Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Chemoselective *O*-Formyl and *O*-Acyl Protection of Alkanolamines, Phenoxyethanols and Alcohols Catalyzed by Nickel-(II) and Copper-(II)-Catalysts

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Supporting Information

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1. General information

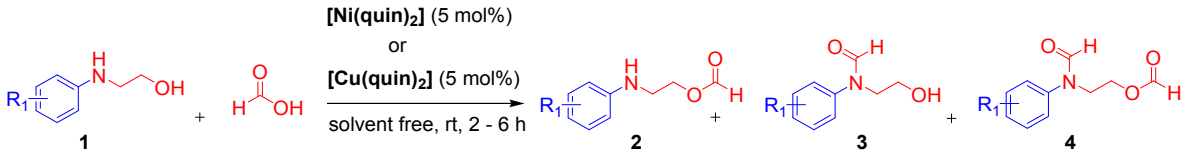
All reactions were carried out under normal conditions and no any stringent conditions were used. The starting materials alkanolamines and phenoxyethanols were synthesized by our reported method and characterized by ^{1}H and ^{13}C NMR spectroscopy, FT-IR and GCMS techniques and used as such for reactions.[1]Lab reagent grade solvents used for reaction, extraction and column chromatography were purchased from *Finar* chemicals. Lab reagent grade reagents used for reaction workup were purchased from *S. D. Fine Chem Ltd.*The progress of reactions was checked by analytical thin-layer chromatography (TLC Silica gel 60 F_{254} plates).The plates were visualized first with short wavelength UV light followed by iodine stain.

Melting points were uncorrected and determined in an open capillary tube. GC-MS spectra were recorded on Shimadzu QP-Ultra 2010 GC-MS system with MS detector (EI mode, 70 ev) and Rxi-624Sil MS column (30 m, 0.32 mm ID, 1.80 μ). The major signals are quoted in m/z with the relative intensity in parentheses. The method used for analysis an injector temperature 250 °C; ion source temperature 200 °C, interface temperature 260 °C, column flow 2 mL/min Helium, the column oven temperature: initial temperature (T_0) = 60 °C, hold time (t) = 2 min, ramp = 20 °C/min, final temperature (T_1) = 240 °C, hold time (t) = 19 min. HRMS spectra were recorded on Waters SYNAPT G2 HDMS system with triple quadrupole mass spectrometer (Electrospray ionization (ESI) mode).

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker Avance-III 500 MHz spectrometer using TMS as an internal standard. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.16-7.32 ppm, DMSO-d_6: δ_H = 2.51 ppm). Infrared spectra were recorded on a Shimadzu FTIR MIRacle 10 with diamond ATR.

2. General Procedures

2.1. Chemoselective *O*-formylation of alkanolamines:



To a mixture of alkanolamine (**1**)(0.2 g, 1 equiv), catalyst (**C1**) [$Ni(quin)_2$] (5 mol%), and formic acid (1 mL, 5 volume) were added.

Or

To a mixture of alkanolamine (**1**) (0.2 g, 1 equiv), catalyst (**C2**) [$Cu(quin)_2$] (5 mol%), and formic acid (1 mL, 5 volume) were added.

The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine stain. After completion, the mixture was diluted with 5 mL of MDC and powdered $NaHCO_3$wasadded slowly with stirring until pHwas between= 5 to 6, confirmed by pH paper. Theorganic layer was then decanted and residue was washed with MDC (2 X 5 mL). All collected organic layers were concentrated under vacuum to obtain the crude *O*-formyl product (**2**).Column purification afforded pure compound of *O*-formyl product (**2**).

Recovery of formic acid in the form of sodium formate: The slurry obtained during reaction workup was collected in a round bottom flask and was neutralized by using saturated $NaHCO_3$ solution in water. The water was then evaporated under vacuum and crude solid was isolated. It was further dissolved in 5mL of methanol and filtered under vacuum using Whatman filter paper. Thus the inorganic salts and catalyst were separated. The filtrate was then evaporated under vacuum that afforded pure crystalline white solid of sodium formate with more than 96% yield. The assay was determined above 99% by titration method using 0.1N HCl solution and phenolphthalein as indicator.

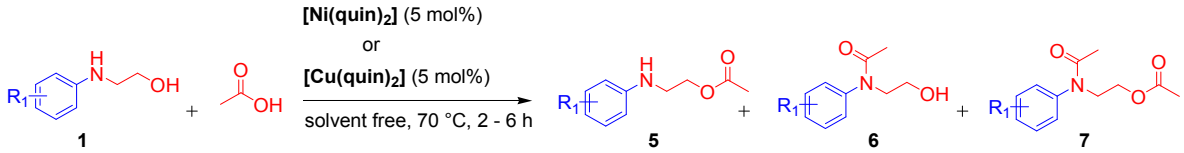
2.2. Gram-scale experimental procedure for Chemoselective *O*-formylation of alkanolamines:

Charged 2.01g of alkanolamine (**1a**) (13.30 mol,1 equiv), 0.26 g of catalyst (**C1**) [$Ni(quin)_2$] (0.66 mol, 5 mol%), and 10 mL of formic acid (5 volume) in a 100 mL round bottom flask. The mixture was stirred at room temperature and the progress of the reaction was monitored up to 6 h by TLC visualized with UV short wavelength followed by iodine stain. After completion, the mixture was diluted with 15 mL of MDC and powdered $NaHCO_3$wasadded

slowly with stirring up to pHwas about 6, confirmed by pH paper. The organic layer was then decanted and residue was washed with MDC (2 X 10 mL). All collected organic layers were concentrated under vacuum to obtain the crude *O*-formyl product (**2a**) with2.53 g. Column purification was done by using 60-120 mesh silica gel and eluent as hexanes/EtOAc (80:20) afforded pure compound of *O*-formyl product (**2a**) with 2.27 g isolated yield.

Recovery of formic acid in the form of sodium formate: The slurry obtained during reaction workup was collected in a 100 mL round bottom flask and was neutralized by using saturated $NaHCO_3$ solution in water. The water was then evaporated under vacuum and 17.02 g crude solid was isolated. It was further dissolved in 50 mL of methanol and filtered under vacuum using Whatman filter paper. Thus the inorganic salts and catalyst were separated. The filtrate was then evaporated under vacuum that afforded pure crystalline white solid of sodium formate with 96.7% yield, 16.42 g. The assay was determined 99.6% by titration method using 0.1N HCl solution and phenolphthalein as indicator.

2.3. Chemoselective *O*-acylation of alkanolamines:



To a mixture of alkanolamine (**1**)(0.2 g, 1 equiv), catalyst (**C1**) [$Ni(quin)_2$] (5 mol%), and acetic acid (1 mL, 5 volume) were added.

Or

To a mixture of alkanolamine (**1**)(0.2 g, 1 equiv), catalyst (**C2**) [$Cu(quin)_2$] (5 mol%), and acetic acid (1 mL, 5 volume) were added.

The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine stain. After completion, the mixture was diluted with 5 mL of MDC and powdered $NaHCO_3$ wasadded slowly with stirring until pHwas between= 5 to 6, confirmed by pH paper. The organic layer was then decanted and residue was washed with MDC for twice (2 X 5 mL). All collected organic layers were concentrated under vacuum to obtain the crude*O*-acyl product (**5**). Column purification afforded pure compound of*O*-acyl product (**5**).

Recovery of acetic acid in the form of sodium acetate: The slurry obtained during reaction workup was collected in a round bottom flask and was neutralized by using

saturated $NaHCO_3$ solution in water. The water was then evaporated under vacuum and crude solid was isolated. It was further dissolved in 5mL of methanol and filtered under vacuum using Whatman filter paper. Thus the inorganic salts and catalyst were separated. The filtrate was then evaporated under vacuum that afforded pure crystalline white solid of sodium acetate with more than 96% yield. The assay was determined above 99% by titration method using 0.1N HCl solution and phenolphthalein as indicator.

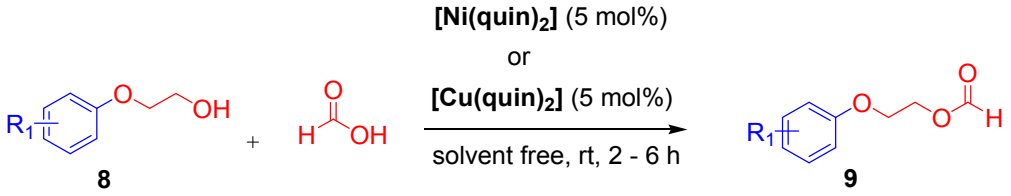
2.4. Gram-scale experimental procedure for Chemoselective *O*-acylation of alkanolamines:

Charged 2.02 g of alkanolamine (**1a**) (13.33 mol, 1 equiv), 0.26 g of catalyst (**C1**) $[Ni(quin)_2]$ (5 mol%), and 10 mL of acetic acid (5 volume) in a 100 mL round bottom flask and the flask. The mixture was stirred at room temperature and the progress of the reaction was monitored up to 6 h by TLC visualized with UV short wavelength followed by iodine stain. After completion, the mixture was diluted with 15 mL of MDC and powdered $NaHCO_3$ wasadded slowly with stirring up to pHwas about 6, confirmed by pH paper. The organic layer was then decanted and residue was washed with MDC for twice (2 X 10 mL). All collected organic layers were concentrated under vacuum to obtain the crude *O*-acyl product (**5a**) with 2.62g. Column purification was done by using 60-120 mesh silica gel and eluent as hexanes/EtOAc (70:30) afforded pure compound of *O*-acyl product (**5a**) with 2.42 g isolated yield.

Recovery of acetic acid in the form of sodium acetate:

The slurry obtained during reaction workup was collected in a 100 mL round bottom flask and was neutralized by using saturated $NaHCO_3$ solution in water. The water was then evaporated under vacuum and 13.07 g crude solid was isolated. It was further dissolved in 50 mL of methanol and filtered under vacuum using Whatman filter paper. Thus the inorganic salts and catalyst were separated. The filtrate was then evaporated under vacuum that afforded pure crystalline white solid of sodium acetate with 96.5% yield, 12.59 g. The assay was determined 99.5% by titration method using 0.1N HCl solution and phenolphthalein as indicator.

2.5. *O*-acylation of phenoxyethanols:



To the phenoxyethanol (**8**) (0.2 g, 1 equiv); catalyst (**C1**) [Ni(quin)$_2$] (5 mol%) and formic acid (1 mL, 5 volume) were added.

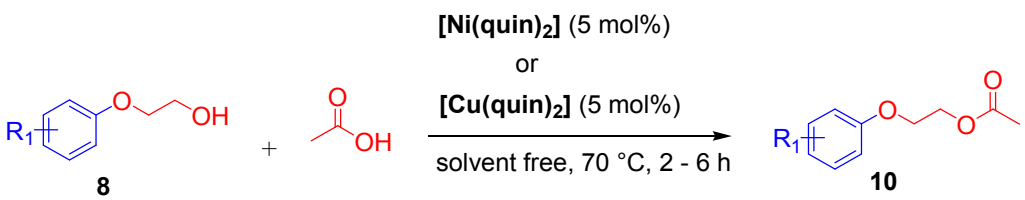
Or

To the phenoxyethanol (**8**) (0.2 g, 1 equiv); catalyst (**C2**) [Cu(quin)$_2$] (5 mol%), and formic acid (1 mL, 5 volume) were added.

The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine stain. After completion, the mixture was diluted with 5 mL of MDC followed by slow addition of 1N HCl under stirring. The organic layer was then separated and washed with water (2 X 5 mL). All collected organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum to obtain the crude *O*-formyl product (**9**). Column purification afforded the pure compound of *O*-formyl product (**9**).

Recovery of formic acid in the form of sodium formate: The aqueous layer obtained during reaction workup was collected in a round bottom flask and was neutralized by using saturated $NaHCO_3$ solution in water. The water was then evaporated under vacuum and crude solid was isolated. It was further dissolved in 5mL of methanol and filtered under vacuum using Whatman filter paper. Thus the inorganic salts and catalyst were separated. The filtrate was then evaporated under vacuum that afforded pure crystalline white solid of sodium formate with more than 96% yield. The assay was determined above 99% by titration method using 0.1N HCl solution and phenolphthalein as indicator.

2.6. *O*-acylation of phenoxyethanols:



To the phenoxyethanol (**8**) (0.2 g, 1 equiv); catalyst (**C1**) [Ni(quin)$_2$] (5 mol%), and acetic acid (1 mL, 5 volume) were added.

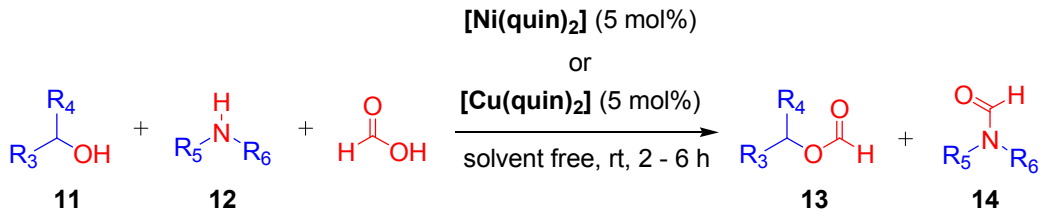
Or

To the phenoxyethanol (**8**) (0.2 g, 1 equiv); catalyst (**C2**) [$Cu(quin)_2$] (5 mol%), and acetic acid (1 mL, 5 volume) were added.

The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine stain. After completion, the mixture was diluted with 5 mL of MDC followed by slow addition of 1N HCl under stirring. Then organic layer separated and washed with water (2 X 5 mL). All collected organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum to obtain the crude *O*-acyl product (**10**). Column purification afforded the pure compound of *O*-acyl product (**10**).

Recovery of acetic acid in the form of sodium acetate: The aqueous layer obtained during reaction workup was collected in a round bottom flask and was neutralized by using saturated $NaHCO_3$ solution in water. The water was then evaporated under vacuum and crude solid was isolated. It was further dissolved in 5mL of methanol and filtered under vacuum using Whatman filter paper. Thus the inorganic salts and catalyst were separated. The filtrate was then evaporated under vacuum that afforded pure crystalline white solid of sodium acetate with more than 96% yield. The assay was determined above 99% by titration method using 0.1N HCl solution and phenolphthalein as indicator.

2.7. Competitive chemoselective *O*-formylation of alcohols in presence of amines



To a mixture of alcohol (**11**) (0.2 g, 1 equiv) and amine (**12**) (0.2 g, 1 equiv); catalyst (**C1**) [$Ni(quin)_2$] (5 mol%) and formic acid (1 mL, 5 volume) were added.

Or

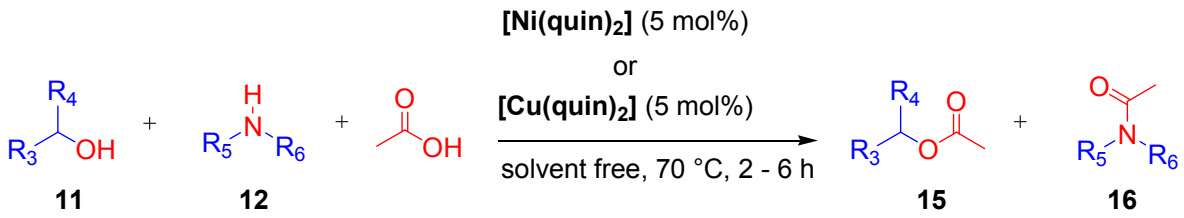
To a mixture of alcohol (**11**) (0.2 g, 1 equiv) and amine (**12**) (0.2 g, 1 equiv); catalyst (**C2**) [$Cu(quin)_2$] (5 mol%) and formic acid (1 mL, 5 volume) were added.

The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine stain. After completion, the mixture was diluted with 5 mL of MDC and powdered $NaHCO_3$ was added slowly with stirring until the pHwas adjusted between 5 to 6, confirmed by pH paper. The organic layer

was then decanted and residue was washed with MDC (2 X 5 mL). All collected organic layers were concentrated under vacuum to obtain the crude *O*-formyl product (**13**). Column purification afford pure compound of *O*-formyl product (**13**).

Recovery of formic acid in the form of sodium formate: The slurry obtained during reaction workup was collected in a round bottom flask and was neutralized by using saturated $NaHCO_3$ solution in water. The water was then evaporated under vacuum and crude solid was isolated. It was further dissolved in 5mL of methanol and filtered under vacuum using Whatman filter paper. Thus the inorganic salts and catalyst were separated. The filtrate was then evaporated under vacuum that afforded pure crystalline white solid of sodium formate with more than 96% yield. The assay was determined above 99% by titration method using 0.1N HCl solution and phenolphthalein as indicator.

2.8. Competitive chemoselective *O*-acylation of alcohols in presence of amines



To a mixture of alcohol (**11**) (0.2 g, 1 equiv) and amine (**12**) (0.2 g, 1 equiv); catalyst (**C1**) $[Ni(quin)_2]$ (5 mol%), and acetic acid (1 mL, 5 volume) was added.

Or

To a mixture of alcohol (**11**) (0.2 g, 1 equiv) and amine (**12**) (0.2 g, 1 equiv); catalyst (**C2**) $[Cu(quin)_2]$ (5 mol%) and acetic acid (1 mL, 5 volume) were added.

After completion, the mixture was diluted with 5 mL of MDC and powdered $NaHCO_3$ was added slowly with stirring until the pHwas adjusted between 5 to 6, confirmed by pH paper. The organic layer was then decanted and residue was washed with MDC (2 X 5 mL). All collected organic layers were concentrated under vacuum to obtain the crude *O*-acyl product (**15**). Column purification afforded pure compound of *O*-acyl product (**15**).

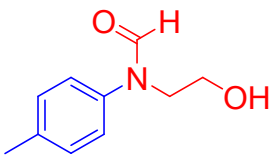
Recovery of acetic acid in the form of sodium acetate: The slurry obtained during reaction workup was collected in a round bottom flask and was neutralized by using saturated $NaHCO_3$ solution in water. The water was then evaporated under vacuum and crude solid was isolated. It was further dissolved in 5mL of methanol and filtered under vacuum using Whatman filter paper. Thus the inorganic salts and catalyst were separated.

The filtrate was then evaporated under vacuum that afforded pure crystalline white solid of sodium acetate with more than 96% yield. The assay was determined above 99% by titration method using 0.1N HCl solution and phenolphthalein as indicator.

3. Characterization of products

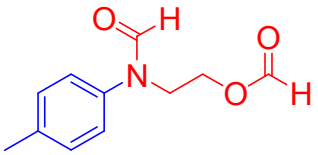
3.1. *N*-and *N*,*O*-formylatedalkanolamines(Table 1,Compounds 3a and 4a)

2-(p-toluidino-*N*-formyl)ethyl alcohol(Table 1, Compound 3a)



The product was obtained as yellow liquid in 65% yield (0.1557 g); **R_F** (eluent hexanes/EtOAc 60:40): 0.55;**^{1}H NMR(500 MHz, $CDCl_3$):**δ 8.27 (s, 1H, N-CHO), 7.13 (t, *J* = 5.1 Hz, 2H, H_{Ar}), 7.05 – 7.03 (m, 2H, H_{Ar}), 3.85 (t, *J* = 5.5 Hz, 2H, O-CH_2), 3.69 (br t, *J* = 5.2 Hz, 2H, N-CH_2), 3.17 (br s, 1H, OH), 2.29 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 162.74, 137.46, 136.27, 129.25, 123.63, 59.37, 48.02, 19.91;**FTIR (cm^{-1}):**3393, 2922, 2855, 2247, 1662, 1611, 1583, 1445, 1410, 1354, 1293, 1262, 1207, 1068, 1021, 909, 864, 821, 734;**HRMS (ESI) m/z:** ratio calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$ 180.1024; found: 180.1030.

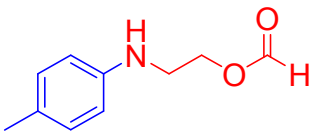
2-(p-toluidino-*N*-formyl)ethyl formate(Table 1, Compound 4a)



The product was obtained as yellow liquid in 61% yield (0.1681 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.68;**^{1}H NMR(500 MHz, $CDCl_3$):**δ 8.28 (s, 1H, N-CHO), 7.90 (s, 1H, O-CHO), 7.15 (dt, *J* = 6.4, 2.8 Hz, 2H, H_{Ar}), 7.03 – 6.99 (m, 2H, H_{Ar}), 4.25 (t, *J* = 5.6 Hz, 2H, O-CH_2), 4.00 (t, *J* = 5.7 Hz, 2H, N-CH_2), 2.30 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):**δ 161.76, 159.60, 136.93, 136.40, 129.35, 123.59, 59.57, 43.17, 19.92; **FTIR (cm^{-1}):**2924, 1722, 1674, 1611, 1584, 1515, 1457, 1348, 1295, 1264, 1222, 1163, 1105, 1018, 821, 718; **HRMS (ESI) m/z:** ratio calcd for $C_{11}H_{14}NO_3$ $[M+H]^+$ 208.0973; found: 208.0978.

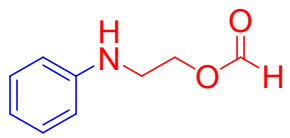
3.2. *O*-formylatedalkanolamines (Scheme 1, entries 2a-2k)

2-(p-toluidino)ethyl formate (Scheme1, entry 2a)



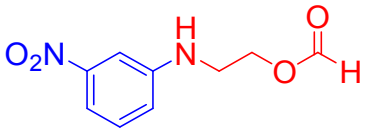
The product was obtained as yellow liquidin95% yield (0.2253 g);**R_F** (eluent hexanes/EtOAc 80:20): 0.65;**^{1}H NMR(500 MHz, $CDCl_3$):**δ 8.02 (s, 1H, CHO), 6.93 (d, J = 8.2 Hz, 2H, H_{Ar}), 6.50 (d,J = 8.4 Hz, 2H, H_{Ar}), 4.29 (t, J = 5.4 Hz, 2H, O-CH_2), 3.70 (br s, 1H, NH), 3.35 (t, J = 5.5 Hz, 2H, N-CH_2), 2.17 (s, 3H,CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 159.92, 144.06, 128.83, 126.36, 112.20, 61.61, 42.00, 19.35; **FTIR (cm^{-1}):**3364, 2920, 2859, 2361, 2338, 1721, 1659, 1609, 1512, 1443, 1412, 1350, 1246, 1169, 1057, 941, 918, 814, 752, 718, 648, 613, 555, 509;**HRMS (ESI) m/z:** ratio calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$ 180.1024; found: 180.1028.

2-(phenylamino)ethyl formate (Scheme 1, entry 2b)



The product was obtained as colorless liquidin 94% yield (0.2267 g);**R_F** (eluent hexanes/EtOAc 80:20): 0.63; **^{1}H NMR(500 MHz, $CDCl_3$):**δ 8.03 (s, 1H, CHO), 7.18 – 7.10 (m, 2H, H_{Ar}), 6.67 (tt, J= 7.4, 1.0 Hz, 1H, H_{Ar}), 6.58 – 6.56 (m, 2H, H_{Ar}), 4.30 (t, J = 5.8 Hz, 2H, O-CH_2), 3.84 (br s, H, NH), 3.37 (t, J = 5.5 Hz, 2H, N-CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 159.92, 146.36, 128.36, 117.06, 111.96, 61.54, 41.62; **FTIR (cm^{-1}):**3391, 2924, 2870, 2361, 2342, 1717, 1663, 1601, 1497, 1454, 1358, 1319, 1246, 1169, 1057, 991, 910, 868, 748, 694, 652, 602, 571, 548, 505; **GC-MS (EI,70ev) *m/z* :** found: 165 ($C_9H_{11}NO_2$), calculated: 165.19 ($C_9H_{11}NO_2$).

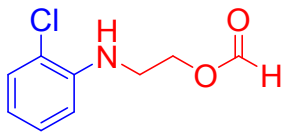
2-(3-nitrophenylamino)ethyl formate (Scheme 1, entry 2c)



The product was obtained as dark yellow liquidin 85% yield (0.1966 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.65; **^{1}H NMR(500 MHz, $CDCl_3$):**δ 8.12 (s, 1H, CHO), 7.56 (dd, J = 8.0, 1.6Hz, 1H, H_{Ar}), 7.43 (t, J = 2.2 Hz, 1H, H_{Ar}), 7.29 (dd, J = 17.3, 9.2 Hz, 1H, H_{Ar}), 6.91 (dd, J = 8.1, 2.1 Hz, 1H, H_{Ar}), 4.42 (t, J = 5.3 Hz, 2H, O-CH_2), 4.33 – 4.31 (m, 1H, NH), 3.52 (dd, J = 9.6, 4.6 Hz, 2H, N-CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.88, 149.44, 148.29, 129.92, 118.92, 112.60, 106.45, 62.11, 42.56; **FTIR (cm^{-1}):**3406, 3078, 2997, 2916, 2851, 2361, 2338, 1709, 1620, 1578, 1535, 1497, 1447, 1385, 1346, 1281,

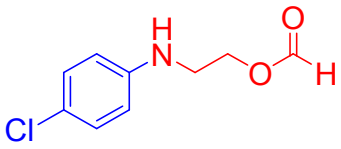
1242, 1169, 1134, 1092, 1015, 988, 945, 895, 856, 833, 787, 729, 671, 610, 548, 525, 463;**HRMS (ESI) m/z:** ratio calcd for $C_9H_{11}N_2O_4$ $[M+H]^+$ 211.0719; found: 211.0722.

2-(2-chlorophenylamino)ethyl formate (Scheme 1, entry 2d)



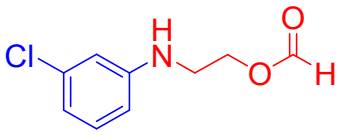
The product was obtained as pale yellow liquidin 90% yield (0.2097 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 75:25): 0.70;**^{1}H NMR (500 MHz, $CDCl_3$)**: δ 8.09 (s, 1H, CHO), 7.26 (dd, J = 7.8, 1.3 Hz, 1H,H_{Ar}),7.14 (m, 1H,H_{Ar}), 6.66 (m, 2H, H_{Ar}), 4.56 (br s, 1H, NH), 4.38 (t, J = 5.5 Hz, 2H, O-CH_2), 3.48 (dd, J = 11.3, 5.7 Hz, 2H, N-CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.93,143.34, 129.37, 127.84, 119.49, 117.91, 111.15, 62.20, 42.34; **FTIR (cm^{-1}):**3402, 2924, 2361, 2338, 1717, 1597, 1508, 1458, 1435, 1381, 1323, 1288, 1238, 1161, 1111, 1034, 922, 876, 849, 795, 741, 648, 613, 525, 463; **HRMS (ESI) m/z:** ratio calcd for $C_9H_{11}ClNO_2$ $[M+H]^+$ 200.0478; found: 200.0482.

2-(4-chlorophenylamino)ethyl formate (Scheme 1, entry 2e)



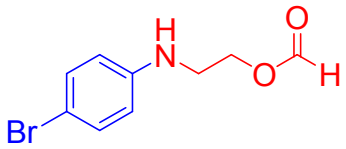
The product was obtained as brown liquid in91% yield (0.2119 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 75:25): 0.70;**^{1}H NMR (500 MHz, CDCl3):** δ 8.09 (s, 1H, CHO), 7.15 – 7.12(m, 2H, H_{Ar}), 6.57 –6.54(m, 2H,H_{Ar}), 4.36 (t, J = 5.4 Hz, 2H, O-CH_2), 3.94 (br s, 1H, NH), 3.41 (t, J = 5.4 Hz, 2H, N-CH_2); **^{13}C NMR (126 MHz, CDCl3):** δ 160.99, 146.00, 129.21, 122.65, 114.06, 62.36, 42.79; **FTIR (cm^{-1}):**3391, 2916, 2361, 2342, 1717, 1663, 1597, 1493, 1358, 1323, 1288, 1246, 1173, 1092, 1061, 1011, 922, 818, 745, 660, 598, 505; **HRMS (ESI) m/z:** ratio calcd for $C_9H_{11}ClNO_2$ $[M+H]^+$ 200.0478; found: 200.0481.

2-(3-chlorophenylamino)ethyl formate (Scheme 1, entry 2f)



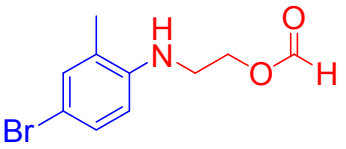
The product was obtained as yellow liquidin 95% yield (0.2216 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 75:25): 0.70;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.00 (s, 1H, CHO), 7.00 (t, J = 8.0 Hz, 1H, H_{Ar}), 6.61(d, J = 9.5 Hz, 1H, H_{Ar}), 6.51 (t, J = 2.0 Hz, 1H, H_{Ar}), 6.41 (dd, J = 8.2, 2.2 Hz, 1H, H_{Ar}), 4.26 (t, J = 5.4 Hz, 2H, O-CH_2), 4.02 (br s, 1H, NH), 3.32 (t, J = 5.5 Hz, 2H, N-CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):**δ 160.98, 148.65, 135.10, 130.37, 117.82, 112.58, 111.29, 62.33, 42.48; **FTIR (cm^{-1}):**3387, 2924, 2878, 1659, 1589, 1481, 1342, 1288, 1250, 1188, 1057, 934, 864, 779, 733, 687, 586, 525;**HRMS (ESI) m/z:** ratio calcd for $C_9H_{11}ClNO_2$ $[M+H]^+$ 200.0478; found: 200.0480.

2-(4-bromophenylamino)ethyl formate (Scheme 1, entry 2g)



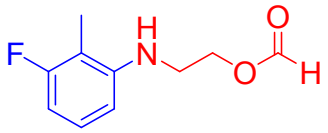
The product was obtained as colorless liquidin 95% yield (0.2148 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 75:25): 0.65;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.09 (s, 1H, CHO), 7.27 –7.24 (m, 2H, H_{Ar}), 6.52 – 6.49 (m, 2H, H_{Ar}), 4.35 (t, J = 5.4 Hz, 2H, O-CH_2), 3.97 (br s, 1H, NH), 3.40 (t, J = 5.5 Hz, 2H, N-CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.94, 146.46, 132.07, 114.54, 109.63, 62.33, 42.67;**FTIR (cm^{-1}):**3395, 2943, 2361, 2334, 1717, 1666, 1593, 1489, 1319, 1285, 1246, 1169, 1072, 1007, 934, 910, 814, 752, 555, 505; **HRMS (ESI) m/z:** ratio calcd for $C_9H_{11}BrNO_2$ $[M+H]^+$ 243.9973; found: 243.9978.

2-(4-bromo-2-methylphenylamino)ethyl formate (Scheme 1, entry 2h)



The product was obtained asyellow liquid in 92% yield (0.2059g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.65;**^{1}H NMR (500 MHz, $CDCl_3$): δ** 8.11 (s, 1H, CHO), 7.21 (dd, *J* = 8.5, 2.2 Hz,1H, H_{Ar}),7.18 – 7.17 (m, 1H, H_{Ar}), 6.48 (d, *J* = 8.6 Hz, 1H, H_{Ar}), 4.42 – 4.40 (m, 2H,O-CH_2), 3.82 (br s, 1H, NH), 3.45 (t, *J* = 5.4 Hz, 2H, N-CH_2), 2.11 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 161.03, 144.46, 132.73, 129.70, 124.53, 111.12, 109.26, 62.36, 42.82, 17.22; **FTIR (cm^{-1}):**3410, 2924, 2851, 2361, 2006, 1944, 1717, 1666, 1574, 1504, 1400, 1277, 1169, 1065, 995, 930, 860, 802, 752, 648, 540; **HRMS (ESI) m/z:** ratio calcd for $C_{10}H_{13}BrNO_2$ $[M+H]^+$ 258.0129; found: 258.0133.

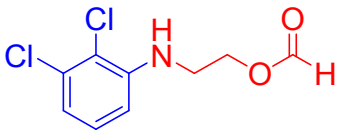
2-(3-fluoro-2-methylphenylamino)ethyl formate (Scheme 1, entry 2i)



The product was obtained as yellow liquidin 95% yield (0.2212 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.67; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.07 (d, J = 12.8 Hz, 1H, CHO), 7.04 (dd, J =14.9, 8.1Hz, 1H, H_{Ar}), 6.46 (t, J = 8.8 Hz, 1H, H_{Ar}), 6.38 (d, J = 8.2 Hz, 1H, H_{Ar}), 4.39 (t, J = 5.4 Hz, 2H, O-CH_2), 3.90 (br s, 1H, NH), 3.45 (t, J = 5.4 Hz, 2H, N-CH_2), 2.02 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 162.49, 161.10, 160.57, 147.12 (d, J = 28.4 Hz), 127.29 (d, J = 42.6 Hz), 108.99 (d, J = 74.9 Hz), 105.33 (d, J = 9.4 Hz), 104.69, 104.50, 62.42, 42.98, 8.12 (d, J = 25.65 Hz); **FTIR (cm^{-1}):**3422, 2932, 2859, 2361, 2338, 2187, 1975, 1948, 1717, 1620, 1585, 1516, 1474, 1373, 1327, 1292, 1234, 1169, 1142,

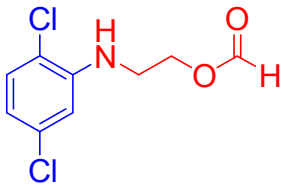
1057, 937, 826, 764, 706, 610, 498, 463; **HRMS (ESI) m/z:** ratio calcd for $C_{10}H_{13}FNO_2$ $[M+H]^+$ 198.093; found: 198.098.

2-(2,3-dichlorophenylamino)ethyl formate (Scheme 1, entry 2j)



The product was obtained as white solid in 85% yield (0.1935 g); **MP:**47-51°C;**R_F** (eluent hexanes/EtOAc 70:30): 0.70; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.11 (s, 1H, CHO), 7.07 (t, J = 8.0 Hz, 1H,H_{Ar}), 6.82 (d, J = 7.8 Hz, 1H, H_{Ar}), 6.58 (d, J = 8.1 Hz, 1H, H_{Ar}), 4.73 (br s, 1H, NH), 4.40 (t, J = 5.2 Hz, 2H, O-CH_2), 3.50 (d, J = 5.4 Hz, 2H, N-CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.87, 144.85, 133.14, 127.81, 118.59, 117.54, 108.91, 61.98, 42.52; **FTIR (cm^{-1}):**3372, 2913, 2874, 2851, 1697, 1585, 1501, 1454, 1381, 1319, 1234, 1196, 1130, 1015, 953, 837, 752, 694, 644, 528, 490; **HRMS (ESI) m/z:** ratio calcd for $C_9H_{10}Cl_2NO_2$ $[M+H]^+$ 234.0088; found: 234.0092.

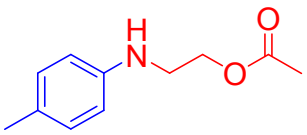
2-(2,5-dichlorophenylamino)ethyl formate (Scheme 1, entry 2k)



The product was obtained as colorless liquid in 88% yield (0.2005 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.68;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.10 (s, 1H, CHO), 7.15 (d, J = 8.2 Hz, 1H, H_{Ar}), 6.62 (dt,J = 8.2, 2.2 Hz, 2H, H_{Ar}), 4.63 (br s, 1H, NH), 4.38 (t, J = 5.5 Hz, 2H,O-CH_2), 3.45 (dd, J = 11.2, 5.6 Hz, 2H, N-CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.88, 144.17, 133.64, 130.05, 117.57, 117.52, 110.97, 61.95, 42.27; **FTIR (cm^{-1}):**3402, 2932, 2855, 2361, 2334, 1987, 1913, 1717, 1593, 1508, 1450, 1416, 1381, 1358, 1285, 1238, 1169, 1096, 953, 883, 756, 671, 648, 590,501; **HRMS (ESI) m/z:** ratio calcd for $C_9H_{10}Cl_2NO_2$ $[M+H]^+$ 234.0088; found: 234.0090.

3.3. O-acylatedalkanolamines (Scheme 2, entries 5a-5i)

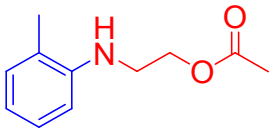
2-(p-toluidino)ethyl acetate (Scheme 2, entry 5a)



The product was obtained as colorless liquidin 94% yield (0.2407 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.65;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.00 (d, J = 8.0 Hz, 2H, H_{Ar}), 6.56 – 6.55 (m, 2H, H_{Ar}),4.26 (t, *J* = 5.5 Hz, 2H, O-CH_2), 3.76 (br s, 1H, NH), 3.37 (t, *J* = 5.5 Hz, 2H, N-CH_2), 2.24 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.15, 145.38, 129.84, 127.17, 113.18, 63.25, 43.26, 20.95, 20.40;**FTIR (cm^{-1}):**3391, 3017, 2916,

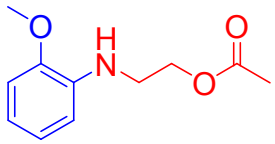
2855, 2335, 2361, 1732, 1616, 1520, 1450, 1366, 1227, 1134, 1045, 953, 806, 644, 606, 505; **GC-MS (EI, 70ev) *m/z* :** found: 193 ($C_{11}H_{15}NO_2$), calculated: 193.24 ($C_{11}H_{15}NO_2$).

2-(o-toluidino)ethyl acetate (Scheme 2, entry 5b)



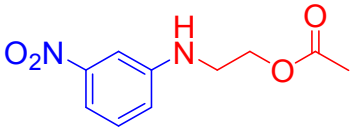
The product was obtained as white solidin 92% yield (0.2355g); **R_F** (eluent hexanes/EtOAc 65:35): 0.29;**^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.12 (td, *J* = 7.6, 1.1 Hz, 1H, H_{Ar}), 7.05 (dd, *J* = 7.3, 0.5 Hz, 1H, H_{Ar}),6.67 (td, *J* = 7.4, 0.9 Hz, 1H, H_{Ar}), 6.61 (d, *J* = 8.0 Hz, 1H, H_{Ar}), 4.31 (m, 2H, O-CH_2), 3.82 (br s, 1H, NH), 3.42 (m, 2H, N-CH_2), 2.13 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.31, 145.69, 130.28, 127.22, 122.30, 117.45, 109.70, 63.17, 43.08, 20.94, 17.48;**FTIR (cm^{-1}):**3402, 3021, 2970, 2928, 2847, 2361, 1732, 1585, 1524, 1454, 1362, 1323, 1242, 1138, 1042, 984, 910, 841, 745, 648, 602, 505;**GC-MS (EI, 70ev) *m/z* :** found: 193 ($C_{11}H_{15}NO_2$), calculated: 193.24 ($C_{11}H_{15}NO_2$).

2-(2-methoxyphenylamino)ethyl acetate (Scheme 2, entry 5c)



The product was obtained as brown liquidin 98% yield (0.2450 g); **R_F** (eluent hexanes/EtOAc 60:40): 0.60;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.87 (td, *J* = 7.7, 1.4 Hz, 1H, H_{Ar}), 6.77 (dd, *J* = 7.9, 1.3 Hz, 1H, H_{Ar}), 6.69 (td, *J* = 7.8, 1.5 Hz, 1H, H_{Ar}), 6.63 (dd, *J* = 7.8, 1.4 Hz, 1H, H_{Ar}), 4.44 (br, s, 1H, NH), 4.28 (t, *J* = 5.6 Hz, 2H, O-CH_2), 3.83 (s, 3H, CH_3), 3.40 (t, *J* = 5.6 Hz, 2H, N-CH_2), 2.07 (s, 3H,CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.13, 147.00, 137.63, 121.31, 117.03, 109.90, 109.63, 63.24, 55.46, 42.54, 20.95; **FTIR (cm^{-1}):**3410, 2936, 2835, 2361, 2342, 2261, 2137, 2033, 1940, 1736, 1601, 1512, 1431, 1366, 1223, 1177, 1099, 953, 903, 799, 644, 606, 579, 463;**HRMS (ESI) m/z:** ratio calcd for $C_{11}H_{16}NO_3$ $[M+H]^+$ 210.113; found: 210.117.

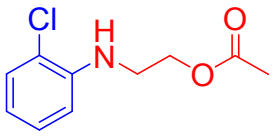
2-(3-nitrophenylamino)ethyl acetate (Scheme 2, entry 5d)



The product was obtained as darkyellow liquidin 85% yield (0.2089g); **R_F** (eluent hexanes/EtOAc 70:30): 0.62;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.52 (ddd, J = 8.1, 2.2, 0.8 Hz, 1H, H_{Ar}),7.42 (t, J = 2.3 Hz, 1H, H_{Ar}), 7.28 (t, J = 8.1 Hz, 1H, H_{Ar}), 6.92 (ddd, J = 8.2, 2.4, 0.7 Hz, 1H, H_{Ar}), 4.55 (br, s, 1H, NH), 4.31 (t, *J* = 5.5 Hz, 2H, O-CH_2), 3.46 (t, *J* = 5.4 Hz, 2H,

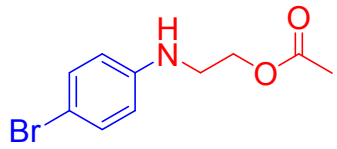
N-CH_2), 2.09 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.25, 149.33, 148.64, 129.80, 118.82, 112.13, 106.34, 62.81, 42.69, 20.84;**FTIR (cm^{-1}):**3395, 2361, 2334, 2087, 1728, 1620, 1582, 1342, 1242, 1130, 1096, 991, 968, 914, 887, 853, 787, 671, 606, 521; **HRMS (ESI) m/z:** ratio calcd for $C_{10}H_{13}N_2O_4$ $[M+H]^+$ 224.0797; found: 224.0800.

2-(2-chlorophenylamino)ethyl acetate (Scheme 2, entry 5e)



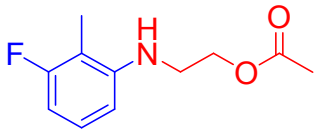
The product was obtained as yellow liquidin 92% yield (0.2292 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.67; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.26 – 7.24 (m, 1H, H_{Ar}), 7.15 – 7.12 (m, 1H, H_{Ar}), 6.68 –6.63 (m, 2H, H_{Ar}), 4.56 (br, s, 1H, NH), 4.29 (t, J = 5.6 Hz, 2H, O-CH_2), 3.44 (br s, 2H, N-CH_2), 2.08 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.12, 143.55, 129.29, 127.87, 119.43, 117.74, 111.21, 62.76, 42.58, 20.88;**FTIR (cm^{-1}):**3406, 2851, 2523, 2361, 2330, 2187, 1987, 1736, 1597, 1458, 1323, 1288, 1165, 953, 922, 841, 741, 637, 606, 525; **GC-MS (EI, 70ev) *m/z* :** found: 213 ($C_{10}H_{12}ClNO_2$), calculated: 213.66 ($C_{10}H_{12}ClNO_2$).

2-(4-bromophenylamino)ethyl acetate (Scheme 2, entry 5f)



The product was obtained as brown oil in 90% yield (0.2154 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.67;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.18 – 7.15 (m, 2H, H_{Ar}), 6.42 – 6.40 (m, 2H, H_{Ar}),4.17 (t, J = 5.5 Hz, 2H, O-CH_2), 3.90 (br, s, 1H, NH), 3.26 (t, J =5.5 Hz, 2H, N-CH_2), 1.99 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.17, 146.72, 132.00, 114.47, 109.34, 62.95, 42.89, 20.93; **FTIR (cm^{-1}):**3387, 2951, 2361, 2338, 1732, 1593, 1501, 1369, 1319, 1238, 1180, 1134, 1045, 999, 949, 814, 733, 694, 633, 606, 501; **GC-MS (EI, 70ev) *m/z* :** found: 258 ($C_{10}H_{12}BrNO_2$), calculated: 258.11 ($C_{10}H_{12}BrNO_2$).

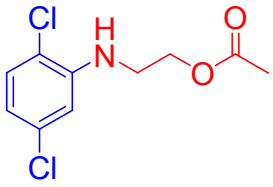
2-(3-fluoro-2-methylphenylamino)ethyl acetate (Scheme 2, entry 5g)



The product was obtained as white solidin 95% yield (0.2376 g); **MP:**85-89°C; **R_F** (eluent hexanes/EtOAc 70:30): 0.70; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.04 (dd, J = 14.9, 8.1 Hz, 1H, H_{Ar}), 6.46 (t,J = 8.8 Hz, 1H, H_{Ar}), 6.39 (d, J = 8.1 Hz, 1H, H_{Ar}), 4.32 (t, *J* = 5.5 Hz, 2H, O-CH_2), 3.92 (br, s, 1H, NH), 3.43 (t, J = 5.4 Hz, 2H, N-CH_2), 2.09 (s, 3H, CH_3), 2.03 (d, J = 1.4 Hz, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.34, 162.46, 160.55, 147.27, 127.24 (d, J = 42.7 Hz), 108.85 (d, J = 74.5 Hz), 105.30, 104.53, 104.34, 62.98, 43.32, 20.90, 8.16; **FTIR (cm^{-1}):**3399, 2994, 2866, 1728, 1582, 1528, 1458, 1366, 1234, 1142, 1053, 922, 814,

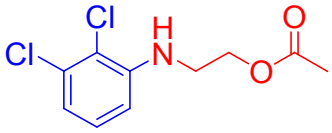
764, 706, 644, 602, 563, 501;**HRMS (ESI) m/z:** ratio calcd for $C_{11}H_{15}FNO_2$ $[M+H]^+$ 212.1087; found: 212.1092.

2-(2,5-dichlorophenylamino)ethyl acetate (Scheme 2, entry 5h)



The product was obtained as yellow liquid in 85% yield (0.2050 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.67;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.13 (d, *J* = 8.4 Hz, 1H, H_{Ar}), 6.64 (d, *J* = 2.3 Hz, 1H, H_{Ar}), 6.60 (dd, *J* = 8.4, 2.3 Hz, 1H, H_{Ar}), 4.68 (br, s, 1H, NH), 4.28 (t, *J* = 5.5 Hz, 2H, CH_2), 3.40 (t, *J* = 5.5 Hz, 2H, CH_2), 2.08 (s, 3H, CH_3);**^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.15, 144.39, 133.68, 129.86, 117.45, 117.27, 111.00, 62.63, 42.48, 20.79;**FTIR (cm^{-1}):**3399, 2851, 2361, 2334, 2207, 2183, 2091, 2045, 1736, 1593, 1447, 1393, 1366, 1234, 1138, 1042, 964, 910, 829, 787, 602, 548, 467; **HRMS (ESI) m/z:** ratio calcd for $C_{10}H_{12}Cl_2NO_2$ $[M+H]^+$ 248.0245; found: 248.0248.

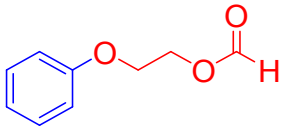
2-(2,3-dichlorophenylamino)ethyl acetate (Scheme 2, entry 5i)



The product was obtained as colorless solid in 83% yield (0.1990 g); **MP:**62-66°C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.65; **^{1}H NMR (500 MHz, $CDCl_3$):**δ 7.13 (d, J = 8.4 Hz, 1H, H_{Ar}), 6.64 (d,J = 2.3 Hz, 1H, H_{Ar}), 6.60 (dd, J = 8.4, 2.3 Hz, 1H, H_{Ar}), 4.69 (br, s, 1H, NH), 4.28 (t, *J* = 5.5 Hz, 2H, O-CH_2), 3.40 (t, J = 5.5 Hz, 2H, N-CH_2), 2.08 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.13, 145.06, 133.04, 127.78, 118.39, 117.44, 108.96, 62.54, 42.78, 20.87; **FTIR (cm^{-1}):**3391, 2947, 2338, 1902, 1736, 1589, 1501, 1454, 1366, 1323, 1227, 1126, 1038, 957, 853,760, 606, 498;**HRMS (ESI) m/z:** ratio calcd for $C_{10}H_{12}Cl_2NO_2$ $[M+H]^+$ 248.0245; found: 248.0247.

3.4. *O*-formylated phenoxyethanols (Scheme 3, entries 9a-9l)

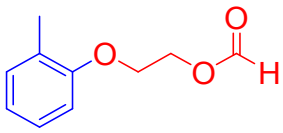
2-phenoxyethyl formate (Scheme 3, entry 9a)



The product was obtained as paleyellow liquidin 99% yield (0.2385 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 98:2): 0.85;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.12 – 8.11 (m, 1H, CHO), 7.31 – 7.24 (m, 2H, H_{Ar}), 6.98(tt, J = 7.5, 1.0 Hz, 1H, H_{Ar}), 6.91 (ddd, J = 4.5, 3.3, 1.8 Hz, 2H, H_{Ar}), 4.52 – 4.50 (m, 2H, CH_2),4.20 – 4.18 (m, 2H, CH_2);**^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.87, 158.30,

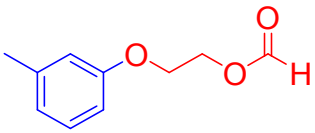
129.60, 121.36, 114.58, 65.53, 62.28; **FTIR (cm^{-1}):**2361, 2342, 1755, 1721, 1597, 1493, 1454, 1366, 1335, 1288, 1242, 1165, 1115, 1088, 1065, 926, 883, 841, 795, 756, 691, 644, 602, 548, 509, 471;**GC-MS (EI, 70ev)** ***m/z*** **:** found: 166 ($C_9H_{10}O_3$), calculated: 166.17 ($C_9H_{10}O_3$).

2-(o-tolyloxy)ethyl formate (Scheme 3, entry 9b)



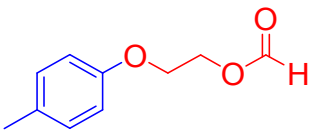
The product was obtained as colorless liquidin 98% yield (0.2327g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 98:2): 0.78; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.10 (s, 1H, CHO), 7.16 (dd, J = 25.7, 19.4 Hz, 2H,H_{Ar}), 6.89 –6.77 (m, 2H, H_{Ar}), 4.52 (t, *J* = 4.6 Hz, 2H, CH_2), 4.16 (t, *J* = 4.7 Hz, 2H, CH_2), 2.22 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.92, 156.51, 130.91, 127.13, 126.84, 121.07, 111.22, 65.82, 62.36, 16.16; **FTIR (cm^{-1}):**2924, 2361, 2342, 1759, 1721, 1589, 1493, 1454, 1377, 1285, 1242, 1165, 1123, 1069, 988, 930, 837, 752, 714, 667, 610, 536, 513, 486;**GC-MS (EI, 70ev)** ***m/z*** **:** found: 180 ($C_{10}H_{12}O_3$), calculated: 180.2 ($C_{10}H_{12}O_3$).

2-(m-tolyloxy)ethyl formate (Scheme 3, entry 9c)



The product was obtained as colorless liquidin 99% yield (0.2349 g);$\mathbf{R_F}$ (eluent hexanes/EtOAc 98:2): 0.81;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.11 (s, 1H, CHO), 7.17 (t, J = 7.8 Hz, 1H, H_{Ar}), 6.80 –6.70 (m, 3H, H_{Ar}), 4.50 (ddd, J = 4.8, 3.5, 0.7 Hz, 2H, CH_2), 4.17 (dd, J = 7.2, 2.3 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.88, 158.33, 139.68, 129.32, 122.19, 115.50, 111.40, 65.50, 62.32, 21.52; **FTIR (cm^{-1}):**2924, 2870, 2361, 2342, 2018, 1840, 1755, 1585, 1489, 1454, 1369, 1288, 1246, 1153, 1069, 880, 849, 772, 733, 691, 606;**GC-MS (EI, 70ev)** ***m/z*** **:** found: 180 ($C_{10}H_{12}O_3$), calculated: 180.2 ($C_{10}H_{12}O_3$).

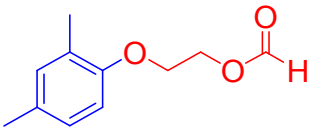
2-(p-tolyloxy)ethyl formate (Scheme 3, entry 9d)



The product was obtained as white solidin 99% yield (0.2342 g);MP: 54-58°C;$\mathbf{R_F}$ (eluent hexanes/EtOAc 98:2): 0.82; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.12 (s, 1H, CHO), 7.09 (d, J = 8.6 Hz, 2H,H_{Ar}), 6.82 – 6.80 (m, 2H, H_{Ar}), 4.50 (t, *J* = 4.7 Hz, 2H, CH_2), 4.17 (t, *J* = 4.7 Hz, 2H, CH_2), 2.29 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.88, 156.20, 130.65, 130.02, 114.49, 65.75, 62.35, 20.49; **FTIR (cm^{-1}):**2928, 2878, 2361, 2342, 1767, 1701,

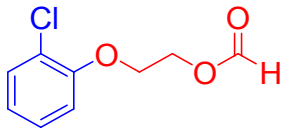
1589, 1485, 1447, 1412, 1373, 1281, 1250, 1177, 1069, 1042, 930, 841, 795, 752, 691, 602, 548, 474; **GC-MS (EI, 70ev)** ***m/z :*** found: 180 ($C_{10}H_{12}O_3$), calculated: 180.2 ($C_{10}H_{12}O_3$).

2-(2,4-dimethylphenoxy)ethyl formate (Scheme 3, entry 9e)



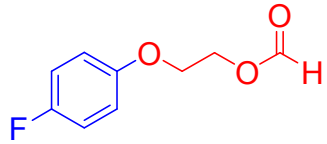
The product was obtained as colorless solid in 99% yield (0.2316 g); **MP:**26-30°C;**R_F** (eluent hexanes/EtOAc 98:2): 0.85; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.12 (s, 1H, CHO), 6.94 (dd, J = 12.9,4.8 Hz, 2H, H_{Ar}), 6.69 (d, J = 8.2 Hz, 1H, H_{Ar}), 4.52 (ddd, J = 4.7, 3.6, 0.7 Hz, 2H, CH_2), 4.16 (t, *J* = 4.7 Hz, 2H, CH2), 2.25 (s, 3H, CH3), 2.19 (s, 3H, CH3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.92, 154.41, 131.72, 130.34, 126.98, 126.94, 111.45, 66.11, 62.46, 20.48, 16.06; **FTIR (cm^{-1}):**3009, 2924, 2882, 1991, 1709, 1612, 1504, 1462, 1373, 1300, 1254, 1134, 1076, 1030, 918, 845, 806, 764, 714, 579, 540;**GC-MS (EI, 70ev)** ***m/z*** **:** found: 194 ($C_{11}H_{14}O_3$), calculated: 194.23 ($C_{11}H_{14}O_3$).

2-(2-chlorophenoxy)ethyl formate (Scheme 3, entry 9f)



The product was obtained as white solidin 98% yield (0.2271 g);**MP:**49-53°C;RF (eluent hexanes/EtOAc 98:2): 0.90; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.07 (s, 1H, CHO), 7.31 – 7.29 (m, 1H, H_{Ar}), 7.14(ddd, J = 8.3, 7.5, 1.6 Hz, 1H, H_{Ar}), 6.88 – 6.85 (m, 2H, H_{Ar}), 4.51 – 4.49 (m, 2H, CH_2), 4.20 (t, *J* = 4.7 Hz, 2H, CH2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 159.80, 152.92, 129.50, 126.72, 122.36, 121.22, 113.00, 65.93, 60.97; **FTIR (cm^{-1}):**2994, 2955, 2920, 2874, 2361, 2342, 1886, 1763, 1705, 1612, 1589, 1512, 1443, 1408, 1373, 1292, 1242, 1177, 1115, 1072, 1030, 930, 849, 810, 737, 555, 513; **GC-MS (EI, 70ev)** ***m/z*** **:** found: 200 ($C_9H_9ClO_3$), calculated: 200.62 ($C_9H_9ClO_3$).

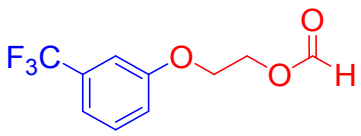
2-(4-fluorophenoxy)ethyl formate (Scheme 3, entry 9g)



The product was obtained as colorless liquid in 99% yield (0.2338 g); **R_F** (eluent hexanes/EtOAc 98:2): 0.88;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.12 (s, 1H,CHO), 7.05 – 6.96 (m,2H, H_{Ar}), 6.87 –6.83 (m, 2H, H_{Ar}), 4.51 – 4.49 (m, 2H, CH_2), 4.17 – 4.15 (m, 2H, CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.80, 157.58 (d, J = 239.4 Hz), 154.44 (d, J = 2.14 Hz), 115.96 (d, J = 23.21 Hz),115.69 (d, J = 8.08 Hz), 66.31, 62.18; **FTIR (cm^{-1}):**2932, 2361,

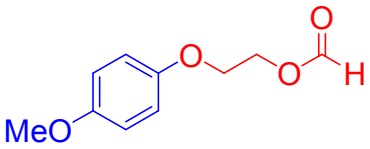
2338, 1994, 1721, 1601, 1504, 1458, 1366, 1288, 1246, 1165, 1099, 1069, 926, 826, 745, 667, 555, 513;**GC-MS (EI, 70ev) *m/z* :** found: 184 ($C_9H_9FO_3$), calculated: 184.16 ($C_9H_9FO_3$).

2-(3-(trifluoromethyl)phenoxy)ethyl formate (Scheme 3, entry 9h)



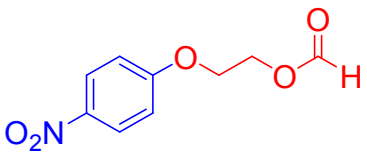
The product was obtained as colorless liquid in 97% yield (0.2209 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 98:2): 0.90;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.12 (s, 1H, CHO), 7.40 (t, J = 8.0 Hz, 1H, H_{Ar}), 7.25 (t, J = 8.8 Hz, 1H, H_{Ar}), 7.15 (s, 1H, H_{Ar}), 7.08 (dd, J = 8.3, 2.3 Hz, 1H, H_{Ar}), 4.54 (t, *J* = 4.7 Hz, 2H, CH_2), 4.24 (t, *J* = 4.7 Hz, 2H, CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.72, 158.43, 131.94 (q, J = 32.44 Hz), 130.13, 123.88 (q, J = 272.88 Hz), 118.02 (q, *J* = 4.0 Hz), 111.38 (q, *J* = 3.8 Hz), 65.87, 61.91; **FTIR (cm^{-1}):**2940, 2361, 2342, 1724, 1593, 1493, 1450, 1369, 1327, 1242, 1161, 1119, 1065, 999, 945, 864, 787, 745, 698, 656, 610, 575, 521; **GC-MS (EI, 70ev) *m/z* :** found: 234 ($C_{10}H_9F_3O_3$), calculated: 234.17 ($C_{10}H_9F_3O_3$).

2-(4-methoxyphenoxy)ethyl formate (Scheme 3, entry 9i)



The product was obtained as white shiny solidin 99% yield (0.2309 g);**MP:**40-43 °C;$\mathbf{R_F}$ (eluent hexanes/EtOAc 85:15): 0.75;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.12 (s, 1H, CHO), 6.87 –6.82 (m, 4H, H_{Ar}), 4.50 (t, *J* = 4.7 Hz, 2H, CH_2), 4.15 (t, *J* =4.7 Hz, 2H, CH_2), 3.77 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.87, 154.29, 152.43, 115.72, 114.72, 66.41, 62.38, 55.71; **FTIR (cm^{-1}):**3017, 2990, 2963, 2932, 2839, 2361, 2338, 1759, 1717, 1593, 1508, 1458, 1377, 1315, 1288, 1231, 1177, 1111, 1069, 1026, 953, 918, 853, 826, 729, 567, 521; **GC-MS (EI, 70ev) *m/z* :** found: 196($C_{10}H_{12}O_4$), calculated: 196.2 ($C_{10}H_{12}O_4$).

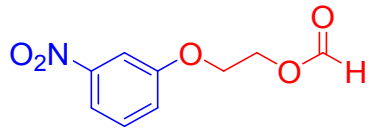
2-(4-nitrophenoxy)ethyl formate (Scheme 3, entry 9j)



The product was obtained as white solidin 97% yield (0.2237g);**MP:**82-86 °C;$\mathbf{R_F}$ (eluent hexanes/EtOAc 85:15): 0.78;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.24 – 8.21 (m, 2H, H_{Ar}), 8.13 (s, 1H, CHO), 7.01 – 6.97 (m, 2H, H_{Ar}),

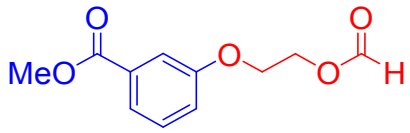
4.58 (t, *J* = 4.6 Hz, 2H,CH_2), 4.31 (t, *J* = 4.6 Hz, 2H, CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 163.21, 160.60, 141.98, 126.00, 114.53, 66.27, 61.61;**FTIR (cm^{-1}):**3719, 3113, 3082, 2936, 2361, 2338, 1759, 1713, 1593, 1512, 1462, 1412, 1373, 1335, 1308, 1261, 1177, 1111, 1061, 1030, 957, 926, 849, 791, 752, 691, 660, 625, 532, 498;**GC-MS (EI, 70ev) *m/z* :** found: 211 ($C_9H_9NO_5$), calculated: 211.17 ($C_9H_9NO_5$).

2-(3-nitrophenoxy)ethyl formate (Scheme 3, entry 9k)



The product was obtained as white solid in 97% yield (0.2231 g); **MP:**66-70 °C;**R_F** (eluent hexanes/EtOAc 85:15): 0.75; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.14 – 8.13 (m, 1H, CHO), 7.86(ddd, J = 8.1, 2.1, 0.9 Hz, 1H, H_{Ar}), 7.75 (t, J = 2.3 Hz, 1H, H_{Ar}), 7.46 (t, J = 8.2 Hz, 1H, H_{Ar}), 7.27 – 7.25 (m, 1H, H_{Ar}), 4.58 – 4.56 (m, 2H, CH_2), 4.30 (t, *J* = 4.5 Hz, 2H, CH2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.64, 158.82, 149.20, 130.16, 121.71, 116.40, 108.83, 66.26, 61.73; **FTIR (cm^{-1}):**3406, 3109, 3071, 2361, 2342, 2014, 1759, 1709, 1609, 1528, 1481, 1447, 1412, 1346, 1292, 1246, 1111, 1069, 995, 961, 910, 872, 841, 791, 733, 671, 610, 548, 463;**GC-MS (EI, 70ev) *m/z* :** found: 211 ($C_9H_9NO_5$), calculated: 211.17($C_9H_9NO_5$).

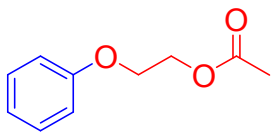
***N,N*-bis(2-chlorobenzyl)-4-methylbenzenamine (Scheme 3, entry 9l)**



The product was obtained as colorless liquidin 97% yield (0.2214 g); **R_F** (eluent hexanes/EtOAc 95:5): 0.75; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.13 (s, 1H, CHO), 7.67 – 7.66 (m,1H, H_{Ar}), 7.57 – 7.56 (m, 1H, H_{Ar}), 7.35 (t, J = 8.0 Hz, 1H, H_{Ar}), 7.13 – 7.11 (m, 1H, H_{Ar}), 4.54 (t, *J* = 4.5 Hz, 2H, CH2), 4.25 (t, *J* = 4.6 Hz, 2H, CH2), 3.91 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 166.75, 160.78, 158.26, 131.54, 129.57, 122.61, 120.04, 114.59, 65.80, 62.04, 52.22;**GC-MS (EI, 70ev) *m/z* :** found: 224 ($C_{11}H_{12}O_5$), calculated: 224.21 ($C_{11}H_{12}O_5$).

3.5. *O*-acylated phenoxyethanols (Scheme 4, entries 10a-10h)

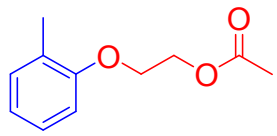
2-phenoxyethyl acetate (Scheme 4, entry 10a)



The product was obtained as colorless liquidin 96% yield (0.2507 g); **R_F** (eluent hexanes/EtOAc 95:5): 0.85; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.30 – 7.24 (m, 2H, H_{Ar}), 6.98 – 6.94 (m, 1H, H_{Ar}), 6.92

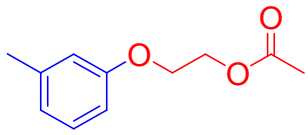
– 6.90 (m,2H, H_{Ar}), 4.42 – 4.40 (m, 2H, CH_2), 4.16 – 4.14 (m, 2H, CH_2), 2.08 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.05, 158.49, 129.56, 121.21, 114.61, 65.83, 62.90, 20.90; **FTIR (cm^{-1}):**1736, 1597, 1493, 1458, 1373, 1223, 1173, 1053, 961, 918, 883, 833, 756, 691, 644, 602, 509;**GC-MS (EI, 70ev) *m/z* :** found: 180 ($C_{10}H_{12}O_3$), calculated: 180.2 ($C_{10}H_{12}O_3$).

2-(o-tolyloxy)ethyl acetate (Scheme 4, entry 10b)



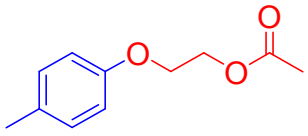
The product was obtained as colorless liquidin 95% yield (0.2426 g); **R_F**(eluent hexanes/EtOAc 95:5): 0.86; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.15 – 7.12 (m, 2H, H_{Ar}), 6.87 (td, J = 7.4, 0.9 Hz, 1H, H_{Ar}), 6.79 –6.78 (m, 1H, H_{Ar}), 4.43 – 4.41 (m, 2H, CH_2), 4.15 – 4.13 (m, 2H, CH_2), 2.22 (s, 3H, CH_3), 2.07 (d, J = 8.0 Hz, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.04, 156.67, 130.84, 127.14, 126.82, 120.94, 111.34, 66.11, 62.93, 20.88, 16.16; **FTIR (cm^{-1}):**2924, 2307, 1987, 1740, 1589, 1493, 1454, 1404, 1373, 1223, 1192, 1123, 1049, 1003, 961, 922, 837, 748, 714, 637, 606, 536, 482;**GC-MS (EI, 70ev) *m/z* :** found: 194 ($C_{11}H_{14}O_3$), calculated: 194.23 ($C_{11}H_{14}O_3$).

2-(m-tolyloxy)ethyl acetate (Scheme 4, entry 10c)



The product was obtained as colorless liquidin 96% yield (0.2455 g); **R_F**(eluent hexanes/EtOAc 95:5): 0.82; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.16 (t, J = 7.8 Hz, 1H, H_{Ar}), 6.80 – 6.70 (m, 3H, H_{Ar}),4.42 – 4.40 (m, 2H, CH_2), 4.15 (dd, J = 5.4, 4.2 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.09 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.05, 158.50, 139.61, 129.28, 122.02, 115.50, 111.43, 65.79, 62.93, 21.53, 20.92; **FTIR (cm^{-1}):** 2920, 2870, 2361, 2342, 2018, 1736, 1585, 1489, 1450, 1400, 1373, 1227, 1157, 1057, 1003, 964, 880, 772, 741, 691, 640, 606, 517;**GC-MS (EI, 70ev) *m/z* :** found: 194 ($C_{11}H_{14}O_3$), calculated: 194.23 ($C_{11}H_{14}O_3$).

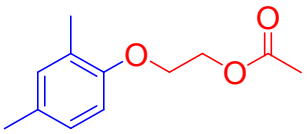
2-(p-tolyloxy)ethyl acetate (Scheme 4, entry 10d)



The product was obtained as colorless liquidin 96% yield (0.2459 g); **R_F**(eluent hexanes/EtOAc 95:5): 0.85; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.07 (dd, J = 8.7, 0.6 Hz, 2H, H_{Ar}), 6.81

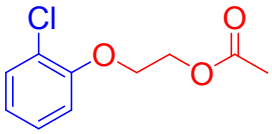
– 6.78 (m, 2H,H_{Ar}), 4.40 – 4.37 (m, 2H, CH_2), 4.12 – 4.10 (m, 2H, CH_2), 2.27 (s, 3H, CH_3), 2.08 (s, 3H, CH_3); **^{13}C NMR(126 MHz, $CDCl_3$):**δ 171.03, 156.41, 130.42, 129.98, 114.51, 66.03, 62.96, 20.89, 20.48; **FTIR (cm^{-1}):**3526, 3063, 2940, 2218, 1921, 1736, 1589, 1485, 1373, 1227, 1057, 961, 833, 748, 694, 602, 517;**GC-MS (EI, 70ev) *m/z* :** found: 194 ($C_{11}H_{14}O_3$), calculated: 194.23 ($C_{11}H_{14}O_3$).

2-(2,4-dimethylphenoxy)ethyl acetate(Scheme 4, entry 10e)



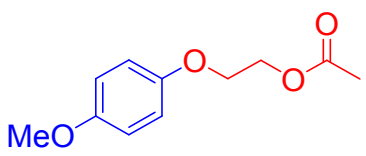
The product was obtained as colorless liquidin 95% yield (0.2383 g); **R_F**(eluent hexanes/EtOAc 95:5): 0.80; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.93 (dd, *J* = 12.7, 4.6 Hz, 2H, H_{Ar}), 6.69 (d, *J* = 8.2 Hz,1H, H_{Ar}), 4.41 (t, *J* = 4.8 Hz, 2H, CH_2), 4.12 (t, *J* = 4.83 Hz, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.09 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.09, 154.57, 131.66, 130.20, 126.97, 111.61, 66.43, 63.02, 20.90, 20.47, 16.06; **FTIR (cm^{-1}):**3017, 2920, 2064, 1740, 1612, 1504, 1454, 1373, 1215, 1134, 1053, 961, 880, 826, 802, 714, 637, 606, 559;**GC-MS (EI, 70ev) *m/z* :** found: 208($C_{12}H_{16}O_3$), calculated: 208.25 ($C_{12}H_{16}O_3$).

2-(2-chlorophenoxy)ethyl acetate (Scheme 4, entry 10f)



The product was obtained as colorless liquidin 94% yield (0.2333 g); **R_F**(eluent hexanes/EtOAc 95:5): 0.81; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.37 – 7.35 (m, 1H, H_{Ar}), 7.20 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1H, H_{Ar}),6.94 – 6.90 (m, 2H, H_{Ar}), 4.46 – 4.45 (m, 2H, CH_2), 4.24 – 4.22 (m, 2H, CH_2), 2.10 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** 171.00, 154.12, 130.46, 127.74, 123.39, 122.11, 114.15, 67.25, 62.54, 20.87;**FTIR (cm^{-1}):**3005, 2916, 2866, 2357, 1740, 1612, 1512, 1454, 1373, 1223, 1057, 961, 818, 737, 606, 559, 513;**GC-MS (EI, 70ev) *m/z* :** found: 214 ($C_{10}H_{11}ClO_3$), calculated: 214.65 ($C_{10}H_{11}ClO_3$).

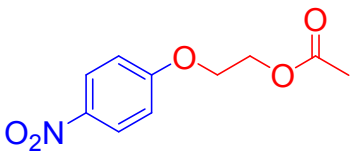
2-(4-methoxyphenoxy)ethyl acetate (Scheme 4, entry 10g)



The product was obtained as white solid in 98% yield (0.2452 g); **MP:** 38-42 °C; RF(eluent hexanes/EtOAc 95:5): 0.85; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.87 – 6.82 (m, 4H, H_{Ar}), 4.41 –4.39 (m, 2H, CH_2), 4.13 – 4.11 (m, 2H,

CH_2), 3.77 (s, 3H,CH_3), 2.10 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.06, 154.18, 152.62, 115.73, 114.68, 66.71, 62.99, 55.72, 20.93; **FTIR (cm^{-1}):**3013, 2963, 2924, 2878, 1728, 1508, 1474, 1439, 1412, 1381, 1285, 1219, 1184, 1107, 1045, 907, 826, 802, 741, 648, 606, 517, 471; **GC-MS (EI, 70ev) *m/z* :** found: 210 ($C_{11}H_{14}O_4$), calculated: 210.23 ($C_{11}H_{14}O_4$).

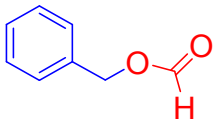
2-(4-nitrophenoxy)ethyl acetate (Scheme 4, entry 10h)



The product was obtained as white solid in 94% yield (0.2314 g);**MP:**76-80 °C; **R_F** (eluent hexanes/EtOAc 90:10): 0.80;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.23 – 8.20 (m, 2H, H_{Ar}), 7.01 – 6.99 (m, 2H, H_{Ar}), 4.48 – 4.46 (m, 2H, CH_2), 4.29 – 4.27 (m,2H, CH_2), 2.12 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):**δ 170.87, 163.43, 141.84, 125.95, 114.54, 66.58, 62.25, 20.84; **FTIR (cm^{-1}):**3017, 2940, 1967, 1736, 1589, 1497, 1458, 1381, 1331, 1265, 1223, 1173, 1107, 1045, 941, 841, 752, 660, 498;**GC-MS (EI, 70ev) *m/z* :** found: 225 ($C_{10}H_{11}NO_5$), calculated: 225.2 ($C_{10}H_{11}NO_5$).

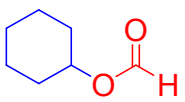
3.6. *O*-formylated alcohols (Scheme 5, entries 13a-13c)

benzyl formate (Scheme 5, entry 13a)



The product was obtained as colorless liquid in 99% yield (0.2496 g); **R_F** (eluent hexanes/EtOAc 80:20): 0.75;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.00 (t, J = 0.9 Hz, 1H, CHO), 7.28 – 7.20 (m, 5H, H_{Ar}), 5.08 (d, J = 0.8 Hz,2H, CH_2);**^{13}C NMR (126 MHz, $CDCl_3$):** δ159.71, 134.18, 127.58, 127.42, 127.30 64.57; **FTIR (cm^{-1}):**3032, 2928, 1717, 1497, 1454, 1369, 1258, 1150, 1026, 899, 741, 698, 594, 482;**GC-MS (EI, 70ev) *m/z* :** found: 136 ($C_8H_8O_2$), calculated: 136.15 ($C_8H_8O_2$).

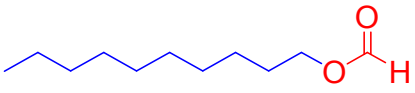
cyclohexyl formate (Scheme 5, entry 13b)



The product was obtained as pale colorless liquid in 97% yield (0.2489 g); **R_F** (eluent hexanes/EtOAc 80:20): 0.70; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.04 (d, J = 0.6 Hz, 1H, CHO), 4.92 – 4.87 (m, 1H, O-CH), 1.90 – 1.86 (m,2H, CH_2), 1.78 – 1.72 (m, 2H, CH_2), 1.58 – 1.53 (m, 1H, CH), 1.51 – 1.44 (m, 2H, CH_2), 1.42 – 1.37 (m, 2H, CH_2), 1.36 – 1.27 (m, 1H, CH); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 160.68, 72.56, 31.53, 25.22, 23.59;**FTIR (cm^{-1}):** 2936, 2859, 2361, 2342, 1755,

1717, 1450, 1369, 1242, 1177, 1123, 1049, 1011, 899, 841, 810, 756, 667, 644, 536, 471;**GC-MS (EI, 70ev) *m/z* :** found: 128 ($C_7H_{12}O_2$), calculated: 128.17 ($C_7H_{12}O_2$).

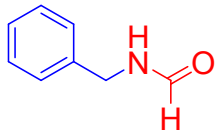
decyl formate (Scheme 5, entry 13c)



The product was obtained as colorless oil in 98% yield (0.2307g); **R_F** (eluent hexanes/EtOAc 80:20): 0.76;**^{1}H NMR (500 MHz, $CDCl_3$):**δ 8.06 (s, 1H, CHO), 4.16 (t, J= 6.7 Hz, 2H, CH_2), 1.69 – 1.63 (m, 2H, CH_2), 1.39 – 1.27 (m, 14H, CH_2), 0.88 (t, J = 6.9 Hz, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 161.20, 64.11, 31.87, 29.50, 29.49, 29.29, 29.18, 28.50, 25.81, 22.66, 14.08; **FTIR (cm^{-1}):**2924, 2855, 1728, 1458, 1381, 1250, 1165, 1049, 910, 718;**GC-MS (EI, 70ev) *m/z* :** found: 186 ($C_{11}H_{22}O_2$), calculated: 186.29 ($C_{11}H_{22}O_2$).

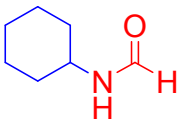
3.7. *N*-formylated amines (Scheme 5, entries 14b-14d)

***N*-benzylformamide(Scheme 5, entry 14b)[2]**



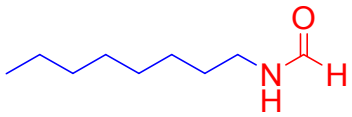
The product was obtained as white solid in 5% yield (0.0138 g); **MP:** 61-64°C; **R_F** (eluent hexanes/EtOAc 70:30): 0.48; **^{1}H NMR(500 MHz, $CDCl_3$):** Mixture of rotamers is observed; Ratio: 8.15/1.5; Major rotamer: δ 8.23 (s, 1H, CHO), 7.38-7.22 (m, 5H, H_{Ar}), 6.05 (br s, 1 H,NH), 4.46 (d, J = 6.0 Hz, 2H, NCH_2); Minor rotamer: δ 8.14 (d, J = 6.0 Hz, CHO), 7.38-7.22 (m, 5H, H_{Ar}), 6.05 (br s, 1 H, NH), 4.39 (d, J = 6.4 Hz, 2H, NCH_2); **FTIR (cm^{-1}):** 3271, 3028, 2359, 2234, 1651, 1530, 1389, 1225, 972, 833, 696, 610; **GC-MS (EI, 70ev) *m/z* :** found: 135 (C_8H_9NO), calculated: 135.16 (C_8H_9NO).

***N*-cyclohexylformamide(Scheme 5, entry 14c)[2]**



The product was obtained asbrown oilin 3% yield (0.0092 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.40; **^{1}H NMR (500 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 7.8/2.2. Major rotamer: δ 8.11(m, 1H, CHO),6.05 (br s, 1H, NH), 3.88 – 3.82 (m, 1H, N-CH), 1.94 – 1.90 (m, 2H, CH_2), 1.75 – 1.70 (m, 2H, CH_2), 1.38 – 1.30 (m, 3H, CH_2), 1.22 – 1.16 (m, 3H, CH_2); Minor rotamer: δ 8.11 (m, 1H, CHO), 6.19 (br s, 1H, NH), 3.34 – 3.28 (m, 1H, N-CH), 1.94 – 1.90 (m, 2H, CH_2), 1.75 – 1.70 (m, 2H, CH_2), 1.63 – 1.61 (m, 4H, CH_2), 1.38 – 1.30 (m, 1H, CH_2), 1.22 – 1.16 (m, 1H, CH_2); **FTIR (cm^{-1}):** 3262, 3048, 2930, 2855, 2357, 2235, 1651, 1531, 1450, 1383, 1252, 1150, 1065, 937, 891, 843, 729; **GC-MS (EI, 70ev) *m/z* :** found: 127 ($C_7H_{13}NO$), calculated: 127.18 ($C_7H_{13}NO$).

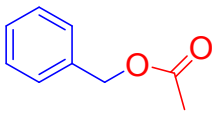
***N*-octylformamide (Scheme 5, entry 14d)[2]**



The product was obtained as yellow brown oil in 4% yield (0.0106 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.47; **^{1}H NMR (500 MHz, $CDCl_3$):** Mixture of rotamers isobserved. Ratio: 8.2/1.8. Major rotamer: δ 8.14 (s, 1H, CHO), 6.21 (s, 1H, NH), 3.27 (q, *J* = 6.9 Hz, 2H, N-CH_2), 1.55 – 1.49 (m, 2H, CH_2), 1.30 – 1.27 (m, 10H, CH_2), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3); Minor rotamer: δ 8.03 (d, *J* = 12.0 Hz, 1H, CHO), 6.21 (s, 1H, NH), 3.21 (q, *J* = 6.7 Hz, 2H, N-CH_2), 1.55 – 1.49 (m, 2H, CH_2), 1.30 – 1.27 (m, 10H, CH_2), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3); **FTIR (cm^{-1}):** 3725, 3275, 3048, 2926, 2857, 2355, 2234, 1659, 1533, 1456, 1383, 1234, 729; **GC-MS (EI, 70ev) *m/z* :** found: 157 ($C_9H_{19}NO$), calculated: 157.25 ($C_9H_{19}NO$).

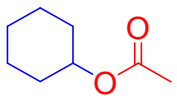
3.8. *O*-acylated alcohols (Scheme 5, entries 15a-15c)

benzyl acetate (Scheme 5, entry 15a)



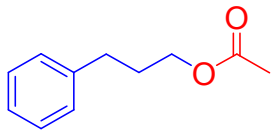
The product was obtained as colorless liquid in 99% yield (0.2747 g); **R_F** (eluent hexanes/EtOAc 80:20): 0.70;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.45 – 7.27 (m, 5H, H_{Ar}), 5.10 (s, 2H, CH_2), 2.09 (s, 3H, CH_3); **^{13}C NMR (126MHz, $CDCl_3$):**δ170.94, 135.97, 128.60, 128.29, 128.19,66.34, 21.02; **FTIR (cm^{-1}):**3059, 3028, 2361, 2338, 1736, 1454, 1381, 1362, 1308, 1227, 1103, 1084, 1026, 918, 964, 903, 833, 737, 698, 640, 610, 579, 540, 498; **GC-MS (EI, 70ev) *m/z* :** found: 150($C_9H_{10}O_2$), calculated: 150.17 ($C_9H_{10}O_2$).

cyclohexyl acetate (Scheme 5, entry 15b)



The product was obtained as colorless liquid in 93% yield (0.2645 g); **R_F** (eluent hexanes/EtOAc 80:20): 0.72;**^{1}H NMR (500 MHz, $CDCl_3$):** δ 4.79 – 4.69 (m, 1H, O-CH), 2.03 (s, 3H, CH_3), 1.91 – 1.80 (m, 2H, CH_2), 1.78 –1.68 (m, 2H, CH_2), 1.55 (ddd, J = 8.5, 6.7, 3.3 Hz, 1H, CH), 1.45 – 1.30 (m, 4H, CH_2), 1.29 – 1.18 (m, 1H, CH); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 170.56, 72.65, 31.63, 25.35, 23.79, 21.40; **FTIR (cm^{-1}):**2936, 2859, 2361, 2342, 1732, 1520, 1450, 1362, 1234, 1123, 1045, 1022, 968, 903, 841, 799, 652, 606, 548;**GC-MS (EI, 70ev) *m/z* :** found: 142 ($C_8H_{14}O_2$), calculated: 142.2 ($C_8H_{14}O_2$).

3-phenylpropyl acetate (Scheme 5, entry 15c)

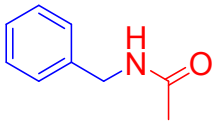


The product was obtained as colorless liquid in 95% yield (0.2488 g); **R_F** (eluent hexanes/EtOAc 80:20): 0.78; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.30 – 7.25 (m, 2H, H_{Ar}), 7.20 – 7.15 (m, 3H, H_{Ar}), 4.08

(t,J = 6.6 Hz, 2H, CH_2), 2.72 – 2.64 (m, 2H, CH_2), 2.04 (s, 3H, CH_3), 1.98 – 1.91 (m, 2H, CH_2); **^{13}C NMR (126 MHz, $CDCl_3$):** δ 171.16, 141.24, 128.47, 128.43,126.04, 63.85, 32.21, 30.22, 20.98; **FTIR (cm^{-1}):**3024, 2943, 1736, 1497, 1454, 1366, 1234, 1034, 745, 698, 606, 482;**GC-MS (EI, 70ev) *m/z* :** found: 178 ($C_{11}H_{14}O_2$), calculated: 178.23 ($C_{11}H_{14}O_2$).

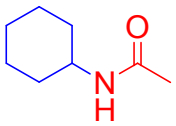
3.9. *N*-acylated amines (Scheme 5, entries 16b-16d)

***N*-benzylacetamide(Scheme 5, entry 16b)[2]**



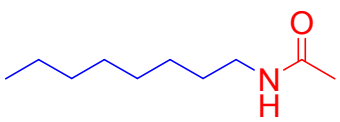
The product was obtained as off-white solid in 3% yield (0.0097 g); **MP:** 59-63 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.55; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.33 – 7.28 (m, 2H, H_{Ar}), 7.25 (t, *J* = 7.5 Hz, 3H, H_{Ar}), 6.43 (brs, 1H, NH), 4.36 (d, *J* = 5.8 Hz, 2H, N-CH_2), 1.96 (s, 3H, CO-CH_3);**FTIR (cm^{-1}):** 3233, 2363, 1709, 1685, 1576, 1507, 1451, 1358, 1229, 1181, 1145, 834, 757, 709; **GC-MS (EI, 70ev) *m/z:*** found: 149 ($C_9H_{11}NO$), calculated: 149.19 ($C_9H_{11}NO$).

***N*-cyclohexylacetamide (Scheme 5, entry 16c)[2]**



The product was obtained as off-white solid in 2% yield (0.0072 g); **MP:** 100-103 °C; **R_F** (eluent hexanes/EtOAc 65:35): 0.50; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.01 (br s, 1H, NH), 3.74 – 3.59 (m, 1H, N-CH), 1.99 (s, 3H, CO-CH_3), 1.82 (d, *J* = 9.7 Hz, 2H, CH_2), 1.67 (d, *J* = 3.1 Hz, 2H, CH_2), 1.53 (s, 1H, CH_2), 1.17 (ddq, *J* = 36.8, 33.8, 12.2 Hz, 5H, CH_2); **FTIR (cm^{-1}):** 3272, 2362, 1667, 1539, 1457, 1355, 1257, 1134, 1062, 967, 871, 853, 735; **GC-MS (EI, 70ev) *m/z*:** found: 141 ($C_8H_{15}NO$), calculated: 141.21 ($C_8H_{15}NO$).

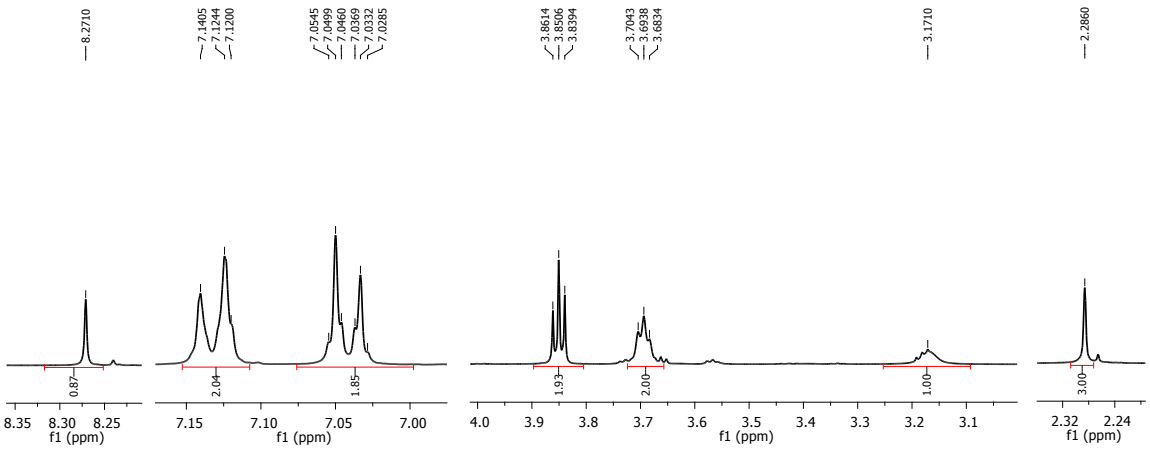
***N*-octylacetamide(Scheme 5, entry 16d)[2]**

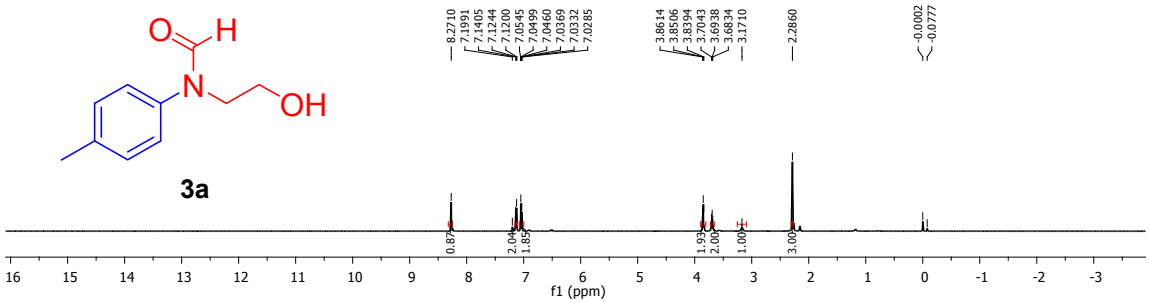


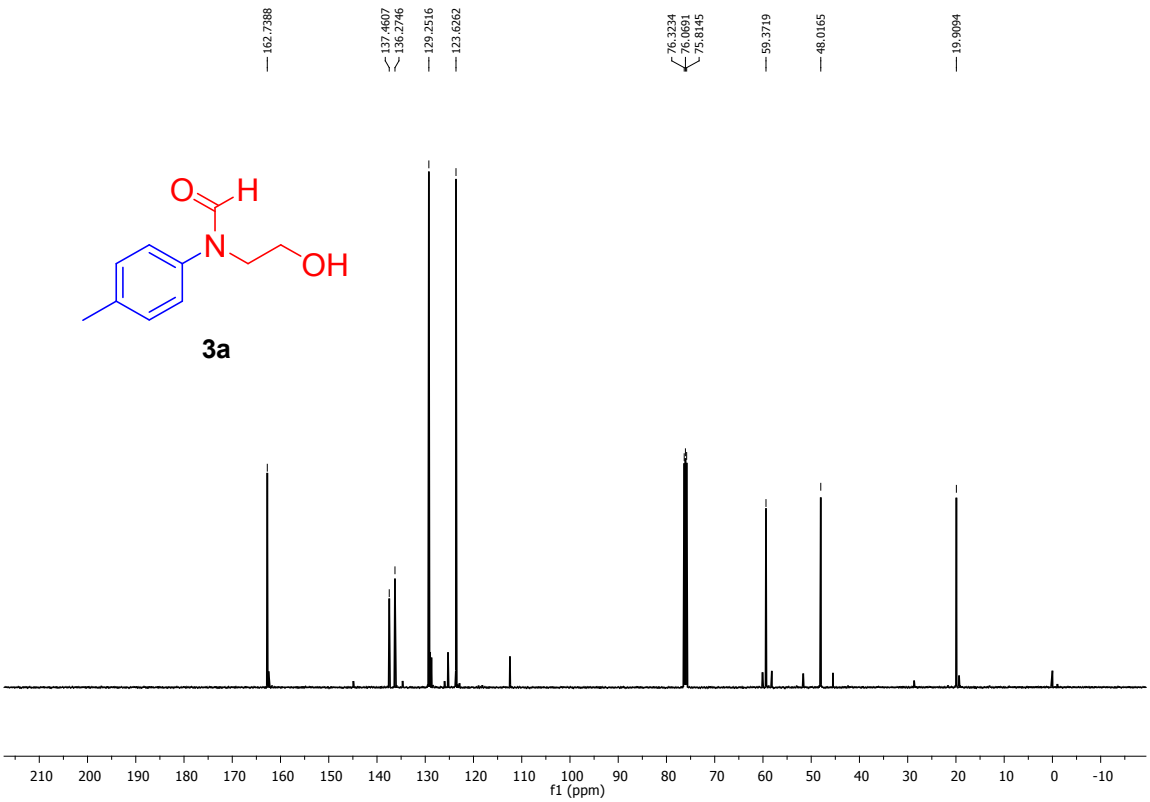
The product was obtained as colourless oil in 4% yield (0.0115 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.53; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 6.04 (s, 1H, NH), 3.22 (dd, *J* = 13.3, 6.9 Hz,2H,N-CH_2), 1.97 (s, 3H, CO-CH_3), 1.54 – 1.45 (m, 2H, CH_2), 1.29 (t, *J* = 10.6 Hz, 11H, CH_2), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3); **FTIR (cm^{-1}):**3225, 2358, 1652, 1537 1451, 1371, 1241, 730; **GC-MS (EI, 70ev) *m/z*:** found: 171 ($C_{10}H_{21}NO$), calculated: 171.28 ($C_{10}H_{21}NO$).

4. ^{1}H NMR and ^{13}C NMR spectra of *N*- and *N,O*-formylatedAlkanolamines

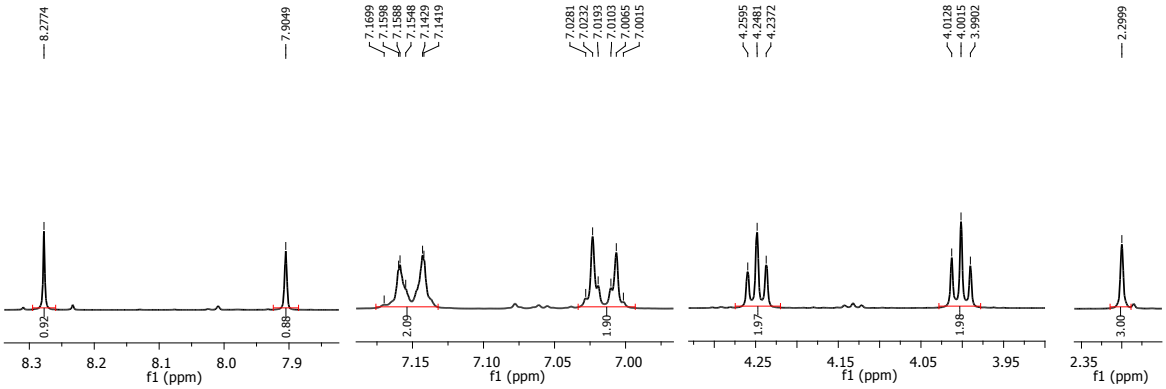
(Table 1, Compound3a)

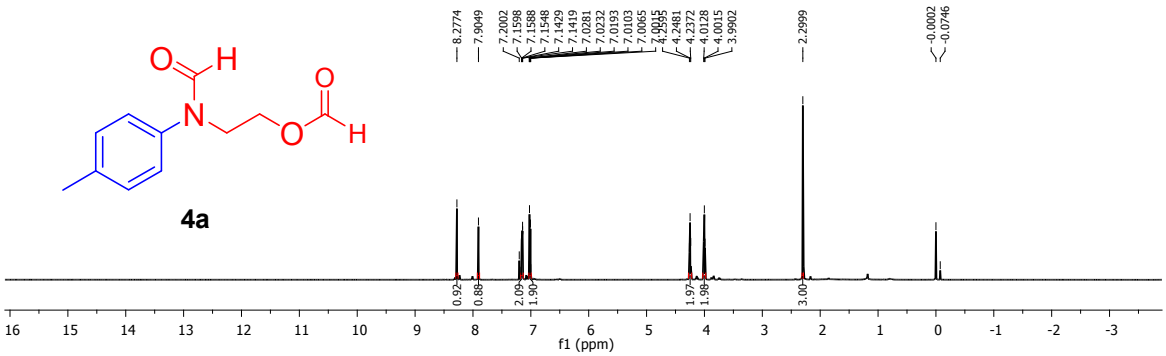


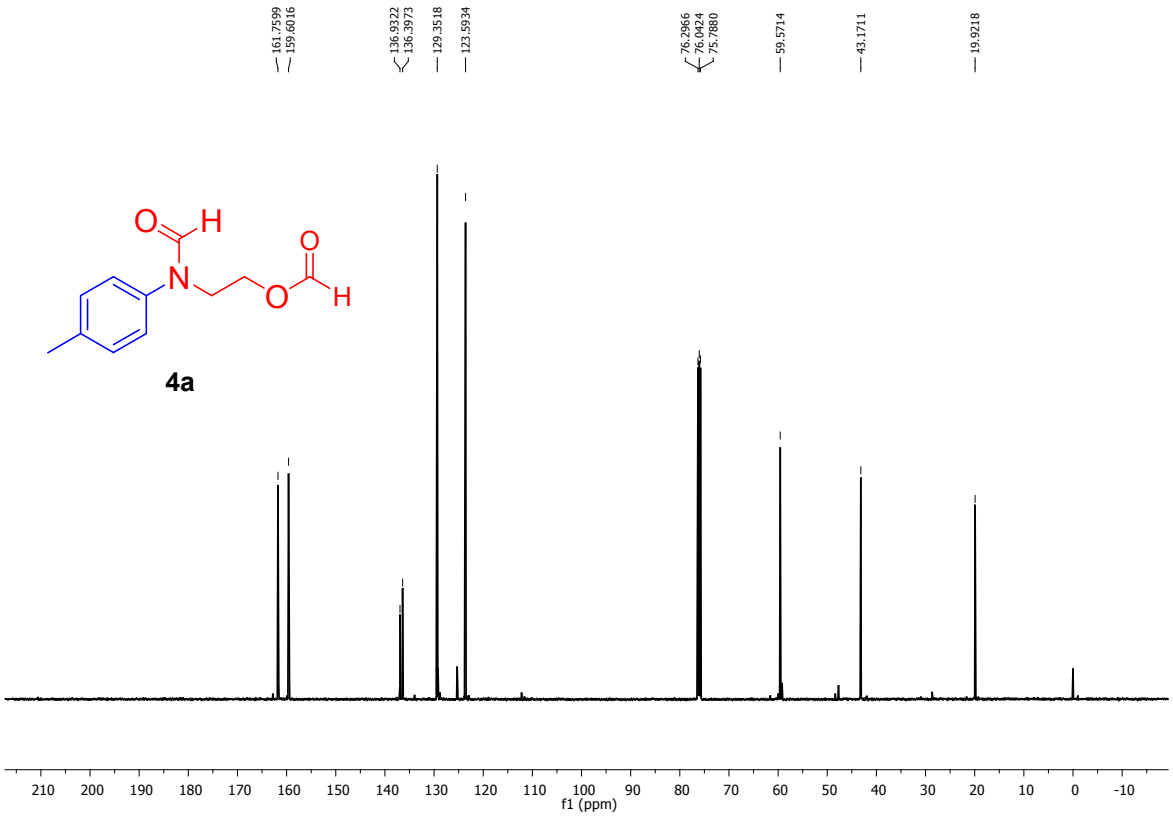




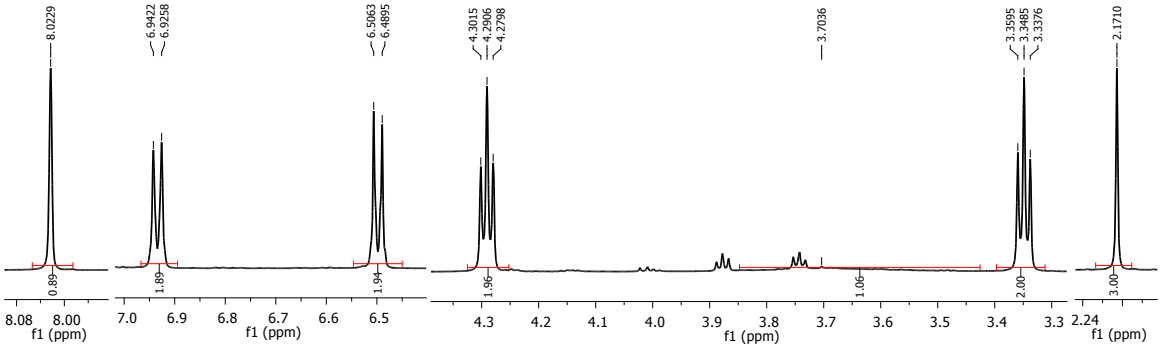
(Table 1, Compound4a)

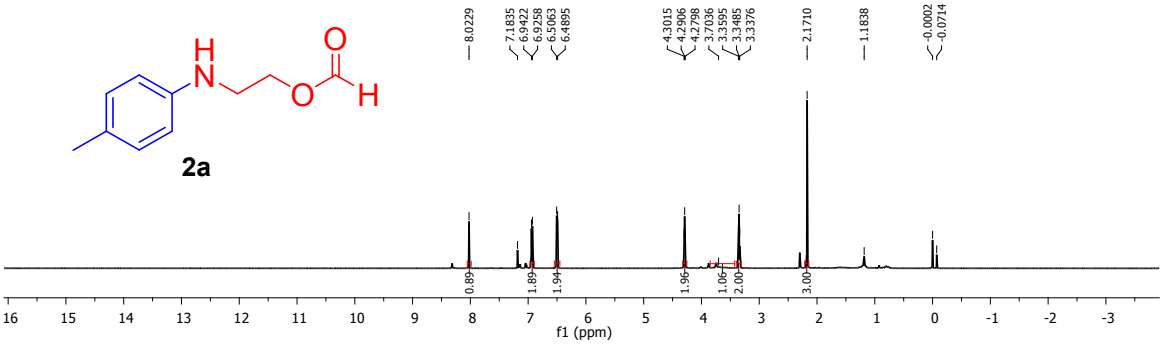


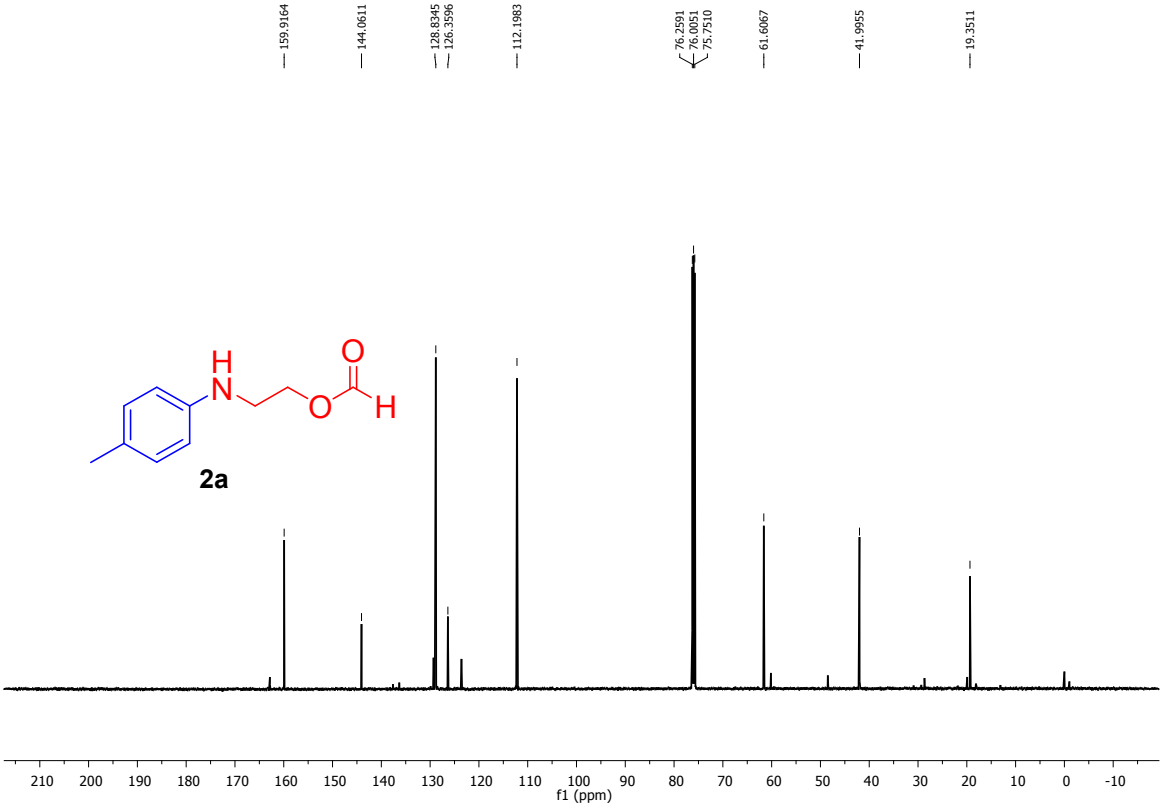




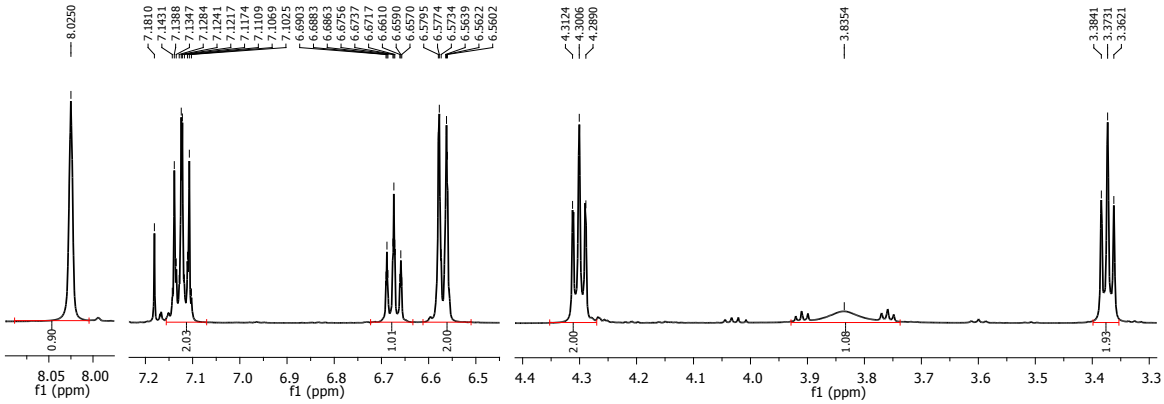
5. ^{1}H NMR and ^{13}C NMR spectra of *O*-formylatedand *O*-Acylated Alkanolamines (Scheme 1, entry 2a)

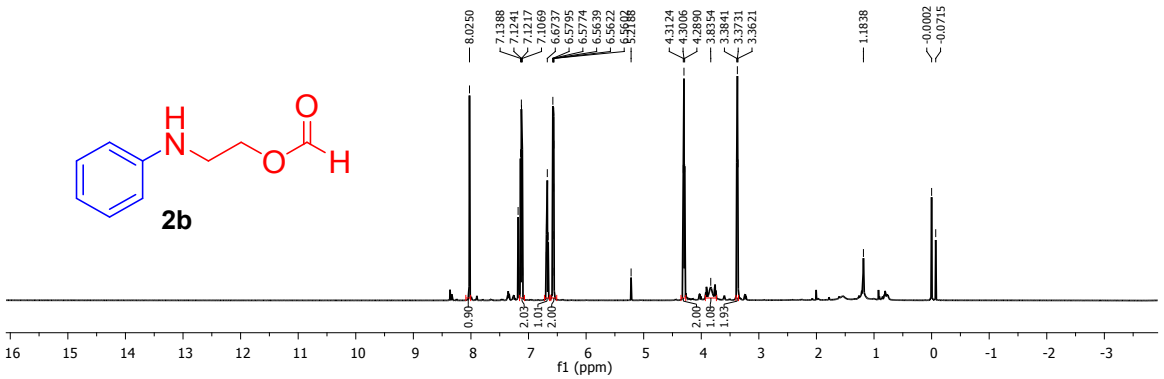


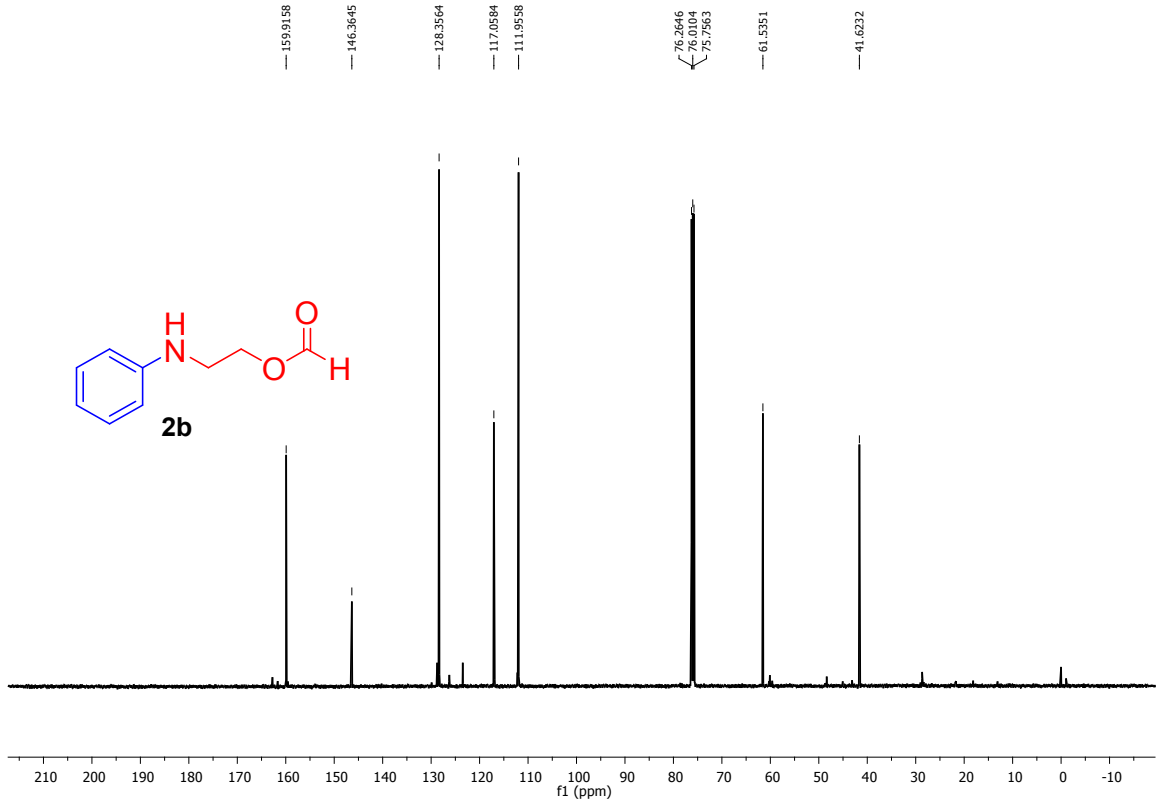




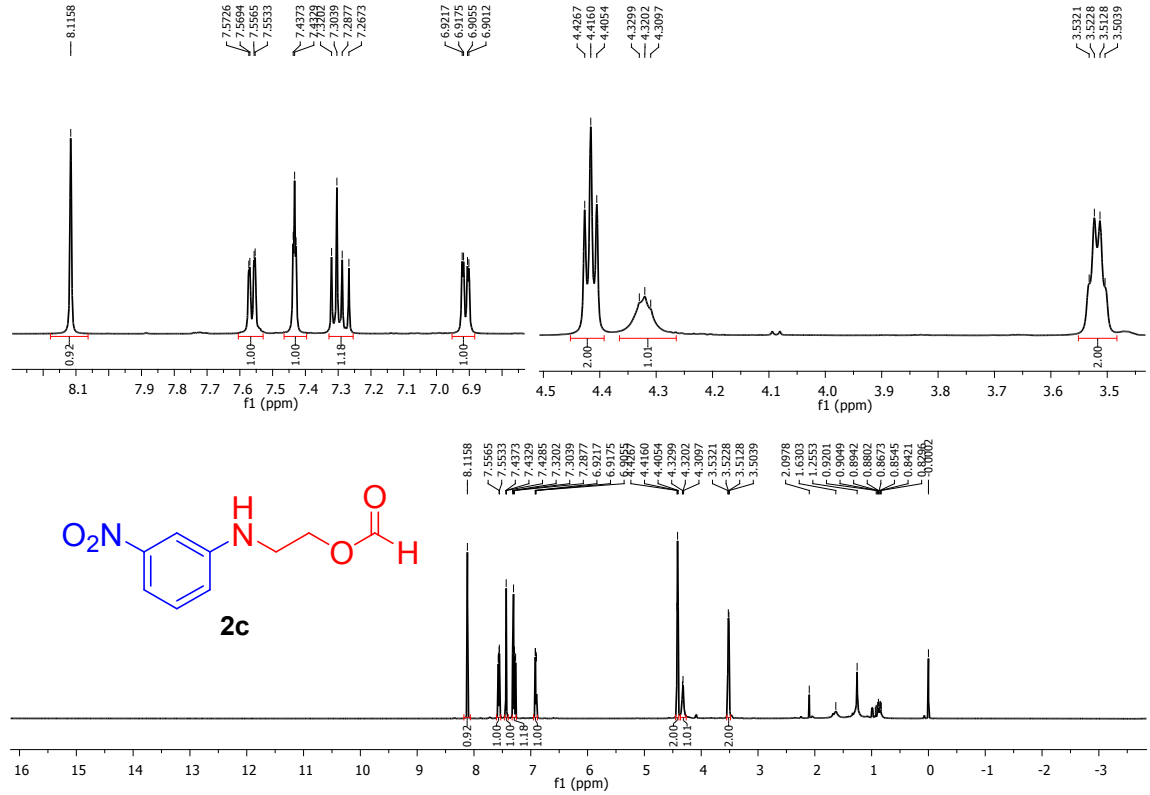
(Scheme 1, entry 2b)

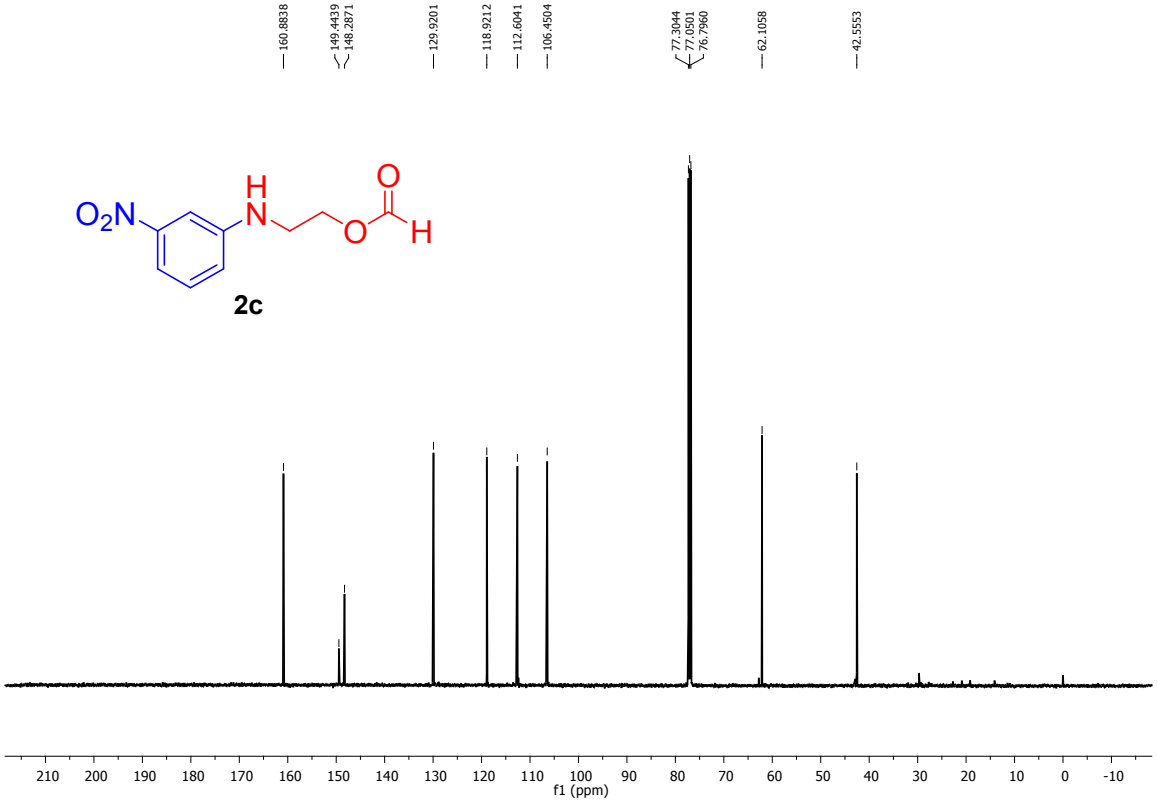




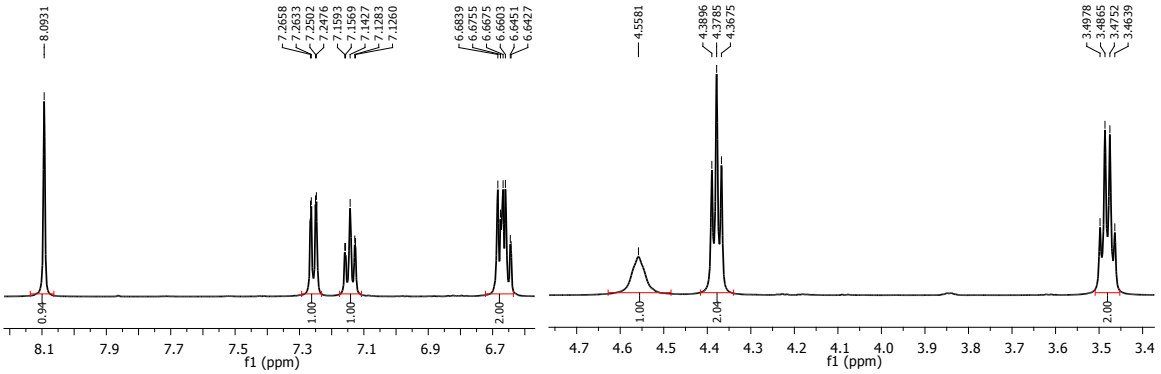


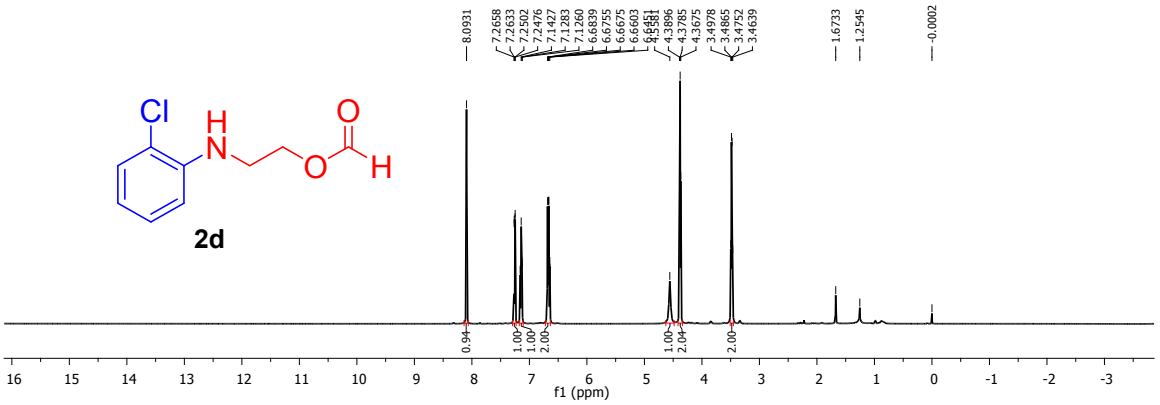
(Scheme 1, entry 2c)

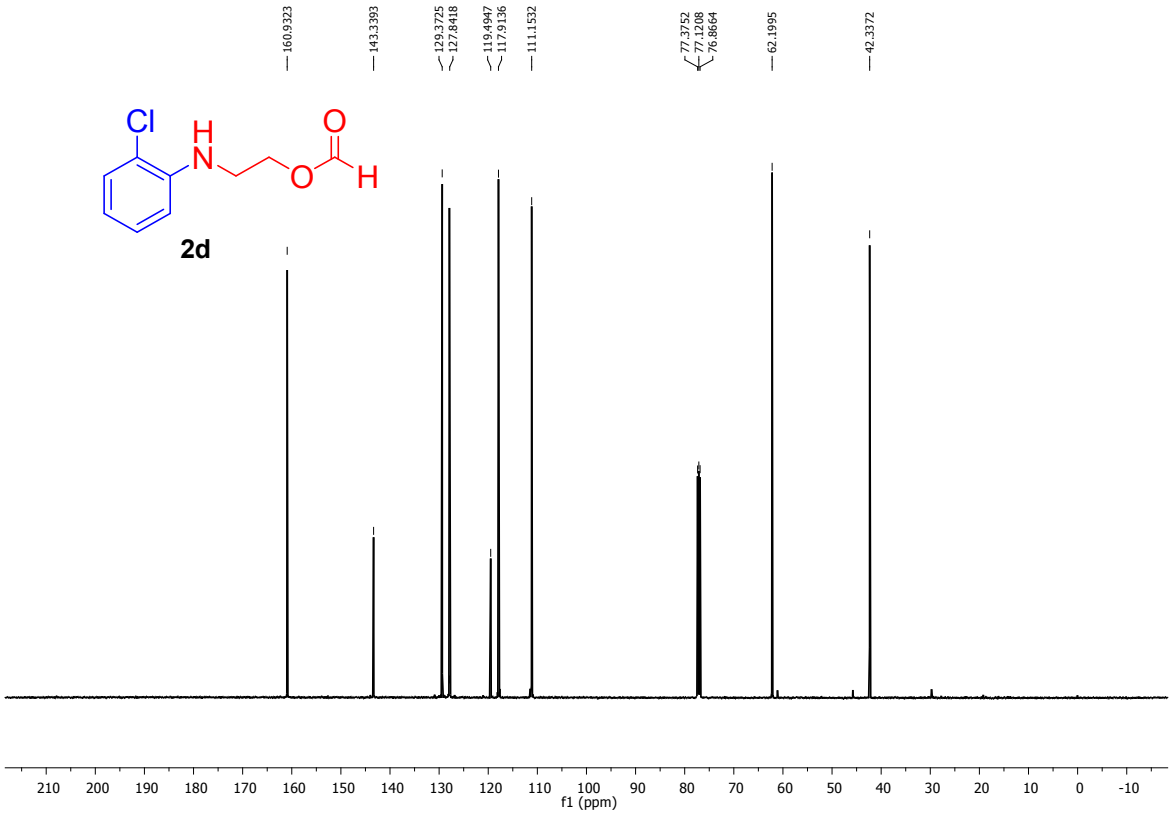




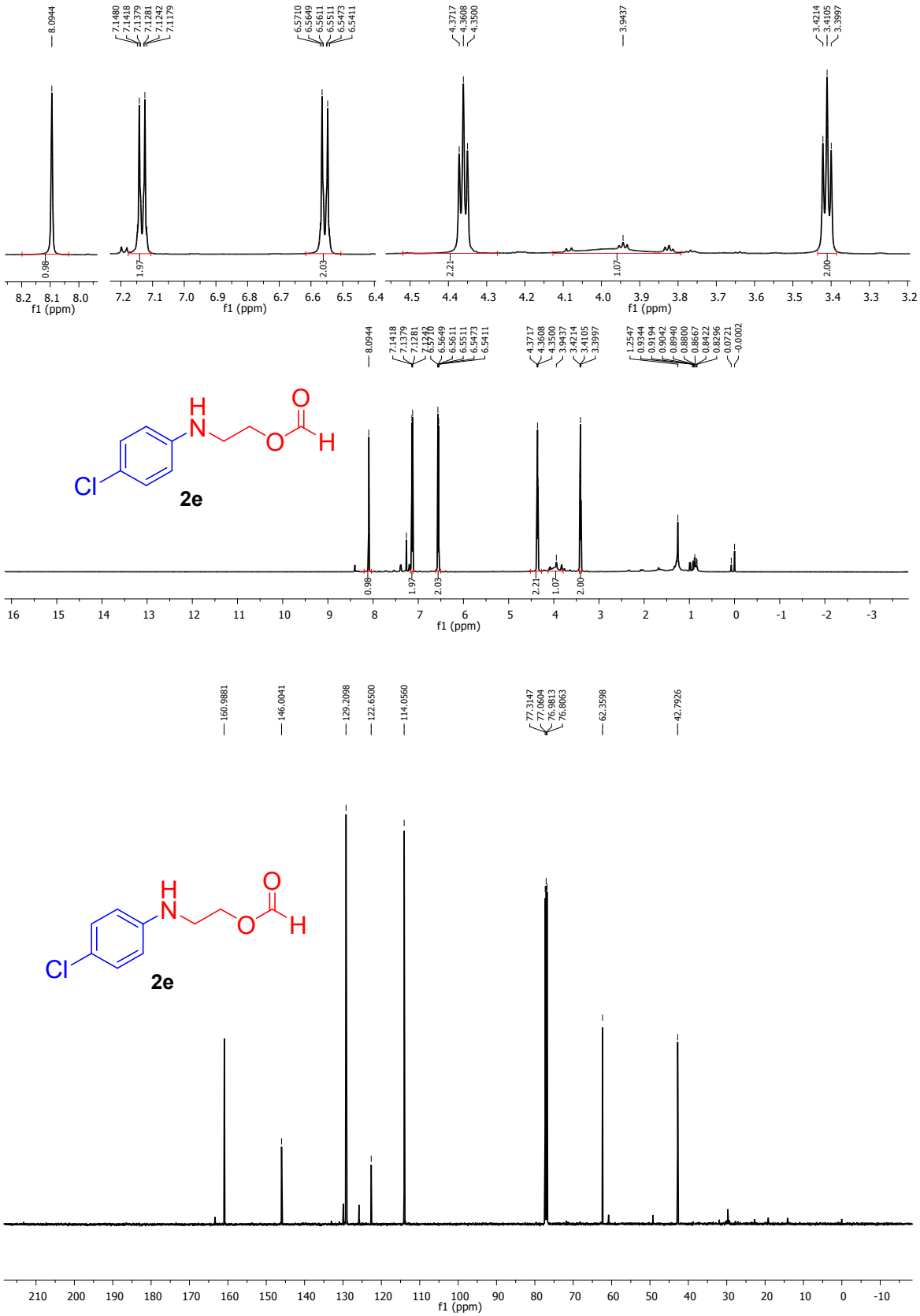
(Scheme 1, entry 2d)



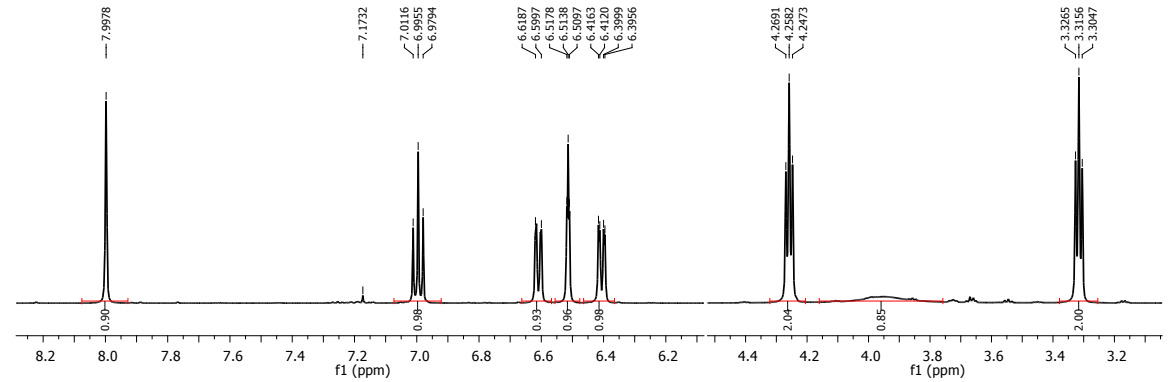


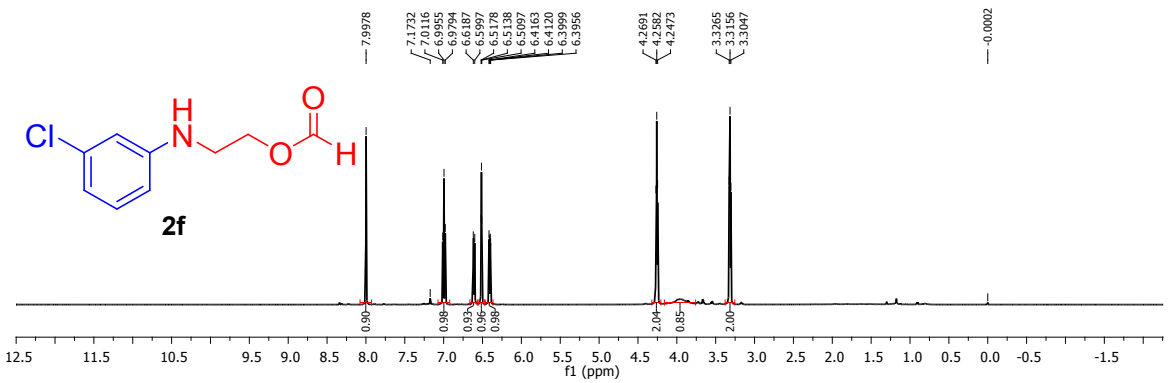


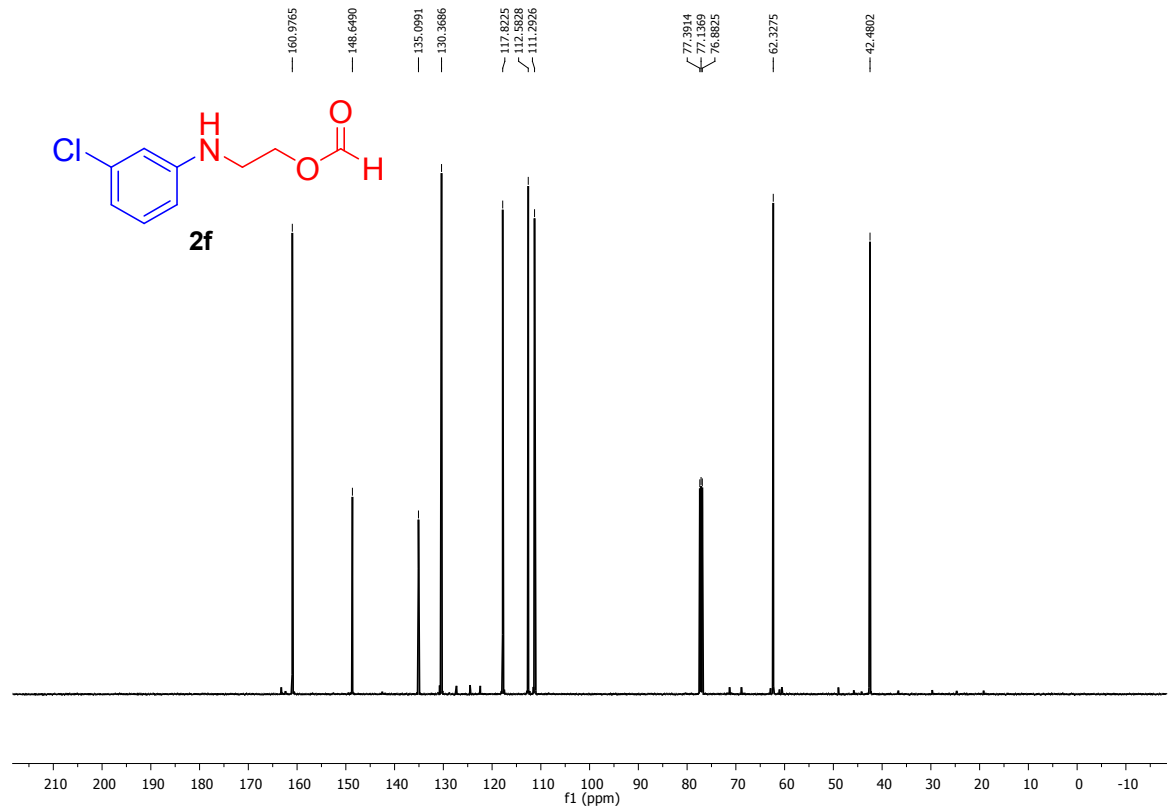
(Scheme 1, entry 2e)



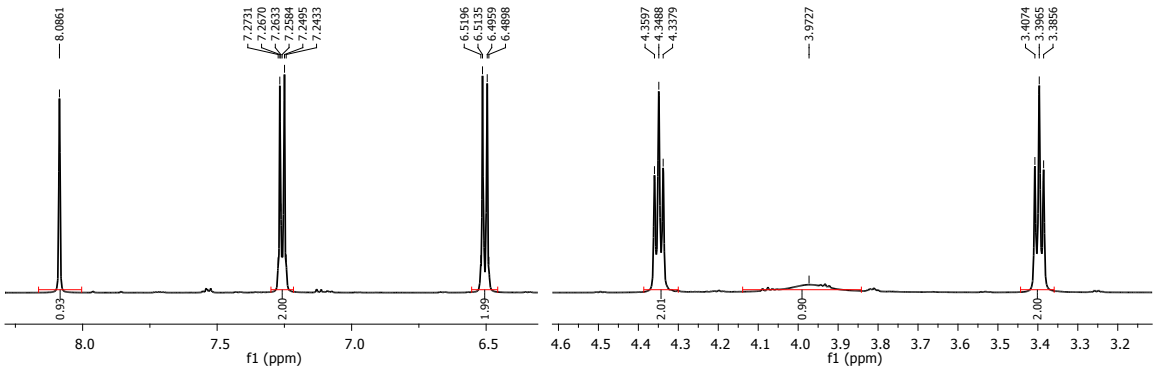
(Scheme 1, entry 2f)

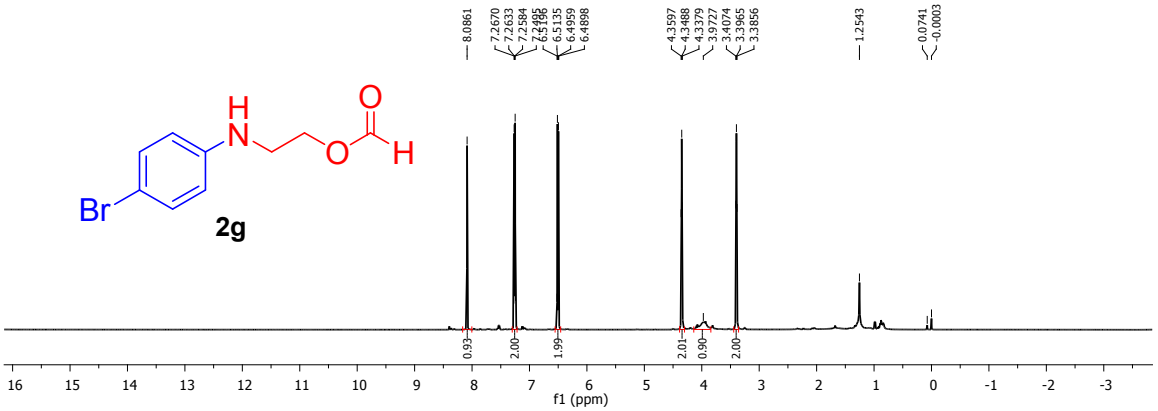


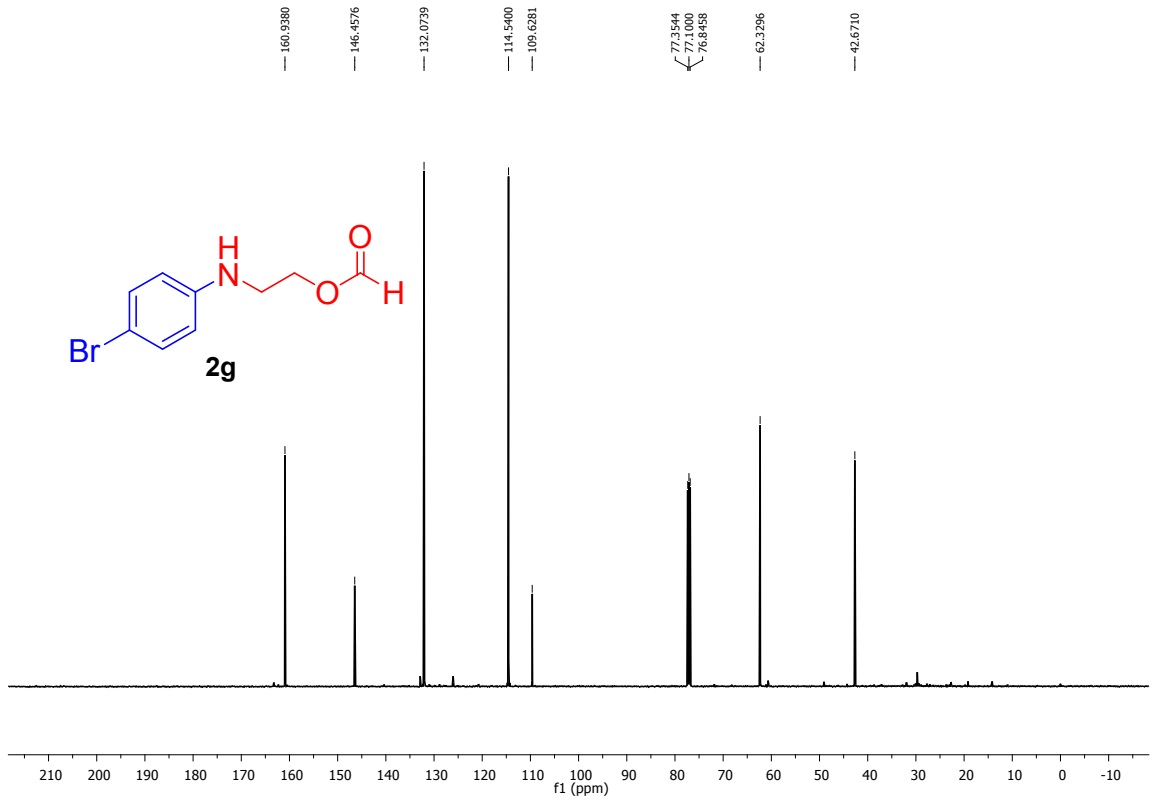




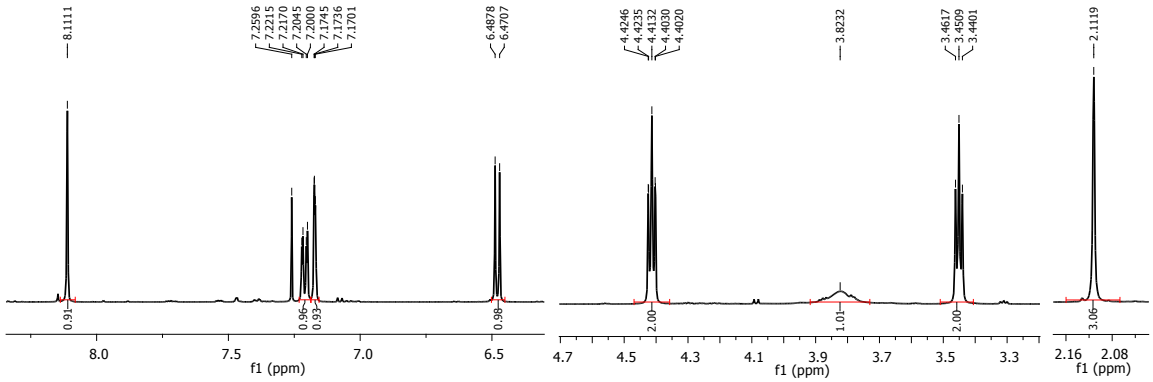
(Scheme 1, entry 2g)

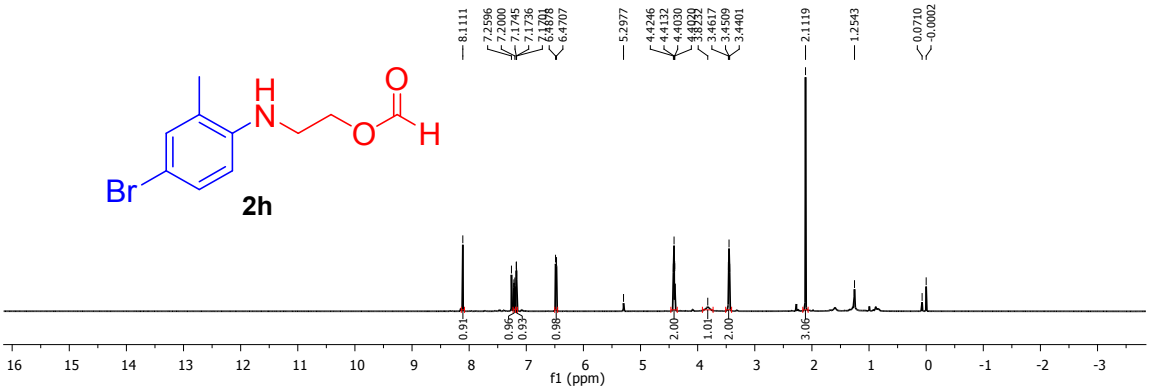


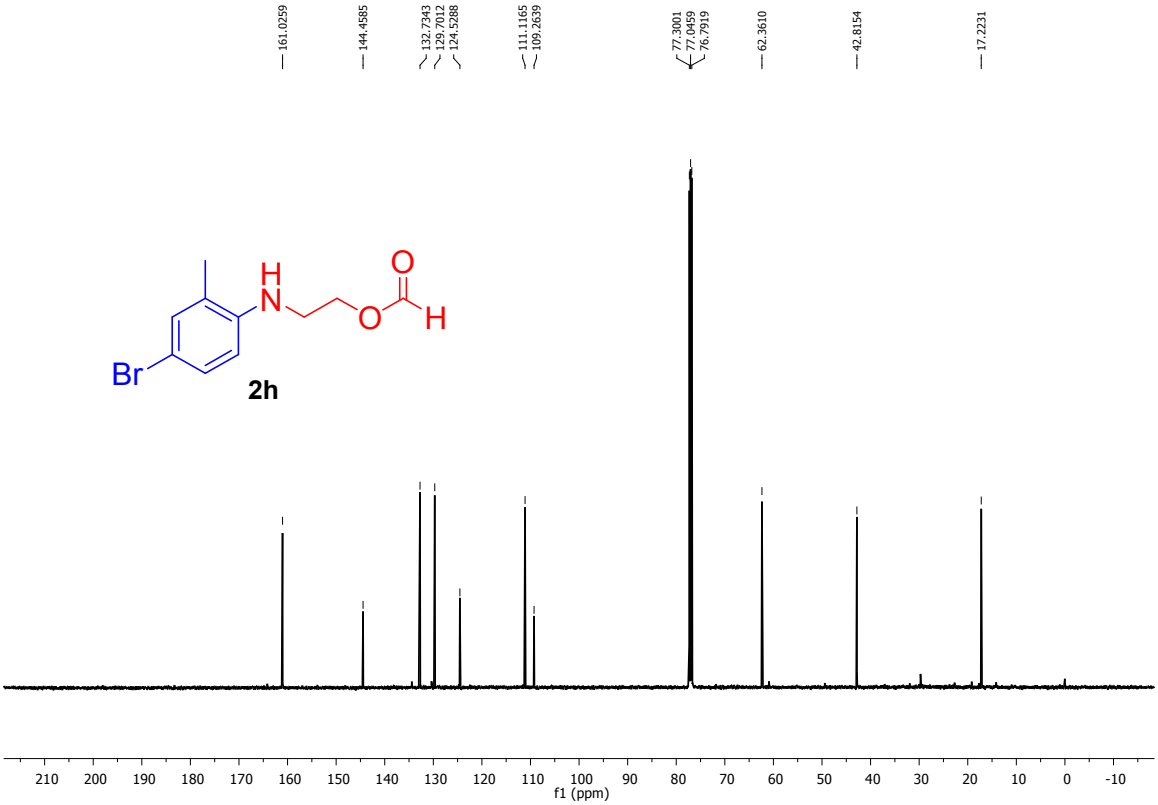




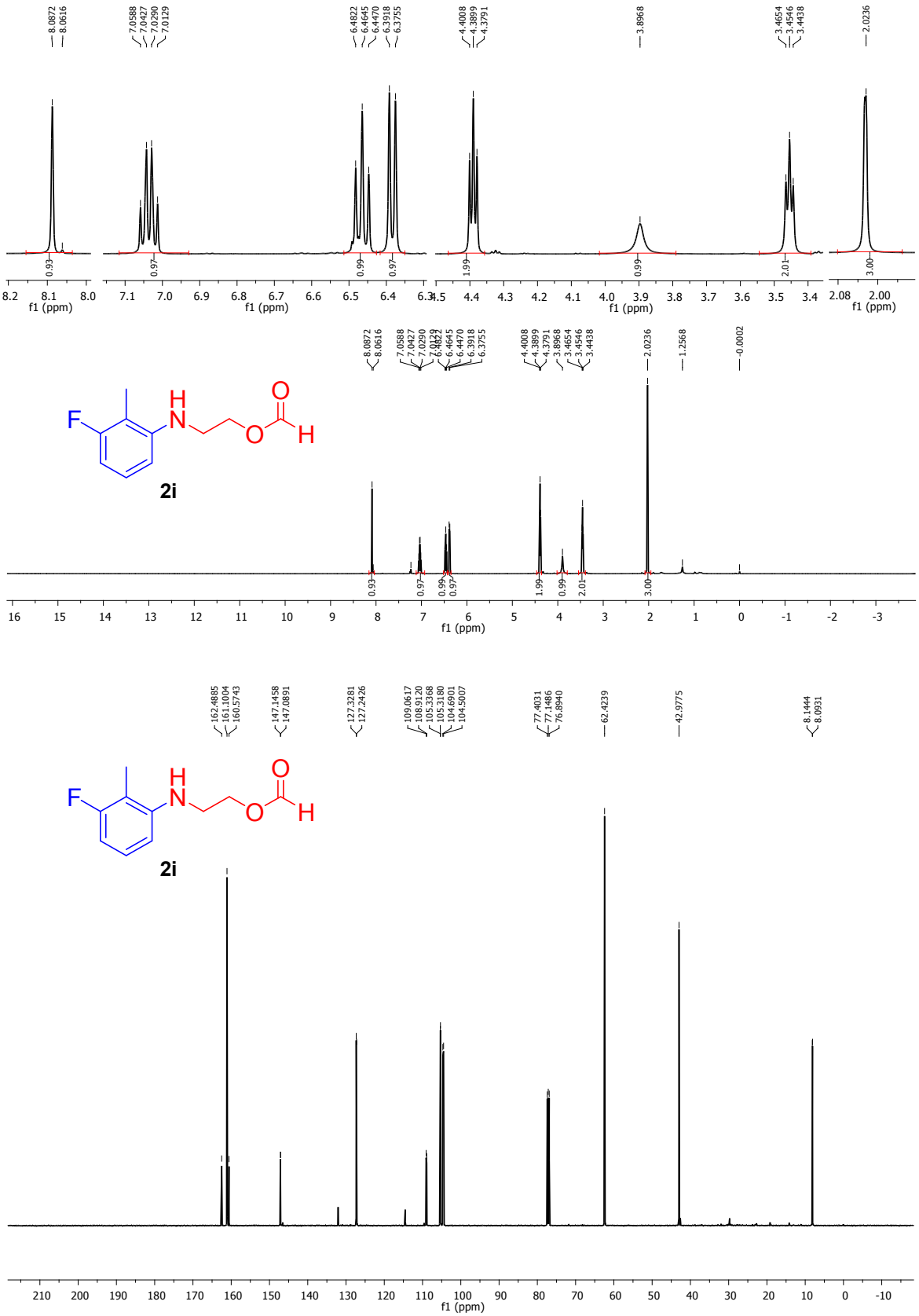
(Scheme 1, entry 2h)



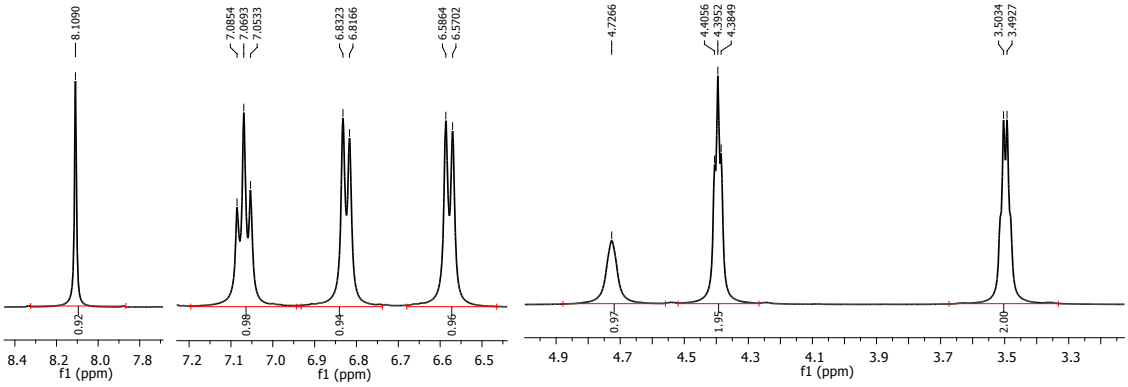


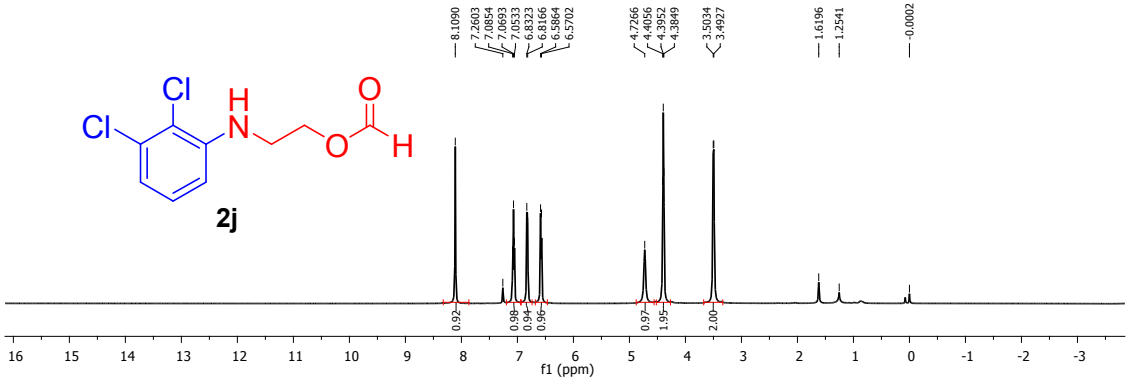


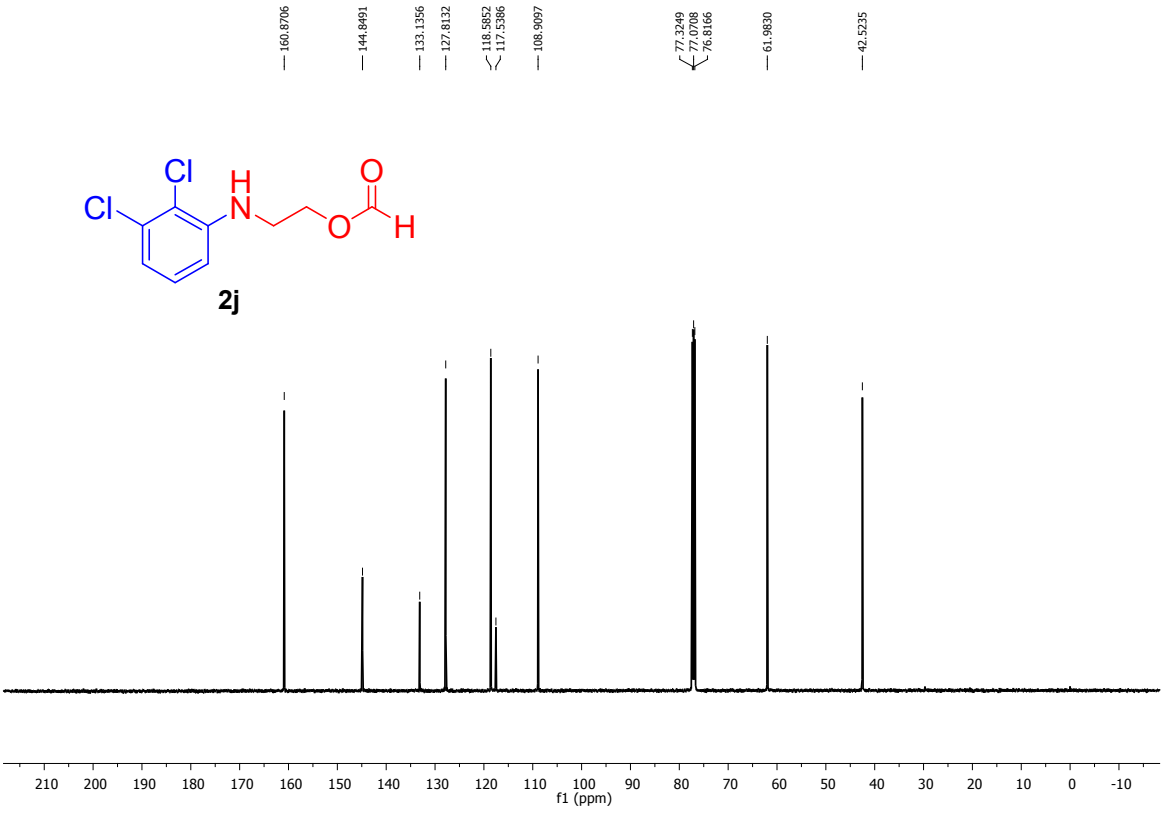
(Scheme 1, entry 2i)



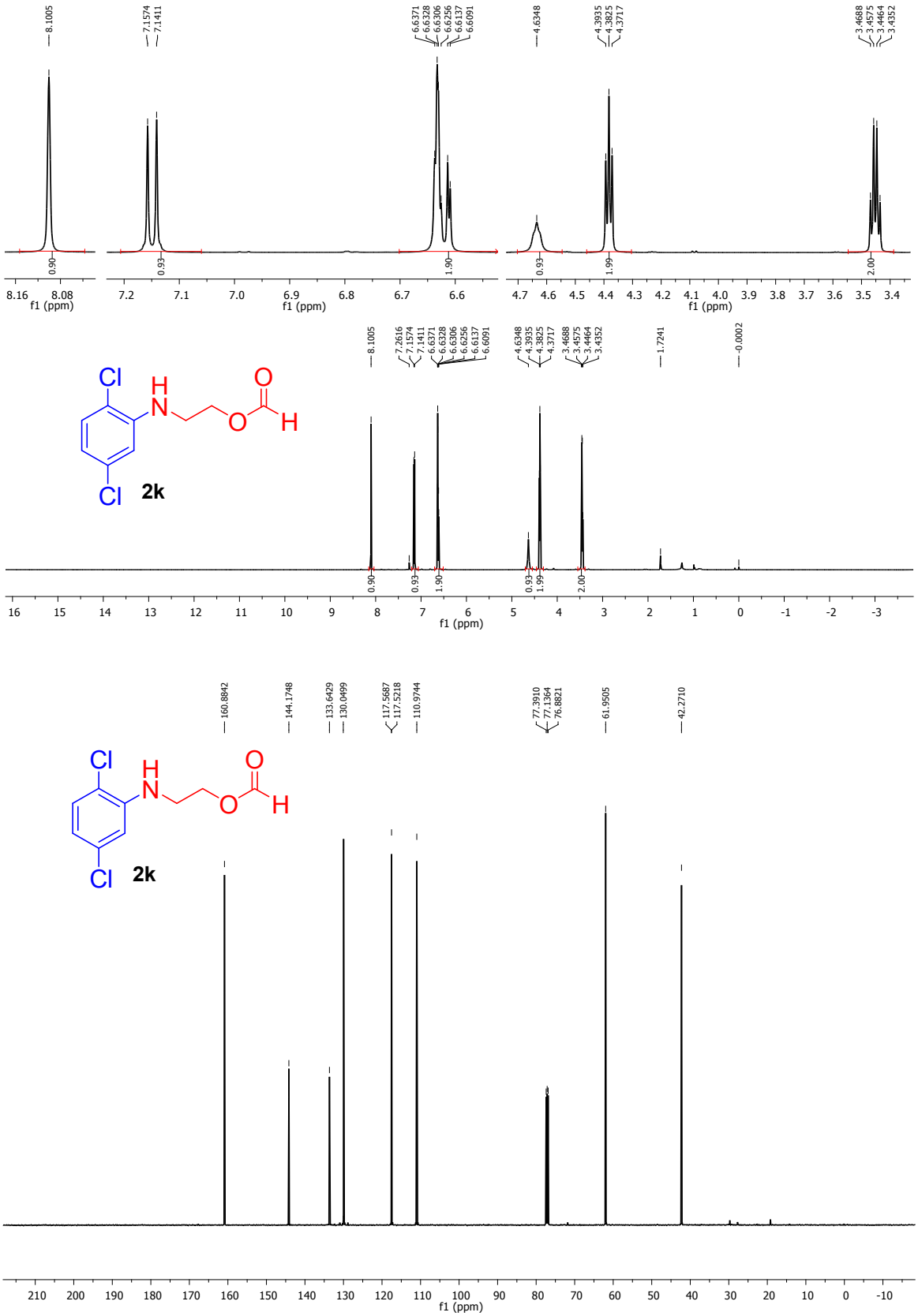
(Scheme 1, entry 2j)



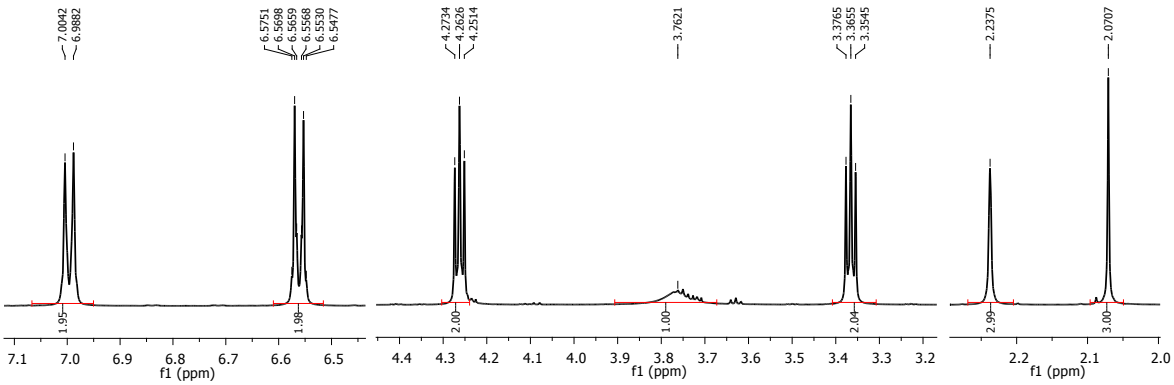


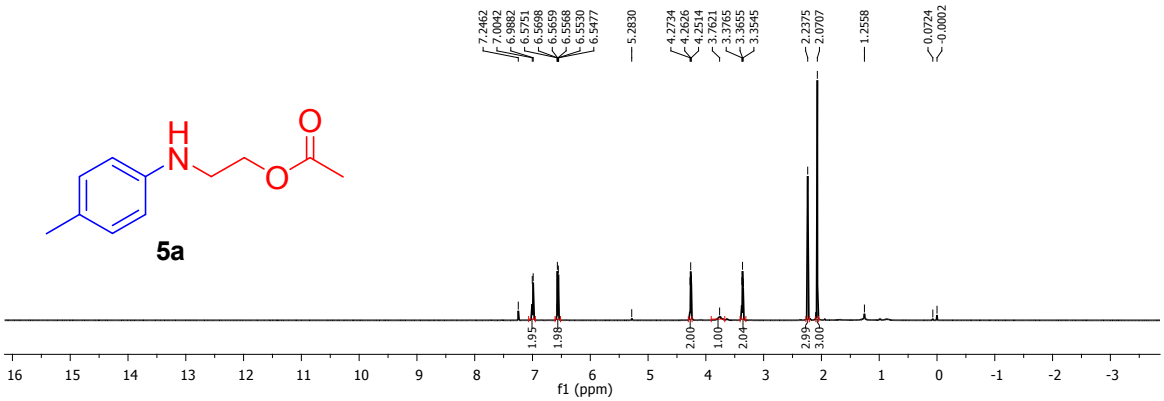


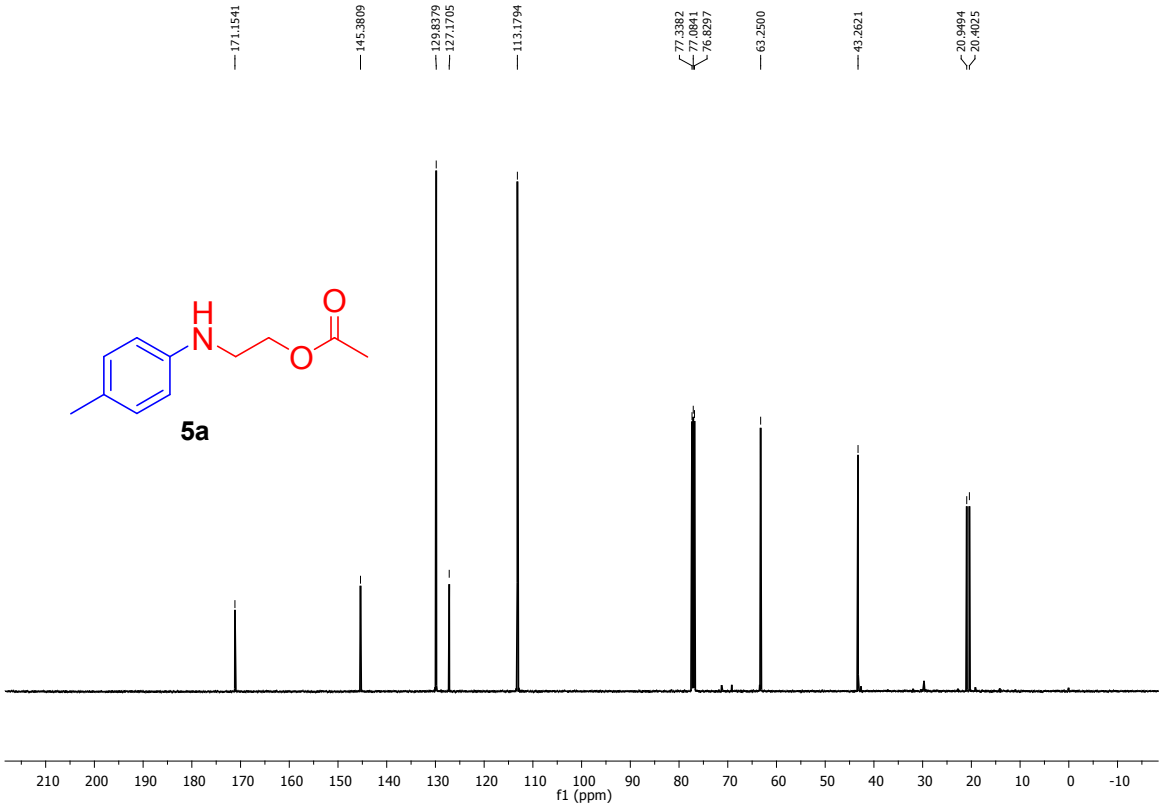
(Scheme 1, entry 2k)



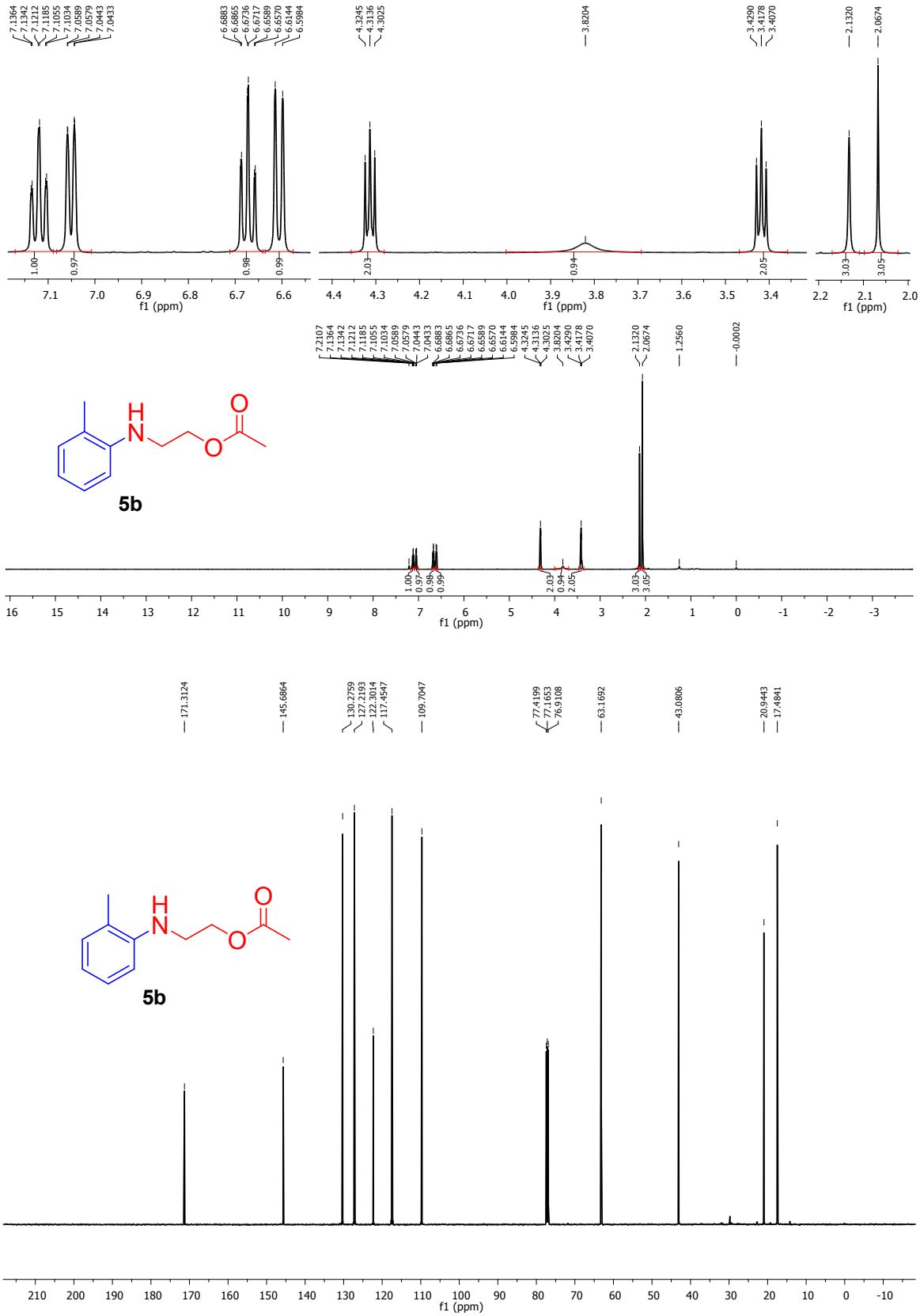
(Scheme 2, entry 5a)



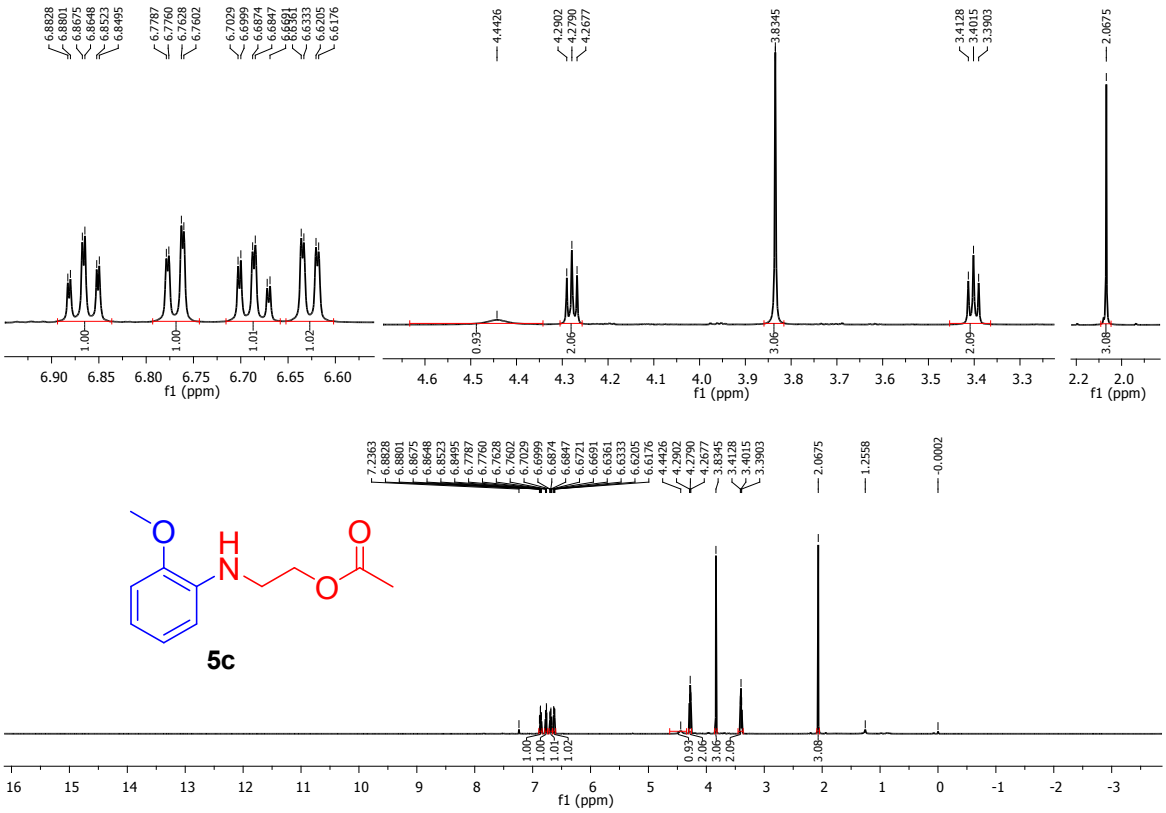


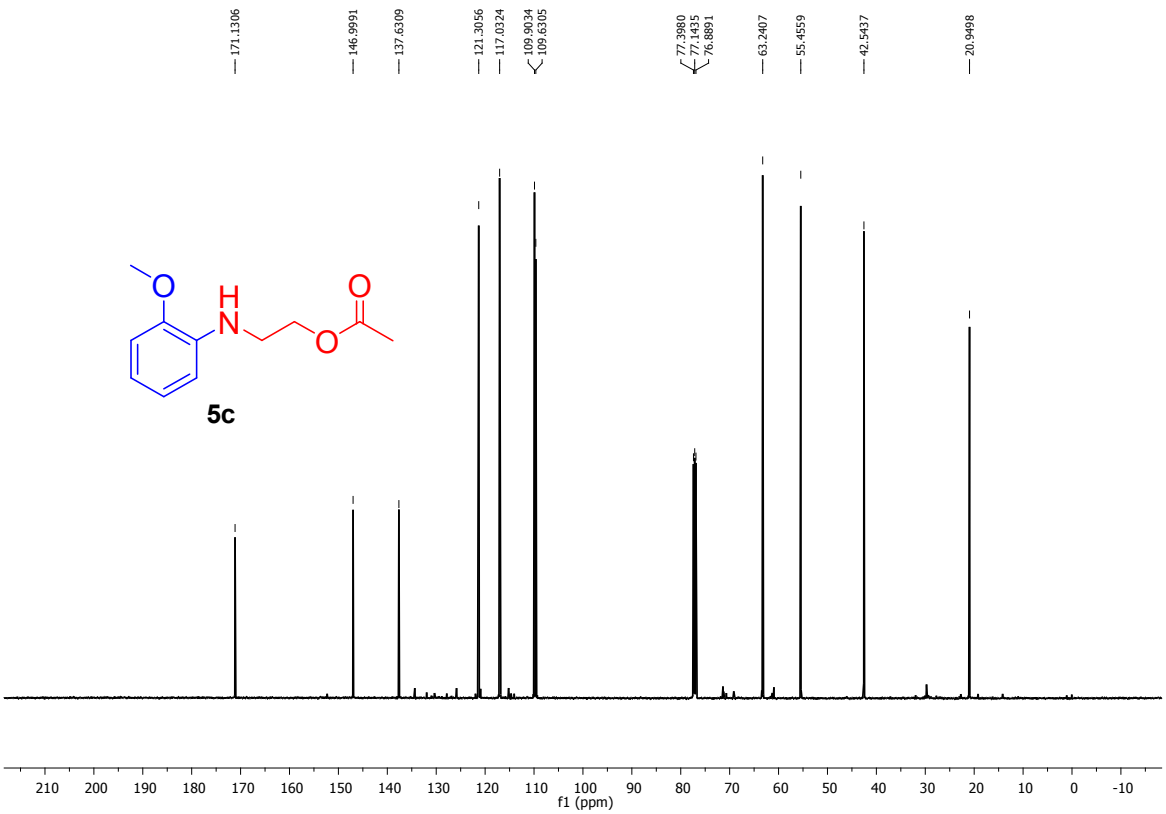


(Scheme 2, entry 5b)

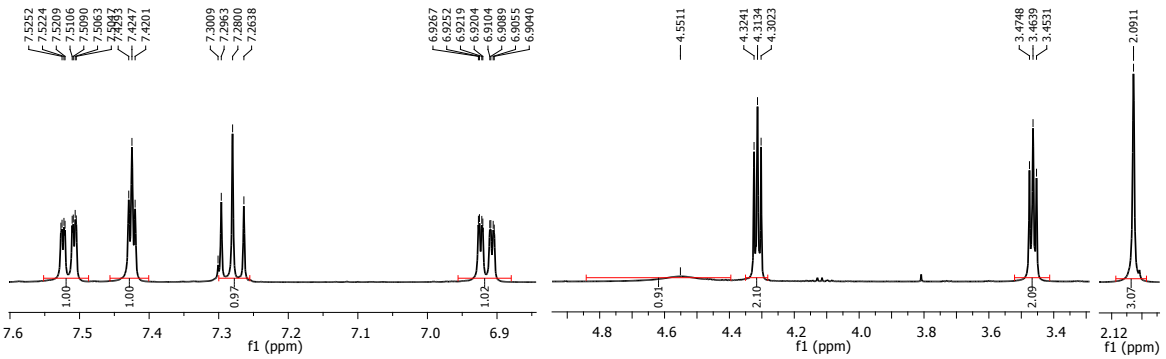


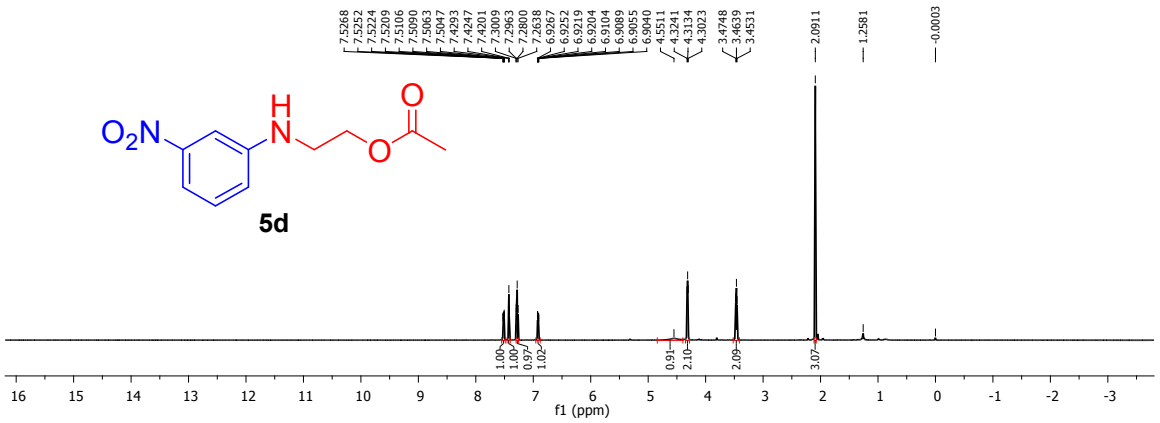
(Scheme 2, entry 5c)

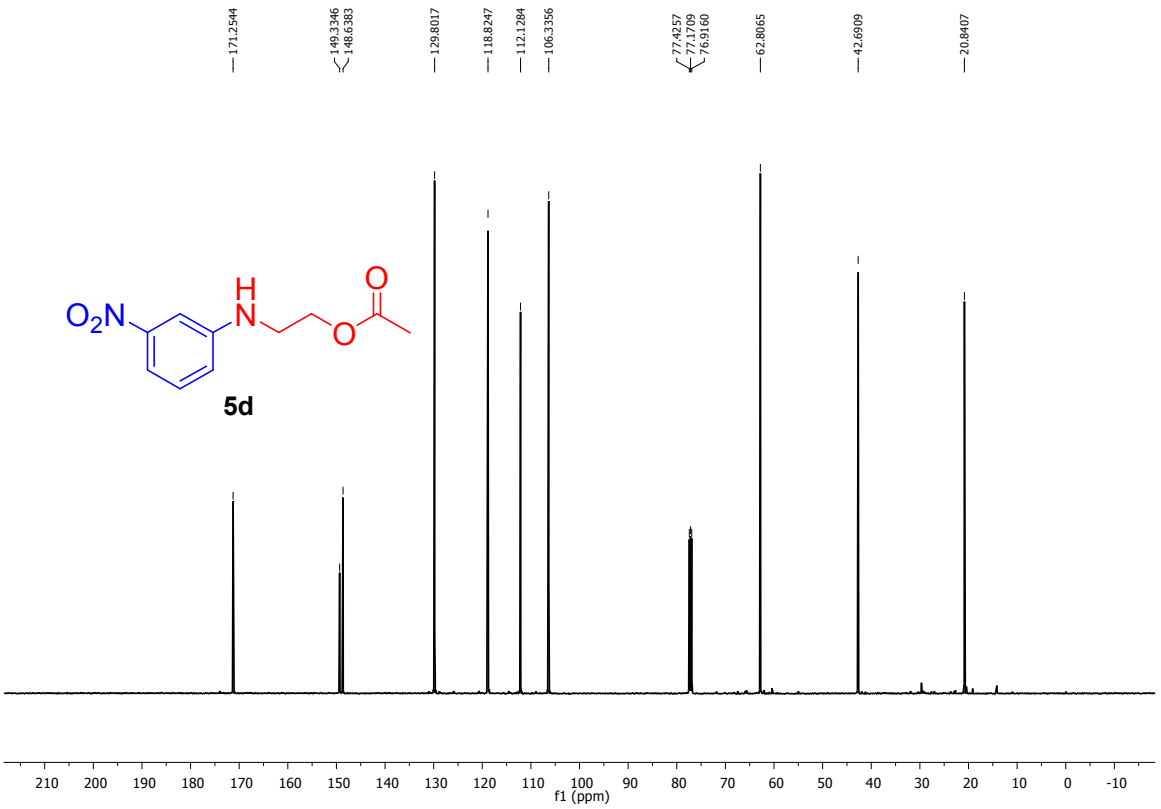




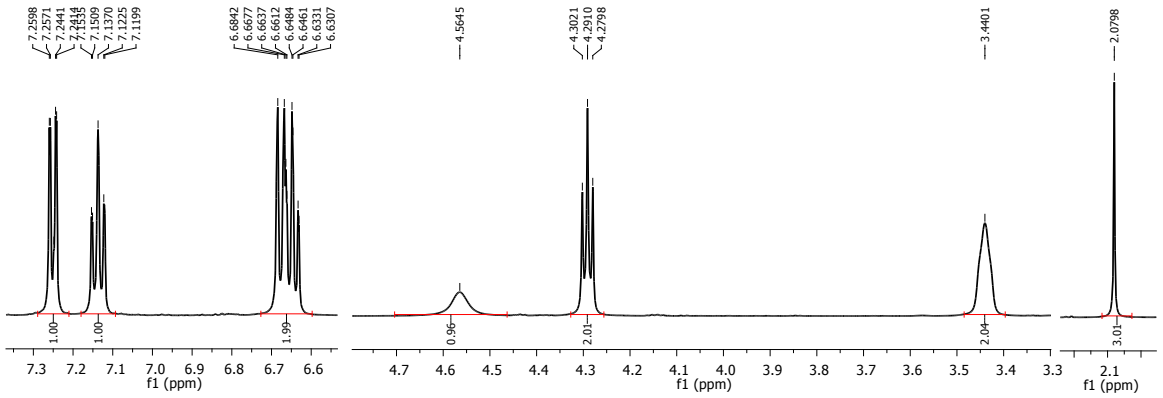
(Scheme 2, entry 5d)

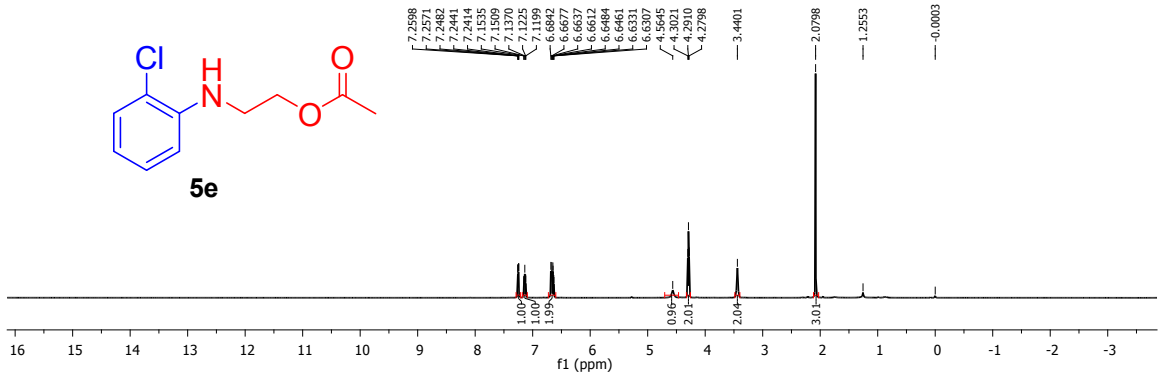


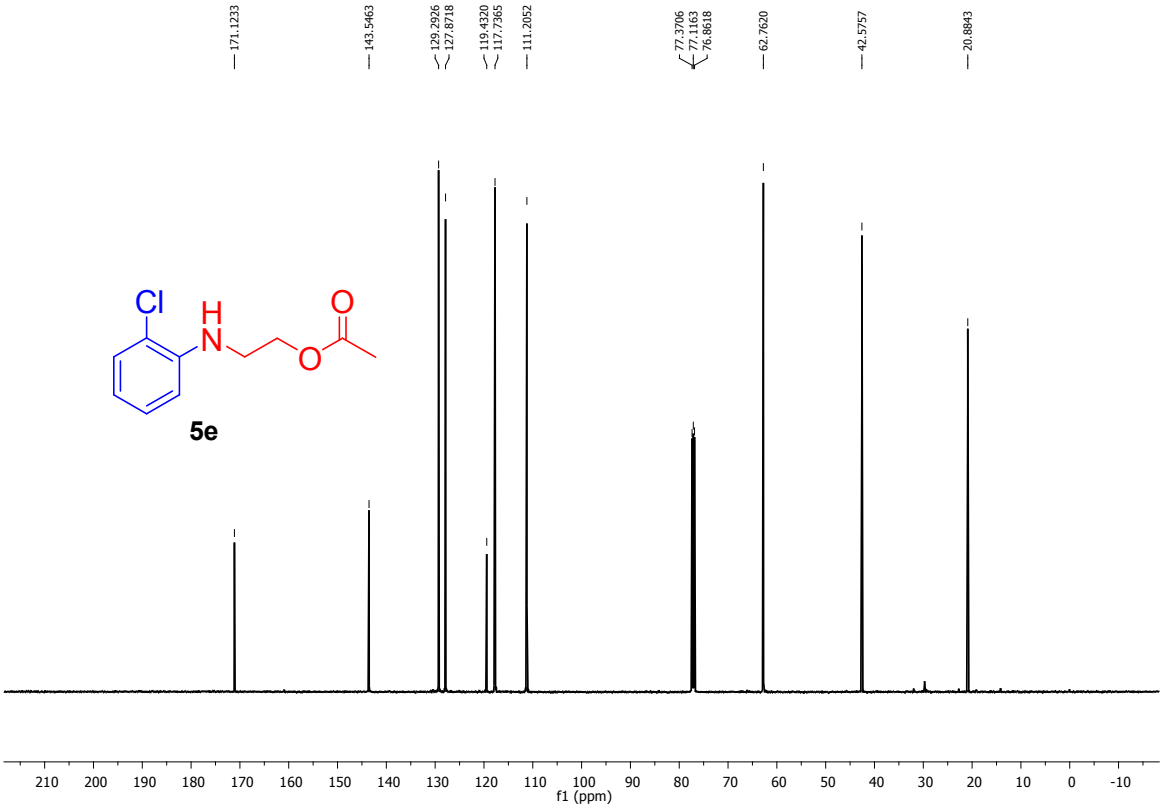




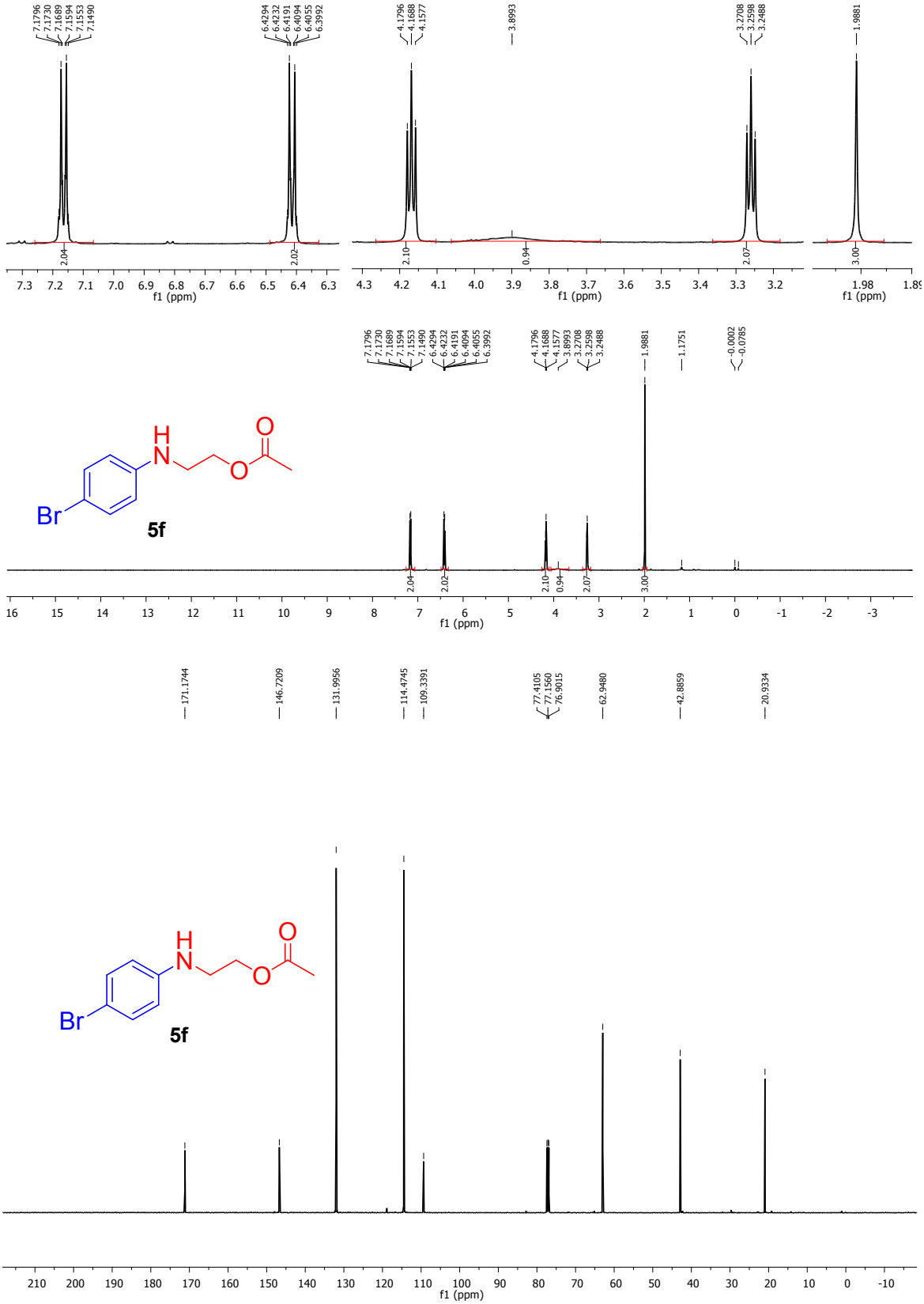
(Scheme 2, entry 5e)



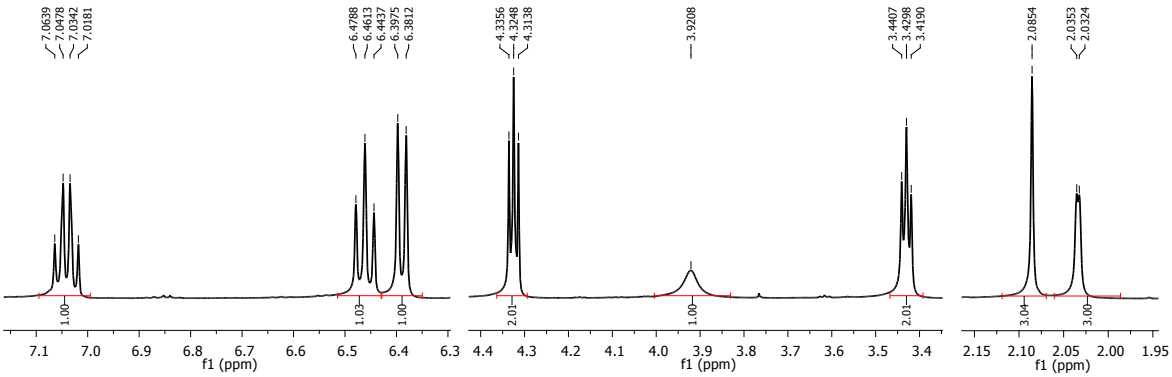


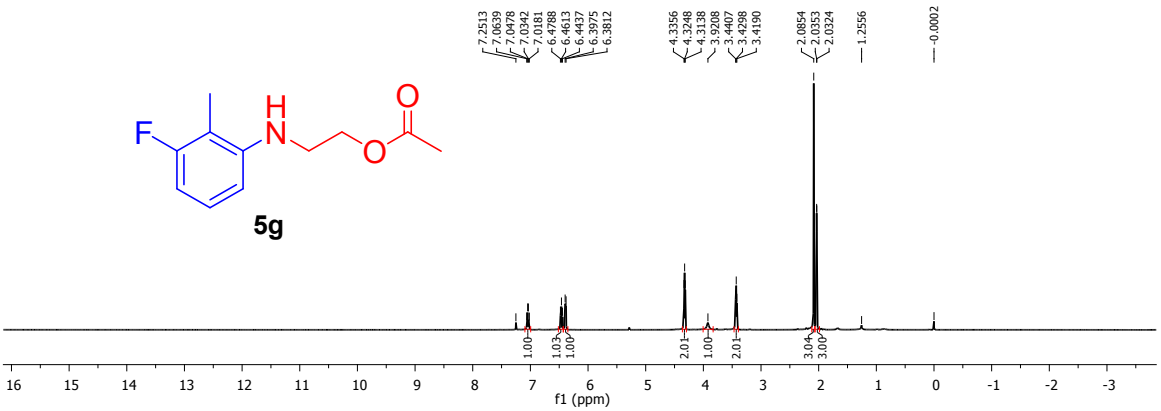


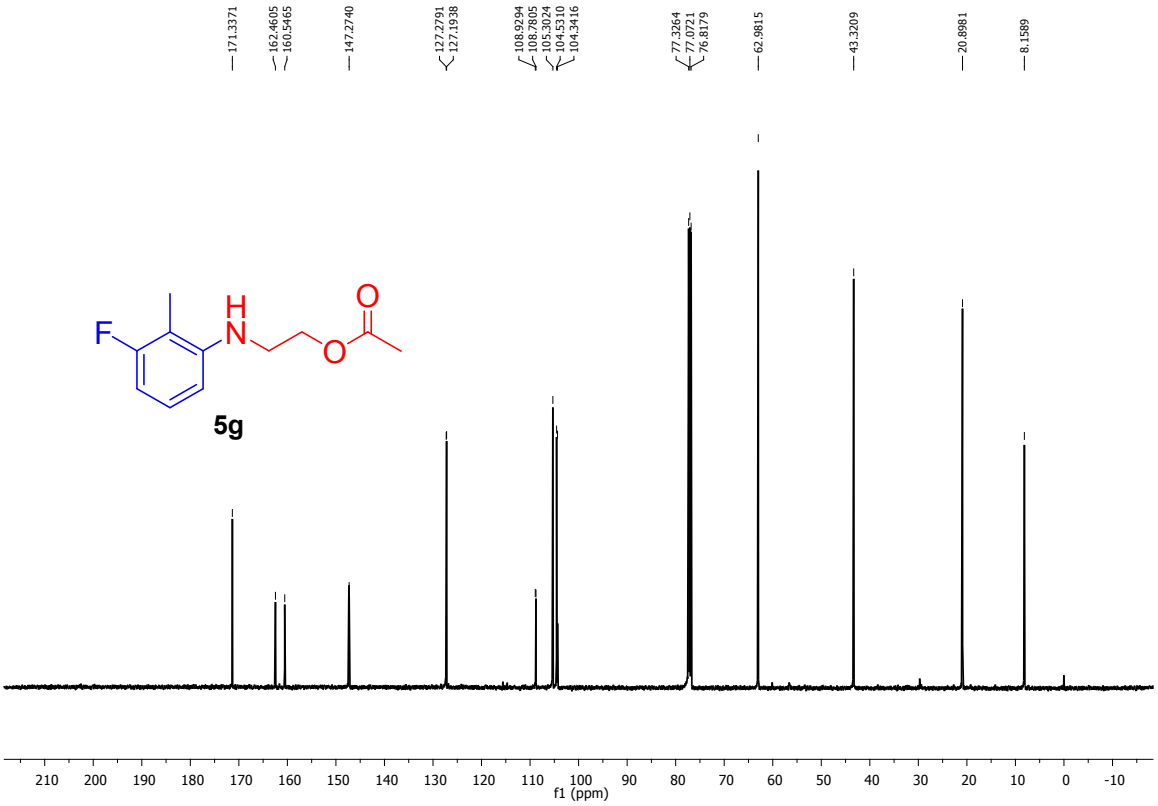
(Scheme 2, entry 5f)



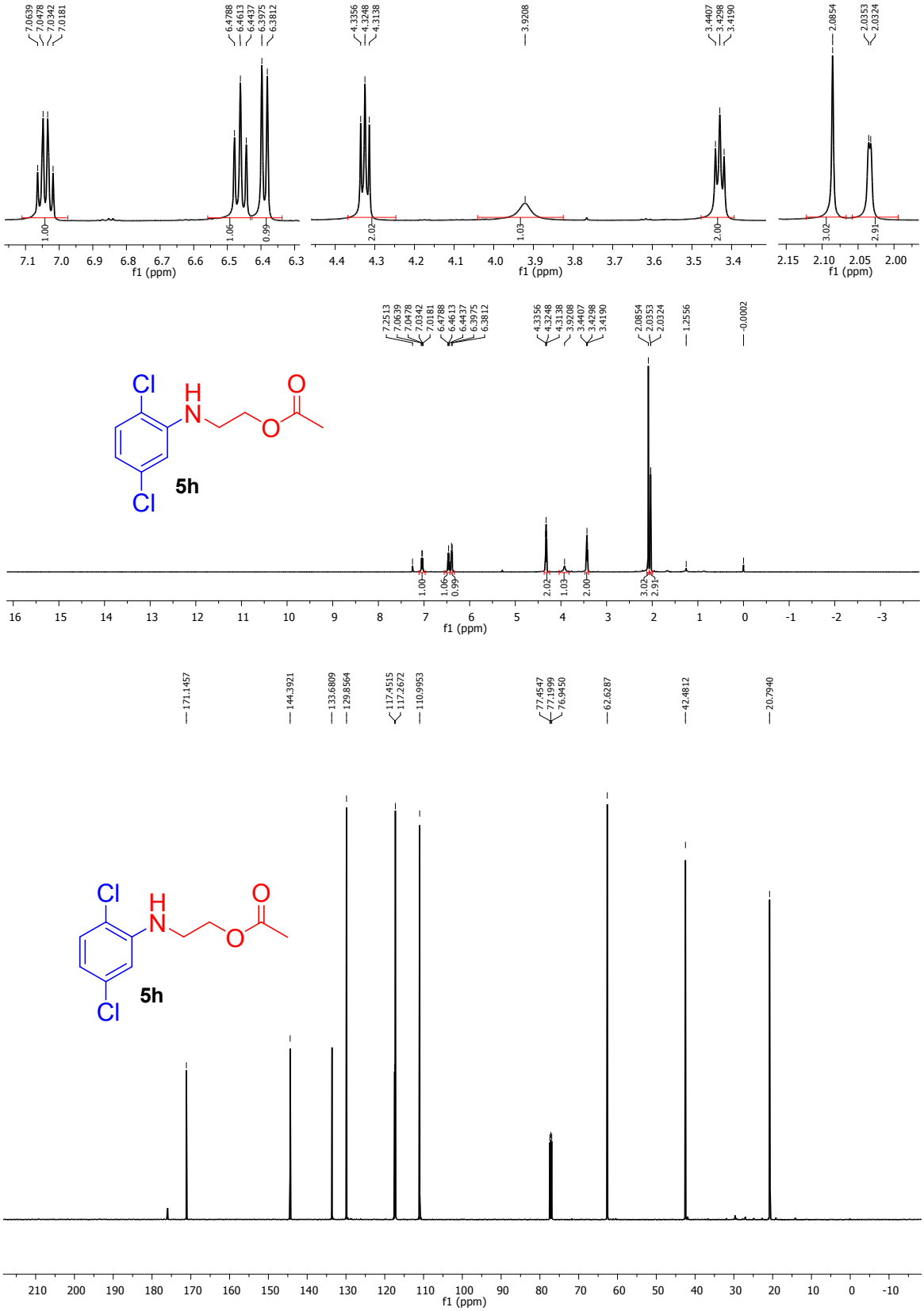
(Scheme 2, entry 5g)



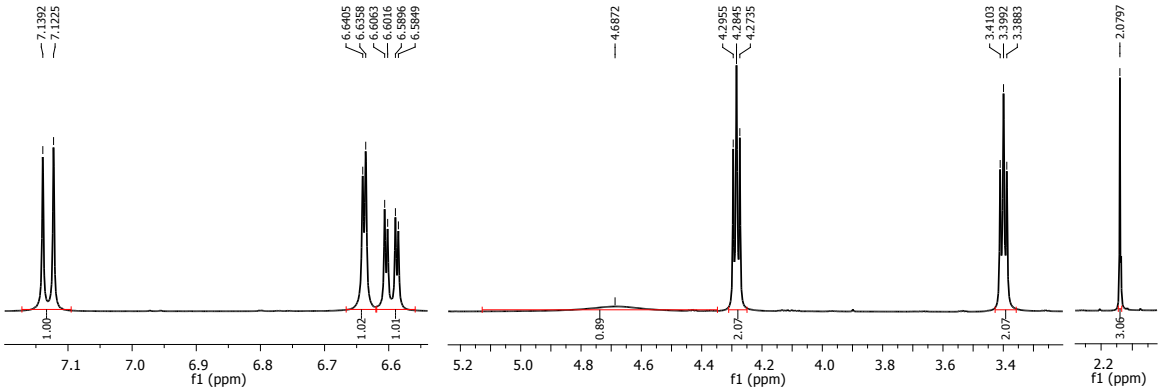


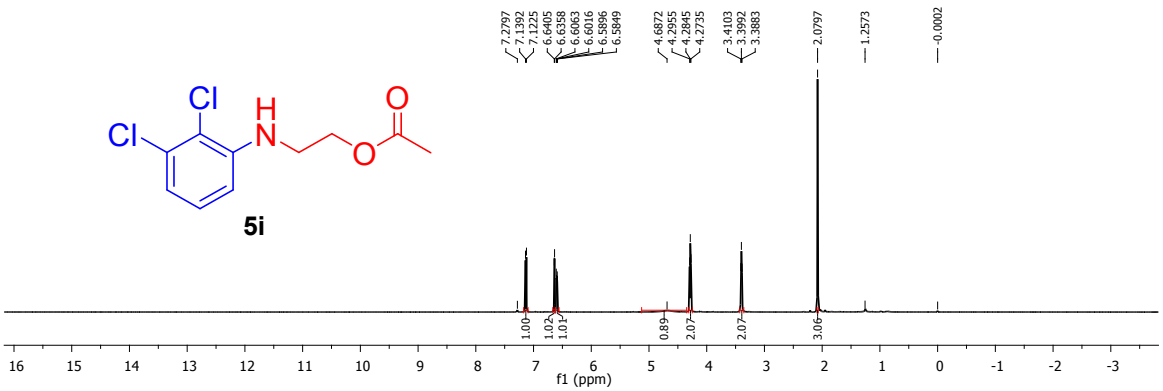


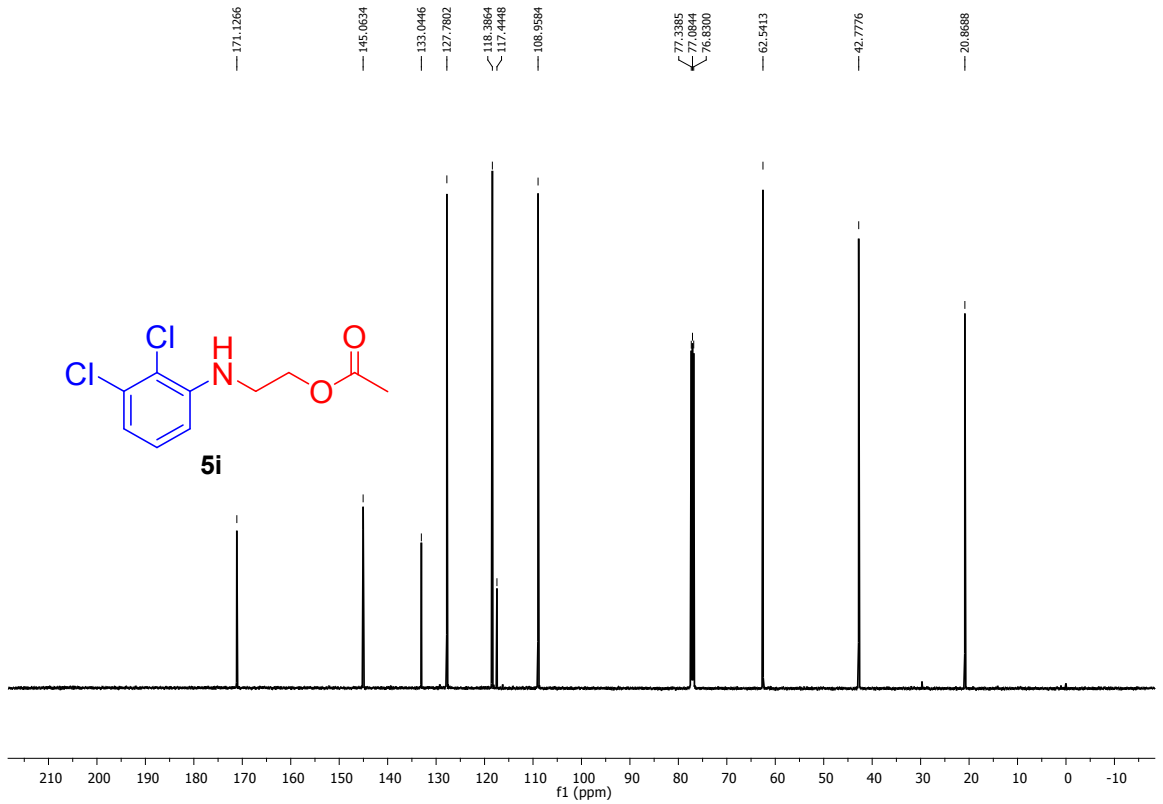
(Scheme 2, entry 5h)



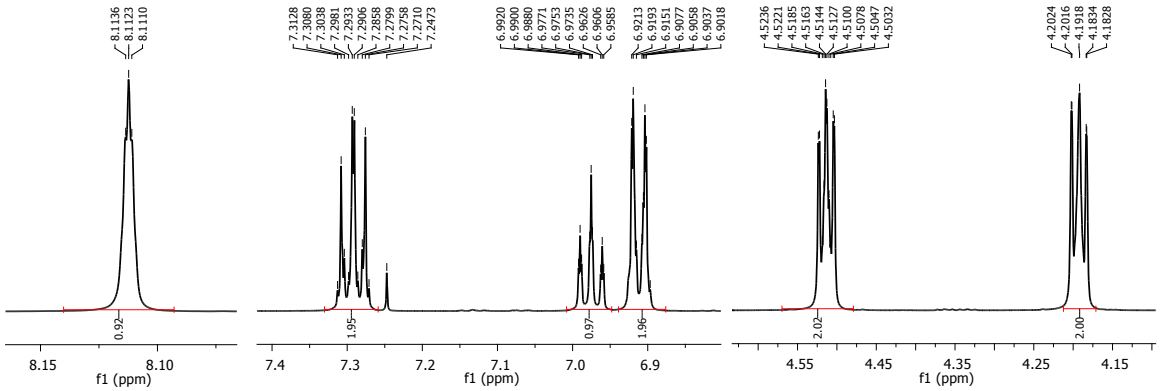
(Scheme 2, entry 5i)

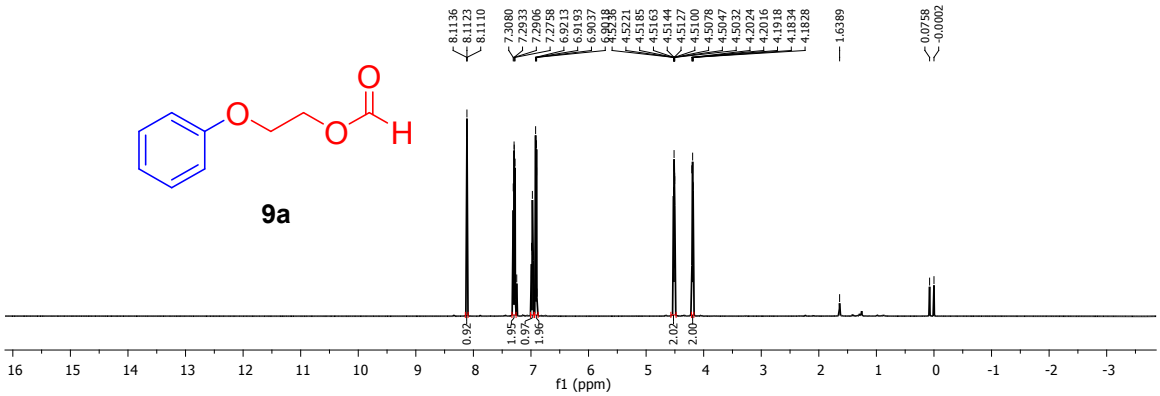


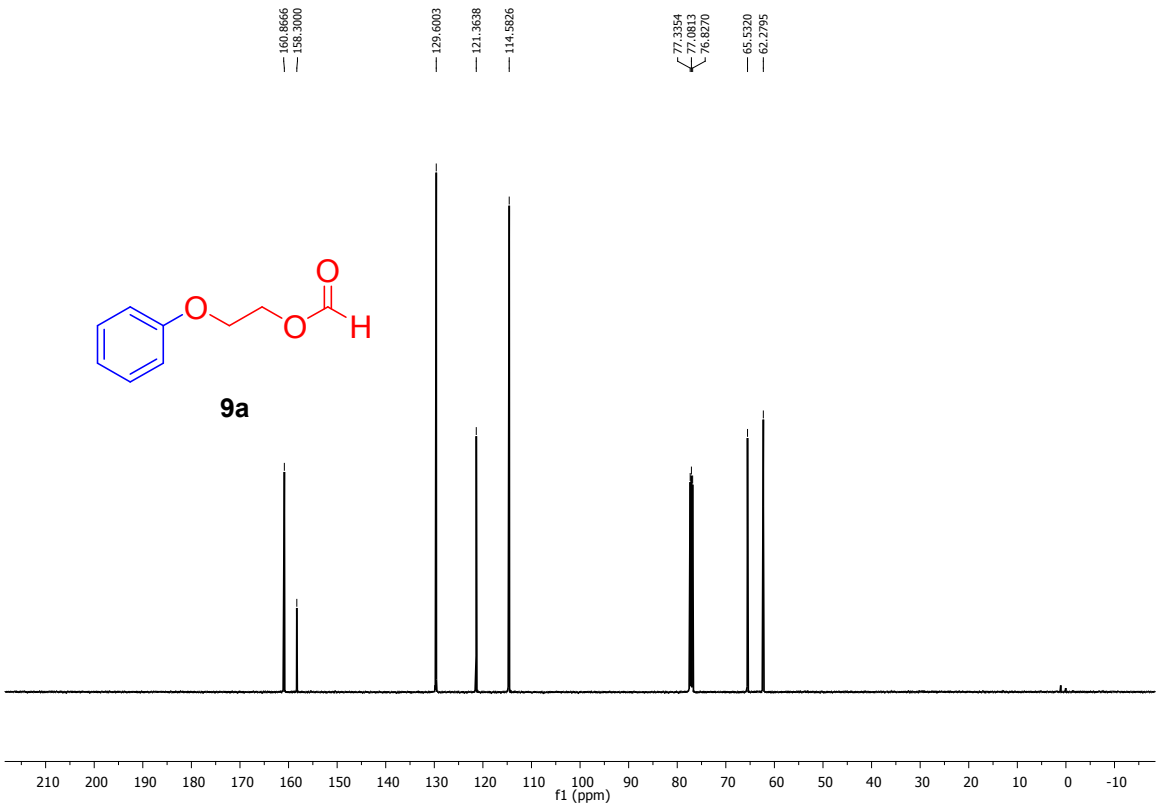




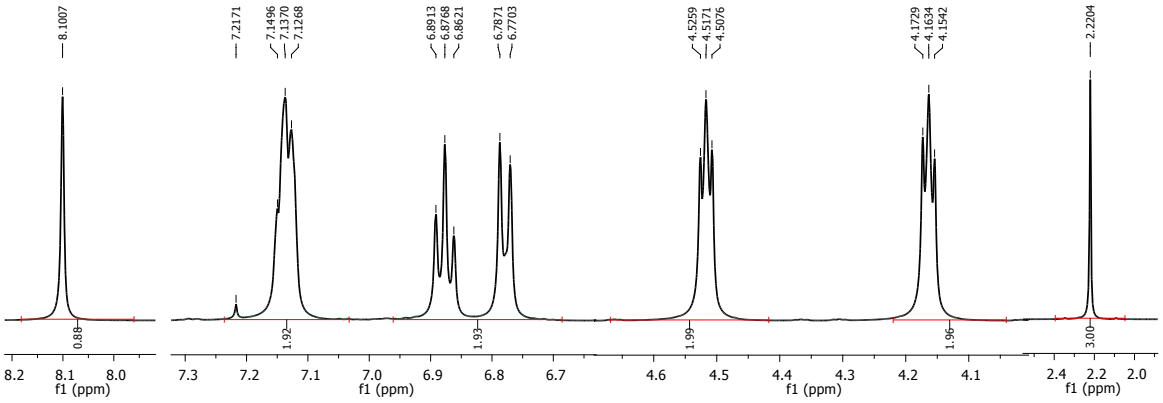
6. ^{1}H NMR and ^{13}C NMR spectra of *O*-formylated and *O*-Acylated Phenoxyethanols (Scheme 3, entry 9a)

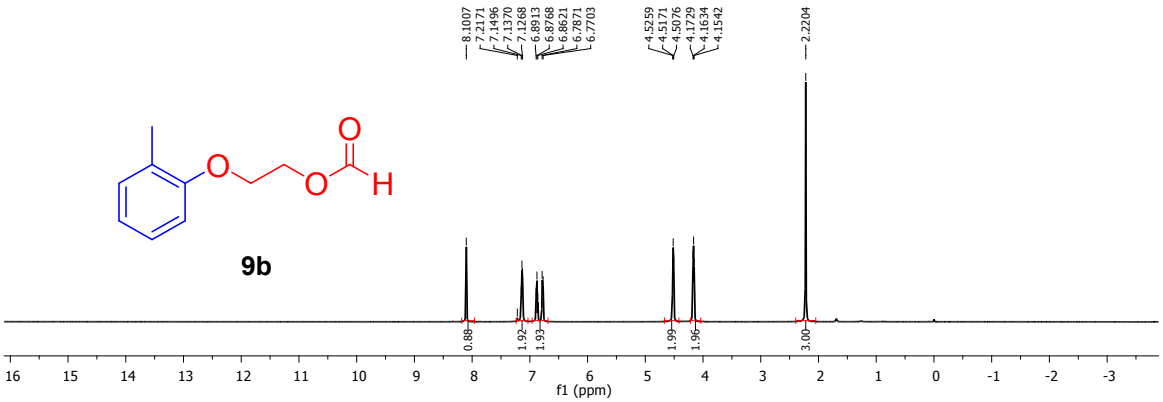


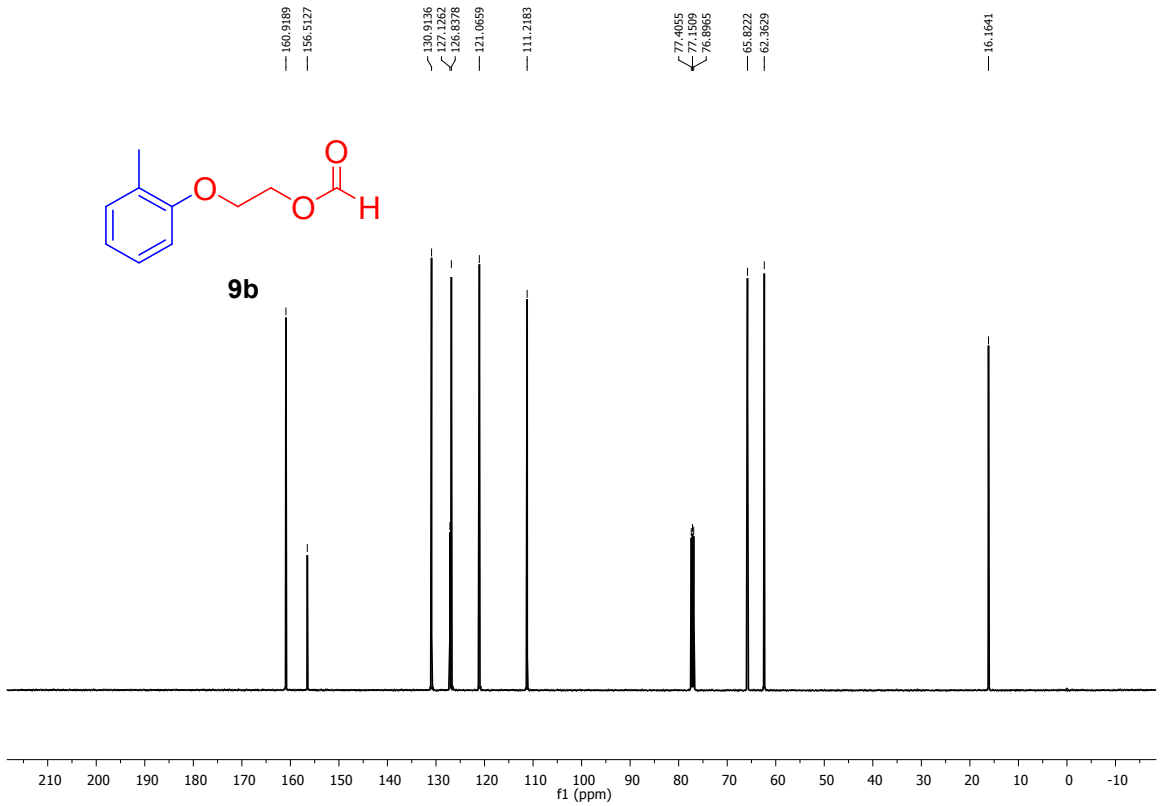




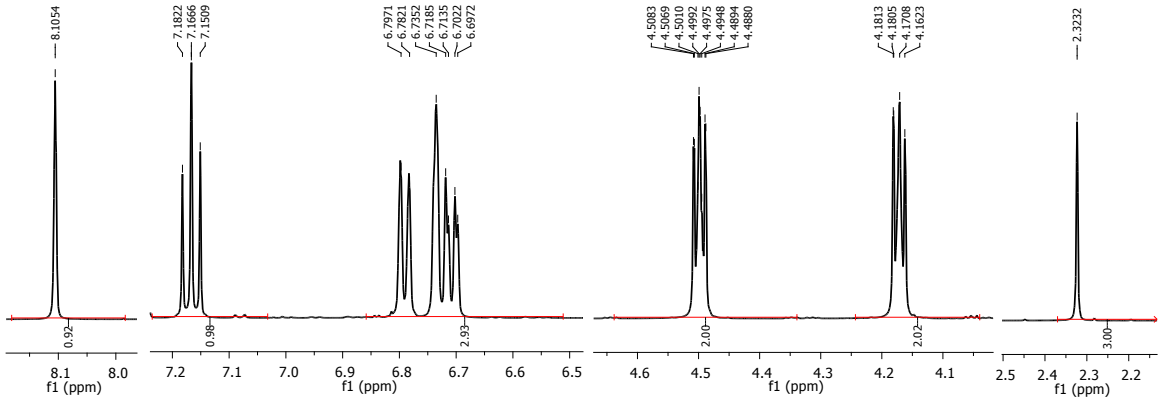
(Scheme 3, entry 9b)

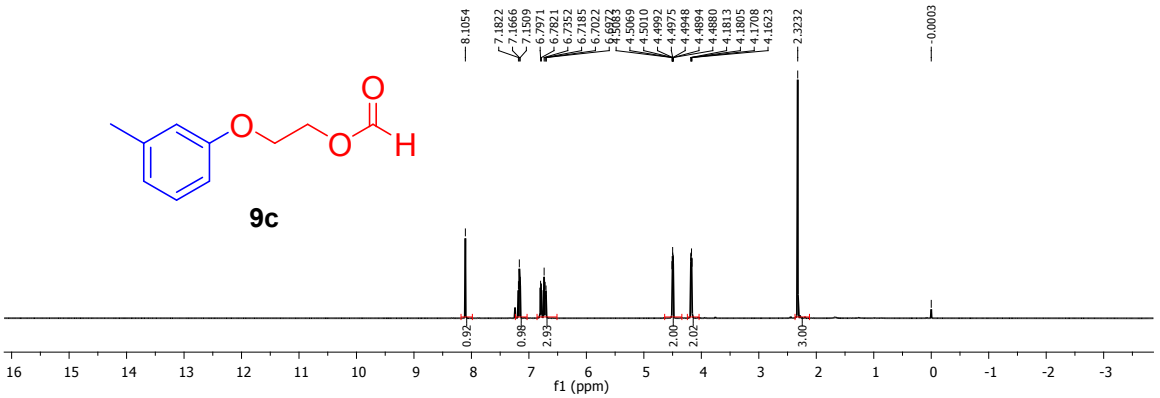


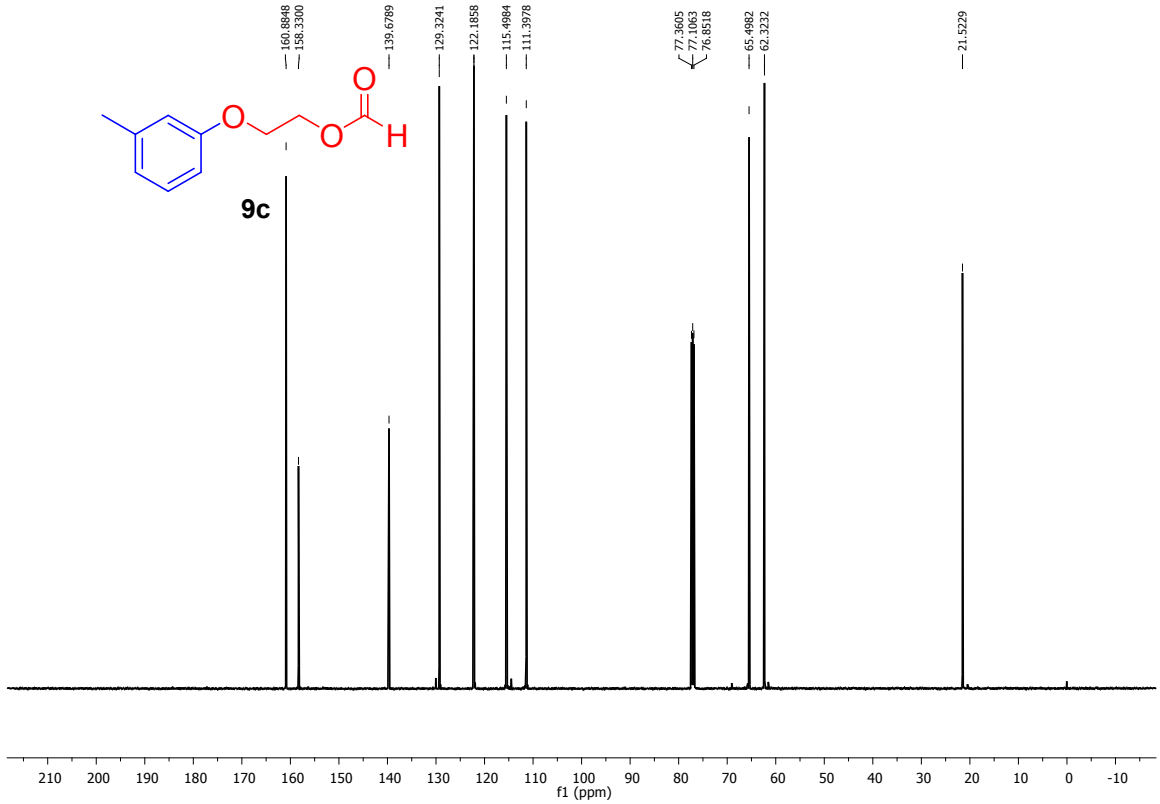




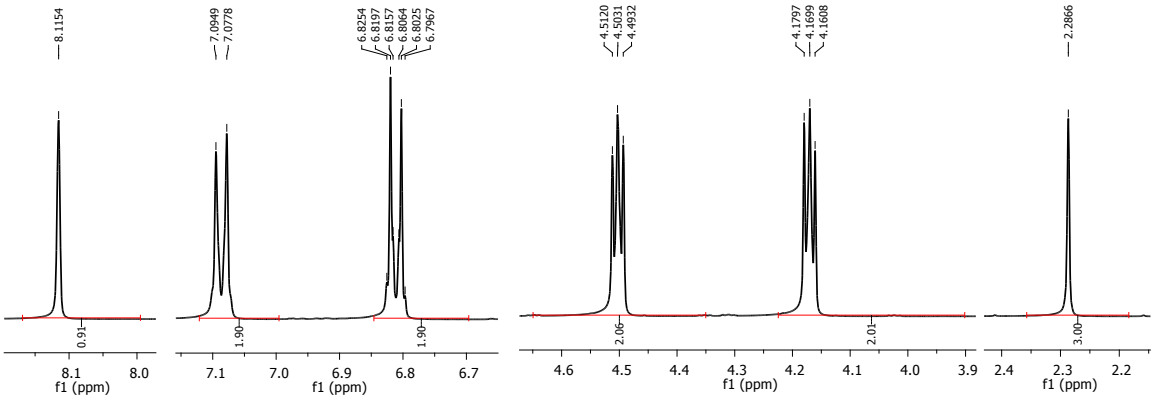
(Scheme 3, entry 9c)

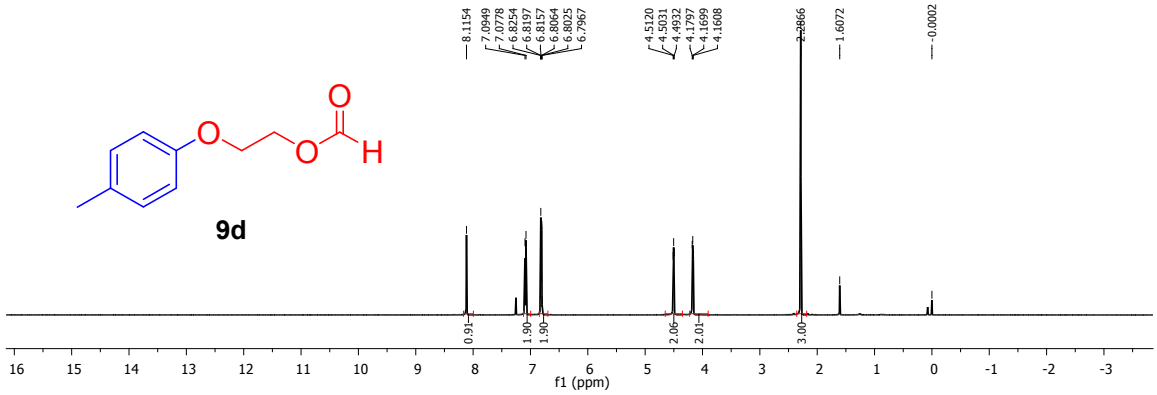


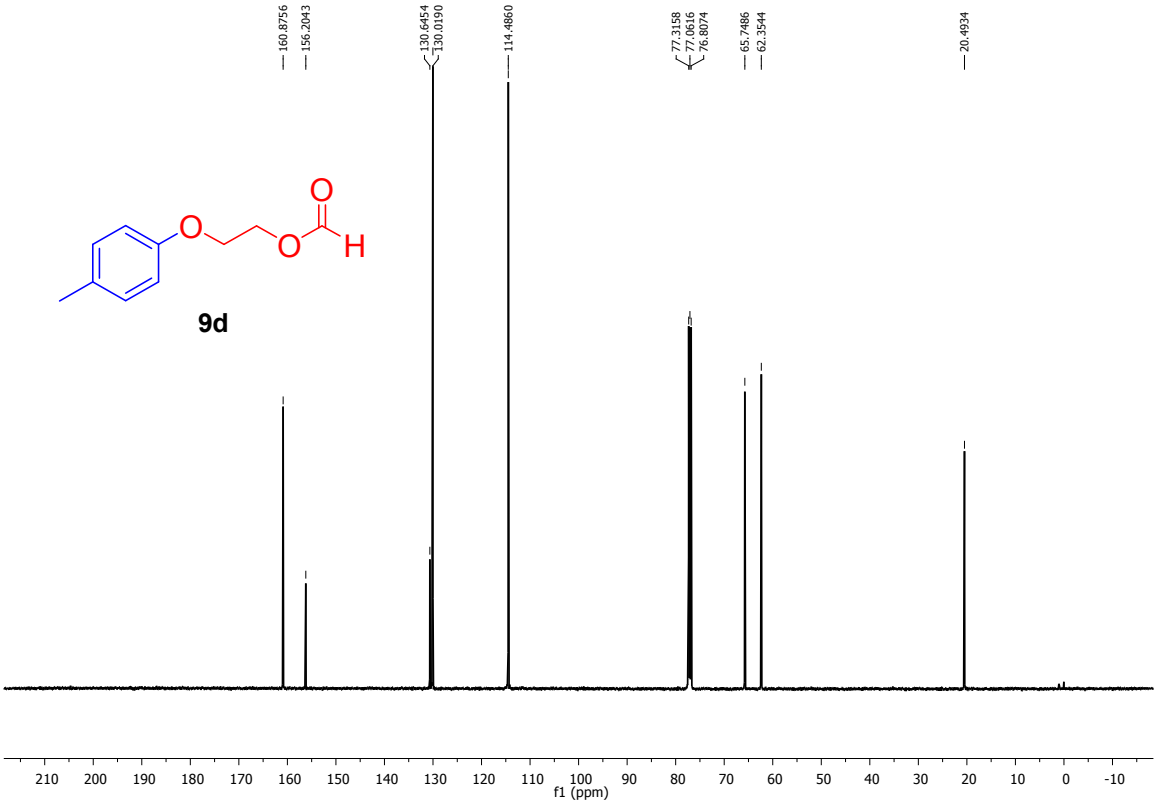




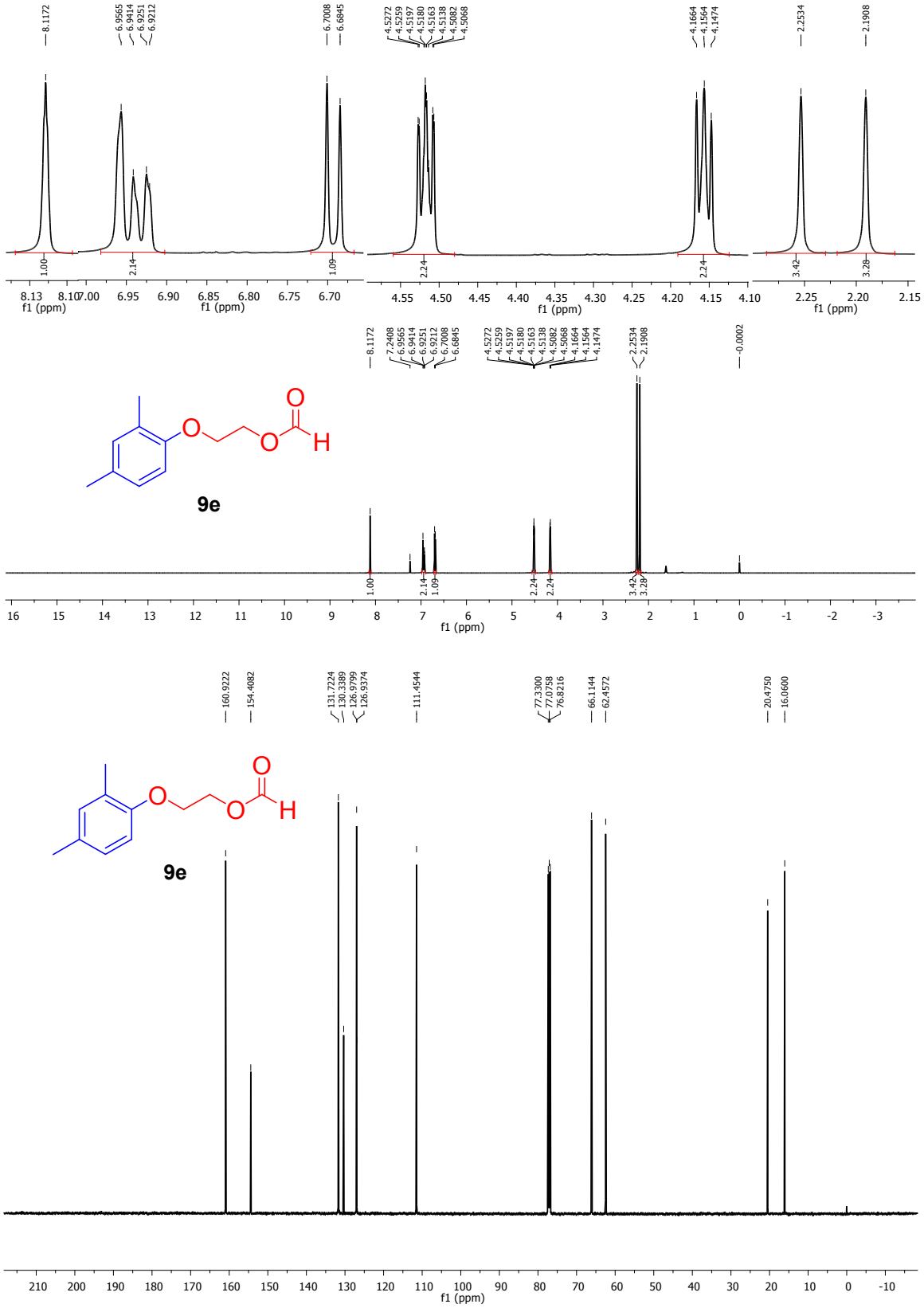
(Scheme 3, entry 9d)



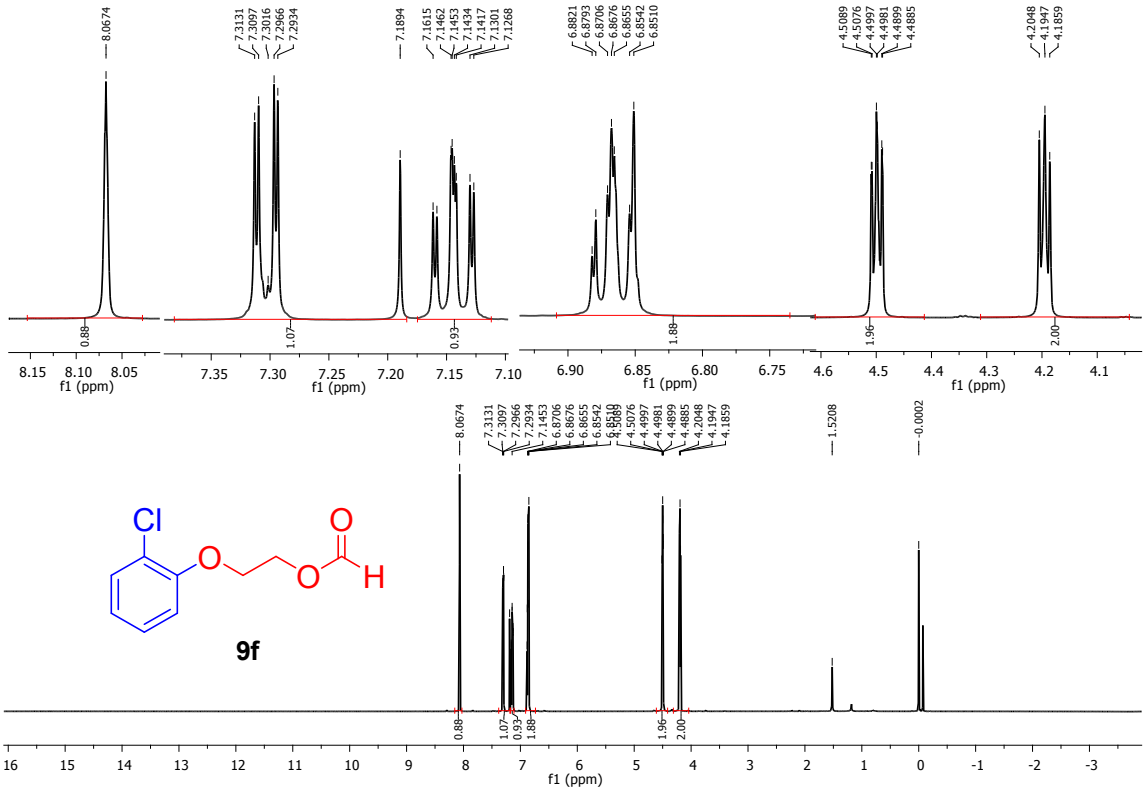


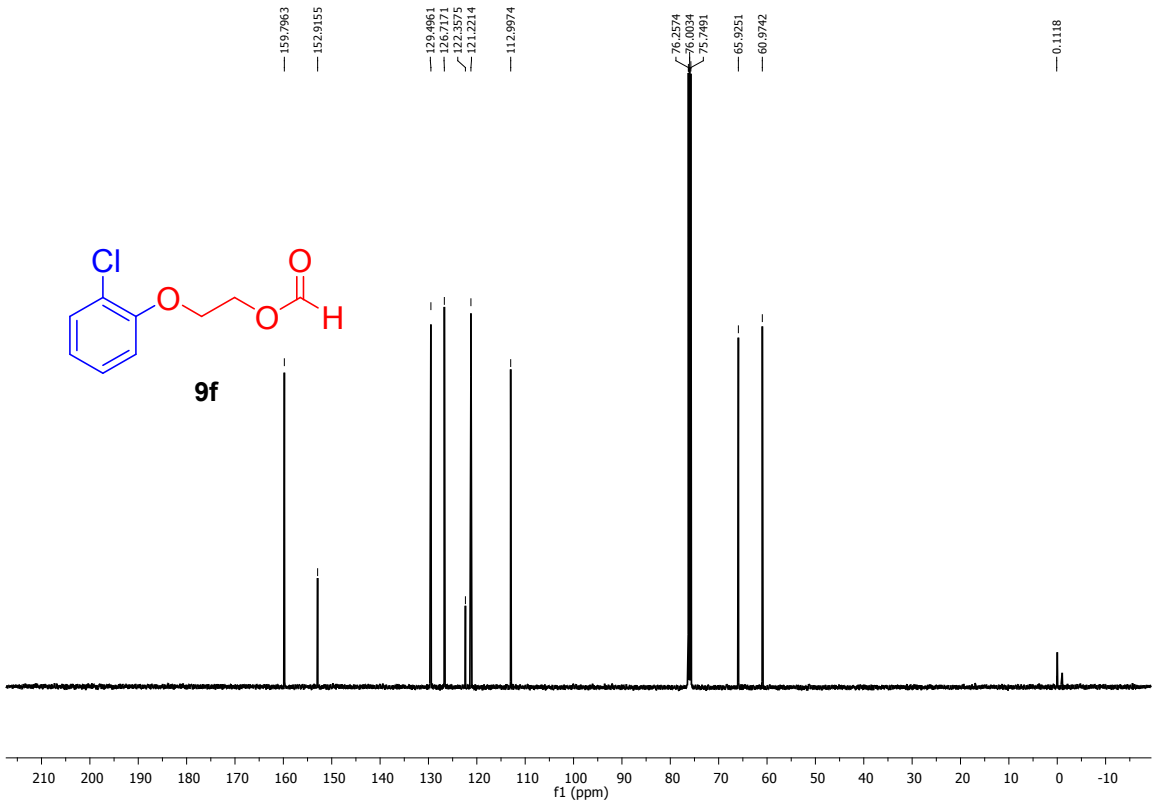


(Scheme 3, entry 9e)

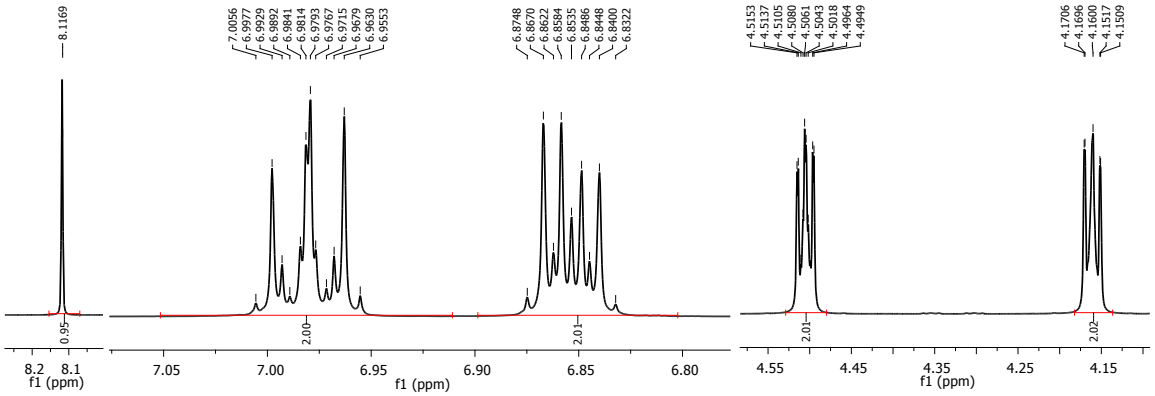


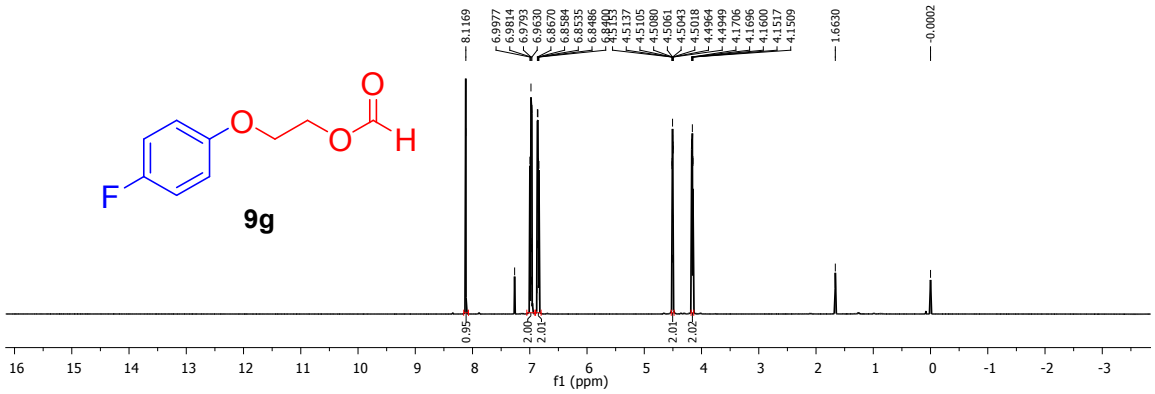
(Scheme 3, entry 9f)

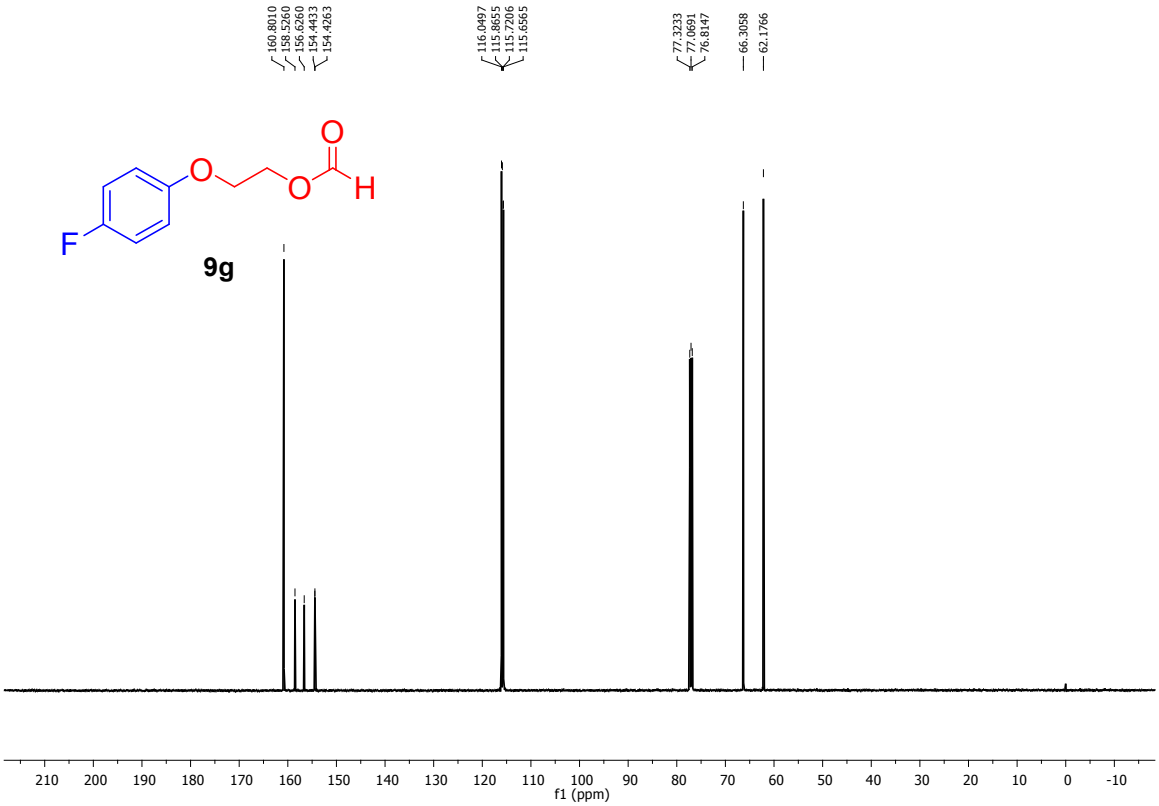




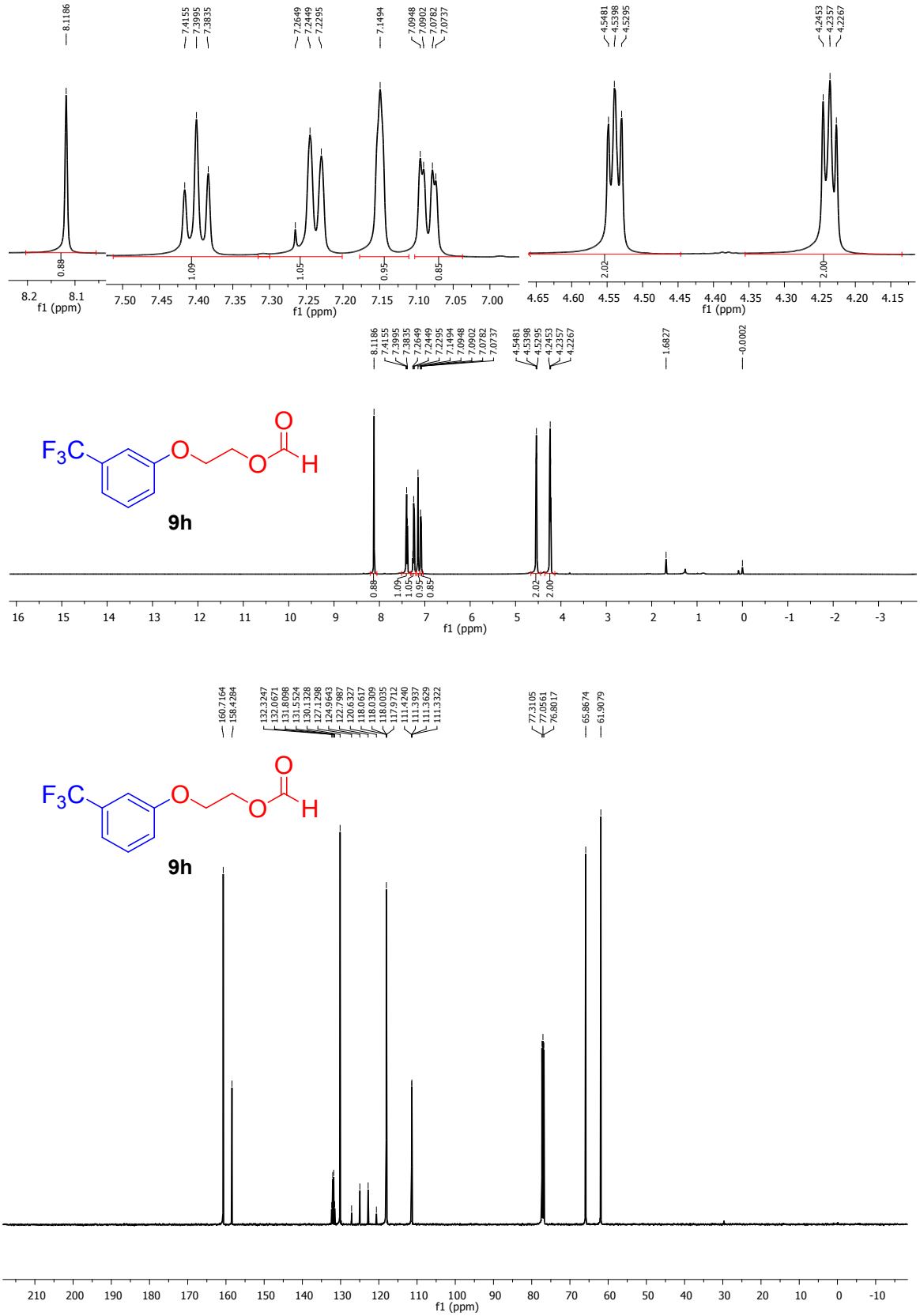
(Scheme 3, entry 9g)



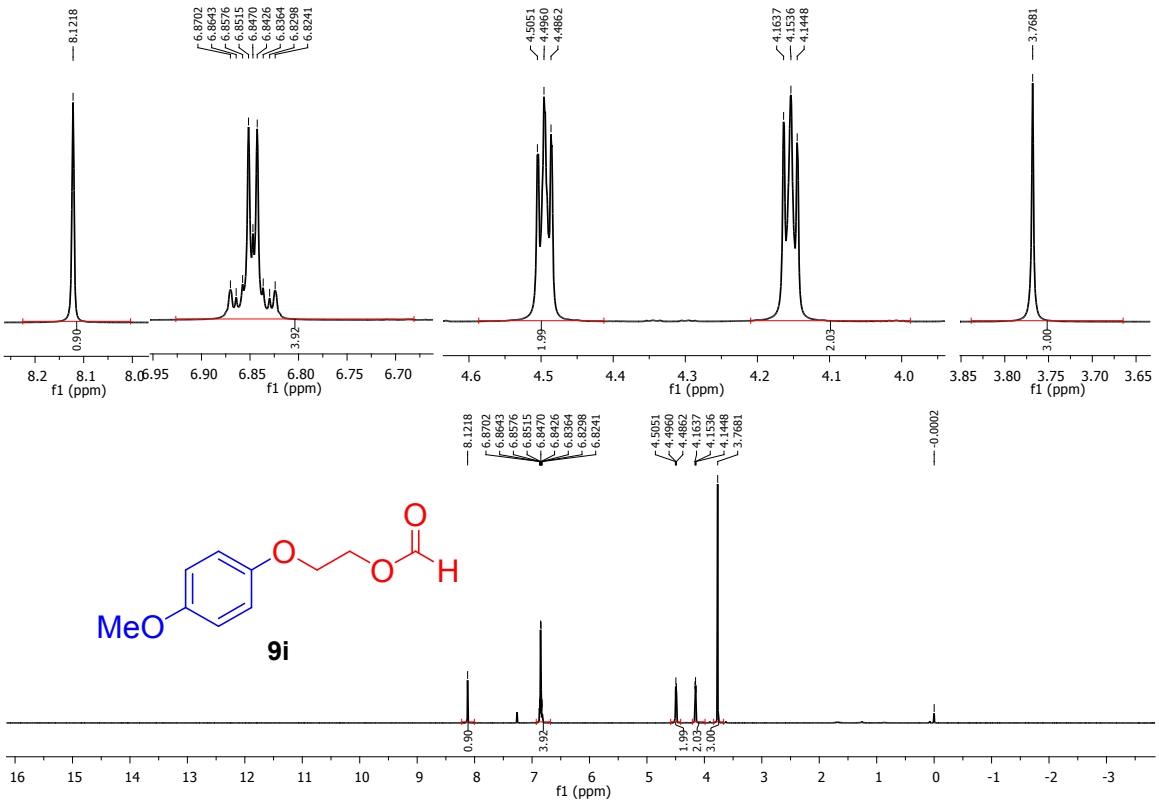


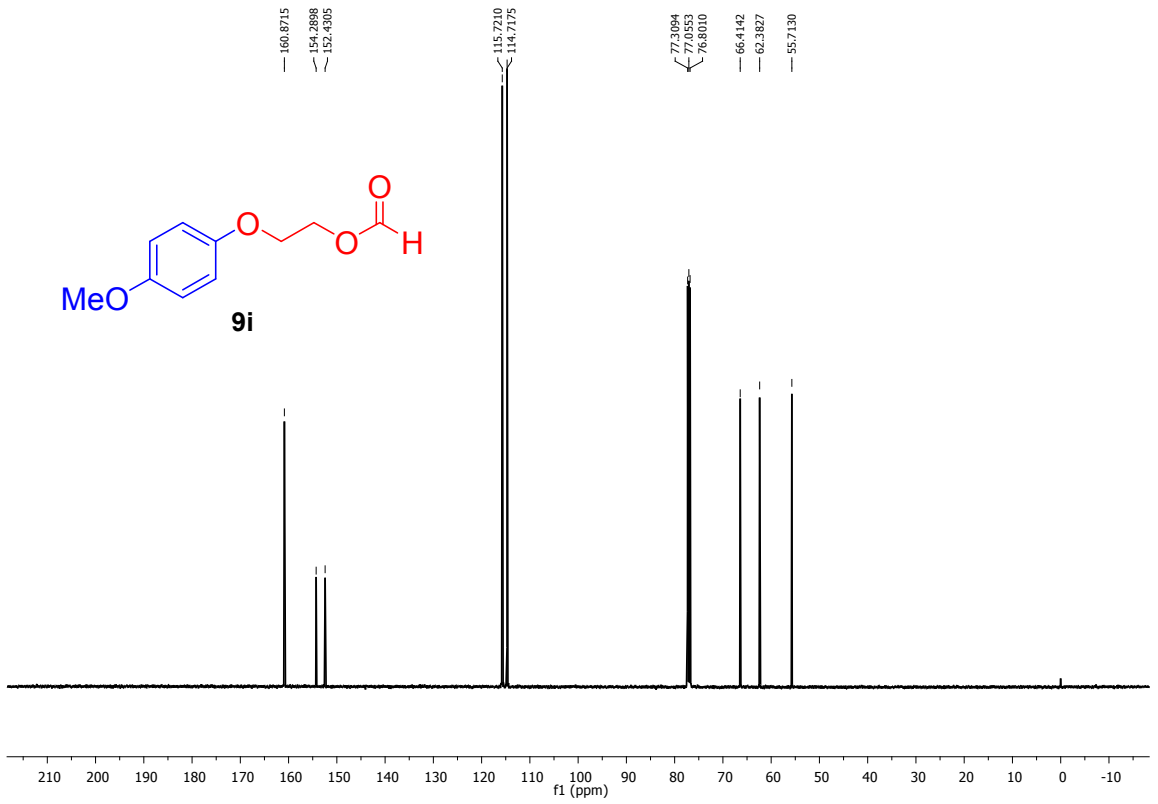


(Scheme 3, entry 9h)

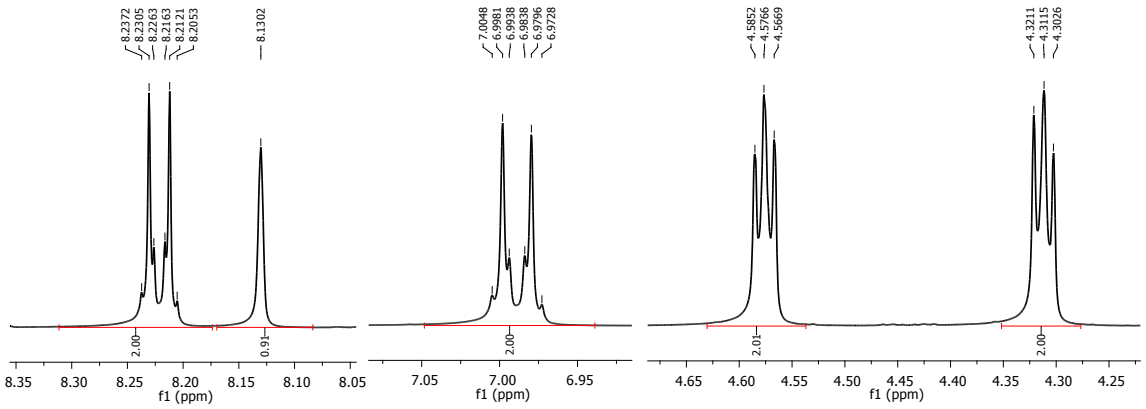


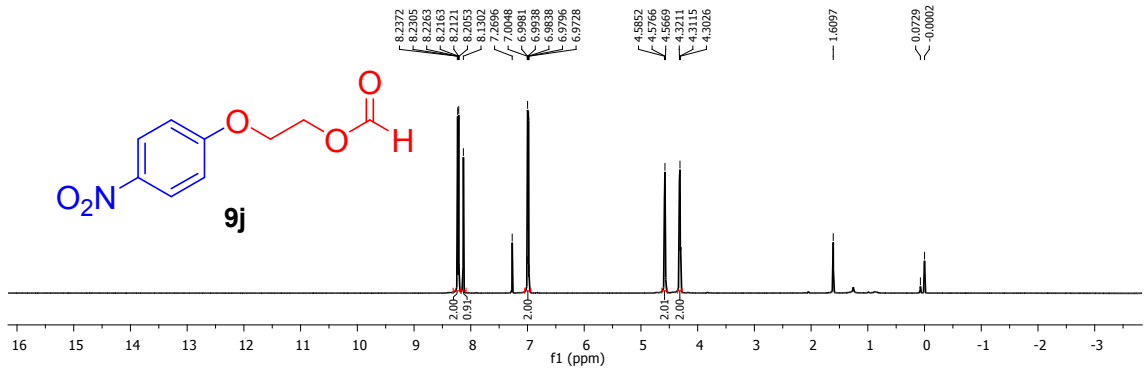
(Scheme 3, entry 9i)

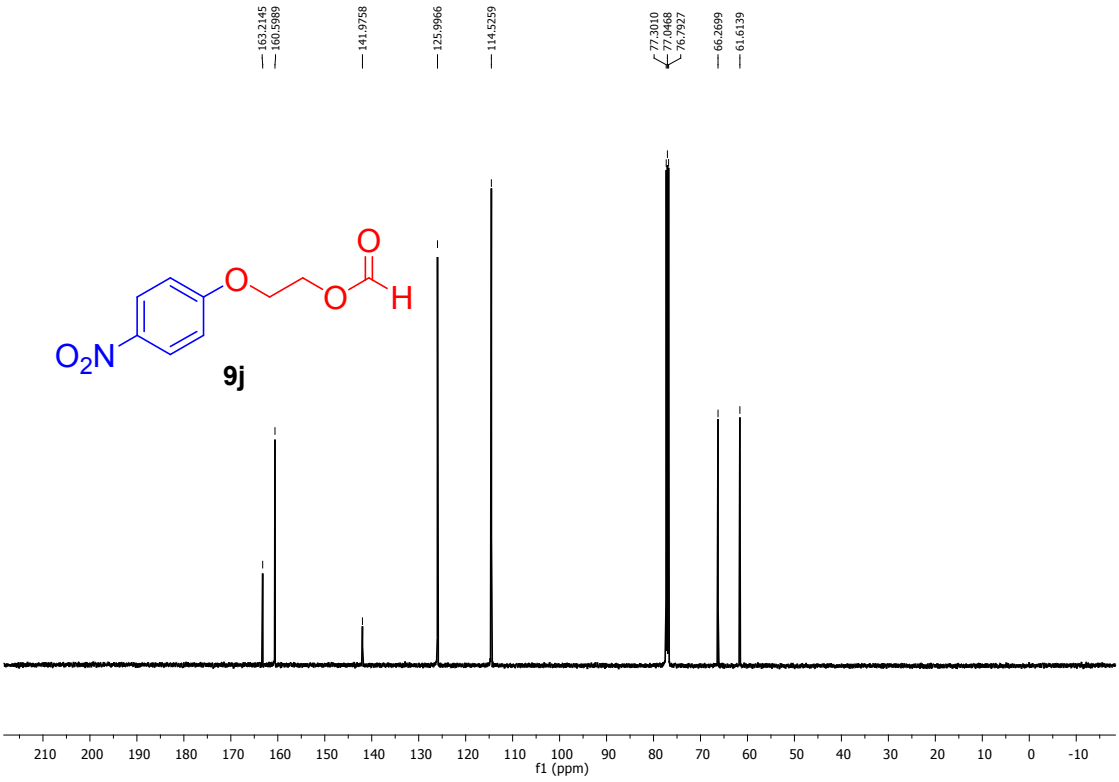




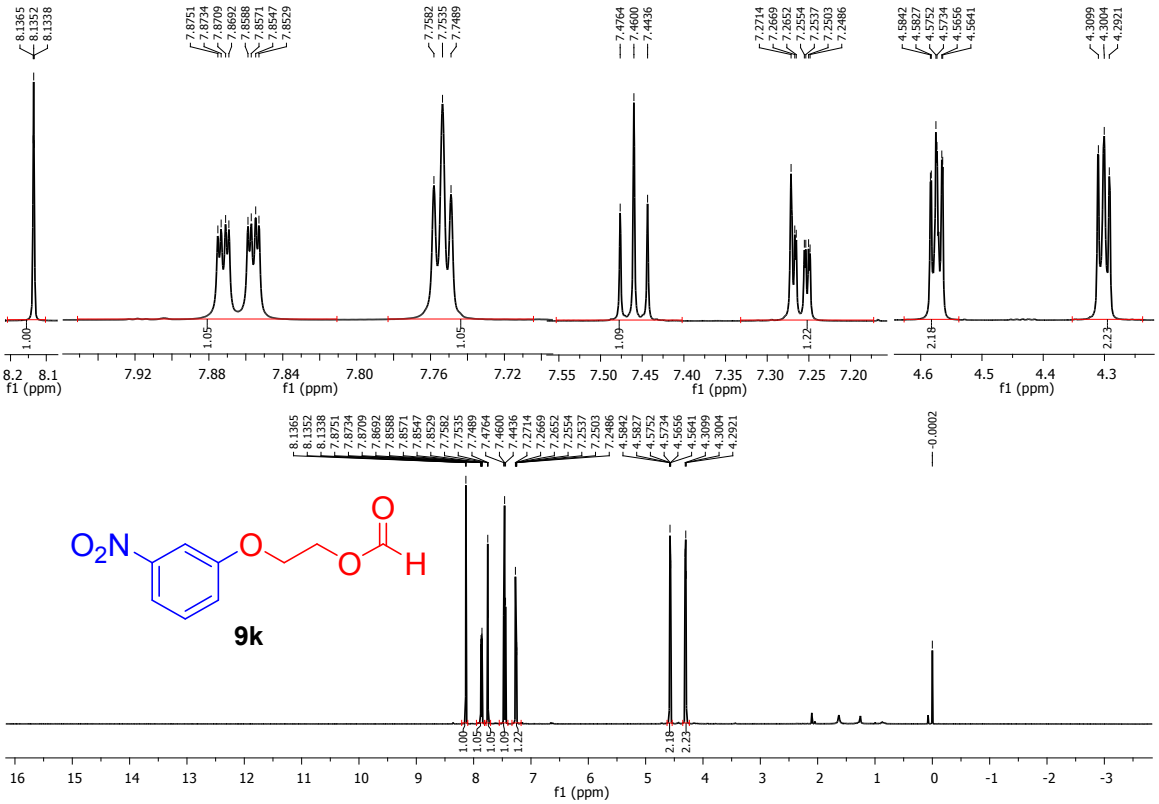
(Scheme 3, entry 9j)



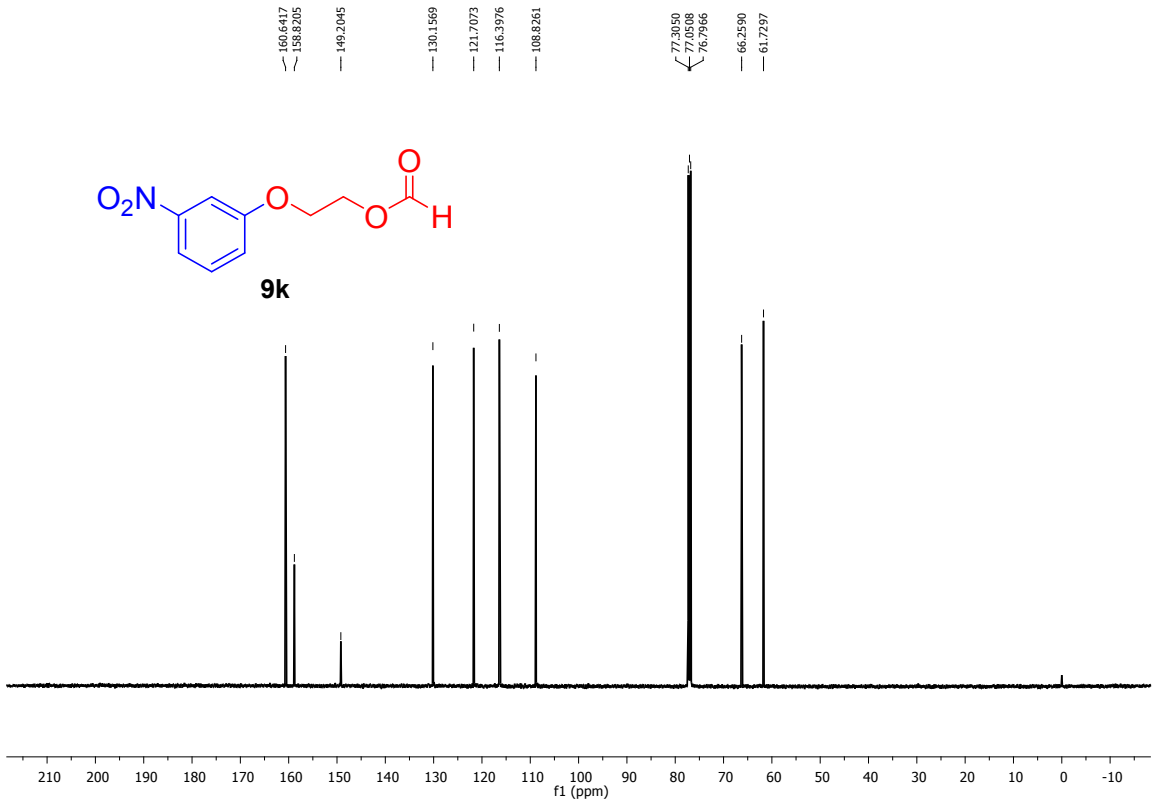




(Scheme 3, entry 9k)

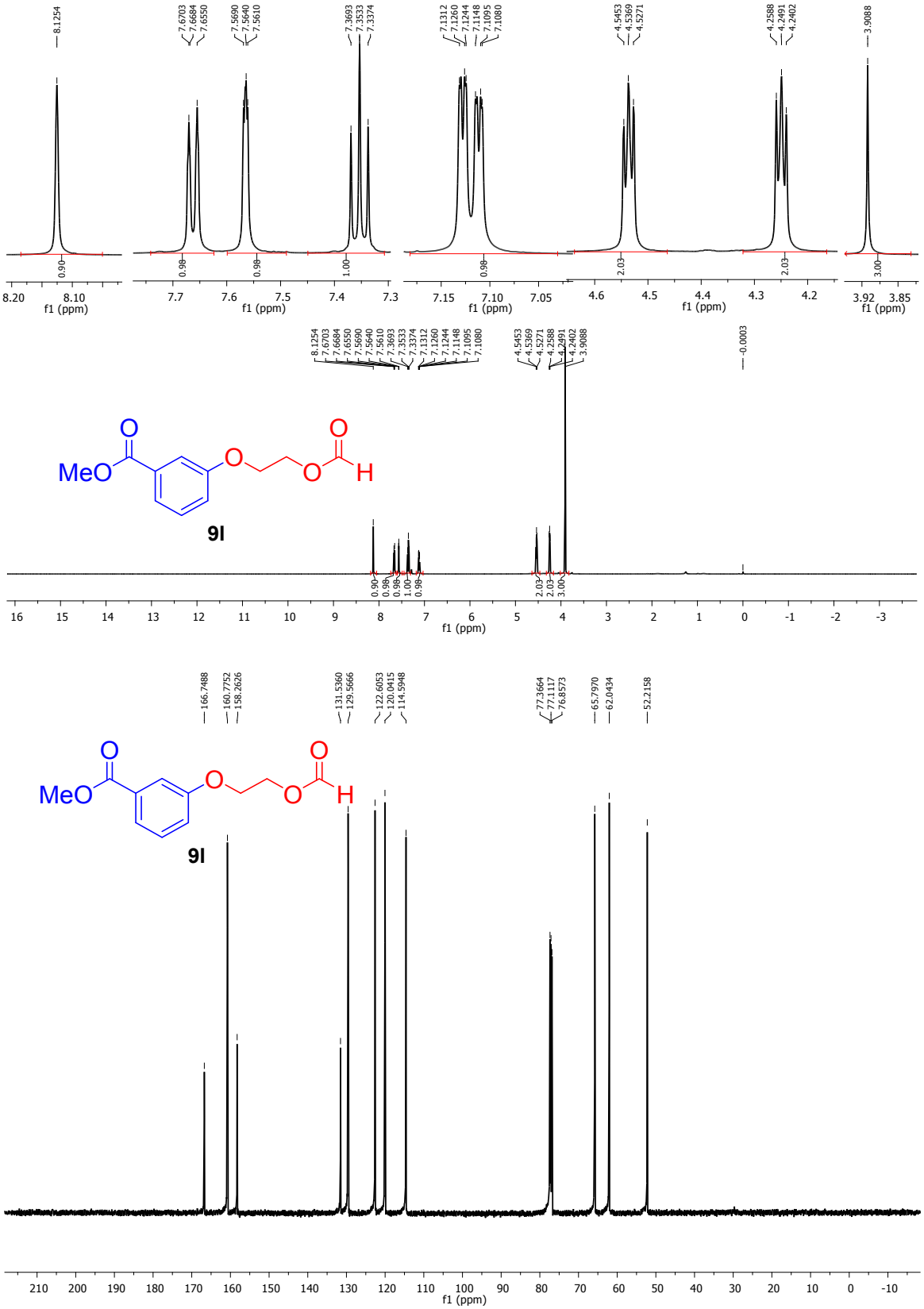


9k

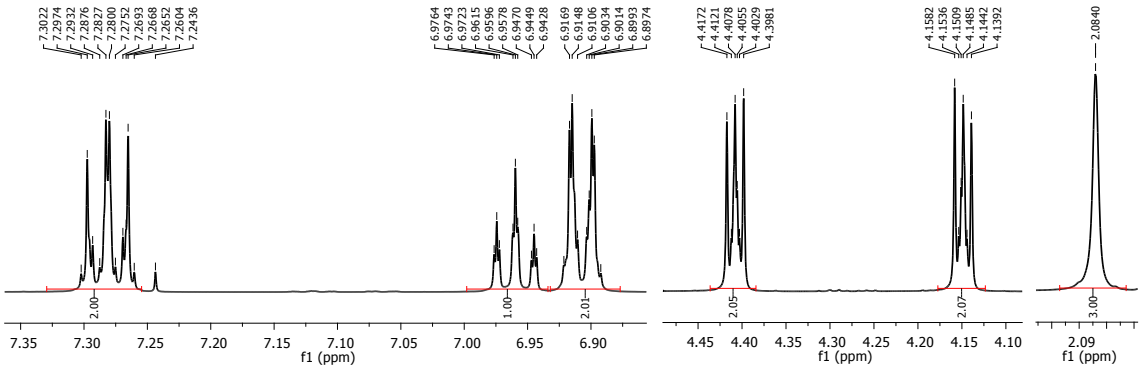


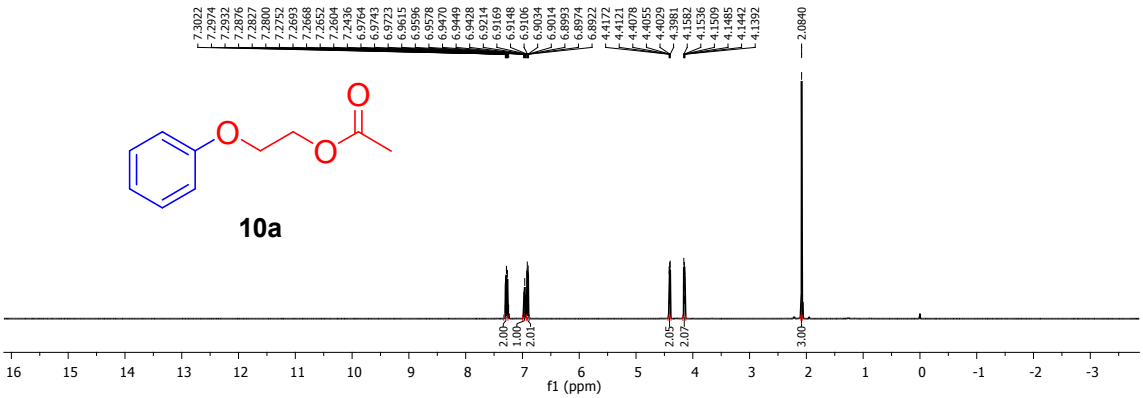
9k

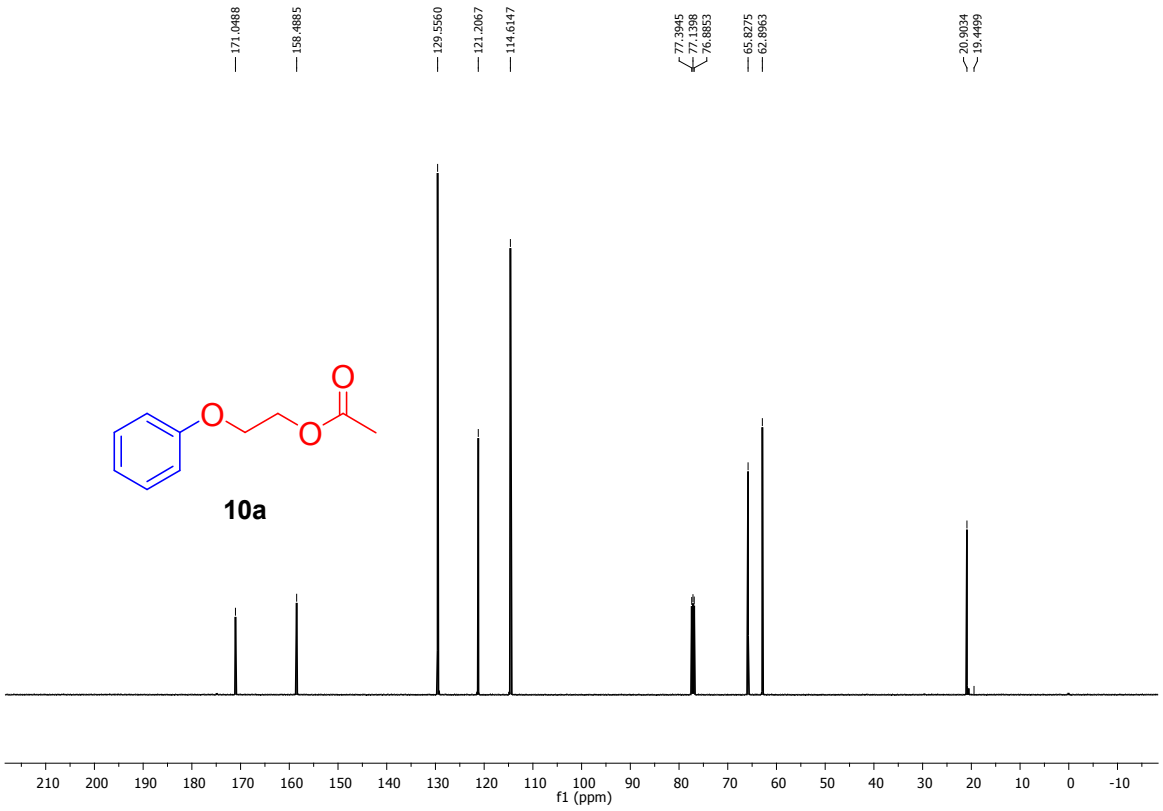
(Scheme 3, entry 9l)



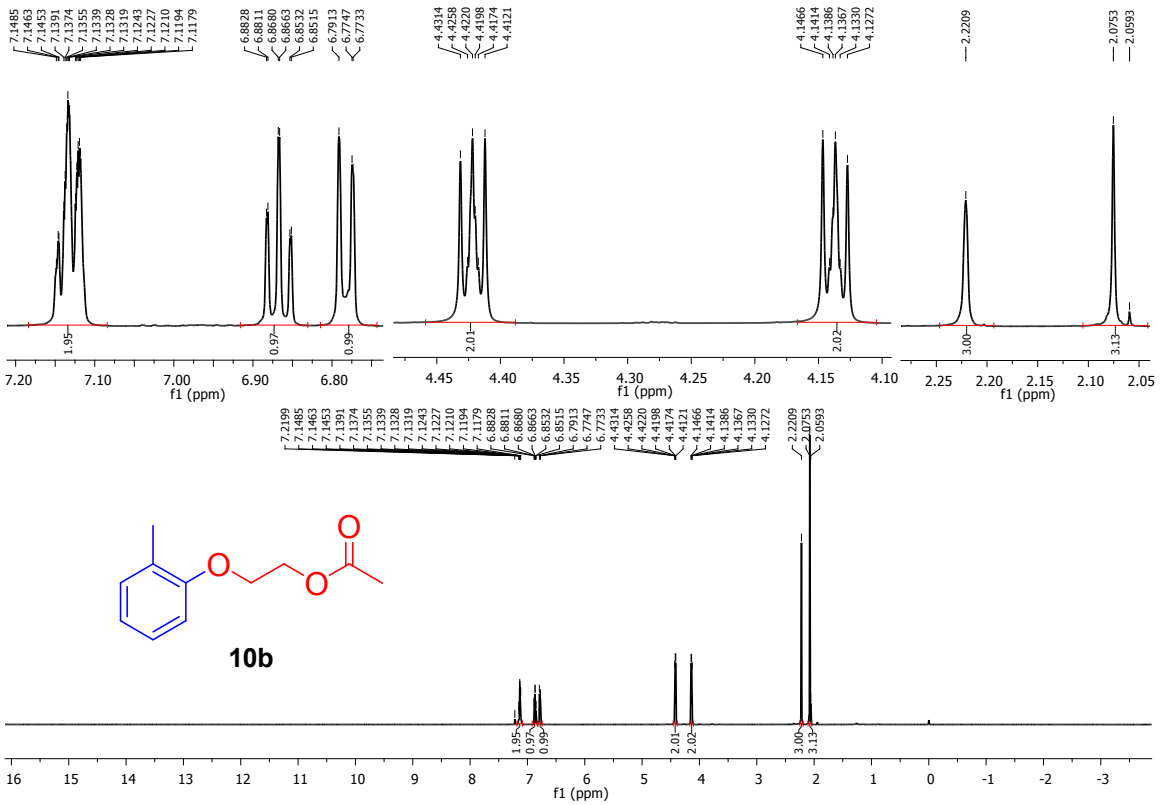
(Scheme 4, entry 10a)

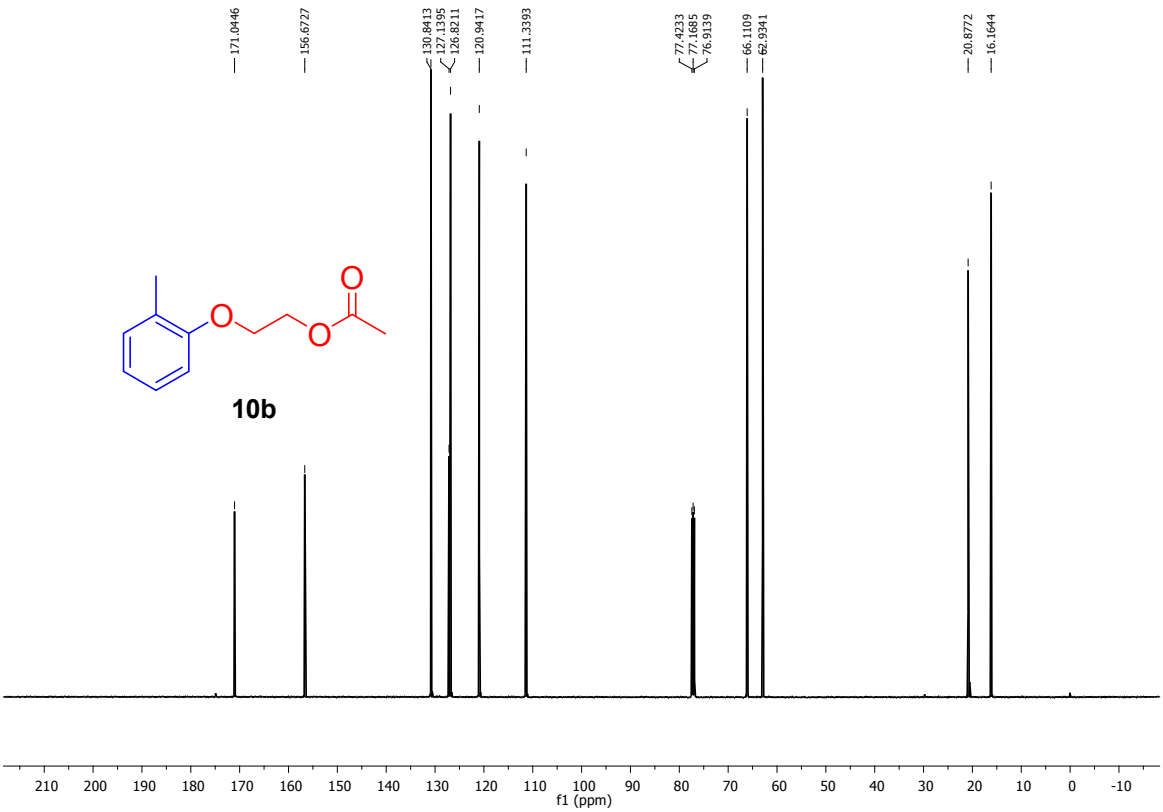




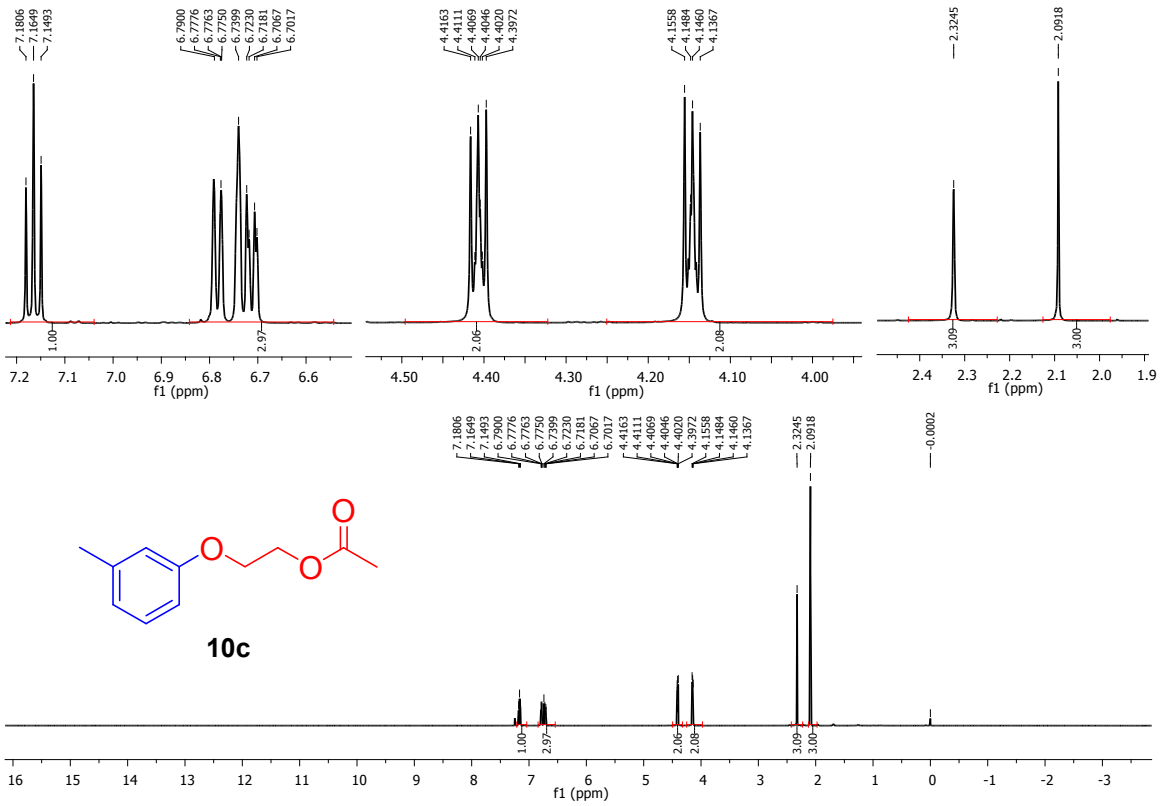


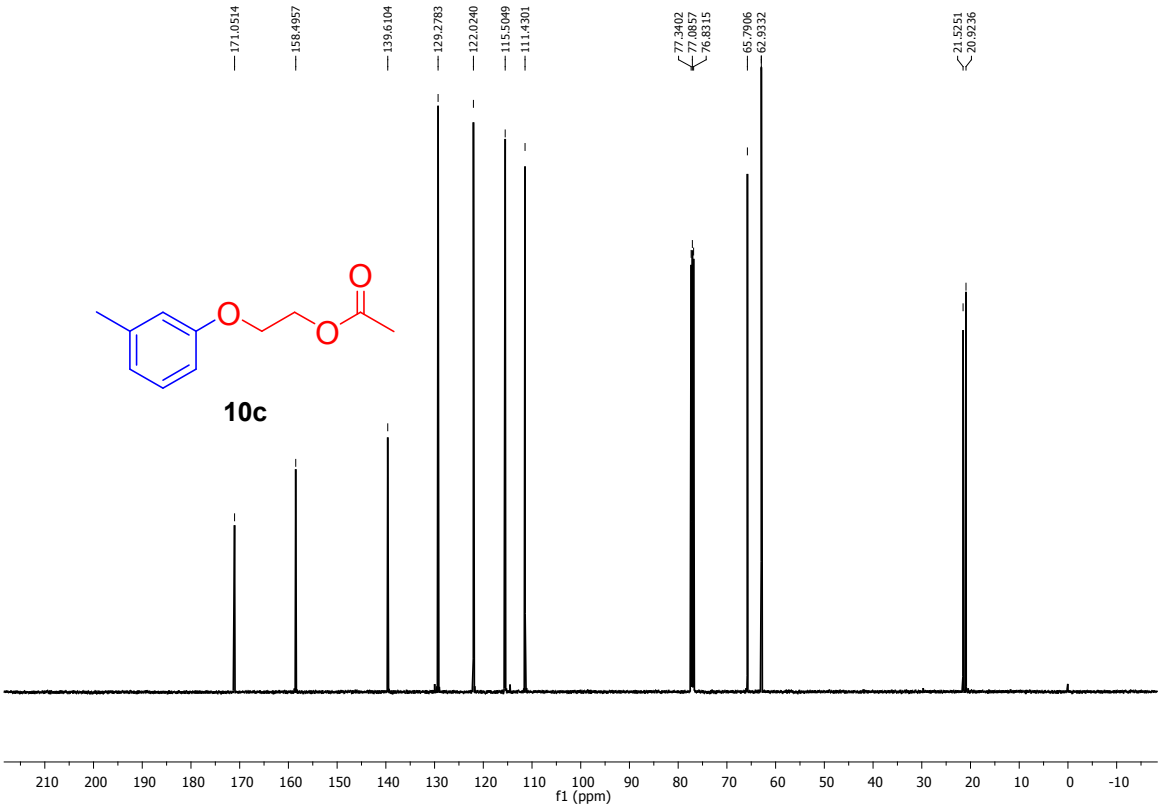
(Scheme 4, entry 10b)



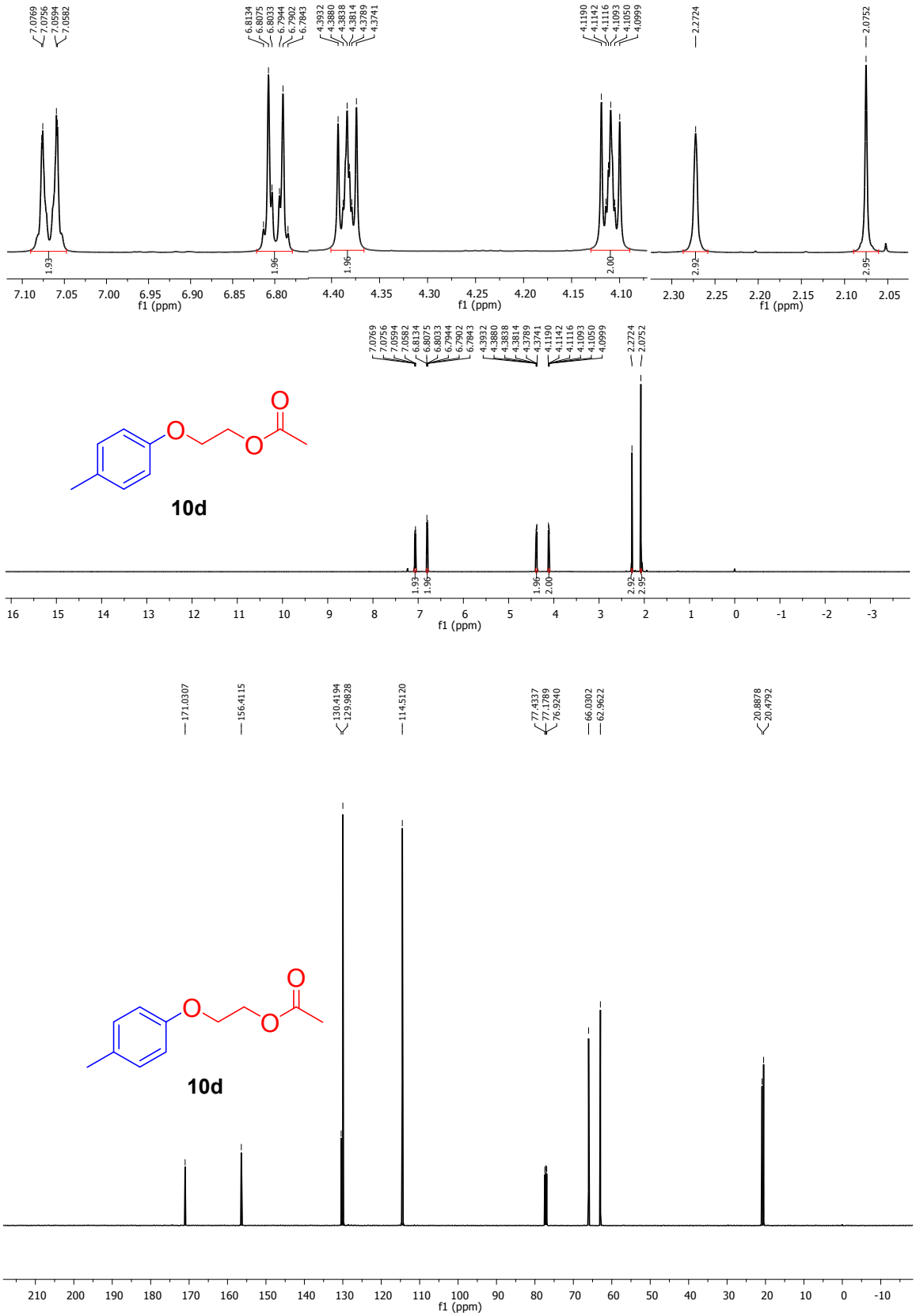


(Scheme 4, entry 10c)

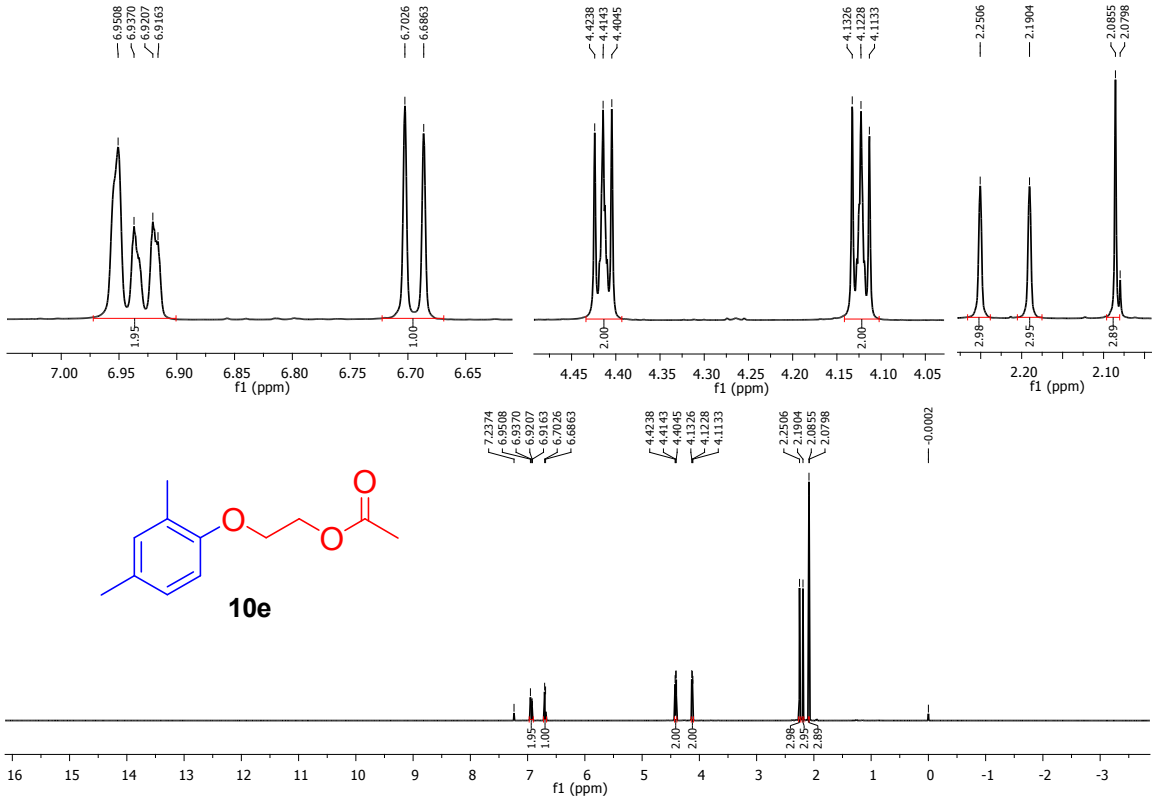


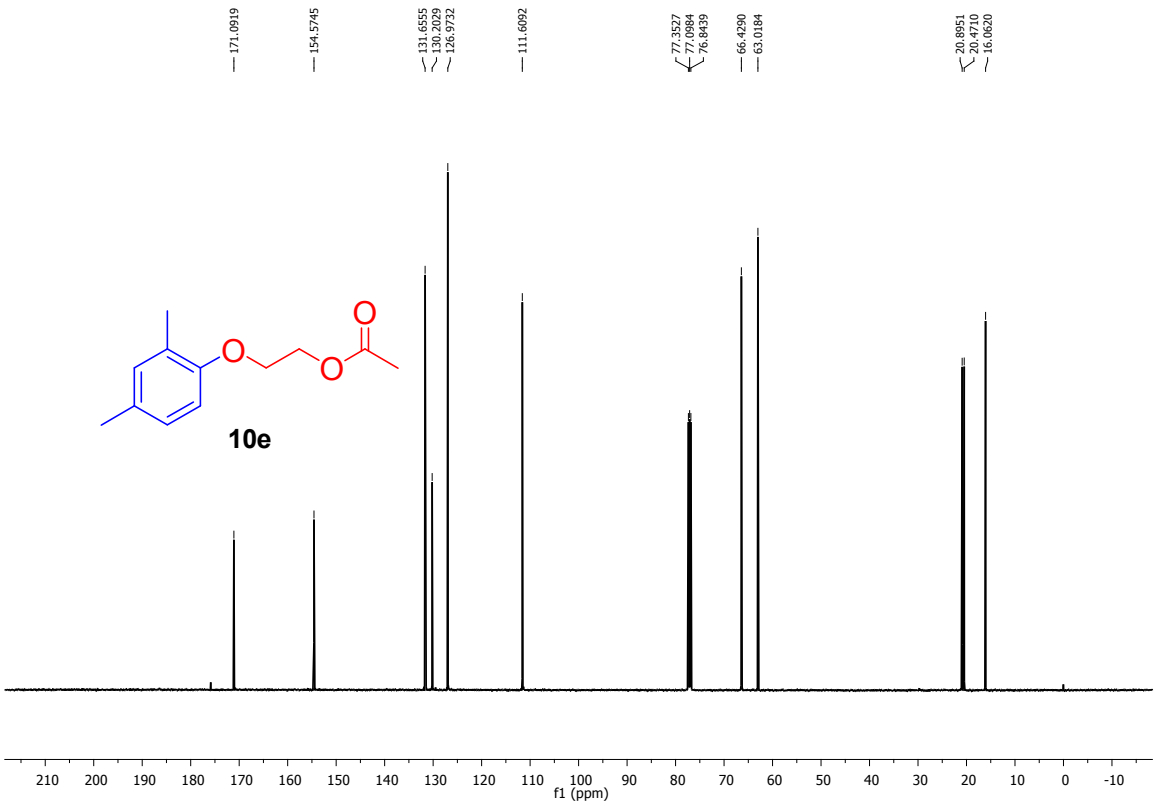


(Scheme 4, entry 10d)

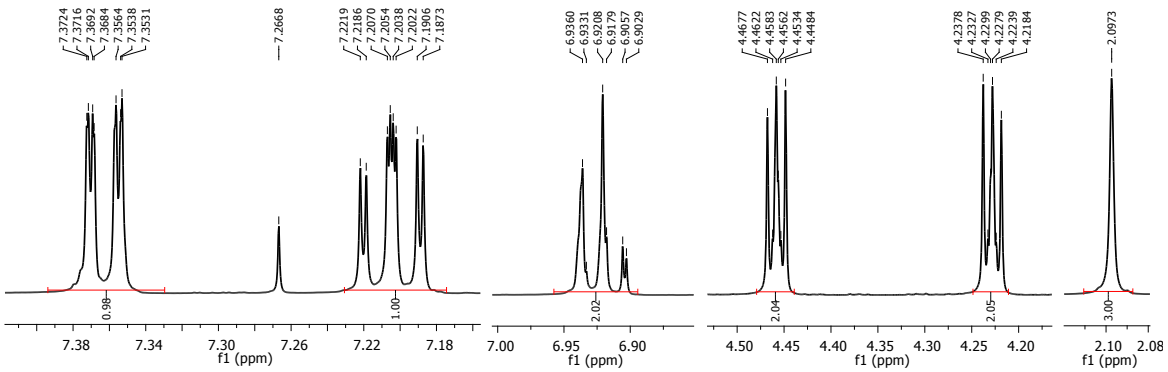


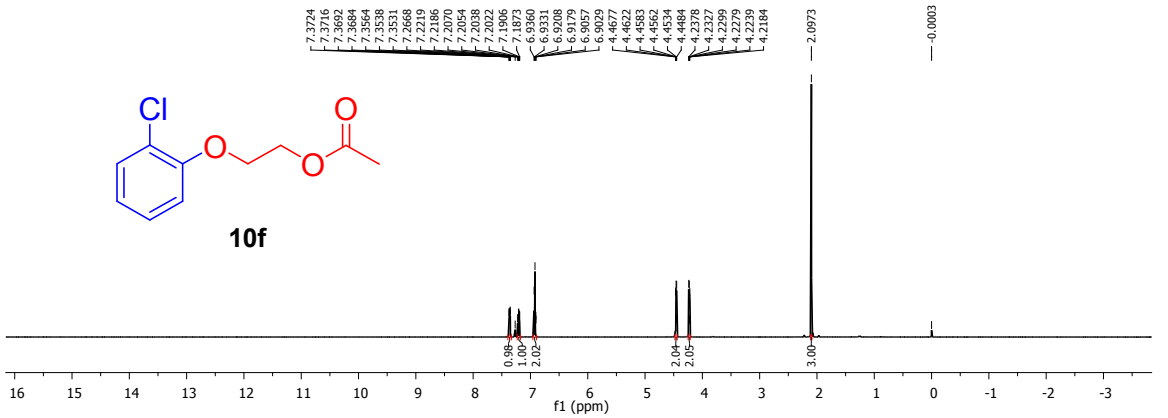
(Scheme 4, entry 10e)

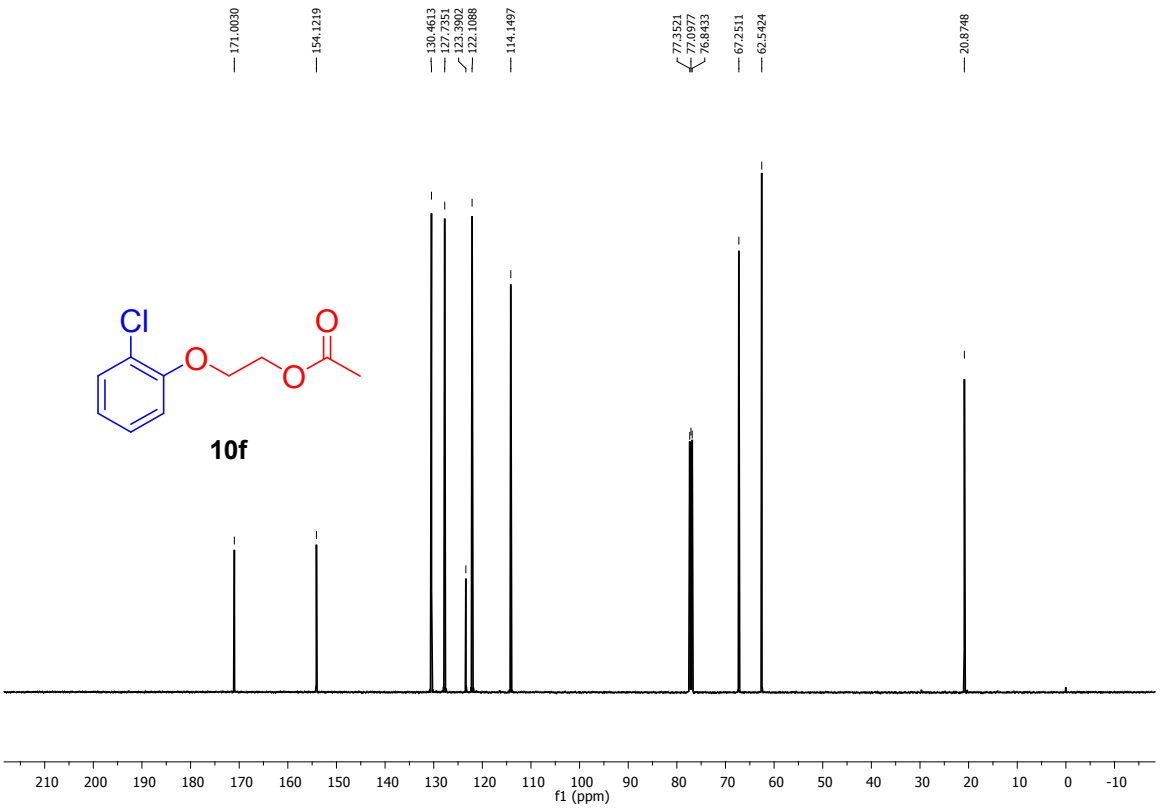




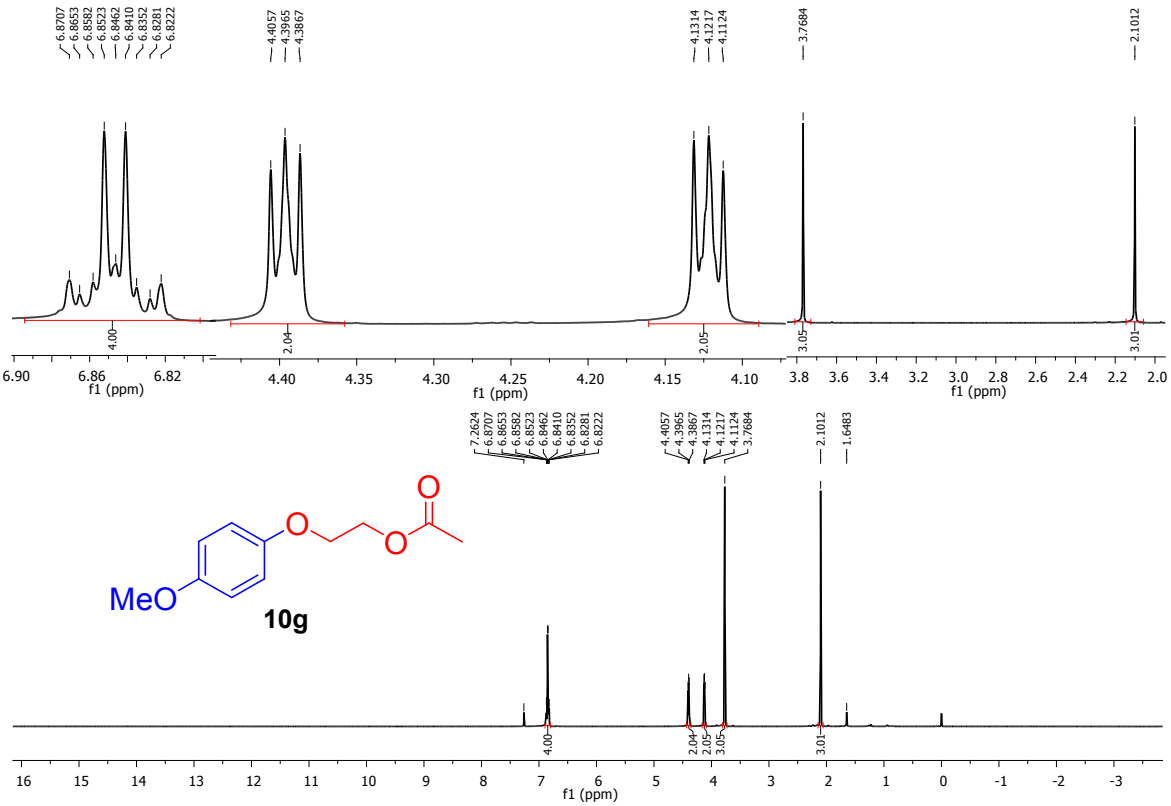
(Scheme 4, entry 10f)

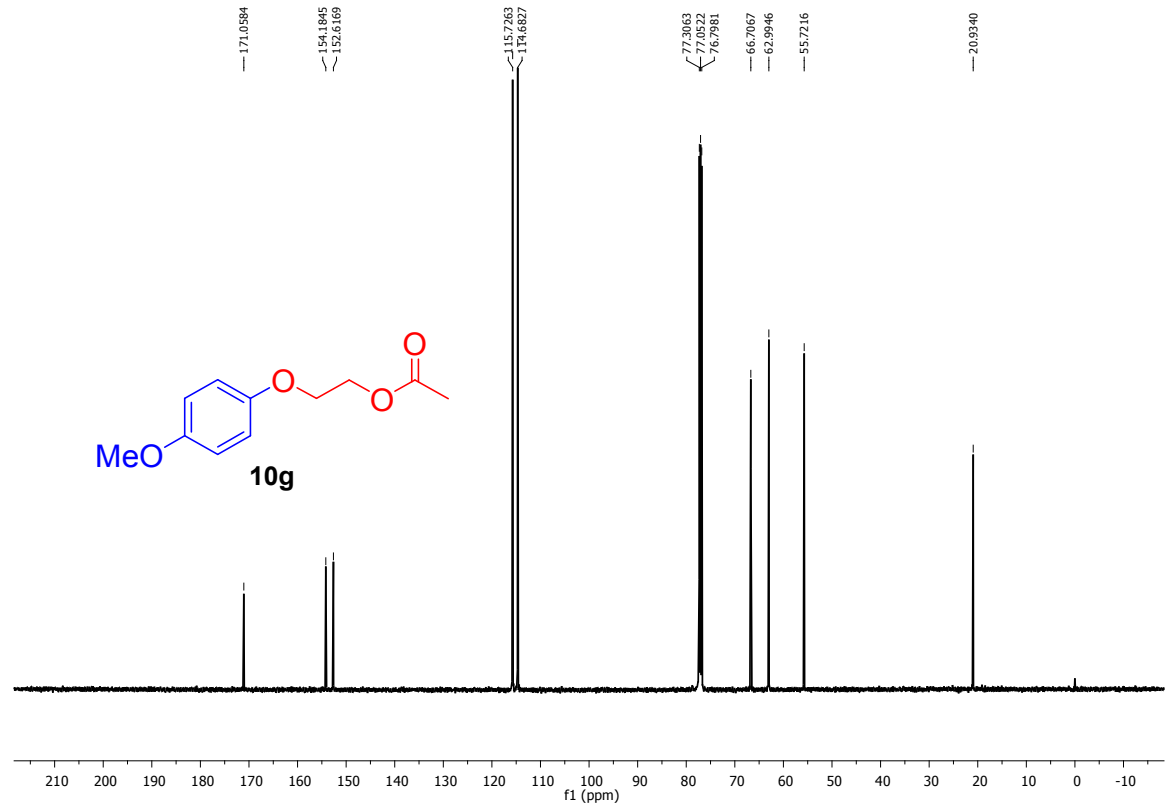




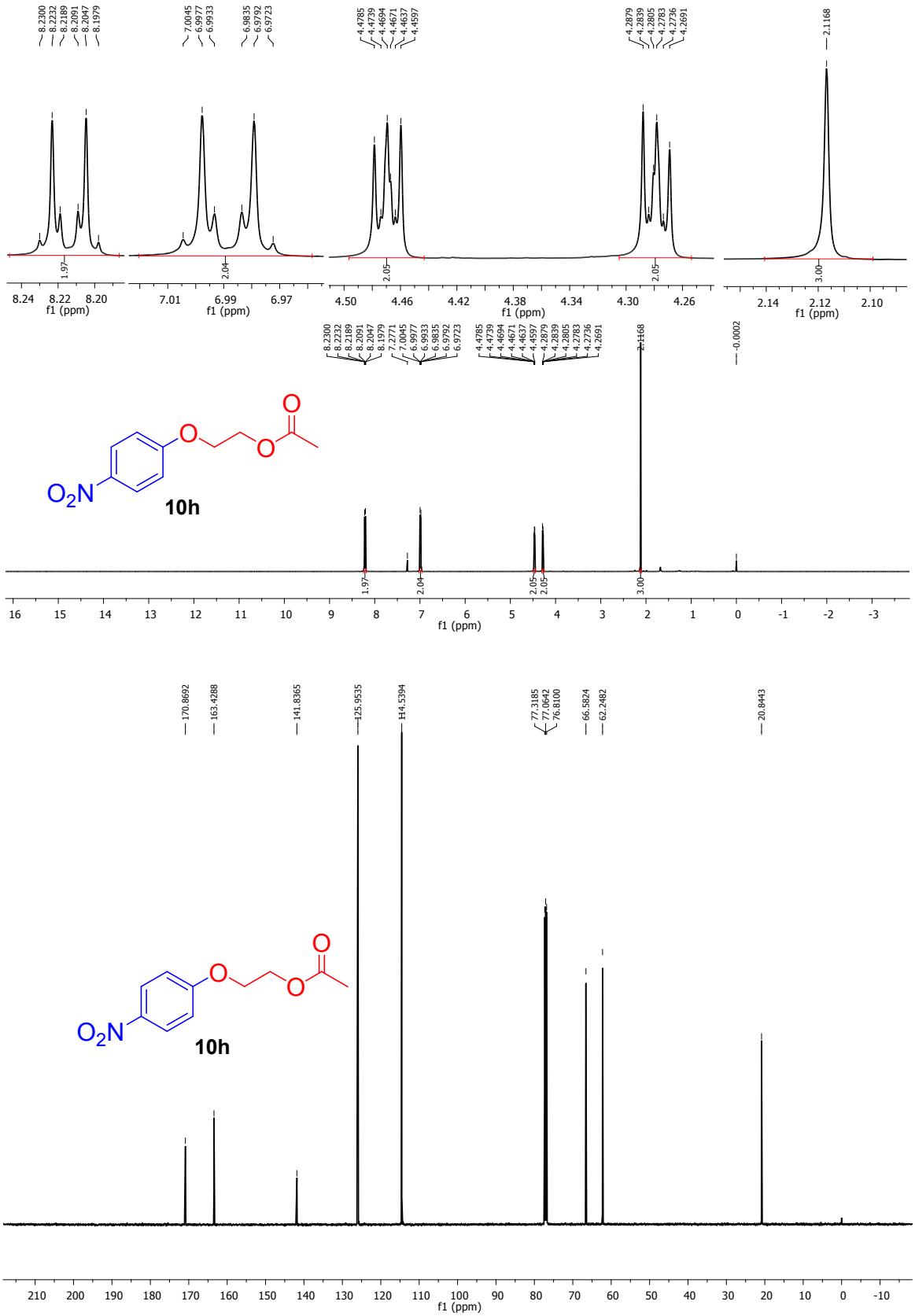


(Scheme 4, entry 10g)



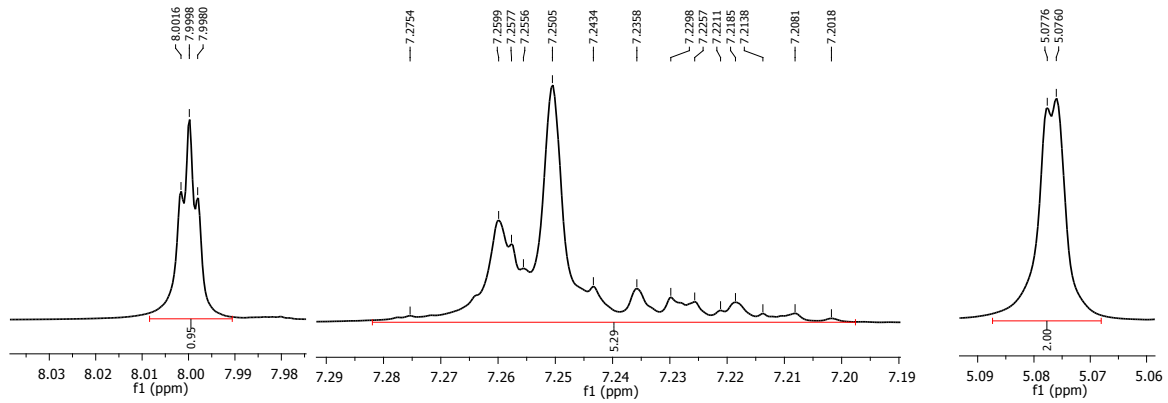


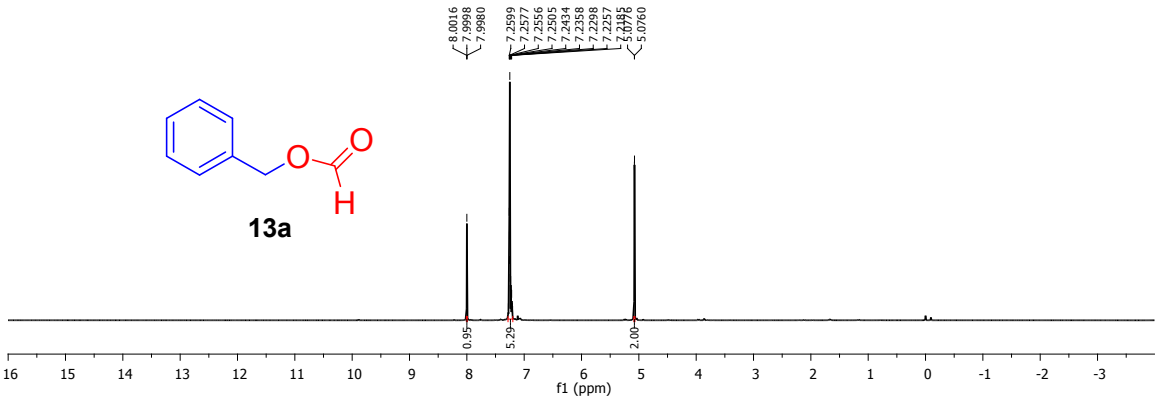
(Scheme 4, entry 10h)

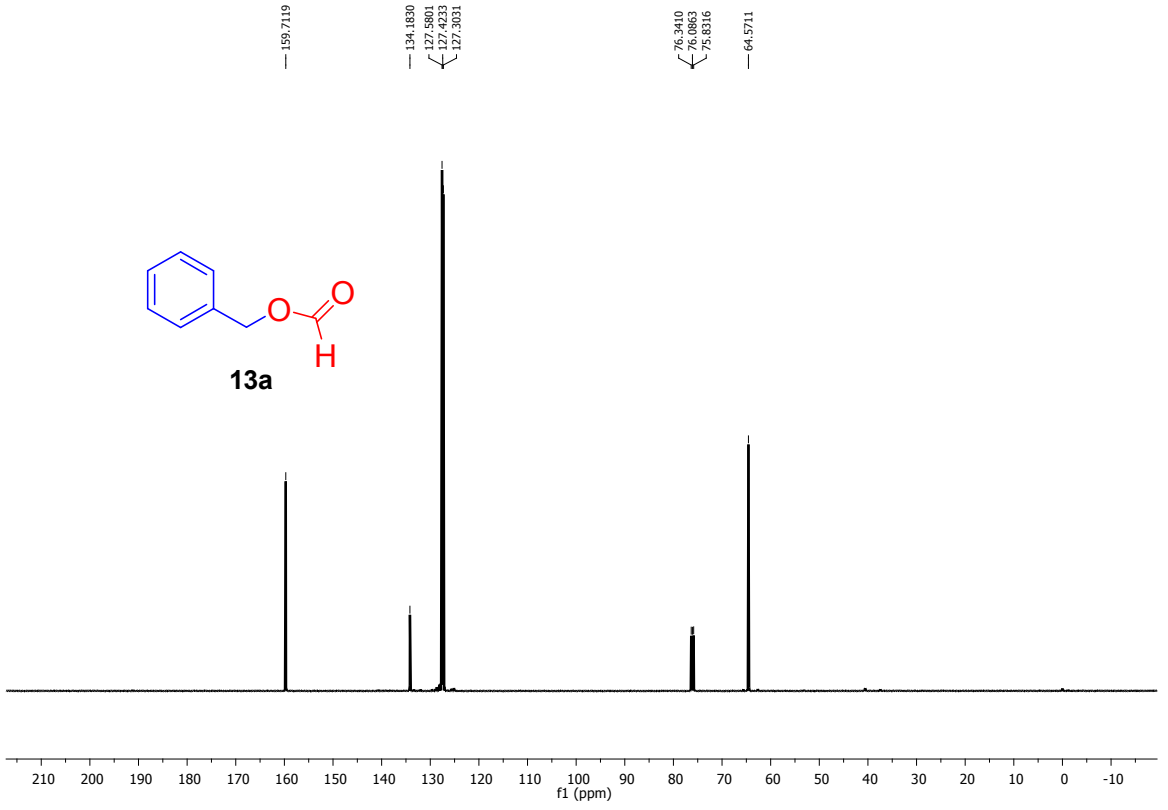


7. ^{1}H NMR and ^{13}C NMR spectra of *O*-formylated and *O*-Acylated alcohols and amines

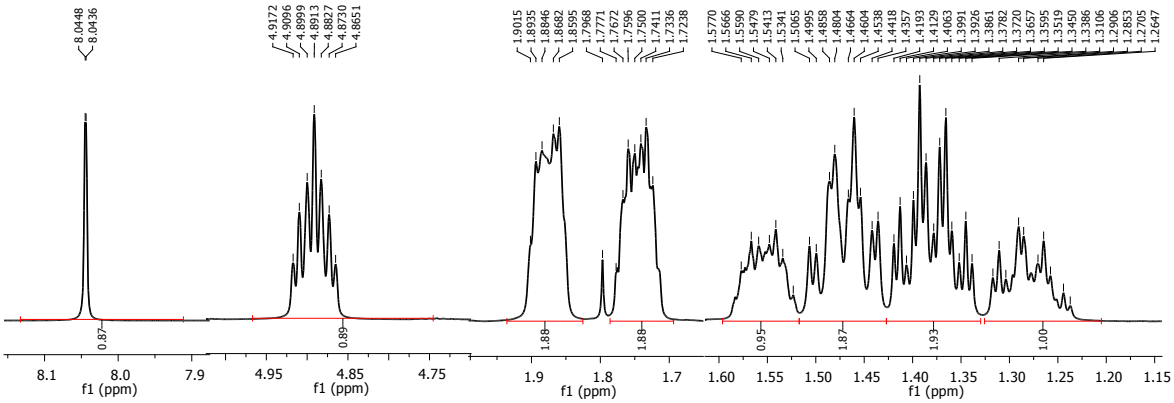
(Scheme 5, entry 13a)

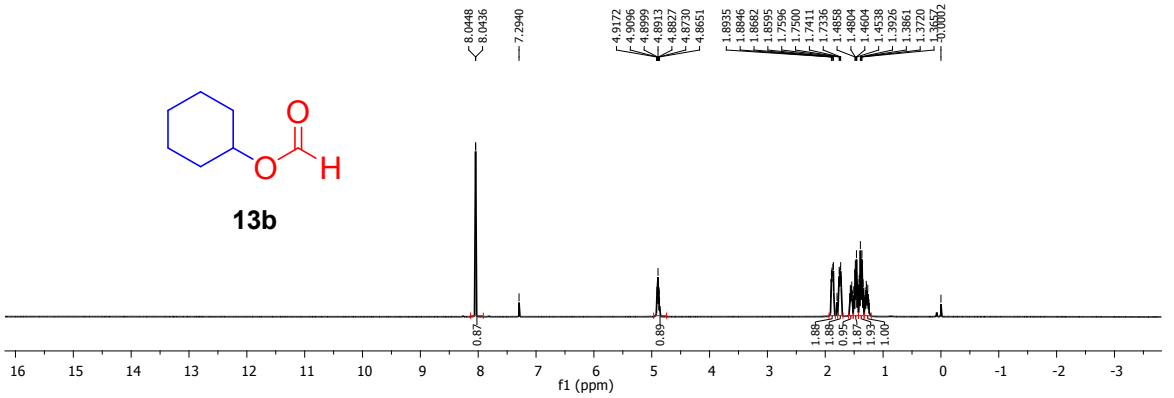


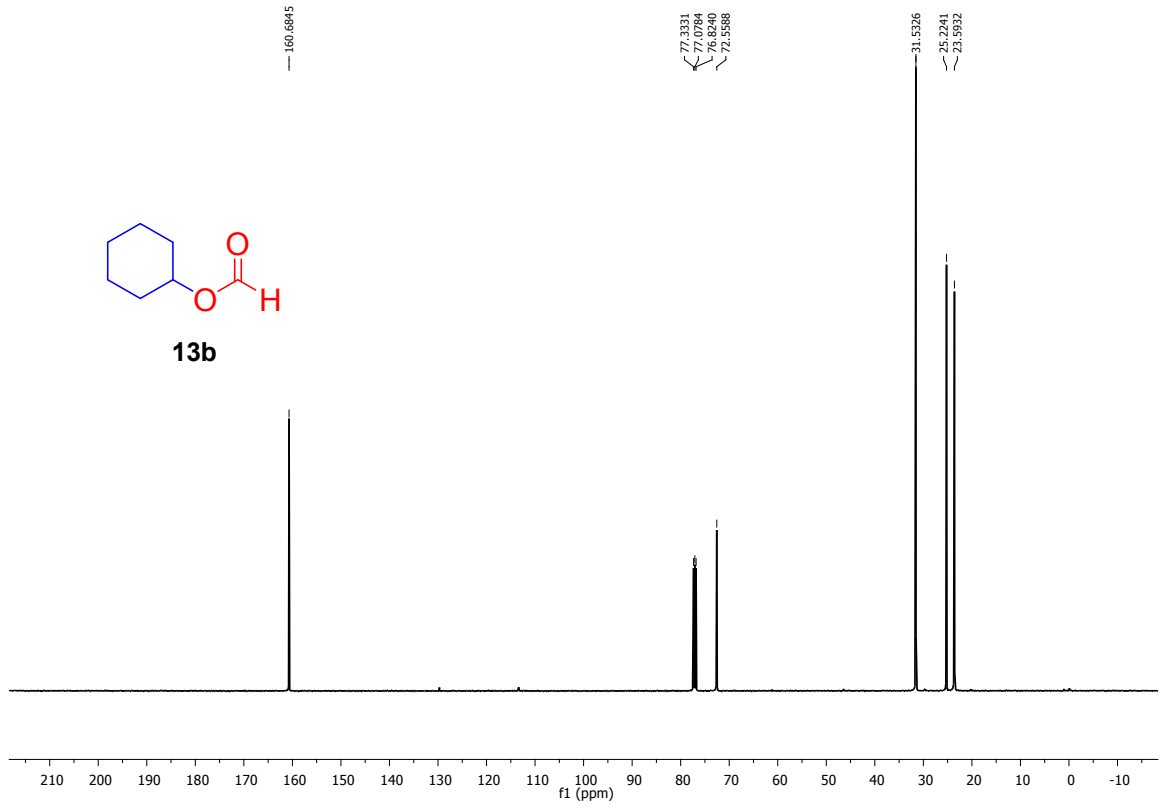




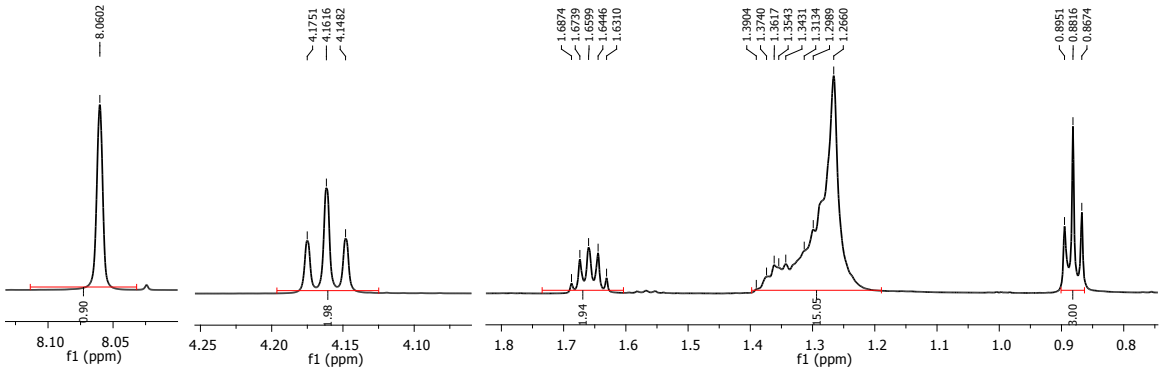
(Scheme 5, entry 13b)

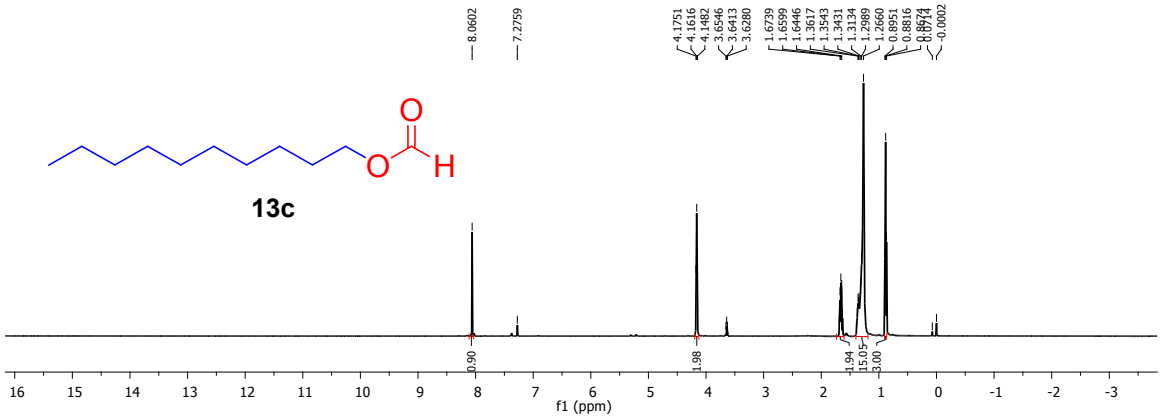


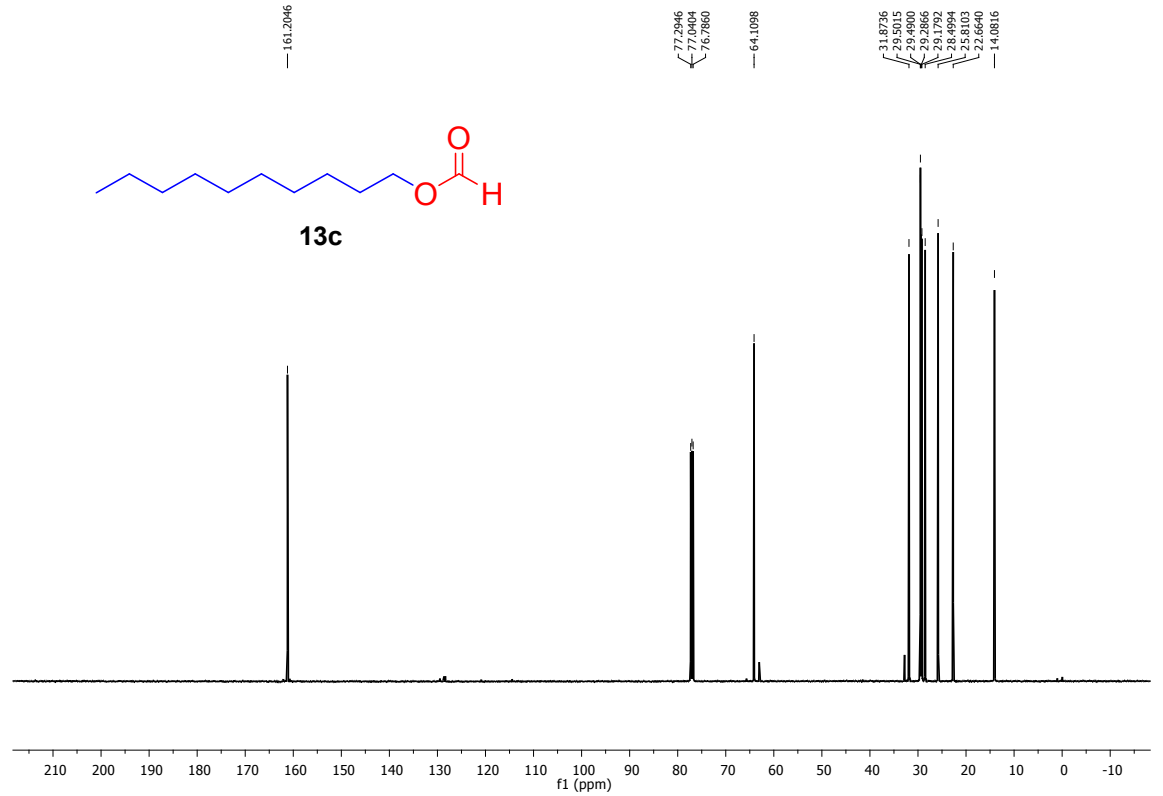




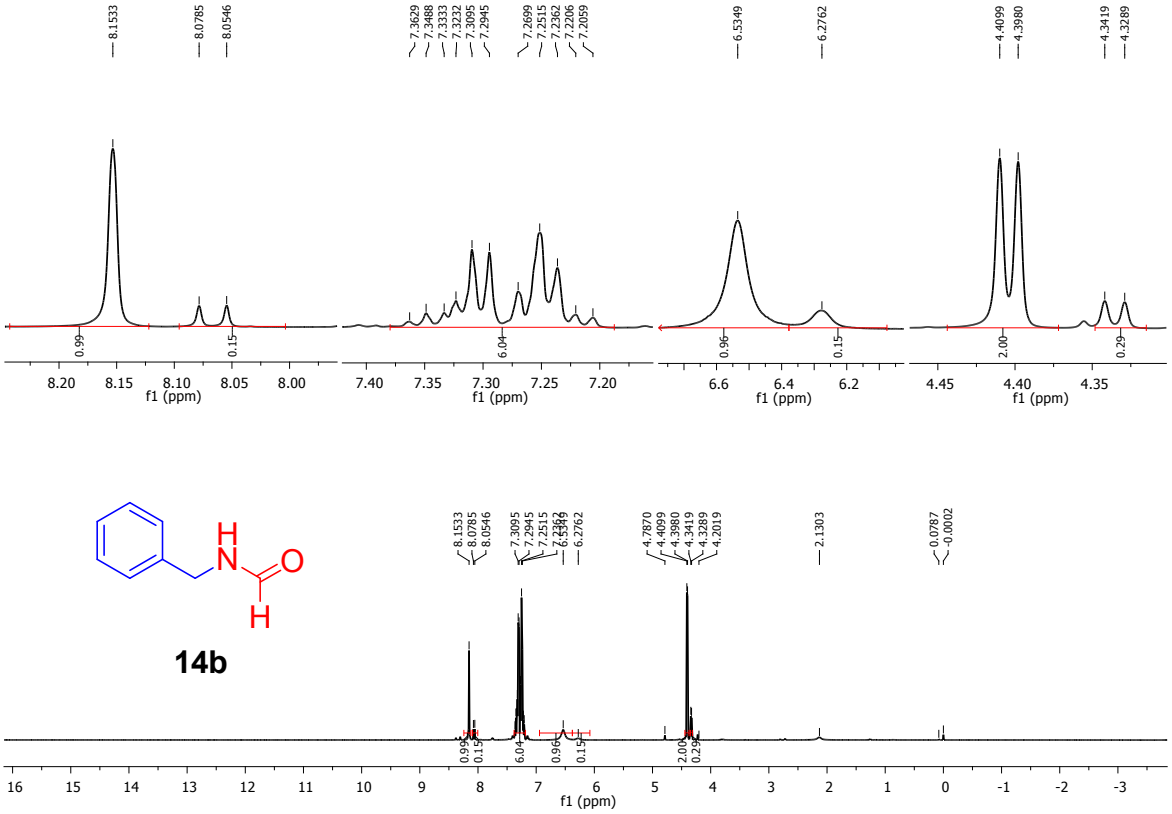
(Scheme 5, entry 13c)



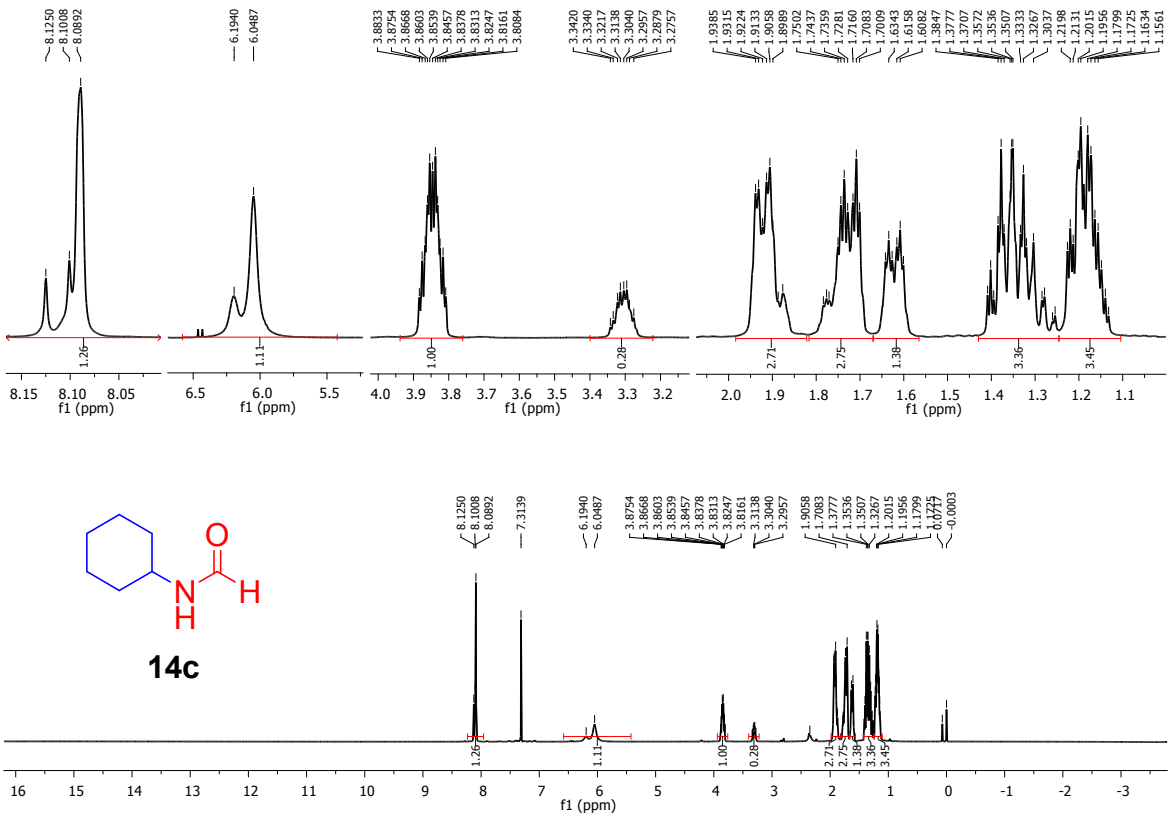




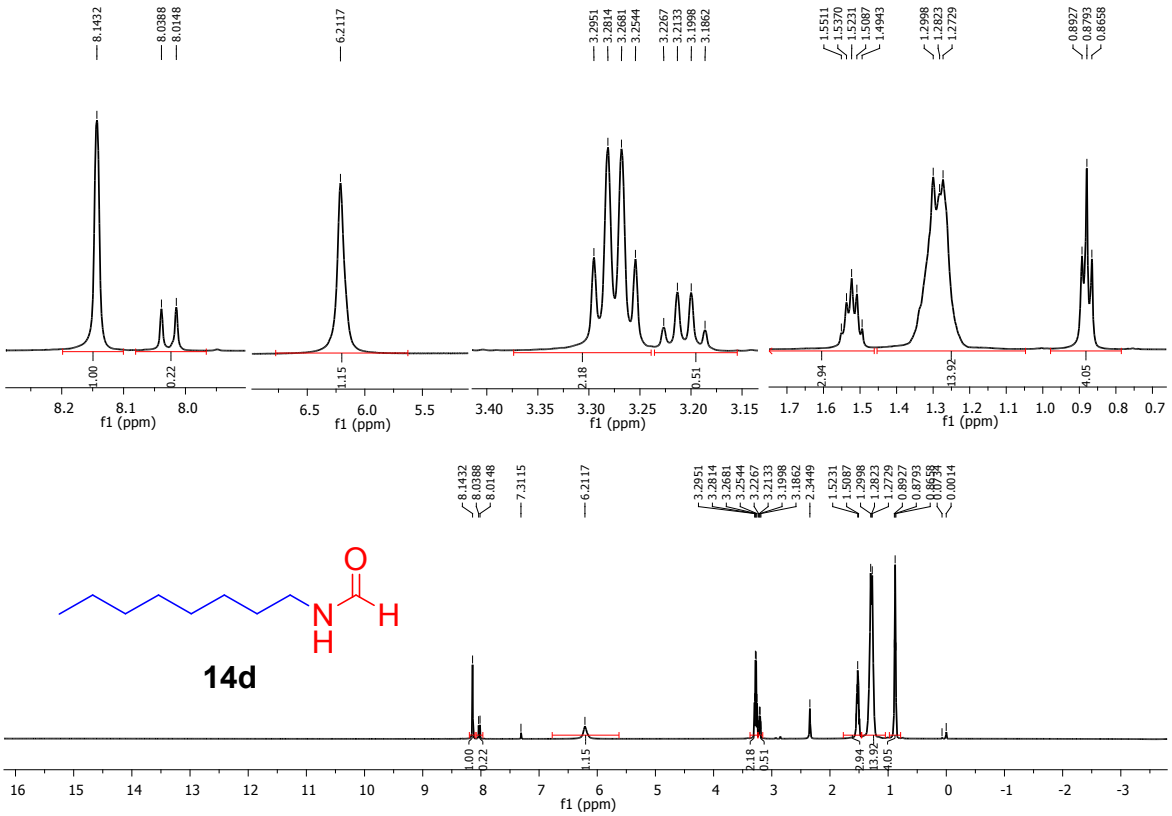
(Scheme 5, entry 14b)



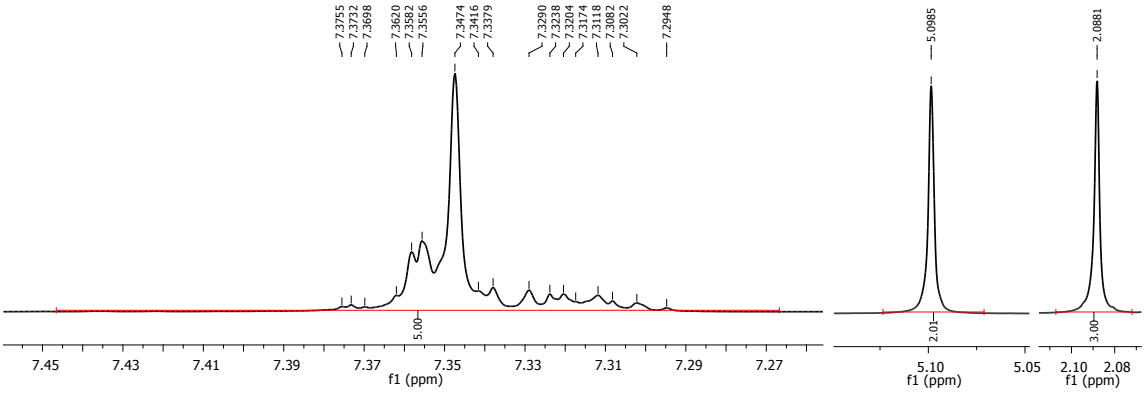
(Scheme 5, entry 14c)

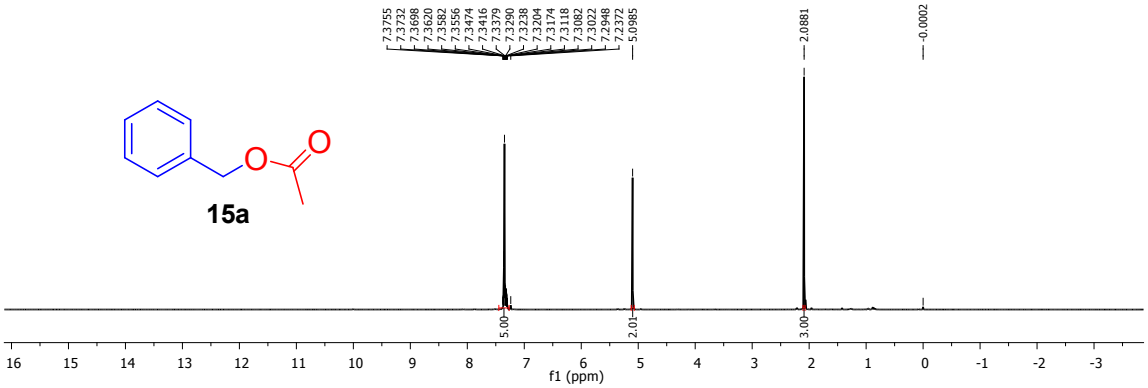


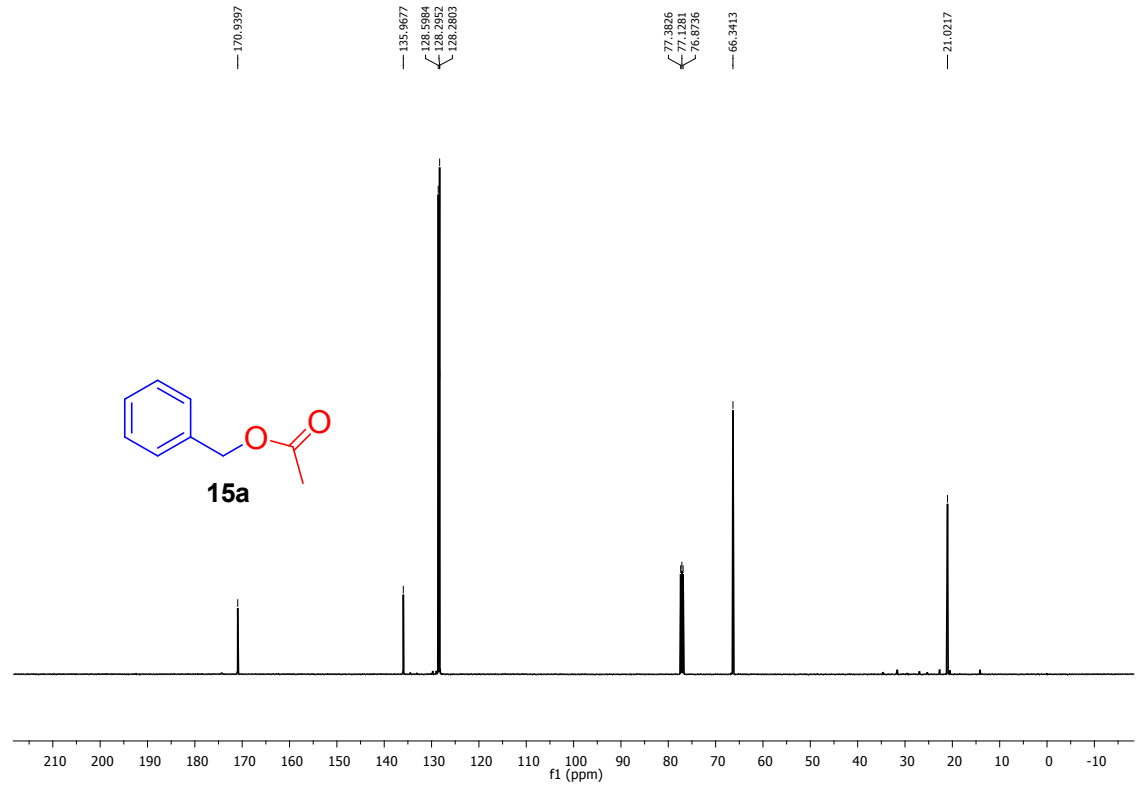
(Scheme 5, entry 14d)



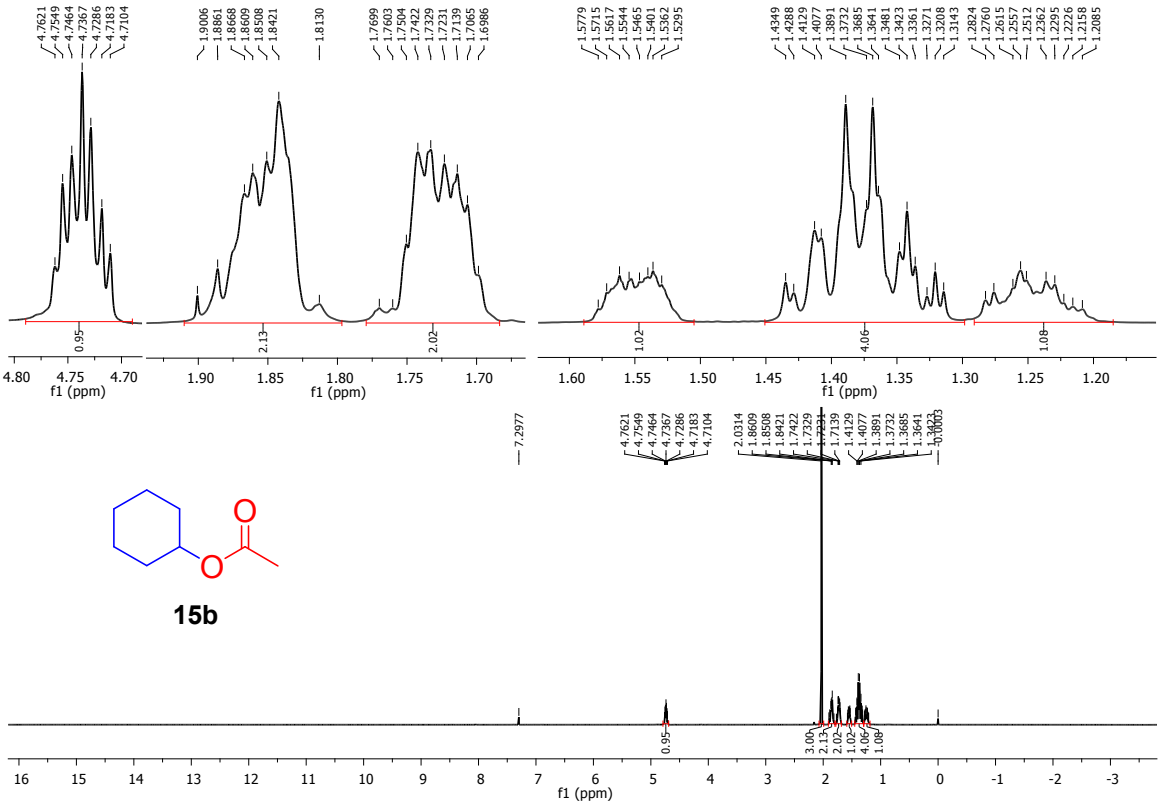
(Scheme 5, entry 15a)

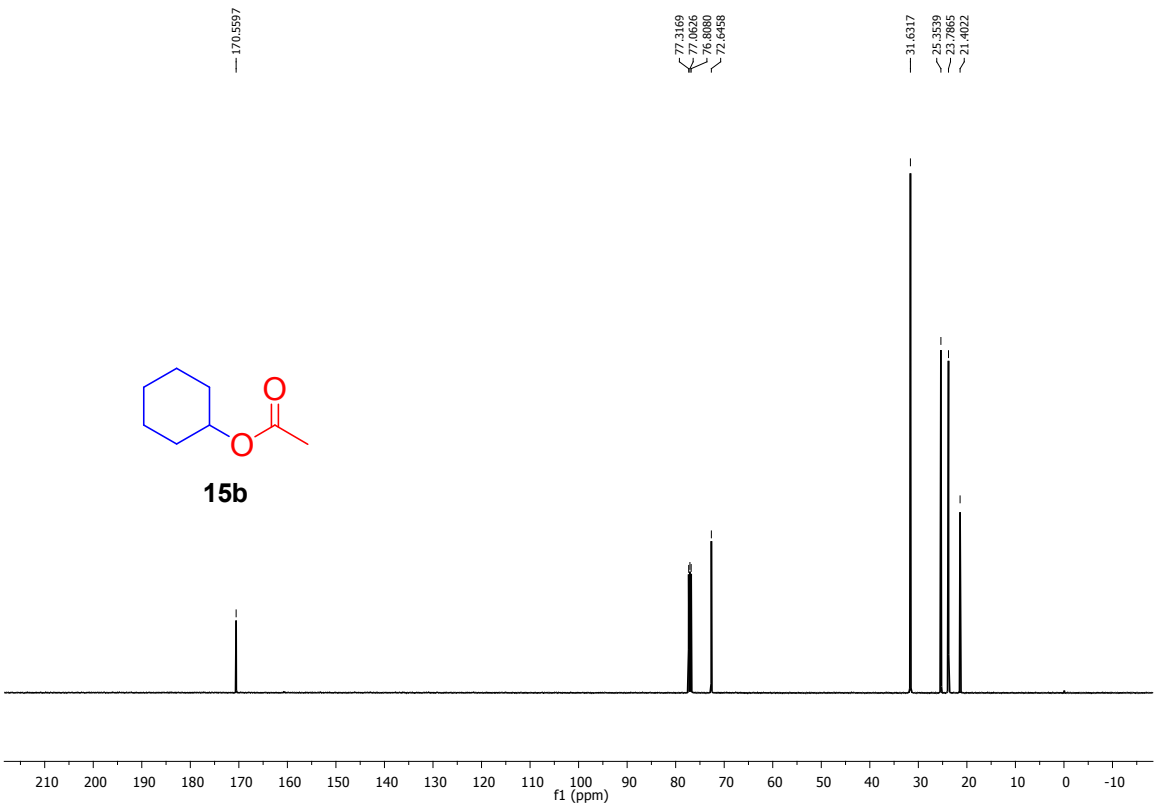




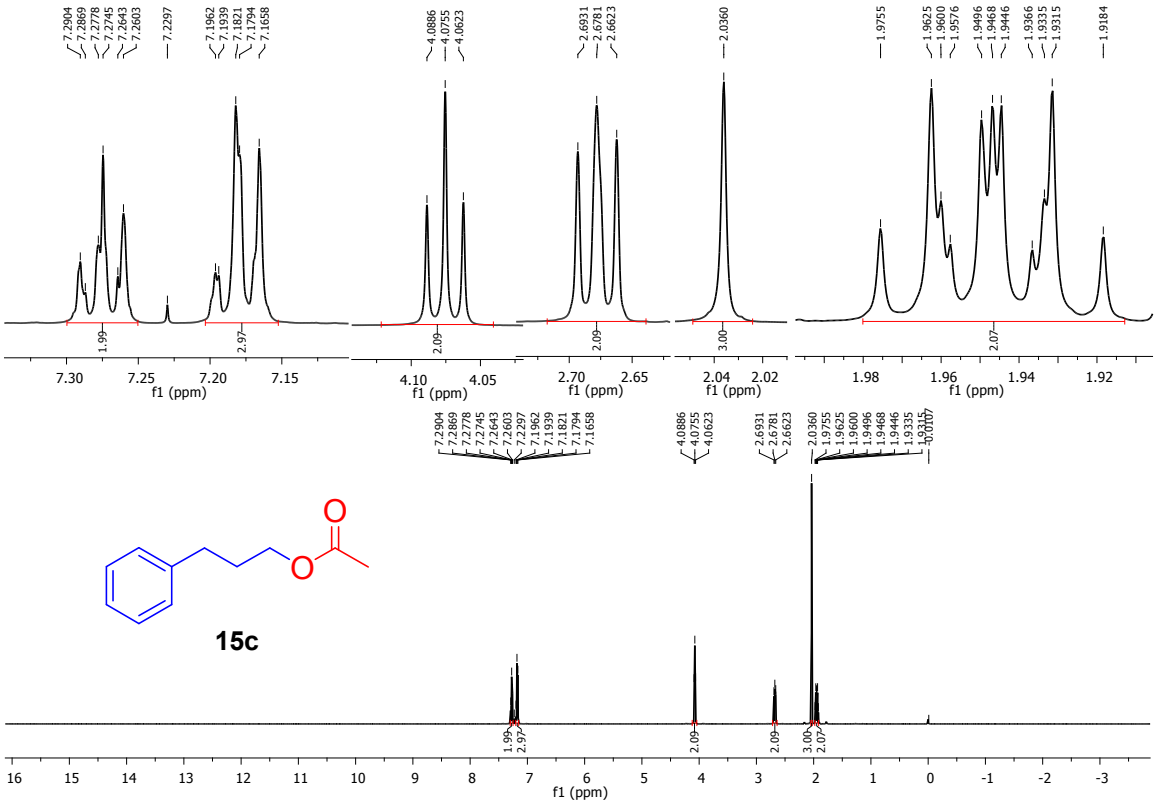


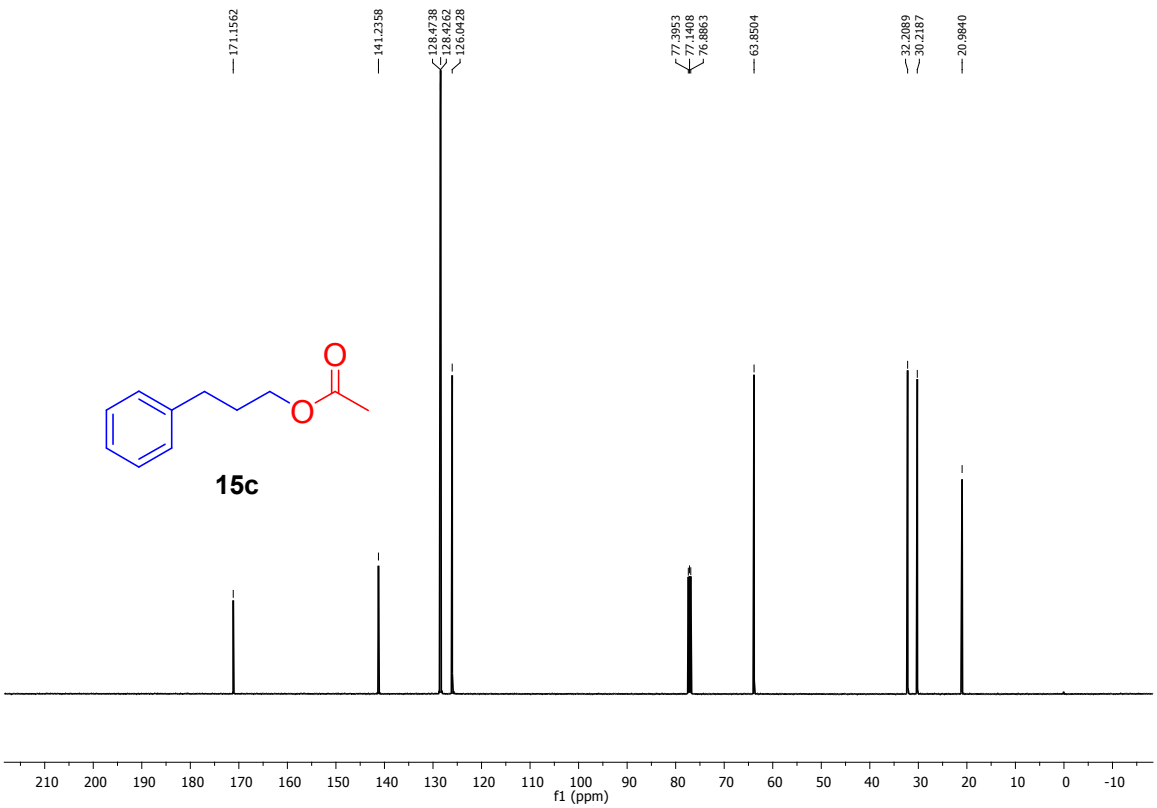
(Scheme 5, entry 15b)



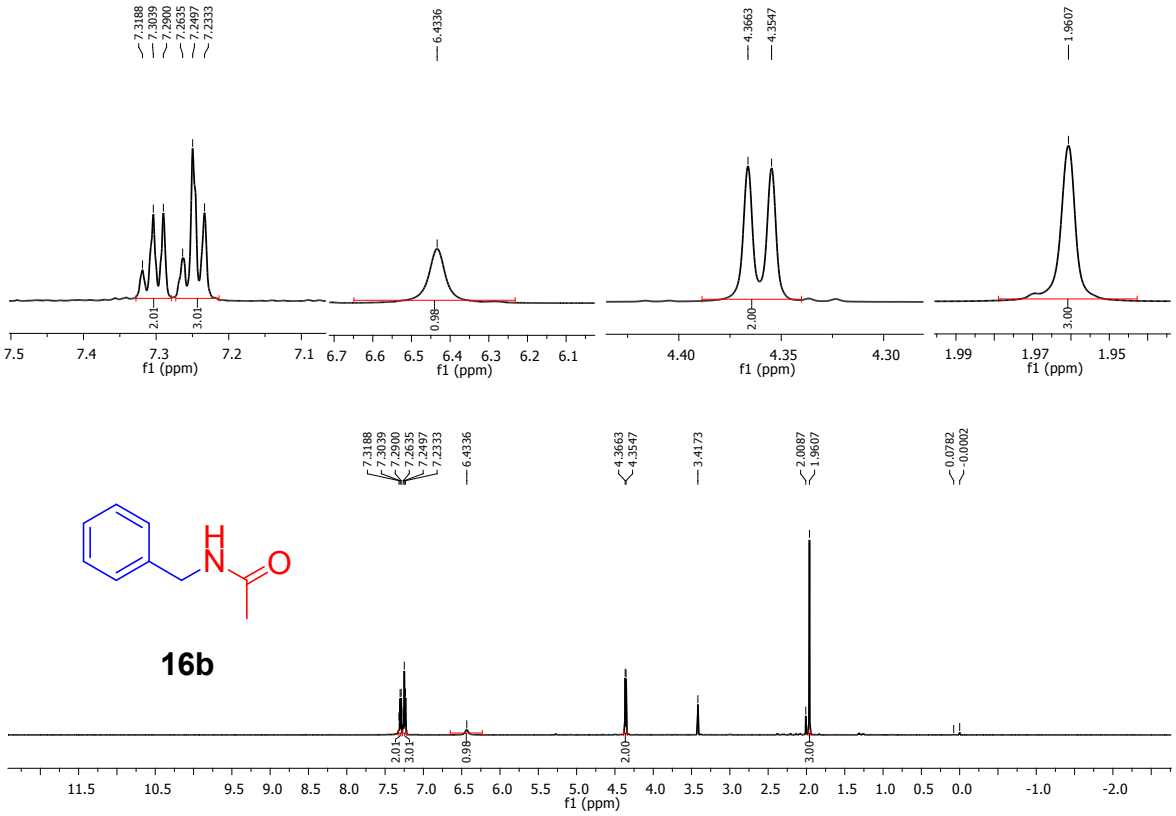


(Scheme 5, entry 15c)

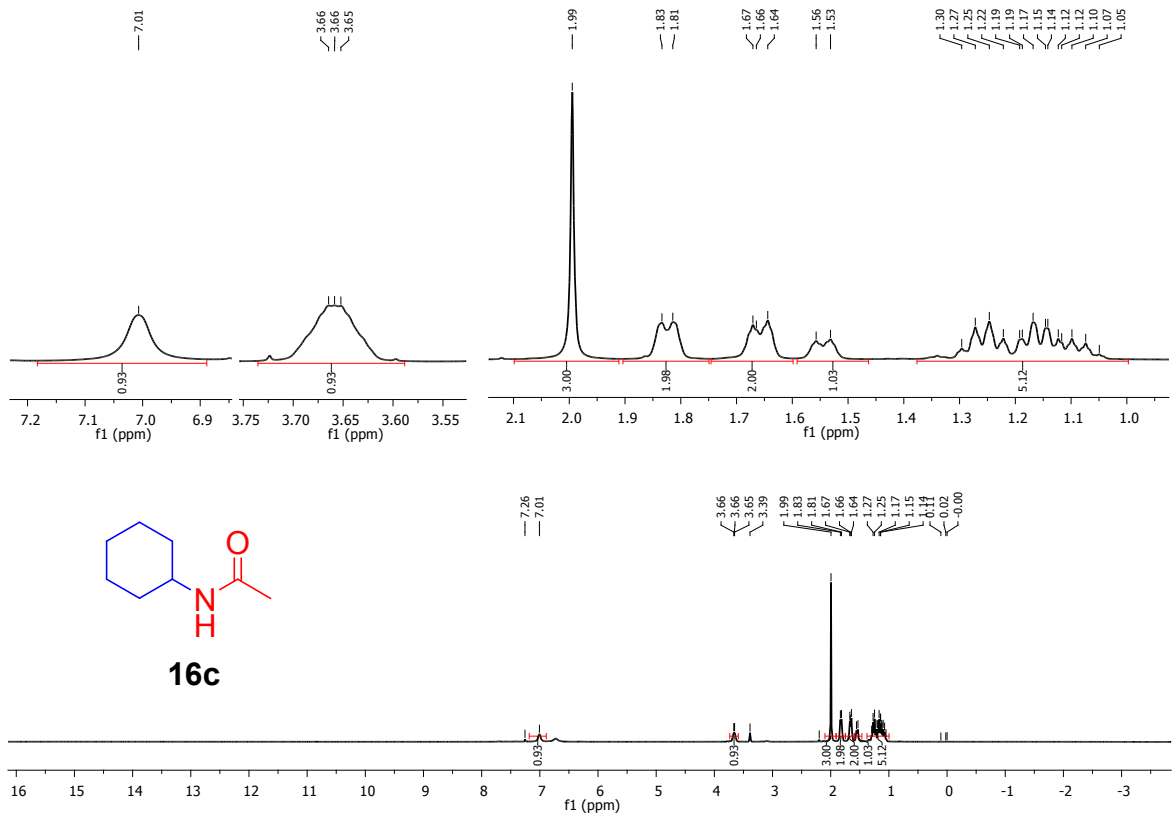




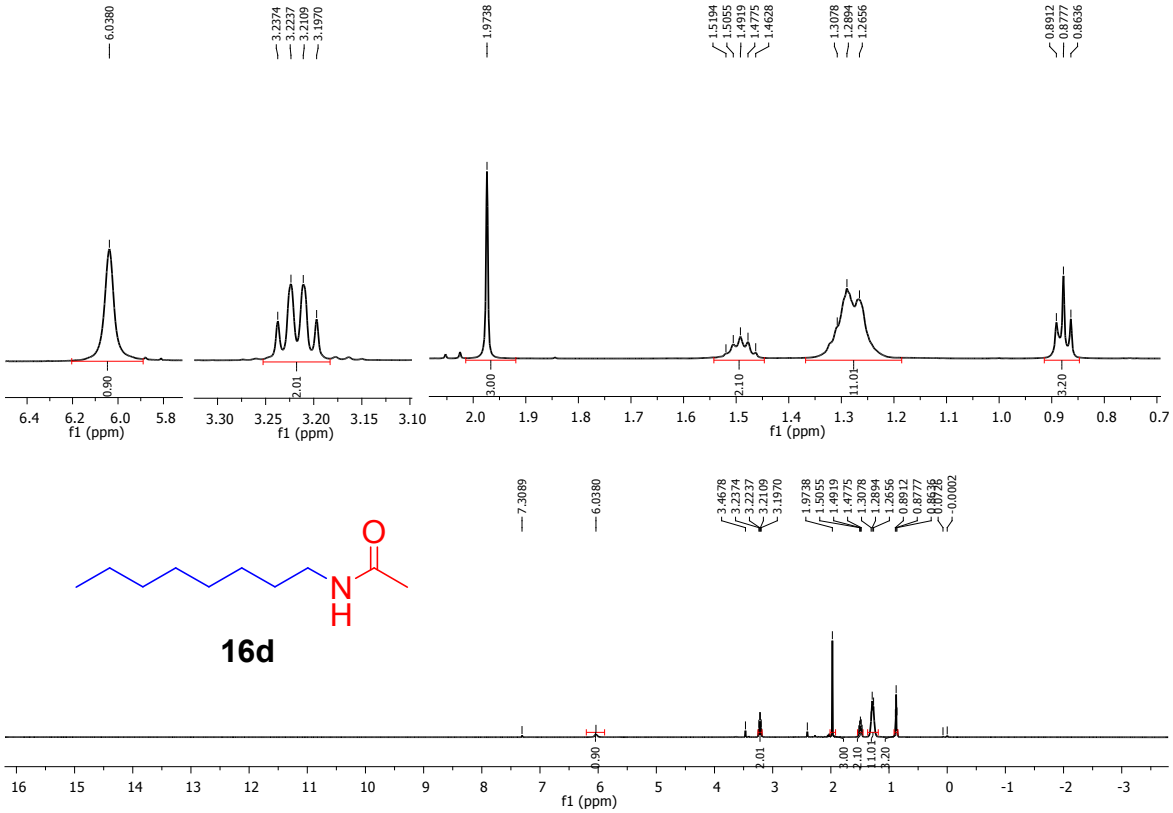
(Scheme 5, entry 16b)



(Scheme 5, entry 16c)



(Scheme 5, entry 16d)



8. References

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