Supporting Information

Rh^{III}-catalyzed site-selective C–H amidation with nitrone as a traceless directing group: an approach to functionalized arylaldehydes

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1. General considerations

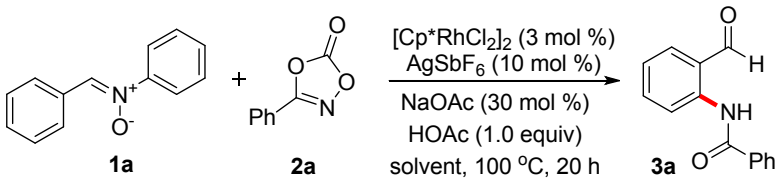
All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz and 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

Arylnitrones were prepared according to reported methods,[1] and they must be recrystallized from ethanol/petroleum ether before use. Dioxazolones were prepared according to reported methods.[2] All chemicals were purchased from commercial suppliers, Aldrich of USA, or Shanghai Chemical Company of China. All the solvents were dried and freshly distilled in N_2 prior to use. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

2. Typical procedure for the reaction of 1a with 2a

A 10 mL Schlenk tube was charged with (Z)-*N*-benzylideneaniline oxide (**1a**, 39.4 mg, 0.20 mmol), 3-phenyl-1,4,2-dioxazol-5-one (**2a**, 40.8 mg, 0.25 mmol), $[Cp^*RhCl_2]_2$ (3.7 mg, 3 mol %), $AgSbF_6$ (6.9 mg, 0.02 mmol), NaOAc (4.9 mg, 0.06 mmol), HOAc (12.0 mg, 0.20 mmol). Then freshly distilled 1,2-dichloroethane (DCE, 1.0 mL) was injected into the Schlenk tube under air atmosphere. The reaction tube was placed in an oil bath. After the reaction was carried out at 100 ^{o}C for 20 h, the sealed tube was cooled to room temperature, detected by TLC, and extracted with dichloromethane (DCM, 3×5.0 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1 to 20:1), affording the desired product **3a** as a white solid (36.0 mg, 80% yield).

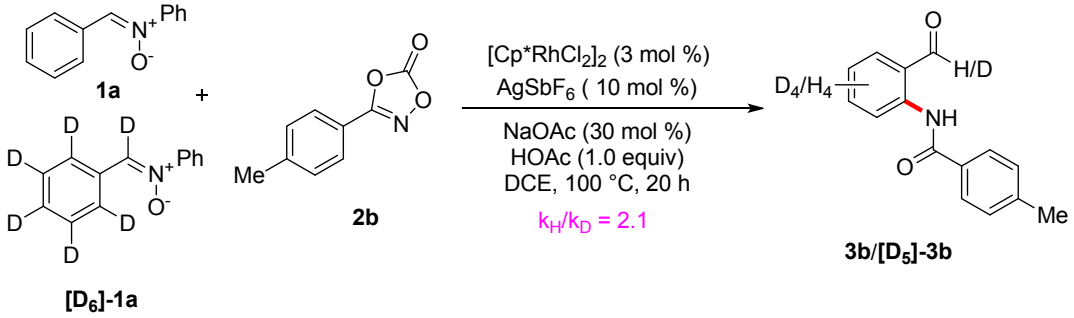
3. Optimization of the solvent on the model reaction



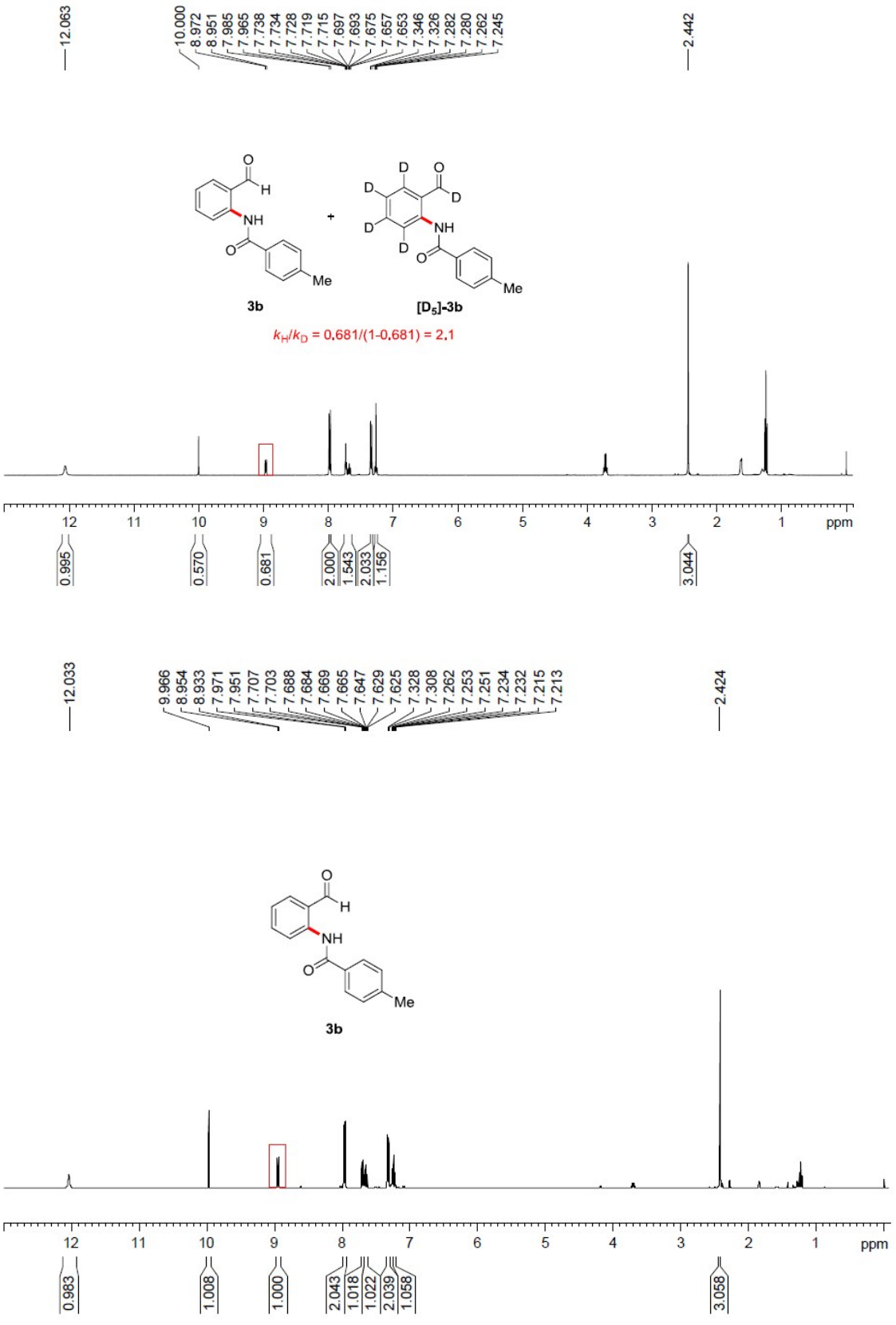
entry	solvent	yield (%)[b]
1	DCE	80
2	MeOH	n.r.
3	CH_3CN	7
4	THF	10
5	dioxane	trace
6	toluene	43
7	$CHCl_3$	65

[a]Reaction conditions: (*Z*)-*N*-benzylideneaniline oxide (**1a**, 0.20 mmol), 3-phenyl-1,4,2-dioxazol-5-one (**2a**, 0.25 mmol), $[Cp^*RhCl_2]_2$ (3 mol %), $AgSbF_6$ (10 mol %), NaOAc (30 mol %), HOAc (1.0 equiv), solvent (1.0 mL), 100 °C for 20 h. [b]Isolated yield.

4. Kinetic isotope effect (KIE) experiments

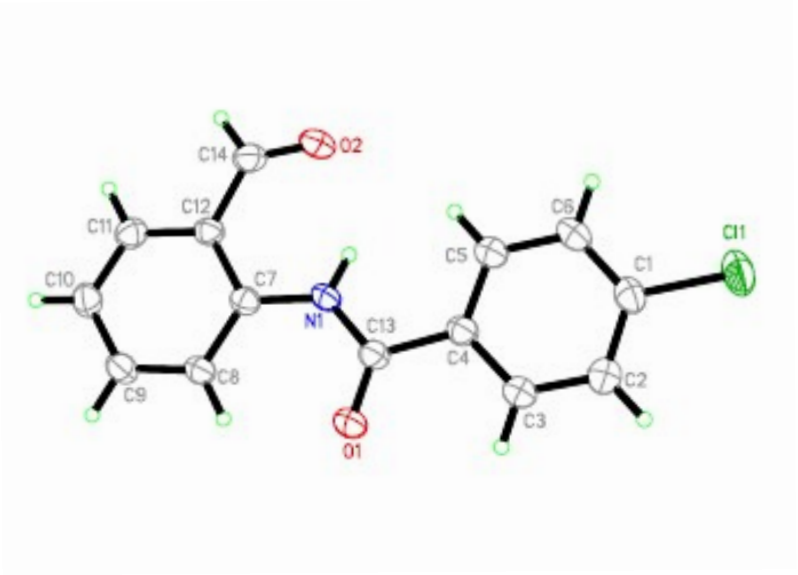


A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with **1a** (0.10 mmol), [D_6]-**1a** (0.10 mmol), 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**2b**, 0.25 mmol), $[Cp^*RhCl_2]_2$ (3.7 mg, 3 mol %), $AgSbF_6$ (6.9 mg, 10 mol %), NaOAc (4.9 mg, 0.06 mmol), HOAc (12.0 mg, 0.20 mmol), and DCE (1.0 mL). The reaction vessel was placed in an oil bath. After the reaction was carried out at 100 °C for 20 h, it was cooled to room temperature, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1 to 20:1) to give the desired product **3b**/[D_5]-**3b**. The KIE value was determined by ^{1}H NMR of **3b** and [D_5]-**3b**.

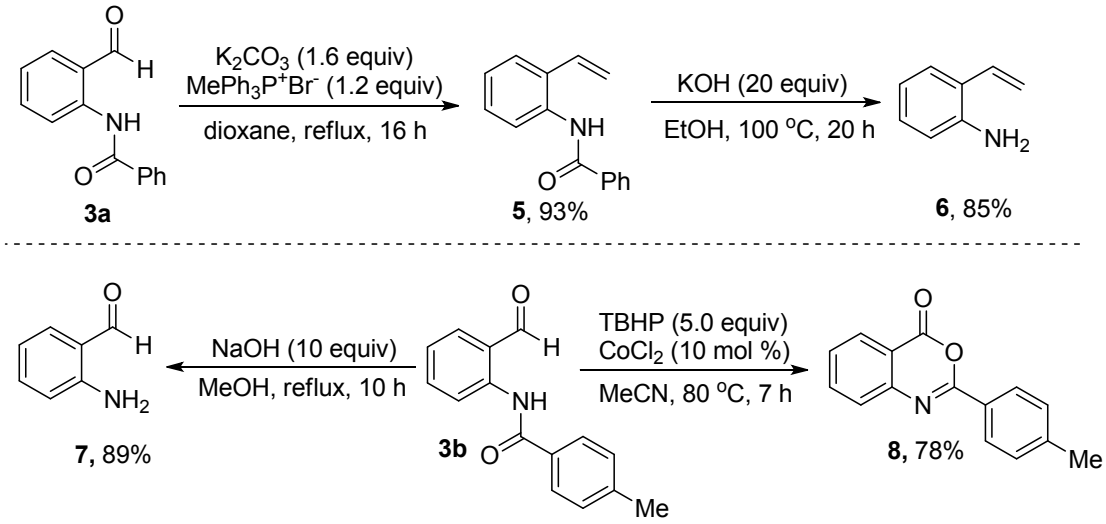


Scheme S1 Kinetic Isotope Effect (KIE) Experiments

5. X-ray single crystal structure of 3e (CCDC Number: 1553921)



6. Design for the transformation of 3a/3b



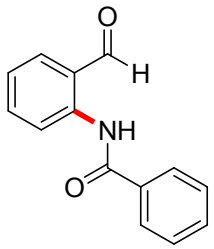
(1) A 10 mL Schlenk tube was charged with **3a** (45.0 mg, 0.2 mmol), K_2CO_3 (1.6 equiv), $MePh_3P^+Br^-$ (1.2 equiv). Then dioxane (1.0 mL) was injected into the Schlenk tube under air atmosphere. The reaction mixture was refluxed for 16h, it was cooled to room temperature, detected by TLC, and extracted with dichloromethane (DCM, 3×5.0 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1 to 9:1), affording the desired product **5** as a white solid (41.4 mg, 93% yield).

(2) A 10 mL Schlenk tube was charged with **5** (44.6 mg, 0.2 mmol), KOH (20 equiv). Then EtOH (1.0 mL) was injected into the Schlenk tube under air atmosphere. The reaction tube was placed in an oil bath. After the reaction was carried out at 100 ^{o}C for 20 h, it was cooled to room temperature and detected by TLC, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1 to 7:1), affording the desired product **6** as a brown oil (20.2 mg, 85% yield).

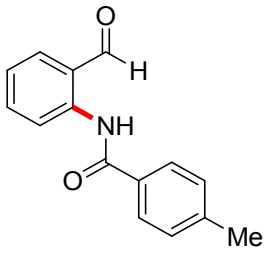
(3) A 10 mL Schlenk tube was charged with **3b** (47.8 mg, 0.2 mmol), NaOH (10 equiv). Then MeOH (1.0 mL) was injected into the Schlenk tube under air atmosphere. The reaction mixture was refluxed for 10 h, it was cooled to room temperature and detected by TLC, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1 to 7:1), affording the desired product **7** as a white solid (21.6 mg, 89% yield).

(4) A 10 mL Schlenk tube was charged with **3b** (47.8 mg, 0.2 mmol), $CoCl_2$ (10 mol %), TBHP (5.0 equiv). Then anhydrous MeCN (1.0 mL) was injected into the Schlenk tube under air atmosphere. The reaction tube was placed in an oil bath. After the reaction was carried out at 80 ^{o}C for 7h, it was cooled to room temperature, detected by TLC. The solvent was evaporated under reduced pressure. The residue was mixed with water (20 mL), and the resulting solution was extracted with ethyl acetate (3 × 5 mL). The combined organic phases were washed with brine and dried with anhydrous $MgSO_4$, and concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1 to 9:1), affording the desired product **8** as a white solid (37.0 mg, 78% yield).

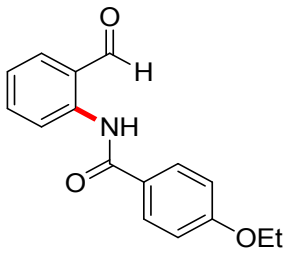
7. Characterization data for the products



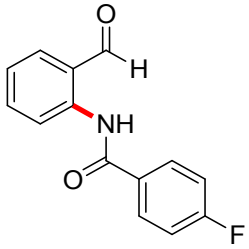
***N*-(2-Formylphenyl)benzamide (3a):** White solid; 36.0 mg, 80% yield; m.p. 69–71 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.09 (s, 1H), 10.00 (s, 1H), 8.97 (d, *J* = 8.4 Hz, 1H), 8.09–8.07 (m, 2H), 7.75–7.73 (m, 1H), 7.71–7.66 (m, 1H), 7.59–7.52 (m, 3H), 7.30–7.26 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.84, 166.10, 141.23 136.34, 136.15, 134.31, 132.18, 128.85, 127.49, 123.01, 121.99, 119.96. The NMR data agree with those in a literature report.[4]



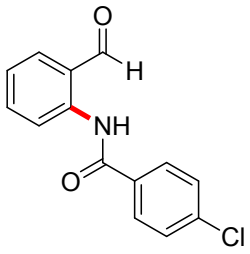
***N*-(2-Formylphenyl)-4-methylbenzamide (3b):** White solid; 34.4 mg, 72% yield; m.p. 83–85 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.03 (s, 1H), 9.97 (s, 1H), 9.94 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.71–7.68 (m, 1H), 7.67–7.63 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25–7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.76, 166.06, 142.73, 141.32, 136.25, 136.09, 131.48, 129.48, 127.47, 122.80, 121.89, 119.87, 21.44. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{15}H_{14}NO_2]^+$: 240.1019, Found: 240.1021. The NMR data agree with those in a literature report.[5]



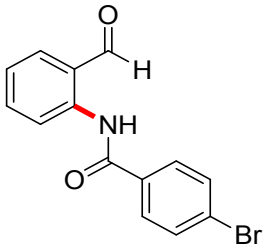
4-Ethoxy-*N*-(2-formylphenyl)benzamide (3c): White solid; 35.0 mg, 65% yield; m.p. 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.02 (s, 1H), 10.01 (s, 1H), 8.96 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.74–7.72 (m, 1H), 7.70–7.66 (m, 1H), 7.27–7.24 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.86, 165.78, 162.27, 141.64, 136.37, 136.15, 129.48, 126.46, 122.71, 121.92, 119.93, 114.57, 63.75, 14.69. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{16}H_{16}NO_3]^+$: 270.1125, Found: 270.1129.



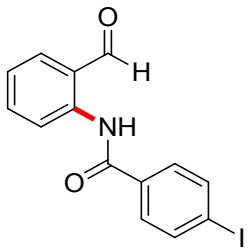
4-Fluoro-*N*-(2-formylphenyl)benzamide (3d): White solid; 34.4 mg, 71% yield; m.p. 90–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.06 (s, 1H), 10.00 (s, 1H), 8.93 (d, *J* = 8.5 Hz, 1H), 8.11–8.07 (m, 2H), 7.75–7.73 (m, 1H), 7.71–7.66 (m, 1H), 7.30–7.28 (m, 1H), 7.23–7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.97, 165.16 (d, *J* = 251.7 Hz), 164.95, 141.12, 136.30 (d, *J* = 23.0 Hz), 130.45 (d, *J* = 2.9 Hz), 129.97, 129.87, 123.12, 121.91, 119.87, 115.92 (d, *J* = 21.9 Hz). HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{14}H_{11}FNO_2]^+$: 244.0768, Found: 244.0771. The NMR data agree with those in a literature report.[5]



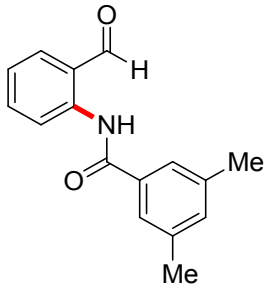
4-Chloro-*N*-(2-formylphenyl)benzamide (3e): White solid; 39.9 mg, 77% yield; m.p. 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.08 (s, 1H), 9.99 (s, 1H), 8.92 (d, *J* = 8.4 Hz, 1H), 8.02–8.00 (m, 2H), 7.75–7.72 (m, 1H), 7.70–7.66 (m, 1H), 7.52–7.49 (m, 2H), 7.30–7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.94, 164.98, 141.03, 138.56, 136.41, 136.16, 132.68, 129.12, 128.90, 123.22, 121.97, 119.94. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{14}H_{11}ClNO_2]^+$: 260.0473, Found: 260.0475. The NMR data agree with those in a literature report.[5]



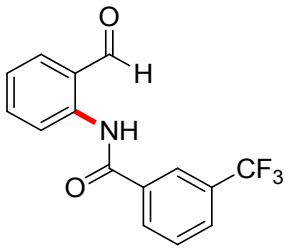
4-Bromo-*N*-(2-formylphenyl)benzamide (3f): White solid; 44.1 mg, 73% yield; m.p. 110–112 °C; ^{1}HNMR (400 MHz, $CDCl_3$) δ: 12.10 (s, 1H), 10.01 (s, 1H), 8.94 (d, *J* = 8.4 Hz, 1H), 7.96–7.94 (m, 2H), 7.77–7.74 (m, 1H), 7.72–7.68 (m, 3H), 7.32–7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.94, 165.05, 140.98, 136.41, 136.17, 133.10, 132.09, 129.04, 127.10, 123.23, 121.93, 119.90. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{14}H_{11}BrNO_2]^+$: 303.9968, Found: 303.9969. The NMR data agree with those in a literature report.[6]



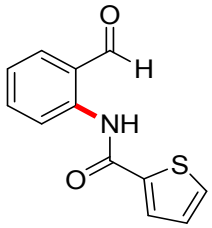
***N*-(2-Formylphenyl)-4-iodobenzamide (3g):** White solid; 43.5 mg, 62% yield; m.p. 124–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.07 (s, 1H), 9.99 (s, 1H), 8.92 (d, *J* = 8.5 Hz, 1H), 7.90–7.88 (m, 2H), 7.79–7.77 (m, 2H), 7.74–7.72 (m, 1H), 7.70–7.66 (m, 1H), 7.30–7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.91, 165.32, 141.05, 138.14, 136.41, 136.17, 133.80, 129.02, 123.26, 122.04, 120.01, 99.54. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{14}H_{11}INO_2]^+$: 351.9829, Found:351.9833.



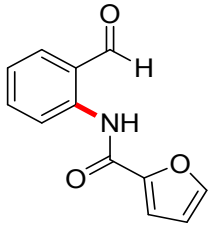
***N*-(2-Formylphenyl)-3,5-dimethylbenzamide (3h):** White solid; 31.9 mg, 63% yield; m.p. 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.01 (s, 1H), 10.00 (s, 1H), 8.95 (d, *J* = 8.4 Hz, 1H), 7.73–7.71 (m, 1H), 7.70–7.65 (m, 3H), 7.28–7.24 (m, 1H), 7.21 (s, 1H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.71, 166.63, 141.36, 138.53, 136.32, 136.11, 134.41, 133.85, 125.30, 122.88, 122.01, 120.02, 21.33. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{16}H_{16}NO_2]^+$: 254.1176, Found: 254.1177.



***N*-(2-Formylphenyl)-3-(trifluoromethyl)benzamide (3i):** White solid; 42.8 mg, 73% yield; m.p. 84–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.21 (s, 1H), 10.01 (s, 1H), 8.93 (d, J = 8.4 Hz, 1H), 8.37 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.76 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.73–7.67 (m, 2H), 7.33–7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.03, 164.55, 140.85, 136.49, 136.20, 135.19, 131.55 (q, J = 32.9 Hz), 130.25, 129.50, 128.71 (q, J = 3.5 Hz), 124.97 (q, J = 4.2 Hz), 123.50, 122.07, 120.02. HRMS (ESI) ([M+H]$^+$) Calcd. For $[C_{15}H_{11}F_3NO_2]^+$: 294.0736, Found: 294.0737.

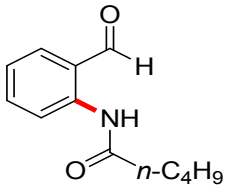


***N*-(2-Formylphenyl)thiophene-2-carboxamide (3j):** White solid; 31.0 mg, 67% yield; m.p. 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.06 (s, 1H), 10.00 (s, 1H), 8.86 (d, J = 8.4 Hz, 1H), 7.86–7.85 (m, 1H), 7.74–7.72 (m, 1H), 7.70–7.65 (m, 1H), 7.62–7.60 (m, 1H), 7.29–7.25 (m, 1H), 7.20–7.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.86, 160.79, 141.10, 139.84, 136.39, 136.13, 131.71, 128.97, 128.05, 123.00, 121.71, 119.84. HRMS (ESI) ([M+H]$^+$) Calcd. For $[C_{12}H_{10}NO_2S]^+$: 232.0427, Found: 232.0426. The NMR data agree with those in a literature report.[6]

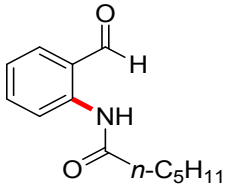


***N*-(2-Formylphenyl)furan-2-carboxamide (3k):** White solid; 26.2 mg, 61% yield; m.p. 98–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.07 (s, 1H), 10.00 (s, 1H), 8.88 (d, J = 8.4 Hz, 1H), 7.73–7.71 (m, 1H), 7.68–7.64 (m, 2H), 7.29–7.25 (m, 2H), 6.58–6.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.42, 157.04, 147.76, 145.10, 140.51, 136.12, 136.01, 123.05, 121.92, 119.95, 115.67, 112.35. HRMS (ESI)

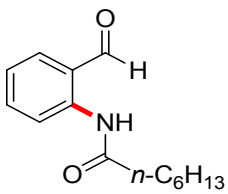
([M+H]$^+$) Calcd. For $[C_{12}H_{10}NO_3]^+$: 216.0655, Found: 216.0652. The NMR data agree with those in a literature report.[6]



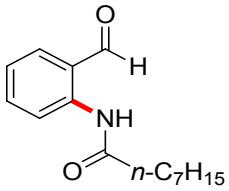
***N*-(2-Formylphenyl)pentanamide (3l):** Colorless liquid; 32.8 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.14 (s, 1H), 9.93 (s, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 7.69–7.66 (m, 1H), 7.64–7.60 (m, 1H), 7.25–7.21 (m, 1H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.80–1.72 (m, 2H), 1.49–1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.51, 172.85, 141.08, 136.18, 135.99, 122.70, 121.57, 119.89, 38.27, 27.49, 22.30, 13.73. The NMR data agree with those in a literature report.[7]



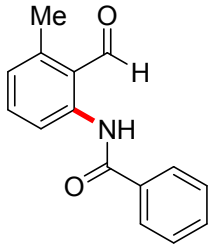
***N*-(2-formylphenyl)hexanamide (3m):** colorless liquid; 37.3 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.14 (s, 1H), 9.92 (s, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 7.67–7.65 (m, 1H), 7.62–7.58 (m, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 2.45 (t, *J* = 7.6 Hz, 2H), 1.80–1.73 (m, 2H), 1.39–1.36 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.41, 172.75, 141.01, 136.08, 135.92, 122.61, 121.51, 119.80, 38.42, 31.25, 25.02, 22.28, 13.79. The NMR data agree with those in a literature report.[5]



***N*-(2-Formylphenyl)heptanamide (3n):** Colorless liquid; 38.7 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.15 (s, 1H), 9.92 (s, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 7.68–7.66 (m, 1H), 7.63–7.59 (m, 1H), 7.24–7.20 (m, 1H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.80–1.72 (m, 2H), 1.42–1.30 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.50, 172.84, 140.99, 136.14, 135.98, 122.66, 121.46, 119.79, 38.50, 31.45, 28.79, 25.33, 22.43, 13.97. The NMR data agree with those in a literature report.[7]

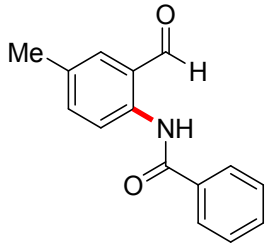


***N*-(2-Formylphenyl)octanamide (3o):** Colorless liquid; 41.0 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.13 (s, 1H), 9.93 (s, 1H), 8.77 (d, *J* = 8.5 Hz, 1H), 7.68–7.66 (m, 1H), 7.63–7.59 (m, 1H), 7.24–7.20 (m, 1H), 2.46 (t, *J* = 7.4 Hz, 2H), 1.78–1.74 (m, 2H), 1.37–1.26 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.50, 172.87, 141.09, 136.18, 135.99, 122.69, 121.57, 119.89, 38.56, 31.65, 29.14, 28.97, 25.43, 22.58, 14.02. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{15}H_{22}NO_2]^+$:248.1645, Found: 248.1642.

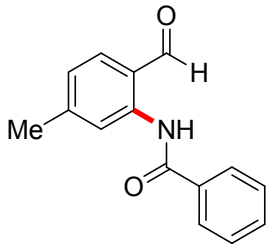


***N*-(2-Formyl-3-methylphenyl)benzamide (4a):** White solid; 33.1 mg, 69% yield; m.p. 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.57 (s, 1H), 10.52 (s, 1H), 8.83 (d, *J* = 8.5 Hz, 1H), 8.09–8.07 (m, 2H), 7.58–7.51 (m, 4H), 6.97 (d, *J* = 7.5 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.72, 166.23, 143.33, 142.08, 136.58,

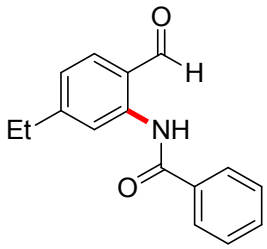
134.62, 132.05, 128.80, 127.52, 125.91, 119.57, 118.54, 19.24. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{15}H_{14}NO_2]^+$: 240.1019, Found:240.1017.



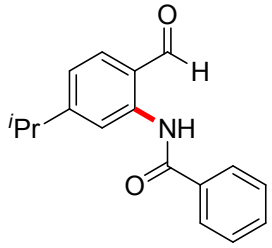
***N*-(2-Formyl-4-methylphenyl)benzamide (4b):** White solid; 35.1 mg, 73% yield; m.p. 104–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.99 (s, 1H), 9.96 (s, 1H), 8.85 (d, *J* = 8.4 Hz, 1H), 8.08–8.06 (m, 2H), 7.58–7.48 (m, 5H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.92, 166.00, 138.93, 137.13, 136.29, 134.47, 132.74, 132.07, 128.83, 127.47, 122.01, 120.03, 20.50. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{15}H_{14}NO_2]^+$: 240.1019, Found:240.1017.



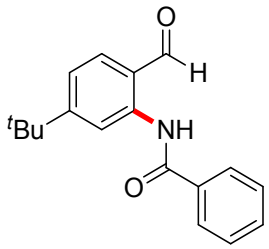
***N*-(2-Formyl-5-methylphenyl)benzamide (4c):** White solid; 35.9 mg, 75% yield; m.p. 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.12 (s, 1H), 9.92 (s, 1H), 8.80 (s, 1H), 8.08–8.06 (m, 2H), 7.60–7.51 (m, 4H), 7.07 (d, *J* = 7.8 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.17, 166.12, 148.18, 141.19, 136.22, 134.34, 132.13, 128.83, 127.47, 124.03, 120.31, 120.01, 22.50. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{15}H_{14}NO_2]^+$: 240.1019, Found:240.1016.



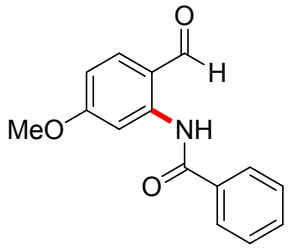
***N*-(5-Ethyl-2-formylphenyl)benzamide (4d):** White solid; 39.5 mg, 78% yield; m.p. 106–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.13 (s, 1H), 9.92 (s, 1H), 8.84 (s, 1H), 8.09–8.07 (m, 2 H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58–7.51 (m, 3H), 7.10–7.08 (m, 1H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.19, 166.12, 154.26, 141.34, 136.34, 134.35, 132.10, 128.82, 127.45, 122.81, 120.18, 119.29, 29.69, 14.95. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{16}H_{16}NO_2]^+$: 254.1176, Found: 254.1176.



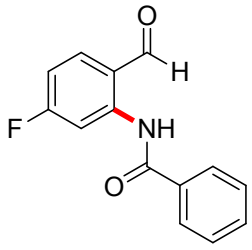
***N*-(2-Formyl-5-isopropylphenyl)benzamide (4e):** White solid; 40.6 mg, 76% yield; m.p. 99–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.13 (s, 1H), 9.94 (s, 1H), 8.89 (s, 1H), 8.08 (d, *J* = 6.8 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58–7.52 (m, 3H), 7.15–7.13 (m, 1H), 3.09–2.98 (m, 1H), 1.33 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.19, 166.21, 158.85, 141.49, 136.39, 134.46, 132.12, 128.86, 127.49, 121.37, 120.40, 118.16, 35.00, 29.67, 23.44. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{17}H_{18}NO_2]^+$: 268.1332, Found: 268.1334.



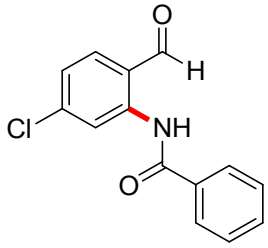
***N*-(5-(*tert*-Butyl)-2-formylphenyl)benzamide (4f):** White solid; 45.1 mg, 80% yield; m.p. 115–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.11 (s, 1H), 9.96 (s, 1H), 9.10 (d, *J* = 1.6 Hz, 1H), 8.11–8.09 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.59–7.53 (m, 3H), 7.32–7.30 (m, 1H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.20, 166.24, 161.04, 141.24, 136.00, 134.45, 132.11, 128.85, 127.46, 120.40, 119.94, 117.17, 35.86, 30.94. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{18}H_{20}NO_2]^+$: 282.1489, Found: 282.1493.



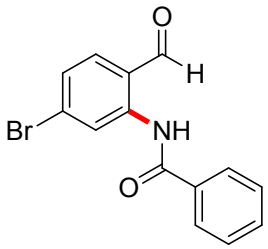
***N*-(2-Formyl-5-methoxyphenyl)benzamide (4g):** White solid; 39.8 mg, 78% yield; m.p. 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.38 (s, 1H), 9.83 (s, 1H), 8.60–8.60 (m, 1H), 8.09–8.07 (m, 2H), 7.60–7.53 (m, 4H), 6.76–6.74 (m, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.70, 166.30, 166.01, 143.69, 137.89, 134.16, 132.16, 128.80, 127.44, 116.06, 110.42, 103.67, 55.74. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{15}H_{14}NO_3]^+$: 256.0968, Found: 256.0966.



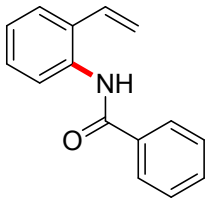
***N*-(5-Fluoro-2-formylphenyl)benzamide (4h):** White solid; 36.0 mg, 74% yield; m.p. 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.27 (s, 1H), 9.94 (s, 1H), 8.77–8.74 (m, 1H), 8.07–8.06 (m, 2H), 7.75–7.71 (m, 1H), 7.62–7.53 (m, 3H), 6.97–6.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.27, 167.43 (d, *J* = 255.3 Hz), 166.20, 143.61 (d, *J* = 13.8 Hz), 138.56 (d, *J* = 12.0 Hz), 133.82, 132.44, 128.90, 127.49, 118.88, 110.48 (d, *J* = 22.9 Hz), 107.49 (d, *J* = 28.7 Hz). HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{14}H_{11}FNO_2]^+$: 244.0768, Found: 244.0765.



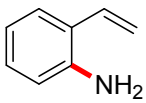
***N*-(5-Chloro-2-formylphenyl)benzamide (4i):** White solid; 40.4 mg, 78% yield; m.p. 99–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.14 (s, 1H), 9.95 (s, 1H), 9.05 (s, 1H), 8.06–8.04 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.60–7.52 (m, 3H), 7.24–7.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.69, 166.10, 143.14, 142.01, 13.6098, 133.83, 132.47, 128.94, 127.51, 123.35, 120.31, 120.11. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{14}H_{11}ClNO_2]^+$: 260.0473, Found: 260.0471.



***N*-(5-Bromo-2-formylphenyl)benzamide (4j):** White solid; 43.1 mg, 71% yield; m.p. 115–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.12 (s, 1H), 9.96 (s, 1H), 9.24 (d, *J* = 1.6 Hz, 1H), 8.08–8.06 (m, 2H), 7.61–7.54 (m, 4H), 7.44–7.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.92, 166.09, 141.87, 136.95, 133.85, 132.49, 132.11, 128.96, 127.53, 126.38, 123.11, 120.64. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{14}H_{11}BrNO_2]^+$: 303.9968, Found: 303.9969.

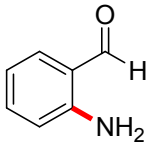


***N*-(2-Vinylphenyl)benzamide (5):** White solid; 41.4 mg, 93% yield; m.p. 156–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 7.89–7.87 (m, 2H), 7.56–7.53 (m, 1H), 7.50–7.44 (m, 3H), 7.34–7.30 (m, 1H), 7.21–7.17 (m, 1H), 6.86 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.70 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.45 (dd, *J* = 11.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.63, 134.70, 134.47, 132.31, 131.85, 130.64, 128.76, 128.52, 127.06, 127.03, 125.41, 123.58, 118.35. The NMR data agree with those in a literature report.[3]

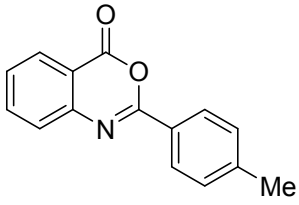


2-Vinylaniline (6): Brown oil; 20.2 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.27 (m, 1H), 7.11–7.06 (m, 1H), 6.81–6.73 (m, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.63 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.31 (dd, *J* = 11.0, 1.4 Hz, 1H), 3.75 (brs, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ: 143.63, 132.74, 128.70, 127.32, 124.09, 118.90, 116.05, 115.66. The NMR data agree with those in a literature report.[8]



2-Aminobenzaldehyde (7): White solid; 21.6 mg, 89% yield; m.p. 39–41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.88 (s, 1H), 7.50–7.48 (m, 1H), 7.34–7.30 (m, 1H), 6.78 (t, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 6.13 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.04, 149.87, 135.68, 135.15, 118.84, 116.35, 115.99. The NMR data agree with those in a literature report.[9]



2-(*p*-Tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (8): White solid; 37.0 mg, 78% yield; m.p. 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24–8.21 (m, 1H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.83–7.87 (m, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.51–7.47 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.66, 157.29, 147.14, 143.36, 136.45, 129.47, 128.53, 128.29, 127.95, 127.44, 127.07, 116.93, 21.65. HRMS (ESI) ($[M+H]^+$) Calcd. For $[C_{15}H_{12}NO_2]^+$: 238.0863, Found: 238.0868

8. References

[1] R. B. Dateer and S. Chang, *J. Am. Chem. Soc*., 2015, **137**, 4908.

[2] Y. Park, K. T. Park, J. G. Kim and S. Chang, *J. Am. Chem. Soc.*, 2015, **137**, 4534.

[3] L. Fra, A. Millán, J. A. Souto and K. Muñiz, *Angew. Chem., Int. Ed*., 2014, **53**, 7349.

[4] P. Seliga and W. Ravenb, *Org. Lett.*, 2014, **16**, 5192.

[5] D. Zhao, Qi. Shen, Y.-R. Zhou and J.-X. Li, *Org. Biomol. Chem.*, 2013, **11**, 5908.

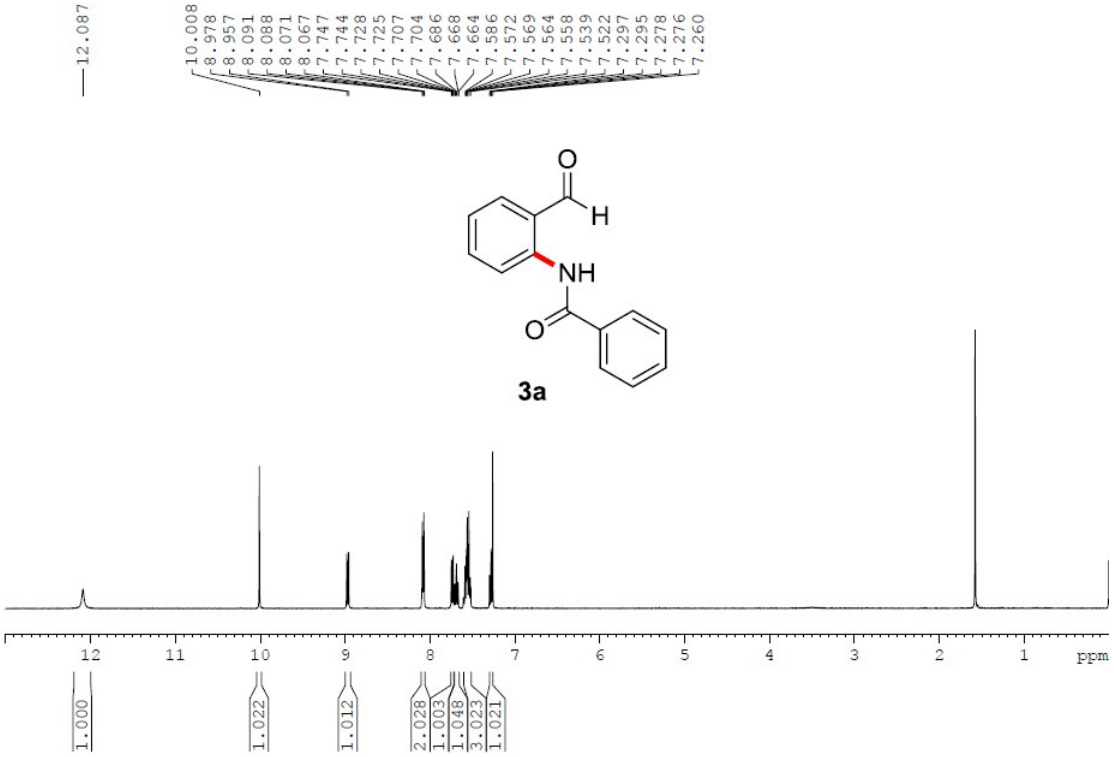
[6] J. Yu, D. Zhang-Negrerie and Y. Du, *Eur. J. Org. Chem.*, 2016, **3**, 562.

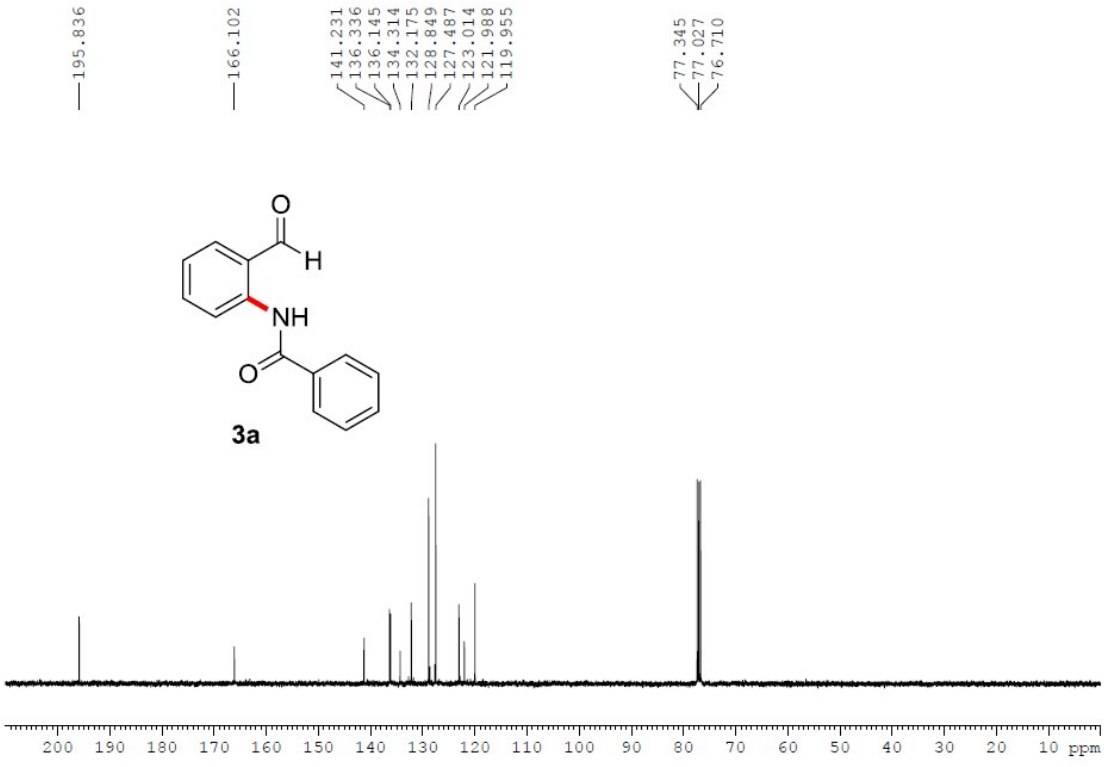
[7] K. K. Park and J. Y. Jung, *Heterocycles*, 2005, **65**, 2095.

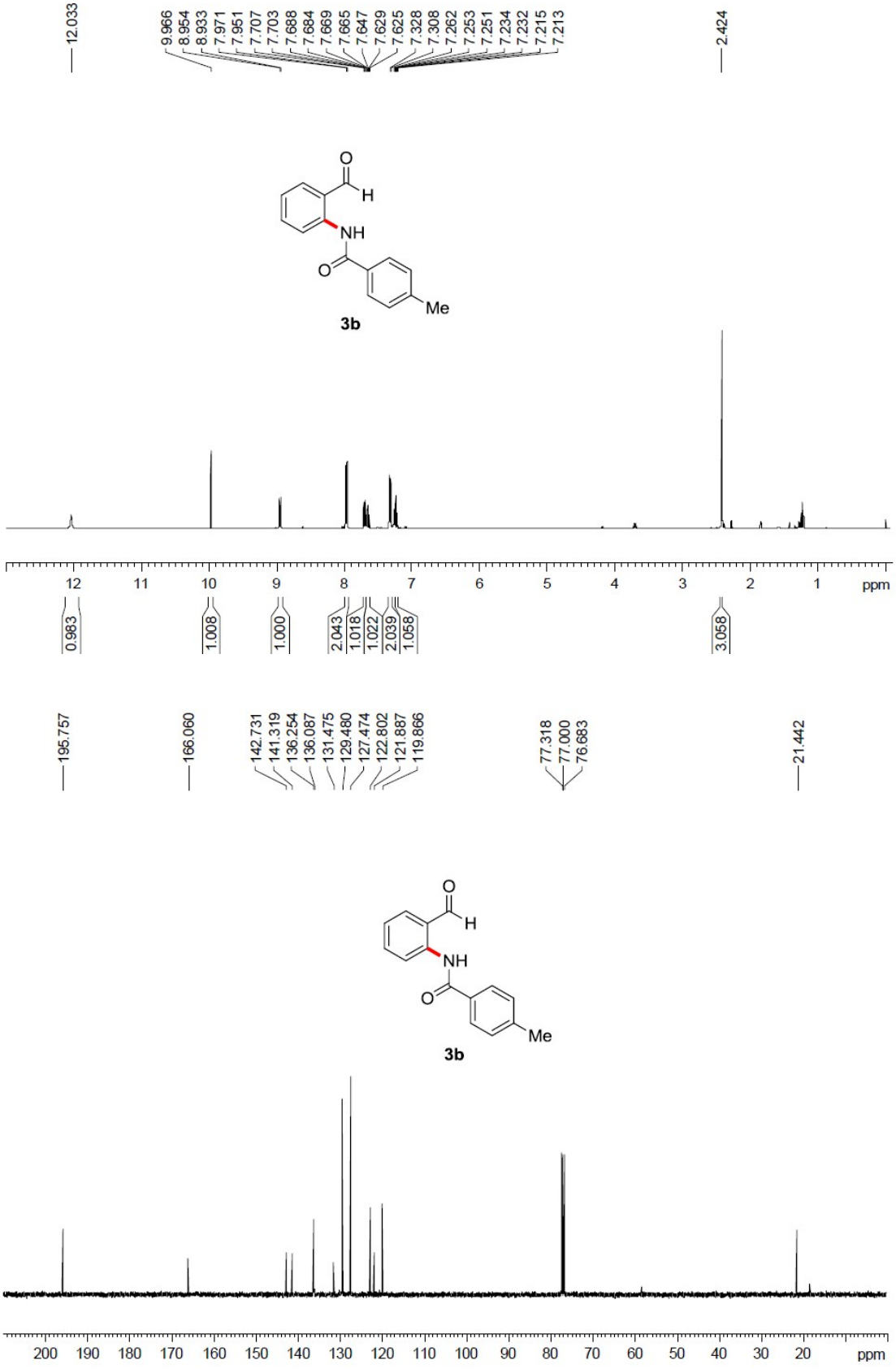
[8] M. Arisawa, Y. Fujii, H. Kato, H. Fukuda, T. Matsumoto, M. Ito, H. Abe, Y. Ito and S. Shuto, *Angew. Chem., Int. Ed*., 2013, **52**, 1003.

[9] Y. Matano and H. Nomura, *Angew. Chem., Int. Ed*., 2002, **41**, 3028.

9. ^{1}H and ^{13}C NMR spectra of the products



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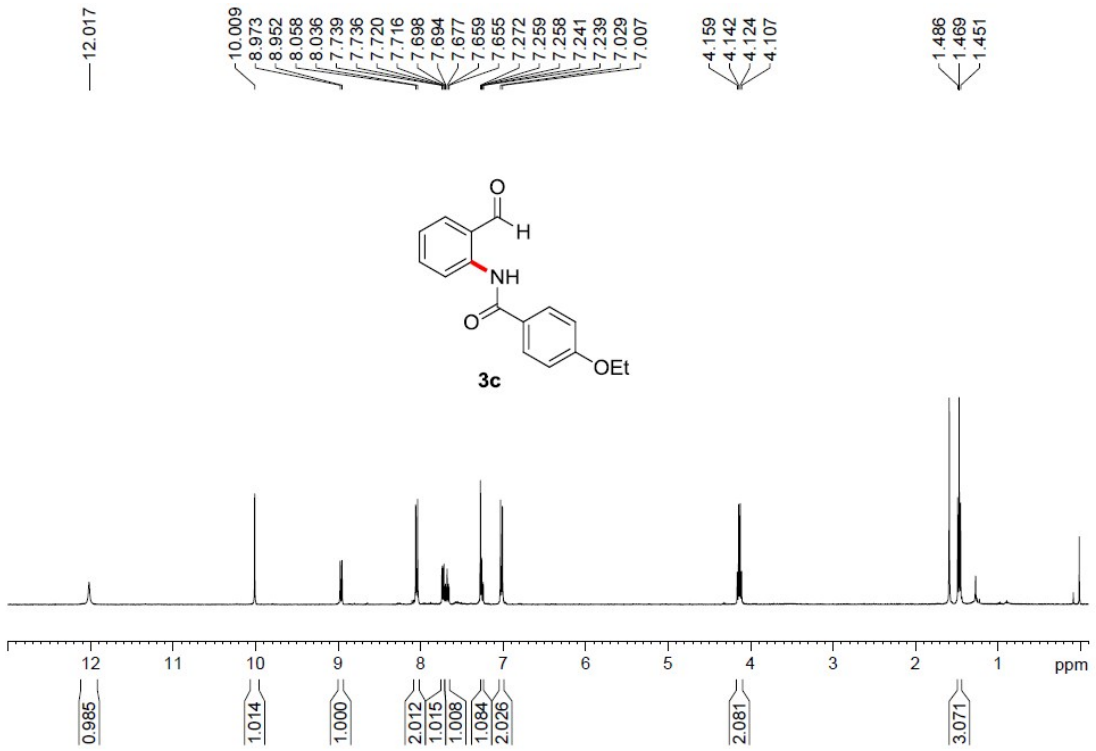
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7.720
7.716
7.698
7.694
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7.655
7.272
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7.241
7.239
7.029
7.007
4.159
4.142
4.124
4.107
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1.469
1.451
O
H
NH
O
OEt
3c
12
11
10
9
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7
6
5
4
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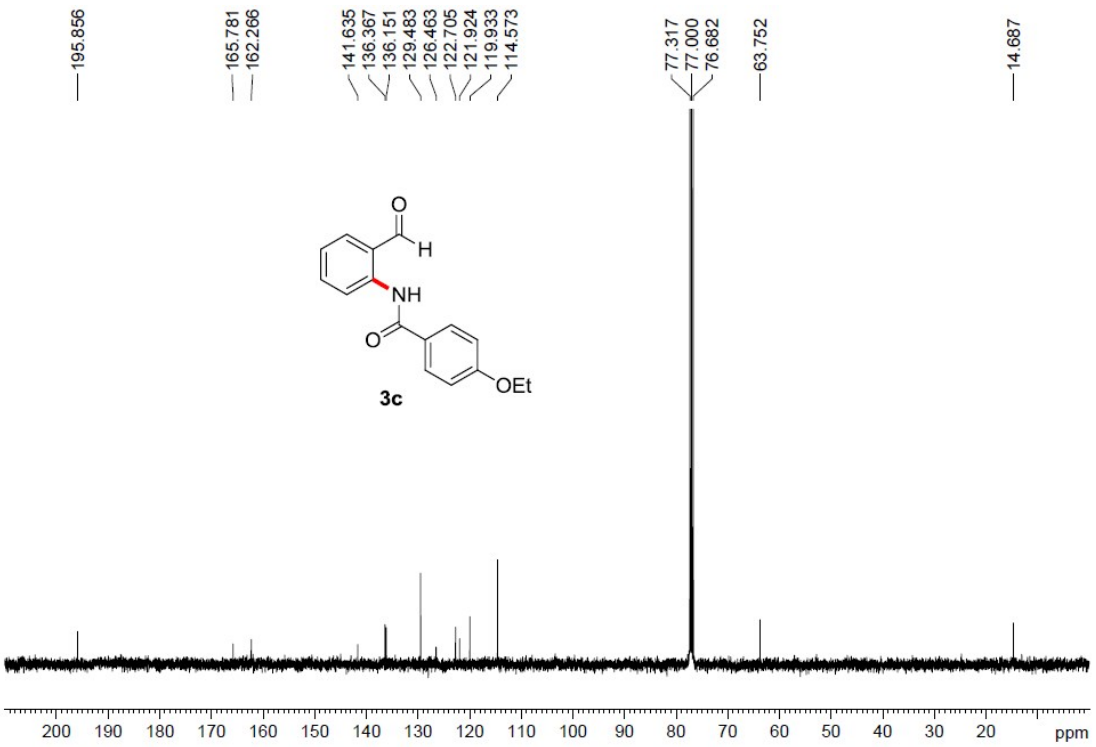
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77.317
77.000
76.682
63.752
14.687
O
H
NH
O
OEt
3c
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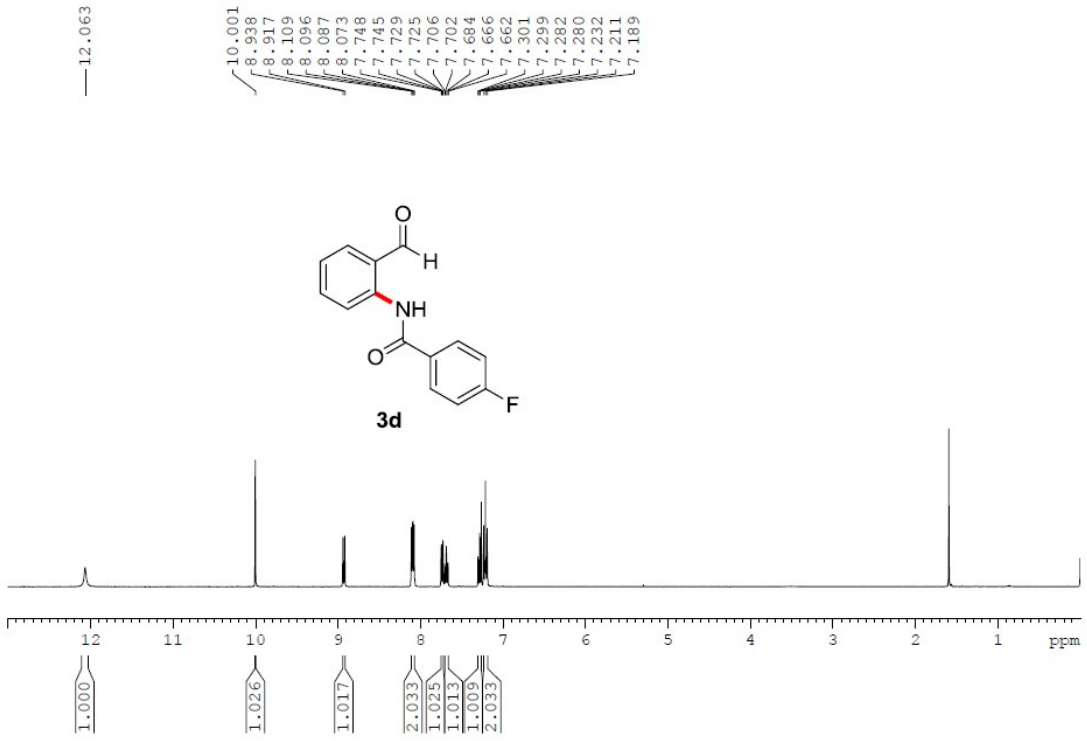
ppm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7.706
7.702
7.684
7.666
7.662
7.301
7.299
7.282
7.280
7.232
7.211
7.189
O
H
NH
O
F
3d
12
11
10
9
8
7
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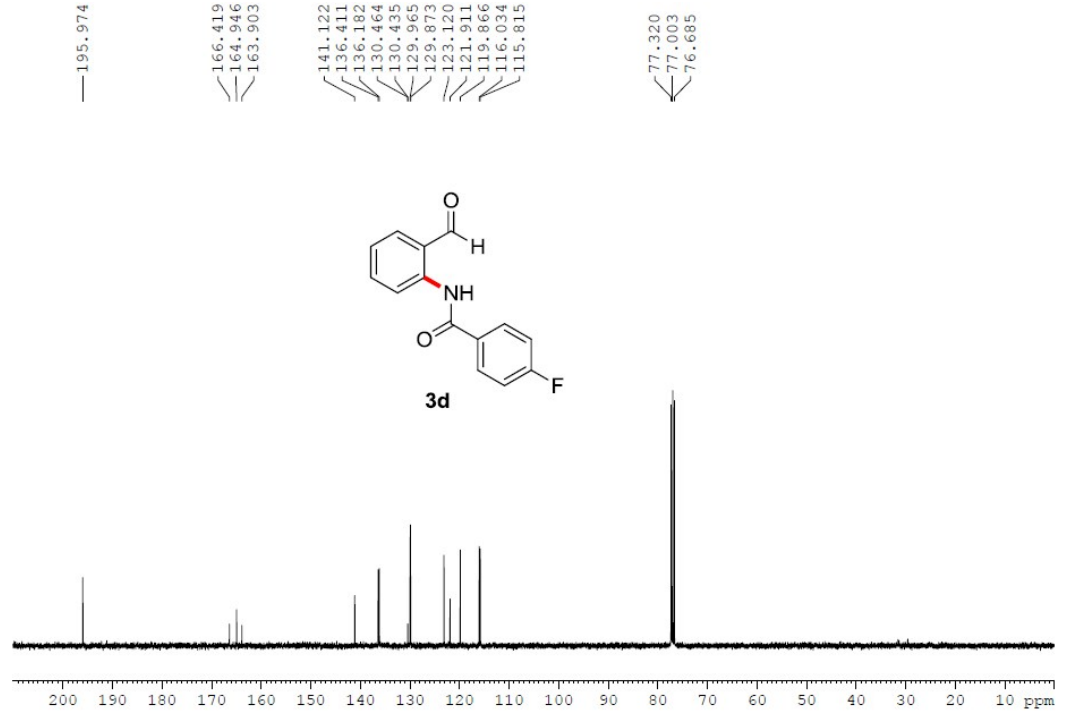
1.009
2.033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121.911
119.866
116.034
115.815
77.320
77.003
76.685
O
H
NH
O
F
3d
200
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180
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160
150
140
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120
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80
70
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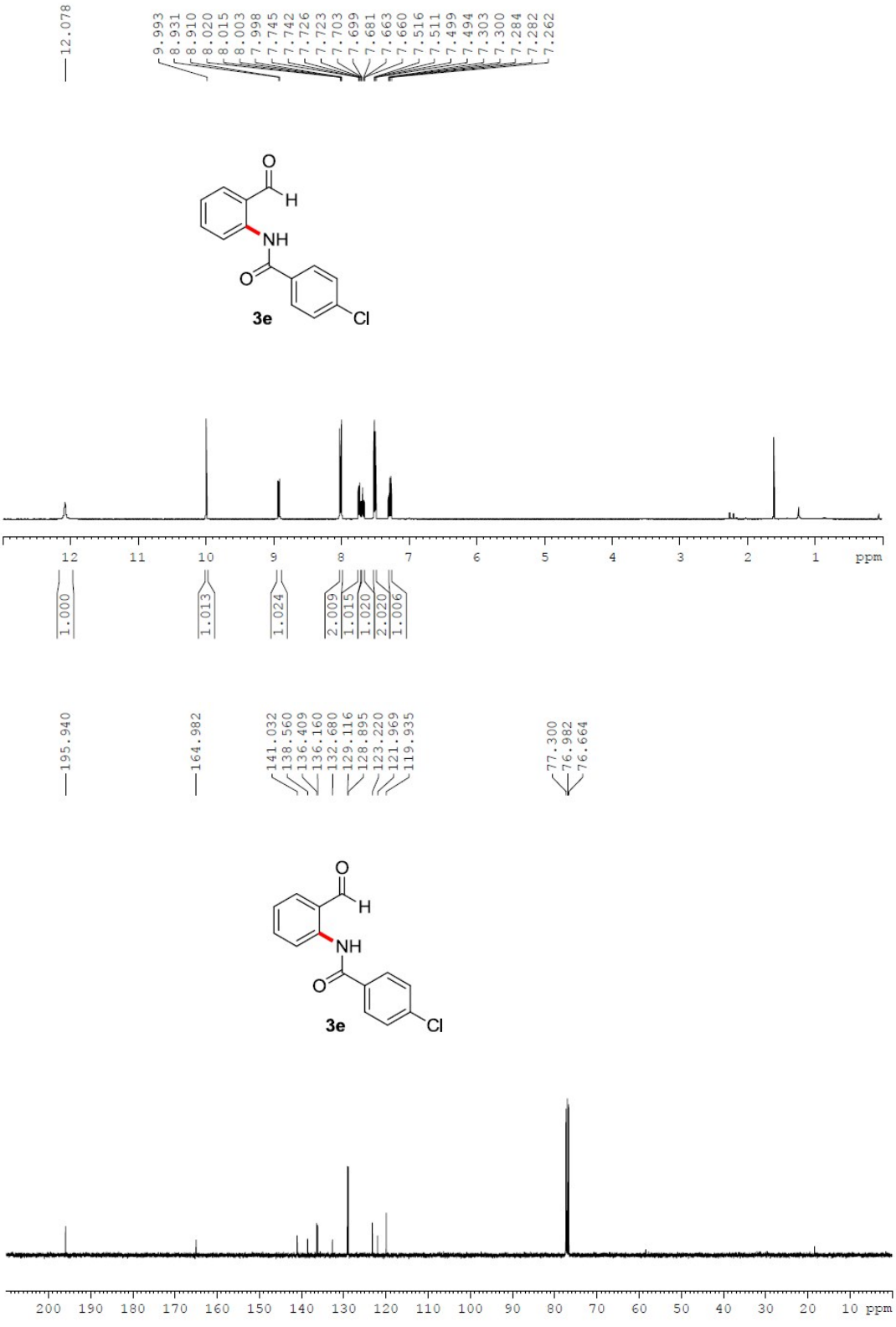
50
40
30
20
10 ppm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7.703
7.699
7.681
7.663
7.660
7.516
7.511
7.499
7.494
7.303
7.300
7.284
7.282
7.262
O
H
NH
O
Cl
3e
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11
10
9
8
7
6
5
4
3
2
1
ppm
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1.013
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2.009
1.015
1.020
2.020
1.006
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141.032
138.560
136.409
136.160
132.680
129.116
128.895
123.220
121.969
119.935
77.300
76.982
76.664
O
H
NH
O
Cl
3e
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160
150
140
130
120
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100
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80
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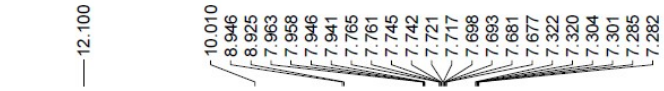
40
30
20
10 ppm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7.958
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7.941
7.765
7.761
7.745
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7.721
7.717
7.698
7.693
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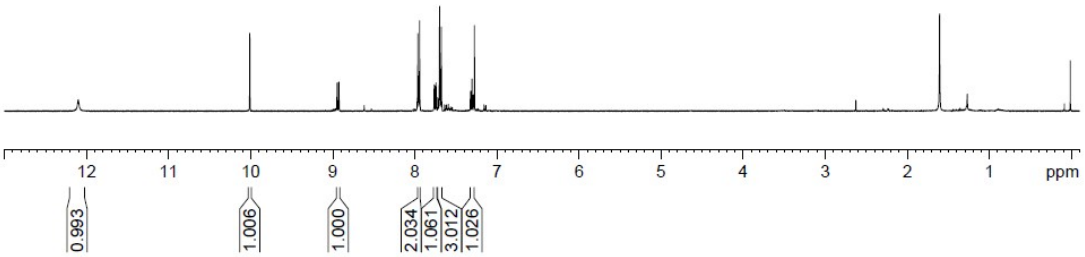
7.322
7.320
7.304
7.301
7.285
7.282


O
H
NH
O
Br

3f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11
10
9
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6
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3
2
1
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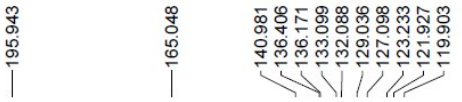
1.026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132.088
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127.098
123.233
121.927
119.903
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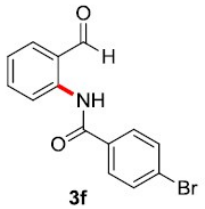
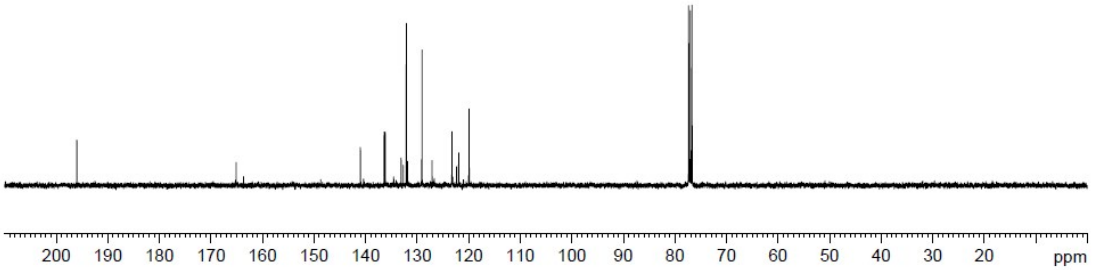
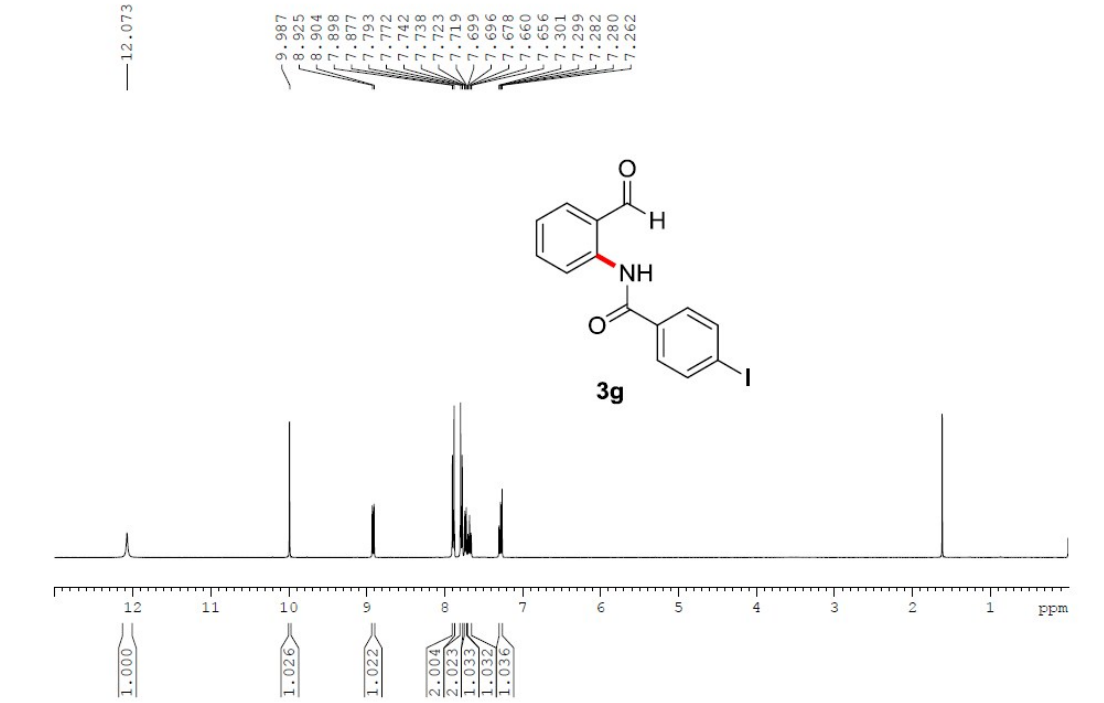
77.005
76.688


O
H
NH
O
Br

3f


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.877
7.793
7.772
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7.738
7.723
7.719
7.699
7.696
7.678
7.660
7.656
7.301
7.299
7.282
7.280
7.262
O
H
NH
O
I
3g
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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2.004
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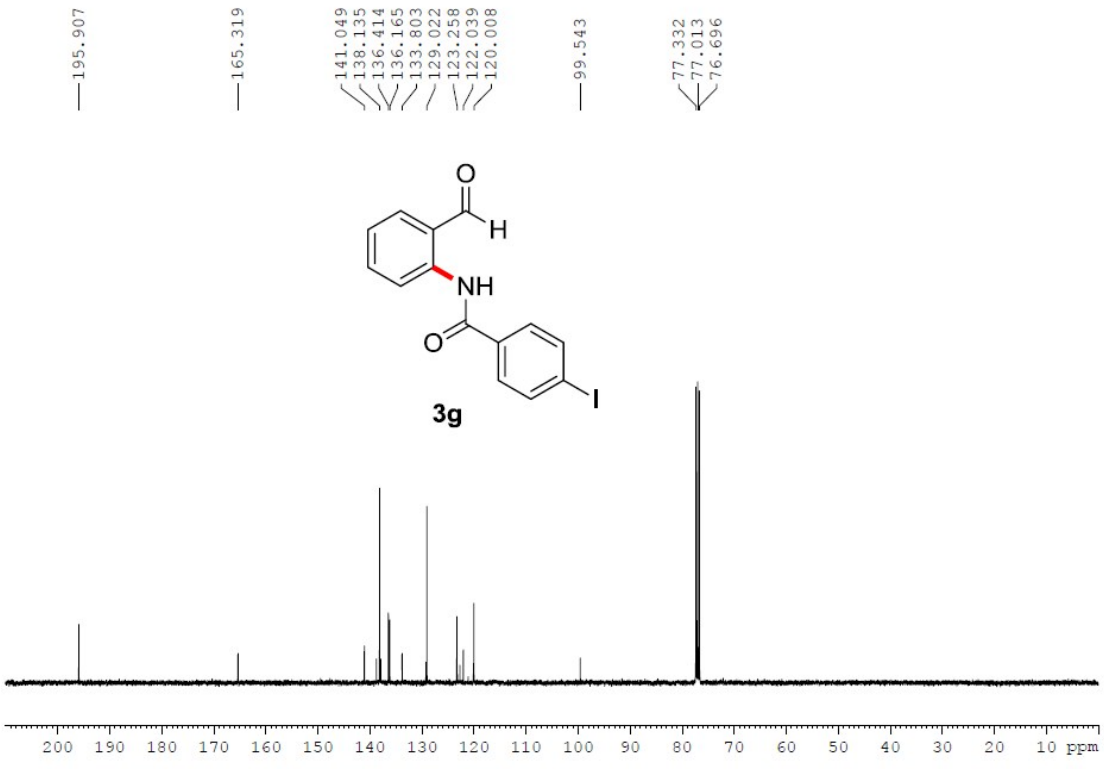
1.033
1.032
1.036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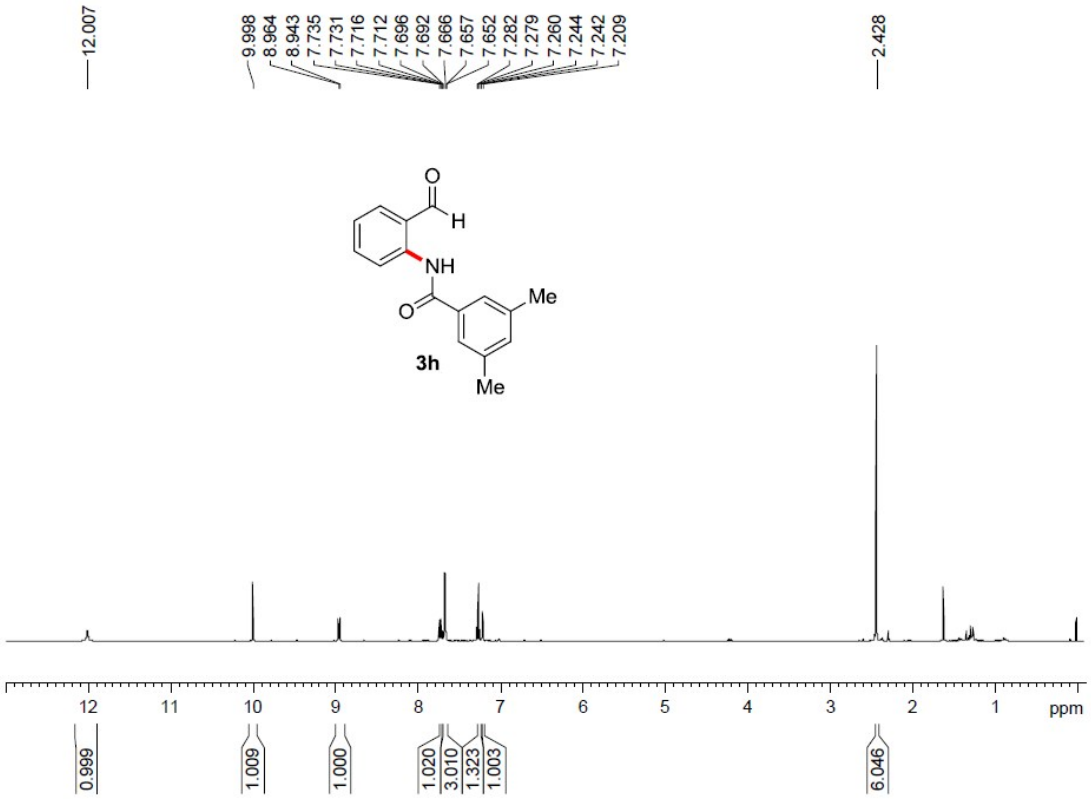
136.414
136.165
133.803
129.022
123.258
122.039
120.008
99.543
77.332
77.013
76.696
O
H
NH
O
I
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.696
7.692
7.666
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7.652
7.282
7.279
7.260
7.244
7.242
7.209
2.428
O
H
NH
O
Me
3h
Me
12
11
10
9
8
7
6
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1
ppm
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1.000
1.020
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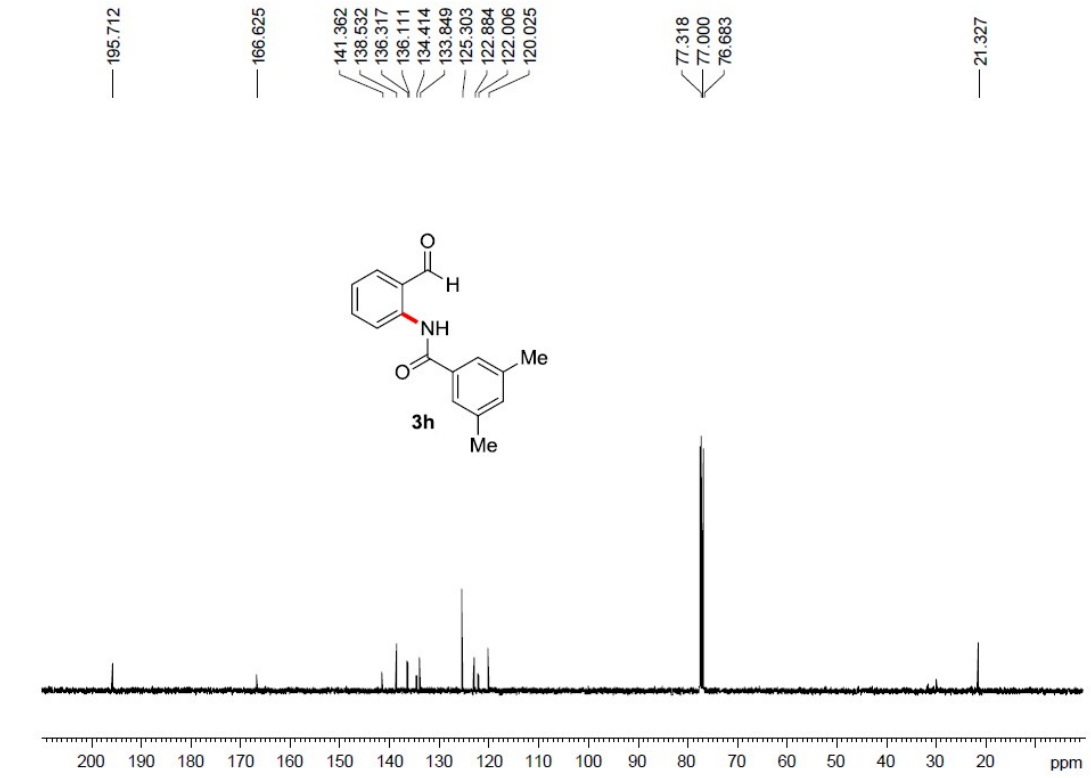
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136.317
136.111
134.414
133.849
125.303
122.884
122.006
120.025
77.318
77.000
76.683
21.327
O
H
NH
O
Me
3h
Me
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150
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130
120
110
100
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80
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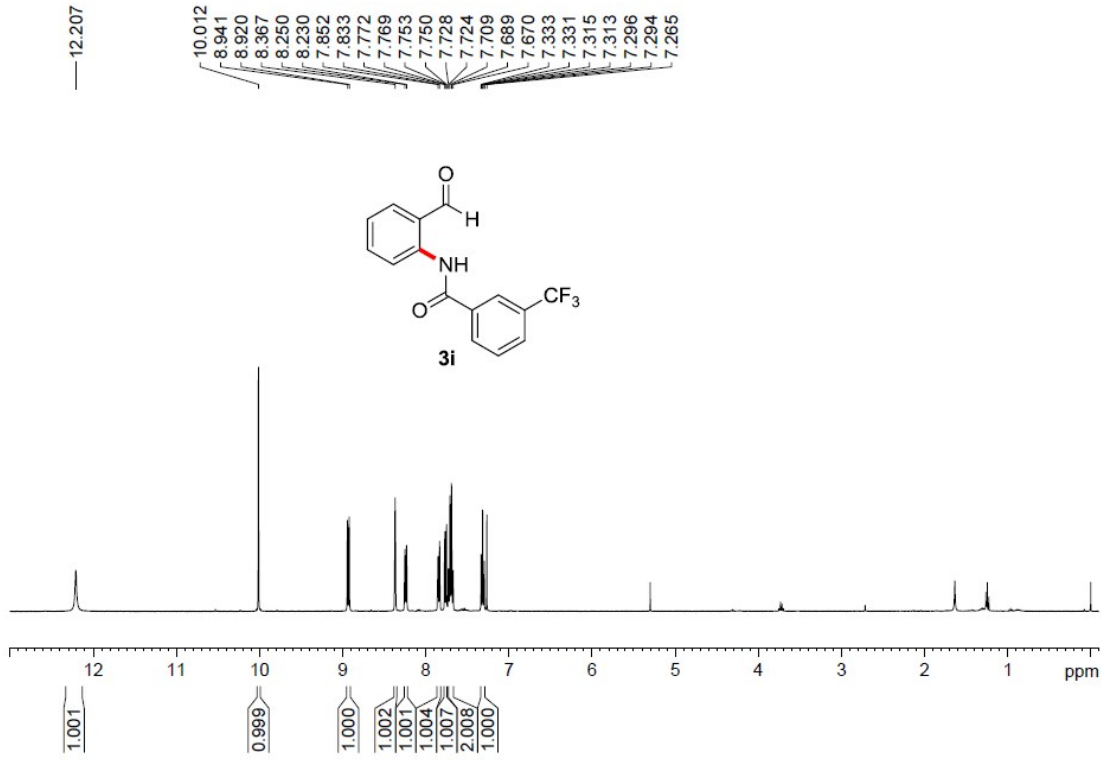
50
40
30
20
ppm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7.852
7.833
7.772
7.769
7.753
7.750
7.728
7.724
7.709
7.689
7.670
7.333
7.331
7.315
7.313
7.296
7.294
7.265
O
H
NH
O
CF3
3i
12
11
10
9
8
7
6
5
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ppm
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1.000
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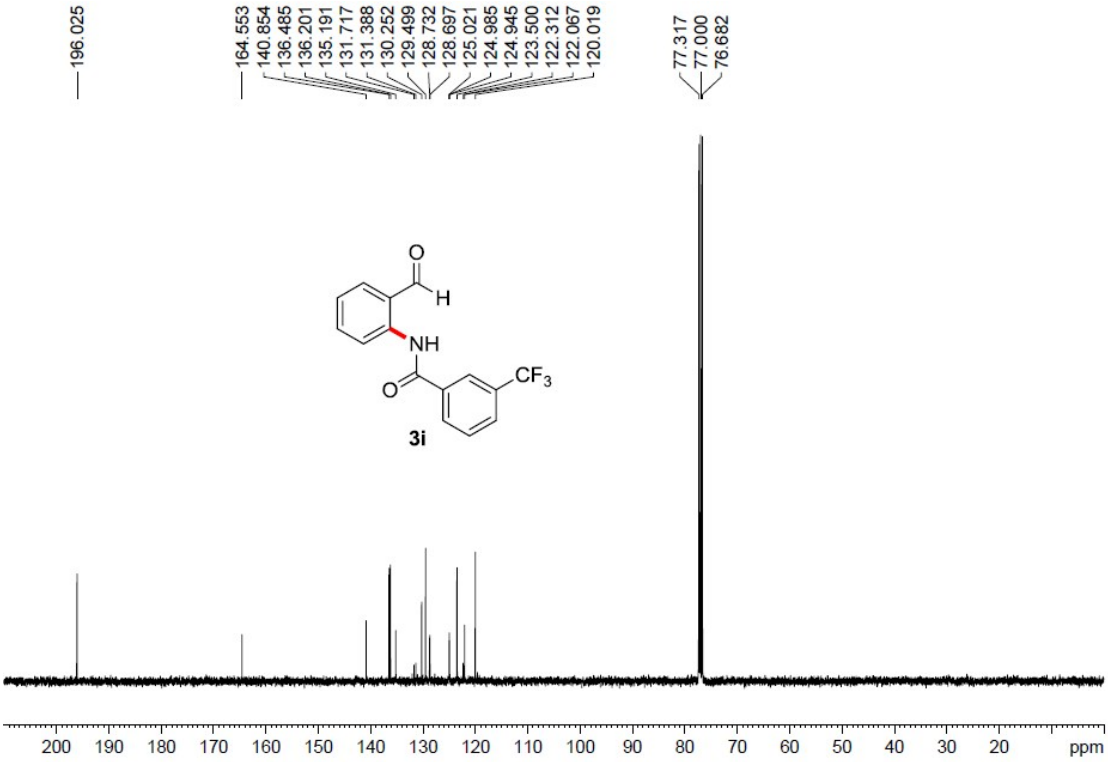
1.001
1.004
1.007
2.008
1.000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135.191
131.717
131.388
130.252
129.499
128.732
128.697
125.021
124.985
124.945
123.500
122.312
122.067
120.019
77.317
77.000
76.682
O
H
NH
O
CF3
3i
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150
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120
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80
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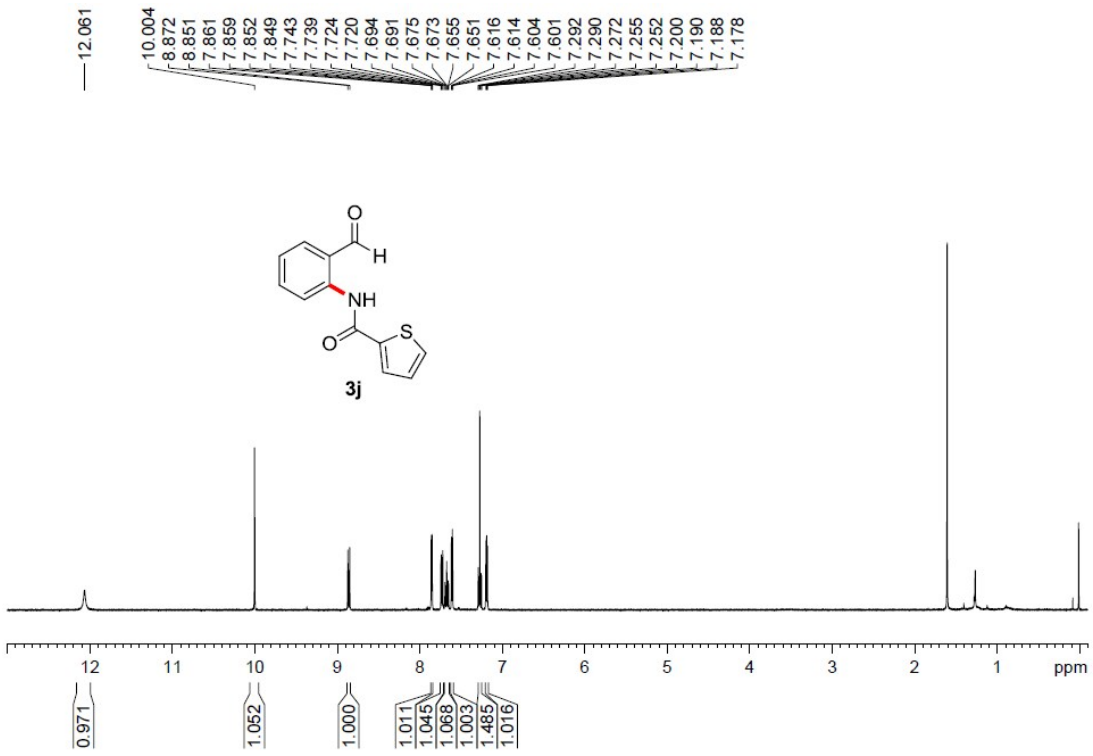
30
20
ppm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7.849
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7.739
7.724
7.720
7.694
7.691
7.675
7.673
7.655
7.651
7.616
7.614
7.604
7.601
7.292
7.290
7.272
7.255
7.252
7.200
7.190
7.188
7.178
O
H
NH
O
S
3j
12
11
10
9
8
7
6
5
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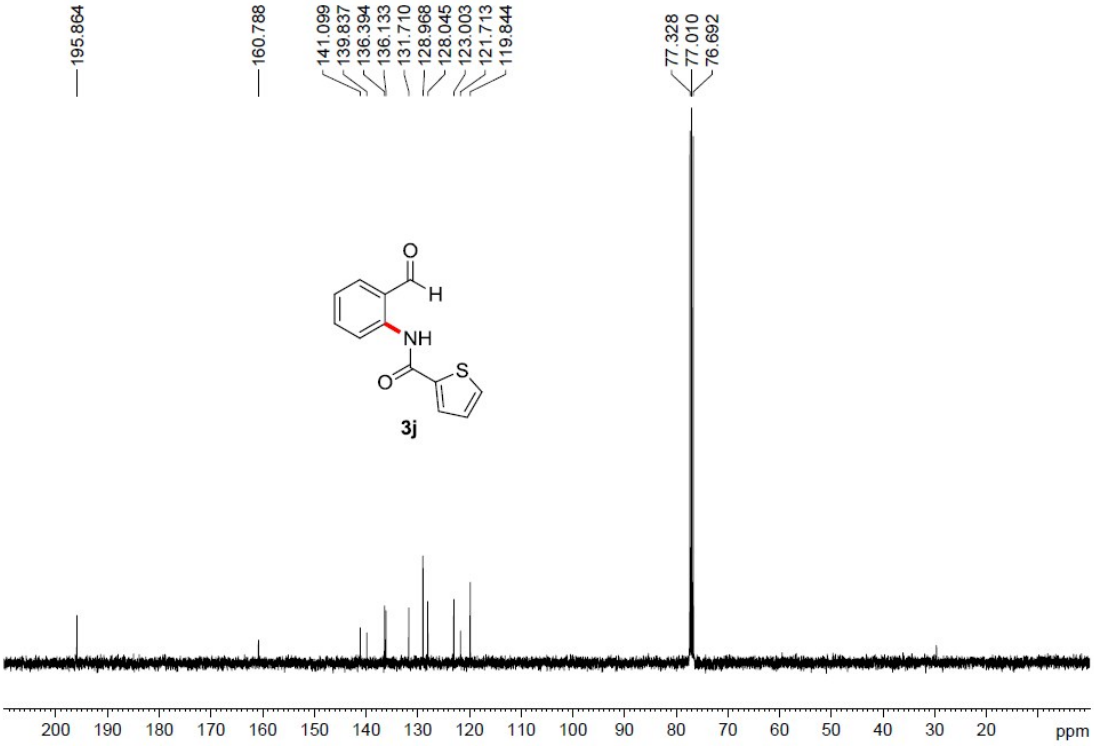
1.016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128.968
128.045
123.003
121.713
119.844
77.328
77.010
76.692
O
H
NH
O
S
3j
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150
140
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110
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90
80
70
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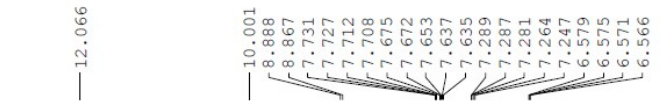
50
40
30
20
ppm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7.708
7.675
7.672
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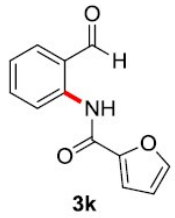
7.287
7.281
7.264
7.247
6.579
6.575
6.571
6.566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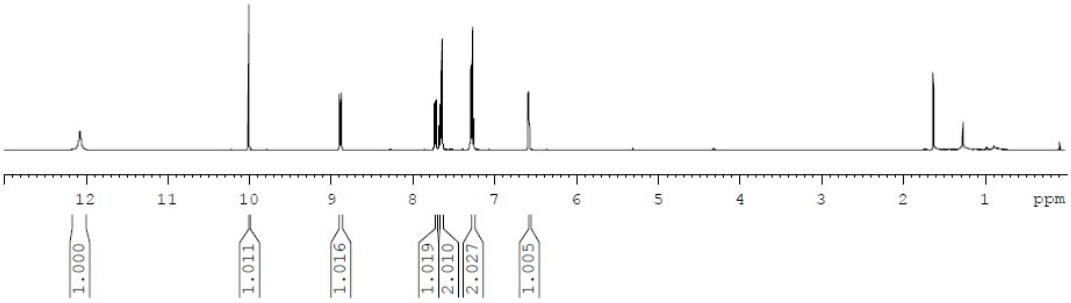
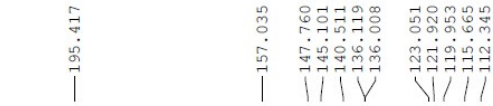
H
NH
O
O

3k


12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.000
1.011
1.016
1.019
2.010
2.027
1.005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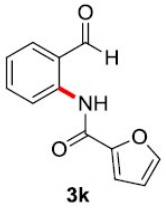
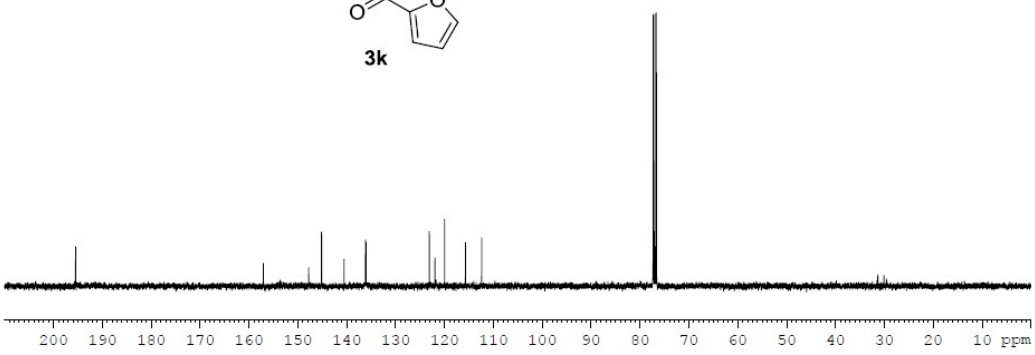
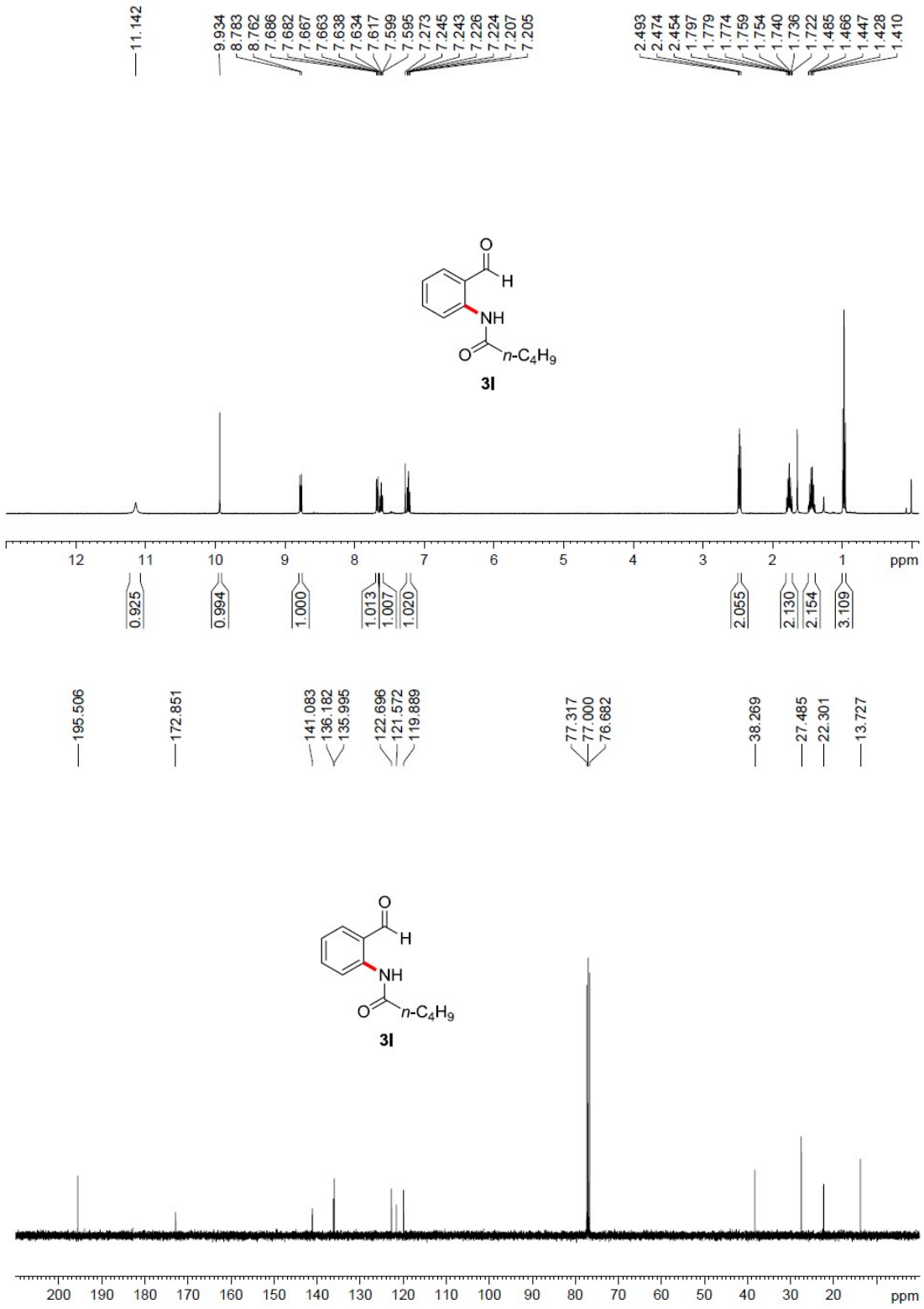
123.051
121.920
119.953
115.665
112.345
77.263
76.946
76.628


O
H
NH
O
O

3k


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.682
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7.663
7.638
7.634
7.617
7.599
7.595
7.273
7.245
7.243
7.226
7.224
7.207
7.205
2.493
2.474
2.454
1.797
1.779
1.774
1.759
1.754
1.740
1.736
1.722
1.485
1.466
1.447
1.428
1.410
O
H
NH
O
n-C4H9
3l
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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0.994
1.000
1.013
1.007
1.020
2.055
2.130
2.154
3.109
195.506
172.851
141.083
136.182
135.995
122.696
121.572
119.889
77.317
77.000
76.682
38.269
27.485
22.301
13.727
O
H
NH
O
n-C4H9
3l
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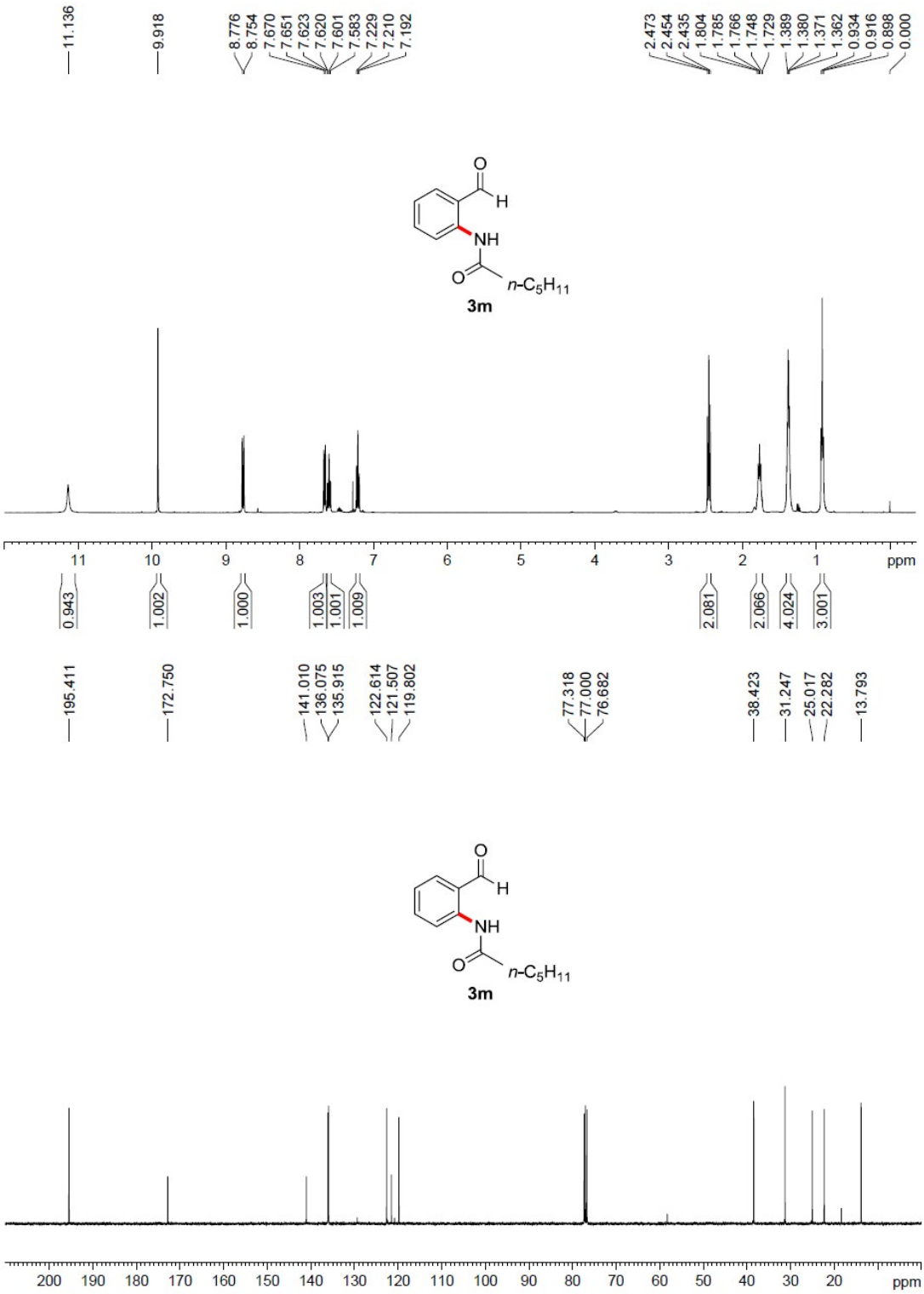
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.620
7.601
7.583
7.229
7.210
7.192
2.473
2.454
2.435
1.804
1.785
1.766
1.748
1.729
1.389
1.380
1.371
1.362
0.934
0.916
0.898
0.000
O
H
NH
O
n-C5H11
3m
11
10
9
8
7
6
5
4
3
2
1
ppm
0.943
1.002
1.000
1.003
1.001
1.009
2.081
2.066
4.024
3.001
195.411
172.750
141.010
136.075
135.915
122.614
121.507
119.802
77.318
77.000
76.682
38.423
31.247
25.017
22.282
13.793
O
H
NH
O
n-C5H11
3m
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160
150
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120
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100
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80
70
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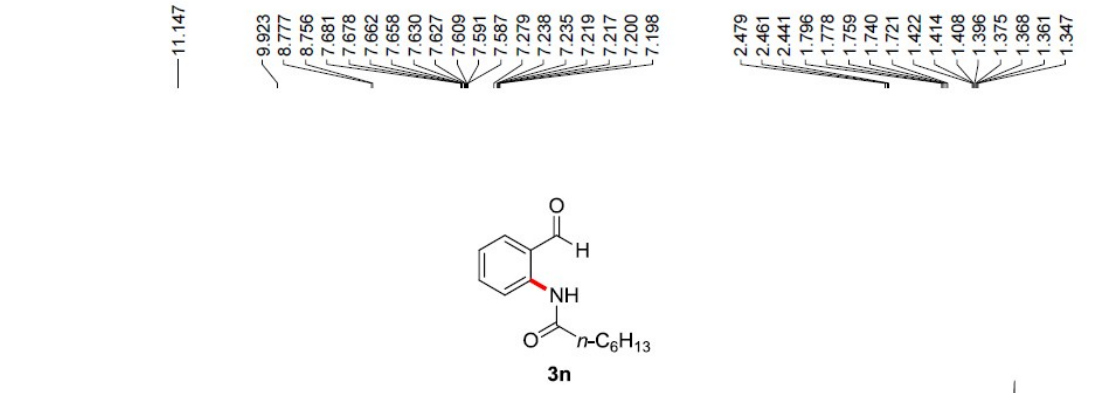
50
40
30
20
ppm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9.923
8.777
8.756
7.681
7.678
7.662
7.658
7.630
7.627
7.609
7.591
7.587
7.279
7.238
7.235
7.219
7.217
7.200
7.198
2.479
2.461
2.441
1.796
1.778
1.759
1.740
1.721
1.422
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1.396
1.375
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1.361
1.347

O
H
NH
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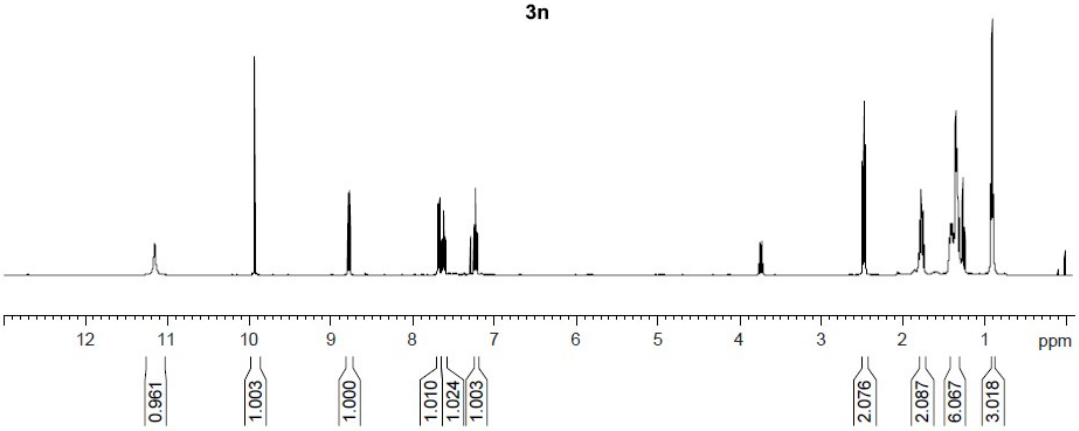
n-C6H13

3n


12
11
10
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8
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6
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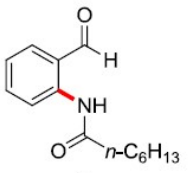
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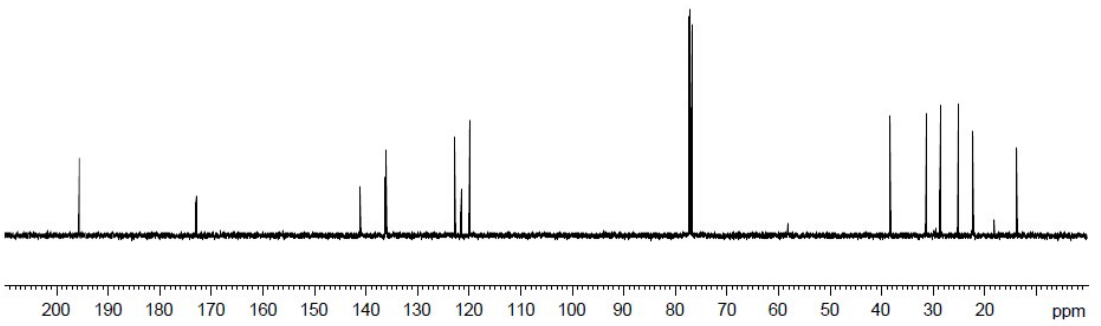
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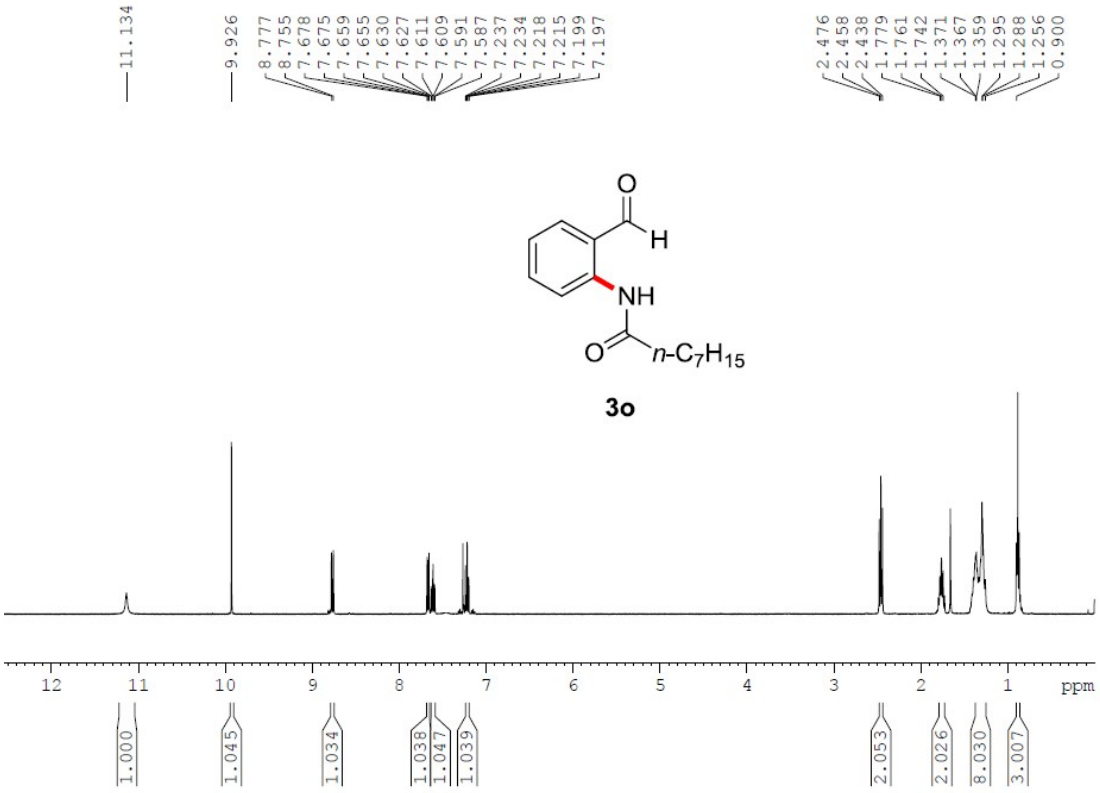
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7.237
7.234
7.218
7.215
7.199
7.197
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2.458
2.438
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1.367
1.359
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H
NH
O
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3o
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11
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5
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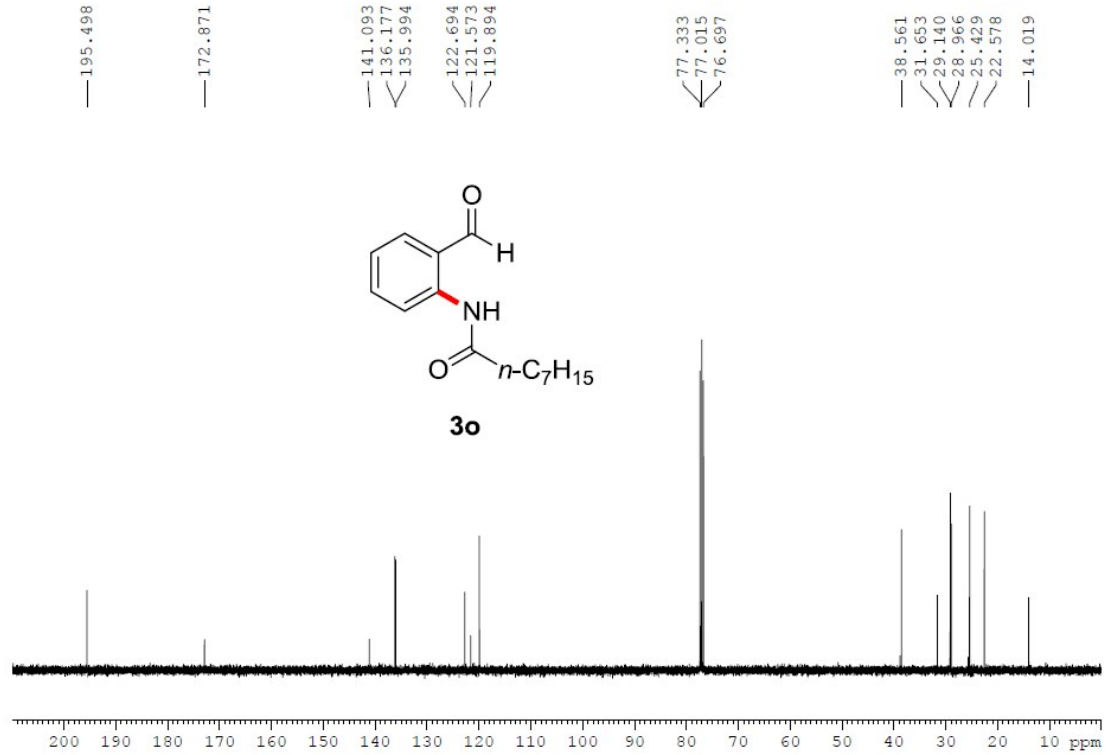
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28.966
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22.578
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H
NH
O
n-C7H15
3o
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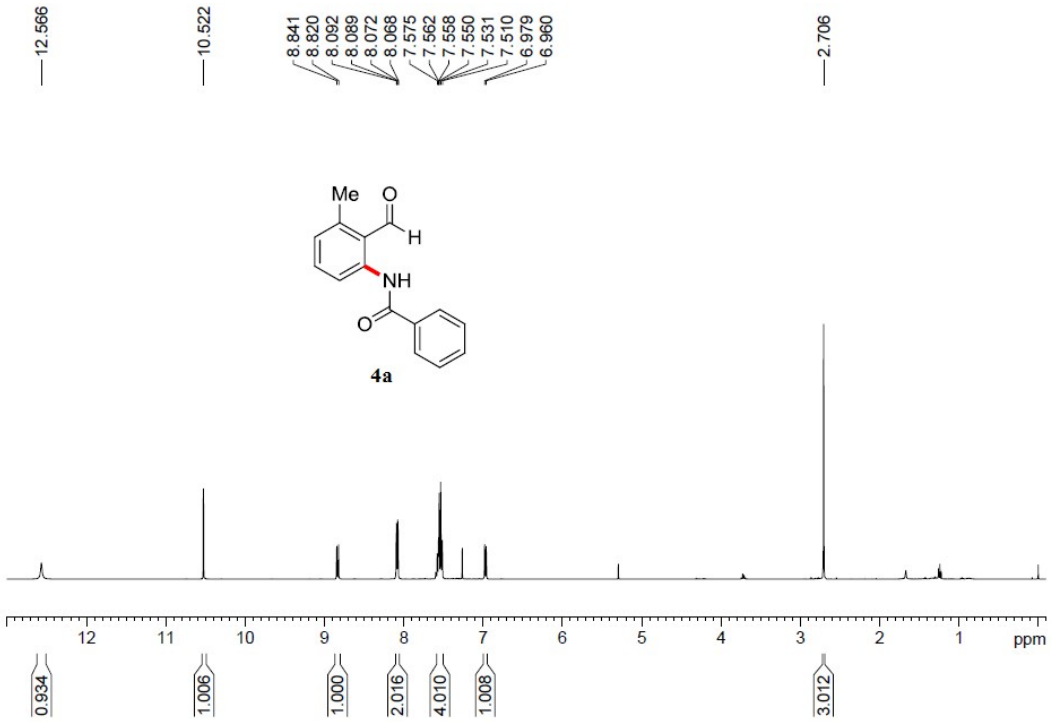
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7.510
6.979
6.960
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H
NH
O
4a
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10
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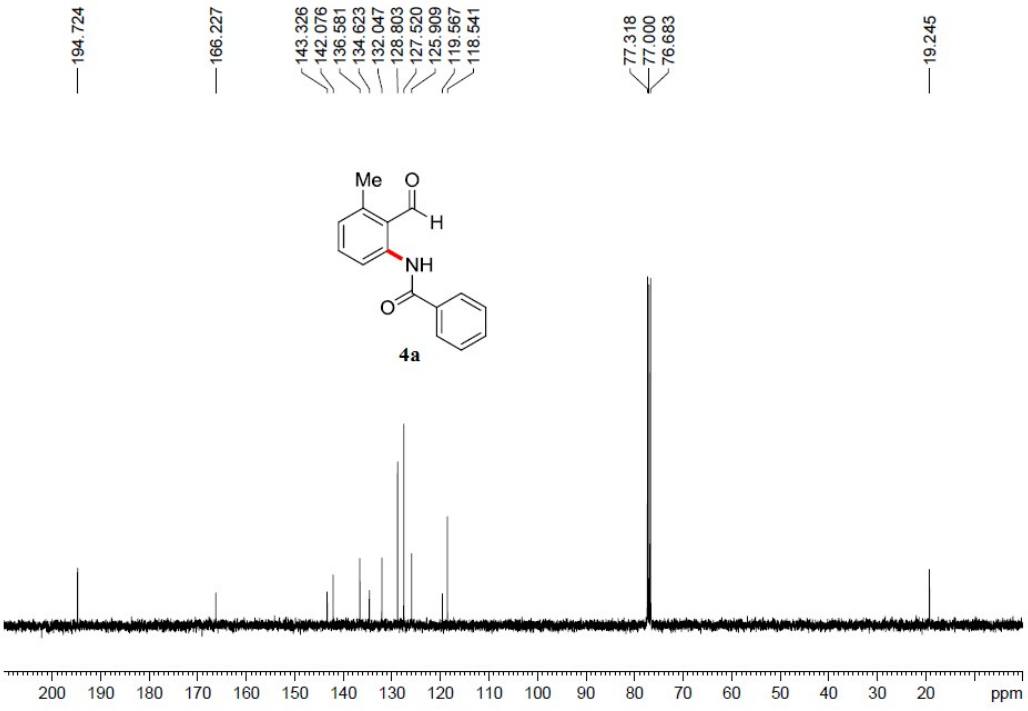
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77.000
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Me
O
H
NH
O
4a
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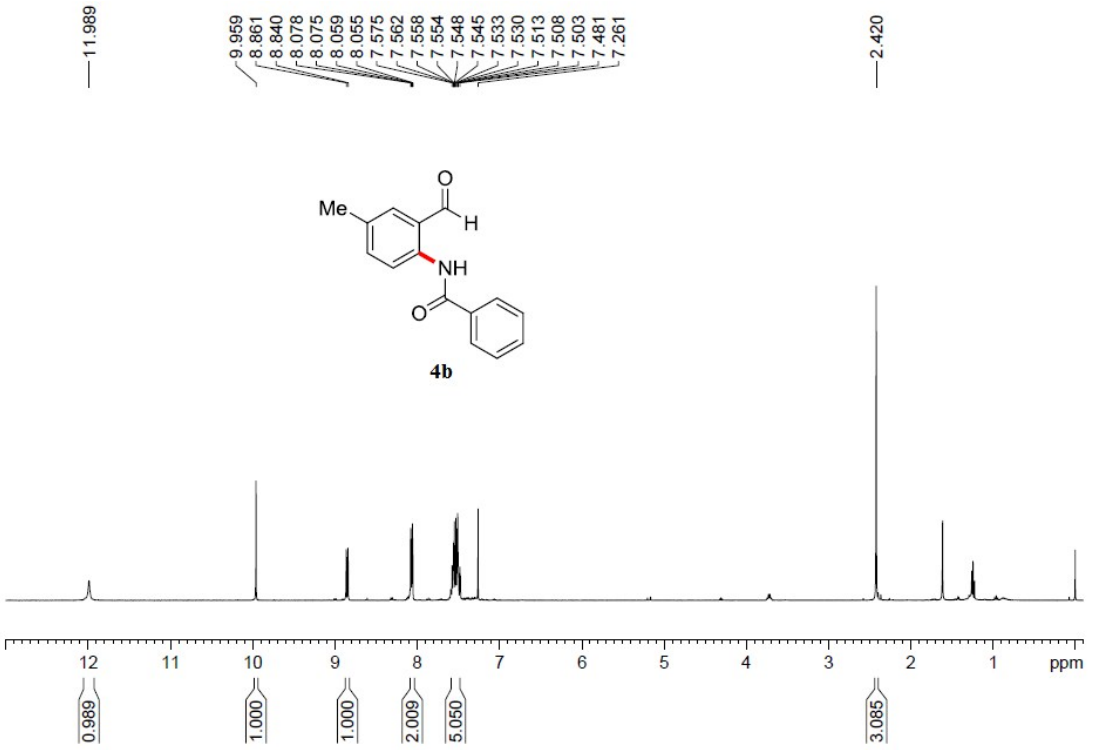
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7.530
7.513
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H
NH
O
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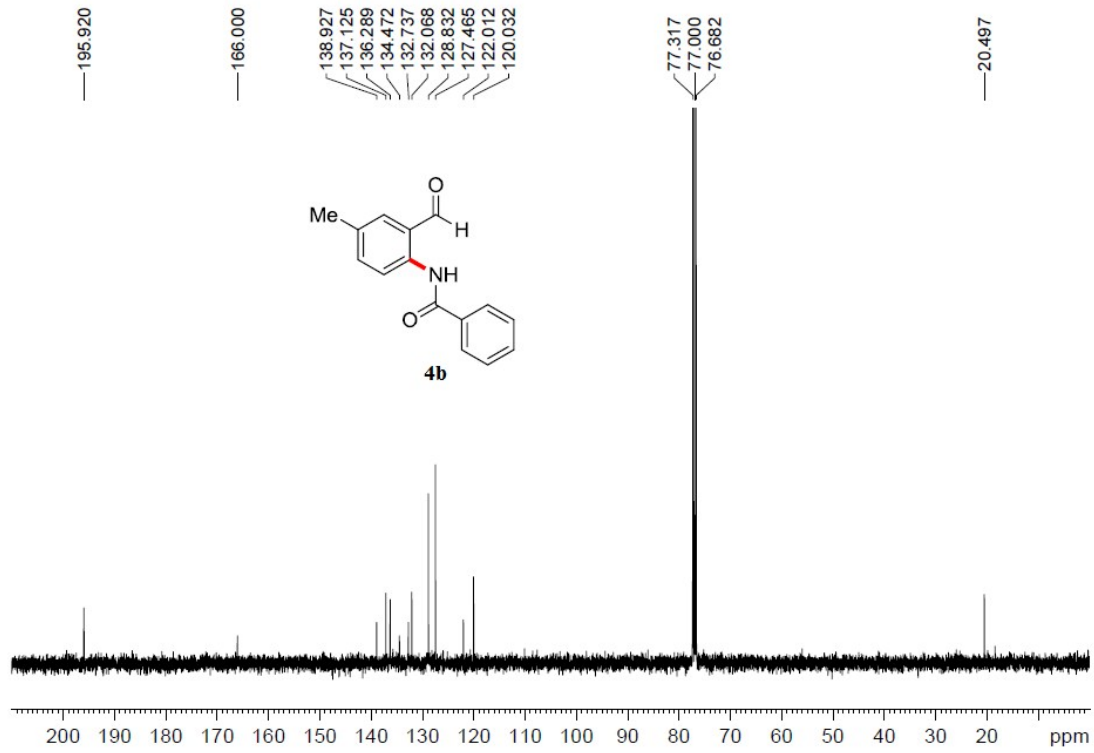
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132.068
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120.032
77.317
77.000
76.682
20.497
Me
O
H
NH
O
4b
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160
150
140
130
120
110
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90
80
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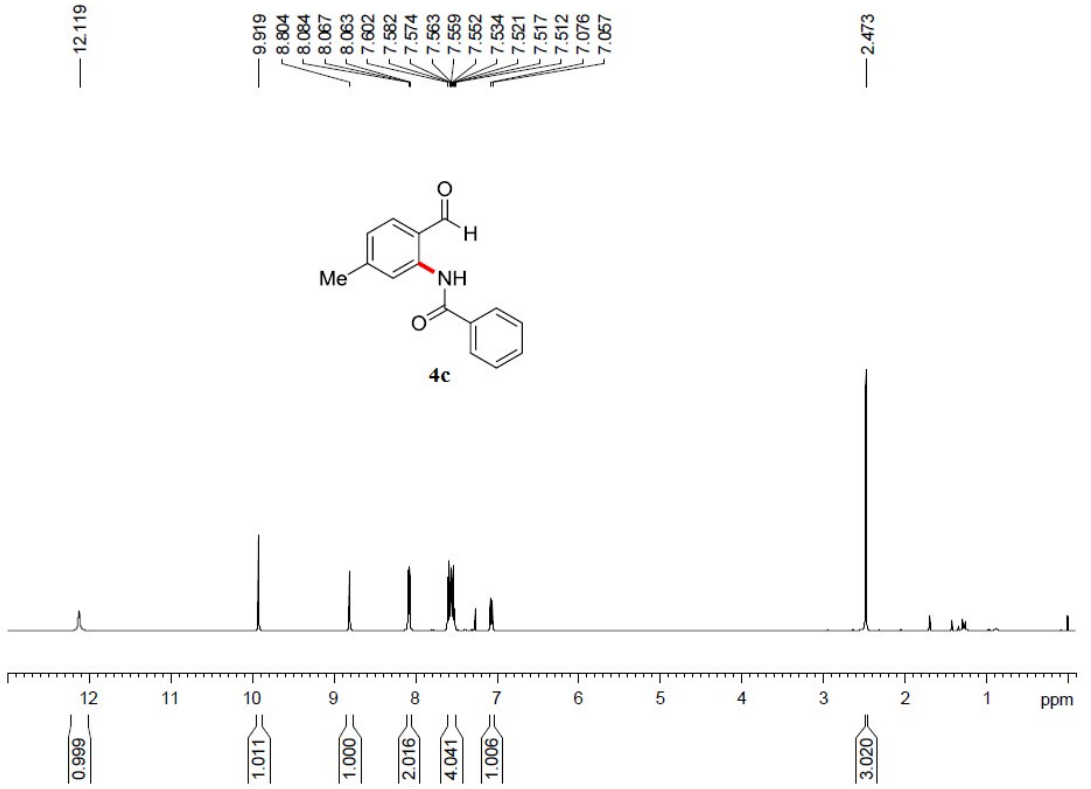
20
ppm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7.552
7.534
7.521
7.517
7.512
7.076
7.057
2.473
O
H
Me
NH
O
4c
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11
10
9
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ppm
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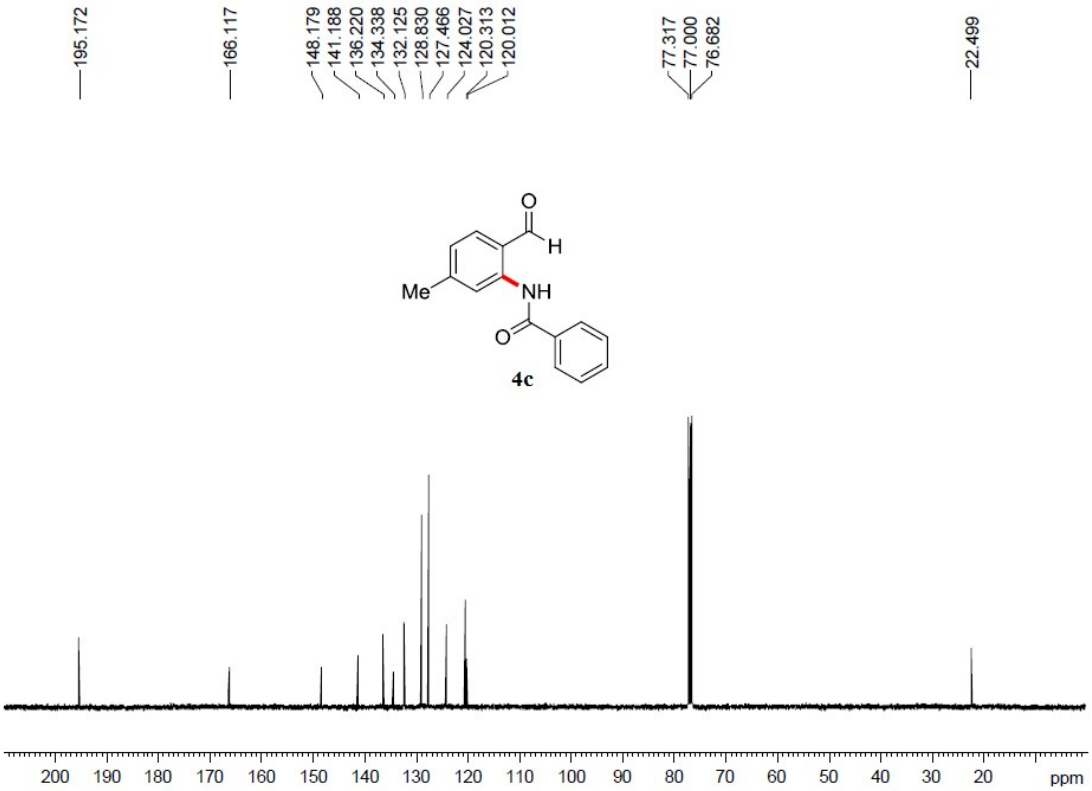
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120.012
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77.000
76.682
22.499
O
H
Me
NH
O
4c
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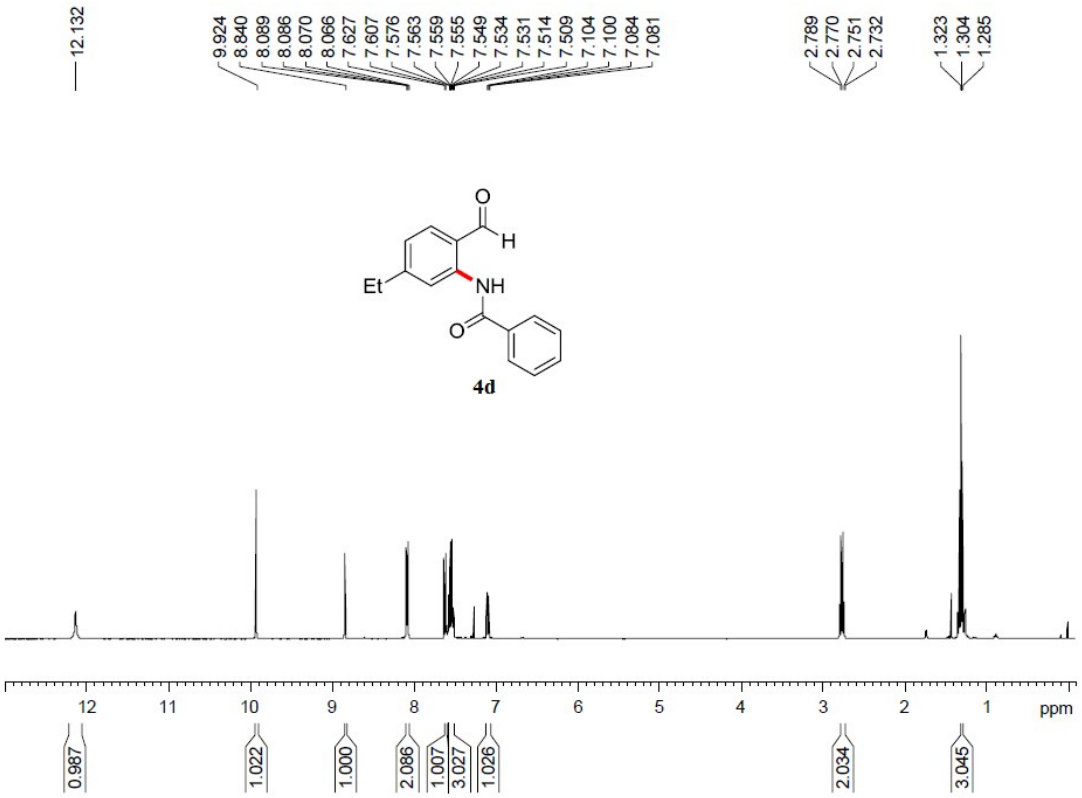
30
20
ppm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7.576
7.563
7.559
7.555
7.549
7.534
7.531
7.514
7.509
7.104
7.100
7.084
7.081
2.789
2.770
2.751
2.732
1.323
1.304
1.285
O
H
Et
NH
O
4d
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11
10
9
8
7
6
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1.007
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1.026
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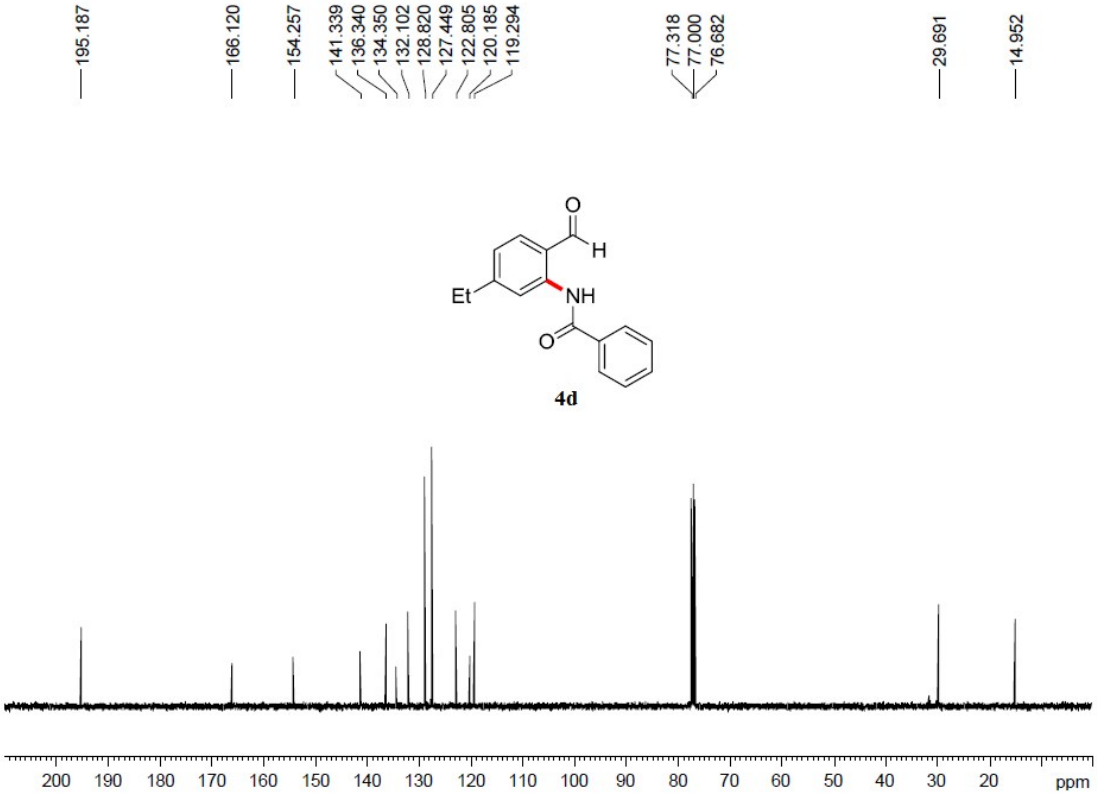
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119.294
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77.000
76.682
29.691
14.952
O
H
Et
NH
O
4d
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150
140
130
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80
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40
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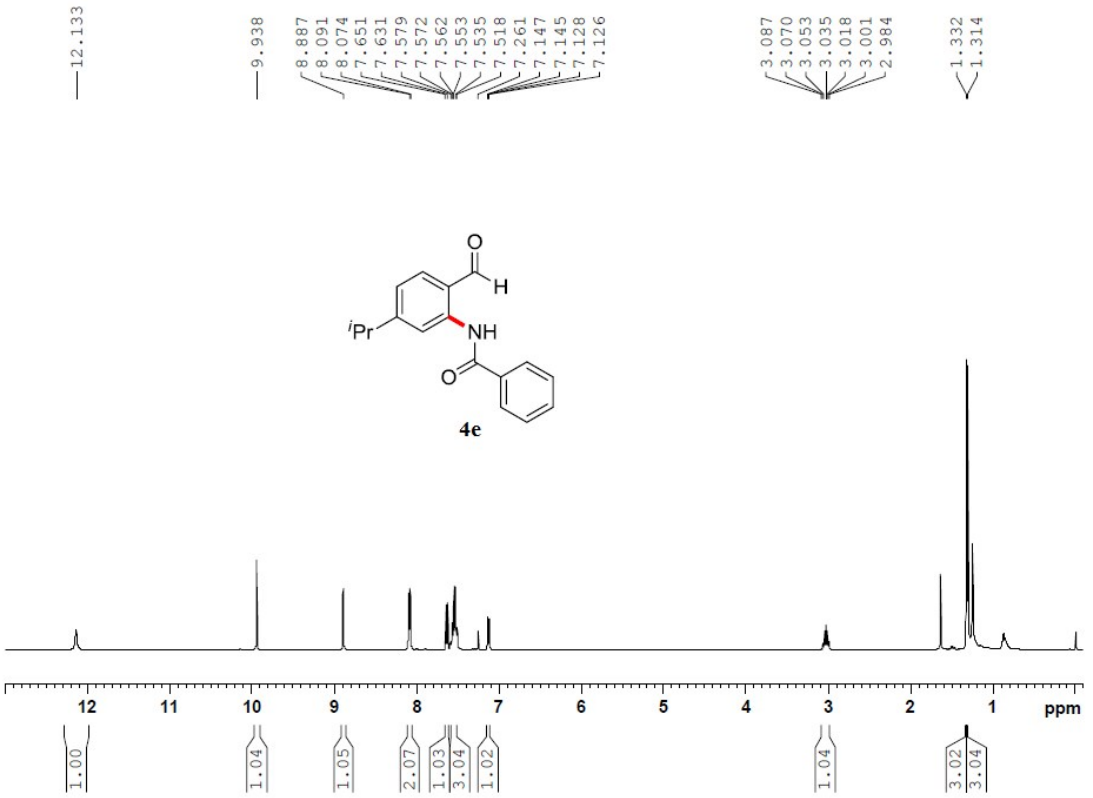
20
ppm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7.572
7.562
7.553
7.535
7.518
7.261
7.147
7.145
7.128
7.126
3.087
3.070
3.053
3.035
3.018
3.001
2.984
1.332
1.314
O
H
iPr
NH
O
4e
12
11
10
9
8
7
6
5
4
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2.07
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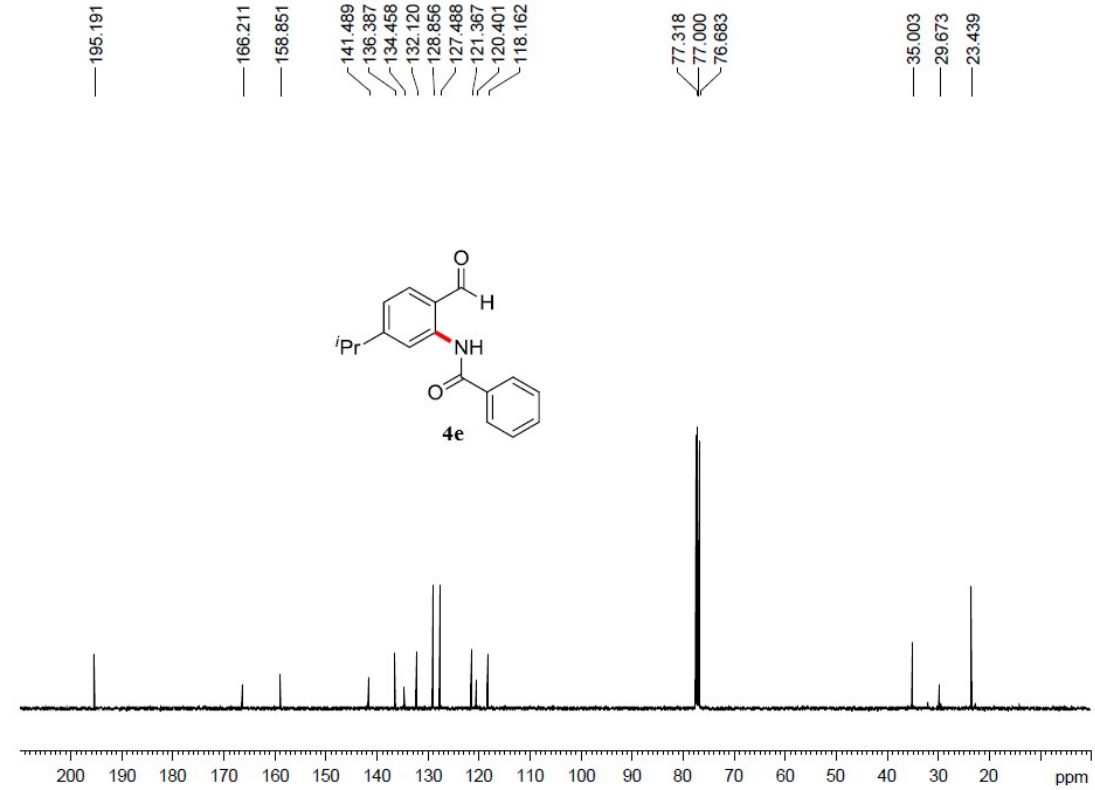
3.04
1.02
1.04
3.02
3.04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120.401
118.162
77.318
77.000
76.683
35.003
29.673
23.439
O
H
iPr
NH
O
4e
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160
150
140
130
120
110
100
90
80
70
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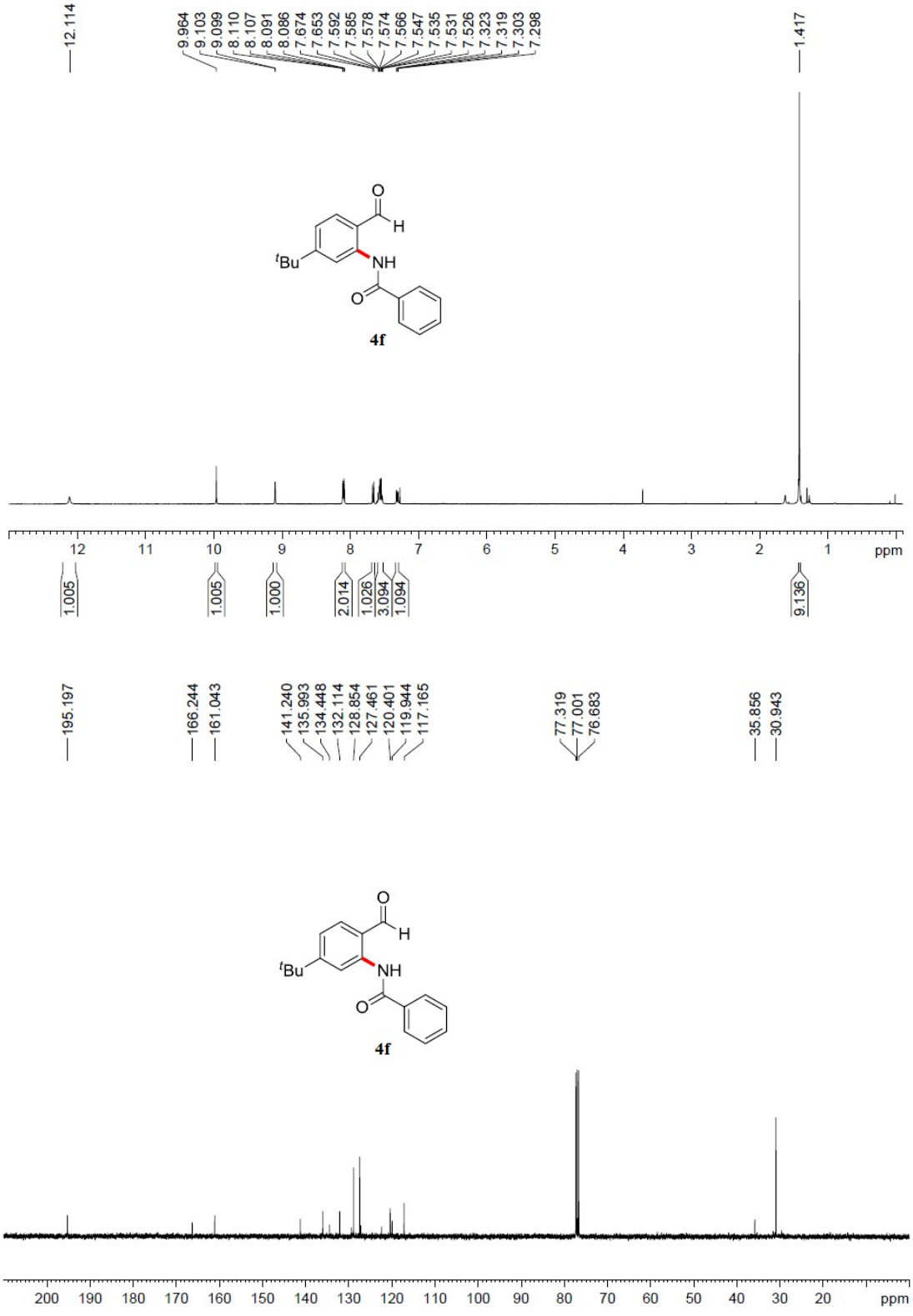
50
40
30
20
ppm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7.578
7.574
7.566
7.547
7.535
7.531
7.526
7.323
7.319
7.303
7.298
1.417
O
H
tBu
NH
O
4f
12
11
10
9
8
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6
5
4
3
2
1
ppm
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1.005
1.000
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1.026
3.094
1.094
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134.448
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127.461
120.401
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117.165
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77.001
76.683
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30.943
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NH
O
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30
20
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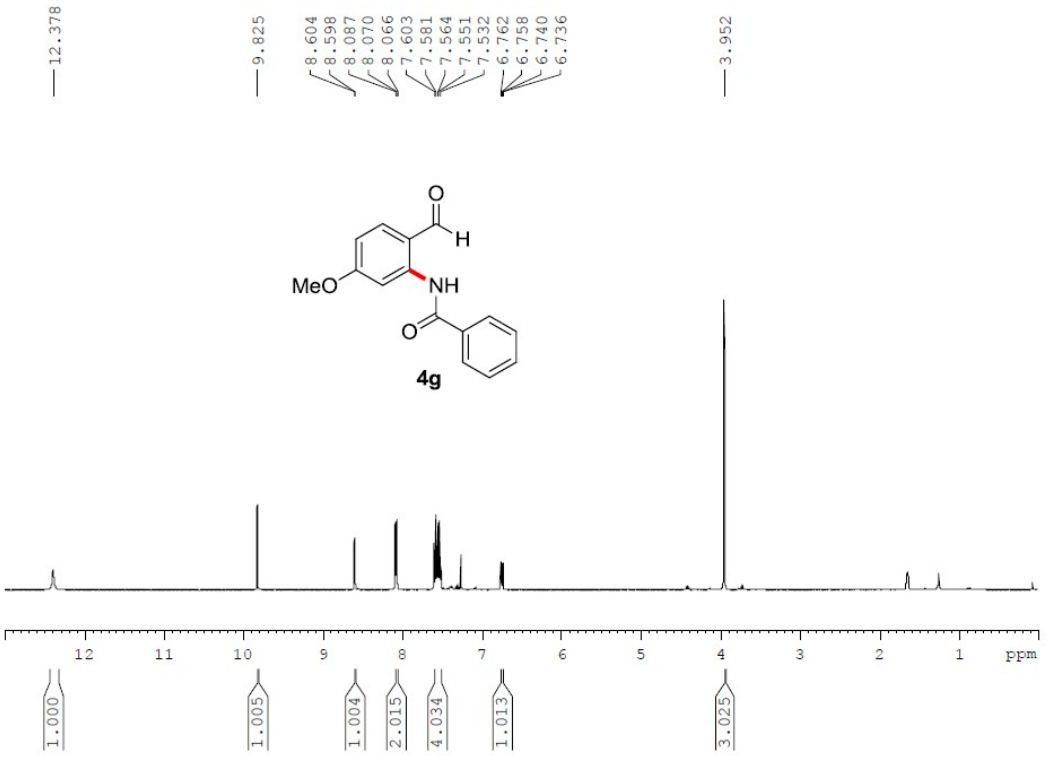
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7.532
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6.758
6.740
6.736
3.952
O
H
MeO
NH
O
4g
12
11
10
9
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3
2
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ppm
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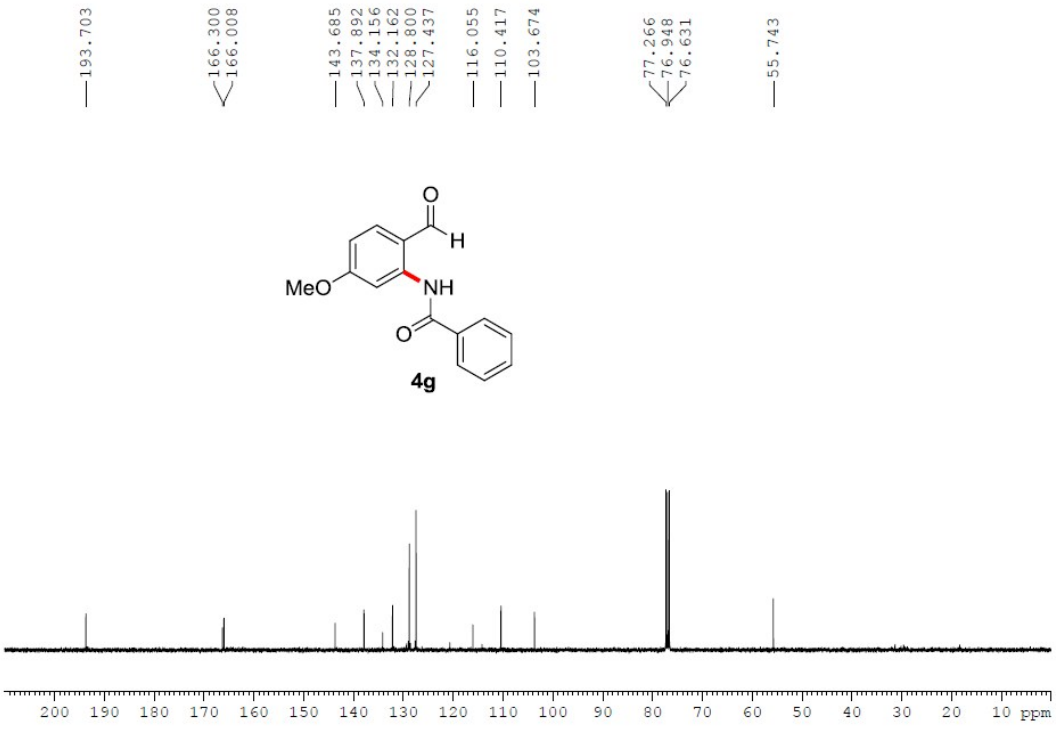
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103.674
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76.631
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H
MeO
NH
O
4g
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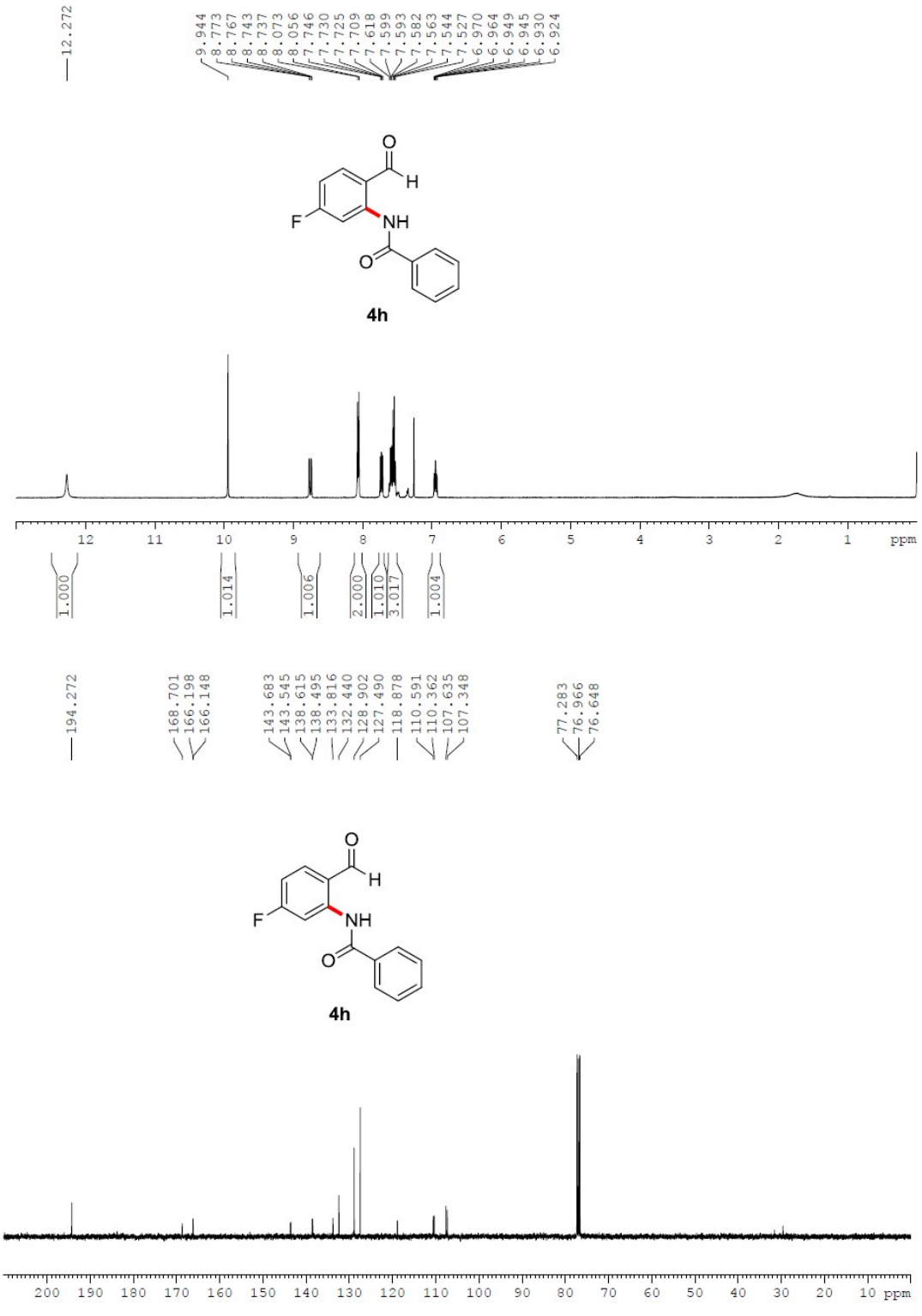
30
20
10
ppm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8.056
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7.618
7.599
7.593
7.582
7.563
7.544
7.527
6.970
6.964
6.949
6.945
6.930
6.924
O
H
F
NH
O
4h
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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1.014
1.006
2.000
1.010
3.017
1.004
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76.966
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H
F
NH
O
4h
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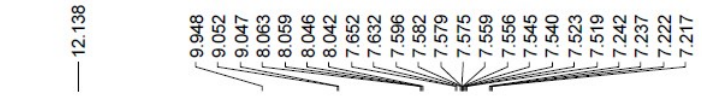
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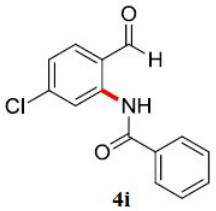
7.217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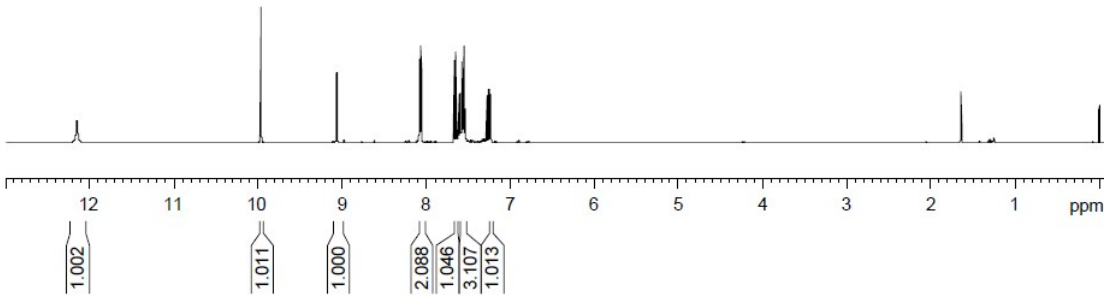
Cl
NH
O

4i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2
1
ppm
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1.000
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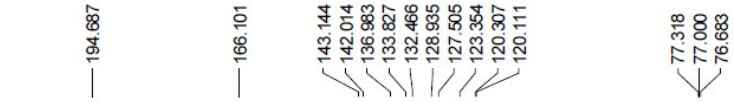
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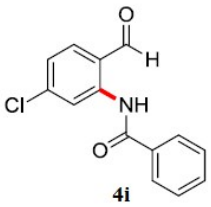
77.000
76.683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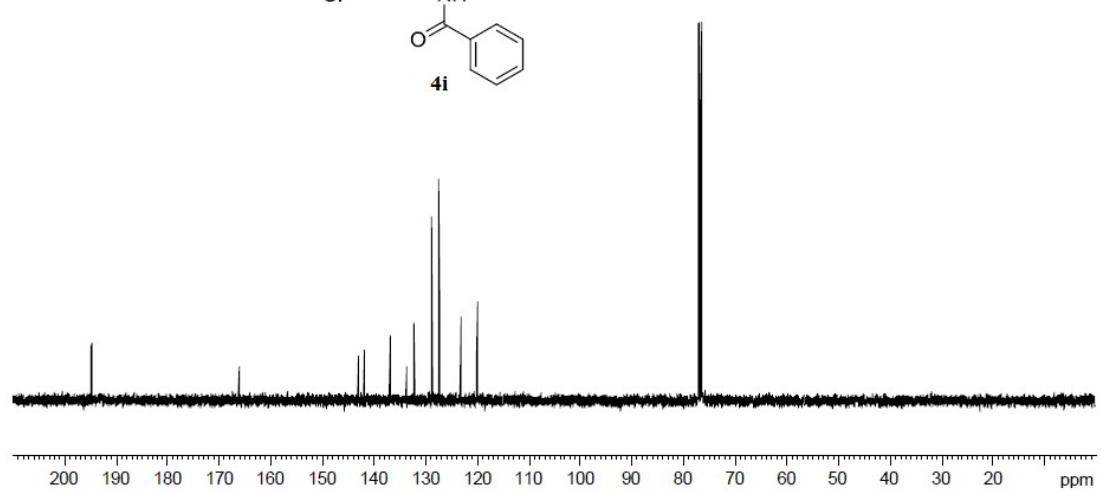
H
Cl
NH
O

4i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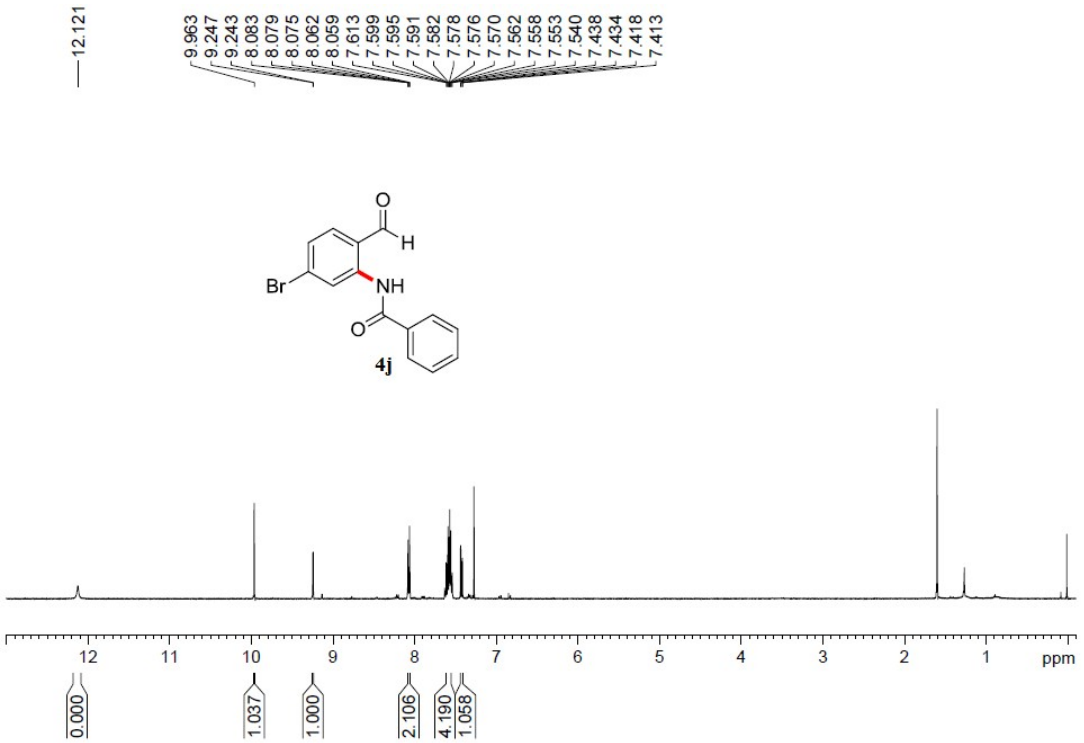
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.613
7.599
7.595
7.591
7.582
7.578
7.576
7.570
7.562
7.558
7.553
7.540
7.438
7.434
7.418
7.413
O
H
Br
NH
O
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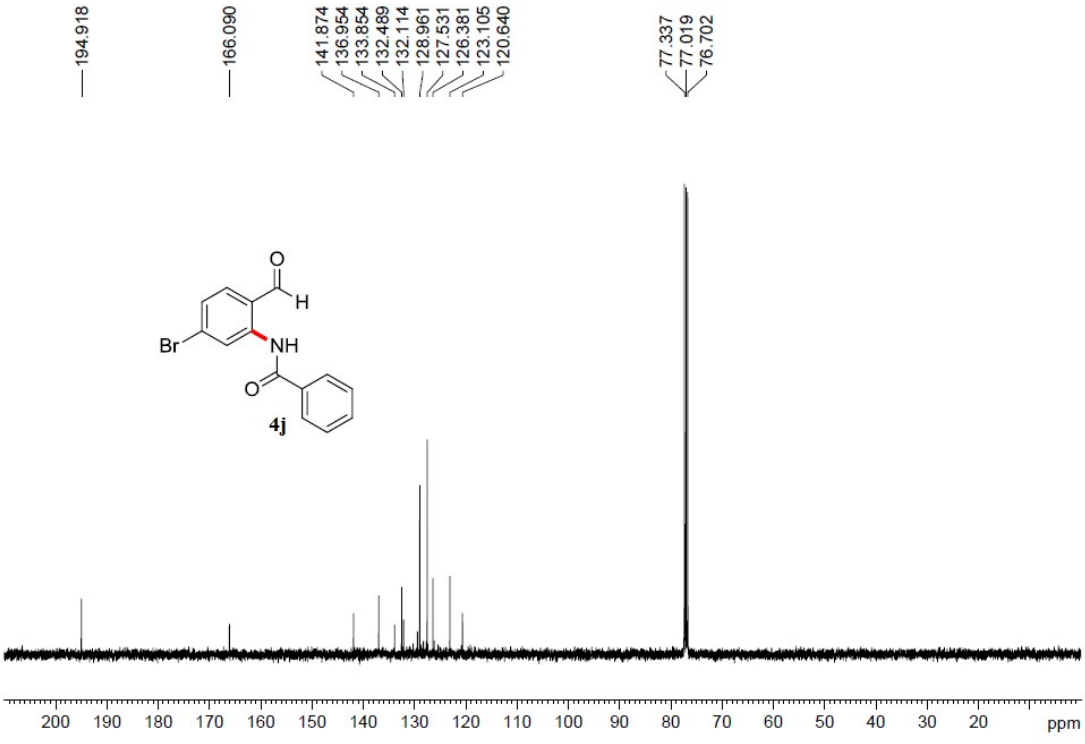
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126.381
123.105
120.640
77.337
77.019
76.702
O
H
Br
NH
O
4j
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80
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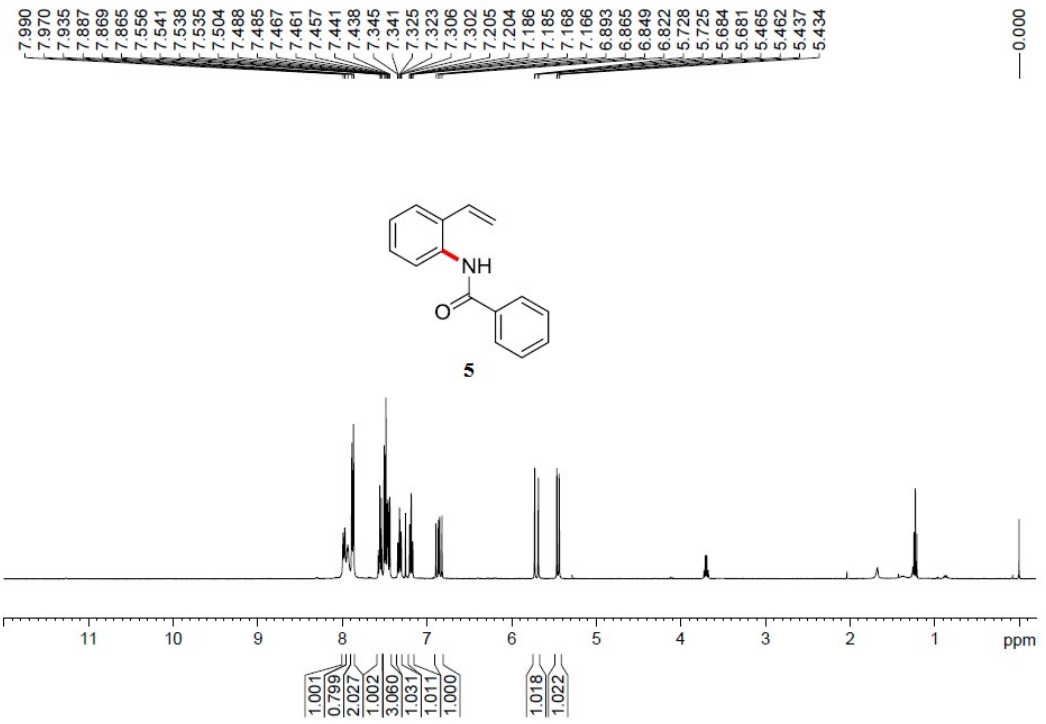
20
ppm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7.467
7.461
7.457
7.441
7.438
7.345
7.341
7.325
7.323
7.306
7.302
7.205
7.204
7.186
7.185
7.168
7.166
6.893
6.865
6.849
6.822
5.728
5.725
5.684
5.681
5.465
5.462
5.437
5.434
0.000
NH
O
5
11
10
9
8
7
6
5
4
3
2
1
ppm
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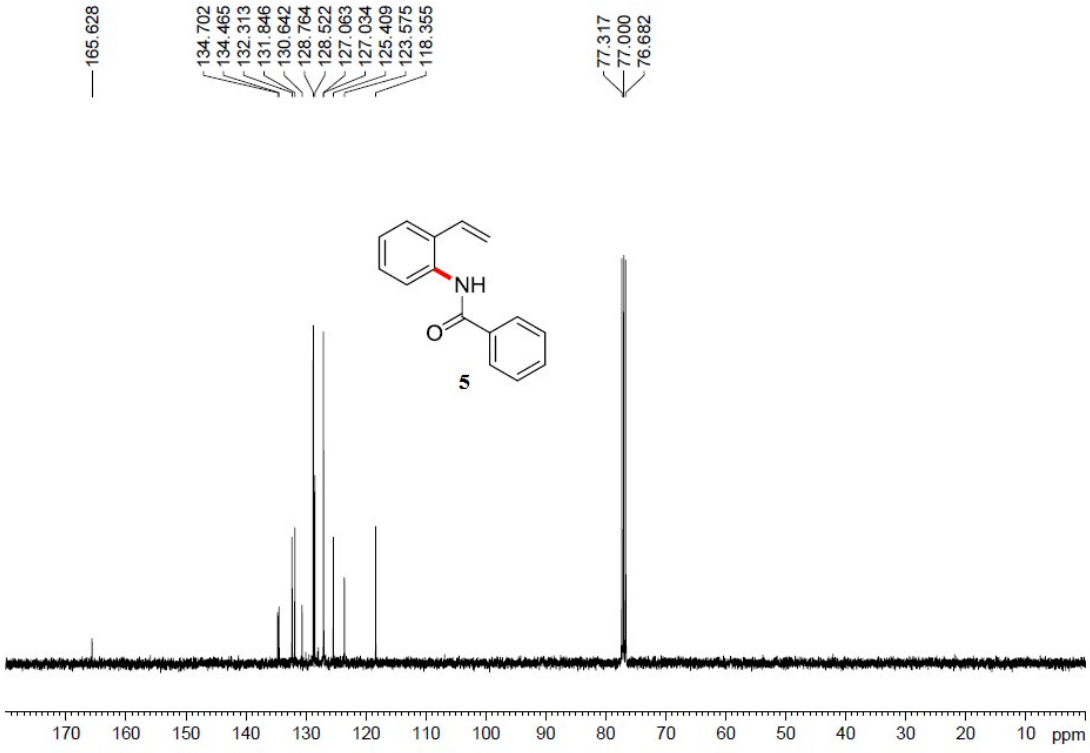
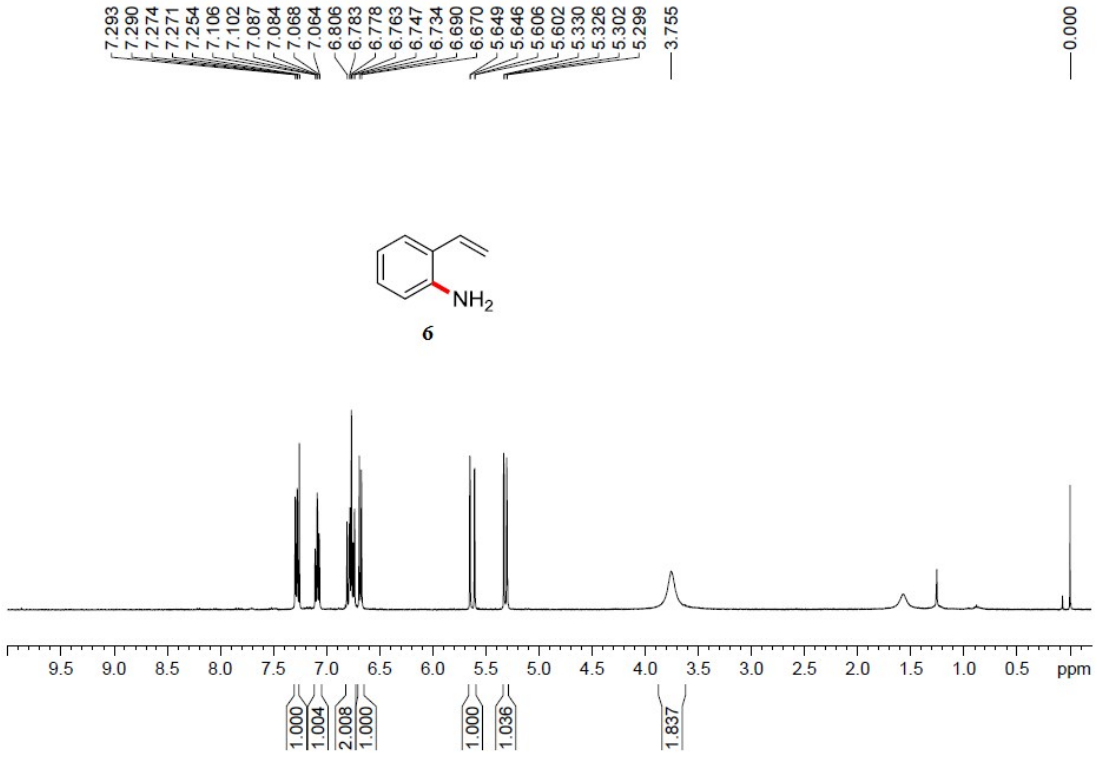
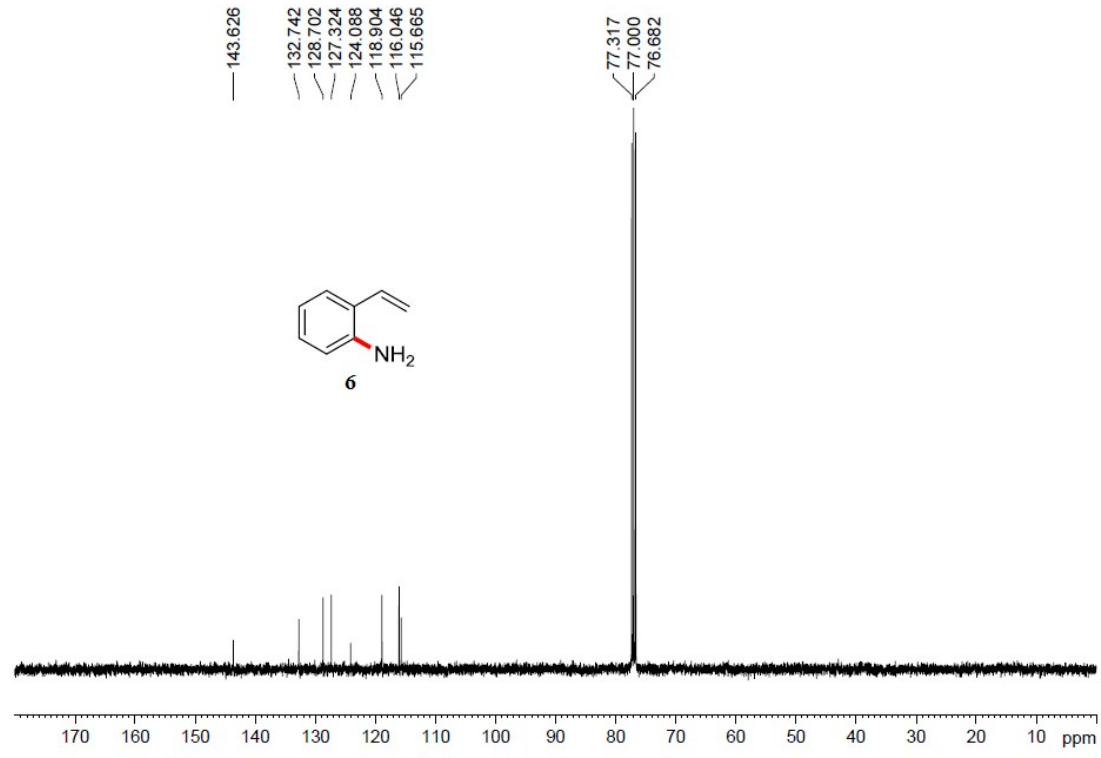
0.799
2.027
1.002
3.060
1.031
1.011
1.000
1.018
1.022

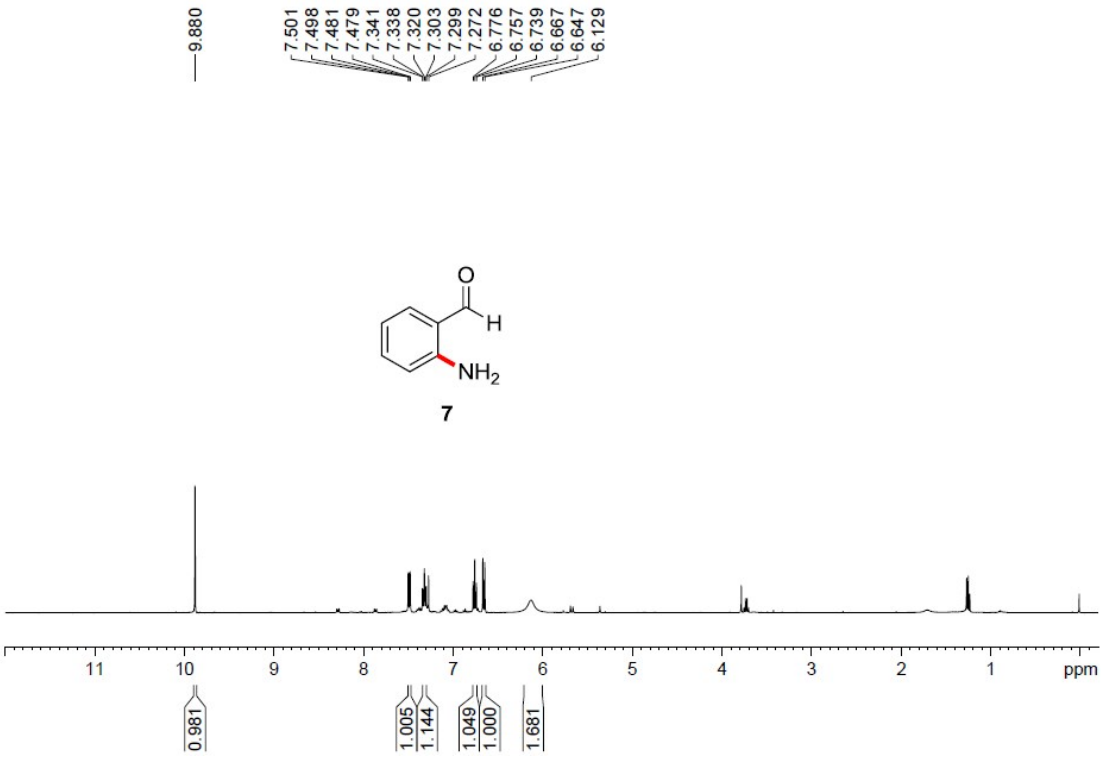

165.628
134.702
134.465
132.313
131.846
130.642
128.764
128.522
127.063
127.034
125.409
123.575
118.355
77.317
77.000
76.682
NH
O
5
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

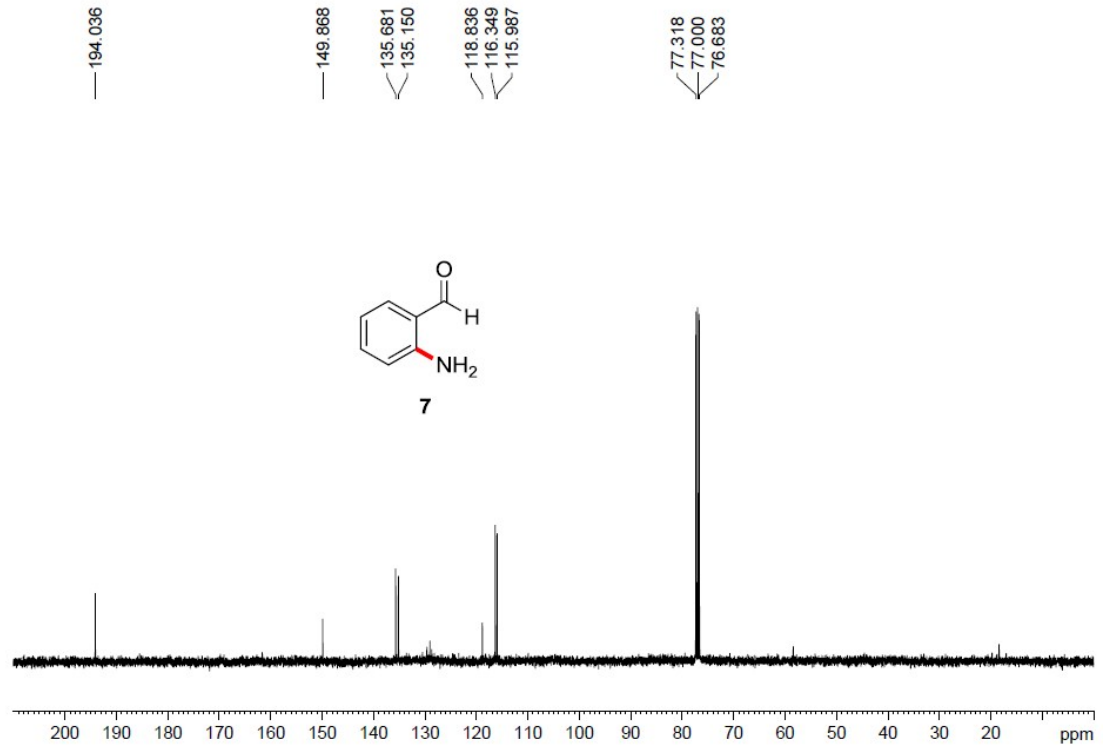

7.293
7.290
7.274
7.271
7.254
7.106
7.102
7.087
7.084
7.068
7.064
6.806
6.783
6.778
6.763
6.747
6.734
6.690
6.670
5.649
5.646
5.606
5.602
5.330
5.326
5.302
5.299
3.755
0.000
NH2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.004
2.008
1.000
1.000
1.036
1.837

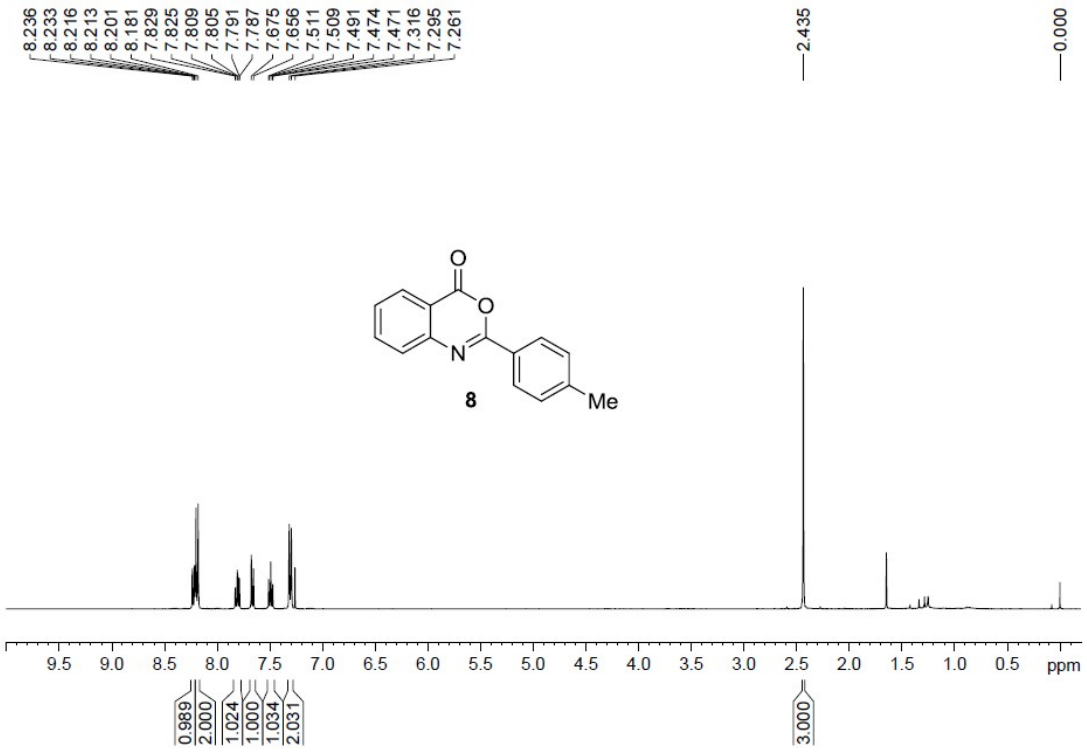
б


143.626
132.742
128.702
127.324
124.088
118.904
116.046
115.665
77.317
77.000
76.682
NH2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

б


9.880
7.501
7.498
7.481
7.479
7.341
7.338
7.320
7.303
7.299
7.272
6.776
6.757
6.739
6.667
6.647
6.129
O
H
NH2
7
11
10
9
8
7
6
5
4
3
2
1
ppm
0.981
1.005
1.144
1.049
1.000
1.681


194.036
149.868
135.681
135.150
118.836
116.349
115.987
77.318
77.000
76.683
O
H
NH2
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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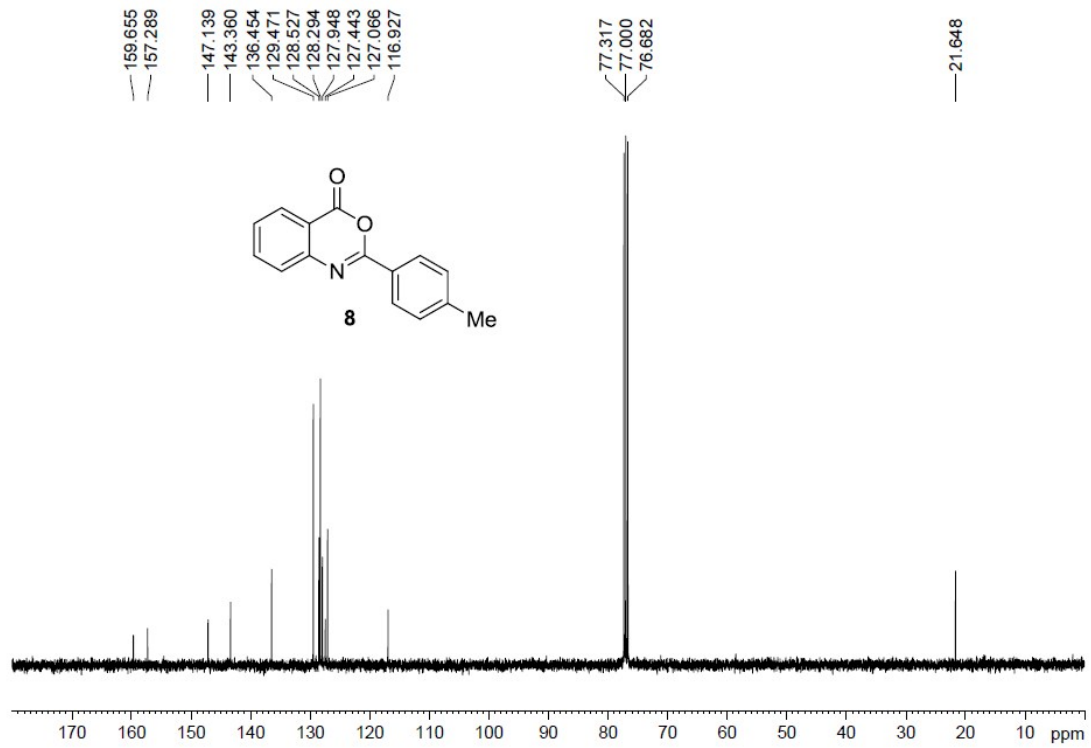
8.233
8.216
8.213
8.201
8.181
7.829
7.825
7.809
7.805
7.791
7.787
7.675
7.656
7.511
7.509
7.491
7.474
7.471
7.316
7.295
7.261
2.435
0.000
O
O
N
Me
8
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.989
2.000
1.024
1.000
1.034
2.031
3.000


159.655
157.289
147.139
143.360
136.454
129.471
128.527
128.294
127.948
127.443
127.066
116.927
77.317
77.000
76.682
21.648
O
O
N
Me
8
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm