Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Fe-Catalyzed Oxidative C-H/N-H Coupling between Aldehydes and Simple Amides

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General information

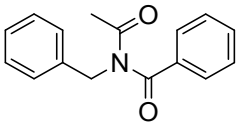
All reactions were isolated from oxygen by a nitrogen atmosphere. All glassware was oven dried at 110 ^{o}C for hours and cooled down under vacuum. DCE was purified by distillation with CaH_2. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp.60-90 ^{o}C). Gas chromatographic analyses were preformed on Varian GC 2000 gas chromatography instrument with a FID detector and dibenzo[b,d]furan was added as internal standard. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. ^{1}H and ^{13}C NMR data were recorded with Varian Mercury (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, chloroform), respectively.

General procedure for the oxidative coupling of amides with aldehydes

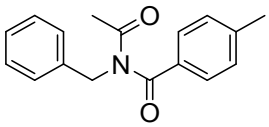
Amide (0.5 mmol) was added to a Schlenk tube equipped with a magnetic stir bar. Then, $FeBr_2$ (5.4 mg, 0.025 mmol) was added to the Schlenk tube in an argon-filled glove box. DCE (2.0 mL) was then injected into the tube by syringe. After stirring for 5 min, aldehyde (1.50 mmol) and TBHP (128.7 mg, 1.0 mmol, a 70% aqueous solution) were consecutively injected into the reaction tube. The reaction was then heated to 60 ºC and stirred for 16 h. Upon completion, the reaction was quenched with water and extracted with ethyl ether (3 × 10 mL). The organic layers were then combined. The pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl acetate= 10:1).

Procedure for eq.3

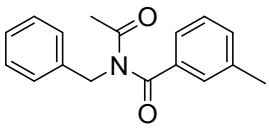
1a (74.6 mg, 0.5 mmol) was added to a Schlenk tube equipped with a magnetic stir bar. Then, $FeBr_2$ (5.4 mg, 0.025 mmol) was added to the Schlenk tube in an argon-filled glove box. DCE (2.0 mL) was then injected into the tube by syringe. After stirring for 5 min, **2a** (159.2 mg, 1.5 mmol) and TBHP (128.7 mg, 1.0 mmol, a 70% aqueous solution) were consecutively injected into the reaction tube. After stirring for 5 min, TEMPO (156.1 mg, 1.0 mmol) was added to the reaction tube in N_2 atmosphere. The reaction was then heated to 60 ºC and stirred for 16 h. Upon completion, the reaction was quenched with water and extracted with ethyl ether (3 × 10 mL). The organic layers were then combined. The pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl acetate= 200:1). The yield of the isolated product was 78% based on TEMPO.



***N*-Acetyl-N-benzylbenzamide (3aa).** Compound **3aa** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 – 7.54 (m, 3H), 7.45 – 7.42 (m, 2H), 7.28 – 7.24 (m, 5H), 5.00 (s, 2H), 2.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.3, 173.2, 137.2, 135.7, 132.4, 128.7, 128.5, 128.3, 127.7, 127.4, 49.2, 26.4 ppm. HRMS (ESI) calcd for $C_{16}H_{15}NO_2$ $[M+H]^+$: 254.1181; found: 254.1172.

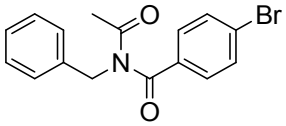


***N*-Acetyl-N-benzyl-4-methylbenzamide (3ab).** Compound **3ab** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 4-methylbenzaldehyde (180.0 mg, 1.5 mmol). Isolated yield = 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, J = 8.1, 2H), 7.31 – 7.18 (m, 6H), 5.00 (s, 2H), 2.39 (s, 3H), 2.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.3, 173.1, 143.4, 137.3, 132.8, 129.4, 128.6, 128.4, 127.8, 127.3, 49.3, 26.3, 21.6 ppm. HRMS (APCI) calcd for $C_{17}H_{17}NO_2$ $[M]^+$: 267.1259 found: 267.1259.

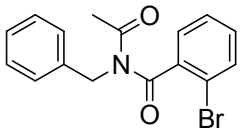


***N*-Acetyl-N-benzyl-3-methylbenzamide (3ac).** Compound **3ac** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 3-methylbenzaldehyde (180.0 mg, 1.5 mmol). Isolated yield = 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.22 (m, 9H), 5.00 (s, 2H), 2.35 (s, 3H), 2.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.6, 173.3, 138.8, 137.4, 135.7, 133.3, 129.0, 128.6, 128.5, 127.8, 127.4, 125.5, 49.3, 26.4, 21.3 ppm. HRMS (APCI) calcd for $C_{17}H_{17}NO_2$ $[M]^+$:

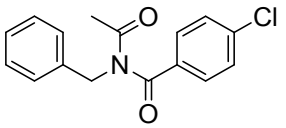
267.1262; found: 267.1264.



***N*-Acetyl-N-benzyl-4-bromobenzamide (3ad).** Compound **3ad** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 4-bromobenzaldehyde (277.5 mg, 1.5 mmol). Isolated yield = 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, *J*=8.5, 2H), 7.41 (d, *J*=8.4, 2H), 7.31 – 7.17 (m, 5H), 4.98 (s, 2H), 2.19 (s, 3H). ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.3, 173.0, 136.9, 134.5, 132.0, 129.7, 128.6, 127.5, 127.2, 49.2, 26.2 ppm. HRMS (APCI) calcd for $C_{16}H_{14}BrNO_2$ $[M]^+$: 331.0211; found: 331.0213.

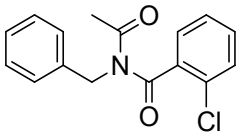


***N*-Acetyl-N-benzyl-2-bromobenzamide (3ae).** Compound **3ae** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 2-bromobenzaldehyde (277.5 mg, 1.5 mmol). Isolated yield = 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 – 7.57 (m, 1H), 7.28 – 7.22 (m, 5H), 7.08 – 7.03 (m, 3H), 4.89 (s, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.0, 171.5, 137.9, 136.9, 132.9, 131.3, 128.5, 128.5(1), 127.5, 127.4, 127.3, 118.7, 48.3, 26.5 ppm. HRMS (APCI) calcd for $C_{16}H_{14}BrNO_2$ $[M]^+$: 331.0209; found: 331.0208.

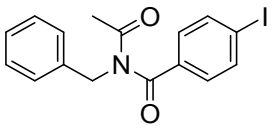


***N*-Acetyl-N-benzyl-4-chlorobenzamide (3af).** Compound **3af** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 4-chlorobenzaldehyde (210.8 mg, 1.5 mmol). Isolated yield = 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.14 (m, 5H), 4.98 (s, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.2,

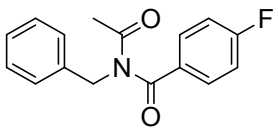
173.0, 138.7, 137.0, 134.0, 129.7, 129.0, 128.6, 127.5, 127.5, 49.2, 26.2 ppm. HRMS (APCI) calcd for $C_{16}H_{14}ClNO_2$ $[M]^+$: 287.0717; found: 287.0720.



***N*-Acetyl-N-benzyl-2-chlorobenzamide (3ag).** Compound **3ag** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 2-chlorobenzaldehyde (210.8 mg, 1.5 mmol). Isolated yield = 43%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 –7.31 (m, 2H), 7.27 – 7.21 (m, 4H), 7.11 – 7.07 (m, 3H), 4.90 (s, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.0, 170.8, 136.9, 135.9, 131.3, 130.1, 129.8, 128.5, 127.4, 127.2, 127.0, 48.3, 26.4 ppm. HRMS (APCI) calcd for $C_{16}H_{14}ClNO_2$ $[M]^+$: 287.0715; found: 287.0713.

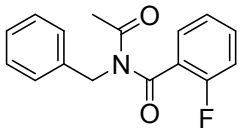


***N*-Acetyl-N-benzyl-4-iodobenzamide (3ah).** Compound **3ah** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 4-iodobenzaldehyde (348.0 mg, 1.5 mmol). Isolated yield = 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, J = 8.5 Hz, 2H), 7.33 – 7.15 (m, 7H), 4.97 (s, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.5, 173.0, 138.0, 136.9, 135.0, 129.6, 128.6, 127.5, 99.6, 49.2, 26.3. ppm. HRMS (APCI) calcd for $C_{16}H_{14}INO_2$ $[M]^+$: 379.0070; found: 379.0069.

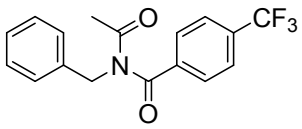


***N*-Acetyl-N-benzyl-4-fluorobenzamide (3ai).** Compound **3ai** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 4-fluorobenzaldehyde (186.2 mg, 1.5 mmol). Isolated yield = 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.56 (m, 2H), 7.30 – 7.20 (m,

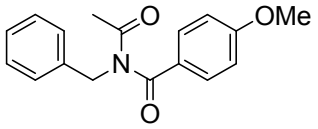
5H), 7.10 (dd, *J* = 11.9, 5.1 Hz, 2H), 4.99 (s, 2H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.2 , 173.0, 166.3, 163.8, 137.0, 131.7(8), 131.7(5), 131.0, 130.9, 128.6, 127.6, 127.5, 116.1, 115.9, 49.3, 26.2 ppm. HRMS (APCI) calcd for $C_{16}H_{14}FNO_2$ $[M]^+$: 271.1014; found: 271.1013.



***N*-Acetyl-N-benzyl-2-fluorobenzamide (3aj).** Compound **3aj** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 2-fluorobenzaldehyde (186.2 mg, 1.5 mmol). Isolated yield = 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 – 7.45 (m, 1H), 7.39 – 7.35 (m, 1H), 7.29 – 7.09 (m, 7H), 4.98 (s, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.1, 169.2, 159.7, 157.2, 133.0, 129.7, 129.6(9), 128.5, 127.4, 127.1, 124.6(3), 124.6(0), 116.0, 115.8, 48.6, 25.8 ppm. HRMS (APCI) calcd for $C_{16}H_{14}FNO_2$ $[M]^+$: 271.1010; found: 271.1009.

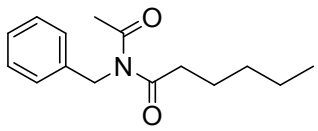


***N*-Acetyl-N-benzyl-4-(trifluoromethyl)benzamide (3ak).** Compound **3ak** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 4-(trifluoromethyl)benzaldehyde (261.2 mg, 1.5 mmol). Isolated yield = 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61-7.52 (m, 4H), 7.22 – 7.09 (m, 5H), 4.91 (s, 2H), 2.17 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.0, 172.8, 139.0, 136.7, 128.6, 128.2, 127.5, 127.2, 125.6, 49.0, 26.2. ppm. HRMS (APCI) calcd for $C_{17}H_{14}F_3NO_2$ $[M]^+$: 321.0982; found: 321.0982.

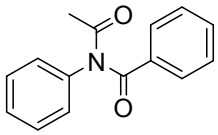


***N*-Acetyl-N-benzyl-4-methoxybenzamide (3al).** Compound **3al** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and 4-methoxybenzaldehyde (204.2 mg,

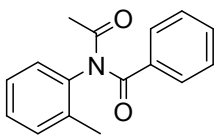
1.5 mmol). Isolated yield = 26%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 – 7.57 (m, 2H), 7.28 – 7.25 (m, 5H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.00 (s, 2H), 3.86 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.8, 173.0, 163.3, 137.4, 131.1, 128.5, 127.9, 127.7, 127.4, 114.1, 55.5, 49.4, 26.1 ppm. HRMS (APCI) calcd for $C_{17}H_{17}NO_3$ $[M]^+$: 283.1207; found: 283.1208.



***N*-Acetyl-N-benzylhexanamide (3am).** Compound **3am** was prepared following the general procedure starting from *N*-benzylacetamide (74.6 mg, 0.5 mmol) and hexanaldehyde (150.2 mg, 1.5 mmol). Isolated yield = 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.28 (m, 3H), 7.16 (d, *J* = 4.0 Hz, 2H), 4.99 (s, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.46 (s, 3H), 1.67 – 1.63 (m, 3H), 1.31 – 1.28 (m, 5H), 0.89 (t, *J* = 8.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.5, 173.6, 137.1, 128.8, 127.4, 126.1, 47.2, 37.8, 31.2, 26.8, 24.5, 22.4, 13.9 ppm. HRMS (APCI) calcd for $C_{15}H_{21}NO_2$ $[M]^+$: 176.0708; found: 176.0712.

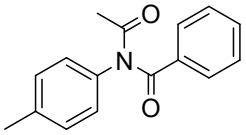


***N*-Acetyl-N-phenylbenzamide (3ba).** Compound **3ba** was prepared following the general procedure starting from *N*-phenylacetamide (67.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.20 (m, 6H), 7.18 (d, *J* = 8.0 Hz, 2H) 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.5, 172.8, 139.1, 134.8, 132.1, 129.4, 129.2, 128.6, 128.3, 128.1, 25.7 ppm. HRMS (ESI) calcd for $C_{15}H_{13}NO_2$ $[M+H]^+$: 240.1025; found: 240.1018.

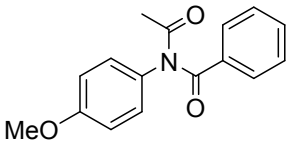


***N*-Acetyl-N-(o-tolyl)benzamide (3ca).** Compound **3ca** was prepared following the general procedure

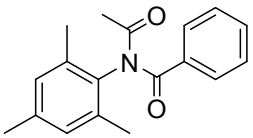
starting from *N*-(o-tolyl)acetamide (74.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.11 (m, 7H), 2.36 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.4, 172.5, 138.1, 135.7, 135.0, 131.7, 131.2, 129.1, 128.7, 128.4, 128.0, 127.0, 25.4, 17.9 ppm. HRMS (APCI) calcd for $C_{16}H_{15}NO_2$ $[M]^+$: 253.1106; found: 253.1108.



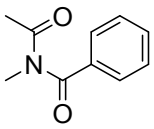
***N*-Acetyl-N-(p-tolyl)benzamide (3da).** Compound **3da** was prepared following the general procedure starting from *N*-(p-tolyl)acetamide (74.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.0 Hz , 2H), 7.41 – 7.11 (m, 7H), 2.36 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.7, 173.0, 138.1, 136.5, 135.0, 132.0, 130.1, 129.2, 128.2(7), 128.2(6), 25.6, 21.1 ppm. HRMS (APCI) calcd for $C_{16}H_{15}NO_2$ $[M]^+$: 253.1105; found: 253.1108.



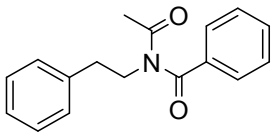
***N*-Acetyl-N-(4-methoxyphenyl)benzamide (3ea).** Compound **3ea** was prepared following the general procedure starting from *N*-(4-methoxyphenyl)acetamide (82.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 – 7.59 (m, 2H), 7.38 – 7.28 (m, 3H), 7.09 – 7.05 (m, 2H), 6.84 – 6.82 (m, 2H), 3.73 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.6, 172.8, 158.9, 134.8, 131.8, 131.5, 129.4, 128.9, 128.1, 114.5, 55.2, 25.4 ppm. HRMS (APCI) calcd for $C_{16}H_{15}NO_3$ $[M]^+$: 269.1051; found: 269.1052.



***N*-Acetyl-N-mesitylbenzamide (3fa).** Compound **3fa** was prepared following the general procedure starting from *N*-mesitylacetamide (88.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.37 (m, 3H), 6.96 (s, 2H), 2.31 – 2.25 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.7, 172.1, 138.8, 135.7, 135.6, 134.9, 131.7, 129.8, 128.3, 128.1, 25.3, 21.1, 18.3 ppm. HRMS (APCI) calcd for $C_{18}H_{19}NO_2$ $[M]^+$: 281.1412; found: 281.1416.

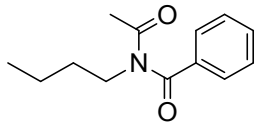


***N*-Acetyl-N-methylbenzamide (3ga).** Compound **3ga** was prepared following the general procedure starting from *N*-methylacetamide (36.5 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.47 (m, 5H), 3.22 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 173.6, 135.2, 132.4, 128.8, 128.4, 34.4, 25.9 ppm. HRMS (APCI) calcd for $C_{10}H_{11}NO_2$ $[M]^+$: 177.0788; found: 177.0790.

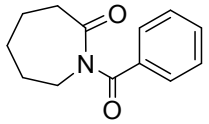


***N*-Acetyl-N-phenethylbenzamide (3ha).** Compound **3ha** was prepared following the general procedure starting from *N*-phenethylacetamide (81.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.37 (m, 5H), 7.25 – 7.18 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.02 – 4.00 (m, 2H), 2.93 – 2.88 (m, 2H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$)

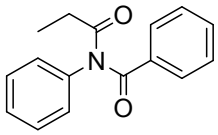
δ = 174.1, 173.1, 138.0, 135.4, 132.0, 128.9, 128.5, 128.3, 128.0, 126.3, 47.7, 34.9, 26.1 ppm. HRMS (APCI) calcd for $C_{17}H_{17}NO_2$ $[M]^+$: 267.1264; found: 267.1264.



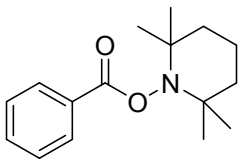
***N*-Acetyl-N-butylbenzamide (3ia).** Compound **3ia** was prepared following the general procedure starting from *N*-butylacetamide (65.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 – 7.53 (m, 3H), 7.48 – 7.44 (m, 2H), 3.77 – 3.74 (m, 2H), 2.15 (s, 3H), 1.58 – 1.54 (m, 2H), 1.27 – 1.25 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.6, 173.2, 135.8, 132.4, 128.8, 128.4, 46.2, 31.1, 26.2, 20.1, 13.6 ppm. HRMS (APCI) calcd for $C_{13}H_{17}NO_2$ $[M]^+$: 219.1263; found: 219.1264.



1-Benzoylazepan-2-one (3ja). Compound **3ja** was prepared following the general procedure starting from azepan-2-one (56.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 – 7.53 (m, 2H), 7.46 – 7.37 (m, 3H), 4.00 – 3.97 (m, 2H), 2.71 – 2.68 (m, 2H), 1.85 – 1.83 (m, 6H). ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.5, 174.1, 136.5, 131.3, 128.1, 127.6, 45.1, 38.8, 29.5, 29.1, 23.7 ppm. HRMS (APCI) calcd for $C_{13}H_{15}NO_2$ $[M]^+$: 217.1098; found: 217.1103.



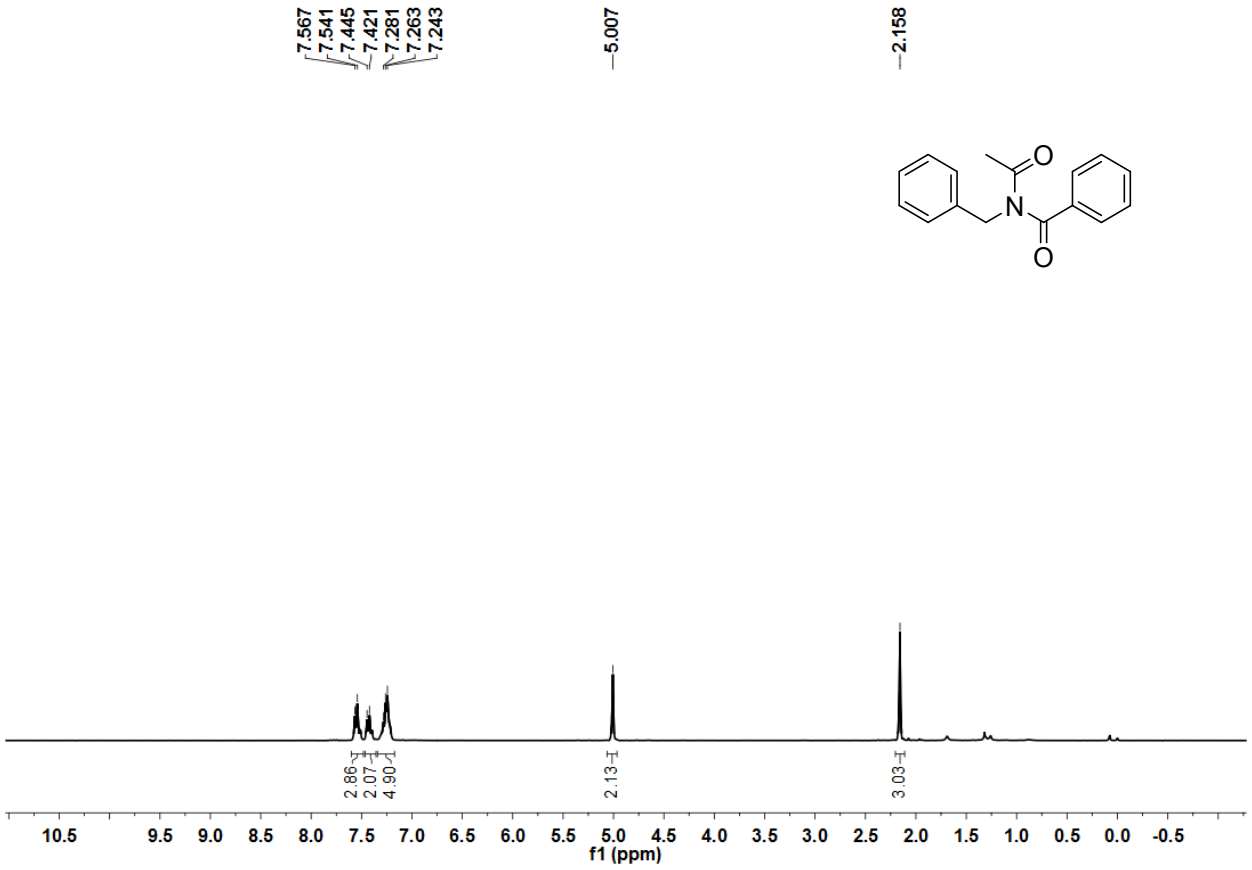
***N*-Phenyl-N-propionylbenzamide (3ka).** Compound **3ka** was prepared following the general procedure starting from *N*-phenylpropionamide (74.6 mg, 0.5 mmol) and benzaldehyde (159.2 mg, 1.5 mmol). Isolated yield = 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.63 (m, 2H), 7.44 – 7.31 (m, 6H), 7.20-7.18 (m, 2H), 2.71 (q, *J* = 7.4 Hz, 2H), 1.23 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.4, 173.0, 139.1, 135.1, 131.9, 129.4, 129.0, 128.7, 128.3, 128.1, 31.0, 9.5 ppm. HRMS (APCI) calcd for $C_{16}H_{15}NO_2$ $[M]^+$: 253.1101; found: 253.1103.

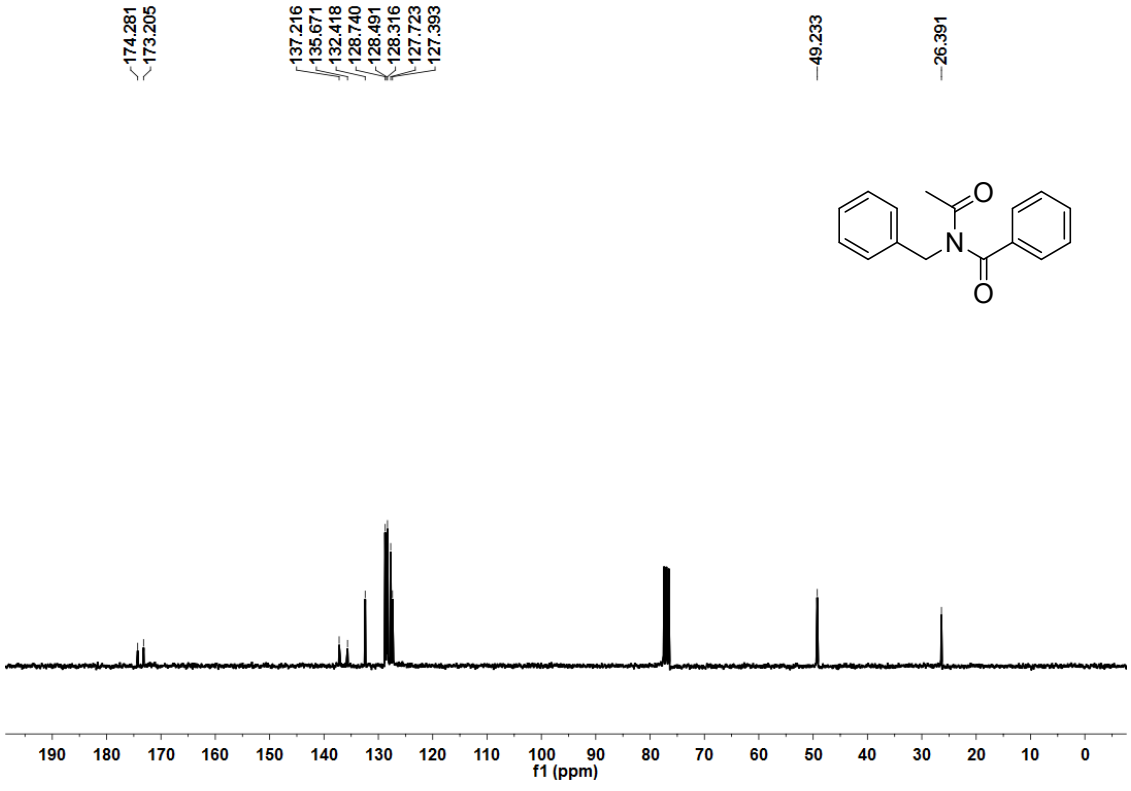


2,2,6,6-Tetramethylpiperidin-1-yl benzoate (4)[1]. Isolated yield = 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 – 8.08 (m, 2H), 7.59 – 7.57 (m, 1H), 7.50 – 7.46 (m, 2H), 1.97 – 1.46 (m, 6H), 1.29 (s, 6H), 1.14 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.3, 132.8, 129.6, 129.5, 128.4, 60.3, 39.0, 31.9, 20.8, 16.9 ppm.

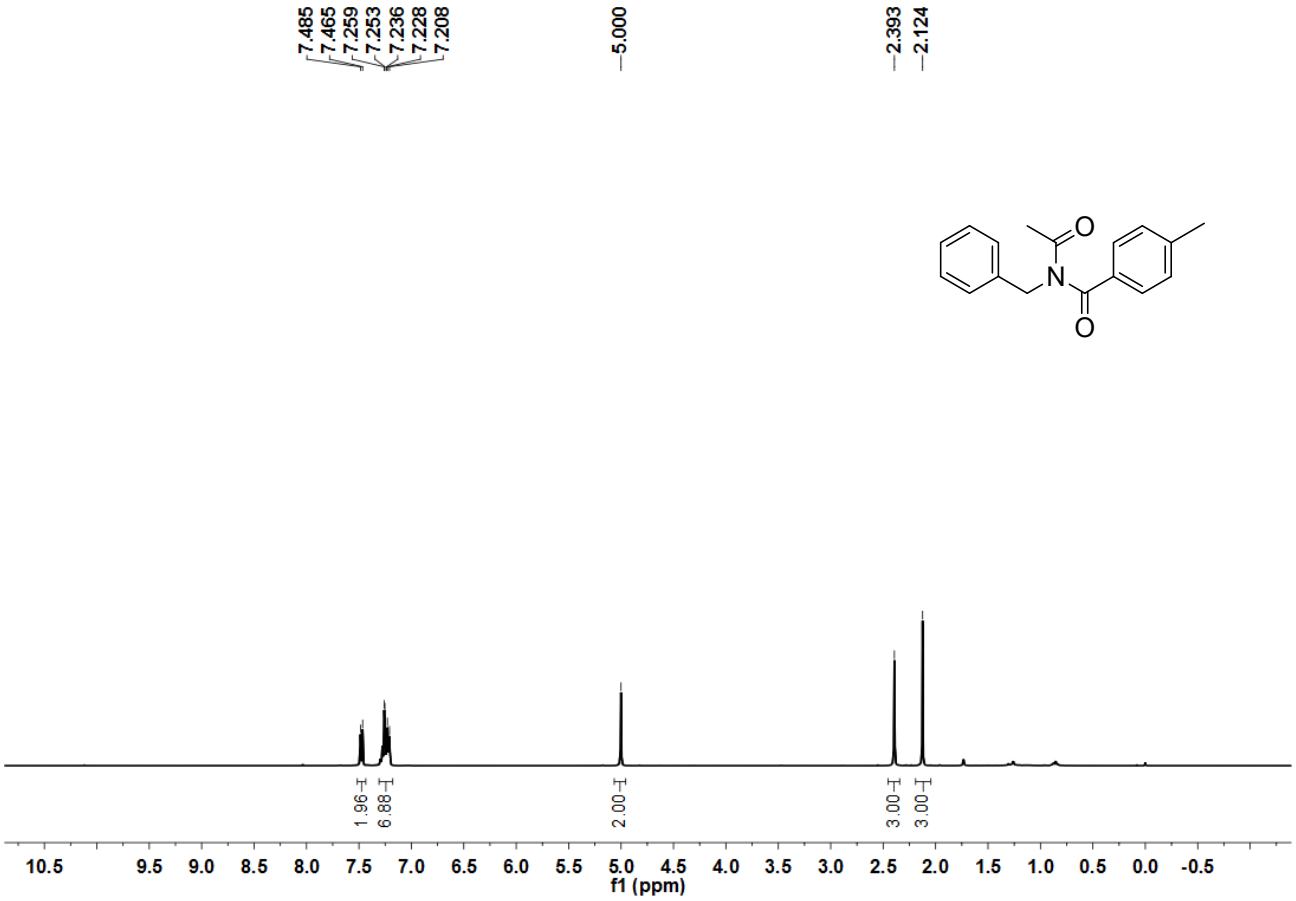
Copies of product ^{1}H and ^{13}C NMR

3aa





3ab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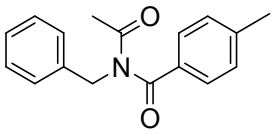
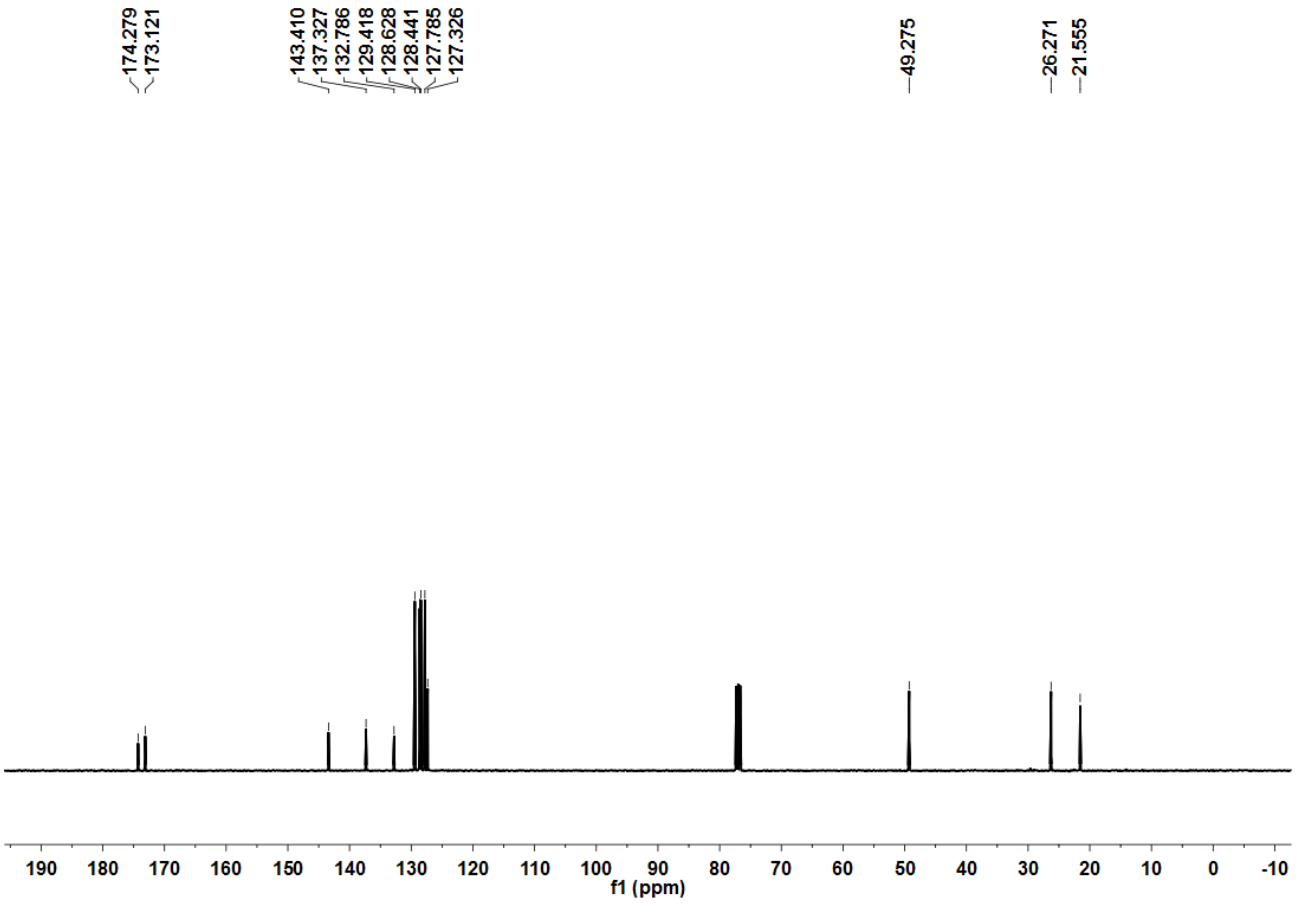
7.465
7.259
7.253
7.236
7.228
7.208
5.000
2.393
2.124
O
N
O
1.96
6.88
2.00
3.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
N
O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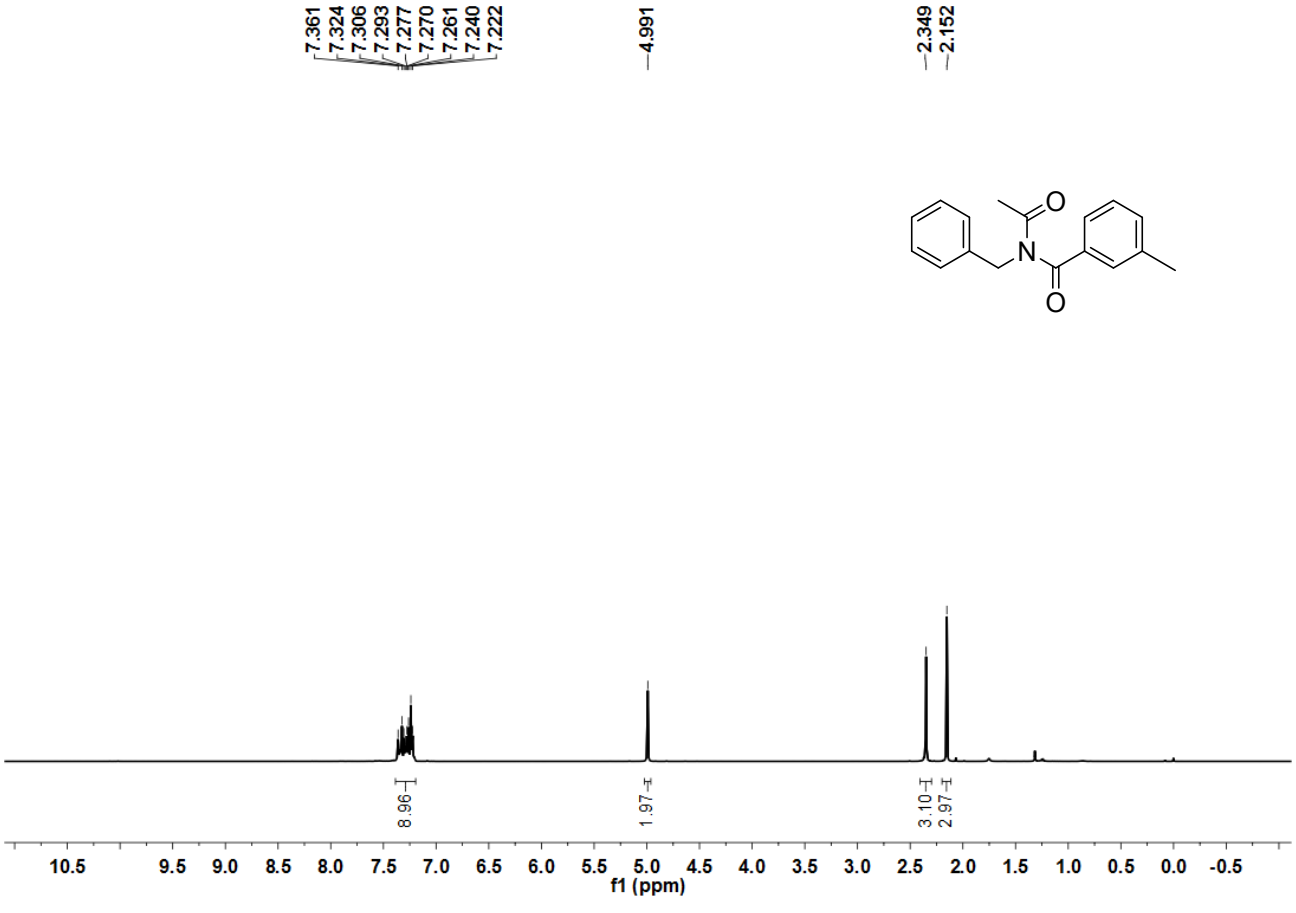
173.121
143.410
137.327
132.786
129.418
128.628
128.441
127.785
127.326
49.275
26.271
21.555
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ac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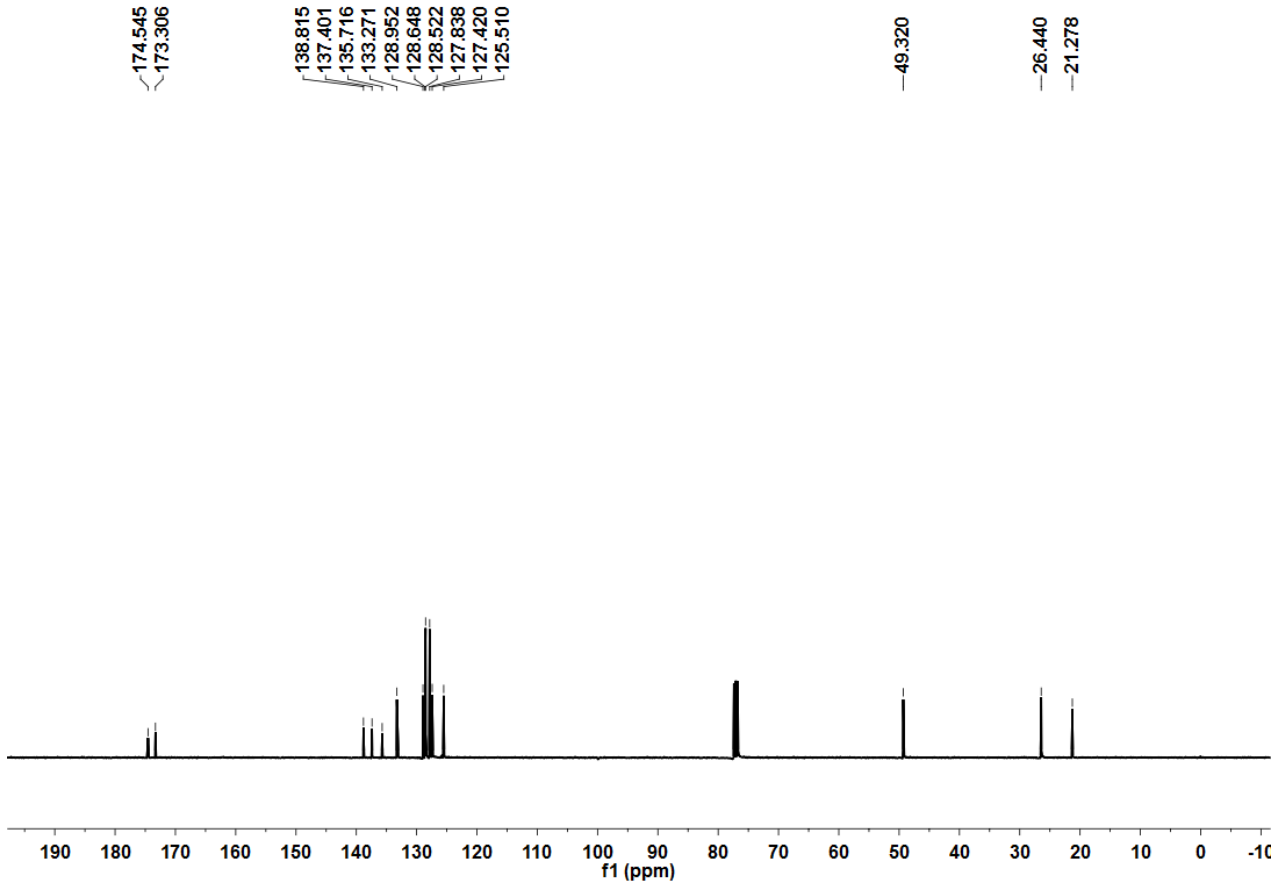
7.306
7.293
7.277
7.270
7.261
7.240
7.222
4.991
2.349
2.152
O
N
O
8.96
1.97
3.10
2.97
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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173.306
138.815
137.401
135.716
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128.952
128.648
128.522
127.838
127.420
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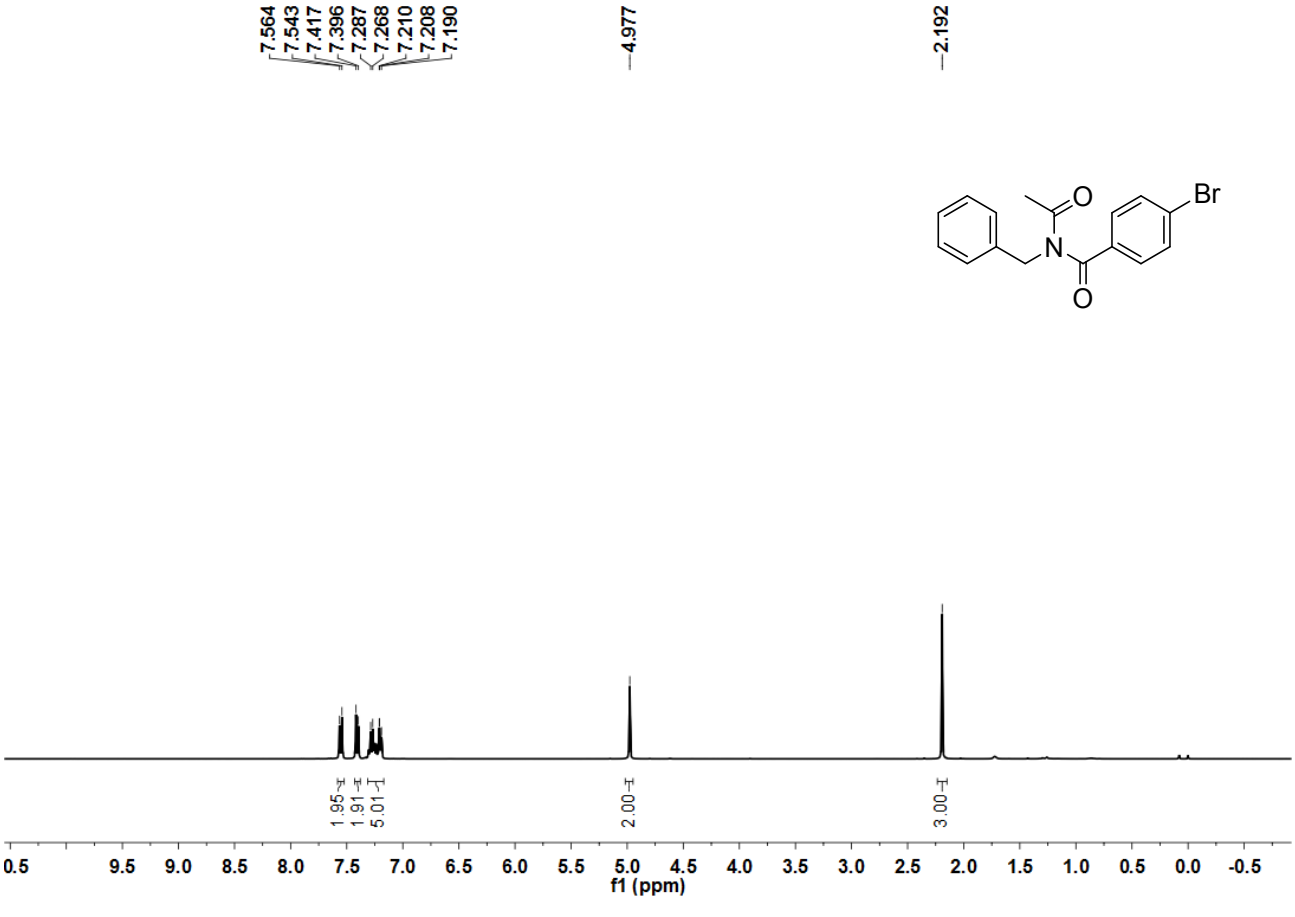
49.320
26.440
21.278
f1 (ppm)

3ad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7.417
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7.287
7.268
7.210
7.208
7.190
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Br
O
N
O
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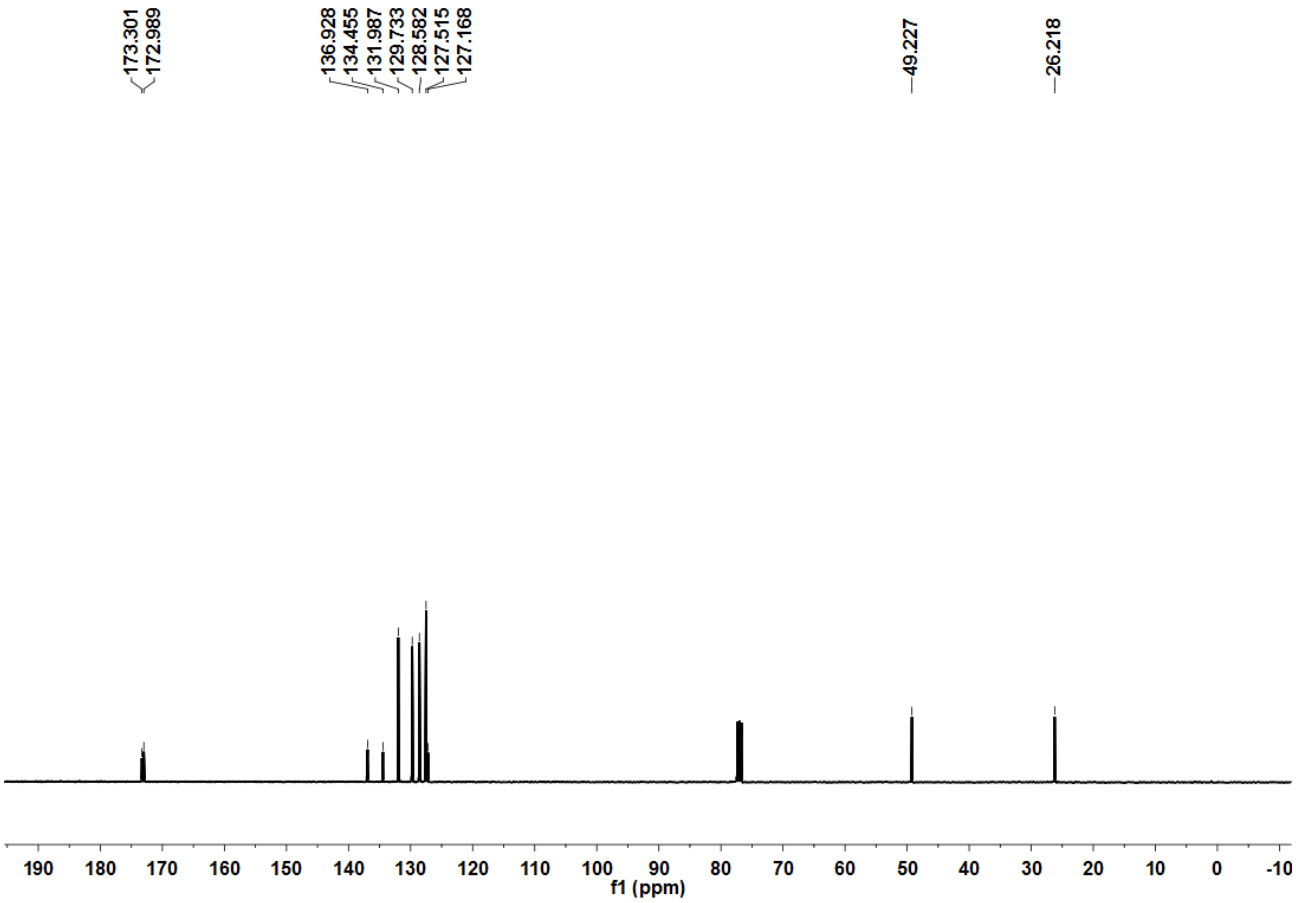
1.91
5.01
2.00
3.00
f1 (ppm)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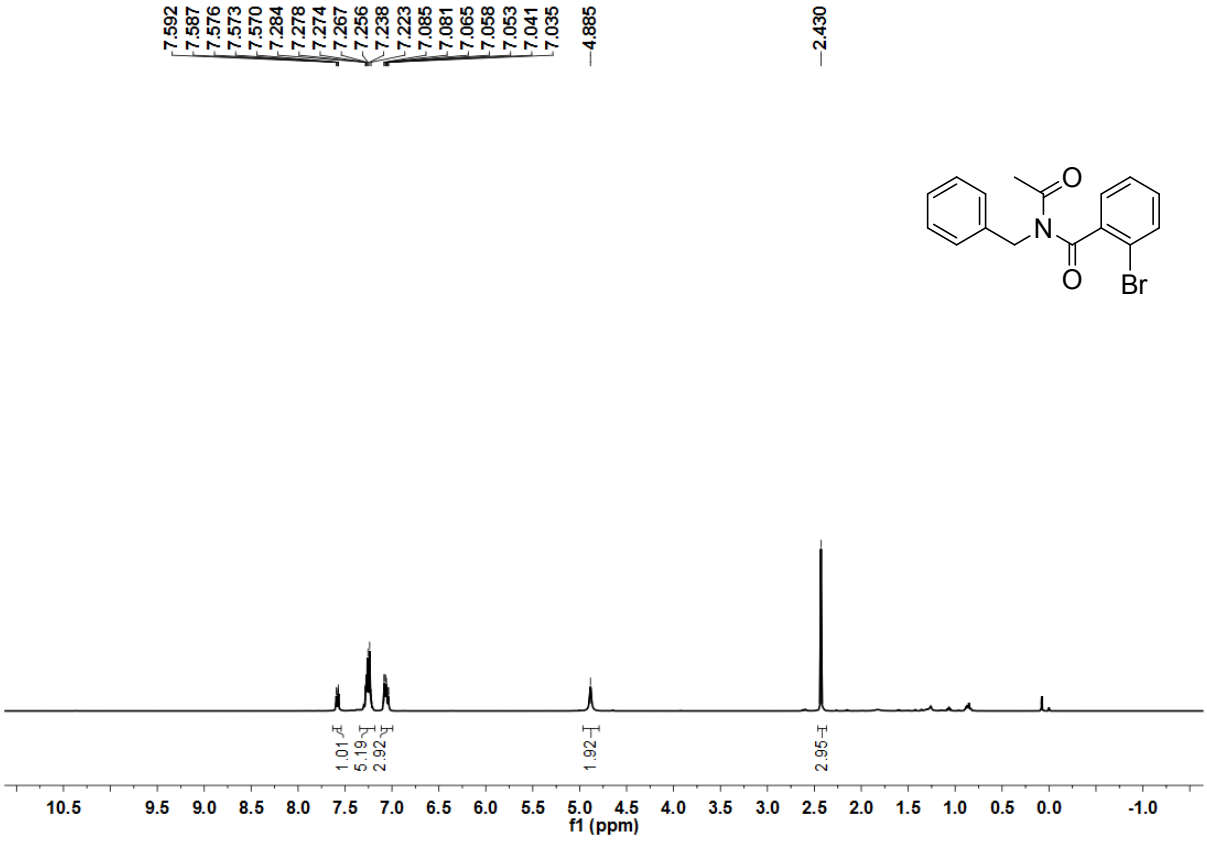
172.989
136.928
134.455
131.987
129.733
128.582
127.515
127.168
49.227
26.218
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ae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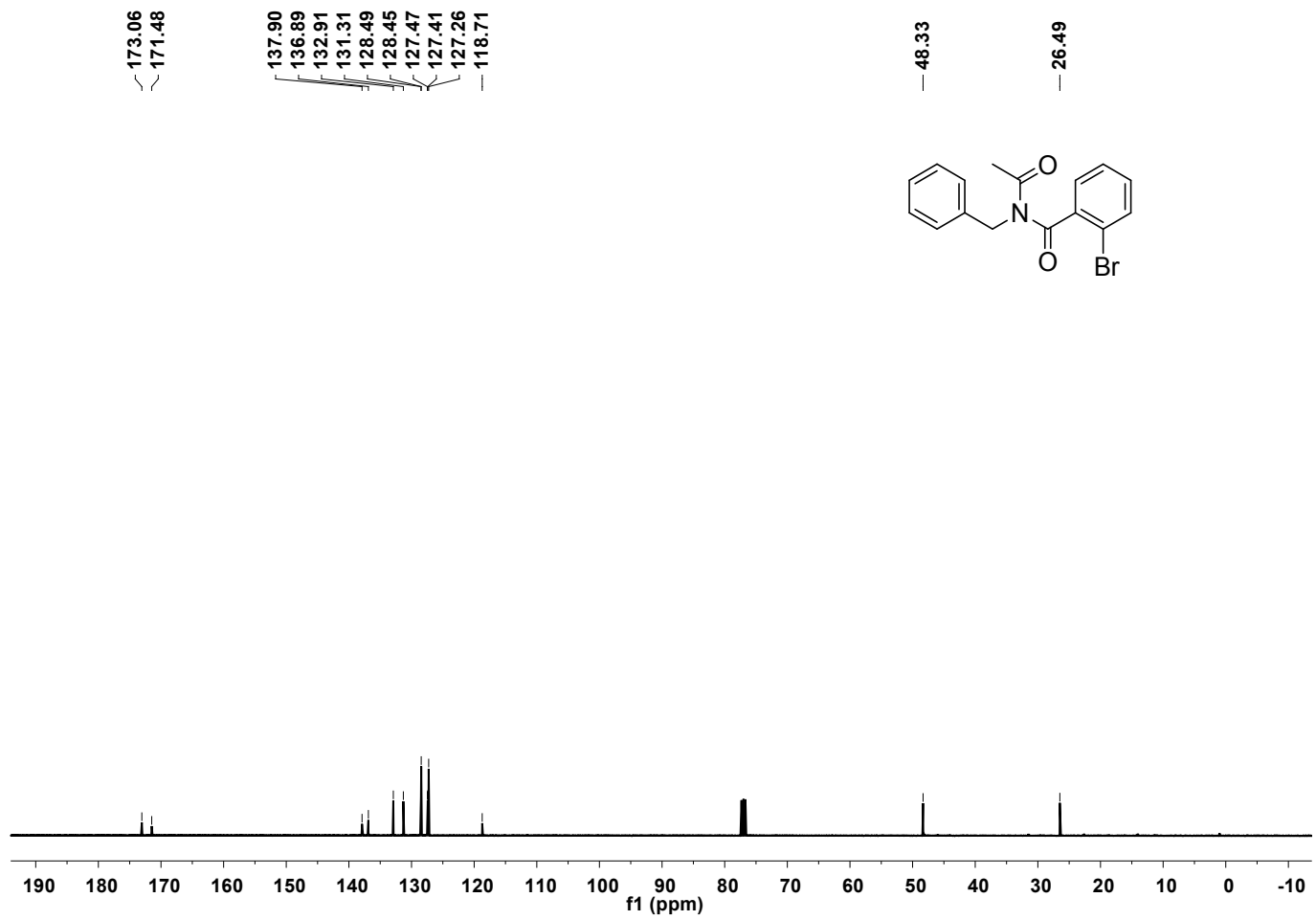
7.573
7.570
7.284
7.278
7.274
7.267
7.256
7.238
7.223
7.085
7.081
7.065
7.058
7.053
7.041
7.035
4.885
2.430
O
N
O
Br
1.01
5.19
2.92
1.92
2.95
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)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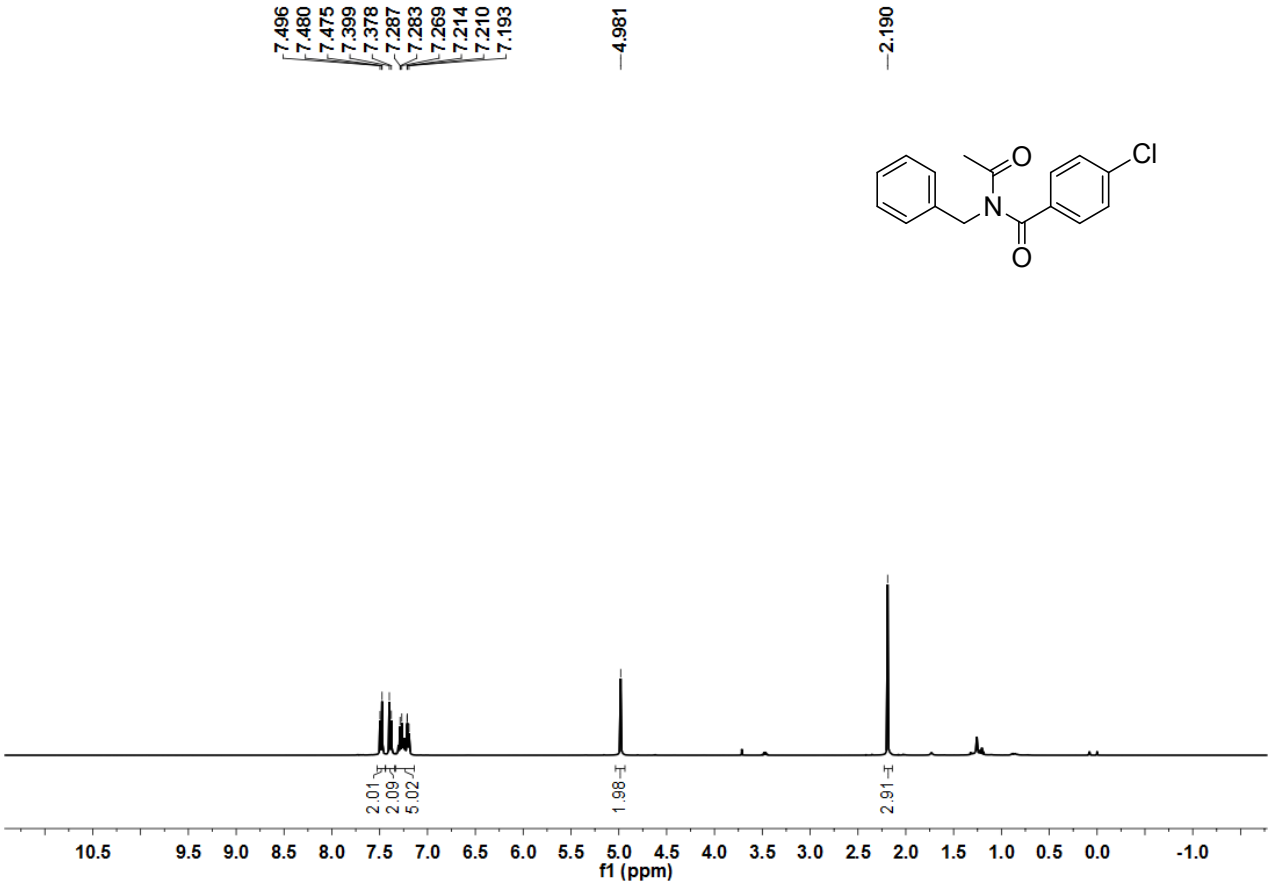
171.48
137.90
136.89
132.91
131.31
128.49
128.45
127.47
127.41
127.26
118.71
48.33
26.49
O
N
O
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3af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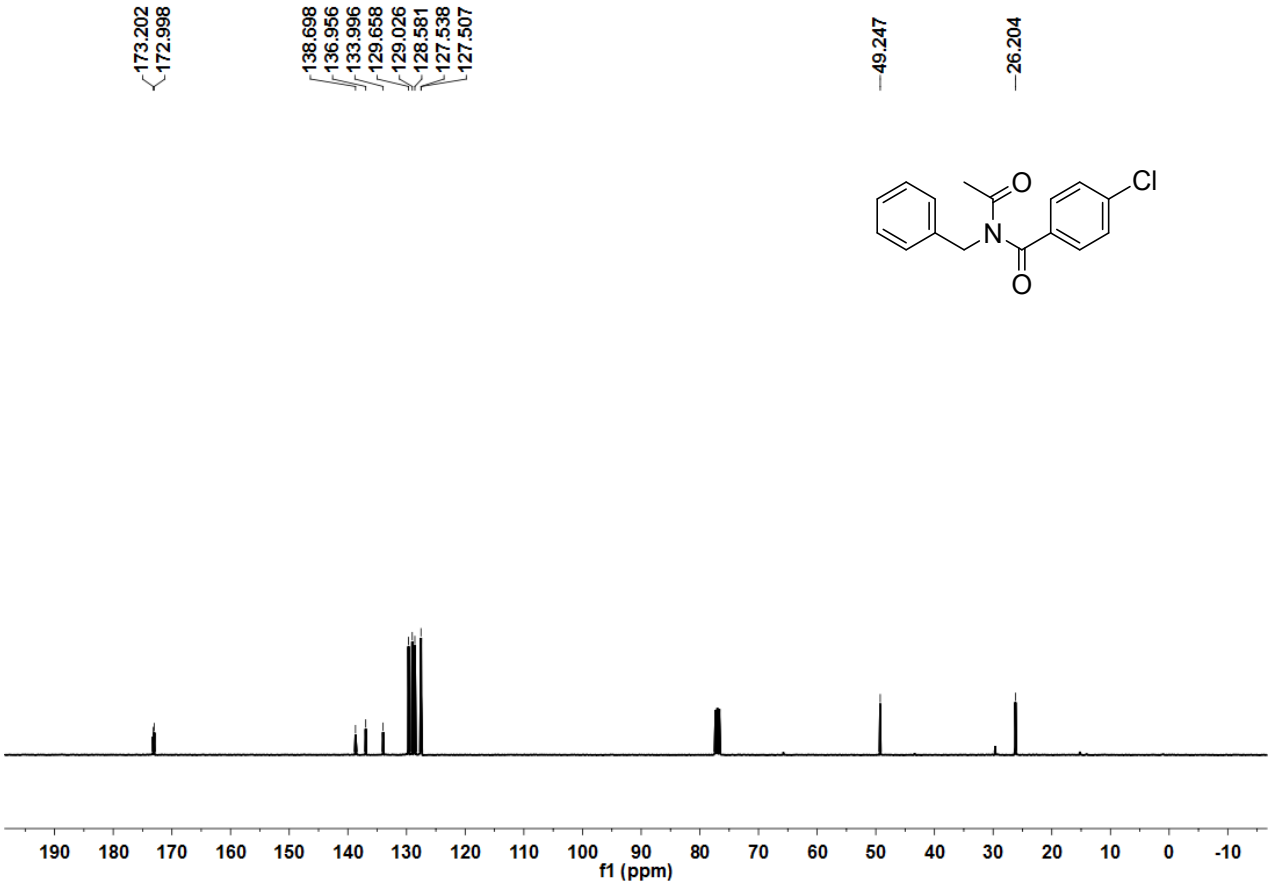
7.283
7.269
7.214
7.210
7.193
4.981
2.190
O
N
O
Cl
2.01
2.09
5.02
1.98
2.91
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)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136.956
133.996
129.658
129.026
128.581
127.538
127.507
49.247
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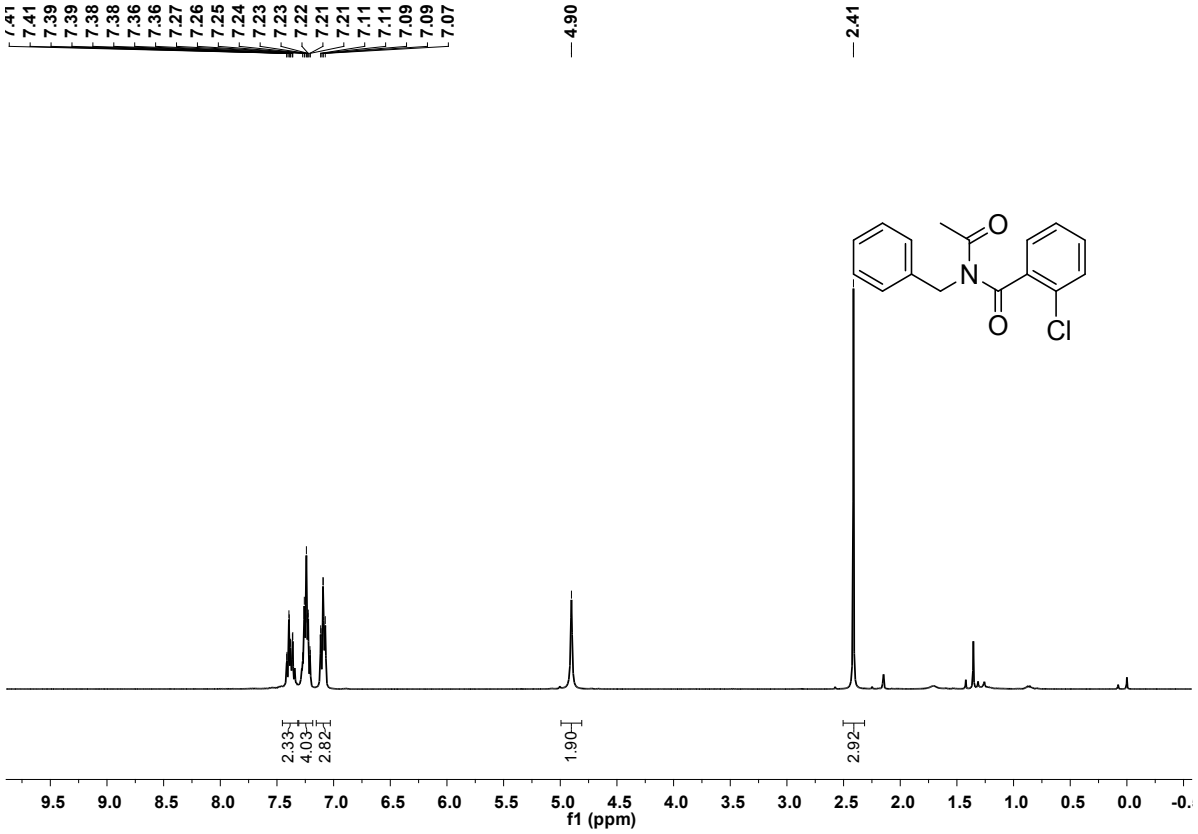
O
N
O
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ag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7.39
7.39
7.38
7.38
7.36
7.36
7.27
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.11
7.11
7.09
7.09
7.07
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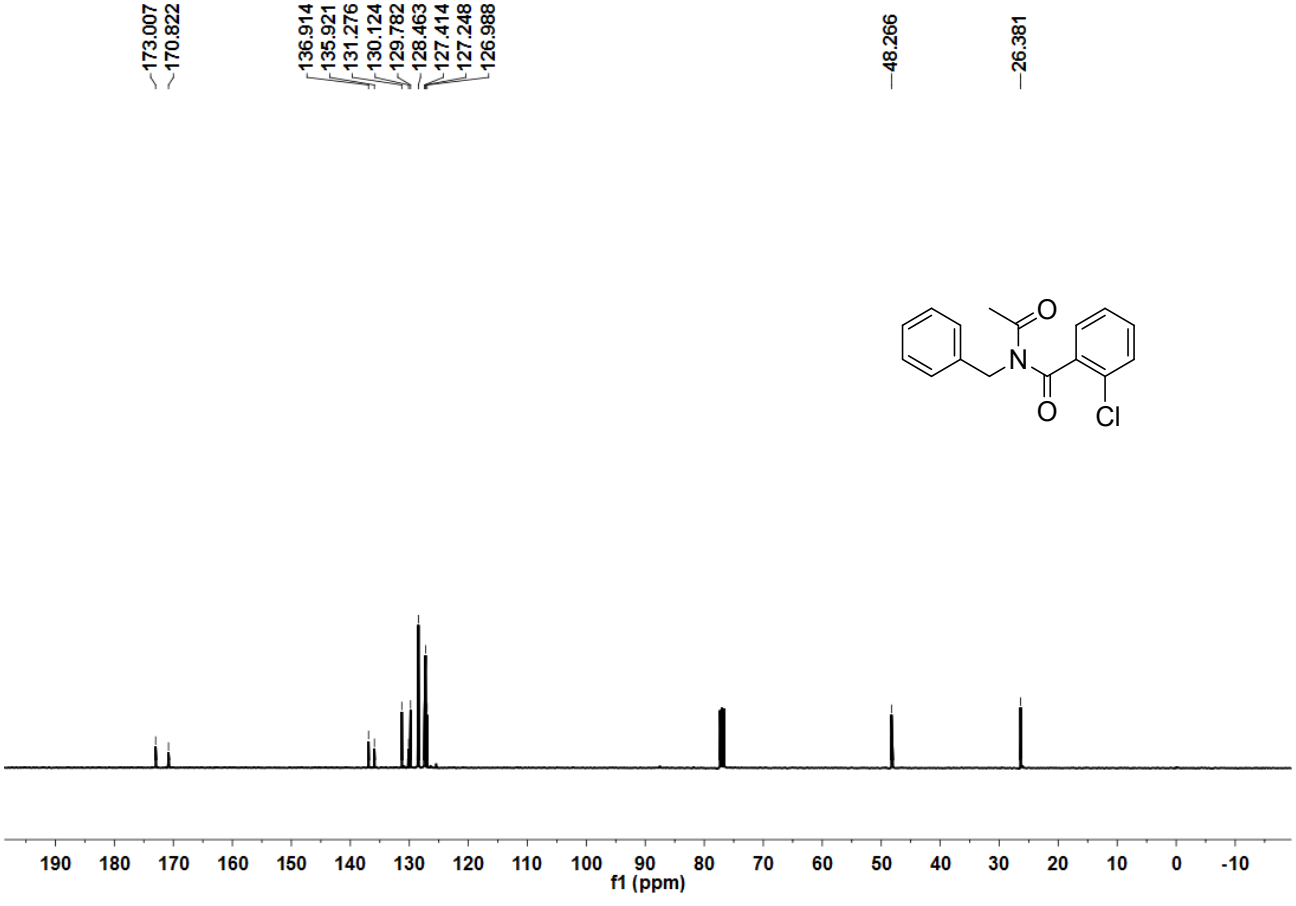
O
N
O
Cl
2.33
4.03
2.82
1.90
2.92
f1 (ppm)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131.276
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O
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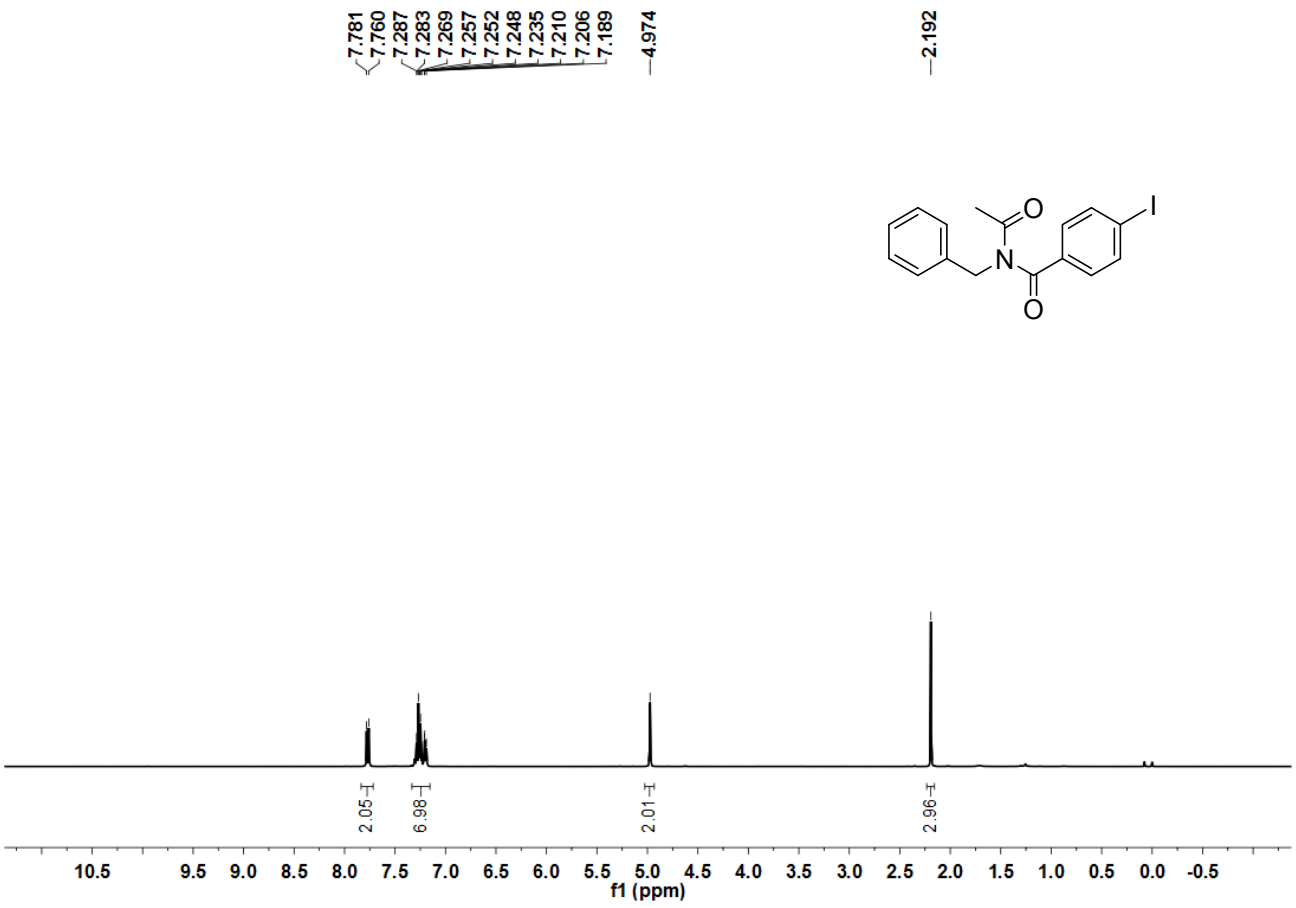
O
Cl
f1 (ppm)

3ah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7.248
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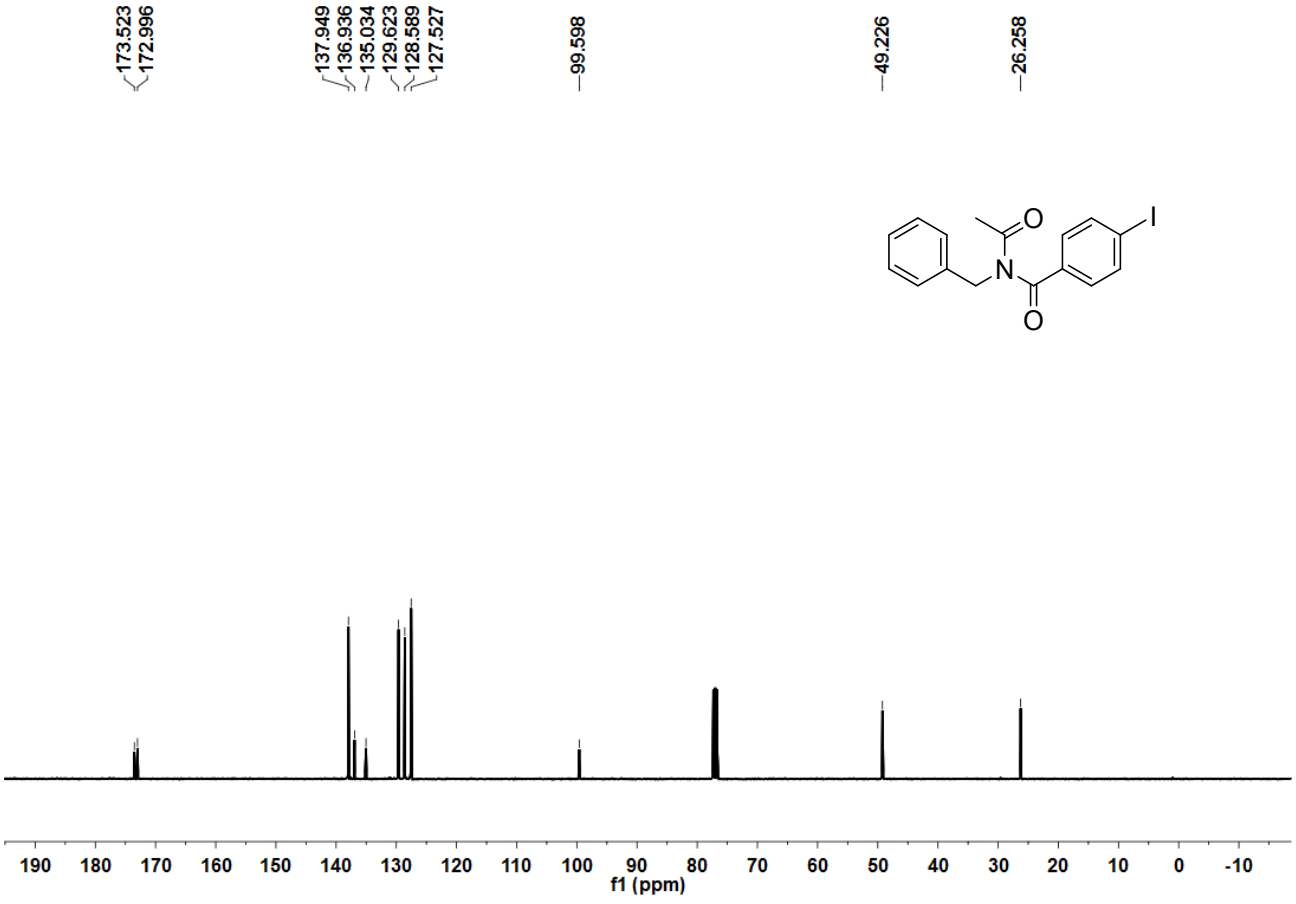
7.210
7.206
7.189
4.974
2.192
O
N
O
I
2.05
6.98
2.01
2.96
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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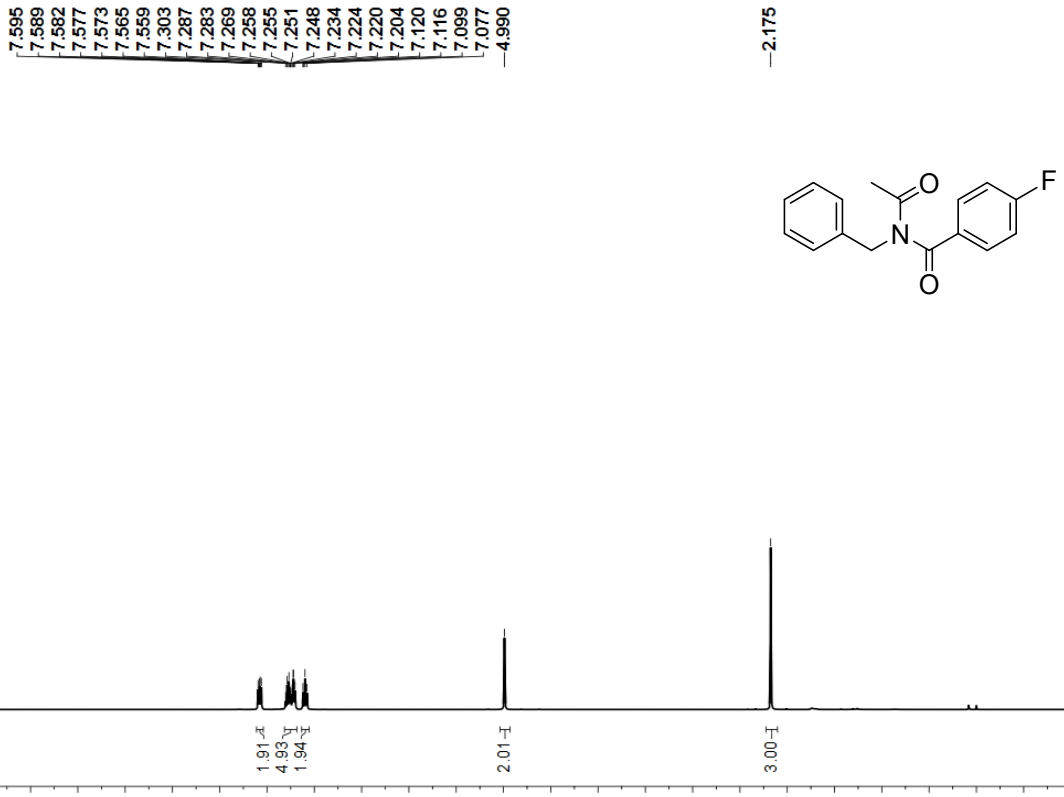
26.258
O
N
O
I
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ai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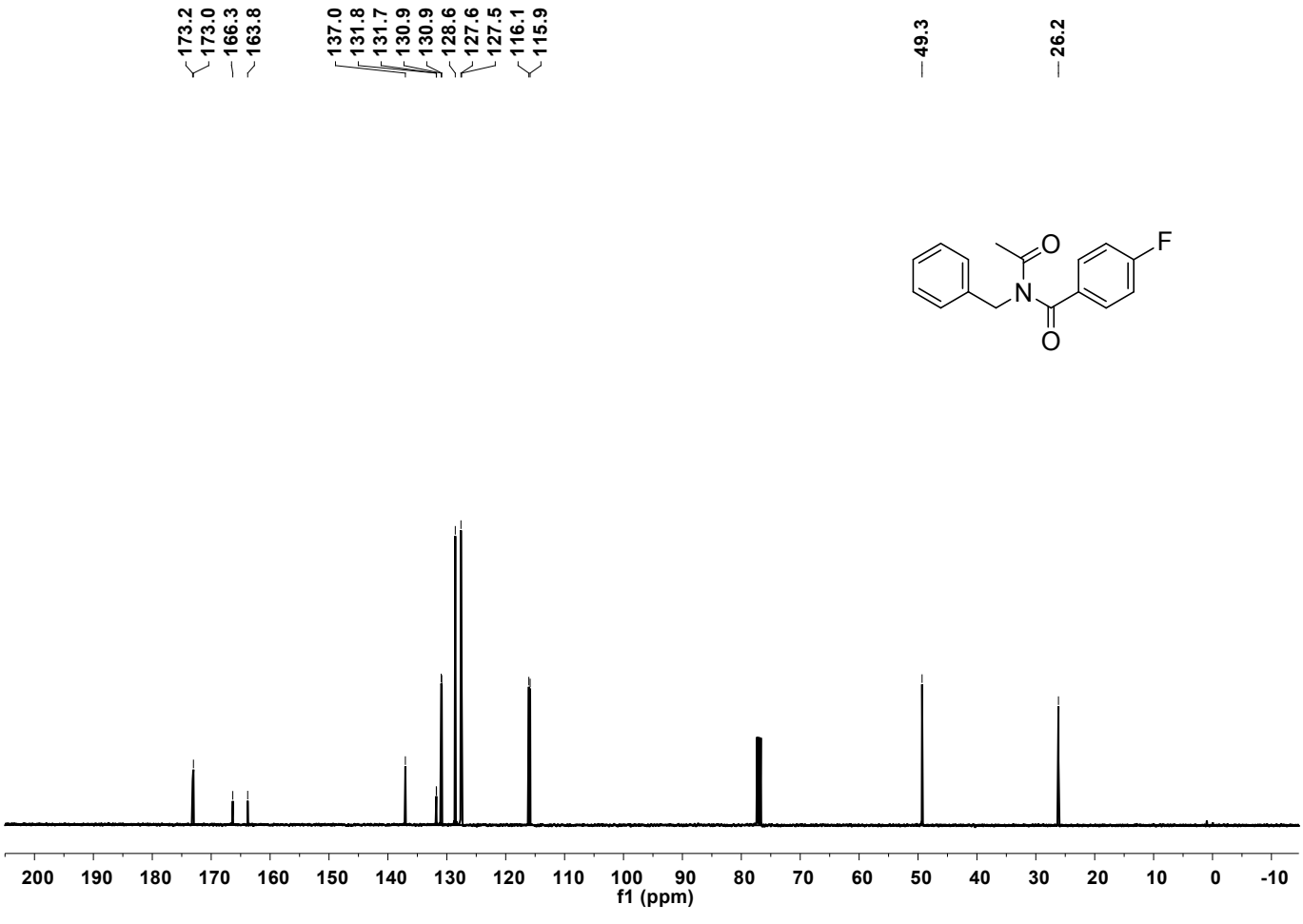
7.559
7.303
7.287
7.283
7.269
7.258
7.255
7.251
7.248
7.234
7.224
7.220
7.204
7.120
7.116
7.099
7.077
4.990
2.175
O
N
O
F
1.91
4.93
1.94
2.01
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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163.8
137.0
131.8
131.7
130.9
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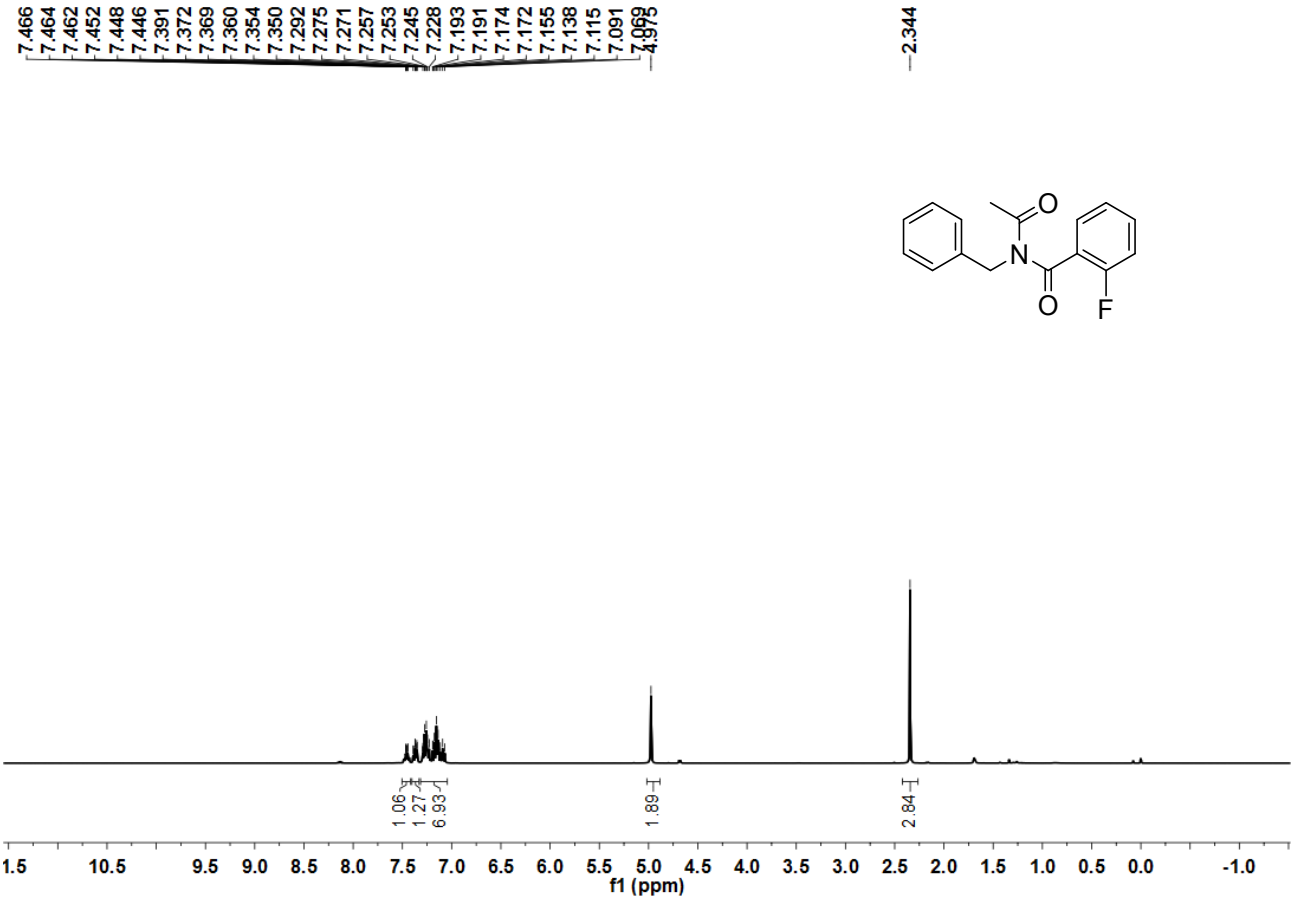
128.6
127.6
127.5
116.1
115.9
49.3
26.2
O
N
O
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3aj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7.462
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7.369
7.360
7.354
7.350
7.292
7.275
7.271
7.257
7.253
7.245
7.228
7.193
7.191
7.174
7.172
7.155
7.138
7.115
7.091
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N
O
F
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6.93
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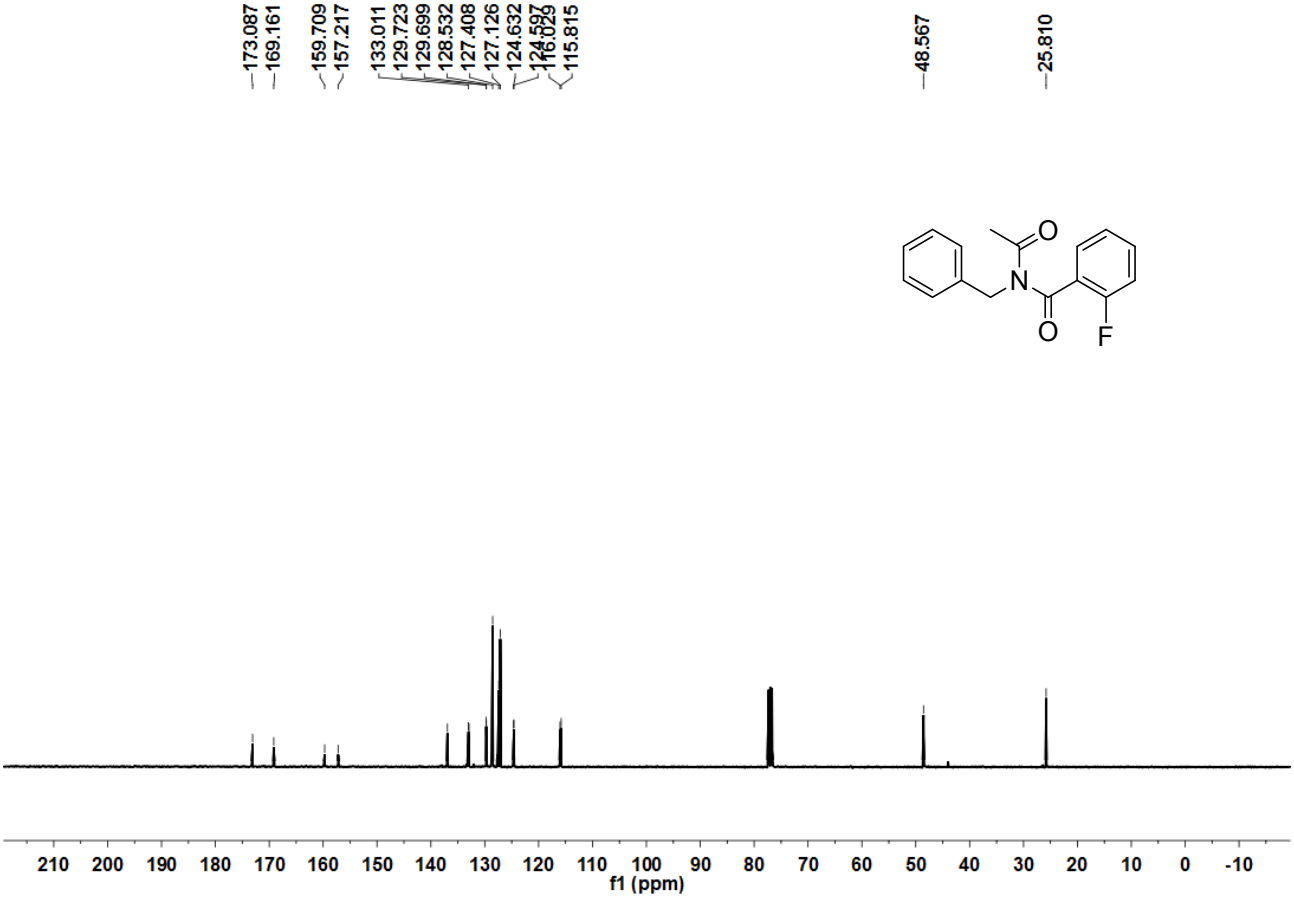
f1 (ppm)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127.126
124.632
115.815
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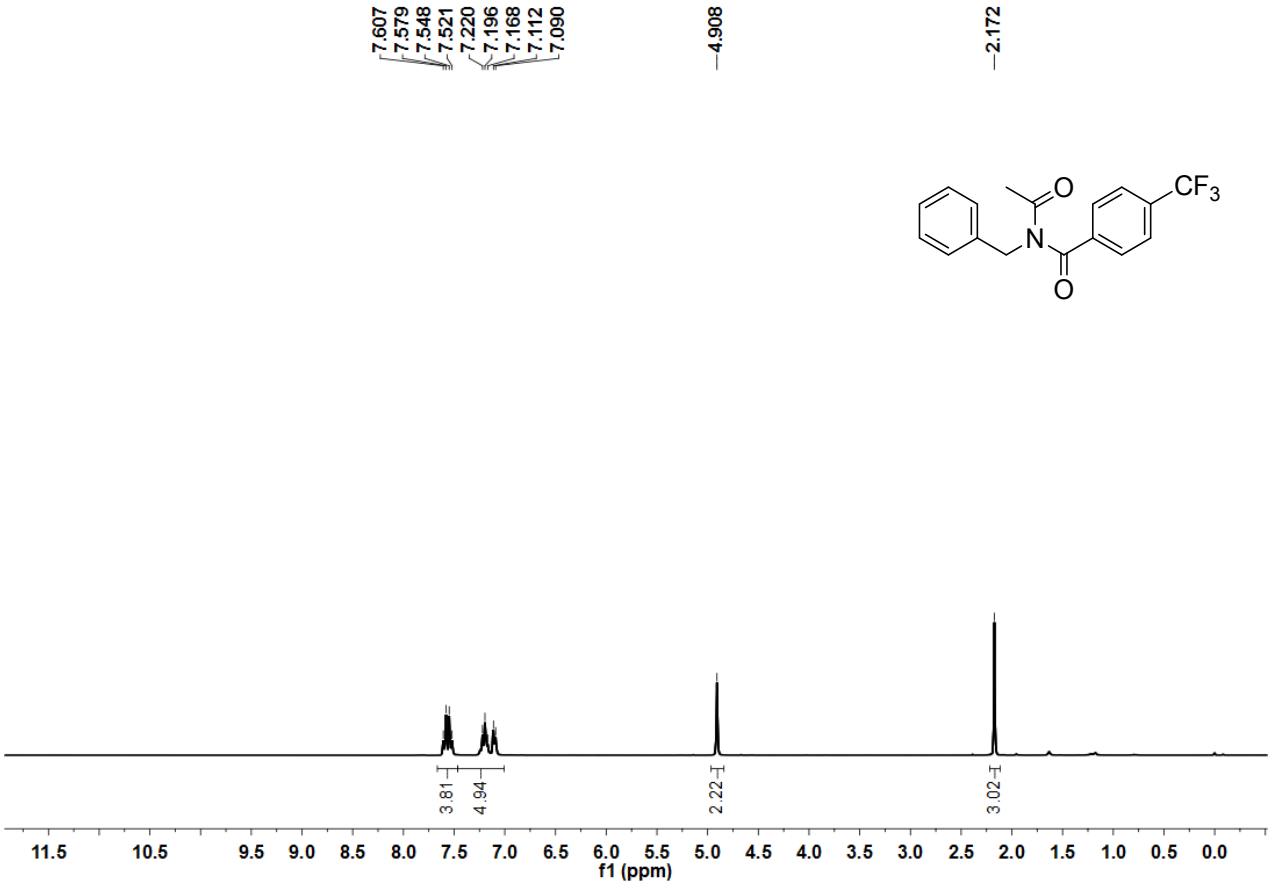
25.810
O
N
O
F
f1 (ppm)

3ak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7.168
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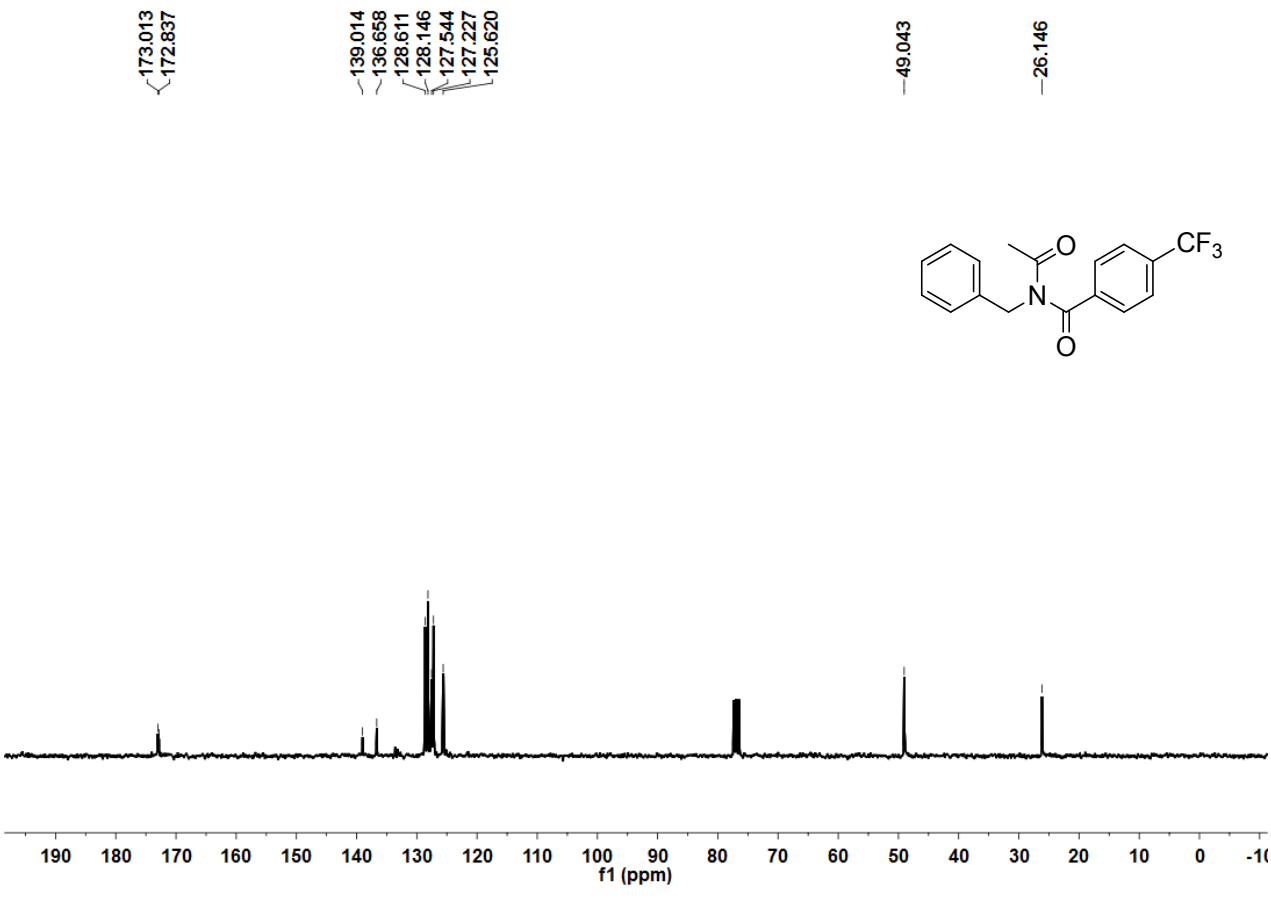
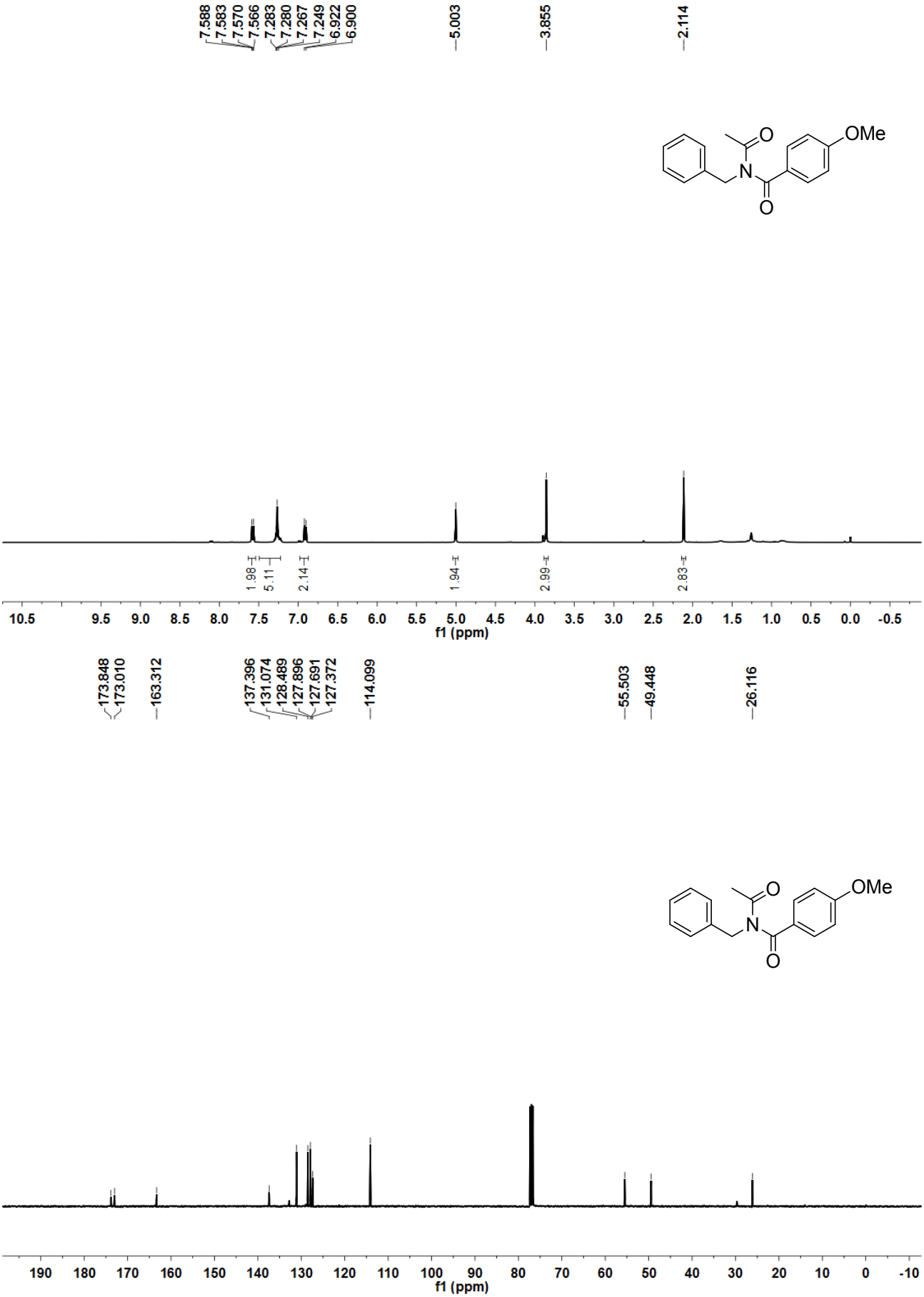
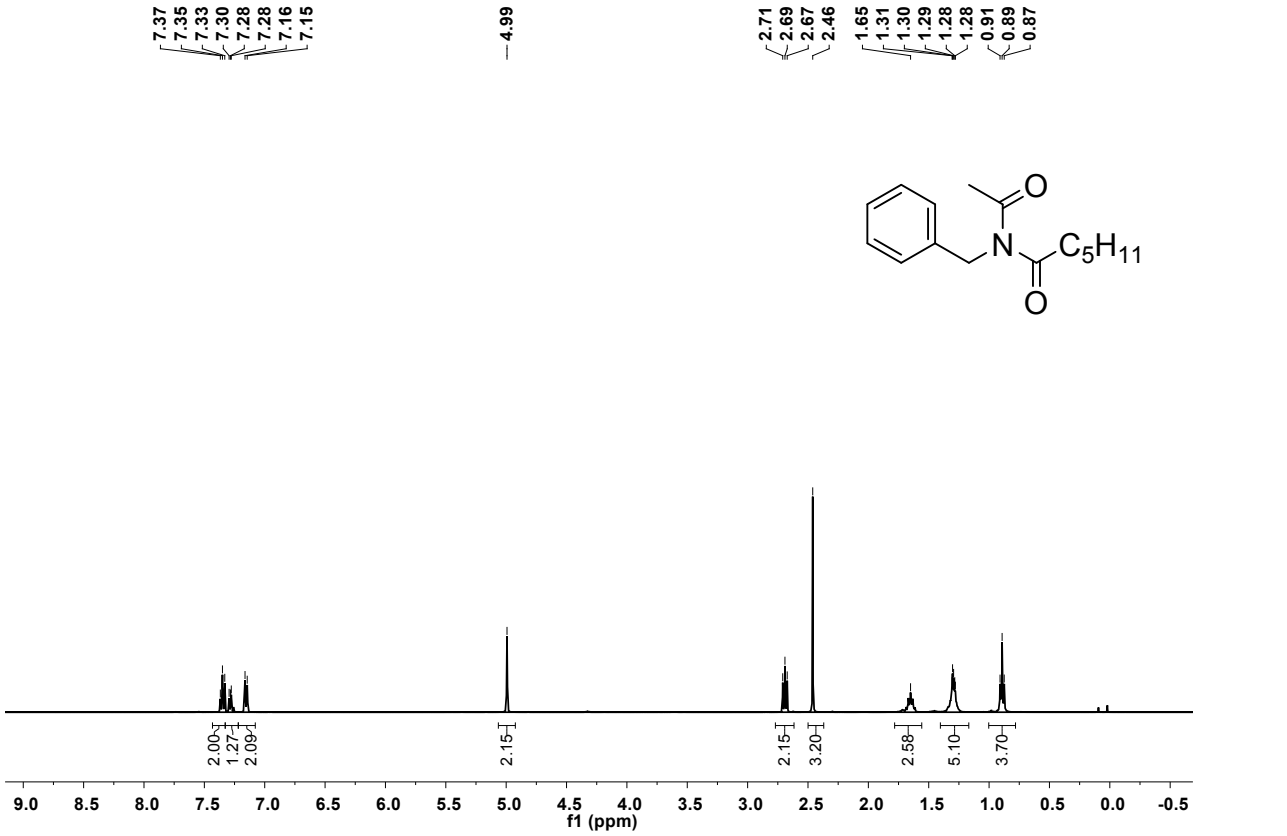
N
O
CF3
3.81
4.94
2.22
3.02
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.013
172.837
139.014
136.658
128.611
128.146
127.544
127.227
125.620
49.043
26.146
O
N
O
CF3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3al

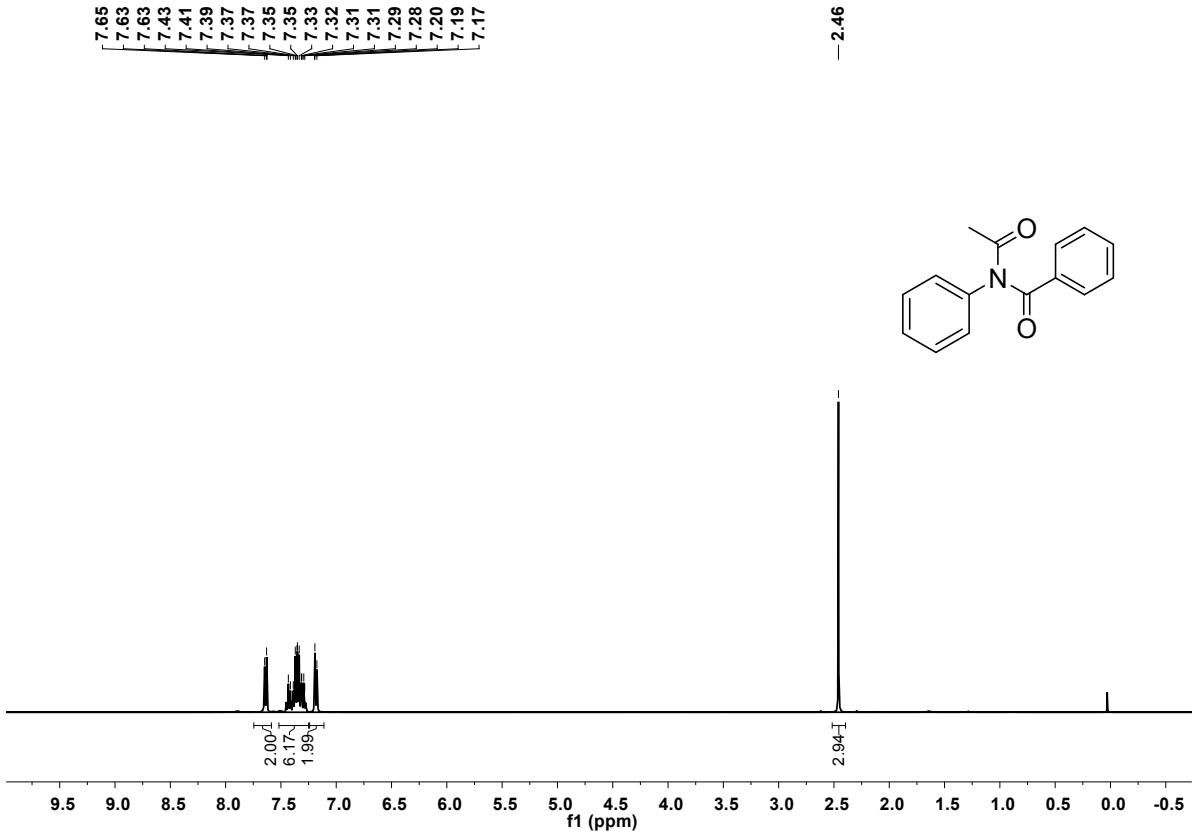

7.588
7.583
7.570
7.566
7.283
7.280
7.267
7.249
6.922
6.900
5.003
3.855
2.114
OMe
O
N
O
1.98
5.11
2.14
1.94
2.99
2.83
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
173.848
173.010
163.312
137.396
131.074
128.489
127.896
127.691
127.372
114.099
55.503
49.448
26.116
OMe
O
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

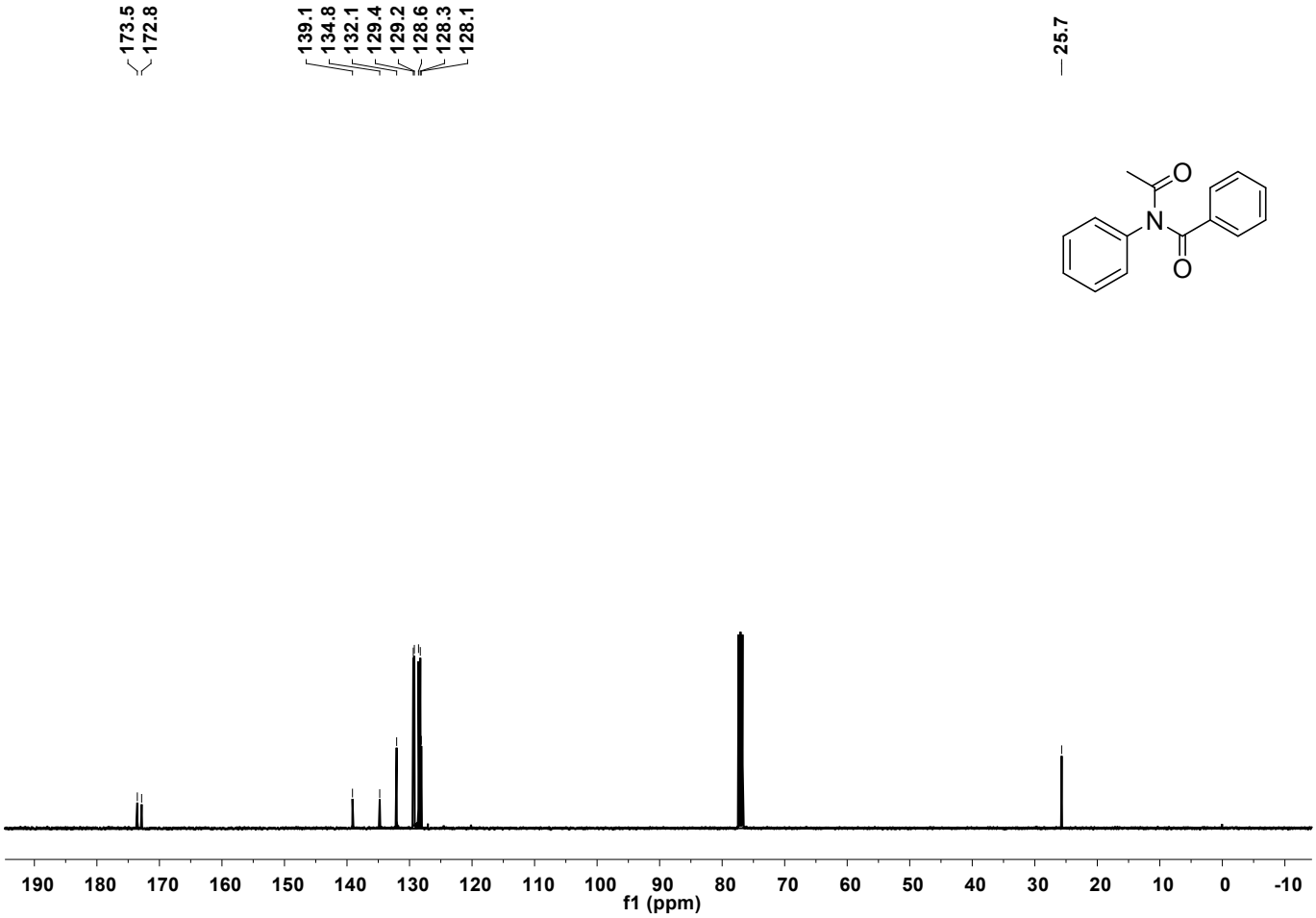
3am


7.37
7.35
7.33
7.30
7.28
7.28
7.16
7.15
4.99
2.71
2.69
2.67
2.46
1.65
1.31
1.30
1.29
1.28
1.28
0.91
0.89
0.87
O
N
C5H11
O
2.00
1.27
2.09
2.15
2.15
3.20
2.58
5.10
3.70
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


176.5
173.6
137.1
128.8
127.4
126.1
47.2
37.8
31.2
26.8
24.5
22.4
13.9
O
N
C5H11
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ba

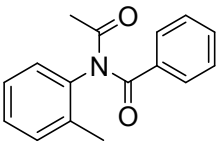

7.65
7.63
7.63
7.43
7.41
7.39
7.37
7.37
7.35
7.35
7.33
7.32
7.31
7.31
7.29
7.28
7.20
7.19
7.17
2.46
2.00
6.17
1.99
2.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

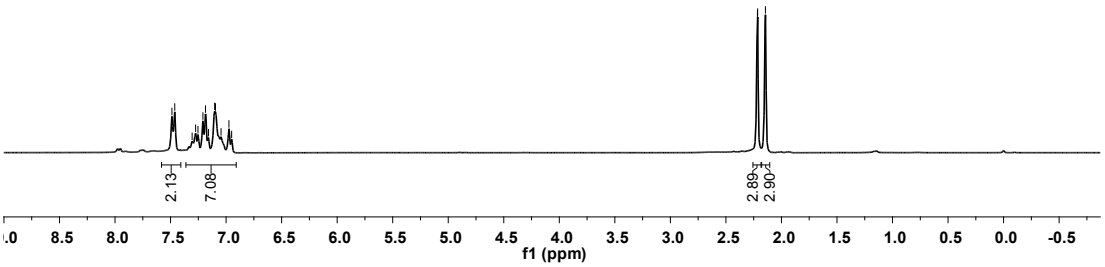

173.5
172.8
139.1
134.8
132.1
129.4
129.2
128.6
128.3
128.1
25.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

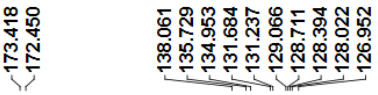
3ca


7.49
7.46
7.31
7.27
7.25
7.21
7.19
7.16
7.10
7.10
7.05
6.97
6.95

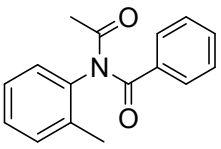

2.22
2.21
2.14

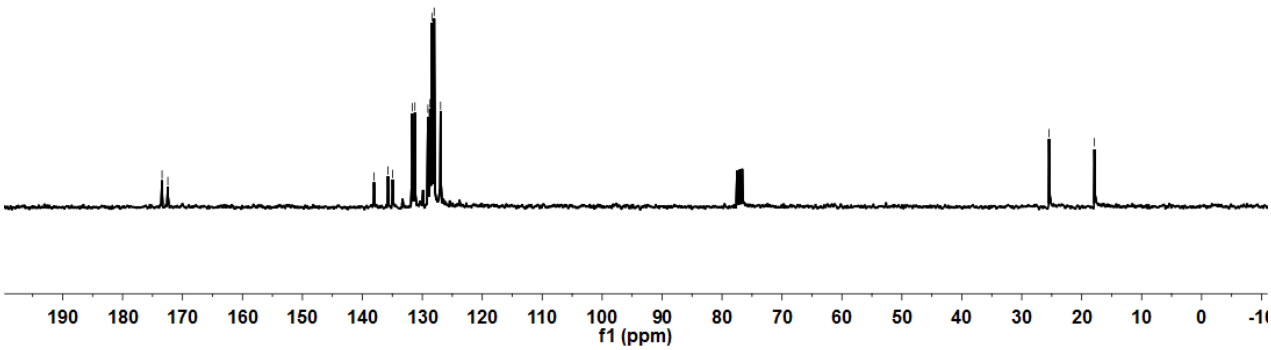

O
N
O


2.13
7.08
2.89
2.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

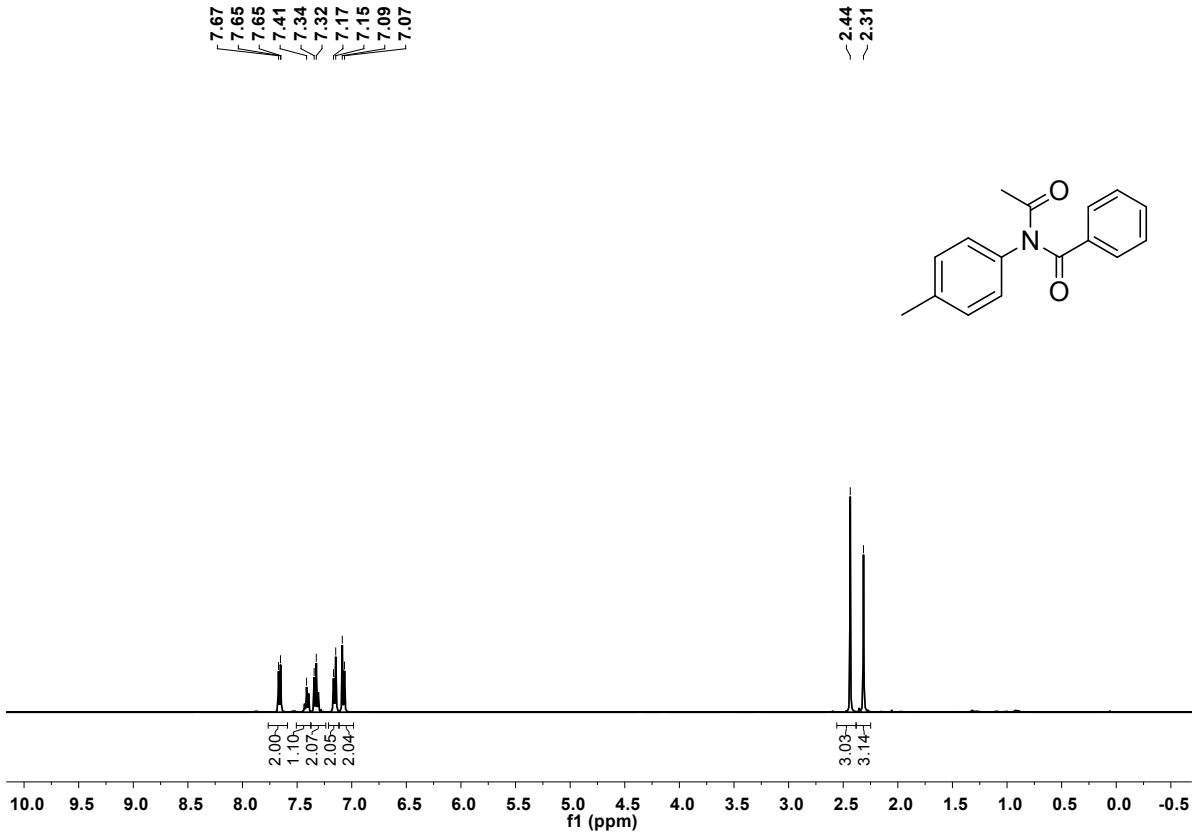

173.418
172.450
138.061
135.729
134.953
131.684
131.237
129.066
128.711
128.394
128.022
126.952

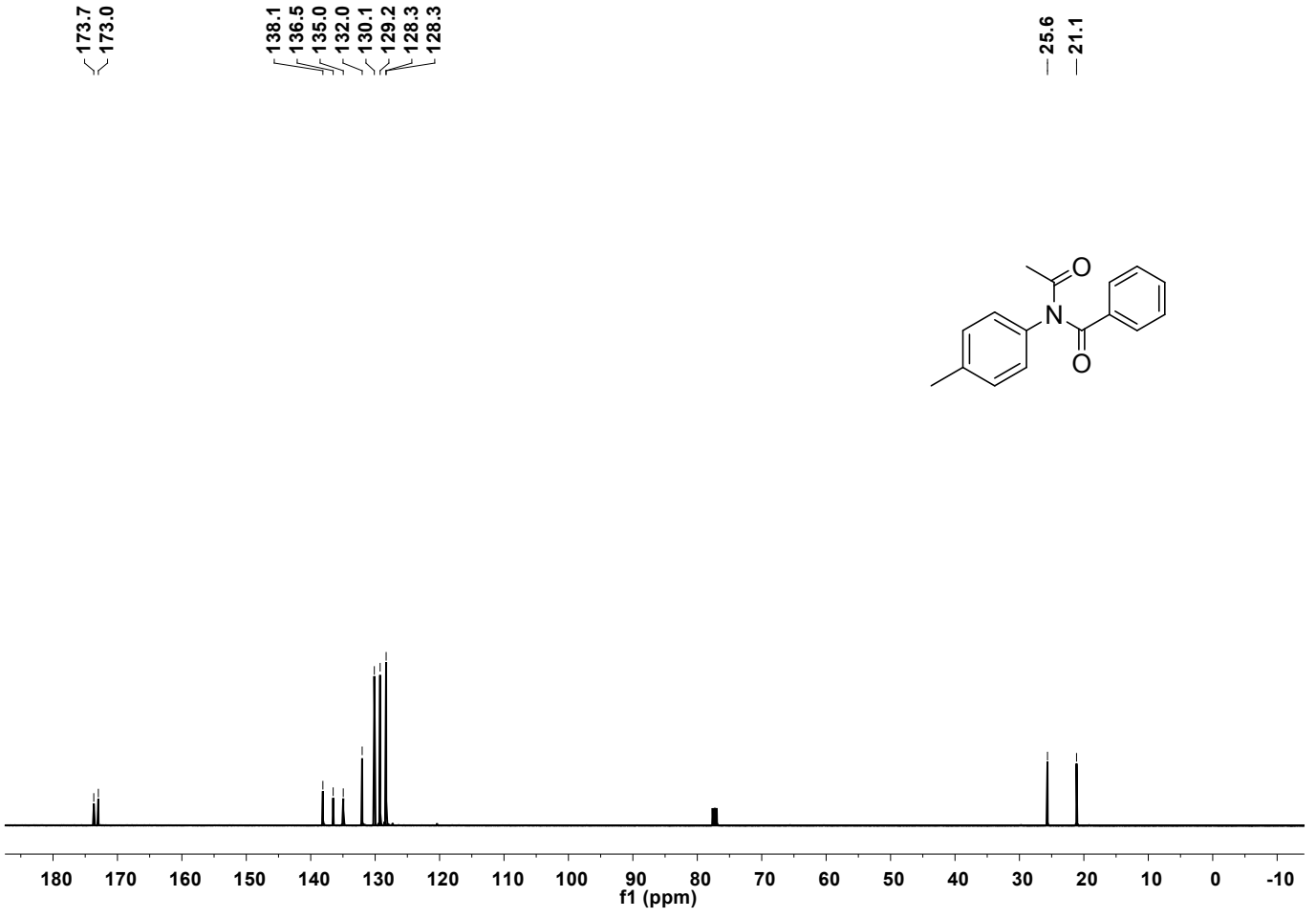

25.442
17.871


O
N
O

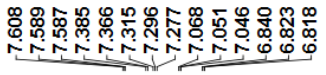

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3da


7.67
7.65
7.65
7.41
7.34
7.32
7.17
7.15
7.09
7.07
2.44
2.31
O
N
O
2.00
1.10
2.07
2.05
2.04
3.03
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

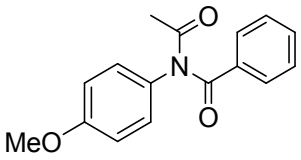

173.7
173.0
138.1
136.5
135.0
132.0
130.1
129.2
128.3
128.3
25.6
21.1
O
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

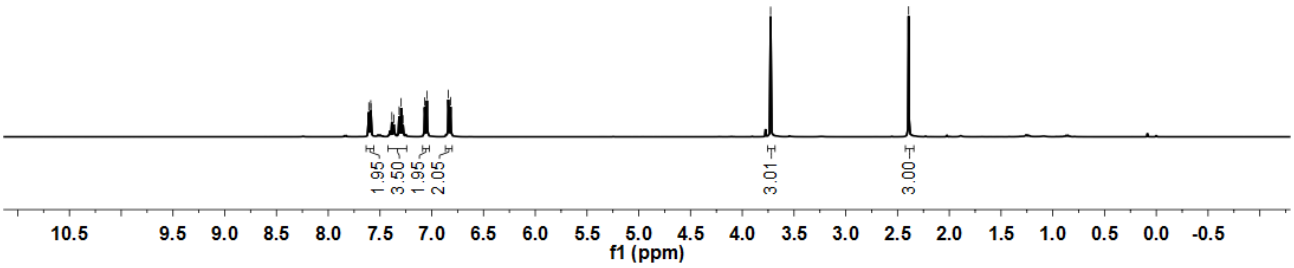
3ea


7.608
7.589
7.587
7.385
7.366
7.315
7.296
7.277
7.068
7.051
7.046
6.840
6.823
6.818

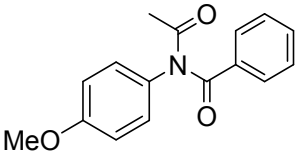

3.726

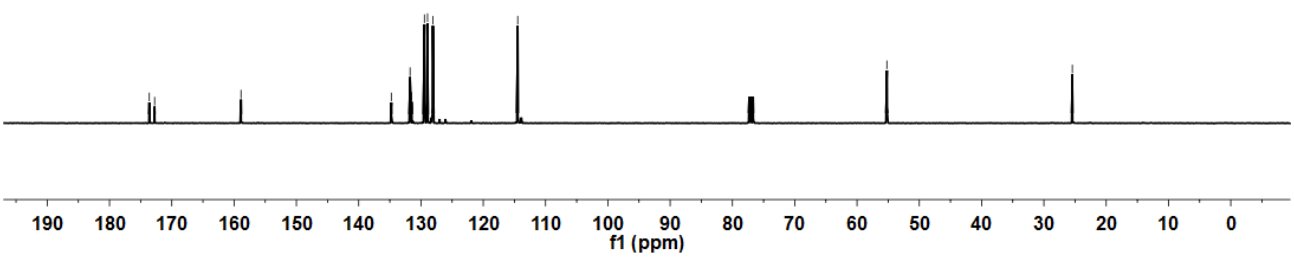
2.393


O
N
O
MeO

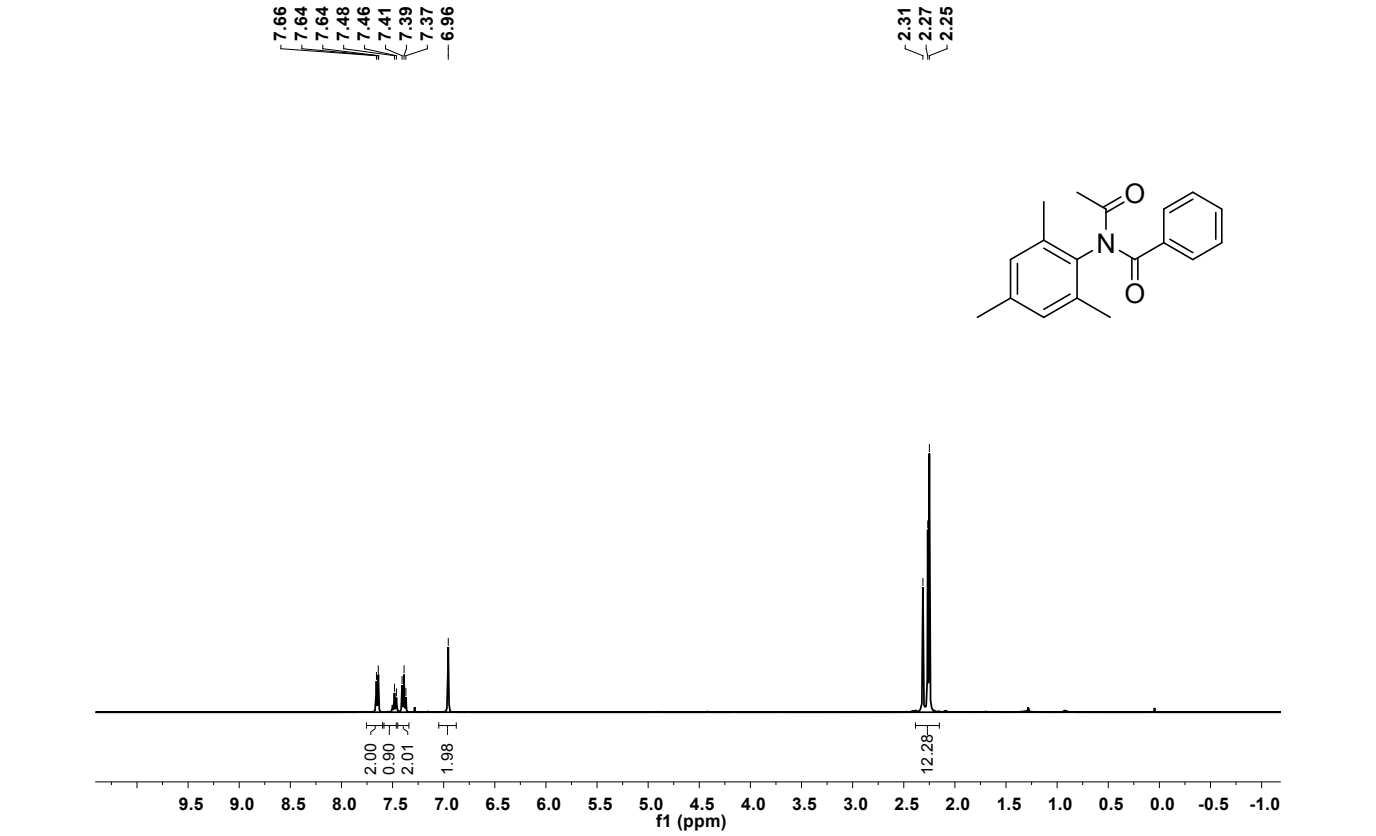

1.95
3.50
1.95
2.05
3.01
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

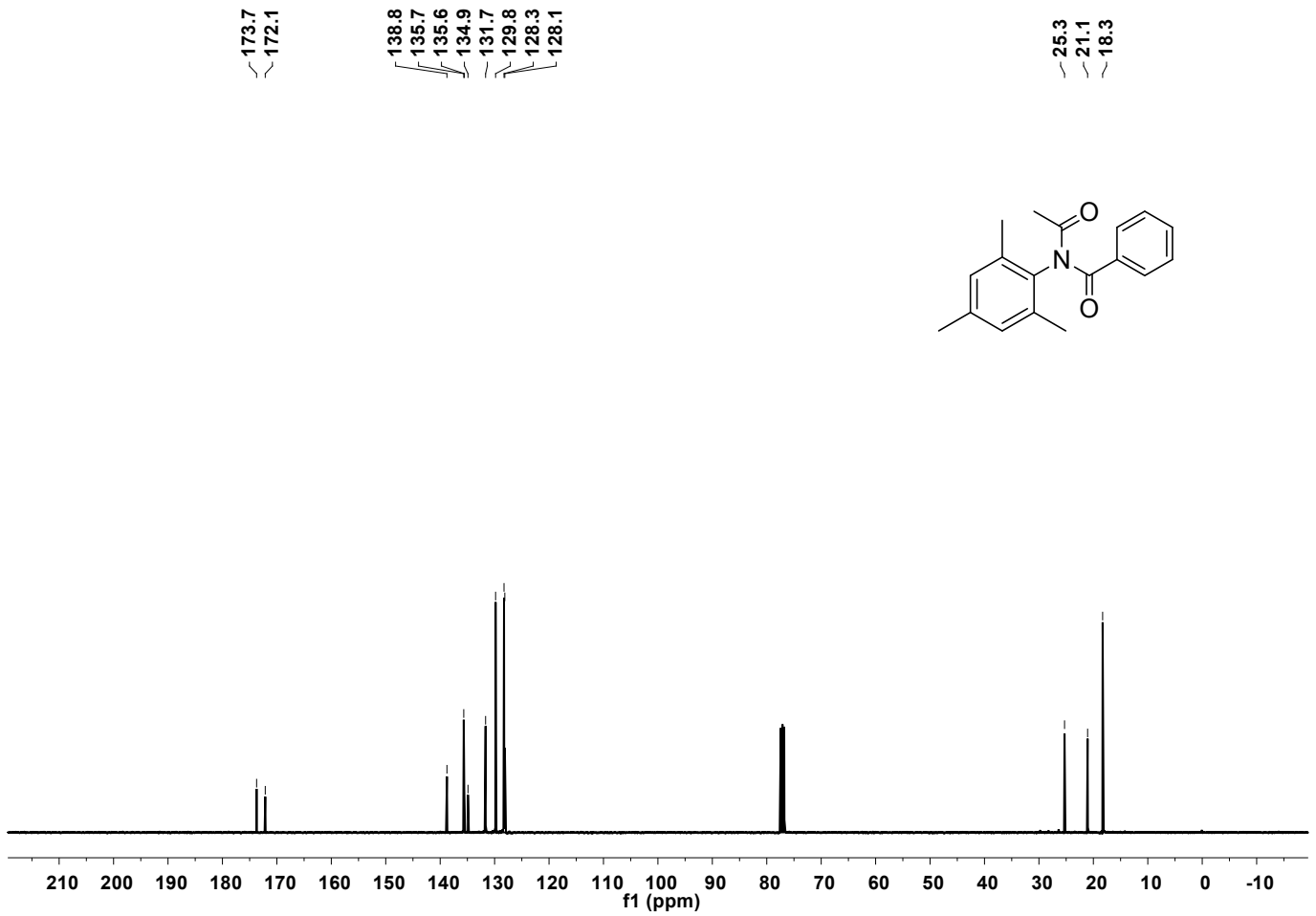

173.608
172.754
158.887
134.757
131.749
131.519
129.447
128.947
128.088
114.469
55.208
25.436


O
N
O
MeO

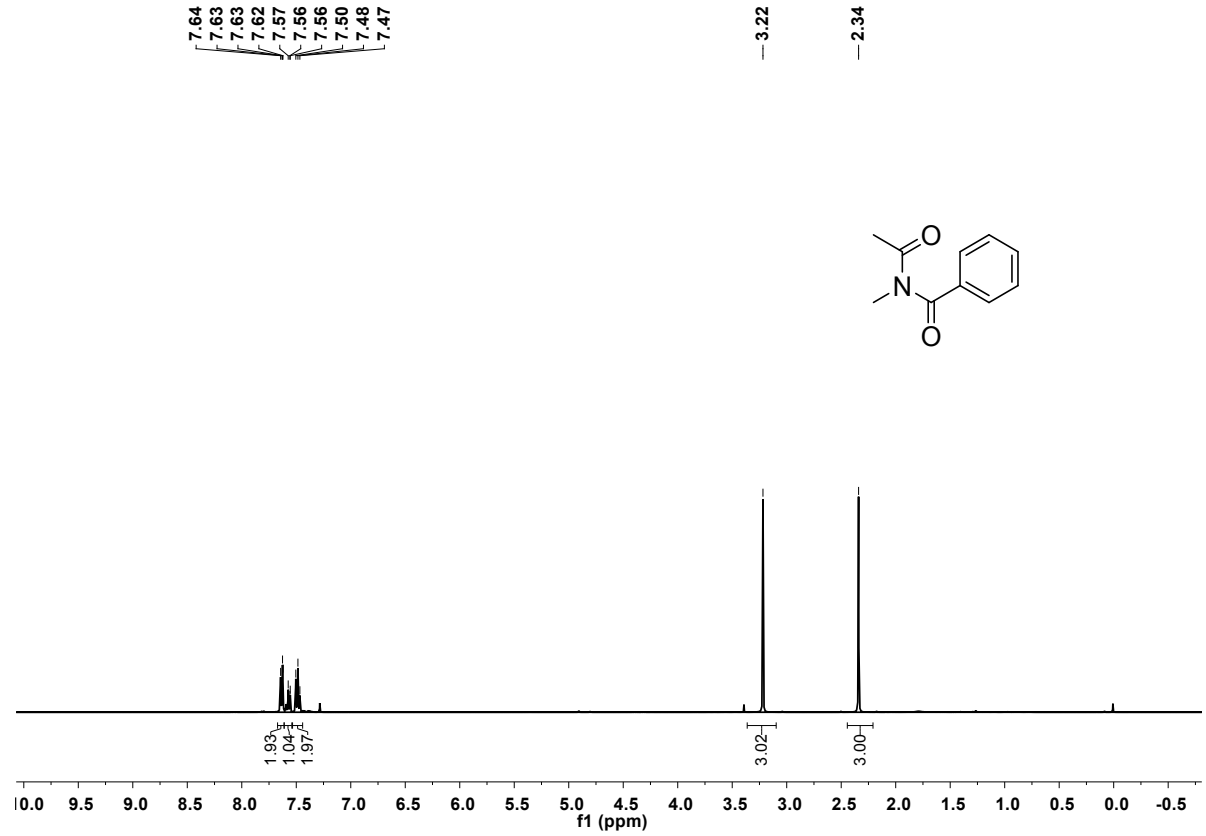

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

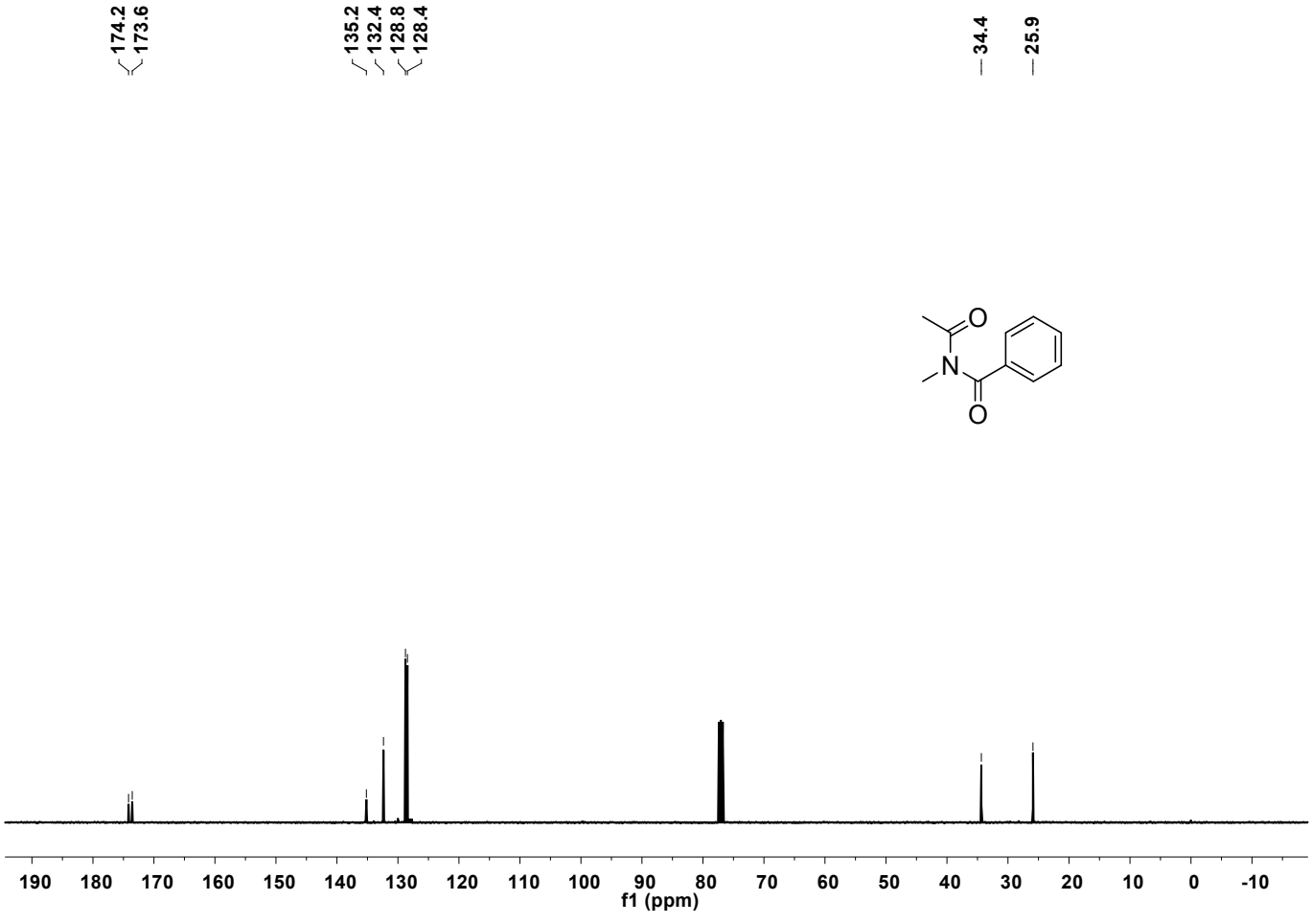
3fa


7.66
7.64
7.64
7.48
7.46
7.41
7.39
7.37
6.96
2.31
2.27
2.25
O
N
O
2.00
0.90
2.01
1.98
12.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

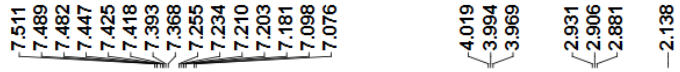

173.7
172.1
138.8
135.7
135.6
134.9
131.7
129.8
128.3
128.1
25.3
21.1
18.3
O
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

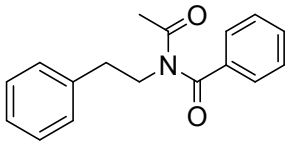
3ga

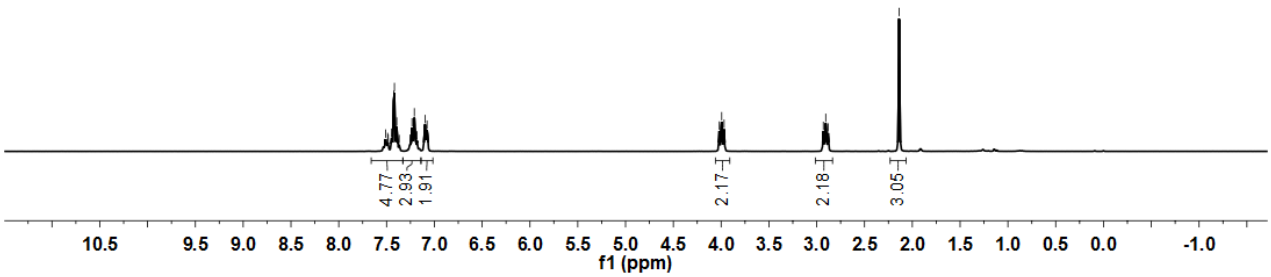

7.64
7.63
7.63
7.62
7.57
7.56
7.56
7.50
7.48
7.47
3.22
2.34
O
N
O
1.93
1.04
1.97
3.02
3.00
f1 (ppm)


174.2
173.6
135.2
132.4
128.8
128.4
34.4
25.9
O
N
O
f1 (ppm)

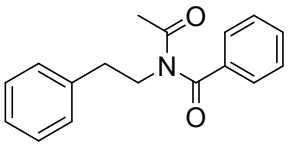
3ha

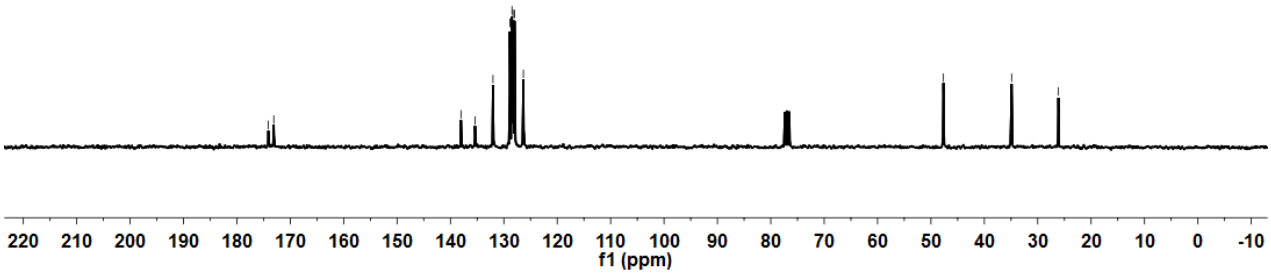

7.511
7.489
7.482
7.447
7.425
7.418
7.393
7.368
7.255
7.234
7.210
7.203
7.181
7.098
7.076
4.019
3.994
3.969
2.931
2.906
2.881
2.138


O
N
O

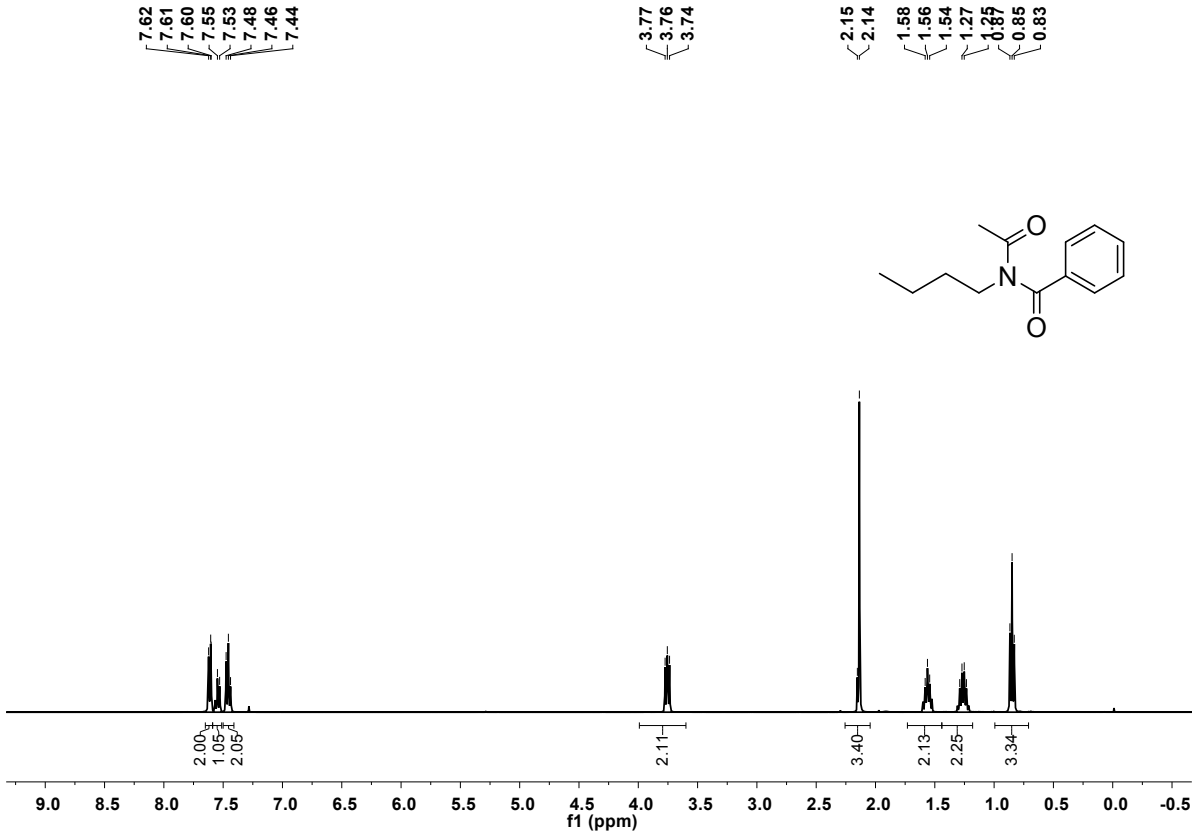

4.77
2.93
1.91
2.17
2.18
3.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

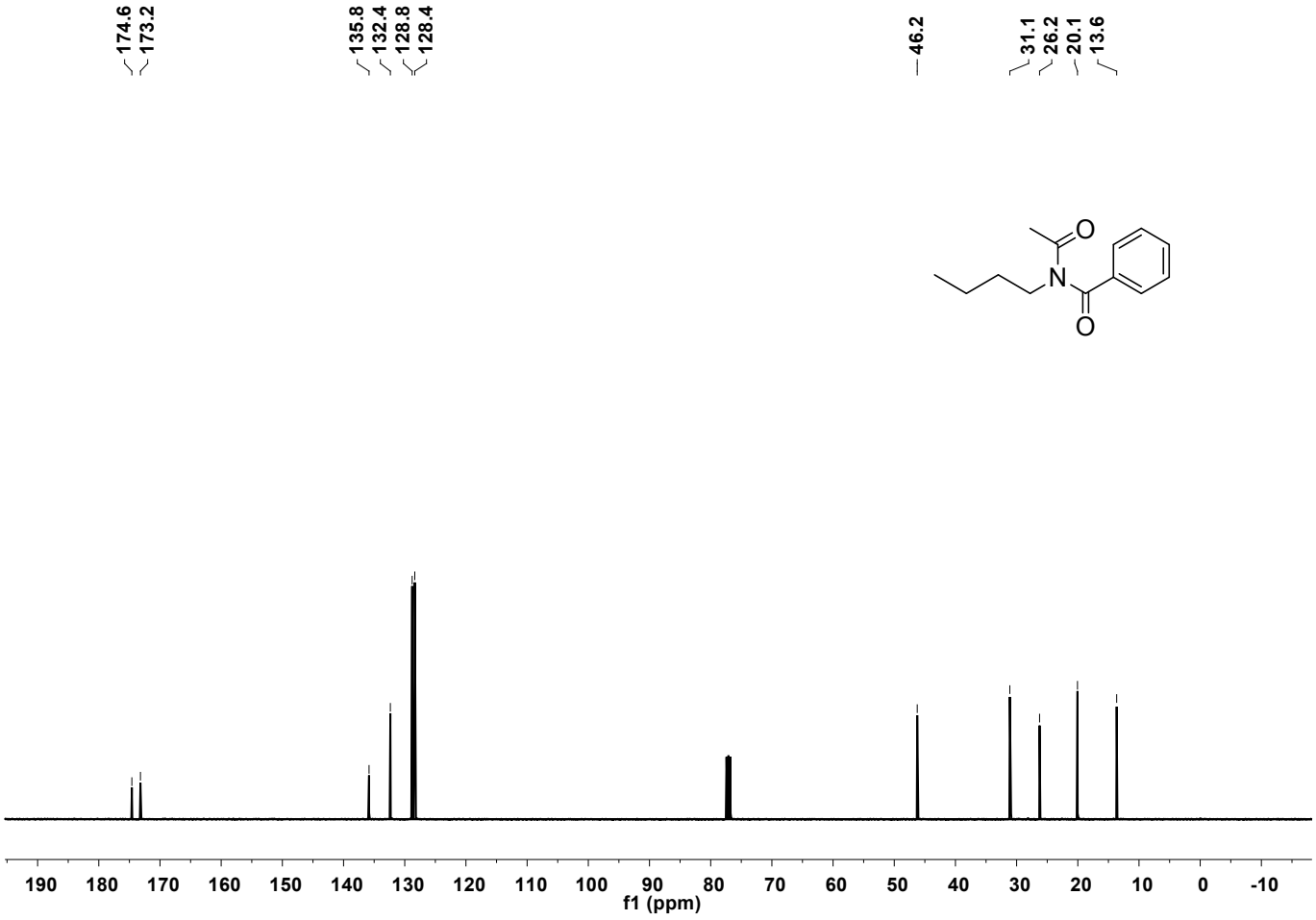

174.100
173.094
138.032
135.397
132.030
128.865
128.478
128.290
128.001
126.342
47.658
34.895
26.118


O
N
O

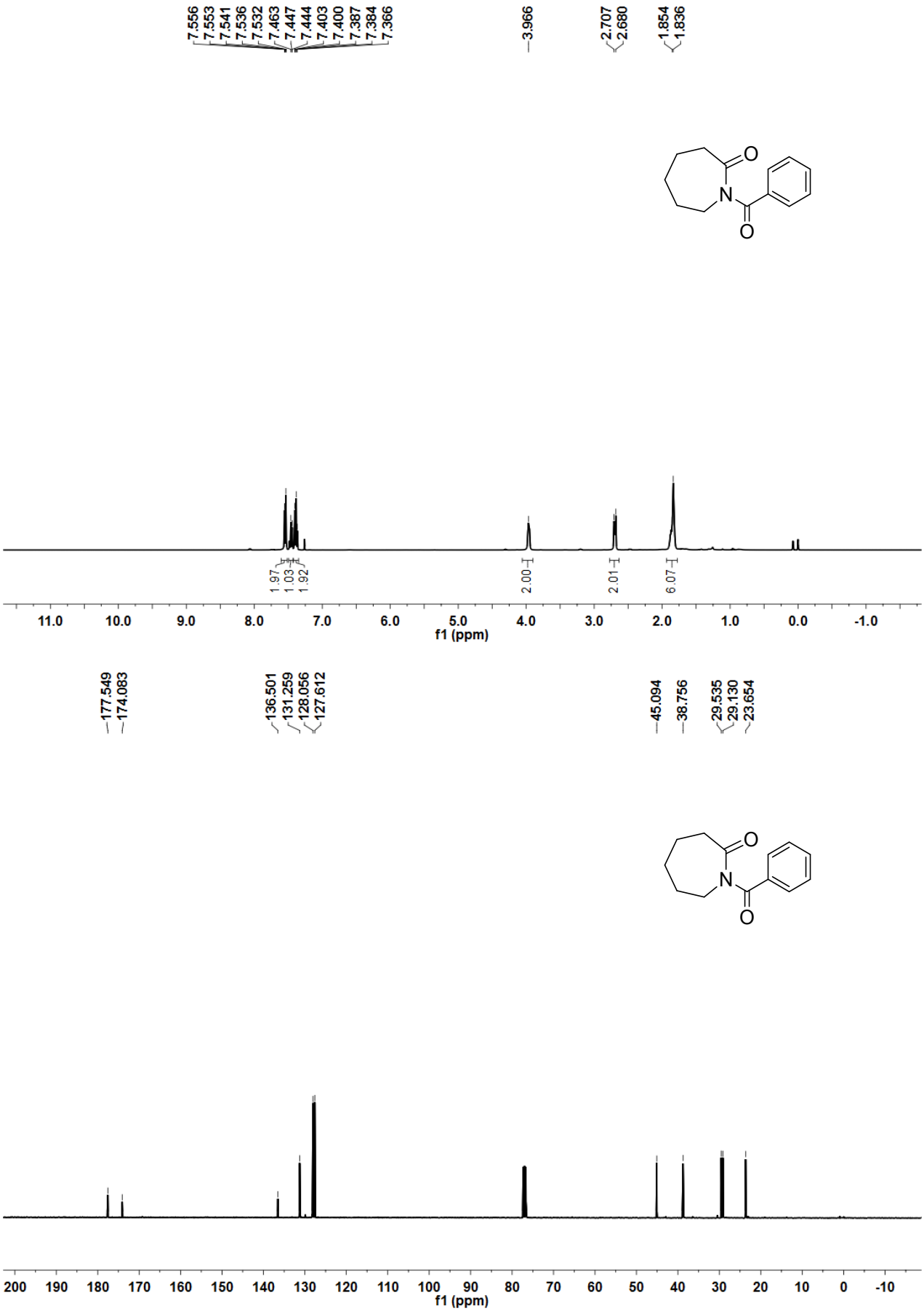

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3ia

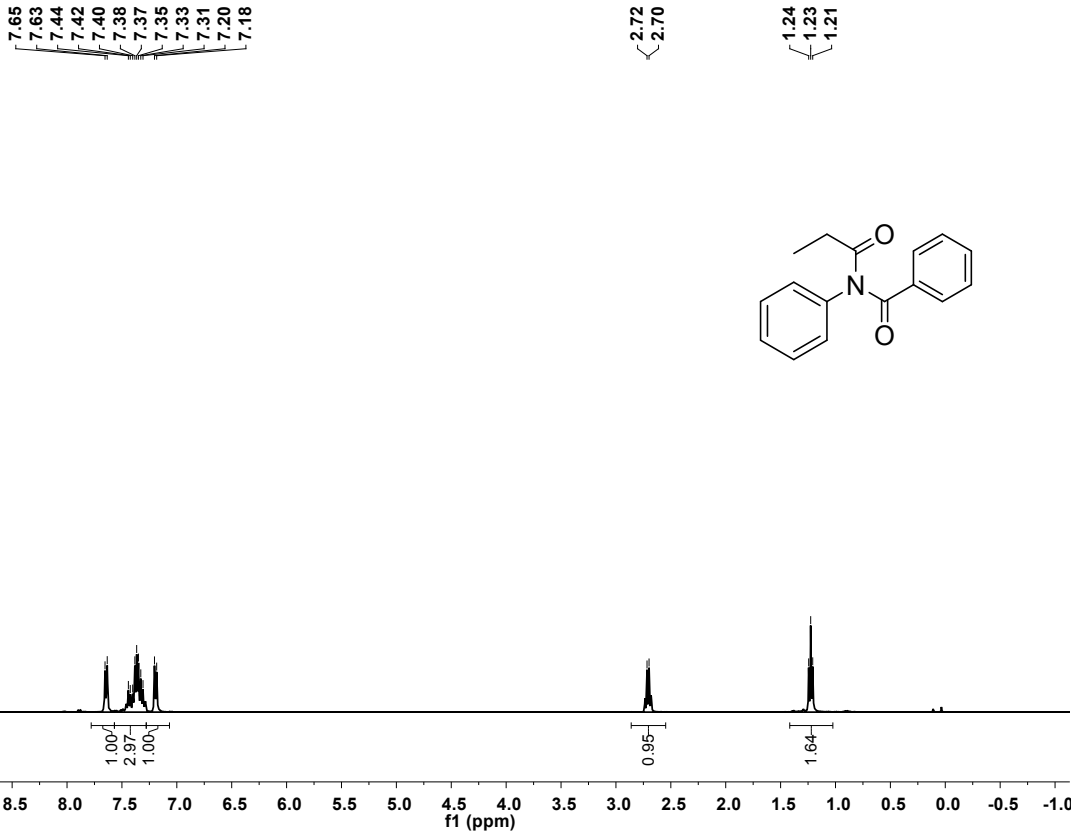

7.62
7.61
7.60
7.55
7.53
7.48
7.46
7.44
3.77
3.76
3.74
2.15
2.14
1.58
1.56
1.54
1.27
0.87
0.85
0.83
O
N
O
2.00
1.05
2.05
2.11
3.40
2.13
2.25
3.34
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

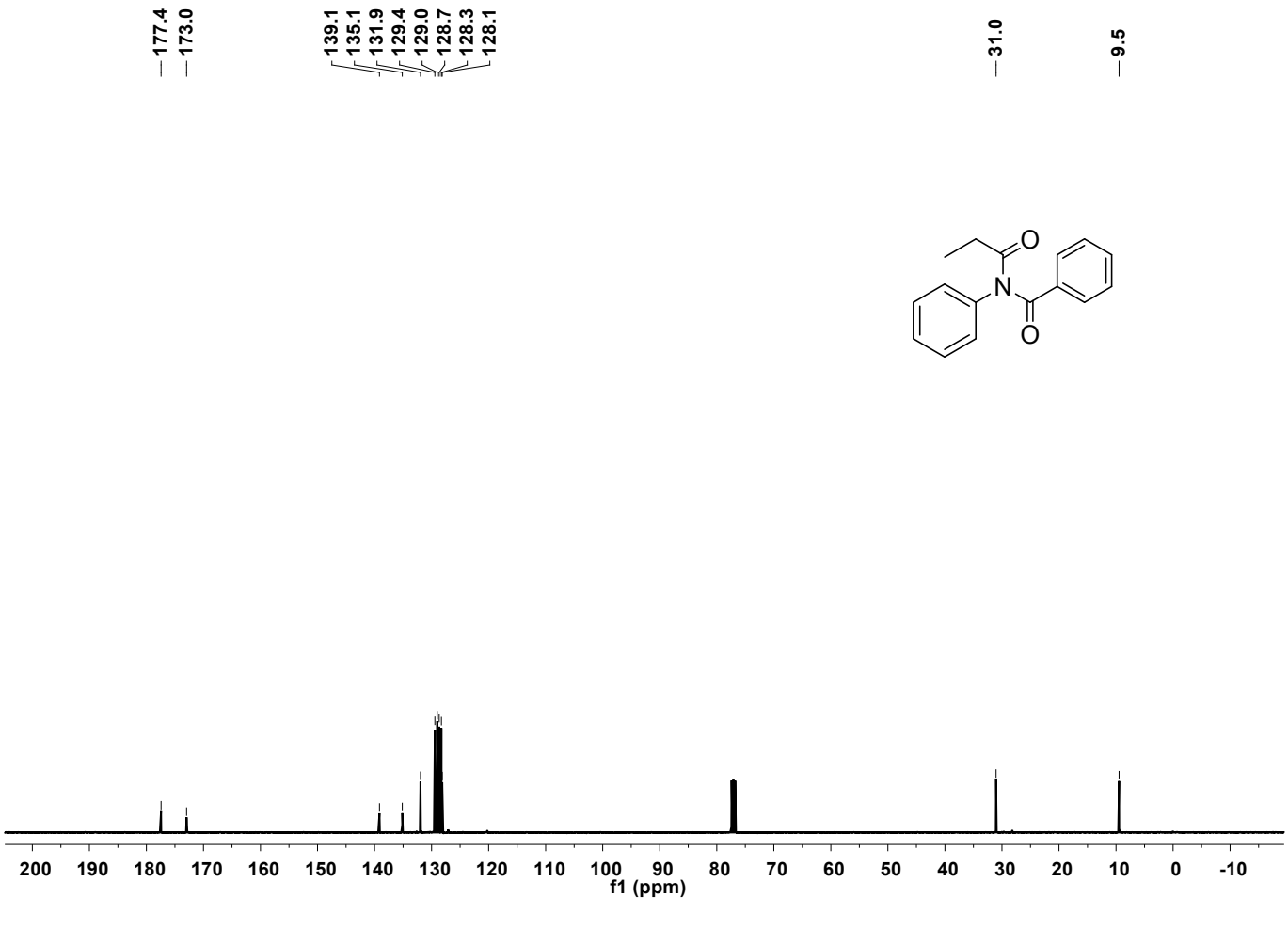

174.6
173.2
135.8
132.4
128.8
128.4
46.2
31.1
26.2
20.1
13.6
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

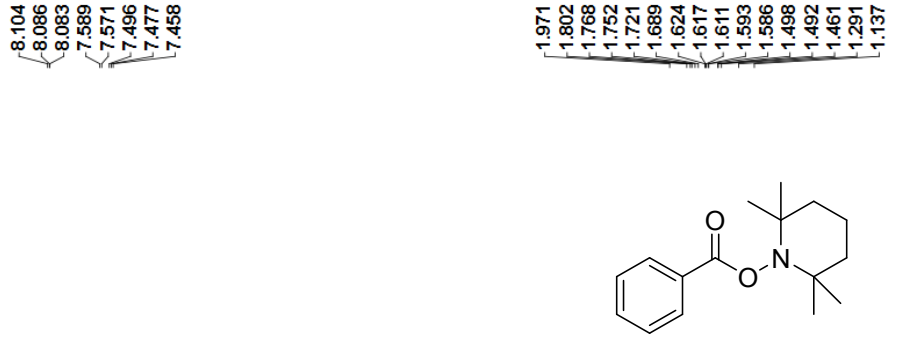
3ja

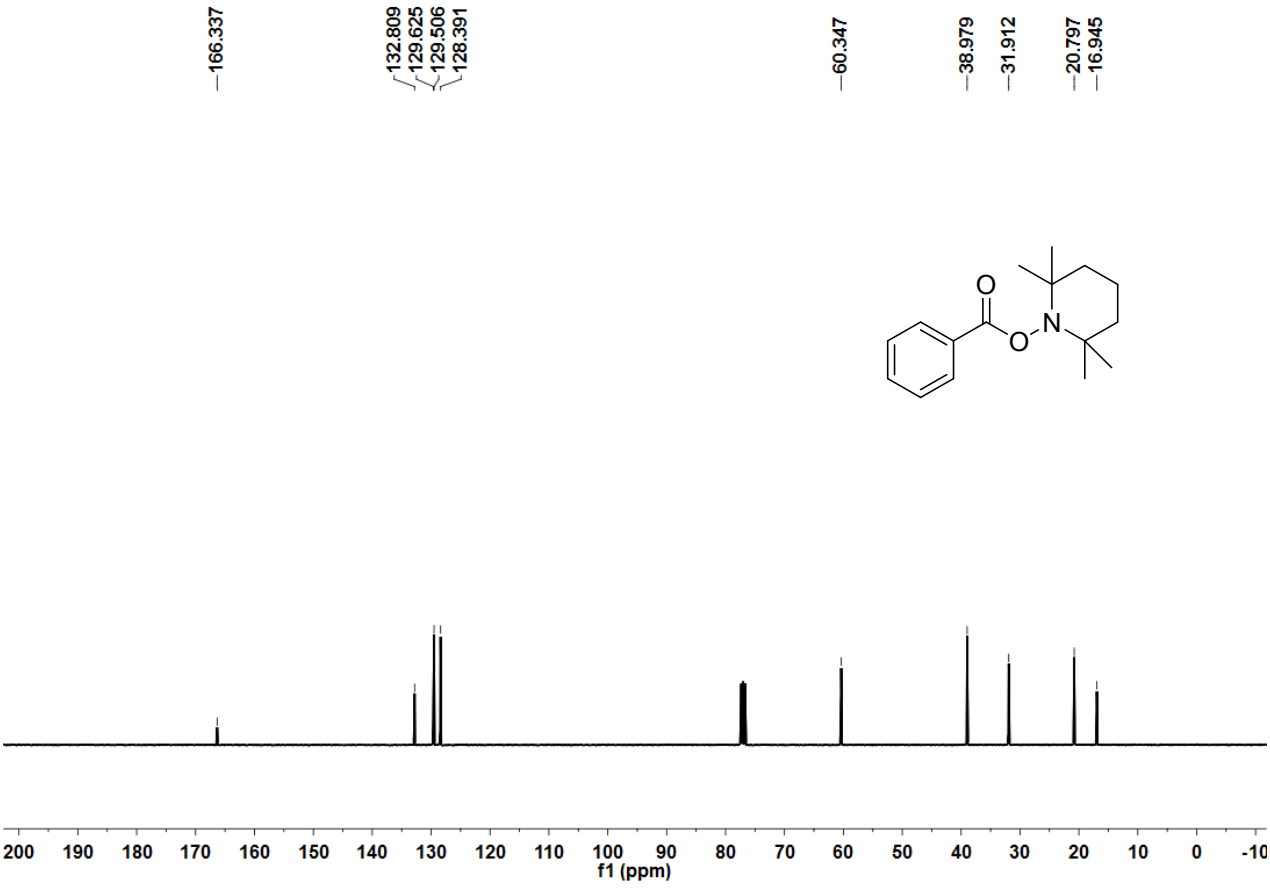

7.556
7.553
7.541
7.536
7.532
7.463
7.447
7.444
7.403
7.400
7.387
7.384
7.366
3.966
2.707
2.680
1.854
1.836
O
N
O
1.97
1.03
1.92
2.00
2.01
6.07
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
177.549
174.083
136.501
131.259
128.056
127.612
45.094
38.756
29.535
29.130
23.654
O
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3la


7.65
7.63
7.44
7.42
7.40
7.38
7.37
7.35
7.33
7.31
7.20
7.18
2.72
2.70
1.24
1.23
1.21
O
N
O
1.00
2.97
1.00
0.95
1.64
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


177.4
173.0
139.1
135.1
131.9
129.4
129.0
128.7
128.3
128.1
31.0
9.5
O
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.104
8.086
8.083
7.589
7.571
7.496
7.477
7.458
1.971
1.802
1.768
1.752
1.721
1.689
1.624
1.617
1.611
1.593
1.586
1.498
1.492
1.461
1.291
1.137
O
N
O
1.89
0.92
1.94
6.25
6.02
6.04
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.337
132.809
129.625
129.506
128.391
60.347
38.979
31.912
20.797
16.945
O
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1 W. Liu, Y. Li, K. Liu, Z. Li, *J. Am. Chem. Soc.* **2011**, *5*, 10756-10759.