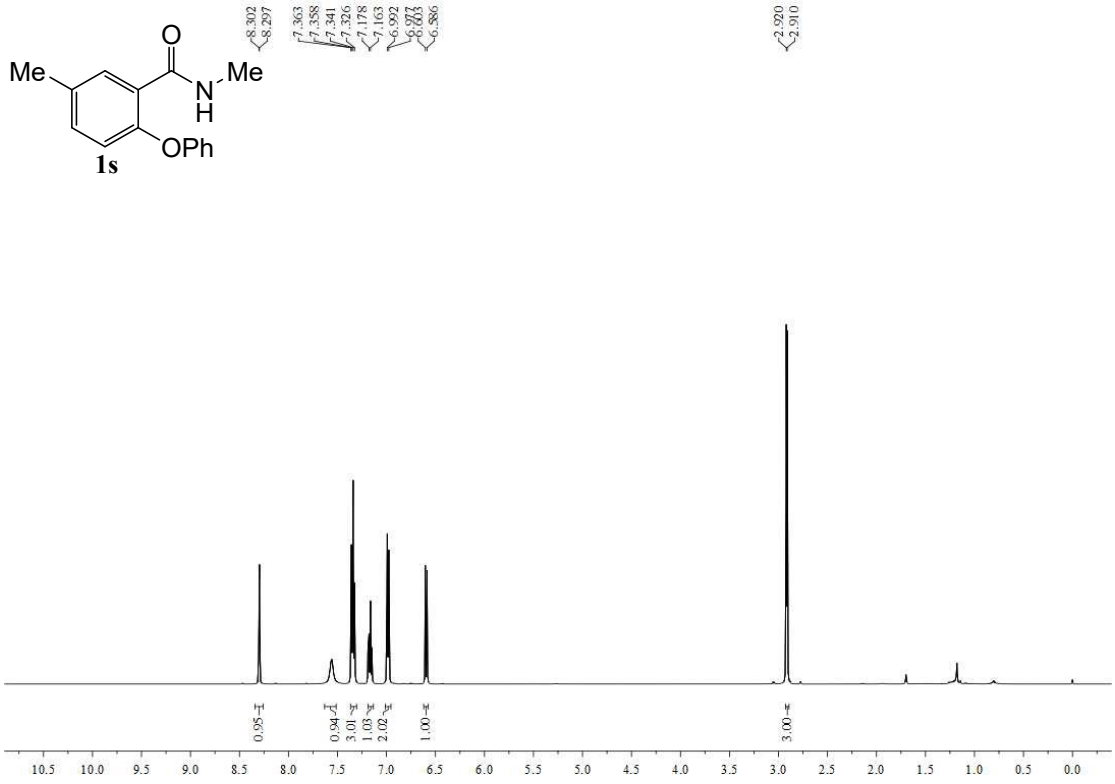
^{19}F NMR spectra in $CDCl_3$ for compound 1q

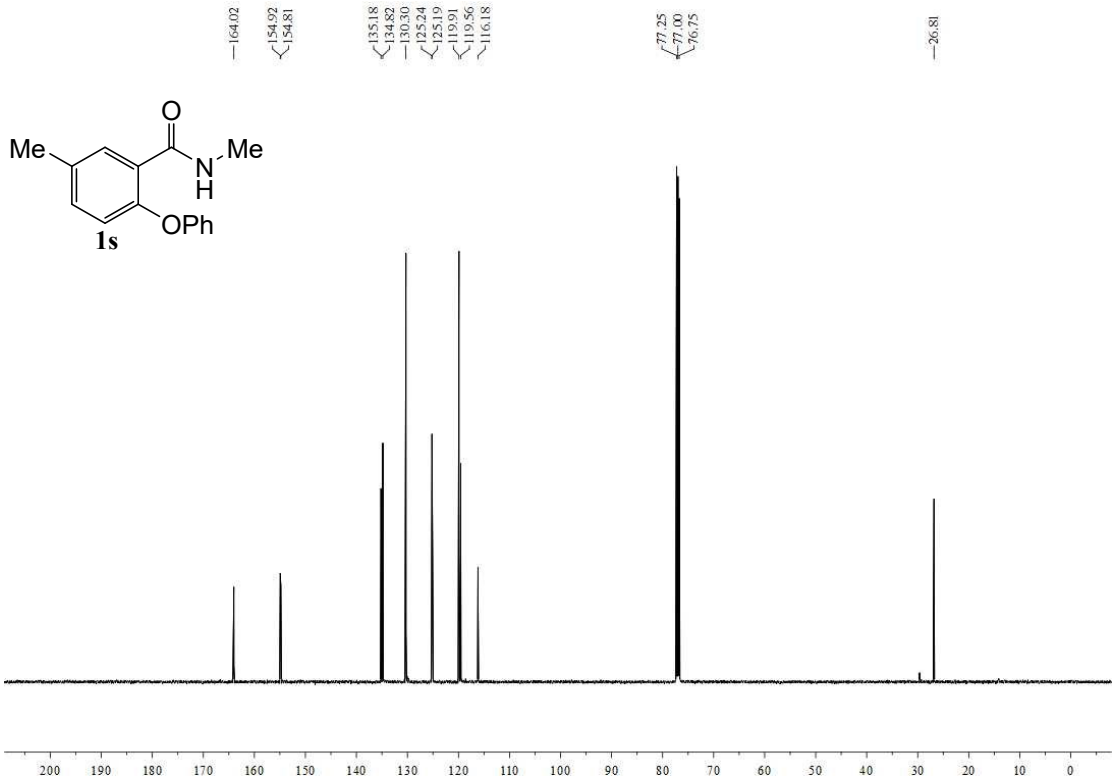


1r

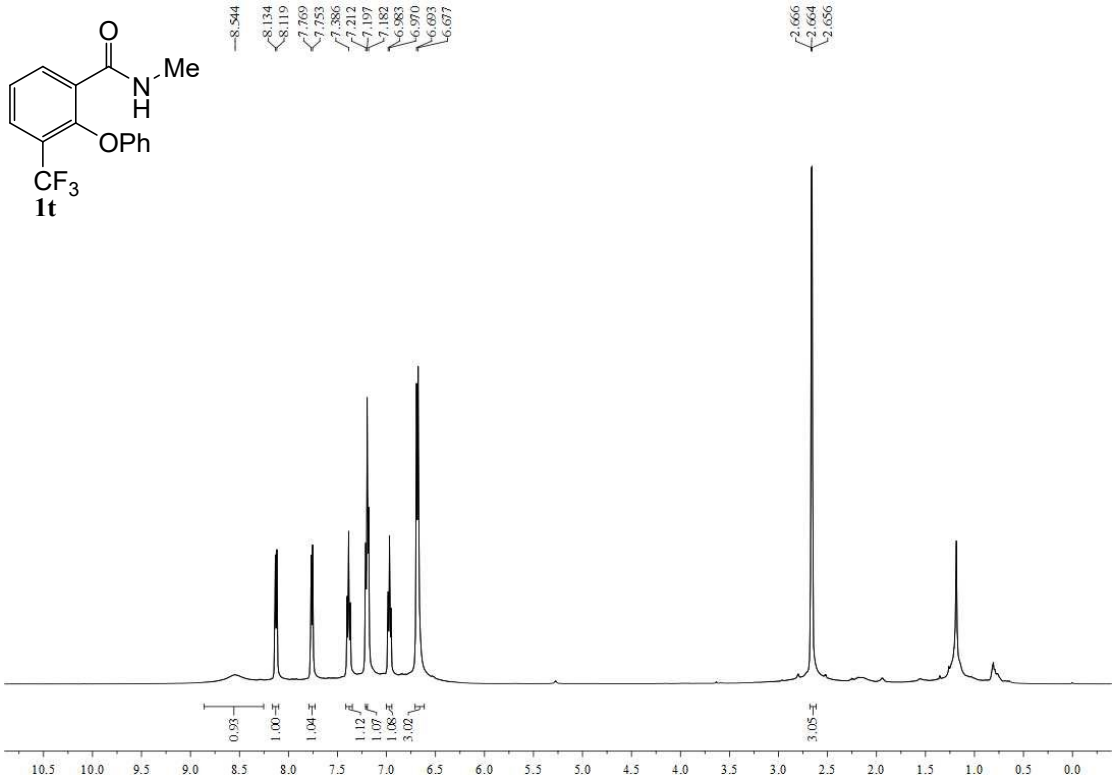


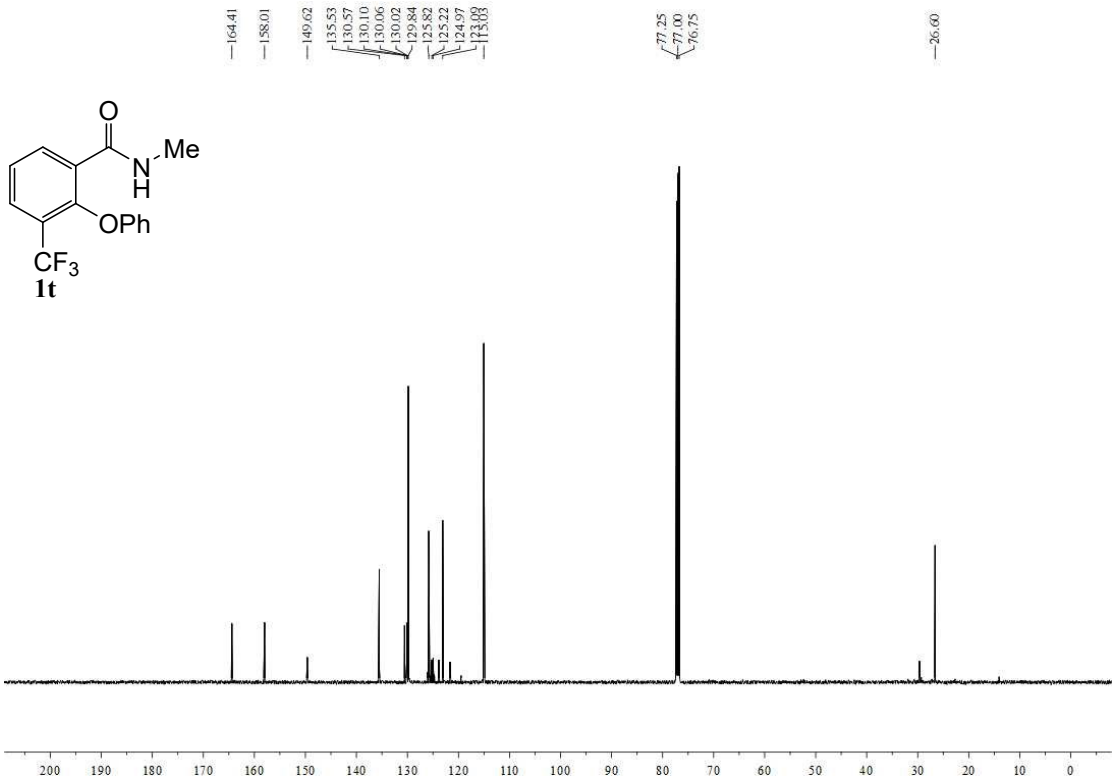
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1r



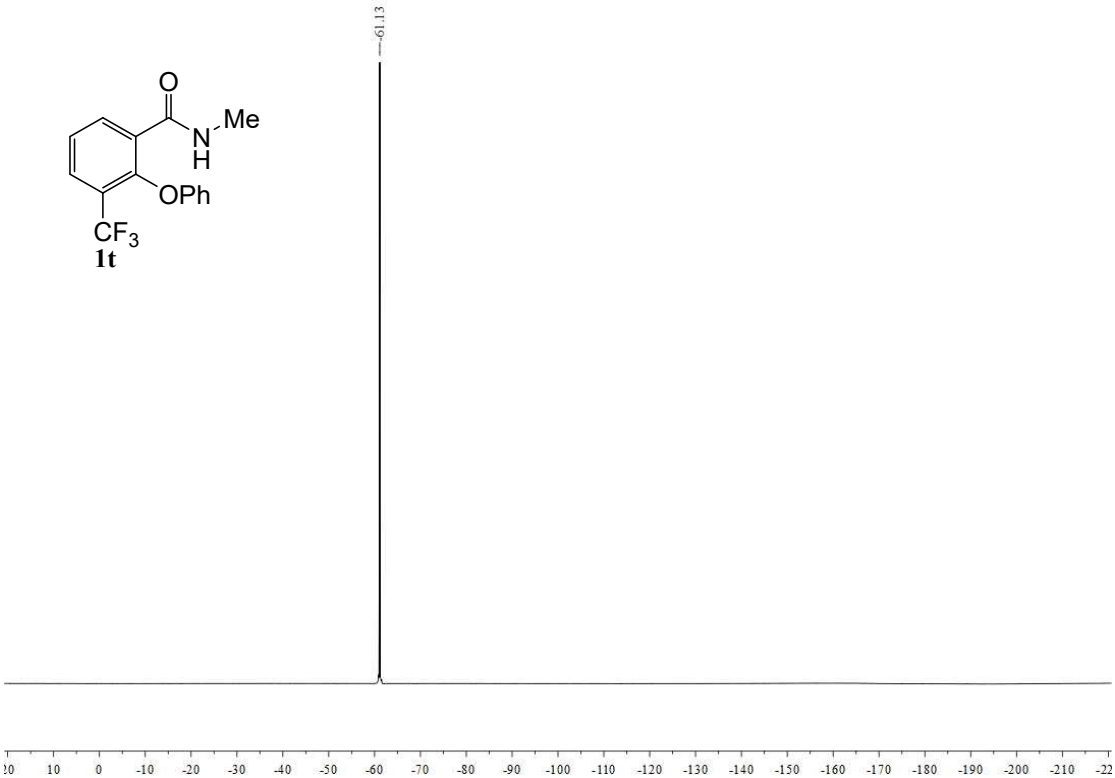


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1s



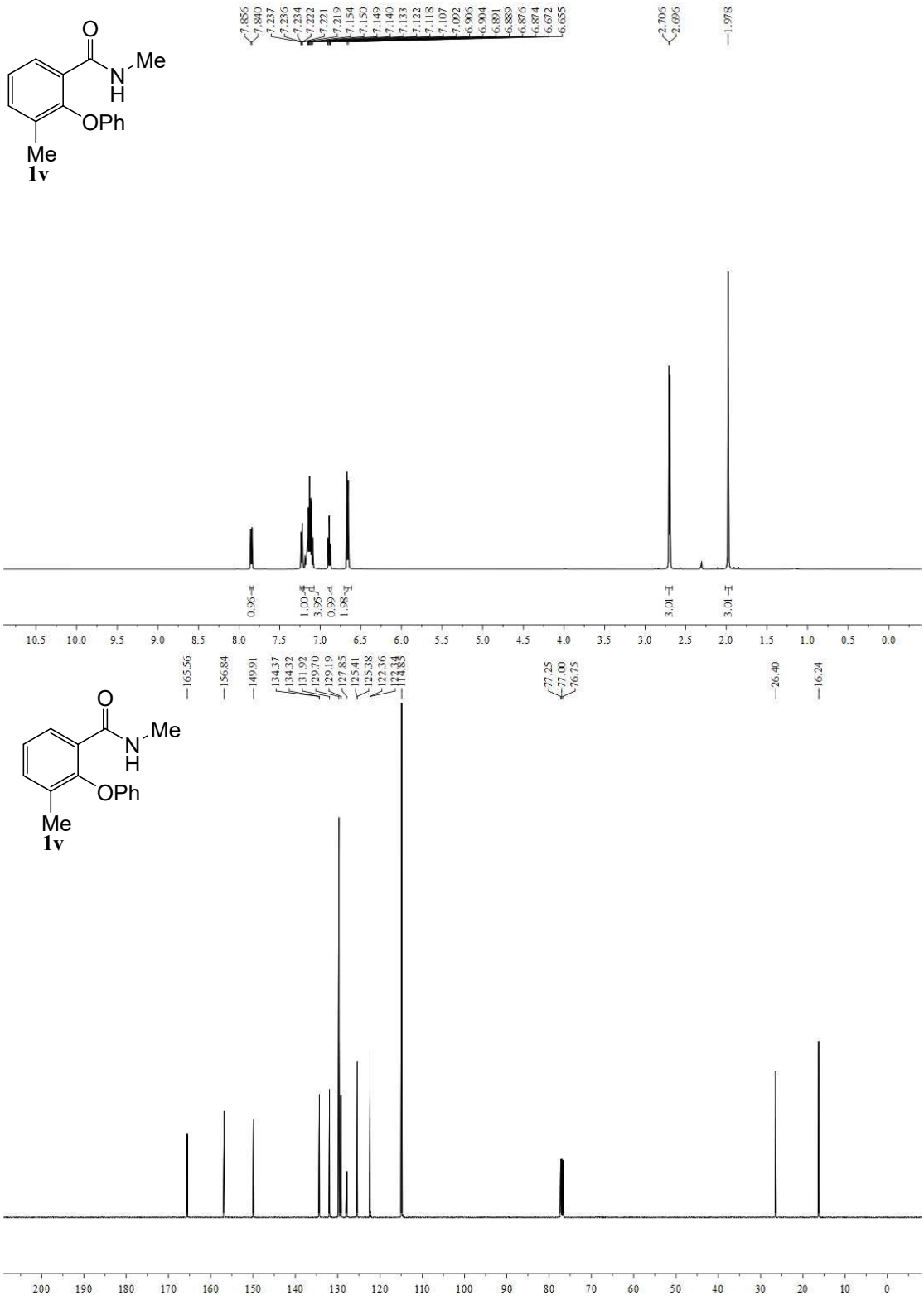


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1t

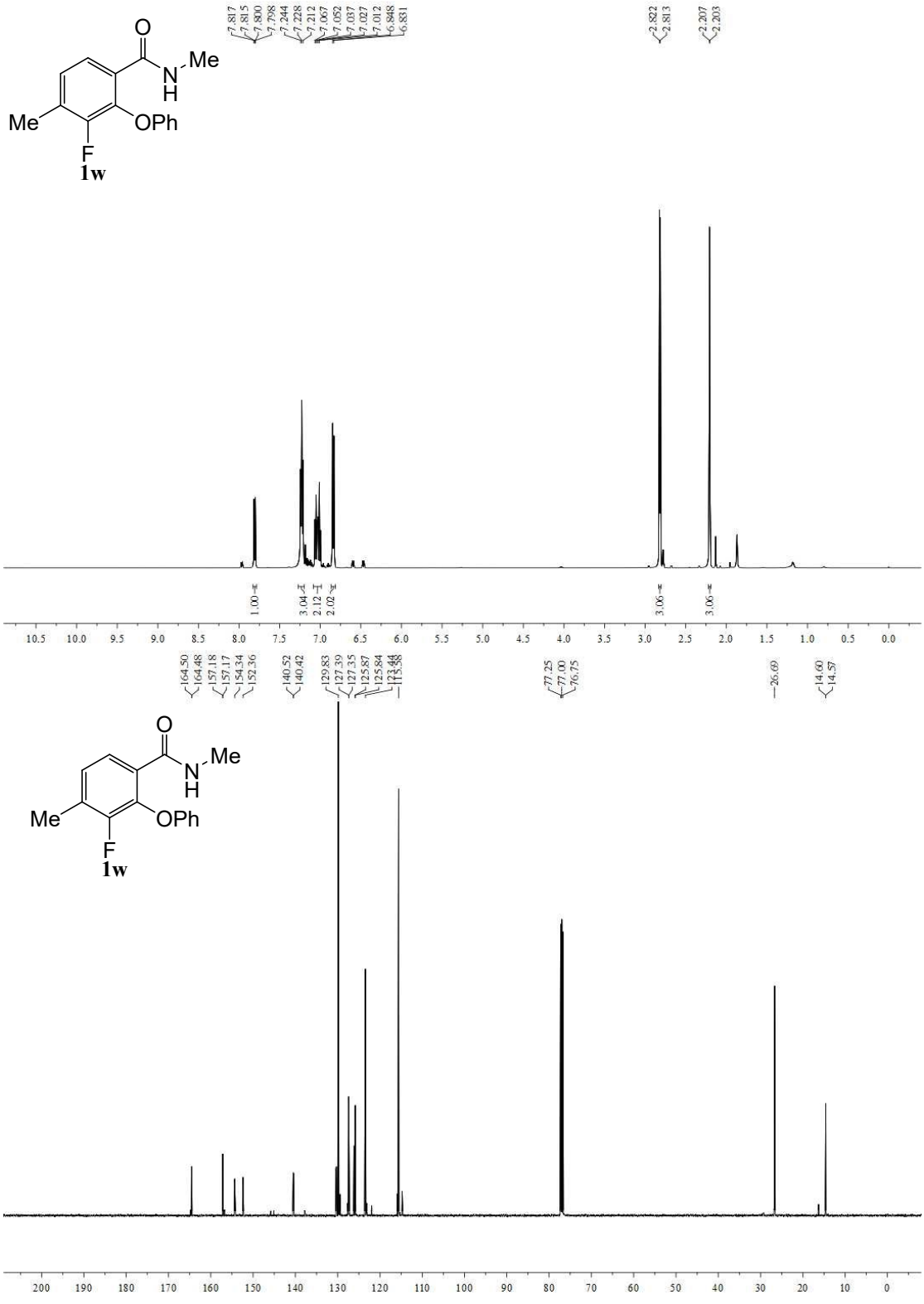


^{19}F NMR spectra in $CDCl_3$ for compound 1t

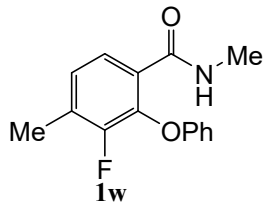
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1u



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1v

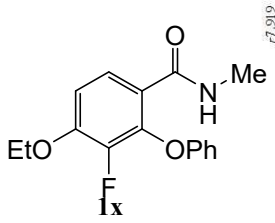


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1w

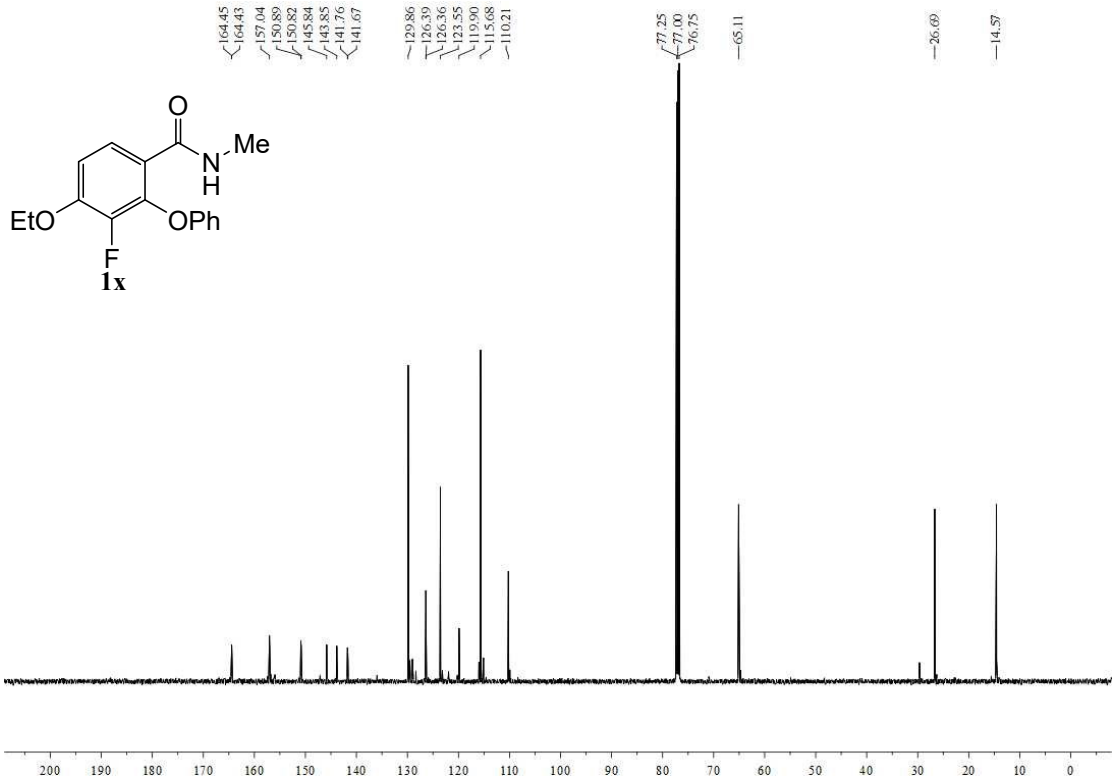


1w

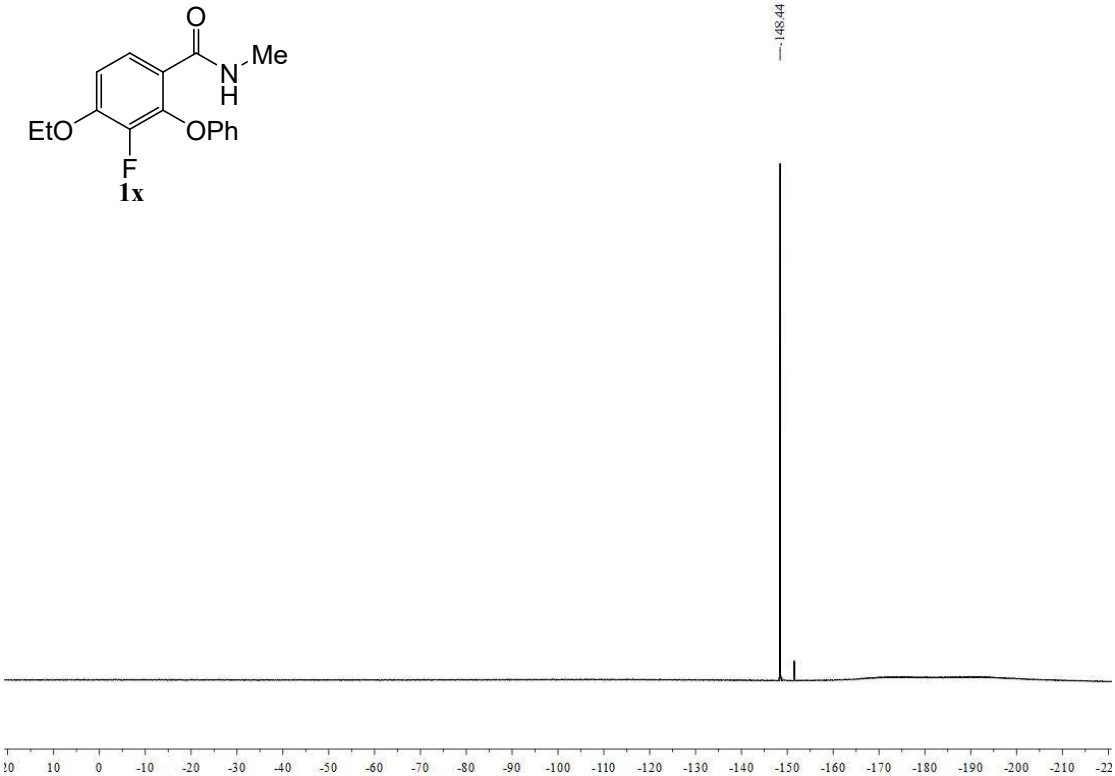
^{19}F NMR spectra in $CDCl_3$ for compound 1w



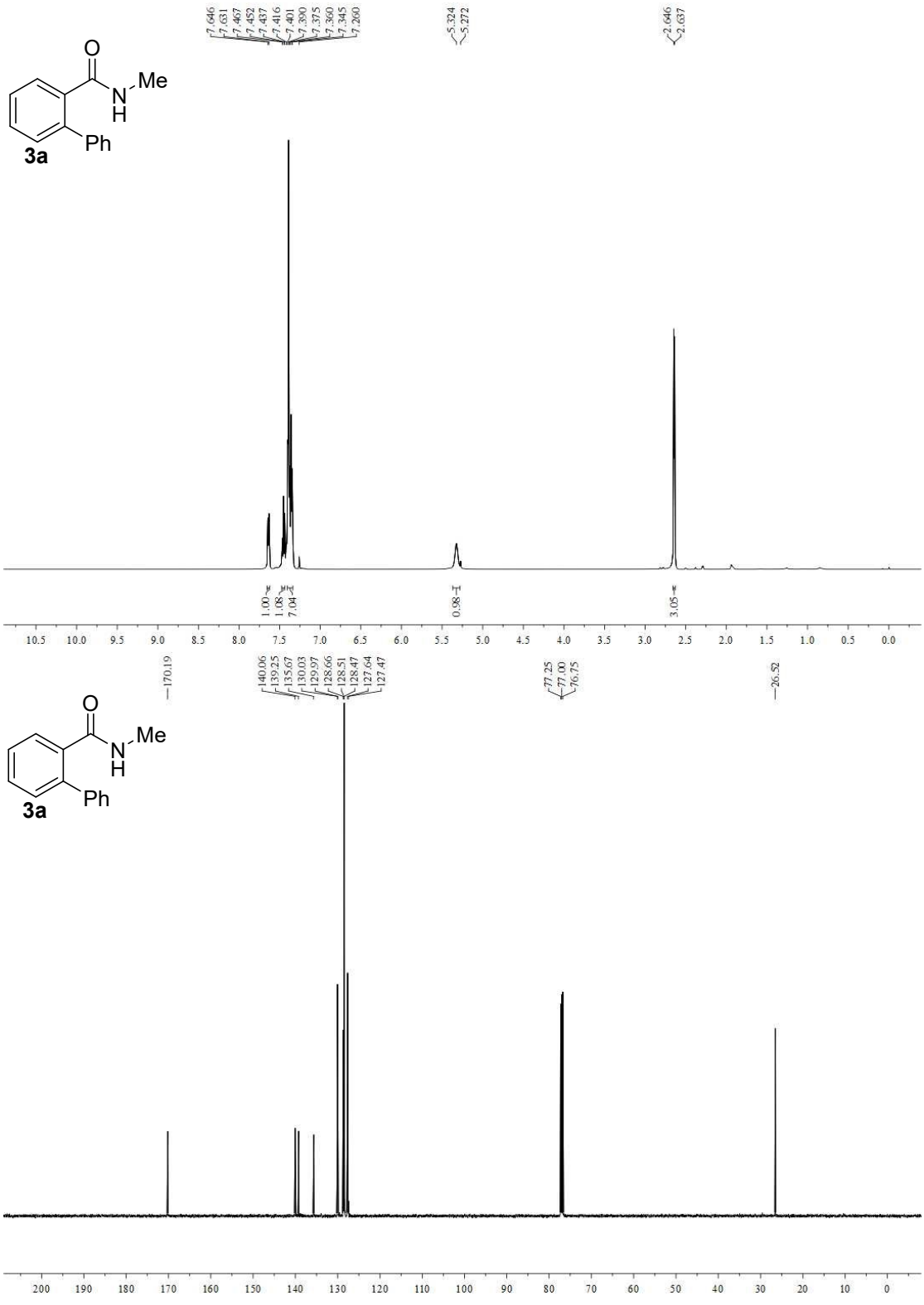
1x



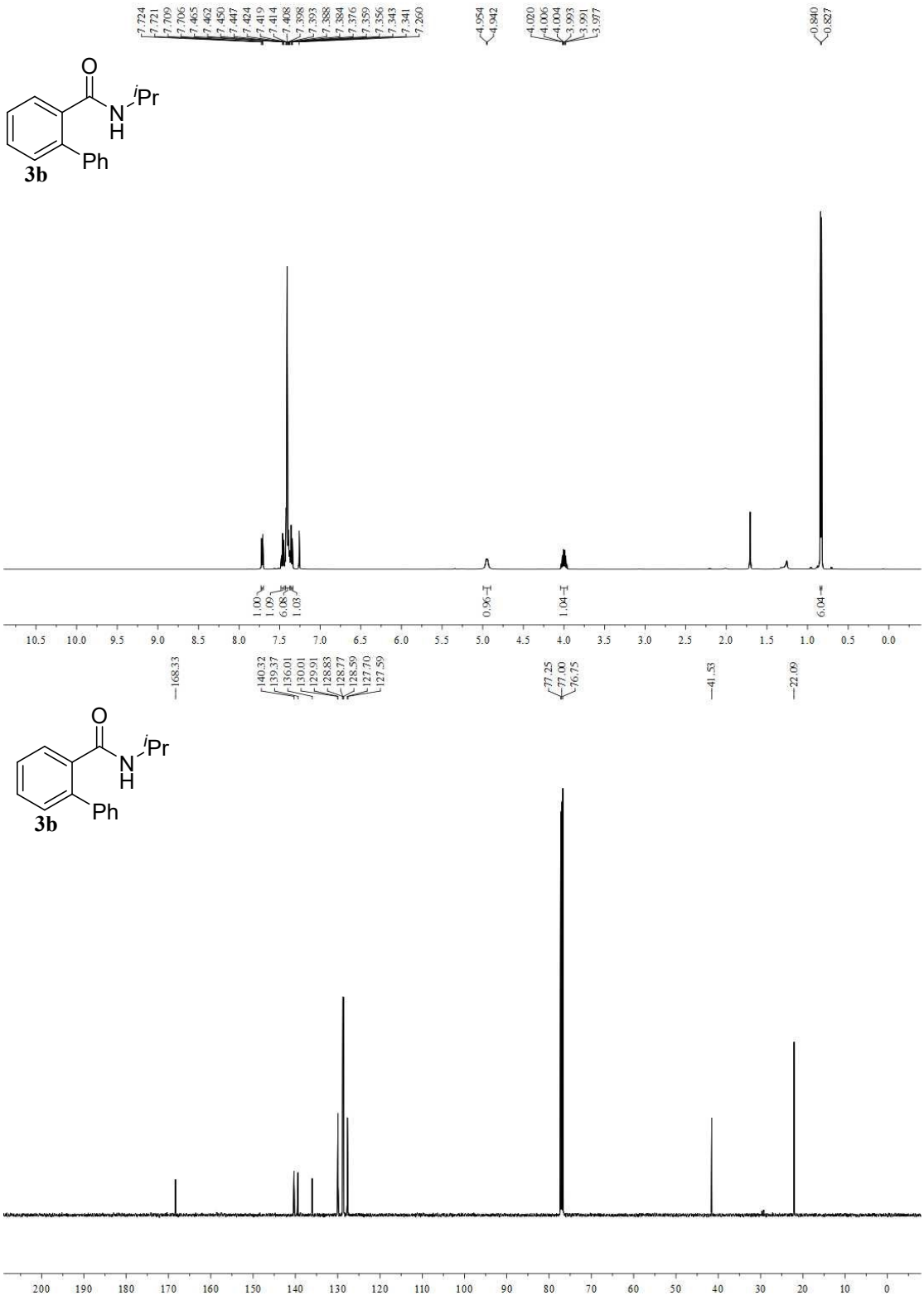
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 1x



^{19}F NMR spectra in $CDCl_3$ for compound 1x

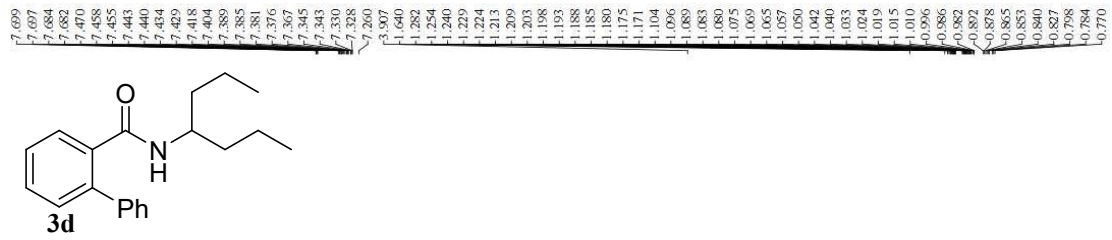


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3a

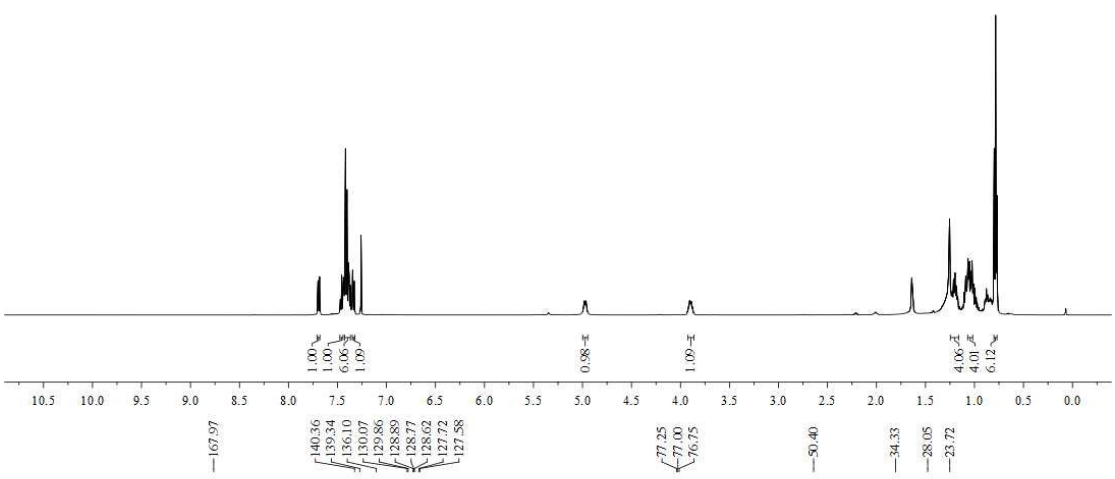


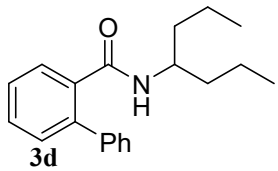
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3b

^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3c

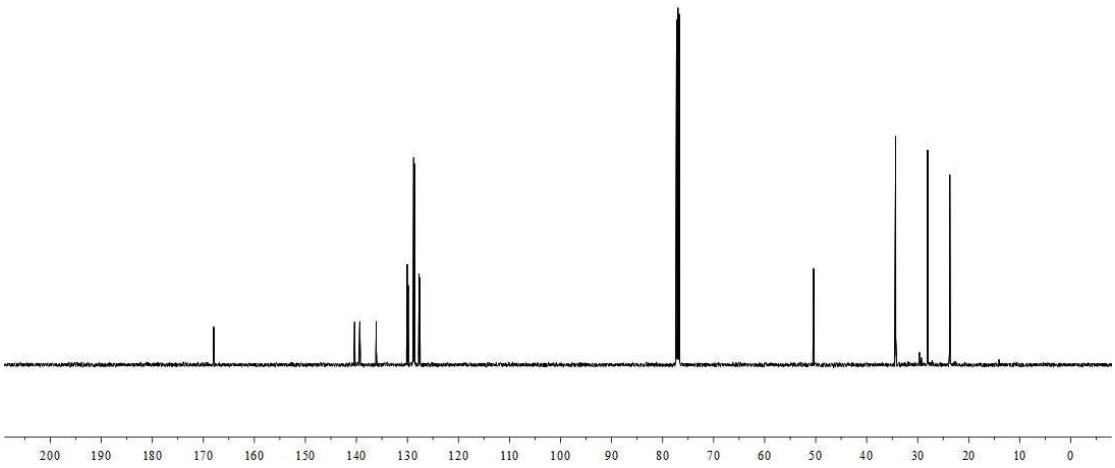


3d

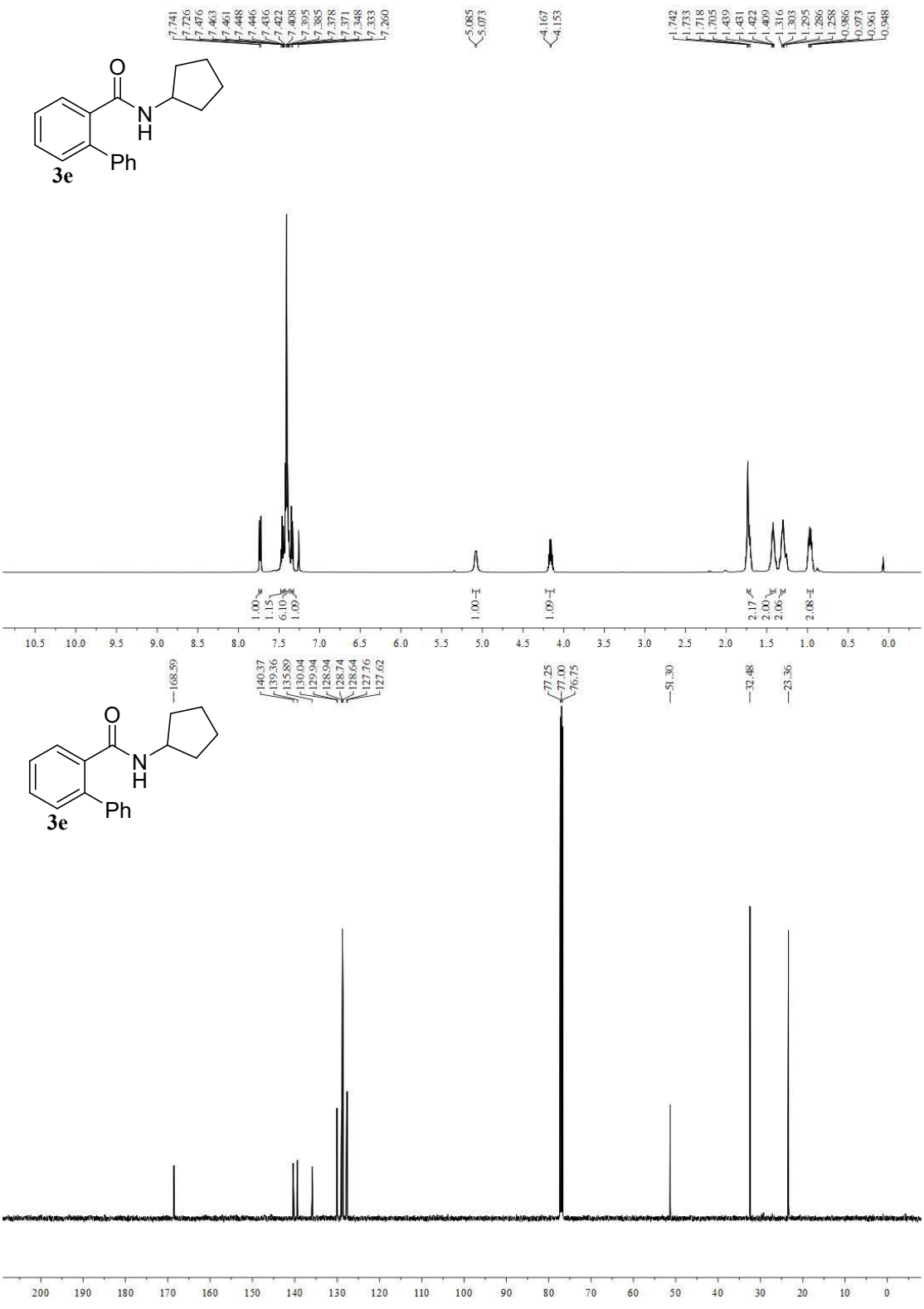




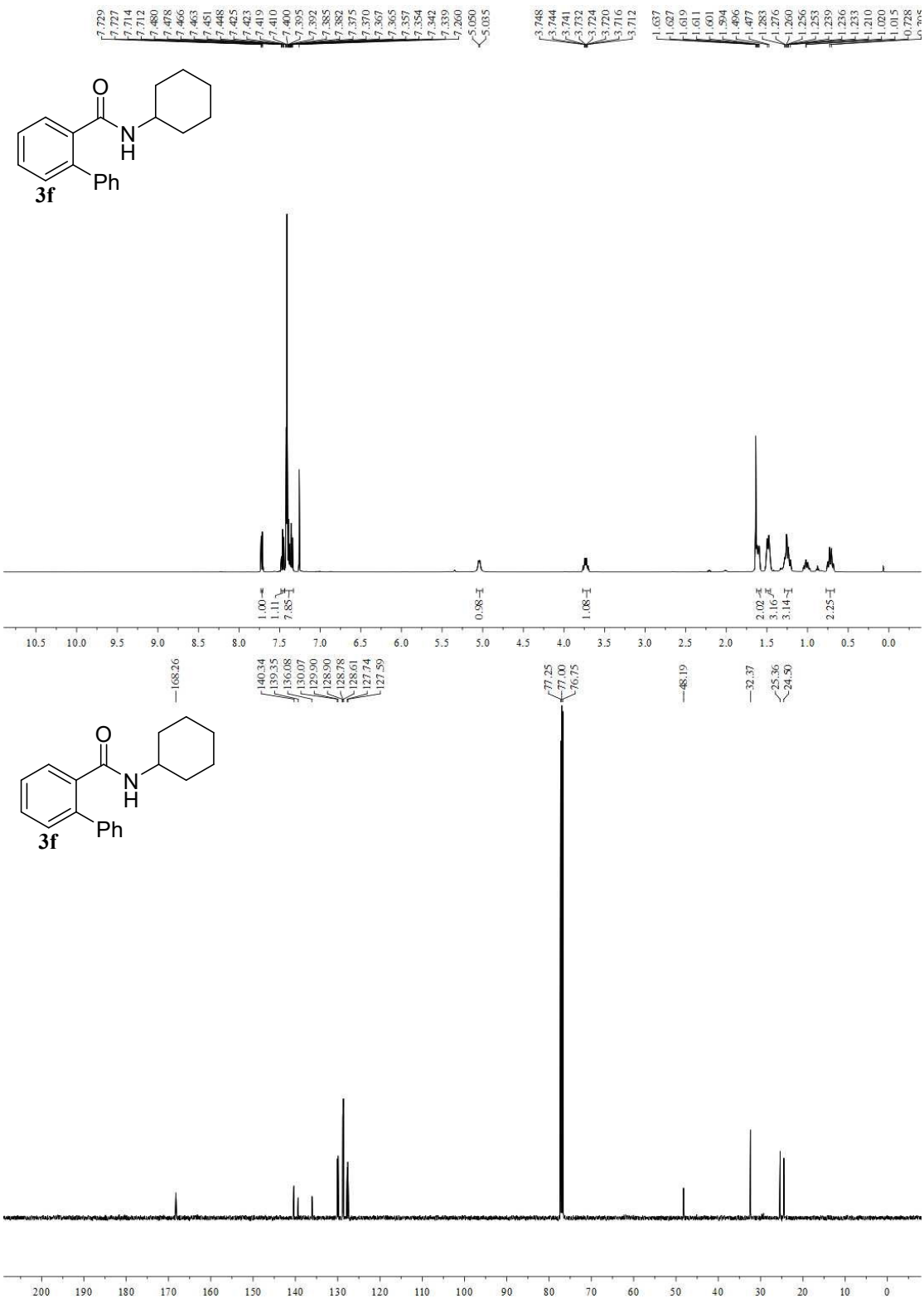
3d



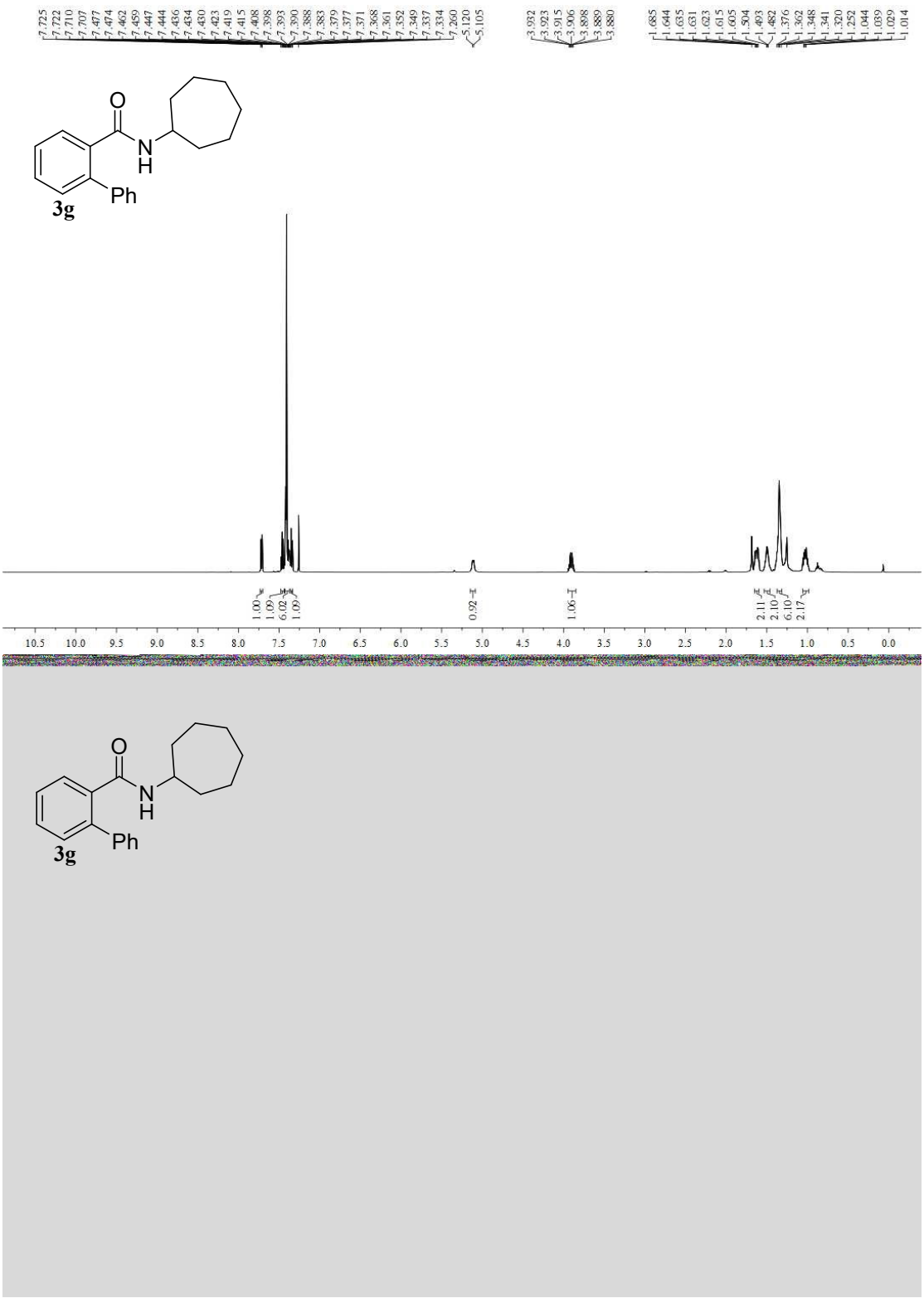
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3d



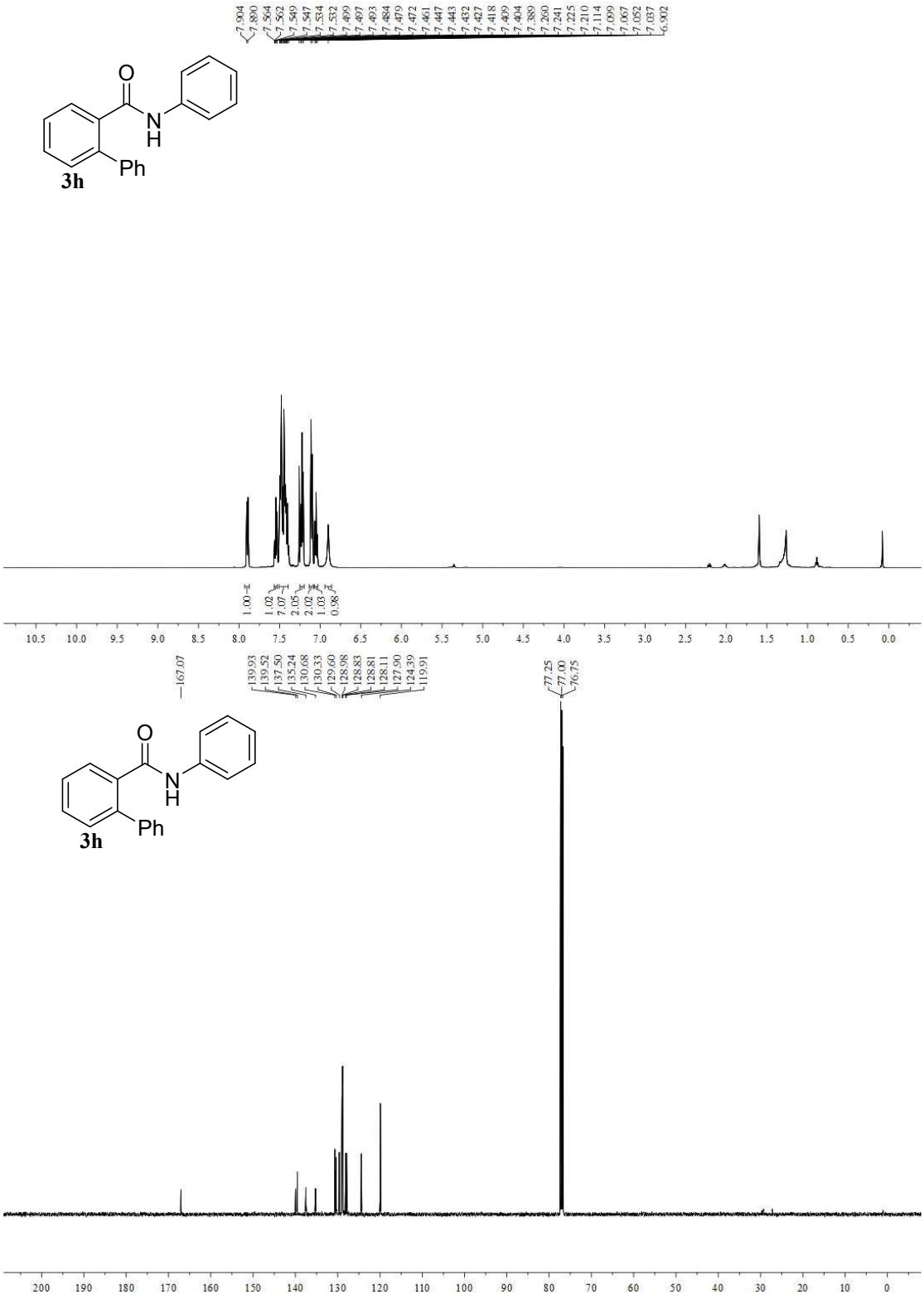
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3e



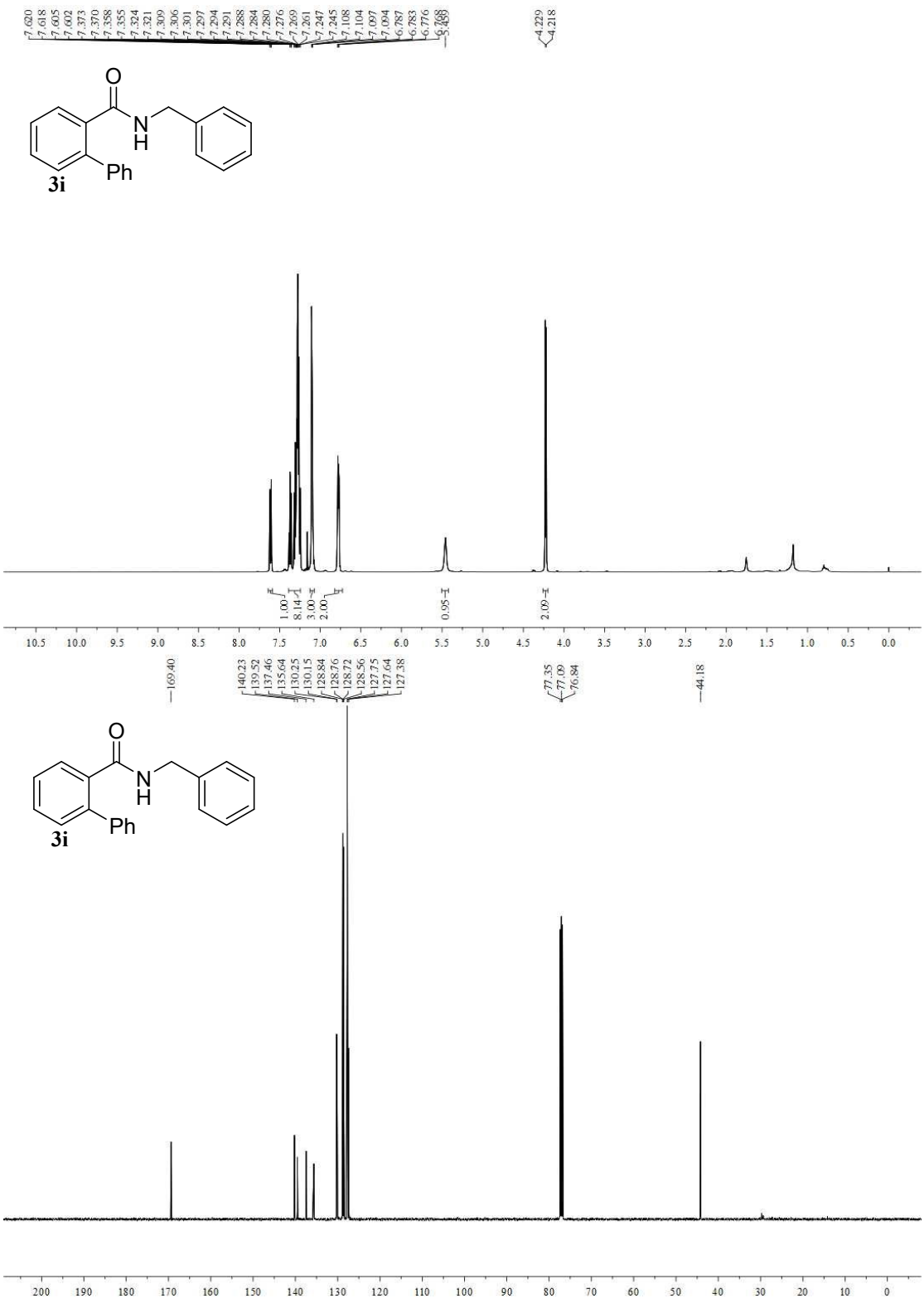
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3f



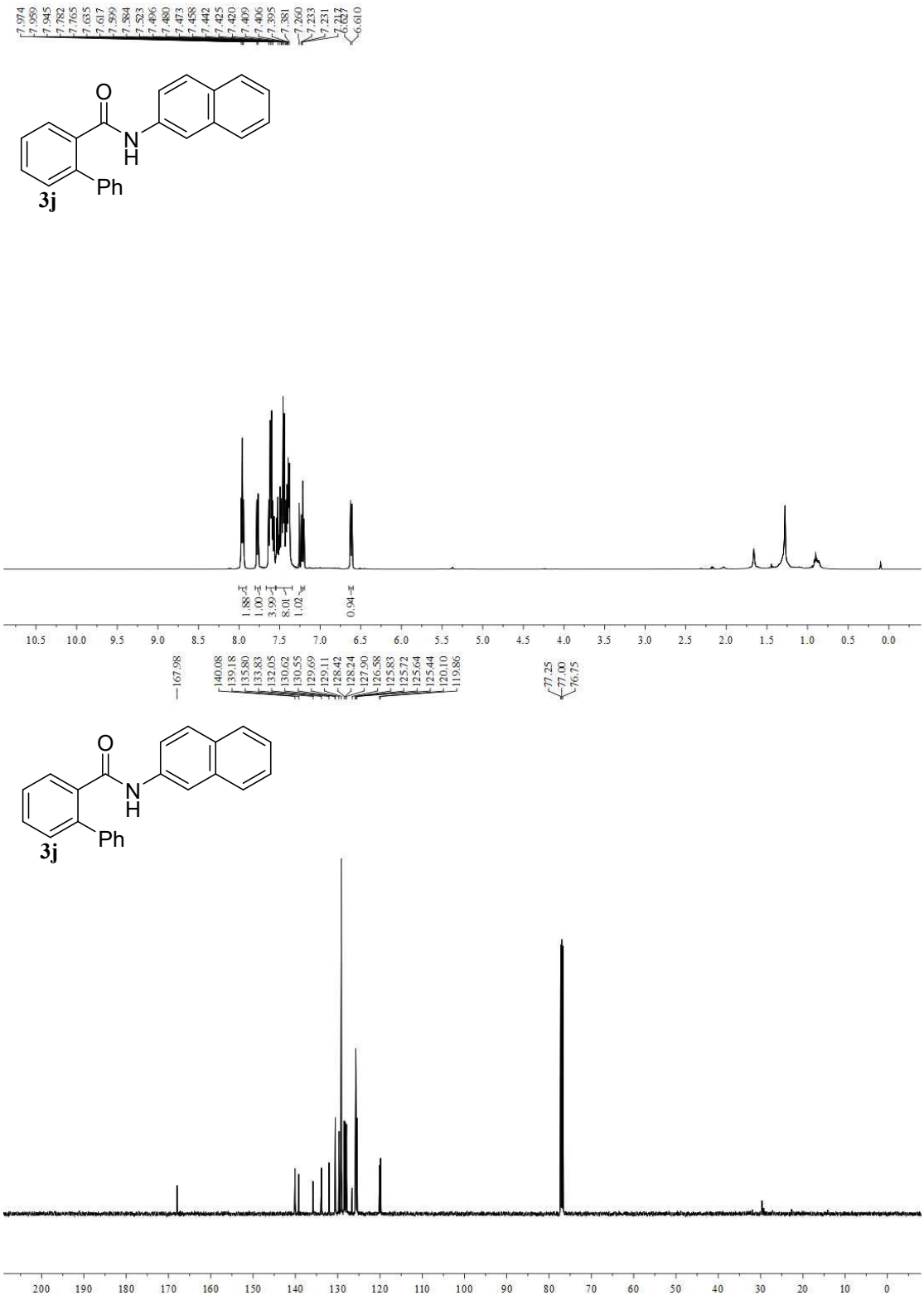
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3g



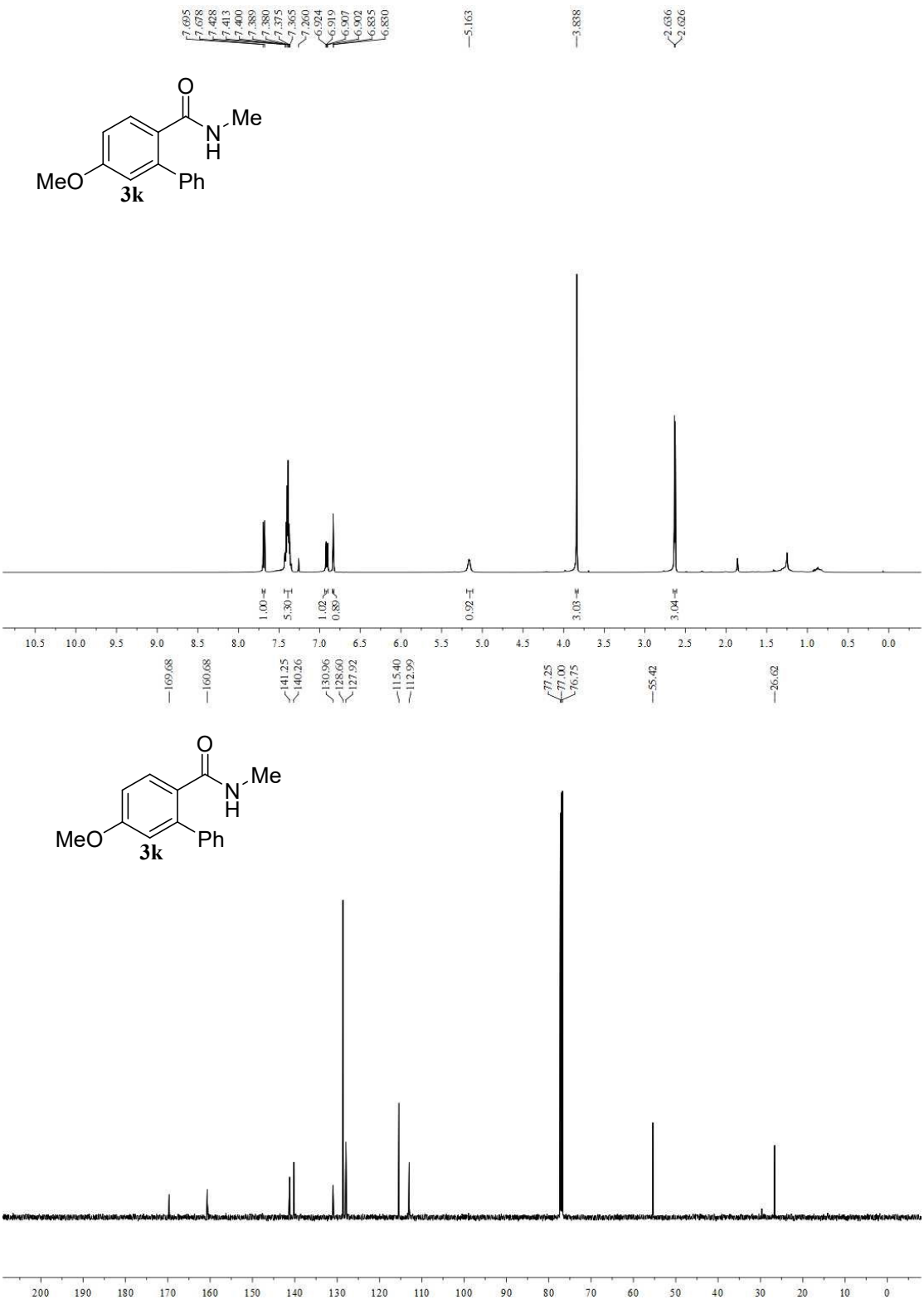
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3h



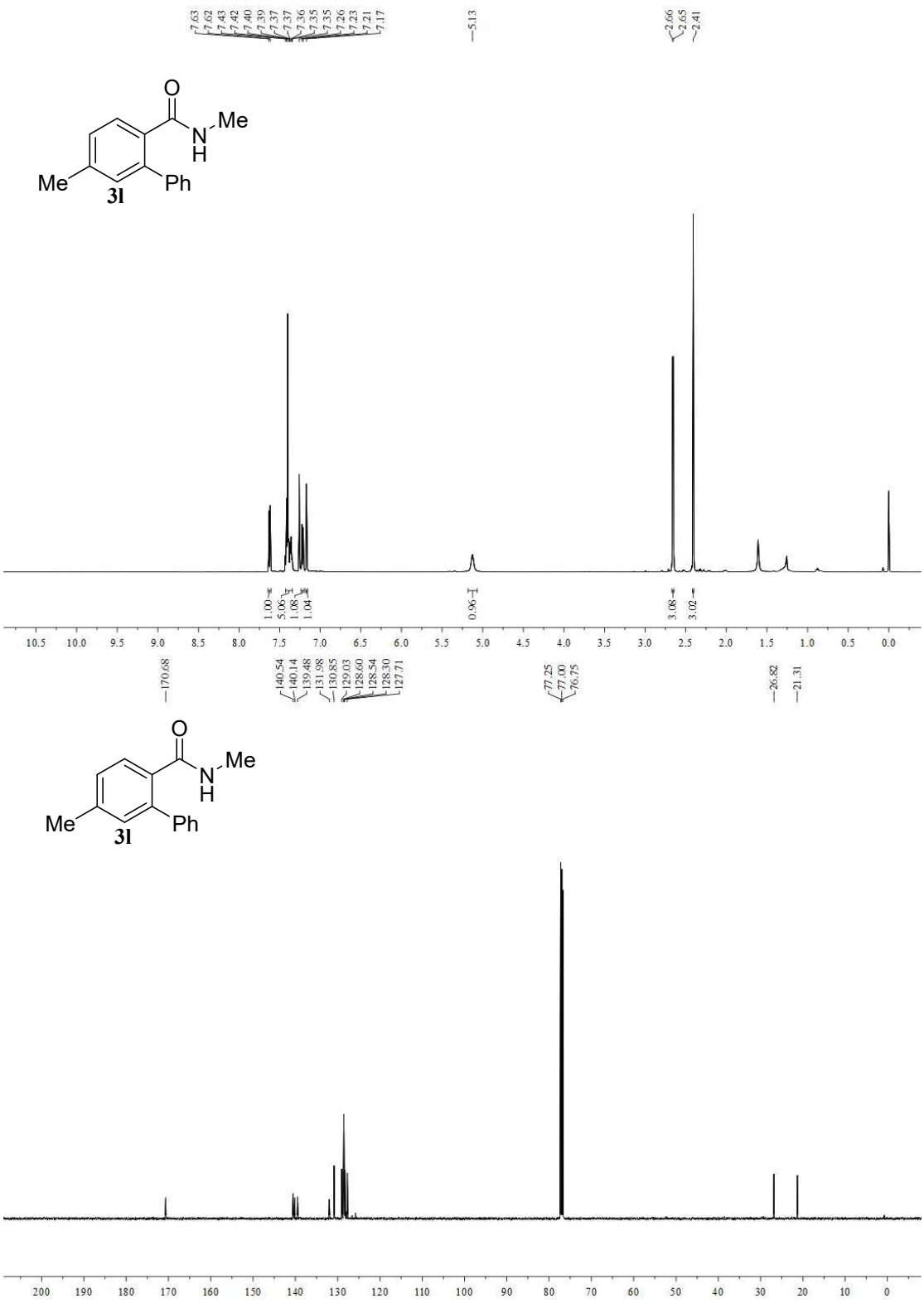
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3l



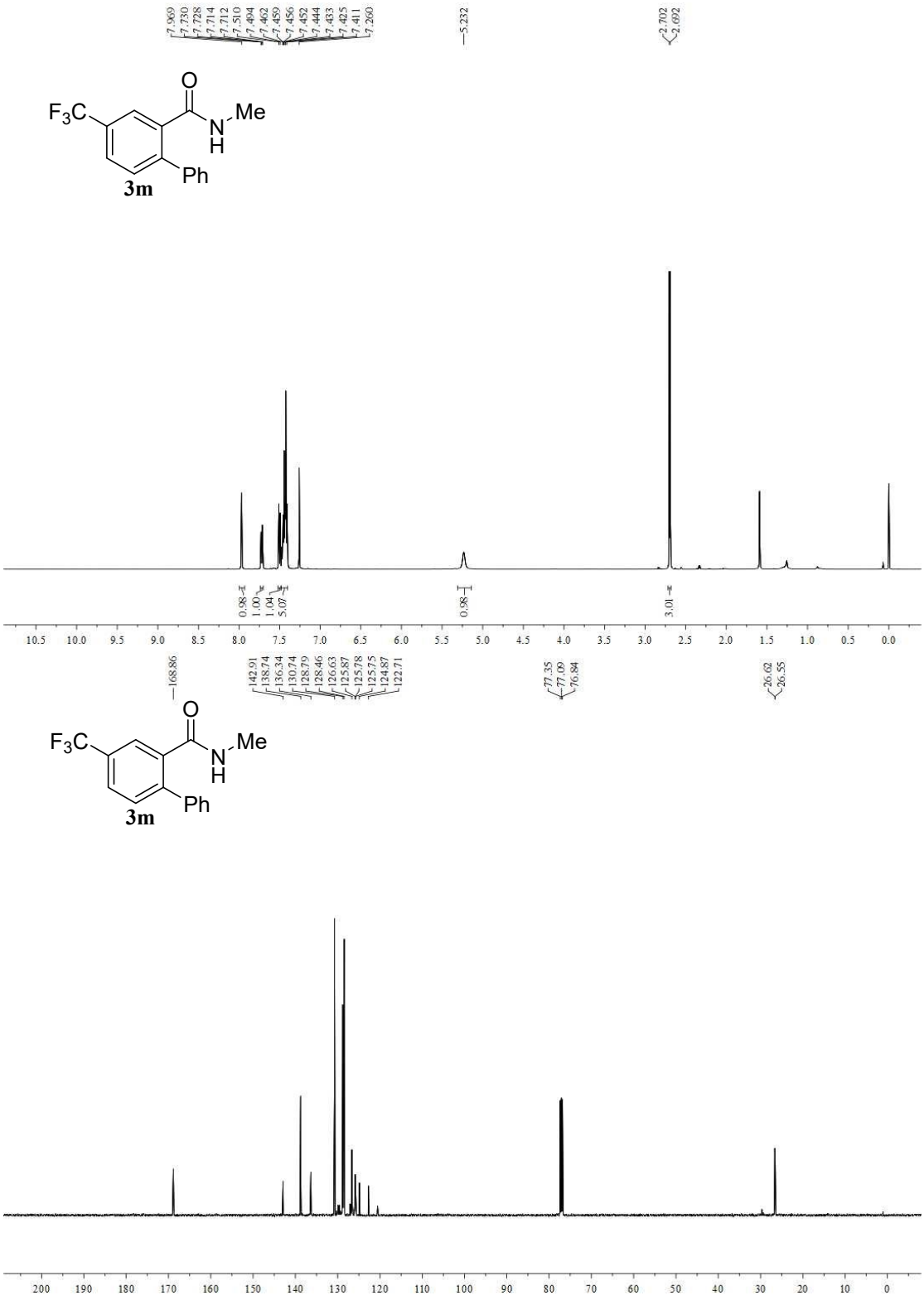
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3j



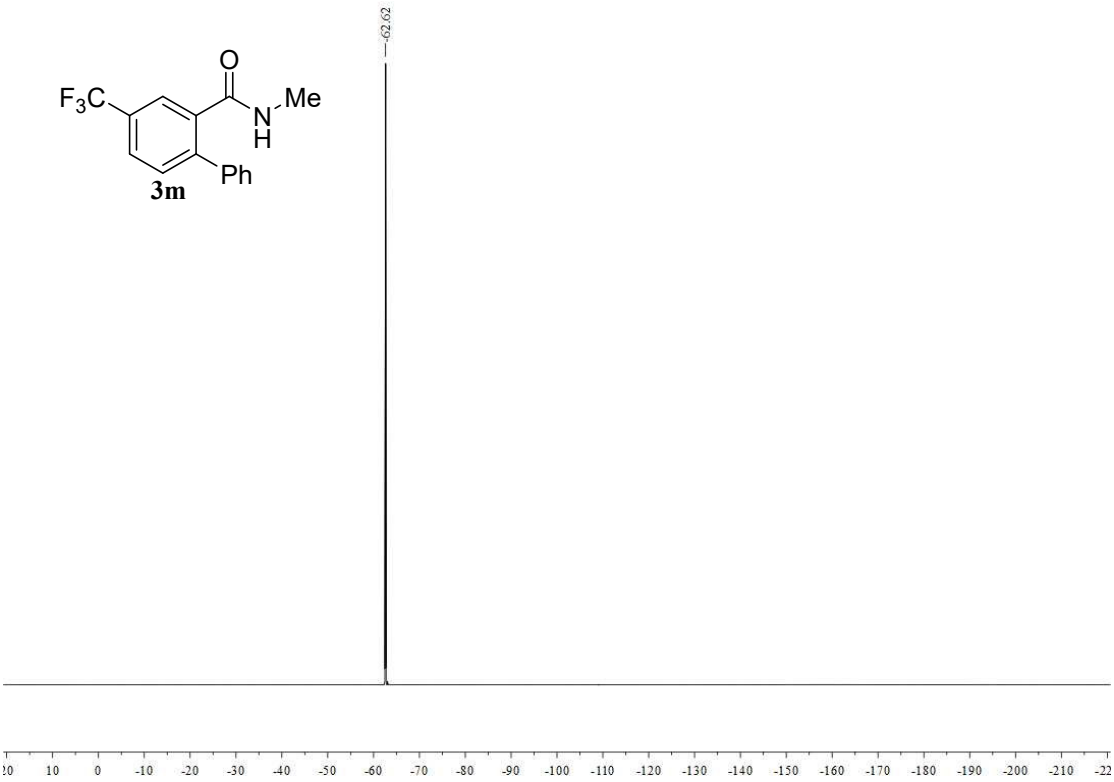
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3k



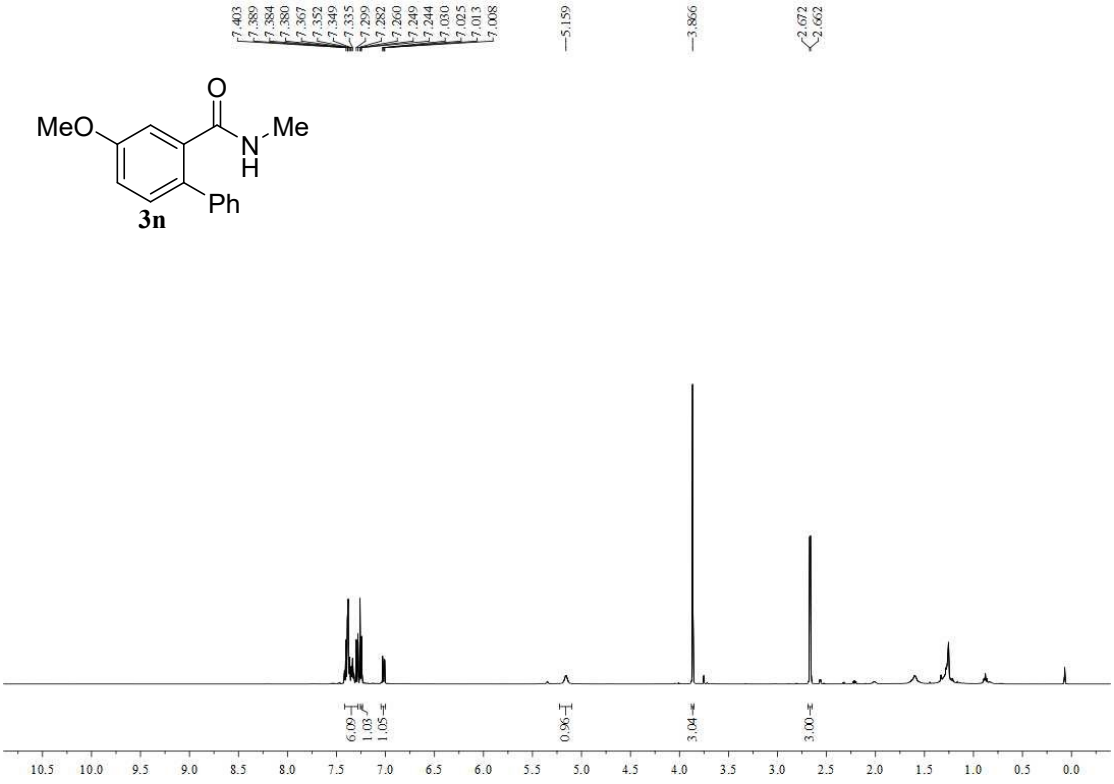
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3l

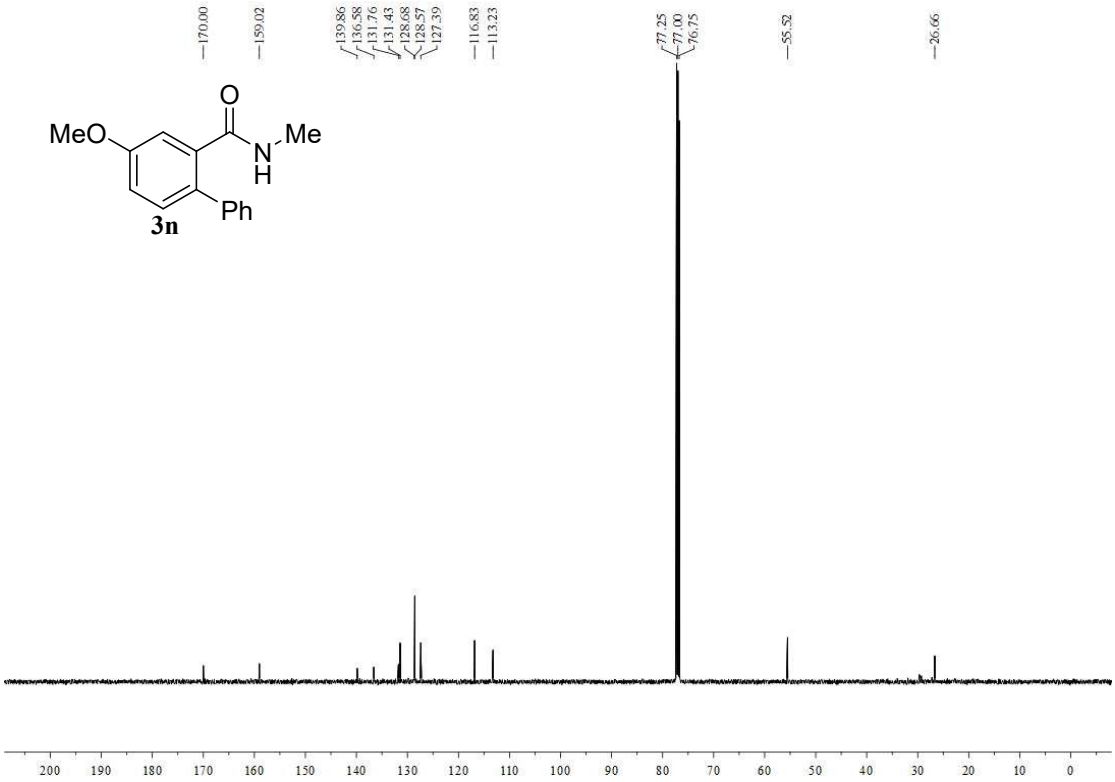


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3m

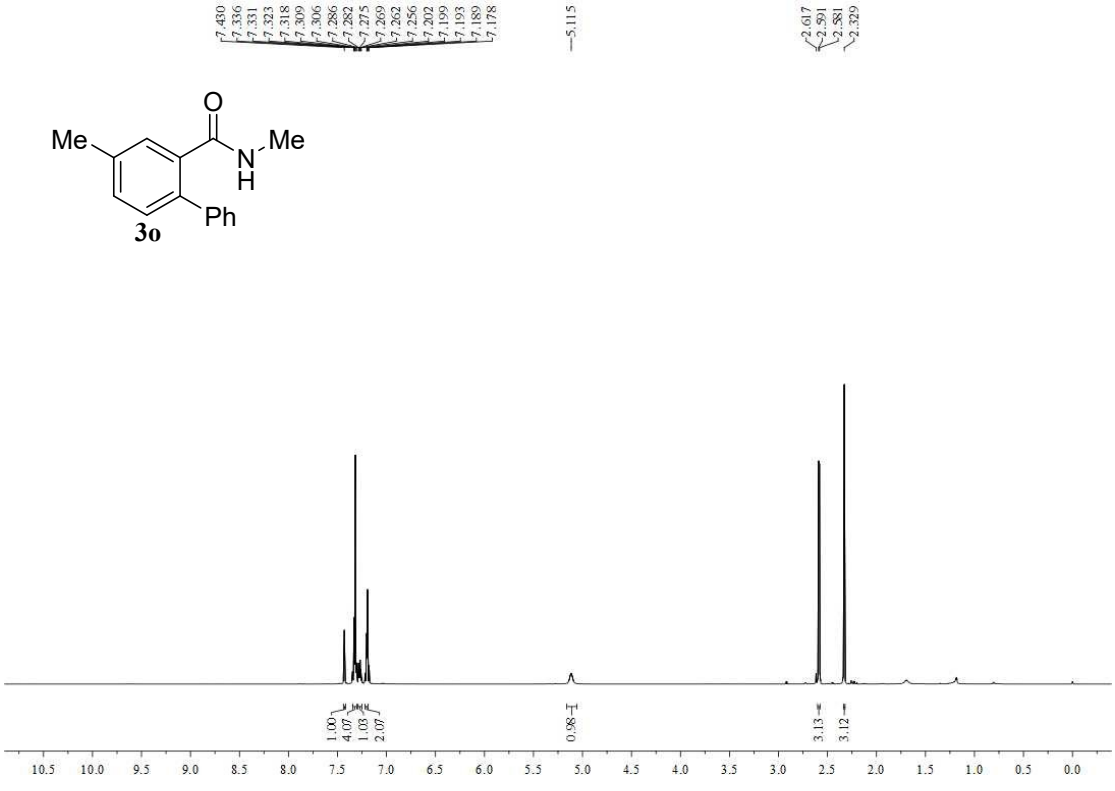


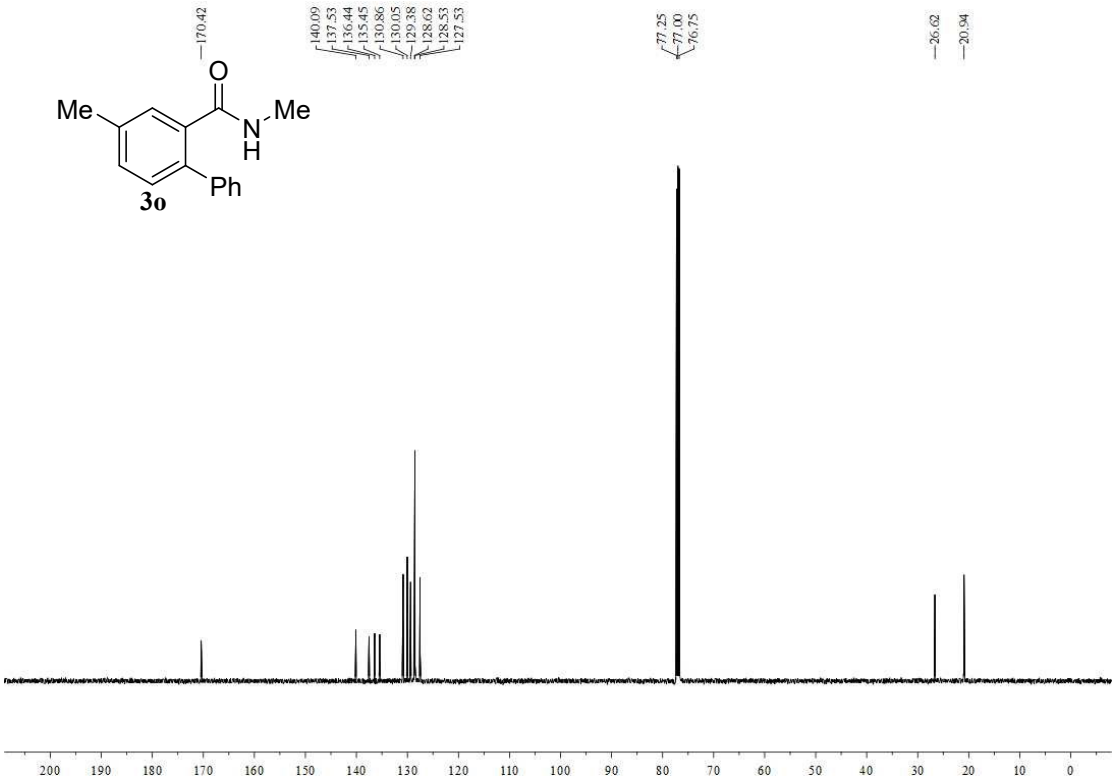
^{19}F NMR spectra in $CDCl_3$ for compound 3m



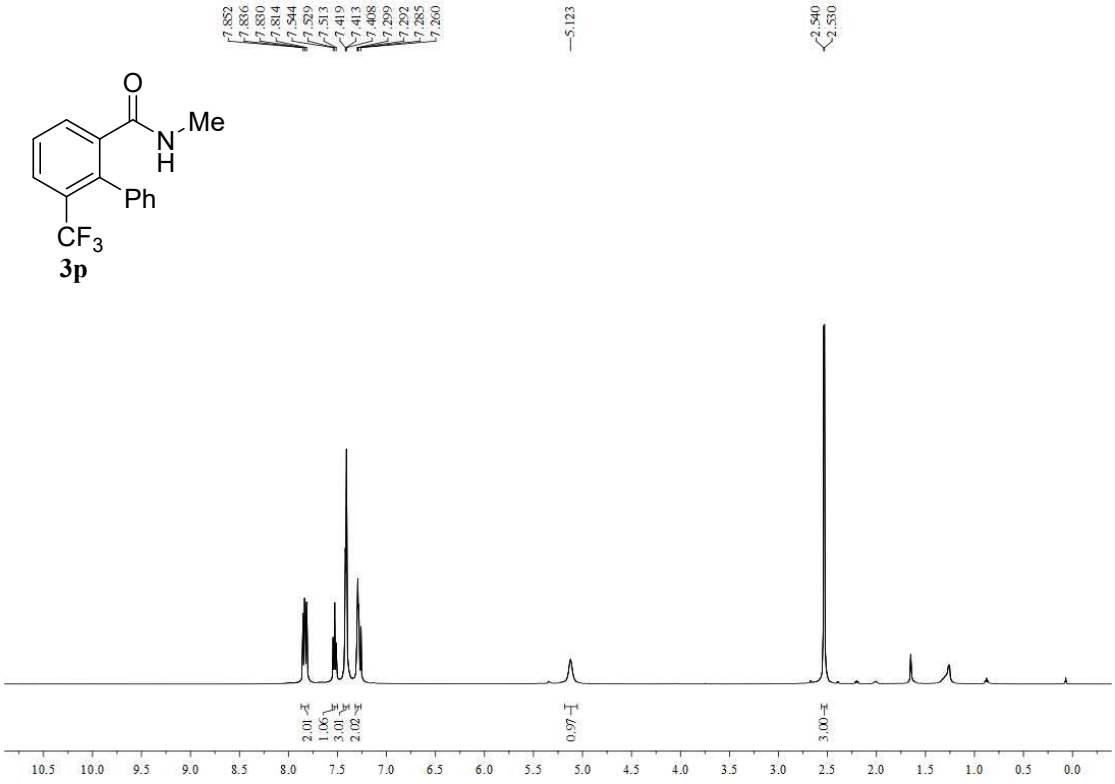


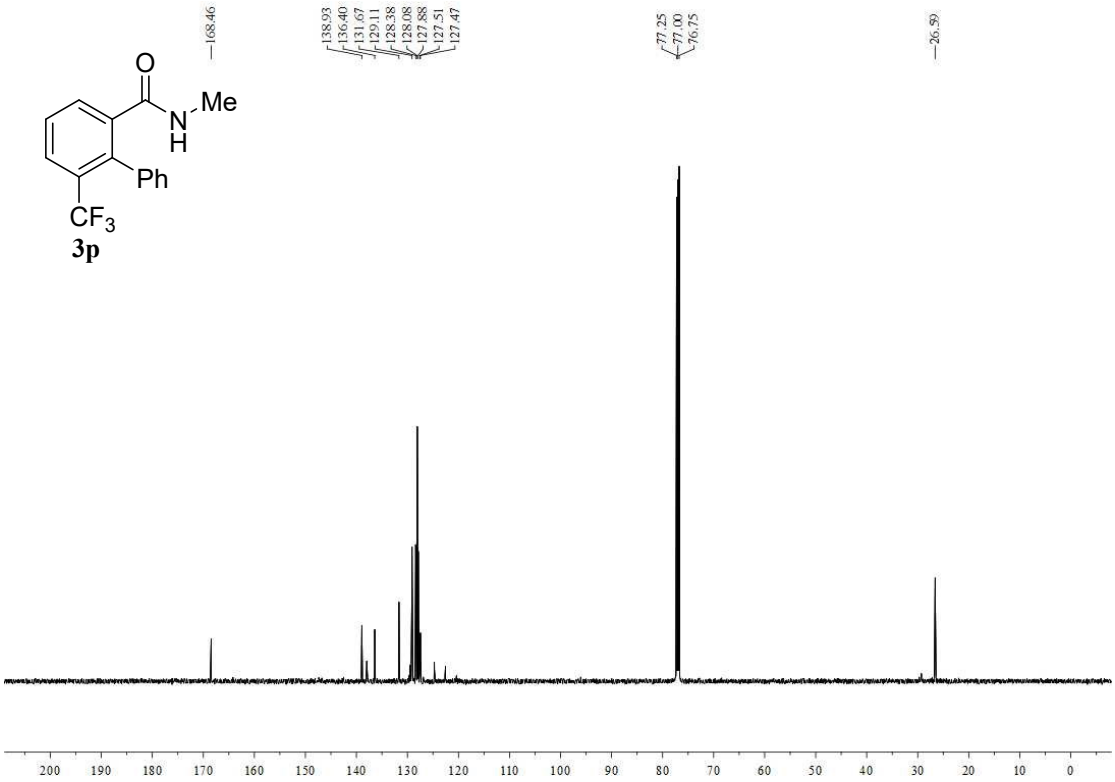
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3n



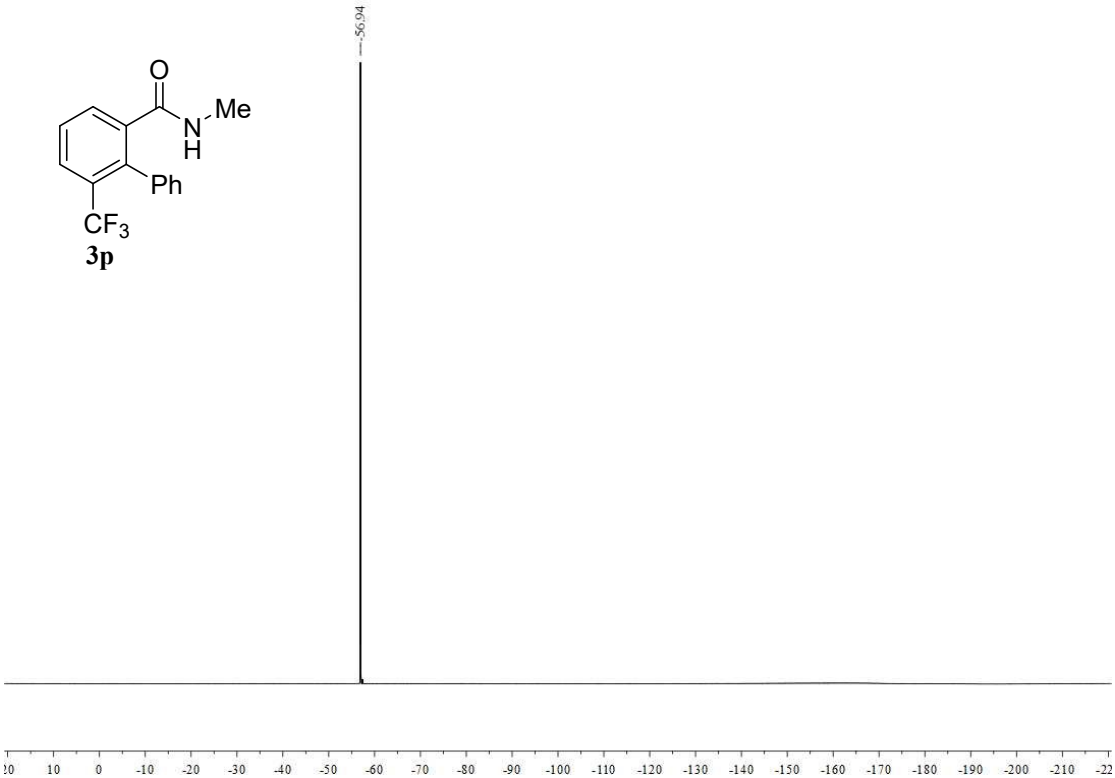


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3o

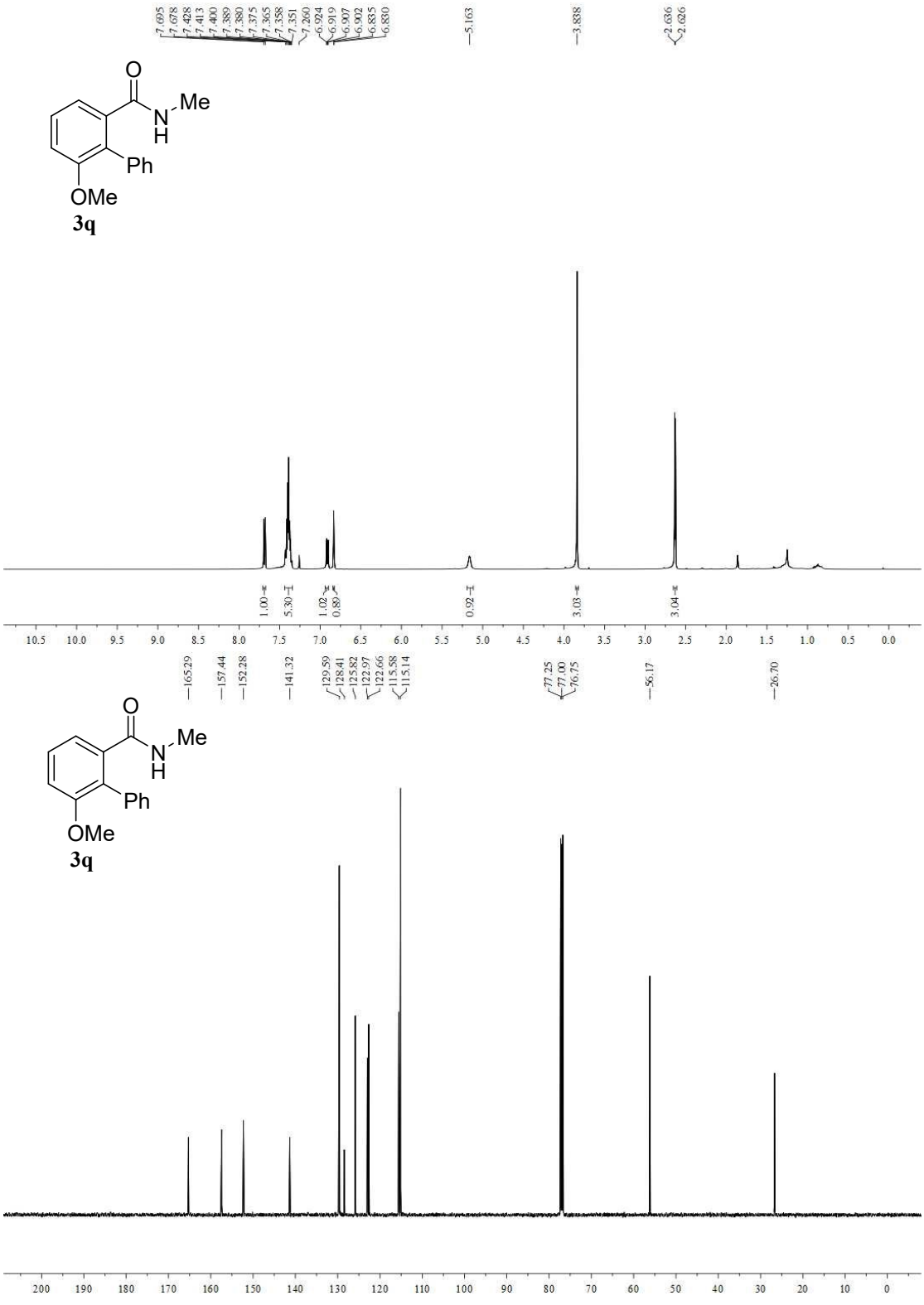




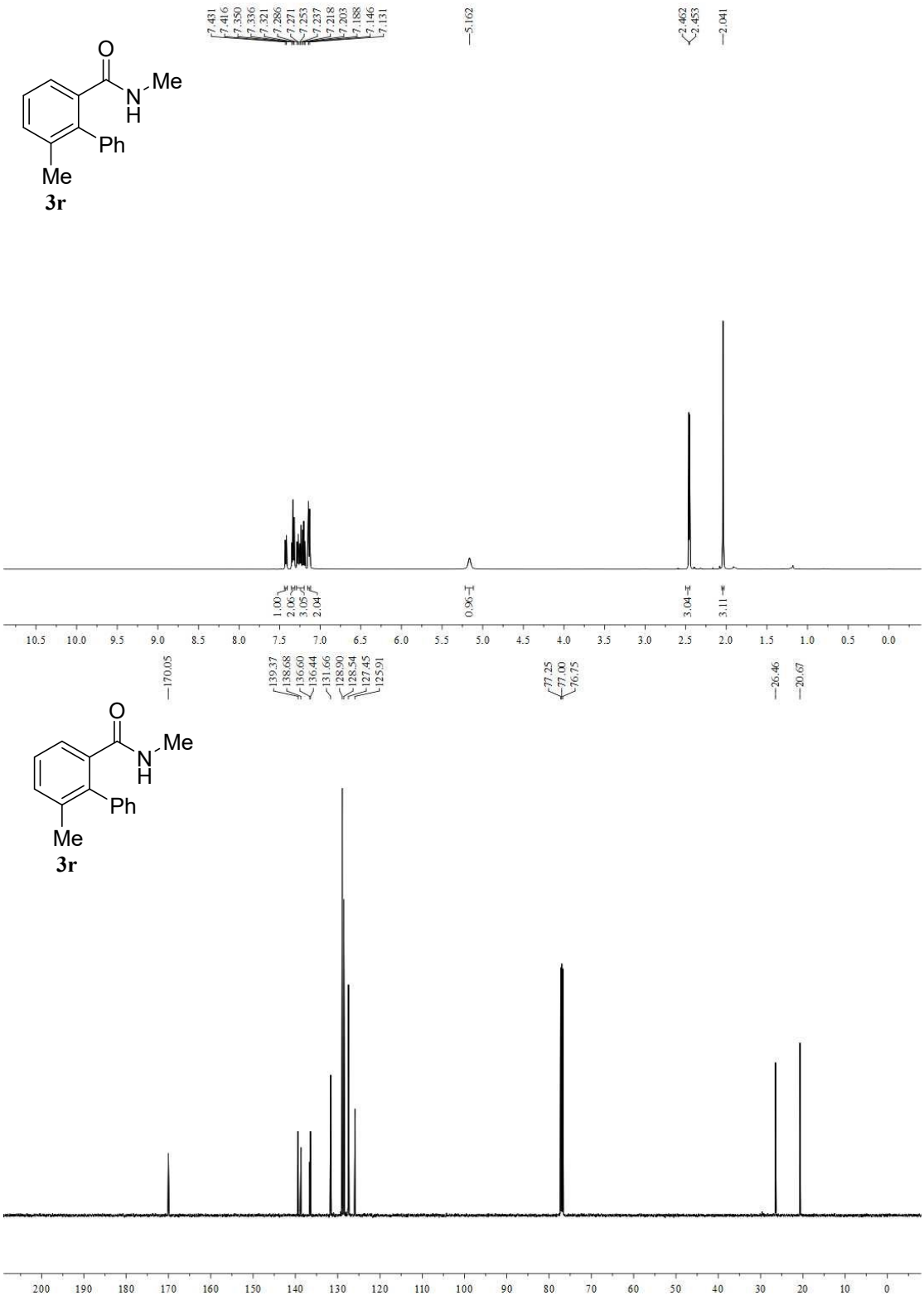
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3p



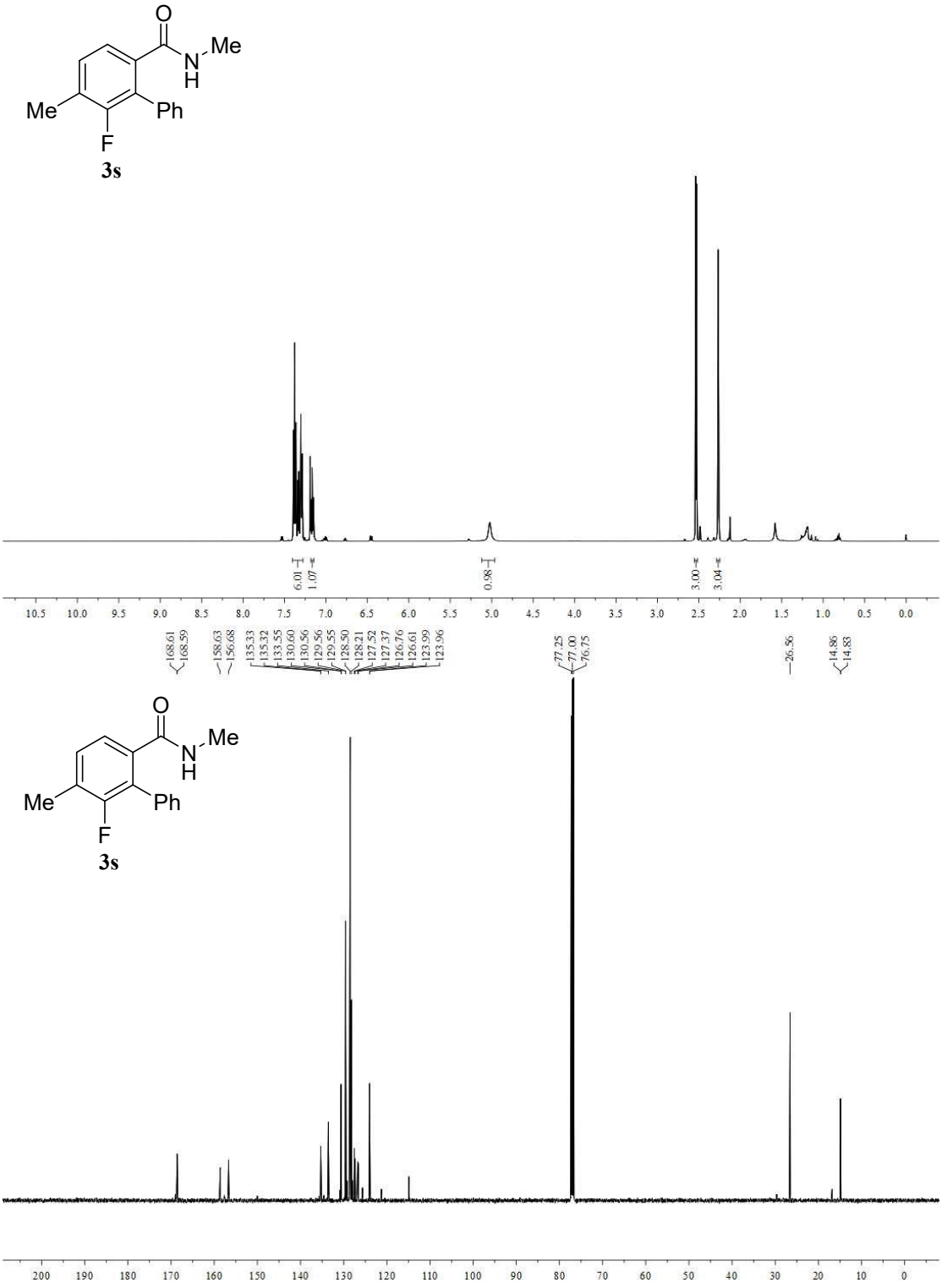
^{19}F NMR spectra in $CDCl_3$ for compound 3p



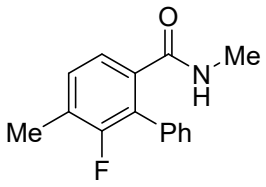
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3q



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3f

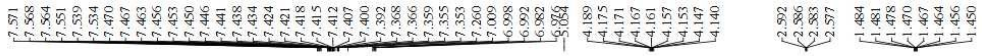


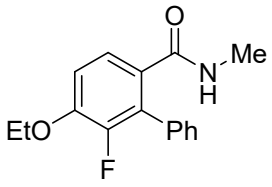
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3s



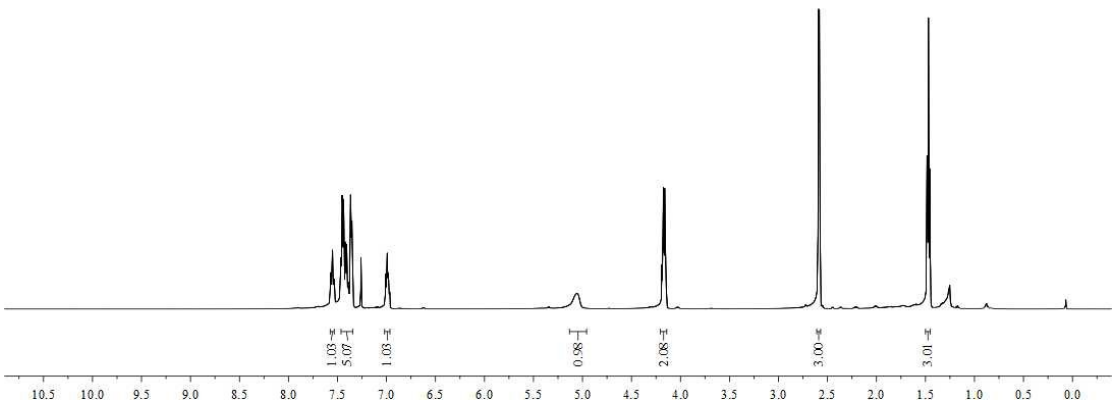
3s

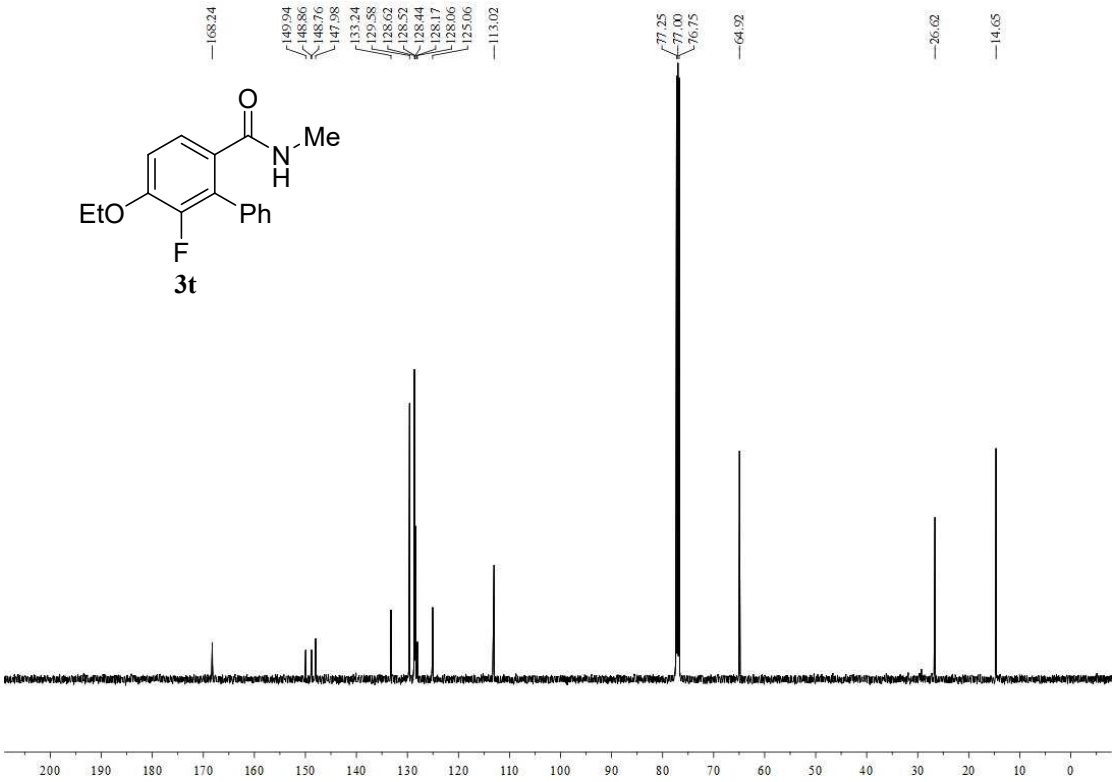
^{19}F NMR spectra in $CDCl_3$ for compound 3s



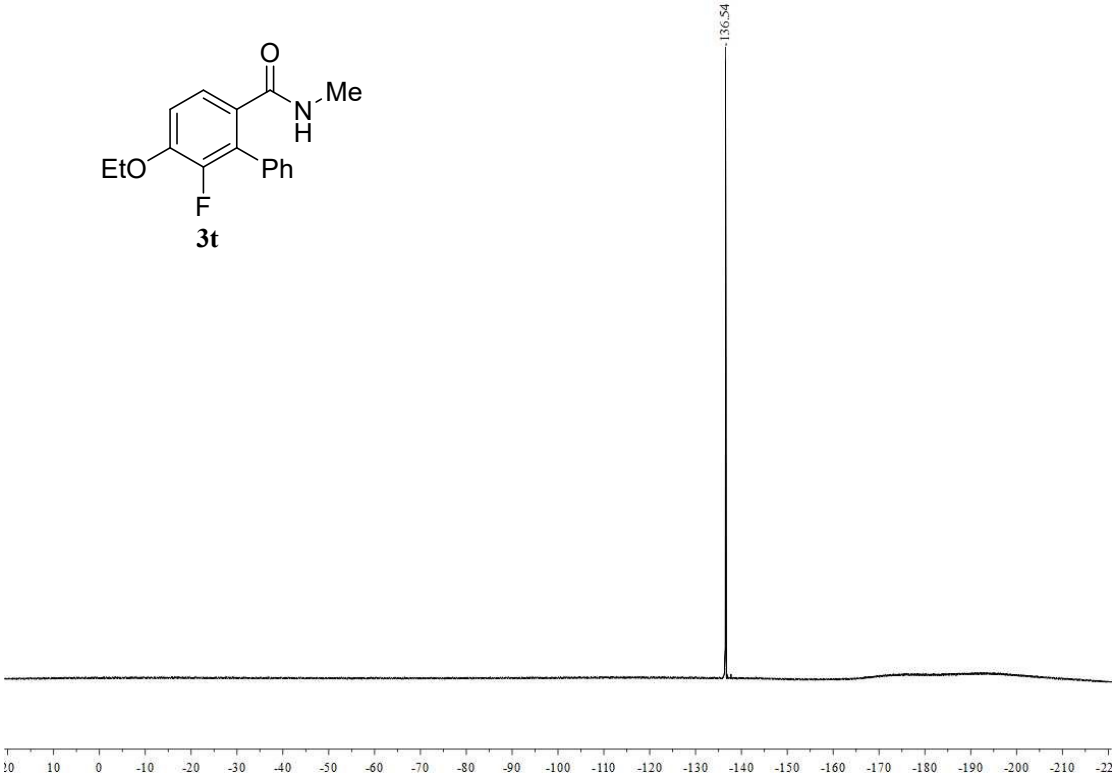


3t

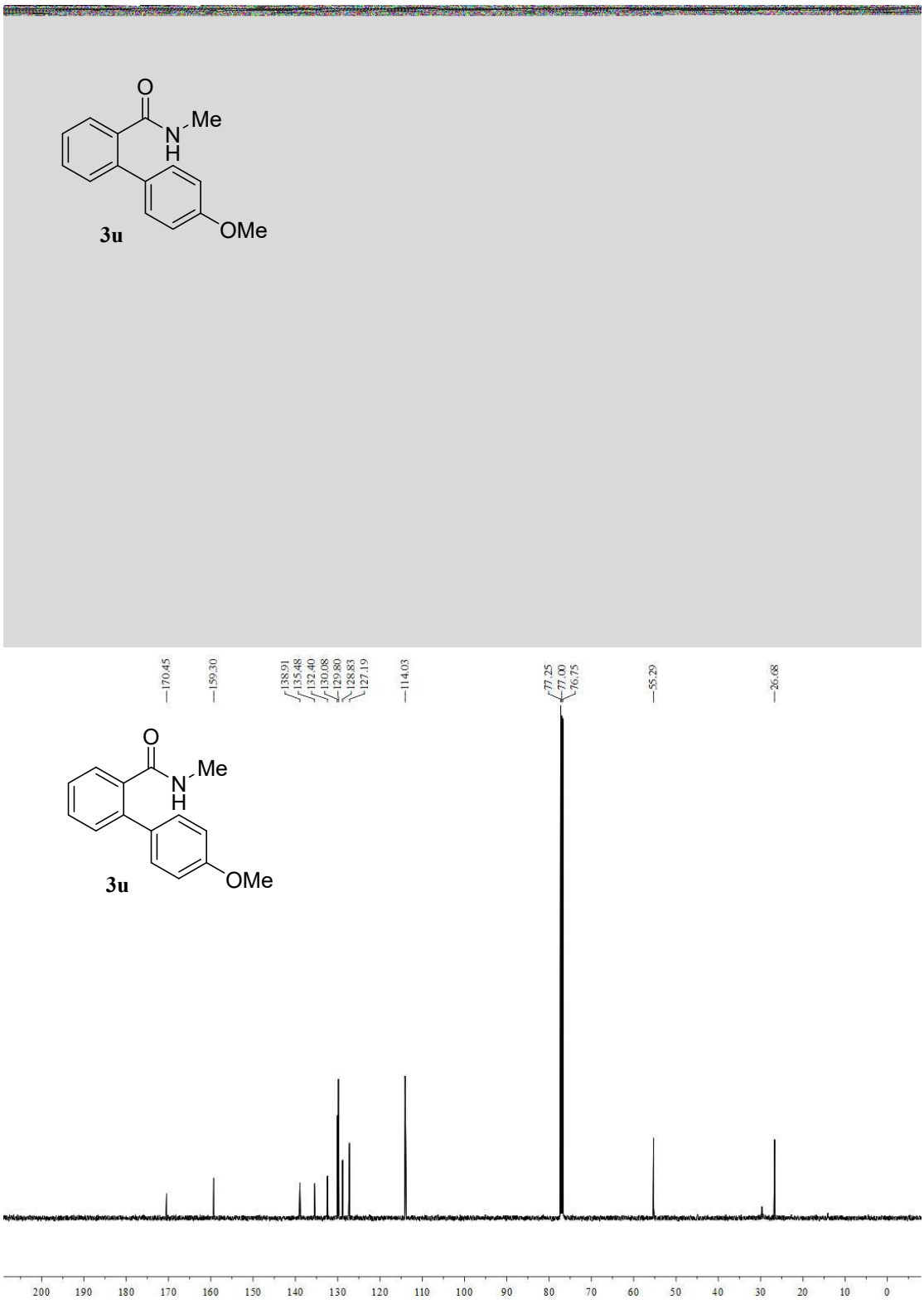




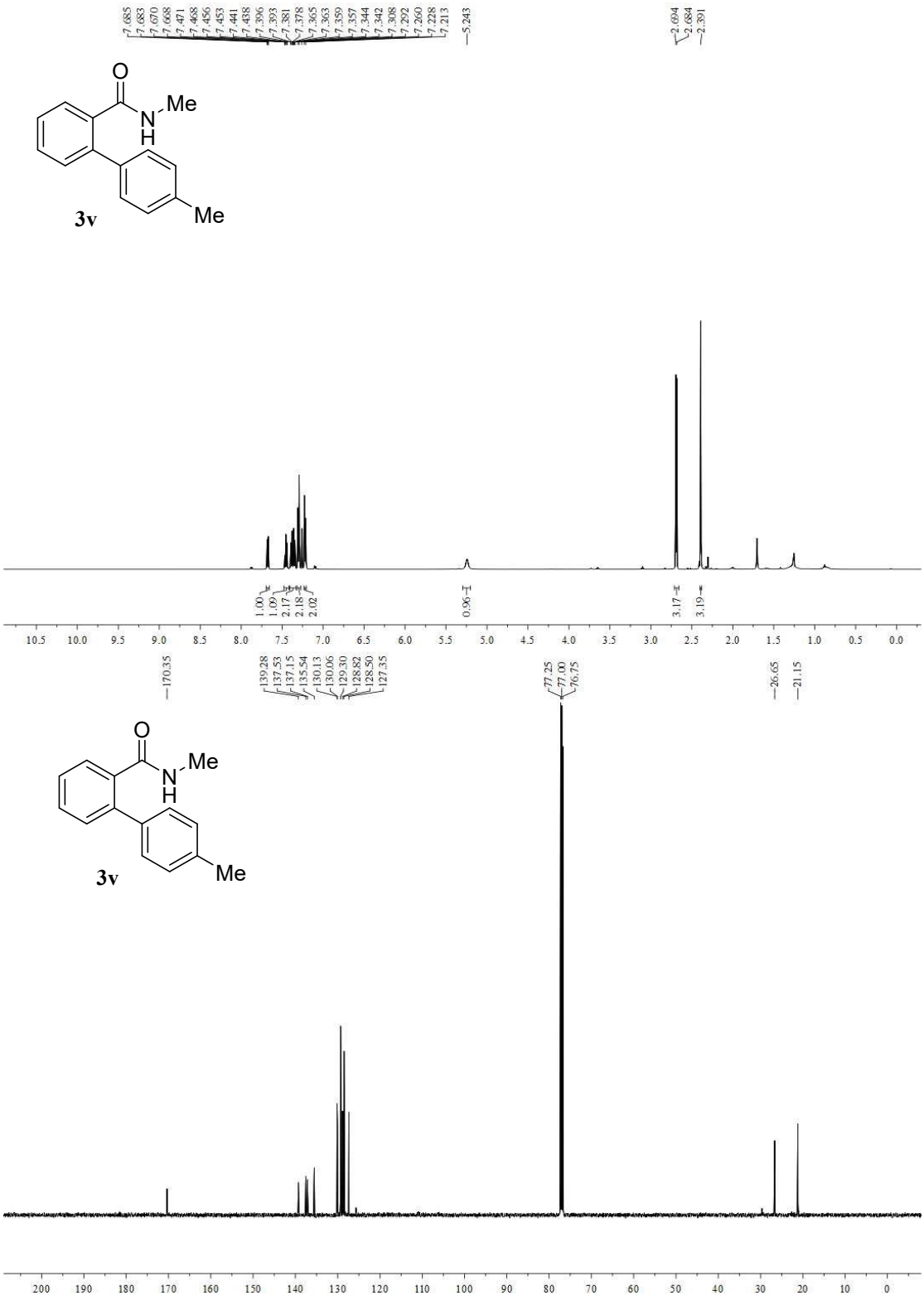
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3t



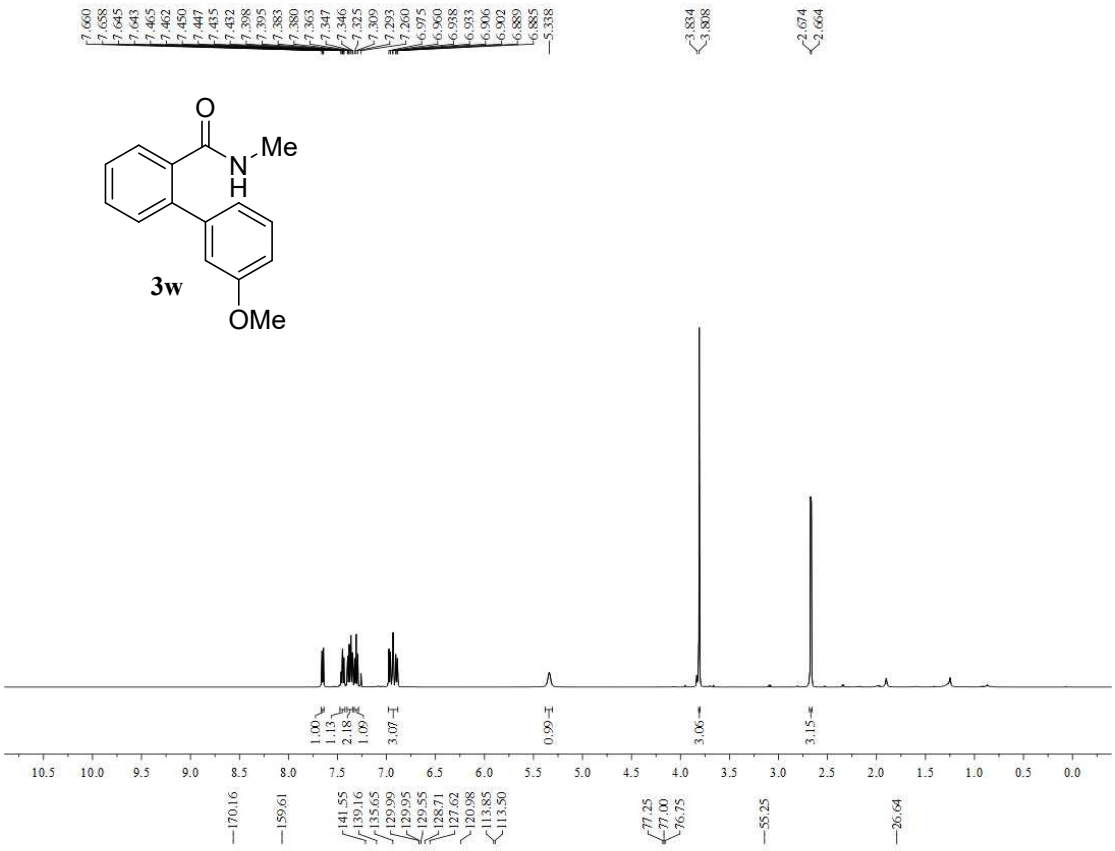
^{19}F NMR spectra in $CDCl_3$ for compound 3t

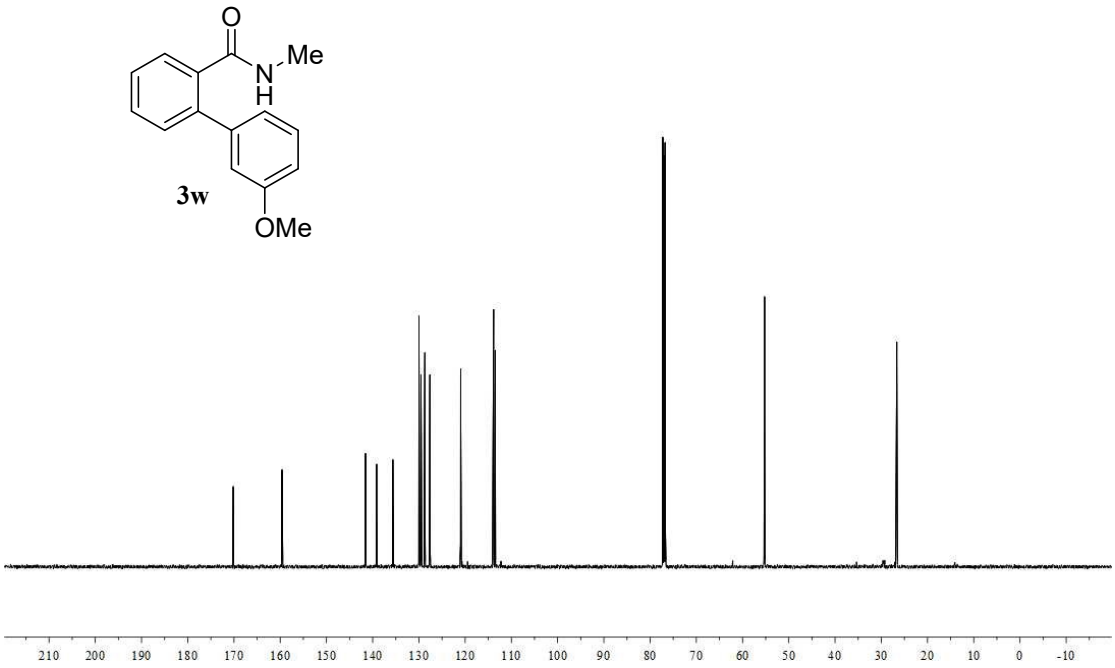


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3u

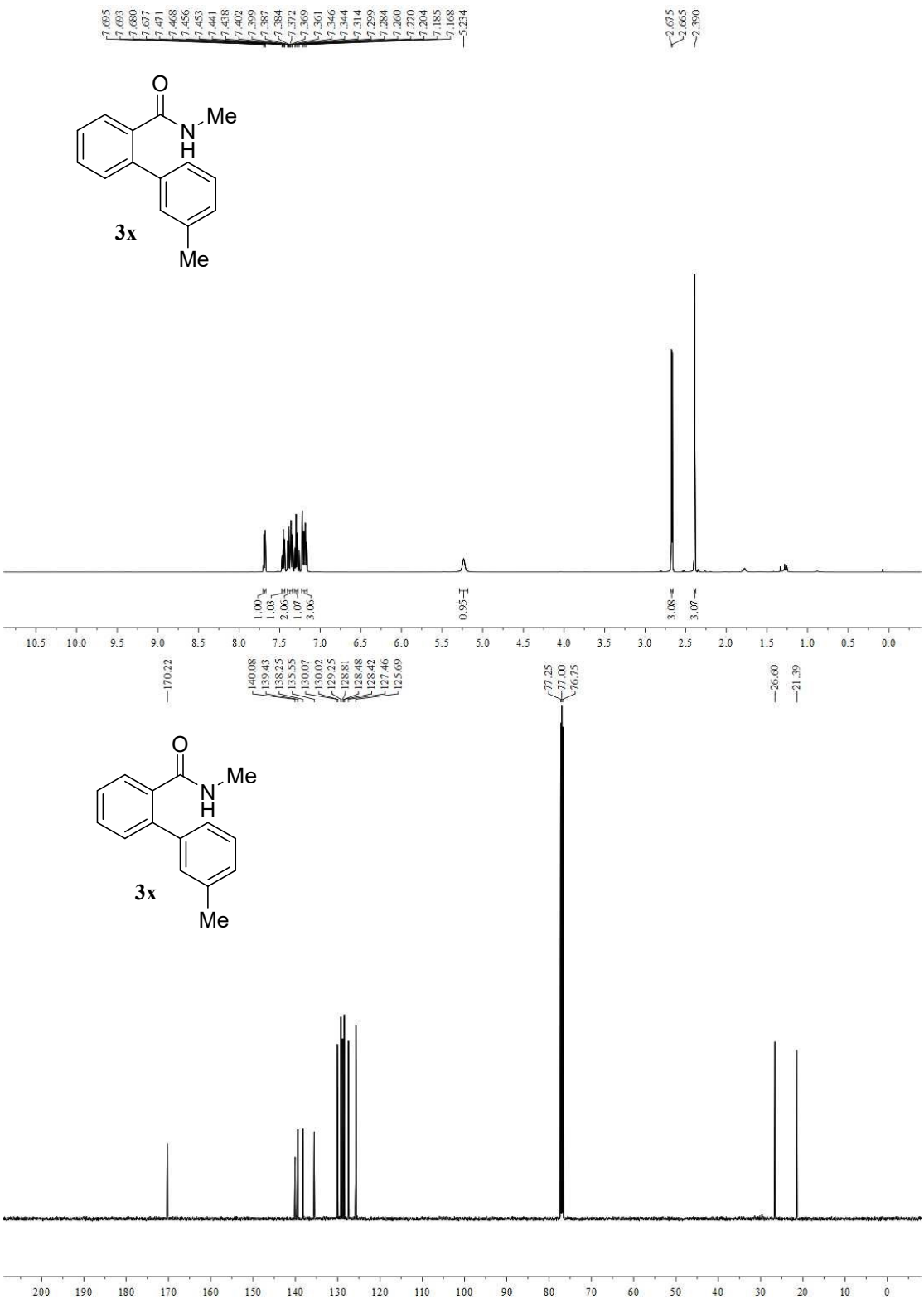


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3v

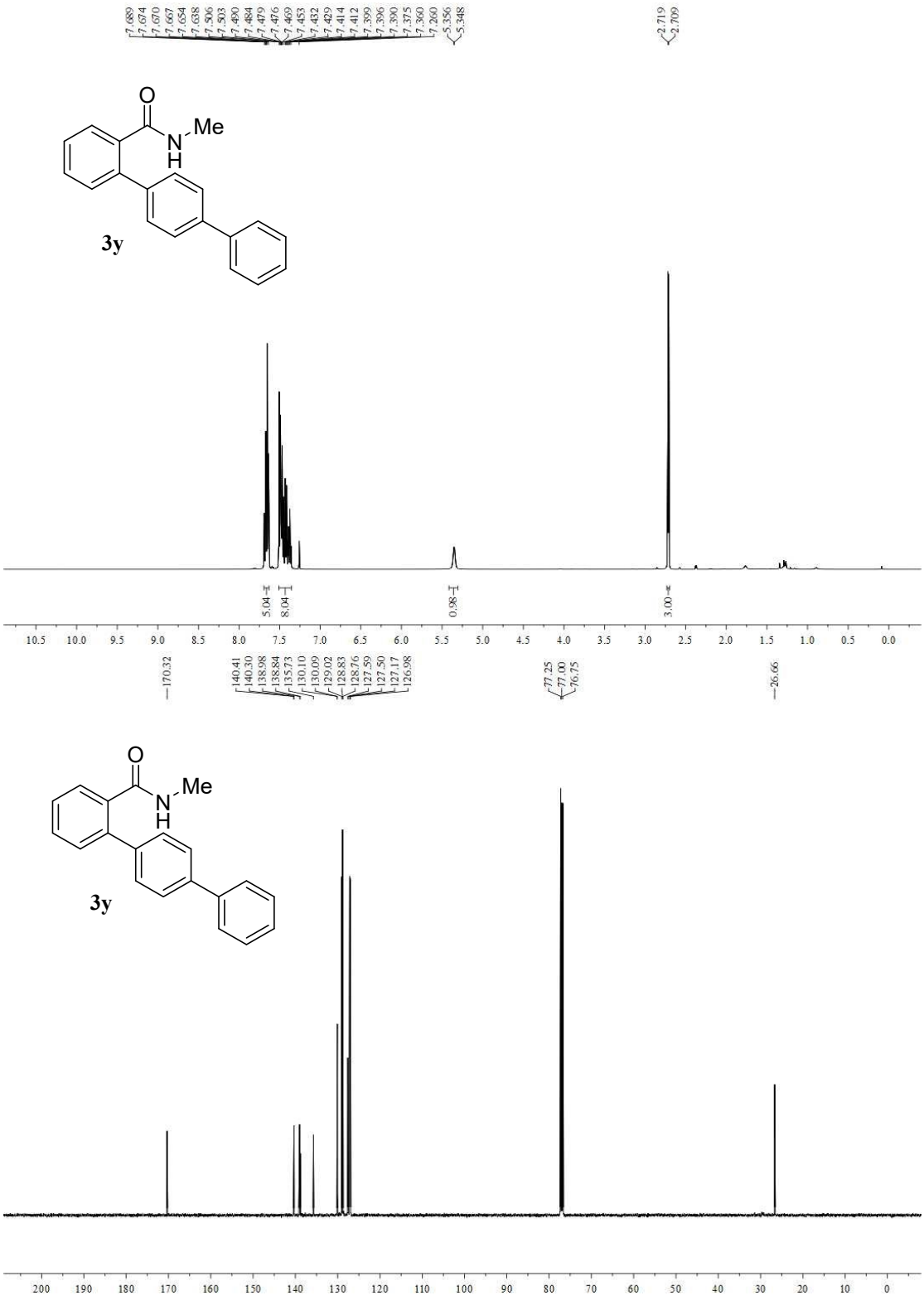




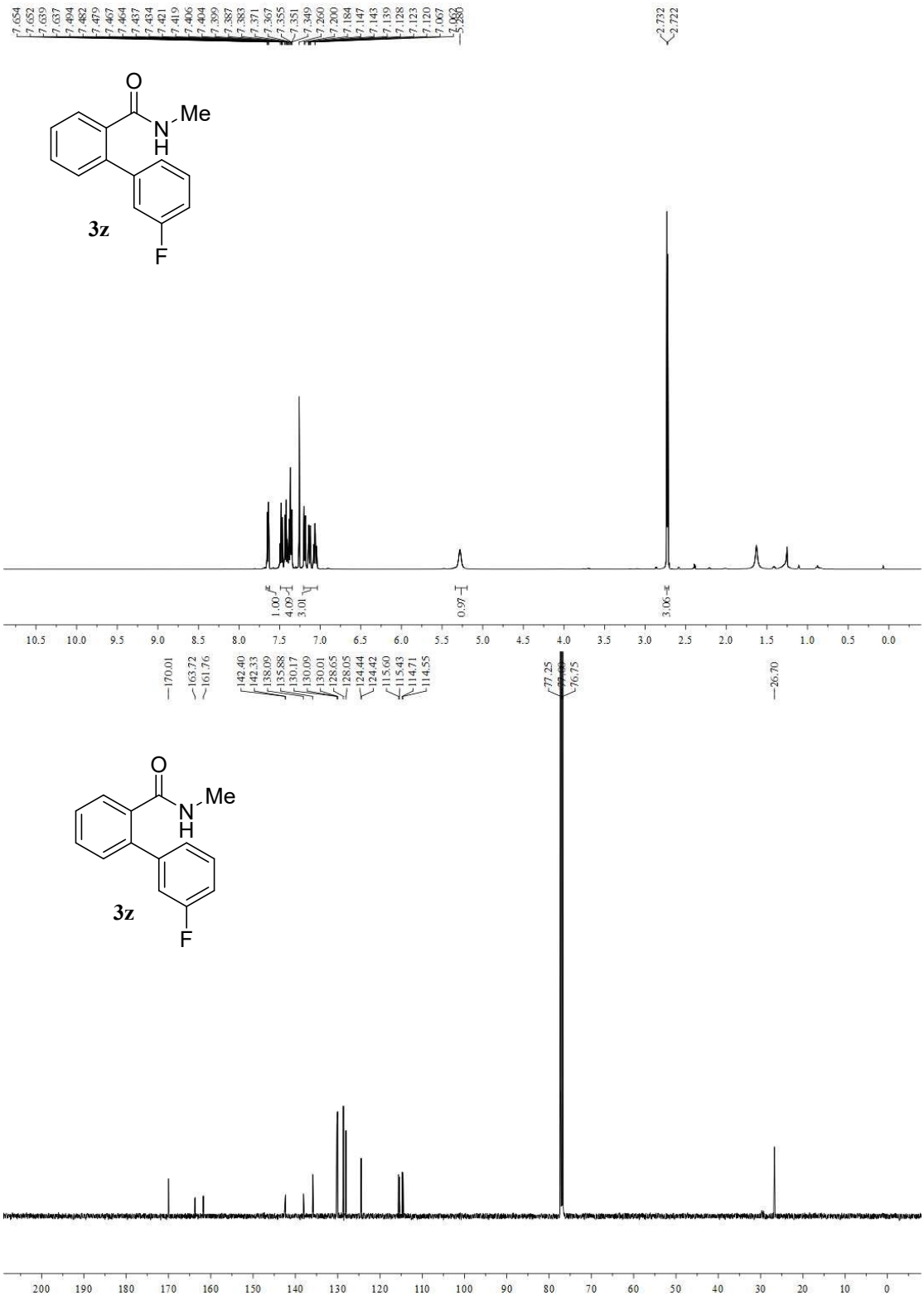
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3w



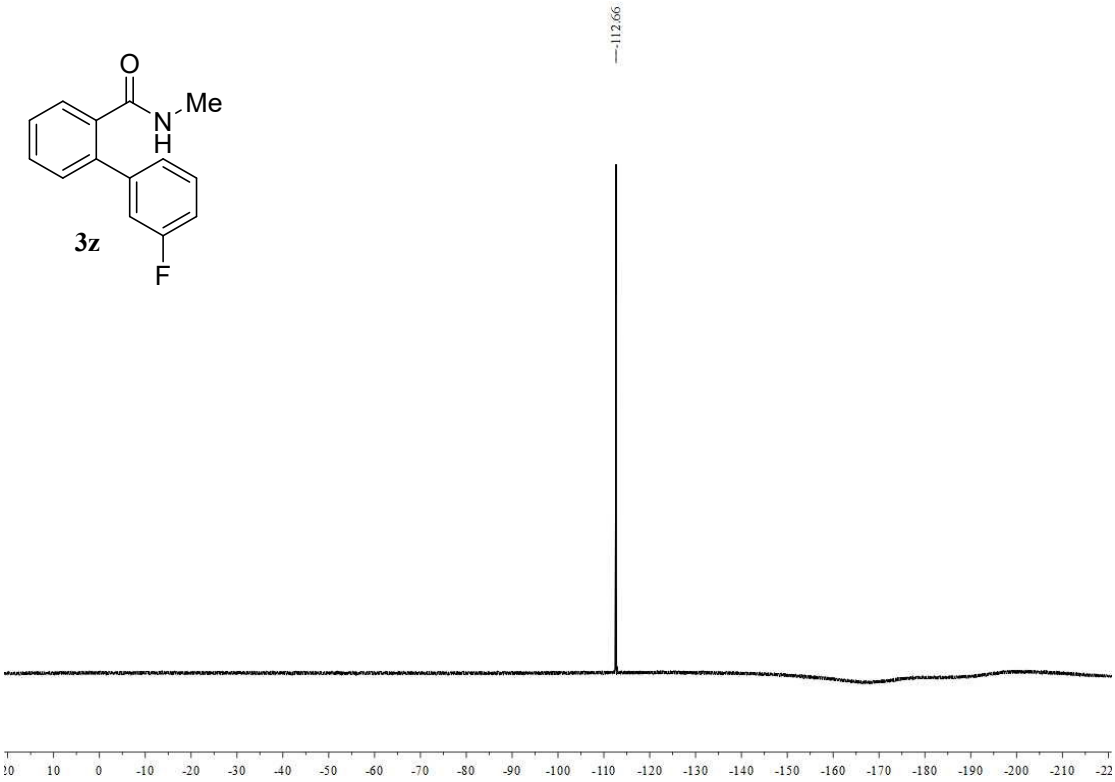
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3x



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3y

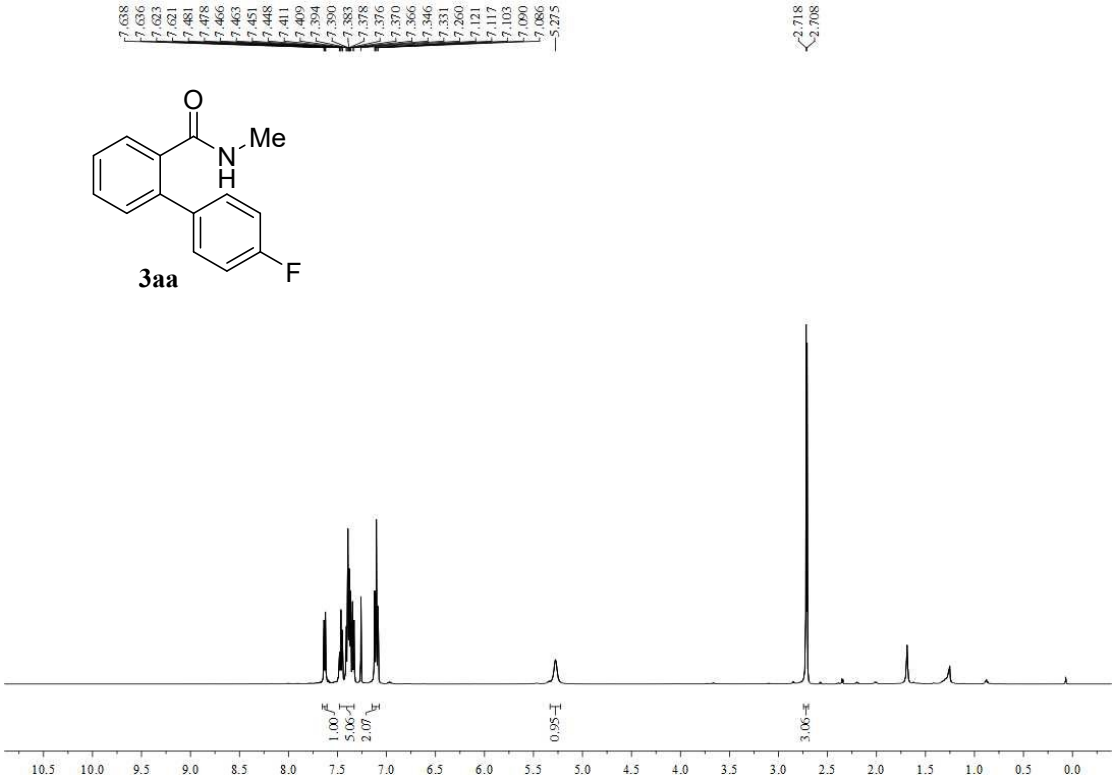


^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3z

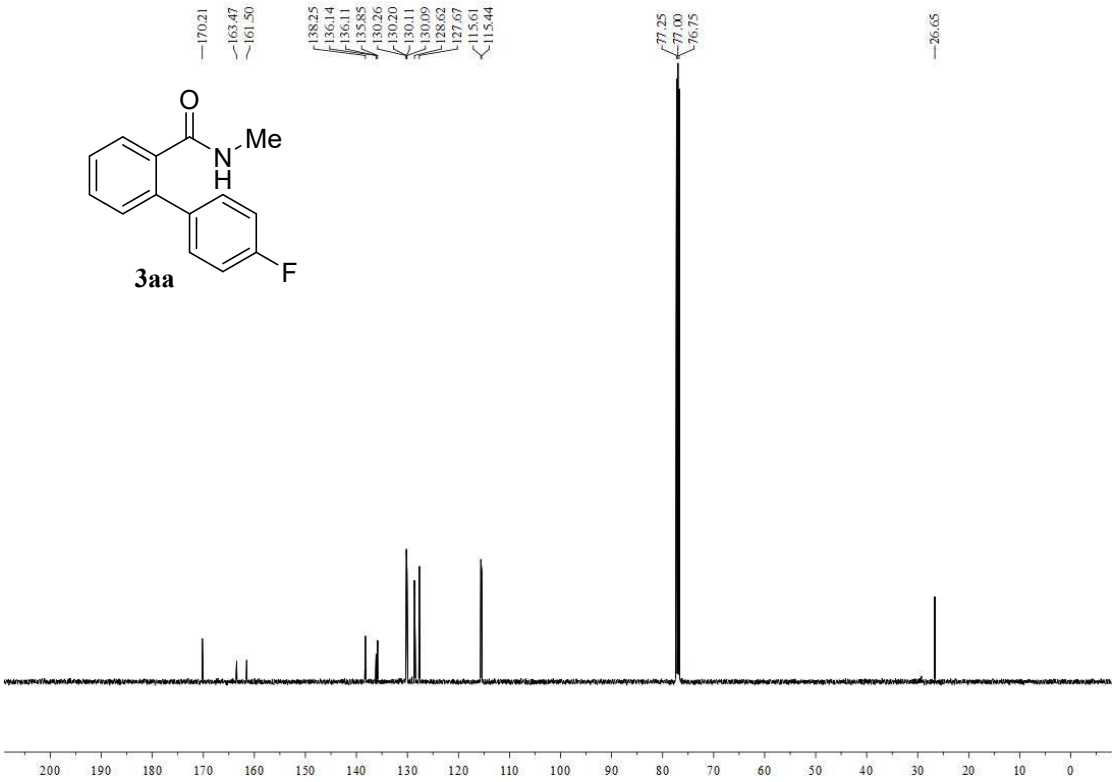


3z

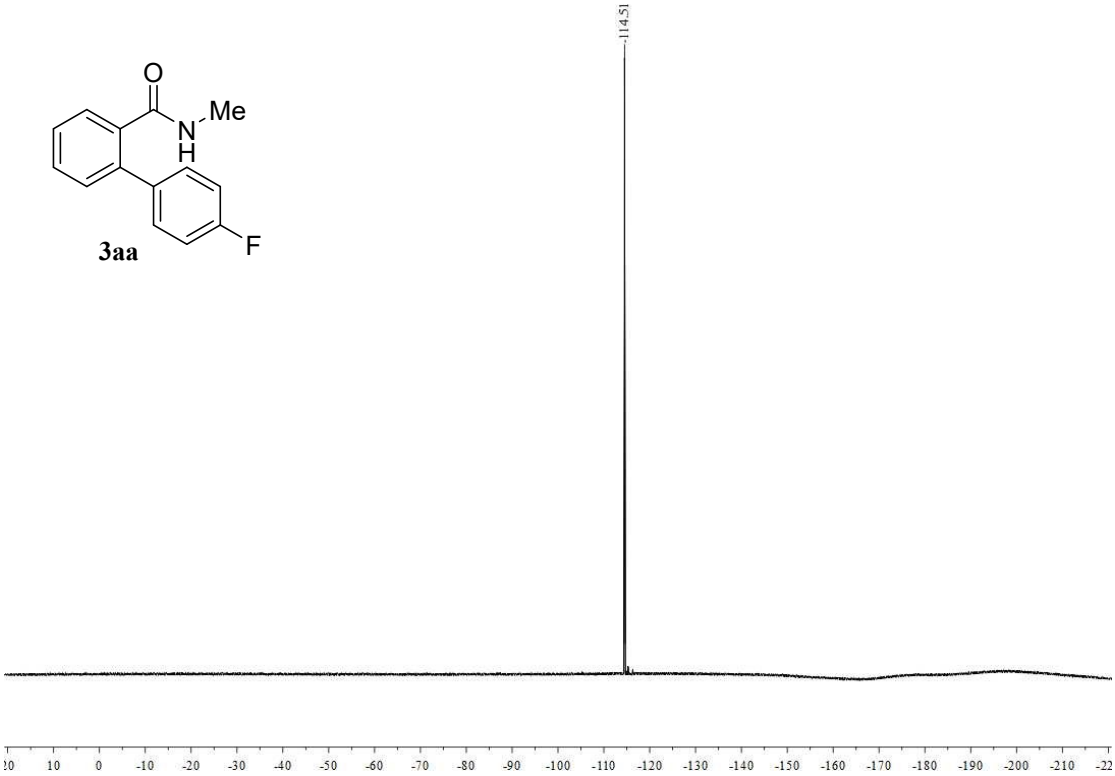
^{19}F NMR spectra in $CDCl_3$ for compound 3z



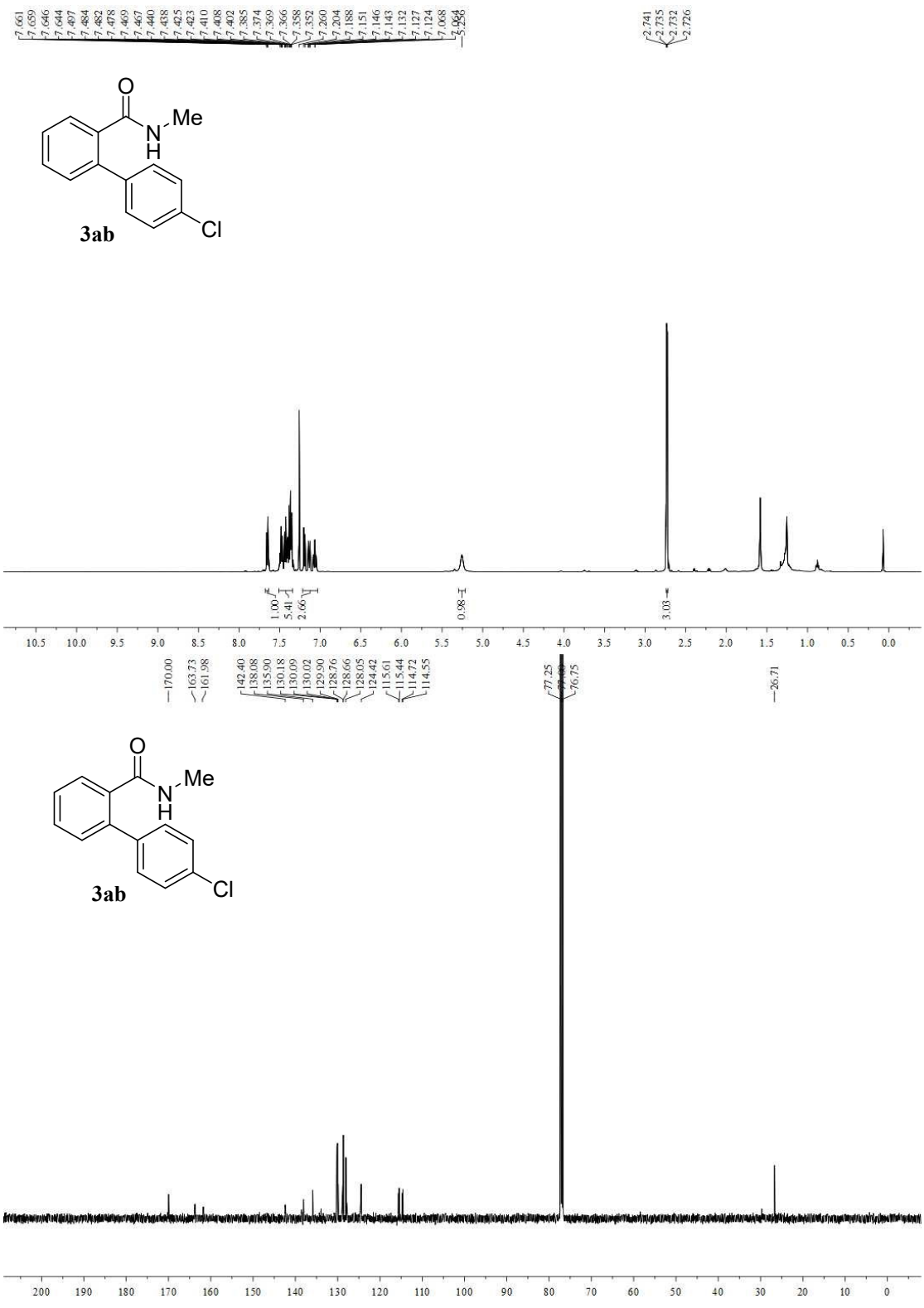
3aa



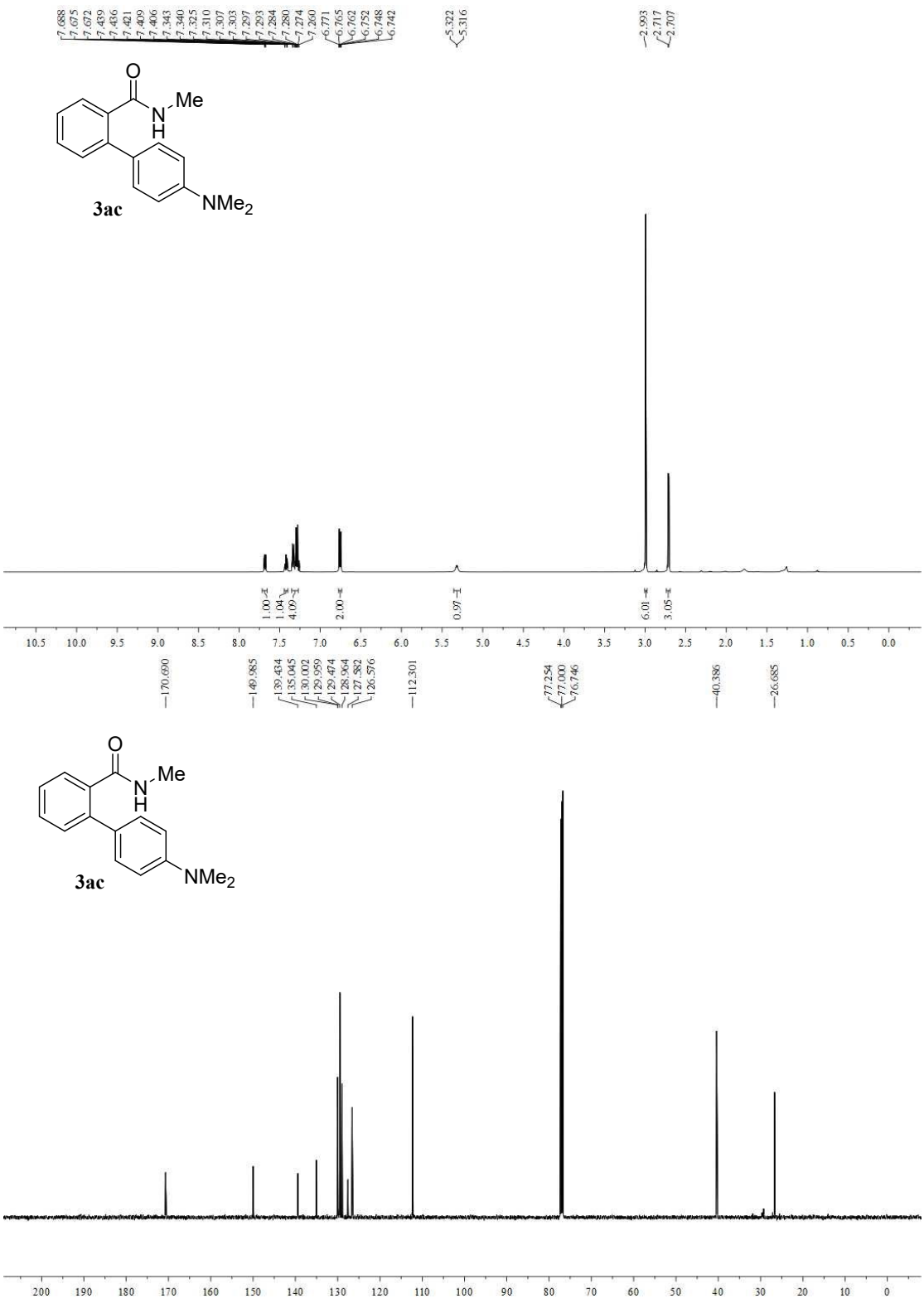
^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3aa



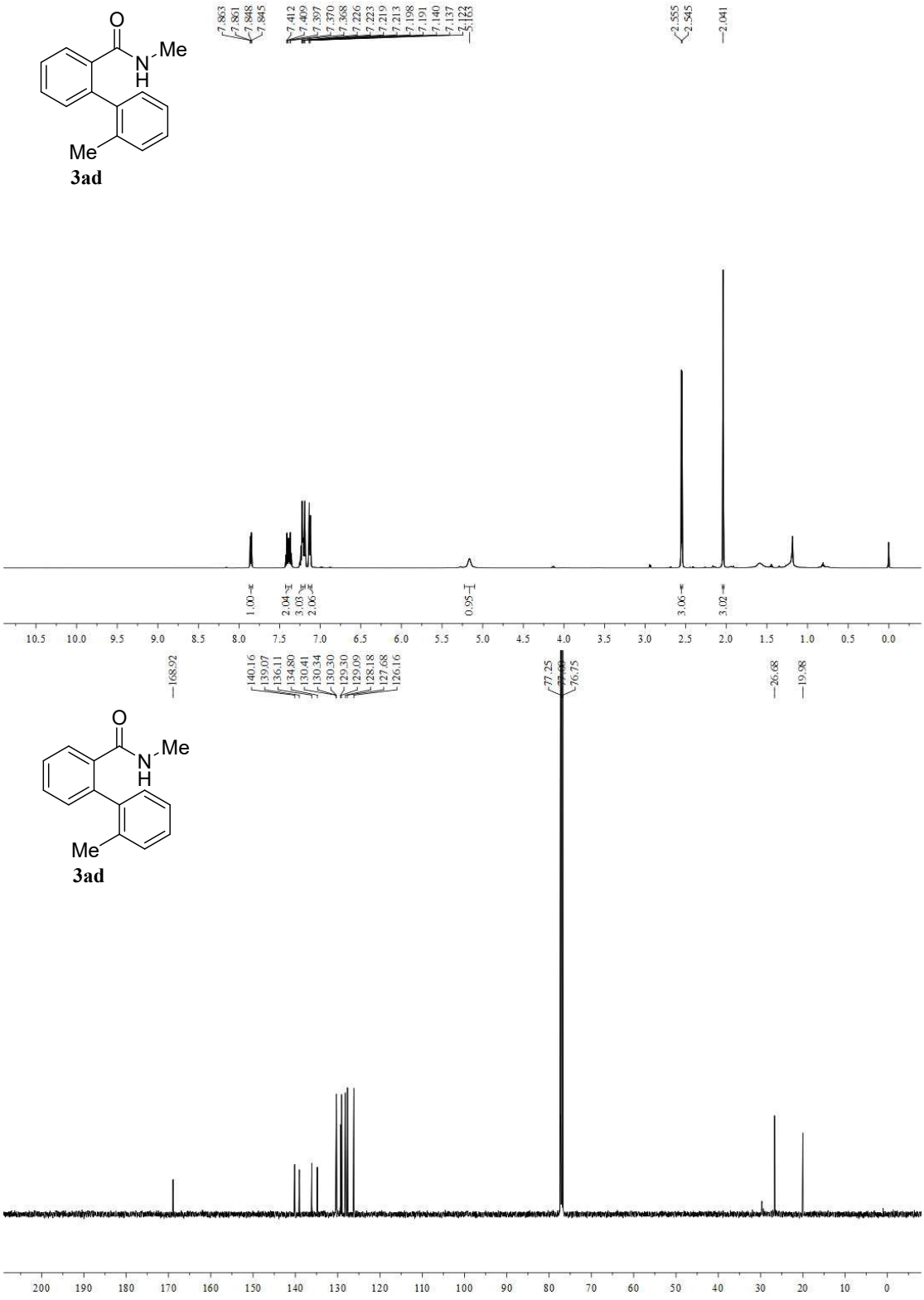
^{19}F NMR spectra in $CDCl_3$ for compound 3aa



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ab



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ac



^{1}H and ^{13}C NMR spectra in $CDCl_3$ for compound 3ad