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Supporting Information
for

Carbon Nitride Photoredox Catalysis Enables the Generation of the Dioxolanyl Radical in Conjugate Addition Reactions

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1. General Practical Considerations

All reagents were purchased from commercial suppliers (ABCR, Acros, Alfa-Aesar, Fluorochem, Merck, TCI, Sigma-Aldrich) and were used without further purification unless stated. Dioxolane was distilled prior to use to remove BHT and stored under N₂. General procedures for catalyst testing are provided as supporting information. Reactions were monitored by thin-layer chromatography (TLC) performed on Merck silica gel 60 F254 glass plates. Spots were visualized with UV light ($\lambda = 254$ nm) or through staining with KMnO₄ or Cerium Ammonium Molybdate.

Chromatographic purification of products was performed using silica gel (SiliaFlash P60, particle size 40–63 μm) for preparative column chromatography under 0.30 bar overpressure. Solvents were removed under reduced pressure by rotatory evaporation at 40 °C.

¹H and ¹³C NMR spectra were recorded in CDCl₃ on Bruker AVIII HD 500 and 400 MHz spectrometers, as well as Bruker Neo 500 and 400 MHz spectrometers operating at the given spectrometer frequency at room temperature. Signal assignment was achieved through ¹H correlation spectroscopy (COSY), heteronuclear single quantum correlation spectroscopy (HSQC), and heteronuclear multiple bond correlation spectroscopy (HMBC). Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS with the solvent resonance employed as the internal standard (chloroform, $\delta = 7.26$ ppm for ¹H and $\delta = 77.16$ ppm for ¹³C). All ¹³C-NMR spectra were measured with complete proton decoupling. Data for NMR spectra are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz as absolute values.

Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum TWO FT-IR (UATR) instrument as thin films.

High-resolution mass spectrometry (HRMS) data were obtained at the ETH Zurich mass spectrometry service on a Bruker Daltonics maXis ESI-Q-TOF or a Thermo Scientific Q Exactive GC Orbitrap with direct Probe (ESI), respectively, and are reported as (*m/z*).

Gas Chromatography (GC) was performed on an Agilent Intuvo 9000 GC-Gas chromatography System with a FI detector using a CP-Chirasil-Dex CB column.

X-ray diffraction (XRD) patterns of the powders were obtained in a PANalytical X'Pert PRO MPD diffractometer with Bragg-Brentano geometry using Ni-filtered CuK α radiation ($\lambda = 0.1541$ nm). The instrument was operated at 30 mA and 10 kV and the patterns were recorded in the 5–70° 2 θ range with an angular step size of 0.05° and an integration time of ~1.38 s per step or ~5.53 s per step.

UV–visible spectrophotometry (UV-Vis) spectra were collected with an Agilent Cary 5000 UV-vis-NIR spectrophotometer in diffuse reflectance mode with a Harrick Scientific Praying Mantis accessory.

Elemental analyses were performed by the microanalytical laboratory of the ETH Zürich on a LECO TruSpec Micro elemental analyzer.

Scanning electron microscopy was performed on a SEM Magellan 400 FEI instrument.

High-Intensity Photoreactor

Photoreactors were custom designed and built by Benson Jelier and the mechanical workshop in the Department of Chemistry and Applied Biosciences at ETH Zürich having blue LEDs, equally spaced in a circle design, powered by a 10.3A power supply, emitting 350 W of light with the measured UV-Vis spectrum. The LEDs were water cooled and further cooled by built-in fans to maintain an ambient temperature.

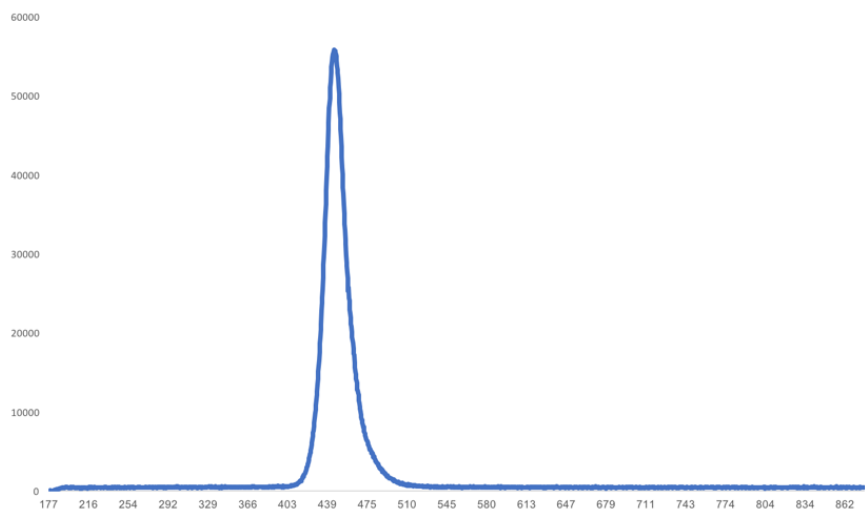


Figure S1: UV-Vis emission spectrum of high-intensity blue LED photoreactors ($\lambda_{max} = 466 \text{ nm}$).¹

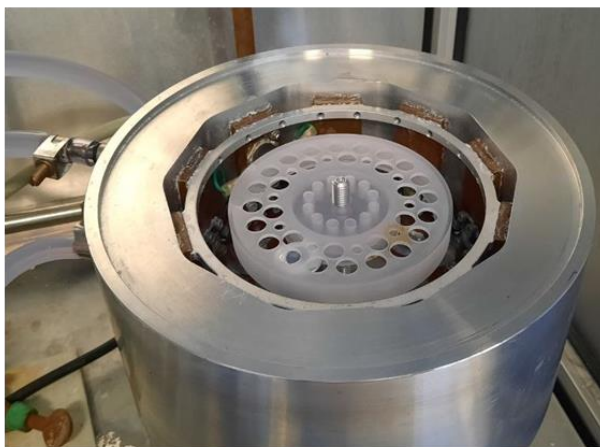
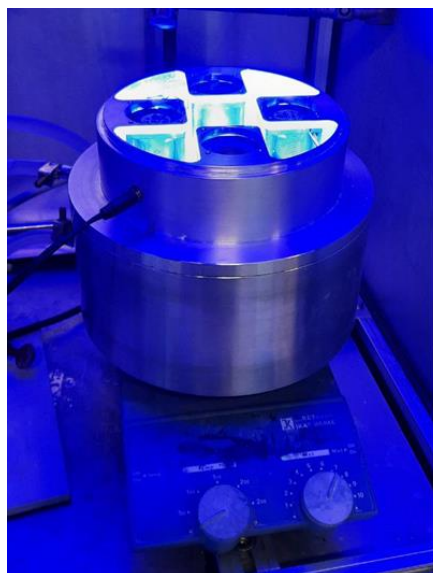


Figure S2: Custom-built blue LED photoreactors for reaction optimization and scale-up.

2. General Reaction Procedures

Synthesis of g-C₃N₄

g-C₃N₄ was prepared by calcination of dicyandiamide at 550 °C (2.3 °C min⁻¹ ramp rate) in a crucible for 4 h under a nitrogen flow.

General procedure A for substrate evaluation

A 20 ml crimp vial was charged with carbon nitride (5.0 mg) and the starting material (0.30 mmol, if solid). The vial was sealed, evacuated, and purged with N₂. Dioxolane (15 ml, distilled) was added, along with the starting material (0.30 mmol, if liquid). The reaction mixture was degassed by bubbling with N₂ for 15 minutes. The vial was placed in the photoreactor and irradiated with blue LEDs ($\lambda_{\text{max}} = 466 \text{ nm}$) for 12 to 24 hours. After completion of the reaction, as indicated by TLC analysis, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (ethyl acetate:hexane)

General procedure B for reaction optimization and control studies

A 5 ml crimp vial was charged with carbon nitride (2.0 mg). The vial was sealed, evacuated, and purged with N₂. Dioxolane (5.0 ml, distilled to remove BHT) was added, along with diethyl fumarate (0.15 mmol, 25 μl) and dodecane (17 μl). The reaction mixture was degassed by bubbling with N₂ for 15 minutes. The vial was placed in the photoreactor and irradiated with blue LEDs ($\lambda_{\text{max}} = 466 \text{ nm}$) for 1 hour. An aliquot was diluted with ethyl acetate and analyzed by gas chromatography.

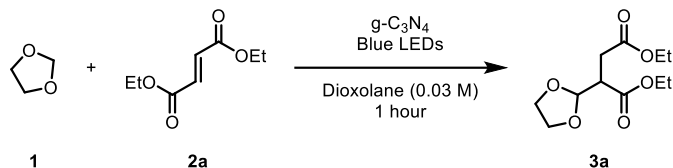
General procedure C for large scale reaction and recycling studies

A 150 ml Schlenk flask was charged with carbon nitride (0.200 g). The vial was sealed, evacuated, and purged with N₂. Dioxolane (0.100 l, distilled) was added, along with diethyl fumarate (3.00 mmol, 0.492 ml) and dodecane (0.500 equiv, 0.340 ml). The reaction mixture was degassed by bubbling with N₂ for 30 minutes. The vial was placed in the photoreactor and irradiated with blue LEDs ($\lambda_{\text{max}} = 466 \text{ nm}$) for 12 hours.

For recycling studies, an aliquot was diluted with ethyl acetate and analyzed by gas chromatography. To recover the catalyst, the remaining reaction mixture was filtered over 0.2 μm nylon membrane filters, the residue was washed with ethyl acetate (3x 20 ml) and dried under vacuum.

For evaluation of the large scale reaction, the reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (ethyl acetate:hexane).

3. Extended Reaction Optimization and Control Studies



Entry	Variation from standard Conditions ^a	Yield ^b
1	None	84%
2	No Carbon Nitride	28%
3	dark	0%
4	20 min, then dark	33%, then 33%
5	Under air	71%
6	Ir(ppy) ₃ as photocatalyst	78%
7	Mes-Acr ⁺ as photocatalyst	40%
8	Ru(bpy) ₃ (PF ₆) ₂ as photocatalyst	75%
9	Mesoporous carbon nitride ¹ as photocatalyst	88%
10	Exfoliated carbon nitride ² as photocatalyst	89%
11	CN-OA-m ³ as photocatalyst	88%
12	Porous C ₃ N ₄ ⁴ as photocatalyst	86%
13	CM ₁ B _{0.033} ⁵ as photocatalyst	88%
14	CM ₁ B _{0.25} as photocatalyst	85%
15	CM ₁ B _{0.5} as photocatalyst	86%
16	C-ZIF/g-C ₃ N ₄ ⁶ as photocatalyst	88%
17	Dioxolane:MeCN (1:1) as solvent	83%
18	Dioxolane:MeCN (1:3) as solvent	24%
19	Dioxolane:MeCN (1:5) as solvent	21%
20	Dioxolane:MeCN (1:10) as solvent	4%
21	0.5 M concentration	3%
22	0.1 M concentration	43%
23	0.05 M concentration	80%
24	0.02 M concentration	84%
25	2 mg catalyst loading	82%
26	5 mg catalyst loading	81%
27	20 mg catalyst loading	82%
28	50 mg catalyst loading	84%

^aReactions were conducted on a 0.15 mmol scale according to general procedure B. ^bYields were determined by gas chromatography using dodecane (0.5 equiv.) as an internal standard.

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² G. Lei, Y. Cao, W. Zhao, Z. Dai, L. Shen, Y. Xiao, L. Jiang, *ACS Sustainable Chem. Eng.* **2019**, *7*, 4941–4950.

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⁶ F. He, G. Chen, Y. Zhou, Y. Yu, L. Li, S. Hao, B. Lu, *J. Mater. Chem. A*, **2016**, *4*, 3822–3827.

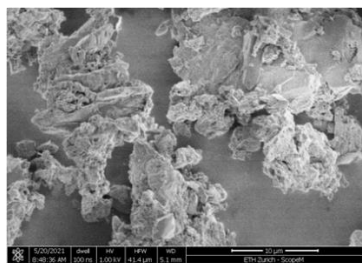
4. Supplementary Figures



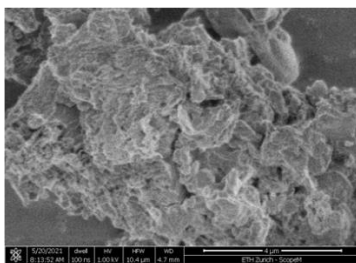
Figure S3: Effect of $g\text{-C}_3\text{N}_4$ loading



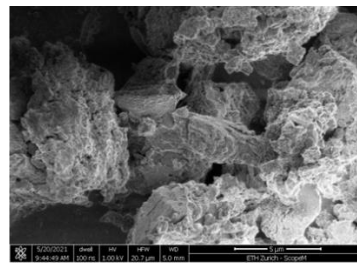
Figure S4: Picture of $g\text{-C}_3\text{N}_4$



Fresh catalyst



After 1° cycle

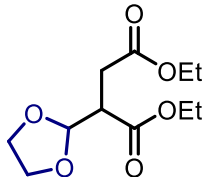


After 5° cycle

Figure S5: Scanning Electron microscopy images of $g\text{-C}_3\text{N}_4$.

5. Characterization Data

Diethyl 2-(1,3-dioxolan-2-yl)succinate (3a)



The title compound was prepared according to general procedure A from diethyl fumarate (51.7 mg, 49.2 ml) and diethyl maleate (51.7 mg, 48.5 μ l). The crude product was purified by flash column chromatography (1:5, ethyl acetate:hexane) to afford a colorless oil (72.0 mg, 97% for fumarate and 68.2 mg, 92% for maleate).

TLC (ethyl acetate:hexane, 1:5): R_f = 0.25.

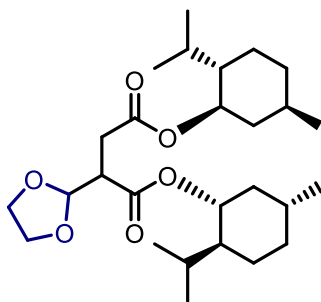
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 5.20 (d, J = 4.1 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 4.13 (qd, J = 7.2, 0.9 Hz, 2H), 4.02 – 3.92 (m, 2H), 3.92 – 3.84 (m, 2H), 3.22 (ddd, J = 9.1, 4.8, 4.1 Hz, 1H), 2.77 (dd, J = 16.8, 9.3 Hz, 1H), 2.59 (dd, J = 16.8, 4.8 Hz, 1H), 1.25 (dt, J = 9.4, 7.2 Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 172.0, 171.0, 103.0, 65.4, 65.4, 61.2, 60.7, 45.9, 30.4, 14.2, 14.2.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2982, 2896, 1734, 1394, 1372, 1261, 1226, 1160, 1147, 1032.

HRMS (ESI): m/z calculated for $\text{C}_{11}\text{H}_{18}\text{NaO}_6$ [$\text{M}+\text{Na}$] $^+$: 269.0996; found: 269.0990.

Bis((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) 2-(1,3-dioxolan-2-yl)succinate (3b)



The title compound was prepared according to general procedure A from dimethyl fumarate (118 mg). The reaction mixture was irradiated for 24 hours. The crude product was purified by flash column chromatography (1:10, ethyl acetate:hexane) to afford a colorless oil (122 mg, 87%) as a mixture of diastereomers.

TLC (ethyl acetate:hexane, 1:10): $R_f = 0.25$

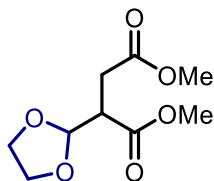
$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 5.19$ (dd, $J = 4.0, 1.8$ Hz, 1H), 4.71 (dtd, $J = 15.5, 10.9, 4.4$ Hz, 2H), 4.02 – 3.91 (m, 2H), 3.91 – 3.82 (m, 2H), 3.31 – 3.19 (m, 1H), 2.76 (ddd, $J = 16.4, 9.3, 7.1$ Hz, 1H), 2.56 (ddd, $J = 16.9, 9.4, 4.8$ Hz, 1H), 2.06 – 1.81 (m, 4H), 1.67 (dp, $J = 13.1, 3.3$ Hz, 4H), 1.52 – 1.29 (m, 4H), 1.06 – 0.79 (m, 18H), 0.75 (d, $J = 6.9$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 171.5, 170.3, 103.3, 75.0, 74.5, 65.4, 47.1, 47.0, 46.0, 40.9, 40.8, 40.7, 34.4, 34.4, 31.5, 31.5, 30.7, 30.4, 26.3, 26.1, 23.6, 23.5, 22.1, 20.9, 20.9, 16.5, 16.3$.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2954, 2928, 2870, 1732, 1456, 1387, 1369, 1260, 1224, 1166, 1146, 1097, 1037, 983.

HRMS (ESI): m/z calculated for $\text{C}_{27}\text{H}_{47}\text{O}_6$ $[\text{M}+\text{H}]^+$: 467.3367; found: 467.3364.

Dimethyl 2-(1,3-dioxolan-2-yl)succinate (3c)



The title compound was prepared according to general procedure A from dimethyl maleate (43.2 mg, 37.6 ml). The crude product was purified by flash column chromatography (1:5 to 1:1, ethyl acetate:hexane) to afford a colorless oil (64.0 mg, 97%).

TLC (ethyl acetate:hexane, 1:5): $R_f = 0.12$.

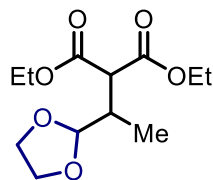
$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 5.19$ (d, $J = 4.2$ Hz, 1H), 4.01 – 3.93 (m, 2H), 3.91 – 3.83 (m, 2H), 3.74 (s, 3H), 3.68 (s, 3H), 3.25 (ddd, $J = 9.1, 4.9, 4.2$ Hz, 1H), 2.80 (dd, $J = 16.9, 9.2$ Hz, 1H), 2.62 (dd, $J = 16.9, 4.9$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 172.5, 171.5, 102.9, 65.5, 65.5, 52.4, 52.0, 45.8, 30.2$.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2955, 2894, 1736, 1437, 1265, 1163, 1147, 1034.

HRMS (ESI): m/z calculated for $\text{C}_9\text{H}_{14}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 241.0683; found: 241.0678.

Diethyl 2-(1-(1,3-dioxolan-2-yl)ethyl)malonate (3d)



The title compound was prepared according to general procedure A from diethyl ethylidenemalonate (55.9 mg, 54.8 μ l). The crude product was purified by flash column chromatography (1:5, ethyl acetate:hexane) to afford a colorless oil (60.7 mg, 78%).

TLC (ethyl acetate:hexane, 1:4): R_f = 0.25.

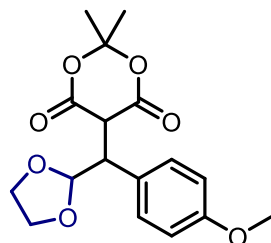
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 4.88 (d, J = 4.2 Hz, 1H), 4.18 (qd, J = 7.2, 3.4 Hz, 4H), 3.96 – 3.88 (m, 2H), 3.88 – 3.80 (m, 2H), 3.51 (d, J = 7.9 Hz, 1H), 2.66 – 2.55 (m, 1H), 1.26 (td, J = 7.1, 3.0 Hz, 6H), 1.06 (d, J = 7.0 Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 168.8, 168.7, 105.5, 65.3, 65.2, 61.4, 61.4, 52.9, 37.3, 14.2, 14.2, 12.3.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2982, 2888, 1731, 1465, 1369, 1226, 1154, 1094, 1066, 1031, 943.

HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{21}\text{O}_6$ $[\text{M}+\text{H}]^+$: 261.1333; found: 261.1324.

5-((1,3-dioxolan-2-yl)(4-methoxyphenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3e)



The title compound was prepared according to general procedure A from 5-(4-methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (78.7 mg). The crude product was purified by flash column chromatography (1:1, ethyl acetate:hexane) to afford a yellow oil (98.0 mg, 97%).

TLC (ethyl acetate:hexane, 1:1): R_f = 0.21.

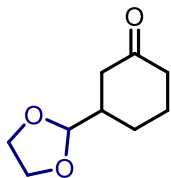
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.43 – 7.32 (m, 2H), 6.89 – 6.79 (m, 2H), 5.88 (d, J = 8.3 Hz, 1H), 4.09 (d, J = 2.6 Hz, 1H), 4.05 – 3.89 (m, 4H), 3.84 (dd, J = 8.3, 2.6 Hz, 1H), 3.76 (s, 3H), 1.71 (d, J = 0.8 Hz, 3H), 1.48 (d, J = 0.8 Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 165.3, 165.0, 159.3, 130.8, 128.6, 114.3, 105.3, 104.1, 65.7, 65.2, 55.3, 49.4, 48.4, 28.3, 27.6.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2957, 1782, 1742, 1612, 1515, 1299, 1250, 1181, 1143, 1114.

HRMS (ESI): m/z calculated for $\text{C}_{17}\text{H}_{20}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$: 359.1101; found: 359.1101.

3-(1,3-dioxolan-2-yl)cyclohexan-1-one (3f)



The title compound was prepared according to general procedure A from cyclohexanone on a 0.2 mmol scale (19.2 mg, 19.4 μ l). The reaction mixture was irradiated for 24 hours. The crude product was purified by flash column chromatography (1:3, ethyl acetate:hexane) to afford a colorless oil (30.0 mg, 88%).

TLC (ethyl acetate:hexane, 1:3): R_f = 0.24.

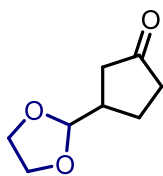
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 4.77 (d, J = 3.7 Hz, 1H), 3.96 – 3.83 (m, 4H), 2.47 – 2.21 (m, 4H), 2.16 – 2.05 (m, 2H), 1.99 – 1.86 (m, 1H), 1.71 – 1.52 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 211.2, 106.0, 65.4, 65.2, 42.3, 41.7, 41.5, 25.8, 24.8.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2949, 2882, 1709, 1146, 1095, 1031, 946.

HRMS (ESI): m/z calculated for $\text{C}_9\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 171.1016; found: 171.1015.

3-(1,3-dioxolan-2-yl)cyclopentan-1-one (3g)



The title compound was prepared according to general procedure A from cyclopentenone (24.6 mg, 25.1 μ l). The crude product was purified by flash column chromatography (1:3, ethyl acetate:hexane) to afford a colorless oil (36.7 mg, 78%).

TLC (ethyl acetate:hexane, 1:3): R_f = 0.20.

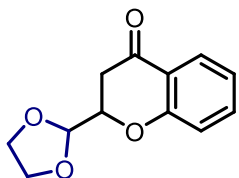
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 4.88 (d, J = 3.9 Hz, 1H), 4.03 – 3.82 (m, 4H), 2.62 – 2.49 (m, 1H), 2.41 – 2.07 (m, 5H), 1.97 – 1.84 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ = 219.0, 106.1, 65.5, 65.3, 39.8, 39.3, 37.6, 24.0.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2957, 2886, 1738, 1404, 1240, 1149, 1128, 1112, 1089, 1032, 995, 963, 944.

HRMS (ESI): m/z calculated for $C_8H_{13}O_3$ $[M+H]^+$: 157.0859; found: 157.0860.

2-(1,3-dioxolan-2-yl)chroman-4-one (3h)



The title compound was prepared according to general procedure A from chromone (43.8 mg). The crude product was purified by flash column chromatography (1:3, ethyl acetate:hexane) to afford an off-white solid (63.0 mg, 95%).

TLC (ethyl acetate:hexane, 1:3): R_f = 0.28

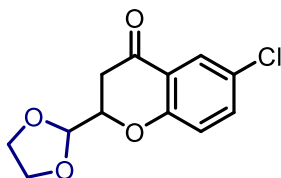
1H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.79 (m, 1H), 7.57 – 7.41 (m, 1H), 7.10 – 6.95 (m, 2H), 5.20 (d, J = 3.5 Hz, 1H), 4.53 (dt, J = 12.0, 3.6 Hz, 1H), 4.11 – 3.91 (m, 4H), 2.89 (dd, J = 16.9, 12.0 Hz, 1H), 2.77 (dd, J = 16.9, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.5, 160.9, 136.2, 127.0, 121.7, 121.3, 118.1, 103.2, 77.8, 65.9, 65.6, 37.3.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2958, 2889, 1688, 1605, 1462, 1302, 1114, 763.

HRMS (ESI): m/z calculated for $C_{12}H_{13}KO_6$ $[M+H]^+$: 221.0808; found: 221.0801.

6-chloro-2-(1,3-dioxolan-2-yl)chroman-4-one (3i)



The title compound was prepared according to general procedure A from 6-chlorochromone (54.2 mg). The crude product was purified by flash column chromatography (1:4, ethyl acetate:hexane) to afford an off-white solid (76.0 mg, 99%).

TLC (ethyl acetate:hexane, 1:4): R_f = 0.20

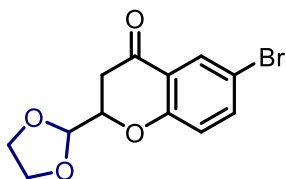
1H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, J = 2.7 Hz, 1H), 7.41 (dd, J = 8.8, 2.7 Hz, 1H), 6.98 (d, J = 8.8 Hz, 1H), 5.18 (d, J = 3.4 Hz, 1H), 4.52 (dt, J = 11.4, 3.7 Hz, 1H), 4.08 – 3.92 (m, 4H), 2.93 – 2.72 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 190.3, 159.3, 136.0, 127.3, 126.3, 122.0, 119.8, 103.0, 77.9, 66.0, 65.6, 36.9.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2892, 1697, 1603, 1469, 1423, 1275, 1129.

HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{11}\text{ClNaO}_4$ $[\text{M}+\text{Na}]^+$: 277.0238; found: 277.0235.

6-bromo-2-(1,3-dioxolan-2-yl)chroman-4-one (3j)



The title compound was prepared according to general procedure A from 6-bromochromone (67.5 mg). The crude product was purified by flash column chromatography (1:4, ethyl acetate:hexane) to afford an off-white solid (79.3 mg, 88%).

TLC (ethyl acetate:hexane, 1:4): R_f = 0.2

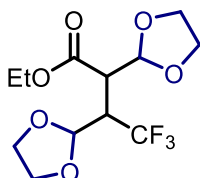
^1H NMR (400 MHz, CDCl_3) δ = 8.00 – 7.93 (m, 1H), 7.55 (dd, J = 8.8, 2.6 Hz, 1H), 6.93 (dd, J = 8.8, 0.3 Hz, 1H), 5.18 (d, J = 3.3 Hz, 1H), 4.52 (ddd, J = 11.3, 4.1, 3.3 Hz, 1H), 4.08 – 3.93 (m, 4H), 2.92 – 2.71 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ = 190.1, 159.7, 138.8, 129.4, 122.5, 120.1, 114.4, 103.0, 77.9, 66.0, 65.6, 36.8.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2891, 1697, 1599, 1466, 1417, 1273, 1129.

HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{11}\text{BrNaO}_4$ $[\text{M}+\text{Na}]^+$: 320.9733; found: 320.9732.

ethyl 2,3-di(1,3-dioxolan-2-yl)-4,4,4-trifluorobutanoate (3k)



The title compound was prepared according to general procedure A from methyl 4,4,4-trifluorobut-2-ynoate (42.6 mg, 36.9 μl). The crude product was purified by flash column chromatography (1:3, ethyl acetate:hexane) to afford a colorless oil (57.0 mg, 60%).

TLC (ethyl acetate:hexane, 1:3): R_f = 0.23

^1H NMR (400 MHz, CDCl_3) δ = 5.50 – 5.40 (m, 1H), 5.33 (dd, J = 4.6, 2.2 Hz, 1H), 4.27 – 4.13 (m, 2H), 4.04 – 3.85 (m, 8H), 3.18 – 2.97 (m, 2H), 1.27 (td, J = 7.1, 1.3 Hz, 3H).

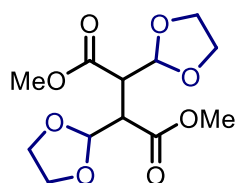
¹³C NMR (101 MHz, CDCl₃) δ = 169.4 (d, *J* = 16.0 Hz), 127.0 (q, *J* = 281.5 Hz), 102.14 (d, *J* = 2.1 Hz), 100.61 (dd, *J* = 10.6, 3.0 Hz), 65.62 – 64.97 (m, 4C), 61.33, 47.46 – 46.07 (m, 2C), 14.10.

¹⁹F NMR (376 MHz, CDCl₃) δ = -62.63 (d, *J* = 9.7 Hz), -64.22 (d, *J* = 9.7 Hz). mixture of diastereomers

IR (ATR, neat): ν_{\max} (cm⁻¹) = 2897, 1737, 1373, 1250, 1115, 1031, 944.

HRMS (ESI): *m/z* calculated for C₁₂H₁₈F₃O₆ [M+H]⁺: 315.1050; found: 315.1048.

dimethyl 2,3-di(1,3-dioxolan-2-yl)succinate (3l)



The title compound was prepared according to general procedure A from dimethyl but-2-ynedioate (49.8 mg, 42.9 μl). The crude product was purified by flash column chromatography (1:1, ethyl acetate:hexane) to afford a colorless oil (38.2 mg, 44%).

TLC (ethyl acetate:hexane, 1:1): *R_f* = 0.28

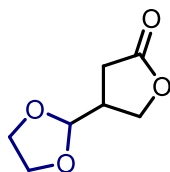
¹H NMR (400 MHz, CDCl₃) δ = 5.43 – 5.35 (m, 2H), 4.02 – 3.89 (m, 8H), 3.73 (s, 6H), 3.22 – 3.13 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 170.9, 102.4, 65.3, 65.3, 52.3, 48.2.

IR (ATR, neat): ν_{\max} (cm⁻¹) = 2955, 2894, 1738, 1437, 1198, 1133, 1030.

HRMS (ESI): *m/z* calculated for C₁₂H₁₈KO₈ [M+K]⁺: 329.0633; found: 329.0627

4-(1,3-dioxolan-2-yl)dihydrofuran-2(3H)-one (3m)



The title compound was prepared according to general procedure A from 2-furanone (25.2 mg, 21.3 μl). The crude product was purified by flash column chromatography (1:1, ethyl acetate:hexane) to afford a colorless oil (44.8 mg, 94%).

TLC (ethyl acetate:hexane, 1:1): *R_f* = 0.21.

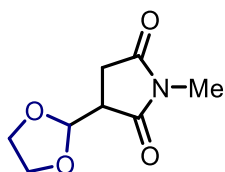
¹H NMR (400 MHz, CDCl₃) δ = 4.90 (d, *J* = 4.0 Hz, 1H), 4.37 (dd, *J* = 9.5, 7.9 Hz, 1H), 4.30 (dd, *J* = 9.5, 5.3 Hz, 1H), 4.06 – 3.96 (m, 2H), 3.96 – 3.86 (m, 2H), 2.85 (dddd, *J* = 9.2, 7.9, 6.3, 5.3, 4.0 Hz, 1H), 2.65 – 2.49 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 176.6, 103.8, 68.4, 65.7, 65.5, 38.5, 29.3.

IR (ATR, neat): ν_{\max} (cm⁻¹) = 2975, 2893, 1765, 1478, 1418, 1399, 1379, 1173, 1133, 1056, 1018, 942.

HRMS (ESI): *m/z* calculated for C₇H₁₀NaO₄ [M+Na]⁺: 181.0471; found: 181.0507

3-(1,3-dioxolan-2-yl)-1-methylpyrrolidine-2,5-dione (3n)



The title compound was prepared according to general procedure A from *N*-methyl maleimide (33.3 mg). The crude product was purified by flash column chromatography (1:1, ethyl acetate:hexane) to afford a colorless oil (26.9 mg, 48%).

TLC (ethyl acetate:hexane, 1:1): *R_f* = 0.2

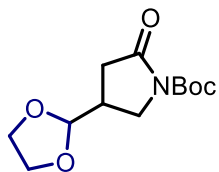
¹H NMR (400 MHz, CDCl₃) δ = 5.31 (d, *J* = 2.4 Hz, 1H), 4.08 – 3.96 (m, 2H), 3.96 – 3.87 (m, 2H), 3.26 (ddd, *J* = 8.8, 4.7, 2.5 Hz, 1H), 3.00 (s, 3H), 2.77 – 2.59 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ = 177.2, 175.8, 101.7, 65.8, 65.7, 44.1, 28.6, 25.0.

IR (ATR, neat): ν_{\max} (cm⁻¹) = 2893, 1698, 1439, 1378, 1290, 1124, 1020.

HRMS (ESI): *m/z* calculated for C₈H₁₂NO₄ [M+H]⁺: 186.0761; found: 186.0759

tert-butyl 4-(1,3-dioxolan-2-yl)-2-oxopyrrolidine-1-carboxylate (3o)



The title compound was prepared according to general procedure A from tert-butyl 2-oxopyrrolidine-1-carboxylate (36.6 mg). The crude product was purified by flash column chromatography (1:1, ethyl acetate:hexane) to afford a colorless oil (48.0 mg, 93%).

TLC (ethyl acetate:hexane, 1:1): $R_f = 0.26$

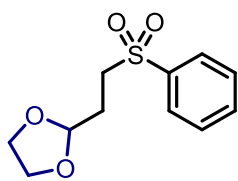
$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 4.92 - 4.83$ (m, 1H), $4.11 - 3.96$ (m, 2H), $3.96 - 3.86$ (m, 2H), $3.86 - 3.77$ (m, 1H), $3.74 - 3.63$ (m, 1H), $2.68 - 2.50$ (m, 3H), 1.54 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 173.0, 150.0, 104.2, 82.9, 65.5, 65.3, 46.8, 33.9, 33.5, 28.0$.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2979, 2891, 1782, 1748, 1711, 1367, 1313, 1255, 1149, 1045, 1024, 941, 778.

HRMS (ESI): m/z calculated for $\text{C}_{12}\text{H}_{20}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 258.1336; found: 258.1332.

2-(2-(phenylsulfonyl)ethyl)-1,3-dioxolane (3p)



The title compound was prepared according to general procedure A from phenyl vinyl sulfone (33.6 mg) on a 0.2 mmol scale. The crude product was purified by flash column chromatography (1:1, ethyl acetate:hexane) to afford a white solid (47.7 mg, 98%).

TLC (ethyl acetate:hexane, 1:1): $R_f = 0.32$

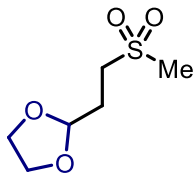
$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 7.94 - 7.87$ (m, 2H), $7.69 - 7.62$ (m, 1H), $7.62 - 7.54$ (m, 2H), 4.96 (t, $J = 3.9$ Hz, 1H), $3.98 - 3.79$ (m, 4H), $3.26 - 3.19$ (m, 2H), $2.13 - 2.04$ (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 139.1, 133.9, 129.5, 128.3, 101.9, 65.3, 50.8, 27.2$.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2962, 2889, 1447, 1306, 1143, 1084.

HRMS (ESI): m/z calculated for $\text{C}_{11}\text{H}_{15}\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 243.0686; found: 243.0683.

2-(2-(methylsulfonyl)ethyl)-1,3-dioxolane (3q)



The title compound was prepared according to general procedure A from methyl vinyl sulfone (21.2 mg) on a 0.2 mmol scale. The crude product was purified by flash column chromatography (1:1, ethyl acetate:hexane) to afford a white solid (28.5 mg, 79%).

TLC (ethyl acetate:hexane, 1:1): $R_f = 0.12$

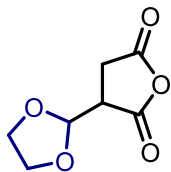
$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 5.04$ (t, $J = 3.8$ Hz, 1H), 4.05 – 3.82 (m, 4H), 3.19 – 3.12 (m, 2H), 2.92 (d, $J = 0.8$ Hz, 3H), 2.29 – 2.16 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 101.8, 65.4, 49.2, 40.7, 26.8$.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2963, 2891, 1301, 1278, 1126, 1054, 945.

HRMS (ESI): m/z calculated for $\text{C}_6\text{H}_{13}\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 181.0529; found: 181.0527.

3-(1,3-dioxolan-2-yl)dihydrofuran-2,5-dione (3r)



The title compound was prepared according to general procedure A from maleic anhydride (29.4 mg). The crude product was purified by flash column chromatography (1:1, ethyl acetate:hexane) to afford an off-white solid (40.5 mg, 78%).

TLC (ethyl acetate:hexane, 1:1): R_f was not determined (smears)

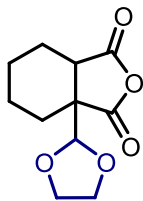
$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 5.28$ (d, $J = 2.4$ Hz, 1H), 4.10 – 4.01 (m, 2H), 3.99 – 3.89 (m, 2H), 3.52 (ddd, $J = 9.0, 5.9, 2.4$ Hz, 1H), 2.99 – 2.88 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 169.9, 169.9, 101.0, 66.0, 65.9, 45.0, 28.7$.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2960, 2900, 1864, 1781, 1221, 1137, 1067, 912.

HRMS (ESI): m/z calculated for $\text{C}_7\text{H}_{12}\text{NO}_5$ $[\text{M}+\text{NH}_4]^+$: 190.0710; found: 190.0709.

3a-(1,3-dioxolan-2-yl)hexahydroisobenzofuran-1,3-dione (3s)



The title compound was prepared according to general procedure A from 1-cyclohexene-1,2-dicarboxylic anhydride (45.6 mg). The crude product was purified by flash column chromatography (1:5, ethyl acetate:hexane) to afford an off-white solid (62.6 mg, 93%).

TLC (ethyl acetate:hexane, 1:5): $R_f = 0.18$

$^1\text{H NMR}$ (400 MHz, CDCl_3) $\delta = 4.97$ (s, 1H), 4.05 – 3.90 (m, 4H), 3.06 (t, $J = 7.0$ Hz, 1H), 2.04 – 1.93 (m, 2H), 1.85 – 1.69 (m, 3H), 1.56 – 1.34 (m, 3H).

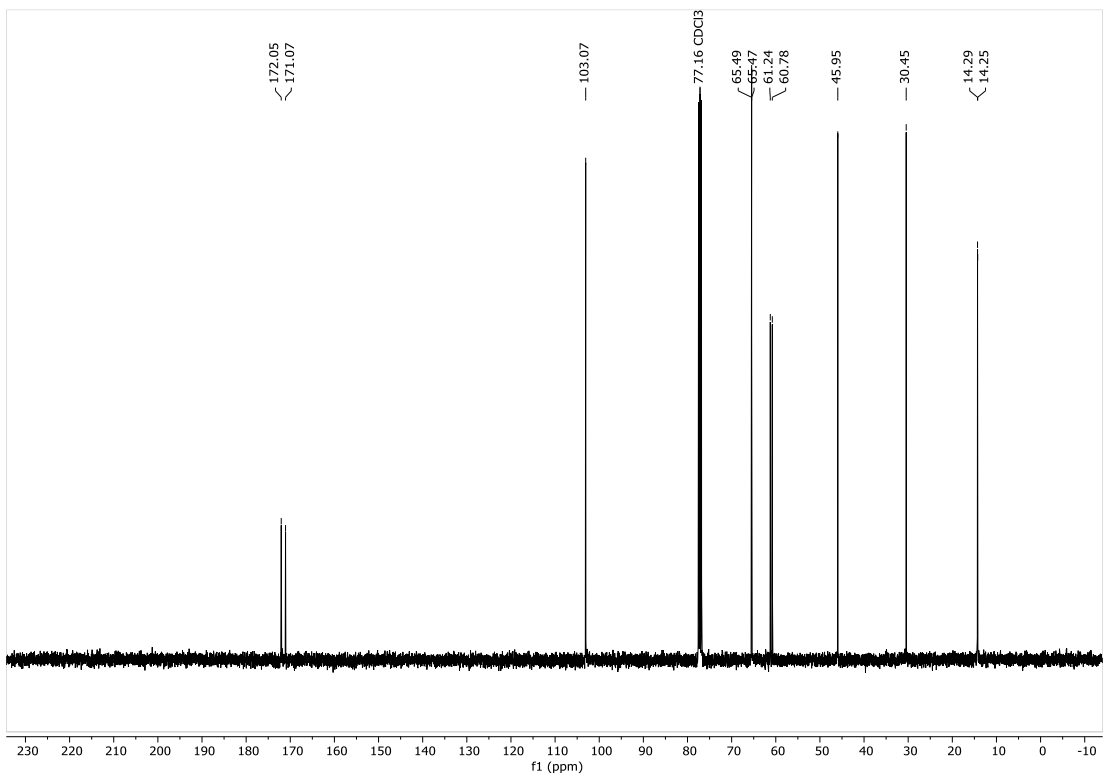
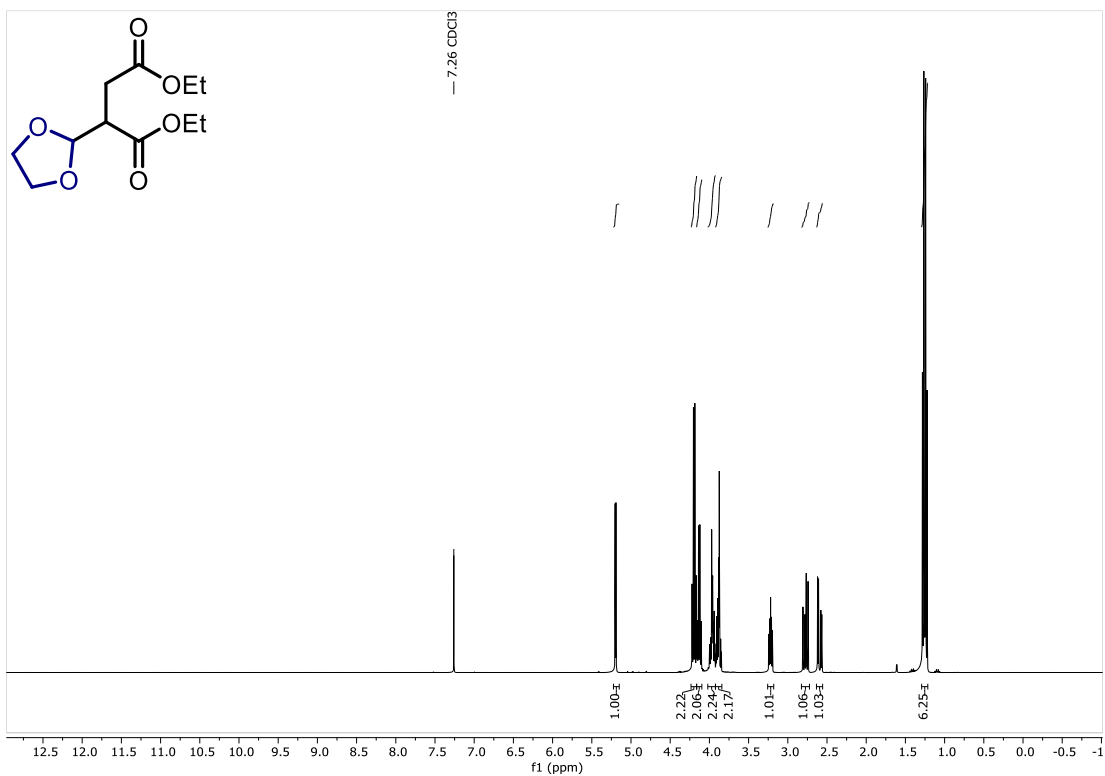
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) $\delta = 172.8, 172.9, 105.2, 65.9, 65.7, 52.5, 40.3, 26.4, 24.0, 21.5, 20.7$.

IR (ATR, neat): ν_{max} (cm^{-1}) = 2944, 2899, 2864, 1855, 1777, 1450, 1228, 1146, 1128, 1119, 1031, 999, 915, 904, 746.

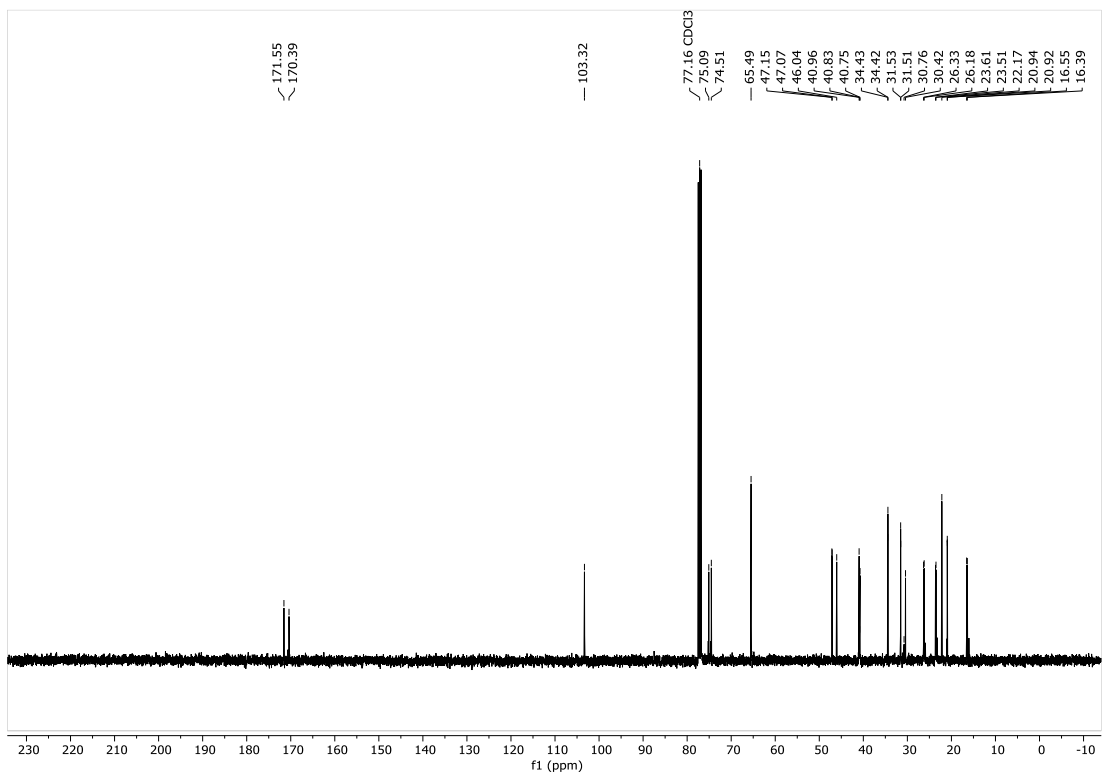
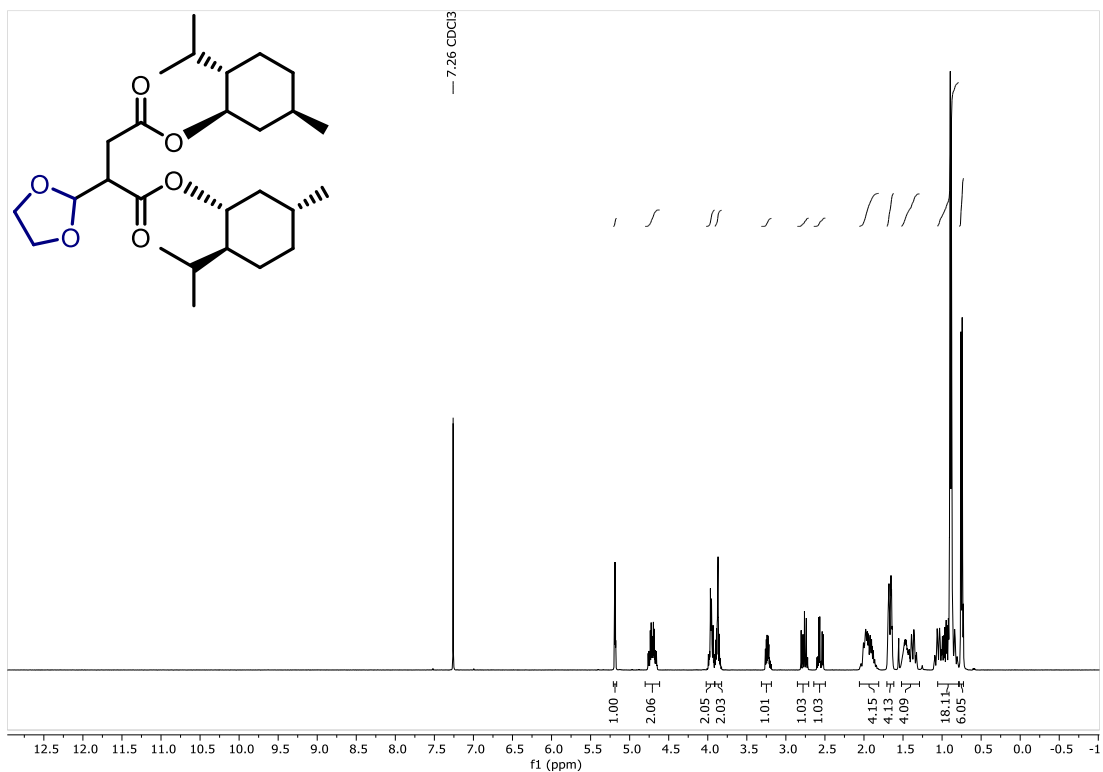
HRMS (ESI): m/z calculated for $\text{C}_{11}\text{H}_{14}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 249.0733; found: 249.0729.

6. NMR Spectra

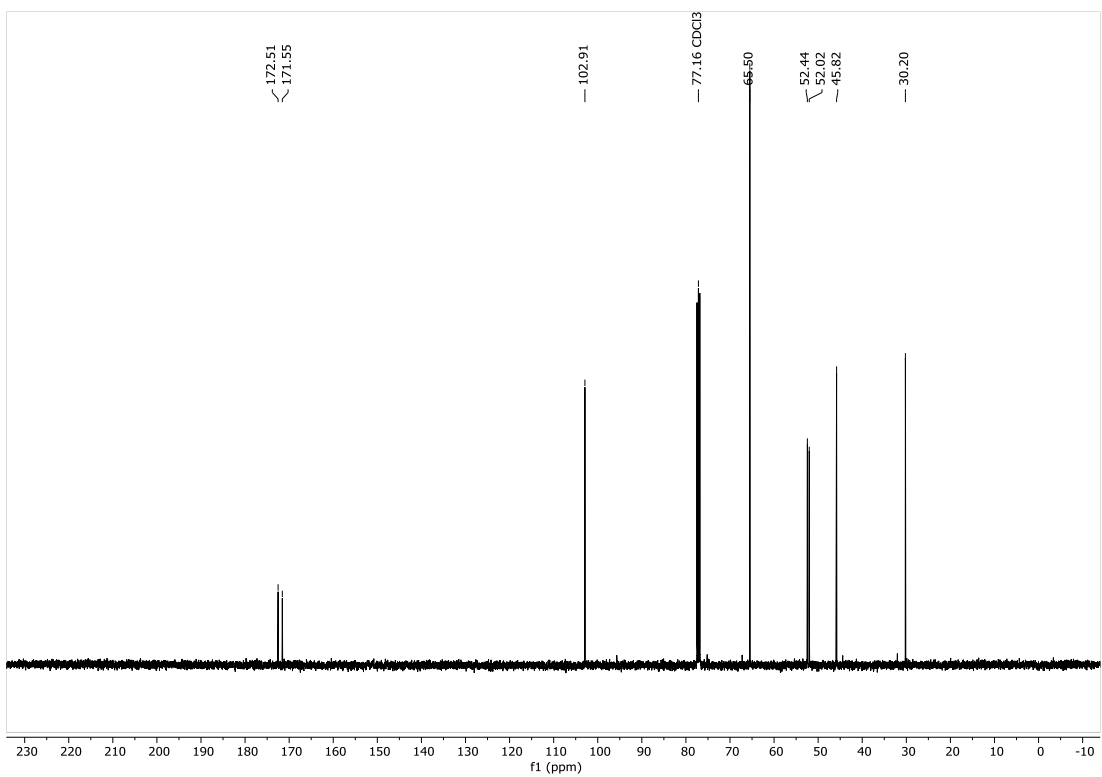
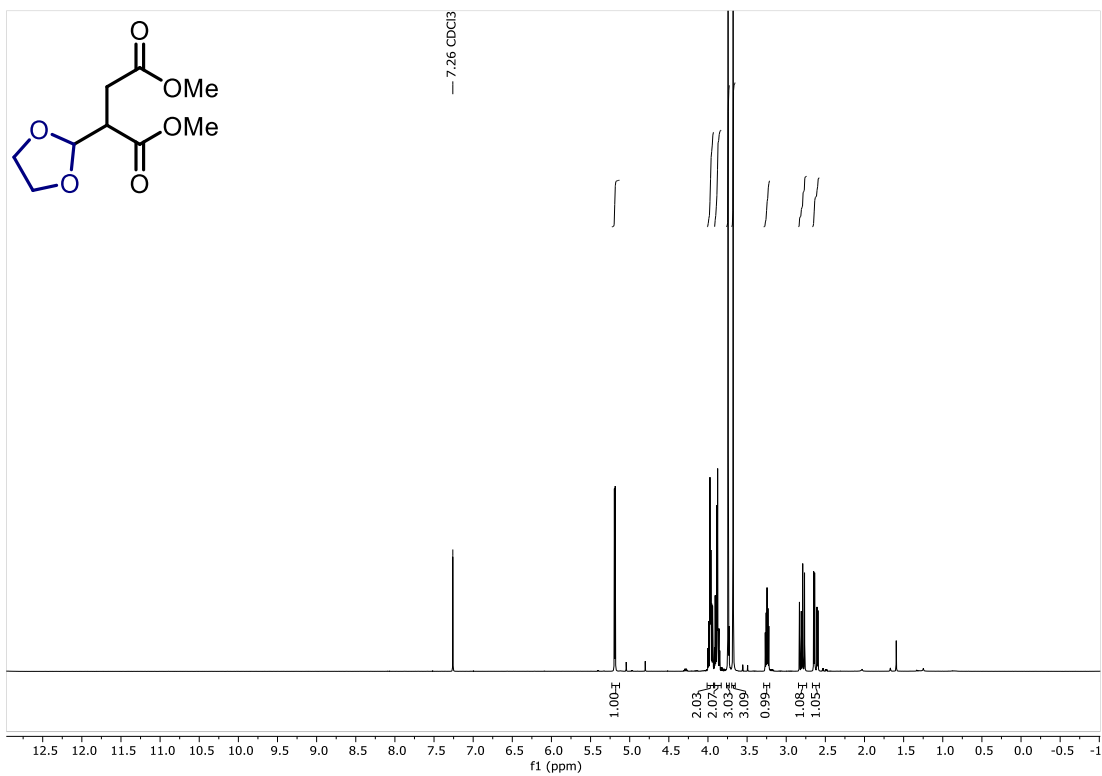
Diethyl 2-(1,3-dioxolan-2-yl)succinate (3a)



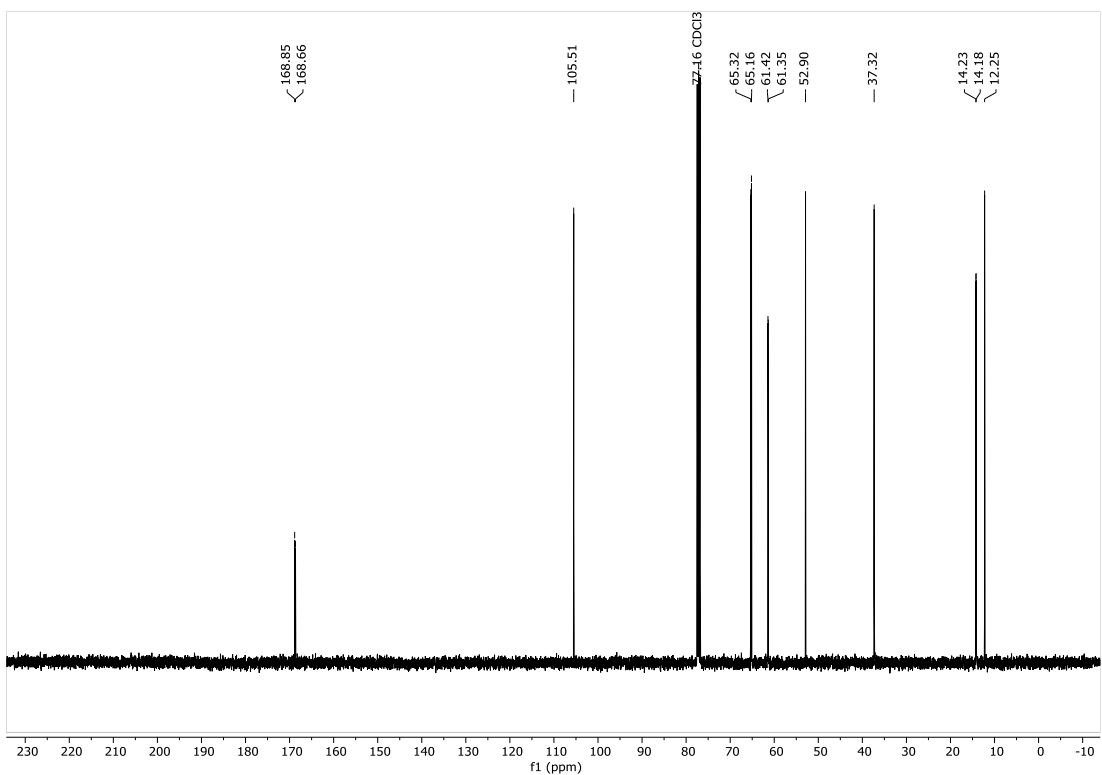
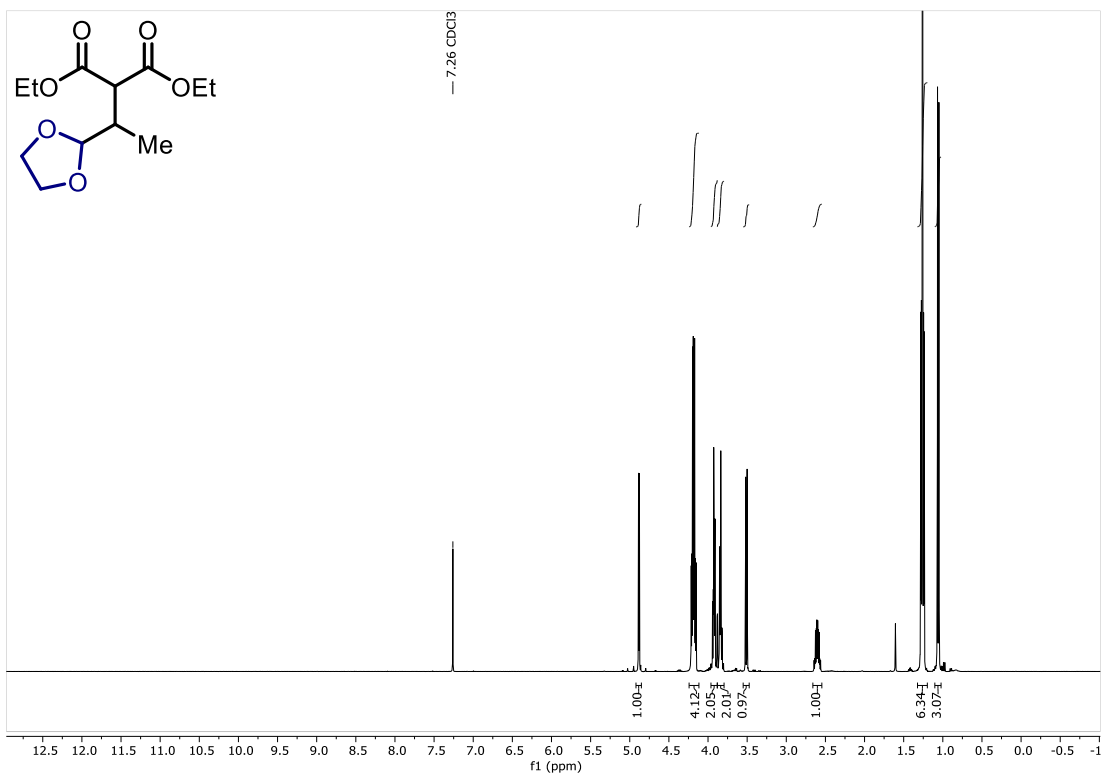
Bis((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) 2-(1,3-dioxolan-2-yl)succinate (3b)



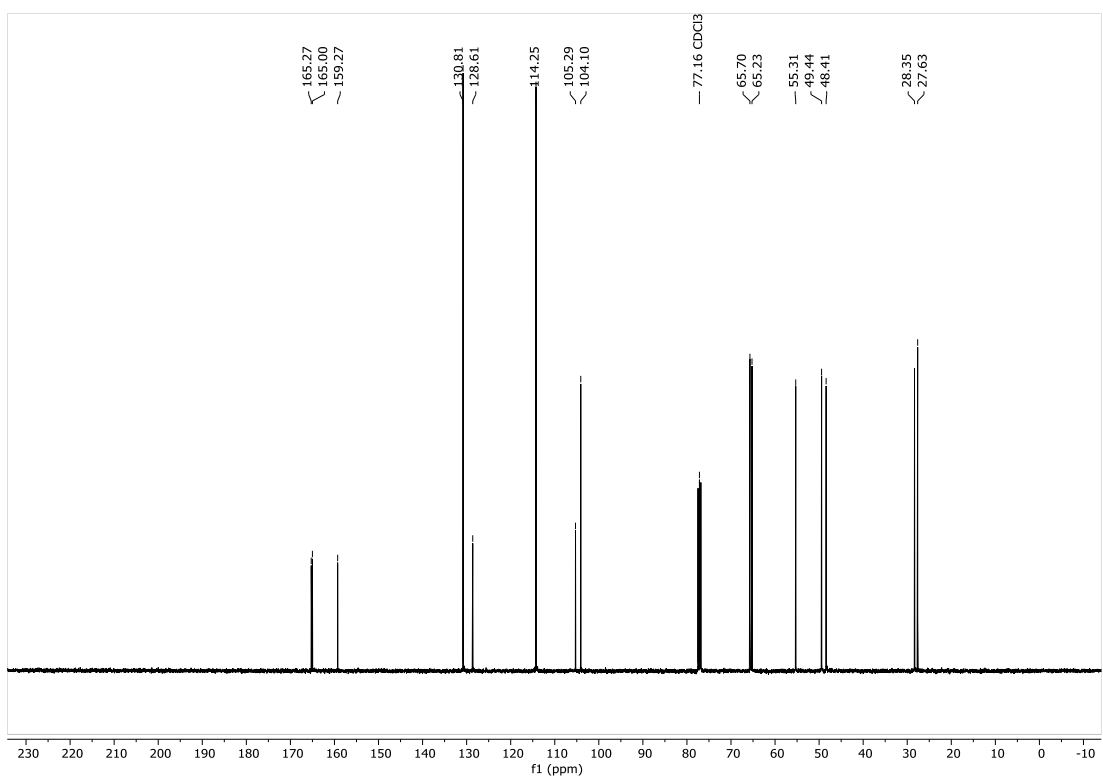
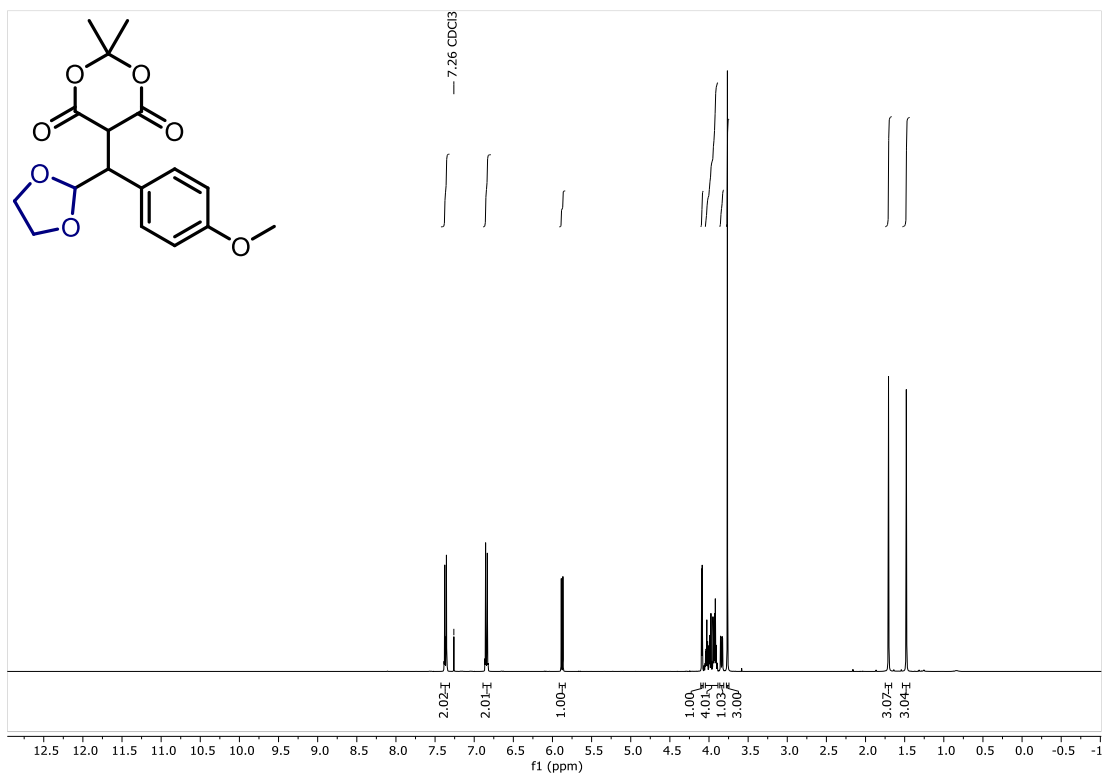
Dimethyl 2-(1,3-dioxolan-2-yl)succinate (3c)



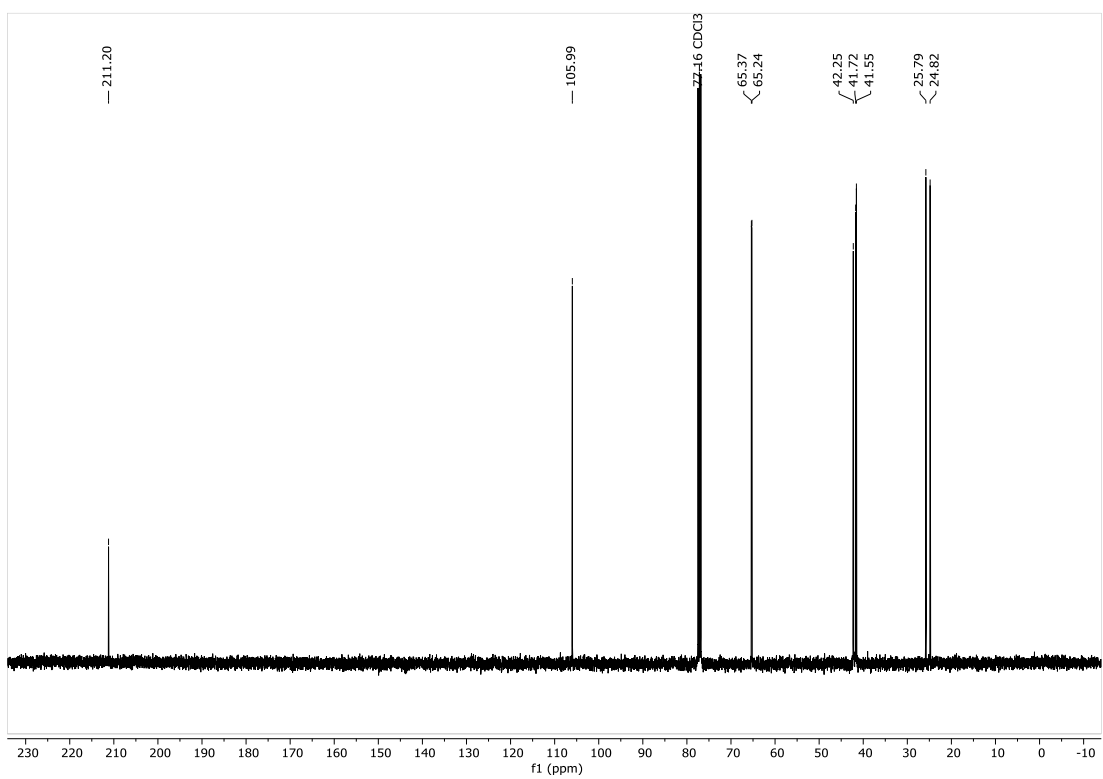
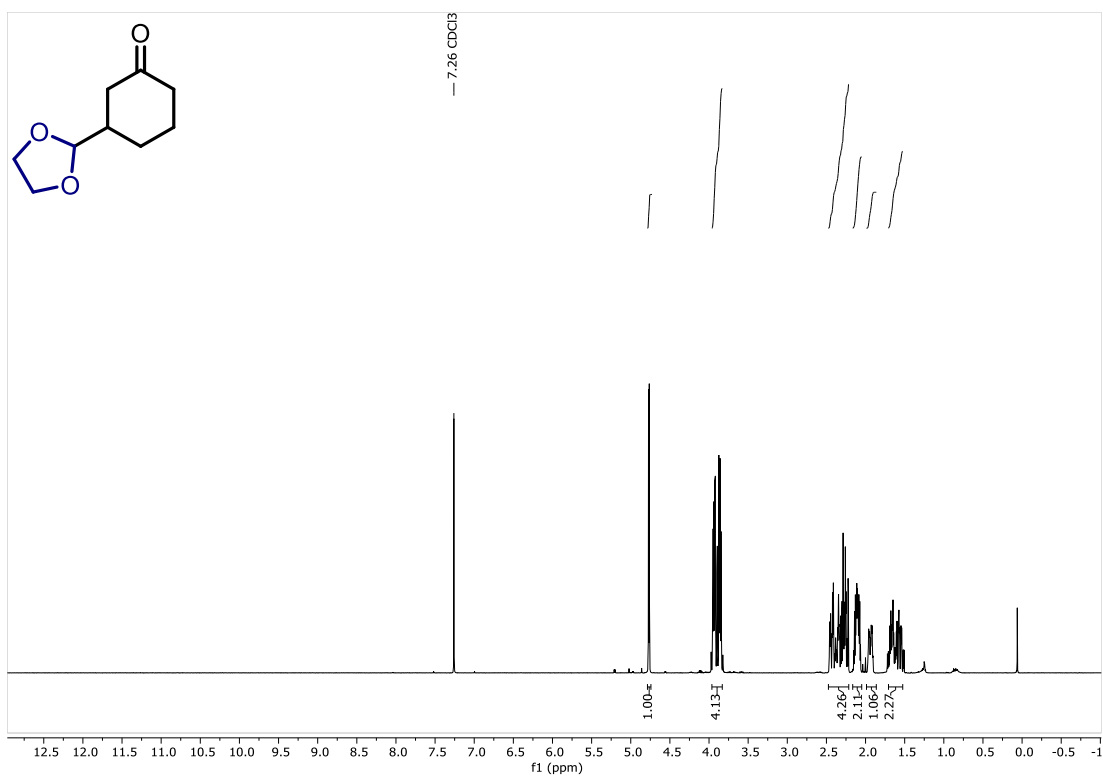
Diethyl 2-(1-(1,3-dioxolan-2-yl)ethyl)malonate (3d)



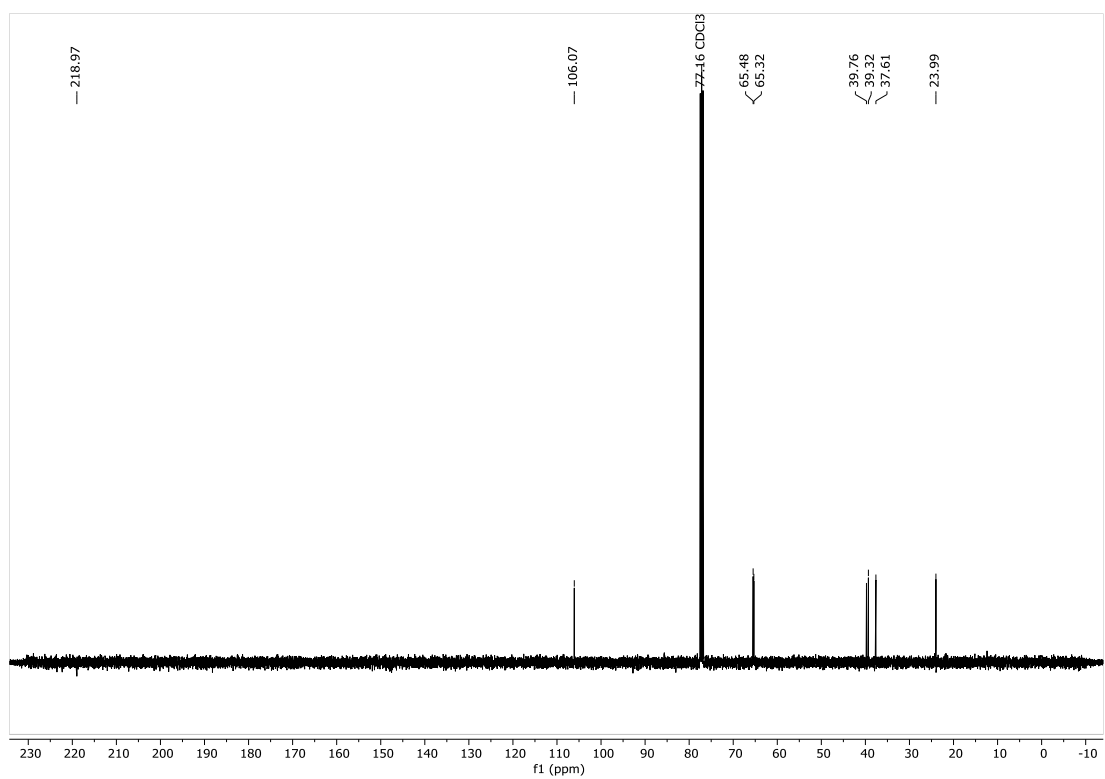
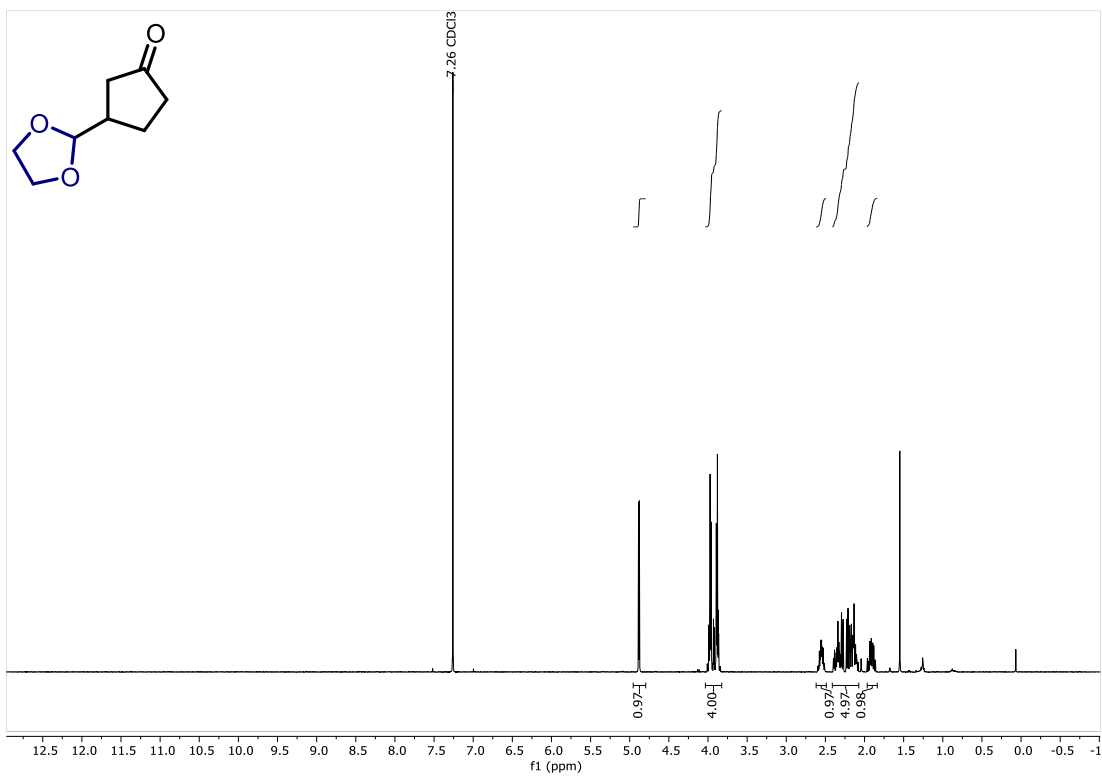
5-((1,3-dioxolan-2-yl)(4-methoxyphenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (3e)



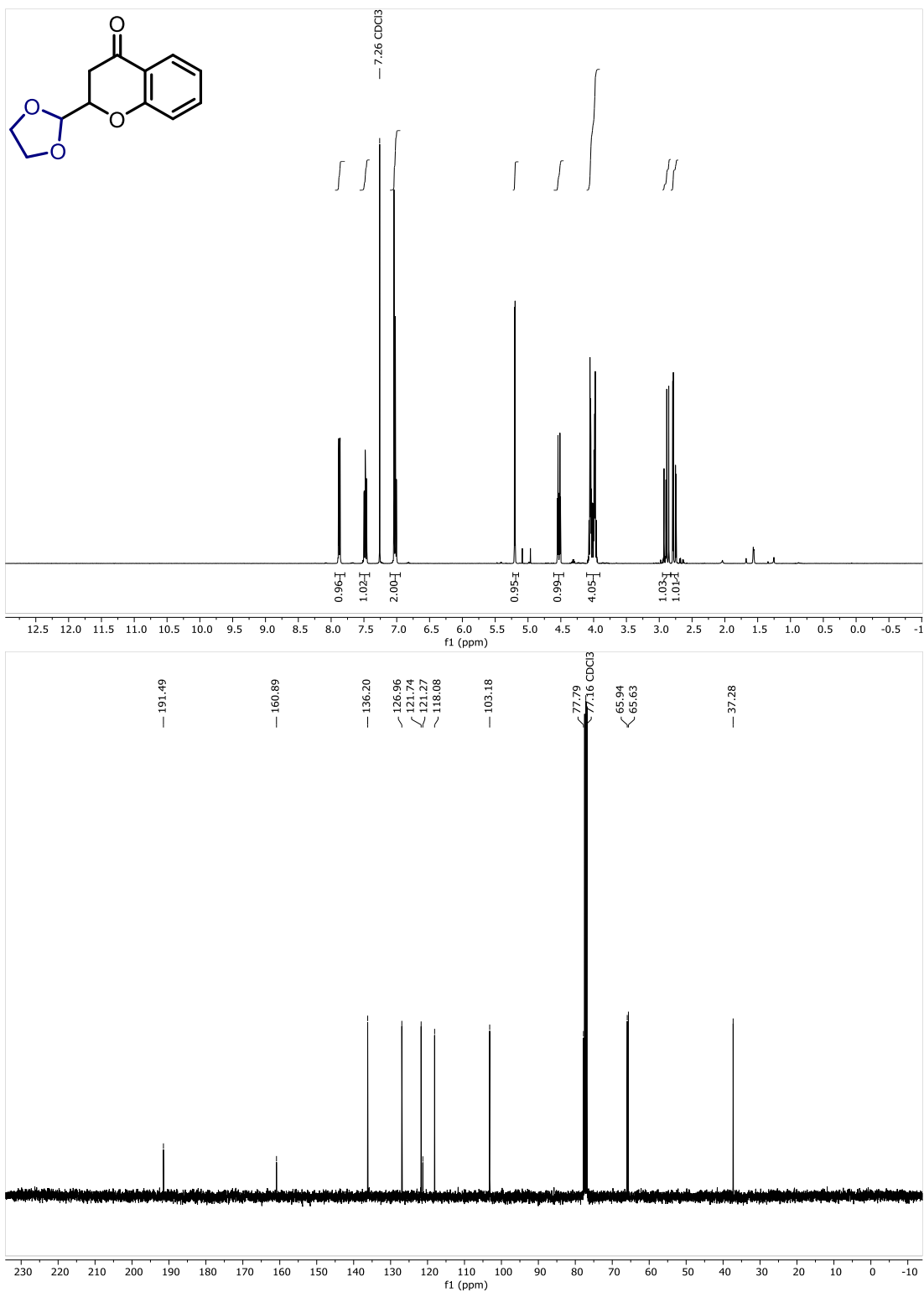
3-(1,3-dioxolan-2-yl)cyclohexan-1-one (3f)



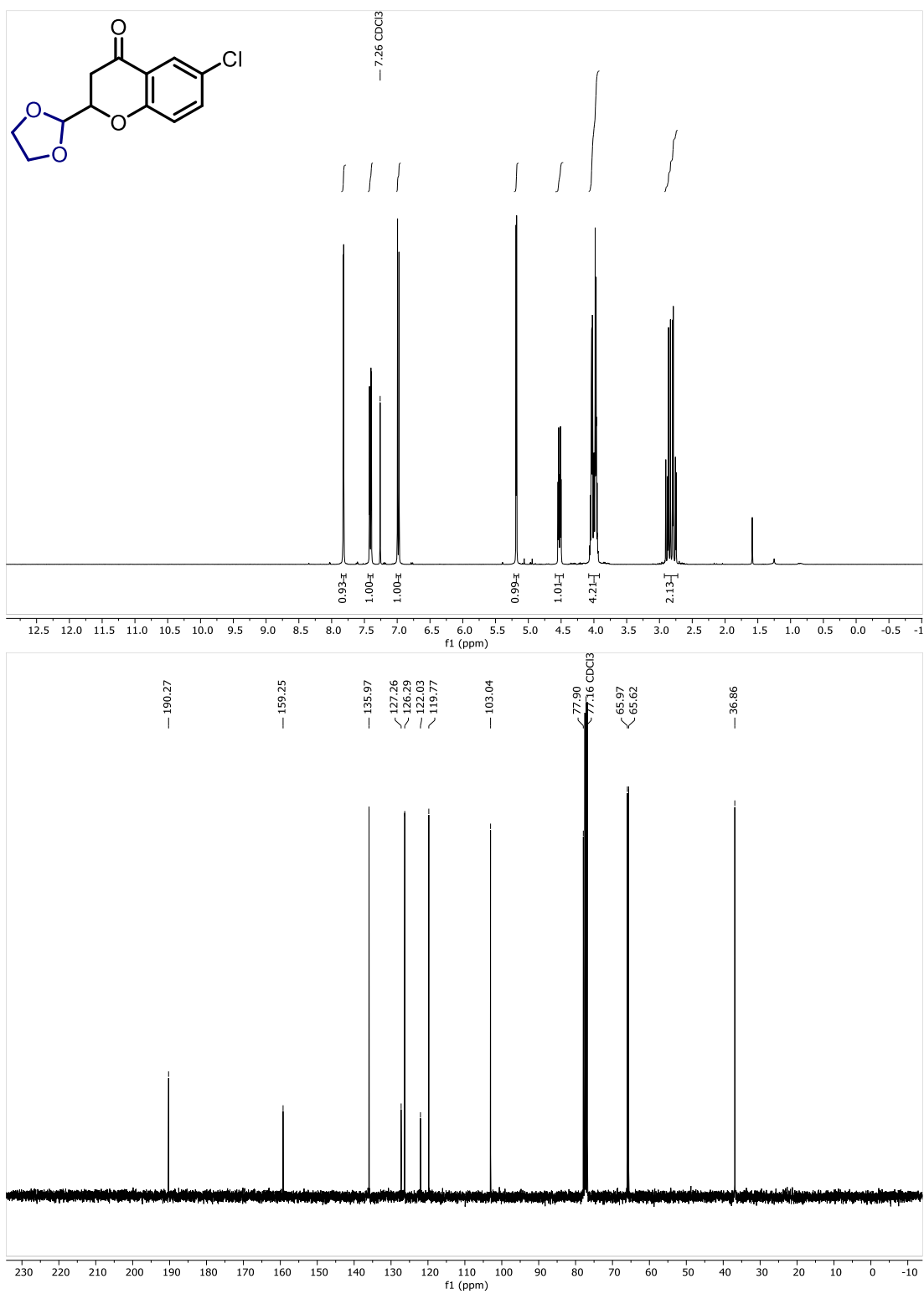
3-(1,3-dioxolan-2-yl)cyclopentan-1-one (3g)



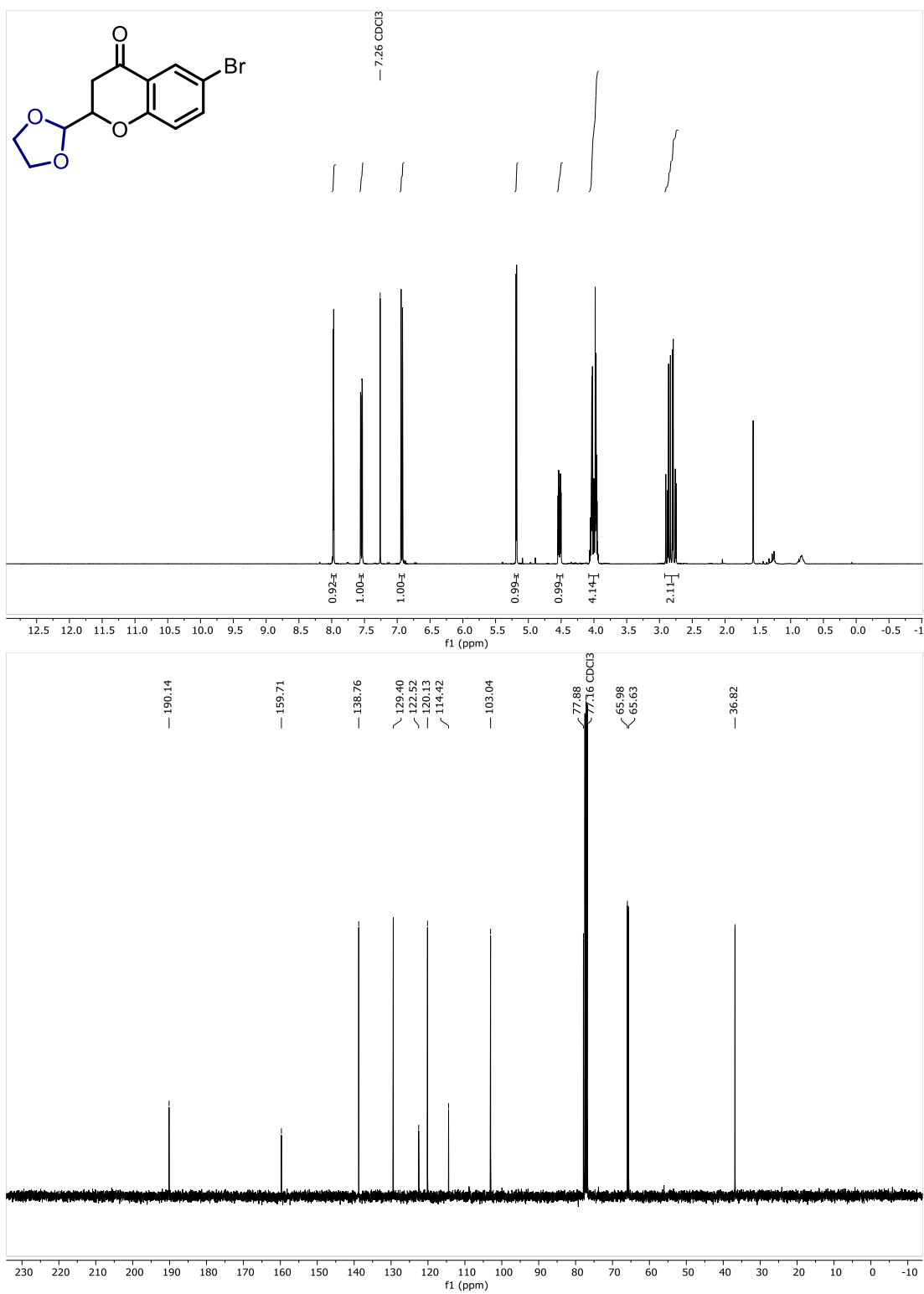
2-(1,3-dioxolan-2-yl)chroman-4-one (3h)



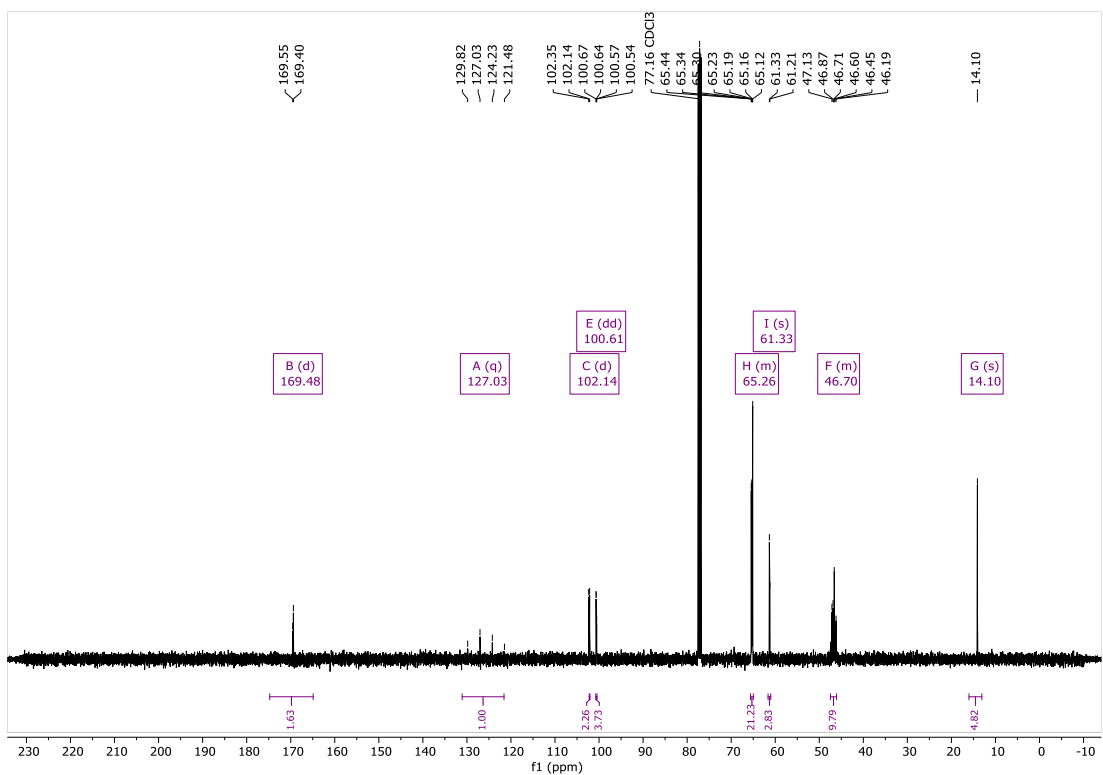
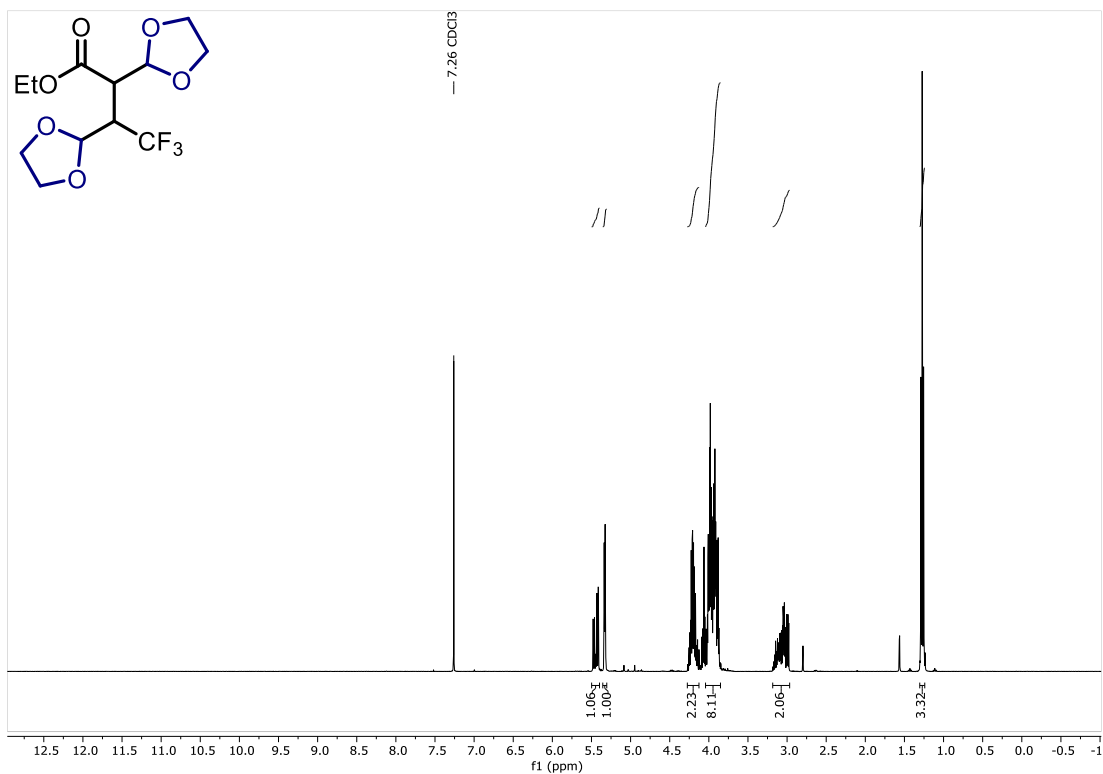
6-chloro-2-(1,3-dioxolan-2-yl)chroman-4-one (3i)

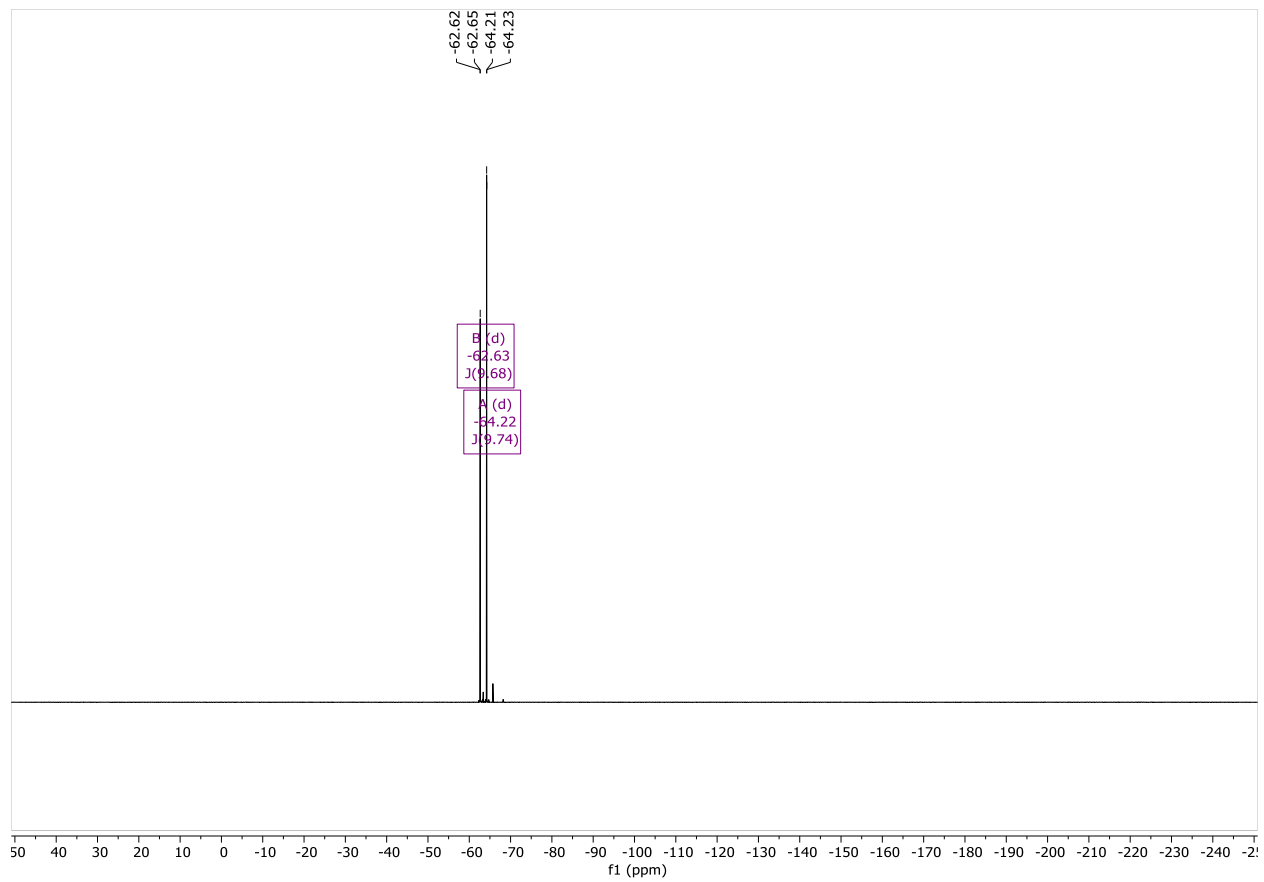


6-bromo -2-(1,3-dioxolan-2-yl)chroman-4-one (3j)

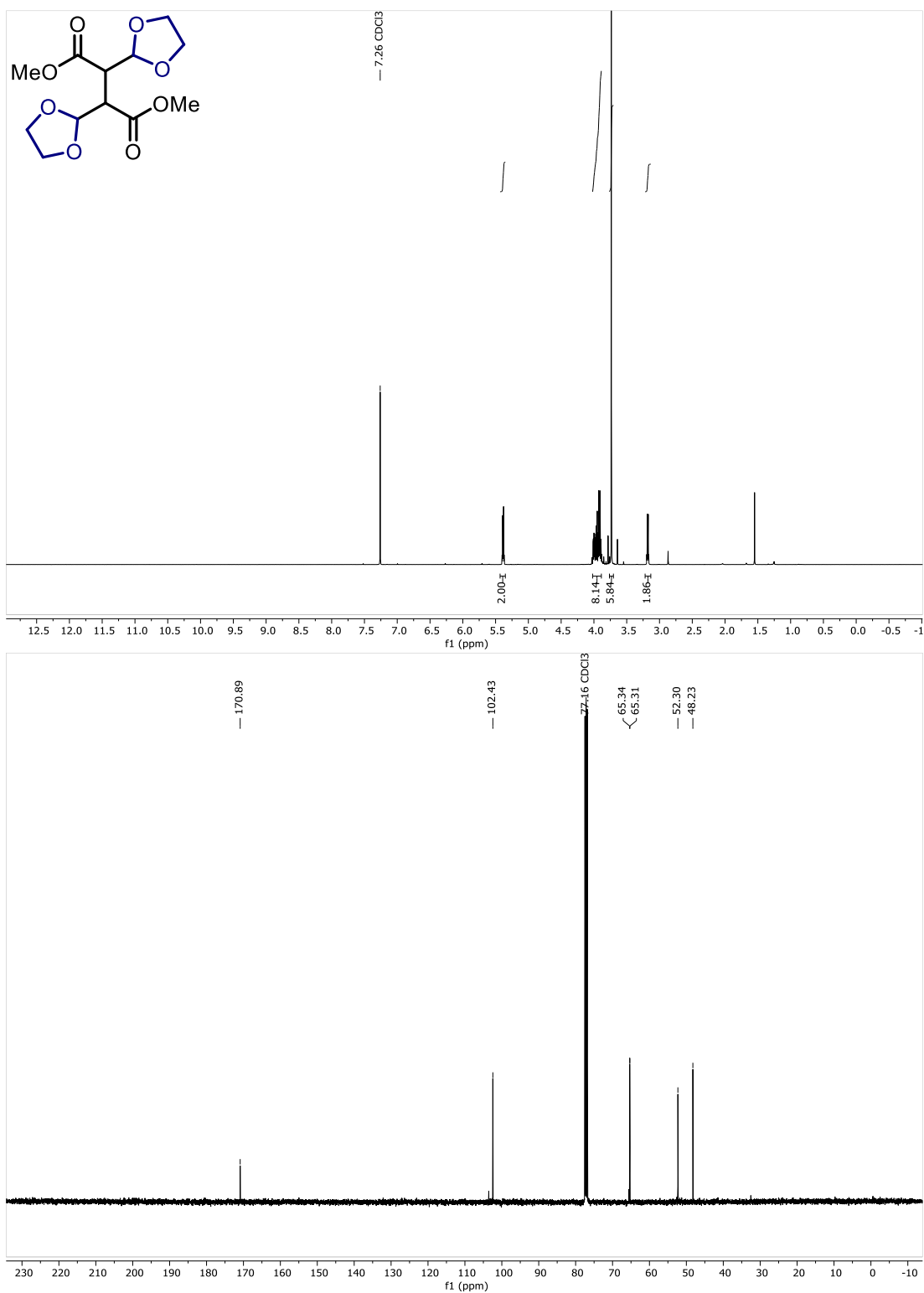


ethyl 2,3-di(1,3-dioxolan-2-yl)-4,4,4-trifluorobutanoate (3k)

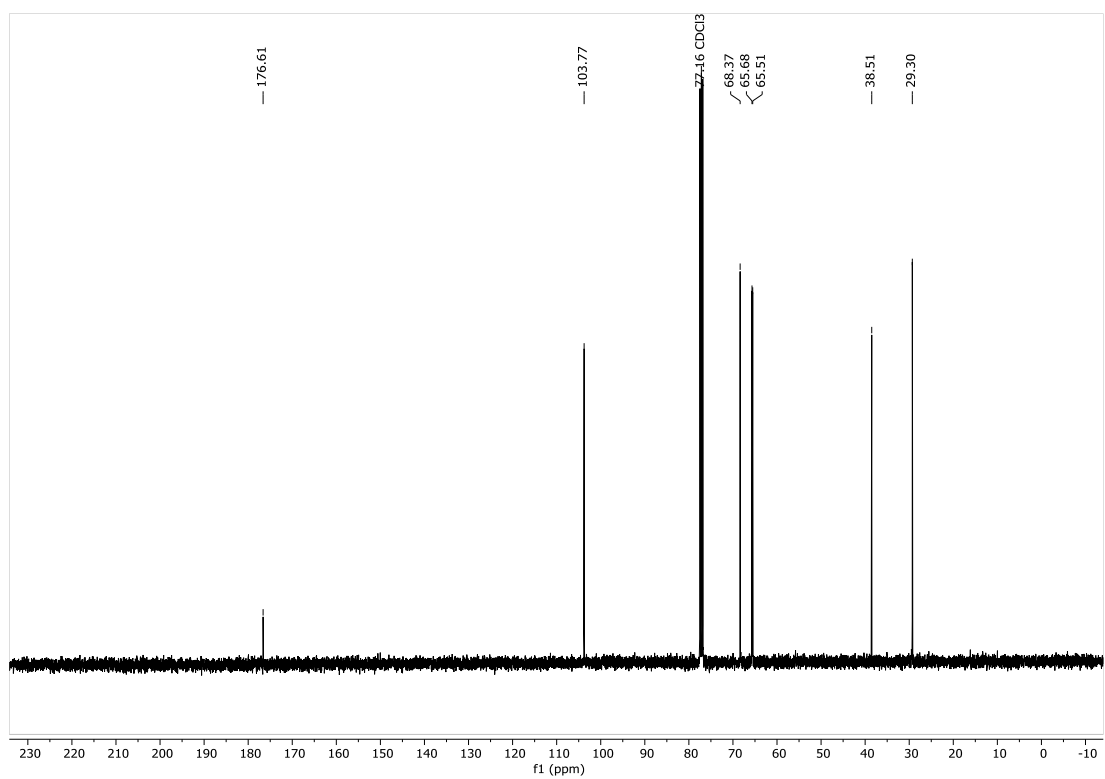
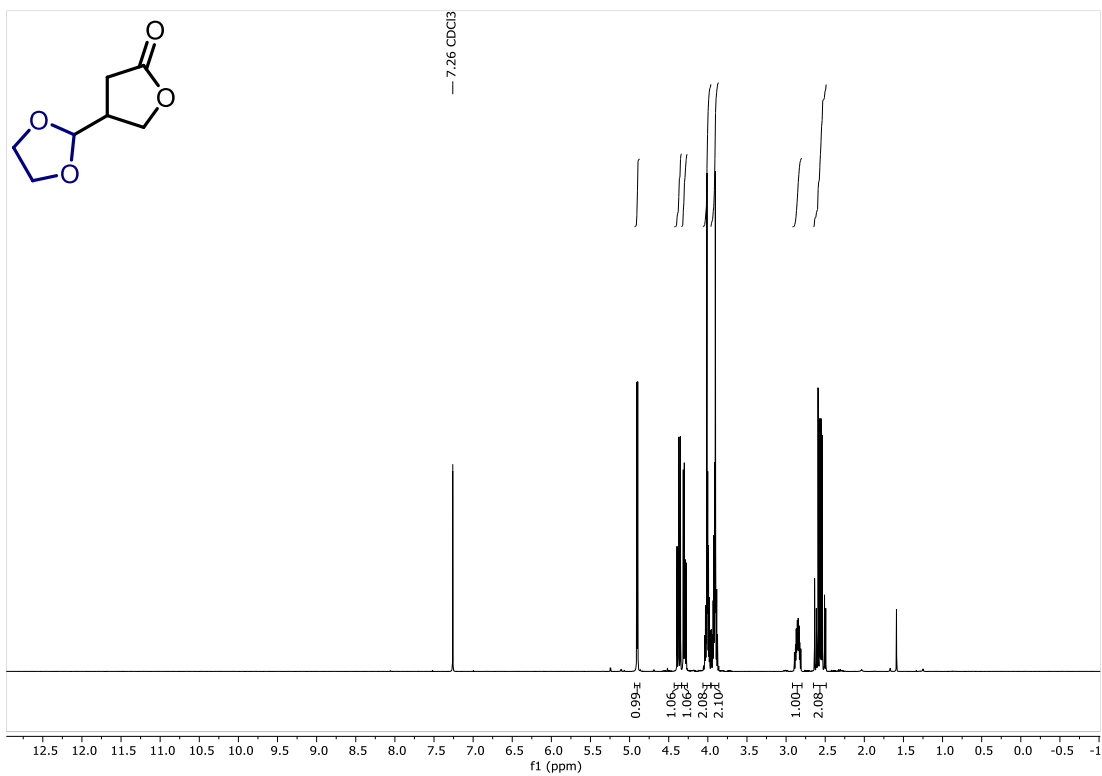




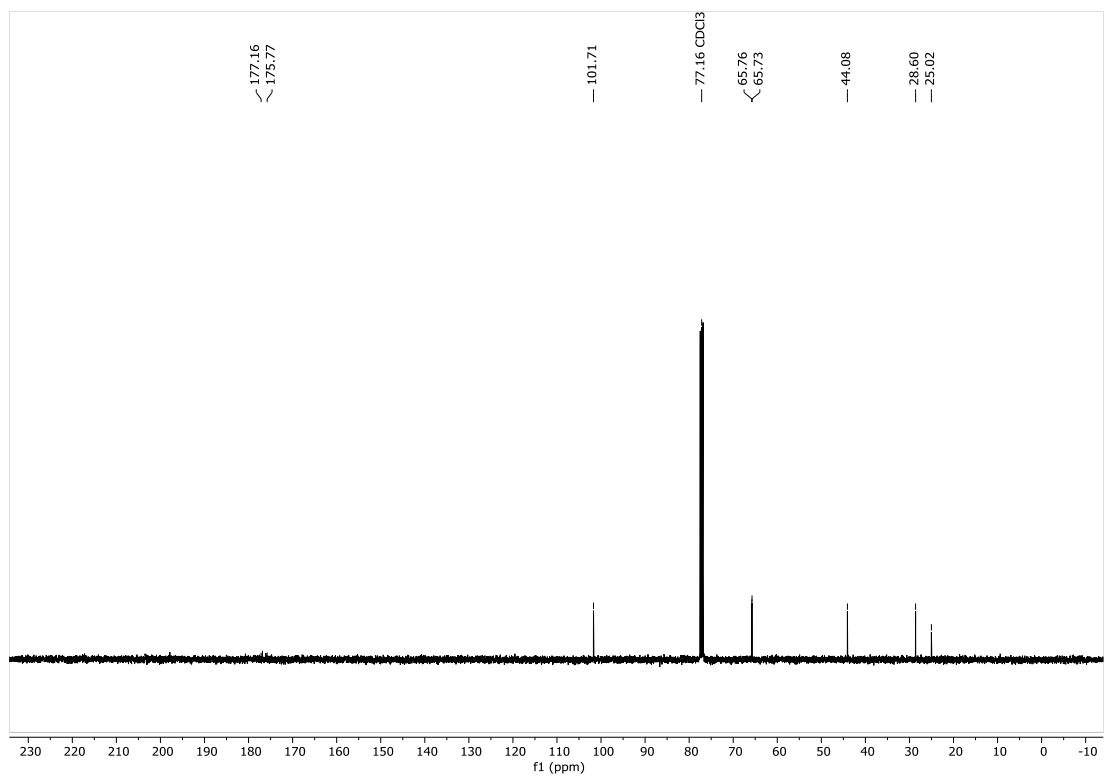
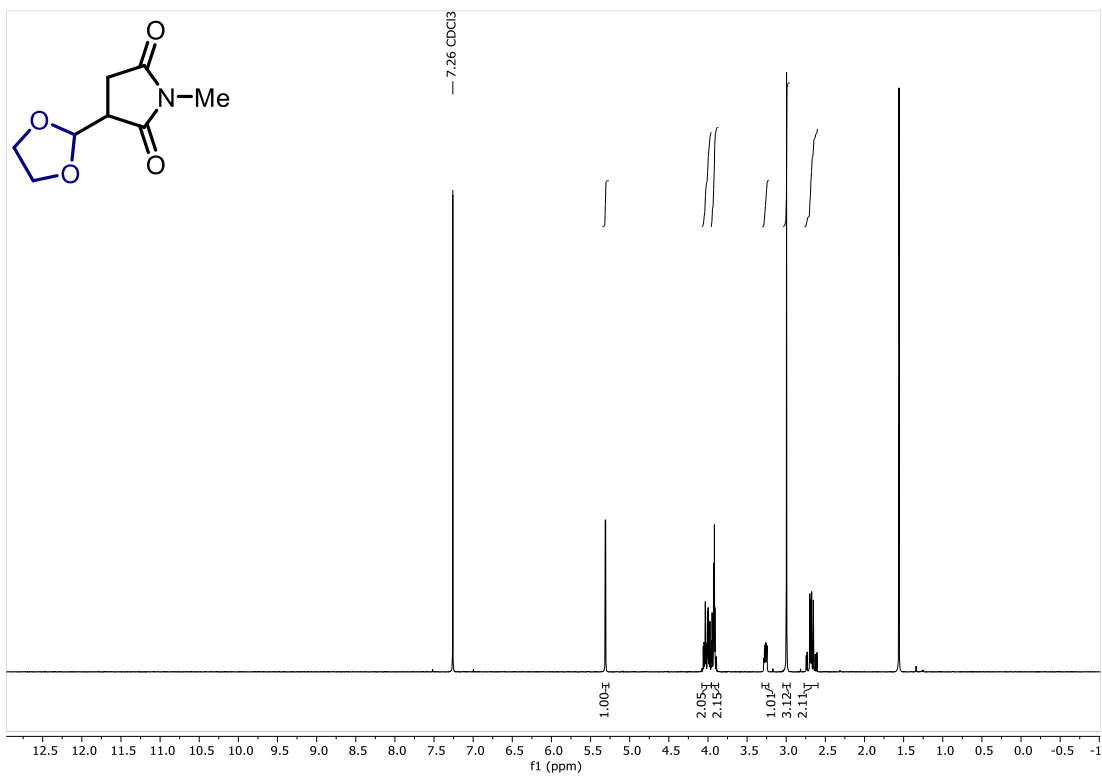
dimethyl 2,3-di(1,3-dioxolan-2-yl)succinate (3l)



4-(1,3-dioxolan-2-yl)dihydrofuran-2(3H)-one (3m)

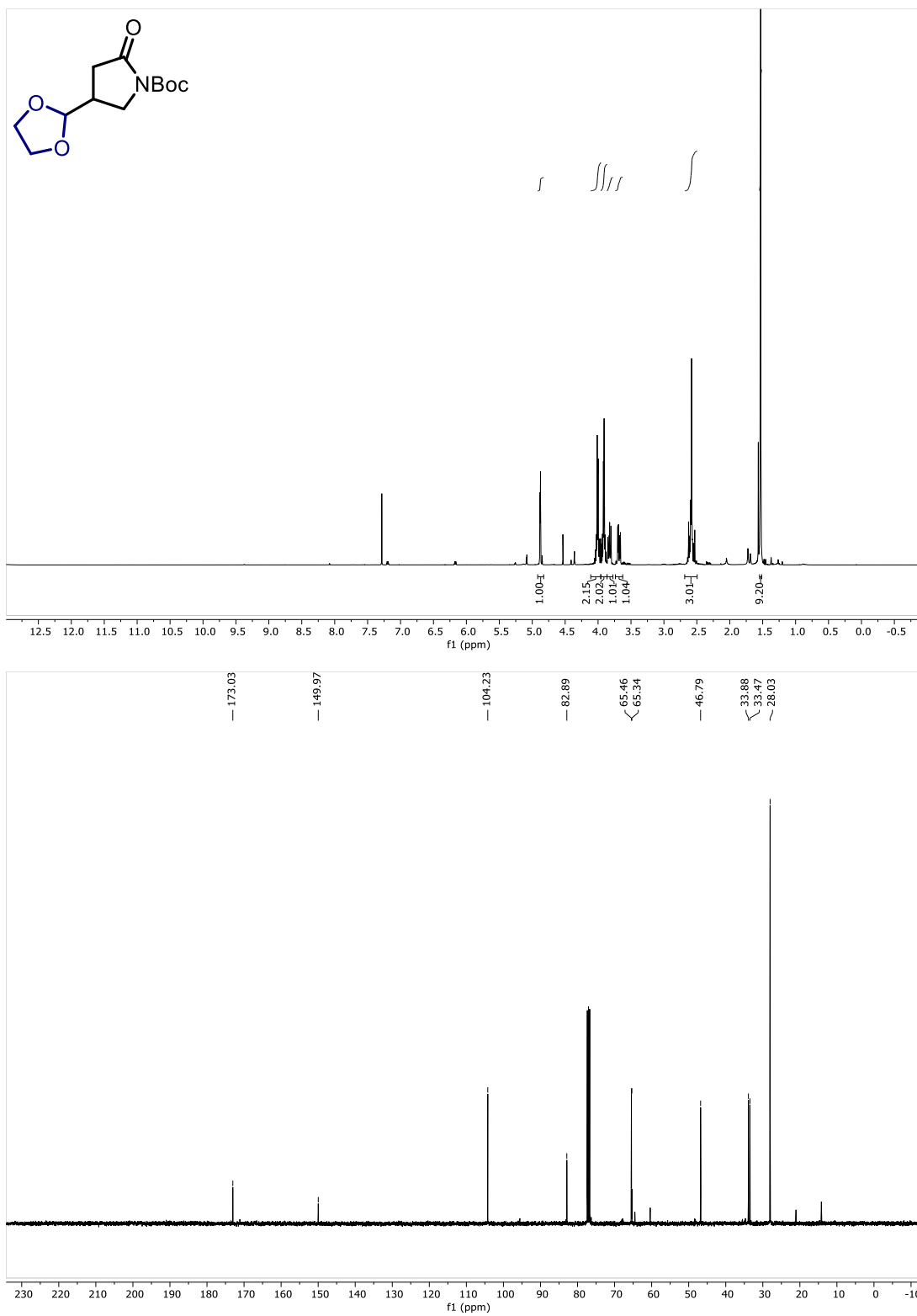


3-(1,3-dioxolan-2-yl)-1-methylpyrrolidine-2,5-dione (3n)

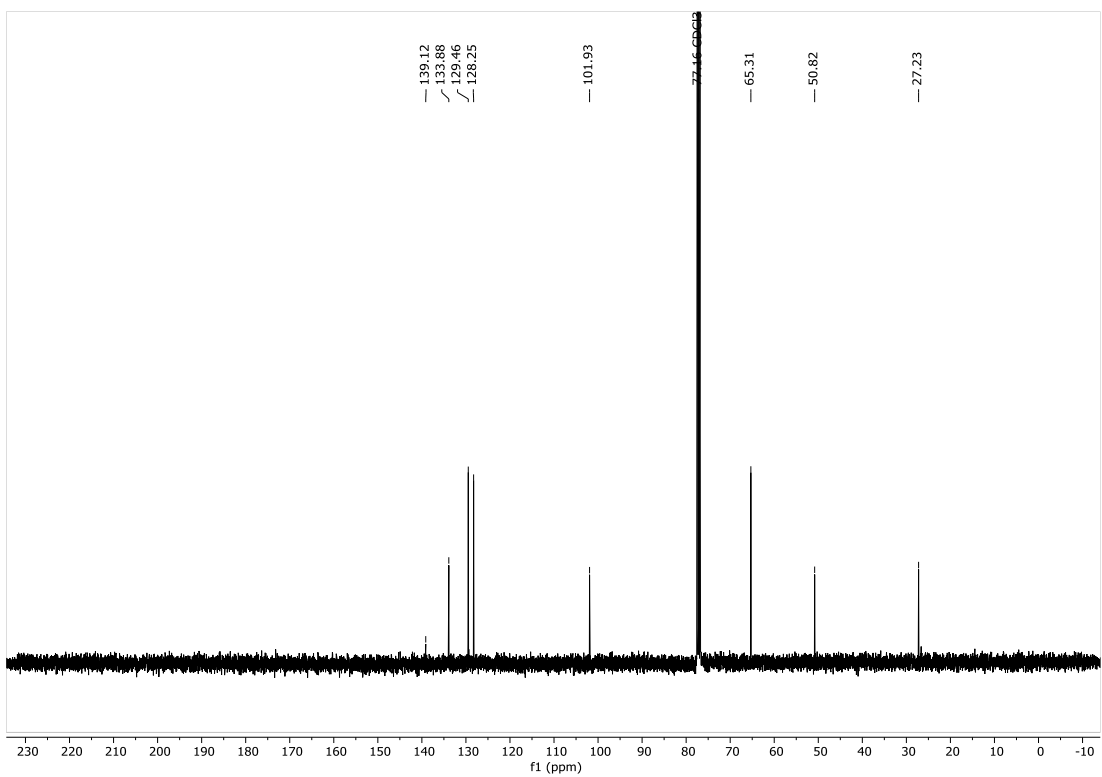
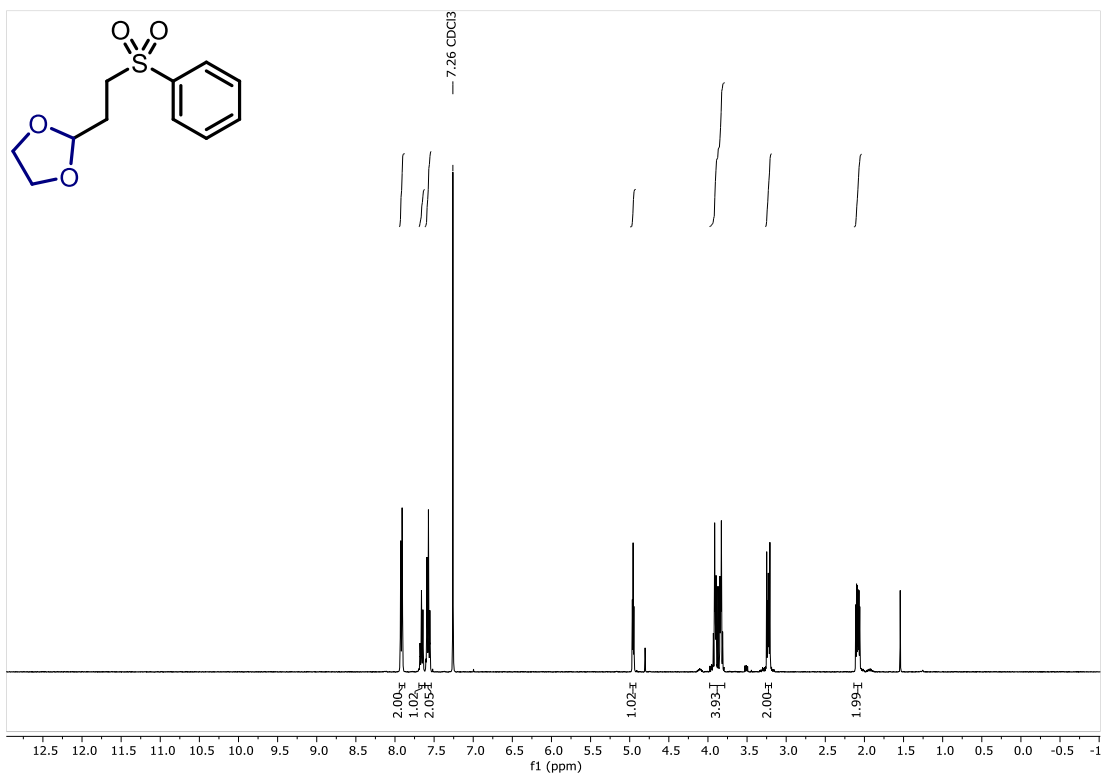


tert-butyl 4-(1,3-dioxolan-2-yl)-2-oxopyrrolidine-1-carboxylate (3o)

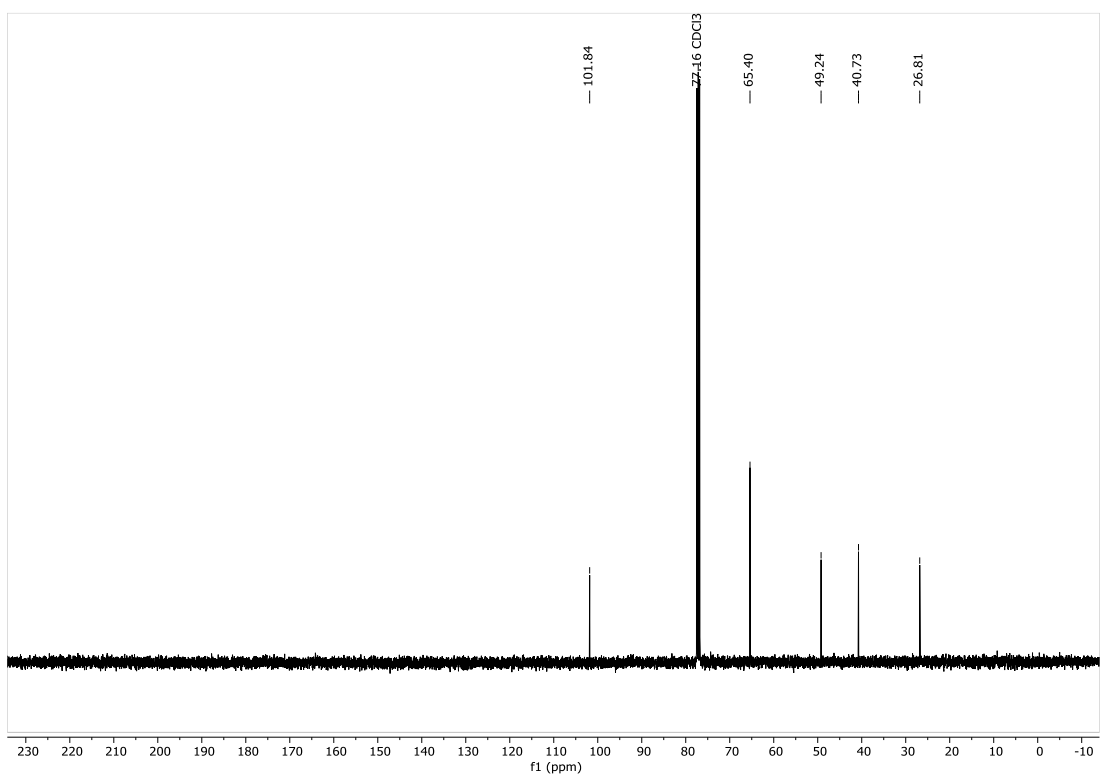
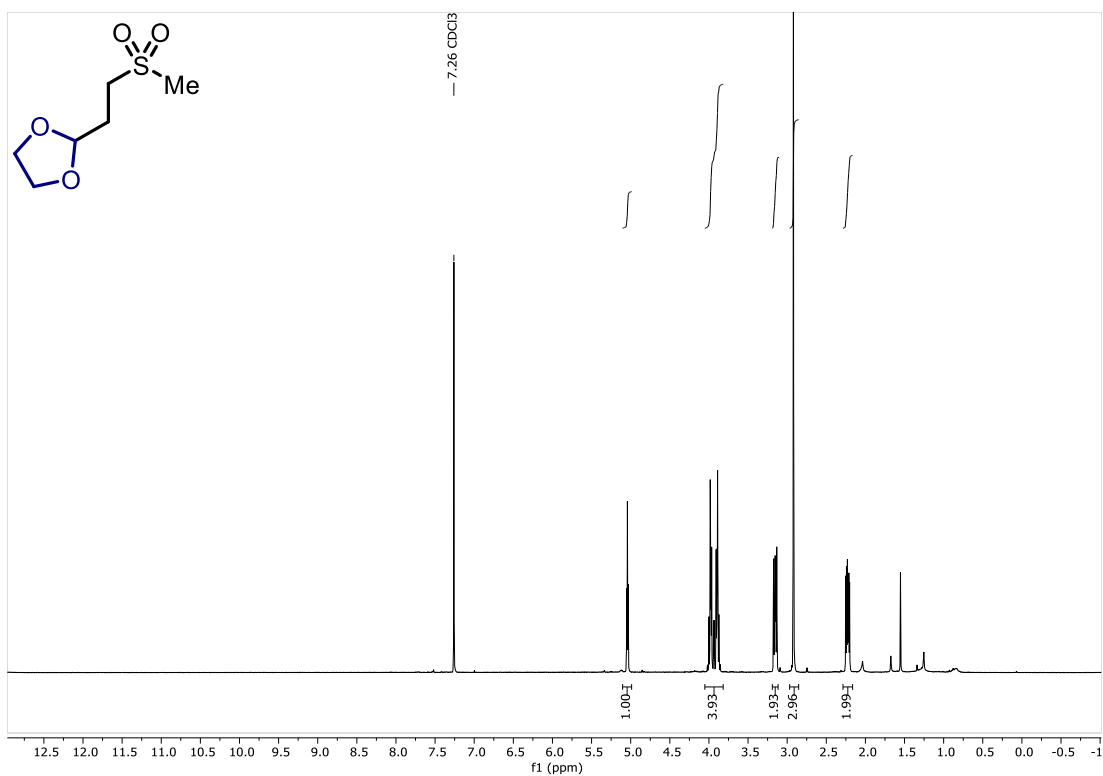
Note: the imide product decomposes slowly on silica gel, resulting in slightly impure spectra.



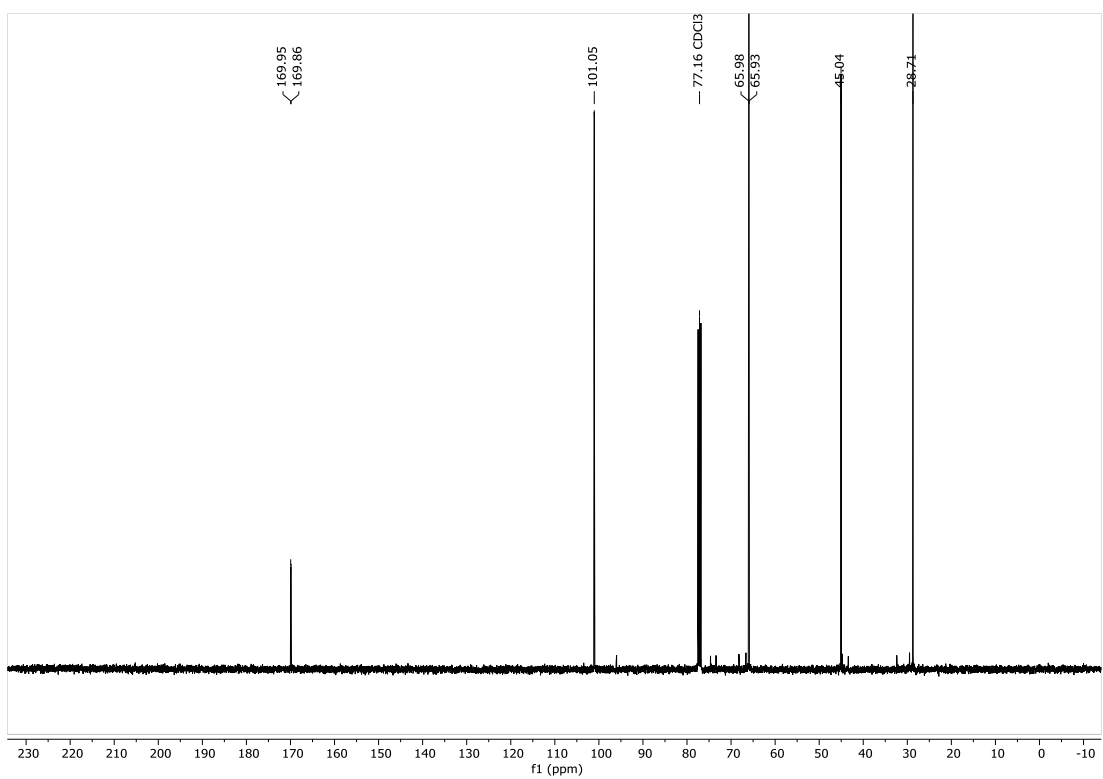
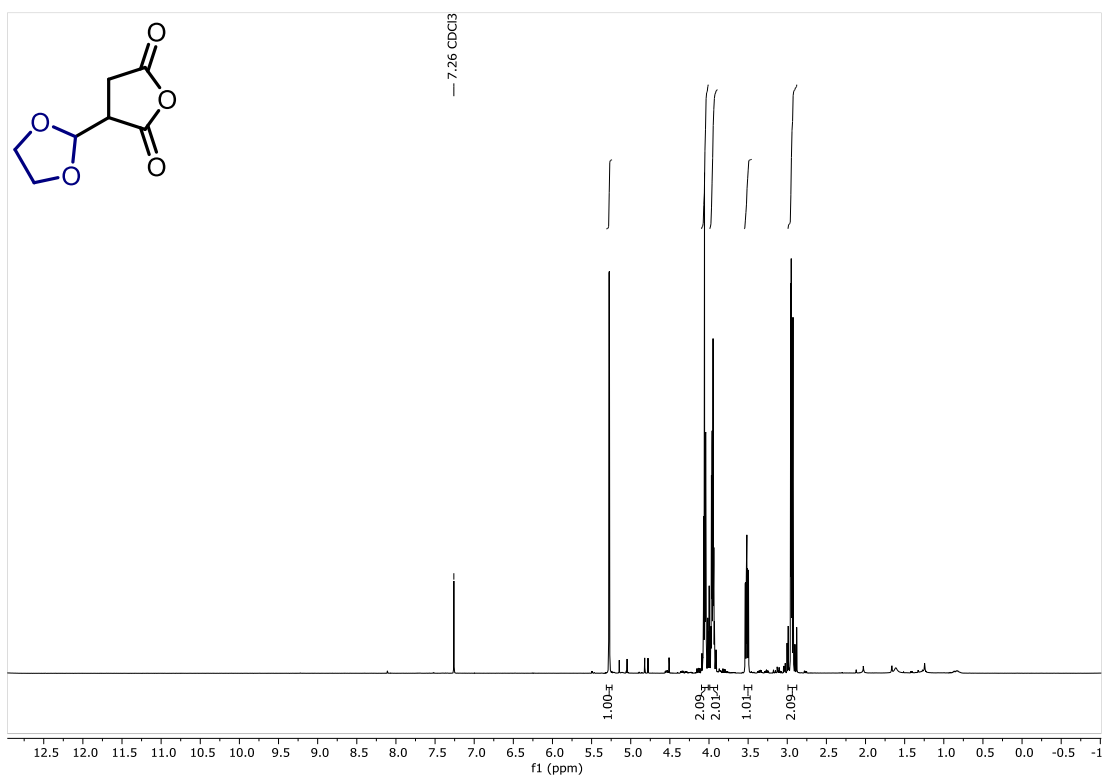
2-(2-(phenylsulfonyl)ethyl)-1,3-dioxolane (3p)



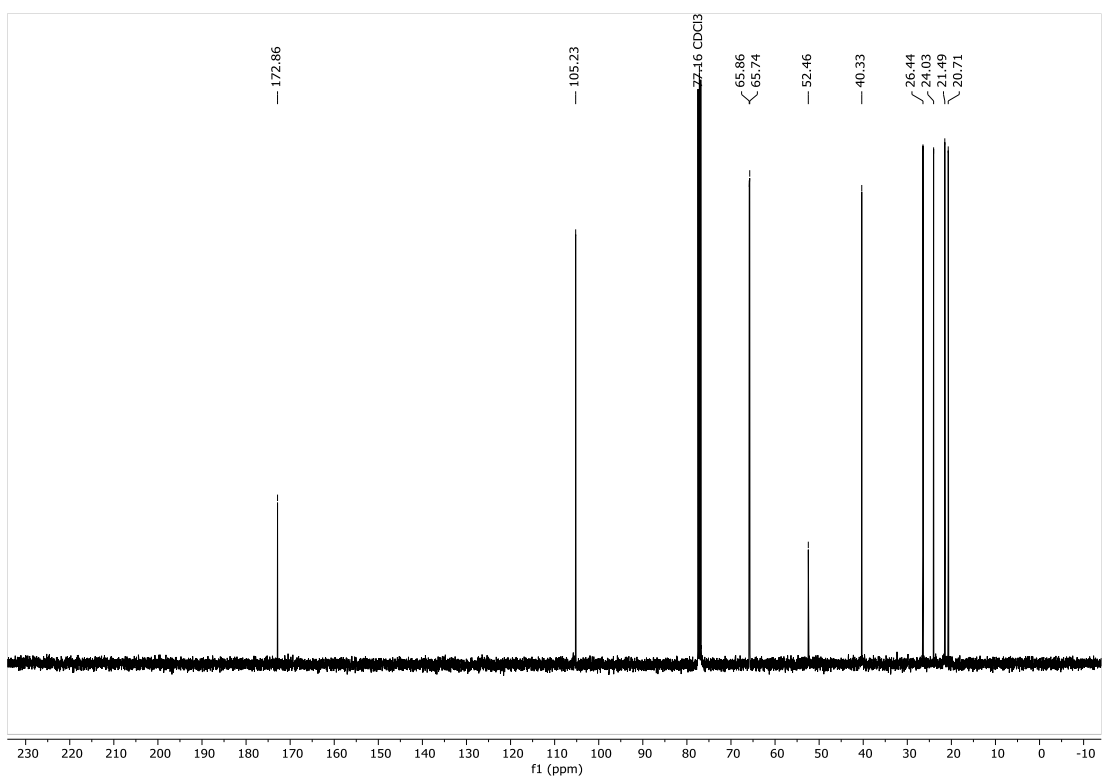
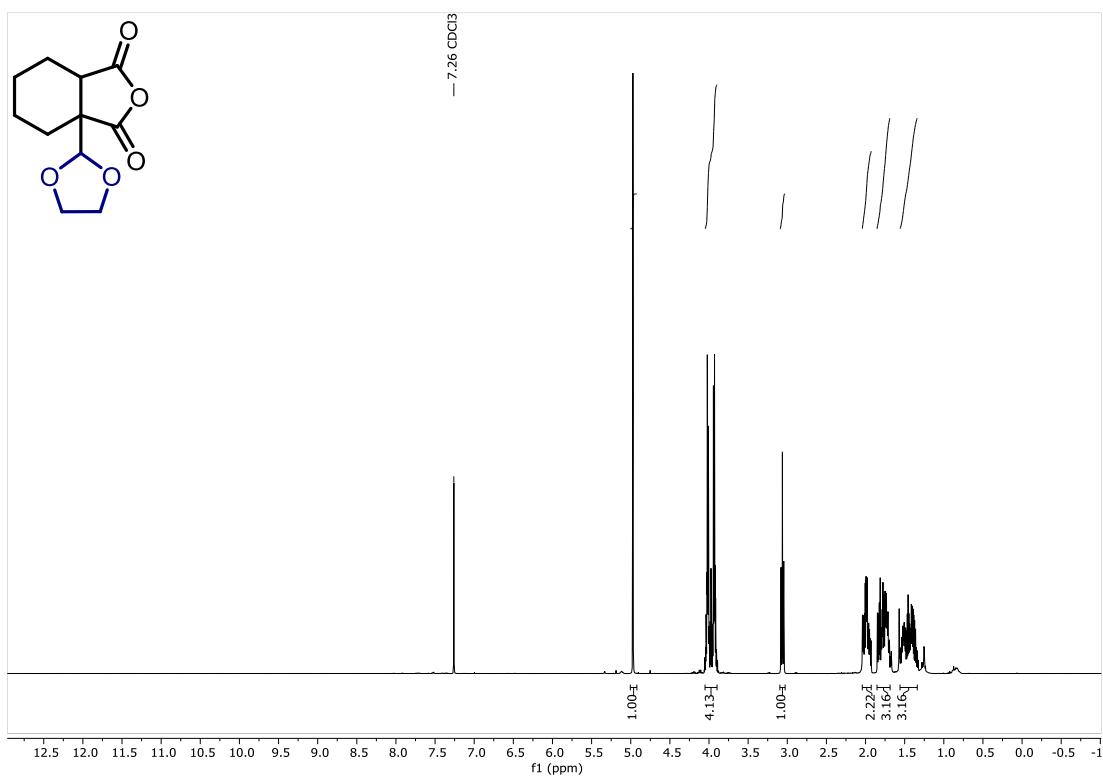
2-(2-(methylsulfonyl)ethyl)-1,3-dioxolane (3q)



3-(1,3-dioxolan-2-yl)dihydrofuran-2,5-dione (3r)



3a-(1,3-dioxolan-2-yl)hexahydroisobenzofuran-1,3-dione (3s)



7. References

- (1) Adapted from: S.L. Rössler, B.J. Jelier, E. Magnier, G. Dagousset, E. M. Carreira, A. Togni, *Angew. Chem. Int. Ed.* **2020**, *59*, 9264–9280.