Electronic Supplementary Information

Photoinduced iodine-mediated tandem dehydrogenative Povarov cyclisation / C–H oxygenation reactions

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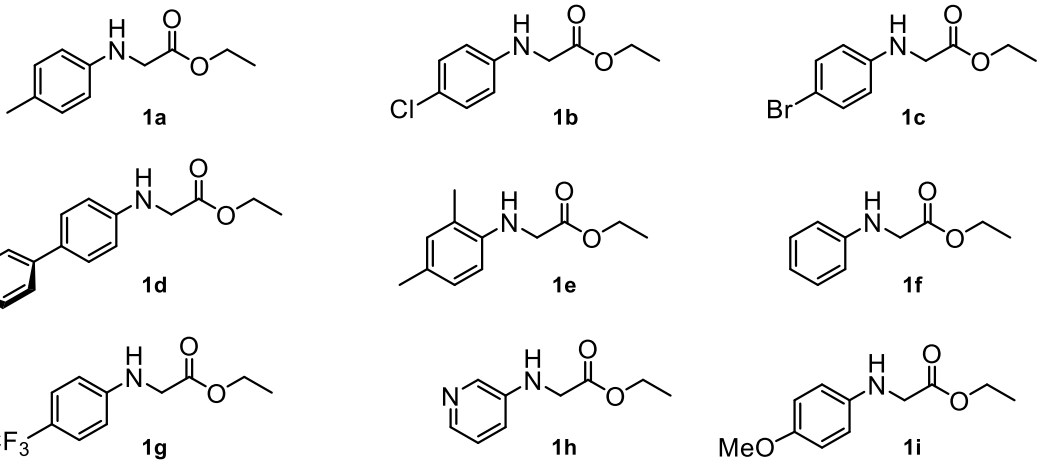
1. Synthesis of substrates 1

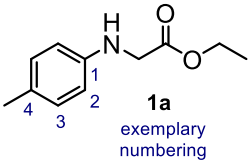
N-aryl glycine esters **1a-i** were prepared according to standard literature procedures.[1]



General procedure (GP 1):

Aniline (1.0 eq.) and NaOAc (1.1 eq.) were suspended in EtOH. Ethyl bromoacetate (1.0 eq.) was added and the mixture was stirred at reflux for 15 h under argon atmosphere. EtOH was removed in vacuo and the residue was partitioned between CH_2Cl_2 and NaCl aq. The aqueous layer was extracted with CH_2Cl_2 (3×) and the combined organic layers were dried with Na_2SO_4, filtered and evaporated. Column chromatography (silica) furnished the product **1**.

Ethyl-*p*-tolylglycinate (1a)

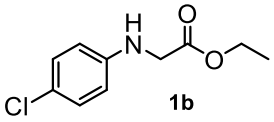


According to GP 1: 2.00 g *p*-Toluidine (18.7 mmol), 1.61 g NaOAc (19.6 mmol) and 2.07 mL ethyl bromoacetate (18.7 mmol) in 2.00 mL EtOH gave **1a** (2.53 g, 70%) after chromatography (EtOAc/heptane 1:5 + 0.5 Vol.-% NEt_3, R_f = 0.70) as colorless solid, m.p. 44 °C. **^{1}H-NMR (600 MHz, chloroform-*d*)** δ = 1.30 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 2.24 (q, 3 H, 4-CH_3), 3.88 (s, 2 H, CH_2), 4.15 (bs, 1 H, NH), 4.24 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 6.54 (d, ^3J = 8.3 Hz, 2 H, 2-H), 7.00 (d, ^3J = 8.3 Hz, 2 H, 3-H) ppm. **^{13}C-NMR (150 MHz, chloroform-*d*)** δ = 14.3 (q, CH_3-Et), 20.5 (q, CH_3), 46.4 (t, CH_2), 61.4 (t, CH_2-Et), 113.3 (d, C-2), 127.6 (s, C-4), 130.0 (d, C-3), 145.0 (s, C-1), 171.5 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[1a]

1 a) L. K. Baumann, H. M. Mbuvi, G. Du and L. K. Woo, *Organometallics*, 2007, **26**, 3995–4002. b) R. Rohlmann, T. Stopka, H. Richter and O. García Mancheño, *J. Org. Chem.*, 2013, **78**, 6050–6064. c) E. Schendera, L.-N. Unkel, P. P. Huyen Quyen, G. Salkewitz, F. Hoffmann, A. Villinger and M. Brasholz, *Chem. Eur. J.*, 2020, **26**, 269–274. d) I. Aviv and Z. Gross, *Chem. Eur. J.*, 2008, **14**, 3995–4005. e) J. S. M. Samec, L. Mony and J.-E. Bäckvall, *Can. J. Chem.*, 2005, **83**, 909–916.

Ethyl-(4-chlorophenyl)glycinate (1b)

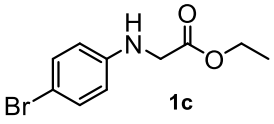


1b

According to GP 1: 1.13 g 4-Chloroaniline (8.83 mmol), 761 mg NaOAc (9.27 mmol) and 979 µL ethyl bromoacetate (8.83 mmol) in 1.00 mL EtOH gave **1b** (1.42 g, 75%) after chromatography (EtOAc/heptane 1:5 + 0.5 Vol.-% NEt_3, R_f = 0.30) as colorless solid, m.p. 92 °C. **^{1}H-NMR (400 MHz, chloroform-*d*)** δ = 1.30 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 3.86 (s, 2 H, CH_2), 4.24 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 6.50–6.55 (m, 2 H, 3-H), 7.10–7.16 (m, 2 H, 2-H) ppm. **^{13}C-NMR (101 MHz, chloroform-*d*)** δ = 14.3 (q, CH_3-Et), 46.0 (t, CH_2), 61.6 (t, CH_2-Et), 114.2 (d, C-3), 123.0 (s, C-4) 129.3 (d, C-2), 145.7 (s, C-1), 171.0 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[1b]

Ethyl-(4-bromophenyl)glycinate (1c)

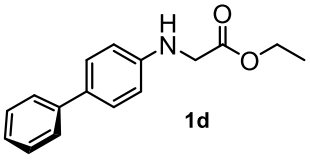


1c

According to GP 1: 972 mg 4-Bromoaniline (5.65 mmol), 487 mg NaOAc (5.93 mmol) and 627 µL ethyl bromoacetate (5.65 mmol) in 800 µL EtOH gave **1c** (1.19 g, 82%) after chromatography (Et_2O/PE 1:5 + 0.5 Vol.-% NEt_3, R_f = 0.49) as colorless solid, m.p. 98 °C. **^{1}H-NMR (400 MHz, chloroform-*d*)** δ = 1.30 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 3.86 (s, 2 H, CH_2), 4.25 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 6.50 (d, ^3J = 8.9 Hz, 2 H, 3-H), 7.27 (d, ^3J = 8.9 Hz, 2 H, 2-H) ppm. **^{13}C-NMR (101 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 45.8 (t, CH_2), 61.5 (t, CH_2-Et), 110.4 (s, C-4), 114.7 (d, C-3), 132.1 (d, C-2), 145.9 (s, C-1), 170.7 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[1b]

Ethyl-[1,1'-biphenyl]-4-ylglycinate (1d)



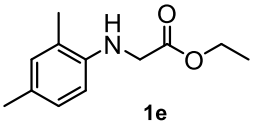
1d

According to GP 1: 508 mg 4-Phenylaniline (3.00 mmol), 258 mg NaOAc (3.15 mmol) and 474 µL ethyl bromoacetate (3.00 mmol) in 500 µL EtOH gave **1d** (342 mg, 45%) after chromatography (Et_2O/heptane 1:1+ 0.5 Vol.-% NEt_3, R_f = 0.33) as colorless solid, m.p. 100 °C. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.32 (t, ^3J = 7.2 Hz, 3 H, Et-CH_3), 3.96 (s, 2 H, CH_2), 4.28 (q, ^3J = 7.2 Hz, 2 H, Et-CH_2), 6.70 (d, ^3J = 8.6 Hz, 2 H, 2-H), 7.25–7.30 (m, 1 H, 4'-H), 7.40 (dd, ^3J = 7.0 Hz, ^3J = 8.5 Hz, 2 H, 3'-H), 7.45–7.49 (m, 2 H, 3-H), 7.52–7.57 (m, 2 H, 2'-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.4 (q, CH_3-Et), 46.0 (t, CH_2), 61.6 (t, CH_2-Et), 113.4 (d, C-2), 126.4 (d, C-4'), 126.5 (d, C-2'), 128.3 (d, C-3), 128.8 (d, C-3'), 131.3 (s, C-4), 141.2 (s, C-1'), 146.6 (s, C-1), 171.2 (s, CO_2Et) ppm.

1b R. Rohlmann, T. Stopka, H. Richter and O. García Mancheño, *J. Org. Chem*., 2013, **78**, 6050–6064.

Spectroscopic data are in agreement with the literature.[1b]

Ethyl-(2,4-dimethylphenyl)glycinate (1e)

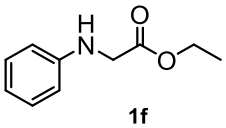


1e

According to GP 1: 606 mg 2,4-Dimethylaniline (5.00 mmol), 431 mg NaOAc (5.25 mmol) and 554 µL ethyl bromoacetate (5.00 mmol) in 800 µL EtOH gave **1e** (849 mg, 82%) after chromatography (Et_2O/heptane 1:1+ 0.5 Vol.-% NEt_3, R_f = 0.67) as light-red liquid. **^{1}H-NMR (500 MHz, acetone-d_6)** δ = 1.24 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 2.13 (s, 3 H, 2-CH_3), 2.16 (s, 3 H, 4-CH_3), 3.93 (d, ^3J = 5.9 Hz, 2 H, CH_2), 4.17 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 4.50 (bs, 1 H, NH), 6.38 (d, ^3J = 8.7 Hz, 1 H, 6-H), 6.81–6.86 (m, 2 H, 3-H, 5-H) ppm. **^{13}C-NMR (126 MHz, acetone-d_6)** δ = 14.5 (q, CH_3-Et), 17.5 (q, CH_3-2), 20.4 (q, CH_3-4), 46.4 (t, CH_2), 61.3 (t, CH_2-Et), 110.7 (d, C-6), 123.0 (s, C-2), 126.5 (s, C-4), 128.0 (d, C-5), 131.6 (d, C-3), 144.5 (s, C-1), 172.1 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[1c]

Ethyl phenylglycinate (1f)

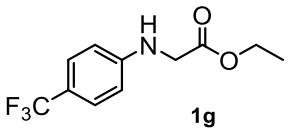


1f

According to GP 1: 1.68 g Aniline (18.0 mmol), 1.67 g NaOAc (20.4 mmol) and 2.00 mL ethyl bromoacetate (18.0 mmol) in 4.0 mL EtOH gave **1f** (2.3 g, 70%) after chromatography (EtOAc/PE 1:5 + 0.5 Vol.-% NEt_3, R_f = 0.60) as orange solid, m.p. 49–51 °C. **^{1}H-NMR (600 MHz, chloroform-d)** δ = 1.30 (t, ^3J = 7.1 Hz, 3-H, Et-CH_3), 3.90 (d, ^3J = 5.5 Hz, 2 H, CH_2), 4.25 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 4.27 (bs, 1 H, NH), 6.58–6.65 (m, 2 H, 2-H), 6.75 (tt, ^4J = 1.1 Hz, ^3J = 7.3 Hz, 1 H, 4-H), 7.16–7.23 (m, 2 H, 3-H) ppm. **^{13}C-NMR (150 MHz, chloroform-d)** δ = 14.4 (q, CH_3-Et), 46.1 (t, CH_2), 61.5 (t, CH_2-Et), 113.0 (d, C-2), 118.2 (d, C-4), 129.3 (d, C-3), 147.0 (s, C-1), 171.3 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[1d]

Ethyl (4-(trifluoromethyl)phenyl)glycinate (1g)



1g

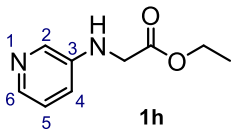
According to GP 1: 483 mg 4-(Trifluoromethyl)aniline (3.00 mmol), 258 mg NaOAc (3.15 mmol) and 333 µL ethyl bromoacetate (3.00 mmol) in 500 µL EtOH gave **1g** (350 mg, 47%) after chromatography (EtOAc/heptane 1:2 +

1b R. Rohlmann, T. Stopka, H. Richter and O. García Mancheño, *J. Org. Chem*., 2013, **78**, 6050–6064.
1c E. Schendera, L.-N. Unkel, P. P. Huyen Quyen, G. Salkewitz, F. Hoffmann, A. Villinger and M. Brasholz, *Chem. Eur. J.*, 2020, **26**, 269–274.
1d I. Aviv and Z. Gross, *Chem. Eur. J.*, 2008, **14**, 3995–4005.

0.5 Vol.-% NEt_3, R_f = 0.35) as colorless solid, m.p. 86 °C. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.31 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 3.93 (s, 2 H, CH_2), 4.28 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 4.56 (bs, 1 H, NH), 6.56–6.69 (m, 2 H, 2-H), 7.38–7.51 (m, 2 H, 3-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.3 (q, CH_3-Et), 45.4 (t, CH_2), 61.5 (t, CH_2-Et), 112.3 (d, C-2), 119.9 (d, ^2J = 32.7 Hz, C-4) 126.1 (q, ^1J = 270.5 Hz, CF_3-4), 126.8 (q, ^3J = 3.9 Hz, C-3), 149.5 (s, C-1), 170.6 (s, CO_2Et) ppm. **^{19}F-NMR (471 MHz, chloroform-*d*)** δ = -61.2 (s, 1 F, CF_3) ppm.

Spectroscopic data are in agreement with the literature.[1b]

Ethyl pyridin-3-ylglycinate (1h)

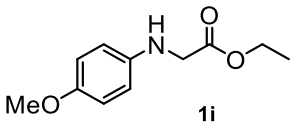


1h

940 mg 3-Aminopyridine (10.0 mmol) was solved in 28 mL DMF and the solution was added to a refluxing solution of 8.17 mL ethyl glyoxylate (50% solution in toluene, 40.0 mmol). The resulting mixture was cooled to room temperature and stirred for 30 min. 2.51 g Sodium cyanoborohydride (40.0 mmol) was added and the resulting mixture was stirred for 1 h. The solution was diluted with 300 mL EtOAc and quenched with 200 ml saturated aqueous $NaHCO_3$. The organic layer was washed with 0.5 M aqueous $NaHCO_3$, brine, dried with Na_2SO_4, filtered and evaporated to dryness. Column chromatography (EE, R_f = 0.42) furnished the product **1h** (329 mg, 18%) as yellow oil. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.30 (t, ^3J = 7.2 Hz, 3 H, Et-CH_3), 3.91 (s, 2 H, CH_2), 4.25 (q, ^3J = 7.2 Hz, 2 H, Et-CH_2), 4.38 (bs, 1 H, NH), 6.87 (ddd, ^4J = 1.4 Hz, ^4J = 2.9 Hz, ^3J = 8.3 Hz, 1 H, 4-H), 7.10 (dd, ^3J = 4.7 Hz, ^3J = 8.3 Hz, 2 H, 5-H), 8.01 (dd, ^4J = 1.4 Hz, ^3J = 4.7 Hz, 2 H, 6-H), 8.05 (d, ^4J = 2.9 Hz, 1 H, 2-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.3 (q, CH_3-Et), 44.4 (t, CH_2), 61.7 (t, CH_2-Et), 119.2 (d, C-4), 123.9 (d, C-5), 136.0 (d, C-2), 139.6 (d, C-6), 143.1 (s, C-3), 170.7 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[2]

Ethyl-(4-methoxyphenyl)glycinate (1i)



1i

According to GP 1: 616 mg *p*-Anisidine (5.00 mmol), 431 mg NaOAc (5.25 mmol) and 554 µL Ethyl bromoacetate (5.00 mmol) in 800 µL EtOH gave **1i** (905 mg, 87%) after chromatography (Et_2O/heptane 1:1 + 0.5 Vol.-% NEt_3, R_f = 0.57) as yellow solid, m.p. 49 °C. **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 1.30 (t, ^3J = 7.3 Hz,

1b R. Rohlmann, T. Stopka, H. Richter and O. García Mancheño, *J. Org. Chem*., 2013, **78**, 6050–6064.

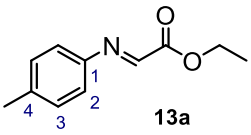
2 J. R. Tata, K. Chapman, J. L. Duffy, N. J. Kevin, Y. Cheng, T. A. Rano, F. Zhang, T. Huening, B. A. Kirk, Z. Lu, S. Raghavan, F. J. Fleitz, D. E. Petrillo, J. D. I. Armstrong, R. J. Varsolona, D. Askin, R. S. Hoerrner and R. Purick WO 2001038332 A1, May 31, 2001.

3 H, Et-CH_3), 3.75 (q, 3 H, OCH_3), 3.87 (s, 2 H, CH_2), 4.11 (bs, 1 H, NH), 4.24 (q, ^3J = 7.3 Hz, 2 H, Et-CH_2), 6.61 (ddd, ^4J = 2.6 Hz, ^4J = 3.4 Hz, ^3J = 9.2 Hz, 2 H, 3-H), 6.80 (ddd, ^4J = 2.6 Hz, ^4J = 3.4 Hz, ^3J = 9.2 Hz, 2 H, 2-H) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 46.8 (t, CH_2), 55.7 (q, C-OCH_3), 61.2 (t, CH_2-Et), 114.4 (d, C-3), 114.9 (d, C-2), 141.2 (s, C-1), 152.6 (s, C-4), 171.4 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[1e]

2. Synthesis of Imine 13

Ethyl (*E*)-2-(p-tolylimino)acetate (13a)



13a

198 µL Ethyl glyoxylate (1.00 mmol) was solved in 10 mL DCM. 204 mg *p*-Toluidine (1.00 mmol) and 205 mg $MgSO_4$ (1.70 mmol) were added and the reaction mixture was stirred at room temperature for 2 h. $MgSO_4$ was filtered off and the solvent was removed in vacuo. The desired product **13a** (177 mg, 93%) was used without further purification as yellow oil, R_f = 0.68 (EtOAc/toluene 1:10). **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 1.41 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 2.38 (s, 3 H, 4-CH_3), 4.42 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 7.19–7.25 (m, 4 H, 2-H, 3-H), 7.93 (s, 1 H, CH) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 14.4 (q, CH_3-Et), 21.3 (q, CH_3-4), 62.2 (t, CH_2-Et), 121.7 (d, C-2), 130.0 (d, C-3), 139.2 (s, C-4), 146.4 (s, C-1), 150.2 (d, CH), 163.6 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[3]

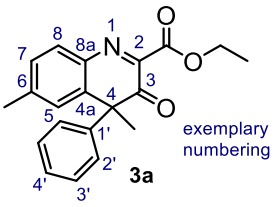
1e J. S. M. Samec, L. Mony and J.-E. Bäckvall, *Can. J. Chem.*, 2005, **83**, 909–916.
3 C. Retich and S. Bräse, *Eur. J. Org. Chem.*, 2018, 60–77.

3. Synthesis of products 3

General procedure (GP 2):

In a 10 mL crimp cap vial, *N*-aryl glycine ester **1** (typically 0.20 mmol) and styrene derivative **2** (or β-methylstyrene **9** or 2,3-dihydrofuran **11** respectively; typically 0.10 mmol) were dissolved in MeCN (3.50 mL per 0.10 mmol of **2**). I_2 (50 mol-%) was added, the vial was sealed and fitted with an O_2-balloon (septum pierced by needle). The mixture was irradiated between two blue CFL lamps (2×18 W, 450±50 nm) with rapid stirring for 48 h. The mixture was poured into $NaHCO_3$ aq. and $Na_2S_2O_3$ aq. followed by extraction with EtOAc (3×). The combined organic layers were dried with Na_2SO_4, filtered and evaporated to dryness. Column chromatography (silica) furnished the product **3**.

Ethyl 4,6-dimethyl-3-oxo-4-phenyl-3,4-dihydroquinoline-2-carboxylate (3a)

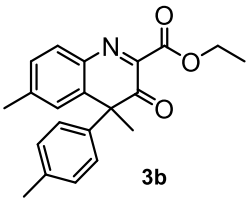


3a

According to GP 2: 43.2 mg (223 µmol) **1a**, 13.2 mg (111 µmol) **2a**, 14.1 mg (56.0 µmol) I_2 in 3.70 mL MeCN gave **3a** (23.7 mg, 74%) after chromatography (EtOAc/toluene 1:10, R_f = 0.52) as yellow oil. **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 1.33 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.86 (s, 3 H, 4-CH_3), 2.42 (s, 3 H, 6-CH_3), 4.35 (m_c, 2 H, Et-CH_2), 6.95–7.03 (m, 2 H, 2'-H), 7.11–7.15 (m, 1 H, 5-H), 7.22–7.31 (m, 4 H, 3'-H, 4'-H, 7-H), 7.65 (d, ^3J = 7.9 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 22.0 (q, CH_3-6), 22.5 (q, CH_3-4), 55.4 (s, C-4), 62.3 (t, CH_2-Et), 127.5 (d, C-2'), 128.1 (d, C-4'), 128.9 (d, C-5), 129.0 (d, C-3'), 129.6 (d, C-7), 131.8 (d, C-8), 137.9 (s, C-Ar), 138.0 (s, C-Ar), 139.3 (s, C-Ar), 142.3 (s, C-6), 150.9 (s, C-2), 163.0 (s, CO_2Et), 194.0 (s, C-3) ppm. **HR-MS (ESI+):** *m/z* calc.: $C_{20}H_{19}NO_3$ $[M+H]^+$: 322.1443, found: 322.1439. **IR:** $\tilde{\nu}$ = 3007 (=C-H), 2938 (-C-H), 1735 (-C=O), 1704 (-C=O), 1565 (-C=C), 1496 (-C=C), 1448 (-C=C), 1370 (-CH_3), 1330 (C-N), 1017 (-C-O-C), 829 (=C-H) cm^{-1}.

Spectroscopic data are in agreement with the literature.[4]

Ethyl 4,6-dimethyl-3-oxo-4-(p-tolyl)-3,4-dihydroquinoline-2-carboxylate (3b)


3b

According to GP 2: 39.5 mg (204 µmol) **1a**, 13.5 mg (102 µmol) **2b**, 12.9 mg (51.2 µmol) I_2 in 3.40 mL MeCN gave **3b** (19.9 mg, 59%) after chromatography (EtOAc/toluene 1:20, R_f = 0.54) as yellow oil. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = = 1.34 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.84 (s, 3 H, 4-CH_3), 2.28 (s, 3 H, 4'-CH_3), 2.42 (s, 3 H, 6-CH_3), 4.35 (m_c, 2 H, Et-CH_2), 6.87 (d, ^3J = 8.3 Hz, 2 H, 2'-H), 7.06 (d, ^3J = 8.3 Hz, 2 H, 3'-H), 7.14 (d, ^4J = 1.9 Hz, 1 H, 5-H), 7.26 (d, ^3J = 7.9 Hz, 1 H, 7-H), 7.64 (d, ^3J = 7.9 Hz, 1 H, 8-H) ppm. **^{13}C-NMR**

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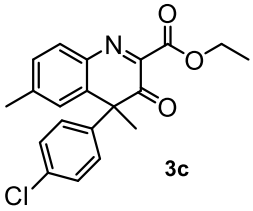
(126 MHz, chloroform-*d*) δ = 14.2 (q, CH_3-Et), 21.1 (q, CH_3-4'), 22.0 (q, CH_3-6), 22.4 (q, CH_3-4), 55.1 (s, C-4), 62.3 (t, CH_2-Et), 127.4 (d, C-2'), 128.8 (d, C-5), 129.5 (d, C-7), 129.7 (d, C-3'), 131.8 (d, C-8), 136.2 (s, C-1'), 137.9 (s, C-4a), 138.0 (s, C-4'), 138.2 (s, C-8a), 142.2 (s, C-6), 151.0 (s, C-2), 163.0 (s, CO_2Et), 193.9 (s, C-3) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{21}H_{21}NO_3$ $[M+H]^+$: 358.1418, found: 358.1422. **IR:** $\tilde{\nu}$ = 3010 (=C-H), 2936 (CH_3), 1735 (-C=O), 1701 (-C=O), 1565 (-C=C), 1510 (-C=C), 1373 (-CH_3), 1328 (C-N), 1022 (-C-O-C), 954 (=C-H), 829 (=C-H) cm^{-1}.

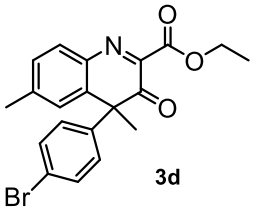
Ethyl 4-(4-chlorophenyl)-4,6-dimethyl-3-oxo-3,4-dihydroquinoline-2-carboxylate (3c)



3c

According to GP 2: 38.5 mg (204 µmol) **1a**, 15.2 mg (99.6 µmol) **2c**, 12.7 mg (50.0 µmol) I_2 in 3.30 mL MeCN gave **3c** (23.6 mg, 67%) after chromatography (EtOAc/toluene 1:20, R_f = 0.55) as yellow oil. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.35 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.84 (s, 3 H, 4-CH_3), 2.42 (s, 3 H, 6-CH_3), 4.36 (m_c, 2 H, Et-CH_2), 6.89–6.97 (m, 2 H, 2'-H), 7.08 (d, ^4J = 1.9 Hz, 1 H, 5-H), 7.22–7.25 (m, 2 H, 3'-H), 7.28 (dd, ^4J = 1.9 Hz, ^3J = 8.0 Hz, 1 H, 7-H), 7.65 (d, ^3J = 8.0 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 22.0 (q, CH_3-6), 22.8 (q, CH_3-4), 54.9 (s, C-4), 62.4 (t, CH_2-Et), 128.8 (d, C-5), 129.0 (d, C-2'), 129.2 (d, C-3'), 129.9 (d, C-7), 132.0 (d, C-8), 134.3 (s, C-Ar), 137.6 (s, C-Ar), 137.8 (s, C-Ar), 138.0 (s, C-Ar), 142.5 (s, C-6), 150.7 (s, C-2), 162.9 (s, CO_2Et), 193.5 (s, C-3) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{20}H_{18}BrNO_3$ $[M+H]^+$: 356.1053; found: 356.1052. **IR:** $\tilde{\nu}$ = 3011 (=C-H), 1735 (-C=O), 1704 (-C=O), 1565 (-C=C), 1493 (-C=C), 1330 (C-N), 1097 (-C-O-C), 829 (-C-Cl) cm^{-1}.

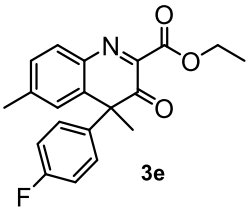
Ethyl 4-(4-bromophenyl)-4,6-dimethyl-3-oxo-3,4-dihydroquinoline-2-carboxylate (3d)



3d

According to GP 2: 43.3 mg (224 µmol) **1a**, 22.0 mg (112 µmol) **2d**, 14.2 mg (56.0 µmol) I_2 in 3.70 mL MeCN gave **3d** (28.5 mg, 64%, R_f = 0.49) after chromatography (Et_2O/toluene 1:10, R_f = 0.49) as yellow oil. **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 1.35 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.83 (s, 3 H, 4-CH_3), 2.42 (s, 3 H, 6-CH_3), 4.30–4.43 (m, 2 H, Et-CH_2), 6.80–6.92 (m, 2 H, 2'-H), 7.07 (d, ^4J = 1.9 Hz, 1 H, 5-H), 7.24–7.31 (m, 1 H, 7-H), 7.35–7.43 (m, 2 H, 3'-H) 7.65 (d, ^3J = 8.0 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 22.0 (q, CH_3-6), 22.7 (q, CH_3-4), 55.0 (s, C-4), 62.4 (t, CH_2-Et), 122.5 (s, C-4'), 128.8 (d, C-5), 129.3 (d, C-2'), 129.9 (d, C-7), 132.0 (d, C-8), 132.1 (d, C-3'), 137.6 (s, C-Ar), 137.8 (s, C-Ar), 138.6 (s, C-1'), 142.5 (s, C-6), 150.7 (s, C-2), 162.9 (s, CO_2Et), 193.4 (s, C-3) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{20}H_{18}BrNO_3$ $[M+H]^+$: 400.0548, found: 400.0547. **IR:** $\tilde{\nu}$ = 3001 (=C-H), 1736 (-C=O), 1700 (-C=O), 1563 (-C=C), 1490 (-C=C), 1374 (CH_3), 1333 (-C-O), 1282 (-C-O-C), 1010 (=C-H), 826 (-C-Br) cm^{-1}.

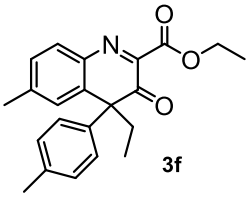
Ethyl 4-(4-fluorophenyl)-4,6-dimethyl-3-oxo-3,4-dihydroquinoline-2-carboxylate (3e)



3e

According to GP 2: 39.0 mg (202 µmol) **1a**, 13.8 mg (101 µmol) **2e**, 12.8 mg (50.5 µmol) I_2 in 3.40 mL MeCN gave **3e** (21.8 mg, 64%) after chromatography (Et_2O/toluene 1:20, R_f = 0.48) as yellow solid, m.p. 114 °C. **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 1.34 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.84 (s, 3 H, 4-CH_3), 2.42 (s, 3 H, 6-CH_3), 4.36 (m_c, 2 H, Et-CH_2), 6.89–7.02 (m, 4 H, 2'-H, 3'-H), 7.10 (d, ^4J = 1.9 Hz, 1 H, 5-H), 7.24–7.31 (m, 1 H, 7-H), 7.65 (d, ^3J = 7.9 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 22.0 (q, CH_3-6), 22.8 (q, CH_3-4), 54.8 (s, C-4), 62.4 (t, CH_2-Et), 115.9 (d, $^2J_{CF}$ = 21.6 Hz, C-3'), 128.8 (d, C-5), 129.3 (d, $^3J_{CF}$ = 8.3 Hz, C-2'), 129.8 (d, C-7), 131.9 (d, C-8), 135.0 (d, $^4J_{CF}$ = 3.2 Hz, C-1'), 137.8 (s, C-4a), 142.5 (s, C-6, C-8a), 150.8 (s, C-2), 162.5 (d, $^1J_{CF}$ = 247.9 Hz, C-4'), 163.0 (s, CO_2Et), 193.4 (s, C-3) ppm. **^{19}F-NMR (282 MHz, chloroform-*d*)** δ = -114.0 (s, 1 F, C-F) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{20}H_{18}BrNO_3$ $[M+H]^+$: 340.1349, found: 340.1335. **IR:** $\tilde{\nu}$ = 2990 (=C-H), 1738 (-C=O), 1704 (-C=O), 1601 (-C=C), 1565 (-C=C), 1507 (-C=C), 1236 (-C-O-C), 1014 (=C-H), 835 (-C-F) cm^{-1}.

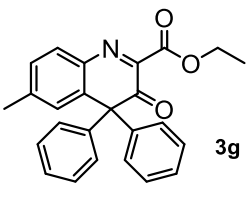
Ethyl 4-ethyl-6-methyl-3-oxo-4-(p-tolyl)-3,4-dihydroquinoline-2-carboxylate (3f)



3f

According to GP 2: 39.8 mg (206 µmol) **1a**, 13.6 mg (103 µmol) **2f**, 12.8 mg (51.4 µmol) I_2 in 3.40 mL MeCN gave **3f** (22.4 mg, 65%) after chromatography (Et_2O/toluene 1:20, R_f = 0.54) as yellow oil. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 0.79 (t, ^3J = 7.2 Hz, 3 H, 4-Et-CH_3), 1.35 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 2.19 (dq, ^3J = 7.3 Hz, ^2J = 14.5 Hz, 1 H, 4-Et-CH_2^a), 2.42 (s, 3 H, 6-CH_3), 2.81 (dq, ^3J = 7.3 Hz, ^2J = 14.5 Hz, 1 H, 4-Et-CH_2^b), 4.36 (m_c, 2 H, Et-CH_2), 7.00–7.05 (m, 3 H, 2'-H, Ar-H), 7.20–7.30 (m, 4 H, 3'-H, 7-H, Ar-H), 7.67 (d, ^3J = 8.0 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 10.0 (q, CH_3-Et-4), 14.2 (q, CH_3-Et), 22.0 (q, CH_3-6), 31.0 (t, CH_2-Et-4), 60.2 (s, C-4), 62.3 (t, CH_2-Et), 127.8 (d, C-2'), 128.0 (d, C-Ar), 129.0 (d, C-3'), 129.5 (d, C-Ar), 129.6 (d, C-Ar), 132.0 (d, C-8), 136.5 (s, C-Ar), 138.8 (s, C-Ar), 139.8 (s, C-Ar), 142.2 (s, C-6), 150.4 (s, C-2), 163.4 (s, CO_2Et), 193.2 (s, C-3) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{21}H_{21}NO_3$ $[M+H]^+$: 336.1599, found: 336.1600. **IR:** $\tilde{\nu}$ = 3033 (=C-H), 2988 (-C-H), 2940 (-C-H), 1735 (-C=O), 1691 (-C=O), 1564 (-C=C), 1328 (C-N), 1285 (-C-O-C), 1020 (=C-H), 828 (=C-H) cm^{-1}.

Ethyl 6-methyl-3-oxo-4,4-diphenyl-3,4-dihydroquinoline-2-carboxylate (3g)



3g

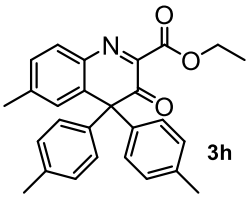
According to GP 2: 41.2 mg (213 µmol) **1a**, 19.2 mg (107 µmol) **2g**, 13.5 mg (53.3 µmol) I_2 in 3.60 mL MeCN gave **3g** (18.9 mg, 47%) after chromatography (Et_2O/toluene 1:20, R_f = 0.54) as yellow solid, m.p. 124 °C. **^{1}H-NMR (500 MHz, acetone-d_6)** δ = 1.28 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 2.31 (s, 3 H, 6-CH_3), 4.28 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 6.65 (d, ^4J = 1.9 Hz, 1 H, 5-H), 6.90–6.99 (m, 4 H, 2'-H), 7.34–7.40 (m, 7 H, 3'-H,

4'-H, 7-H), 7.59 (d, ^3J = 7.9 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (126 MHz, acetone-d_6)** δ = 14.3 (q, CH_3-Et), 21.7 (q, CH_3-6), 62.4 (t, CH_2-Et), 67.9 (s, C-4), 129.1 (d, C-4'), 129.3 (d, C-3'), 130.7 (d, C-7), 131.2 (d, C-2'), 132.1 (d, C-8), 132.6 (d, C-5), 138.4 (s, C-8a), 138.6 (s, C-1'), 139.2 (s, C-4a), 142.5 (s, C-6), 152.3 (s, C-2), 163.5 (s, CO_2Et), 193.2 (s, C-3) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{25}H_{21}NO_3$ $[M+H]^+$: 384.1599, found: 384.1599. **IR:** $\tilde{\nu}$ = 3003 (=C-H), 2926 (-C-H), 1732 (-C=O), 1715 (-C=O), 1564 (-C=C), 1499 (-C=C), 1447 (-C=C), 1330 (C-N), 1042 (-C-O-C), 831 (=C-H) cm^{-1}.

Ethyl 6-methyl-3-oxo-4,4-di-p-tolyl-3,4-dihydroquinoline-2-carboxylate (3h) and **Di-*p*-tolylmethanone**

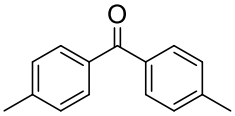
According to GP 2: 42.7 mg (221 µmol) **1a**, 23.0 mg (110 µmol) **2h**, 14.0 mg (55.1 µmol) I_2 in 3.70 mL MeCN gave **3h** (21.6 mg, 48%) and di-*p*-tolylmethanone (1.2 mg, 5%) after chromatography (Et_2O/toluene 1:20).

Ethyl 6-methyl-3-oxo-4,4-di-p-tolyl-3,4-dihydroquinoline-2-carboxylate (3h)



Yellow oil, R_f = 0.44 (Et_2O/toluene 1:20). **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.32 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 2.31 (s, 3 H, 6-CH_3), 2.34 (s, 6 H, 4'-CH_3), 4.27–4.47 (m, 2 H, Et-CH_2), 6.59 (d, ^3J = 8.3 Hz, 4 H, 2'-H), 6.77 (d, ^3J = 8.3 Hz, 4 H, 3'-H), 7.10 (d, ^4J = 1.9 Hz, 1 H, 5-H), 7.24 (d, ^3J = 7.9 Hz, 1 H, 7-H), 7.64 (d, ^3J = 7.9 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 21.2 (q, CH_3-4'), 21.9 (q, CH_3-6), 62.3 (t, CH_2-Et), 66.8 (s, C-4), 129.3 (d, C-3'), 129.7 (d, C-7), 130.4 (d, C-2'), 131.7 (d, C-5), 131.8 (d, C-8), 134.2 (s, C-1'), 138.2 (s, C-4', C-8a), 138.5 (s, C-4a), 141.7 (s, C-6), 151.3 (s, C-2), 162.8 (s, CO_2Et), 193.1 (s, C-3) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{27}H_{25}NO_3$ $[M+H]^+$: 412.1913, found: 412.1913. **IR:** $\tilde{\nu}$ = 3004 (=C-H), 2927 (-C-H), 1736 (-C=O), 1710 (-C=O), 1565 (-C=C), 1510 (-C=C), 1374 (-CH_3), 1331 (C-N), 1043 (-C-O-C), 1022 (=C-H), 912 (=C-H), 832 (=C-H) cm^{-1}.

4,4'-Dimethylbenzophenone

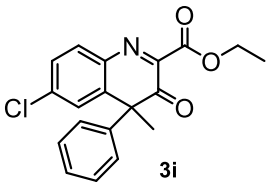


Colorless solid, m.p. 98 °C, R_f = 0.54 (Et_2O/heptane 1:10). **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 2.44 (s, 6 H, CH_3), 7.27 (d, ^3J = 8.1 Hz, 4 H, 3-H), 7.70 (d, ^3J = 8.1 Hz, 4 H, 2-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 21.8 (q, C-4), 129.1 (d, C-3), 130.3 (d, C-2), 135.4 (s, C-1), 143.1 (s, C-4), 196.5 (s, C=O) ppm.

Spectroscopic data are in agreement with the literature.[5]

5 G. A. Babu and P. Ramasamy, *J. Cryst. Growth*, 2008, **310**, 3561–3567.

Ethyl 6-chloro-4-methyl-3-oxo-4-phenyl-3,4-dihydroquinoline-2-carboxylate (3i)

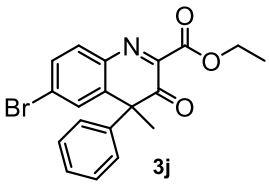


3i

According to GP 2: 47.4 mg (222 µmol) **1b**, 13.1 mg (111 µmol) **2a**, 14.1 mg (57.1 µmol) I_2 in 3.70 mL MeCN gave **3i** (8.9 mg, 23%) after chromatography (Et_2O/toluene 1:20, R_f = 0.52) as yellow oil. **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 1.34 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.87 (s, 3 H, 4-CH_3), 4.36 (m_c, 2 H, Et-CH_2), 6.94–7.03 (m, 2 H, 2'-H), 7.27–7.33 (m, 4 H, 3'-H, 4'-H, 5-H), 7.45 (dd, ^4J = 2.3 Hz, ^3J = 8.4 Hz, 1 H, 7-H), 7.70 (d, ^3J = 8.4 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 22.5 (q, CH_3-4), 55.3 (s, C-4), 62.6 (t, CH_2-Et), 127.4 (d, C-2'), 128.5 (d, C-4'), 128.5 (d, C-5), 129.2 (d, C-3'), 129.3 (d, C-7), 133.0 (d, C-8), 137.6 (s, C-Ar), 138.4 (s, C-Ar), 138.6 (s, C-Ar), 139.9 (s, C-6), 149.8 (s, C-2), 162.7 (s, CO_2Et), 192.8 (s, C-3) ppm.

Spectroscopic data are in agreement with the literature.[3]

Ethyl 6-bromo-4-methyl-3-oxo-4-phenyl-3,4-dihydroquinoline-2-carboxylate (3j)

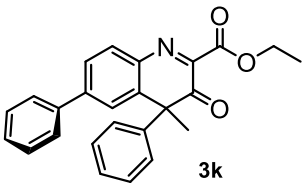


3j

According to GP 2: 47.4 mg (220 µmol) **1c**, 13.0 mg (110 µmol) **2a**, 14.1 mg (57.1 µmol) I_2 in 3.70 mL MeCN gave **3j** (13.4 mg, 32%) after chromatography (Et_2O/toluene 1:20, R_f = 0.57) as yellow oil. **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 1.34 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.87 (s, 3 H, 4-CH_3), 4.30–4.43 (m, 2 H, Et-CH_2), 6.98 (dd, ^4J = 2.0 Hz, ^3J = 7.7 Hz, 2 H, 2'-H), 7.27–7.30 (m, 3 H, 3'-H, 4'-H), 7.47–7.49 (m, 1 H, 5-H), 7.61–7.64 (m, 2 H, 7-H, 8-H) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 22.5 (q, CH_3-4), 55.3 (s, C-4), 62.6 (t, CH_2-Et), 126.1 (s, C-4a), 127.4 (d, C-2'), 128.5 (d, C-4'), 129.3 (d, C-3'), 131.4 (d, C-5), 132.4 (d, C-7), 133.1 (d, C-8), 138.4 (s, C-1'), 139.0 (s, C-6), 140.0 (s, C-8a), 152.2 (s, C-2), 162.7 (s, CO_2Et), 192.8 (s, C-3) ppm.

Spectroscopic data are in agreement with the literature.[4]

Ethyl 4-methyl-3-oxo-4,6-diphenyl-3,4-dihydroquinoline-2-carboxylate (3k)



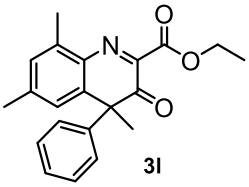
3k

According to GP 256.2 mg (220 µmol) **1d**, 13.0 mg (110 µmol) **2a**, 14.0 mg (55.0 µmol) I_2 in 3.70 mL MeCN gave **3k** (14.1 mg, 34%) after chromatography (Et_2O/toluene 1:20, R_f = 0.49) as yellow oil. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.35 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.94 (s, 3 H, 4-CH_3), 4.37 (m_c, 2 H, Et-CH_2), 7.00–7.08 (m, 2 H, 2'-H), 7.25–7.30 (m, 3 H, 3'-H, 4'-H), 7.38–7.43 (m, 1 H, 4''-H), 7.45–7.49 (m, 2 H, 3''-H), 7.56 (d, ^4J = 2.0 Hz, 1 H, 5-H), 7.60–7.63 (m, 2 H, 2''-H), 7.71 (dd, ^4J = 2.0 Hz,

4 X. Jia, W. Hou, Y. Shao, Y. Yuan, Q. Chen, P. Li, X. Liu and H. Ji, *Chem. Eur. J.*, 2017, **23**, 12980–12984.

^3J = 8.1 Hz, 1 H, 7-H), 7.84 (d, ^3J = 8.1 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 22.6 (q, CH_3-4), 55.6 (s, C-4), 62.5 (t, CH_2-Et), 126.9 (d, C-5), 127.4 (d, C-2''), 127.5 (d, C-7), 127.6 (d, C-2'), 128.3 (d, C-4'), 128.6 (d, C-4''), 129.1 (d, C-3''), 129.2 (d, C-3'), 132.3 (d, C-8), 138.6 (s, C-8a), 139.1 (s, C-1'), 139.3 (s, C-4a), 139.7 (s, C-1''), 144.6 (s, C-6), 151.6 (s, C-2), 162.9 (s, CO_2Et), 193.8 (s, C-3) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{25}H_{21}NO_3$ $[M+H]^+$: 384.1599, found: 384.1603. **IR:** $\tilde{\nu}$ = 3001 (=C-H), 2940 (-C-H), 1738 (-C=O), 1704 (-C=O), 1559 (-C=C), 1493 (-C=C), 1445 (-C=C), 1373 (-CH_3), 1197 (C-N), 1020 (-C-O-C), 849 (=C-H) cm^{-1}.

Ethyl 4,6,8-trimethyl-3-oxo-4-phenyl-3,4-dihydroquinoline-2-carboxylate (3l)

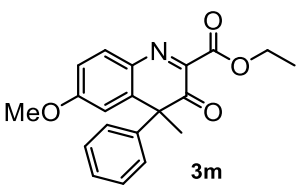

3l

According to GP 2: 44.5 mg (215 µmol) **1e**, 12.7 mg (107 µmol) **2a**, 13.4 mg (52.8 µmol) I_2 in 3.60 mL MeCN gave **3l** (11.5 mg, 30%) after chromatography (Et_2O/toluene 1:20, R_f = 0.60) as yellow oil. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.32 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.83 (s, 3 H, 4-CH_3), 2.36 (s, 3 H, 6-CH_3), 2.56 (s, 3 H, 8-CH_3), 4.33 (m_c, 2 H, Et-CH_2), 6.93 (d, ^4J = 1.9 Hz, 1 H, 5-H), 7.00 (dd, ^4J = 1.8 Hz, ^3J = 7.7 Hz, 2 H, 2'-H), 7.11 (d, ^4J = 1.9 Hz, 1 H, 7-H), 7.21–7.29 (m, 3 H, 3'-H, 4'-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.2 (q, CH_3-Et), 17.8 (q, CH_3-8), 21.9 (q, CH_3-6), 22.8 (q, CH_3-4), 55.5 (s, C-4), 62.0 (t, CH_2-Et), 126.7 (d, C-5), 127.6 (d, C-2'), 128.0 (d, C-4'), 128.9 (d, C-3'), 131.4 (d, C-7), 136.4 (s, C-8), 138.5 (s, C-4a), 139.7 (s, C-1'), 140.6 (s, C-8a), 141.9 (s, C-6), 149.3 (s, C-2), 163.4 (s, CO_2Et), 194.5 (s, C-3) ppm. **HR-MS (ESI+)**: *m/z* calc. $C_{21}H_{21}NO_3$ $[M+H]^+$: 336.1599, found: 336.1606. **IR:** $\tilde{\nu}$ = 3004 (=C-H), 2990 (-C-H), 1735 (-C=O), 1698 (-C=O), 1570 (-C=C), 1448 (-C=C), 1371 (-CH_3), 1126 (C-N), 1020 (-C-O-C), 863 (=C-H) cm^{-1}.

Ethyl 6-methoxy-4-methyl-3-oxo-4-phenyl-3,4-dihydroquinoline-2-carboxylate (3m) and **Ethyl 6-methoxy-4-methyl-3-phenylquinoline-2-carboxylate (5)**

According to GP 2: 39.9 mg (206 µmol) **1h**, 21.5 mg (103 µmol) **2a**, 13.1 mg (51.6 µmol) I_2 in 3.40 mL MeCN gave **3m** (10.9 mg, 28%) and **5** (8.3 mg, 23%) after chromatography (Et_2O/toluene 1:20 → 1:10).

Ethyl 6-methoxy-4-methyl-3-oxo-4-phenyl-3,4-dihydroquinoline-2-carboxylate (3m)

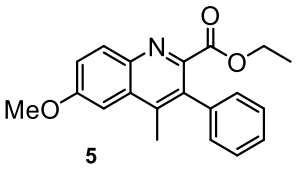

3m

Yellow oil, R_f = 0.32 (Et_2O/toluene 1:20). **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.34 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 1.86 (s, 3 H, 4-CH_3), 3.87 (s, 3 H, 6-OCH_3), 4.35 (m_c, 2 H, Et-CH_2), 6.85 (d, ^4J = 2.7 Hz, 1 H, 5-H), 6.97 (dd, ^4J = 2.7 Hz, ^3J = 8.7 Hz, 1 H, 7-H), 7.01 (dd, ^4J = 1.9 Hz, ^3J = 7.8 Hz, 2 H, 2'-H), 7.23–7.30 (m, 3 H, 3'-H, 4'-H), 7.73 (d, ^3J = 8.7 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.2 (q,

CH_3-Et), 22.6 (q, CH_3-4), 55.7 (s, C-4), 55.8 (q, OCH_3-6), 62.2 (t, CH_2-Et), 112.9 (d, C-7), 115.0 (d, C-5), 127.5 (d, C-2'), 128.2 (d, C-4'), 129.0 (d, C-3'), 133.9 (d, C-8), 134.1 (s, C-4a), 139.2 (s, C-1'), 140.7 (s, C-8a), 148.8 (s, C-2), 162.6 (s, C-6), 163.1 (s, CO_2Et), 193.8 (s, C-3) ppm.

Spectroscopic data are in agreement with the literature.[4]

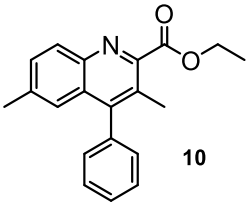
Ethyl 6-methoxy-4-methyl-3-phenylquinoline-2-carboxylate (5)



5

Colorless solid, m.p. 138 °C, R_f = 0.21 (Et_2O/toluene 1:10). **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 0.99 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 2.49 (s, 3 H, 4-CH_3), 3.98 (s, 3 H, 6-OCH_3), 4.10 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 7.25 (d, ^4J = 2.8 Hz, 1 H, 5-H), 7.27–7.28 (m, 2 H, 2'-H), 7.38–7.48 (m, 4 H, 3'-H, 4'-H, 7-H), 8.21 (d, ^3J = 9.3 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 13.8 (q, CH_3-Et), 16.3 (q, CH_3-4), 55.8 (q, OCH_3-6), 61.7 (t, CH_2-Et), 102.3 (d, C-5), 122.6 (d, C-7), 127.9 (d, C-4'), 128.3 (d, C-3'), 129.6 (s, C-Ar), 129.8 (d, C-2'), 131.9 (d, C-8), 133.0 (s, C-4), 137.7 (s, C-Ar), 141.4 (s, C-Ar), 142.5 (s, C-Ar), 159.3 (s, C-6), 167.0 (s, CO_2Et) ppm. **HR-MS (ESI+):** *m/z* calc. $C_{27}H_{25}NO_3$ $[M+H]^+$: 322.1443, found: 322.1450. **IR:** $\tilde{\nu}$ = 3006 (=C-H), 2987 (-C-H), 1726 (-C=O), 1624 (-C=C), 1499 (-C=C), 1445 (-C=C), 1415 (-C-H), 1379 (-CH_3), 1299 (-C-O), 1173, 1113, 1024 (-C-O-C), 834 (=C-H), 701 (=C-H) cm^{-1}.

Ethyl 3,6-dimethyl-4-phenylquinoline-2-carboxylate (10)



10

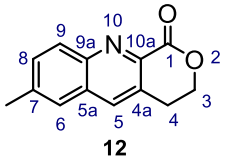
According to GP 2: 39.8 mg (206 µmol) **1a**, 12.6 mg (102 µmol) **9**, 13.2 mg (51.4 µmol) I_2 in 3.40 mL MeCN gave **10** (22.4 mg, 65%) after chromatography (Et_2O/toluene 1:20, R_f = 0.29) as colorless solid, m.p. 115 °C. **^{1}H-NMR (500 MHz, chloroform-*d*)** δ = 1.47 (t, ^3J = 7.1 Hz, 3 H, Et-CH_3), 2.29 (s, 3 H, 3-CH_3), 2.39 (s, 3 H, 6-CH_3), 4.54 (q, ^3J = 7.1 Hz, 2 H, Et-CH_2), 7.08–7.13 (m, 1 H, 5-H), 7.22–7.25 (m, 2 H, 2'-H), 7.47–7.57 (m, 4 H, 3'-H, 4'-H, 7-H), 8.08 (d, ^3J = 8.6 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (126 MHz, chloroform-*d*)** δ = 14.4 (q, CH_3-Et), 17.0 (q, CH_3-3), 22.1 (q, CH_3-6), 62.1 (t, CH_2-Et), 124.9 (d, C-5), 126.5 (s, C-3), 128.2 (d, C-4'), 128.3 (d, C-4a), 128.8 (d, C-3'), 129.4 (d, C-2'), 129.7 (d, C-8), 131.5 (d, C-7), 137.7 (s, C-1'), 138.0 (s, C-6), 144.4 (s, C-8a), 148.1 (s, C-4), 150.7 (s, C-2), 167.7 (s, CO_2Et) ppm.

Spectroscopic data are in agreement with the literature.[6]

4 X. Jia, W. Hou, Y. Shao, Y. Yuan, Q. Chen, P. Li, X. Liu and H. Ji, *Chem. Eur. J.*, 2017, **23**, 12980–12984.

6 X. Yang, L. Li, Y. Li, Y. Zhang, *J. Org. Chem*., 2016, **81**, 12433–12442.

7-Methyl-3,4-dihydro-1*H*-pyrano[3,4-*b*]quinoline-1-one (12)



12

According to GP 2: 39.0 mg (202 µmol) **1a**, 7.1 mg (101 µmol) **11**, 12.8 mg (50.5 µmol) I_2 in 3.40 mL MeCN gave **12** (8.3 mg, 39%) after chromatography (Et_2O/toluene 1:20, R_f = 0.28) as colorless solid, m.p. 115 °C. **^{1}H-NMR (300 MHz, chloroform-*d*)** δ = 2.57 (s, 3 H, 7-CH_3), 3.31 (t, ^3J = 5.7 Hz, 2 H, 4-H), 4.65 (t, ^3J = 5.7 Hz, 2 H, 3-H), 7.51–7.68 (m, 2 H, 6-H, 9-H), 7.99 (s, 1 H, 5-H), 8.24 (d, ^3J = 9.5 Hz, 1 H, 8-H) ppm. **^{13}C-NMR (75 MHz, chloroform-*d*)** δ = 22.1 (q, CH_3-7), 28.2 (t, CH_2-4), 67.3 (t, CH_2-3), 125.8 (d, C-9), 129.8 (s, C-9a), 130.8 (d, C-8), 131.3 (s, C-10a), 132.9 (d, C-6), 134.1 (d, C-5), 140.1 (s, C-7), 142.4 (s, C-4a), 147.0 (s, C-5a), 163.2 (s, C-1) ppm.

Spectroscopic data are in agreement with the literature.[7]

7 C. Huo, F. Chen, Y. Yuan, H. Xie, Y. Wang, *Org. Lett.*, 2015, **17**, 5028–5031.

4. X-Ray crystal structure of compound 3l

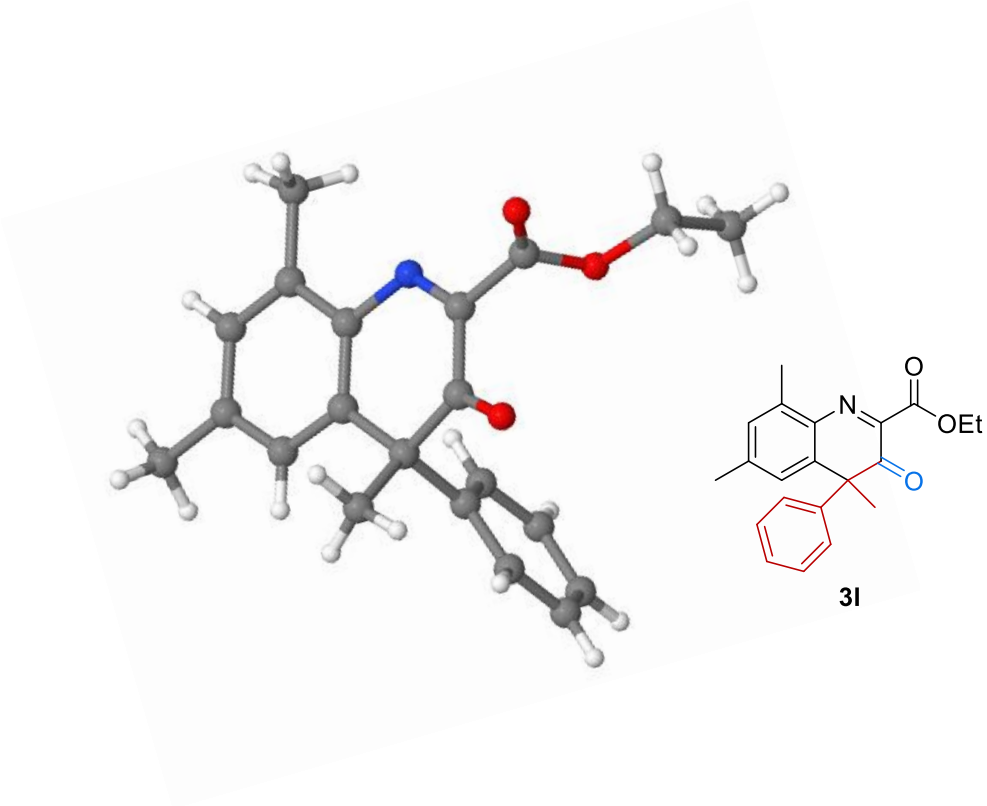
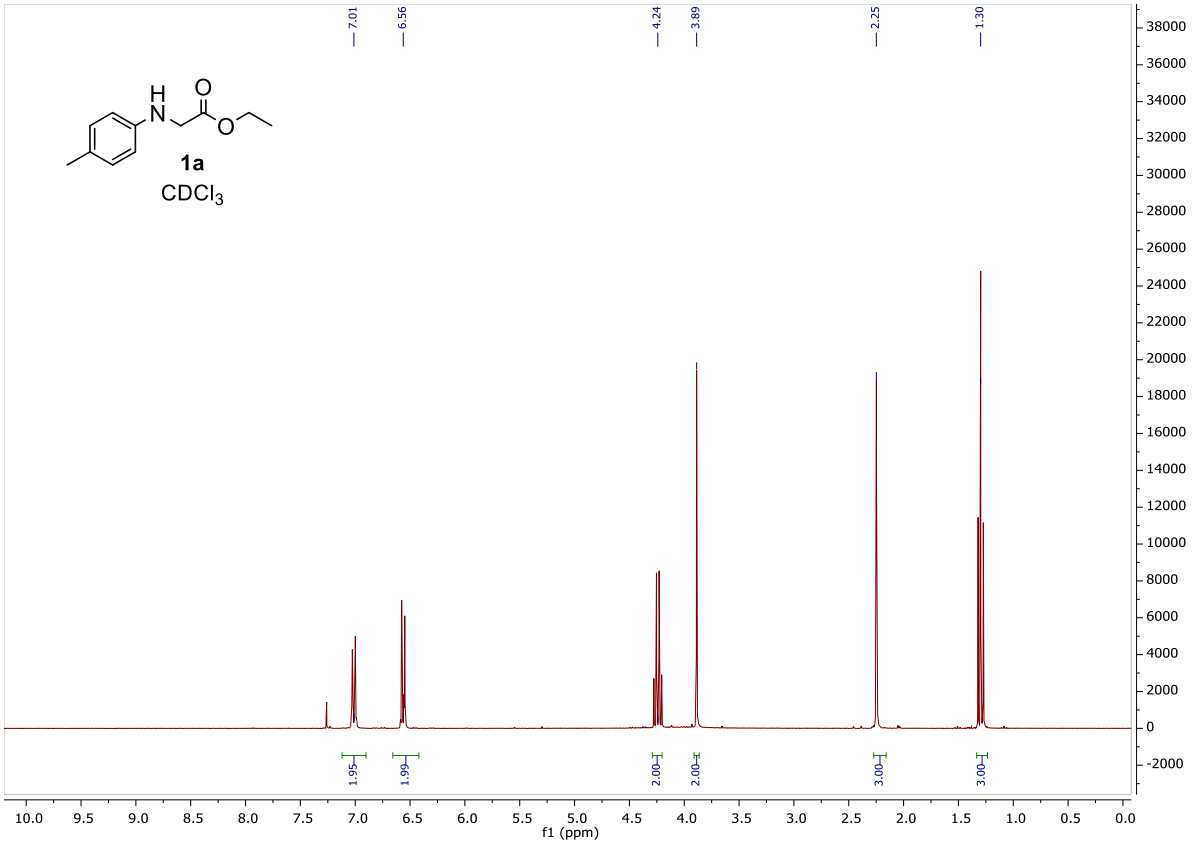
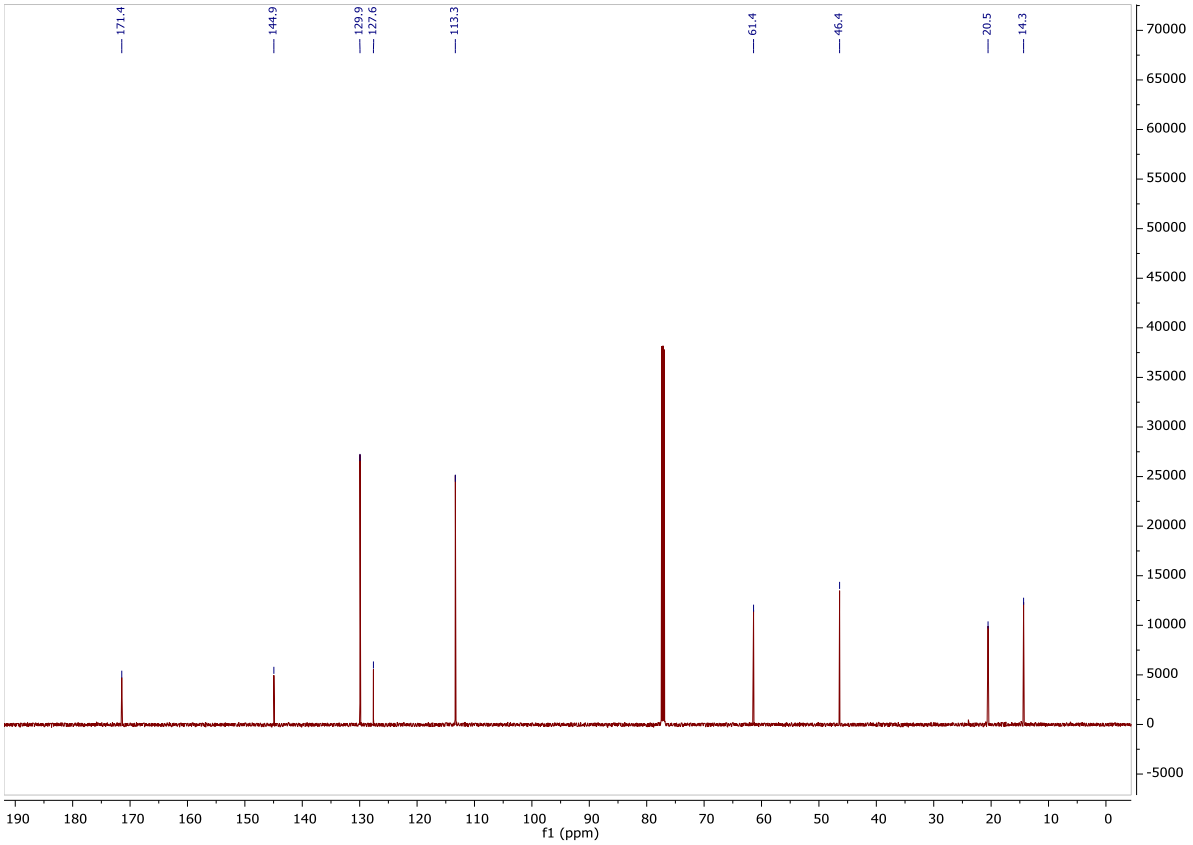
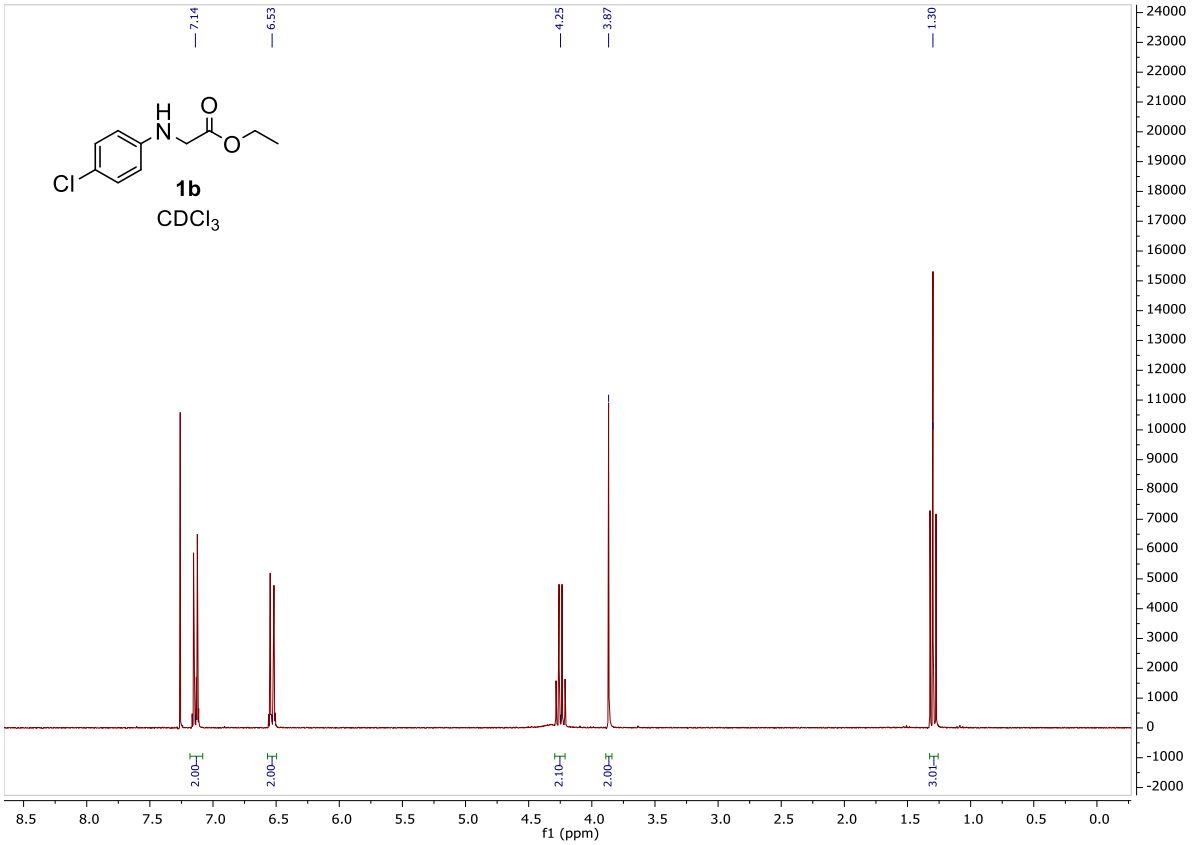


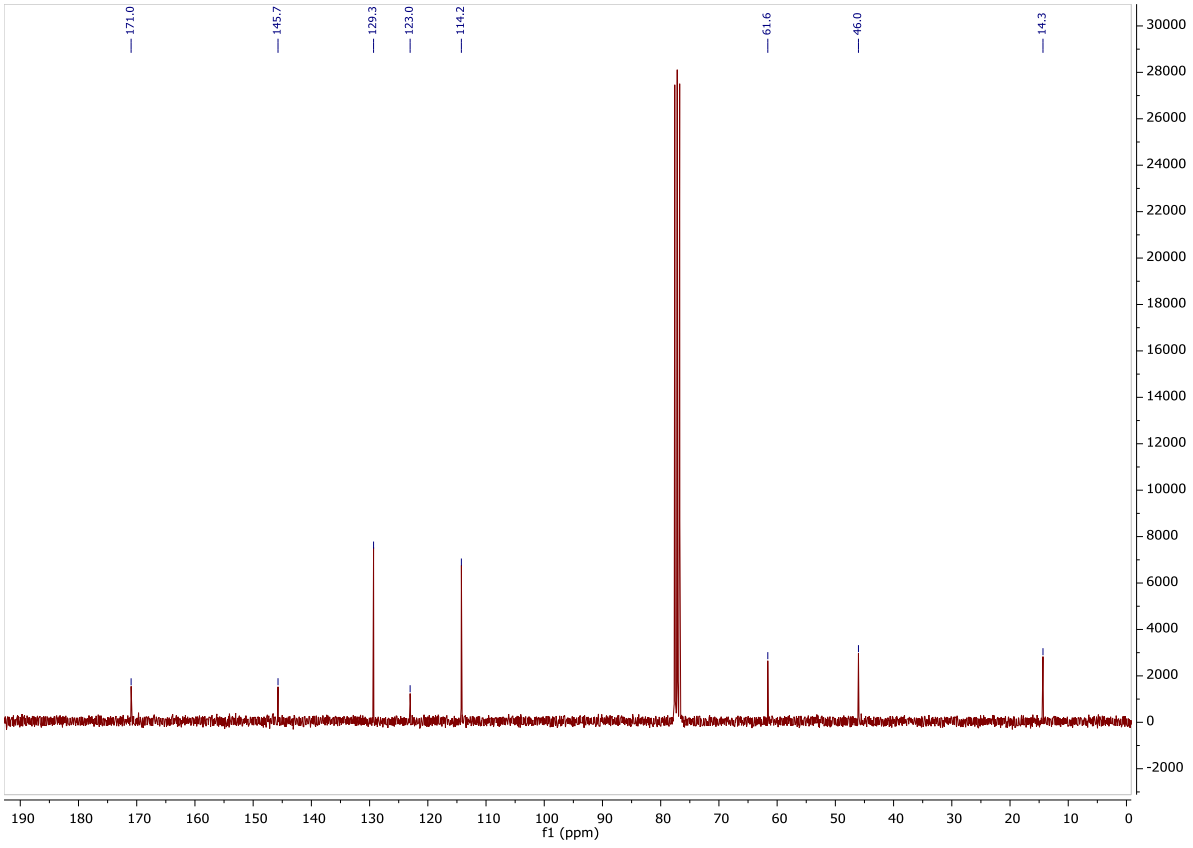
Figure S1. Crystal structure of product **3l.** CCDC 2022869 contains the supplementary crystallographic data for this compound. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

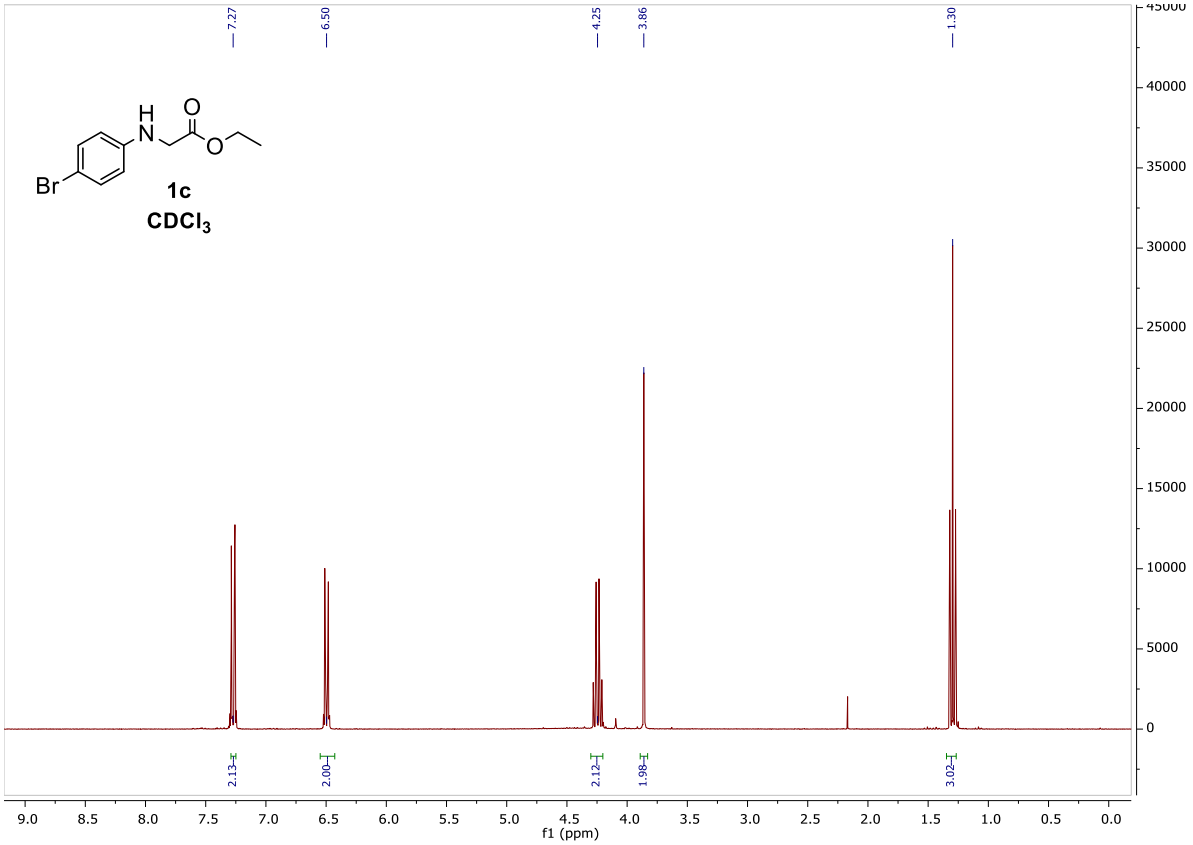
5. NMR spectra






7.14
6.53
4.25
3.87
1.30
Cl
H
N
O
O
1b
CDCl3
2.00
2.00
2.10
2.00
3.01
f1 (ppm)


171.0
145.7
129.3
123.0
114.2
61.6
46.0
14.3
f1 (ppm)


7.27
6.50
4.25
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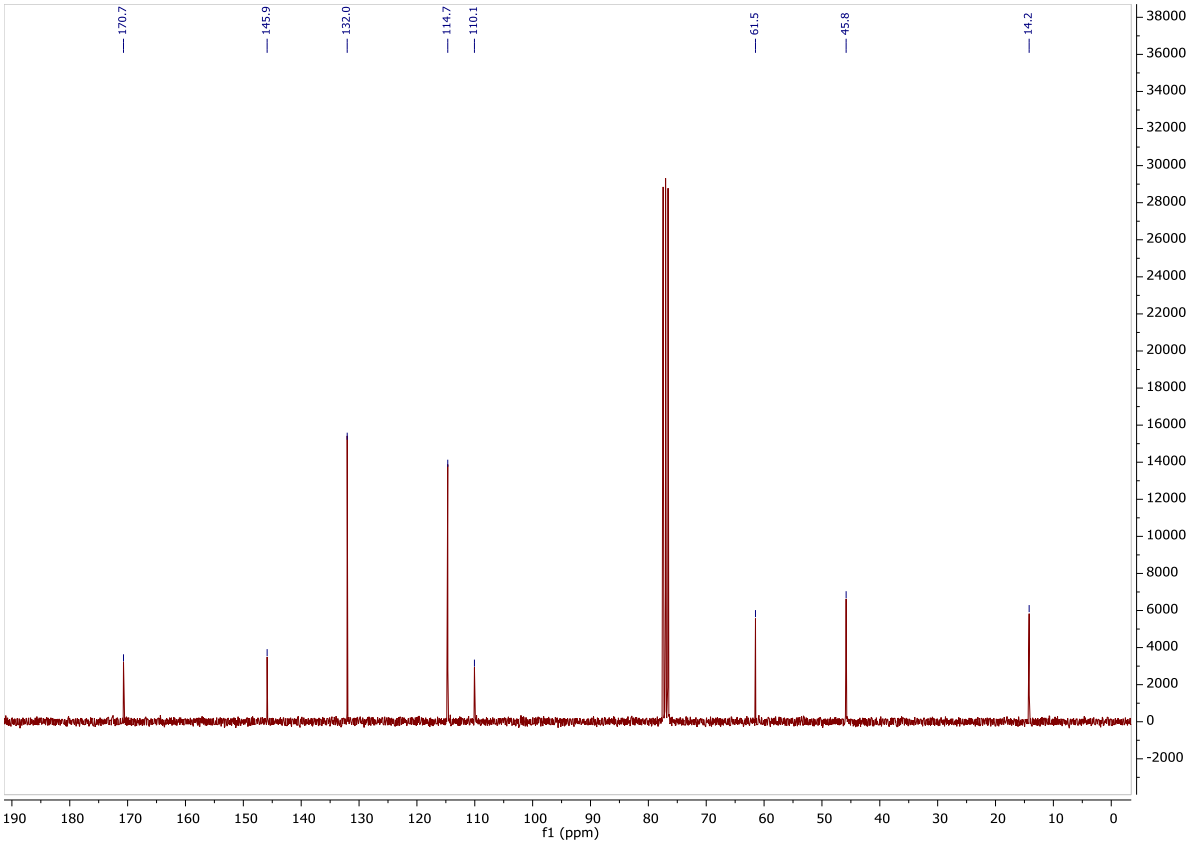
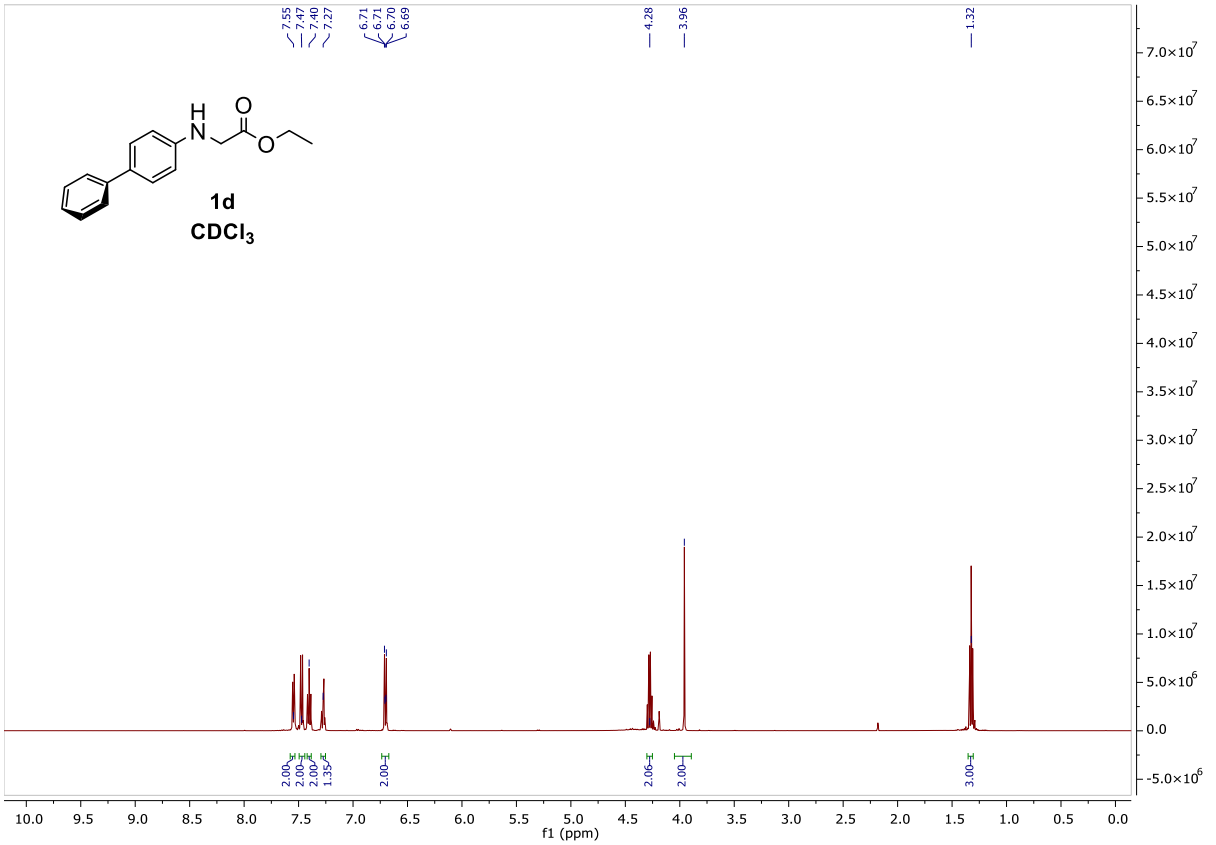
1.30
Br
1c
CDCl3
2.13
2.00
2.12
1.98
3.02
f1 (ppm)


170.7
145.9
132.0
114.7
110.1
61.5
45.8
14.2
f1 (ppm)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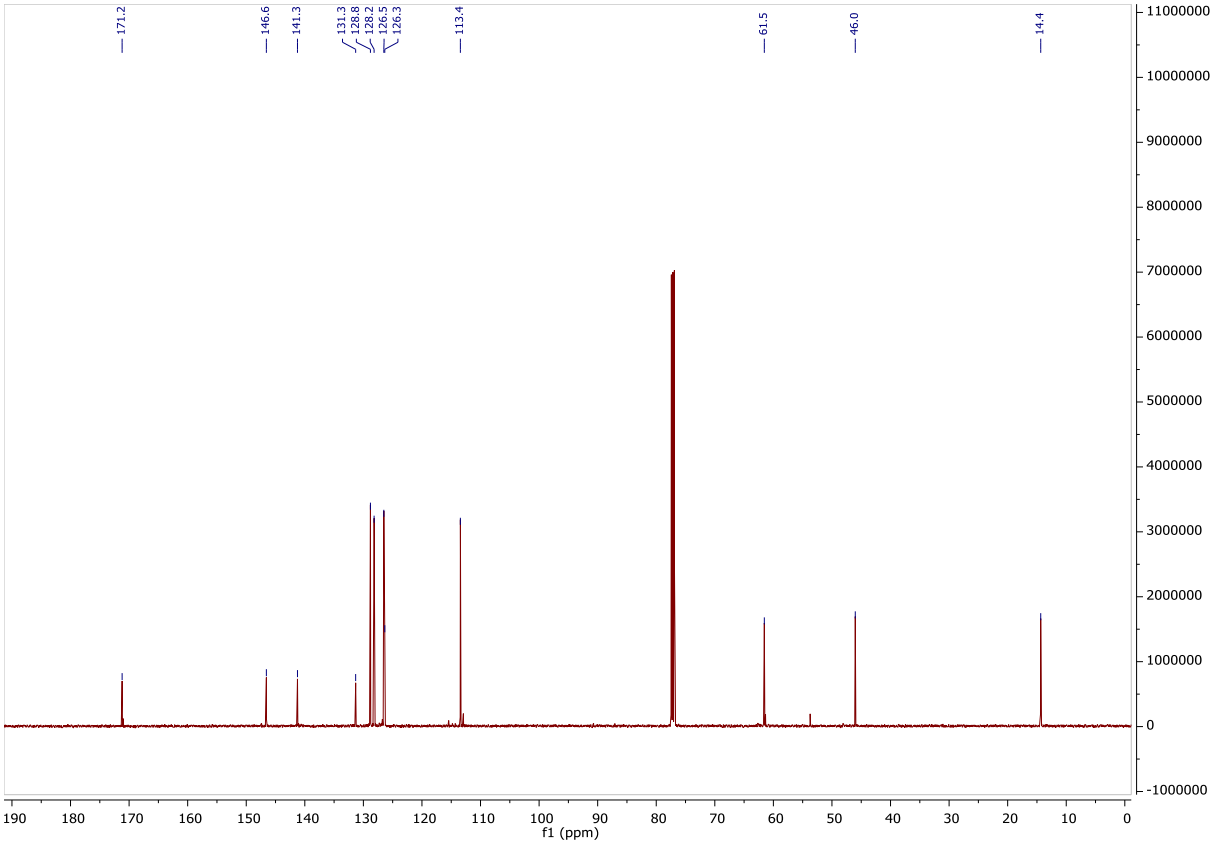
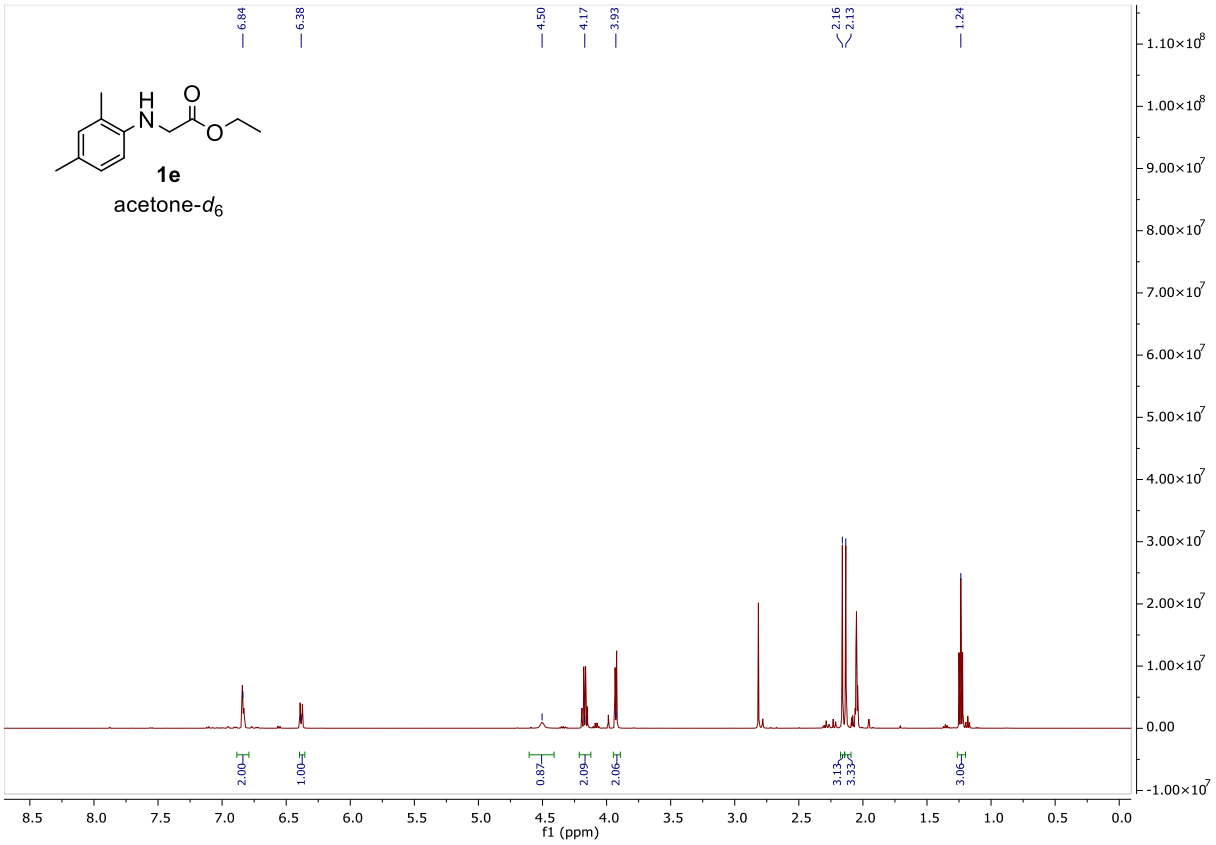
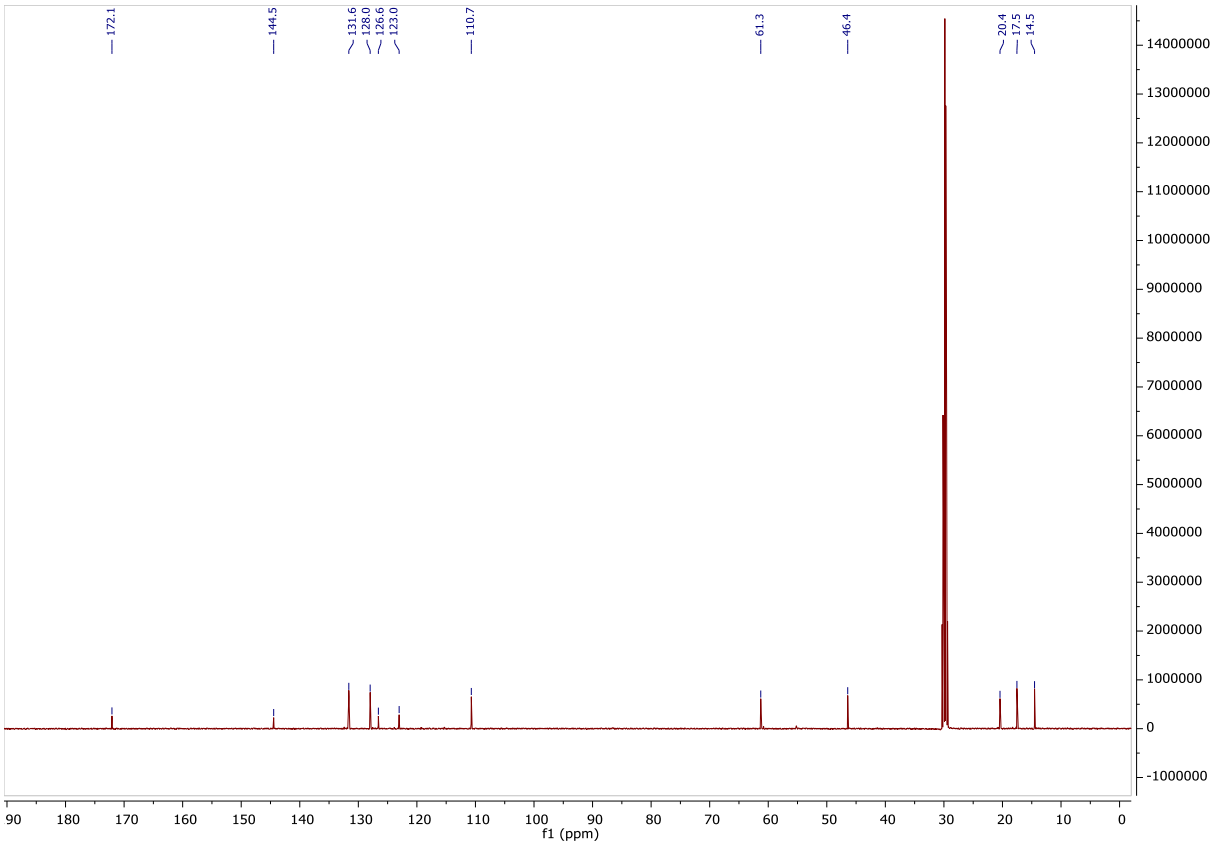
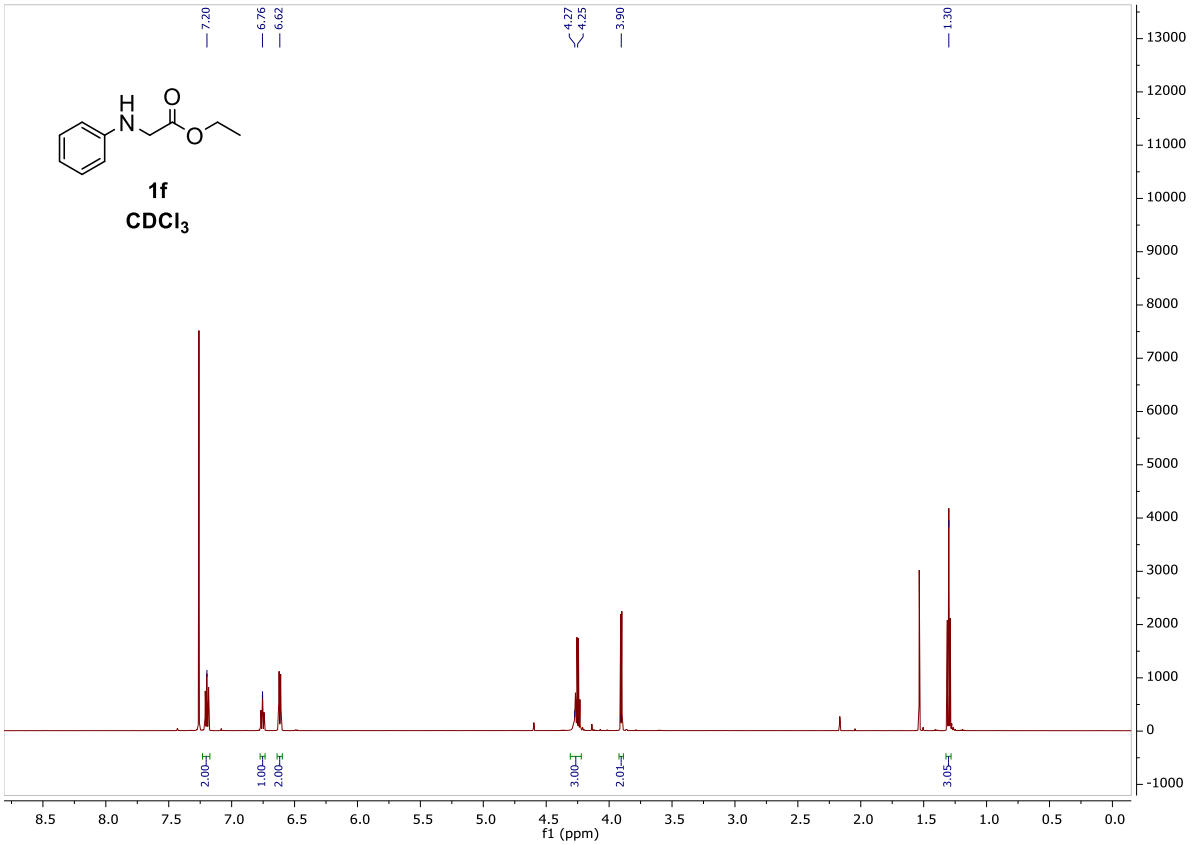
6.71
6.71
6.70
6.69
4.28
3.96
1.32
1d
CDCl3
f1 (ppm)


171.2
146.6
141.3
131.3
128.8
128.2
126.5
126.3
113.4
61.5
46.0
14.4
f1 (ppm)


6.84
6.38
4.50
4.17
3.93
2.16
2.13
1.24
1e
acetone-d_6
f1 (ppm)


172.1
144.5
131.6
128.0
126.6
123.0
110.7
61.3
46.4
20.4
17.5
14.5
f1 (ppm)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6.62
4.27
4.25
3.90
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1f
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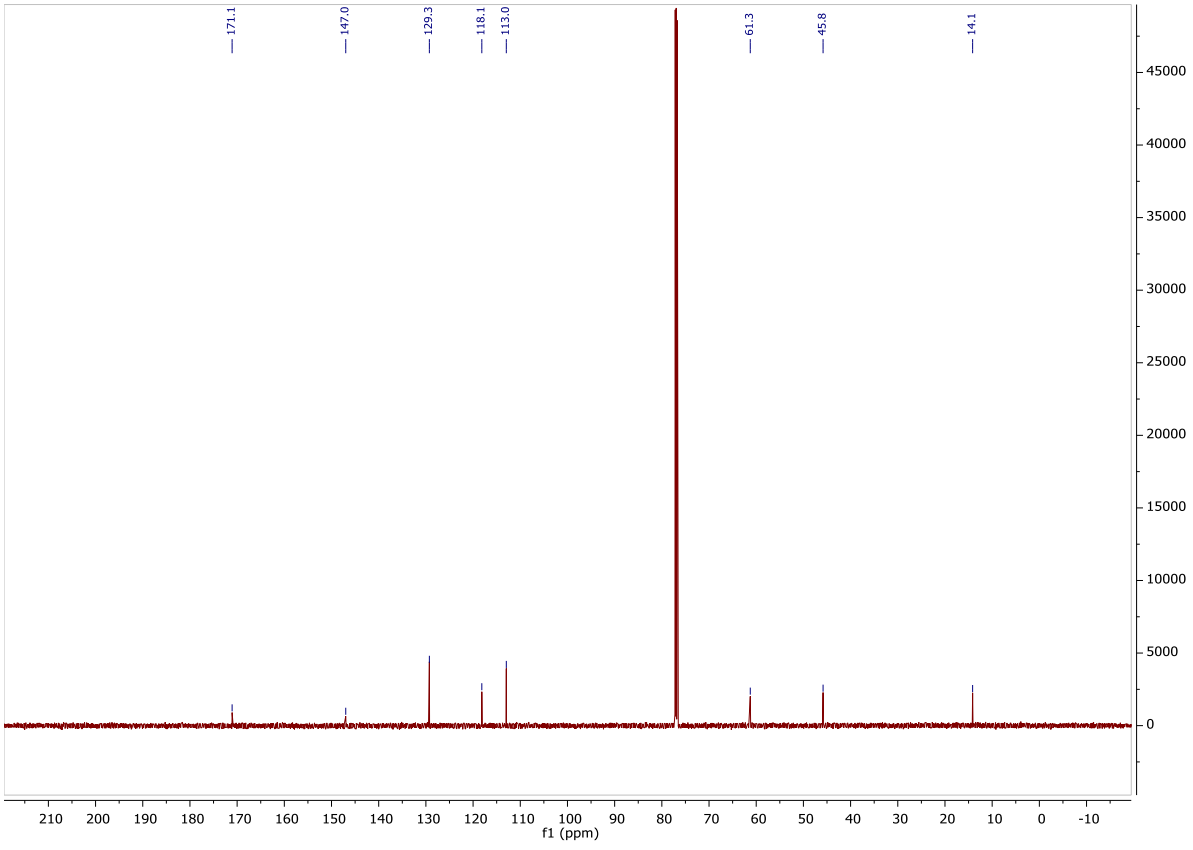
2.00
1.00
2.00
3.00
2.01
3.05
f1 (ppm)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147.0
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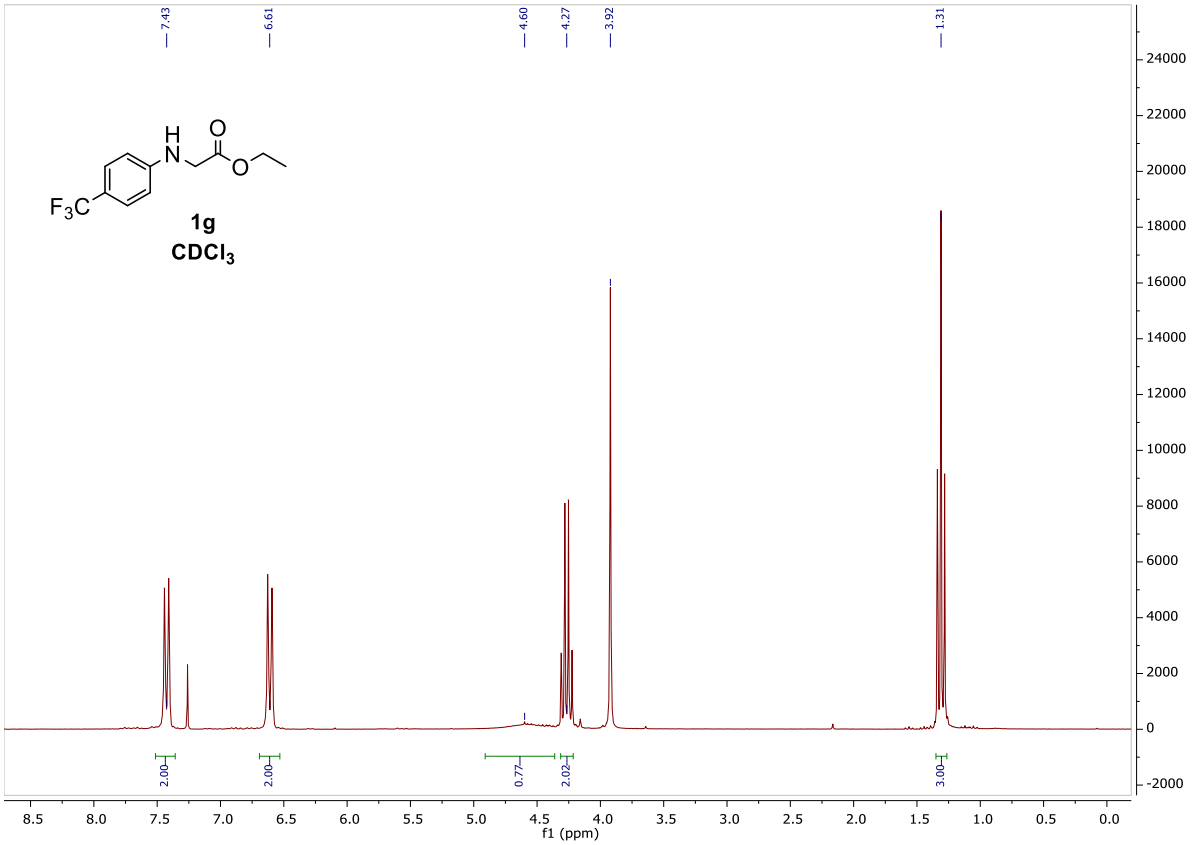
118.1
113.0
61.3
45.8
14.1
f1 (ppm)


7.43
6.61
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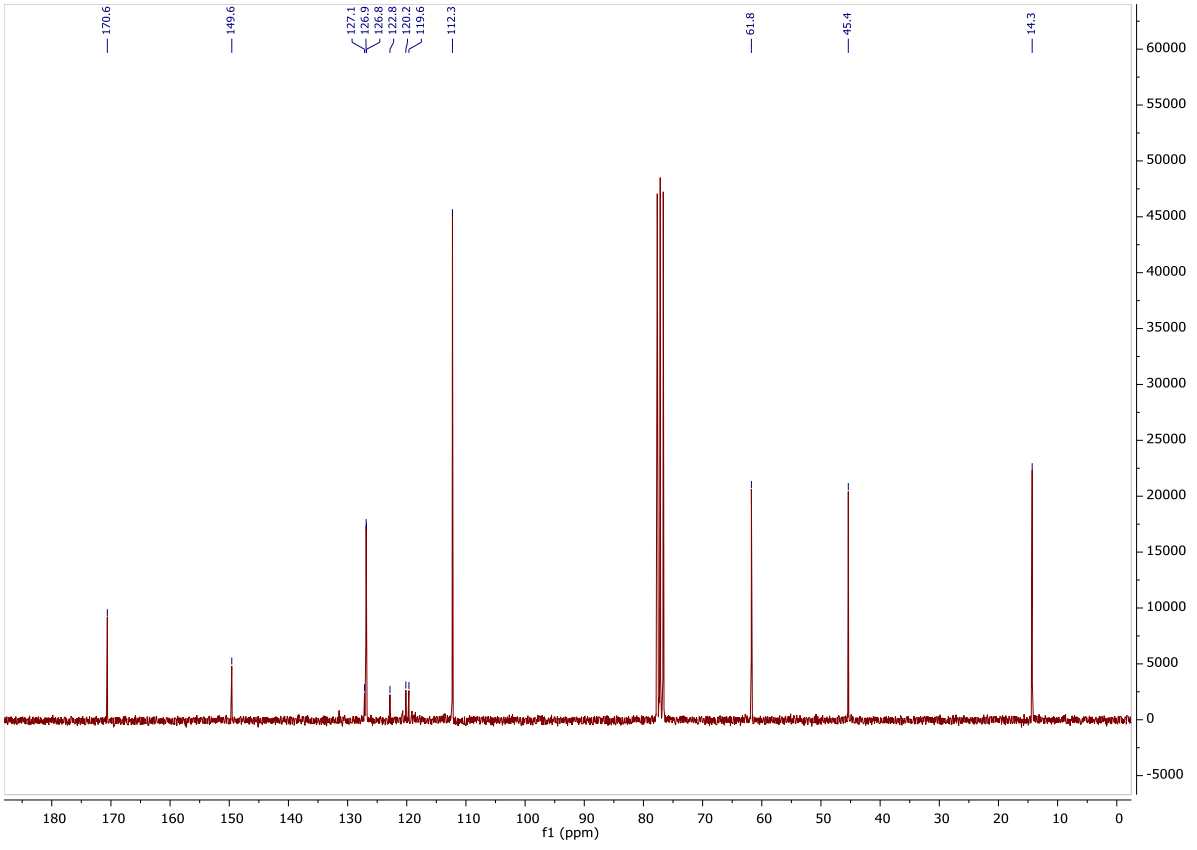
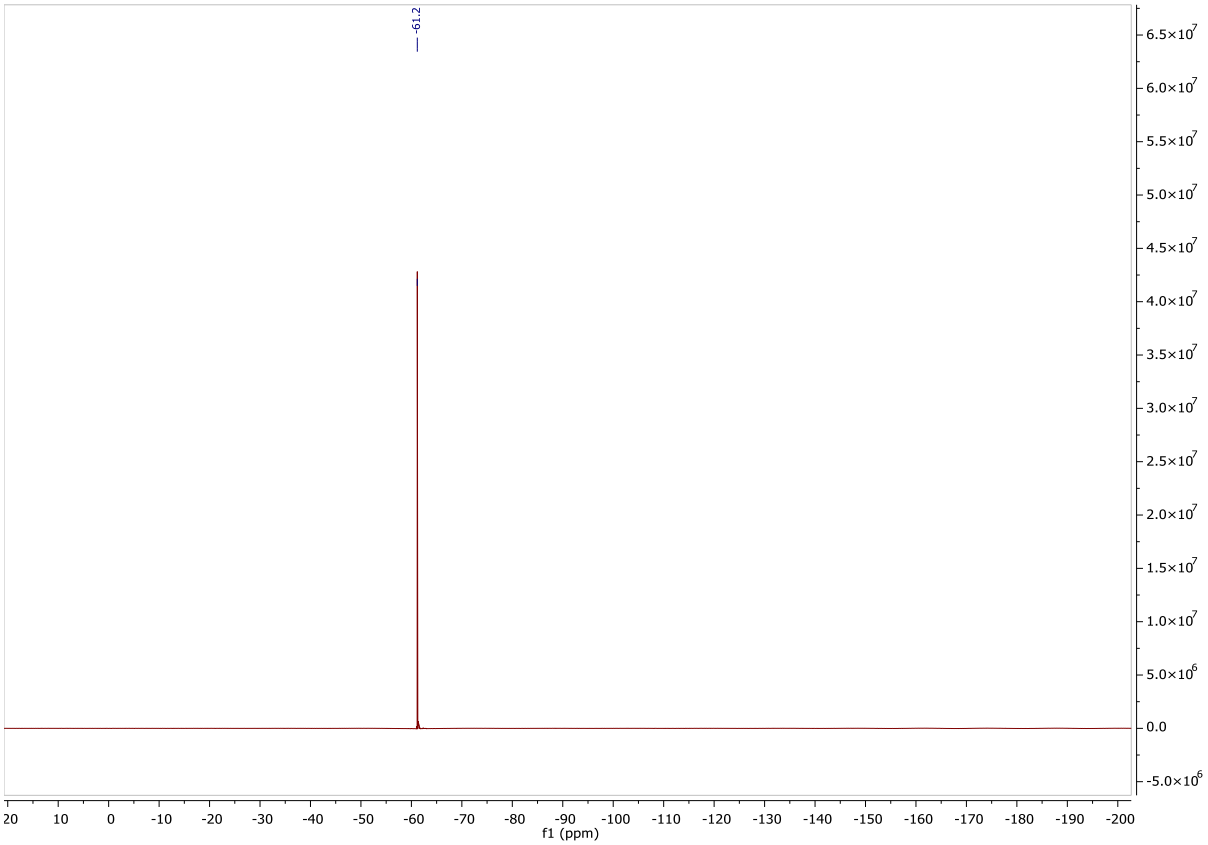
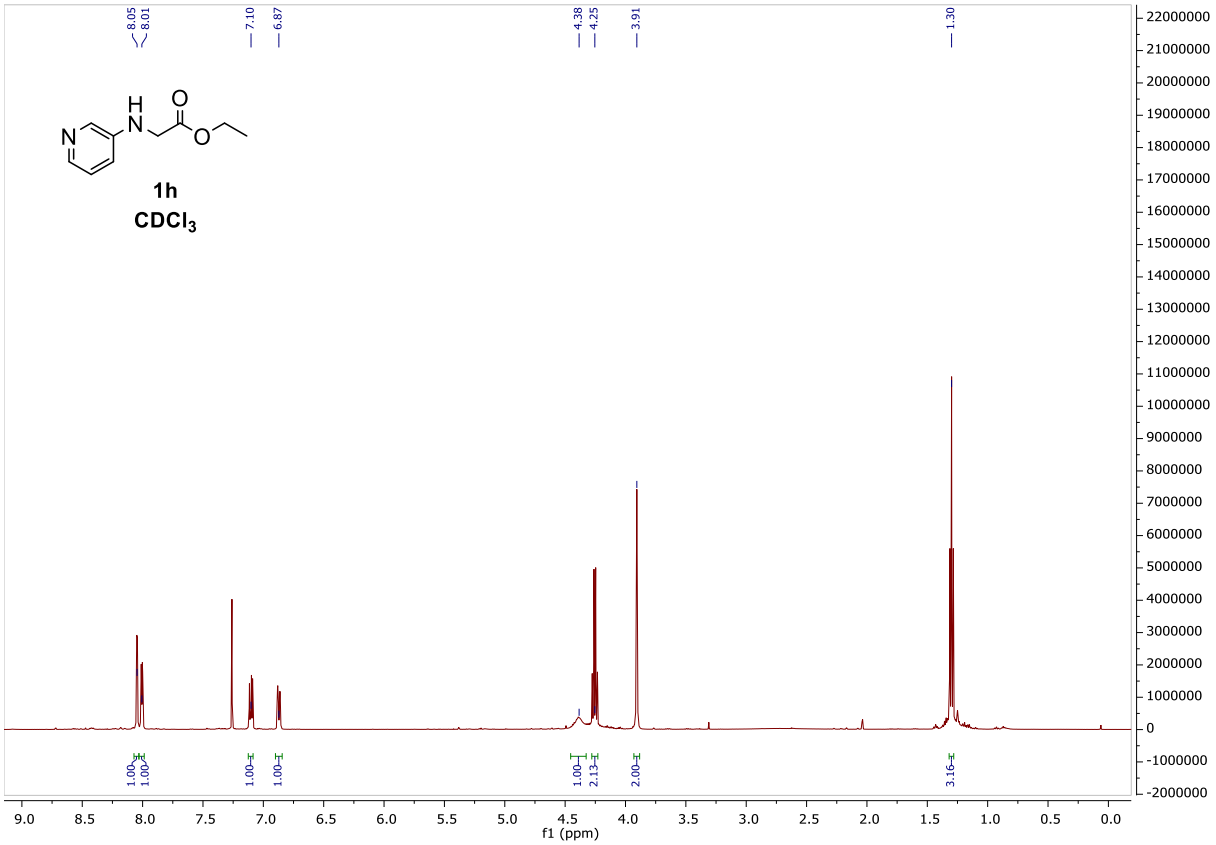
4.27
3.92
1.31
1g
CDCl3
2.00
2.00
0.77
2.02
3.00
f1 (ppm)


170.6
149.6
127.1
126.9
126.8
122.8
120.2
119.6
112.3
61.8
45.4
14.3
f1 (ppm)


-61.2
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


8.05
8.01
7.10
6.87
4.38
4.25
3.91
1.30
1.00
1.00
1.00
1.00
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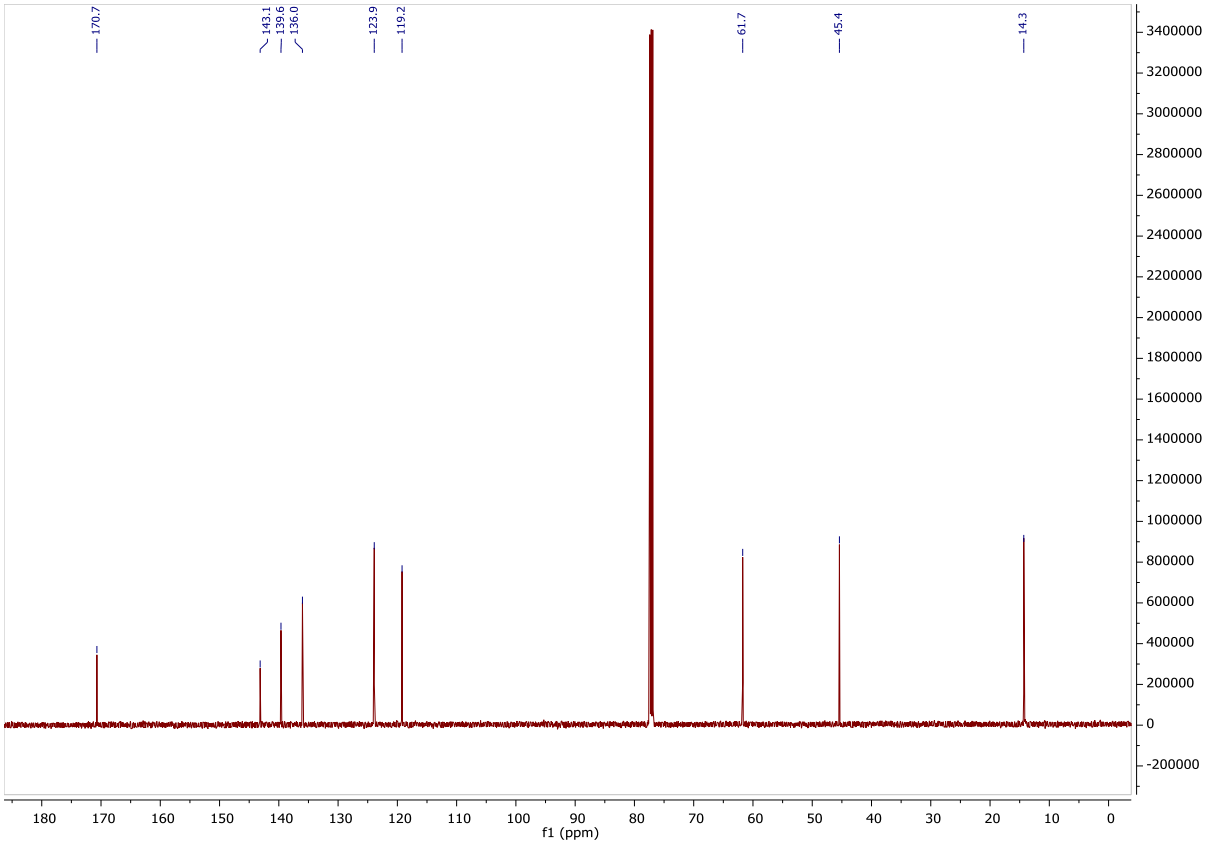
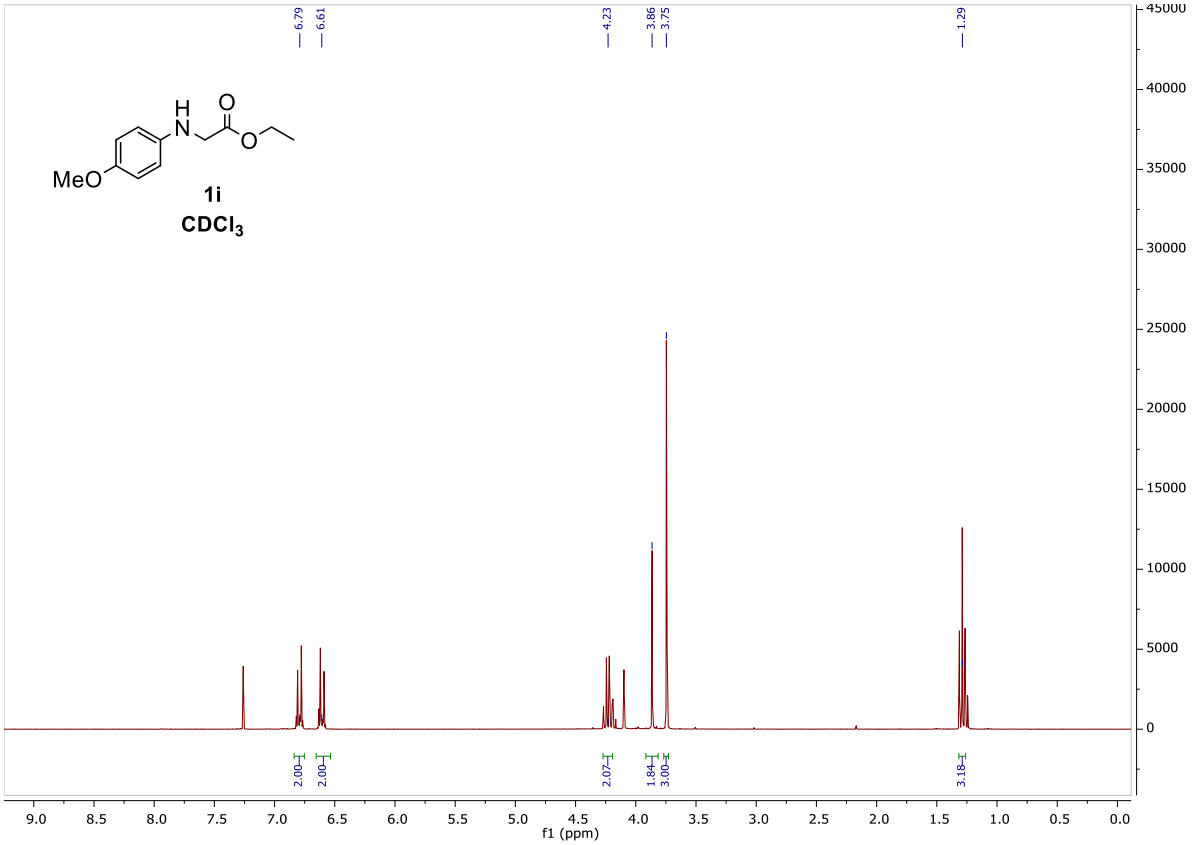
2.00
3.16
1h
CDCl3
f1 (ppm)


170.7
143.1
139.6
136.0
123.9
119.2
61.7
45.4
14.3
f1 (ppm)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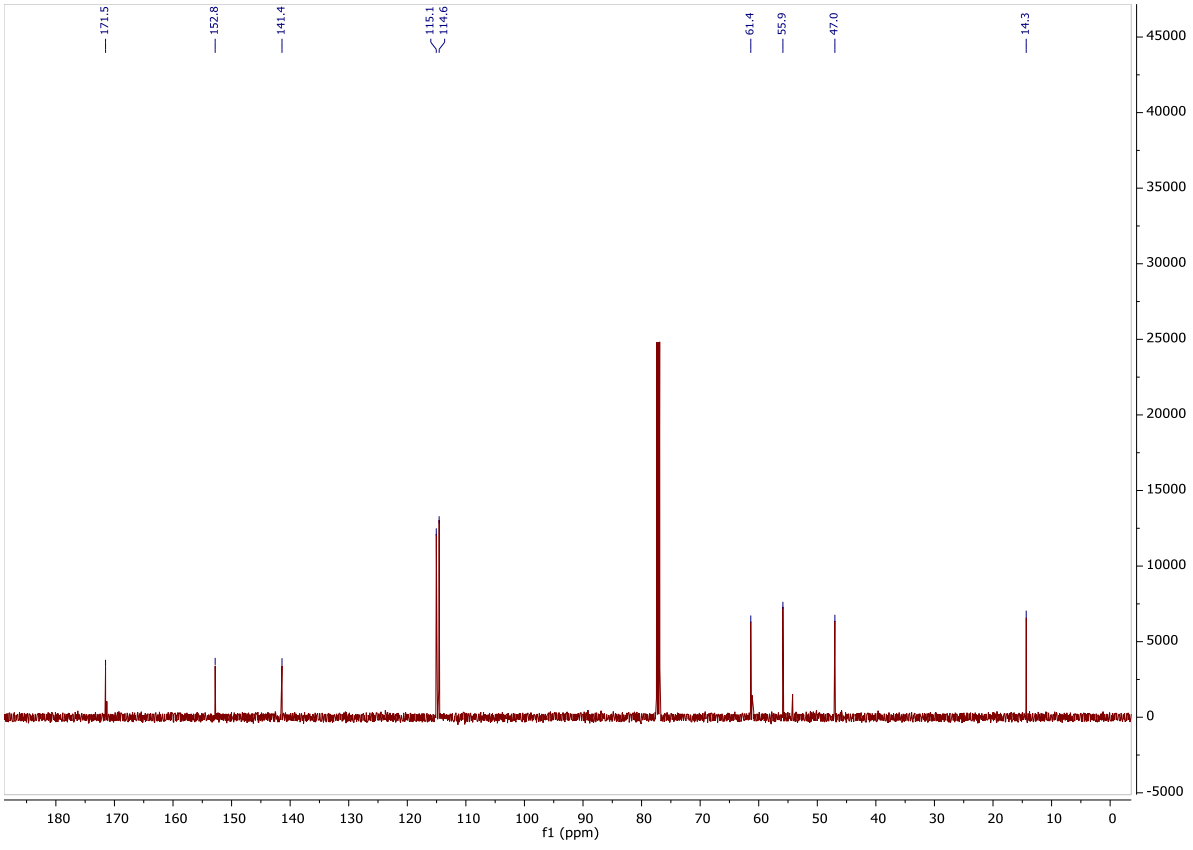
6.61
4.23
3.86
3.75
1.29
MeO
1i
CDCl3
2.00
2.00
2.07
1.84
3.00
3.18
f1 (ppm)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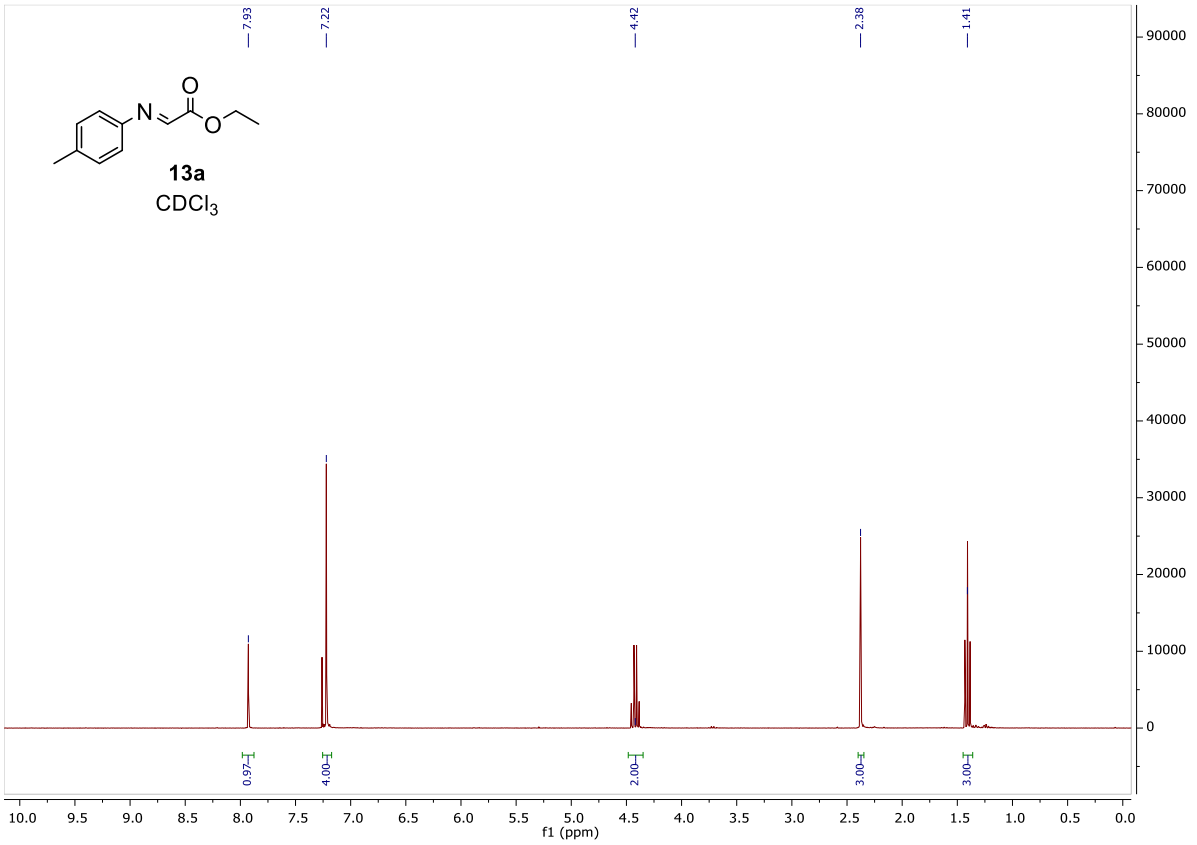
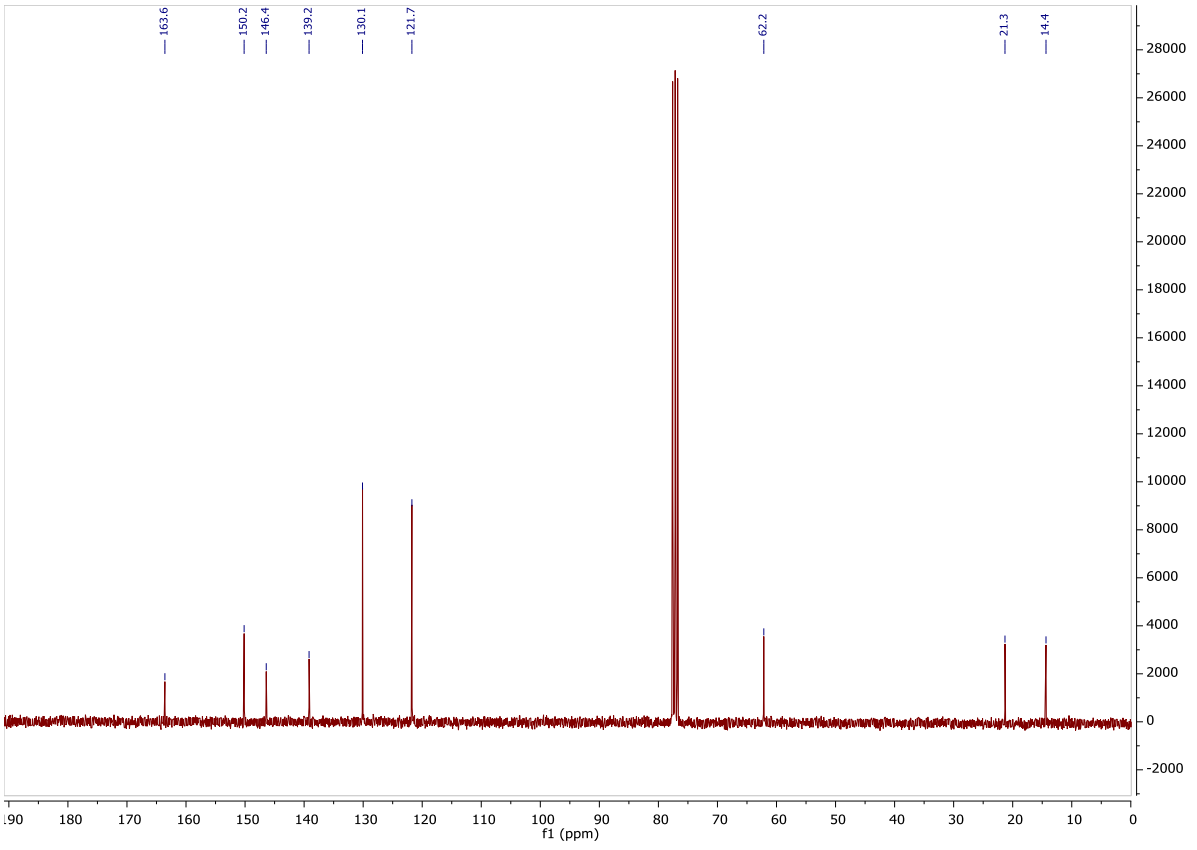
141.4
115.1
114.6
61.4
55.9
47.0
14.3
f1 (ppm)


7.93
7.22
4.42
2.38
1.41
13a
CDCl3
0.97
4.00
2.00
3.00
3.00
f1 (ppm)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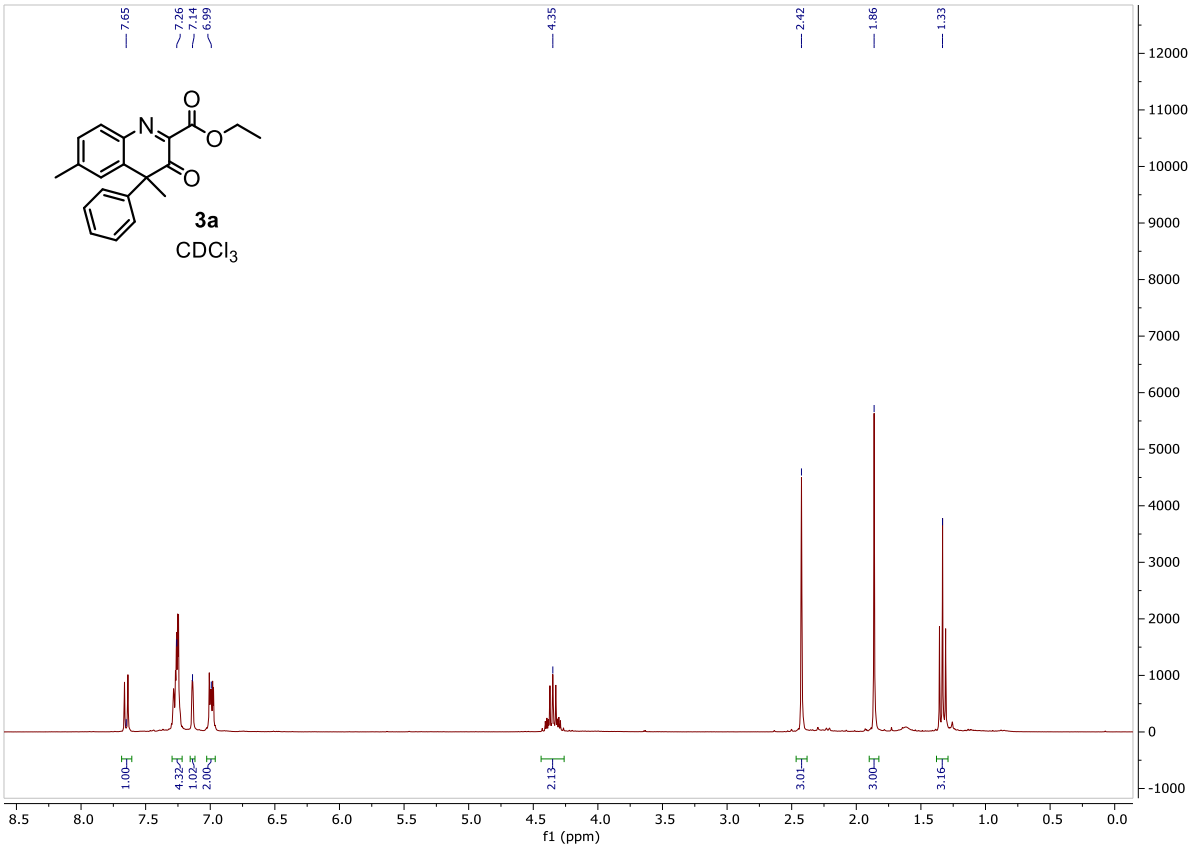
146.4
139.2
130.1
121.7
62.2
21.3
14.4
f1 (ppm)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7.26
7.14
6.99
4.35
2.42
1.86
1.33
3a
CDCl3
1.00
4.32
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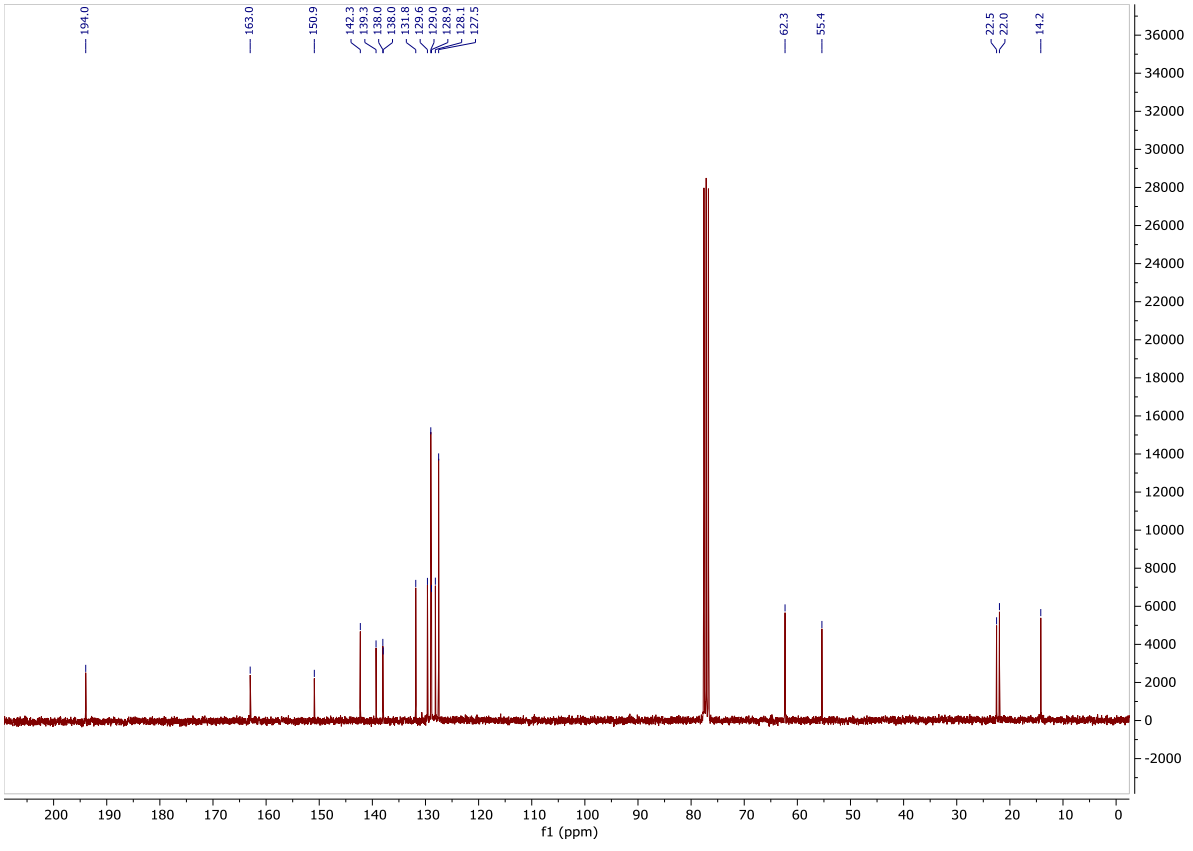
2.13
3.01
3.00
3.16
f1 (ppm)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150.9
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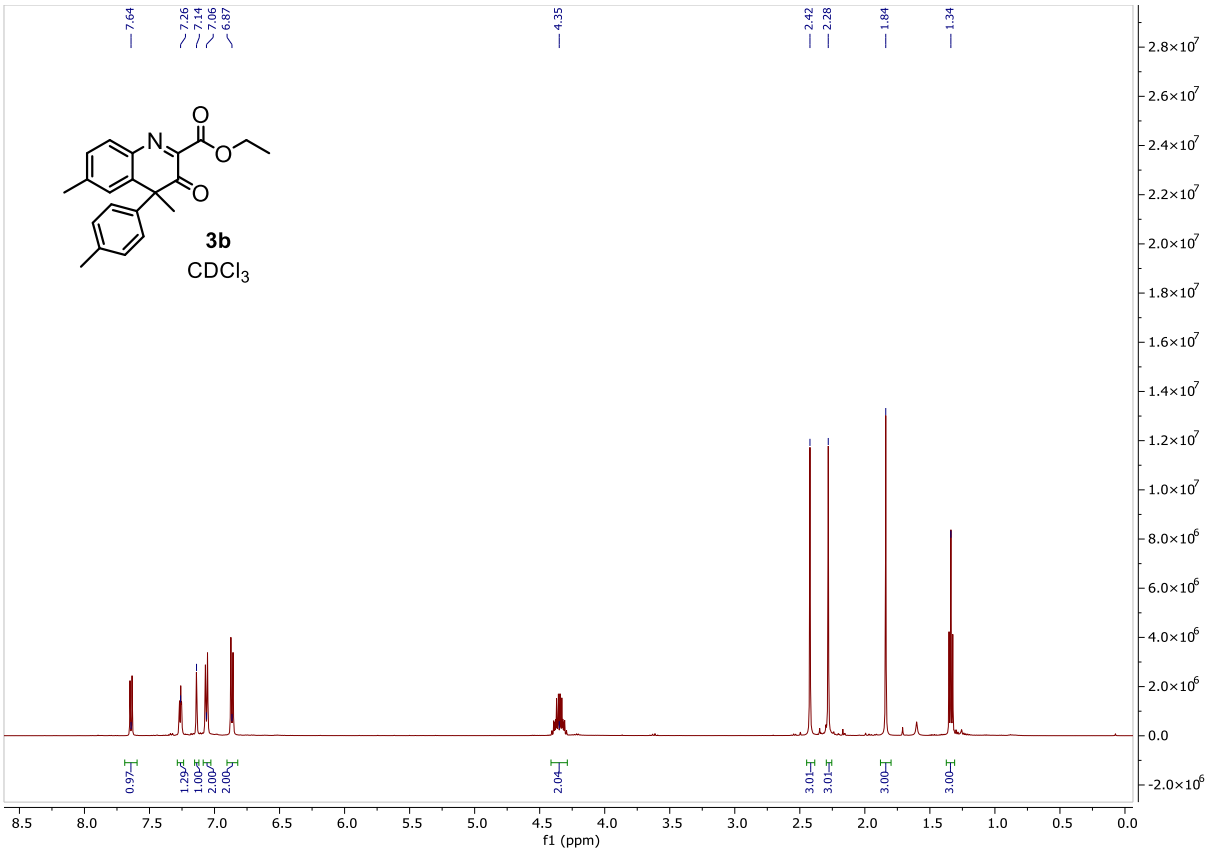
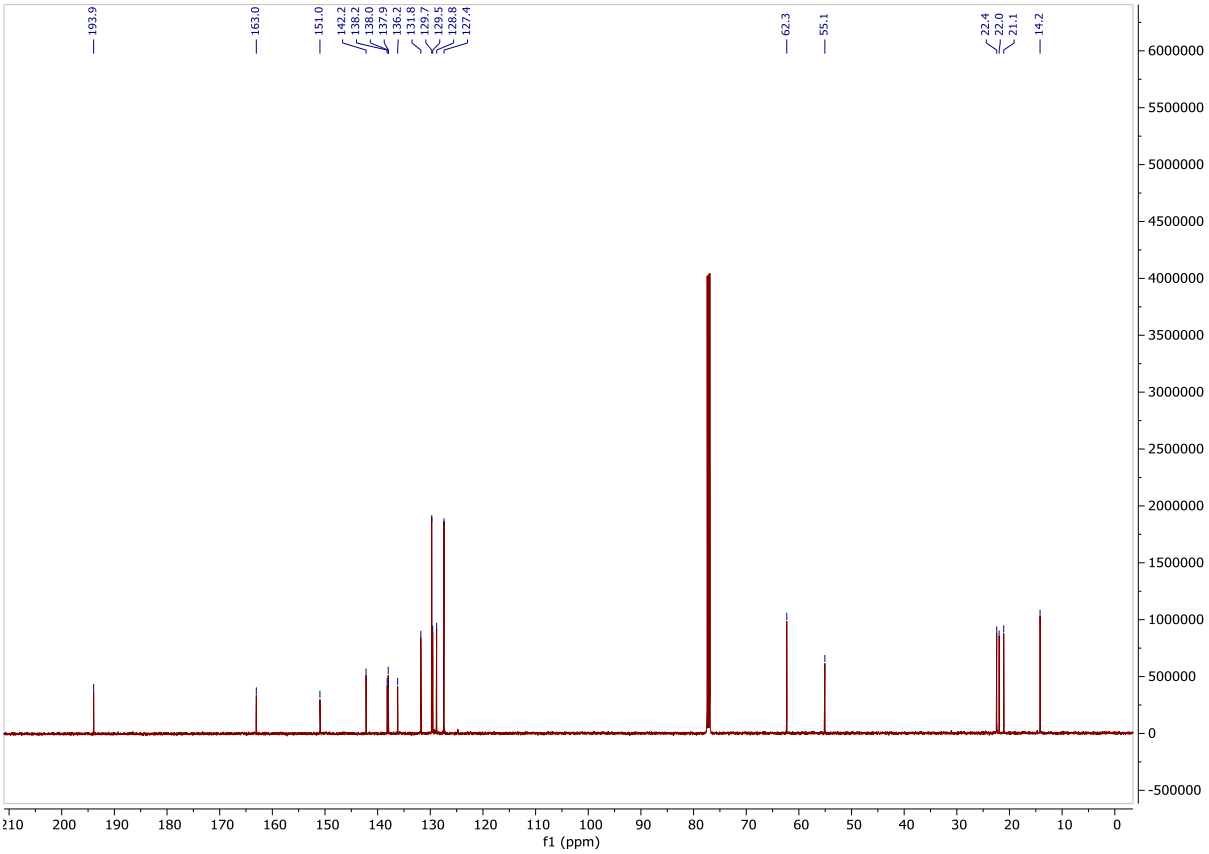
139.3
138.0
138.0
131.8
129.6
129.0
128.9
128.1
127.5
62.3
55.4
22.5
22.0
14.2
f1 (ppm)


7.64
7.26
7.14
7.06
6.87
4.35
2.42
2.28
1.84
1.34
3b
CDCl3
0.97
1.29
1.00
2.00
2.00
2.04
3.01
3.01
3.00
3.00
f1 (ppm)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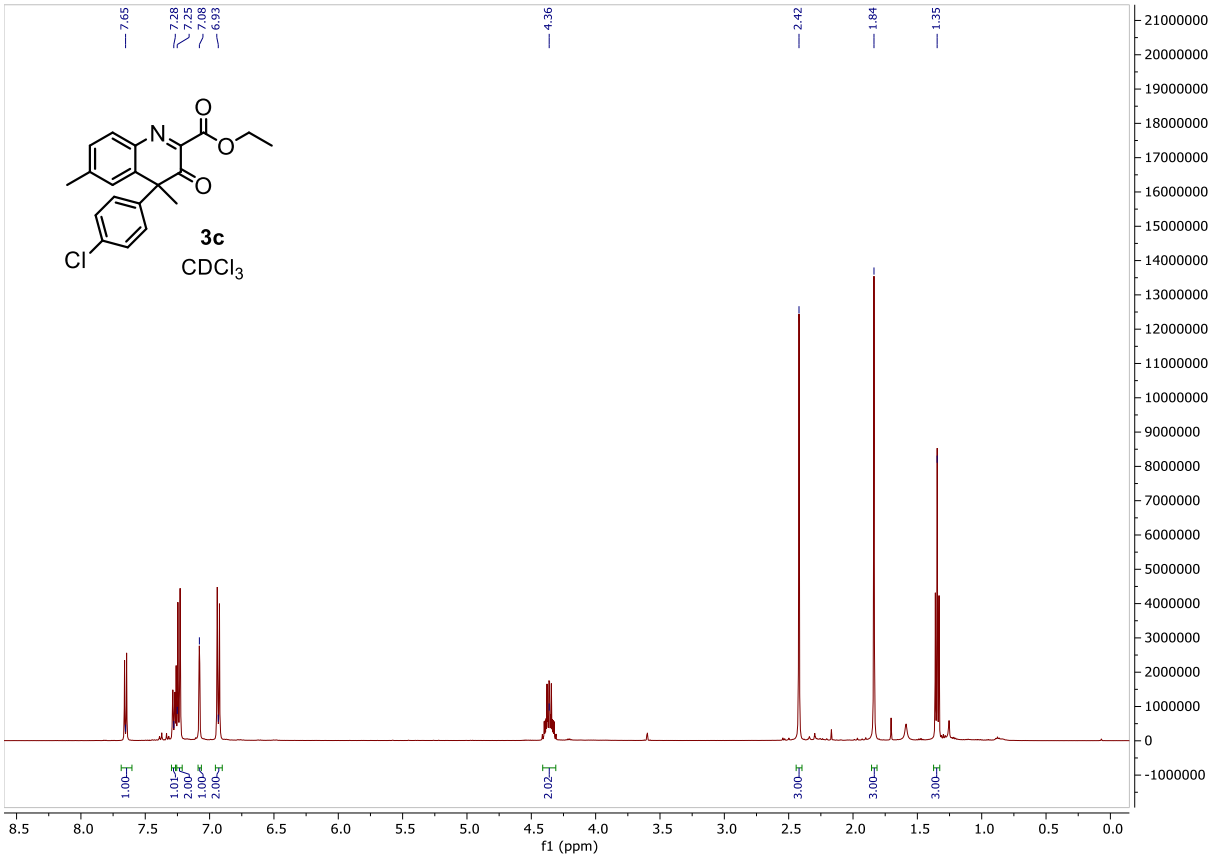
163.0
151.0
142.2
138.2
138.0
137.9
136.2
131.8
129.7
129.5
128.8
127.4
62.3
55.1
22.4
22.0
21.1
14.2
f1 (ppm)


7.65
7.28
7.25
7.08
6.93
4.36
2.42
1.84
1.35
3c
CDCl3
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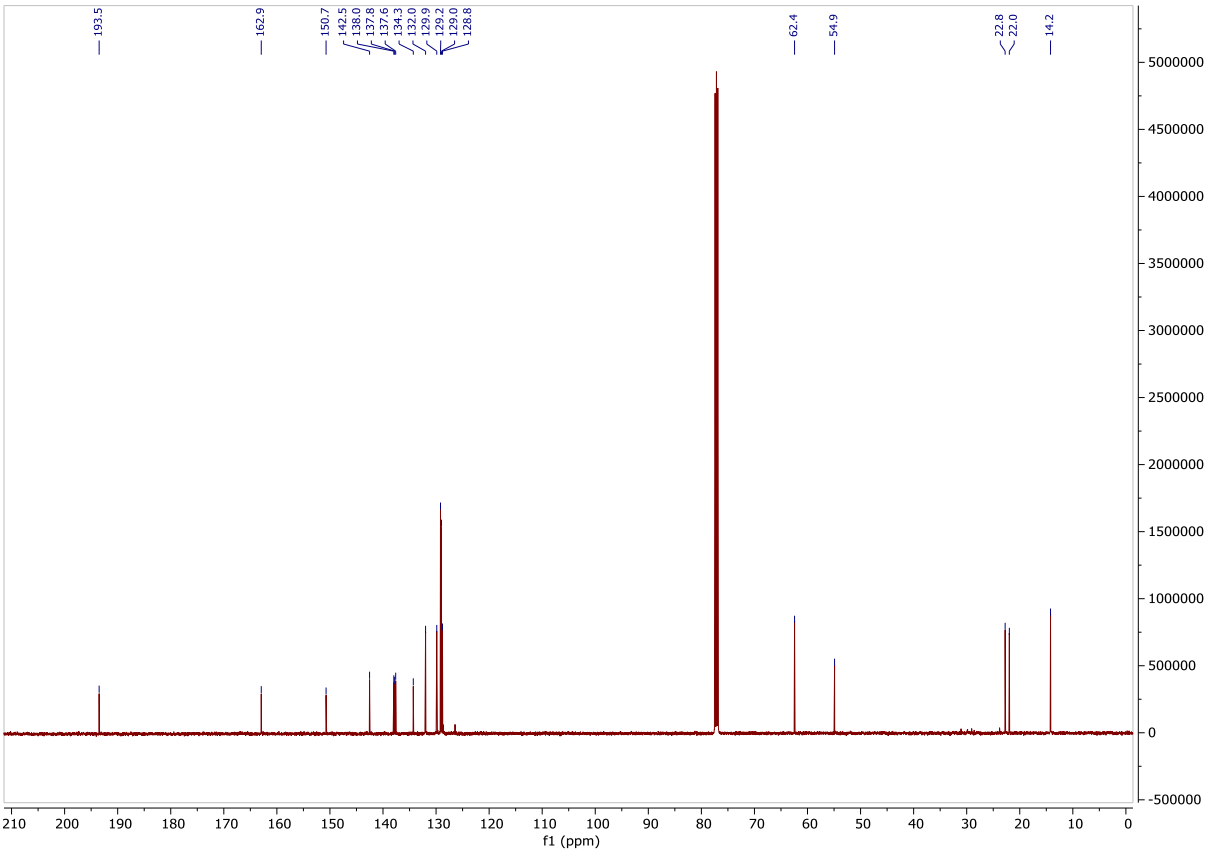
2.02
3.00
3.00
3.00
f1 (ppm)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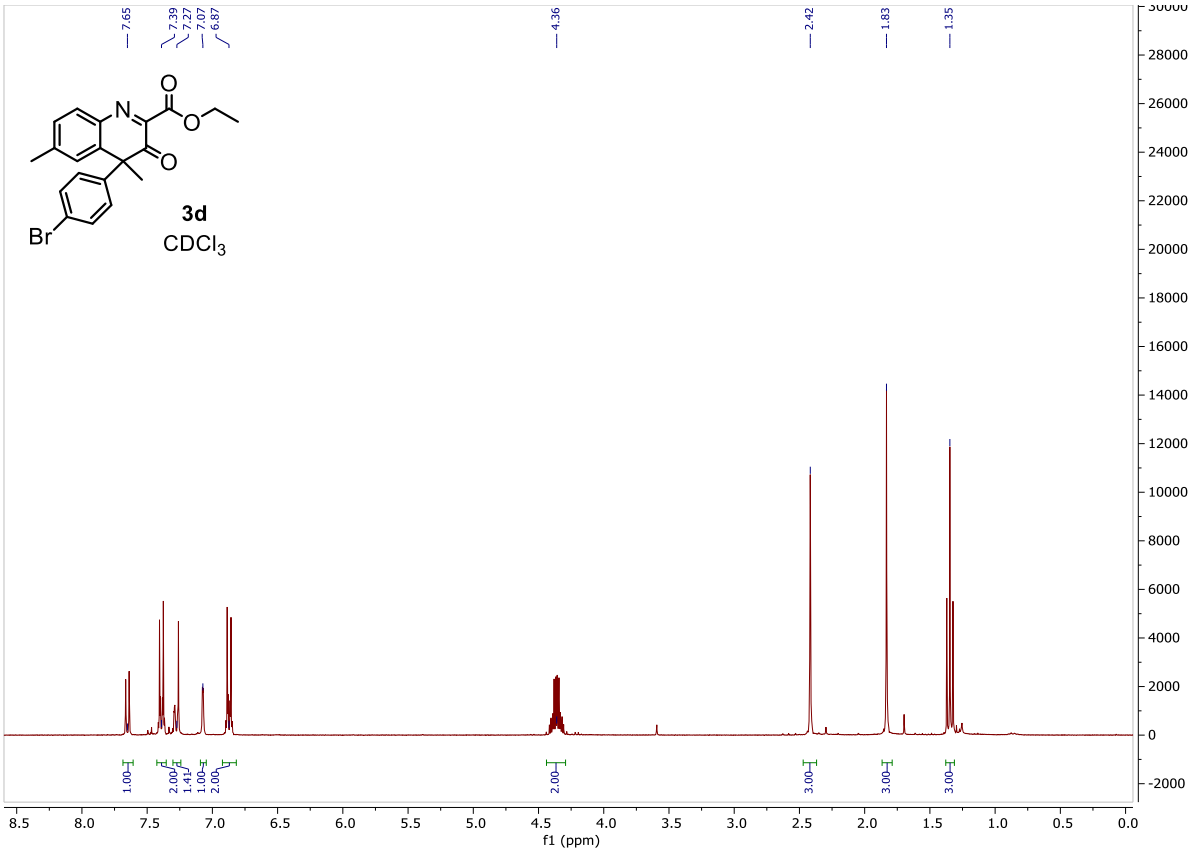
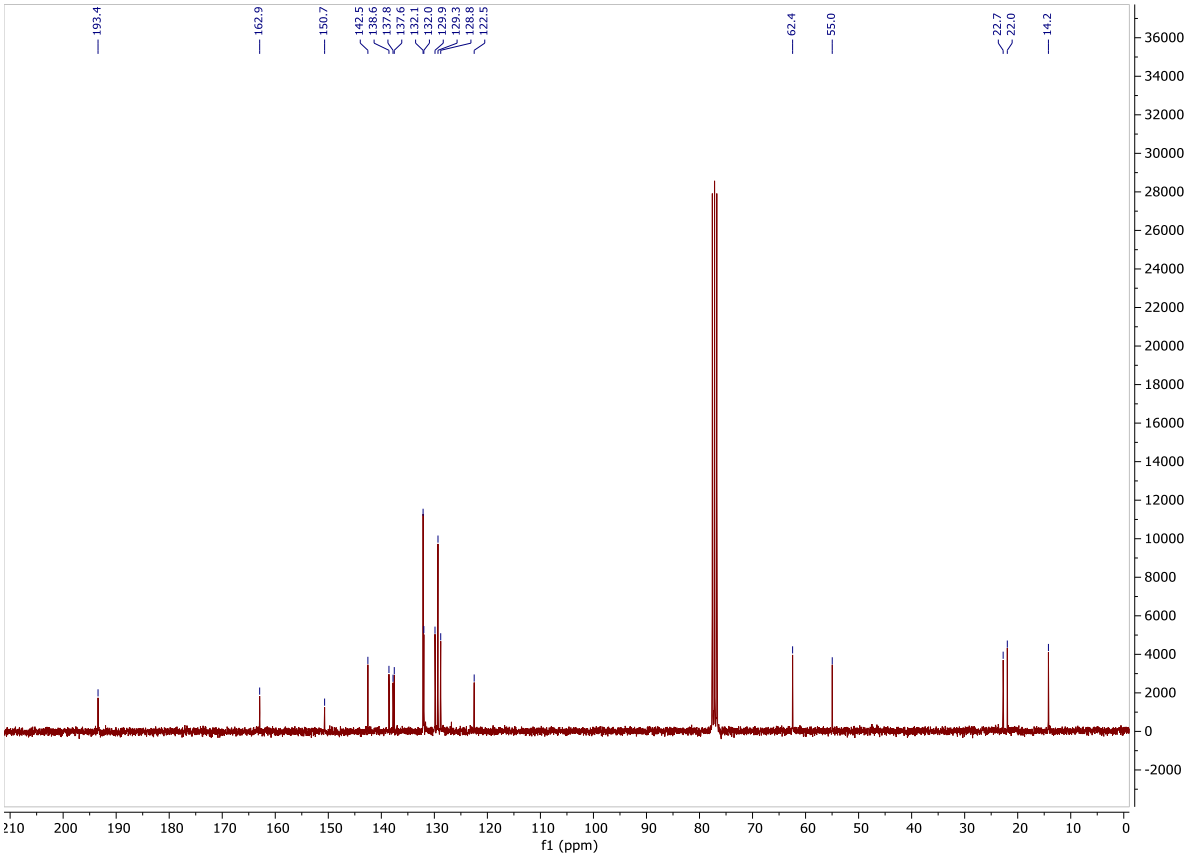
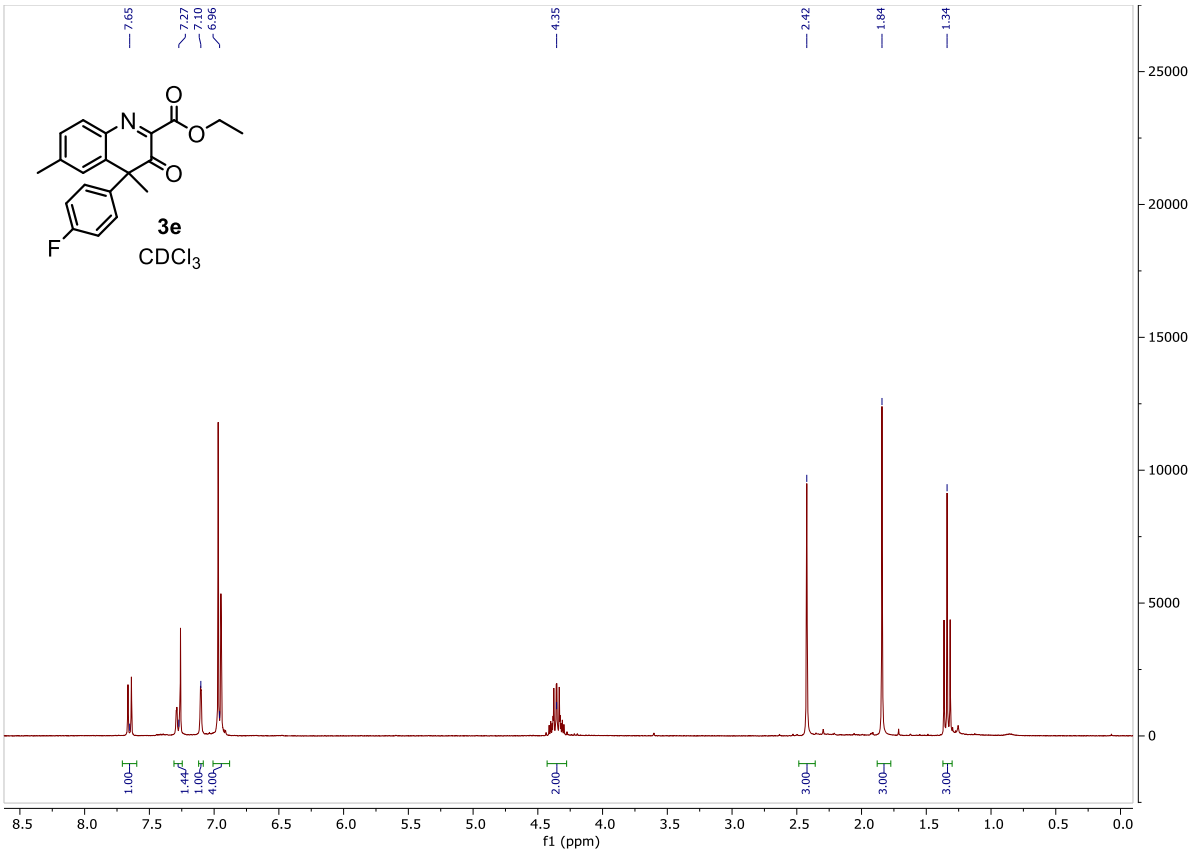
162.9
150.7
142.5
138.0
137.8
137.6
134.3
132.0
129.9
129.2
129.0
128.8
62.4
54.9
22.8
22.0
14.2
f1 (ppm)


7.65
7.39
7.27
7.07
6.87
4.36
2.42
1.83
1.35
3d
CDCl3
Br
f1 (ppm)


193.4
162.9
150.7
142.5
138.6
137.8
137.6
132.1
132.0
129.9
129.3
128.8
122.5
62.4
55.0
22.7
22.0
14.2
f1 (ppm)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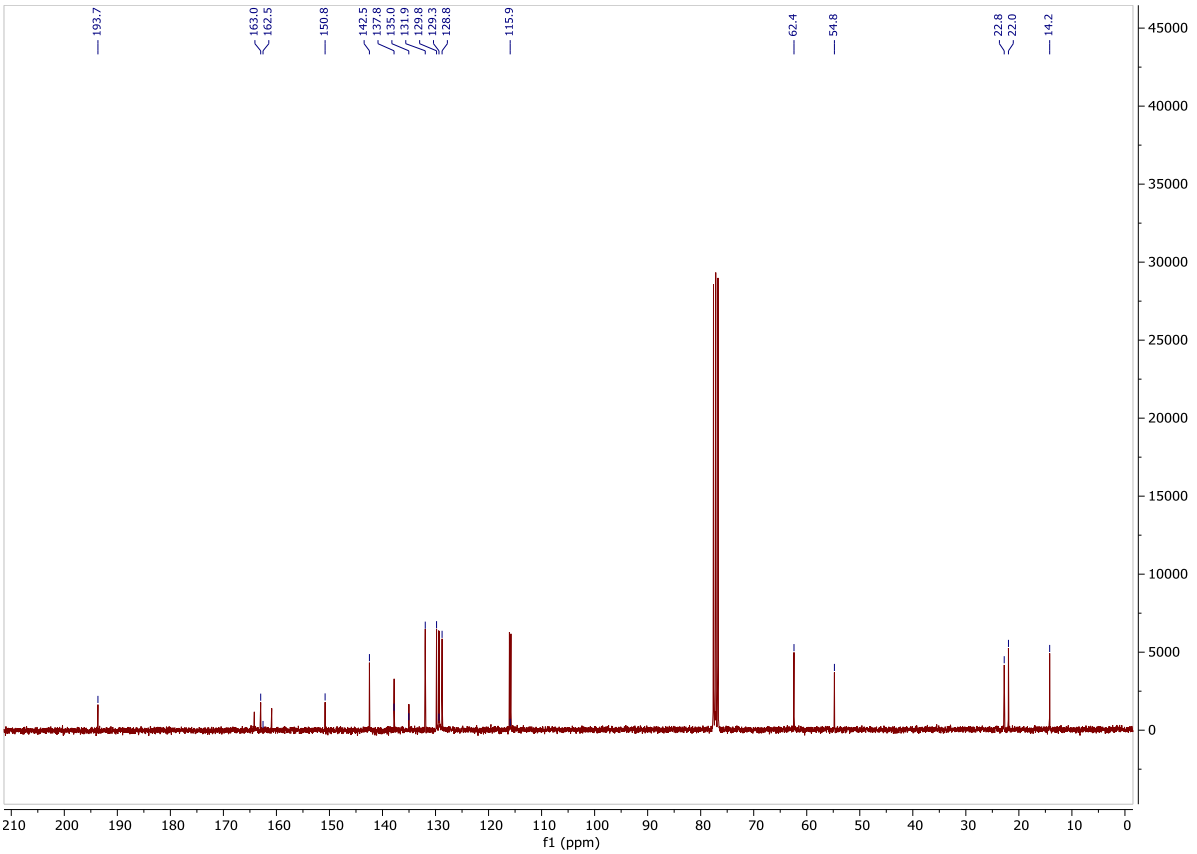
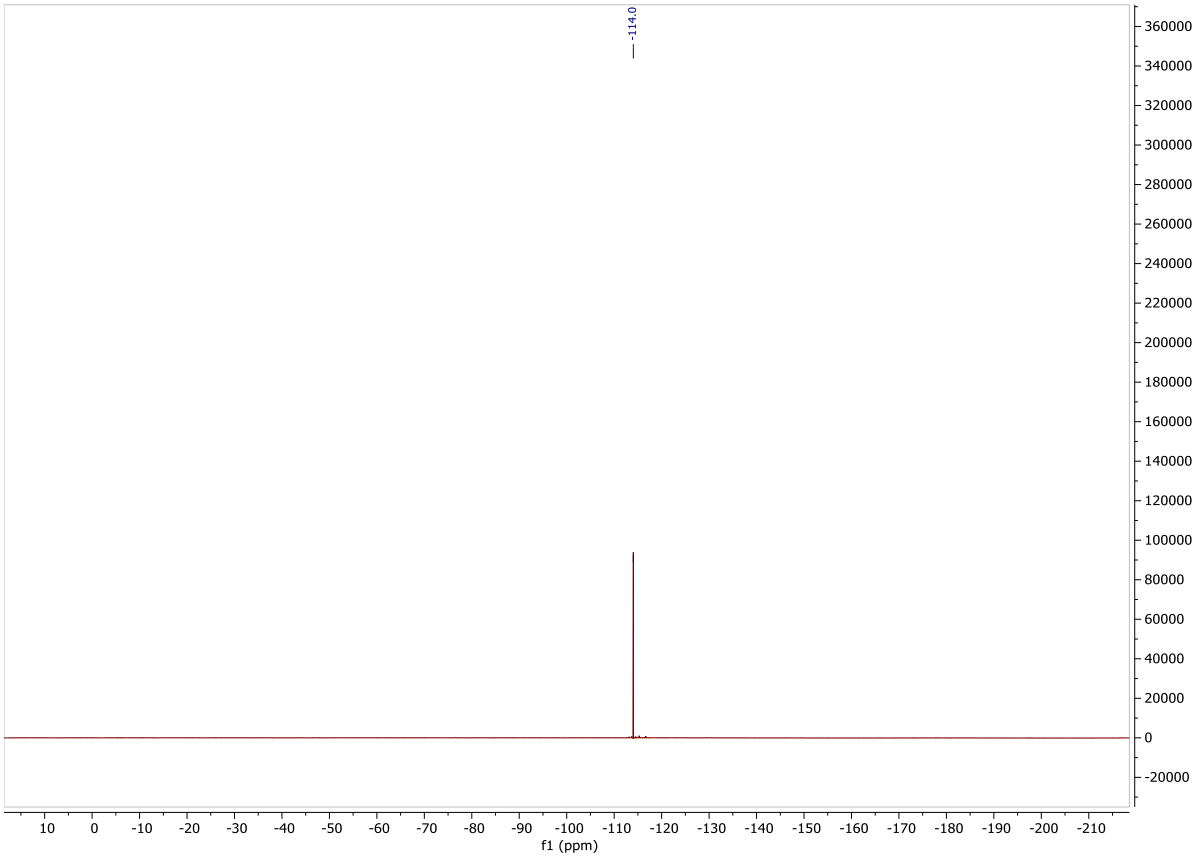
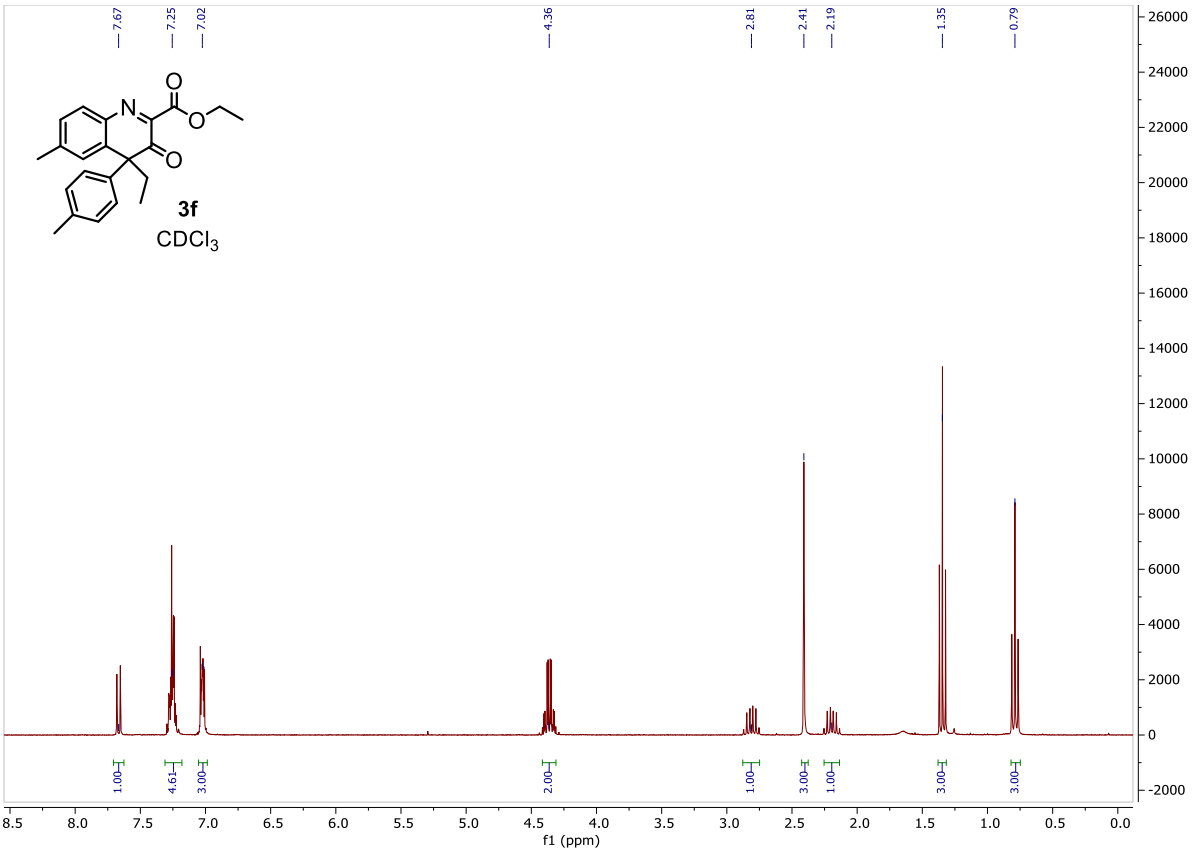
7.27
7.10
6.96
4.35
2.42
1.84
1.34
3e
CDCl3
f1 (ppm)


193.7
163.0
162.5
150.8
142.5
137.8
135.0
131.9
129.8
129.3
128.8
115.9
62.4
54.8
22.8
22.0
14.2
f1 (ppm)


-114.0
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.67
7.25
7.02
4.36
2.81
2.41
2.19
1.35
0.79
O
N
O
O
3f
CDCl3
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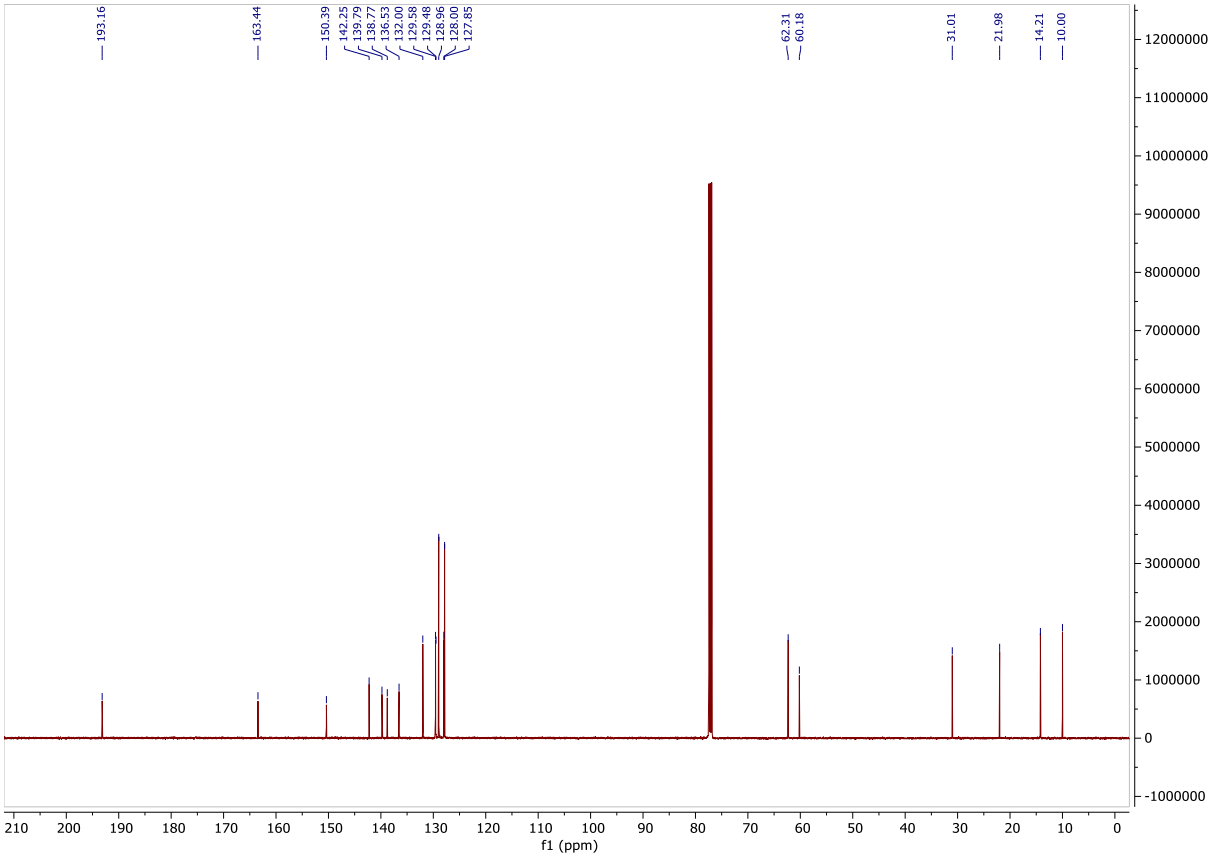
4.61
3.00
2.00
1.00
3.00
1.00
3.00
3.00
f1 (ppm)


193.16
163.44
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142.25
139.79
138.77
136.53
132.00
129.58
129.48
128.96
128.00
127.85
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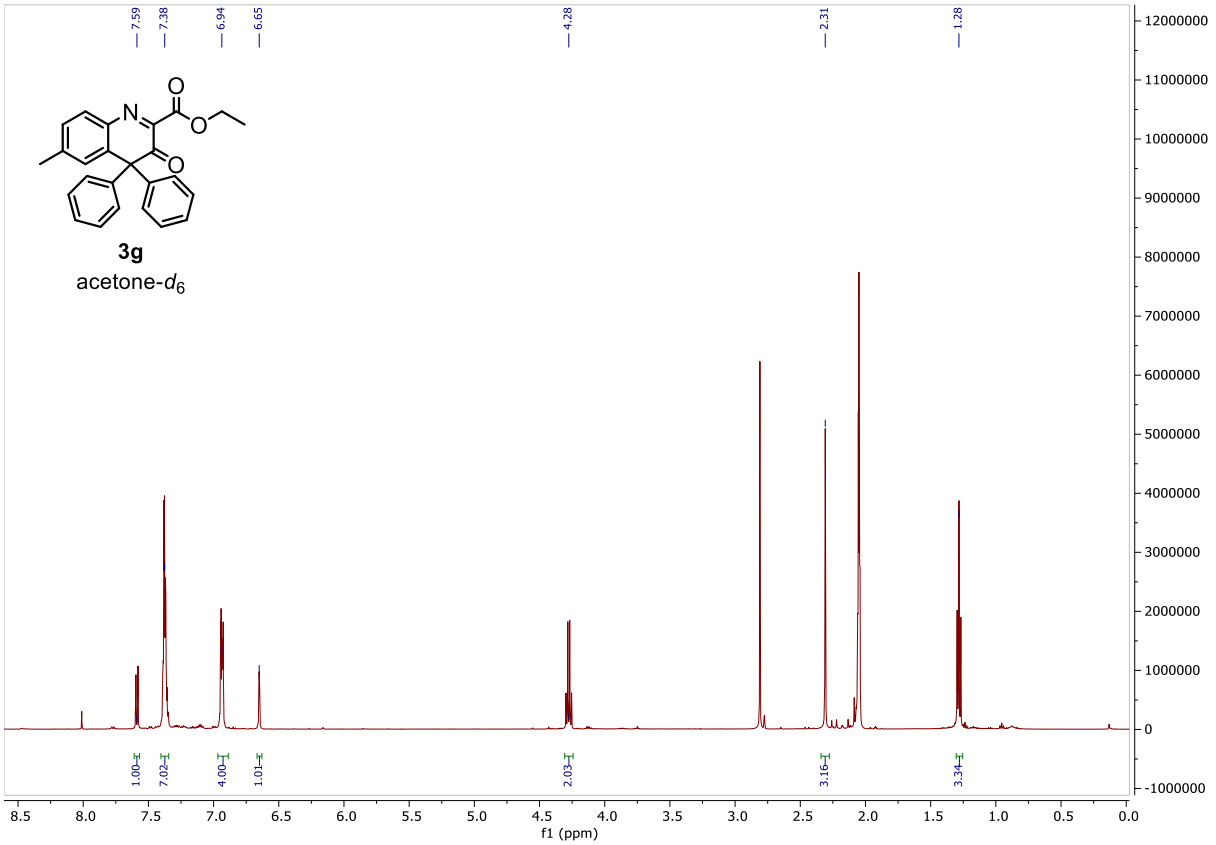
60.18
31.01
21.98
14.21
10.00
f1 (ppm)


7.59
7.38
6.94
6.65
4.28
2.31
1.28
3g
acetone-d_6
1.00
7.02
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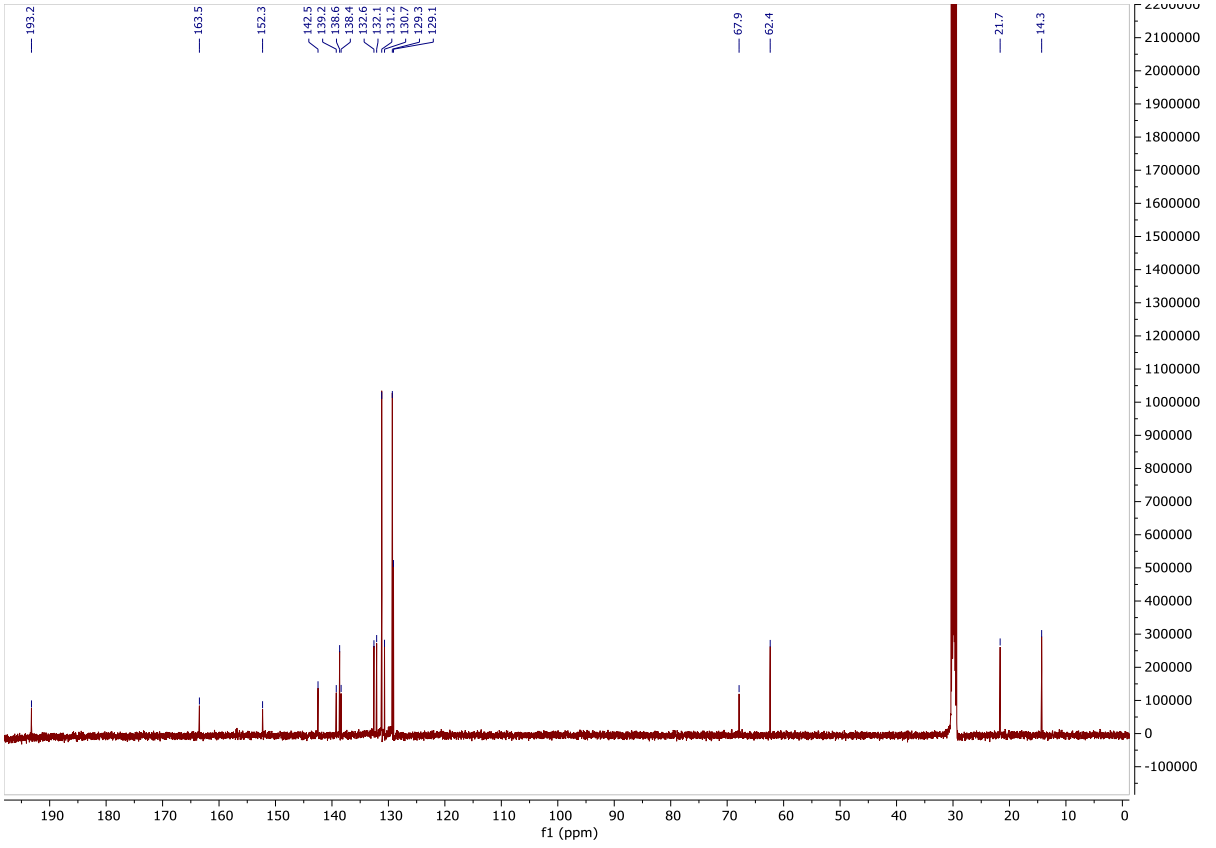
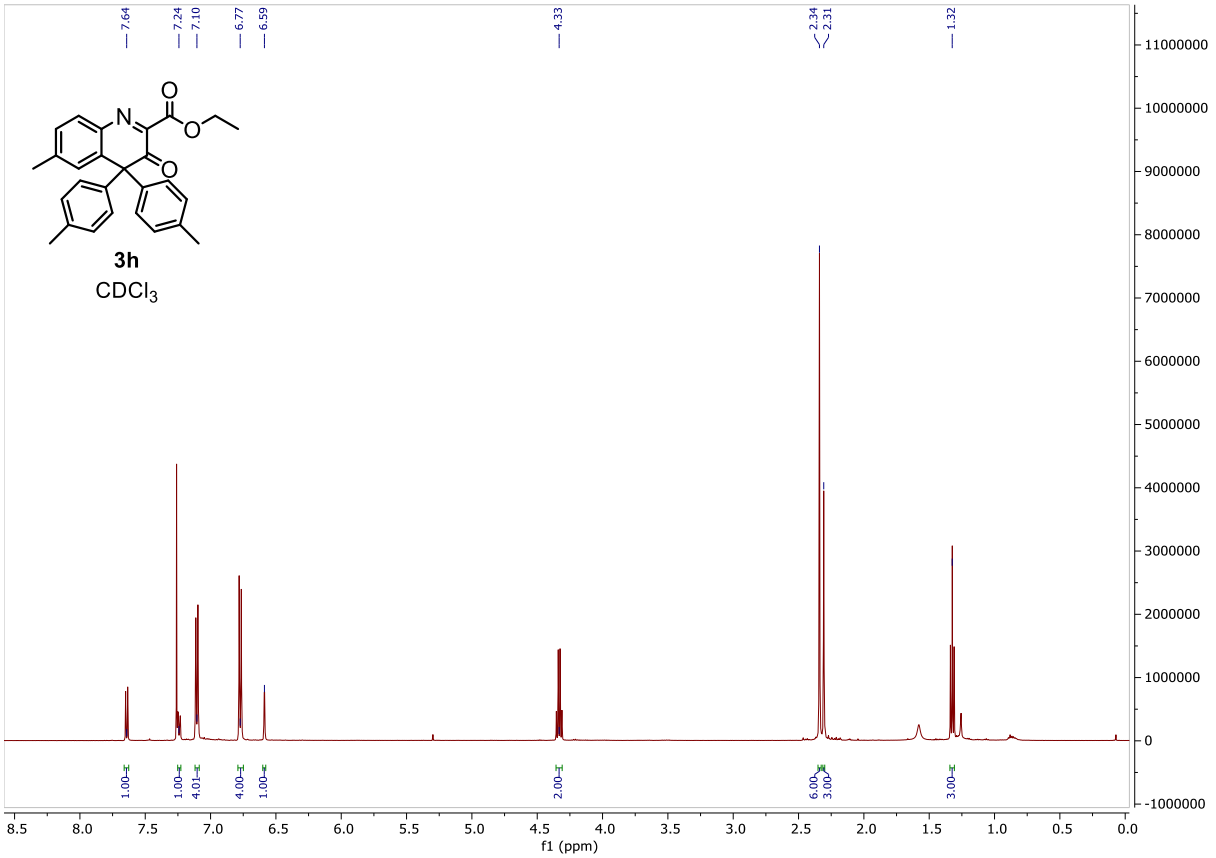
1.01
2.03
3.16
3.34
f1 (ppm)


193.2
163.5
152.3
142.5
139.2
138.6
138.4
132.6
132.1
131.2
130.7
129.3
129.1
67.9
62.4
21.7
14.3
f1 (ppm)


7.64
7.24
7.10
6.77
6.59
4.33
2.34
2.31
1.32
3h
CDCl3
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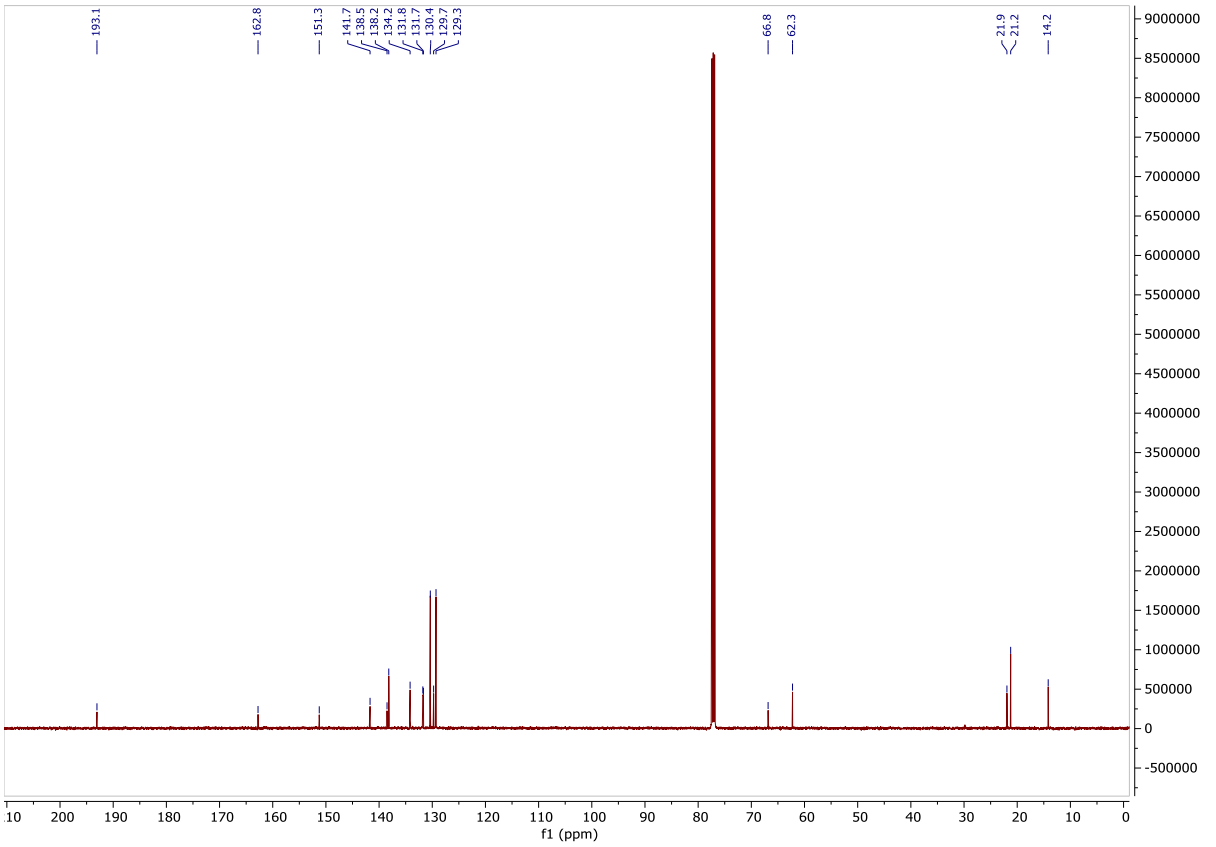
2.00
6.00
3.00
3.00
f1 (ppm)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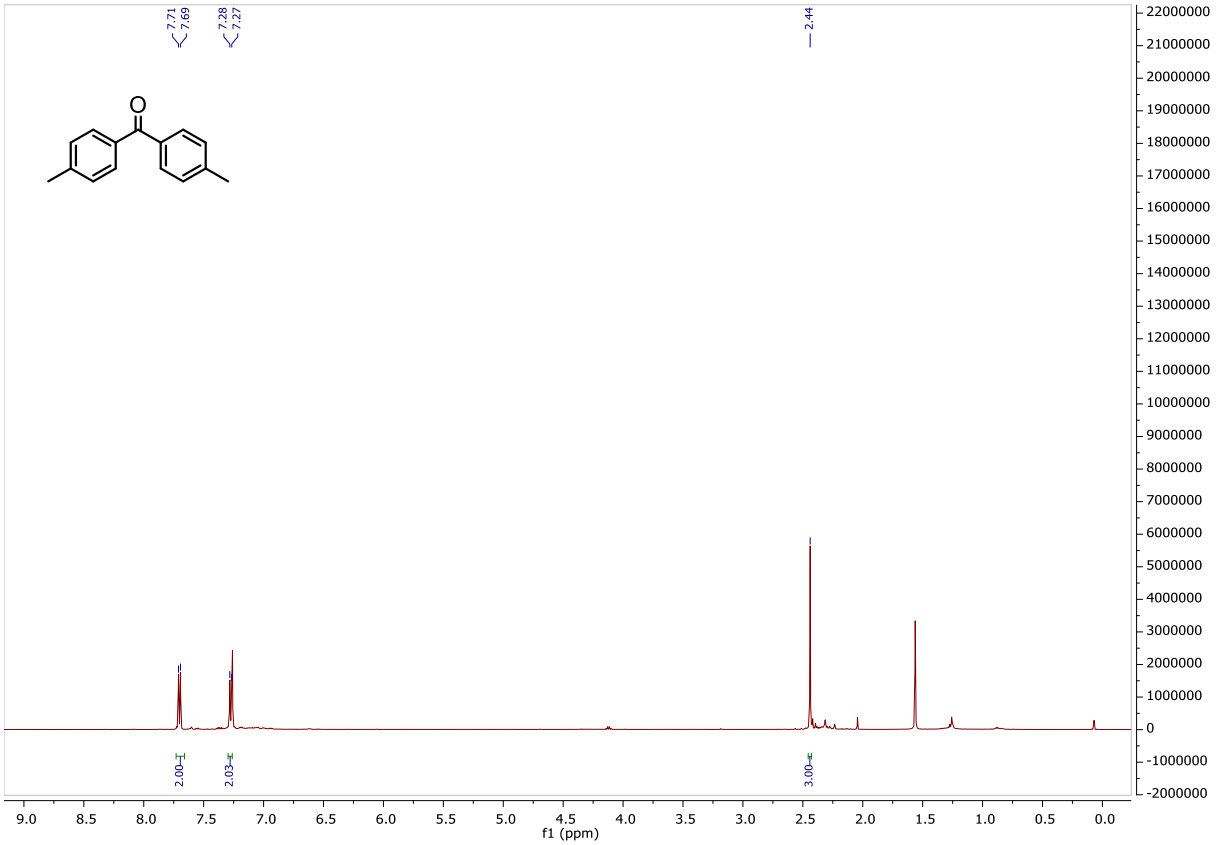
162.8
151.3
141.7
138.5
138.2
134.2
131.8
131.7
130.4
129.7
129.3
66.8
62.3
21.9
21.2
14.2
f1 (ppm)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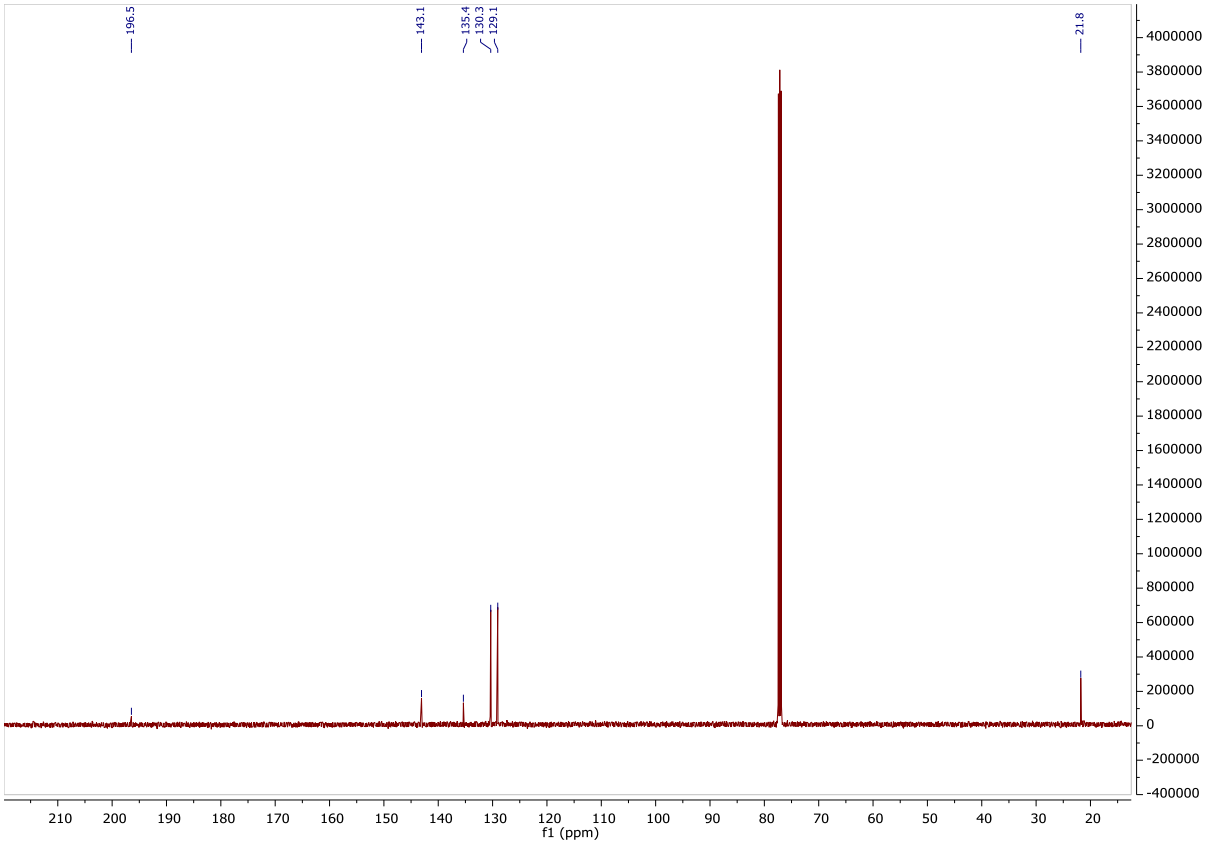
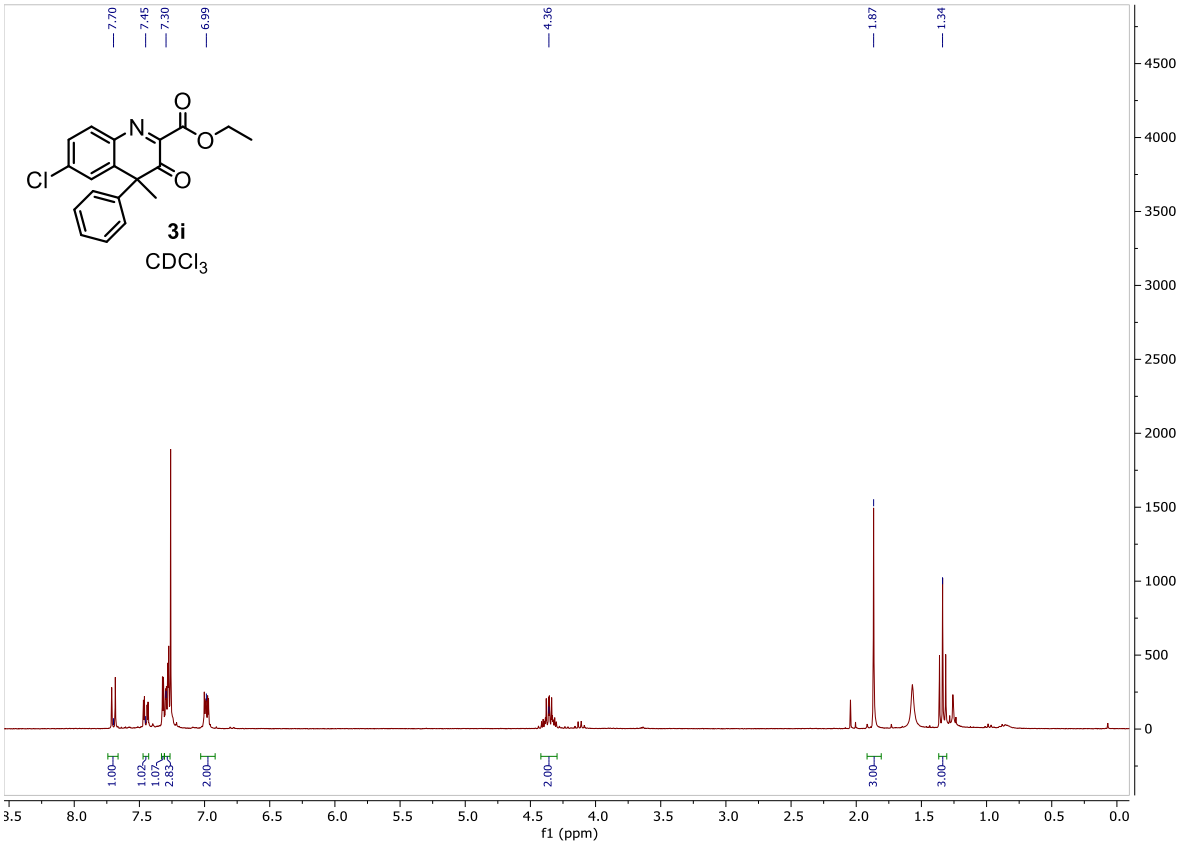
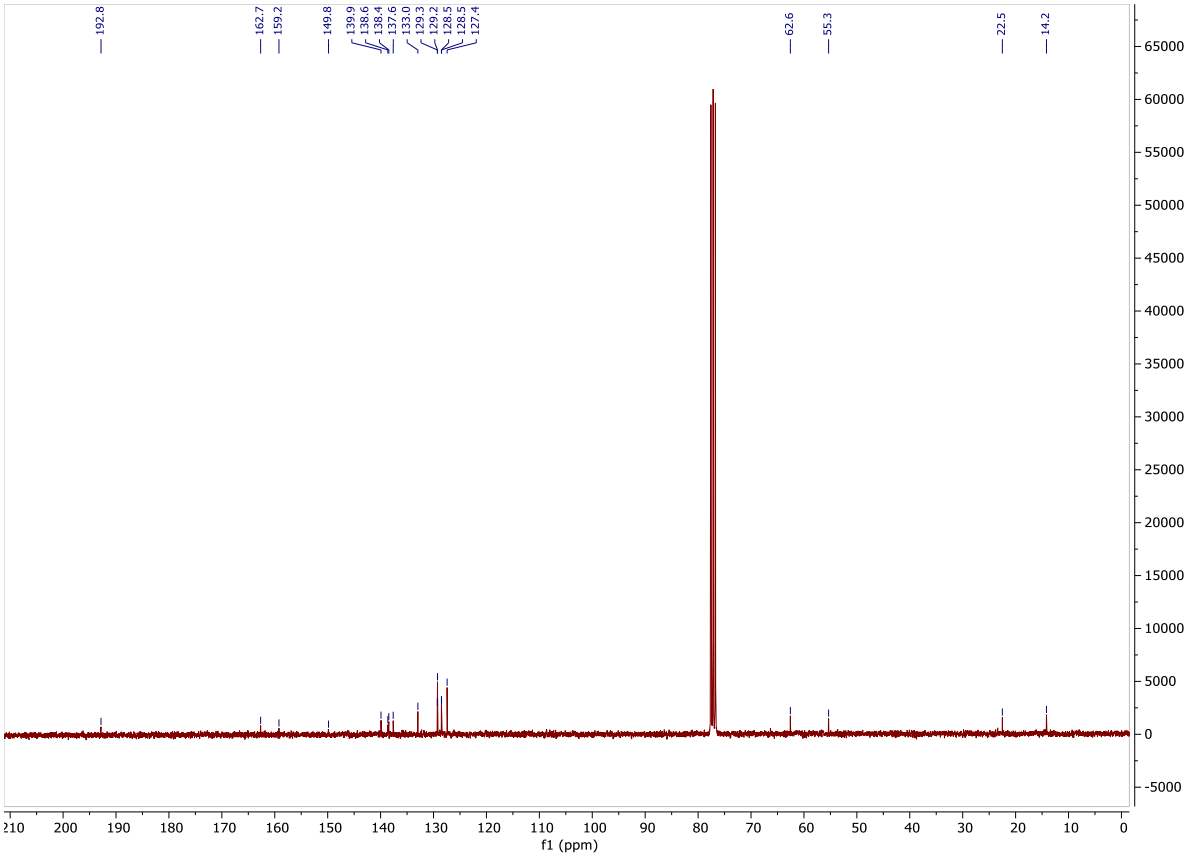
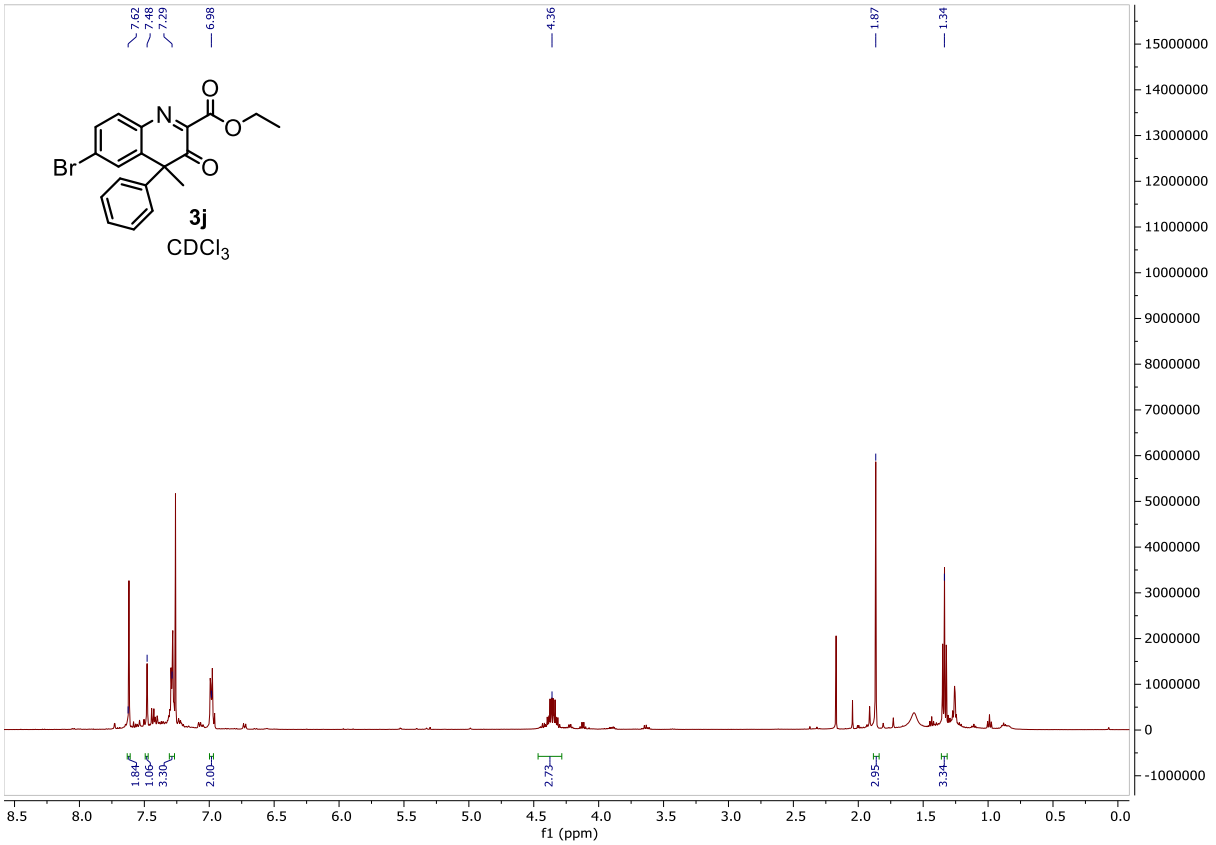
7.69
7.28
7.27
2.44
2.00
2.03
3.00
f1 (ppm)


196.5
143.1
135.4
130.3
129.1
21.8
f1 (ppm)


7.70
7.45
7.30
6.99
4.36
1.87
1.34
3i
CDCl3
1.00
1.02
1.07
2.83
2.00
2.00
3.00
3.00
f1 (ppm)


192.8
162.7
159.2
149.8
139.9
138.6
138.4
137.6
133.0
129.3
129.2
128.5
128.5
127.4
62.6
55.3
22.5
14.2
f1 (ppm)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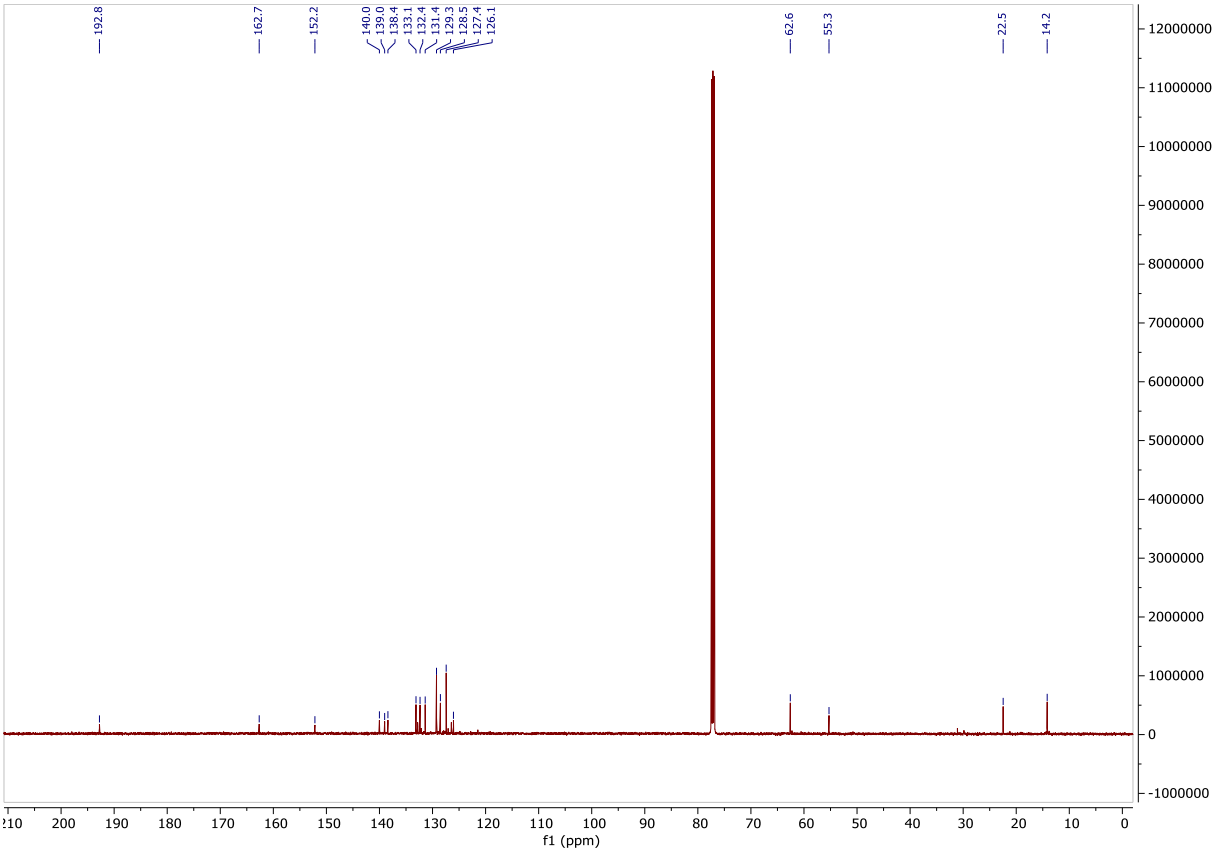
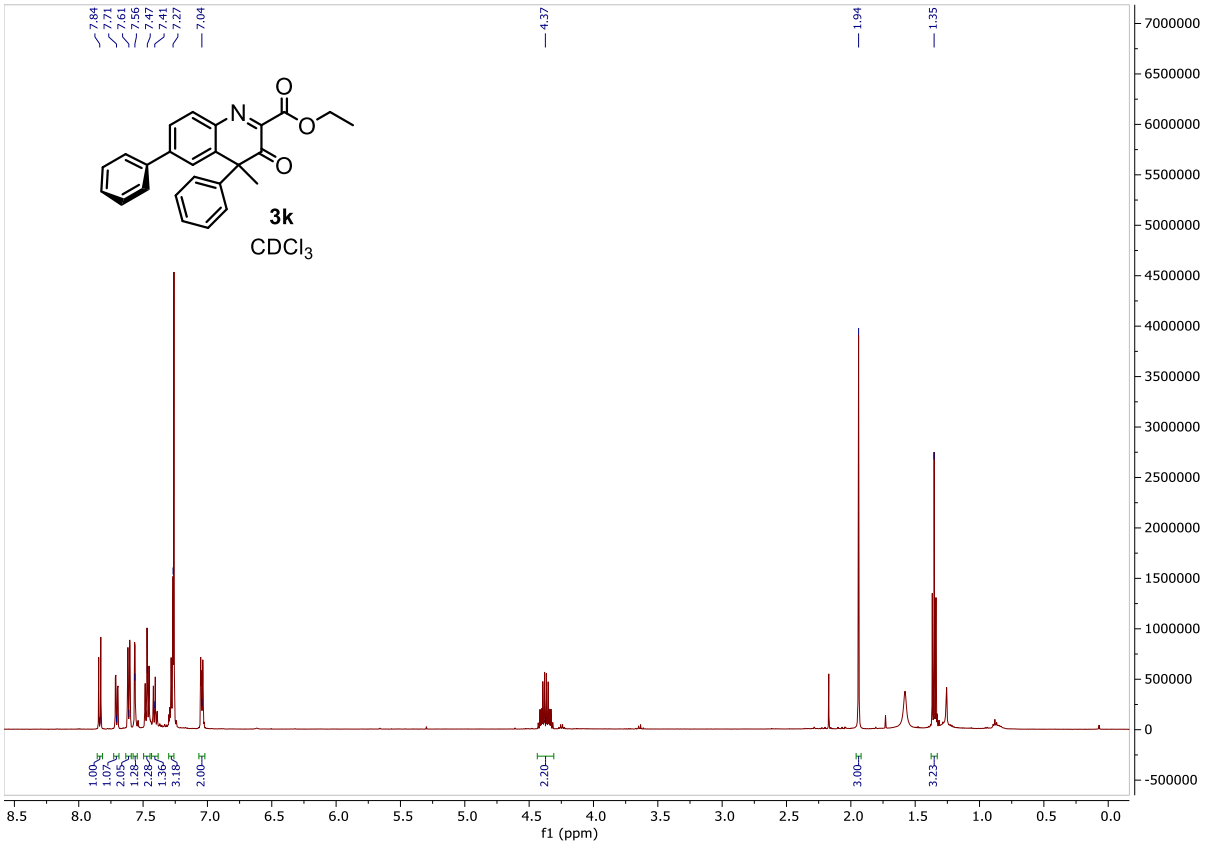
7.48
7.29
6.98
4.36
1.87
1.34
Br
O
N
O
O
3j
CDCl3
1.84
1.06
3.30
2.00
2.73
2.95
3.34
f1 (ppm)


192.8
162.7
152.2
140.0
139.0
138.4
133.1
132.4
131.4
129.3
128.5
127.4
126.1
62.6
55.3
22.5
14.2
f1 (ppm)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7.71
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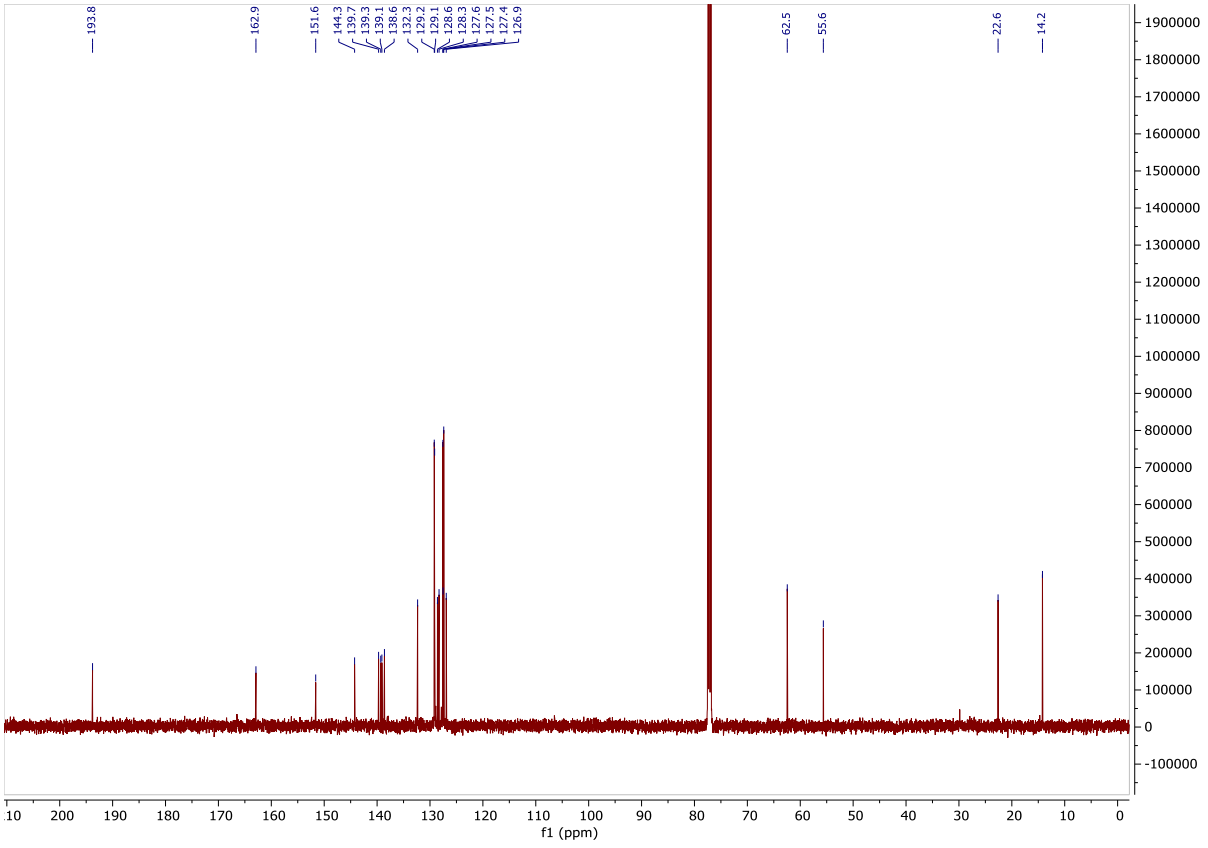
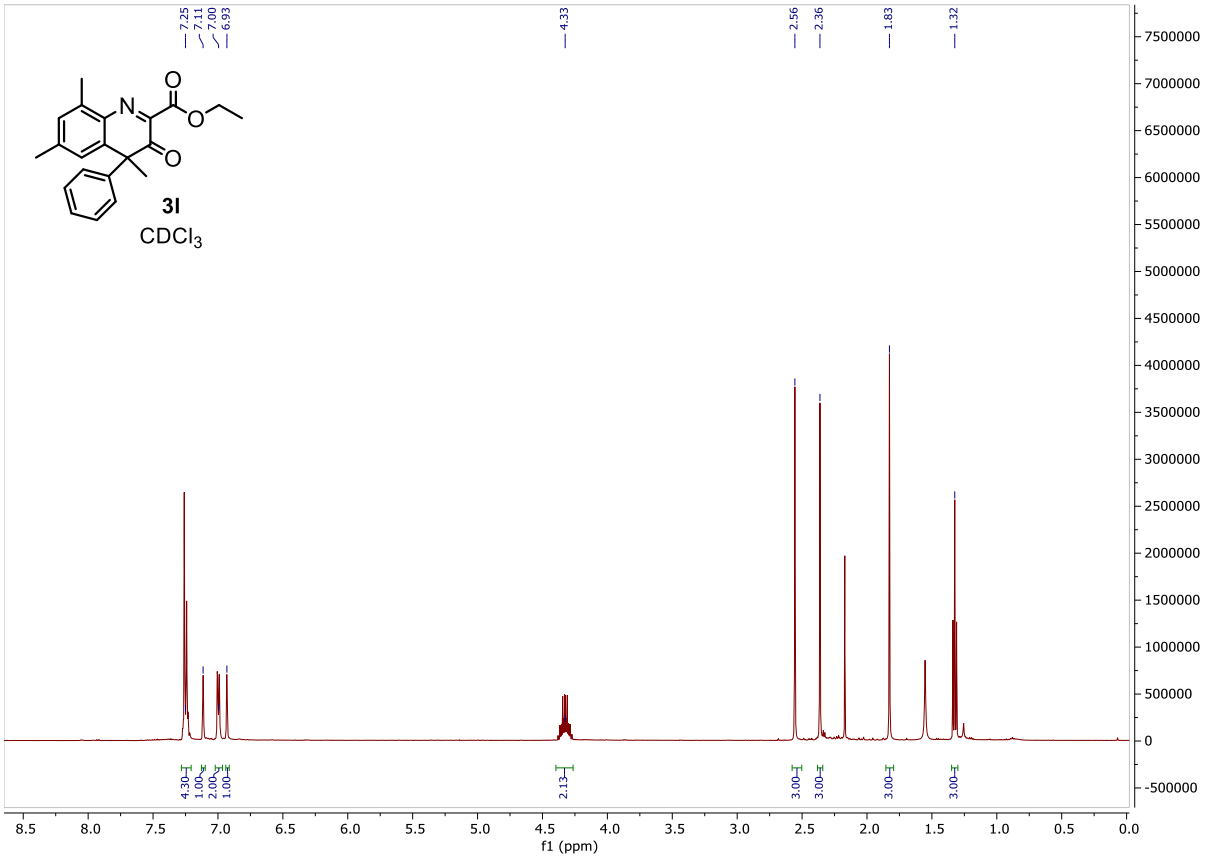
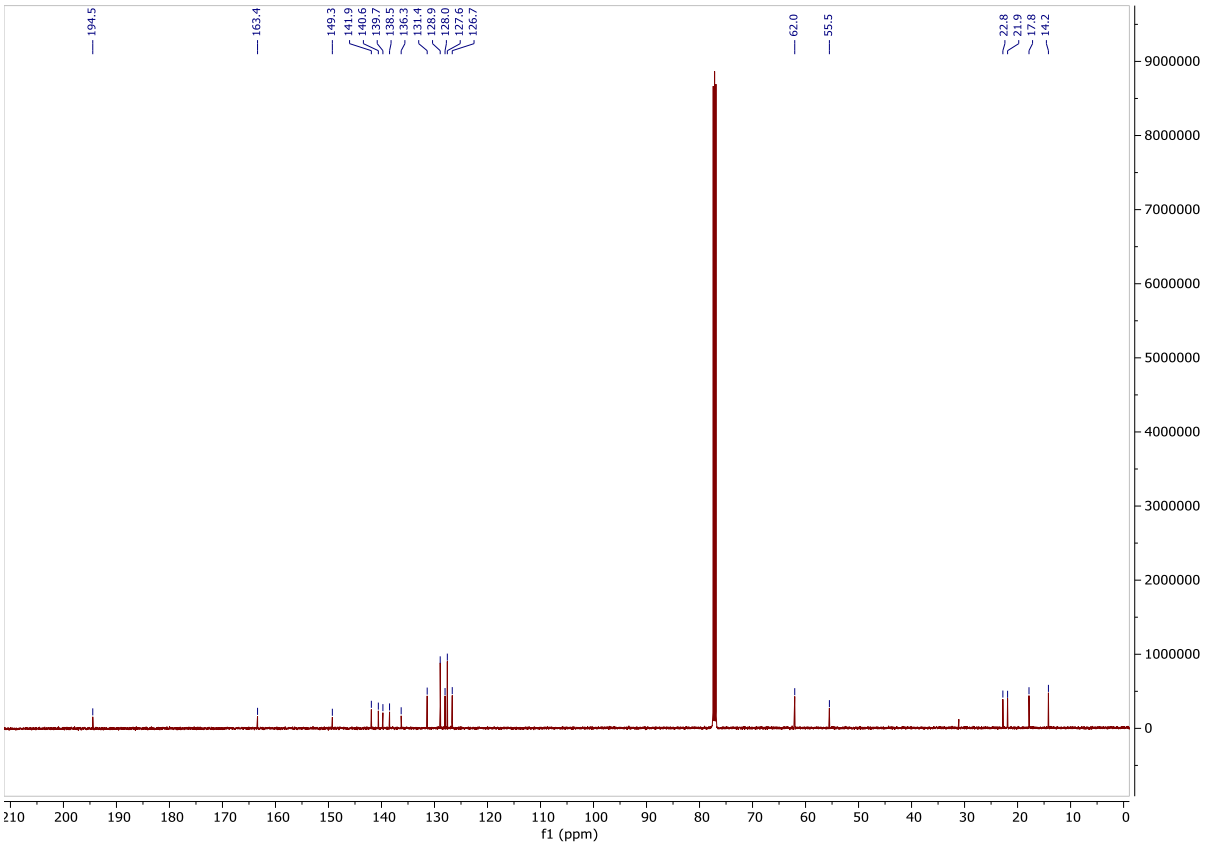
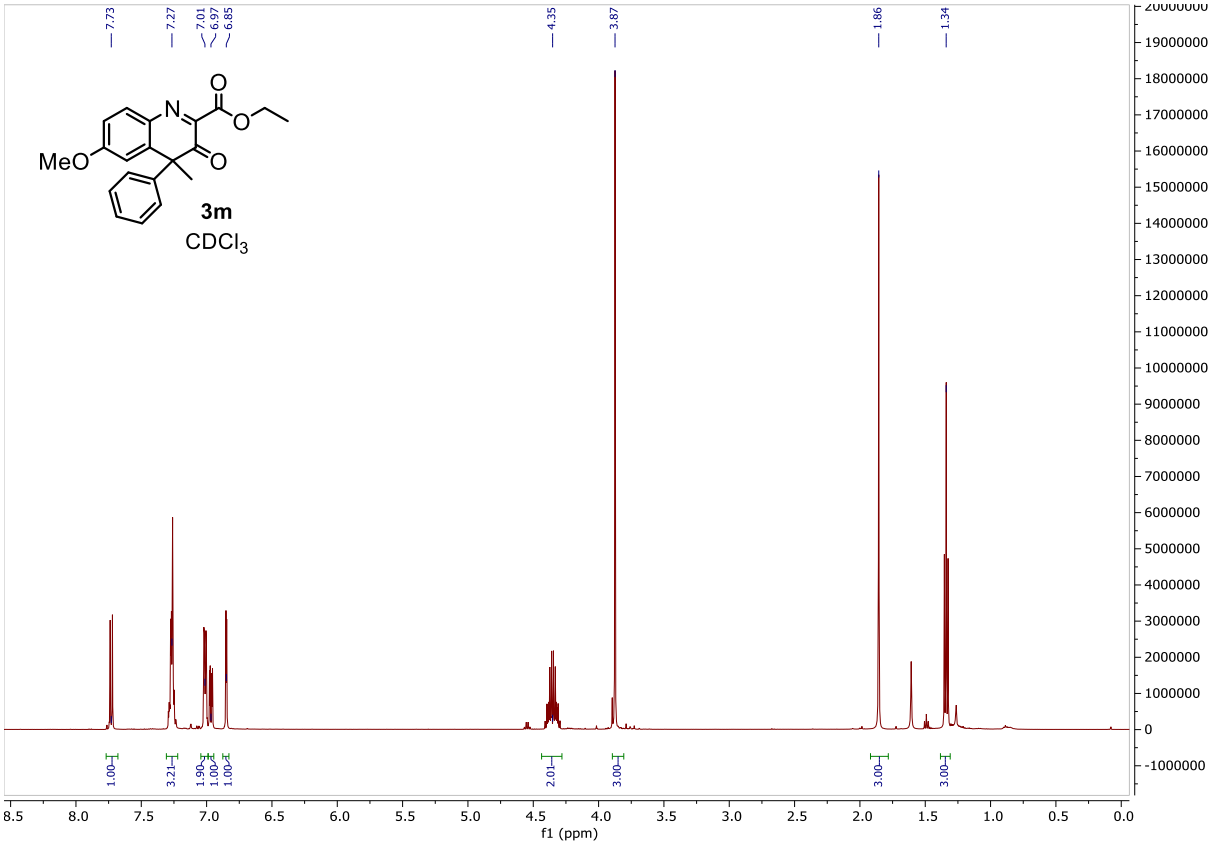
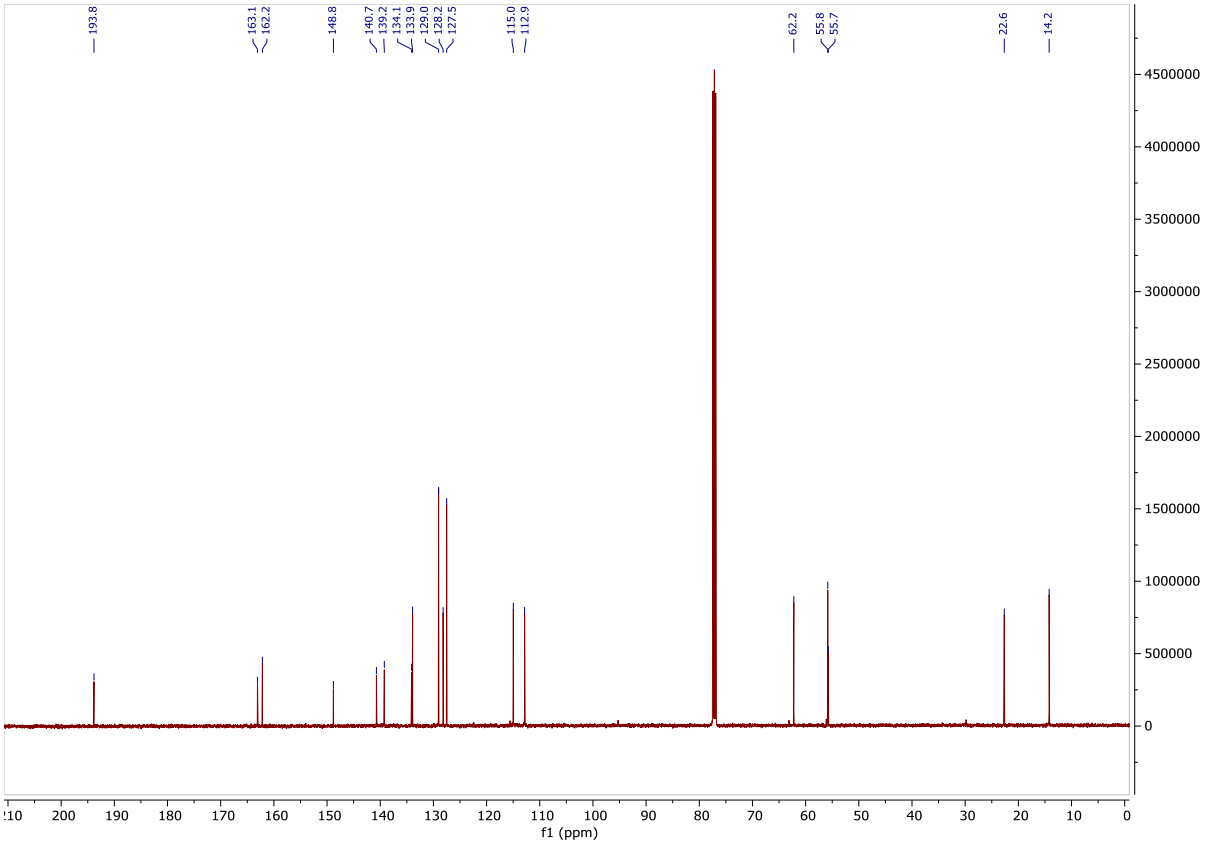
7.56
7.47
7.41
7.27
7.04
4.37
1.94
1.35
3k
CDCl3
1.00
1.07
2.05
1.28
2.28
1.36
3.18
2.00
2.20
3.00
3.23
f1 (ppm)

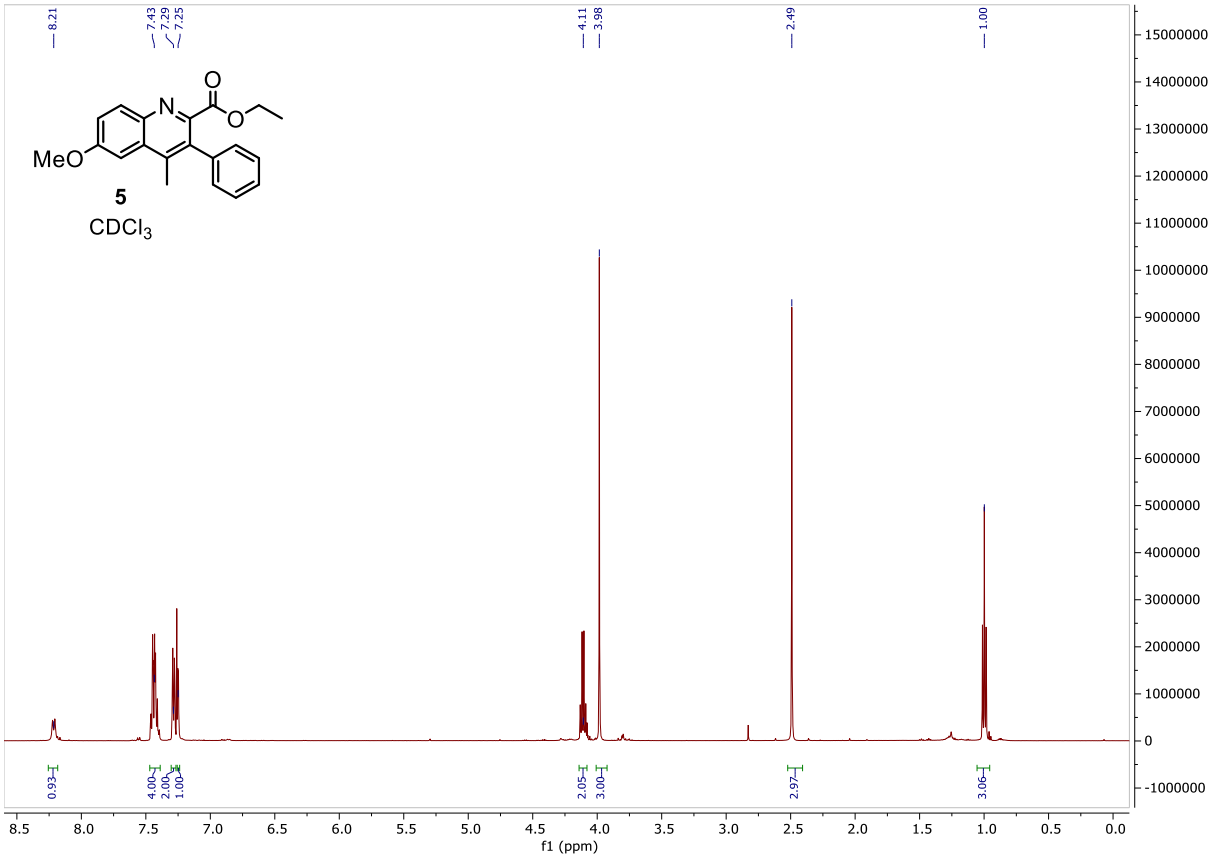

193.8
162.9
151.6
144.3
139.7
139.3
139.1
138.6
132.3
129.2
129.1
128.6
128.3
127.6
127.5
127.4
126.9
62.5
55.6
22.6
14.2
f1 (ppm)

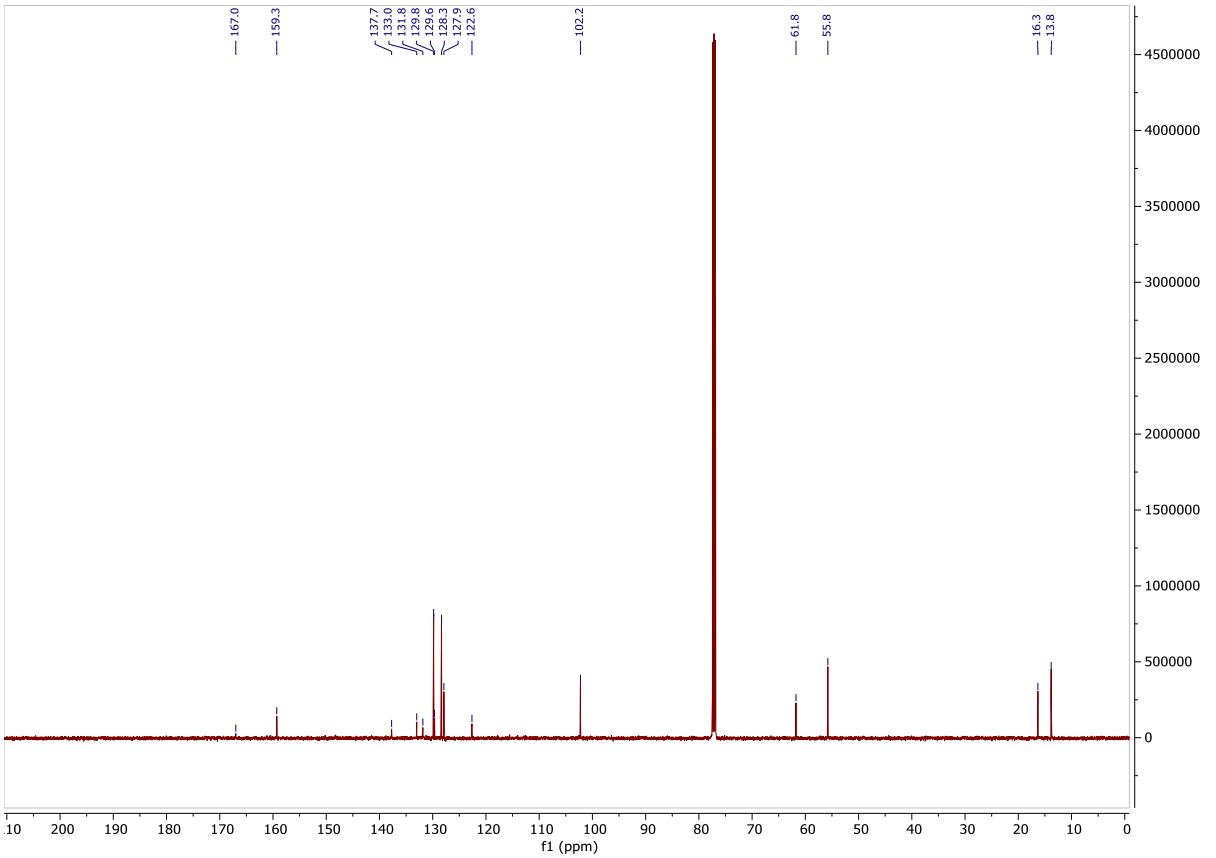

7.25
7.11
7.00
6.93
4.33
2.56
2.36
1.83
1.32
3I
CDCl3
4.30
1.00
2.00
1.00
2.13
3.00
3.00
3.00
3.00
f1 (ppm)

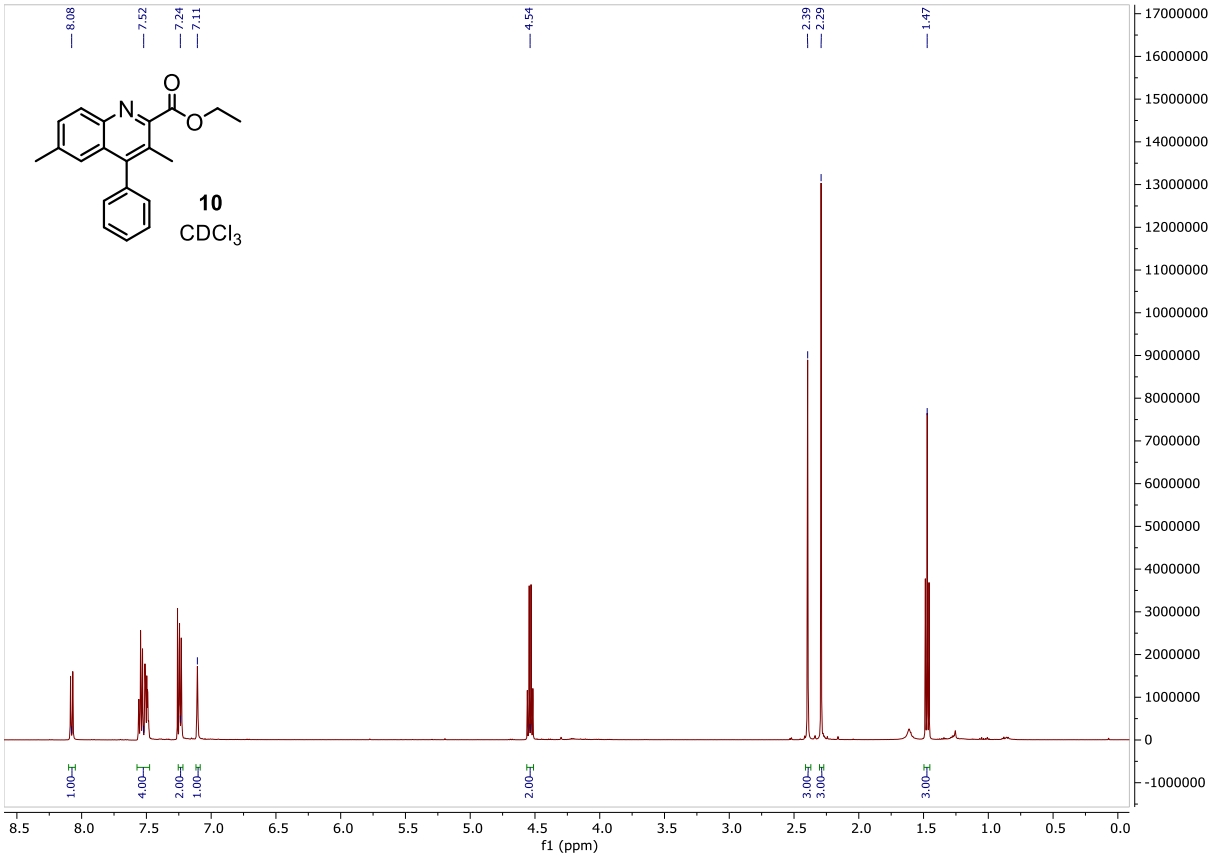

194.5
163.4
149.3
141.9
140.6
139.7
138.5
136.3
131.4
128.9
128.0
127.6
126.7
62.0
55.5
22.8
21.9
17.8
14.2
f1 (ppm)

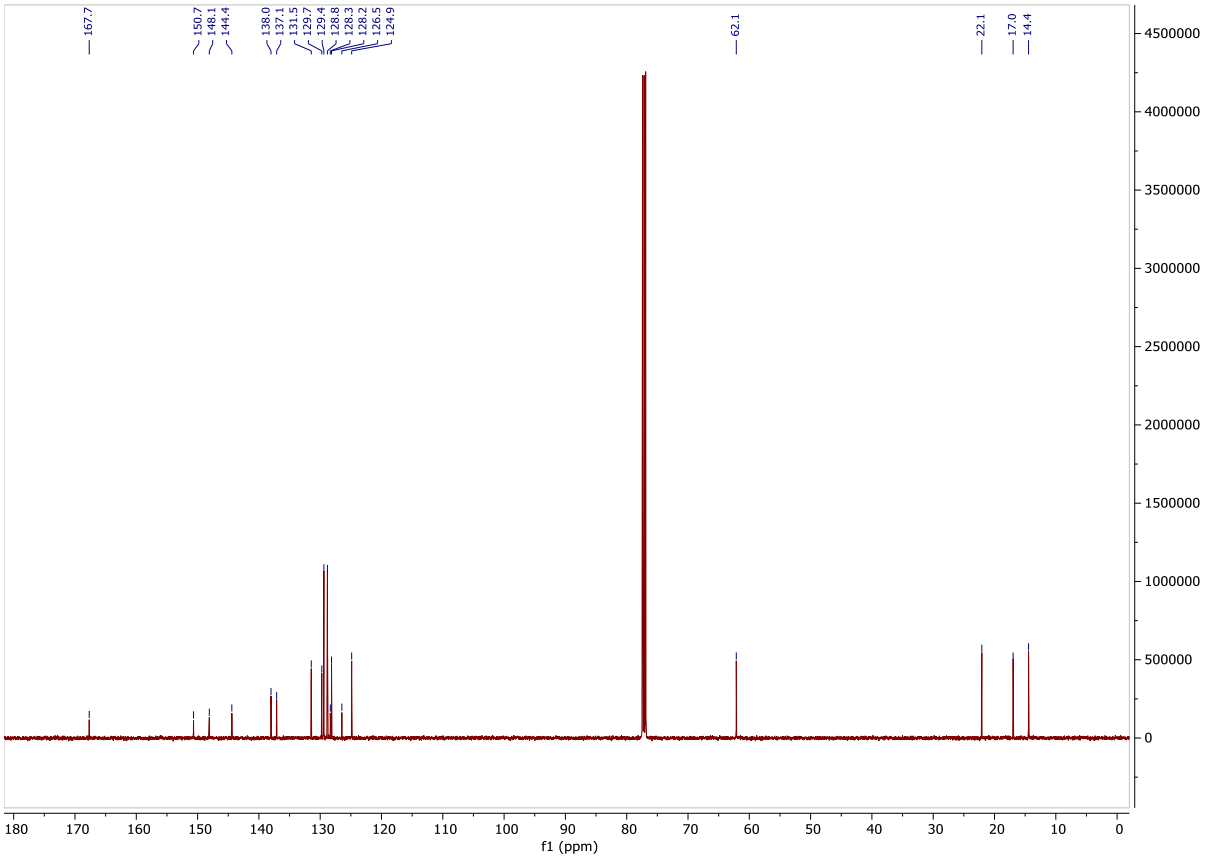

7.73
7.27
7.01
6.97
6.85
4.35
3.87
1.86
1.34
MeO
O
N
O
O
3m
CDCl3
1.00
3.21
1.90
1.00
1.00
2.01
3.00
3.00
3.00
f1 (ppm)

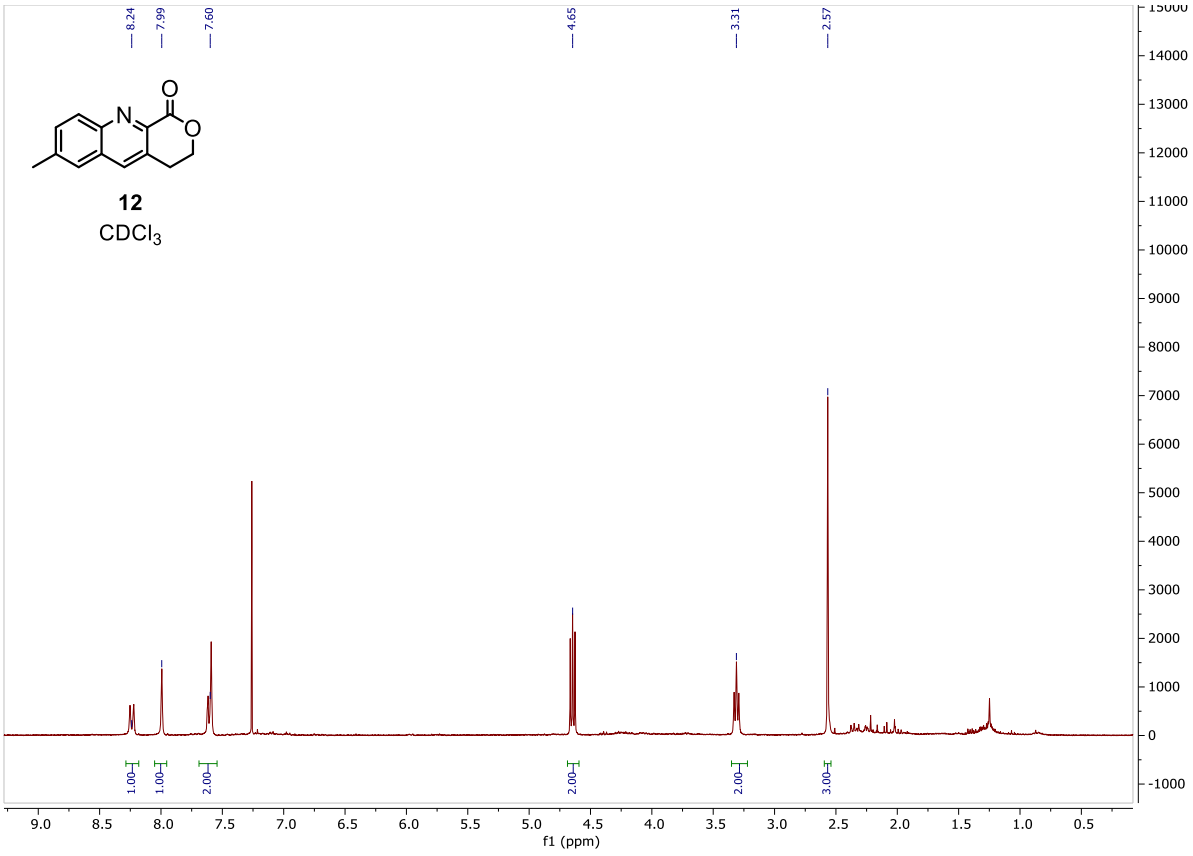

193.8
163.1
162.2
148.8
140.7
139.2
134.1
133.9
129.0
128.2
127.5
115.0
112.9
62.2
55.8
55.7
22.6
14.2
f1 (ppm)

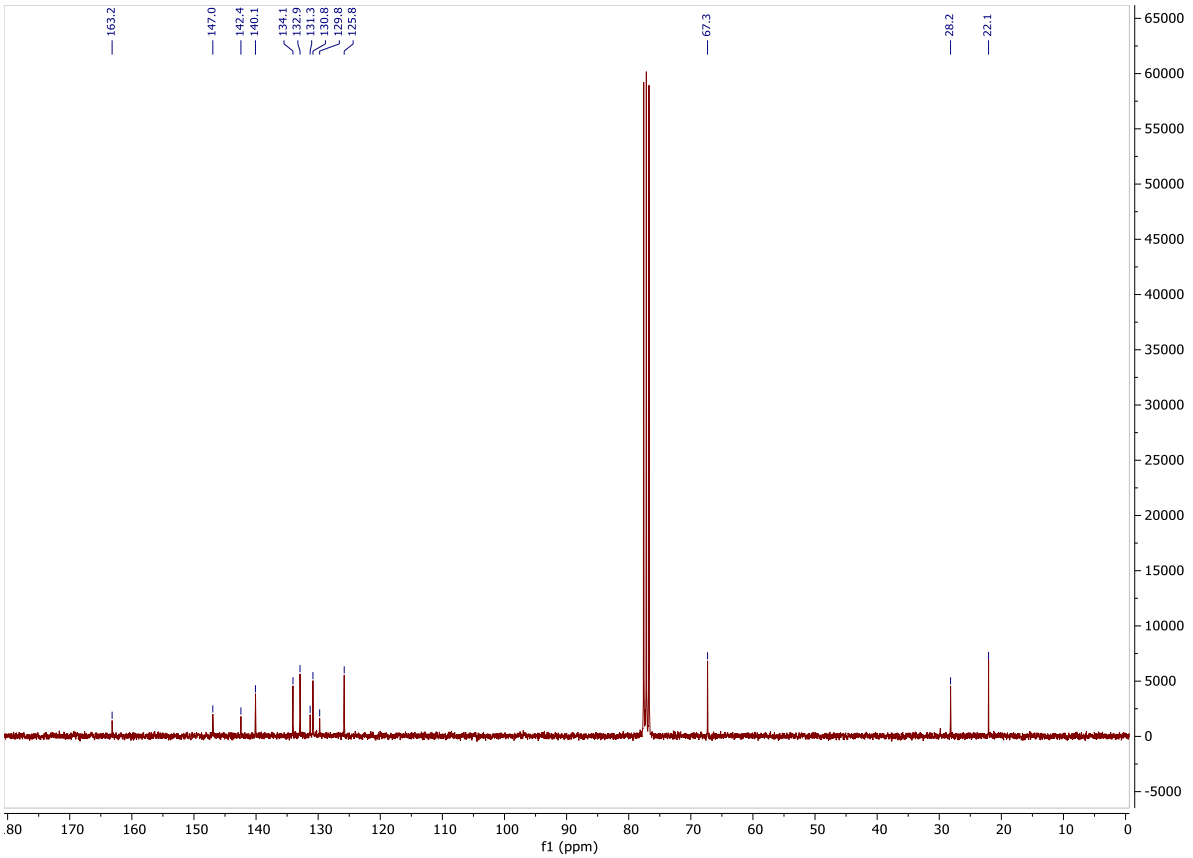

8.21
7.43
7.29
7.25
4.11
3.98
2.49
1.00
MeO
N
O
O
5
CDCl3
0.93
4.00
2.00
1.00
2.05
3.00
2.97
3.06
f1 (ppm)


167.0
159.3
137.7
133.0
131.8
129.8
129.6
128.3
127.9
122.6
102.2
61.8
55.8
16.3
13.8
f1 (ppm)


8.08
7.52
7.24
7.11
4.54
2.39
2.29
1.47
10
CDCl3
1.00
4.00
2.00
1.00
2.00
3.00
3.00
3.00
f1 (ppm)


167.7
150.7
148.1
144.4
138.0
137.1
131.5
129.7
129.4
128.8
128.3
128.2
126.5
124.9
62.1
22.1
17.0
14.4
f1 (ppm)


8.24
7.99
7.60
4.65
3.31
2.57
O
N
O
12
CDCl3
1.00
1.00
2.00
2.00
2.00
3.00
f1 (ppm)


163.2
147.0
142.4
140.1
134.1
132.9
131.3
130.8
129.8
125.8
67.3
28.2
22.1
f1 (ppm)