Supporting Information

Bu_4NI-catalyzed decarboxylative acyloxylation of sp^3 C-H bond adjacent to heteroatom with α-oxocarboxylic acids

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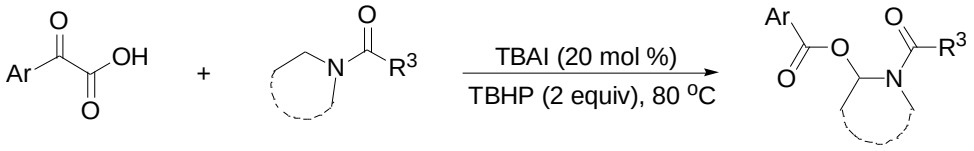
General Information

All Reactions were carried out under an atmosphere of nitrogen with the strict exclusion of moisture. The dry DMF were distilled from CaH_2 under nitrogen and stored over molecular sieves under nitrogen. Column chromatography was carried out on silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III-400 in solvents as indicate. Chemical shift are reported in ppm from $CDCl_3$ using TMS as internal standard. IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm^{-1}. HRMS were obtained on a Q-TOF micro spectrometer. Melting points were determined on a microscopic apparatus and were uncorrected.

Starting Materials

N-formylpiperidine, and *N*,*N*-dimethylacetamide were purchased from Sigma-Aldrich. Phenylglyoxylic acid **1a** was purchased from Sigma-Aldrich. Other α-oxocarboxylic acids were prepared from the corresponding methyl ketones according to the reported procedure.[1]

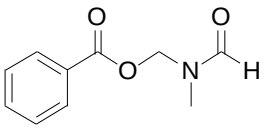
General Procedure for the Decarboxylative Acyloxylation of Formamides



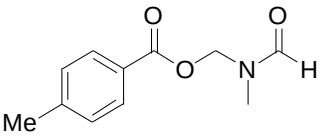
1 **2** **3**

A 10 mL oven-dried Schlenk-tube was charged with TBAI (14.8 mg, 20 mol %). The tube was evacuated and backfilled with nitrogen (three times). α-Oxocarboxylic acids (**1**, 0.2 mmol, 1.0 equiv) and *tert*-butyl hydroperoxide (TBHP, 0.4 mmol, 2.0 equiv) in substituted formamides (2 mL) were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 3 h at 80 ^{o}C. Upon completion of the reaction (monitored by TLC), the mixture was diluted with EtOAc, filtered through a pad of Celite, and the filtrate was washed with water, dried over Na_2SO_4. After the solvent was removed, the residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/10 to 1/5) to give the corresponding products **3** in yields listed in Table 2.

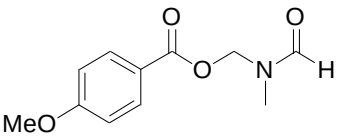
Characterization of Products 3



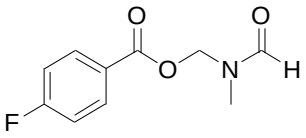
***N*-Benzoyloxymethyl-*N*-methylformamide** (**3a**): A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 8.04-8.02 (d, *J* = 7.2 Hz, 2H), 7.62-7.58 (t, *J* = 7.2 Hz, 1H), 7.48-7.44 (t, *J* = 7.6 Hz, 2H), 5.55 (s, 2H), 3.03 (s, 3H); The ^{1}H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 164.0, 133.6, 129.8, 129.1, 128.5, 74.2, 29.8 ppm; IR (KBr): υ_{max} 1724, 1689, 1396, 1262, 1067 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{11}NNaO_3$ $[M+Na]^+$ 216.0631, found 216.0638.



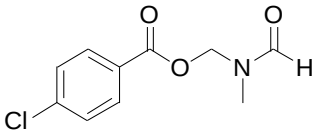
4-Methyl-*N*-benzoyloxymethyl-*N*-methylformamide (**3b**): A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.92-7.90 (d, *J* = 8.0 Hz, 2H), 7.26-7.24 (d, *J* = 8.0 Hz, 2H), 5.53 (s, 2H), 3.02 (s, 3H), 2.41 (s, 3H); The ^{1}H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 164.1, 144.5, 129.7, 129.2, 126.3, 74.0, 29.8, 21.7 ppm; IR (KBr): υ_{max} 1722, 1691, 1398, 1264, 1069 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{13}NNaO_3$ $[M+Na]^+$ 230.0788, found 230.0780.



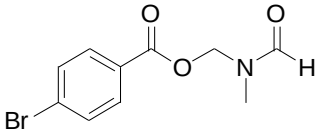
4-Methoxyl-*N*-benzoyloxymethyl-*N*-methylformamide (**3c**): A pale yellow solid, R_f 0.1 (EtOAc/petroleum ether = 1:5), mp = 38-39 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 7.98-7.96 (d, *J* = 8.8 Hz, 2H), 6.93-6.91 (d, *J* = 8.4 Hz, 2H), 5.51 (s, 2H), 3.86 (s, 3H), 3.01 (s, 3H); The ^{1}H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 164.1, 163.9, 131.8, 121.4, 113.7, 73.9, 55.5, 29.8 ppm; IR (KBr): υ_{max} 1710, 1691, 1425, 1261, 1070 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{13}NNaO_4$ $[M+Na]^+$ 246.0737, found 246.0730.



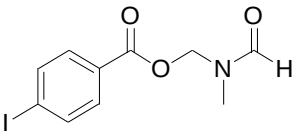
4-Fluoro-*N*-benzoyloxymethyl-*N*-methylformamide (**3d**): A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 8.05-8.03 (m, 2H), 7.15-7.11 (t, *J* = 8.4 Hz, 2H), 5.54 (s, 2H), 3.02 (s, 3H); The ^{1}H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1 (d, $J_{C, F}$ = 253.8 Hz), 165.1, 164.0, 132.4 (d, $J_{C, F}$ = 9.5 Hz), 125.3, 115.8 (d, $J_{C, F}$ = 20.9 Hz), 74.3, 29.9 ppm; IR (KBr): υ_{max} 1726, 1683, 1397, 1263, 1072 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}FNNaO_3$ $[M+Na]^+$ 234.0537, found 234.0532.



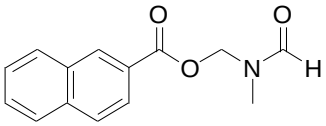
4-Chloro-*N*-benzoyloxymethyl-*N*-methylformamide (**3e**): A pale yellow solid, R_f 0.3 (EtOAc/petroleum ether = 1:5), mp = 34-35 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 7.97-7.94 (d, *J* = 8.4 Hz, 2H), 7.44-7.42 (t, *J* = 8.8 Hz, 2H), 5.54 (s, 2H), 3.02 (s, 3H); The ^{1}H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 164.0, 140.2, 131.1, 128.9, 127.5, 74.4, 29.9 ppm; IR (KBr): υ_{max} 1725, 1672, 1400, 1265, 1096 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}ClNNaO_3$ $[M+Na]^+$ 250.0241, found 250.0236.



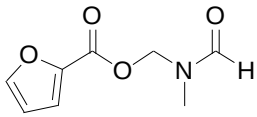
4-Bromo-*N*-benzoyloxymethyl-*N*-methylformamide (**3f**): A pale yellow solid, R_f 0.3 (EtOAc/petroleum ether = 1:5), mp = 45-46 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.89-7.87 (d, *J* = 8.4 Hz, 2H), 7.61-7.59 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 2H), 3.02 (s, 3H); The ^{1}H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 164.0, 131.9, 131.2, 128.9, 128.0, 74.4, 29.9 ppm; IR (KBr): υ_{max} 1724, 1671, 1398, 1262, 1074 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}BrNNaO_3$ $[M+Na]^+$ 293.9736, found 293.9735.



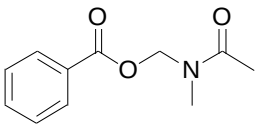
4-Iodo-*N*-benzoyloxymethyl-*N*-methylformamide (**3g**): A pale yellow solid, R_f 0.3 (EtOAc/petroleum ether = 1:5), mp = 50-51 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.84-7.82 (d, *J* = 8.4 Hz, 2H), 7.73-7.71 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 2H), 3.02 (s, 3H); The ^1H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 164.0, 138.0, 131.1, 128.6, 101.7, 74.4, 29.9 ppm; IR (KBr): υ_{max} 1719, 1673, 1395, 1262, 1072 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{10}INNaO_3$ $[M+Na]^+$ 341.9598, found 341.9591.



***N*-2-naphthoyloxymethyl-*N*-methylformamide** (**3i**): A pale yellow solid, R_f 0.15 (EtOAc/petroleum ether = 1:5), mp = 92-93 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 8.48 (s, 1H), 8.04-8.03 (d, *J* = 1.2 Hz, 1H), 8.02-8.01 (d, *J* = 1.6 Hz, 1H), 7.97-7.88 (m, 2H), 7.64-7.55 (m, 2H), 5.61 (s, 2H), 3.07 (s, 3H); The ^1H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 164.1, 135.7, 132.3, 131.5, 129.4, 128.7, 128.4, 127.8, 126.9, 126.2, 124.9, 74.3, 29.9 ppm; IR (KBr): υ_{max} 1720, 1676, 1397, 1270, 1070 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{13}NNaO_3$ $[M+Na]^+$ 266.0788, found 266.0785.

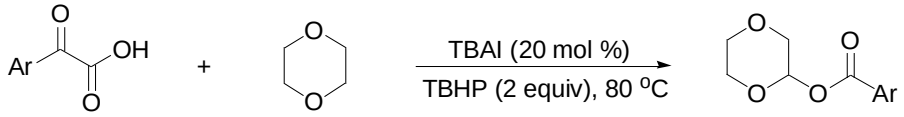


***N*-furoyloxymethyl-*N*-methylformamide** (**3j**): A pale yellow oil, R_f 0.1 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.64 (s, 1H), 7.25 (m, 1H), 6.56 (m, 1H), 5.54 (s, 2H), 3.03 (s, 3H); The ^1H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 158.0, 147.1, 143.5, 119.2, 112.1, 74.0, 29.9 ppm; IR (KBr): υ_{max} 1733, 1686, 1397, 1299, 1072 cm^{-1}; HRMS (ESI) calcd for $C_8H_9NNaO_4$ $[M+Na]^+$ 206.0424, found 206.0424.



***N*-Benzoyloxymethyl-*N*-methylacetamide** (**3l**): A pale yellow oil, R_f 0.3 (EtOAc/petroleum ether = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01-8.00 (d, *J* = 6.8 Hz, 2H), 7.59-7.52 (m, 1H), 7.45-7.38 (m, 2H), 5.59 (s, 2H), 3.07 (s, 3H), 2.27 (s, 3H); The ^{1}H NMR spectrum also displayed a minor set of signals due to amide rotamers. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 165.9, 133.5, 129.7, 129.1, 128.4, 75.3, 33.7, 21.1 ppm; IR (KBr): υ_{max} 1722, 1675, 1397, 1267, 1095 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{13}NNaO_3$ $[M+Na]^+$ 230.0788, found 230.0786.

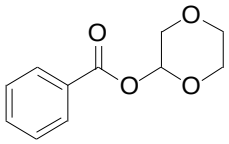
General Procedure for the Decarboxylative Acyloxylation of 1,4-Dioxane



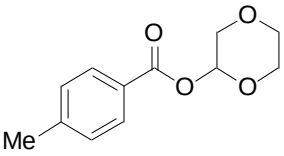
1 **4a** **5**

A 10 mL oven-dried Schlenk-tube was charged with TBAI (14.8 mg, 20 mol %). The tube was evacuated and backfilled with nitrogen (three times). *α*-Oxocarboxylic acids (**1**, 0.2 mmol, 1.0 equiv) and *tert*-butyl hydroperoxide (TBHP, 0.4 mmol, 2.0 equiv) in 1,4-dioxane (1 mL) were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 4 h at 80 ^{o}C. Upon completion of the reaction (monitored by TLC), the mixture was diluted with EtOAc, filtered through a pad of Celite. After the solvent was removed, the residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/15 to 1/6) to give the corresponding products **5** in yields listed in Table 3.

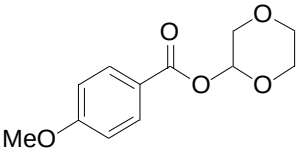
Characterization of Products 5



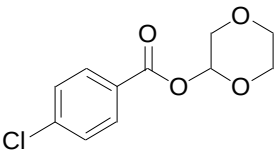
Benzoic acid [1,4]dioxan-2-yl ester (**5a**):[2a] R_f 0.3 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14-8.12 (d, *J* = 7.6 Hz, 2H), 7.60-7.57 (t, *J* = 7.2 Hz, 1H), 7.48-7.44 (t, *J* = 7.6 Hz, 2H), 6.10 (s, 1H), 4.25-4.19 (m, 1H), 3.89 (s, 2H), 3.84-3.82 (m, 2H), 3.70-3.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 133.4, 129.9, 129.7, 128.4, 89.8, 67.8, 66.1, 61.7 ppm.



4-Methyl-benzoic acid [1,4]dioxan-2-yl ester (**5b**):[2b] R_f 0.3 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02-8.00 (d, *J* = 8.0 Hz, 2H), 7.26-7.24 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 1H), 4.24-4.18 (m, 1H), 3.88 (s, 2H), 3.83-3.81 (m, 2H), 3.69-3.65 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 144.1, 129.9, 129.1, 126.9, 89.5, 67.8, 66.1, 61.7, 21.6 ppm.

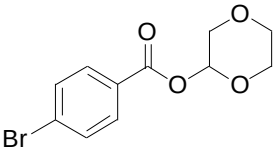


4-Methoxy-benzoic acid [1,4]dioxan-2-yl ester (**5c**):[2a] R_f 0.1 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-8.68 (m, 2H), 6.95-6.92 (m, 2H), 6.07 (s, 1H), 4.24-4.18 (m, 1H), 3.89-3.87 (m, 5H), 3.83-3.81 (m, 2H), 3.69-3.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 163.7, 132.0, 122.0, 113.7, 89.4, 67.9, 66.1, 61.8, 55.4 ppm.

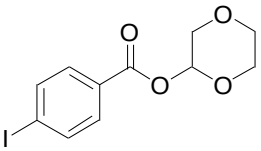


4-Chloro-benzoic acid [1,4]dioxan-2-yl ester (**5d**):[2a] R_f 0.2 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.04(d, *J* = 8.8 Hz, 2H), 7.44-7.42 (d, *J*

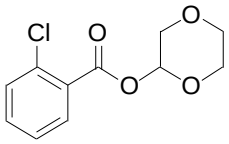
= 8.8 Hz, 2H), 6.09-6.08 (t, *J* = 1.6 Hz, 1H), 4.23-4.17 (m, 1H), 3.89 (s, 2H), 3.84-3.82 (m, 2H), 3.70-3.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 139.9, 131.3, 128.8, 128.1, 90.0, 67.7, 66.1, 61.7 ppm.



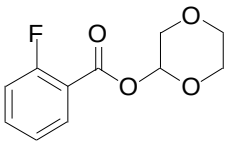
4-Bromo-benzoic acid [1,4]dioxan-2-yl ester (**5e**):[2a] R_f 0.2 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98-7.96(d, *J* = 8.0 Hz, 2H), 7.60-7.58 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.22-4.16 (m, 1H), 3.88 (s, 2H), 3.83-3.81 (m, 2H), 3.68-3.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 131.8, 131.3, 128.6, 90.0, 67.7, 66.0, 61.7 ppm.



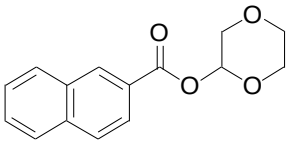
4-Iodo-benzoic acid [1,4]dioxan-2-yl ester (**5f**): A pale yellow solid, R_f 0.3 (EtOAc/petroleum ether = 1:6); mp = 115-117 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 4H), 6.08 (s, 1H), 4.21-4.16 (m, 1H), 3.88 (s, 2H), 3.83-3.82 (m, 2H), 3.69-3.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 137.8, 131.3, 129.1, 101.4, 90.0, 67.7, 66.1, 61.7 ppm; IR (KBr): υ_{max} 2967, 2855, 1725, 1585, 1258 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}INaO_4$ $[M+Na]^+$ 356.9594, found 356.9588.



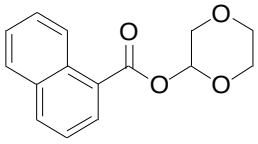
2-Chloro-benzoic acid [1,4]dioxan-2-yl ester (**5g**): A pale yellow oil, R_f 0.2 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94-7.92 (m, 1H), 7.47-7.42 (m, 2H), 7.35-7.31 (m, 1H), 6.11 (s, 1H), 4.28-4.21 (m, 1H), 3.89 (s, 2H), 3.83-3.81 (m, 2H), 3.70-3.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 134.0, 132.9, 131.8, 131.2, 129.4, 126.6, 90.4, 67.6, 66.0, 61.8 ppm; IR (KBr): υ_{max} 2975, 2857, 1737, 1571, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}ClNaO_4$ $[M+Na]^+$ 265.0238, found 265.0243.



2-Fluoro-benzoic acid [1,4]dioxan-2-yl ester (**5h**): A pale yellow oil, R_f 0.2 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03-7.99 (t, *J* = 7.6 Hz, 1H), 7.58-7.53 (m, 1H), 7.26-7.14 (m, 2H), 6.12 (s, 1H), 4.28-4.22 (m, 1H), 3.89 (s, 2H), 3.84-3.83 (m, 2H), 3.70-3.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0 (d, $J_{C,F}$ = 4.0 Hz), 162.2 (d, $J_{C,F}$ = 260.0 Hz), 134.9 (d, $J_{C,F}$ = 9.0 Hz), 132.3, 124.0 (d, $J_{C,F}$ = 4.0 Hz), 118.3 (d, $J_{C,F}$ = 10.0 Hz), 117.1 (d, $J_{C,F}$ = 22.0 Hz), 90.2, 67.7, 66.1, 61.7 ppm; IR (KBr): υ_{max} 2975, 2859, 1736, 1584, 1296 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}FNaO_4$ $[M+Na]^+$ 249.0534, found 249.0543.

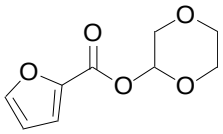


Naphthalene-2-carboxylic acid [1,4]dioxan-2-yl ester (**5i**): A pale yellow solid, R_f 0.2 (EtOAc/petroleum ether = 1:6); mp = 88-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 8.15-8.12 (d, *J* = 8.8 Hz, 1H), 7.99-7.97 (d, *J* = 8.0 Hz, 1H), 7.91-7.87 (m, 2H), 7.62-7.53 (m, 2H), 6.18 (s, 1H), 4.32-4.26 (m, 1H), 3.95 (s, 2H), 3.87-3.86 (m, 2H), 3.73-3.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 135.7, 132.4, 131.5, 129.4, 128.4, 128.2, 127.7, 126.9, 126.7, 125.3, 89.8, 67.9, 66.1, 61.8 ppm; IR (KBr): υ_{max} 2974, 2857, 1724, 1582, 1263 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{14}NaO_4$ $[M+Na]^+$ 281.0784, found 281.0787.

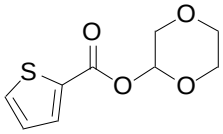


Naphthalene-1-carboxylic acid [1,4]dioxan-2-yl ester (**5j**):[2b] R_f 0.2 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.04-9.02 (d, *J* = 7.6 Hz, 1H), 8.37-8.35 (d, *J* = 7.2 Hz, 1H), 8.07-8.05 (d, *J* = 8.0 Hz, 1H), 7.91-7.89 (d, *J* = 8.4 Hz, 1H), 7.66-7.62 (t, *J* = 7.6 Hz, 1H), 7.57-7.51 (m, 2H), 6.22 (s, 1H), 4.31-4.25 (m, 1H), 3.97 (s, 2H), 3.87-3.85 (m, 2H), 3.75-3.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 134.0, 133.8, 131.5, 130.9, 128.6, 128.0, 126.3, 126.1,

125.7, 124.4, 89.8, 67.9, 66.1, 61.9 ppm.



Furan-2-carboxylic acid [1,4]dioxan-2-yl ester (**5k**):[2a] R_f 0.1 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 1H), 7.30-7.29 (d, *J* = 3.6 Hz, 1H), 6.54-6.52 (q, *J* = 1.6 Hz, 1H), 6.06 (s, 1H), 4.23-4.16 (m, 1H), 3.86 (s, 2H), 3.82-3.80 (m, 2H), 3.68-3.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 146.9, 144.0, 118.9, 111.9, 89.7, 67.7, 66.0, 61.7 ppm.



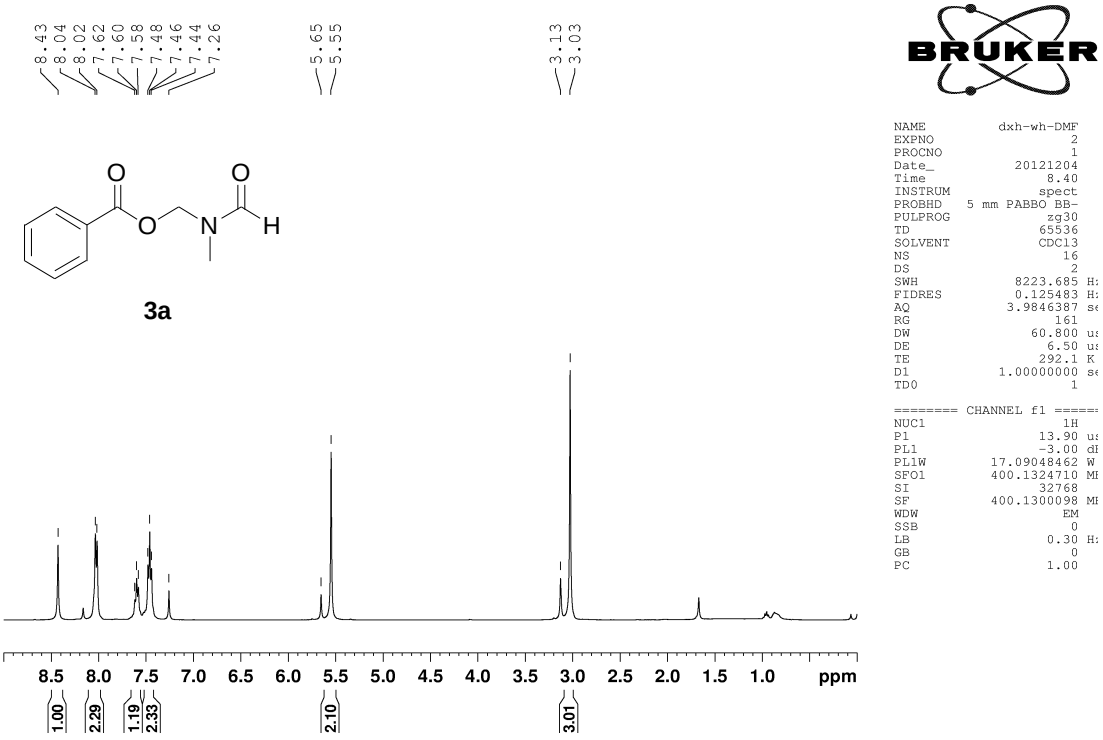
Thiophene-2-carboxylic acid [1,4]dioxan-2-yl ester (**5l**):[2a] R_f 0.1 (EtOAc/petroleum ether = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90-7.89 (m, 1H), 7.61-7.60 (q, *J* = 1.2 Hz, 1H), 7.13-7.11 (t, *J* = 4.0 Hz, 1H), 6.05 (s, 1H), 4.23-4.17 (m, 1H), 3.86 (s, 2H), 3.82-3.80 (m, 2H), 3.68-3.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 134.1, 133.2, 127.8, 89.9, 67.7, 66.0, 61.7 ppm.

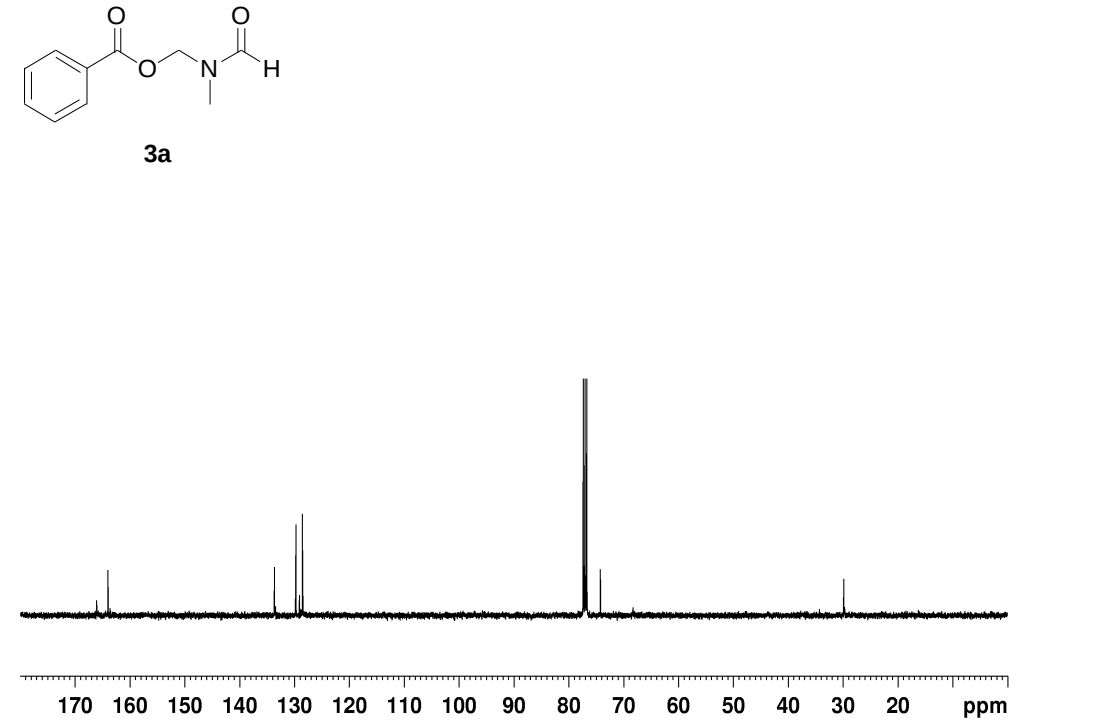
References

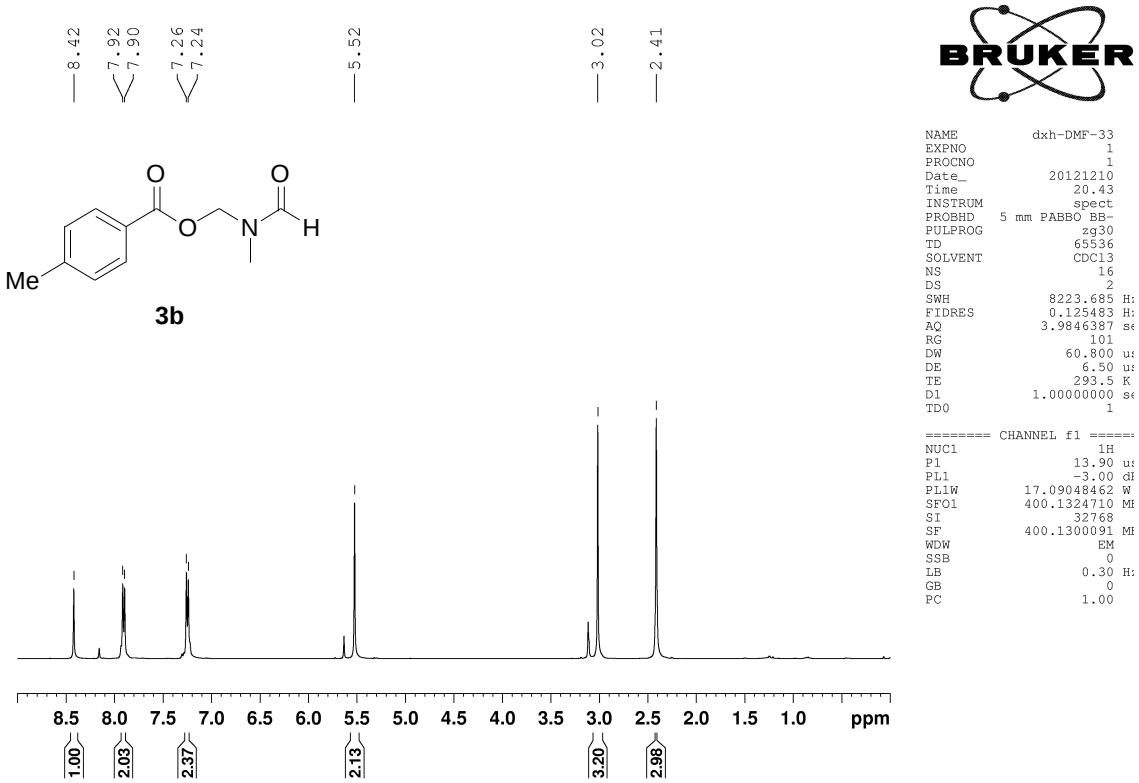
1. K. Wadhwa, C. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun.*, 2008, **38**, 4434.

2. (a) L. Chen, E. Shi, Z. Liu, S. Chen, W. Wei, H. Li, K. Xu and X. Wan, *Chem. Eur. J.*, 2011, **17**, 4085. (b) Z.-Q. Liu, L. Zhao, X. Shang and Z. Cui, *Org. Lett.*, 2012, **14**, 3218.

^{1}H NMR and ^{13}C NMR Spectra of the Products



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3.02
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PROCNO 1
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TD 65536
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FIDRES 0.125483 H
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RG 101
DW 60.800 u
DE 6.50 u
TE 293.5 K
D1 1.00000000 s
TD0 1
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PL1 -3.00 d
PL1W 17.09048462 W
SFO1 400.1324710 M
SI 32768
SF 400.1300091 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
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 ppm
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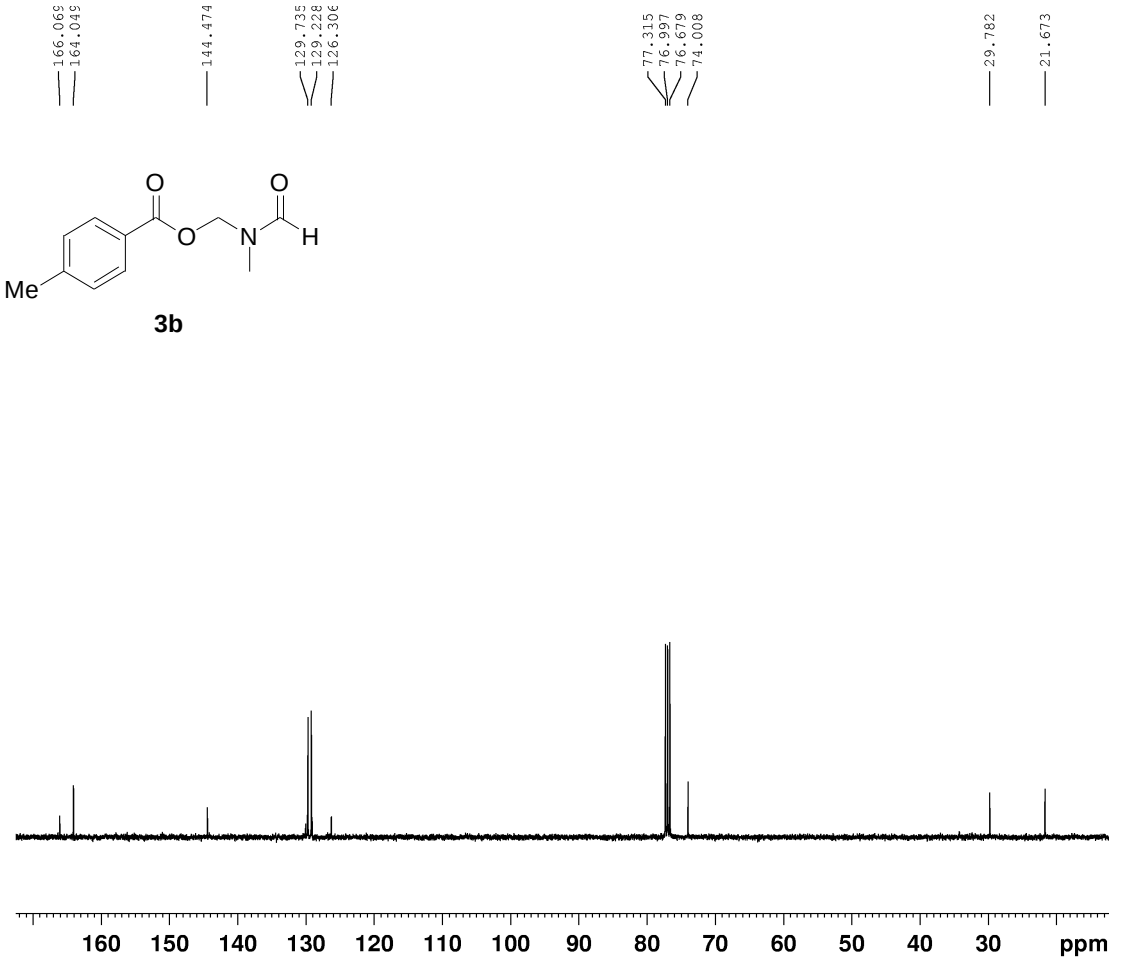
2.13
3.20
2.98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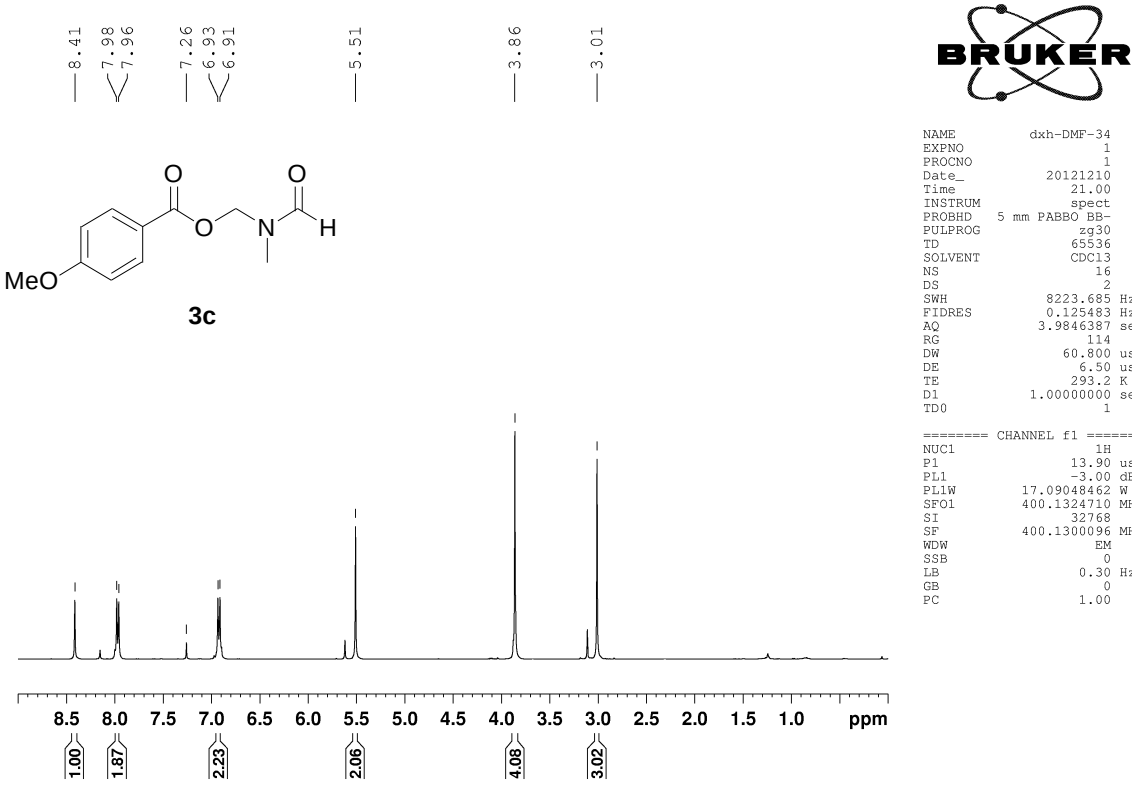
164.049
144.474
129.735
129.228
126.306
77.315
76.997
76.679
74.008
29.782
21.673
Me
3b
160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm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5.51
3.86
3.01
MeO
3c
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PROCNO 1
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Time 21.00
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TD 65536
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DS 2
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FIDRES 0.125483 Hz
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RG 114
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DE 6.50 us
TE 293.2 K
D1 1.00000000 sec
TD0 1
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SFO1 400.1324710 MHz
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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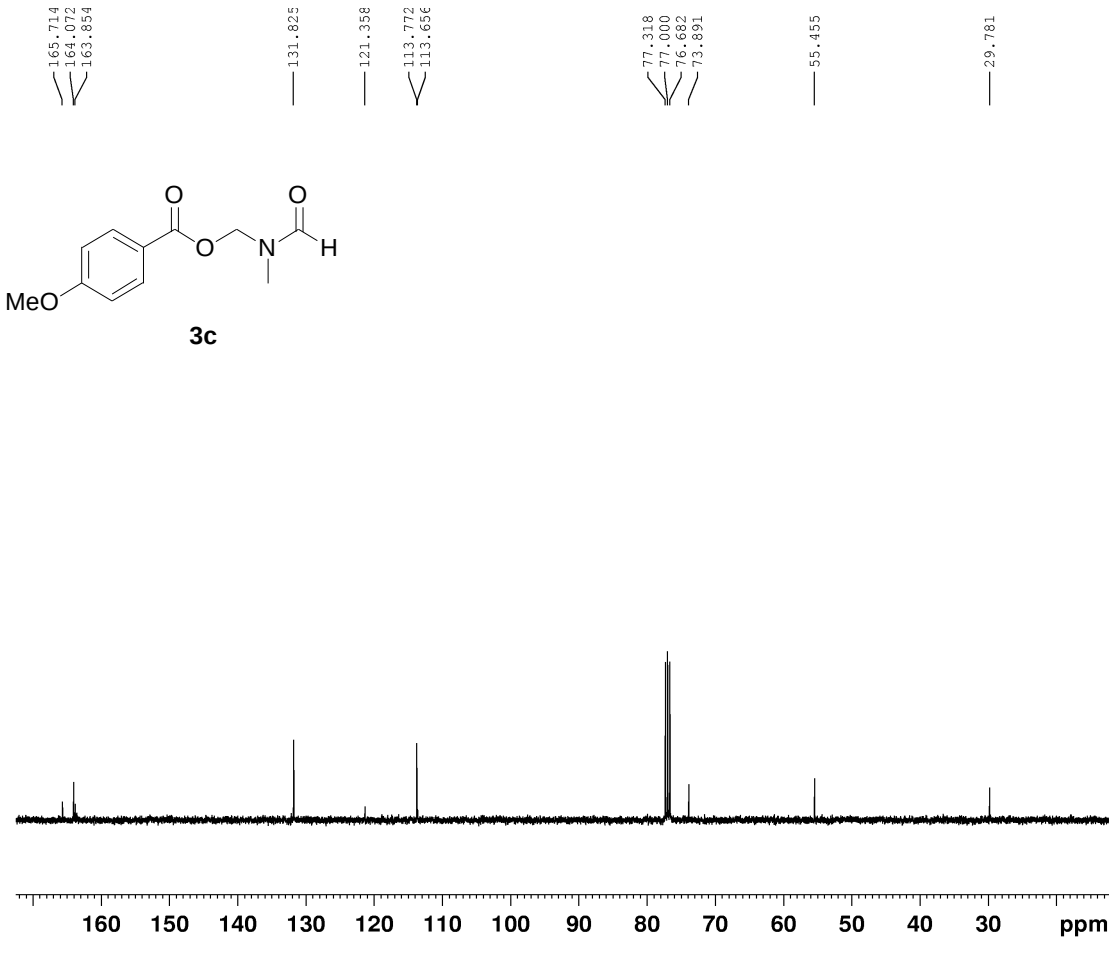
4.08
3.02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MeO
3c
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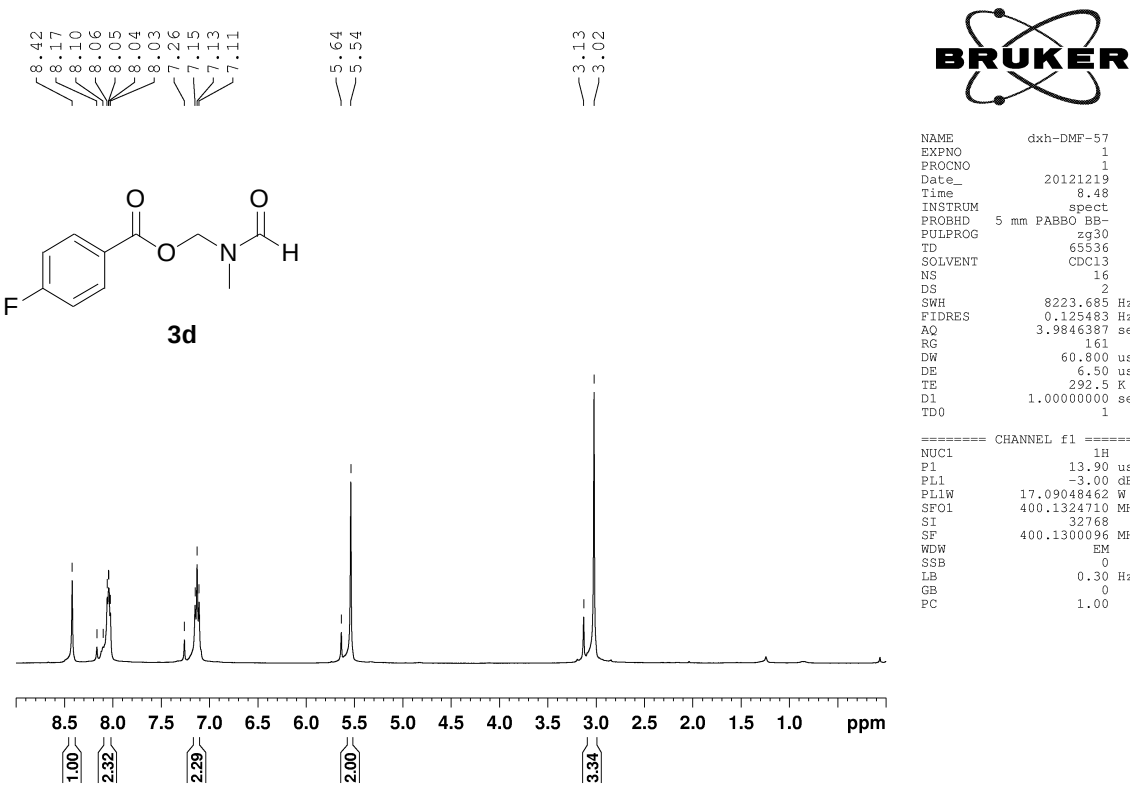
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8.17
8.10
8.06
8.05
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8.03
7.26
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7.13
7.11
5.64
5.54
3.13
3.02
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PROCNO 1
Date_ 20121219
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FIDRES 0.125483 Hz
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RG 161
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DE 6.50 us
TE 292.5 K
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TD0 1
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PL1 -3.00 dB
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SFO1 400.1324710 MH
SI 32768
SF 400.1300096 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
O
N
H
F
3d
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
1.0
ppm
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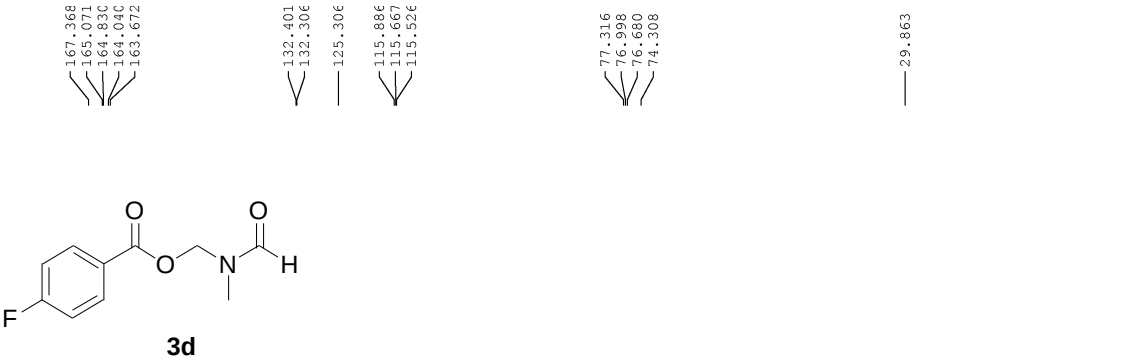
2.29
2.00
3.34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164.04C
163.672
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132.30E
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115.88E
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77.316
76.998
76.680
74.308
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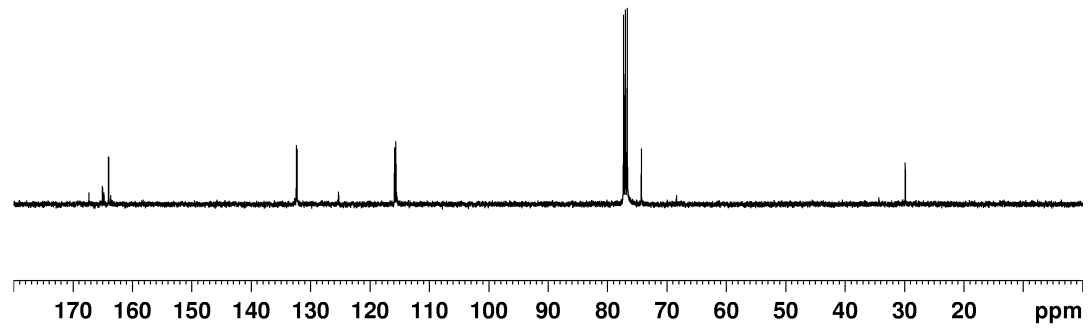
O
O
O
N
H
F
3d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160
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120
110
100
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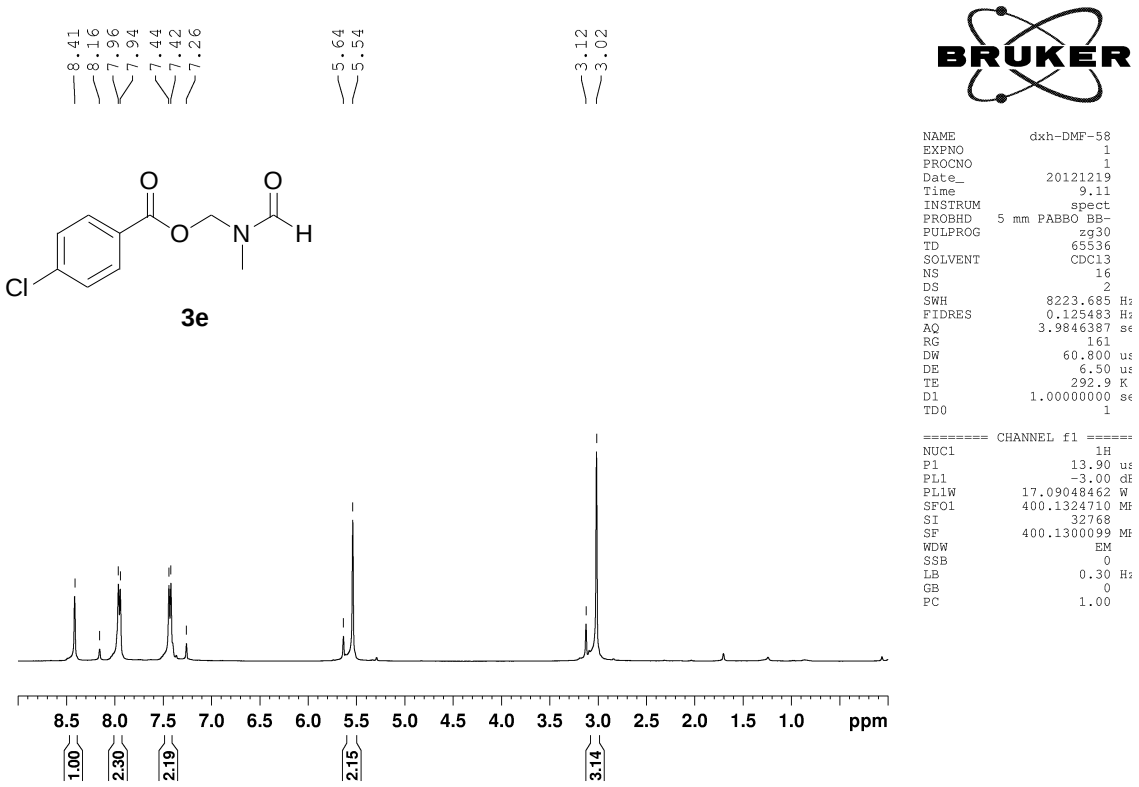
80
70
60
50
40
30
20
ppm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EXPNO 1
PROCNO 1
Date_ 20121219
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SI 32768
SF 400.1300099 MH
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LB 0.30 Hz
GB 0
PC 1.00
O
O
O
N
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Cl
3e
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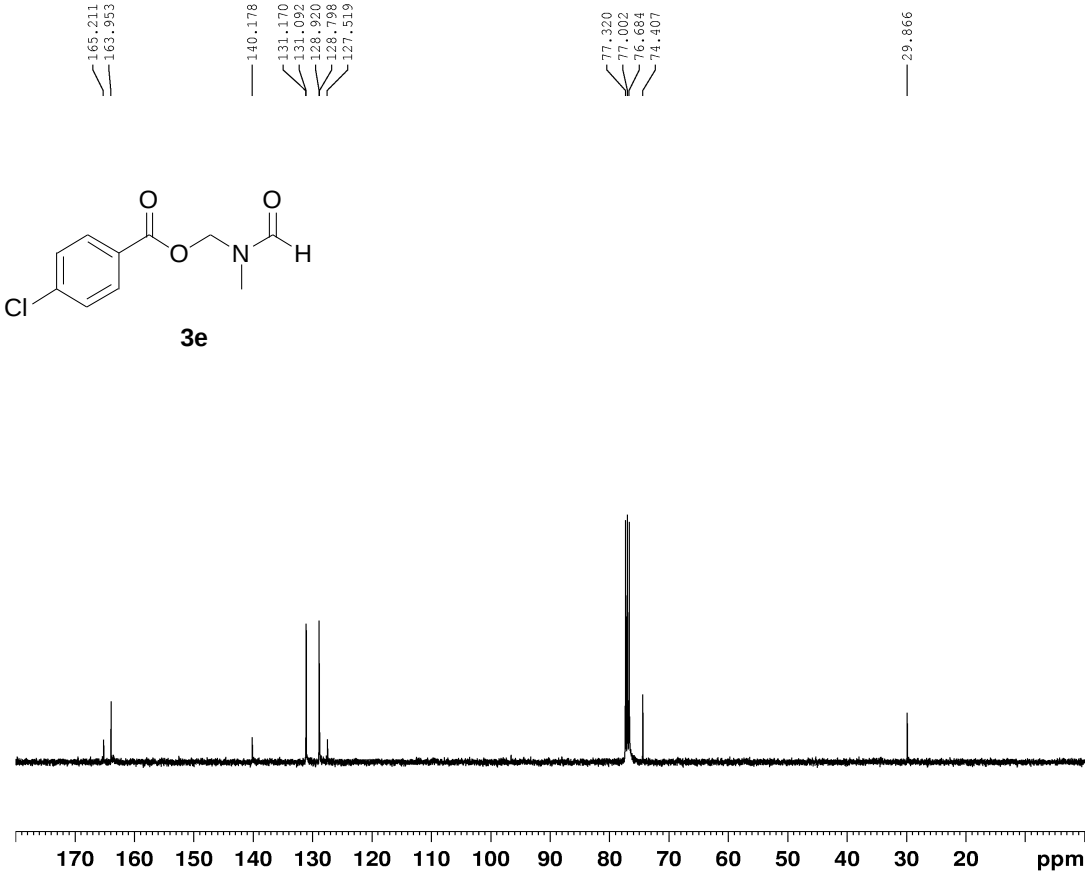
3.14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O
O
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H
Cl
3e
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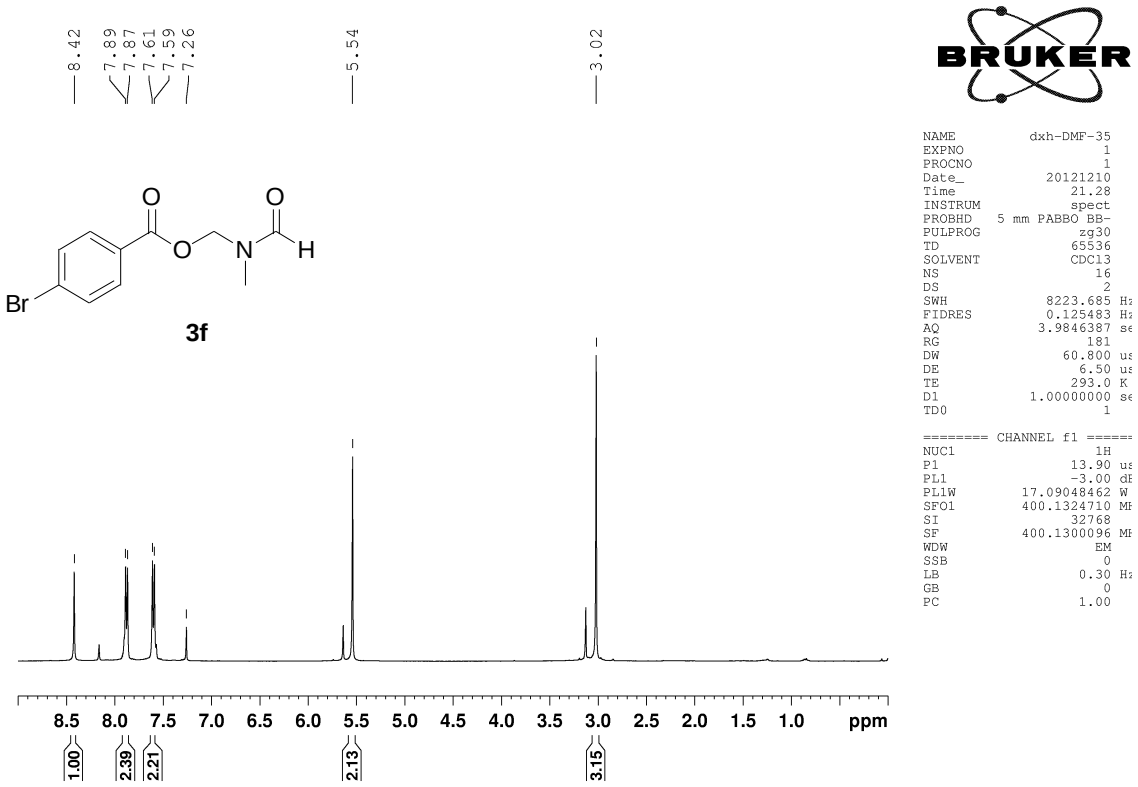
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H
Br
3f
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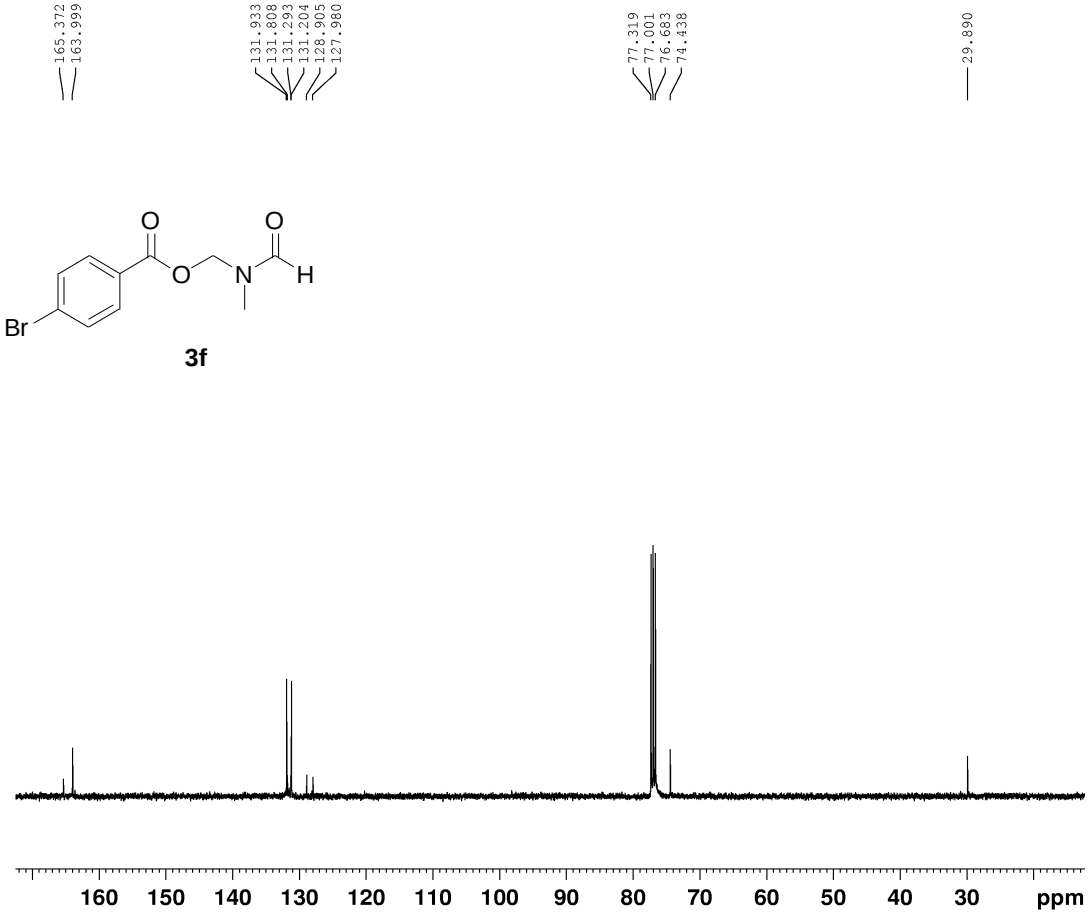
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Br
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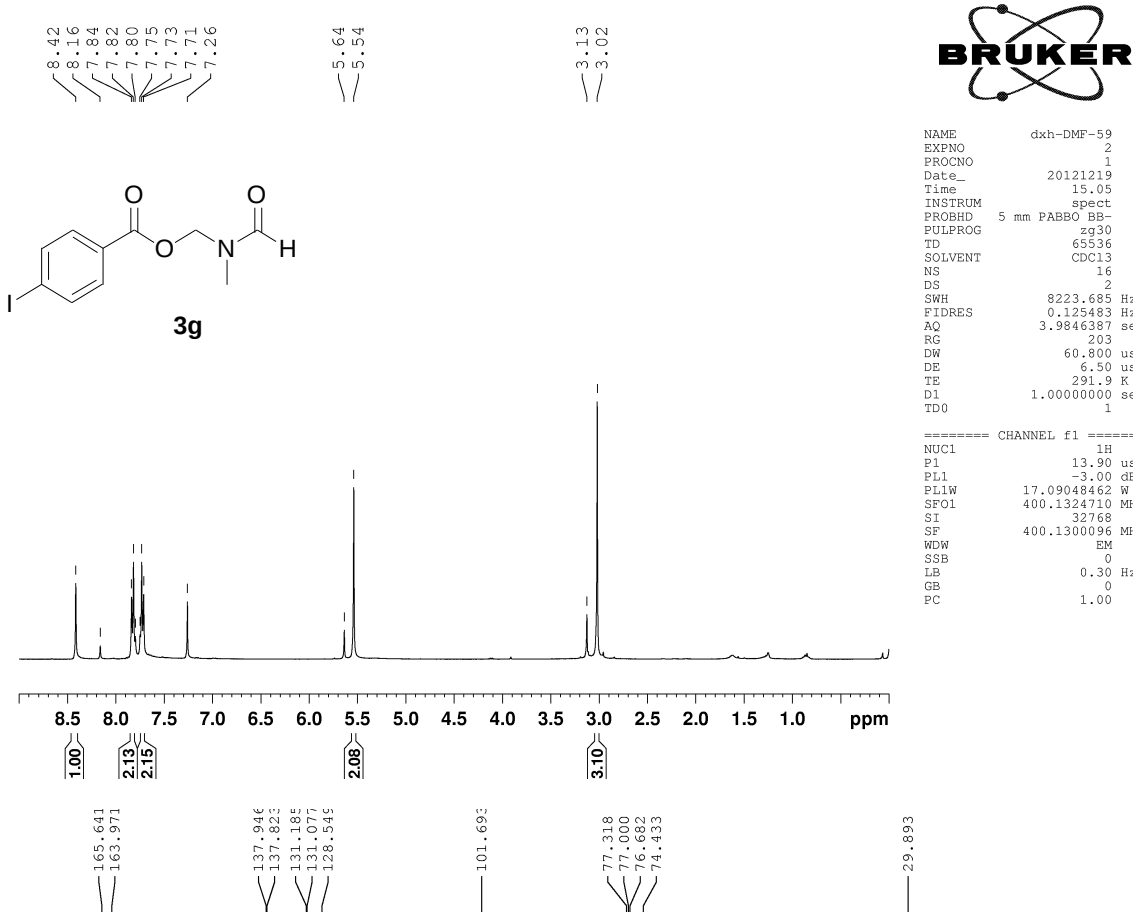
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SI 32768
SF 400.1300096 MH
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PC 1.00
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2.13
2.15
2.08
3.10

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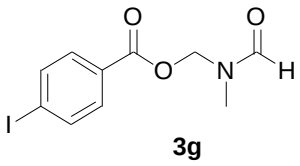
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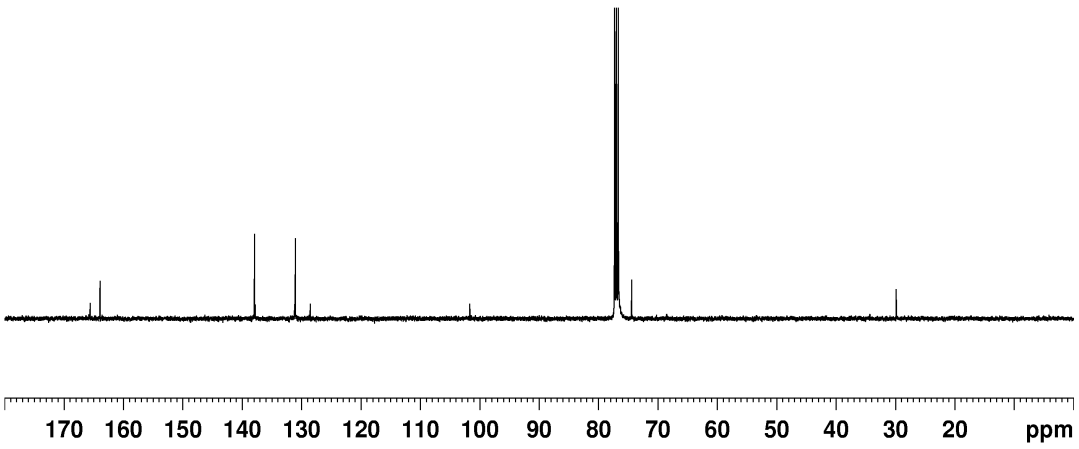
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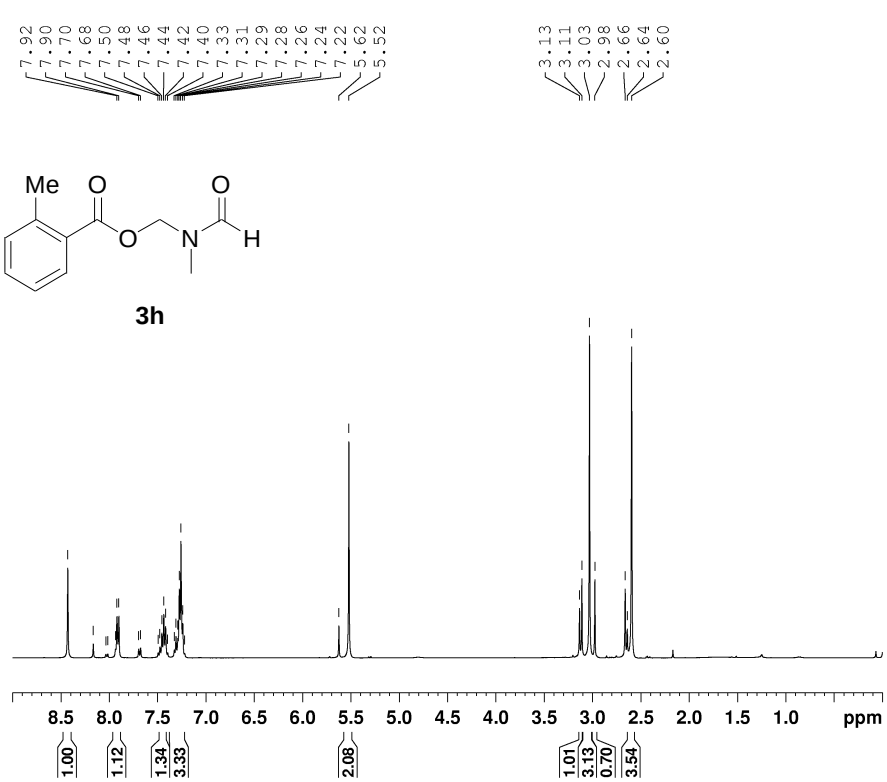


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SI                   32768
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WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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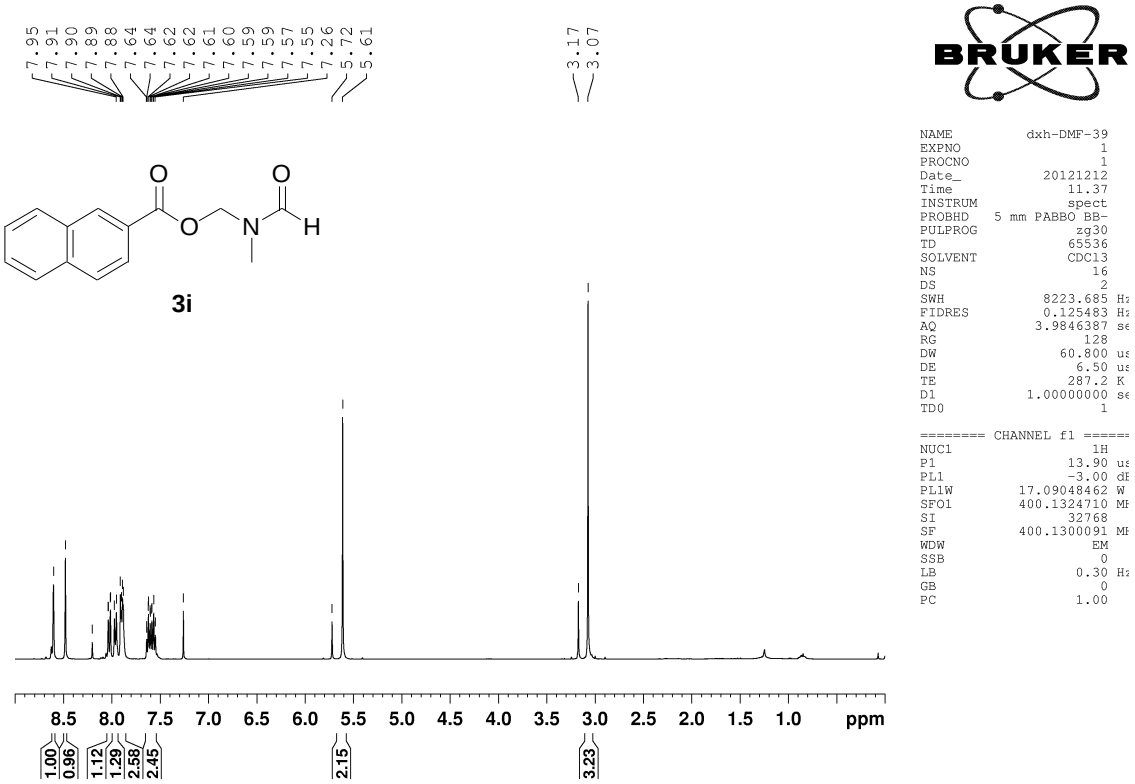
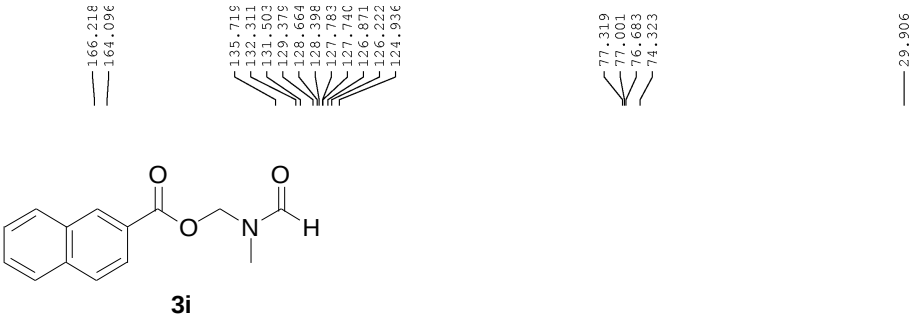
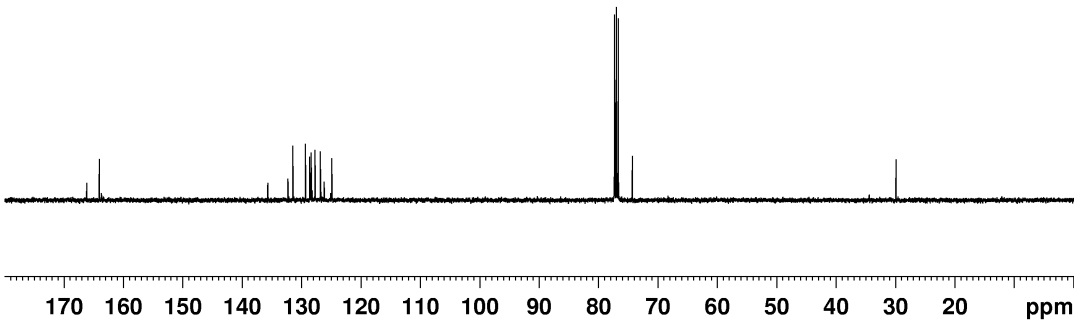
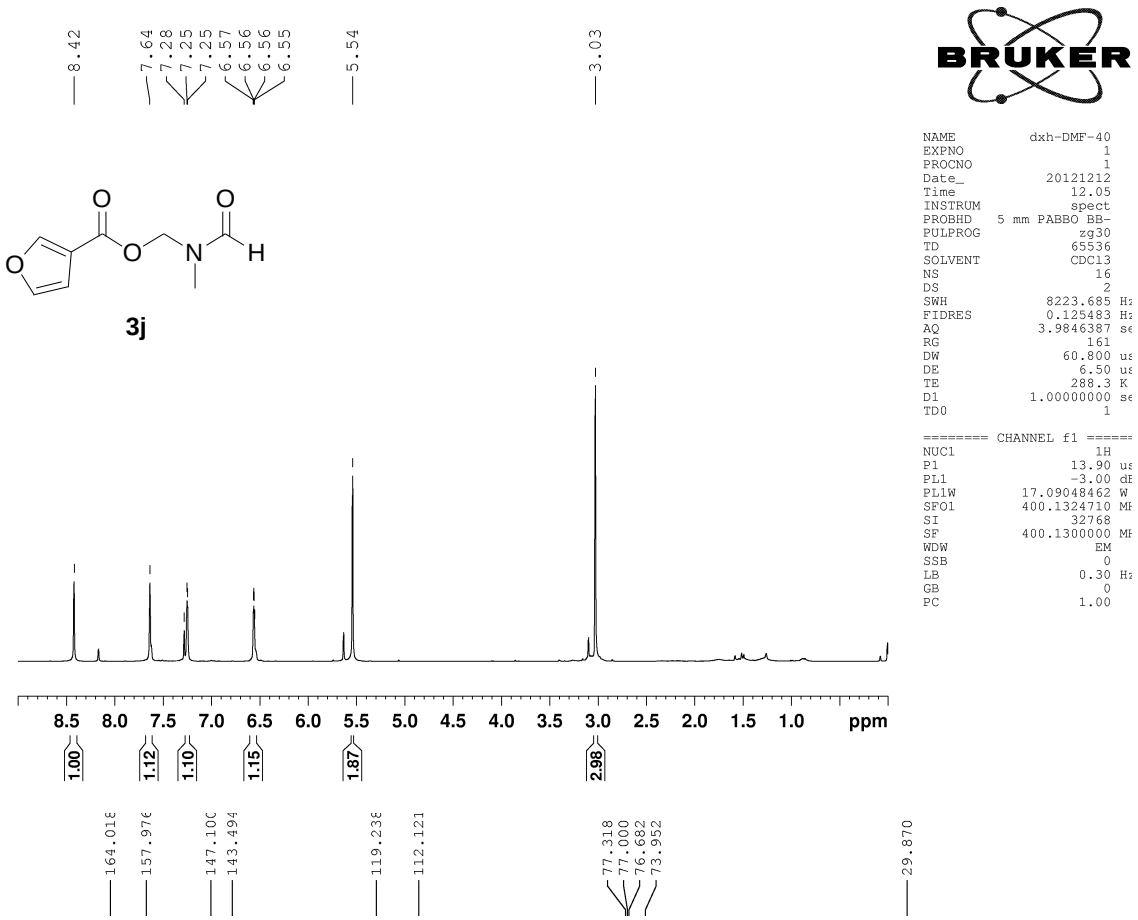
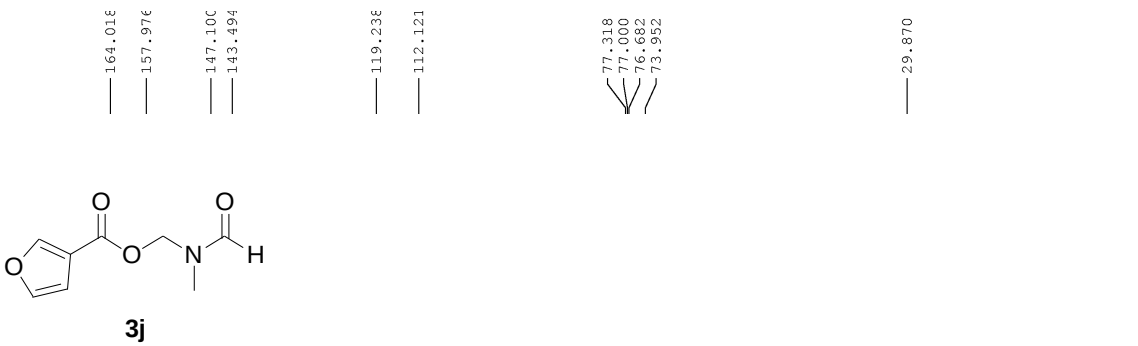
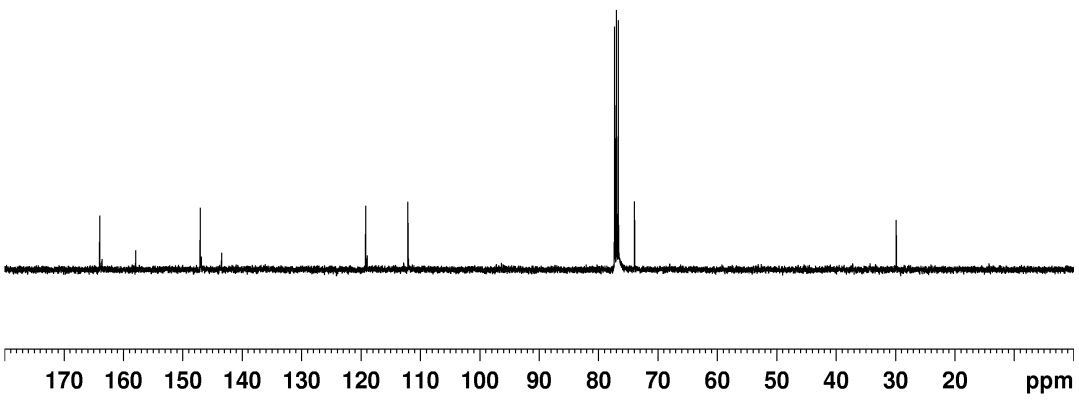

7.95
7.91
7.90
7.89
7.88
7.64
7.64
7.62
7.62
7.61
7.60
7.59
7.59
7.57
7.55
7.26
5.72
5.61
3.17
3.07
O
O
O
N
H
3i
NAME dxh-DMF-39
EXPNO 1
PROCNO 1
Date_ 20121212
Time 11.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 se
RG 128
DW 60.800 us
DE 6.50 us
TE 287.2 K
D1 1.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 13.90 us
PL1 -3.00 dB
PL1W 17.09048462 W
SFO1 400.1324710 MH
SI 32768
SF 400.1300091 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
1.00 0.96 1.12 1.29 2.58 2.45 2.15 3.23

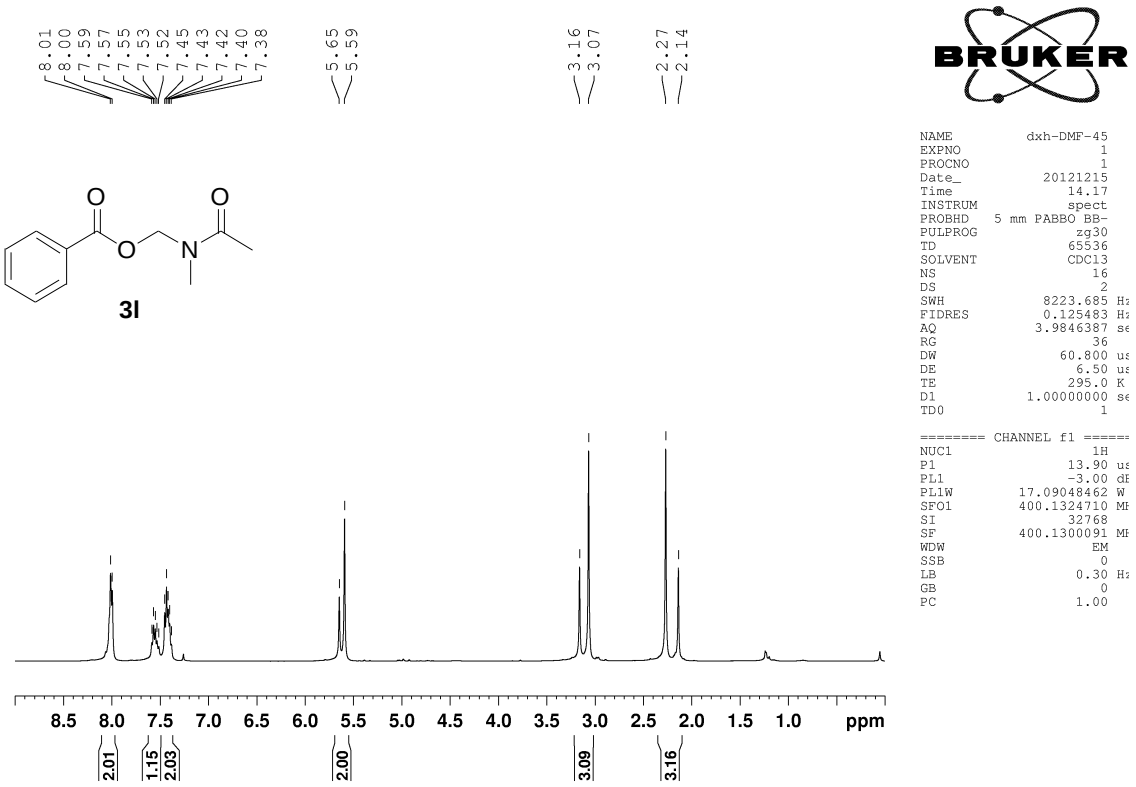

166.218
164.096
135.719
132.311
131.503
129.379
128.664
128.398
127.783
127.740
126.871
126.222
124.936
77.319
77.001
76.683
74.323
29.906
O
O
O
N
H
3i

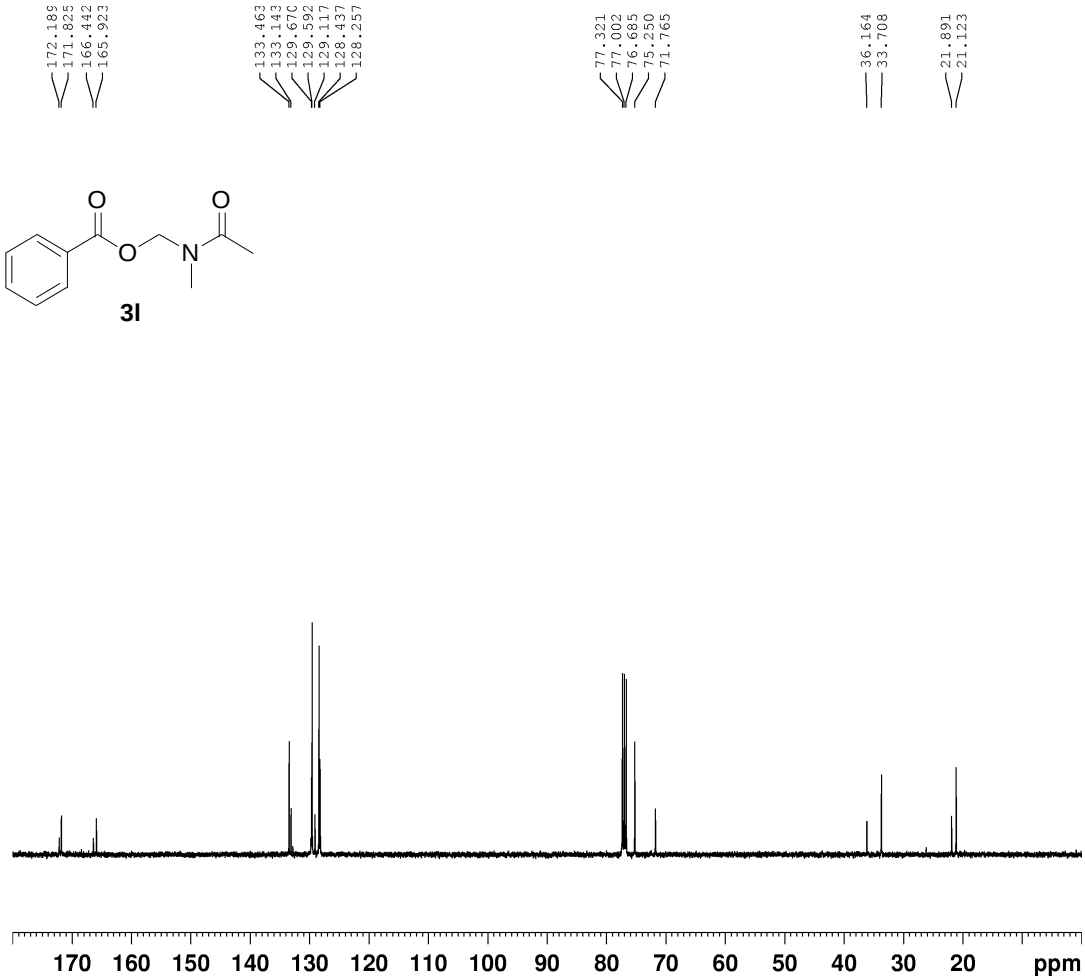

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

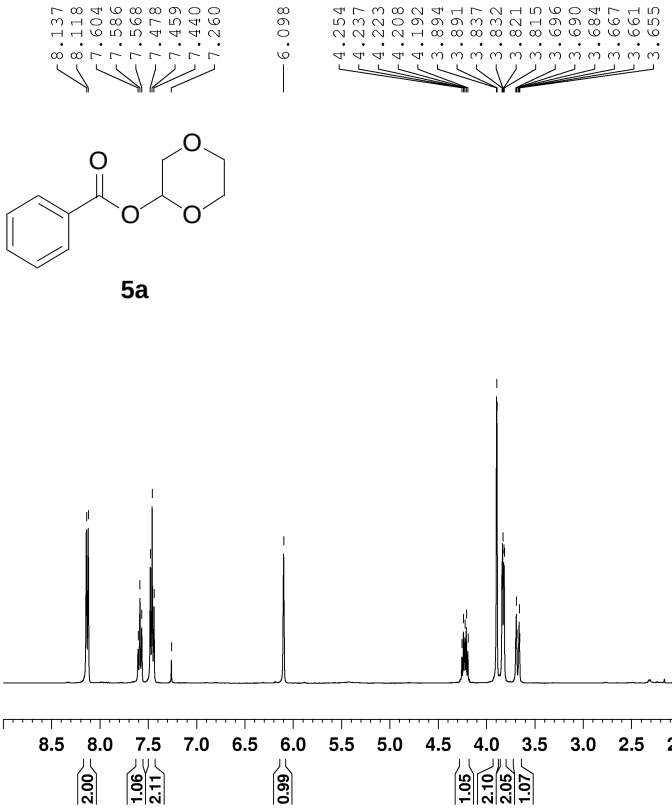

8.42
7.64
7.28
7.25
7.25
6.57
6.56
6.56
6.55
5.54
3.03
BRUKER
NAME dxh-DMF-40
EXPNO 1
PROCNO 1
Date_ 20121212
Time 12.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 161
DW 60.800 us
DE 6.50 us
TE 288.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 13.90 us
PL1 -3.00 dB
PL1W 17.09048462 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
O
O
N
H
3j
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 ppm
1.00
1.12
1.10
1.15
1.87
2.98


164.018
157.976
147.100
143.494
119.238
112.121
77.318
77.000
76.682
73.952
29.870
O
O
O
O
N
H
3j

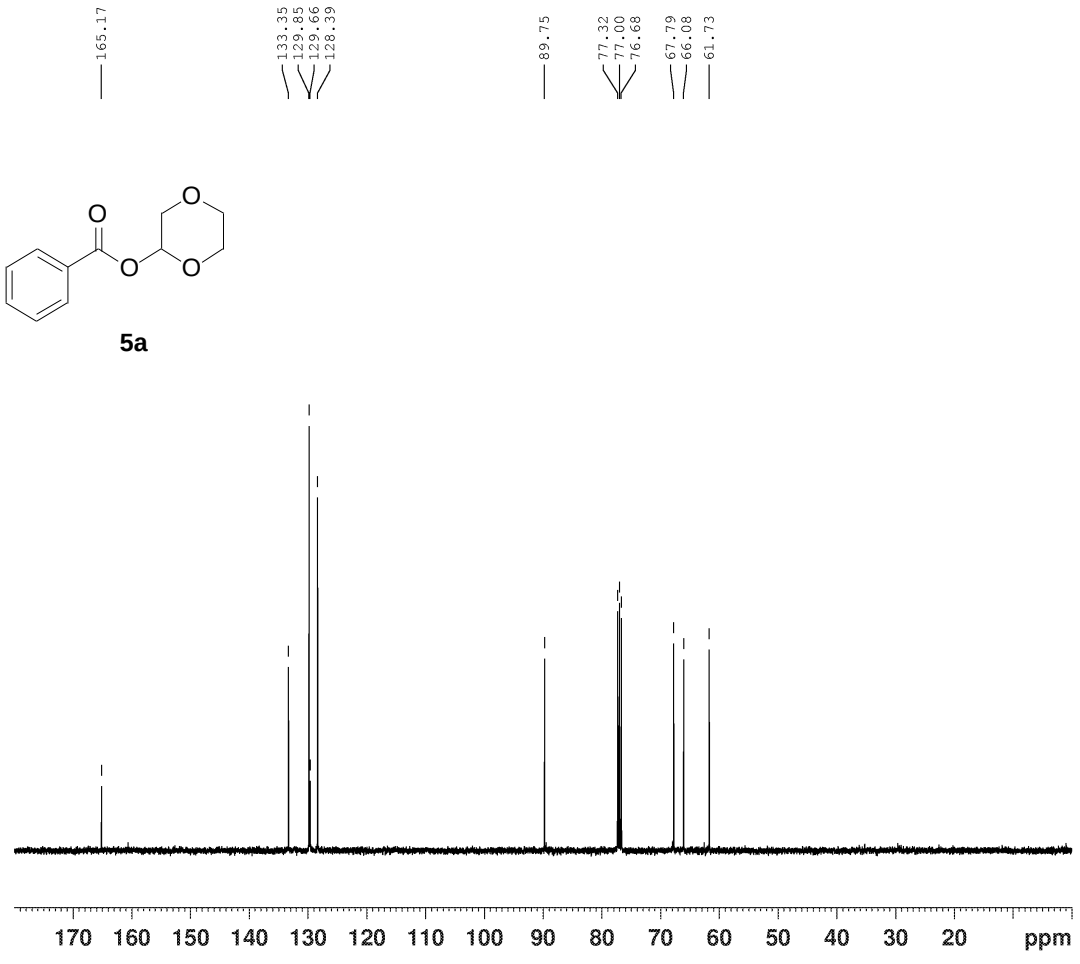

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

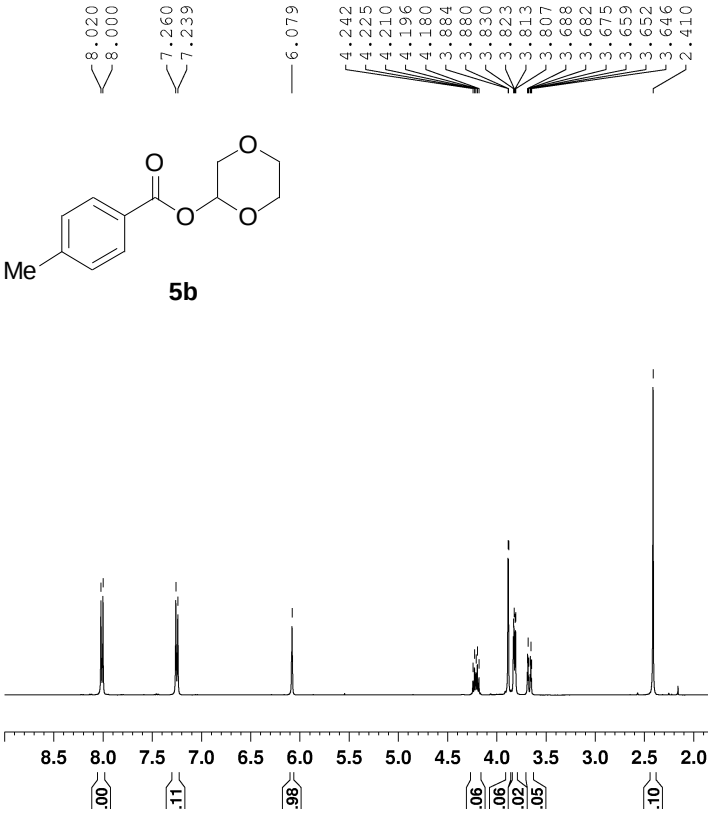

8.01
8.00
7.59
7.57
7.55
7.53
7.52
7.45
7.43
7.42
7.40
7.38
5.65
5.59
3.16
3.07
2.27
2.14
BRUKER
NAME dxh-DMF-45
EXPNO 1
PROCNO 1
Date_ 20121215
Time 14.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 se
RG 36
DW 60.800 us
DE 6.50 us
TE 295.0 K
D1 1.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 13.90 us
PL1 -3.00 dB
PL1W 17.09048462 W
SFO1 400.1324710 MH
SI 32768
SF 400.1300091 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
O
N
3l
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
ppm
2.01
1.15
2.03
2.00
3.09
3.16

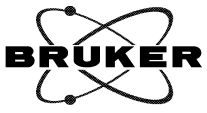

172.188
171.825
166.442
165.923
133.463
133.143
129.670
129.592
129.117
128.437
128.257
77.321
77.002
76.685
75.250
71.765
36.164
33.708
21.891
21.123
O
O
O
N
3l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



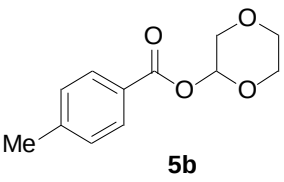
```
NAME          dxh-Dioxone-1
EXPNO                     2
PROCNO                    1
Date_              20121122
Time                  21.52
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 H
FIDRES             0.125483 H
AQ                 3.9846387 s
RG                      45.2
DW                    60.800 u
DE                     6.50 u
TE                   295.2 K
D1                1.00000000 s
TD0                       1

======== CHANNEL f1 =====
NUC1                      1H
P1                     13.90 u
PL1                    -3.00 d
PL1W          17.09048462 W
SFO1          400.1324710 M
SI                     32768
SF            400.1300096 M
WDW                       EM
SSB                        0
LB                     0.30 H
GB                         0
PC                      1.00
```

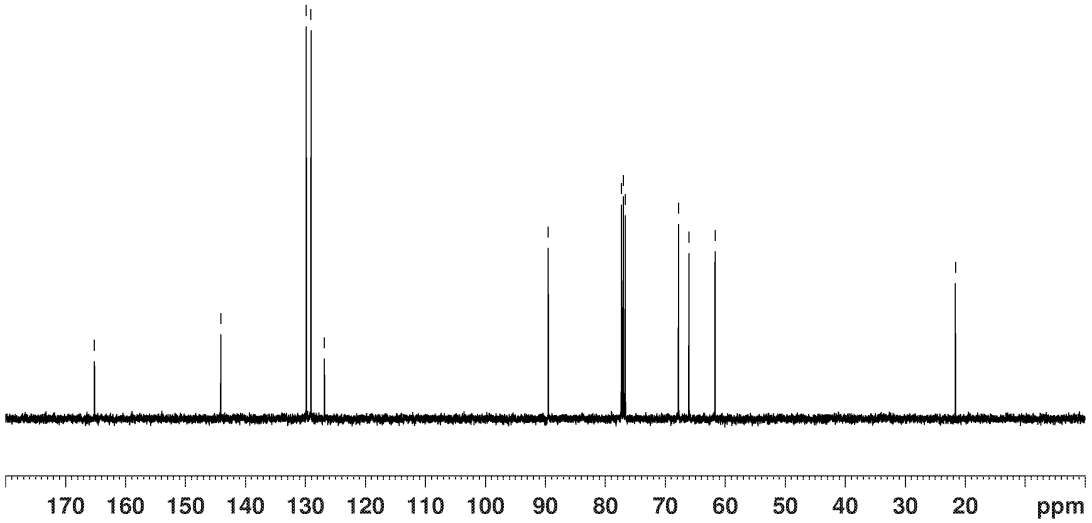


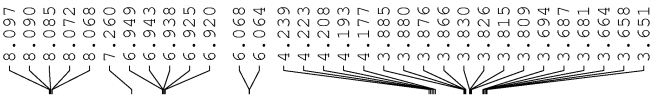


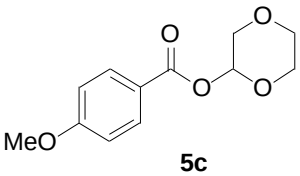



```
NAME      dxh-dioxone-32
EXPNO                  1
PROCNO                 1
Date_           20121130
Time               21.43
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 H
FIDRES          0.125483 H
AQ              3.9846387 s
RG                  40.3
DW                60.800 u
DE                 6.50 u
TE                292.8 K
D1           1.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                13.90 u
PL1               -3.00 d
PL1W        17.09048462 W
SFO1        400.1324710 M
SI                 32768
SF          400.1300094 M
WDW                   EM
SSB                    0
LB                0.30 H
GB                     0
PC                1.00
```

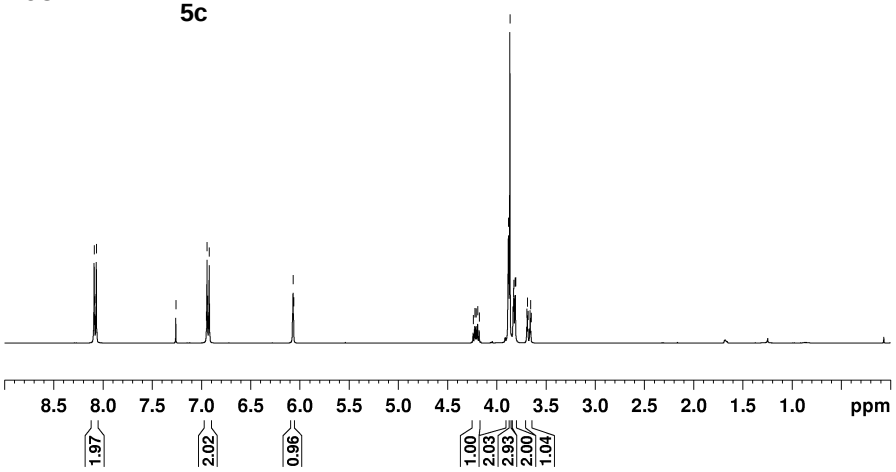




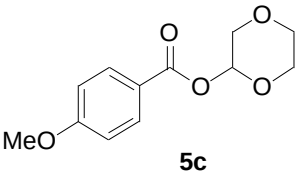




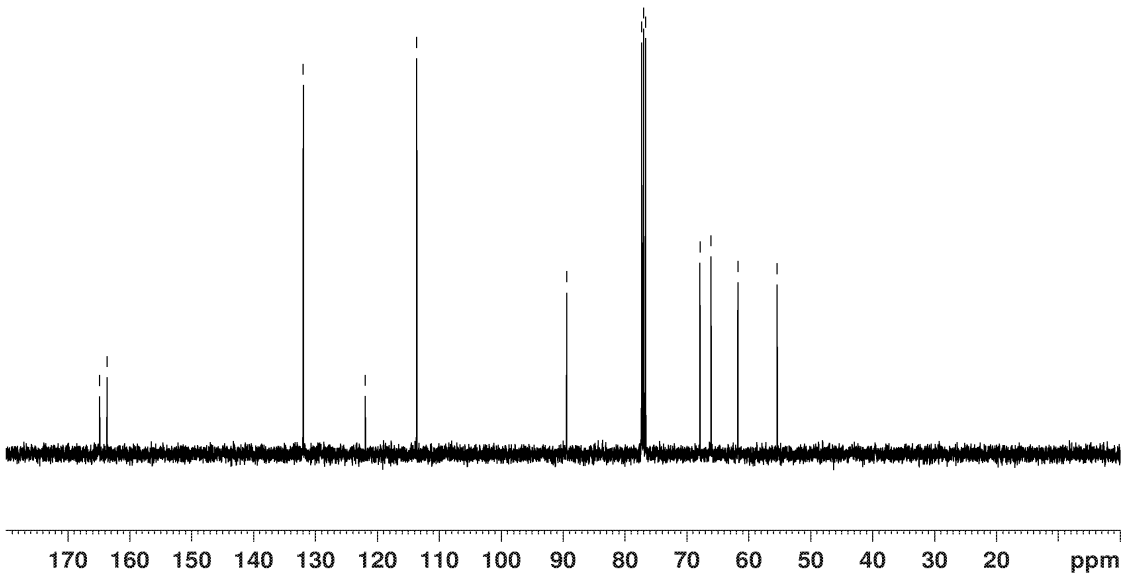
5c

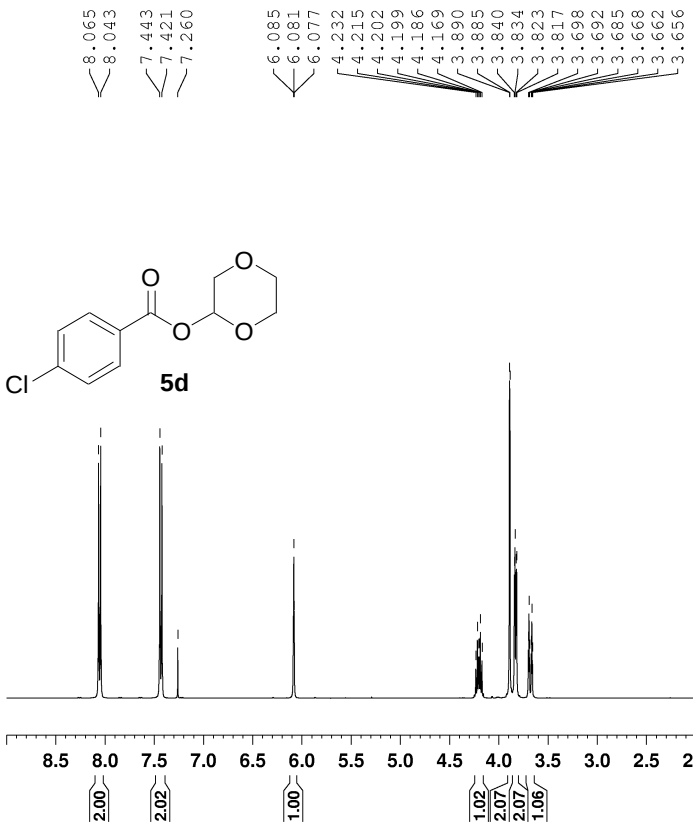



```
NAME        dxh-dioxone-3
EXPNO                   1
PROCNO                  1
Date_            20121130
Time                21.57
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 H
FIDRES           0.125483 H
AQ               3.9846387 s
RG                    114
DW                 60.800 u
DE                  6.50 u
TE                 292.8 K
D1              1.00000000 s
TD0                     1

======== CHANNEL f1 =====
NUC1                   1H
P1                 13.90 u
PL1                -3.00 d
PL1W         17.09048462 W
SFO1         400.1324710 M
SI                   32768
SF           400.1300096 M
WDW                   EM
SSB                    0
LB                  0.30 H
GB                     0
PC                  1.00
```

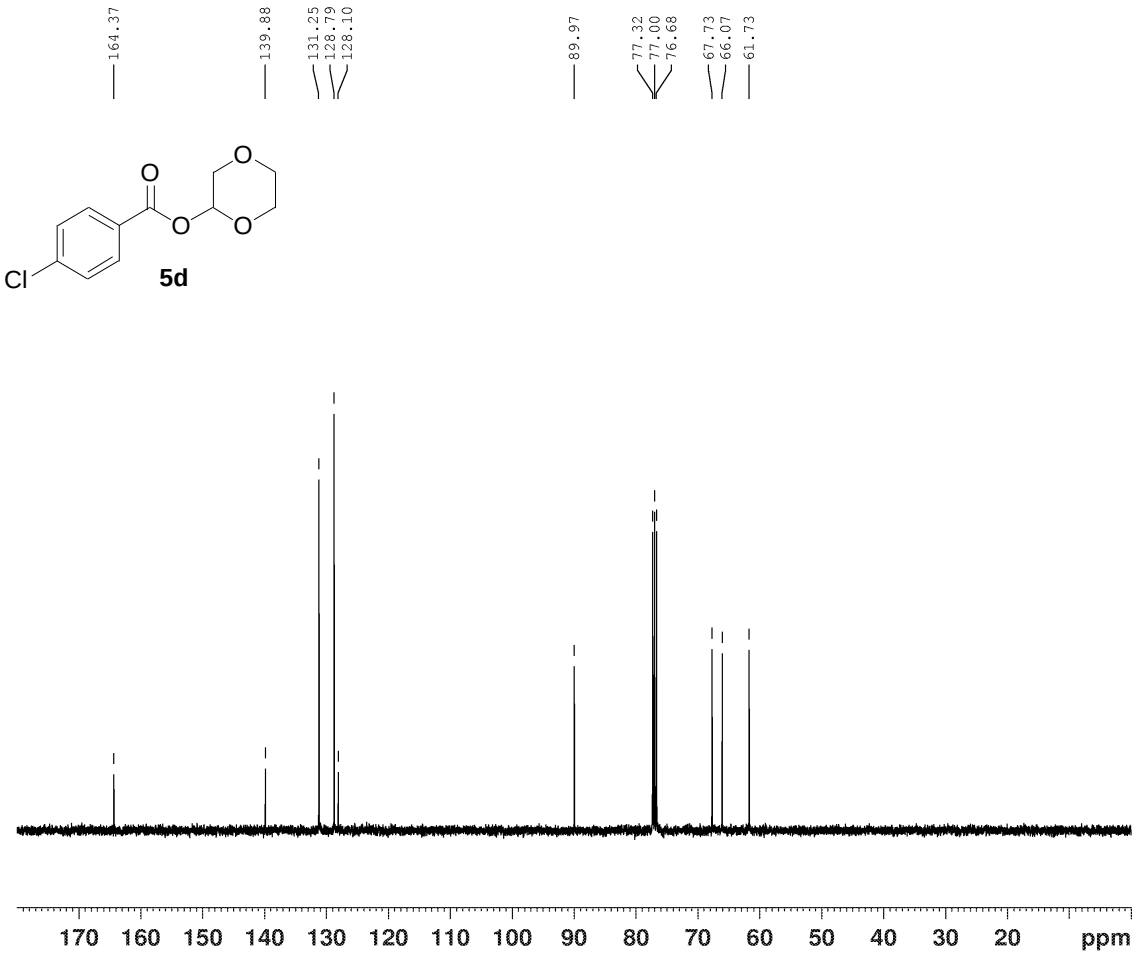


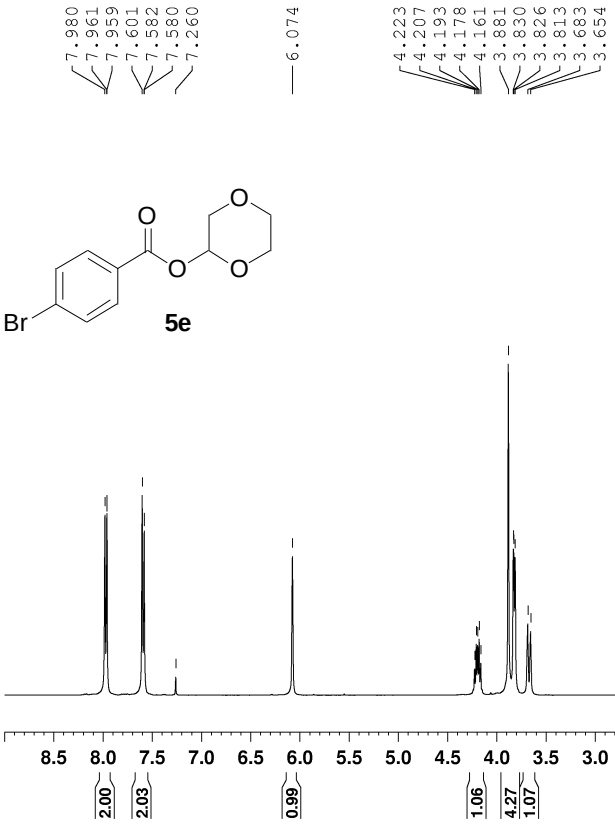
5c



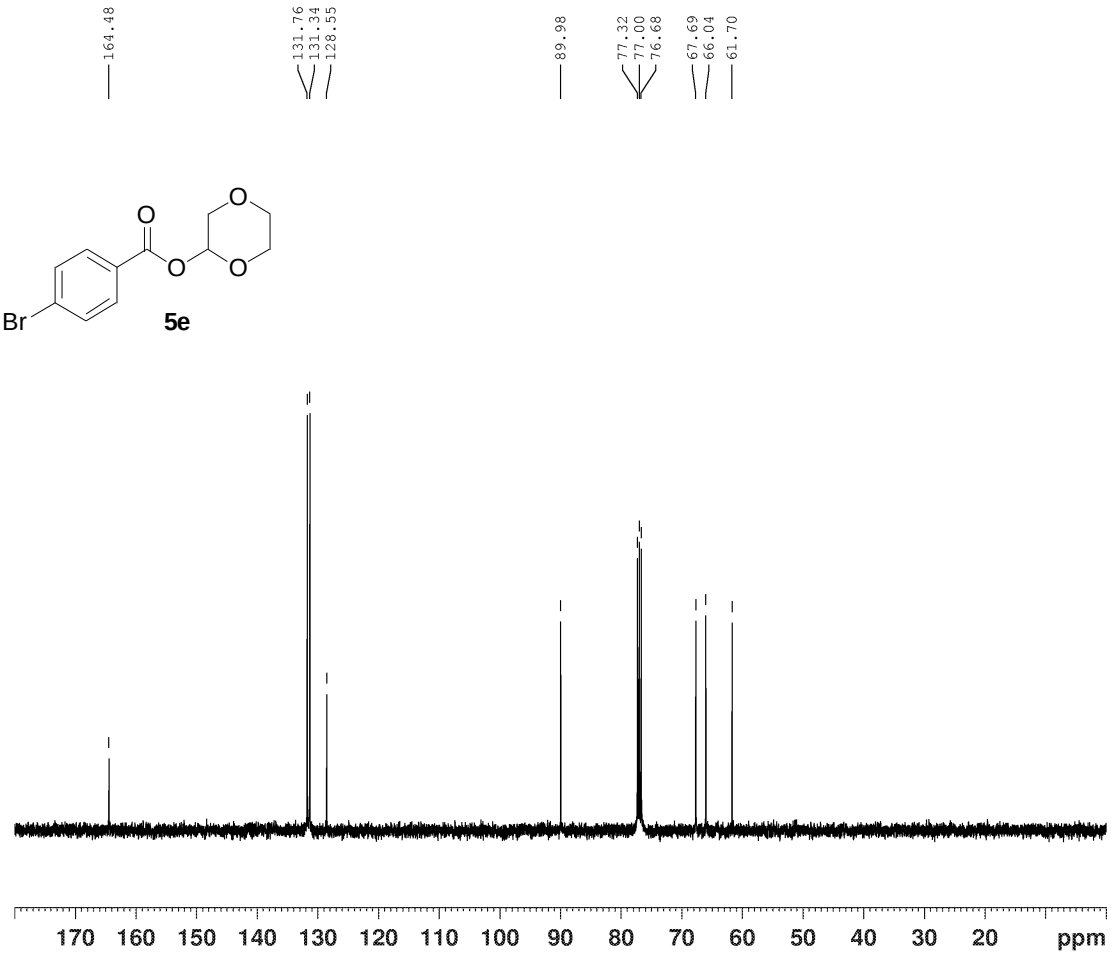


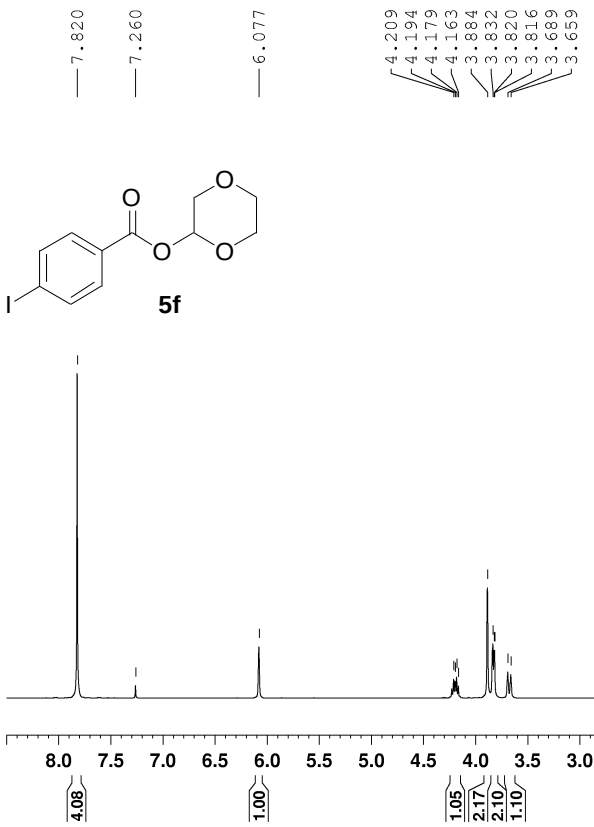
```
NAME          dxh-dioxone-4
EXPNO                    1
PROCNO                   1
Date_             20121130
Time                 22.11
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              8223.685 H
FIDRES           0.125483 H
AQ               3.9846387 s
RG                     101
DW                  60.800 u
DE                   6.50 u
TE                  292.8 K
D1              1.00000000 s
TD0                      1

======== CHANNEL f1 =====
NUC1                    1H
P1                  13.90 u
PL1                 -3.00 d
PL1W         17.09048462 W
SFO1        400.1324710 M
SI                   32768
SF          400.1300096 M
WDW                    EM
SSB                     0
LB                   0.30 H
GB                      0
PC                   1.00
```



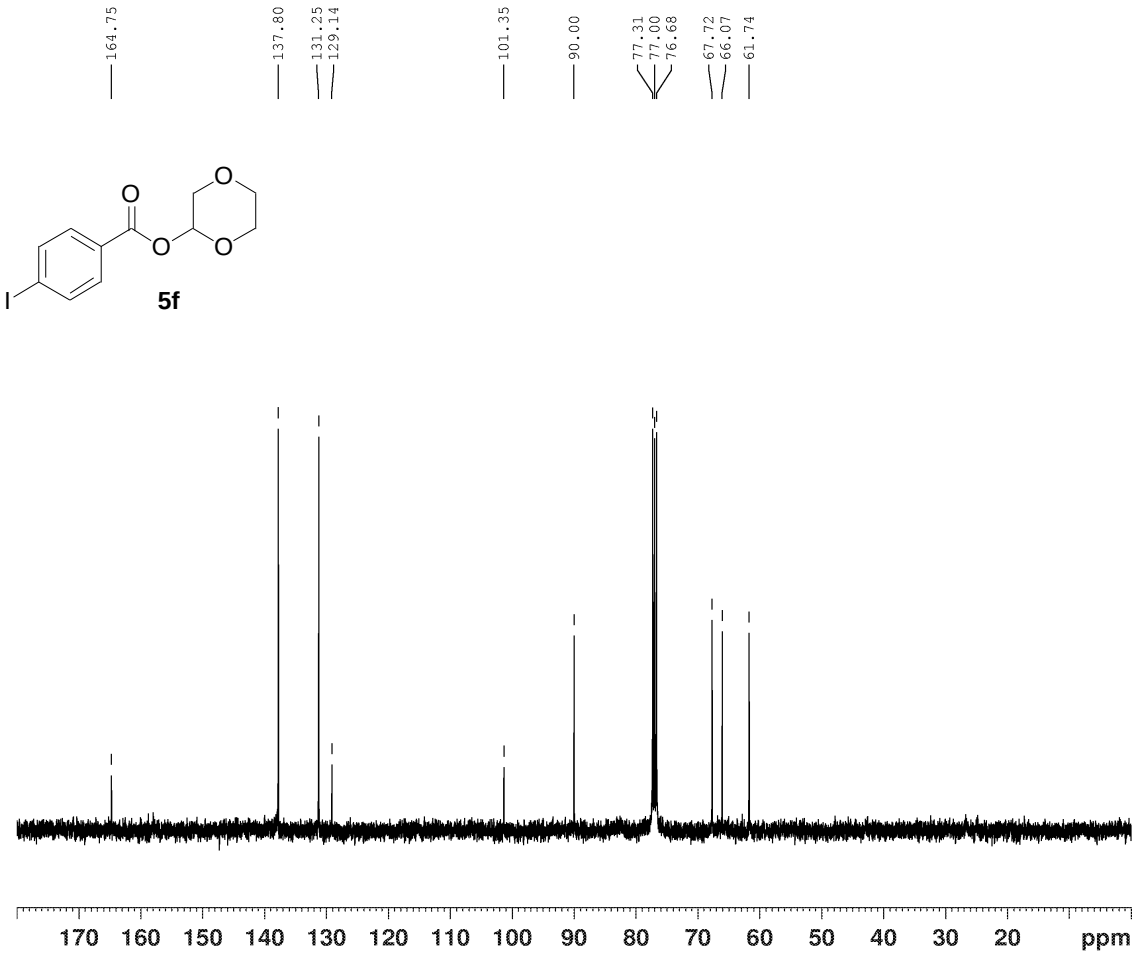


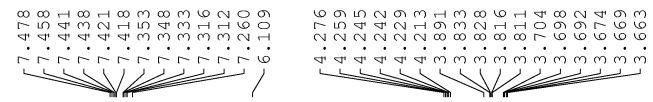
```
NAME          dxh-dioxone-5
EXPNO                    1
PROCNO                   1
Date_             20121208
Time                  9.25
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 H
FIDRES            0.125483 H
AQ                3.9846387 s
RG                     71.8
DW                  60.800 u
DE                   6.50 u
TE                  294.3 K
D1              1.00000000 s
TD0                      1

======== CHANNEL f1 =====
NUC1                    1H
P1                  13.90 u
PL1                 -3.00 d
PL1W          17.09048462 W
SFO1          400.1324710 M
SI                    32768
SF            400.1300086 M
WDW                     EM
SSB                      0
LB                  0.30 H
GB                       0
PC                   1.00
```

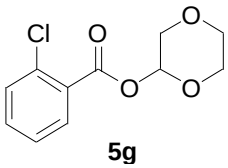





```
NAME        dxh-dioxone-6
EXPNO                  1
PROCNO                 1
Date_           20121207
Time              17.32
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 H
FIDRES          0.125483 H
AQ              3.9846387 s
RG                   114
DW                60.800 u
DE                 6.50 u
TE                293.8 K
D1           1.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                13.90 u
PL1               -3.00 d
PL1W        17.09048462 W
SFO1       400.1324710 M
SI               32768
SF         400.1300096 M
WDW                 EM
SSB                    0
LB                0.30 H
GB                     0
PC                1.00
```

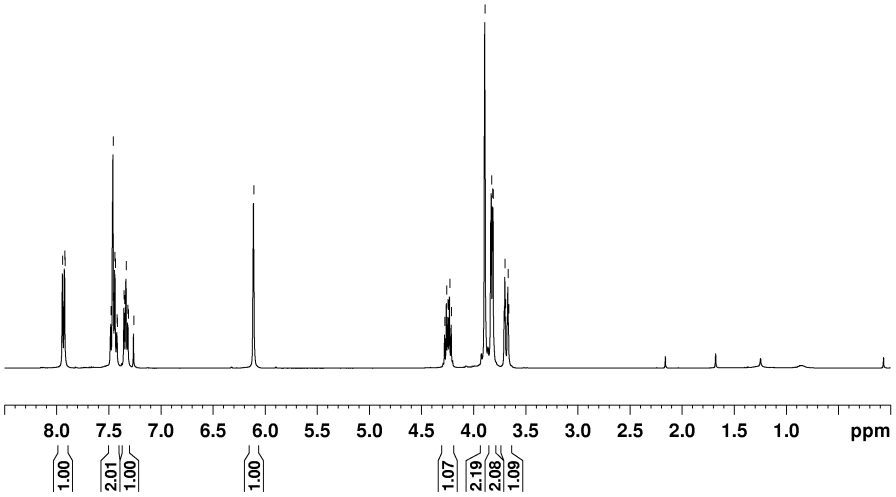


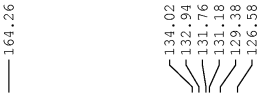


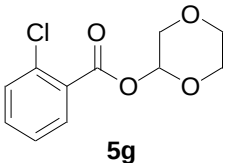


5g

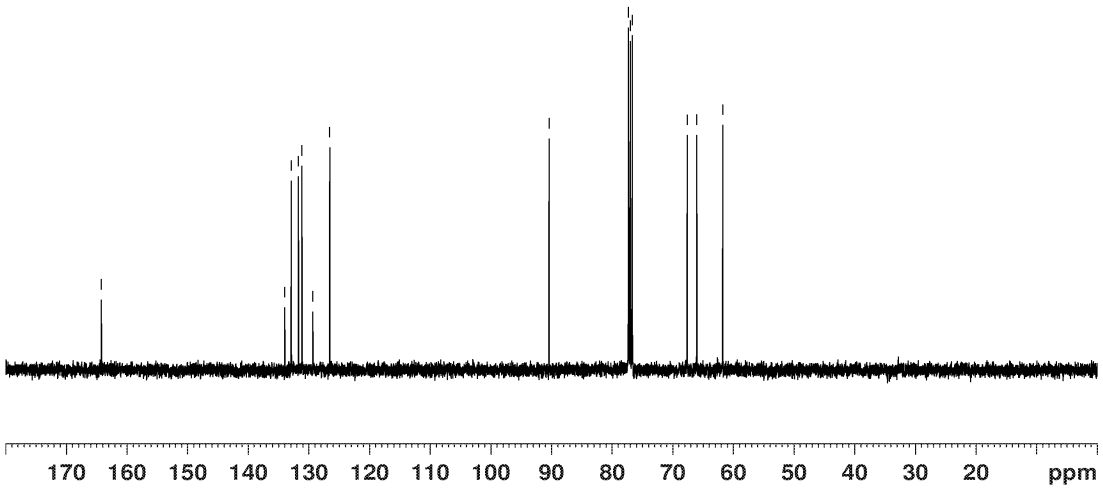
```
NAME        dxh-dioxone-7
EXPNO                   1
PROCNO                  1
Date_            20121208
Time                9.38
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 H
FIDRES           0.125483 H
AQ               3.9846387 s
RG                    90.5
DW                  60.800 u
DE                   6.50 u
TE                  293.9 K
D1             1.00000000 s
TD0                     1

======== CHANNEL f1 =====
NUC1                   1H
P1                  13.90 u
PL1                 -3.00 d
PL1W         17.09048462 W
SFO1        400.1324710 M
SI                  32768
SF          400.1300091 M
WDW                    EM
SSB                     0
LB                   0.30 H
GB                      0
PC                   1.00
```

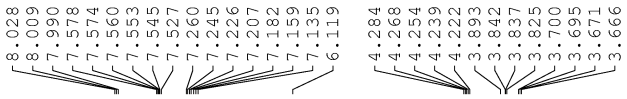


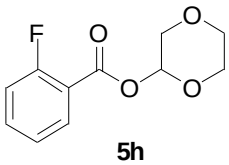




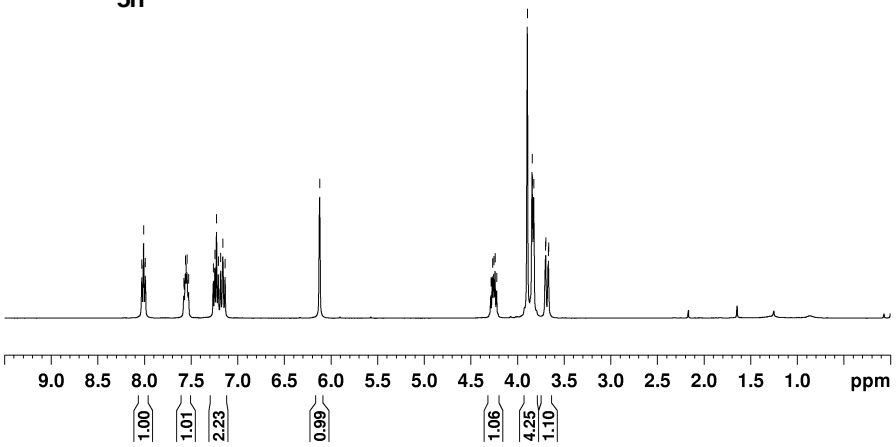
5g



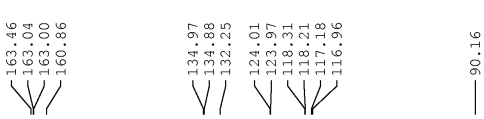


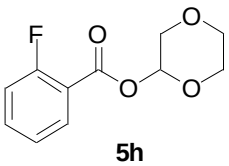


5h

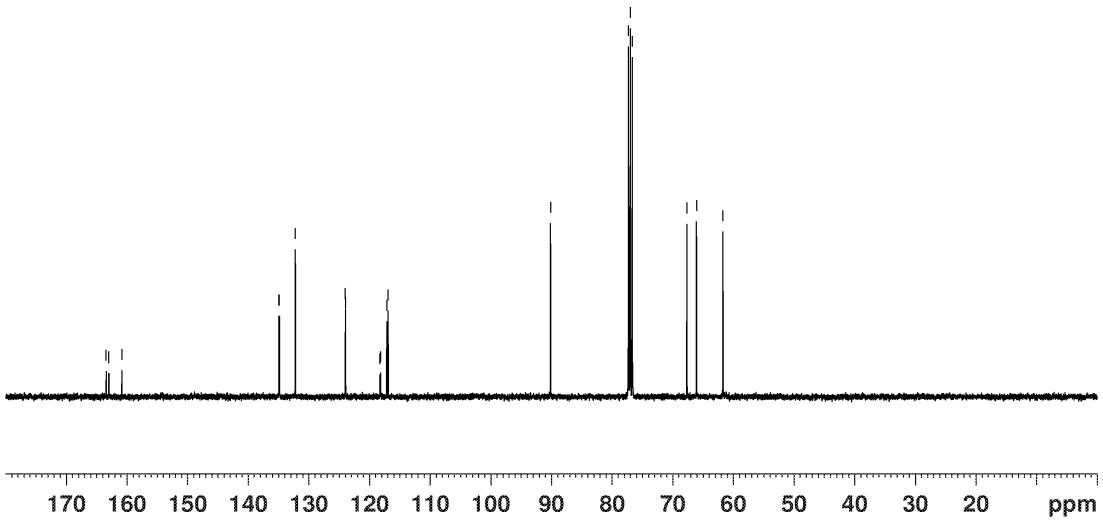


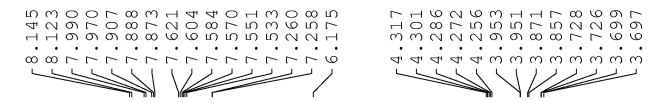

```
NAME        dxh-dioxone-9
EXPNO                  1
PROCNO                 1
Date_           20121208
Time               10.13
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 H
FIDRES          0.125483 H
AQ              3.9846387 s
RG                   144
DW                60.800 u
DE                 6.50 u
TE                294.2 K
D1           1.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                13.90 u
PL1               -3.00 d
PL1W        17.09048462 W
SFO1       400.1324710 M
SI               32768
SF         400.1300089 M
WDW                  EM
SSB                   0
LB                 0.30 H
GB                    0
PC                 1.00
```

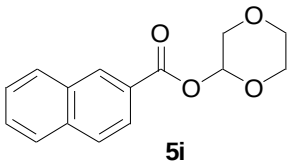




5h



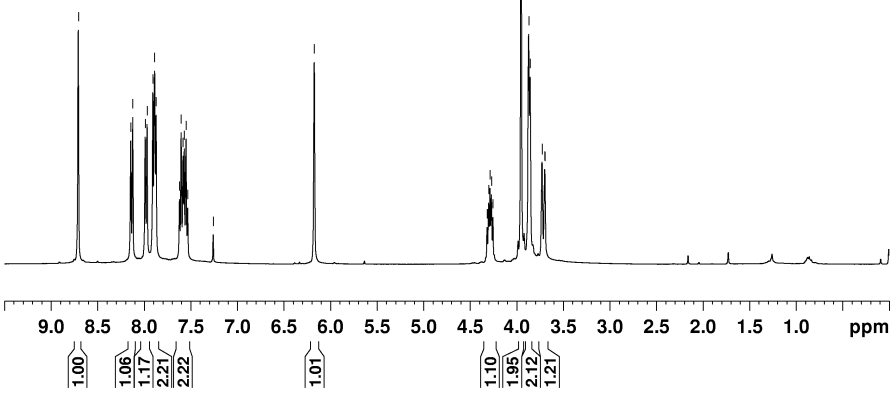


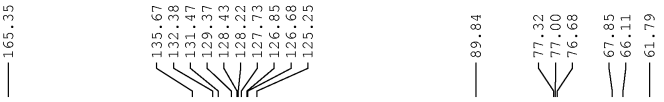


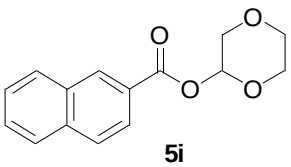
5i

NAME dxh-dioxone-8
EXPNO 1
PROCNO 1
Date_ 20121208
Time 9.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685
FIDRES 0.125483
AQ 3.9846387
RG 45.2
DW 60.800
DE 6.50
TE 293.8
D1 1.00000000
TD0 1

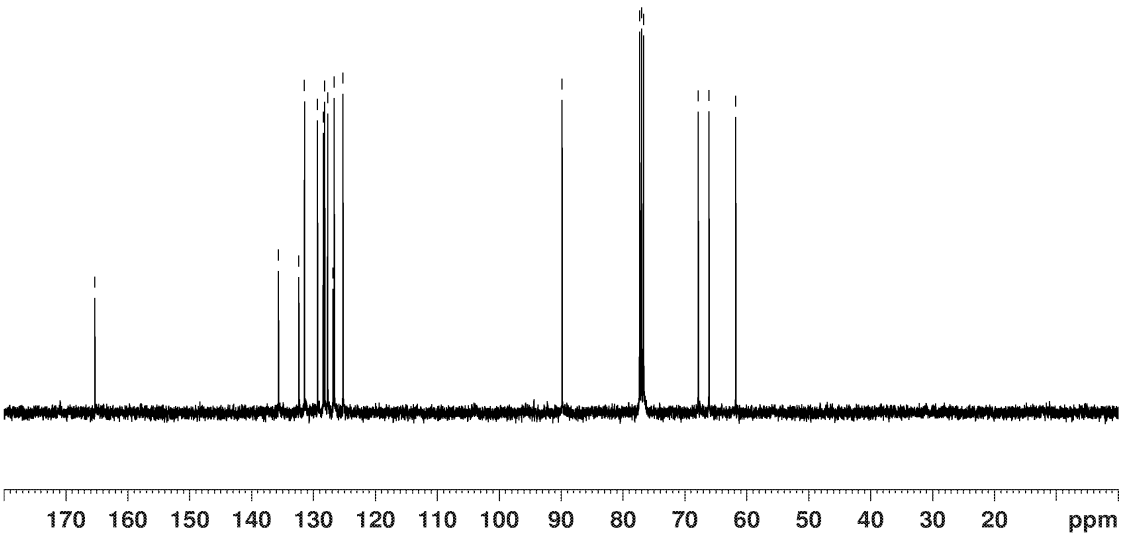
======== CHANNEL f1 ====
NUC1 1H
P1 13.90
PL1 -3.00
PL1W 17.09048462
SFO1 400.1324710
SI 32768
SF 400.1300100
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00

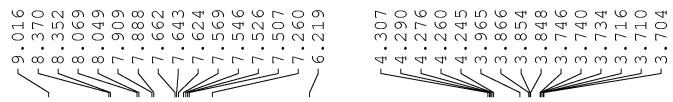


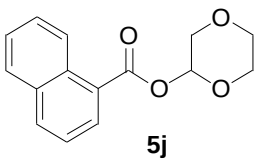




5i

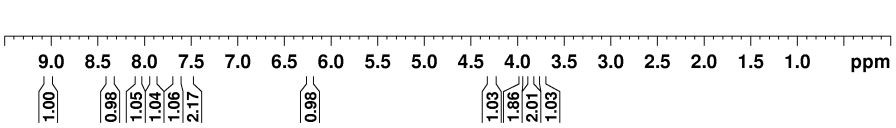


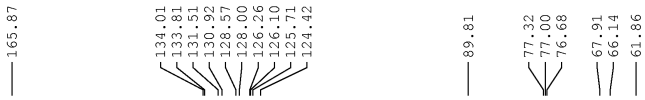


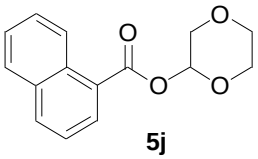


5j

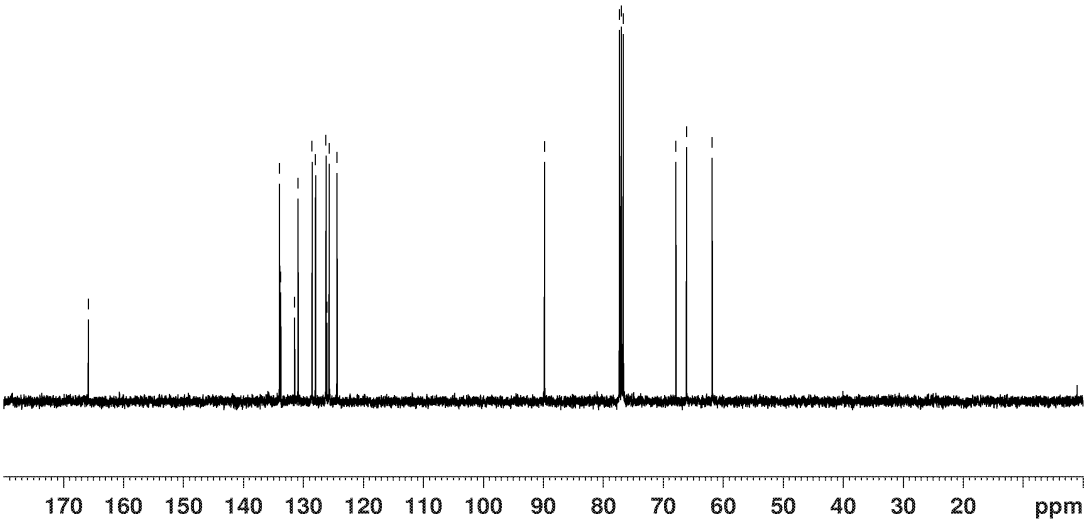
```
NAME      dxh-dioxone-10
EXPNO                  1
PROCNO                 1
Date_           20121208
Time              10.38
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 H
FIDRES          0.125483 H
AQ              3.9846387 s
RG                  80.6
DW                60.800 u
DE                 6.50 u
TE                293.8 K
D1           1.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                13.90 u
PL1               -3.00 d
PL1W        17.09048462 W
SFO1       400.1324710 M
SI               32768
SF         400.1300096 M
WDW                  EM
SSB                   0
LB                 0.30 H
GB                    0
PC                 1.00
```

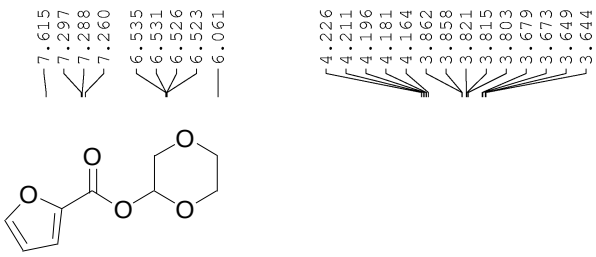






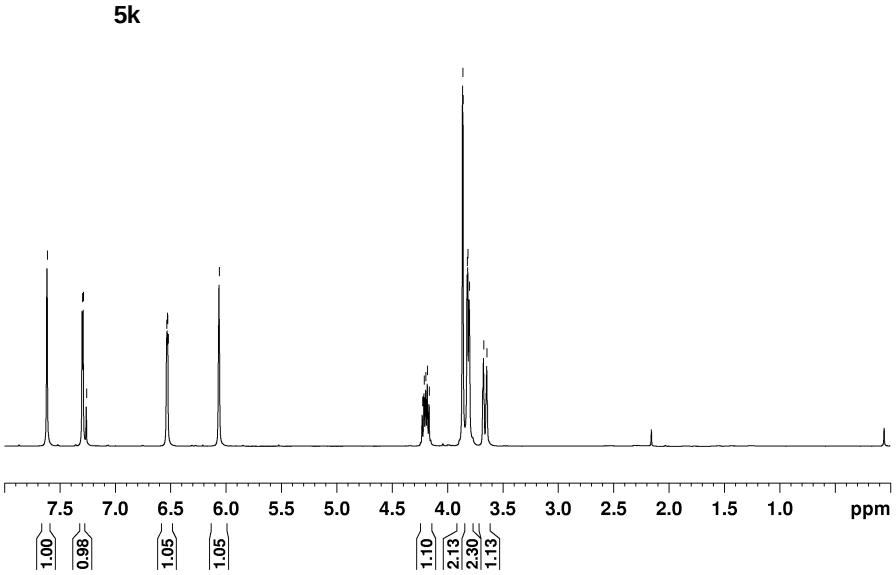
5j

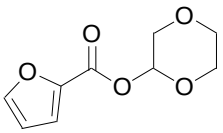




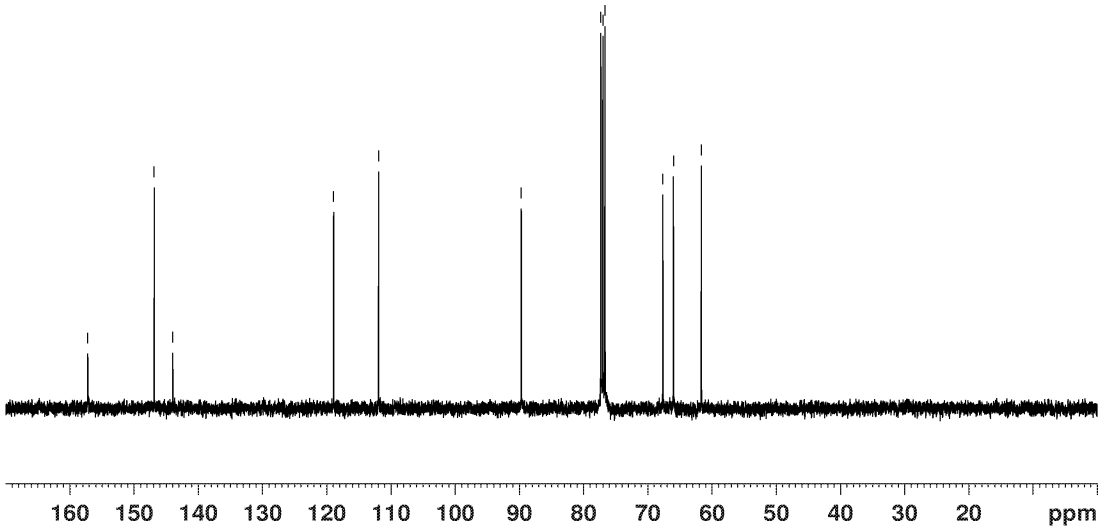
5k

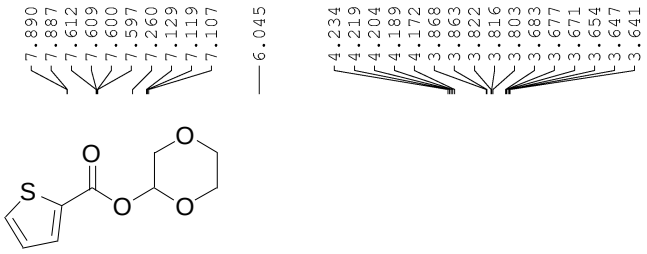
```
NAME        dxh-dioxone-12
EXPNO                    1
PROCNO                   1
Date_             20121218
Time                 16.17
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      16
DS                       2
SWH              8223.685 H
FIDRES           0.125483 H
AQ               3.9846387 s
RG                    90.5
DW                  60.800 u
DE                   6.50 u
TE                  291.9 K
D1             1.00000000 s
TD0                      1

======== CHANNEL f1 =====
NUC1                    1H
P1                   13.90 u
PL1                  -3.00 d
PL1W         17.09048462 W
SFO1         400.1324710 M
SI                   32768
SF           400.1300099 M
WDW                     EM
SSB                      0
LB                    0.30 H
GB                       0
PC                    1.00
```



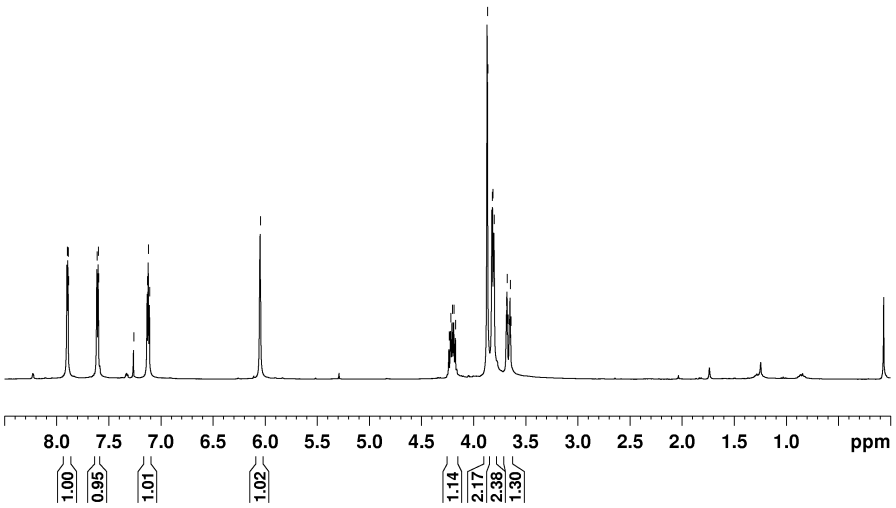


5k

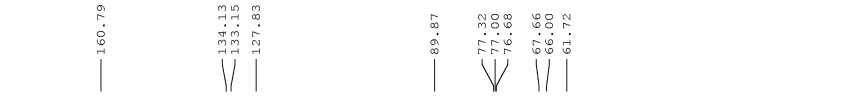


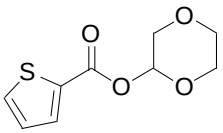


5l

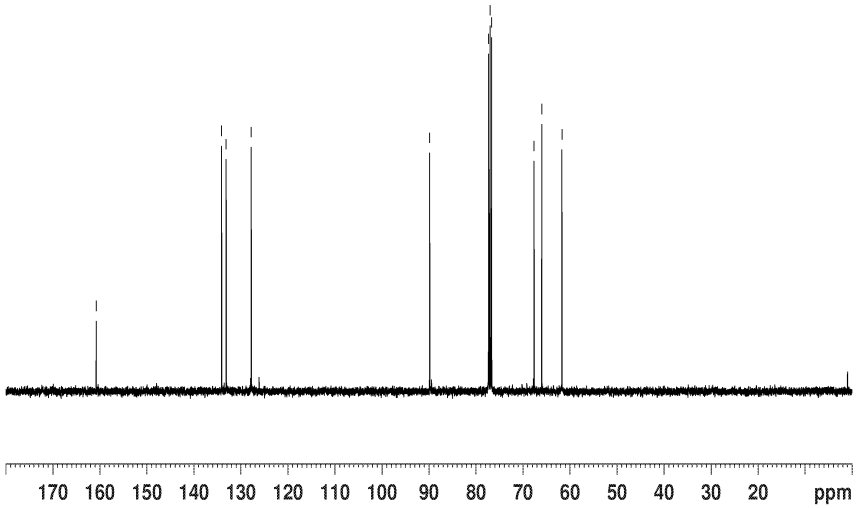



```
NAME      dxh-dioxone-13
EXPNO                  1
PROCNO                 1
Date_           20121215
Time               21.51
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 H
FIDRES          0.125483 H
AQ              3.9846387 s
RG                  50.8
DW                60.800 u
DE                 6.50 u
TE                294.0 K
D1             1.00000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                  1H
P1                 13.90 u
PL1                -3.00 d
PL1W         17.09048462 W
SFO1        400.1324710 M
SI                 32768
SF          400.1300094 M
WDW                   EM
SSB                    0
LB                 0.30 H
GB                     0
PC                 1.00
```





5l




```
NAME      dxh-dioxone-13
EXPNO                  2
PROCNO                 1
Date_           20121215
Time               22.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    78
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 se
RG                   203
DW                20.800 us
DE                 6.50 us
TE                295.0 K
D1             2.00000000 se
D11            0.03000000 se
TD0                    1

======== CHANNEL f1 ======
NUC1                  13C
P1                 8.90 us
PL1               -3.00 dB
PL1W         66.65790558 W
SFO1        100.6228298 MH

======== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 us
PL2               -3.00 dB
PL12              12.20 dB
PL13              13.00 dB
PL2W         17.09048462 W
PL12W         0.51612443 W
PL13W         0.42929357 W
SFO2        400.1316005 MH
SI                 32768
SF          100.6127773 MH
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```