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Supporting Information

Selective cleavage and reconstruction of C–N/C–C bonds in saturated cyclic amines: tunable synthesis of lactams and functionalized acyclic amines

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I. General experimental information

TEMPO salts were synthesized with a previously described procedure.[1] *N*-Aryl cyclic amines (**1**) were prepared based on a literature procedure.[2] Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz, and the ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 376 MHz. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. High-resolution mass spectra (HRMS) were performed on a microTOF mass spectrometer. All the reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. A typical procedure for the synthesis of 2a the spectroscopic data of 2a-2v

To a reaction tube equipped with a stir bar were added 1-(4-chlorophenyl)piperidine (**1a**, 39 mg, 0.2 mmol), toluene (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (120 μL, 0.6 mmol, 5 mol/L in decane), and TFA (15 μL, 0.2 mmol). The resulting mixture was then stirred at 100 ^oC under air for 4 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford **2a** as yellow solid in 28 mg (72%). **2b-2v** were obtained in an analogous manner.

1-(4-Chlorophenyl)pyrrolidin-2-one (2a)[3]

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (28 mg, 72%), mp 95-96 ℃ (lit.[3] 95-97 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 7.32 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 2H), 3.84 (t, J = 7.2 Hz, 2H), 2.61 (t, J = 8.0 Hz, 2H), 2.21-2.15 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 174.3, 138.0, 129.6, 128.8, 121.0, 48.7, 32.7, 17.9. MS: m/z 196 $[M+H]^+$.

1-Phenylpyrrolidin-2-one (2b)[3]

Eluent: petroleum ether/ethyl acetate (2:1). White solid (18 mg, 56%), mp 67-68 ℃ (lit.[3] 68-69 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 3.87 (t, J = 7.2 Hz, 2H), 2.62 (t, J = 8.0 Hz, 2H), 2.21-2.13 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 174.3, 139.4, 128.8, 124.5, 120.0, 48.8, 32.8, 18.1. MS: m/z 162 $[M+H]^+$.

1-(*p*-Tolyl)pyrrolidin-2-one (2c)[3]

Eluent: petroleum ether/ethyl acetate (2:1). White solid (19 mg, 54%), mp 89-90 ℃ (lit.[3] 88-90 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 3.84 (t, J = 7.2 Hz,

2H), 2.59 (t, J = 8.4 Hz, 2H), 2.32 (s, 3H), 2.17-2.13 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 174.1, 136.9, 134.2, 129.4, 120.1, 49.0, 32.7, 20.9, 18.1. MS: m/z 176 $[M+H]^+$.

1-(4-Methoxyphenyl)pyrrolidin-2-one (2d)[3]

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (16 mg, 42%), mp 110-112 ℃ (lit.[3] 112-114 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.8 Hz, 2H), 6.90 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 2H), 3.84-3.80 (m, 5H), 2.59 (t, J = 8.4 Hz, 2H), 2.17-2.13 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 174.0, 156.6, 132.6, 121.9, 114.1, 55.5, 49.2, 32.5, 18.1. MS: m/z 192 $[M+H]^+$.

1-(4-Fluorophenyl)pyrrolidin-2-one (2e)[3]

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (23 mg, 64%), mp 41-43 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.07-7.03 (m, 2H), 3.83 (t, J = 7.2 Hz, 2H), 2.60 (t, J = 8.4 Hz, 2H), 2.20-2.12 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 174.2, 160.0 (d, $^{1}J_{C\text{-}F}$ = 242.9 Hz), 135.5 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 121.7 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 115.5 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 49.0, 32.5, 18.0. $^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz): δ -117.8. MS: m/z 180 $[M+H]^+$.

1-(4-Bromophenyl)pyrrolidin-2-one (2f)[3]

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (27 mg, 56%), mp 101-102 ℃ (lit.[3] 100-101 ℃) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 2H), 7.48-7.45 (m, 2H), 3.83 (t, J = 7.2 Hz, 2H), 2.61 (t, J = 8.4 Hz, 2H), 2.21-2.15 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 174.3, 138.5, 131.8, 121.3, 117.3, 48.6, 32.7, 17.9. MS: m/z 240 $[M+H]^+$.

1-(4-Iodophenyl)pyrrolidin-2-one (2g)[4]

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (32 mg, 56%), mp 138-119 ℃ (lit.[4] 140-142 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.65 (m, 2H), 7.42-7.40 (m, 2H), 3.83 (t, J = 7.2 Hz, 2H), 2.60 (t, J = 8.0 Hz, 2H), 2.18-2.15 (m, 2H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 174.3, 139.2, 137.8, 121.6, 88.0, 48.5, 32.7, 17.9. MS: m/z 288 $[M+H]^+$.

Methyl 4-(2-oxopyrrolidin-1-yl)benzoate (2h)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (25 mg, 57%), mp 118-119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 3.90-3.87 (m, 5H), 2.63 (t, *J* = 8.4 Hz, 2H), 2.22-2.16 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 174.7, 166.7, 143.4, 130.5, 125.5, 118.6, 52.0, 48.5, 32.9, 17.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}NO_3$ 220.0968; Found 220.0969.

4-(2-Oxopyrrolidin-1-yl)benzonitrile (2i)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (17 mg, 46%), mp 99-100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 3.88 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.25-2.17 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 174.9, 143.2, 133.0, 119.3, 118.9, 107.1, 48.3, 32.8, 17.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}N_2O$ 187.0866; Found 187.0867.

1-(4-(Trifluoromethyl)phenyl)pyrrolidin-2-one (2j)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (19 mg, 41%), mp 120-121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 3.90 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.24-2.17 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 174.7, 142.3, 126.1 (q, $^{3}J_{C\text{-}F}$ = 11.0 Hz), 126.0 (q, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 124.1 (q, $^{1}J_{C\text{-}F}$ = 270.2 Hz), 119.2, 48.5, 32.8, 17.9. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}F_3NO$ 230.0787; Found 230.0784.

1-(3-Fluorophenyl)pyrrolidin-2-one (2k)[3]

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (19 mg, 53%), mp 127-129 ℃ (lit.[3] 128-129 ℃) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.51 (m, 1H), 7.35-7.29 (m, 2H), 6.85-6.81 (m, 1H), 3.84 (t, *J* = 7.2 Hz, 2H), 2.61 (t, *J* = 8.4 Hz, 2H), 2.20-2.13 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz,

$CDCl_3$): δ 174.4, 162.9 (d, $^1J_{C\text{-}F}$ = 242.9 Hz), 140.9 (d, $^3J_{C\text{-}F}$ = 11.0 Hz), 129.9 (d, $^3J_{C\text{-}F}$ = 11.0 Hz), 114.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 111.1 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 107.1 (d, $^2J_{C\text{-}F}$ = 25.2 Hz), 48.7, 32.8, 17.8. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz):δ -111.6. MS: m/z 180 $[M+H]^+$.

1-(3-Chlorophenyl)pyrrolidin-2-one (2l)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (20 mg, 51%), mp 64-65 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (t, *J* = 2.0 Hz, 1H), 7.48-7.45 (m, 1H), 7.23-7.18 (m, 1H), 7.05-7.03 (m, 1H), 3.76 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 8.4 Hz, 2H), 2.13-2.07 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 174.4, 140.6, 134.5, 129.8, 124.4, 119.8, 117.7, 48.6, 32.7, 17.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{11}ClNO$ 196.0524; Found 196.0522.

1-(3-Bromophenyl)pyrrolidin-2-one (2m)[3]

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (15 mg, 31%), mp 57-58 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.28-7.20 (m, 2H), 3.83 (t, *J* = 7.2 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.20-2.15 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 174.3, 140.7, 130.1, 127.3, 122.58, 122.56, 118.2, 48.6, 32.7, 17.9. MS: m/z 240 $[M+H]^+$.

1-(*m*-Tolyl)pyrrolidin-2-one (2n)[5]

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (12 mg, 34%), mp 59-60 ℃ (lit.[5] 57-58 ℃). ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, J_1 = 7.9 Hz, J_2 = 2.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 3.85 (t, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.19-2.13 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 174.2, 139.4, 138.7, 128.7, 125.4, 120.9, 117.2, 49.0, 32.8, 21.6, 18.1. MS: m/z 176 $[M+H]^+$.

1-(3-Methoxyphenyl)pyrrolidin-2-one (2o)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (21 mg, 55%), mp 55-56 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 2.0 Hz, 1H), 7.26 (t, *J* = 8.4 Hz, 1H), 7.13-7.10 (m, 1H), 6.70 (dd, J_1 =

8.0 Hz, J_2 = 2.4 Hz, 1H), 3.86-3.82 (m, 5H), 2.61 (t, J = 8.0 Hz, 2H), 2.19-2.11 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 174.3, 160.0, 140.7, 129.5, 112.0, 110.1, 106.1, 55.3, 48.9, 32.9, 18.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}NO_2$ 192.1019; Found 192.1020.

1-(3-Nitrophenyl)pyrrolidin-2-one (2p)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (21 mg, 51%), mp 86-88 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (t, J = 2.0 Hz, 1H), 8.17 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.98 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.53 (t, J = 8.4 Hz, 1H), 3.94 (t, J = 7.2 Hz, 2H), 2.67 (t, J = 8.0 Hz, 2H), 2.28-2.20 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 174.7, 148.5, 140.5, 129.6, 125.3, 118.8, 113.8, 48.5, 32.7, 17.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{11}N_2O_3$ 207.0764; Found 207.0761.

1-([1,1'-Biphenyl]-4-yl)pyrrolidin-2-one (2q)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (19 mg, 40%), mp 165-166 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.8 Hz, 2H), 7.61-7.57 (m, 4H), 7.44 (t, J = 8.0 Hz, 2H), 7.35 (d, J = 7.2 Hz, 1H), 3.91 (t, J = 7.2 Hz, 2H), 2.64 (t, J = 8.4 Hz, 2H), 2.23-2.17 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 174.3, 140.5, 138.7, 137.3, 128.8, 127.5, 127.2, 126.9, 120.2, 48.8, 32.8, 18.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NO$ 238.1226; Found 238.1225.

1-(Naphthalen-2-yl)pyrrolidin-2-one (2r)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (9 mg, 21%), mp 125-126 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 7.86-7.79 (m, 4H), 7.48-7.41 (m, 2H), 3.98 (t, J = 7.2 Hz, 2H), 2.66 (t, J = 8.4 Hz, 2H), 2.25-2.19 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 174.5, 137.2, 133.5, 130.7, 128.6, 127.7, 127.6, 126.4, 125.2, 119.9, 116.8, 49.1, 32.9, 18.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO$ 212.1070; Found 212.1068.

1-(Pyridin-2-yl)pyrrolidin-2-one (2s)

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (18 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40-8.35 (m, 2H), 7.71-7.67 (m, 1H), 7.02 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 1H), 4.11 (t, J = 7.2 Hz, 2H), 2.66 (t, J = 8.0 Hz, 2H), 2.17-2.10 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 175.0, 152.0, 147.5, 137.6, 119.4, 114.7, 47.4, 33.7, 17.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_{11}N_2O$ 163.0866; Found 163.0865.

3-Methyl-1-phenylpyrrolidin-2-one (2t)

Eluent: petroleum ether/ethyl acetate (2:1). Brown solid (17 mg, 49%), mp 93-95 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.62 (m, 2H), 7.38-7.34 (m, 2H), 7.15-7.11 (m, 1H), 3.80-3.76 (m, 2H), 2.70-2.63 (m, 1H), 2.41-2.34 (m, 1H), 1.82-1.74 (m, 1H), 1.31 (d, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.7, 139.7, 128.8, 124.3, 119.7, 46.6, 38.3, 27.0, 16.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}NO$ 176.1070; Found 176.1069.

1-(3-Chlorophenyl)-3-methylpyrrolidin-2-one (2u)

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (15 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (t, J = 2.0 Hz, 1H), 7.57-7.55 (m, 1H), 7.29-7.25 (m, 1H), 7.11-7.09 (m, 1H), 3.77-3.73 (m, 2H), 2.70-2.64 (m, 1H), 2.41-2.35 (m, 1H), 1.82-1.74 (m, 1H), 1.30 (d, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 176.9, 140.8, 134.5, 129.8, 124.2, 119.5, 117.4, 46.4, 38.3, 26.9, 16.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{13}ClNO$ 210.0680; Found 210.0682.**1,3-Diphenylimidazolidin-2-one (2v)**

Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid (13 mg, 27%), mp 208-209 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 4H), 7.38 (t, J = 8.0 Hz, 4H), 7.09 (t, J = 7.6 Hz, 2H), 3.97 (s, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 155.1, 140.1, 128.9, 123.1, 118.1, 42.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}N_2O$ 239.1179; Found 239.1174.

2. A typical procedure for the synthesis of 3a/3a' and the spectroscopic data of 3a-3p, 3a'-3b',

3e'-3f', 3h', 3j'-3l' and 3o'-3p'

To a reaction tube equipped with a stir bar were added 1-(4-chlorophenyl)piperidine (**1a**, 39 mg, 0.2 mmol), CH_3CN (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (80 μL, 0.4 mmol, 5 mol/L in decane), TEMPO (125 mg, 0.8 mmol) and DABCO (22 mg, 0.2 mmol). The resulting mixture was then stirred at 100 ^oC under air for 8 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate and washed with aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **3a** as yellow liquid in 32 mg (42%). Meanwhile, **3a'** was obtained as yellow liquid in 8 mg (13%). **3b-3p, 3b', 3e'-3f', 3h', 3j'-3l' and 3o'-3p'** were obtained in an analogous manner.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(4-chlorophenyl)formamido)butanoate (3a)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (32 mg, 42%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.40-7.37 (m, 2H), 7.17-7.14 (m, 2H), 3.88-3.84 (m, 2H), 2.38 (t, *J* = 7.6 Hz, 2H), 1.96-1.89 (m, 2H), 1.68-1.64 (m, 3H), 1.53-1.51 (m, 2H), 1.42-1.30 (m, 1H), 1.12 (s, 6H), 1.01 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.6, 162.1, 139.3, 132.6, 130.0, 125.0, 60.0, 44.4, 39.0, 31.9, 29.6, 23.0, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{30}ClN_2O_3$ 381.1939; Found 381.1935. IR (neat): υ (cm^{-1}) 2975, 2933, 2872, 1759, 1677, 1594, 1494, 1468, 1363, 1131, 833.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-phenylformamido)butanoate (3b)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (28 mg, 40%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.43-7.39 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.22-7.20 (m, 2H), 3.89 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.6 Hz, 2H), 1.96-1.91 (m, 2H), 1.68-1.62 (m, 3H), 1.53-1.50 (m, 2H), 1.41

(s, 1H), 1.12 (s, 6H), 1.01 (s, 6H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 172.5, 162.5, 140.7, 129.8, 127.0, 123.9, 60.0, 44.4, 39.0, 31.9, 29.8, 23.1, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{31}N_2O_3$ 347.2329; Found 347.2310. IR (neat): υ (cm^{-1}) 2974, 2933, 2872, 2848, 1760, 1675, 1596, 1497, 1458, 1363, 1264, 1129.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-*p*-tolylformamido)butanoate (3c)

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (37 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.85 (t, *J* = 7.6 Hz, 2H), 2.39-2.36 (m, 5H), 1.96-1.90 (m, 2H), 1.68-1.41 (m, 6H), 1.12 (s, 6H), 1.00 (s, 6H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 172.6, 162.5, 138.1, 137.0, 130.3, 124.2, 60.0, 44.5, 39.0, 31.9, 29.8, 23.1, 20.9, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{33}N_2O_3$ 361.2486; Found 361.2484. IR (neat): υ (cm^{-1}) 3005, 2973, 2931, 2870, 1761, 1675, 1612, 1515, 1451, 1363, 1265, 1129, 819.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(4-(*tert*-butyl)phenyl)formamido)butanoate (3d)

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (49 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.86 (t, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.94 (t, *J* = 7.2 Hz, 2H), 1.68-1.50 (m, 6H), 1.41-1.19 (m, 9H), 1.11 (s, 6H), 1.00 (s, 6H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 172.6, 162.5, 150.1, 138.0, 126.7, 123.7, 60.0, 44.4, 39.0, 34.6, 32.0, 31.3, 29.8, 23.2, 20.5, 17.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{39}N_2O_3$ 403.2955; Found 403.2955. IR (neat): υ (cm^{-1}) 3005, 2962, 2935, 2870, 1762, 1676, 1609, 1511, 1462, 1363, 1267, 1130, 837.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(4-methoxyphenyl)formamido)butanoate (3e)

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (23 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.95-6.91 (m, 2H), 3.84-3.80 (m, 5H), 2.38 (t, *J* = 7.6 Hz, 2H), 1.95-1.88 (m, 2H), 1.68-1.39 (m, 6H), 1.12 (s, 6H), 1.01 (s, 6H). $^{13}C\{^{1}H\}$ NMR (150

MHz, $CDCl_3$): δ 172.5, 162.6, 158.7, 133.6, 126.2, 114.9, 59.9, 55.5, 44.8, 39.0, 31.9, 29.8, 23.1, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{33}N_2O_4$ 377.2435; Found 377.2435. IR (neat): υ (cm^{-1}) 3002, 2934, 2869, 2838, 1767, 1662, 1510, 1450, 1363, 1280, 1245, 1121, 1034, 834.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(4-(trifluoromethyl)phenyl)formamido)butanoate (3f)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (27 mg, 33%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 3.93 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 6.8 Hz, 2H), 1.98-1.94 (m, 2H), 1.66-1.26 (m, 6H), 1.12 (s, 6H), 1.01 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.5, 161.9, 143.9, 128.5 (q, $^1J_{C\text{-}F}$ = 192.6 Hz), 127.1 (q, $^4J_{C\text{-}F}$ = 3.3 Hz), 123.9, 122.8, 60.0, 44.0, 39.0, 32.0, 29.4, 22.9, 20.5, 16.9. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz): δ -62.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{30}F_3N_2O_3$ 415.2203; Found 415.2197. IR (neat): υ (cm^{-1}) 2974, 2934, 2859, 1759, 1682, 1614, 1521, 1457, 1364, 1324, 1165, 1119, 1069, 844.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(4-fluorophenyl)formamido)butanoate (3g)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (26 mg, 36%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.20-7.17 (m, 2H), 7.14-7.09 (m, 2H), 3.84 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.94-1.90 (m, 2H), 1.68-1.42 (m, 6H), 1.12 (s, 6H), 1.01 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.6, 162.3, 161.4 (d, $^1J_{C\text{-}F}$ = 246.0 Hz), 136.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 126.2 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 116.7 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 60.0, 44.8, 39.0, 32.0, 29.7, 23.0, 20.5, 16.9. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz): δ -114.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{30}FN_2O_3$ 365.2235; Found 365.2231. IR (neat): υ (cm^{-1}) 2975, 2933, 2872, 2848, 1759, 1676, 1509, 1453, 1364, 1223, 1130, 840.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(4-bromophenyl)formamido)butanoate (3h)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (37 mg, 43%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.54 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 3.86 (t, *J* =

7.6 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.96-1.91 (m, 2H), 1.68-1.42 (m, 6H), 1.12 (s, 6H), 1.01 (s, 6H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 172.6, 162.0, 139.9, 132.9, 125.3, 120.4, 60.0, 53.5, 44.3, 39.0, 32.0, 29.6, 23.0, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{30}BrN_2O_3$ 425.1434; Found 425.1418. IR (neat): υ (cm^{-1}) 2973, 2931, 2869, 2855, 1765, 1666, 1586, 1487, 1451, 1364, 1343, 1226, 1170, 1121, 833, 817.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(3-chlorophenyl)formamido)butanoate (3i)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (34 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.29-7.26 (m, 1H), 7.20 (t, *J* = 2.0 Hz, 1H), 7.12 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 3.88 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.96-1.92 (m, 2H), 1.68-1.50 (m, 6H), 1.12 (s, 6H), 1.01 (s, 6H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 172.5, 162.1, 142.0, 135.4, 130.9, 127.1, 123.8, 121.8, 60.0, 44.4, 39.0, 32.0, 29.7, 23.1, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{30}ClN_2O_3$ 381.1939; Found 381.1938. IR (neat): υ (cm^{-1}) 2972, 2931, 2869, 2850, 1759, 1679, 1592, 1481, 1363, 1350, 1246, 1130, 872, 782, 692.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(3-methoxyphenyl)formamido)butanoate (3j)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (32 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 6.85-6.78 (m, 2H), 6.72 (t, *J* = 2.4 Hz, 1H), 3.89-3.82 (m, 5H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.96-1.93 (m, 2H), 1.67-1.41 (m, 6H), 1.12 (s, 6H), 1.01 (s, 6H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 172.5, 162.4, 160.6, 141.9, 130.5, 116.1, 112.1, 110.1, 60.0, 55.5, 44.4, 39.0, 31.9, 29.9, 23.2, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{33}N_2O_4$ 377.2435; Found 377.2427. IR (neat): υ (cm^{-1}) 3005, 2974, 2934, 2872, 2843, 1759, 1677, 1601, 1490, 1454, 1363, 1129, 1045, 858, 780, 696.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-*m*-tolylformamido)butanoate (3k)

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (33 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.31-7.27 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.00-6.99 (m, 2H), 3.87 (t, *J* = 7.6 Hz, 2H), 2.40-2.36 (m, 5H), 1.97-1.91 (m, 2H), 1.68-1.41 (m, 6H), 1.12 (s, 6H), 1.00 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.5, 162.5, 140.7, 139.9, 129.6, 127.8, 124.8, 121.2, 60.0, 44.4, 39.0, 31.9, 29.9, 23.2, 21.4, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{33}N_2O_3$ 361.2486; Found 361.2481. IR (neat): υ (cm^{-1}) 3005, 2974, 2932, 2869, 1760, 1676, 1606, 1589, 1493, 1452, 1363, 1129, 873, 785, 700.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-([1,1'-biphenyl]-4-yl)formamido)butanoate (3l)

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (32 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.92 (t, *J* = 7.6 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.00-1.96 (m, 2H), 1.68-1.41 (m, 6H), 1.12 (s, 6H), 1.01 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.6, 162.4, 139.95, 139.89, 129.0, 128.4, 127.7, 127.0, 124.1, 60.0, 44.4, 39.0, 32.0, 29.8, 23.2, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{35}N_2O_3$ 423.2642; Found 423.2633. IR (neat): υ (cm^{-1}) 2973, 2931, 2872, 2850, 1759, 1674, 1606, 1522, 1487, 1353, 1246, 1184, 1130, 841, 764, 728, 697.

2,2,6,6-Tetramethylpiperidin-1-yl 4-(*N*-(naphthalen-2-yl)formamido)butanoate (3m)

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (40 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.90-7.82 (m, 3H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.54-7.50 (m, 2H), 7.35 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 3.99 (t, *J* = 7.6 Hz, 2H), 2.42 (t, *J* = 7.6 Hz, 2H), 2.01-1.97 (m, 2H), 1.66-1.48 (m, 6H), 1.09 (s, 6H), 0.98 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.5, 162.7, 138.1, 133.6, 132.0, 130.0, 127.8, 127.7, 127.1, 126.4, 122.4, 122.1, 60.0, 44.4, 39.0, 31.9, 29.9,

23.3, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{33}N_2O_3$ 397.2486; Found 397.2485. IR (neat): υ (cm^{-1}) 2974, 2930, 2872, 2853, 1759, 1675, 1598, 1529, 1509, 1364, 1126, 858, 814, 749.

2,2,6,6-Tetramethylpiperidin-1-yl 5-(*N*-phenylformamido)pentanoate (3o)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (22 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.85 (t, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.71-1.25 (m, 10H), 1.11 (s, 6H), 1.00 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.8, 162.4, 140.9, 129.7, 127.0, 124.3, 59.9, 44.6, 39.0, 32.4, 32.0, 27.3, 22.4, 20.5, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{33}N_2O_3$ 361.2486; Found 361.2481. IR (neat): υ (cm^{-1}) 2974, 2932, 2870, 1760, 1675, 1596, 1497, 1460, 1363, 1265, 1129, 763, 698.

2,2,6,6-Tetramethylpiperidin-1-yl 5-(*N*-(4-fluorophenyl)formamido)pentanoate (3p)

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (29 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.17-7.08 (m, 4H), 3.80 (t, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.72-1.29 (m, 10H), 1.11 (s, 6H), 1.00 (s, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.9, 162.3, 161.5 (d, $^1J_{C\text{-}F}$ = 237.3 Hz), 136.9 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 126.6 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 116.6 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 59.9, 44.9, 39.0, 32.3, 32.0, 27.3, 22.3, 20.5, 16.95, 16.93. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz): δ -114.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{32}FN_2O_3$ 379.2391; Found 379.2390. IR (neat): υ (cm^{-1}) 2972, 2931, 2872, 2850, 1759, 1676, 1509, 1464, 1363, 1221, 1130, 840.

***tert*-Butyl 4-(*N*-(4-chlorophenyl)formamido)butanoate (3a')**

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (8 mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.39 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 2H), 7.13 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 2H), 3.82 (t, *J* = 7.6 Hz, 2H), 2.24 (t, *J* = 7.2 Hz, 2H), 1.85-1.81 (m, 2H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (150

MHz, $CDCl_3$): δ 172.0, 162.1, 139.4, 132.6, 129.9, 125.2, 80.6, 44.3, 32.5, 28.1, 23.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{20}ClNNaO_3$ 320.1024; Found 320.1005.

***tert*-Butyl 4-(*N*-phenylformamido)butanoate (3b')**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (8 mg, 15%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.20-7.18 (m, 2H), 3.85 (t, *J* = 7.6 Hz, 2H), 2.25 (t, *J* = 7.6 Hz, 2H), 1.86-1.83 (m, 2H), 1.42 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.1, 162.4, 140.9, 129.8, 126.9, 124.1, 80.5, 44.3, 32.6, 28.1, 23.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}NO_3$ 264.1594; Found 264.1576.

***tert*-Butyl 4-(*N*-(4-methoxyphenyl)formamido)butanoate (3e')**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (9 mg, 15%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.04-7.02 (m, 2H), 6.86-6.84 (m, 2H), 3.75 (s, 3H), 3.70 (t, *J* = 7.6 Hz, 2H), 2.17 (t, *J* = 7.6 Hz, 2H), 1.76-1.72 (m, 2H), 1.35 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.2, 162.6, 158.7, 133.7, 126.3, 114.9, 80.5, 55.6, 44.7, 32.6, 28.1, 23.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}NO_4$ 294.1700; Found 294.1686.

***tert*-Butyl 4-(*N*-(4-(trifluoromethyl)phenyl)formamido)butanoate (3f')**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (7 mg, 11%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.90 (t, *J* = 7.2 Hz, 2H), 2.26 (t, *J* = 7.2 Hz, 2H), 1.88-1.84 (m, 2H), 1.42 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.0, 161.9, 144.0, 128.5 (q, $^2J_{C\text{-}F}$ = 21.9 Hz), 127.1 (q, $^4J_{C\text{-}F}$ = 2.9 Hz), 126.3 (q, $^1J_{C\text{-}F}$ = 198.3 Hz), 122.9 (q, $^3J_{C\text{-}F}$ = 10.2 Hz), 80.7, 44.0, 32.4, 28.1, 23.0. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz): δ -62.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}F_3NO_3Na$ 354.1287; Found 354.1288.

***tert*-Butyl 4-(*N*-(4-bromophenyl)formamido)butanoate (3h')**

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (14 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.54 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 3.82 (t, J = 7.2 Hz, 2H), 2.24 (t, J = 7.6 Hz, 2H), 1.85-1.81 (m, 2H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.0, 162.0, 140.0, 132.9, 125.4, 120.3, 80.6, 44.2, 32.5, 28.1, 23.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}BrNO_3$ 342.0699; Found 342.0692.

***tert*-Butyl 4-(*N*-(3-methoxyphenyl)formamido)butanoate (3j')**

Eluent: petroleum ether/ethyl acetate (5:1). Brown liquid (6 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.31 (t, J = 8.4 Hz, 1H), 6.83 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.77 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.72 (t, J = 2.4 Hz, 1H), 3.85-3.74 (m, 5H), 2.24 (t, J = 7.2 Hz, 2H), 1.87-1.83 (m, 2H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.2, 162.4, 160.6, 142.1, 130.5, 116.1, 112.1, 110.1, 80.5, 55.5, 44.2, 32.6, 28.1, 23.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{23}NO_4Na$ 316.1519; Found 316.1509.

***tert*-Butyl 4-(*N*-*m*-tolylformamido)butanoate (3k')**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (8 mg, 14%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.28-7.26 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.99-6.97 (m, 2H), 3.83 (t, J = 7.6 Hz, 2H), 2.38 (s, 3H), 2.24 (t, J = 7.6 Hz, 2H), 1.86-1.82 (m, 2H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.2, 162.4, 140.8, 139.8, 129.5, 127.7, 124.8, 121.2, 80.4, 44.3, 32.7, 28.1, 23.1, 21.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}NO_3$ 278.1751; Found 278.1751.

***tert*-Butyl 4-(*N*-([1,1'-biphenyl]-4-yl)formamido)butanoate (3l')**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (6 mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.64-7.62 (m, 2H), 7.59-7.56 (m, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.27-7.25 (m, 2H), 3.88 (t, J = 7.6 Hz, 2H), 2.27 (t, J = 7.6 Hz, 2H), 1.90-1.87 (m, 2H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 172.2, 162.4, 140.00, 139.95, 129.0, 128.4, 127.7, 127.0,

124.2, 80.5, 44.3, 32.6, 28.1, 23.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}NO_3Na$ 362.1727; Found 362.1719.

***tert*-Butyl 5-(*N*-phenylformamido)pentanoate (3o')**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (4 mg, 7%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.18-7.16 (m, 2H), 3.83 (t, *J* = 6.8 Hz, 2H), 2.20 (t, *J* = 7.2 Hz, 2H), 1.59-1.57 (m, 4H), 1.40 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.7, 162.4, 140.9, 129.7, 126.9, 124.3, 80.2, 44.6, 35.0, 28.1, 27.0, 22.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}NO_3$ 278.1751; Found 278.1749.

***tert*-Butyl 5-(*N*-(4-fluorophenyl)formamido)pentanoate (3p')**

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (7 mg, 12%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.16-7.08 (m, 4H), 3.78 (t, *J* = 6.8 Hz, 2H), 2.21 (t, *J* = 6.8 Hz, 2H), 1.59-1.54 (m, 4H), 1.41 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.6, 162.3, 161.4 (d, $^1J_{C\text{-}F}$ = 246.2 Hz), 136.9 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 126.6 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 116.6 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 80.2, 44.9, 35.0, 28.1, 26.9, 22.2. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz):δ -114.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}FNO_3Na$ 318.1476; Found 318.1476.

3. A typical procedure for the synthesis of 2w' and the spectroscopic data of 2w'

To a reaction tube equipped with a stir bar were added 4-phenylmorpholine (**1w**, 33 mg, 0.2 mmol), toluene (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), and TBHP (120 μL, 0.6 mmol, 5 mol/L in decane). The resulting mixture was then stirred at 100 ^oC under air for 4 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford

2w' as yellow liquid in 12 mg (31%).

2-(*N*-Phenylformamido)ethyl formate (2w')

Eluent: petroleum ether/ethyl acetate (2:1). Yellow liquid (12 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.97 (s, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.34-7.33 (m, 1H), 7.22 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 4.34 (t, J = 5.6 Hz, 2H), 4.11 (t, J = 5.6 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 162.7, 160.6, 140.7, 129.9, 127.4, 124.5, 60.6, 44.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{12}NO_3$ 194.0812; Found 194.0821.

4. A typical procedure for the synthesis of 2x' and the spectroscopic data of 2x'

To a reaction tube equipped with a stir bar were added 1-phenethylpiperidine (**1x**, 38 mg, 0.2 mmol), toluene (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), and TBHP (120 μL, 0.6 mmol, 5 mol/L in decane), and TFA (15 μL, 0.2 mmol). The resulting mixture was then stirred at 100 ^{o}C under air for 4 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **2x'** as yellow liquid in 5 mg (12%).

1-Phenethylpiperidine-2,3-dione (2x')

Eluent: petroleum ether/ethyl acetate (5:1). Yellow liquid (5 mg, 12%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.53-7.49 (m, 2H), 3.72-3.70 (m, 2H), 3.31-3.28 (m, 2H), 1.72-1.69 (m, 4H), 1.59-1.54 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 192.0, 165.5, 134.7, 133.3, 129.6, 129.0, 47.1, 42.2, 26.2, 25.5, 24.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NO_2$ 218.1176; Found 218.1151.

5. A typical procedure for the synthesis of 4 and the spectroscopic data of 4

To a reaction tube equipped with a stir bar were added 2,2,6,6-tetramethylpiperidin-1-yl 4-(*N*-phenylformamido)butanoate (**3b**, 57 mg, 0.166 mmol), AcOH/THF/H_2O (1:1:1.5, 7 mL), and zinc powder (261 mg, 4.015 mmol). The mixture was then stirred at 70 ℃ for 2 h. Upon completion, the mixture was cooled to room temperature and quenched with saturated NaOH solution. The precipitate was filtered and the remaining mixture was the extracted with EtOAc (10 mL × 3). The combined organic layers were washed with saturated brine solution and saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtrated, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica-gel with dichloromethane/methanol (20:1) as the eluent to afford **4** as green solid in 20 mg (58%).

4-(*N*-Phenylformamido)butanoic acid (4)

Eluent: dichloromethane/methanol (20:1). Green solid (20 mg, 58%), mp 65-66 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.89 (t, *J* = 7.2 Hz, 2H), 2.39 (t, *J* = 7.6 Hz, 2H), 1.91-1.87 (m, 2H). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.04 (br s, 1H), 8.41 (s, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 3.80 (t, *J* = 7.2 Hz, 2H), 2.20 (t, *J* = 7.2 Hz, 2H), 1.67-1.61 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 177.5, 162.8, 140.5, 129.8, 127.2, 124.2, 44.2, 31.1, 22.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}NO_3$ 208.0968; Found 208.0966.

6. Control Experiments

6.1. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), toluene (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (120 μL, 0.6 mmol, 5 mol/L in decane), TFA (15 μL, 0.2 mmol), and BHT (132 mg, 0.6 mmol). The resulting mixture was then stirred at 100 ^{o}C under air for 4 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and aqueous NaCl. The organic

layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford **2b** as yellow solid in 16 mg (50%).

6.2. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), CH_3CN (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (80 μL, 0.4 mmol, 5 mol/L in decane), TEMPO (125 mg, 0.8 mmol), DABCO (22 mg, 0.2 mmol), and BHT (132 mg, 0.6 mmol). The resulting mixture was then stirred at 100 ^oC under air for 8 h. Subsequent TLC analysis of the resulting mixture showed that there was no desired product **3b** formed from this reaction.

6.3. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), toluene (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (120 μL, 0.6 mmol, 5 mol/L in decane), and TFA (15 μL, 0.2 mmol). The resulting mixture was then stirred at 100 ^oC under air for 0.5 h. Subsequent HRMS analysis of the resulting mixture showed that intermediate (**B**) (calcd, 160.1121; found, 160.1127) was formed (Fig. S1).

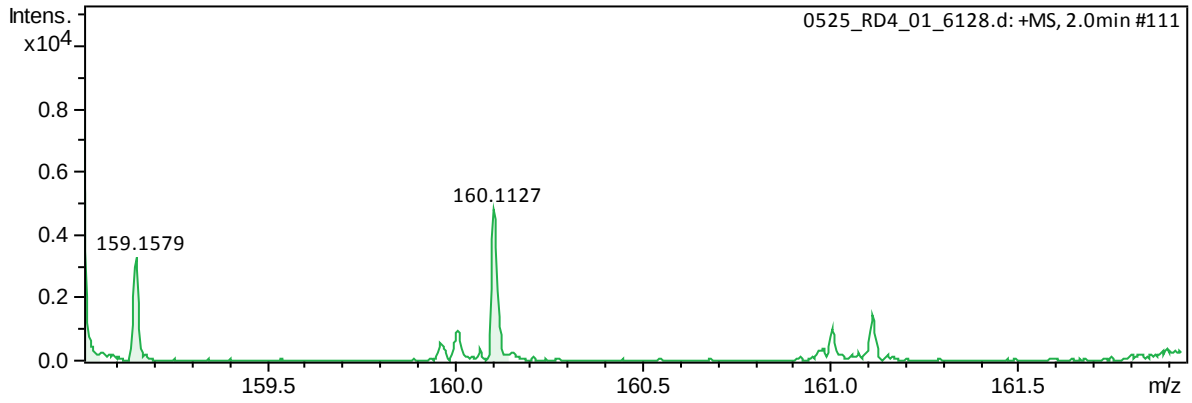


Fig. S1 Copy of HRMS Spectra of the Reaction Mixture

6.4. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), CH_3CN (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (80 μL, 0.4 mmol, 5 mol/L in decane), TEMPO (125 mg, 0.8 mmol) and DABCO (22 mg, 0.2 mmol). The resulting mixture was then stirred at 100 ^oC under air for 0.5 h. Subsequent HRMS analysis of the resulting mixture showed

that intermediate (**B**) (calcd, 160.1121; found, 160.1120) was formed (Fig. S2).

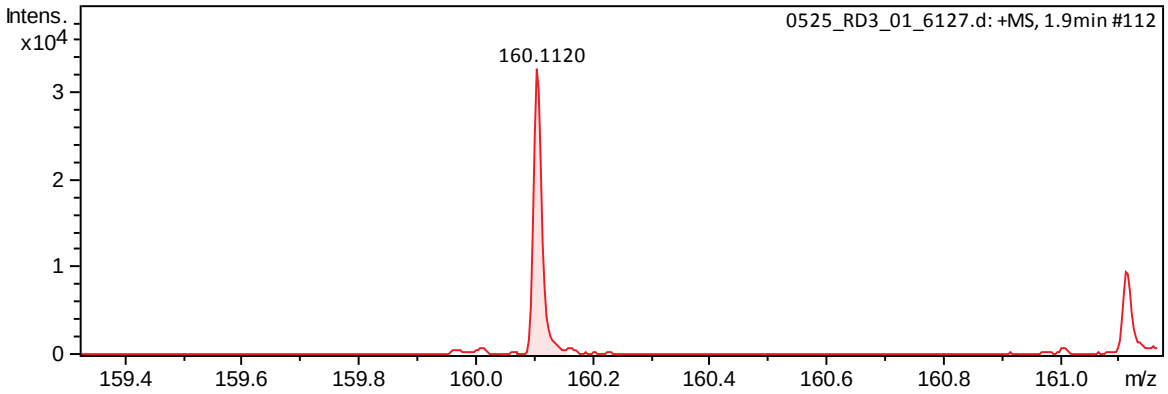


Fig. S2 Copy of HRMS Spectra of the Reaction Mixture

6.5. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), toluene (1 mL), $T^{+}BF_4^{-}$ (59 mg, 0.24 mmol), TBHP (120 μL, 0.6 mmol, 5 mol/L in decane), and TFA (15 μL, 0.2 mmol). The resulting mixture was then stirred at 100 ^{o}C under air for 1 h. Subsequent HRMS analysis of the resulting mixture showed that intermediate (**F**) (calcd, 208.0968; found, 208.0963) was formed (Fig. S3).

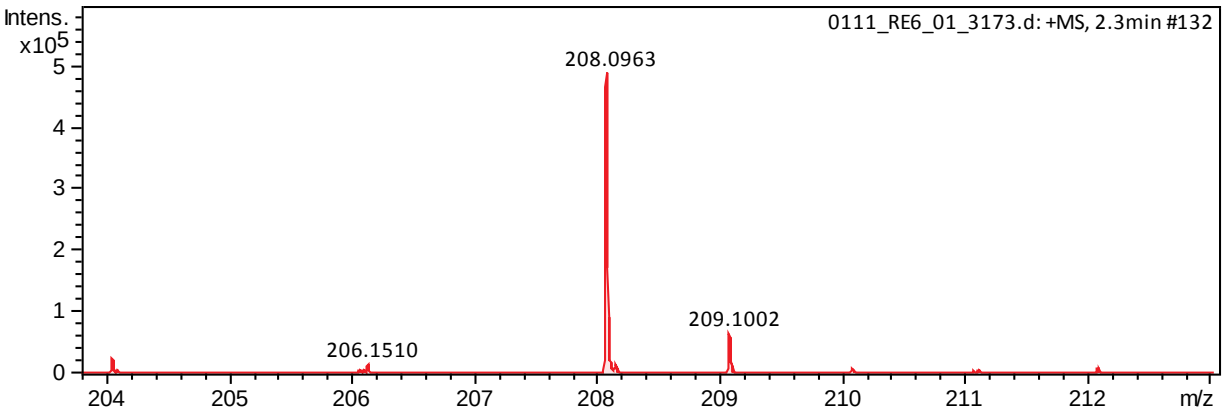


Fig. S3 Copy of HRMS Spectra of the Reaction Mixture

6.6. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), CH_3CN (1 mL), $T^{+}BF_4^{-}$ (59 mg, 0.24 mmol), TBHP (80 μL, 0.4 mmol, 5 mol/L in decane), TEMPO (125 mg, 0.8 mmol) and DABCO (22 mg, 0.2 mmol). The resulting mixture was then stirred at 100 ^{o}C under air for 1 h. Subsequent HRMS analysis of the resulting mixture showed that intermediate (**G**) (calcd, 264.1594; found, 264.1586) was formed (Fig. S4).

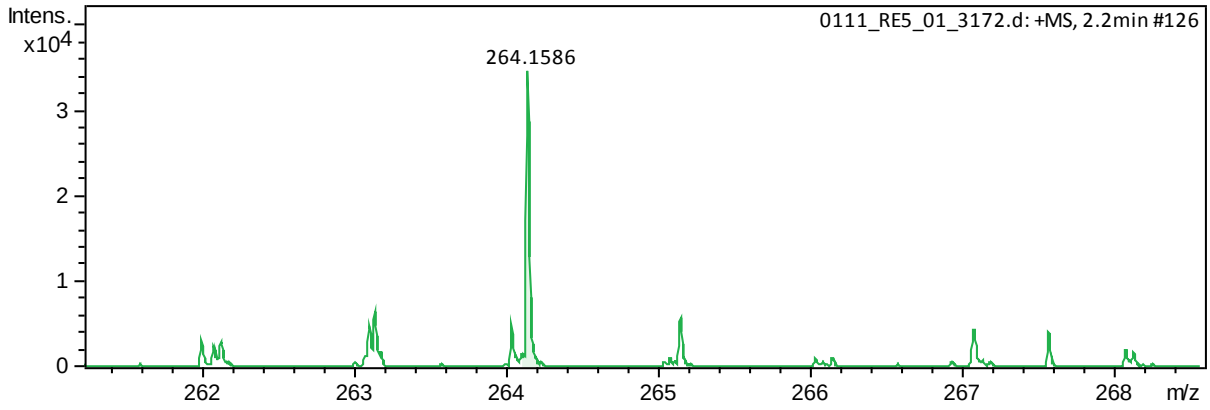


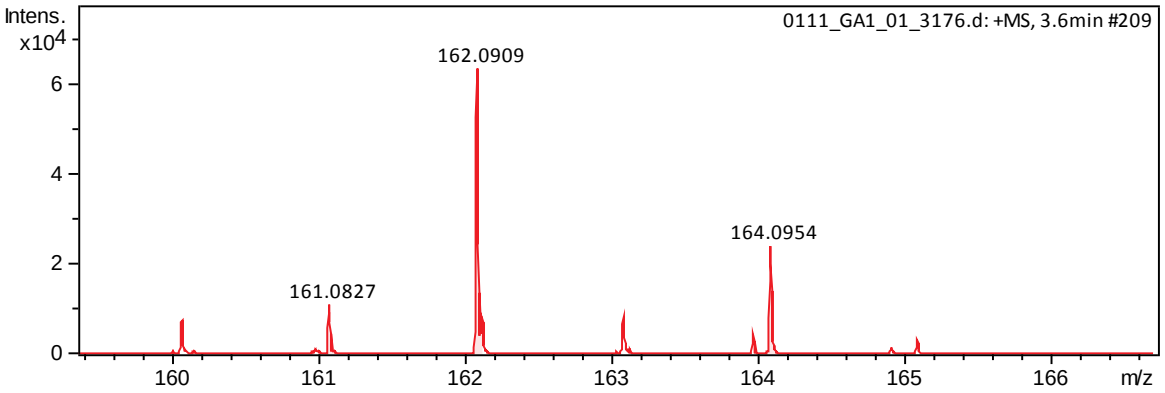
Fig. S4 Copy of HRMS Spectra of the Reaction Mixture

6.7. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), toluene (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (120 μL, 0.6 mmol, 5 mol/L in decane), and TFA (15 μL, 0.2 mmol). The resulting mixture was then stirred at 100 ^oC under N_2 for 4 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate and washed with saturated $NaHCO_3$ solution and aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (2:1) as the eluent to afford **2b** as yellow solid in 17 mg (53%).

6.8. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), CH_3CN (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (80 μL, 0.4 mmol, 5 mol/L in decane), TEMPO (125 mg, 0.8 mmol) and DABCO (22 mg, 0.2 mmol). The resulting mixture was then stirred at 100 ^oC under N_2 for 8 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate and washed with aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and filtered. Then, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica-gel with petroleum ether/ethyl acetate (5:1) as the eluent to afford **3b** as yellow liquid in 18 mg (26%).

6.9. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2

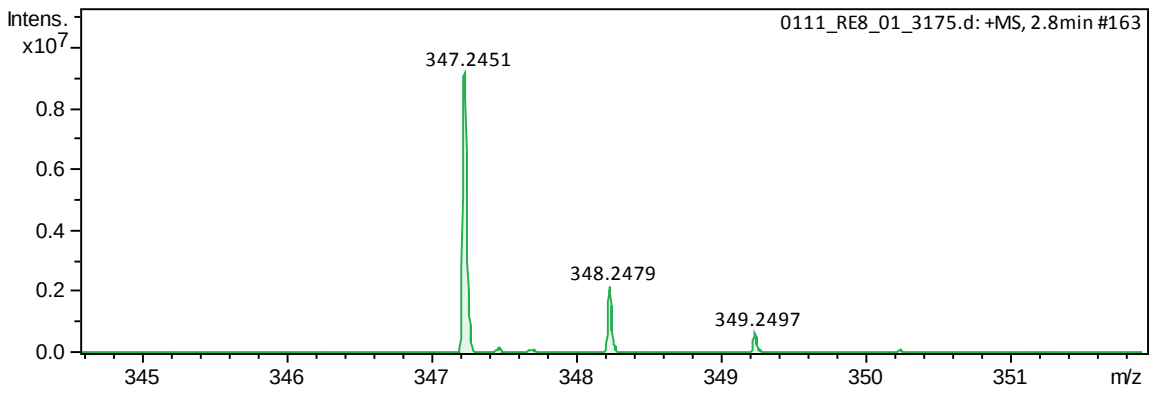
mmol), toluene (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (120 μL, 0.6 mmol, 5 mol/L in decane), TFA (15 μL, 0.2 mmol) and $H_2{}^{18}O$ (20 μL, 1.0 mmol). The resulting mixture was then stirred at 100 ^oC under air for 4 h. Subsequent HRMS analysis of the mixture showed that [^{16}O]-**2b** and [^{18}O]-**2b** were formed in a ratio of 3:1 (Fig. S5).



m/z	Res.	S/N	I	I%	FWHM
162.0909	10568	688.3	62932	0.6	0.0153
164.0954	9990	259.8	24023	0.2	0.0164

Fig. S5 Copy of HRMS Spectra of the Mixture of [^{16}O]-2b/[^{18}O]-2b

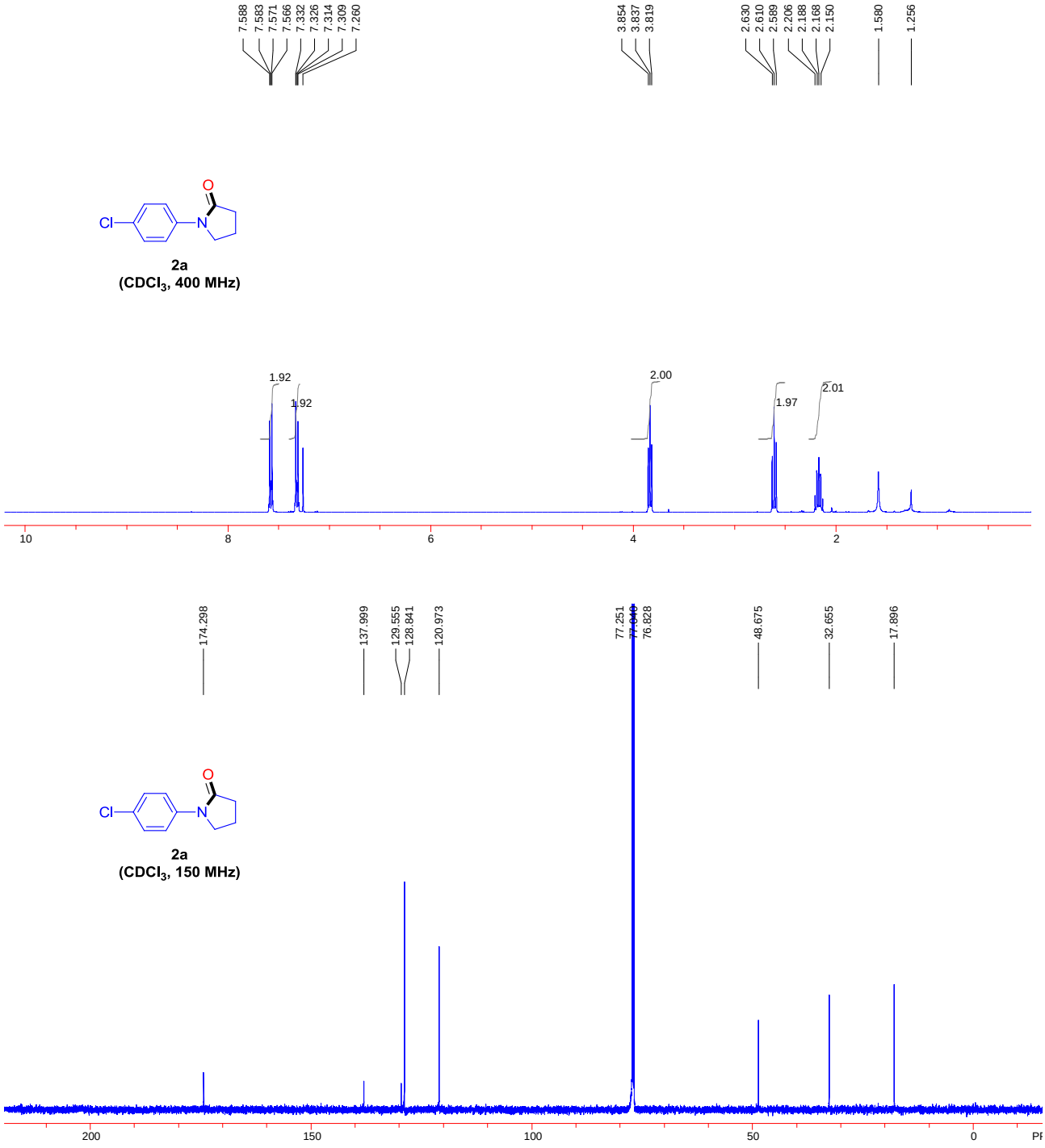
6.10. To a reaction tube equipped with a stir bar were added 1-phenylpiperidine (**1b**, 32 mg, 0.2 mmol), CH_3CN (1 mL), $T^+BF_4^-$ (59 mg, 0.24 mmol), TBHP (80 μL, 0.4 mmol, 5 mol/L in decane), TEMPO (125 mg, 0.8 mmol), DABCO (22 mg, 0.2 mmol) and $H_2{}^{18}O$ (20 μL, 1.0 mmol). The resulting mixture was then stirred at 100 ^oC under air for 8 h. Subsequent HRMS analysis of the mixture showed that [^{16}O]-**3b** and [^{18}O]-**3b** were formed in a ratio of 13:1 (Fig. S6).

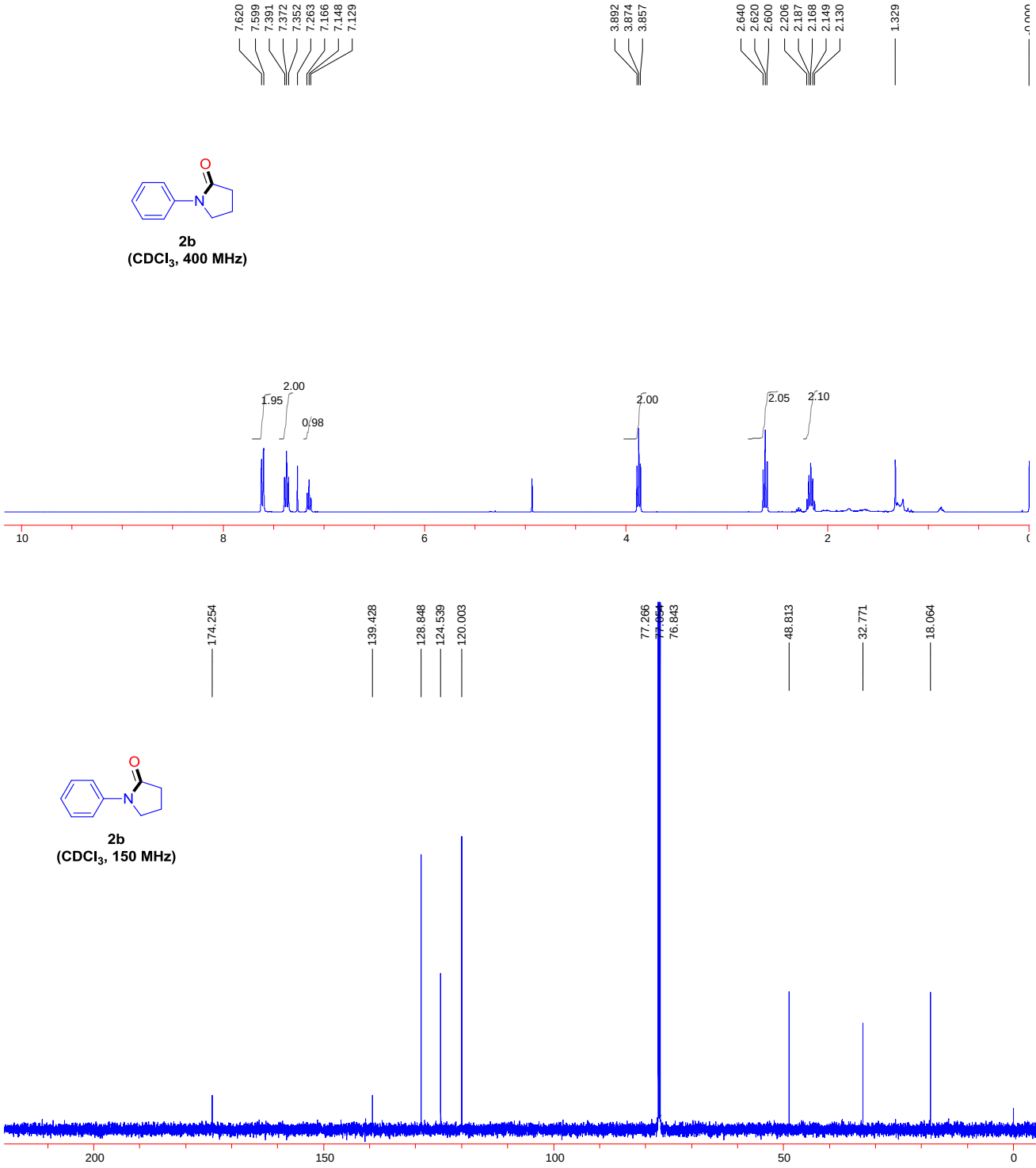


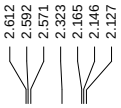
m/z	Res.	S/N	I	I%	FWHM
347.2451	10800	43259.8	9900182	100	0.0321
349.2497	11820	3287.1	752892	7.6	0.0295

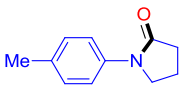
Fig. S6 Copy of HRMS Spectra of the Mixture of [^{16}O]-3b/[^{18}O]-3b

III. Copies of the NMR spectra of 2a-2v

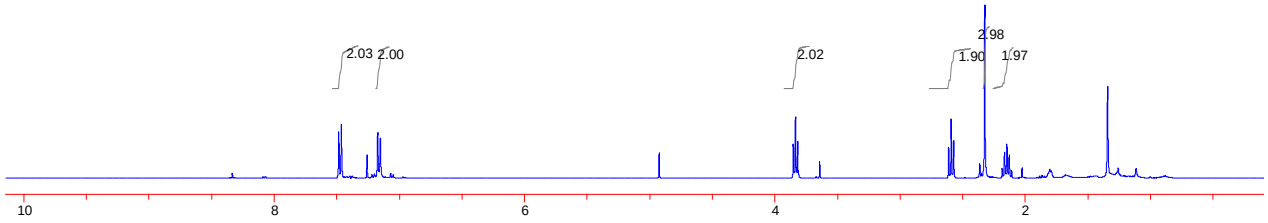


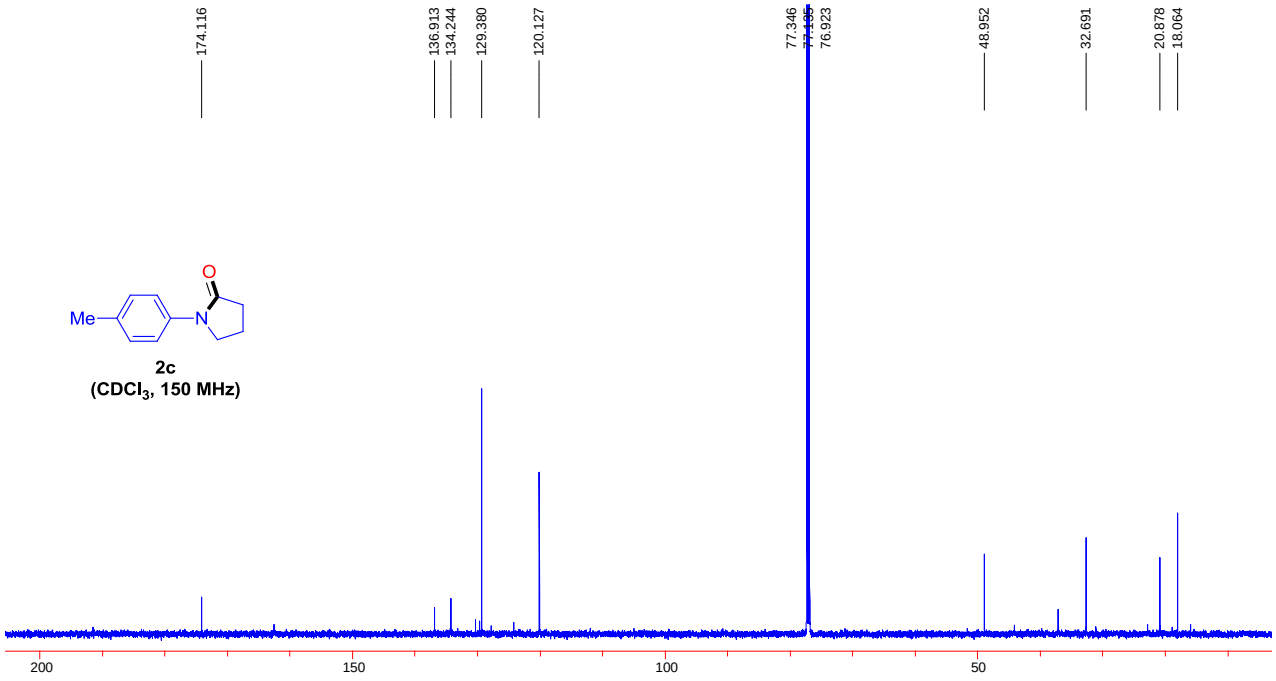

7.620
7.599
7.391
7.372
7.352
7.263
7.166
7.148
7.129
3.892
3.874
3.857
2.640
2.620
2.600
2.206
2.187
2.168
2.149
2.130
1.329
0.000
O
N
2b
(CDCl3, 400 MHz)
2.00
1.95
0.98
2.00
2.05
2.10
10
8
6
4
2
174.254
139.428
128.848
124.539
120.003
77.266
77.054
76.843
48.813
32.771
18.064
O
N
2b
(CDCl3, 150 MHz)
200
150
100
50
0



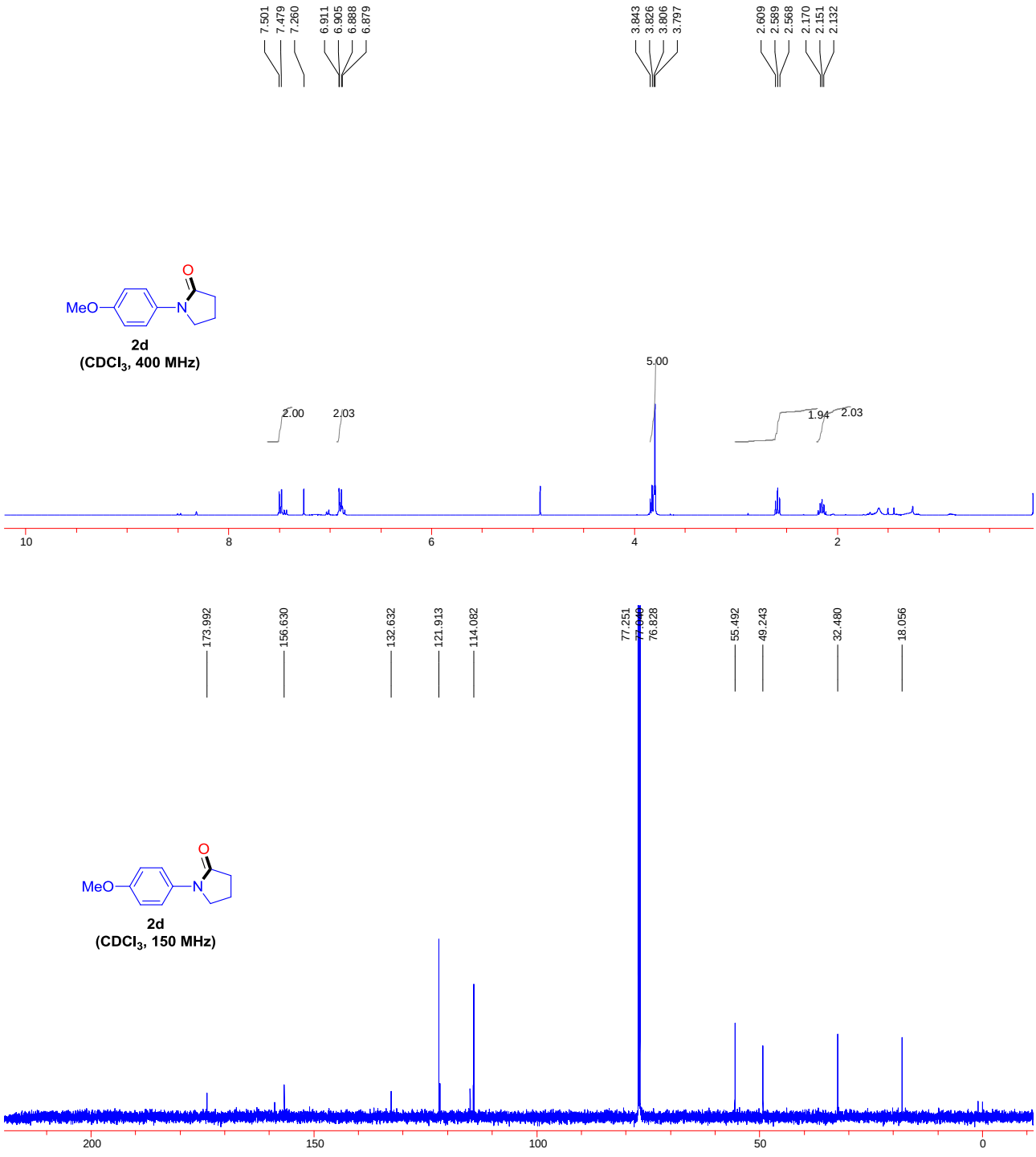


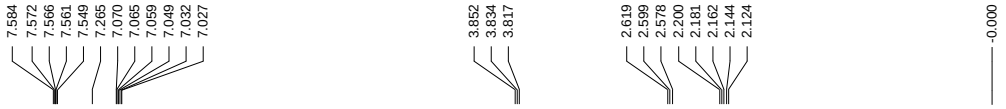
2c
($CDCl_3$, 400 MHz)

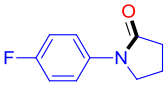




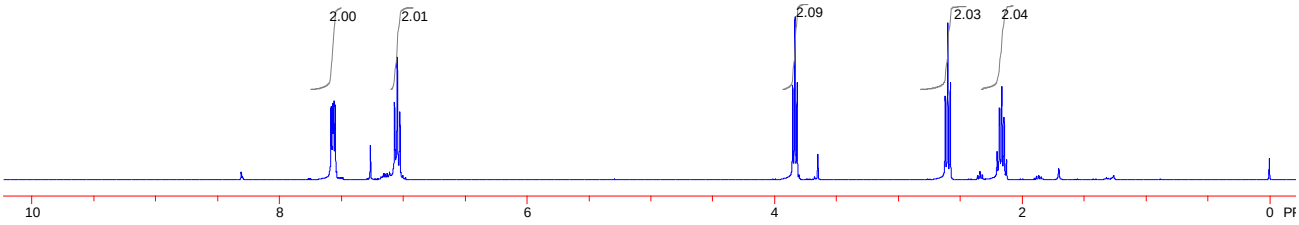
2c
($CDCl_3$, 150 MHz)

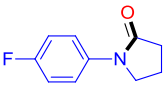

7.501
7.479
7.260
6.911
6.905
6.888
6.879
3.843
3.826
3.806
3.797
2.609
2.589
2.568
2.170
2.151
2.132
MeO
N
O
2d
(CDCl3, 400 MHz)
5.00
2.00
2.03
1.94
2.03
10
8
6
4
2
173.992
156.630
132.632
121.913
114.082
77.251
77.040
76.828
55.492
49.243
32.480
18.056
MeO
N
O
2d
(CDCl3, 150 MHz)
200
150
100
50
0



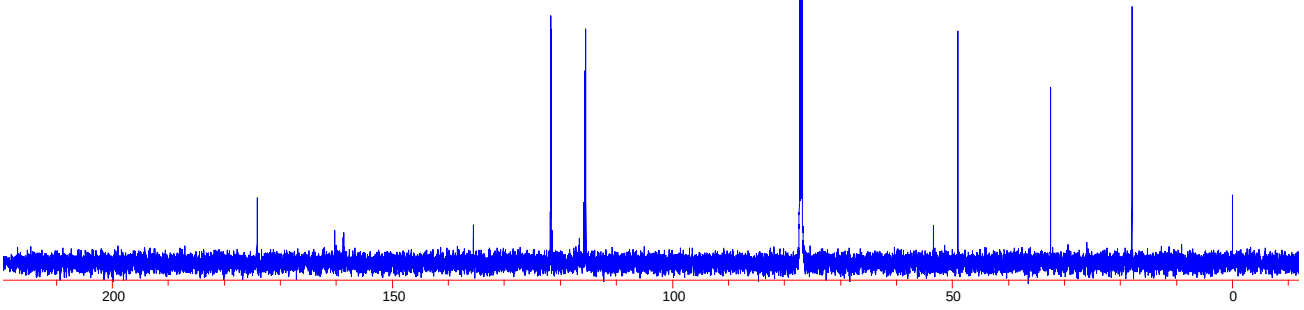


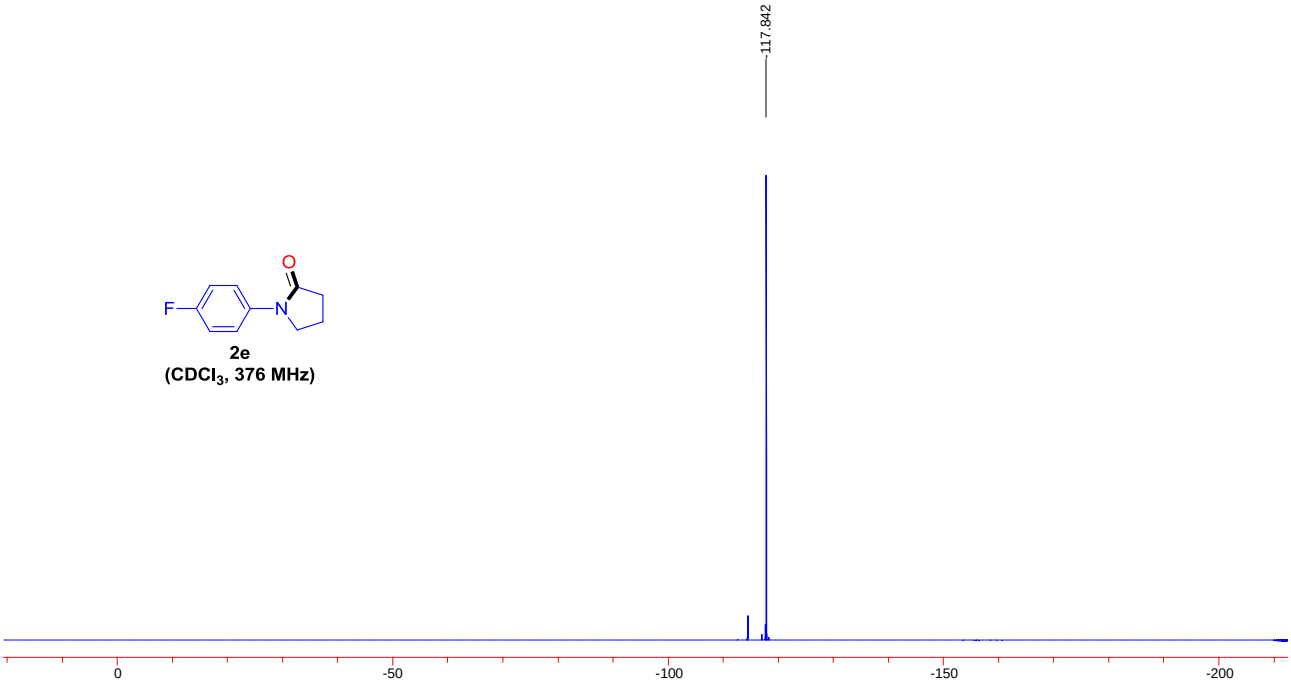
2e
($CDCl_3$, 400 MHz)





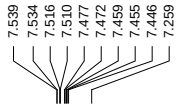
2e
($CDCl_3$, 150 MHz)

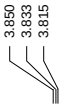


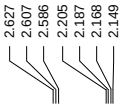


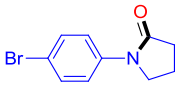
2e

($CDCl_3$, 376 MHz)

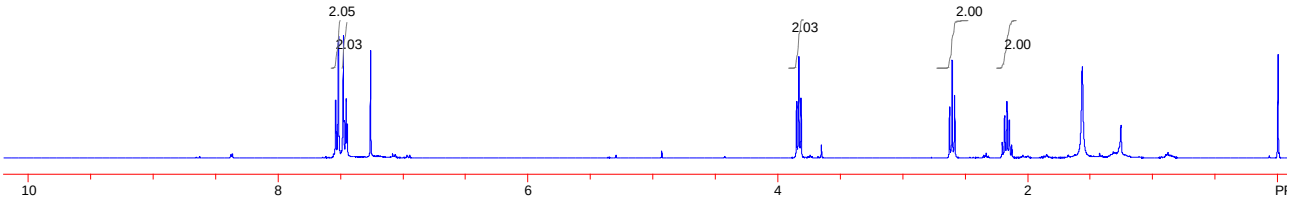


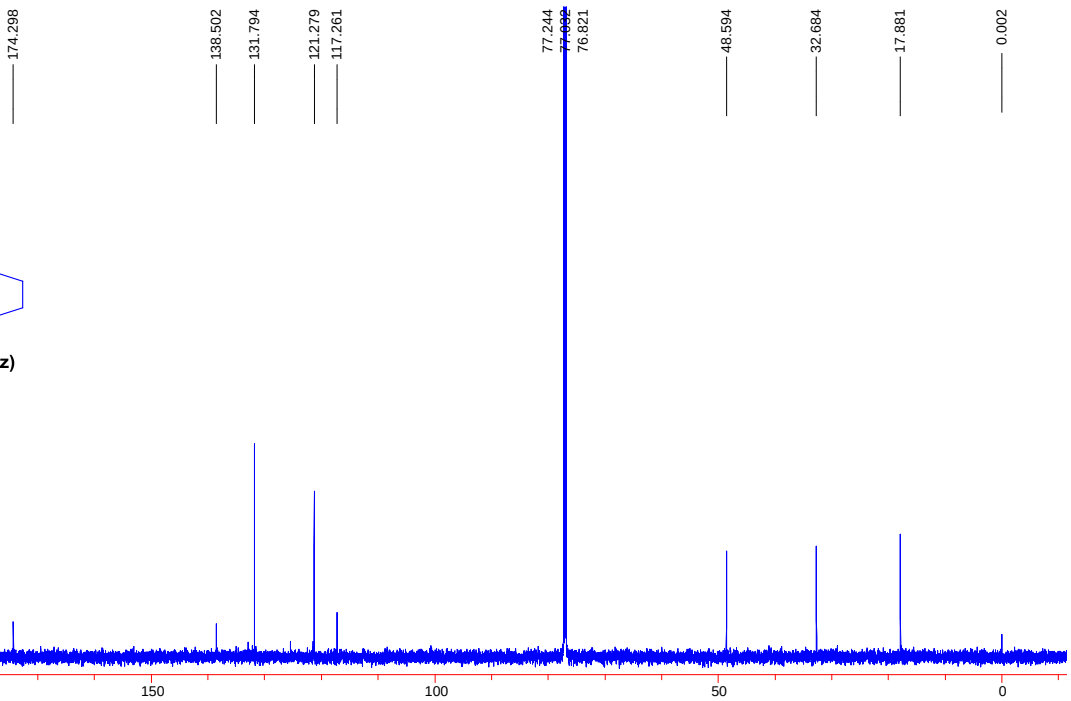


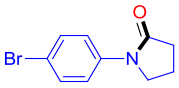




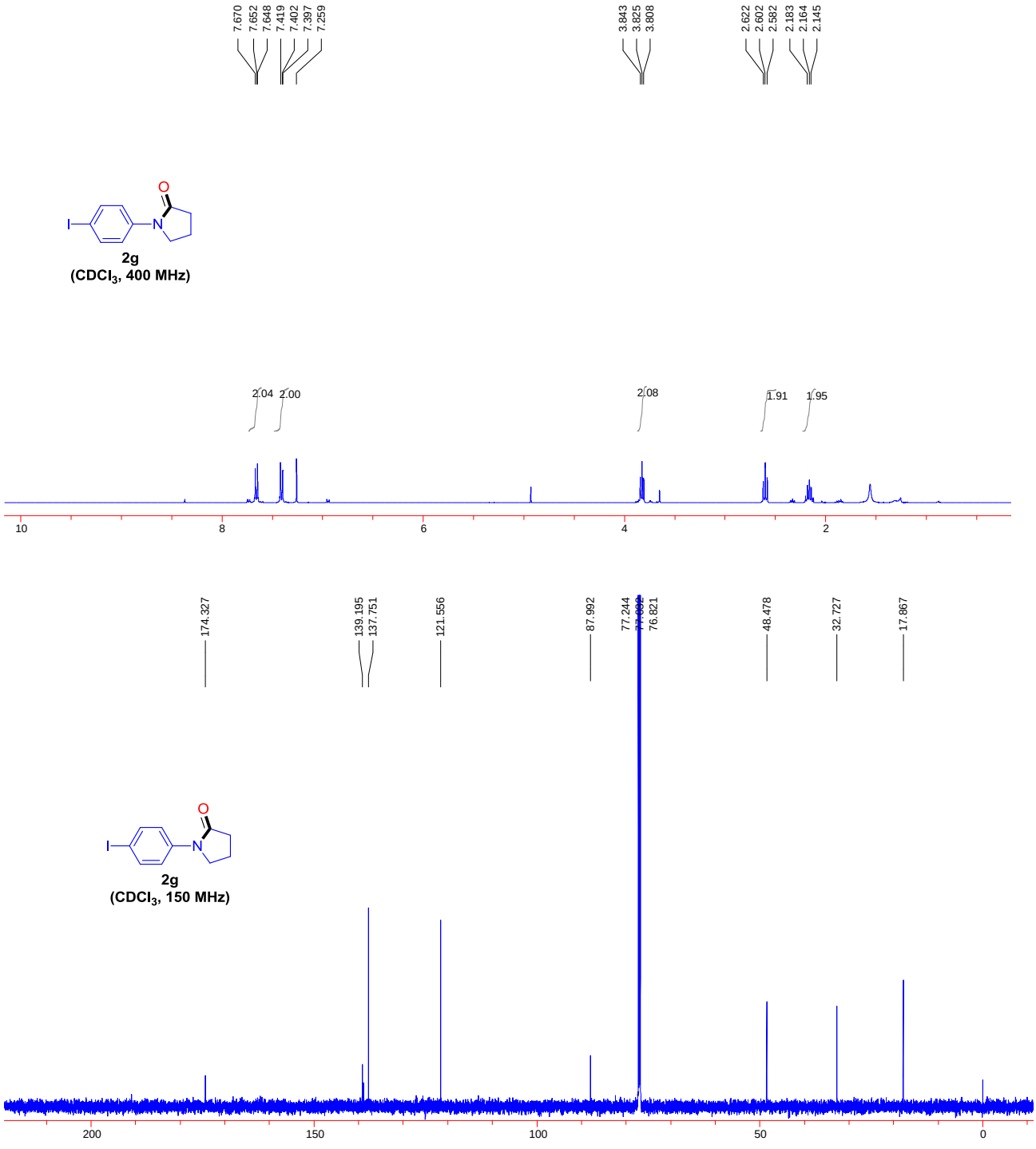
2f
($CDCl_3$, 400 MHz)

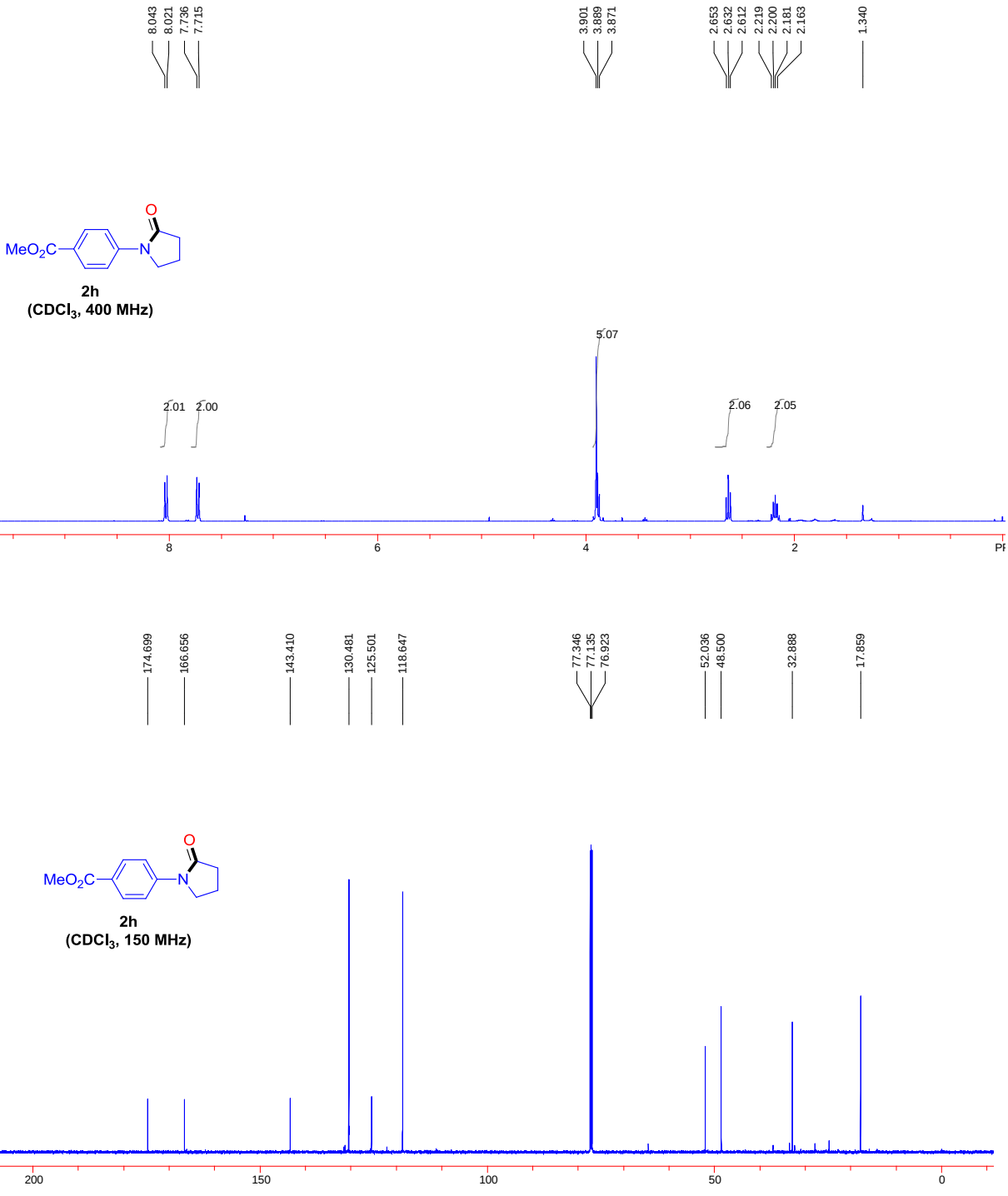


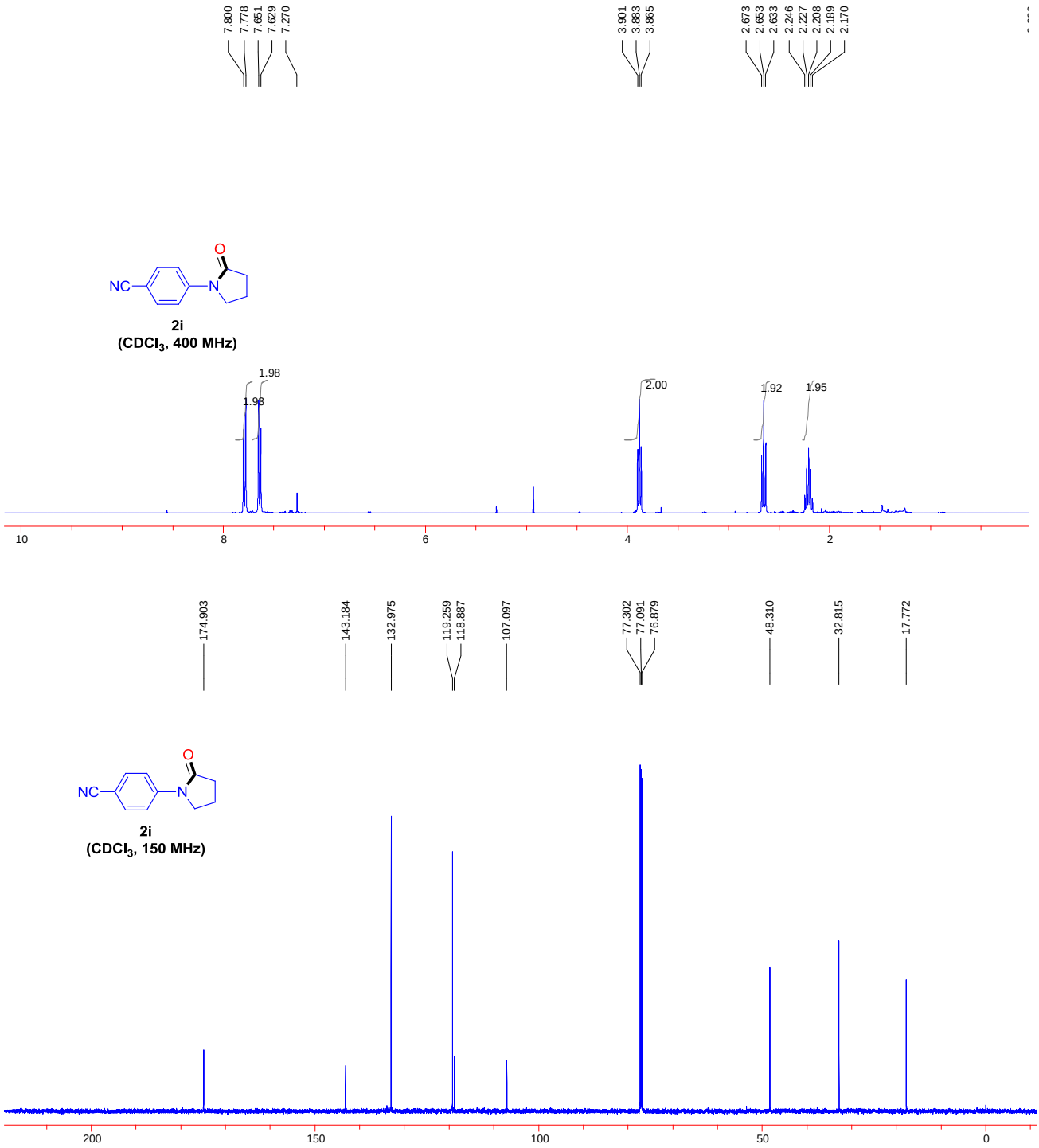


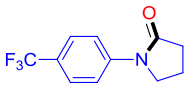


2f
($CDCl_3$, 150 MHz)

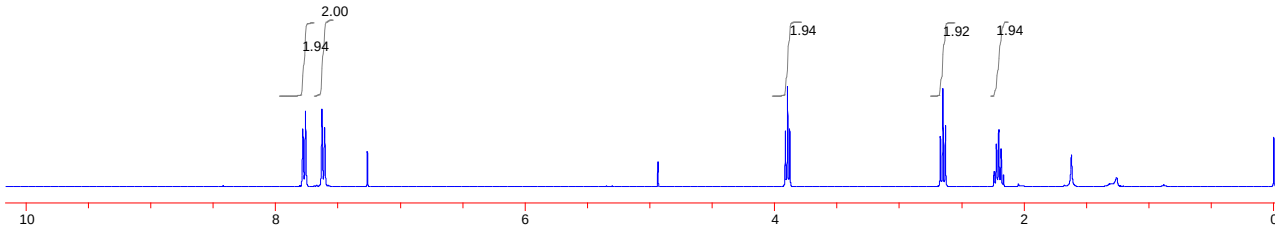

7.670
7.652
7.648
7.419
7.402
7.397
7.259
3.843
3.825
3.808
2.622
2.602
2.582
2.183
2.164
2.145
2g
(CDCl3, 400 MHz)
2.04
2.00
2.08
1.91
1.95
10
8
6
4
2
174.327
139.195
137.751
121.556
87.992
77.244
76.821
48.478
32.727
17.867
2g
(CDCl3, 150 MHz)
200
150
100
50
0

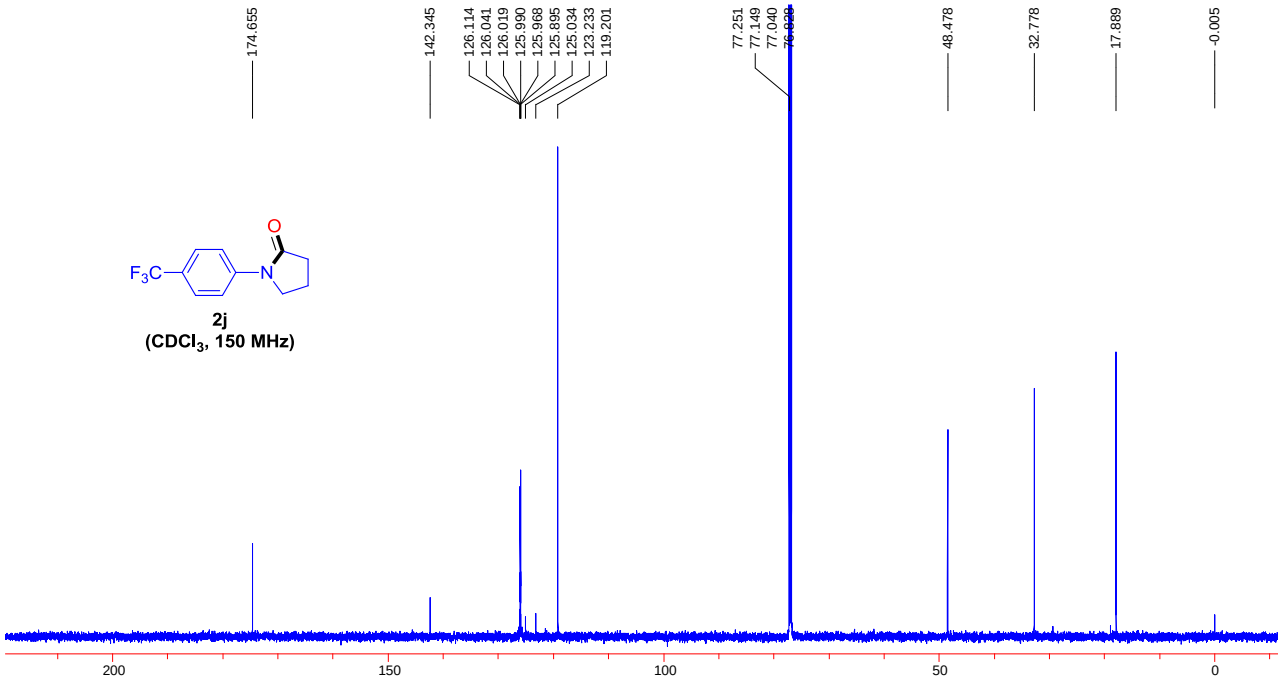

8.043
8.021
7.736
7.715
3.901
3.889
3.871
2.653
2.632
2.612
2.219
2.200
2.181
2.163
1.340
O
MeO2C
N
2h
(CDCl3, 400 MHz)
5.07
2.01
2.00
2.06
2.05
10
8
6
4
2
Pr
174.699
166.656
143.410
130.481
125.501
118.647
77.346
77.135
76.923
52.036
48.500
32.888
17.859
O
MeO2C
N
2h
(CDCl3, 150 MHz)
200
150
100
50
0


7.800
7.778
7.651
7.629
7.270
3.901
3.883
3.865
2.673
2.653
2.633
2.246
2.227
2.208
2.189
2.170
NC
O
N
2i
(CDCl3, 400 MHz)
1.98
1.98
2.00
1.92
1.95
10
8
6
4
2
174.903
143.184
132.975
119.259
118.887
107.097
77.302
77.091
76.879
48.310
32.815
17.772
NC
O
N
2i
(CDCl3, 150 MHz)
200
150
100
50
0

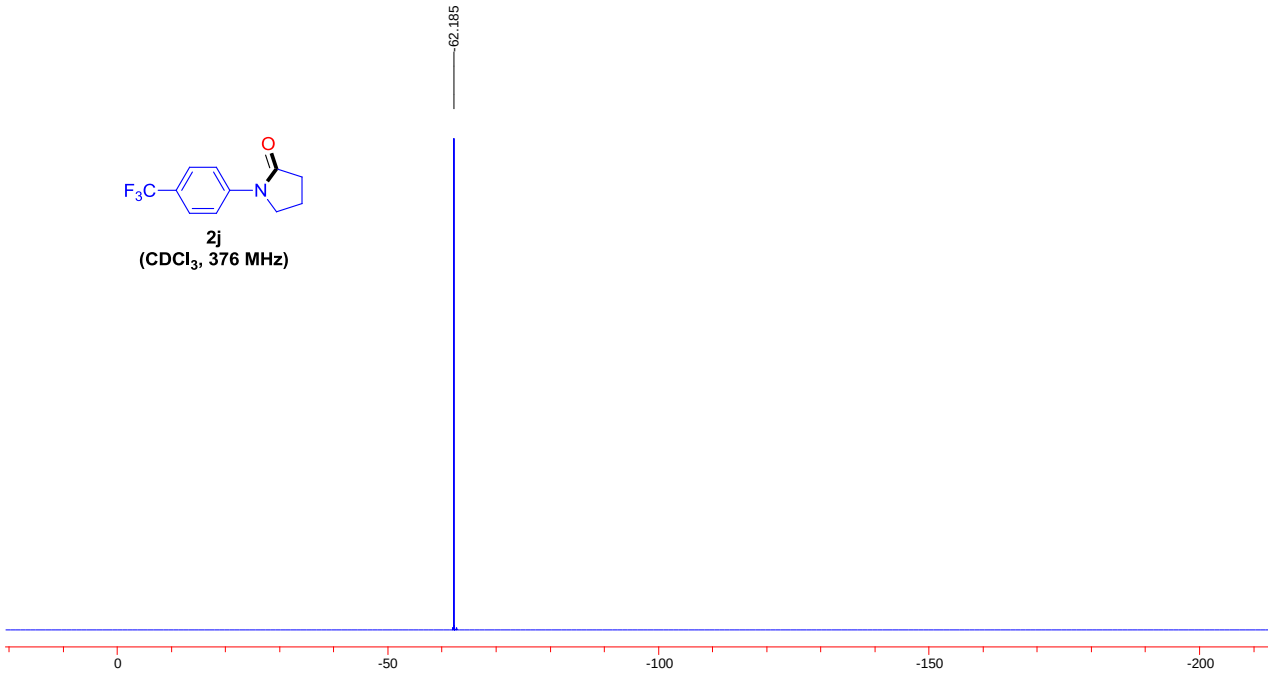


2j
($CDCl_3$, 400 MHz)

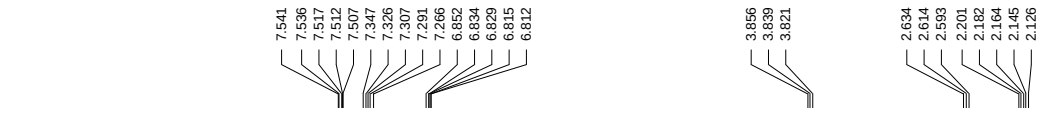


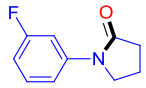


2j
($CDCl_3$, 150 MHz)

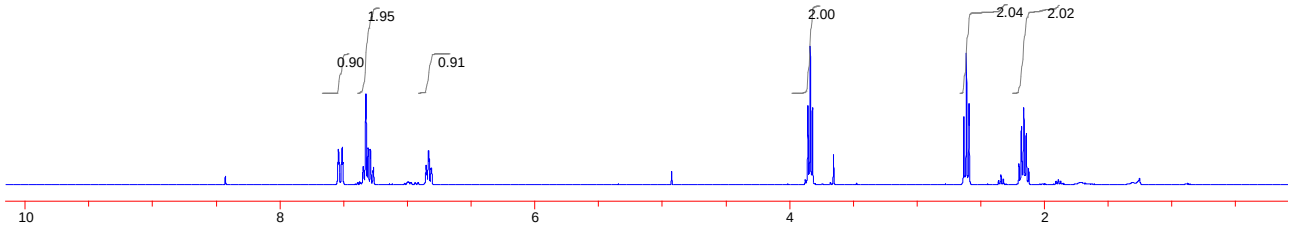


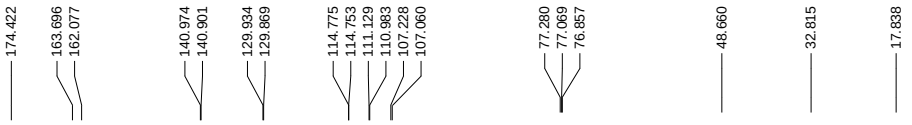
2j
($CDCl_3$, 376 MHz)

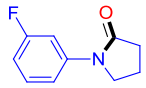




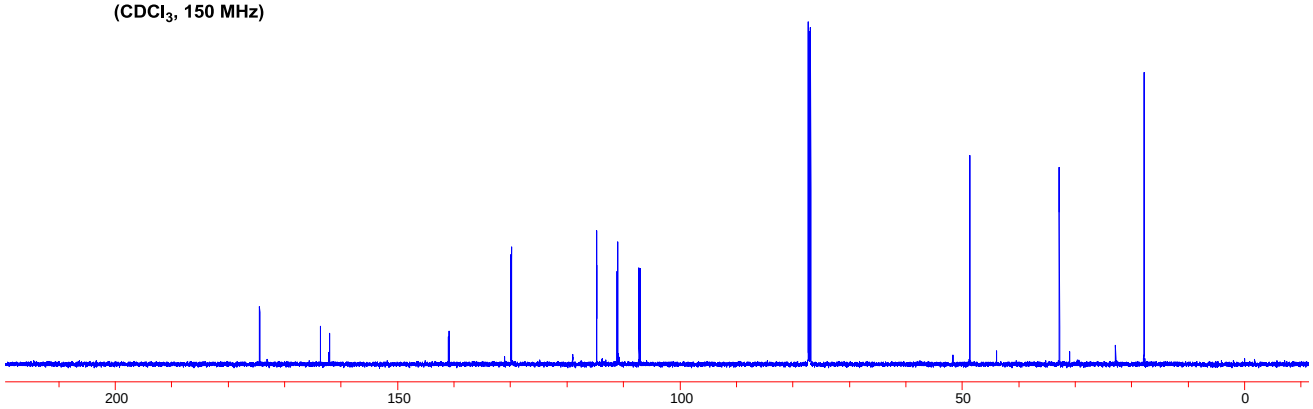
2k
($CDCl_3$, 400 MHz)

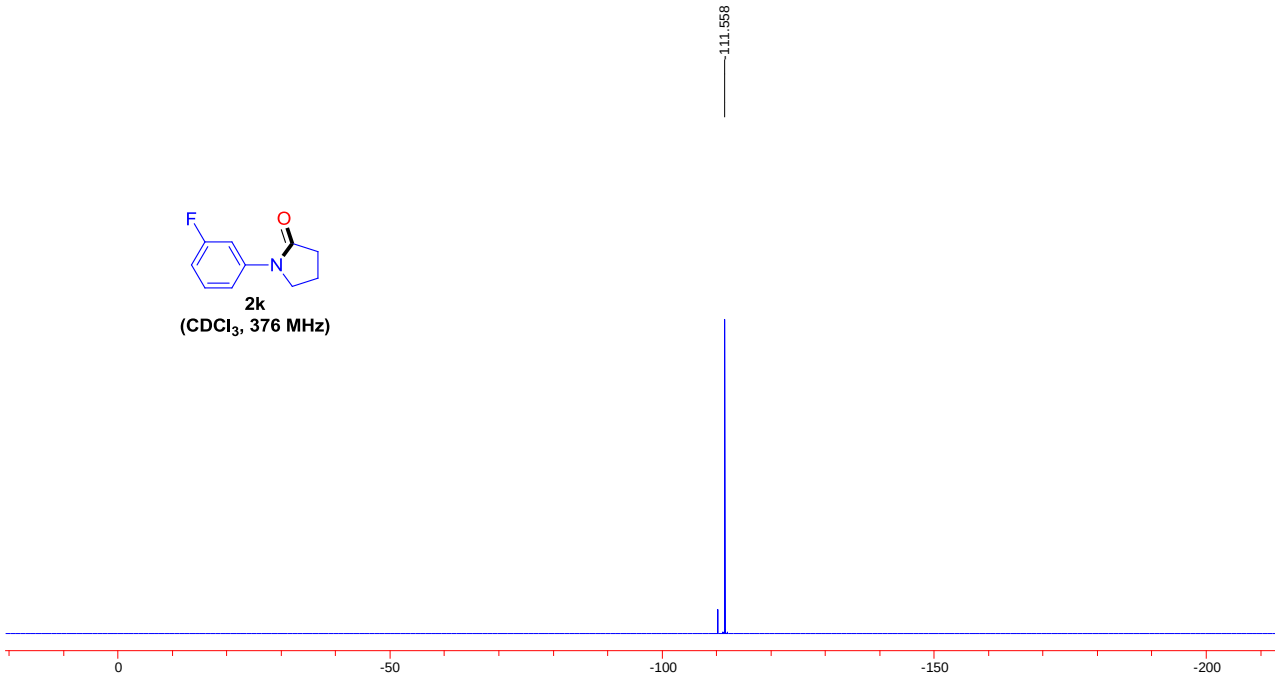




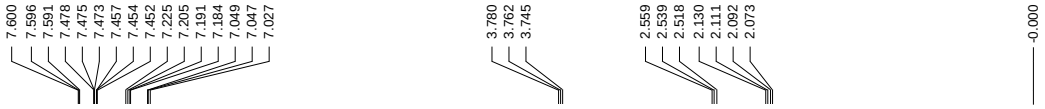


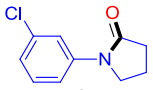
2k
($CDCl_3$, 150 MHz)



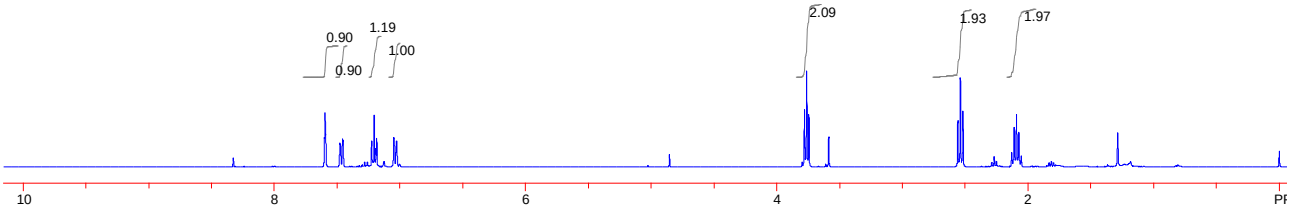


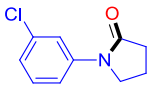
2k
($CDCl_3$, 376 MHz)



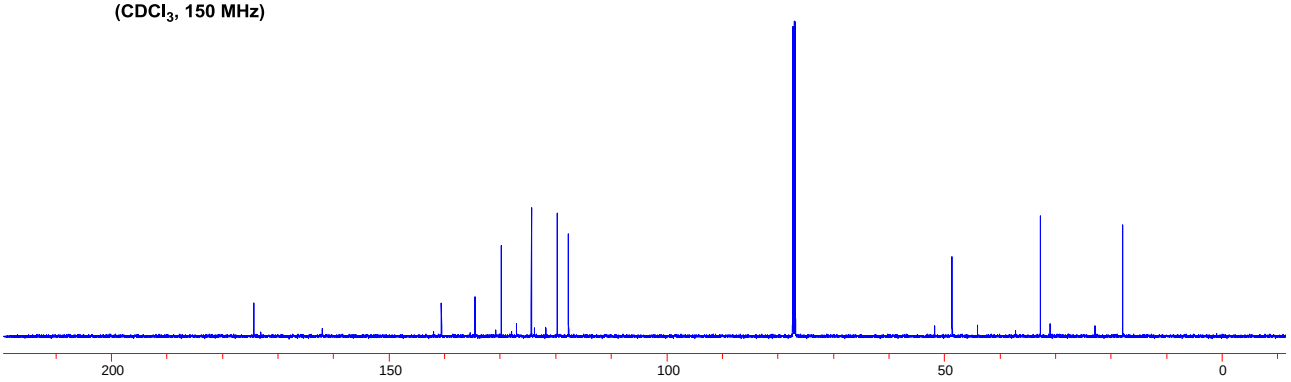


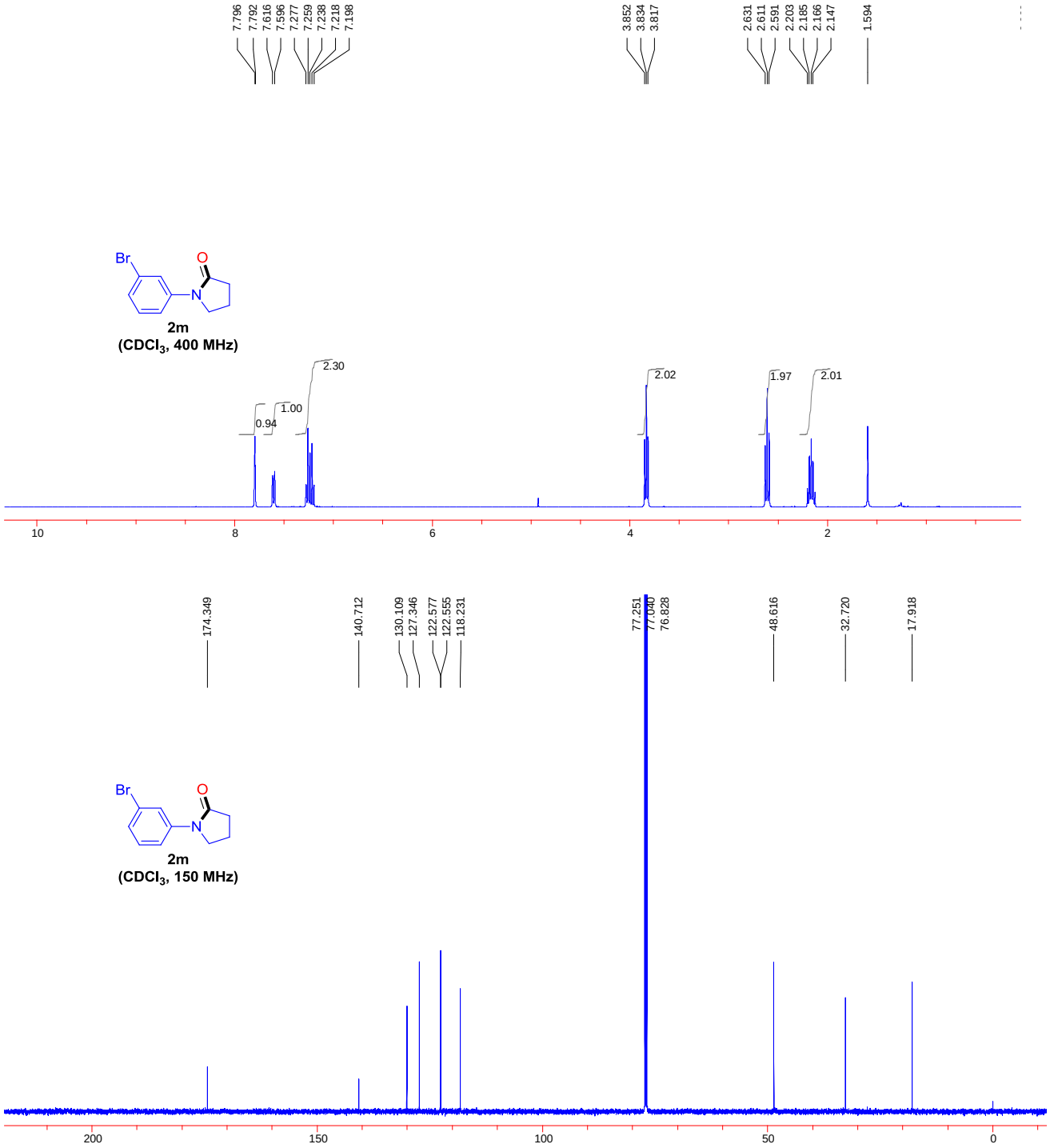
2l
($CDCl_3$, 400 MHz)

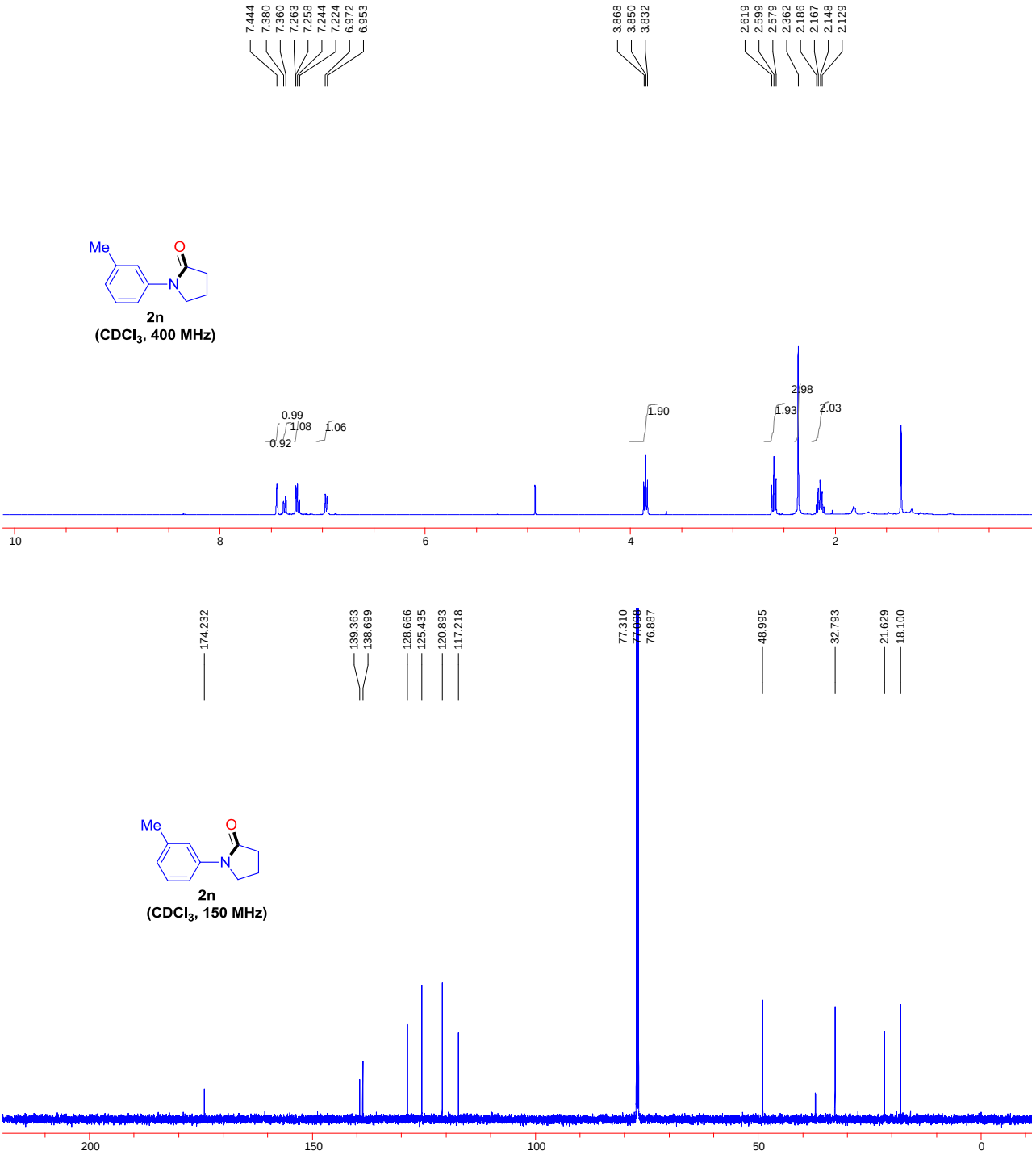


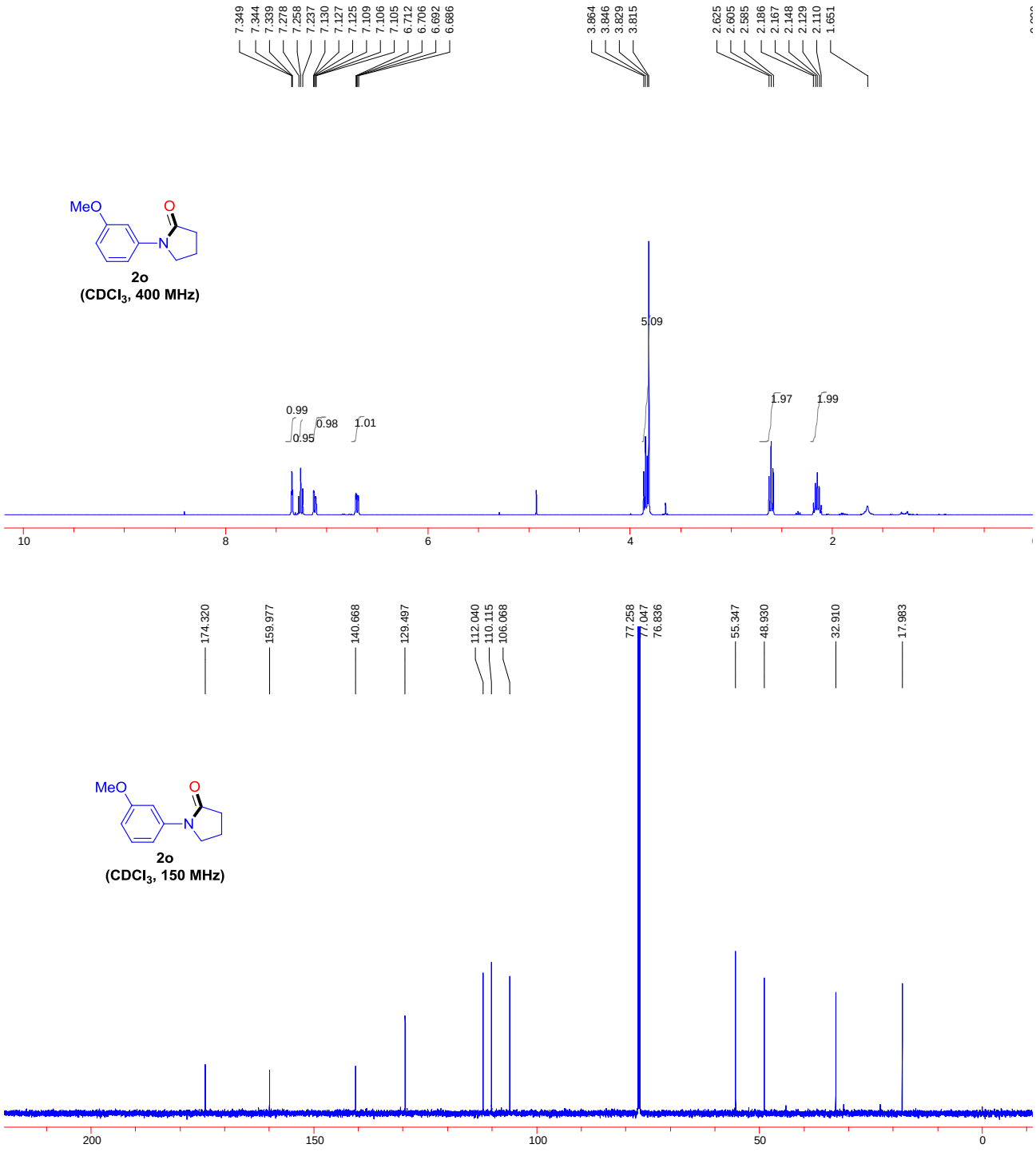


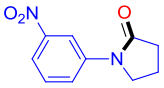
2l
($CDCl_3$, 150 MHz)



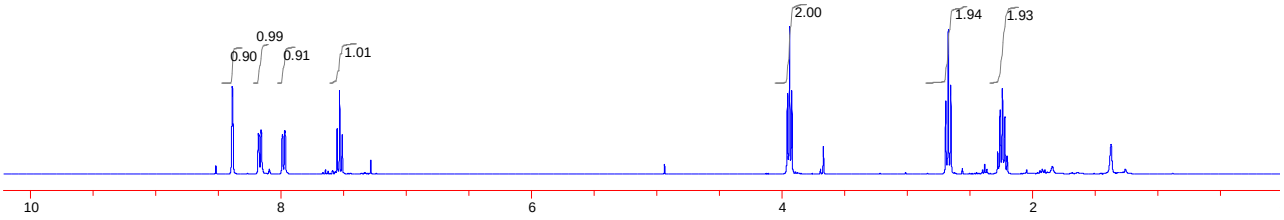

7.796
7.792
7.616
7.596
7.277
7.259
7.238
7.218
7.198
3.852
3.834
3.817
2.631
2.611
2.591
2.203
2.185
2.166
2.147
1.594
Br
O
N
2m
(CDCl3, 400 MHz)
0.94
1.00
2.30
2.02
1.97
2.01
10
8
6
4
2
174.349
140.712
130.109
127.346
122.577
122.555
118.231
77.251
77.040
76.828
48.616
32.720
17.918
Br
O
N
2m
(CDCl3, 150 MHz)
200
150
100
50
0

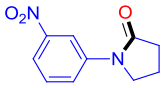

7.444
7.380
7.360
7.263
7.258
7.244
7.224
6.972
6.953
3.868
3.850
3.832
2.619
2.599
2.579
2.362
2.186
2.167
2.148
2.129
Me
O
N
2n
(CDCl3, 400 MHz)
0.99
1.08
1.06
0.92
1.90
2.98
1.93
2.03
10
8
6
4
2
174.232
139.363
138.699
128.666
125.435
120.893
117.218
77.310
77.000
76.687
48.995
32.793
21.629
18.100
Me
O
N
2n
(CDCl3, 150 MHz)
200
150
100
50
0


7.349
7.344
7.339
7.278
7.258
7.237
7.130
7.127
7.125
7.109
7.106
7.105
6.712
6.706
6.692
6.686
3.864
3.846
3.829
3.815
2.625
2.605
2.585
2.186
2.167
2.148
2.129
2.110
1.651
MeO
O
N
2o
(CDCl3, 400 MHz)
5.09
0.99
0.98
0.95
1.01
1.97
1.99
10
8
6
4
2
174.320
159.977
140.668
129.497
112.040
110.115
106.068
77.258
77.047
76.836
55.347
48.930
32.910
17.983
MeO
O
N
2o
(CDCl3, 150 MHz)
200
150
100
50
0

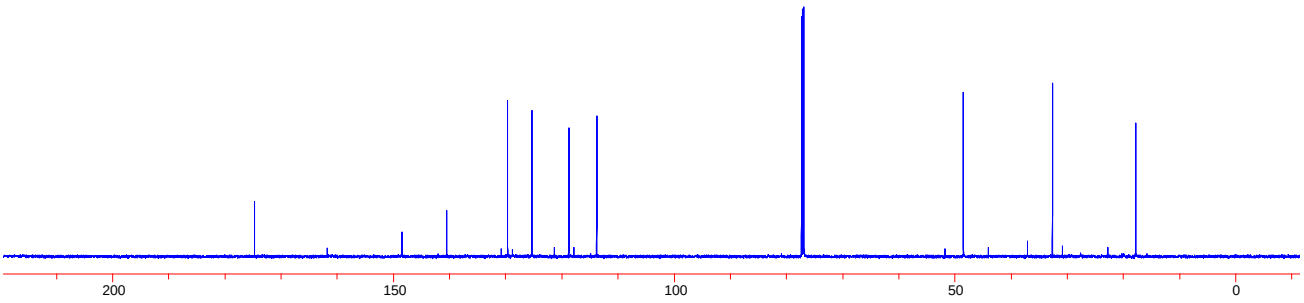


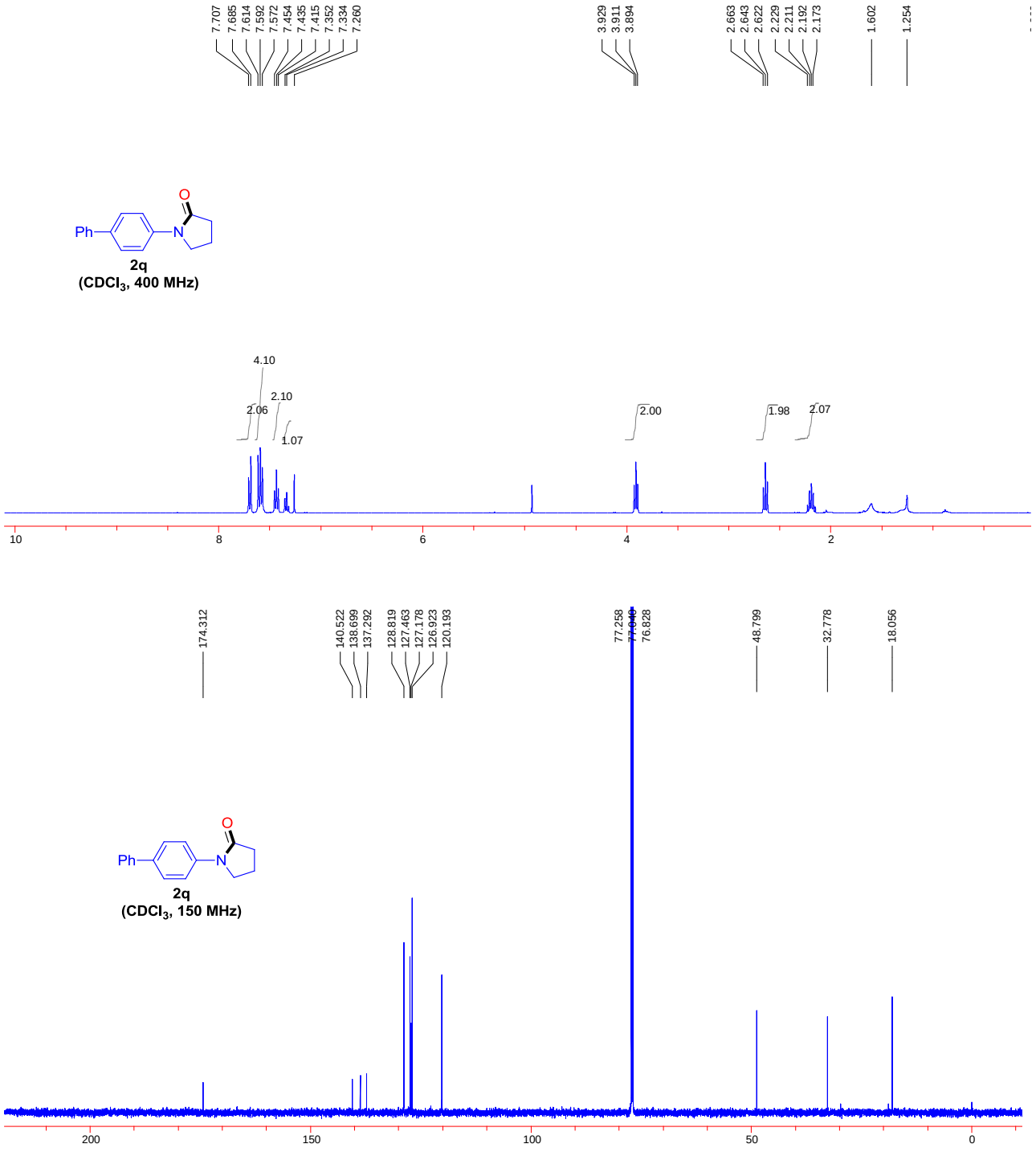
2p
($CDCl_3$, 400 MHz)

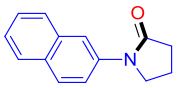




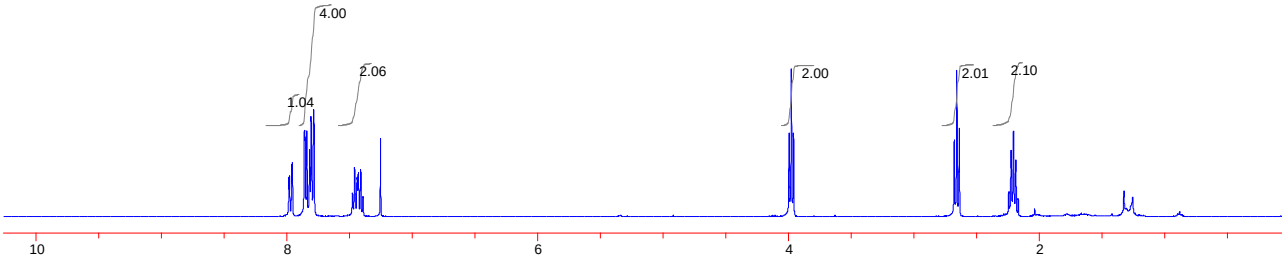
2p
($CDCl_3$, 150 MHz)

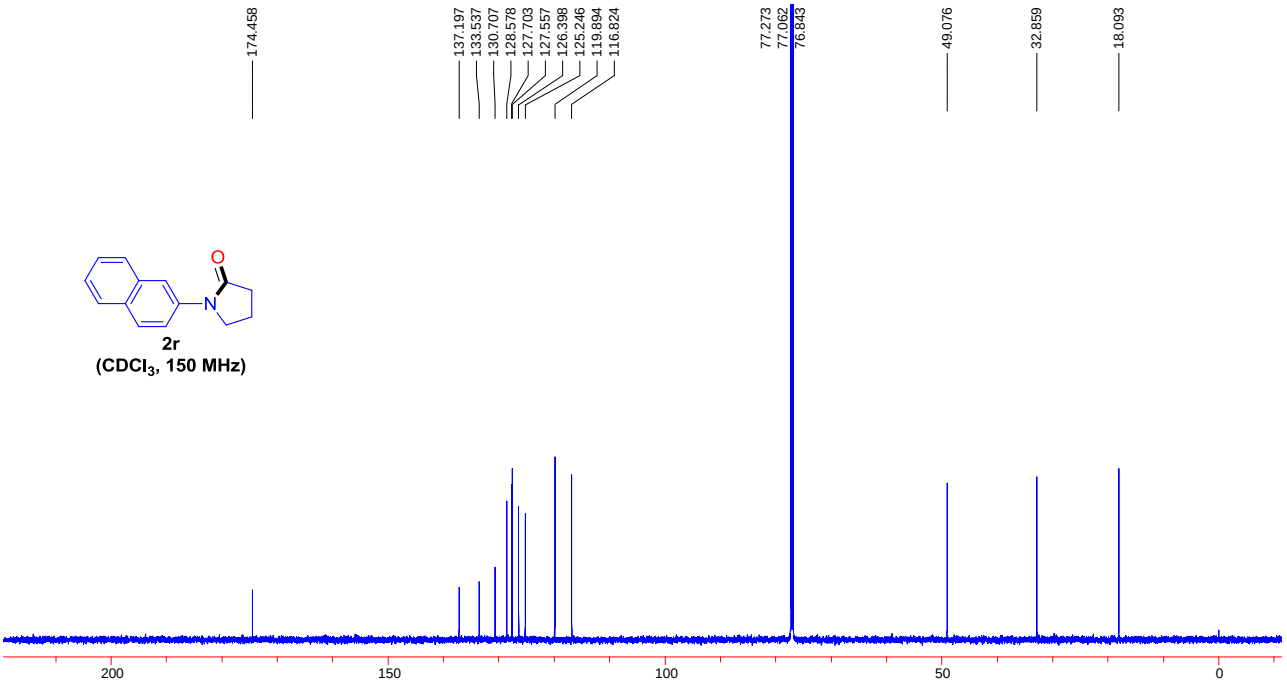



7.707
7.685
7.614
7.592
7.572
7.454
7.435
7.415
7.352
7.334
7.260
3.929
3.911
3.894
2.663
2.643
2.622
2.229
2.211
2.192
2.173
1.602
1.254
Ph
N
O
2q
(CDCl3, 400 MHz)
4.10
2.10
2.06
1.07
2.00
1.98
2.07
10
8
6
4
2
174.312
140.522
138.699
137.292
128.819
127.463
127.178
126.923
120.193
77.258
77.046
76.828
48.799
32.778
18.056
Ph
N
O
2q
(CDCl3, 150 MHz)
200
150
100
50
0

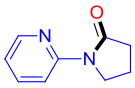


2r
($CDCl_3$, 400 MHz)

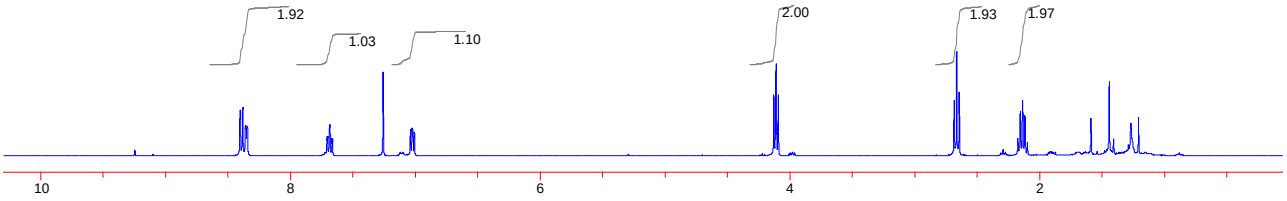


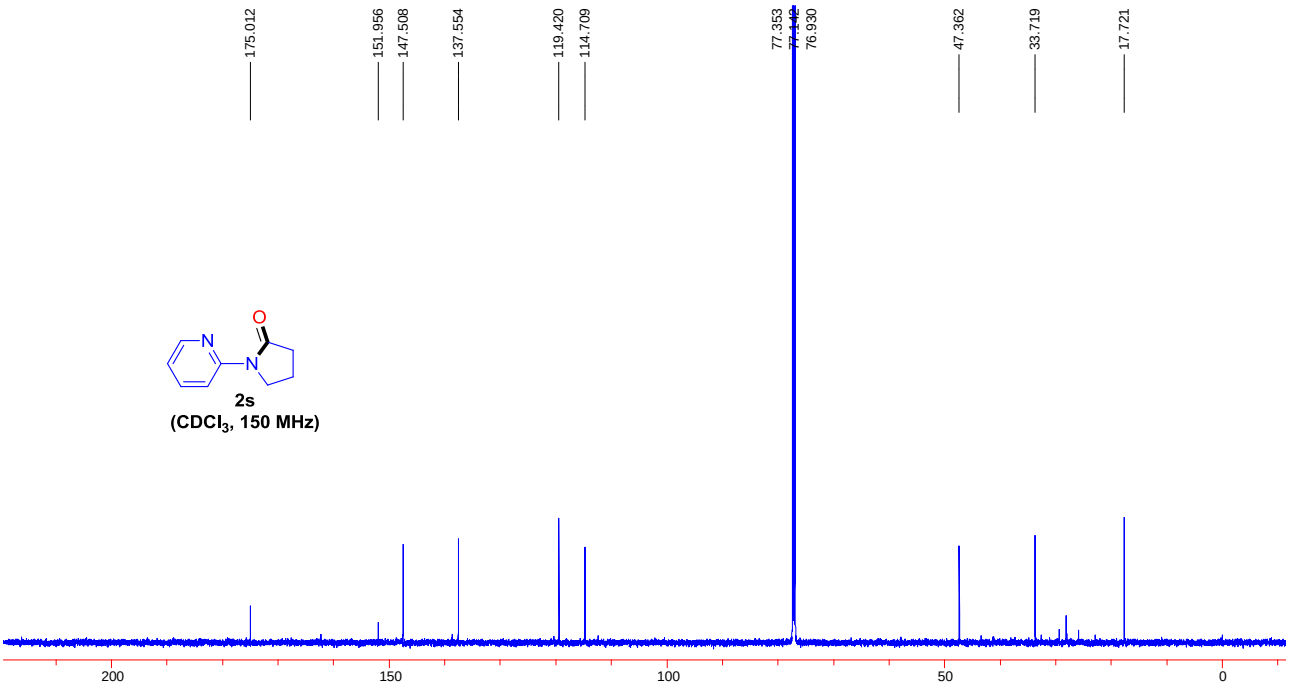


2r
($CDCl_3$, 150 MHz)

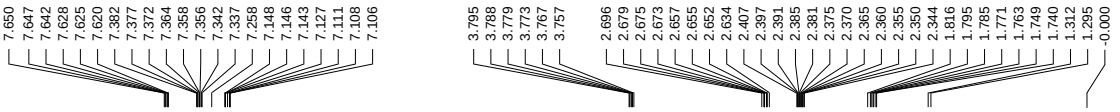


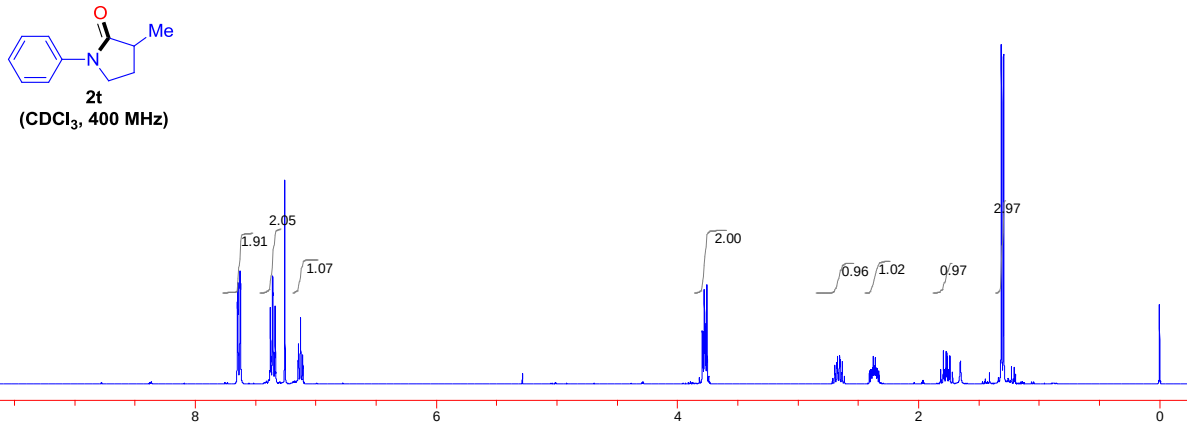
2s
($CDCl_3$, 400 MHz)

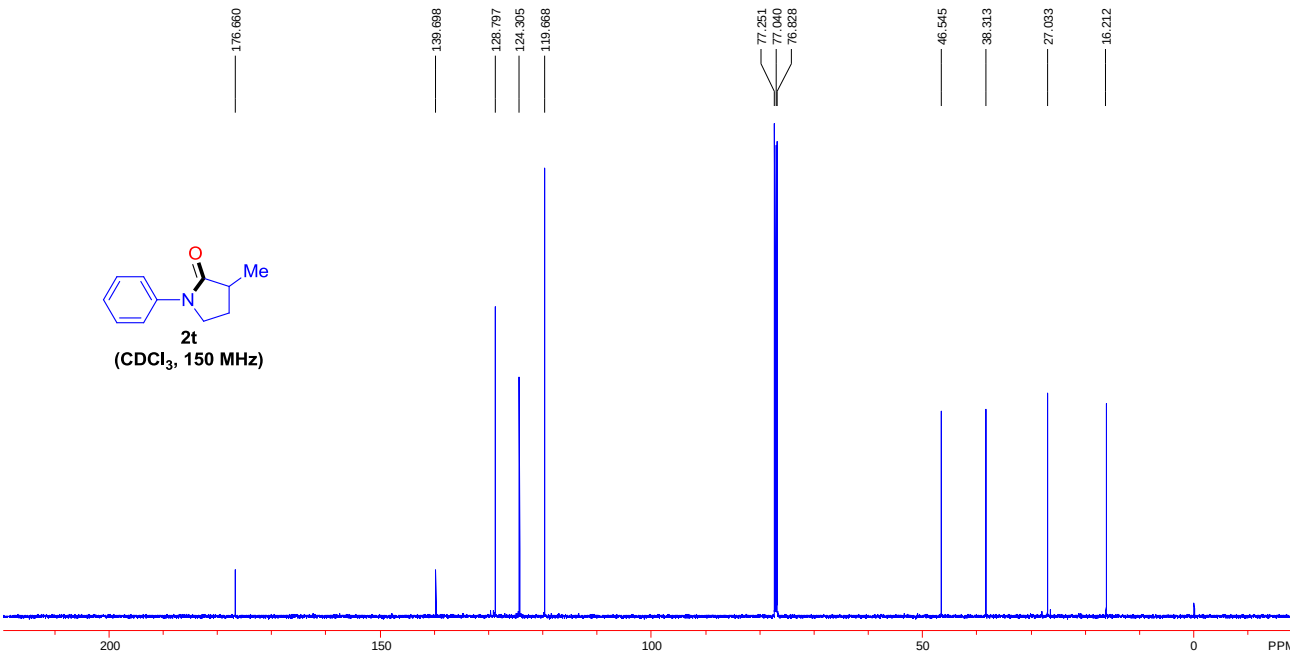


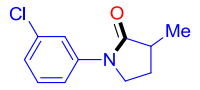


2s
($CDCl_3$, 150 MHz)

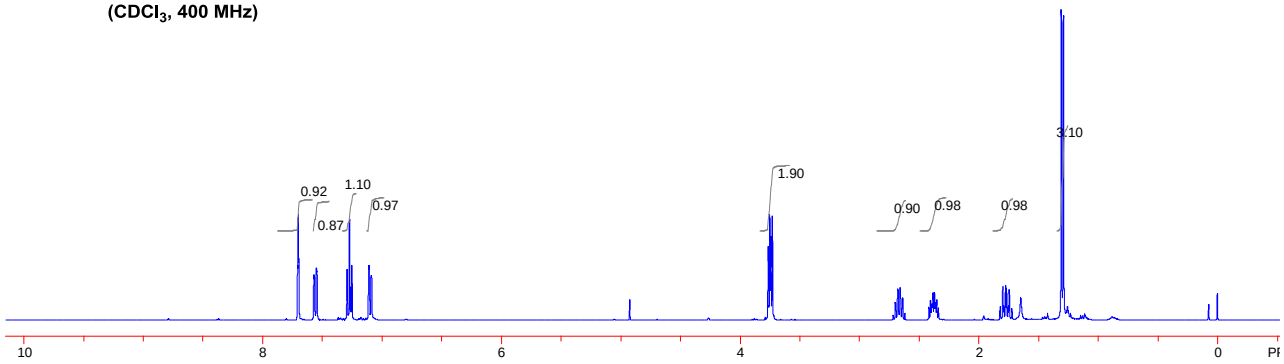

7.650
7.647
7.642
7.628
7.625
7.620
7.382
7.377
7.372
7.364
7.358
7.356
7.342
7.337
7.258
7.148
7.146
7.143
7.127
7.111
7.108
7.106
3.795
3.788
3.779
3.773
3.767
3.757
2.696
2.679
2.675
2.673
2.657
2.655
2.652
2.634
2.407
2.397
2.391
2.385
2.381
2.375
2.370
2.365
2.360
2.355
2.350
2.344
1.816
1.795
1.785
1.771
1.763
1.749
1.740
1.312
1.295
-0.000

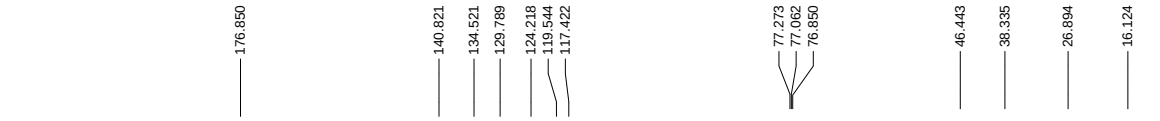

O
Me
N
2t
(CDCl3, 400 MHz)
1.91
2.05
1.07
2.00
0.96
1.02
0.97
2.97
10
8
6
4
2
0

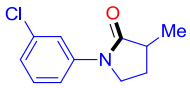

176.660
139.698
128.797
124.305
119.668
77.251
77.040
76.828
46.545
38.313
27.033
16.212
O
Me
N
2t
(CDCl3, 150 MHz)
200
150
100
50
0
PPM



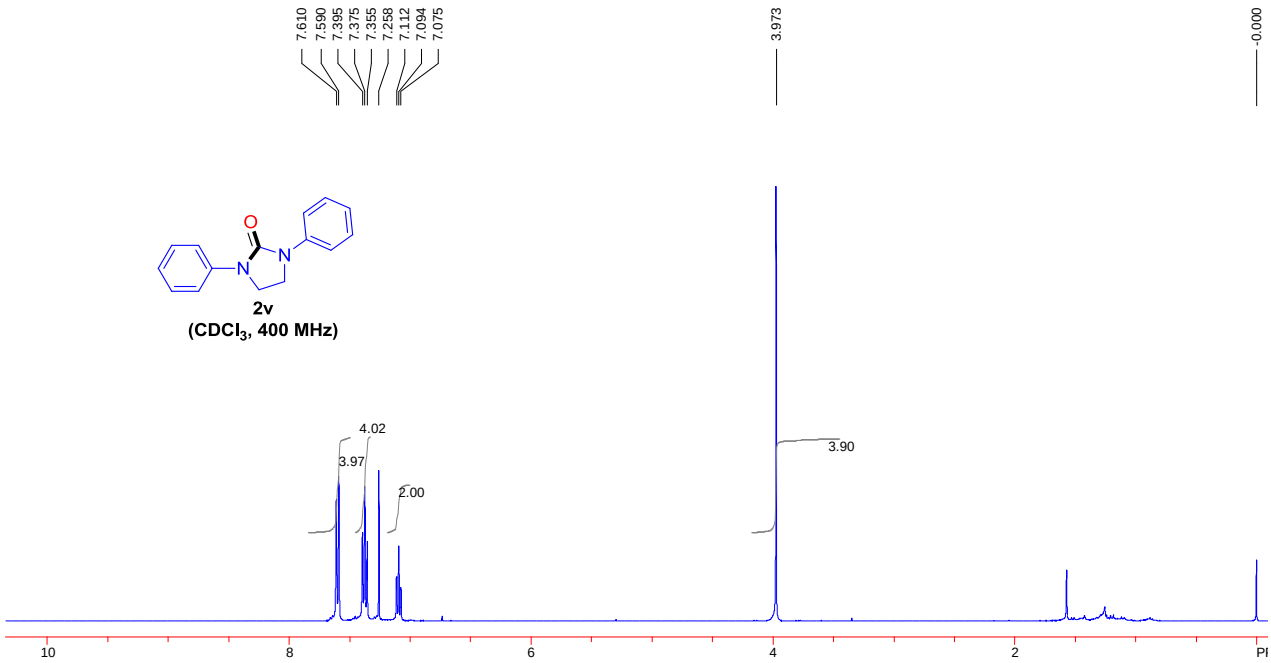
2u
($CDCl_3$, 400 MHz)

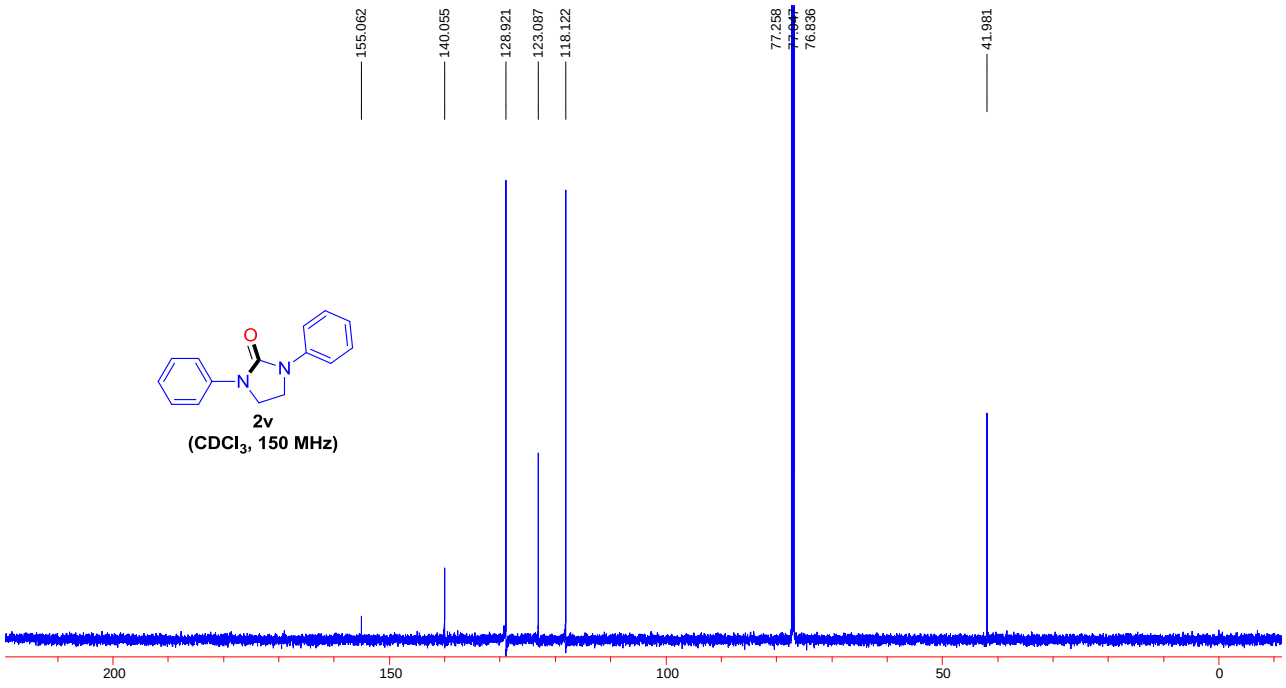




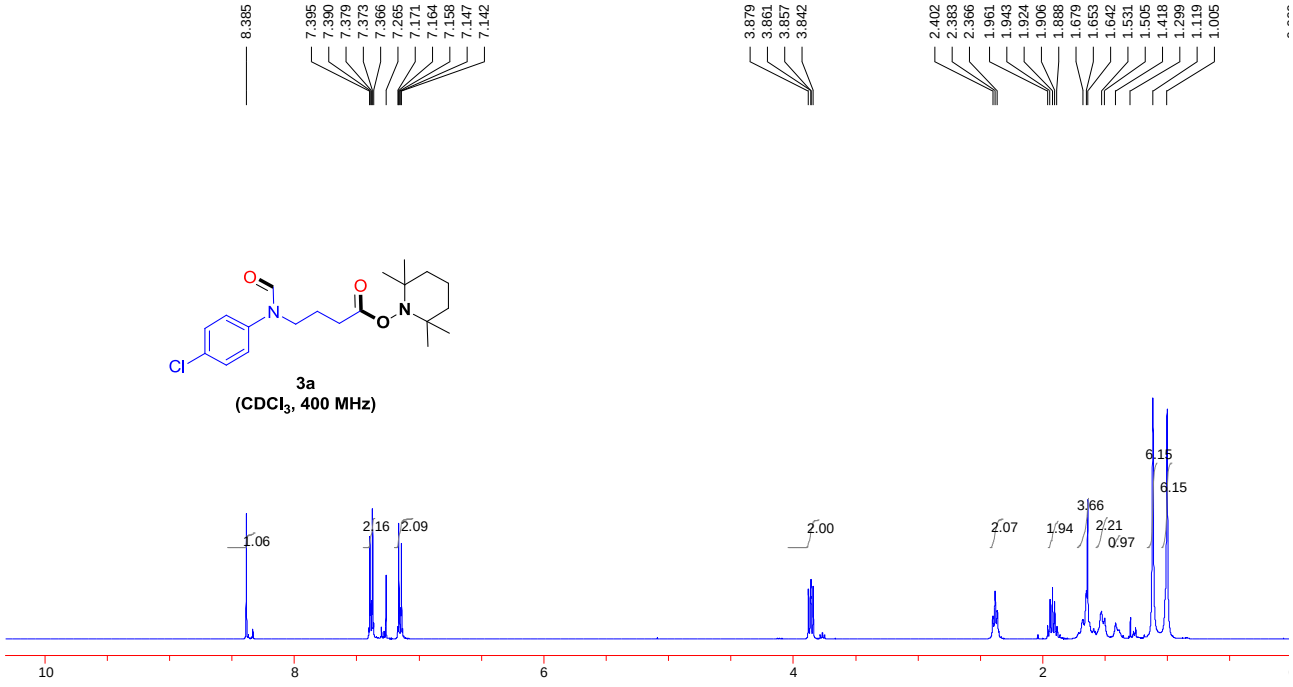


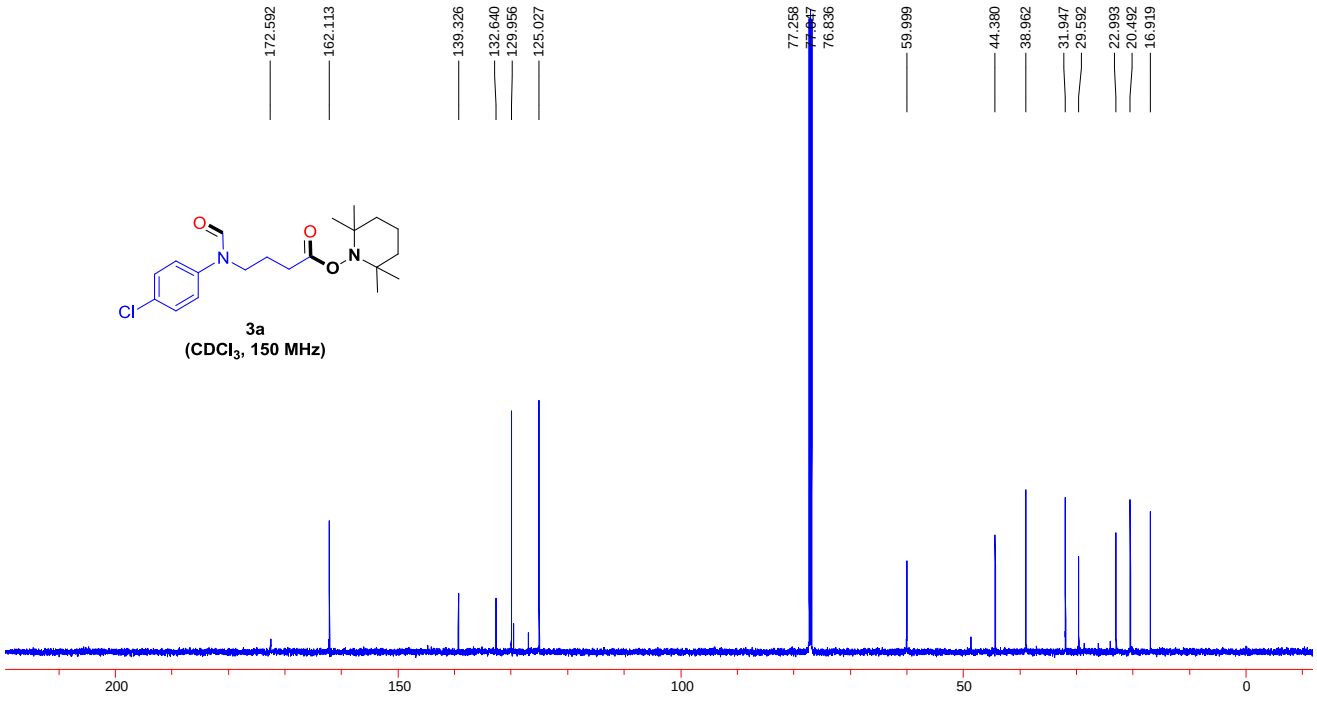
2u
($CDCl_3$, 150 MHz)

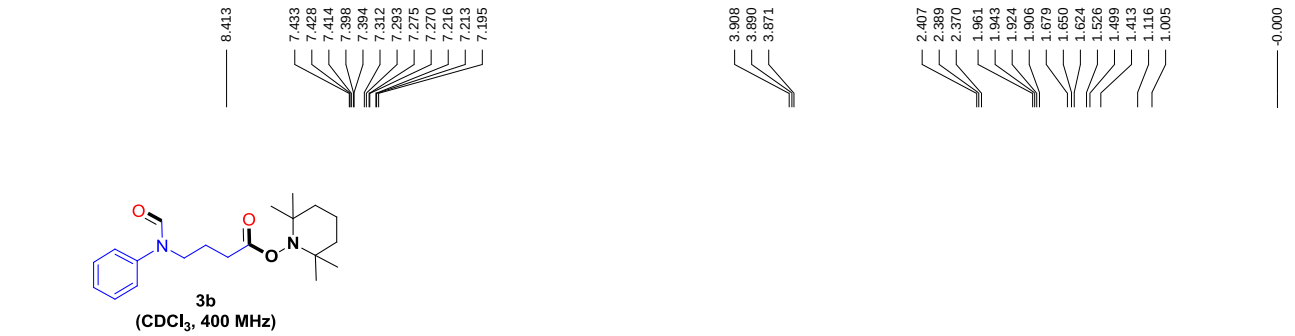

7.610
7.590
7.395
7.375
7.355
7.258
7.112
7.094
7.075
3.973
-0.000
O
N
N
2v
(CDCl3, 400 MHz)
4.02
3.97
2.00
3.90
10
8
6
4
2


155.062
140.055
128.921
123.087
118.122
77.258
77.047
76.836
41.981
O
N
N
2v
(CDCl3, 150 MHz)
200
150
100
50
0

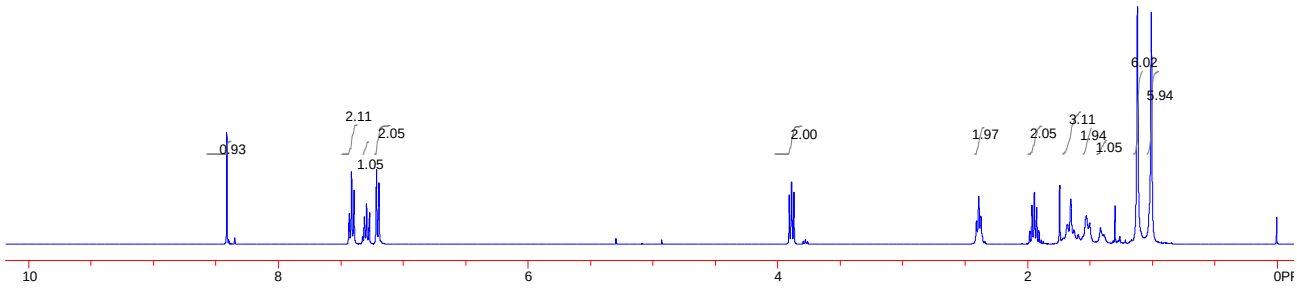
IV. Copies of the NMR spectra of 3a-3p

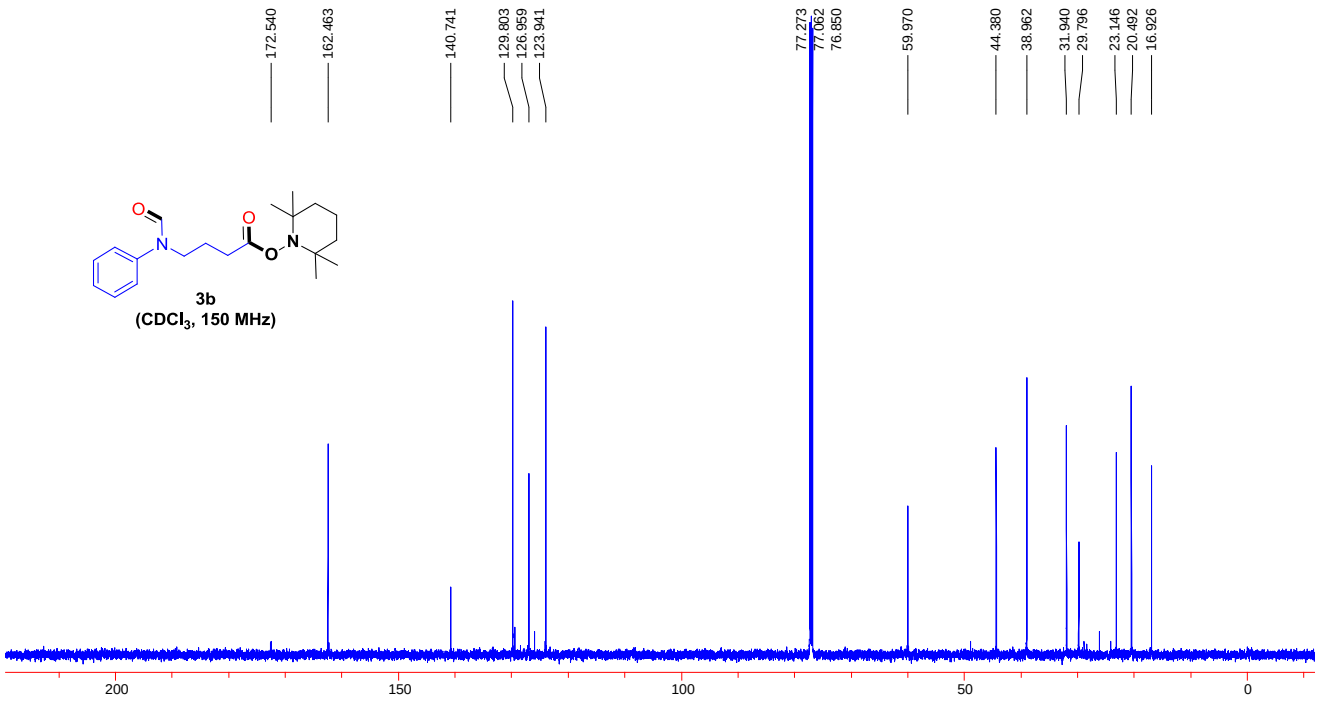




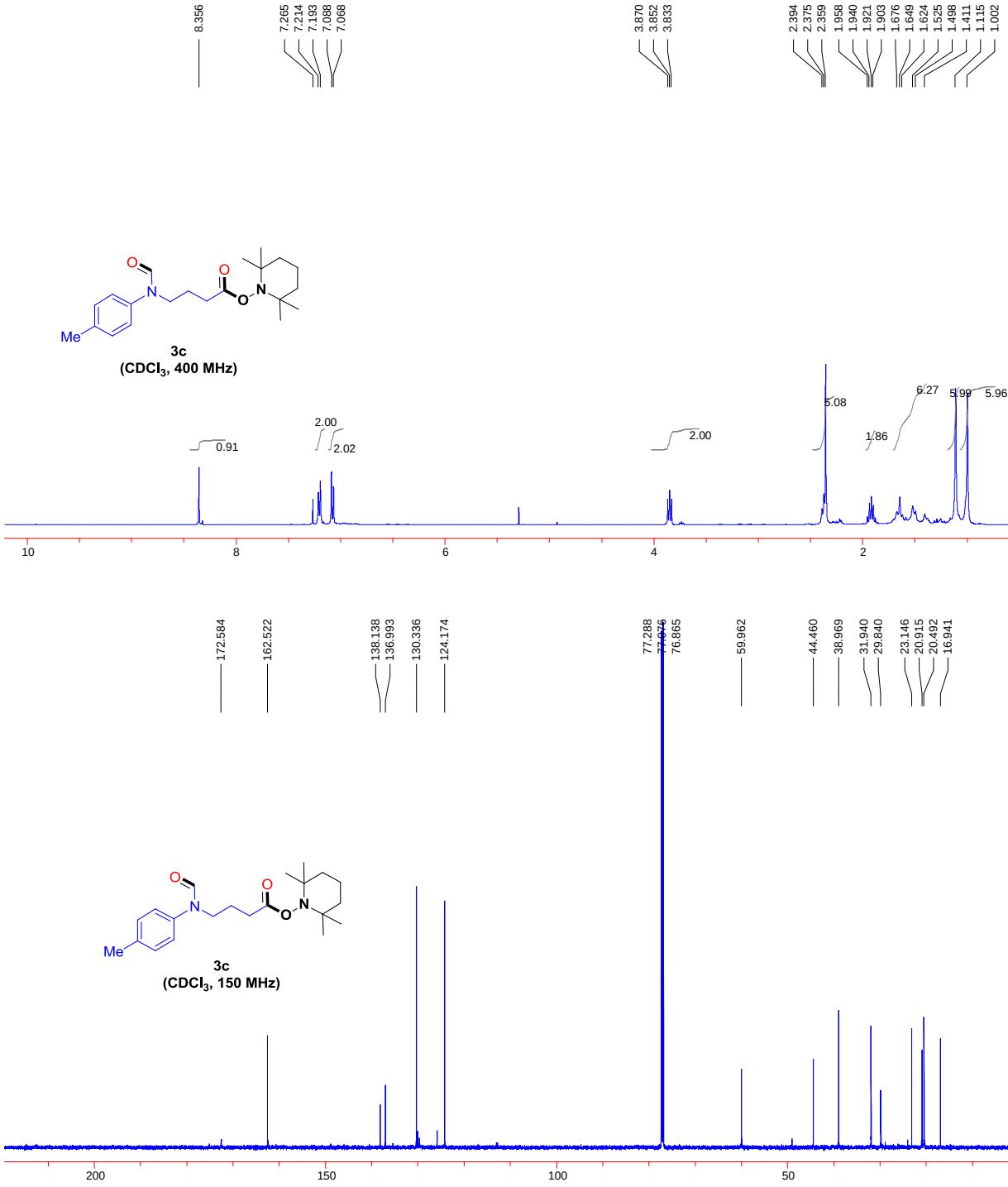


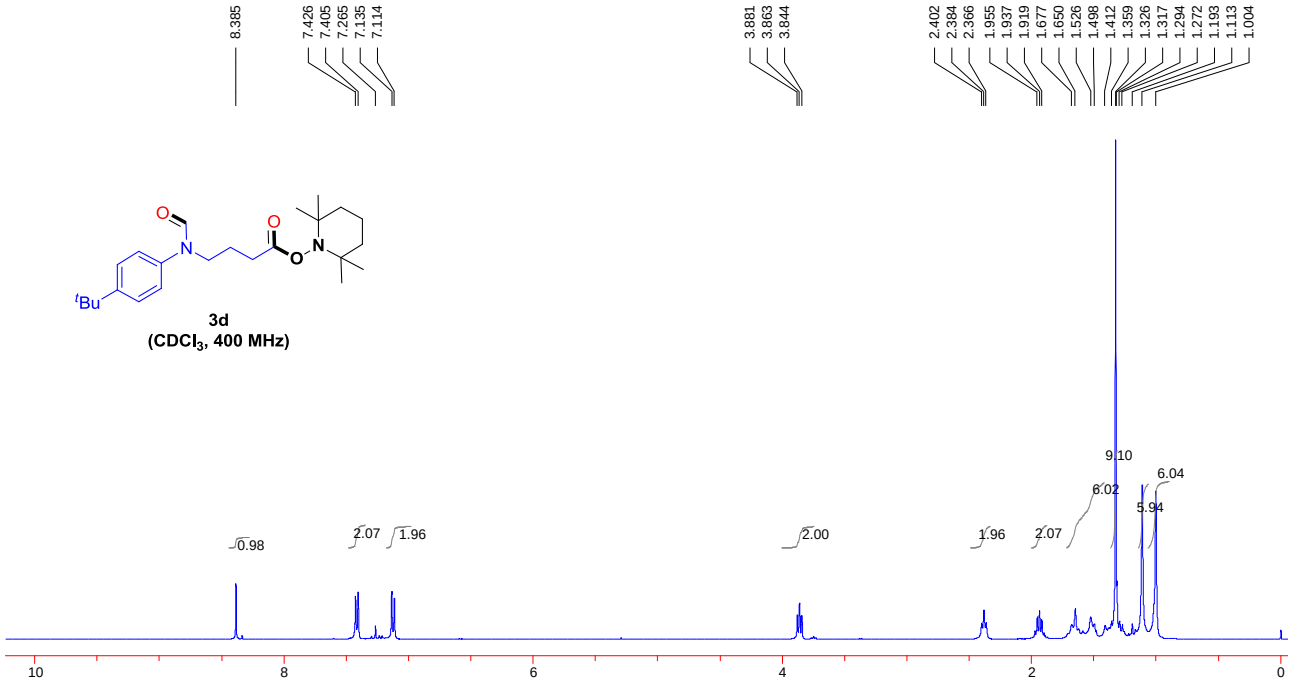
3b
($CDCl_3$, 400 MHz)

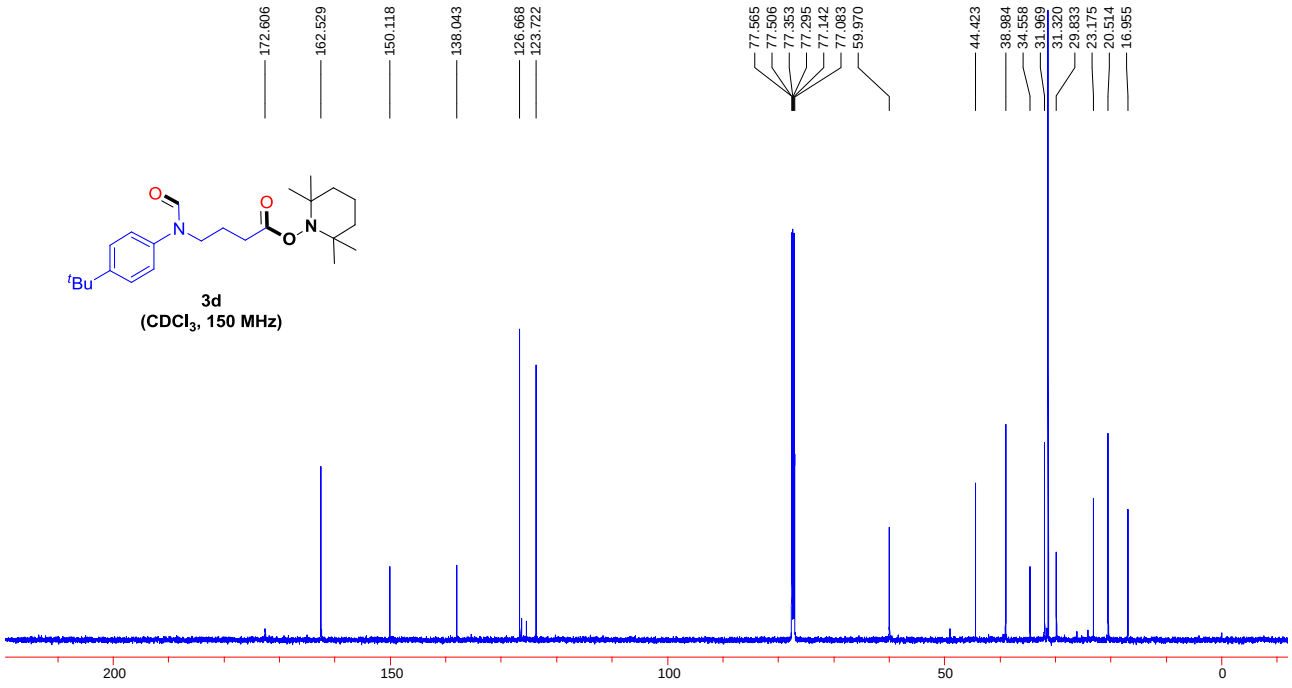


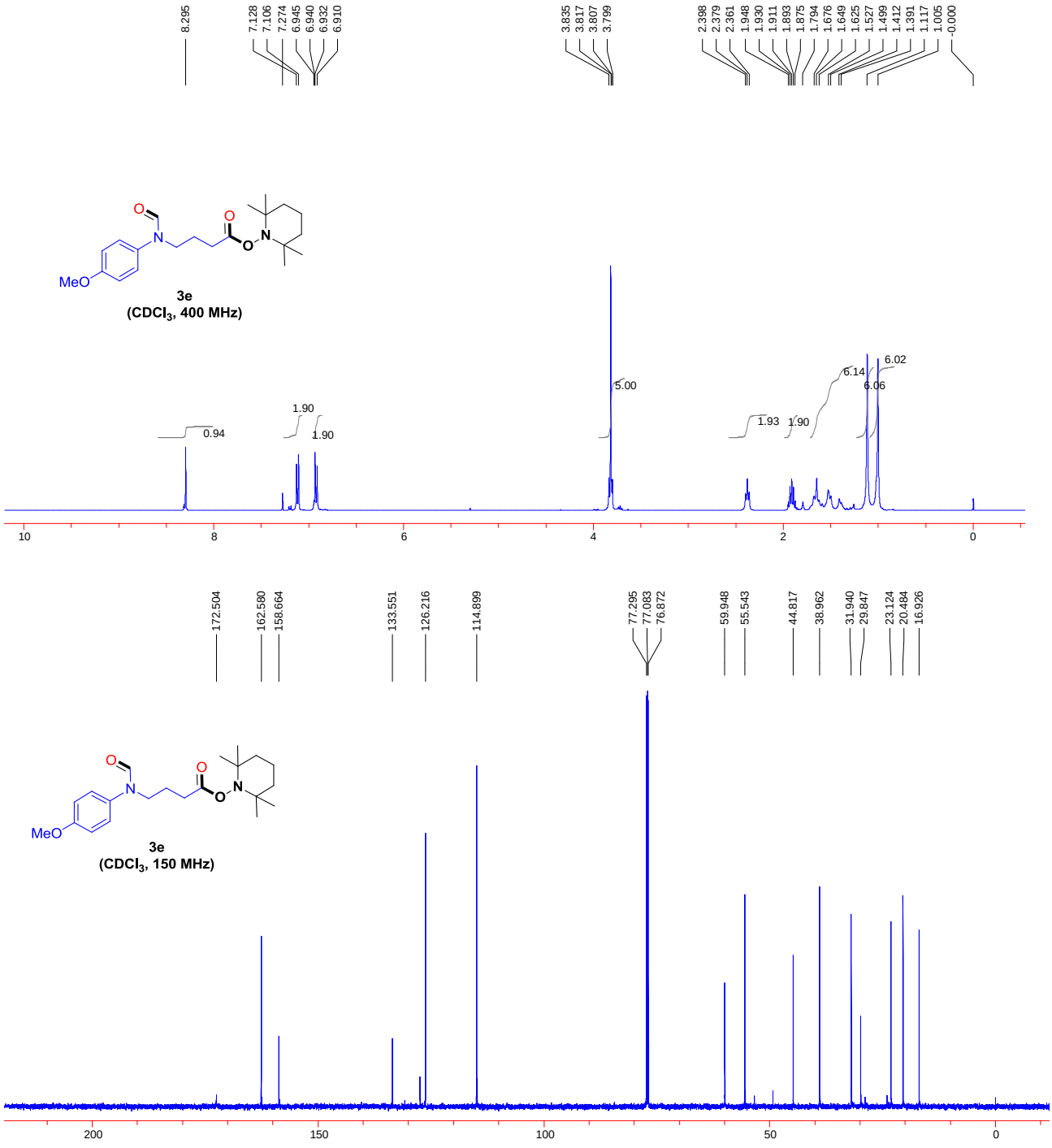


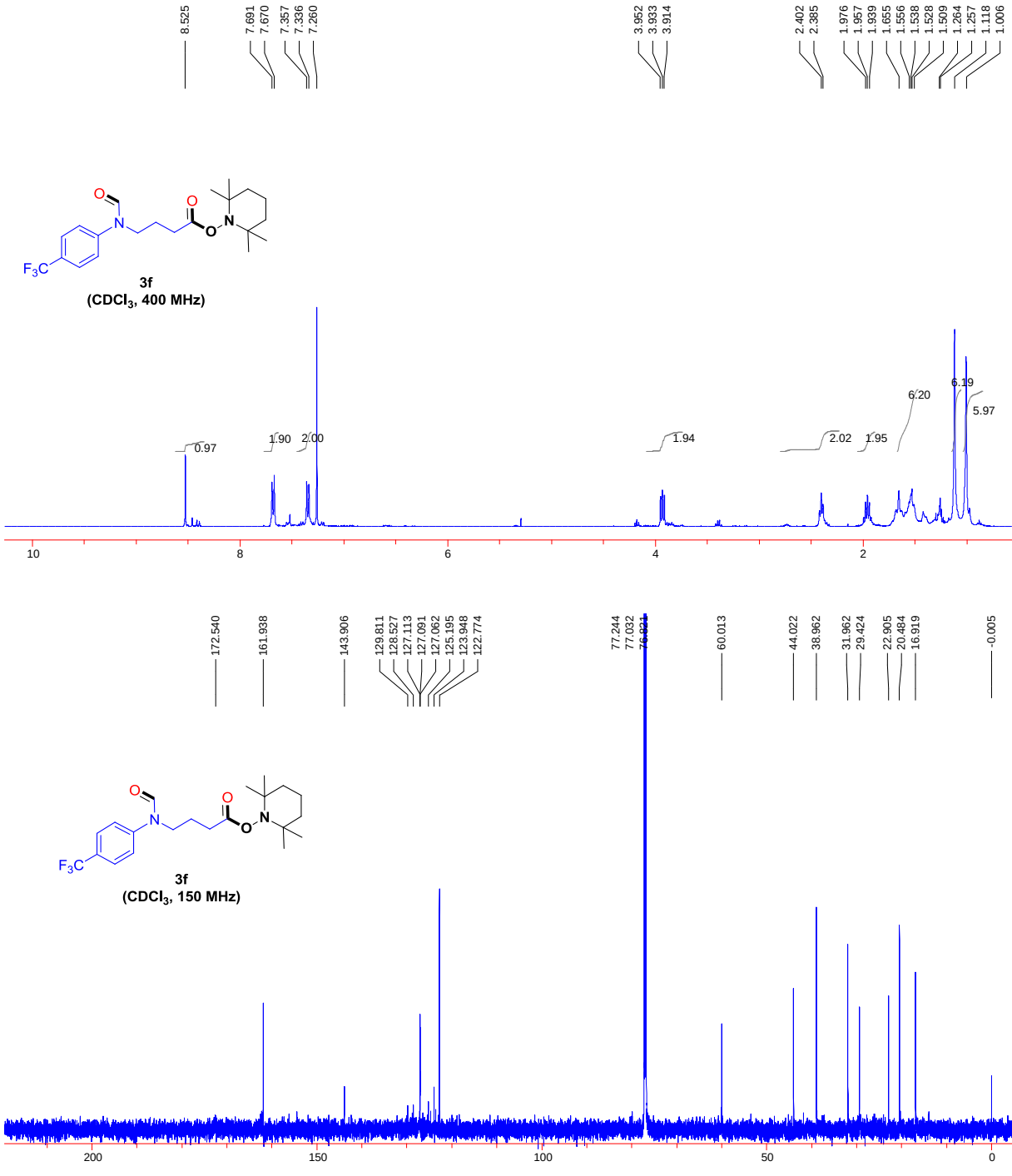
3b
($CDCl_3$, 150 MHz)


8.356
7.265
7.214
7.193
7.088
7.068
3.870
3.852
3.833
2.394
2.375
2.359
1.958
1.940
1.921
1.903
1.676
1.649
1.624
1.525
1.498
1.411
1.115
1.002
Me
3c
(CDCl3, 400 MHz)
0.91
2.00
2.02
2.00
5.08
1.86
6.27
5.99
5.96
10
8
6
4
2
172.584
162.522
138.138
136.993
130.336
124.174
77.288
77.076
76.865
59.962
44.460
38.969
31.940
29.840
23.146
20.915
20.492
16.941
Me
3c
(CDCl3, 150 MHz)
200
150
100
50
0

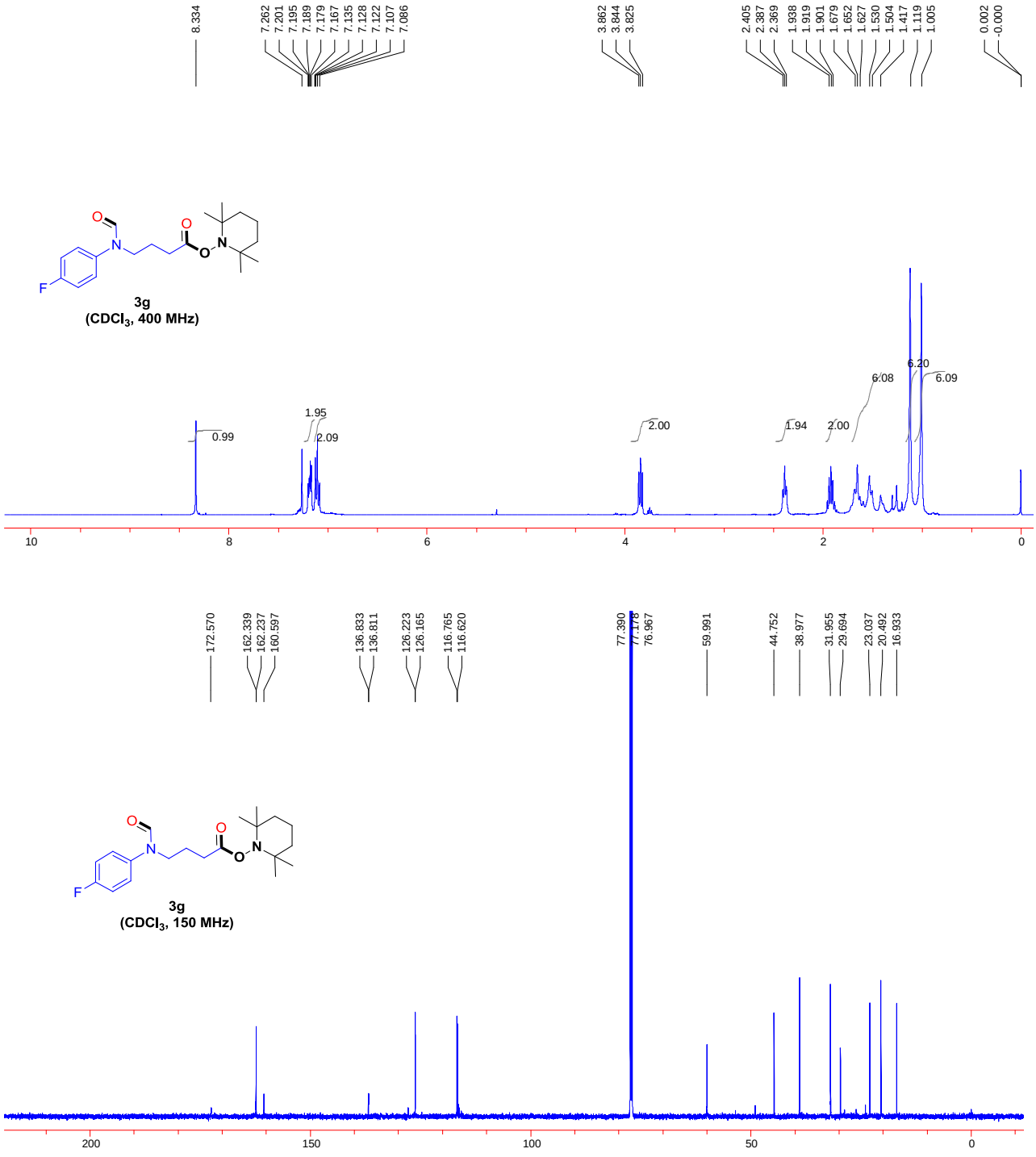

8.385
7.426
7.405
7.265
7.135
7.114
3.881
3.863
3.844
2.402
2.384
2.366
1.955
1.937
1.919
1.677
1.650
1.526
1.498
1.412
1.359
1.326
1.317
1.294
1.272
1.193
1.113
1.004
3d
(CDCl3, 400 MHz)
0.98
2.07
1.96
2.00
1.96
2.07
9.10
6.02
6.04
5.94
10
8
6
4
2
0

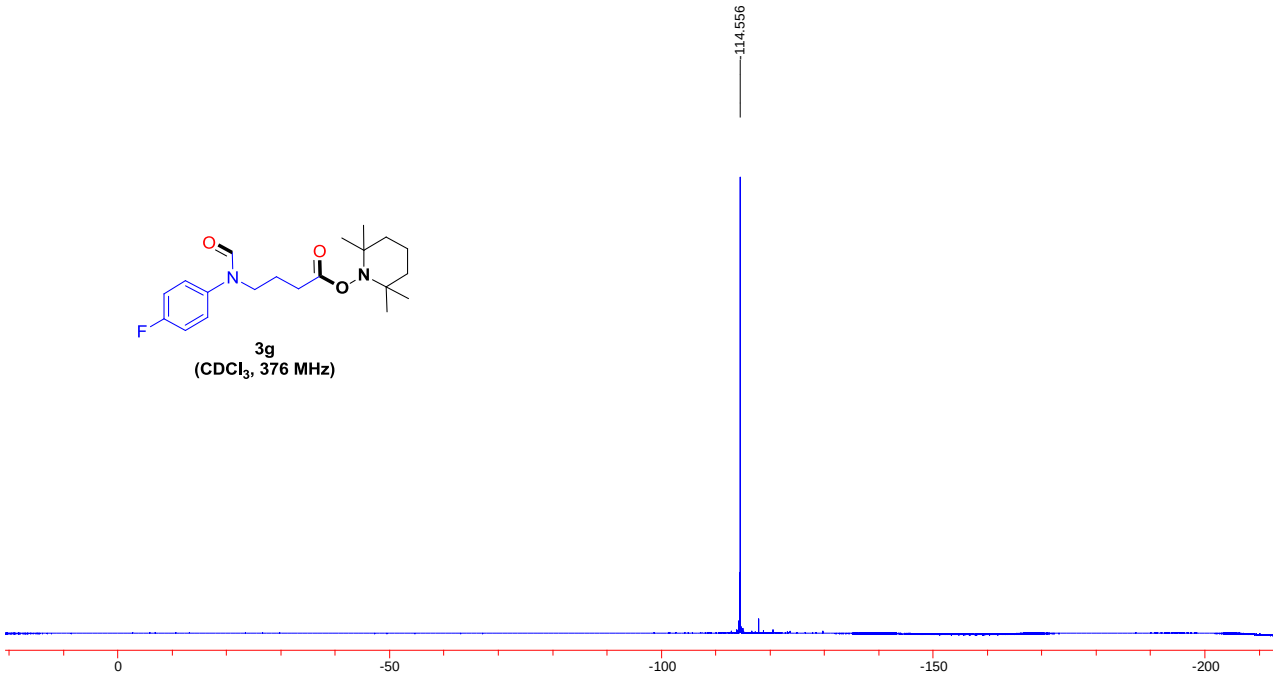

172.606
162.529
150.118
138.043
126.668
123.722
77.565
77.506
77.353
77.295
77.142
77.083
59.970
44.423
38.984
34.558
31.963
31.320
29.833
23.175
20.514
16.955
3d
(CDCl3, 150 MHz)
200
150
100
50
0


8.295
7.128
7.106
7.274
6.945
6.940
6.932
6.910
3.835
3.817
3.807
3.799
2.398
2.379
2.361
1.948
1.930
1.911
1.893
1.875
1.794
1.676
1.649
1.625
1.527
1.499
1.412
1.391
1.117
1.005
-0.000
MeO
3e
(CDCl3, 400 MHz)
0.94
1.90
1.90
5.00
1.93
1.90
6.14
6.06
6.02
10
8
6
4
2
0
172.504
162.580
158.664
133.551
126.216
114.899
77.295
77.083
76.872
59.948
55.543
44.817
38.962
31.940
29.847
23.124
20.484
16.926
MeO
3e
(CDCl3, 150 MHz)
200
150
100
50
0

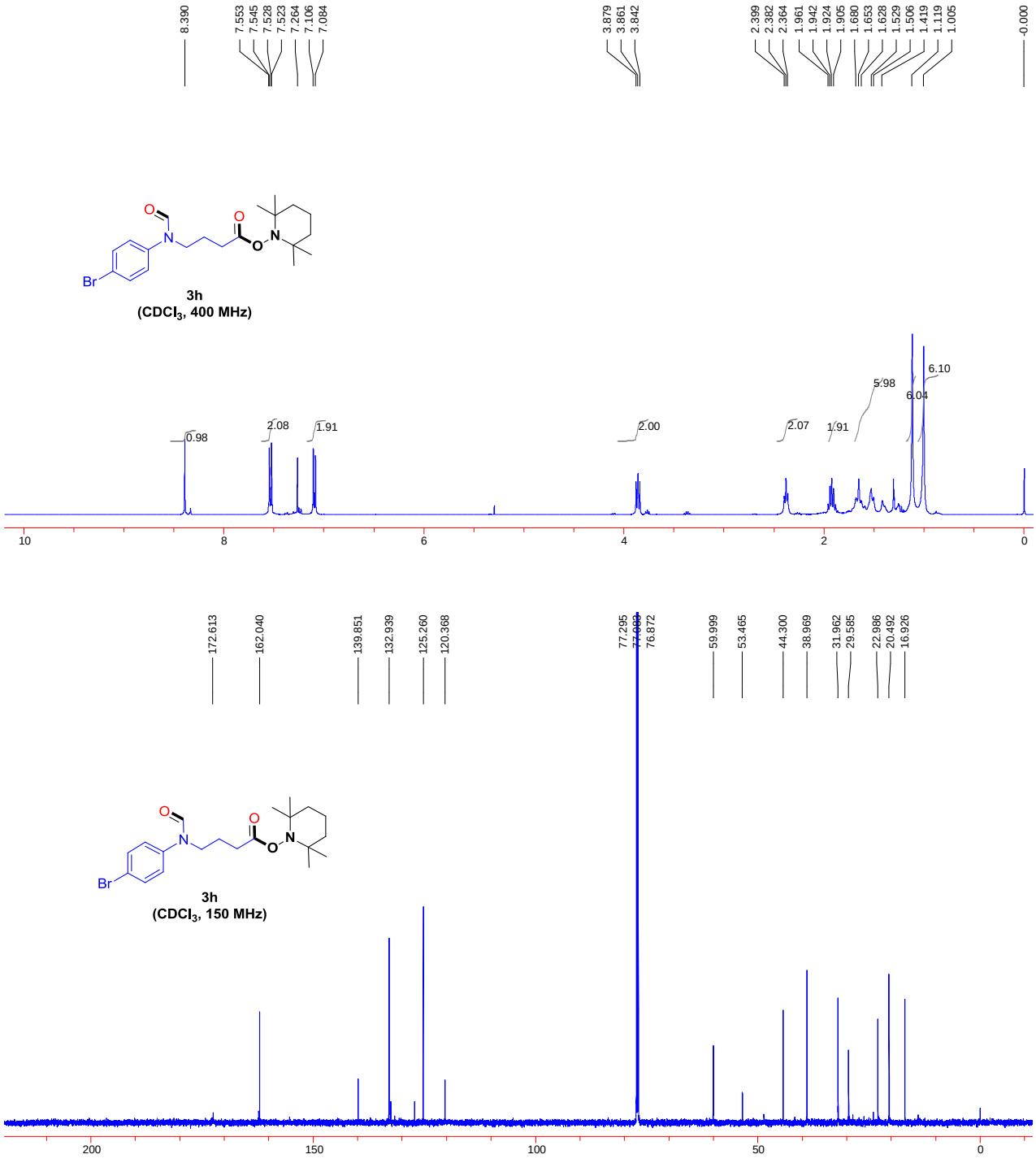

8.525
7.691
7.670
7.357
7.336
7.260
3.952
3.933
3.914
2.402
2.385
1.976
1.957
1.939
1.655
1.556
1.538
1.528
1.509
1.264
1.257
1.118
1.006
3f
(CDCl3, 400 MHz)
0.97
1.90
2.00
1.94
2.02
1.95
6.20
6.19
5.97
10
8
6
4
2
172.540
161.938
143.906
129.811
128.527
127.113
127.091
127.062
125.195
123.948
122.774
77.244
77.032
60.013
44.022
38.962
31.962
29.424
22.905
20.484
16.919
-0.005
3f
(CDCl3, 150 MHz)
200
150
100
50
0

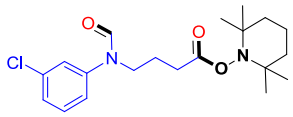
3f
($CDCl_3$, 376 MHz)


8.334
7.262
7.201
7.195
7.189
7.179
7.167
7.135
7.128
7.122
7.107
7.086
3.862
3.844
3.825
2.405
2.387
2.369
1.938
1.919
1.901
1.679
1.652
1.627
1.530
1.504
1.417
1.119
1.005
0.002
-0.000
3g
(CDCl3, 400 MHz)
0.99
1.95
2.09
2.00
1.94
2.00
6.08
6.20
6.09
10
8
6
4
2
0
172.570
162.339
162.237
160.597
136.833
136.811
126.223
126.165
116.765
116.620
77.390
77.176
76.967
59.991
44.752
38.977
31.955
29.694
23.037
20.492
16.933
3g
(CDCl3, 150 MHz)
200
150
100
50
0

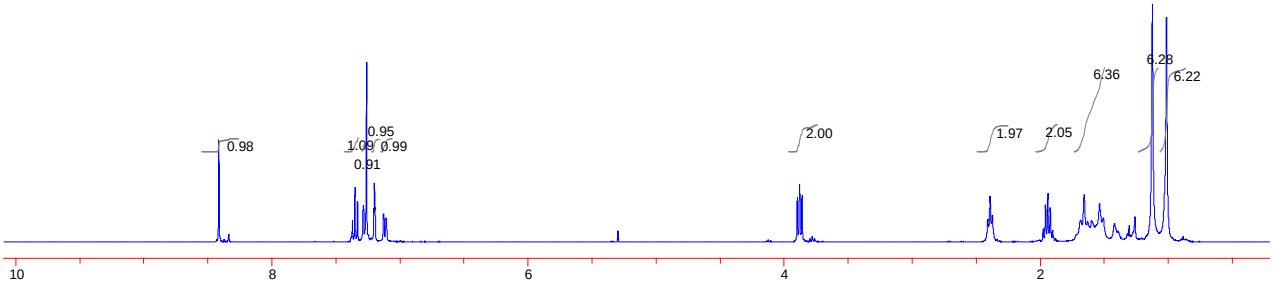


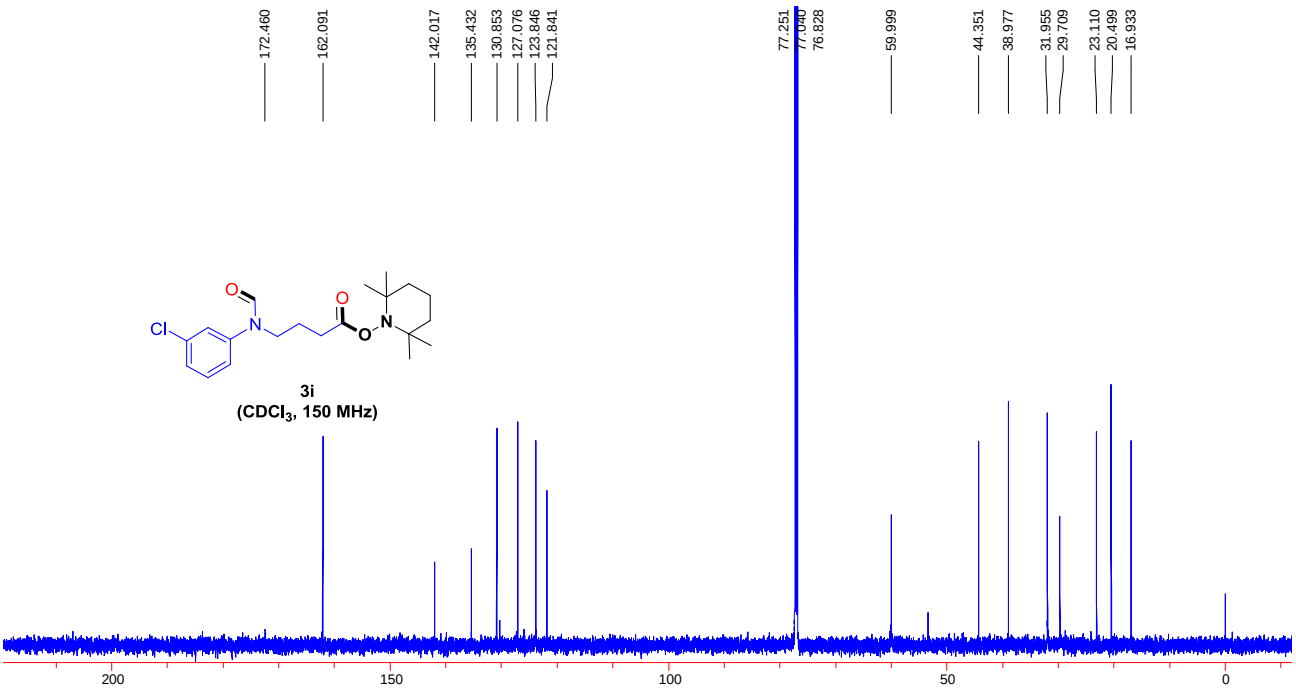
3g
($CDCl_3$, 376 MHz)


8.390
7.553
7.545
7.528
7.523
7.264
7.106
7.084
3.879
3.861
3.842
2.399
2.382
2.364
1.961
1.942
1.924
1.905
1.680
1.653
1.628
1.529
1.506
1.419
1.119
1.005
-0.000
Br
3h
(CDCl3, 400 MHz)
0.98
2.08
1.91
2.00
2.07
1.91
5.98
6.04
6.10
10
8
6
4
2
0
172.613
162.040
139.851
132.939
125.260
120.368
77.295
77.083
76.872
59.999
53.465
44.300
38.969
31.962
29.585
22.986
20.492
16.926
Br
3h
(CDCl3, 150 MHz)
200
150
100
50
0

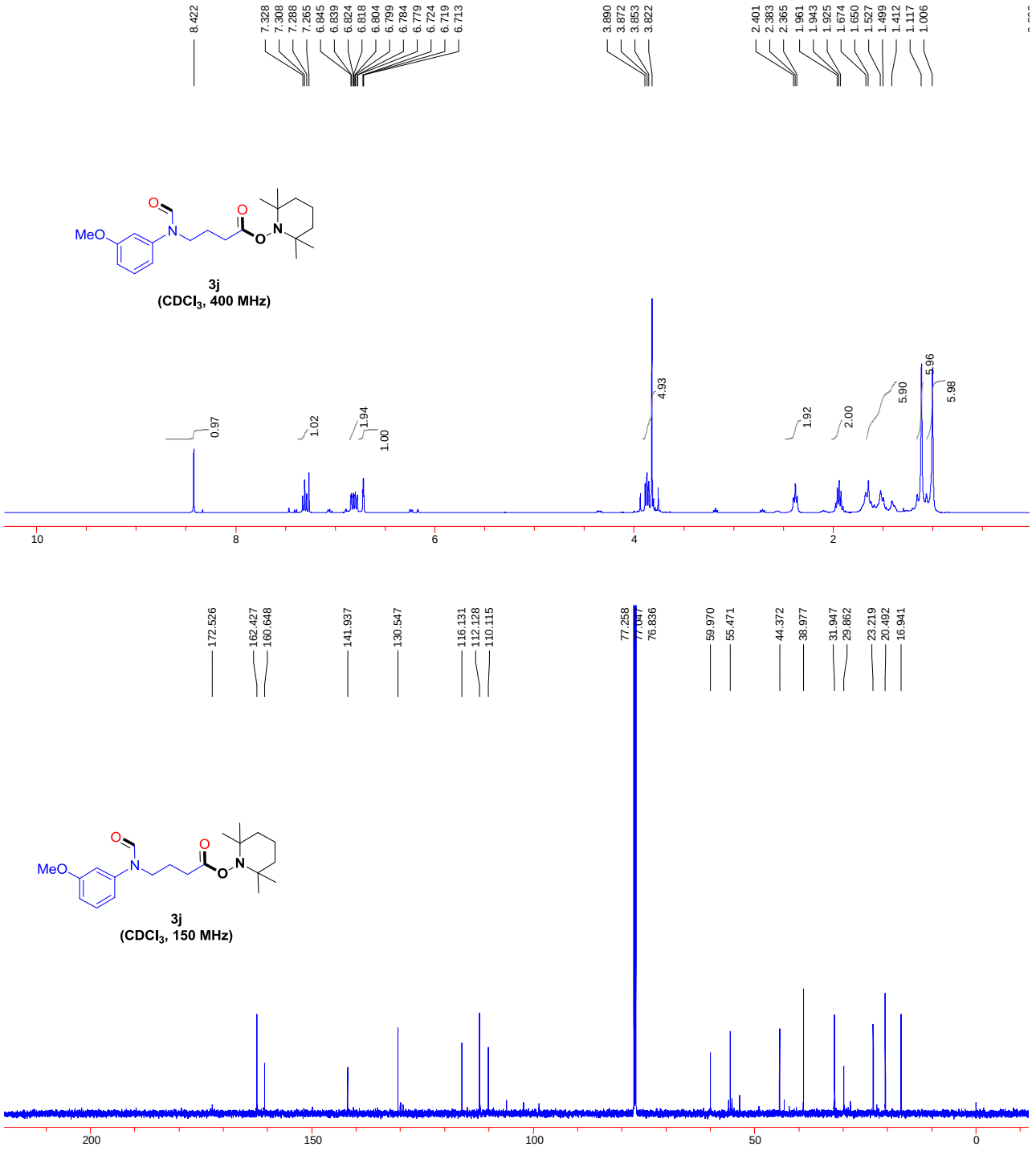


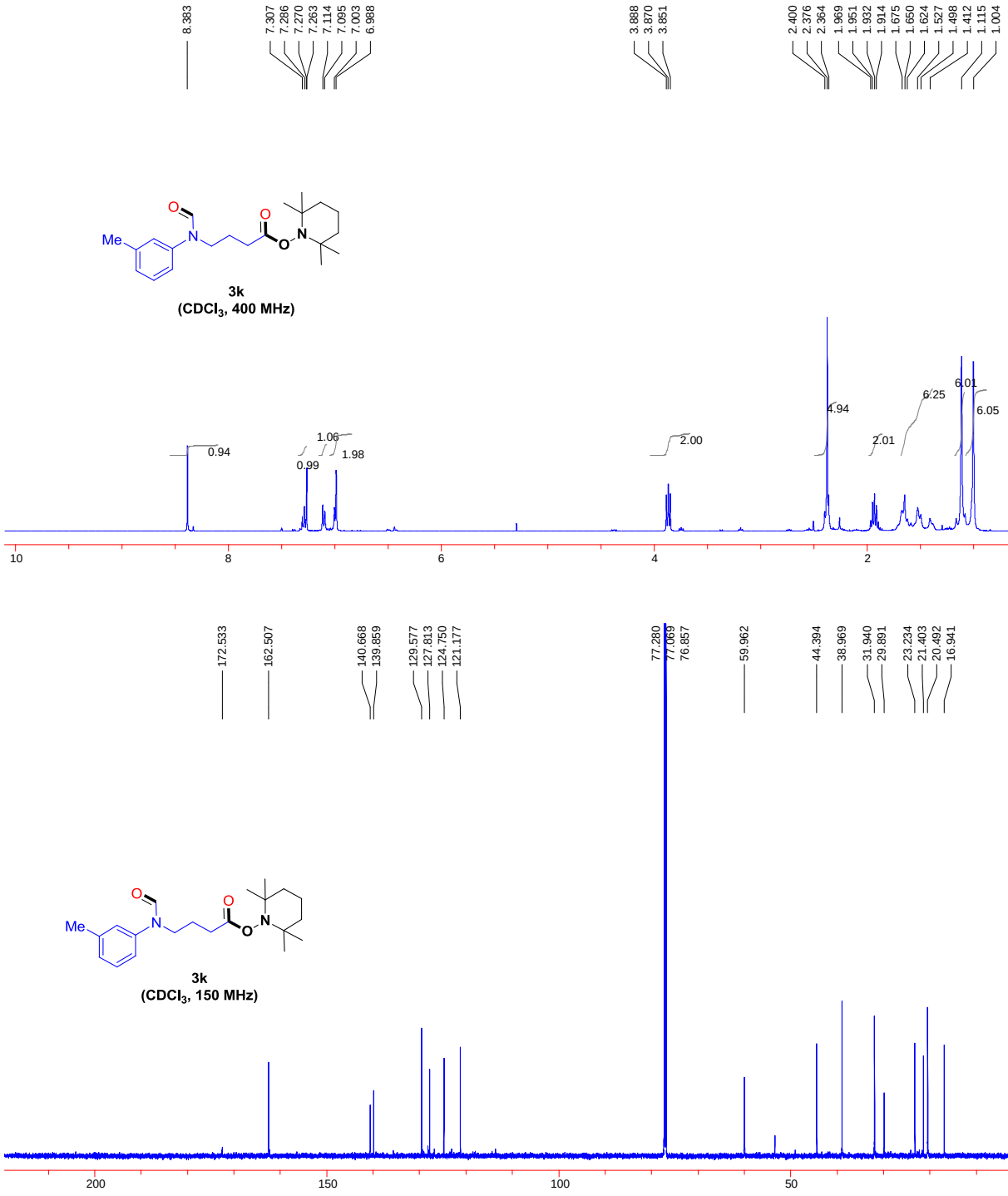
3i
($CDCl_3$, 400 MHz)

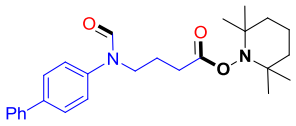




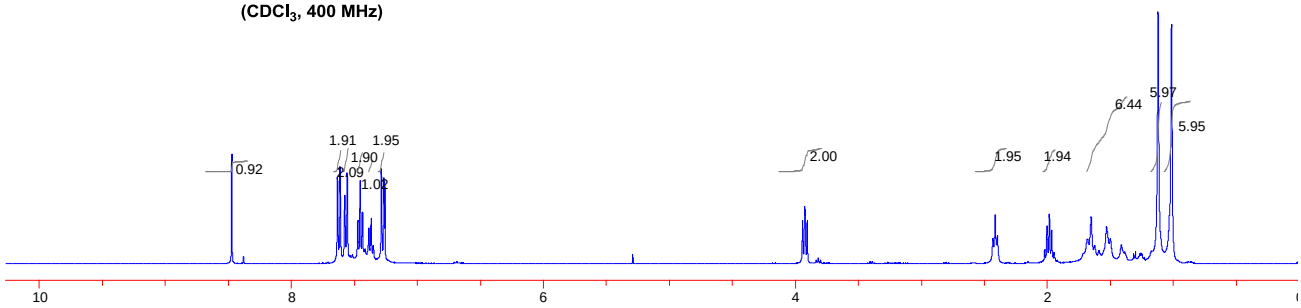
3i
($CDCl_3$, 150 MHz)

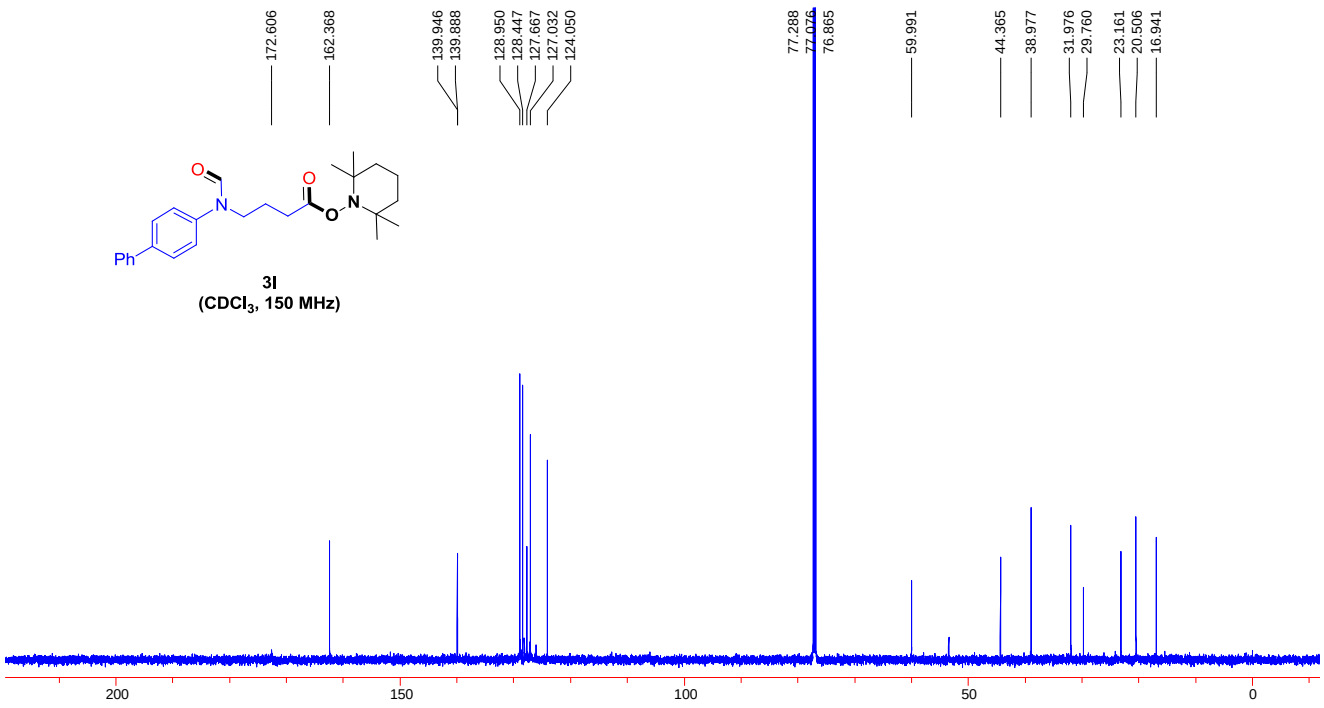

8.422
7.328
7.308
7.288
7.265
6.845
6.839
6.824
6.818
6.804
6.799
6.784
6.779
6.724
6.719
6.713
3.890
3.872
3.853
3.822
2.401
2.383
2.365
1.961
1.943
1.925
1.674
1.650
1.527
1.499
1.412
1.117
1.006
MeO
3j
(CDCl3, 400 MHz)
0.97
1.02
1.94
1.00
4.93
1.92
2.00
5.90
5.96
5.98
10
8
6
4
2
172.526
162.427
160.648
141.937
130.547
116.131
112.128
110.115
77.258
77.047
76.836
59.970
55.471
44.372
38.977
31.947
29.862
23.219
20.492
16.941
MeO
3j
(CDCl3, 150 MHz)
200
150
100
50
0


8.383
7.307
7.286
7.270
7.263
7.114
7.095
7.003
6.988
3.888
3.870
3.851
2.400
2.376
2.364
1.969
1.951
1.932
1.914
1.675
1.650
1.624
1.527
1.498
1.412
1.115
1.004
Me
O
N
O
O
N
3k
(CDCl3, 400 MHz)
0.94
1.06
0.99
1.98
2.00
4.94
2.01
6.25
6.01
6.05
10
8
6
4
2
172.533
162.507
140.668
139.859
129.577
127.813
124.750
121.177
77.280
77.069
76.857
59.962
44.394
38.969
31.940
29.891
23.234
21.403
20.492
16.941
Me
O
N
O
O
N
3k
(CDCl3, 150 MHz)
200
150
100
50
0

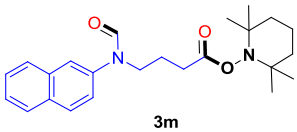


3l
($CDCl_3$, 400 MHz)

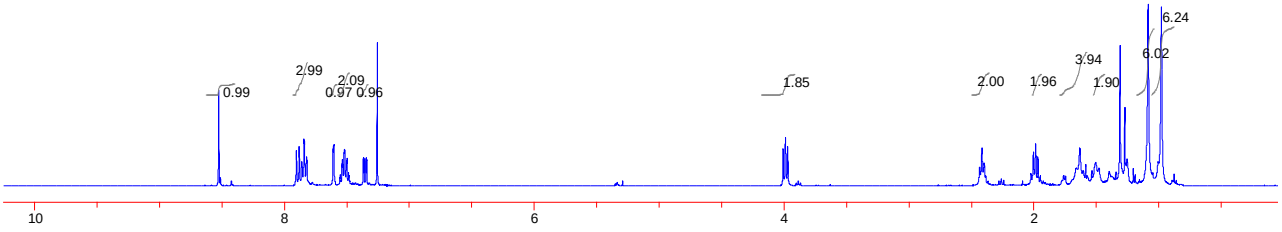


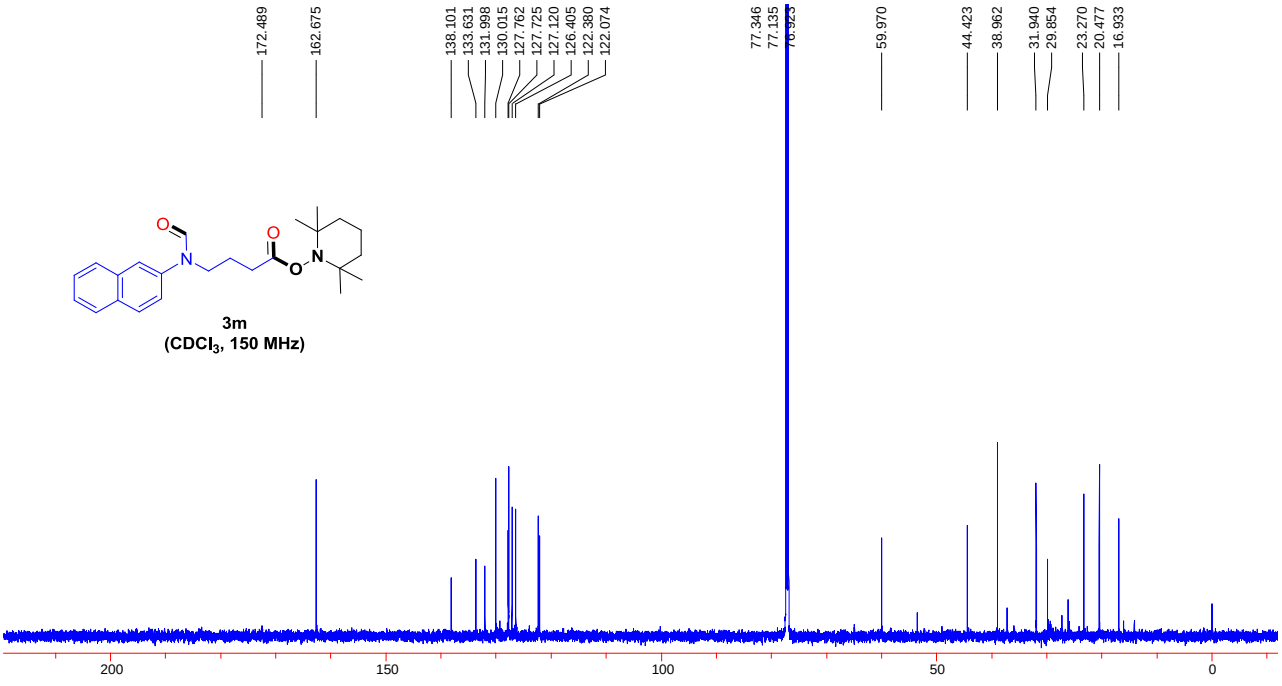


3l
($CDCl_3$, 150 MHz)

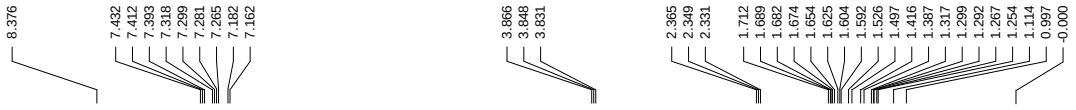


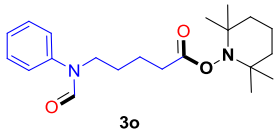
3m
($CDCl_3$, 400 MHz)



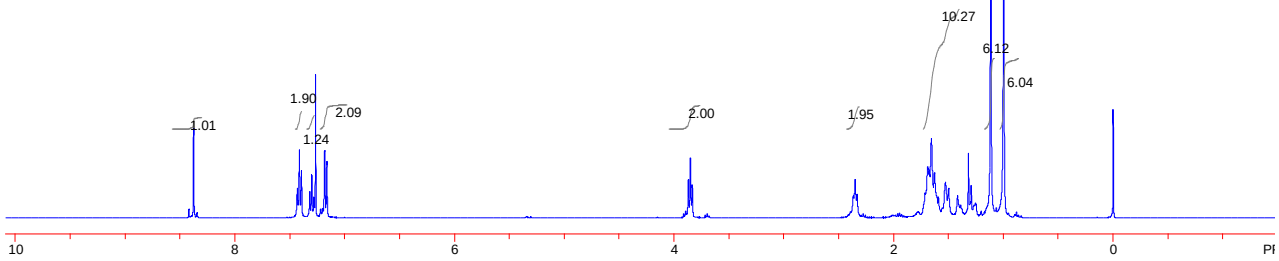


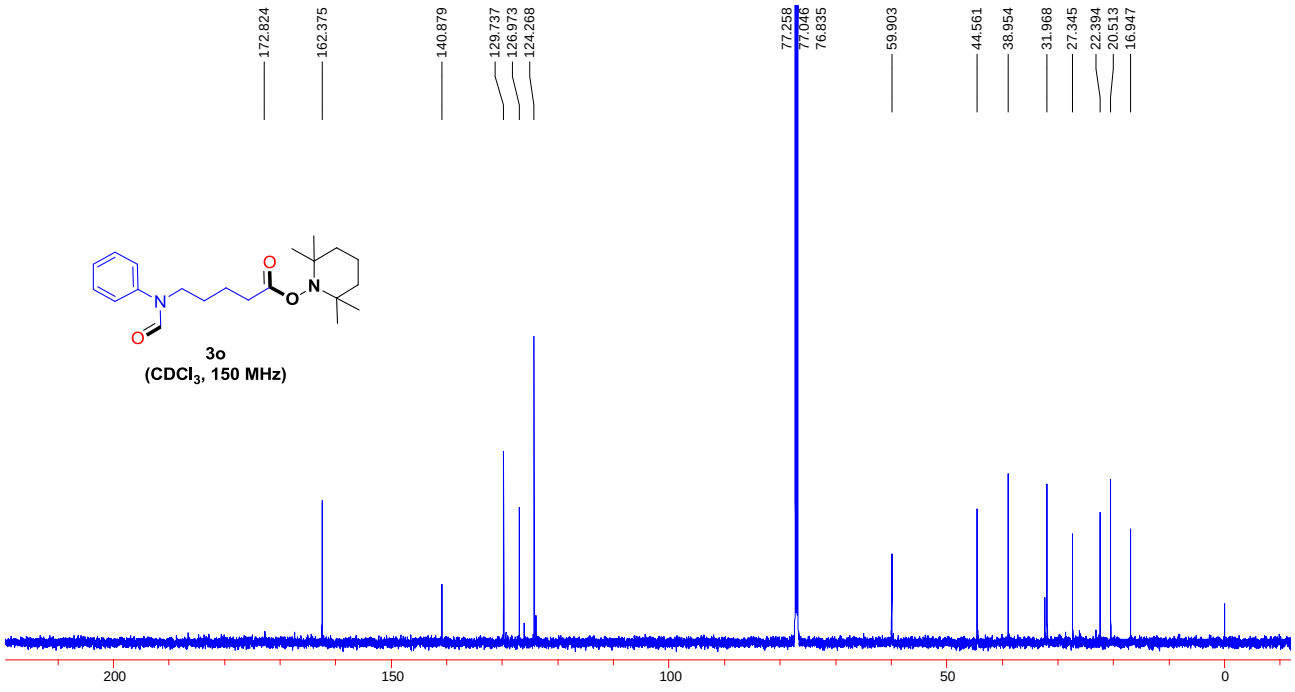
3m
($CDCl_3$, 150 MHz)



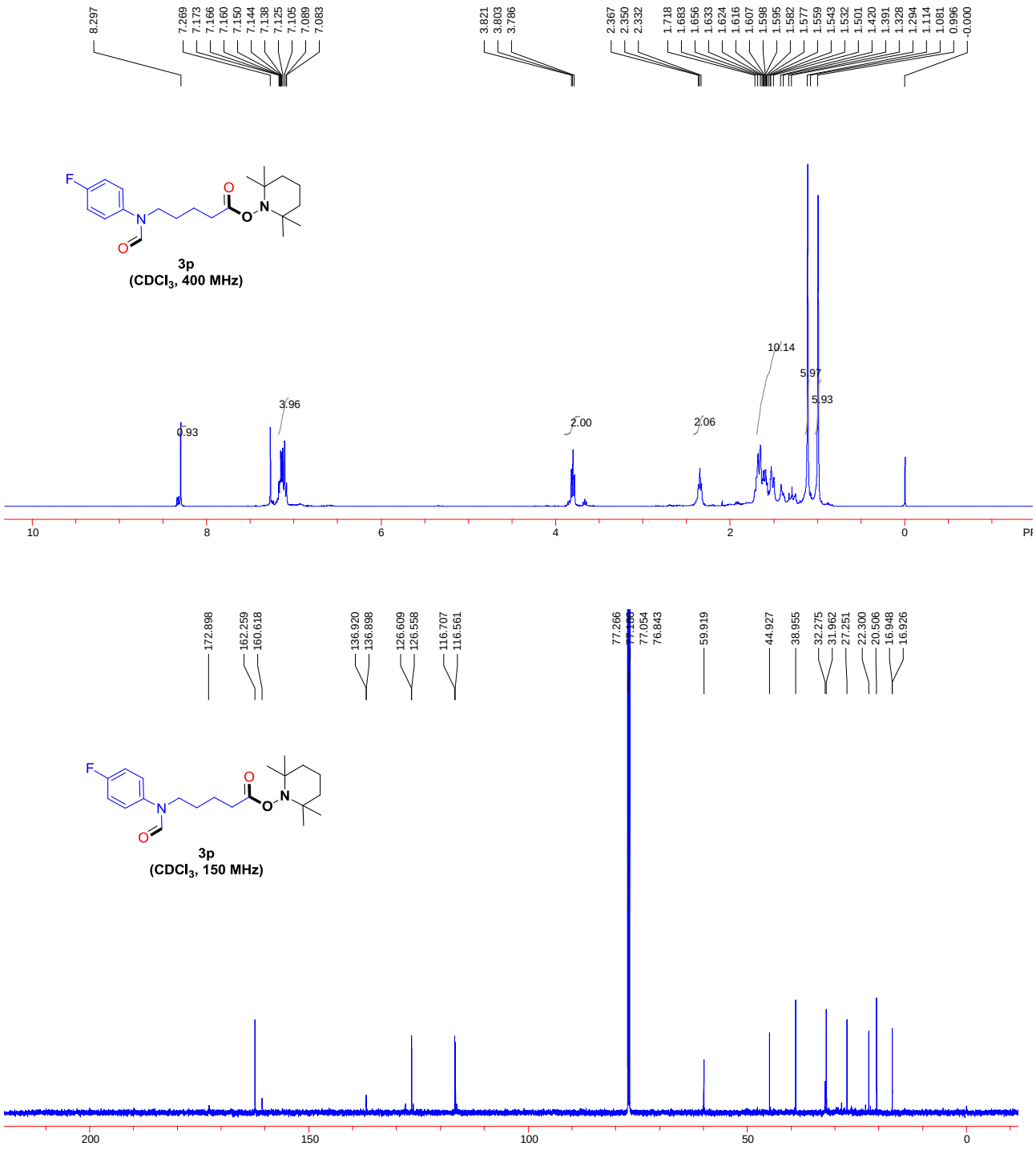


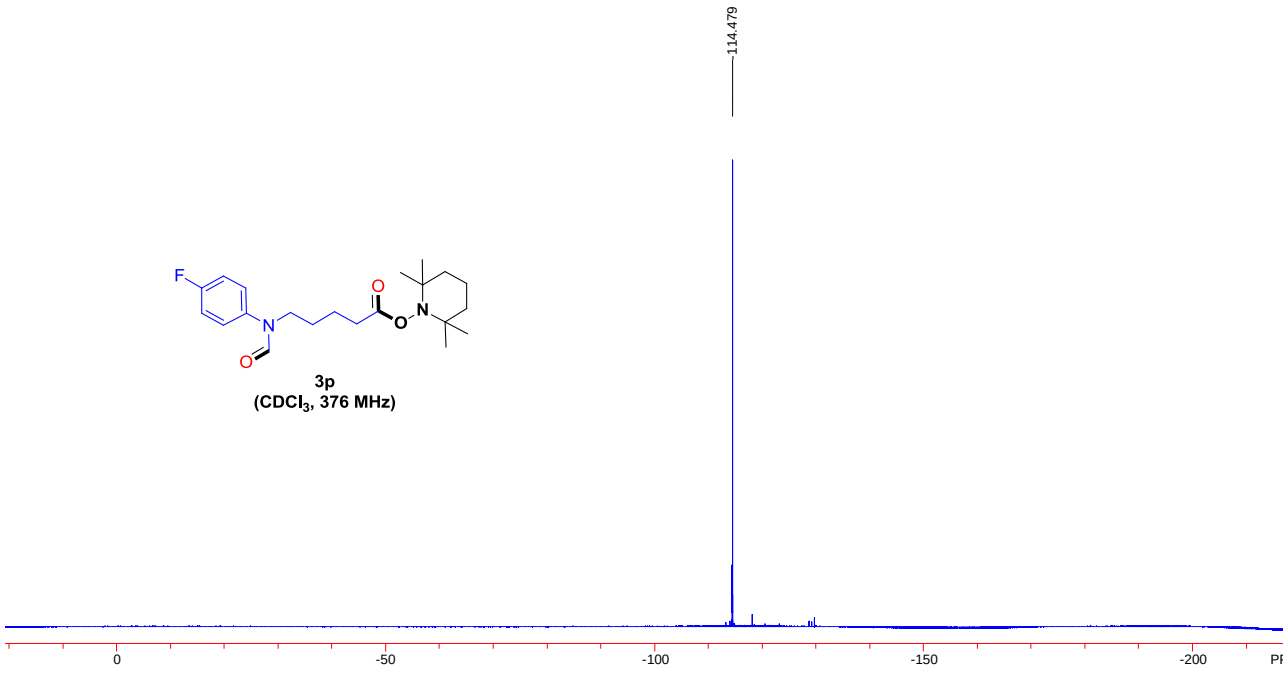
3o
($CDCl_3$, 400 MHz)





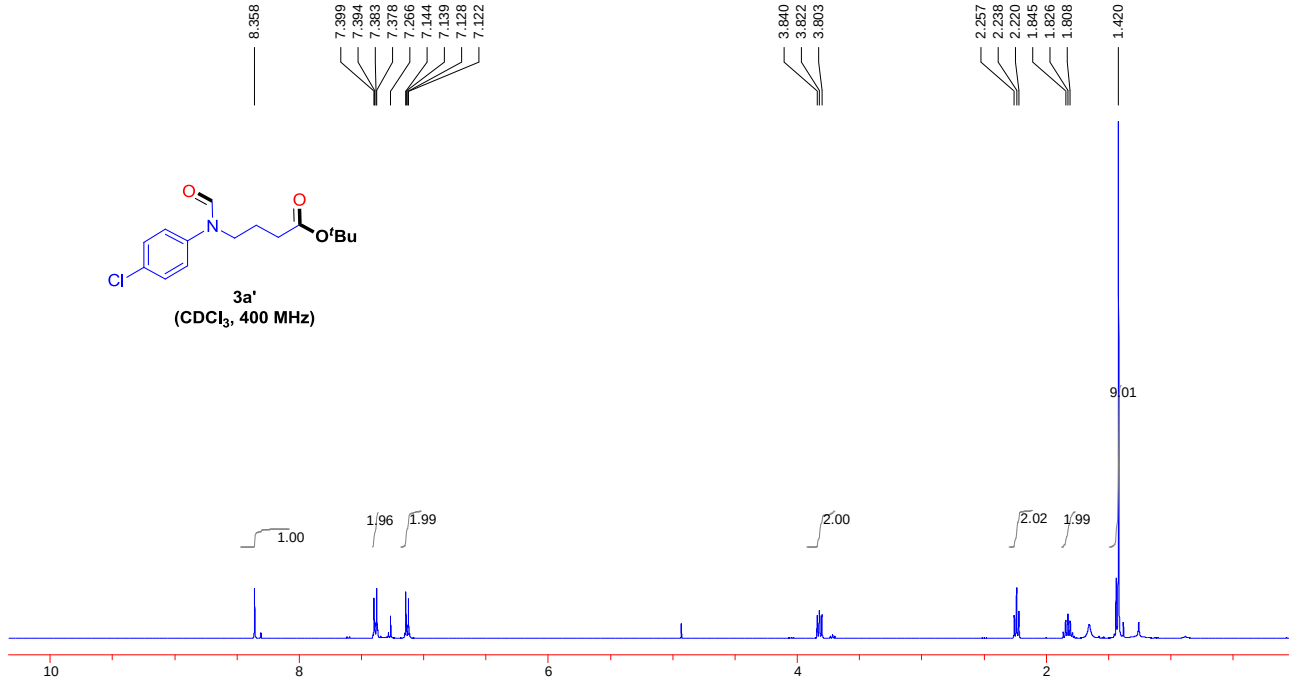
3o
($CDCl_3$, 150 MHz)

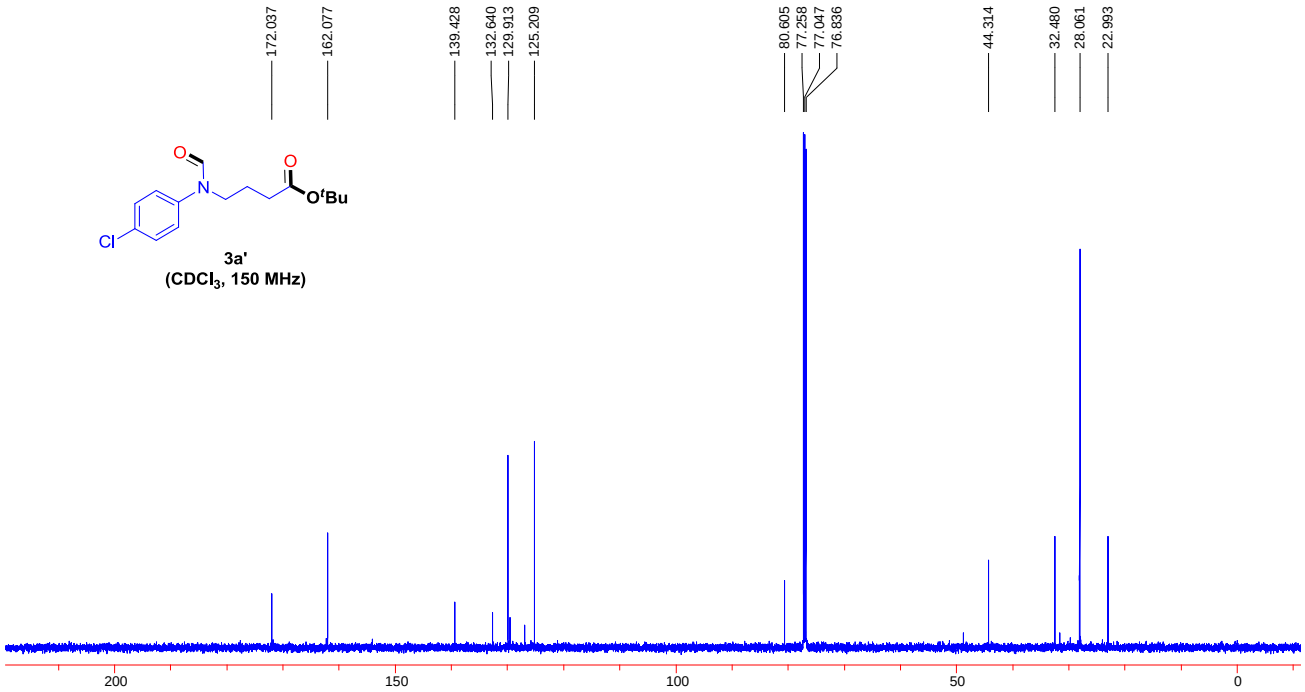

8.297
7.269
7.173
7.166
7.160
7.150
7.144
7.138
7.125
7.105
7.089
7.083
3.821
3.803
3.786
2.367
2.350
2.332
1.718
1.683
1.656
1.633
1.624
1.616
1.607
1.598
1.595
1.582
1.577
1.559
1.543
1.532
1.501
1.420
1.391
1.328
1.294
1.114
1.081
0.996
-0.000
F
O
N
O
O
N
3p
(CDCl3, 400 MHz)
10.14
5.97
5.93
3.96
2.00
2.06
0.93
10
8
6
4
2
0
172.898
162.259
160.618
136.920
136.898
126.609
126.558
116.707
116.561
77.266
77.160
77.054
76.843
59.919
44.927
38.955
32.275
31.962
27.251
22.300
20.506
16.948
16.926
F
O
N
O
O
N
3p
(CDCl3, 150 MHz)
200
150
100
50
0

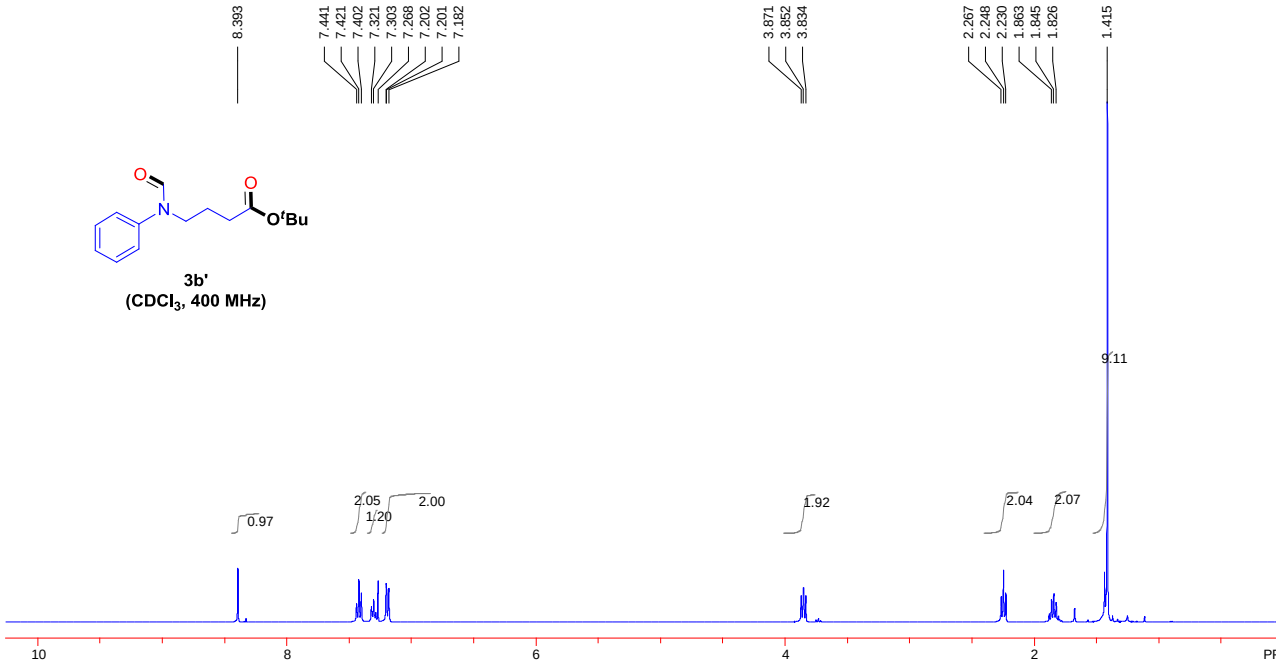


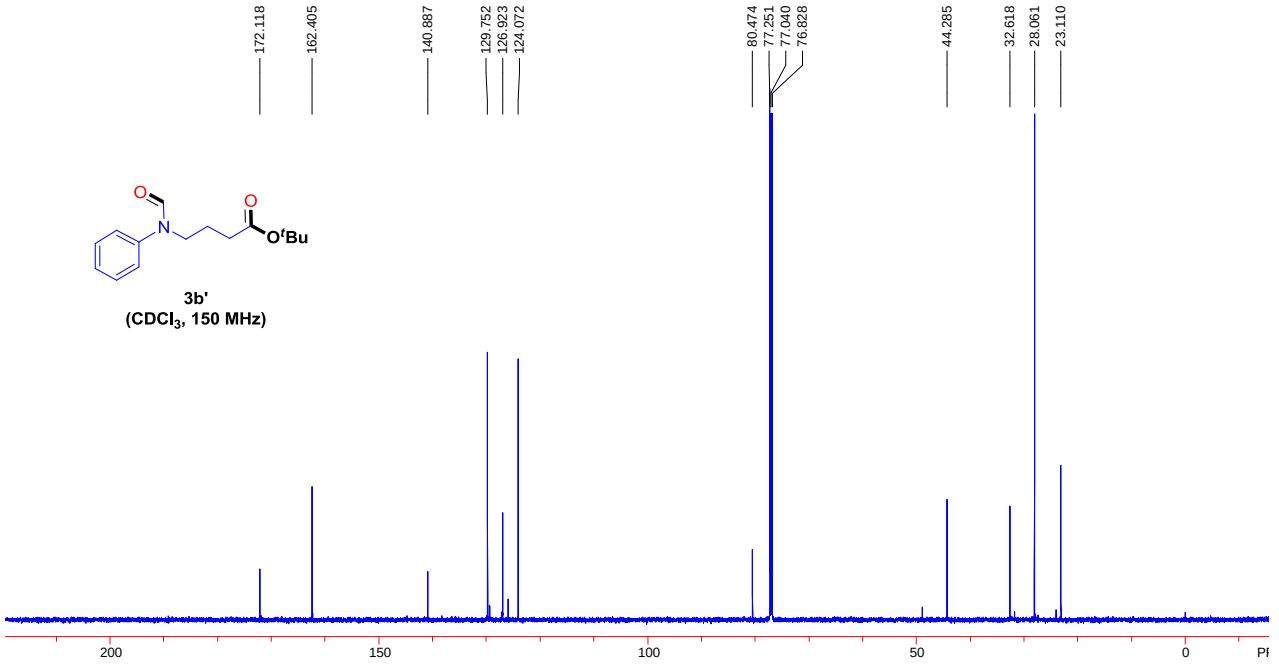
3p
($CDCl_3$, 376 MHz)

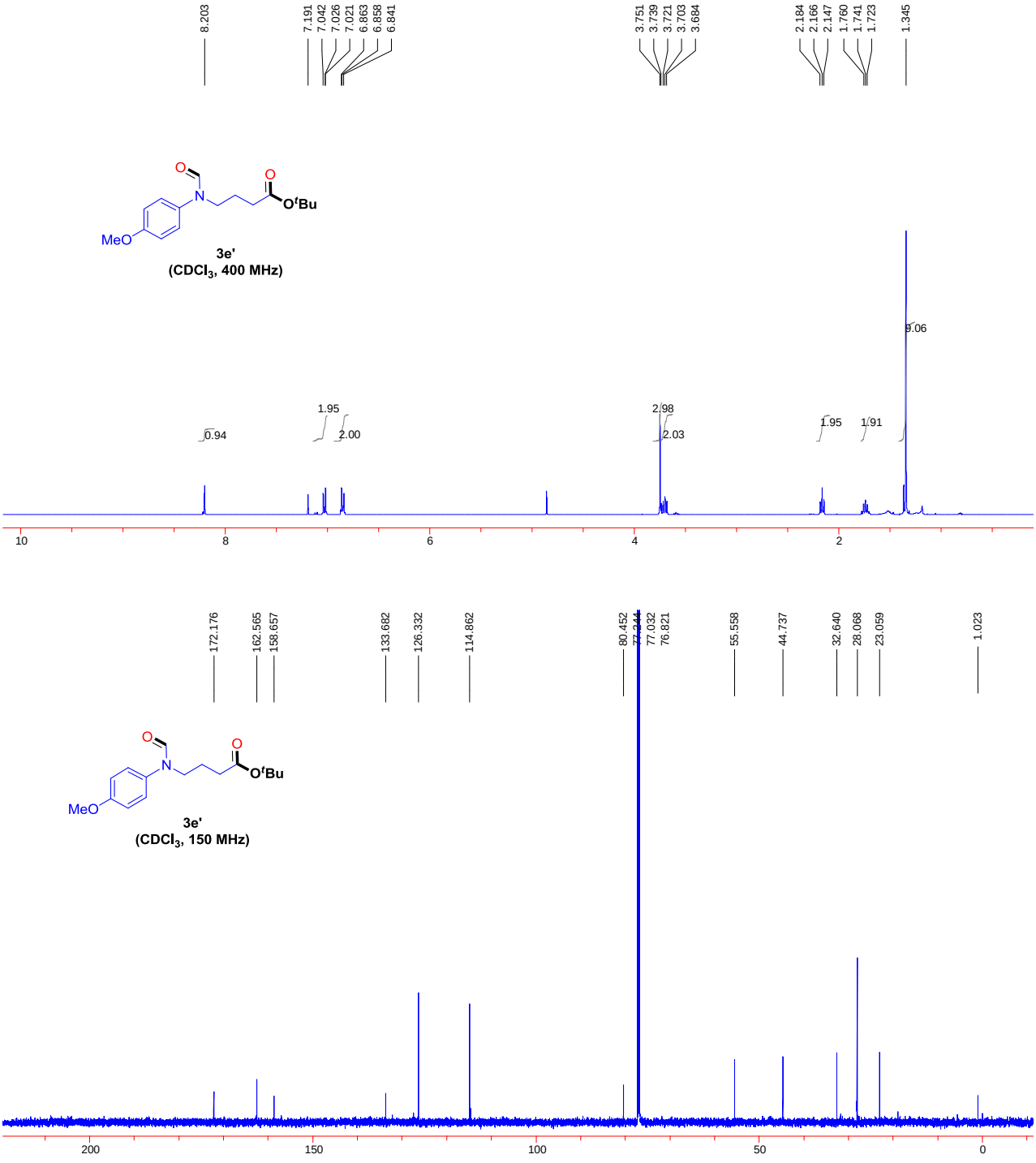
IV. Copies of the NMR spectra of 3a'-3b', 3e'-3f', 3h', 3j'-3l' and 3o'-3p'

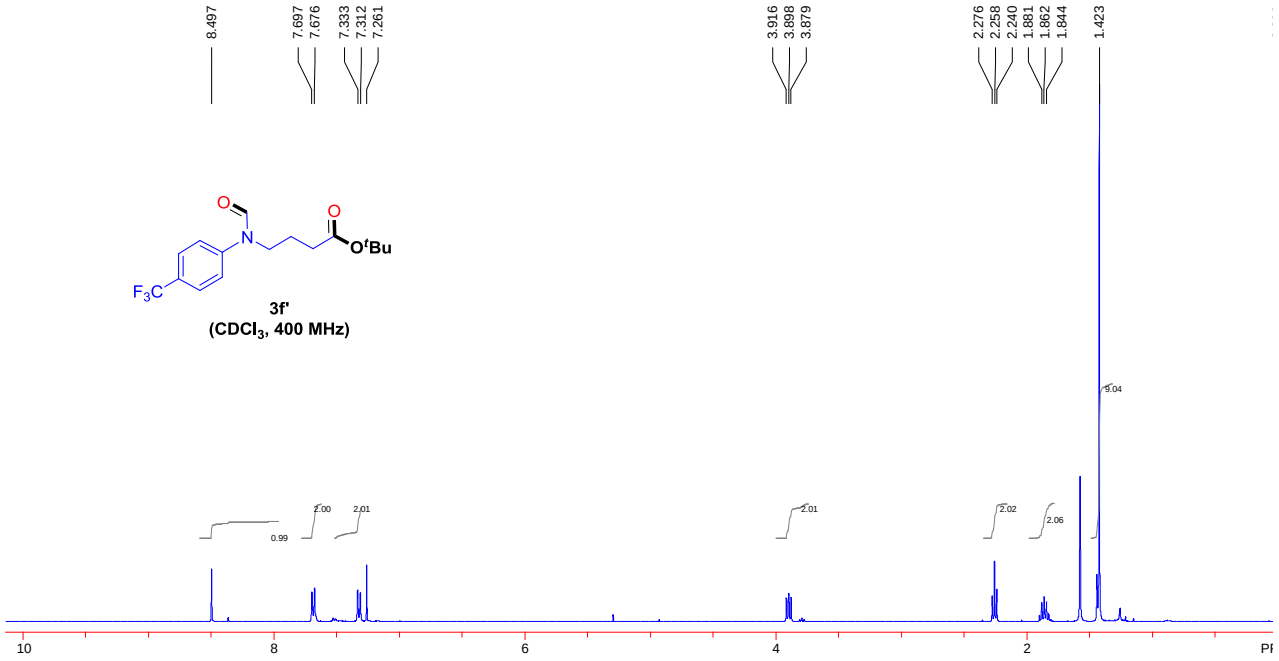




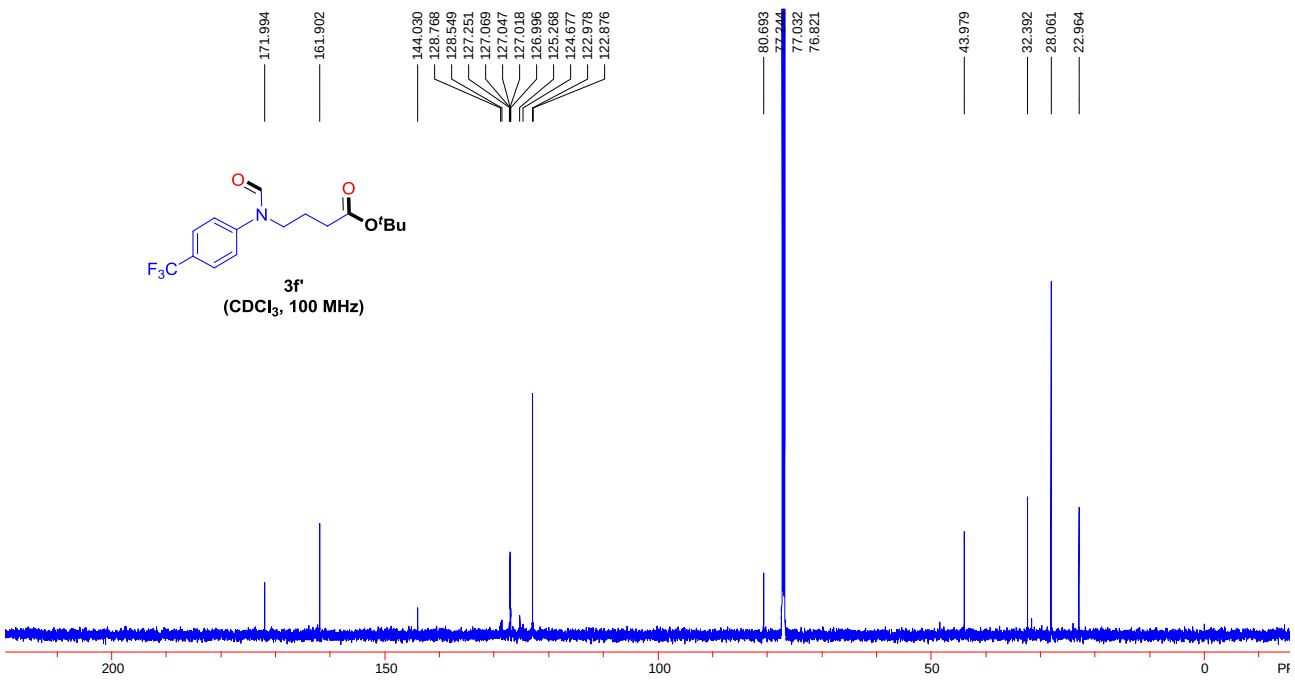

8.393
7.441
7.421
7.402
7.321
7.303
7.268
7.202
7.201
7.182
3.871
3.852
3.834
2.267
2.248
2.230
1.863
1.845
1.826
1.415
O
N
O
O'Bu
3b'
(CDCl3, 400 MHz)
9.11
0.97
2.05
1.20
2.00
1.92
2.04
2.07
10
8
6
4
2


172.118
162.405
140.887
129.752
126.923
124.072
80.474
77.251
77.040
76.828
44.285
32.618
28.061
23.110
O
N
O
O'Bu
3b'
(CDCl3, 150 MHz)
200
150
100
50
0

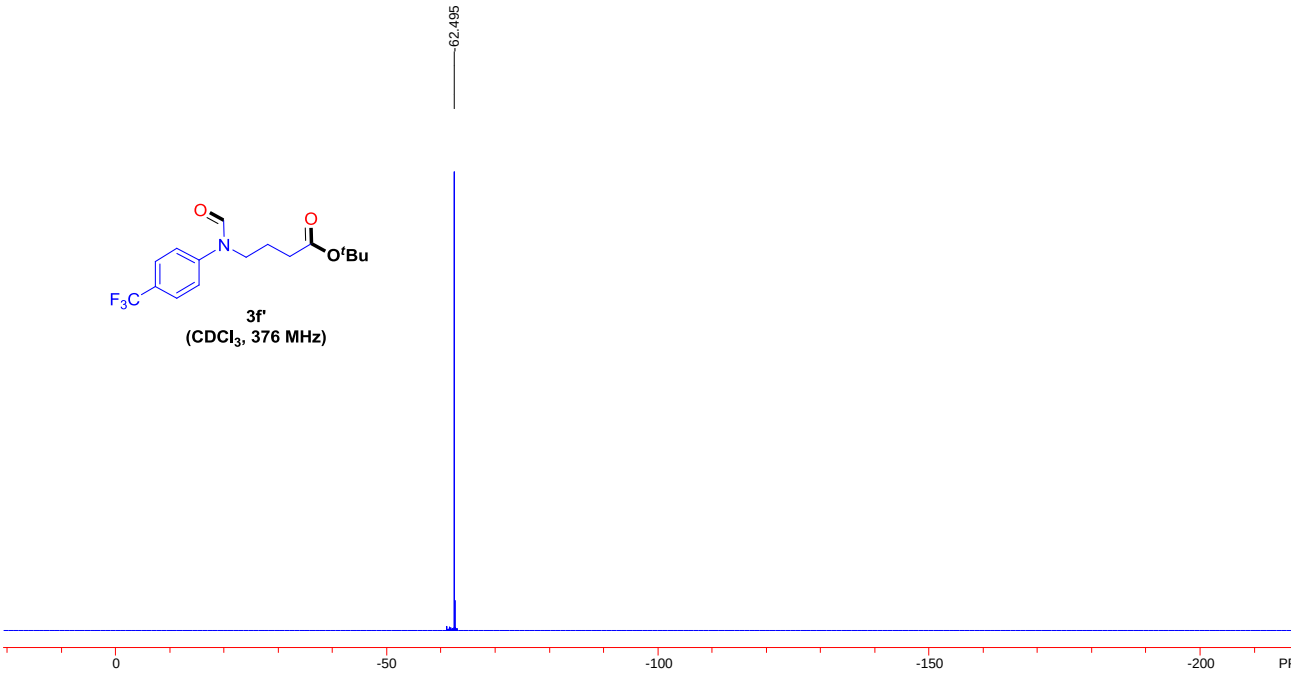

8.203
7.191
7.042
7.026
7.021
6.863
6.858
6.841
3.751
3.739
3.721
3.703
3.684
2.184
2.166
2.147
1.760
1.741
1.723
1.345
O
N
O
O'Bu
MeO
3e'
(CDCl3, 400 MHz)
9.06
1.95
2.98
0.94
2.00
2.03
1.95
1.91
10
8
6
4
2
172.176
162.565
158.657
133.682
126.332
114.862
80.452
77.244
77.032
76.821
55.558
44.737
32.640
28.068
23.059
1.023
O
N
O
O'Bu
MeO
3e'
(CDCl3, 150 MHz)
200
150
100
50
0



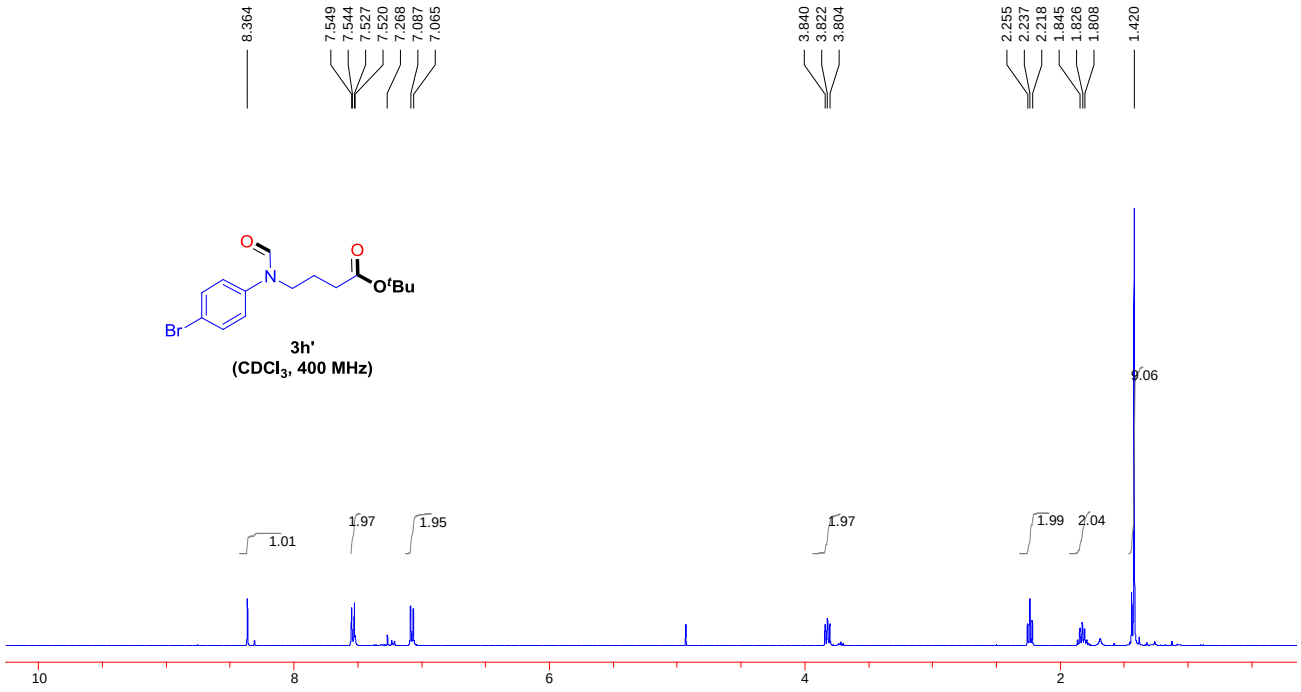
3f'
($CDCl_3$, 400 MHz)

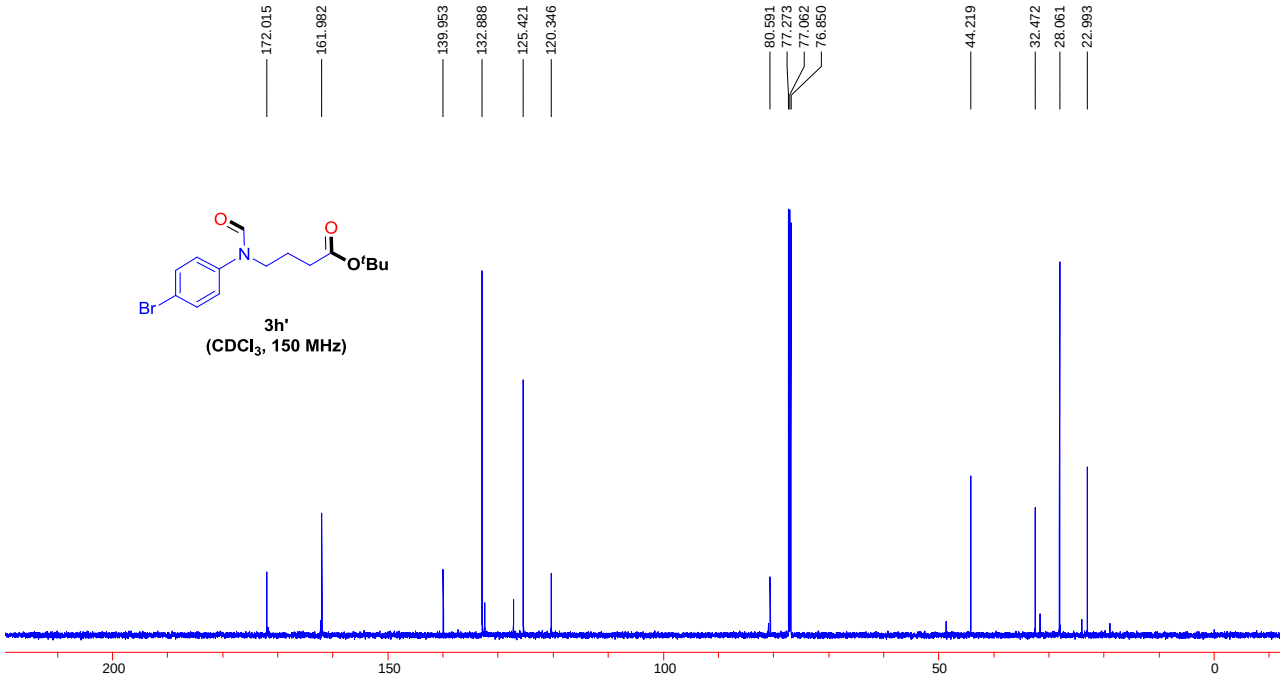


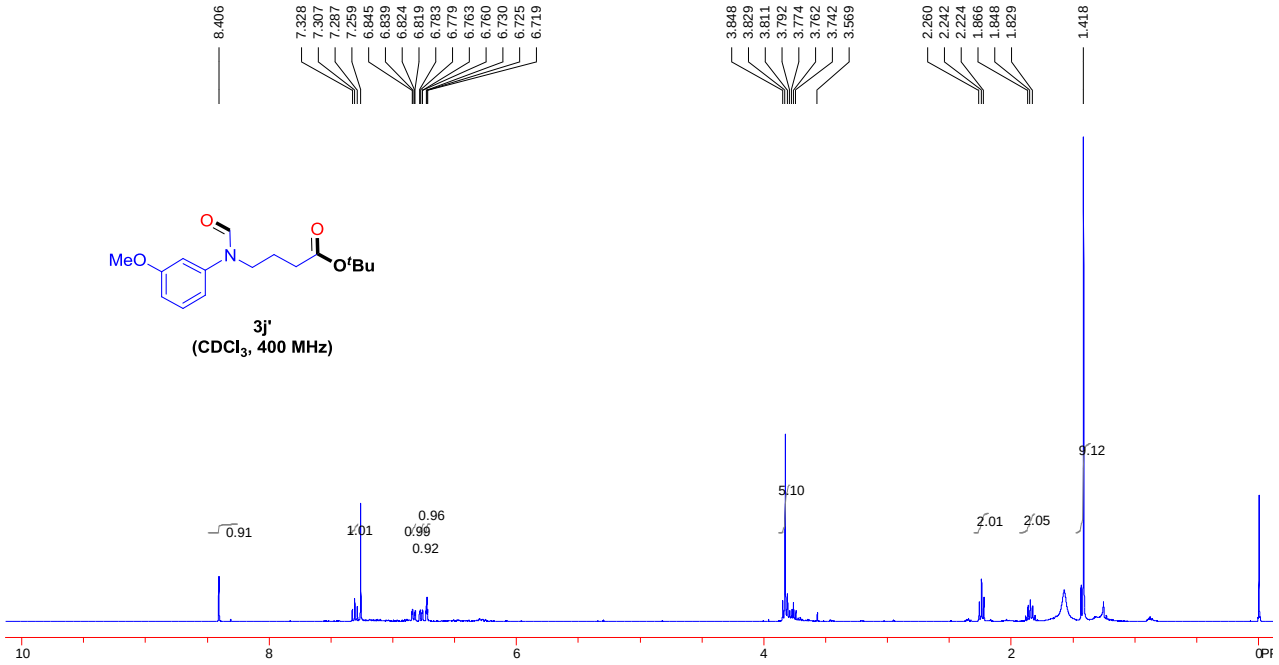
3f'
($CDCl_3$, 100 MHz)



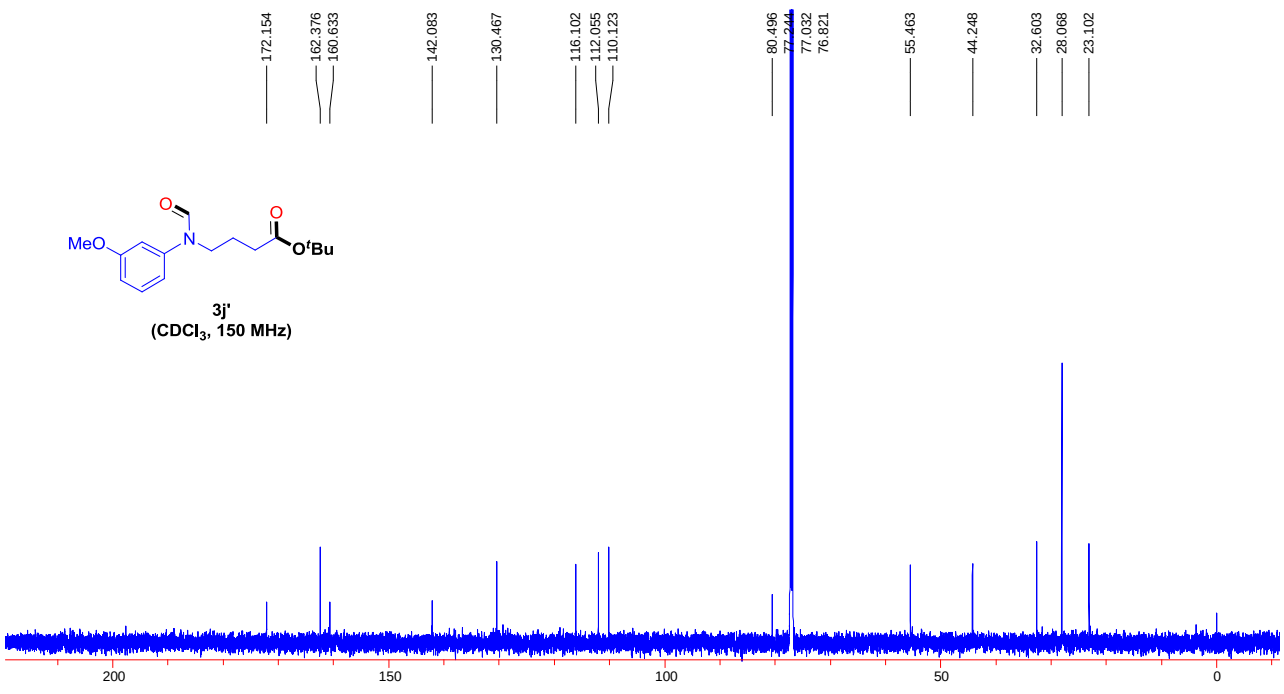
3f'
($CDCl_3$, 376 MHz)


8.364
7.549
7.544
7.527
7.520
7.268
7.087
7.065
3.840
3.822
3.804
2.255
2.237
2.218
1.845
1.826
1.808
1.420
O
N
O
O^{t}Bu
Br
3h'
(CDCl$_3$, 400 MHz)
9.06
1.01
1.97
1.95
1.97
1.99
2.04
10
8
6
4
2

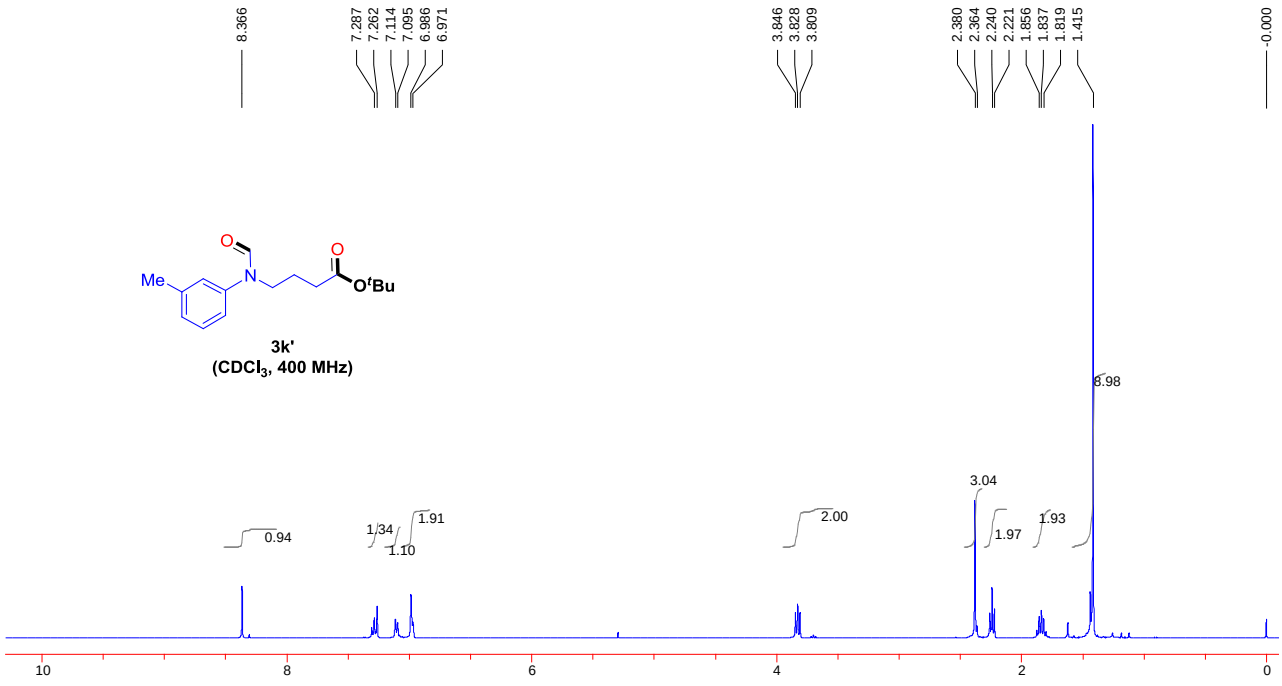

172.015
161.982
139.953
132.888
125.421
120.346
80.591
77.273
77.062
76.850
44.219
32.472
28.061
22.993
O
N
O
O^{t}Bu
Br
3h'
(CDCl$_3$, 150 MHz)
200
150
100
50
0

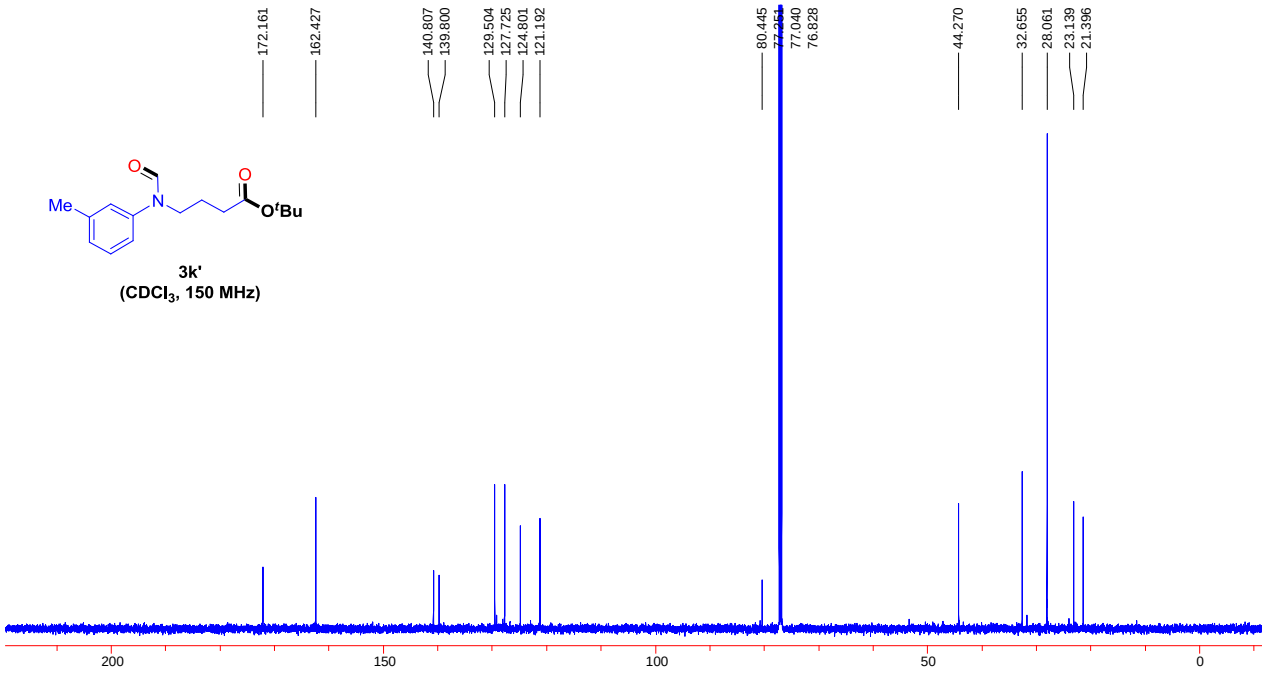


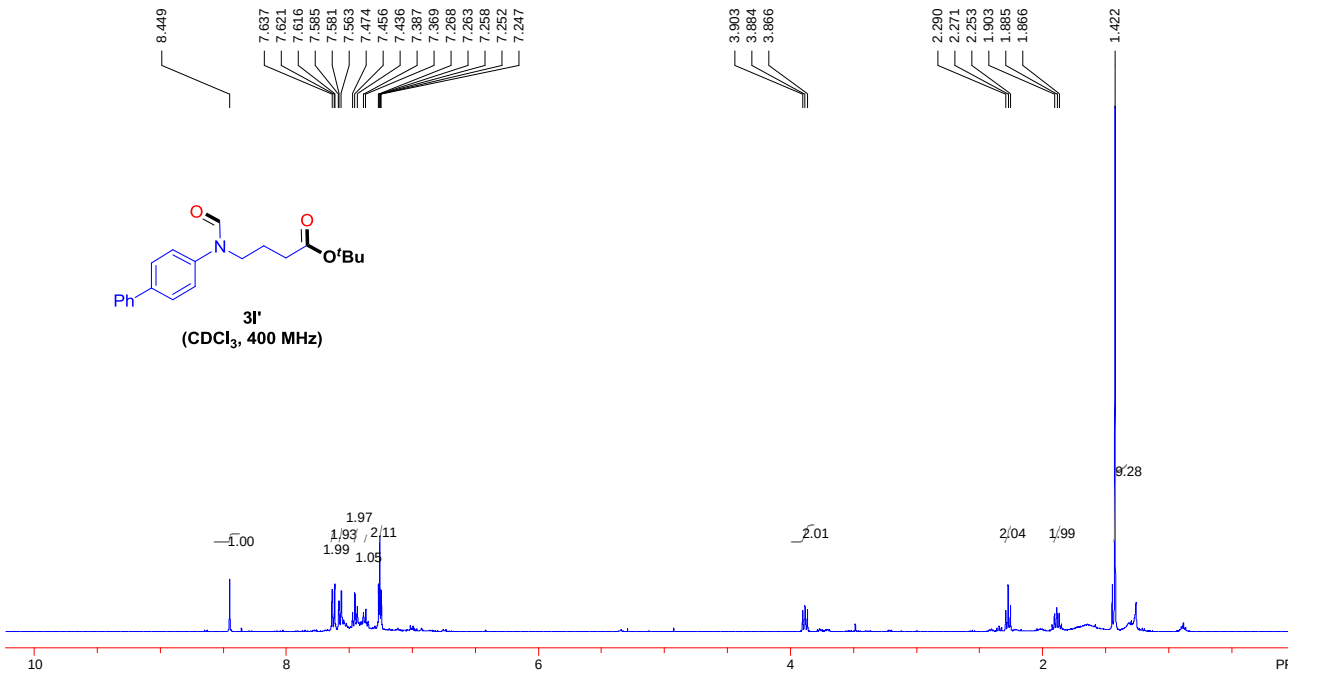
3j'
($CDCl_3$, 400 MHz)



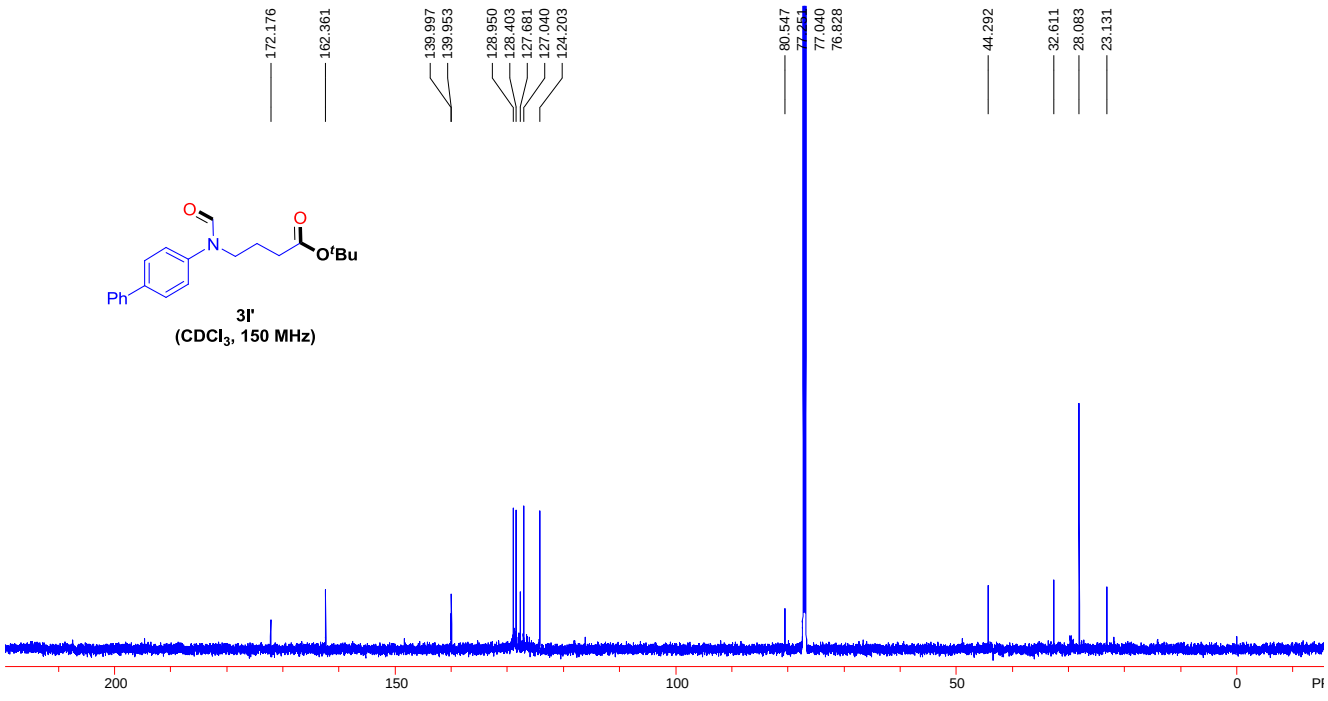
3j'
($CDCl_3$, 150 MHz)


8.366
7.287
7.262
7.114
7.095
6.986
6.971
3.846
3.828
3.809
2.380
2.364
2.240
2.221
1.856
1.837
1.819
1.415
-0.000
Me
O
N
O
O'Bu
3k'
(CDCl3, 400 MHz)
8.98
3.04
2.00
1.97
1.93
1.91
1.34
1.10
0.94
10
8
6
4
2
0

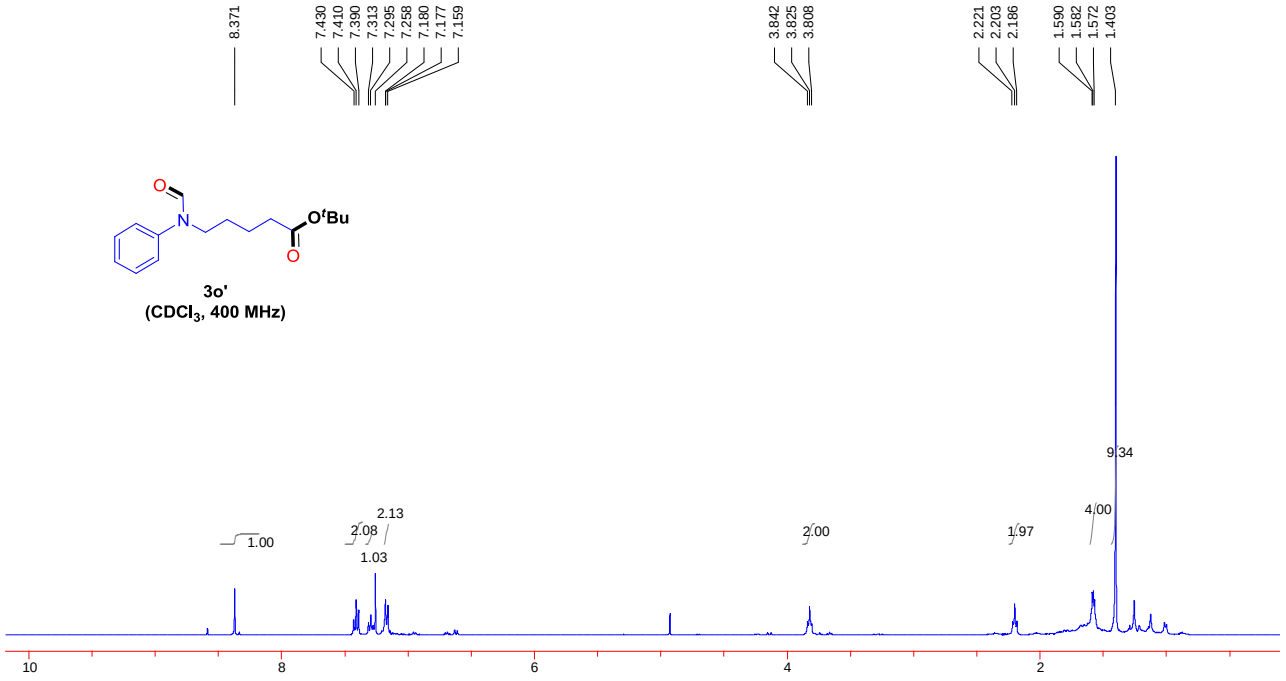

172.161
162.427
140.807
139.800
129.504
127.725
124.801
121.192
80.445
77.254
77.040
76.828
44.270
32.655
28.061
23.139
21.396
Me
O
N
O
O'Bu
3k'
(CDCl3, 150 MHz)
200
150
100
50
0

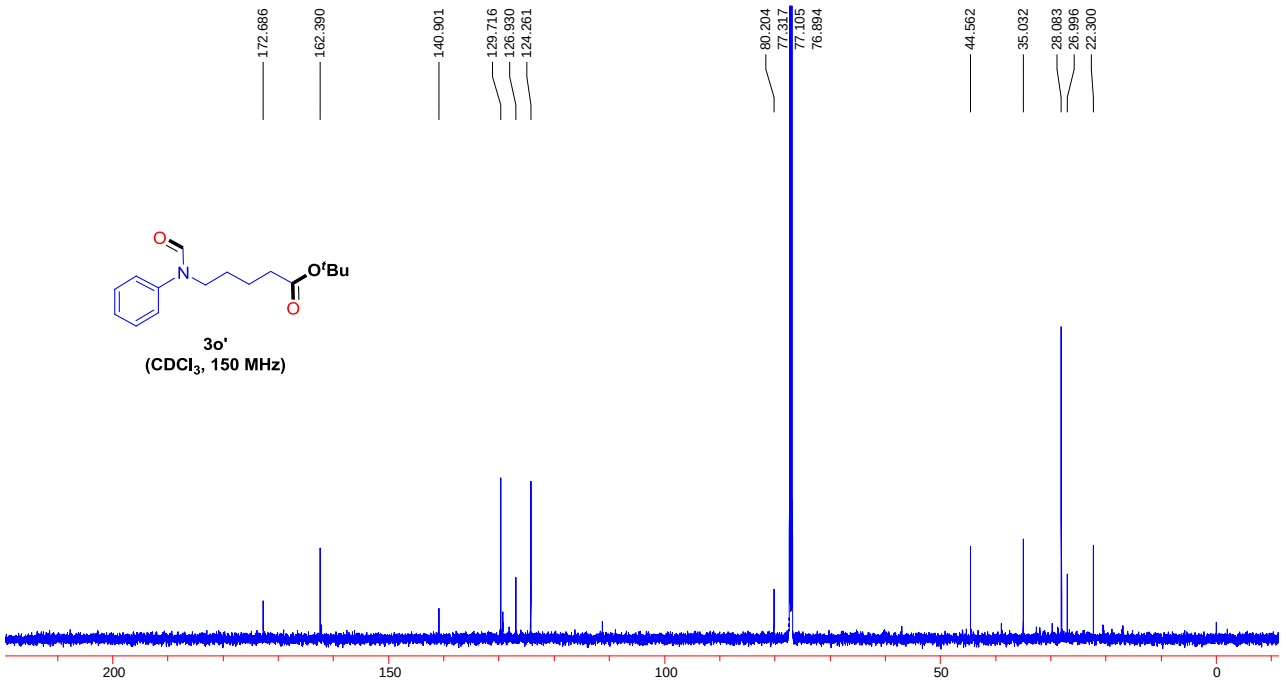


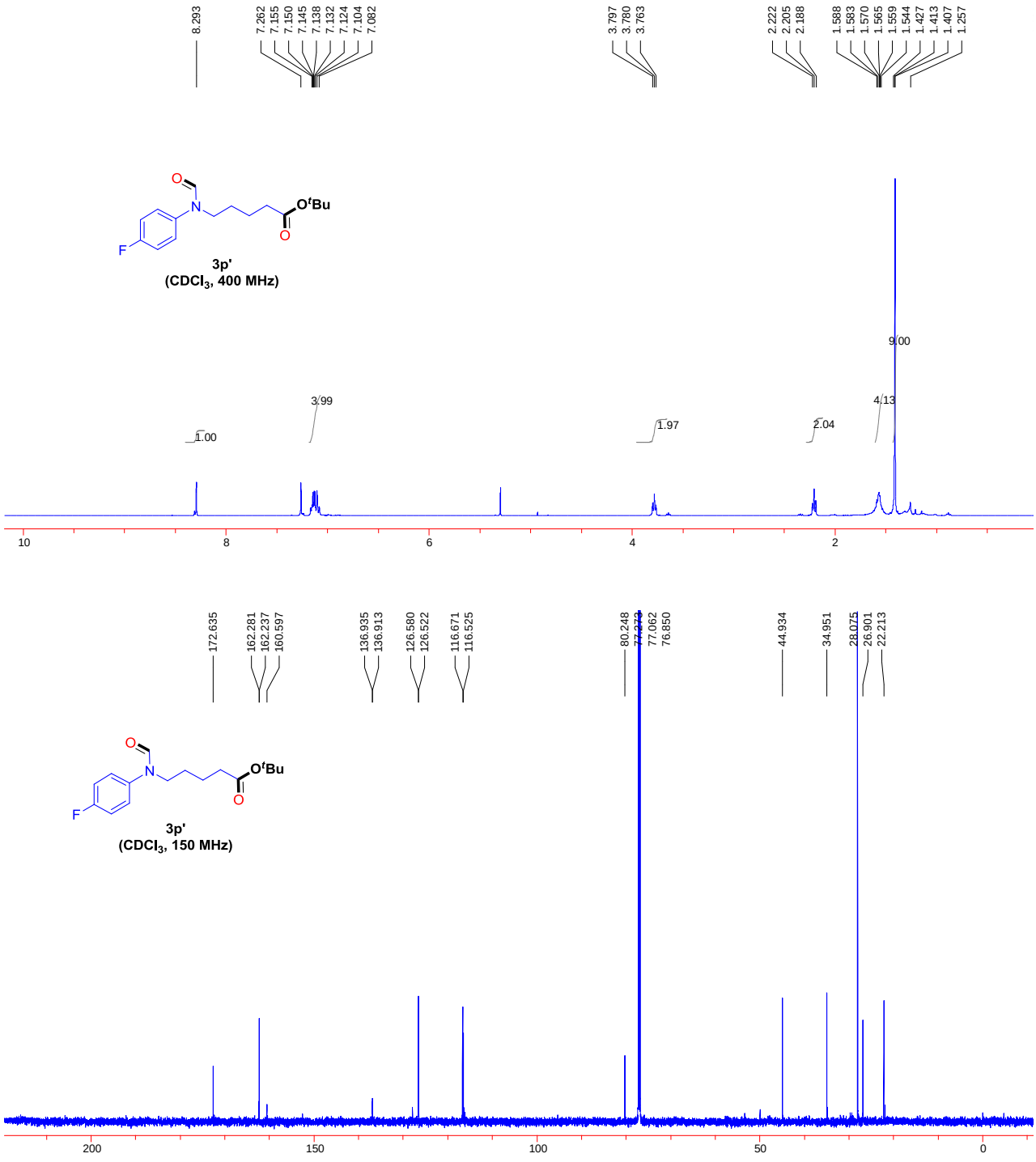
3l'
($CDCl_3$, 400 MHz)

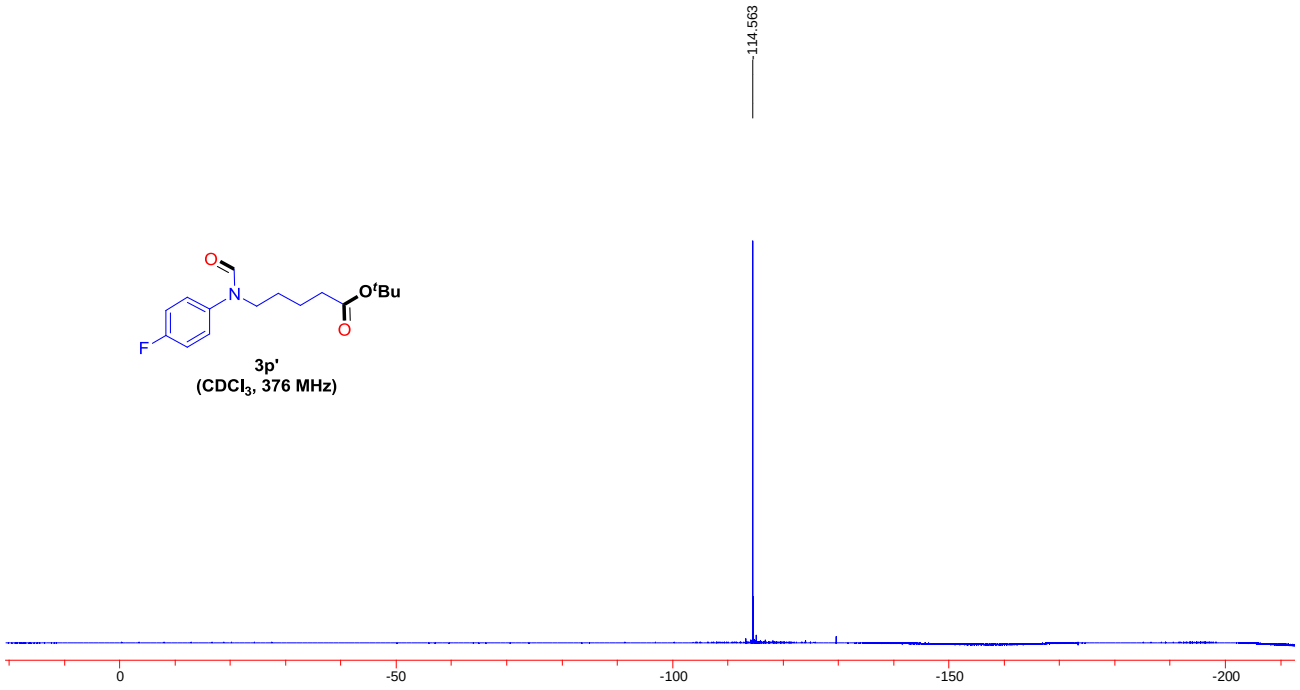


3l'
($CDCl_3$, 150 MHz)


8.371
7.430
7.410
7.390
7.313
7.295
7.258
7.180
7.177
7.159
3.842
3.825
3.808
2.221
2.203
2.186
1.590
1.582
1.572
1.403
O
N
O
O
O
O
tBu
3o'
(CDCl3, 400 MHz)
1.00
2.08
2.13
1.03
2.00
1.97
4.00
9.34
10
8
6
4
2

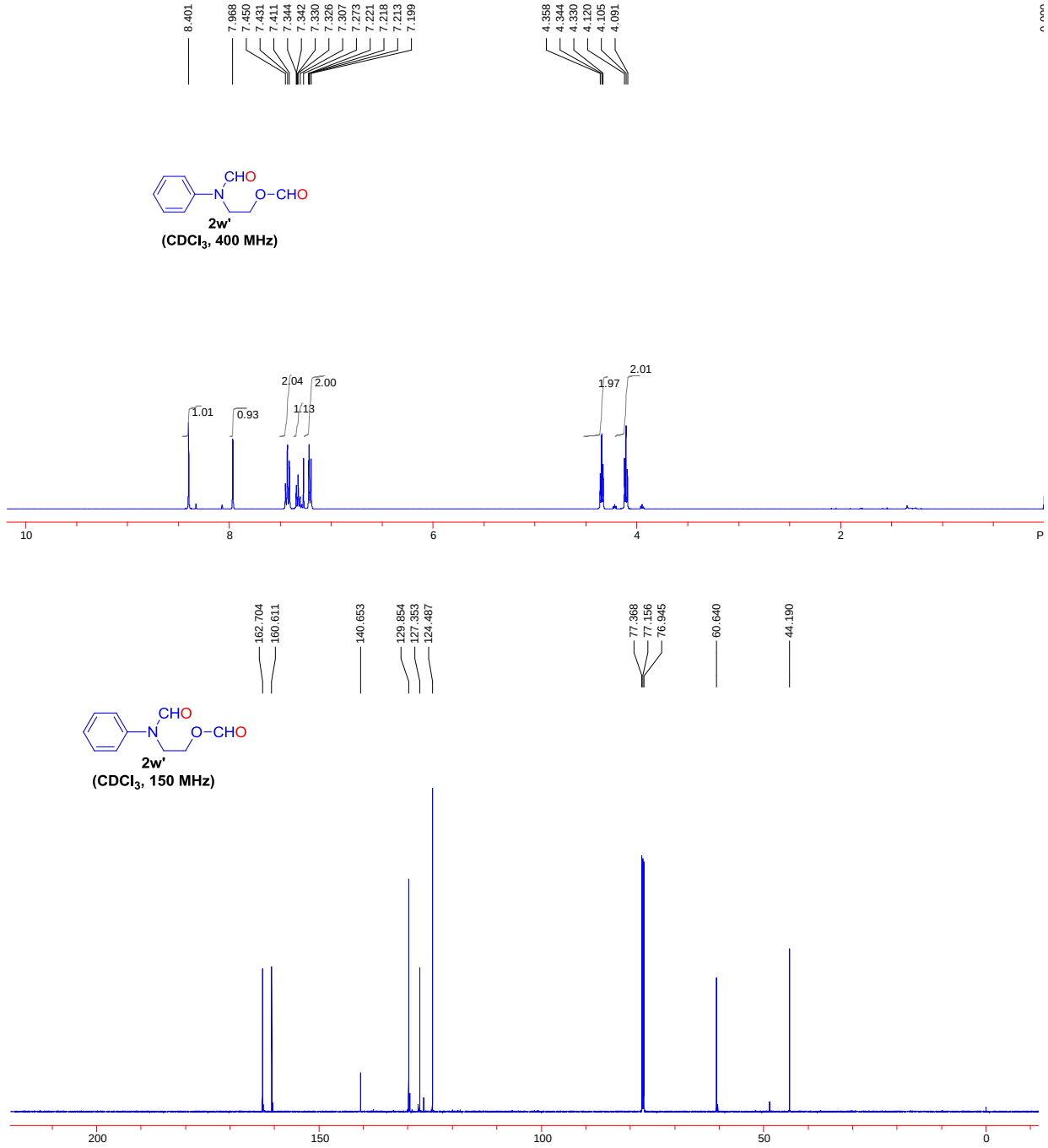

172.686
162.390
140.901
129.716
126.930
124.261
80.204
77.317
77.105
76.894
44.562
35.032
28.083
26.996
22.300
O
N
O
O
O
O
tBu
3o'
(CDCl3, 150 MHz)
200
150
100
50
0


8.293
7.262
7.155
7.150
7.145
7.138
7.132
7.124
7.104
7.082
3.797
3.780
3.763
2.222
2.205
2.188
1.588
1.583
1.570
1.565
1.559
1.544
1.427
1.413
1.407
1.257
O
N
O'Bu
O
F
3p'
(CDCl3, 400 MHz)
1.00
3.99
1.97
2.04
4.13
9.00
10
8
6
4
2
172.635
162.281
162.237
160.597
136.935
136.913
126.580
126.522
116.671
116.525
80.248
77.373
77.062
76.850
44.934
34.951
28.075
26.901
22.213
O
N
O'Bu
O
F
3p'
(CDCl3, 150 MHz)
200
150
100
50
0

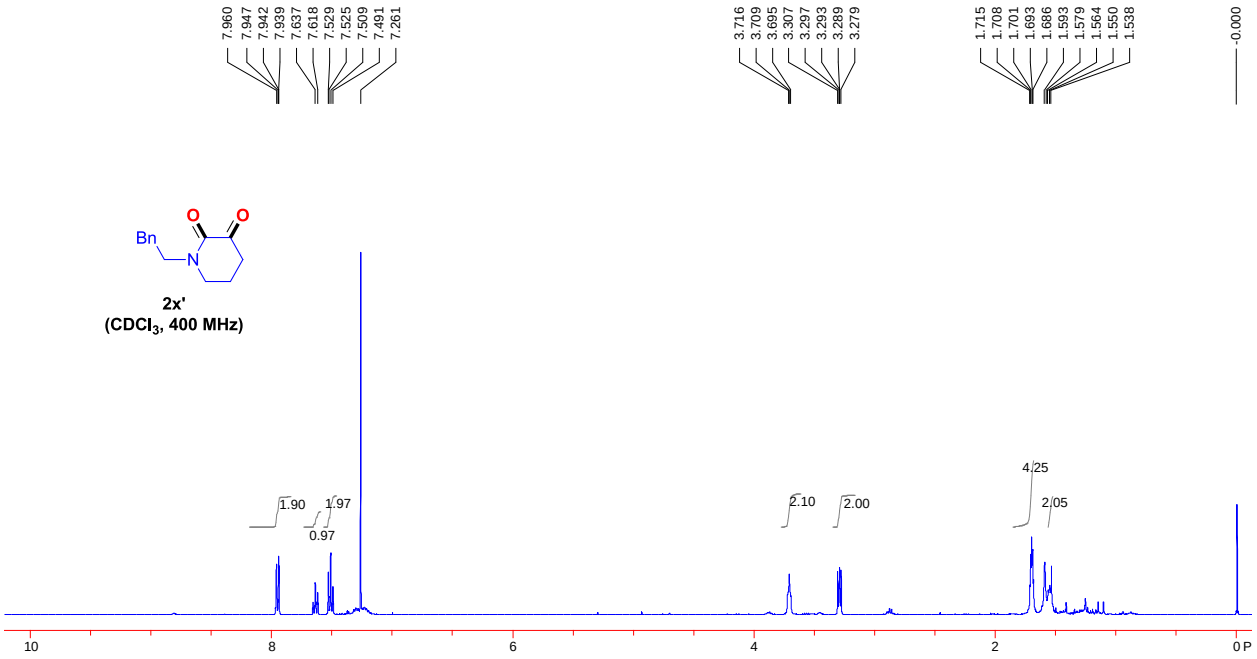


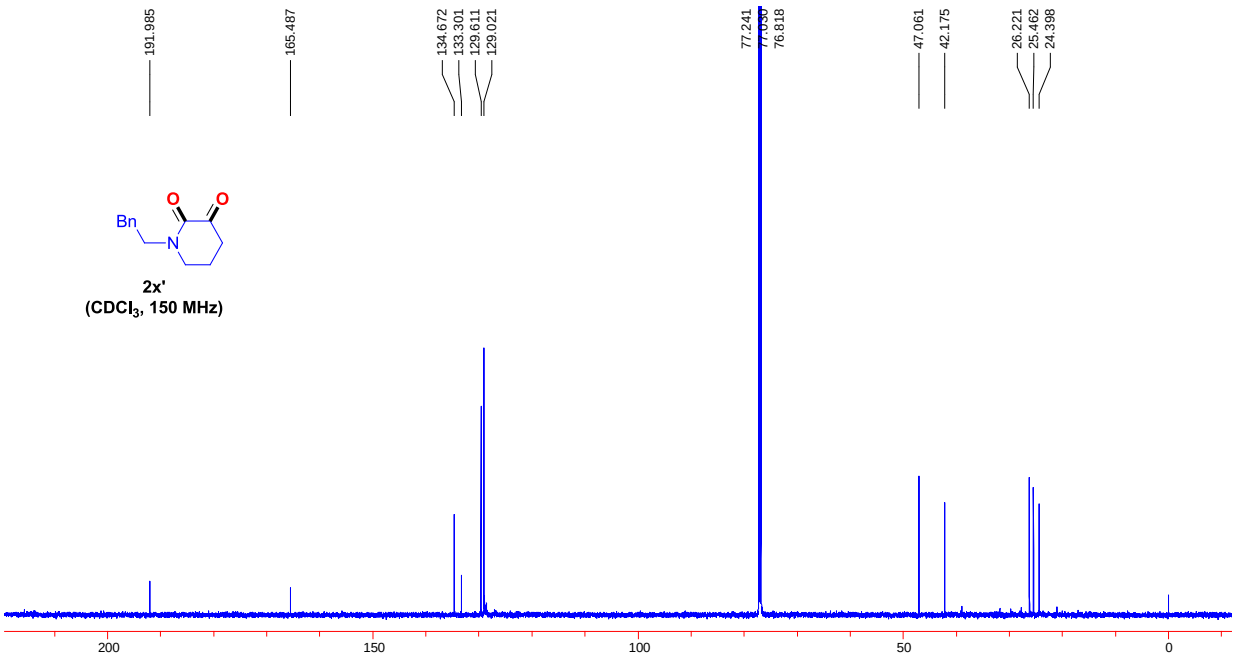
3p'
($CDCl_3$, 376 MHz)

VI. Copies of the NMR spectra of 2w’

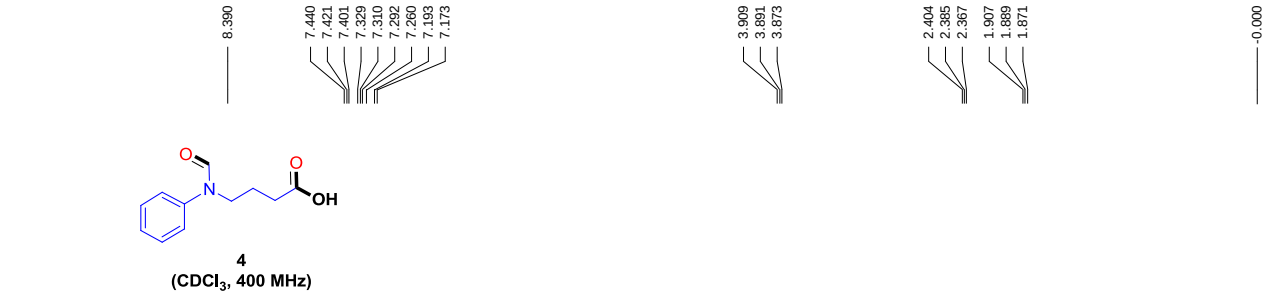


VII. Copies of the NMR spectra of 2x’

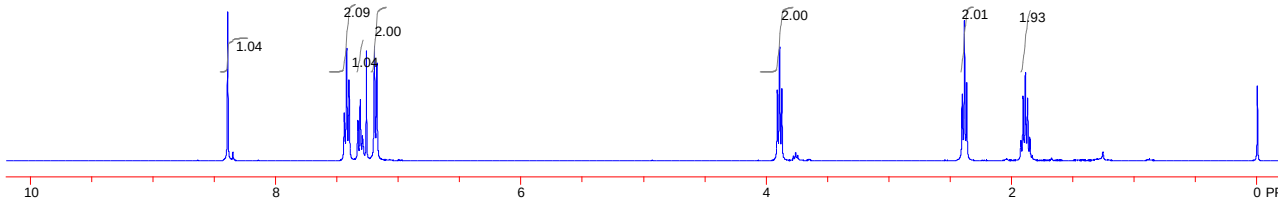


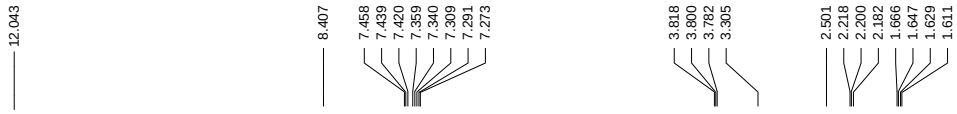


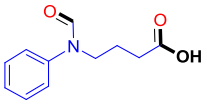
VIII. Copies of the NMR spectra of 4



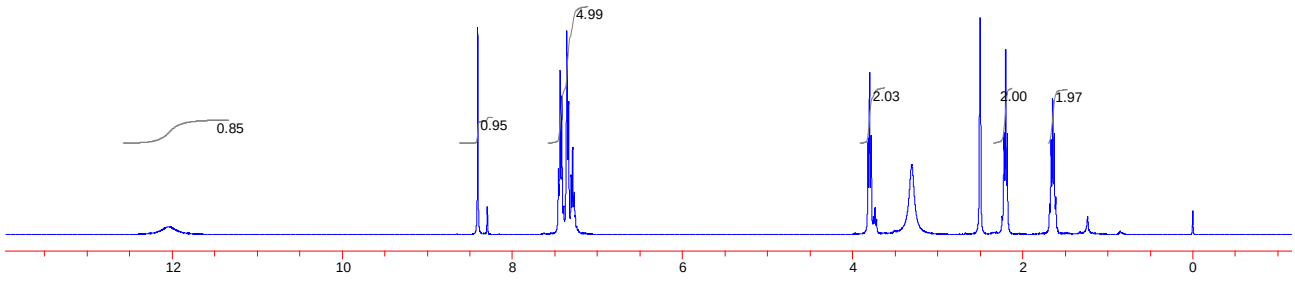
4
($CDCl_3$, 400 MHz)

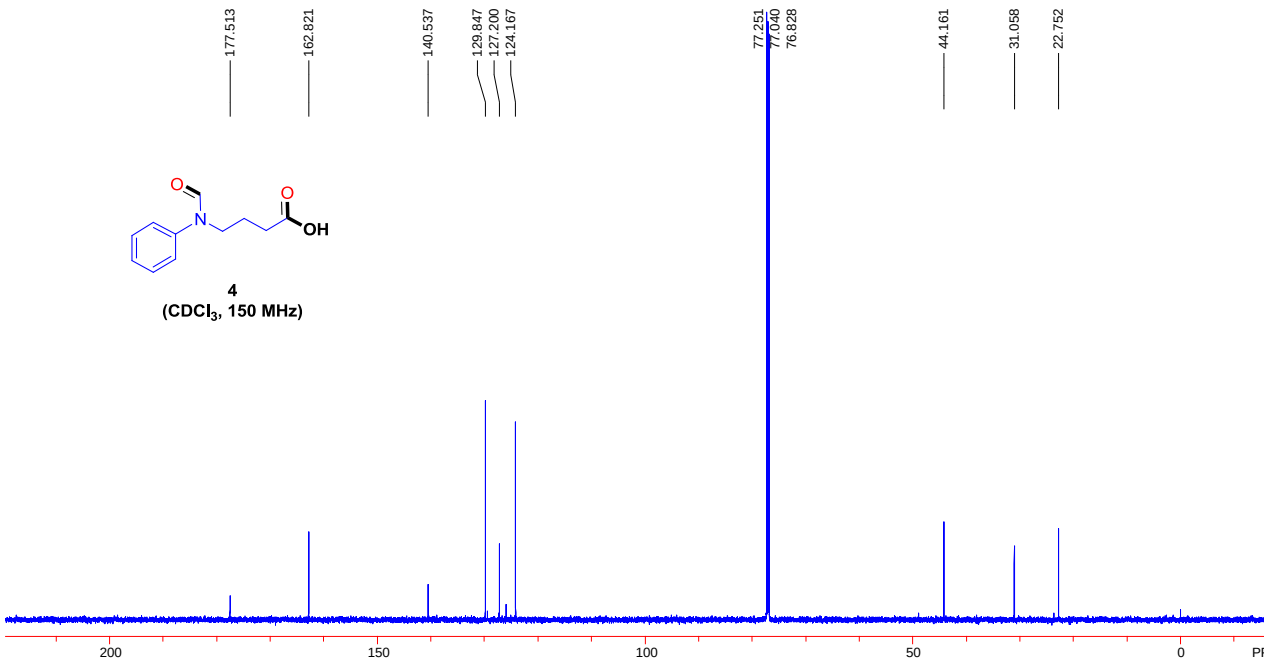






4
(DMSO-d_6, 400 MHz)

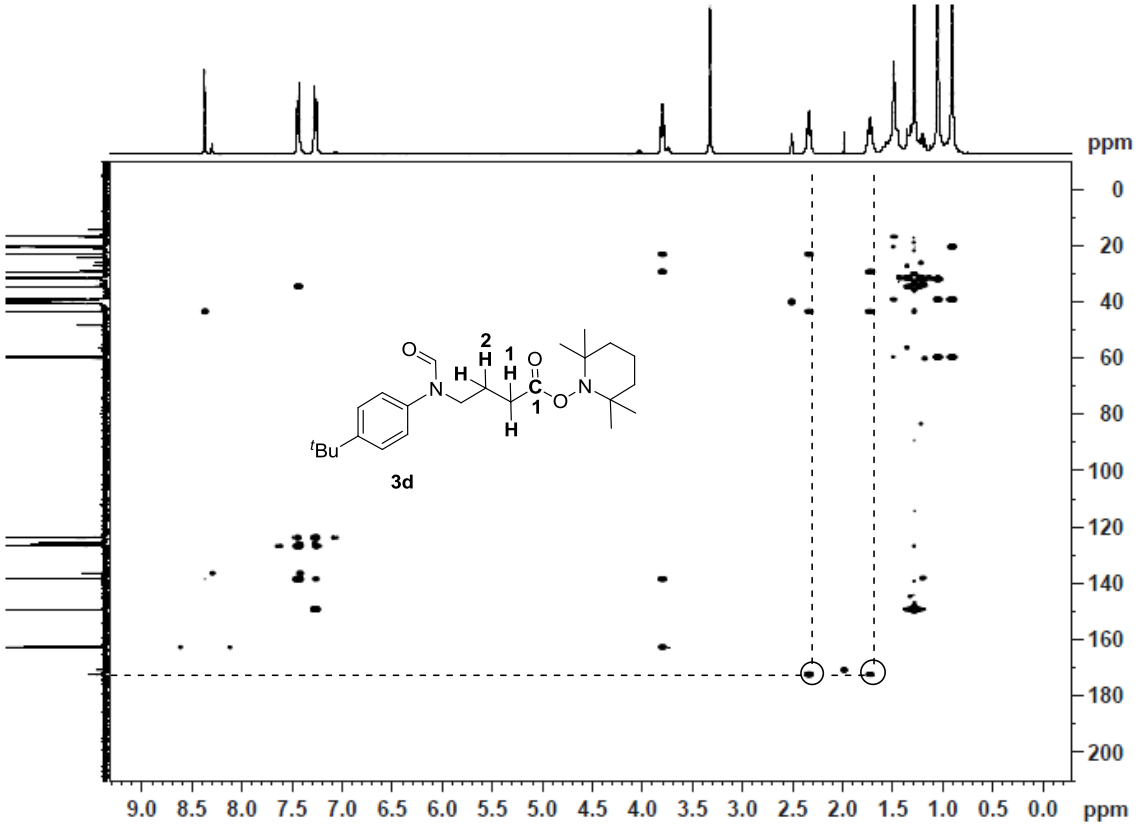




4
($CDCl_3$, 150 MHz)

IX. Copies of C-H HMBC of 3d

According to the cross-peaks of **3d**-H1 to **3d**-C1 and **3d**-H2 to **3d**-C1 appeared on the C-H HMBC spectrum of **3d**, we could deduce that the peak at 172.6 ppm, which is not obvious, should be **3d**-C1.



X. References

(1) H. Richter and O. G. Mancheño, *Eur. J. Org. Chem.*, 2010, 4460.

(2) F. Wang, Y. He, M. Tian, X. Zhang and X. Fan, *Org. Lett.*, 2018, **20**, 864.

(3) F. Wang, X. Zhang, Y. He and X. Fan, *Org. Biomol. Chem.*, 2019, **17**, 156.

(4) D. Kalyani, A. R. Dick, W. Q. Anani and M. S. Sanford. *Tetrahedron*, 2006, **62**, 11483.

(5) A. Correa and C. Bolm, *Angew. Chem., Int. Ed.*, 2007, **46**, 8862.