Supporting Information

$B(C_6F_5)_3$-Catalyzed Michael Reactions: Aromatic C–H as Nucleophiles

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1. General Considerations

All chemicals were purchased from commercial sources with purities ≥95% and used without further purification. Tris(pentafluorophenyl)borane was purchased from TCI in a purity >98.0% (NMR) and used without further purification. Deuterated solvents were ordered from Deutero GmbH and stored over molecular sieves. NMR spectra were received using Bruker 300 Fourier, Bruker AV 300 and Bruker AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s= singlet, d= doublet, t= triplet and m= multiplet. NMR yields very determined by using mesitylene as internal standard. High resolution mass spectra (HRMS) were obtained either from a MAT 95 XP from Thermo (EI) or from an HPLC system 1200 and downstream ESI-TOF-MS 6210 from Agilent (ESI). Thin layer chromatography was performed on Merck TLC-plates with fluorescence indication (silica type 60, F_{254}), spots were visualized using UV-light or vanilline. Column chromatography was performed using silica with a grain size of 40–63 µm from Macherey-Nagel.

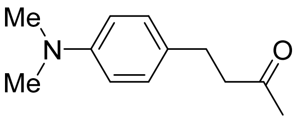
2. General Procedures (GP)

Coupling reaction of aromatic and hetro-aromatic compounds with *α, β*-unsaturated carbonyl-containing compounds:

A 25 cm^3 pressure tube equipped with screw cap and stiring was charged with $B(C_6F_5)_3$ (51 mg, 0.10 mmol 5 mol%) and dissolved in $CHCl_3$ (2 mL). Subsequently 1 equiv of the aromatic or hetro-aromatic compounds **1** (2.0 mmol) and 2 equiv of the *α, β*-unsaturated carbonyl-containing compounds **2** (4.0 mmol) were added. The reaction mixture was stirred for 24 h at 80 °C. The rection mixture was cooled to room temperature and directly purifite by column chromatography (cyclohexane:ethyl acetate = 20:1). to afforded. After removal of all volatiles in vaccuo the desired products **3** were obtained.

3. Characterization of the synthesized compounds

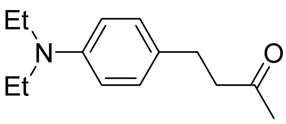
4-(4-(dimethylamino)phenyl)butan-2-one (3a)[1]



According to **GP**, *N,N*-dimethylaniline **1a** (247 mg, 2.04 mmol), $B(C_6F_5)_3$ (51 mg, 0.100 mmol) and but-3-en-2-one **2a** (294 mg, 4.20 mmol) were converted to the desired product. The product **3a** (354 mg, 1.85 mmol, 91%) was obtained (cyclohexane:ethyl acetate = 20:1) as a white solid (m.p. 52-54 ^oC).

^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 2.92 (s, 6H), 2.88 – 2.76 (m, 2H), 2.76 – 2.65 (m, 2H), 2.13 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 149.2, 129.0, 128.9, 113.0, 45.7, 40.9, 30.1, 28.9.

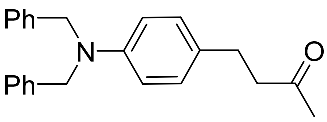
4-(4-(diethylamino)phenyl)butan-2-one (3b)[1]



According to **GP**, *N,N*-diethylaniline **1b** (324 mg, 2.17 mmol), $B(C_6F_5)_3$ (51 mg, 0.100 mmol) and but-3-en-2-one **2a** (282 mg, 4.03 mmol) were converted to the desired product. The product **3b** (360 mg, 1.64 mmol, 76%) was obtained (cyclohexane:ethyl acetate = 20:1) as a colourless liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.14 – 6.92 (m, 2H), 6.74 – 6.52 (m, 2H), 3.33 (q, *J* = 7.1 Hz, 4H), 2.92 – 2.76 (m, 2H), 2.76 – 2.66 (m, 2H), 2.14 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 146.3, 129.1, 127.6, 112.2, 45.8, 44.4, 30.1, 28.9, 12.6.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{14}H_{21}NO$ $[M^{+}+H]$: 220.1696; *m/z* found $C_{14}H_{21}NO$ $[M^{+}+H]$: 220.1696.

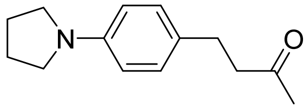
4-(4-(dibenzylamino)phenyl)butan-2-one (3c)



According to **GP**, *N,N*-dibenzylaniline **1c** (555 mg, 2.03 mmol), $B(C_6F_5)_3$ (60 mg, 0.117 mmol) and but-3-en-2-one **2a** (277 mg, 3.96 mmol) were converted to the desired product. The product **3c** (672 mg, 1.96 mmol, 97%) was obtained (cyclohexane:ethyl acetate = 20:1) as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.23 (m, 10H), 7.08 – 6.97 (m, 2H), 6.80 – 6.65 (m, 2H), 4.67 (s, 4H), 2.88 – 2.80 (m, 2H), 2.79 – 2.70 (m, 2H), 2.18 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 146.3, 129.1, 127.61 , 112.2, 45.8, 44.4, 30.1, 28.9, 12.6.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{24}H_{25}NONa$ [M^++Na]: 366.1828; *m/z* found $C_{24}H_{25}NONa$ [M^++Na]: 366.1833.

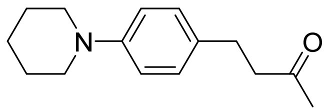
4-(4-(pyrrolidin-1-yl)phenyl)butan-2-one (**3d**)



According to **GP**, 1-phenylpyrrolidine **1d** (293 mg, 1.99 mmol), $B(C_6F_5)_3$ (54 mg, 0.106 mmol) and but-3-en-2-one **2a** (276 mg, 3.94 mmol) were converted to the desired product. The product **3d** (376 mg, 1.73 mmol, 87%) was obtained (cyclohexane:ethyl acetate = 20:1) as a white solid (m.p. 51-53 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 8.7, 0.7 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 2H), 3.39 – 3.13 (m, 4H), 2.81 (ddd, *J* = 7.9, 6.4, 1.9 Hz, 2H), 2.77 – 2.65 (m, 2H), 2.13 (d, *J* = 0.5 Hz, 3H), 2.05 – 1.94 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 146.5, 129.0, 111.8, 47.8, 45.9, 30.2, 29.0, 25.5.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{14}H_{19}NO$ [M^++H]: 218.1539; *m/z* found $C_{14}H_{19}NO$ [M^++H]: 218.1536.

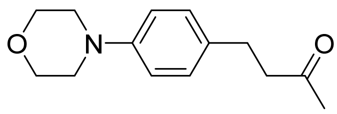
4-(4-(piperidin-1-yl)phenyl)butan-2-one (**3e**)



According to **GP**, 1-phenylpiperidine **1e** (335 mg, 2.08 mmol), $B(C_6F_5)_3$ (52 mg, 0.102 mmol) and but-3-en-2-one **2a** (289 mg, 4.13 mmol) were converted to the desired product. The product **3e** (303 mg, 1.31 mmol, 63%) was obtained (cyclohexane:ethyl acetate = 20:1) as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 – 7.00 (m, 2H), 6.94 – 6.79 (m, 2H), 3.22 – 3.02 (m, 4H), 2.81 (ddd, *J* = 7.9, 6.5, 1.8 Hz, 2H), 2.77 – 2.66 (m, 2H), 2.13 (s, 3H), 1.79 – 1.63 (m, 4H), 1.63 – 1.48 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.4, 150.7, 131.6, 128.8, 116.8, 51.0, 45.5, 30.1, 29.0, 25.9, 24.3.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{15}H_{21}NONa$ [M^++Na]: 254.1515; *m/z* found $C_{15}H_{21}NONa$ [M^++Na]: 254.1509.

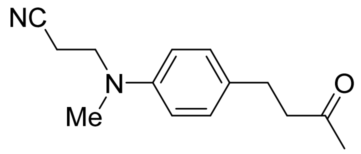
4-(4-morpholinophenyl)butan-2-one (**3f**)



According to **GP**, 4-phenylmorpholine **1f** (342 mg, 2.10 mmol), $B(C_6F_5)_3$ (55 mg, 0.108 mmol) and but-3-en-2-one **2a** (285 mg, 4.07 mmol) were converted to the desired product. The product **3f** (341 mg, 1.46 mmol, 70%) was obtained (cyclohexane:ethyl acetate = 20:1) as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.04 (m, 2H), 6.90 – 6.79 (m, 2H), 3.92 – 3.73 (m, 4H), 3.20 – 3.04 (m, 4H), 2.82 (ddd, *J* = 7.9, 6.6, 1.7 Hz, 2H), 2.71 (ddd, *J* = 9.3, 6.6, 1.8 Hz, 2H), 2.12 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.2, 149.7, 132.5, 129.0, 116.0, 67.0, 49.6, 45.4, 30.1, 28.9.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{14}H_{19}NO_2$ [M^++H]: 234.1489; *m/z* found $C_{14}H_{19}NO_2$ [M^++H]: 234.1484.

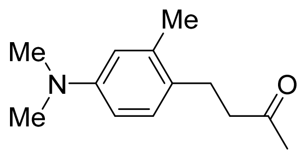
3-(methyl(4-(3-oxobutyl)phenyl)amino)propanenitrile (**3g**)



According to **GP**, 3-(methyl(phenyl)amino)propanenitrile **1g** (326 mg, 2.04 mmol), $B(C_6F_5)_3$ (55 mg, 0.108 mmol) and but-3-en-2-one **2a** (302 mg, 4.31 mmol) were converted to the desired product. The product **3g** (140 mg, 1.46 mmol, 30%) was obtained (cyclohexane:ethyl acetate = 10:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 3.68 (t, *J* = 6.9 Hz, 2H), 2.99 (s, 3H), 2.86 – 2.77 (m, 2H), 2.75 – 2.68 (m, 2H), 2.55 (t, *J* = 6.9 Hz, 2H), 2.13 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.4, 146.1, 130.2, 129.36, 118.5, 113.0, 49.2, 45.5, 38.8, 30.1, 28.8, 15.2.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{14}H_{18}N_2ONa$ [M^++Na]: 253.1311; *m/z* found $C_{14}H_{18}N_2ONa$ [M^++Na]: 253.1312.

4-(4-(dimethylamino)-2-methylphenyl)butan-2-one (**3h**)[(1)]

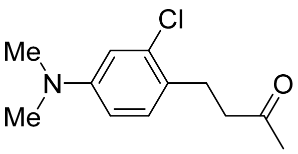


According to **GP**, *N,N,*3-trimethylaniline **1h** (273 mg, 2.02 mmol), $B(C_6F_5)_3$ (54 mg, 0.106 mmol) and but-3-en-2-one **2a** (282 mg, 4.03 mmol) were converted to the desired product. The product **3h** (383 mg, 1.87 mmol, 93%) was obtained (cyclohexane:ethyl acetate = 20:1) as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 – 6.94 (m, 1H), 6.57 (d, *J* = 7.6 Hz, 2H), 2.92 (s, 6H), 2.86 – 2.76 (m, 2H), 2.74 – 2.62 (m, 2H), 2.30 (s, 3H), 2.16 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 149.4, 136.5, 129.3, 127.3, 114.9, 110.8, 44.5, 40.9, 30.1, 26.4, 19.9.

HRMS (ESI-TOF/MS): *m/z* calcd. $C_{13}H_{19}NO$ [M^++H]: 206.1539; *m/z* found $C_{13}H_{19}NO$ [M^++H]: 206.1539.

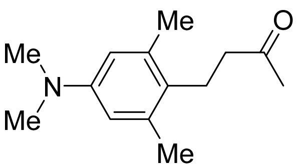
4-(2-chloro-4-(dimethylamino)phenyl)butan-2-one (**3i**)



According to **GP**, 3-chloro-*N,N*-dimethylaniline **1i** (308 mg, 1.99 mmol), $B(C_6F_5)_3$ (50 mg, 0.098 mmol) and but-3-en-2-one **2a** (289 mg, 4.13 mmol) were converted to the desired product. The product **3i** (395 mg, 1.76 mmol, 88%) was obtained (cyclohexane:ethyl acetate = 20:1) as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 2.7 Hz, 1H), 6.55 (dd, *J* = 8.5, 2.7 Hz, 1H), 2.91 (m, 8H), 2.71 (ddt, *J* = 8.4, 7.2, 0.6 Hz, 2H), 2.13 (t, *J* = 0.5 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3, 150.1, 134.4, 130.8, 125.7, 113.2, 111.3, 43.9, 40.5, 30.0, 27.0.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{12}H_{16}ClNO$ [M^++H]: 226.0993; *m/z* found $C_{12}H_{16}ClNO$ [M^++H]: 226.0997.

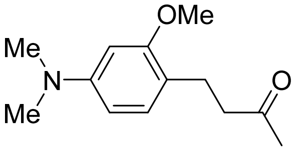
4-(4-(dimethylamino)-2,6-dimethylphenyl)butan-2-one (**3j**)



According to **GP**, *N,N*,3,5-tetramethylaniline **1j** (310 mg, 2.08 mmol), $B(C_6F_5)_3$ (53 mg, 0.104 mmol) and but-3-en-2-one **2a** (291 mg, 4.16 mmol) were converted to the desired product. The product **3j** (420 mg, 1.92 mmol, 92%) was obtained (cyclohexane:ethyl acetate = 20:1) as a white solid (m.p. 57-58 ^{o}C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (s, 2H), 2.90 (d, *J* = 0.5 Hz, 6H), 2.86 – 2.78 (m, 2H), 2.62 – 2.51 (m, 2H), 2.28 (d, *J* = 0.7 Hz, 6H), 2.17 (d, *J* = 0.6 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.8, 149.0, 136.7, 126,0, 113.0, 43.4, 40.8, 29.9, 23.0, 20.3.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{14}H_{21}NONa$ [M^++Na]: 242.1515; *m/z* found $C_{14}H_{21}NONa$ [M^++Na]: 242.1514.

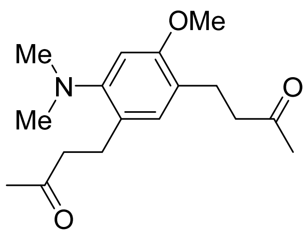
4-(4-(dimethylamino)-2-methoxyphenyl)butan-2-one (**3k**)



According to **GP**, 3-methoxy-*N,N*-dimethylaniline **1k** (302 mg, 2.00 mmol), $B(C_6F_5)_3$ (54 mg, 0.106 mmol) and but-3-en-2-one **2a** (278 mg, 3.97 mmol) were converted to the desired product. The product **3k** (275 mg, 1.24 mmol, 62%) was obtained (cyclohexane:ethyl acetate = 20:1) as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 – 6.91 (m, 1H), 6.35 – 6.08 (m, 2H), 3.82 (s, 3H), 2.93 (s, 6H), 2.79 (ddd, *J* = 8.4, 6.6, 1.8 Hz, 2H), 2.73 – 2.62 (m, 2H), 2.13 (d, *J* = 0.5 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 209.3, 158.1, 150.9, 130.2, 117.5, 104.7, 96.4, 55.1, 44.3, 40.9, 29.9, 24.4.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{13}H_{19}NO_2Na$ [M^++Na]: 244.1308; *m/z* found $C_{13}H_{19}NO_2Na$ [M^++Na]: 244.1307.

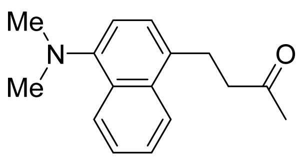
4,4'-(4-(dimethylamino)-6-methoxy-1,3-phenylene)bis(butan-2-one) (**3l**)



According to **GP**, 3-methoxy-*N,N*-dimethylaniline **1l** (302 mg, 2.00 mmol), $B(C_6F_5)_3$ (54 mg, 0.106 mmol) and but-3-en-2-one **2a** (278 mg, 3.97 mmol) were converted to the desired product. The product **3l** (192 mg, 0.660 mmol, 33%) was obtained as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.61 (s, 1H), 3.79 (s, 3H), 2.91 – 2.65 (m, 8H), 2.64 (s, 6H), 2.13 (d, *J* = 3.5 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 208.9, 156.3, 151.9, 130.9, 127.4, 124.2, 102.6, 55.3, 45.2, 44.8, 43.9, 29.9, 24.9, 24.6.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{17}H_{25}NO_3Na$ [M^++Na]: 314.1727; *m/z* found $C_{17}H_{25}NO_3Na$ [M^++Na]: 314.1727.

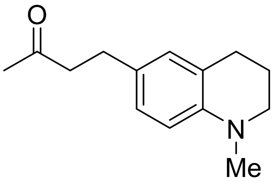
4-(4-(dimethylamino)naphthalen-1-yl)butan-2-one (**3m**)



According to **GP**, *N,N*-dimethylnaphthalen-1-amine **1m** (357 mg, 2.09 mmol), $B(C_6F_5)_3$ (54 mg, 0.106 mmol) and but-3-en-2-one **2a** (280 mg, 4.00 mmol) were converted to the desired product. The product **3m** (428 mg, 1.78 mmol, 85%) was obtained (cyclohexane:ethyl acetate = 10:1) as a colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 – 8.28 (m, 1H), 8.10 – 7.91 (m, 1H), 7.63 – 7.50 (m, 2H), 7.37 – 7.18 (m, 1H), 7.06 (d, J = 7.6 Hz, 1H), 3.44 – 3.25 (m, 2H), 2.93 (m, 8H), 2.21 (d, J = 0.5 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.2, 149.8, 131.5, 129.3, 125.9, 125.0, 124.9, 123.9, 113.8, 45.4, 44.6, 30.1, 26.6.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{16}H_{19}NONa$ [M^++Na]: 264.1359; *m/z* found $C_{16}H_{19}NONa$ [M^++Na]: 264.1354.

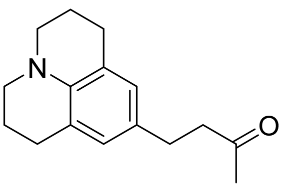
4-(1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)butan-2-one (**3n**)



According to **GP**, *N,N*-dimethylnaphthalen-1-amine **1n** (138 mg, 0.939 mmol), $B(C_6F_5)_3$ (27 mg, 0.053 mmol) and but-3-en-2-one **2a** (164 mg, 2.34 mmol) were converted to the desired product. The product **3n** (84 mg, 0.387 mmol, 39%) was obtained (cyclohexane:ethyl acetate = 20:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (dd, J = 8.3, 2.3 Hz, 1H), 6.78 (d, J = 2.3 Hz, 1H), 6.53 (d, J = 8.2 Hz, 1H), 3.32 – 3.12 (m, 2H), 2.86 (d, J = 2.5 Hz, 3H), 2.83 – 2.62 (m, 6H), 2.14 (s, 3H), 2.08 – 1.88 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 145.2, 128.8, 128.5, 126.7, 123.1, 111.3, 51.4, 45.8, 39.3, 30.1, 28.9, 27.8, 22.6.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{14}H_{19}NONa$ [M^++Na]: 240.1359; *m/z* found $C_{14}H_{19}NONa$ [M^++Na]: 240.1362.

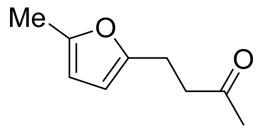
4-(2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)butan-2-one (**3o**)



According to **GP** (130 °C in 2.0 mL mesitylene), julolidine **1o** (345 mg, 1.99 mmol), $B(C_6F_5)_3$ (49 mg, 0.096 mmol) and but-3-en-2-one **2a** (286 mg, 4.08 mmol) were converted to the desired product. The product **3o** (275 mg, 1.13 mmol, 57%) was obtained (cyclohexane:ethyl acetate = 30:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.61 (s, 2H), 3.21 – 3.01 (m, 4H), 2.81 – 2.67 (m, 8H), 2.15 (d, J = 2.4 Hz, 3H), 2.06 – 1.90 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 128.1, 126.8, 121.8, 50.1, 45.9, 30.1, 28.9, 27.6, 22.2.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{16}H_{21}NONa$ [M^++Na]: 266.1515; *m/z* found $C_{16}H_{21}NONa$ [M^++Na]: 266.1510.

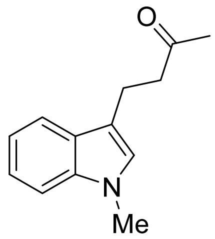
4-(5-methylfuran-2-yl)butan-2-one (**3q**)[2]



According to **GP**, 2-methylfuran **1q** (171 mg, 2.08 mmol), $B(C_6F_5)_3$ (49 mg, 0.096 mmol) and but-3-en-2-one **2a** (292 mg, 4.17 mmol) were converted to the desired product. The product **3q** (180 mg, 1.18 mmol, 57%) was obtained (cyclohexane:ethyl acetate = 30:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 – 5.73 (m, 2H), 2.85 (dd, *J* = 9.1, 6.4 Hz, 2H), 2.80 – 2.69 (m, 2H), 2.23 (d, *J* = 1.1 Hz, 3H), 2.15 (d, *J* = 0.8 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 207.5, 152.6, 150.6, 105.9, 105.8, 41.9, 29.9, 22.3, 13.5.

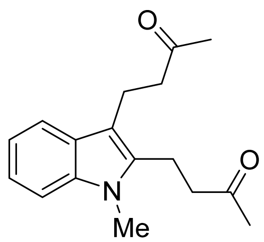
4-(1-methyl-1H-indol-3-yl)butan-2-one (**3r**)[3]



According to **GP**, 1-methyl-indole **1r** (263 mg, 2.01 mmol), $B(C_6F_5)_3$ (50 mg, 0.098 mmol) and but-3-en-2-one **2a** (290 mg, 4.14 mmol) were converted to the desired product. The product **3r** (175 mg, 0.871 mmol, 43%) was obtained (cyclohexane:ethyl acetate = 20:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (ddd, *J* = 10.9, 5.8, 2.3 Hz, 1H), 7.42 – 7.23 (m, 2H), 7.19 (tdd, *J* = 6.5, 3.5, 1.4 Hz, 1H), 6.90 (dd, *J* = 6.4, 3.3 Hz, 1H), 3.90 – 3.71 (m, 3H), 3.19 – 3.04 (m, 2H), 2.90 (td, *J* = 7.8, 3.3 Hz, 2H), 2.30 – 2.09 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.8, 137.0, 126.4, 121.6, 118.8, 118.8, 113.7, 109.3, 44.4, 32.6, 30.1, 19.3.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{13}H_{15}NONa$ $[M^+{+}Na]$: 224.1046; *m/z* found $C_{13}H_{15}NONa$ $[M^+{+}Na]$: 224.1046.

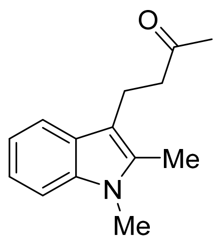
4,4'-(1-methyl-1H-indole-2,3-diyl)bis(butan-2-one) (**3s**)



According to **GP**, 1-methyl-indole **1r** (263 mg, 2.01 mmol), $B(C_6F_5)_3$ (50 mg, 0.098 mmol) and but-3-en-2-one **2a** (290 mg, 4.14 mmol) were converted to the desired product. The product **3s** (235 mg, 0.867 mmol, 43%) was obtained (cyclohexane:ethyl acetate = 10:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.45 (m, 1H), 7.36 – 7.18 (m, 2H), 7.14 (tdd, *J* = 6.6, 2.5, 1.3 Hz, 1H), 3.70 (dd, *J* = 5.1, 2.0 Hz, 3H), 3.18 – 2.97 (m, 4H), 2.79 (ddd, *J* = 21.8, 9.3, 5.4 Hz, 4H), 2.25 – 2.19 (m, 3H), 2.19 – 2.12 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 207.2, 136.9, 135.7, 127.2, 121.1, 119.0, 118.1, 110.3, 108.9, 44.6, 43.6, 30.2, 30.1, 29.7, 18.6, 18.4.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{17}H_{21}NO_2Na$ [M^++Na]: 294.1465; *m/z* found $C_{17}H_{21}NO_2Na$ [M^++Na]: 294.1465.

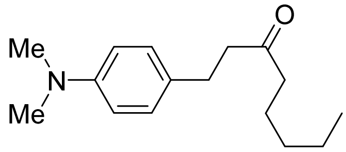
4-(1,2-dimethyl-1H-indol-3-yl)butan-2-one (**3t**)



According to **GP**, 1,2-dimethyl-indole **1t** (295 mg, 2.03 mmol), $B(C_6F_5)_3$ (50 mg, 0.098 mmol) and but-3-en-2-one **2a** (251 mg, 3.59 mmol) were converted to the desired product. The product **3t** (269 mg, 1.25 mmol, 62%) was obtained (cyclohexane:ethyl acetate = 20:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.50 (m, 1H), 7.38 – 7.28 (m, 1H), 7.27 – 7.19 (m, 1H), 7.14 (ddt, *J* = 8.0, 6.9, 0.9 Hz, 1H), 3.81 – 3.68 (m, 3H), 3.06 (dd, *J* = 8.2, 6.7 Hz, 2H), 2.82 (dd, *J* = 8.1, 6.8 Hz, 2H), 2.44 (d, *J* = 2.6 Hz, 3H), 2.17 (d, *J* = 0.7 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 209.0, 133.1, 127.3, 120.6, 118.8, 117.7, 109.7, 108.7, 44.6, 30.3, 29.5, 18.7, 10.2.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{14}H_{17}NONa$ [M^++Na]: 216.1383; *m/z* found $C_{14}H_{17}NONa$ [M^++Na]: 216.1384.

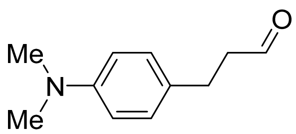
1-(4-(dimethylamino)phenyl)octan-3-one (**3u**)



According to **GP**, *N,N*-dimethylaniline **1a** (247 mg, 2.04 mmol), $B(C_6F_5)_3$ (54 mg, 0.106 mmol) and oct-1-en-3-one **2b** (511 mg, 4.06 mmol) were converted to the desired product. The product **3u** (253 mg, 1.83 mmol, 90%) was obtained (cyclohexane:ethyl acetate = 30:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 – 7.02 (m, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 2.91 (s, 6H), 2.81 (ddd, *J* = 9.2, 7.2, 2.0 Hz, 2H), 2.73 – 2.62 (m, 2H), 2.46 – 2.26 (m, 2H), 1.66 – 1.46 (m, 2H), 1.41 – 1.17 (m, 5H), 0.98 – 0.80 (t, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9, 149.2, 129.2, 128.9, 113.0, 44.8, 43.1, 40.9, 31.4, 28.9, 23.5, 22.5, 14.0.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{16}H_{25}NO$ [M$^+$+H]: 248.2010; *m/z* found $C_{16}H_{25}NO$ [M$^+$+H]: 248.2007.

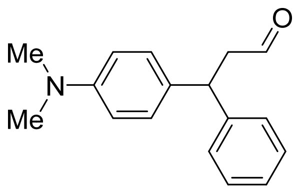
3-(4-(dimethylamino)phenyl)propanal (**3v**)[(4)]



According to **GP**, *N,N*-dimethylaniline **1a** (269 mg, 2.22 mmol), $B(C_6F_5)_3$ (54 mg, 0.106 mmol) and acrylaldehyde **2c** (224 mg, 4.0 mmol) were converted to the desired product. The product **3v** (234 mg, 1.32 mmol, 60%) was obtained (cyclohexane:ethyl acetate = 20:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1.5 Hz, 1H), 7.15 – 6.96 (m, 2H), 6.80 – 6.48 (m, 2H), 2.93 (s, 6H), 2.92 – 2.85 (m, 2H), 2.78 – 2.69 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 202.3, 149.3, 128.9, 128.2, 113.0, 45.7, 40.8, 27.2.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{11}H_{15}NO$ [M$^+$+H]: 178.1226; *m/z* found $C_{11}H_{15}NO$ [M$^+$+H]: 178.1228.

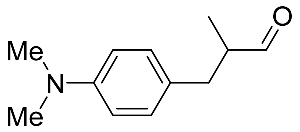
3-(4-(dimethylamino)phenyl)-3-phenylpropanal (**3w**)



According to **GP** (130 ^{o}C in 2.0 mL mesitylene), *N,N*-dimethylaniline **1a** (484 mg, 4.0 mmol), $B(C_6F_5)_3$ (60 mg, 0.117 mmol) and cinnamaldehyde **2d** (262 mg, 1.98 mmol) were converted to the desired product. The product **3w** (242 mg, 0.957 mmol, 48%) was obtained (cyclohexane:ethyl acetate = 30:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (td, *J* = 2.4, 0.8 Hz, 1H), 7.42 – 7.21 (m, 5H), 7.20 – 7.10 (m, 2H), 6.88 – 6.61 (m, 2H), 4.59 (t, *J* = 7.8 Hz, 1H), 3.29 – 3.08 (m, 2H), 3.07 – 2.83 (m, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 149.4, 144.1, 131.0, 128.7, 128.4, 127.6, 126.4, 112.8, 49.6, 44.2, 40.6.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{17}H_{19}NO$ [M$^+$+H]: 254.1539; *m/z* found $C_{17}H_{19}NO$ [M$^+$+H]: 254.1537.

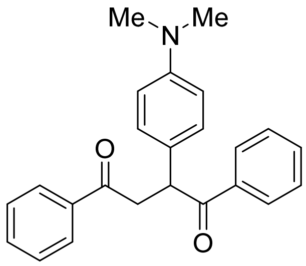
3-(4-(dimethylamino)phenyl)-2-methylpropanal (**3x**)



According to **GP**, *N,N*-dimethylaniline **1a** (238 mg, 1.97 mmol), $B(C_6F_5)_3$ (50 mg, 0.098 mmol) and methacrylaldehyde **2e** (278 mg, 3.97 mmol) were converted to the desired product. The product **3x** (184 mg, 0.963 mmol, 49%) was obtained (cyclohexane:ethyl acetate = 20:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (dd, *J* = 1.7, 0.5 Hz, 1H), 7.14 – 6.98 (m, 2H), 6.84 – 6.60 (m, 2H), 3.03 – 2.88 (m, 7H), 2.72 – 2.48 (m, 2H), 1.15 – 1.03 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 205.1, 149.3, 129.7, 126.6, 112.9, 48.4, 40.8, 35.8, 13.2.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{12}H_{17}NO$ [M^++H]: 192.1383; *m/z* found $C_{12}H_{17}NO$ [M^++H]: 192.1385.

2-(4-(dimethylamino)phenyl)-1,4-diphenylbutane-1,4-dione (**3y**)



According to **GP**, *N,N*-dimethylaniline **1a** (491 mg, 4.06 mmol), $B(C_6F_5)_3$ (58 mg, 0.113 mmol) and (*E*)-1,4-diphenylbut-2-ene-1,4-dione **2f** (456 mg, 1.93 mmol) were converted to the desired product. The product **3y** (626 mg, 1.75 mmol, 91%) was obtained (cyclohexane:ethyl acetate = 20:1) as a yellow solid (m.p. 149-151 ^{o}C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 – 7.98 (m, 4H), 7.68 – 7.53 (m, 1H), 7.55 – 7.39 (m, 5H), 7.32 – 7.21 (m, 2H), 6.82 – 6.64 (m, 2H), 5.39 – 5.23 (m, 1H), 4.25 (dd, *J* = 18.0, 10.1 Hz, 1H), 3.33 (dd, *J* = 18.0, 3.7 Hz, 1H), 2.95 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 198.5, 149.8, 136.7, 136.6, 133.1, 132.7, 129.0, 128.56, 128.5, 125.8, 113.1, 47.8, 43.9, 40.5.
HRMS (ESI-TOF/MS): *m/z* calcd. $C_{24}H_{23}NONa$ [M^++Na]: 380.1621; *m/z* found $C_{24}H_{23}NONa$ [M^++Na]: 380.1623.

Tris(perfluorophenyl)borane[5]

^{19}F NMR (282 MHz, $CDCl_3$) δ -129.80, -145.65, -160.35, -160.40, -160.43, -160.47, -160.51.

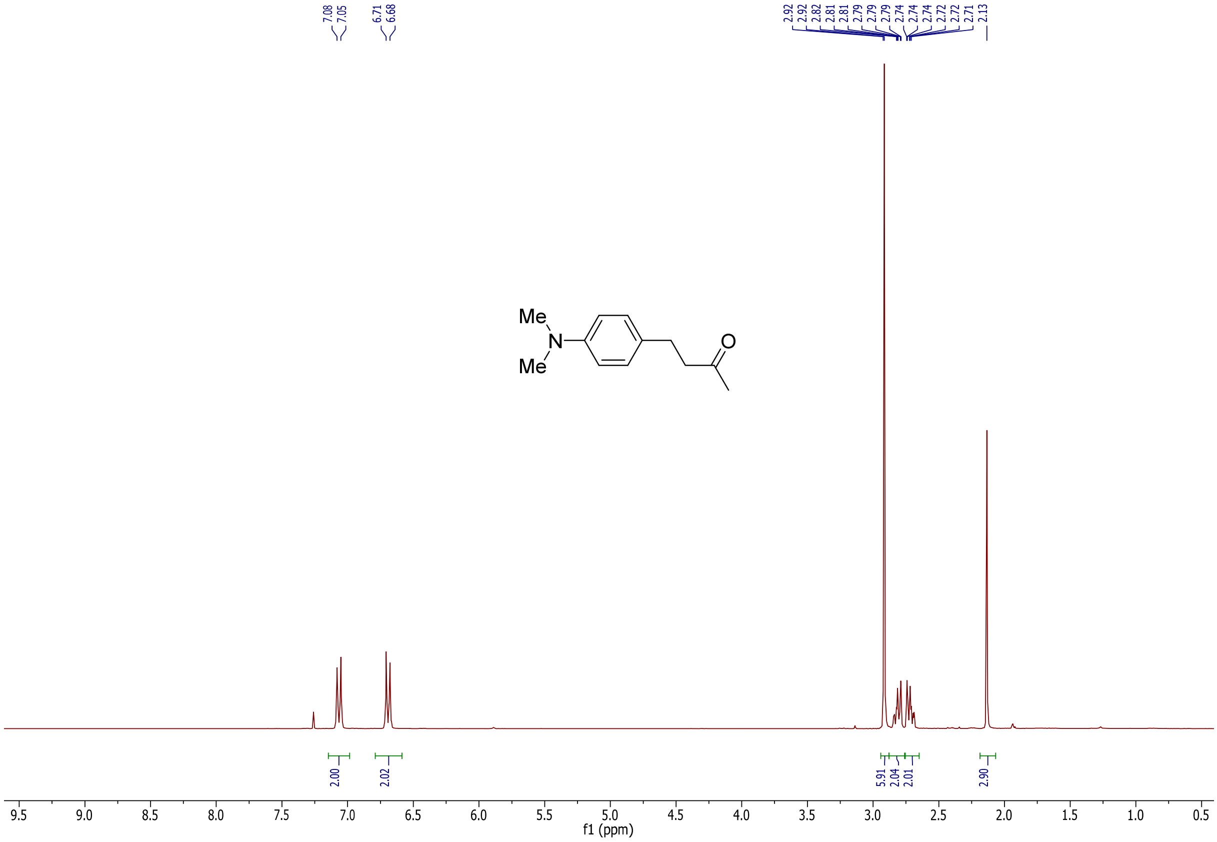
4. Reference

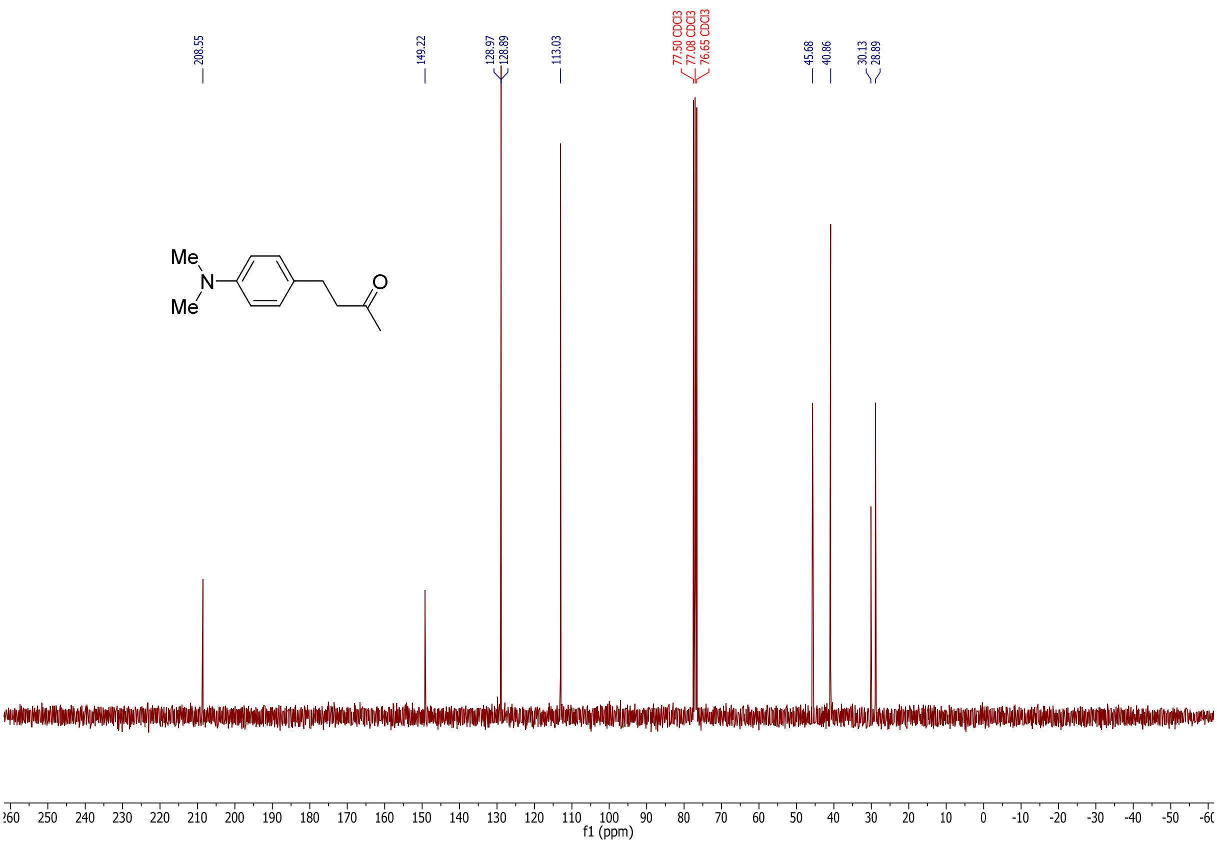
(1) Hu, X.; Martin, D.; Melaimi, M.; Bertrand, G. *J. Am. Chem. Soc.* **2014**, *136*, 13594−13597.
(2) Dyker, G.; Muth, E.; Hashmi, A. S. K.; Ding, L. *Adv. Synth. Catal*. **2003**, *345*, 1247−1252.

(3) Bah, J.; Naidu, V. R.; Teske, J.; Franzén, J. *Adv. Synth. Catal.* **2015**, *357*, 148−158.
(4) Frost, C. G.; Hartley, B. C. *Org. Lett.* **2007**, *9*, 4259–4261.
(5) Bähr, A.; Wilkins, L.C.; Ollegott, K.; Kariuki, B.M.; Melen, R.L. *Molecules* **2015**, *20*, 4530–4547.

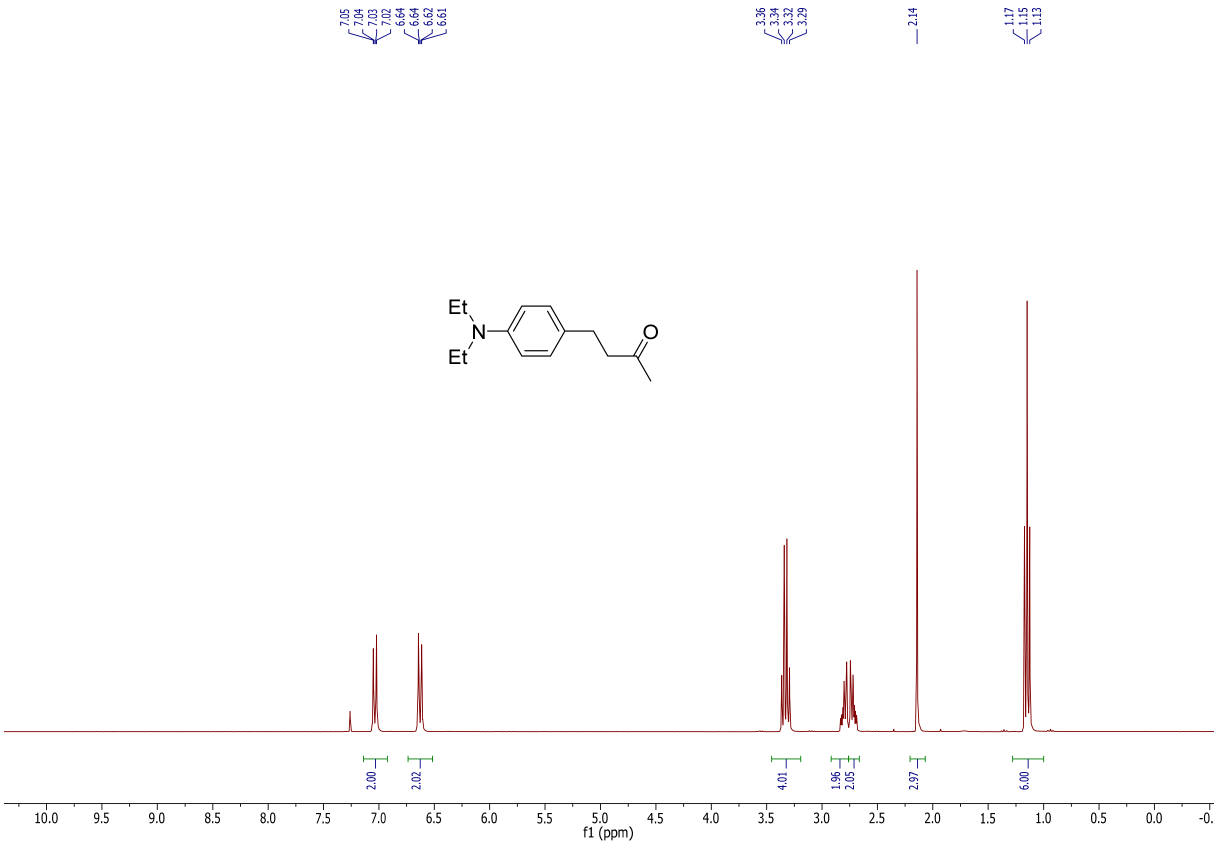
5. ^{1}H NMR and ^{13}C NMR spectra

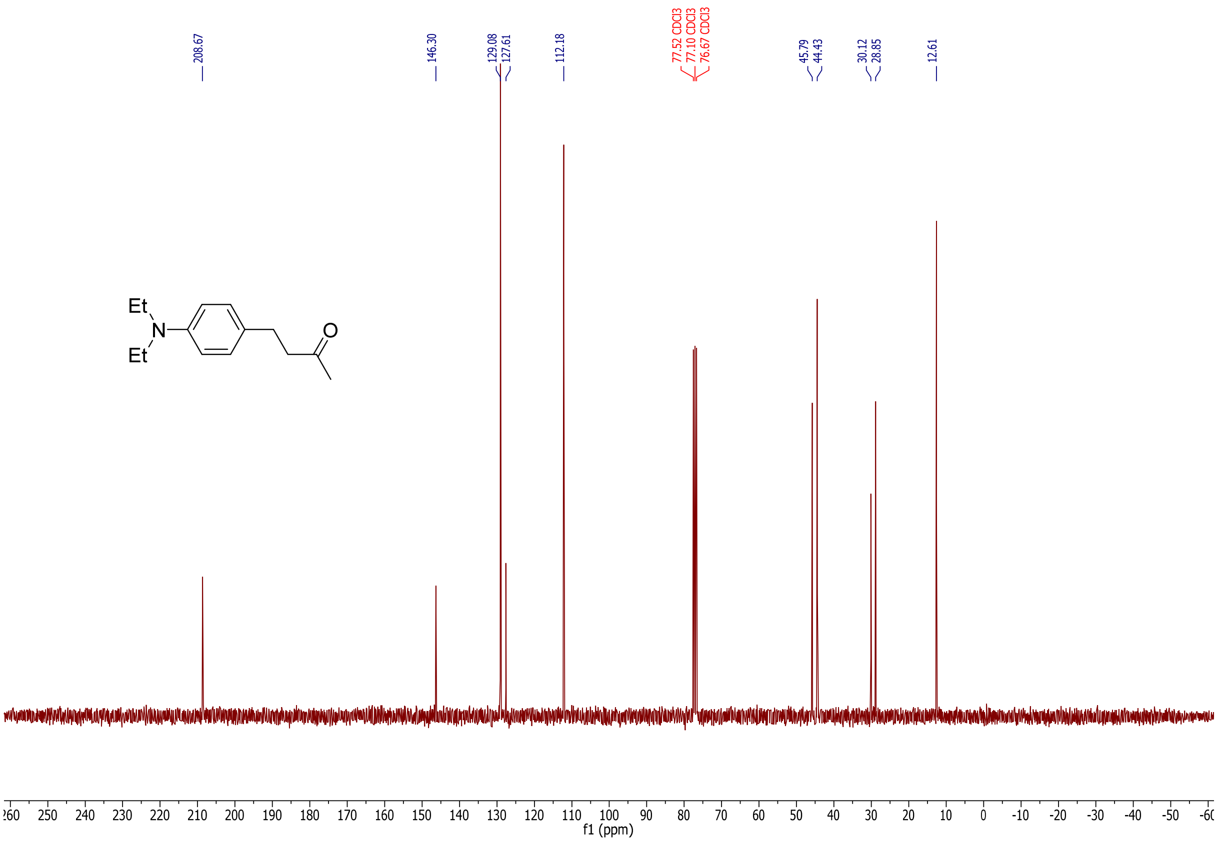
Original spectra for **3a**:



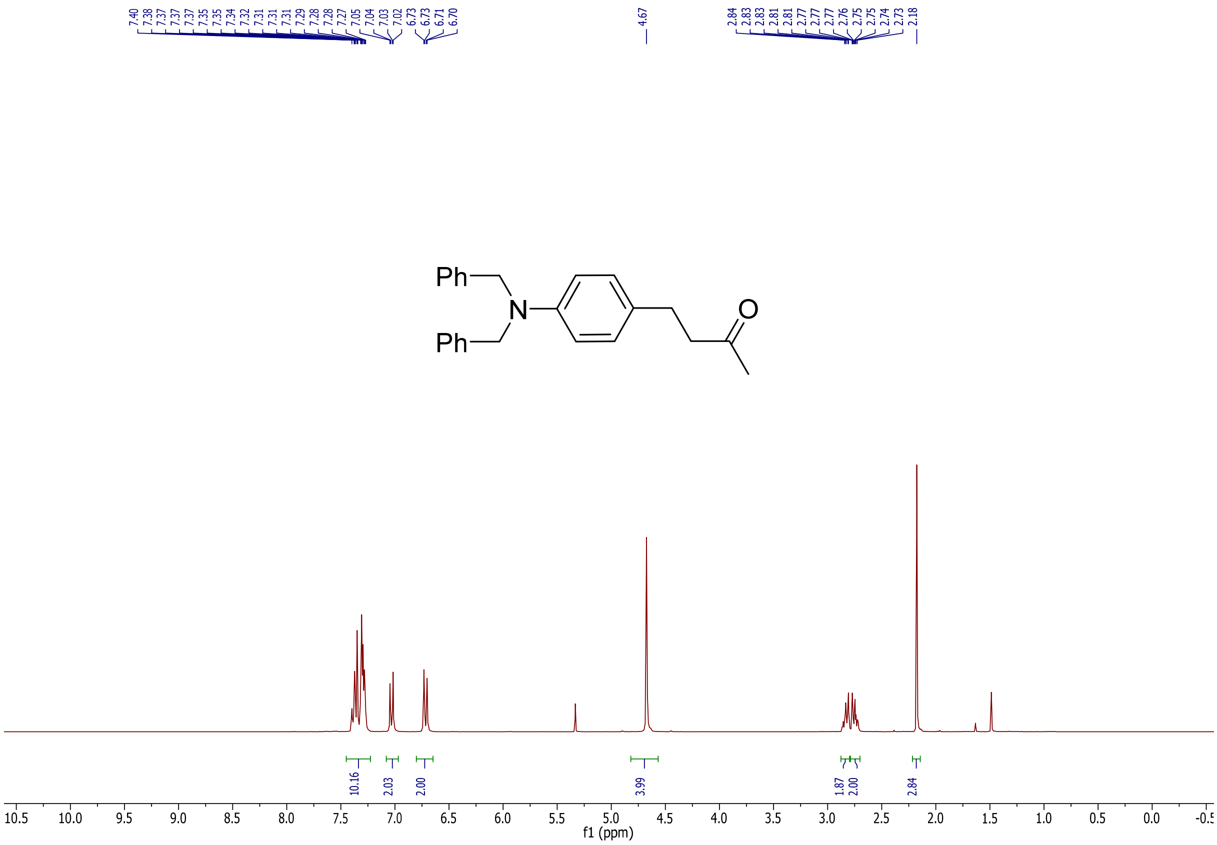


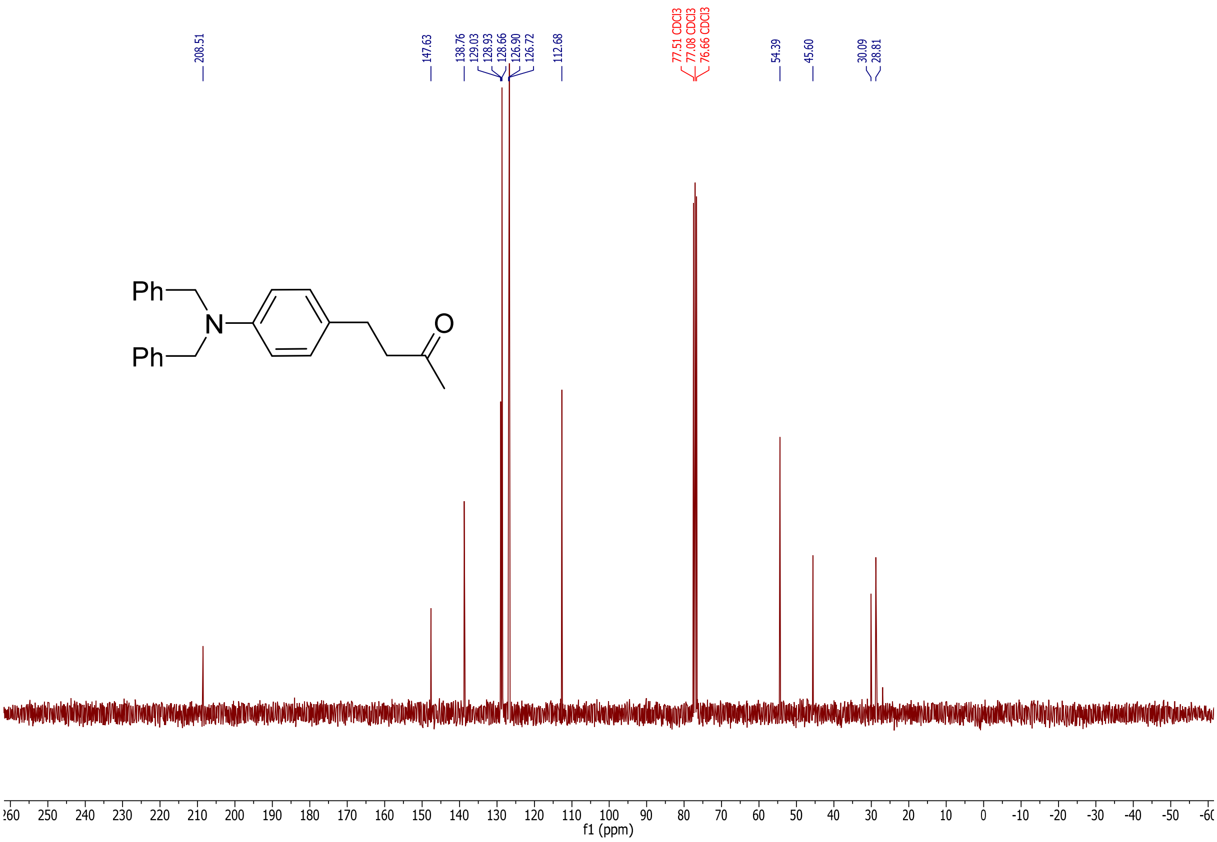
Original spectra for **3b**:



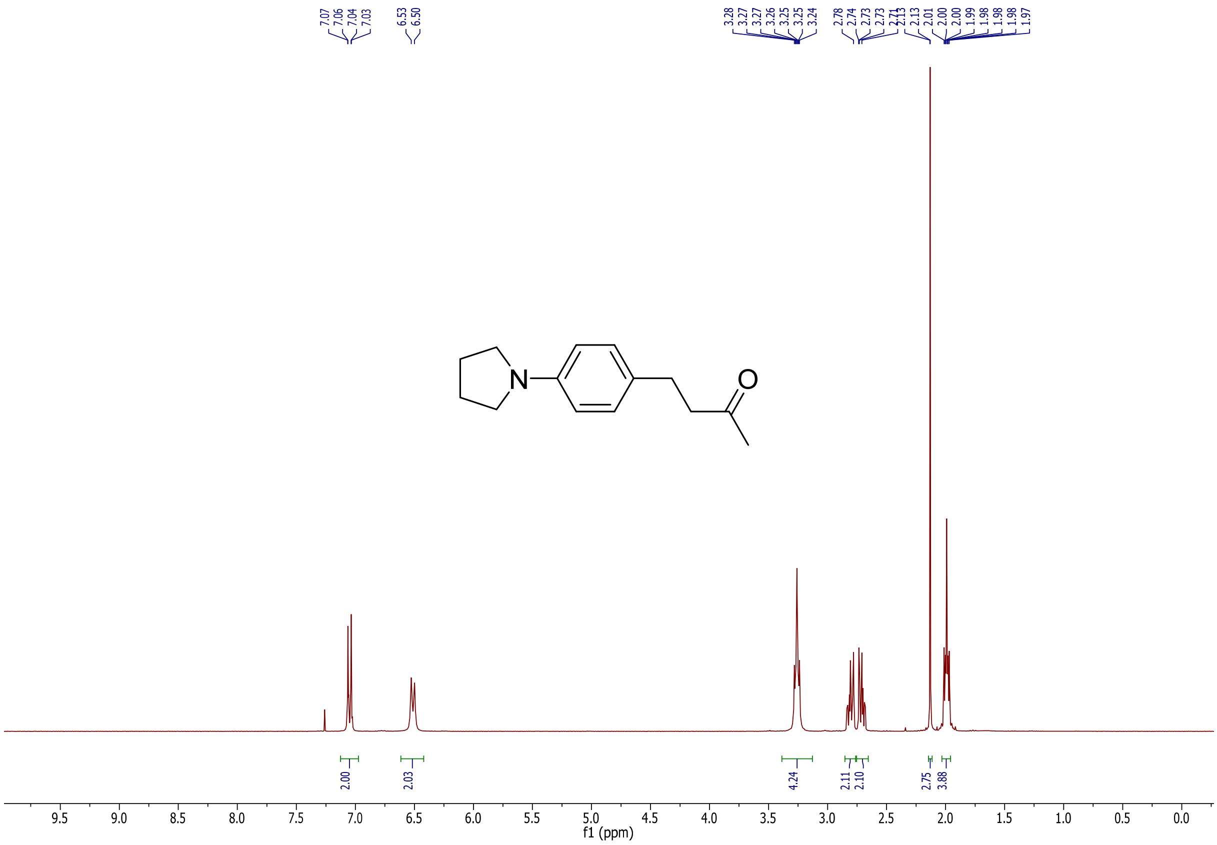


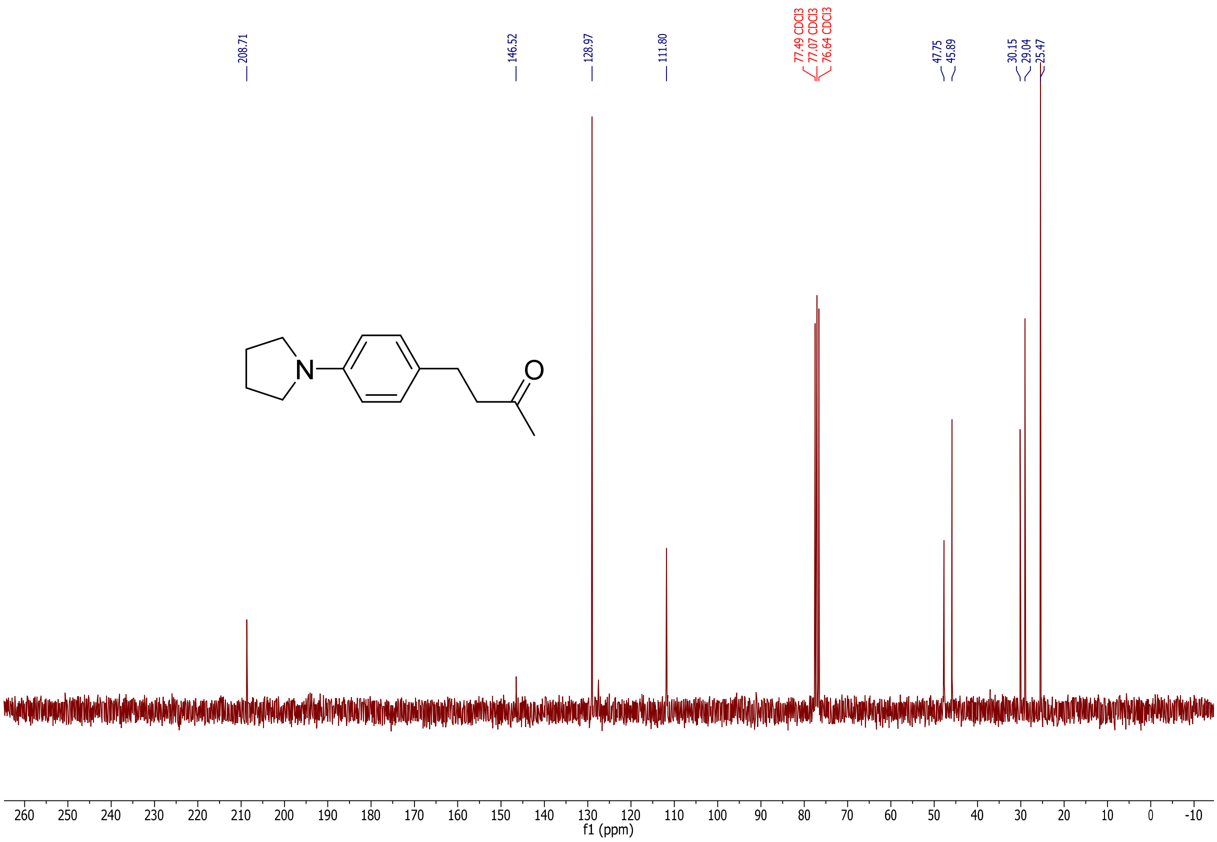
Original spectra for **3c**:



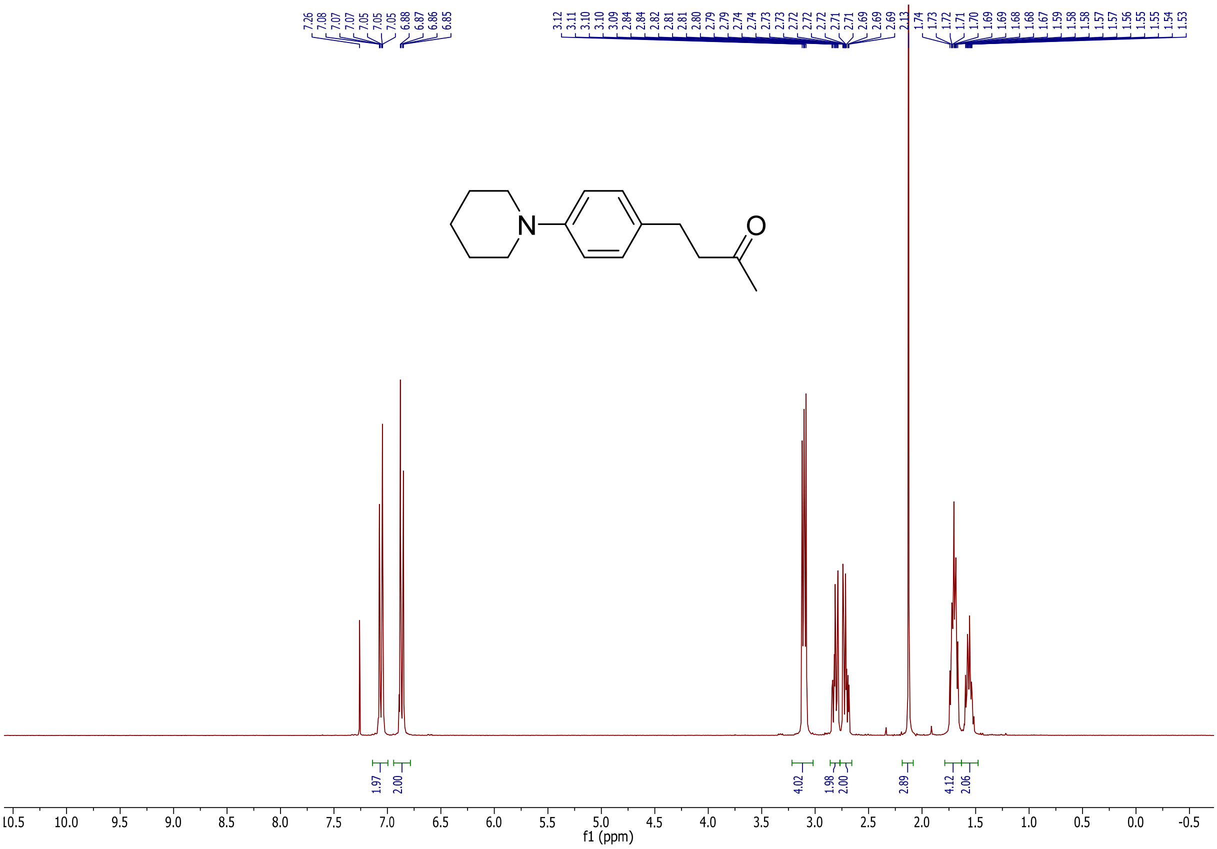


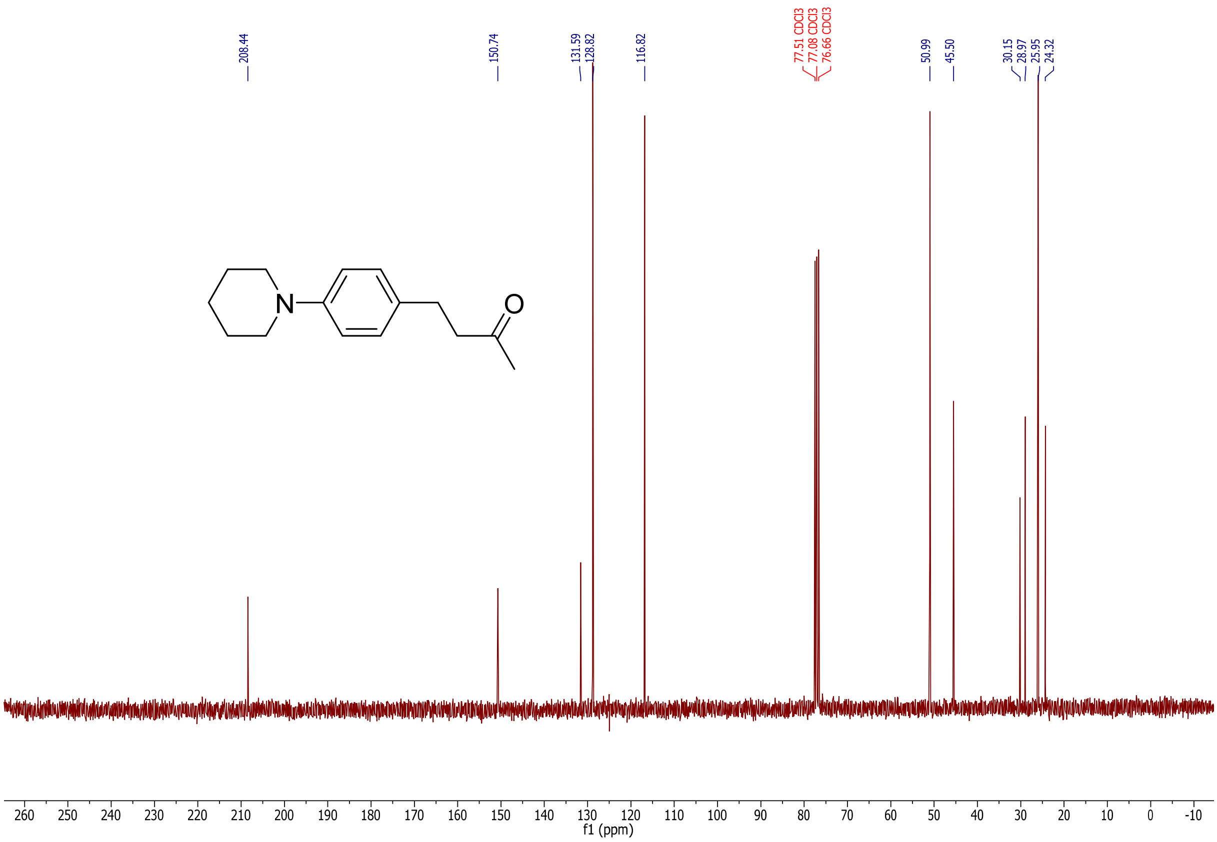
Original spectra for **3d**:



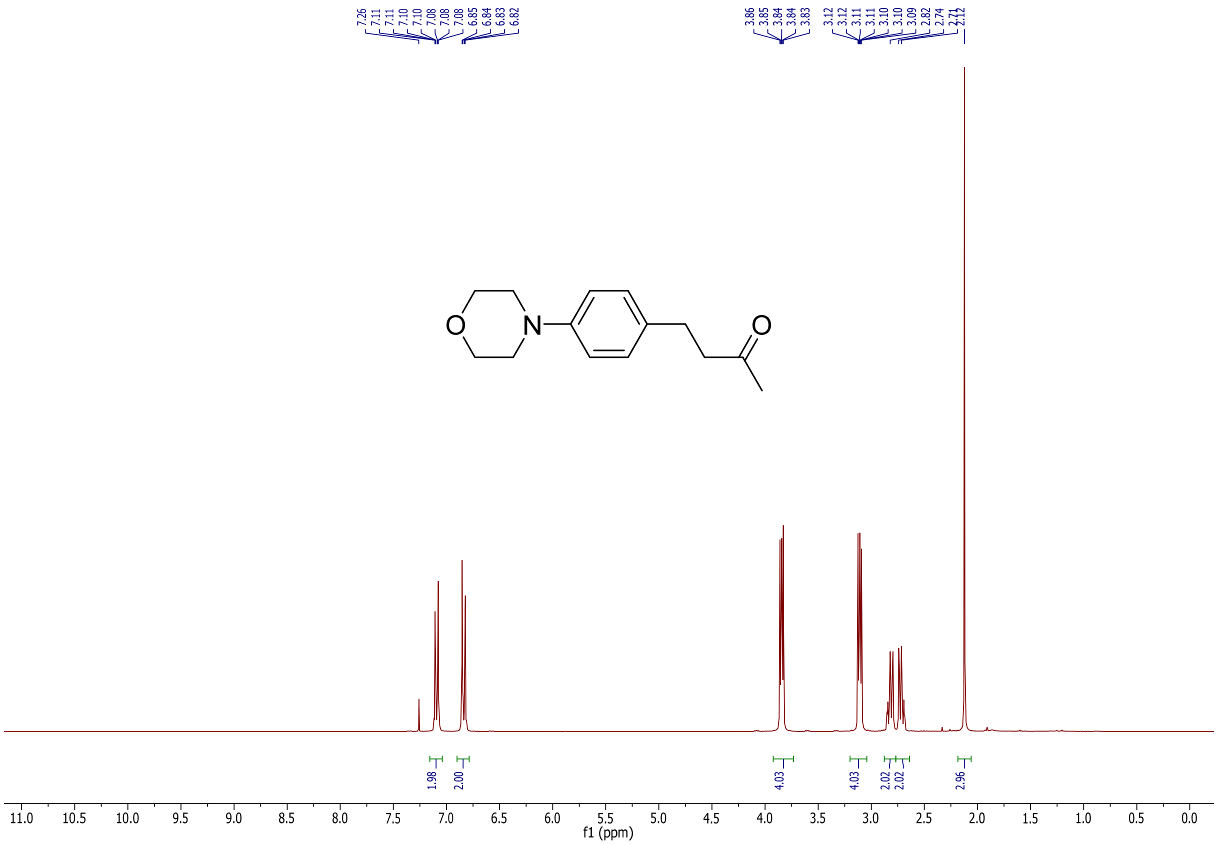


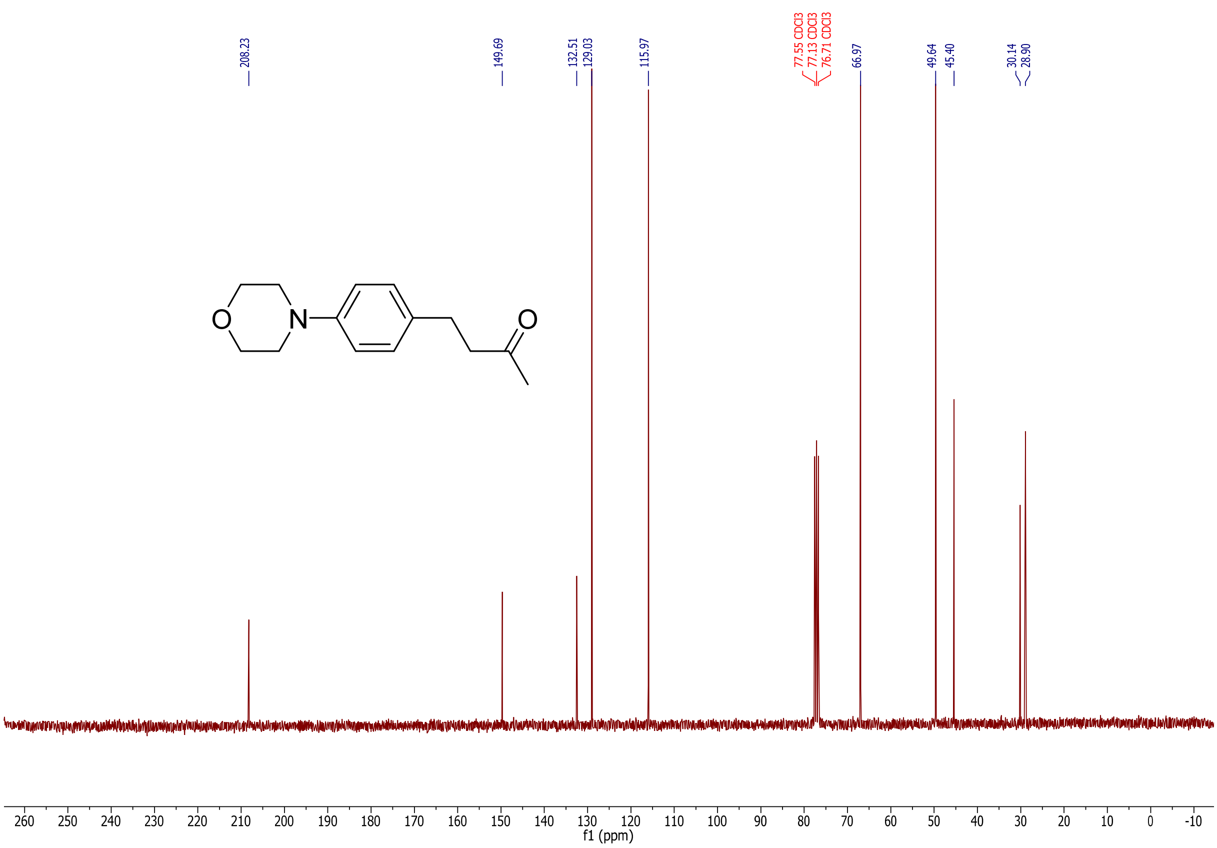
Original spectra for **3e**:



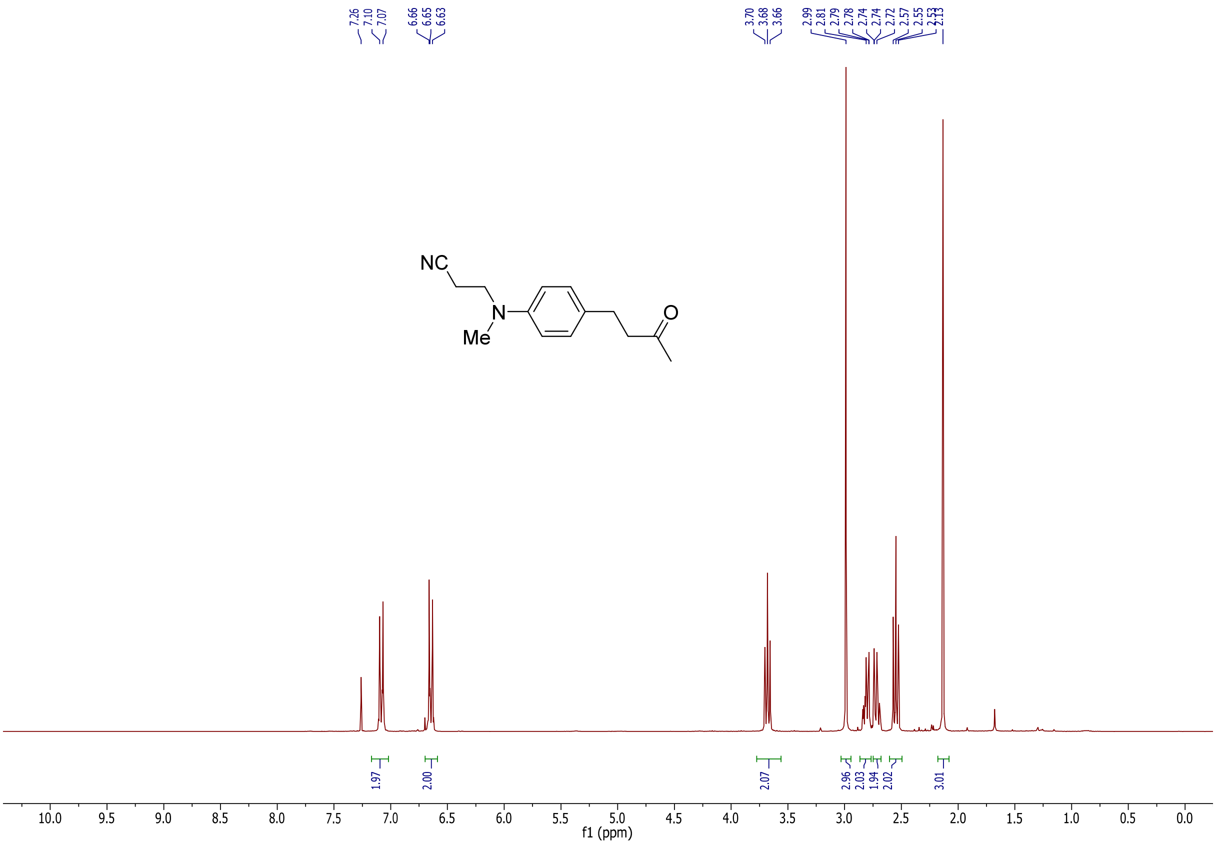


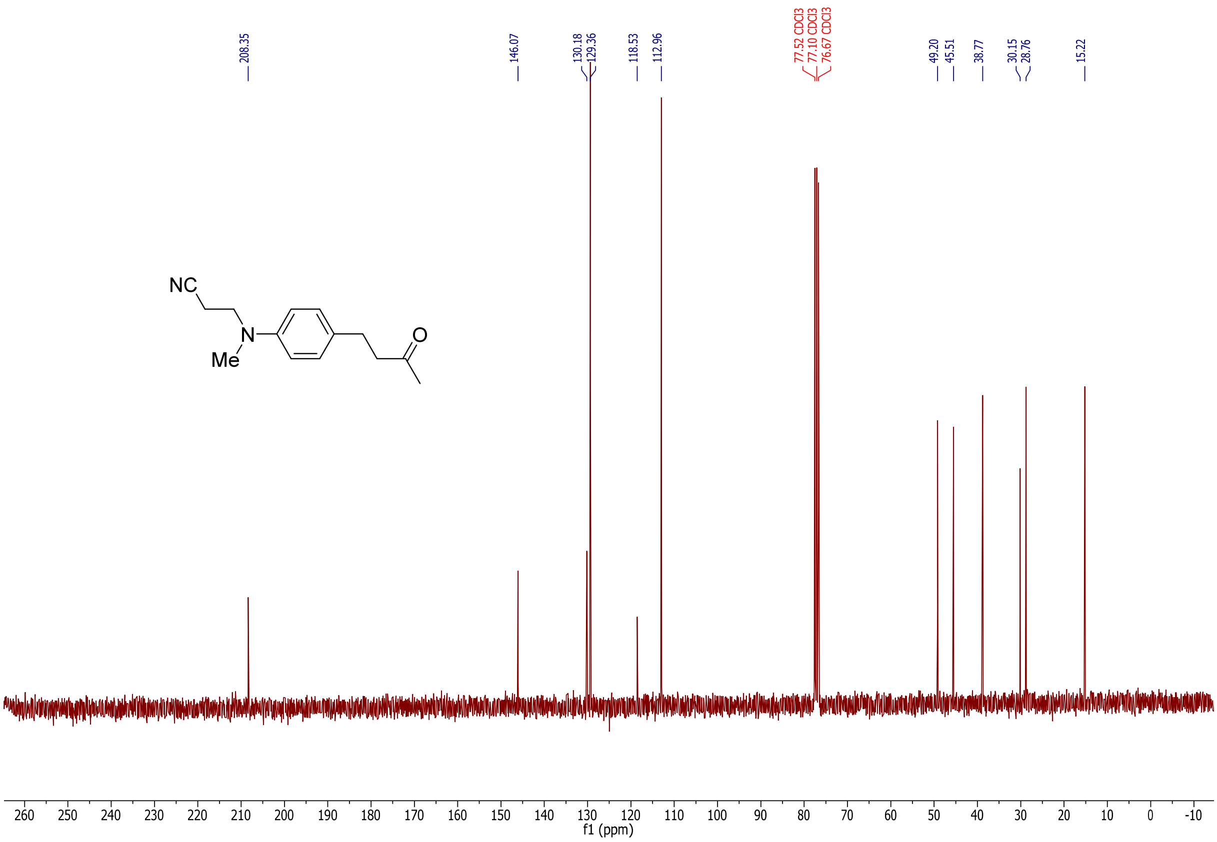
Original spectra for **3f**:



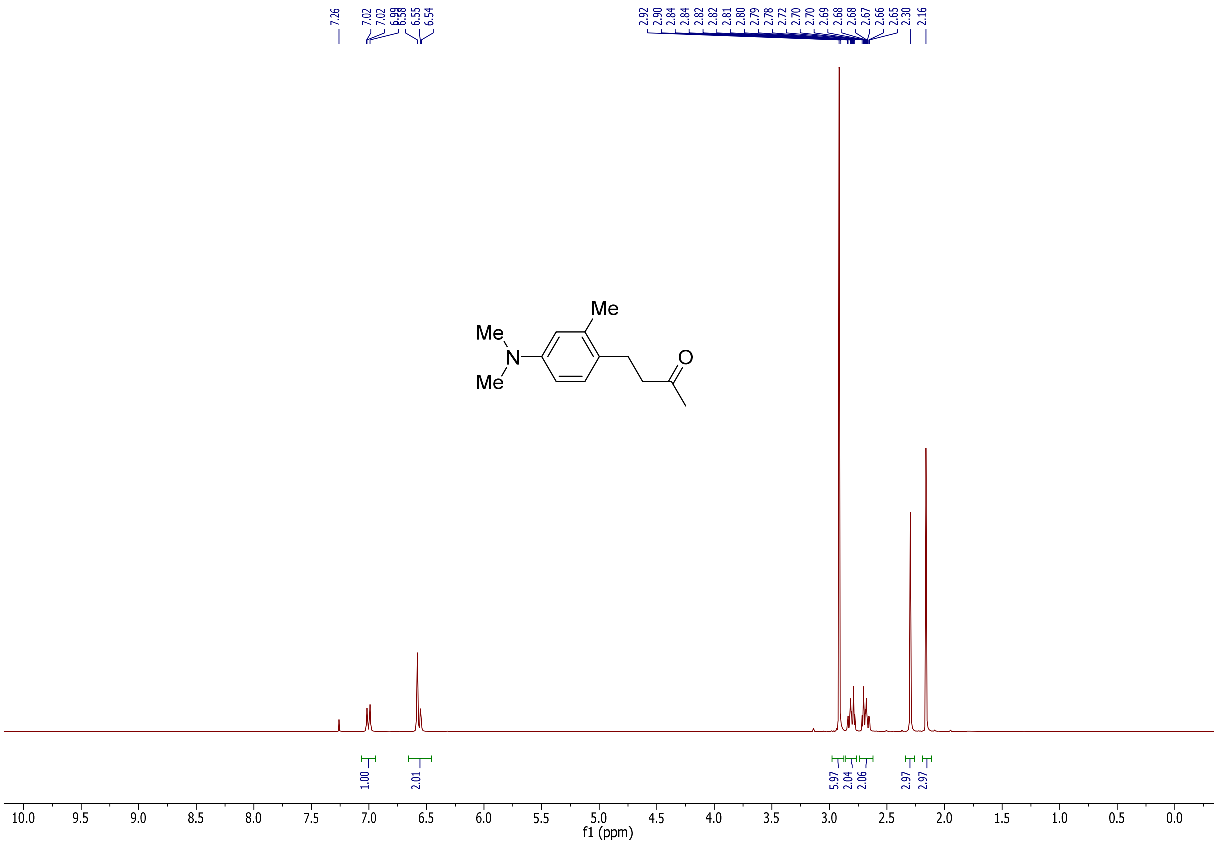


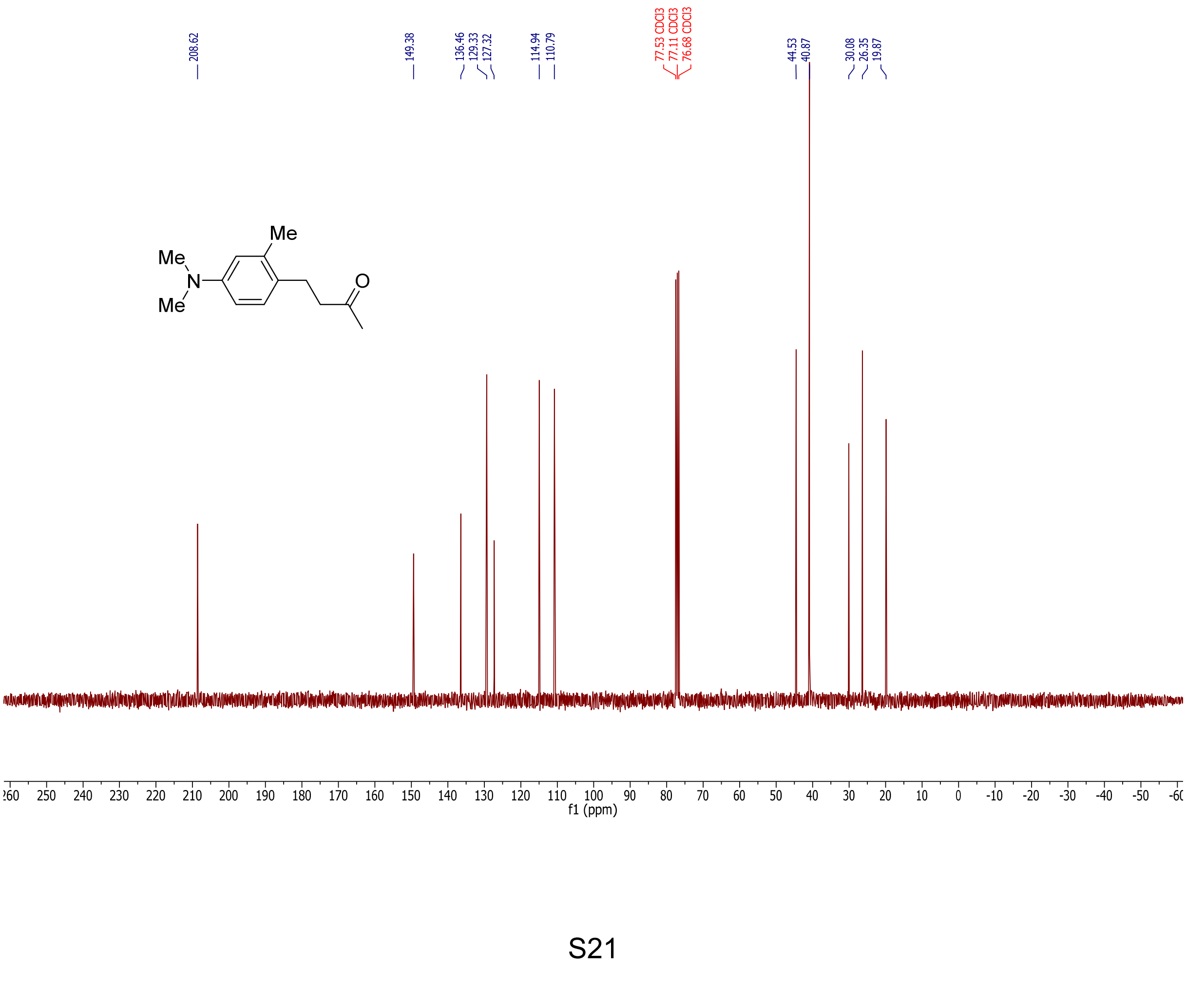
Original spectra for **3g**:



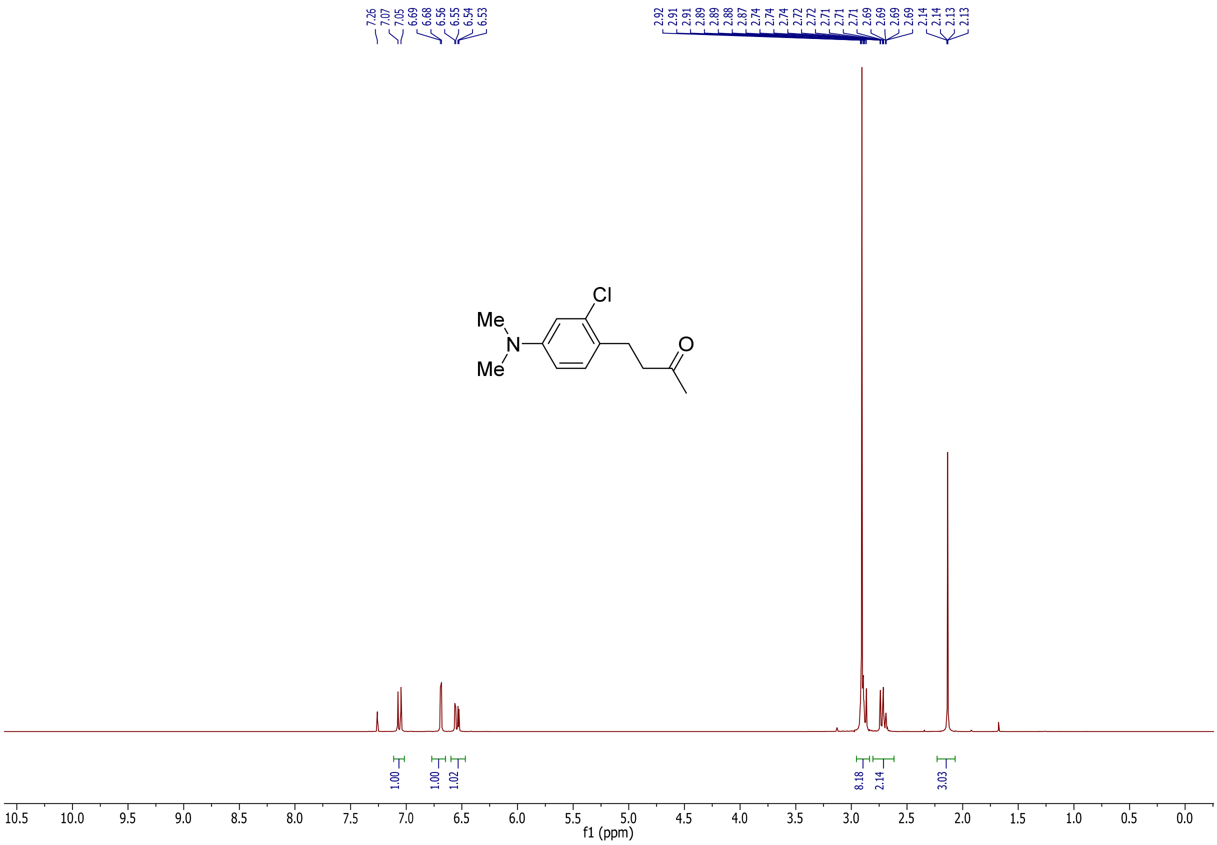


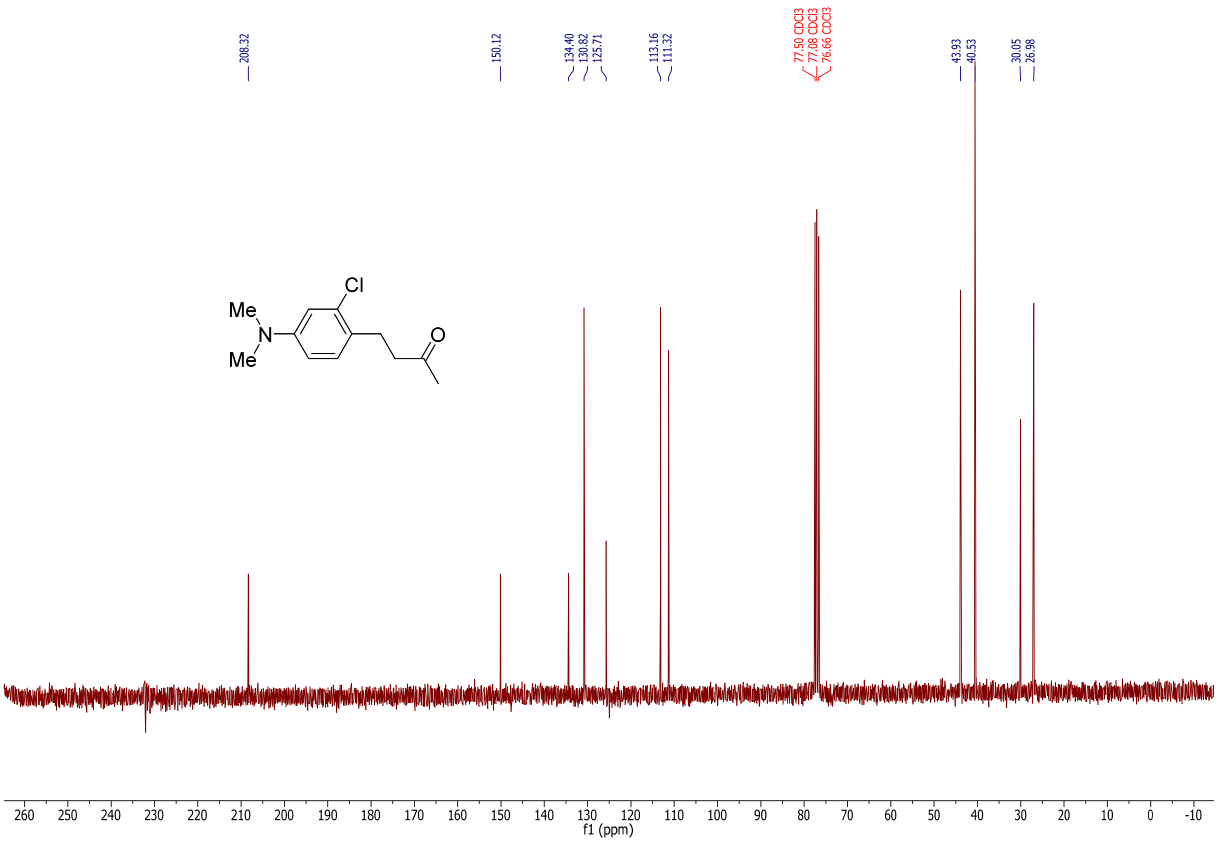
Original spectra for **3h**:



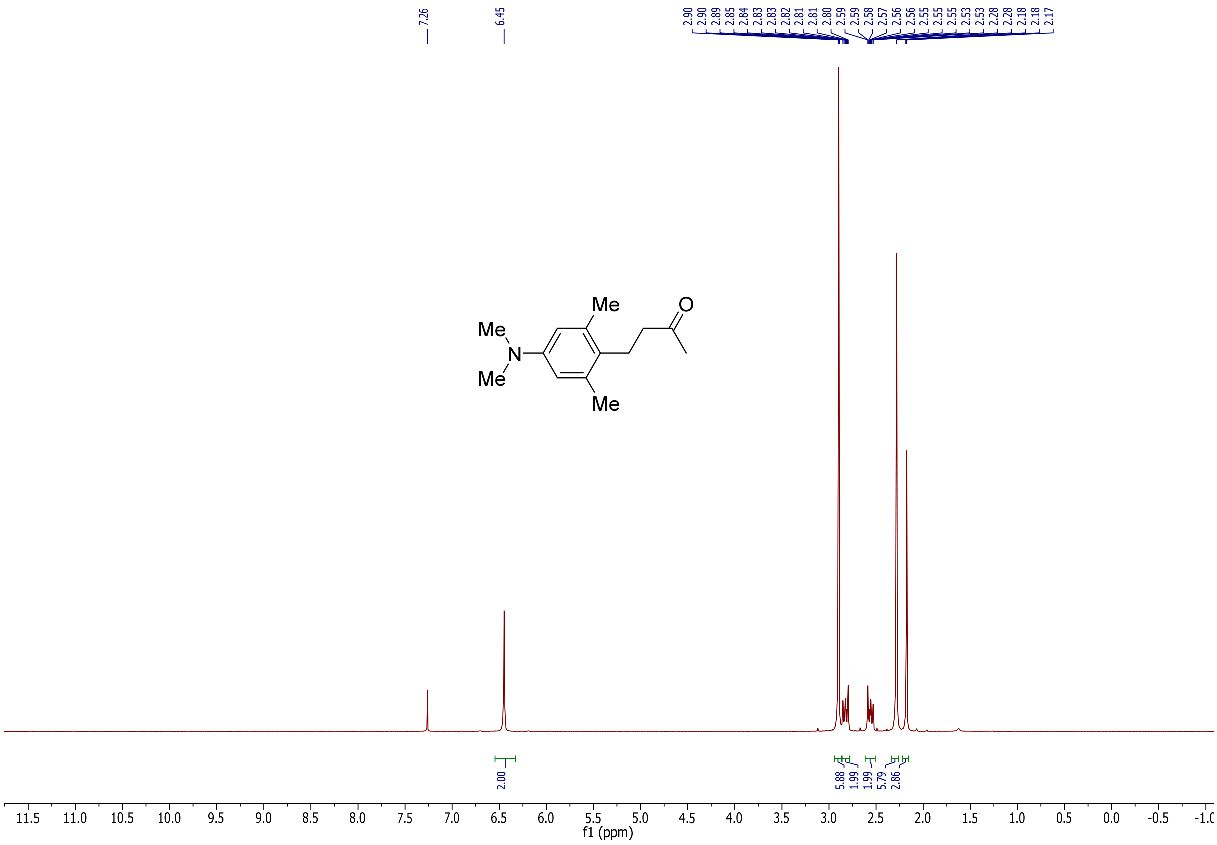


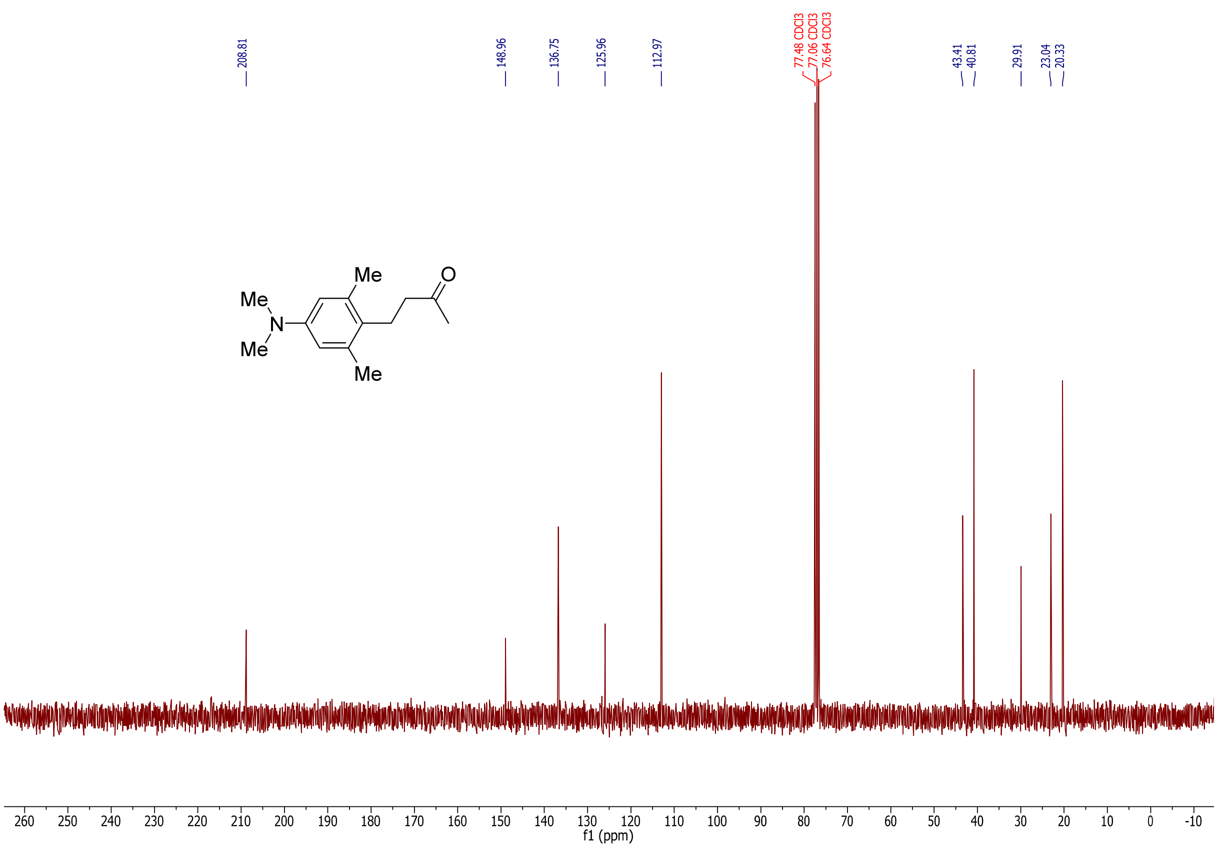
Original spectra for **3i**:



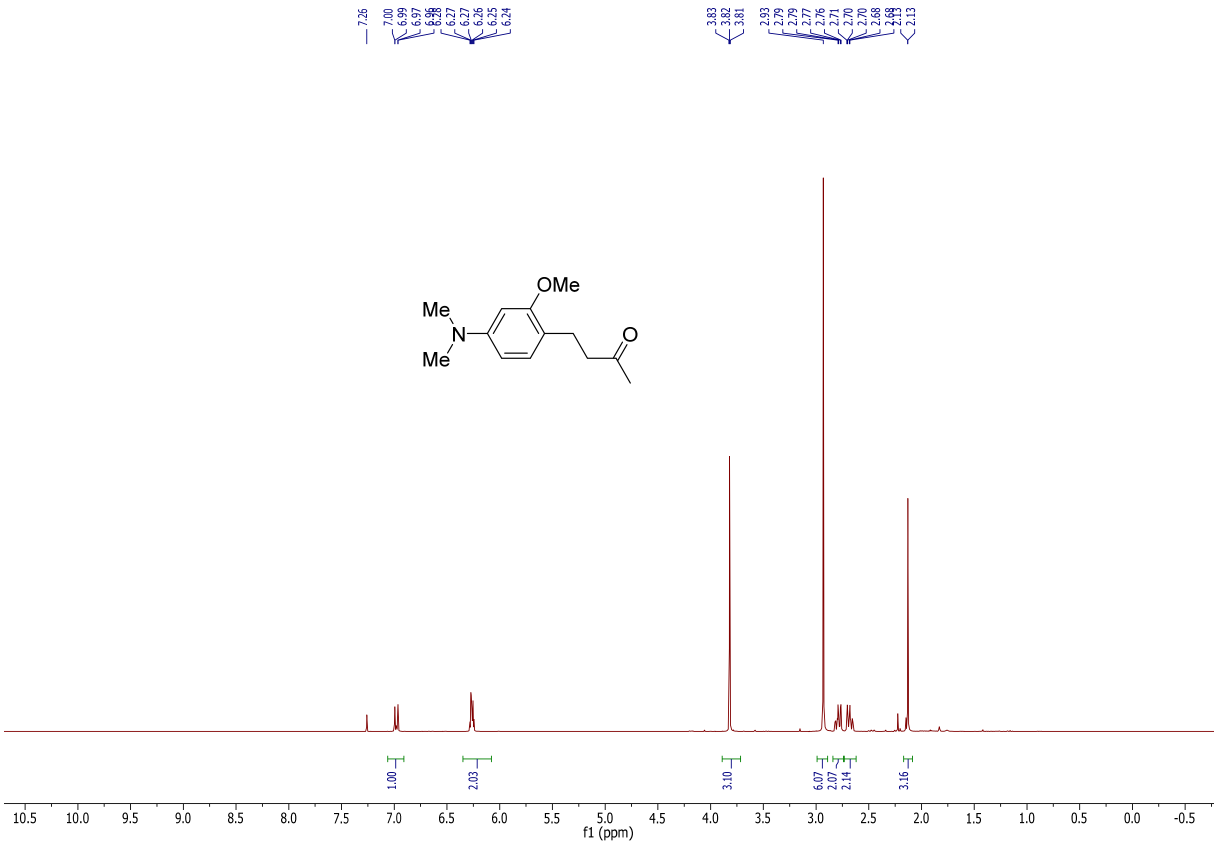


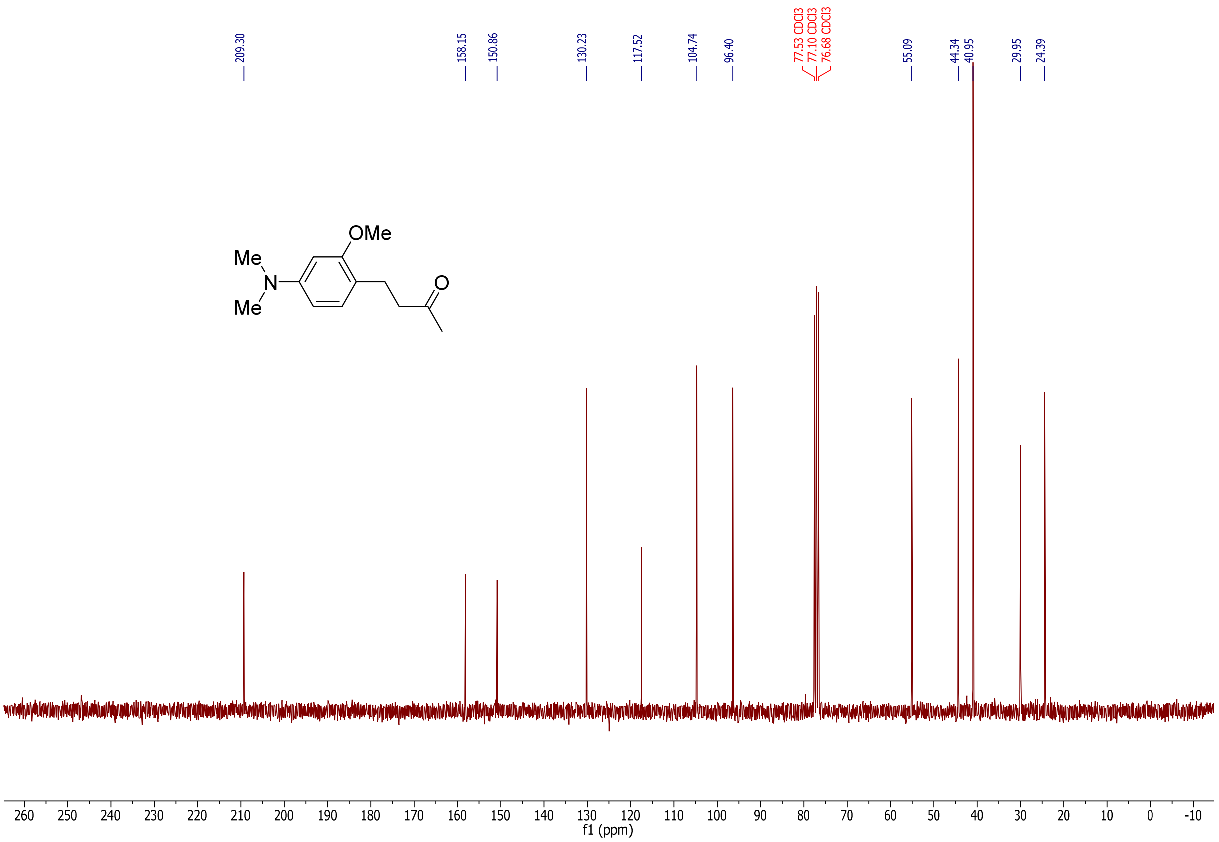
Original spectra for **3j**:



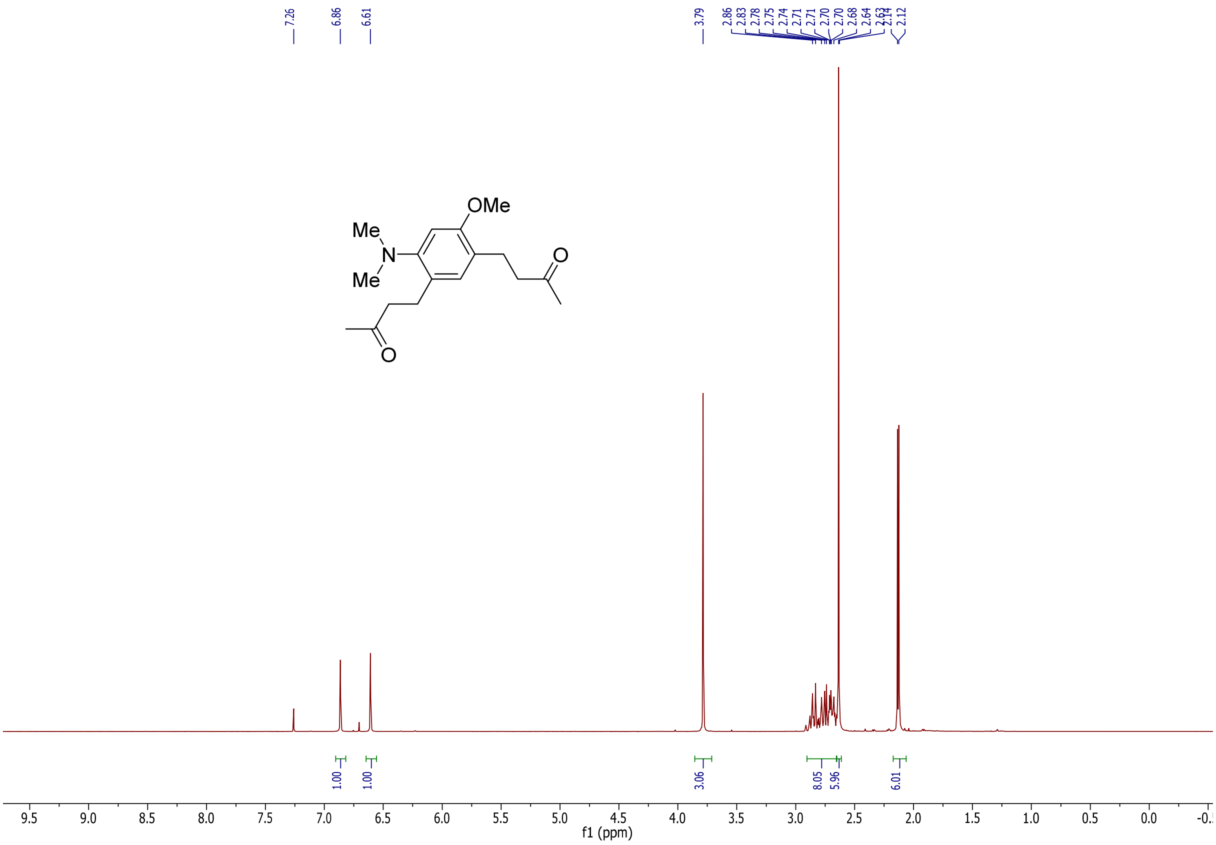


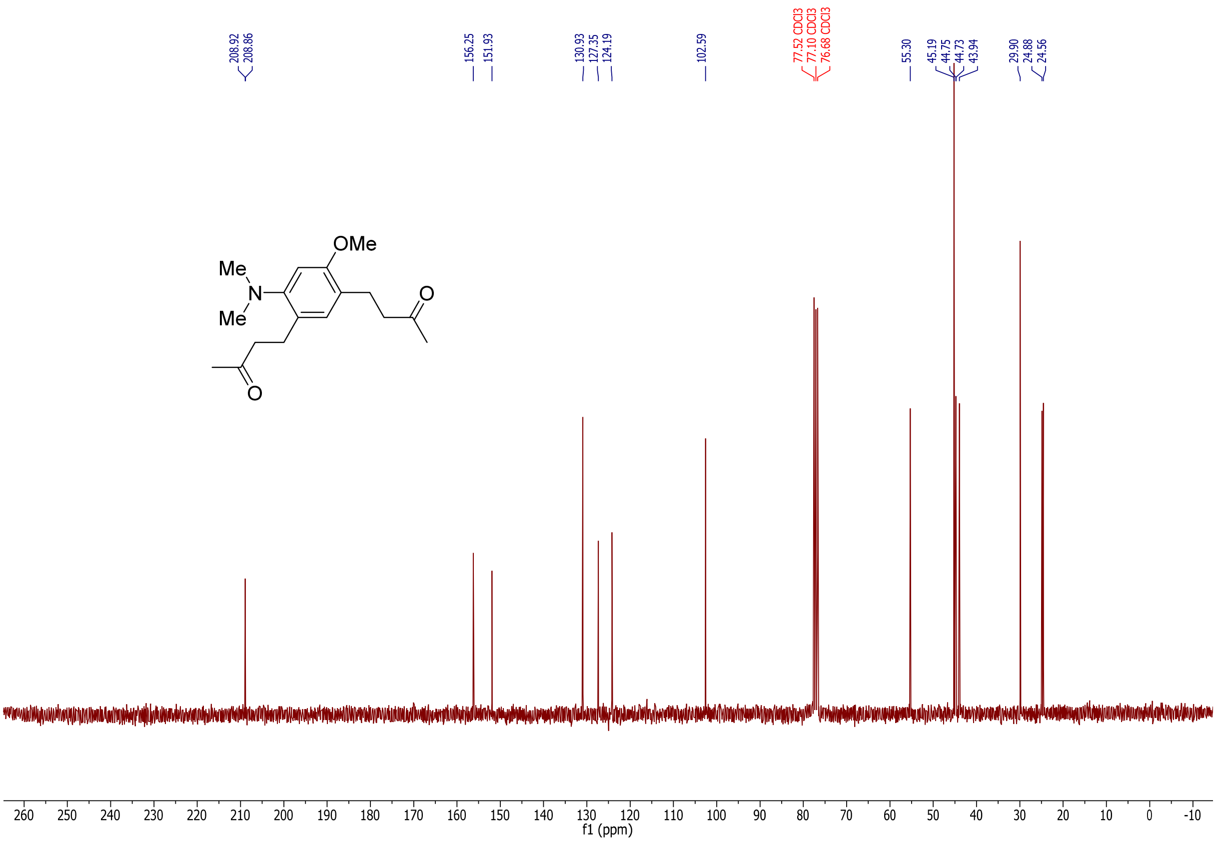
Original spectra for **3k**:



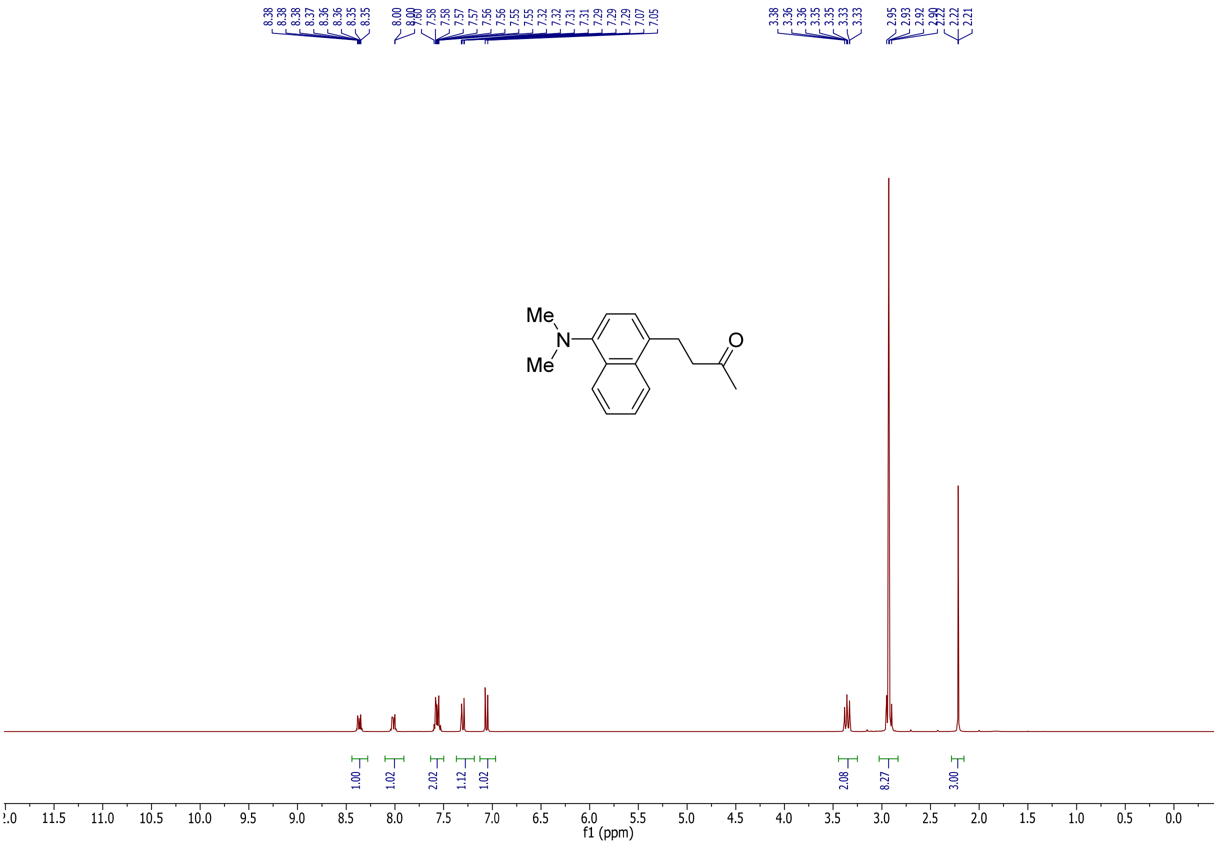


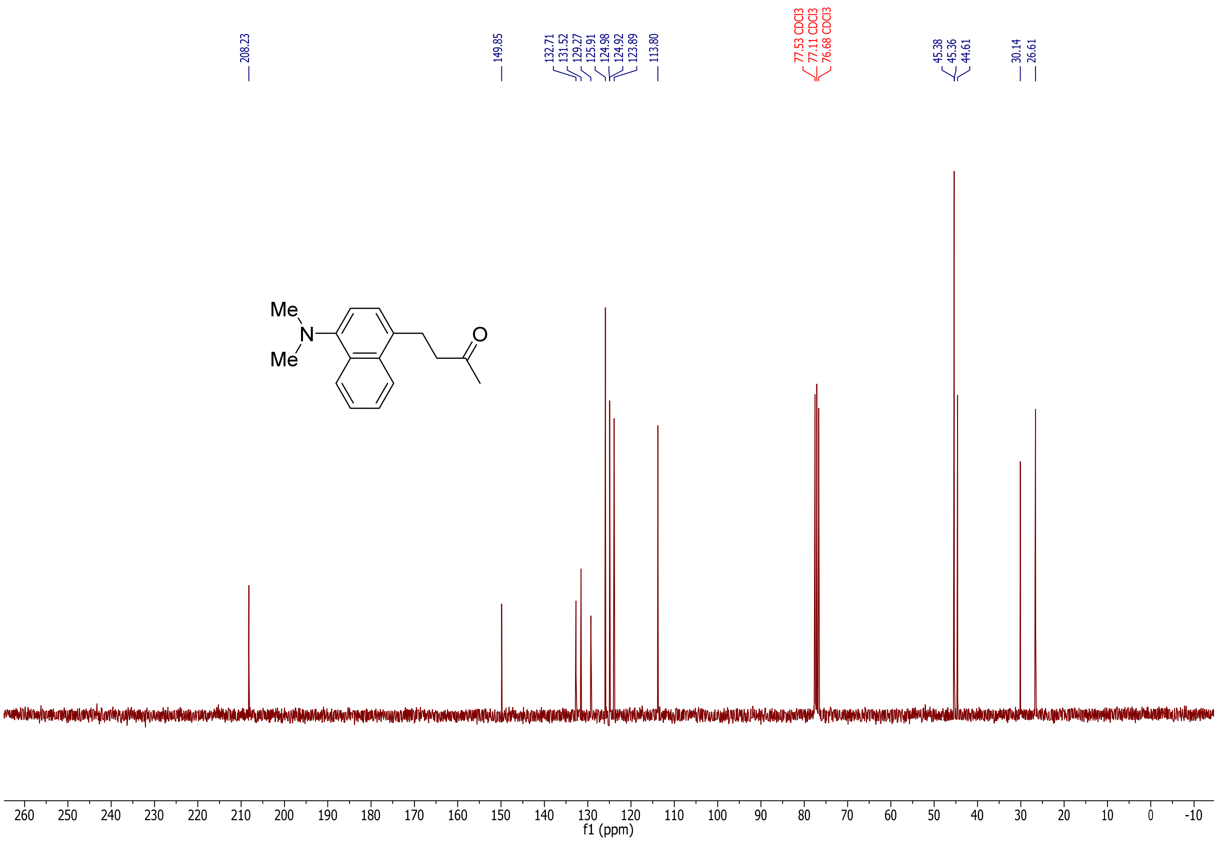
Original spectra for **3l**:



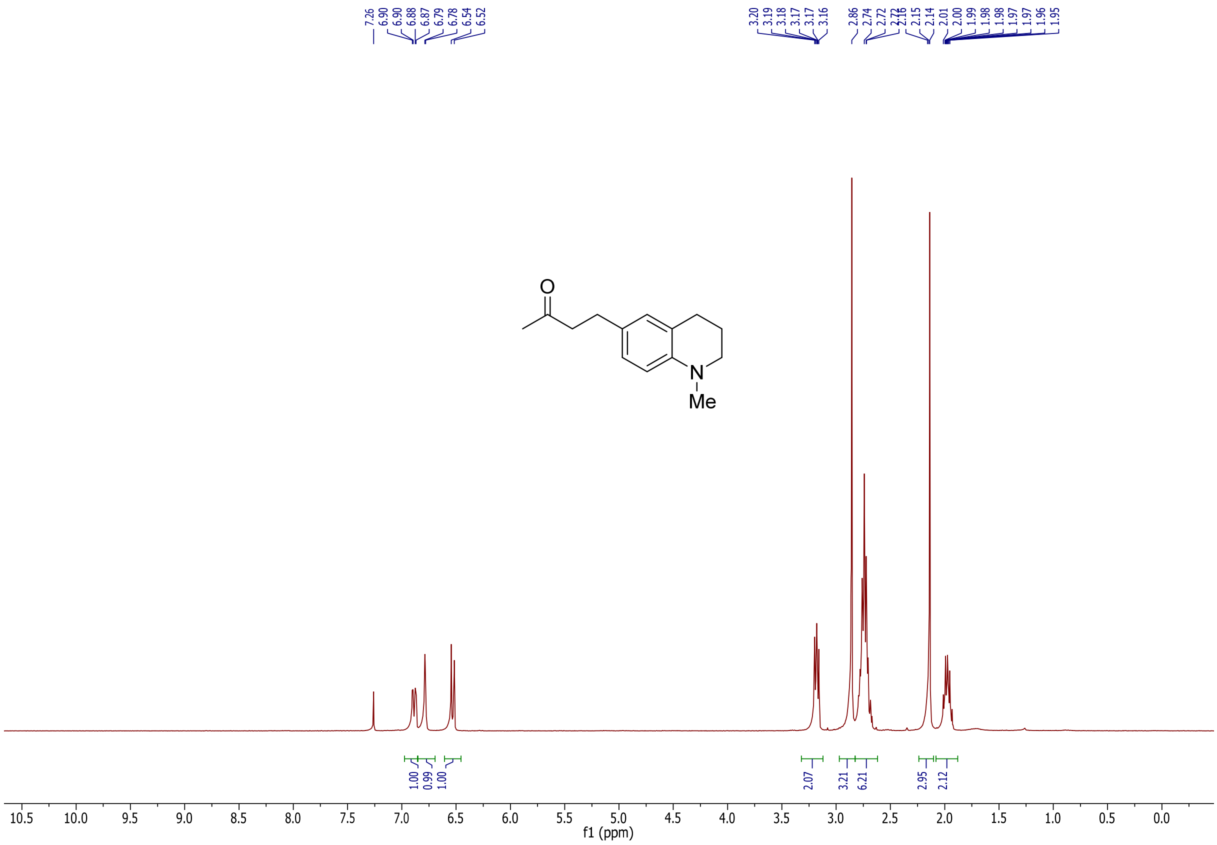


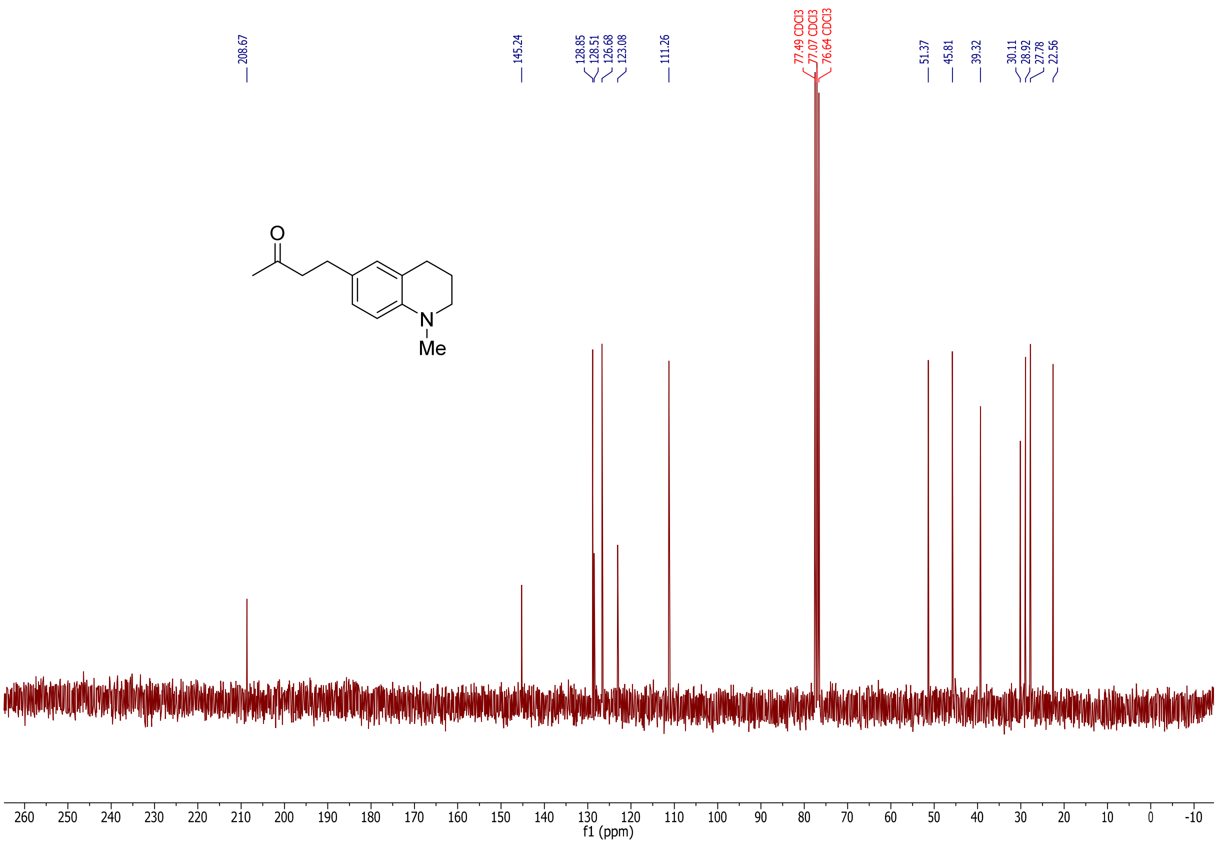
Original spectra for **3m**:



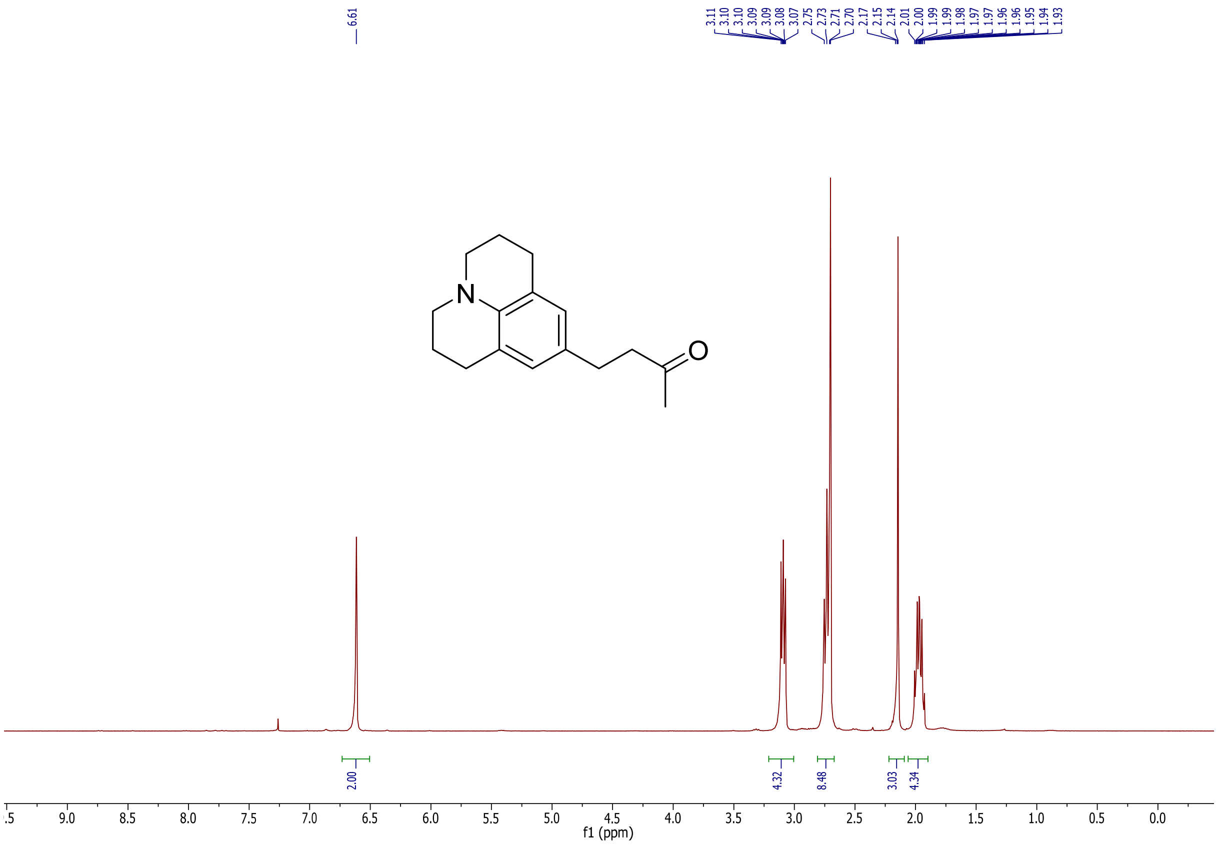


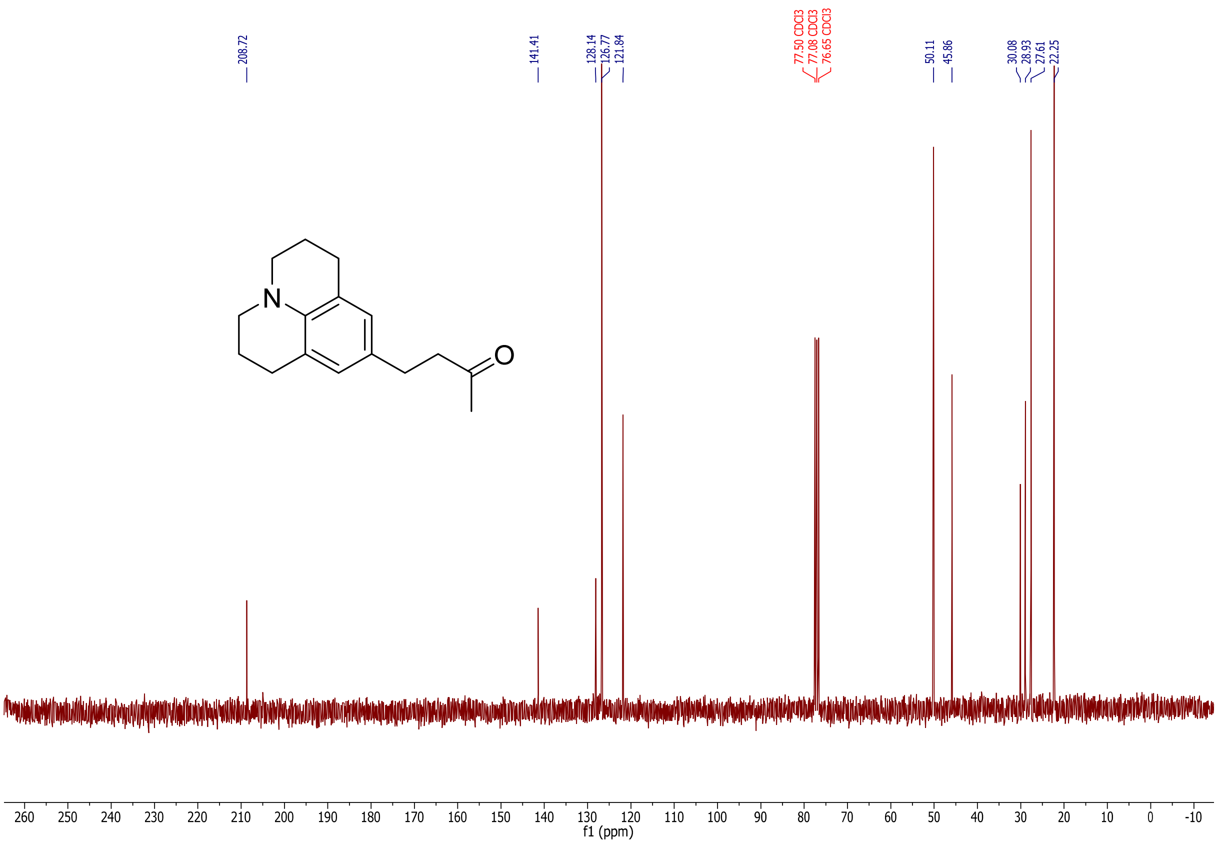
Original spectra for **3n**:



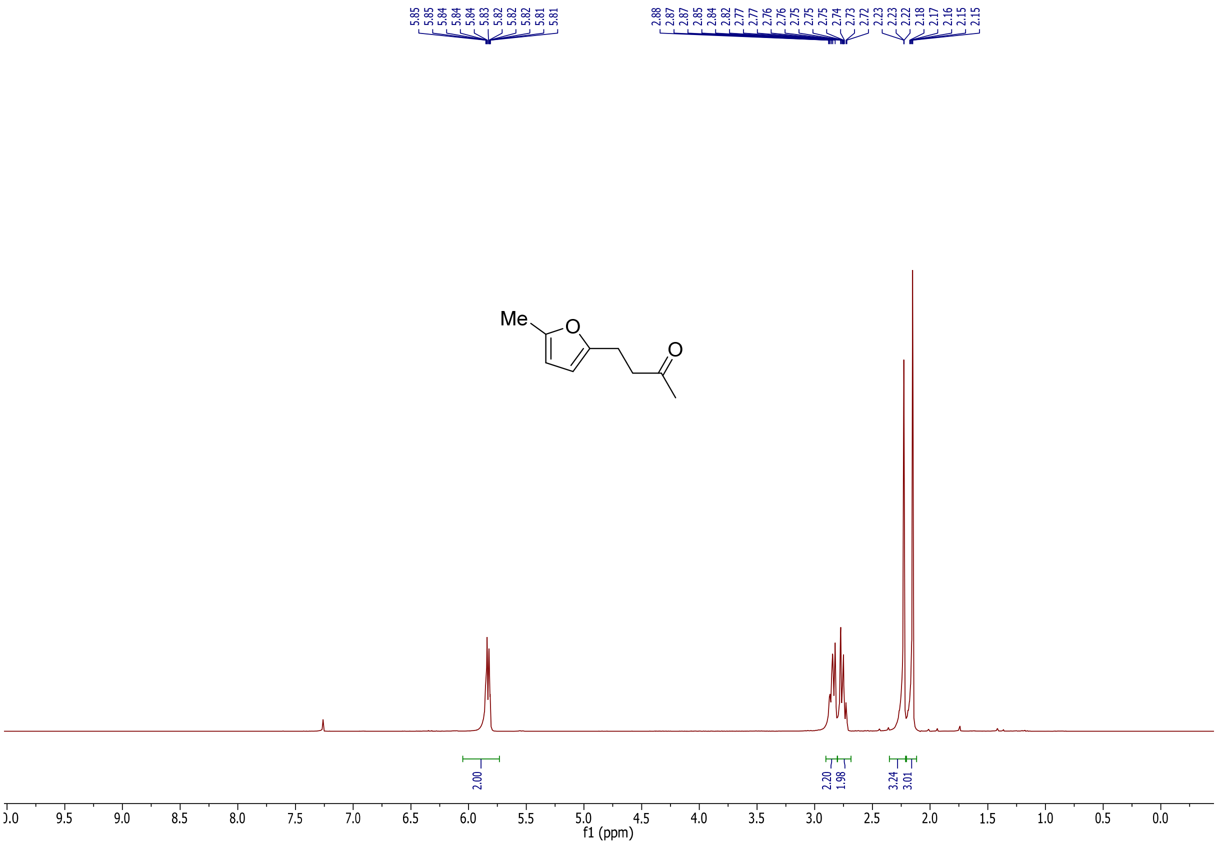


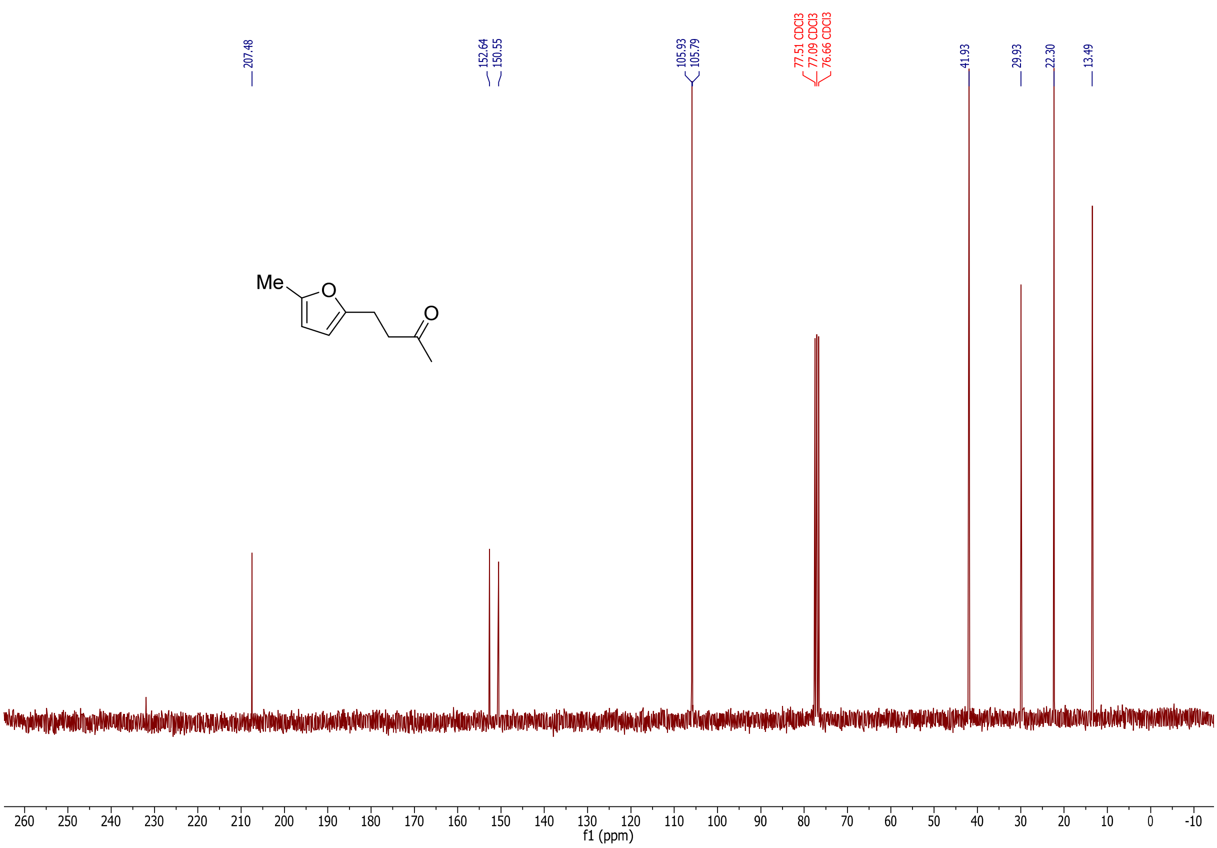
Original spectra for **3o**:



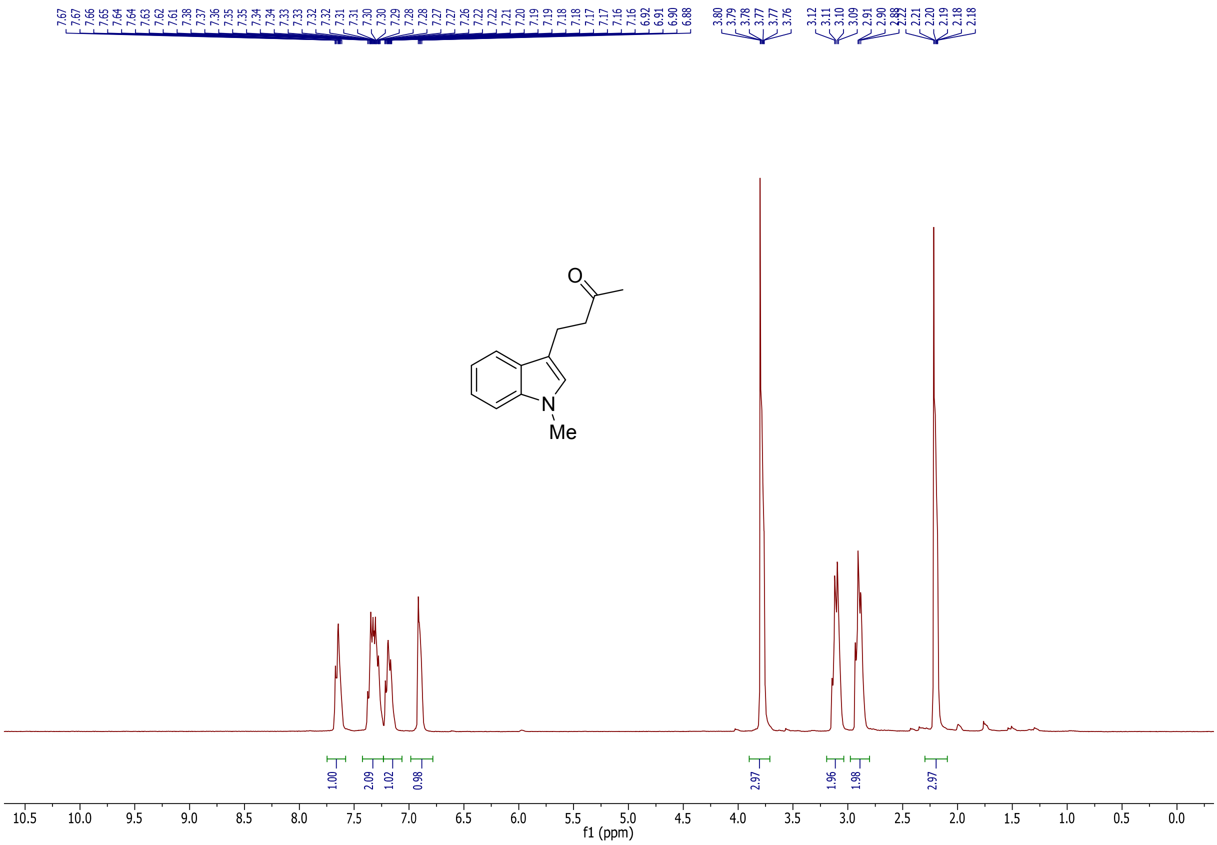


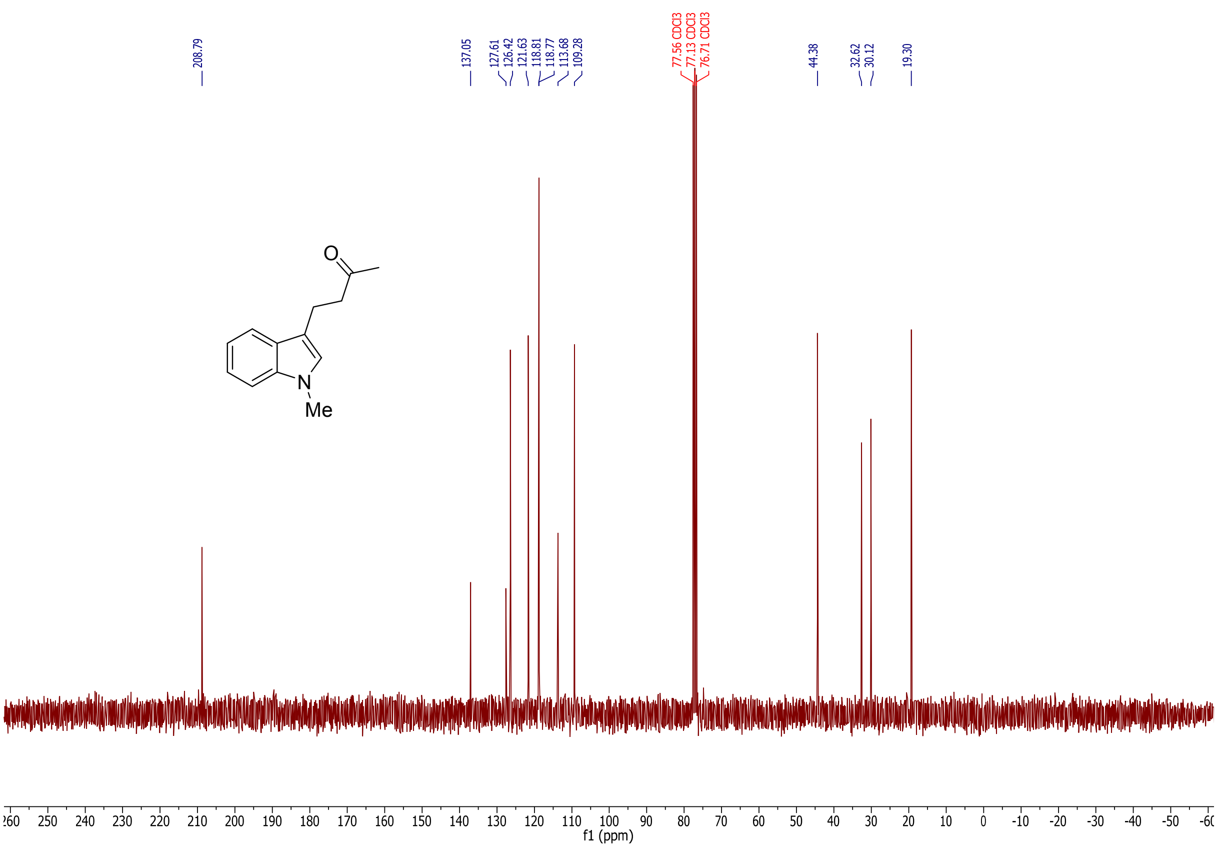
Original spectra for **3q**:



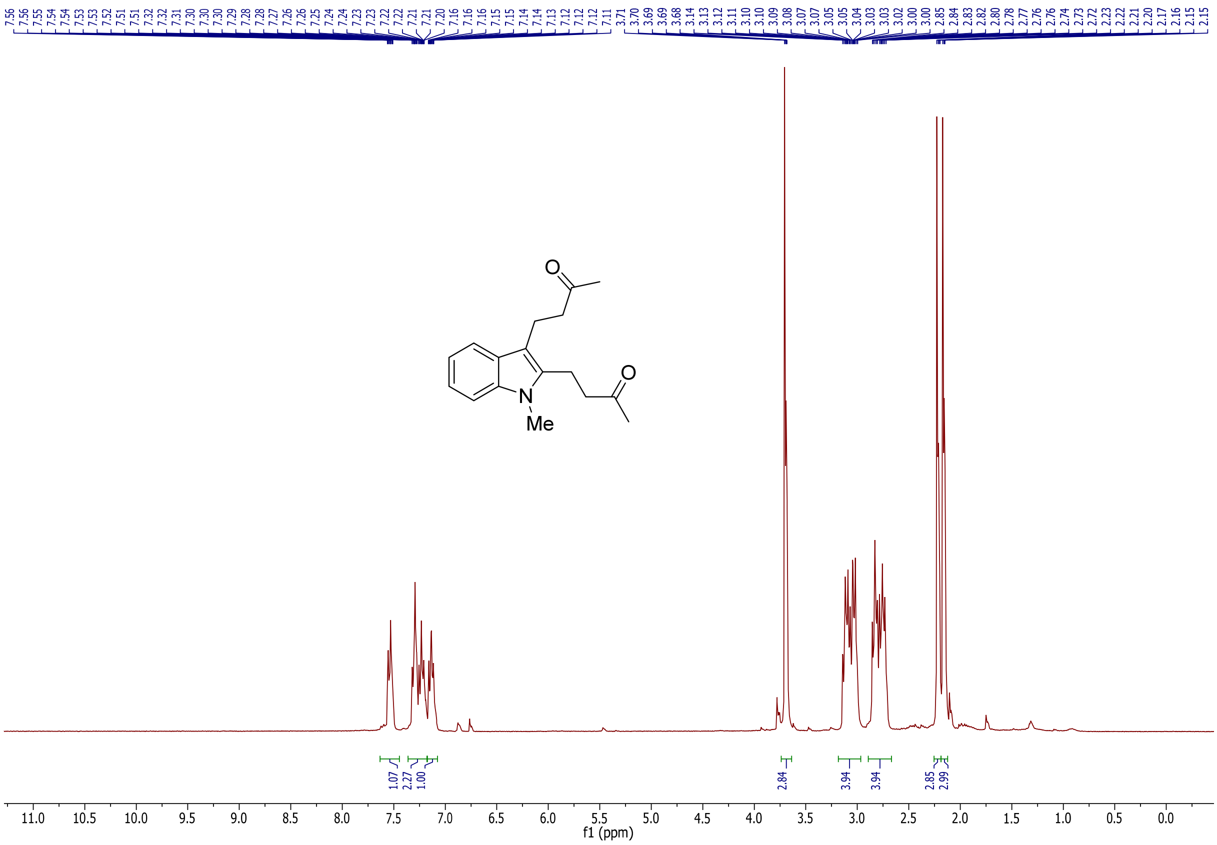


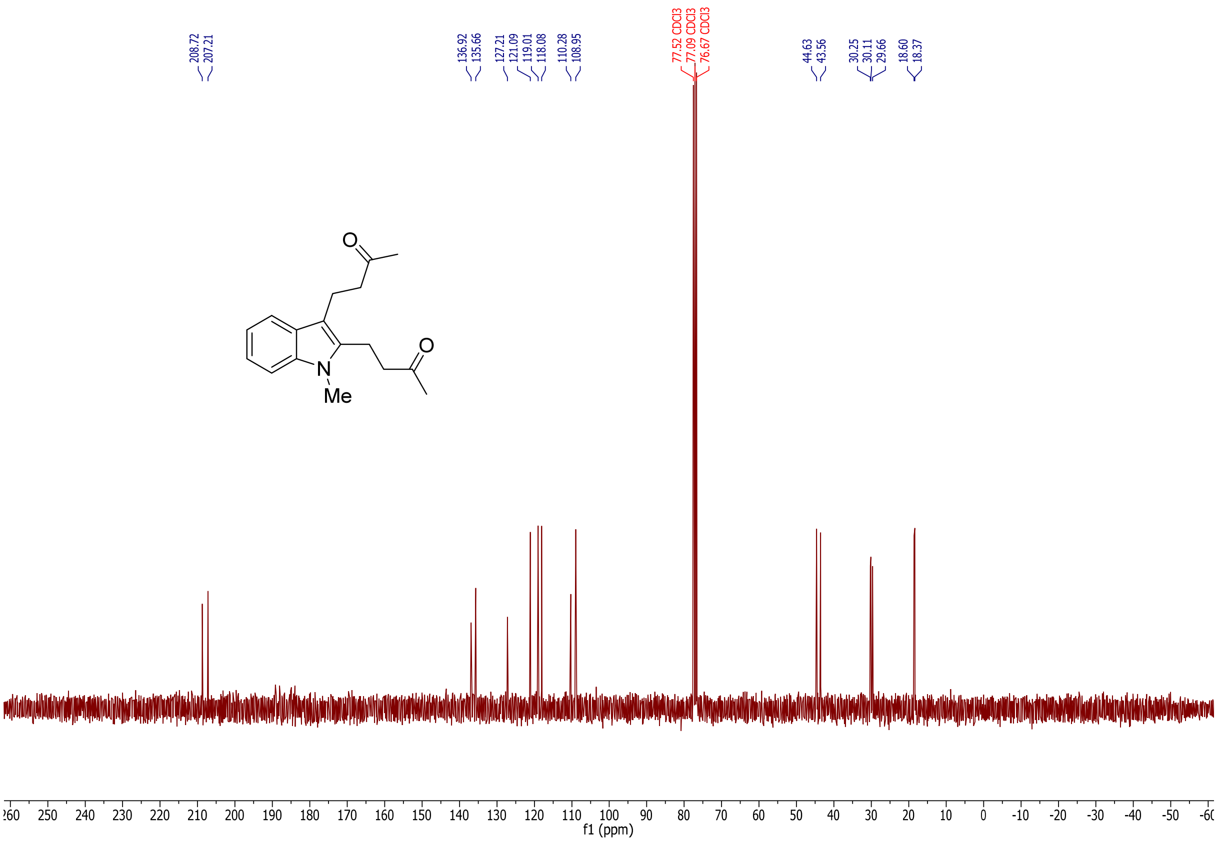
Original spectra for **3r**:



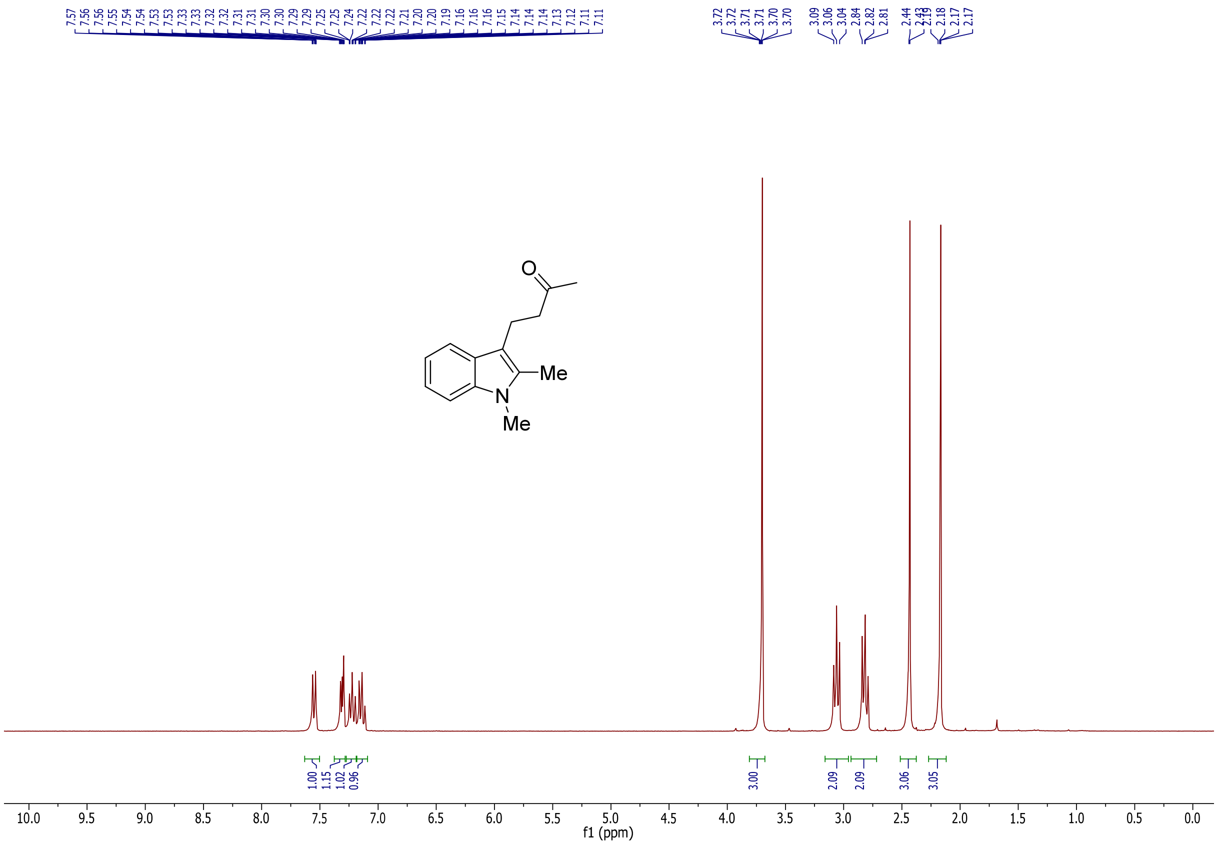


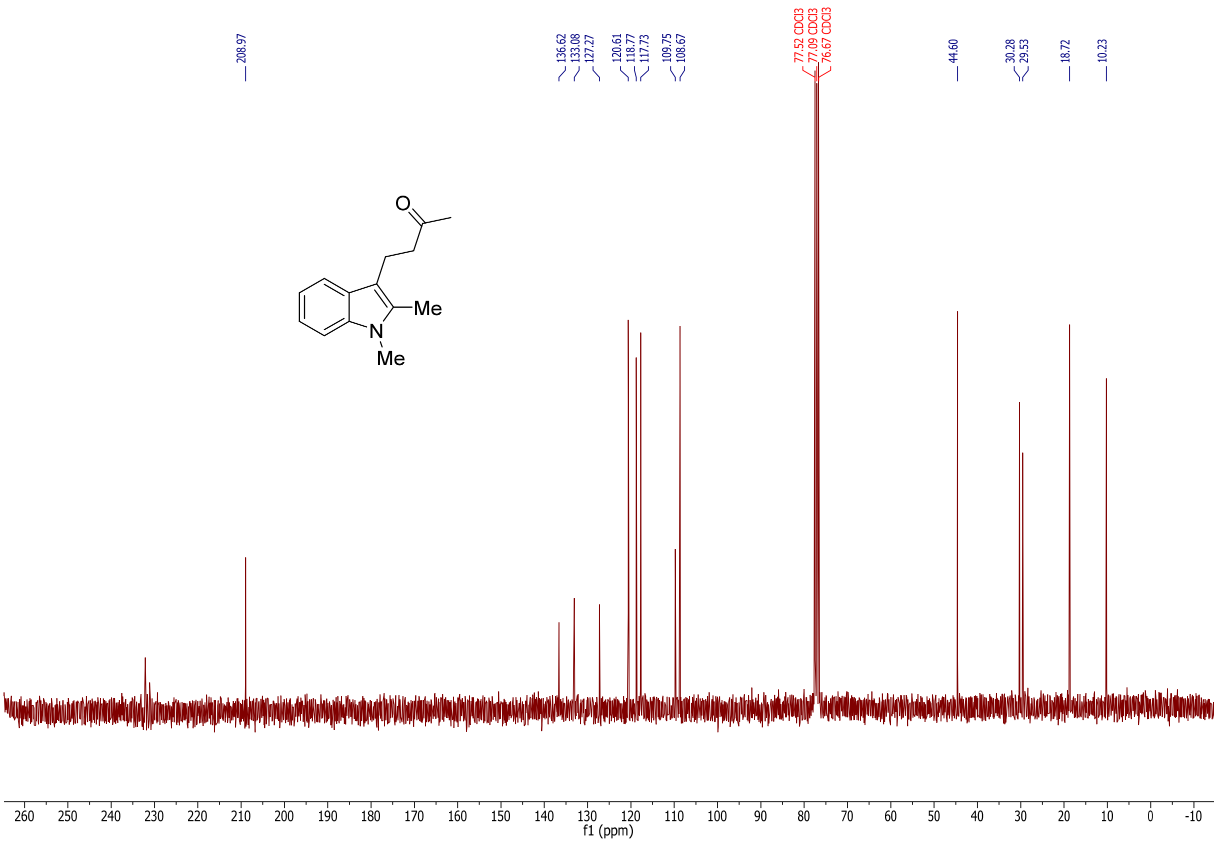
Original spectra for **3s**:



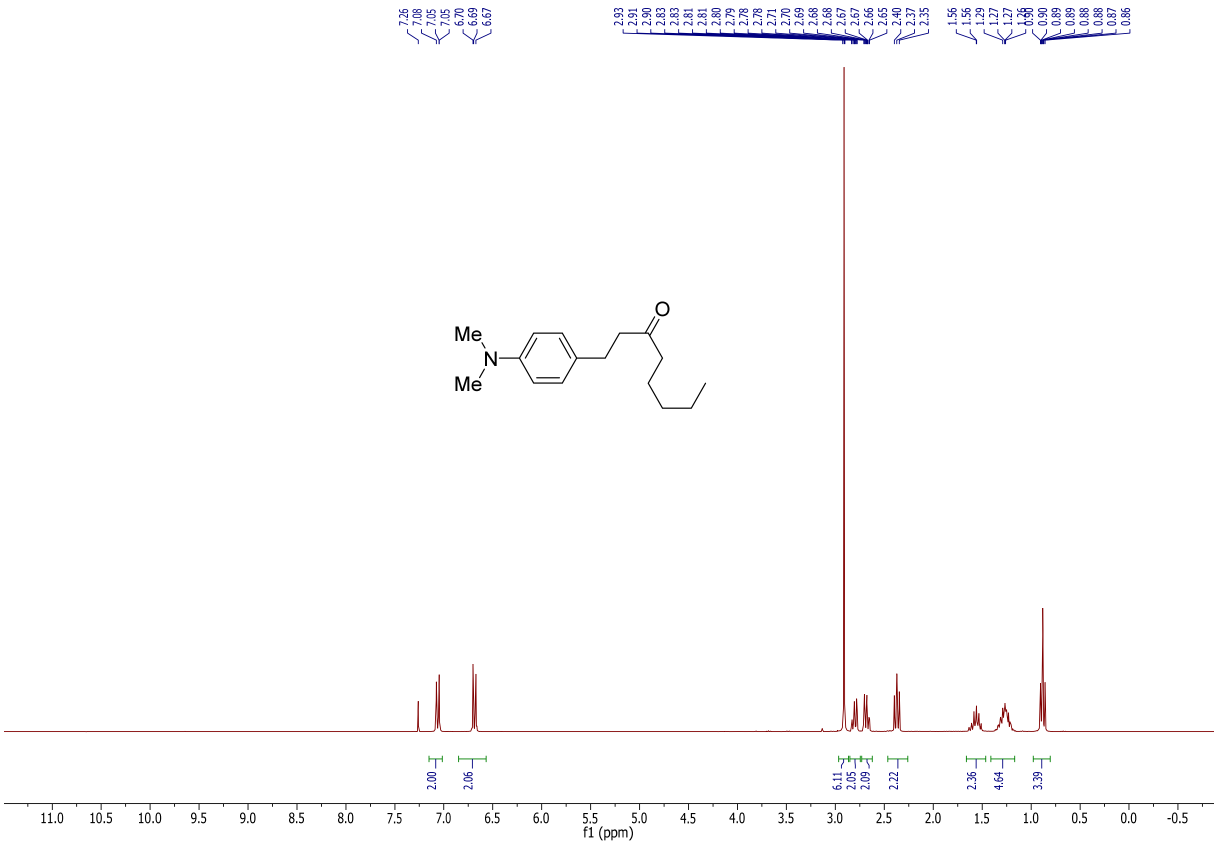


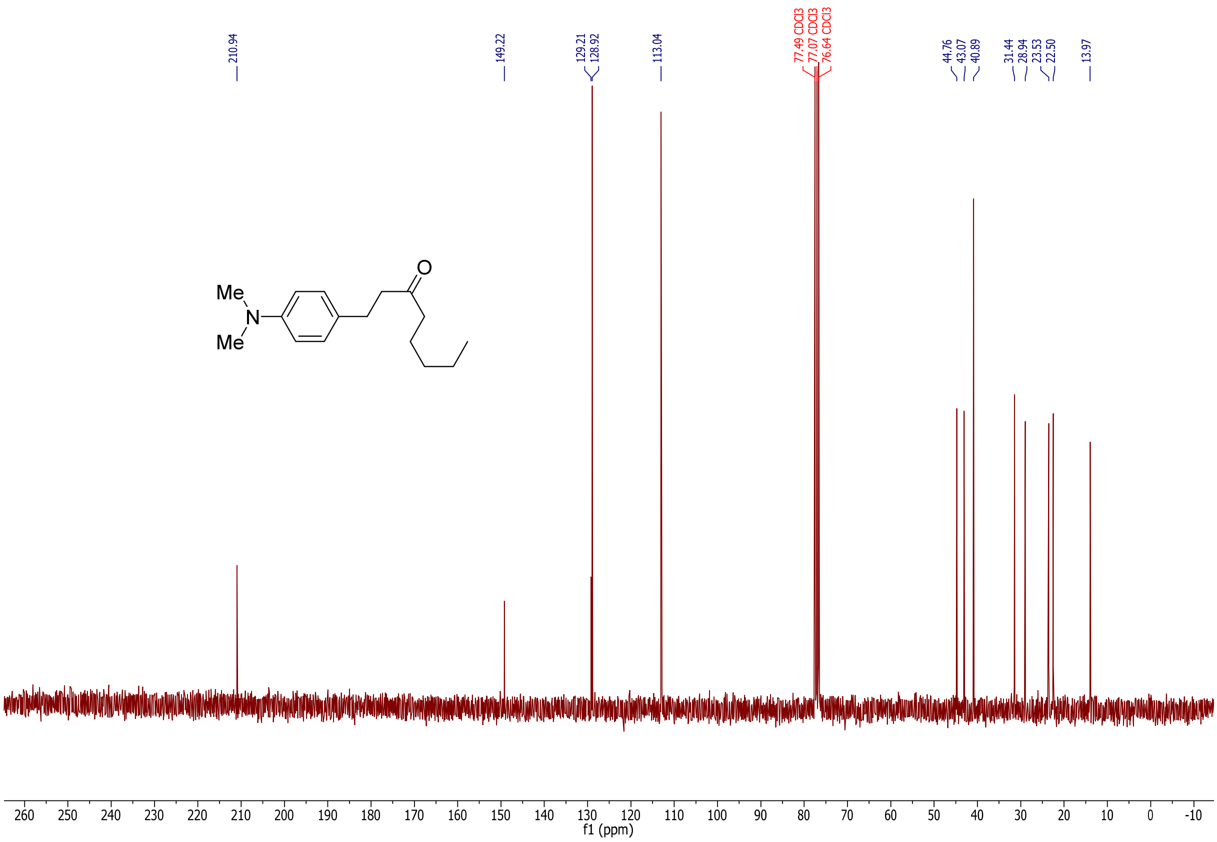
Original spectra for **3t**:



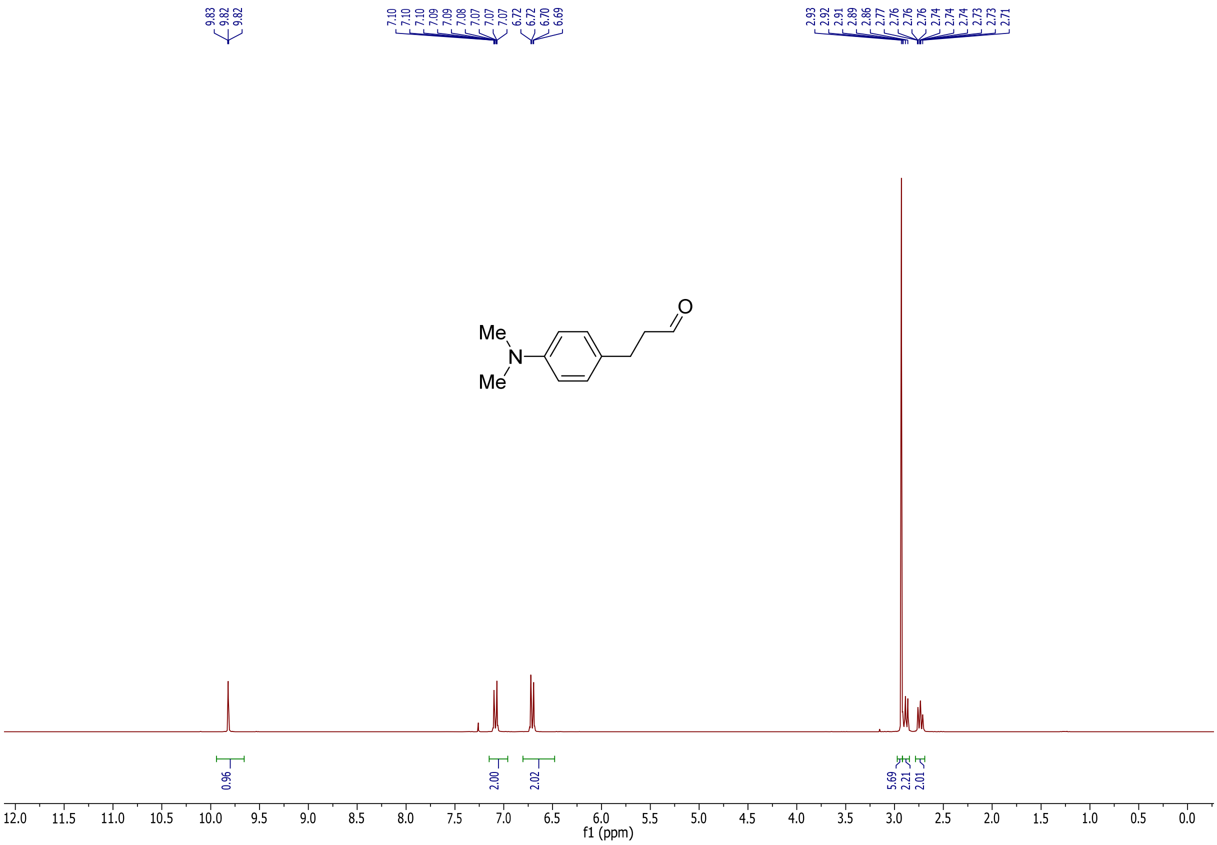


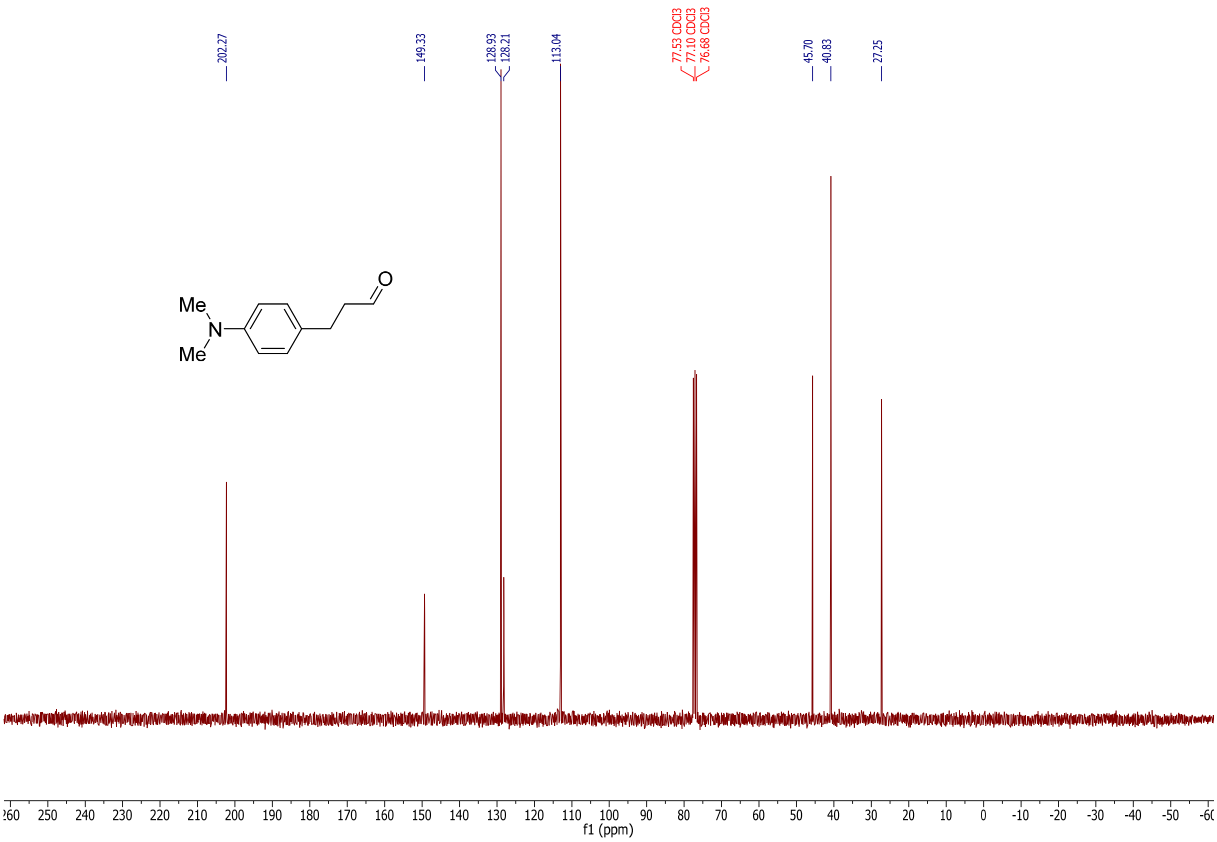
Original spectra for **3u**:



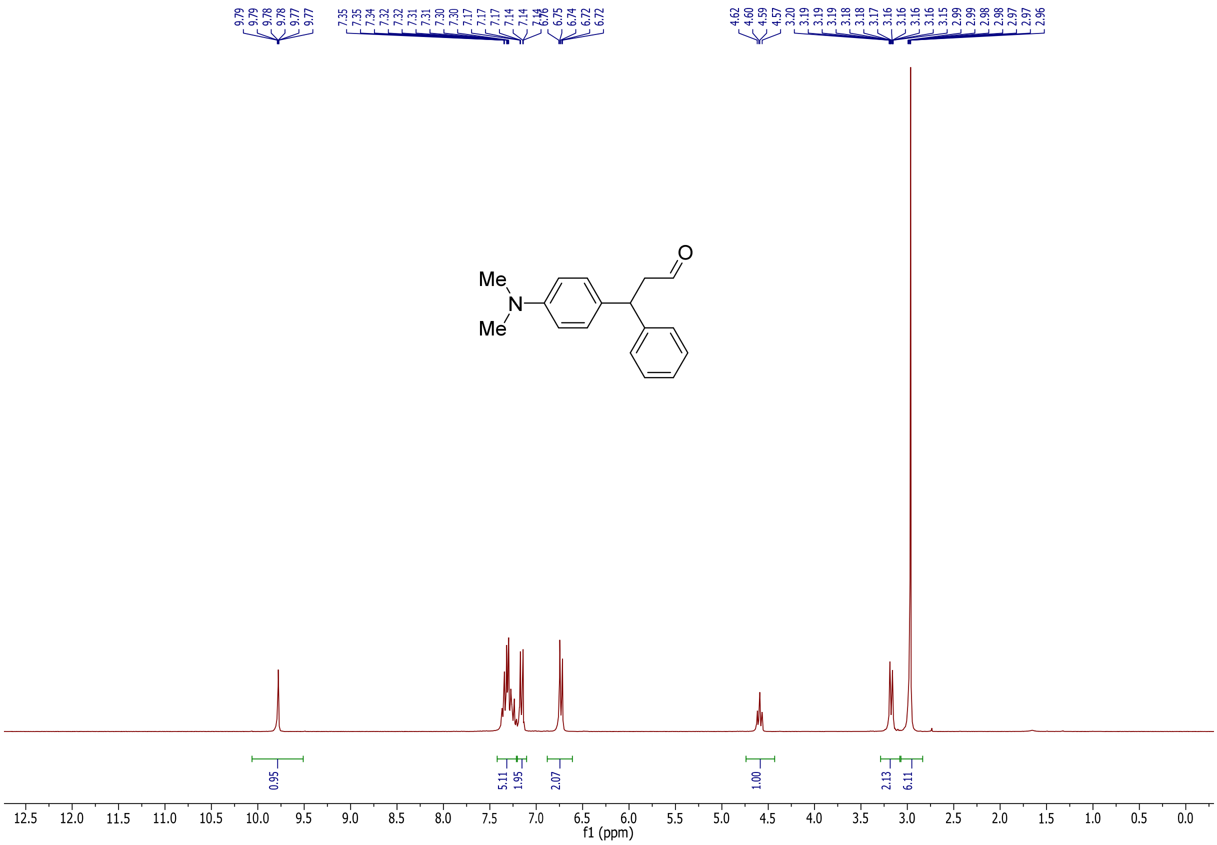


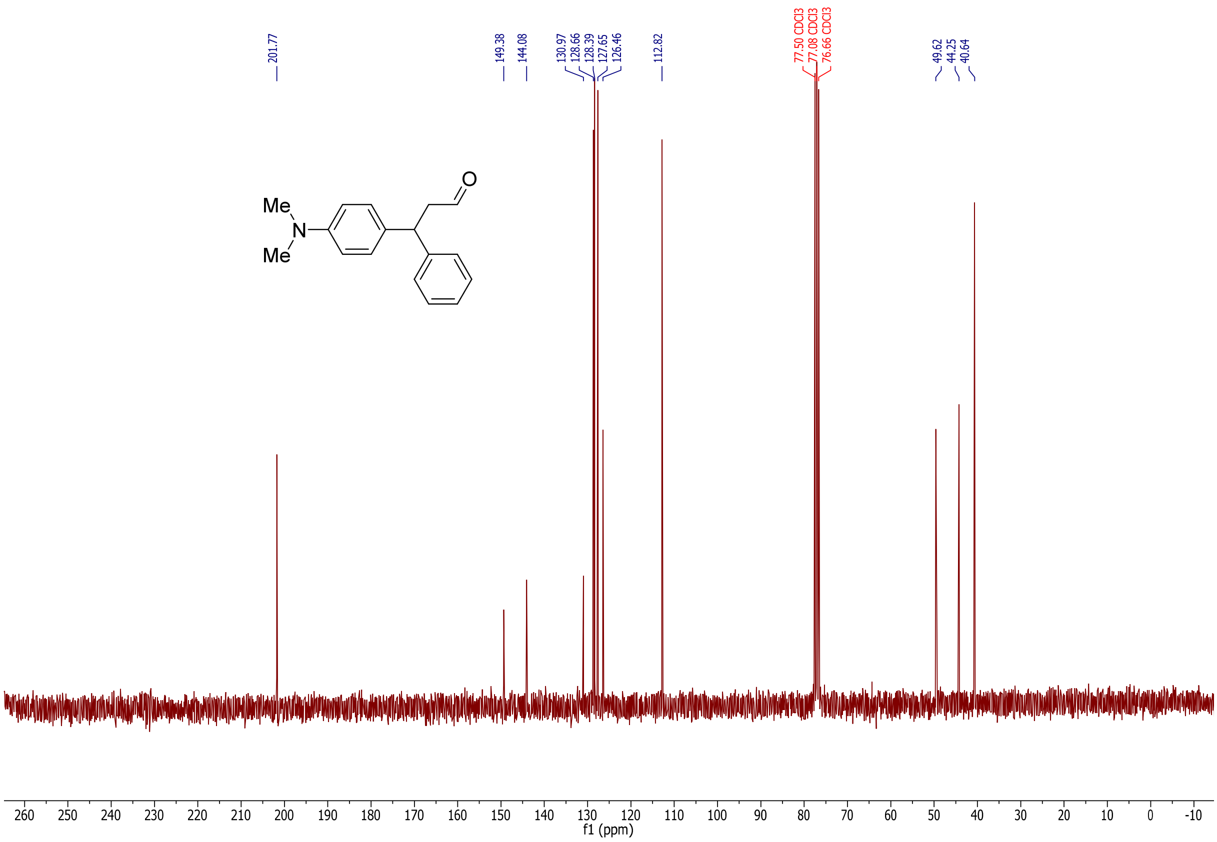
Original spectra for **3v**:



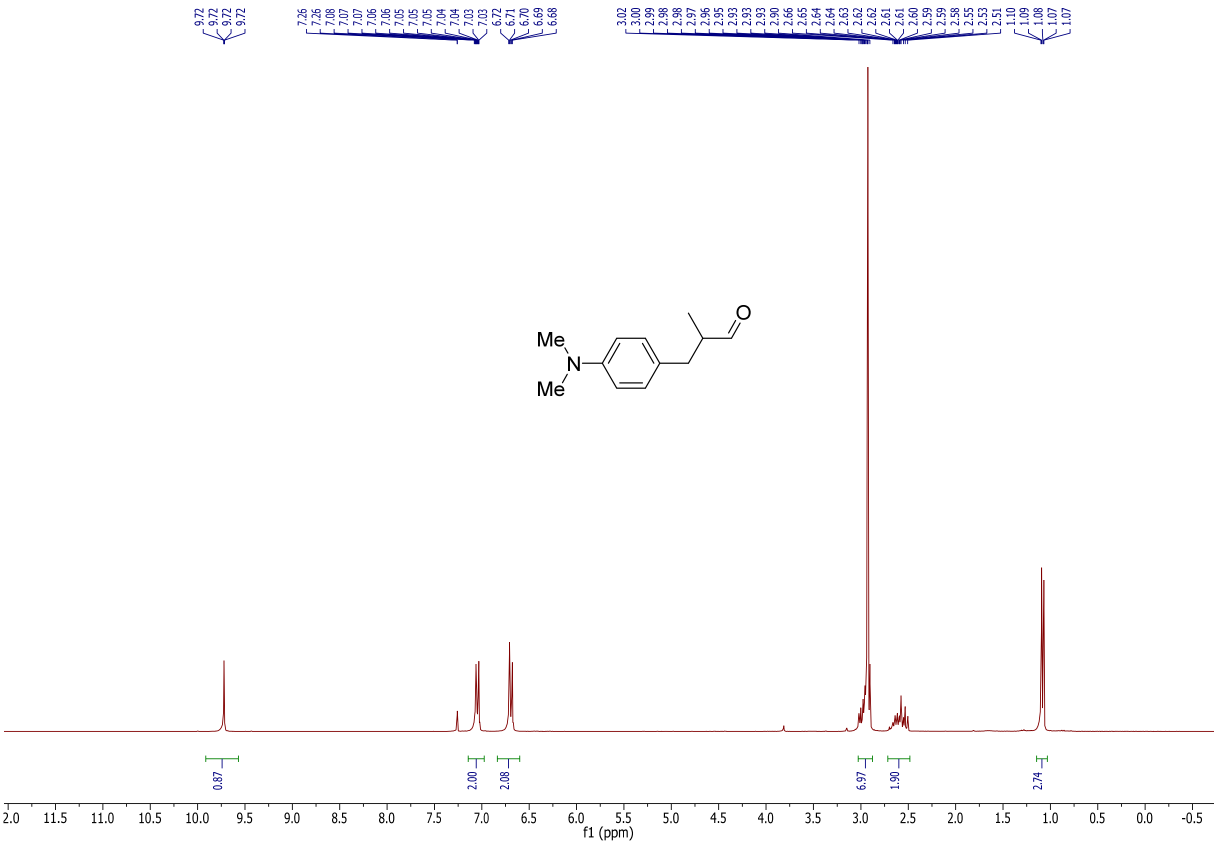


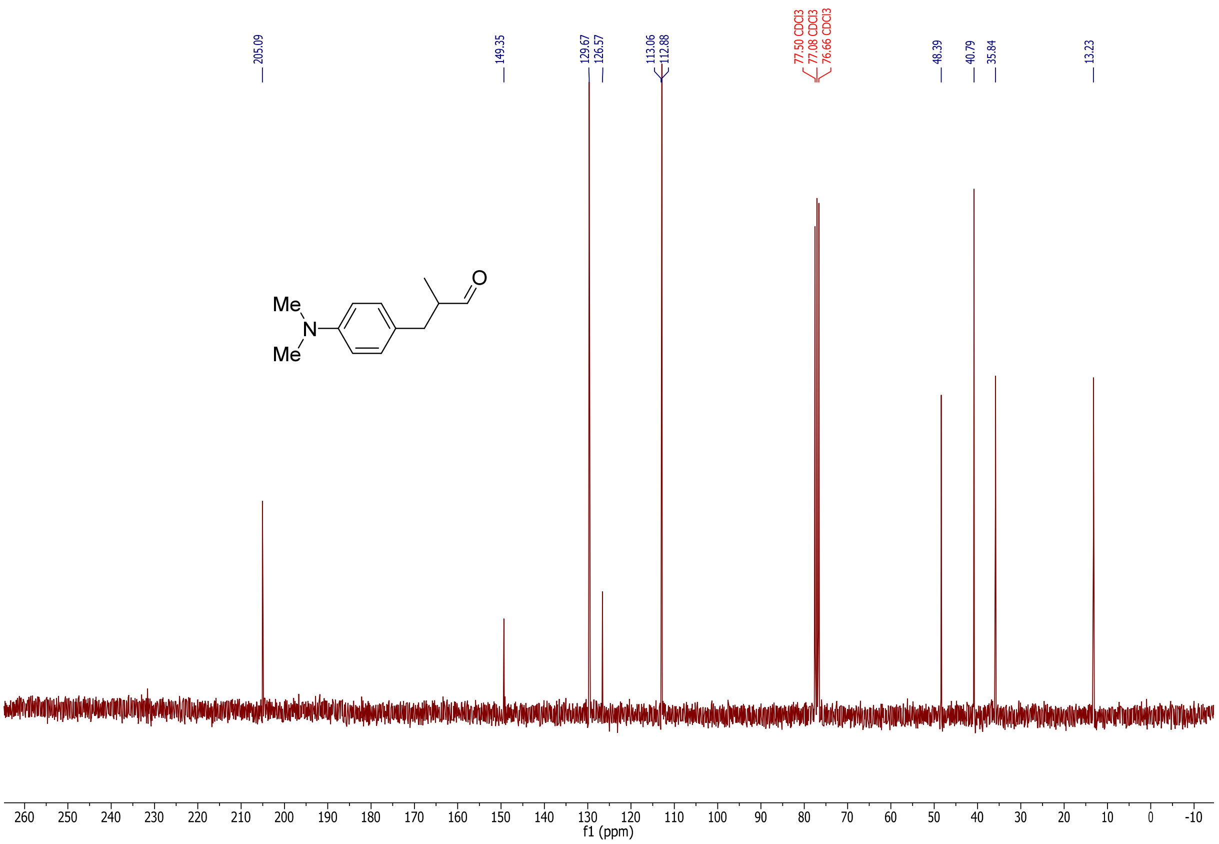
Original spectra for **3w**:



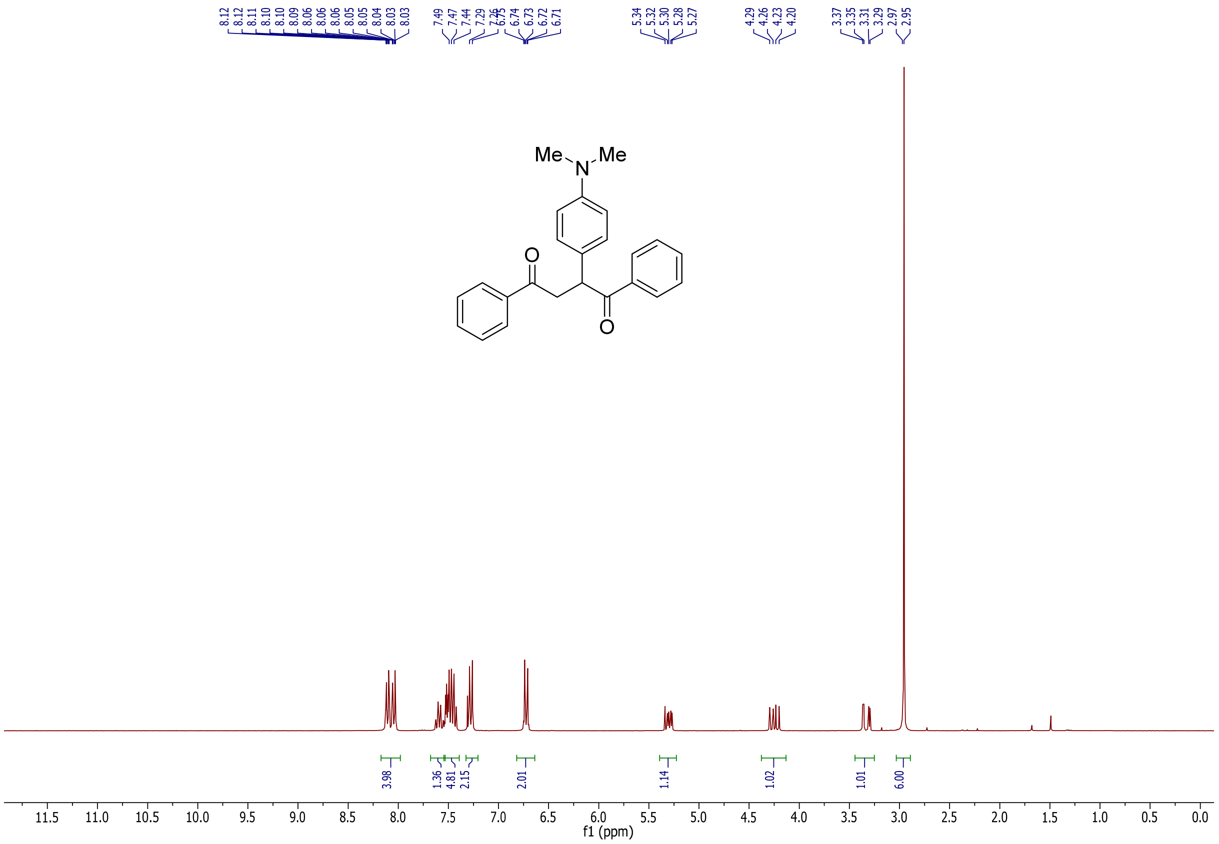


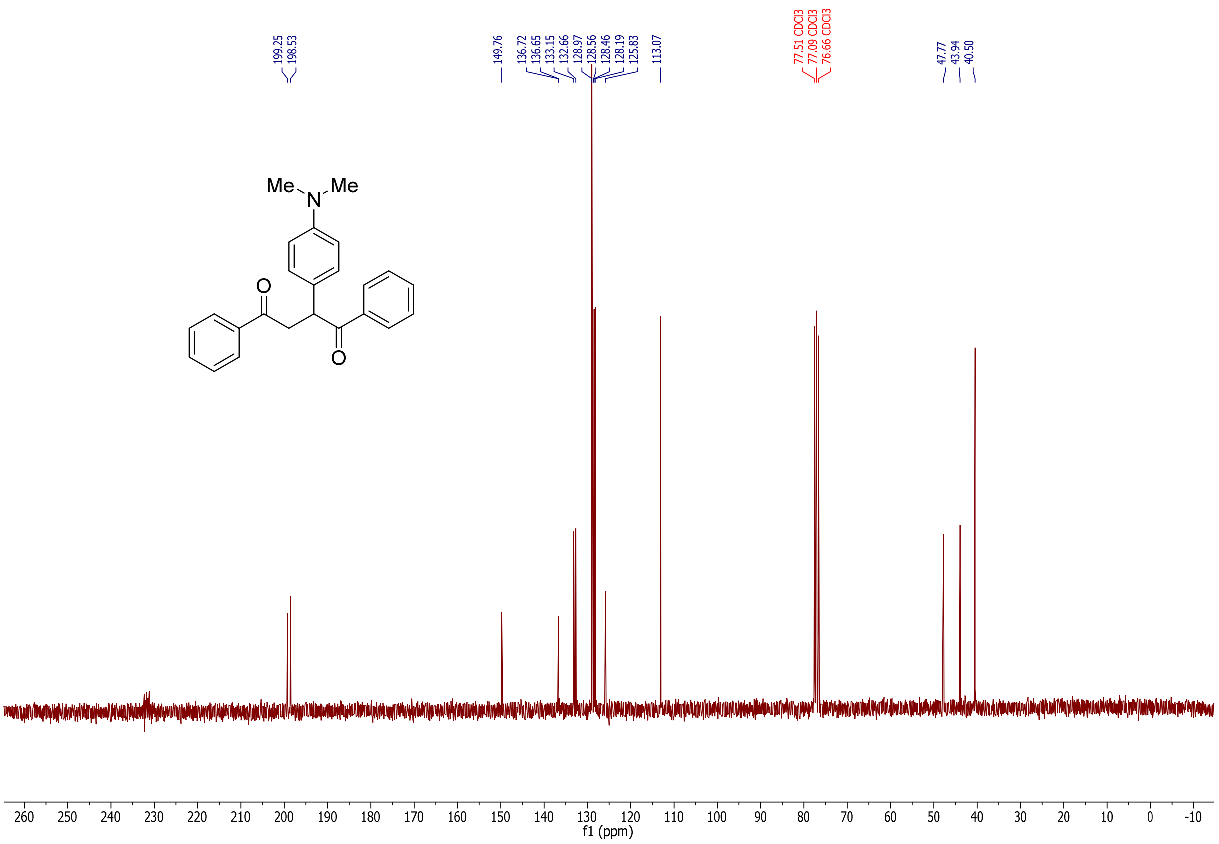
Original spectra for **3x**:





Original spectra for **3y**:





Original ^{19}F NMR spectra for $B(C_6F_5)_3$: