Supplementary Information

Acetonitrile and Benzonitrile as Versatile Amino Sources in the Copper-Catalyzed Mild C−H Amidation Electrochemical Reactions

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Contents of Supplementary Information:

1. General Information

Preparative electrolysis was performed in galvanostatic mode with simultaneous control of the working electrode potential in thermostatically controlled, cylindrical 40 mL cell with separate anodic and cathodic compartments using a B5-49 direct current source at a current of 40 mA. A ceramic plate with the pore size 900 nm was used as a membrane. The potential of the working electrode was detected by a V7-27 DC voltmeter. The platinum cylindrical cathode with a surface area of 20 cm^2 used as a working electrode and the platinum rod was used as the anode. The working electrode potential was determined using reference electrode $Ag/AgNO_3$ in CH_3CN. The catholyte was a saturated solution of the $PyHBF_4$ in the CH_3CN. During electrolysis, the electrolyte was stirred using a magnetic stirrer. Preparative chromatography BUCHI system including Pump Module C-601, ELS Detector C-605, Fraction Collector C-660, Control Unit C-620, Sepacore Control Package and software program were used for products isolation.

2. Materials

Toluene (99%), o-Xylene (99%), m-Xylene (99%), Naphthalene (99%), 2-Phenylpyridine (97%), Copper(II) acetate (anhydrous, 98%) were purchased from Alfa Aesar and used without preliminary purification.
Benzene (anhydrous, 99.8%), 2-Bromotoluene (99%), Mesitylene (98%), 2-Bromomesitylene (98%), 2,6-Lutidine (ReagentPlus®, 98%), 4-Bromoanisole (≥99.0%), Anisole (anhydrous, 99.7%), Benzonitrile (99+%) were purchased from Sigma Aldrich and used without preliminary purification.
Acetonitrile (CHROMASOLV® Plus, ≥99.9%, «extra pure» by Acros Organics) was used without preliminary purification.

3. NMR and Mass measurements

NMR measurements were performed in the NMR department (A.E. Arbuzov Institute Organic and Physical Chemistry) of the Federal Collective Spectral Analysis Center for physical and chemical studies on the structure, properties, and composition of matter and materials. NMR experiments were conducted using Bruker spectrometers AVANCE-400 (399.93 MHz (^{1}H), 100.6 MHz (^{13}C) and AVANCE-600 (600.1 MHz (^{1}H) 150.9 MHz (^{13}C) equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5 G cm^{-1}. All spectra were acquired in a 5 mm gradient inverse broad band probe head. As a result, chemical shifts were reported on the δ (ppm) scale relative to the residual ^{1}H and ^{13}C C_6D_6 signal resulting in external NMR spectra.

Mass spectrometric studies (electrospray ionization) of the samples was carried out on a Bruker Daltonik GmbH AmazonX (Germany). Nitrogen was used as a drying gas in the source with a temperature of 220°C. The source voltage was 4.5 kV. Solutions of the samples were diluted with acetonitrile to a concentration of ~10–3 mg mL^{-1}. The samples were injected using an autosampler of an Agilent 1260 Infinity liquid chromatograph (Agilent Technologies, USA).

GC–MS analysis of the samples was carried out on an Agilent 6890N/5973 gas chromatograph (Agilent Technologies, USA) with a capillary column (30 mm×0.25 mm, film thickness 0.25 μm) equipped with an Agilent 6890N-5973 mass selective detector in the electron impact mode. The GC was operated under the following conditions: manual injection 1 μl; injector temperature, 300 °C; carrier gas (He) flow 1 ml/min, split – 1:5; oven temperature programmed 100–300 °C at a rate of 10 °C/min. The detector temperature was 230 °C. The MS was operated under 70 eV, scan range 29–800 amu.

4. Synthesis

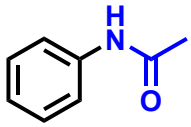
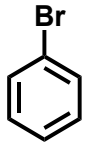
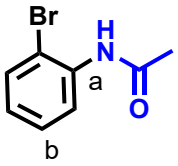
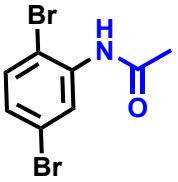
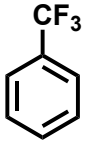
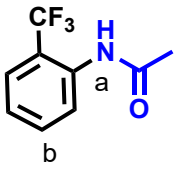
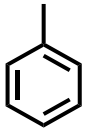
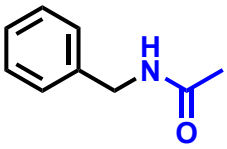
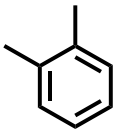
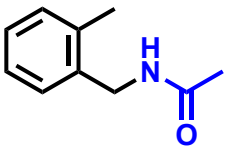
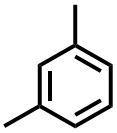
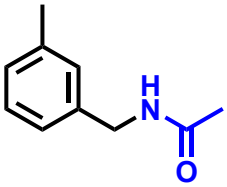
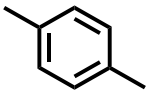
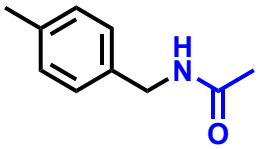
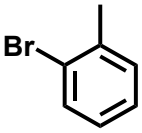
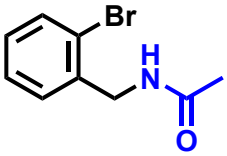
4.1 Electrolysis setup

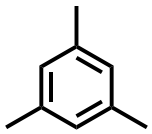
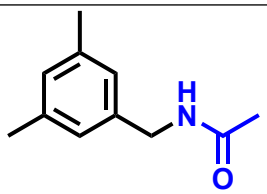
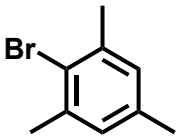
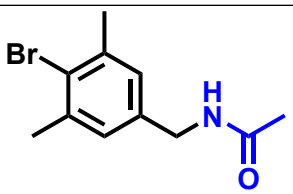
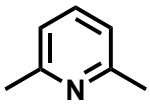
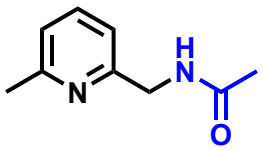
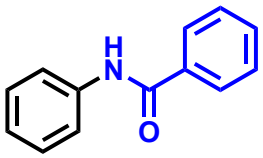
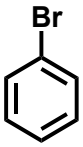
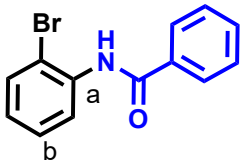
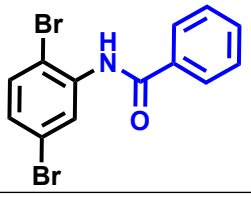
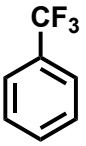
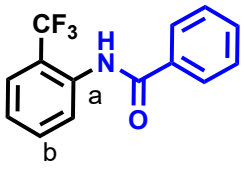
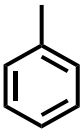
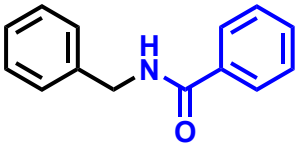
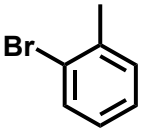
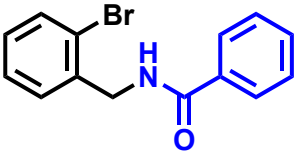
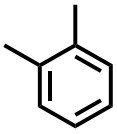
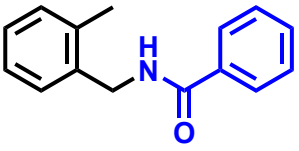
Figure S1. Electrolysis setup: cylindrical cell with divided anodic and cathodic compartments. The ceramic plate with the pore size of 900 nm is a membrane, the cylindrical platinum with a surface area of 20 cm^2 is cathode and the platinum rod is anode. The cell can be thermostatted.

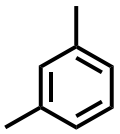
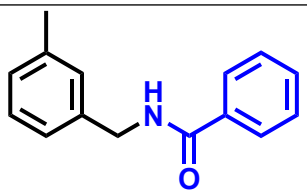
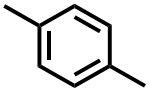
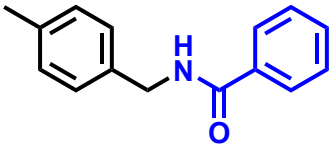
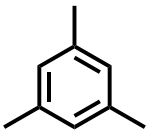
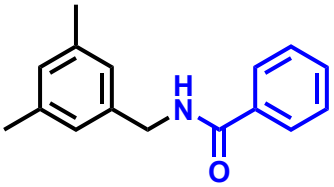
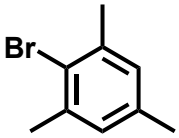
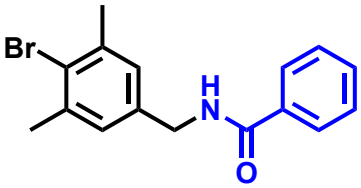
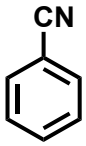
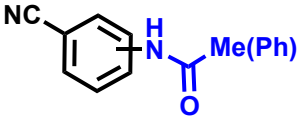
4.2 General electrolysis procedure

The substrate (1.0 mmol, 0.1 g), Copper acetate (0.1 mmol, 0.024 g), R-CN (40 mL) as solvent, were placed into electrochemical cell at 23°C. The electrolysis time is 2 to 4 hours (2F or 4F electricity). At the end of electrolysis the reaction mixture was evaporated on rotary evaporator. The residue was purified through passing through chromatographic column with silica gel (hexane-ethyl acetate). The product yields are given in Table S1.

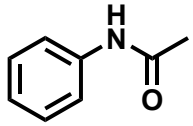
Table S1. Yield of the obtained acetamides. **a** Isolated. **b** by NMR

Entry	Substrate	R-CN	Product	Yield[a], %
1a		MeCN		70
2a,b		MeCN		68 (1:3 a:b)
3a		MeCN		69
4a,b		MeCN		76 (3:1 a:b)
5a		MeCN		78
6a		MeCN		69
7a		MeCN		68
8a		MeCN		72
9a		MeCN		56

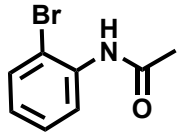
10a		MeCN		62
11a		MeCN		51
12a		MeCN		trace[b]
13a		PhCN		60
14a,b		PhCN		56 (1:3 a:b)
15a		PhCN		59
16a,b		PhCN		64 (3:1 a:b)
17a		PhCN		69
18a		PhCN		48
19a		PhCN		59

20a		PhCN		58
21a		PhCN		61
22a		PhCN		54
23a		PhCN		42
24a		MeCN, PhCN		0

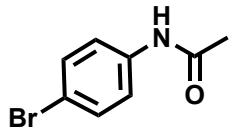
5. Characterization of the products



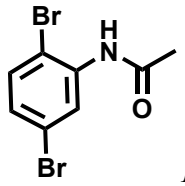
N-Phenylacetamide (**1a**). Light brown powder (70%, 0.121 g), mp 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.51–7.53 (d, *J* = 7.9 Hz, 2H), 7.33–7.36 (t, *J* = 7.8 Hz, 2H), 7.11–7.15 (t, *J* = 7.3 Hz, 1H), 7.22 (s, NH), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 168.18, 137.87, 129.01, 124.32, 119.85, 24.61. MS (ESI) m/z: $[M+H]^+$ 136.0.



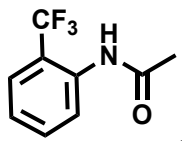
N-(2-bromophenyl)acetamide (**2a**). Light yellow solid (17 %, 0.048 g), mp 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.44 (d, J = 8.1 Hz, 1H), 7.71 (s, NH), 7.64 (d, J = 8.2 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 168.31, 135.82, 132.18, 128.31, 122.32, 113.43, 125.30, 24.50.MS (ESI) m/z: $[M+H]^+$ 214.0.



N-(4-bromophenyl)acetamide (**2b**). Light yellow solid (51%, 0.144 g), mp 167-169°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.53 (d, *J* = 8.5 Hz, 2H), 7. 41 (d, *J* = 8.5 Hz, 2H), 7.26 (s, NH), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 168.82, 139.21, 132.07, 121.32, 114.85, 24.5.MS (ESI) m/z: $[M+H]^+$ 214.0.

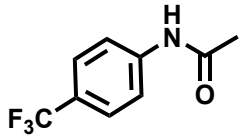


N-(2,5-dibromophenyl)acetamide (**3a**). White solid (69%, 0.267 g), mp 172-174°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.36(s, 1H), 7.95 (s, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.16-7.09 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 168.18, 136.77, 133.08, 124.41, 122.09, 111,41, 24.87.MS (ESI) m/z: $[M+H]^+$ 294.0.

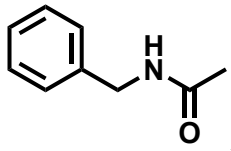


N-(2-(trifluoromethyl)phenyl)acetamide (**4a**). White solid (57%, 0.153 g), mp 95-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.24 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.40 (s, NH), 7.19 (t, J = 7.6 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz,

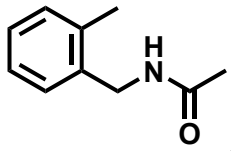
$CDCl_3$): δ_C = 168.44, 135.11, 132.93, 126.14, 124.69, 124.53, 124.43, 24.87. MS (ESI) m/z: $[M+H]^+$ 204.0.



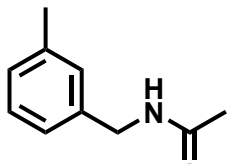
N-(4-(trifluoromethyl)phenyl)acetamide (**4b**). White solid (19%, 0.051 g), mp 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.68 (d, *J* = 7.9 Hz, 2H), 7. 53 (d, *J* = 7.9 Hz, 2H), 7.37 (s, NH), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 168.89, 142.65, 128.80, 123.40, 123.17, 123.00, 122.80, 119.20, 24.87. MS (ESI) m/z: $[M+H]^+$ 204.0.



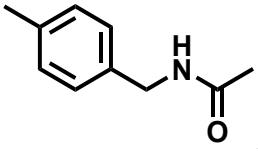
N-benzyl-acetamide (**5a**). Colorless crystals (78%, 0.126 g), mp 43–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.38 – 7.27 (m, 5H), 5.86 (s, 1H), 4.45 (d, *J* = 5.5 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 169.94, 138.23, 128.73, 127.86, 127.56, 43.8, 22.23. MS (ESI) m/z: $[M+H]^+$ 150.0.



N-(2-methylbenzyl)acetamide (**6a**). White solid (69%, 0.106 g), mp 73–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.26 – 7.19 (dt, 4H), 5.58 (s, 1H), 4.46 (d, *J* = 5.4 Hz, 2H), 2.35 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 169.67, 136.5, 135.81, 130.58, 128.66, 127.86, 126.25, 41.92, 23.18, 18.94. MS (ESI) m/z: $[M+H]^+$ 164.0.

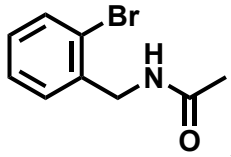


N-(3-methylbenzyl)acetamide (**7a**). White solid (67%, 0.103 g), mp 21–24 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.27-7.21 (m, 1H), 7.14 – 7.07 (m, 3H), 5.85 (s, 1H), 4.41 (d, *J* = 5.7 Hz, 2H), 2.37 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 169.76, 138.49, 138.14, 128.65, 128.32, 124.91, 43.8, 23.29, 21.33. MS (ESI) m/z: $[M+H]^+$ 164.0.

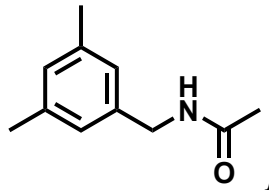


N-(4-methylbenzyl)acetamide (**8a**). White solid (72 %, 0.11 g), mp 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.20 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.59 (s,

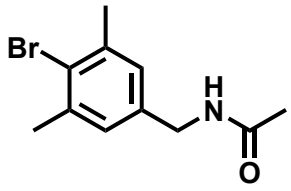
1H), 4.45 (d, *J* = 5.4 Hz, 2H), 2.34 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 169.92, 137.31, 135.2, 129.41, 127.88, 43.53, 23.28, 21.09. MS (ESI) m/z: $[M+H]^+$ 164.0.



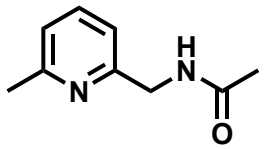
*N-(2-bromobenzyl)acetamid*e (**9a**). White solid (56%, 0.0746), mp. 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.61 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.23-7.17 (m, 1H), 6.31 (s, 1H), 4.64 (d, J = 5.7 Hz, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 170.03, 138.17, 131.6, 129.73, 128.86, 127.56, 124.8, 43.7, 23.37. MS (ESI) m/z: $[M+H]^+$ 228.0.



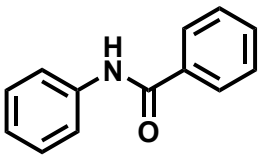
N-(3,5-dimethylbenzyl)acetamide (**10a**). White solid (62%, 0.091 g), mp. 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 6.92 (d, *J* = 20.1 Hz, 3H), 6.24 (s, 1H), 4.37 (d, *J* = 4.5 Hz, 2H), 2.31 (s, 6H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 170.98, 138.46, 137.5, 129.35, 125.75, 44.11, 22.89, 21.1. MS (ESI) m/z: $[M+H]^+$ 178.0.



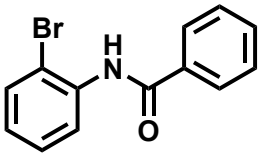
N-(4-bromo-3,5-dimethylbenzyl)acetamide (**11a**). White solid (51%, 0.065 g), mp. 101-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.03 (s, 2H), 5.97 (s, 1H), 4.45 (d, *J* = 5.6 Hz, 2H), 2.48 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 169.98, 139.92, 130.36, 127.48, 122.9, 44.25, 22.33, 20.3.MS (ESI) m/z: $[M+H]^+$ 256.0.



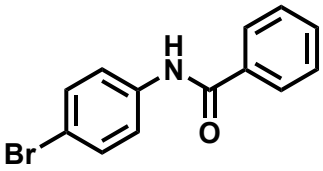
N-((6-methylpyridin-2-yl)methyl)acetamide (**12a**). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.09 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 4.7 (d, *J* = 5.7 Hz, 2H), 2.5 (s, 3H), 2.07 (s, 3H). MS (ESI) m/z: $[M+H]^+$ 165.0.



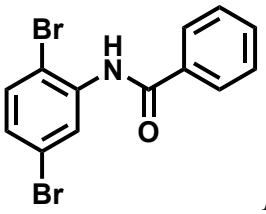
N-Phenylbenzamide (**13a**). White solid (60%, 0.15 g), mp. 163-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.17-8.11 (m, 2H), 7.88-7.82 (m, 2H), 7.64-7.5 (m, 6H), 6.20 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 166.82, 139.17, 135.44, 132.4, 128.77, 128.49, 128.01, 123.71, 120.28. MS (ESI) m/z: $[M+H]^+$ 198.



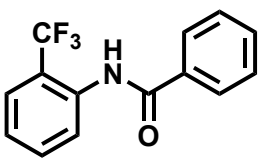
N-(2-bromophenyl)benzamide (**14a**). Light yellow solid (14%, 0.051 g), mp. 109-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.64 (d, J = 7.8 Hz, 1H), 8.26 (s, NH), 8.04 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.0 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 165.31, 136.44, 134.11, 132.78, 131.87, 128.82, 128.47, 128.11, 127.92, 127.63, 120.56. MS (ESI) m/z: $[M+H]^+$ 276.



N-(4-bromophenyl)benzamide (**14b**). Light yellow solid (42%, 0.153 g), mp. 203-205 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.02 (d, J = 7.6 Hz, 2H), 7.9 (s, NH), 7.81 (d, J = 7.6 Hz, 2H), 7.62-7.55 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 166.17, 137.09, 134.58, 131.6, 129.73, 128.86, 127.56, 117.23. MS (ESI) m/z: $[M+H]^+$ 276.

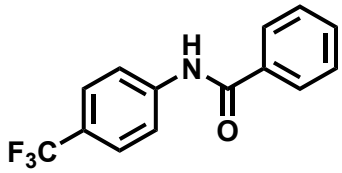


N-(2,5-dibromophenyl)benzamide (**15a**). White solid (59%, 0.277 g), mp. 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.11 (d, J = 7.5 Hz, 2H), 7.85 (d, J = 7.5 Hz, 1H), 7.61-7.58 (m, 2H), 7.53 (s, NH), 7.6 (t, J = 7.0 Hz, 2H), 7.44 (t, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 166.28, 137.21, 134.41, 132.78, 131.87, 128.82, 128.47, 128.11, 127.92, 127.63. MS (ESI) m/z: $[M+H]^+$ 354.

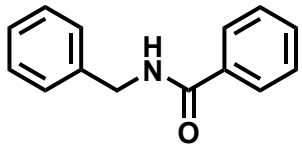


N-(2-(Trifluoromethyl)phenyl)benzamide (**16a**). White solid (48%, 0.168 g), mp. 144-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.41 (d, *J* = 8.2 Hz, 1H), 8.25 (s, 1H), 7.89–7.86 (m, 2H), 7.66–7.49 (m, 5H), 7.26 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C =

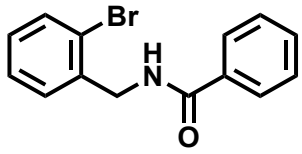
166.73, 136.09, 134.57, 133.9, 132.66, 132.04, 129.67, 129.09, 127.4, 127.17, 127.0, 126.8. MS (ESI) m/z: $[M+H]^+$ 266.



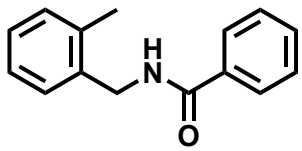
N-(2-(Trifluoromethyl)phenyl)benzamide (**16b**). White solid (16%, 0.056 g), mp. 200-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.01 (s, 1H), 7.91 (d, *J* = 7.0 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.62 (tt, *J* = 7.0, 1.8 Hz, 1H), 751 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 167.89, 144.15, 135.22, 132.73, 128.96, 125.84, 123.97, 121.07. MS (ESI) m/z: $[M+H]^+$ 266.



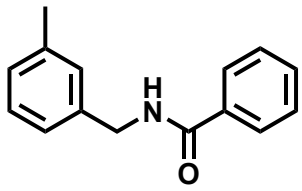
N-benzylbenzamide (**17a**). White solid (69%, 0.158 g), mp. 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.81 (m, 2H), 7.69-7.6 (m, 4H), 7.37 (m, 4H), 6.5 (s, 1H), 4.66 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 166.48, 138.16, 134.38, 133.11, 128.88, 128.61, 127.96, 127.64, 126.96, 44.17. MS (ESI) m/z: $[M+H]^+$ 212.



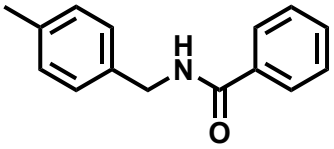
N-(2-bromobenzyl)benzamide (**18a**). White solid (48%, 0.081 g), mp. 105-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.90–7.84 (m, 2H), 7.75-7.32 (m, 6H), 7.25-7.16 (m, 1H), 6.73 (s, 1H), 4.66 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 168.43, 137.72, 135.19, 134.21, 132.77, 131.93, 129.44, 128.62, 128.06, 127.51, 123.87, 44.56. MS (ESI) m/z: $[M+H]^+$ 290.



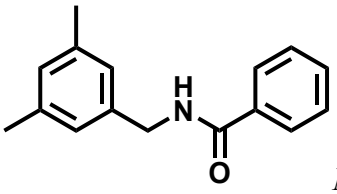
N-(2-methylbenzyl)benzamide (**19a**). White solid (59%, 0.125 g), mp. 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.82–7.76 (m, 2H), 7.43–7.36 (m, 1H), 7.32–7.23 (m, 2H), 7.21–7.16 (m, 1H), 7.12–7.07 (m, 3H), 6.7 (s, 1H), 4.6 (d, *J* = 5.3 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 167.91, 138.47, 137.89, 136.23, 131.58, 130.84, 128.70, 128.60, 128.12, 127.50, 125.79, 42.28, 19.80. MS (ESI) m/z: $[M+H]^+$ 226.



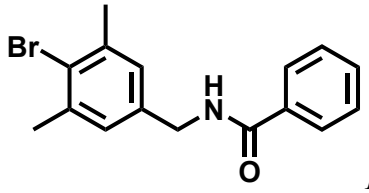
N-(3-methylbenzyl)benzamide (**20a**). Light yellow solid (58%, 0.123 g) mp. 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.93–7.88 (d, 2H), 7.49–7.41 (m, 1H), 7.36-7.29 (m, 2H), 7.27–7.19 (m, 1H), 7.15–7.06 (m, 3H), 6.68 (s, 1H), 4.58 (d, *J* = 5.6 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 167.14, 139.62, 139.19, 134.81, 131.53, 128.78, 128.61, 128.44, 127.50, 125.83, 44.43, 20.88. MS (ESI) m/z: $[M+H]^+$ 226.



N-(4-methylbenzyl)benzamide (**21a**). White solid (61%, 0.129 g) mp. 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.83–7.80 (m, 2H), 7.67–7.65 (m, 1H), 7.46-7.42 (m, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.50 (s, 1H), 4.62 (d, *J* = 5.6 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 167.29, 137.11, 135.12, 134.28, 131.29, 129.32, 128.41, 127.82, 126.93, 43.74, 21.33. MS (ESI) m/z: $[M+H]^+$ 226.



N-(3,5-dimethylbenzyl)benzamide (**22a**). White solid (54%, 0.107 g), mp. 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.83–7.81 (m, 2H), 7.57–7.52 (m, 1H), 7.49-7.46 (m, 2H), 7.03-6.94 (m, 3H), 6.45 (s, 1H), 4.6 (d, *J* = 4.5 Hz, 2H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 167.77, 138.64, 136.24, 131.55, 129.42, 128.68, 127.20, 125.81, 42.32, 19.13. MS (ESI) m/z: $[M+H]^+$ 240.



N-(4-bromo-3,5-dimethylbenzyl)benzamide (**23a**). White solid (42%, 0.067), mp. 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 7.83-7.76 (m, 2H), 7.55–7.52 (m, 1H), 7.51- 7.40 (m, 2H), 6.99-6.87 (m, 2H), 6.59 (s, 1H), 4.59 (d, *J* = 4.5 Hz, 2H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 167.66, 138.85, 135.97, 131.44, 129.42, 128.81, 125.88, 42.56, 20.45. MS (ESI) m/z: $[M+H]^+$ 318.

6. Electrochemical potentials

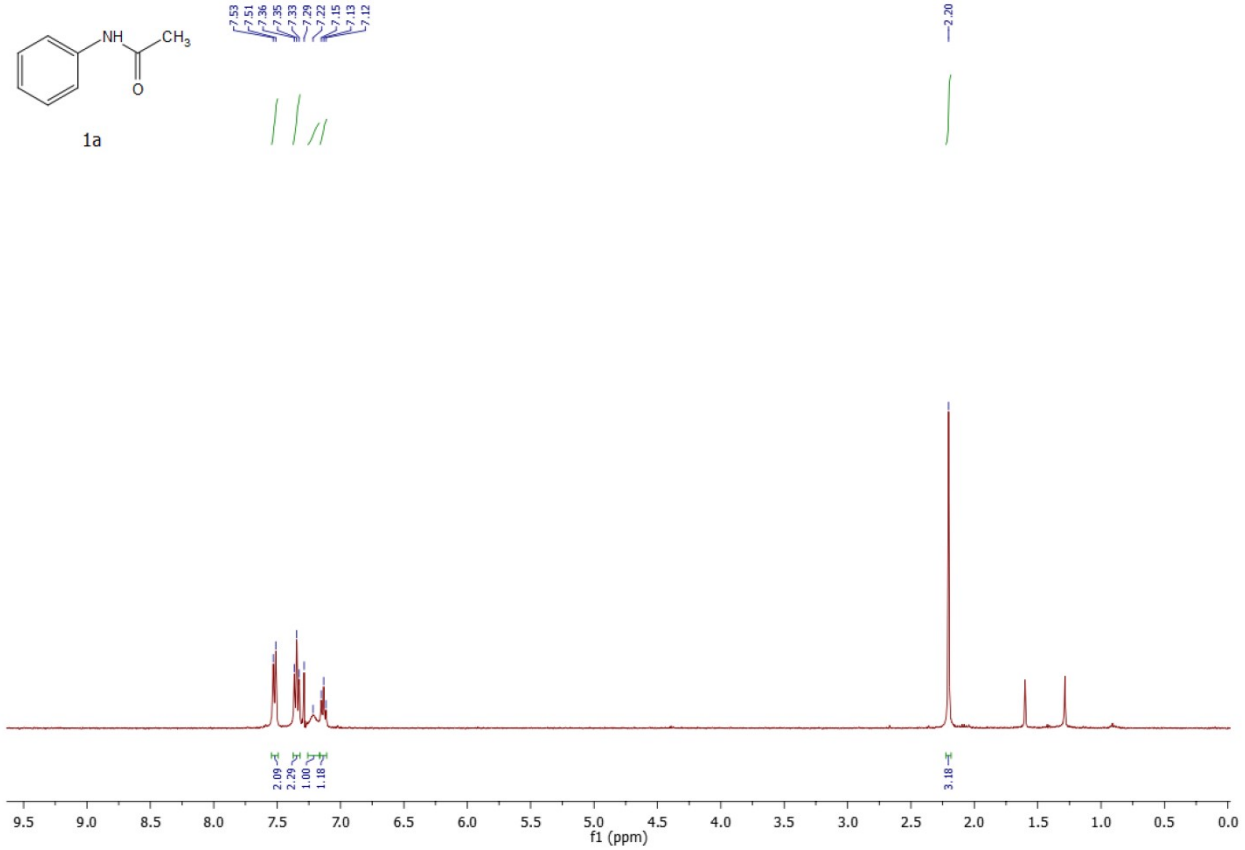
Table S2. Oxidation potentials (V) of compounds; (***a)*** our results, conditions: WE- GC, RE – **Ag/AgCl**, Bu_4NBF_4, CH_3CN; (***b)*** literature data, conditions: WE- Pt, RE – **$Ag/AgNO_3$**, perchlorate salts ($LiClO_4$, $NaClO_4$, $(C_2H_5)_4NClO_4$, $(n\text{-}C_8H_7)_4NClO_4$, $(n\text{-}C_4H_9)_4NClO_4$)), CH_3CN

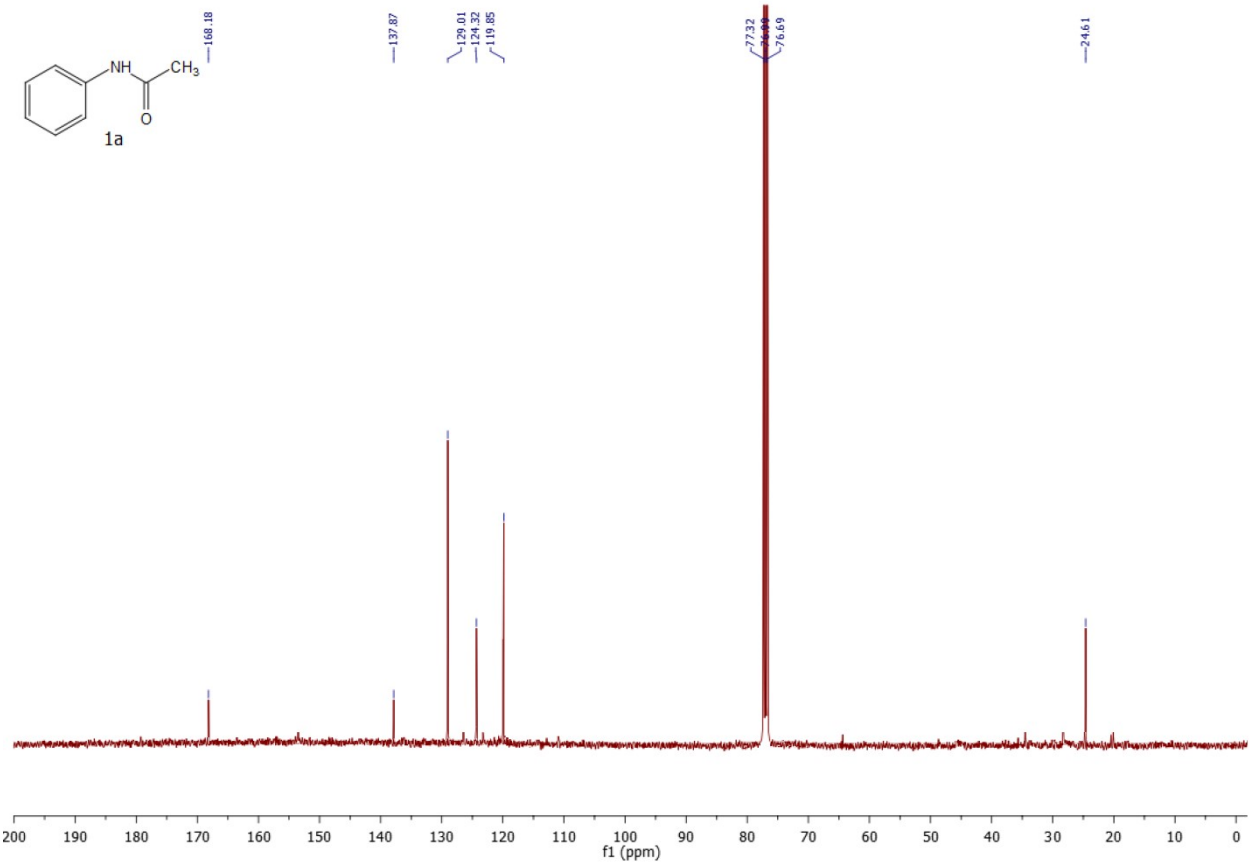
№	Compound	E_{ox}[a], V	E_{ox}[b], V	References
1	Benzene	2.53	2.08	1
2	Toluene	2.20	1.98	1
3	o-Xylene	2.15	1.58	1
4	m-Xylene	2.15	1.58	1, 2
5	p-Xylene	2.14	1.56	1
6	Bromobenzene	2.57	1.98	1
7	2-Bromtoluene	2.25		
8	Mesitylene	2.01	1.55	1
9	2-Bromomesitylene	2.05		
10	Naphthalene	1.70	1.34	1
11	2-Phenylpyridine	2.20, 2.65		
12	$Cu(OAc)_2$	2.35		
13	Benzonitrile	2.35	1.8 **vs SCE**	3

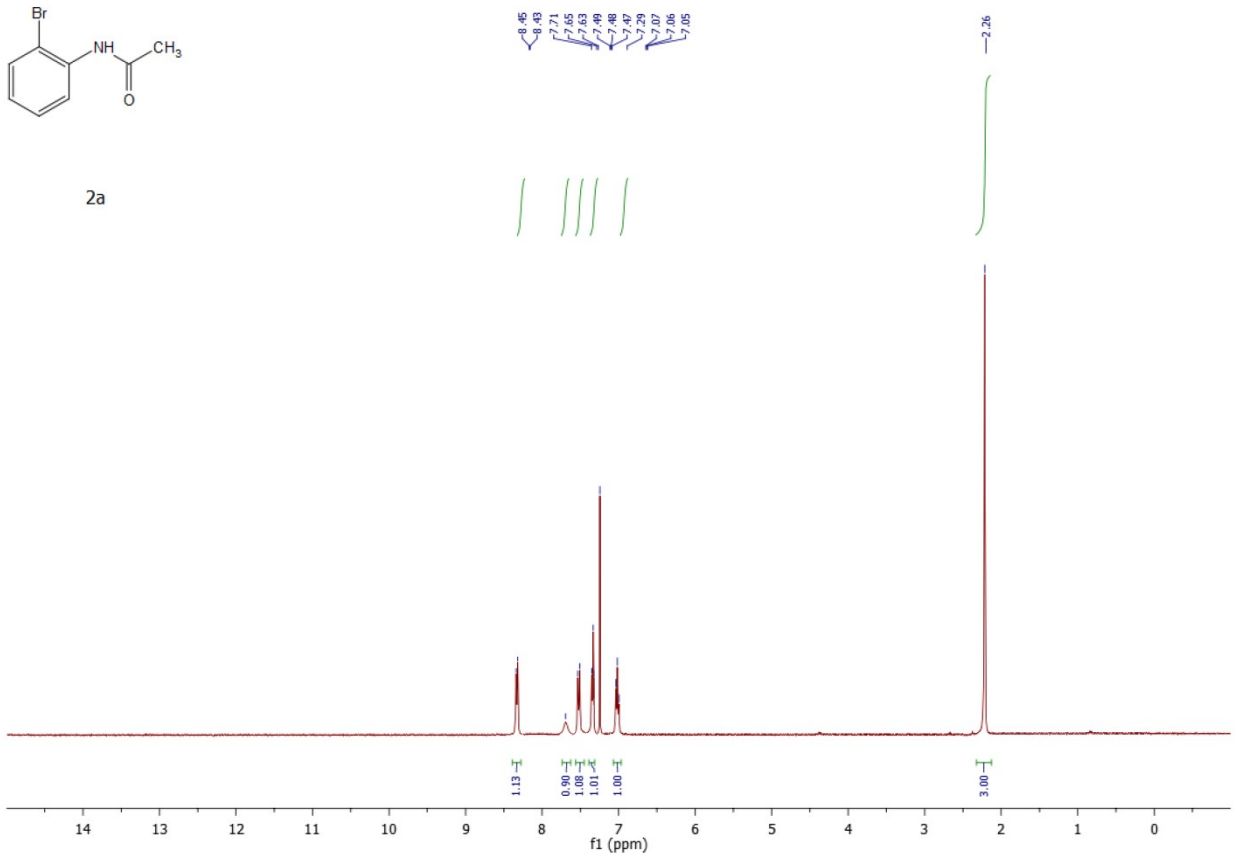
References

1. N.L. Weinberg and H.R. Weinberg, *Chem. Rev.*, 1968, **68**, 449-523.
2. D.M. Heard and A.J.J. Lennox, *Angew. Chem. Int. Ed.*, 2020, **59**, 18866-18884.
3. K.M. Kadish and J.E. Anderson, *Pure Appl. Chem.*, 1987, **59**, 703-714.

7. NMR Spectra



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7.05
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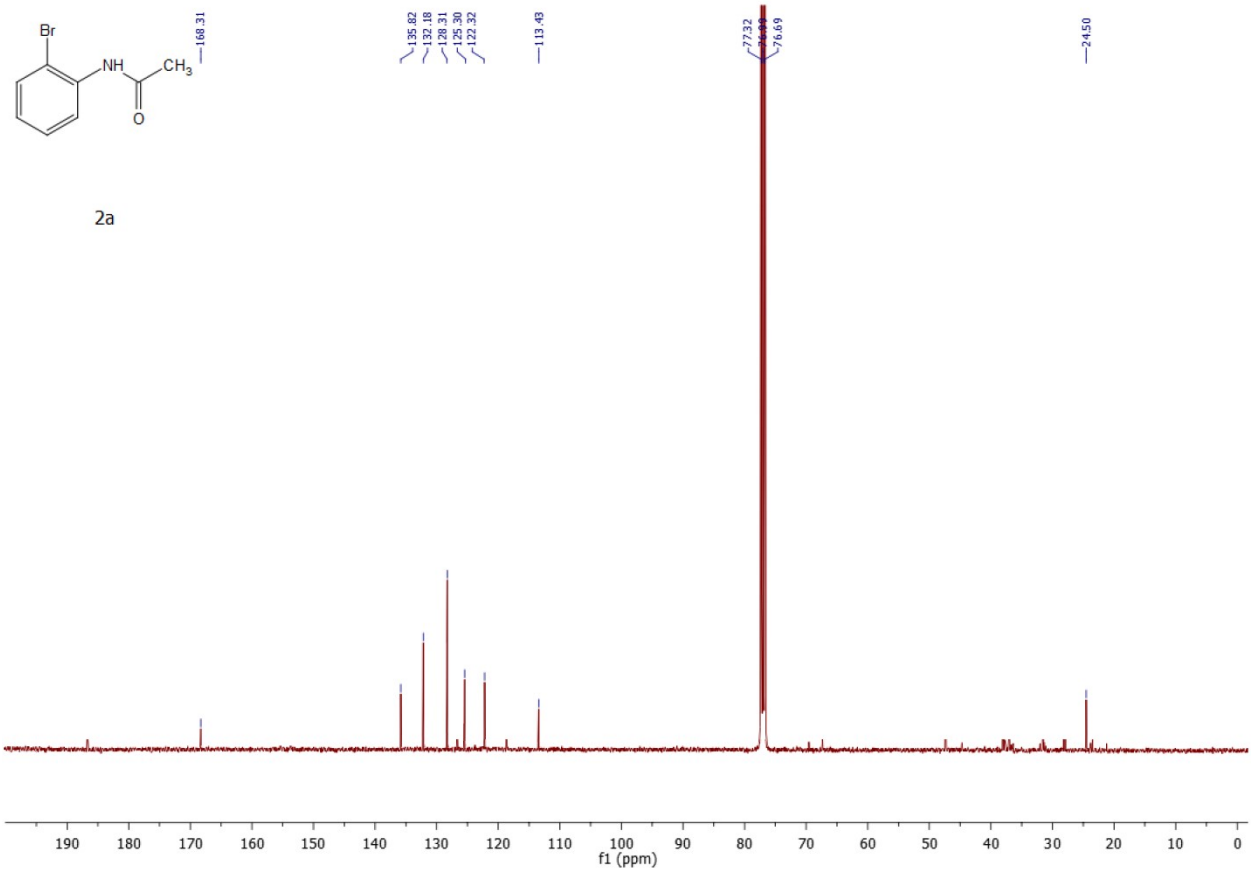
1.01
1.00
3.00
f1 (ppm)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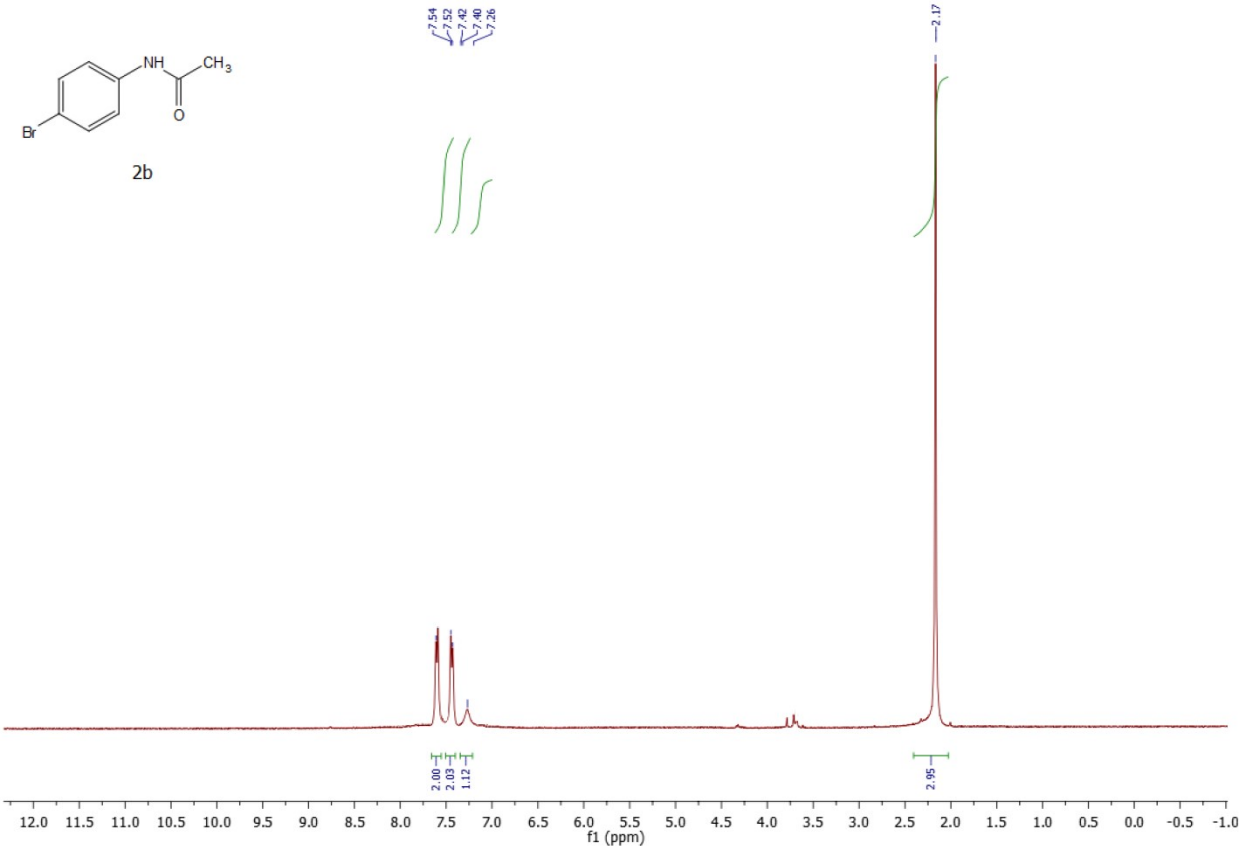
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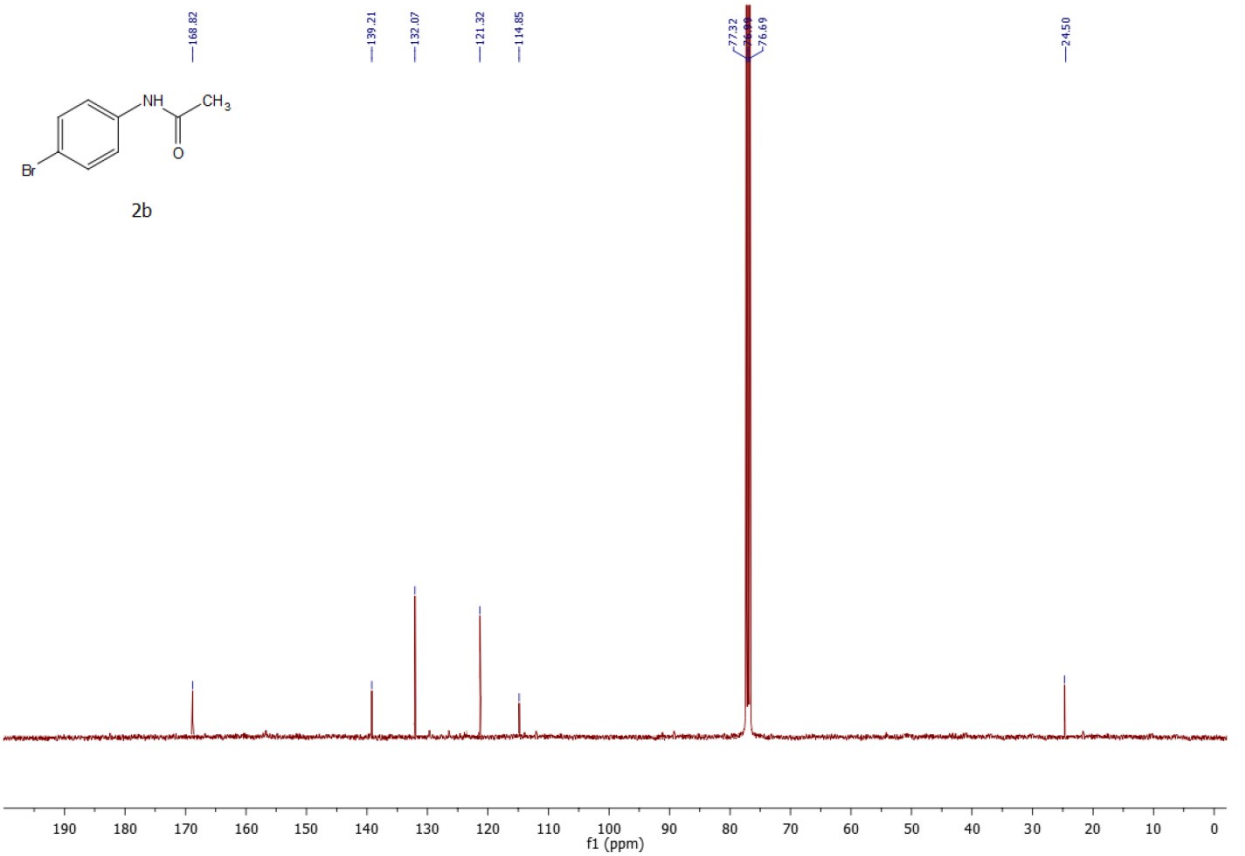
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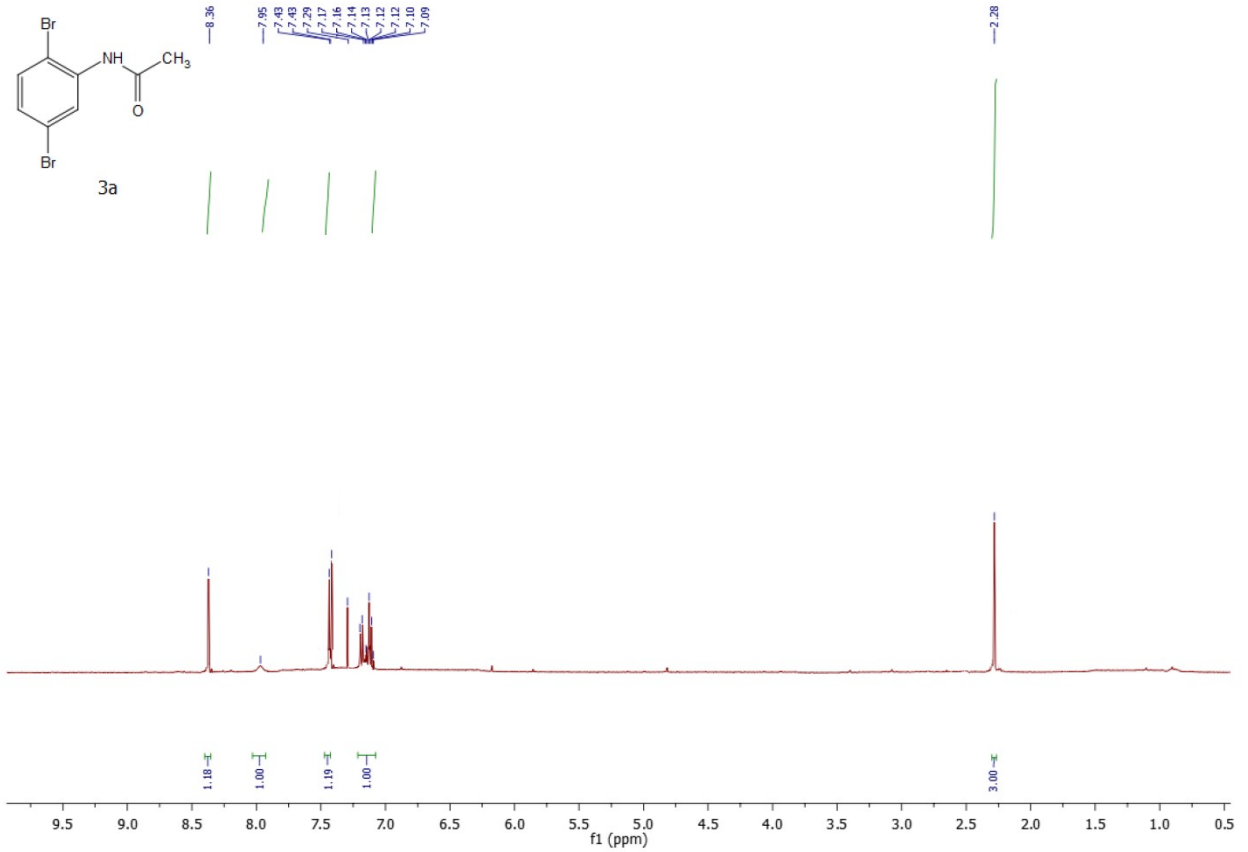
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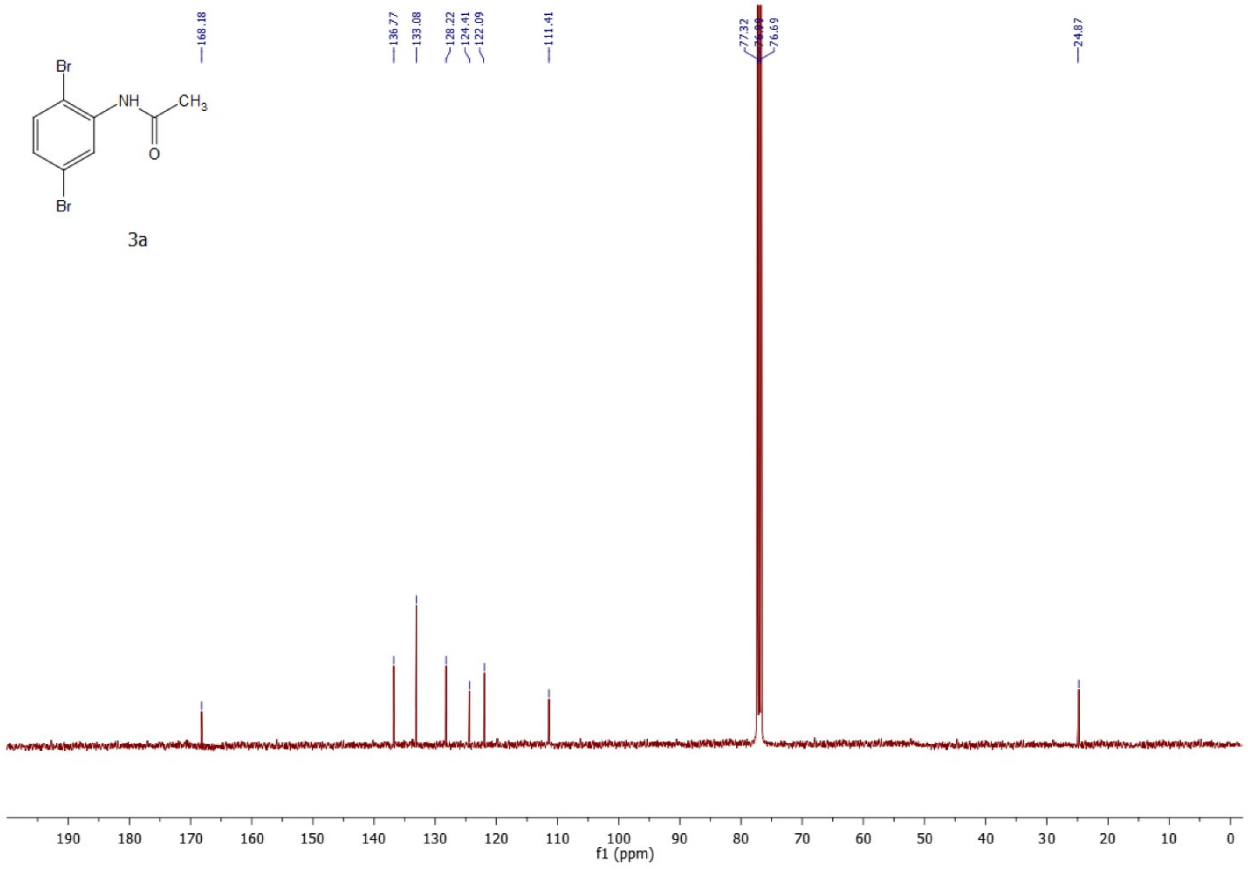
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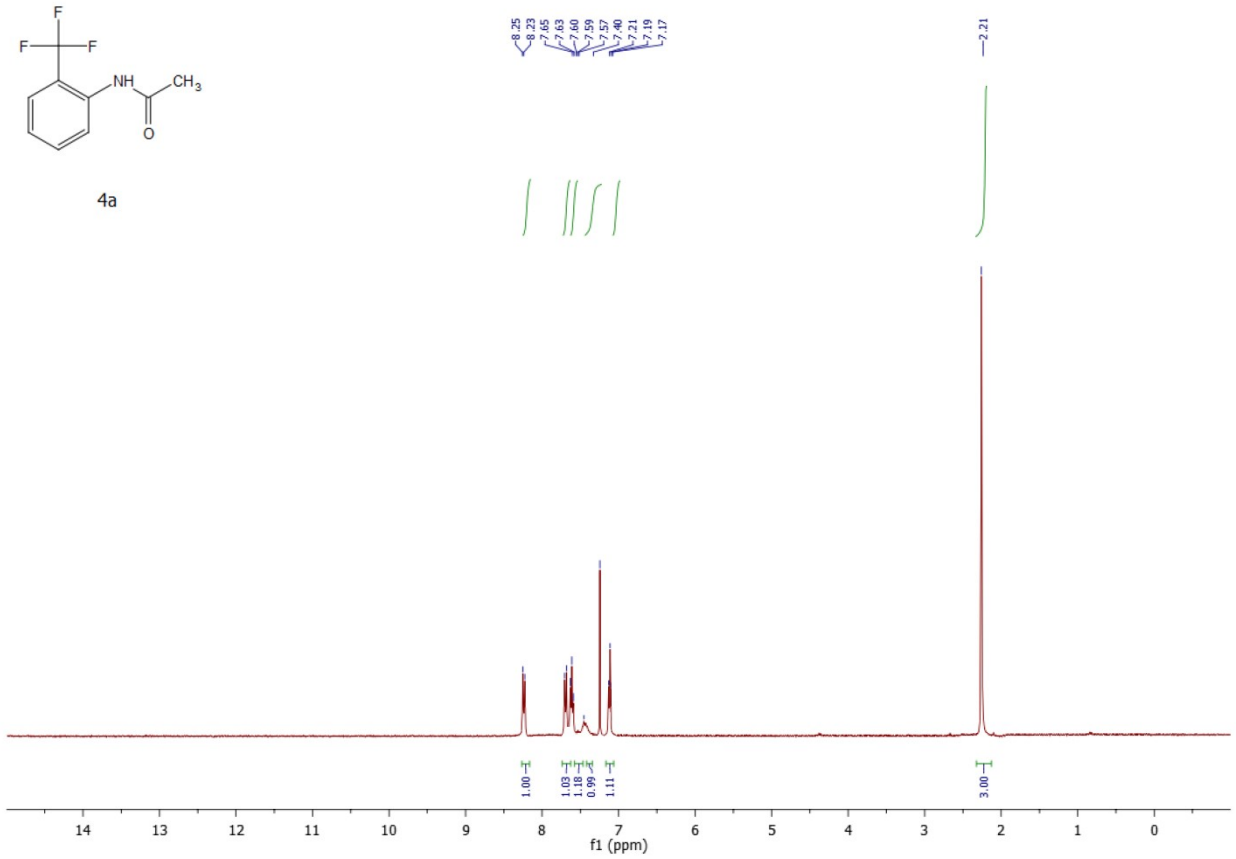
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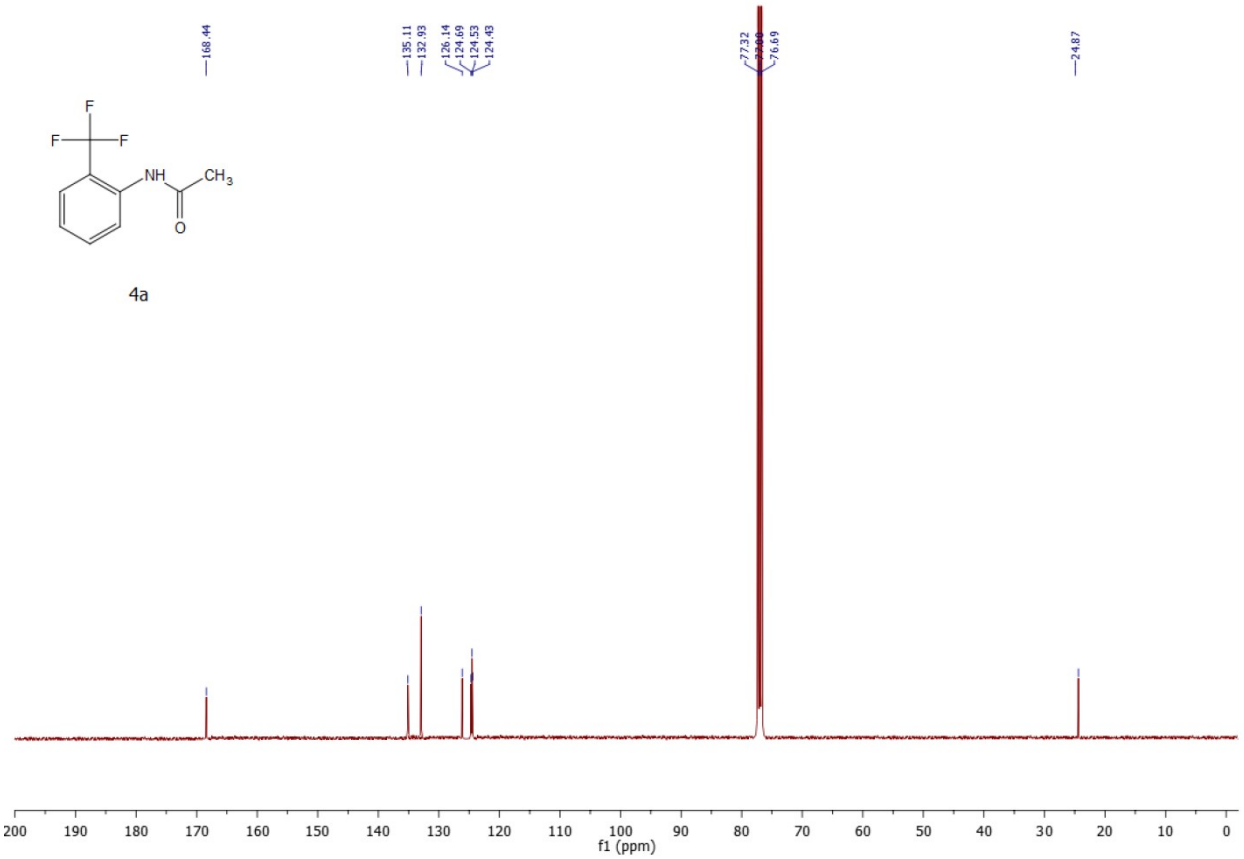
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F
F
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O
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180
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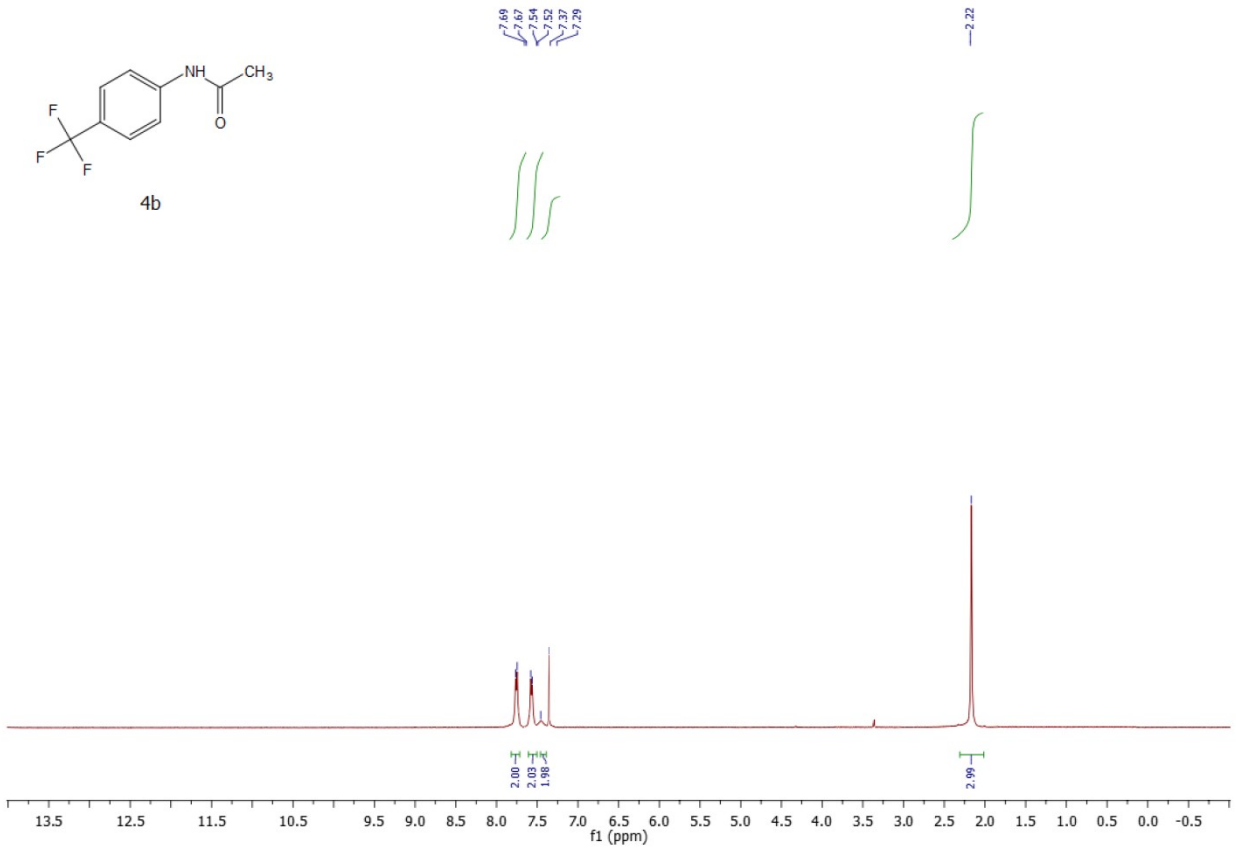
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2.03
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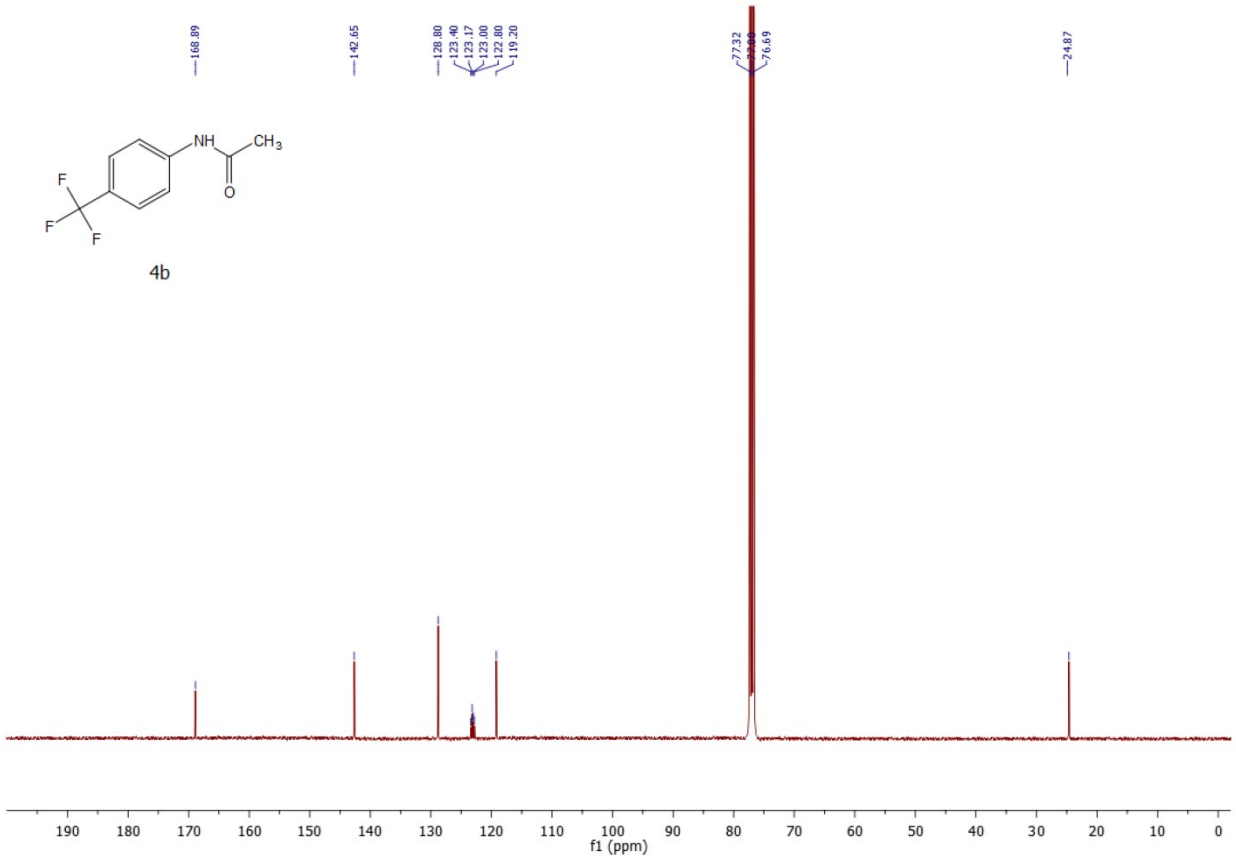
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F
F
F
4b
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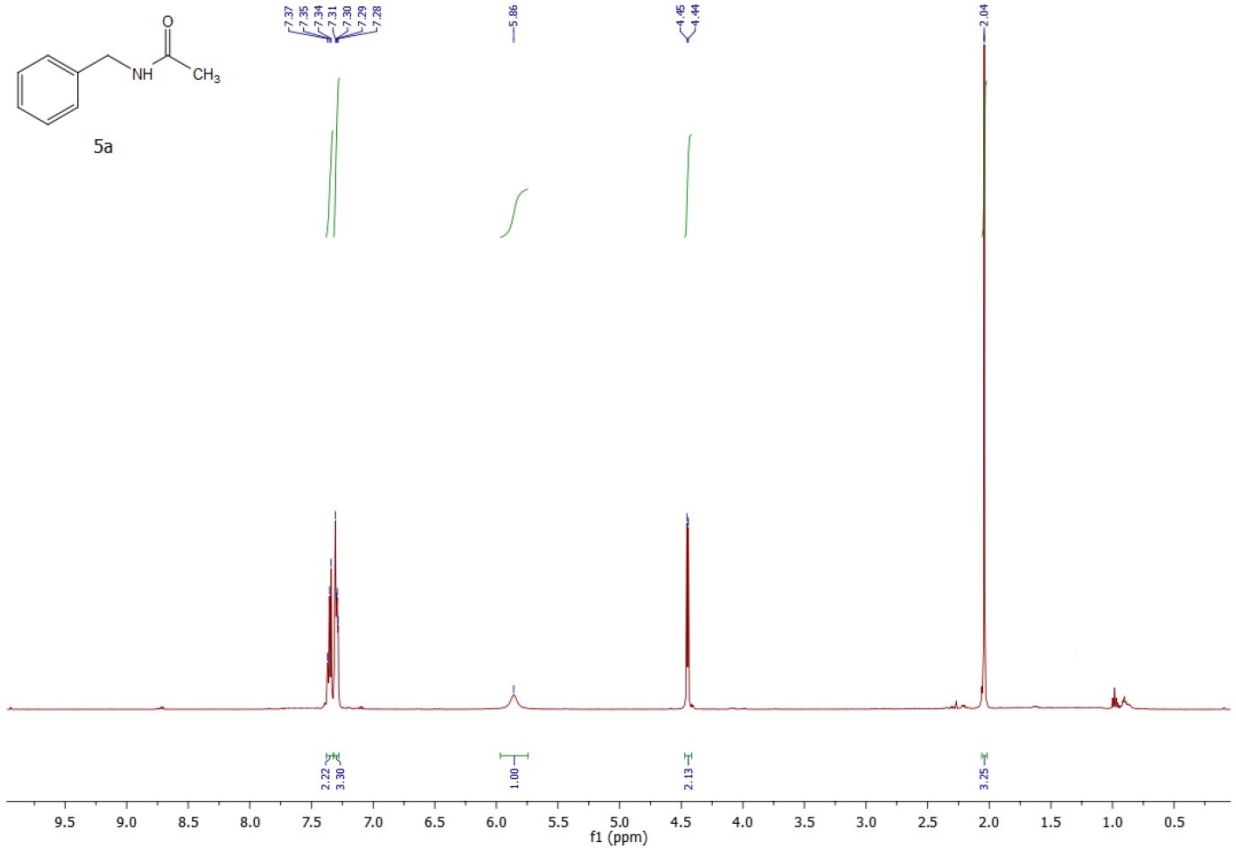
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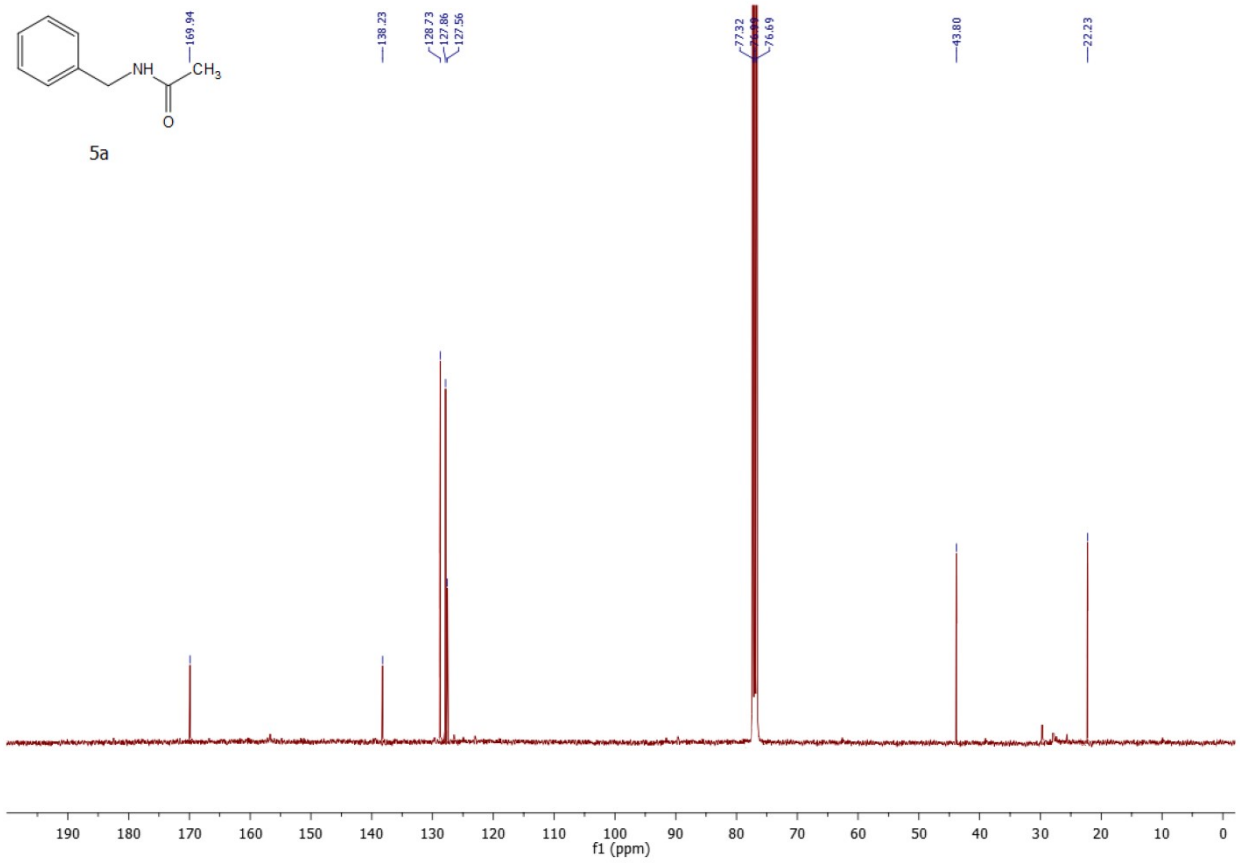
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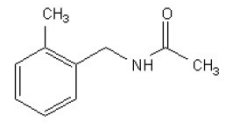
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6a

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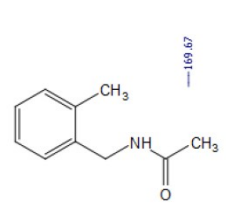
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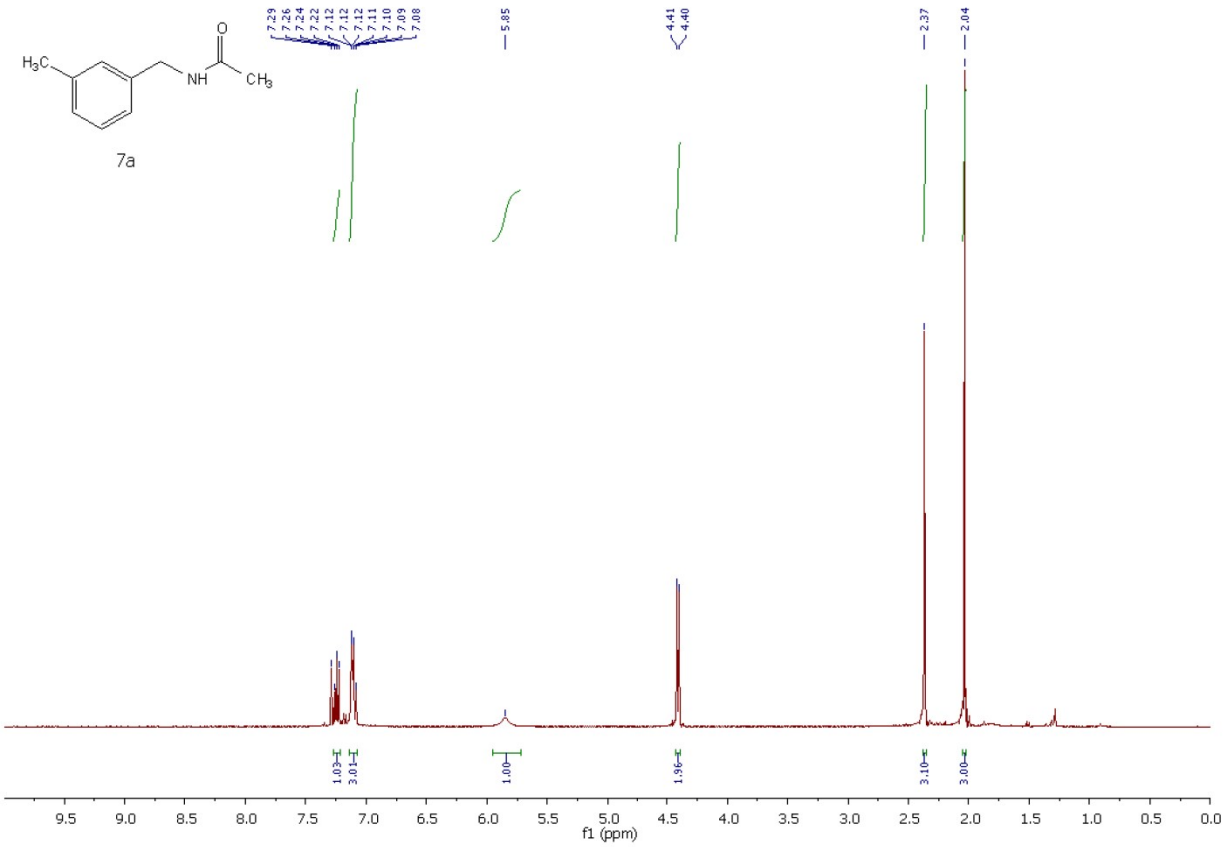
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O
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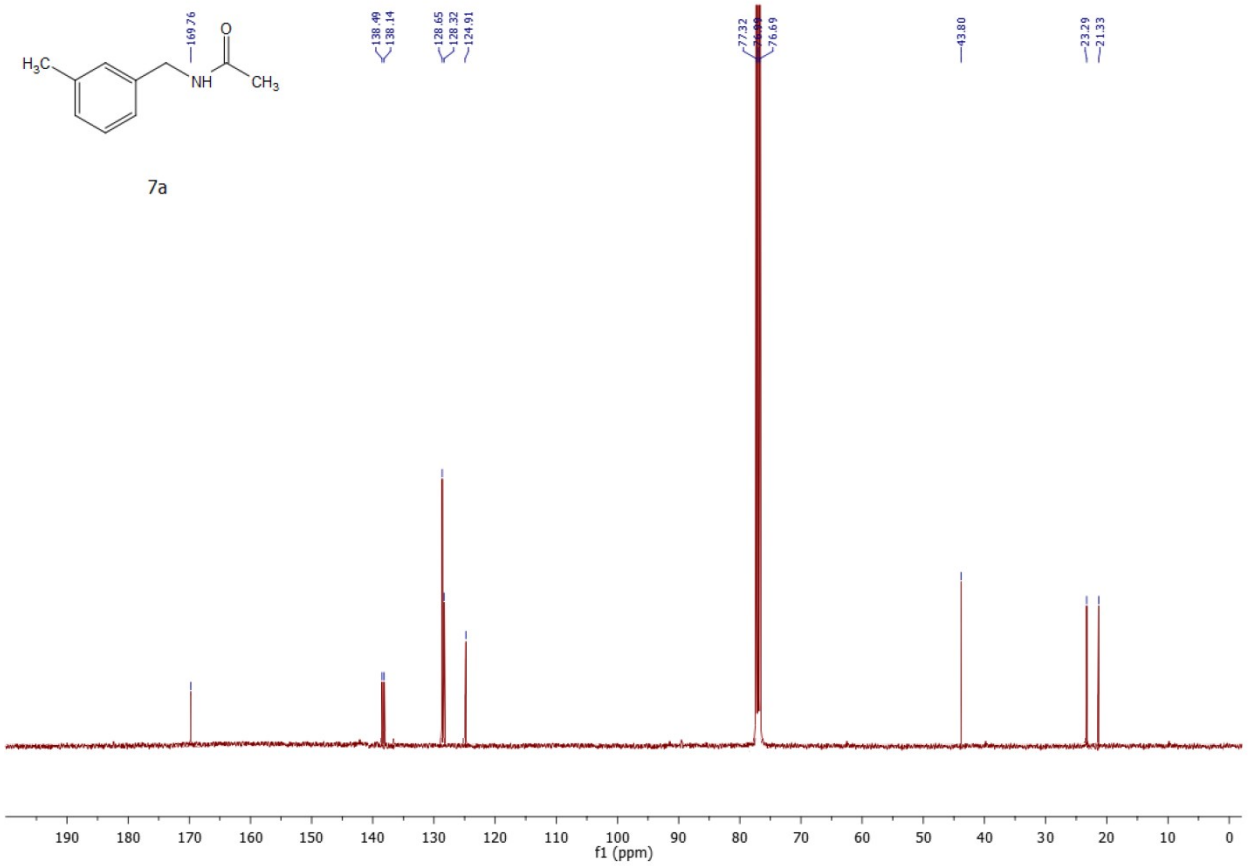
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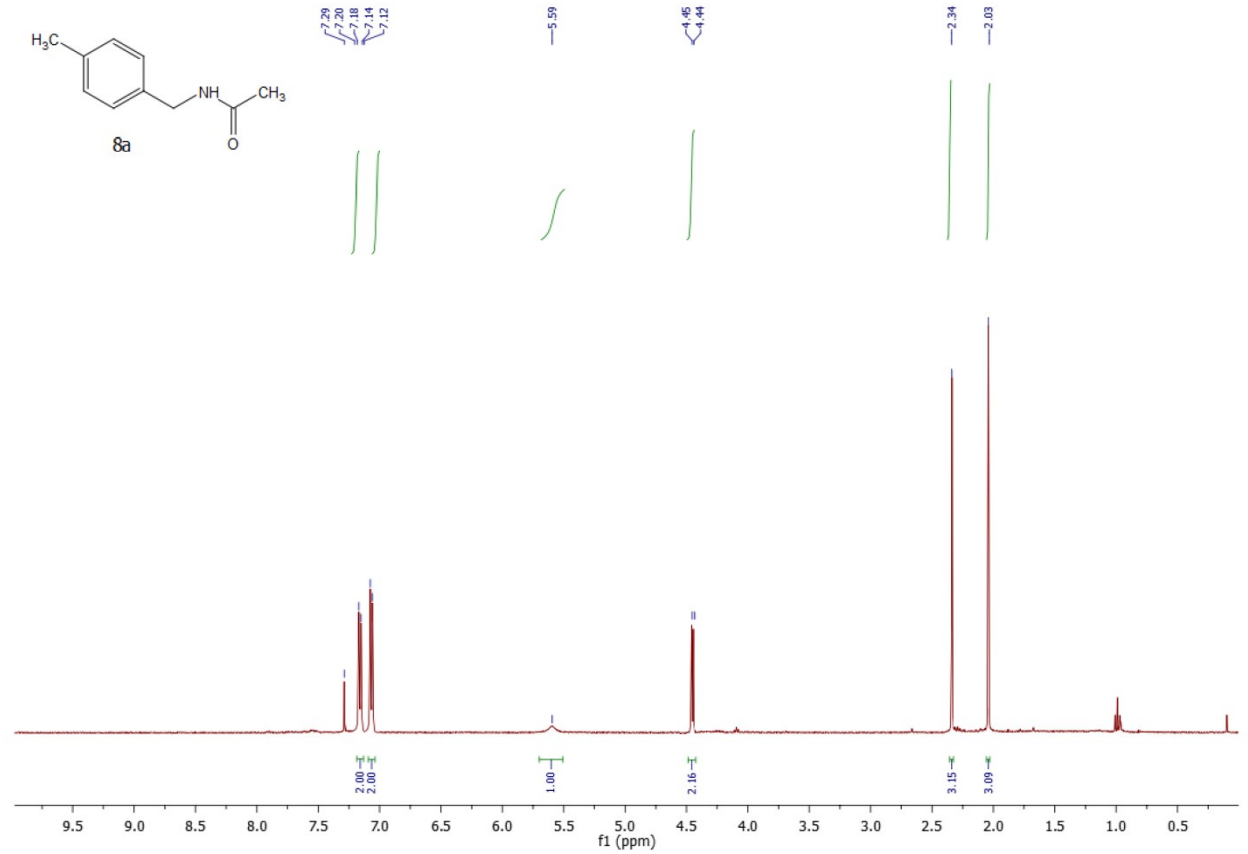
7a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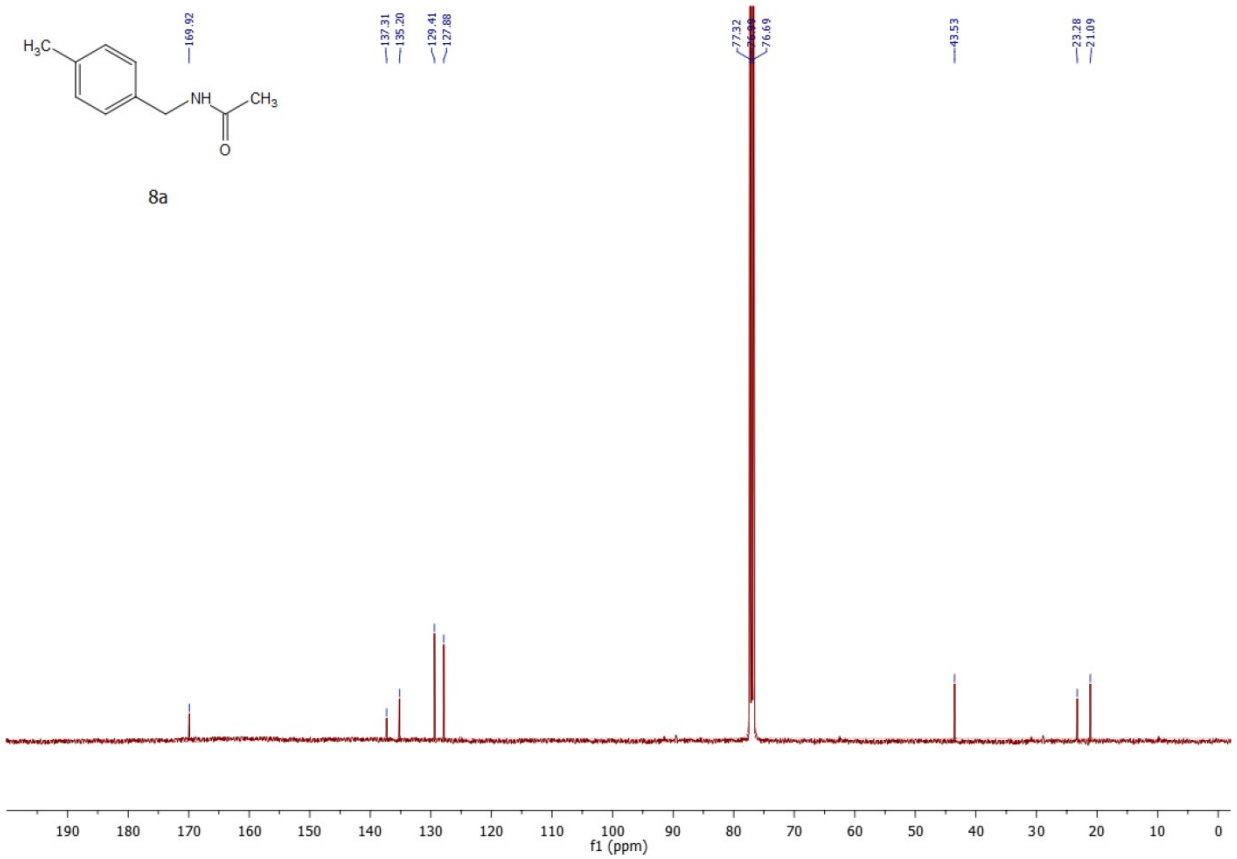
8a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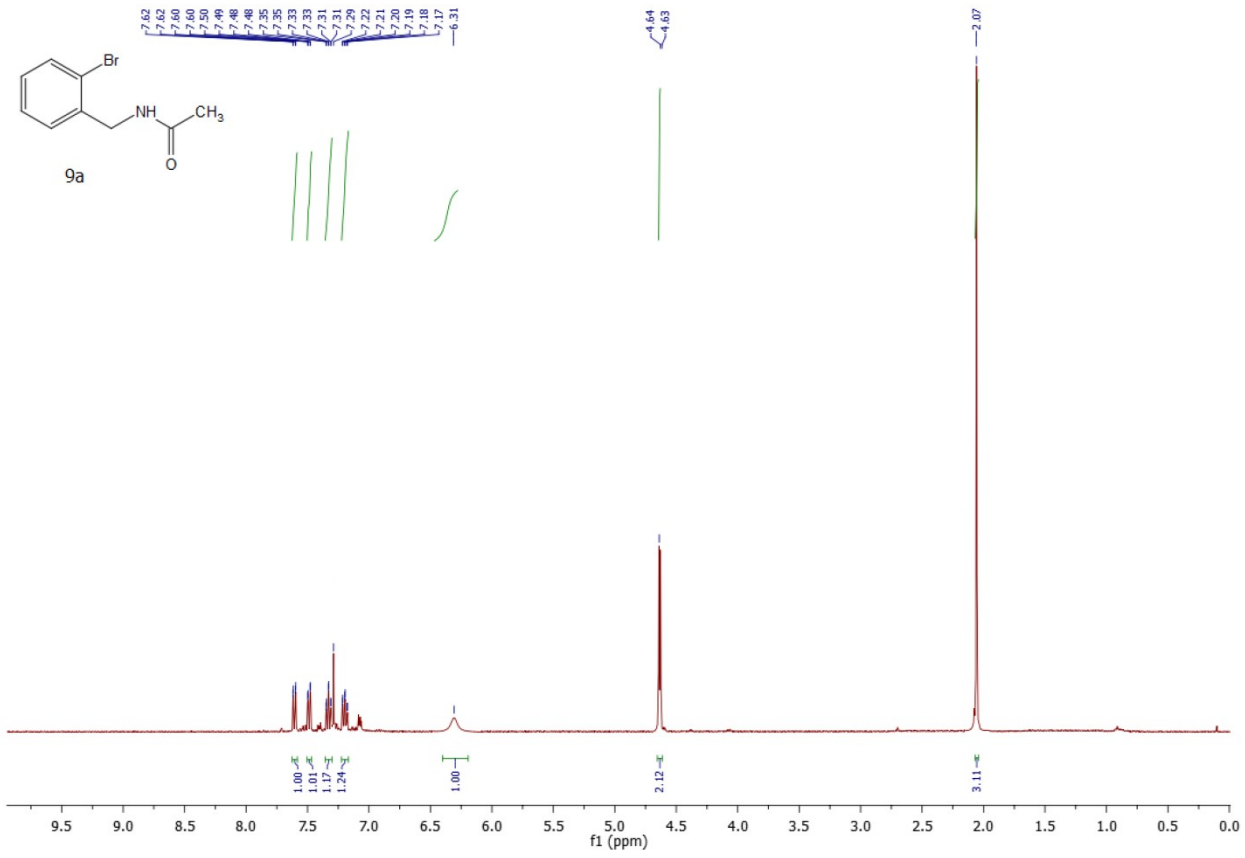
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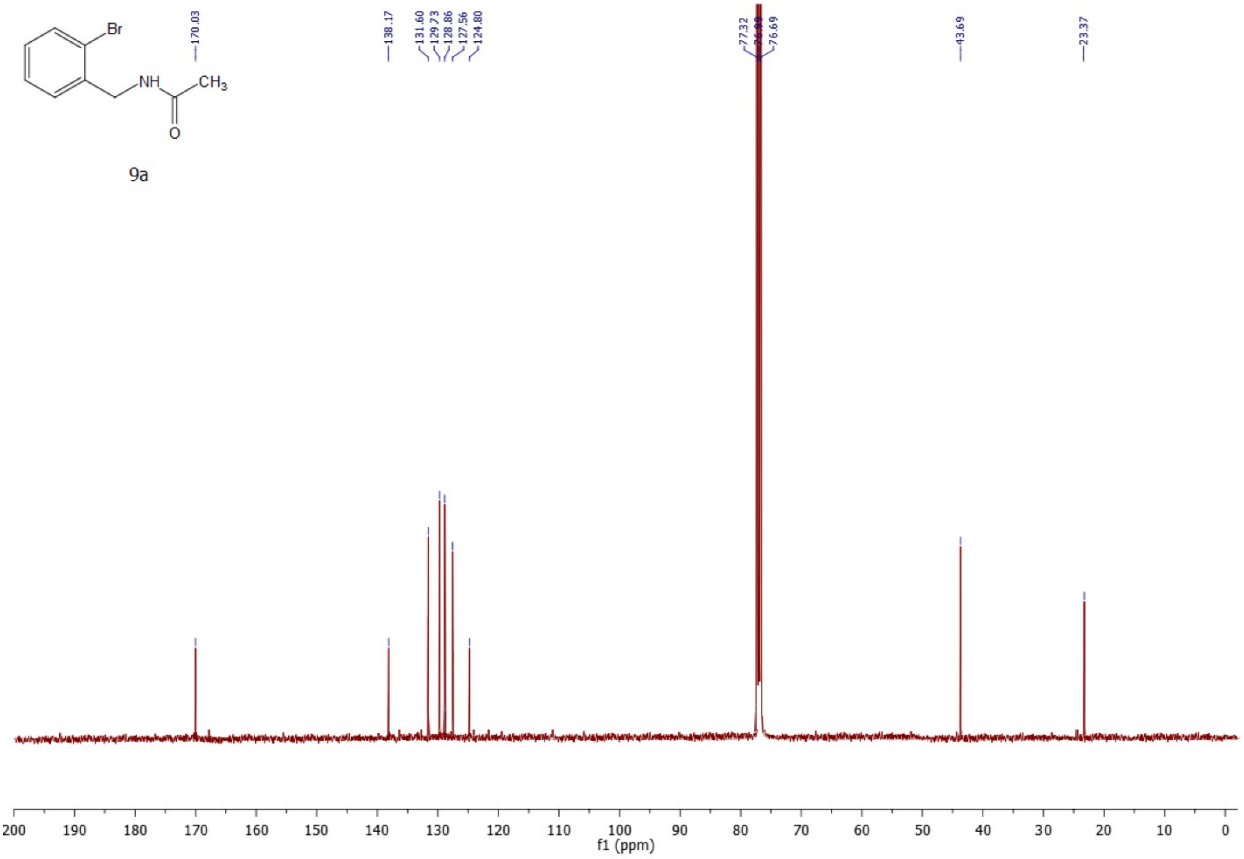
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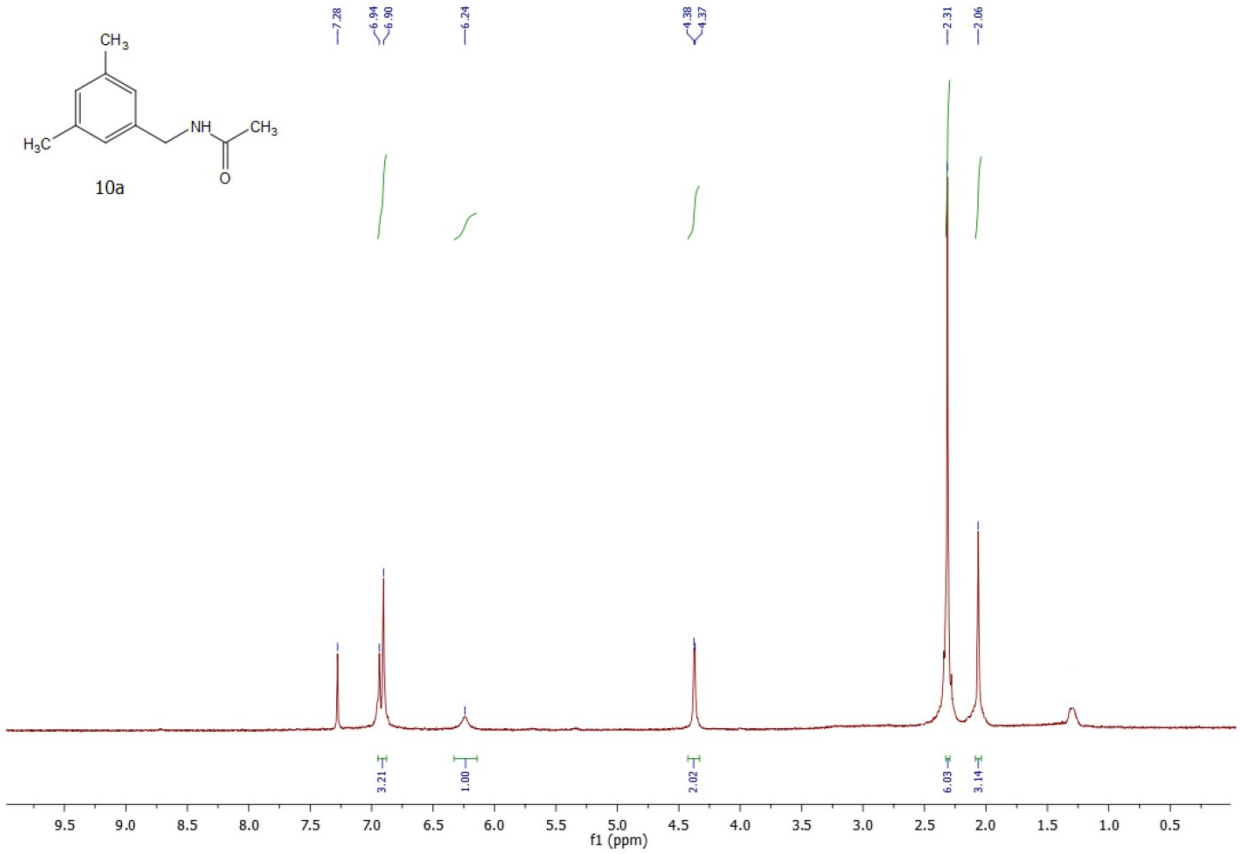
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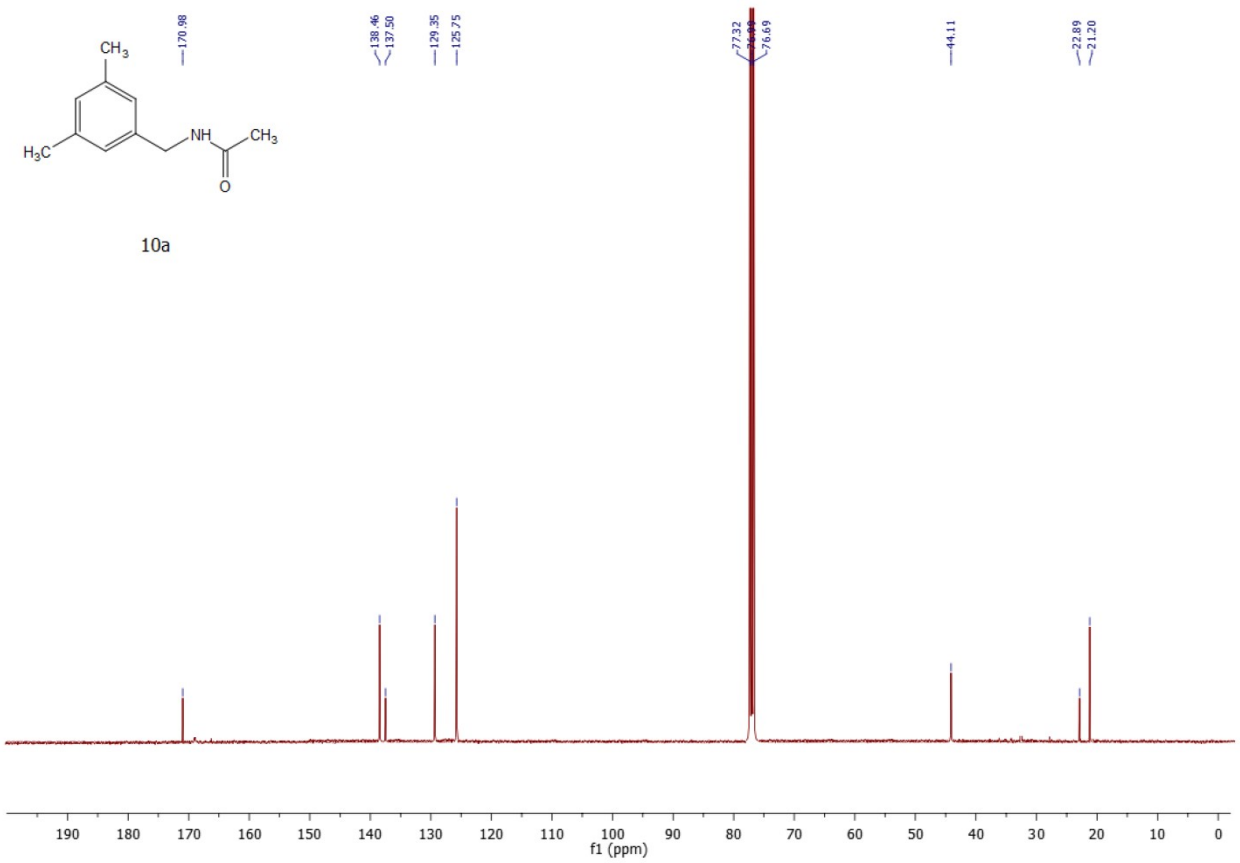
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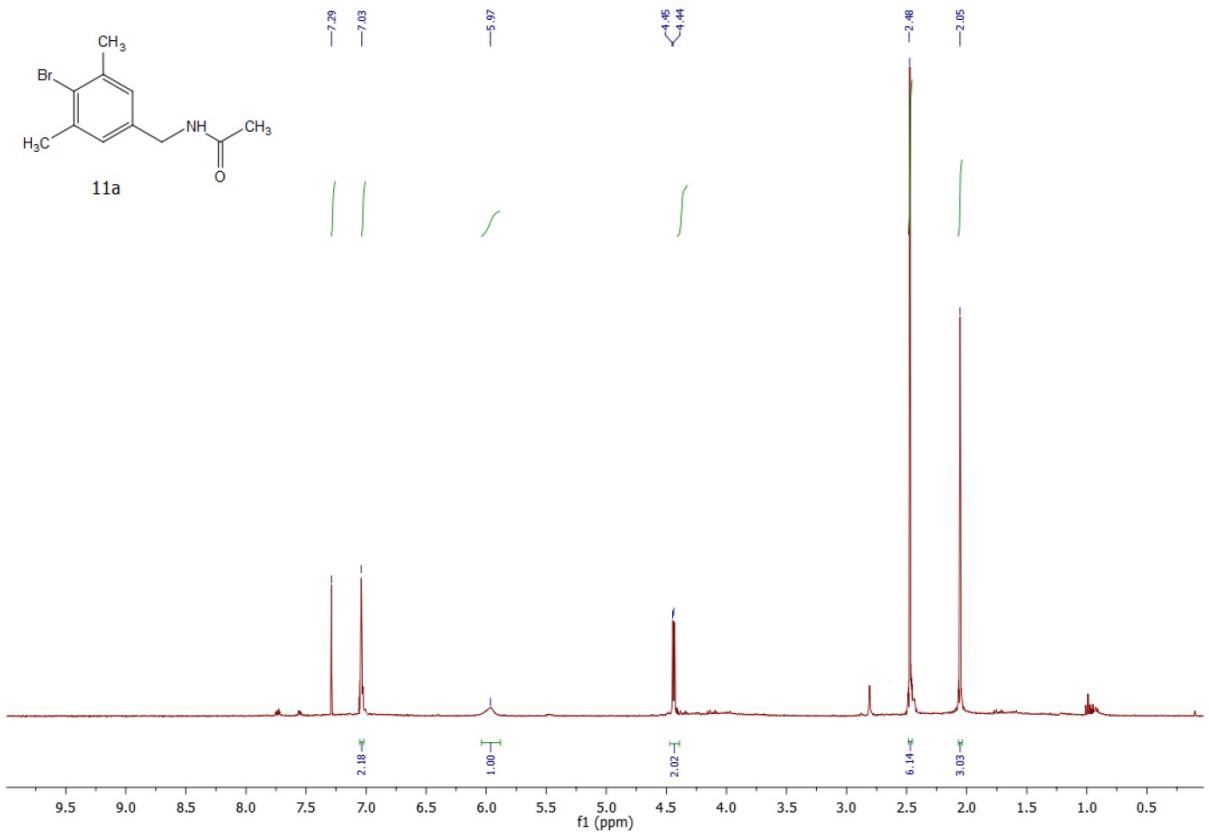
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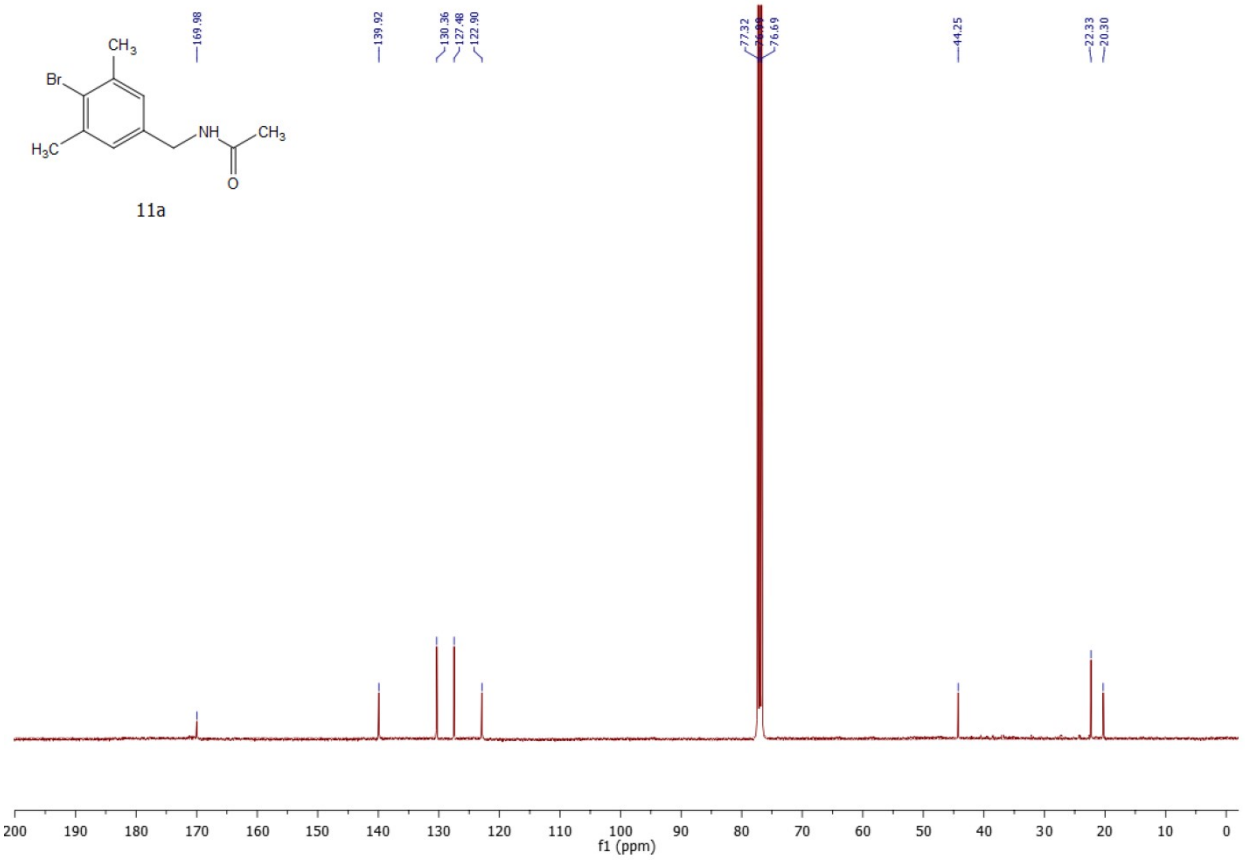
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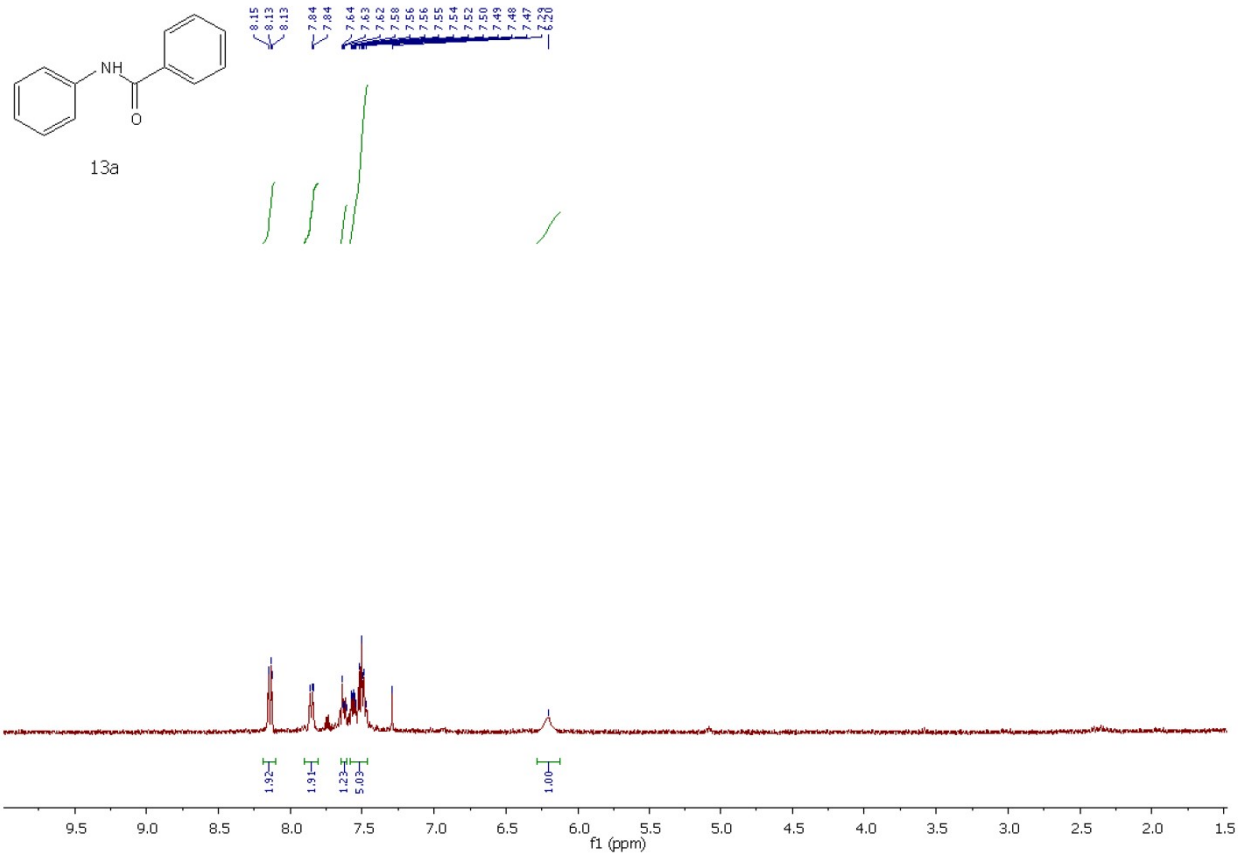
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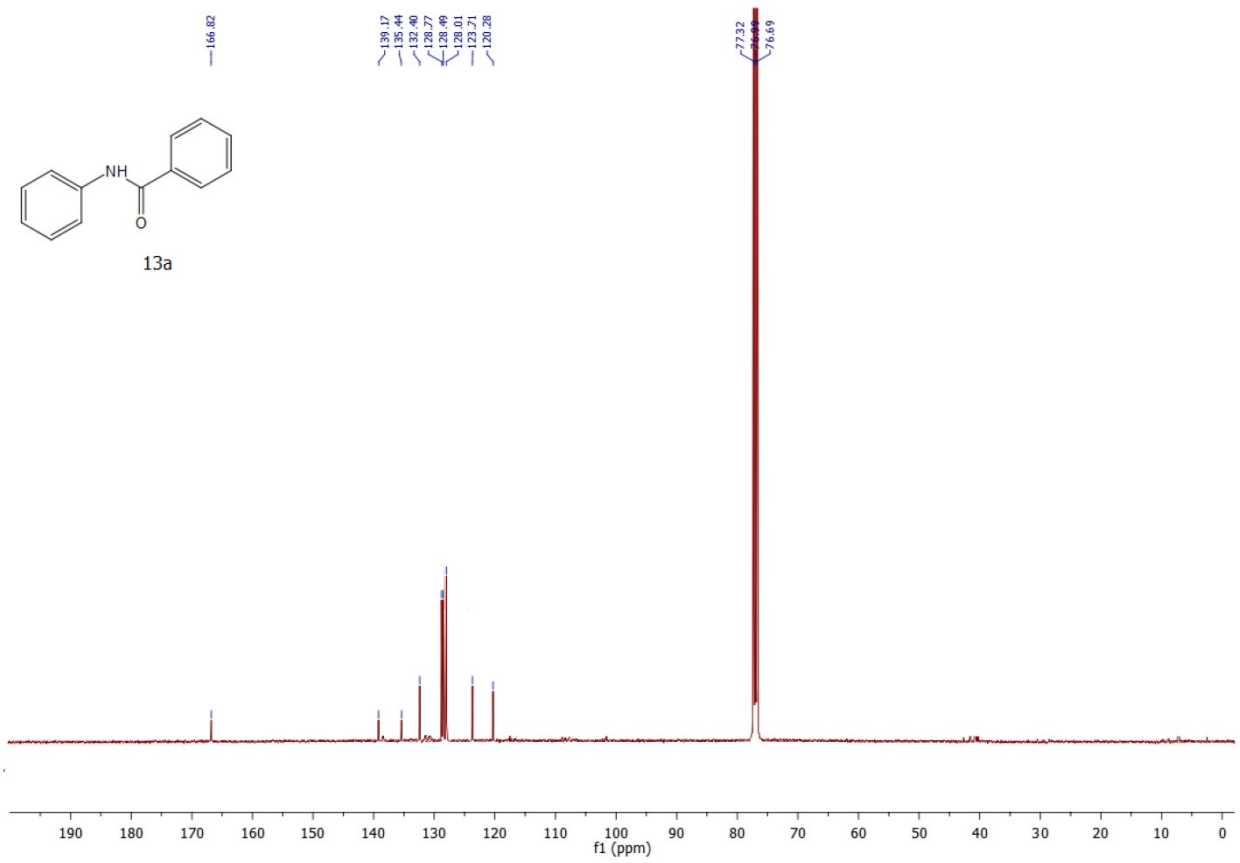
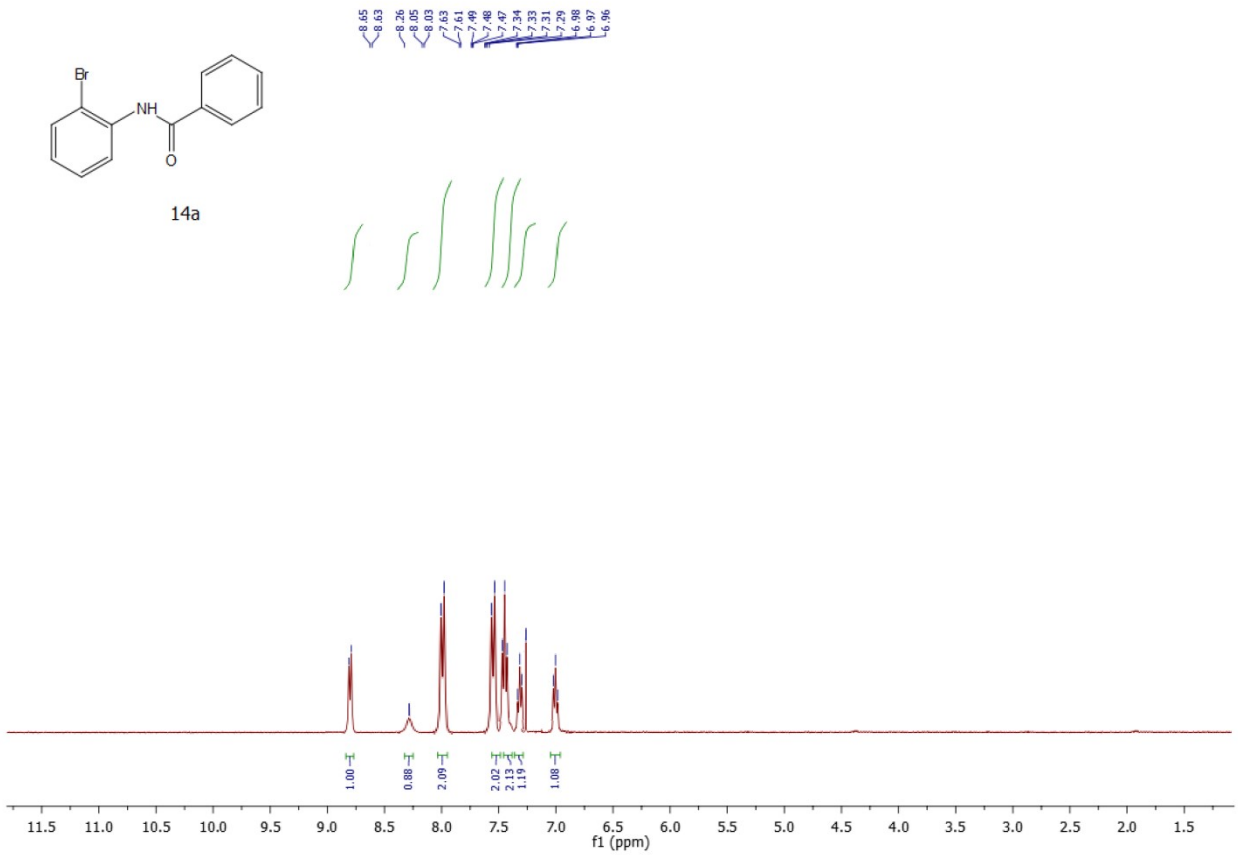
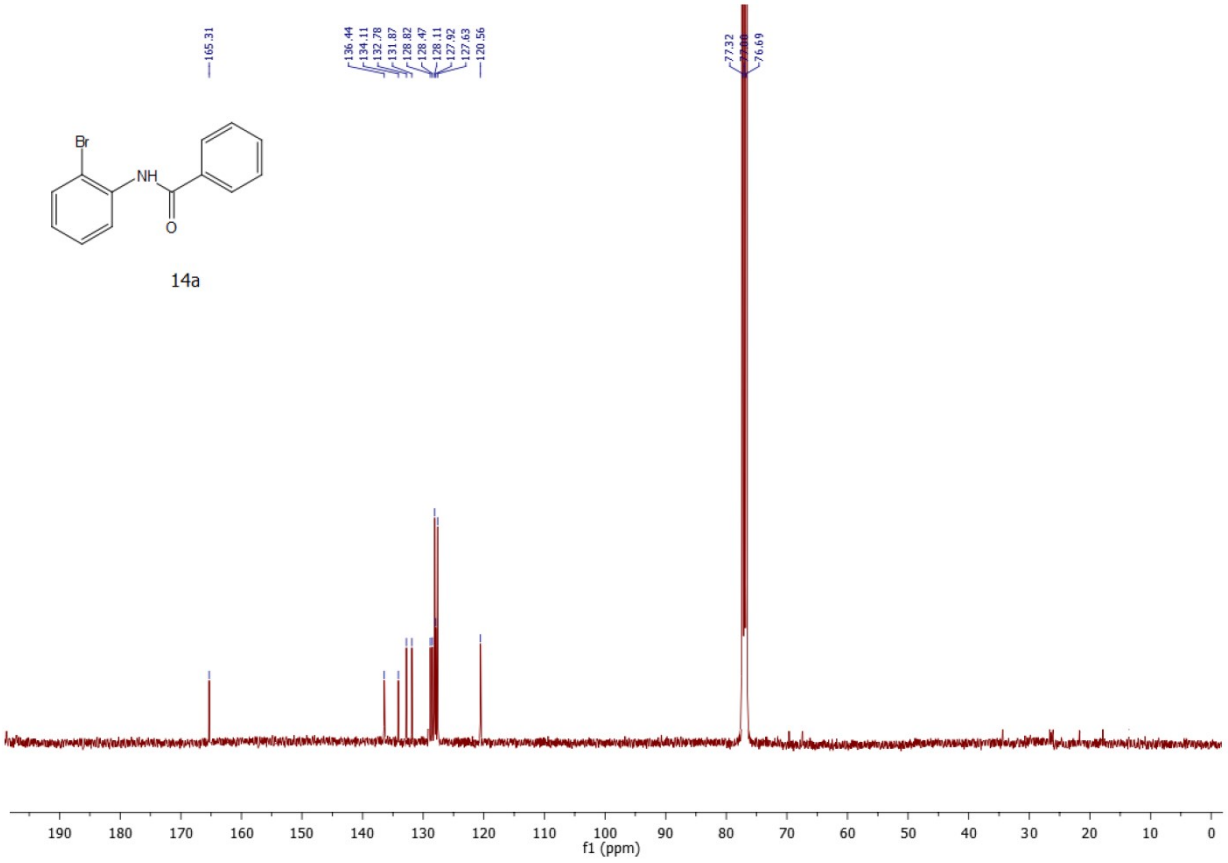
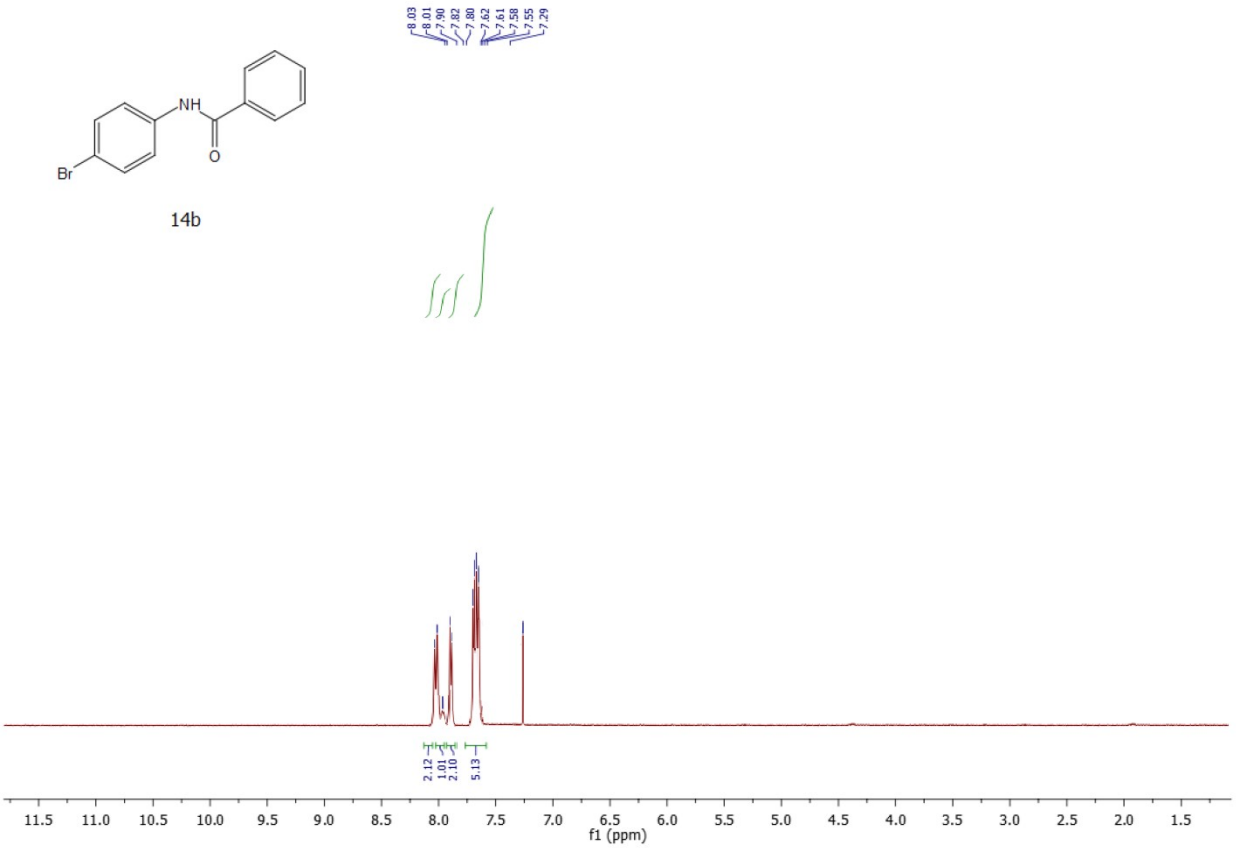
5.03
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)


166.82
139.17
135.44
132.40
128.77
128.49
128.01
123.71
120.28
77.32
76.69
NH
O
13a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

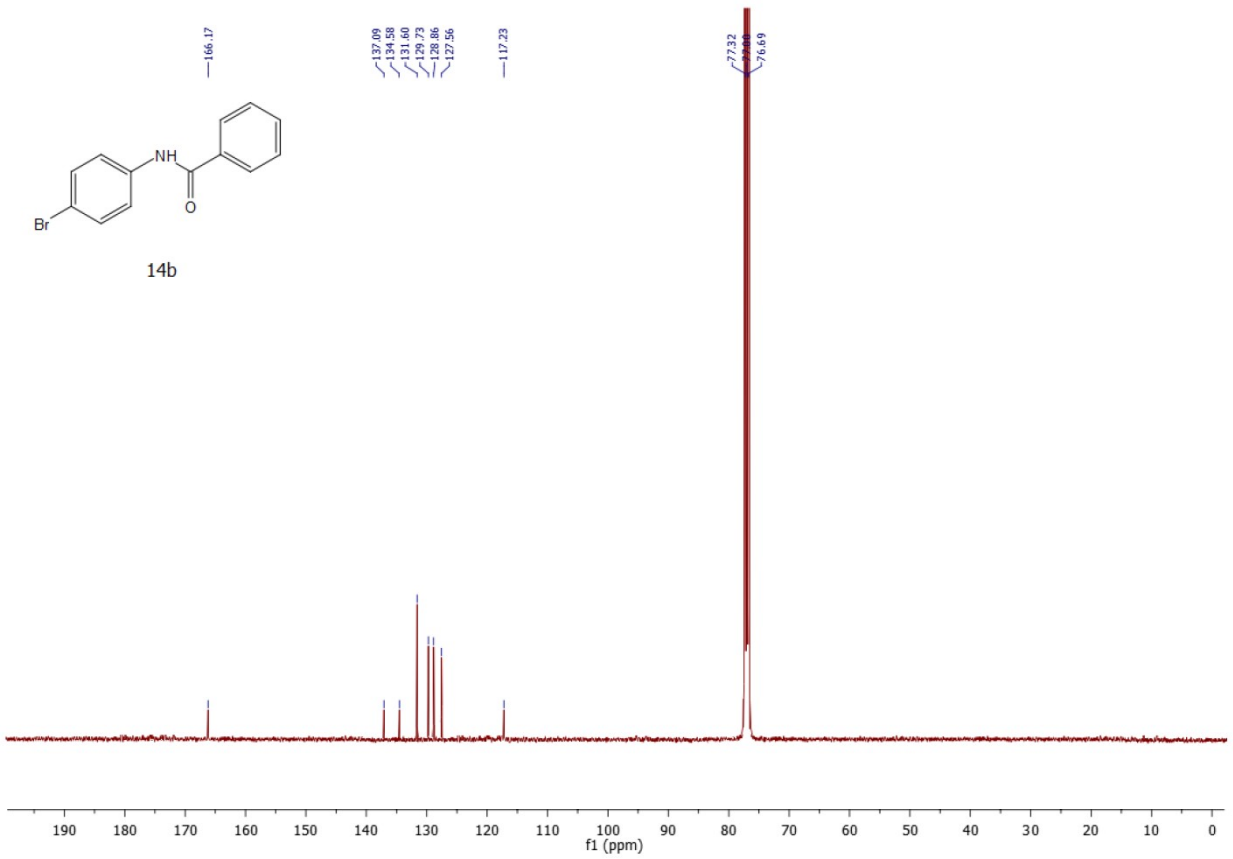

8.65
8.63
8.26
8.05
8.03
7.63
7.61
7.49
7.48
7.47
7.34
7.33
7.31
7.29
6.98
6.97
6.96
Br
NH
O
14a
1.00
0.88
2.09
2.02
2.13
1.19
1.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)


165.31
136.44
134.11
132.78
131.87
128.82
128.47
128.11
127.92
127.63
120.56
77.32
76.69
Br
NH
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

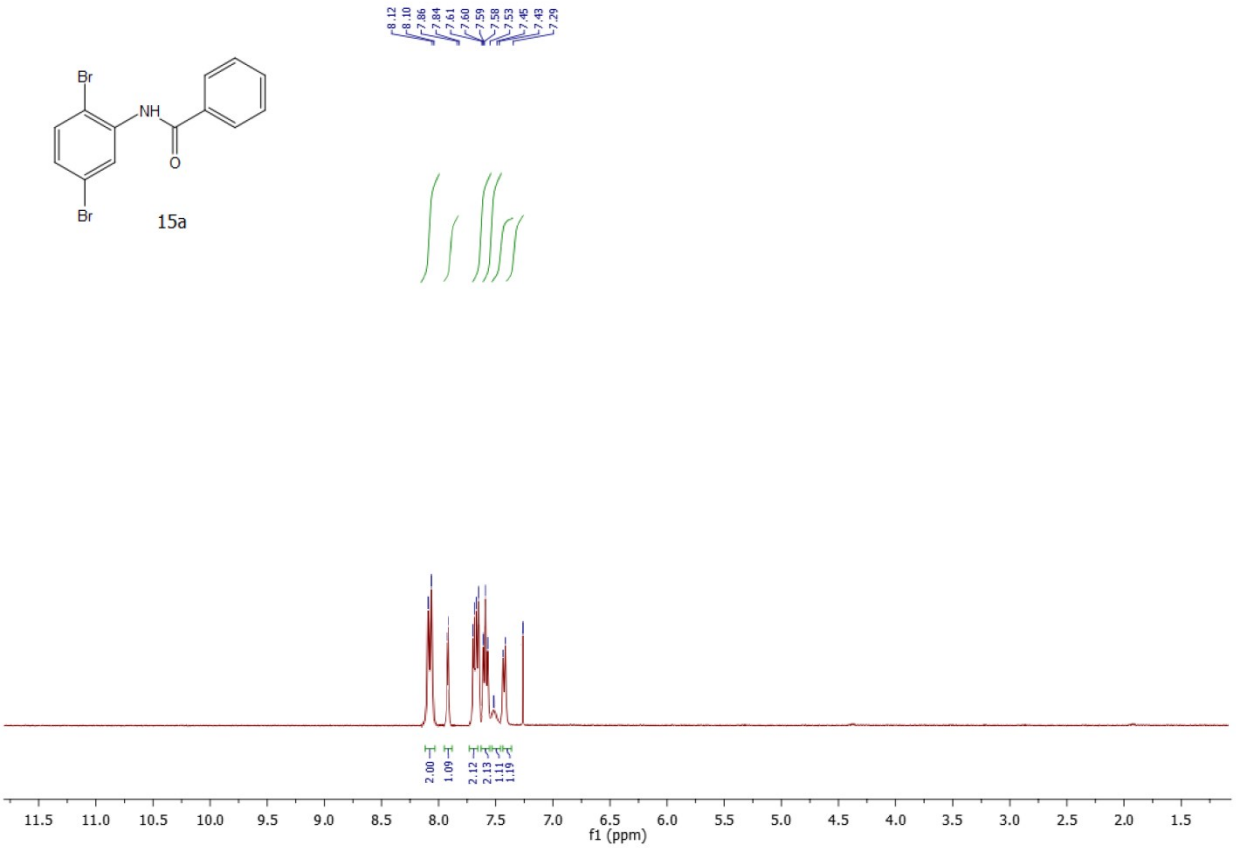
14a


8.03
8.01
7.90
7.82
7.80
7.62
7.61
7.58
7.55
7.29
NH
O
Br
2.12
1.01
2.10
5.13
11.5 11.0 10.5 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
f1 (ppm)

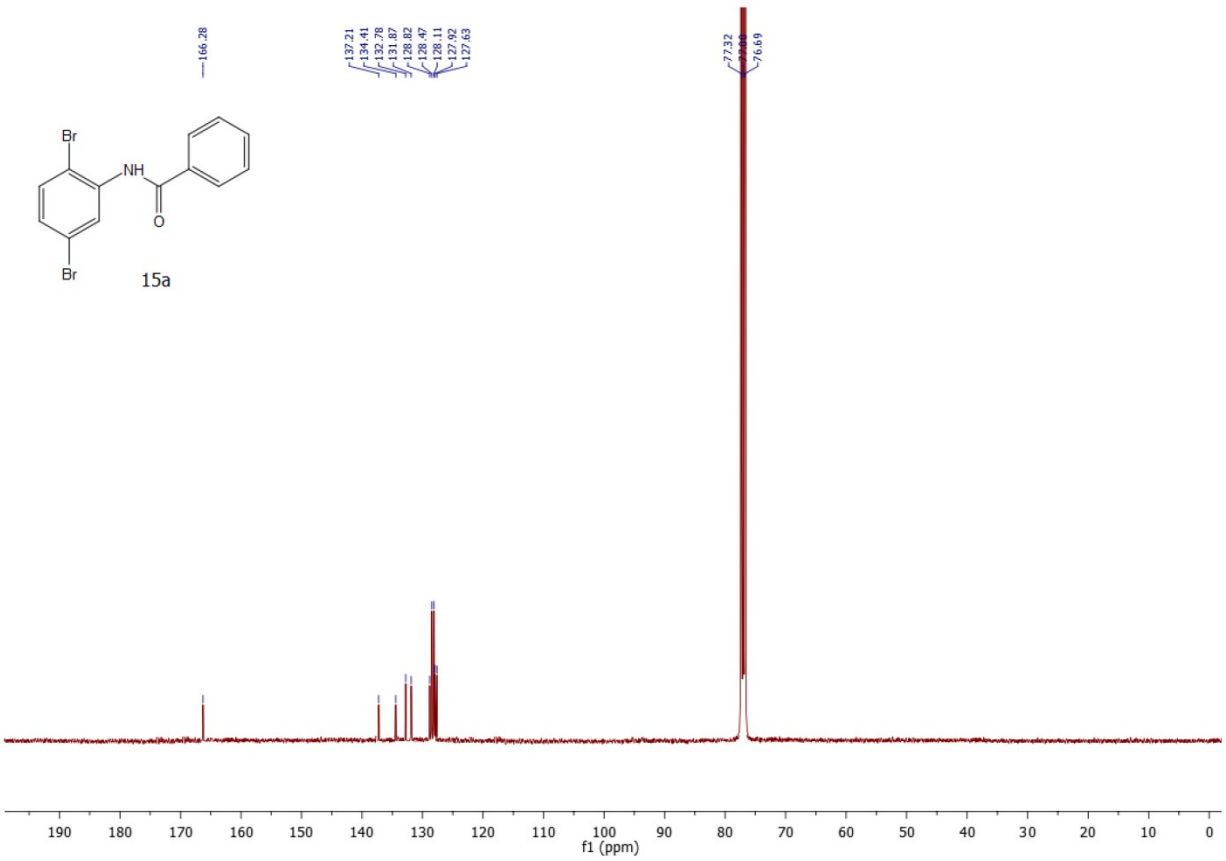
14b

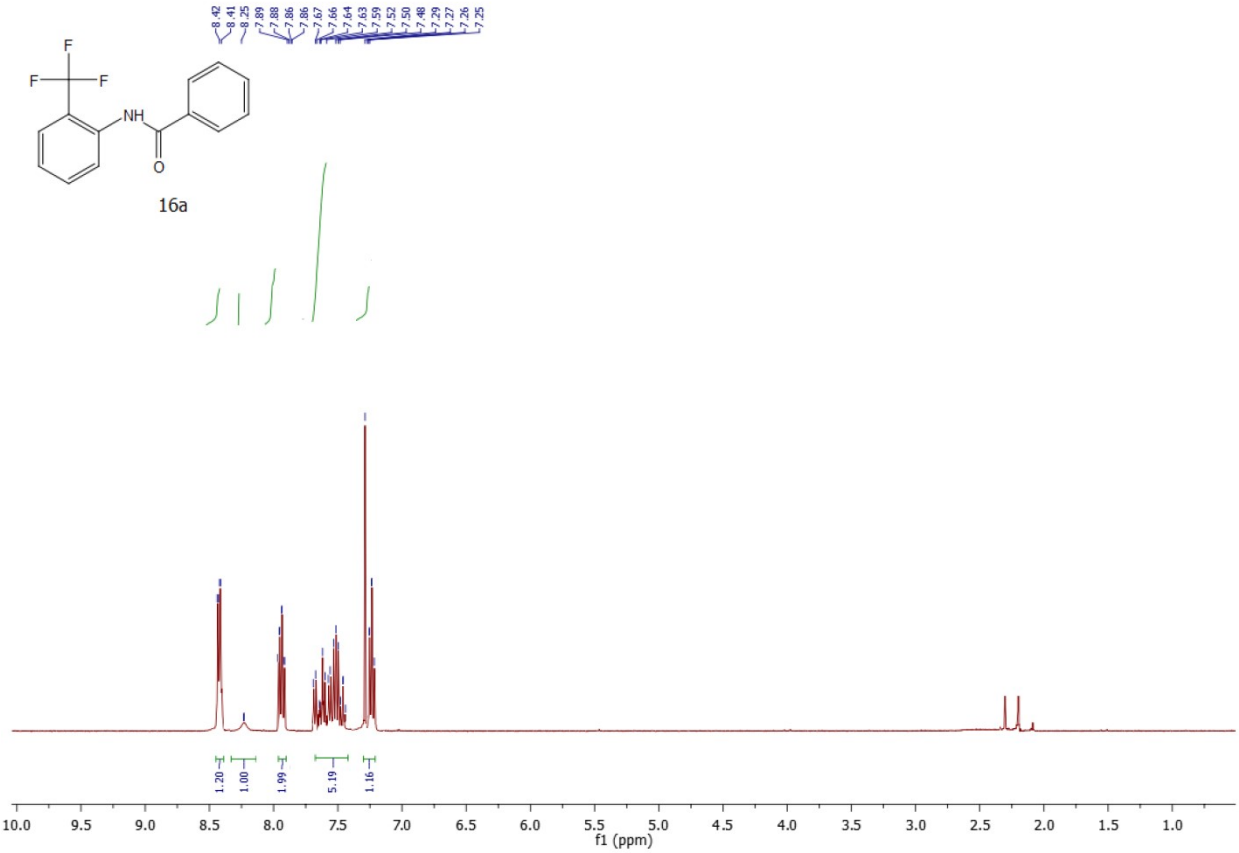

166.17
137.09
134.58
131.60
129.73
128.86
127.56
117.23
77.32
76.69
NH
O
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

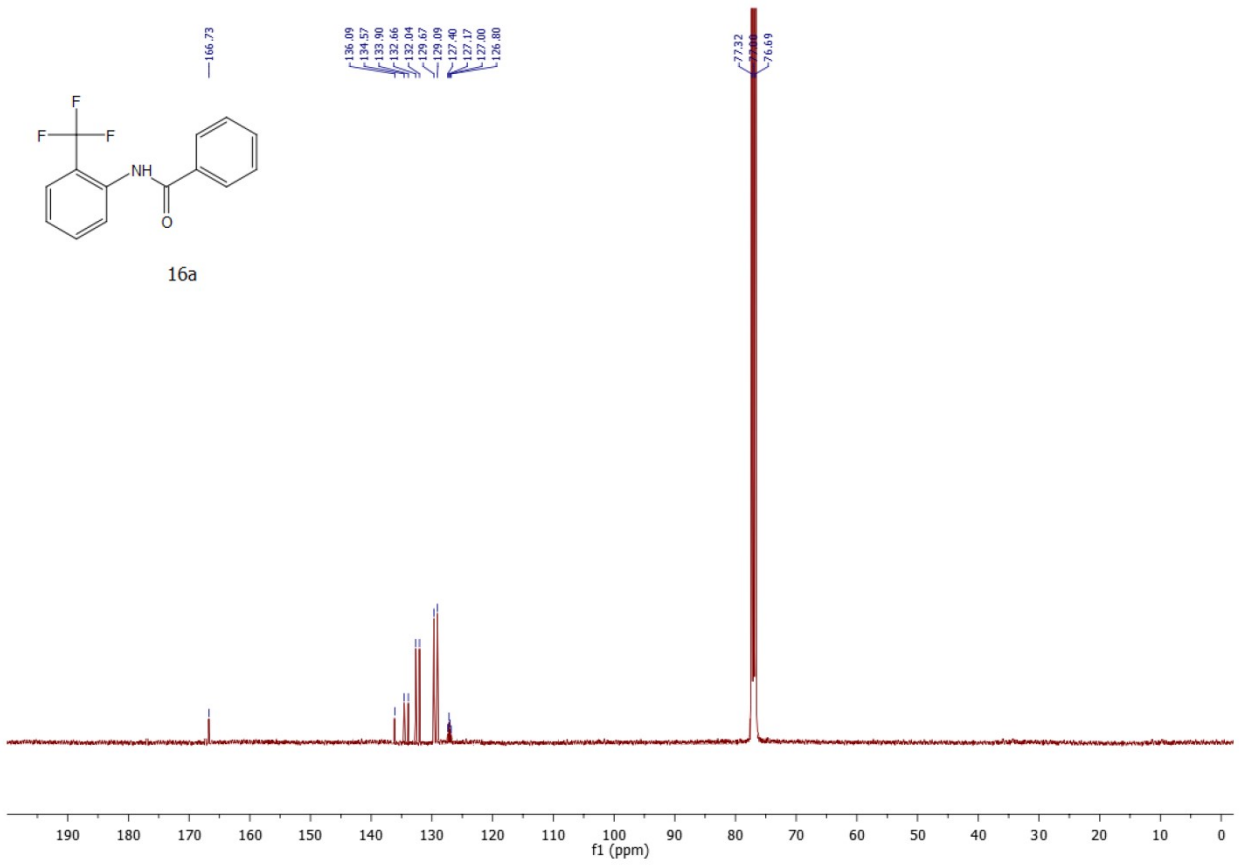
14b


8.12
8.10
7.86
7.84
7.61
7.60
7.59
7.58
7.53
7.46
7.43
7.29
Br
NH
O
Br
2.00
1.09
2.12
2.13
1.11
1.19
11.5 11.0 10.5 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
f1 (ppm)

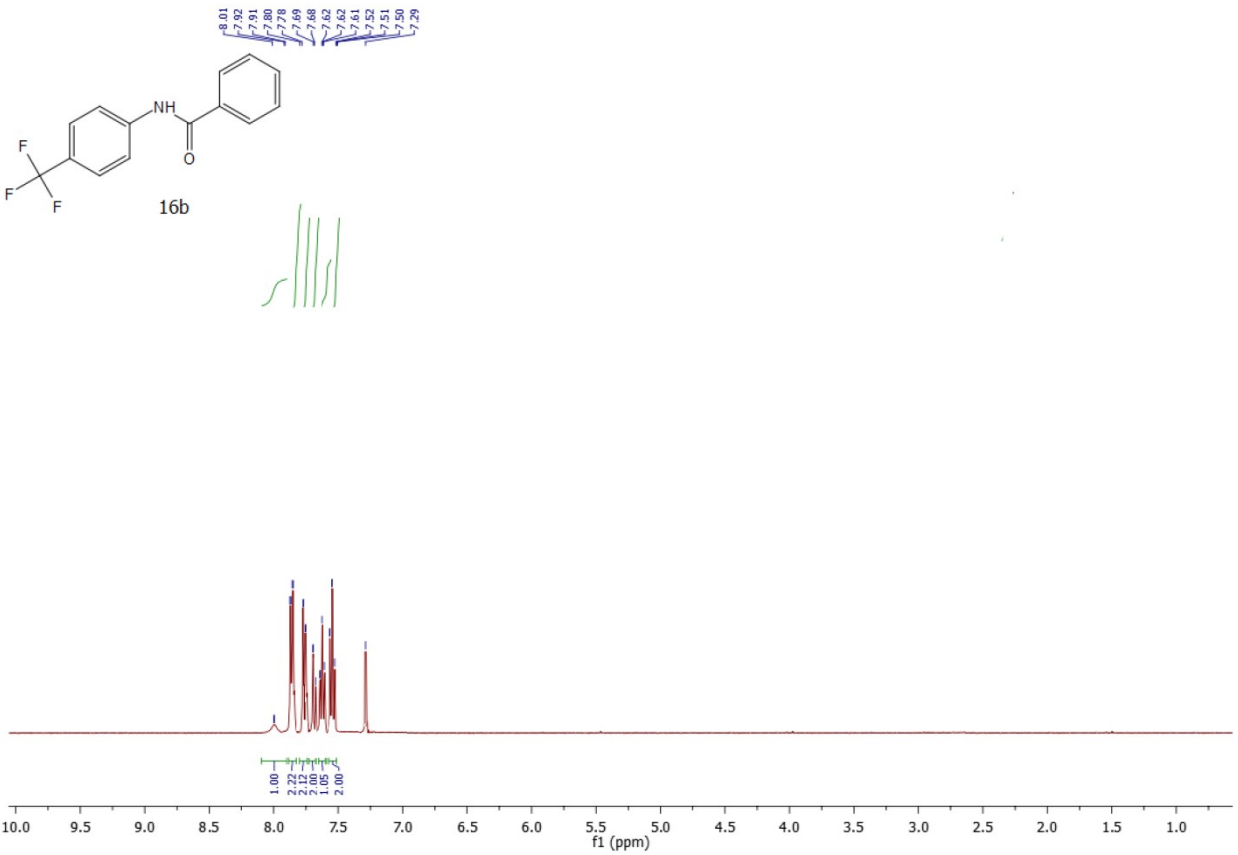
15a


166.28
137.21
134.41
132.78
131.87
128.82
128.47
128.11
127.92
127.63
77.32
77.00
76.69
Br
NH
O
Br
15a
f1 (ppm)

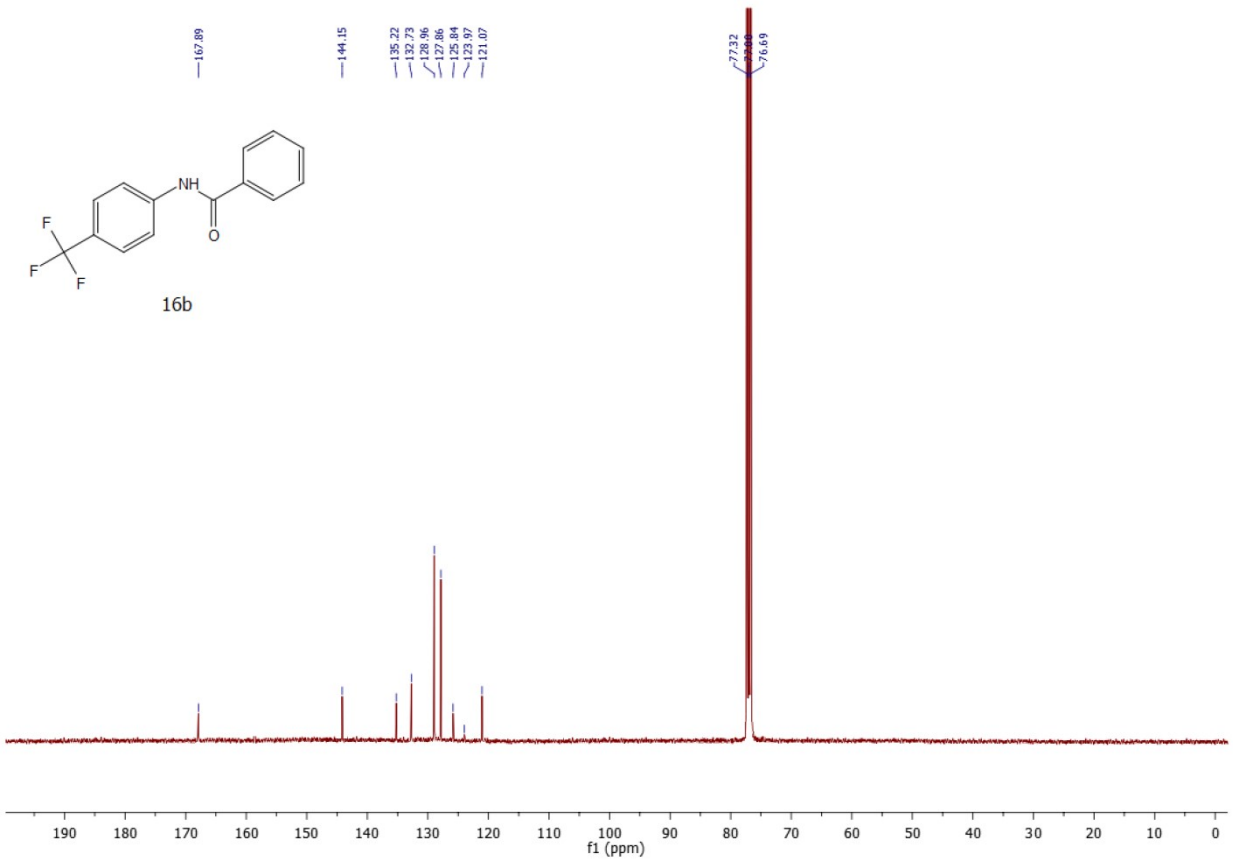

8.42
8.41
8.25
7.89
7.88
7.86
7.86
7.67
7.66
7.64
7.63
7.59
7.52
7.50
7.48
7.29
7.27
7.26
7.25
F
F
F
NH
O
16a
1.20
1.00
1.99
5.19
1.16
f1 (ppm)

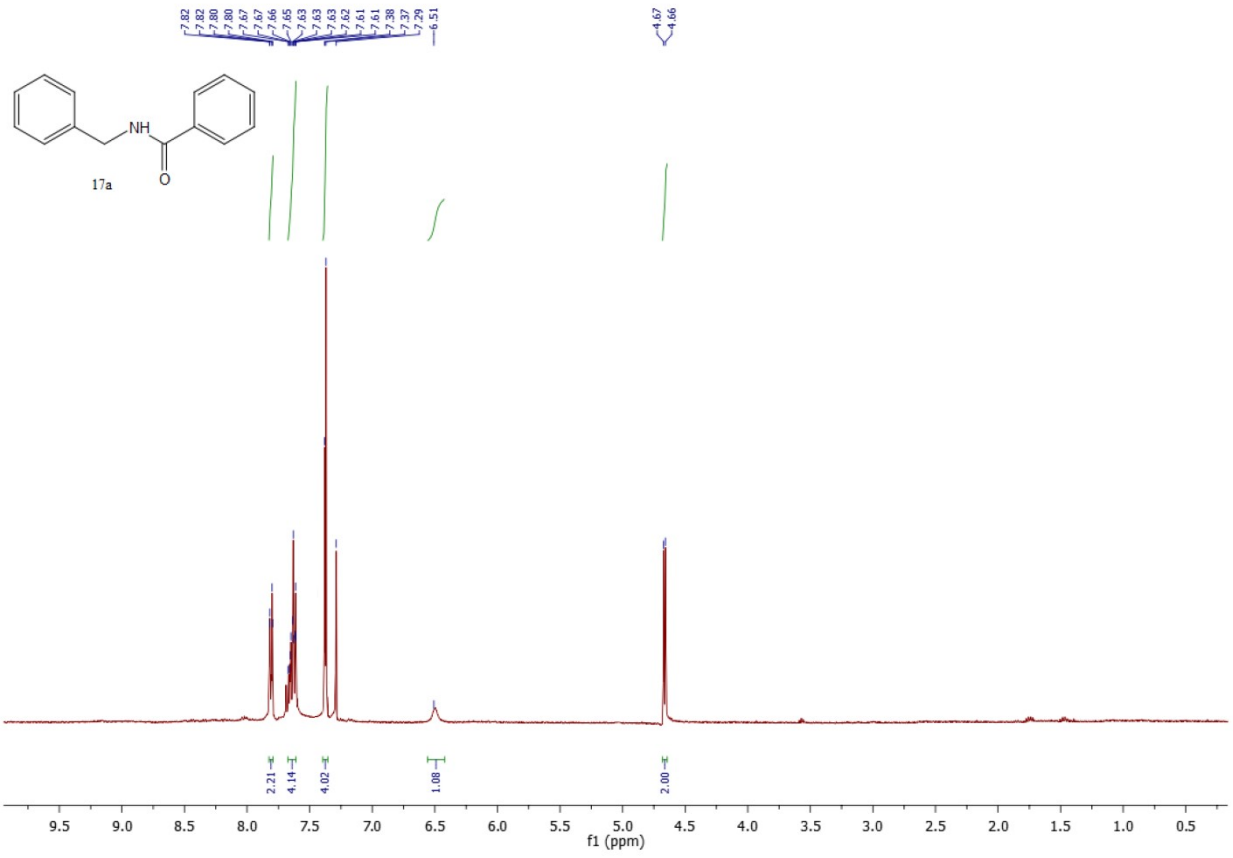

166.73
136.09
134.57
133.90
132.66
132.04
129.67
129.09
127.40
127.17
127.00
126.80
77.32
77.00
76.69
F
F
F
NH
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

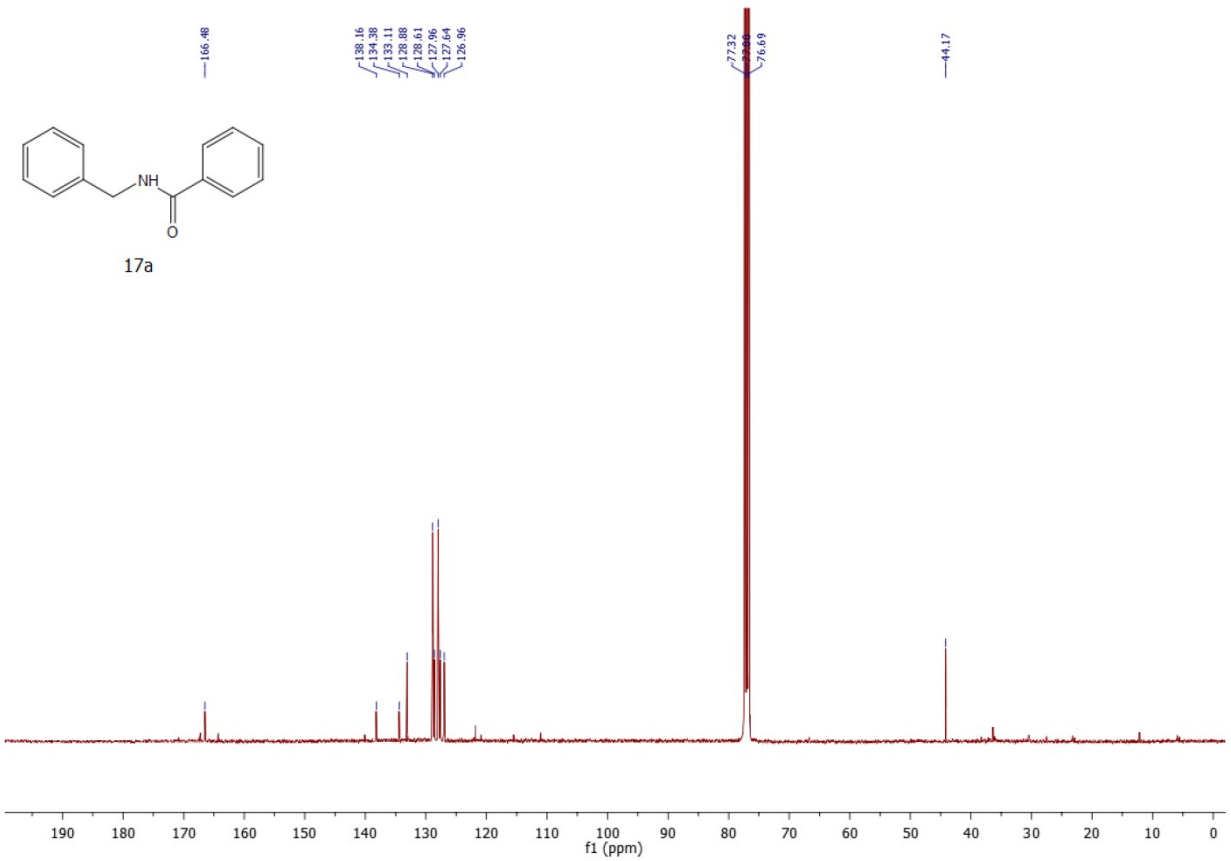
16a

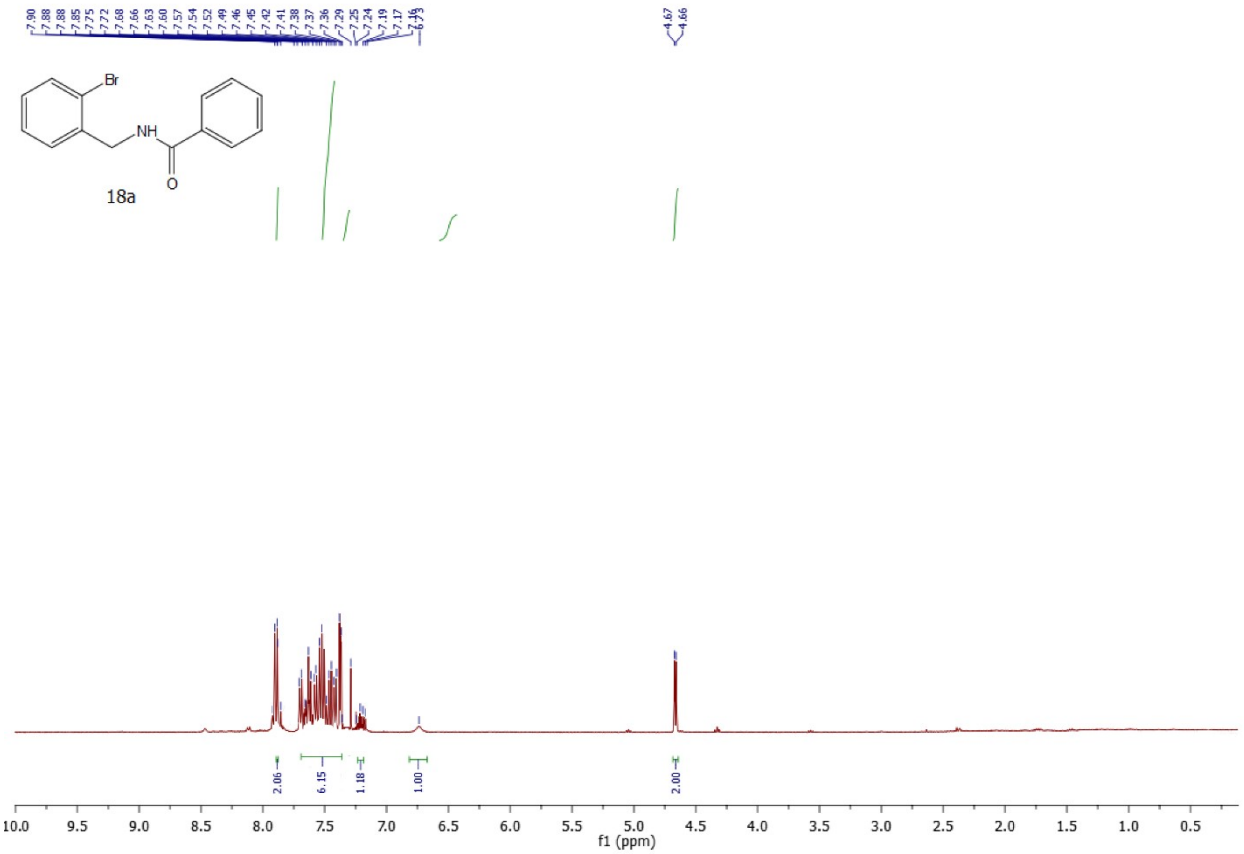

8.01
7.92
7.91
7.80
7.78
7.69
7.68
7.62
7.61
7.52
7.51
7.50
7.29
NH
O
F
F
F
1.00
2.22
2.12
2.00
1.05
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

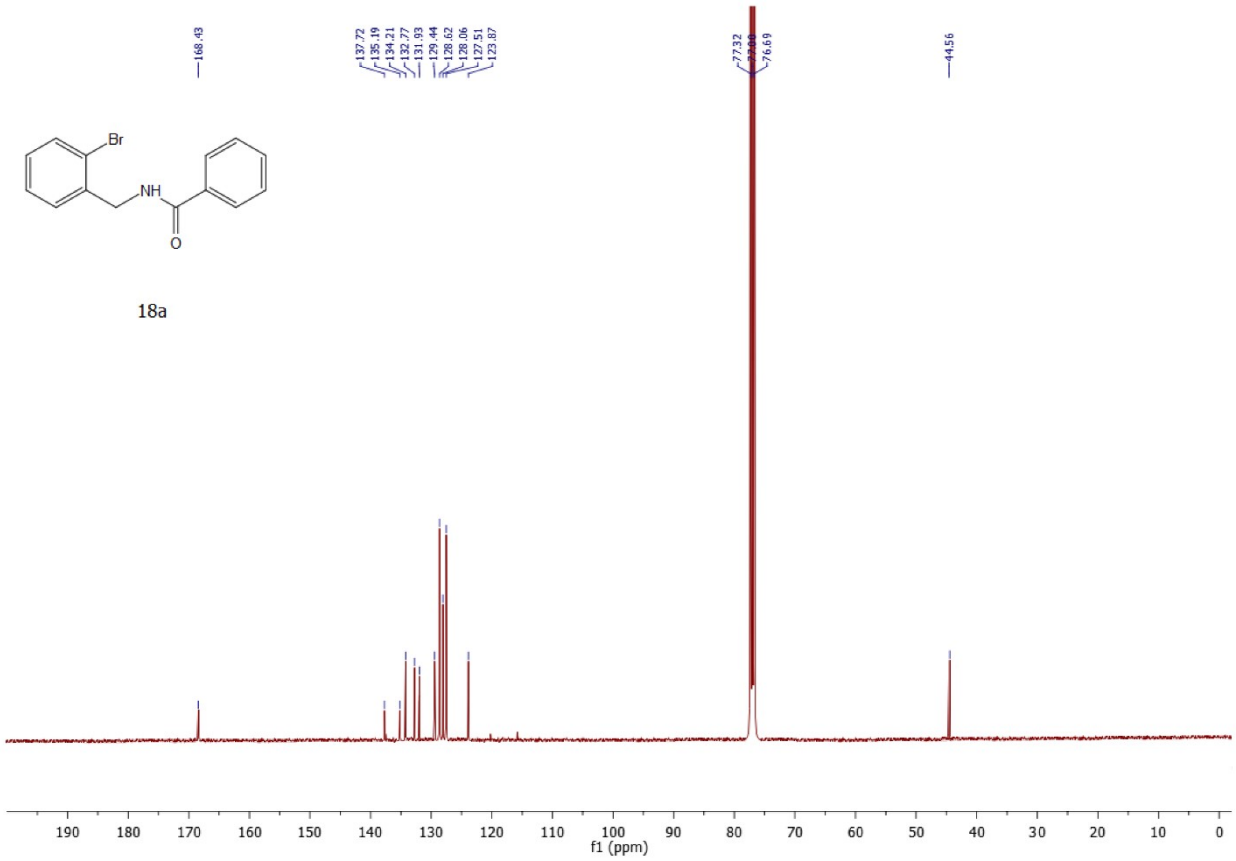
16b

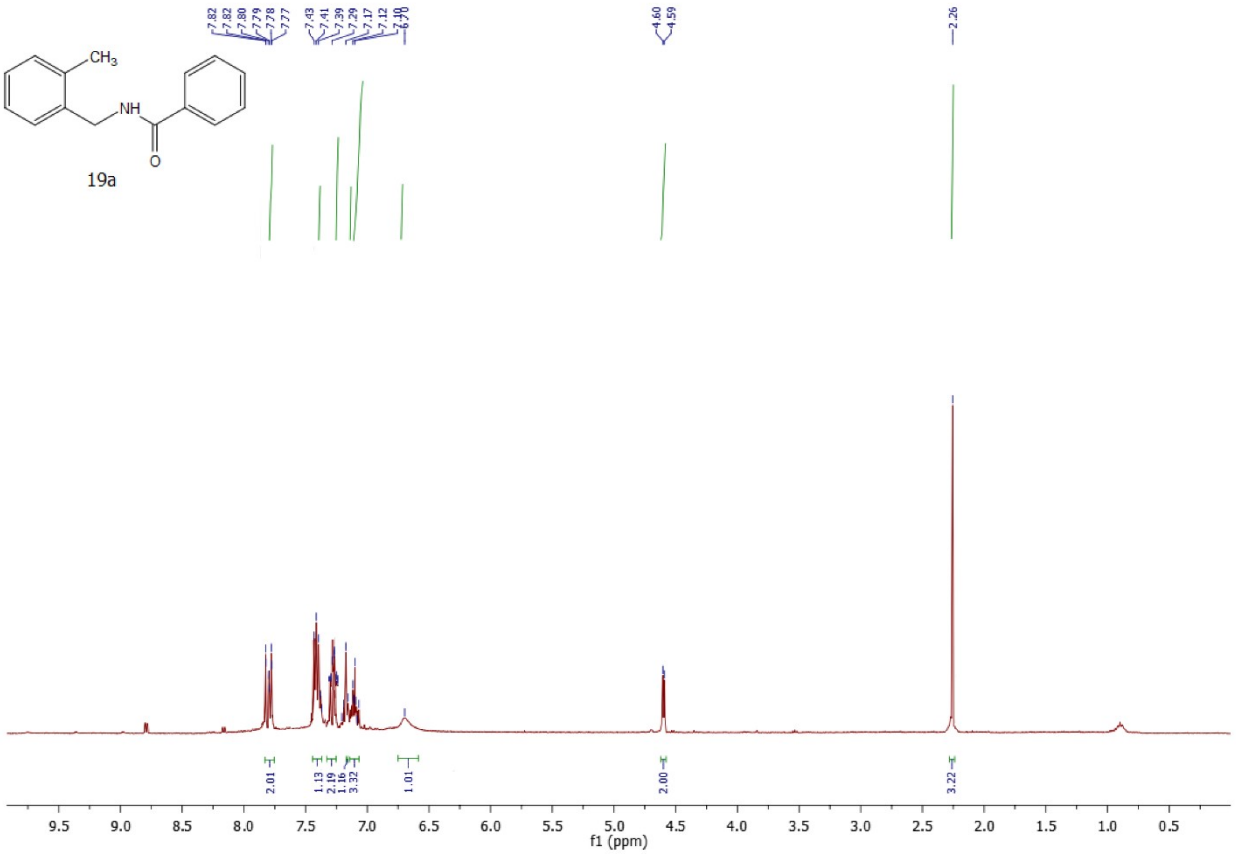

167.89
144.15
135.22
132.73
128.96
127.86
125.84
123.97
121.07
77.32
76.69
NH
O
F
F
F
16b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

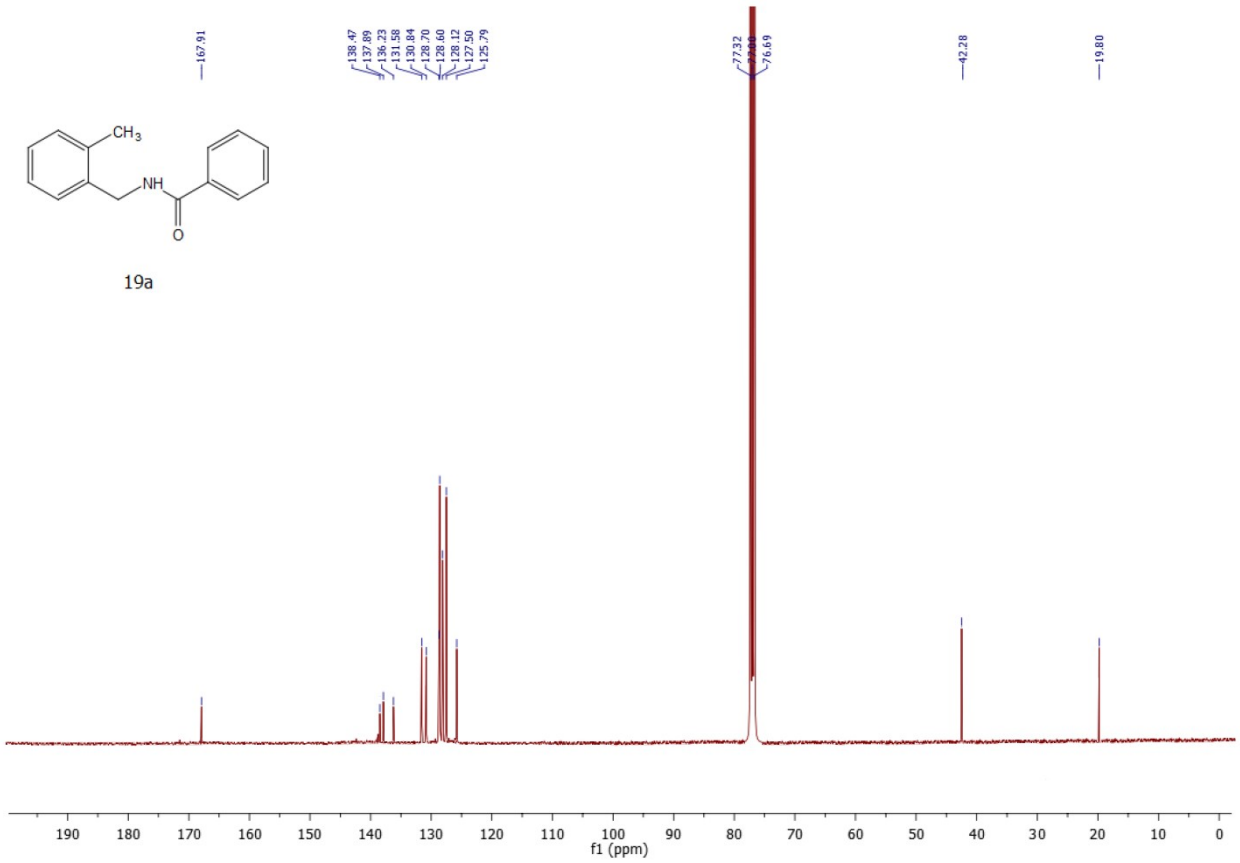

7.82
7.82
7.80
7.80
7.67
7.67
7.66
7.65
7.63
7.63
7.62
7.61
7.61
7.38
7.37
7.29
6.51
4.67
4.66
NH
O
17a
2.21
4.14
4.02
1.08
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

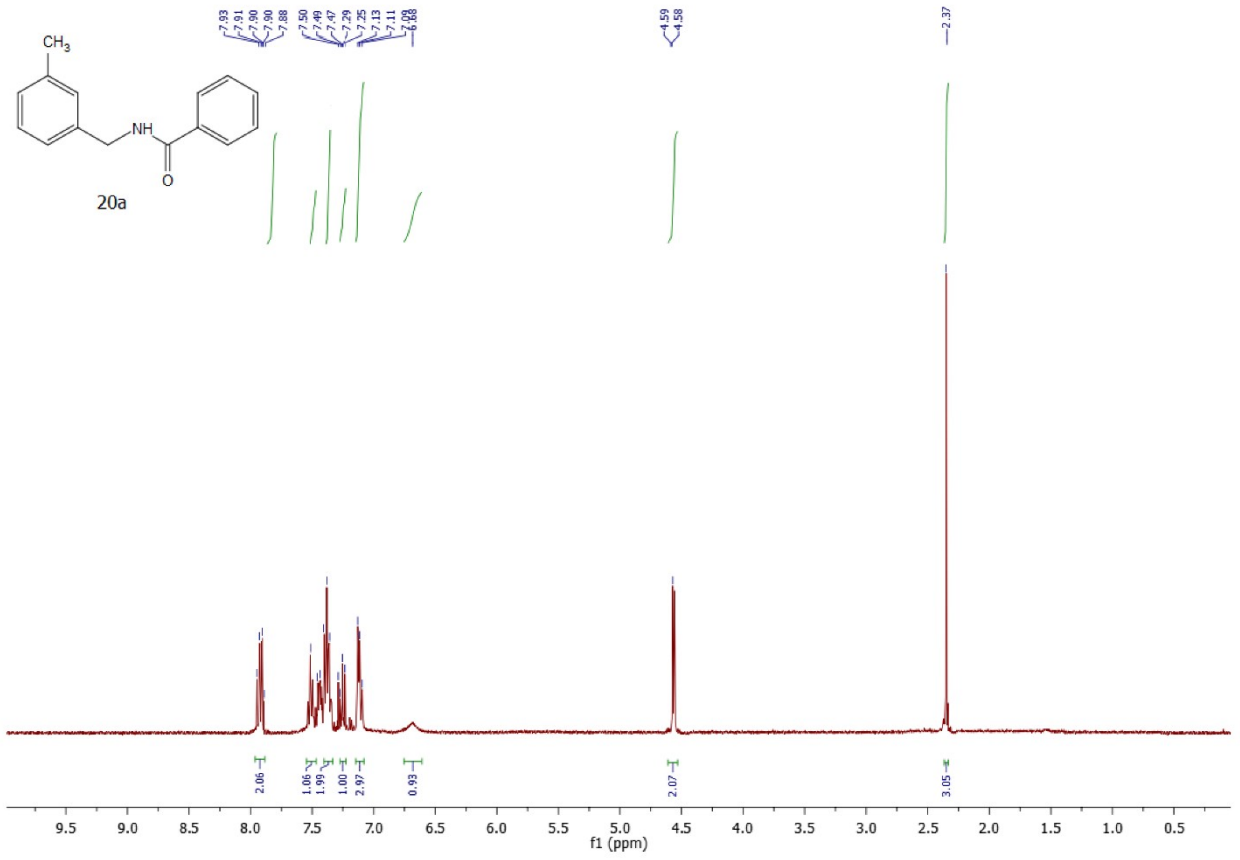

166.48
138.16
134.38
133.11
128.88
128.61
127.96
127.64
126.96
77.32
76.69
44.17
NH
O
17a
f1 (ppm)

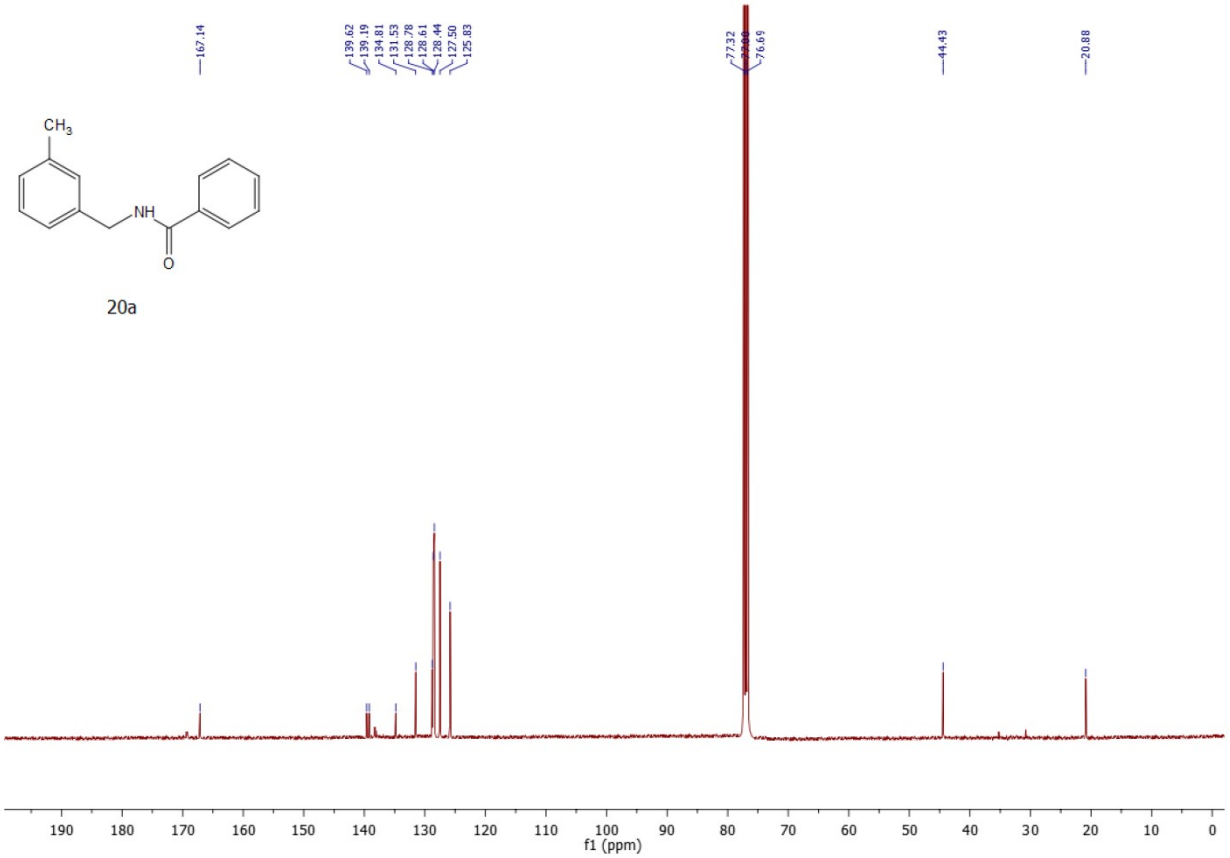

7.90
7.88
7.88
7.85
7.75
7.72
7.68
7.66
7.63
7.60
7.57
7.54
7.52
7.49
7.46
7.45
7.42
7.41
7.38
7.37
7.36
7.29
7.25
7.24
7.19
7.17
4.67
4.66
Br
NH
O
18a
2.06
6.15
1.18
1.00
2.00
f1 (ppm)

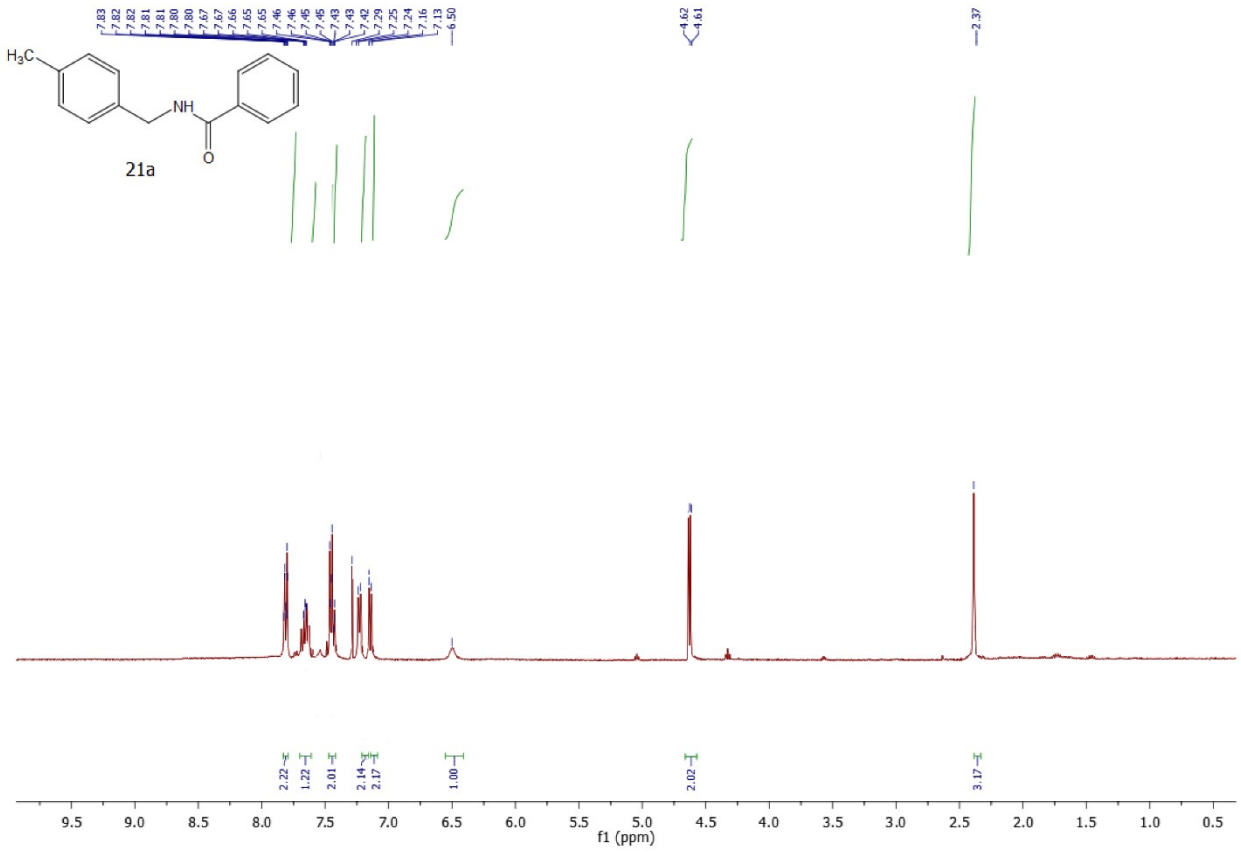

168.43
137.72
135.19
134.21
132.77
131.93
129.44
128.62
128.06
127.51
123.87
77.32
76.69
44.56
Br
NH
O
18a
f1 (ppm)

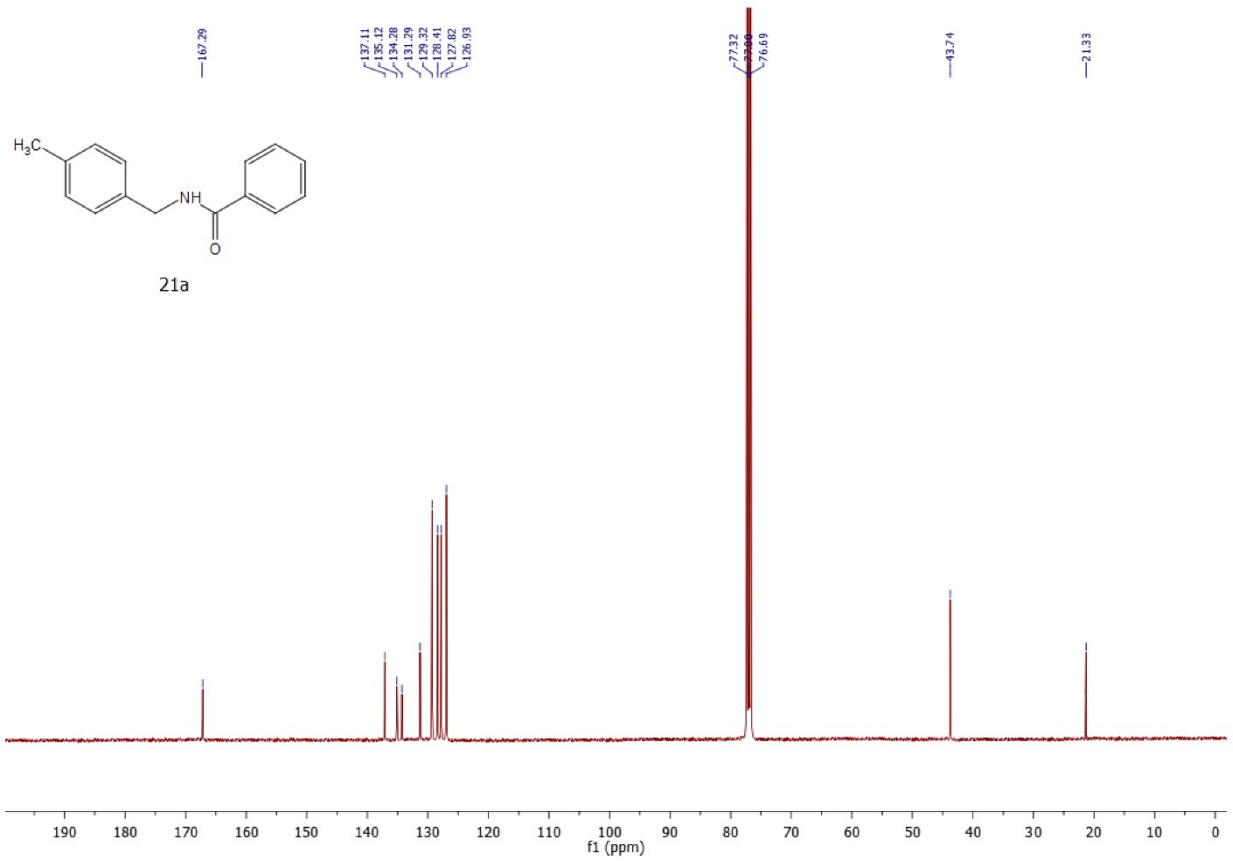

7.82
7.80
7.79
7.78
7.77
7.43
7.41
7.39
7.29
7.17
7.12
4.60
4.59
2.26
CH3
NH
O
19a
2.01
1.13
2.10
1.10
3.32
1.01
2.00
3.22
f1 (ppm)

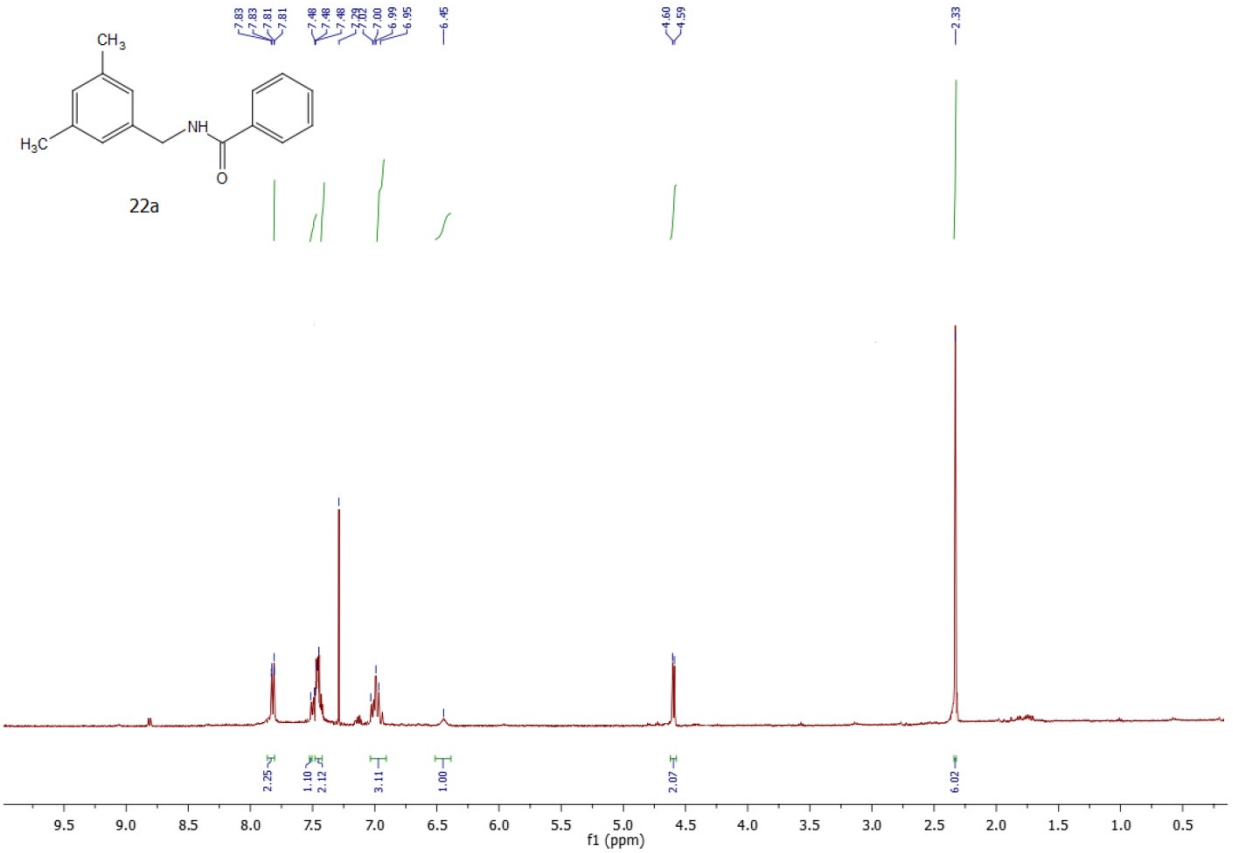

167.91
138.47
137.89
136.23
131.58
130.84
128.70
128.60
128.12
127.50
125.79
77.32
77.00
76.69
42.28
19.80
CH3
NH
O
19a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

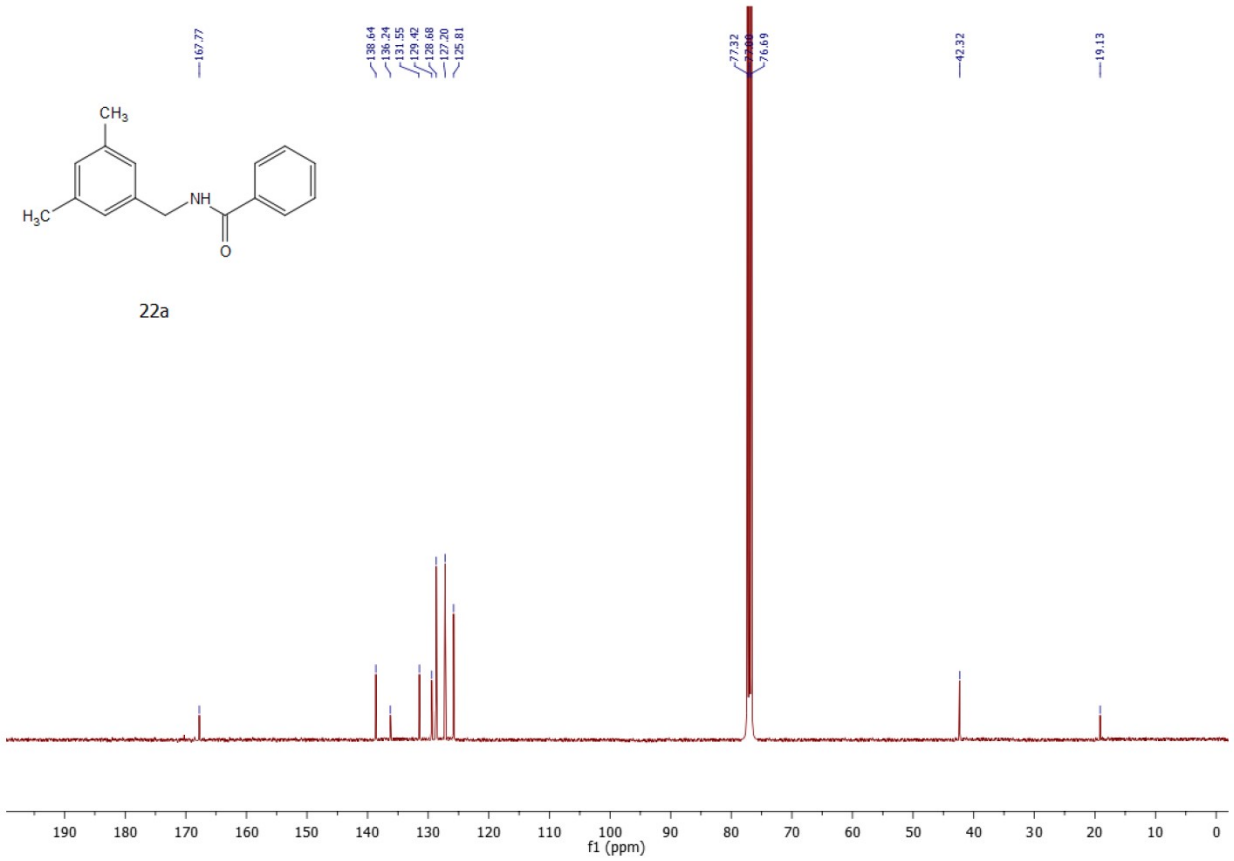

7.93
7.91
7.90
7.90
7.88
7.50
7.49
7.47
7.29
7.25
7.13
7.11
7.08
6.88
4.59
4.58
2.37
CH3
NH
O
20a
2.06
1.06
1.99
1.00
2.97
0.93
2.07
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

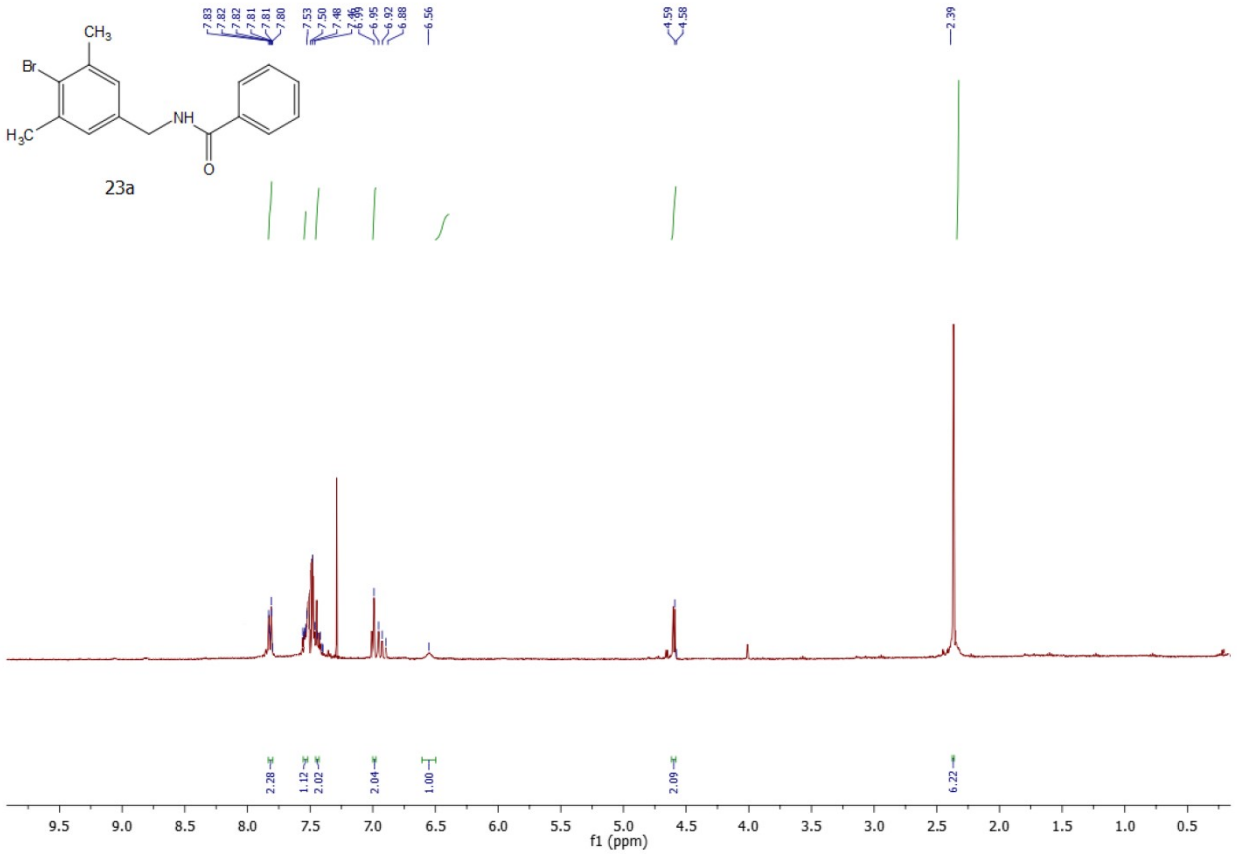

167.14
139.62
139.19
134.81
131.53
128.78
128.61
128.44
127.50
125.83
77.32
76.69
44.43
20.88
CH3
NH
O
20a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

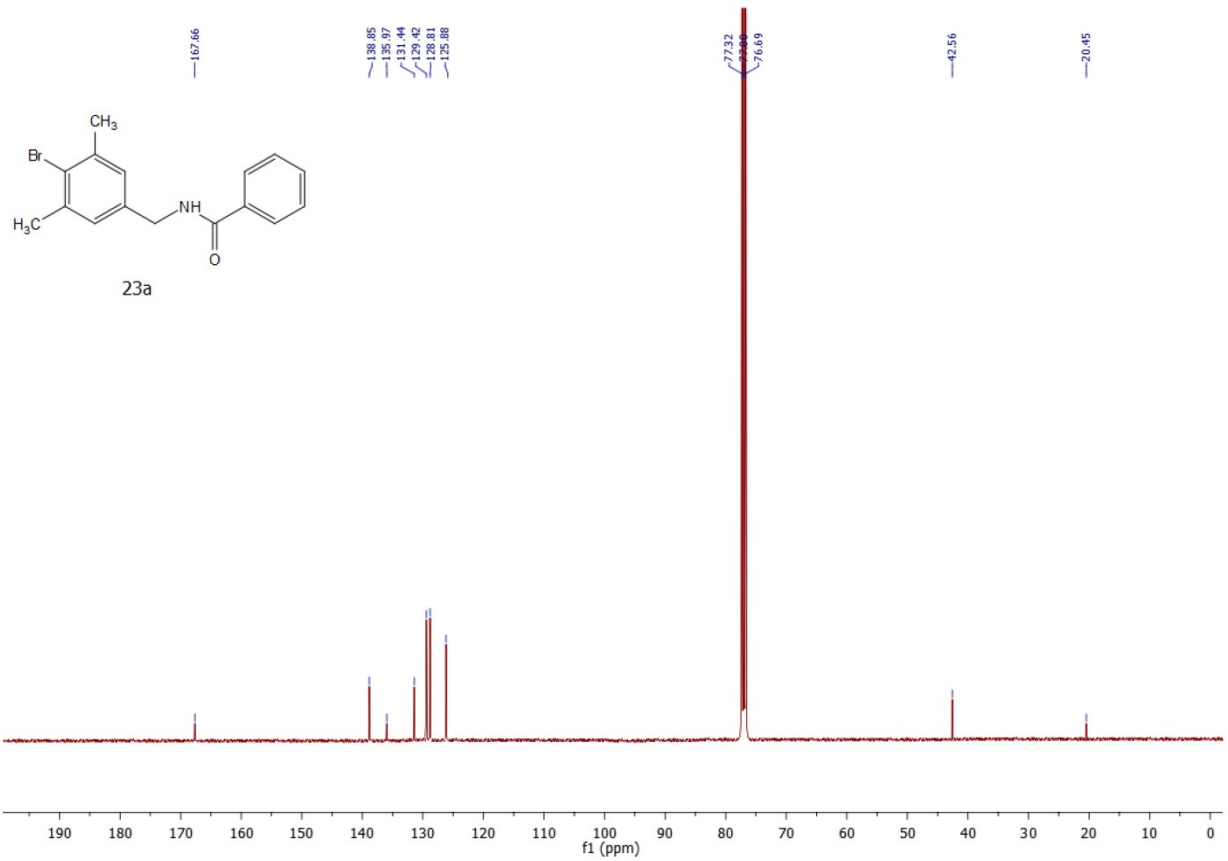

7.83
7.82
7.82
7.81
7.81
7.80
7.80
7.67
7.67
7.66
7.65
7.65
7.46
7.46
7.45
7.45
7.43
7.43
7.42
7.29
7.25
7.24
7.16
7.13
6.50
4.62
4.61
2.37
H3C
NH
O
21a
2.22
1.22
2.01
2.14
2.17
1.00
2.02
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


167.29
137.11
135.12
134.28
131.29
129.32
128.41
127.82
126.93
77.32
76.69
43.74
21.33
H3C
NH
O
21a
f1 (ppm)

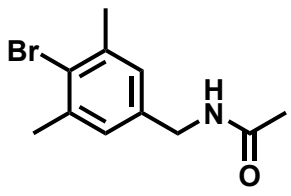

7.83
7.81
7.48
7.46
7.02
7.00
6.99
6.95
6.45
4.60
4.59
2.33
CH3
H3C
NH
O
22a
2.25
1.10
2.12
3.11
1.00
2.07
6.02
f1 (ppm)


167.77
138.64
136.24
131.55
129.42
128.68
127.20
125.81
77.32
76.69
42.32
19.13
CH3
H3C
NH
O
22a
f1 (ppm)

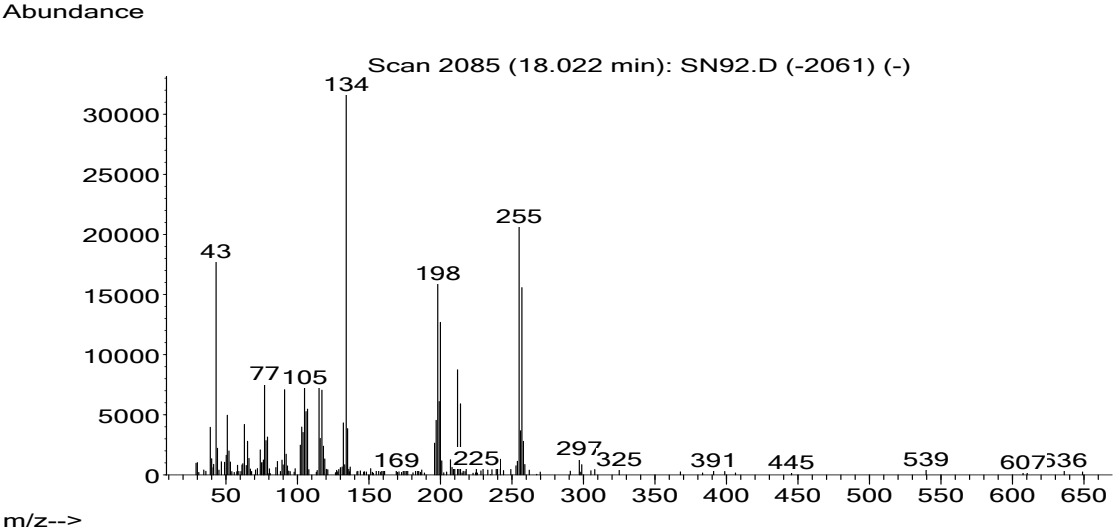

7.83
7.82
7.82
7.81
7.81
7.80
7.53
7.50
7.48
6.95
6.92
6.88
6.56
4.59
4.58
2.39
CH3
Br
H3C
NH
O
23a
2.28
1.12
2.02
2.04
1.00
2.09
6.22
f1 (ppm)

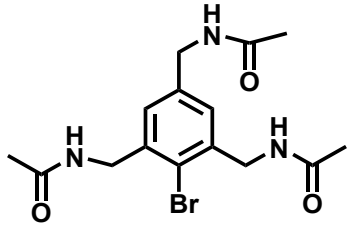


Formation of a product with three substituted CH_3 group of 2-Bromomesitylene was established by GC-MS analysis



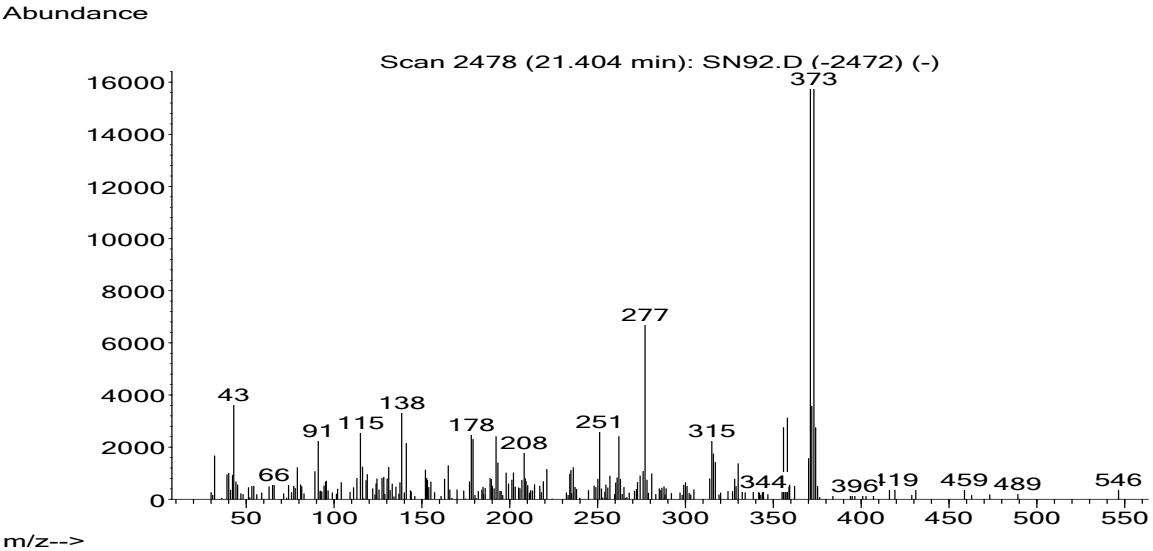
M=255



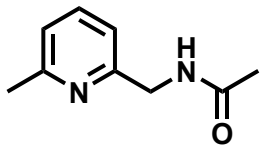


N,N',N''-((2-bromobenzene-1,3,5-triyl)tris(methylene))triacetamide,

M= 370

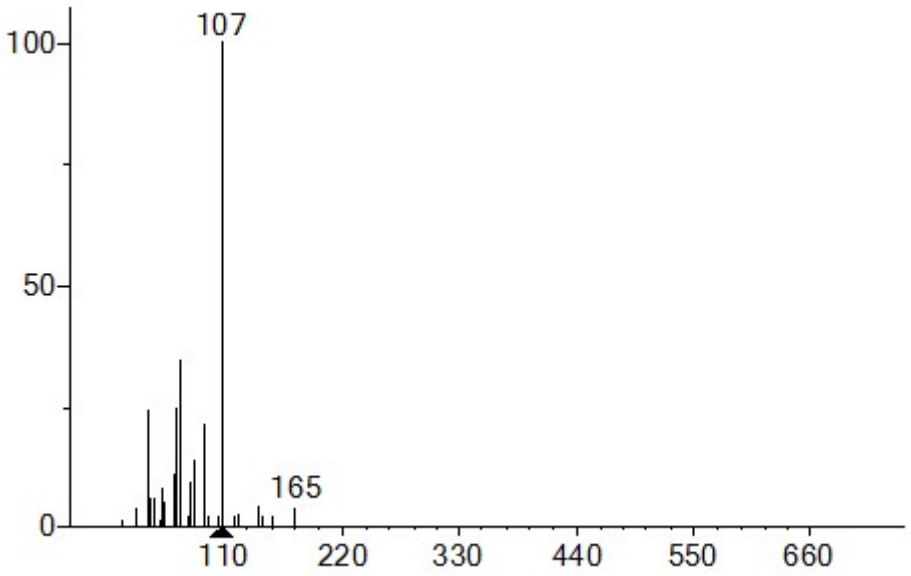


Formation of **12** was determined GC-MC analysis



(12)

M=164


100
50
0
107
165
110
220
330
440
550
660