Pd-Catalyzed Carbonylation for the Construction of Tertiary and Quaternary Carbon Centers with sp^3 Carbon Partners

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1. General information

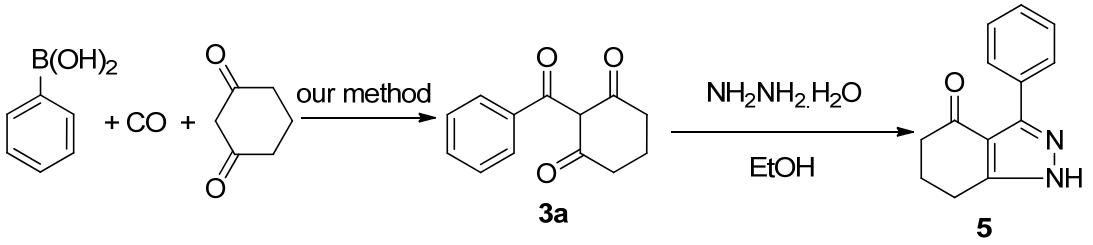
Flash chromatography was performed with freshly distilled solvents. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using $CDCl_3$ as solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Toluene was dried over sodium for 4 h, and distilled under N_2 atmosphere.

2. General procedures

2. 1 Pd-catalyzed carbonylation for the tertiary and quaternary carbon centers

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. *t*-BuOLi (0.5 mmol) and carbon nucleophiles(0.5 mmol) were placed in a 10 mL Teflon reaction tube and then solvent (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, Pd catalyst (0.025 mmol), ligand (0.025 mmol), arylboronic (0.25 mmol) and oxidant (0.5 mmol) were added to the tube, to which was added 2 mL solvent with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, and then pressurized to 5 atm with CO at room temperature and heated in an oil bath at 80 °C for 12 h. The autoclave was then cooled to room temperature and vented to discharge the excess CO in a fume hood. Water (10 mL) was added, and the product was extracted with ethyl acetate (3 x 15 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether as eluent to give the carbonylation products.

2.2 Synthesis of indazole 5



1,3,3'-Triketone **3a** (1 mmol) and hydrazine hydrate (2 mmol) were added to a 25 mL round bottom flask, which was evacuated and refilled with N_2 for 3 times. After the addition, the sealed tube was placed in an oil bath and stirred at 25^{o}C for 4 h. After completion, the reaction mixture was quenched by water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with brine (1 x 45 mL), and dried over $MgSO_4$. After the evaporation, the residue was purified with silica gel chromatography with petroleum ether/ethyl acetate as eluent to afford product **5**.

2.3 Kinetic Experiments

2.3.1 Variation of yield with time in the carbonylation of phenyl boronic acid.

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. *t*-BuOLi (0.5 mmol) and cyclohexane-1, 3-dione(0.5 mmol) were placed in a 10 mL Teflon reaction tube, and then toluene (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, Pd catalyst (0.025 mmol), ligand (0.025 mmol), arylboronic (0.25 mmol) and oxidant (0.5 mmol) were added in the tube, to which was added 2 mL toluene with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, and then pressurized to 5 atm at room temperature and heated in an oil bath at 80 °C with the time shown in Fig 1. The autoclave was then cooled to room temperature and vented to discharge the excess CO in a fumehood. Water (10 mL) was added, and the product

was extracted with ethyl acetate (3 x 15 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The conversion was determined by ^{1}HNMR with 1, 3, 5-trimethoxybenzene as internal standard.

2.3.2 Variation of yield with the amount of base in the carbonylation of phenyl boronic acid.

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. *t*-BuOLi, cyclohexane-1, 3-dione was placed in a 10 mL Teflon reaction tube, then toluene (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, Pd catalyst (0.025 mmol), ligand (0.025 mmol), arylboronic acid (0.25 mmol) and oxidant (0.5 mmol) were added in the tube, which was added 2 mL toluene with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, then pressurized to 1 or 5 atm at room temperature and heated in an oil bath at 80 °C for 10 h. The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with Ethyl acetate (3 x 15 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The conversion was determined by ^{1}HNMR with 1, 3, 5-trimethoxybenzene as internal standard.

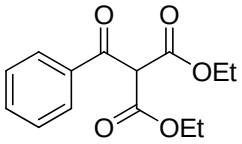
2.3.3 Variation of yield with CO pressure in the carbonylation of phenyl boronic acid

The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. *t*-BuOLi (0.5 mmol), cyclohexane-1, 3-dione (0.5 mmol) was placed in a 10 mL Teflon reaction tube, then toluene (1 mL) was added. The reaction mixture was stirred at room temperature for 1 h. Next, Pd catalyst (0.025 mmol), ligand (0.025 mmol), arylboronic (0.25 mmol) and oxidant (0.5 mmol) were added in the tube, which was added 2 mL toluene with a syringe. The tube was placed in the autoclave. Once sealed, the autoclave was purged several times with CO, and then pressurized to the pressure shown in Fig 3 at room temperature and heated in an oil bath at 80 °C for 10 h. The autoclave was then cooled to room temperature and vented to discharge the excess CO. Water (10 mL) was added, and the product was extracted with Ethyl acetate (3 x 15 mL). The organic layers were washed with brine, dried over Na_2SO_4,

and evaporated. The conversion was determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

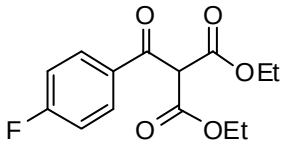
3. Data for products

Diethyl 2-benzoylmalonate (2a)



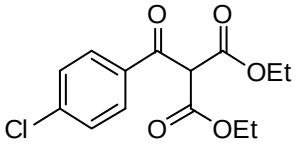
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (d, *J* = 7.2 Hz, 2H), 7.60 (q, *J* = 7.2 Hz, 1H), 7.49 (q, *J* = 7.6 Hz, 2H), 5.28 (s, 1H), 4.27 (q, *J* = 6.9 Hz, 4H), 1.25 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 189.0, 164.9, 135.4, 134.0, 128.9, 128.5, 62.4, 61.8, 13.9; IR (KBr): 3209, 2992, 1796, 1765, 1693, 787, 695, 643 cm^{-1}; HRMS (ESI): calc. for ($M + Na^{+}$) 287.0890; found 287.0893.

Diethyl 2-(4-fluorobenzoyl)malonate (2b)



Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.96-7.93 (m, 2H), 7.27-7.14 (m, 2H), 5.22 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 4H), 1.26-1.24 (t, *J* =7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 187.4, 164.9, 163.7, 131.9, 131.3, 131.2, 130.0, 116.2, 116.0, 62.5, 61.9, 61.3, 13.9, 13.7; IR (KBr): 3070, 2870, 1753, 1733, 1692, 852, 796, 685 cm^{-1}; HRMS (ESI): calc. for ($M + Na^{+}$) 305.0796; found 305.0790.

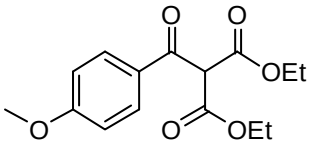
Diethyl 2-(4-chlorobenzoyl)malonate (2c)



Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 5.21 (s, 1H), 4.27 (q, *J* = 6.8 Hz, 4H), 1.26 (t, *J* = 6.8 Hz 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 187.8, 168.4, 133.8, 129.9, 128.6,

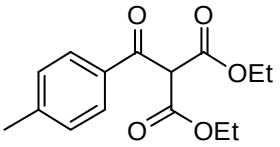
62.5, 61.4, 14.1, 14.0; IR (KBr): 3210, 2983, 1768, 1752, 1695, 960, 823, 702 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 321.0500; found 321.0497.

Diethyl 2-(4-methoxybenzoyl)malonate (2d)



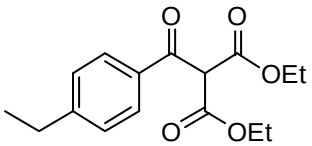
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.24 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 4H), 3.88 (s, 3H), 1.26 (t , *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz , $CDCl_3$) δ (ppm): 187.3, 165.0, 164.2, 130.9, 128.5, 114.1, 62.3, 61.7, 55.6, 13.9; IR (KBr): 3165, 2960, 1764, 1745, 1698, 783, 721, 696 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 317.0996; found 317.0991.

Diethyl 2-(4-meyhylbenzoyl)malonate (2e)



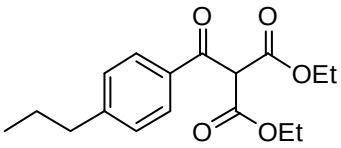
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 9.2 Hz, 2H), 5.25 (s, 1H), 4.29 (q, *J* = 6.8 Hz, 4H), 2.42 (s, 3H), 1.27 (t, *J* =7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.5, 164.9, 145.1, 133.0, 129.6, 128.6, 62.3, 61.9, 21.7, 13.9; IR (KBr): 3062, 2891, 1782, 1765, 1687, 792, 765, 721, 684 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 301.1046; found 301.1043.

Diethyl 2-(4-ethylbenzoyl)malonate (2f)



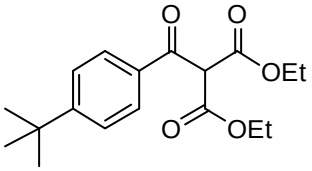
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 5.26 (s, 1H), 4.30-4.18 (m, 4H), 2.74-2.67 (m, 2H), 1.28-1.25 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.5, 165.0, 133.2, 128.8, 128.4, 114.3, 62.3, 61.8, 29.0, 15.0, 13.9; IR (KBr): 3132, 2983, 1792, 1721, 1695, 831, 797, 758, 693, 684 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 315.1203; found 315.1208.

Diethyl 2-(4-propylbenzoyl)malonate (2g)



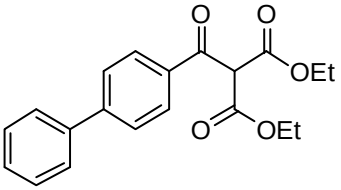
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.26 (s, 1H), 4.29 (m, 4H), 2.67 (t, *J* = 7.2 Hz, 2H), 1.69 (t, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.5, 165.0, 149.7, 133.2, 129.0, 128.7, 127.6, 62.3, 61.8, 38.0, 24.1, 13.9, 13.7; IR (KBr): 3021, 2967, 1795, 1743, 1695, 821, 786, 762, 731, 693, 684 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 329.1359; found 329.1352.

Diethyl 2-(4-(tert-butyl)benzoyl)malonate (2h)



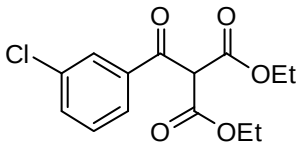
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 5.27 (s, 1H), 4.30 (m, 4H), 1.32 (s, 9H), 1.28 (t, *J* =7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.5, 165.0, 158.0, 132.9, 128.5, 125.9, 62.3, 61.8, 35.2, 31.0, 13.9; IR (KBr): 3024, 2893, 1786, 1745, 1683, 824, 786, 697, 674 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 343.1516; found 343.1519.

Diethyl 2-([1, 1'-biphenyl]-4-carbonyl)malonate (2i)



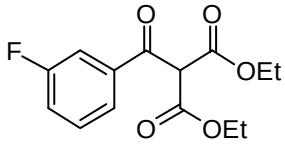
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.96 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.64 (q, *J* = 6.6 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 5.31 (s, 1H), 4.32-4.26 (m, 4H), 1.27 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.5, 164.9, 146.7, 139.5, 134.2, 129.1, 128.2, 128.5, 127.5, 127.3, 62.4, 62.0, 13.9; IR (KBr): 3024, 2986, 2893, 1786, 1745, 1683, 835, 798, 692 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 363.1203; found 363.1211.

Diethyl 2-(3-chlorobenzoyl)malonate (2j)



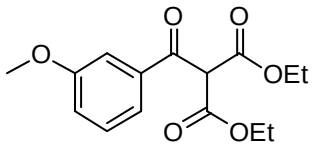
Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, *J* = 8.4 Hz, 2H), 7.27-7.14 (m, 2H), 5.22 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 4H), 1.26-1.24 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 187.4, 164.5, 163.7, 137.0, 135.4, 133.9, 130.2, 128.6, 126.6, 62.6, 61.9, 54.3, 13.9; IR (KBr):3075, 2982, 1752, 1730, 1690, 740, 682, 615 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 321.0500; found 321.0493.

Diethyl 2-(3-fluorobenzoyl)malonate (2k)



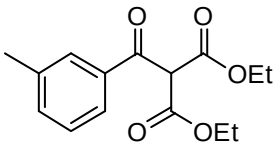
Colorless oil; R_f = 0.2(petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68-7.61 (m, 2H), 7.47 (m, 1H), 5.22 (s, 1H), 4.28 (t, *J* = 7.2 Hz, 4H), 1.30-1.24(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 187.8, 168.4, 137.5 (d, $J_{C\text{-}F}$ = 6.5 Hz), 130.6 (d, $J_{C\text{-}F}$ = 7.2Hz), 124.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 121.2(d, $J_{C\text{-}F}$ = 21.3 Hz), 115.4(d, $J_{C\text{-}F}$ = 22.6 Hz), 62.5, 61.4, 13.9; IR (KBr):3132, 2995, 1797, 1765, 1697, 754, 694, 635 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 305.0796; found 305.0791.

Diethyl 2(3-methoxybenzoyl)malonate (2l)



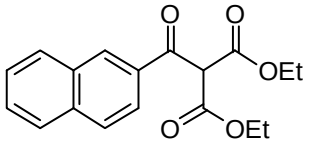
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H), 4.27(t, *J* = 7.2 Hz, 4H), 3.85 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.8, 164.8, 160.1, 129.8, 121.0, 120.8, 116.4, 112.6, 62.4, 55.5, 13.9;IR (KBr):3055, 2992, 1742, 1720, 1690, 832, 764, 696, 654 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 317.0996; found 317.0991.

Diethyl 2-(3-methylbenzoyl)malonate (2m)



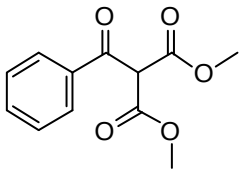
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 15:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73-7.68 (m, 2H), 7.43-7.28 (m, 2H), 5.28 (s, 1H), 4.7 (q, *J* = 5.2 Hz, 4H), 2.41 (s, 3H), 1.25 (t, *J* =7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 189.0, 164.9, 138.8, 135.5, 134.8, 129.0, 128.7,125.7,62.3, 61.9, 21.3, 13.9; IR (KBr):3043, 2983, 1765, 1732, 1698, 798, 764, 696, 654 cm^{-1}; HRMS (ESI): calc. for ($M + Na^+$) 301.1046; found 301.1041.

Diethyl 2-(2-naphthoyl)malonate (2n)



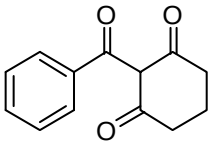
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31(s, 1H), 7.99 (t, *J* =8.8 Hz, 2H), 7.96-7.85 (m, 2H), 7.66-7.56 (m, 2H), 5.45 (s, 1H), 4.28 (q, *J* = 4.0 Hz, 4H), 1.27 (t, *J* =7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.9, 164.9, 135.9, 132.9, 132.4, 130.5, 129.8, 129.1, 128.9, 127.8, 127.1, 123.8, 62.4, 62.0, 54.4, 13.9; IR (KBr):3055, 2992, 2897, 1745, 1730, 1696, 764, 696, 663 cm^{-1}; HRMS (ESI): calc. for ($M + Na^+$) 337.1046; found 337.1041.

Dimethyl 2-benzoylmalonate (2o)



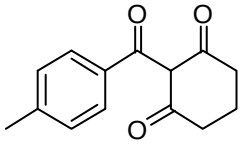
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92-7.90 (m, 2H), 7.51-7.46 (m, 3H), 5.34 (s, 1H), 3.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 188.6, 165.8, 135.3, 133.6, 130.5, 130.2, 127.6, 61.4; IR (KBr):3035, 2987, 1787, 1769, 1698, 832, 764, 696, cm^{-1}; HRMS (ESI) calc. for ($M + Na^+$) 259.0577; found 259.0571.

2-benzoylcyclohexane-1,3-dione (3a)



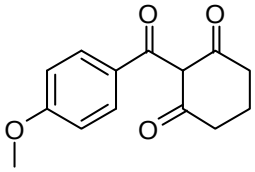
Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 6.05 (s, 1H), 2.69 (t, *J* = 5.6 Hz, 2H), 2.47 (t, *J* = 6.8 Hz, 2H), 2.17-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.4, 170.1, 163.2, 134.1, 130.2, 128.7, 117.9, 36.8, 28.4, 21.4; IR (KBr): 2950, 2928, 1740, 1738, 1669, 1635, 1125, 968, 748, 700 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 239.0679; found 239.0674.

2-(4-Methylbenzoyl) cyclohexane-1,3-dione (3b)



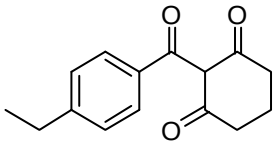
Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.04 (s, 1H), 2.70-2.66 (m, 2H), 2.48-2.44 (m, 5H), 2.16-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.5, 170.3, 163.2, 145.1, 130.3, 129.4, 125.9, 117.8, 36.8, 28.5, 21.8, 21.4 ; IR (KBr): 2956, 2926, 1740, 1769, 1679, 1127, 966, 745, 689 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 253.0835; found 253.0839.

2-(4-Methoxybenzoyl) cyclohexane-1,3-dione (3c)



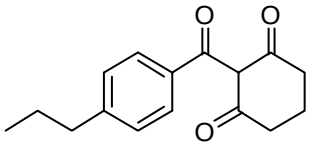
Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.03 (s, 1H), 3.89 (s, 3H), 2.69 (m, 2H), 2.46 (t, *J* = 6.8 Hz, 2H), 2.12 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.6, 170.4, 164.3, 162.9, 132.4, 120.9, 117.7, 114.0, 55.6, 36.8, 28.5, 21.4; IR (KBr): 2956, 2924, 1755, 1711, 1597, 1129, 968, 748, 700 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 269.0784; found 269.0790.

2-(4-Ethylbenzoyl) cyclohexane-1,3-dione (3d)



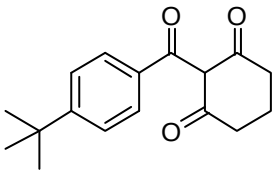
Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.00 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.03 (s, 1H), 2.76-2.66 (m, 4H), 2.46 (t, *J* = 6.8 Hz, 2H), 2.16-2.09 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.5, 170.3, 163.3, 151.3, 130.4, 128.3, 126.1, 117.8, 36.8, 29.1, 28.5, 21.4, 15.2; IR (KBr): 2957, 2921, 1743, 1680, 1604, 1125, 967, 855, 759 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 267.0992; found 267.0996.

2-(4-Propylbenzoyl) cyclohexane-1,3-dione (3e)



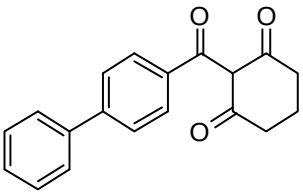
Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 2.68-2.64 (m, 4H), 2.46 (t, *J* = 6.8 Hz, 2H), 2.15-2.09 (m, 2H), 1.70-1.64 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.5, 170.3, 163.3,149.8, 130.3, 128.9, 126.1, 117.8, 38.1, 36.8, 28.5, 24.2, 21.4, 13.7; IR (KBr): 2959, 2924, 1755, 1711, 1158, 847, 800, 710, 513 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 281.1148; found 281.1152.

2-(4-[*Tert*-butyl] benzoyl) cyclohexane (3f)



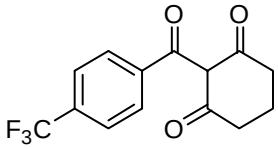
Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 6.03 (s, 1H), 2.68 (t, *J* = 6.2 Hz, 2H), 2.46 (t, *J* = 6.8 Hz, 2H), 2.13 (q, *J* = 6.5 Hz, 2H), 1.35 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.5, 170.3, 163.2, 158.1, 130.2, 125.7, 117.8, 36.8, 35.3, 31.1, 28.5, 21.4; IR (KBr): 2964, 2929, 1740, 1679, 1611, 1064, 966, 853, 757, 699 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 295.1305; found 295.1309.

2-([1,1′-Biphenyl]-4-carbonyl)cyclohexane-1,3-dione (3g)



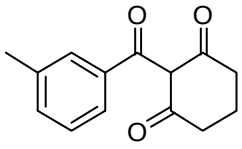
Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 6.0 Hz, 2H), 2.48 (t, *J* = 6.6 Hz, 2H), 2.157-2.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.4, 170.2, 163.1, 146.9, 139.6, 130.8, 129.0, 128.5, 127.4, 127.3, 117.9, 36.8, 28.5, 21.4; IR (KBr): 2955, 2926, 1739, 1668, 1630, 1123, 948, 776, 761 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 315.0992; found 315.0995.

2-(4-[Trifluoromethyl] benzoyl) cyclohexane-1,3-dione (3h)



Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 5.99 (s, 1H), 2.63 (q, *J* = 5.8 Hz, 2H), 2.41 (t, *J* = 6.8 Hz, 2H), 2.11-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.1, 169.6, 162.0, 135.5, 131.9, 130.6, 125.8, 125.8 (t, $J_{C\text{-}F}$ = 3.6 Hz), 118.1, 36.8, 28.3, 21.3; IR (KBr): 2956, 2927, 1748, 1680, 1648, 1127, 967, 862, 769, 698 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 307.0552; found 307.0554.

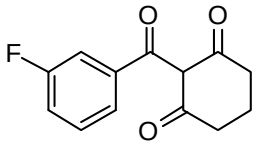
2-(3-Methylbenzoyl) cyclohexane-1,3-dione (3i)



Light yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H),6.03 (s, 1H), 2.67 (t, *J* = 6.2 Hz, 2H), 2.46 (t, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 2.12 (t, *J* = 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.5, 170.3, 163.4, 138.6, 134.9, 130.7, 128.6, 128.6, 127.4, 117.9, 36.8, 28.5, 21.4, 21.6; IR (KBr): 2958, 2924, 1748, 1766, 1672, 1123, 966, 753, 695

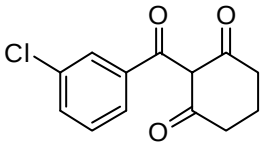
cm^{-1}; IR (KBr): 2958, 2924, 1748, 1766, 1672, 1123, 966, 753, 695 cm^{-1}; HRMS (ESI): calc. for ($M + Na^+$) 253.0835; found 253.0838.

2-(3-Fluorobenzoyl) cyclohexane-1, 3-dione (3j)



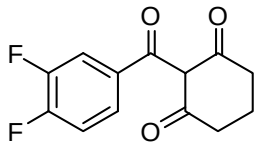
Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88-7.87 (m, 1H), 7.78-7.75 (m, 1H), 7.52-7.46 (m, 1H), 7.38-7.32 (m, 1H), 6.05 (s, 1H), 2.68 (t, *J* = 6.2 Hz, 2H), 2.46 (t, *J* = 6.2 Hz, 2H), 2.17-2.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.3, 169.7, 161.7 (d, J_{C-F} = 70 Hz), 130.5 (d, J_{C-F} = 7.5 Hz), 126.0 (d, J_{C-F} = 3.2 Hz), 121.4 (d, J_{C-F} = 21.1 Hz), 118.1, 117.2 (d, J_{C-F} = 23.2 Hz), 36.8, 28.4, 21.3; IR (KBr): 2967, 2926, 1746, 1693, 1679, 1125, 978, 845, 738 cm^{-1}; HRMS (ESI): calc. for ($M + Na^+$) 257.0584; found 257.0581.

2-(3-Chlorobenzoyl) cyclohexane-1, 3-dione (3k)



Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.05 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.62-7.60 (m, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 6.04 (s, 1H), 2.67 (t, *J* = 6.2 Hz, 2H), 2.47 (t, *J* = 6.6 Hz, 2H), 2.16-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.2, 169.7, 162.0, 135.0, 134.1, 130.2, 130.0, 128.3, 118.1, 36.8, 28.4, 21.3; IR (KBr): 2968, 2928, 1748, 1678, 1576, 1126, 968, 881, 739 cm^{-1}; HRMS (ESI): calc. for ($M + Na^+$) 273.0289; found 273.0294.

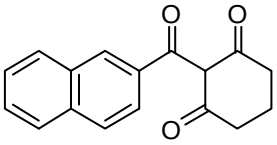
2-(3, 4-Difluorobenzoyl) cyclohexane-1, 3-dione (3l)



Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86-7.80 (m, 2H), 7.26-7.19 (m, 1H), 5.97 (s, 1H), 2.62-2.58 (m, 2H), 2.40 (t, *J* = 6.8 Hz, 2H), 2.10-2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.2, 169.5, 161.3, 155.6 (d, J_{C-F} =

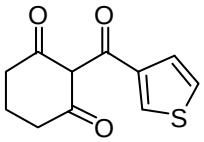
12.5 Hz), 152.6 (dd, J_{C-F} = 228, 13.1 Hz), 149.0 (d, J_{C-F} = 12.9 Hz), 127.4 (t, J_{C-F} = 3.8 Hz), 125.7 (t, J_{C-F} = 2.1 Hz), 119.6 (t, J_{C-F} = 17.6 Hz), 118.1,117.9 (d, J_{C-F} = 18 Hz), 36.8, 28.3, 21.3; IR (KBr):2958, 2932, 1745, 1677, 1617, 1124, 934, 774, 752 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 275.0490; found 275.0498.

2-(2-Naphthoyl) cyclohexane-1, 3-dione (3m)



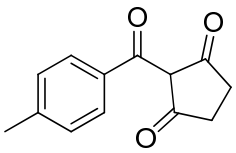
White solid; m.p = 101-102 ^oC, R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.59 (s, 1H), 8.00-7.98 (m, 1H), 7.91 (t, *J* = 8.0 Hz, 1H), 7.86-7.82 (m, 2H), 7.57-7.51 (m, 2H), 6.03 (s, 1H), 2.67 (t, *J* = 6.2 Hz, 2H), 2.42 (t, *J* = 6.8 Hz, 2H), 2.11-2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.5, 170.3, 163.4, 136.0, 132.4, 132.3, 129.5, 129.0, 128.6, 127.9, 127.1, 125.8, 125.2, 117.9, 36.8, 28.5, 21.4; IR (KBr): 2960, 2926, 1745, 1677, 1617, 1124, 934, 774, 752 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 289.0835; found 289.840.

2-(Thiophene-3-carbonyl) cyclohexane-1, 3-dione (3n)



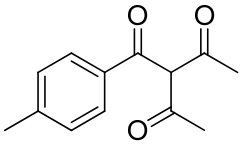
Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.23 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 4.8 Hz, 1H), 7.37 (t, *J* = 2.0 Hz, 1H), 6.03 (s, 1H), 2.66 (t, *J* = 6.0 Hz, 2H), 2.45 (t, *J* = 6.6 Hz, 2H), 2.15-2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 199.4, 169.8, 158.9, 134.8, 132.0, 128.1, 126.7, 117.8, 36.8, 28.5, 21.4; IR (KBr):2958, 2926, 1745, 1677, 1617, 1124, 934, 774, 752 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 245.0243; found 245.0251.

2-(4-Methylbenzoyl) cyclopentane-1, 3-dione (3o)



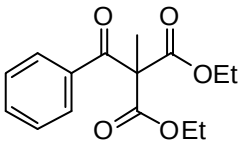
Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.00 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.37 (s, 1H), 2.91-2.88 (m, 2H), 2.52-2.50 (m, 2H), 2.44 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm): 206.8, 180.1, 162.2, 145.6, 130.5, 129.6, 125.3, 116.6, 33.4, 28.9, 21.8; IR (KBr):2958, 2924, 17405, 1768, 1674, 1123, 968, 755, 684 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 239.0679; found 239.0672.

3-(4-Methylbenzoyl) pentane-2, 4-dione (3p)



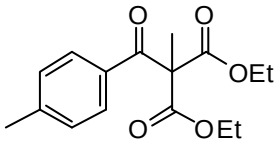
Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.79 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.3, 192.1, 144.8, 136.2, 129.5, 127.1, 115.5, 24.6, 21.7; IR (KBr):2958, 2924, 17405, 1768, 1674, 1123, 968, 755, 684 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 239.0679; found 239.0672.

Diethyl 2-benzoyl-2-methylmalonate (4a)



Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.25 (q, *J* = 5.2 Hz, 4H), 1.84 (s, 3H), 1.20 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.5, 168.9, 135.3, 132.9, 129.0, 128.3, 62.6, 62.2, 20.2, 13.8. IR (KBr):3051, 2972, 1764, 1726, 1675, 887, 792, 687, 646 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 301.1046; found 301.1041.

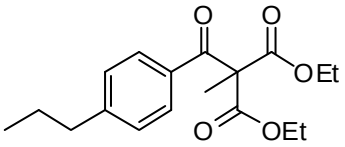
Diethyl 2-methyl-2-(4-methylbenzoyl)malonate (4b)



Colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.71 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 2H), 4.28-4.19 (m, 4H), 2.40 (s, 3H), 1.83 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.0, 169.0,

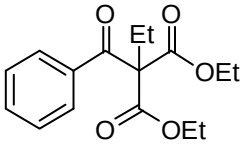
143.8, 132.6, 129.2, 129.0, 65.6, 62.2, 21.6, 20.2, 13.8; IR (KBr):3044, 2965, 1767, 1731, 1699, 862, 792, 681, 654 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 315.1203; found 315.1210.

Diethyl 2-methyl-2-(4-propylbenzoyl)malonate (4c)



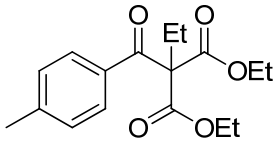
Colorless oil.. R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (d, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 4.27-4.19 (m, 4H)，2.62 (t, *J* = 7.4 Hz, 2H), 1.83 (s, 3H), 1.65 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 6H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):193.1, 169.0, 148.4, 132.8, 129.2, 128.4, 65.6, 62.2, 38.0, 24.1, 20.1, 13.8, 13.7; IR (KBr):3042, 2978, 1761, 1744, 1691, 916, 877, 768, 657, 632 cm^{-1}; HRMS (ESI): calc. for (M + Na+) 343.1516; found 343.1519.

Diethyl 2-ethyl-2-(4-ethylbenzoyl)malonate (4d)



Colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43-7.41 (m, 2H), 4.22-4.16 (m, 4H), 2.34 (q, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 6H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.2, 167.9, 136.2, 132.8, 128.6, 128.3, 68.9, 61.8, 27.9, 13.8, 9.5. IR (KBr): 3042, 2968, 1769, 1728, 1694, 856, 783, 685, 662 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 314.1125; found 314.1131.

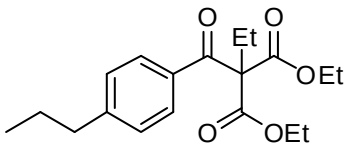
Diethyl 2-ethyl-2-(4-methylbenzoyl)malonate (4e)



Colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 (d, *J* = 6.8 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 4.18 (q, *J* = 6.5 Hz, 4H)，2.83 (s, 3H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 6H) 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 191.7, 168.1, 143.7, 133.3, 129.0, 128.9, 68.8, 61.8, 27.9, 21.6, 13.8, 9.5; IR

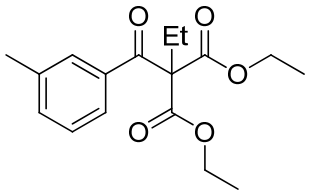
(KBr):3054, 2982, 1762, 1730, 1684, 842, 761, 687, 654 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 329.1359; found 329.1353.

Diethyl 2-ethyl-2-(4-propylbenzoyl)malonate (4f)



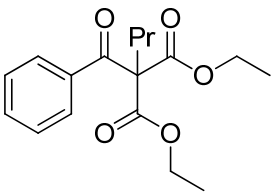
Colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 8.4 Hz, 2H), 4.21-4.18 (m, 4H)， 2.62 (t, *J* = 7.6 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.69-1.60 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 6H), 1.65 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 6H), 1.04 (t, *J* = 7.4 Hz, 3H); 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):191.8, 168.0, 148.3, 133.7, 128.8, 128.4, 68.8, 61.8, 37.9, 27.9, 24.1, 13.8, 13.7, 9.5; IR (KBr): 3041, 2975, 1768, 1749, 1698, 873, 762, 677, 642 cm^{-1}; HRMS (ESI): calc. for (M + Na+) 357.1672; found 357.1679.

Diethyl 2-ethyl-2-(3-methylbenzoyl)malonate (4g)



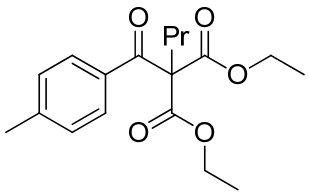
Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^1H NMR (400 MHz, CDCl3) δ (ppm): 7.67 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.24 (s, 1H), 4.22-4.17 (m, 4H), 2.38 (s, 3H), 2.34 (d, *J* = 7.6 Hz, 2H), 1.62 (t, *J* = 7.2 Hz, 6H), 1.06 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.5, 168.0, 138.2, 136.2, 133.6, 129.2, 128.1, 125.8, 61.8, 28.0, 21.4, 13.8, 9.5; IR (KBr):3046, 2976, 1768, 1727, 1684, 851, 766, 682, 651 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 328.1281; found 328.1275.

Diethyl 2-benzoyl-2-propylmalonate (4h)



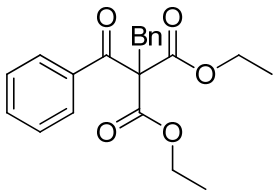
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 4.21-4.15 (m, 4H)， 2.23 (t, *J* = 7.6 Hz, 2H), 1.44 (t, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.0 Hz, 6H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.2, 168.2, 136.1, 132.8, 128.6, 128.3, 68.5, 61.9, 36.6, 18.3, 14.4, 13.8; IR (KBr):3051, 2972, 1763, 1721, 1674, 857, 786, 692, 656 cm^{-1}; HRMS (ESI): calc. for (M + Na+) 329.1359; found 329.1352.

Diethyl 2-(4-methylbenzoyl) -2-propylmalonate (4i)



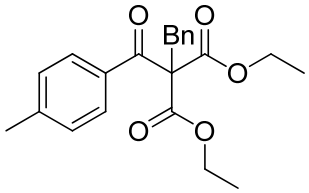
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.11 (q, *J* = 6.9 Hz, 4H)， 2.32 (s, 3H), 2.18-2.14 (m, 2H), 1.36 (t, *J* = 7.7 Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 6H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 191.6, 168.1, 143.7, 133.4, 129.0, 128.8, 68.4, 61.8, 36.6, 21.6, 18.3, 14.4, 13.8; IR (KBr): 3052, 2976, 1767, 1726, 1682, 841, 763, 684, 643 cm^{-1}; HRMS (ESI): calc. for (M + Na+) 343.1516; found 343.1512.

Diethyl 2-benzoyl-2-benzylmalonate (4j)



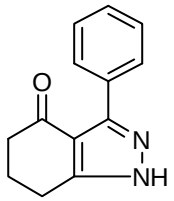
Colorless oil; R_f = 0.3 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 6.8 Hz, 2H), 7.51 (t, *J* = 6.8 Hz, 1H), 7.39 (t, *J* = 6.8 Hz, 2H), 7.25-7.22 (m, 5H)，4.11-4.01(m, 4H), 3.67 (s, 2H), 0.99 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 191.3, 167.2, 136.0, 135.6, 132.9, 130.5, 128.8, 128.3, 128.3, 127.1, 69.7, 61.9, 40.0, 13.6; IR (KBr): 3046, 2968, 1764, 1734, 1695, 912, 867, 798, 687, 656 cm^{-1}; HRMS (ESI): calc. for (M + Na+) 377.1359; found 377.1354.

Diethyl 2-benzyl-2-(4-methylbenzoyl) malonate (4k)



Colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.76 (d, *J* = 8.4 Hz, 2H), 7.23-7.17 (m, 7H), 4.11-4.02 (m, 4H), 3.66 (s, 2H), 2.38 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.6, 167.3, 143.8, 135.8, 133.3, 130.5, 129.0, 128.5, 128.0, 127.1, 61.8, 40.0, 21.6, 13.6; IR (KBr): 3047, 2978, 1767, 1724, 1698, 887, 795, 688, 646 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 390.1438; found 390.1443.

3-Phenyl-6,7-dihydro-1*H*-indazol-4(5*H*)-one (5)



White solid; R_f = 0.2 (petroleum ether/ethyl acetate 1:1); 9.40 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.530 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 5.16 (s, 1H), 5.485 (s, 1H), 2.45 (s, 2H) , 2.31 (t, *J* = 5.6 Hz, 2H), 2.00 (t, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.6, 165.7, 163.4, 131.5, 130.3, 127.7, 126.5, 98.0, 35.5, 25.5, 20.7.

4. References.

Entry	Products	Reference
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2	2b	[S2]
3	2c	[S1]
4	2d	[S3]
5	2e	[S3]

6	2f	[S4]
7	2g	[S5]
8	2h	[S6]
9	2i	[S7]
10	2j	[S8]
11	2k	[S9]
12	2l	[S8]
13	2m	[S10]
14	2n	[S11]
15	2o	[S3]
16	3a	[S1]
17	3b	[S12]
18	3c	[S13]
19	3d	[S14]
20	3e	[S15]
21	3f	[S16]
22	3g	[S17]
23	3h	[S12]

24	3i	[S18]
25	3j	[S19]
26	3k	[S20]
27	3l	[S21]
28	3m	[S22]
29	3n	[S23]
30	3o	[S12]
31	3p	[S1]
32	4a	[S24]
33	4b	[S24]
34	4c	[S25]
35	4d	[S26]
36	4e	[S27]
37	4f	[S28]
38	4g	[S29]
39	4h	[S30]
40	4i	[S31]
41	4j	[S32]

42	4k	[S33]
43	5a	[S34]

[S1] Q. Shen, W. Huang, J. Wang, X. Zhou, *Org. Lett.,* 2007. **9**. 22.

[S2] S. S. More, T. K. Mohan, S. Kumar, U. K. S. Kumar, N. B. Patel, *Beilstein J. Org. Chem.*, 2011, **7**, 831.

[S3] Y.T. Tao, H.William, Jr. Saunders, *J. Am. Chem. Soc.,* 1983, **105**, 10.

[S4] No reference was found via SCI finder.

[S5] No reference was found via SCI finder.

[S6] No reference was found via SCI finder.

[S7] No reference was found via SCI finder.

[S8] S. S. More, T. K. Mohan, S. Kumar, U. K. S. Kumar, N. B. Patel, *Beilstein J. Org. Chem.*, 2011, **7**, 831.

[S9] No reference was found via SCI finder.

[S10] No reference was found via SCI finder.

[S11] No reference was found via SCI finder.

[S12] T. H. Kim, R. Oh, H. S. Na, H. C. Lee, *Arch Pharm Res.,* 2003, **26**, 3..

[S13] No reference was found via SCI finder.

[S14] No reference was found via SCI finder.

[S15] No reference was found via SCI finder.

[S16] No reference was found via SCI finder.

[S17] No reference was found via SCI finder.

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[S20] No reference was found via SCI finder.

[S21] No reference was found via SCI finder.

[S22] No reference was found via SCI finder.

[S23] No reference was found via SCI finder.

[S24] T. Kobayashi, M. Tanaka, *Tetrahedron Letters.,*1986, **27**, 4745.

[S25] No reference was found via SCI finder.

[S26] D.Tarbell, Stanley, J. A. Pricez, *J. Org. Chem.,* 1957, **22**, 245.

[S27] No reference was found via SCI finder.

[S28] No reference was found via SCI finder.

[S29] No reference was found via SCI finder.

[S30] No reference was found via SCI finder.

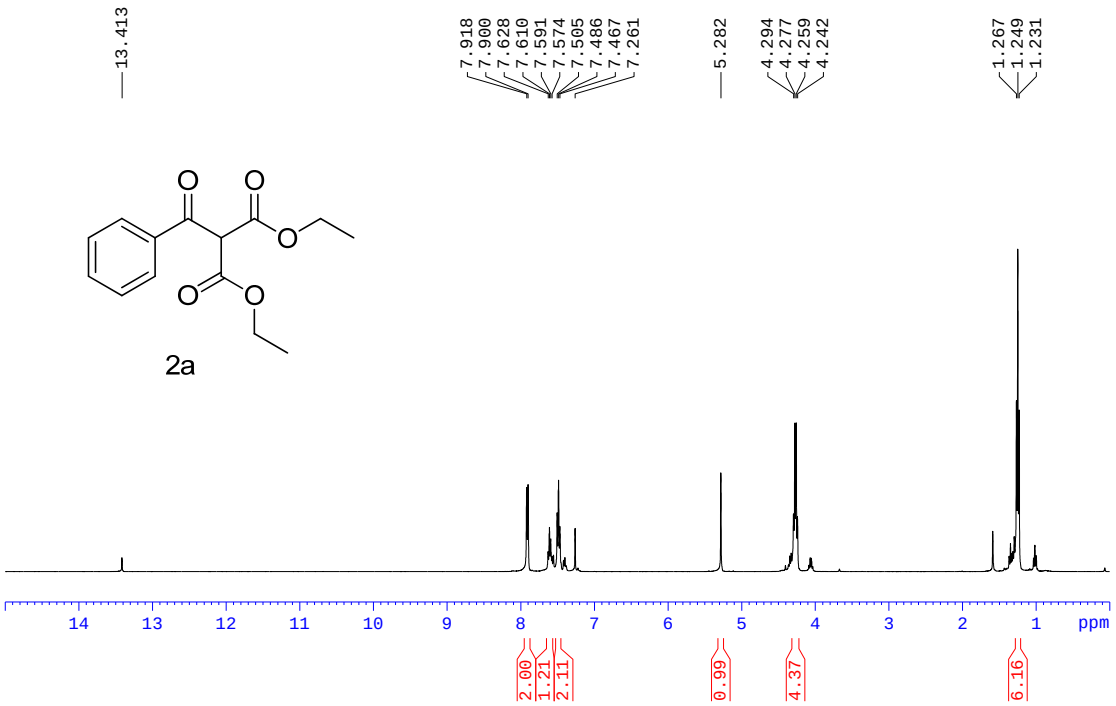
[S31] No reference was found via SCI finder.

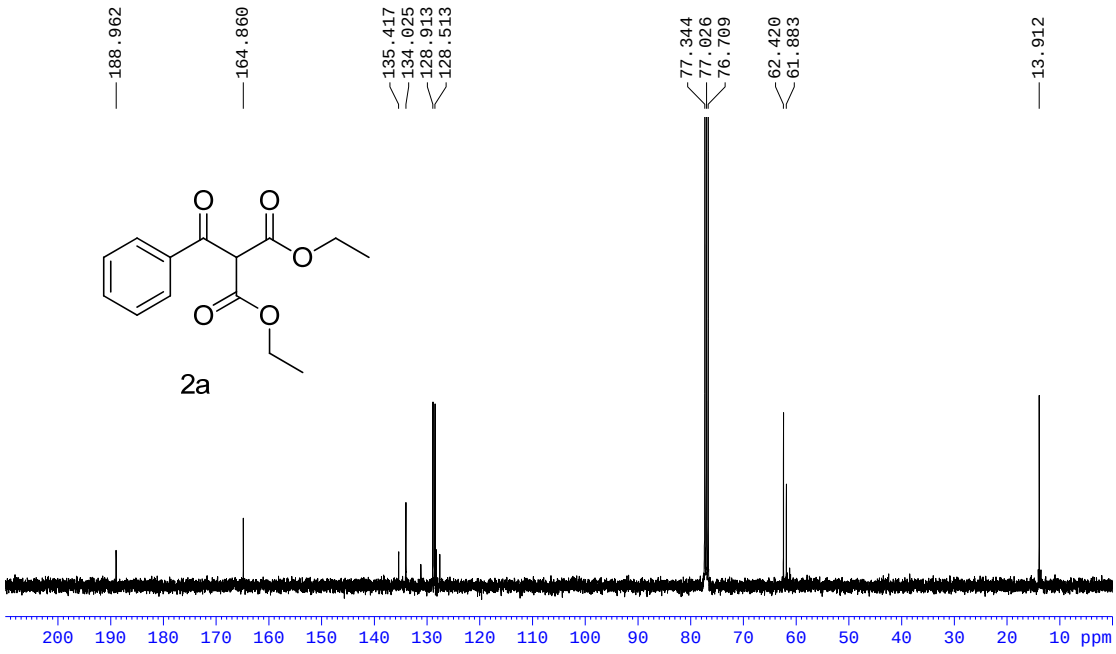
[S32] No reference was found via SCI finder.

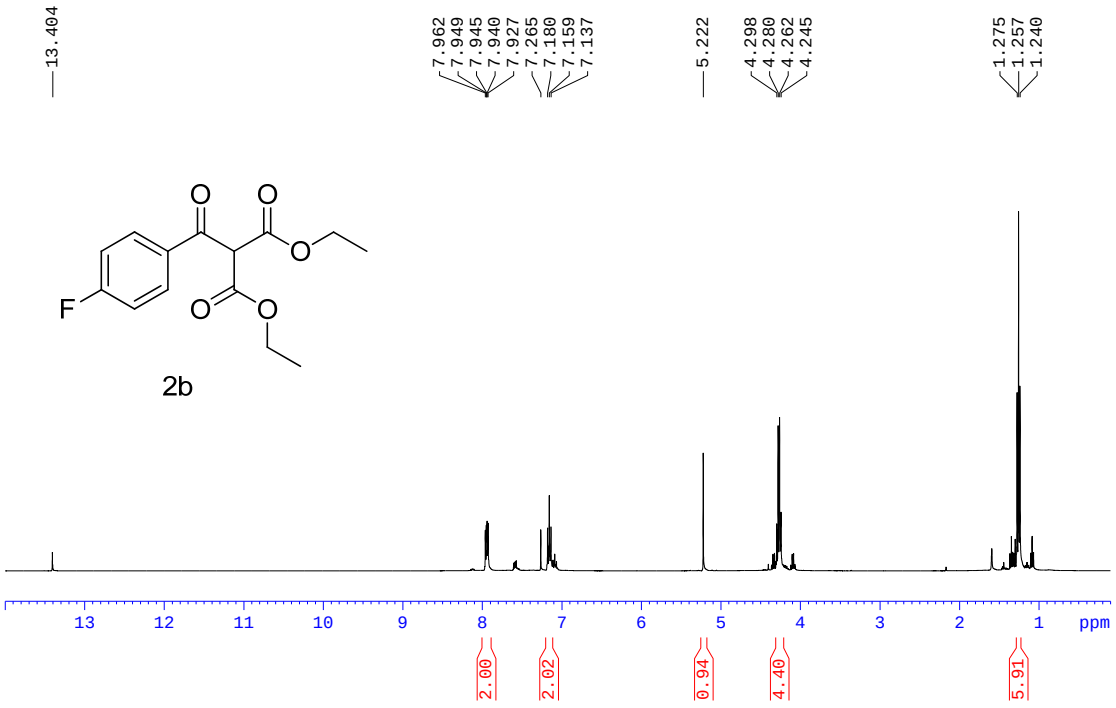
[S33] No reference was found via SCI finder.

[S34] J. II. Kim, B. C. Kim, S. W. Moon, Y. Jahng, *Heterocycles,* 1995, **41**, 1471.

5. Copies of the ^{1}H NMR and ^{13}C NMR spectra of products



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4.280
4.262
4.245
1.275
1.257
1.240
O
O
O
O
O
F
2b
13
12
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2.00
2.02
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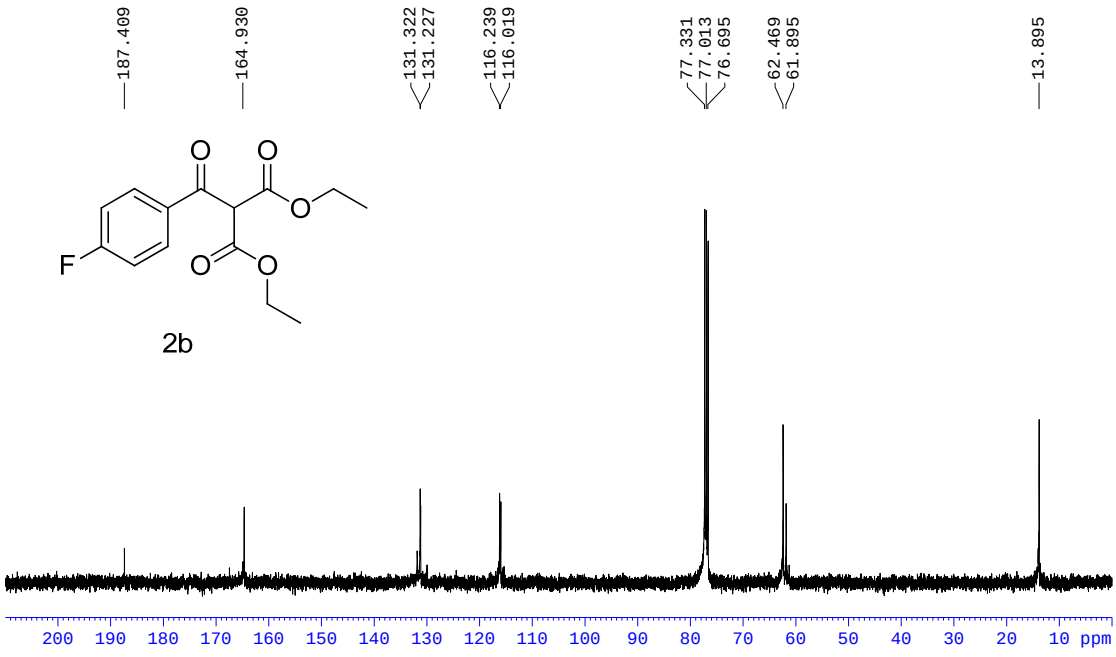
4.40
5.91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62.469
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O
O
O
O
O
F
2b
200
190
180
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160
150
140
130
120
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100
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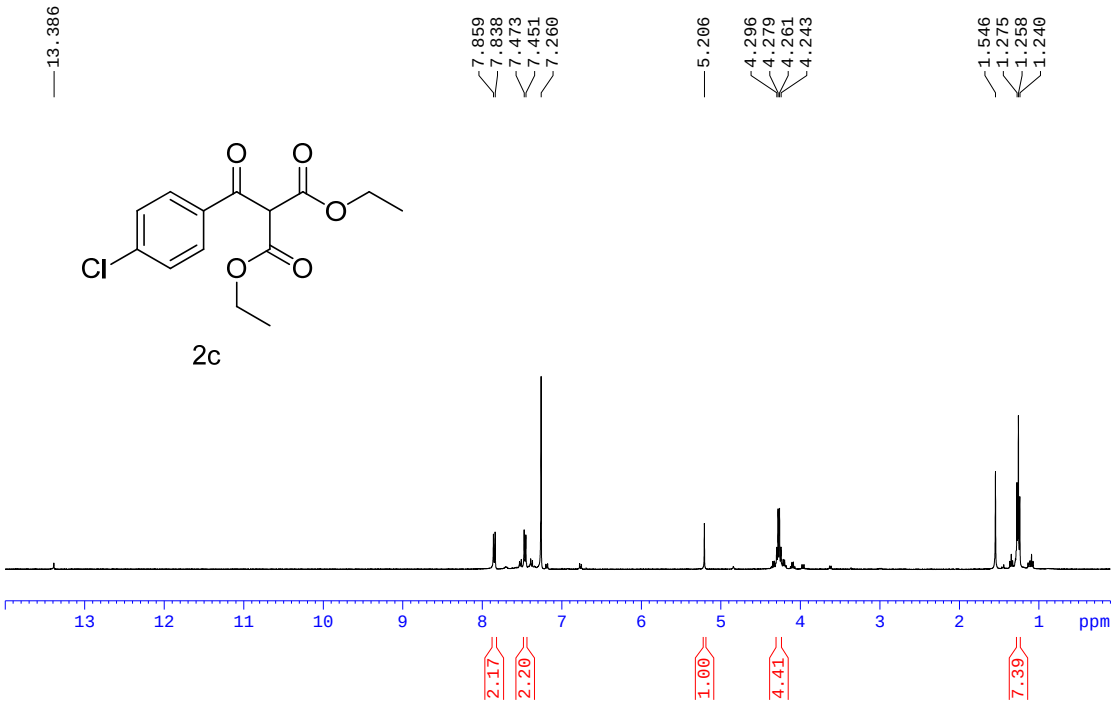
80
70
60
50
40
30
20
10 ppm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1.258
1.240
Cl
O
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O
O
2c
13
12
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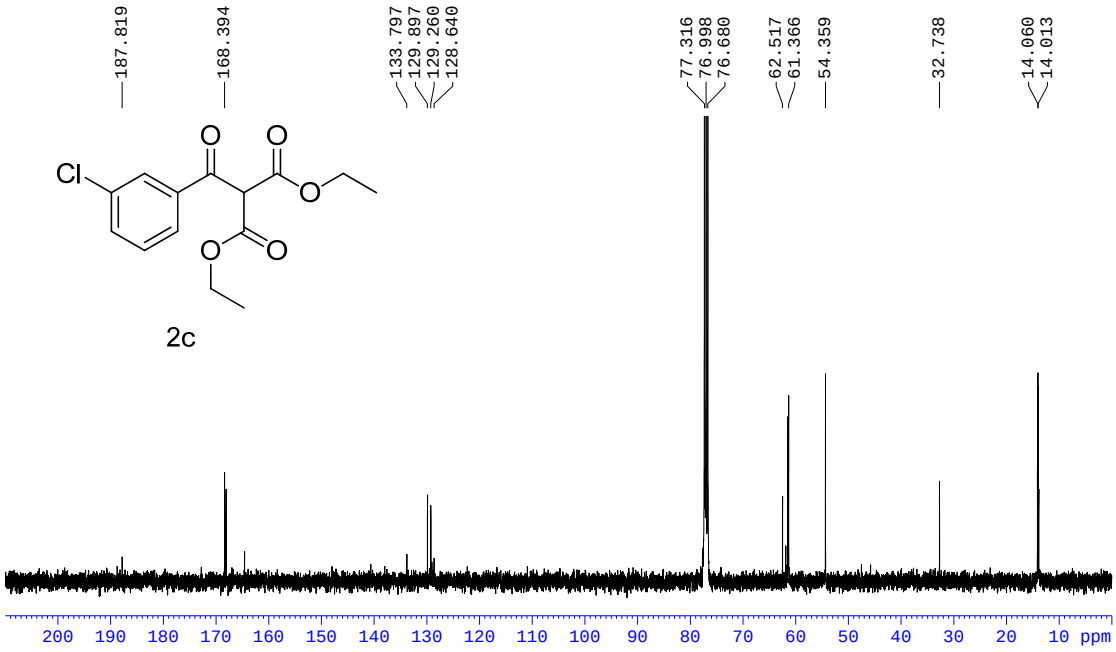
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14.060
14.013
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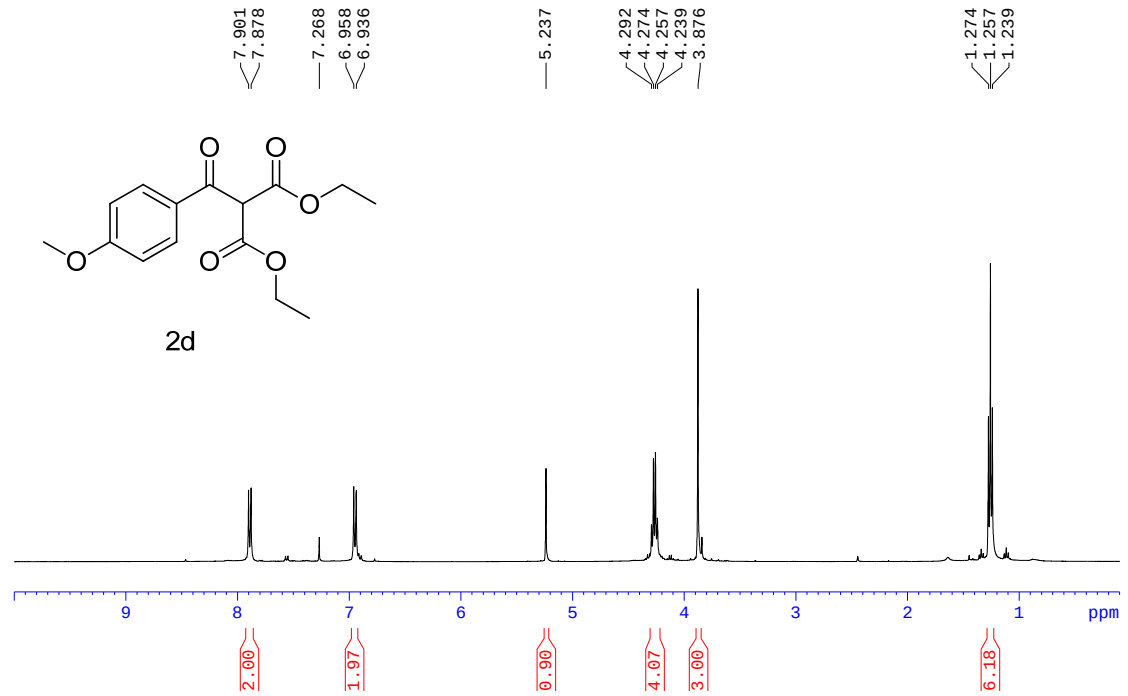
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2d
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3
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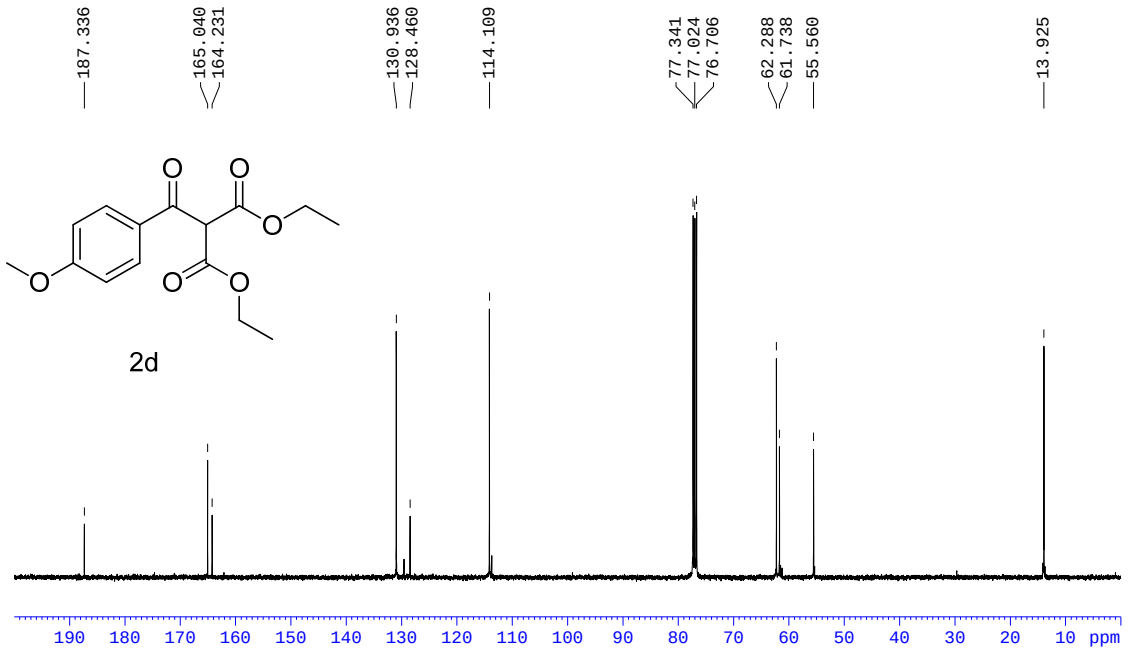
6.18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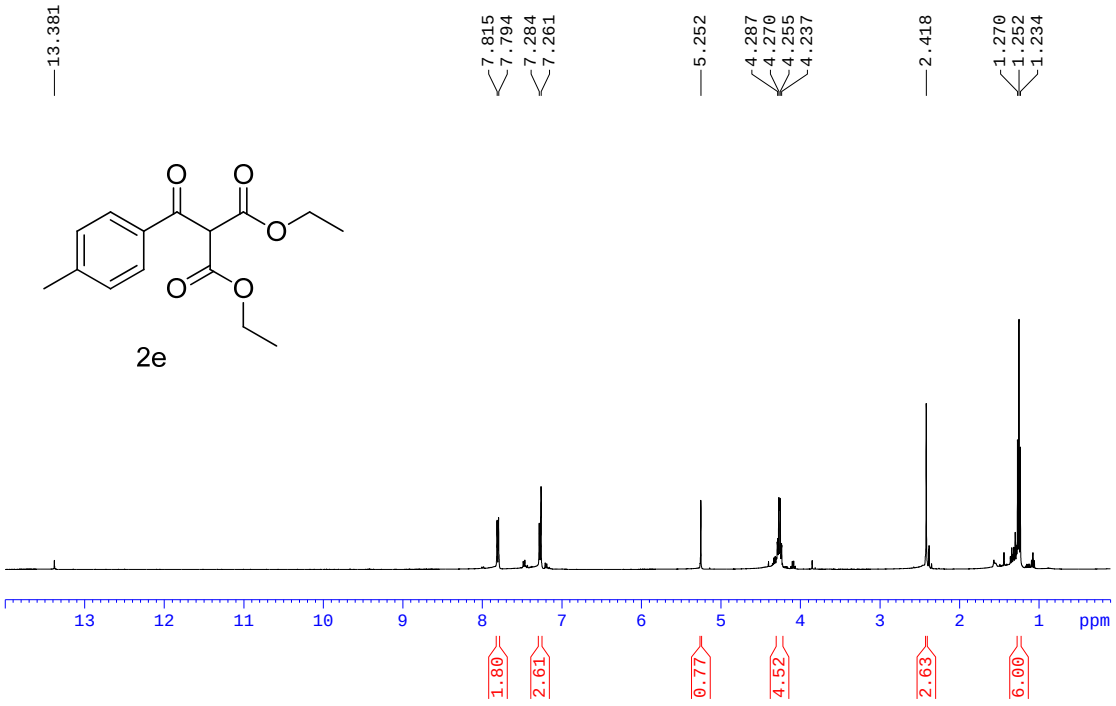
90
80
70
60
50
40
30
20
10
ppm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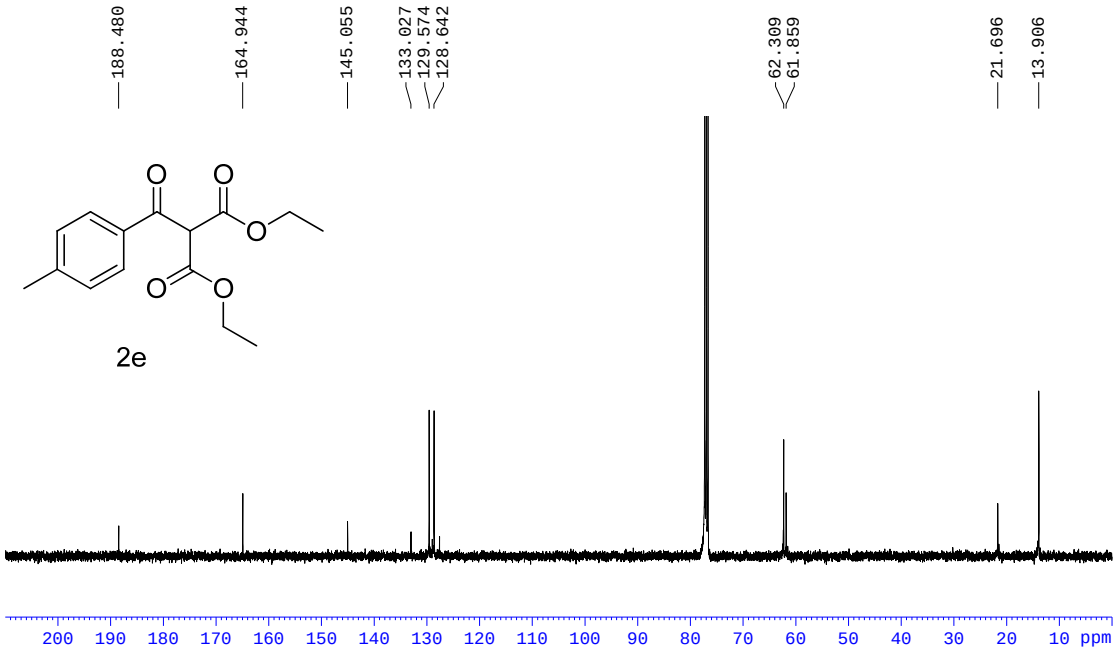
6.00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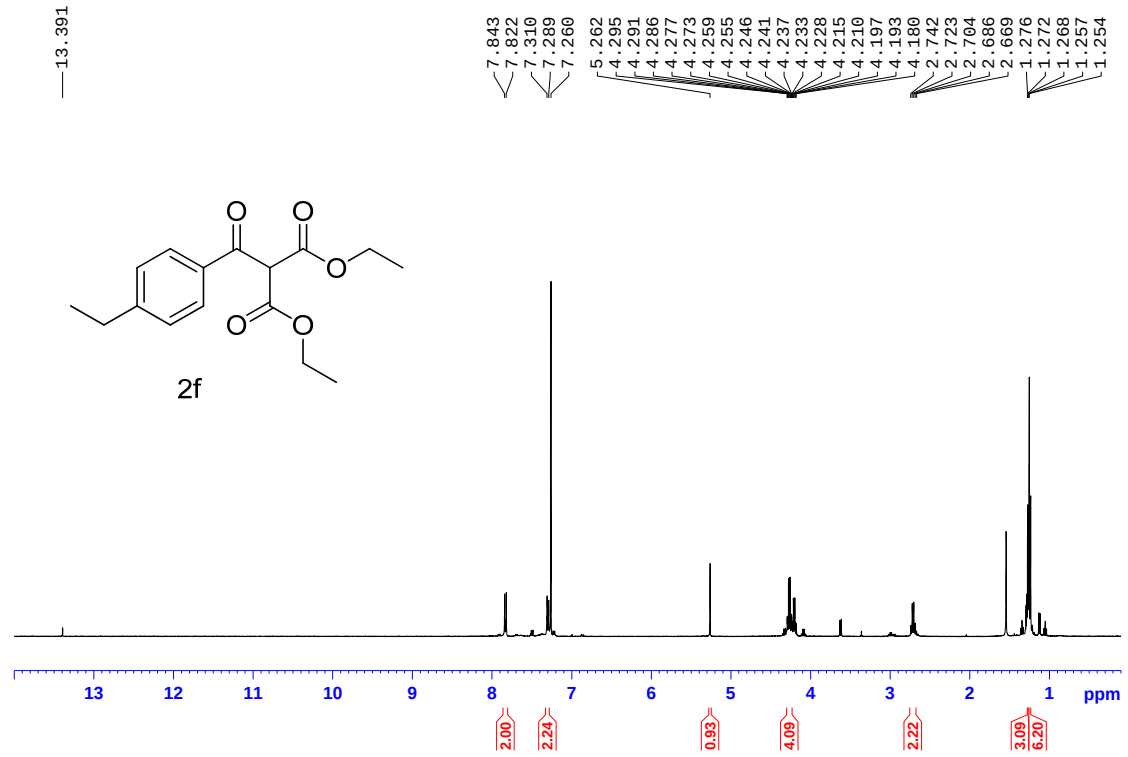
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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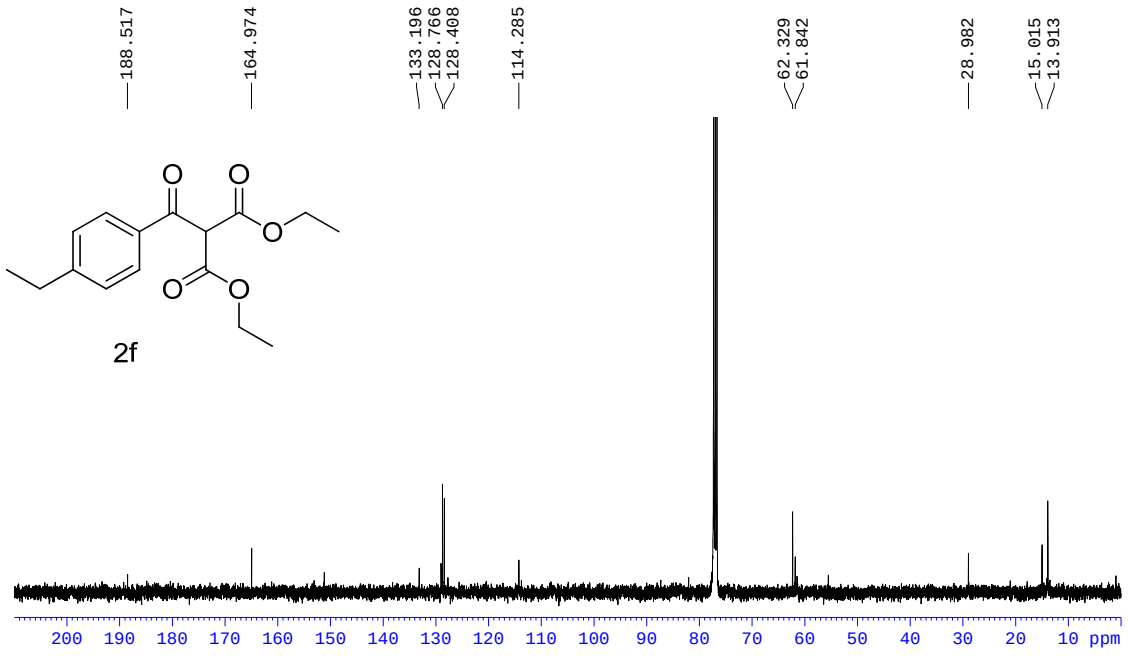
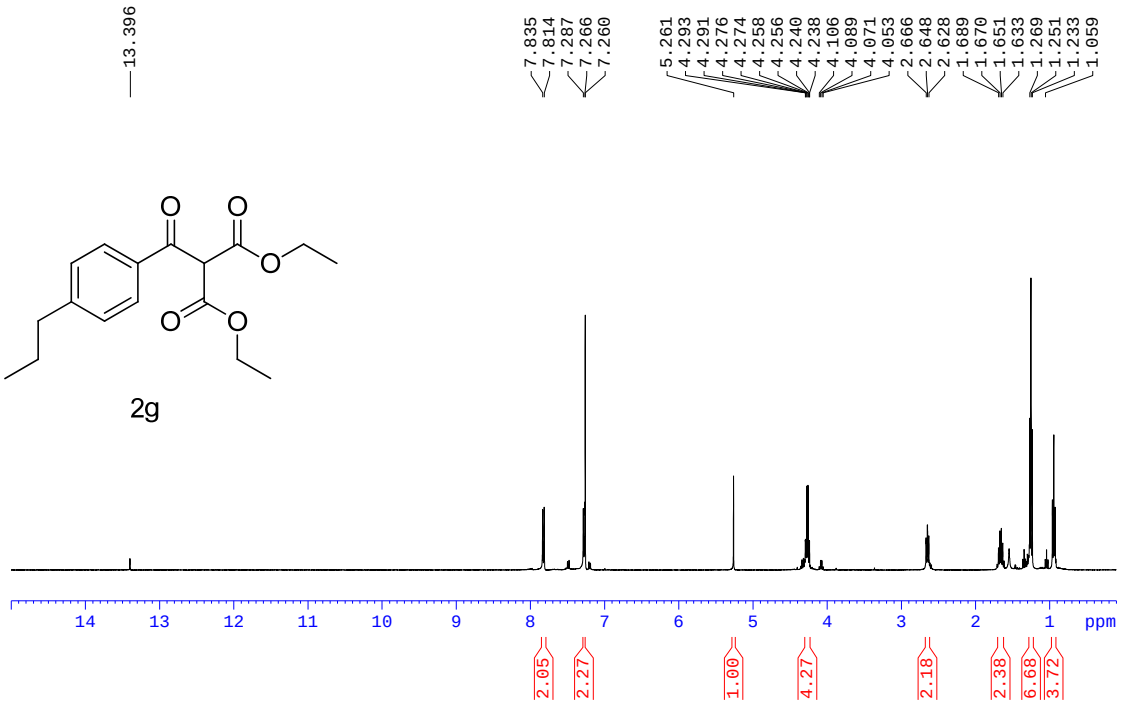
7.843
7.822
7.310
7.289
7.260
5.262
4.295
4.291
4.286
4.277
4.273
4.259
4.255
4.246
4.241
4.237
4.233
4.228
4.215
4.210
4.197
4.193
4.180
2.742
2.723
2.704
2.686
2.669
1.276
1.272
1.268
1.257
1.254
2f
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.24
0.93
4.09
2.22
3.09
6.20


188.517
164.974
133.196
128.766
128.408
114.285
62.329
61.842
28.982
15.015
13.913
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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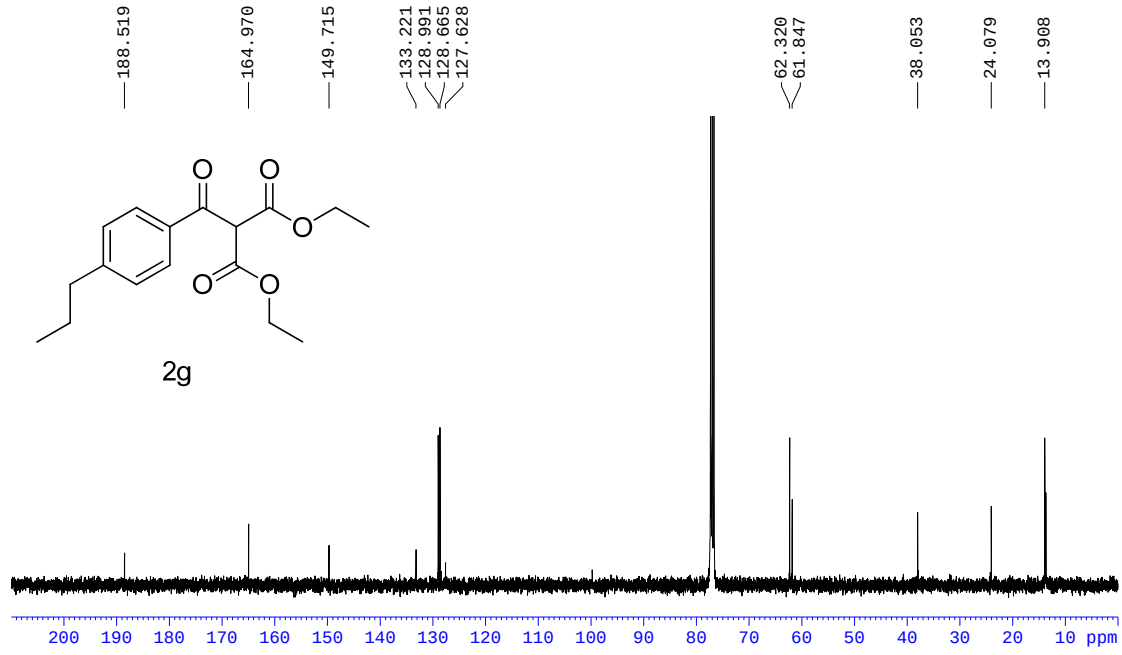
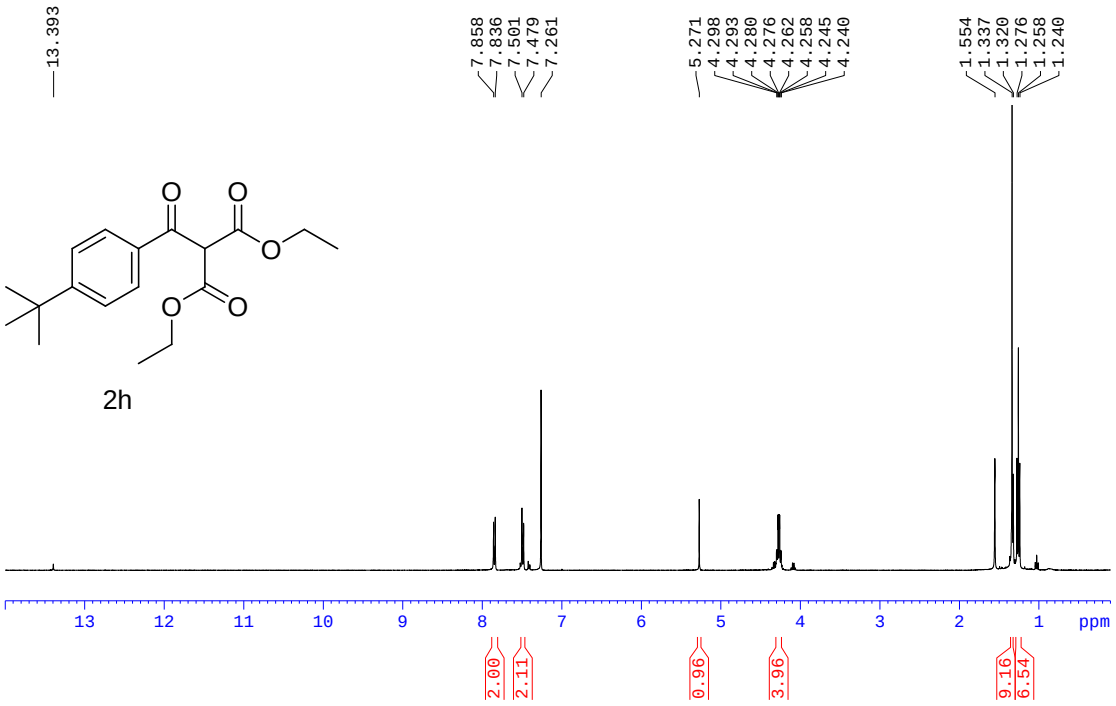
7.835
7.814
7.287
7.266
7.260
5.261
4.293
4.291
4.276
4.274
4.258
4.256
4.240
4.238
4.106
4.089
4.071
4.053
2.666
2.648
2.628
1.689
1.670
1.651
1.633
1.269
1.251
1.233
1.059
2g
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.05
2.27
1.00
4.27
2.18
2.38
6.68
3.72


188.519
164.970
149.715
133.221
128.991
128.665
127.628
62.320
61.847
38.053
24.079
13.908
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


13.393
7.858
7.836
7.501
7.479
7.261
5.271
4.298
4.293
4.280
4.276
4.262
4.258
4.245
4.240
1.554
1.337
1.320
1.276
1.258
1.240
2h
13
12
11
10
9
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4
3
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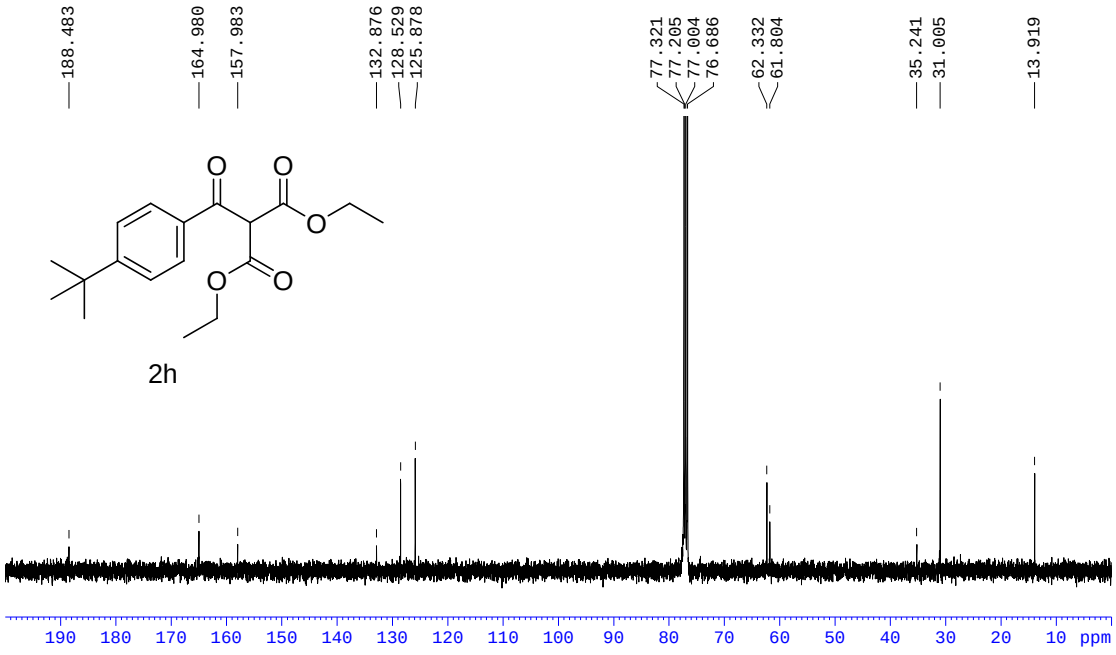
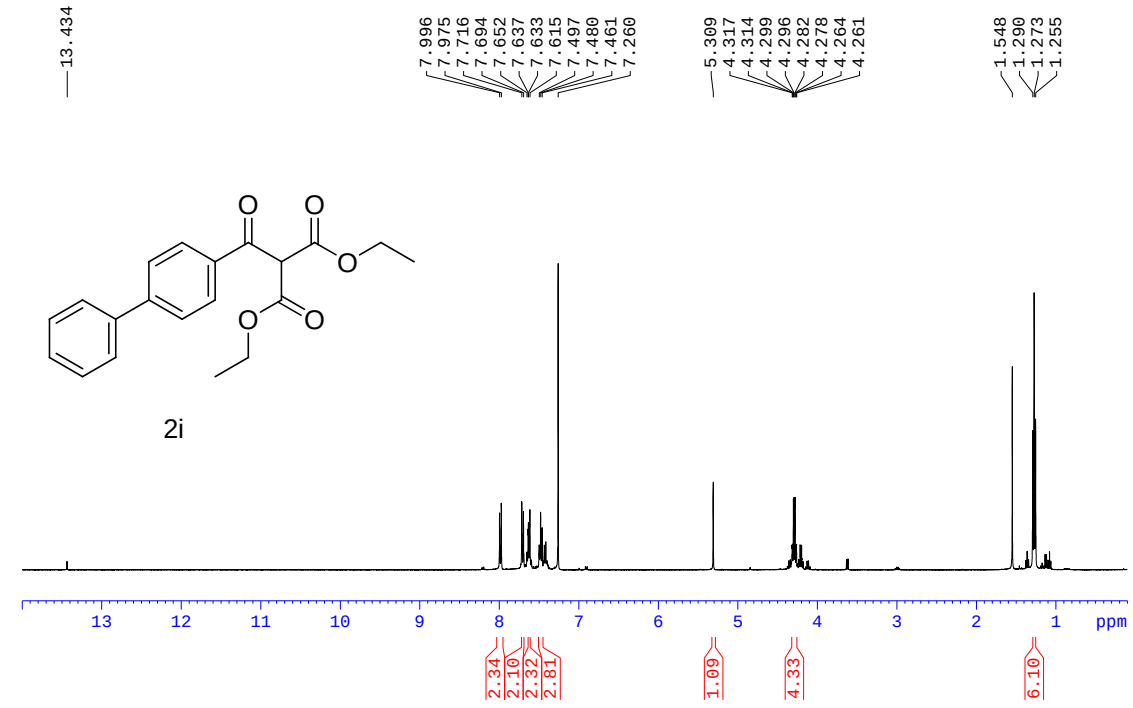
ppm
2.00
2.11
0.96
3.96
9.16
6.54


188.483
164.980
157.983
132.876
128.529
125.878
77.321
77.205
77.004
76.686
62.332
61.804
35.241
31.005
13.919
2h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13.434
7.996
7.975
7.716
7.694
7.652
7.637
7.633
7.615
7.497
7.480
7.461
7.260
5.309
4.317
4.314
4.299
4.296
4.282
4.278
4.264
4.261
1.548
1.290
1.273
1.255
2i
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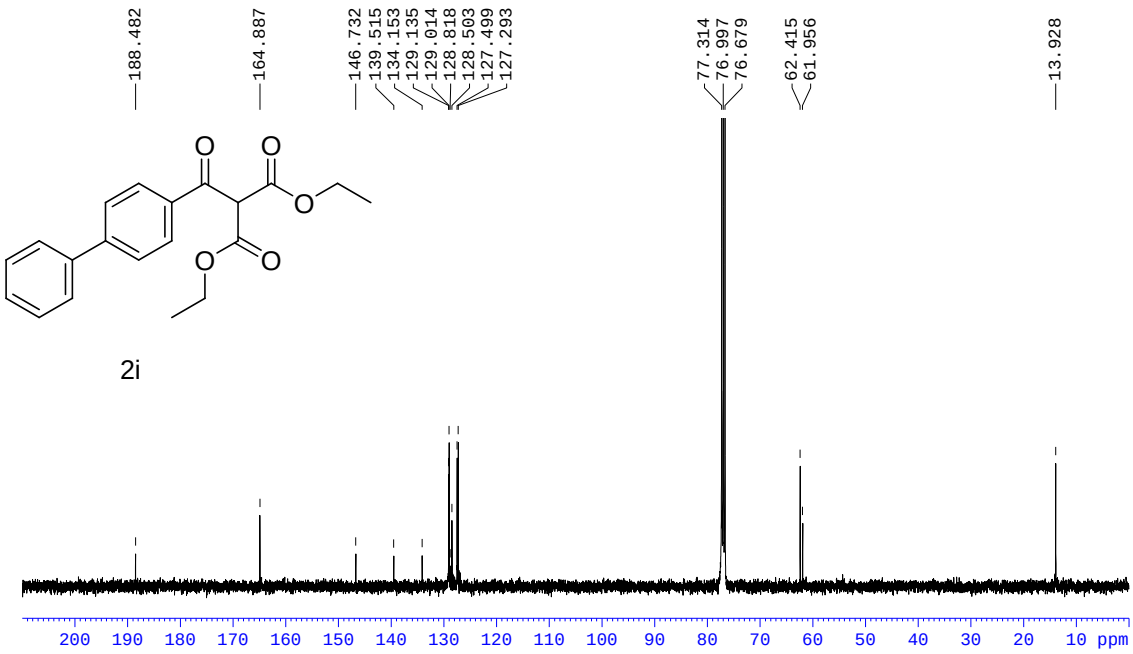
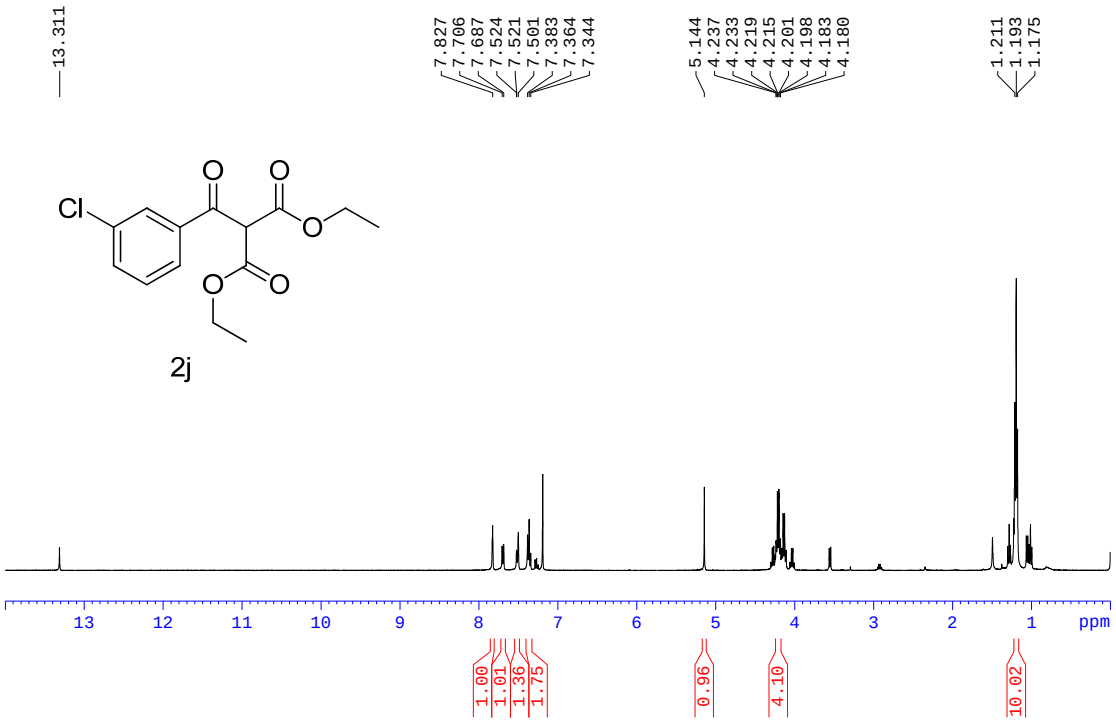
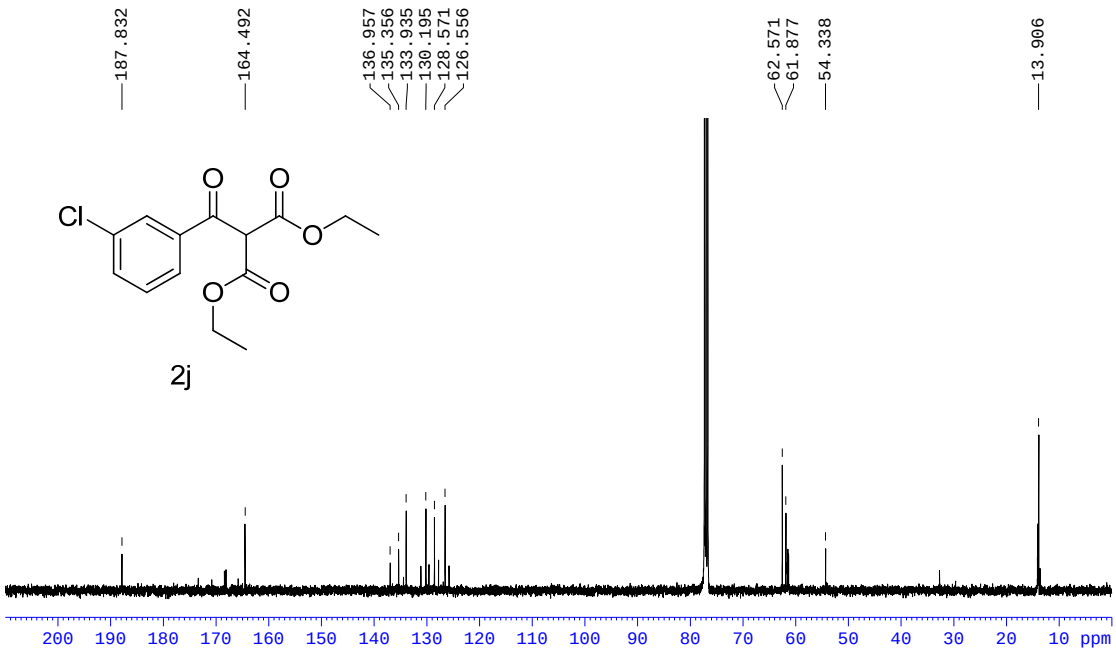
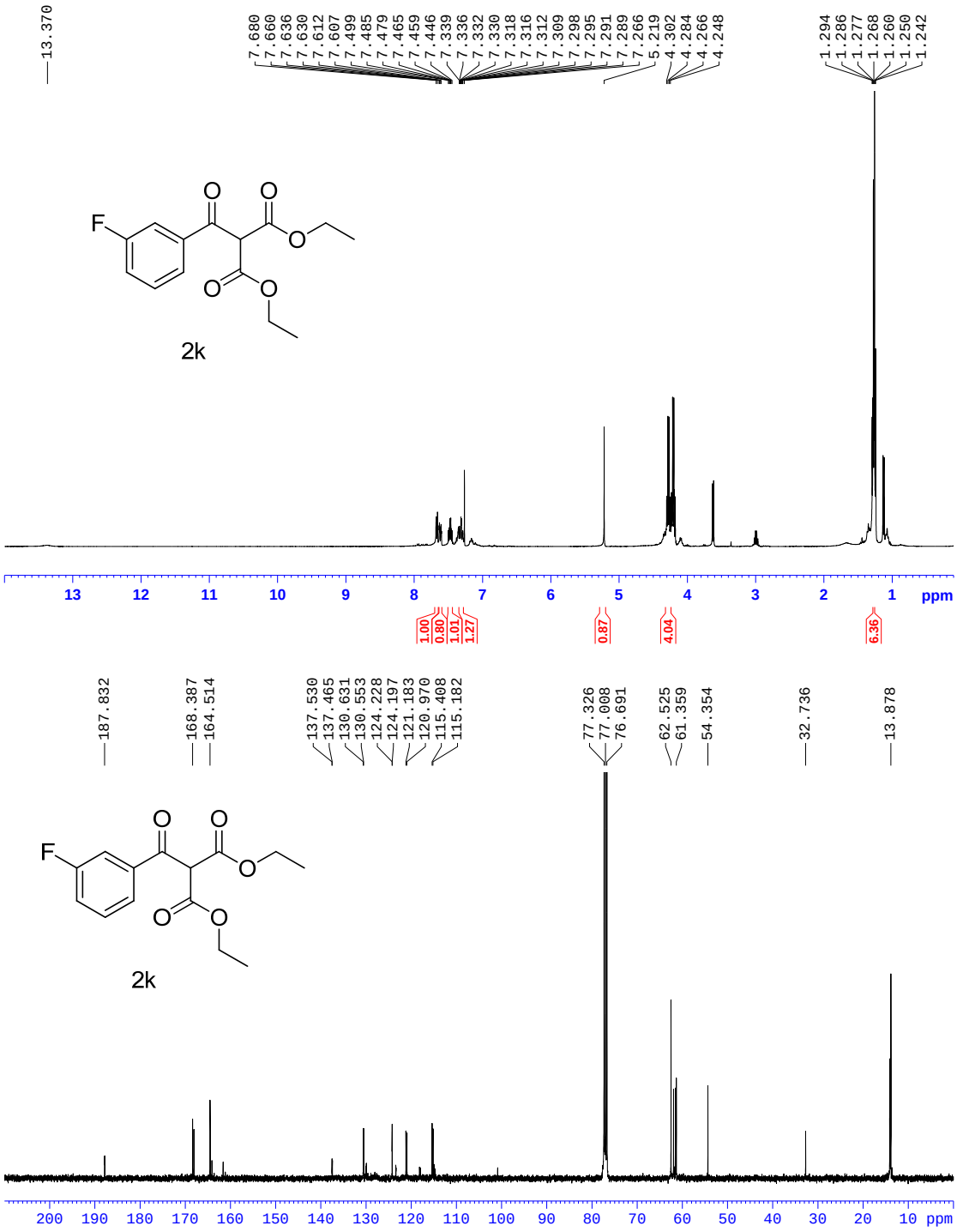
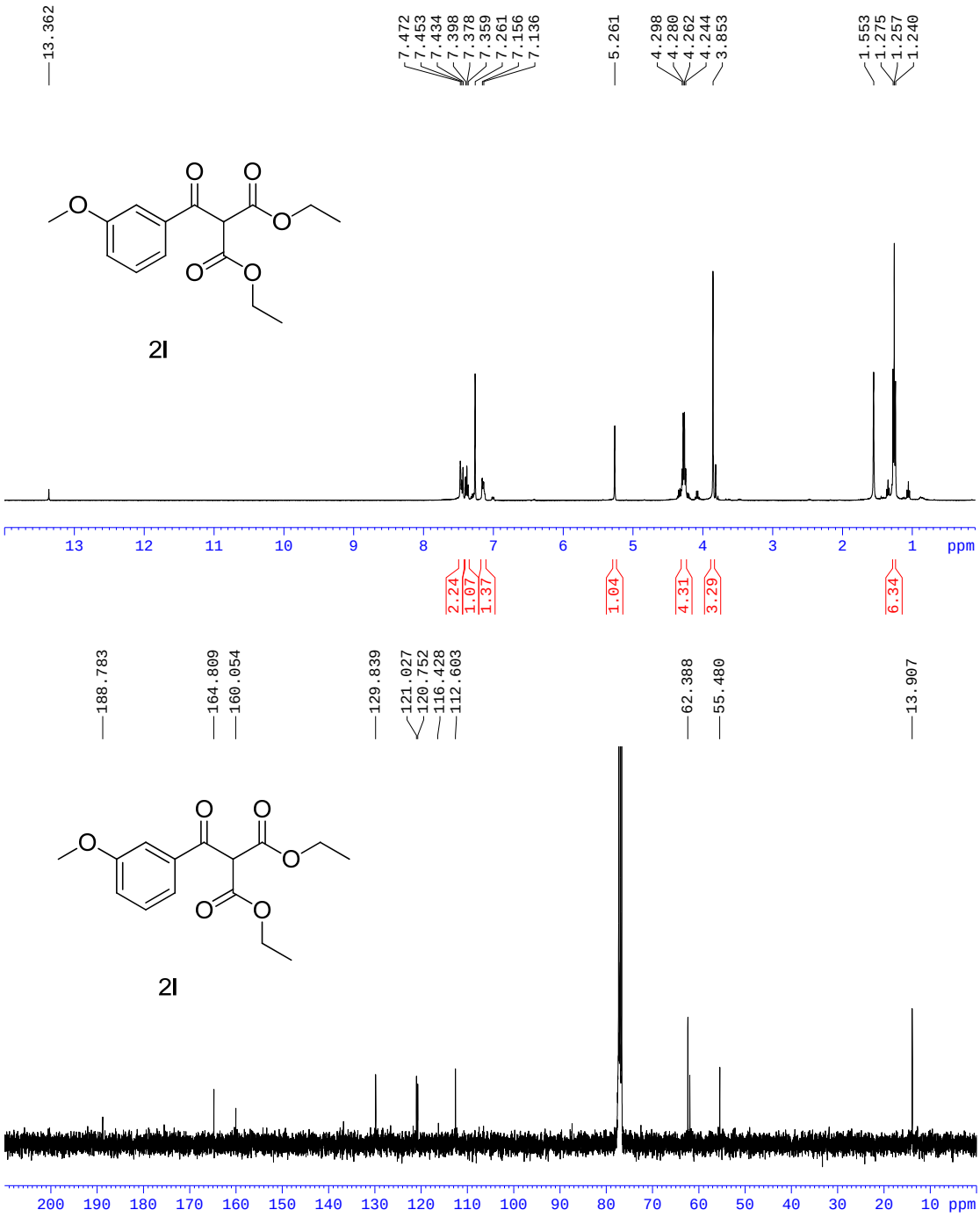
2.34
2.10
2.32
2.81
1.09
4.33
6.10

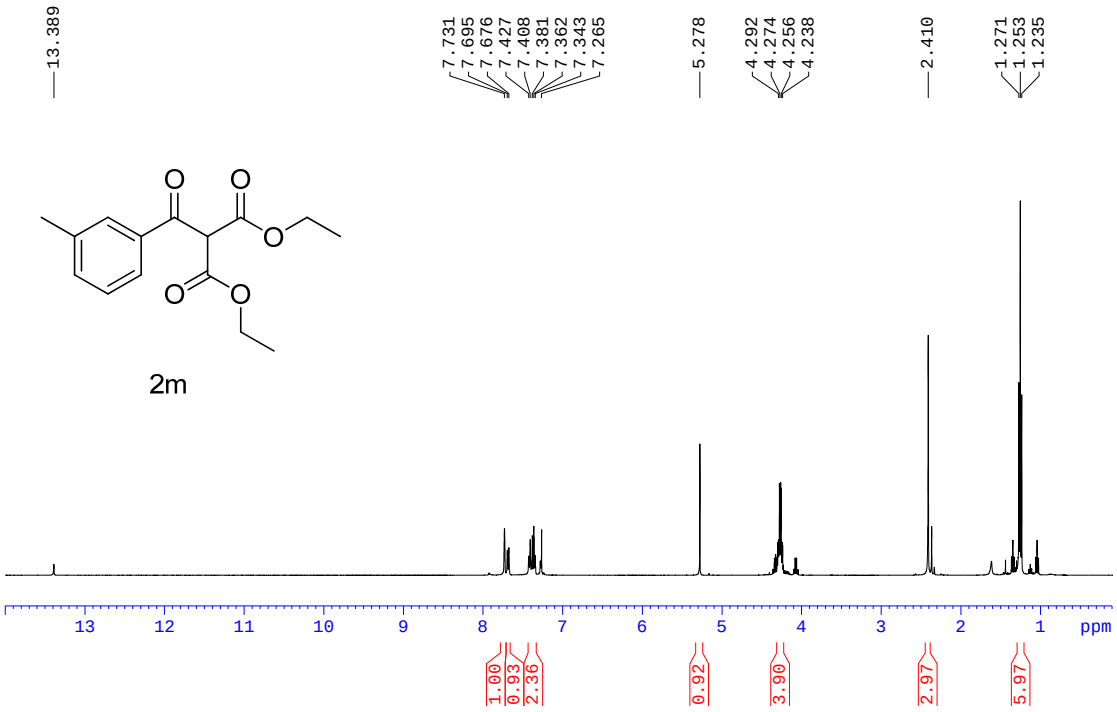

188.482
164.887
146.732
139.515
134.153
129.135
129.014
128.818
128.503
127.499
127.293
77.314
76.997
76.679
62.415
61.956
13.928
2i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

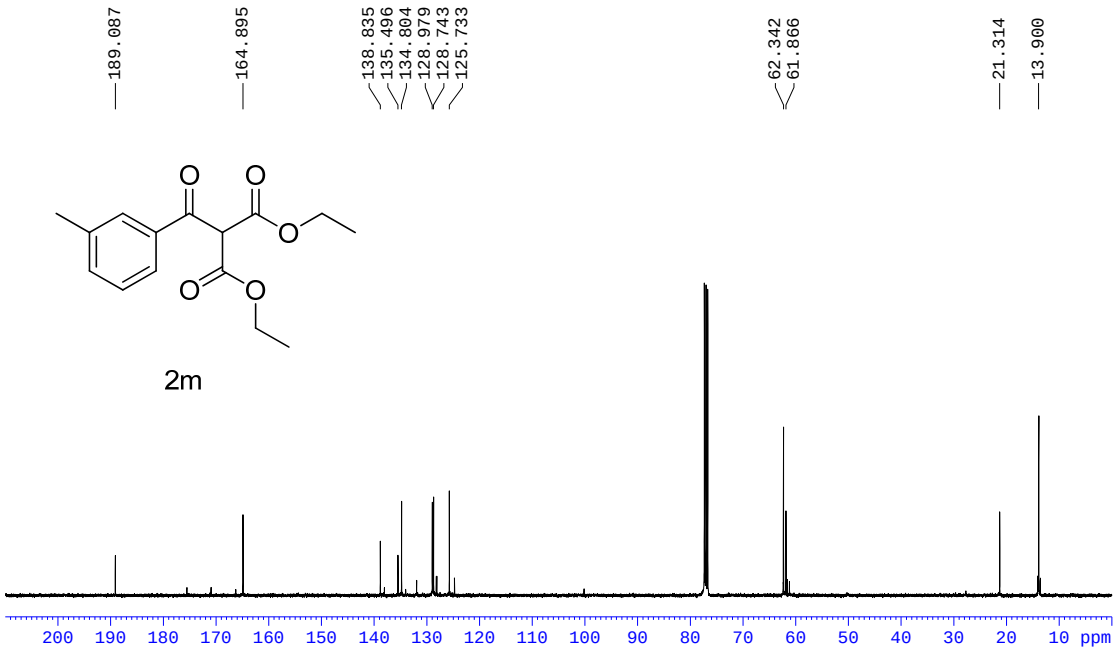

13.311
7.827
7.706
7.687
7.524
7.521
7.501
7.383
7.364
7.344
5.144
4.237
4.233
4.219
4.215
4.201
4.198
4.183
4.180
1.211
1.193
1.175
Cl
O
O
O
O
O
2j
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.36
1.75
0.96
4.10
10.02

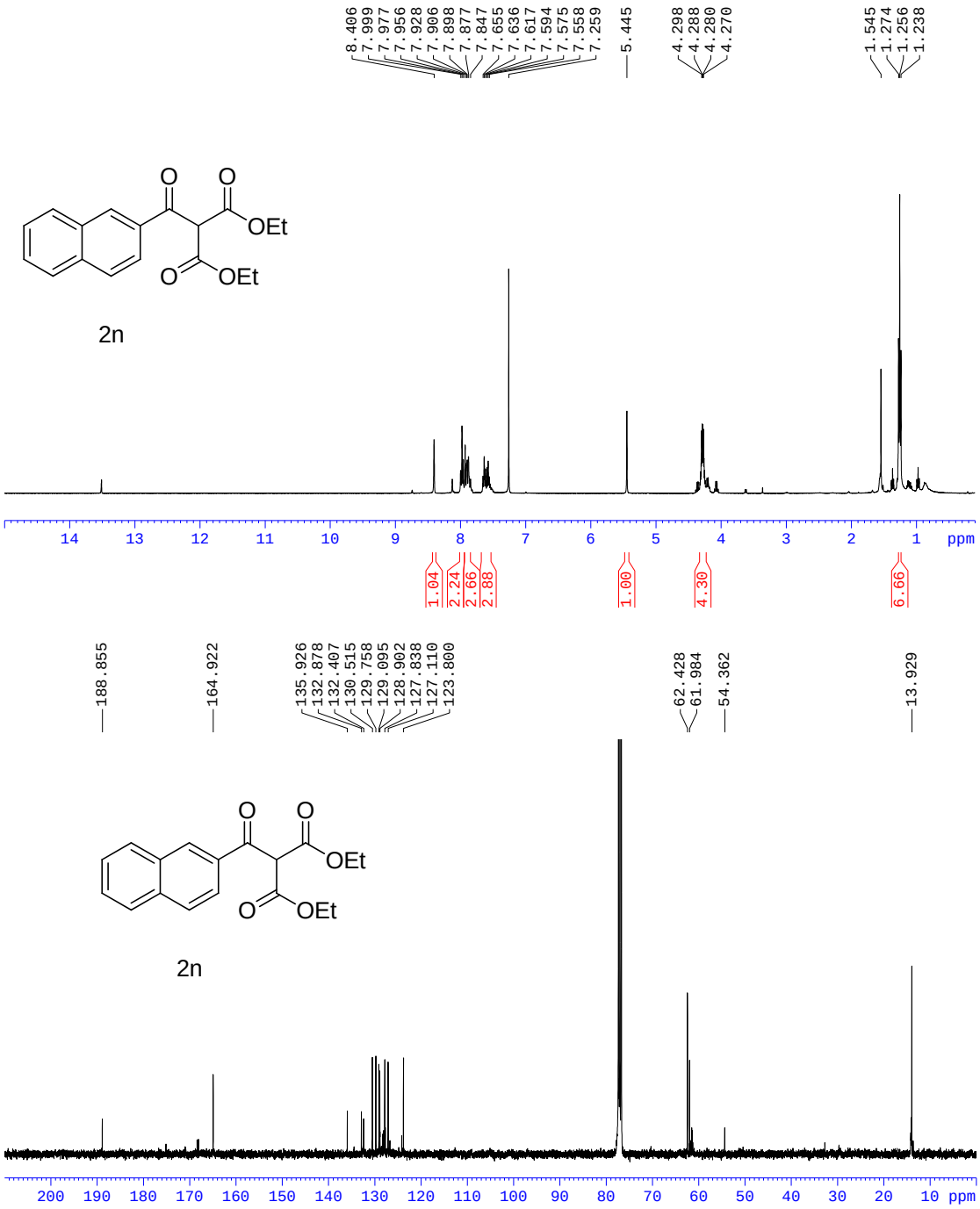

187.832
164.492
136.957
135.356
133.935
130.195
128.571
126.556
62.571
61.877
54.338
13.906
Cl
O
O
O
O
O
2j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

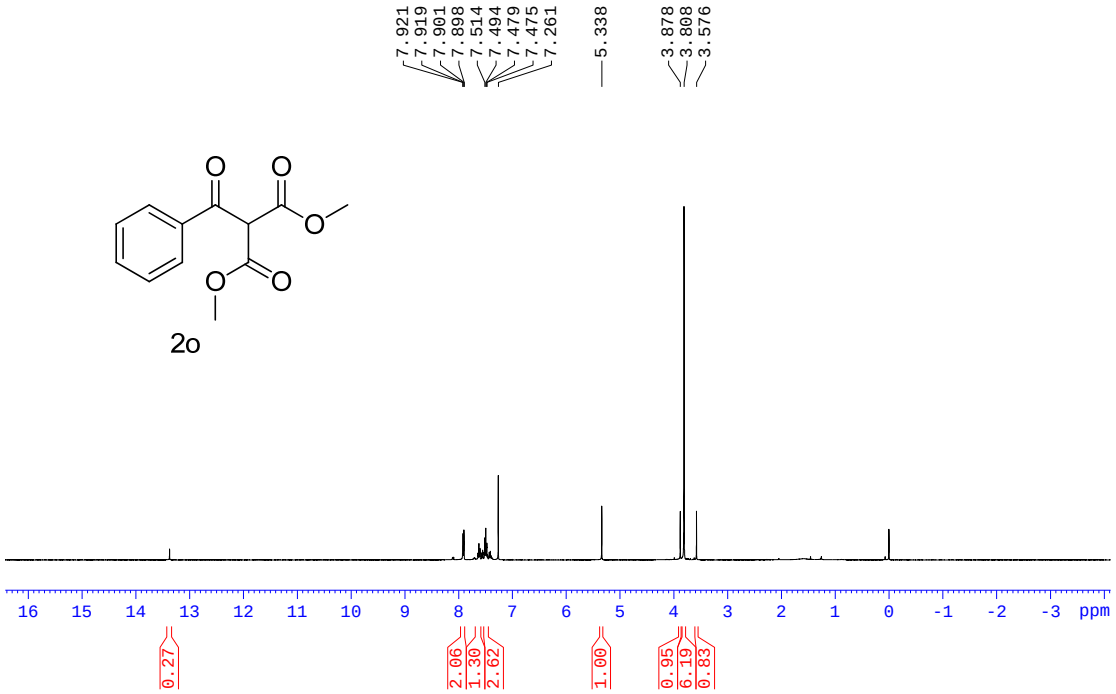

13.370
7.680
7.660
7.636
7.630
7.612
7.607
7.499
7.485
7.479
7.465
7.459
7.446
7.339
7.336
7.332
7.330
7.318
7.316
7.312
7.309
7.298
7.295
7.291
7.289
7.266
5.219
4.302
4.284
4.266
4.248
1.294
1.286
1.277
1.268
1.260
1.250
1.242
F
O
O
O
O
O
2k
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.80
1.01
1.27
0.87
4.04
6.36
187.832
168.387
164.514
137.530
137.465
130.631
130.553
124.228
124.197
121.183
120.970
115.408
115.182
77.326
77.008
76.691
62.525
61.359
54.354
32.736
13.878
F
O
O
O
O
O
2k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

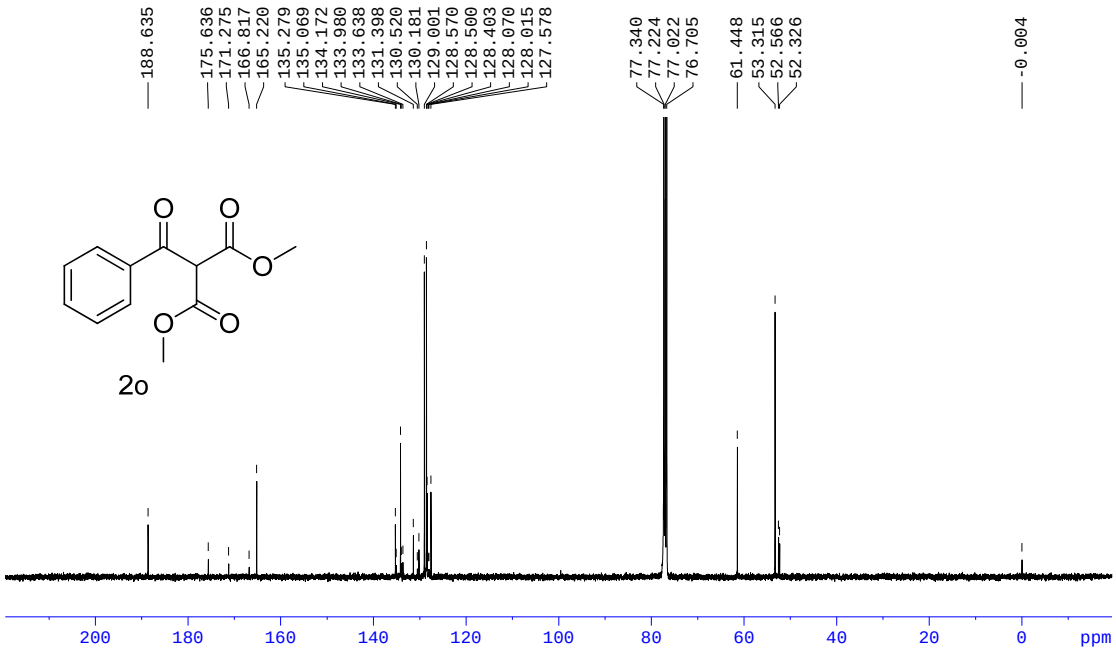

13.362
7.472
7.453
7.434
7.398
7.378
7.359
7.261
7.156
7.136
5.261
4.298
4.280
4.262
4.244
3.853
1.553
1.275
1.257
1.240
2I
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.24
1.07
1.37
1.04
4.31
3.29
6.34
188.783
164.809
160.054
129.839
121.027
120.752
116.428
112.603
62.388
55.480
13.907
2I
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

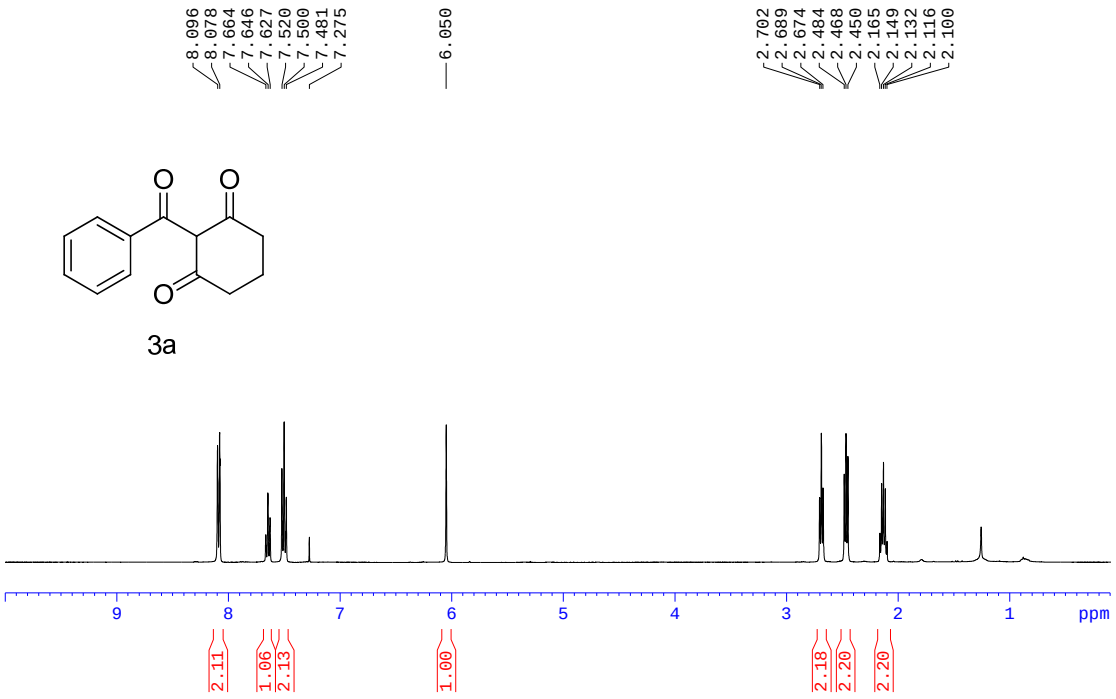

13.389
7.731
7.695
7.676
7.427
7.408
7.381
7.362
7.343
7.265
5.278
4.292
4.274
4.256
4.238
2.410
1.271
1.253
1.235
2m
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.93
2.36
0.92
3.90
2.97
5.97

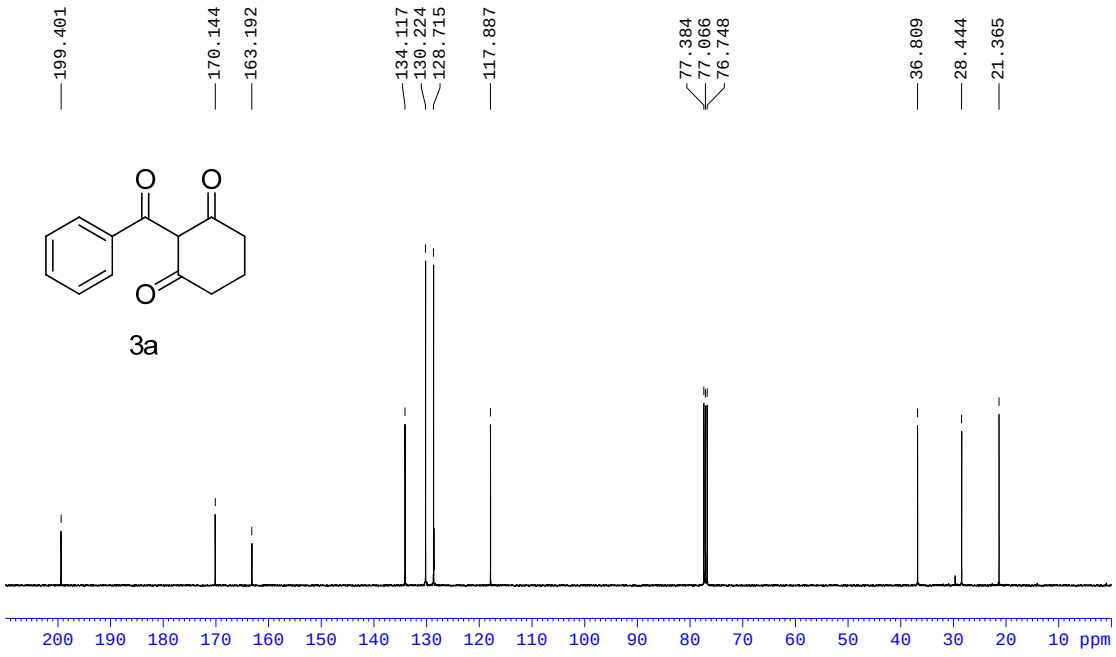

189.087
164.895
138.835
135.496
134.804
128.979
128.743
125.733
62.342
61.866
21.314
13.900
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.406
7.999
7.977
7.956
7.928
7.906
7.898
7.877
7.847
7.655
7.636
7.617
7.594
7.575
7.558
7.259
5.445
4.298
4.288
4.280
4.270
1.545
1.274
1.256
1.238
O
O
OEt
O
OEt
2n
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.04
2.24
2.66
2.88
1.00
4.30
6.66
188.855
164.922
135.926
132.878
132.407
130.515
129.758
129.095
128.902
127.838
127.110
123.800
62.428
61.984
54.362
13.929
O
O
OEt
O
OEt
2n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


7.921
7.919
7.901
7.898
7.514
7.494
7.479
7.475
7.261
5.338
3.878
3.808
3.576
2o
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
0.27
2.06
1.30
2.62
1.00
0.95
6.19
0.83


188.635
175.636
171.275
166.817
165.220
135.279
135.069
134.172
133.980
133.638
131.398
130.520
130.181
129.001
128.570
128.500
128.403
128.070
128.015
127.578
77.340
77.224
77.022
76.705
61.448
53.315
52.566
52.326
-0.004
2o
200 180 160 140 120 100 80 60 40 20 0 ppm


8.096
8.078
7.664
7.646
7.627
7.520
7.500
7.481
7.275
6.050
2.702
2.689
2.674
2.484
2.468
2.450
2.165
2.149
2.132
2.116
2.100
3a
9
8
7
6
5
4
3
2
1
ppm
2.11
1.06
2.13
1.00
2.18
2.20
2.20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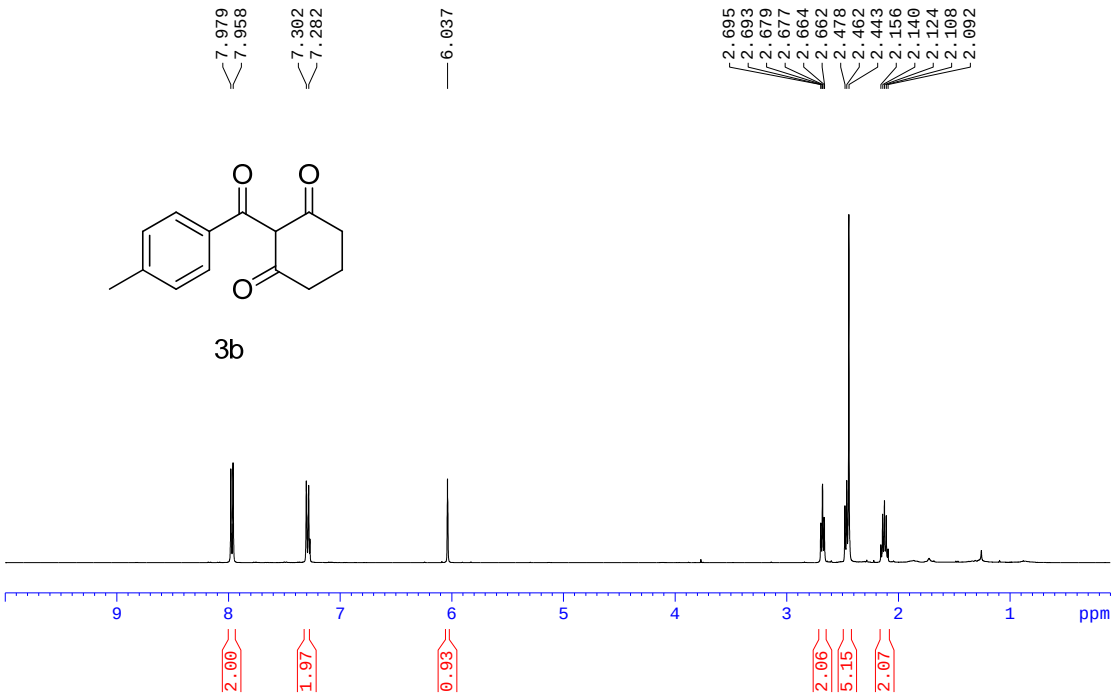
170.144
163.192
134.117
130.224
128.715
117.887
77.384
77.066
76.748
36.809
28.444
21.365
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.958
7.302
7.282
6.037
2.695
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2.679
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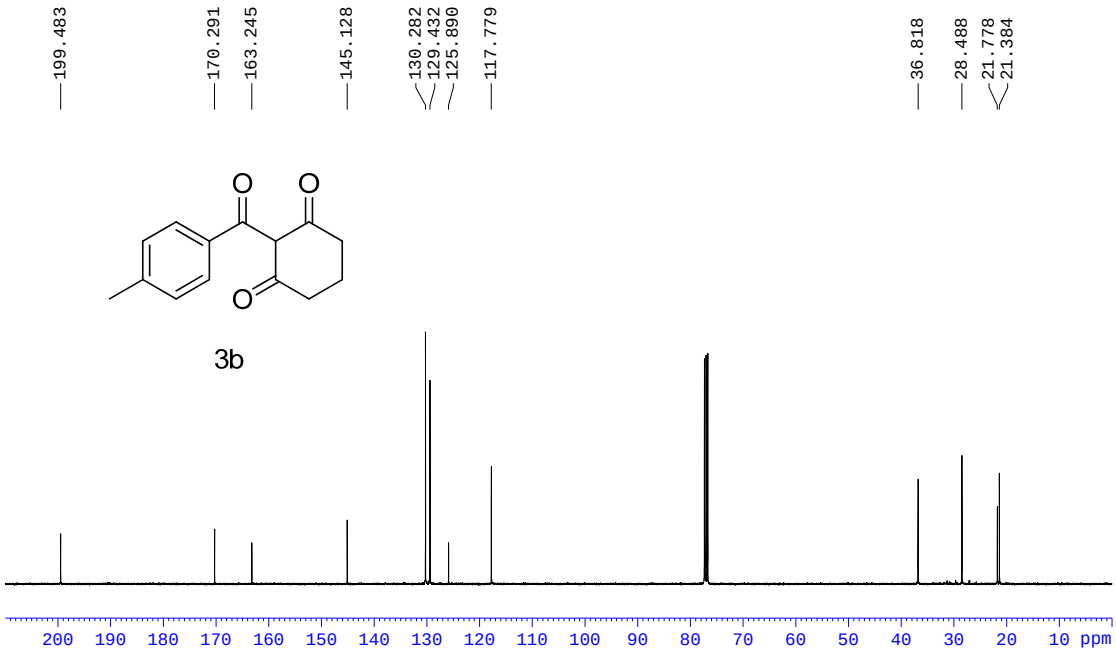
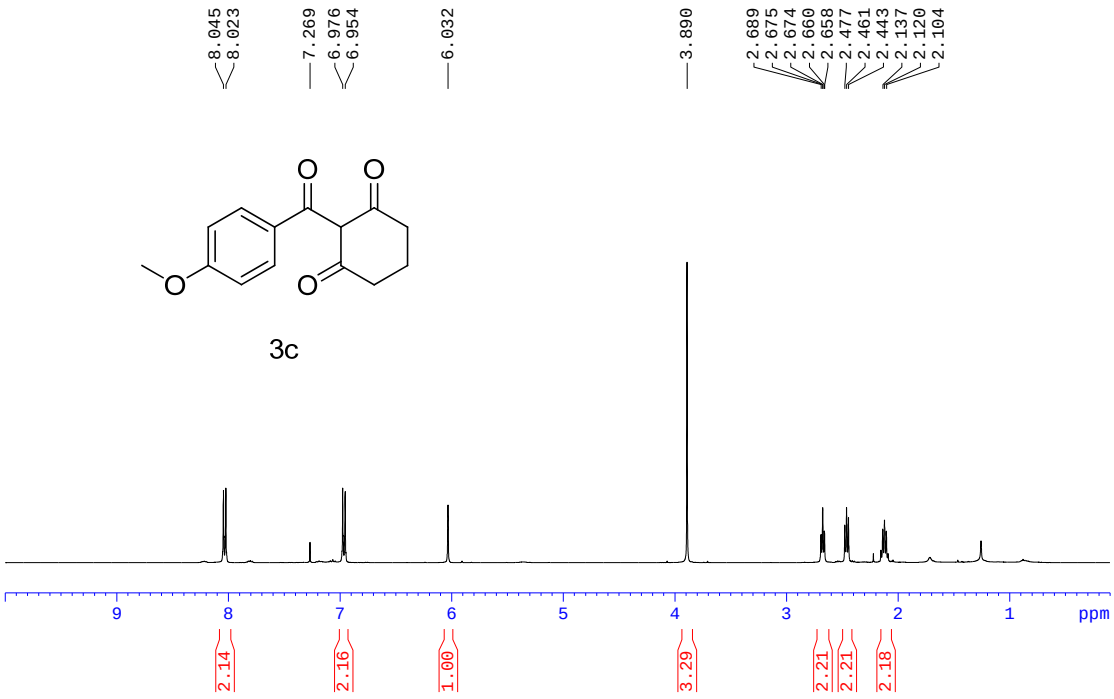
2.664
2.662
2.478
2.462
2.443
2.156
2.140
2.124
2.108
2.092
3b
9
8
7
6
5
4
3
2
1
ppm
2.00
1.97
0.93
2.06
5.15
2.07


199.483
170.291
163.245
145.128
130.282
129.432
125.890
117.779
36.818
28.488
21.778
21.384
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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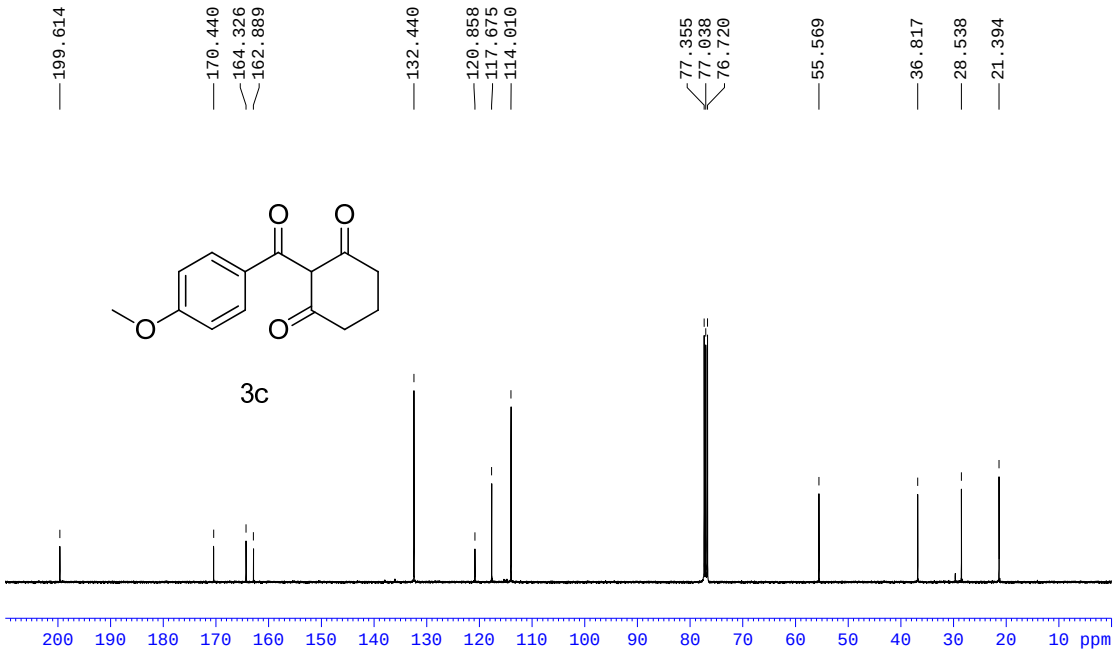
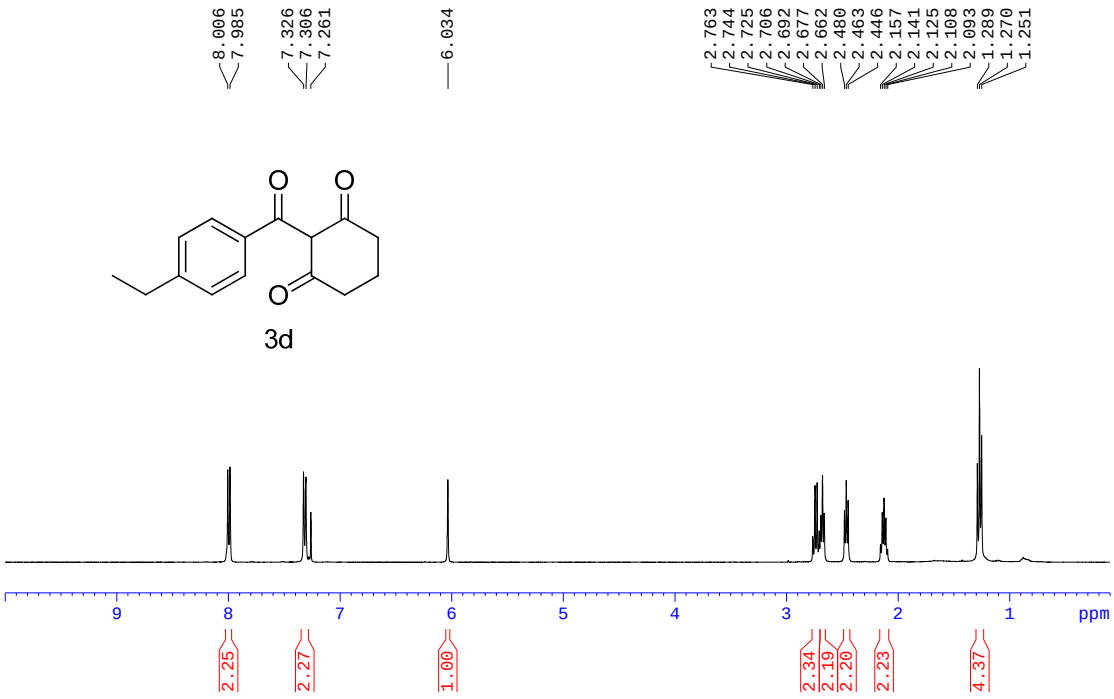
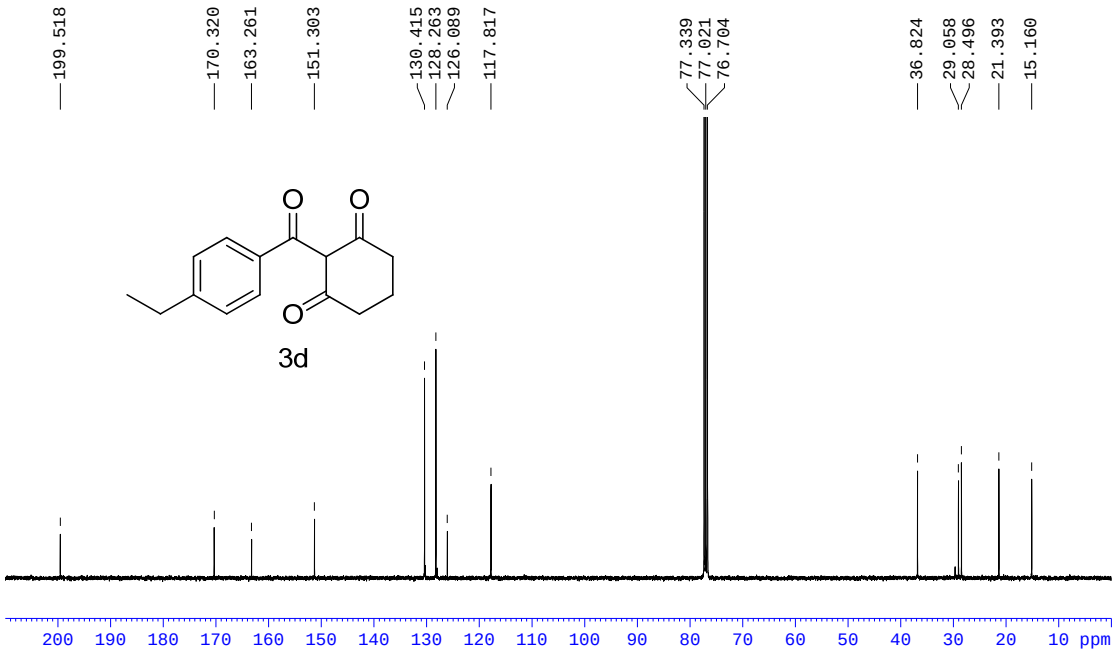
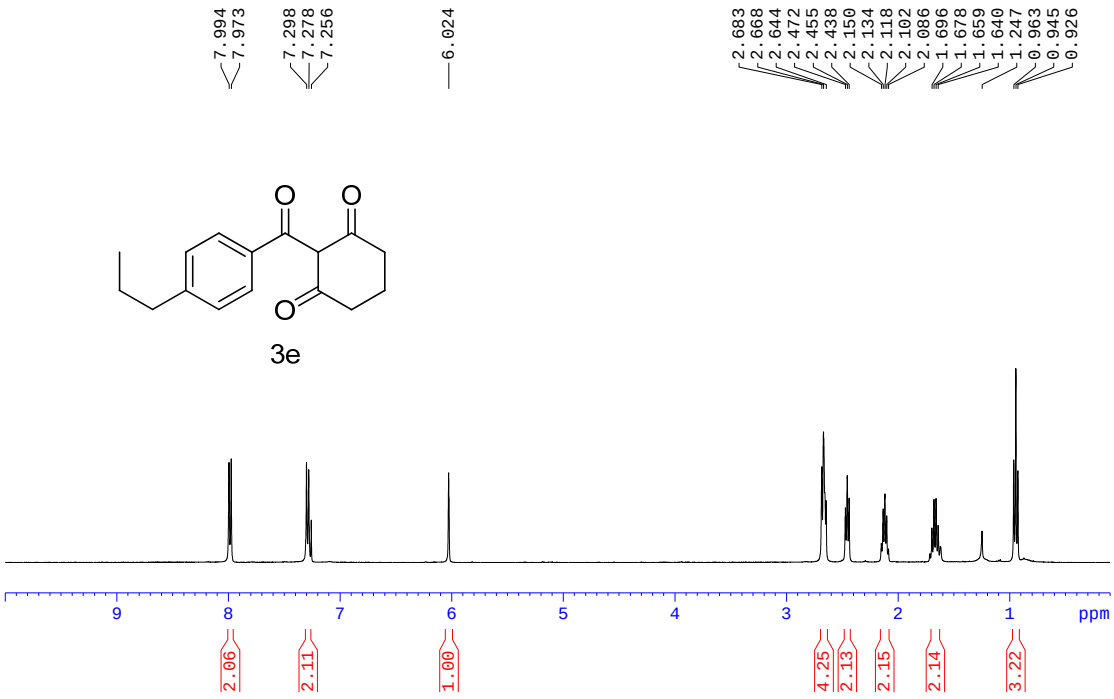
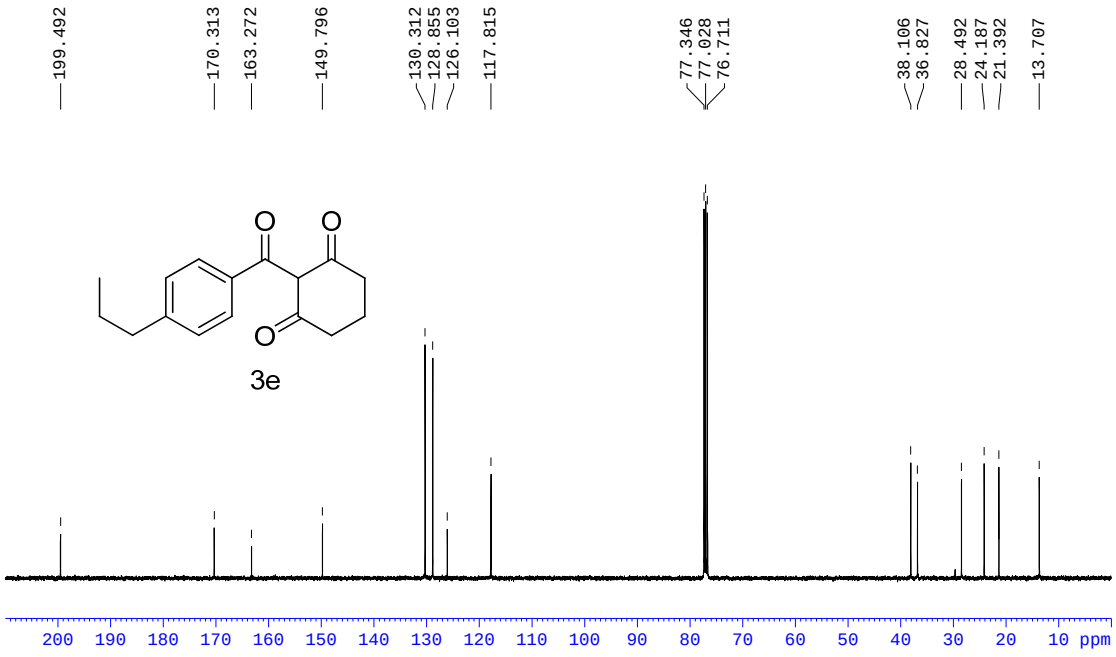
8.023
7.269
6.976
6.954
6.032
3.890
2.689
2.675
2.674
2.660
2.658
2.477
2.461
2.443
2.137
2.120
2.104
3c
9
8
7
6
5
4
3
2
1
ppm
2.14
2.16
1.00
3.29
2.21
2.21
2.18


199.614
170.440
164.326
162.889
132.440
120.858
117.675
114.010
77.355
77.038
76.720
55.569
36.817
28.538
21.394
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.006
7.985
7.326
7.306
7.261
6.034
2.763
2.744
2.725
2.706
2.692
2.677
2.662
2.480
2.463
2.446
2.157
2.141
2.125
2.108
2.093
1.289
1.270
1.251
3d
9
8
7
6
5
4
3
2
1
ppm
2.25
2.27
1.00
2.34
2.19
2.20
2.23
4.37


199.518
170.320
163.261
151.303
130.415
128.263
126.089
117.817
77.339
77.021
76.704
36.824
29.058
28.496
21.393
15.160
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


7.994
7.973
7.298
7.278
7.256
6.024
2.683
2.668
2.644
2.472
2.455
2.438
2.150
2.134
2.118
2.102
2.086
1.696
1.678
1.659
1.640
1.247
0.963
0.945
0.926
3e
9
8
7
6
5
4
3
2
1
ppm
2.06
2.11
1.00
4.25
2.13
2.15
2.14
3.22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21.392
13.707
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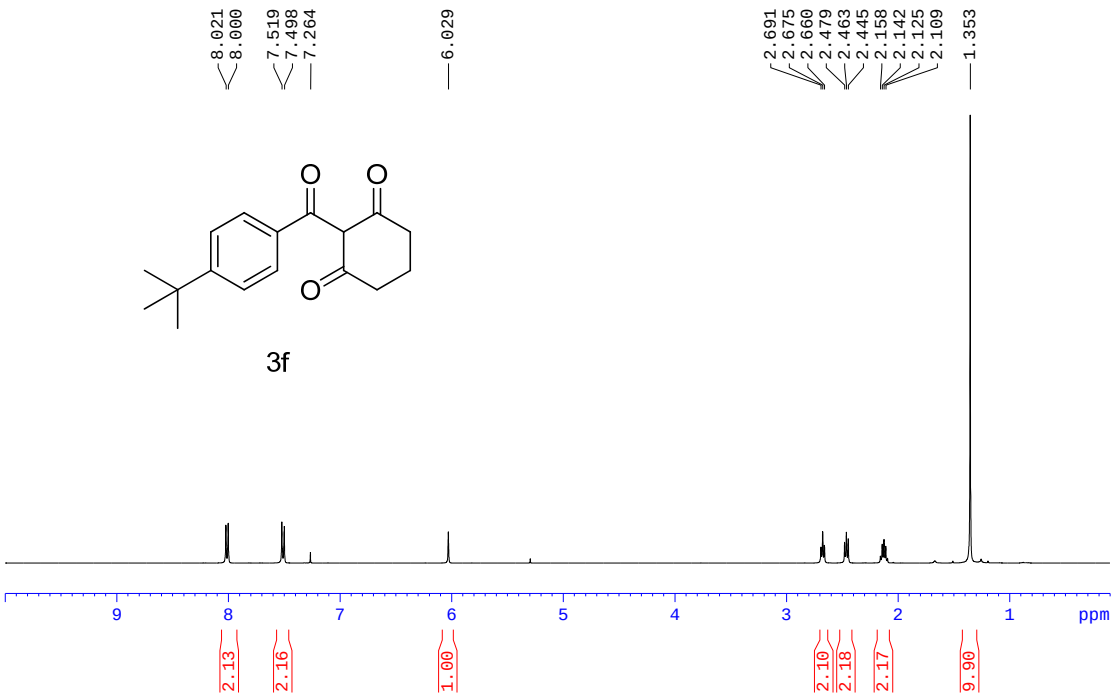
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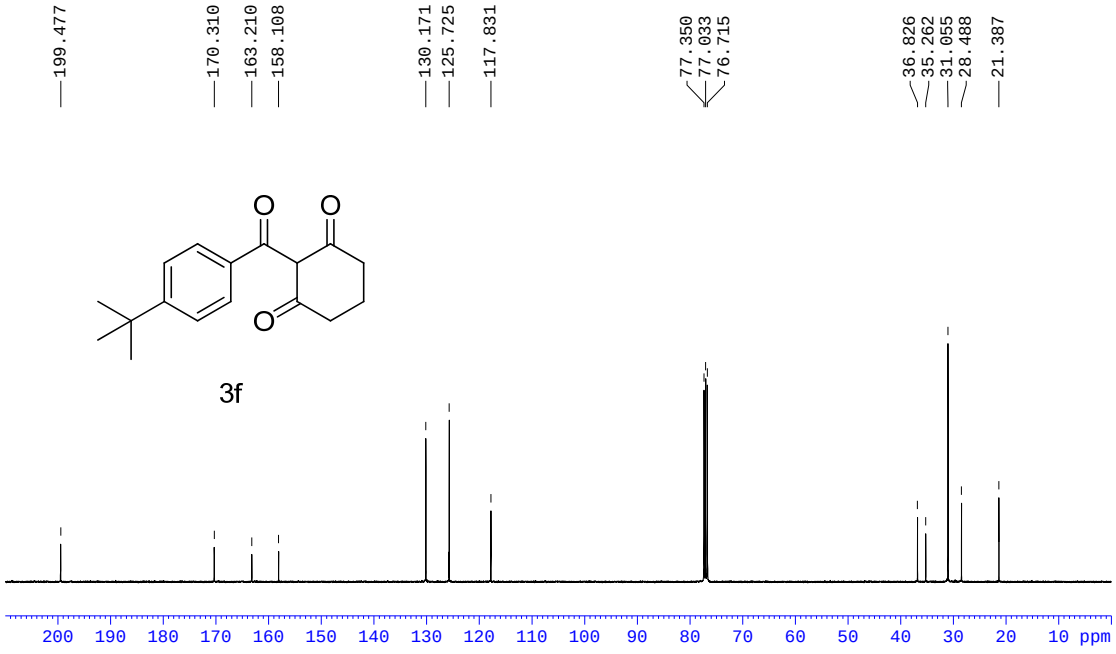
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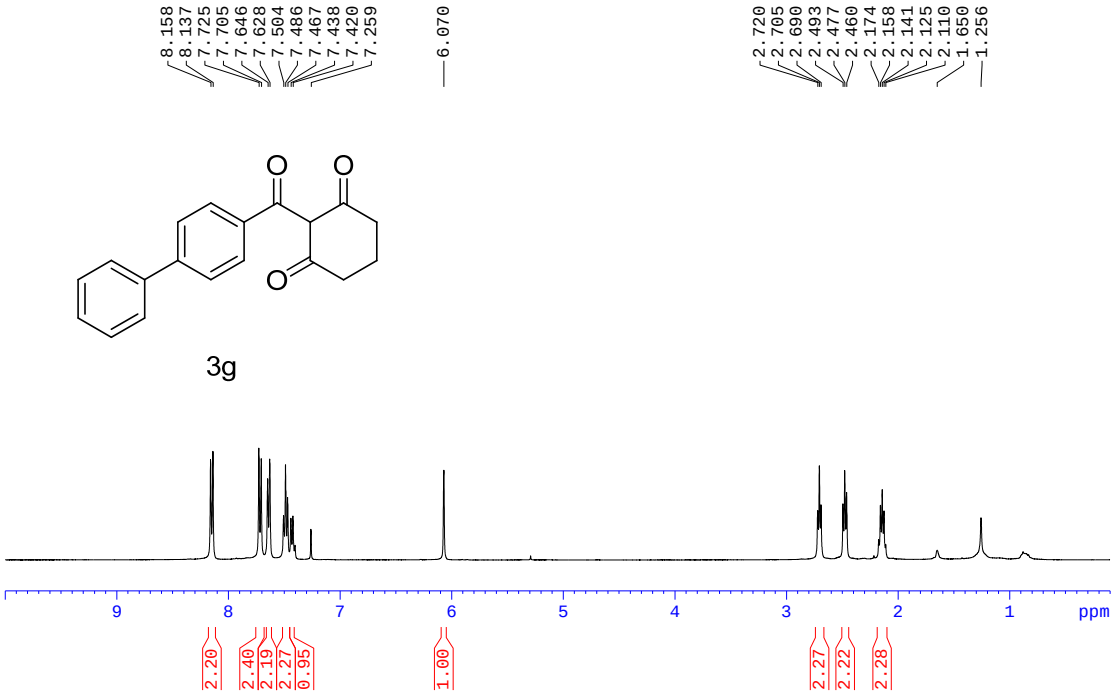
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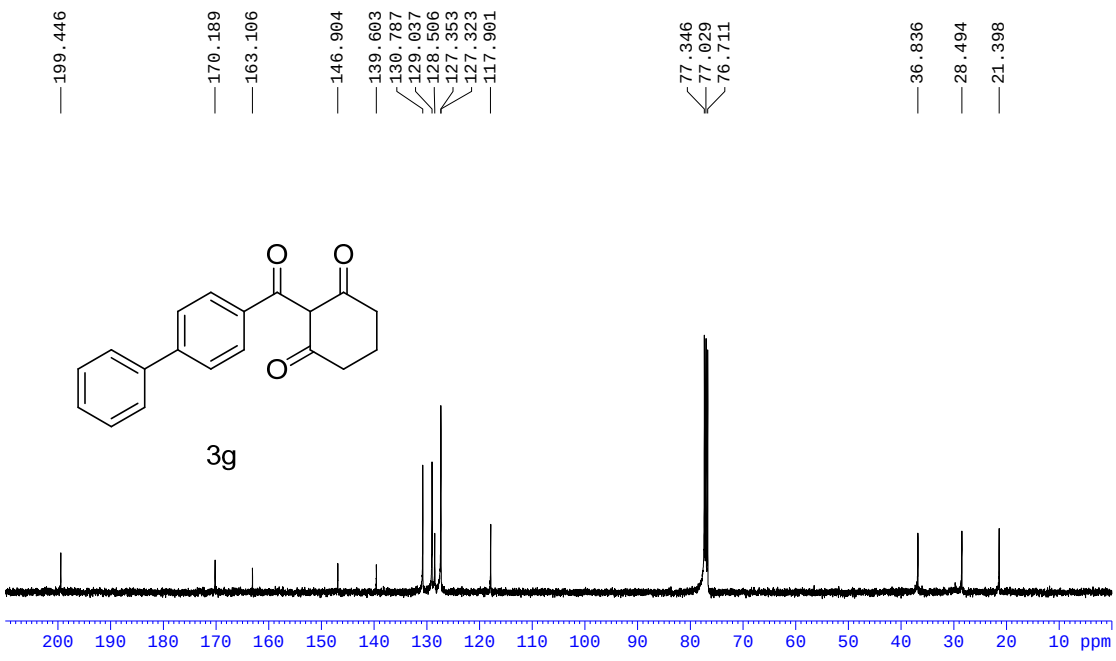
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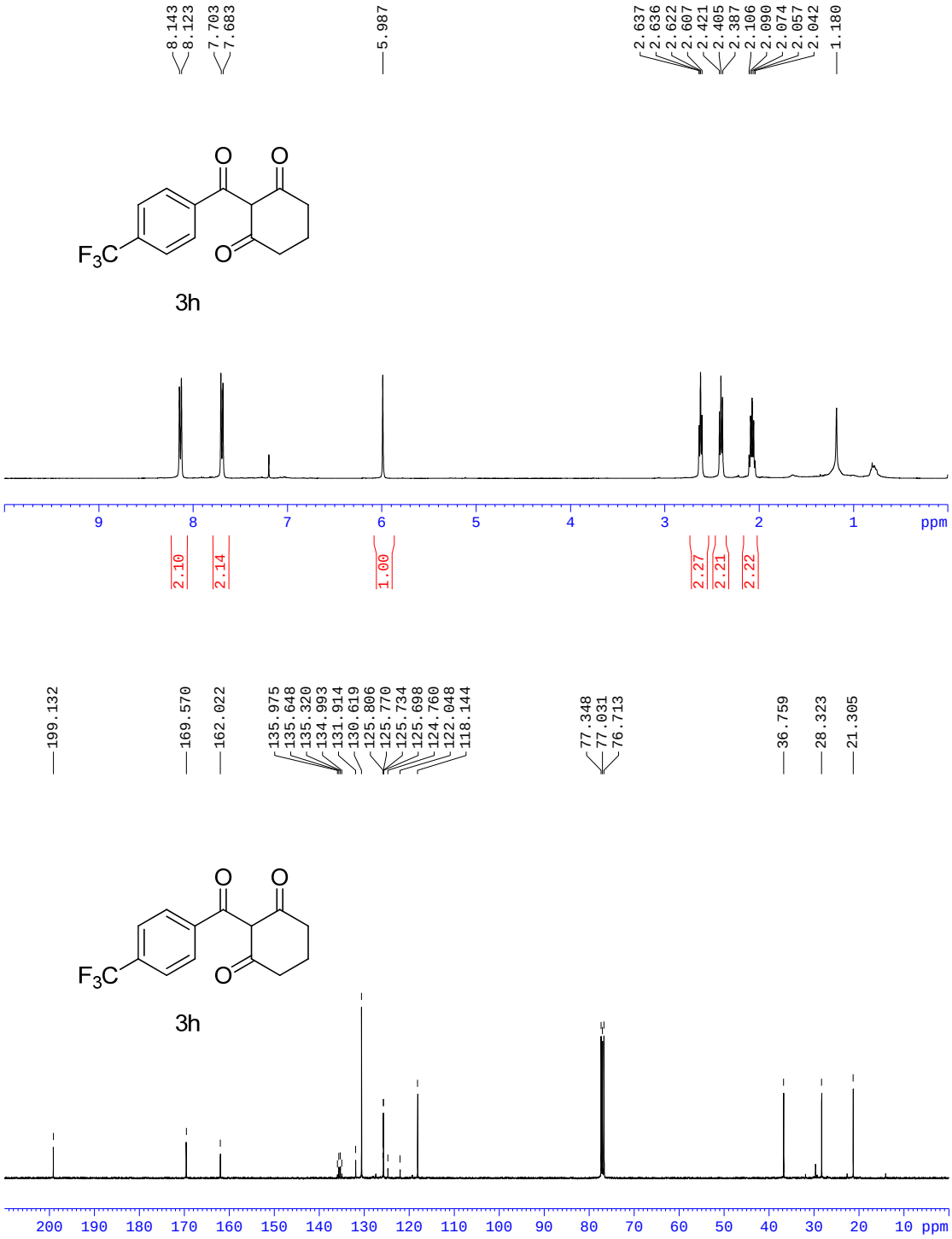
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O
O
F3C
3h
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5
4
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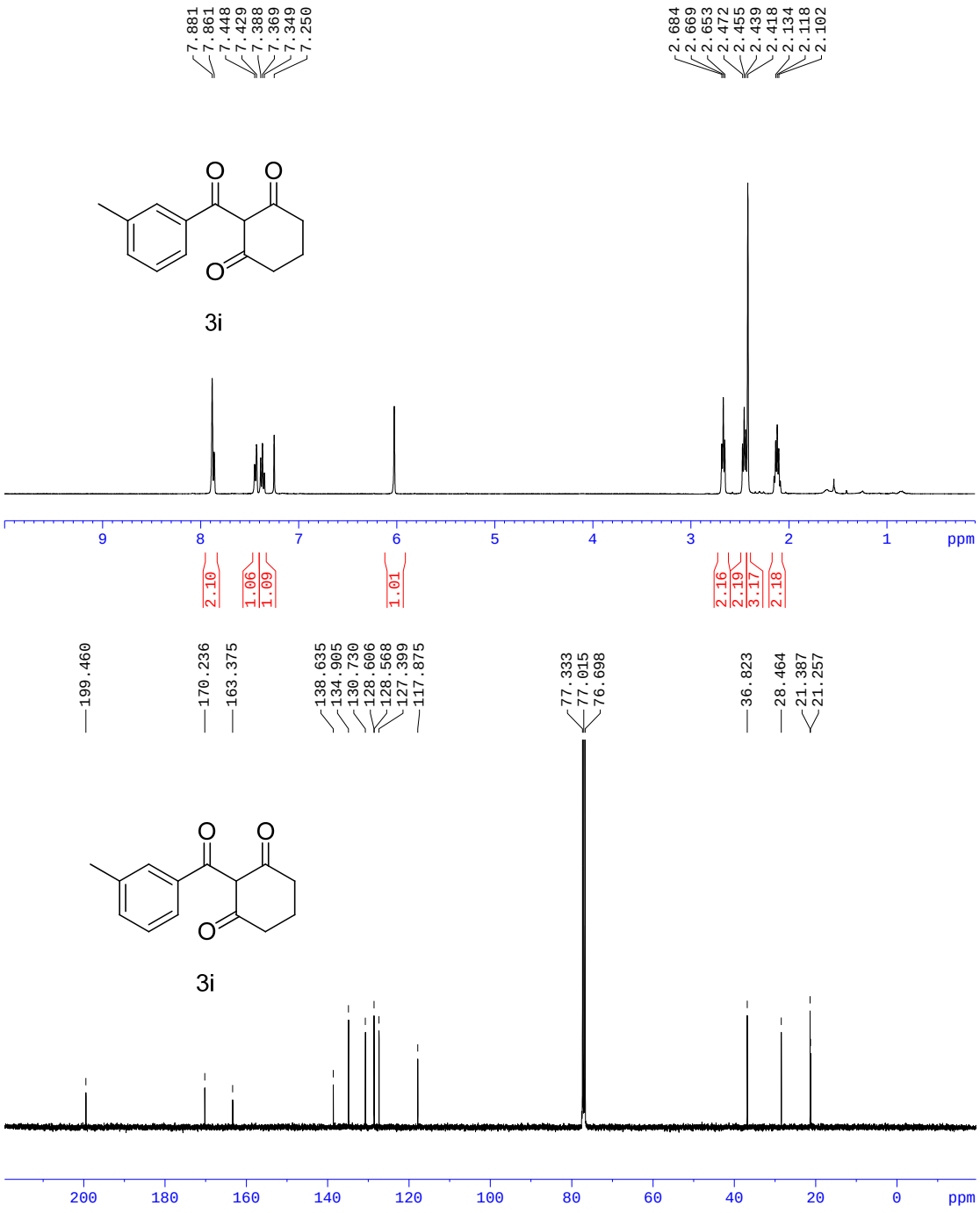
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2.455
2.439
2.418
2.134
2.118
2.102
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8
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5
4
3
2
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2.10
1.06
1.09
1.01
2.16
2.19
3.17
2.18
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128.568
127.399
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76.698
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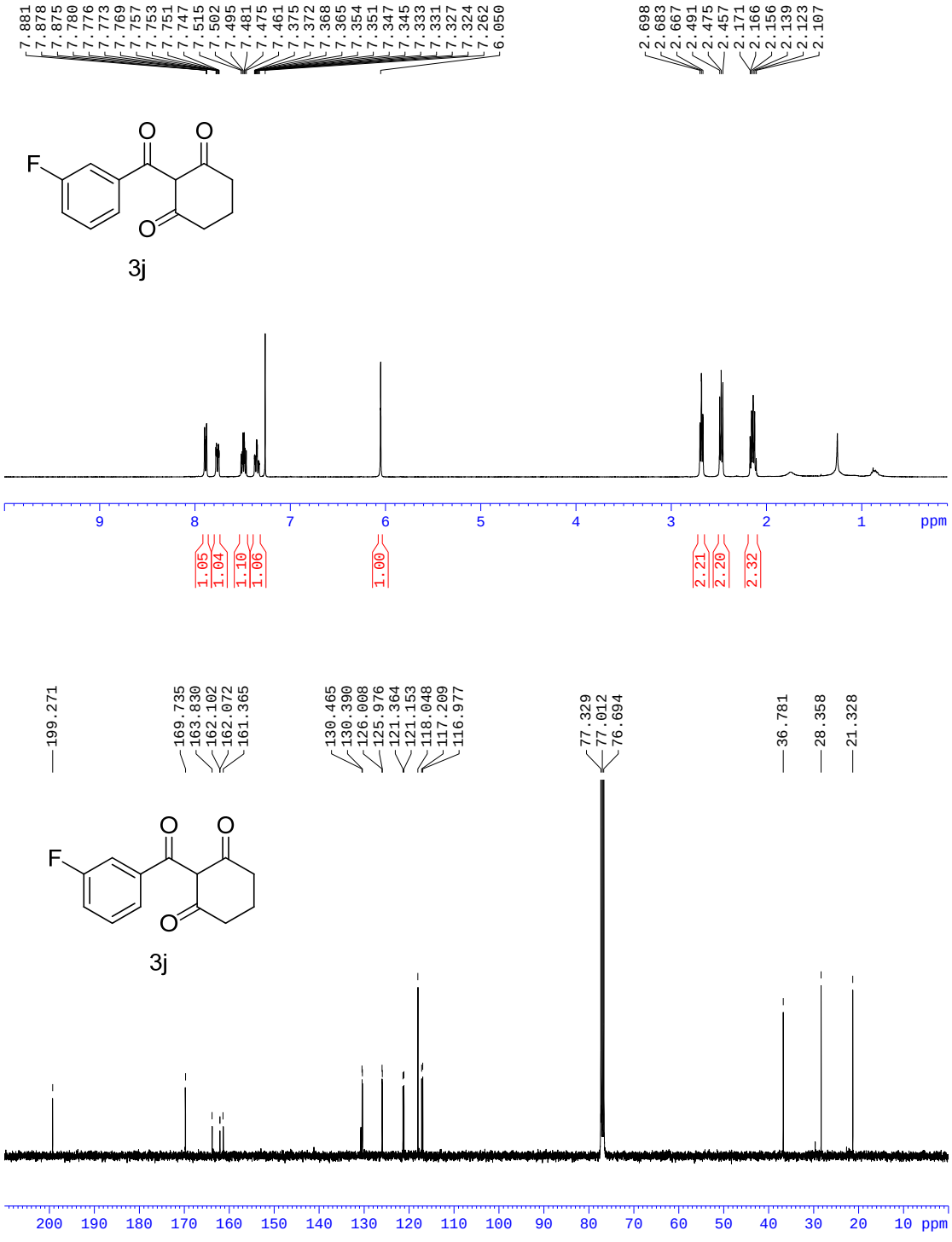
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7.502
7.495
7.481
7.475
7.461
7.375
7.372
7.368
7.365
7.354
7.351
7.347
7.345
7.333
7.331
7.327
7.324
7.262
6.050
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2.475
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2.107
O
O
F
O
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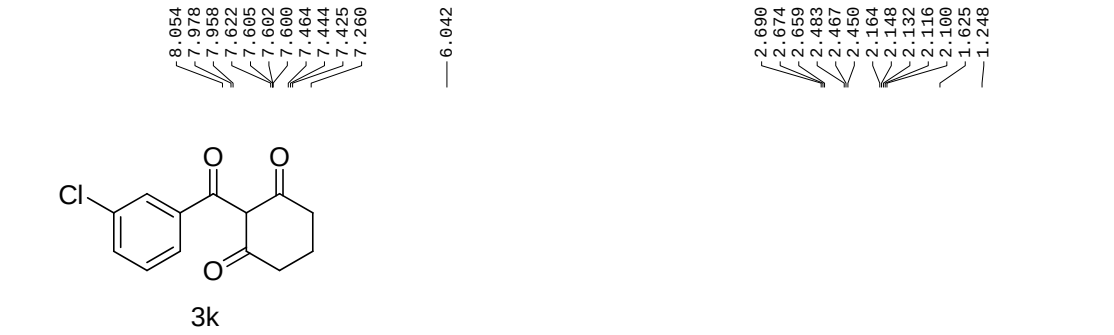
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2.450
2.164
2.148
2.132
2.116
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1.248
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O
O
O
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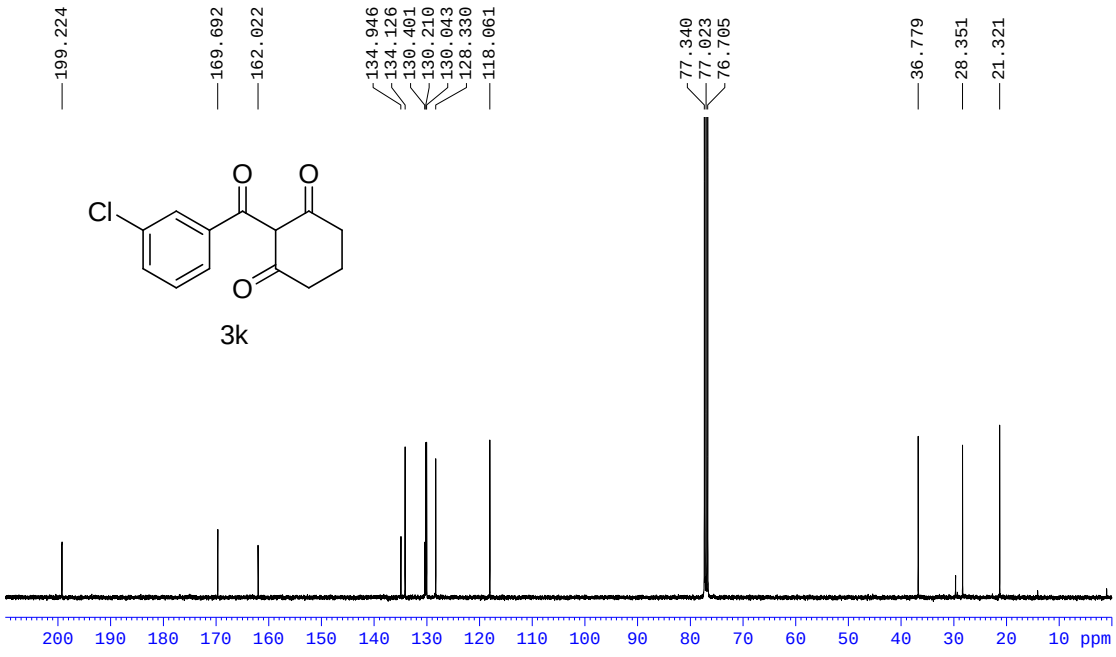
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Cl
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O
O
3k
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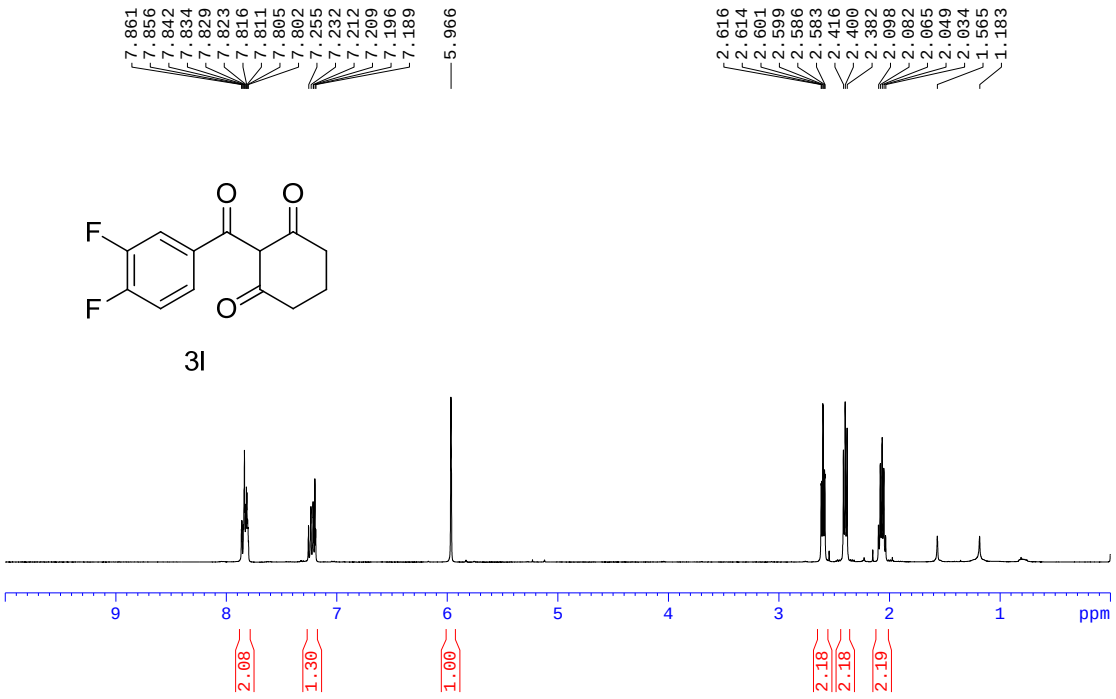
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7.189
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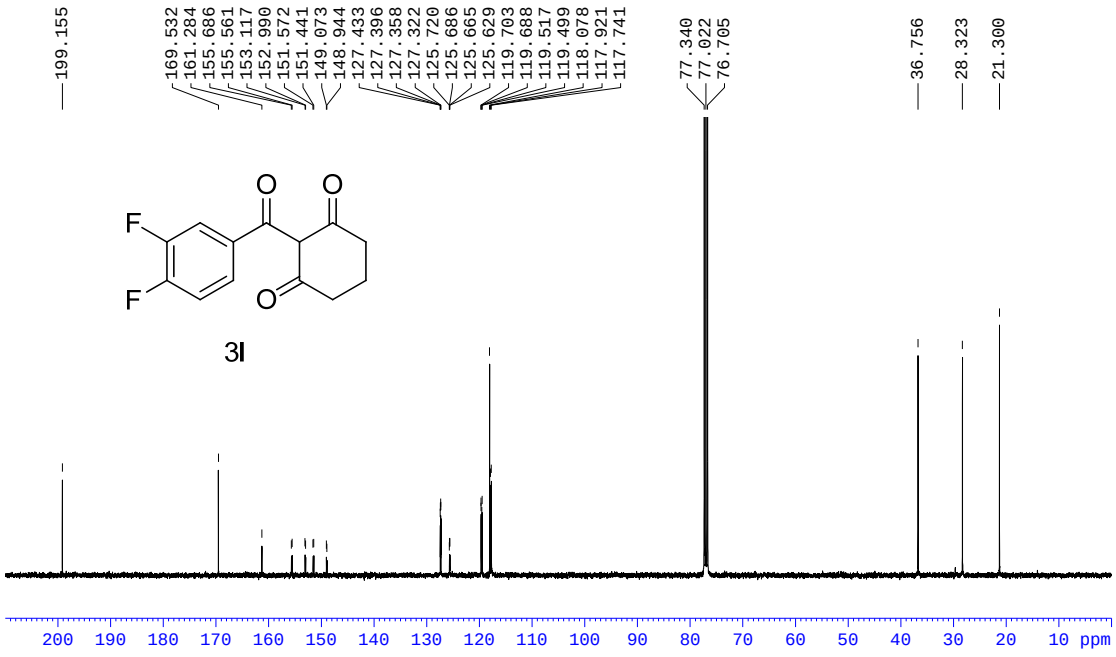
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O
F
F
O
3l
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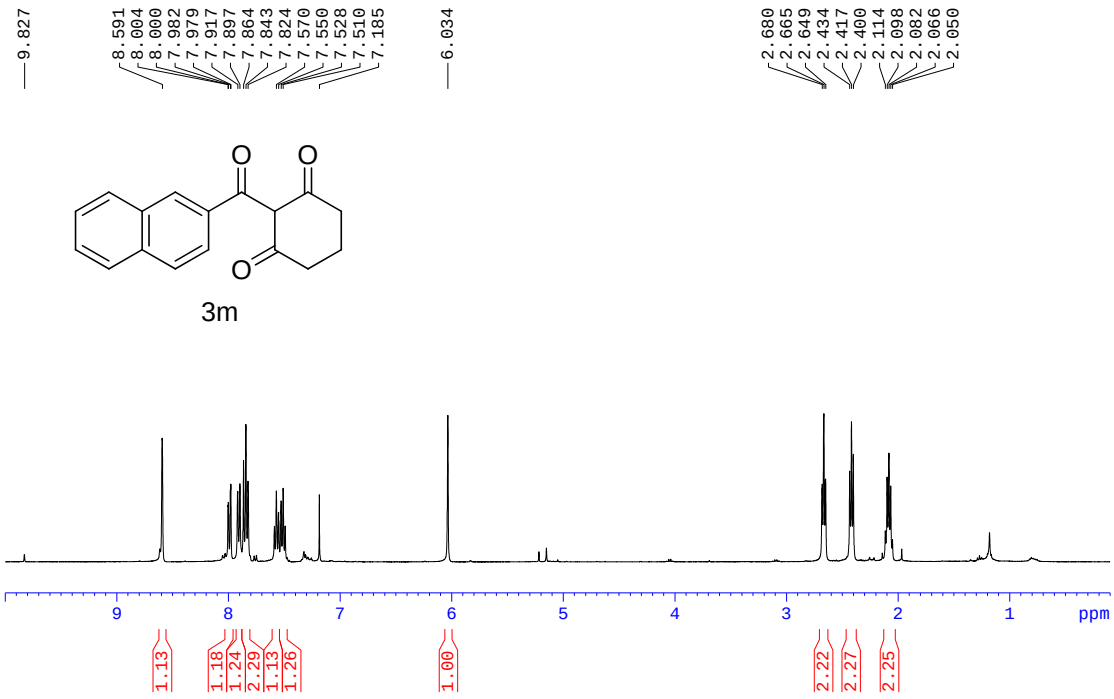
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7.550
7.528
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7.185
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2.434
2.417
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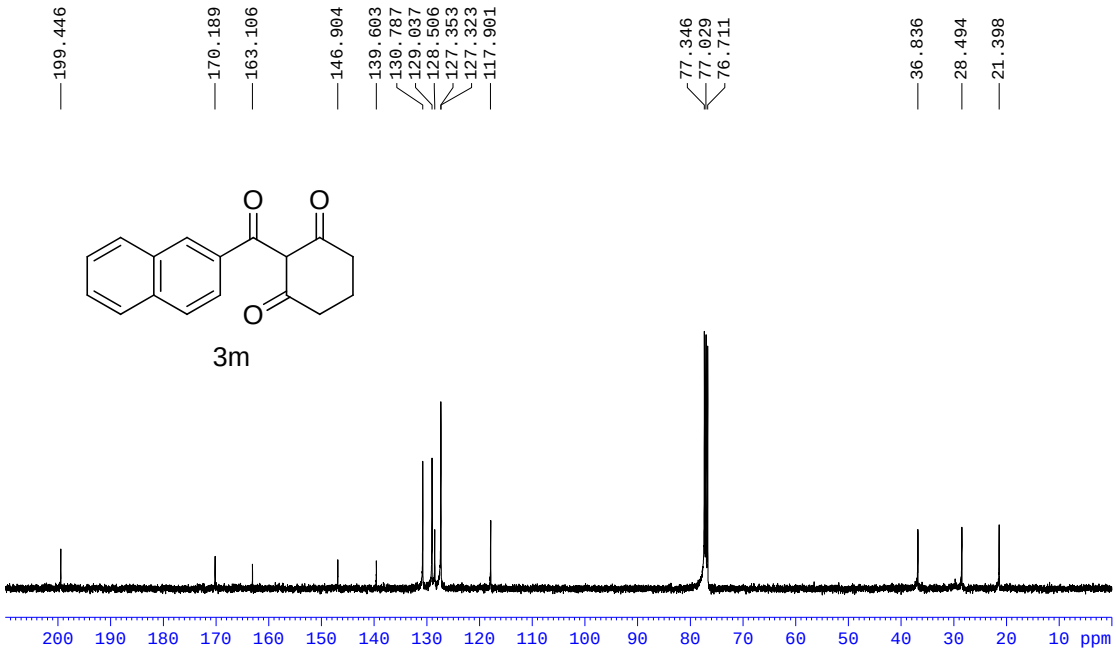
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77.029
76.711
36.836
28.494
21.398
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180
170
160
150
140
130
120
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100
90
80
70
60
50
40
30
20
10 ppm


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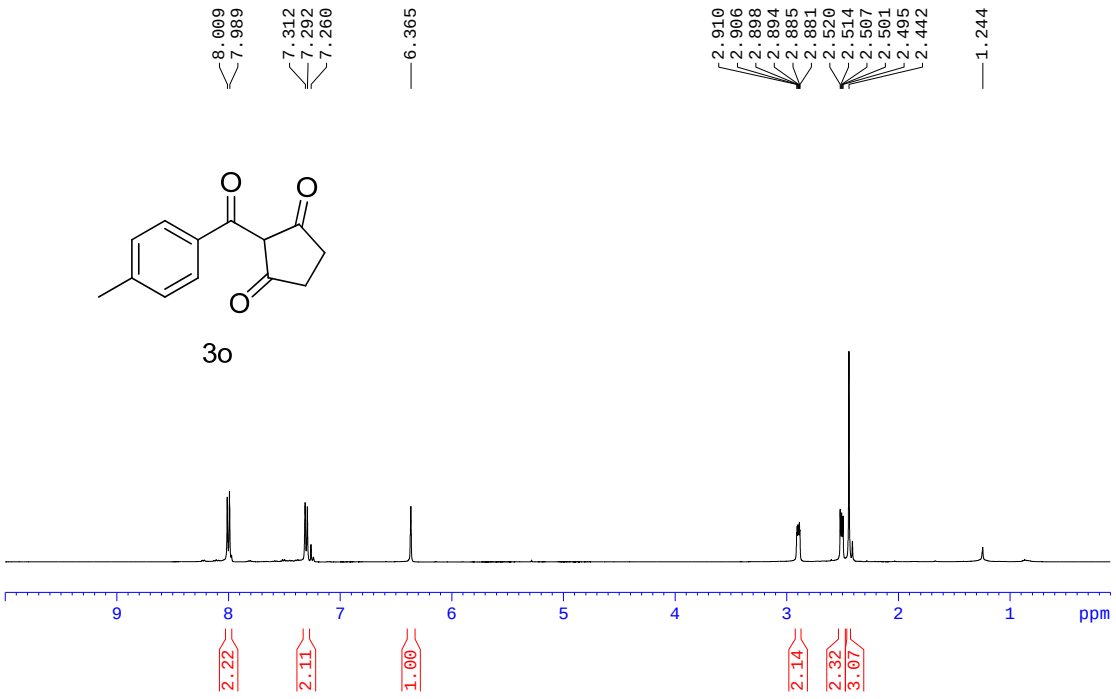
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2.507
2.501
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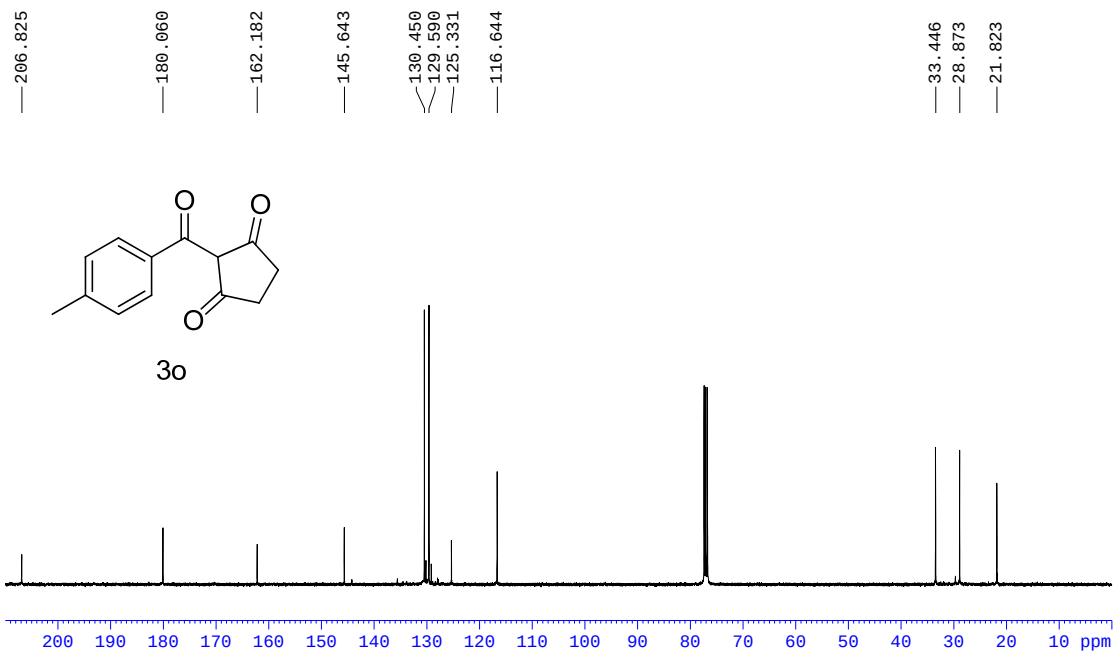
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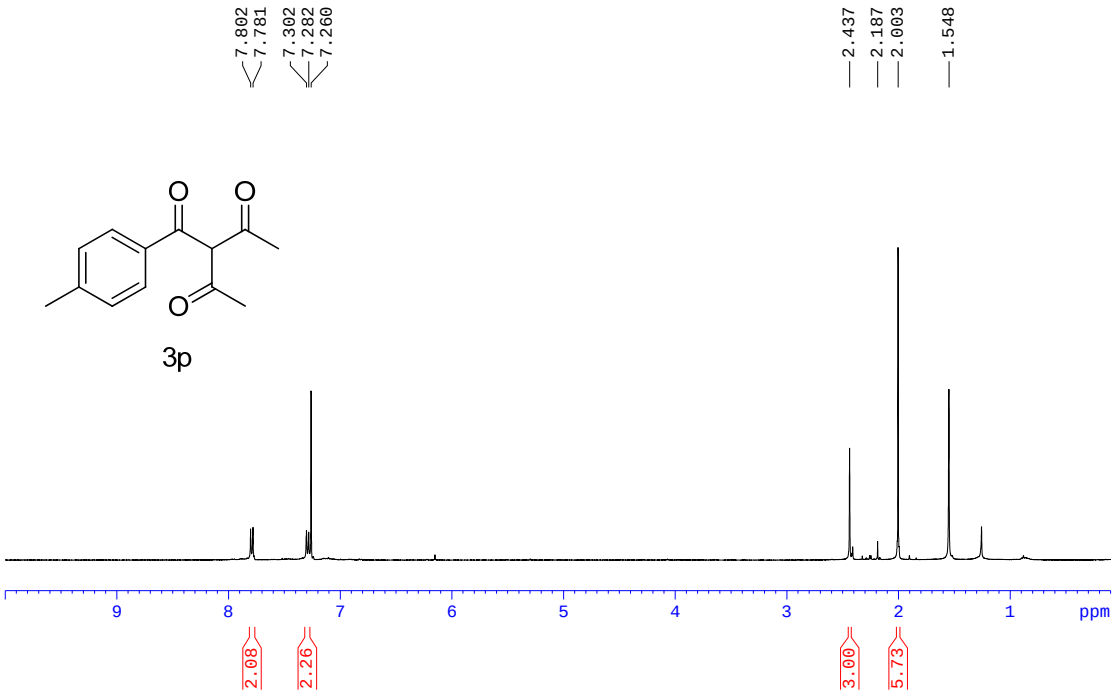
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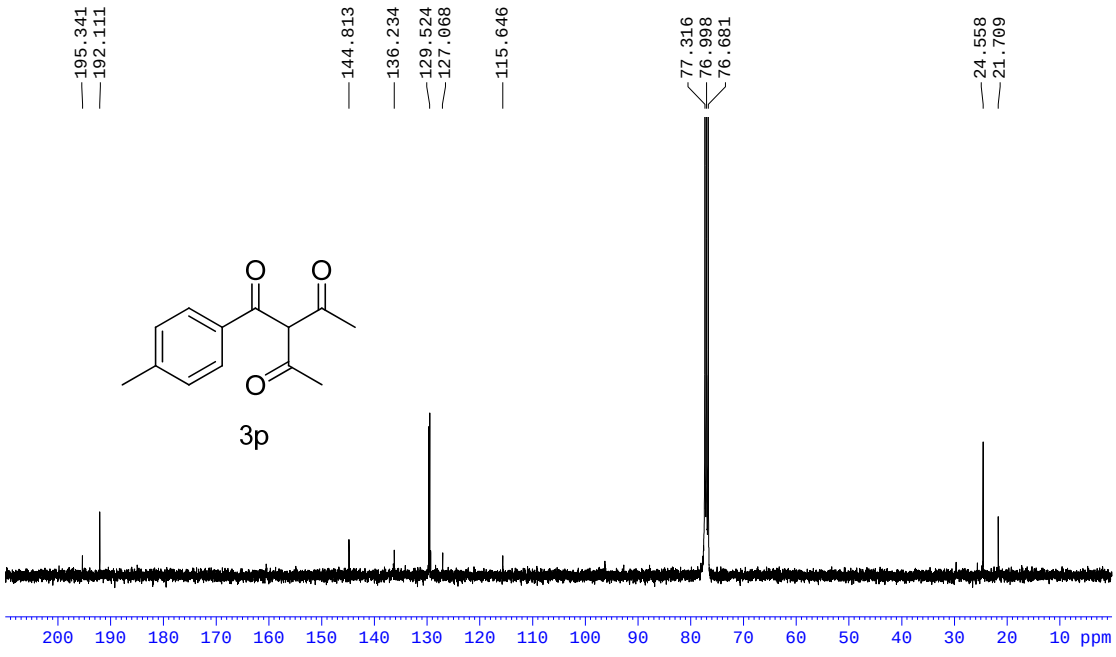
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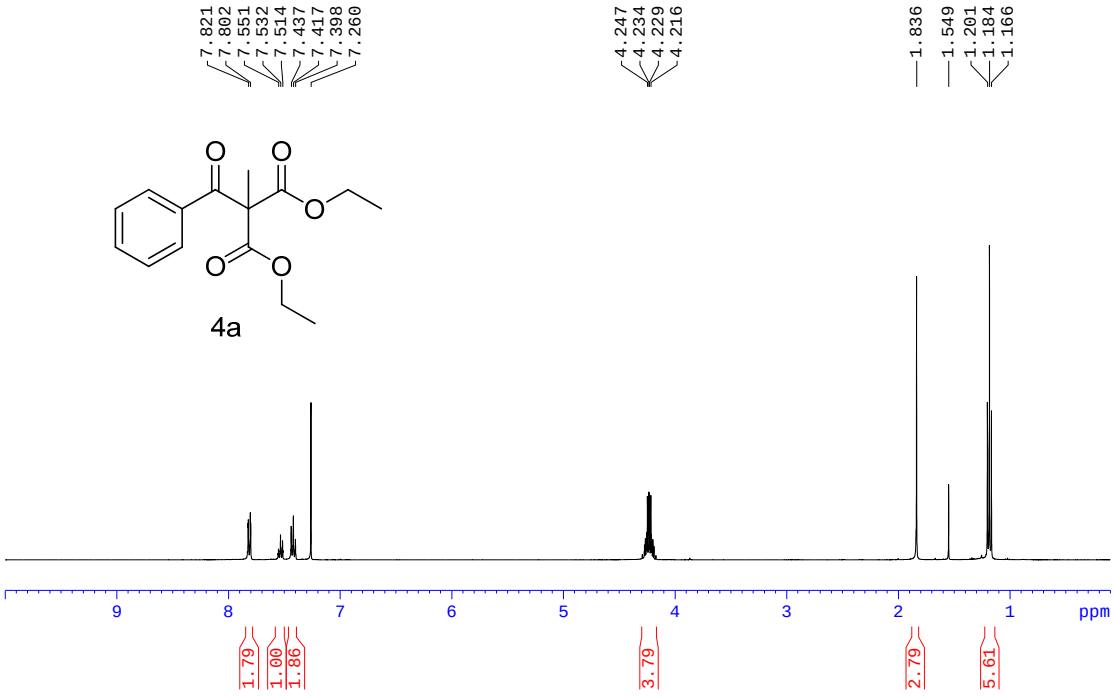
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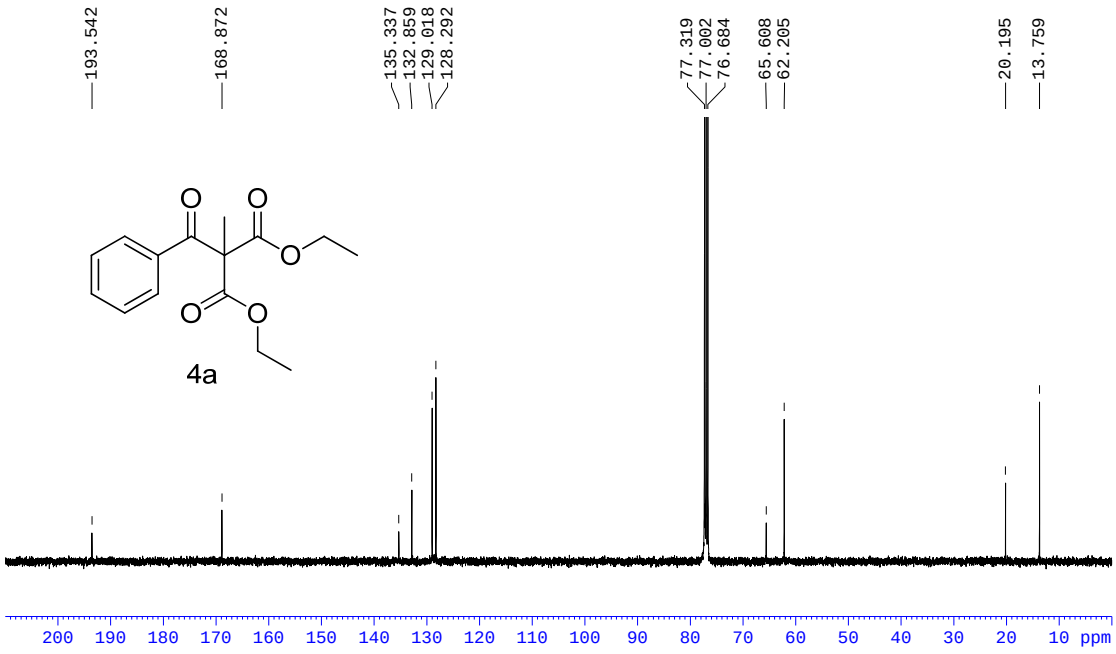
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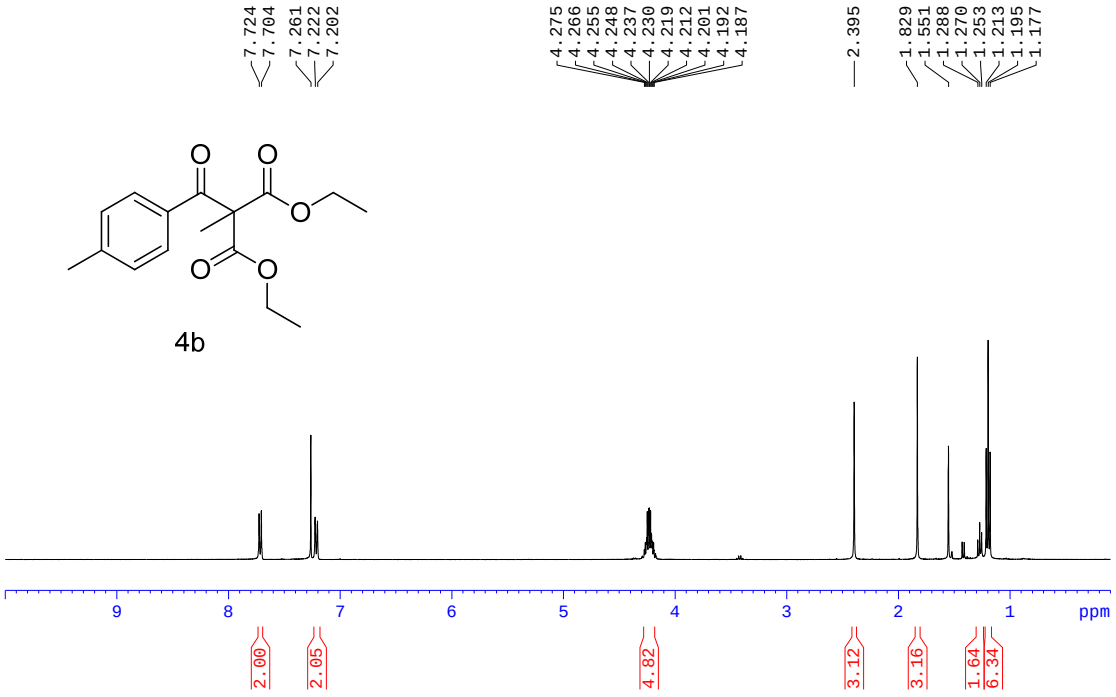
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1.270
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1.177
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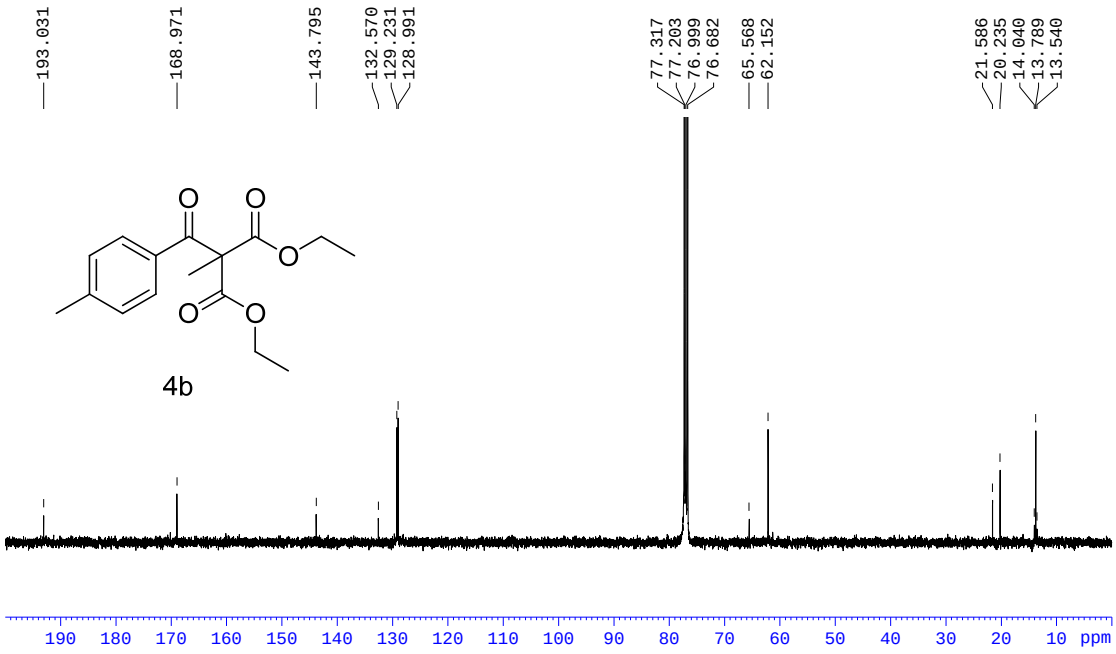
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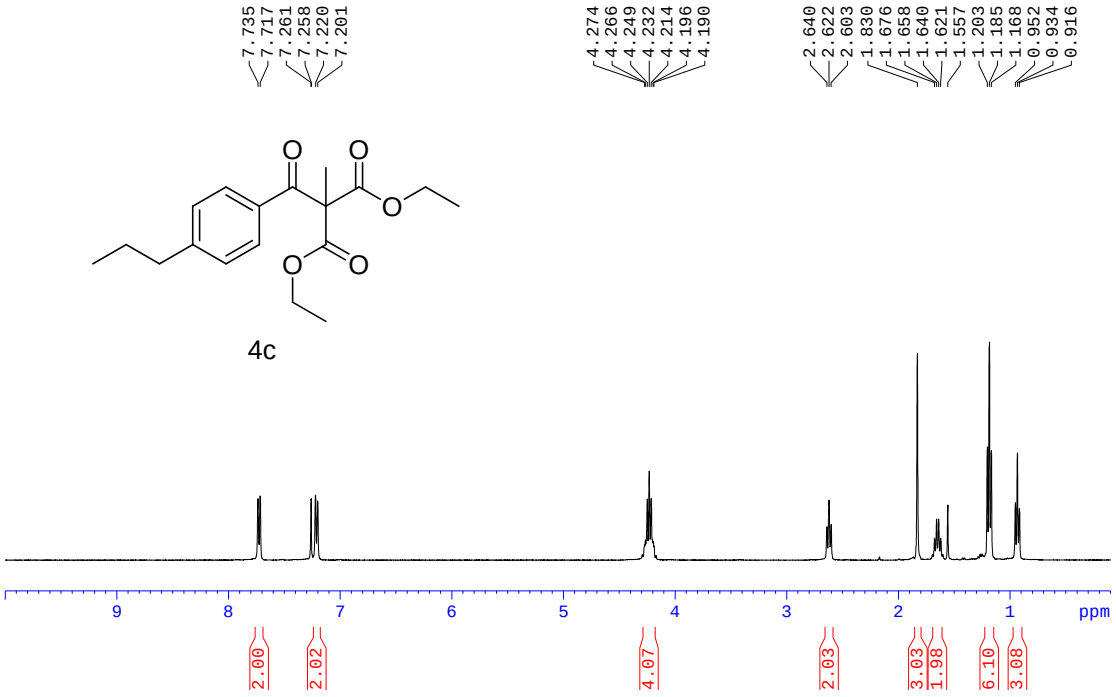
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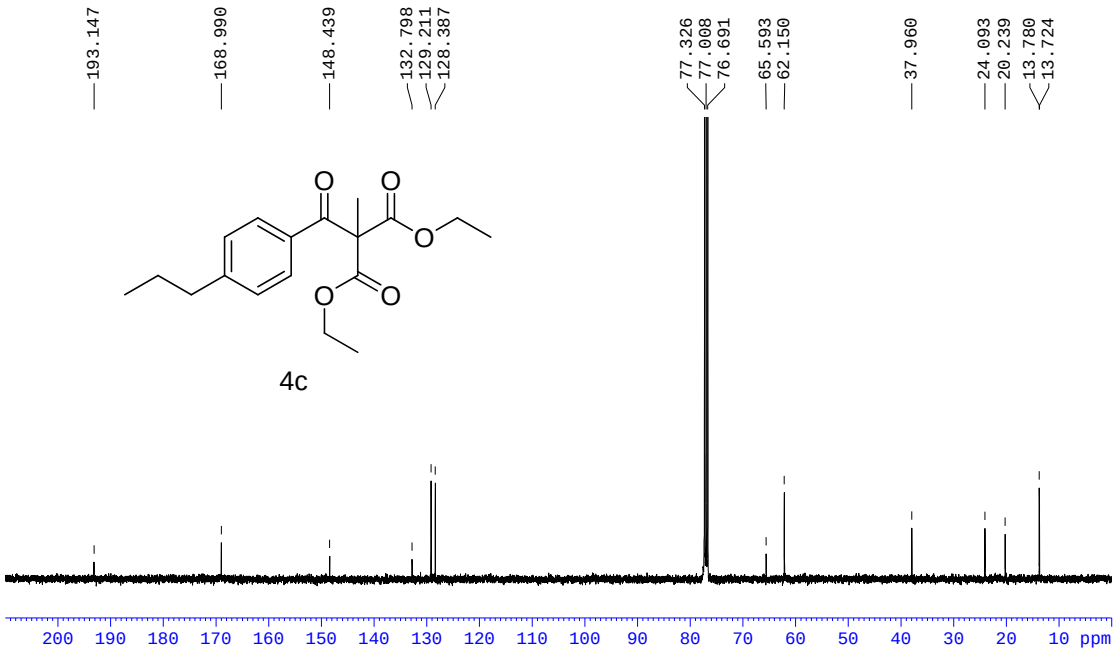
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13.724
4c
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180
170
160
150
140
130
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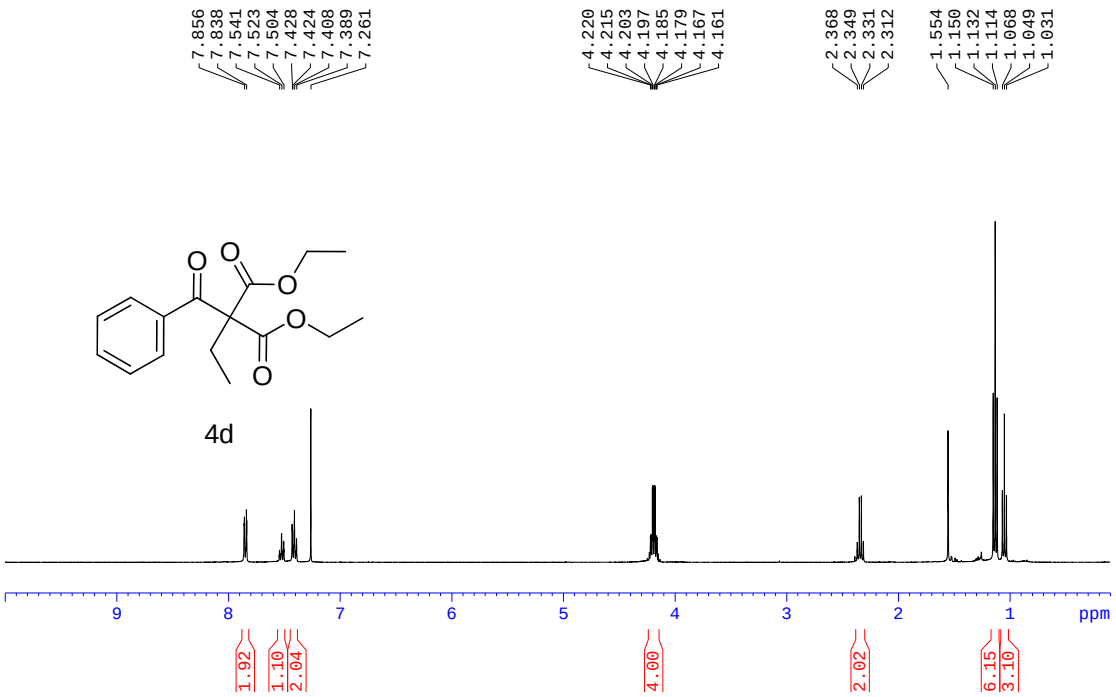
110
100
90
80
70
60
50
40
30
20
10 ppm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7.541
7.523
7.504
7.428
7.424
7.408
7.389
7.261
4.220
4.215
4.203
4.197
4.185
4.179
4.167
4.161
2.368
2.349
2.331
2.312
1.554
1.150
1.132
1.114
1.068
1.049
1.031
4d
9
8
7
6
5
4
3
2
1
ppm
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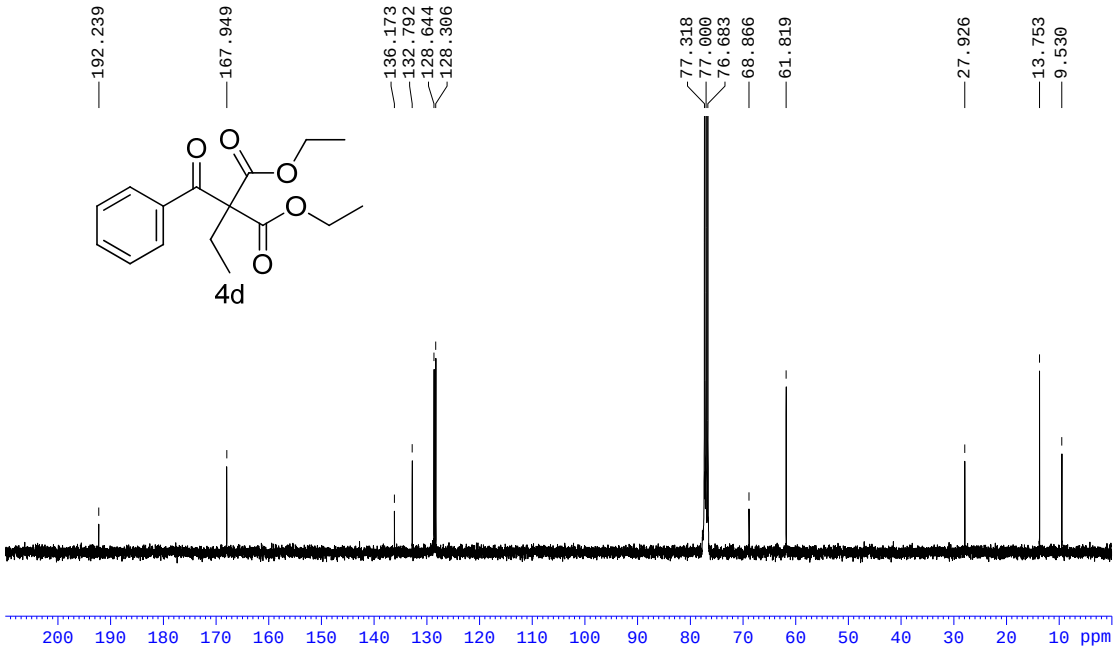
1.10
2.04
4.00
2.02
6.15
3.10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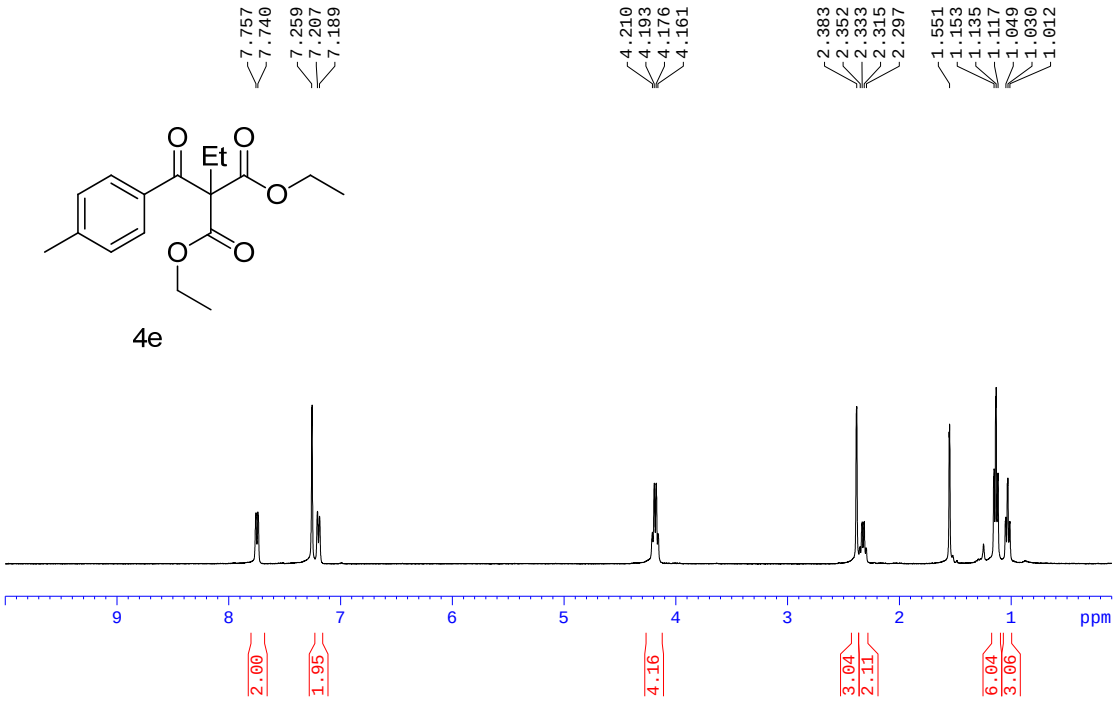
167.949
136.173
132.792
128.644
128.306
77.318
77.000
76.683
68.866
61.819
27.926
13.753
9.530
4d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.740
7.259
7.207
7.189
4.210
4.193
4.176
4.161
2.383
2.352
2.333
2.315
2.297
1.551
1.153
1.135
1.117
1.049
1.030
1.012
Et
4e
9
8
7
6
5
4
3
2
1
ppm
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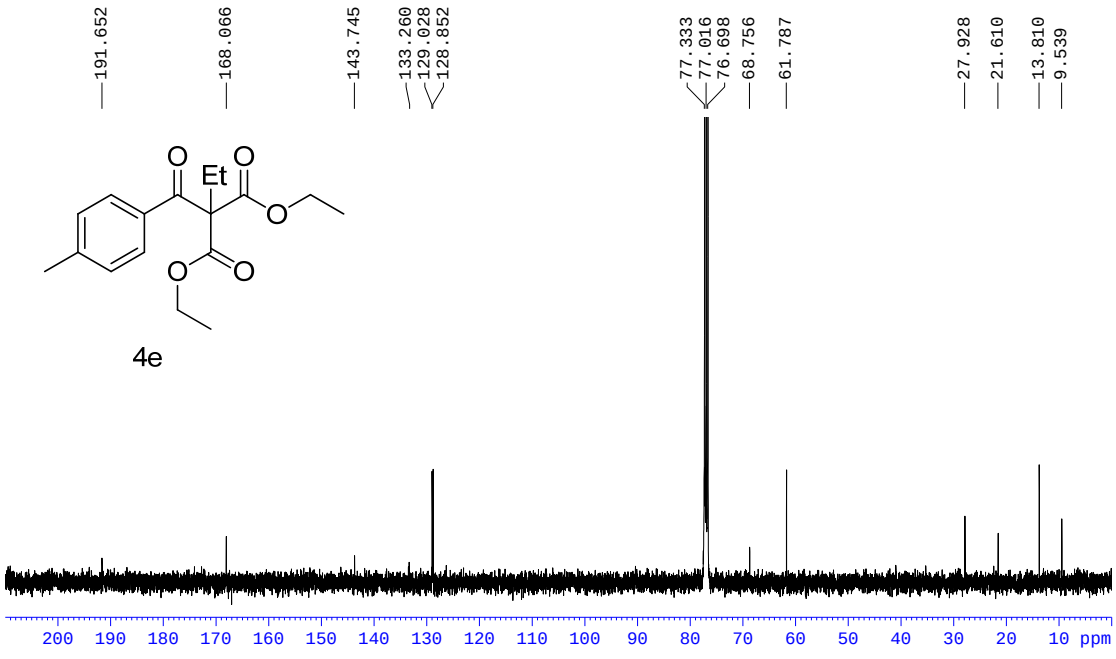
4.16
3.04
2.11
6.04
3.06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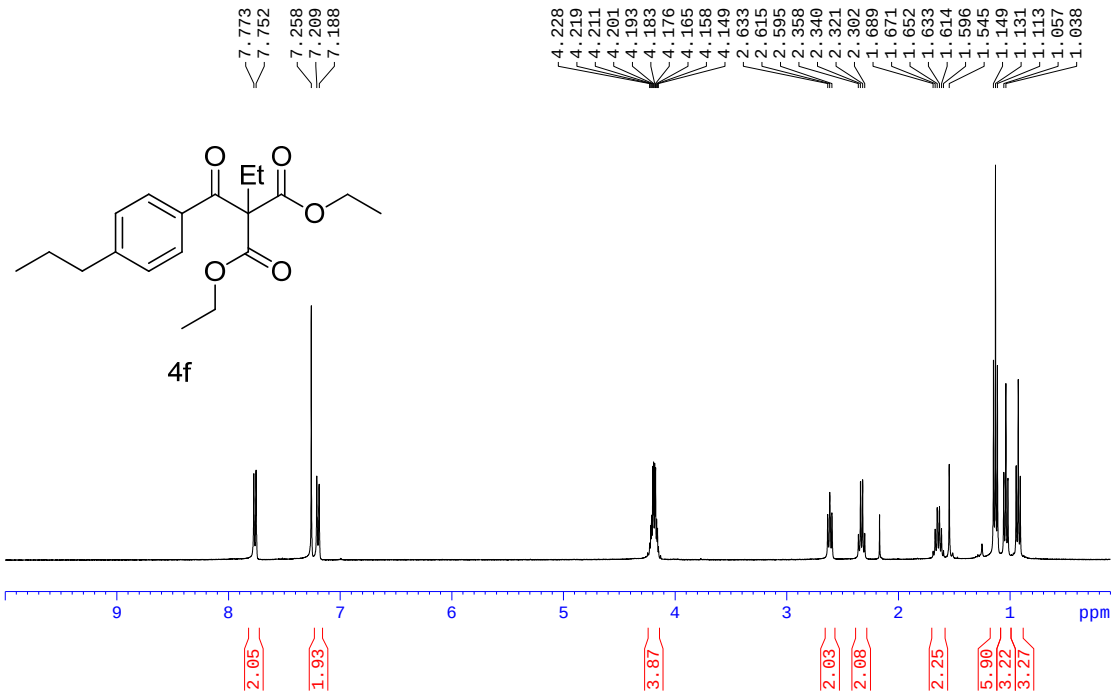
143.745
133.260
129.028
128.852
77.333
77.016
76.698
68.756
61.787
27.928
21.610
13.810
9.539
Et
4e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.752
7.258
7.209
7.188
4.228
4.219
4.211
4.201
4.193
4.183
4.176
4.165
4.158
4.149
2.633
2.615
2.595
2.358
2.340
2.321
2.302
1.689
1.671
1.652
1.633
1.614
1.596
1.545
1.149
1.131
1.113
1.057
1.038
O
Et
O
O
O
O
4f
9
8
7
6
5
4
3
2
1
ppm
2.05
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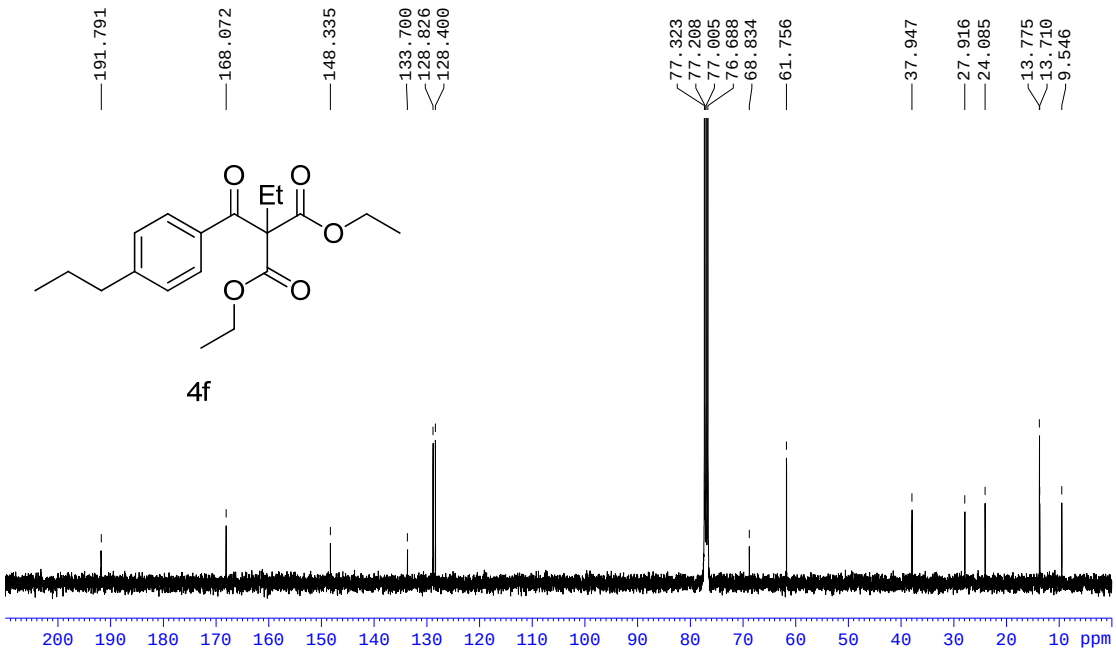
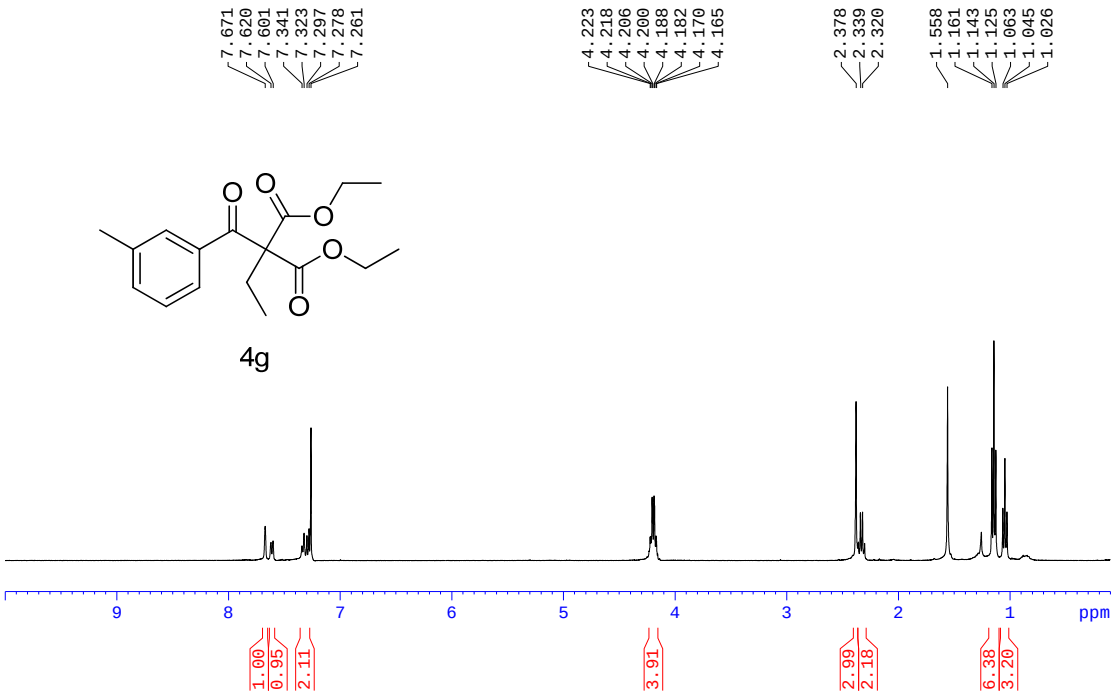
2.03
2.08
2.25
5.90
3.22
3.27


191.791
168.072
148.335
133.700
128.826
128.400
77.323
77.208
77.005
76.688
68.834
61.756
37.947
27.916
24.085
13.775
13.710
9.546
O
Et
O
O
O
O
4f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


7.671
7.620
7.601
7.341
7.323
7.297
7.278
7.261
4.223
4.218
4.206
4.200
4.188
4.182
4.170
4.165
2.378
2.339
2.320
1.558
1.161
1.143
1.125
1.063
1.045
1.026
4g
9
8
7
6
5
4
3
2
1
ppm
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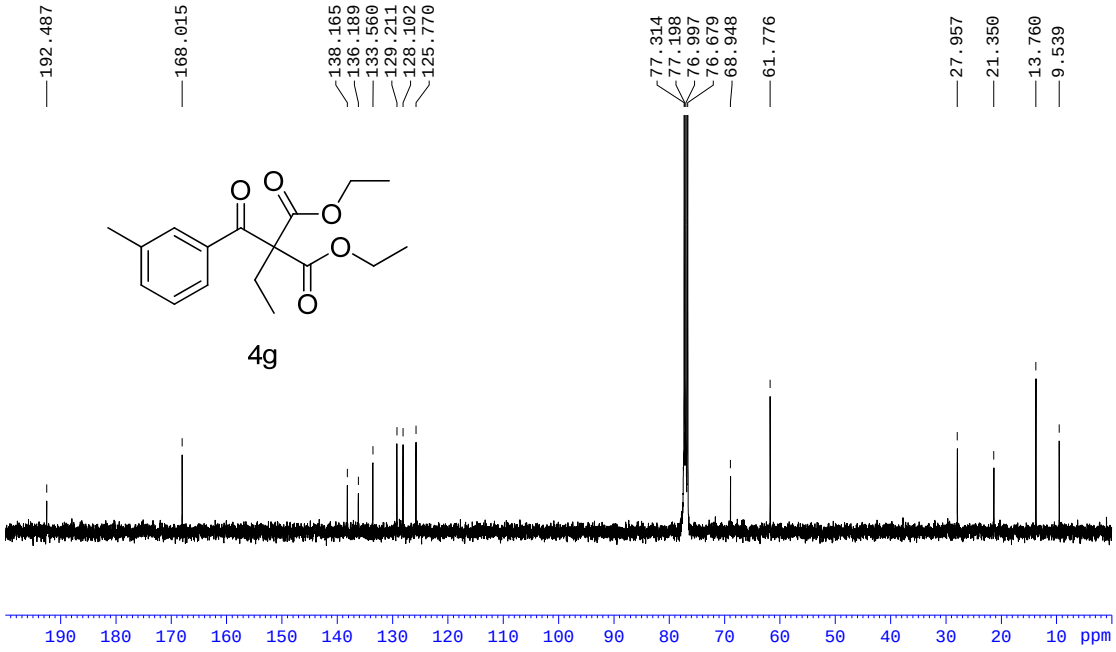
2.11
3.91
2.99
2.18
6.38
3.20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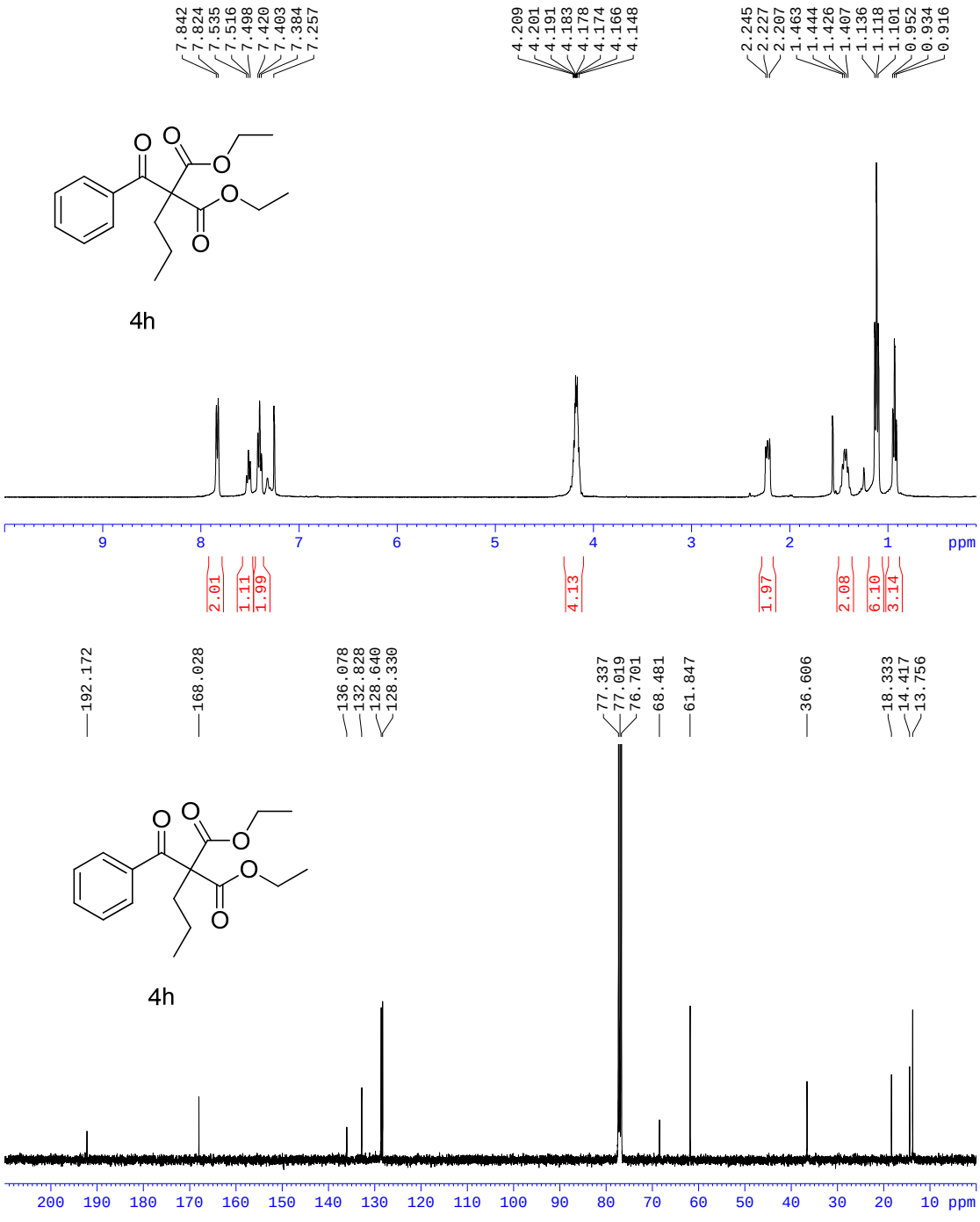
168.015
138.165
136.189
133.560
129.211
128.102
125.770
77.314
77.198
76.997
76.679
68.948
61.776
27.957
21.350
13.760
9.539
4g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.824
7.535
7.516
7.498
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7.403
7.384
7.257
4.209
4.201
4.191
4.183
4.178
4.174
4.166
4.148
2.245
2.227
2.207
1.463
1.444
1.426
1.407
1.136
1.118
1.101
0.952
0.934
0.916
4h
ppm
2.01
1.11
1.99
4.13
1.97
2.08
6.10
3.14
192.172
168.028
136.078
132.828
128.640
128.330
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77.019
76.701
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36.606
18.333
14.417
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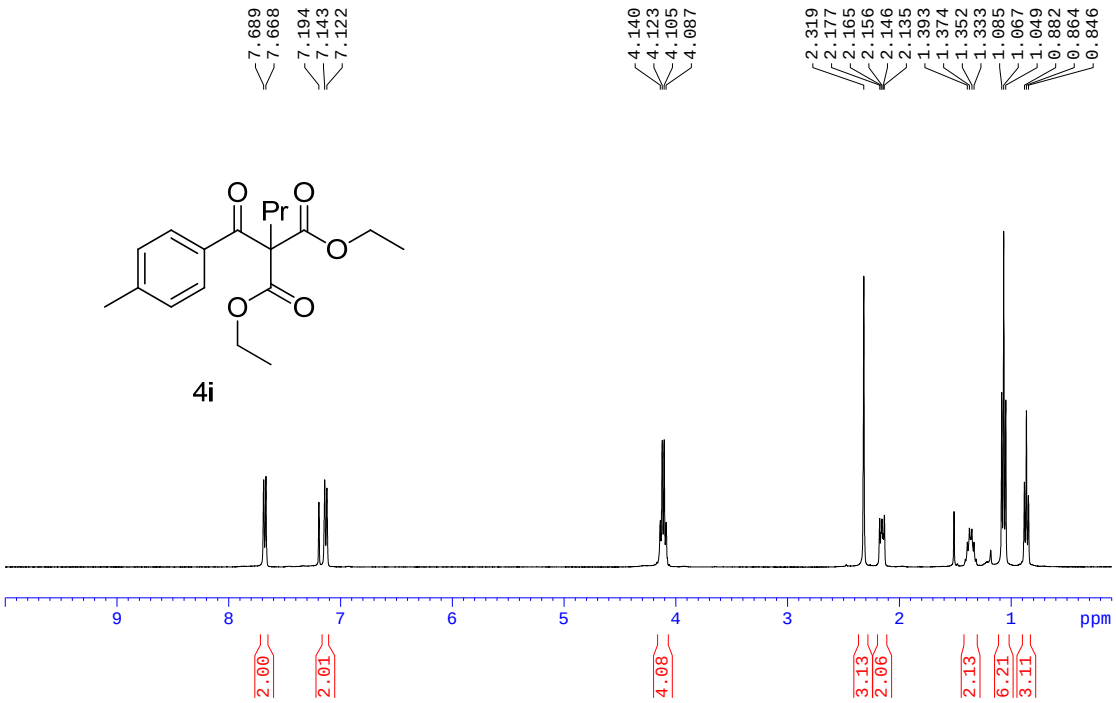
4h
ppm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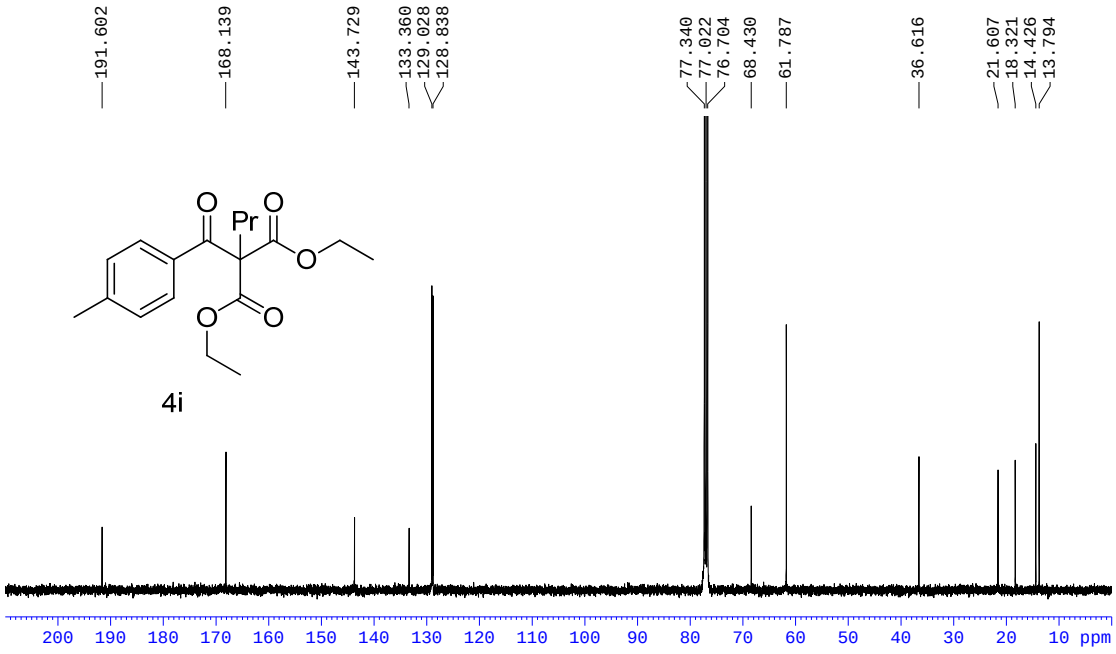
7.668
7.194
7.143
7.122
4.140
4.123
4.105
4.087
2.319
2.177
2.165
2.156
2.146
2.135
1.393
1.374
1.352
1.333
1.085
1.067
1.049
0.882
0.864
0.846
O
Pr
O
O
O
O
O
4i
9
8
7
6
5
4
3
2
1
ppm
2.00
2.01
4.08
3.13
2.06
2.13
6.21
3.11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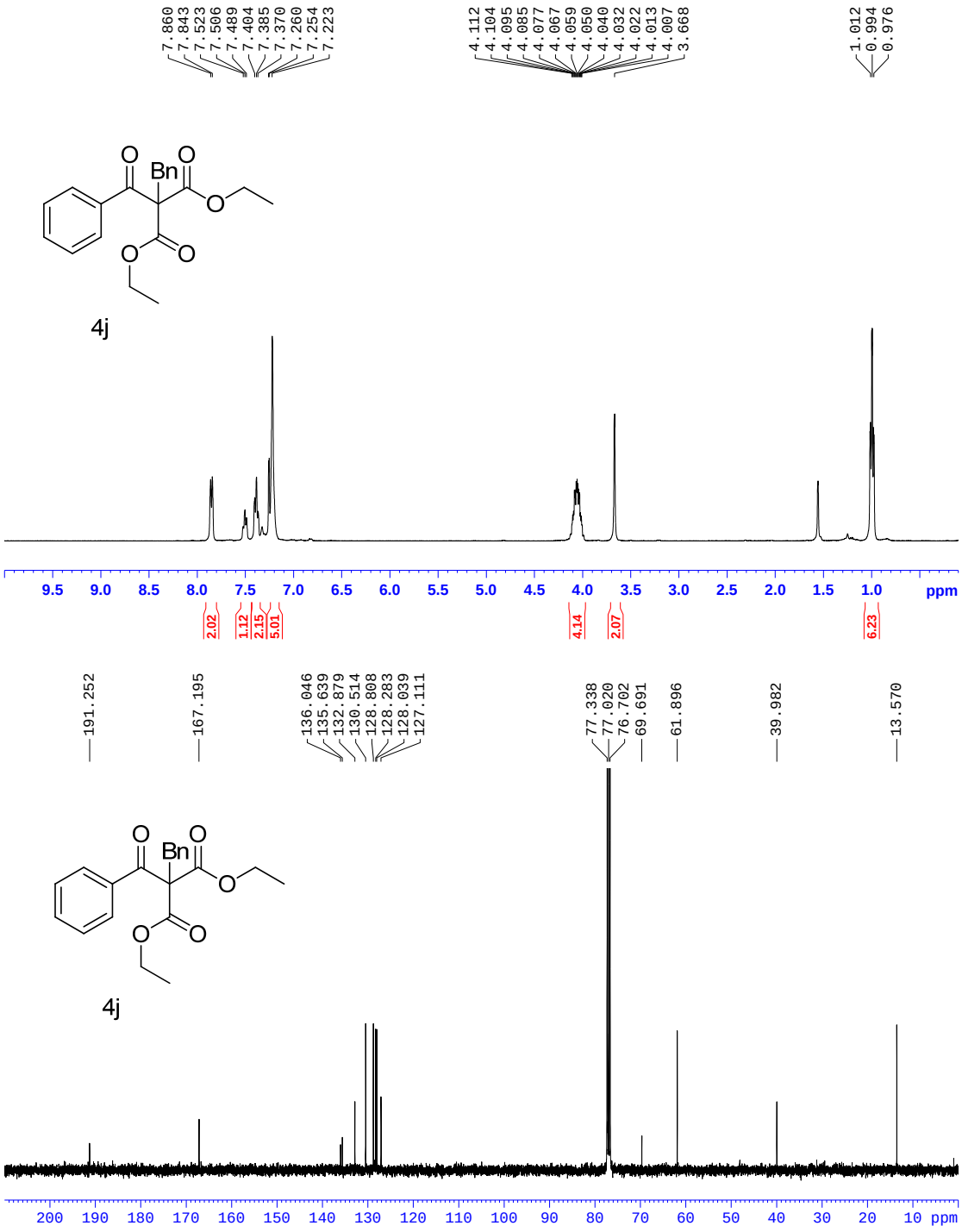
128.838
77.340
77.022
76.704
68.430
61.787
36.616
21.607
18.321
14.426
13.794
O
Pr
O
O
O
O
O
4i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm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7.506
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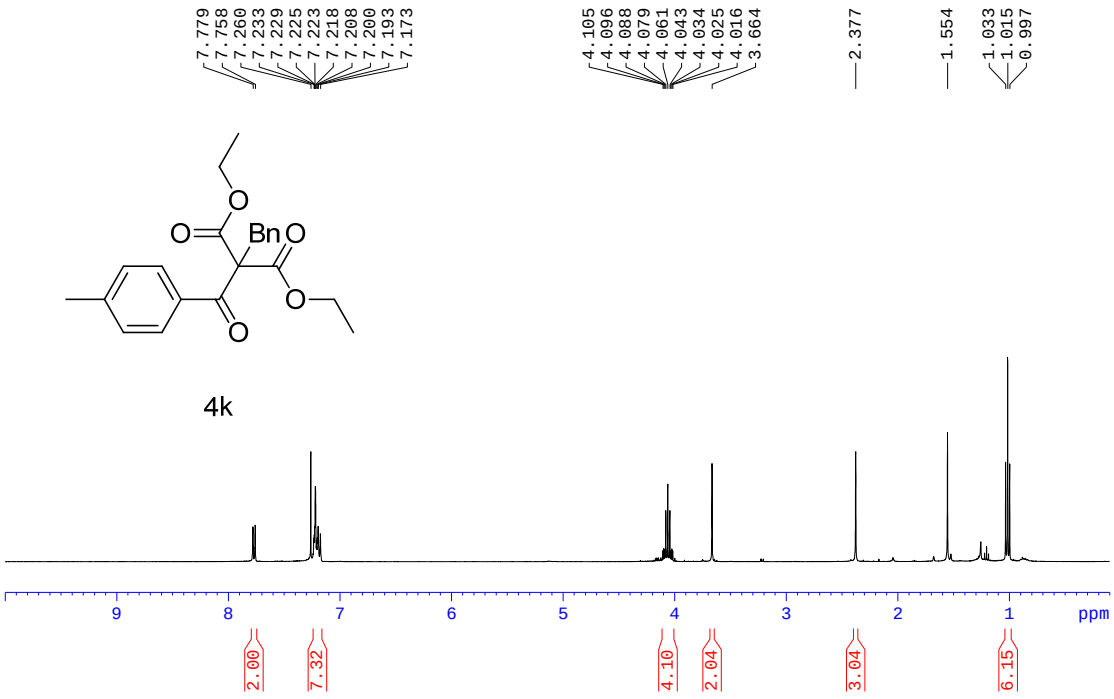
7.385
7.370
7.260
7.254
7.223
4.112
4.104
4.095
4.085
4.077
4.067
4.059
4.050
4.040
4.032
4.022
4.013
4.007
3.668
1.012
0.994
0.976
Bn
4j
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02
1.12
2.15
5.01
4.14
2.07
6.23
191.252
167.195
136.046
135.639
132.879
130.514
128.808
128.283
128.039
127.111
77.338
77.020
76.702
69.691
61.896
39.982
13.570
Bn
4j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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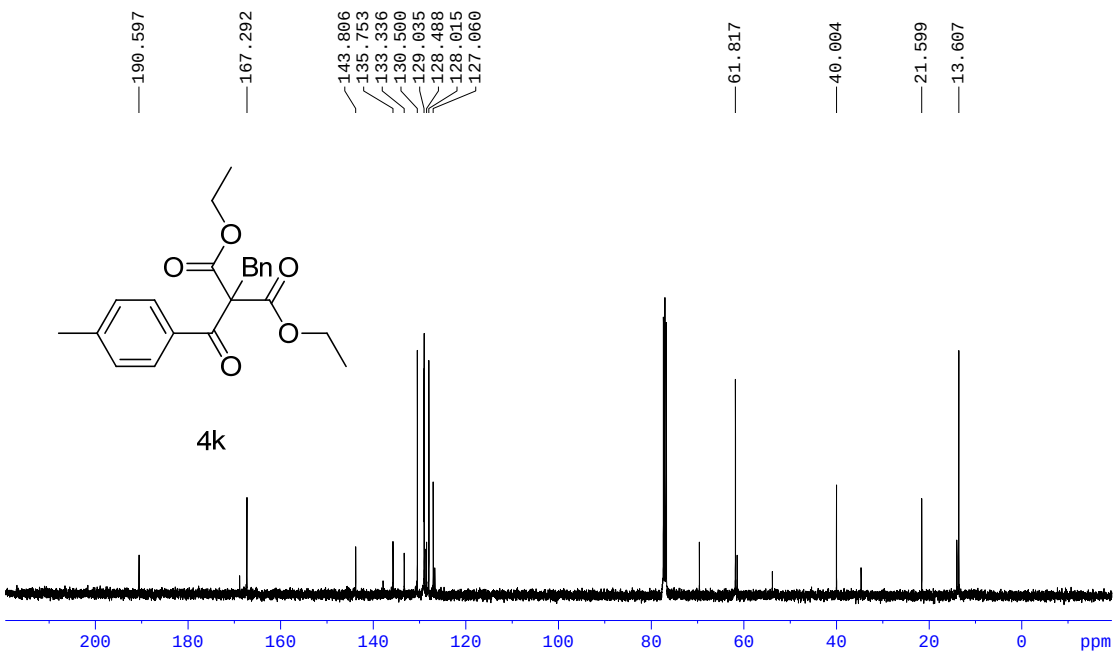
7.233
7.229
7.225
7.223
7.218
7.208
7.200
7.193
7.173
4.105
4.096
4.088
4.079
4.061
4.043
4.034
4.025
4.016
3.664
2.377
1.554
1.033
1.015
0.997
O
O
Bn O
O
O
4k
9
8
7
6
5
4
3
2
1
ppm
2.00
7.32
4.10
2.04
3.04
6.15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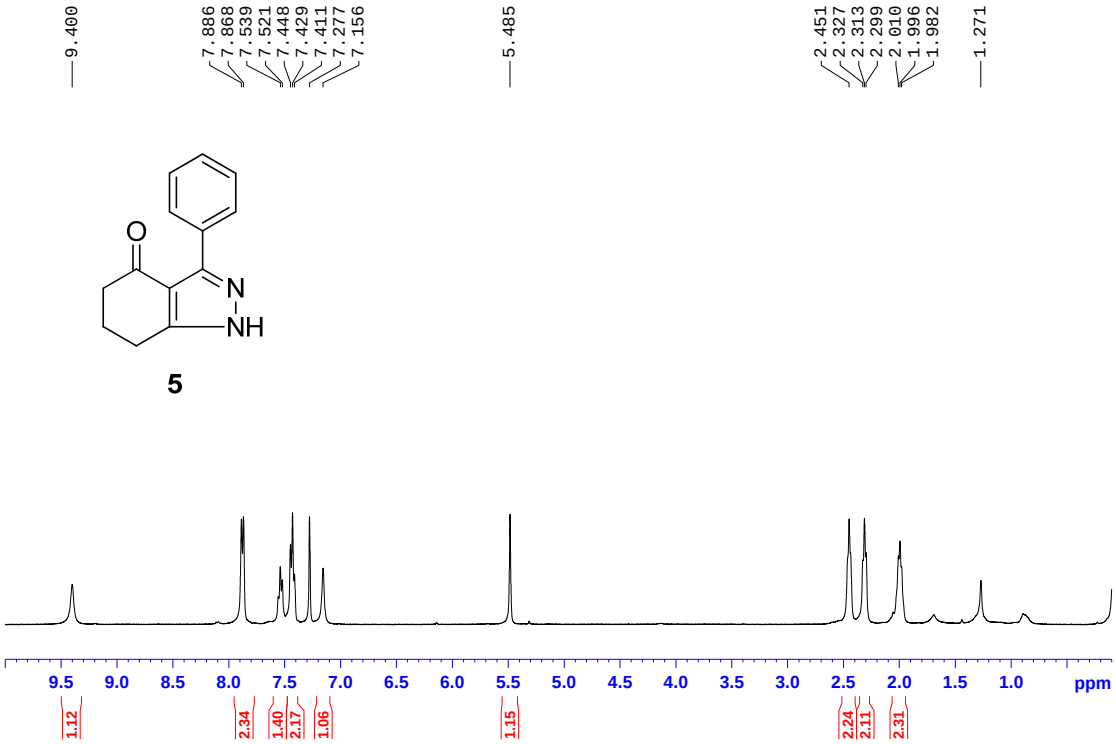
143.806
135.753
133.336
130.500
129.035
128.488
128.015
127.060
61.817
40.004
21.599
13.607
O
O
Bn O
O
O
4k
200
180
160
140
120
100
80
60
40
20
0
ppm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7.429
7.411
7.277
7.156
5.485
2.451
2.327
2.313
2.299
2.010
1.996
1.982
1.271
O
N
NH
5
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
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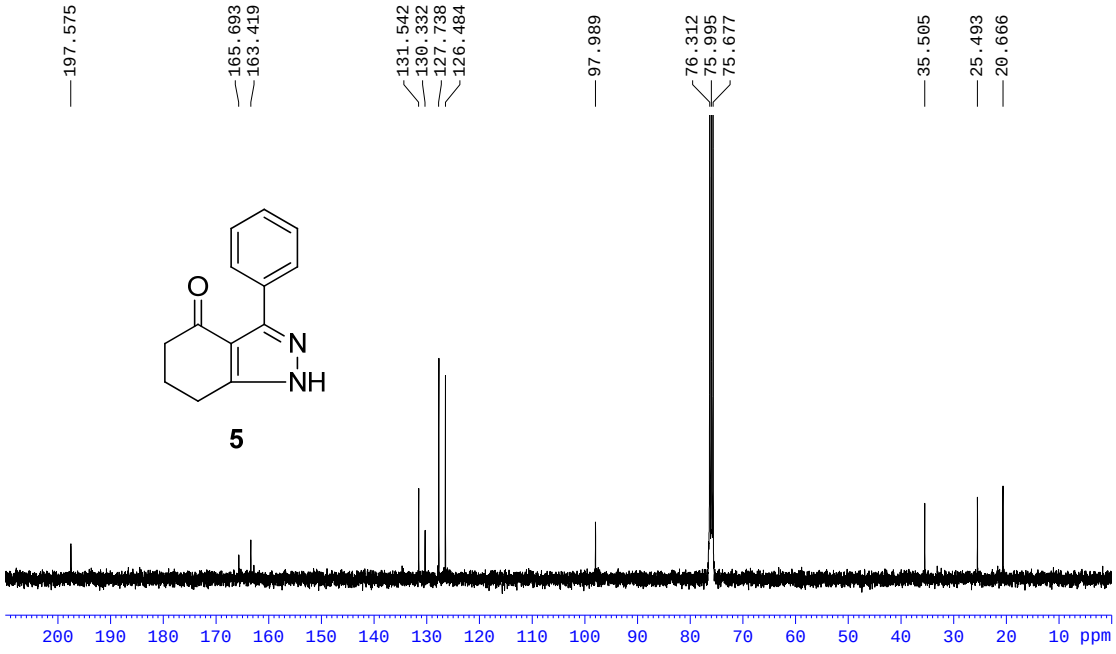
2.34
1.40
2.17
1.06
1.15
2.24
2.11
2.31


197.575
165.693
163.419
131.542
130.332
127.738
126.484
97.989
76.312
75.995
75.677
35.505
25.493
20.666
O
N
NH
5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm