Electronic Supplementary Material (ESI) for ChemComm.

Directing Group Assistated Copper-Mediated Aroylation of Phenols Using 2-Bromoacetophenones

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Supporting Information

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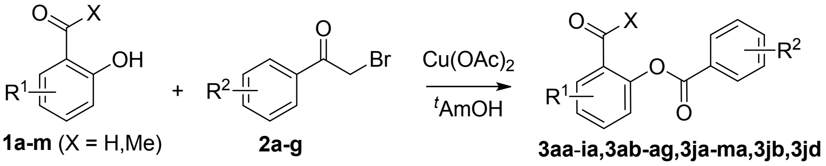
1. General Information

Melting points were measured with a Buchi B-540 melting point apparatus and are uncorrected. NMR spectra were recorded on Bruker Avance III 500 MHz FTNMR spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on Trace DSQ GCMS instrument. All the commercially available regents were used as received. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Merck). Column chromatography was performed on silica gel (100-200 mesh, Merck).

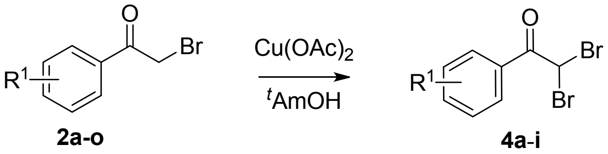
2. Reaction Procedures

2.1 General procedure for the synthesis of aryl esters (Procedure A):



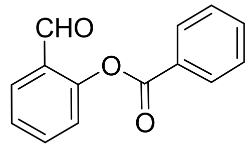
A solution of α-hydroxybenzaldehyde or α-hydroxyacetophenone (1.0 mmol), 2-bromoacetophenone (2.0 mmol) and $Cu(OAc)_2.H_2O$ (1.0 mmol) in ^{t}AmOH (6.0 mL) was stirred at 100 ^{o}C under open air for 10 hours. The solvent was removed under vacuo and the crude reaction mixture was poured into water and extracted with ethyl acetate (25 mL x 3). The ethyl acetate layer was then washed with brine. Finally, it was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuo. The crude product obtained was purified by silica gel (100-200 mesh) column chromatography using EtOAc/Hexane (1:9) as the eluant to afford chromones. Using this general procedure compounds **3** were synthesized.

2.2 General procedure for the synthesis of 2,2-dibromoacetophenones (Procedure B):



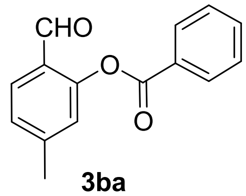
A solution of 2-bromoacetophenone (2.0 mmol) and $Cu(OAc)_2.H_2O$ (1.0 mmol) in ^{t}AmOH (6.0 mL) was stirred at 100 ^{o}C under open air for 5 hours. The solvent was removed under vacuo and the crude reaction mixture was poured into water and extracted with ethyl acetate (25 mL x 3). The ethyl acetate layer was then washed with brine. Finally, it was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuo. The crude product obtained was purified by silica gel (100-200 mesh) column chromatography using EtOAc/Hexane (1:9) as the eluant to afford 2,2-dibromoacetophenones. Using this general procedure compounds **2a**-**i** were synthesized.

2.3 Spectral and Analytical Data:



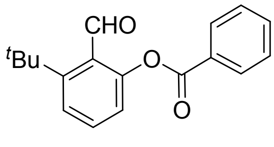
3aa

2-Formylphenyl benzoate (3aa): Following the general procedure, the reaction was carried out by heating a mixture of salicylaldehyde (**1a**, 122 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol) and $Cu(OAc)_{2.}H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 12 h under air to afford the title compound in 78% yield (Yellow oil, 176 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.32-8.16 (m, 2H), 7.97 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.77-7.62 (m, 2H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 8.2, 1.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 164.9, 152.2, 135.3, 134.0, 130.2, 130.1, 128.7, 128.5, 128.2, 126.4, 123.5. IR ($CHCl_3$, cm^{-1}): 1743, 1698, 1604, 1260. MS (EI, m/z): 226. Anal. calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46; Found: C, 74.12; H, 4.23.



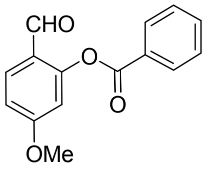
3ba

2-Formyl-5-methylphenyl benzoate (3ab): Following the general procedure, the reaction was carried out by heating a mixture of 2-hydroxy-4-methylbenzaldehyde (**1b**, 136 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol) and $Cu(OAc)_{2.}H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 10 h under air to afford the title compound in 62% yield (Yellow oil, 149 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.23 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.72-7.65 (m, 1H), 7.57-7.51 (m, 2H), 7.25 (d, *J* = 15.0 Hz, 1H), 7.13 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.0, 166.0, 152.1, 147.0, 133.9, 130.2, 130.1, 128.6, 127.3, 126.3, 125.8, 123.9, 21.8. IR ($CHCl_3$, cm^{-1}): 1742, 1695, 1614, 1262, 1231. MS (EI, m/z): 240. Anal. calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03; Found: C, 74.82; H, 4.94.



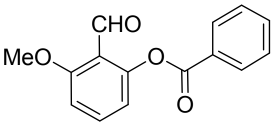
3ca

3-(*tert*-Butyl)-2-formylphenyl benzoate (3ca): Following the general procedure, the reaction was carried out by heating a mixture of 5-*tert*-butyl-2-hydroxybenzaldehyde (**1c**, 178 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 54% yield (Yellow oil, 152 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1H NMR (500 MHz, Chloroform-d) δ 10.22 (s, 1H), 8.24 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 2.6 Hz, 1H), 7.71-7.65 (m, 2H), 7.59-7.51 (m, 3H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.7, 165.0, 150.1, 149.6, 133.9, 132.6, 130.2, 129.9, 129.0, 128.7, 127.5, 126.6, 122.9, 34.7, 31.1. IR ($CHCl_3$, cm^{-1}): 1744, 1693, 1259, 1023. MS (EI, m/z): 282. Anal. calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; Found: C, 76.71; H, 6.22.



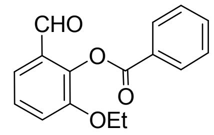
3da

2-Formyl-5-methoxyphenyl benzoate (3da): Following the general procedure, the reaction was carried out by heating a mixture of 2-hydroxy-6-methoxybenzaldehyde (**1e**, 152 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 59% yield (solid, 151 mg). M.p.: 112–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.23 (dd, J = 8.4, 1.2 Hz, 2H), 7.90 (d, J = 8.7 Hz, 1H), 7.73-7.65 (m, 1H), 7.58-7.52 (m, 2H), 6.94 (dd, J = 8.7, 2.4 Hz, 1H), 6.82 (d, J = 2.4 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, CDCl3) δ 187.1, 165.2, 154.0, 133.97, 131.9, 130.2, 128.7, 121.7, 112.6, 108.5, 77.1, 76.9, 76.6, 55.8. IR ($CHCl_3$, cm^{-1}): 1742, 1692, 1604, 1009. MS (EI, m/z): 256. Anal. calcd. for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72; Found: C, 70.25; H, 4.64.



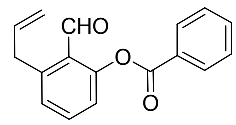
3ea

2-Formyl-3-methoxyphenyl benzoate (3ea): Following the general procedure, the reaction was carried out by heating a mixture of 2-hydroxy-6-methoxybenzaldehyde (**1e**, 152 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 68% yield (solid, 174 mg). M.p.: 112–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.28-8.13 (m, 2H), 7.67-7.60 (m, 1H), 7.57 (t, J = 8.3 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 6.94 (d, J = 8.6 Hz, 1H), 6.88-6.78 (d, J = 8.0 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.0, 165.0, 162.8, 150.9, 135.4, 133.4, 130.2, 129.3, 128.4, 117.5, 115.8, 109.3, 56.1. IR ($CHCl_3$, cm^{-1}): 1743, 1692, 1607. MS (EI, m/z): 256. Anal. calcd. for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72; Found: C, 70.49; H, 4.78.



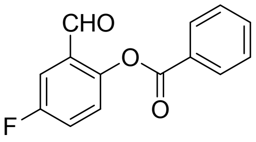
3fa

2-Ethoxy-6-formylphenyl benzoate (3fa): Following the general procedure, the reaction was carried out by heating a mixture of 2-hydroxy-6-ethoxybenzaldehyde (**1f**, 166 mg, 1.0 mmol) 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 58% yield (Yellow oil, 157 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.25 (d, J = 8.1 Hz, 2H), 7.73-7.65 (m, 1H), 7.60-7.48 (m, 3H), 7.35 (t, J = 7.9 Hz, 1H), 7.24 (s, 1H), 4.15-4.04 (m, 2H), 1.34-1.27 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 164.4, 151.1, 142.6, 133.8, 130.3, 129.4, 128.6, 126.7, 126.6, 120.2, 118.9, 64.9, 14.5. IR ($CHCl_3$, cm^{-1}): 1743, 1694, 1583, 1262, 1055. MS (EI, m/z): 270. Anal. calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; Found: C, 71.19; H, 5.35.



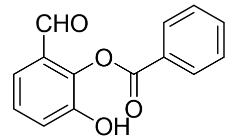
3ga

3-Allyl-2-formylphenyl benzoate (3ga): Following the general procedure, the reaction was carried out by heating a mixture of 3-allylsalicylaldehyde (**1g**, 122 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 50% yield (Yellow oil, 133 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.34-8.17 (m, 2H), 7.89-7.79 (m, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.64-7.50 (m, 3H), 7.44-7.37 (m, 1H), 6.02-5.84 (m, 1H), 5.16-5.00 (m, 2H), 3.39 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.7, 164.8, 150.1, 136.3, 134.9, 134.0, 130.2, 129.1, 128.7, 128.3, 128.0, 126.5, 126.3, 117.1, 34.0. IR ($CHCl_3$, cm^{-1}): 1742, 1698, 1261. MS (EI, m/z): 266. Anal. calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30; Found: C, 76.53; H, 5.22.

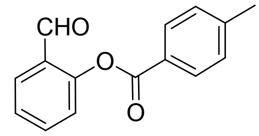


3ha

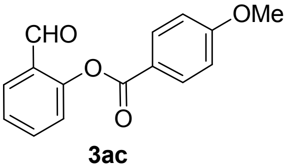
4-Fluoro-2-formylphenyl benzoate (3ha): Following the general procedure, the reaction was carried out by heating a mixture of 5-fluorosalicylaldehyde (**1h**, 140 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 53% yield (Solid, 129 mg). M.p.: 68-69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.23 (d, *J* = 8 Hz, 2H), 7.70 (t, *J* = 7.45 Hz, 1H), 7.66-7.62 (m, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.39 (m, 1H), 7.35-7.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.0, 164.9, 160.7 (d, *J* = 247.5 Hz), 148.3, 134.2, 130.3, 128.8, 128.15, 125.3 (d, *J* = 8.8 Hz), 122.2 (d, *J* = 23.4 Hz), 115.4 (d, *J* = 23.8 Hz). IR ($CHCl_3$, cm^{-1}): 1745, 1694, 1604, 1262, 1054. MS (EI, m/z): 244. Anal. calcd. for $C_{14}H_9FO_3$: C, 68.85; H, 3.71;Found: C, 68.93; H, 3.79.


3ia

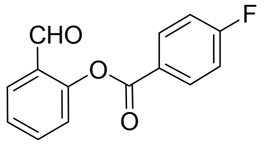
2-Formyl-6-hydroxyphenyl benzoate (3ia): Following the general procedure, the reaction was carried out by heating a mixture of 2,3-dihydroxybenzaldehyde (**1i**, 138 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 10 h under air to afford the title compound in 57% yield (138 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ. 11.1 (s, 1H), 9.88 (s, 1H), 8.17 (d, J = 8.5 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.48-7.36 (m, 4H), 7.01 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 164.3, 153.4, 139.0, 133.7, 131.0, 130.3, 130.0, 128.7, 128.5, 121.8, 119.5. IR ($CHCl_3$, cm^{-1}): 1742, 1661, 1456, 1227, 1061. MS (EI, m/z): 242. Anal. calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16; Found: C, 69.32; H, 4.09.


3ab

2-Formylphenyl 4-methylbenzoate (3ab): Following the general procedure, the reaction was carried out by heating a mixture of salicylaldehyde (**1a**, 122 mg, 1.0 mmol), 4-′methyl-2-bromoacetophenone (**2b**, 428 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) 100 ^{o}C for 10 h to afford the title compound in 60% yield (solid, 144 mg). M.p.: 64 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.12 (d, J = 7.5 Hz, 2H), 8.01-7.91 (m, 1H), 7.74-7.63 (m, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 8.1 Hz, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 164.9, 152.4, 145.0, 135.3, 130.3, 129.8, 129.4, 128.2, 126.3, 125.7, 123.5, 21.7. IR ($CHCl_3$, cm^{-1}): 1740, 1702, 1605, 1263, 1177, 1063. MS (EI, m/z): 240. Anal. calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03; Found: C, 75.12; H, 5.19.

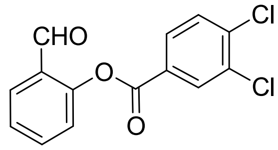

3ac

2-Formylphenyl 4-methoxybenzoate (3ac): Following the general procedure, the reaction was carried out by heating a mixture of salicylaldehyde (**1a**, 122 mg, 1.0 mmol), 4′-methoxy-2-bromoacetophenone (**2c**, 456 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 10 h to afford the title compound in 65% yield (solid, 166 mg). M.p.: 75 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.19 (d, *J* = 8.9 Hz, 2H), 7.96 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.71-7.63 (m, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 164.5, 164.2, 152.5, 135.2, 132.4, 129.7, 128.3, 126.2, 123.5, 120.7, 114.0, 55.5. IR ($CHCl_3$, cm^{-1}): 1735, 1697, 1605, 1256, 1167, 1009. MS (EI, m/z): 256. Anal. calcd. for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72; Found: C, 70.44; H, 4.85.



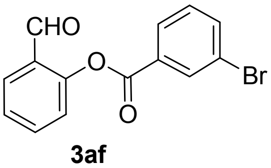
3ad

2-Formylphenyl 4-fluorobenzoate (3ad): Following the general procedure, the reaction was carried out by heating a mixture of salicylaldehyde (**1a**, 122 mg, 1.0 mmol), 4′-fluoro-2-bromoacetophenone (**2d,** 432 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 10 h to afford the title compound in 62% yield (Yellow oil, 151 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.32-8.22 (m, 2H), 7.96 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.73-7.67 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 166.3 (d, *J* = 255.0 Hz), 163.9, 151.8, 135.3, 133.0, 132.9 (d, *J* = 10.0 Hz), 130.7, 128.1, 126.5, 123.4, 115.9 (d, *J* = 21.2 Hz), 115.8. IR ($CHCl_3$, cm^{-1}): 1743, 1698, 1604, 1260, 1154. MS (EI, m/z): 244. Anal. calcd. for $C_{14}H_9FO_3$: C, 68.85; H, 3.71; Found: C, 68.67; H, 3.64.



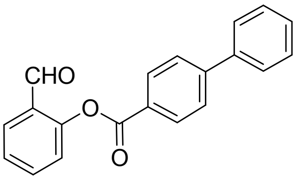
3ae

2-Formylphenyl 3,4-dichlorobenzoate (3ae): Following the general procedure, the reaction was carried out by heating a mixture of salicylaldehyde (**1a**, 122 mg, 1.0 mmol), 3′,4′-dichloro-2-bromoacetophenone (**2e,** 532 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 10 h to afford the title compound in 52% yield (solid, 153 mg). M.p.: 74-76 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.31 (d, *J* = 2.0 Hz, 1H), 8.06 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.95 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 163.1, 151.1, 138.7, 135.3, 133.3, 132.1, 131.6, 130.8, 129.2, 128.6, 128.0, 126.8, 123.3. IR ($CHCl_3$, cm^{-1}): 1744, 1698, 1605, 1465, 1206. MS (EI, m/z): 294. Anal. calcd. for $C_{14}H_8Cl_2O_3$: C, 56.98; H, 2.73; Found: C, 56.82; H, 2.61.



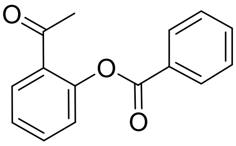
3af

2-Formylphenyl 3-bromobenzoate (3af): Following the general procedure, the reaction was carried out by heating a mixture of salicylaldehyde (**1a**, 122 mg, 1.0 mmol), 3′-bromo-2-bromoacetophenone (**2f,** 552 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h to afford the title compound in 45% yield (Yellow oil, 137 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.37 (t, *J* = 1.8 Hz, 1H), 8.20-8.13 (m, 1H), 7.96 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.83-7.78 (m, 1H), 7.70 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 163.6, 151.5, 136.9, 135.3, 133.1, 131.0, 130.2, 128.8, 128.0, 126.7, 123.4. IR ($CHCl_3$, cm^{-1}): 1743, 1704, 1605, 1246, 1207. MS (EI, m/z): 303. Anal. calcd. for $C_{14}H_9BrO_3$: C, 55.11; H, 2.97; Found: C, 55.18; H, 3.17.



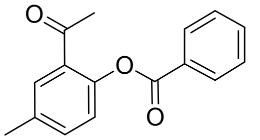
3ag

2-Formylphenyl [1,1'-biphenyl]-4-carboxylate (3ag): Following the general procedure, the reaction was carried out by heating a mixture of salicylaldehyde (**1a**, 122 mg, 1.0 mmol), 4′-phenyl-2-bromoacetophenone (**2g,** 548 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h to afford the title compound in 68% yield (solid, 205 mg). M.p.: 93-94 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.30 (d, *J* = 8.3 Hz, 2H), 7.98 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.38 (m, 5H), 7.36 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 164.8, 152.2, 146.7, 139.6, 135.3, 130.8, 130.2, 128.9, 128.3, 127.4, 127.3, 126.4, 123.5. IR ($CHCl_3$, cm^{-1}): 1739, 1700, 1605, 1265, 1065. MS (EI, m/z): 302. Anal. calcd. for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67; Found: C, 77.61; H, 4.40.



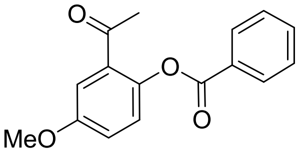
3ja

2-Acetylphenyl benzoate (3ja): Following the general procedure, the reaction was carried out by heating a mixture of 2-hydroxyacetophenone (**1j**, 136 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (192 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 10 h under air to afford the title compound in 76% yield (Yellow oil, 182 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.71-7.63 (m, 1H), 7.62-7.58 (m, 1H), 7.57-7.49 (m, 2H), 7.42-7.35 (m, 1H), 7.29-7.21 (m, 1H), 2.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 165.1, 149.3, 133.7, 133.3, 131.1, 130.2, 129.1, 128.6, 126.1, 123.8, 29.7 IR ($CHCl_3$, cm^{-1}): 1740, 1688, 1602, 1449, 1261, 799. MS (EI, m/z): 240. Anal. calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03; Found: C, 74.87; H, 4.92.



3ka

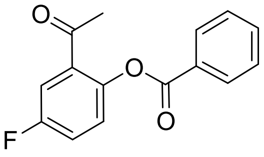
2-Acetyl-4-methylphenyl benzoate (3ka): Following the general procedure, the reaction was carried out by heating a mixture of 2′-hydroxy-5′-methylacetophenone (**1k**, 150 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 10 h under air to afford the title compound in 70% yield (Yellow oil, 178 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.67-7.63 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.41-7.35 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 2.53 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 165.2, 147.1, 135.9, 133.9, 133.7, 130.5, 130.2, 129.2, 128.6, 123.5, 29.8, 20.8. IR ($CHCl_3$, cm^{-1}): 1741, 1689, 1268, 1202, 1060, 708. MS (EI, m/z): 254. Anal. calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; Found: C, 75.64; H, 5.60.



3la

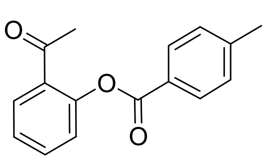
2-Acetyl-4-methoxyphenyl benzoate (3la): Following the general procedure, the reaction was carried out by heating a mixture of 2′-hydroxy-5′-methoxyacetophenone (**1l**, 166 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 ^{o}C for 10 h under air to afford the title compound in 63% yield

(Yellow oil, 170 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32-8.13 (m, 2H), 7.71-7.61 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 3.0 Hz, 1H), 7.19-7.07 (m, 2H), 3.87 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.2, 165.4, 157.1, 142.8, 133.7, 131.7, 130.2, 129.1, 128.6, 124.7, 119.1, 114.2, 55.7, 29.9. IR ($CHCl_3$, cm^{-1}): 1740, 1689, 1489, 1266, 1233, 707. MS (EI, m/z): 270. Anal. calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; Found: C, 71.18; H, 5.41.



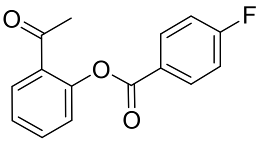
3ma

2-Acetyl-4-fluorophenyl benzoate (3ma): Following the general procedure, the reaction was carried out by heating a mixture of 2′-hydroxy-5′-fluoroacetophenone (**1m**, 154 mg, 1.0 mmol), 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 61% yield (Yellow oil, 157 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.70-7.65 (m, 1H), 7.59-7.50 (m, 3H), 7.33-7.26 (m, 1H), 7.22 (dd, *J* = 8.9, 4.6 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 165.1, 159.8 (d, *J* = 246.3), 158.9, 145.1, 133.9, 132.4, 130.2, 128.7, 125.5 (d, *J* = 7.5 Hz), 120.2 (d, *J* = 23.8 Hz), 116.5 (d, *J* = 25.0 Hz), 29.7. IR ($CHCl_3$, cm^{-1}): 1741, 1692, 1484, 1266, 1172. MS (EI, m/z): 258. Anal. calcd. for $C_{15}H_{11}FO_3$: C, 69.76; H, 4.29; Found: C, 69.83; H, 4.37.



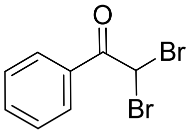
3jb

2-Acetylphenyl 4-methylbenzoate (3jb): Following the general procedure, the reaction was carried out by heating a mixture of 2′-hydroxyacetophenone (**1j**, 136 mg, 1.0 mmol), 4′-methyl-2-bromoacetophenone (**2b**, 428 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 71% yield (Yellow oil, 180 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.86 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.62-7.55 (m, 1H), 7.41-7.30 (m, 3H), 7.27-7.18 (m, 2H), 2.54 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 165.1, 149.4, 144.7, 133.3, 131.3, 130.3, 130.1, 129.3, 126.3, 126.0, 123.8, 29.8, 21.7. IR ($CHCl_3$, cm^{-1}): 1736, 1688, 1604, 1449, 1268, 1177 745. MS (EI, m/z): 254. Anal. calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; Found: C, 75.63; H, 5.59.



3jd

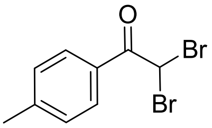
2-Acetylphenyl 4-fluorobenzoate (3jd): Following the general procedure, the reaction was carried out by heating a mixture of 2′-hydroxyacetophenone (**1j**, 136 mg, 1.0 mmol), 4′-fluoro-2-bromoacetophenone (**2d**, 432 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in *t*AmOH (6.0 mL) at 100 °C for 10 h under air to afford the title compound in 70% yield (Yellow oil, 181 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 8.30-8.18 (m, 2H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.27-7.14 (m, 3H), 2.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 166.2 (d, *J* = 251.2 Hz), 164.2, 149.1, 133.4, 132.8 (d, *J* = 10.0 Hz), 130.9, 130.3, 126.2, 125.4, 123.8, 115.8 (d, *J* = 22.5 Hz), 29.5. IR ($CHCl_3$, cm^{-1}): 1741, 1688, 1603, 1507, 1267, 757. MS (EI, m/z): 258. Anal. calcd. for $C_{15}H_{11}FO_3$: C, 69.76; H, 4.29; Found: C, 69.71; H, 4.54.



4a

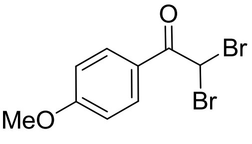
2,2-Dibromo-1-phenylethanone (4a): Following the general procedure, the reaction was carried out by heating a mixture of 2-bromoacetophenone (**2a**, 396 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in *t*AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 42% yield (Yellow oil, 234 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.71-7.58 (m, 1H), 7.57-7.41 (m, 2H), 6.73 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.9, 134.4, 130.7, 129.6, 128.9, 39.6. IR ($CHCl_3$, cm^{-1}): 1698, 1595, 1449. MS (EI, m/z): 276. Anal. calcd. for $C_8H_6Br_2O$: C, 34.57; H, 2.18; Found: C, 34.71; H, 2.10.

2,2-dibromo-1-(*p*-tolyl)ethanone (4b): Following the general procedure, the reaction was carried out by heating a mixture of 4′-metyl-2-bromoacetophenone (**2b**, 424 mg, 2.0 mmol), and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in *t*AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 41% yield (Solid, 238 mg). M.p.: 88-89 °C. ^1H NMR (500 MHz, $CDCl_3$) δ

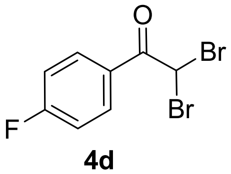


4b

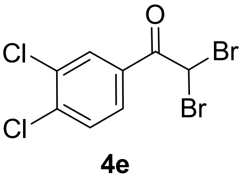
7.97 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.5, 145.7, 129.7, 129.6, 128.8, 39.9, 21.8. IR ($CHCl_3$, cm^{-1}): 1740, 1688, 1602, 1449, 1261, 799. IR ($CHCl_3$, cm^{-1}): 1687, 1604, 1278, 1196, 753. MS (EI, m/z): 290. Anal. calcd. for $C_9H_8Br_2O$: C, 37.02; H, 2.76; Found: C, 37.11; H, 2.84.


4c

2,2-Dibromo-1-(4-methoxyphenyl)ethanone (4c): Following the general procedure, the reaction was carried out by heating a mixture of 4′-methoxy-2-bromoacetophenone (**2c**, 456 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 39% yield (Yellow oil, 239 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.04 (m, 2H), 6.98 (dd, J = 8.9, 1.4 Hz, 2H), 6.69 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 164.4, 132.1, 123.2, 114.1, 55.6, 39.9. IR ($CHCl_3$, cm^{-1}): 1679, 1599, 1509, 1264, 1179, 846. MS (EI, m/z): 306. Anal. calcd. for $C_9H_8Br_2O_2$: C, 35.10; H, 2.62; Found: C, 35.24; H, 2.65. HRMS Calcd (ESI) m/z for $C_9H_9Br_2O_2$: $[M+H]^+$ 306.8965, found: 366.8969.

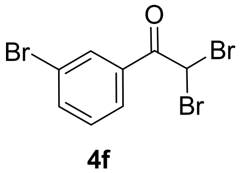

4d

2,2-Dibromo-1-(4-fluorophenyl)ethanone (4d): Following the general procedure, the reaction was carried out by heating a mixture of 4′-fluoro-2-bromoacetophenone (**2d**, 432 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 40% yield (Yellow oil, 238 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-8.10 (m, 2H), 7.23-7.14 (m, 2H), 6.65 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.5, 166.2 (d, J = 257.5 Hz), 132.6 (d, J = 10.0 Hz), 126.94, 116.1 (d, J = 22.5 Hz), 39.3. IR ($CHCl_3$, cm^{-1}): 1698, 1598, 1507, 1271, 1241, 1190, 1160, 850. MS (EI, m/z): 294. Anal. calcd. for $C_8H_5Br_2FO$: C, 32.47; H, 1.70; Found: C, 32.64; H, 1.78.


4e

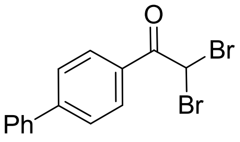
2,2-Dibromo-1-(3,4-dichlorophenyl)ethanone (4e): Following the general procedure, the reaction was carried out by heating a mixture of 3′,4′-dichloro-2-bromoacetophenone

(**2e**, 532 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in *ᵗ*AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 39% yield (Solid, 265 mg). M.p.: 68˚C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.1 Hz, 1H), 7.95 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 6.57 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.9, 139.1, 133.6, 131.6, 130.8, 130.1, 128.6, 38.7. IR ($CHCl_3$, cm^{-1}): 1706, 1582, 1466, 1388, 1277, 1194, 1032. MS (EI, m/z): 345. Anal. calcd. for $C_8H_4Br_2Cl_2O$: C, 27.70; H, 1.16; Found: C, 27.87; H, 1.19.



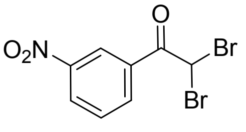
4f

2,2-Dibromo-1-(3-bromophenyl)ethanone (4f): Following the general procedure, the reaction was carried out by heating a mixture of 3′-bromo-2-bromoacetophenone (**2f**, 552 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in *ᵗ*AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 42% yield (Yellow oil, 294 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27-8.17 (m, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 6.64 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 137.2, 132.5, 132.4, 130.3, 128.1, 123.1, 39.0. IR ($CHCl_3$, cm^{-1}): 1703, 1567, 1419, 1253, 1192. MS (EI, m/z): 354. Anal. calcd. for $C_8H_5Br_3O$: C, 26.93; H, 1.41; Found: C, 27.15; H, 1.38.



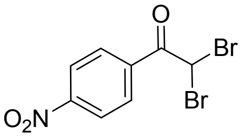
4g

1-([1,1'-Biphenyl]-4-yl)-2,2-dibromoethanone(4g): Following the general procedure, the reaction was carried out by heating a mixture of 4′-phenyl-2-bromoacetophenone (**2g**, 548 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in *ᵗ*AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 37% yield (Solid, 260 mg). M.p.: 116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23-8.11 (m, 2H), 7.79-7.68 (m, 2H), 7.67-7.59 (m, 2H), 7.54-7.38 (m, 3H), 6.73 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.5, 147.1, 139.2, 130.3, 129.3, 129.0, 128.6, 127.4, 127.2, 39.7. IR ($CHCl_3$, cm^{-1}): 1682, 1600, 1486, 1407, 1208. MS (EI, m/z): 354. Anal. calcd. for $C_{14}H_{10}Br_2O$: C, 47.50; H, 2.85; Found: C, 47.80; H, 2.80. HRMS Calcd (ESI) m/z for $C_{14}H_{11}Br_2O$: $[M+H]^+$ 352.9172, found: 352.9177.



4h

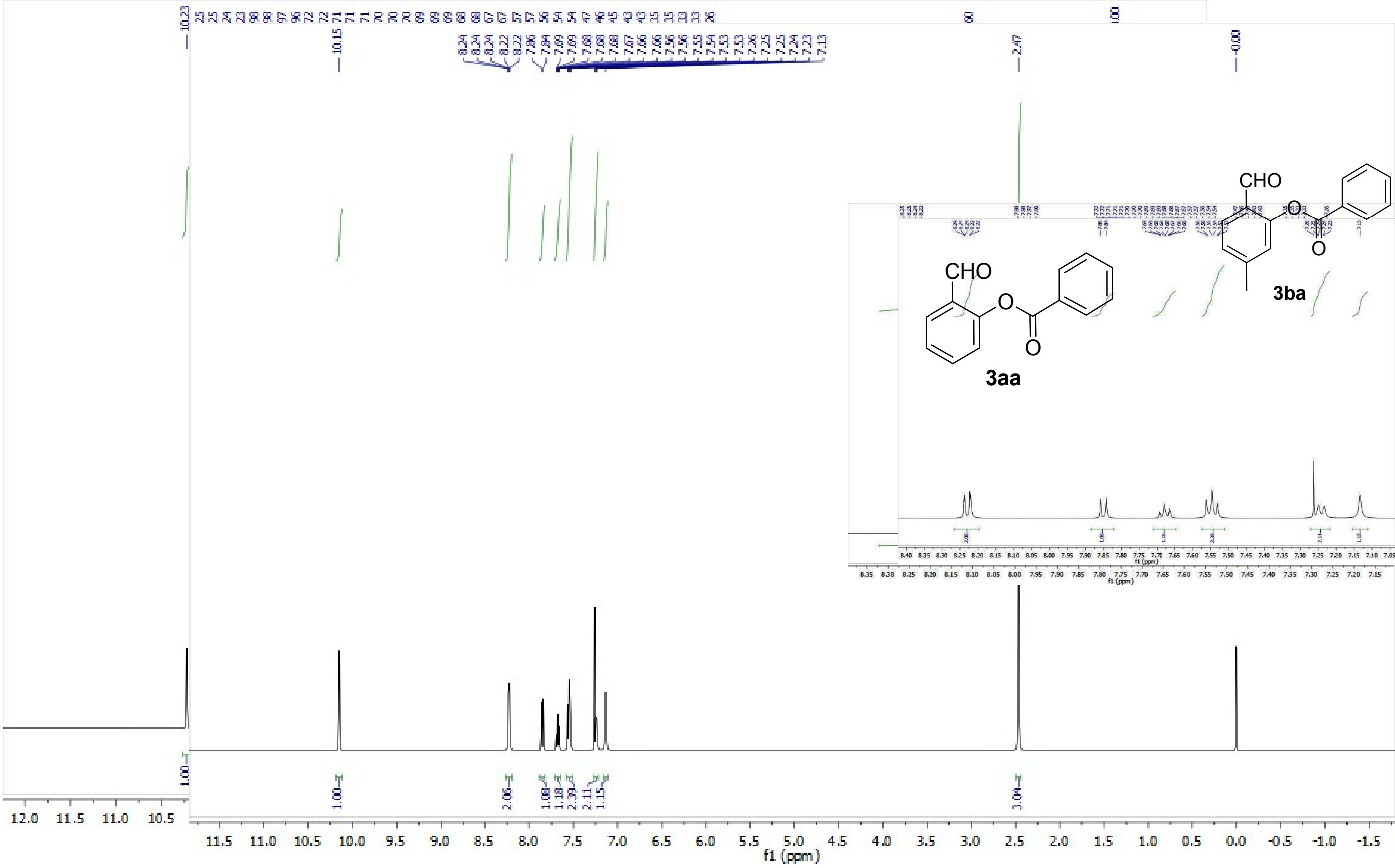
2,2-Dibromo-1-(3-nitrophenyl)ethanone (4h): Following the general procedure, the reaction was carried out by heating a mixture of 3′-nitro-2-bromoacetophenone (**2h**, 486 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 44% yield (Yellow oil, 282 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.58-8.42 (m, 2H), 7.77 (t, *J* = 8.0 Hz, 1H), 6.64 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.9, 148.3, 135.3, 132.0, 130.1, 128.4, 124.6, 38.5. IR ($CHCl_3$, cm^{-1}): 1706, 1613, 1531, 1350. MS (EI, m/z): 321. Anal. calcd. for $C_8H_5Br_2NO_3$: C, 29.75; H, 1.56; N, 4.34; Found: C, 29.87; H, 1.31; N, 4.31.

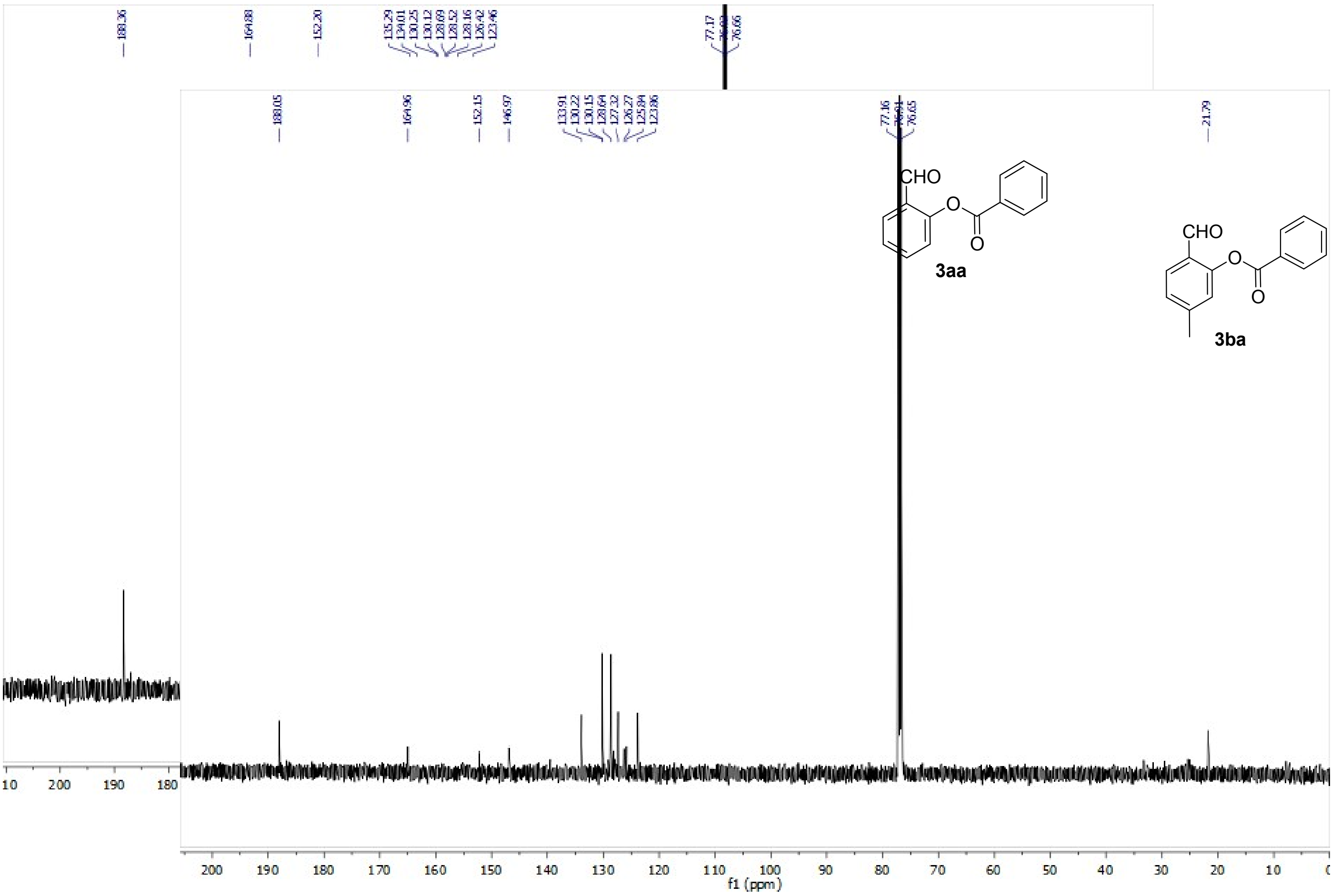


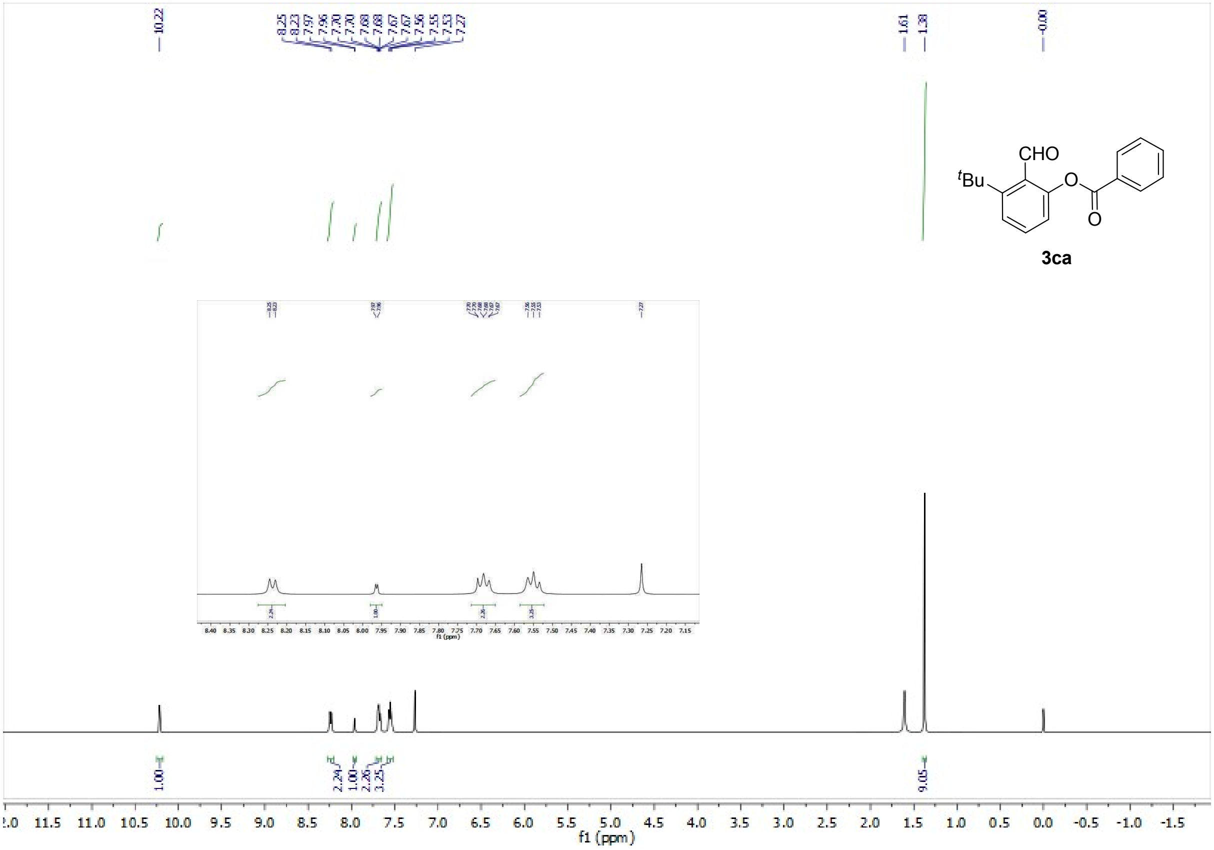
4i

2,2-Dibromo-1-(4-nitrophenyl)ethanone (4i): Following the general procedure, the reaction was carried out by heating a mixture of 4′-nitro-2-bromoacetophenone (**2i**, 486 mg, 2.0 mmol) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in ^{t}AmOH (6.0 mL) at 100 °C for 5 h under air to afford the title compound in 43% yield (Yellow oil, 276 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.25 (m, 4H), 6.62 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.4, 150.7, 135.5, 130.9, 123.8, 38.7. IR ($CHCl_3$, cm^{-1}): 1705, 1602, 1525, 1346, 1262. MS (EI, m/z): 321. Anal. calcd. for $C_8H_5Br_2NO_3$: C, 29.75; H, 1.56; N, 4.34; Found: C, 29.80; H, 1.62; N, 4.09.

6. NMR-spectra



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7.68
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7.55
7.53
7.27
1.61
1.38
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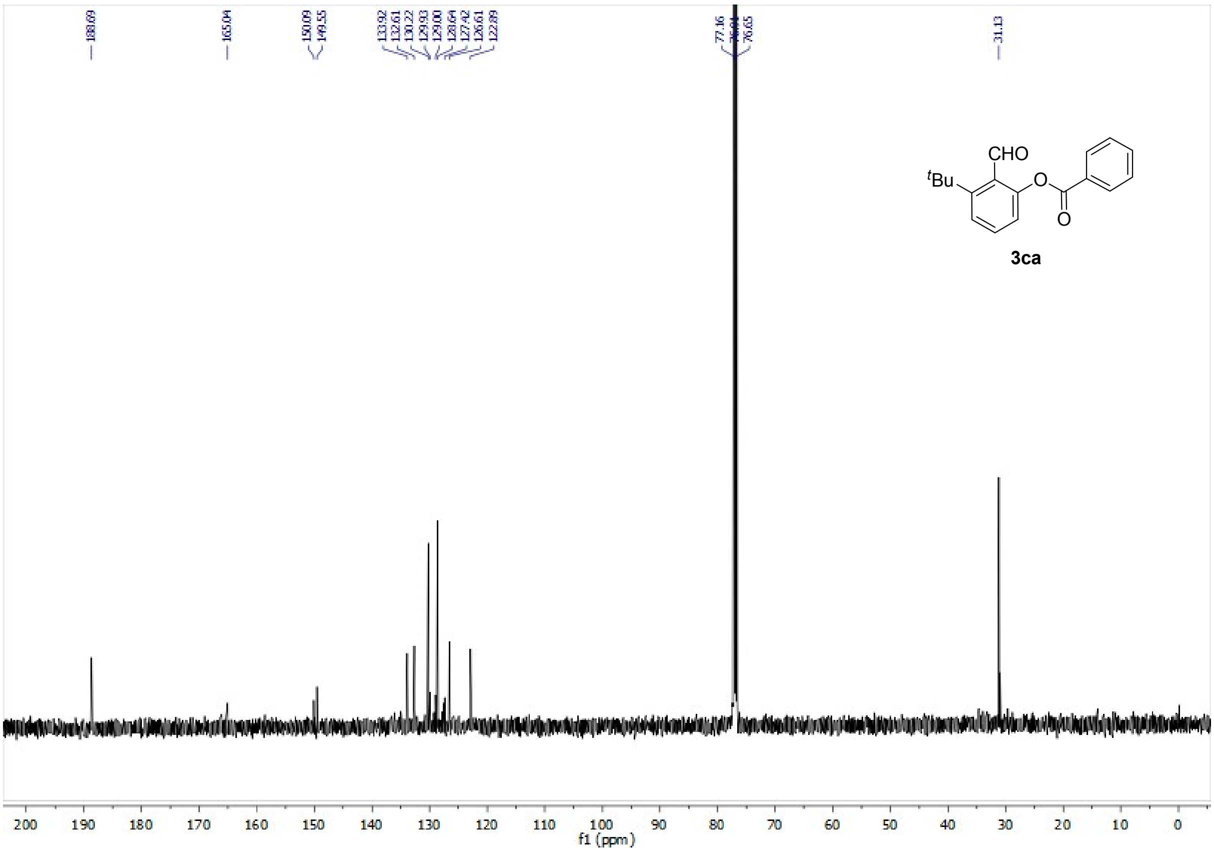
O
O
3ca
1.00
2.24
1.00
2.26
3.25
9.05
f1 (ppm)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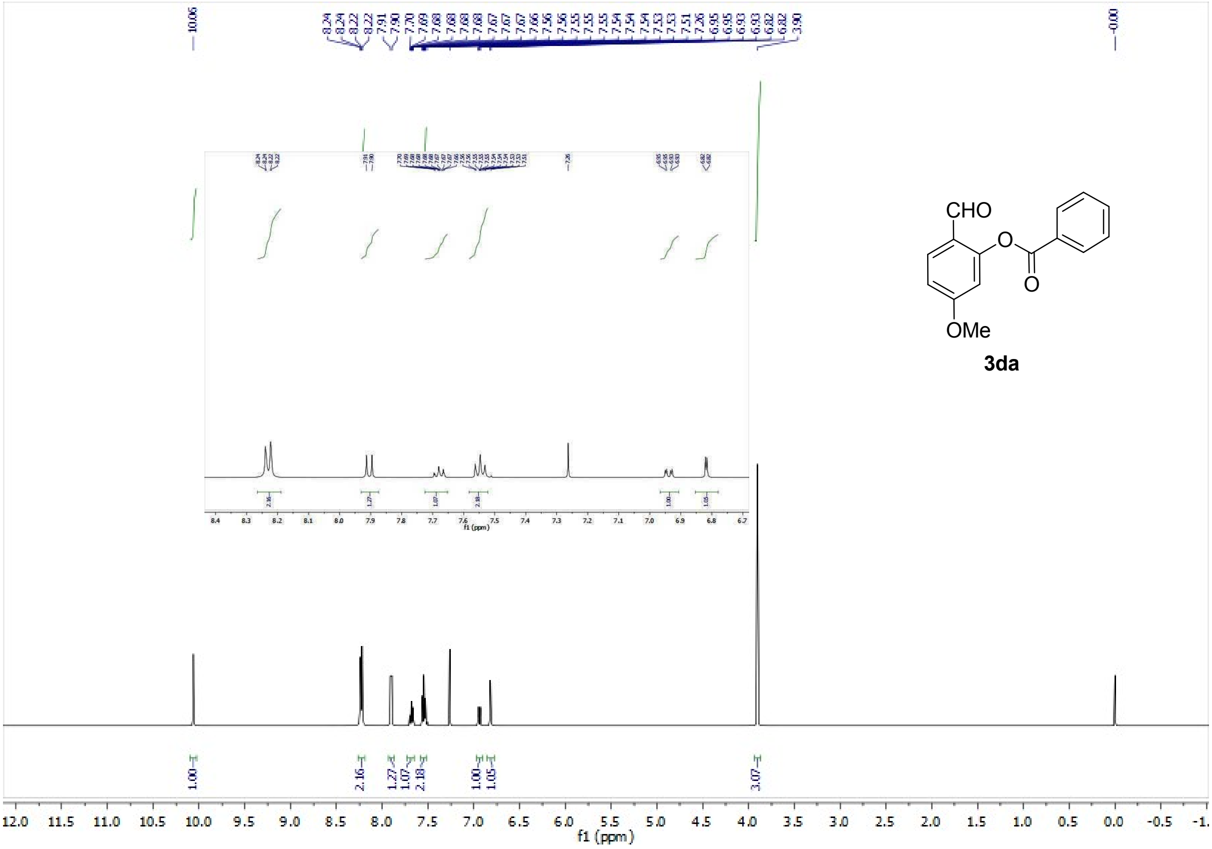
O
3ca
f1 (ppm)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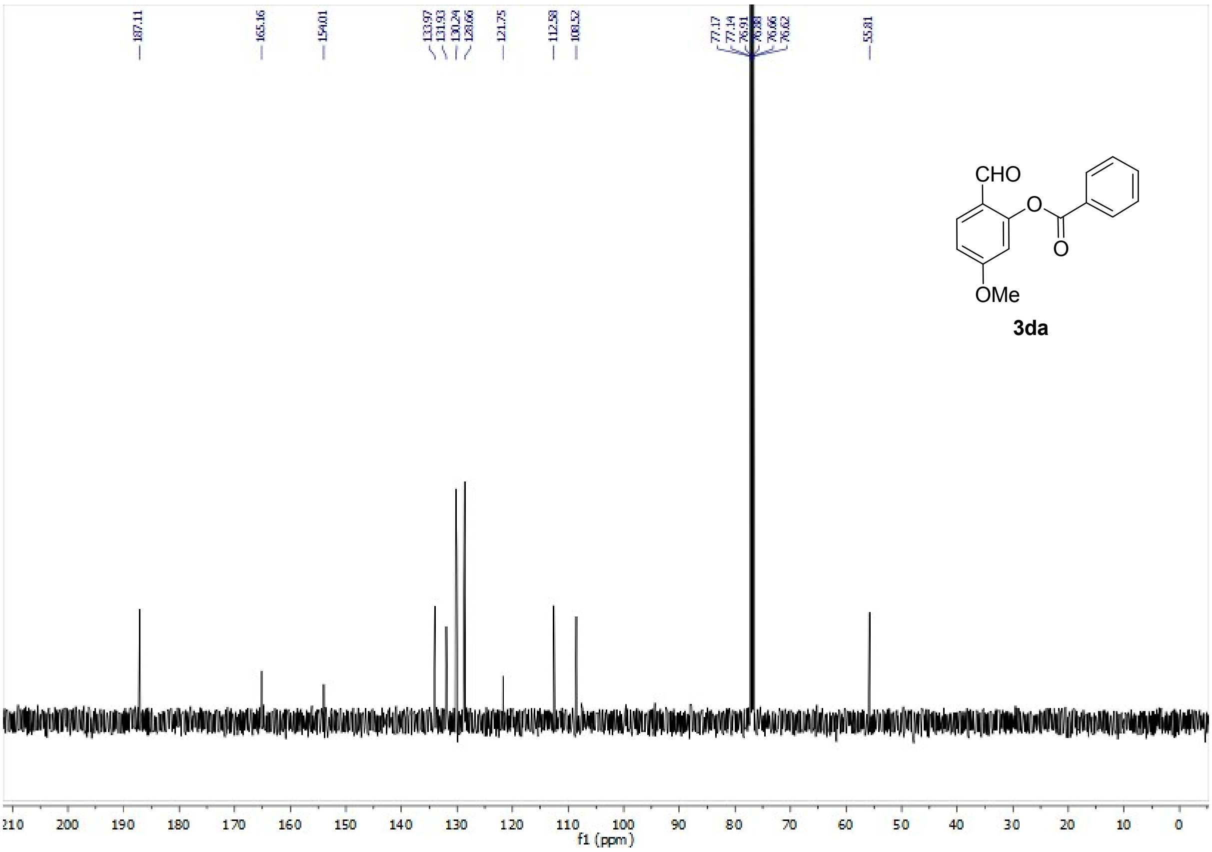
7.67
7.67
7.66
7.56
7.56
7.55
7.55
7.55
7.54
7.54
7.54
7.53
7.53
7.53
7.51
7.26
6.95
6.95
6.93
6.93
6.82
6.82
3.90
0.00
CHO
O
O
OMe
3da
1.00
2.16
1.27
1.07
2.18
1.00
1.05
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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76.88
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CHO
O
O
OMe
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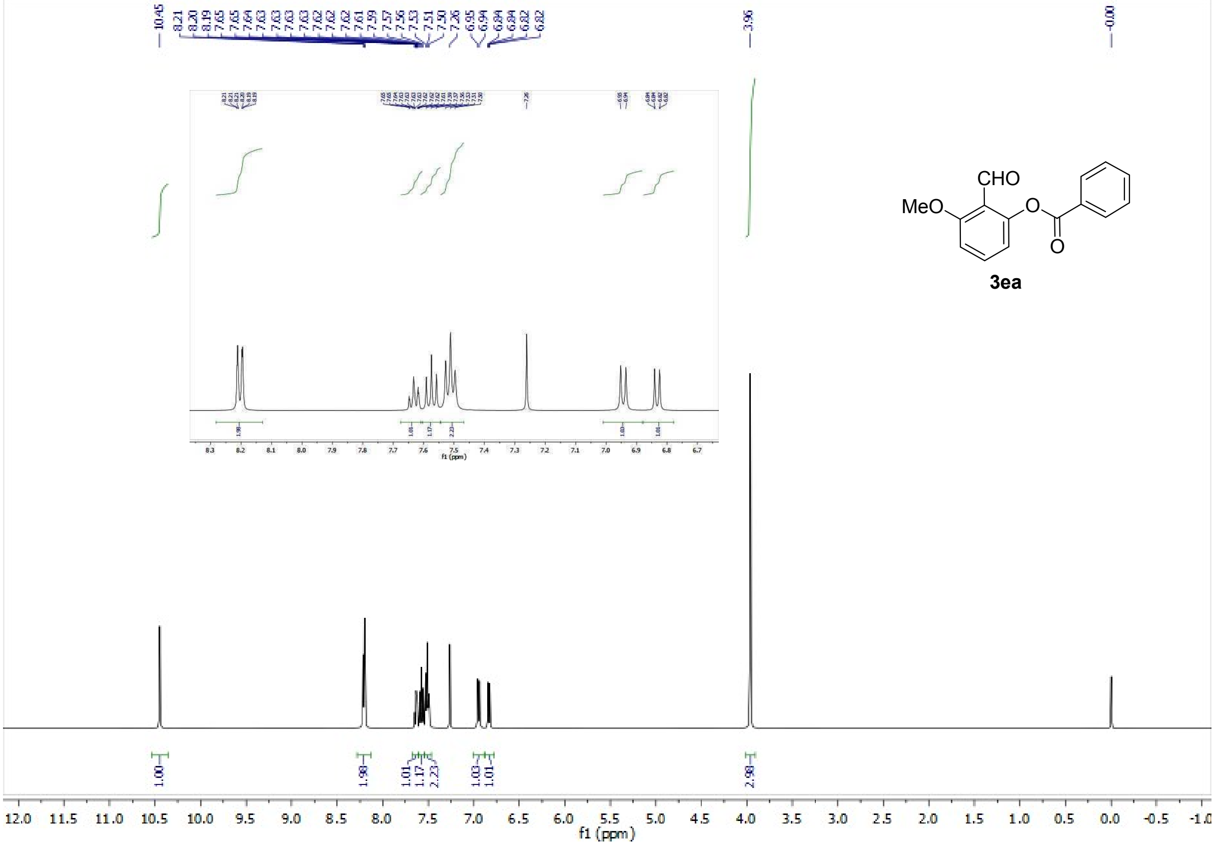
f1 (ppm)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7.57
7.56
7.53
7.51
7.50
7.26
6.95
6.94
6.84
6.84
6.82
6.82
3.96
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CHO
MeO
O
O
3ea
1.00
1.98
1.01
1.17
2.23
1.03
1.01
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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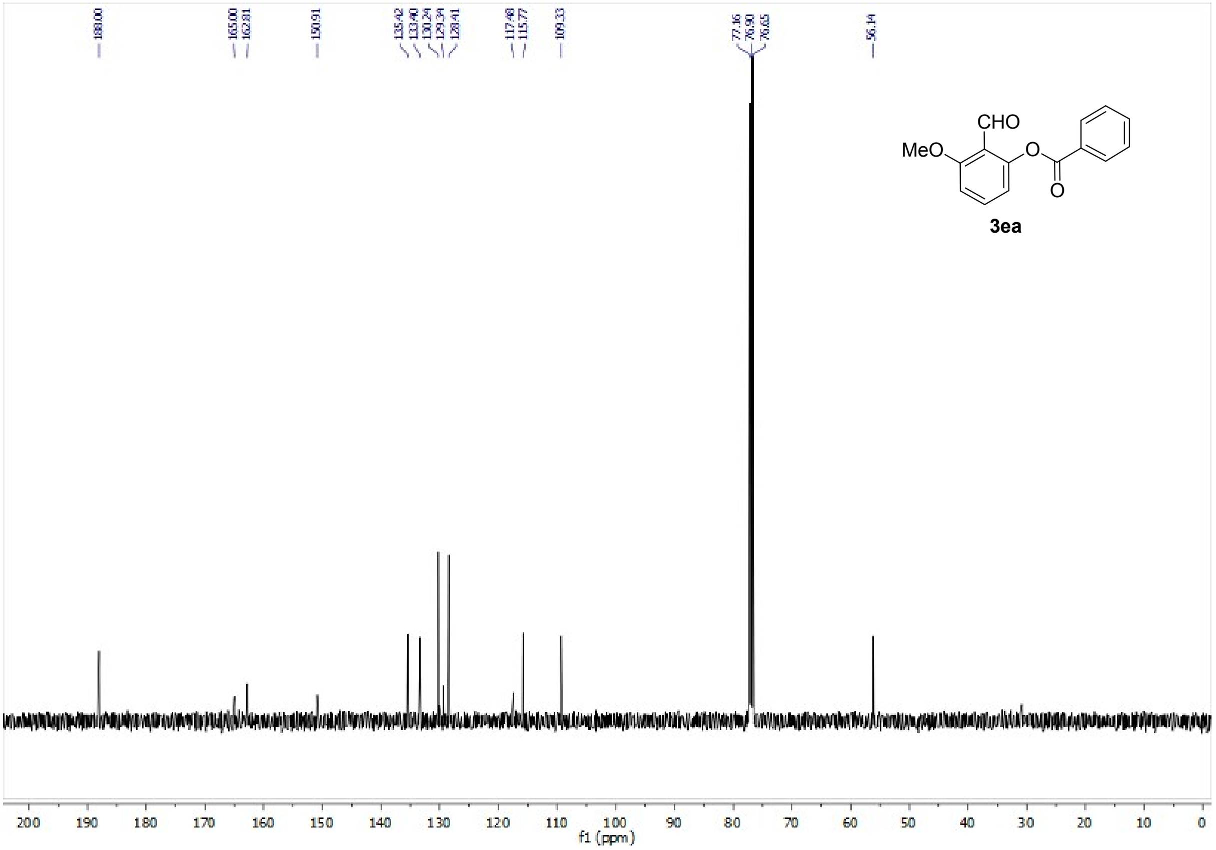
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77.16
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CHO
MeO
O
O
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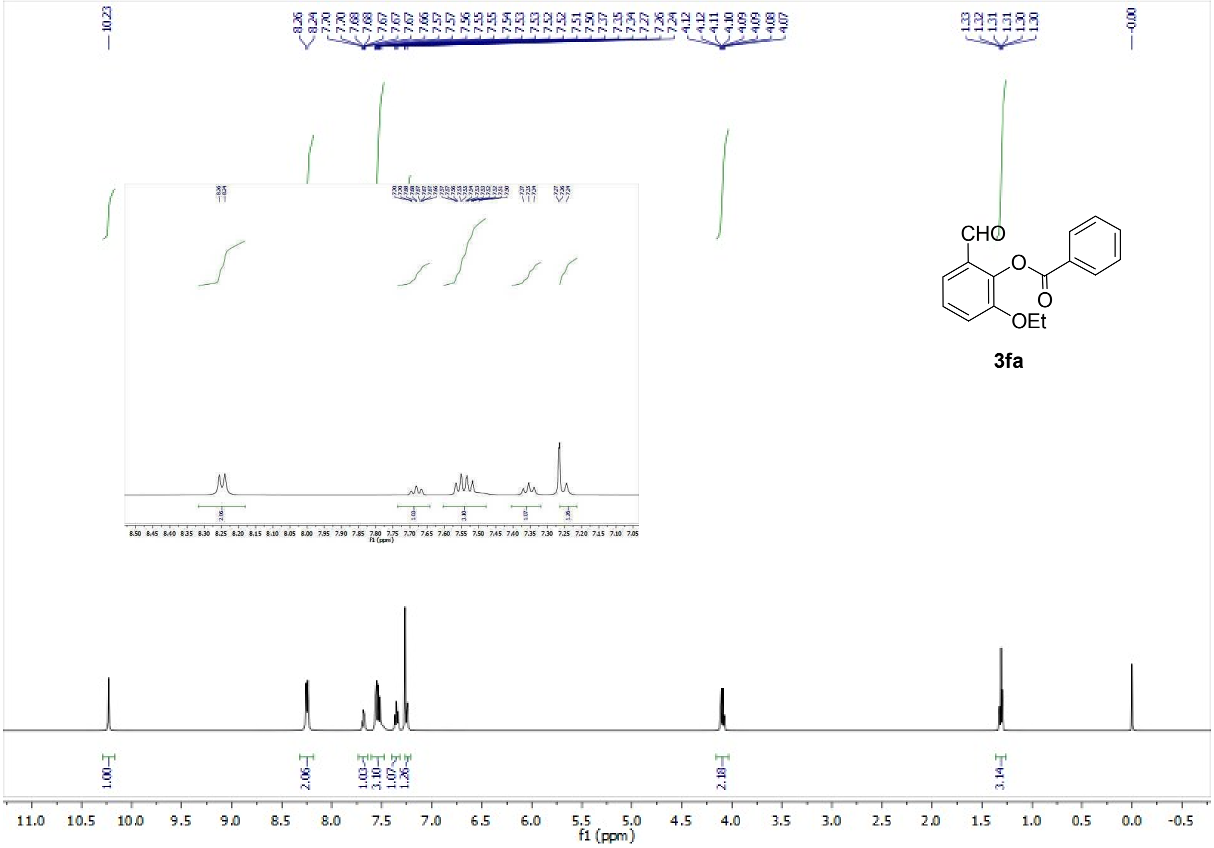
f1 (ppm)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7.53
7.52
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7.34
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7.26
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4.11
4.10
4.09
4.09
4.08
4.07
1.33
1.32
1.31
1.31
1.30
1.30
0.00
CHO
O
O
OEt
3fa
1.00
2.06
1.03
3.10
1.07
1.26
2.18
3.14
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
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2.5
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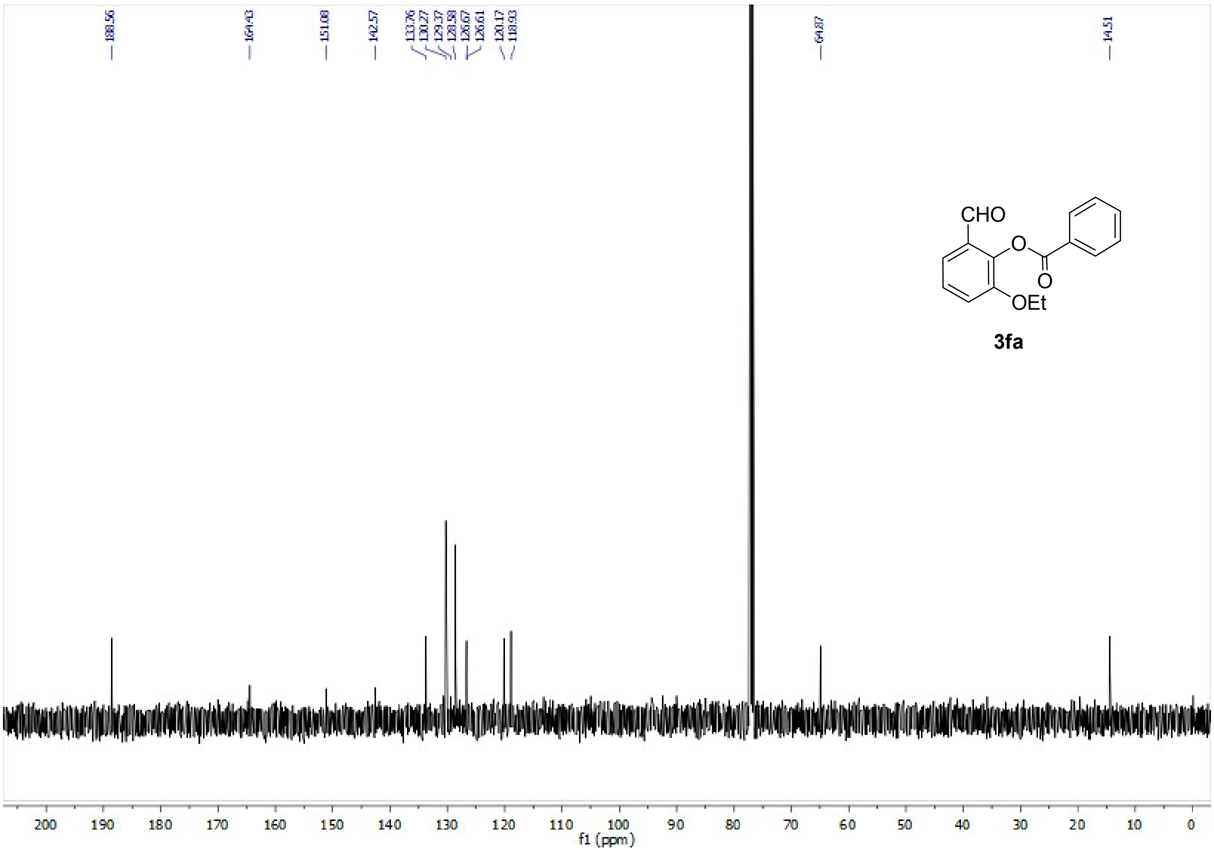
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64.87
14.51
CHO
O
O
OEt
3fa
200
190
180
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130
120
110
100
90
80
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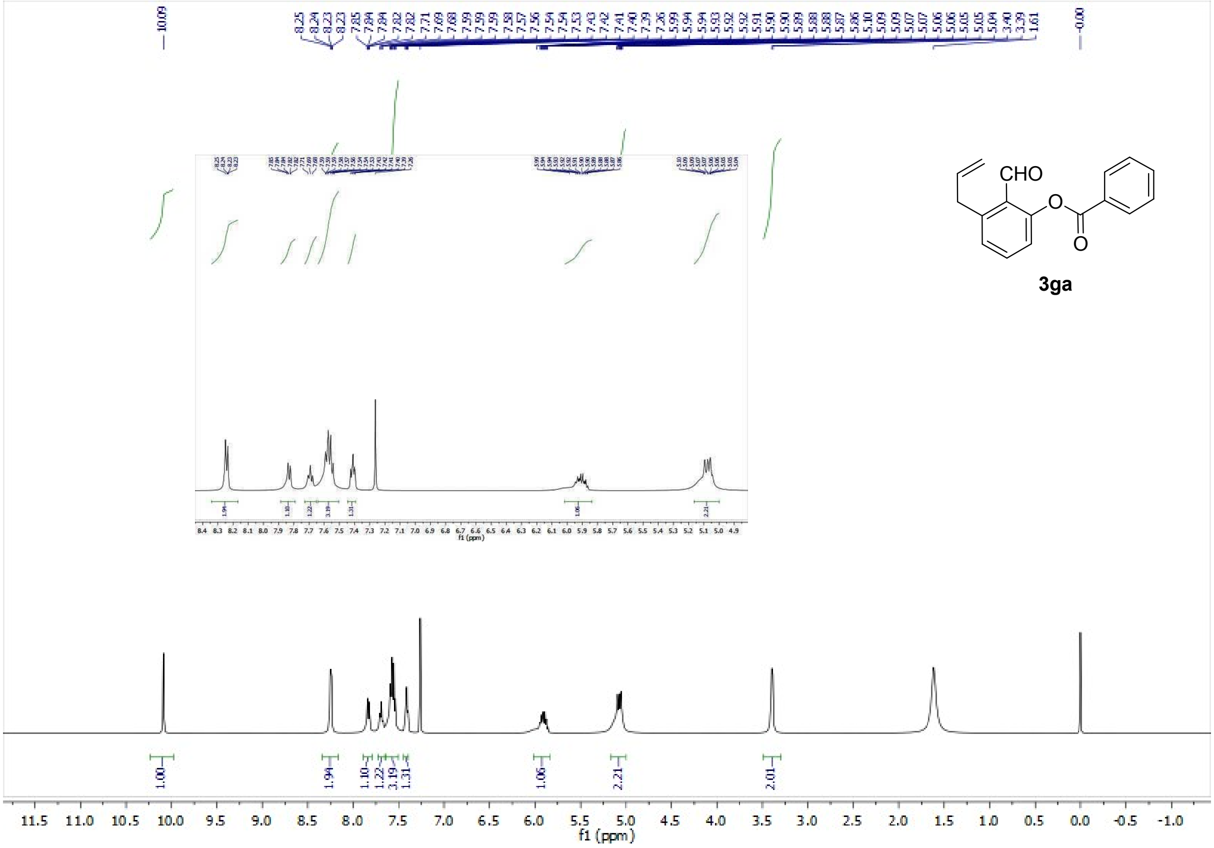
50
40
30
20
10
0
f1 (ppm)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-0.00
CHO
O
O
3ga
1.00
1.94
1.10
1.22
3.19
1.31
1.06
2.21
2.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9
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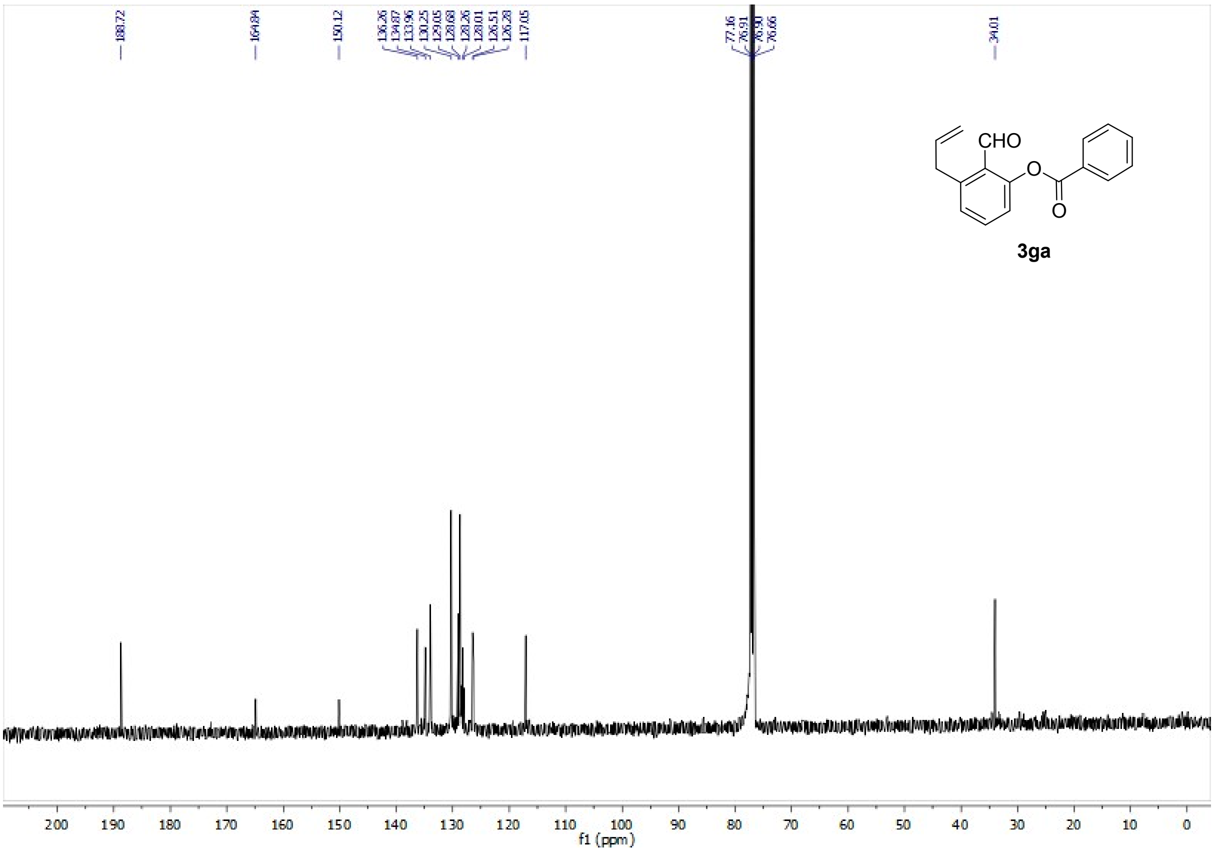
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117.05
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34.01
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O
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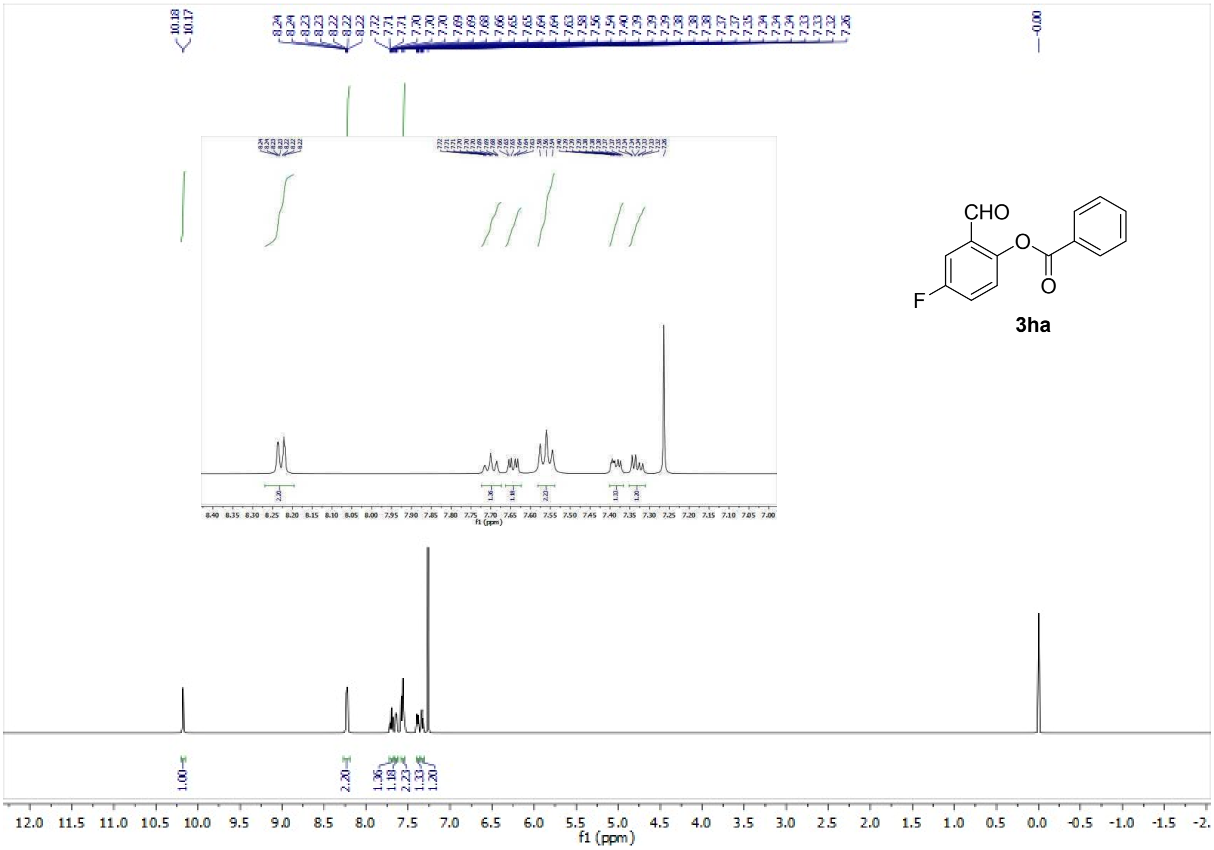
f1 (ppm)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O
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1.20
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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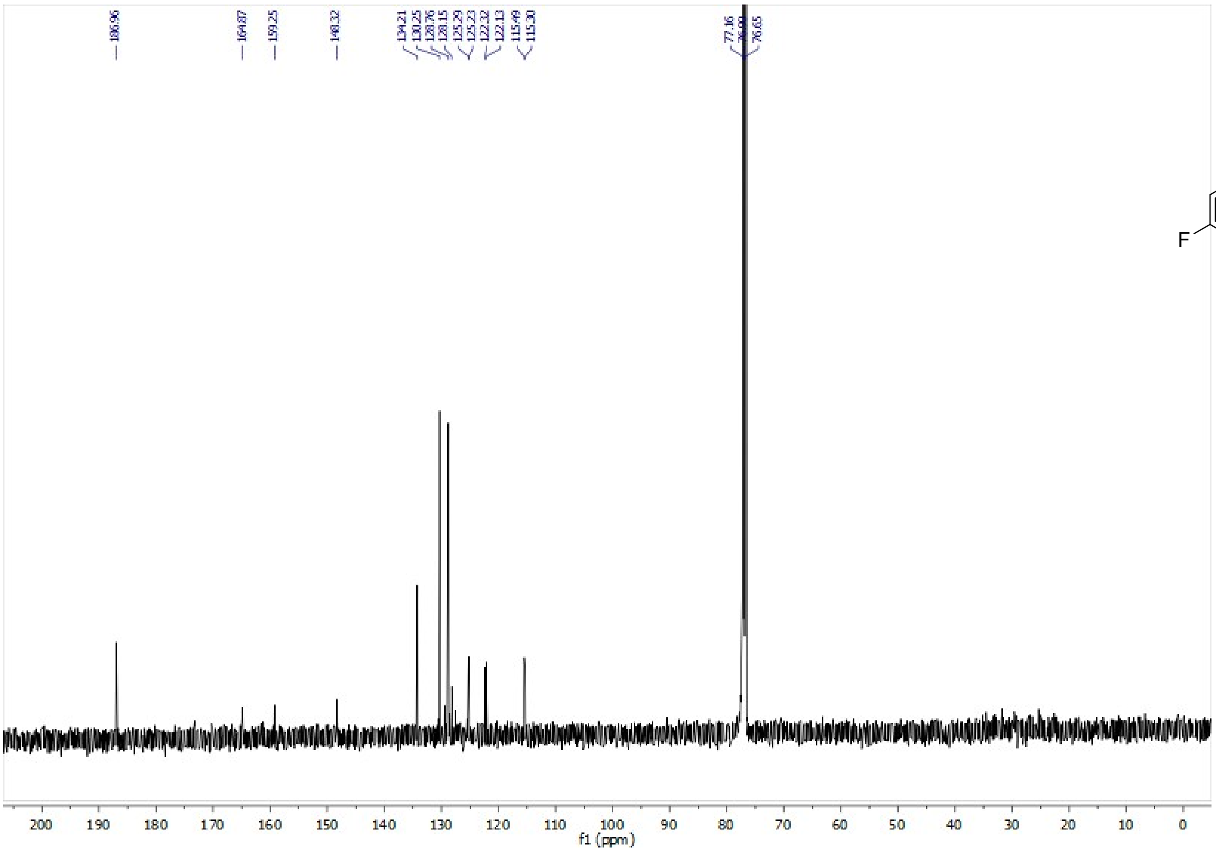
f1 (ppm)

3ha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125.23
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122.13
115.49
115.30
77.16
76.65
200
190
180
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30
20
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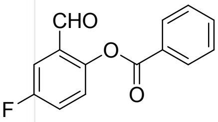
f1 (ppm)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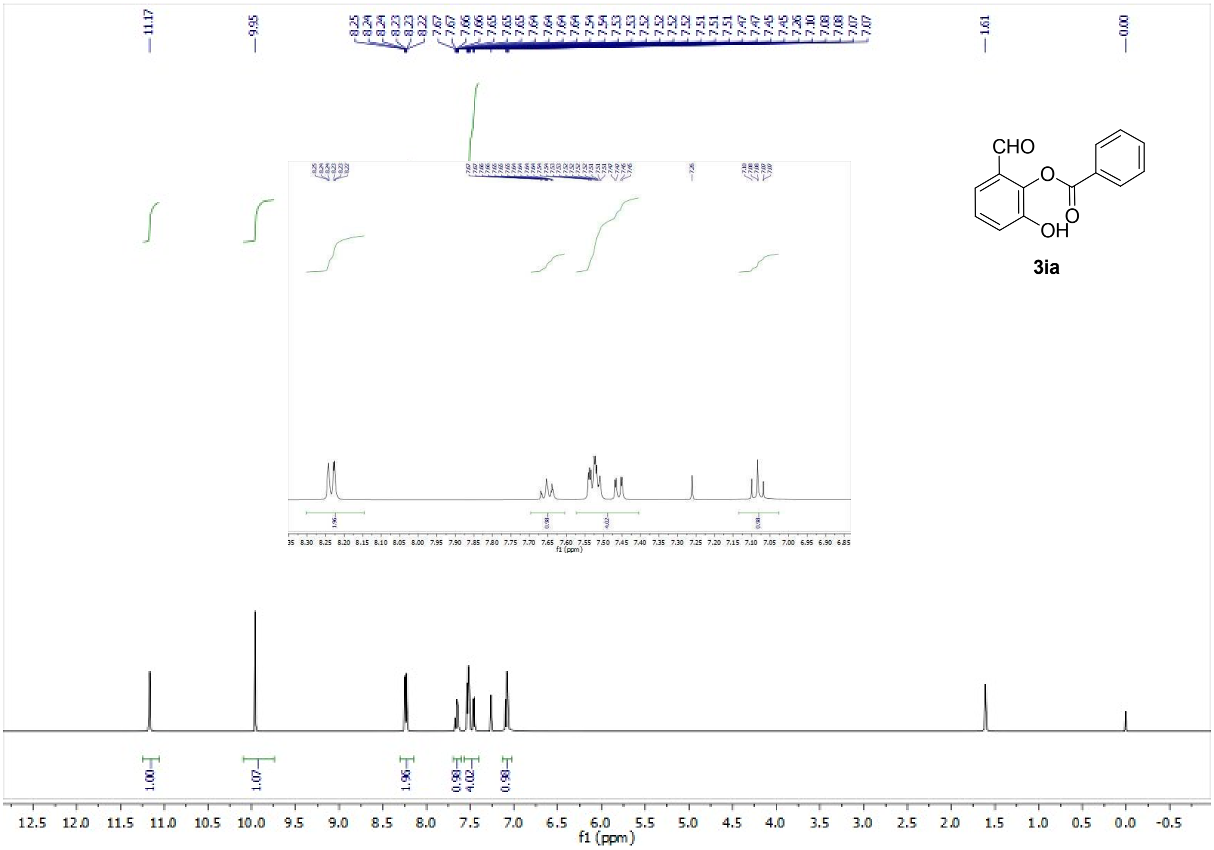
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7.08
7.08
7.07
7.07
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CHO
O
O
OH
3ia
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1.07
1.96
0.98
4.02
0.98
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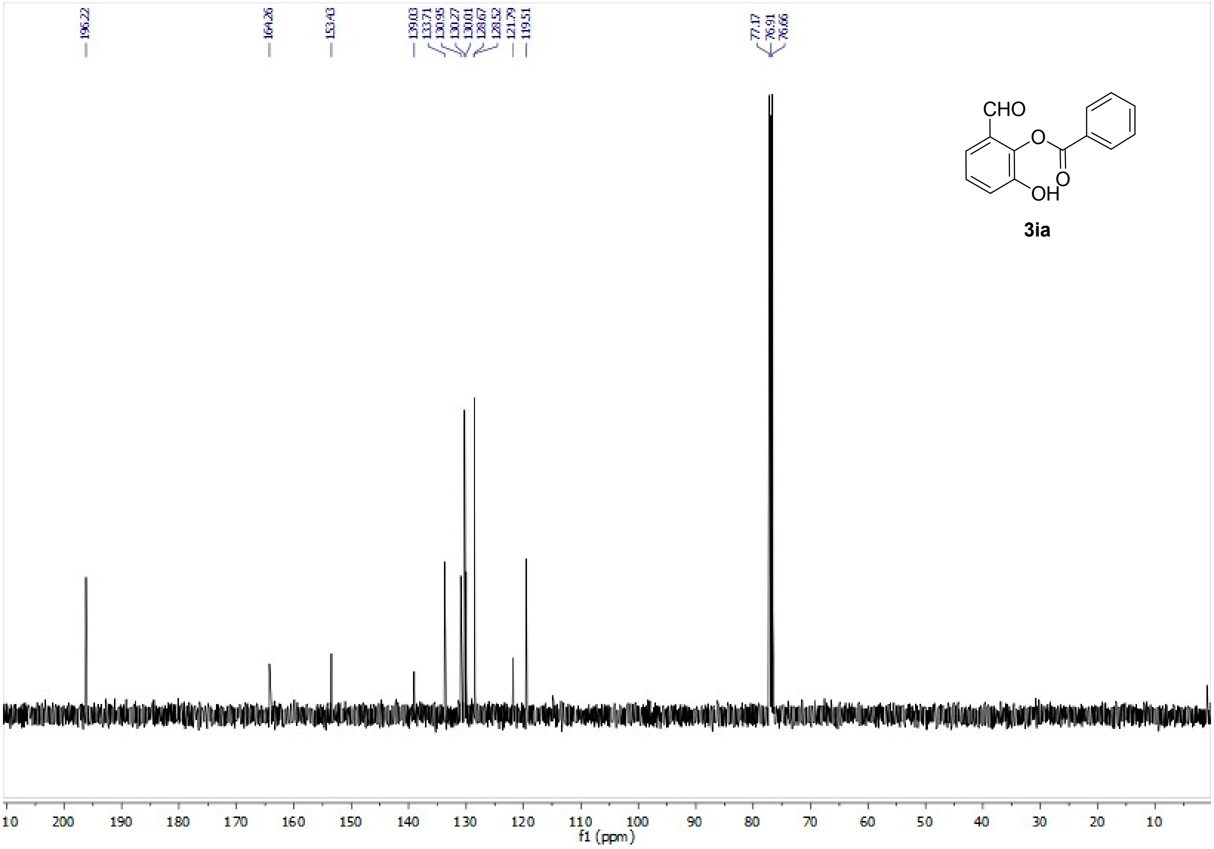
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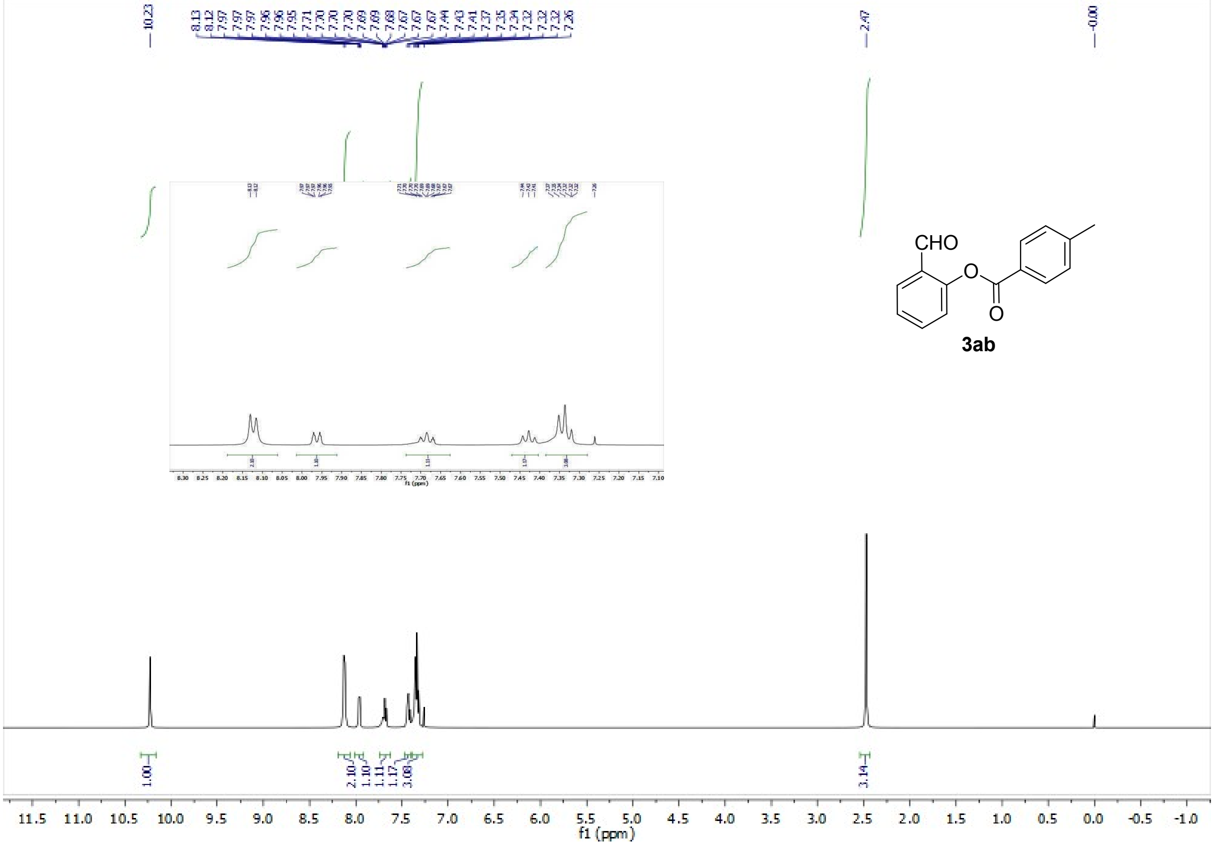
f1 (ppm)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7.41
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7.35
7.34
7.32
7.32
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7.26
2.47
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O
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2.10
1.10
1.11
1.17
3.08
3.14
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 1.0 0.5 0.0 -0.5 -1.0
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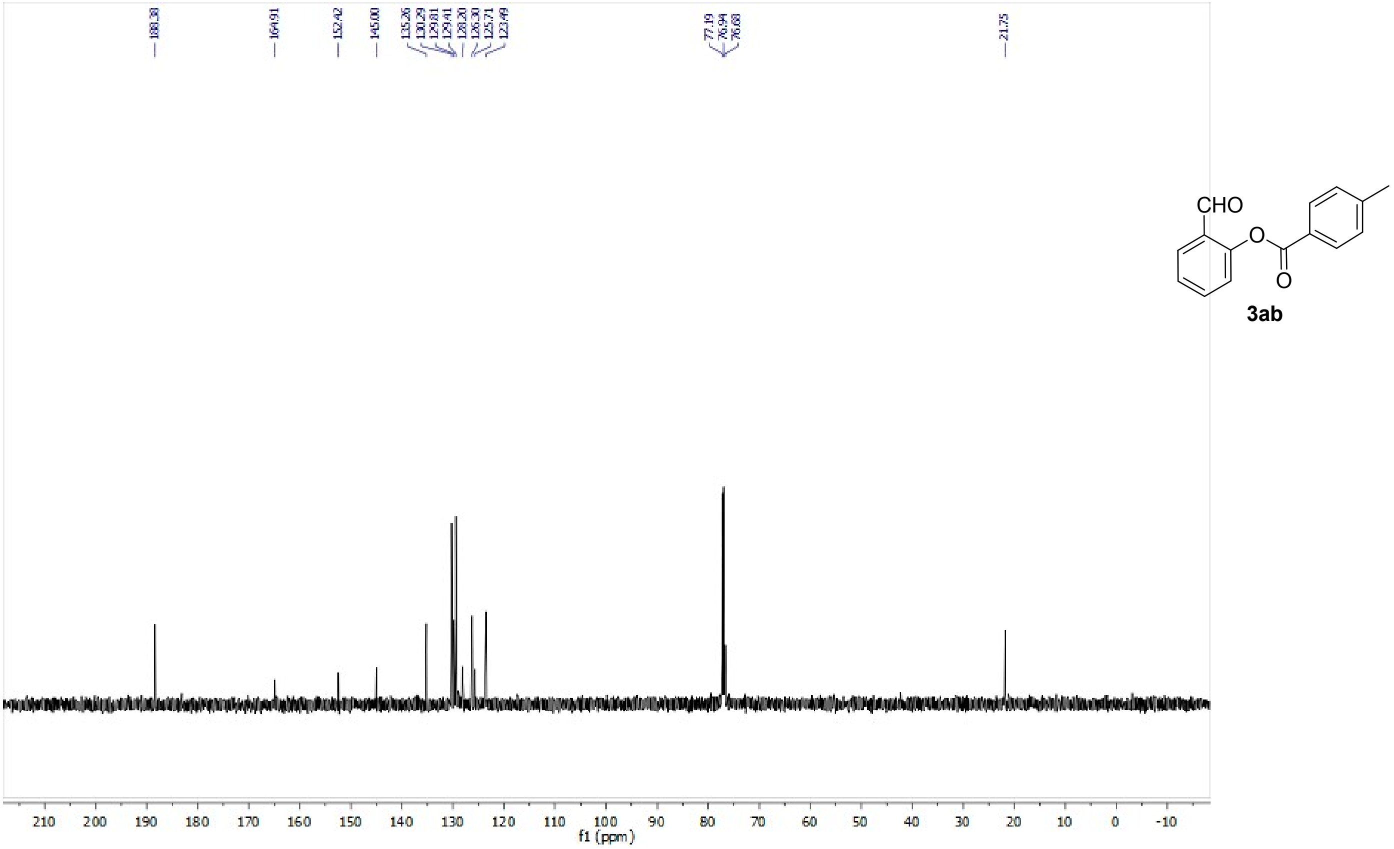
3ab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77.19
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O
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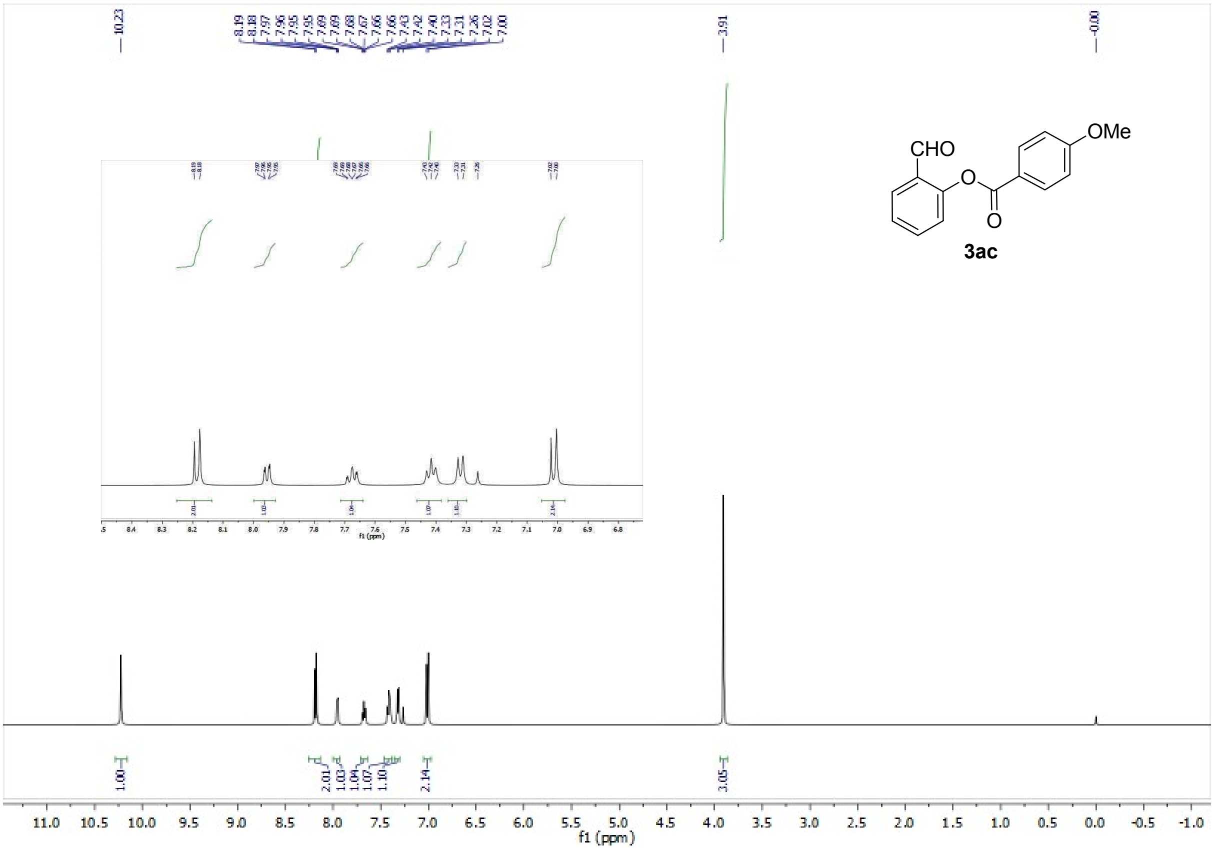
3ab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7.66
7.43
7.42
7.40
7.33
7.31
7.26
7.02
7.00
3.91
-0.00
CHO
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O
OMe
3ac
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2.01
1.03
1.04
1.07
1.10
2.14
3.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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6.0
5.5
5.0
4.5
4.0
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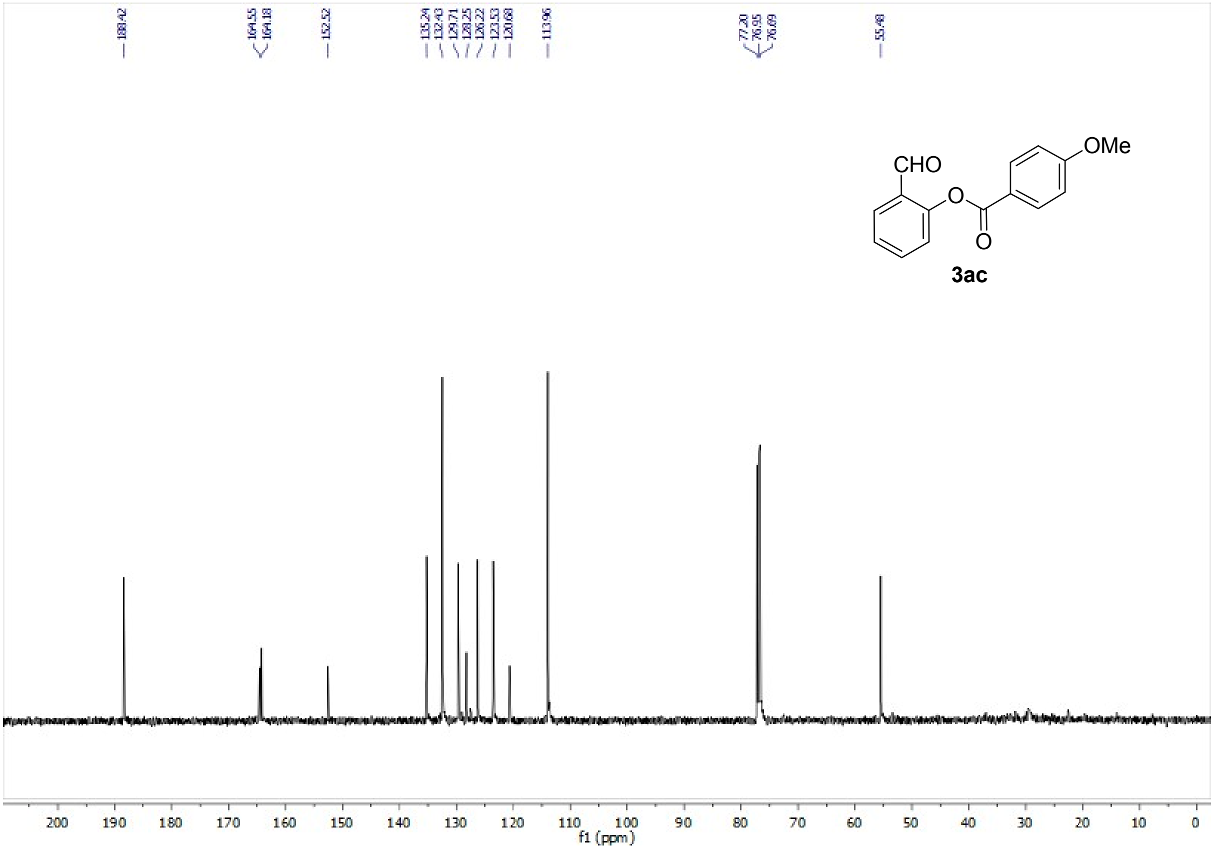
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76.69
55.48
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O
OMe
3ac
200
190
180
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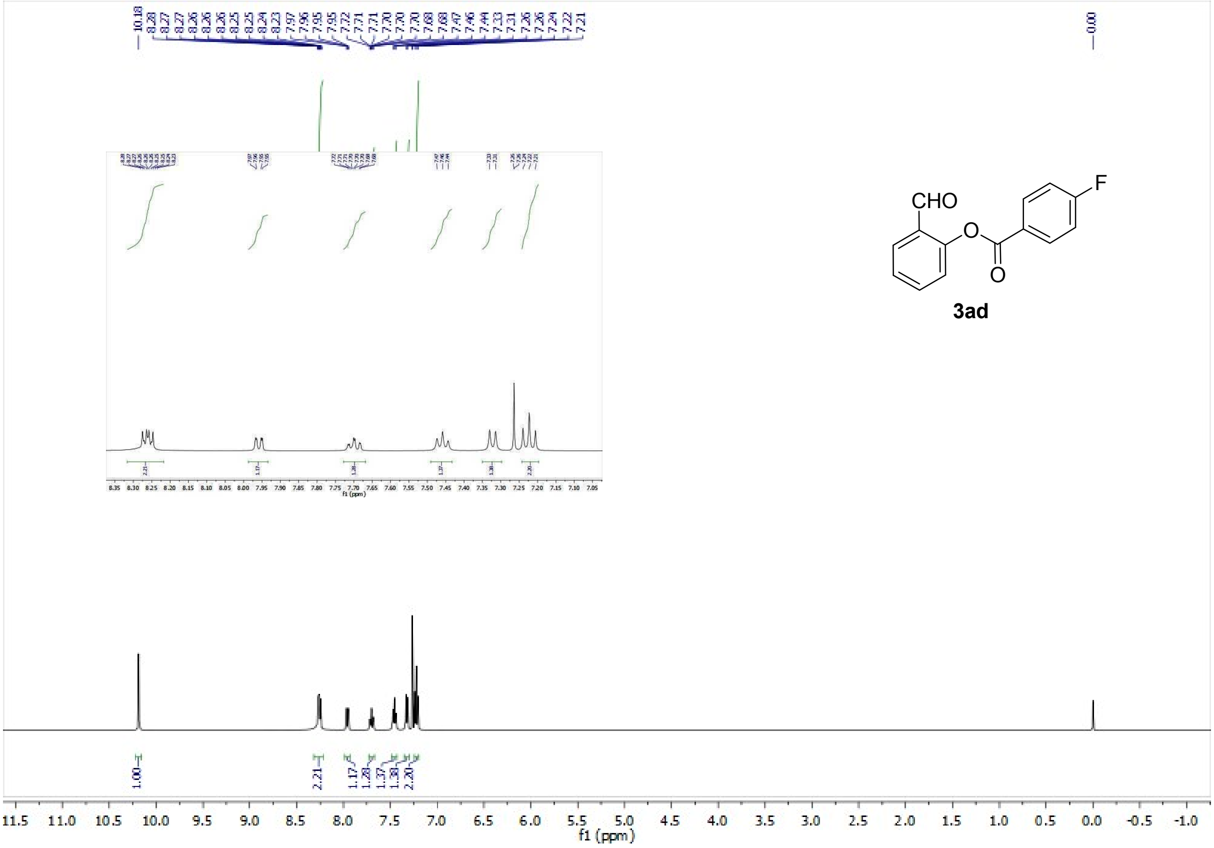
f1 (ppm)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7.68
7.68
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7.26
7.24
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7.21
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4.0
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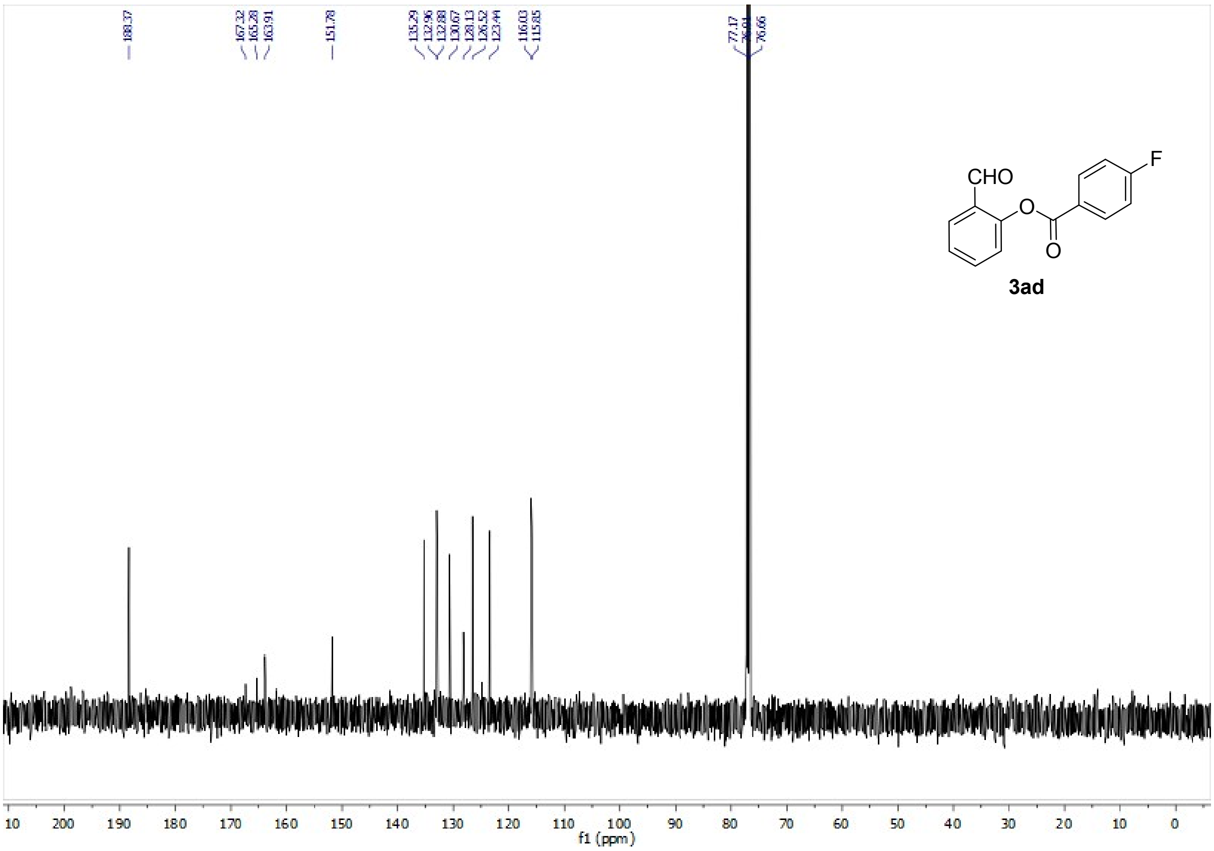
f1 (ppm)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115.85
77.17
76.91
76.66
CHO
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O
F
3ad
10
200
190
180
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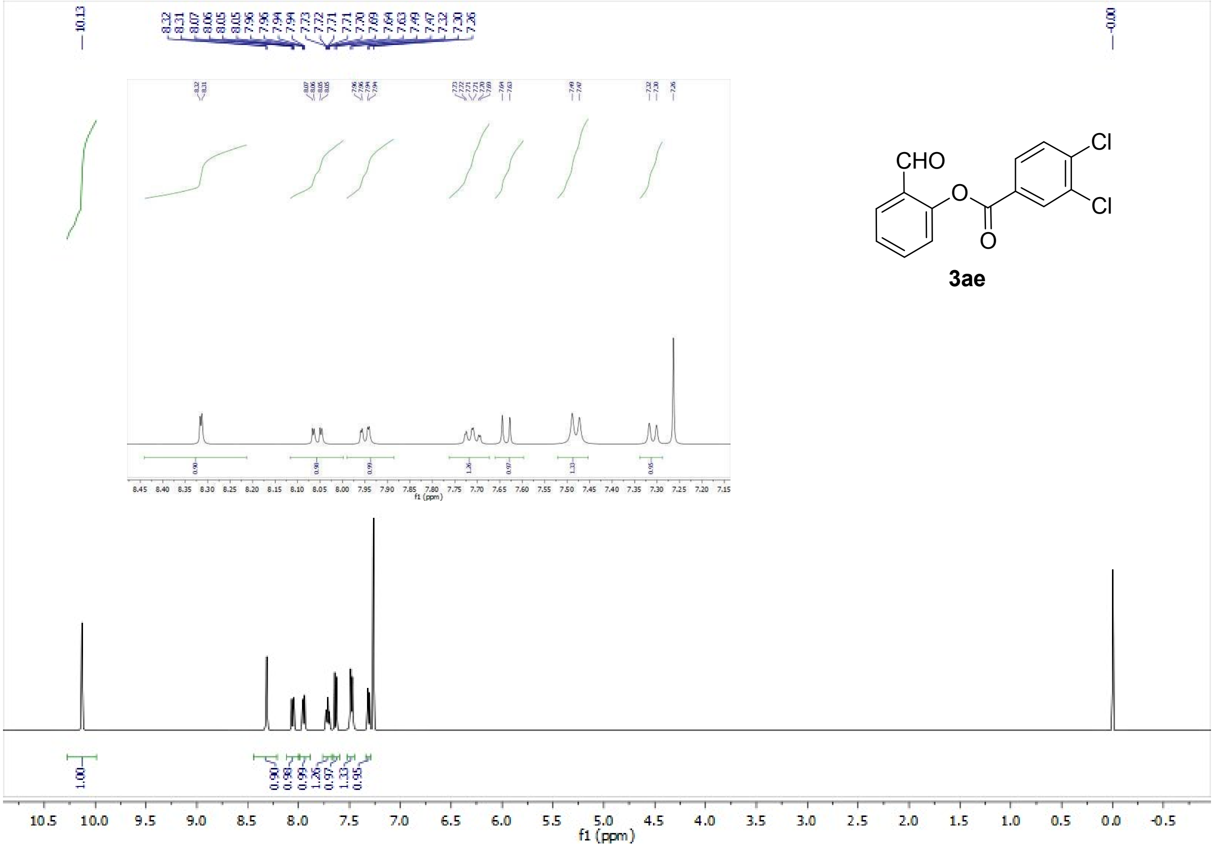
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7.32
7.30
7.26
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CHO
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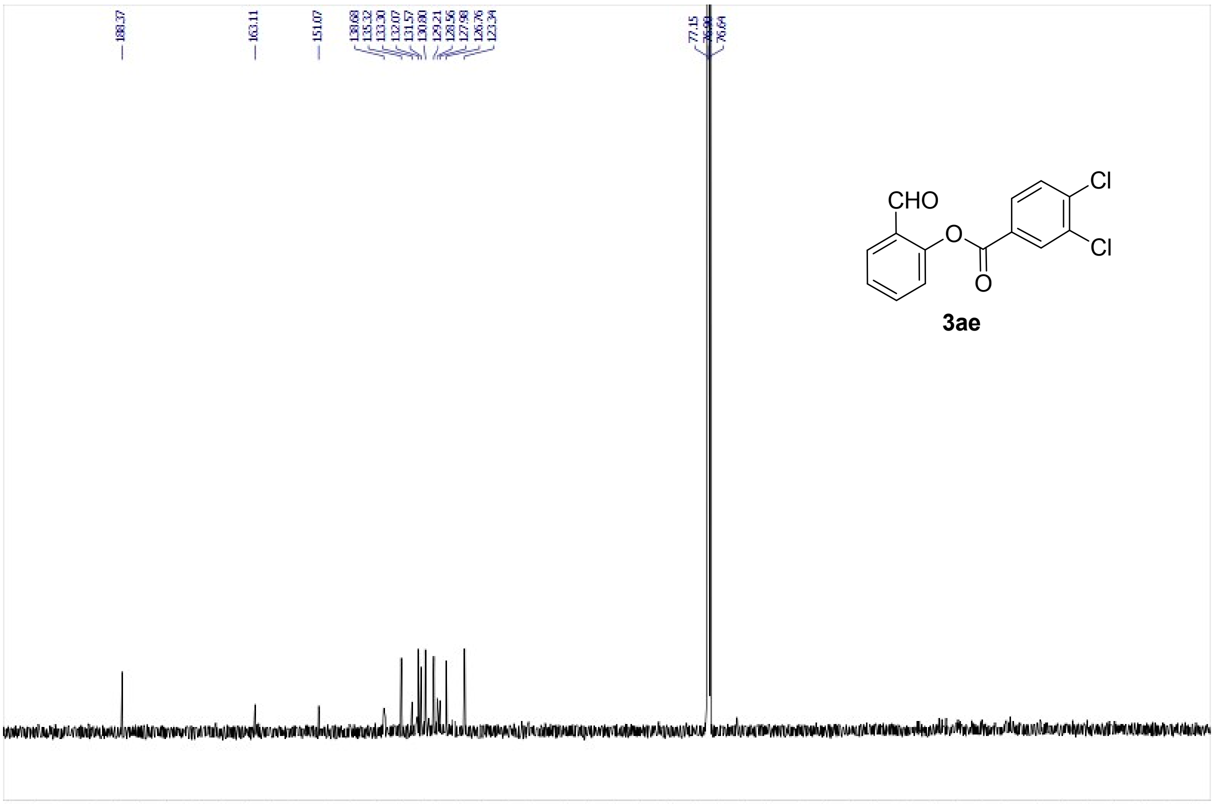
f1 (ppm)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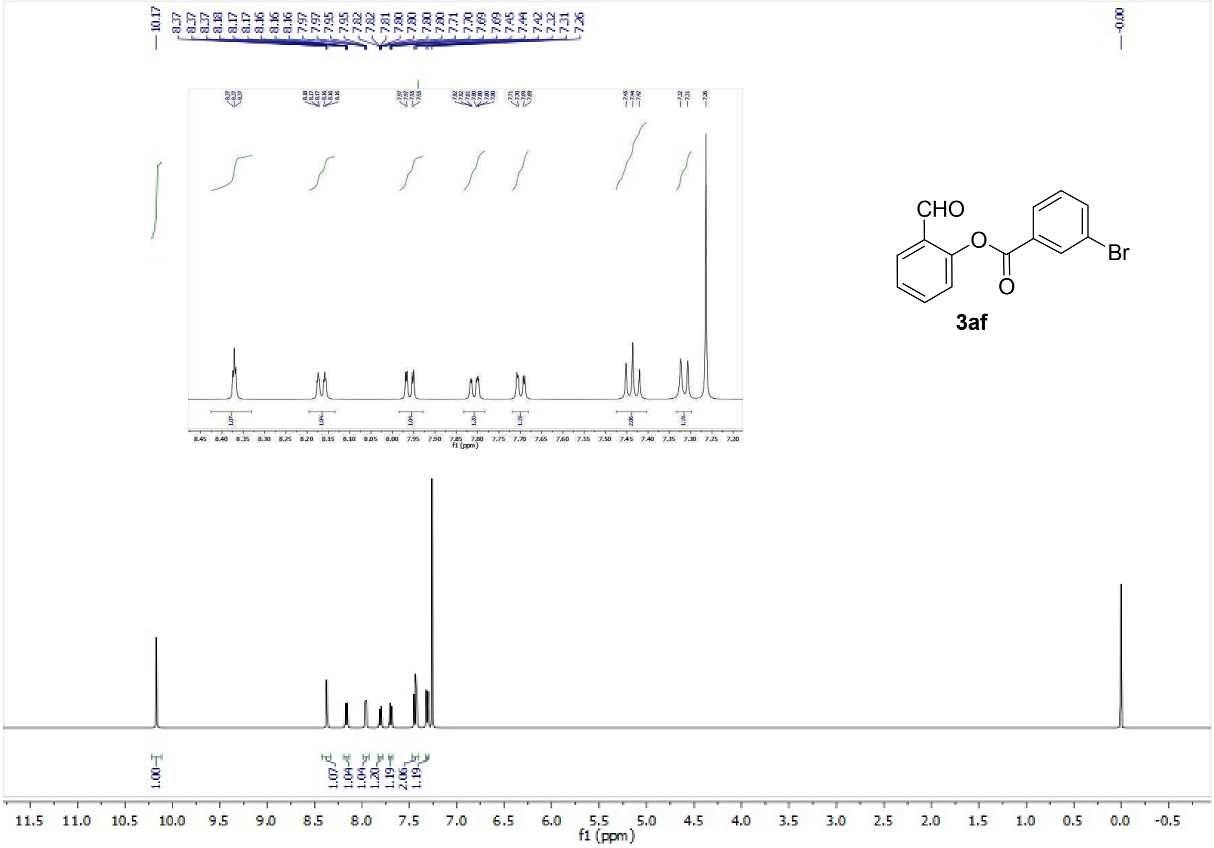
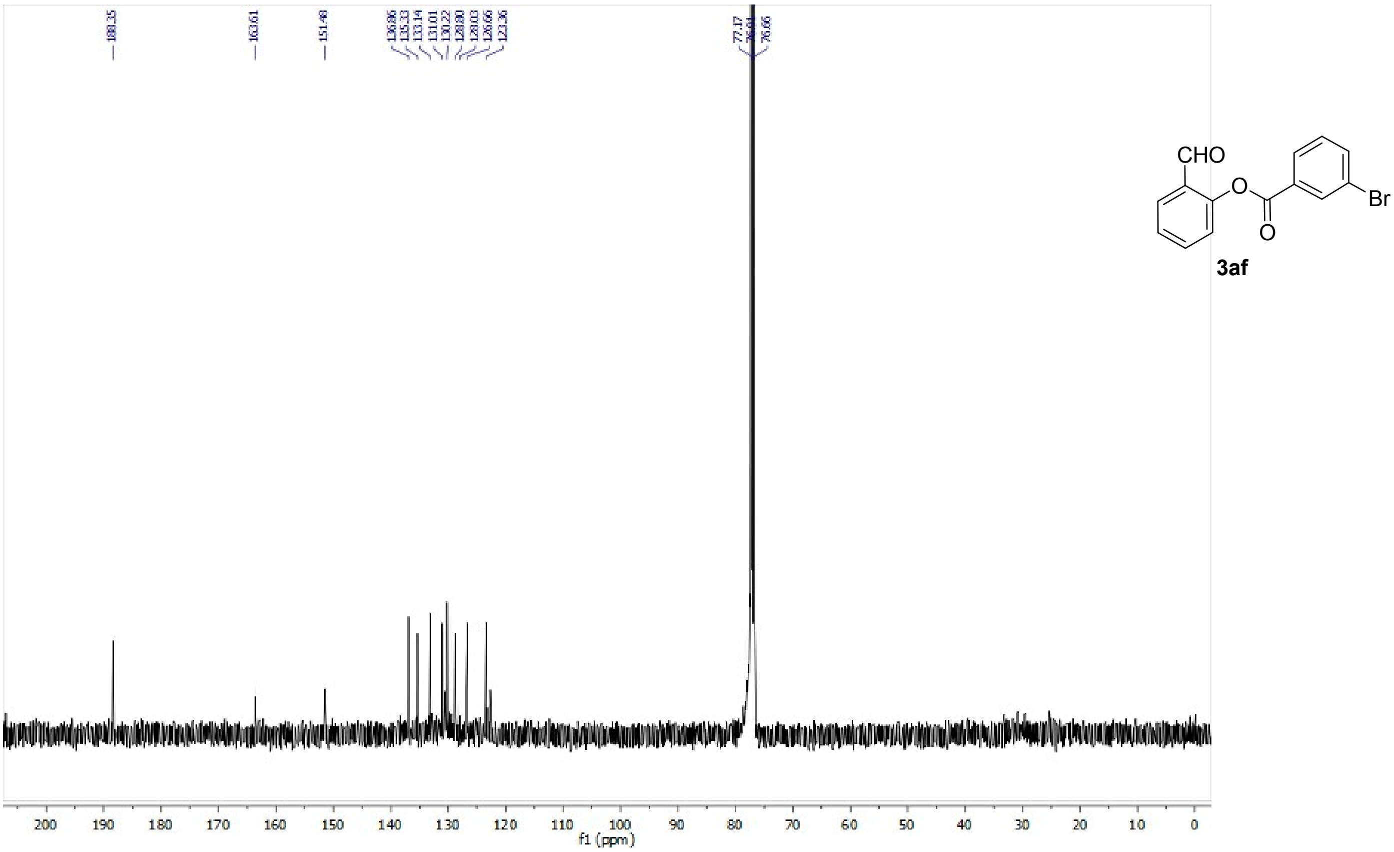
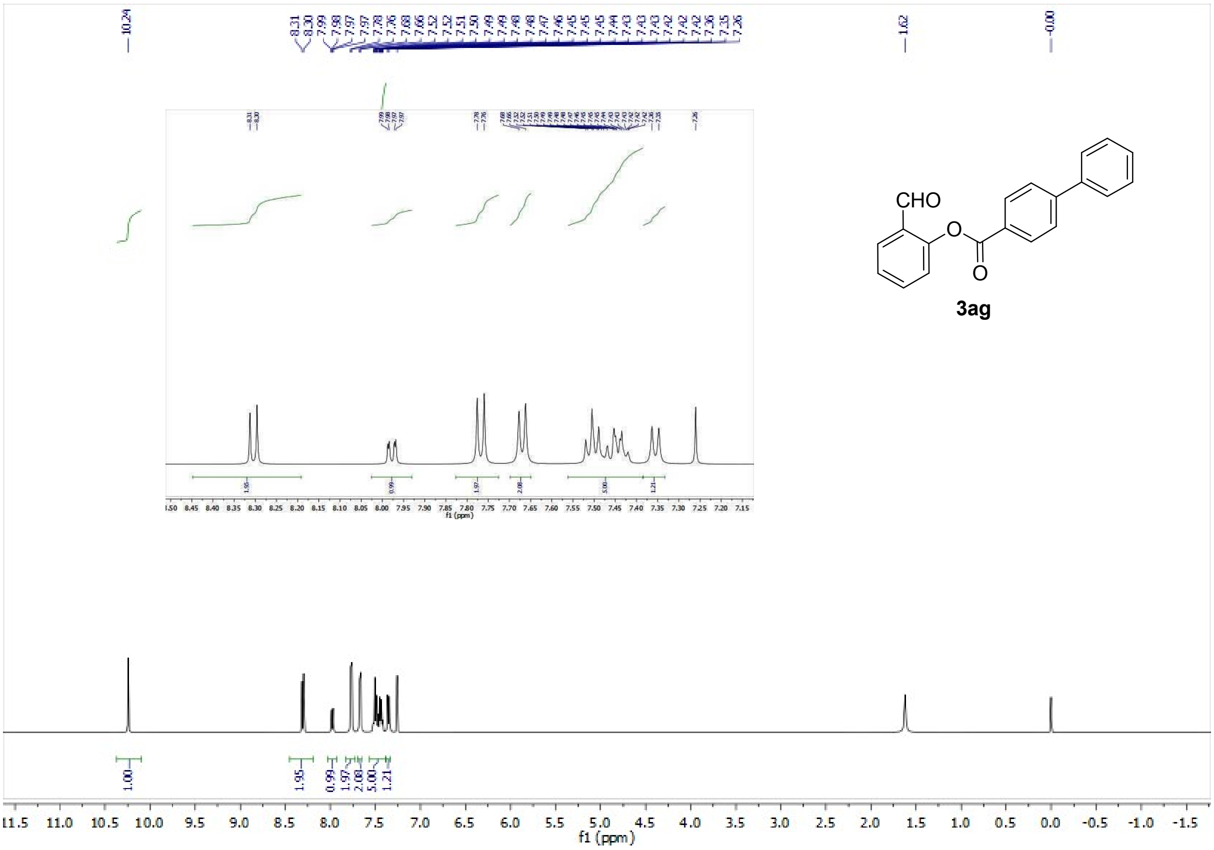
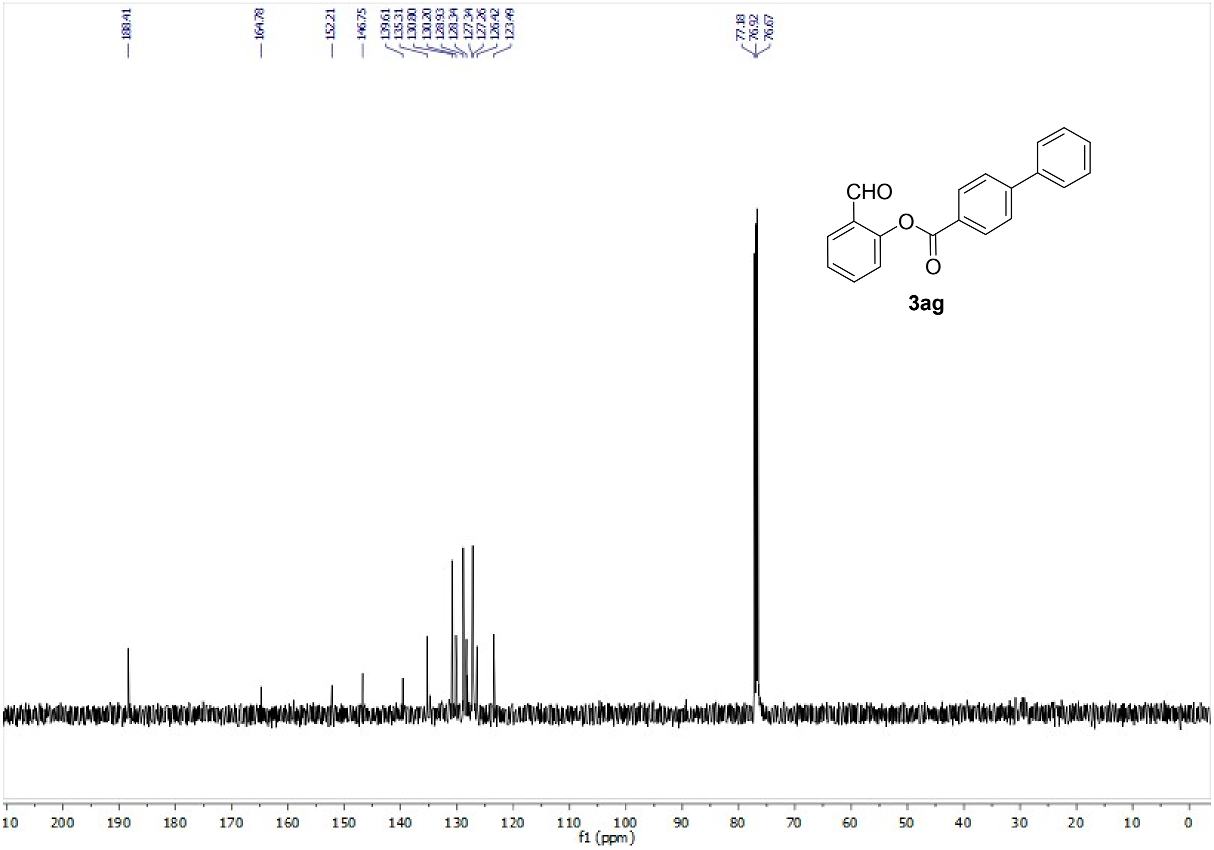
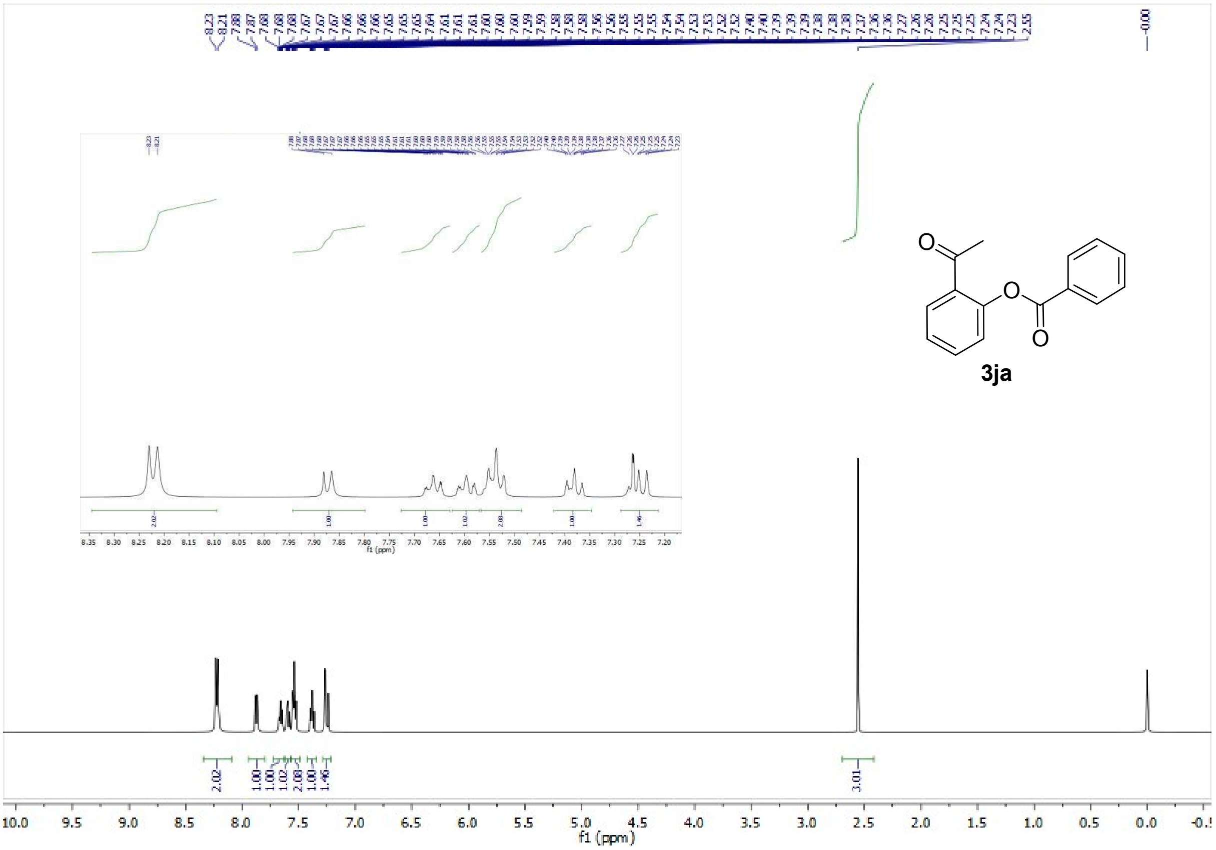
126.76
123.34
77.15
76.90
76.64
CHO
O
O
Cl
Cl
3ae
f1 (ppm)


10.17
8.37
8.37
8.37
8.18
8.17
8.17
8.16
8.16
8.16
7.97
7.97
7.95
7.95
7.82
7.82
7.81
7.80
7.80
7.80
7.80
7.71
7.70
7.69
7.69
7.45
7.44
7.42
7.32
7.31
7.26
0.00
CHO
O
O
Br
3af
1.00
1.07
1.04
1.04
1.20
1.19
2.06
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 1.0 0.5 0.0 -0.5
f1 (ppm)

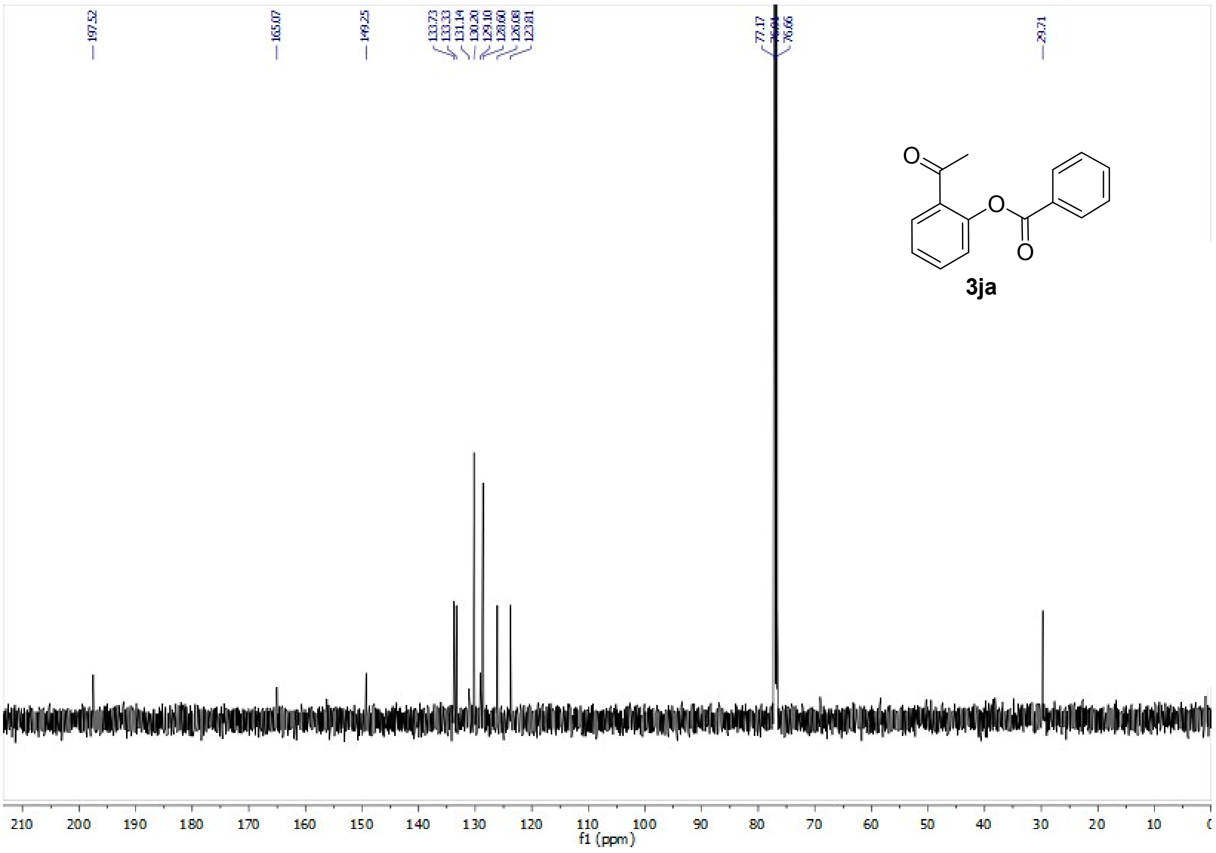

188.35
163.61
151.48
136.86
135.33
133.14
131.01
130.22
128.80
128.03
126.66
123.36
77.17
76.91
76.66
CHO
O
O
Br
3af
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.24
8.31
8.30
7.99
7.98
7.97
7.97
7.78
7.76
7.68
7.66
7.52
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.36
7.35
7.26
1.62
0.00
1.00
1.95
0.99
1.97
2.08
5.00
1.21
CHO
O
O
3ag
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 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

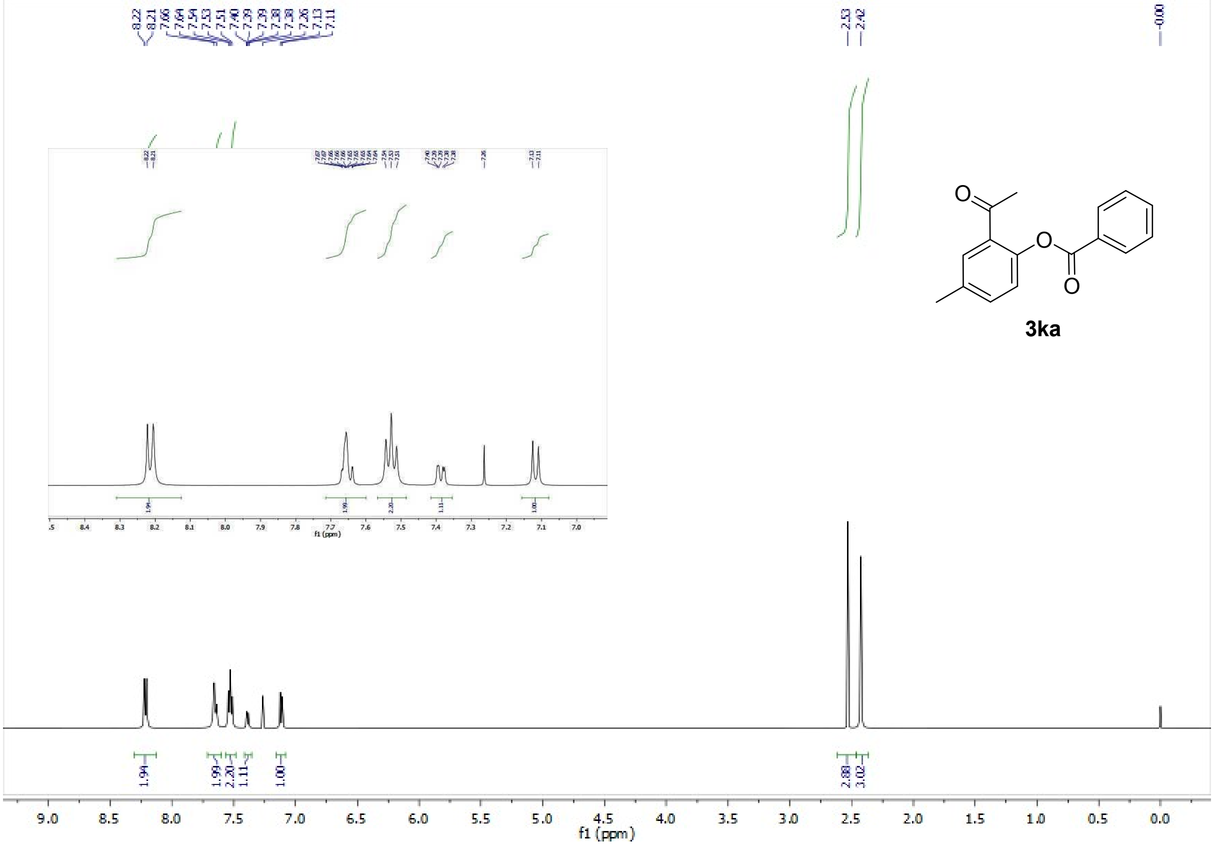

188.41
164.78
152.21
146.75
139.61
135.31
130.80
130.20
128.93
128.34
127.34
127.26
126.42
123.49
77.18
76.92
76.67
CHO
O
O
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

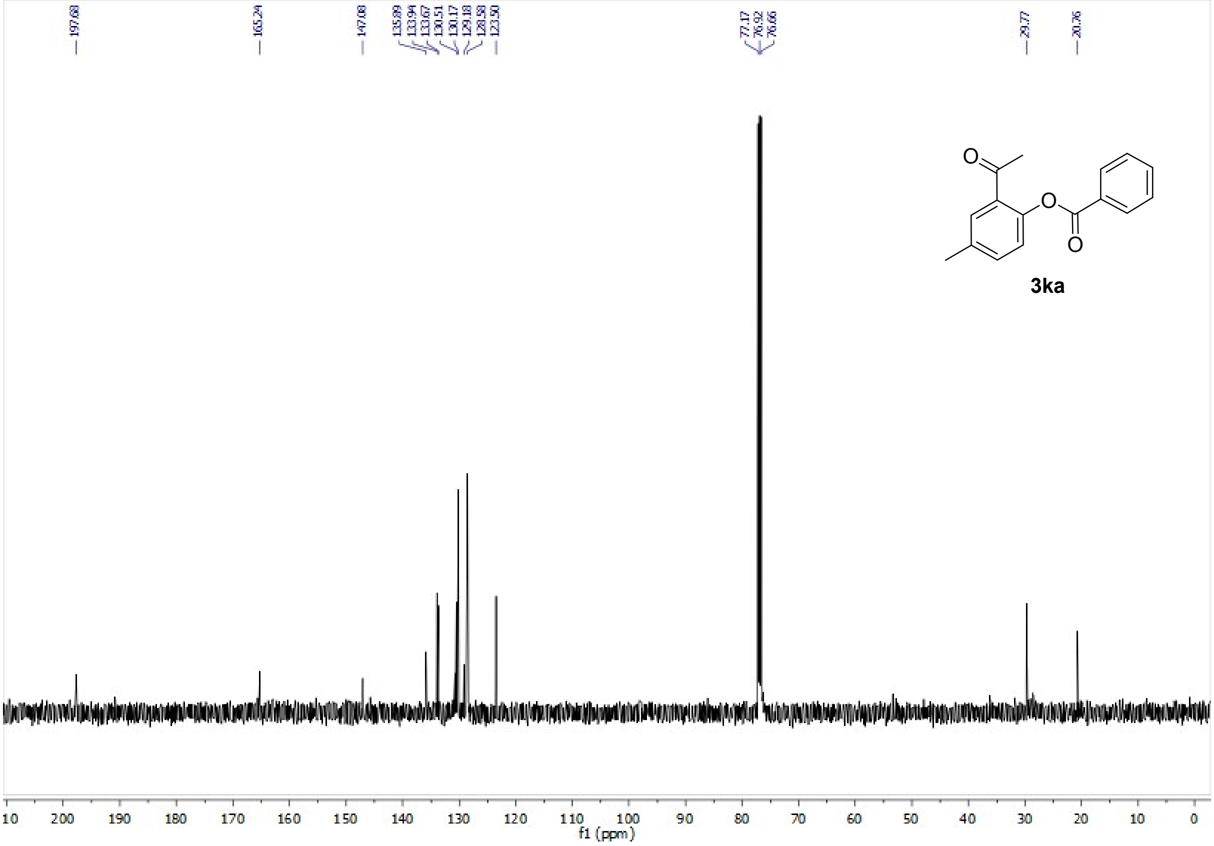

8.23
8.21
7.88
7.87
7.68
7.55
7.40
7.37
7.27
7.23
2.55
0.00
2.02
1.00
1.00
1.02
2.08
1.00
1.46
3.01
O
O
O
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

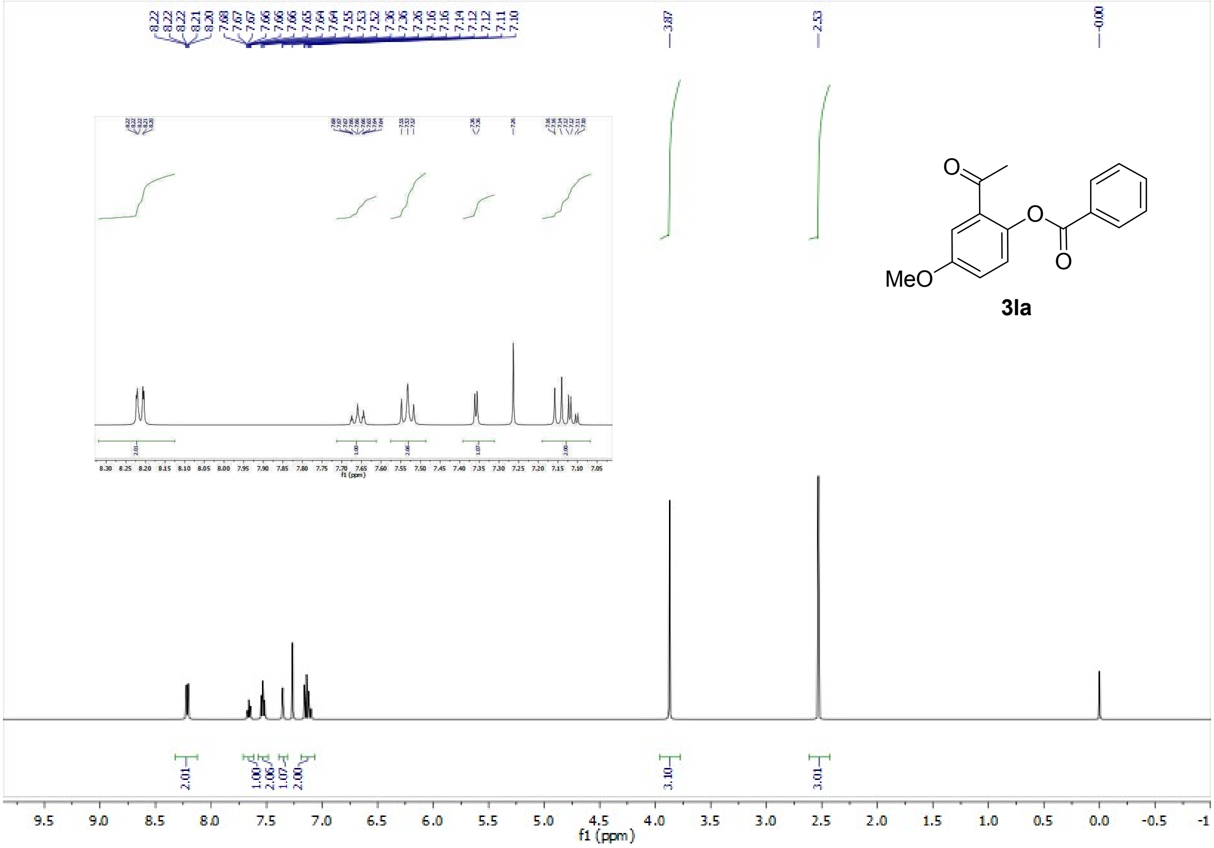
3ja


197.52
165.07
149.25
133.73
133.33
131.14
130.20
129.10
128.60
126.08
123.81
77.17
76.91
76.66
29.71
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

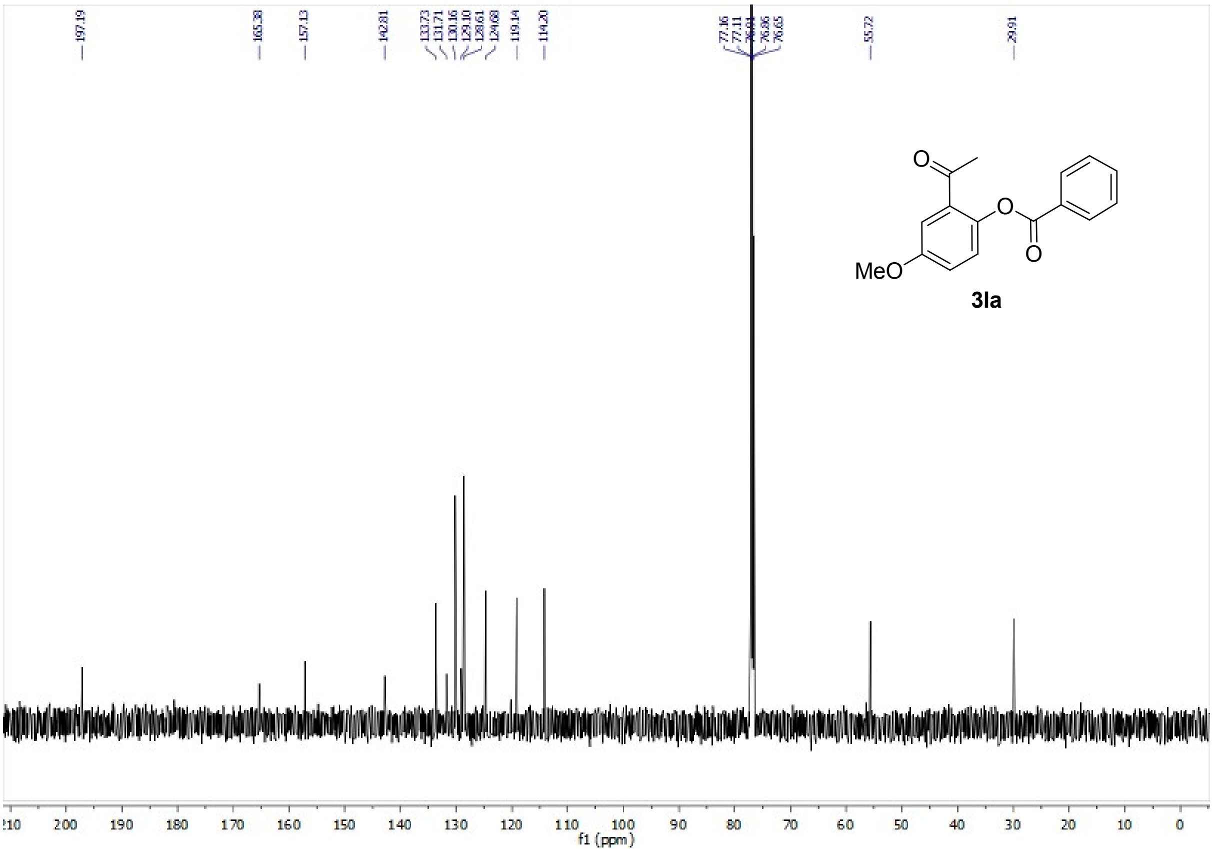
3ja


8.22
8.21
7.66
7.64
7.54
7.53
7.51
7.40
7.39
7.39
7.38
7.38
7.26
7.13
7.11
2.53
2.42
0.00
1.94
1.99
2.20
1.11
1.00
2.88
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
O
O
3ka

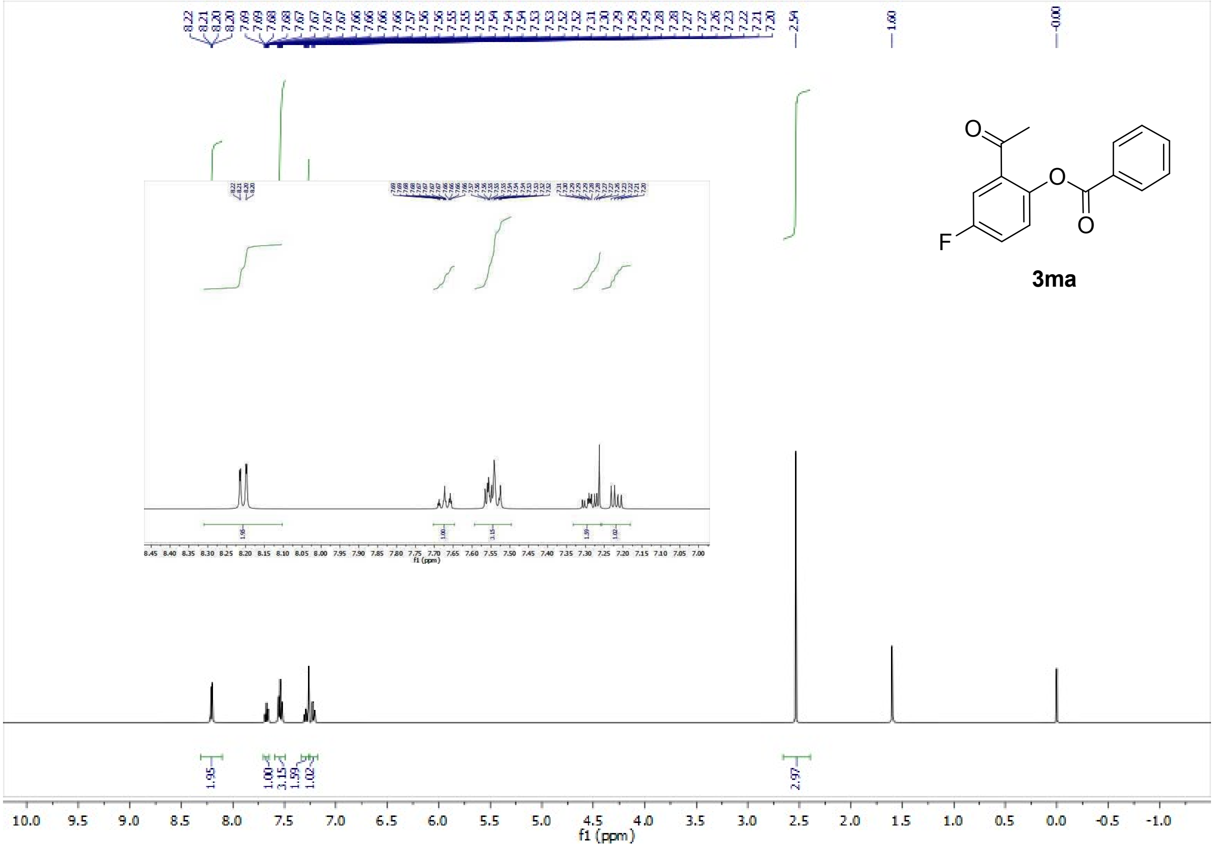

197.68
165.24
147.08
135.89
133.94
133.67
130.51
130.17
129.18
128.58
123.50
77.17
76.92
76.66
29.77
20.76
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
O
3ka


8.22
8.22
8.22
8.21
8.20
7.68
7.67
7.66
7.66
7.66
7.65
7.64
7.55
7.53
7.52
7.36
7.36
7.26
7.16
7.16
7.14
7.12
7.12
7.11
7.10
3.87
2.53
0.00
MeO
O
O
O
2.01
1.00
2.06
1.07
2.00
3.10
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

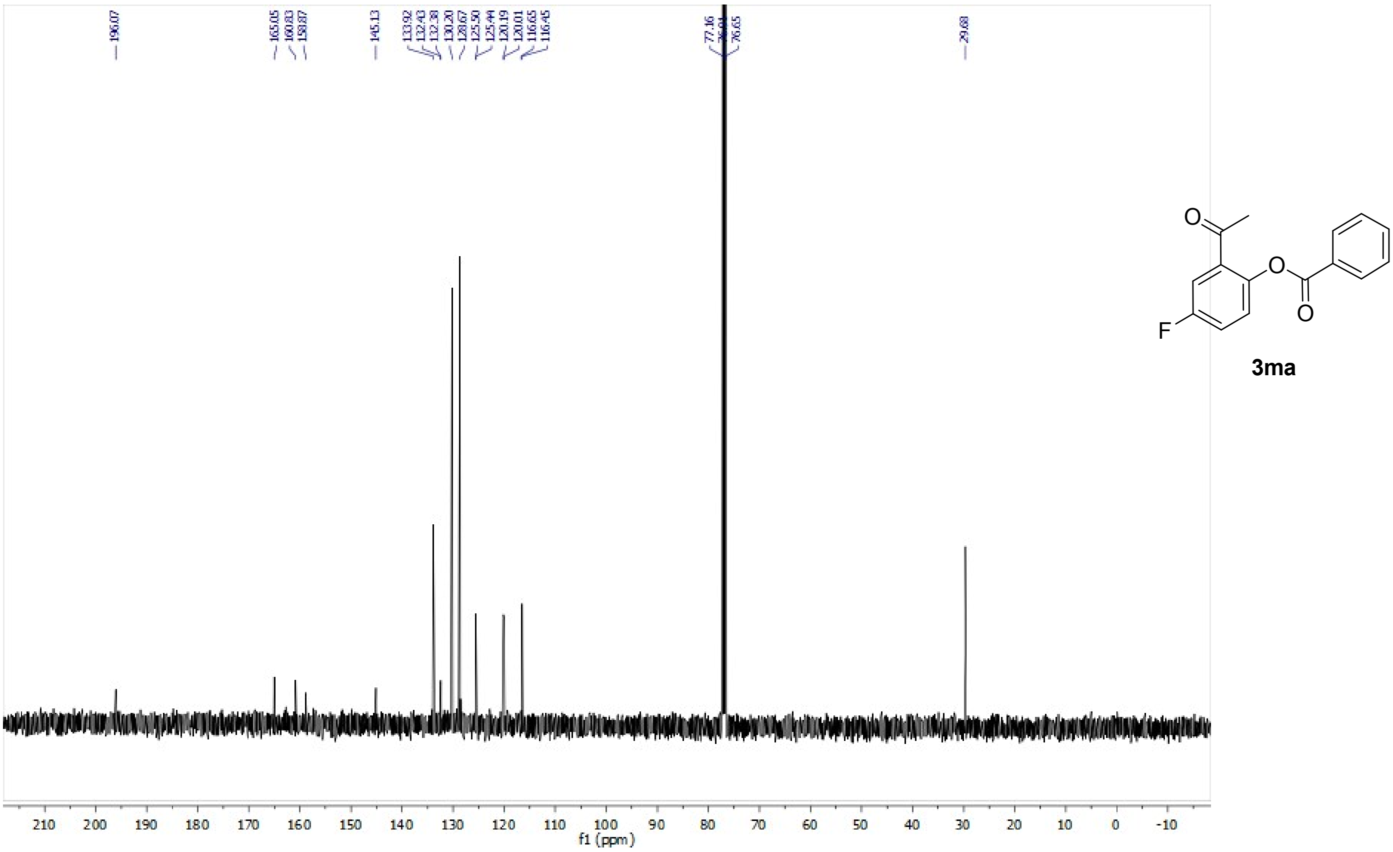
3la


197.19
165.38
157.13
142.81
133.73
131.71
130.16
129.10
128.61
124.68
119.14
114.20
77.16
77.11
76.91
76.86
76.65
55.72
29.91
MeO
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

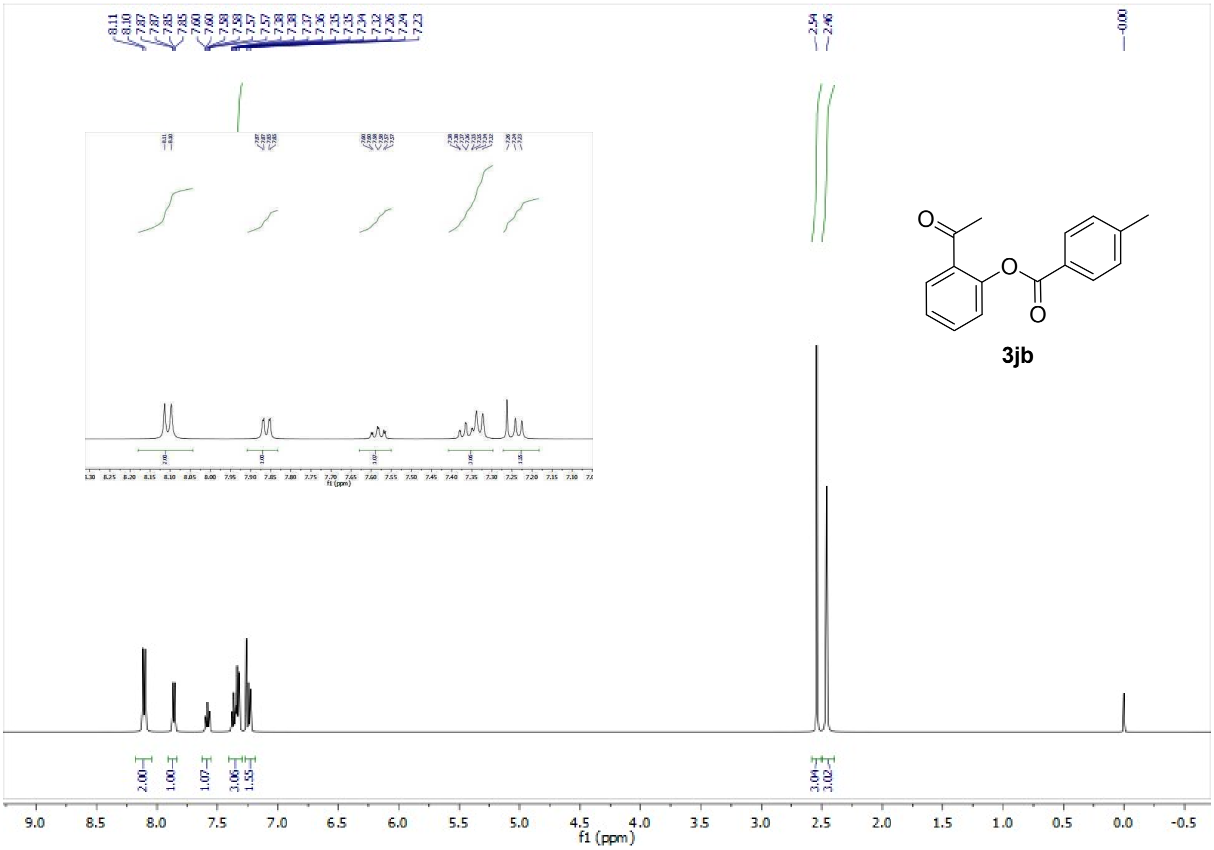
3la

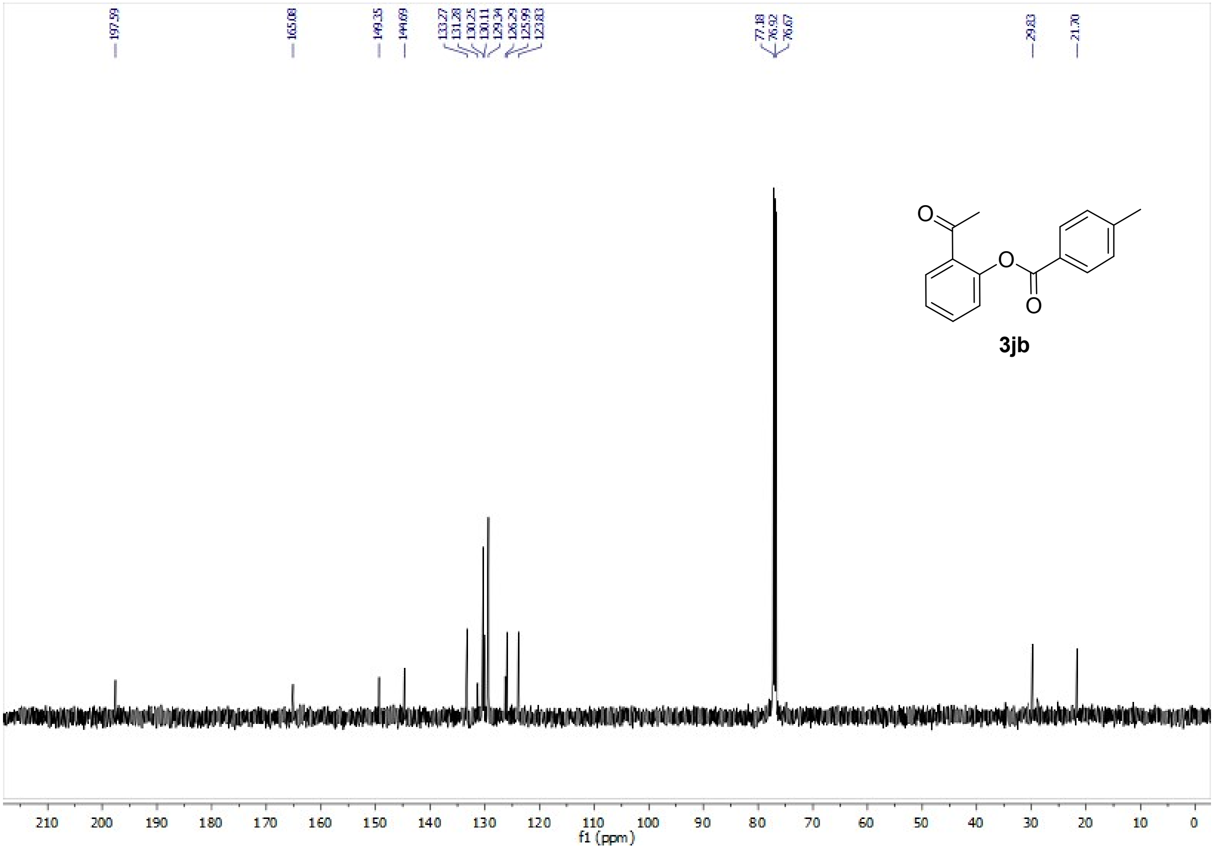

8.22
8.21
8.20
8.20
7.69
7.69
7.68
7.68
7.67
7.67
7.67
7.66
7.66
7.66
7.57
7.56
7.56
7.55
7.55
7.55
7.54
7.54
7.54
7.53
7.53
7.52
7.52
7.31
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.23
7.22
7.21
7.20
2.54
1.60
0.00
O
O
O
F
1.95
1.00
3.15
1.59
1.02
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

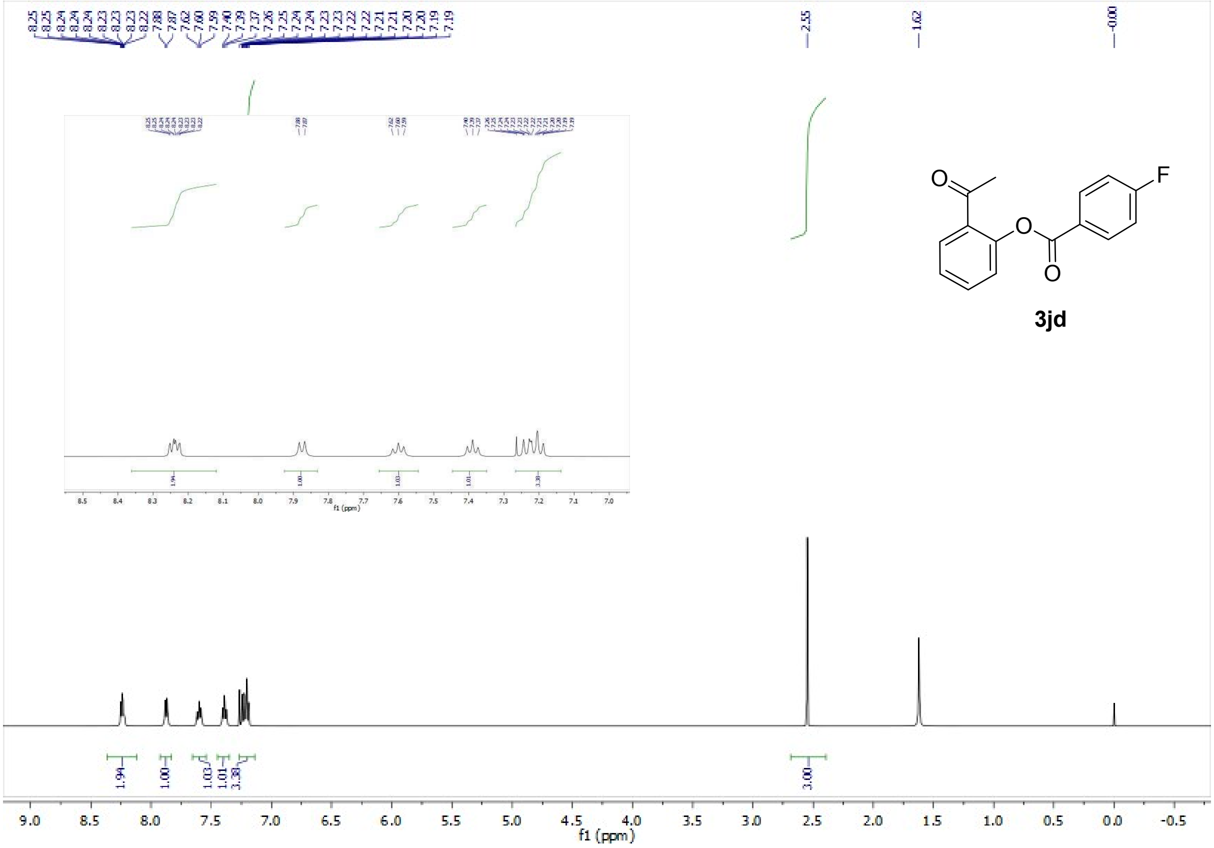
3ma

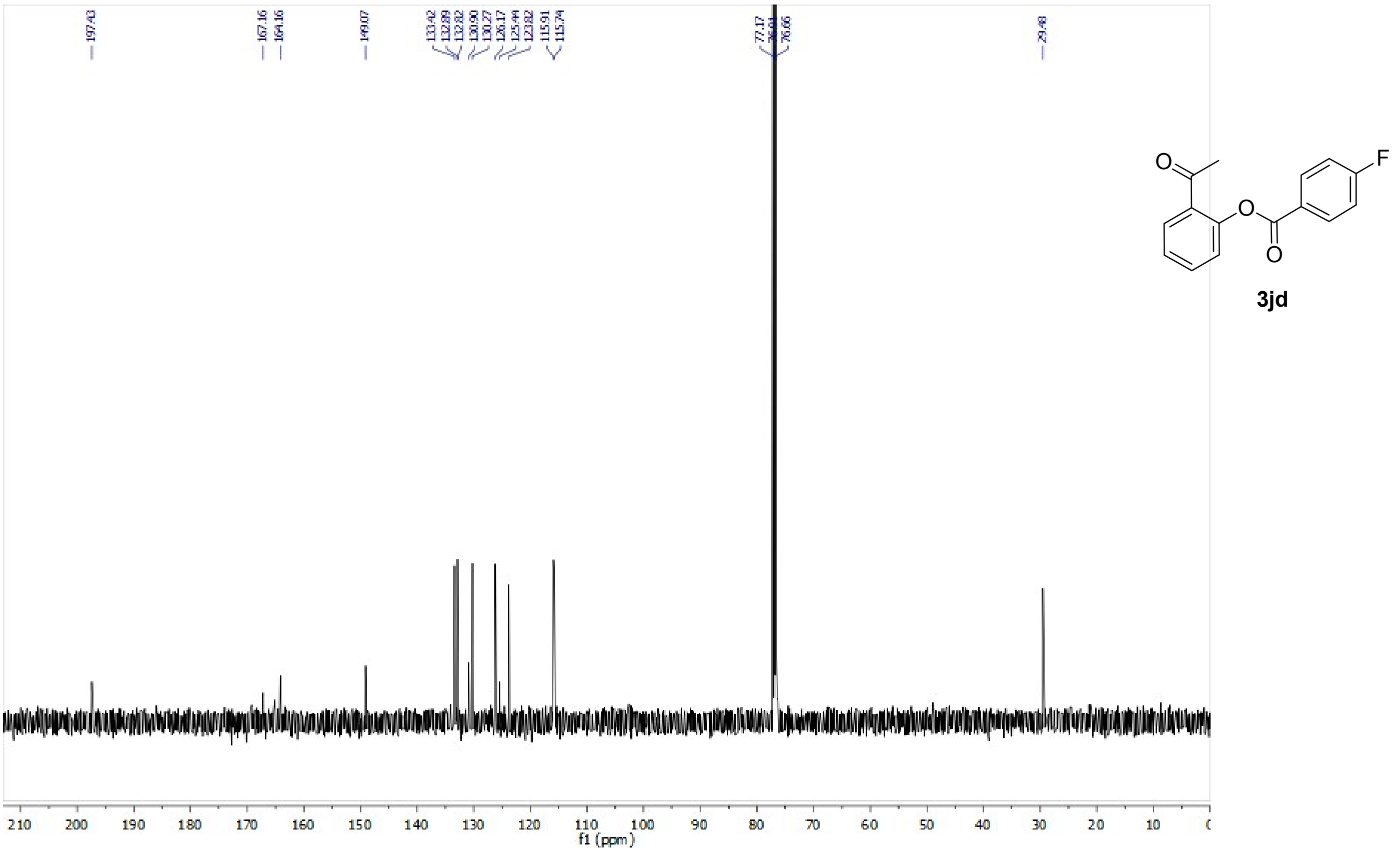

196.07
165.05
160.83
158.87
145.13
133.92
132.43
132.38
130.20
128.67
125.50
125.44
120.19
120.01
116.65
116.45
77.16
76.91
76.65
29.68
O
O
O
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

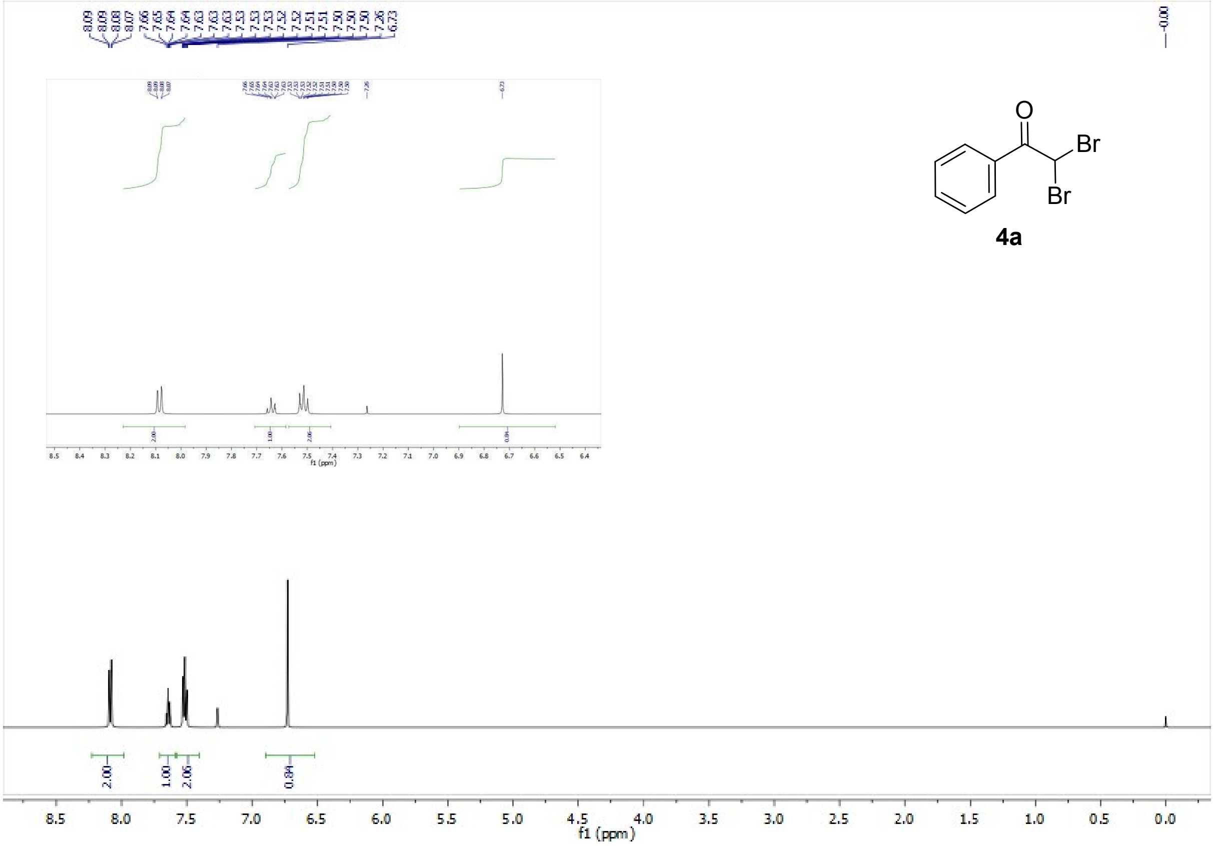
3ma

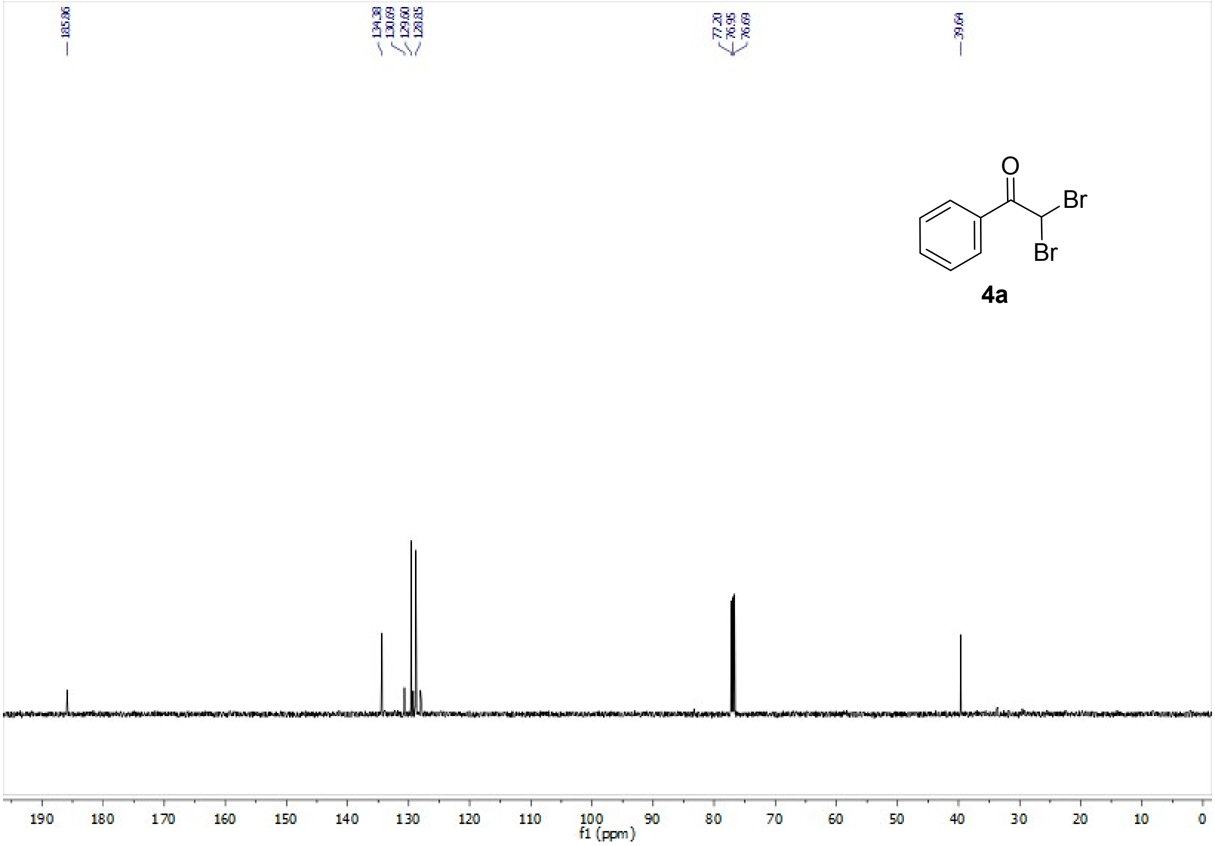

8.11
8.10
7.87
7.87
7.85
7.85
7.60
7.60
7.58
7.58
7.57
7.57
7.38
7.38
7.37
7.36
7.35
7.35
7.34
7.32
7.26
7.24
7.23
2.54
2.46
0.00
2.00
1.00
1.07
3.06
1.55
3.04
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
O
O
O
3jb

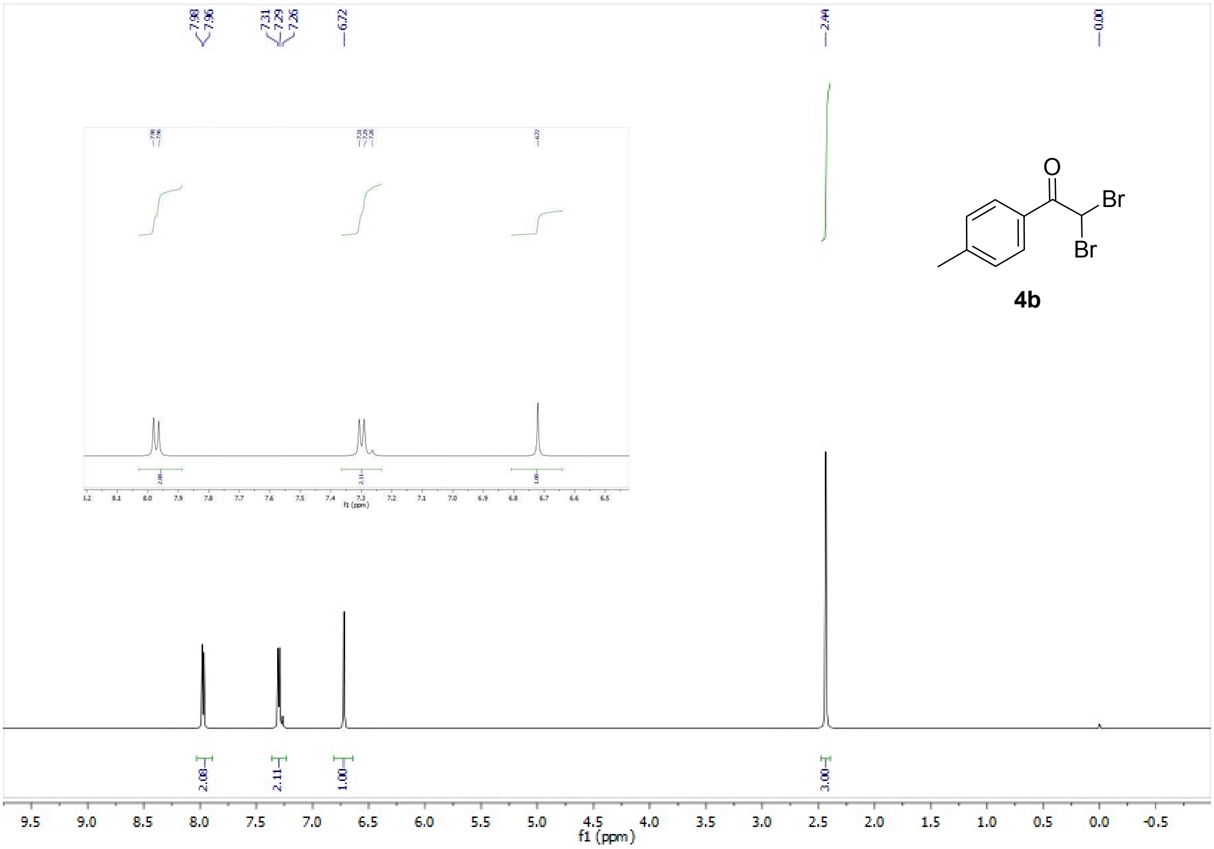

197.59
165.08
149.35
144.69
133.27
131.28
130.25
130.11
129.34
126.29
125.99
123.83
77.18
76.92
76.67
29.83
21.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
O
O
3jb

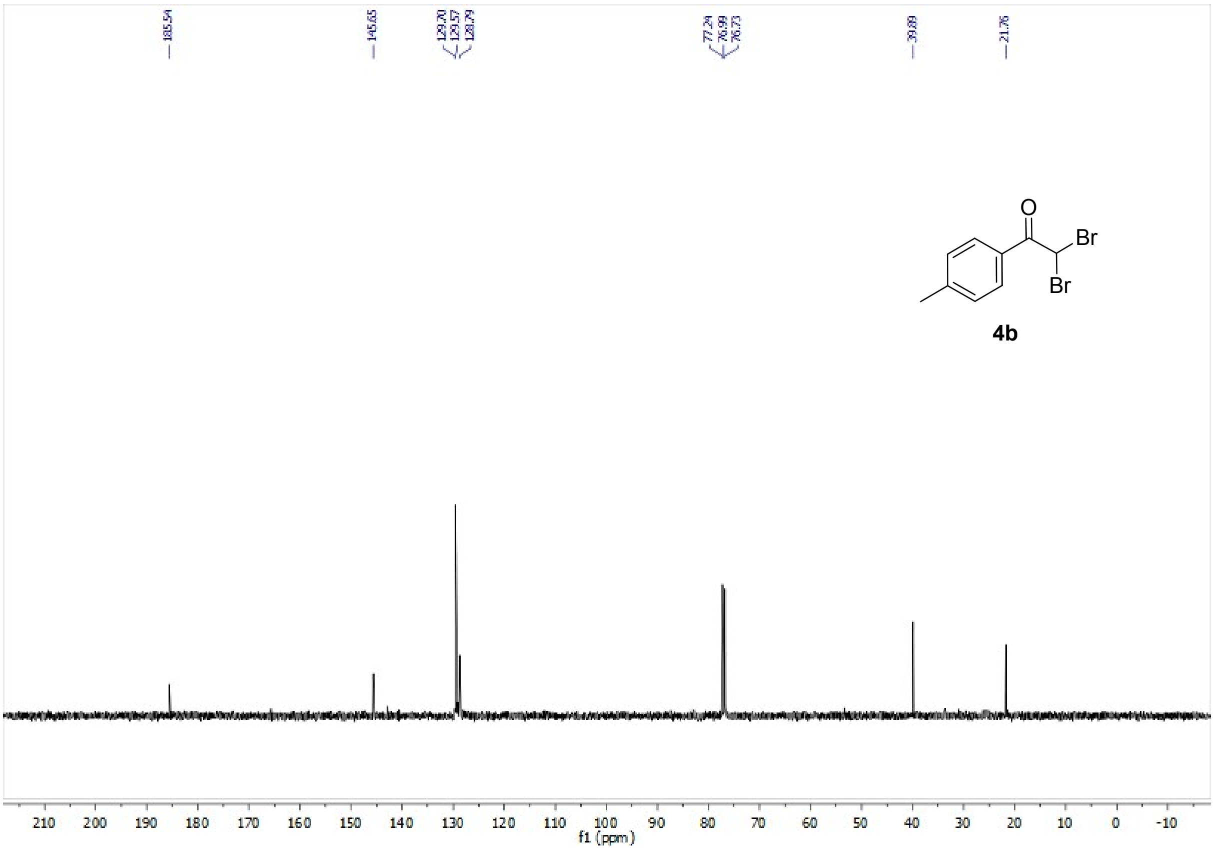

8.25
8.25
8.24
8.24
8.24
8.23
8.23
8.23
8.22
7.88
7.87
7.62
7.60
7.59
7.40
7.39
7.37
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
2.55
1.62
0.00
O
O
O
F
3jd
1.94
1.00
1.03
1.01
3.38
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

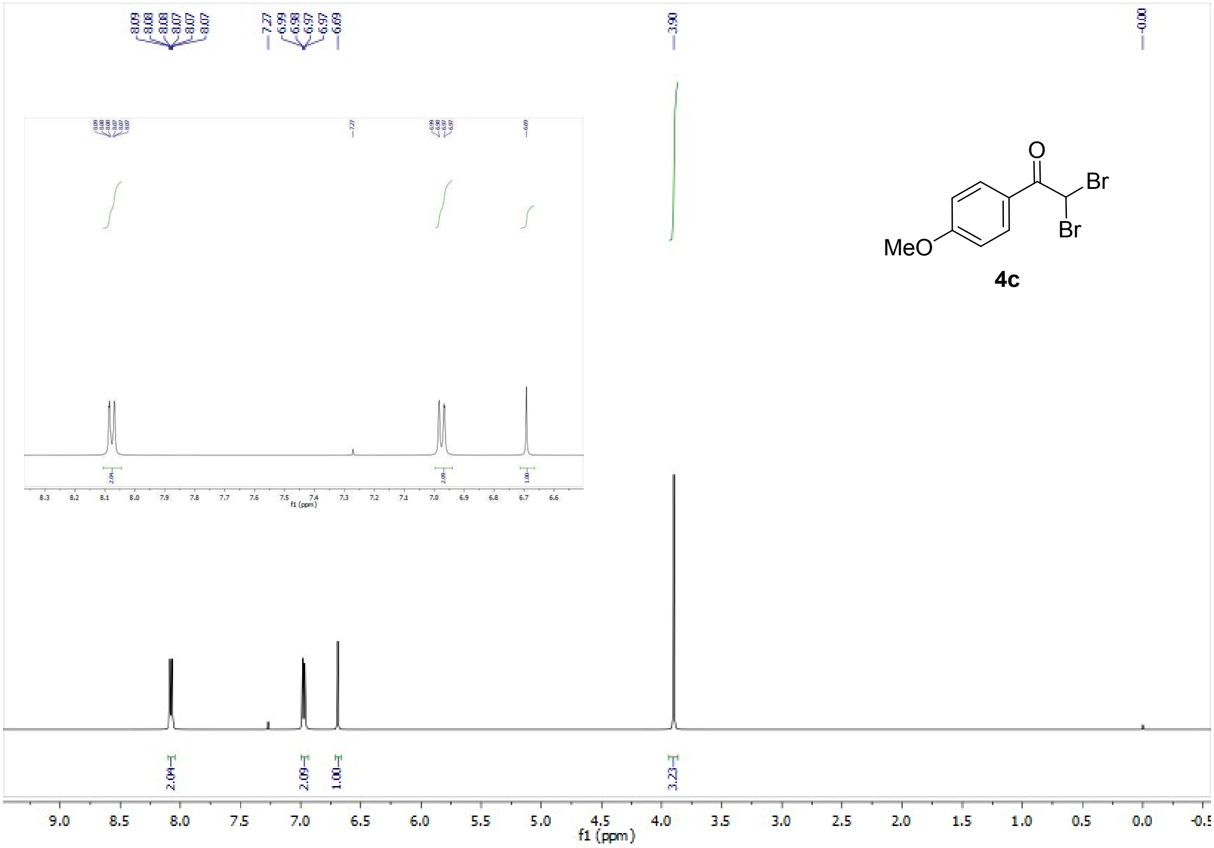

197.43
167.16
164.16
149.07
133.42
132.89
132.82
130.90
130.27
126.17
125.44
123.82
115.91
115.74
77.17
76.91
76.66
29.48
O
O
O
F
3jd
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.09
8.09
8.08
8.07
7.66
7.65
7.64
7.64
7.63
7.63
7.63
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.50
7.26
6.73
0.00
2.00
1.00
2.06
0.84
f1 (ppm)
O
Br
Br
4a

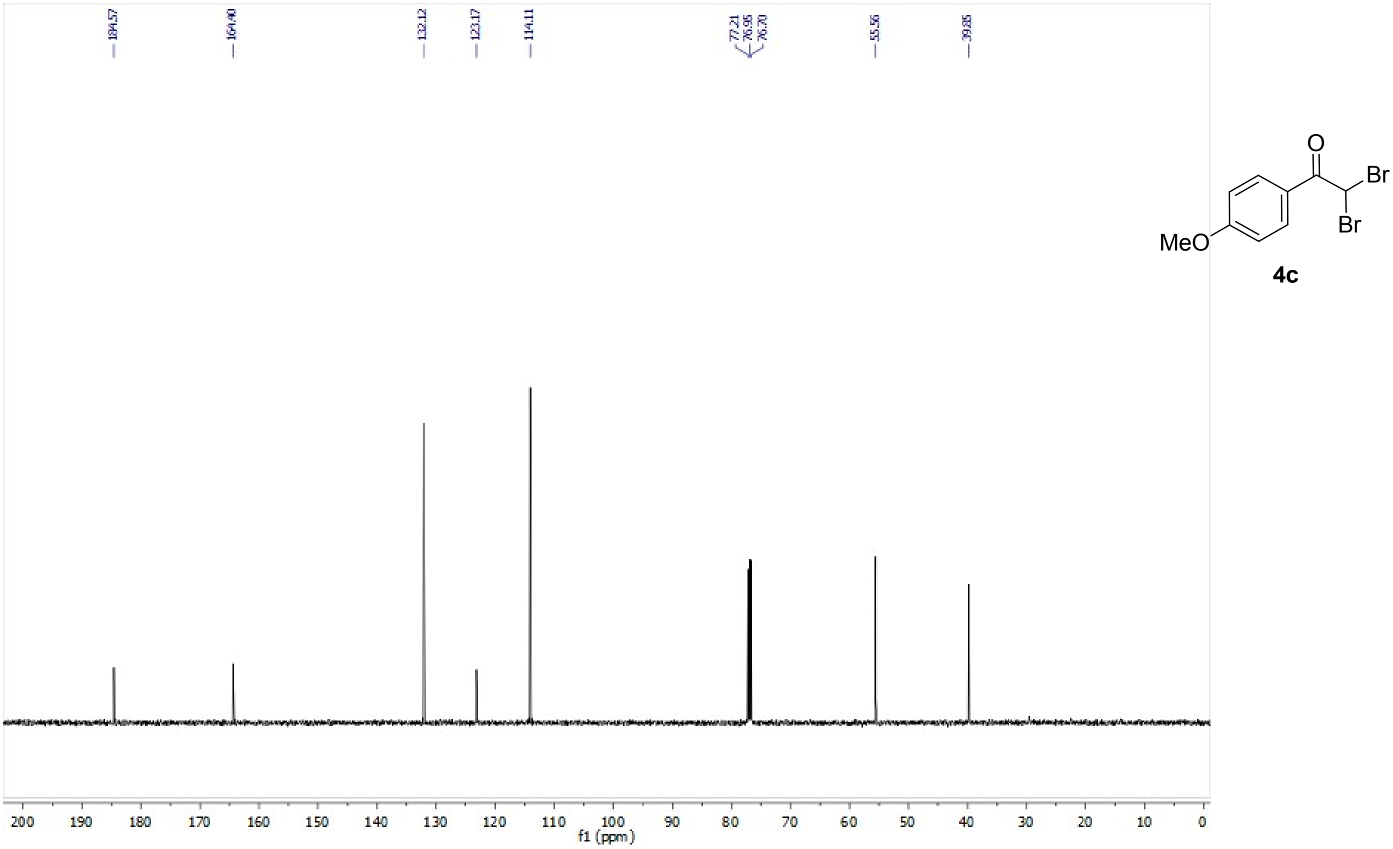

185.86
134.38
130.69
129.60
128.85
77.20
76.95
76.69
39.64
O
Br
Br
4a
f1 (ppm)


7.98
7.96
7.31
7.29
7.26
6.72
2.44
0.00
O
Br
Br
4b
2.08
2.11
1.00
3.00
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
0.0
-0.5
f1 (ppm)

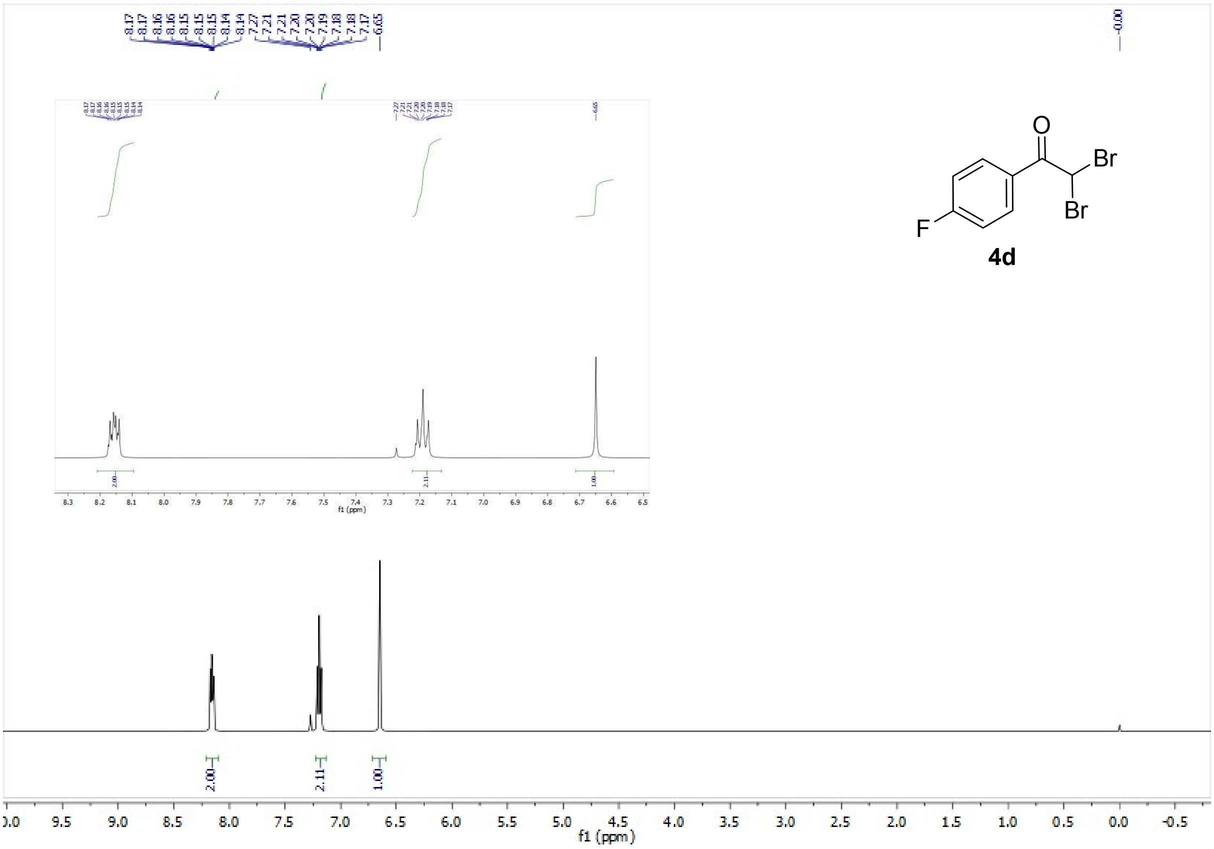

185.54
145.65
129.70
129.57
128.79
77.24
76.99
76.73
39.89
21.76
O
Br
Br
4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.09
8.08
8.08
8.07
8.07
8.07
7.27
6.99
6.98
6.97
6.97
6.69
3.90
-0.00
2.04
2.09
1.00
3.23
MeO
O
Br
Br
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

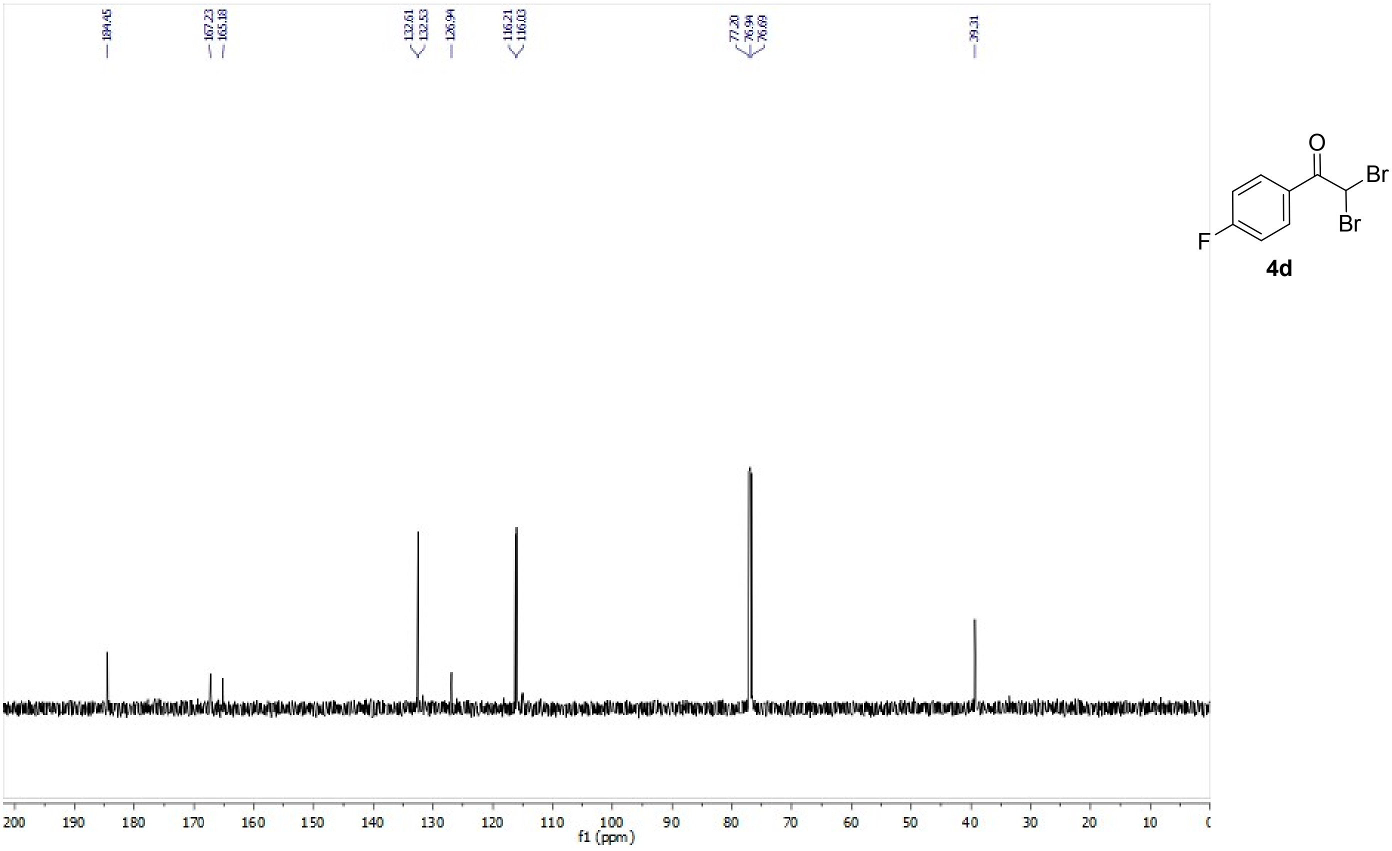
4c


184.57
164.40
132.12
123.17
114.11
77.21
76.95
76.70
55.56
39.85
MeO
O
Br
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

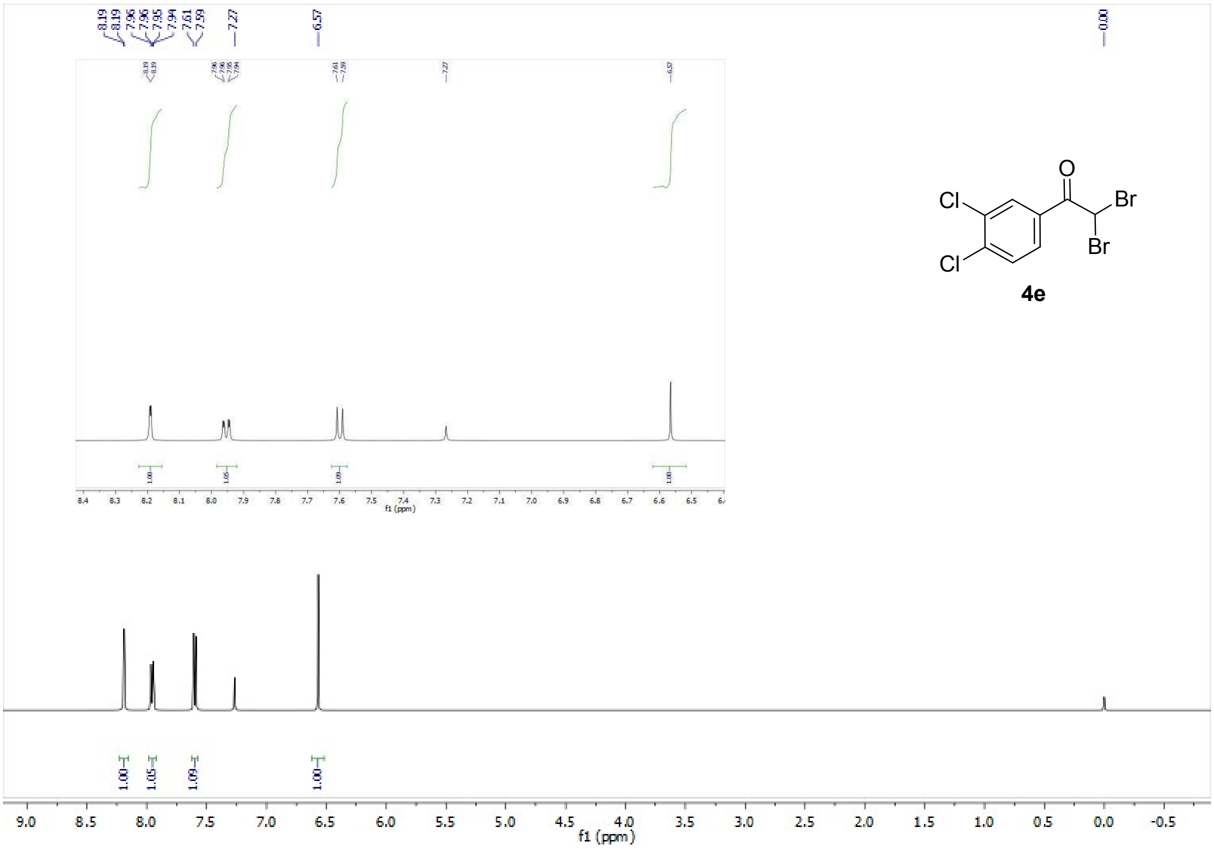
4c


8.17
8.17
8.16
8.16
8.15
8.15
8.14
8.14
7.27
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
6.65
0.00
2.00
2.11
1.00
O
Br
Br
F
f1 (ppm)

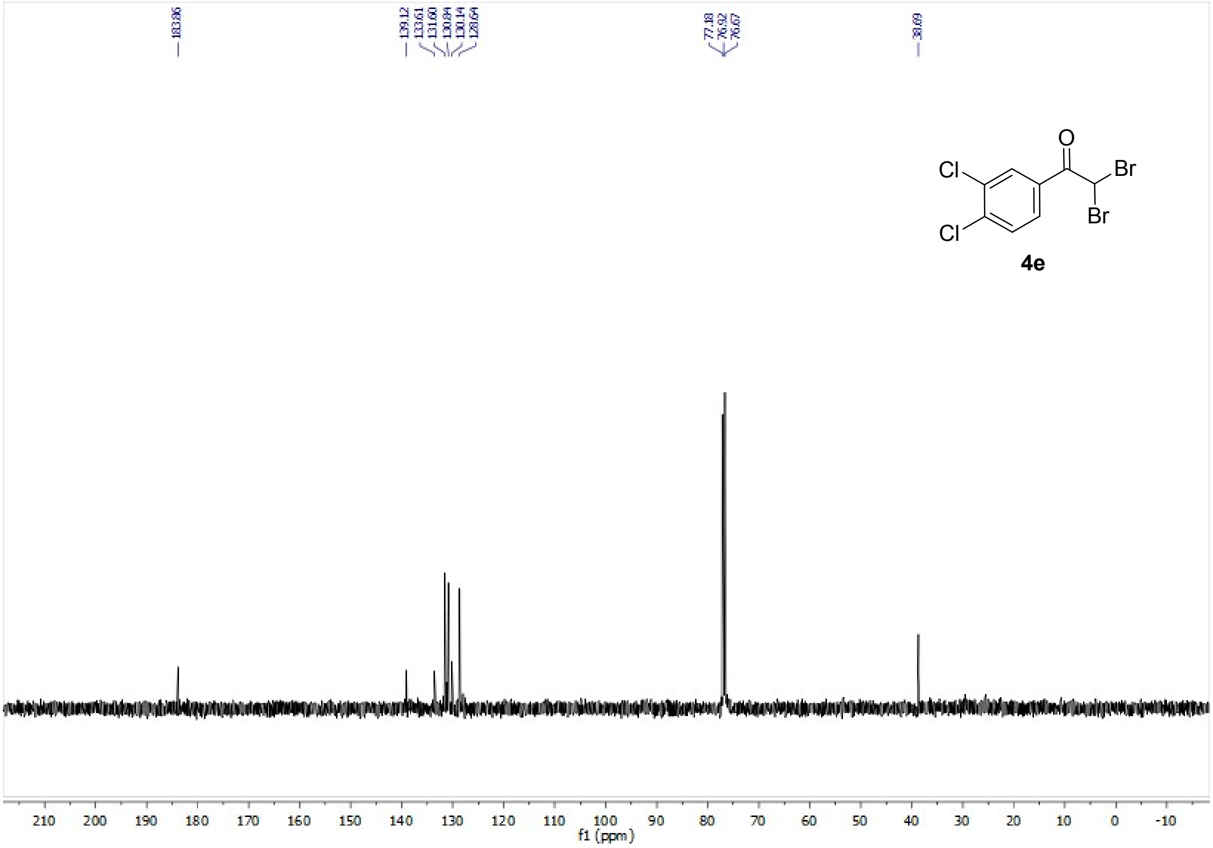
4d


184.45
167.23
165.18
132.61
132.53
126.94
116.21
116.03
77.20
76.94
76.69
39.31
O
Br
Br
F
f1 (ppm)

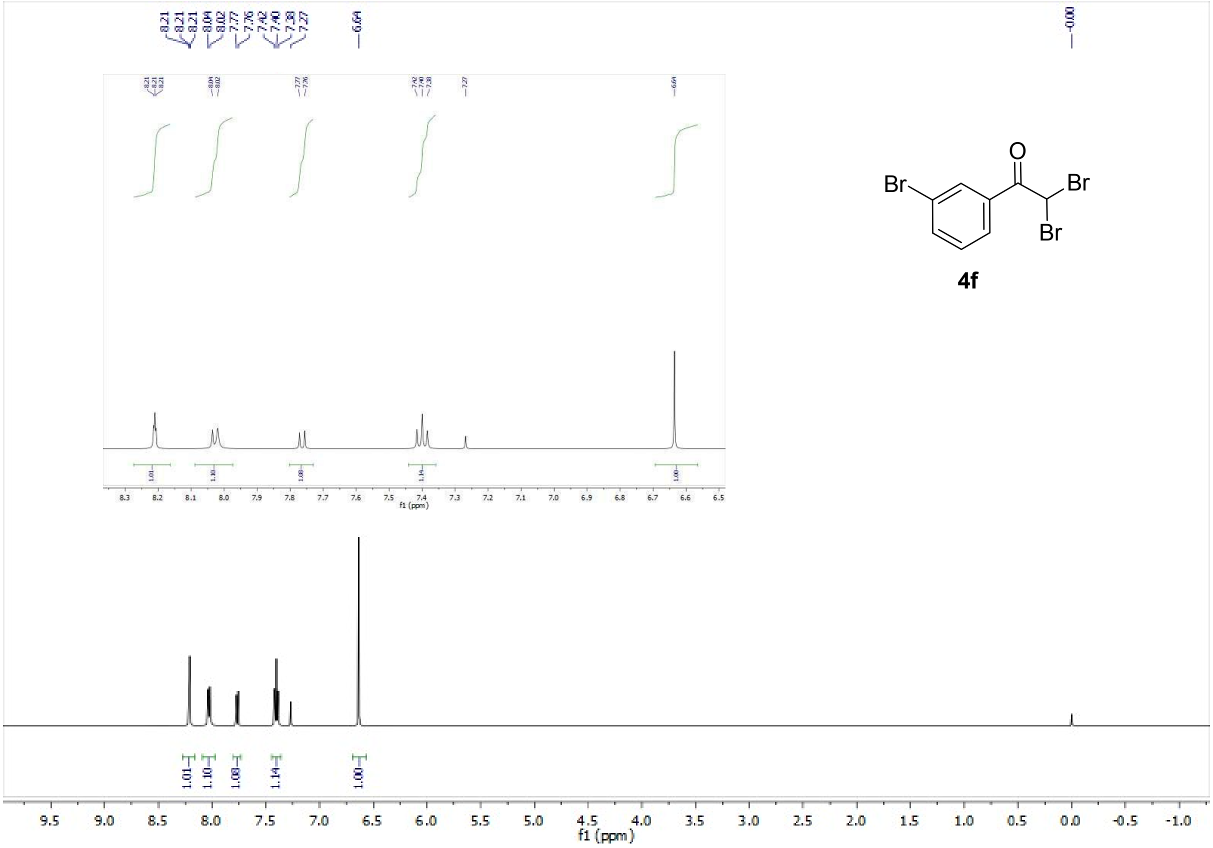
4d

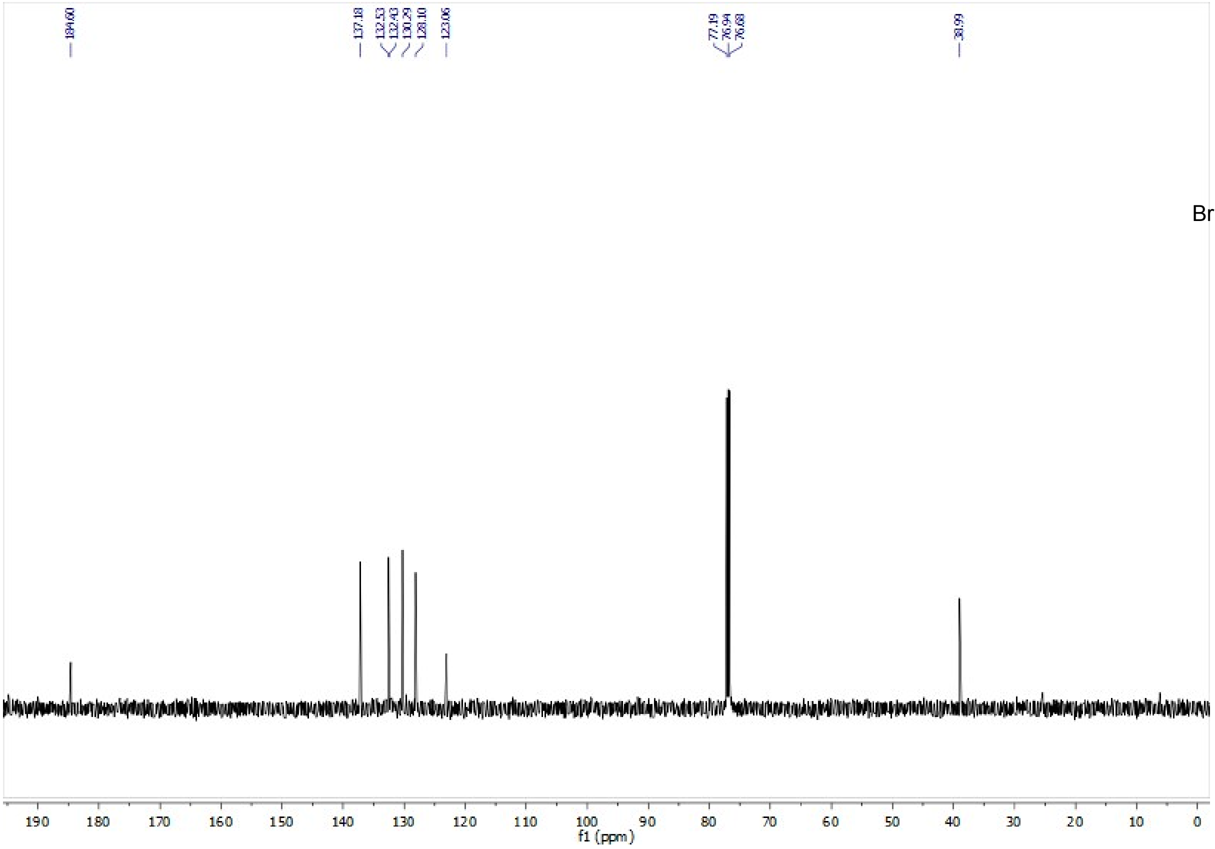

8.19
8.19
7.96
7.96
7.95
7.94
7.61
7.59
7.27
6.57
0.00
1.00
1.05
1.09
1.00
f1 (ppm)
Cl
Cl
O
Br
Br

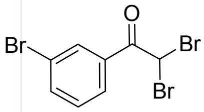
4e


183.86
139.12
133.61
131.60
130.84
130.14
128.64
77.18
76.92
76.67
38.69
f1 (ppm)
Cl
Cl
O
Br
Br

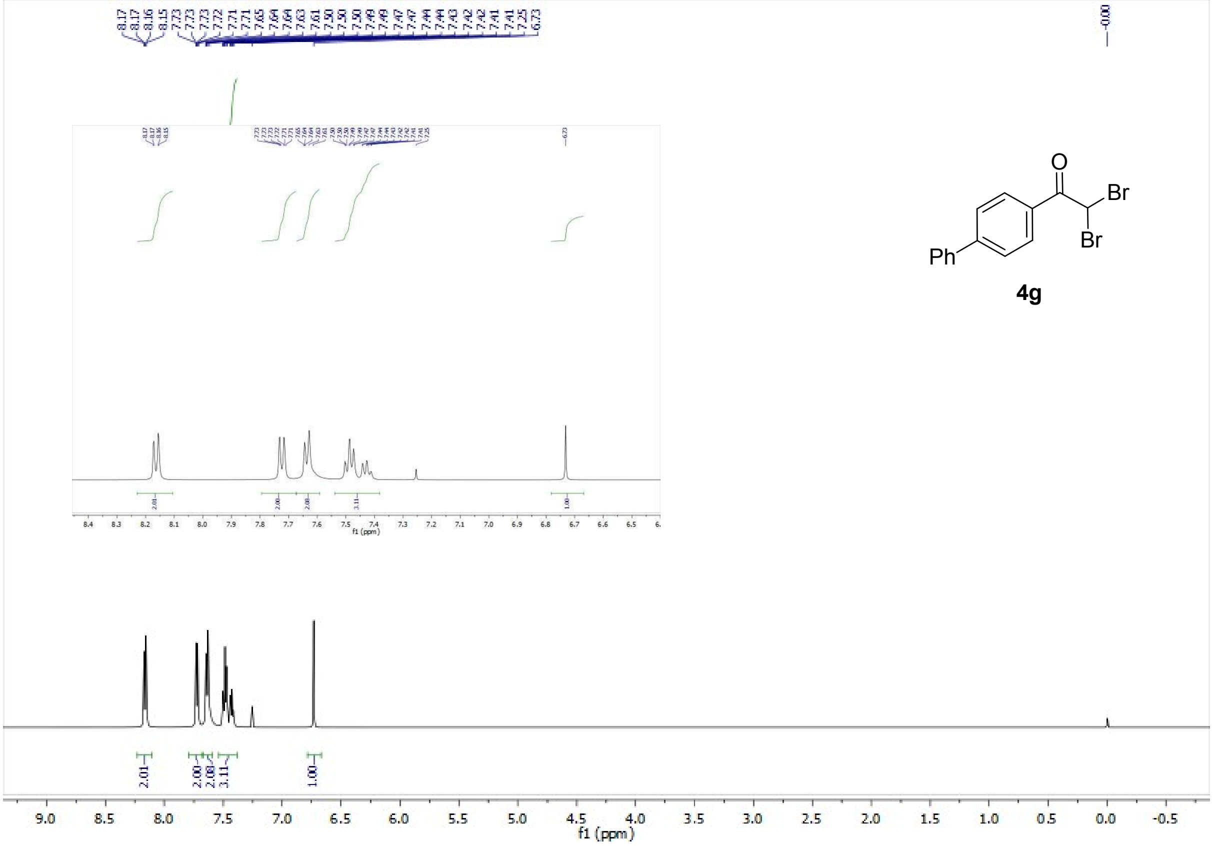
4e


8.21
8.21
8.21
8.04
8.02
7.77
7.76
7.42
7.40
7.38
7.27
6.64
0.00
O
Br
Br
Br
4f
1.01
1.10
1.08
1.14
1.00
f1 (ppm)

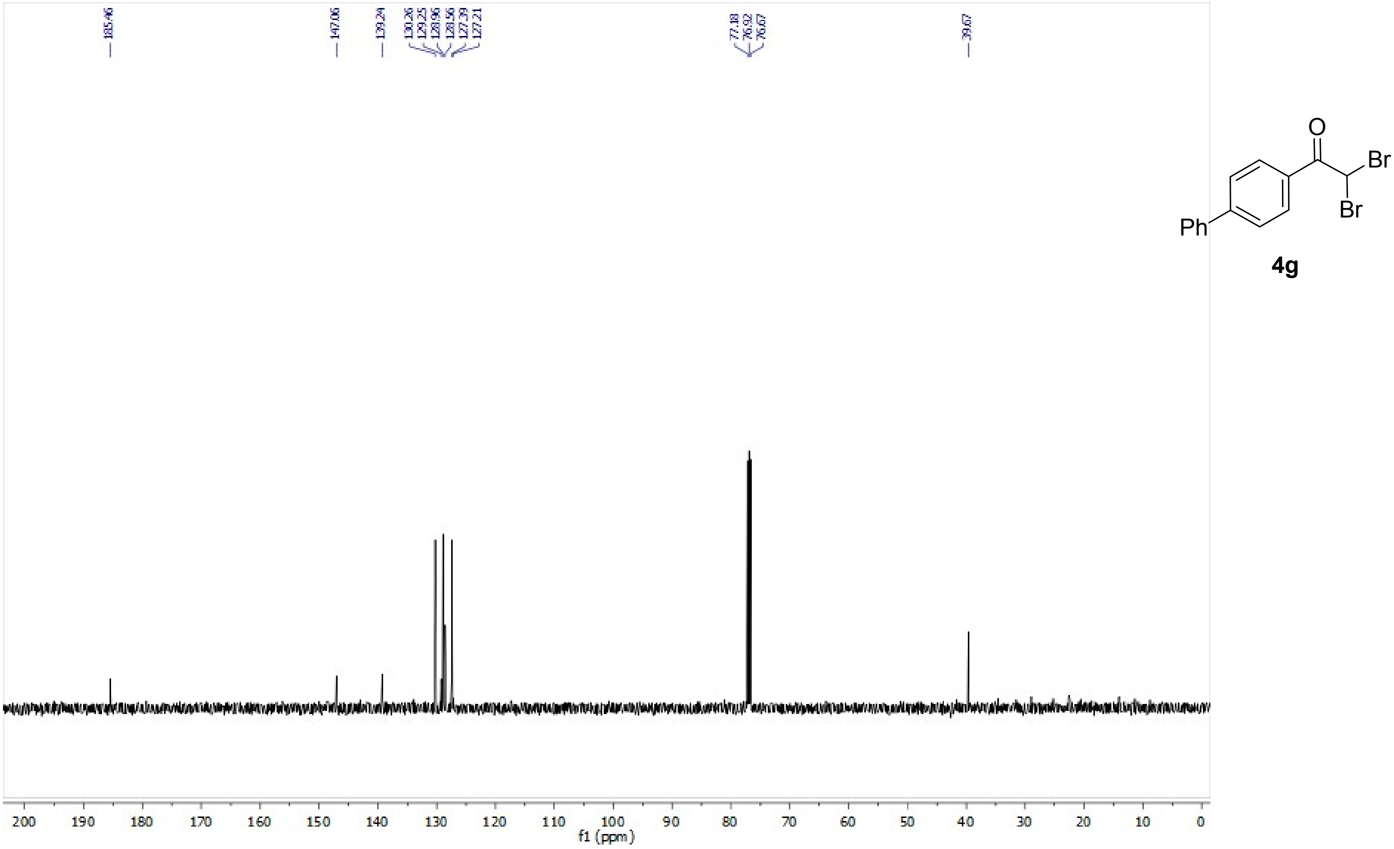

184.60
137.18
132.53
132.43
130.29
128.10
123.06
77.19
76.94
76.68
38.99
f1 (ppm)


O
Br
Br
Br

4f


8.17
8.17
8.16
8.15
7.73
7.73
7.73
7.72
7.71
7.71
7.65
7.64
7.64
7.63
7.61
7.50
7.50
7.50
7.49
7.49
7.47
7.47
7.44
7.44
7.43
7.42
7.42
7.41
7.25
6.73
0.00
O
Br
Br
Ph
2.01
2.00
2.08
3.11
1.00
f1 (ppm)

4g


185.46
147.06
139.24
130.26
129.25
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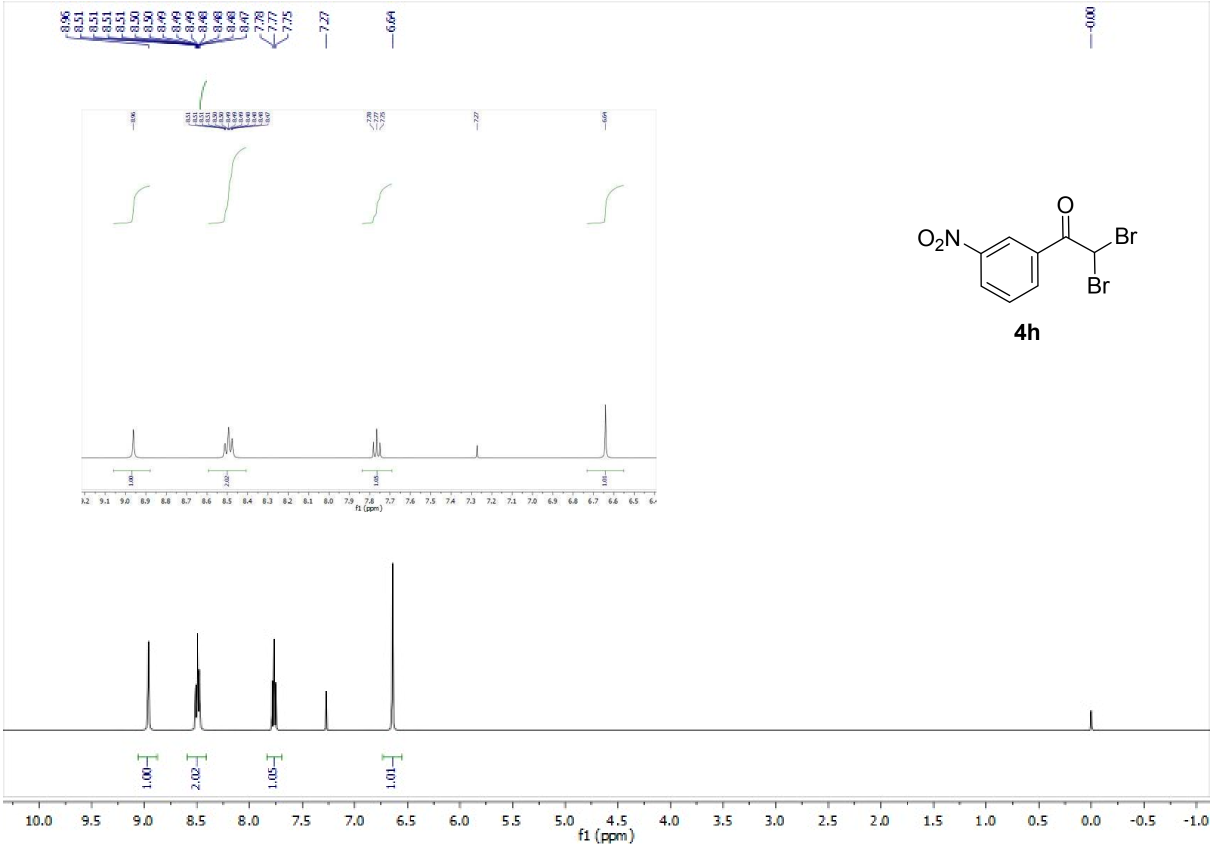
127.39
127.21
77.18
76.92
76.67
39.67
O
Br
Br
Ph
f1 (ppm)

4g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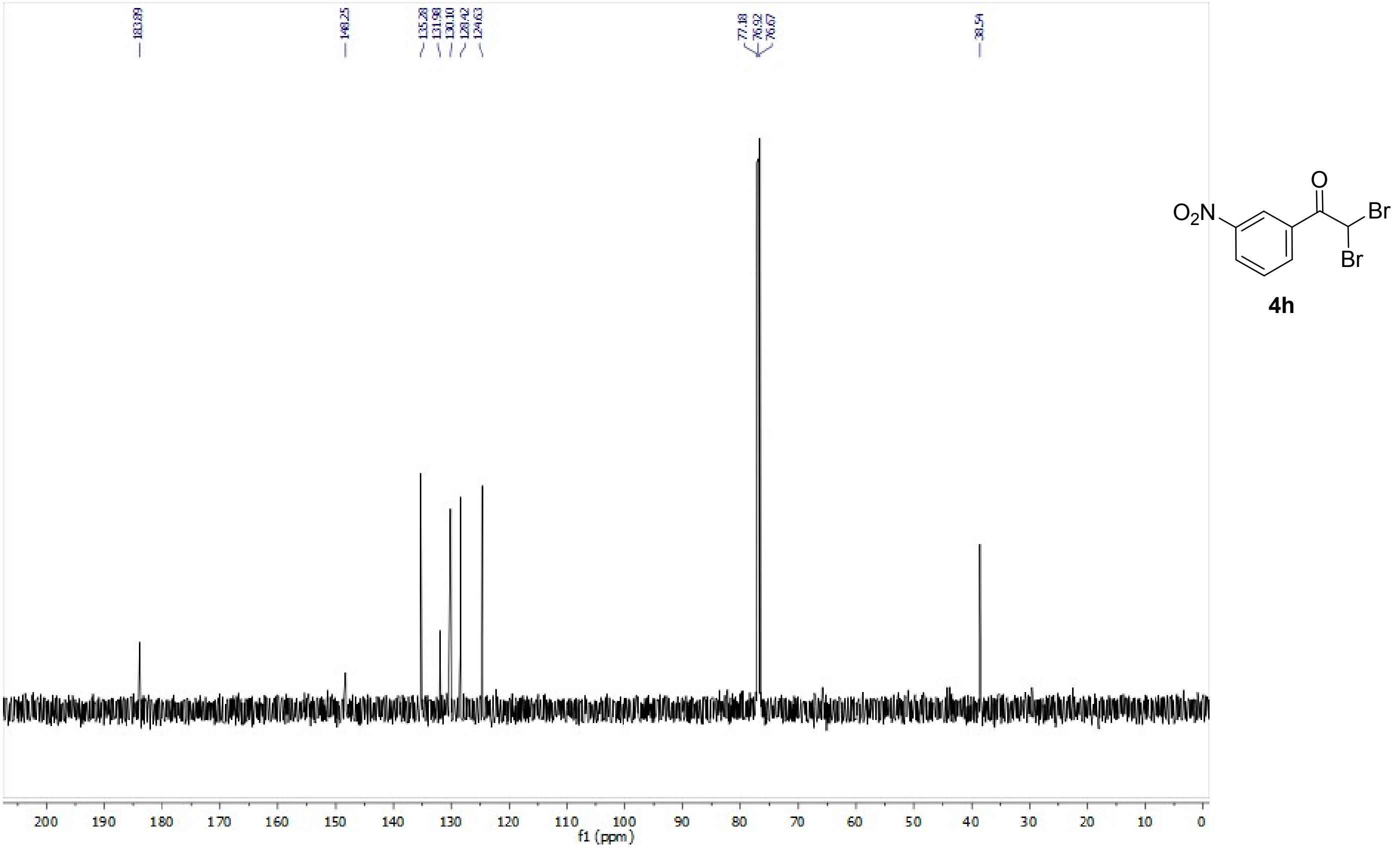
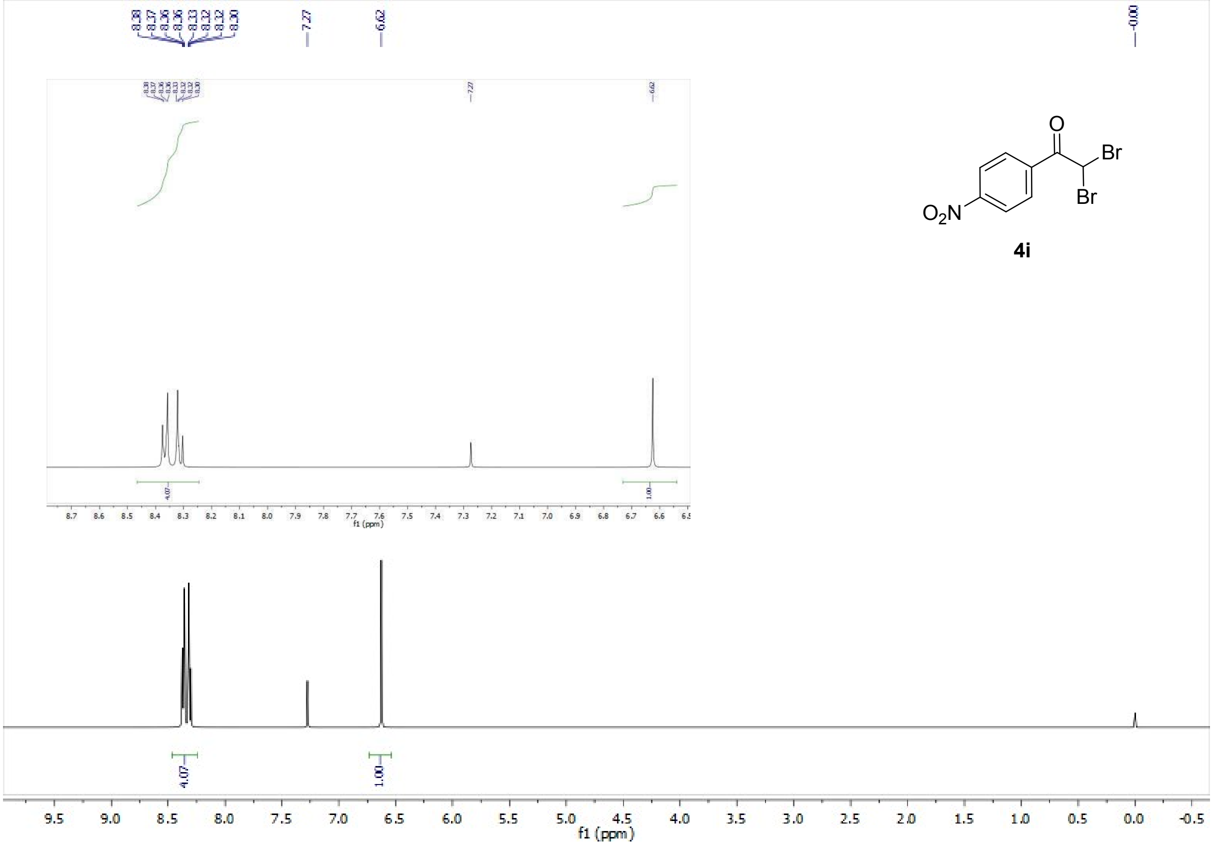
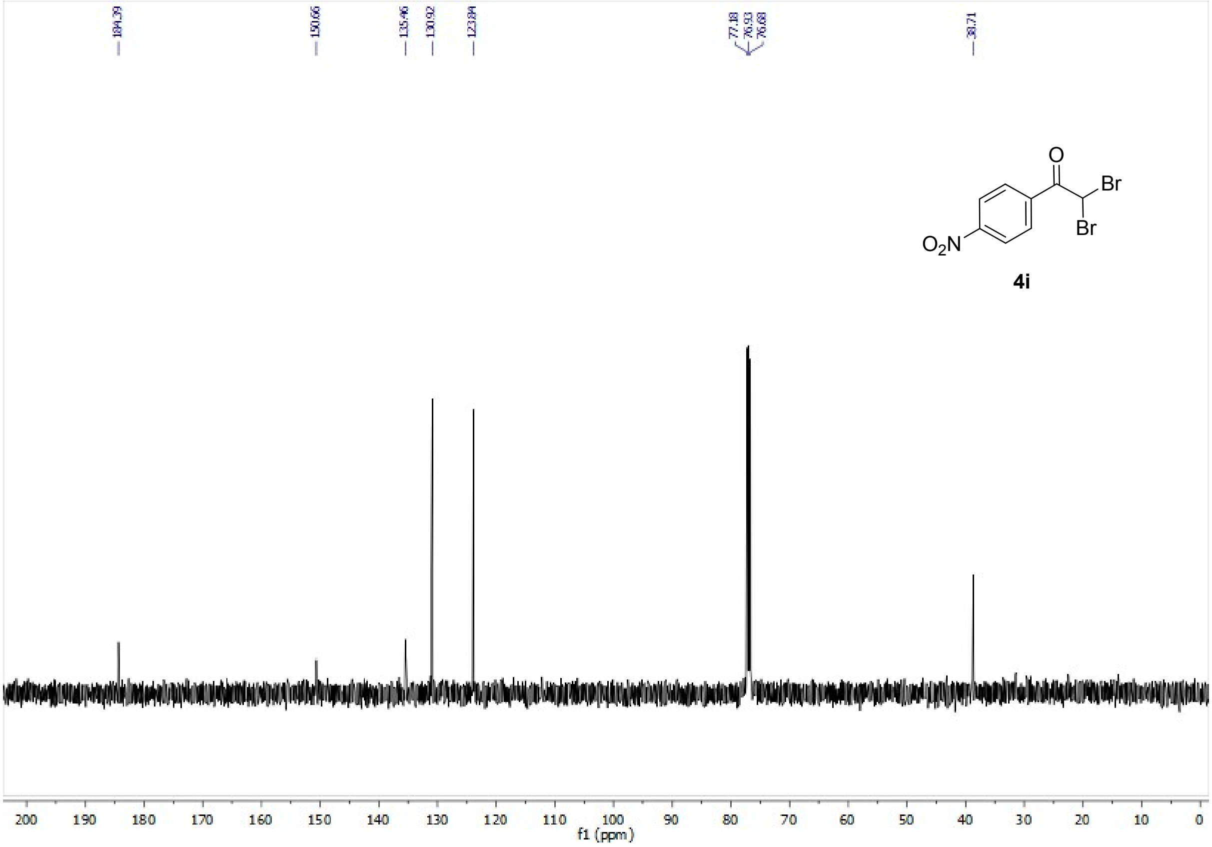
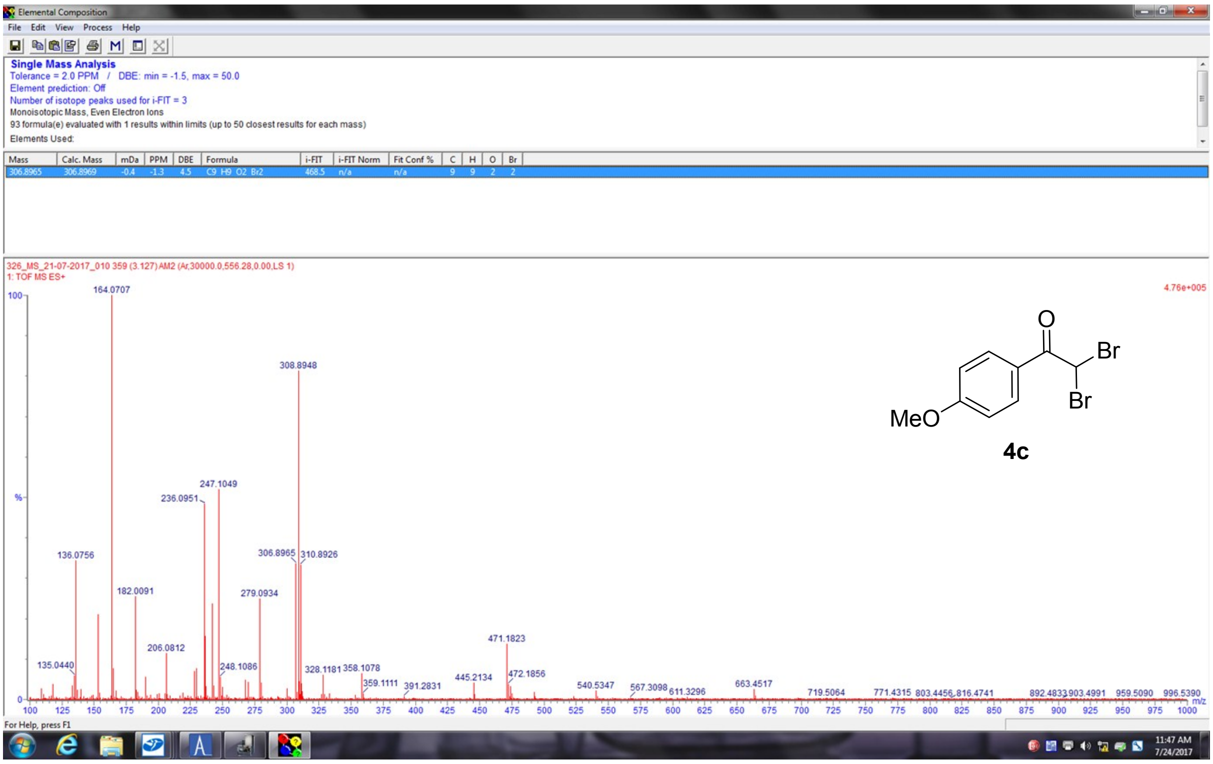
8.51
8.51
8.51
8.51
8.50
8.50
8.49
8.49
8.49
8.48
8.48
8.48
8.47
7.78
7.77
7.75
7.27
6.64
0.00
1.00
2.02
1.05
1.01
O2N
O
Br
Br
4h
f1 (ppm)


183.89
148.25
135.28
131.98
130.10
128.42
124.63
77.18
76.92
76.67
38.54
O2N
O
Br
Br
4h
f1 (ppm)


8.38
8.37
8.36
8.36
8.33
8.32
8.32
8.30
7.27
6.62
0.00
O
Br
Br
O2N
4i
4.07
1.00
f1 (ppm)


184.39
150.66
135.46
130.92
123.84
77.18
76.93
76.68
38.71
O
Br
Br
O2N
4i
f1 (ppm)



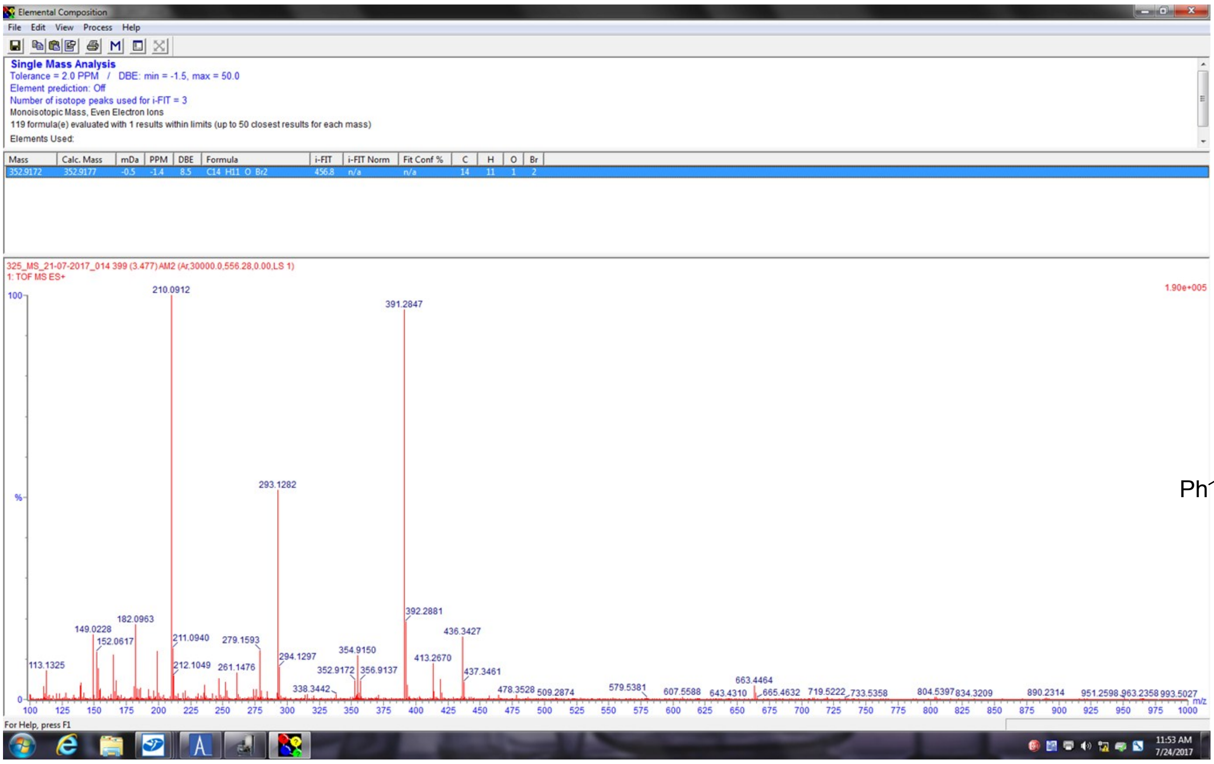
Single Mass Analysis
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
93 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Br
306.8965	306.8969	-0.4	-1.3	4.5	C9 H9 O2 Br2	468.5	n/a	n/a	9	9	2	2

326_MS_21-07-2017_010 359 (3.127) AM2 (Ar,30000.0,556.28,0.00,LS 1)
1: TOF MS ES+

For Help, press F1

4c

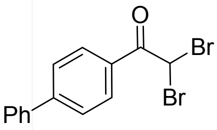


Single Mass Analysis
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
119 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Br
352.9172	352.9177	-0.5	-1.4	8.5	C14 H11 O Br2	456.8	n/a	n/a	14	11	1	2

325_MS_21-07-2017_014 399 (3.477) AM2 (Ar,30000.0,556.28,0.00,LS 1)
1: TOF MS ES+

For Help, press F1



4g