Supporting Information

Copper-Catalyzed Direct Alkylation of Heteroarenes

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General Information.

All reactions were carried out in oven-dried glassware under an argon atmosphere employing standard techniques in handling air-sensitive materials.

All solvents were reagent grade. 1,4-Dioxane (99.5%, Extra Dry over Molecular Sieve, AcroSeal) was purchased from ACROS Organics and used as supplied. Ethanol, absolute was purchased from Fischer Chemical and distilled over magnesium/iodine.

Copper(I) iodide (99,999% purity) and tris(2-pyridylmethyl)amine (>98.0% purity) were respectively purchased from Aldrich and TCI and used as supplied. All other reagents were used as supplied.

Reactions were magnetically stirred and monitored by thin layer chromatography using Merck-Kiesegel 60F_{254} plates. Flash chromatography was performed with silica gel 60 (particle size 35-70 μm) supplied by Merck. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated.

Proton NMR spectra were recorded using an internal deuterium lock at ambient temperature on Bruker 300 MHz spectrometer. Internal reference of δ_H 7.26 was used for $CDCl_3$. Data are presented as follows: chemical shift (in ppm on the δ scale relative to δ_{TMS} = 0), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, sext. = sextuplet, sept. = septuplet, m = multiplet, br. = broad, app. = apparent), coupling constant (*J*/Hz) and integration. Resonances that are either partially or fully obscured are denoted obscured (obs.). Carbon-13 NMR spectra were recorded at 75 MHz using $CDCl_3$ (δ_C 77.16) as internal reference. Fluorine-19 NMR spectra were recorder at 377 MHz using C_6F_6 (δ_F - 164.92) as external reference.

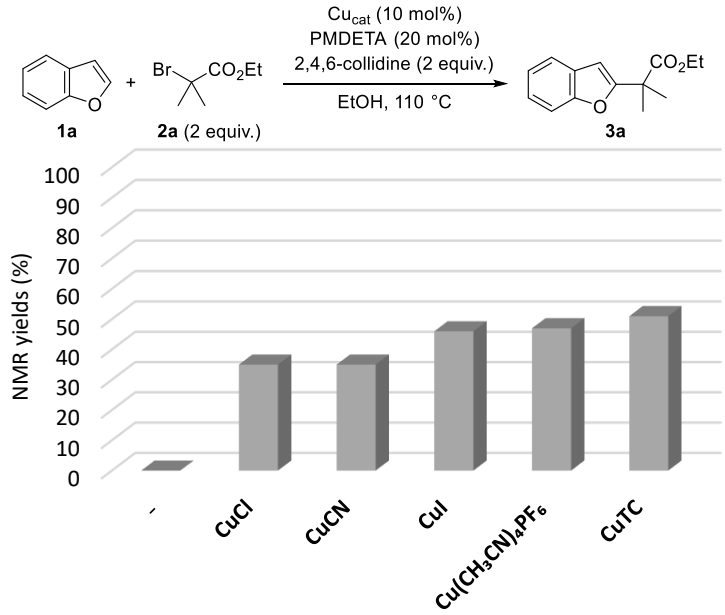
Optical rotations were recorded on an Atago AP-100 automatic polarimeter at 589 nm and reported as follows: $[\alpha]_D^{25}$, concentration (*c* in g/100 mL), and solvent. Melting points were recorded on a Stuart Scientific Analogue SMP11. Infrared spectra were recorded on a Bruker Alpha (ATR). High-resolution mass-spectra were obtained on Agilent QTOF 6520.

Optimization of the Reaction Conditions:

General procedure:

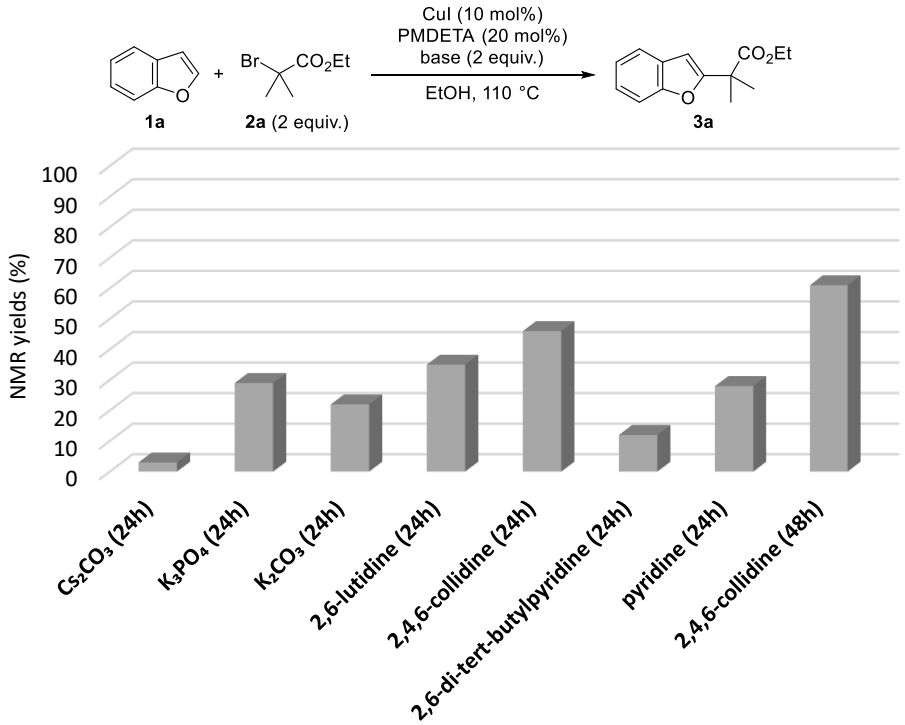
A 15 mL pressure tube was charged with the copper source (0.1 mmol). If solids, the base (2.0 mmol) and/or the ligand (0.2 mmol) were added at this stage. The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon before adding the solvent (1.6 mL), benzofuran (110 µL, 1.0 mmol) and ethyl α-bromoisobutyrate (290 µL, 2.0 mmol). If liquids, the base (2.0 mmol) and/or the ligand (0.2 mmol) were added at this stage. The rubber septum was replaced by Teflon-coated screw cap and the mixture was heated at 110 °C for 24 or 48 hours. The brownish suspension was cooled to room temperature, filtered over a plug of silica gel (washed with EtOAc) and concentrated. The yields were determined by NMR spectroscopy using benzyl acetate as an internal standard.

Optimization of the copper source:



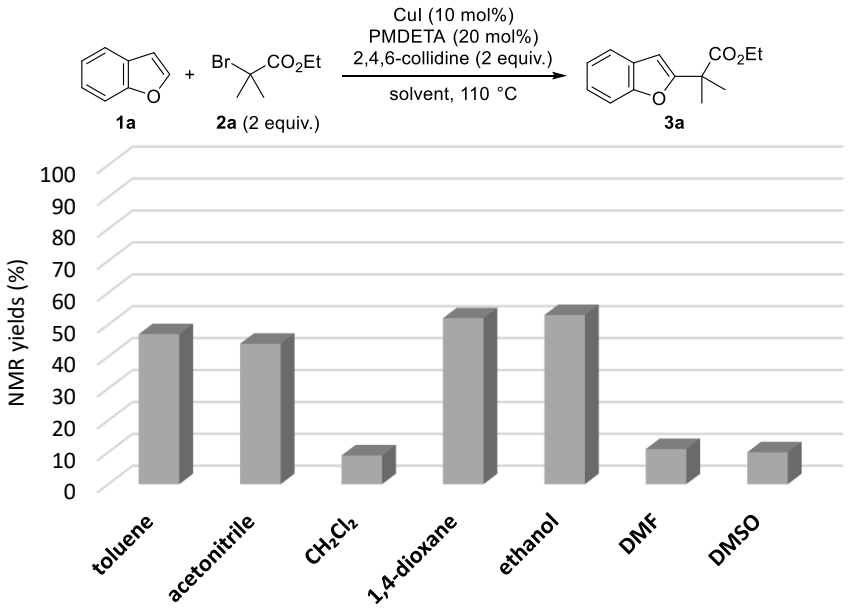
*Optimization of the copper source. Reactions performed using **1a** (1.0 mmol), **2a** (2.0 mmol), copper source (10 mol%), PMDETA (20 mol%), 2,4,6-collidine (2 equiv.) in ethanol (1.6 mL) at 110 °C for 48h. Yields determined by NMR spectroscopy using benzyl acetate as an internal standard. PMDETA: N,N,N',N'',N''-pentamethyldiethylenetriamine.*

Optimization of the base:



*Optimization of the base. Reactions performed using **1a** (1.0 mmol), **2a** (2.0 mmol), copper iodide (10 mol%), PMDETA (20 mol%), base (2 equiv.) in ethanol (1.6 mL) at 110 °C for 24 or 48h. Yields determined by NMR spectroscopy using benzyl acetate as an internal standard. PMDETA: N,N,N',N'',N''-pentamethyldiethylenetriamine.*

Optimization of the solvent:



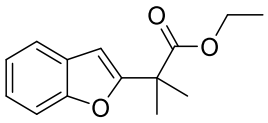
*Optimization of the solvent. Reactions performed using **1a** (1.0 mmol), **2a** (2.0 mmol), copper iodide (10 mol%), PMDETA (20 mol%), 2,4,6-collidine (2 equiv.) in solvent (1.6 mL) at 110 °C for 48h. Yields determined by NMR spectroscopy using benzyl acetate as an internal standard. PMDETA: N,N,N',N'',N''-pentamethyldiethylenetriamine.*

Experimental Procedure and Characterization Data:

Alkylation of Heteroarenes

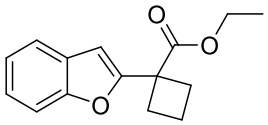
General procedure:

A 15 mL pressure tube was charged with copper(I) iodide (10 mg, 50 µmol) and tris(2-pyridylmethyl)amine (29 mg, 0.1 mmol). If solids, the heteroarene (0.5 mmol) and/or the alkyl halide (1.0 mmol) were added at this stage. The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon before adding anhydrous 1,4-dioxane or distilled ethanol (0.8 mL). If liquids, the heteroarene (0.5 mmol) and/or the alkyl halide (1.0 mmol) were added at this stage. 2,4,6-Collidine (130 µL, 1.0 mmol) was finally added and the rubber septum was replaced by Teflon-coated screw cap before heating the reaction mixture at the appropriate temperature (110 °C or 150 °C) for 48 hours. The brownish suspension was cooled to room temperature, filtered over a plug of silica gel (washed with EtOAc) and concentrated. The crude residue was finally purified by flash column chromatography over silica gel.



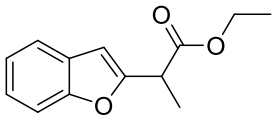
3a

Ethyl 2-(benzofuran-2-yl)-2-methylpropanoate 3a. Yield: 81% (1,4-dioxane or EtOH, 110 °C, 187 mg, 805 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.28 (app. quint. d, *J* = 7.5 and 1.8 Hz, 2H), 6.61 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.72 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ174.4, 160.9, 154.8, 128.5, 123.9, 122.7, 120.8, 111.2, 101.8, 61.3, 44.0, 24.5, 14.2; IR (ATR): ν_{max} 2982, 1733, 1454, 1385, 1252, 1143, 1084, 804, 751 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{17}O_3$ $[M+H]^+$ 233.1172, found 233.1180.



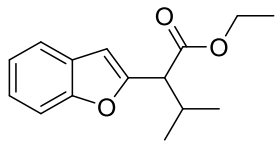
3b

Ethyl 1-(benzofuran-2-yl)cyclobutane-1-carboxylate 3b. Yield: 93% (1,4-dioxane, 110 °C, 226 mg, 925 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.57 (d, *J* = 7.1 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.26 (app. quint. d, *J* = 7.4 and 1.8 Hz, 2H), 6.66 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.95-2.78 (m, 2H), 2.71-2.56 (m, 2H), 2.21-2.02 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ173.6, 158.9, 155.1, 128.6, 123.9, 122.7, 120.8, 111.2, 102.7, 61.4, 48.1, 30.8, 16.7, 14.2; IR (ATR): ν_{max} 2953, 1730, 1454, 1250, 1211, 1100, 751 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{17}O_3$ $[M+H]^+$ 245.1172, found 245.1172.



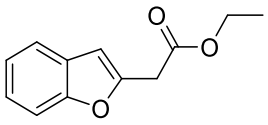
3c

Ethyl 2-(benzofuran-2-yl)propanoate 3c. Yield: 76% from ethyl-2-bromopropionate (1,4-dioxane, 110 °C, 166 mg, 760 µmol) and 54% from ethyl-2-chloropropionate (1,4-dioxane, 110 °C, 58 mg, 266 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.56 (d, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.26 (app. quint. d, *J* = 7.7 and 2.0 Hz, 2H), 6.61 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.98 (q, *J* = 7.8 Hz, 1H), 1.66 (d, *J* = 7.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 156.6, 154.8, 128.5, 124.0, 122.8, 120.8, 111.2, 103.1, 61.4, 40.1, 15.9, 14.2; IR (ATR): ν_{max} 2985, 1737, 1455, 1254, 1186, 1067, 1024, 941, 751 cm^{-1}; ESIHRMS *m/z* calcd for $C_{13}H_{15}O_3$ $[M+H]^+$ 219.1016, found 219.1015.



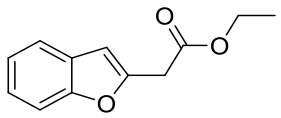
3d

Ethyl 2-(benzofuran-2-yl)-3-methylbutanoate 3d. Yield: 87% (1,4-dioxane, 110 °C, 215 mg, 873 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.24 (app. quint. d, *J* = 7.1 and 1.8 Hz, 2H), 6.68 (s, 1H), 4.28-4.15 (m, 2H), 3.57 (d, *J* = 9.3 Hz, 1H), 2.54 (d. sept., *J* = 9.3 and 6.7 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.3, 154.9, 154.8, 128.6, 123.9, 122.8, 120.8, 111.2, 104.6, 61.1, 53.6, 31.0, 21.0, 20.4, 14.3; IR (ATR): ν_{max} 2965, 1737, 1454, 1187, 1131, 1031, 750 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{19}O_3$ $[M+H]^+$ 247.1329, found 247.1331.



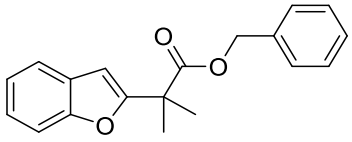
3e

Ethyl 2-(benzofuran-2-yl)-3,3-dimethylbutanoate 3e. Yield: 33% (EtOH, 110 °C, 41 mg, 166 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane: 90/10; White solid; Mp: 60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.22 (app. quint. d, *J* = 7.4 and 0.8 Hz, 2H), 6.75 (s, 1H), 3.74 (s, 1H), 3.71 (s, 3H), 1.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.4, 154.6, 154.1, 128.6, 123.4, 122.8, 120.8, 111.2, 105.6, 56.1, 51.9, 35.3, 28.1; IR (ATR): ν_{max} 2956, 1732, 1474, 1242, 1152, 1131, 755, 747 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{19}O_3$ $[M+H]^+$ 247.1329, found 247.1333.



3g

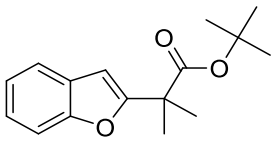
Ethyl 2-(benzofuran-2-yl)acetate 3g. Yield: 4% (1,4-dioxane, 110 °C, 9 mg, 44 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, *J* = 6.9 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.23 (app. quint. d, *J* = 7.5 and 1.4 Hz, 2H), 6.63 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 155.0, 150.9, 128.7, 124.1, 122.8, 120.9, 111.2, 105.2, 61.6, 34.9, 14.3; This compound has been previously reported.[1]



3h

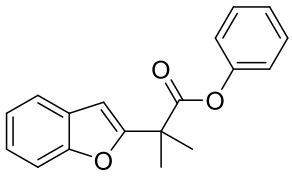
Benzyl 2-(benzofuran-2-yl)-2-methylpropanoate 3h. Yield: 62% (1,4-dioxane, 110 °C, 92 mg, 312 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane: 80/20; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.37-7.23 (m, 7H), 6.61 (d, *J* = 0.9 Hz, 1H), 5.21 (s, 2H), 1.74 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.2, 160.6, 154.9, 136.1, 128.6, 128.5, 128.1, 127.7, 124.0, 122.7, 120.9, 111.2, 102.0, 66.8, 44.2, 24.5; IR (ATR): ν_{max} 2966, 1736, 1454, 1253, 1139, 1083, 797, 750, 697 cm^{-1}; ESIHRMS *m/z* calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1329, found 295.1329.

[1] Ramella, V.; He, Z.; Daniliuc, C. G.; Studer, A. *Eur. J. Org. Chem.* **2016**, 2268.



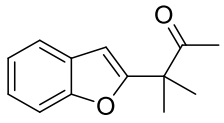
3i

***tert*-Butyl 2-(benzofuran-2-yl)-2-methylpropanoate 3i.** Yield: 58% (EtOH, 110 °C, 76 mg, 292 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; Mp: 52 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.0 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.26 (app. quint. d, *J* = 7.3 and 1.9 Hz, 2H), 6.57 (s, 1H), 1.66 (s, 6H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6, 161.5, 154.8, 128.6, 123.7, 122.6, 120.8, 111.1, 101.5, 81.1, 44.8, 28.0, 24.6, ; IR (ATR): ν_{max} 2979, 1723, 1454, 1367, 1254, 1139, 847, 752 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{21}O_3$ $[M+H]^+$ 261.1485, found 261.1483.



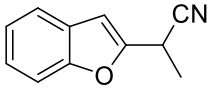
3j

Phenyl 2-(benzofuran-2-yl)-2-methylpropanoate 3j. Yield: 79% (1,4-dioxane, 110 °C, 111 mg, 396 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; Mp: 54 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* =7.1 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43-7.20 (m, 5H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.70 (d, *J* = 0.8 Hz, 1H), 1.84 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1, 160.2, 155.0, 151.0, 129.5, 128.5, 126.0, 124.1, 122.9, 121.5, 121.0, 111.3, 102.2, 44.4, 24.6; IR (ATR): ν_{max} 2991, 1750, 1488, 1455, 1256, 1232, 1190, 1163, 1127, 1084, 814, 744, 716, 691 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{17}O_3$ $[M+H]^+$ 281.1172, found 281.1174.



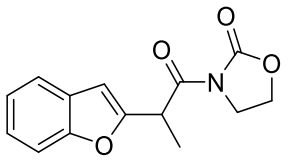
3k

3-(Benzofuran-2-yl)-3-methylbutan-2-one 3k. Yield: 78% (EtOH, 110 °C, 79 mg, 391 µmol). Solvent system for flash column chromatography: pentane/Et_2O: 90/10; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, *J* =6.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.26 (app. quint. d, *J* = 7.4 and 1.9 Hz, 2H), 6.63 (s, 1H), 2.08 (s, 3H), 1.58 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.7, 161.2, 155.0, 128.5, 124.2, 122.9, 120.9, 111.3, 102.6, 49.7, 25.8, 23.3; IR (ATR): ν_{max} 2980, 1717, 1455, 1354, 1254, 1171, 1126, 1082, 940, 804, 752, 742 cm^{-1}; ESIHRMS *m/z* calcd for $C_{13}H_{15}O_2$ $[M+H]^+$ 203.1067, found 203.1071.



3l

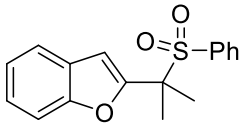
2-(Benzofuran-2-yl)propanenitrile 3l. Yield: 42% (1,4-dioxane, 110 °C, 36 mg, 210 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.32 (td, *J* = 7.3 and 1.5 Hz, 1H), 7.25 (td, *J* = 7.5 and 1.4 Hz, 1H), 6.72 (t, *J* = 0.93 Hz, 1H), 4.13 (qd, *J* = 7.2 and 0.9 Hz, 1H), 1.77 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 151.8, 127.8, 124.9, 123.3, 121.3, 119.1, 111.4, 104.0, 25.8, 17.6; IR (ATR): ν_{max} 1454, 1255, 1173, 1082, 1010, 943, 813, 751 cm^{-1}; ESIHRMS *m/z* calcd for $C_{10}H_9O$ $[M-CN]^+$ 145.0648, found 145.0646.



3m

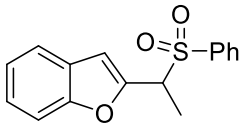
3-[2-(Benzofuran-2-yl)propanoyl]oxazolidin-2-one 3m. Yield: 60% (1,4-dioxane, 110 °C, 78 mg, 301 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane:

35/65; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 7.5 H, 1H), 7.21 (app. quint. d, *J* = 7.9 and 1.7 Hz, 2H), 6.69 (s, 1H), 5.40 (q, *J* =7.0 Hz, 1H), 4.51-4.36 (m, 2H), 4.14-4.02 (m, 2H), 1.68 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 155.9, 154.9, 153.2, 128.4, 124.0, 122.8, 120.9, 111.3, 104.2, 62.1, 43.0, 38.0, 15.8; IR (ATR): ν_{max} 2989, 1176, 1702, 1455, 1386, 1364, 1252, 1221, 1116, 1009, 753 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{14}NO_4$ $[M+H]^+$ 260.0917, found 260.0917.



3o

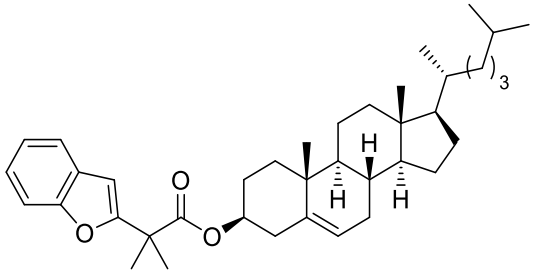
2-[2-(Phenylsulfonyl)propan-2-yl]benzofuran 3o. Yield: 58% (EtOH, 110 °C, 175 mg, 583 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane: 60/40; White solid; Mp: 102 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.48 (m, 4H), 7.38-7.29 (m, 3H), 7.23 (app. quint. d, *J* = 6.7 and 1.4 Hz, 2H), 6.66 (d, *J* = 0.7 Hz, 1H), 1.84 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8, 154.0, 135.5, 133.8, 130.2, 128.5, 127.9, 125.0, 123.1, 121.3, 111.4, 107.3, 64.1, 20.9; IR (ATR): ν_{max} 1448, 1300, 1159, 1129, 1074, 765, 754, 727, 689, 620 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{16}O_2SNa$ $[M+Na]^+$ 323.0712, found 323.0711.



3p

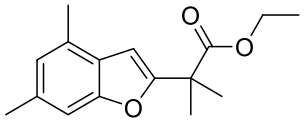
2-[1-(Phenylsulfonyl)ethyl]benzofuran 3p. Yield: 47% (EtOH, 110 °C, 67 mg, 234 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane: 50/50; White solid; Mp: 88 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.60 (tt, *J* = 7.6 and 1.1 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 8.2 Hz, 2H), 7.34-7.29 (m, 1H), 7.23 (app. quint. d, *J* = 7.2 and 1.4 Hz, 2H), 6.65 (s, 1H), 4.52 (q, *J* = 7.3 Hz, 1H), 1.81 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 150.2, 136.9, 134.0, 129.3, 129.0, 127.8, 125.0, 123.2, 121.3, 111.4, 107.6, 61.0,

12.8; IR (ATR): ν_{max} 1448, 1317, 1151, 1070, 1044, 808, 760, 732, 686, 649 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{18}NO_3S$ $[M+NH_4]^+$ 304.1002, found 304.1001.



3q

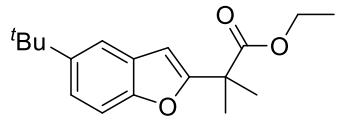
Cholestyl 2-(benzofuran-2-yl)-2-methylpropanoate 3q. Yield: 51% (EtOH, 110 °C, 133 mg, 232 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane: 90/10; White solid; Mp: 122 °C; $[\alpha]_D^{25}$ - 14 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.23 (app. quint. d, *J* = 7.4 and 1.6 Hz, 2H), 6.55 (s, 1H), 5.41-5.34 (m, 1H), 4.66 (sept., *J* = 4.6 Hz, 1H), 2.37-2.21 (m, 2H), 2.09-1.93 (m, 2H), 1.92-1.77 (m, 3H), 1.66 (s, 6H), 1.62-0.91 (m, 21H), 0.99 (s, 3H), 0.93 (obs. d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.7, 161.0, 154.8, 139.7, 128.5, 123.8, 122.8, 122.6, 120.8, 111.1, 101.7, 74.8, 56.7, 56.2, 50.1, 44.2, 42.4, 39.8, 39.6, 37.9, 37.0, 36.7, 36.3, 35.9, 32.0, 32.0, 28.4, 28.1, 27.6, 24.6, 24.4, 24.0, 23.0, 22.7, 21.1, 19.5, 18.8, 12.0; IR (ATR): ν_{max} 2938, 1739, 1467, 1253, 1153, 1082, 1002, 920, 805, 749, 733 cm^{-1}; ESIHRMS *m/z* calcd for $C_{39}H_{60}NO_3$ $[M+H]^+$ 590.4568, found 590.4554.



3r

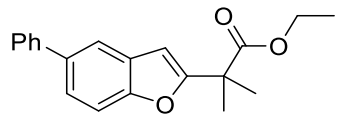
Ethyl 2-(4,6-dimethylbenzofuran-2-yl)-2-methylpropanoate 3r. Yield: 78% (EtOH, 110 °C, 102 mg, 392 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (s, 1H), 6.85 (s, 1H), 6.53 (d, *J* = 0.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 2.43 (s, 3H), 1.66 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ174.6, 159.7, 155.1, 134.0, 130.2, 125.7, 124.4, 108.9, 100.2, 61.3, 44.0, 24.6, 21.7, 18.6, 14.2; IR (ATR): ν_{max} 2982, 1733, 1469, 1292, 1249, 1147, 1128, 1054, 1026, 837, 802, 757 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{21}O_3$ $[M+H]^+$ 261.1485, found 261.1484.



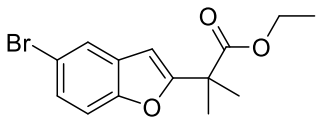
3s

Ethyl 2-[5-(*tert*-butyl)benzofuran-2-yl]-2-methylpropanoate 3s. Yield: 85% (EtOH, 110 °C, 122 mg, 423 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.56 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.33 (dd, *J* = 8.7 and 1.9 Hz, 1H), 6.54 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.66 (s, 6H), 1.39 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ174.4, 161.0, 153.1, 145.7, 128.2, 121.7, 117.1, 110.5, 101.9, 61.3, 44.1, 34.8, 32.0, 24.6, 14.2; IR (ATR): ν_{max} 2963, 1734, 1477, 1254, 1148, 1089, 1026, 808, 752 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{25}O_3$ $[M+H]^+$ 289.1798, found 289.1798.



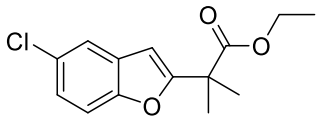
3t

Ethyl 2-methyl-2-(5-phenylbenzofuran-2-yl)propanoate 3t. Yield: 74% (EtOH, 110 °C, 114 mg, 370 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; Mp: 76 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.72 (t, *J* = 1.2 Hz, 1H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.51-7.41 (m, 4H), 7.35 (tt, *J* = 7.3 and 1.3 Hz, 1H), 6.60 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.68 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ174.4, 161.7, 154.5, 141.9, 136.5, 129.1, 128.8, 127.6, 126.9, 123.6, 119.4, 111.3, 102.1, 61.4, 44.2, 24.6, 14.2; IR (ATR): ν_{max} 2989, 1733, 1462, 1241, 1140, 1085, 1027, 814, 761, 699 cm^{-1}; ESIHRMS *m/z* calcd for $C_{20}H_{21}O_3$ $[M]^+$ 309.1485, found 309.1486.



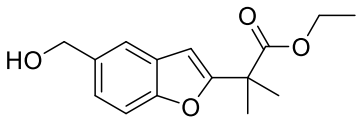
3u

Ethyl 2-(5-bromobenzofuran-2-yl)-2-methylpropanoate 3u. Yield: 79% (1,4-dioxane, 110 °C, 245 mg, 787 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, *J* = 1.7 Hz, 1H), 7.37-7.29 (m, 2H), 6.49 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.64 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 162.3, 153.6, 130.5, 126.8, 123.5, 115.7, 112.6, 101.5, 61.5, 44.1, 24.5, 14.2; IR (ATR): ν_{max} 2982, 1733, 1444, 1252, 1145, 1088, 1025, 798, 673 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{16}O_3Br$ $[M+H]^+$ 311.0277, found 311.0280.



3v

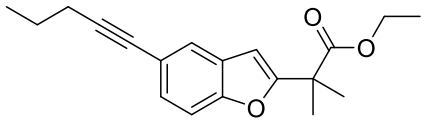
Ethyl 2-(5-chlorobenzofuran-2-yl)-2-methylpropanoate 3v. Yield: 76% (EtOH, 110 °C, 102 mg, 382 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 2.1 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.19 (dd, *J* = 8.7 and 2.2 Hz, 1H), 6.50 (d, *J* = 0.8 Hz, 1H), 4.16 (q, *J* =7.1 Hz, 2H), 1.64 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 162.5, 153.2, 129.9, 128.3, 124.1, 120.5, 112.1, 101.6, 61.5, 44.2, 24.5, 14.2; IR (ATR): ν_{max} 2983, 1733, 1446, 1257, 1145, 1089, 865, 799, 697 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{16}O_3Cl$ $[M+H]^+$ 267.0782, found 267.0783.



3w

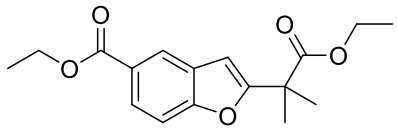
Ethyl 2-[5-(hydroxymethyl)benzofuran-2-yl]-2-methylpropanoate 3w. Yield: 72% (EtOH, 110 °C, 3 equiv. of ethyl α-bromoisobutyrate during 72h, 51 mg, 194 µmol). Solvent system for flash

column chromatography: petroleum ether/dichloromethane: 85/15; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (app. s, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.25 (dd, *J* = 8.2 and 1.8 Hz, 1H), 6.53 (d, *J* = 0.8 Hz, 1H), 4.74 (s, 2H), 4.15 (q, *J* =7.4 Hz, 2H), 1.73 (br. s, 1H), 1.64 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4, 161.5, 154.5, 135.5, 128.7, 123.4, 119.6, 111.2, 101.9, 65.8, 61.4, 44.1, 24.5, 14.2; IR (ATR): ν_{max} 3335, 2982, 1732, 1474, 1445, 1257, 1148, 1088, 1024, 808, 772 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{19}O_4$ $[M+H]^+$ 263.1278, found 263.1282.



3x

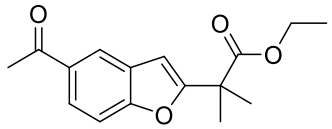
Ethyl 2-methyl-2-[5-(pent-1-yn-1-yl)benzofuran-2-yl]propanoate 3x. Yield: 66% (EtOH, 110 °C, 98 mg, 328 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane: 95/5; Pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 1.1 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.28 (dd, *J* = 8.5 and 1.6 Hz, 1H), 6.49 (d, *J* = 0.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.39 (t, *J* = 7.0 Hz, 2H), 1.64 (obs. app. sext, *J* = 7.2 Hz, 2H), 1.63 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.3, 161.7, 154.1, 128.6, 127.7, 124.1, 118.5, 111.1, 101.7, 88.6, 81.1, 61.4, 44.1, 24.5, 22.5, 21.6, 14.2, 13.7; IR (ATR): ν_{max} 2965, 1734, 1467, 1254, 1218, 1142, 1087, 1026, 810 cm^{-1}; ESIHRMS *m/z* calcd for $C_{19}H_{23}O_3$ $[M+H]^+$ 299.1642, found 299.1643.



3z

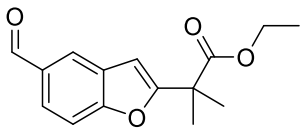
Ethyl 2-(1-ethoxy-2-methyl-1-oxopropan-2-yl)benzofuran-5-carboxylate 3z. Yield: 71% (EtOH, 110 °C, 35 mg, 354 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; Mp: 44 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, *J* = 1.3 Hz, 1H),

7.98 (dd, *J* = 8.6 and 1.7 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 6.60 (d, *J* = 0.8 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.65 (s, 6H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.1, 167.0, 162.4, 157.4, 128.5, 125.8, 125.5, 123.3, 111.0, 102.4, 61.5, 61.0, 44.1, 24.5, 14.5, 14.2; IR (ATR): ν_{max} 2974, 1733, 1713, 1445, 1299, 1276, 1246, 1168, 1147, 1090, 1029, 765 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{21}O_5$ $[M+H]^+$ 305.1384, found 305.1389.



3aa

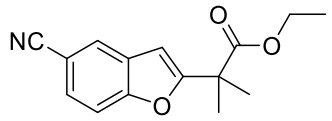
Ethyl 2-(5-acetylbenzofuran-2-yl)-2-methylpropanoate 3aa. Yield: 64% (EtOH, 110 °C, 88 mg, 321 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; Mp: 64 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, *J* = 1.0 Hz, 1H), 7.92 (dd, *J* = 8.6 and 1.5 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 6.62 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.65 (s, 3H), 1.66 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.8, 174.1, 162.6, 157.5, 132.7, 128.6, 124.8, 122.2, 111.2, 102.5, 61.5, 44.2, 26.9, 24.5, 14.2; IR (ATR): ν_{max} 2986, 1738, 1677, 1595, 1441, 1270, 1254, 1168, 1145, 1087, 1021, 811 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{19}O_4$ $[M+H]^+$ 275.1278, found 275.1280.



3ab

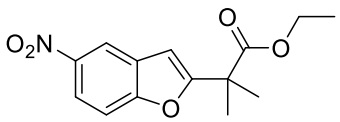
Ethyl 2-(5-formylbenzofuran-2-yl)-2-methylpropanoate 3ab. Yield: 46% (EtOH, 110 °C, 60 mg, 230 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.04 (s, 1H), 8.07 (d, *J* = 1.1 Hz, 1H), 7.82 (dd, *J* = 8.5 and 1.5 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 6.66 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.66 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 174.0, 163.1, 158.3, 132.2, 129.1, 125.8, 124.0,

111.9, 102.5, 61.6, 44.2, 24.5, 14.2; IR (ATR): ν_{max} 2983, 1732, 1695, 1445, 1302, 1266, 1148, 1113, 1024, 813, 790 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{17}O_4$ $[M+H]^+$ 261.1121, found 261.1116.



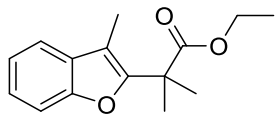
3ac

Ethyl 2-(5-cyanobenzofuran-2-yl)-2-methylpropanoate 3ac. Yield: 47% (EtOH, 110 °C, 61mg, 237 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; Mp: 42 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 1.3 and 0.9 Hz, 1H), 7.54-7.50 (m, 2H), 6.61 (d, *J* = 0.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.66 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 163.6, 156.6, 129.3, 127.8, 126.0, 119.8, 112.5, 106.7, 102.0, 61.7, 44.3, 24.5, 14.3; IR (ATR): ν_{max} 2985, 2227, 1732, 1590, 1467, 1445, 1269, 1254, 1148, 1086, 1024, 816 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{16}NO_3$ $[M+H]^+$ 258.1125, found 258.1129.



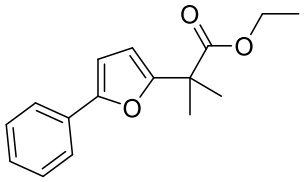
3ad

Ethyl 2-methyl-2-(5-nitrobenzofuran-2-yl)propanoate 3ad. Yield: 19% (EtOH, 110 °C, 26 mg, 94 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 98/2; Brown solid; Mp: 45 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, *J* = 2.3 Hz, 1H), 8.19 (dd, *J* = 9.0 and 2.4 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 6.69 (d, *J* = 0.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.67 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.8, 164.4, 157.7, 144.2, 128.9, 120.0, 117.4, 111.5, 102.9, 61.7, 44.3, 24.4, 14.2; IR (ATR): ν_{max} 2977, 1728, 1593, 1350, 1264, 1148, 1070, 925, 810 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{16}NO_5$ $[M+H]^+$ 278.1023, found 278.1022.



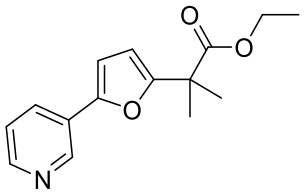
3ae

Ethyl 2-methyl-2-(3-methylbenzofuran-2-yl)propanoate 3ae. Yield: 74% (1,4-dioxane, 110 °C, 183 mg, 743 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.52-7.38 (m, 2H), 7.32-7.19 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.21 (s, 3H), 1.70 (s, 6H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ175.1, 154.2, 153.1, 131.0, 123.7, 122.2, 118.9, 110.9, 109.7, 61.3, 44.4, 25.0, 14.2, 8.3; IR (ATR): ν_{max} 2982, 1732, 1455, 1247, 1147, 1097, 745 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{19}O_3$ $[M+H]^+$ 247.1329, found 247.1329.



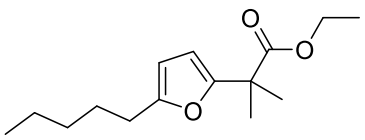
5a

Ethyl 2-methyl-2-(5-phenylfuran-2-yl)propanoate 5a. Yield: 84% (1,4-dioxane, 110 °C, 218 mg, 844 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 90/10; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.64 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.62 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ174.8, 157.4, 152.9, 131.1, 128.7, 127.2, 123.7, 107.0, 105.7, 61.2, 43.8, 24.7, 14.2; IR (ATR): ν_{max} 2982, 1731, 1249, 1150, 1119, 1026, 759, 692 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{19}O_3$ $[M+H]^+$ 259.1329, found 259.1330.



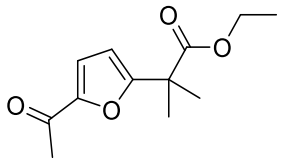
5b

Ethyl 2-methyl-2-[5-(pyridin-3-yl)furan-2-yl]propanoate 5b. Yield: 93% (EtOH, 110 °C, 120 mg, 463 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 70/30; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ8.86 (dd, *J* = 2.2 and 0.8 Hz, 1H), 8.43 (dd, *J* = 4.8 and 1.6 Hz, 1H), 7.84 (ddd, *J* = 8.0, 2.2 and 1.7 Hz, 1H), 7.24 (ddd, *J* = 8.0, 4.8 and 0.8 Hz, 1H), 6.64 (d, *J* = 3.4 Hz, 1H), 6.24 (d, *J* = 3.4 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.58 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ174.5, 158.5, 149.9, 148.0, 145.3, 130.5, 127.0, 123.5, 107.2, 107.1, 61.2, 43.7, 24.6, 14.1; IR (ATR): ν_{max} 2982, 1730, 1486, 1250, 1151, 1115, 1024, 787, 707 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{18}NO_3$ $[M+H]^+$ 260.1281, found 260.1281.



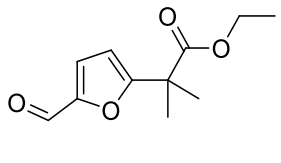
5c

Ethyl 2-methyl-2-(5-pentylfuran-2-yl)propanoate 5c. Yield: 54% (EtOH, 110 °C, 68 mg, 269 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ6.00 (d, *J* = 3.1 Hz, 1H), 5.87 (d, *J* = 3.1 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 1.66-1.55 (m, 2H), 1.52 (s, 6H), 1.37-1.26 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ175.2, 155.8, 155.7, 105.1, 105.0, 61.0, 43.5, 31.4, 28.1, 27.9, 24.6, 22.5, 14.2, 14.1; IR (ATR): ν_{max} 2933, 1734, 1468, 1252, 1150, 1119, 1022, 782 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{25}O_3$ $[M+H]^+$ 253.1798, found 253.1809.



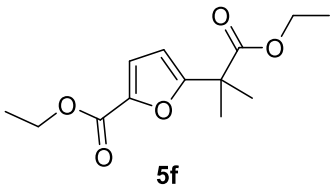
5d

Ethyl 2-(5-acetylfuran-2-yl)-2-methylpropanoate 5d. Yield: 68% (EtOH, 110 °C, 77 mg, 340 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 80/20; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (d, *J* = 3.5 Hz, 1H), 6.29 (d, *J* = 3.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.56 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.5, 173.8, 162.2, 152.0, 118.1, 108.1, 61.4, 44.1, 25.9, 24.4, 14.1; IR (ATR): ν_{max} 2984, 1732, 1677, 1513, 1366, 1250, 1153, 1024, 803, 628 cm^{-1}; ESIHRMS *m/z* calcd for $C_{12}H_{17}O_4$ $[M+H]^+$ 225.1121, found 225.1121.



5e

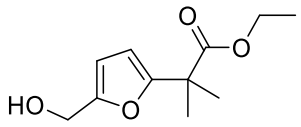
Ethyl 2-(5-formylfuran-2-yl)-2-methylpropanoate 5e. Yield: 70% (EtOH, 110 °C, 73 mg, 350 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 85/15; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.18 (d, *J* = 3.6 Hz, 1H), 6.38 (d, *J* = 3.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.60 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.7, 173.7, 164.4, 152.3, 122.2, 108.6, 61.6, 44.3, 24.5, 14.1; IR (ATR): ν_{max} 2984, 1732, 1681, 1515, 1388, 1249, 1152, 1087, 1026, 805, 764 cm^{-1}; ESIHRMS *m/z* calcd for $C_{11}H_{15}O_4$ $[M+H]^+$ 211.0965, found 211.0970.



5f

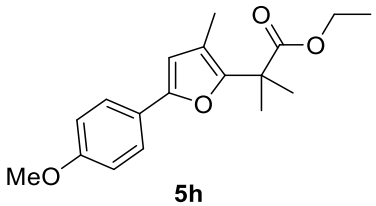
Ethyl 5-(1-ethoxy-2-methyl-1-oxopropan-2-yl)furan-2-carboxylate 5f. Yield: 53% (EtOH, 110 °C, 68 mg, 267 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc:

90/10; Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.09 (d, *J* = 3.4 Hz, 1H), 6.26 (d, *J* = 3.5 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.60 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.1, 162.0, 158.9, 143.9, 118.7, 107.5, 61.5, 60.8, 44.1, 24.6, 14.5, 14.2; IR (ATR): ν_{max} 2984, 1729, 1519, 1301, 1252, 1152, 1136, 1023, 762 cm^{-1}; ESIHRMS *m/z* calcd for $C_{13}H_{19}O_5$ $[M+H]^+$ 255.1227, found 255.1223



5g

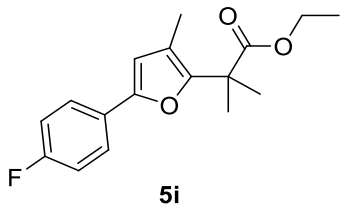
Ethyl 2-(5-(hydroxymethyl)furan-2-yl)-2-methylpropanoate 5g. Yield: 40% (EtOH, 110 °C, 42 mg, 198 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 70/30; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.20 (d, *J* = 3.2 Hz, 1H), 6.09 (d, *J* = 3.2 Hz, 1H), 4.55 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.91 (br. s, 1H), 1.54 (s, 6H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.9, 157.8, 153.3, 108.5, 105.7, 61.2, 57.7, 43.7, 24.6, 14.2; IR (ATR): ν_{max} 3427, 2982, 1731, 1386, 1253, 1151, 1115, 1020, 859, 791 cm^{-1}; ESIHRMS *m/z* calcd for $C_{11}H_{17}O_4$ $[M+H]^+$ 213.1121, found 213.1118.



5h

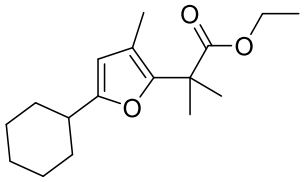
Ethyl 2-[5-(4-methoxyphenyl)-3-methylfuran-2-yl]-2-methylpropanoate 5h. Yield: 93% (1,4-dioxane, 110 °C, 141 mg, 466 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; Mp: 50 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.30 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.02 (s, 3H), 1.63 (s, 6H), 1.23 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.4, 158.8, 150.5, 150.1, 124.9, 124.2, 116.4, 114.1, 108.5, 61.1, 55.4, 44.1, 24.9, 14.3, 10.9; IR (ATR): ν_{max} 2979, 1732, 1500, 1246,

1181, 1147, 1115, 1027, 837, 804 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{23}O_4$ $[M+H]^+$ 303.1591, found 303.1591.



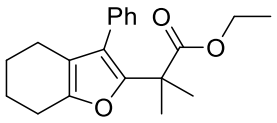
5i

Ethyl 2-[5-(4-fluorophenyl)-3-methylfuran-2-yl]-2-methylpropanoate 5i. Yield: 86% (1,4-dioxane, 110 °C, 99 mg, 340 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 8.9 and 5.3 Hz, 2H), 7.04 (t, *J* = 8.8 Hz, 2H), 6.37 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.02 (s, 3H), 1.63 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3, 162.0 (d, *J* = 244.7 Hz), 150.3 (d, *J* = 98.2 Hz), 127.5 (d, *J* = 3.0 Hz), 125.1 (d, *J* = 7.5 Hz), 116.6, 115.8, 115.5, 109.7, 61.2, 44.2, 24.9, 14.3, 10.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -118.25 (m); IR (ATR): ν_{max} 2982, 1731, 1497, 1230, 1149, 1095, 1026, 837, 811 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{20}O_3F$ $[M+H]^+$ 291.1391, found 291.1390.



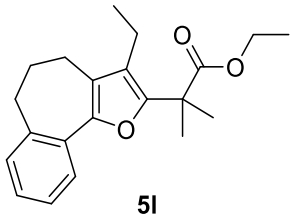
5j

Ethyl 2-(5-cyclohexyl-3-methylfuran-2-yl)-2-methylpropanoate 5j. Yield: 73% (EtOH, 110 °C, 101 mg, 363 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.70 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.60-2.46 (m, 1H), 2.02-1.96 (m, 2H), 1.94 (s, 3H), 1.85-1.60 (m, 3H), 1.54 (s, 6H), 1.41-1.24 (m, 5H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.7, 157.7, 148.6, 114.3, 107.6, 60.9, 44.1, 37.1, 31.5, 26.3, 26.0, 25.0, 14.3, 10.9; IR (ATR): ν_{max} 2929, 1732, 1449, 1252, 1147, 1027, 780, 733 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{27}O_3$ $[M+H]^+$ 279.1955, found 279.1953.



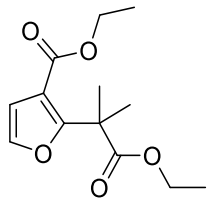
5k

Ethyl 2-methyl-2-(3-phenyl-4,5,6,7-tetrahydrobenzofuran-2-yl)propanoate 5k. Yield: 76% (1,4-dioxane, 110 °C, 119 mg, 381 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.29 (m, 2H), 7.28-7.25 (m, 1H), 7.24-7.18 (m, 2H), 3.78 (q, *J* = 7.1 Hz, 2H), 2.60 (tt, *J* = 6.1 and 1.6 Hz, 2H), 2.19 (tt, *J* = 6.0 and 1.6 Hz, 2H), 7.90-1.78 (m, 2H), 1.75-1.64 (m, 2H), 1.47 (s, 6H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.4, 149.7, 148.3, 134.3, 130.0, 128.0, 126.9, 121.4, 118.7, 60.9, 44.4, 26.0, 23.2, 23.1 (2C), 21.3, 14.1; IR (ATR): ν_{max} 2934, 1732, 1444, 1249, 1173, 1144, 1106, 1027, 759, 702 cm^{-1}; ESIHRMS *m/z* calcd for $C_{20}H_{25}O_3$ $[M+H]^+$ 313.1798, found 313.1799.



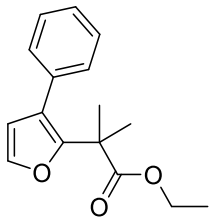
5l

Ethyl 2-(3-ethyl-5,6-dihydro-4H-benzo[6,7]cyclohepta[1,2-b]furan-2-yl)-2-methylpropanoate 5l. Yield: 70% (EtOH, 110 °C, 92 mg, 282 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.23 (dt, *J* = 8.1 and 4.3 Hz, 1H), 7.10 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.93-2.85 (m, 2H), 2.69 (t, *J* = 6.4 Hz, 2H), 2.39 (q, *J* = 7.5 Hz, 2H), 2.06-1.95 (m, 2H), 1.67 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.6, 149.8, 145.4, 138.7, 130.6, 129.3, 126.2, 126.1, 124.8, 123.7, 123.0, 61.1, 44.2, 26.3, 25.3 (2C), 24.7, 16.9, 14.5, 14.2; IR (ATR): ν_{max} 2977, 2932, 1730, 1445, 1254, 1147, 1095, 1026, 761, 733 cm^{-1}; ESIHRMS *m/z* calcd for $C_{21}H_{27}O_3$ $[M+H]^+$ 327.1955, found 327.1956.

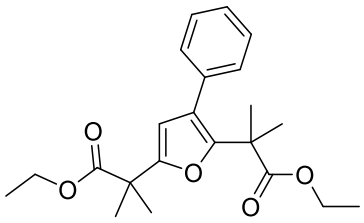


5m

Ethyl 2-(1-ethoxy-2-methyl-1-oxopropan-2-yl)furan-3-carboxylate 5m. Yield: 54% (EtOH, 110 °C, 3 equiv. of ethyl α-bromoisobutyrate during 72h, 69 mg, 271 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 (d, *J* = 1.9 Hz, 1H), 6.72 (d, *J* = 1.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.60 (s, 6H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.9, 163.4, 163.1, 140.0, 113.1, 111.9, 61.1, 60.5, 45.1, 24.6, 14.4, 14.2; IR (ATR): ν_{max} 2984, 1737, 1716, 1514, 1298, 1247, 1192, 1159, 1060, 1034, 736 cm^{-1}; ESIHRMS *m/z* calcd for $C_{13}H_{19}O_5$ $[M+H]^+$ 255.1227, found 255.1231.



5n

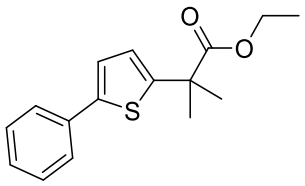


5n'

Ethyl 2-methyl-2-(3-phenylfuran-2-yl)propanoate 5n and **diethyl 2,2'-(3-phenylfuran-2,5-diyl)bis(2-methylpropanoate) 5n'.** Two separable compounds are obtained.

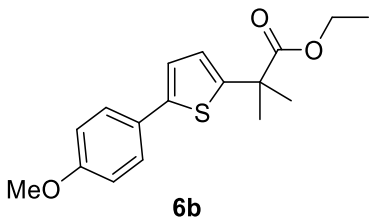
- **Ethyl 2-methyl-2-(3-phenylfuran-2-yl)propanoate 5n** (*faster eluting compound*). Yield: 29% (EtOH, 110 °C, 38 mg, 147 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.23 (m, 6H), 6.36 (d, *J* = 1.8 Hz, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 1.52 (s, 6H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.2, 151.7, 139.9, 134.9, 129.4, 128.1, 127.1, 121.6, 113.9, 61.1, 44.4, 25.7, 14.0; IR (ATR): ν_{max} 2983, 1731, 1515, 1446, 1257, 1145, 1027, 893, 766, 745, 700 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{19}O_3$ $[M+H]^+$ 259.1329, found 259.1329.

- **Diethyl 2,2'-(3-phenylfuran-2,5-diyl)bis(2-methylpropanoate) 5n'** (*slower eluting compound*). Yield: 39% (EtOH, 110 °C, 72 mg, 193 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 90/10; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.21 (m, 5H), 6.09 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.77 (q, *J* = 7.1 Hz, 2H), 1.55 (s, 6H), 1.48 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ175.1, 174.8, 154.7, 150.3, 135.0, 129.3, 128.0, 126.9, 121.8, 108.9, 61.1, 61.0, 44.4, 43.5, 25.7, 24.5, 14.3, 14.0; IR (ATR): ν_{max} 2982, 1731, 1469, 1386, 1254, 1147, 1027, 766, 701 cm^{-1}; ESIHRMS *m/z* calcd for $C_{22}H_{29}O_5$ $[M+H]^+$ 373.2010, found 373.2011.



6a

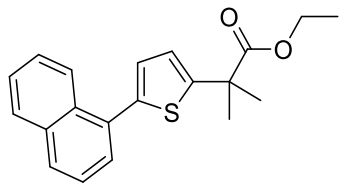
Ethyl 2-methyl-2-(5-phenylthiophen-2-yl)propanoate 6a. Yield: 83% (1,4-dioxane, 150 °C, 114 mg, 415 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.57 (m, 2H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.26 (tt, *J* = 7.5 and 1.4 Hz, 1H), 7.15 (d, *J* = 3.7 Hz, 1H), 6.93 (d, *J* = 3.7 Hz, 1H), 4.17 (q, *J* =7.1 Hz, 2H), 1.69 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ175.3, 148.9, 143.0, 134.5, 128.9, 127.4, 125.7, 124.7, 122.6, 61.4, 45.0, 27.6, 14.2; IR (ATR): ν_{max} 2978, 1727, 1250, 1144, 1027, 756, 690 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{19}O_2S$ $[M+H]^+$ 275.1100, found 275.1101.



6b

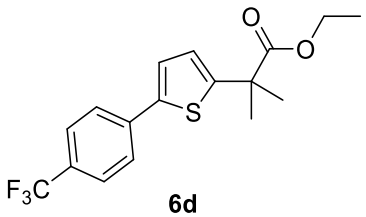
Ethyl 2-[5-(4-methoxyphenyl)thiophen-2-yl]-2-methylpropanoate 6b. Yield: 65% (1,4-dioxane, 150 °C, 99 mg, 325 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; Mp: 47 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.49 (d, *J* = 8.8 Hz, 2H),

7.02 (d, *J* = 3.7 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 3.7 Hz, 1H), 4.16 (q, *J* =7.1 Hz, 2H), 3.82 (s, 3H), 1.67 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ175.4, 159.2, 147.9, 143.0, 127.5, 127.0, 124.6, 121.5, 114.3, 61.3, 55.4, 45.0, 27.6, 14.2; IR (ATR): ν_{max} 2981, 1721, 1509, 1265, 1245, 1180, 1158, 1031, 826, 802 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{21}O_3S$ $[M+H]^+$ 305.1206, found 305.1207.



6c

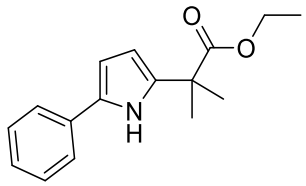
Ethyl 2-methyl-2-[5-(naphthalen-1-yl)thiophen-2-yl]propanoate 6c. Yield: 62% (1,4-dioxane, 150 °C, 82 mg, 308 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 97/3; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34-8.26 (m, 1H), 7.94-7.82 (m, 2H), 7.60-7.45 (m, 4H), 7.10 (d, *J* = 3.6 Hz, 1H), 7.04 (d, *J* = 3.6 Hz, 1H), 4.22 (q, *J* =7.1 Hz, 2H), 1.75 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.4, 149.6, 140.5, 134.0, 132.6, 131.8, 128.4, 128.4, 128.1, 126.9, 126.5, 126.1, 125.9, 125.3, 124.0, 61.4, 45.1, 27.7, 14.2; IR (ATR): ν_{max} 2979, 1728, 1471, 1391, 1255, 1144, 1022, 797, 775 cm^{-1}; ESIHRMS *m/z* calcd for $C_{20}H_{21}O_2S$ $[M+H]^+$ 325.1257, found 325.1258.



6d

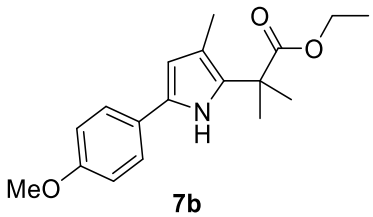
Ethyl 2-methyl-2-{5-[4-(trifluoromethyl)phenyl]thiophen-2-yl}propanoate 6d. Yield: 55% (1,4-dioxane, 150 °C, 94 mg, 274 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 98/2; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 3.8 Hz, 1H), 6.96 (d, *J* = 3.8 Hz, 1H), 4.17 (q, *J* =7.1 Hz, 2H), 1.69 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.1, 150.6, 141.1, 137.9, 129.1 (q, *J*

= 32.3 Hz), 125.9 (q, *J* = 3.8 Hz), 125.7, 125.1, 124.3 (q, *J* = 270.1 Hz), 124.0, 61.5, 45.1, 27.6, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ-62.56 (s); IR (ATR): ν_{max} 2960, 1729, 1324, 1254, 1123, 1068, 1015, 839, 803 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{18}O_2SF_3$ $[M+H]^+$ 343.0974, found 343.0979.



7a

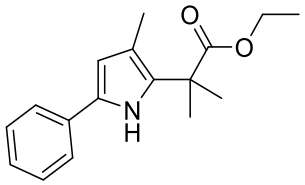
Ethyl 2-methyl-2-(5-phenyl-1*H*-pyrrol-2-yl)propanoate 7a. Yield: 53% (EtOH, 150 °C, 57 mg, 221 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5 + 1% Et_3N; Beige solid; Mp: 48 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ8.91 (br. s, 1H), 7.47 (m, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.19 (tt, *J* = 7.3 and 1.2 Hz, 1H), 6.41 (dd, *J* = 3.4 and 2.9 Hz, 1H), 6.10 (dd, *J* = 3.5 and 2.7 Hz, 1H), 4.19 (q, *J* =7.1 Hz, 2H), 1.61 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ176.2, 135.8, 132.9, 132.0, 129.0, 126.2, 123.8, 106.5, 105.6, 61.4, 42.5, 26.3, 14.3; IR (ATR): ν_{max} 3355, 2986, 2930, 1704, 1509, 1261, 1165, 1022, 774, 757, 695 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{20}NO_2$ $[M+H]^+$ 258.1489, found 258.1486.



7b

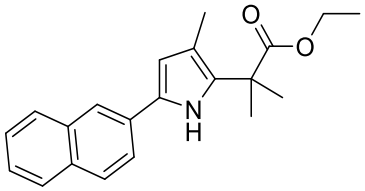
Ethyl 2-[5-(4-methoxyphenyl)-3-methyl-1*H*-pyrrol-2-yl]-2-methylpropanoate 7b. Yield: 58% (EtOH, 110 °C, 88 mg, 292 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 90/10 + 1% Et_3N; Yellow solid; Mp: 82 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ8.27 (br. s, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.15 (d, *J* = 3.0 Hz, 1H), 4.18 (q, *J* =7.1 Hz, 2H), 3.82 (s, 3H), 2.12 (s, 3H), 1.64 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ176.1, 158.1, 129.2, 129.1, 126.0, 125.0, 116.4, 114.4, 108.8, 61.2, 55.4, 43.1, 25.8, 14.3, 12.8; IR (ATR):

ν_{max} 3395, 2977, 1725, 1521, 1243, 1176, 1144, 1028, 821 cm^{-1}; ESIHRMS *m/z* calcd for $C_{18}H_{24}NO_3$ $[M+H]^+$ 302.1751, found 302.1751.



7c

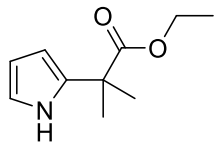
Ethyl 2-methyl-2-(3-methyl-5-phenyl-1*H*-pyrrol-2-yl)propanoate 7c. Yield: 62% (EtOH, 110 °C, 84 mg, 309 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5 + 1% Et_3N; Pale yellow solid; Mp: 35 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.40 (br. s, 1H), 7.44 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.17 (tt, *J* = 7.3 and 1.3 Hz, 1H), 6.29 (d, *J* = 3.0 Hz, 1H), 4.19 (q, *J* =7.1 Hz, 2H), 2.14 (s, 3H), 1.65 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.0, 132.8, 130.1, 129.1, 128.9, 125.9, 123.5, 116.7, 109.9, 61.3, 43.1, 25.7, 14.3, 12.8; IR (ATR): ν_{max} 3365, 2978, 1704, 1511, 1253, 1149, 1024, 795, 759, 694 cm^{-1}; ESIHRMS *m/z* calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$ 272.1645, found 272.1649.



7d

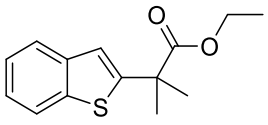
Ethyl 2-methyl-2-[3-methyl-5-(naphthalen-2-yl)-1*H*-pyrrol-2-yl]propanoate 7d. Yield: 52% (EtOH, 110 °C, 83 mg, 258 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5 + 1% Et_3N; Blue solid; Mp: 99 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.56 (br. s, 1H), 7.82 (s, 1H), 7.81-7.77 (m, 3H), 7.62 (dd, *J* = 8.6 and 1.9 Hz, 1H), 7.47 (td, *J* = 6.9 and 1.5 Hz, 1H), 7.40 (td, *J* = 8.2 and 1.6 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 4.21 (q, *J* =7.1 Hz, 2H), 2.17 (s, 3H), 1.70 (s, 6H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.0, 134.0, 132.0, 130.6, 130.2, 129.1, 128.6, 127.8, 127.7, 126.5, 125.3, 123.1, 120.4, 116.9, 110.7, 61.3, 43.2, 25.8, 14.3, 12.9;

IR (ATR): ν_{max} 3371, 2983, 1710, 1627, 1251, 1145, 1023, 832, 809, 745 cm^{-1}; ESIHRMS *m/z* calcd for $C_{21}H_{24}NO_2$ $[M+H]^+$ 322.1802, found 322.1800.



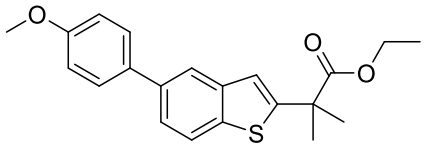
7e

Ethyl 2-methyl-2-(1*H*-pyrrol-2-yl)propanoate 7e. Yield: 24% (EtOH, 110 °C, 22 mg, 121 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 90/10; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (br. s, 1H), 6.74 (app. td, *J* = 2.7 and 1.6 Hz, 1H), 6.12 (dd, *J* = 6.1 and 2.8 Hz, 1H), 6.07-6.02 (m, 1H), 4.15 (q, *J* =7.1 Hz, 2H), 1.57 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.2, 134.7, 117.7, 108.0, 104.6, 61.3, 42.3, 26.2, 14.2; IR (ATR): ν_{max} 3350, 2975, 1694, 1475, 1388, 1267, 1163, 1148, 1126, 1020, 799, 734 cm^{-1}; ESIHRMS *m/z* calcd for $C_{10}H_{16}NO_2$ $[M+H]^+$ 182.1176, found 182.1174.



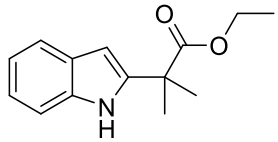
8a

Ethyl 2-(benzo[*b*]thiophen-2-yl)-2-methylpropanoate 8a. Yield: 44% (1,4-dioxane, 150 °C, 55 mg, 221 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5. Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.3 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.31 (app. quint. d, *J* = 7.2 and 1.4 Hz, 2H), 7.18 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.73 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.1, 150.2, 139.7, 139.4, 124.3, 124.1, 123.4, 122.2, 120.3, 61.5, 45.4, 27.5, 14.2; IR (ATR): ν_{max} 2980, 1729, 1458, 1386, 1248, 1144, 1026, 746.4 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{17}O_2S$ $[M+H]^+$ 249.0944, found 249.0946.



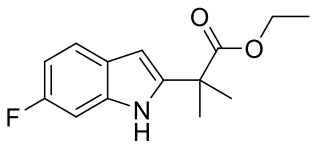
8b

Ethyl 2-[5-(4-methoxyphenyl)benzo[*b*]thiophen-2-yl]-2-methylpropanoate 8b. Yield: 41% (1,4-dioxane, 150 °C, 73 mg, 221 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5. White solid; Mp: 40 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 1.4 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.50 (dd, *J* = 8.4 and 1.8 Hz, 1H), 7.22 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.75 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0, 159.1, 150.9, 140.3, 137.9, 137.5, 134.1, 128.4, 123.5, 122.4, 121.3, 120.5, 114.4, 61.5, 55.5, 45.5, 27.5, 14.2; IR (ATR): ν_{max} 2980, 1752, 1600, 1455, 1222, 1141, 1038, 1018, 854, 810 cm^{-1}; ESIHRMS *m/z* calcd for $C_{21}H_{23}O_3S$ $[M+H]^+$ 355.1362, found 355.1358.



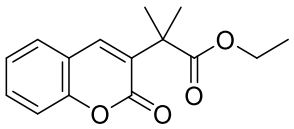
9a

Ethyl 2-(1*H*-indol-2-yl)-2-methylpropanoate 9a. Yield: 24% (1,4-dioxane, 150 °C, 14 mg, 61 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane: 65/35; White solid; Mp: 113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (br. s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.34 (dd, *J* = 8.1 and 0.8 Hz, 1H), 7.16 (td, *J* =7.9 and 1.1 Hz, 1H), 7.08 (td, *J* = 7.9 and 1.2 Hz, 1H), 6.38 (dd, *J* = 2.1 and 0.8 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.68 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.8, 141.7, 136.3, 128.1, 121.9, 120.4, 119.9, 110.9, 99.1, 61.6, 43.0, 26.0, 14.2; IR (ATR): ν_{max} 3360, 2979, 1697, 1270, 1155, 1019, 788, 778, 751, 734, 712 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{18}NO_2$ $[M+H]^+$ 232.1332, found 232.1330.



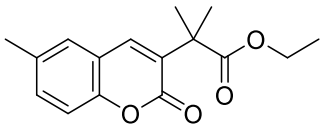
9b

Ethyl 2-(6-fluoro-1*H*-indol-2-yl)-2-methylpropanoate 9b. Yield: 30% (1,4-dioxane, 150 °C, 38 mg, 152 µmol). Solvent system for flash column chromatography: petroleum ether/dichloromethane: 60/40; White solid; Mp: 127 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (br. s, 1H), 7.45 (dd, *J* = 8.6 and 5.4 Hz, 1H), 7.02 (dd, *J* = 9.7 and 2.2 Hz, 1H), 7.85 (ddd, *J* = 9.7, 8.6 and 2.3 Hz, 1H), 6.34 (dd, *J* = 2.2 and 0.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.66 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.8, 159.9 (d, *J* = 235.5 Hz), 142.1 (d, *J* = 3.8 Hz), 136.2 (d, *J* = 12.0 Hz), 124.5, 120.0 (d, *J* = 10.5 Hz), 108.5 (d, *J* = 24.8 Hz), 99.0, 97.3 (d, *J* = 26.2 Hz), 61.7, 43.0, 26.0, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ -124.55 (m); IR (ATR): ν_{max} 3350, 2975, 1699, 1505, 1456, 1267, 1244, 1155, 1141, 1021, 853, 807, 713 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{17}FNO_2$ $[M+H]^+$ 250.1238, found 250.1240.



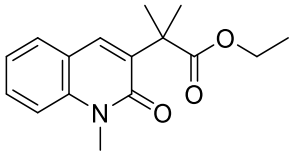
10a

Ethyl 2-methyl-2-(2-oxo-2*H*-chromen-3-yl)propanoate 10a. Yield: 77% (EtOH, 110 °C, 100 mg, 384 µmol). Solvent system for flash column chromatography: dichloromethane; White solid; Mp: 75 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.49 (td, *J* = 7.4 and 1.6 Hz, 2H), 7.33-7.24 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.55 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.5, 160.4, 153.2, 136.6, 133.5, 131.1, 127.9, 124.5, 119.2, 116.5, 61.2, 44.8, 24.7, 14.1; IR (ATR): ν_{max} 2979, 1781, 1723, 1704, 1273, 1223, 1175, 1138, 1032, 1015, 758 cm^{-1}; ESIHRMS *m/z* calcd for $C_{15}H_{17}O_4$ $[M+H]^+$ 261.1121, found 261.1124.



10b

Ethyl 2-methyl-2-(6-methyl-2-oxo-2*H*-chromen-3-yl)propanoate 10b. Yield: 59% (EtOH, 110 °C, 80 mg, 294 µmol). Solvent system for flash column chromatography: dichloromethane; White solid; Mp: 79 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.31-7.26 (m, 2H), 7.22-7.17 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.54 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.5, 160.6, 151.3, 136.6, 134.1, 133.3, 132.1, 127.7, 119.0, 116.2, 61.1, 44.7, 24.7, 20.8, 14.1; IR (ATR): ν_{max} 2982, 1705, 1584, 1472, 1274, 1221, 1178, 1157, 1131, 1026, 818, 785 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{19}O_4$ $[M+H]^+$ 275.1278, found 275.1277.



11

Ethyl 2-methyl-2-(1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)propanoate 11. Yield: 48% (1,4-dioxane, 150 °C, 65 mg, 234 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 70/30; White solid; Mp: 117 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.60-7.49 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.23 (td, *J* = 7.7 and 1.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 1.56 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.5, 161.2, 139.3, 137.7, 132.9, 130.0, 128.8, 122.1, 120.5, 113.9, 60.7, 44.9, 29.8, 25.0, 14.2; IR (ATR): ν_{max} 2979, 1728, 1642, 1593, 1473, 1378, 1255, 1163, 1140, 751 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{20}NO_3$ $[M+H]^+$ 274.1438, found 274.1437.

Experimental Procedure: Gram Scale Synthesis of 3a

General procedure:

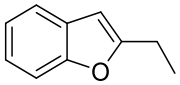
An oven dried 250 mL flask equipped with a condenser and fitted with a rubber septum was charged with copper(I) iodide (403 mg, 2.1 mmol) and tris(2-pyridylmethyl)amine (1.23 g, 4.2 mmol). The flask was evacuated under high vacuum and backfilled with argon before adding anhydrous 1,4-dioxane (67 mL), benzofuran (4.7 mL, 42.3 mmol), ethyl α-bromoisobutyrate (12.4 mL, 84.6 mmol) and 2,4,6-collidine (11.2 mL, 84.6 mL). The reaction mixture was then heated at reflux for 96h. The brownish suspension was cooled to room temperature, filtered over a plug of silica gel (washed with EtOAc) and concentrated. The crude residue was finally purified by flash column chromatography over silica gel (petroleum ether/dichloromethane: 95/5 then 75/25) to afford the desired product **3a** as yellow oil (4.0 g, 17.2 mmol, 41%).

Experimental Procedure and Characterization Data:

Reductive Desulfonylation of 3o and 3p

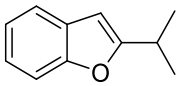
General procedure:

The reductive desulfonylation of **3o** and **3p** was performed based on a previously reported procedure.[2] KH_2PO_4 (15 equiv.) and 5% Na/Hg amalgam (20 equiv.) were added to a dry solution of **3o** or **3p** (1 equiv.) in distilled MeOH (12.5 mL/mmol). The mixture was vigorously stirred at room temperature until completion (monitored by TLC), filtered over a plug of Celite® (washed with MeOH) and concentrated under vacuum. The crude residue was finally purified by flash column chromatography over silica gel.



4

2-Ethylbenzofuran 4. Yield: 79% (23 mg, 157 µmol). Solvent system for flash column chromatography: pentane; Volatile colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.46 (m, 1H), 7.44-7.38 (m, 1H), 7.23-7.14 (m, 2H), 6.38 (d, *J* = 1.0 Hz, 1H), 2.80 (qd, *J* = 7.6 and 1.0 Hz, 1H), 1.34 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.1, 154.8, 129.1, 123.2, 122.5, 120.3, 110.8, 101.1, 21.9, 12.1; This compound has been previously reported.[3]



4'

2-Isopropylbenzofuran 4'. Yield: 69% (22 mg, 137 µmol). Solvent system for flash column chromatography: pentane; Volatile colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.46 (m, 1H), 7.44-7.38 (m, 1H), 7.24-7.14 (m, 2H), 6.36 (app. t, *J* = 1.0 Hz, 1H), 3.08 (sept. d, *J* = 6.9 and 0.9 Hz,

[2] Karoyan, P.; Chassaing, G. *Tetrahedron Lett.* **2002**, *43*, 1221.
[3] Lee, D.-H.; Kwon, K.-H.; Yi, C. S. *J. Am. Chem. Soc.* **2012**, *134*, 7325.

1H), 1.35 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.1, 154.7, 129.0, 123.2, 122.4, 120.4, 110.9, 99.8, 28.4, 21.1; This compound has been previously reported.[4]

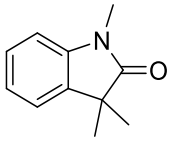
[4] Ortega, N.; Urban, S.; Beiring, B.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 1710.

Experimental Procedure and Characterization Data:

Intramolecular Alkylation of α-Bromoacetanilides to Indolones

General procedure:

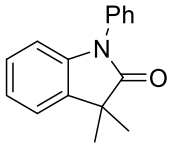
A 15 mL pressure tube was charged with the α-bromoacetanilide (0.5 mmol), copper(I) iodide (10 mg, 50 µmol) and tris(2-pyridylmethyl)amine (29 mg, 0.1 mmol). The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Distilled ethanol (0.8 mL) and 2,4,6-collidine (130 µL, 1.0 mmol) were next added. The rubber septum was replaced by Teflon-coated screw cap and the mixture was heated at 110 °C for 48 hours. The brownish suspension was cooled to room temperature, filtered over a plug of silica gel (washed with EtOAc) and concentrated. The crude residue was finally purified by flash column chromatography over silica gel.



13a

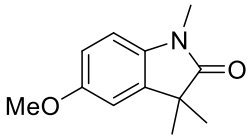
1,3,3-Trimethylindolin-2-one 13a. Yield: 80% (EtOH, 110 °C, 70 mg, 399 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 85/15; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (td, *J* = 7.7 and 1.3 Hz, 1H), 7.19 (dd, *J* = 7.3 and 0.8 Hz, 1H), 7.05 (td, *J* = 7.5 and 0.9 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 3.20 (s, 3H), 1.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 142.7, 135.9, 127.7, 122.5, 122.3, 108.1, 44.2, 26.2, 24.4; This compound has been previously reported.[5]

[5] Liu, C.; Liu, D.; Zhang, W.; Zhou, L.; Lei, A. *Org. Lett.* **2013**, *15*, 6166.



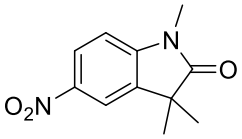
13b

3,3-Dimethyl-1-phenylindolin-2-one 13b. Yield: 84% (EtOH, 110 °C, 100 mg, 421 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 95/5; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.49 (m, 2H), 7.47-7.39 (m, 3H), 7.29 (dd, *J* = 7.1 and 0.9 Hz, 1H), 7.20 (td, *J* = 7.7 and 1.4 Hz, 1H), 7.11 (td, *J* = 7.4 and 1.1 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 1.51 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.8, 142.6, 135.7, 134.8, 129.6, 127.9, 127.7, 126.6, 123.0, 122.7, 109.5, 44.4, 24.9; This compound has been previously reported.[5]



13c

5-Methoxy-1,3,3-trimethylindolin-2-one 13c. Yield: 78% (EtOH, 110 °C, 80 mg, 390 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 85/15; White solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.81 (d, *J* = 2.3 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 6.74 (s, 1H), 3.79 (s, 3H), 3.17 (s, 3H), 1.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.1, 156.1, 137.3, 136.2, 111.6, 110.1, 108.3, 55.9, 44.7, 26.3, 24.5; This compound has been previously reported.[5]



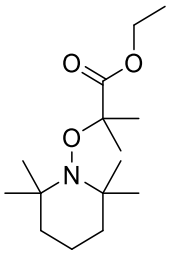
13d

1,3,3-Trimethyl-5-nitroindolin-2-one 13d. Yield: 65% (EtOH, 110 °C, 72 mg, 327 µmol). Solvent system for flash column chromatography: petroleum ether/EtOAc: 90/10; Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (dd, *J* = 8.6 and 2.3 Hz, 1H), 8.08 (d, *J* = 2.2 Hz, 1H), 6.92 (d, *J* = 8.6 Hz,

1H), 3.27 (s, 3H), 1.41 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ181.3, 148.5, 143.5, 136.5, 125.3, 118.4, 107.7, 44.3, 26.7, 24.2;This compound has been previously reported.[5]

Experimental Procedure and Characterization Data:

Radical Trapping Experiments



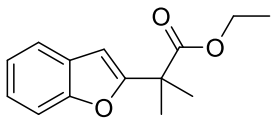
14

Ethyl 2-methyl-2-[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]propanoate 14. A 15 mL pressure tube was charged with TEMPO (156 mg, 1.0 mmol), copper(I) iodide (19 mg, 0.1 mmol) and tris(2-pyridylmethyl)amine (58 mg, 0.2 mmol). The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Dry 1,4-dioxane (1.6 mL), benzofuran (110 µL, 1.0 mmol), ethyl α-bromoisobutyrate (290 µL, 2.0 mmol) and 2,4,6-collidine (260 µL, 2.0 mmol) were next added. The rubber septum was replaced by Teflon-coated screw cap and the mixture was heated at 110 °C for 48 hours. The brownish suspension was cooled to room temperature, filtered over a plug of silica gel (washed with EtOAc) and concentrated. The crude residue was finally purified by flash column chromatography over silica gel (petroleum ether/AcOEt 95/5) yielding the adduct **13** as a colorless oil (120 mg, 442 µmol, 44%).[1]H NMR (300 MHz, $CDCl_3$): δ 4.23 (q, *J* = 7.1 Hz, 2H), 1.52 (s, 12H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 6H), 1.06 (s, 6H); [13]C NMR (75 MHz, $CDCl_3$): δ 176.1, 81.2, 60.7, 59.6, 40.7, 33.6, 24.6, 20.6, 17.2, 14.3; This compound has been previously reported.[6]

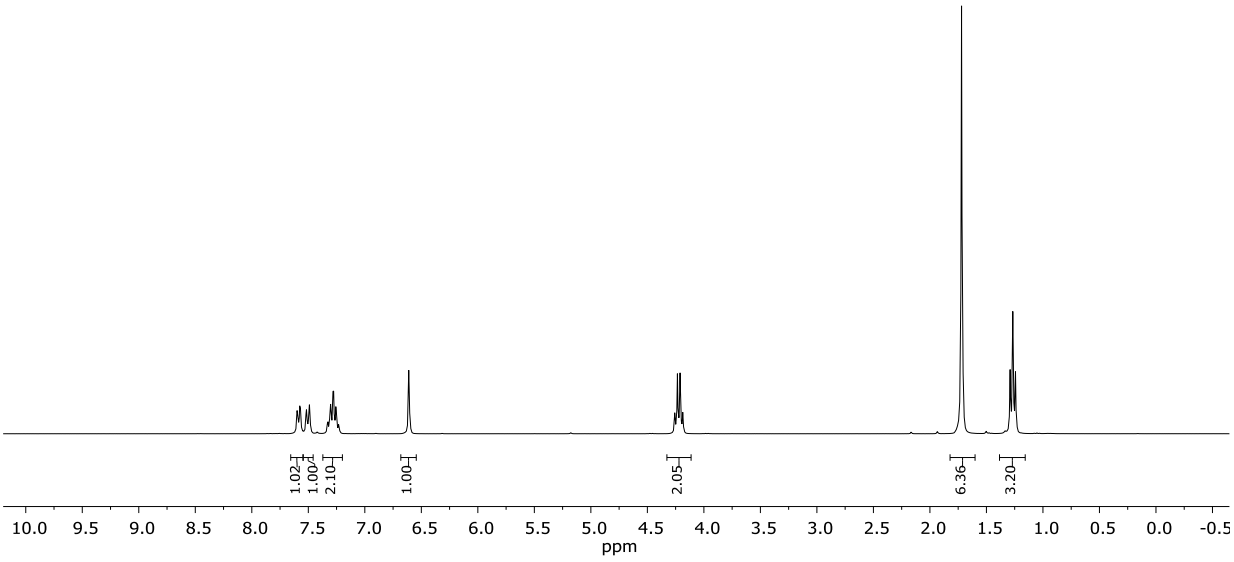
[6] Yamago, S.; Ukai, Y.; Matsumoto, A.; Nakamura, Y. *J. Am. Chem. Soc.* **2009**, *131*, 2100.

Supporting Information

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



3a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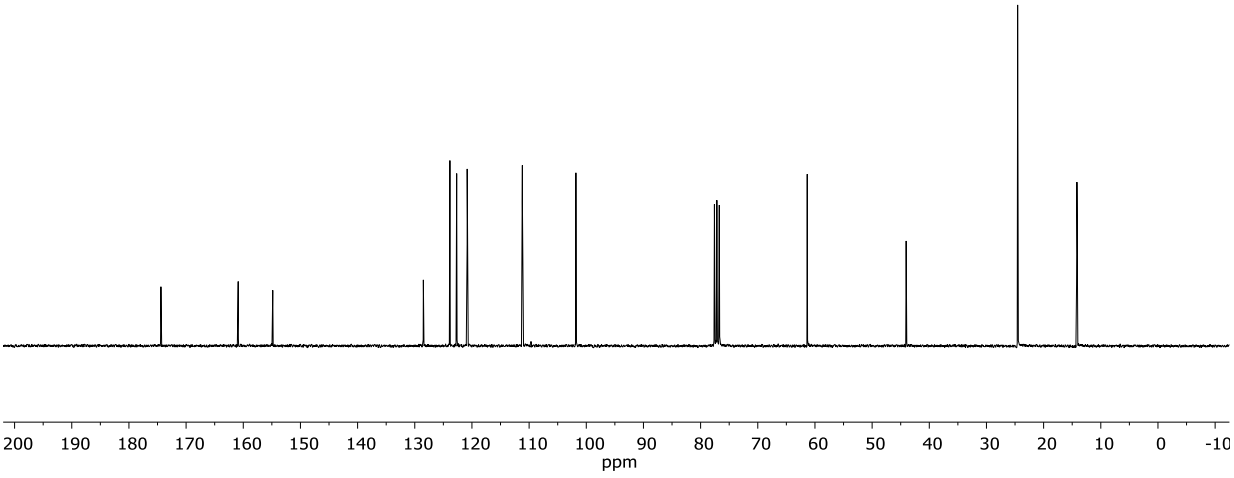
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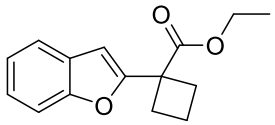
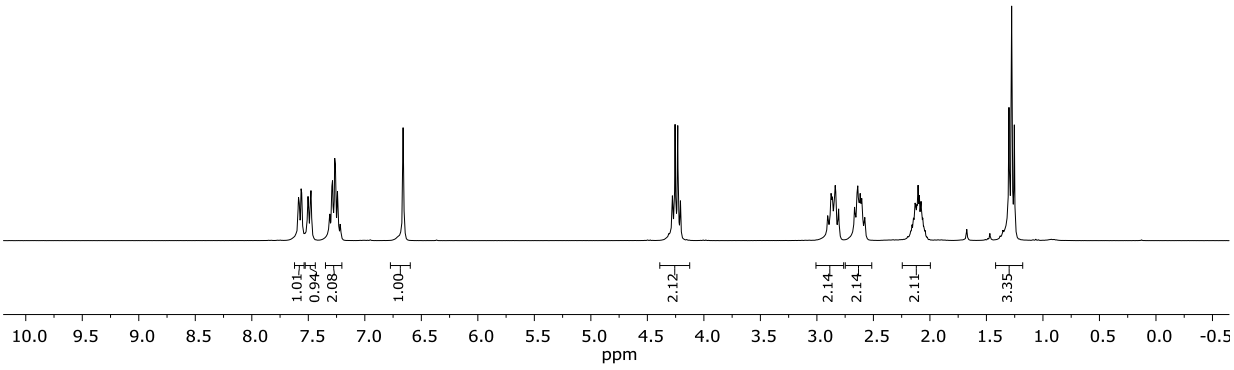


3b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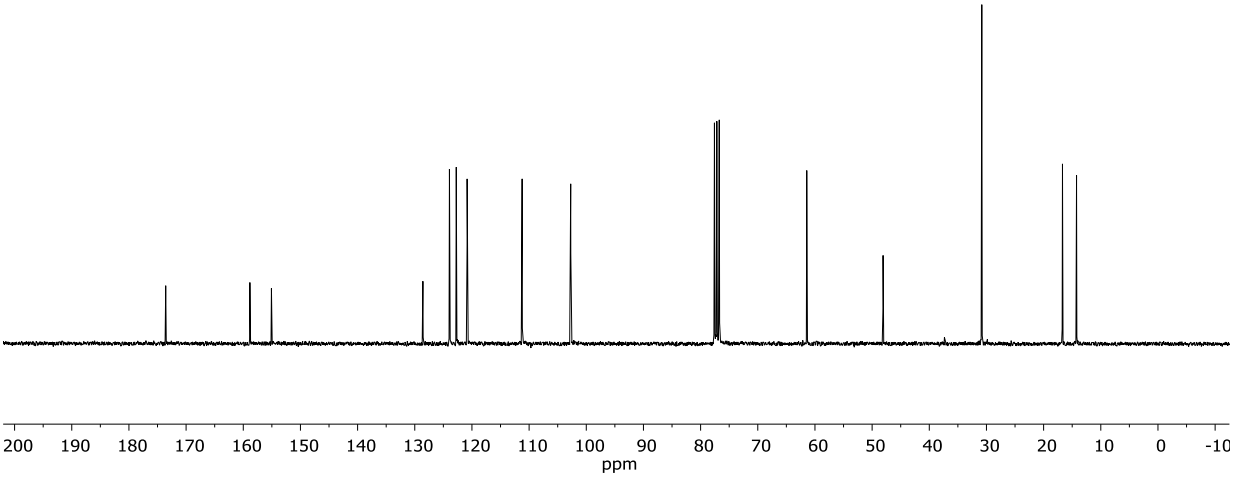
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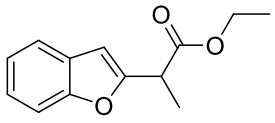
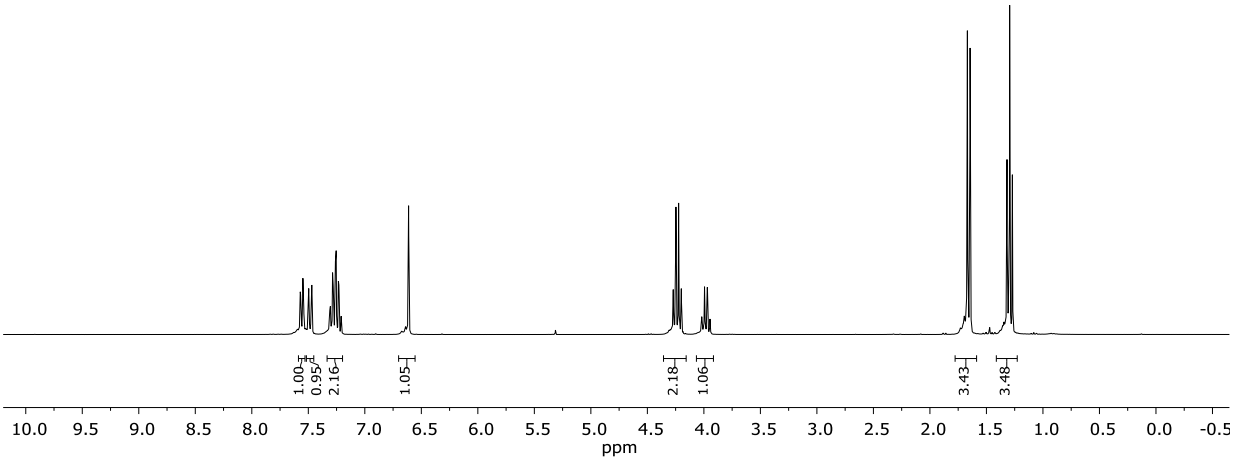


3c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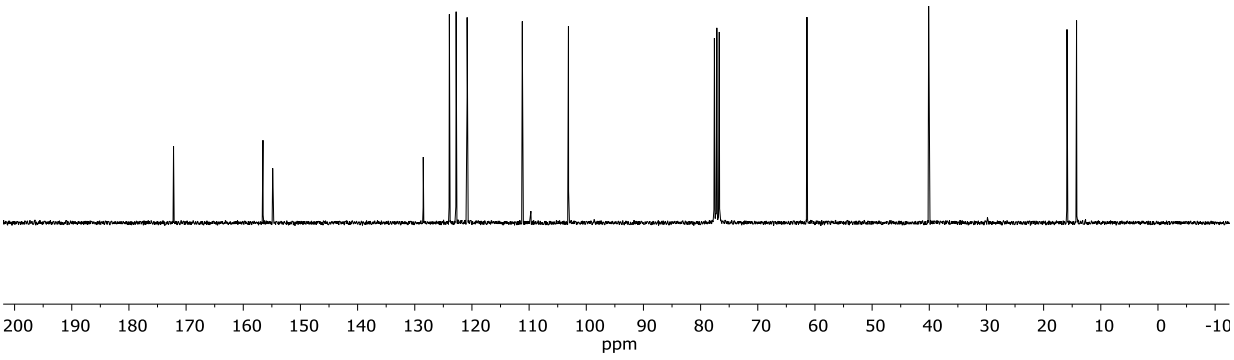
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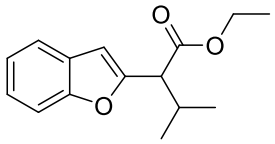

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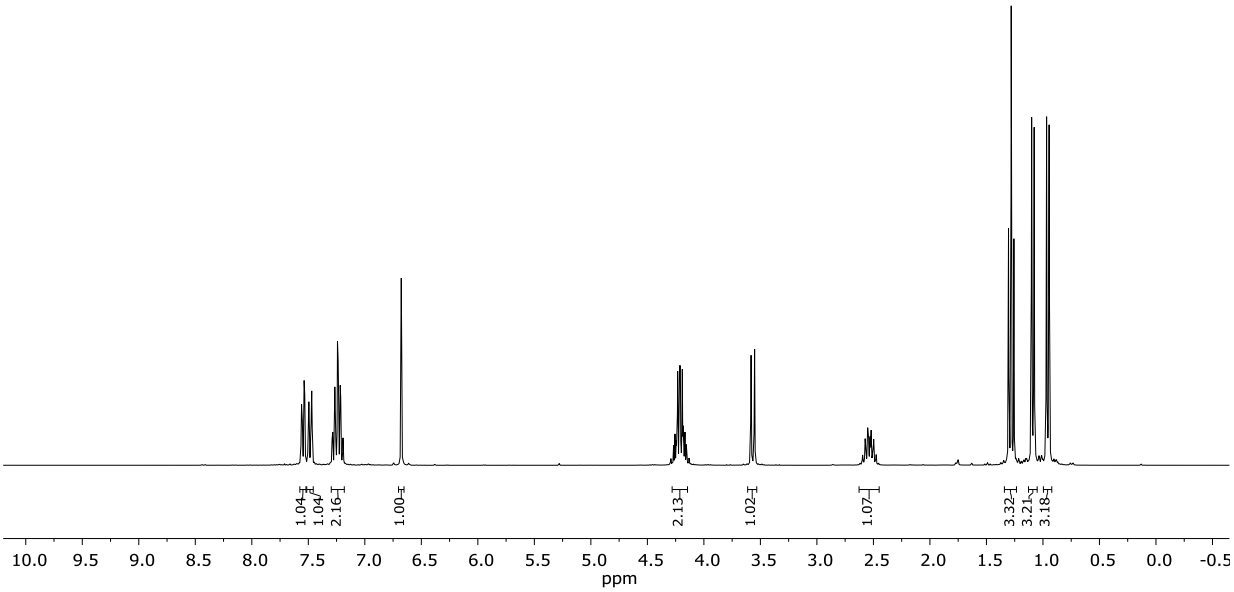
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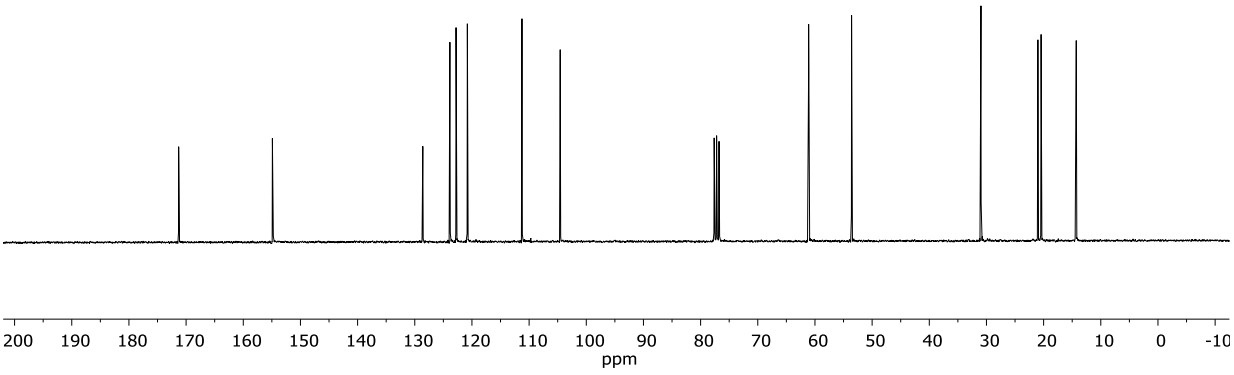
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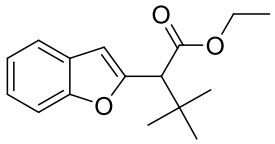

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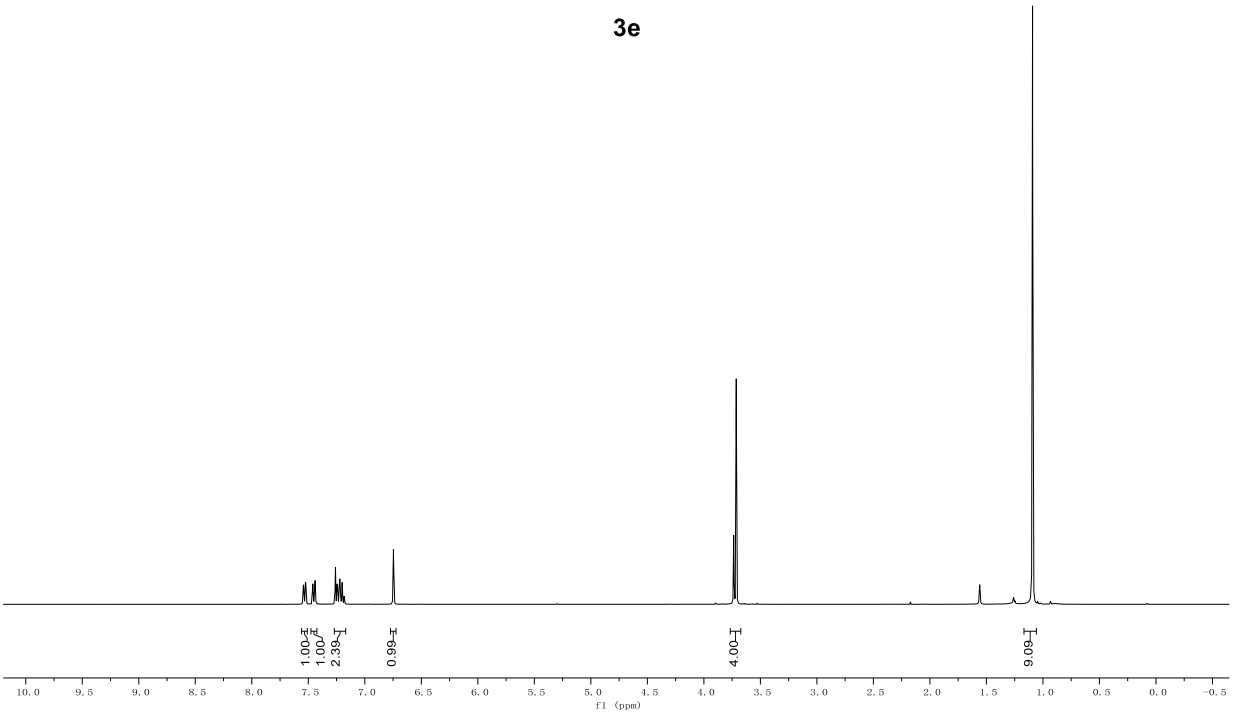

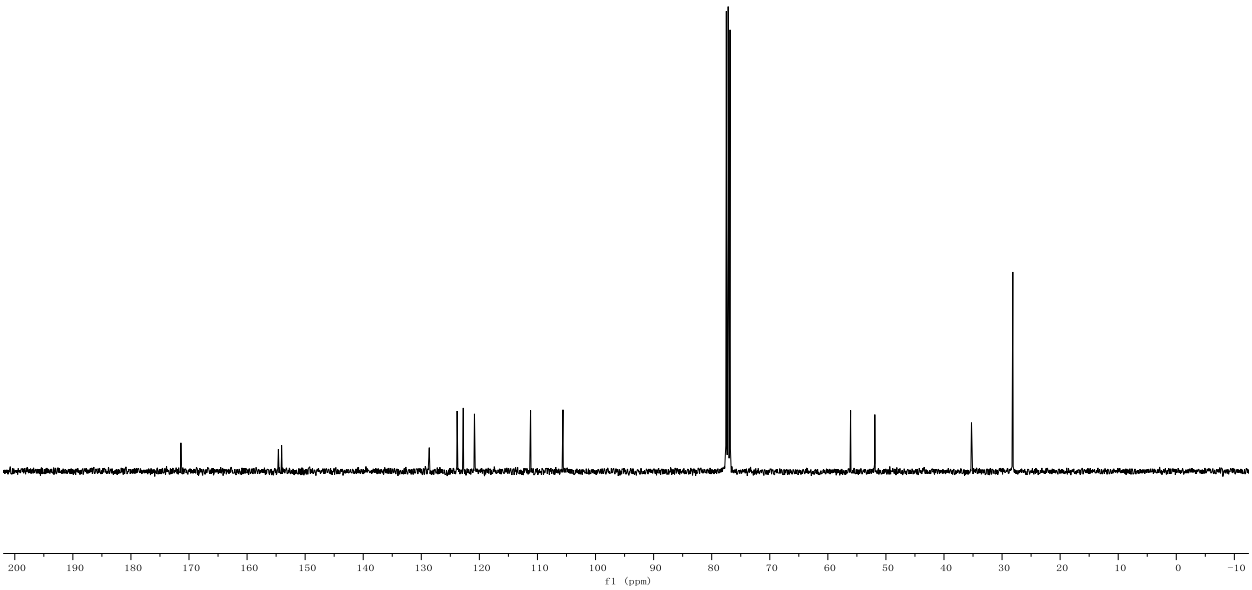

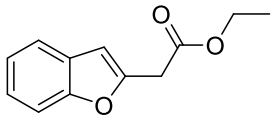

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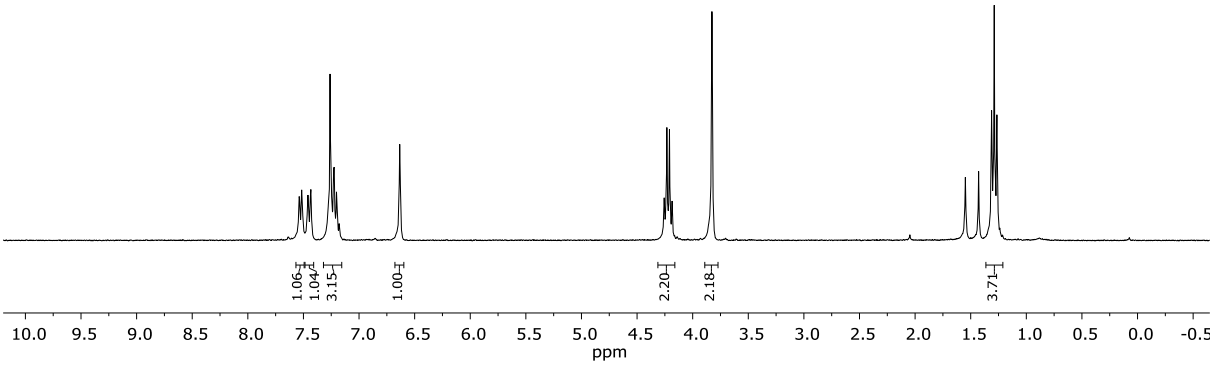
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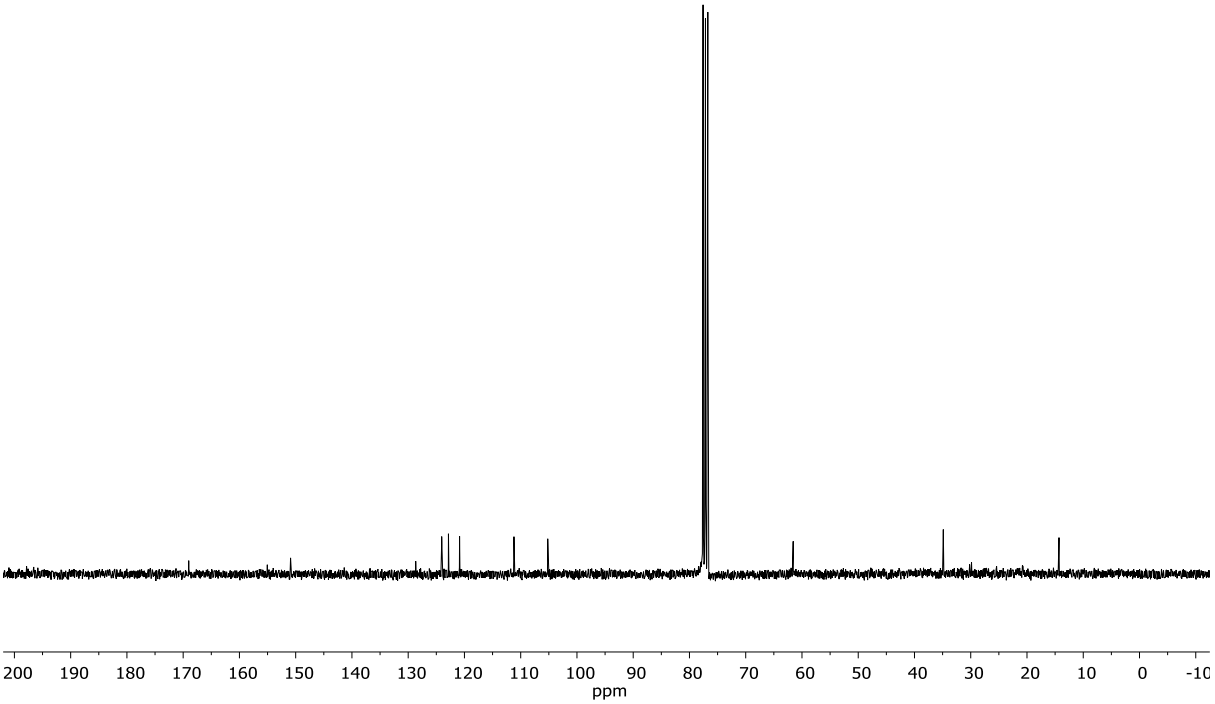
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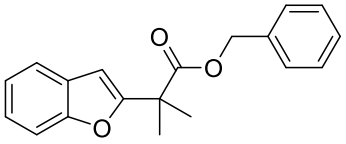
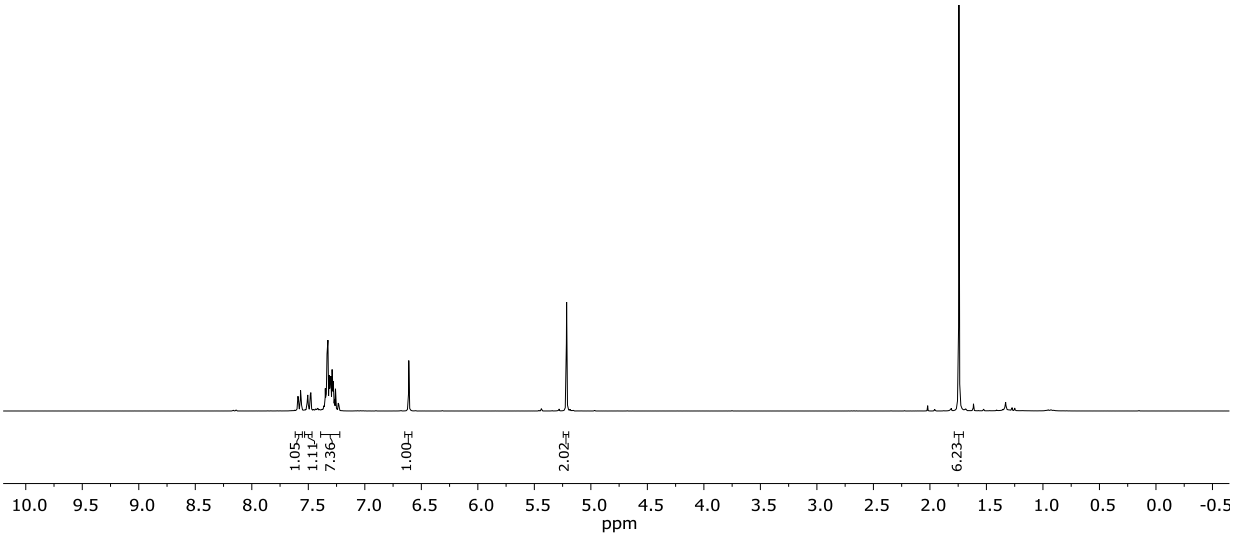
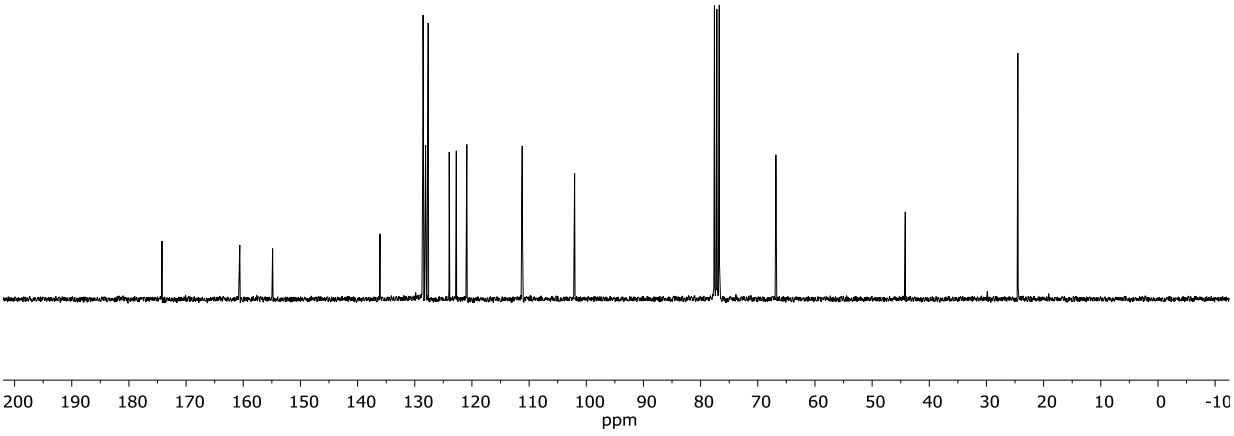


3h


1.05
1.11
7.36
1.00
2.02
6.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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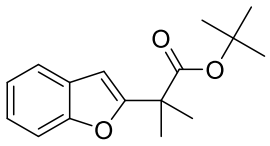
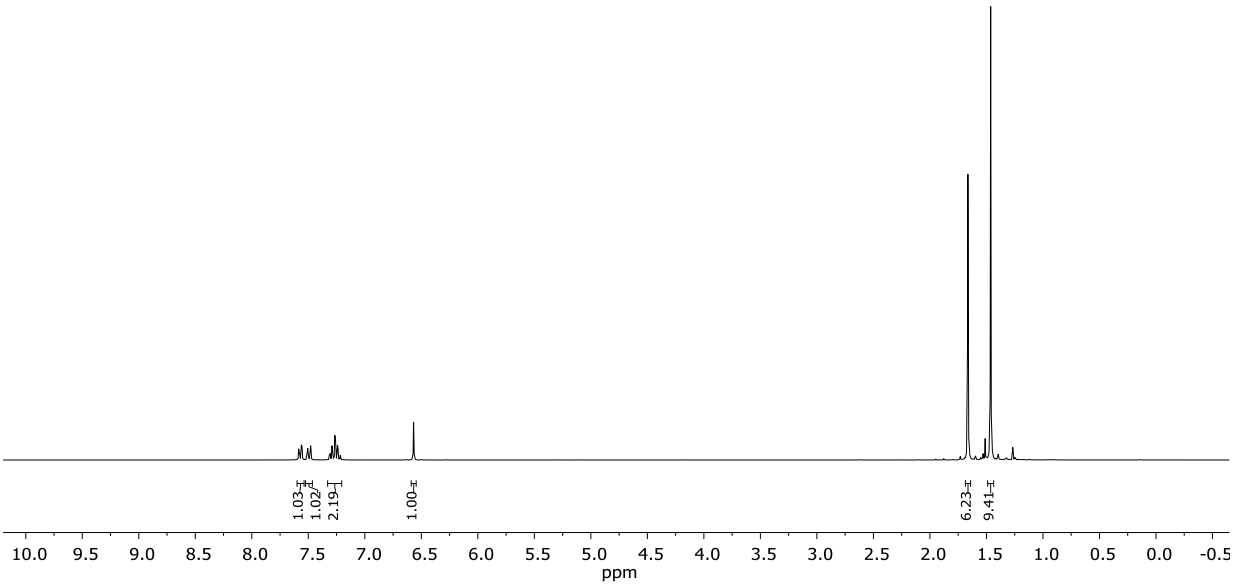
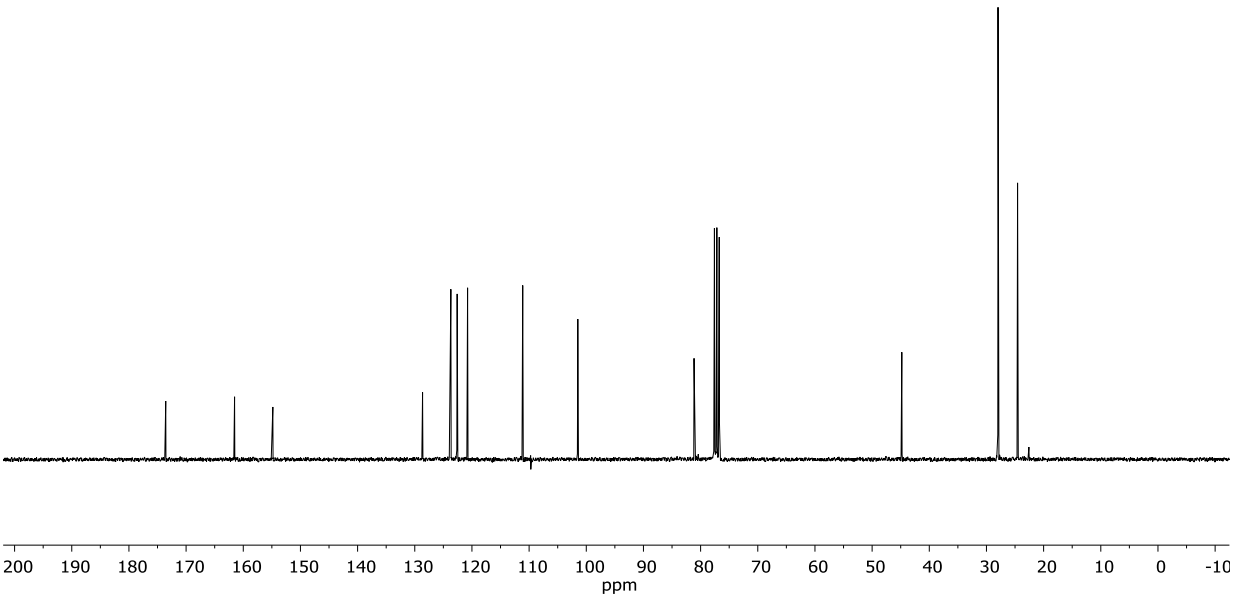
ppm



3i


1.03
1.02
2.19
1.00
6.23
9.41
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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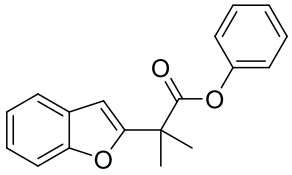
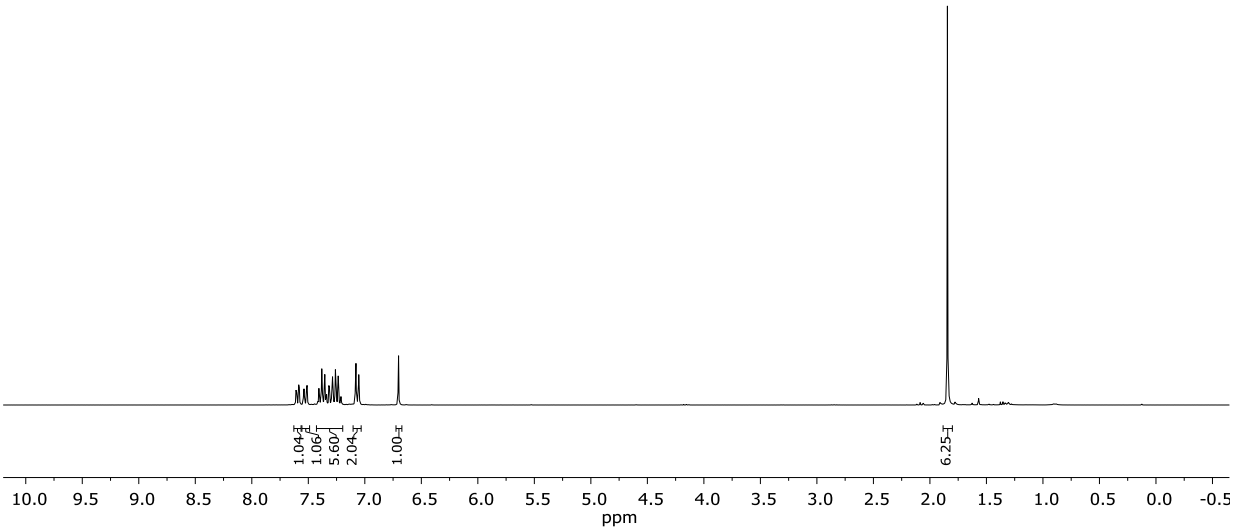
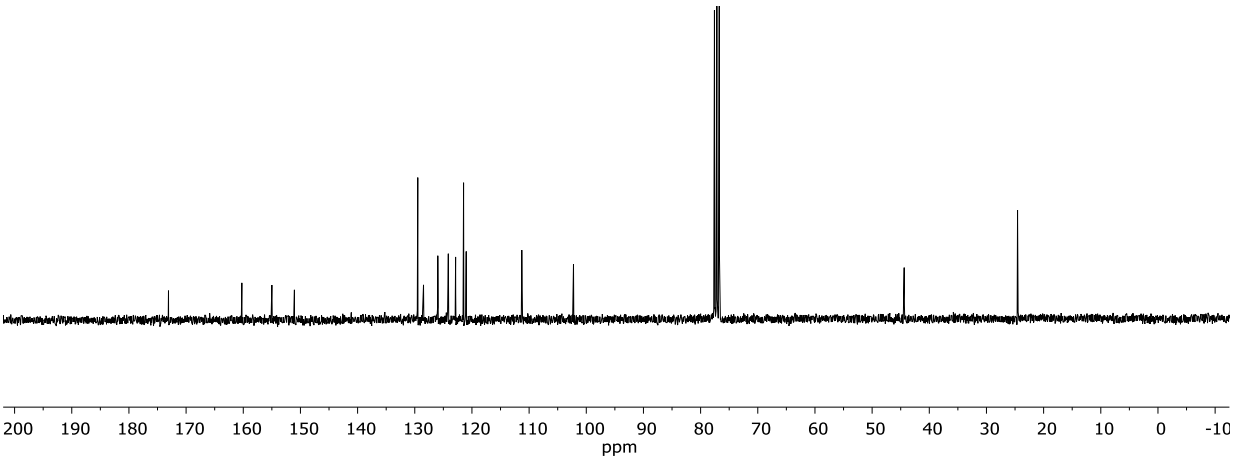
ppm



3j


1.04
1.06
5.60
2.04
1.00
6.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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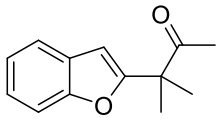
ppm



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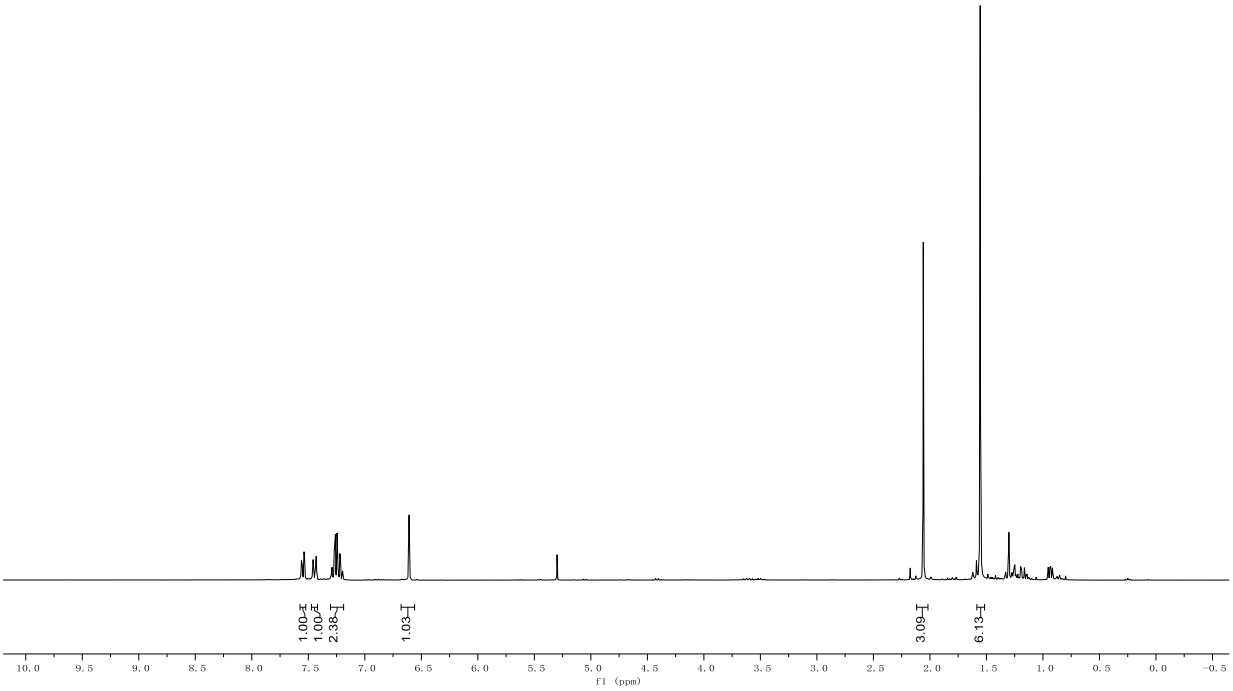
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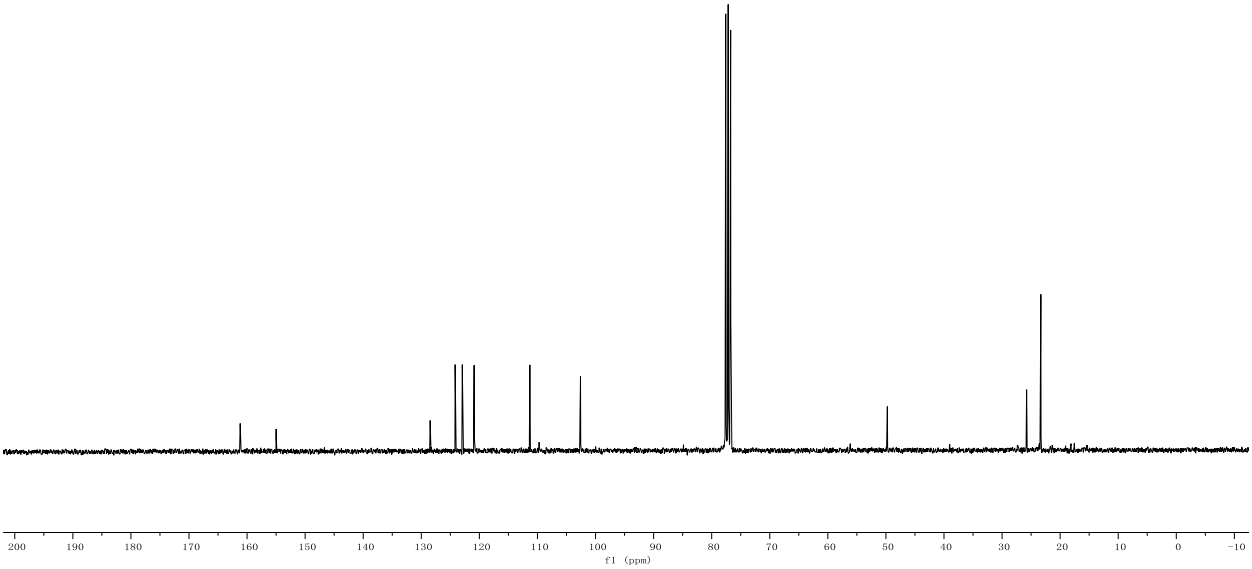
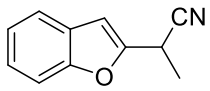
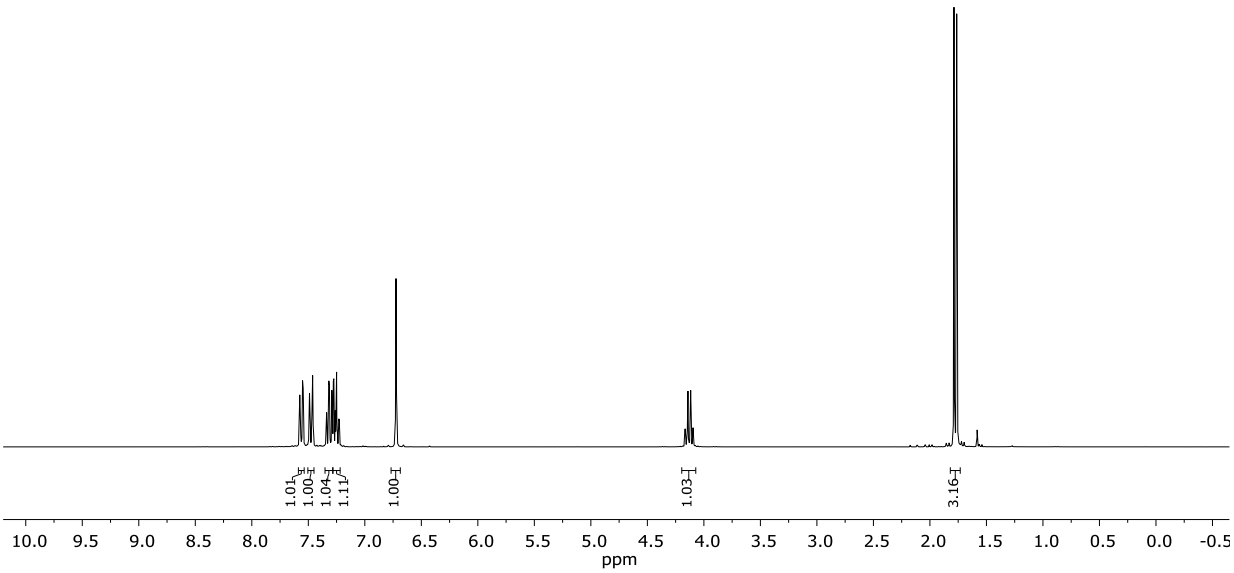
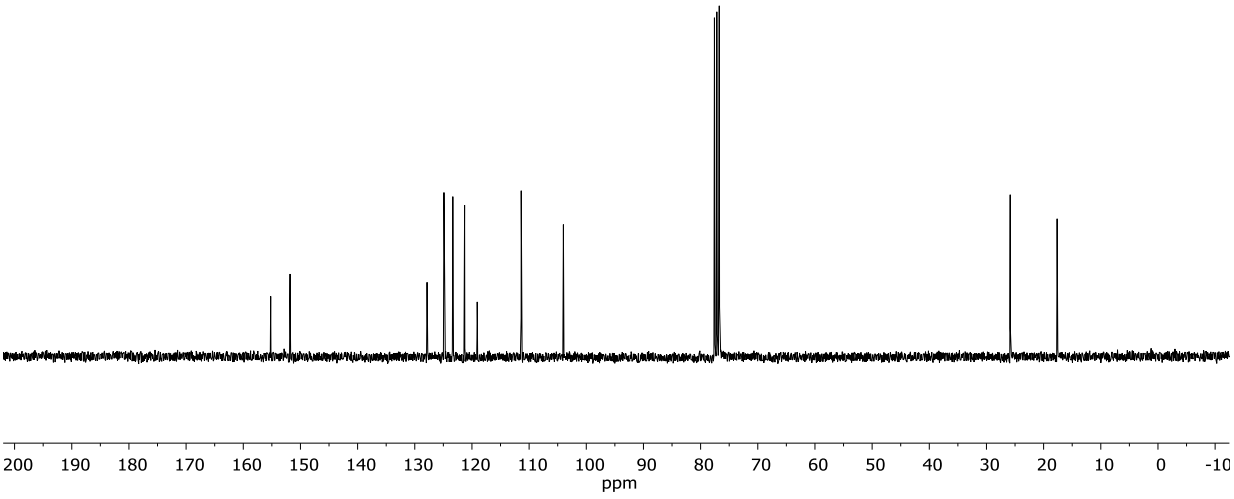
1.00
2.38
1.03
3.09
6.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CN
O

3l


1.01
1.00
1.04
1.11
1.00
1.03
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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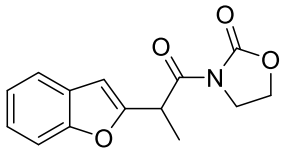
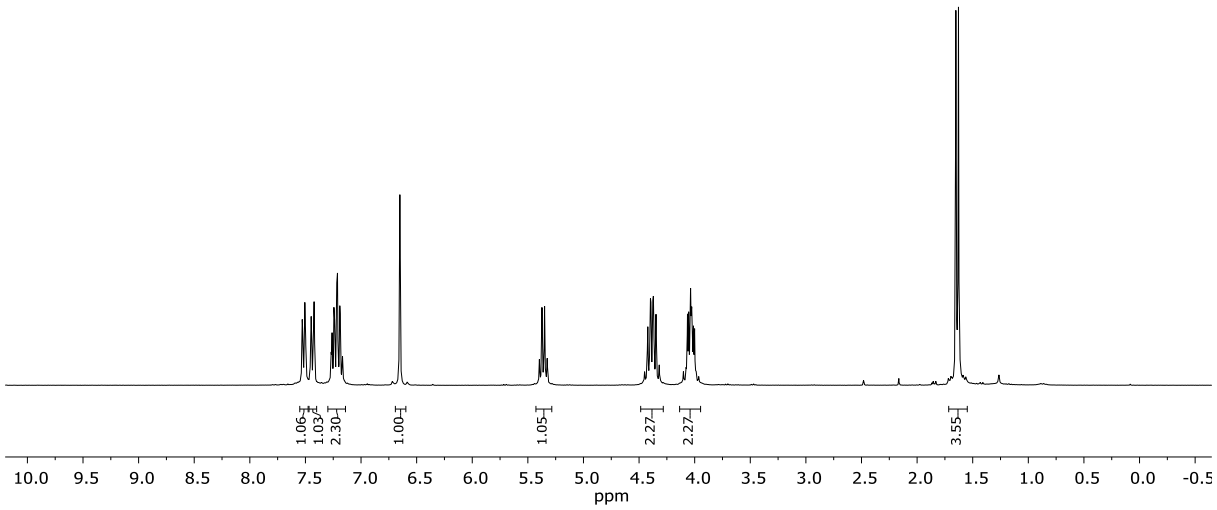
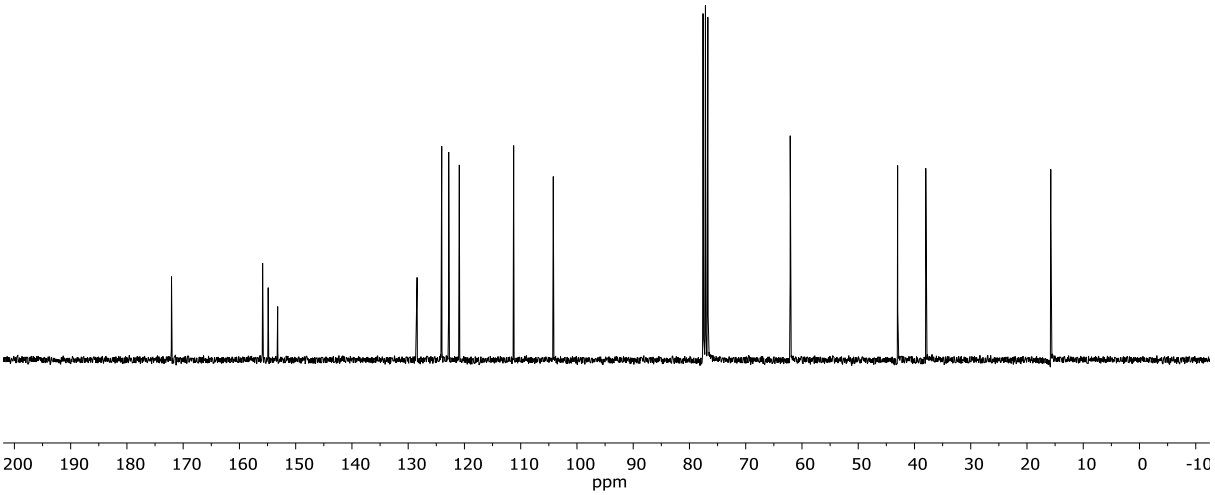
ppm



3m


1.06
1.03
2.30
1.00
1.05
2.27
2.27
3.55
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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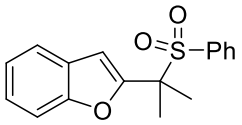
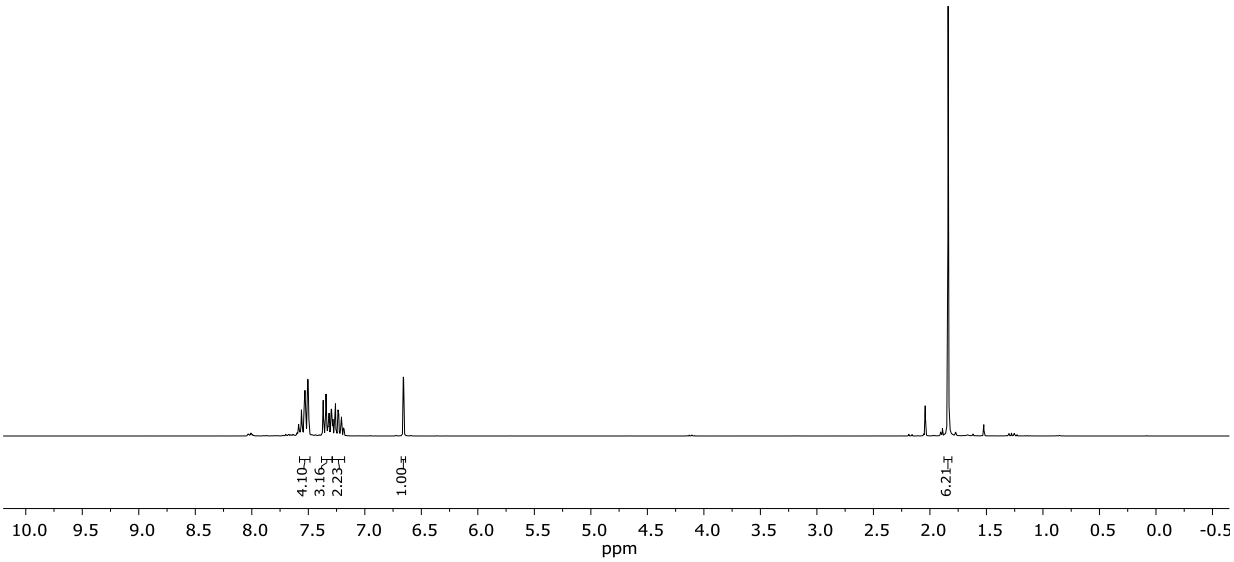
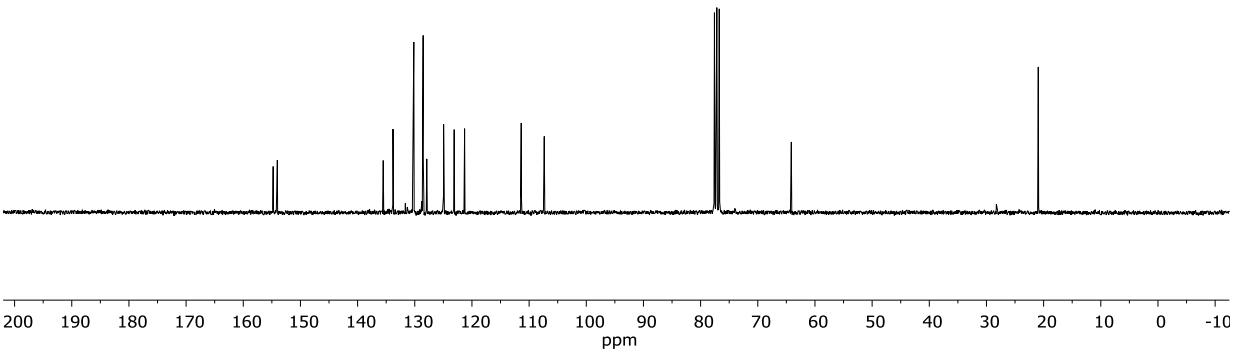
ppm


O
O
S
Ph
O

3o


4.10
3.16
2.23
1.00
6.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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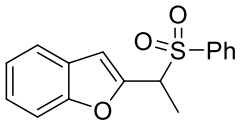
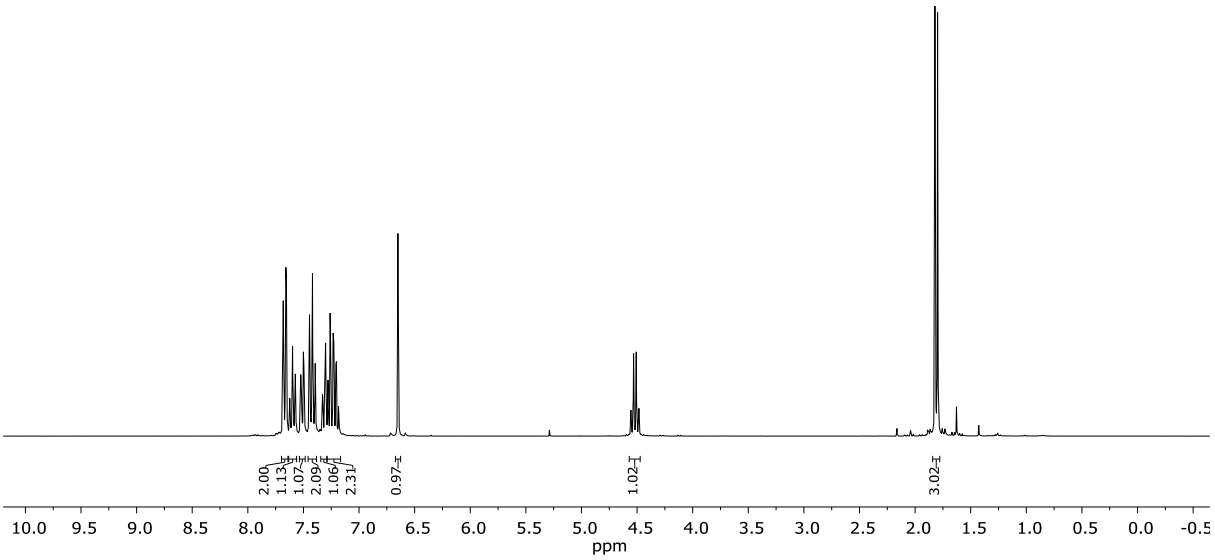
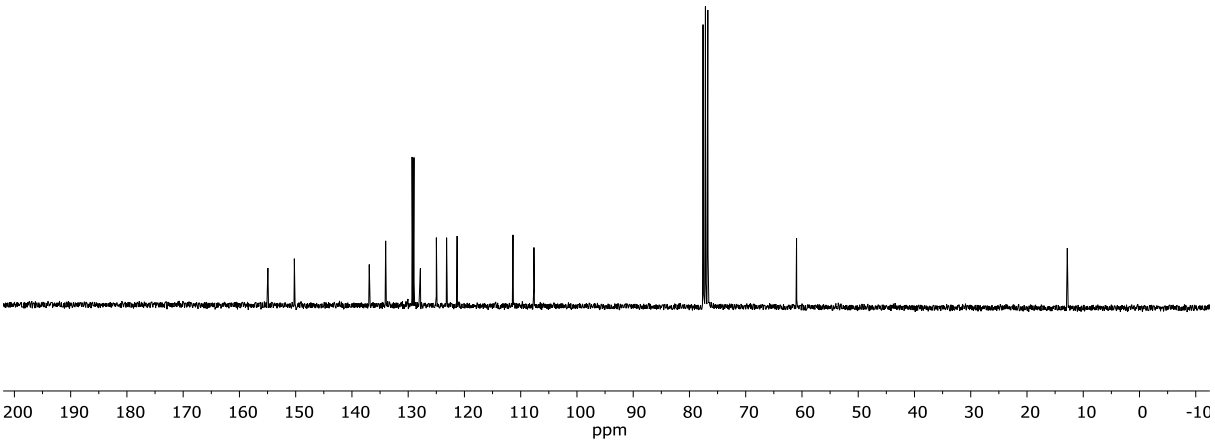
ppm



3p


2.00
1.13
1.07
2.09
1.06
2.31
0.97
1.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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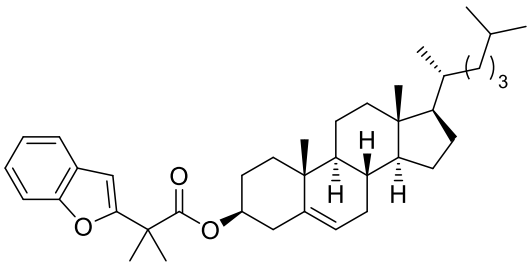
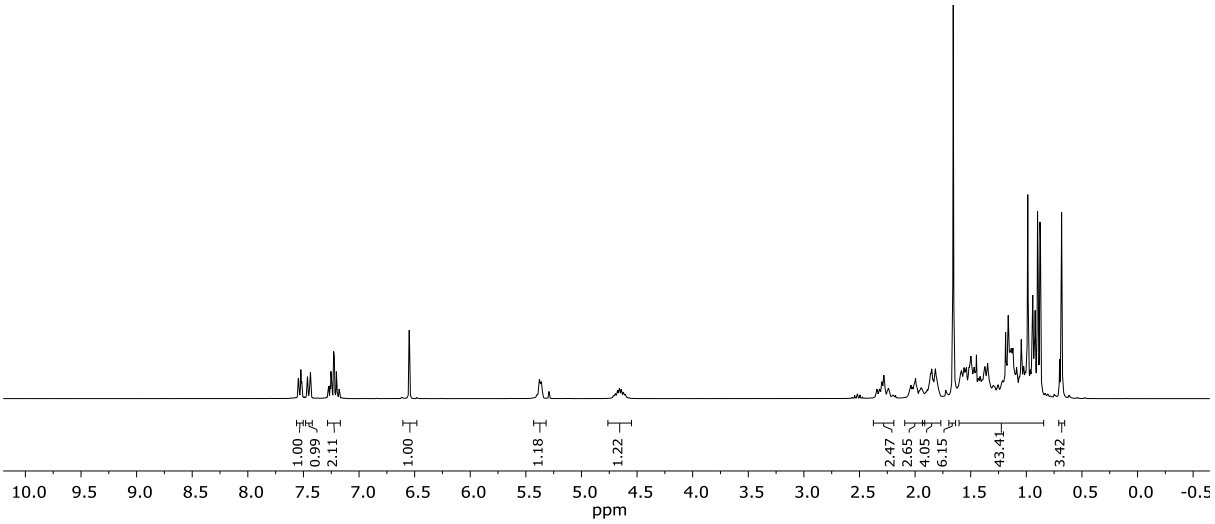
ppm



3q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0.99
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1.00
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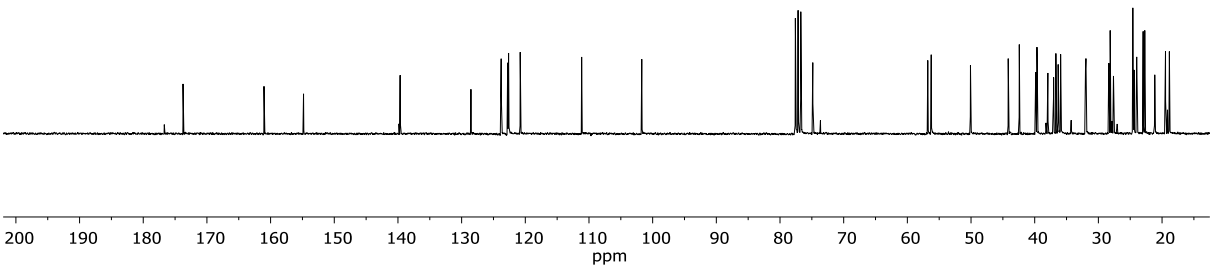
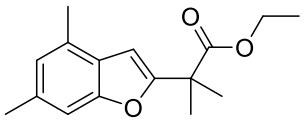
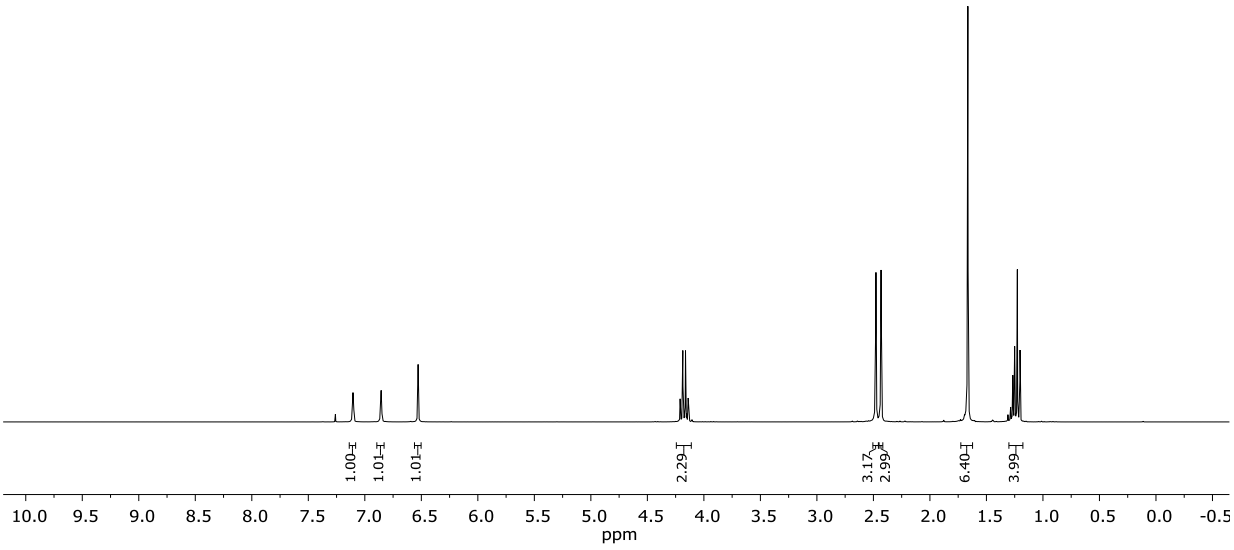
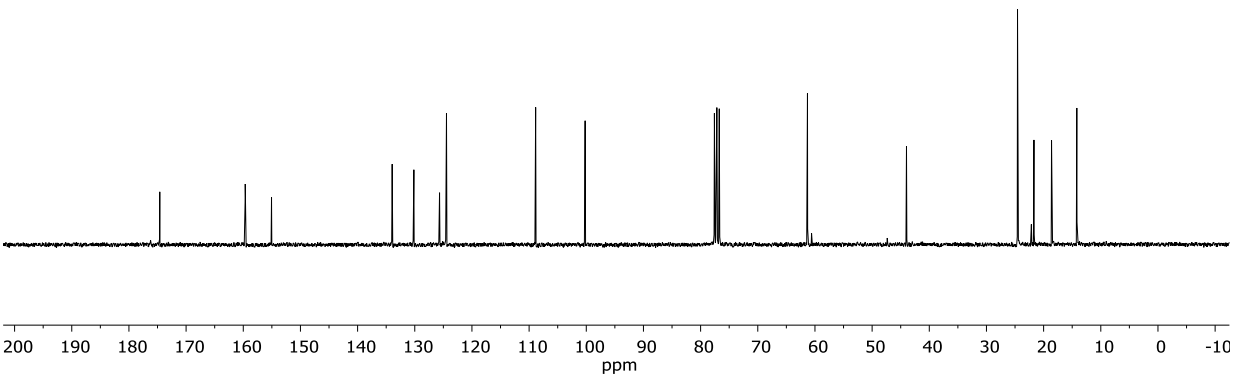
1.22
2.47
2.65
4.05
6.15
43.41
3.42
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm



3r


1.00
1.01
1.01
2.29
3.17
2.99
6.40
3.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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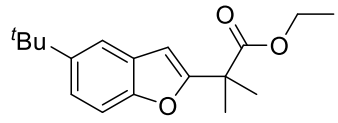
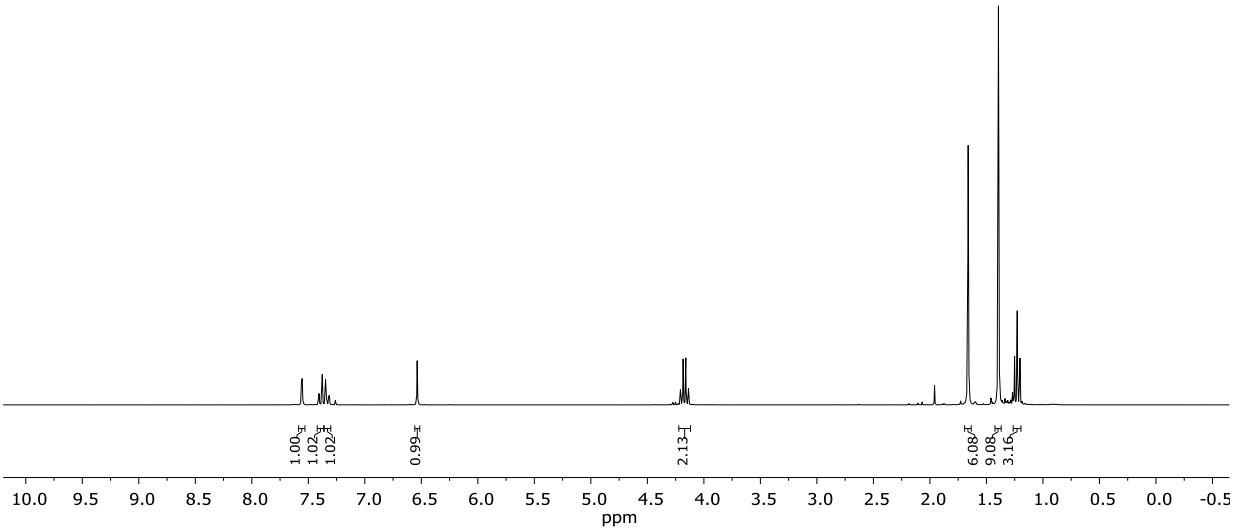
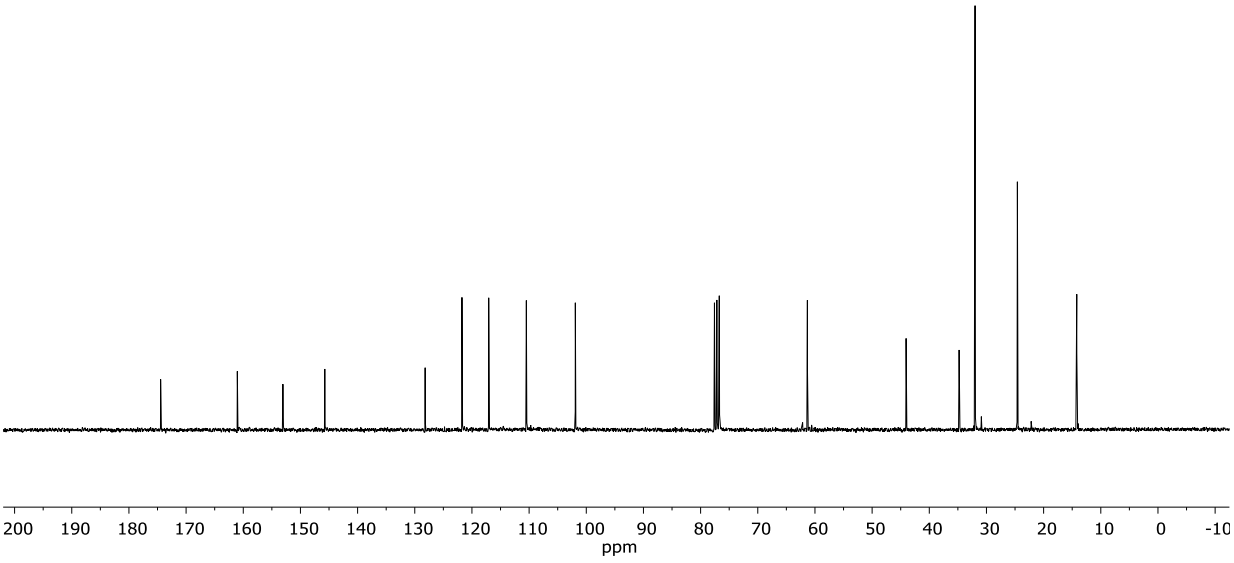
ppm


tBu
O
O
O

3s


1.00
1.02
1.02
0.99
2.13
6.08
9.08
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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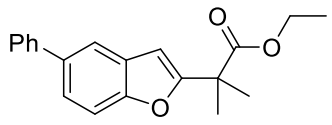
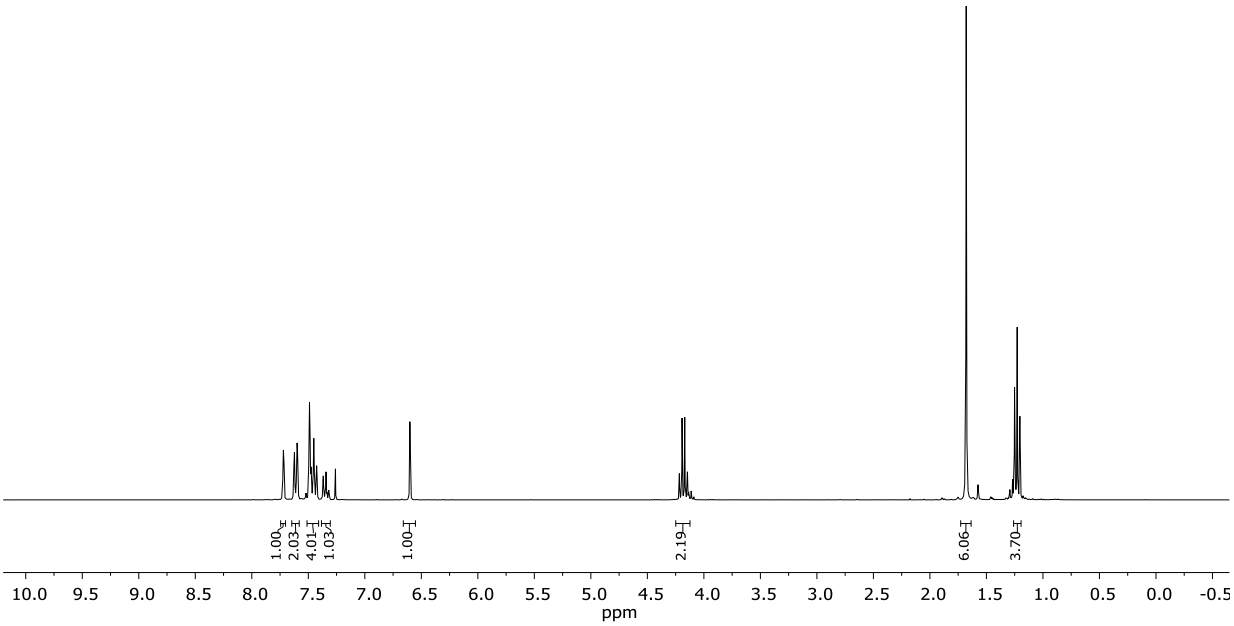
ppm


Ph
O
O
O

3t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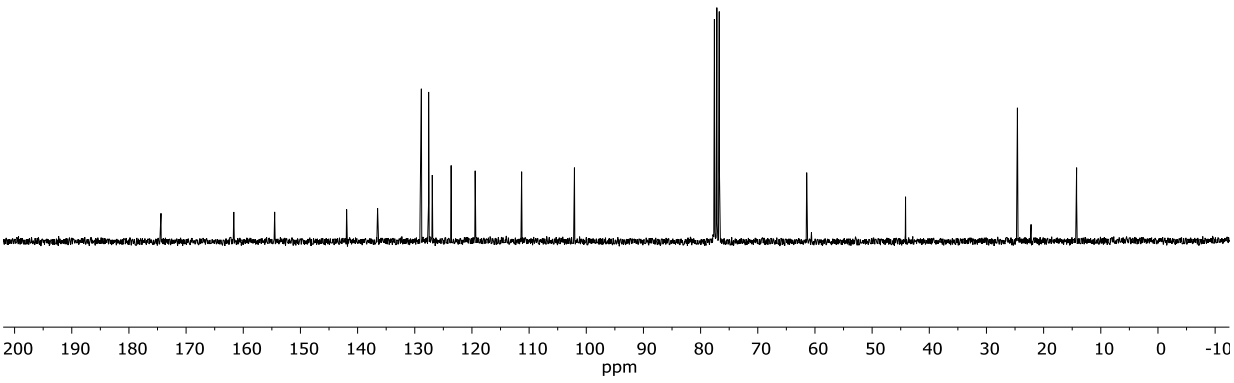
2.03
4.01
1.03
1.00
2.19
6.06
3.70
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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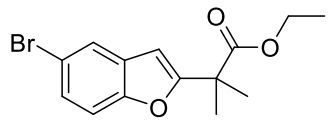
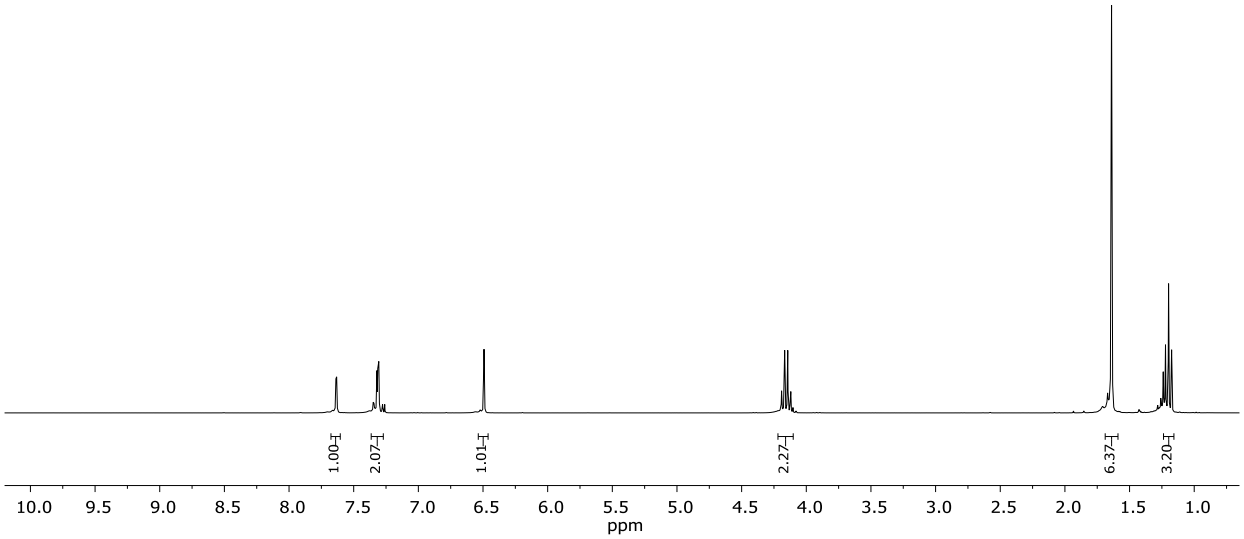
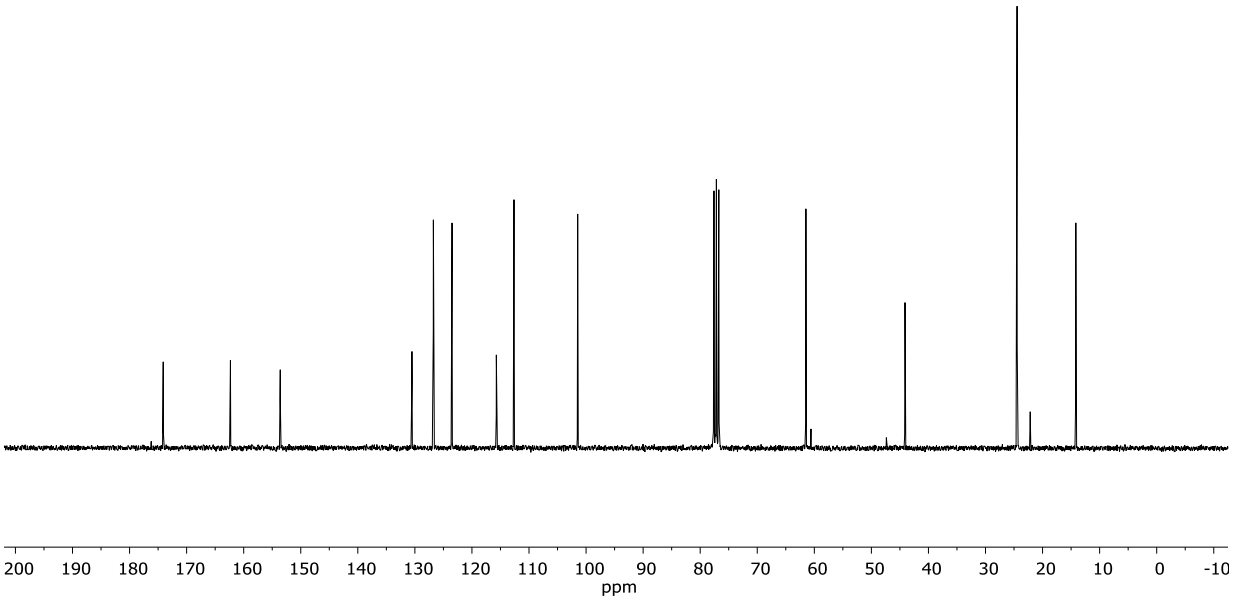
ppm


Br
O
O
O

3u


1.00
2.07
1.01
2.27
6.37
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm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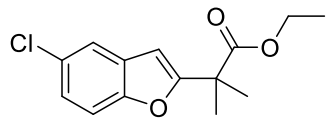
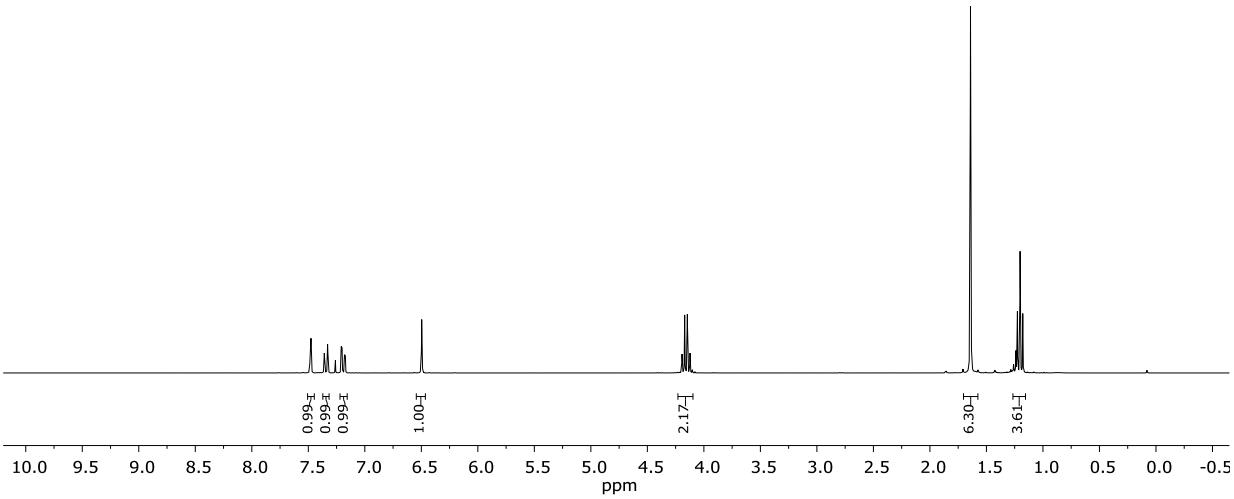
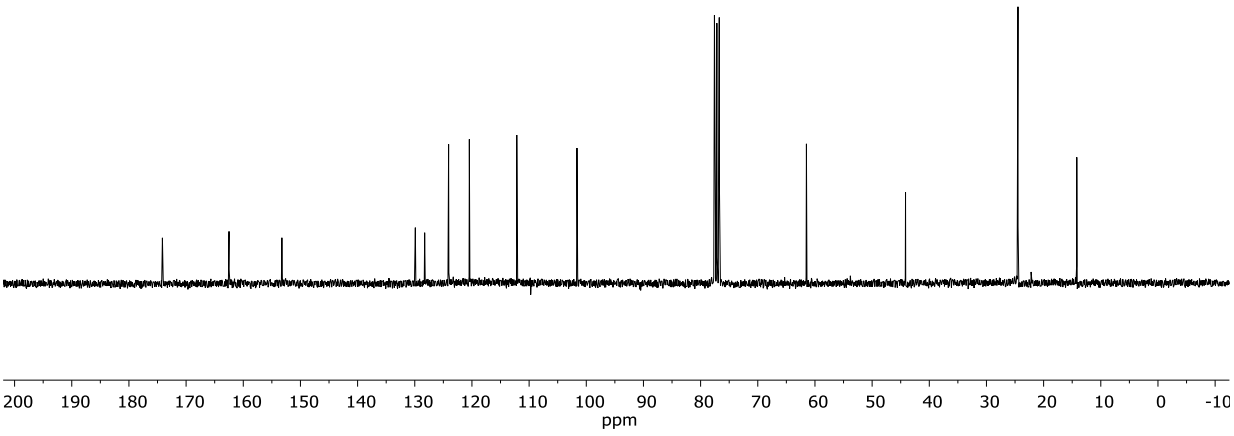
ppm


Cl
O
O
O

3v


0.99
0.99
0.99
1.00
2.17
6.30
3.61
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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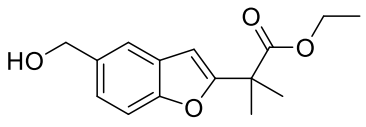
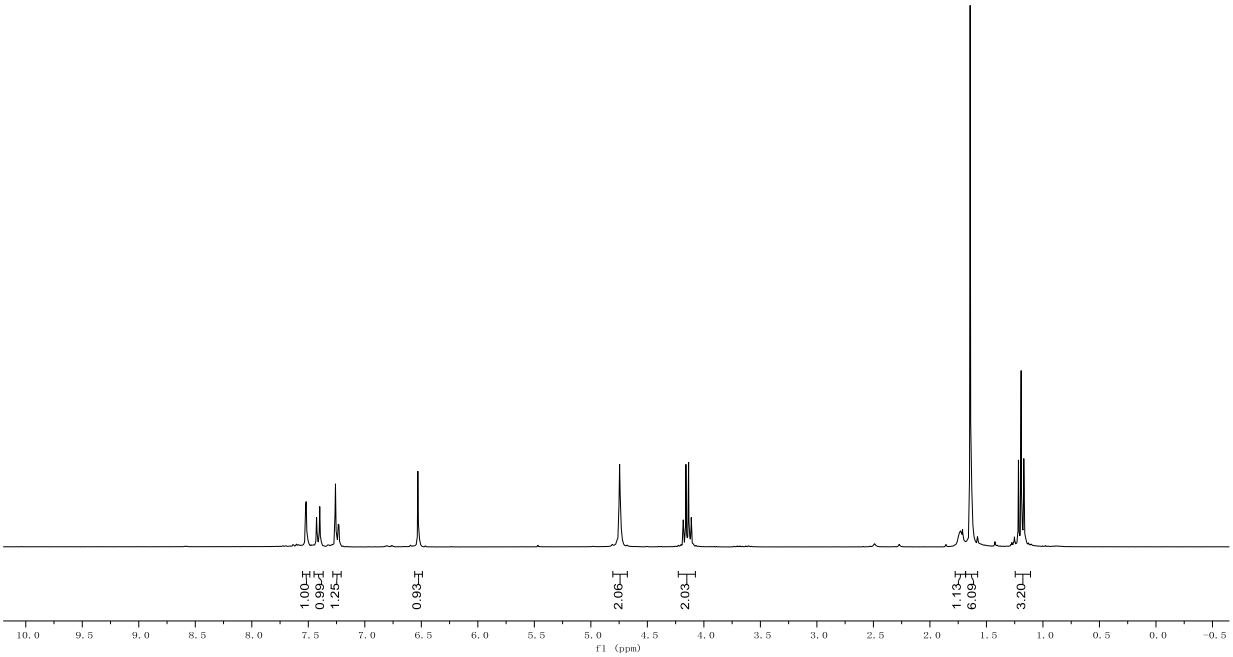
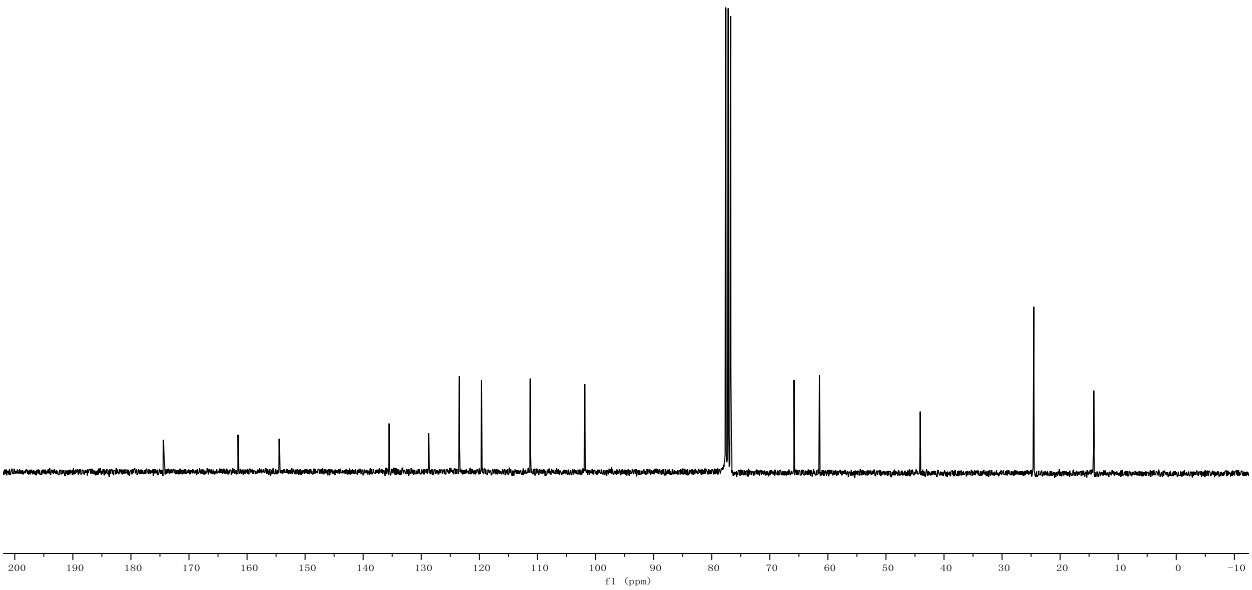
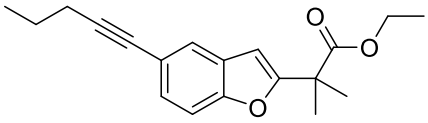
ppm



3w







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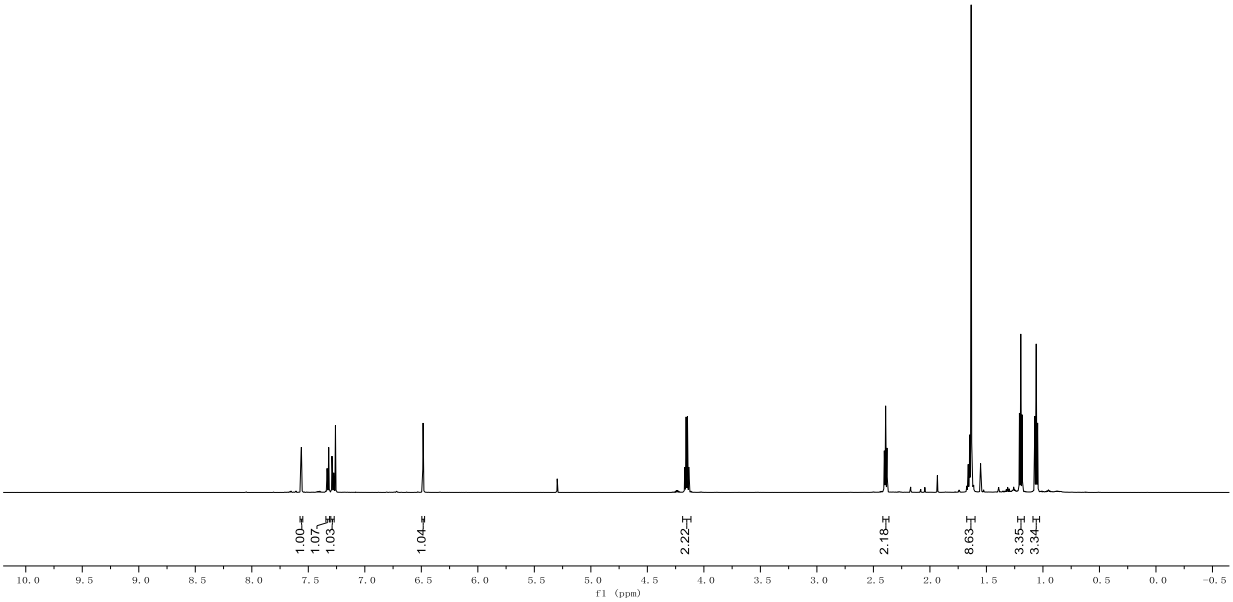

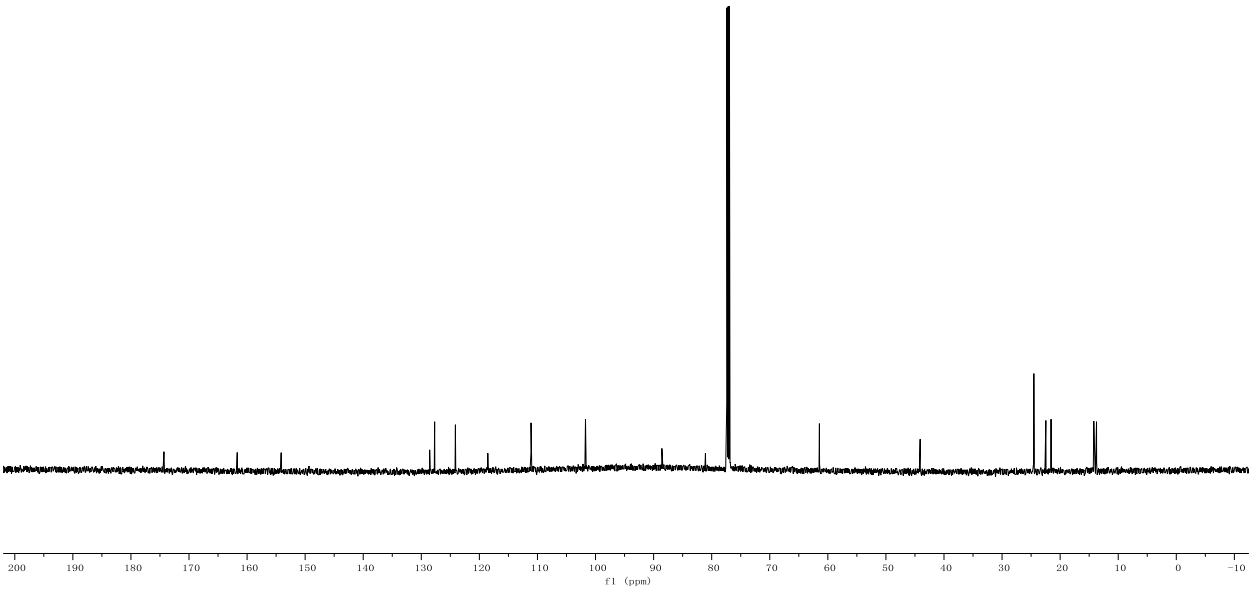

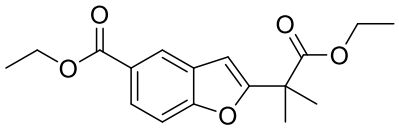

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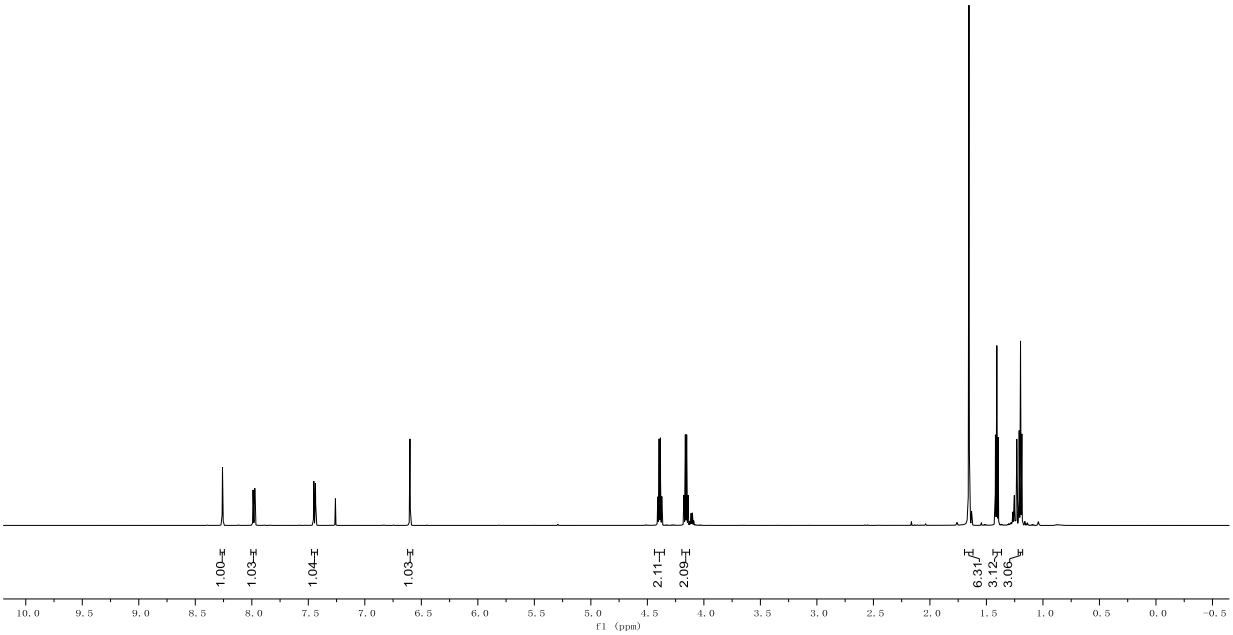
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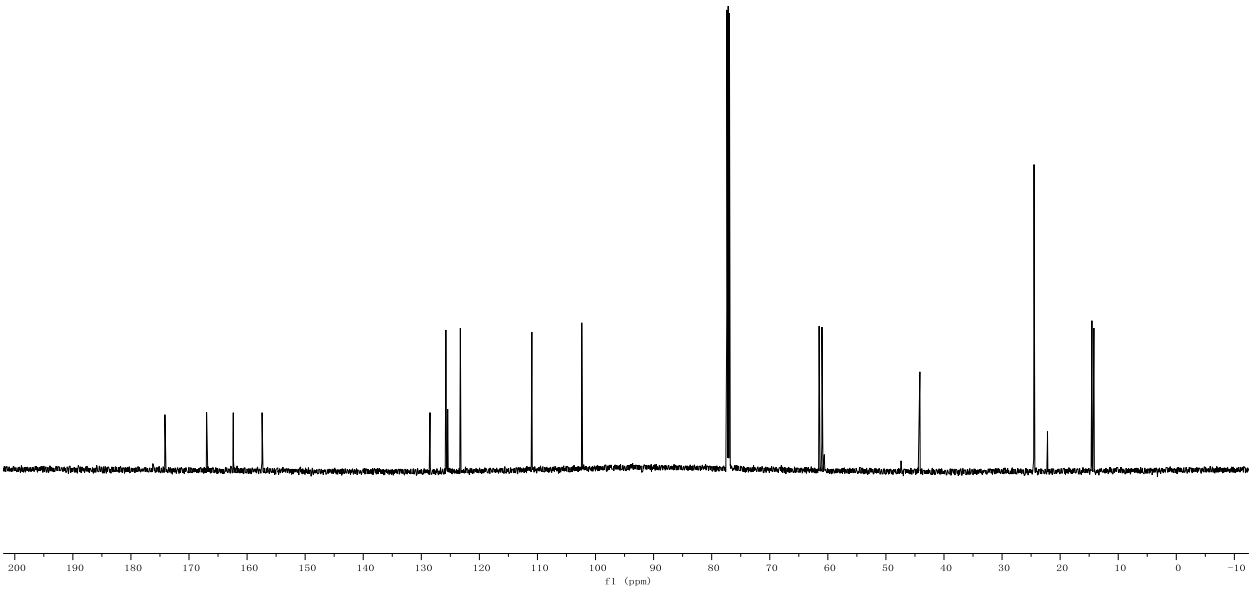
1.03
1.04
1.03
2.11
2.09
6.31
3.12
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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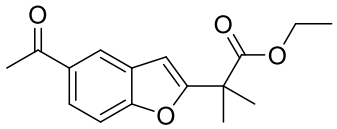
f1 (ppm)



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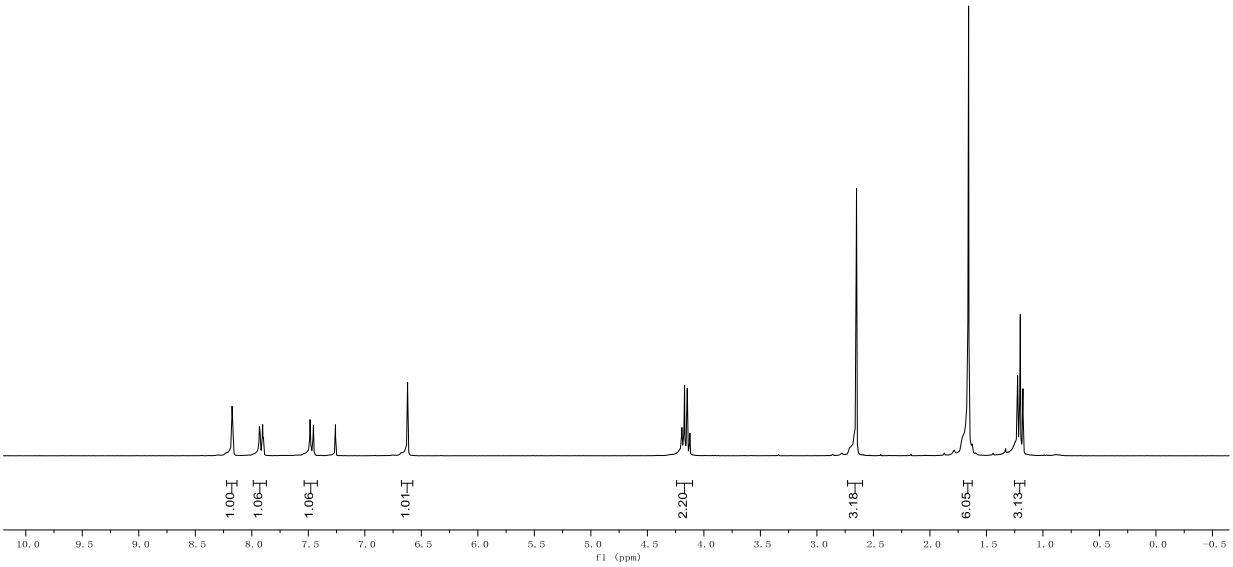
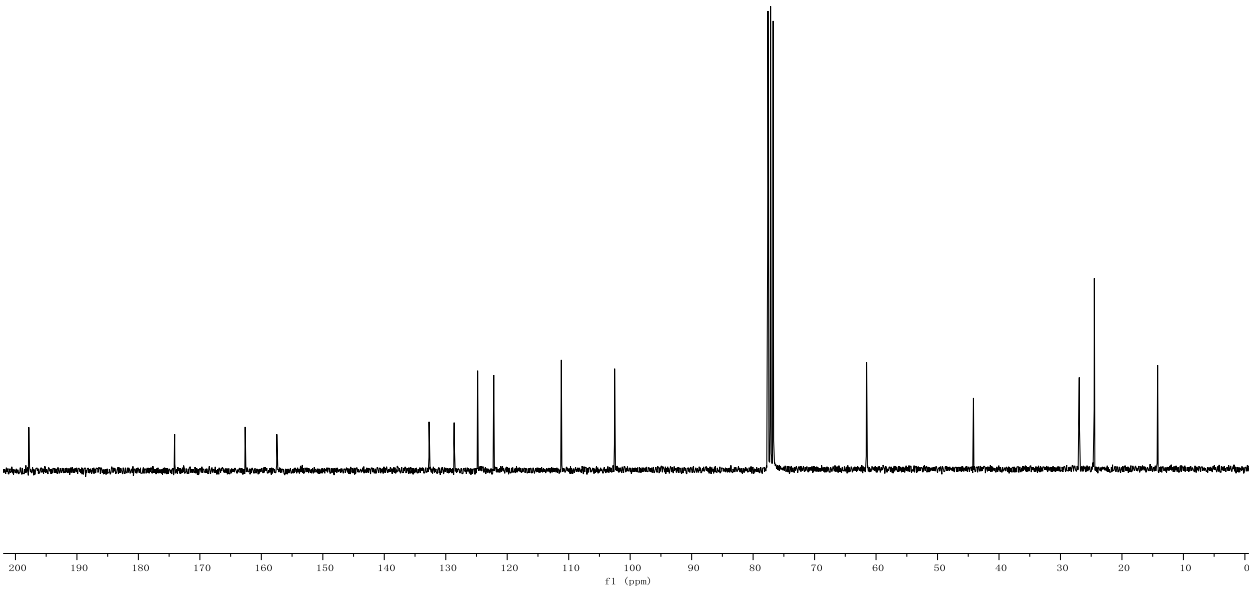

1.00
1.06
1.06
1.01
2.20
3.18
6.05
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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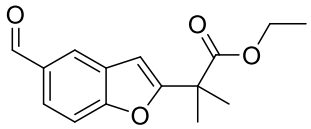
f1 (ppm)



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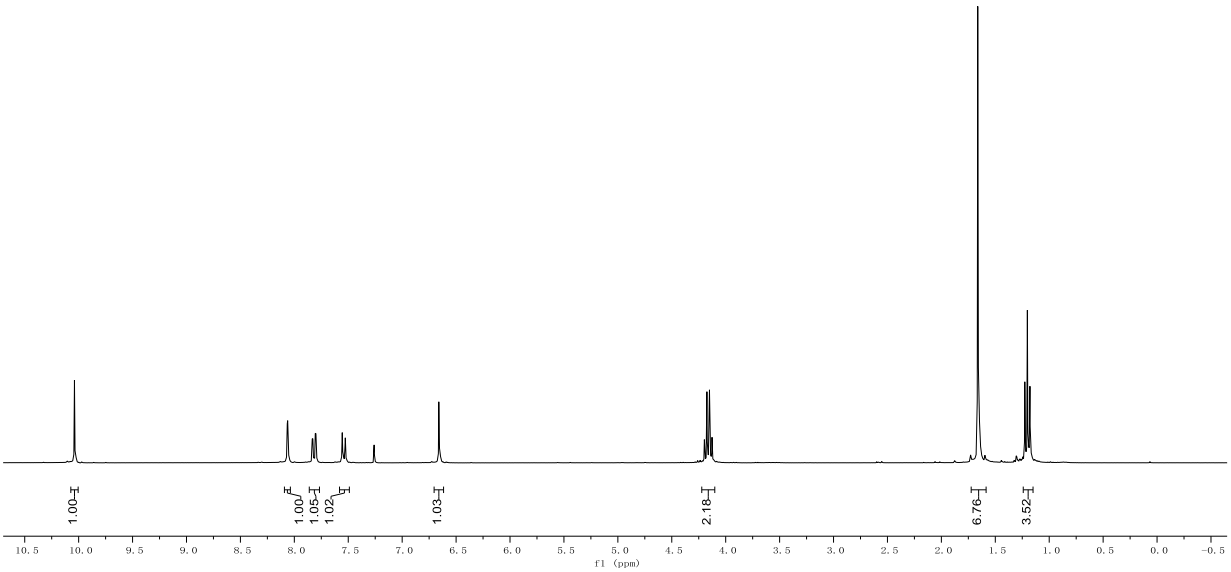

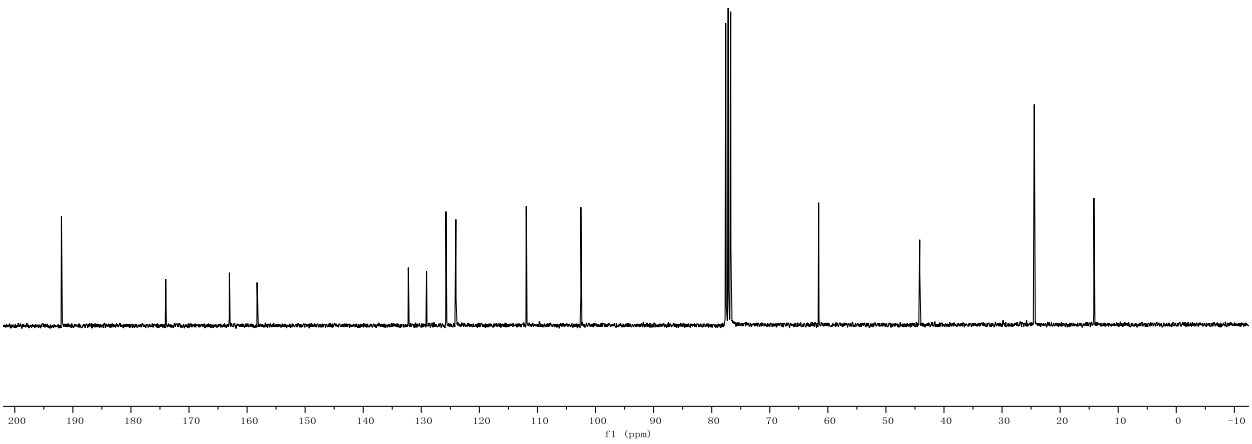

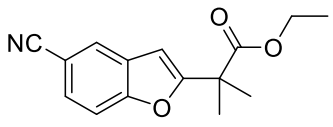

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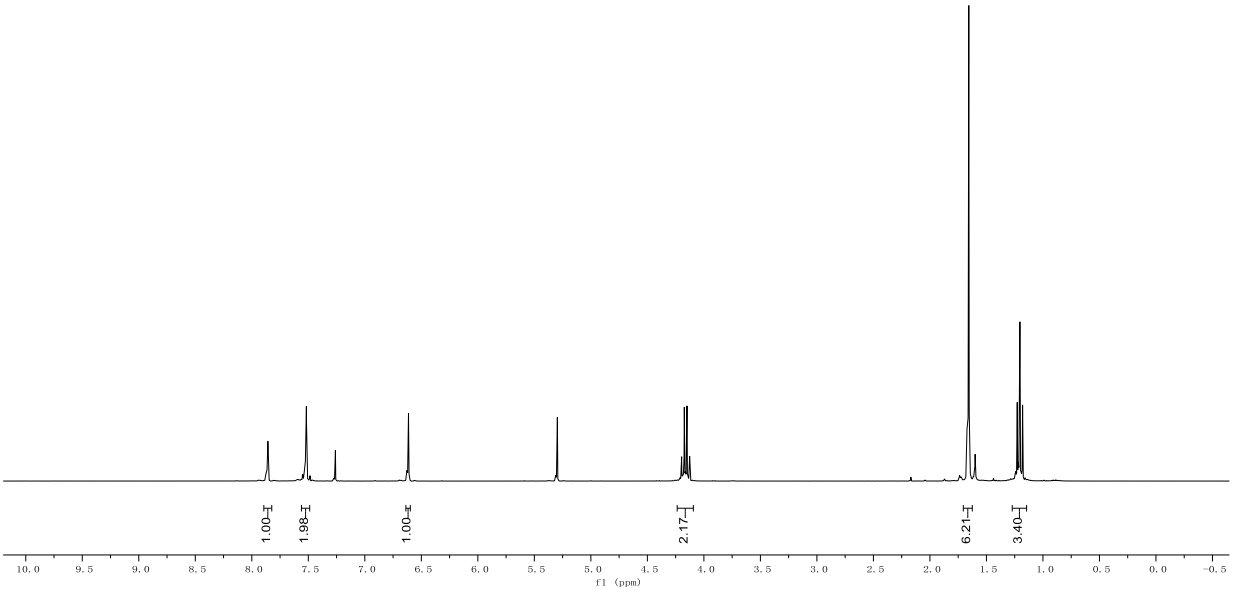

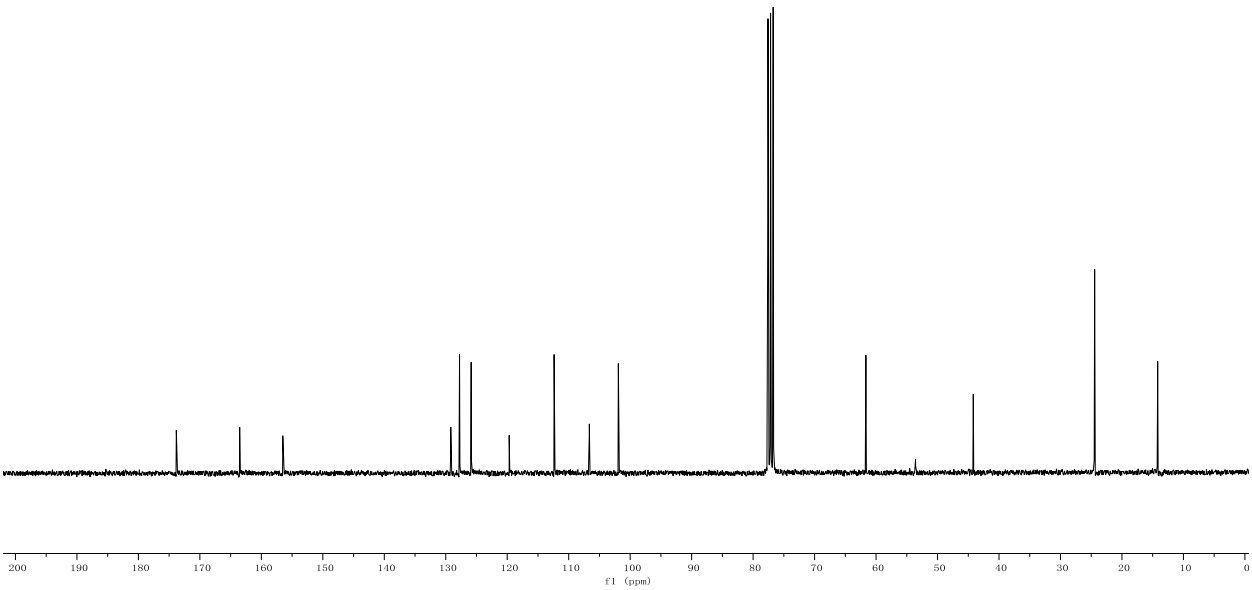

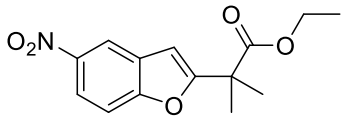

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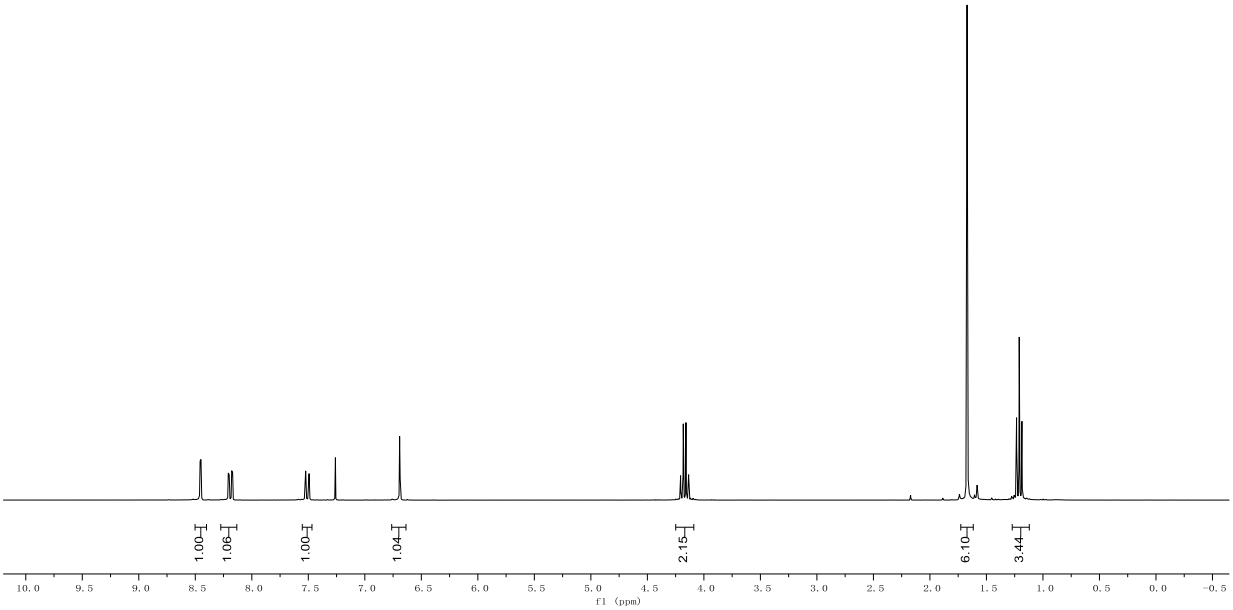

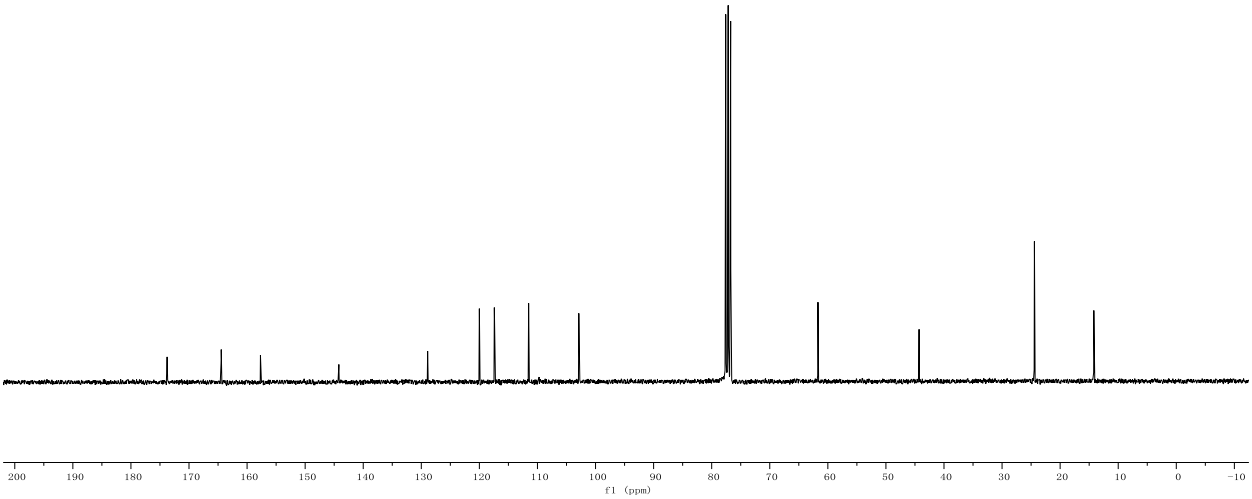

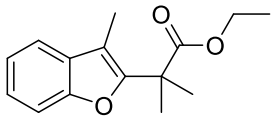

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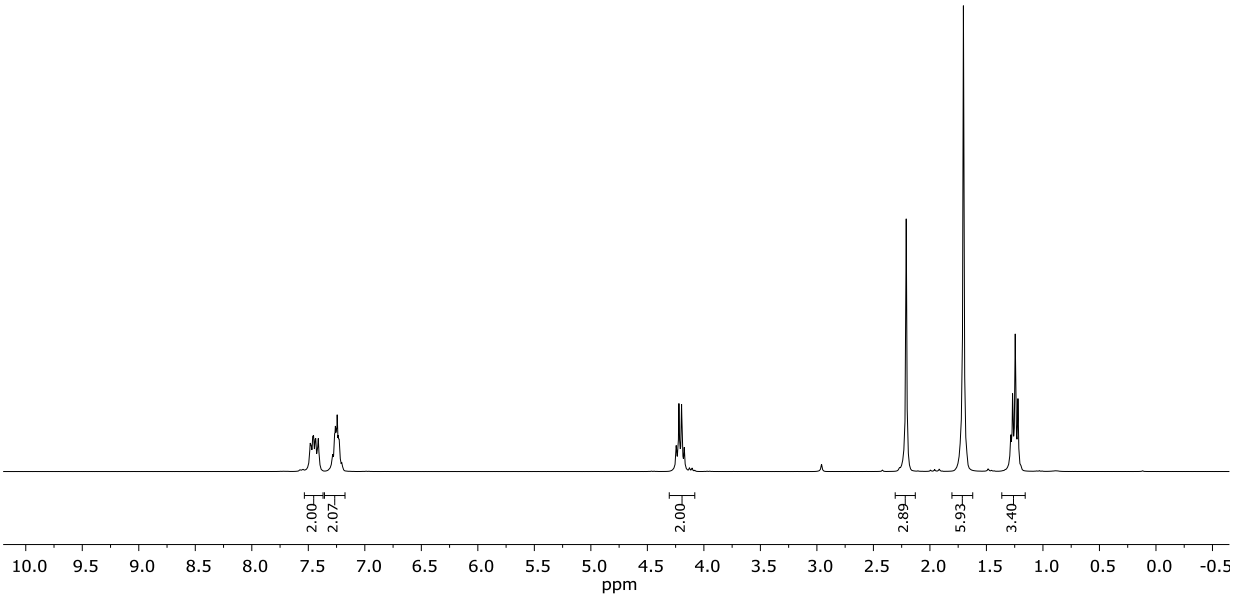
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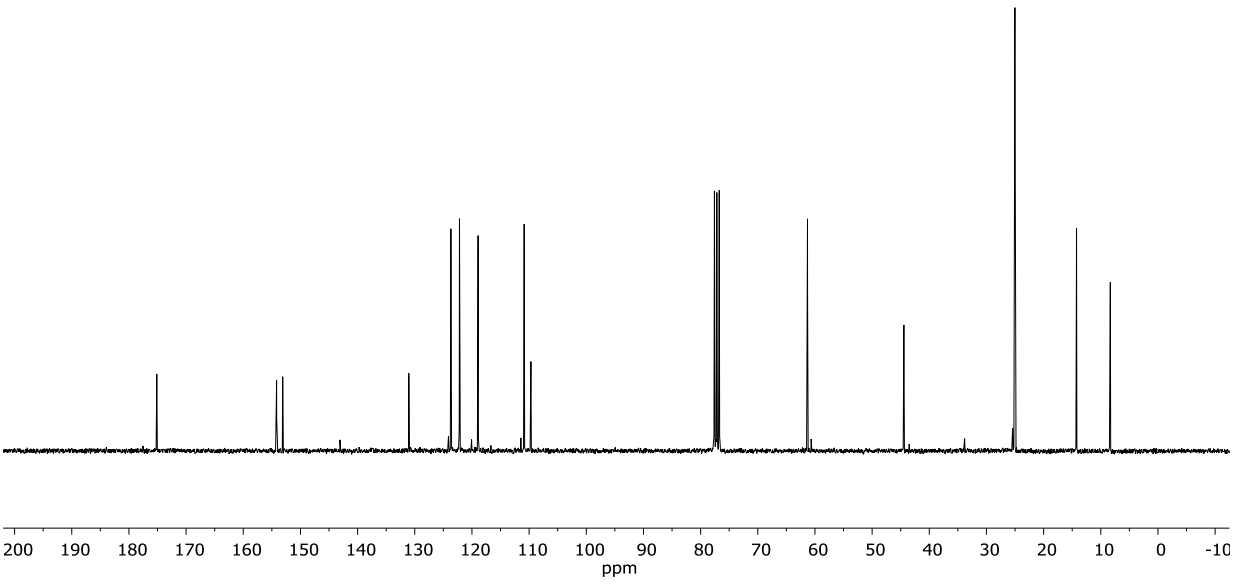
2.07
2.00
2.89
5.93
3.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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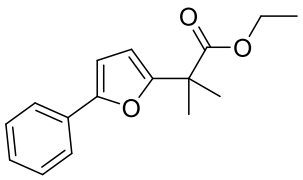
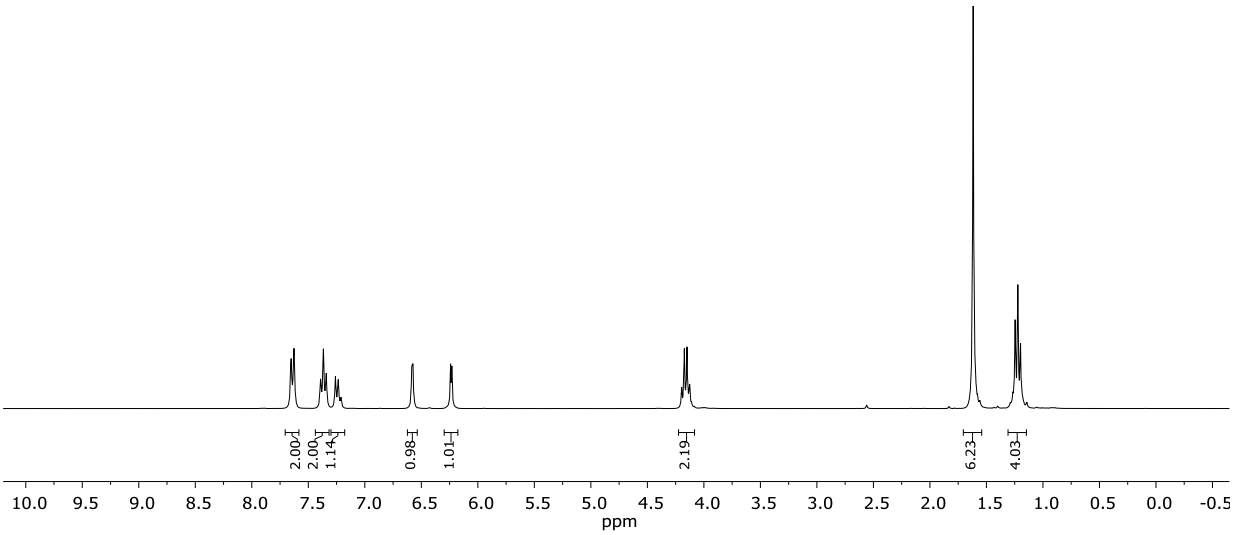
ppm



5a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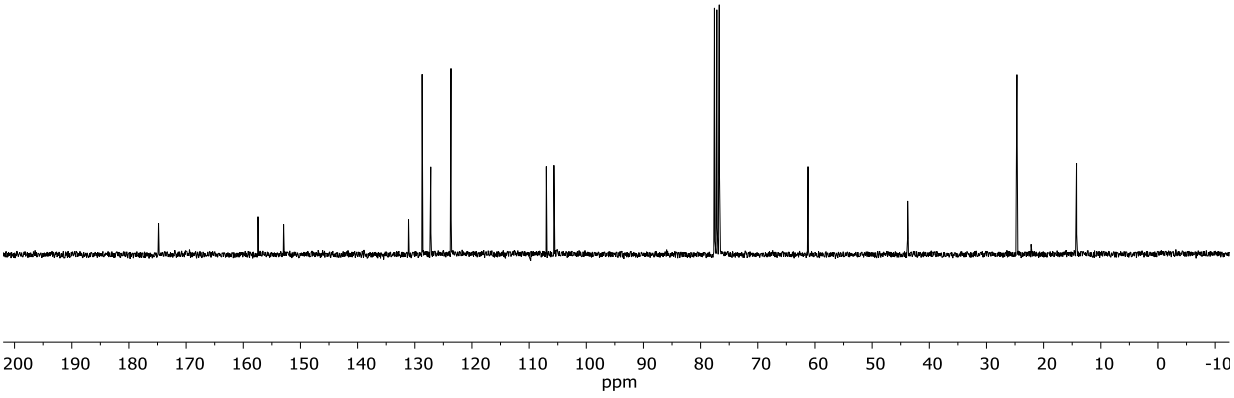
2.00
1.14
0.98
1.01
2.19
6.23
4.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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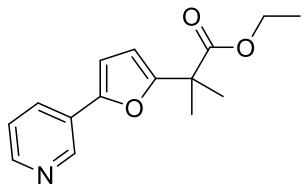
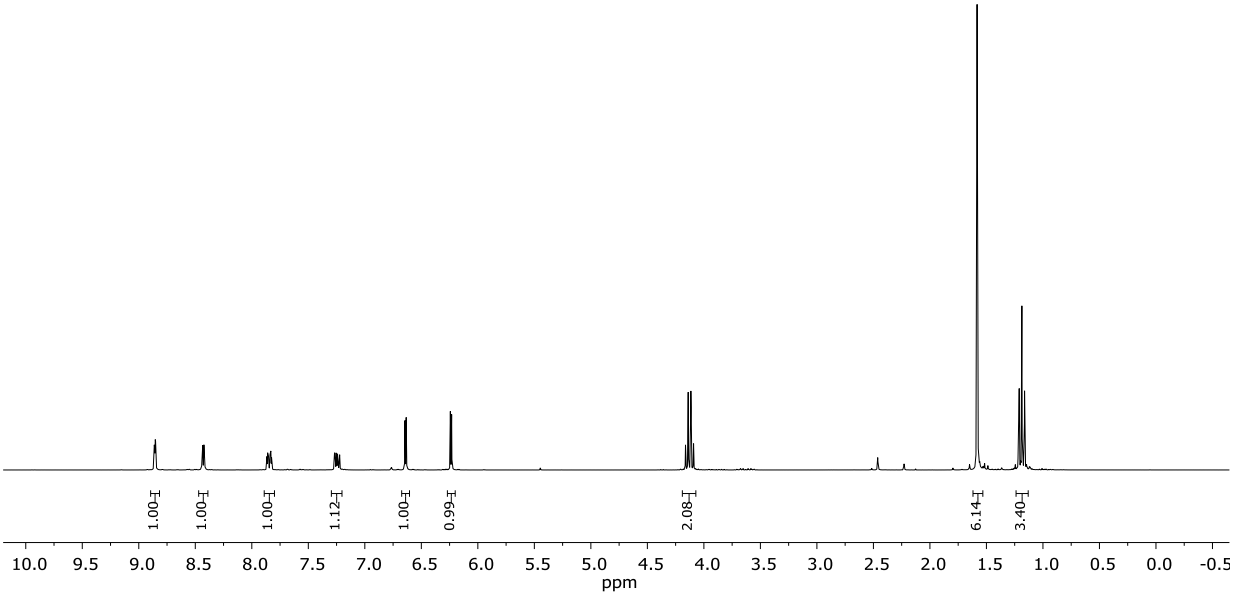
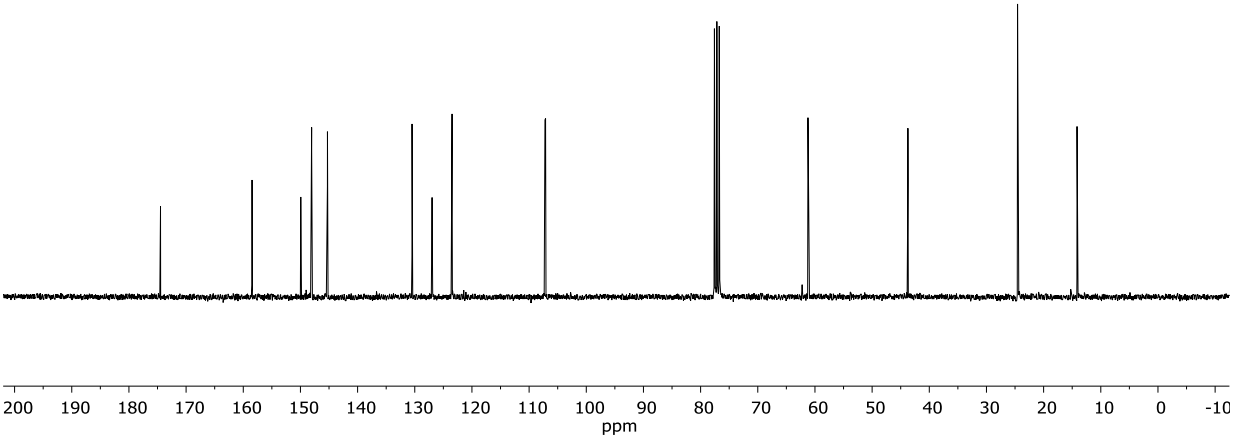
ppm



5b


1.00
1.00
1.00
1.12
1.00
0.99
2.08
6.14
3.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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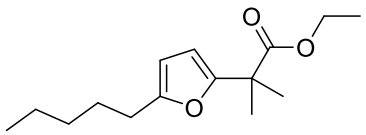
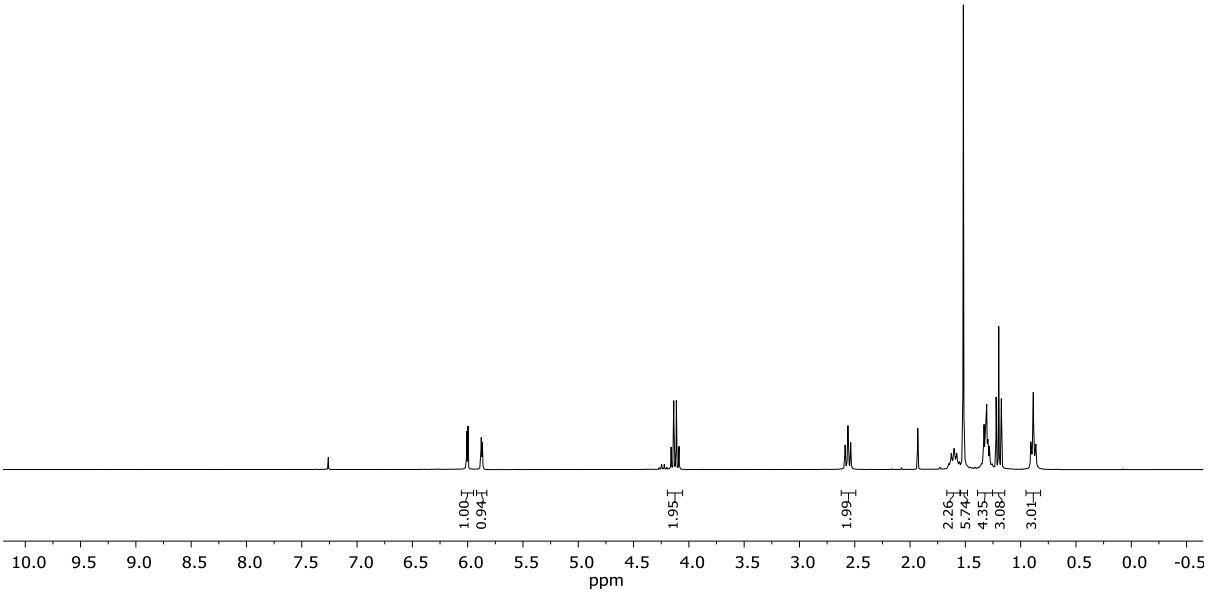
ppm



5c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0.94
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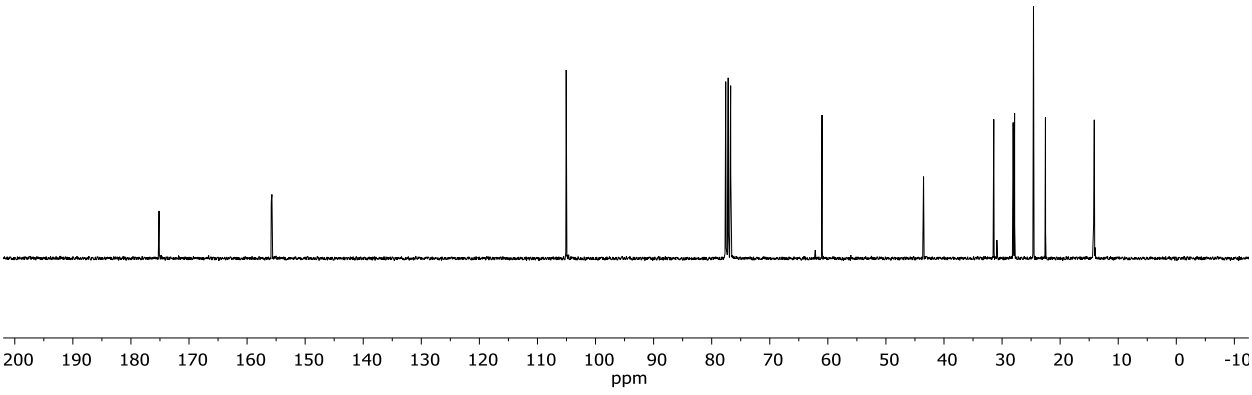
1.99
2.26
5.74
4.35
3.08
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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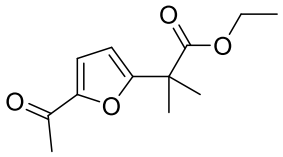
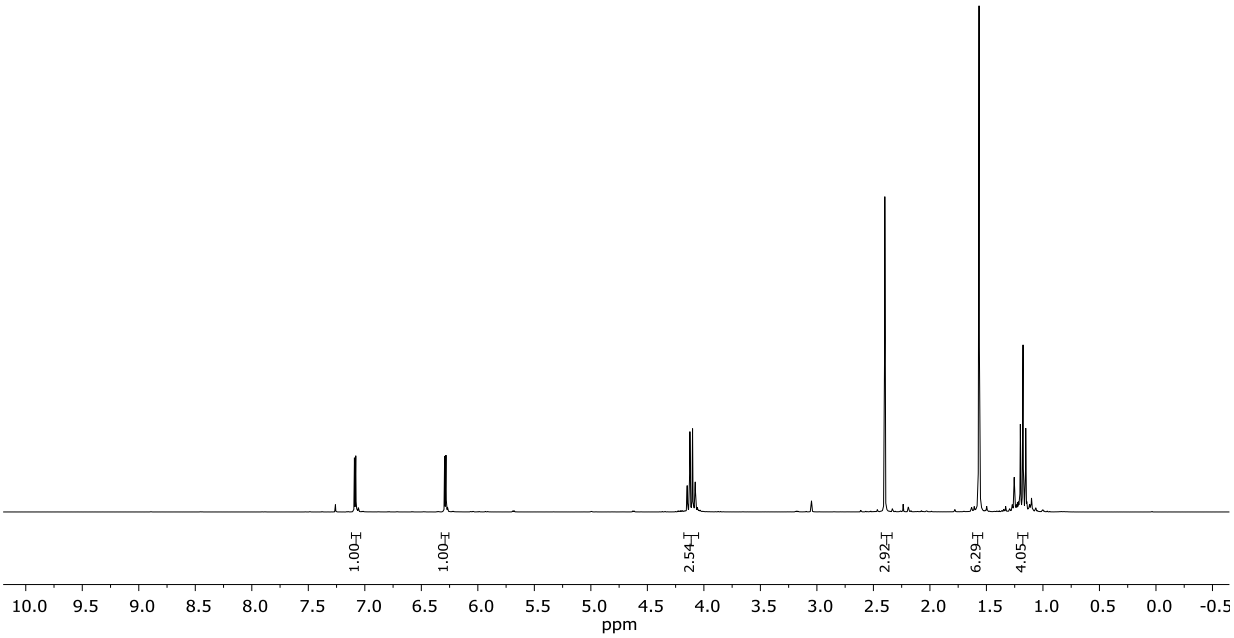
ppm



5d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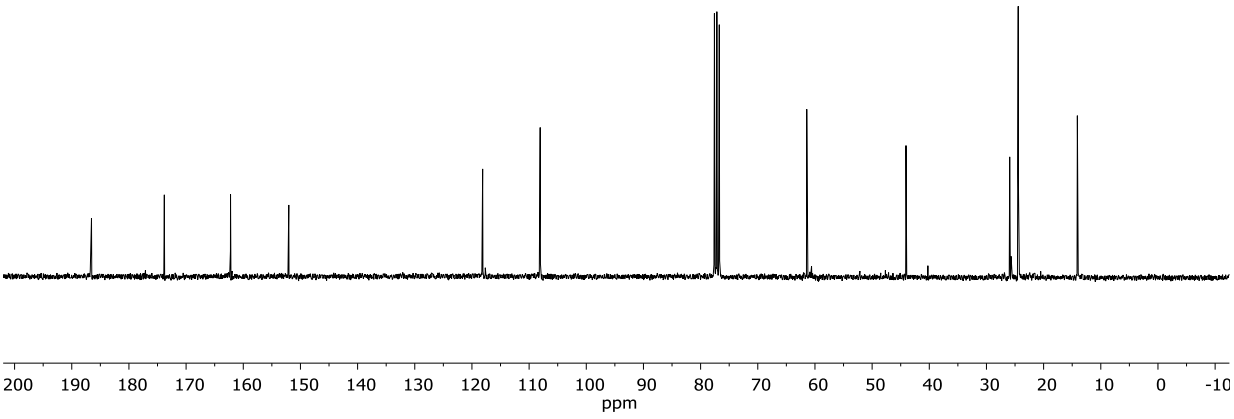
1.00
2.54
2.92
6.29
4.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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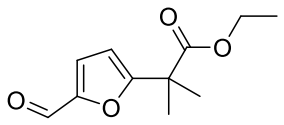
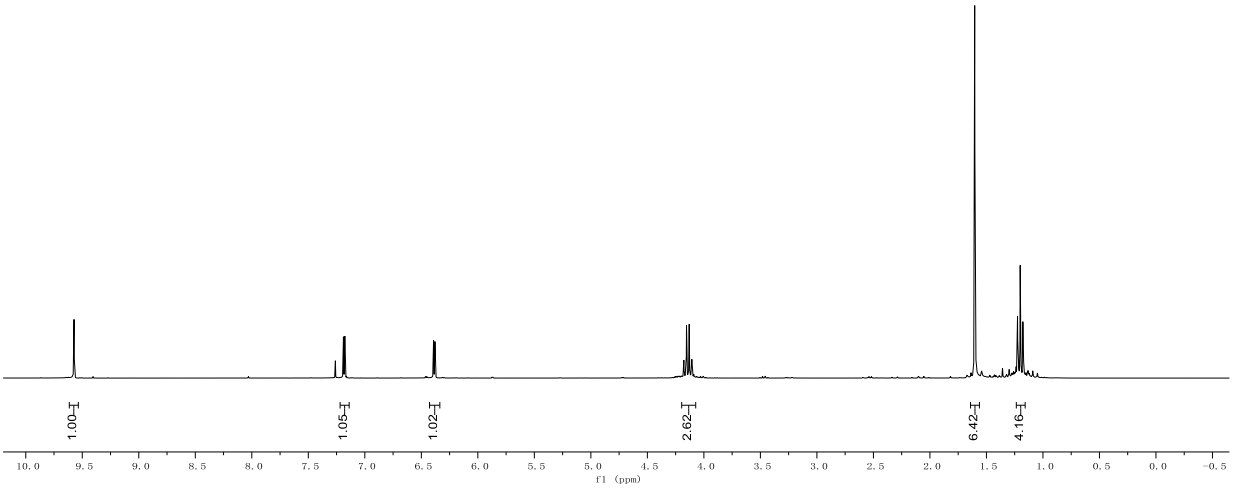
ppm



5e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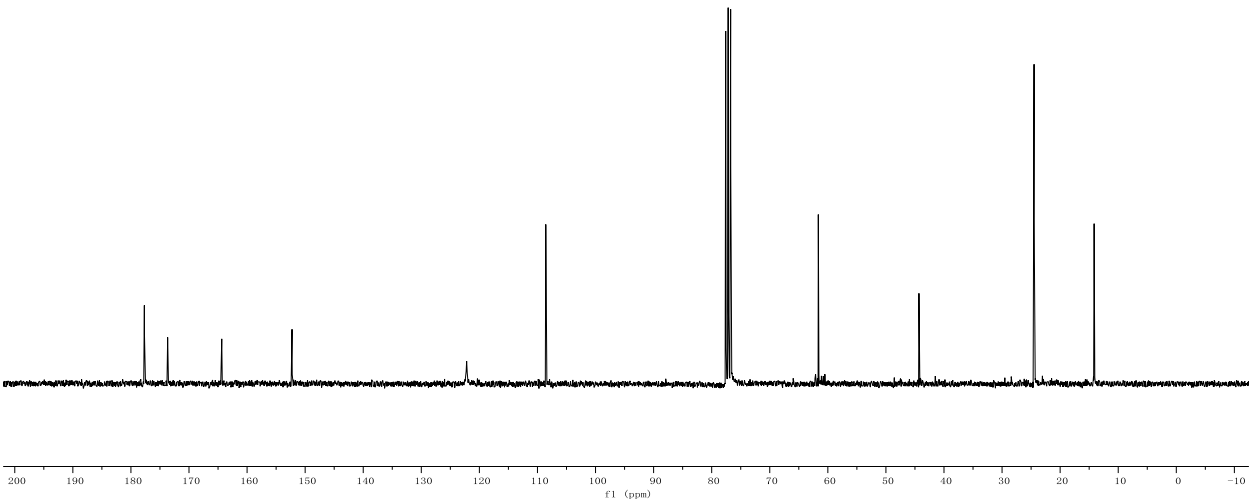
1.05
1.02
2.62
6.42
4.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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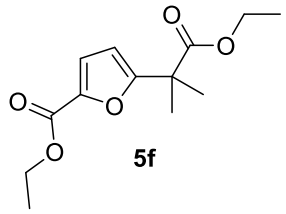
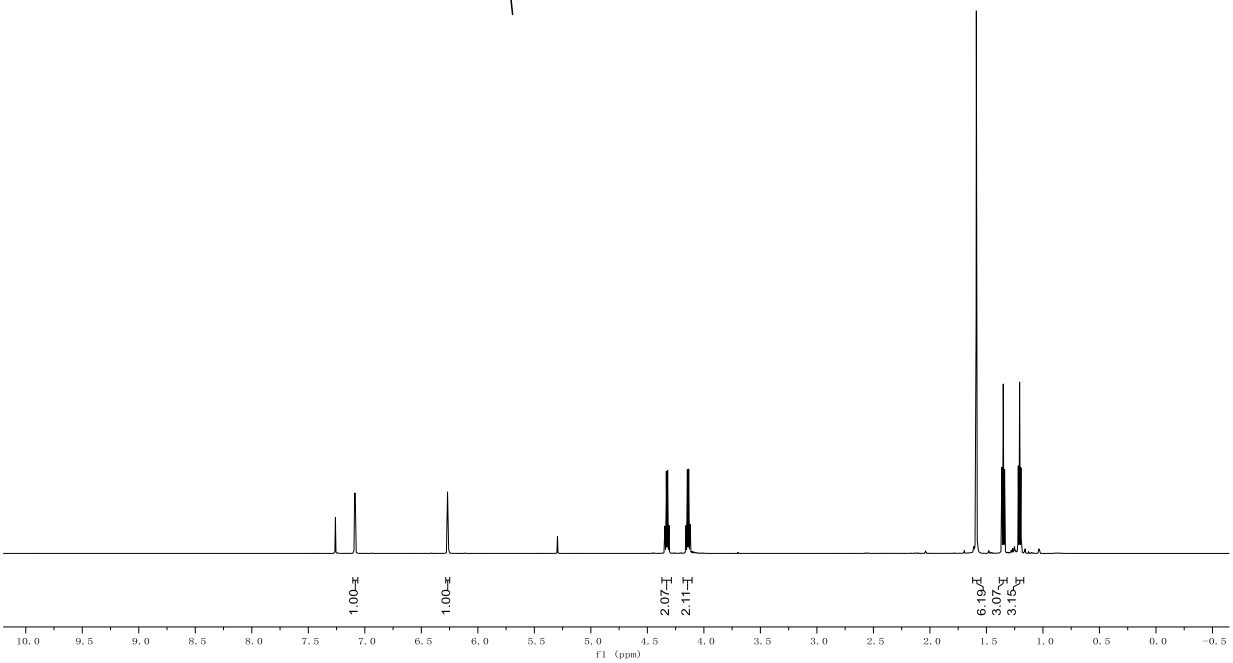
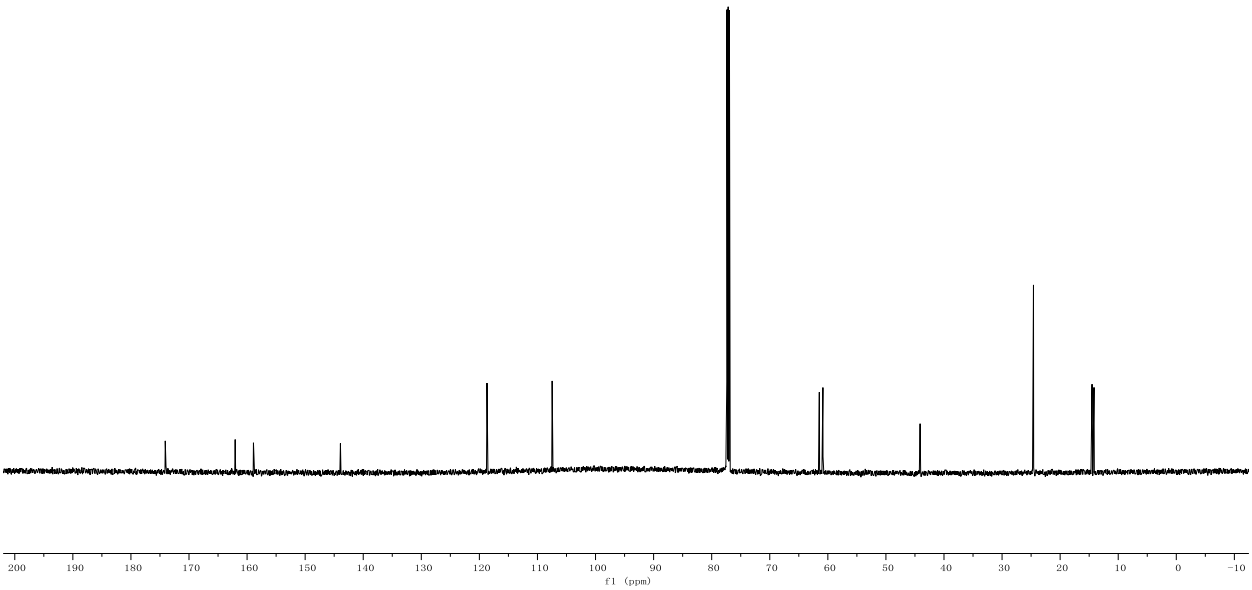
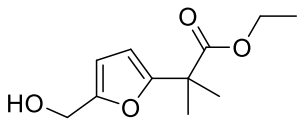
f1 (ppm)



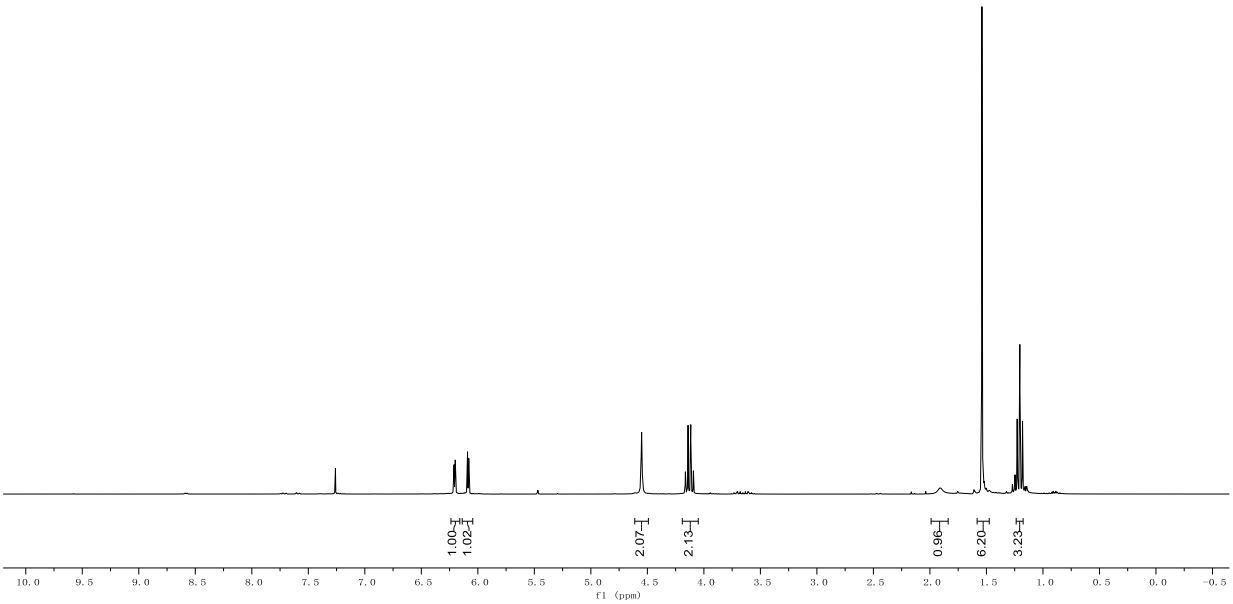
5f

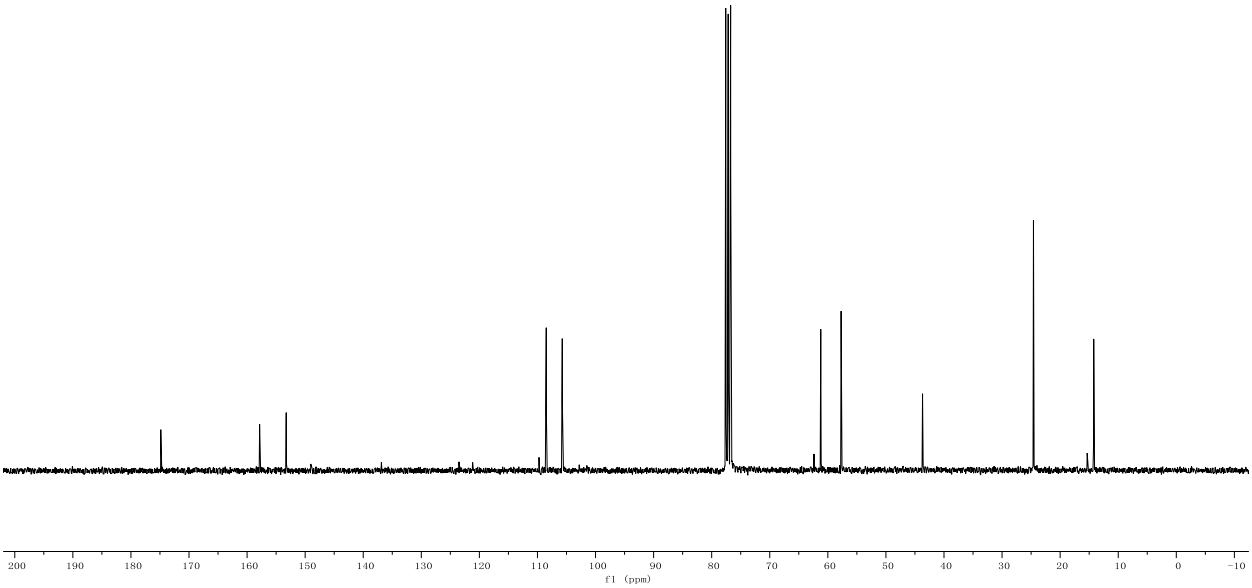





HO
O
O
O

5g


1.00
1.02
2.07
2.13
0.96
6.20
3.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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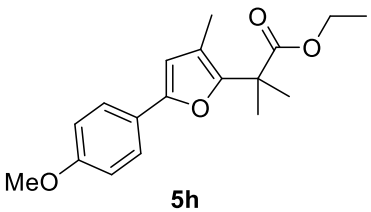
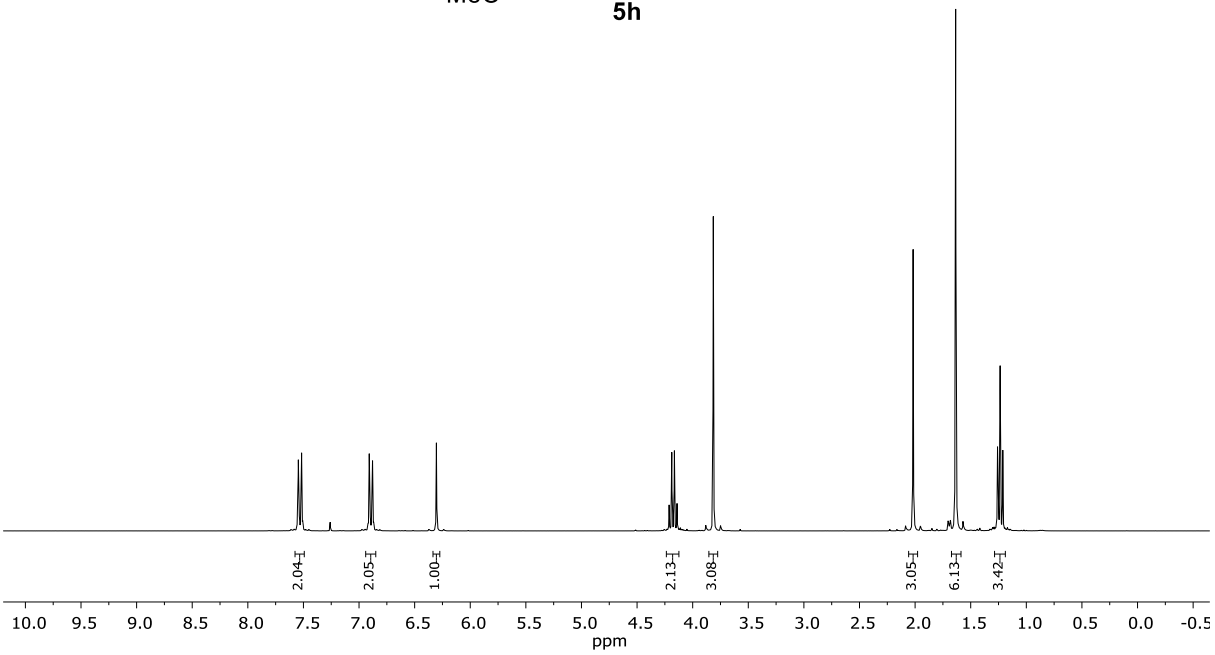
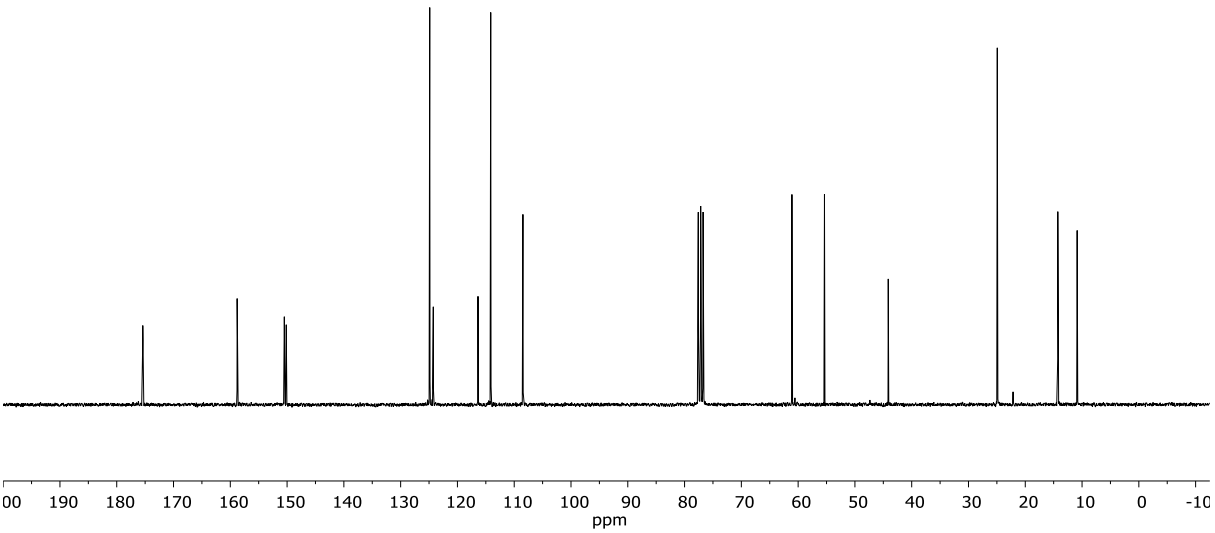
f1 (ppm)


O
O
O
MeO

5h


2.04
2.05
1.00
2.13
3.08
3.05
6.13
3.42
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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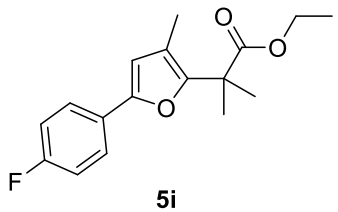
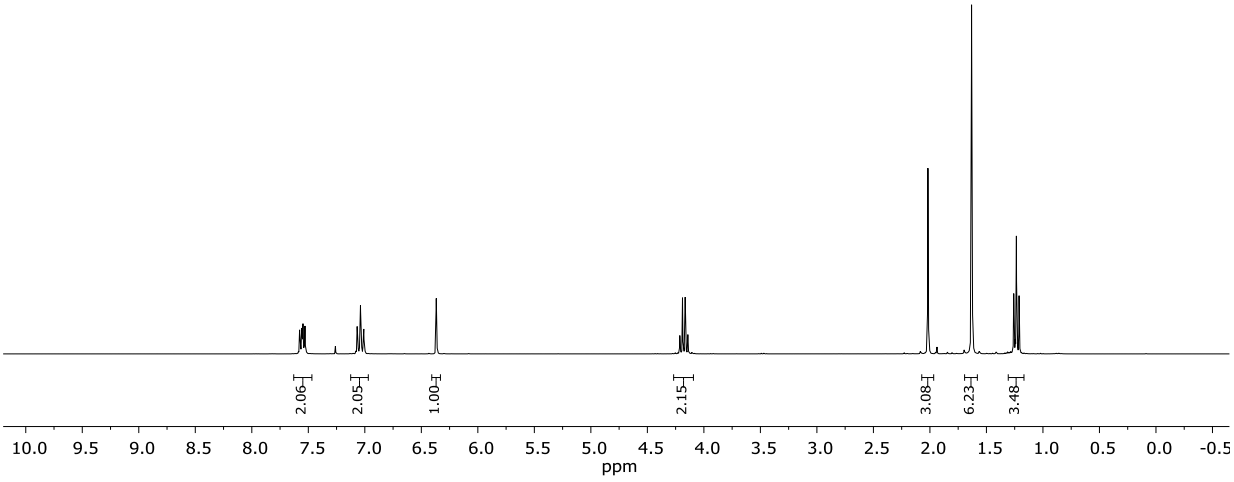
ppm


O
O
O
F

5i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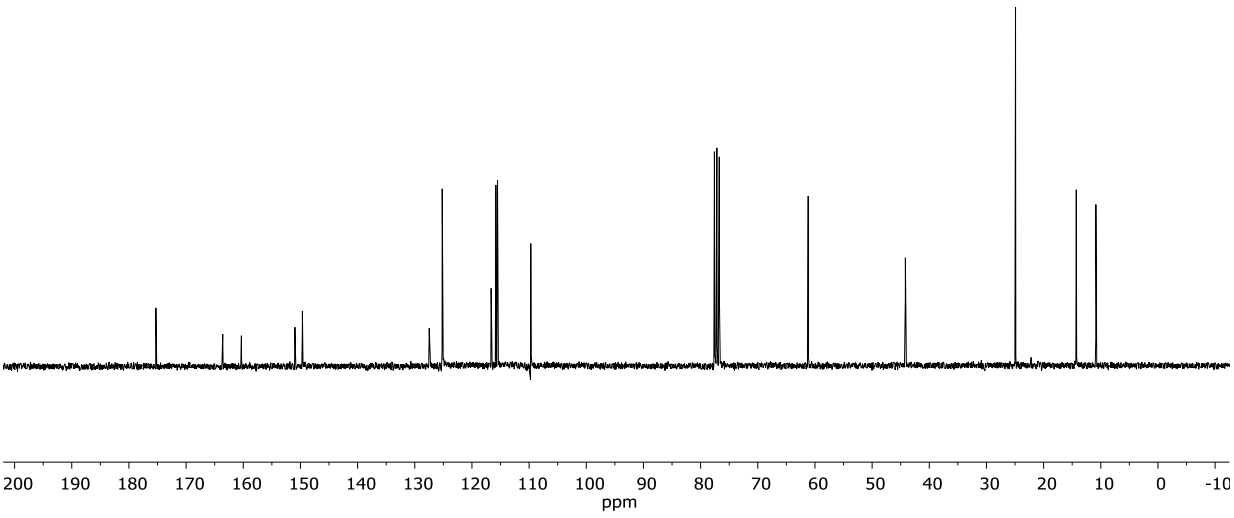
2.05
1.00
2.15
3.08
6.23
3.48
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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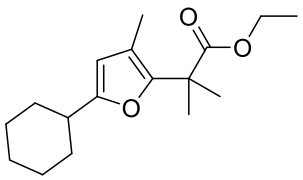
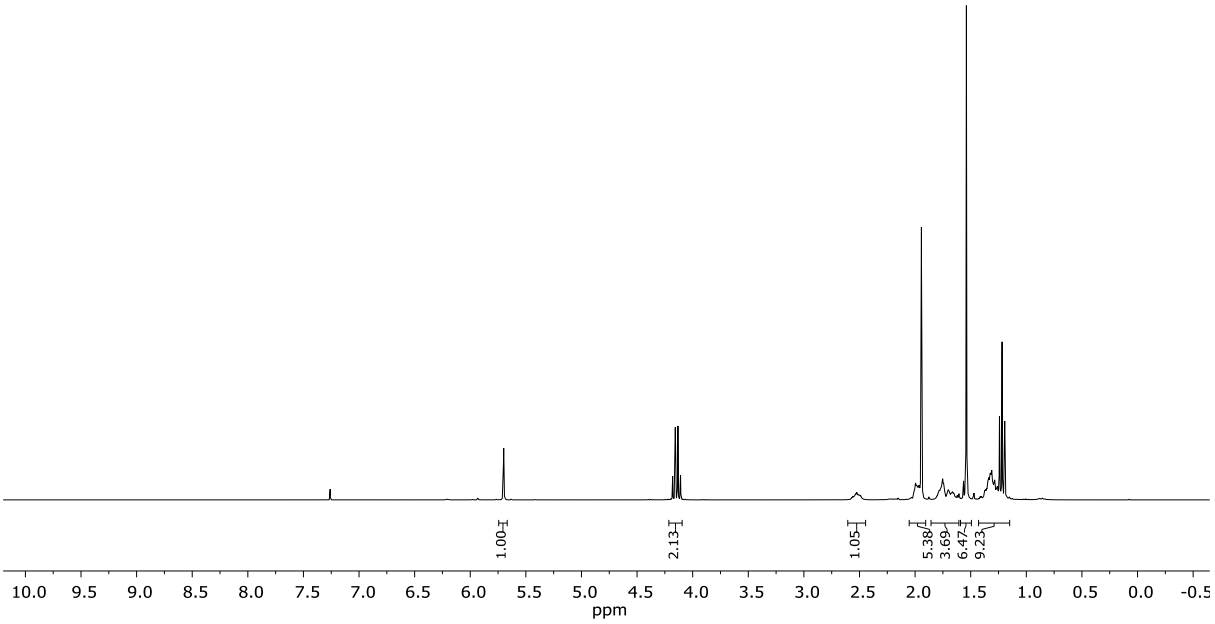
ppm



5j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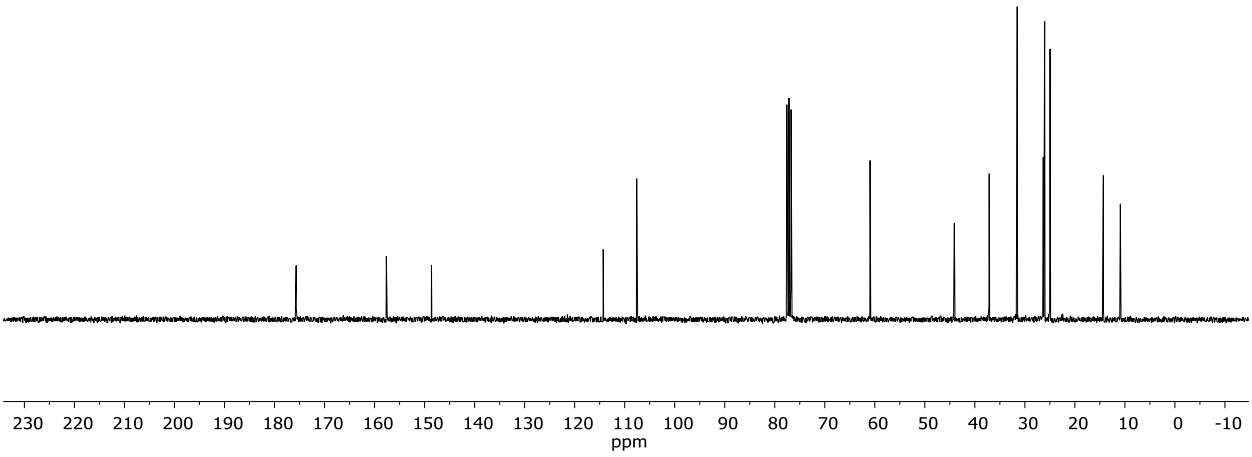
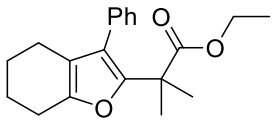
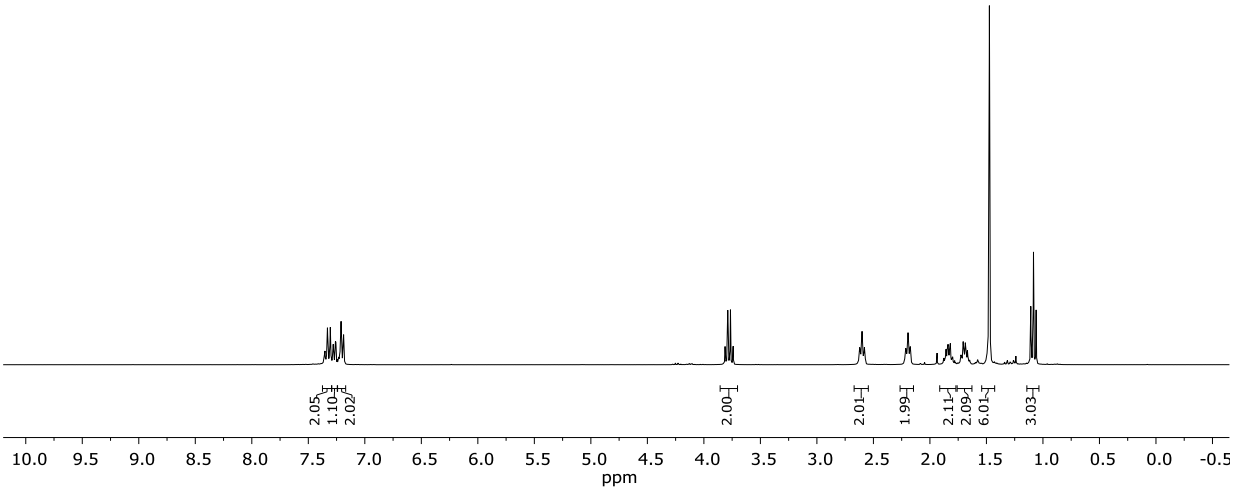
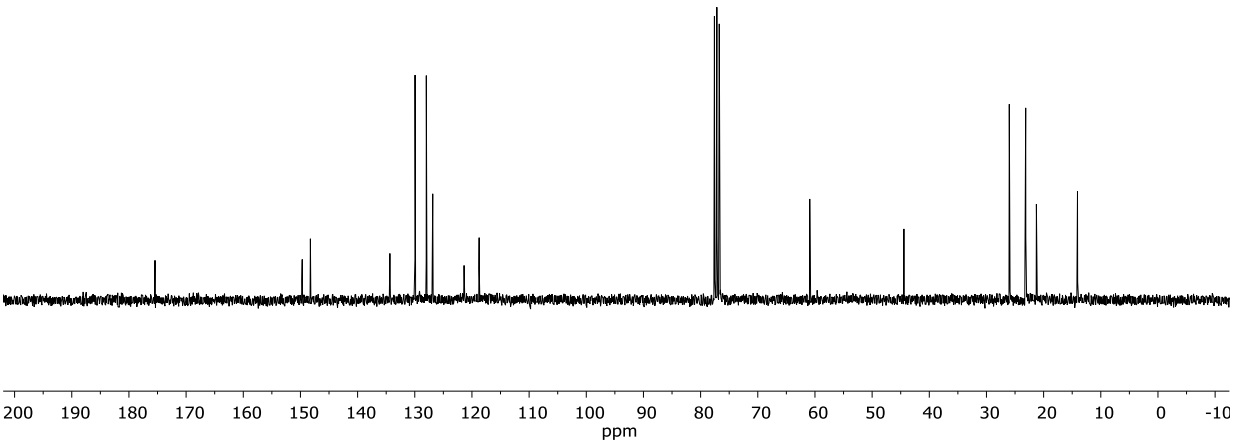
2.13
1.05
5.38
3.69
6.47
9.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


Ph
O
O
O

5k


2.05
1.10
2.02
2.00
2.01
1.99
2.11
2.09
6.01
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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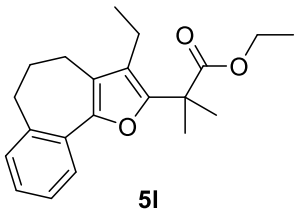
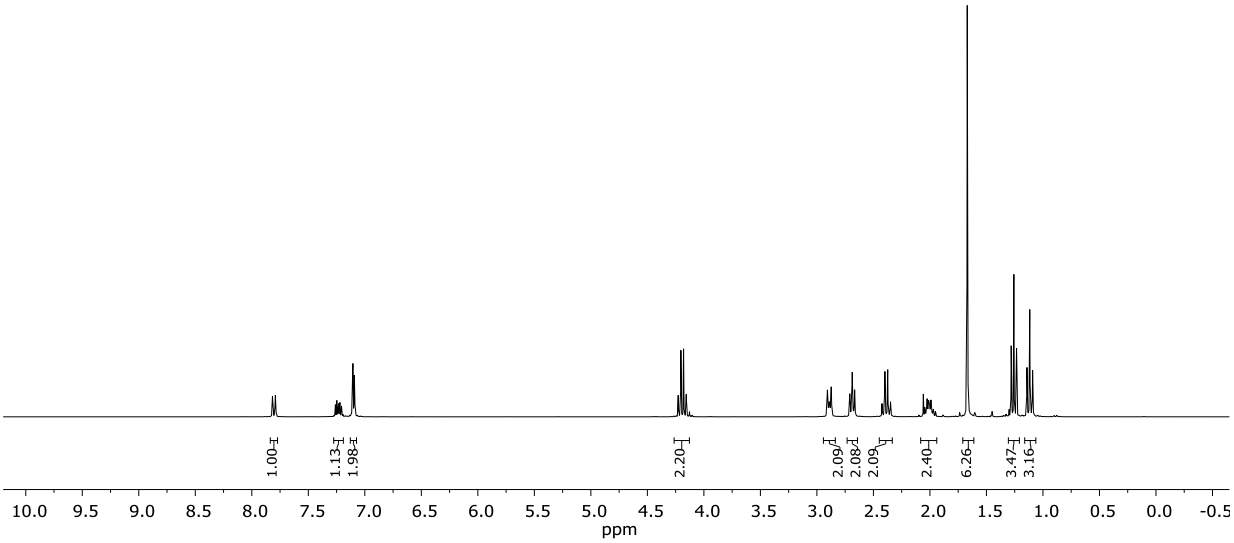
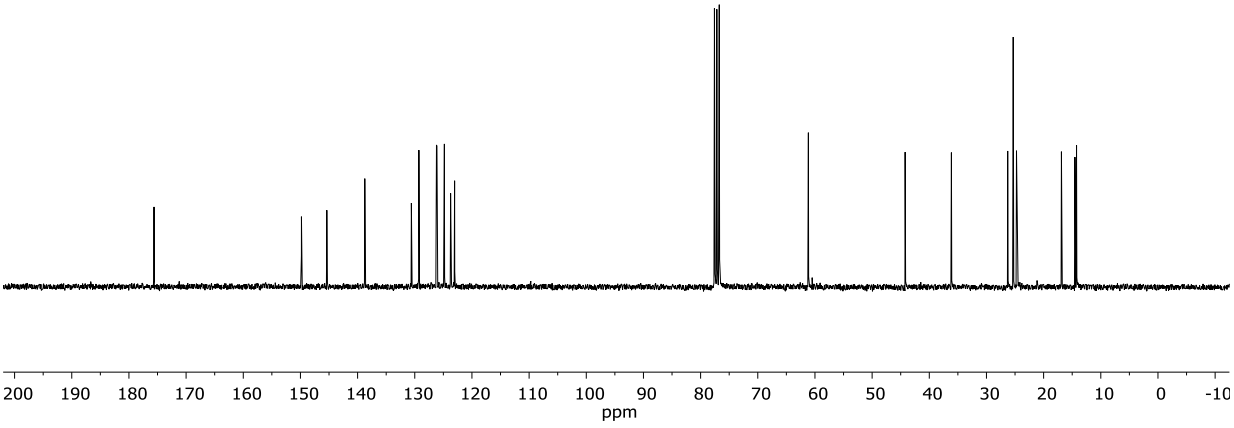
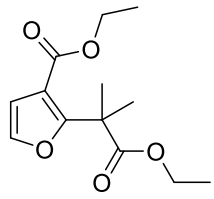
ppm



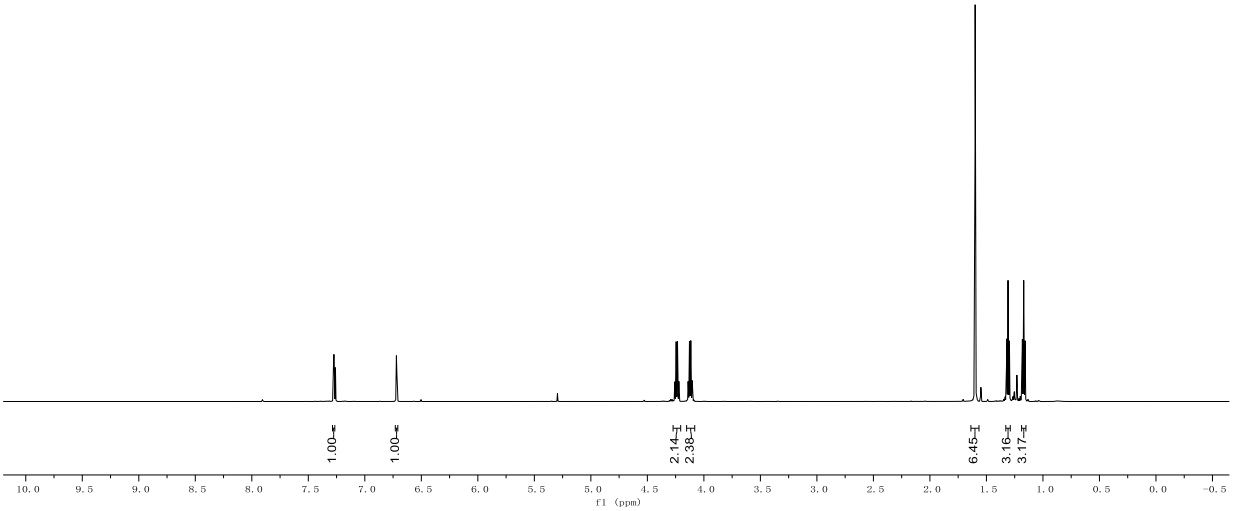
5l

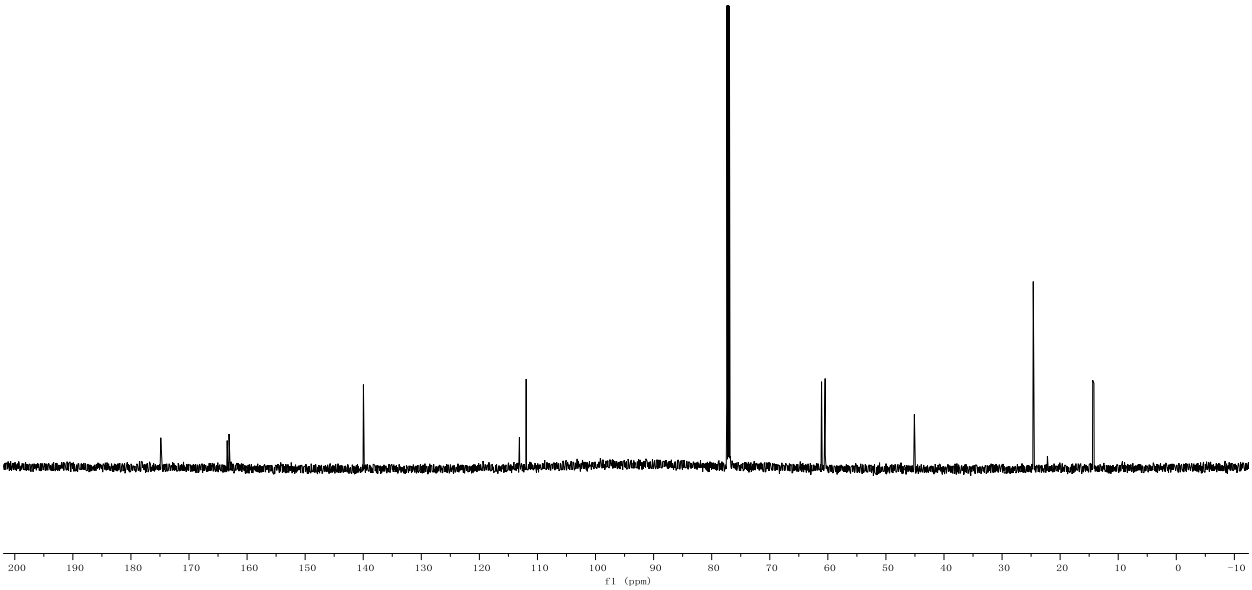

1.00
1.13
1.98
2.20
2.09
2.08
2.09
2.40
6.26
3.47
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

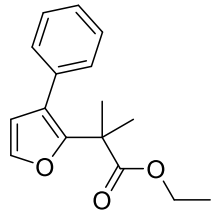

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



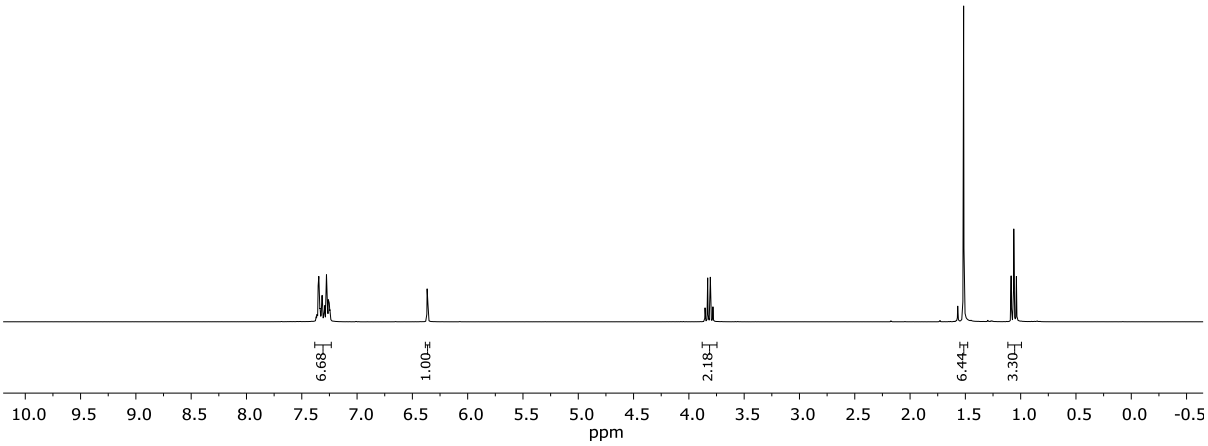
5m

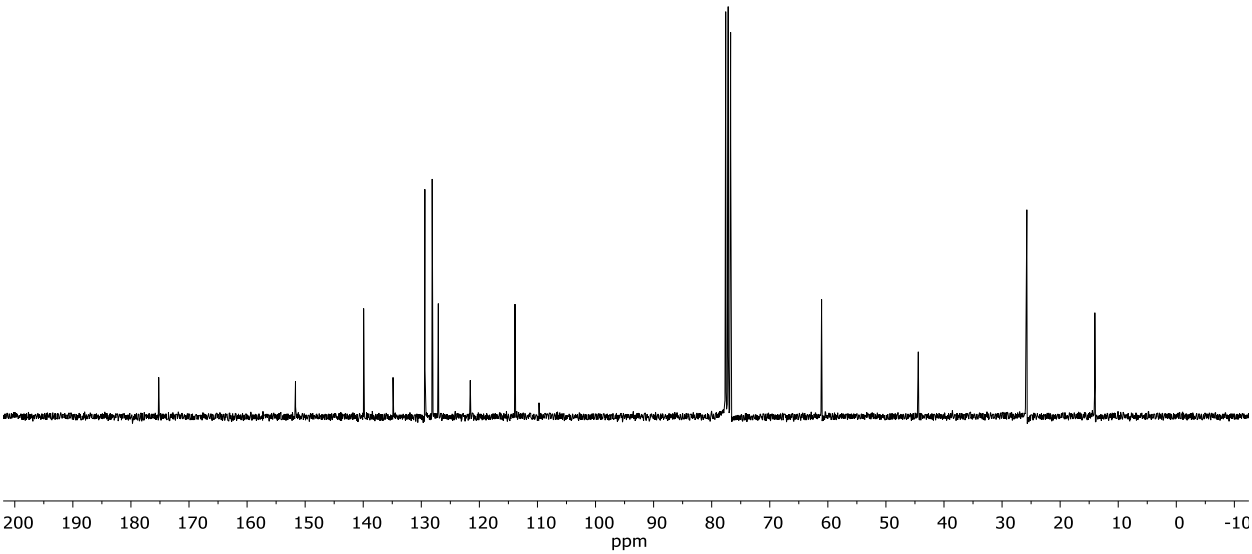

1.00
1.00
2.14
2.38
6.45
3.16
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

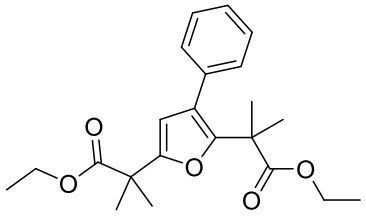

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



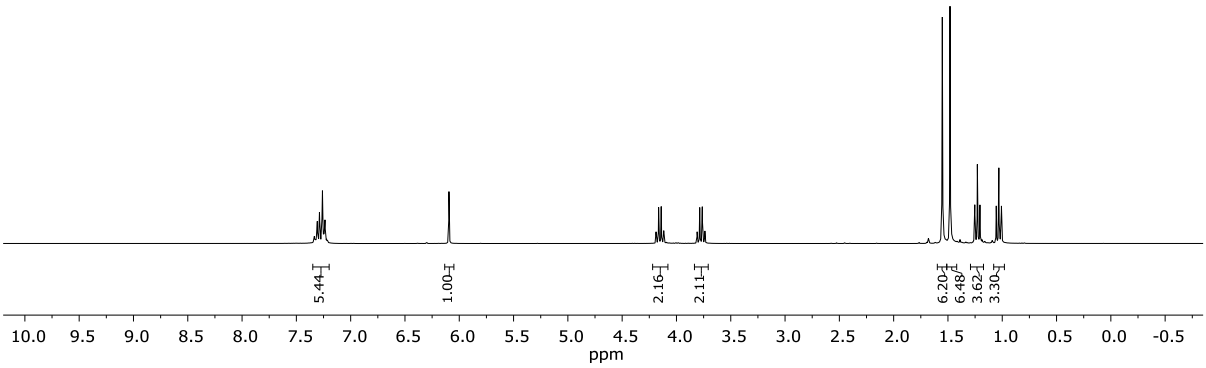
5n

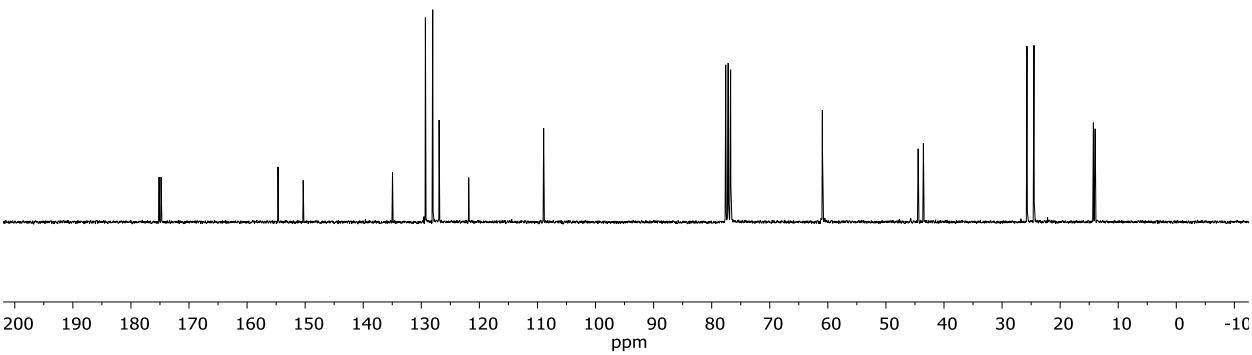

6.68
1.00
2.18
6.44
3.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

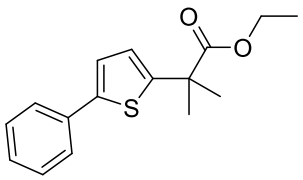

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



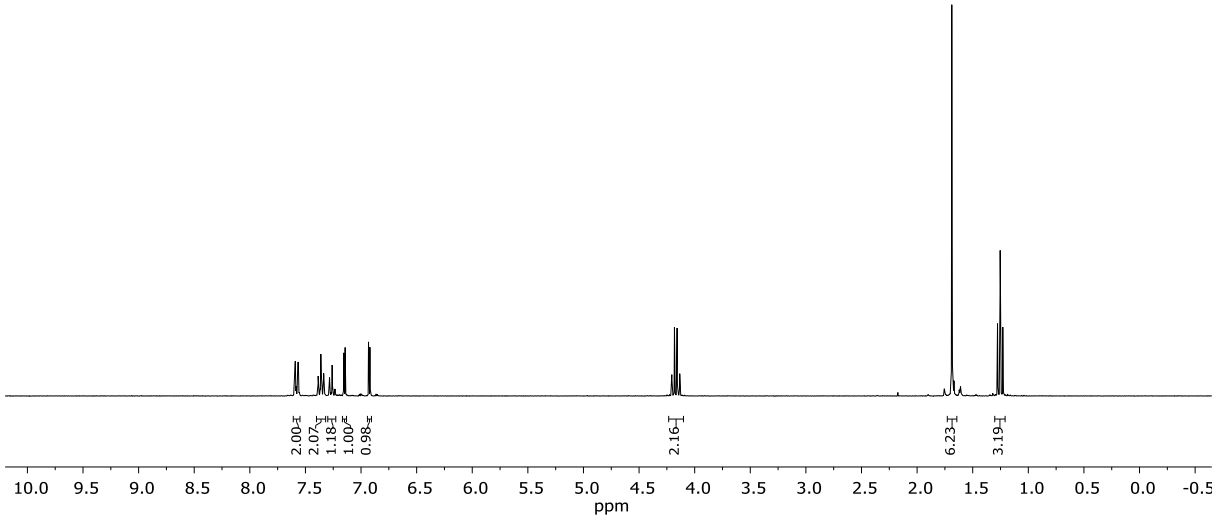
5n'

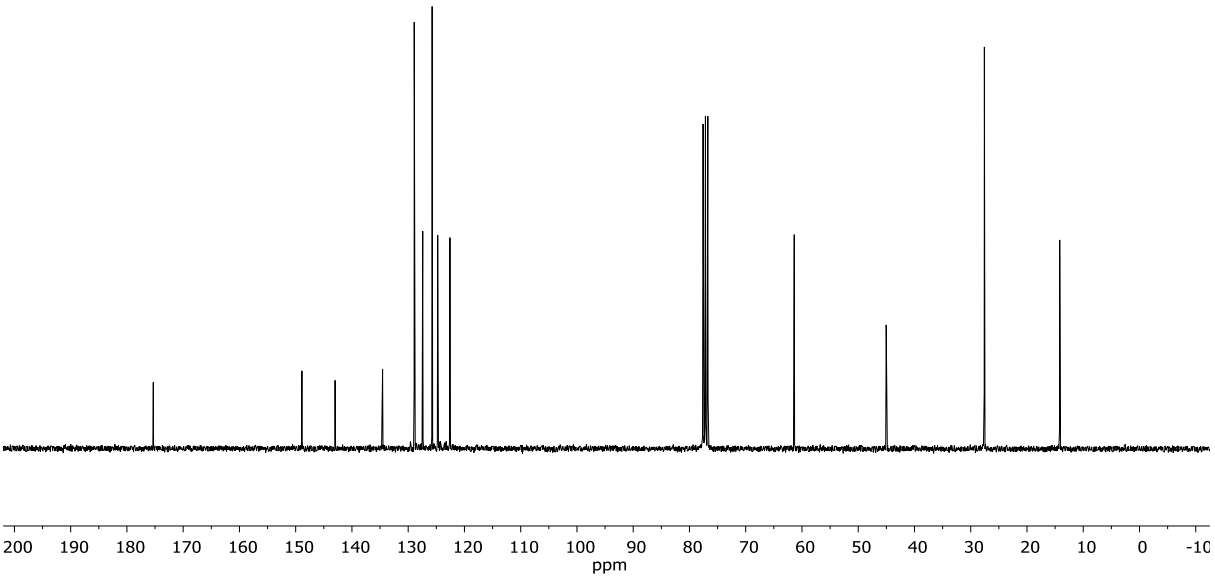

5.44
1.00
2.16
2.11
6.20
6.48
3.62
3.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

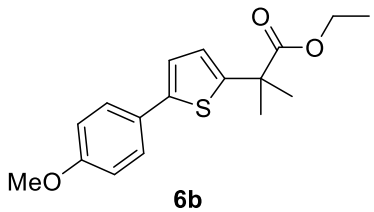

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



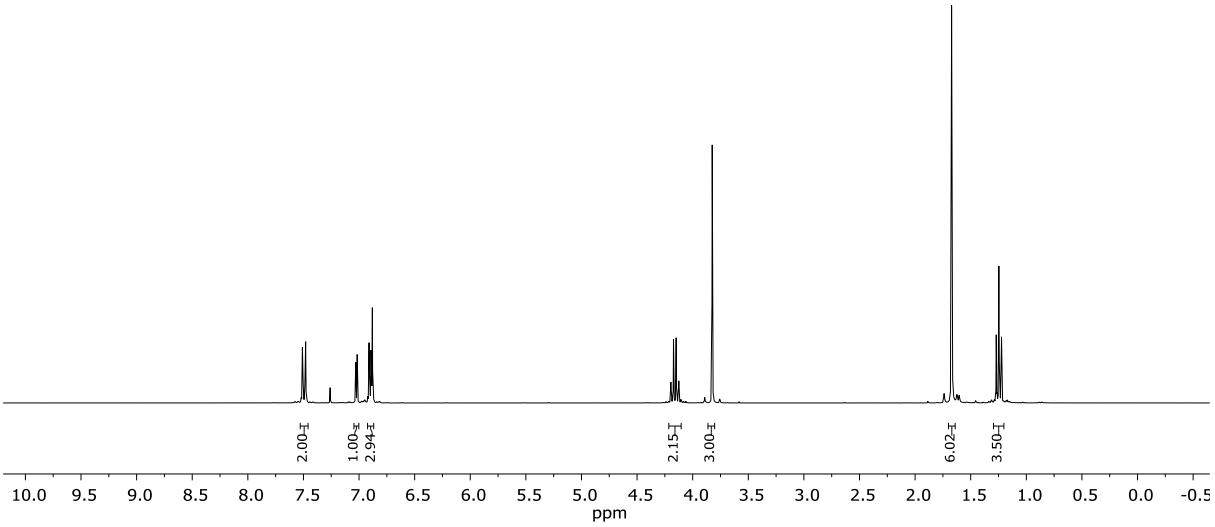
6a

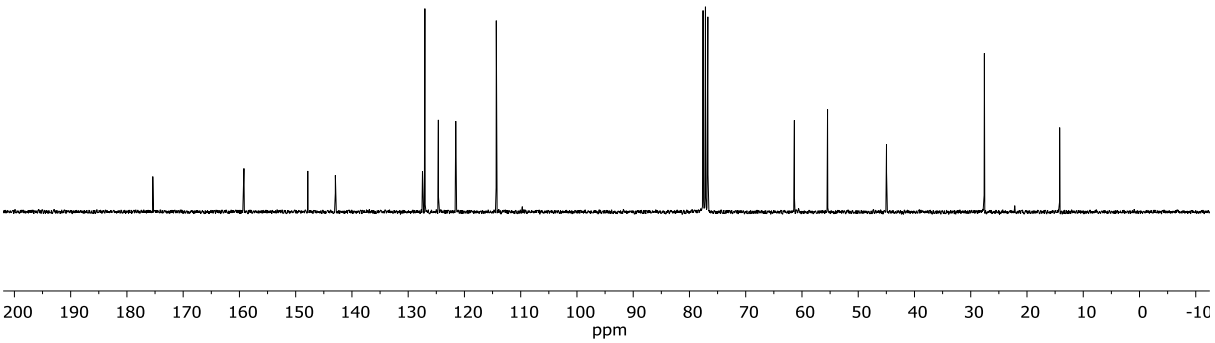

2.00
2.07
1.18
1.00
0.98
2.16
6.23
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

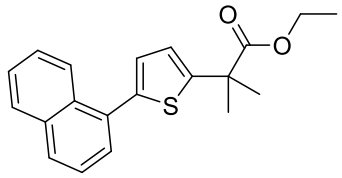

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


O
O
S
MeO

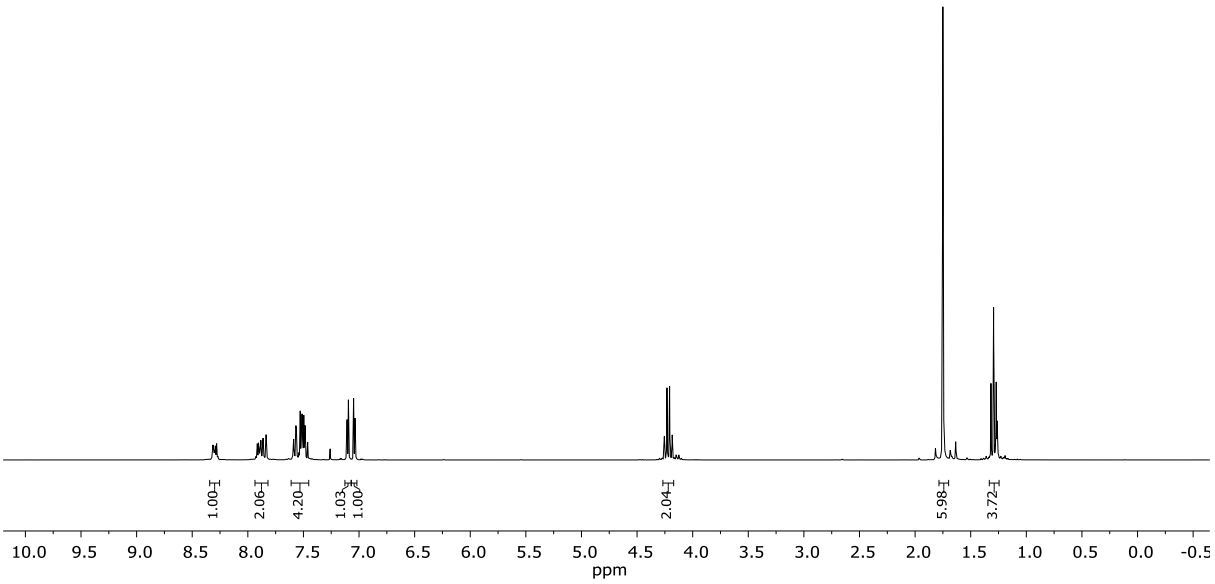
6b

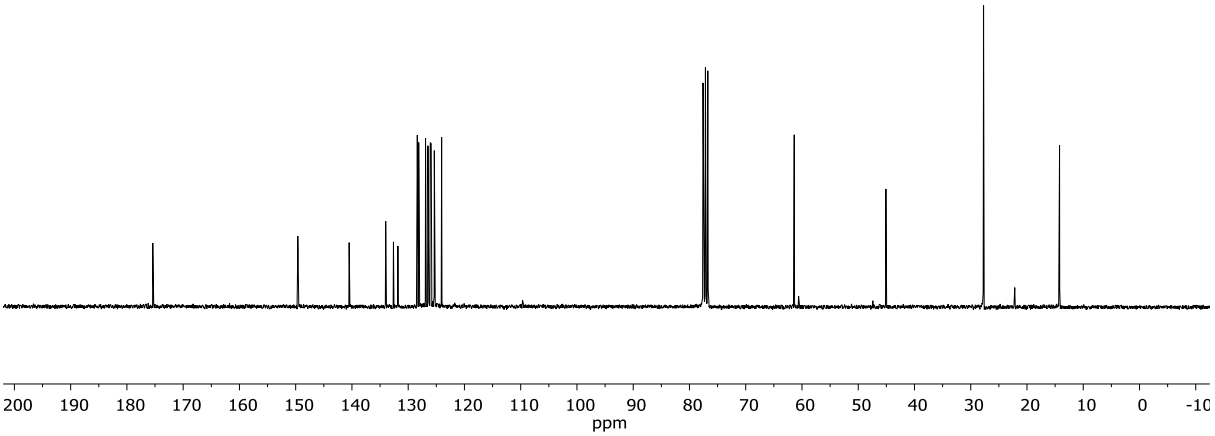

2.00
1.00
2.94
2.15
3.00
6.02
3.50
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



6c


1.00
2.06
4.20
1.03
1.00
2.04
5.98
3.72
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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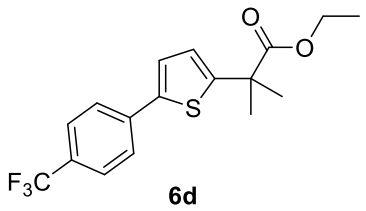
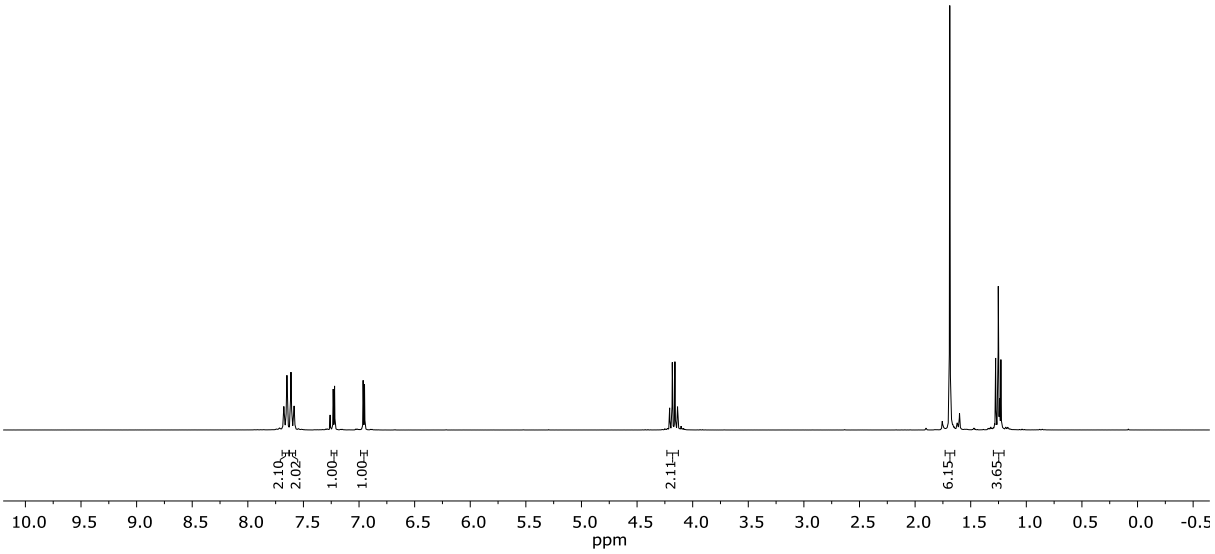
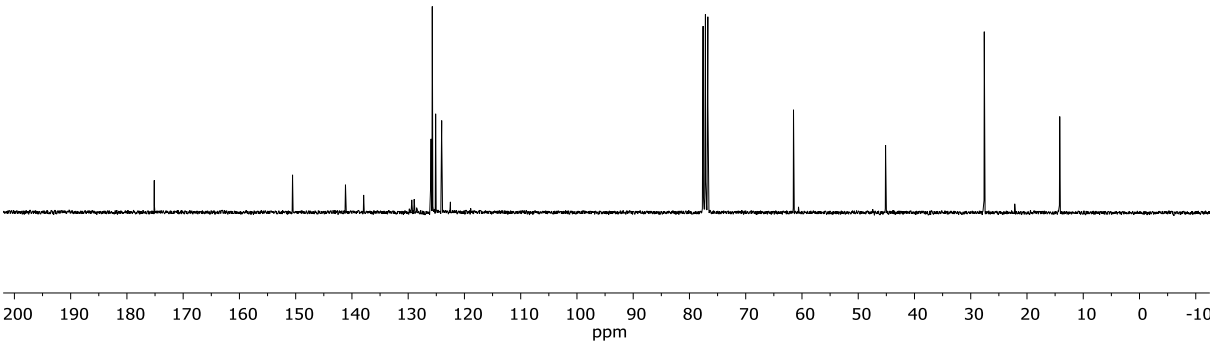
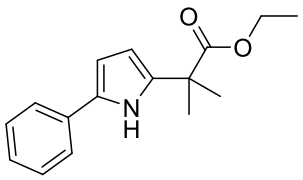
ppm


O
O
S
F3C

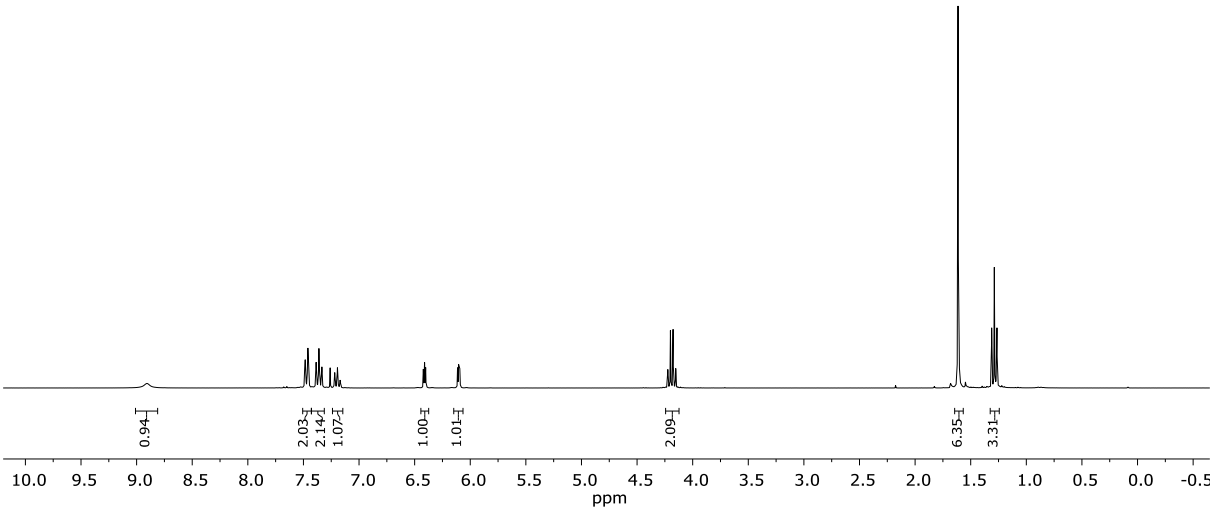
6d

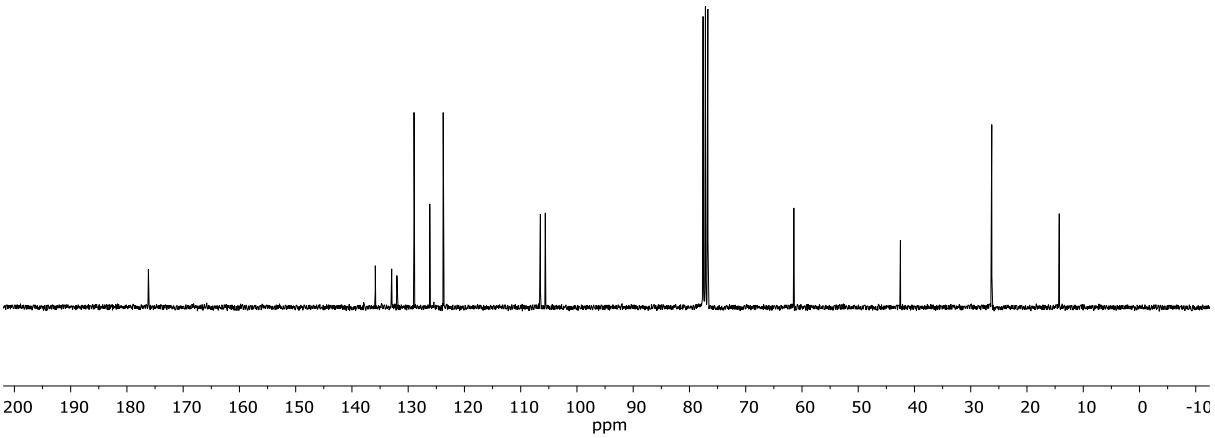

2.10
2.02
1.00
1.00
2.11
6.15
3.65
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

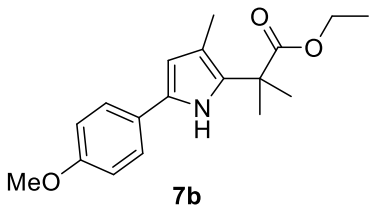

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



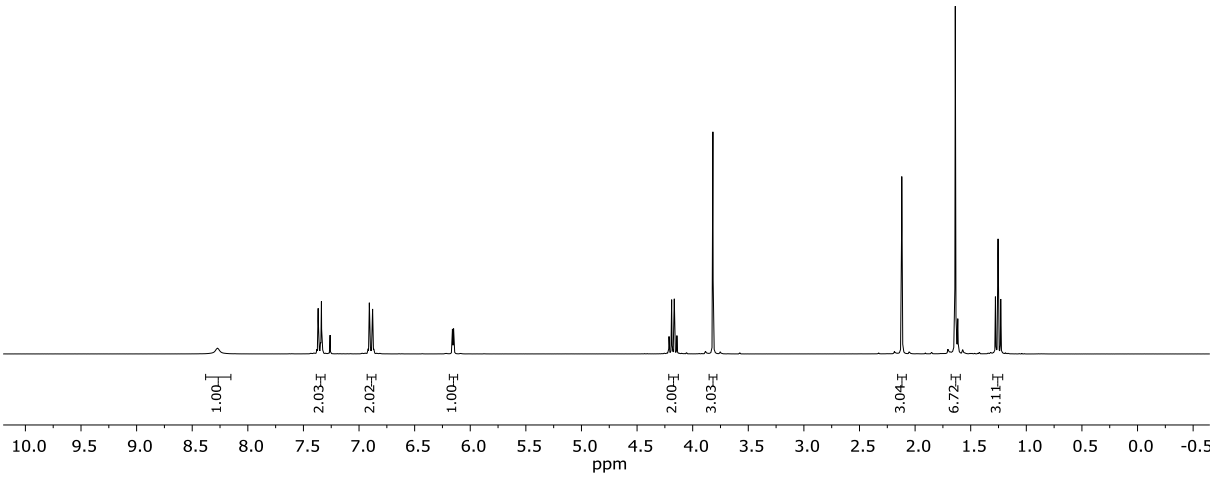
7a

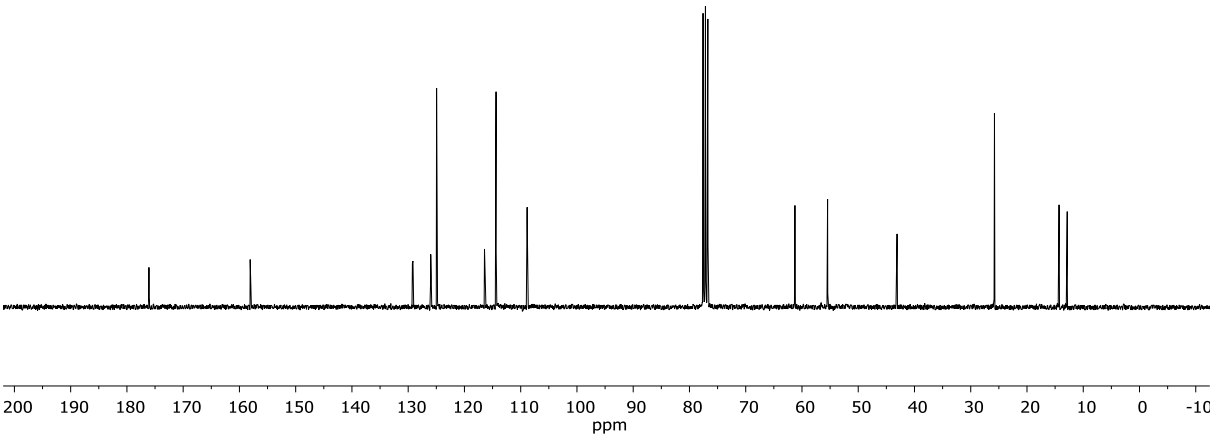

0.94
2.03
2.14
1.07
1.00
1.01
2.09
6.35
3.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

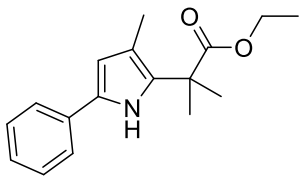

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


O
O
N
H
MeO

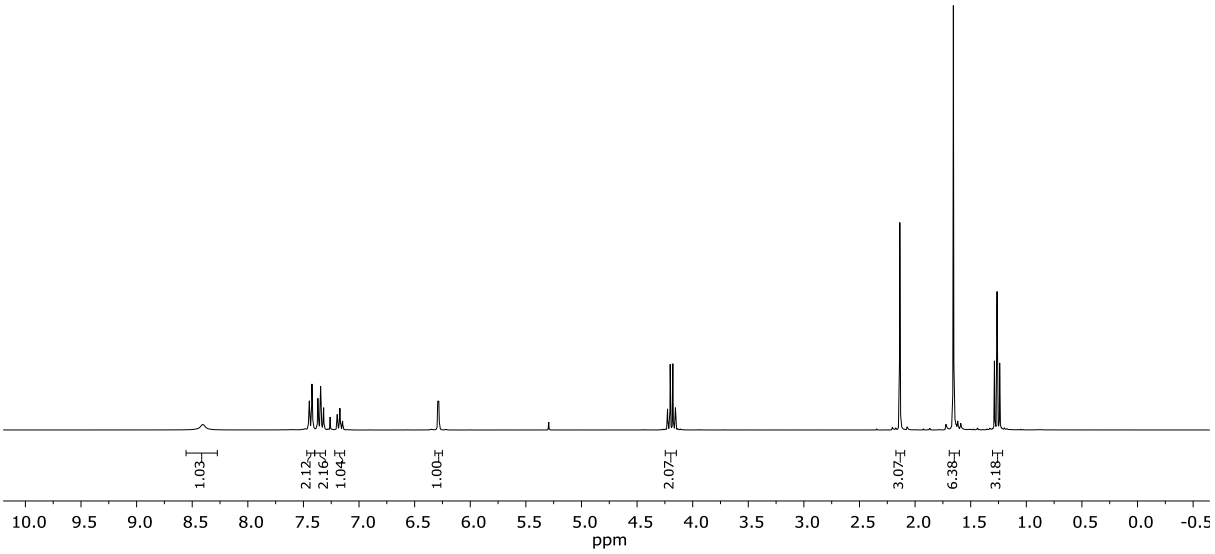
7b

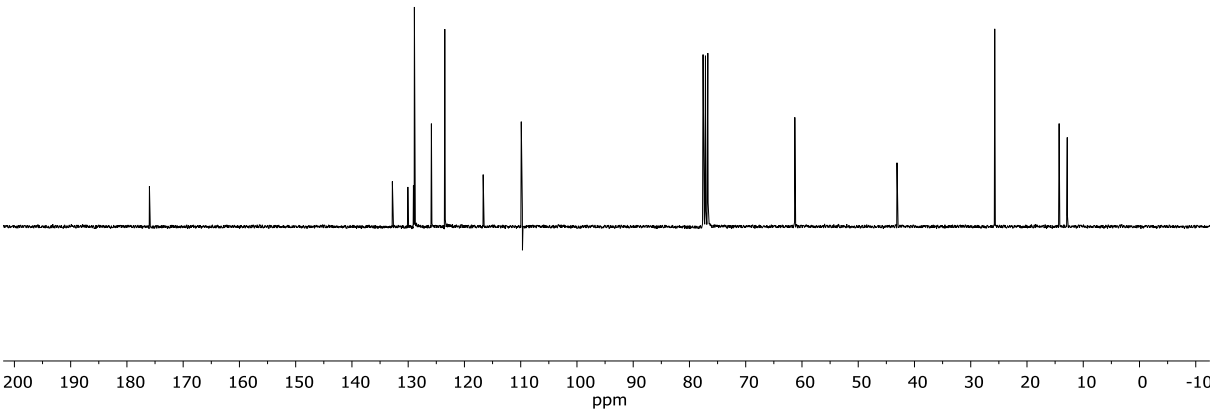

1.00
2.03
2.02
1.00
2.00
3.03
3.04
6.72
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

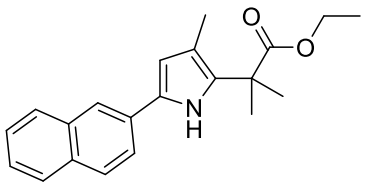

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



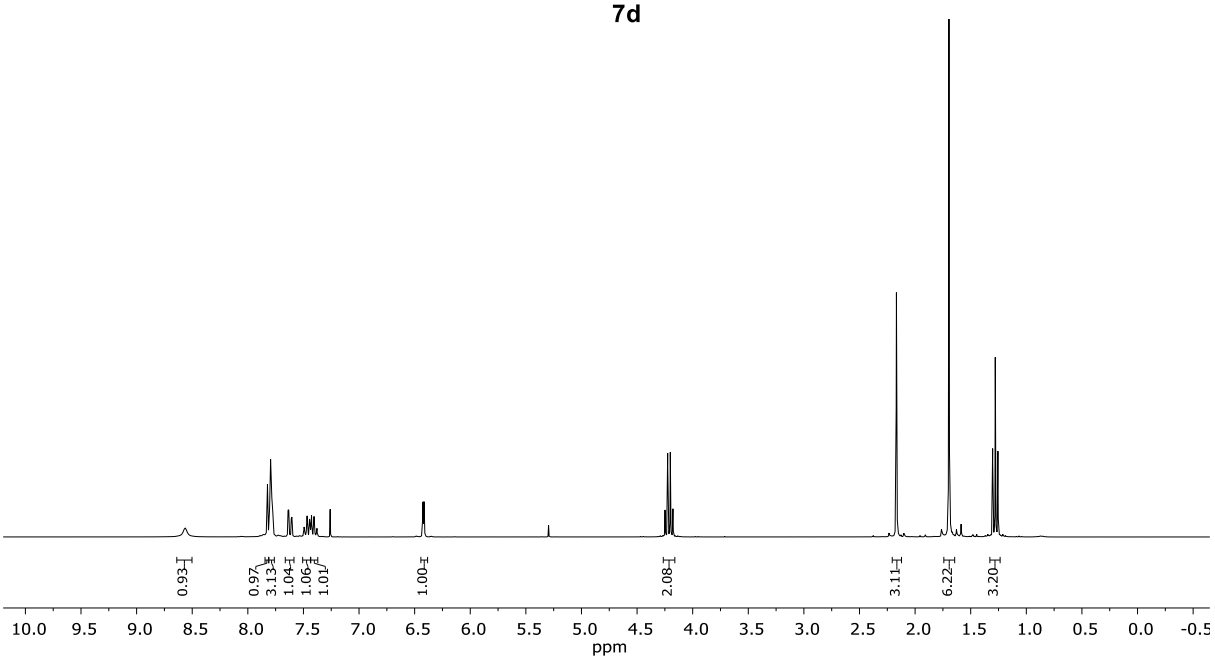
7c

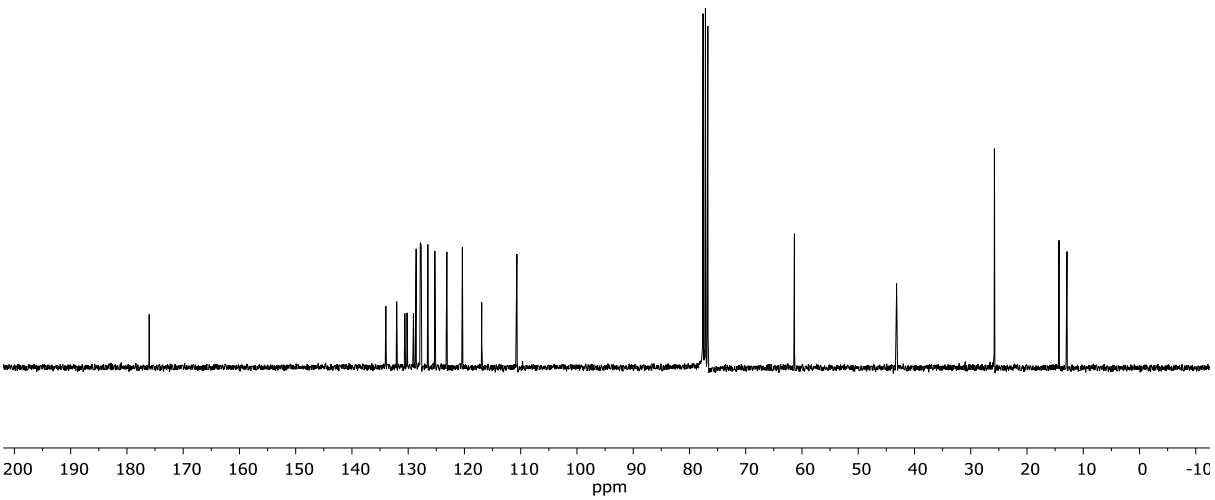

1.03
2.12
2.16
1.04
1.00
2.07
3.07
6.38
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

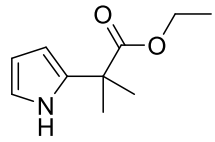

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


O
O
N
H

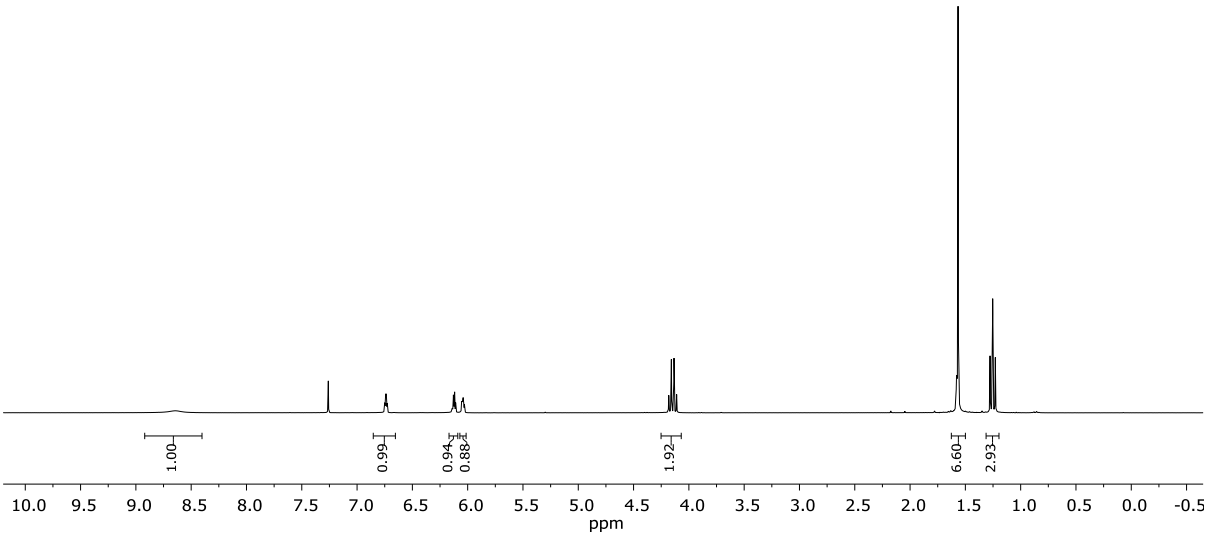
7d

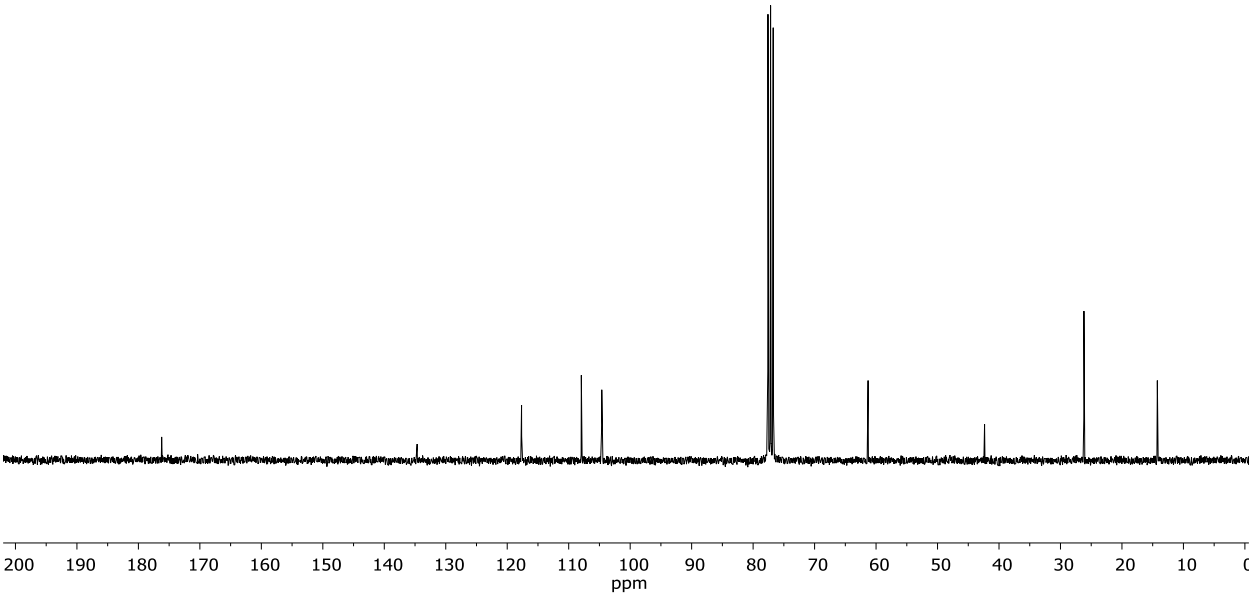

0.93
0.97
3.13
1.04
1.06
1.01
1.00
2.08
3.11
6.22
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

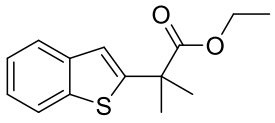

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



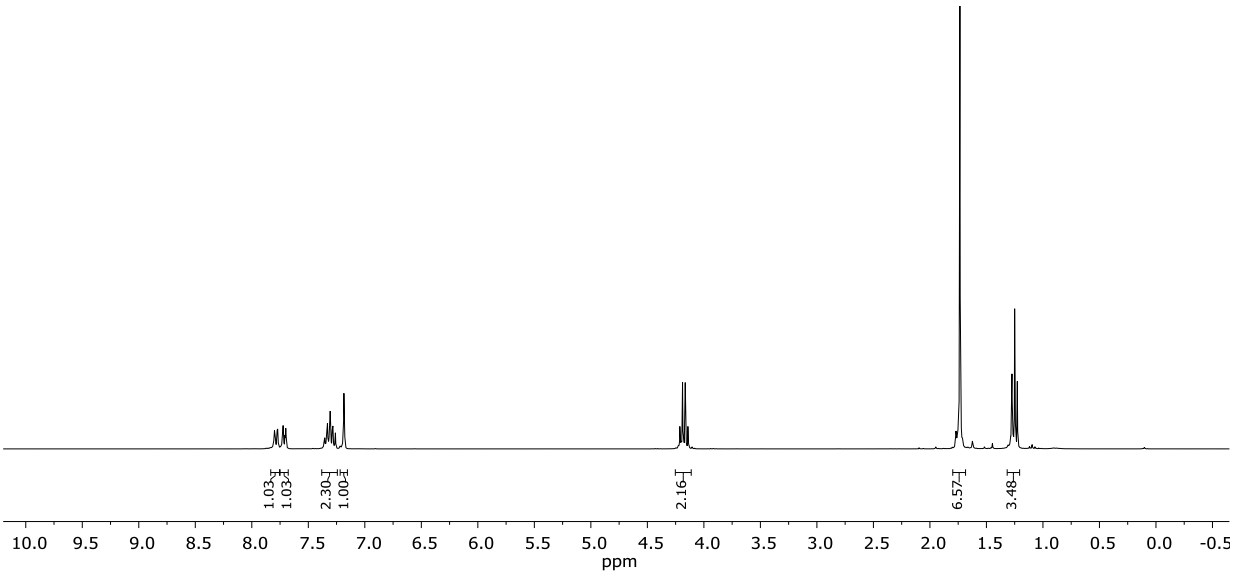
7e

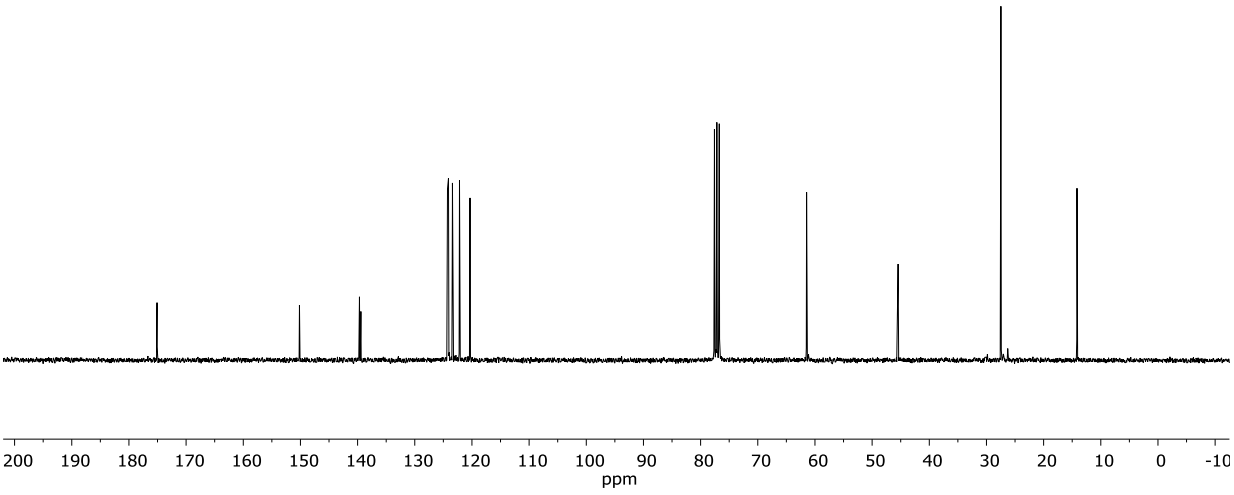

1.00
0.99
0.94
0.88
1.92
6.60
2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm



8a


1.03
1.03
2.30
1.00
2.16
6.57
3.48
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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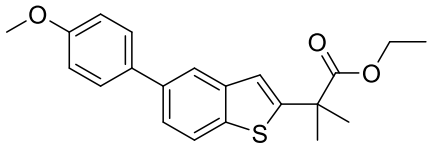
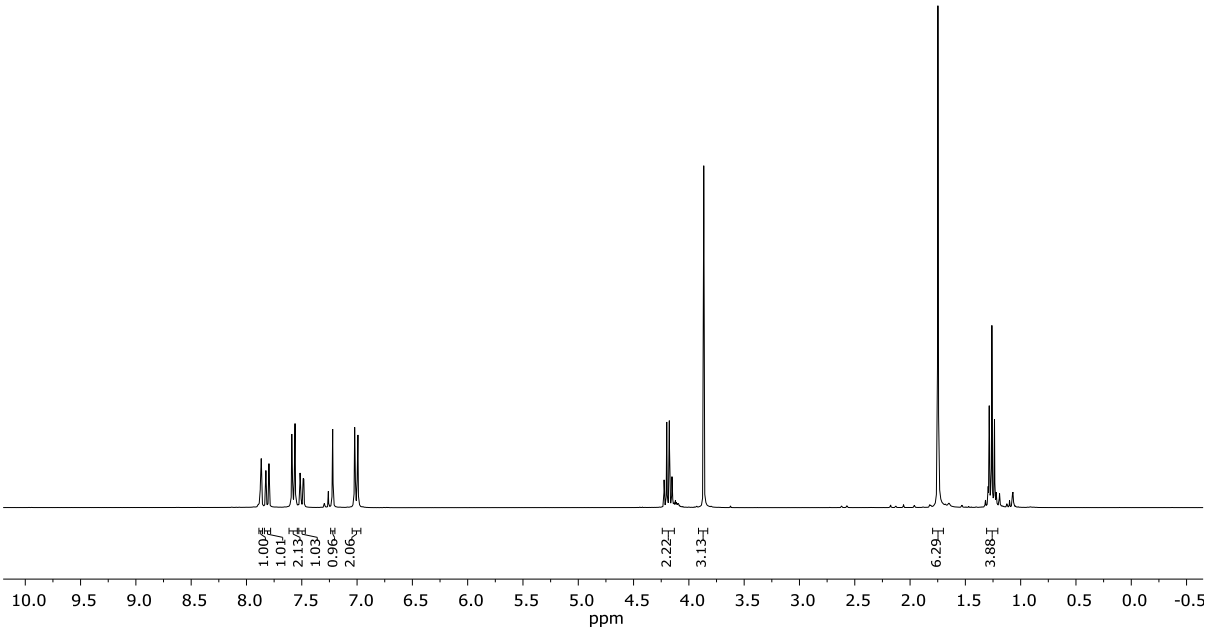
ppm


O
O
O
S

8b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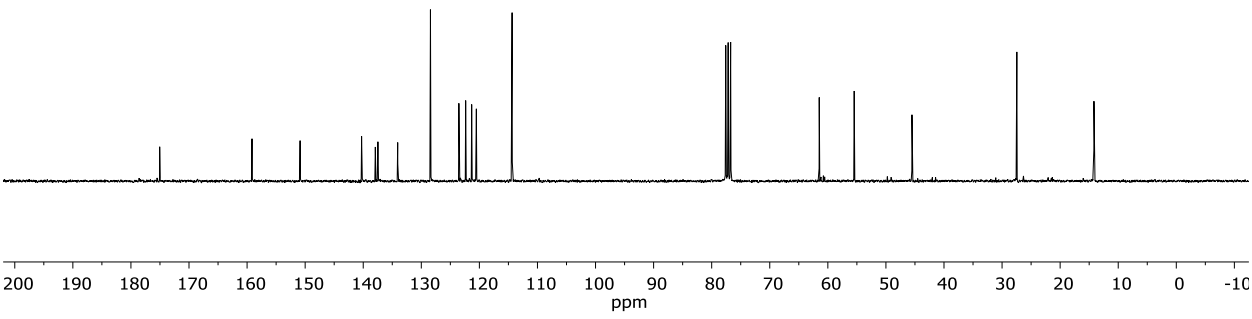
1.01
2.13
1.03
0.96
2.06
2.22
3.13
6.29
3.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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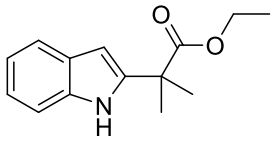
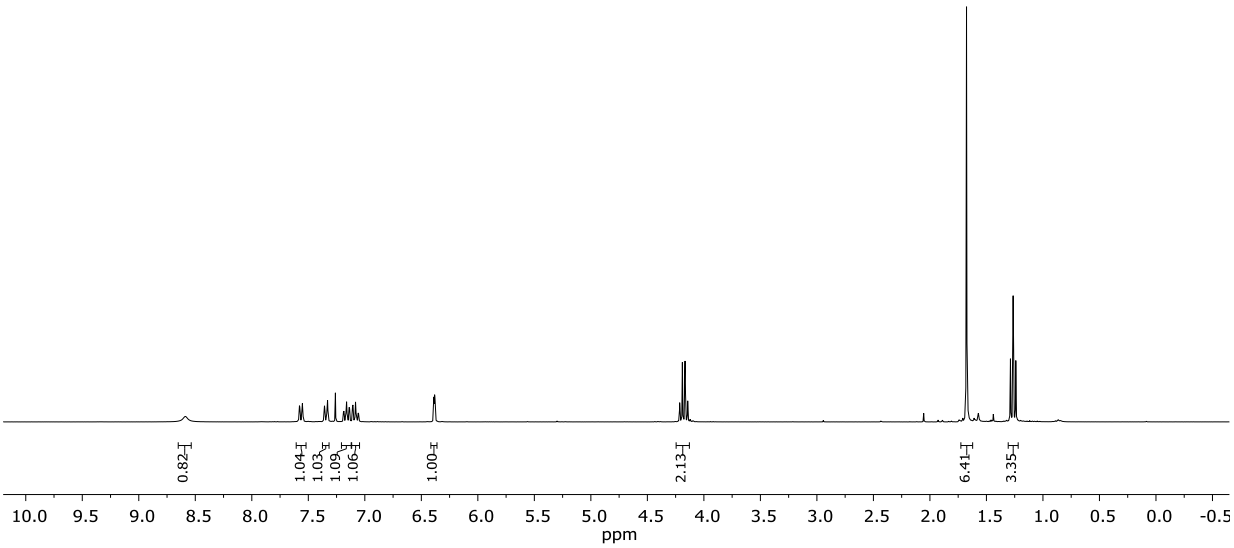
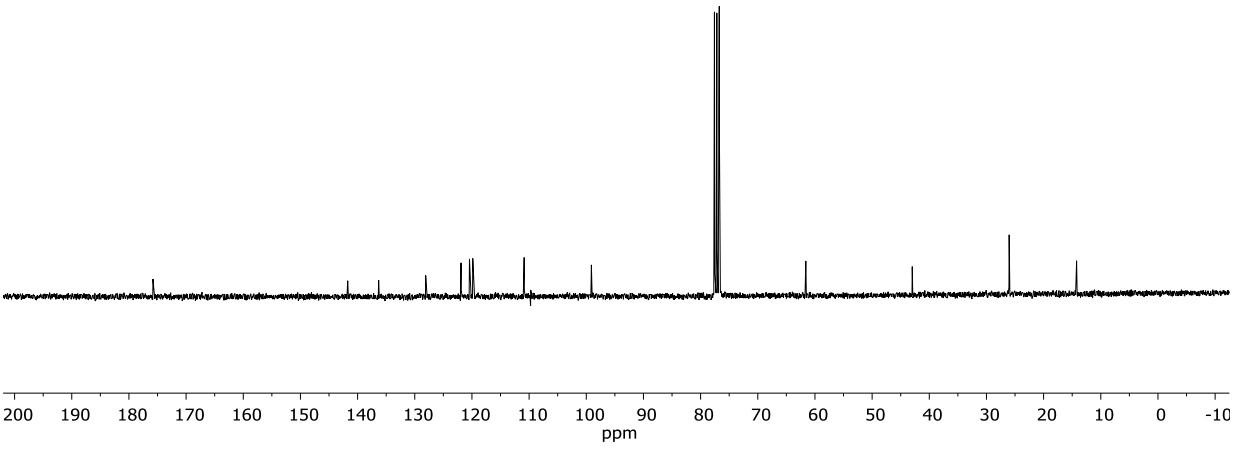
ppm



9a


0.82
1.04
1.03
1.09
1.06
1.00
2.13
6.41
3.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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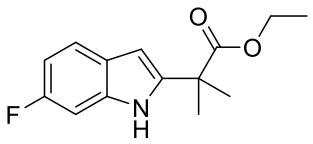
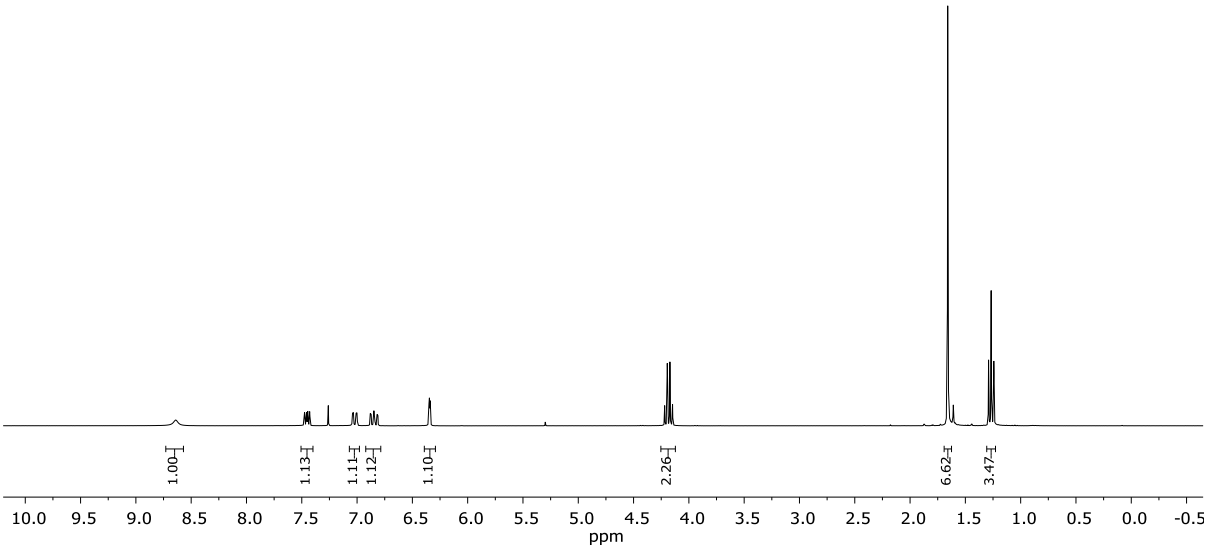
ppm


O
O
F
N
H

9b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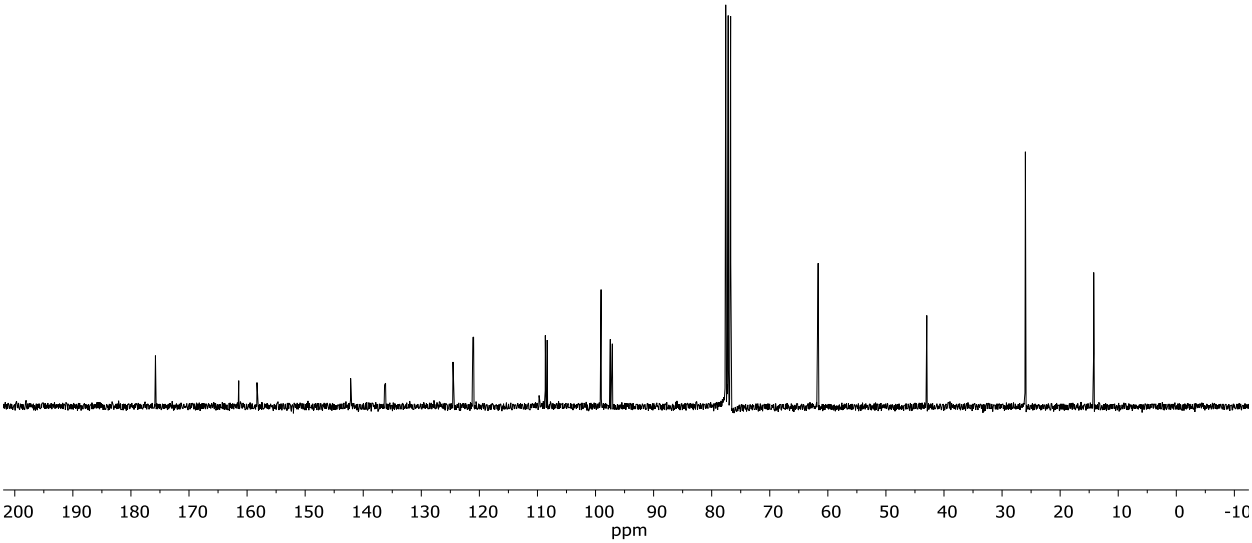
1.13
1.11
1.12
1.10
2.26
6.62
3.47
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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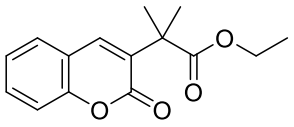
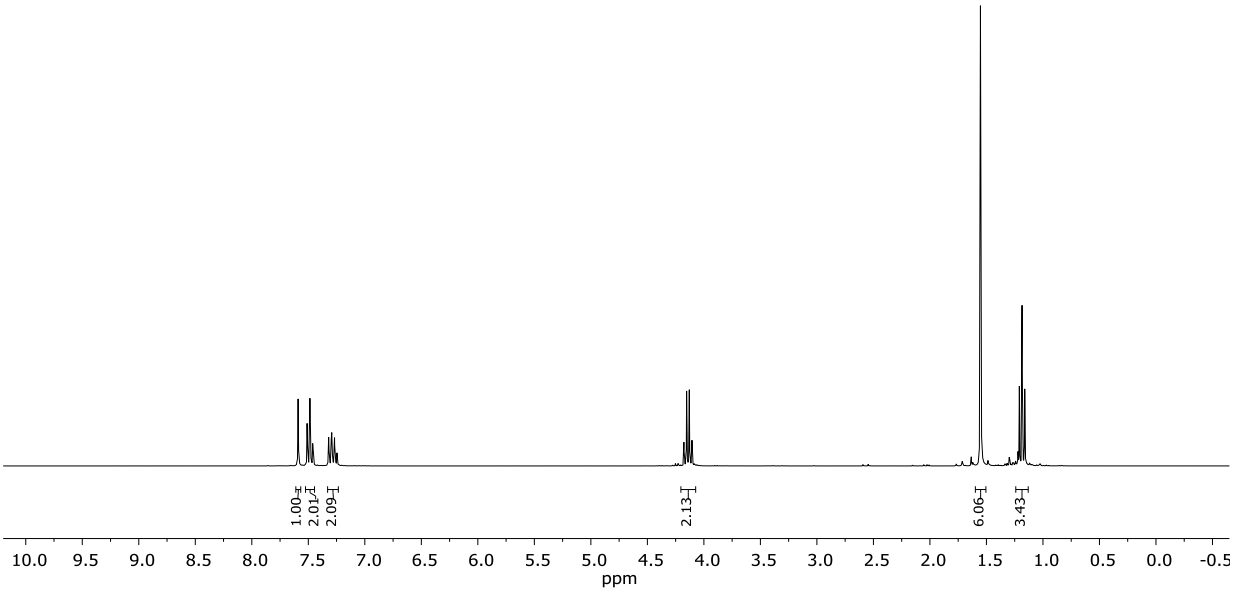
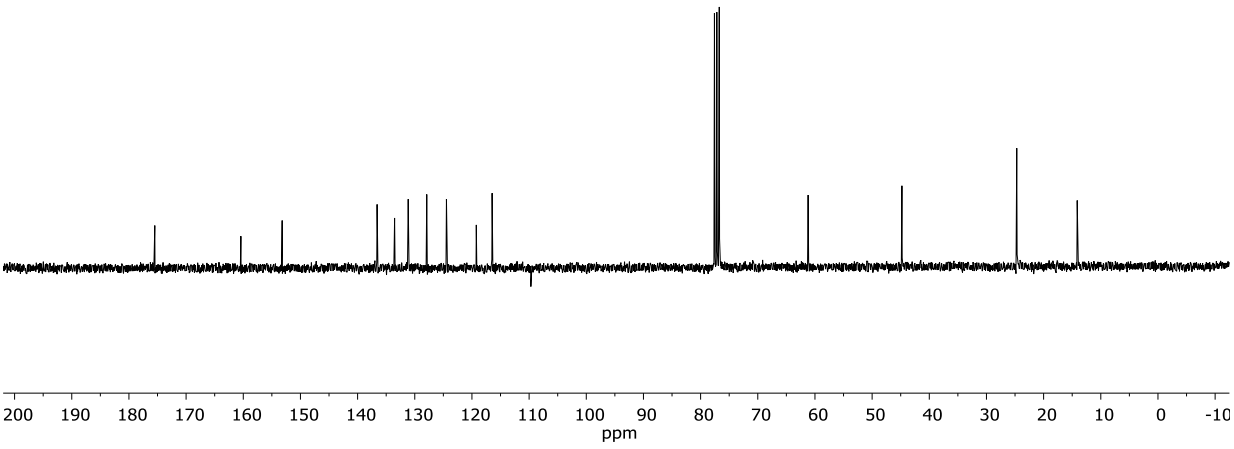
ppm



10a


1.00
2.01
2.09
2.13
6.06
3.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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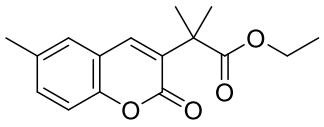
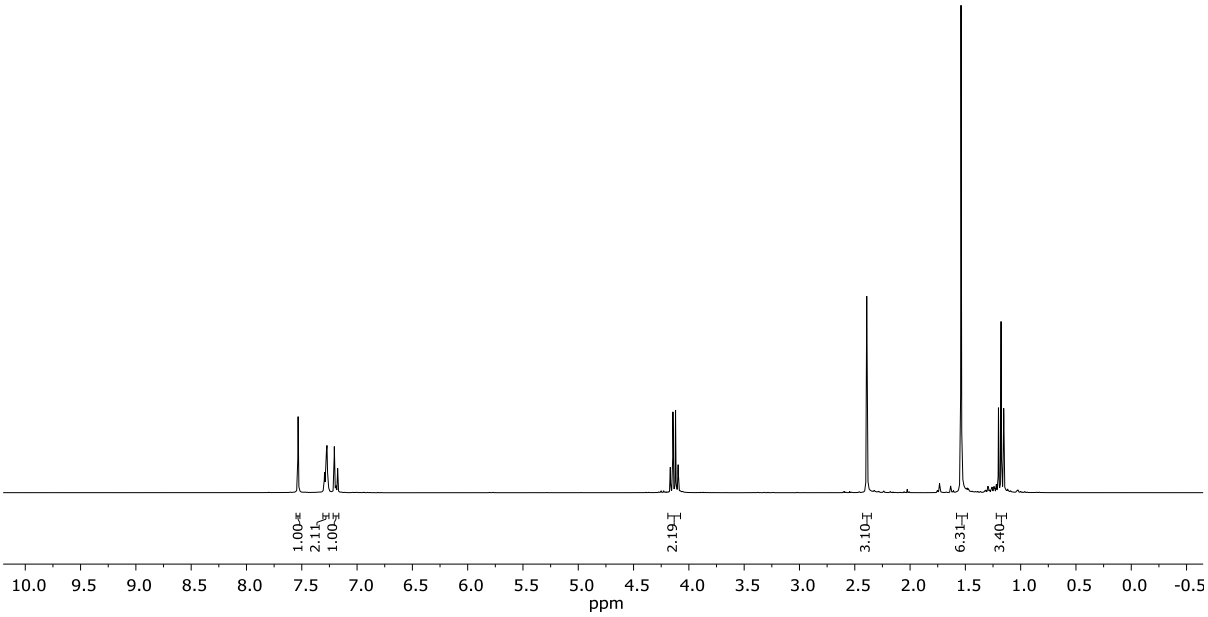
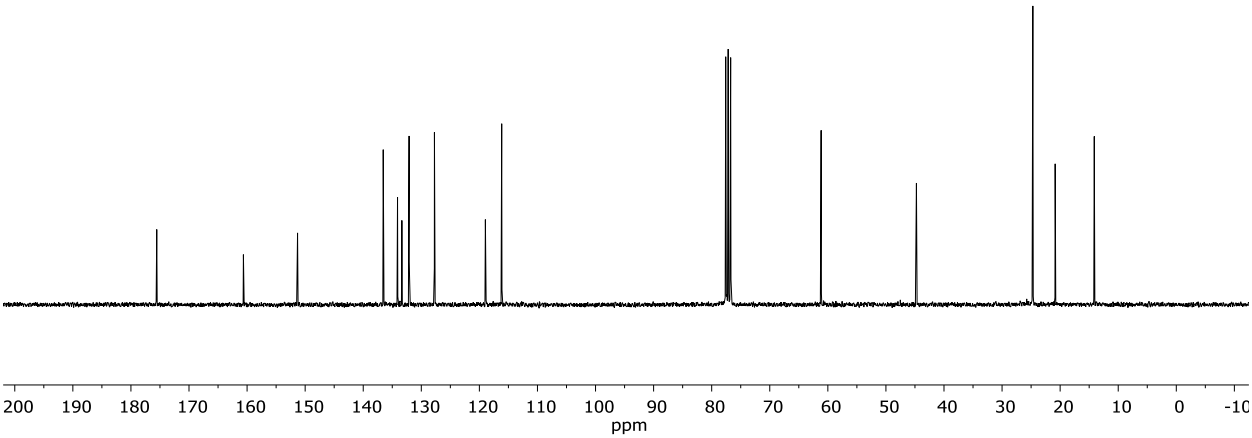
ppm



10b


1.00
2.11
1.00
2.19
3.10
6.31
3.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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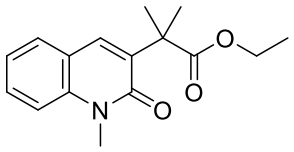
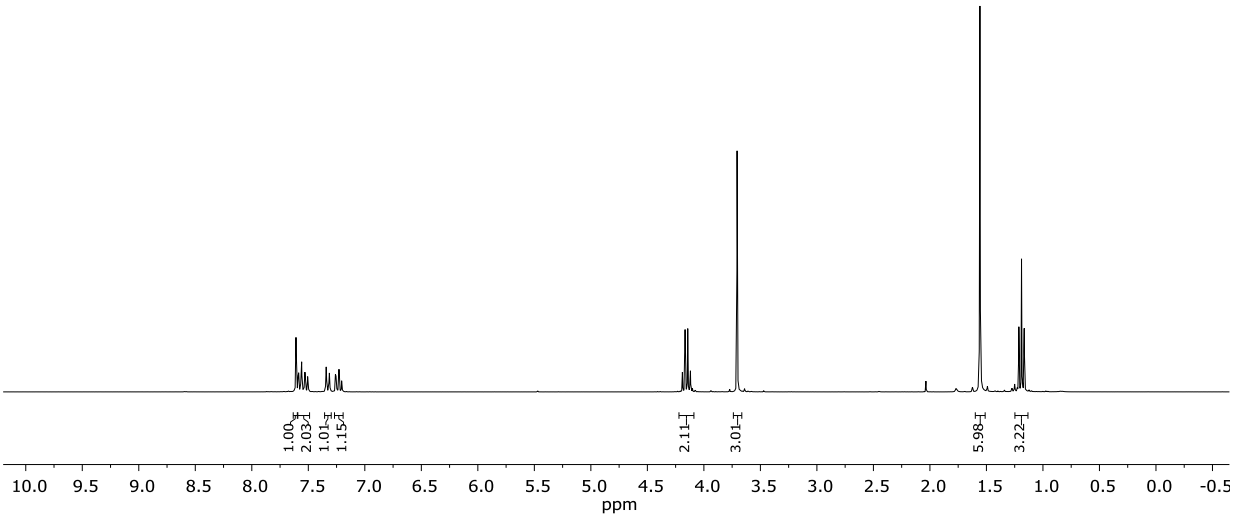
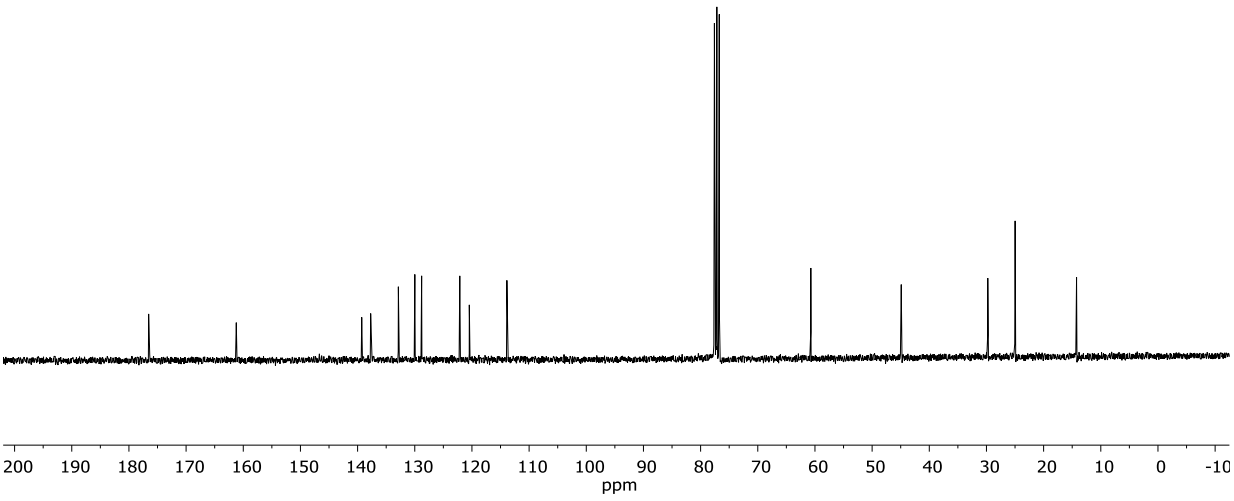
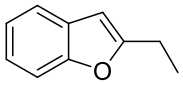
ppm



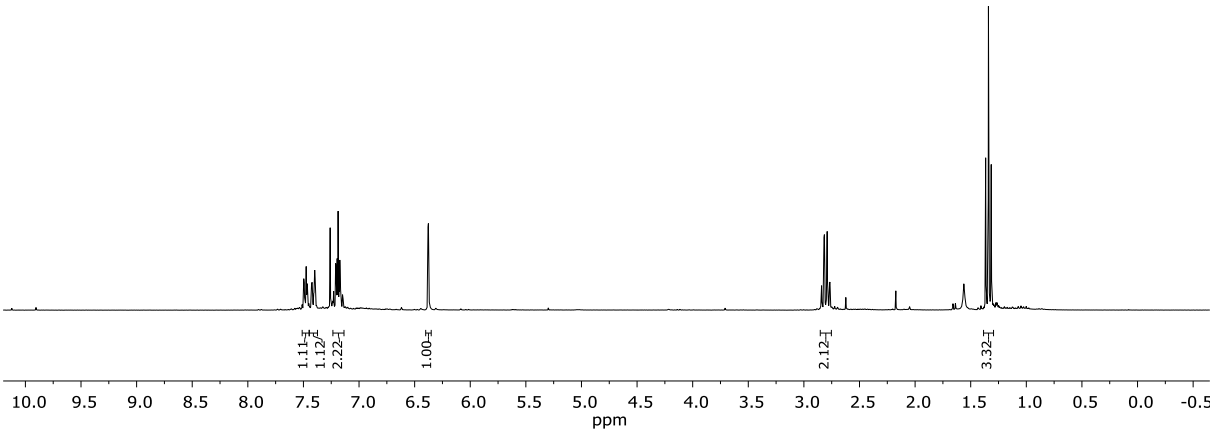
11

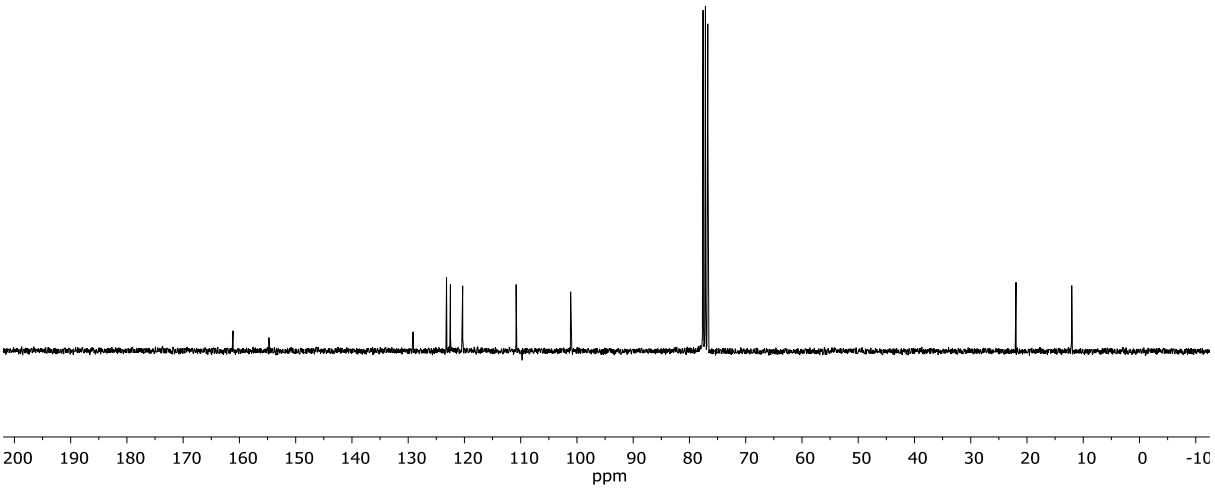

1.00
2.03
1.01
1.15
2.11
3.01
5.98
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

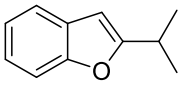

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



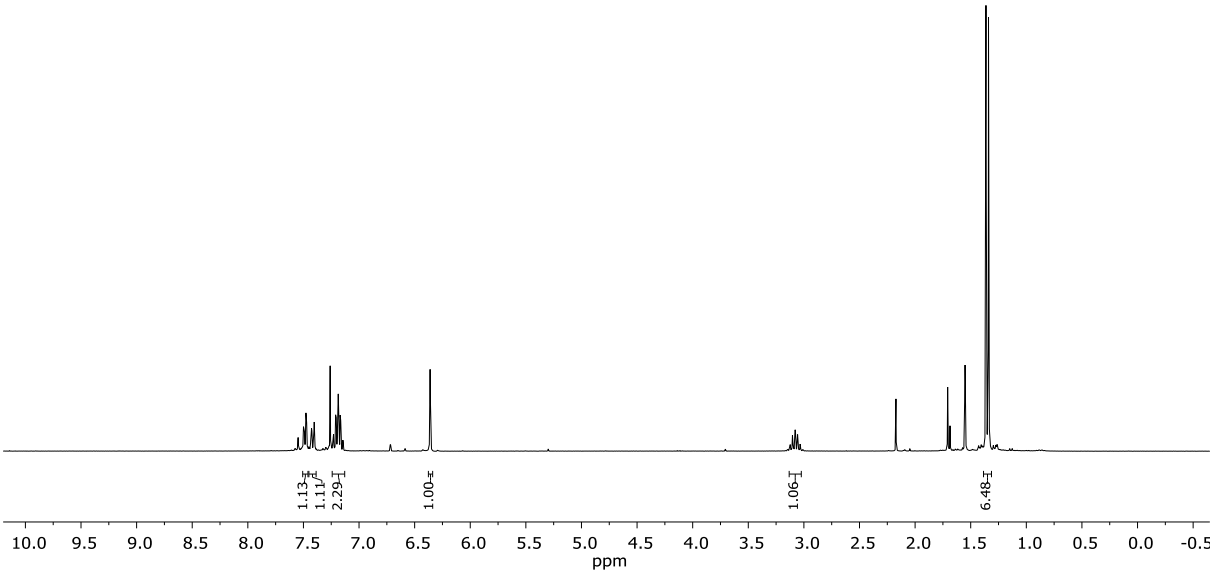
4

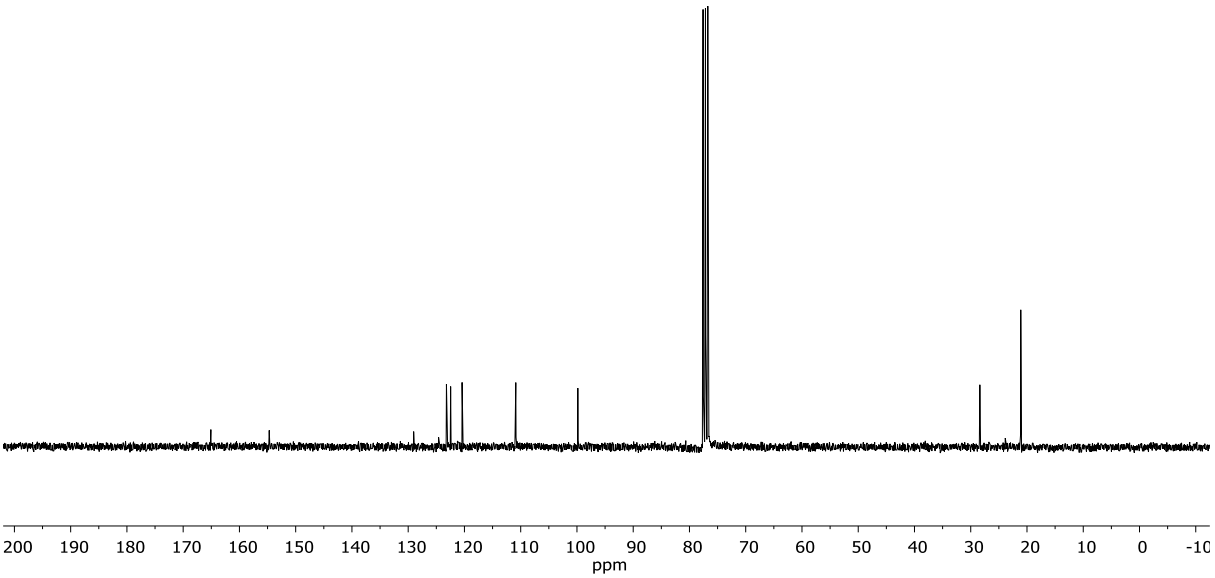

1.11
1.12
2.22
1.00
2.12
3.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



4'


1.13
1.11
2.29
1.00
1.06
6.48
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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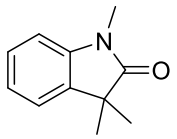
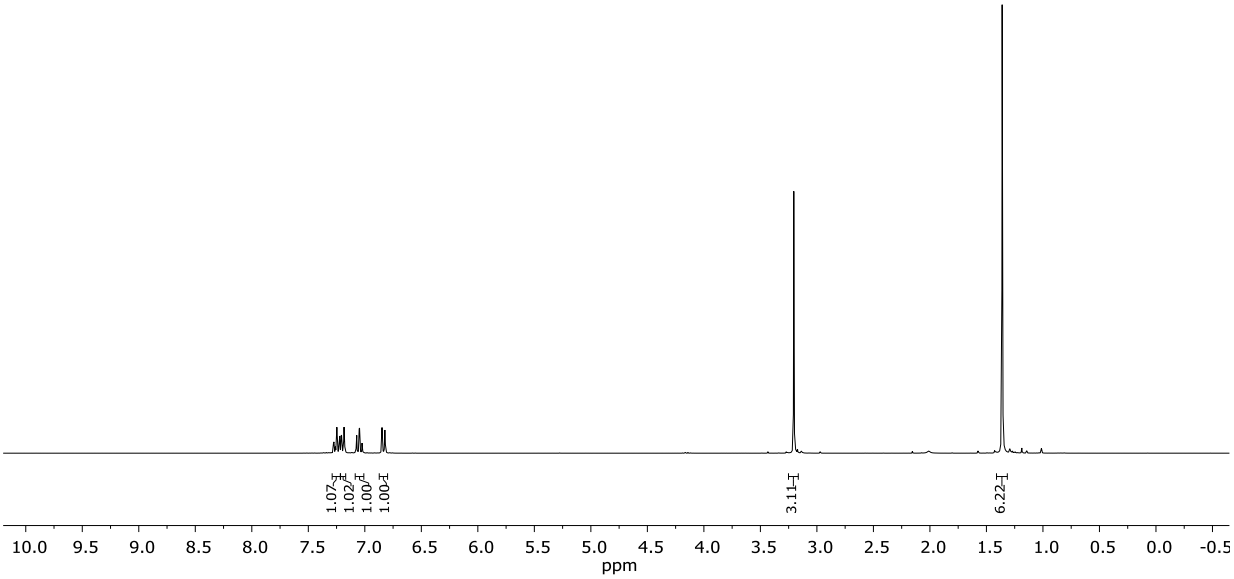
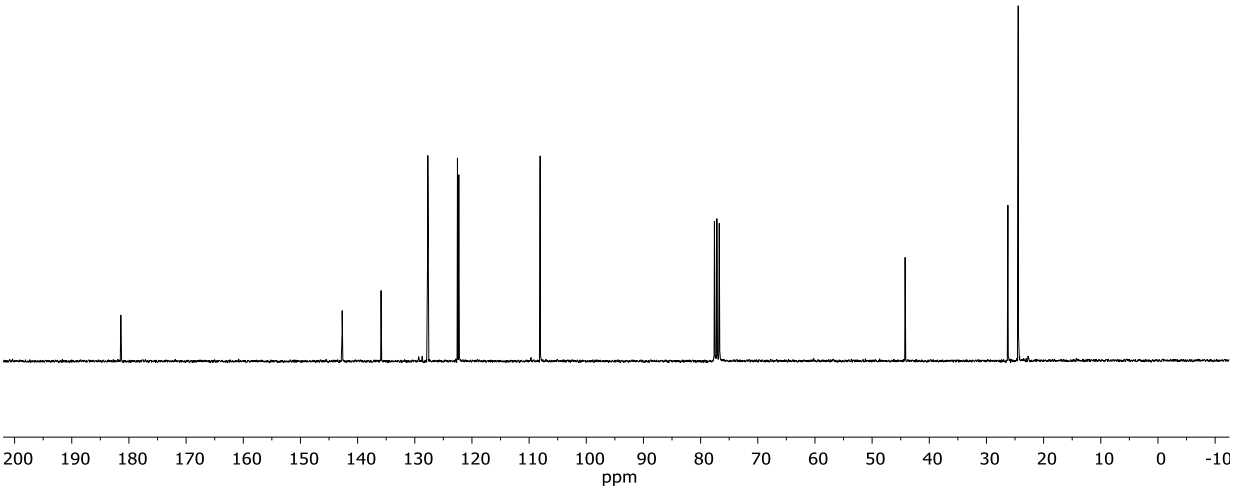
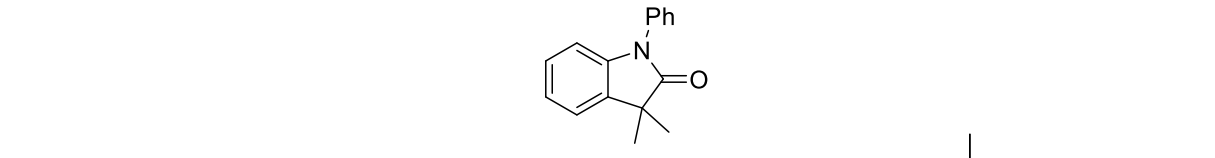
ppm



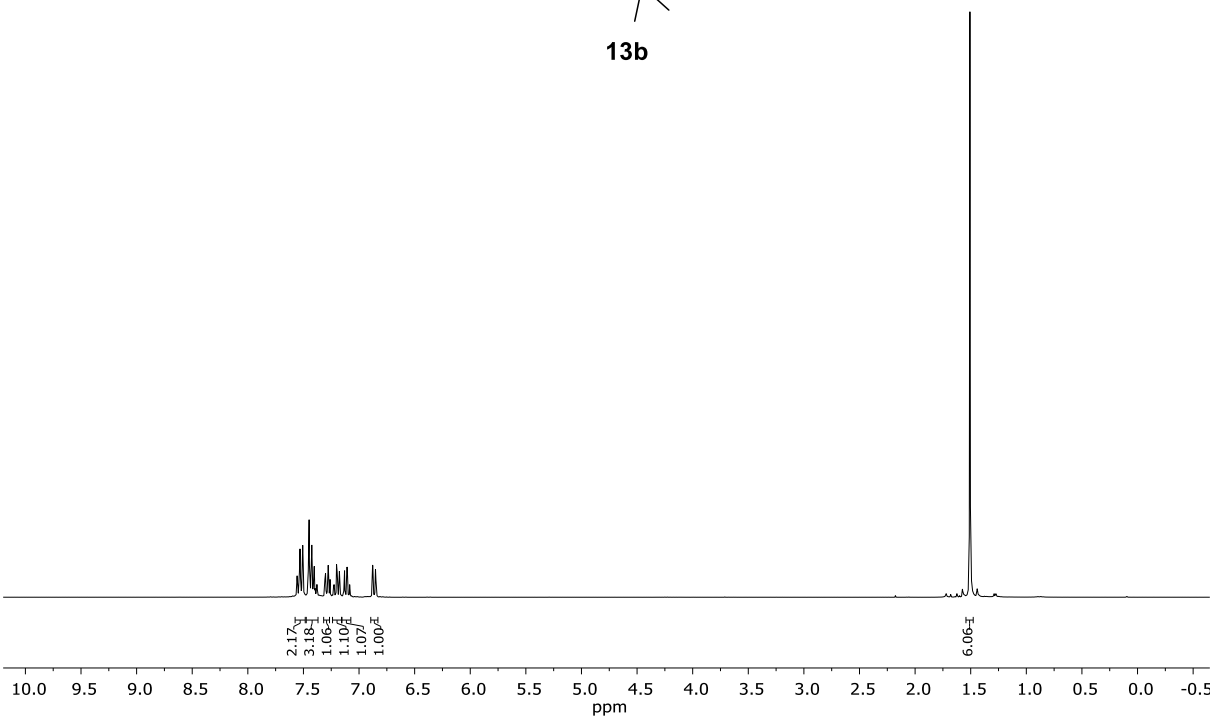
13a

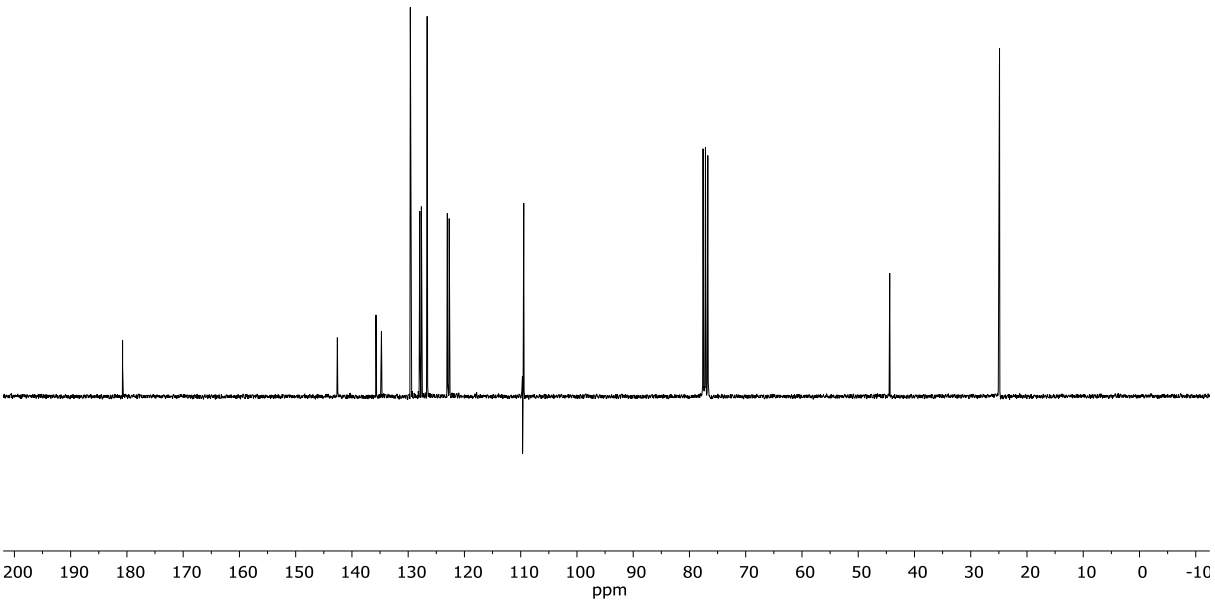

1.07
1.02
1.00
1.00
3.11
6.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

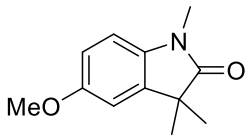

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


Ph
N
O

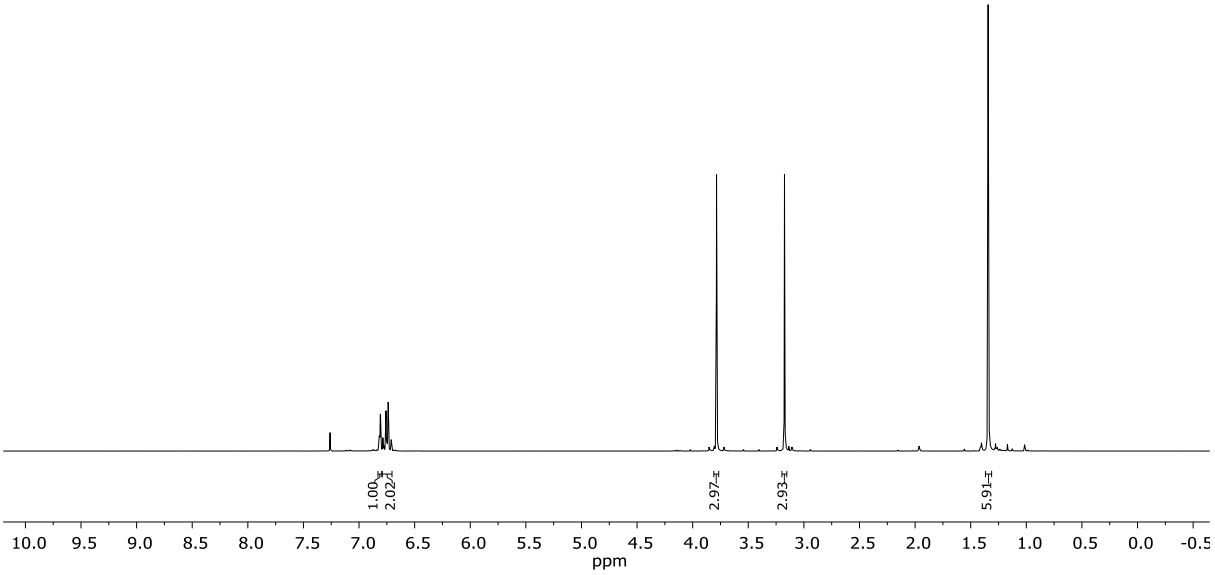
13b

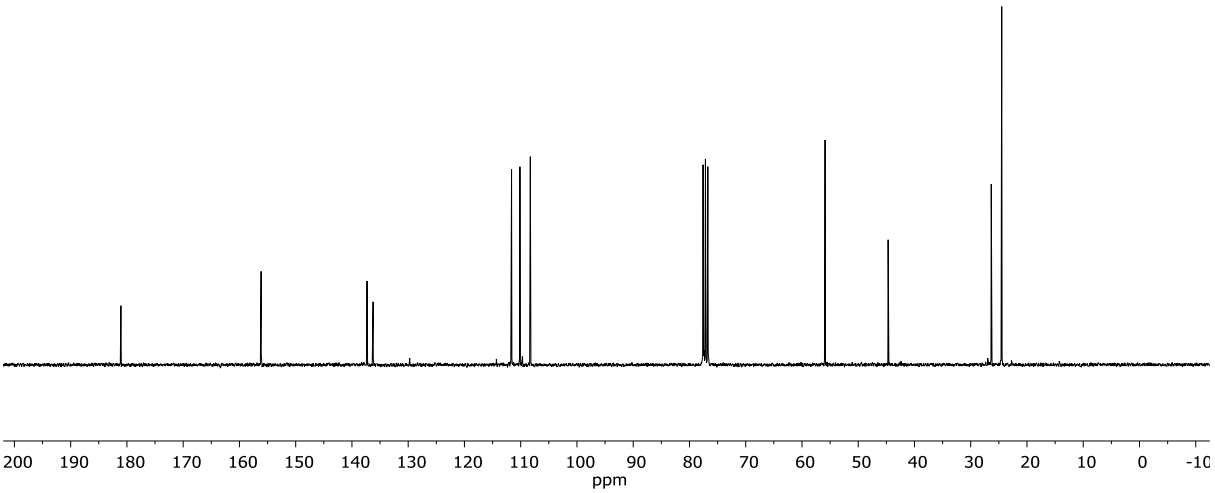

2.17
3.18
1.06
1.10
1.07
1.00
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


N
O
MeO

13c


1.00
2.02
2.97
2.93
5.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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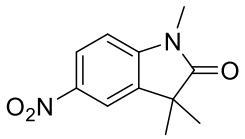
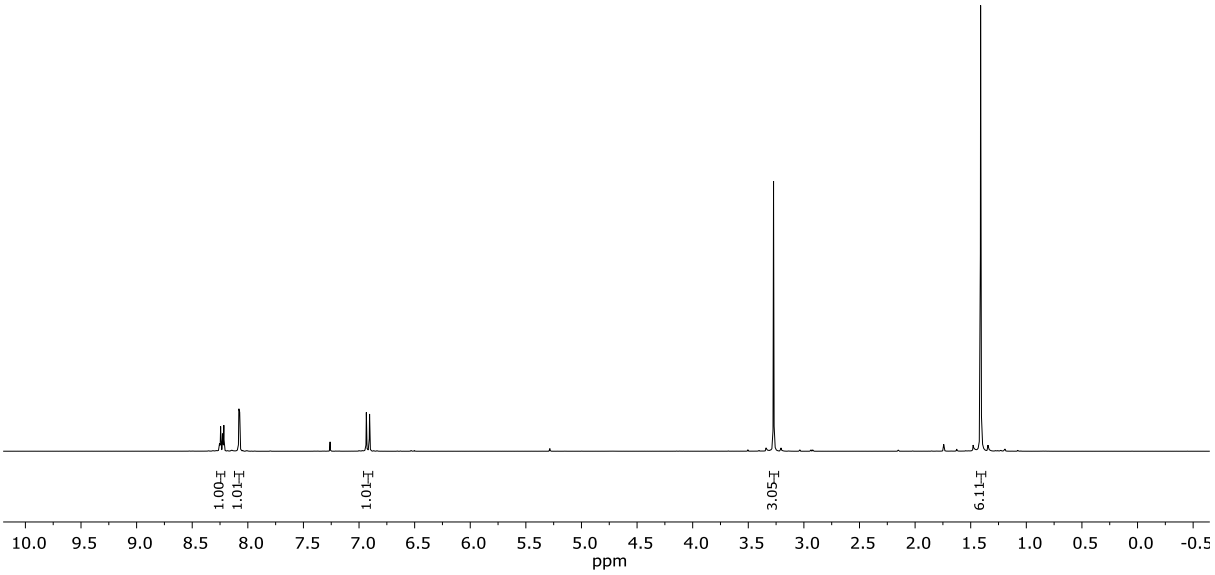
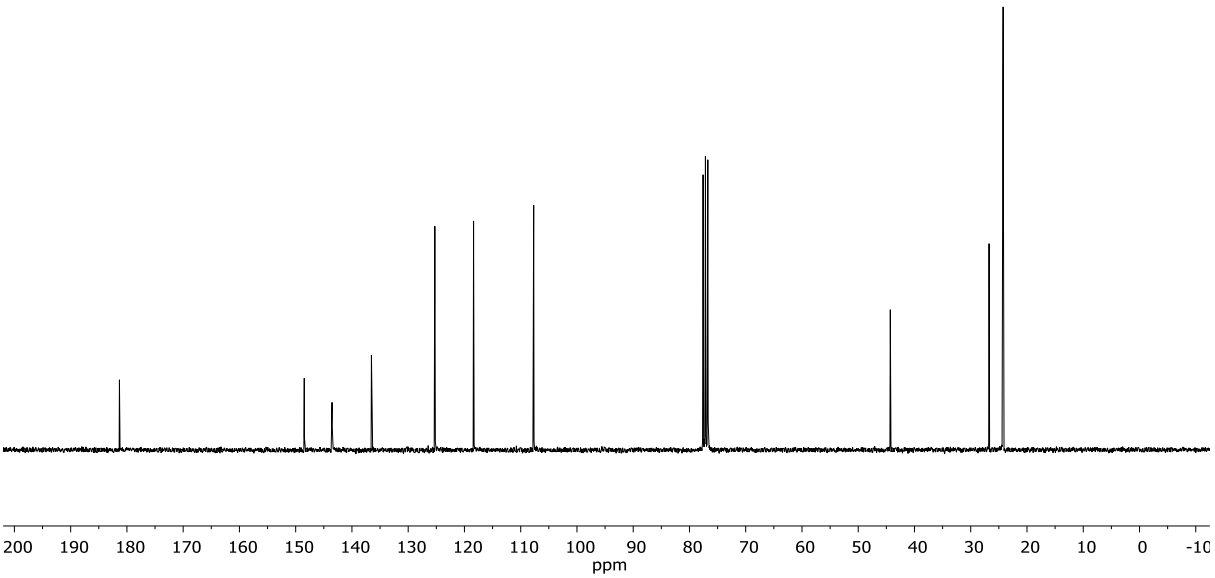
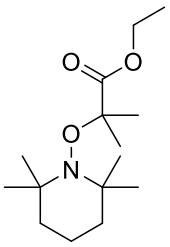
ppm


N
O
O_2N

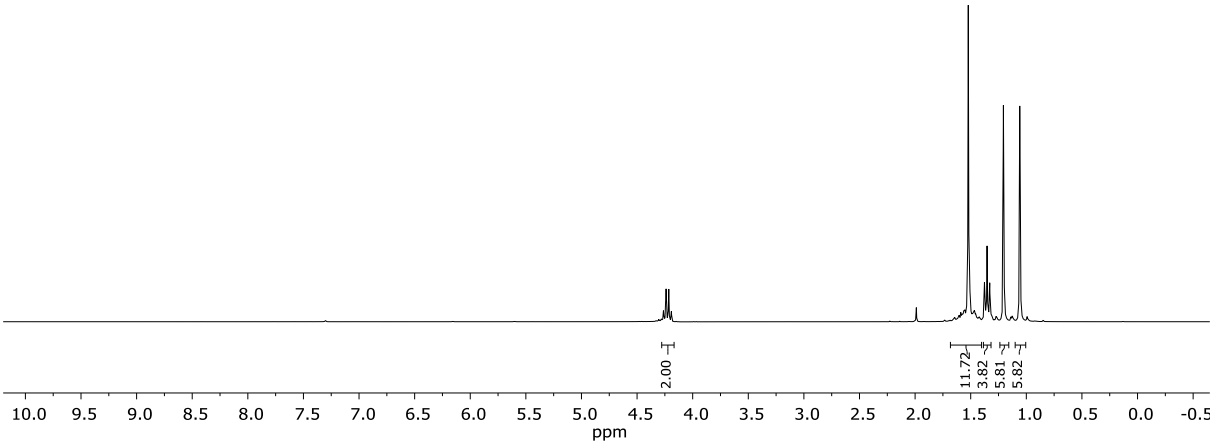
13d

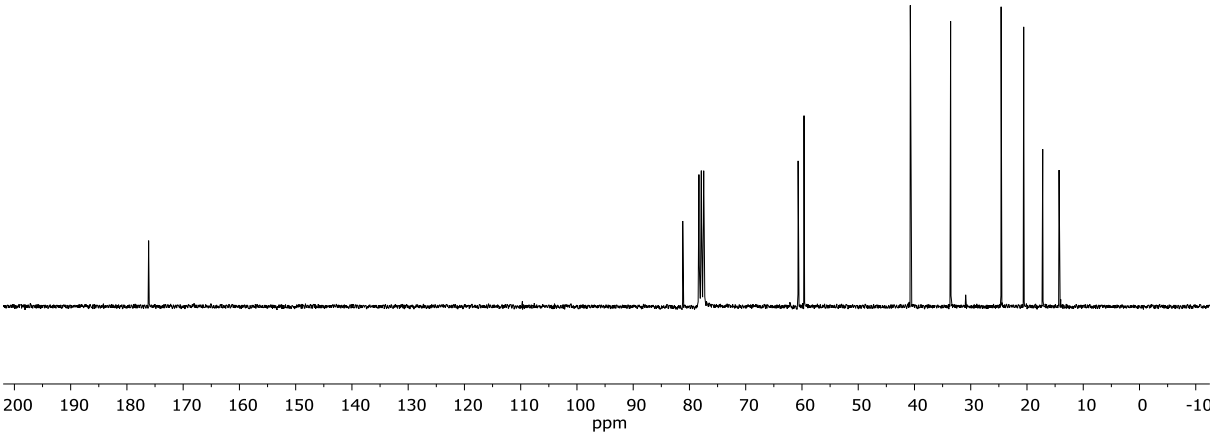

1.00
1.01
1.01
3.05
6.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



14


2.00
11.72
3.82
5.81
5.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm