Supporting Information for

Phenazinium Salt-Catalyzed Aerobic Oxidative Amidation of Aromatic Aldehydes

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1. General Information

All commercial reagents were purchased from Sigma-Aldrich, Fluka, Alfa Aesar, TCI, and Acros of the highest purity grade. They were used without further purification unless specified. Anhydrous solvents and tetrahydrofuran (THF, inhibitor-free) were obtained from Sigma-Aldrich and used as received. Phenazine ethosulfate (PES) was purchased from MP Biomedicals and used as received. Phenazine methosulfate (PMS) and Basic Red 2 (Safranin O) was purchased from TCI and used as received. All reactions were conducted in 35 mL sealed tubes (Chemglass). All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, Merck 60 F_{254}. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining with iodine or $KMnO_4$ stain. Preparative TLC was performed on 0.5 mm silica gel (Analtech). Columns for flash chromatography (FC) contained silica gel (32–63µ, Merck). Columns were packed as slurry of silica gel in hexane and equilibrated with the appropriate solvent/solvent mixture prior to use. The analyte was loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with constant flow of nitrogen gas.

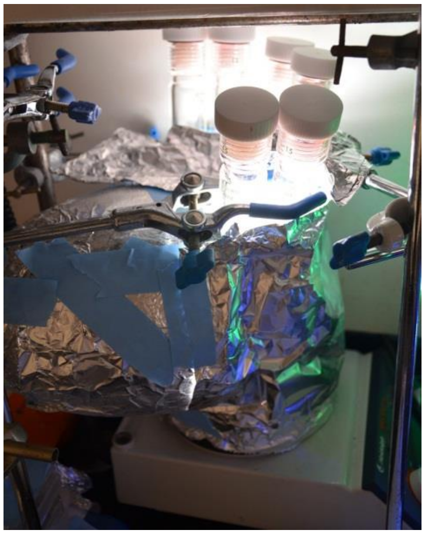
Solid reagents were weighed using Mettler Toledo AX205 analytical balance, with accuracy of 0.01 mg. Liquid reagents were measured using Eppendorf Research® pipettes. ^{1}H and ^{13}C attached proton test (APT) NMR spectra were recorded on Bruker AV-400 (400 MHz and 100 MHz, respectively) equipped with a 5mm DCH cryoprobe instrument. The peaks were internally referenced to TMS (0.00 ppm) or residual solvent signal. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. In ^{13}C APT NMR spectra, quaternary (CH_0) and methylene (CH_2) signals are negative; whereas methine (CH) and methyl (CH_3) signals are positive. High resolution mass spectra were recorded on an Agilent LC 1200 series and 6210 ESI-TOF (electrospray ionization-time of flight). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer. Frequencies were given in reciprocal centimeters (cm^{-1}). The solar experiments were conducted in ambient environment using Newport 92250A 2 × 2 inches Oriel® class A solar simulator equipped with a Newport 69907 arc lamp power supply and Newport 6255 150 W xenon lamp. The irradiation intensity was measured by a Newport Oriel® 91150V reference cell. The solar simulator irradiance is given in "Sun" units, where one Sun is equal to 1000 W/m^2 at 25 °C and Airmass 1.5 Global Reference. Fluorescence quenching experiments were conducted on a HORIBA Jobin Yvon FluoroMax®-4 spectrofluorometer.

2. Experimental Section

2.1. Standard reaction set-up

In a typical experiment, a 24 W compact fluorescent light (CFL) bulb (Philips Tornado 24W cool daylight, model 872790090880000, 6500K color temperature, 1450 Lm) was used. The lamp was purchased from IKEA (Tertial work lamp). The reaction tubes (35 mL sealed tubes, Chemglass) were placed approximately 2 cm from the light source. The setup was then covered with aluminum foil to reduce the glares. For set-up with colored LEDs, a 50 cm flexible strip consisting of 30 LEDs (mono color, 5050 tri-chip) was coiled around the reaction tube and wrapped with aluminum foil.

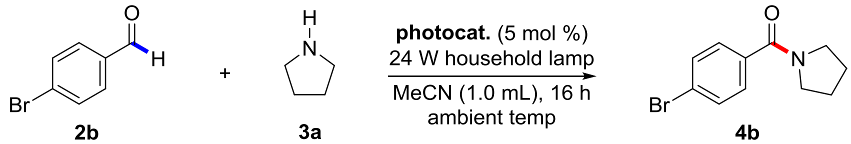
Typical experimental set-up with a 24 W CFL bulb:

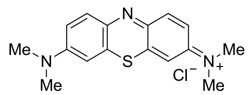
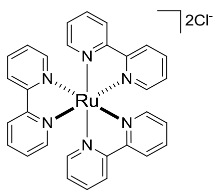
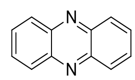
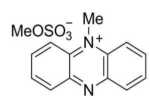
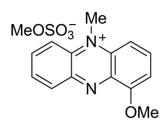
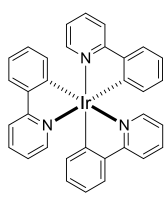
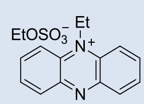
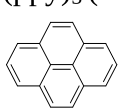
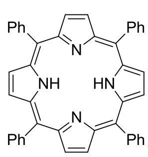


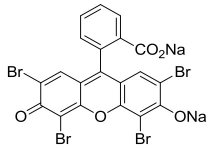
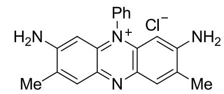
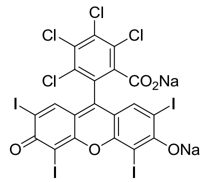
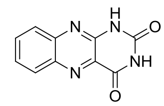
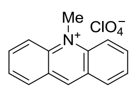
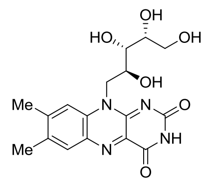
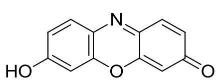
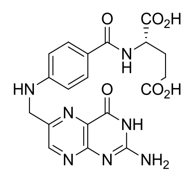
Typical experimental set-up with colored LEDs:

2.2. Optimization studies

Table S1 Identification of optimal photocatalyst[a]

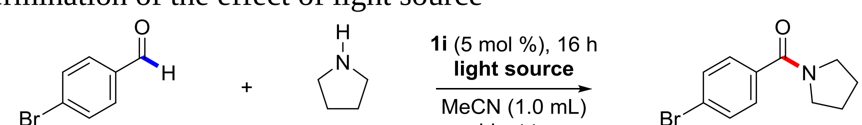


entry	photocat.	oxidant (equiv.)	yield (%)[b]	entry	photocat.	oxidant (equiv.)	yield (%)[b]
1[c]	—	air (1 atm)	7	12	 methylene blue (**S1c**)	air (1 atm)	20
2	 $Ru(bpy)_3Cl_2$ (**1a**)	air (1 atm)	22	13	 phenazine (**1g**)	air (1 atm)	37
3	**1a**	$MVCl_2$ (1.0)	38	14	 PMS (**1h**)	air (1 atm)	58
4	**1a**	*o*-DNB (1.2)	14	15	 1-OMe PMS (**S1d**)	air (1 atm)	62
5	 $Ir(ppy)_3$ (**1b**)	air (1 atm)	30	**16**	 PES (**1i**)	**air (1 atm)**	**64**
6	 pyrene (**1c**)	air (1 atm)	47	17[c,d]	**1i**	degassed (Ar, 1 atm)	11
7	 TPP (**1d**)	air (1 atm)	58	18[c,d]	**1i**	O_2 (1 atm)	93

entry	photocat.	oxidant (equiv.)	yield (%)[b]	entry	photocat.	oxidant (equiv.)	yield (%)[b]
8	 eosin Y (**1e**)	air (1 atm)	28	19	 safranin O (**1j**)	air (1 atm)	62
9	 rose bengal (**1f**)	air (1 atm)	44	20	 alloxazine (**S1e**)	air (1 atm)	26
10	 10-Me-acridinium perchlorate (**S1a**)	air (1 atm)	18	21	 riboflavin (**S1f**)	air (1 atm)	29
11	 resorufin (**S1b**)	air (1 atm)	17	22	 folic acid (**S1g**)	air (1 atm)	25

[a] Unless otherwise noted, the reaction conditions were as followed: aldehyde **2b** (0.10 mmol), amine **3a** (3.0 equiv.), **photocatalyst** (5 mol %), MeCN (1.0 mL), 16 h, ambient temperature, irradiated with a 24 W compact fluorescent bulb. [b] Yield determined by ^{1}H NMR analysis of unpurified reaction mixture using CH_2Br_2 or $MeNO_2$ as internal standard. [c] THF (inhibitor-free) was used as solvent instead of MeCN. [d] Photocatalyst **1i** (1 mol %) was used. Abbreviations: bpy, 2,2'-bipyridyl; $MVCl_2$, methyl viologen dichloride; *o*-DNB, 1,2-dinitrobenzene; ppy, 2-phenylpyridinyl; TPP, *meso*-tetraphenylporphyrin; Me, methyl; Et, ethyl; Ph, phenyl; PMS, phenazine methosulfate; PES, phenazine ethosulfate.

Table S2 Determination of the effect of light source[a]

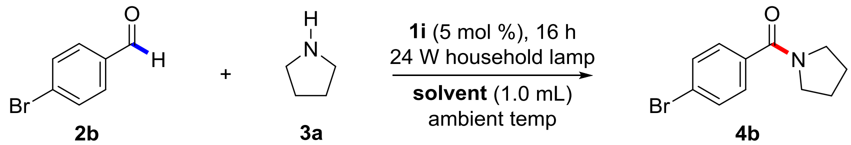


2b **3a** **4b**

entry	light source	yield (%)[b]	entry	light source	yield (%)[b]
1	no light	8	4	blue LEDs (450–495 nm)	56
2[c]	no light	5	5	green LEDs (495–570 nm)	69
3	**24 W household lamp**	**64**	6	red LEDs (620–750 nm)	23

[a] Unless otherwise noted, the reaction conditions were as followed: aldehyde **2b** (0.10 mmol), amine **3a** (3.0 equiv.), photocatalyst **1i** (5 mol %), MeCN (1.0 mL), 16 h, ambient temperature, irradiated with a light source. [b] Yield determined by ^{1}H NMR analysis of unpurified reaction mixture using CH_2Br_2 or $MeNO_2$ as internal standard. [c] Photocatalyst **1i** (1 mol %) and THF (inhibitor-free) were used.

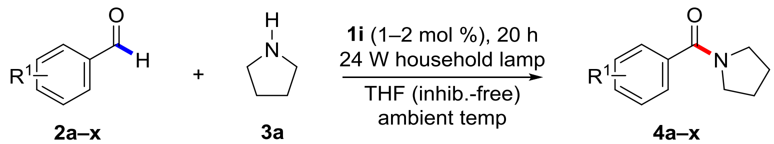
Table S3 Solvent screening[a]



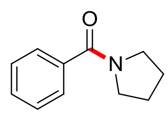
entry	solvent	yield (%)[b]	entry	solvent	yield (%)[b]
1	MeCN	64	5	$MeNO_2$	0
2	DCE	33	6	THF (with 250 ppm BHT)	65
3	DMSO	30	7[c]	THF (with 250 ppm BHT)	74
4	MeOH	10	**8**[c]	**THF (inhib.-free)**	**81**

[a] Unless otherwise noted, the reaction conditions were as followed: aldehyde **2b** (0.10 mmol), amine **3a** (3.0 equiv.), photocatalyst **1i** (5 mol %), **solvent** (1.0 mL), 16 h, ambient temperature, irradiated with a 24 W compact fluorescent bulb. [b] Yield determined by ^{1}H NMR analysis of unpurified reaction mixture using CH_2Br_2 or $MeNO_2$ as internal standard. [c] Photocatalyst **1i** (1 mol %) was used. Abbreviations: DCE, 1,2-dichloroethane; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; BHT, butylated hydroxytoluene.

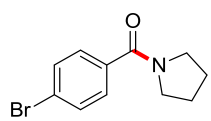
*2.3. **General procedure for phenazinium salt-catalyzed aerobic amidation of aromatic and heteroaromatic aldehydes***



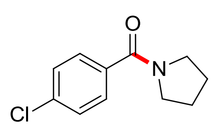
A 35 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with aldehyde **2** (0.12 mmol, 1.0 equiv.) and photocatalyst **1i** (0.40 mg, 1.2×10^{-4} mmol, 1 mol %). Amine **3a** (0.30 mmol, 2.5 equiv., 25.1 μL) was added and THF (inhibitor-free, 1.2 mL) was used to wash down the solids on the sides of wall. The tube was then capped and placed approximately 2 cm from the light source. After stirring for 20 h, the crude reaction mixture was filtered through a short pad of silica gel. EtOAc (3 × 2 mL) was used for washing. The filtrate was concentrated *in vacuo*. For the optimization studies, either CH_2Br_2 or $MeNO_2$ (0.12 mmol) was added into a solution of unpurified reaction mixture in $CDCl_3$ The product yield was determined by integration of the pyrrolidinyl α-methylene ^{1}H NMR peak against the methylene peak of CH_2Br_2 or methyl peak of $MeNO_2$. For the isolation of product, the resulting residue was purified by preparative TLC using hexanes/EtOAc as the eluent.



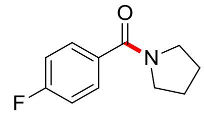
phenyl(pyrrolidin-1-yl)methanone (4a)[1]: Colorless oil; 15.1 mg; 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.42 – 7.35 (m, 3H), 3.64 (br s, 2H), 3.42 (br s, 2H), 1.94 – 1.88 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.7, 137.2, 129.7, 128.2, 127.0, 49.6, 46.1, 26.3, 24.4 ppm; IR (film): 3470 (br s), 1616, 1424 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{11}H_{14}NO^+$ [M+H$^+$] 176.1070, found 176.1077.



(4-bromophenyl)(pyrrolidin-1-yl)methanone (4b)[2]: White solid; 24.7 mg; 81% yield; mp: 77–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.40 – 7.37 (m, 2H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.84 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.6, 135.9, 131.4, 128.8, 124.1, 49.6, 46.3, 26.4, 24.4 ppm; IR (film): 3470 (br s), 1623, 1424 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{11}H_{13}BrNO^+$ [M+H$^+$] 254.0175, found 254.0181.

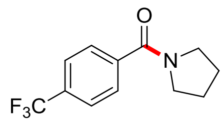


(4-chlorophenyl)(pyrrolidin-1-yl)methanone (4c)[2]: Colorless oil; 21.9 mg; 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.37 – 7.34 (m, 2H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.83 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.6, 135.8, 135.5, 128.7, 128.5, 49.6, 46.3, 26.4, 24.4 ppm; IR (film): 3470 (br s), 1622, 1425 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{11}H_{13}ClNO^+$ [M+H$^+$] 210.0680, found 210.0679.

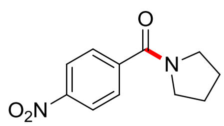


After stirring the reaction for 16 h, another portion of **1i** (1 mol %) was added. The reaction was continued for additional 6 h.

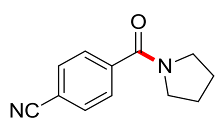
(4-fluorophenyl)(pyrrolidin-1-yl)methanone (4d)[2]: Yellow oil; 18.1 mg; 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.10 – 7.04 (m, 2H), 3.63 (t, J = 6.8 Hz, 2H), 3.42 (t, J = 6.8 Hz, 2H), 1.99 – 1.84 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.7, 163.4 (d, $J_{C–F}$ = 248 Hz, 1C), 133.2 (d, $J_{C–F}$ = 3.4 Hz, 1C), 129.4 (d, $J_{C–F}$ = 8.5 Hz, 1C), 115.2 (d, $J_{C–F}$ = 21.6 Hz, 1C), 49.7, 46.3, 26.4, 24.4 ppm; IR (film): 3470 (br s), 1623, 1429 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{11}H_{13}FNO^+$ [M+H$^+$] 194.0976, found 194.0975.



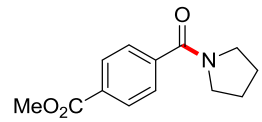
pyrrolidin-1-yl(4-(trifluoromethyl)phenyl)methanone (4e)[3]: Yellow oil; 24.2 mg; 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 2H), 7.62 – 7.60 (m, 2H), 3.65 (t, J = 6.4 Hz, 2H), 3.38 (t, J = 6.4 Hz, 2H), 1.99 – 1.87 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.3, 140.6, 131.6 (q, $J_{C–F}$ = 32.4 Hz, 1C), 127.4, 125.4 (q, $J_{C–F}$ = 3.7 Hz, 1C), 123.8 (q, $J_{C–F}$ = 271 Hz, 1C), 49.5, 46.3, 26.4, 24.4 ppm; IR (film): 3470 (br s), 1628, 1434, 1324 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{13}F_3NO^+$ [M+H$^+$] 244.0944, found 244.0939.



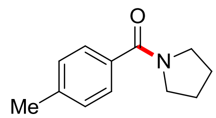
(4-nitrophenyl)(pyrrolidin-1-yl)methanone (4f)[2]: Yellow solid; 19.8 mg; 75% yield; mp: 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.24 (m, 2H), 7.68 – 7.65 (m, 2H), 3.65 (t, J = 6.8 Hz, 2H), 3.37 (t, J = 6.8 Hz, 2H), 2.02 – 1.88 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 167.3, 148.3, 143.1, 128.1, 123.6, 49.4, 46.3, 26.3, 24.3 ppm; IR (film): 3470 (br s), 1628, 1520, 1433, 1350 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{11}H_{13}N_2O_3^+$ [M+H$^+$] 221.0921, found 221.0918.



4-(pyrrolidine-1-carbonyl)benzonitrile (4g)[2]: Colorless oil; 22.3 mg; 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.61 – 7.59 (m, 2H), 3.63 (t, J = 6.8 Hz, 2H), 3.36 (t, J = 6.8 Hz, 2H), 2.00 – 1.85 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 167.6, 141.4, 132.3, 127.8, 118.2, 113.5, 49.5, 46.4, 26.4, 24.4 ppm; IR (film): 3467 (br s), 2230, 1739, 1625, 1435, 1217 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{13}N_2O^+$ [M+H$^+$] 201.1022, found 201.1013.

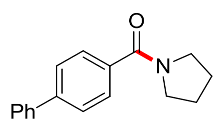


methyl 4-(pyrrolidine-1-carbonyl)benzoate (4h): Light yellow oil; 20.7 mg; 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.36 (t, *J* = 6.8 Hz, 2H), 1.99 – 1.84 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.6, 166.4, 141.3, 131.1, 129.6, 127.0, 52.3, 49.4, 46.2, 26.3, 24.4 ppm; IR (film): 3470 (br s), 1725, 1626, 1433, 1280 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{13}H_{16}NO_3^+$ [M+H$^+$] 234.1125, found 234.1122.

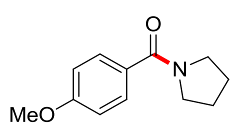


Amine (4.0 equiv.) was used. After stirring the reaction for 14 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 20 h.

pyrrolidin-1-yl(p-tolyl)methanone (4i)[2]: Colorless oil; 18.2 mg; 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.17 (m, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H), 1.98 – 1.82 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.8, 139.8, 134.2, 128.8, 127.2, 49.6, 46.1, 26.4, 24.4, 21.3 ppm; IR (film): 3470 (br s), 1737, 1614, 1424 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{16}NO^+$ [M+H$^+$] 190.1226, found 190.1228.

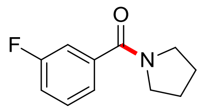


[1,1'-biphenyl]-4-yl(pyrrolidin-1-yl)methanone (4j): Light yellow solid; 24.7 mg; 82% yield; mp: 70–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 6H), 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 1H), 3.67 (t, *J* = 6.8 Hz, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 2.01 – 1.85 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.4, 142.6, 140.3, 135.9, 128.8, 127.68, 127.65, 127.1, 126.9, 49.6, 46.2, 26.4, 24.4, ppm; IR (film): 3470 (br s), 1739, 1619, 1426, 1016 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{17}H_{18}NO^+$ [M+H$^+$] 252.1383, found 252.1383.

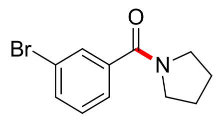


Amine (4.0 equiv.) was used. After stirring the reaction for 14 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 20 h.

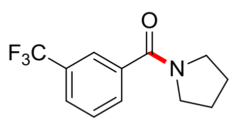
(4-methoxyphenyl)(pyrrolidin-1-yl)methanone (4k)[2]: Colorless oil; 17.7 mg; 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 1.97 – 1.82 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.4, 160.7, 129.3, 129.1, 113.3, 55.3, 49.8, 46.3, 26.5, 24.4 ppm; IR (film): 3470 (br s), 1738, 1609, 1429, 1217 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{16}NO_2^+$ [M+H$^+$] 206.1176, found 206.1180.



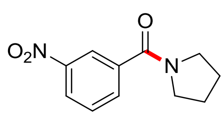
(3-fluorophenyl)(pyrrolidin-1-yl)methanone (4l)[2]: Yellow oil; 18.5 mg; 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 1H), 7.29 – 7.27 (m, 1H), 7.22 – 7.19 (m, 1H), 7.12 – 7.07 (m, 1H), 3.63 (t, J = 6.8 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.99 – 1.84 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.2, 162.3 (d, $J_{C–F}$ = 245.8 Hz, 1C), 139.1 (d, $J_{C–F}$ = 6.8 Hz, 1C), 130.0 (d, $J_{C–F}$ = 8.0 Hz, 1C), 122.7 (d, $J_{C–F}$ = 3.1 Hz, 1C), 116.7 (d, $J_{C–F}$ = 21.0 Hz, 1C), 114.3 (d, $J_{C–F}$ = 22.5 Hz, 1C), 49.5, 46.2, 26.3, 24.4 ppm; IR (film): 3470 (br s), 1738, 1624, 1448 cm^{-1}; HRMS(m/z, ESI-TOF): Calcd for $C_{11}H_{13}FNO^+$ [M+H$^+$] 194.0976, found 194.0980.



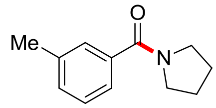
(3-bromophenyl)(pyrrolidin-1-yl)methanone (4m)[4]: Yellow oil; 28.1 mg; 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, J = 1.8 Hz, 1H), 7.54 – 7.52 (m, 1H), 7.44 – 7.41 (m, 1H), 7.28 – 7.24 (m, 1H), 3.62 (t, J = 6.8 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.99 – 1.84 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 167.9, 139.1, 132.8, 130.1, 129.9, 125.6, 122.3, 49.5, 46.2, 26.3, 24.4 ppm; IR (film): 3470 (br s), 1739, 1627, 1433, 1217 cm^{-1}; HRMS(m/z, ESI-TOF): Calcd for $C_{11}H_{13}BrNO^+$ [M+H$^+$] 254.0175, found 254.0185.



pyrrolidin-1-yl(3-(trifluoromethyl)phenyl)methanone (4na): Yellow oil; 26.3 mg; 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.71 – 7.65 (m, 2H), 7.53 (t, J = 7.8 Hz, 1H), 3.65 (t, J = 6.8 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 2.01 – 1.86 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.1, 137.9, 130.7 (q, $J_{C–F}$ = 33.4 Hz, 1C), 130.4 (d, $J_{C–F}$ = 1.0 Hz, 1C), 126.5 (q, $J_{C–F}$ = 3.6 Hz, 1C), 124.1 (q, $J_{C–F}$ = 3.8 Hz, 1C), 123.7 (q, $J_{C–F}$ = 270.8 Hz, 1C), 49.5, 46.3, 26.4, 24.4 ppm; IR (film): 3470 (br s), 1739, 1632, 1328 cm^{-1}; HRMS(m/z, ESI-TOF): Calcd for $C_{12}H_{13}F_3NO^+$ [M+H$^+$] 244.0944, found 244.0941.

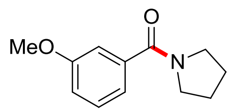


(3-nitrophenyl)(pyrrolidin-1-yl)methanone (4o)[5]: Yellow solid; 22.5 mg; 85% yield; mp: 56–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (t, J = 1.7 Hz, 1H), 8.28 – 8.25 (m, 1H), 7.88 – 7.85 (m, 1H), 7.60 (t, J = 8.1 Hz, 1H), 3.66 (t, J = 6.8 Hz, 2H), 3.43 (t, J = 6.8 Hz, 2H), 2.03 – 1.88 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 166.9, 147.8, 138.6, 133.2, 129.6, 124.6, 122.2, 49.6, 46.4, 26.4, 24.3 ppm; IR (film): 3470 (br s), 1738, 1626, 1531, 1349 cm^{-1}; HRMS(m/z, ESI-TOF): Calcd for $C_{11}H_{13}N_2O_3^+$ [M+H$^+$] 221.0921, found 221.0928.



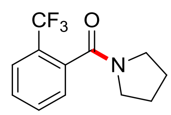
Amine (4.0 equiv.) was used. After stirring the reaction for 14 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 20 h.

pyrrolidin-1-yl(m-tolyl)methanone (4p)[4]: Colorless oil; 17.9 mg; 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 0.6 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.21 – 7.19 (m, 1H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.35 (s, 3H), 1.97 – 1.81 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.9, 138.0, 137.1, 130.4, 128.0, 127.6, 123.9, 49.5, 46.1, 26.3, 24.4, 21.3 ppm; IR (film): 3470 (br s), 1738, 1623, 1436, 1018 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{16}NO^+$ [M+H$^+$] 190.1226, found 190.1219.



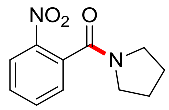
After stirring the reaction for 20 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 4 h.

(3-methoxyphenyl)(pyrrolidin-1-yl)methanone (4q)[2]: Colorless oil; 19.5 mg; 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 1H), 7.07 – 7.04 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.63 (t, *J* = 6.7 Hz, 2H), 3.42 (t, *J* = 6.7 Hz, 2H), 1.97 – 1.84 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.4, 159.4, 138.5, 129.3, 119.2, 115.7, 112.3, 55.3, 49.6, 46.1, 26.3, 24.4 ppm; IR (film): 3470 (br s), 1739, 1623, 1435, 1366, 1217 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{16}NO_2^+$ [M+H$^+$] 206.1176, found 206.1176.



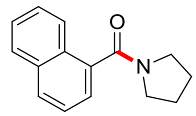
Amine (4.0 equiv.) was used. After stirring the reaction for 20 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 20 h.

pyrrolidin-1-yl(2-(trifluoromethyl)phenyl)methanone (4r): Yellow oil; 17.5 mg; 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 3.64 (t, *J* = 6.9 Hz, 2H), 3.11 (t, *J* = 6.9 Hz, 2H), 1.99 – 1.82 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 167.2, 136.3 (d, $J_{C–F}$ = 2.3 Hz, 1C), 132.2 (d, $J_{C–F}$ = 0.7 Hz, 1C), 128.9, 127.1, 126.6 (q, $J_{C–F}$ = 4.6 Hz, 1C), 126.1 (q, $J_{C–F}$ = 31.7 Hz, 1C), 122.6 (q, $J_{C–F}$ = 272.1 Hz, 1C), 48.5, 45.6, 25.8, 24.5 ppm; IR (film): 3470 (br s), 1739, 1639, 1432, 1318 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{13}F_3NO^+$ [M+H$^+$] 244.0944, found 244.0936.



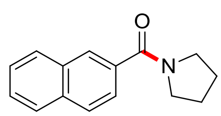
The reaction components were mixed together in a 25 mL Schlenk-type sealed tube (Synthware). The tube was purged and refilled with O_2 (×3). After stirring the reaction for 14 h, another portion of photocatalyst **1i** (1 mol %) was added. Then the tube was refilled with O_2 and the reaction was continued for additional 20 h.

(2-nitrophenyl)(pyrrolidin-1-yl)methanone (4s)[2]: Yellow oil; 15.3 mg; 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.16 (m, 1H), 7.73 – 7.69 (m, 1H), 7.58 – 7.54 (m, 1H), 7.45 – 7.43 (m, 1H), 3.69 (t, *J* = 6.8 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H), 2.03 – 1.87 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 166.1, 144.9, 134.5, 134.0, 129.6, 128.1, 124.6, 48.1, 45.7, 25.8, 24.4 ppm; IR (film): 3452 (br s), 1737, 1638, 1530, 1350 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{11}H_{13}N_2O_3^+$ [M+H$^+$] 221.0921, found 221.0914.

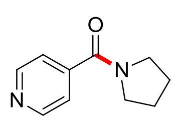


After stirring the reaction for 16 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 6 h.

naphthalen-1-yl(pyrrolidin-1-yl)methanone (4t)[2]: Yellow oil; 18.4 mg; 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.85 (m, 3H), 7.54 – 7.44 (m, 4H), 3.79 (t, *J* = 7.0 Hz, 2H), 3.12 (t, *J* = 7.0 Hz, 2H), 2.03 – 1.97 (m, 2H), 1.86 – 1.79 (m, 2H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.2, 135.7, 133.5, 129.1, 129.0, 128.4, 126.9, 126.2, 125.2, 124.8, 123.7, 48.5, 45.6, 26.0, 24.6 ppm; IR (film): 3470 (br s), 1738, 1630, 1439, 1384, 1218 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{15}H_{16}NO^+$ [M+H$^+$] 226.1226, found 226.1240.

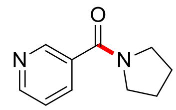


naphthalen-2-yl(pyrrolidin-1-yl)methanone (4u)[2]: Yellow oil; 22.7 mg; 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 0.8 Hz, 1H), 7.87 – 7.84 (m, 3H), 7.63 – 7.60 (m, 1H), 7.55 – 7.49 (m, 2H), 3.70 (t, *J* = 6.9 Hz, 2H), 3.48 (t, *J* = 6.9 Hz, 2H), 2.02 – 1.84 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.7, 134.4, 133.7, 132.5, 128.4, 128.0, 127.7, 127.0, 126.9, 126.5, 124.4, 49.7, 46.2, 26.4, 24.4 ppm; IR (film): 3470 (br s), 1738, 1613, 1421, 1365, 1218 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{15}H_{16}NO^+$ [M+H$^+$] 226.1226, found 226.1218.

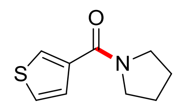


After stirring the reaction for 16 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 8 h.

pyridin-4-yl(pyrrolidin-1-yl)methanone (4v)[6]: Yellow oil; 17.1 mg; 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.66 (m, 2H), 7.36 – 7.35 (m, 2H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.35 (t, *J* = 6.7 Hz, 2H), 1.99 – 1.85 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 167.1, 150.1, 144.4, 121.1, 49.2, 46.2, 26.3, 24.3 ppm; IR (film): 3470 (br s), 1738, 1623, 1444, 1218 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{10}H_{13}N_2O^+$ [M+H$^+$] 177.1022, found 177.1016.

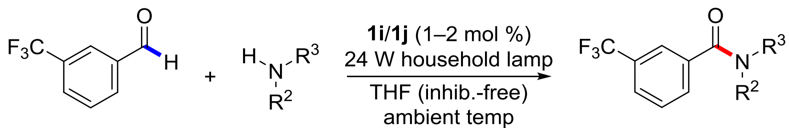


The reaction components were mixed together in a 25 mL Schlenk-type sealed tube (Synthware). The tube was purged and refilled with O_2 (×3). After stirring the reaction for 24 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 24 h.
pyridin-3-yl(pyrrolidin-1-yl)methanone (4w)[2]: Colorless oil; 16.5 mg; 78% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 1.2 Hz, 1H), 8.65 – 8.63 (m, 1H), 7.36 – 7.33 (m, 1H), 7.86 – 7.84 (m, 1H), 3.65 (t, *J* = 6.7 Hz, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 2.01 – 1.87 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 167.1, 150.8, 148.0, 135.0, 132.9, 123.3, 49.5, 46.3, 26.4, 24.3 ppm; IR (film): 3470 (br s), 1738, 1617, 1447, 1217 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{10}H_{13}N_2O^+$ [M+H$^+$] 177.1022, found 177.1025.

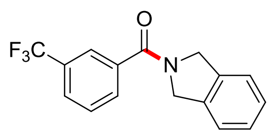


After stirring the reaction for 16 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 20 h.
pyrrolidin-1-yl(thiophen-3-yl)methanone (4x): Yellow oil; 15.9 mg; 73% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.65 (m, 1H), 7.36 (d, *J* = 5.0 Hz, 1H), 7.31 – 7.29 (m, 1H), 3.65 – 3.58 (m, 4H), 1.96 – 1.90 (m, 4H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 164.4, 137.9, 127.6, 127.2, 125.3, 49.2, 46.5, 26.5, 24.3 ppm; IR (film): 3470 (br s), 1738, 1609, 1443, 1365, 1218 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_9H_{12}NOS^+$ [M+H$^+$] 182.0634, found 182.0625.

2.4. General procedure for phenazinium salt-catalyzed aerobic amidation of aromatic aldehyde with various secondary amines

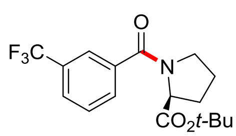


A 35 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with aldehyde **2n** (16.1 μL, 0.12 mmol, 1.0 equiv.) and photocatalyst **1j** (0.42 mg, 1.2×10^{-4} mmol, 1 mol %). Amine **3** (0.30 mmol, 2.5 equiv.) was added and THF (inhibitor-free, 1.2 mL) was used to wash down the solids on the sides of wall. The tube was then capped and placed approximately 2 cm from the light source. After stirring for 20 h, the crude reaction mixture was filtered through a short pad of silica gel. EtOAc (3 × 2 mL) was used for washing. The filtrate was concentrated *in vacuo*, and the resulting residue was purified by preparative TLC using hexanes/EtOAc as the eluent.



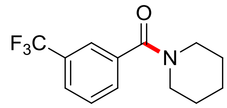
Amine (3.0 equiv.) was used.

isoindolin-2-yl(3-(trifluoromethyl)phenyl)methanone (4nb): Yellow oil; 28.7 mg; 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.78 – 7.72 (m, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.17 (d, J = 7.3 Hz, 1H), 5.03 (s, 2H), 4.76 (s, 2H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.7, 137.4, 136.0, 131.1 (q, $J_{C–F}$ = 32.6 Hz, 1C), 130.2 (d, $J_{C–F}$ = 1.0 Hz, 1C), 129.2, 128.0, 127.6, 126.8 (q, $J_{C–F}$ = 3.7 Hz, 1C), 123.9 (q, $J_{C–F}$ = 3.8 Hz, 1C), 123.7 (q, $J_{C–F}$ = 270.8 Hz, 1C), 123.0, 122.5, 54.9, 52.6 ppm; IR (film): 3483 (br s), 1638, 1411, 1326, 1124 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{16}H_{13}F_3NO^+$ [$M+H^+$] 292.0944, found 292.0943.



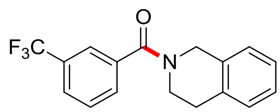
Photocatalyst **1i** (1 mol %) was used. After stirring the reaction for 14 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 20 h.

(*S*)-*tert*-butyl 1-(3-(trifluoromethyl)benzoyl)pyrrolidine-2-carboxylate (4nc): Yellow oil; 28.8 mg; 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.76 – 7.61 (m, 2H), 7.56 – 7.48 (m, 1H), 4.55 (dd, J = 8.3, 5.6 Hz, 0.7H, major), 4.20 (dd, J = 8.2, 2.6 Hz, 0.3H, minor), 3.81 – 3.77 (m, 0.6H), 3.64 – 3.58 (m, 0.7H), 3.50 – 3.44 (m, 0.7H), 2.35 – 2.22 (m, 1H), 2.07 – 1.96 (m, 2H), 1.93 – 1.84 (m, 1H), 1.50 (s, 6H, major), 1.29 (s, 3H, minor) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 171.1 (major), 171.0 (minor), 167.9, 137.8 (minor), 137.1 (major), 130.8 (q, $J_{C–F}$ = 32.6 Hz, 1C), 130.5 (major), 130.2 (minor), 128.9 (minor), 128.8 (major), 126.8 (q, $J_{C–F}$ = 3.7 Hz, 1C, major), 126.4 (q, $J_{C–F}$ = 3.7 Hz, 1C, minor), 124.2 (q, $J_{C–F}$ = 3.8 Hz, 1C, major), 123.8 (q, $J_{C–F}$ = 3.8 Hz, 1C, minor), 123.7 (q, $J_{C–F}$ = 270.7 Hz, 1C), 82.1 (minor), 81.6 (major), 61.9 (minor), 60.0 (major), 49.9 (major), 46.8 (minor), 31.6 (minor), 29.3 (major), 28.0 (major), 27.6 (minor), 25.3 (major), 22.5 (minor) ppm; IR (film): 3470 (br s), 1738, 1641, 1329, 1218 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{13}H_{13}F_3NO_3^+$ [$M+H^+$] 288.0848, found 288.0843. HPLC analysis: Chiralpak AS-H (Hex/IPA = 95/5, 1.0 mL/min, 254 nm, 25°C) 38.3, 42.7 (major) min, 91% *ee*.

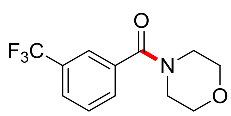


The reaction components were mixed together in a 25 mL Schlenk-type sealed tube (Synthware). The tube was purged and refilled with O_2 (×3). After stirring the reaction for 24 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 12 h.

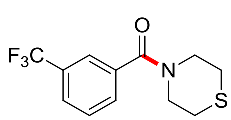
piperidin-1-yl(3-(trifluoromethyl)phenyl)methanone (4nd): Yellow oil; 25.6 mg; 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.66 (m, 2H), 7.59 – 7.51 (m, 2H), 3.72 (br s, 2H), 3.32 (br s, 2H), 1.69 – 1.53 (m, 6H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.6, 137.2, 130.9 (q, $J_{C–F}$ = 32.5 Hz, 1C), 130.0, 129.0, 126.1 (q, $J_{C–F}$ = 3.7 Hz, 1C), 123.8 (q, $J_{C–F}$ = 3.8 Hz, 1C), 123.7 (q, $J_{C–F}$ = 270.8 Hz, 1C), 48.7, 43.2, 26.4, 25.4, 24.3 ppm; IR (film): 3470 (br s), 1738, 1636, 1331 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{13}H_{15}F_3NO^+$ [M+H$^+$] 258.1100, found 258.1098.



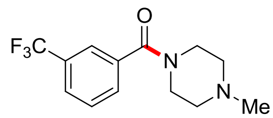
(3,4-dihydroisoquinolin-2(1H)-yl)(3-(trifluoromethyl)phenyl)methanone (4ne): Yellow oil; 33.3 mg; 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.56 (m, 4H), 7.20 – 7.16 (m, 3.7H), 6.91 (br s, 0.3H, minor), 4.89 (br s, 1.2H, major), 4.54 (br s, 0.8H, minor), 4.00 (br s, 0.8H, minor), 3.61 (br s, 1.2H, major), 2.99 – 2.88 (m, 2H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.3 (major), 168.8 (minor), 136.8, 134.6 (minor), 133.5 (major), 132.6 (major), 132.4 (minor), 131.1 (q, $J_{C–F}$ = 32.7 Hz, 1C), 130.5 (minor), 130.1 (major), 129.2 (major), 128.6 (minor), 127.1, 126.7, 126.6, 126.4, 125.8, 124.2 (minor), 123.9 (major), 123.6 (q, $J_{C–F}$ = 270.8 Hz, 1C), 49.7 (minor), 45.3 (major), 44.9 (major), 40.7 (minor), 29.5 (major), 28.1 (minor) ppm; IR (film): 3470 (br s), 1738, 1639, 1330, 1218 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{17}H_{15}F_3NO^+$ [M+H$^+$] 306.1100, found 306.1095.



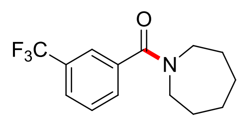
morpholino(3-(trifluoromethyl)phenyl)methanone (4nf): White solid; 26.4 mg; 85% yield; mp: 68–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.60 – 7.54 (m, 2H), 3.79 (br s, 4H), 3.64 (br s, 2H), 3.43 (br s, 2H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.8, 136.0, 131.2 (q, $J_{C–F}$ = 32.5 Hz, 1C), 130.4 (d, $J_{C–F}$ = 1.0 Hz, 1C), 129.2, 126.7 (q, $J_{C–F}$ = 3.7 Hz, 1C), 124.1 (q, $J_{C–F}$ = 3.8 Hz, 1C), 123.7 (q, $J_{C–F}$ = 270.9 Hz, 1C), 66.8, 48.2, 42.6 ppm; IR (film): 3470 (br s), 1738, 1638, 1333, 1218 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{13}F_3NO_2^+$ [M+H$^+$] 260.0893, found 260.0886.



thiomorpholino(3-(trifluoromethyl)phenyl)methanone (4ng): Yellow oil; 17.5 mg; 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (br s, 1H), 7.68 (s, 1H), 7.56 (br s, 1H), 4.04 (br s, 2H), 3.65 (br s, 2H), 2.75 (br s, 2H), 2.57 (br s, 2H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 169.2, 136.5, 131.2 (q, $J_{C–F}$ = 32.7 Hz, 1C), 130.1, 129.3, 126.6 (q, $J_{C–F}$ = 3.6 Hz, 1C), 123.8 (q, $J_{C–F}$ = 3.8 Hz, 1C), 123.6 (q, $J_{C–F}$ = 270.9 Hz, 1C), 50.1, 44.7, 28.0, 27.4 ppm; IR (film): 3470 (br s), 1739, 1638, 1334, 1218 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{12}H_{13}F_3NOS^+$ [M+H^+] 276.0664, found 276.0670.

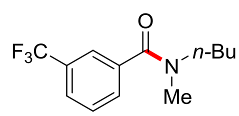


(4-methylpiperazin-1-yl)(3-(trifluoromethyl)phenyl)methanone (4nh): Colorless oil; 28.1 mg; 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (br s, 2H), 7.57 – 7.52 (m, 2H), 7.56 (br s, 1H), 3.80 (br s, 2H), 3.41 (br s, 2H), 2.49 (br s, 2H), 2.35 (br s, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 168.7, 136.5, 131.0 (q, $J_{C–F}$ = 32.5 Hz, 1C), 130.3, 129.1, 126.4 (q, $J_{C–F}$ = 3.6 Hz, 1C), 124.0 (q, $J_{C–F}$ = 3.8 Hz, 1C), 123.6 (q, $J_{C–F}$ = 270.9 Hz, 1C), 55.1, 54.5, 47.6, 45.9, 42.1 ppm; IR (film): 3470 (br s), 1638, 1332, 1265, 1129 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{13}H_{16}F_3N_2O^+$ [M+H^+] 273.1209, found 273.1210.



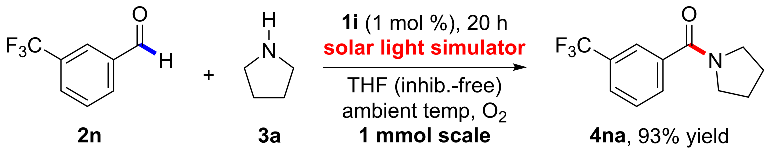
Photocatalyst **1i** (1 mol %) was used.

azepan-1-yl(3-(trifluoromethyl)phenyl)methanone (4ni): Yellow oil; 25.1 mg; 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.64 (m, 2H), 7.57 – 7.50 (m, 2H), 3.68 (t, *J* = 5.9 Hz, 2H), 3.34 (t, *J* = 5.8 Hz, 2H), 1.87 – 1.82 (m, 2H), 1.68 – 1.57 (m, 6H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 170.0, 138.0, 130.8 (q, $J_{C–F}$ = 32.5 Hz, 1C), 129.8 (d, $J_{C–F}$ = 1.1 Hz, 1C), 129.0, 125.8 (q, $J_{C–F}$ = 3.7 Hz, 1C), 123.5 (q, $J_{C–F}$ = 3.8 Hz, 1C), 124.2 (q, $J_{C–F}$ = 270.8 Hz, 1C), 49.7, 46.4, 29.4, 27.8, 27.1, 26.4 ppm; IR (film): 3470 (br s), 1738, 1633, 1331, 1128 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{14}H_{17}F_3NO^+$ [M+H^+] 272.1277, found 272.1271.



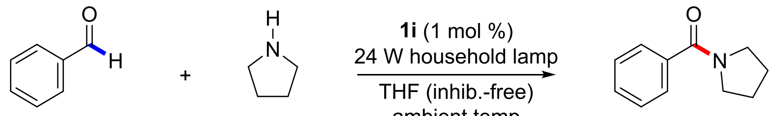
***N*-butyl-*N*-methyl-3-(trifluoromethyl)benzamide (4nj)**: Colorless oil; 17.4 mg; 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 2H), 7.57 – 7.50 (m, 2H), 3.53 (t, *J* = 1.8 Hz, 0.9H, minor), 3.18 (t, *J* = 1.8 Hz, 1.1H, major), 3.07 (s, 1.6H, major), 2.91 (s, 1.4H, minor), 1.65 – 1.62 (m, 1H), 1.56 – 1.50 (m, 1H), 1.42 – 1.37 (m, 1H), 1.18 – 1.13 (m, 1H), 0.97 (t, *J* = 1.8 Hz, 1.4H, minor), 0.78 (t, *J* = 1.8 Hz, 1.6H, major) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 170.2 (major), 169.6 (minor), 137.5, 130.8 (q, $J_{C–F}$ = 32.5 Hz, 1C), 130.1 (minor), 130.0 (major), 129.0, 126.0, 123.8 (minor), 123.6 (major), 123.7 (q, $J_{C–F}$ = 270.8 Hz, 1C), 51.0 (major), 47.3 (minor), 37.3 (minor), 32.7 (major), 30.3 (major), 29.0 (minor), 20.0 (minor), 19.5 (major), 13.8 (minor), 13.5 (major) ppm; IR (film): 3470 (br s), 1639, 1332, 1128 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_{13}H_{17}F_3NO^+$ [M+H^+] 260.1257, found 260.1264.

2.5. Scalable oxidative amidation of aldehyde using solar energy



A 35 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with aldehyde **2n** (133.8 μL, 1.00 mmol, 1.0 equiv.) and photocatalyst **1i** (3.34 mg, 0.010 mmol, 1 mol %). Amine **3a** (208.7 μL, 2.50 mmol, 2.5 equiv.) was added and THF (inhibitor-free, 8.0 mL) was used to wash down the solids on the sides of wall. The tube was purged and refilled with O_2 (×3). It was then placed under irradiation of the solar simulator (**CAUTION**: UV safety spectacles should be worn to protect eyes from exposure). The tube was tilted at an angle of 15° from the horizontal plane for maximum light exposure. The solar irradiance was measured before and after the reaction. It remained at 0.90 Sun constantly. After stirring for 20 h, the crude reaction mixture was filtered through a short pad of silica gel. EtOAc (3 × 2 mL) was used for washing. The filtrate was concentrated *in vacuo*, and the resulting residue was purified by flash chromatography using hexanes/EtOAc as the eluent to give amide **4na** as yellow oil (225.0 mg, 93% yield).

2.6. Initial rates and kinetic isotope effect



2a 3a 4a

Entry	T (s)	Yield (Avg of 2 runs)	[**2a**] (M)
1	0	0.0	0.0000
2	1800	0.4	0.0004
3	3600	1.2	0.0012
4	5400	2.5	0.0025
5	7620	4.3	0.0043

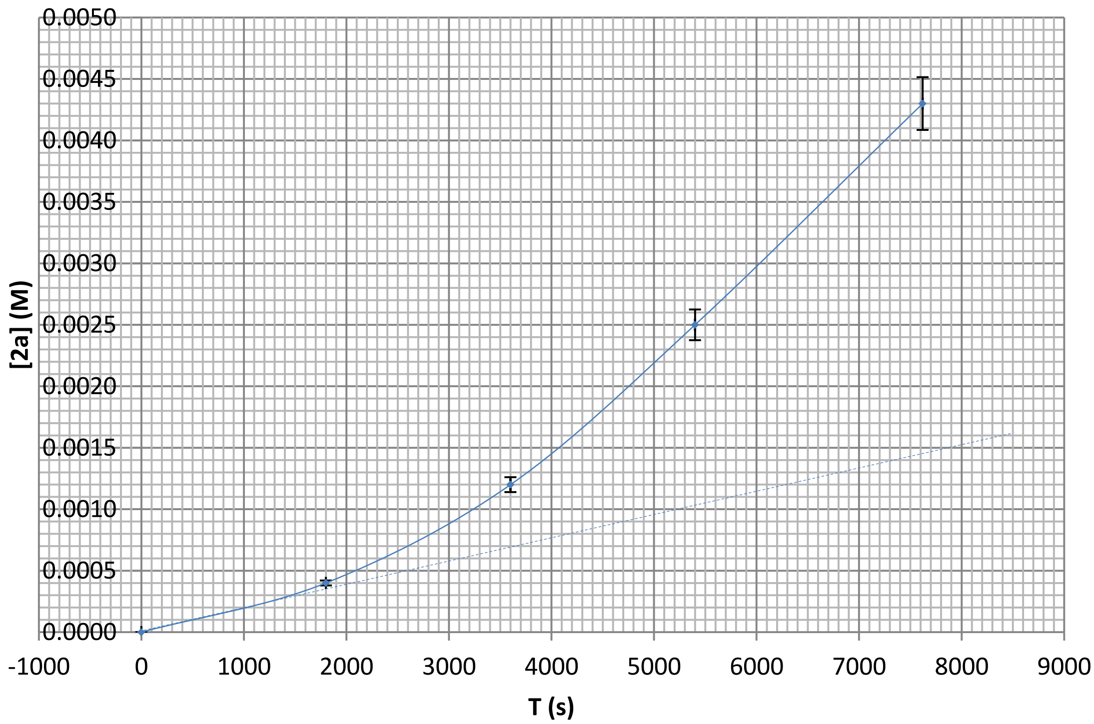
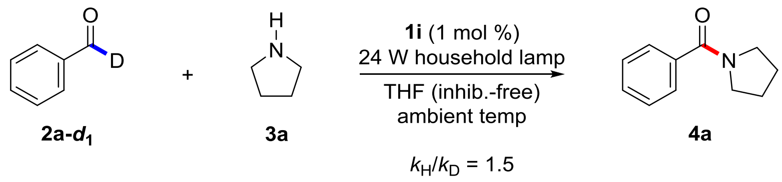


Figure S1 Initial rate of reaction between aldehyde **2a** and amine **3a**.



Entry	T (s)	Yield (Avg of 2 runs)	[**2a**] (M)
1	0	0.0	0.0000
2	5700	0.9	0.0009
3	11580	3.0	0.0030
4	15360	5.0	0.0050
5	21600	8.9	0.0089

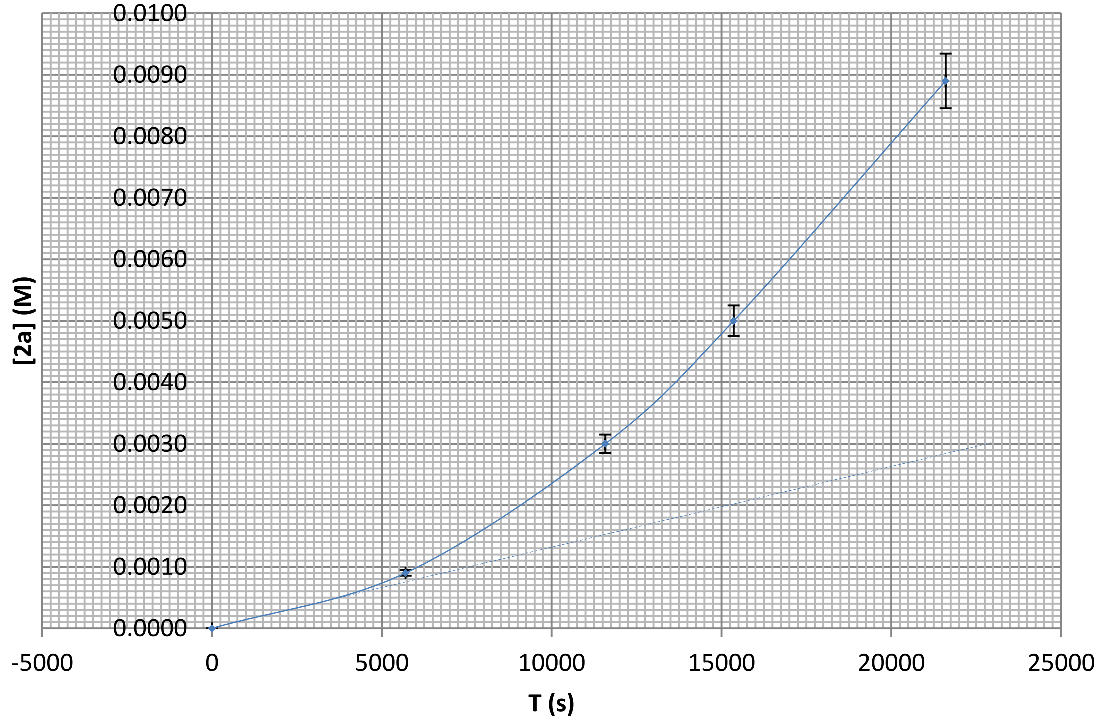
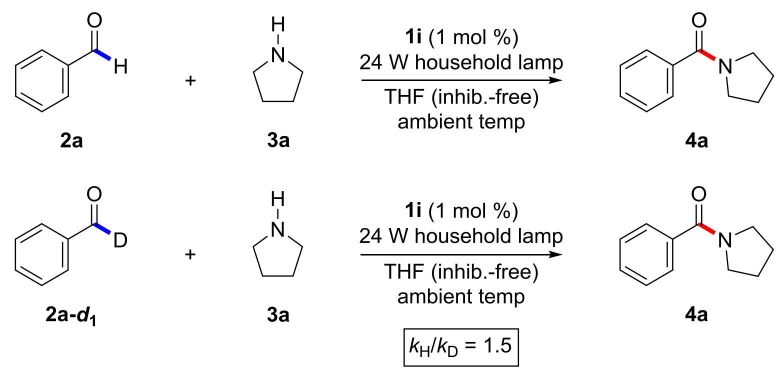


Figure S2 Initial rate of reaction between aldehyde **2a-d$_1$** and amine **3a**.

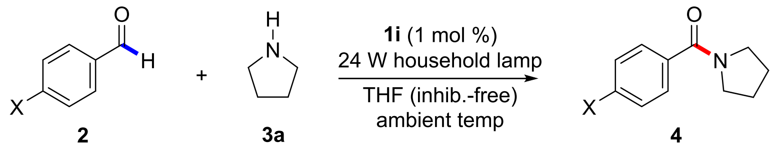


KIE = k_H / k_D

= (1.92 x 10^{-7} Ms^{-1}) / (1.30 x 10^{-7} Ms^{-1})

= 1.5

2.7. Hammett plot for the oxidative amidation of aldehydes



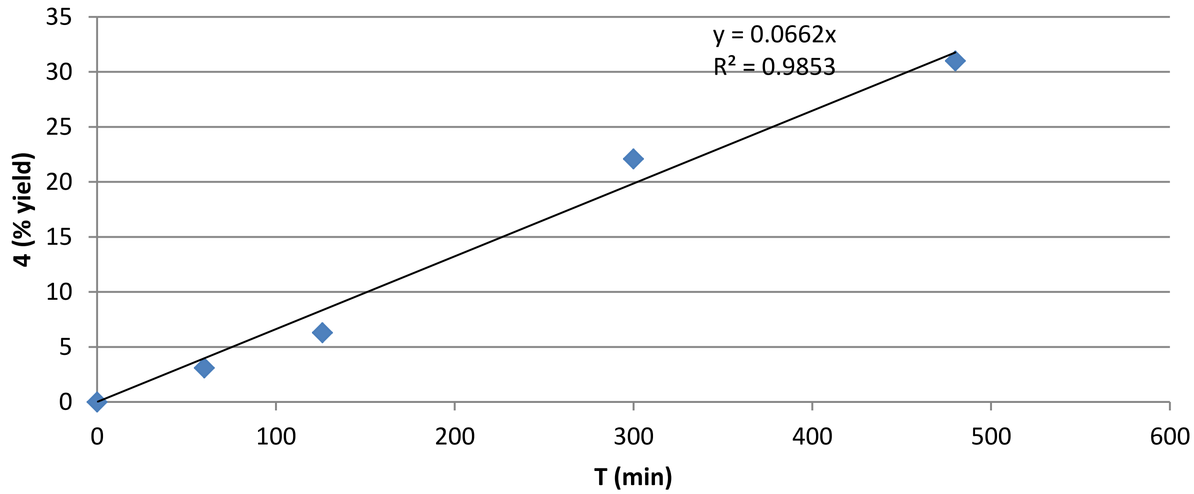


Figure S3 Rate of reaction between aldehyde **2** (X = NO_2) and amine **3a**.

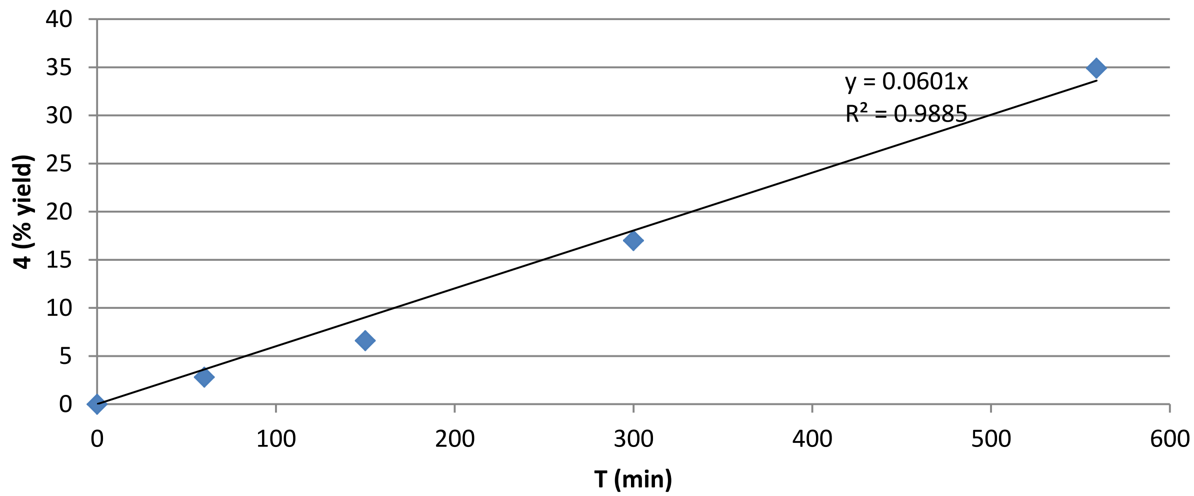


Figure S4 Rate of reaction between aldehyde **2** (X = CF_3) and amine **3a**.

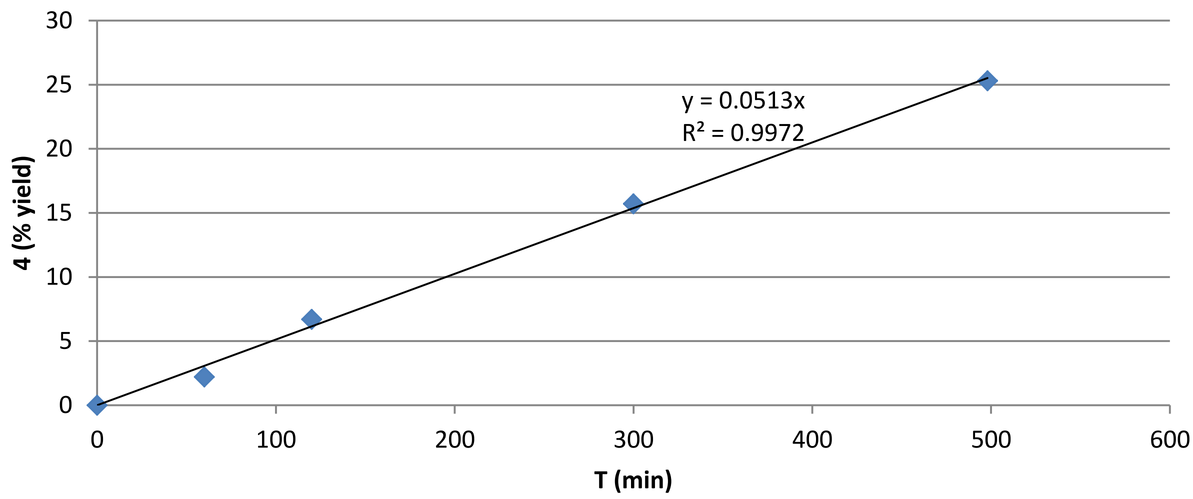


Figure S5 Rate of reaction between aldehyde **2** (X = Br) and amine **3a**.

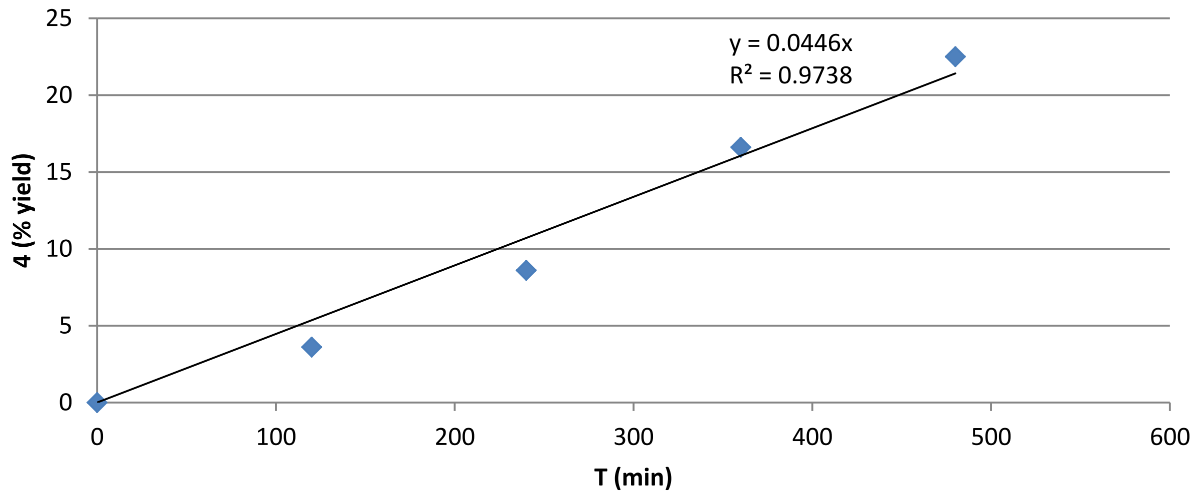


Figure S6 Rate of reaction between aldehyde **2** (X = H) and amine **3a**.

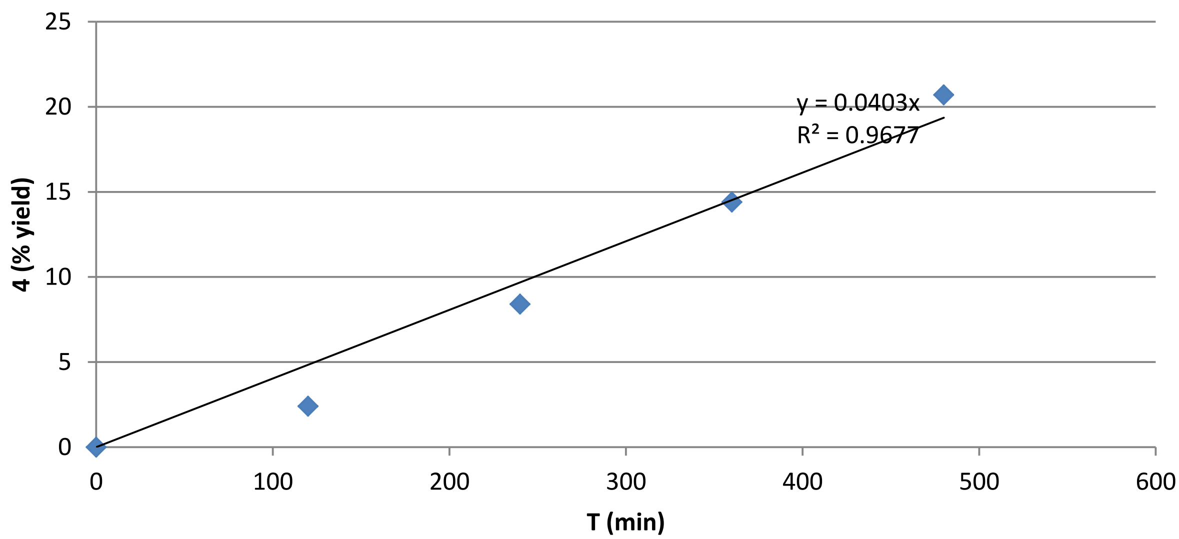
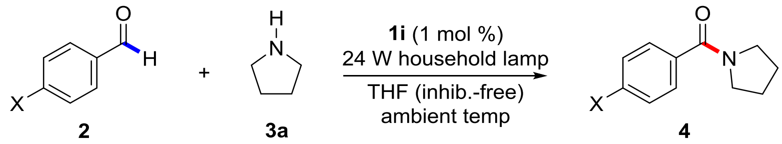


Figure S7 Rate of reaction between aldehyde **2** (X = CH_3) and amine **3a**.

Hammett plot:



X	σ_p	k/k_0	$\log(k/k_0)$
4–NO_2	0.778	1.484304933	0.171523131
4–CF_3	0.540	1.347533632	0.129539613
4–Br	0.232	1.150224215	0.060782506
H	0.000	1	0
4–Me	-0.170	0.903587444	-0.044029813

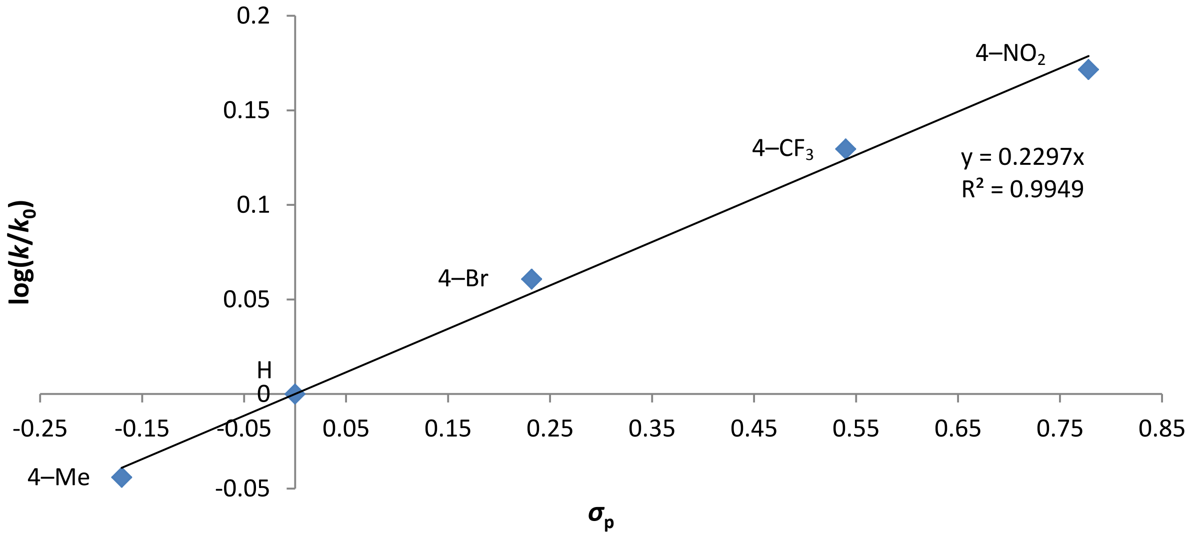
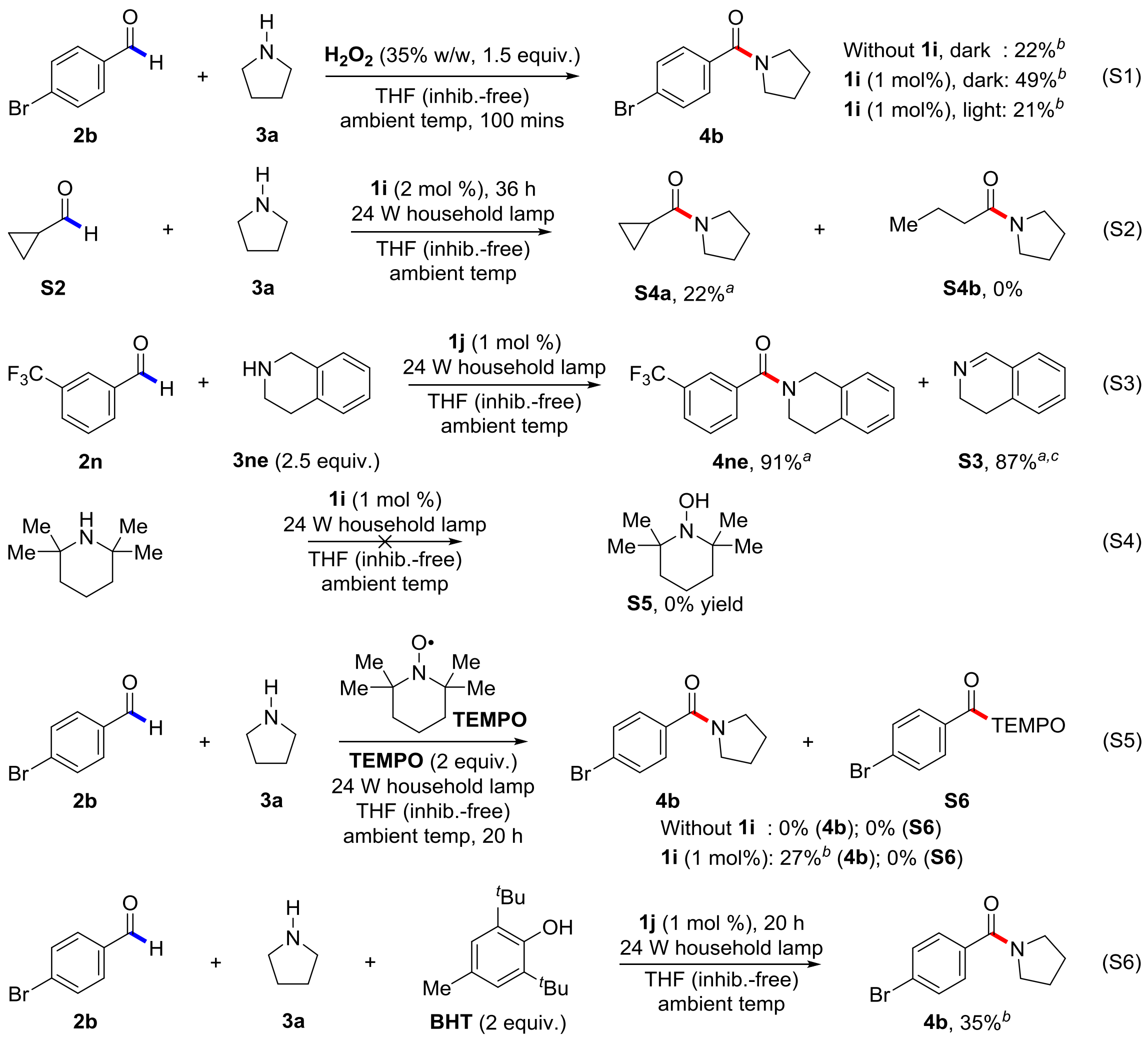
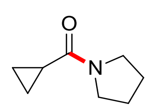


Figure S8 Hammett plot for the oxidative amidation of aldehydes.

2.8. Mechanistic studies

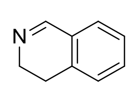


[a] Isolated yield. [b] Yield determined by ^{1}H NMR analysis of unpurified reaction mixture using CH_2Br_2 or $MeNO_2$ as internal standard. [c] Yield based on recovered starting materials.



The procedure in Section 2.3 was followed. Amine (4.0 equiv.) was used. After stirring the reaction for 16 h, another portion of photocatalyst **1i** (1 mol %) was added. The reaction was continued for additional 20 h.

cyclopropyl(pyrrolidin-1-yl)methanone (S4a): Colorless oil; 3.7 mg; 22% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (t, *J* = 6.8 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 2.01 – 1.94 (m, 2H), 1.89 – 1.82 (m, 2H), 1.64 – 1.58 (m, 1H), 1.00 – 0.97 (m, 2H), 0.76 – 0.72 (m, 2H) ppm; ^{13}C NMR (APT, 100 MHz, $CDCl_3$) δ 172.1, 46.5, 45.9, 26.0, 24.4, 12.5, 7.3 ppm; IR (film): 3437 (br s), 1617, 1454 cm^{-1}; HRMS(*m/z*, ESI-TOF): Calcd for $C_8H_{14}NO^+$ [M+H$^+$] 140.1070, found 140.1070.



3,4-dihydroisoquinoline (S3)[7]: Yellow solid; 20.5 mg; 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.38 – 7.15 (m, 4H), 3.78 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H) ppm.

2.9. UV–visible spectrum of photocatalyst

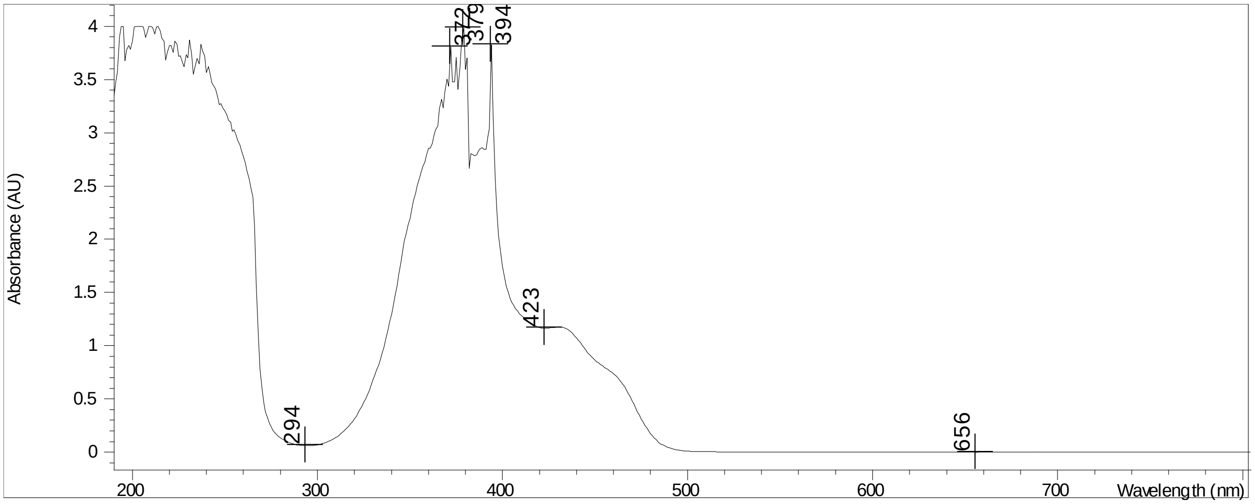


Figure S9 UV-visible spectrum of photocatalyst **1i** in MeCN

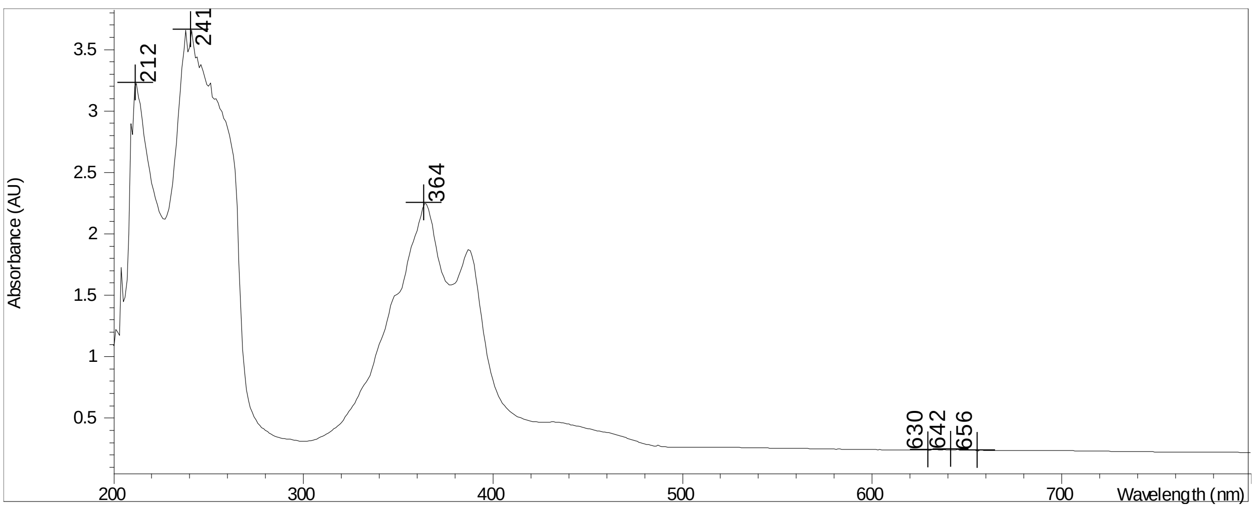


Figure S10 UV-visible spectrum of photocatalyst **1i** in THF

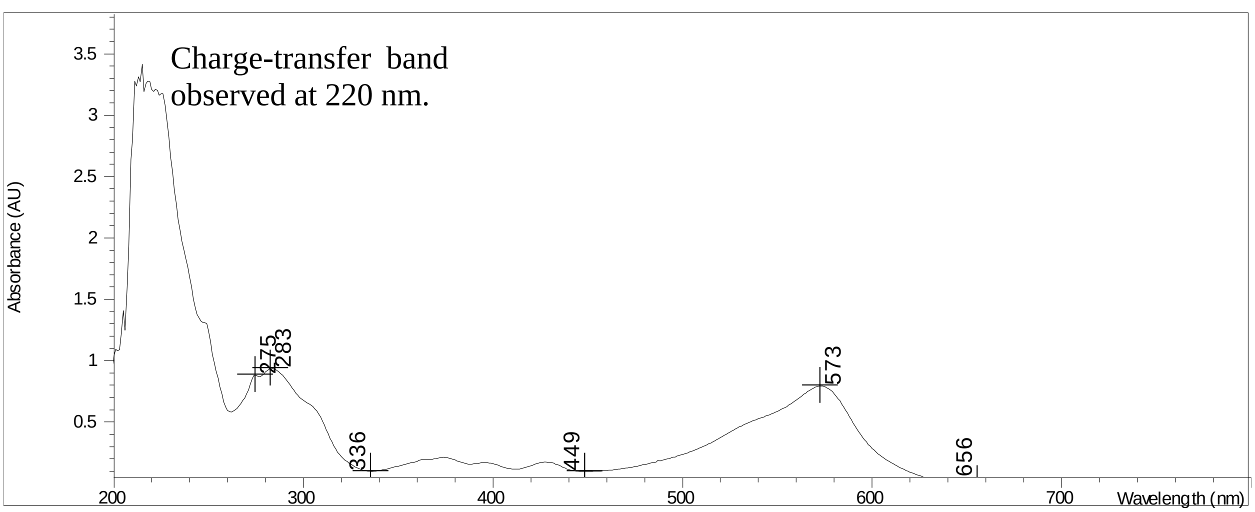


Figure S11 UV-visible spectrum of photocatalyst **1i** in the presence of amine **3a** in THF

2.10. Fluorescence quenching experiments

A solution of photocatalyst **1i** (33.44 mg, 0.100 mmol) in MeCN was prepared in a 100 mL volumetric flask (stock solution A, 0 μM amine **3a**). Another solution of photocatalyst **1i** (33.44 mg, 0.100 mmol) in MeCN was prepared in a 100 mL volumetric flask and amine **3a** (8.35 μL, 0.100 mmol) was added to it (stock solution B, 1000 μM amine **3a**). Next, solution B (5, 10, 15, and 20 mL) was added to four 25 mL volumetric flasks respectively. Then they were filled to the mark with solution A to give a series of solutions with the amine **3a** concentration of 200, 400, 600, and 800 μM. In a typical experiment, a Hellma® fluorescence micro cuvette (10×2 mm pathlength, 4 windows) was filled with the appropriate solution. Then the fluorescence emission spectrum (450 nm – 700 nm) was recorded at excitation wavelength of 379 nm.

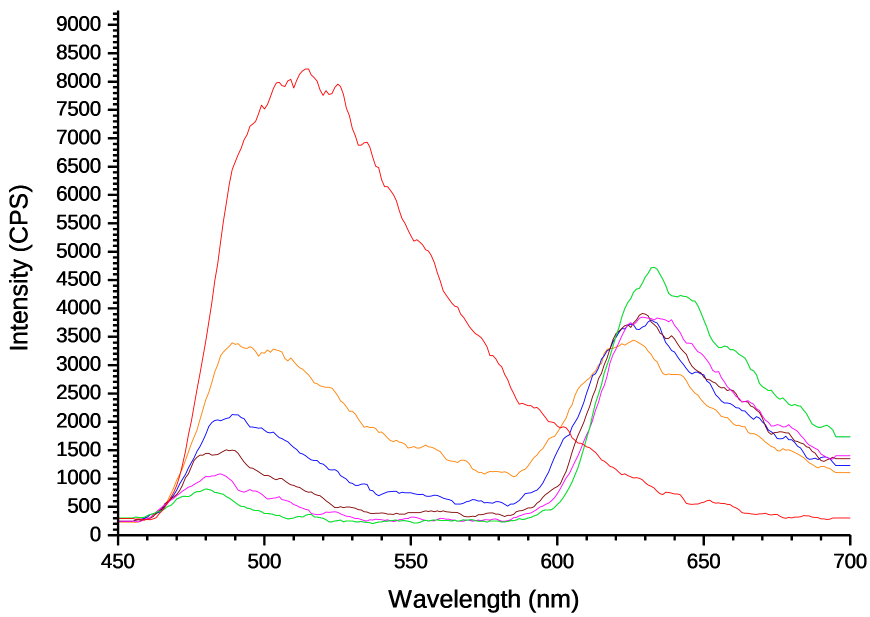


Figure S12 Fluorescence quenching of photocatalyst **1i** (1000 μM) by amine **3a**. Amine **3a** concentration: red color line, 0 μM; orange color line, 200 μM; blue color line, 400 μM; brown color line, 600 μM; magenta color line, 800 μM; green color line, 1000 μM.

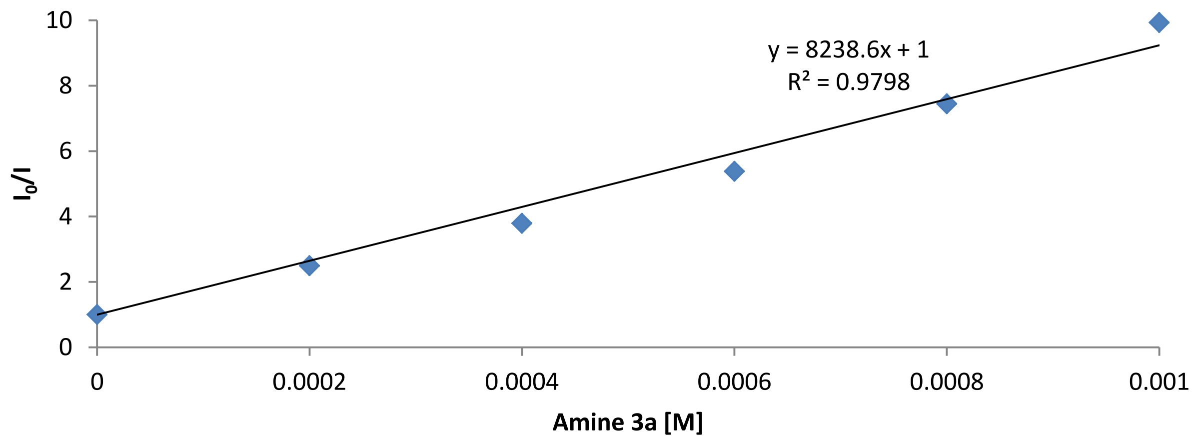
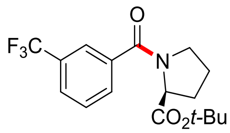
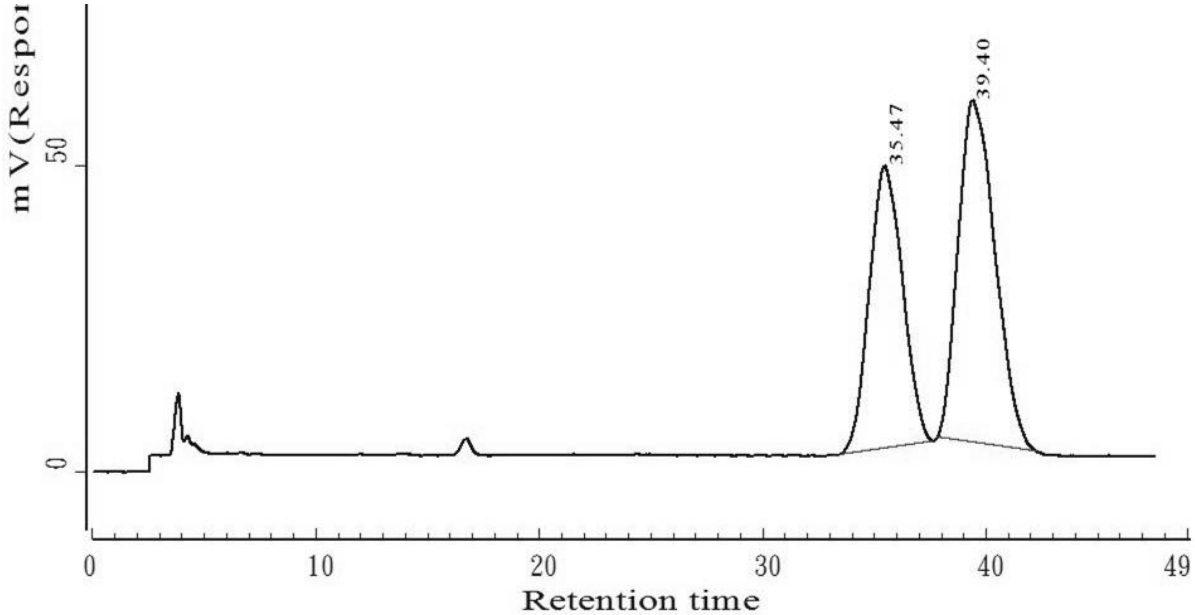


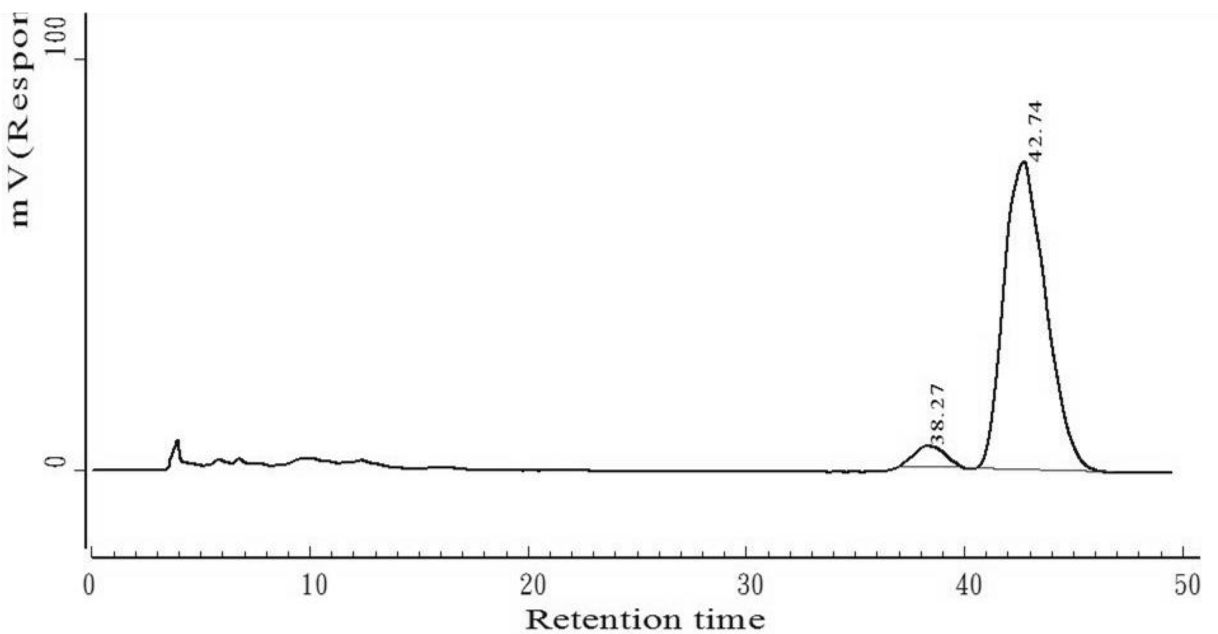
Figure S13 Plot of fluorescence intensity of photocatalyst **1i** versus concentration of amine **3a**.

2.11. Chiral HPLC chromatogram

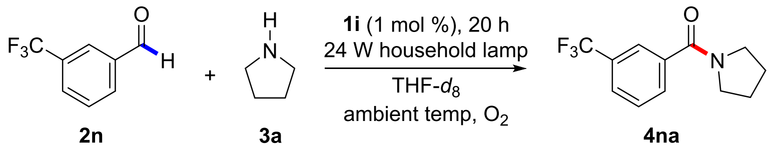


4nc



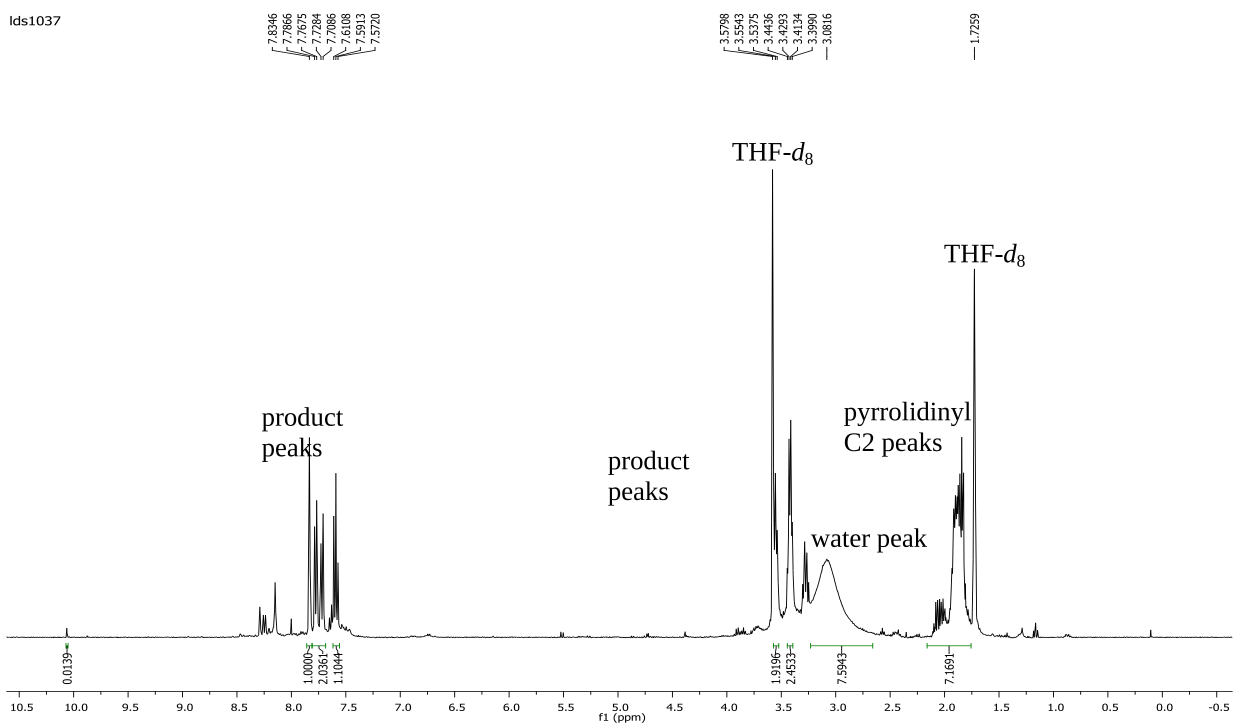


2.12. Detection of water byproduct



A flame-dried 35 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was purged with N_2. Then it was charged with aldehyde **2n** (13.4 μL, 0.10 mmol, 1.0 equiv.) and photocatalyst **1i** (0.33 mg, 0.001 mmol, 1 mol %) under constant flow of dry N_2. Following that, amine **3a** (20 μL, 0.250 mmol, 2.5 equiv.) was added and ampoule-sealed anhydrous THF-d_8 (1.0 mL) was used to wash down the solids on the sides of wall. The tube was purged and refilled with dry O_2 (×3). It was then placed approximately 2 cm from the light source. After stirring for 20 h, the crude reaction was transferred directly to an oven-dried NMR tube under constant flow of dry N_2.

In THF-$d_{8,}$ the literature reported that H_2O proton NMR peak appears at 2.46 ppm.[8] From the ^{1}H NMR, a broad peak at δ 3.08 (3.58–2.58) ppm was observed and this was assigned to be the water peak. However it was more downfield and this could possibly due to the proton chemical exchange with H_2O_2 as well as protons from the remaining unreacted pyrrolidine.



3. References

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(7) Product is commercially available.

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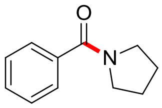
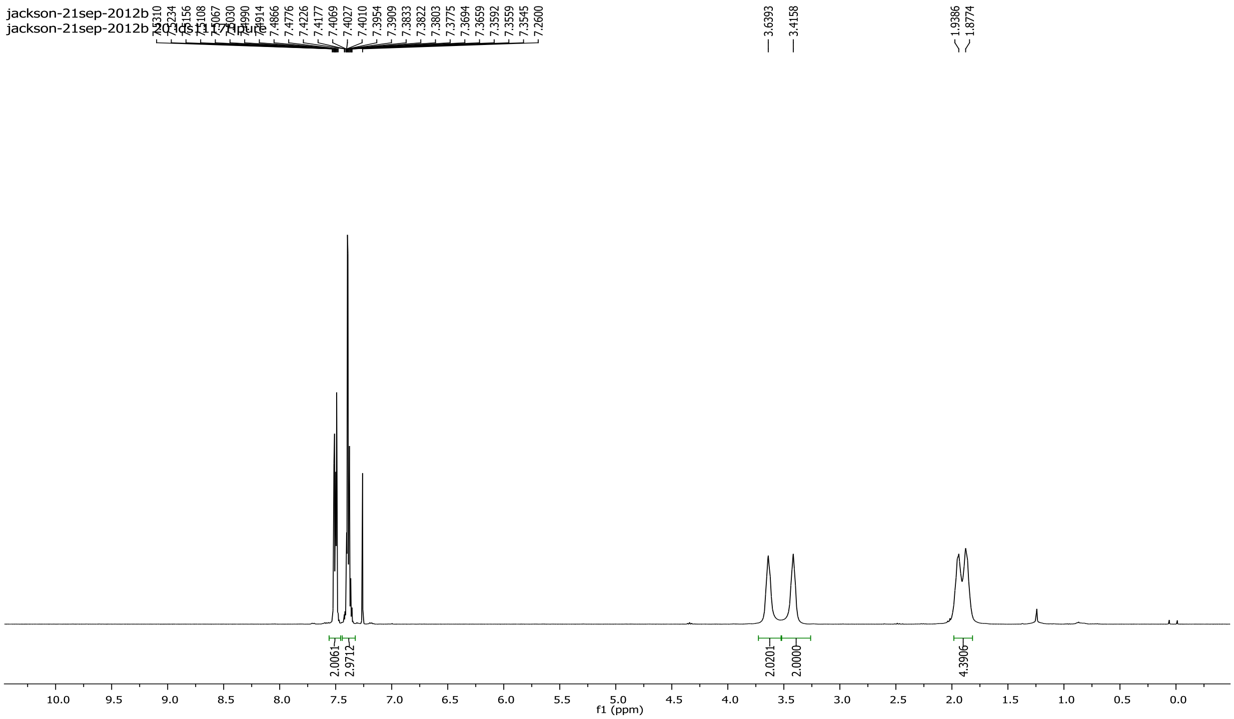
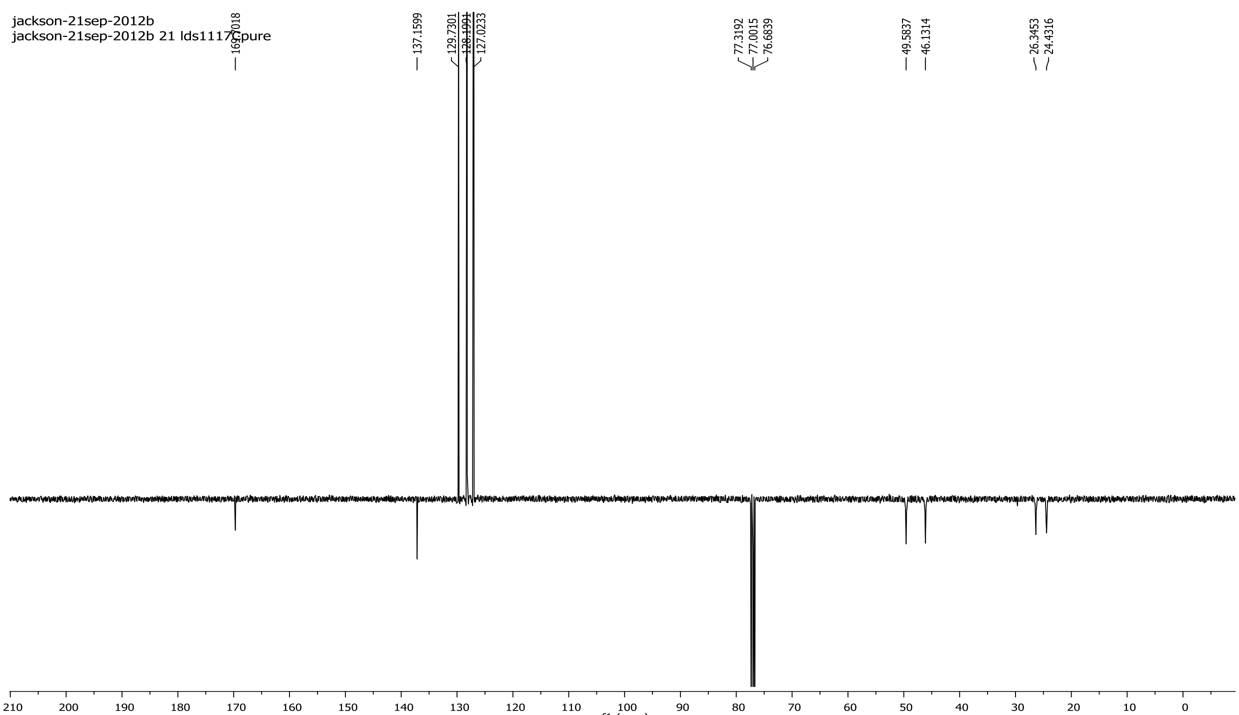
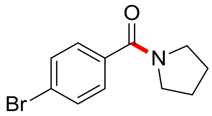
4. NMR Spectra of New Compounds



4a

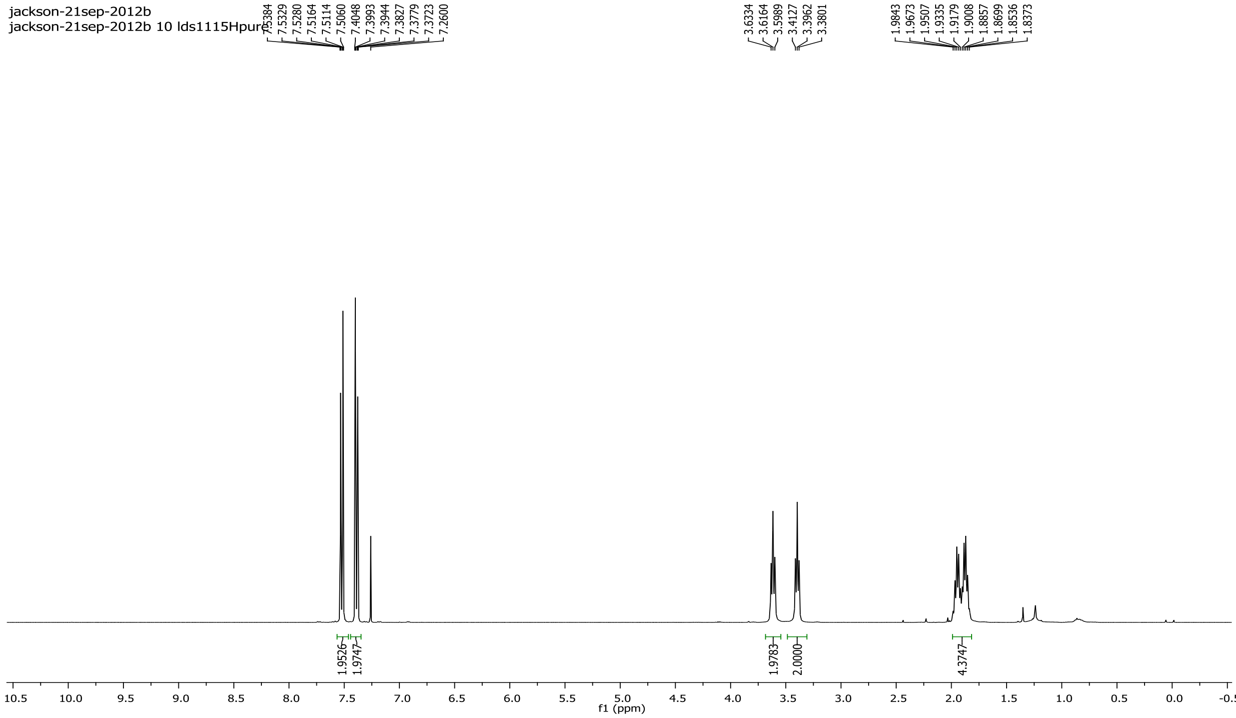






O
N
Br

4b



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jackson-21sep-2012b 10 lds1115Hpure
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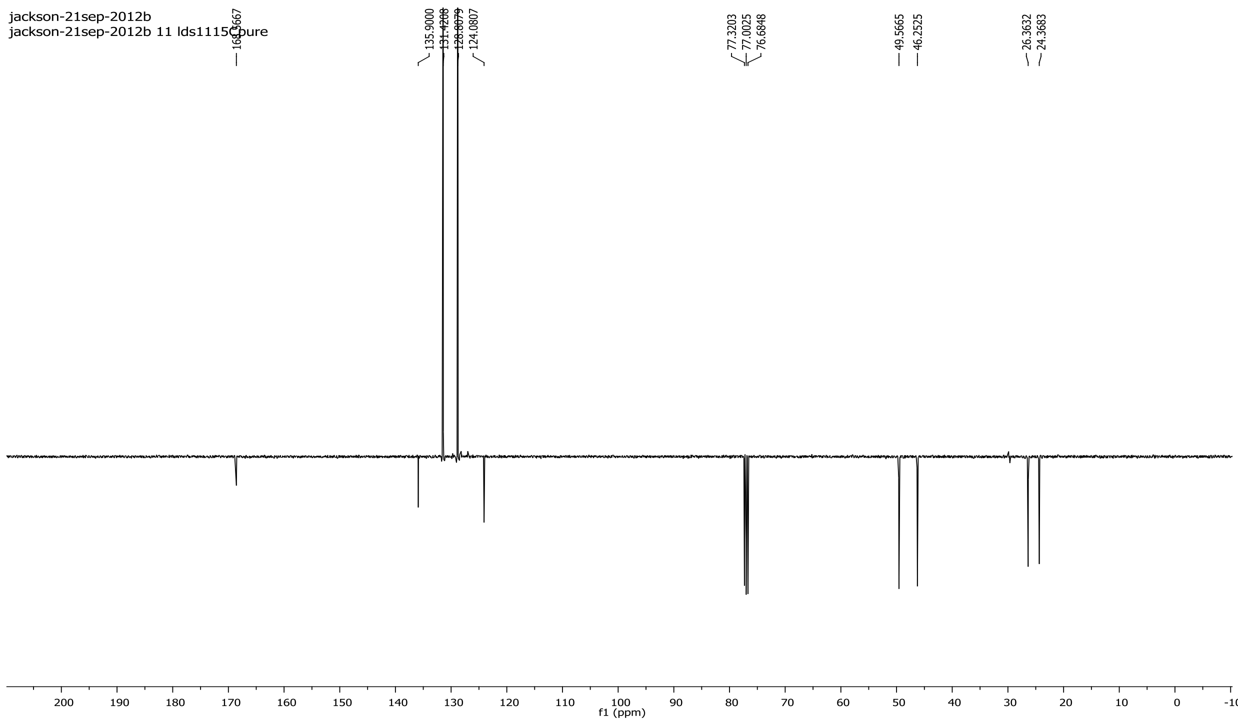
7.5280
7.5164
7.5114
7.5060
7.4048
7.3993
7.3944
7.3827
7.3779
7.3723
7.2600
3.6334
3.6164
3.5989
3.4127
3.3962
3.3801
1.9843
1.9673
1.9507
1.9335
1.9179
1.9008
1.8857
1.8699
1.8536
1.8373
1.9526
1.9747
1.9783
2.0000
4.3747
f1 (ppm)



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jackson-21sep-2012b 11 lds1115Cpure
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76.6848
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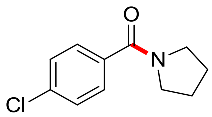
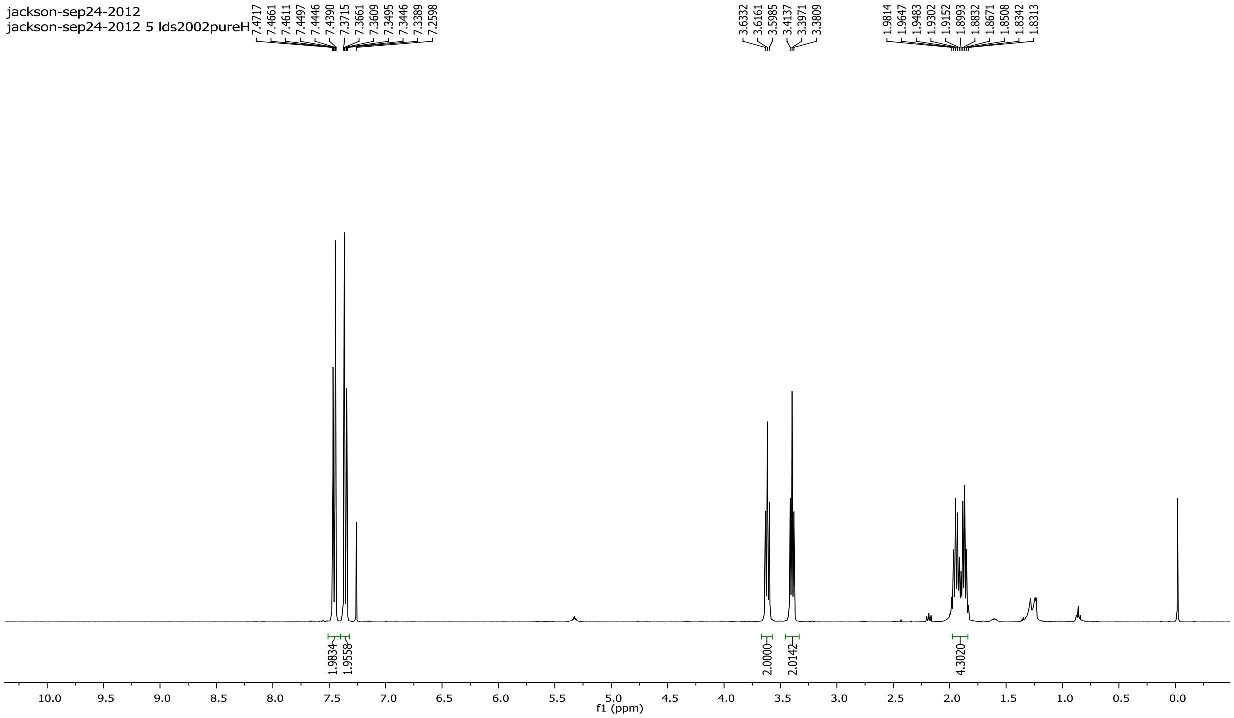
46.2525
26.3632
24.3683
f1 (ppm)


O
N
Cl

4c


jackson-sep24-2012
jackson-sep24-2012 5 lds2002pureH
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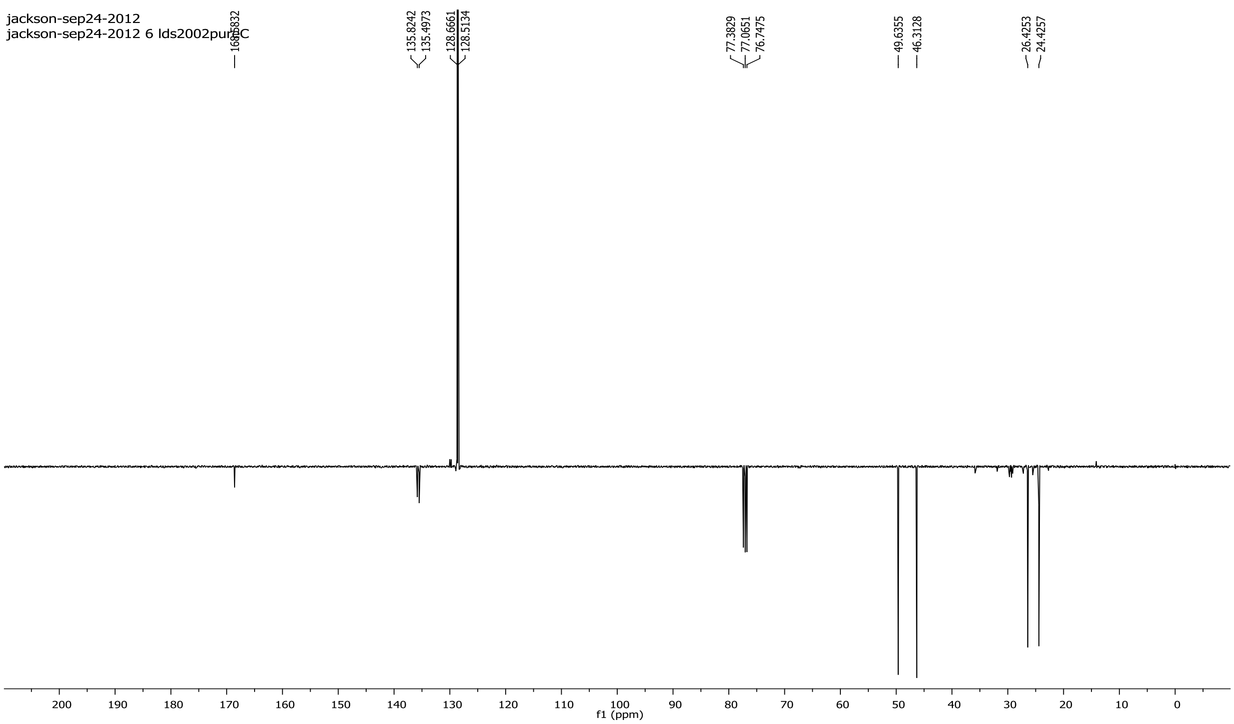
7.4611
7.4497
7.4446
7.4390
7.3715
7.3661
7.3609
7.3495
7.3446
7.3389
7.2598
3.6332
3.6161
3.5985
3.4137
3.3971
3.3809
1.9814
1.9647
1.9483
1.9302
1.9152
1.8993
1.8832
1.8671
1.8508
1.8342
1.8313
1.9834
1.9558
2.0000
2.0142
4.3020
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


jackson-sep24-2012
jackson-sep24-2012 6 lds2002pureC
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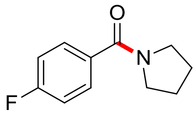
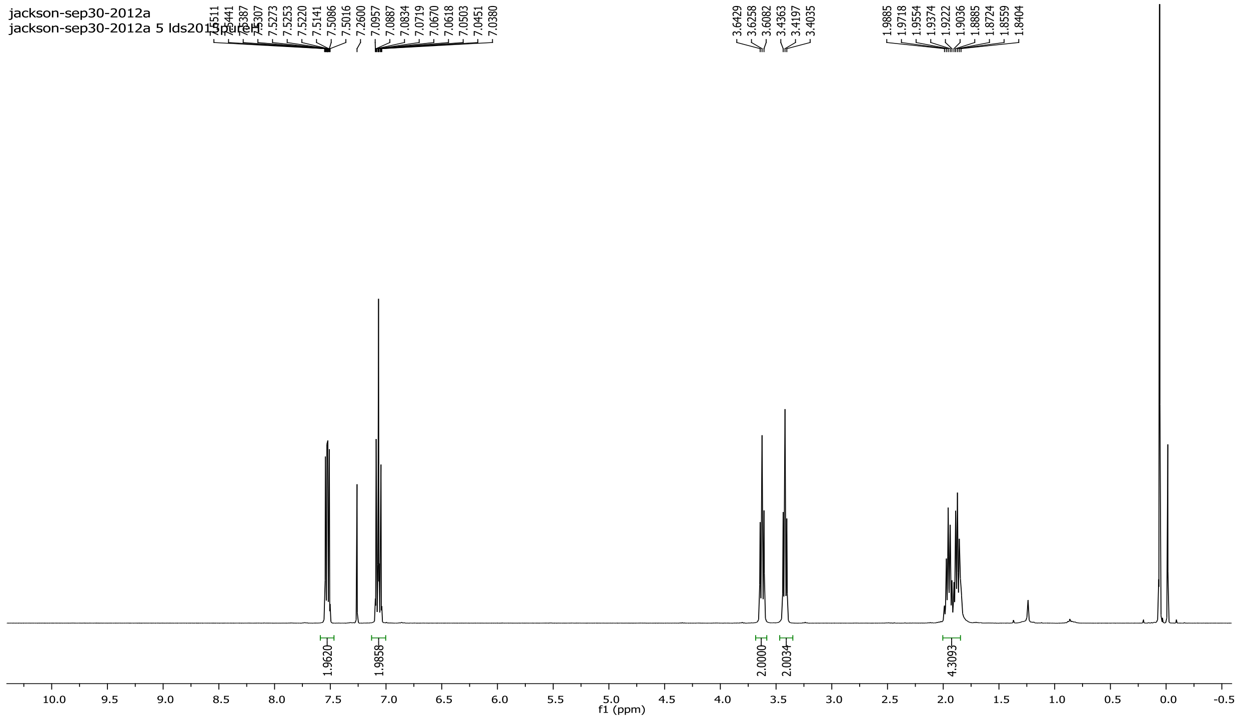
135.4973
128.6661
128.5134
77.3829
77.0651
76.7475
49.6355
46.3128
26.4253
24.4257
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4d



jackson-sep30-2012a
jackson-sep30-2012a 5 lds2015pureH
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7.5273
7.5253
7.5220
7.5141
7.5086
7.5016
7.2600
7.0957
7.0887
7.0834
7.0719
7.0670
7.0618
7.0503
7.0451
7.0380
3.6429
3.6258
3.6082
3.4363
3.4197
3.4035
1.9885
1.9718
1.9554
1.9374
1.9222
1.9036
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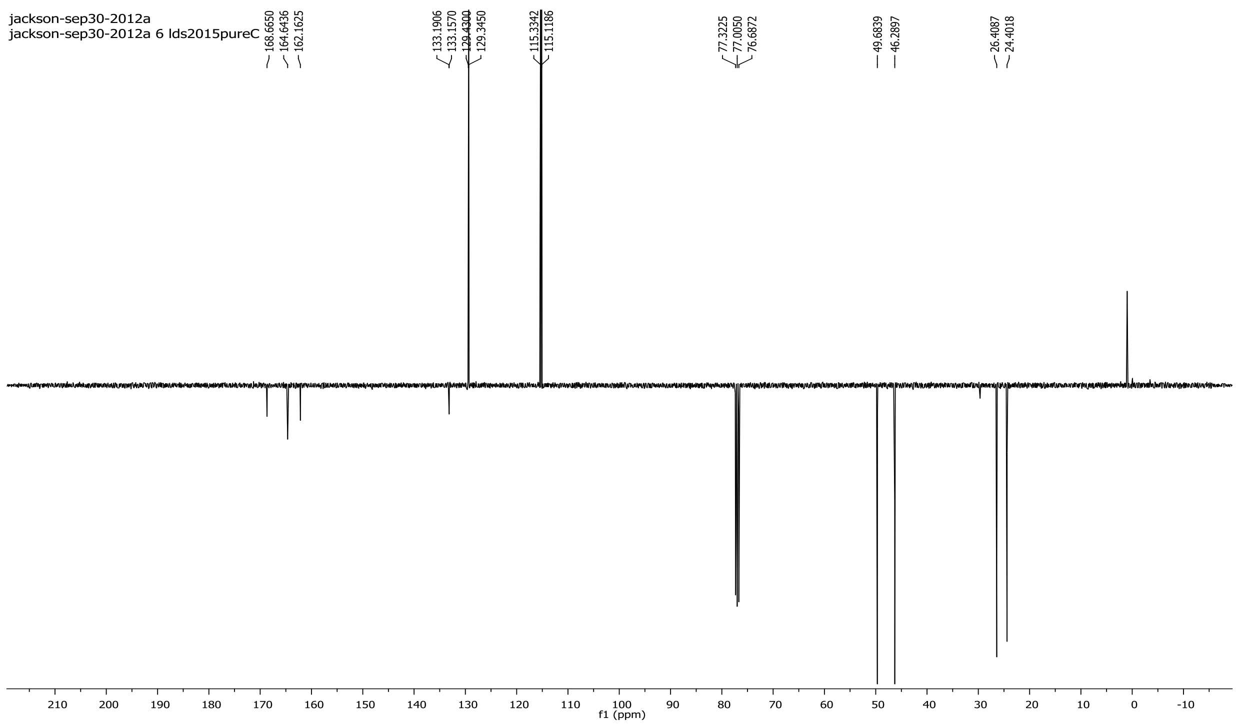
4.3093
f1 (ppm)



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jackson-sep30-2012a 6 lds2015pureC
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162.1625
133.1906
133.1570
129.4300
129.3450
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77.3225
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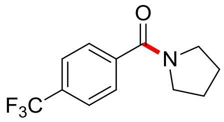
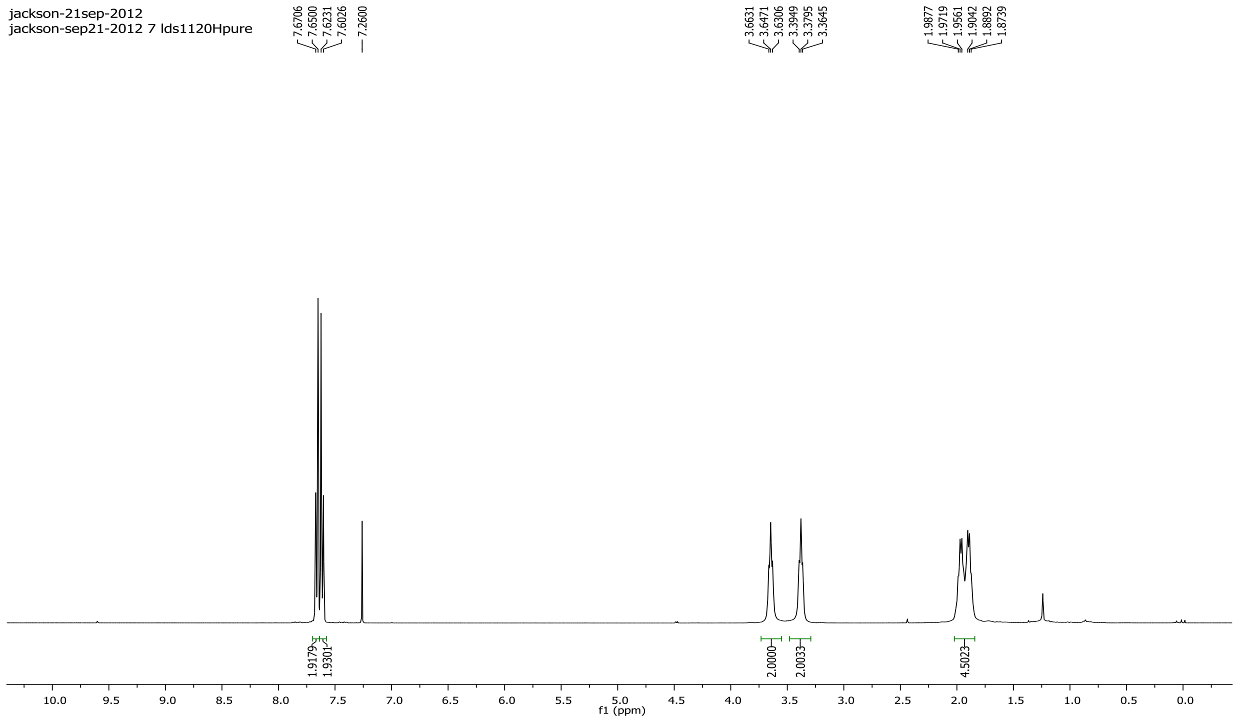
76.6872
49.6839
46.2897
26.4087
24.4018
f1 (ppm)


F3C
O
N

4e


jackson-21sep-2012
jackson-sep21-2012 7 lds1120Hpure
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7.6026
7.2600
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3.6471
3.6306
3.3949
3.3795
3.3645
1.9877
1.9719
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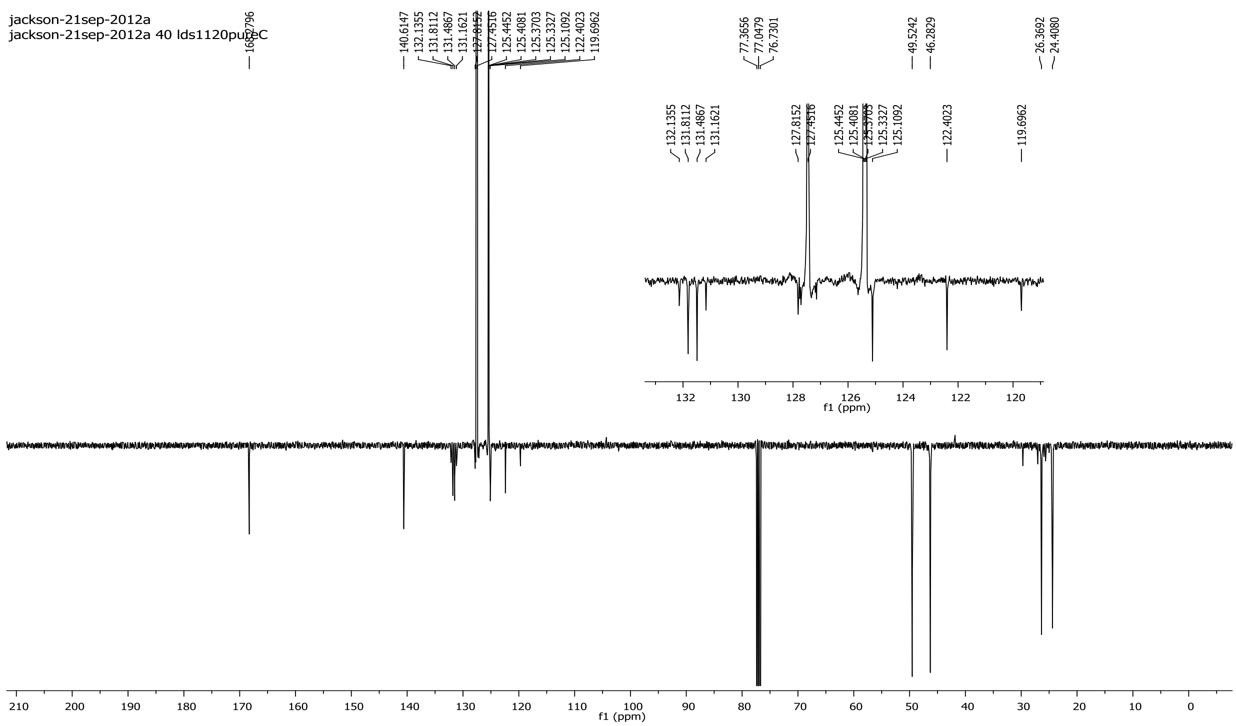
f1 (ppm)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jackson-21sep-2012a 40 lds1120pureC
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125.1092
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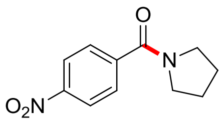
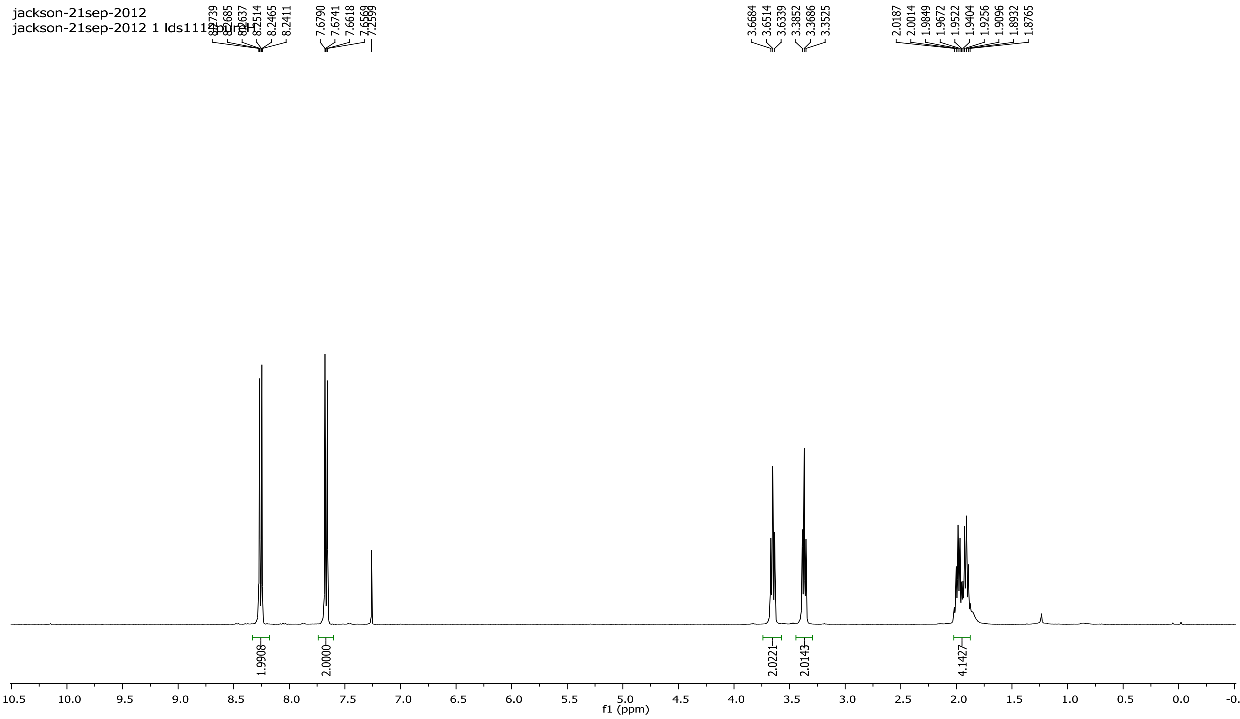
26.3692
24.4080
f1 (ppm)



4f



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3.3686
3.3525
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2.0014
1.9849
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2.0221
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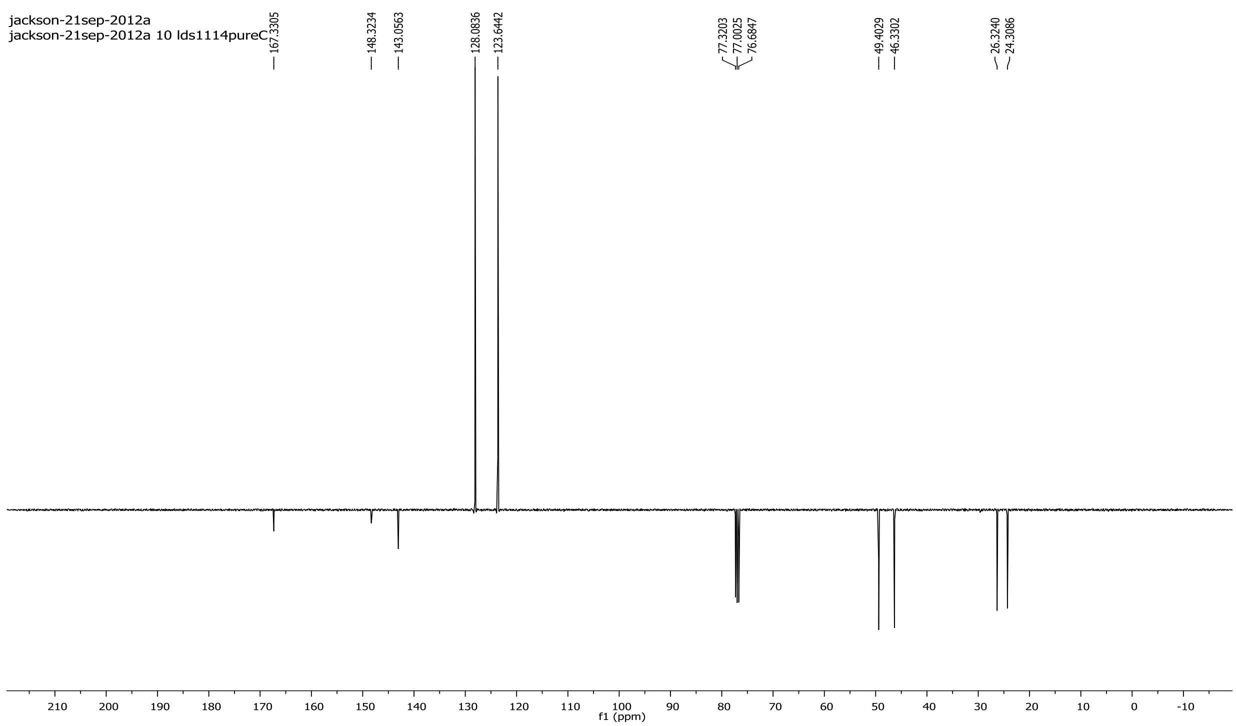
4.1427
f1 (ppm)



jackson-21sep-2012a
jackson-21sep-2012a 10 lds1114pureC
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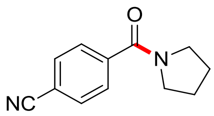
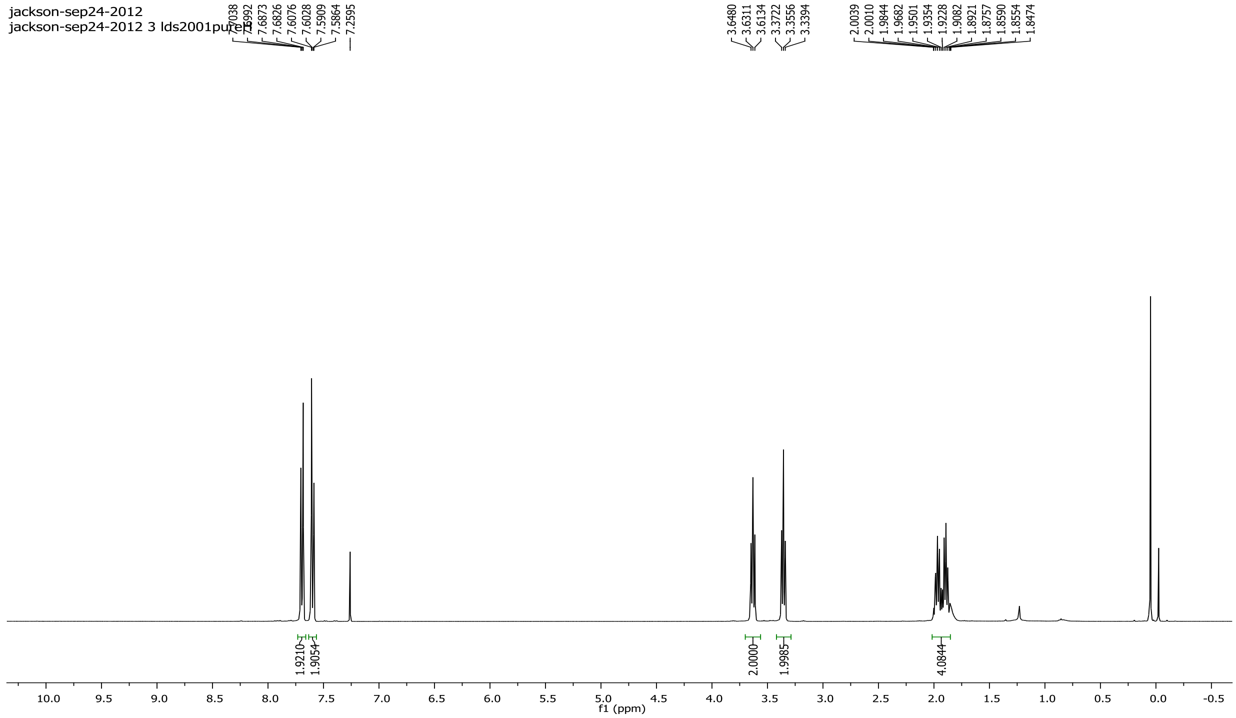
24.3086
f1 (ppm)



NC
O
N

4g



jackson-sep24-2012
jackson-sep24-2012 3 lds2001pureH
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7.6826
7.6076
7.6028
7.5909
7.5864
7.2595
3.6480
3.6311
3.6134
3.3722
3.3556
3.3394
2.0039
2.0010
1.9844
1.9682
1.9501
1.9354
1.9228
1.9082
1.8921
1.8757
1.8590
1.8554
1.8474
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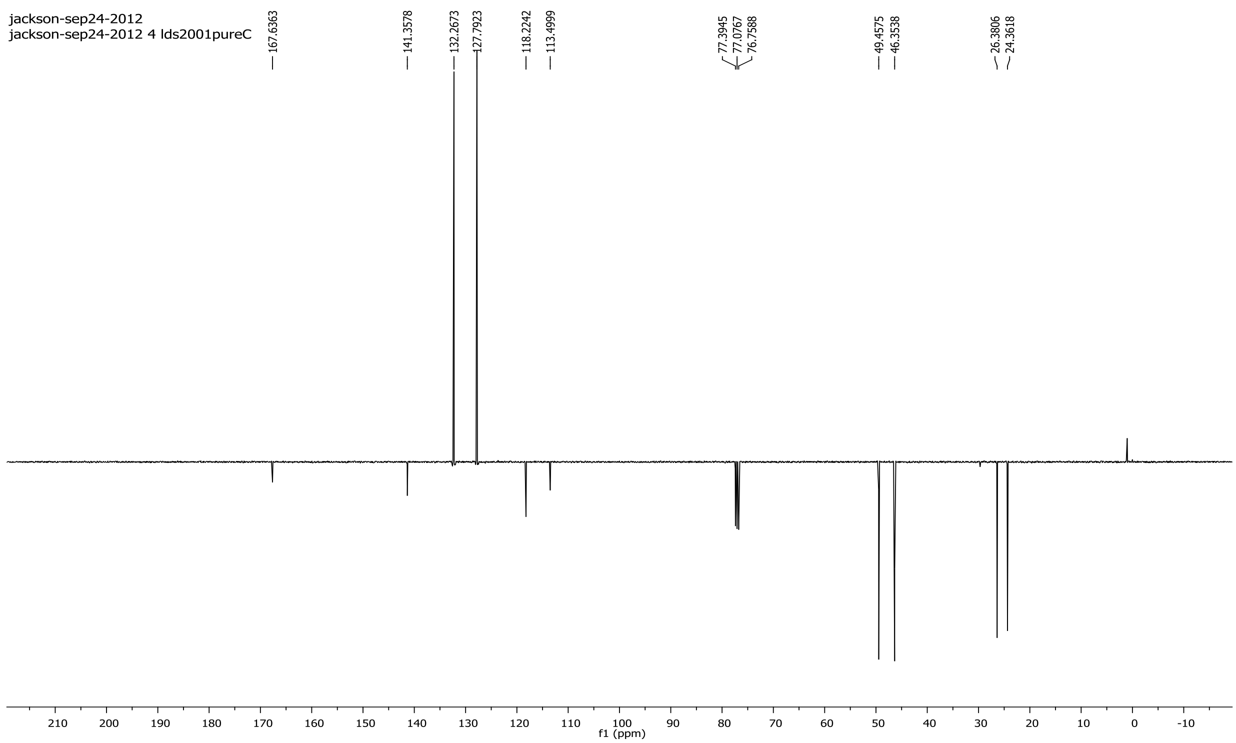
1.9054
2.0000
1.9985
4.0844
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



jackson-sep24-2012
jackson-sep24-2012 4 lds2001pureC
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77.3945
77.0767
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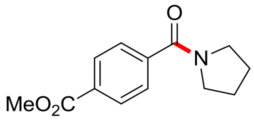
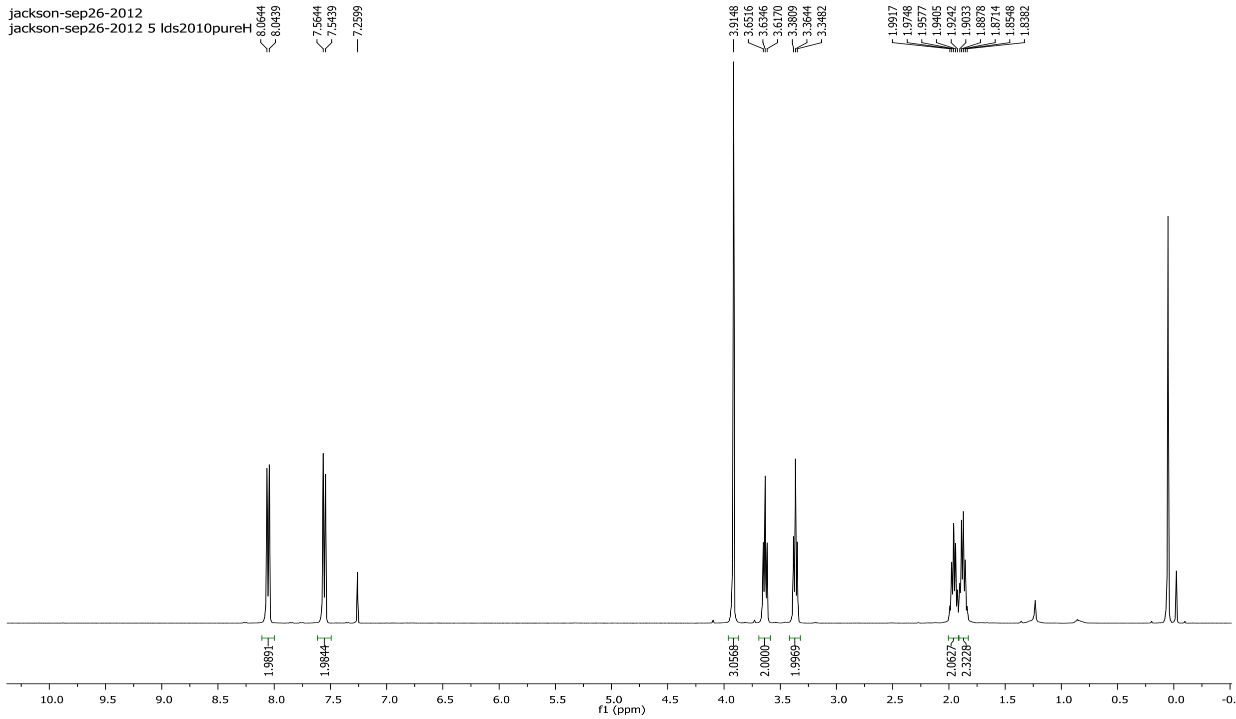
26.3806
24.3618
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



MeO2C
N
O

4h



jackson-sep26-2012
jackson-sep26-2012 5 lds2010pureH
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1.9748
1.9577
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1.9242
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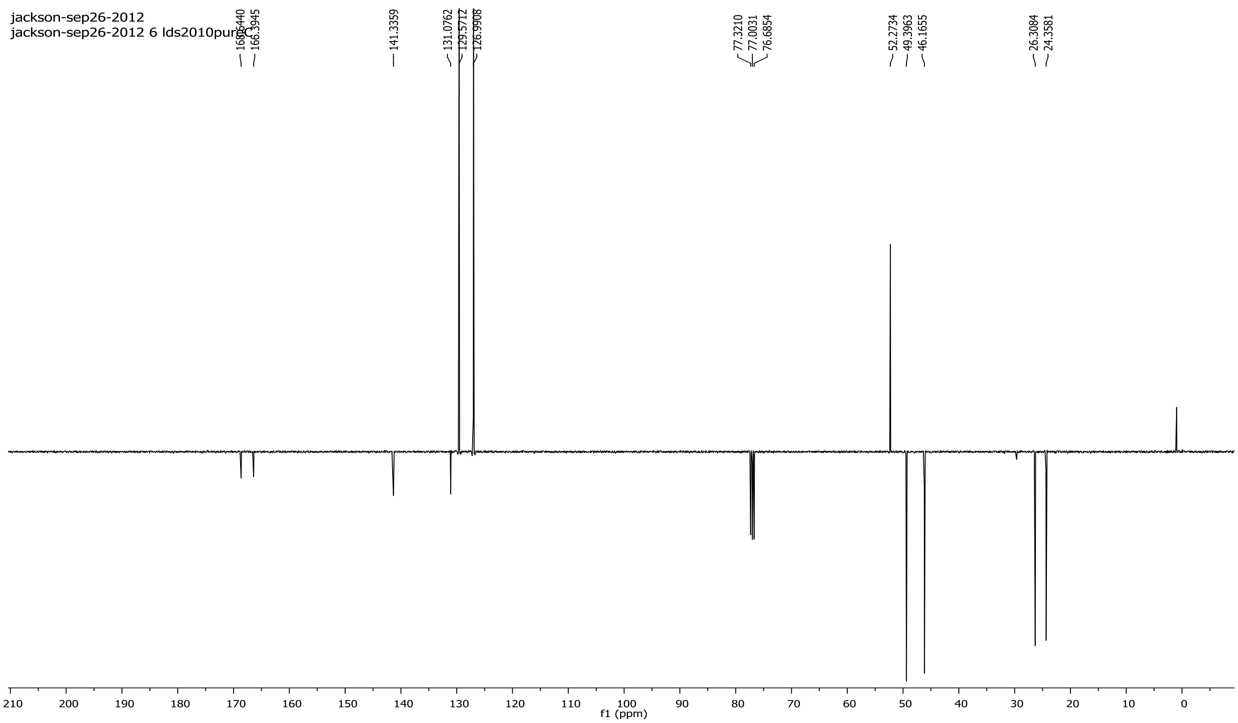
f1 (ppm)



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jackson-sep26-2012 6 lds2010pure
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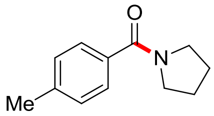
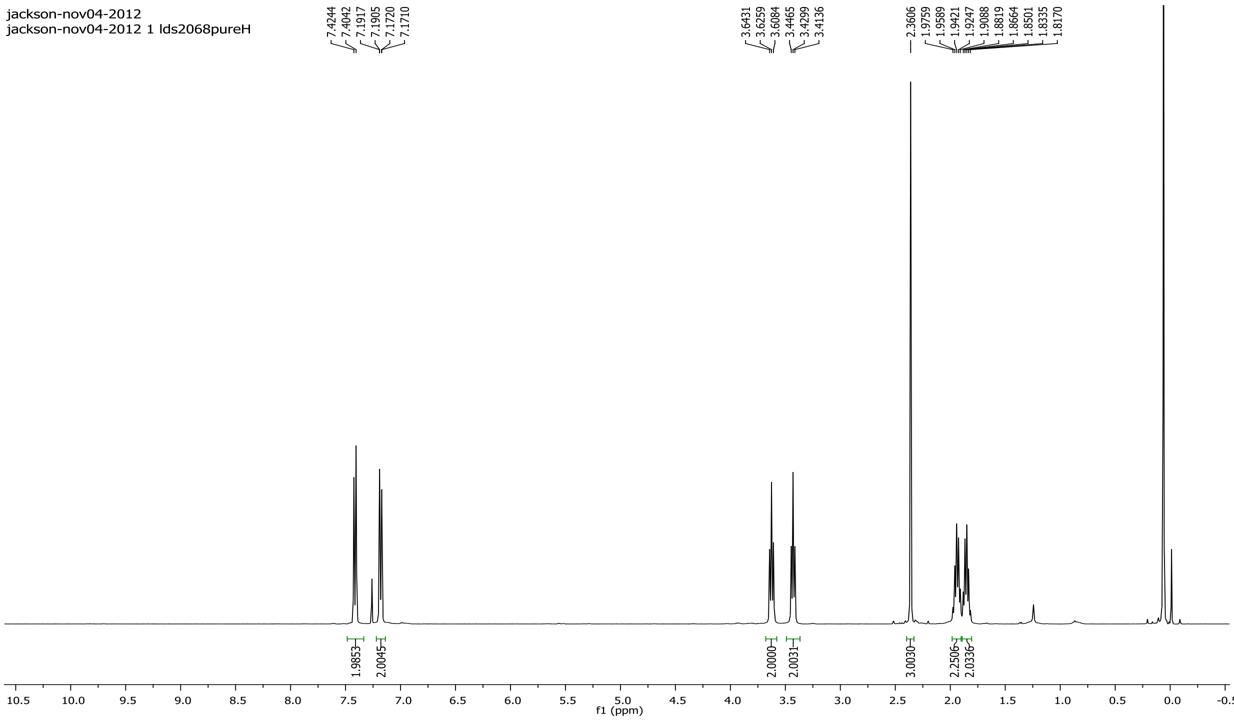
24.3581
f1 (ppm)


O
N
Me

4i


jackson-nov04-2012
jackson-nov04-2012 1 lds2068pureH
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7.1710
3.6431
3.6259
3.6084
3.4465
3.4299
3.4136
2.3606
1.9759
1.9589
1.9421
1.9247
1.9088
1.8819
1.8664
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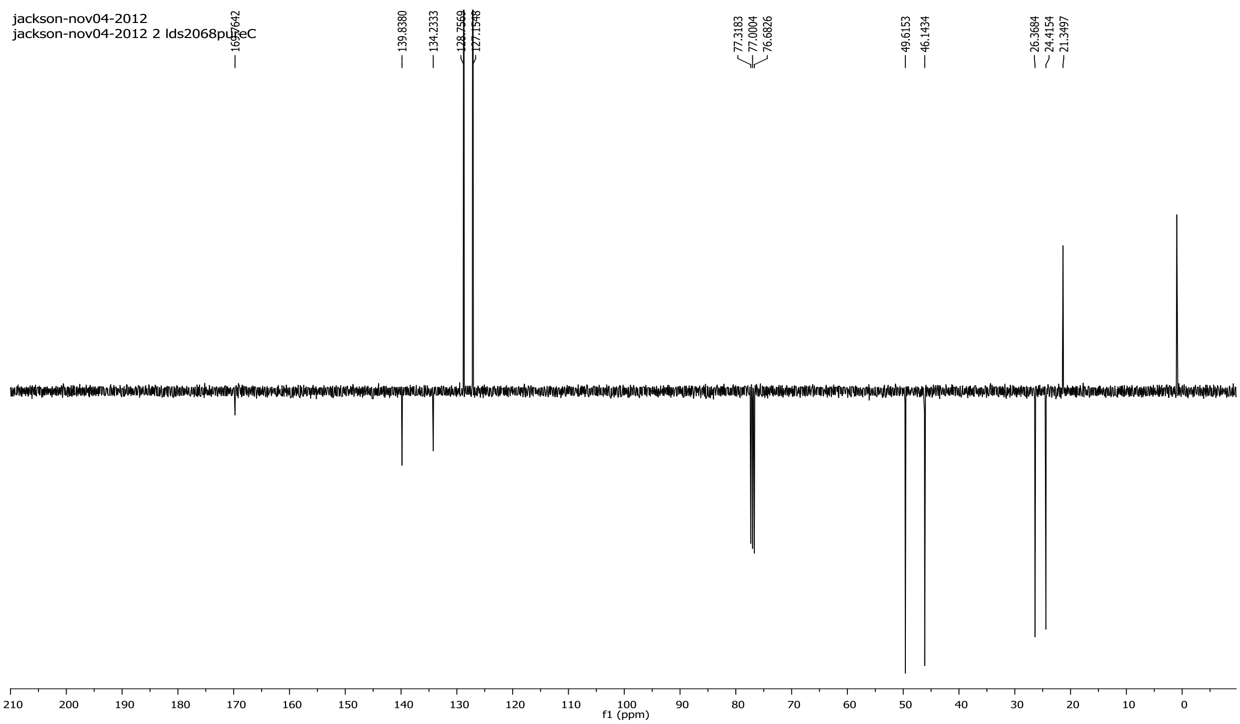
f1 (ppm)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jackson-nov04-2012 2 lds2068pureC
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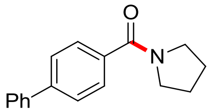
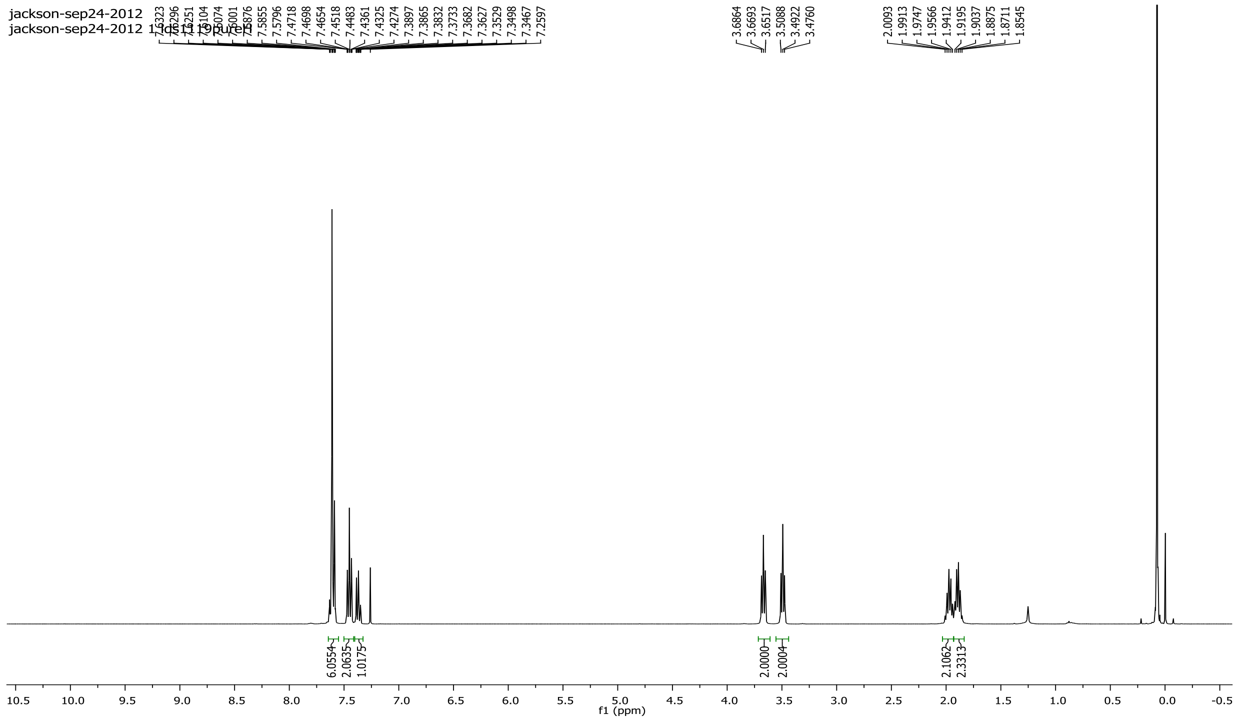
21.3497
f1 (ppm)


O
N
Ph

4j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1.9913
1.9747
1.9566
1.9412
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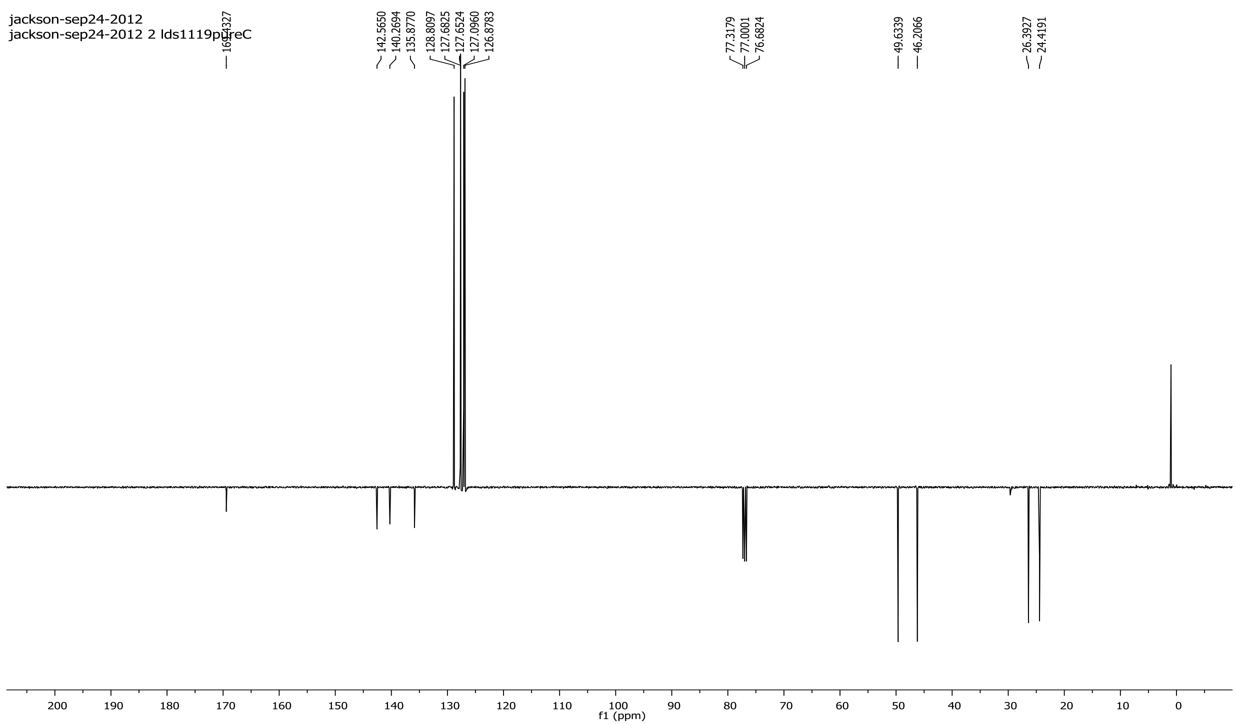
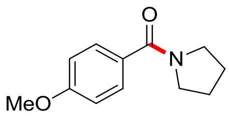
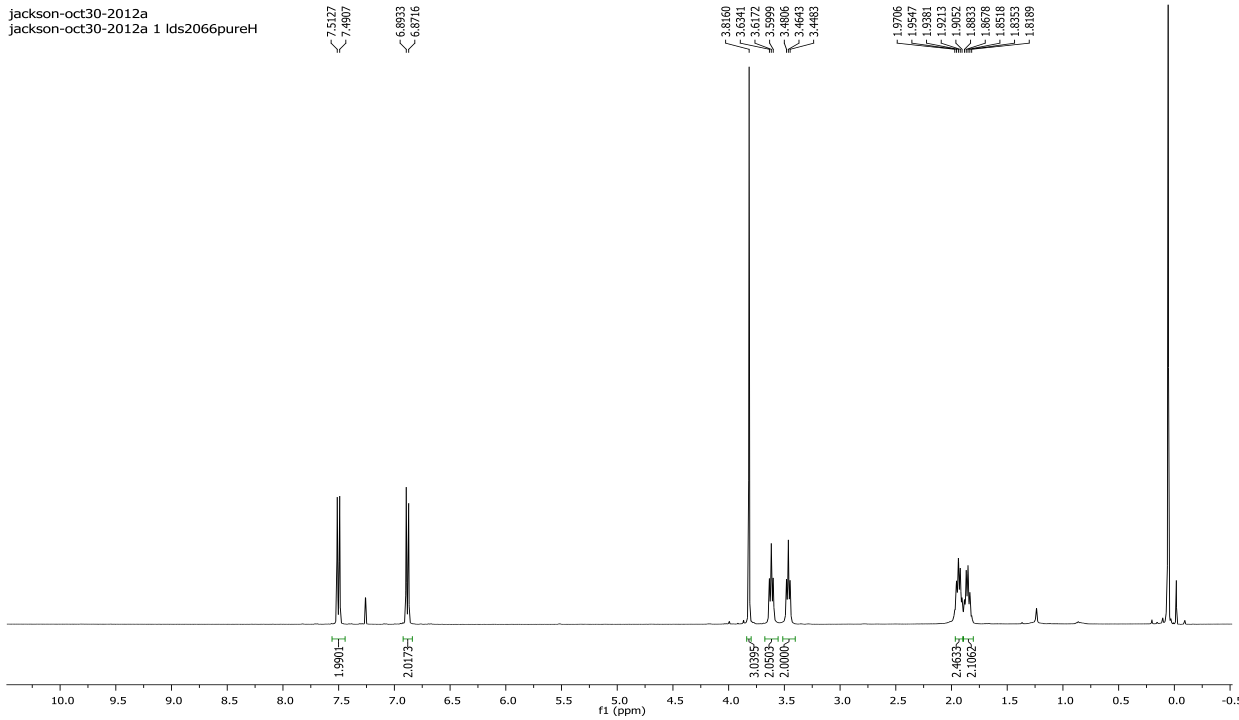
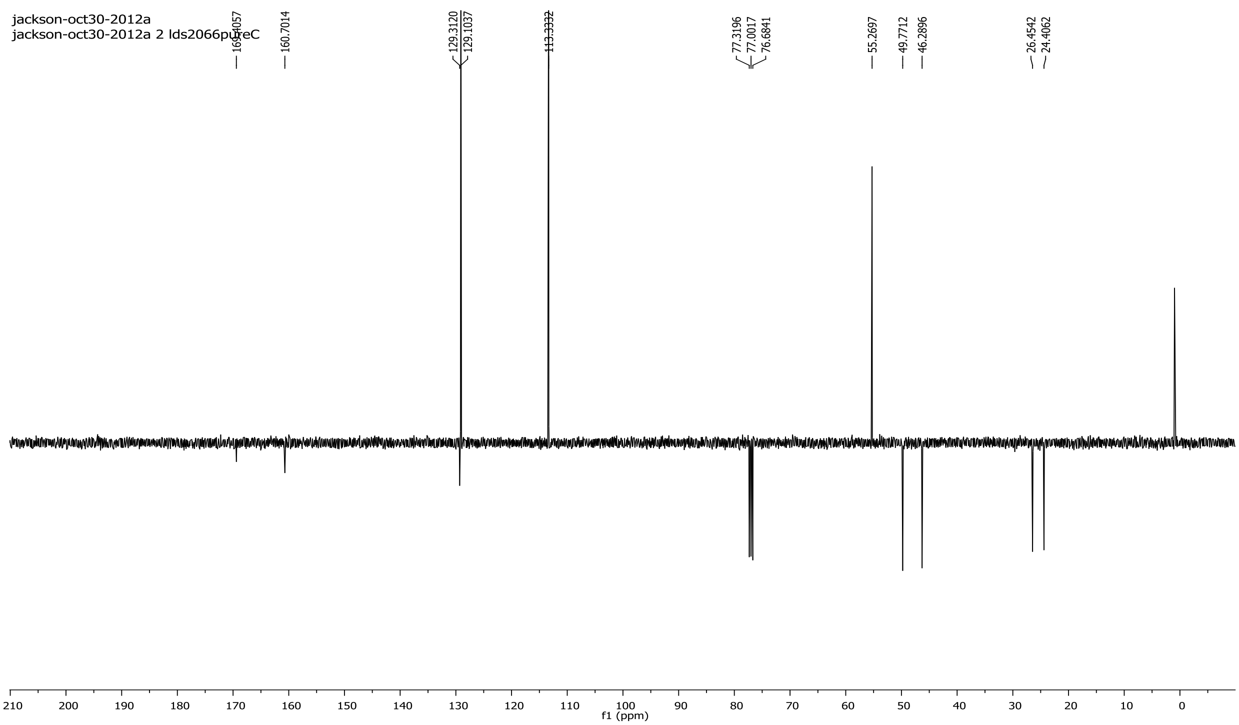
1.8711
1.8545
6.0554
2.0635
1.0175
2.0000
2.0004
2.1062
2.3313
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

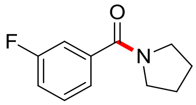

jackson-sep24-2012
142.5650
140.2694
135.8770
128.8097
127.6825
127.6524
127.0960
126.8783
77.3179
77.0001
76.6824
49.6339
46.2066
26.3927
24.4191
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
MeO

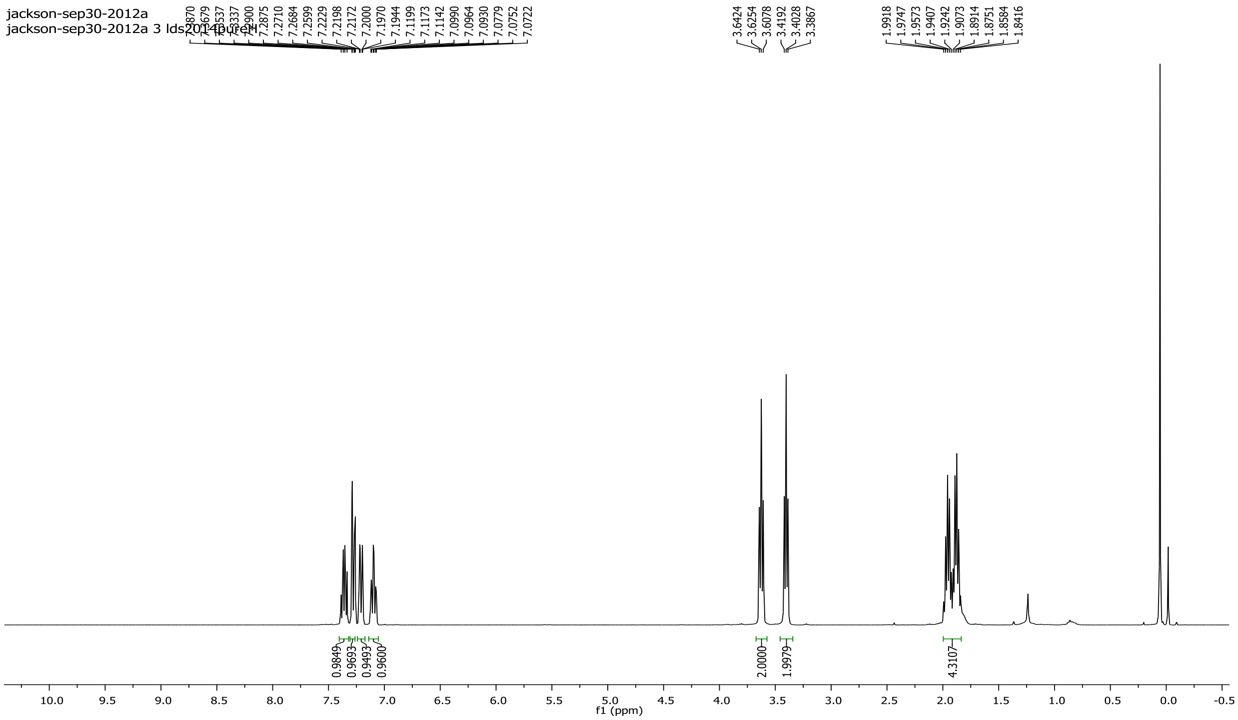
4k


jackson-oct30-2012a
jackson-oct30-2012a 1 lds2066pureH
7.5127
7.4907
6.8933
6.8716
3.8160
3.6341
3.6172
3.5999
3.4806
3.4643
3.4483
1.9706
1.9547
1.9381
1.9213
1.9052
1.8833
1.8678
1.8518
1.8353
1.8189
1.9901
2.0173
3.0395
2.0503
2.0000
2.4633
2.1062
f1 (ppm)

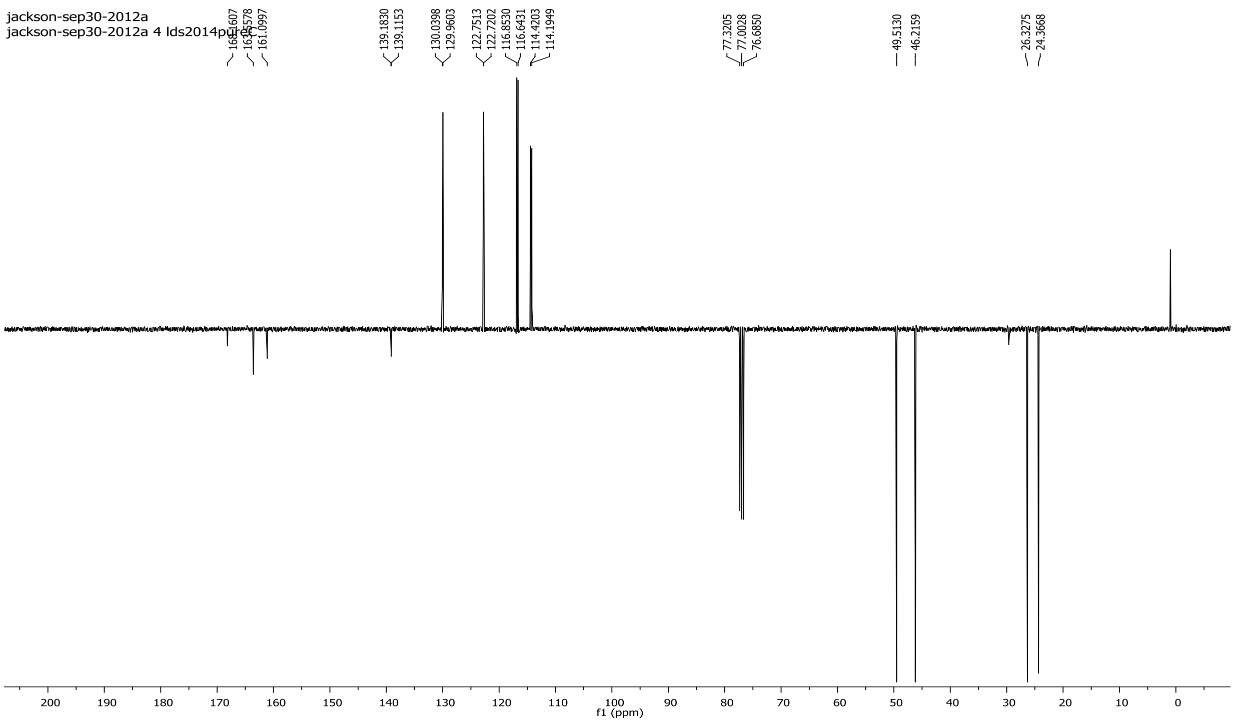

jackson-oct30-2012a
jackson-oct30-2012a 2 lds2066pureC
160.7014
129.3120
129.1037
77.3196
77.0017
76.6841
55.2697
49.7712
46.2896
26.4542
24.4062
f1 (ppm)



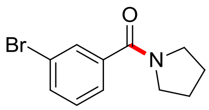
4l



jackson-sep30-2012a
7.2710
7.2684
7.2599
7.2229
7.2198
7.2172
7.2000
7.1970
7.1944
7.1199
7.1173
7.1142
7.0990
7.0964
7.0930
7.0779
7.0752
7.0722
3.6424
3.6254
3.6078
3.4192
3.4028
3.3867
1.9918
1.9747
1.9573
1.9407
1.9242
1.9073
1.8914
1.8751
1.8584
1.8416
0.9849
0.9693
0.9493
0.9600
2.0000
1.9979
4.3107
f1 (ppm)

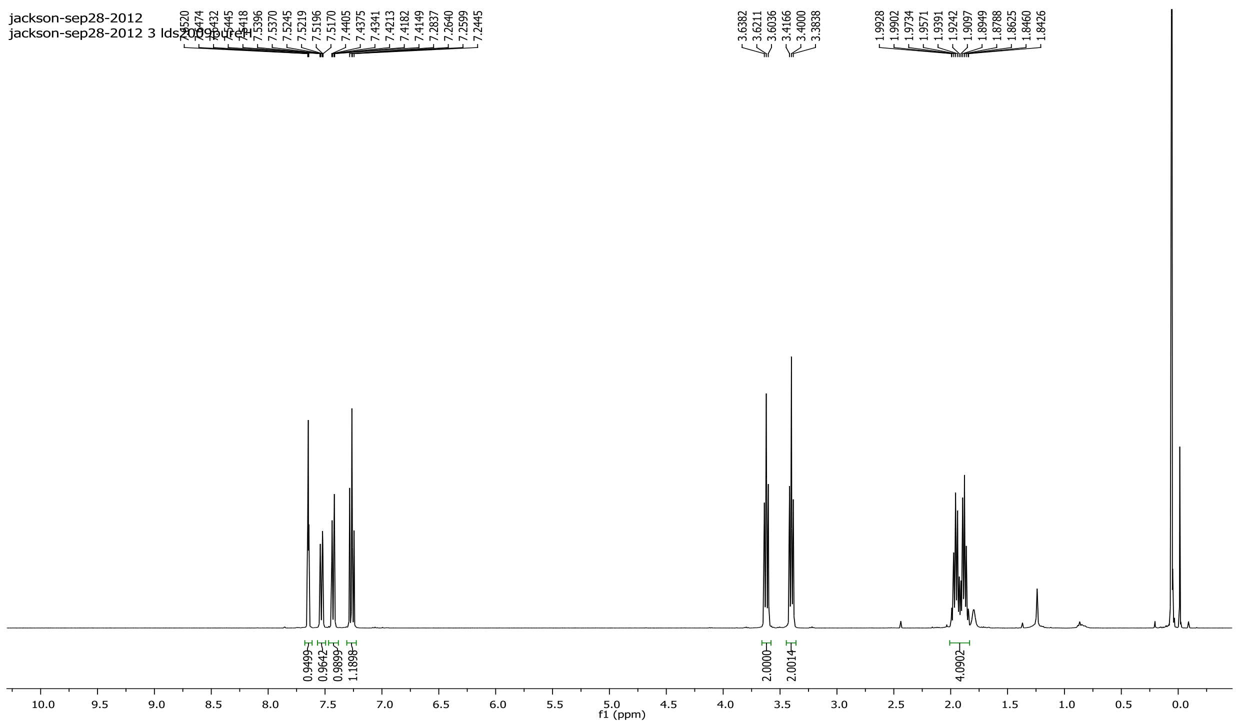


jackson-sep30-2012a
161.0997
139.1830
139.1153
130.0398
129.9603
122.7513
122.7202
116.8530
116.6431
114.4203
114.1949
77.3205
77.0028
76.6850
49.5130
46.2159
26.3275
24.3668
f1 (ppm)

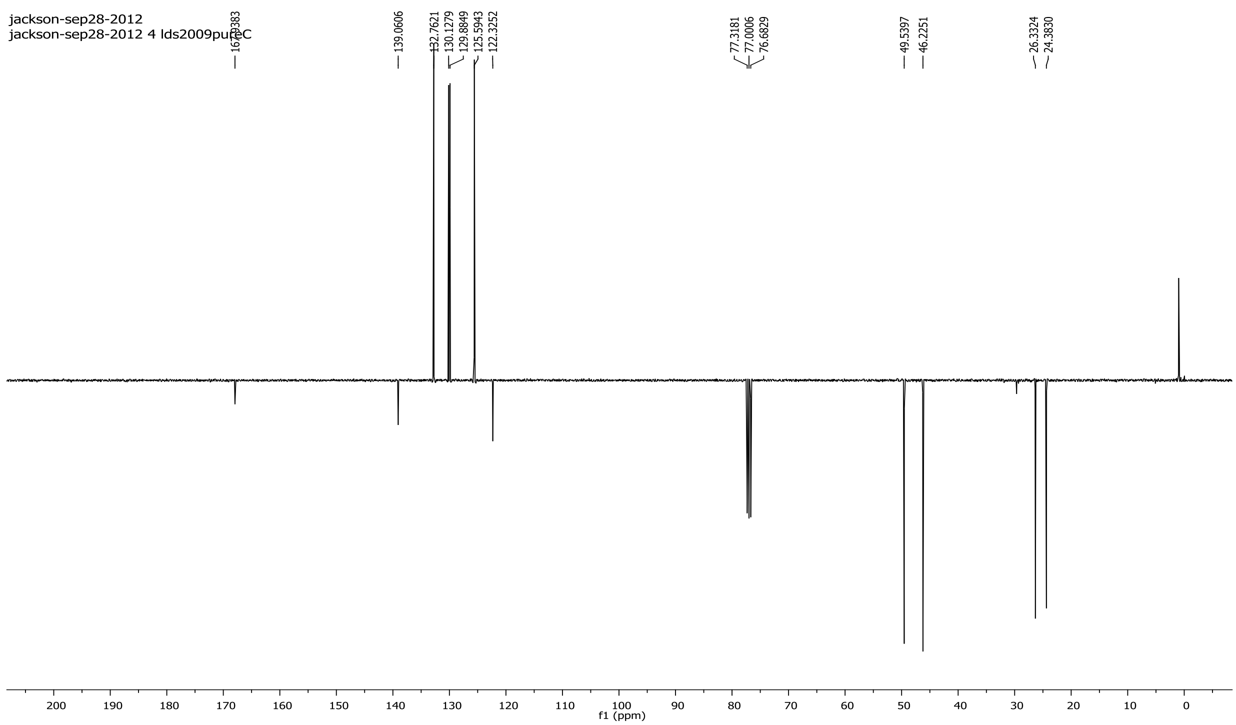


Br
O
N

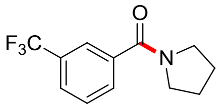
4m



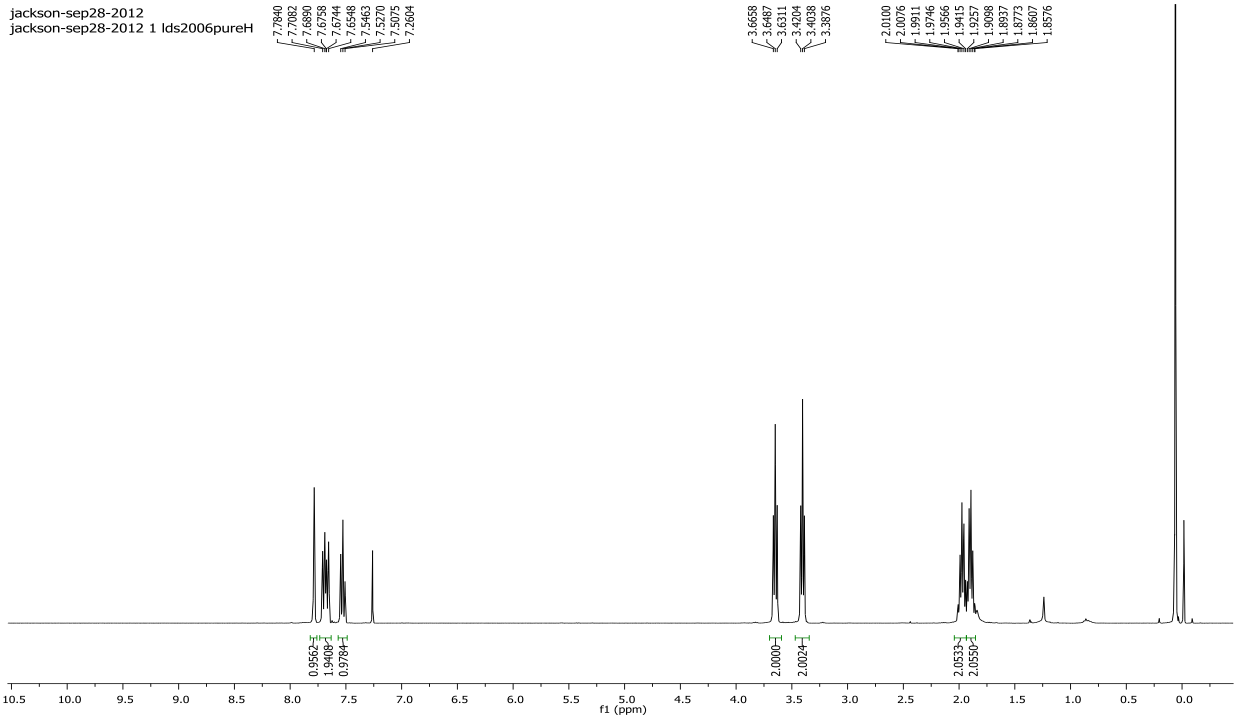
jackson-sep28-2012
jackson-sep28-2012 3 lds2009pureH
7.6474
7.5445
7.5418
7.5396
7.5370
7.5245
7.5219
7.5196
7.5170
7.4405
7.4375
7.4341
7.4213
7.4182
7.4149
7.2837
7.2640
7.2599
7.2445
3.6382
3.6211
3.6036
3.4166
3.4000
3.3838
1.9928
1.9902
1.9734
1.9571
1.9391
1.9242
1.9097
1.8949
1.8788
1.8625
1.8460
1.8426
0.9499
0.9642
0.9899
1.1898
2.0000
2.0014
4.0902
f1 (ppm)

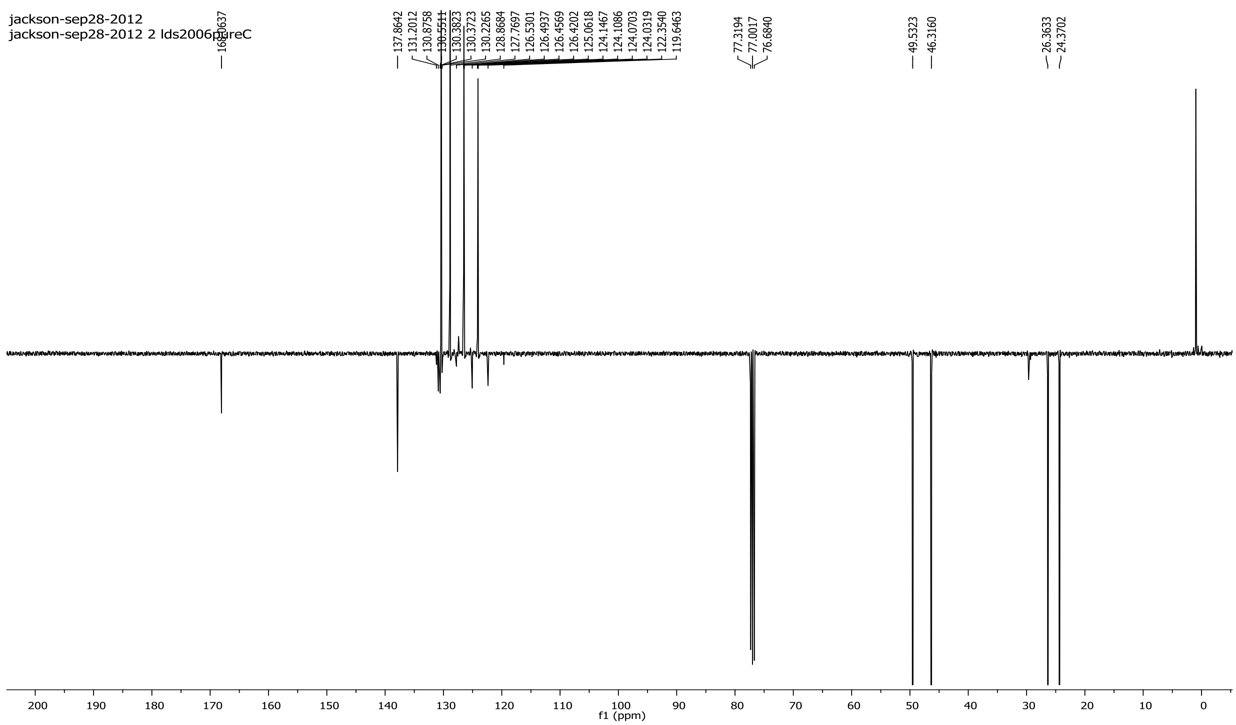


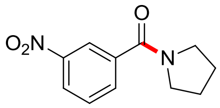
jackson-sep28-2012
jackson-sep28-2012 4 lds2009pureC
139.0606
132.7621
130.1279
129.8849
125.5943
122.3252
77.3181
77.0006
76.6829
49.5397
46.2251
26.3324
24.3830
f1 (ppm)


O
F3C
N

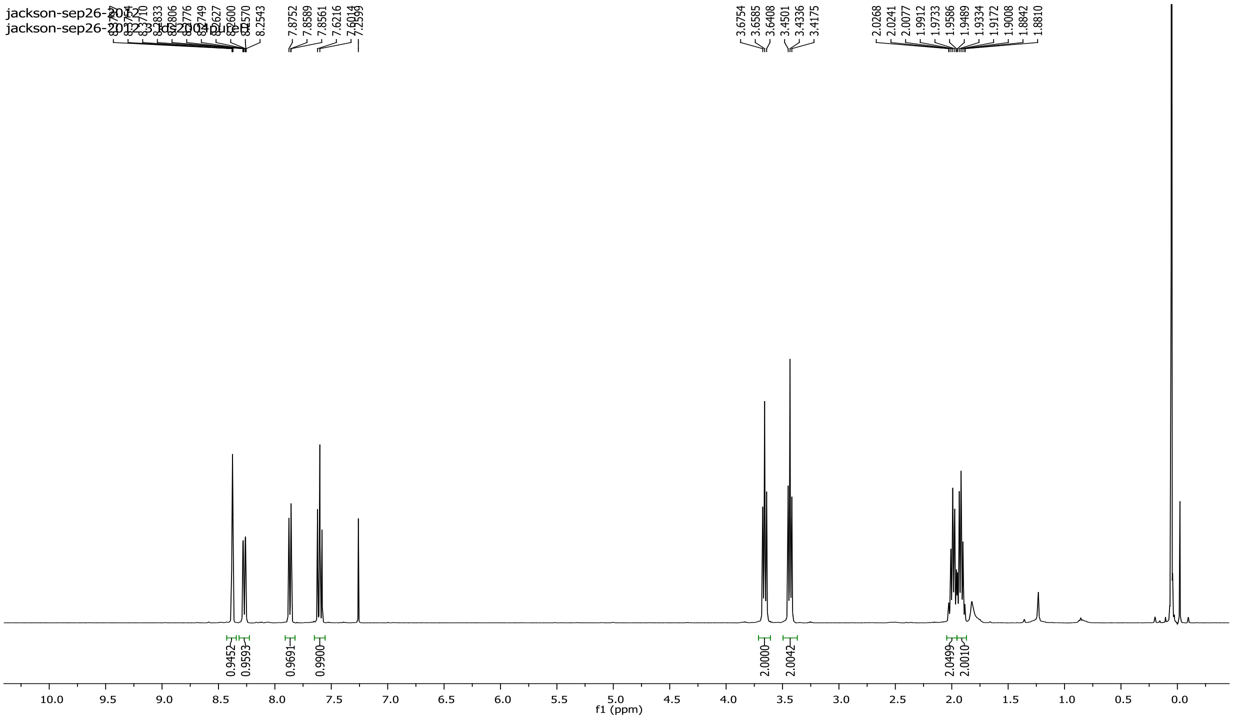
4na

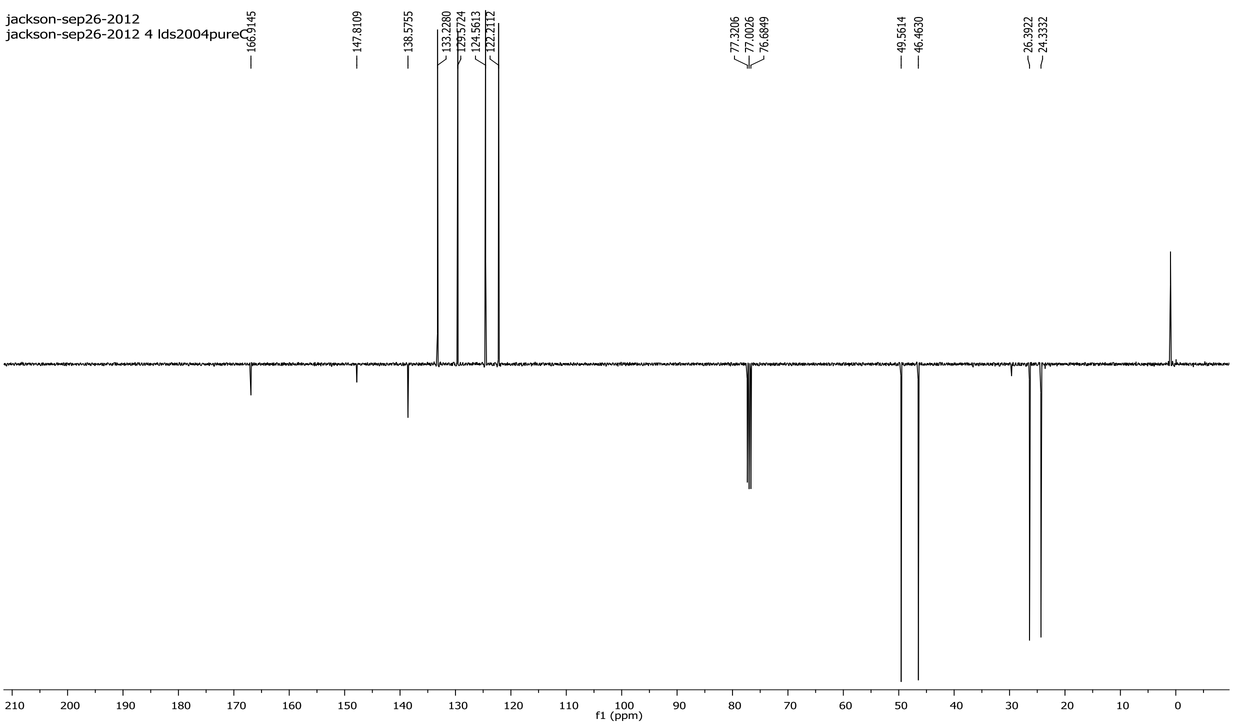

jackson-sep28-2012
jackson-sep28-2012 1 lds2006pureH
7.7840
7.7082
7.6890
7.6758
7.6744
7.6548
7.5463
7.5270
7.5075
7.2604
3.6658
3.6487
3.6311
3.4204
3.4038
3.3876
2.0100
2.0076
1.9911
1.9746
1.9566
1.9415
1.9257
1.9098
1.8937
1.8773
1.8607
1.8576
0.9562
1.9408
0.9784
2.0000
2.0024
2.0533
2.0550
f1 (ppm)

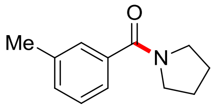

jackson-sep28-2012
jackson-sep28-2012 2 lds2006pureC
137.8642
131.2012
130.8758
130.5511
130.3823
130.3723
130.2265
128.8684
127.7697
126.5301
126.4937
126.4569
126.4202
125.0618
124.1467
124.1086
124.0703
124.0319
122.3540
119.6463
77.3194
77.0017
76.6840
49.5323
46.3160
26.3633
24.3702
f1 (ppm)


O
O_2N
N

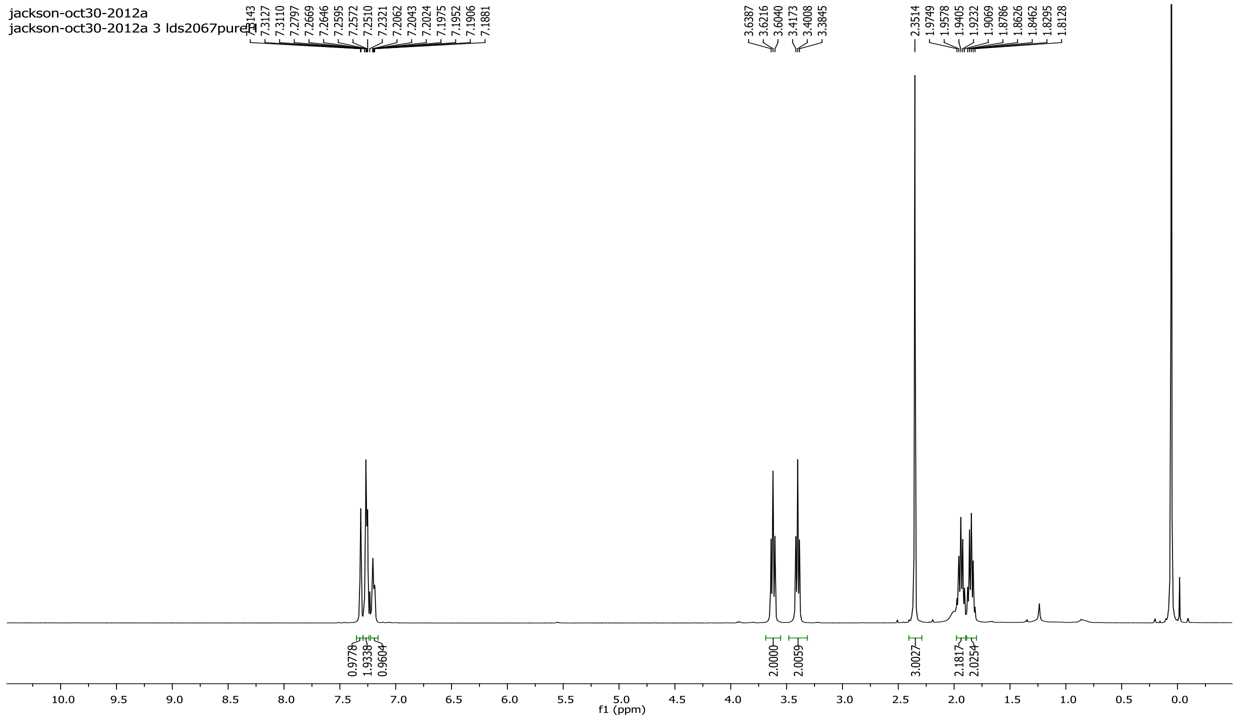
4o

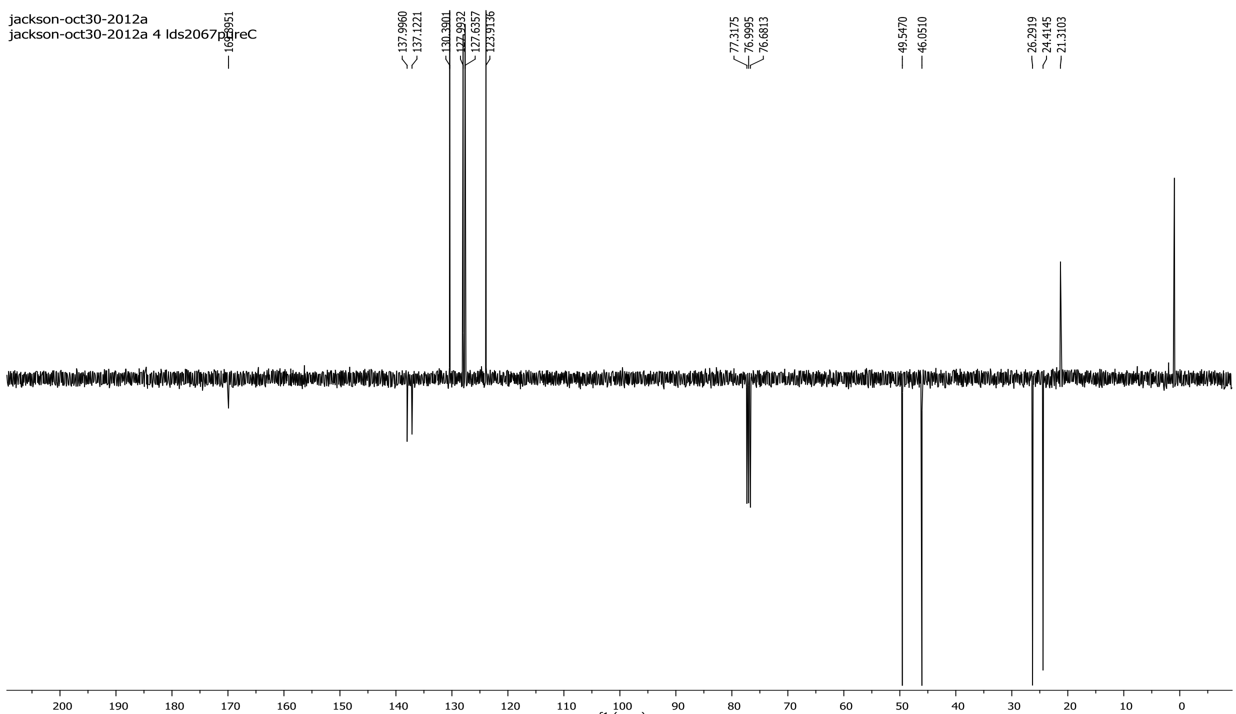

jackson-sep26-2012
8.3833
8.3806
8.3776
8.3749
8.2627
8.2600
8.2570
8.2543
7.8752
7.8589
7.8561
7.6216
7.6014
7.2599
3.6754
3.6585
3.6408
3.4501
3.4336
3.4175
2.0268
2.0241
2.0077
1.9912
1.9733
1.9586
1.9489
1.9334
1.9172
1.9008
1.8842
1.8810
0.9452
0.9593
0.9691
0.9900
2.0000
2.0042
2.0499
2.0010
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

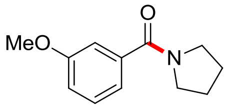

jackson-sep26-2012
jackson-sep26-2012 4 lds2004pureC
166.9145
147.8109
138.5755
133.2280
129.5724
124.5613
122.2112
77.3206
77.0026
76.6849
49.5614
46.4630
26.3922
24.3332
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



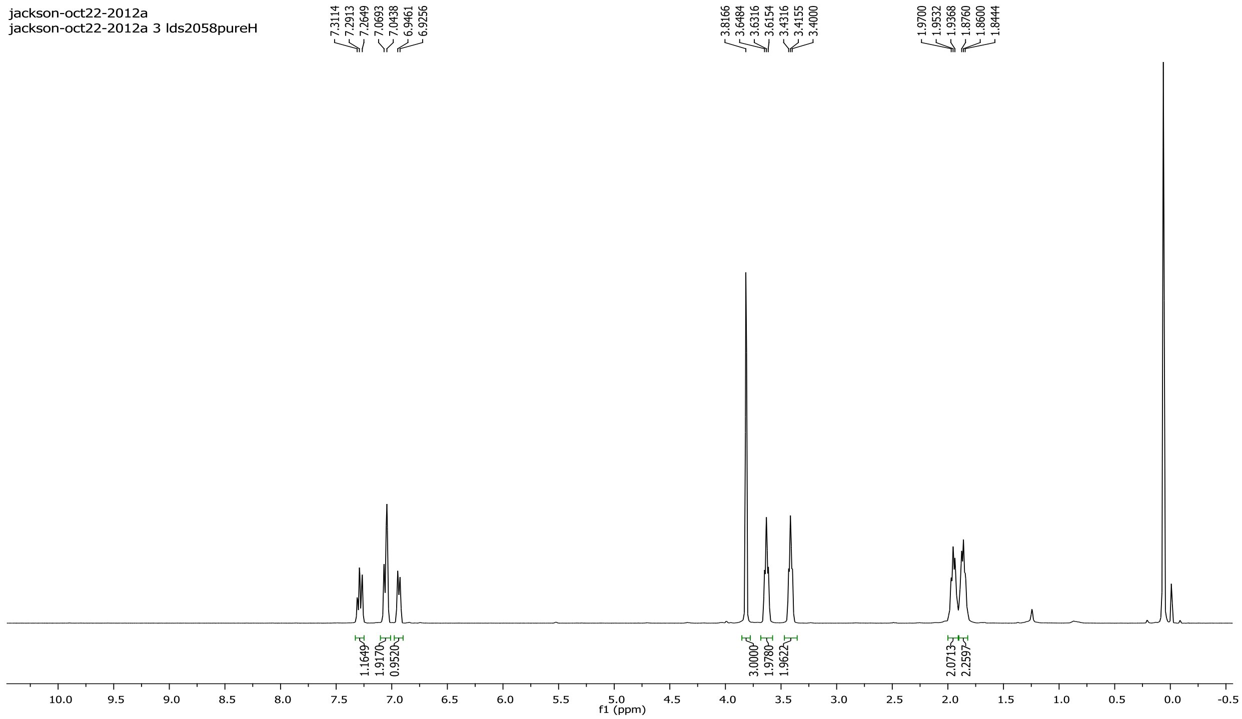
4p

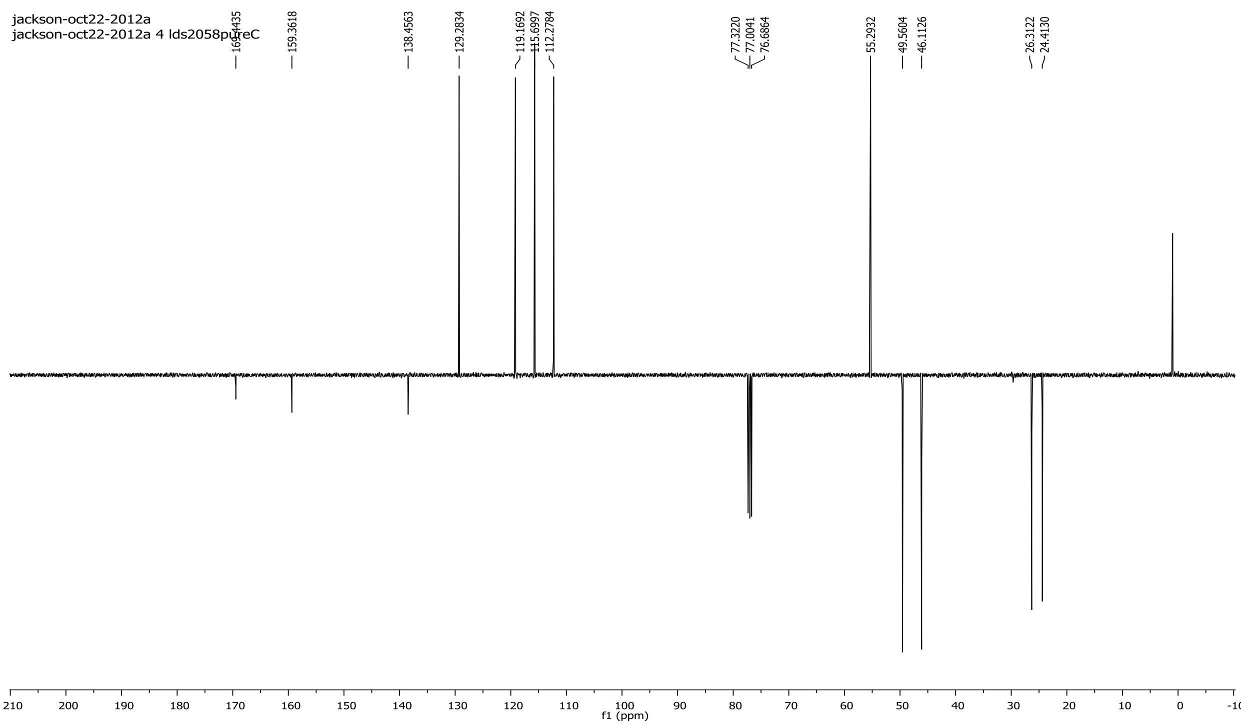

jackson-oct30-2012a
jackson-oct30-2012a 3 lds2067pureH
7.3143 7.3127 7.3110 7.2797 7.2669 7.2646 7.2595 7.2572 7.2510 7.2321 7.2062 7.2043 7.2024 7.1975 7.1952 7.1906 7.1881
3.6387 3.6216 3.6040 3.4173 3.4008 3.3845
2.3514 1.9749 1.9578 1.9405 1.9232 1.9069 1.8786 1.8626 1.8462 1.8295 1.8128
0.9778 1.9338 0.9604
2.0000 2.0059
3.0027
2.1817 2.0254
f1 (ppm)

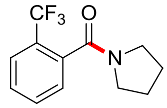

jackson-oct30-2012a
jackson-oct30-2012a 4 lds2067pureC
137.9960 137.1221
130.3901 127.9932 127.6357 123.9136
77.3175 76.9995 76.6813
49.5470 46.0510
26.2919 24.4145 21.3103
f1 (ppm)


MeO
O
N

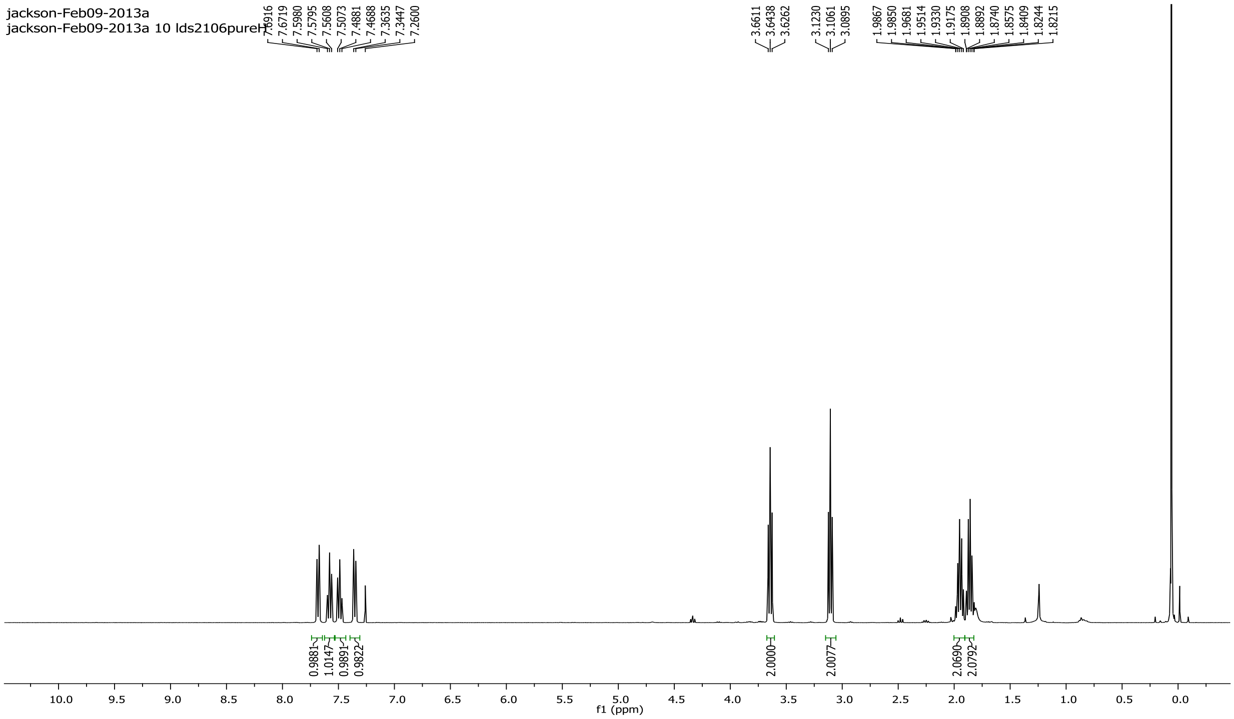
4q

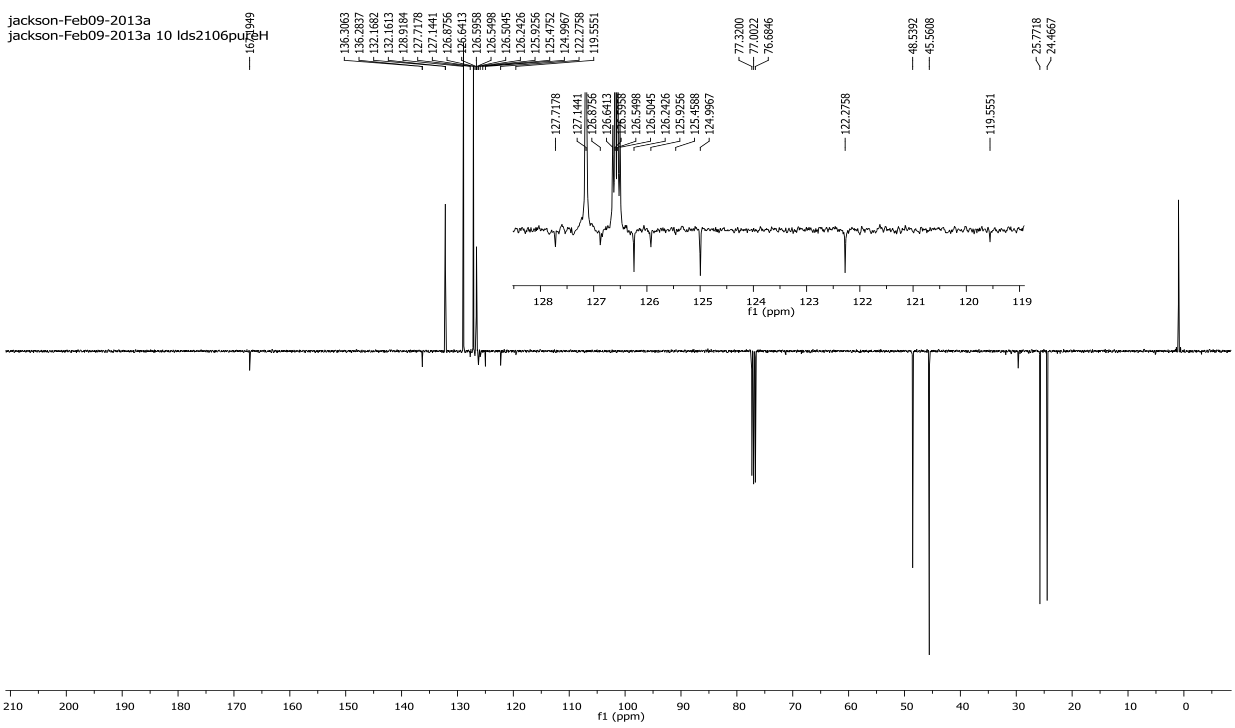

jackson-oct22-2012a
jackson-oct22-2012a 3 lds2058pureH
7.3114
7.2913
7.2649
7.0693
7.0438
6.9461
6.9256
3.8166
3.6484
3.6316
3.6154
3.4316
3.4155
3.4000
1.9700
1.9532
1.9368
1.8760
1.8600
1.8444
1.1649
1.9170
0.9520
3.0000
1.9780
1.9622
2.0713
2.2597
f1 (ppm)

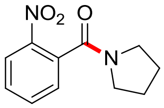

jackson-oct22-2012a
jackson-oct22-2012a 4 lds2058pureC
169.4435
159.3618
138.4563
129.2834
119.1692
115.6997
112.2784
77.3220
77.0041
76.6864
55.2932
49.5604
46.1126
26.3122
24.4130
f1 (ppm)


CF3
O
N

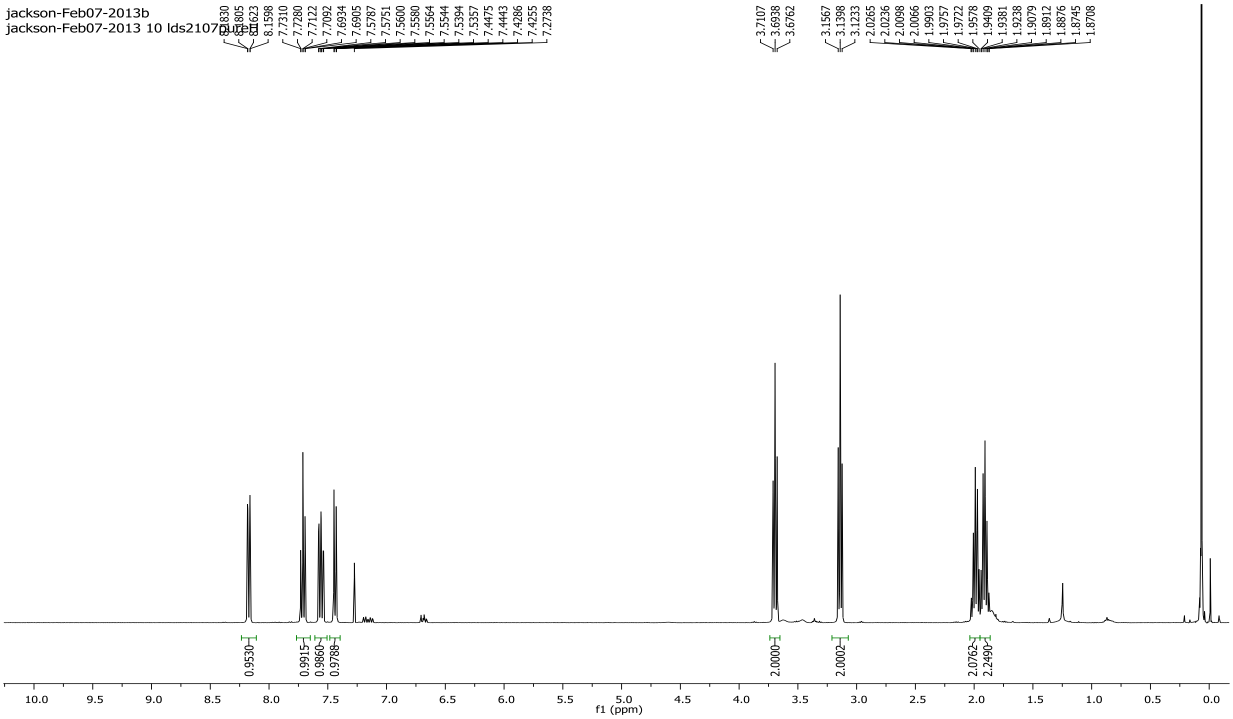
4r

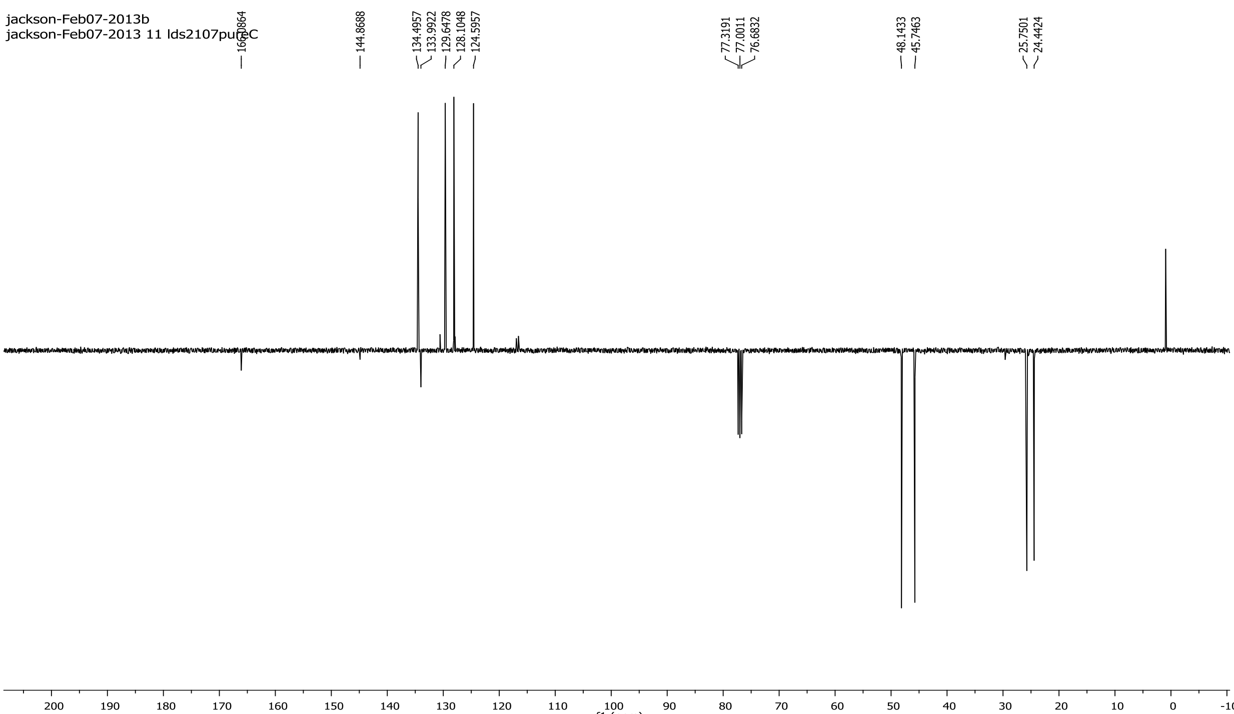

jackson-Feb09-2013a
jackson-Feb09-2013a 10 lds2106pureH
f1 (ppm)

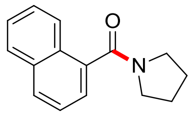

jackson-Feb09-2013a
jackson-Feb09-2013a 10 lds2106pureH
f1 (ppm)


NO2
O
N

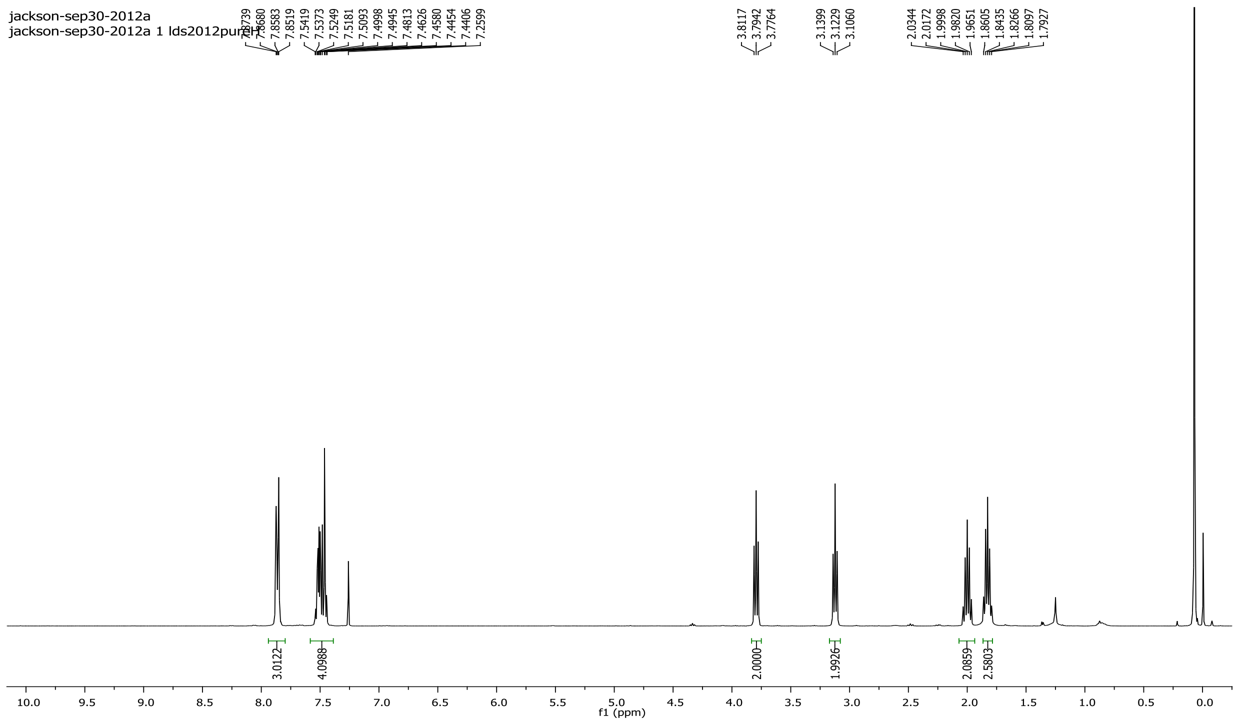
4s

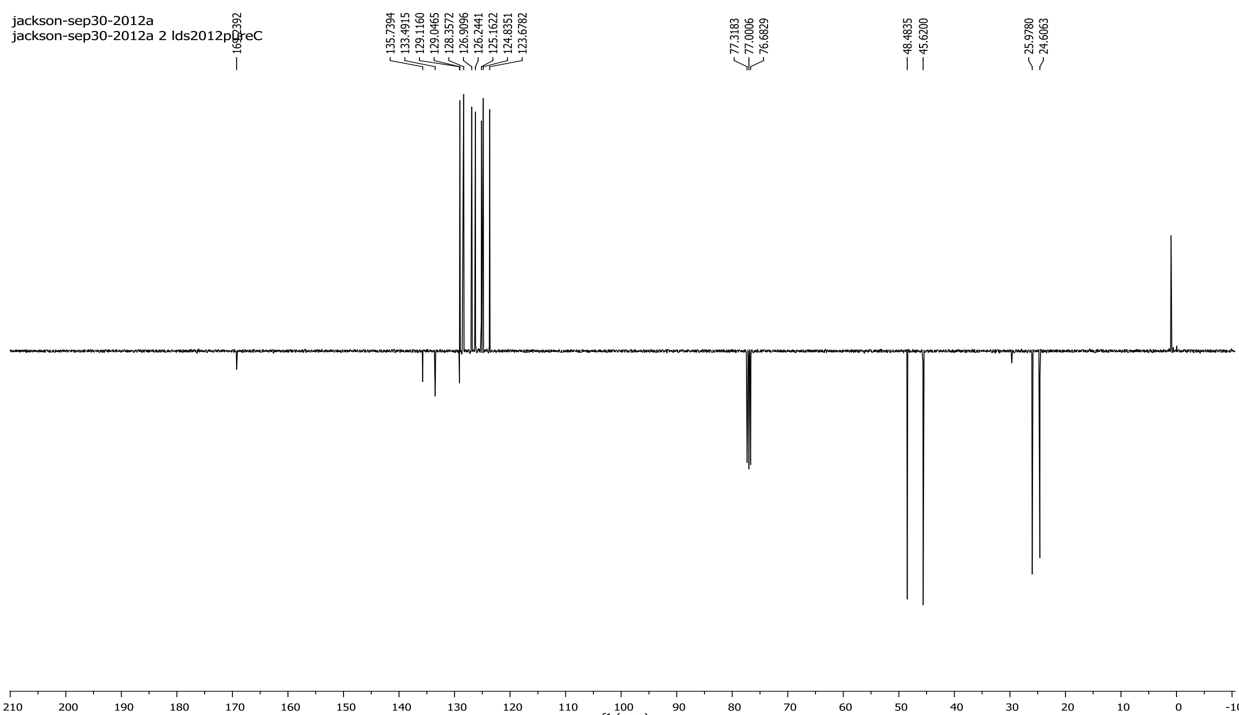

jackson-Feb07-2013b
jackson-Feb07-2013 10 lds2107pureH
f1 (ppm)

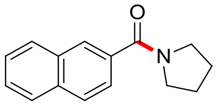

jackson-Feb07-2013b
jackson-Feb07-2013 11 lds2107pureC
f1 (ppm)



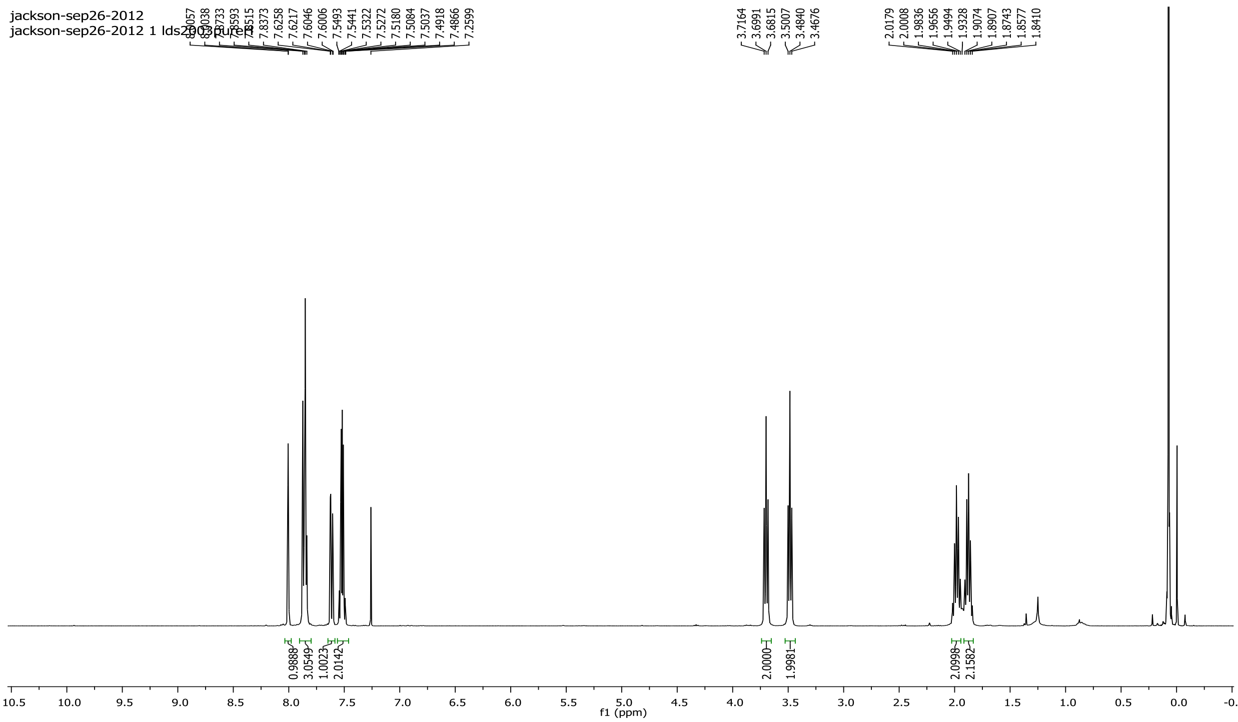
4t


jackson-sep30-2012a
jackson-sep30-2012a 1 lds2012pureH
7.8739
7.8680
7.8583
7.8519
7.5419
7.5373
7.5249
7.5181
7.5093
7.4998
7.4945
7.4813
7.4626
7.4580
7.4454
7.4406
7.2599
3.8117
3.7942
3.7764
3.1399
3.1229
3.1060
2.0344
2.0172
1.9998
1.9820
1.9651
1.8605
1.8435
1.8266
1.8097
1.7927
3.0122
4.0988
2.0000
1.9926
2.0859
2.5803
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

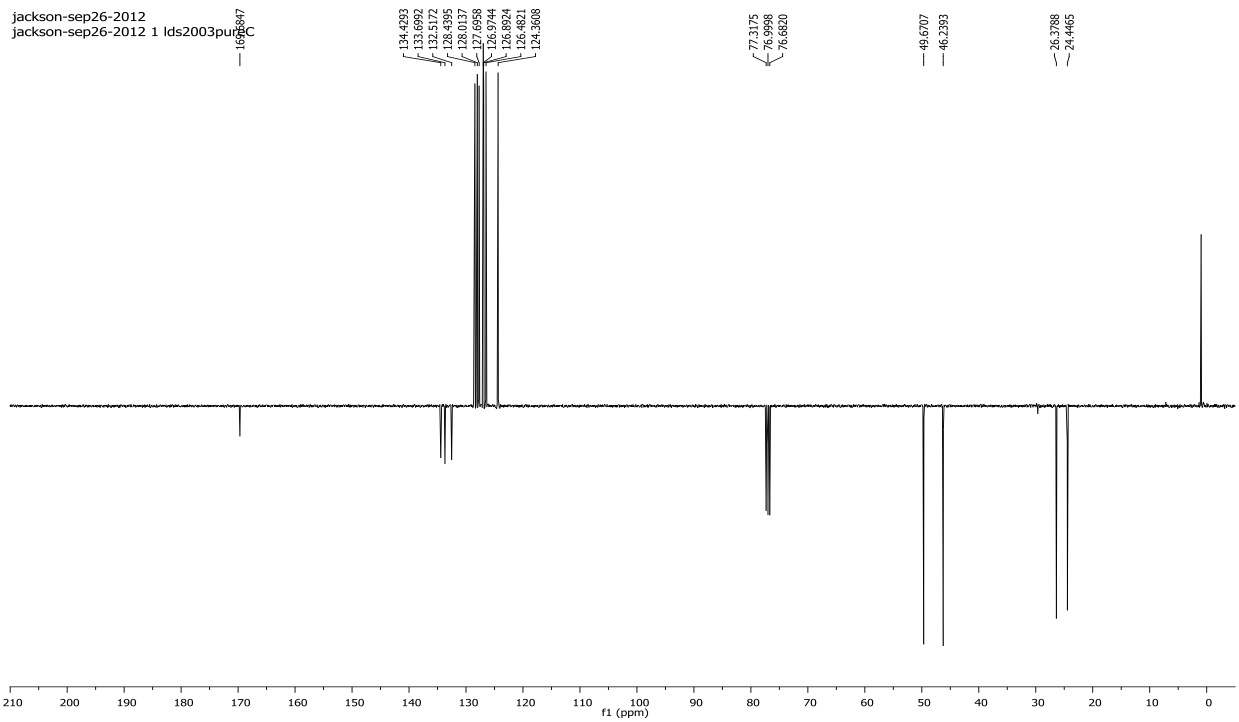

jackson-sep30-2012a
jackson-sep30-2012a 2 lds2012pureC
169.2392
135.7394
133.4915
129.1160
129.0465
128.3572
126.9096
126.2441
125.1622
124.8351
123.6782
77.3183
77.0006
76.6829
48.4835
45.6200
25.9780
24.6063
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



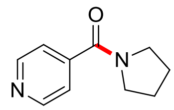
4u



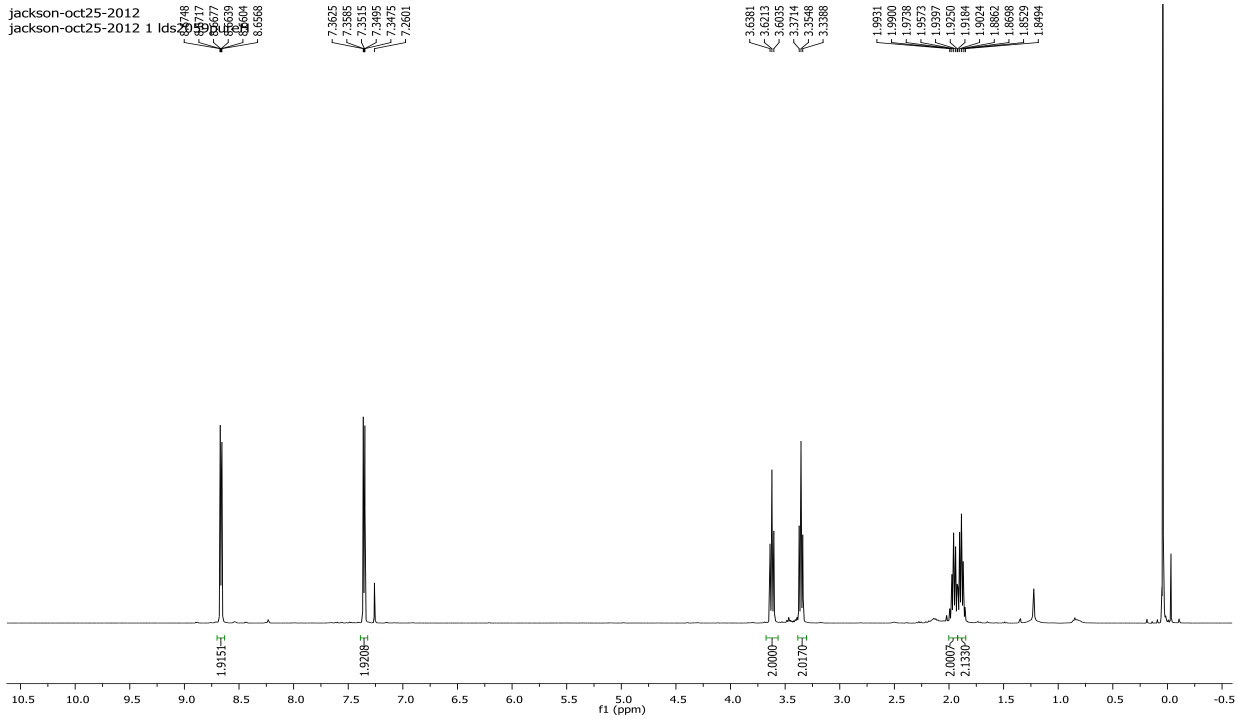
jackson-sep26-2012
jackson-sep26-2012 1 lds2003pureH
7.8373
7.6258
7.6217
7.6046
7.6006
7.5493
7.5441
7.5322
7.5272
7.5180
7.5084
7.5037
7.4918
7.4866
7.2599
3.7164
3.6991
3.6815
3.5007
3.4840
3.4676
2.0179
2.0008
1.9836
1.9656
1.9494
1.9328
1.9074
1.8907
1.8743
1.8577
1.8410
0.9888
3.0549
1.0023
2.0142
2.0000
1.9981
2.0998
2.1582
f1 (ppm)



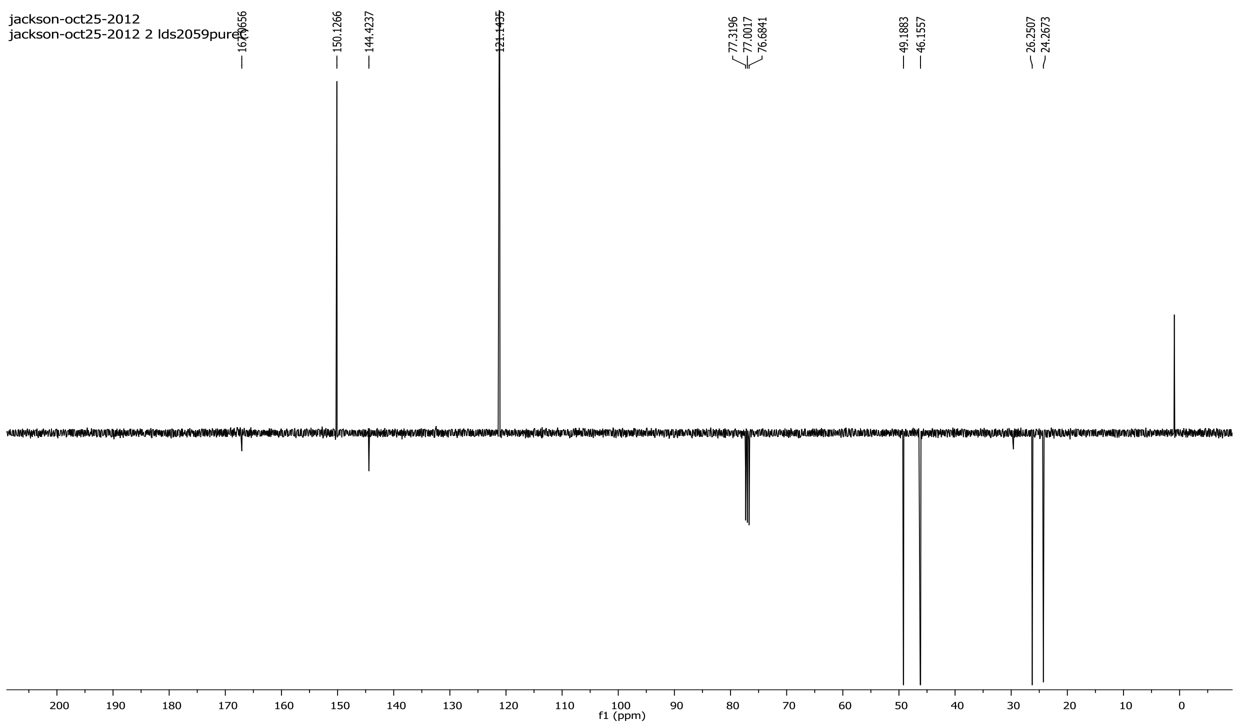
jackson-sep26-2012
jackson-sep26-2012 1 lds2003pureC
134.4293
133.6992
132.5172
128.4395
128.0137
127.6958
126.9744
126.8924
126.4821
124.3608
77.3175
76.9998
76.6820
49.6707
46.2393
26.3788
24.4465
f1 (ppm)



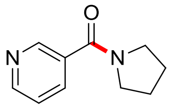
4v



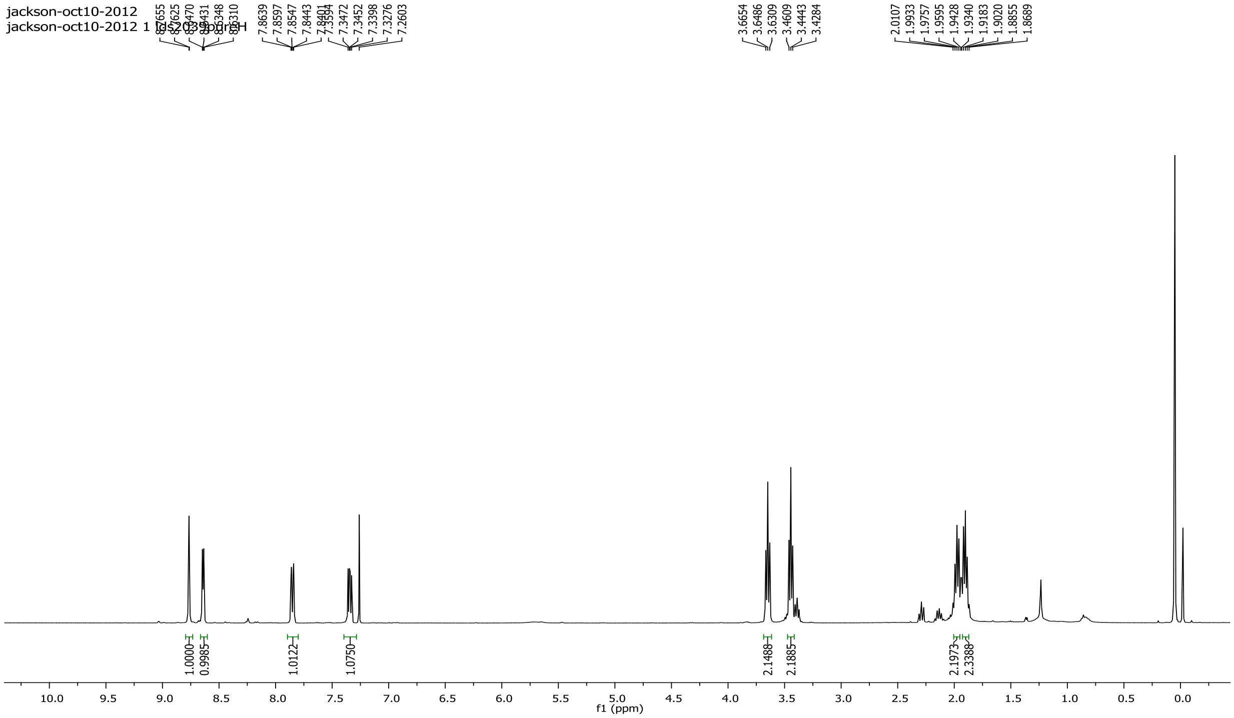
jackson-oct25-2012
jackson-oct25-2012 1 lds2059pureH
8.6677
8.6639
8.6604
8.6568
7.3625
7.3585
7.3515
7.3495
7.3475
7.2601
3.6381
3.6213
3.6035
3.3714
3.3548
3.3388
1.9931
1.9900
1.9738
1.9573
1.9397
1.9250
1.9184
1.9024
1.8862
1.8698
1.8529
1.8494
1.9151
1.9208
2.0000
2.0170
2.0007
2.1330
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

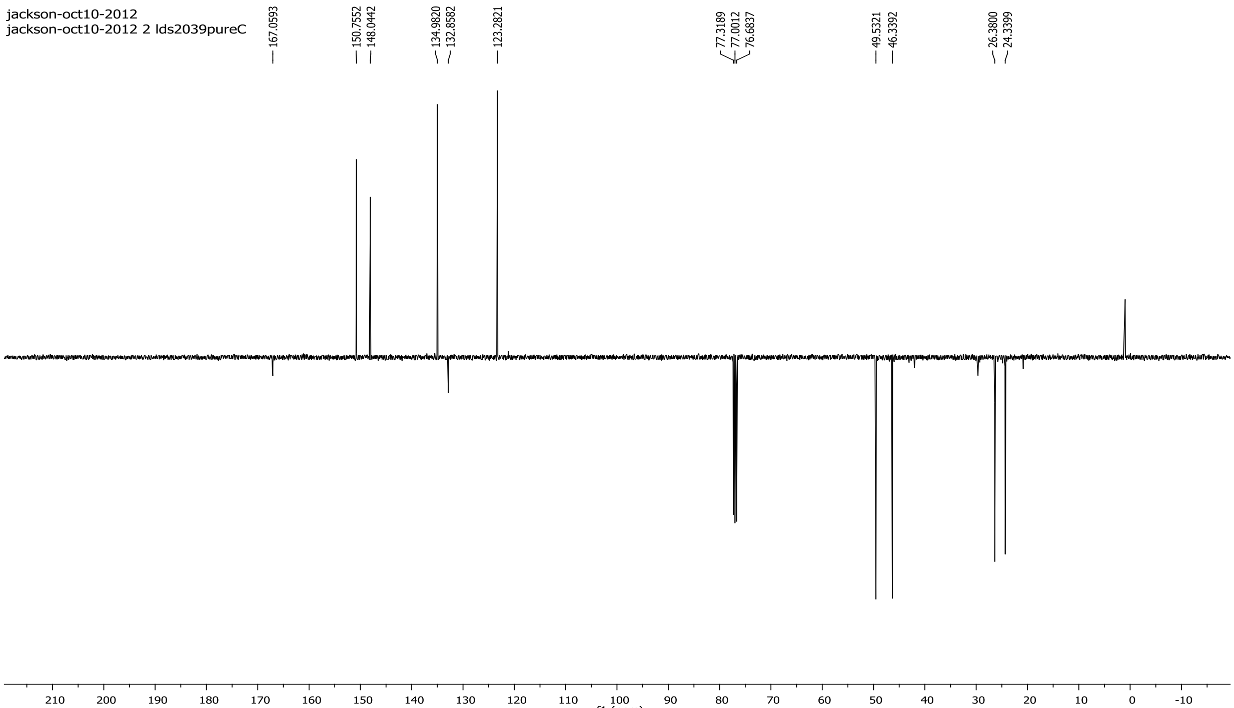


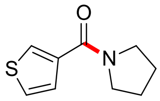
jackson-oct25-2012
jackson-oct25-2012 2 lds2059pureC
150.1266
144.4237
77.3196
77.0017
76.6841
49.1883
46.1557
26.2507
24.2673
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



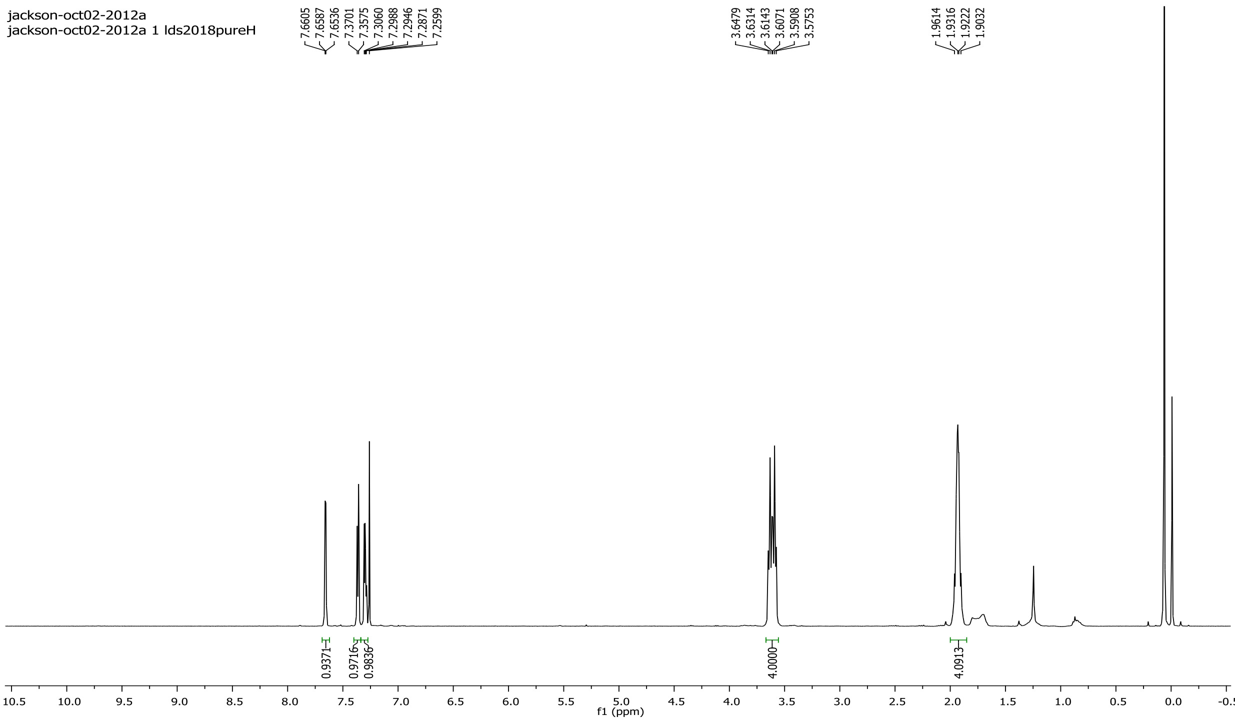
4w

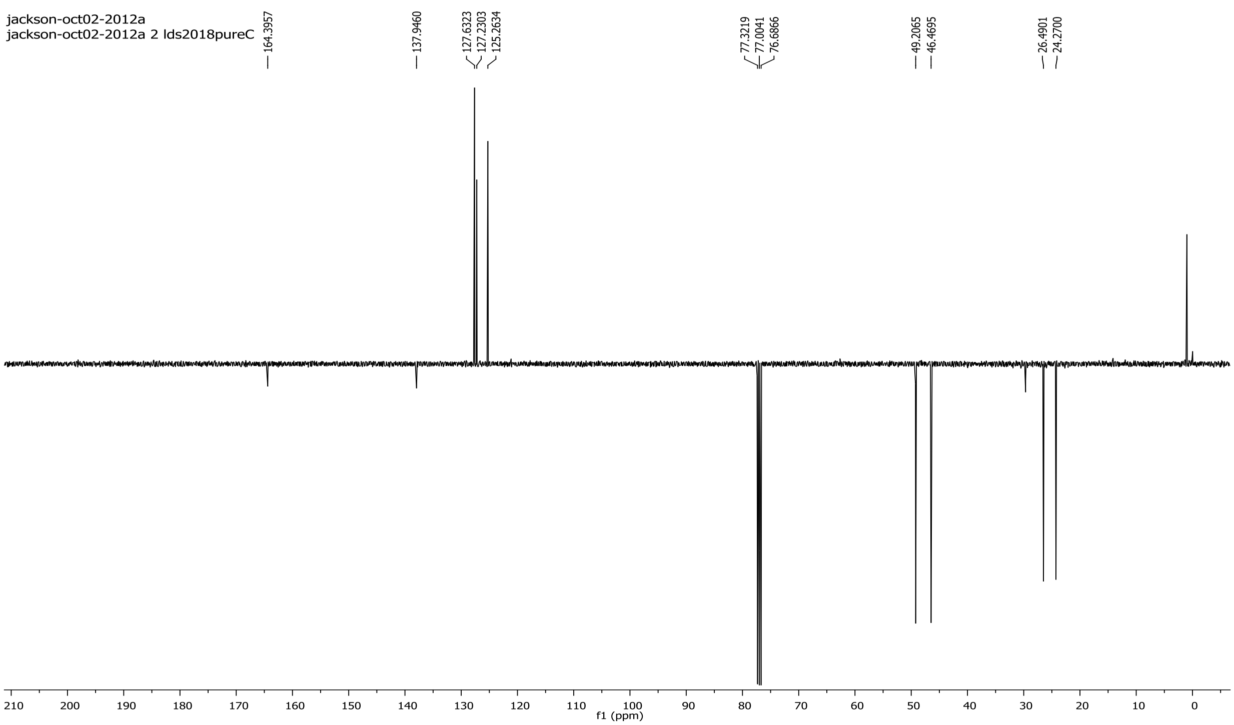

jackson-oct10-2012
jackson-oct10-2012 1 lds2039pureH
7.8639
7.8597
7.8547
7.8443
7.3472
7.3452
7.3398
7.3276
7.2603
3.6654
3.6486
3.6309
3.4609
3.4443
3.4284
2.0107
1.9933
1.9757
1.9595
1.9428
1.9340
1.9183
1.9020
1.8855
1.8689
1.0000
0.9985
1.0122
1.0750
2.1488
2.1885
2.1973
2.3388
f1 (ppm)

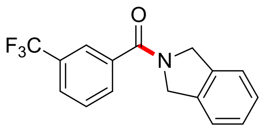

jackson-oct10-2012
jackson-oct10-2012 2 lds2039pureC
167.0593
150.7552
148.0442
134.9820
132.8582
123.2821
77.3189
77.0012
76.6837
49.5321
46.3392
26.3800
24.3399
f1 (ppm)


O
S
N

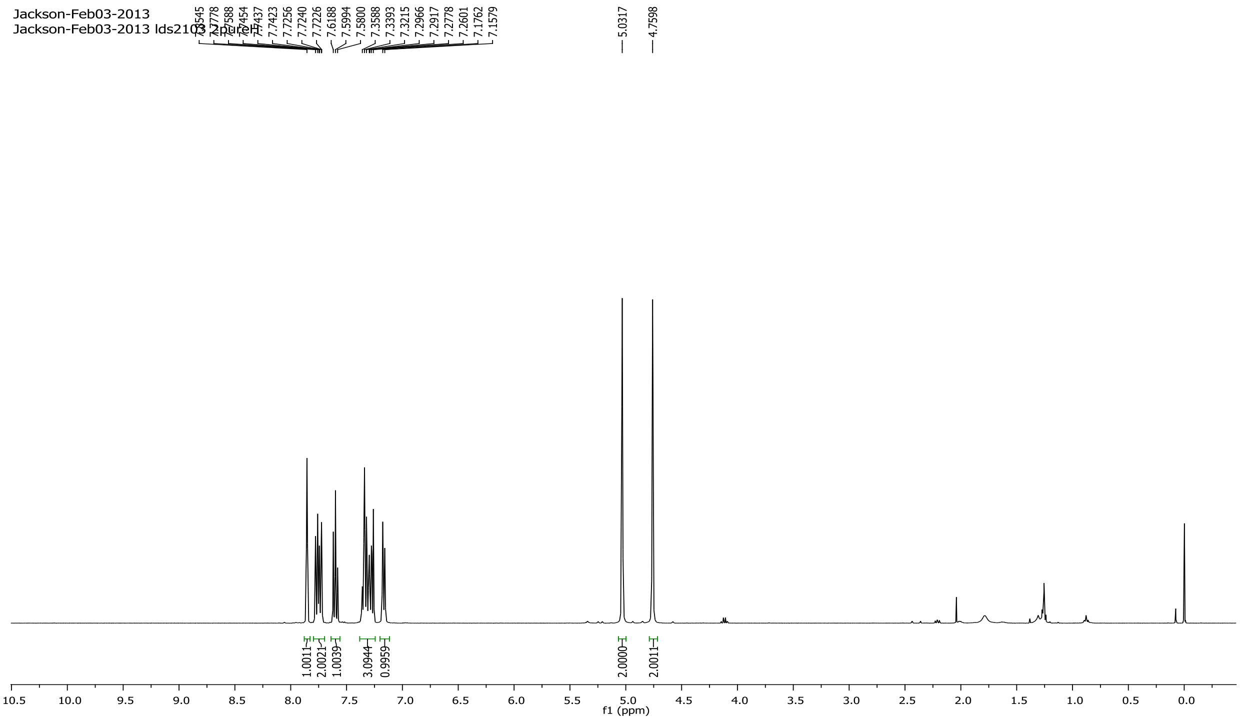
4x

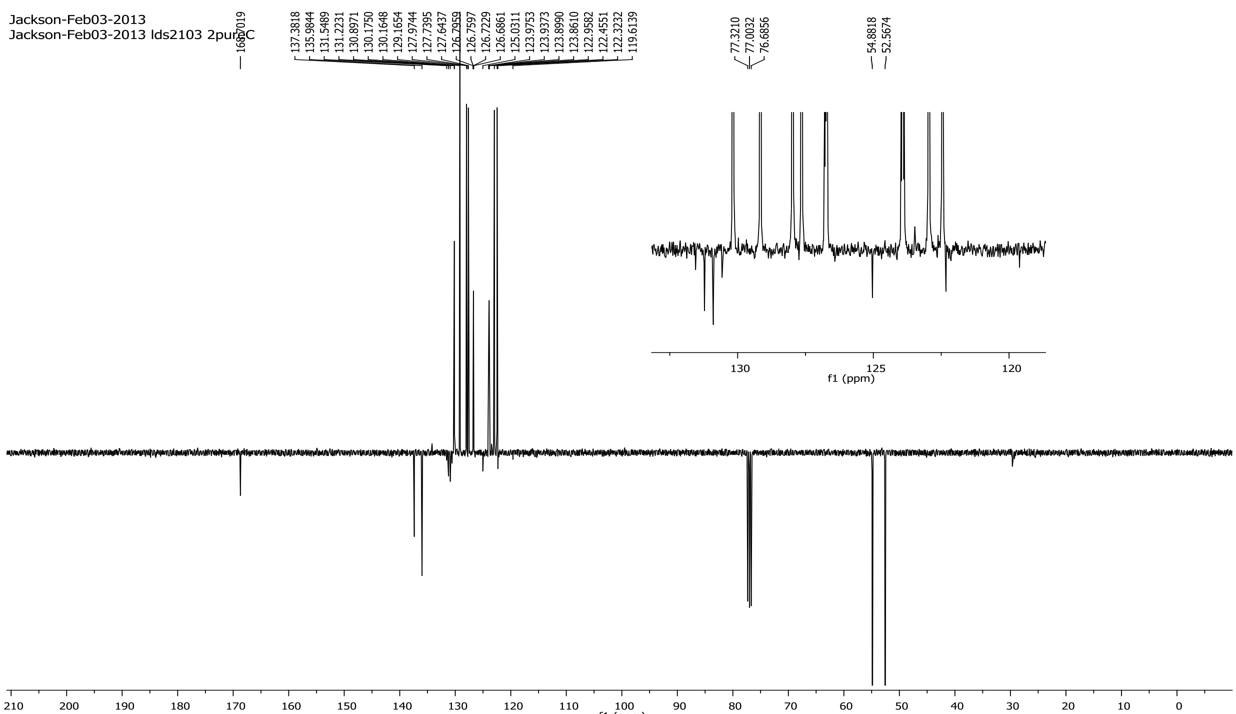

jackson-oct02-2012a
jackson-oct02-2012a 1 lds2018pureH
7.6605
7.6587
7.6536
7.3701
7.3575
7.3060
7.2988
7.2946
7.2871
7.2599
3.6479
3.6314
3.6143
3.6071
3.5908
3.5753
1.9614
1.9316
1.9222
1.9032
0.9371
0.9716
0.9836
4.0000
4.0913
f1 (ppm)

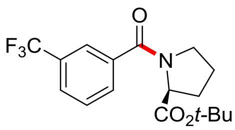

jackson-oct02-2012a
jackson-oct02-2012a 2 lds2018pureC
164.3957
137.9460
127.6323
127.2303
125.2634
77.3219
77.0041
76.6866
49.2065
46.4695
26.4901
24.2700
f1 (ppm)



4nb

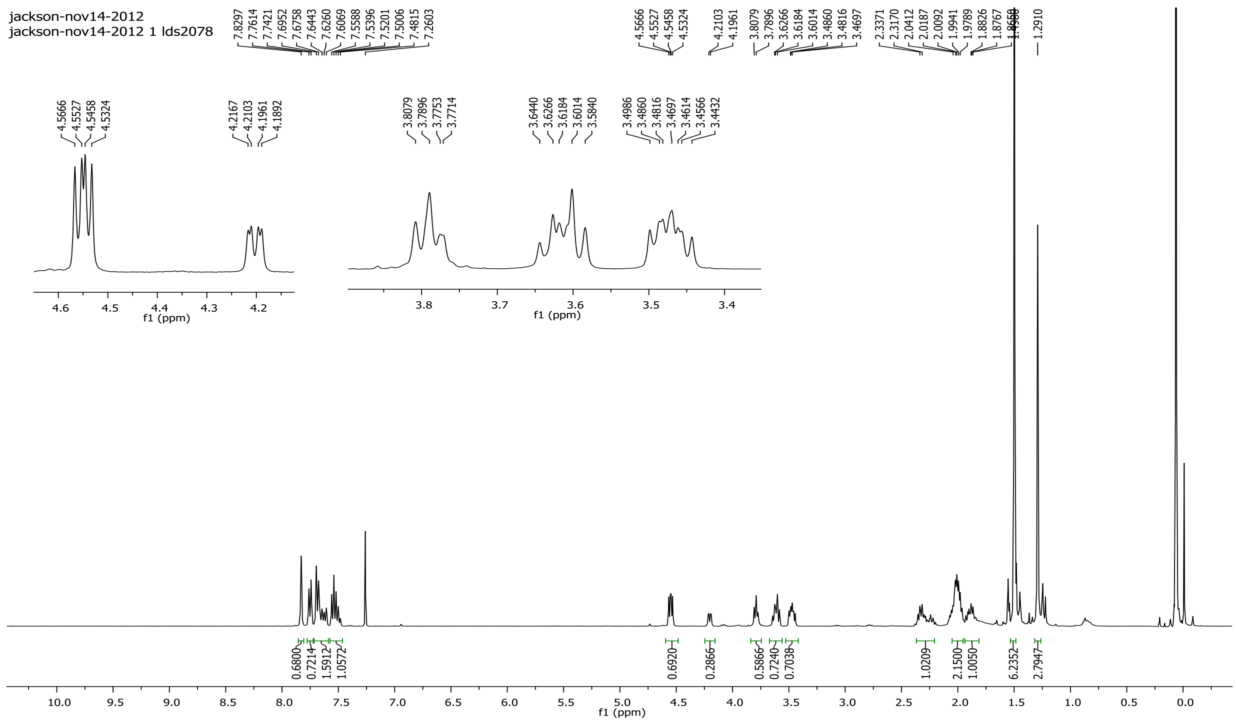

Jackson-Feb03-2013
Jackson-Feb03-2013 lds2103 2pureH
7.8545
7.7778
7.7588
7.7454
7.7437
7.7423
7.7256
7.7240
7.7226
7.6188
7.5994
7.5800
7.3588
7.3393
7.3215
7.2966
7.2917
7.2778
7.2601
7.1762
7.1579
5.0317
4.7598
1.0011
2.0021
1.0039
3.0944
0.9959
2.0000
2.0011
f1 (ppm)


Jackson-Feb03-2013
Jackson-Feb03-2013 lds2103 2pureC
168.7019
137.3818
135.9844
131.5489
131.2231
130.8971
130.1750
130.1648
129.1654
127.9744
127.7395
127.6437
126.7959
126.7597
126.7229
126.6861
125.0311
123.9753
123.9373
123.8990
123.8610
122.9582
122.4551
122.3232
119.6139
77.3210
77.0032
76.6856
54.8818
52.5674
f1 (ppm)

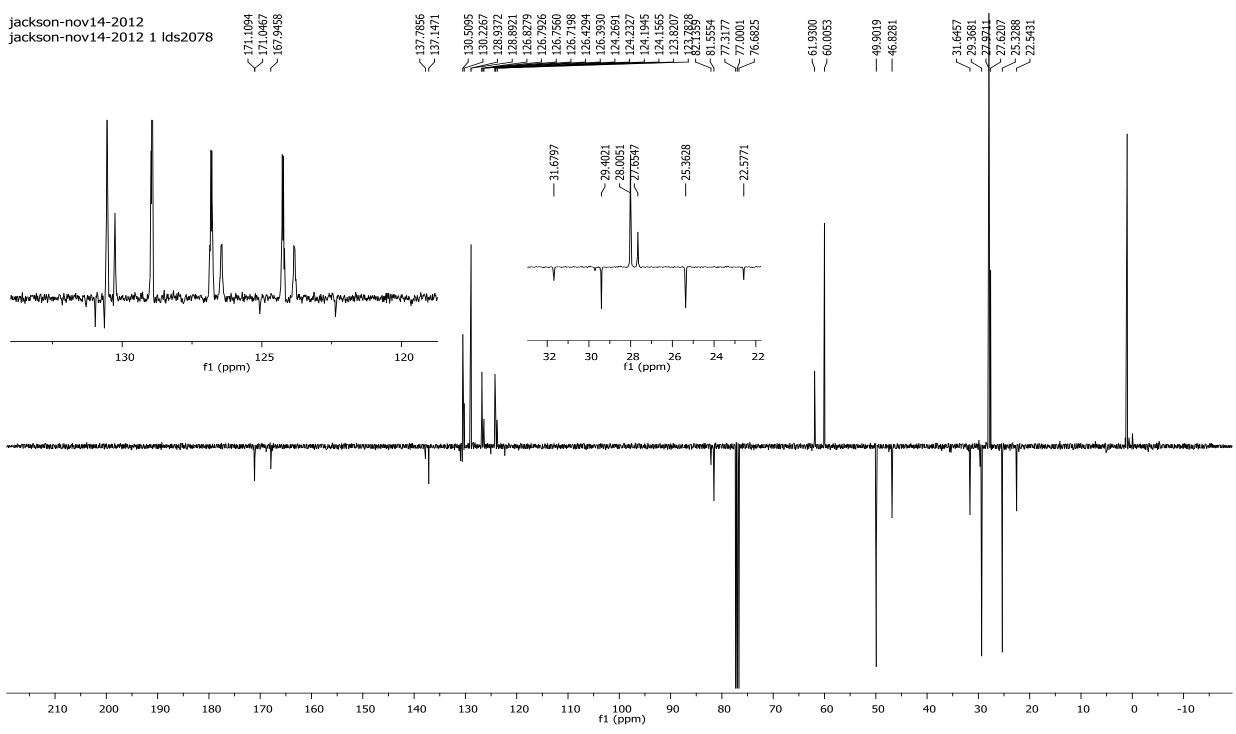


O
F3C
N
CO2t-Bu

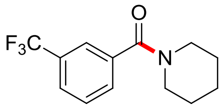
4nc



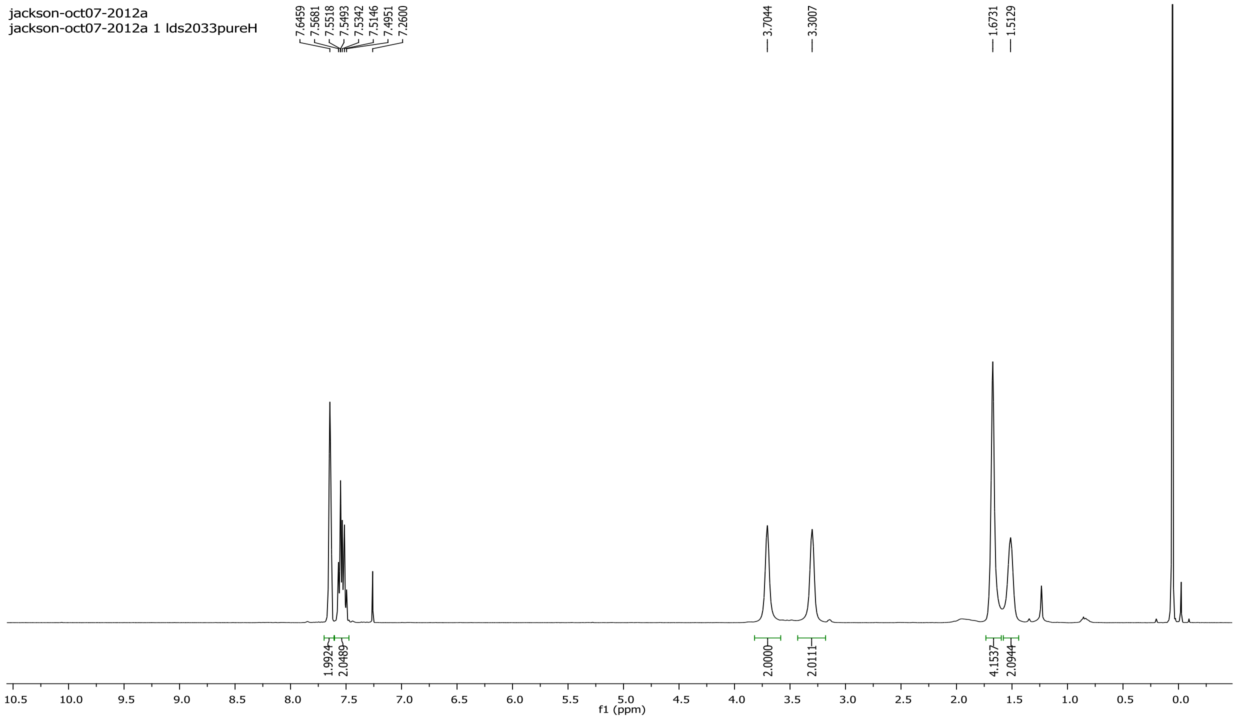
jackson-nov14-2012
jackson-nov14-2012 1 lds2078
7.8297 7.7614 7.7421 7.6952 7.6758 7.6443 7.6260 7.6069 7.5588 7.5396 7.5201 7.5006 7.4815 7.2603
4.5666 4.5527 4.5458 4.5324 4.2103 4.1961 3.8079 3.7896 3.6266 3.6184 3.6014 3.4860 3.4816 3.4697
2.3371 2.3170 2.0412 2.0187 2.0092 1.9941 1.9789 1.8826 1.8767 1.4569 1.2910
4.5666 4.5527 4.5458 4.5324
4.2167 4.2103 4.1961 4.1892
3.8079 3.7896 3.7753 3.7714
3.6440 3.6266 3.6184 3.6014 3.5840
3.4986 3.4860 3.4816 3.4697 3.4614 3.4566 3.4432
f1 (ppm)
0.6800 0.7214 1.5912 1.0572 0.6920 0.2866 0.5866 0.7240 0.7038 1.0209 2.1500 1.0050 6.2352 2.7947
f1 (ppm)

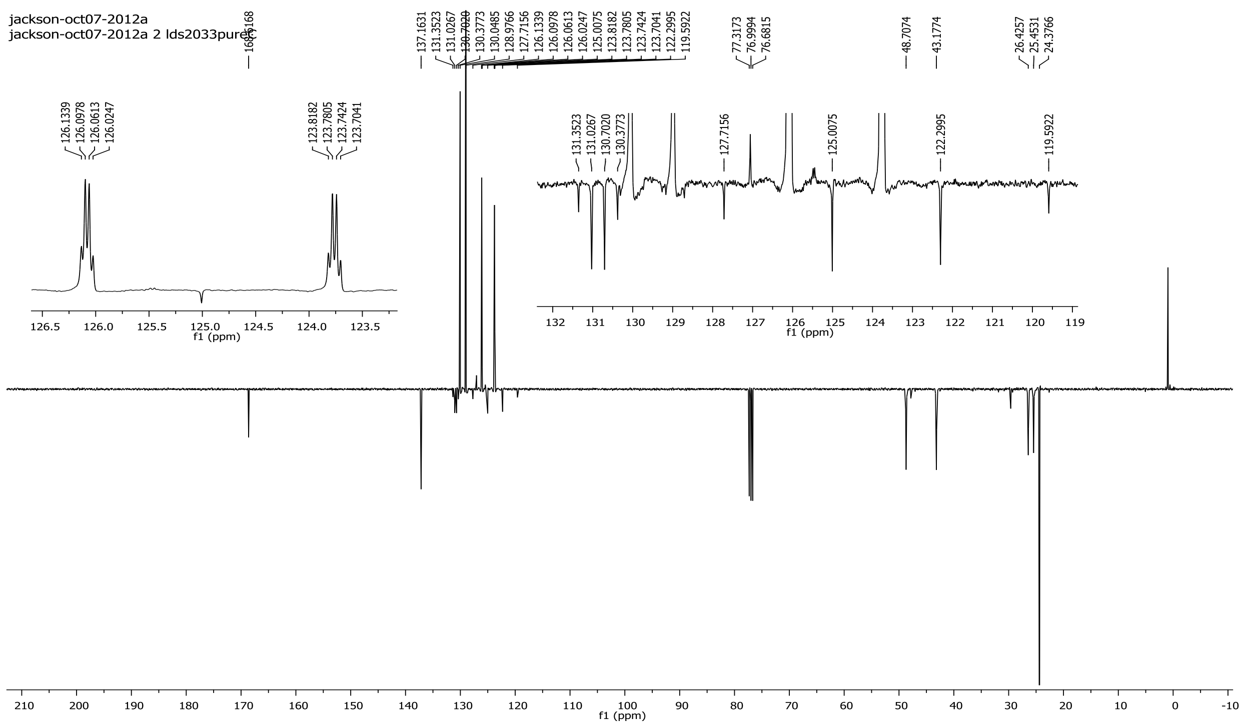


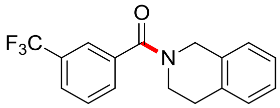
jackson-nov14-2012
jackson-nov14-2012 1 lds2078
171.1094 171.0467 167.9458
137.7856 137.1471
130.5095 130.2267 128.9372 128.8921 126.8279 126.7926 126.7560 126.7198 126.4294 126.3930 124.2691 124.2327 124.1945 124.1565 123.8207 123.7828 82.1539 81.5554 77.3177 77.0001 76.6825
61.9300 60.0053
49.9019 46.8281
31.6457 29.3681 27.9711 27.6207 25.3288 22.5431
31.6797 29.4021 28.0051 27.6547 25.3628 22.5771
f1 (ppm)
f1 (ppm)
f1 (ppm)


F3C
O
N

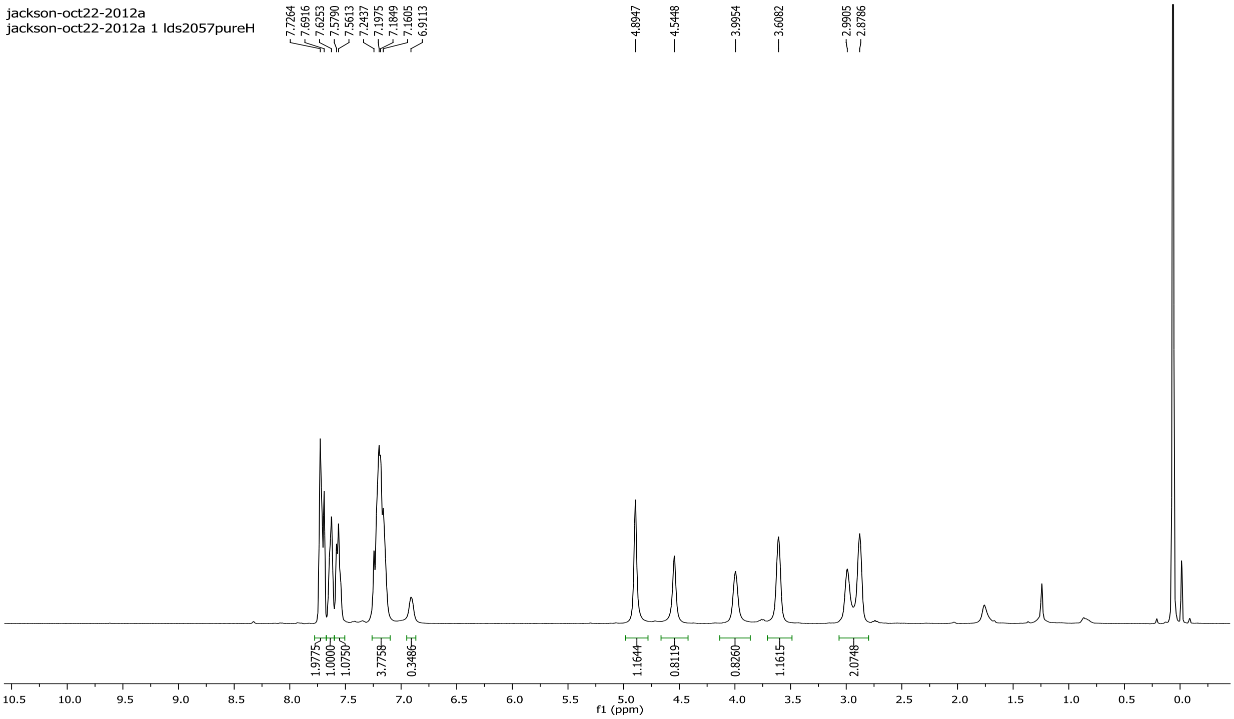
4nd


jackson-oct07-2012a
jackson-oct07-2012a 1 lds2033pureH
7.6459
7.5681
7.5518
7.5493
7.5342
7.5146
7.4951
7.2600
3.7044
3.3007
1.6731
1.5129
1.9924
2.0489
2.0000
2.0111
4.1537
2.0944
f1 (ppm)

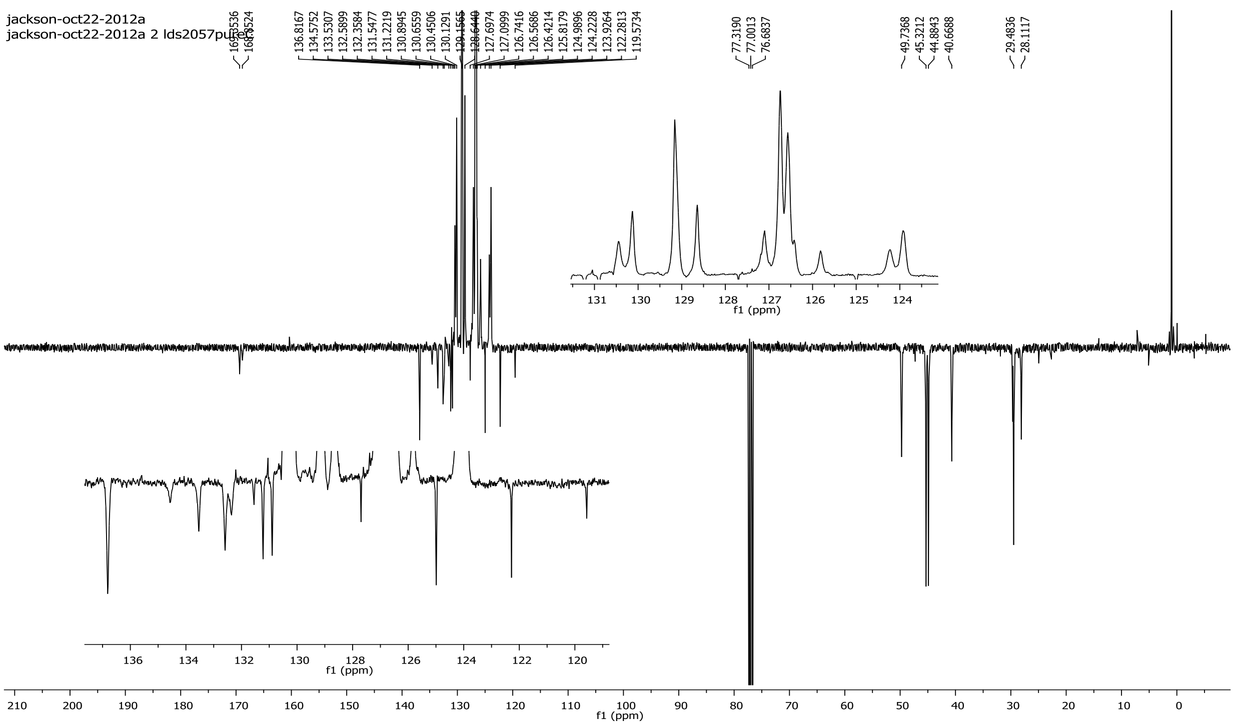

jackson-oct07-2012a
jackson-oct07-2012a 2 lds2033pureC
137.1631
131.3523
131.0267
130.7020
130.3773
130.0485
128.9766
127.7156
126.1339
126.0978
126.0613
126.0247
125.0075
123.8182
123.7805
123.7424
123.7041
122.2995
119.5922
77.3173
76.9994
76.6815
48.7074
43.1774
26.4257
25.4531
24.3766
f1 (ppm)



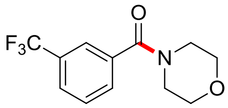
4ne



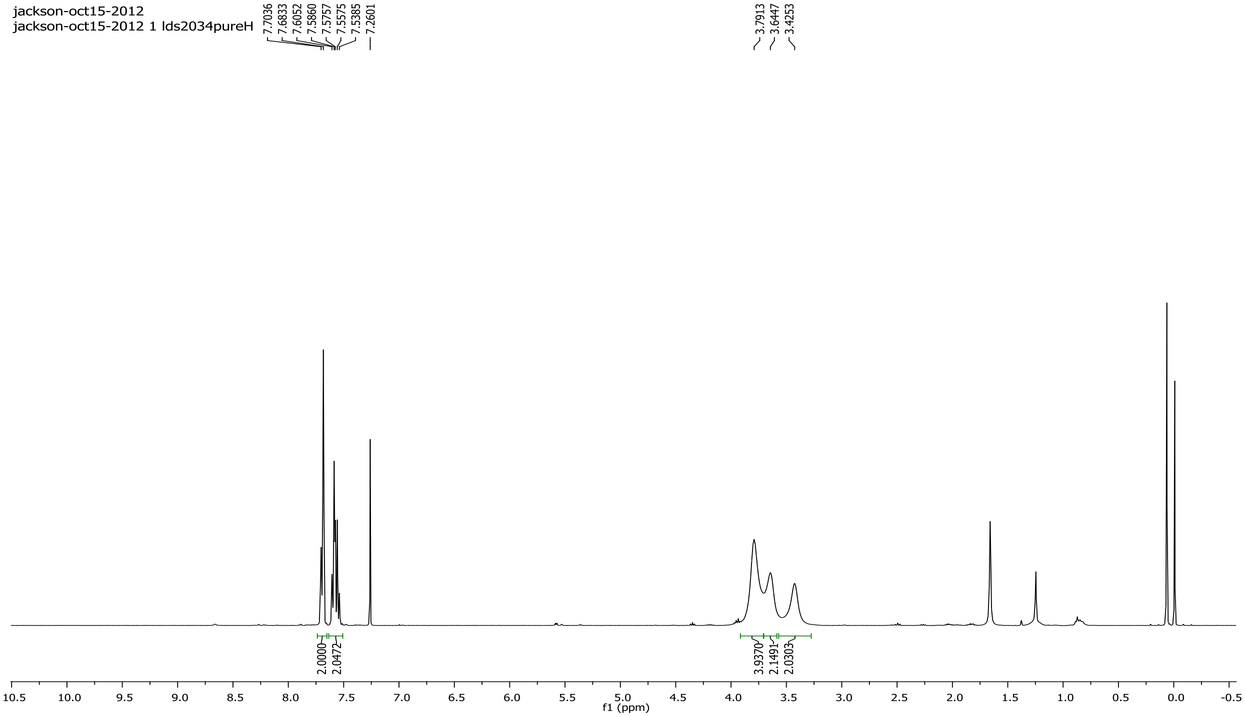
jackson-oct22-2012a
jackson-oct22-2012a 1 lds2057pureH
7.7264
7.6916
7.6253
7.5790
7.5613
7.2437
7.1975
7.1849
7.1605
6.9113
4.8947
4.5448
3.9954
3.6082
2.9905
2.8786
1.9775
1.0000
1.0750
3.7758
0.3486
1.1644
0.8119
0.8260
1.1615
2.0748
f1 (ppm)

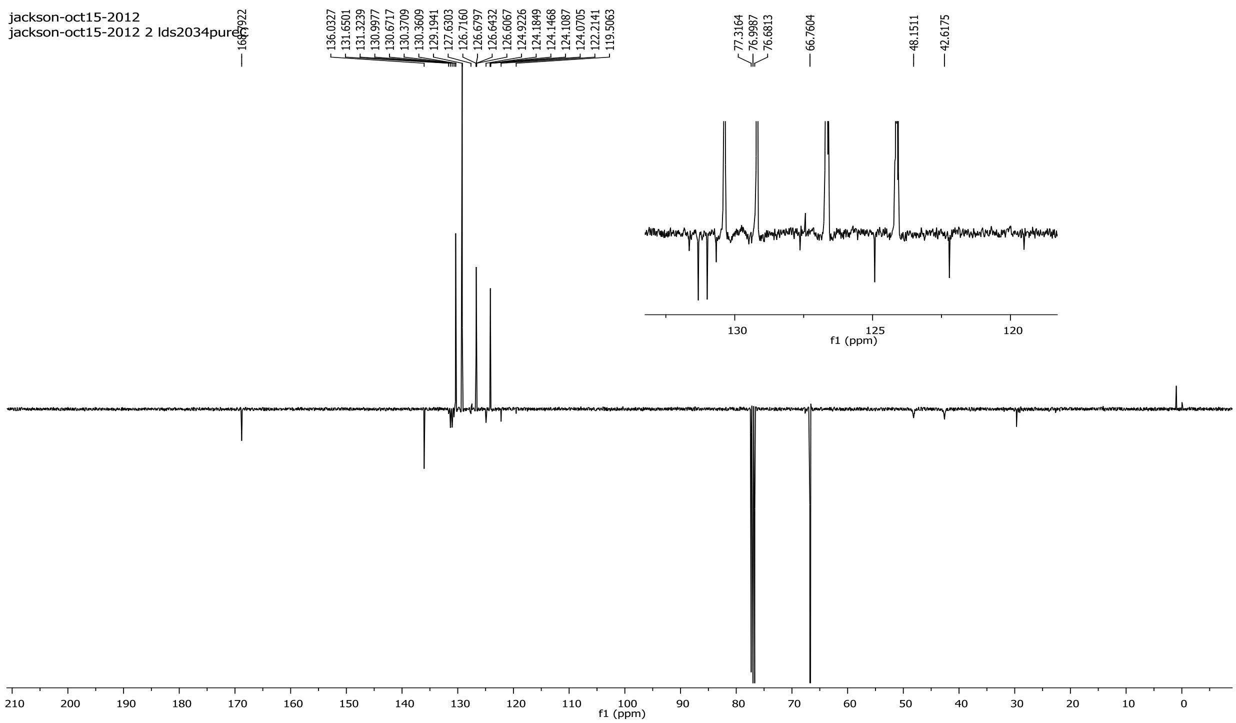


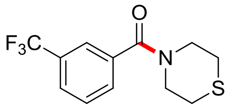
jackson-oct22-2012a
jackson-oct22-2012a 2 lds2057pureC
136.8167
134.5752
133.5307
132.5899
132.3584
131.5477
131.2219
130.8945
130.6559
130.4506
130.1291
128.6440
127.6974
127.0999
126.7416
126.5686
126.4214
125.8179
124.9896
124.2228
123.9264
122.2813
119.5734
77.3190
77.0013
76.6837
49.7368
45.3212
44.8843
40.6688
29.4836
28.1117
f1 (ppm)


F3C
O
N
O

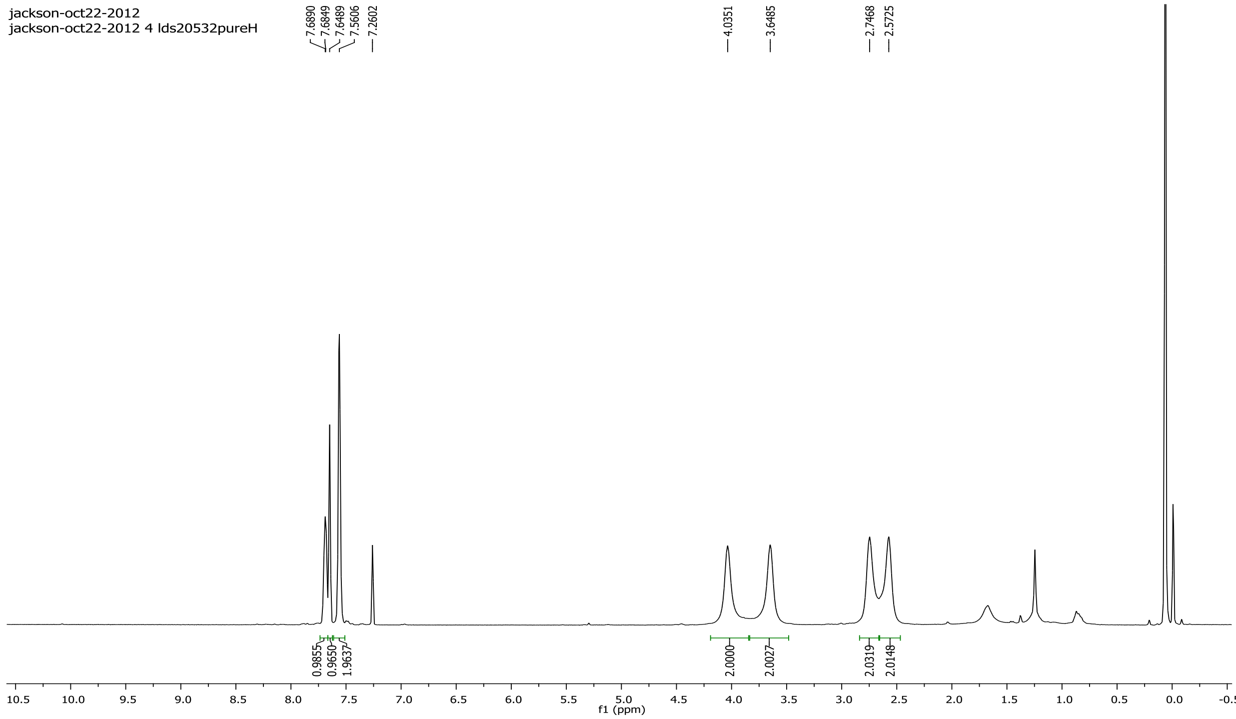
4nf

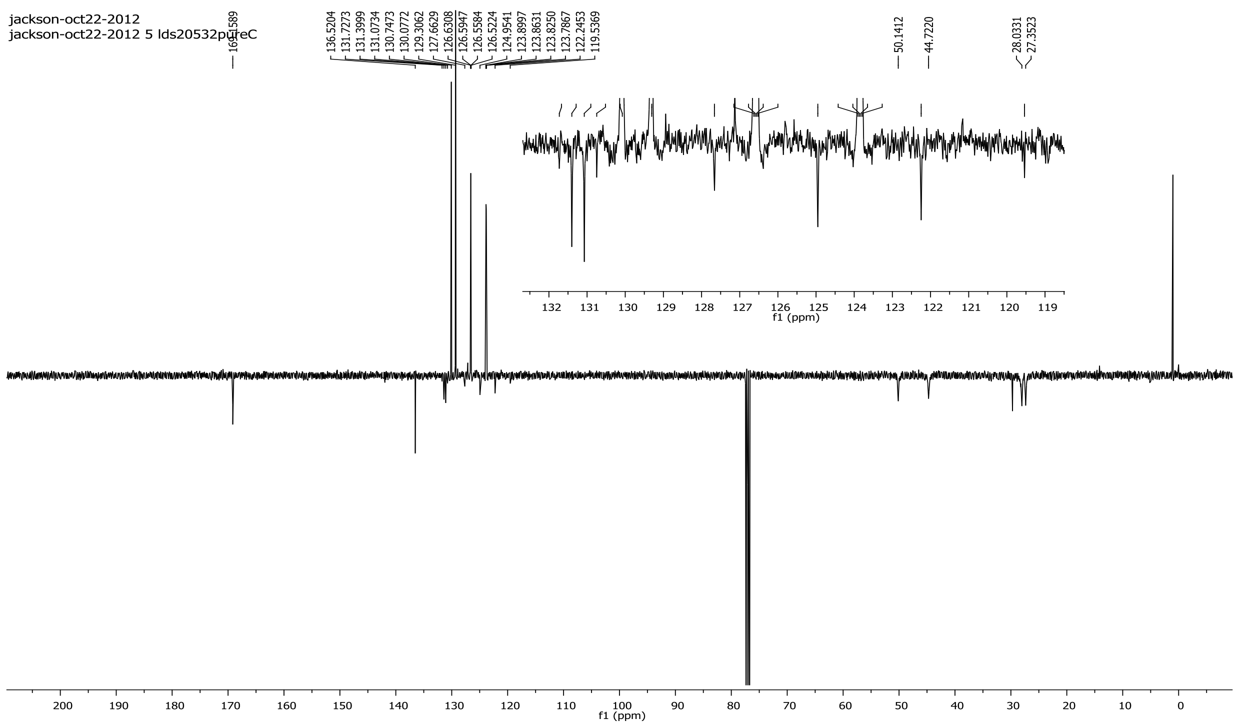

jackson-oct15-2012
jackson-oct15-2012 1 lds2034pureH
7.7036
7.6833
7.6052
7.5860
7.5757
7.5575
7.5385
7.2601
3.7913
3.6447
3.4253
2.0000
2.0472
3.9370
2.1491
2.0303
f1 (ppm)

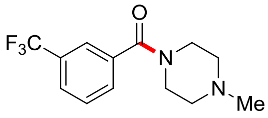

jackson-oct15-2012
jackson-oct15-2012 2 lds2034pureC
136.0327
131.6501
131.3239
130.9977
130.6717
130.3709
130.3609
129.1941
127.6303
126.7160
126.6797
126.6432
126.6067
124.9226
124.1849
124.1468
124.1087
124.0705
122.2141
119.5063
77.3164
76.9987
76.6813
66.7604
48.1511
42.6175
f1 (ppm)


O
F3C
N
S

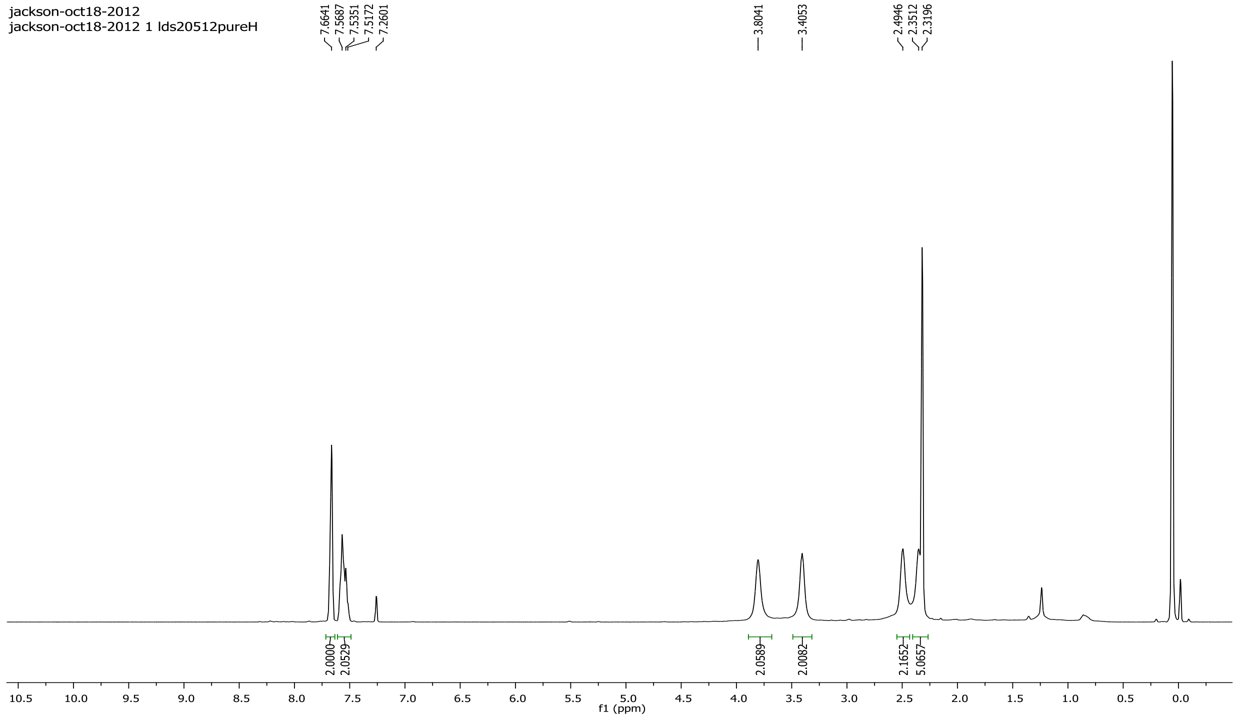
4ng

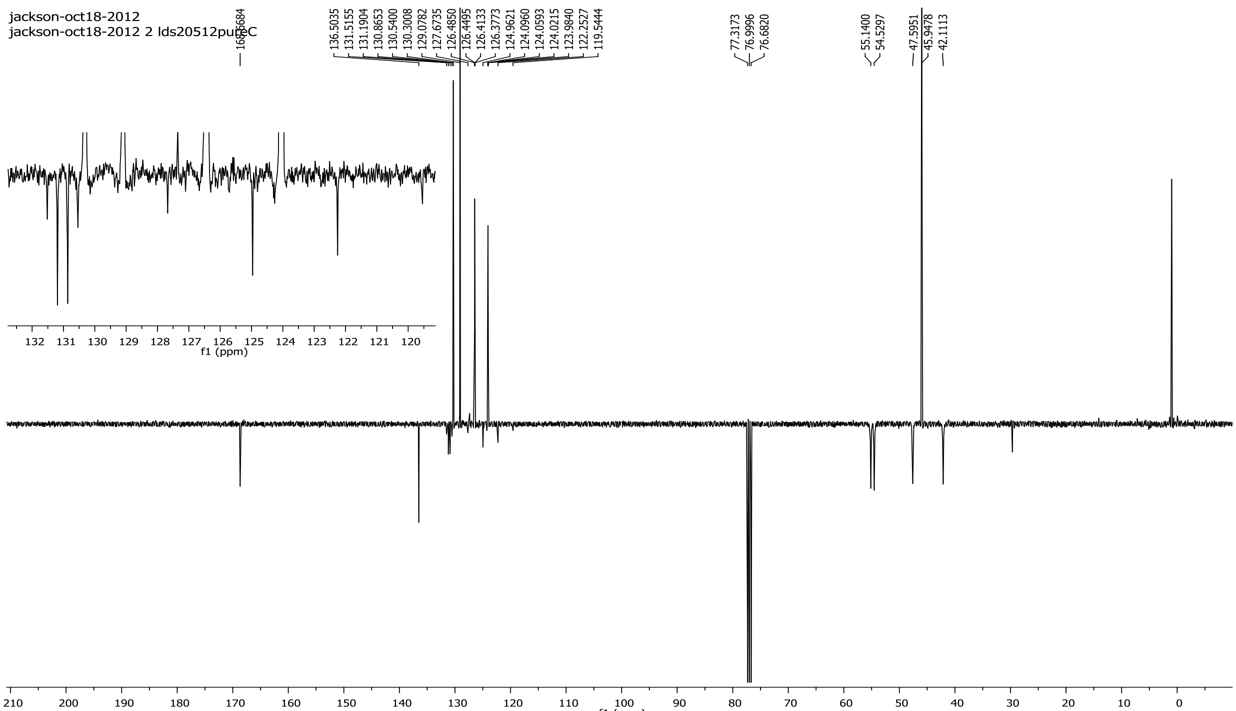

jackson-oct22-2012
jackson-oct22-2012 4 lds20532pureH
7.6890
7.6849
7.6489
7.5606
7.2602
4.0351
3.6485
2.7468
2.5725
0.9855
0.9650
1.9637
2.0000
2.0027
2.0319
2.0148
f1 (ppm)

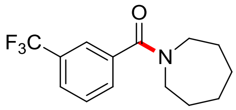

jackson-oct22-2012
jackson-oct22-2012 5 lds20532pureC
169.1589
136.5204
131.7273
131.3999
131.0734
130.7473
130.0772
129.3062
127.6629
126.6308
126.5947
126.5584
126.5224
124.9541
123.8997
123.8631
123.8250
123.7867
122.2453
119.5369
50.1412
44.7220
28.0331
27.3523
f1 (ppm)


F3C
O
N
N
Me

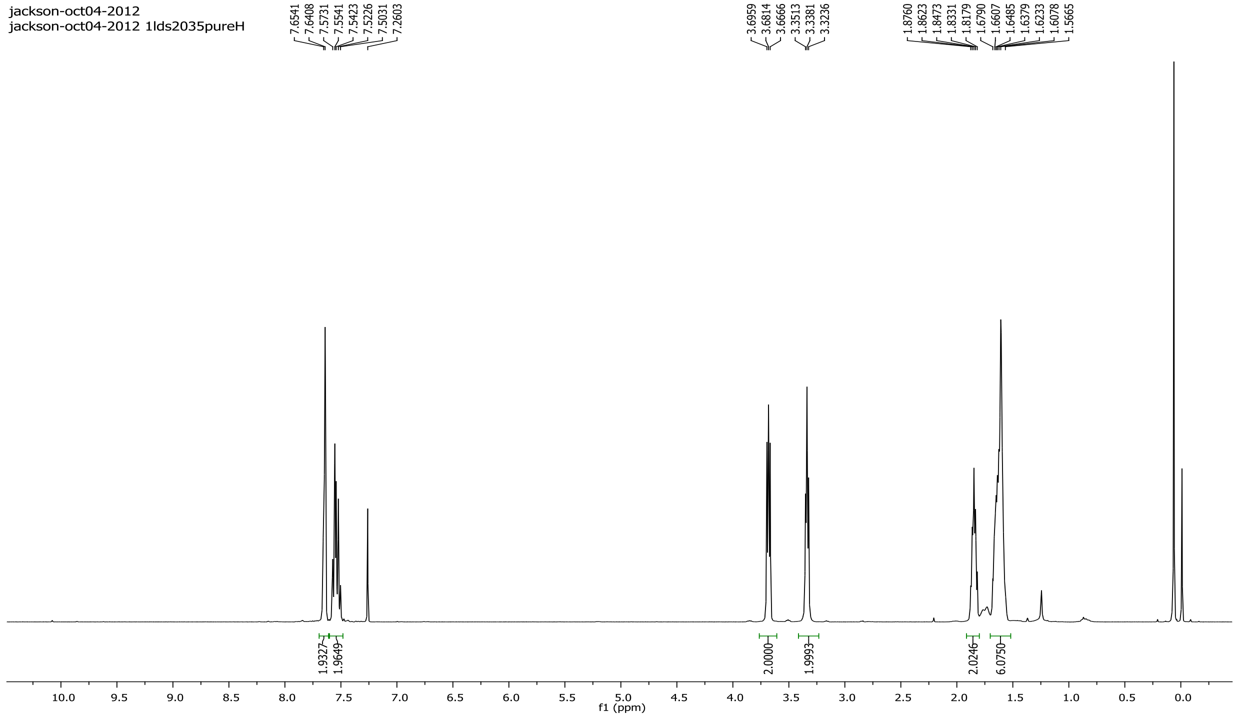
4nh

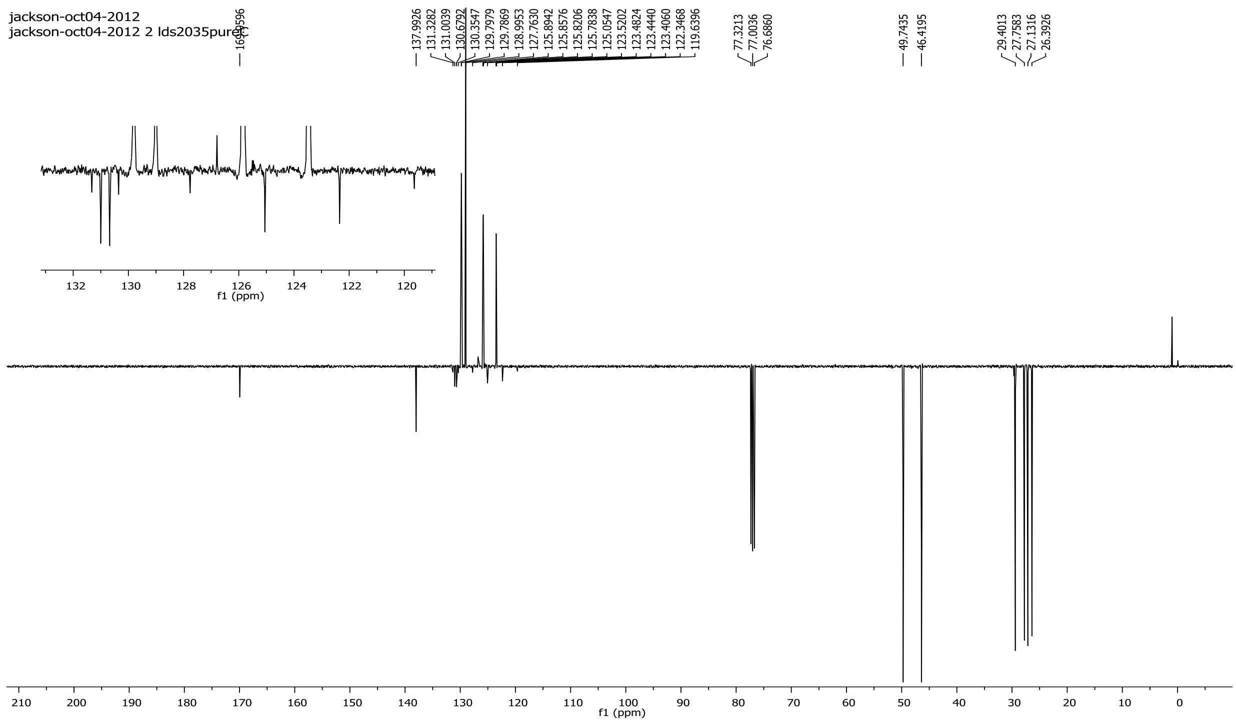

jackson-oct18-2012
jackson-oct18-2012 1 lds20512pureH
7.6641
7.5687
7.5351
7.5172
7.2601
3.8041
3.4053
2.4946
2.3512
2.3196
2.0000
2.0529
2.0589
2.0082
2.1652
5.0657
f1 (ppm)

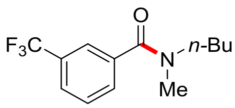

jackson-oct18-2012
jackson-oct18-2012 2 lds20512pureC
136.5035
131.5155
131.1904
130.8653
130.5400
130.3008
129.0782
127.6735
126.4850
126.4495
126.4133
126.3773
124.9621
124.0960
124.0593
124.0215
123.9840
122.2527
119.5444
77.3173
76.9996
76.6820
55.1400
54.5297
47.5951
45.9478
42.1113
f1 (ppm)


F3C
O
N

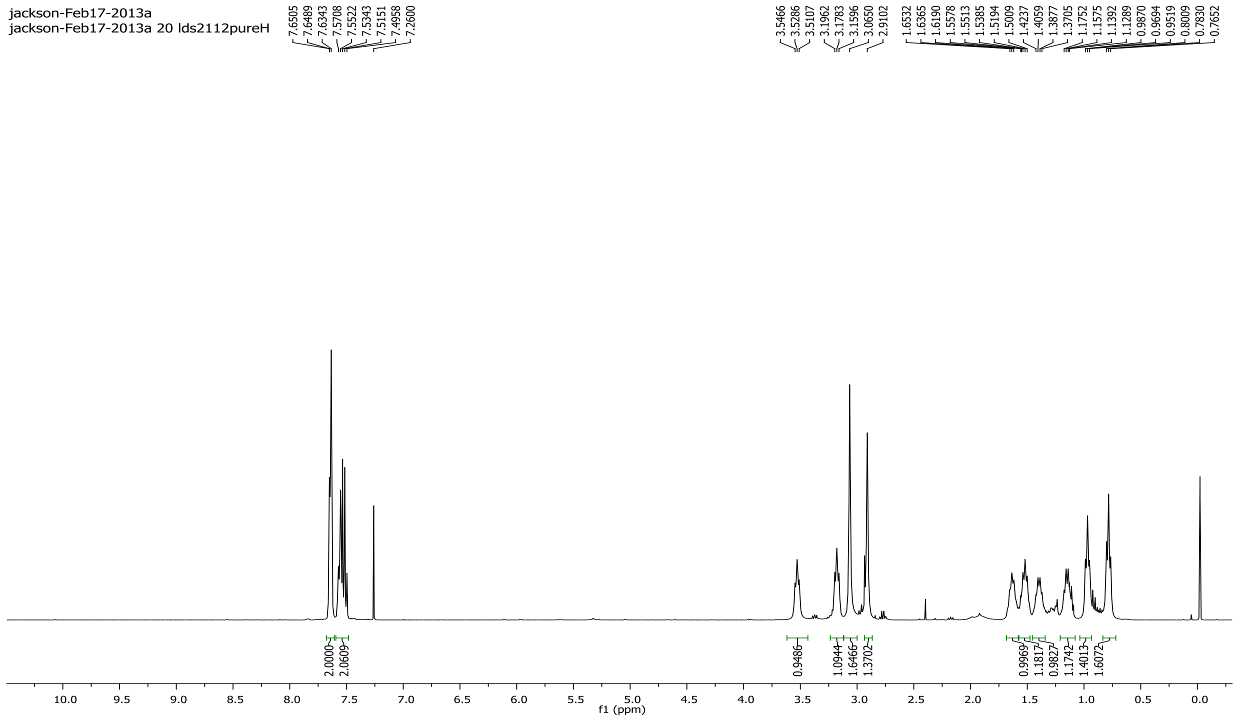
4ni

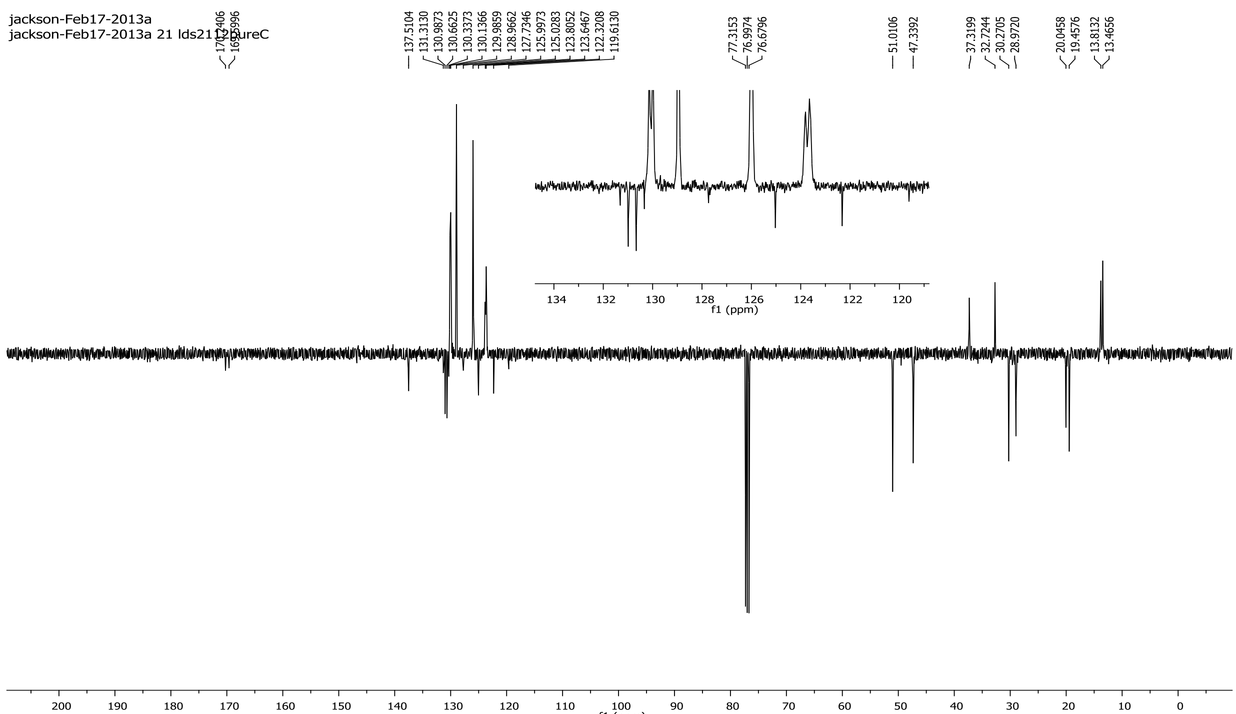

jackson-oct04-2012
jackson-oct04-2012 1lds2035pureH
7.6541
7.6408
7.5731
7.5541
7.5423
7.5226
7.5031
7.2603
3.6959
3.6814
3.6666
3.3513
3.3381
3.3236
1.8760
1.8623
1.8473
1.8331
1.8179
1.6790
1.6607
1.6485
1.6379
1.6233
1.6078
1.5665
1.9327
1.9649
2.0000
1.9993
2.0246
6.0750
f1 (ppm)

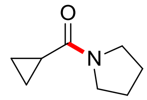

jackson-oct04-2012
jackson-oct04-2012 2 lds2035pureC
137.9926
131.3282
131.0039
130.6792
130.3547
129.7979
129.7869
128.9953
127.7630
125.8942
125.8576
125.8206
125.7838
125.0547
123.5202
123.4824
123.4440
123.4060
122.3468
119.6396
77.3213
77.0036
76.6860
49.7435
46.4195
29.4013
27.7583
27.1316
26.3926
f1 (ppm)



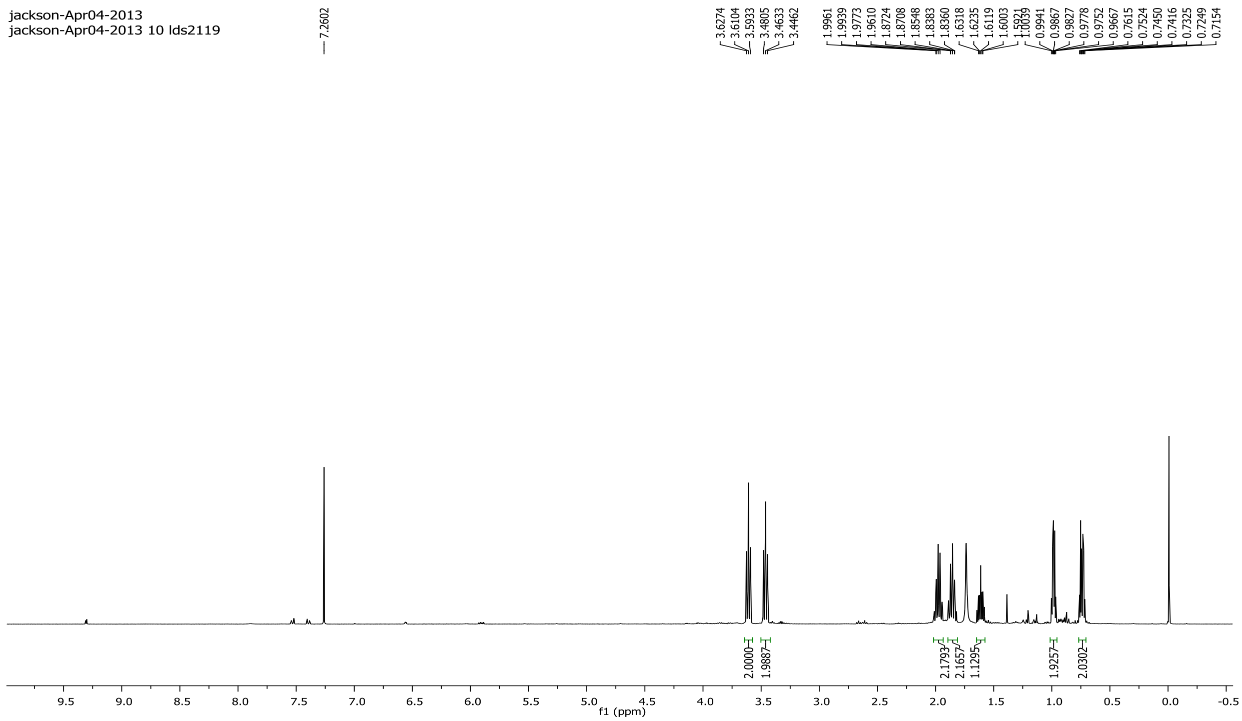
4nj

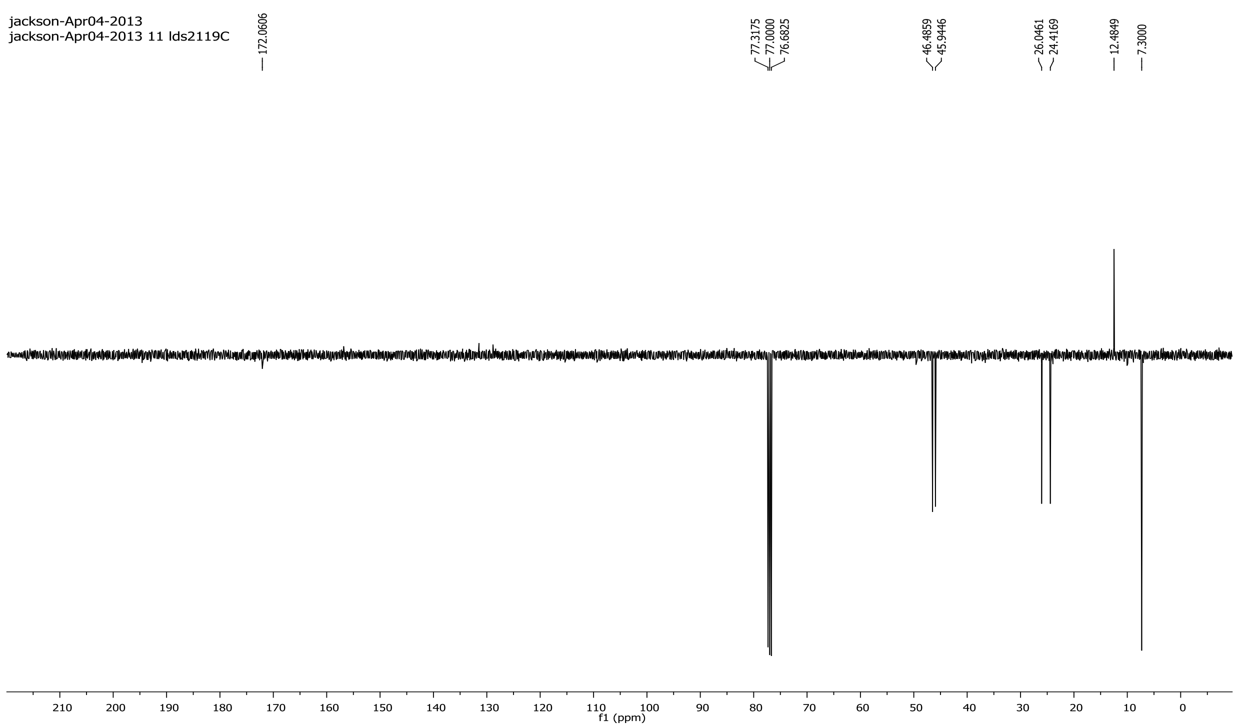

jackson-Feb17-2013a
jackson-Feb17-2013a 20 lds2112pureH
f1 (ppm)

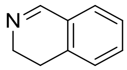

jackson-Feb17-2013a
jackson-Feb17-2013a 21 lds2112pureC
f1 (ppm)



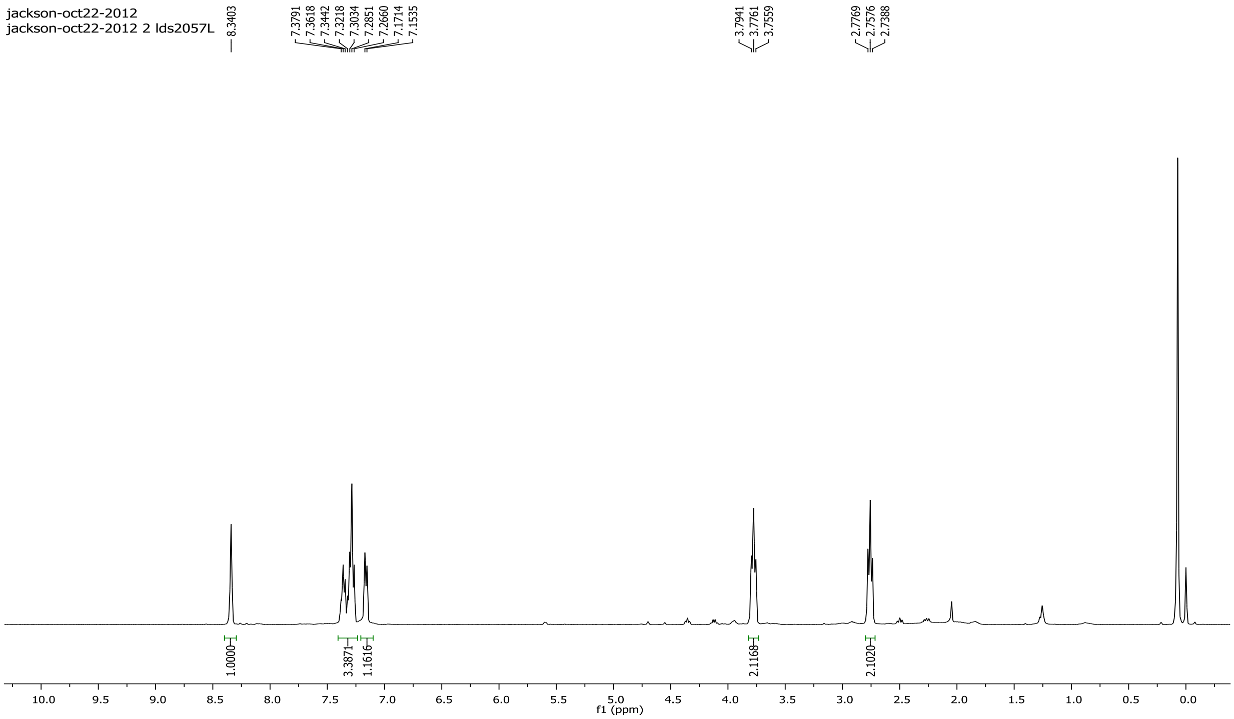
S4a


jackson-Apr04-2013
jackson-Apr04-2013 10 lds2119
7.2602
3.6274
3.6104
3.5933
3.4805
3.4633
3.4462
1.9961
1.9939
1.9773
1.9610
1.8724
1.8708
1.8548
1.8383
1.8360
1.6318
1.6235
1.6119
1.6003
1.5921
1.0039
0.9941
0.9867
0.9827
0.9778
0.9752
0.9667
0.7615
0.7524
0.7450
0.7416
0.7325
0.7249
0.7154
2.0000
1.9887
2.1793
2.1657
1.1295
1.9257
2.0302
f1 (ppm)


jackson-Apr04-2013
jackson-Apr04-2013 11 lds2119C
172.0606
77.3175
77.0000
76.6825
46.4859
45.9446
26.0461
24.4169
12.4849
7.3000
f1 (ppm)



S3


jackson-oct22-2012
jackson-oct22-2012 2 lds2057L
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