

Enantioselective [3+2]-Cycloaddition of 2,3-Disubstituted Cyclobutenones: Vicinal Quaternary Stereocenters Construction and Skeletal Functionalization

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1. Experiment Procedure and Characterization data

1.1 General Information

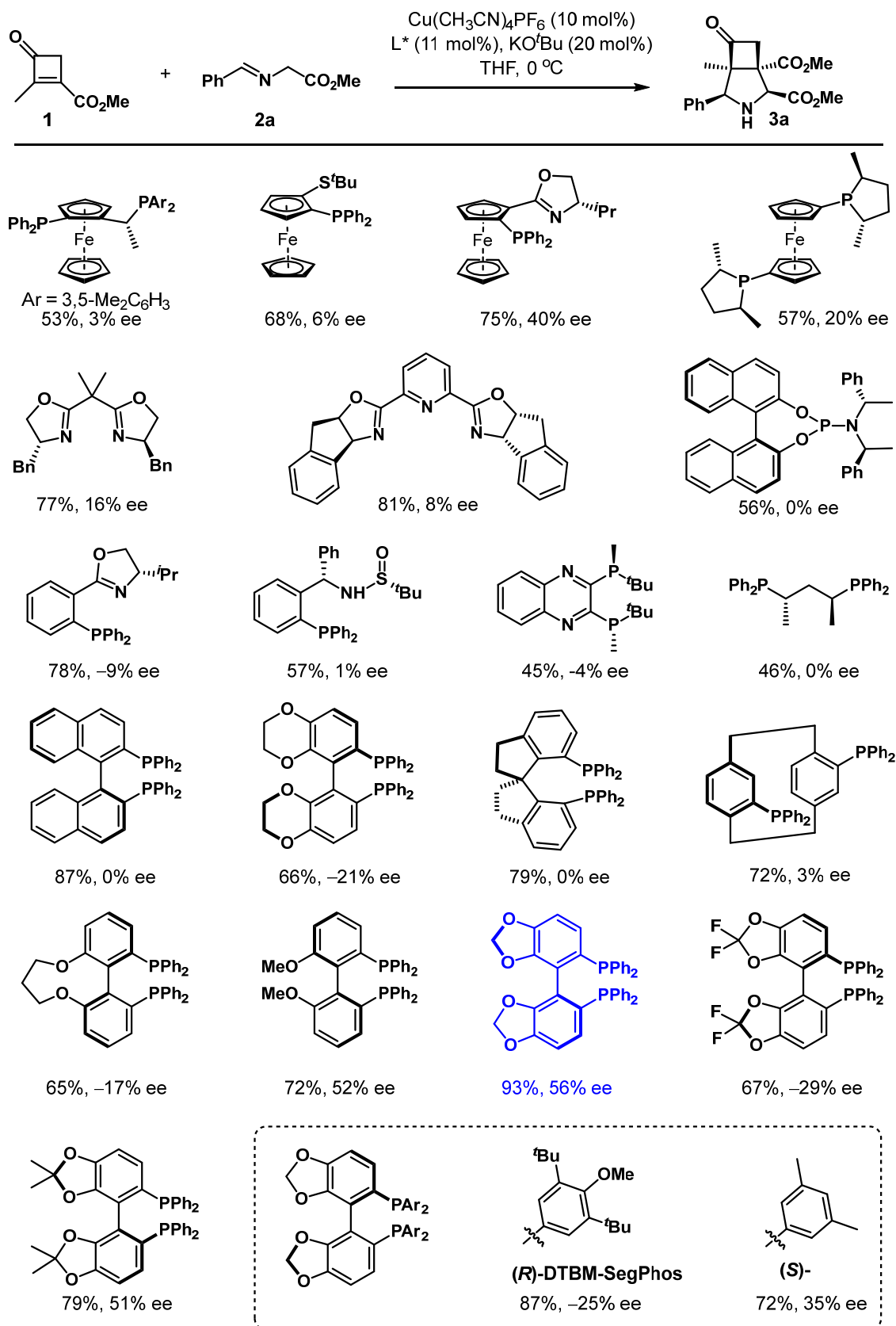
All reactions were carried out under an inert atmosphere of dry argon in the oven or flame-dried glassware unless the reaction procedure states otherwise. Tetrahydrofuran (THF), toluene, ether (diethyl ether), and dichloromethane were purified from a solvent purification system (Innovative Technology: PS-MD-5, China). Triethylamine was distilled from calcium hydride in a continuous still under an atmosphere of argon. Reaction temperatures were controlled by Heidolph MR Hei-Standard. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC plates and visualized using combinations of UV, anisaldehyde, ceric ammonium molybdate (CAM), and potassium permanganate. Flash column chromatography was performed using 300-400 mesh silica gel (Huanghai, Shandong) as the stationary phase. Proton and carbon nuclear magnetic resonance spectra were recorded at Bruker-400 MHz spectrometer and Agilent-400 MHz spectrometer. Optical Rotations were measured on a Rudolph Autopol III S2 polarimeter. The enantiomeric excess (*ee*) of the products was determined by chiral stationary phase HPLC (SHIMADZU LC 20AB). HRMS-DART was recorded at Thermo Fisher Scientific LTQ FT Ultra.

Abbreviations:

Tf = trifluoromethanesulfonyl; TES = triethylsilyl; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; (*S*)-DTBM-Segphos = (*S*)-(+)-5,5'-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole; TBDPSCl = *tert*-butyldiphenylsilyl chloride; DDQ = 1,2-dichloro-4,5-dicyanobenzoquinone; mCPBA = *meta*-chloroperoxybenzoic acid; TBAF = tetrabutylammonium fluoride; HTIB = phenyliodosohydroxy tosylate; TsCl = *p*-toulenesulfonyl chloride.

1.2 Summary of Reaction Optimization

Table S1 Optimization of cycloaddition of **1** with **2a**



Conditions: **1** (0.2 mmol), **2a** (0.4 mmol), [Cu] (10 mol%), L^* (11 mol%), base (20 mol%), THF (4 mL) 0 °C, 8–12 h.

Table S2 Base effect for the cycloaddition of 1 with 2a

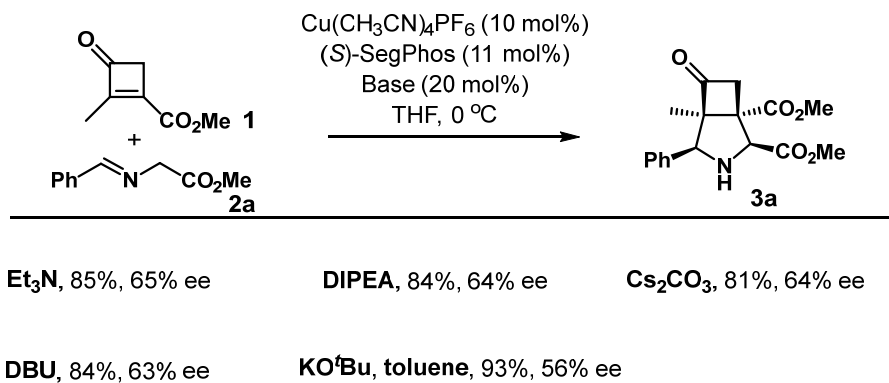


Table S3 Screening of metal catalysts

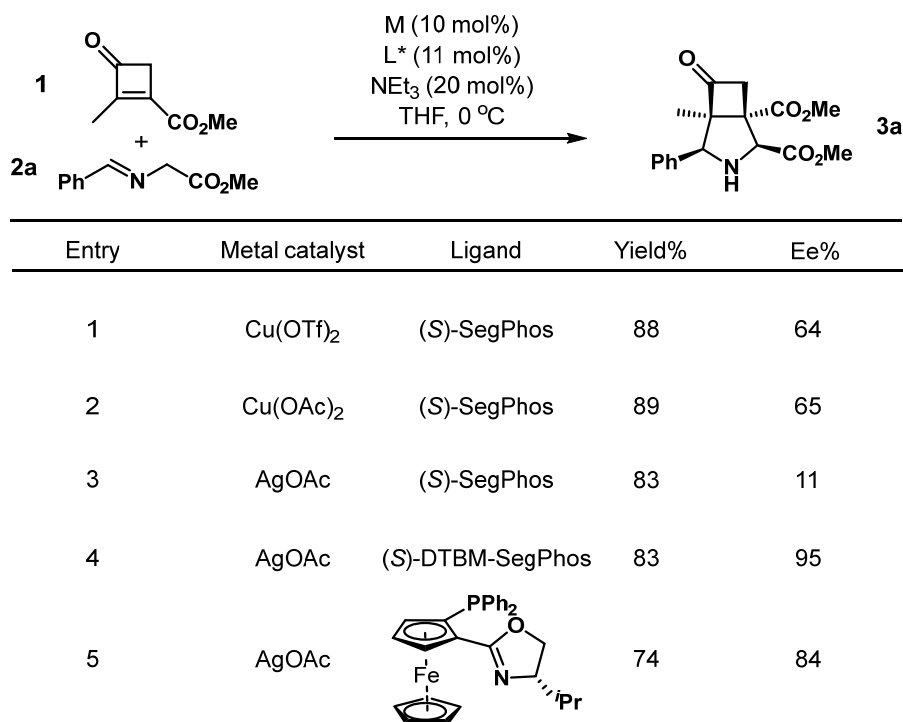
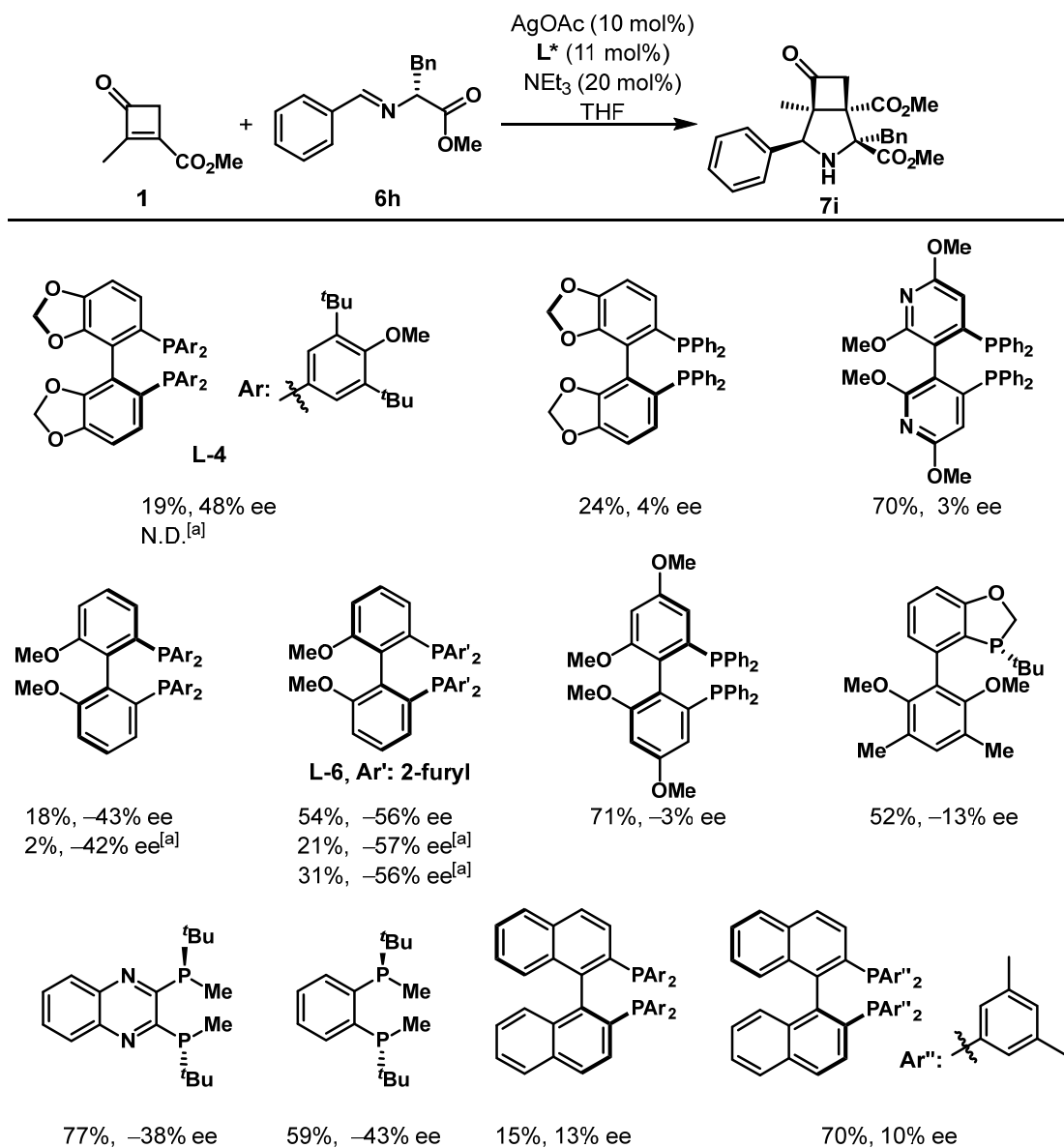


Table S4 Ligand screening for the cycloaddition of **1** with **6h**

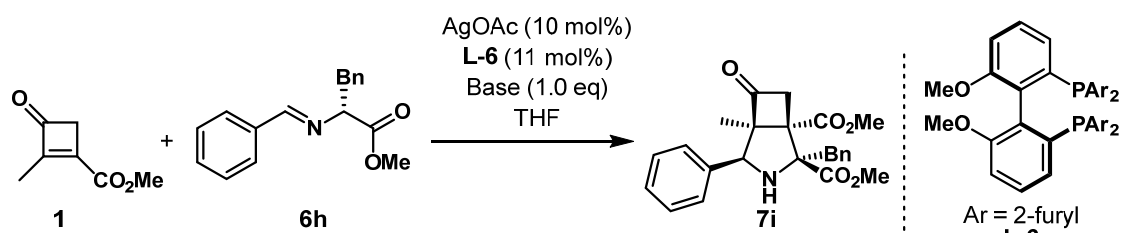


Conditions: **1** (1.0 equiv), **6h** (2.0 equiv), [Ag] (10 mol%), L* (11 mol%), base (20 mol%), THF (0.05–0.065 M), 0 °C, 9–14 h.

^[a] Reproducing of the reaction using NEt₃ (20 mol%) as a base.

Comments: The Ligands were screened using NEt₃ as a base, and **L-6** gave the best results. However, the yield of reaction was lack of reproducibility, and enantioselectivity was within the margin of error.

Table S5 Base effect for the cycloaddition of **1** with **6h**

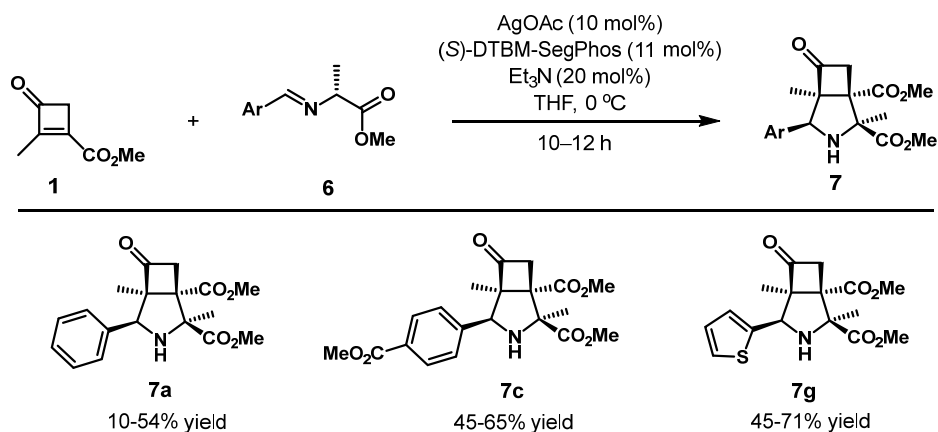


entry	Base	T (°C)	Yield [%]	Ee [%]
1	CsF	0	98	-58
2	K ₃ PO ₄	0	99	-51
3	KO ^t Bu	0	66	0
4	Imidazole	0	trace	-
5	K ₂ CO ₃	0	93	-59
6	NEt ₃	0	26	-53
7	Na ₂ CO ₃	0	99	-59
8	Na ₂ CO ₃	-40	27	-46
9	<i>N</i> -methylpiperidine	0	89	-61
10 ^[a]	<i>N</i> -methylpiperidine	0	37	-52
11	<i>N</i> -methylpiperidine	-20	74	-65

[a] *N*-methylpiperidine (20 mol%) was used.

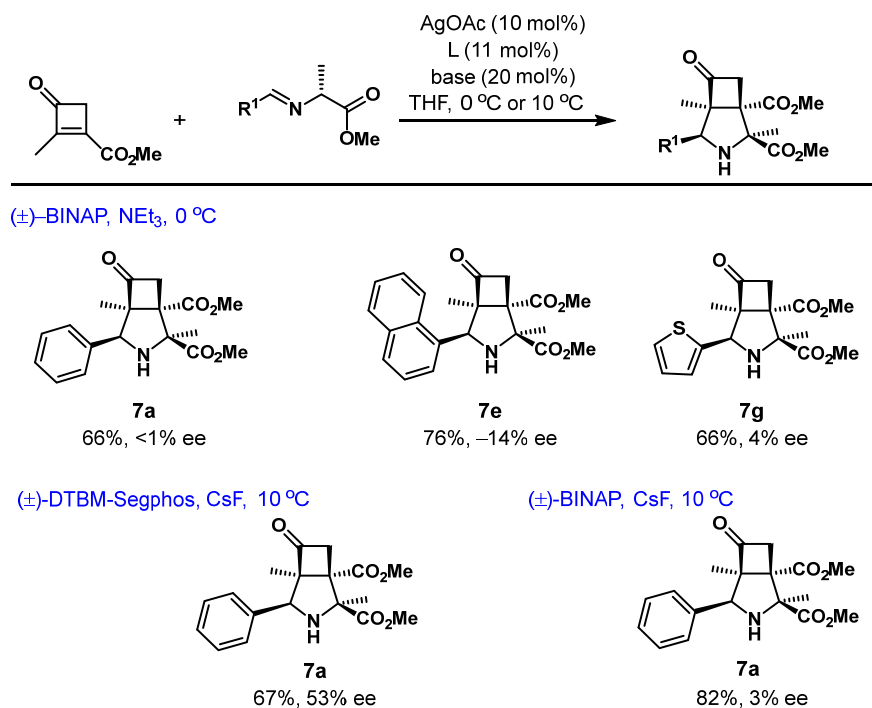
Comments: When strong base *t*-BuOK was used, the background reaction took place smoothly, giving the cycloadduct in 68% yield in the absence of Lewis acid and ligand (not shown).

Table S6 The cycloaddition of **1** with **6** using NEt_3 as a base



Comments: The yield of reaction was lack of reproducibility using NEt_3 as a base.

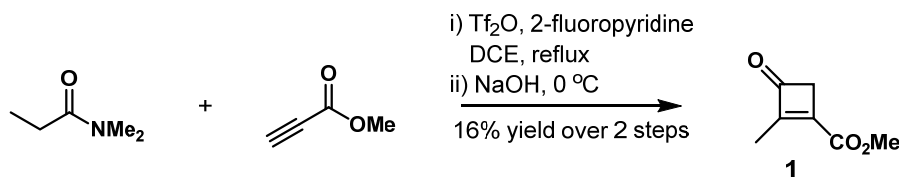
Table S7 The cycloaddition of **1** with **6** in the presence of racemic ligands



Comments: In the presence of $(\pm)\text{-BINAP}$ and NEt_3 at $0\text{ }^\circ\text{C}$, the reaction of **1** with different substrates **R-6** gave distinct results. In the case of **7e**, up to 14% ee was obtained. The reaction of **1** and **R-6a** gave **7a** in 53% ee when using $(\pm)\text{-Segphos}$ and CsF at $10\text{ }^\circ\text{C}$. We attributed these observations to the memory of chirality effect. As suggested by one referee, chiral **R-6a** might act as a chiral ligand in cycloaddition, thus leading to the above results. We cannot rule out this possibility at this point.

1.3 Synthesis of Cyclobutenones and Azomethine Ylides

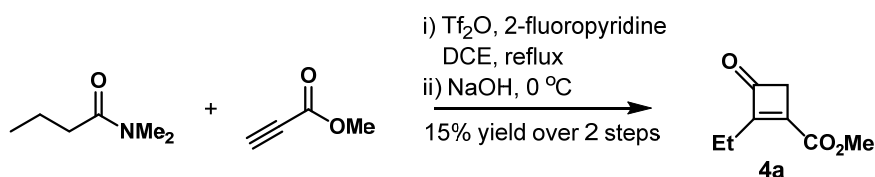
1.3.1 General procedure (GP1) for the synthesis of cyclobutenones **1** and **4a**:¹



Methyl 2-methyl-3-oxocyclobut-1-ene-1-carboxylate (**1**)²

2-Fluoropyridine (6.5 mL, 7.28 g, 75.0 mmol) was added dropwise to a solution of *N,N*-dimethylpropionamide (8.2 mL, 7.59 g, 75.0 mmol) in DCE (80 mL) at 0 °C, followed with methyl propiolate (2.2 mL, 2.10 g, 25.0 mmol). Then Tf_2O (12.6 mL, 21.2 g, 75.0 mmol) was added dropwise over 30 min. The resulting solution was stirred at reflux overnight. The resulting mixture was then cooled to 0 °C, and an aqueous solution of NaOH (1 M) was added until pH = 9. The resulting mixture was stirred at 0 °C for 4 h, before diluted with H_2O (20 mL). The reaction mixture was extracted with DCM and the combined organic phase was washed with brine, dried over Na_2SO_4 , concentrated, and the residue was purified by column chromatography on silica gel (PE:ether = 30:1) to afford the pure product **1** (0.575 g, 4.10 mmol, 16% yield).

¹H NMR (400 MHz, CDCl_3) δ (ppm): 3.87 (s, 3H), 3.39 (d, $J = 2.3$ Hz, 2H), 1.95 (s, 3H).



Methyl 2-ethyl-3-oxocyclobut-1-ene-1-carboxylate (**4a**)³

Prepared according to **General Procedure GP1** using *N,N*-dimethylbutyramide (4.82 g, 41.8 mmol), 2-Fluoropyridine (3.6 mL, 4.05 g, 41.8 mmol), methyl propiolate (1.9 mL, 1.80 g, 21.4 mmol), and Tf_2O (7.0 mL, 11.7 g, 41.5 mmol) in DCE (66 mL) at reflux for 15 h. The reaction mixture was then cooled to 0 °C and an aqueous solution of NaOH (1M) was added until pH = 9. The resulting mixture was stirred at 0 °C for another 4 h; flash chromatography on silica gel (PE/EA = 30/1) afforded **4a** (0.510 g, 3.31 mmol, 15% yield).

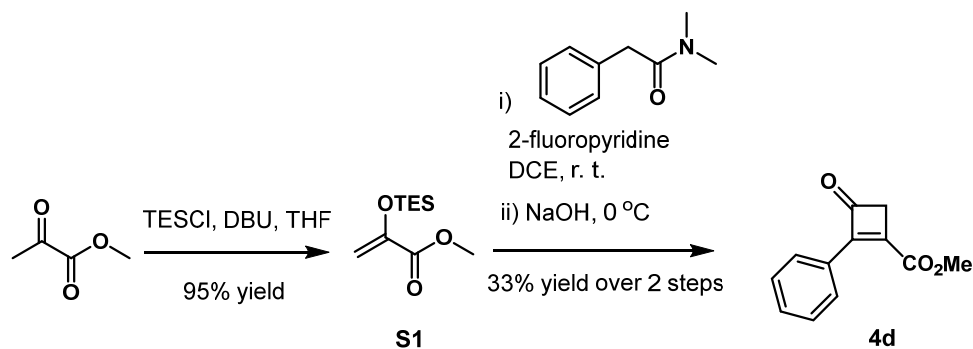
¹H NMR (400 MHz, CDCl_3) δ (ppm): 3.37 (s, 3H), 3.08 (s, 2H), 2.32 – 2.17 (q, $J = 7.6$ Hz, 2H), 1.14 – 1.01 (t, $J = 7.6$ Hz, 3H).

¹B.-C. Yan, M. Zhou, J. Li, X.-Nian. Li, S.-J. He, J.-P. Zuo, H.-D. Sun, A. Li, P.-T. Puno, *Angew. Chem. Int. Ed.* **2021**, *60*, 12859–12867.

²J. Vidal, H. Huet, *J. Org. Chem.* **1988**, *53*, 611–616.

³P. Yan, J. Zhang, L. Lu, H. Fang, P. Lu, *Acs Catal.* **2022**, *12*, 15416–15423.

1.3.2 General procedure (GP2) for the synthesis of cyclobutenones 4b–4e:



Methyl 3-oxo-2-phenylcyclobut-1-ene-1-carboxylate (4d)

To a solution of methyl pyruvate (0.9 mL, 1.02 g, 10.0 mmol) and chlorotriethylsilane (2.1 mL, 1.84 g, 12.2 mmol) in THF (45 mL) was added a solution of DBU (2.2 mL, 2.28 g, 15.0 mmol) in THF (7.5 mL) dropwise. The resulting mixture was stirred at room temperature for 8 h before diluted with Et₂O (10 mL). The reaction mixture was filtered through a pad of Celite®. The filtrate was washed sequentially with a cold aqueous solution of HCl (1M), H₂O, brine, dried over Na₂SO₄, and concentrated to afford the crude product **S1** (2.06 g, 9.52 mmol, 95% yield), which was directly submitted to the next step without further purification.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.49 (s, 1H), 4.87 (s, 1H), 3.77 (s, 3H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.72 (q, *J* = 7.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 164.93, 147.27, 103.47, 52.13, 6.50, 4.71.

IR (neat cm⁻¹): 2959, 2878, 1736, 1626, 1331, 1199, 1168, 1015.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₁₀H₂₁SiO₃, 217.1254; found, 217.1255.

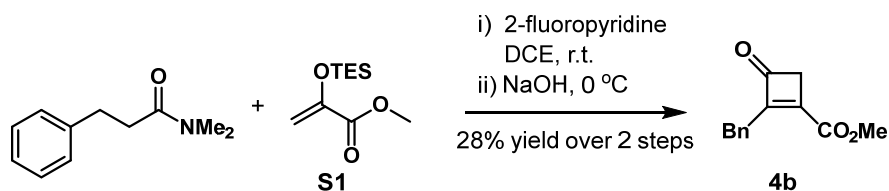
To a solution of *N,N*-dimethylphenylacetamide (1.60 g, 9.80 mmol) in DCE (5 mL) at 0 °C was added sequentially 2-fluoropyridine (0.9 mL, 1.02 g, 10.5 mmol) and a solution of **S1** (0.95 g, 4.39 mmol) in DCE (5 mL). Then a solution of Tf₂O (1.7 mL, 2.85 g, 10.1 mmol) in DCE (8 mL) was added dropwise over 30 min. The resulting mixture was stirred at room temperature for 15 h. The solution was cooled to 0 °C, and an aqueous solution of NaOH (1 M) was added until pH = 9. The resultant solution was stirred at 0 °C for 4 h, before diluted with H₂O (10 mL). The reaction mixture was extracted with DCM three times. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated, and the residue was purified by column chromatography on silica gel (PE:EA = 15:1) to afford the pure product **4d** (0.293 g, 1.45 mmol, 33% yield).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.14 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.35 – 7.30 (m, 3H), 3.83 (s, 3H), 3.47 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 189.70, 163.28, 151.62, 146.73, 130.96, 129.53, 128.45, 128.03, 52.30, 49.96.

IR (neat cm⁻¹): 2878, 1759, 1712, 1627, 1612, 1489, 1437, 1201, 1179, 1146.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₂H₁₀O₃, 202.0624; found, 202.0624.



Methyl 2-benzyl-3-oxocyclobut-1-ene-1-carboxylate (**4b**)

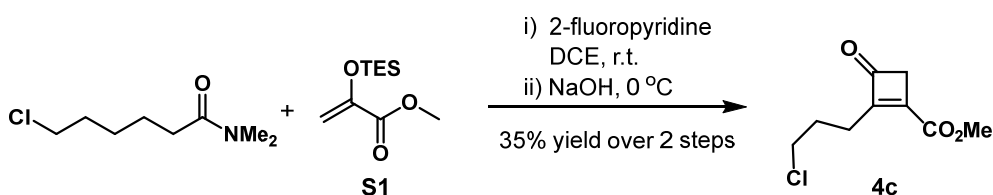
Prepared according to **General Procedure GP2** using **S1** (0.472 g, 2.18 mmol), *N,N*-dimethyl-3-phenylpropanamide (0.762 g, 4.30 mmol), Tf₂O (0.72 mL, 1.21 g, 4.30 mmol), 2-fluoropyridine (0.37 mL, 0.417 g, 4.30 mmol) in DCE (8 mL) at room temperature for 10 h. The reaction mixture was then cooled to 0 °C and an aqueous solution of NaOH (1M) was added until pH = 9. The resulting mixture was stirred at 0 °C for another 4 h; flash chromatography on silica gel (PE/EA = 10/1) afforded **4b** (0.133 g, 0.613 mmol, 28% yield).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.52 – 6.97 (m, 5H), 3.89 (s, 3H), 3.73 (s, 2H), 3.40 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 189.85, 163.10, 157.31, 151.82, 135.86, 128.90, 128.74, 126.81, 52.33, 48.85, 31.01.

IR (neat cm⁻¹): 3031, 1766, 1712, 1639, 1601, 1496, 1436, 1239, 1182, 1128.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₃H₁₂O₃, 216.0781; found, 216.0781.



Methyl 2-(3-chloropropyl)-3-oxocyclobut-1-ene-1-carboxylate (**4c**)

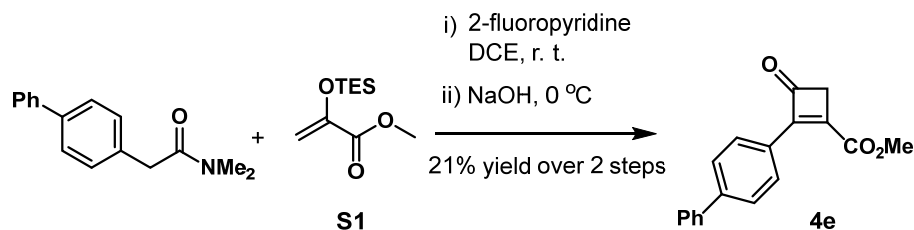
Prepared according to **General Procedure GP2** using **S1** (1.10 g, 5.07 mmol), 6-chloro-*N,N*-dimethylhexanamide (1.75 g, 10.7 mmol), Tf₂O (1.68 mL, 2.82 g, 10.0 mmol), 2-fluoropyridine (0.86 mL, 0.970 g, 10.0 mmol) in DCE (16 mL) at room temperature for 10 h. The reaction mixture was then cooled to 0 °C and an aqueous solution of NaOH (1M) was added until pH = 9. The resulting mixture was stirred at 0 °C for another 4 h; flash chromatography on silica gel (PE/EA = 10/1) afforded **4c** (0.357 g, 1.76 mmol, 35% yield).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.87 (s, 3H), 3.53 (t, *J* = 6.4 Hz, 2H), 3.39 (t, *J* = 1.8 Hz, 2H), 2.56 (tt, *J* = 7.8, 1.8 Hz, 2H), 2.09 – 2.00 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 190.17, 162.99, 158.17, 152.88, 52.34, 48.73, 44.20, 29.17, 22.44.

IR (neat cm⁻¹): 2959, 1764, 1715, 1437, 1217, 1130.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₉H₁₁ClO₃, 202.0391; found, 202.0392.



Methyl 2-([1,1'-biphenyl]-4-yl)-3-oxocyclobut-1-ene-1-carboxylate (**4e**)

Prepared according to **General Procedure GP2** using **S1** (1.63 g, 7.52 mmol), 2-([1,1'-biphenyl]-4-yl)-*N,N*-dimethylacetamide (3.56 g, 14.9 mmol), Ti_2O (2.60 mL, 4.36 g, 15.5 mmol), 2-fluoropyridine (1.30 mL, 1.47 g, 15.1 mmol) in DCE (25 mL) at room temperature for 12 h. The reaction mixture was then cooled to 0 °C and an aqueous solution of NaOH (1M) was added until pH = 9. The resulting mixture was stirred at 0 °C for another 4 h; flash chromatography on silica gel (PE/EA = 10/1) afforded **4e** (0.438 g, 1.57 mmol, 21% yield).

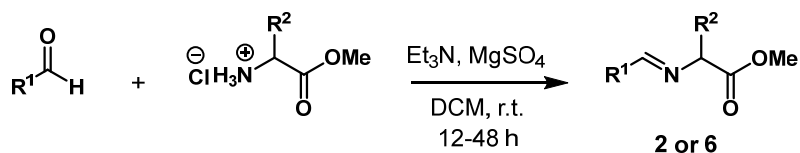
^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.37 – 8.27 (m, 2H), 7.71 – 7.55 (m, 4H), 7.52 – 7.42 (m, 2H), 7.42 – 7.34 (m, 1H), 3.95 (s, 3H), 3.61 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 190.06, 163.56, 151.57, 146.42, 143.70, 140.11, 130.19, 128.90, 128.00, 127.22, 127.14, 127.01, 52.48, 50.18.

IR (neat cm^{-1}): 2952, 2879, 1760, 1708, 1605, 1483, 1436, 1337, 1200, 1176, 1147.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_3$, 278.0937; found, 278.0936.

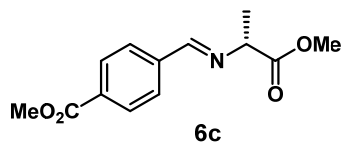
1.3.3 The synthesis of azomethine ylides **2** and **6**:⁴⁻⁵



To the suspension of amino acid ester hydrochloride (6.0 mmol, 1.2 equiv.), and MgSO_4 (0.758 g, 6.25 mmol, 1.25 equiv.) in DCM (10 mL) was added Et_3N (0.84 mL, 6.0 mmol, 1.2 equiv.). The mixture was stirred at room temperature for 1 h. Then the corresponding aldehyde (5.0 mmol, 1.0 equiv.) was added and the mixture was allowed to stir at room temperature for 16 h. Then the reaction mixture was filtrated through a pad of Celite[®], and the filtrate was washed with water. The aqueous phase was extracted three times with DCM and the combined organic layer was washed once with brine, dried over Na_2SO_4 , and concentrated. The α -iminoesters were used for [3+2]-cycloadditions without further purification. For **6c**, the pure product was obtained via further recrystallization from ethyl acetate/petroleum ether.

⁴M. Potowski, C. Merten, A.P. Antonchick, H. Waldmann, *Chem. Eur. J.* **2015**, *21*, 4913–4917.

⁵M. González-Esguevillas, J. Adrio, J. C. Carretero, *Chem. Commun.* **2013**, *49*, 4649–4651.



Methyl (*R,E*)-4-(((1-methoxy-1-oxopropan-2-yl)imino)methyl)benzoate (6c**)**

Prepared using methyl 4-formylbenzoate (0.816 g, 4.97 mmol), *D*-alanine methyl ester hydrochloride (0.838g, 6.00 mmol), MgSO₄ (0.786 g, 6.53 mmol), and NEt₃ (0.85 mL, 0.619 g, 6.12 mmol) in DCM (10 mL) at room temperature for 24 h. The reaction mixture was worked up to afford the crude product of **6b** (1.19 g, 4.49 mmol, 90% yield). Pure product was obtained via further recrystallization from ethyl acetate/petroleum ether.

[α]_D²⁶ 1.20 (*c* 1.0, CHCl₃).

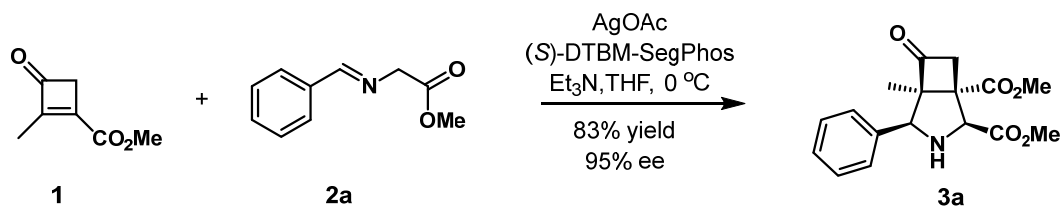
¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.34 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 4.18 (q, *J* = 6.8 Hz, 1H), 3.90 (s, 3H), 3.73 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 172.59, 166.46, 161.92, 139.46, 132.14, 129.74, 128.29, 67.92, 52.19, 19.30.

IR (neat, cm⁻¹): 1720, 1638, 1432, 1281, 1202, 1107.

HRMS-EI (*m/z*): [M+H]⁺ calcd. for C₁₃H₁₆NO₄, 250.1074; found, 250.1074.

1.4 [3+2] Cycloaddition



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-methyl-6-oxo-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3a**)

General Procedure A: A suspension of AgOAc (3.5 mg, 21.0 μ mol) and (*S*)-DTBM-SegPhos (26.4 mg, 22.4 μ mol) in THF (1 mL) was cooled to 0 °C, and a solution of **2a** (70.7 mg, 0.399 mmol) in THF (1 mL), a solution of NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol) in THF (0.1 mL), and a solution of **1** (27.7 mg, 0.198 mmol) in THF (1 mL) were sequentially added dropwise. The reaction mixture was stirred at 0 °C for 12 h before quenched with H₂O and diluted with DCM. The organic layer was separated, and the aqueous phase was extracted with DCM three times. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated and the residue was purified by column chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:acetone = 8:1) to afford the **3a** (51.9 mg, 0.164 mmol, 83% yield).

Ee: 95% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 28.0 min (major); t₂ = 33.1 min (minor)).

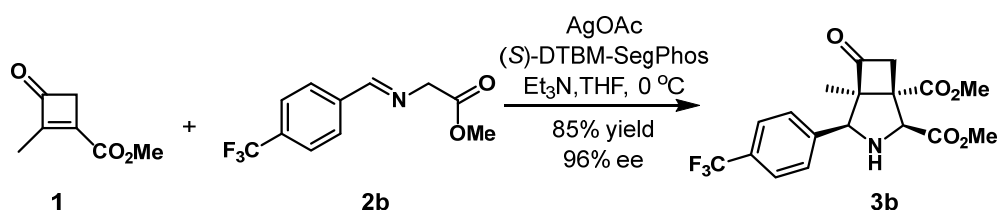
[α]_D²⁵ -12.5 (c 1.2, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.30 – 7.21 (m, 5H), 4.71 (s, 1H), 4.01 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.67 (d, *J* = 18.5 Hz, 1H), 3.03 (d, *J* = 18.5 Hz, 1H), 2.62 (brs, 1H), 1.13 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.04, 171.27, 170.42, 136.02, 128.43, 128.18, 127.43, 79.23, 70.93, 64.53, 52.52, 52.30, 50.70, 49.29, 13.21.

IR (neat, cm⁻¹): 3346, 2955, 1781, 1750, 1724, 1433, 1255, 1213, 1103, 703.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₇H₁₉NO₅, 317.1258; found, 317.1259.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-methyl-6-oxo-4-(4-(trifluoromethyl)phenyl)-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3b**)

Prepared according to **General Procedure A** using **1** (28.3 mg, 0.202 mmol), **2b** (97.5 mg, 0.398 mmol), AgOAc (4.2 mg, 25.2 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (24.4 mg, 20.7 μ mol) in THF (3.1 mL) at 0 °C for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3b** (66.2 mg, 0.172 mmol, 85% yield).

Ee: 96% (Chiralcel[®]AD-H; 5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 19.8 min (major); t_2 = 22.0 min (minor)).

$[\alpha]_D^{31}$ -4.2 (c 1.1, CHCl₃).

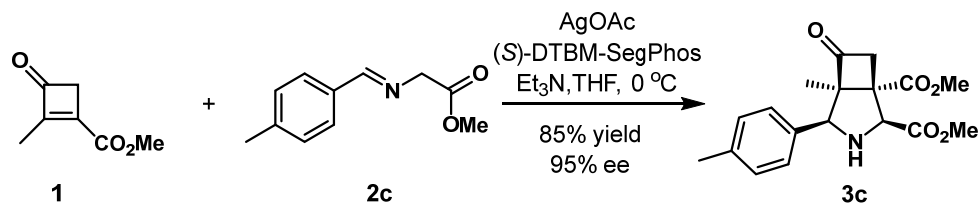
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.56 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 4.72 (s, 1H), 4.06 (s, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.69 (d, J = 18.6 Hz, 1H), 3.01 (d, J = 18.6 Hz, 1H), 2.66 (brs, 1H), 1.13 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.83, 171.03, 170.20, 140.20, 130.48 (q, J = 32.4 Hz), 127.82, 125.13 (q, J = 3.8 Hz), 123.98 (q, J = 272.1 Hz), 78.71, 70.11, 64.51, 52.66, 52.40, 50.46, 49.42, 13.00.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.54.

IR (neat, cm⁻¹): 1781, 1750, 1724, 1622, 1439, 1324, 1114.

HRMS-EI (m/z): [M]⁺ calcd. for C₁₈H₁₈F₃NO₅, 385.1132; found, 385.1125.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-methyl-6-oxo-4-(*p*-tolyl)-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3c**)

Prepared according to **General Procedure A** using **1** (27.9 mg, 0.199 mmol), **2c** (76.3 mg, 0.399 mmol), AgOAc (3.3 mg, 19.8 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (25.3 mg, 23.0 μ mol) in THF (3.1 mL) at 0 °C for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3c** (56.2 mg, 0.170 mmol, 85% yield).

Ee: 95% (Chiralcel[®]IC; 20% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 18.7 min (major); t_2 = 22.2 min (minor)).

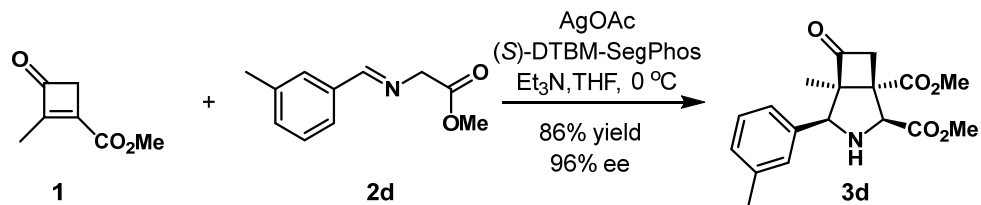
$[\alpha]_D^{30}$ 2.9 (c 1.2, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.21 – 7.15 (m, 2H), 7.15 – 7.07 (m, 2H), 4.70 (d, J = 4.4 Hz, 1H), 3.98 (d, J = 4.0 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.66 (d, J = 18.5 Hz, 1H), 3.02 (d, J = 18.5 Hz, 1H), 2.59 (brs, 1H), 2.33 (s, 3H), 1.12 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.33, 171.34, 170.50, 138.17, 132.94, 128.95, 127.32, 79.26, 70.82, 64.52, 52.54, 52.34, 50.71, 49.27, 21.15, 13.23.

IR (neat cm⁻¹): 3332, 2961, 2879, 1789, 1745, 1724, 1627, 1507, 1379, 1323, 1206, 1176.

HRMS-EI (m/z): [M]⁺ calcd. for C₁₈H₂₁NO₅, 331.1414; found, 331.1415.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-methyl-6-oxo-4-(*m*-tolyl)-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3d**)

Prepared according to **General Procedure A** using **1** (28.4 mg, 0.203 mmol), **2d** (76.7 mg, 0.408 mmol), AgOAc (3.6 mg, 21.6 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (25.3 mg, 21.4 μ mol) in THF (3.1 mL) at 0 °C for 12 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3d** (58.0 mg, 0.175 mmol, 86% yield).

Ee: 96% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 27.9 min (major); t₂ = 34.0 min (minor)).

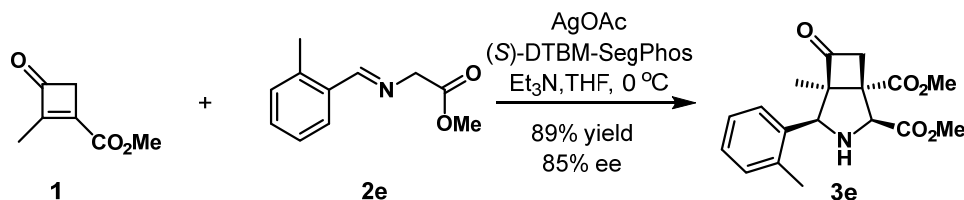
[α]_D²¹ -10.9 (c 1.1, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.24 – 7.17 (m, 1H), 7.15 – 7.05 (m, 3H), 4.70 (d, *J* = 4.2 Hz, 1H), 3.98 (d, *J* = 3.8 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.66 (d, *J* = 18.5 Hz, 1H), 3.03 (d, *J* = 18.4 Hz, 1H), 2.60 (brs, 1H), 2.33 (s, 3H), 1.13 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.09, 171.29, 170.47, 137.76, 135.90, 129.22, 128.03, 124.53, 79.23, 70.90, 64.50, 52.51, 52.31, 50.67, 49.23, 21.35, 13.24.

IR (neat cm⁻¹): 2976, 2885, 1781, 1751, 1721, 1609, 1437, 1376, 1324, 1242, 1201, 1171, 1051.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₈H₂₁NO₅, 331.1414; found, 331.1415.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-methyl-6-oxo-4-(*o*-tolyl)-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3e**)

Prepared according to **General Procedure A** using **1** (28.0 mg, 0.200 mmol), **2e** (76.7 mg, 0.401 mmol), AgOAc (3.1 mg, 18.6 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (29.0 mg, 23.8 μ mol) in THF (3.1 mL) at 0 °C for 12 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3e** (58.9 mg, 0.178 mmol, 89% yield).

Ee: 85% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 31.9 min (major); t₂ = 38.4 min (minor)).

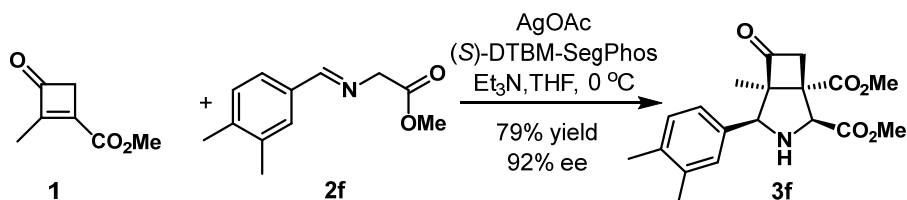
[α]_D²² -15.1 (c 1.2, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.44 – 7.35 (m, 1H), 7.22 – 7.07 (m, 3H), 4.73 (s, 1H), 4.41 (s, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 3.69 (d, *J* = 18.5 Hz, 1H), 3.08 (d, *J* = 18.5 Hz, 1H), 2.53 (brs, 1H), 2.35 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 207.34, 171.33, 170.45, 135.77, 133.91, 130.54, 128.17, 127.99, 125.83, 80.38, 65.91, 64.75, 52.58, 52.36, 50.84, 49.29, 19.91, 13.61.

IR (neat cm^{-1}): 3332, 3203, 2976, 2878, 1779, 1742, 1732, 1627, 1439, 1326, 1201.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_5$, 331.1414; found, 331.1416.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-4-(3,4-dimethylphenyl)-5-methyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3f**)

Prepared according to **General Procedure A** using **1** (28.3 mg, 0.202 mmol), **2f** (84.4 mg, 0.411 mmol), AgOAc (4.6 mg, 27.6 μmol), NEt_3 (5.6 μL , 4.1 mg, 40.0 μmol), (S)-DTBM-SegPhos (26.2 mg, 22.2 μmol) in THF (3.1 mL) at $0\text{ }^\circ\text{C}$ for 9 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 6:1) provided **3f** (55.1 mg, 0.160 mmol, 79% yield).

Ee: 92% (Chiralcel[®]OD-H; 5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 18.8 min (minor); t_2 = 30.3 min (major)).

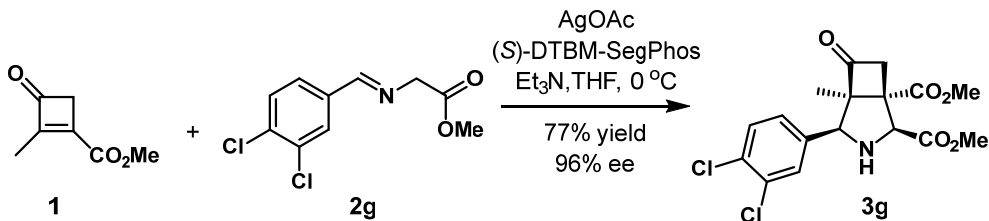
$[\alpha]_D^{33}$ 4.3 (c 1.1, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.10 – 6.98 (m, 3H), 4.68 (d, J = 3.5 Hz, 1H), 3.95 (d, J = 3.1 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.65 (d, J = 18.5 Hz, 1H), 3.03 (d, J = 18.5 Hz, 1H), 2.57 (t, J = 4.5 Hz, 1H), 2.23 (s, 6H), 1.12 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 207.37, 171.34, 170.53, 136.78, 136.35, 133.30, 129.47, 128.58, 124.83, 79.27, 70.82, 64.49, 52.51, 52.32, 50.70, 49.18, 19.73, 19.46, 13.25.

IR (neat cm^{-1}): 3008, 1780, 1747, 1721, 1440, 1329, 1250, 1215, 1013.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}_5$, 345.1571; found, 345.1569.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-4-(3,4-dichlorophenyl)-5-methyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3g**)

Prepared according to **General Procedure A** using **1** (28.3 mg, 0.202 mmol), **2g** (99.0 mg, 0.402 mmol), AgOAc (4.4 mg, 26.3 μmol), NEt_3 (5.6 μL , 4.1 mg, 40.0 μmol), (S)-DTBM-SegPhos (25.4 mg, 21.5 μmol) in THF (3.1 mL) at $0\text{ }^\circ\text{C}$ for 8 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 6:1) provided **3g** (60.1 mg, 0.156 mmol, 77% yield).

Ee: 96% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 21.3 min (major); t_2 = 30.0 min (minor)).

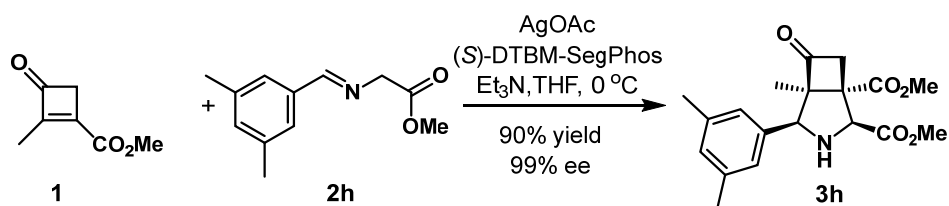
$[\alpha]_D^{28}$ 17.9 (c 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.42 – 7.31 (m, 2H), 7.14 (dd, J = 8.3, 2.1 Hz, 1H), 4.69 (d, J = 2.8 Hz, 1H), 3.95 (s, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.68 (d, J = 18.7 Hz, 1H), 2.98 (d, J = 18.6 Hz, 1H), 2.60 (brs, 1H), 1.12 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.74, 170.96, 170.11, 136.48, 132.39, 132.36, 130.18, 129.26, 126.68, 78.50, 69.39, 64.39, 52.68, 52.43, 50.36, 49.47, 13.01.

IR (neat, cm⁻¹): 1777, 1751, 1724, 1438, 1325, 1231, 1108, 1067, 1030.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for C₁₇H₁₈Cl₂NO₅, 386.0557; found, 386.0555.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-4-(3,5-dimethylphenyl)-5-methyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3h**)

Prepared according to **General Procedure A** using **1** (28.5 mg, 0.203 mmol), **2h** (82.4 mg, 0.401 mmol), AgOAc (3.9 mg, 23.4 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (25.6 mg, 21.7 μ mol) in THF (3.1 mL) at 0 °C for 11 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3h** (63.0 mg, 0.182 mmol, 90% yield).

Ee: 99% (Chiralcel[®]IC; 2.5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 60.0 min (major); t_2 = 94.1 min (minor)).

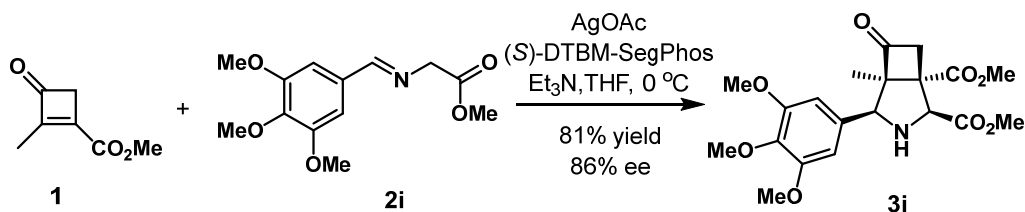
$[\alpha]_D^{32}$ -7.3 (c 1.3, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.97 – 6.85 (m, 3H), 4.69 (s, 1H), 3.94 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.65 (d, J = 18.5 Hz, 1H), 3.04 (d, J = 18.4 Hz, 1H), 2.58 (brs, 1H), 2.29 (s, 6H), 1.13 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.18, 171.35, 170.56, 137.66, 135.84, 130.22, 125.21, 79.31, 70.95, 64.52, 52.54, 52.36, 50.72, 49.22, 21.26, 13.32.

IR (neat cm⁻¹): 1780, 1745, 1732, 1369, 1324, 1219, 1033, 1000.

HRMS-EI (m/z): $[M]^+$ calcd. for C₁₉H₂₃NO₅, 345.1571; found, 345.1567.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-methyl-6-oxo-4-(3,4,5-trimethoxyphenyl)-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3i**)

Prepared according to **General Procedure A** using **1** (27.9 mg, 0.199 mmol), **2i** (107.4 mg, 0.402 mmol), AgOAc (3.3 mg, 20.0 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (25.9 mg, 22.0 μ mol) in THF (3.1 mL) at 0 °C for 9 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3i** (66.0 mg, 0.162 mmol, 81% yield).

Ee: 86% (Chiralcel[®]IC; 30% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 42.8 min (major); t₂ = 68.2 min (minor)).

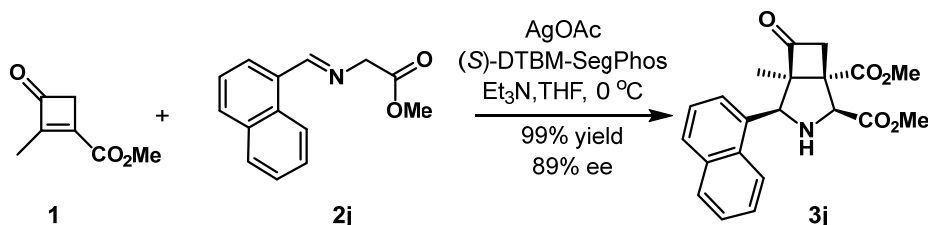
[α]_D³⁰ 0.32 (c 1.2, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.48 (s, 2H), 4.66 (s, 1H), 3.90 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.79 (s, 6H), 3.74 (s, 3H), 3.64 (d, *J* = 18.5 Hz, 1H), 2.99 (d, *J* = 18.5 Hz, 1H), 2.59 (brs, 1H), 1.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.23, 171.15, 170.30, 152.84, 137.83, 131.47, 104.57, 78.87, 71.10, 64.35, 60.66, 56.03, 52.51, 52.27, 50.32, 49.21, 13.18.

IR (neat, cm⁻¹): 3337, 1783, 1723, 1591, 1216, 1132, 1013.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₀H₂₅NO₈, 407.1575; found, 407.1576.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-methyl-4-(naphthalen-1-yl)-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3j**)

Prepared according to **General Procedure A** using **1** (28.1 mg, 0.201 mmol), **2j** (92.3 mg, 0.406 mmol), AgOAc (3.8 mg, 22.8 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (25.4 mg, 21.5 μ mol) in THF (3.1 mL) at 0 °C for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3j** (73.3 mg, 0.200 mmol, 99% yield).

Ee: 89% (Chiralcel[®] AD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 254 nm; t₁ = 17.5 min (minor); t₂ = 22.9 min (major)).

[α]_D²⁷ 25.5 (c 1.3, CHCl₃).

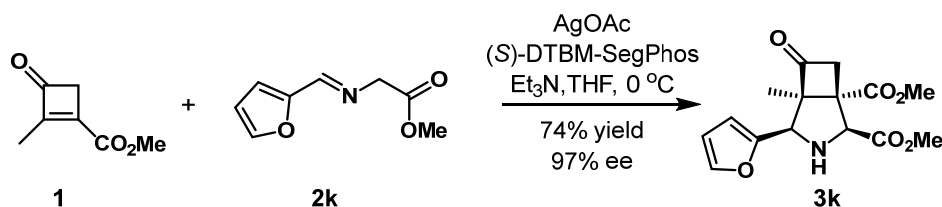
¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.15 – 7.98 (m, 1H), 7.94 – 7.84 (m, 1H), 7.84 – 7.75 (m, 2H), 7.52 – 7.42 (m, 3H), 5.03 (d, *J* = 3.1 Hz, 1H), 4.84 (d, *J* = 3.6 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.73 (d, *J* = 18.5 Hz, 1H), 3.11 (d, *J* = 18.5 Hz, 1H), 2.62 (brs,

1H), 1.19 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.23, 171.27, 170.47, 133.78, 131.69, 131.62, 129.15, 128.70, 125.97, 125.91, 125.27, 125.23, 122.55, 80.06, 64.70, 64.62, 52.64, 52.40, 50.93, 49.33, 13.86.

IR (neat, cm⁻¹): 3350, 3338, 1783, 1745, 1727, 1439, 1318, 1259, 1207, 1102.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₁H₂₁NO₅, 367.1414; found, 367.1418.



Dimethyl (1*S*,2*S*,4*R*,5*S*)-4-(furan-2-yl)-5-methyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3k**)

Prepared according to **General Procedure A** using **1** (28.0 mg, 0.200 mmol), **2k** (67.7 mg, 0.405 mmol), AgOAc (3.8 mg, 22.8 μmol), NEt₃ (5.6 μL, 4.1 mg, 40.0 μmol), (S)-DTBM-SegPhos (28.1 mg, 23.8 μmol) in THF 3.1 (3.1 mL) at 0 °C for 9 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3k** (45.5 mg, 0.148 mmol, 74% yield).

Ee: 97% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 30.8 min (major); t₂ = 58.1 min (minor)).

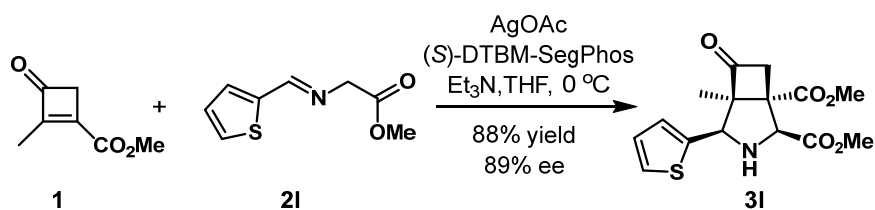
[α]_D²⁵ -19.0 (c 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.37 (t, *J* = 1.4 Hz, 1H), 6.34 (d, *J* = 1.4 Hz, 2H), 4.71 (d, *J* = 4.4 Hz, 1H), 4.13 (d, *J* = 4.3 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.66 (d, *J* = 18.5 Hz, 1H), 2.99 (d, *J* = 18.6 Hz, 1H), 2.88 (brs, 1H), 1.21 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.02, 170.94, 170.13, 149.57, 142.57, 110.35, 107.72, 79.40, 64.92, 52.67, 52.50, 51.79, 48.78, 13.66.

IR (neat, cm⁻¹): 2953, 1785, 1729, 1260, 1096, 1020.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₅H₁₇NO₆, 307.1050; found, 307.1051.



Dimethyl (1*S*,2*S*,4*R*,5*S*)-5-methyl-6-oxo-4-(thiophen-2-yl)-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3l**)

Prepared according to **General Procedure A** using **1** (28.1 mg, 0.201 mmol), **2l** (75.0 mg, 0.410 mmol), AgOAc (4.0 mg, 24.0 μmol), NEt₃ (5.6 μL, 4.1 mg, 40.0 μmol), (S)-DTBM-SegPhos (27.6 mg, 23.4 μmol) in THF (3.1 mL) at 0 °C for 10 h; flash

chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3I** (57.3 mg, 0.177 mmol, 88% yield).

Ee: 89% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 52.6 min (major); t₂ = 57.4 min (minor)).

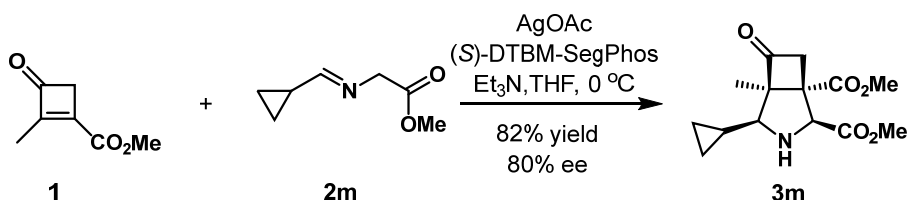
[α]_D²⁷ -10.5 (c 1.2, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.24 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.04 – 6.92 (m, 2H), 4.70 (d, *J* = 3.7 Hz, 1H), 4.32 (d, *J* = 3.2 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.66 (d, *J* = 18.5 Hz, 1H), 3.02 (d, *J* = 18.6 Hz, 1H), 2.83 (brs, 1H), 1.19 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.45, 171.03, 170.01, 139.54, 126.77, 125.05, 124.88, 78.99, 66.60, 64.47, 52.60, 52.39, 50.88, 49.46, 13.37.

IR (neat, cm⁻¹): 3340, 1784, 1731, 1442, 1352, 1263, 1230, 1108.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₅H₁₇NO₅S, 323.0822; found, 323.0822.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-4-cyclopropyl-5-methyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3m**)

Prepared according to **General Procedure A** using **1** (28.1 mg, 0.201 mmol), **2m** (56.8 mg, 0.402 mmol), AgOAc (3.5 mg, 20.9 μmol), NEt₃ (5.6 μL, 4.1 mg, 40.0 μmol), (S)-DTBM-SegPhos (27.0 mg, 22.9 μmol) in THF (3.1 mL) at 0 °C for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3m** (46.3 mg, 0.165 mmol, 82% yield).

Ee: 80% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 29.2 min (major); t₂ = 34.2 min (minor)).

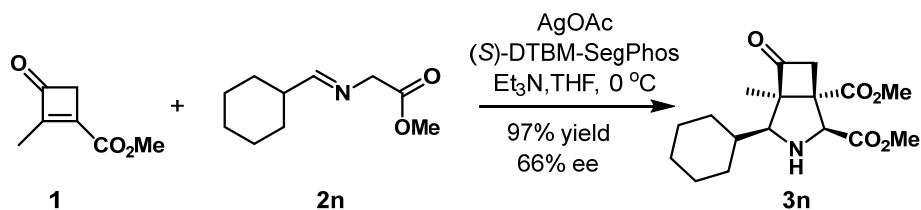
[α]_D²² -37.8 (c 1.1, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.52 (s, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.65 (d, *J* = 18.7 Hz, 1H), 2.82 (d, *J* = 18.7 Hz, 1H), 2.57 – 2.27 (brs, 1H), 2.18 (d, *J* = 9.2 Hz, 1H), 1.15 (s, 3H), 0.93 – 0.81 (m, 1H), 0.65 – 0.56 (m, 1H), 0.56 – 0.46 (m, 1H), 0.24 (dq, *J* = 9.8, 4.9 Hz, 1H), 0.12 (dq, *J* = 9.8, 4.9 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 208.82, 171.27, 170.55, 79.10, 72.48, 64.53, 52.50, 52.32, 52.07, 48.57, 13.41, 10.03, 2.65, 2.17.

IR (neat, cm⁻¹): 3354, 3005, 2940, 1781, 1729, 1437, 1321, 1251, 1221.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₄H₁₉NO₅, 281.1258; found, 281.1255.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-4-cyclohexyl-5-methyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3n**)

Prepared according to **General Procedure A** using **1** (28.0 mg, 0.200 mmol), **2n** (73.5 mg, 0.401 mmol), AgOAc (3.3 mg, 20.0 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (25.9 mg, 22.0 μ mol) in THF (3.1 mL) at 0 °C for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3n** (62.5 mg, 0.193 mmol, 97% yield).

Ee: 66% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 15.0 min (major); t_2 = 18.3 min (minor)).

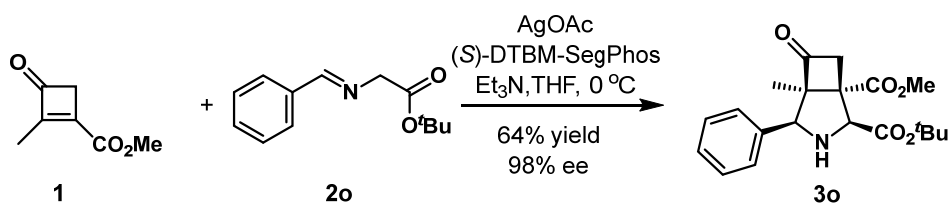
$[\alpha]_D^{26}$ -59.2 (c 1.2, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.52 (s, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.49 (d, J = 18.3 Hz, 1H), 2.80 (d, J = 18.4 Hz, 1H), 2.72 (d, J = 8.7 Hz, 1H), 2.44 (s, 1H), 2.06 – 1.91 (m, 1H), 1.86 (d, J = 12.7 Hz, 1H), 1.76 – 1.52 (m, 3H), 1.41 – 1.30 (m, 1H), 1.27 – 1.06 (m, 6H), 1.02 – 0.91 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.48, 171.20, 170.69, 79.93, 72.91, 64.26, 53.17, 52.45, 52.36, 47.95, 40.91, 31.38, 30.27, 26.00, 25.75, 25.69, 16.11.

IR (neat, cm⁻¹): 2971, 2931, 2902, 1743, 1735, 1724, 1434, 1257, 1095, 1052.

HRMS-EI (m/z): [M]⁺ calcd. for C₁₇H₂₅NO₅, 323.1727; found, 323.1725.



2-(*Tert*-butyl) 1-methyl (1*S*,2*S*,4*S*,5*S*)-5-methyl-6-oxo-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**3o**)

Prepared according to **General Procedure A** using **1** (27.5 mg, 0.196 mmol), **2o** (87.1 mg, 0.397 mmol), AgOAc (3.5 mg, 20.9 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (25.6 mg, 23.0 μ mol) in THF (3.1 mL) at 0 °C for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3o** (45.5 mg, 0.127 mmol, 64% yield).

Ee: 98% (Chiralcel[®]IC; 5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 22.8 min (major); t_2 = 26.4 min (minor)).

$[\alpha]_D^{34}$ 1.9 (c 1.1, CHCl₃).

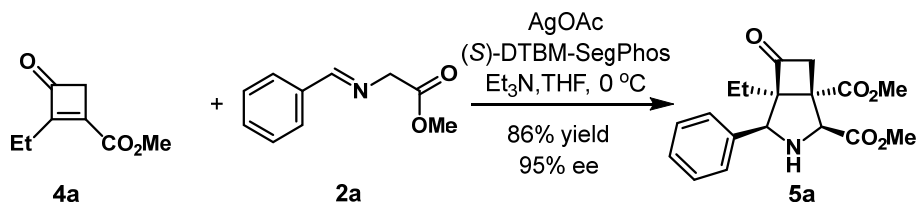
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.35 – 7.27 (m, 5H), 4.60 (s, 1H), 4.01 (s, 1H), 3.83 (s, 3H), 3.66 (d, J = 18.4 Hz, 1H), 3.02

(d, $J = 18.4$ Hz, 1H), 2.55 (brs, 1H), 1.46 (s, 9H), 1.13 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 207.33, 171.43, 169.17, 136.19, 128.37, 128.16, 127.45, 82.06, 79.01, 71.01, 65.41, 52.38, 51.08, 48.90, 27.91, 13.23.

IR (neat cm^{-1}): 3342, 2879, 1778, 1747, 1730, 1626, 1376, 1323, 1224, 1200, 1170.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{26}\text{NO}_5$, 360.1805; found, 360.1801.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-ethyl-6-oxo-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**5a**)

Prepared according to **General Procedure A** using **4a** (30.4 mg, 0.197 mmol), **2a** (71.3 mg, 0.402 mmol), AgOAc (4.0 mg, 24.0 μmol), NEt_3 (5.6 μL , 4.1 mg, 40.0 μmol), (S)-DTBM-SegPhos (26.5 mg, 22.5 μmol) in THF (3.1 mL) at $0\text{ }^\circ\text{C}$ for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 6:1) provided **5a** (55.9 mg, 0.169 mmol, 86% yield).

Ee: 95% (Chiralcel[®]IA; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; $t_1 = 11.5$ min (minor); $t_2 = 12.5$ min (major)).

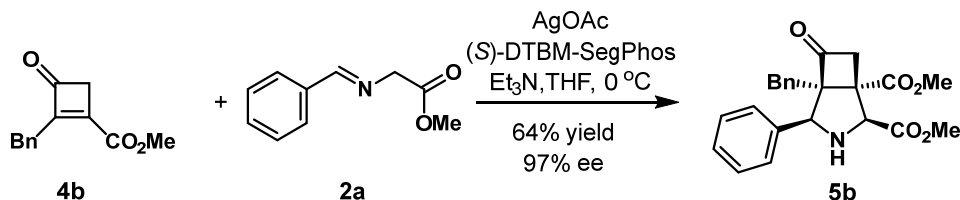
$[\alpha]_{\text{D}}^{28}$ 4.8 (c 1.2, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.35 – 7.27 (m, 5H), 4.63 (d, $J = 2.0$ Hz, 1H), 4.19 – 4.04 (m, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.61 (d, $J = 18.6$ Hz, 1H), 2.98 (d, $J = 18.6$ Hz, 1H), 2.58 (t, $J = 4.5$ Hz, 1H), 1.80 – 1.58 (m, 2H), 0.79 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 207.52, 171.80, 170.33, 136.17, 128.38, 128.06, 127.87, 83.99, 68.99, 65.30, 52.62, 52.30, 49.80, 49.61, 21.23, 8.56.

IR (neat, cm^{-1}): 3329, 1784, 1722, 1438, 1372, 1255, 1229, 1106.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_5$, 331.1414; found, 331.1412.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-benzyl-6-oxo-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**5b**)

Prepared according to **General Procedure A** using **5b** (43.9 mg, 0.203 mmol), **2a** (70.5 mg, 0.398 mmol), AgOAc (3.1 mg, 18.6 μmol), NEt_3 (5.6 μL , 4.1 mg, 40.0 μmol), (S)-DTBM-SegPhos (25.4 mg, 21.5 μmol) in THF (3.1 mL) at $0\text{ }^\circ\text{C}$ for 9 h; flash

chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **5b** (51.5 mg, 0.131 mmol, 64% yield).

Ee: 97% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 31.7 min (minor); t₂ = 34.3 min (major)).

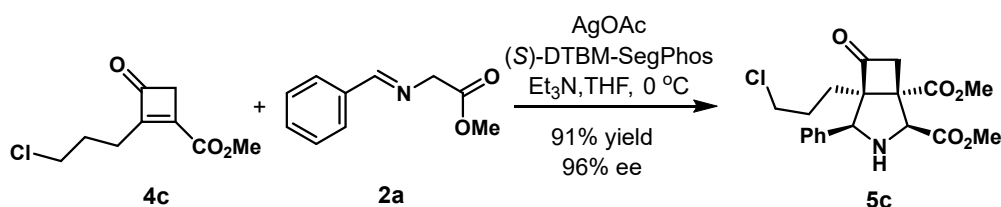
[α]_D²¹ -17.9 (c 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.37 – 7.24 (m, 3H), 7.24 – 7.11 (m, 5H), 7.10 – 7.01 (m, 2H), 4.67 (d, *J* = 3.5 Hz, 1H), 4.22 (d, *J* = 3.3 Hz, 1H), 3.74 (s, 3H), 3.62 (s, 3H), 3.39 (d, *J* = 18.6 Hz, 1H), 3.12 (d, *J* = 14.7 Hz, 1H), 3.02 – 2.91 (m, 2H), 2.59 (brs, 1H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.36, 171.58, 170.24, 136.01, 135.31, 130.37, 128.39, 128.21, 128.04, 128.02, 126.77, 83.60, 70.28, 65.80, 52.46, 52.31, 50.38, 50.00, 35.23.

IR (neat cm⁻¹): 3358, 3049, 1782, 1725, 1436, 1257, 1214, 1030.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₃H₂₃NO₅, 393.1571; found, 393.1573.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-(3-chloropropyl)-6-oxo-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**5c**)

Prepared according to **General Procedure A** using **4c** (40.2 mg, 0.198 mmol), **2a** (69.6 mg, 0.404 mmol), AgOAc (4.1 mg, 24.6 μmol), NEt₃ (5.6 μL, 4.1 mg, 40.0 μmol), (S)-DTBM-SegPhos (27.6 mg, 23.4 μmol) in THF (3.1 mL) at 0 °C for 11 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **5c** (68.5 mg, 0.180 mmol, 91% yield).

Ee: 96% (Chiralcel[®]IA; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 13.9 min (minor); t₂ = 15.4 min (major)).

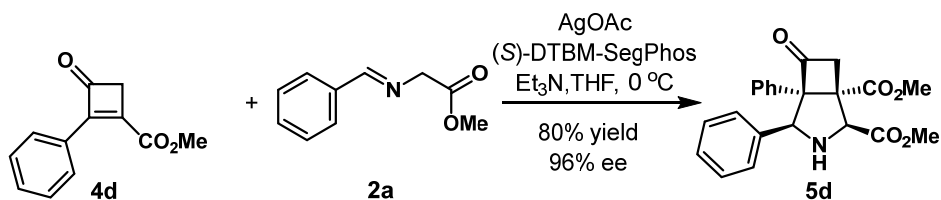
[α]_D²⁴ -21.8 (c 1.1, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.35 – 7.27 (m, 5H), 4.65 (d, *J* = 4.4 Hz, 1H), 4.11 (d, *J* = 4.1 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.64 (d, *J* = 18.7 Hz, 1H), 3.43 (dt, *J* = 11.1, 5.7 Hz, 1H), 3.34 (dt, *J* = 10.9, 6.3 Hz, 1H), 3.00 (d, *J* = 18.7 Hz, 1H), 2.61 (t, *J* = 4.5 Hz, 1H), 1.93 – 1.80 (m, 1H), 1.79 – 1.68 (m, 1H), 1.63 (td, *J* = 9.1, 4.3 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.90, 171.49, 170.16, 135.88, 128.58, 128.17, 128.01, 82.37, 69.80, 65.21, 52.86, 52.35, 50.12, 49.59, 44.84, 27.11, 26.24.

IR (neat cm⁻¹): 3340, 2878, 1779, 1741, 1719, 1626, 1437, 1323, 1212.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₉H₂₂ClNO₅, 379.1181; found, 379.1185.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-6-oxo-4,5-diphenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**5d**)

Prepared according to **General Procedure A** using **1c** (40.6 mg, 0.201 mmol), **2a** (70.9 mg, 0.400 mmol), AgOAc (4.3 mg, 25.8 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (26.6 mg, 22.6 μ mol) in THF (3.1 mL) at 0 °C for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **5d** (60.7 mg, 0.160 mmol, 80% yield). Ee: 96% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 19.4 min (minor); t₂ = 36.3 min (major)).

[α]_D²⁷ 3.3 (c 1.1, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.27 – 7.04 (m, 8H), 6.97 – 6.83 (m, 2H), 4.99 (s, 1H), 4.54 (s, 1H), 3.71 (s, 3H), 3.69 (d, *J* = 18.7 Hz, 1H), 3.34 (s, 3H), 3.03 (d, *J* = 18.7 Hz, 1H)..

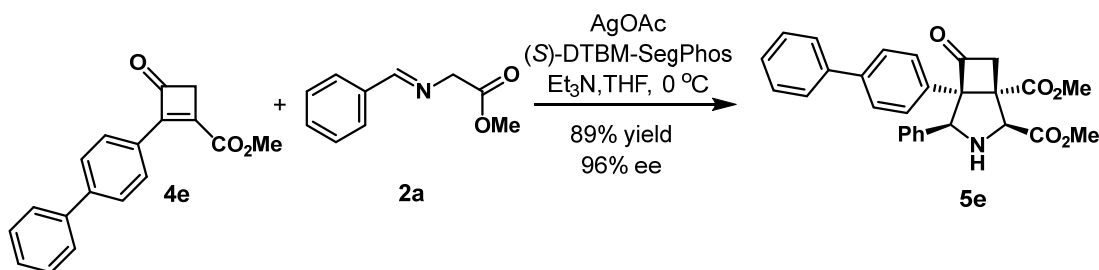
¹³C NMR (101 MHz, CDCl₃) δ (ppm): 204.47, 170.69, 170.08, 135.11, 134.29, 128.41, 128.23, 127.87, 127.84, 126.95, 126.50, 86.17, 72.96, 64.39, 53.76, 52.43, 52.21, 50.10.

IR (neat cm⁻¹): 1787, 1725, 1438, 1253, 1226.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₂H₂₁NO₅, 379.1414; found, 379.1416.

Synthesis of **5d** on a 1.4 mmol scale:

Prepared according to **General Procedure A** using **4d** (0.282 g, 2.01 mmol), **6a** (0.283 g, 1.40 mmol), AgOAc (12.5 mg, 74.9 μ mol), (*S*)-DTBM-SegPhos (92.2 mg, 78.2 μ mol) in THF (15 mL) and NEt₃ (40 μ L, 29.1 mg, 0.288 mmol) at 0 °C for 11 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 6:1) provided **3d** (0.469 g, 1.24 mmol, 89% yield). Ee: 95% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 22.1 min (minor); t₂ = 44.1 min (major)).



Dimethyl (1*S*,2*S*,4*S*,5*S*)-5-([1,1'-biphenyl]-4-yl)-6-oxo-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**5e**)

Prepared according to **General Procedure A** using **4e** (55.5 mg, 0.199 mmol), **2a** (69.6 mg, 0.393 mmol), AgOAc (3.6 mg, 21.6 μmol), NEt_3 (5.6 μL , 4.1 mg, 40.0 μmol), (*S*)-DTBM-SegPhos (27.2 mg, 23.1 μmol) in THF (3.1 mL) at 0 °C for 10 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 6:1) provided **5e** (81 mg, 0.178 mmol, 89% yield).

Ee: 96% (Chiralcel[®]IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 254 nm; t_1 = 25.4 min (minor); t_2 = 49.7 min (major)).

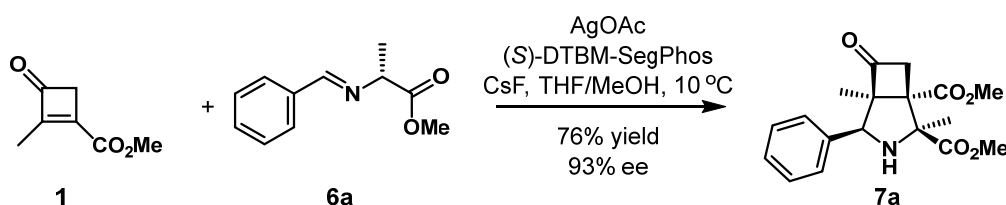
$[\alpha]_{\text{D}}^{23}$ -61.7 (c 1.0, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.63 – 7.48 (m, 4H), 7.48 – 7.38 (m, 2H), 7.38 – 7.28 (m, 3H), 7.27 – 7.09 (m, 3H), 7.05 – 6.92 (m, 2H), 5.06 (s, 1H), 4.61 (s, 1H), 3.80 (s, 3H), 3.78 (d, J = 18.7 Hz, 1H), 3.44 (s, 3H), 3.09 (d, J = 18.7 Hz, 1H), 2.77 (brs, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 204.62, 170.81, 170.28, 140.41, 140.11, 135.37, 133.32, 128.80, 128.25, 127.89, 127.52, 126.98, 126.91, 126.88, 86.08, 72.97, 64.46, 53.85, 52.45, 52.31, 50.09.

IR (neat cm^{-1}): 3350, 2959, 2870, 1736, 1627, 1497, 1437, 1375, 1333, 1200, 1171, 1051.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{28}\text{H}_{25}\text{NO}_5$, 455.1724; found, 455.1727.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-2,5-dimethyl-6-oxo-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**7a**)

General Procedure B: A suspension of AgOAc (3.3 mg, 20.0 μmol) and (*S*)-DTBM-SegPhos (27.7 mg, 23.4 μmol) in THF (1 mL) was stirred at room temperature for 10 min. The resulting mixture was cooled to 10 °C and a solution of **6a** (76.5 mg, 0.400 mmol) in THF (1 mL), a solution of CsF (12.4 mg, 81.6 μmol) in MeOH (0.3 mL), and a solution of **1** (28.3 mg, 0.202 mmol) in THF (1 mL) were sequentially added dropwise. The reaction mixture was stirred at 10 °C for 21 h before quenched with H_2O and diluted with DCM. The organic layer was separated, and the aqueous phase was extracted with DCM three times. The combined organic phase was washed with brine, dried over Na_2SO_4 , concentrated and the residue was purified by column chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 8:1) to afford the **7a** (50.8 mg, 0.153 mmol, 76% yield).

Ee: 93% (Chiralcel[®]OD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 11.9 min (minor); t_2 = 25.3 min (major)).

$[\alpha]_{\text{D}}^{27}$ -20.4 (c 1.0, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.38 – 7.28 (m, 5H), 4.29 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.54 (d, J = 18.1 Hz, 1H), 3.23 (d, J = 18.1 Hz, 1H), 2.37 (brs, 1H), 1.76 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 206.83, 173.22, 170.53, 136.57, 128.43, 128.26, 127.18, 78.47, 69.93, 68.31, 53.56, 53.22, 52.45, 52.13, 22.99, 15.32.

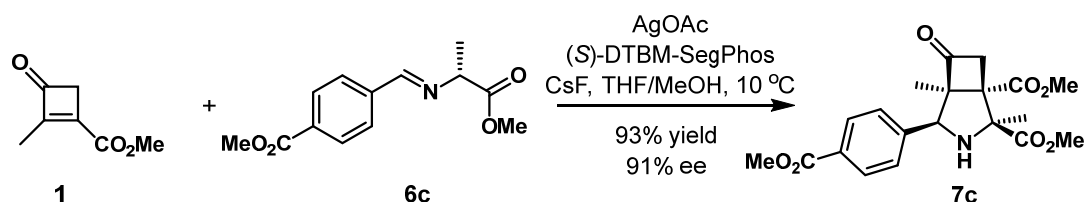
IR (neat cm^{-1}): 2959, 1792, 1743, 1717, 1494, 1451, 1288, 1200, 1153.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_5$, 331.1414; found, 331.1422.

Synthesis of **7a** on a 2 mmol scale:

Prepared according to **General Procedure B** using **1** (0.282 g, 2.01 mmol), **6a** (0.764 g, 4.00 mmol), AgOAc (16.7 mg, 0.100 mmol), CsF (0.120 mg, 0.790 mmol), (*S*)-DTBM-SegPhos (138.8 mg, 0.118 mmol) in THF (15 mL) and MeOH (1.5 mL) at 10 °C for 33 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 10:1) provided **7a** (0.519 g, 1.57 mmol, 78% yield).

Ee: 93% (Chiralcel[®]OD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 10.6 min (minor); t_2 = 21.2 min (major)).



Dimethyl (1*S*,2*S*,4*S*,5*S*)-4-(4-(methoxycarbonyl)phenyl)-2,5-dimethyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**7c**)

Prepared according to **General Procedure B** using **1** (28.3 mg, 0.202 mmol), **6c** (99.7 mg, 0.400 mmol), AgOAc (3.4 mg, 20.4 μmol), CsF (11.6 mg, 76.4 μmol), (*S*)-DTBM-SegPhos (26.6 mg, 22.6 μmol) in THF (3.0 mL) and MeOH (0.3 mL) at 10 °C for 21 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 8:1) provided **7c** (73.3 mg, 0.188 mmol, 93% yield).

Ee: 91% (Chiralcel[®]IA; 20% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 10.3 min (minor); t_2 = 15.0 min (major)).

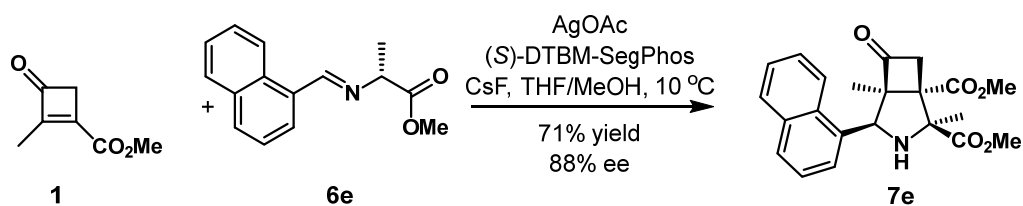
$[\alpha]_D^{31}$ 9.1 (c 1.0, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.01 - 7.88 (m, 2H), 7.43 - 7.29 (m, 2H), 4.33 (d, J = 3.8 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.55 (d, J = 18.3 Hz, 1H), 3.19 (d, J = 18.3 Hz, 1H), 2.33 (d, J = 4.4 Hz, 1H), 1.74 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 206.47, 173.11, 170.35, 166.70, 141.95, 130.16, 129.55, 127.17, 78.18, 70.04, 67.79, 53.48, 53.35, 52.49, 52.19, 52.01, 23.08, 15.22.

IR (neat cm^{-1}): 3338, 2815, 1790, 1743, 1723, 1706, 1435, 1270, 1194, 1147, 1134, 1107.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{24}\text{NO}_7$, 390.1547; found, 390.1547.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-2,5-dimethyl-4-(naphthalen-1-yl)-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (7e**)**

Prepared according to **General Procedure B** using **1** (28.7 mg, 0.205 mmol), **6e** (97.8 mg, 0.405 mmol), AgOAc (3.9 mg, 23.4 μ mol), CsF (12.6 mg, 82.9 μ mol), (*S*)-DTBM-SegPhos (27.1 mg, 23.0 μ mol) in THF (3.1 mL) and MeOH (0.3 mL) at 10 °C for 21 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 8:1) provided **7e** (55.4 mg, 0.145 mmol, 71% yield).

Ee: 88% (Chiralcel[®]IA; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 254 nm; t₁ = 10.5 min (minor); t₂ = 12.6 min (major)).

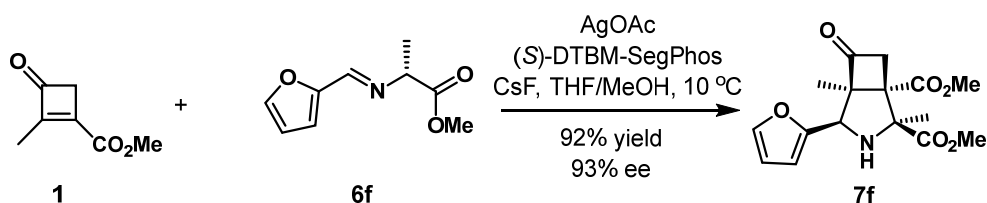
[α]_D²⁵ 23.1 (c 1.2, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.18 – 8.06 (m, 1H), 7.92 – 7.83 (m, 1H), 7.83 – 7.72 (m, 2H), 7.54 – 7.37 (m, 3H), 5.35 (d, *J* = 4.4 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.63 (d, *J* = 18.2 Hz, 1H), 3.31 (d, *J* = 18.2 Hz, 1H), 2.35 (d, *J* = 4.5 Hz, 1H), 1.88 (s, 3H), 1.30 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 207.00, 173.34, 170.47, 133.87, 132.43, 131.84, 129.18, 128.67, 125.89, 125.49, 125.28, 125.22, 122.53, 79.42, 70.02, 61.83, 53.95, 53.33, 52.44, 52.13, 23.18, 16.03.

IR (neat cm⁻¹): 1781, 1732, 1595, 1297, 1146, 1116, 1106, 1017.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₂H₂₃NO₅, 381.1571; found, 381.1568.



Dimethyl (1*S*,2*S*,4*R*,5*S*)-4-(furan-2-yl)-2,5-dimethyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (7f**)**

Prepared according to **General Procedure B** using **1** (28.6 mg, 0.204 mmol), **6f** (73.7 mg, 0.407 mmol), AgOAc (3.8 mg, 22.8 μ mol), CsF (12.5 mg, 82.3 μ mol), (*S*)-DTBM-SegPhos (26.5 mg, 22.5 μ mol) in THF (3.0 mL) and MeOH (0.3 mL) at 10 °C for 21 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 8:1) provided **7f** (60.0 mg, 0.187 mmol, 92% yield).

Ee: 93% (Chiralcel[®]OD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 10.1 min (minor); t₂ = 12.5

min (major)).

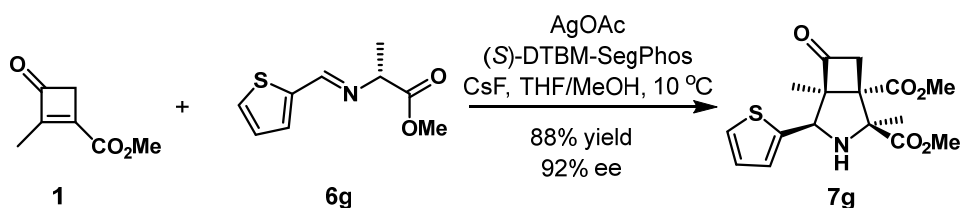
$[\alpha]_D^{23}$ -38.3 (c 1.0, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.43 – 7.29 (m, 1H), 6.34 – 6.24 (m, 2H), 4.32 (d, $J = 7.9$ Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.46 (d, $J = 18.3$ Hz, 1H), 3.20 (d, $J = 18.3$ Hz, 1H), 3.04 (d, $J = 8.2$ Hz, 1H), 1.66 (s, 3H), 1.29 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm): 205.56, 172.61, 170.29, 149.85, 142.61, 110.29, 107.62, 78.69, 70.48, 63.48, 55.02, 52.63, 52.24, 52.20, 22.39, 15.84.

IR (neat cm^{-1}): 2958, 2917, 2849, 1784, 1728, 1540, 1506, 1437, 1281, 1150, 1174, 1013.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{16}\text{H}_{20}\text{NO}_6$, 322.1285; found, 322.1285.



Dimethyl (1*S*,2*S*,4*R*,5*S*)-2,5-dimethyl-6-oxo-4-(thiophen-2-yl)-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**7g**)

Prepared according to **General Procedure B** using **1** (28.0 mg, 0.200 mmol), **6g** (79.4 mg, 0.403 mmol), AgOAc (3.6 mg, 21.6 μmol), CsF (12.0 mg, 79.0 μmol), (*S*)-DTBM-SegPhos (26.1 mg, 22.1 μmol) in THF (3.0 mL) and MeOH (0.3 mL) at 10 °C for 21 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 8:1) provided **7g** (59.1 mg, 0.175 mmol, 88% yield).

Ee: 92% (Chiralcel[®] AD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 10.2 min (minor); t_2 = 11.7 min (major)).

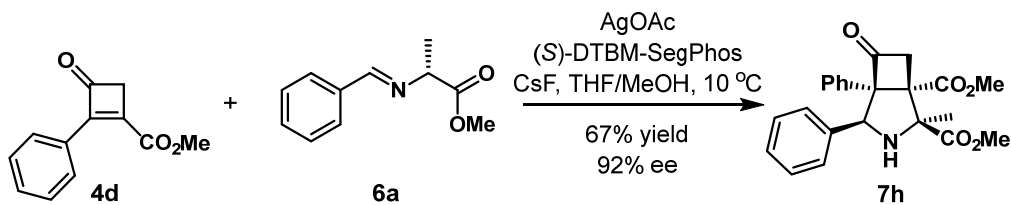
$[\alpha]_D^{22}$ -29.0 (c 1.3, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.24 – 7.16 (m, 1H), 7.09 – 6.91 (m, 2H), 4.59 (d, $J = 4.2$ Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.51 (d, $J = 18.1$ Hz, 1H), 3.25 (d, $J = 18.1$ Hz, 1H), 2.59 (d, $J = 4.8$ Hz, 1H), 1.73 (s, 3H), 1.29 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm): 205.95, 172.77, 170.30, 140.75, 126.87, 124.78, 124.42, 78.26, 69.93, 64.25, 53.98, 53.46, 52.49, 52.15, 23.02, 15.55.

IR (neat cm^{-1}): 3326, 1783, 1735, 1437, 1310, 1289, 1261, 1140, 1098, 1018.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{16}\text{H}_{20}\text{SNO}_5$, 338.1057; found, 338.1057.



Dimethyl (1*S*,2*S*,4*S*,5*S*)-2-methyl-6-oxo-4,5-diphenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**7h**)

Prepared according to **General Procedure B** using **4d** (40.9 mg, 0.202 mmol), **6a** (78.3 mg, 0.409 mmol), AgOAc (3.9 mg, 23.4 μmol), CsF (11.6 mg, 76.3 μmol), (*S*)-DTBM-SegPhos (28.0 mg, 23.7 μmol) in THF (3.0 mL) and MeOH (0.3 mL) at 10 °C for 21 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:acetone = 20:1) provided **7h** (53.6 mg, 0.136 mmol, 67% yield).

Ee: 92% (Chiralcel[®]OD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 7.5 min (minor); t_2 = 17.8 min (major)).

$[\alpha]_D^{21}$ -44.6 (c 0.9, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.35 – 7.17 (m, 8H), 7.06 – 6.90 (m, 2H), 4.71 (d, J = 4.1 Hz, 1H), 3.82 (s, 3H), 3.67 (d, J = 18.2 Hz, 1H), 3.31 (s, 3H), 3.21 (d, J = 18.3 Hz, 1H), 2.36 (d, J = 4.1 Hz, 1H), 2.13 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm): 204.45, 173.51, 170.53, 135.89, 135.33, 128.37, 128.31, 127.92, 127.52, 127.14, 126.40, 85.60, 70.00, 69.58, 55.44, 54.48, 52.55, 51.65, 23.50.

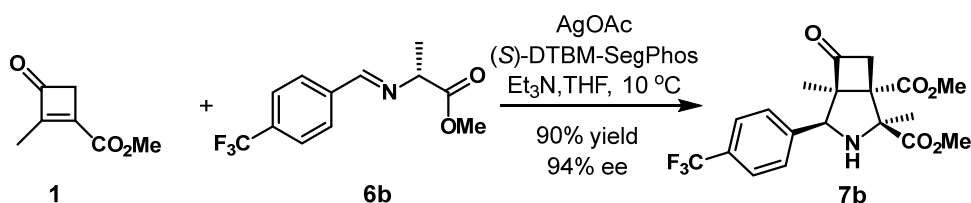
IR (neat cm^{-1}): 3339, 1783, 1735, 1497, 1447, 1435, 1373, 1274, 1124, 1106, 1073.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{23}\text{H}_{24}\text{NO}_5$, 394.1649; found, 394.1645.

Synthesis of **7h** on a 1 mmol scale:

Prepared according to **General Procedure B** using **4d** (0.204 g, 1.01 mmol), **6a** (0.382 g, 2.00 mmol), AgOAc (16.9 mg, 0.101 mmol), CsF (60.9 mg, 0.401 mmol), (*S*)-DTBM-SegPhos (0.131 g, 0.111 mmol) in THF (15 mL) and MeOH (1.5 mL) at 10 °C for 22 h; flash chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:acetone = 20:1) provided **7h** (0.288 g, 0.732 mmol, 72% yield).

Ee: 94% (Chiralcel[®]OD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 7.5 min (minor); t_2 = 17.8 min (major)).



Dimethyl (1*S*,2*S*,4*S*,5*S*)-2,5-dimethyl-6-oxo-4-(4-(trifluoromethyl)phenyl)-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (7b)

Prepared according to **General Procedure A** using **1** (27.8 mg, 0.198 mmol), **6b** (104.3 mg, 0.403 mmol), AgOAc (3.6 mg, 21.6 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (26.2 mg, 22.2 μ mol) in THF (3.1 mL) at 10 °C for 22 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:A = 8:1) provided **7b** (71.5 mg, 0.179 mmol, 90% yield).

Ee: 94% (Chiralcel[®]IA; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 8.1 min (minor); t₂ = 9.3 min (major)).

[α]_D²² -10.8 (c 1.1, CHCl₃).

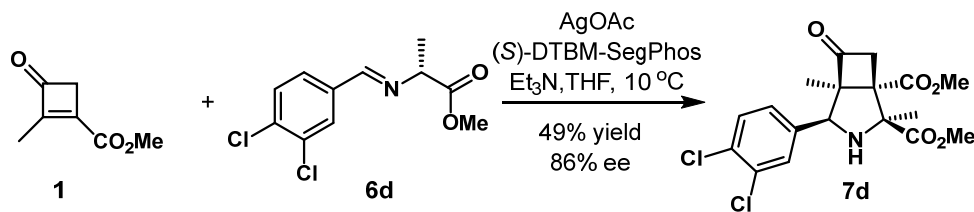
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.56 (d, *J* = 8.1 Hz, 4H), 7.43 (d, *J* = 8.1 Hz, 4H), 4.34 (d, *J* = 3.9 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.57 (d, *J* = 18.3 Hz, 1H), 3.20 (d, *J* = 18.3 Hz, 1H), 2.30 (d, *J* = 4.3 Hz, 1H), 1.76 (s, 3H), 1.24 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.52, 173.08, 170.31, 140.90, 130.51 (q, *J* = 32.5 Hz), 127.60, 125.23 (q, *J* = 3.8 Hz), 124.00 (q, *J* = 273.2), 78.06, 70.04, 67.66, 53.46, 53.38, 52.50, 52.22, 23.11, 15.18.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.54.

IR (neat cm⁻¹): 2976, 2879, 1773, 1748, 1626, 1438, 1323, 1202, 1160, 1142, 1131, 1109, 1162.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₁₉H₂₁F₃NO₅, 400.1366; found, 400.1364.

**Dimethyl (1*S*,2*S*,4*S*,5*S*)-4-(3,4-dichlorophenyl)-2,5-dimethyl-6-oxo-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (7d)**

Prepared according to **General Procedure A** using **1** (28.1 mg, 0.201 mmol), **6d** (104.2 mg, 0.401 mmol), AgOAc (3.4 mg, 20.4 μ mol), NEt₃ (5.6 μ L, 4.1 mg, 40.0 μ mol), (*S*)-DTBM-SegPhos (28.1 mg, 23.8 μ mol) in THF (3.1 mL) at 10 °C for 21 h; flash chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 8:1) provided **7d** (39.0 mg, 97.4 μ mol, 49% yield).

Ee: 86% (Chiralcel[®]IA; 5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t₁ = 13.0 min (minor); t₂ = 14.5 min (major)).

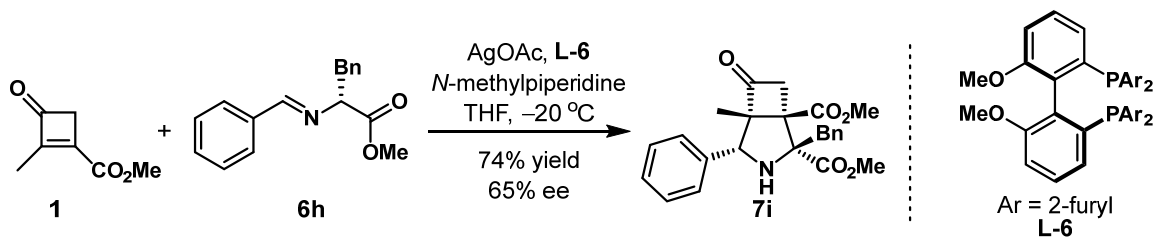
[α]_D²⁵ 7.8 (c 1.2, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.44 – 7.32 (m, 2H), 7.20 – 7.08 (m, 1H), 4.23 (d, *J* = 3.4 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.57 (d, *J* = 18.3 Hz, 1H), 3.18 (d, *J* = 18.3 Hz, 1H), 2.24 (d, *J* = 4.1 Hz, 1H), 1.74 (s, 3H), 1.22 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.48, 173.01, 170.24, 137.20, 132.48, 132.31, 130.25, 129.09, 126.49, 77.82, 69.95, 66.96, 53.44, 53.33, 52.51, 52.24, 23.15, 15.16.

IR (neat cm⁻¹): 2988, 2879, 1778, 1737, 1619, 1437, 1373, 1332, 1297, 1198, 1159, 1144, 1029.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{18}H_{20}Cl_2NO_5$, 400.0713; found, 400.0709.



Dimethyl (1*R*,2*R*,4*R*,5*R*)-2-benzyl-5-methyl-6-oxo-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (**7i**)

Procedure C: A suspension of AgOAc (3.8 mg, 22.8 μmol) and L-6 (13.0 mg, 24.0 μmol) in THF (1.6 mL) was cooled to $-20\text{ }^\circ\text{C}$, and a solution of **6h** (106.3 mg, 0.398 mmol) in THF (1 mL), a solution of *N*-methylpiperidine (24 μL , 19.6 mg, 0.198 mmol) in THF (0.4 mL), and a solution of **1** (27.8 mg, 0.198 mmol) in THF (1 mL) were sequentially added dropwise. The reaction mixture was stirred at $-20\text{ }^\circ\text{C}$ for 33 h before quenched with H₂O and diluted with DCM. The organic layer was separated, and the aqueous phase was extracted with DCM three times. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated and the residue was purified by column chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:EA = 10:1) to afford product **7i** (59.9 mg, 0.147 mmol, 74% yield).

Ee: 65% (Chiralcel[®] AD-H; 5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; t_1 = 11.8 min (major); t_2 = 41.3 min (minor)).

$[\alpha]_D^{25}$ 63.5 (c 1.1, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.40 – 7.29 (m, 5H), 7.29 – 7.16 (m, 3H), 7.06 – 6.97 (m, 2H), 4.43 (d, J = 3.2 Hz, 1H), 3.87 (s, 3H), 3.73 (s, 3H), 3.59 (d, J = 18.2 Hz, 1H), 3.51 – 3.37 (m, 2H), 3.21 (d, J = 18.2 Hz, 1H), 2.49 (d, J = 3.6 Hz, 1H), 1.31 (s, 3H).

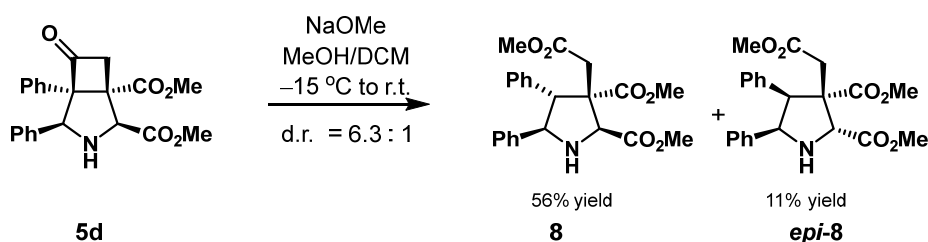
¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.81, 171.99, 170.22, 136.60, 135.82, 129.45, 128.84, 128.56, 128.30, 127.30, 127.29, 78.21, 74.17, 68.44, 54.15, 53.02, 52.40, 52.15, 38.68, 15.17.

IR (neat cm⁻¹): 1780, 1736, 1496, 1448, 1372, 1321, 1278, 1262, 1201, 1091, 1062, 1046, 1031.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{24}H_{26}NO_5$, 408.1805; found, 408.1802.

1.5 Further Transformations of Cycloadducts

Dimethyl (2*S*,3*S*,4*R*,5*R*)-3-(2-methoxy-2-oxoethyl)-4,5-diphenylpyrrolidine-2,3-dicarboxylate (**8**) and dimethyl (2*R*,3*S*,4*S*,5*R*)-3-(2-methoxy-2-oxoethyl)-4,5-diphenylpyrrolidine-2,3-dicarboxylate (*epi*-**8**)



A solution of NaOMe (65.2 mg, 1.21 mmol) in MeOH (2 mL) was added dropwise to a solution of compound **5d** (0.295g, 0.777 mmol) in MeOH (2 mL) and DCM (2 mL) at $-15\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-15\text{ }^{\circ}\text{C}$ for 1 h, then stirred at room temperature for another 16 h before quenched with an aqueous solution of HCl (2M). The organic solvent was removed, and the resulting mixture was neutralized with an aqueous solution of NaHCO_3 and diluted with DCM. The organic layer was separated, and the aqueous phase was extracted with DCM three times. The combined organic phase was washed with brine, dried over Na_2SO_4 , concentrated and the residue was purified by column chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:Et₂O = 3:1) to afford product **8** (0.178 g, 0.432 mmol, 56% yield) and *epi*-**8** (34.6 mg, 84.1 μmol , 11% yield). ¹H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 6.3:1.

8:

Ee: 97% (Chiralcel[®]AD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; $t_1 = 26.7$ min (minor); $t_2 = 29.7$ min (major)).

$[\alpha]_{\text{D}}^{33} -34.9$ (c 1.0, CHCl_3).

¹H NMR (400 MHz, CDCl_3) δ (ppm): 7.43 – 7.36 (m, 2H), 7.29 – 7.10 (m, 6H), 7.10 – 7.00 (m, 2H), 5.07 – 4.55 (m, 2H), 3.74 (s, 3H), 3.63 (s, 3H), 3.48 – 3.35 (m, 4H), 3.03 (d, $J = 17.8$ Hz, 1H), 2.70 (d, $J = 17.8$ Hz, 1H).

¹³C NMR (101 MHz, CDCl_3) δ (ppm): 173.97, 172.59, 171.51, 141.74, 134.98, 128.92, 128.26, 128.18, 127.74, 127.24, 64.67, 64.59, 61.42, 59.25, 51.94, 51.79, 51.68, 37.65.

IR (neat cm^{-1}): 3030, 2948, 1736, 1603, 1492, 1436, 1362, 1214, 1201, 1174.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{23}\text{H}_{25}\text{NO}_6$, 411.1676; found, 411.1675.

epi-**8:**

Ee: 96% (Chiralcel[®]AD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 210 nm; $t_1 = 16.2$ min (minor); $t_2 = 19.2$ min (major)).

$[\alpha]_{\text{D}}^{26} -123.4$ (c 1.2, CHCl_3).

¹H NMR (400 MHz, CDCl_3) δ (ppm): 7.36 – 7.19 (m, 2H), 7.14 – 6.78 (m, 8H), 5.64 (d, $J = 6.7$ Hz, 1H), 4.50 (d, $J = 6.7$ Hz, 1H),

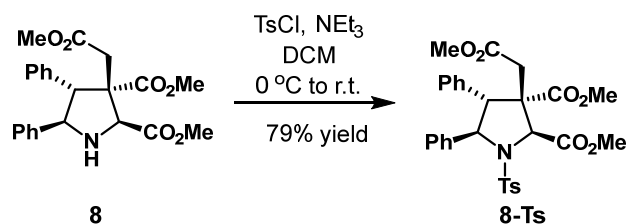
4.07 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.52 (s, 3H), 3.08 (d, $J = 17.6$ Hz, 1H), 2.91 (brs, 1H), 2.00 (d, $J = 17.5$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 173.26, 173.21, 171.42, 141.91, 136.91, 130.39, 127.82, 127.45, 126.87, 126.70, 125.59, 67.23, 63.79, 60.17, 56.03, 52.70, 52.47, 51.49, 38.14.

IR (neat cm^{-1}): 3341, 3029, 2900, 2876, 1743, 1604, 1494, 1436, 1357, 1213, 1174.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{23}\text{H}_{25}\text{NO}_6$, 411.1676; found, 411.1678.

Dimethyl (2S,3S,4R,5R)-3-(2-methoxy-2-oxoethyl)-4,5-diphenyl-1-tosylpyrrolidine-2,3-dicarboxylate (8-Ts):



A solution of **8** (34.0 mg, 82.6 μmol) in DCM (0.7 mL) was added sequentially a solution of *p*-touenesulfonyl chloride (18.3 mg, 96.0 μmol) in DCM (0.3 mL) and NEt_3 at 0 $^\circ\text{C}$. The reaction mixture was warmed to room temperature and stirred for 3 h before it was quenched with water. The mixture was extracted with DCM, washed with brine, dried over Na_2SO_4 , concentrated, and the residue was purified by column chromatography on silica gel (PE:EA = 4:1) to afford product **8-Ts** (36.9 mg, 65.2 μmol , 79% yield). $[\alpha]_{\text{D}}^{22} -45.1$ (c 0.8, CHCl_3).

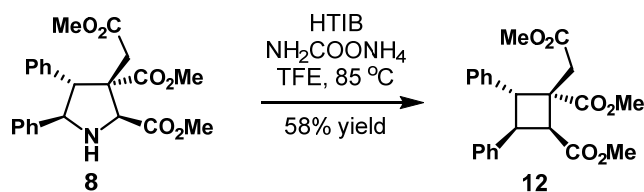
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.34 – 7.24 (m, 4H), 7.23 – 7.14 (m, 3H), 7.09 – 6.90 (m, 7H), 5.56 (s, 1H), 5.15 (d, $J = 11.0$ Hz, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 3.59 (d, $J = 11.0$ Hz, 1H), 3.55 (s, 3H), 3.02 (d, $J = 17.9$ Hz, 1H), 2.42 (d, $J = 17.9$ Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 171.85, 170.59, 170.49, 142.76, 137.96, 137.12, 132.24, 128.81, 128.44, 128.36, 128.20, 127.91, 127.54, 127.46, 66.33, 65.59, 61.77, 55.81, 52.36, 52.16, 51.93, 37.48, 21.42.

IR (neat cm^{-1}): 1736, 1599, 1436, 1345, 1223, 1201, 1179, 1162, 1104.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{30}\text{H}_{32}\text{NO}_8\text{S}$, 566.1843; found, 566.1838.

Dimethyl (1S,2S,3S,4R)-1-(2-methoxy-2-oxoethyl)-3,4-diphenylcyclobutane-1,2-dicarboxylate (12)



A solution of phenyliodosohydroxy tosylate (101.1 mg, 0.258 mmol), ammonium carbamate (62.5 mg, 0.801 mmol), and **8** (40.8 mg, 99.2 μmol) in TFE (1 mL) was heated at 85 $^\circ\text{C}$ for 3 h. Then TFE was removed, and H_2O (5 mL) and DCM were added to the

residue. The organic layer was separated, and the aqueous phase was extracted with DCM three times. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 8:1) to afford product **12** (22.6 mg, 57.1 μmol, 58% yield).

Ee: 96% (Chiralcel® AD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min, detection at 230 nm; t₁ = 11.2 min (minor); t₂ = 14.3 min (major)).

[α]_D²¹ -5.6 (c 1.1, CHCl₃).

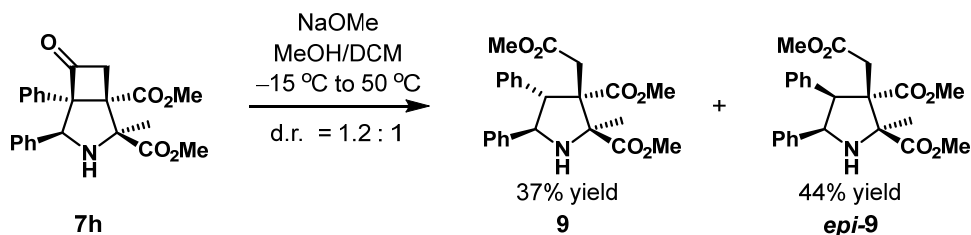
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.34 – 7.21 (m, 5H), 7.21 – 7.10 (m, 5H), 4.72 (dd, *J* = 11.7, 9.9 Hz, 1H), 4.35 (s, 1H), 4.34 – 4.29 (m, 1H), 3.61 (s, 3H), 3.67 – 3.54 (m, 1H), 3.34 (s, 3H), 3.32 (s, 3H), 3.33 – 3.24 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 172.41, 172.00, 171.80, 138.84, 137.46, 128.40, 128.17, 127.48, 127.08, 126.81, 126.67, 51.97, 51.64, 51.57, 51.24, 50.66, 47.47, 41.36, 37.30.

IR (neat cm⁻¹): 3030, 2998, 1731, 1604, 1497, 1435, 1358, 1205, 1166.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₂₃H₂₅O₆, 397.1646; found, 397.1646.

Dimethyl (2*S*,3*S*,4*R*,5*R*)-3-(2-methoxy-2-oxoethyl)-2-methyl-4,5-diphenylpyrrolidine-2,3-dicarboxylate (9) and dimethyl (2*S*,3*S*,4*S*,5*R*)-3-(2-methoxy-2-oxoethyl)-2-methyl-4,5-diphenylpyrrolidine-2,3-dicarboxylate (*epi*-9)



A solution of NaOMe (0.114 g, 2.11 mmol) in MeOH (8 mL) was added dropwise to a solution of compound **7h** (0.266g, 0.676 mmol) in DCM (4 mL) at -15 °C. The reaction mixture was warmed to 50 °C stirred for 24 h before quenched with an aqueous solution of HCl (1M) and neutralized with a saturated aqueous solution of NaHCO₃. The organic solvent was removed, and the resulting mixture was extracted with DCM, washed with brine, dried over Na₂SO₄, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 6:1) to afford product **9** (0.105 g, 0.247 mmol, 37% yield) and *epi*-**9** (0.127 g, 0.298 mmol, 44% yield). ¹H NMR analysis of the crude reaction mixture revealed a diastereomer ratio of 1:1.2.

9:

[α]_D²⁴ -30.9 (c 1.1, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.59 – 7.37 (m, 2H), 7.28 – 7.07 (m, 8H), 5.13 (d, *J* = 11.1 Hz, 1H), 3.77 (s, 3H), 3.64 (d, *J* = 11.1 Hz, 1H), 3.61 (s, 3H), 3.53 (s, 3H), 2.97 (d, *J* = 17.9 Hz, 1H), 2.91 – 2.68 (brs, 1H), 2.42 (d, *J* = 17.9 Hz, 1H), 1.82 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 175.99, 170.76, 170.54, 142.53, 134.87, 129.17, 128.34, 128.10, 127.88, 127.42, 126.96, 71.54, 63.71, 62.27, 61.50, 52.20, 51.44, 51.38, 38.27, 21.91.

IR (neat cm^{-1}): 3375, 1724, 1602, 1495, 1454, 1435, 1364, 1214, 1174, 1124, 1052.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{28}\text{NO}_6$, 426.1911; found, 426.1907.

epi-9:

$[\alpha]_{\text{D}}^{24}$ -70.6 (c 1.0, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.24 – 7.11 (m, 4H), 7.09 – 7.03 (m, 2H), 7.03 – 6.88 (m, 4H), 5.08 (d, $J = 6.3$ Hz, 1H), 4.51 (d, $J = 6.3$ Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.21 (s, 3H), 3.17 (d, $J = 16.9$ Hz, 2H), 2.29 (d, $J = 16.8$ Hz, 1H), 1.59 (s, 3H).

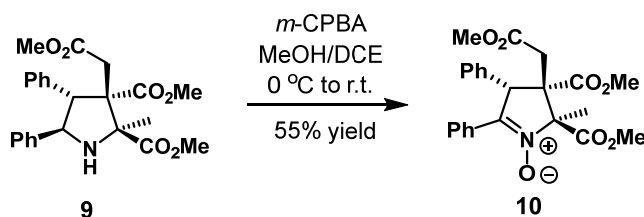
^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 174.31, 174.23, 171.53, 138.84, 136.70, 127.57, 127.31, 126.74, 126.46, 126.12, 70.04, 64.30, 62.95, 58.26, 52.70, 52.31, 51.35, 38.28, 23.76.

IR (neat cm^{-1}): 3333, 1733, 1497, 1455, 1435, 1356, 1267, 1221, 1197, 1175, 1124, 1061.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{28}\text{NO}_6$, 426.1911; found, 426.1910.

(2*S*,3*S*,4*R*)-3-(2-methoxy-2-oxoethyl)-2,3-bis(methoxycarbonyl)-2-methyl-4,5-diphenyl-3,4-dihydro-2*H*-pyrrole 1-oxide

(10)



A solution of **9** (15.1 mg, 35.5 μmol) in DCE (0.5 mL) was added a solution of *m*-CPBA (85%, 22.4 mg, 0.110 mmol) in DCE (0.7 mL) at 0 $^{\circ}\text{C}$. Then the reaction mixture was warmed to room temperature and stirred for 23 h before quenched with a cold 5% aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$. The resulting mixture was extracted with DCM, and the combined organic phase was washed with a cold 5% aqueous solution of K_2CO_3 , brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (PE:acetone = 4:1) to afford product **10** (8.6 mg, 19.6 μmol , 55% yield).

$[\alpha]_{\text{D}}^{25}$ 158.8 (c 0.3, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.02 – 7.78 (m, 2H), 7.39 – 7.13 (m, 6H), 7.07 – 6.90 (m, 2H), 4.82 (s, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.46 (d, $J = 17.7$ Hz, 1H), 3.29 (s, 3H), 2.66 (d, $J = 17.7$ Hz, 1H), 2.15 (s, 3H).

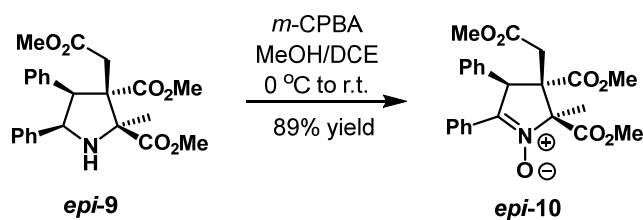
^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 169.82, 169.61, 168.17, 141.29, 134.45, 129.84, 129.62, 128.50, 128.48, 128.30, 128.15, 127.88, 84.71, 57.67, 56.02, 53.49, 51.89, 51.87, 38.03, 17.67.

IR (neat cm^{-1}): 1736, 1578, 1553, 1495, 1436, 1363, 1261, 1211, 1178, 1141, 1051.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{24}\text{H}_{25}\text{NO}_7$, 439.1626; found, 439.1625.

(2*S*,3*S*,4*S*)-3-(2-methoxy-2-oxoethyl)-2,3-bis(methoxycarbonyl)-2-methyl-4,5-diphenyl-3,4-dihydro-2*H*-pyrrole 1-oxide

(*epi*-10)



A solution of *epi*-9 (18.2 mg, 42.8 μ mol) in DCE (0.7 mL) was added a solution of *m*-CPBA (85%, 27.7 mg, 0.136 mmol) in DCE (0.8 mL) at 0 °C. Then the reaction mixture was warmed to room temperature and stirred for 12 h before it was quenched with a cold 5% aqueous solution of Na₂S₂O₃. The resulting mixture was extracted with DCM, and the combined organic phase was washed with a cold 5% aqueous solution of K₂CO₃, brine, dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel (PE:Acetone = 4:1) to afford product *epi*-10 (16.8 mg, 38.2 μ mol, 89% yield).

$[\alpha]_D^{25}$ -226.9 (c 0.7, CHCl₃).

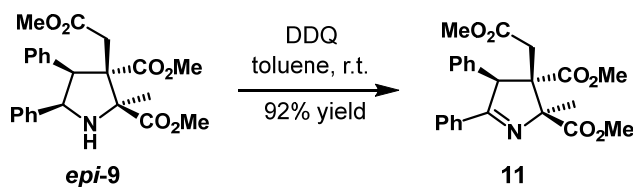
¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.43 – 8.07 (m, 2H), 7.37 – 7.27 (m, 5H), 7.24 – 7.14 (m, 3H), 5.62 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.45 (s, 3H), 3.11 (d, *J* = 17.3 Hz, 1H), 2.00 (d, *J* = 17.3 Hz, 1H), 1.80 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 171.99, 171.00, 169.07, 143.76, 136.05, 131.09, 130.40, 128.63, 128.32, 128.17, 128.04, 84.46, 53.84, 53.09, 52.91, 52.79, 51.84, 36.55, 20.26.

IR (neat cm⁻¹): 1737, 1556, 1438, 1363, 1287, 1252, 1216, 1050.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₄H₂₅NO₇, 439.1626; found, 439.1627.

Dimethyl (2*S*,3*S*,4*S*)-3-(2-methoxy-2-oxoethyl)-2-methyl-4,5-diphenyl-3,4-dihydro-2*H*-pyrrole-2,3-dicarboxylate (**11**)



A solution of *epi*-9 (42.9 mg, 0.101 mmol) in toluene (3 mL) was added DDQ (45.5 mg, 0.200 mmol) at room temperature. The reaction mixture was stirred at room temperature for another 9 h before quenched with a saturated aqueous solution of NaHCO₃. The resulting mixture was extracted with DCM, washed with brine, dried over Na₂SO₄, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 6:1) to afford product **11** (39.3 mg, 92.8 μ mol, 92% yield).

$[\alpha]_D^{26}$ -259.7 (c 0.5, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.72 – 7.62 (m, 2H), 7.29 – 7.05 (m, 8H), 5.59 (s, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.29 (s, 3H), 3.06 (d, *J* = 17.4 Hz, 1H), 1.96 (d, *J* = 17.4 Hz, 1H), 1.56 (s, 3H).

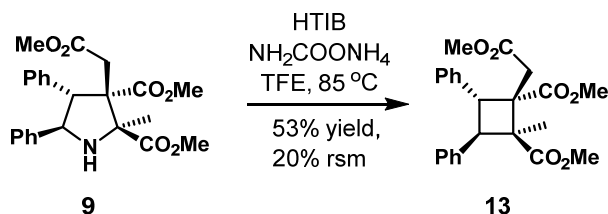
¹³C NMR (101 MHz, CDCl₃) δ (ppm): 174.25, 173.38, 172.65, 171.49, 135.67, 132.98, 130.56, 128.89, 128.23, 128.21, 127.51,

82.94, 60.75, 60.11, 52.35, 52.33, 51.52, 36.67, 23.16.

IR (neat cm^{-1}): 1735, 1632, 1578, 1496, 1447, 1435, 1359, 1286, 1202, 1178, 1119, 1054.

HRMS-EI (m/z): $[M]^+$ calcd. for $\text{C}_{24}\text{H}_{25}\text{NO}_6$, 423.1676; found, 423.1675.

Dimethyl (1*S*,2*S*,3*R*,4*R*)-1-(2-methoxy-2-oxoethyl)-2-methyl-3,4-diphenylcyclobutane-1,2-dicarboxylate (13**)**



A solution of phenyliodosohydroxy tosylate (95.9 mg, 0.245 mmol), ammonium carbamate (60.6 mg, 0.776 mmol), and **9** (36.8 mg, 86.5 μmol) in TFE (1 mL) was stirred at 85 °C for 7 h before quenched with water. The resulting mixture was extracted with DCM, washed with brine, dried over Na_2SO_4 , concentrated and the residue was purified by column chromatography on silica gel (PE:Acetone = 10:1) to afford product **13** (18.7 mg, 45.6 μmol , 53% yield) and recovered starting material **9** (7.5 mg, 17.6 μmol , 20% yield)

$[\alpha]_{\text{D}}^{23}$ 15.7 (c 0.8, CHCl_3).

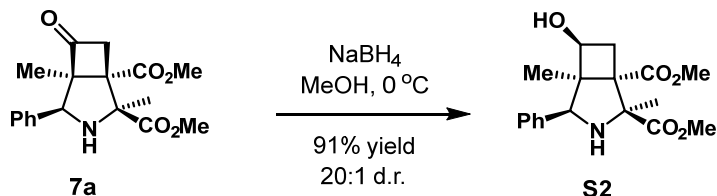
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.29 – 7.22 (m, 4H), 7.21 – 7.13 (m, 4H), 7.12 – 7.05 (m, 2H), 4.49 (s, 2H), 3.64 (s, 3H), 3.55 (d, $J = 16.9$ Hz, 1H), 3.36 (s, 3H), 3.29 (s, 3H), 3.25 (d, $J = 16.9$ Hz, 1H), 1.78 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 172.95, 171.97, 171.94, 139.08, 138.94, 128.13, 128.12, 126.74, 126.70, 126.59, 56.61, 55.20, 51.53, 51.51, 51.48, 49.80, 47.60, 39.15, 20.67.

IR (neat cm^{-1}): 1728, 1604, 1497, 1448, 1434, 1356, 1252, 1201, 1170, 1155, 1126, 1053.

HRMS-EI (m/z): $[M]^+$ calcd. for $\text{C}_{24}\text{H}_{26}\text{O}_6$, 410.1724; found, 410.1725.

Dimethyl (1*S*,2*S*,4*S*,5*S*,6*S*)-6-hydroxy-2,5-dimethyl-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (S2**)**



A solution of sodium borohydride (0.113 g, 2.98 mmol) in MeOH (15 mL) was cooled to 0 °C, then a solution of **7a** (0.483 g, 1.46 mmol) in MeOH (35 mL) was added. The reaction mixture was stirred at 0 °C for 45 min before quenched with a saturated aqueous solution of NH_4Cl . The mixture was concentrated, then extracted with DCM. The combined organic phase was washed with brine, dried over Na_2SO_4 , concentrated and the residue was purified by column chromatography on silica gel (pre-neutralized with 1% NEt_3 in PE, PE:EA = 2:1) to afford product **S2** (0.442 g, 1.33 mmol, 91% yield). ^1H NMR analysis of the crude reaction mixture

revealed a diastereomer ratio of 20:1.

$[\alpha]_D^{23}$ -1.8 (c 1.2, CHCl₃).

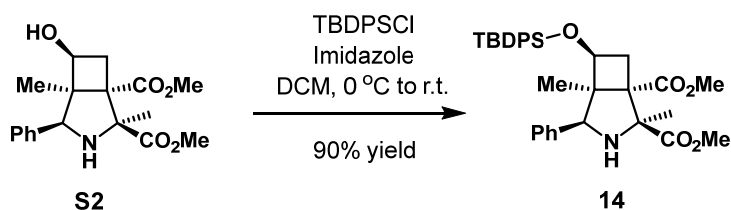
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.61 – 7.52 (m, 2H), 7.40 – 7.32 (m, 2H), 7.31 – 7.21 (m, 1H), 4.41 (s, 1H), 3.85 (ddd, J = 10.3, 9.0, 6.6 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.91 (dd, J = 13.2, 9.0 Hz, 1H), 2.49 (d, J = 10.7 Hz, 1H), 2.48 (brs, 1H), 1.97 (dd, J = 13.2, 6.6 Hz, 1H), 1.61 (s, 3H), 1.41 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 173.85, 171.80, 138.32, 128.61, 127.59, 126.79, 72.27, 69.05, 66.54, 58.00, 55.79, 52.29, 51.71, 36.97, 23.55, 22.67.

IR (neat cm⁻¹): 1724, 1449, 1436, 1281, 1196, 1157, 1137.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for C₁₈H₂₄NO₅, 334.1649; found, 334.1649.

Dimethyl (1*S*,2*S*,4*S*,5*S*,6*S*)-6-((*tert*-butyldiphenylsilyl)oxy)-2,5-dimethyl-4-phenyl-3-azabicyclo[3.2.0]heptane-1,2-dicarboxylate (14**)**



A solution of **S2** (0.182 g, 0.547 mmol) and imidazole (83.2 mg, 1.22 mmol) in DCM (6 mL) was added TBDPSCI (0.301g, 0.28 mL, 1.09 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 10 min then stirred at rt for another 6 h. The reaction mixture was quenched with water and extracted with DCM. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated and the residue was purified by column chromatography on silica gel (pre-neutralized with 1% NEt₃ in PE, PE:Acetone = 8:1) to afford product **14** (0.280 g, 0.490 mmol, 90% yield).

$[\alpha]_D^{22}$ -10.3 (c 1.0, CHCl₃).

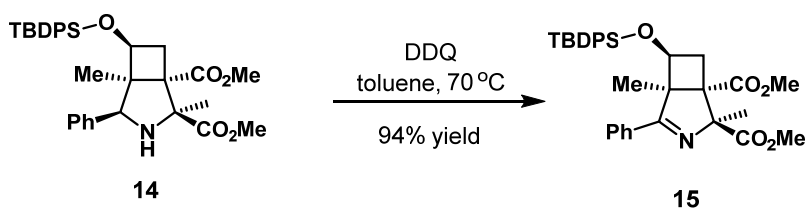
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.56 – 7.49 (m, 2H), 7.41 – 7.32 (m, 2H), 7.32 – 7.19 (m, 8H), 7.17 – 7.06 (m, 3H), 4.30 (s, 1H), 3.90 (dd, J = 8.9, 7.1 Hz, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.32 (brs, 1H), 2.46 (dd, J = 12.8, 9.0 Hz, 1H), 2.02 (dd, J = 11.8, 6.0 Hz, 1H), 1.56 (s, 3H), 1.26 (s, 3H), 0.83 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 173.85, 171.98, 138.26, 135.72, 135.51, 133.54, 133.37, 129.57, 129.28, 128.00, 127.71, 127.40, 127.23, 126.66, 72.75, 69.61, 67.62, 60.22, 56.84, 52.29, 51.49, 36.29, 26.93, 23.92, 23.02, 18.67.

IR (neat cm⁻¹): 1730, 1589, 1451, 1428, 1268, 1139, 1113.

HRMS-EI (m/z): $[M]^+$ calcd. for C₃₄H₄₁NO₅Si, 571.2749; found, 571.2746.

Dimethyl (1*S*,2*S*,5*S*,6*S*)-6-((*tert*-butyldiphenylsilyloxy)-2,5-dimethyl-4-phenyl-3-azabicyclo[3.2.0]hept-3-ene-1,2-dicarboxylate (**15**)



15 was prepared according to a literature procedure⁶. DDQ (0.111 g, 0.487 mmol) was added to a solution of **14** (0.135 g, 0.236 mmol) in toluene (3 mL) at 50 °C. The reaction mixture was heated to 70 °C and stirred for 10 h before quenched with a saturated aqueous solution of NaHCO₃ and extracted with DCM. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 8:1) to afford product **15** (0.126 g, 0.221 mmol, 94% yield).

$[\alpha]_D^{27}$ -44.5 (c 1.3, CHCl₃).

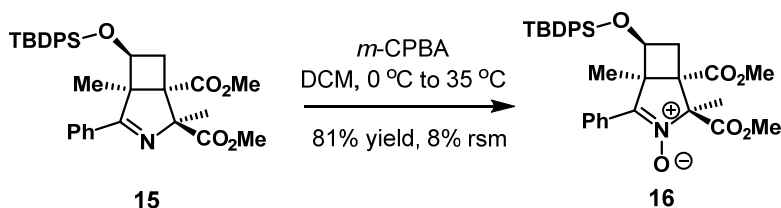
¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.16 – 8.06 (m, 2H), 7.65 – 7.57 (m, 2H), 7.56 – 7.49 (m, 2H), 7.48 – 7.23 (m, 9H), 4.28 (dd, J = 8.8, 7.7 Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 2.36 (dd, J = 11.9, 7.7 Hz, 1H), 1.87 (dd, J = 11.9, 8.9 Hz, 1H), 1.50 (s, 3H), 1.38 (s, 3H), 0.94 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 173.91, 172.90, 171.25, 135.73, 135.63, 133.61, 133.33, 133.21, 130.46, 130.23, 129.86, 129.84, 127.81, 127.67, 127.58, 83.01, 71.91, 70.02, 53.25, 52.25, 51.93, 37.49, 26.82, 24.61, 20.85, 18.87.

IR (neat cm⁻¹): 1729, 1604, 1573, 1428, 1296, 1267, 1195, 1130, 1113, 1062.

HRMS-EI (m/z): [M]⁺ calcd. for C₃₄H₃₉NO₅Si, 569.2592; found, 569.2596.

(1*S*,4*S*,5*S*,7*S*)-7-((*Tert*-butyldiphenylsilyloxy)-4,5-bis(methoxycarbonyl)-1,4-dimethyl-2-phenyl-3-azabicyclo[3.2.0]hept-2-ene 3-oxide (**16**)



A solution of *m*-CPBA (85%, 36.7 mg, 0.180 mmol) in DCM (2 mL) was added to a solution of **15** (92.0 mg, 0.161 mmol) in DCM (1 mL) at 0 °C. After 30 min, the reaction mixture was heated to 35 °C and stirred for another 24 h before quenched with a cold 5% aqueous solution of Na₂S₂O₃. The resulting mixture was extracted with DCM, and the combined organic phase was washed sequentially with a cold 5% aqueous solution of K₂CO₃, brine, dried over Na₂SO₄ and concentrated. The residue was purified by

⁶ S. Xu, Z.-M. Zhang, B. Xu, B. Liu, Y. Liu, J. Zhang, *J. Am. Chem. Soc.* **2018**, *140*, 2272–2283.

column chromatography on silica gel (PE:EA = 3:1) to afford product **16** (76.2 mg, 0.130 mmol, 81% yield) and recovered starting material **16** (7.3 mg, 12.8 μ mol, 8% yield).

$[\alpha]_D^{24}$ 2.9 (c 1.0, CHCl₃).

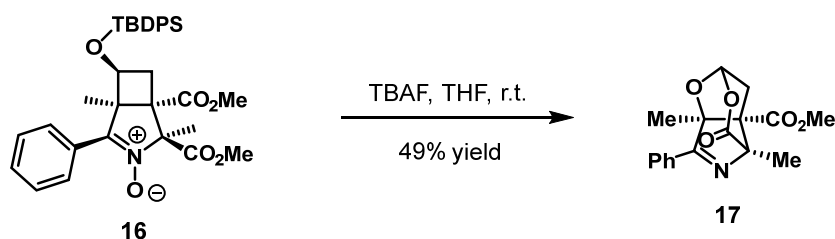
¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.62–8.49 (m, 2H), 7.66–7.55 (m, 2H), 7.55–7.49 (m, 2H), 7.49–7.28 (m, 9H), 4.45 (dd, J = 9.3, 7.6 Hz, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 2.84 (dd, J = 12.3, 9.3 Hz, 1H), 2.09 (dd, J = 12.4, 7.7 Hz, 1H), 1.78 (s, 3H), 1.58 (s, 3H), 0.92 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 169.92, 167.45, 143.11, 135.73, 135.59, 133.10, 132.91, 129.97, 129.93, 129.87, 128.85, 127.74, 127.67, 83.32, 73.05, 62.45, 52.86, 52.27, 48.72, 37.09, 26.77, 21.24, 20.99, 18.84.

IR (neat cm⁻¹): 2952, 2858, 1741, 1520, 1428, 1302, 1266, 1228, 1133, 1111, 1061.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for C₃₄H₄₀NO₆Si, 586.2619; found, 586.2627.

Methyl (3*S*,3*aR*,7*aS*)-3,7*a*-dimethyl-7-oxo-2-phenyl-4,5,7,7*a*-tetrahydro-3,5-epoxypyrano[3,4-*b*]pyrrole-3*a*(3*H*)-carboxylate (17**)**



A solution of **16** (37.2 mg, 63.5 μ mol) in THF (1 mL) was added a solution of TBAF (33.2 mg, 0.105 mmol) in THF (0.3 mL). The reaction mixture was stirred at room temperature for 3.5 h before quenched with water and extracted with DCM. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 2:1) to afford product **17** (9.9 mg, 31.4 μ mol, 49% yield).

$[\alpha]_D^{29}$ 50.7 (c 0.2, CHCl₃).

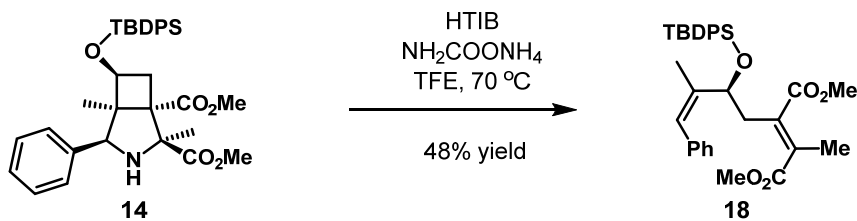
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.85–7.65 (m, 2H), 7.53–7.37 (m, 3H), 5.78 (dd, J = 2.9, 1.0 Hz, 1H), 3.75 (s, 3H), 2.56–2.50 (m, 2H), 1.79 (s, 3H), 1.46 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 177.18, 168.57, 168.55, 132.12, 130.89, 128.47, 128.00, 100.22, 97.41, 83.17, 65.08, 52.44, 35.78, 19.77, 18.63.

IR (neat cm⁻¹): 1736, 1612, 1575, 1458, 1376, 1318, 1272, 1206, 1139, 1108, 1055.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for C₁₇H₁₈NO₅, 316.1179; found, 316.1178.

Dimethyl 2-((*S,Z*)-2-((*tert*-butyldiphenylsilyloxy)-3-methyl-4-phenylbut-3-en-1-yl)-3-methylfumarate (**18**)



Asolution of phenyliodosohydroxy tosylate (62.3 mg, 0.159 mmol), ammonium carbamate (38.5 mg, 0.493 mmol) and **14** (33.1 mg, 57.3 μmol) in TFE (0.8 mL) was stirred at 70 °C for 3 h before quenched with water. The resulting mixture was extracted with DCM, washed with brine, dried over Na_2SO_4 , concentrated and the residue was purified by column chromatography on silica gel (PE:EA = 30:1) to afford product **18** (15.4 mg, 27.7 μmol , 48% yield).

$[\alpha]_D^{25}$ 17.9 (c 0.8, CHCl_3).

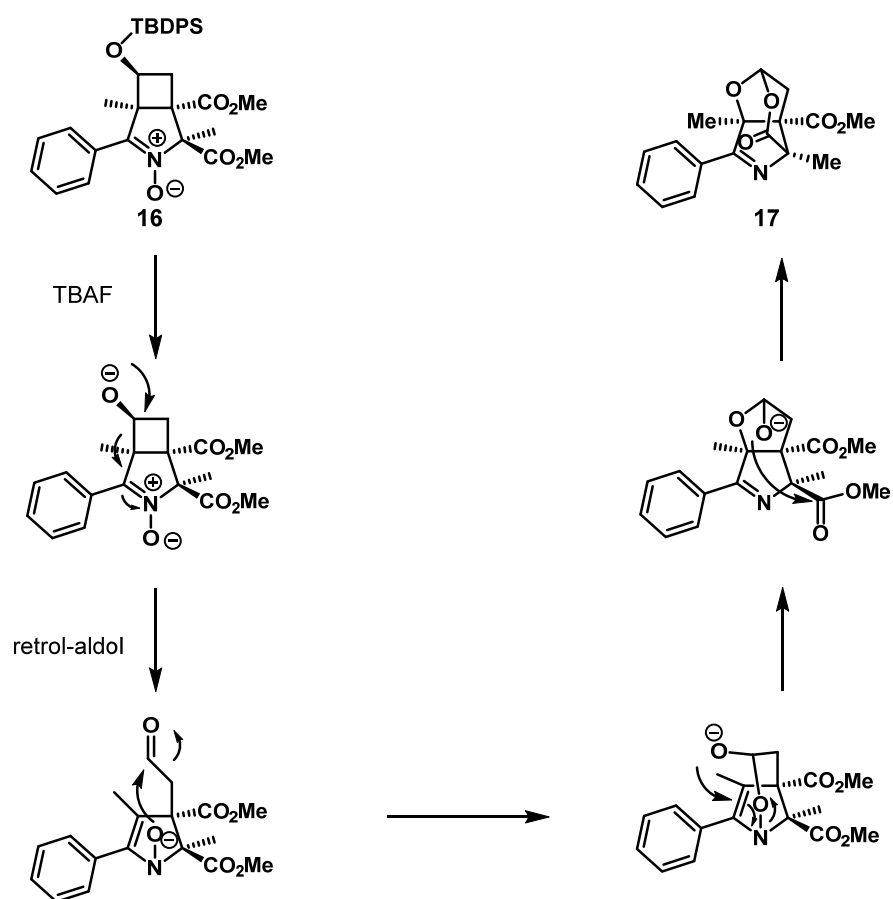
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.59 – 7.50 (m, 4H), 7.40 – 7.33 (m, 2H), 7.32 – 7.23 (m, 4H), 7.11 – 6.95 (m, 3H), 6.79 – 6.62 (m, 2H), 6.16 (s, 1H), 5.04 (t, $J = 7.1$ Hz, 1H), 3.62 (s, 3H), 3.25 (s, 3H), 2.90 (qd, $J = 13.7, 7.2$ Hz, 2H), 1.97 (s, 3H), 1.90 (d, $J = 1.4$ Hz, 3H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 169.44, 167.81, 138.70, 137.66, 137.05, 135.95, 133.85, 133.79, 132.07, 129.38, 129.36, 128.61, 127.74, 127.66, 127.32, 127.24, 125.89, 69.83, 51.80, 51.22, 37.29, 26.86, 19.35, 18.24, 18.12.

IR (neat cm^{-1}): 1722, 1493, 1473, 1428, 1253, 1222, 1203, 1111, 1068.

HRMS-ESI (m/z): $[\text{M}+\text{NH}_4]^+$ calcd. for $\text{C}_{34}\text{H}_{44}\text{SiNO}_5$, 574.2983; found, 574.2976.

1.6 Proposed Mechanism for the Formation of 17



Scheme S1

1.7 X-ray Data of structures 3a, 5d, 7a, 8-Ts, *epi*-8, 16, and 17

X-ray Structure 3a:

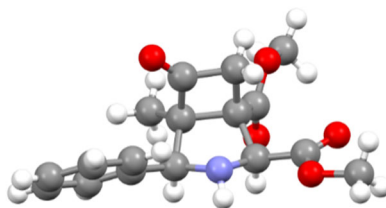
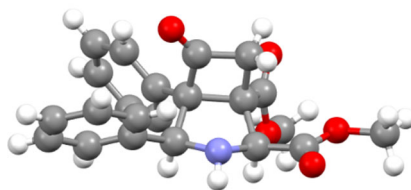
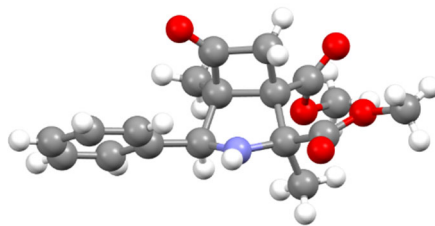


Table S5 Crystal data and structure refinement.

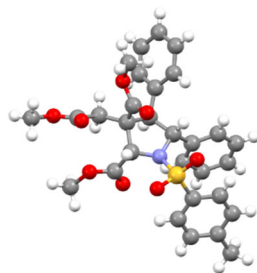
Identification code	exp_2574
Empirical formula	C ₁₇ H ₁₉ NO ₅
Formula weight	317.33
Temperature/K	173.00(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.10160(10)
b/Å	9.87230(10)
c/Å	17.9089(2)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1609.18(3)
Z	4
ρ _{calc} /cm ³	1.310
μ/mm ⁻¹	0.804
F(000)	672.0
Crystal size/mm ³	0.42 × 0.36 × 0.24
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.878 to 134.154
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -21 ≤ l ≤ 21
Reflections collected	37119
Independent reflections	2857 [R _{int} = 0.0486, R _{sigma} = 0.0161]
Data/restraints/parameters	2857/0/216
Goodness-of-fit on F ²	1.056
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0256, wR ₂ = 0.0687
Final R indexes [all data]	R ₁ = 0.0259, wR ₂ = 0.0690
Largest diff. peak/hole / e Å ⁻³	0.17/-0.14
Flack parameter	0.02(5)

**Table S6 Crystal data and structure refinement.**

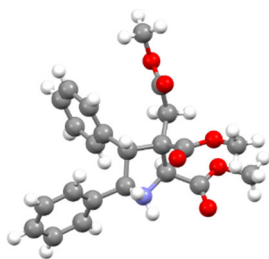
Identification code	cu_llc_3_36_0m_a
Empirical formula	C ₂₂ H ₂₁ NO ₅
Formula weight	379.40
Temperature/K	250
Crystal system	monoclinic
Space group	P2 ₁
a/Å	10.5662(7)
b/Å	6.4254(4)
c/Å	14.2474(9)
α /°	90
β /°	91.616(3)
γ /°	90
Volume/Å ³	966.90(11)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.303
μ/mm^{-1}	0.762
F(000)	400.0
Crystal size/mm ³	0.08 × 0.05 × 0.05
Radiation	Cu K α (λ = 1.54178)
2 θ range for data collection/°	6.21 to 133.91
Index ranges	-12 ≤ h ≤ 12, -7 ≤ k ≤ 7, -16 ≤ l ≤ 16
Reflections collected	27515
Independent reflections	3421 [R_{int} = 0.0502, R_{sigma} = 0.0760]
Data/restraints/parameters	3421/1/259
Goodness-of-fit on F ²	1.074
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0283, wR_2 = 0.0742
Final R indexes [all data]	R_1 = 0.0431, wR_2 = 0.0768
Largest diff. peak/hole / e Å ⁻³	0.14/-0.16
Flack parameter	0.14(6)

**Table S7 Crystal data and structure refinement.**

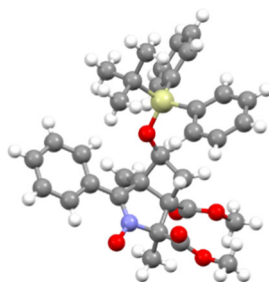
Identification code	cu_d8v22363_0m
Empirical formula	C ₁₈ H ₂₁ NO ₅
Formula weight	331.36
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	6.5148(3)
b/Å	18.6775(10)
c/Å	7.3961(4)
α/°	90
β/°	100.321(2)
γ/°	90
Volume/Å ³	885.40(8)
Z	2
ρ _{calc} /cm ³	1.243
μ/mm ⁻¹	0.751
F(000)	352.0
Crystal size/mm ³	0.2 × 0.15 × 0.08
Radiation	Cu Kα (λ = 1.54178)
2θ range for data collection/°	13.06 to 134.94
Index ranges	-7 ≤ h ≤ 7, -22 ≤ k ≤ 22, -8 ≤ l ≤ 8
Reflections collected	11336
Independent reflections	3026 [R _{int} = 0.0559, R _{sigma} = 0.0536]
Data/restraints/parameters	3026/1/222
Goodness-of-fit on F ²	1.074
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0525, wR ₂ = 0.1364
Final R indexes [all data]	R ₁ = 0.0531, wR ₂ = 0.1379
Largest diff. peak/hole / e Å ⁻³	0.21/-0.34
Flack parameter	0.10(10)

**Table S8 Crystal data and structure refinement.**

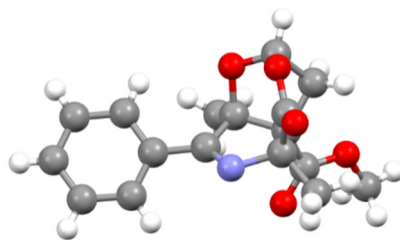
Identification code	exp_3074
Empirical formula	C ₃₀ H ₃₁ NO ₈ S
Formula weight	565.62
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	12.63180(10)
b/Å	7.14960(10)
c/Å	15.68420(10)
α/°	90
β/°	101.2370(10)
γ/°	90
Volume/Å ³	1389.32(2)
Z	2
ρ _{calc} /cm ³	1.352
μ/mm ⁻¹	1.482
F(000)	596.0
Crystal size/mm ³	0.39 × 0.36 × 0.28
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	5.744 to 134.138
Index ranges	-15 ≤ h ≤ 15, -8 ≤ k ≤ 8, -18 ≤ l ≤ 18
Reflections collected	29729
Independent reflections	4977 [R _{int} = 0.0396, R _{sigma} = 0.0225]
Data/restraints/parameters	4977/1/366
Goodness-of-fit on F ²	1.025
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0240, wR ₂ = 0.0628
Final R indexes [all data]	R ₁ = 0.0242, wR ₂ = 0.0631
Largest diff. peak/hole / e Å ⁻³	0.19/-0.19
Flack parameter	0.000(6)

**Table S9 Crystal data and structure refinement.**

Empirical formula	C ₂₃ H ₂₅ NO ₆
Formula weight	411.46
Temperature/K	172.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.9746(3)
b/Å	9.7722(3)
c/Å	12.9941(4)
α/°	89.169(2)
β/°	76.315(2)
γ/°	69.111(3)
Volume/Å ³	1031.41(6)
Z	2
ρ _{calc} /cm ³	1.3248
μ/mm ⁻¹	0.791
F(000)	437.5
Crystal size/mm ³	0.42 × 0.36 × 0.32
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.02 to 134.12
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	22027
Independent reflections	3656 [R _{int} = 0.0345, R _{sigma} = 0.0217]
Data/restraints/parameters	3656/0/274
Goodness-of-fit on F ²	1.039
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0317, wR ₂ = 0.0778
Final R indexes [all data]	R ₁ = 0.0336, wR ₂ = 0.0792
Largest diff. peak/hole / e Å ⁻³	0.24/-0.15

**Table S11 Crystal data and structure refinement.**

Identification code	exp_3145
Empirical formula	C ₃₄ H ₃₉ NO ₆ Si
Formula weight	585.75
Temperature/K	173.00(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.65320(10)
b/Å	12.55440(10)
c/Å	25.5448(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3095.78(5)
Z	4
ρ _{calc} /cm ³	1.257
μ/mm ⁻¹	1.040
F(000)	1248.0
Crystal size/mm ³	0.32 × 0.29 × 0.26
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.92 to 134.154
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -30 ≤ l ≤ 30
Reflections collected	81298
Independent reflections	5514 [R _{int} = 0.0601, R _{sigma} = 0.0201]
Data/restraints/parameters	5514/0/386
Goodness-of-fit on F ²	1.067
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0282, wR ₂ = 0.0757
Final R indexes [all data]	R ₁ = 0.0285, wR ₂ = 0.0759
Largest diff. peak/hole / e Å ⁻³	0.21/-0.21
Flack parameter	0.023(7)

**Table S12 Crystal data and structure refinement.**

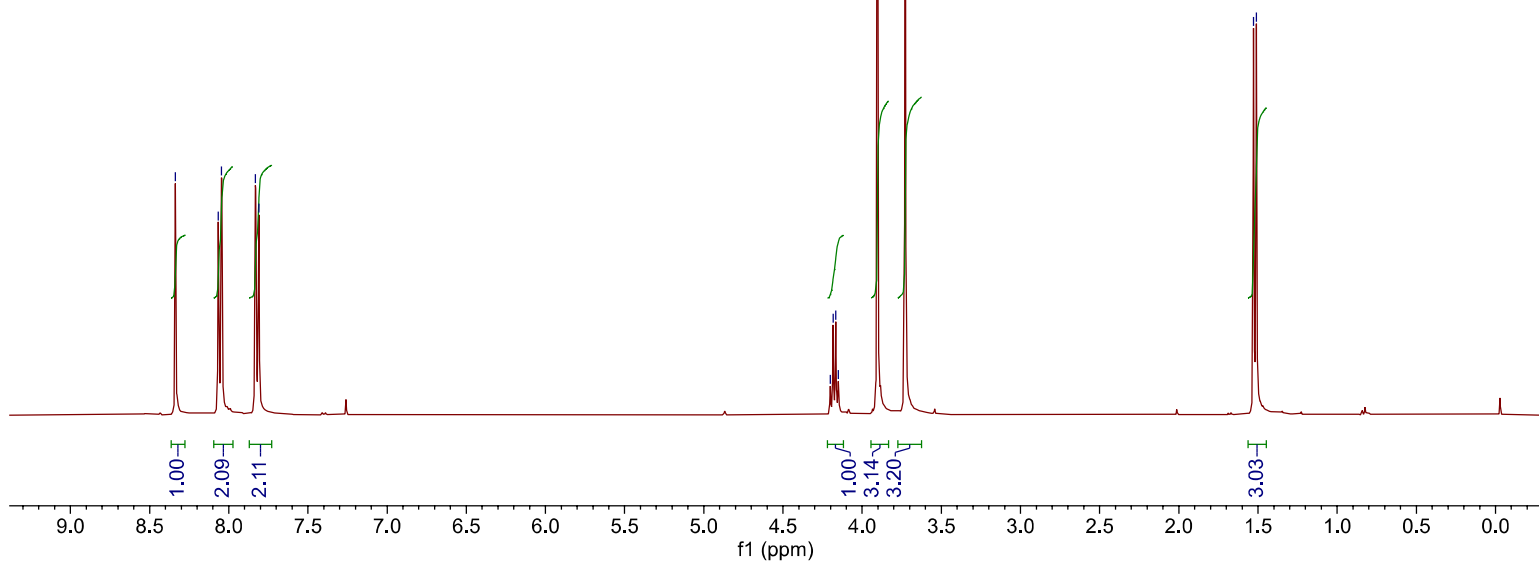
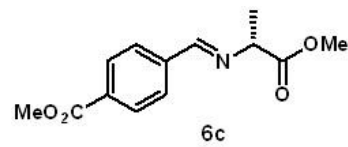
Identification code	exp_3132
Empirical formula	C ₁₇ H ₁₇ NO ₅
Formula weight	315.31
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	7.03880(10)
b/Å	31.5073(3)
c/Å	7.15720(10)
α/°	90
β/°	103.3610(10)
γ/°	90
Volume/Å ³	1544.32(3)
Z	4
ρ _{calc} /cm ³	1.356
μ/mm ⁻¹	0.837
F(000)	664.0
Crystal size/mm ³	0.39 × 0.32 × 0.27
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	11.234 to 134.118
Index ranges	-8 ≤ h ≤ 8, -37 ≤ k ≤ 37, -8 ≤ l ≤ 8
Reflections collected	32400
Independent reflections	2759 [R _{int} = 0.0478, R _{sigma} = 0.0214]
Data/restraints/parameters	2759/0/211
Goodness-of-fit on F ²	1.045
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0342, wR ₂ = 0.0809
Final R indexes [all data]	R ₁ = 0.0360, wR ₂ = 0.0820
Largest diff. peak/hole / e Å ⁻³	0.25/-0.21

8.34
8.07
8.05
7.83
7.81

4.20
4.18
4.17
4.15
3.90
3.73

1.53
1.51

Parameter	Value
1 Title	c-2-98-ap.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.9
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-10-05T19:54:07
8 Spectrometer Frequency	400.13



172.59
166.46
161.92

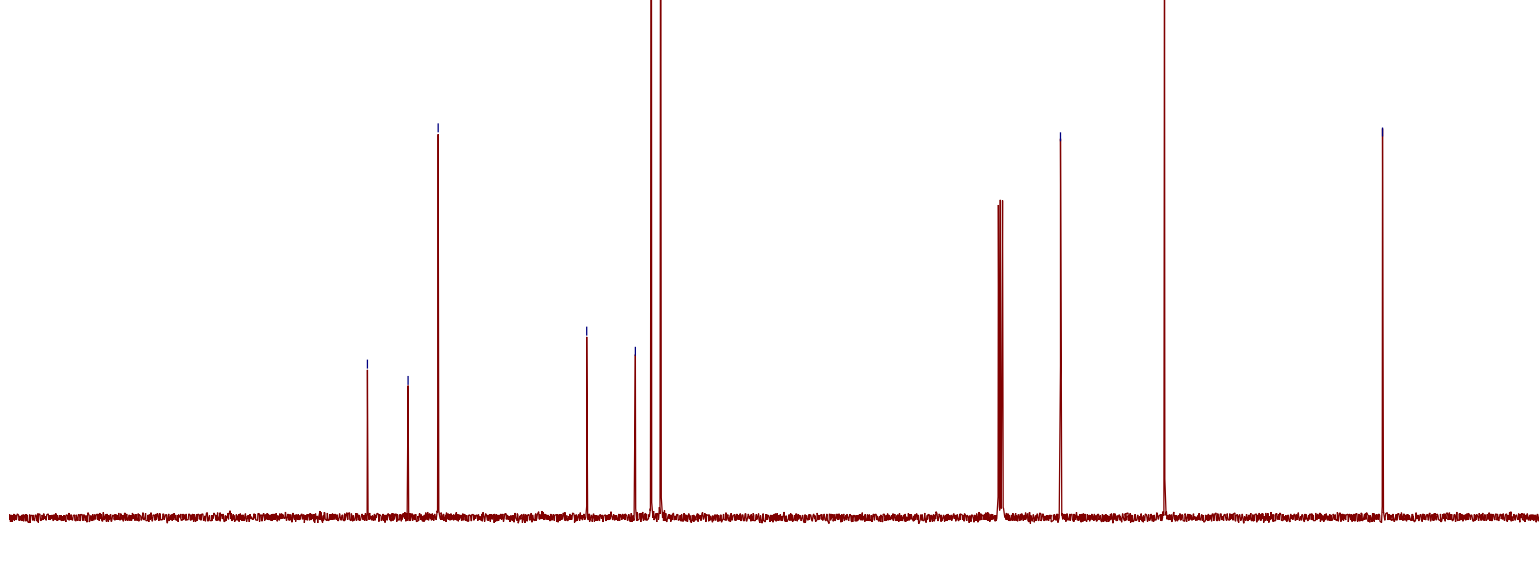
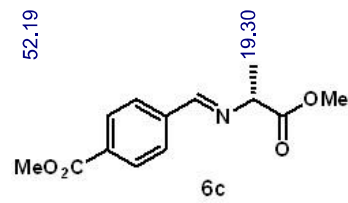
139.46
132.14
129.74
128.29

67.92

52.19

19.30

Parameter	Value
1 Title	c-2-98-ap-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.4
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-10-05T20:06:50
8 Spectrometer Frequency	100.62



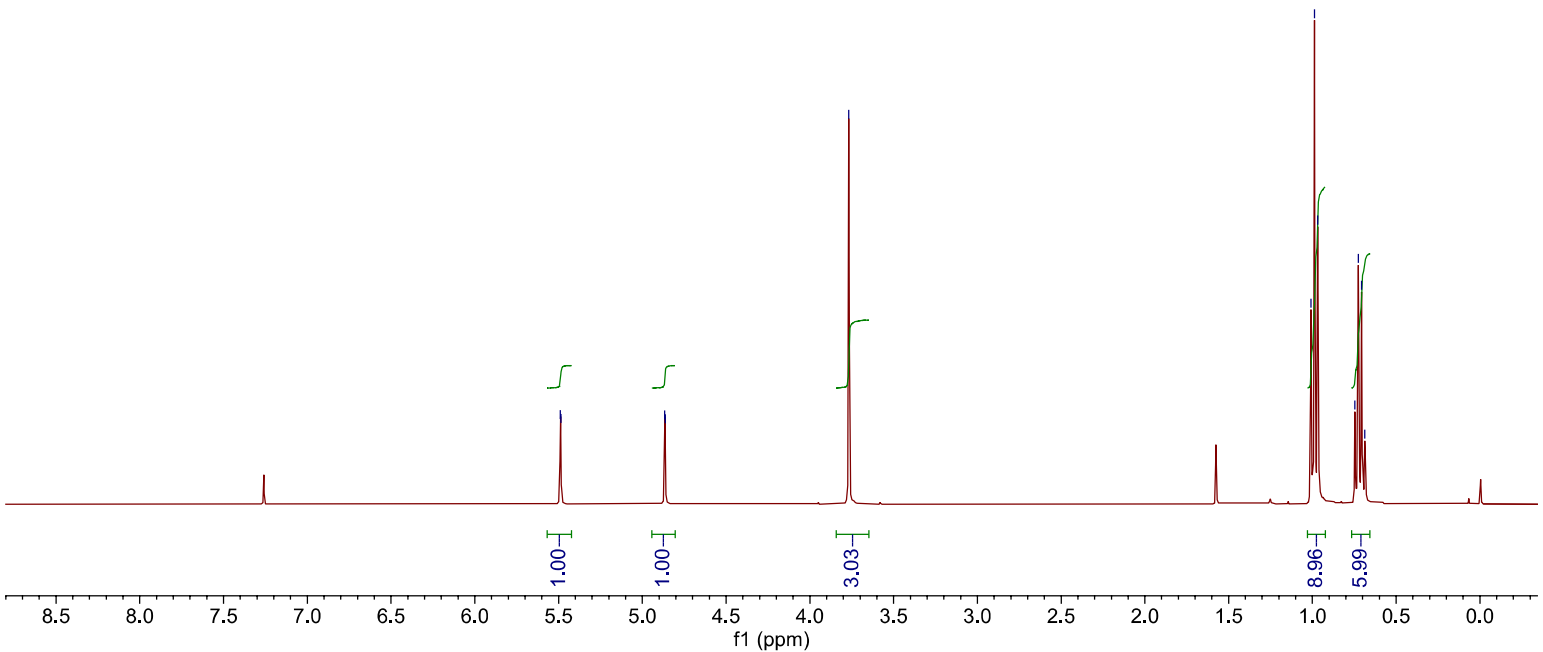
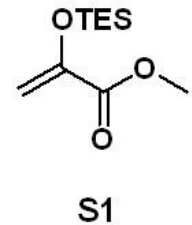
5.49
5.49

4.87
4.86

3.77

1.01
0.99
0.97
0.75
0.73
0.71
0.69

Parameter	Value
1 Title	LLC-2-36-AP.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.2
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-10-07T05:11:09
8 Spectrometer Frequency	400.13



164.93

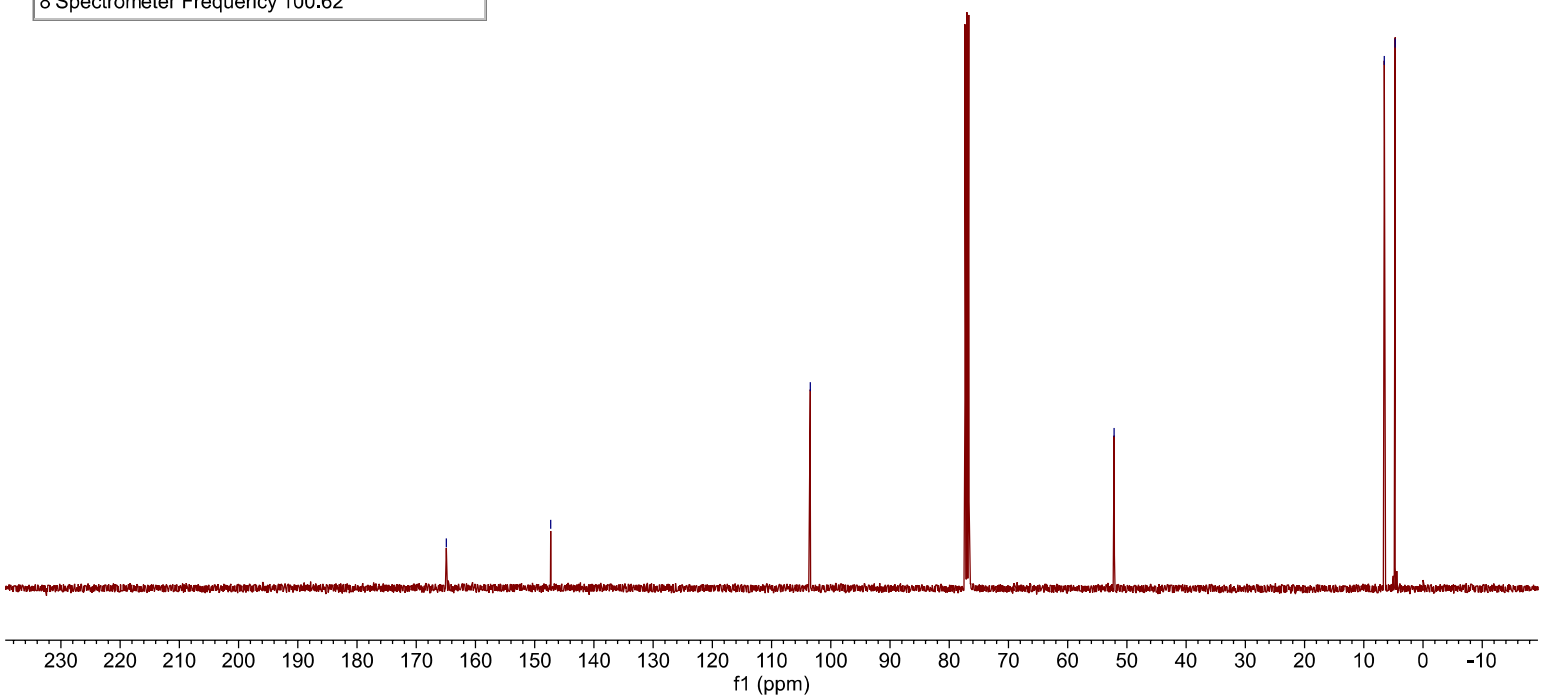
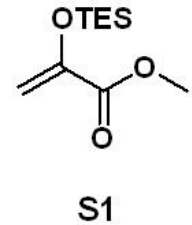
147.27

103.47

52.13

6.50
4.71

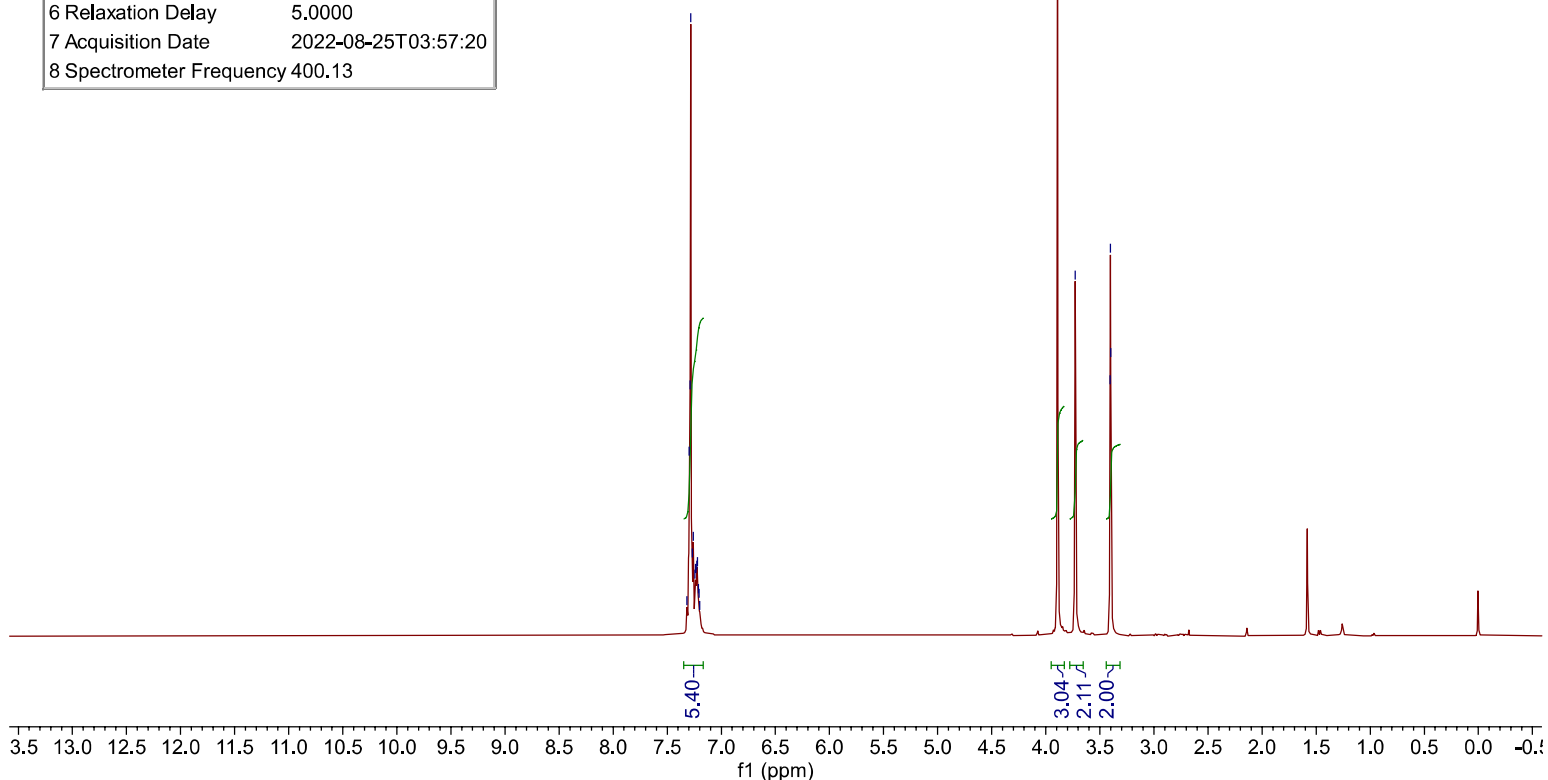
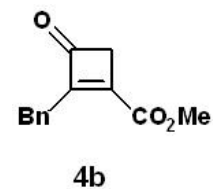
Parameter	Value
1 Title	llc-2-36-ap-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.7
5 Number of Scans	1000
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-10-20T10:59:34
8 Spectrometer Frequency	100.62



Parameter	Value
1 Title	c-2-21-ap-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.2
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-08-25T03:57:20
8 Spectrometer Frequency	400.13

7.32
7.30
7.29
7.28
7.27
7.26
7.24
7.24
7.24
7.23
7.22
7.21
7.21
7.20

3.89
3.73
3.41
3.40
3.40



189.85

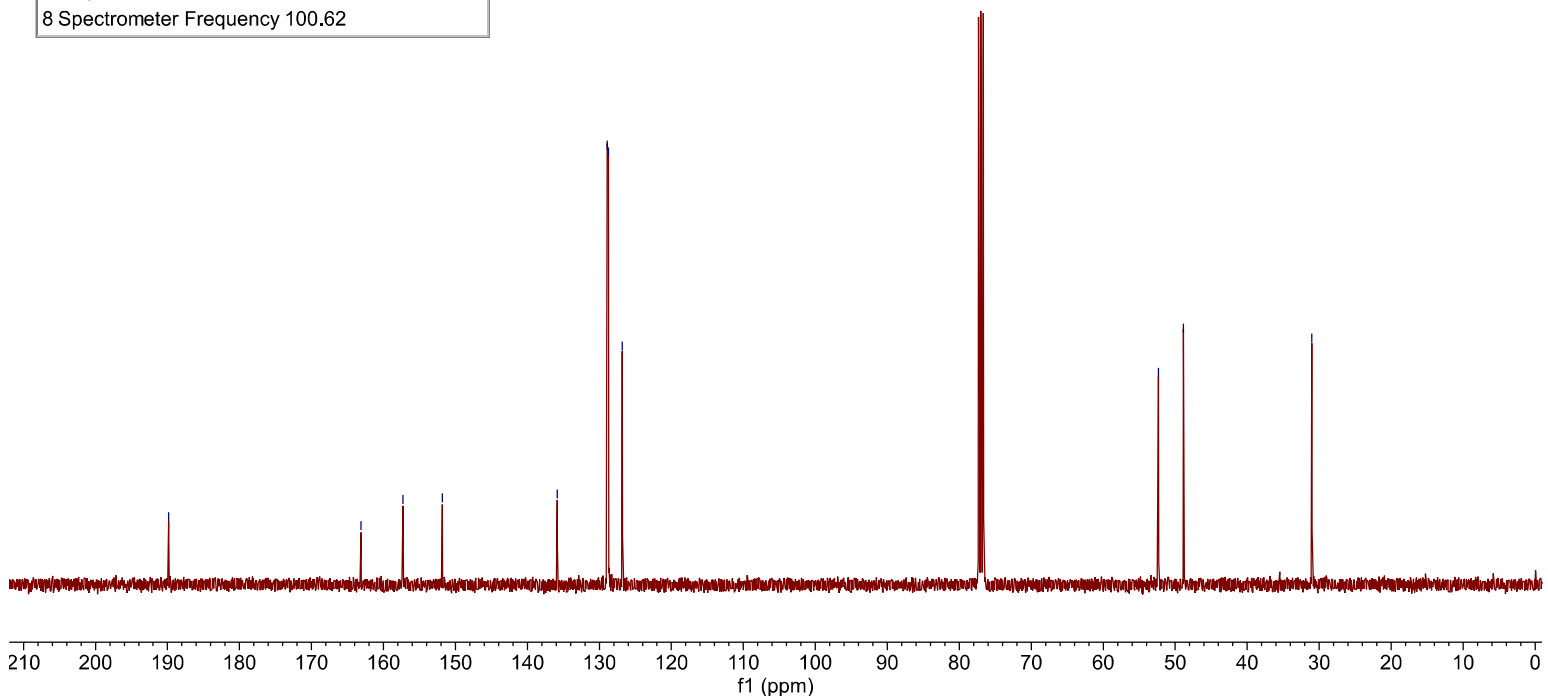
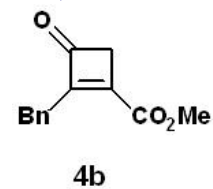
163.10
157.31
151.82

135.86
128.90
128.74
126.81

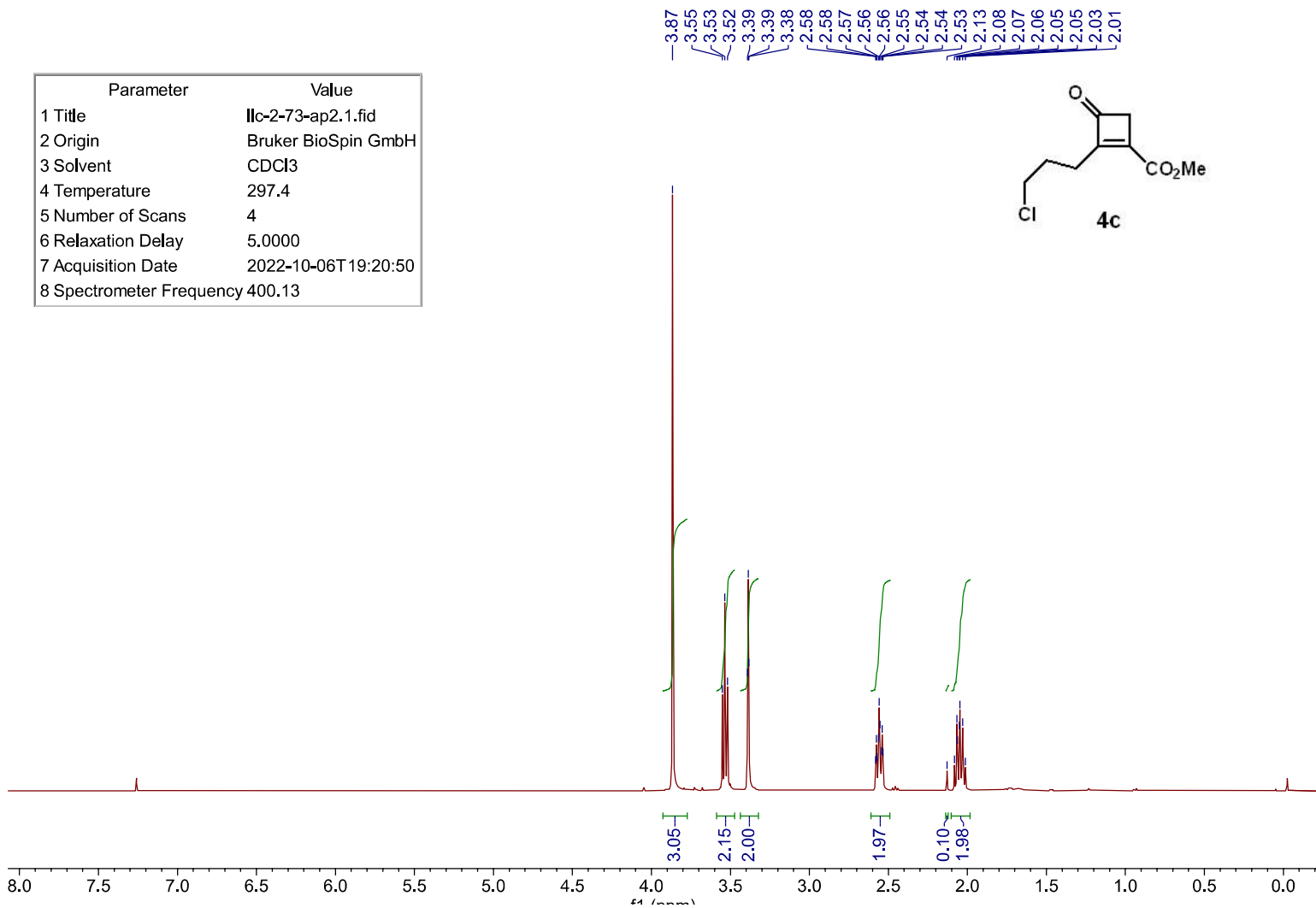
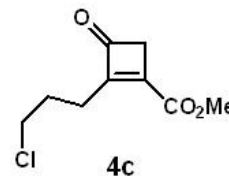
52.33
48.85

31.01

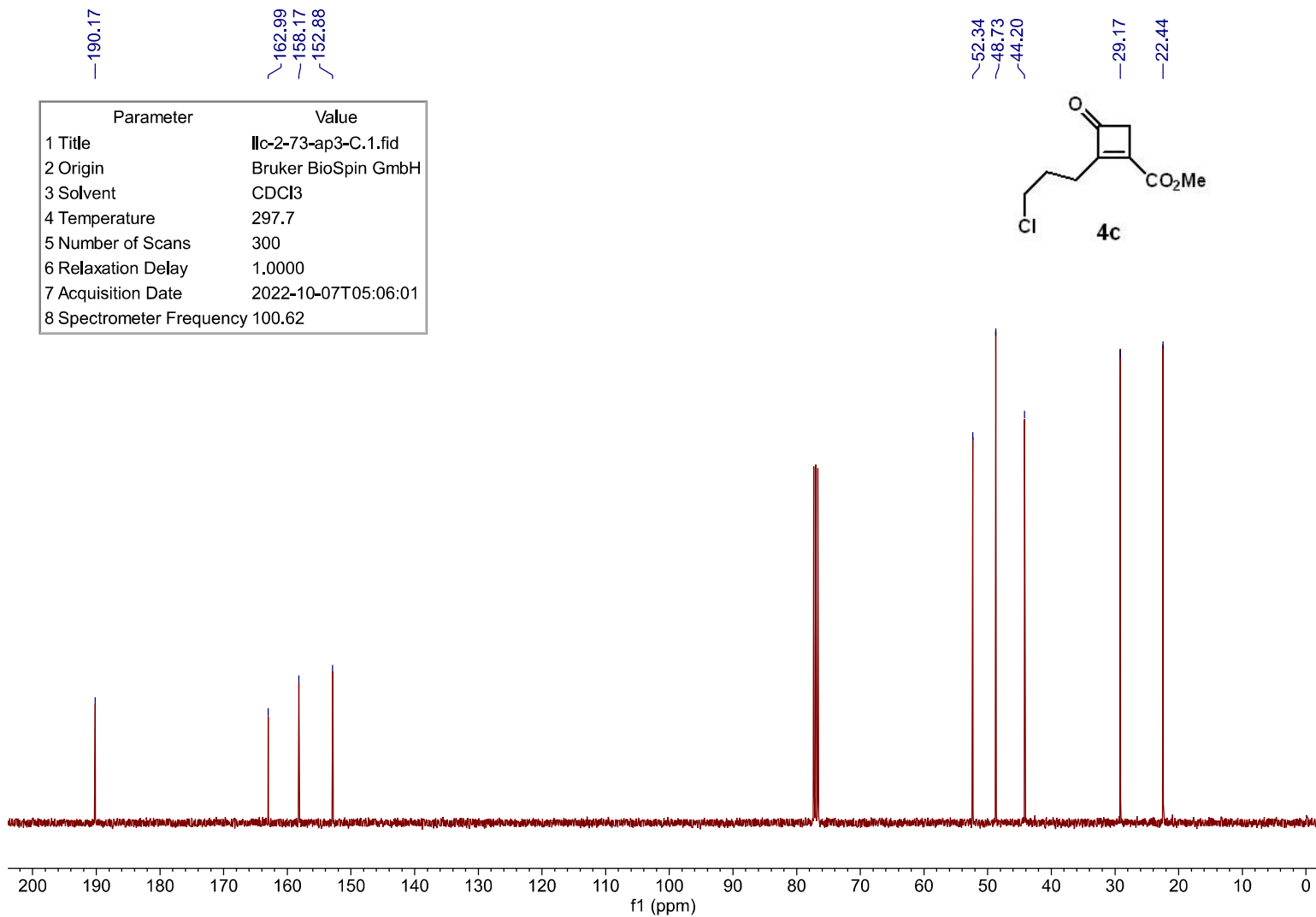
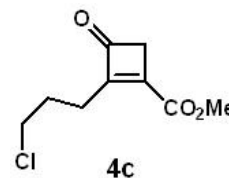
Parameter	Value
1 Title	c-2-21-ap-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.7
5 Number of Scans	400
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-08-25T04:13:38
8 Spectrometer Frequency	100.62



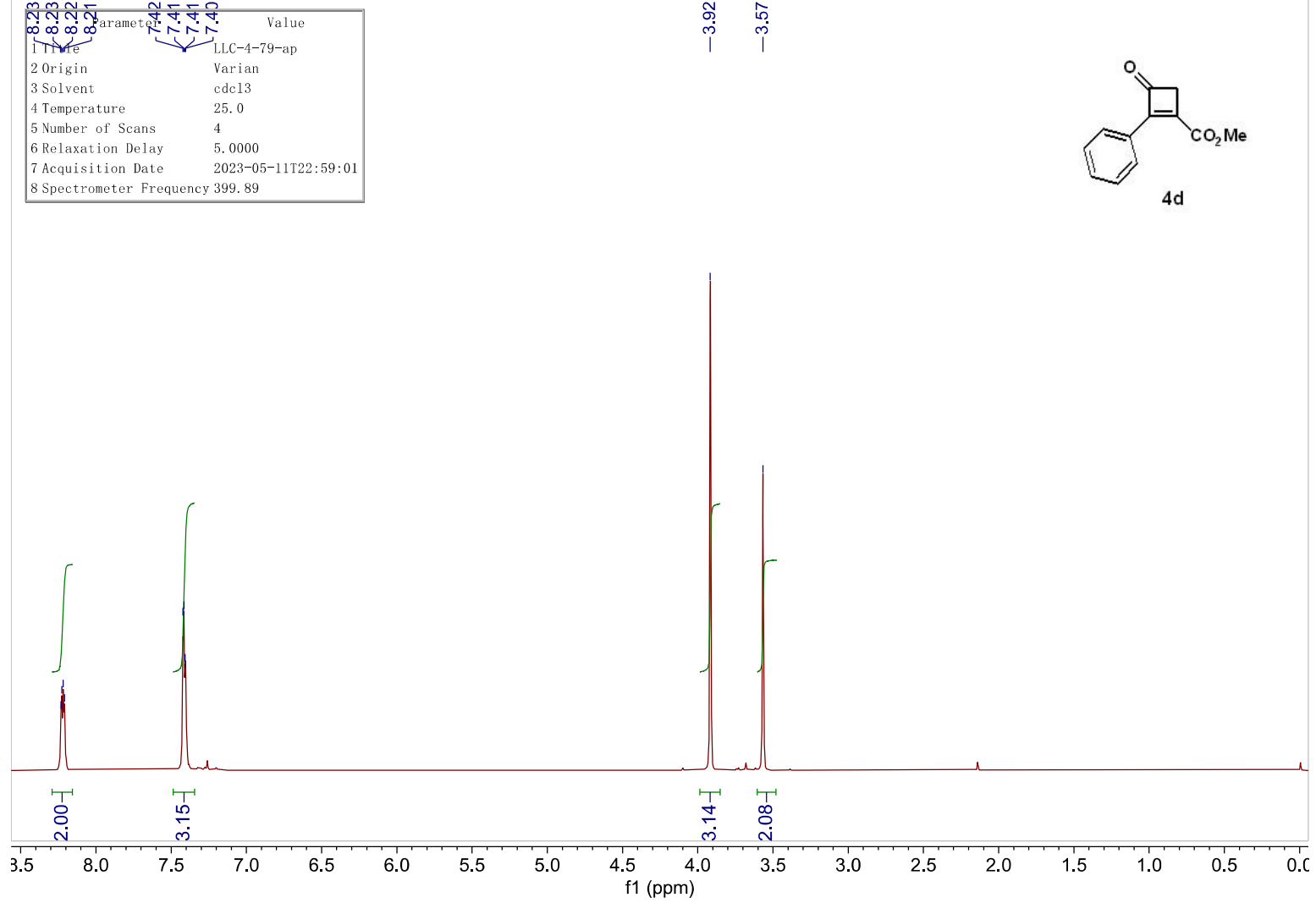
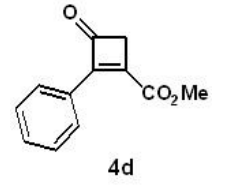
Parameter	Value
1 Title	llc-2-73-ap2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.4
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-10-06T19:20:50
8 Spectrometer Frequency	400.13



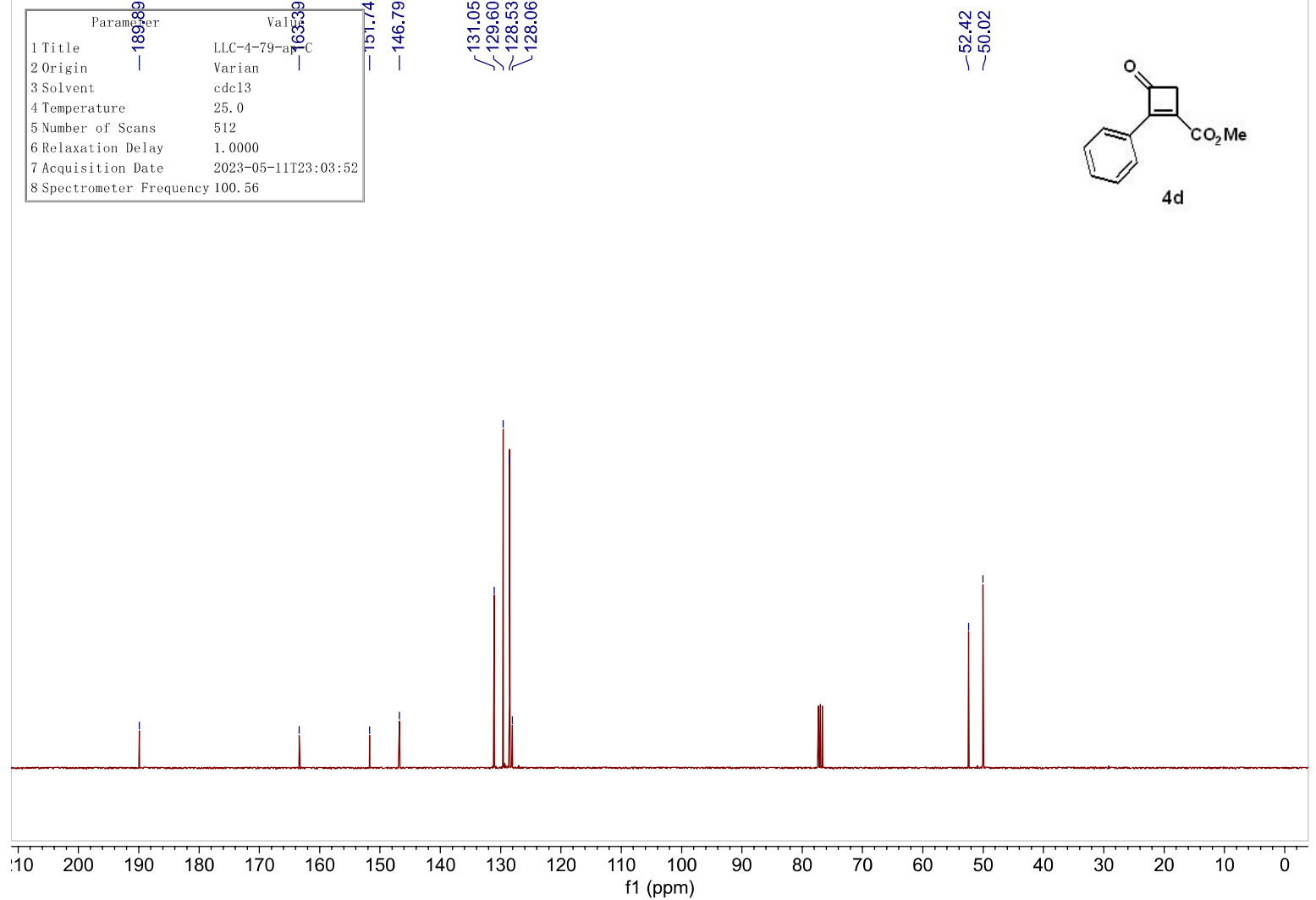
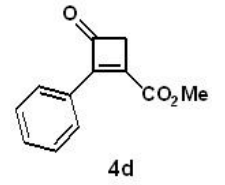
Parameter	Value
1 Title	llc-2-73-ap3-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.7
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-10-07T05:06:01
8 Spectrometer Frequency	100.62



Parameter	Value
1 Title	LLC-4-79-ap
2 Origin	Varian
3 Solvent	cdcl3
4 Temperature	25.0
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2023-05-11T22:59:01
8 Spectrometer Frequency	399.89

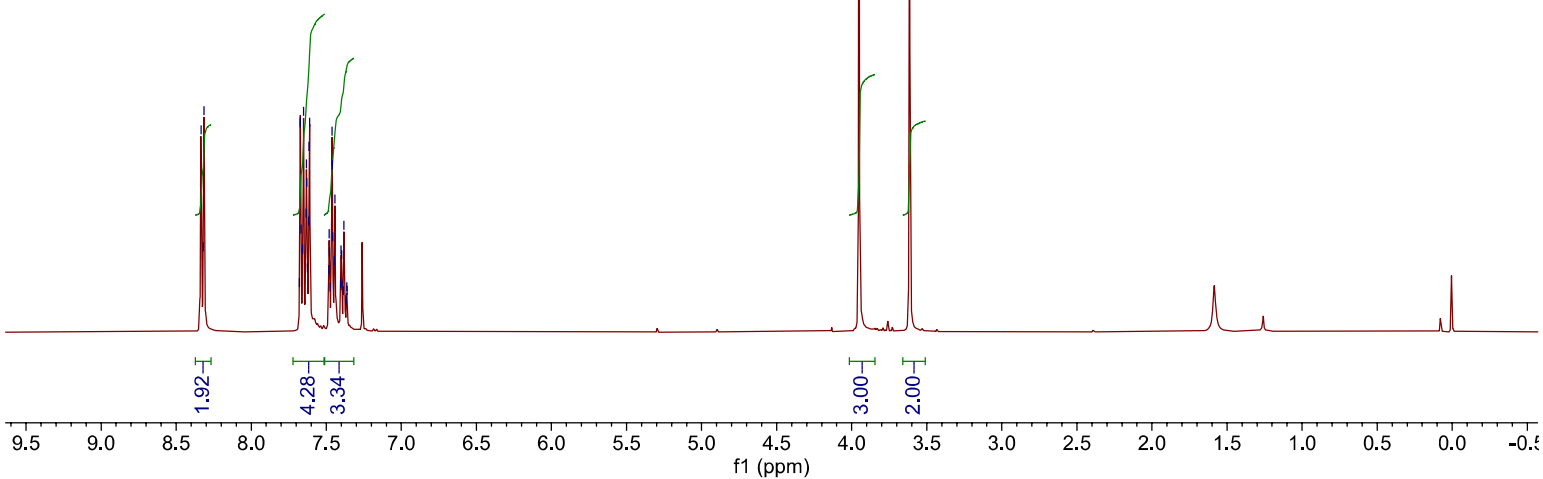
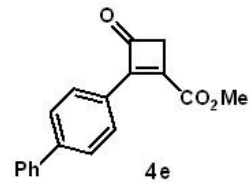


Parameter	Value
1 Title	LLC-4-79-ap
2 Origin	Varian
3 Solvent	cdcl3
4 Temperature	25.0
5 Number of Scans	512
6 Relaxation Delay	1.0000
7 Acquisition Date	2023-05-11T23:03:52
8 Spectrometer Frequency	100.56



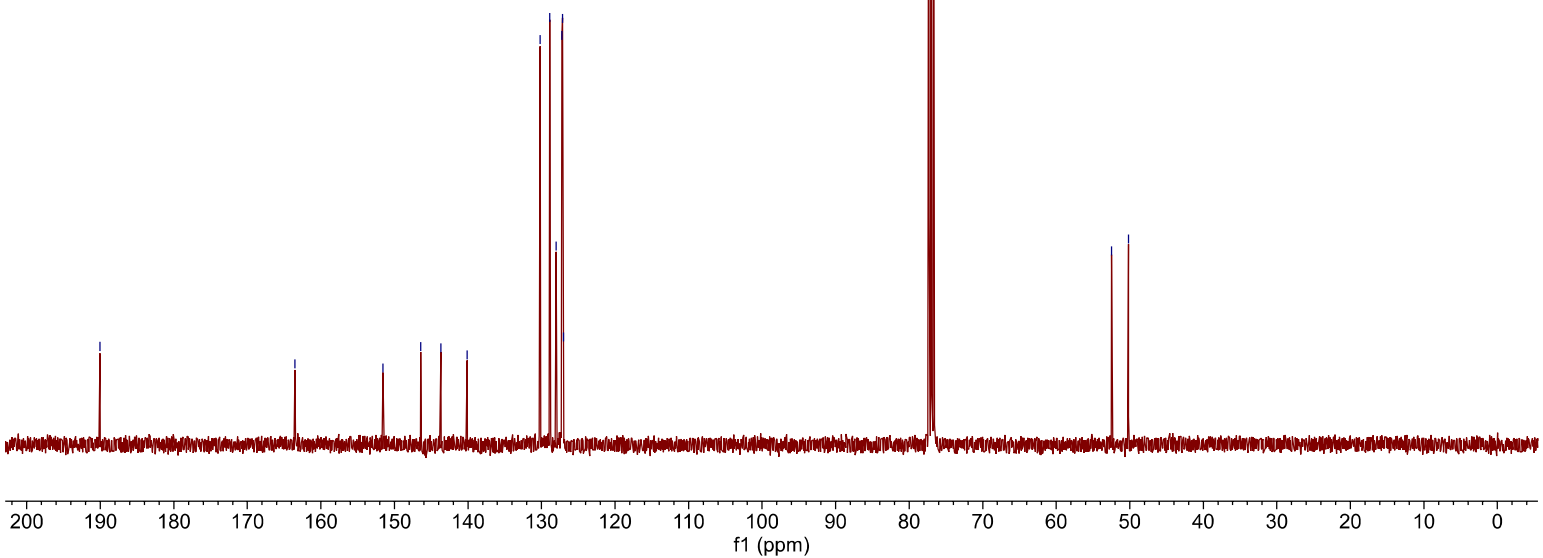
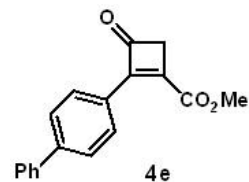
8.33
8.32
8.31
7.68
7.67
7.67
7.66
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.40
7.40
7.40
7.39
7.38
7.37
7.36
3.95
3.95
3.61

Parameter	Value
1 Title	llc-1-142-2-b-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.9
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-07-12T13:03:41
8 Spectrometer Frequency	400.13



190.06
163.56
151.57
146.42
143.70
140.11
130.19
128.90
128.00
127.22
127.14
127.01
52.48
50.18

Parameter	Value
1 Title	llc-1-142-2-b-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.4
5 Number of Scans	300
6 Relaxation Delay	2.0000
7 Acquisition Date	2022-07-12T13:21:12
8 Spectrometer Frequency	100.62



7.26

4.66

3.97

3.80

3.80

3.72

3.64

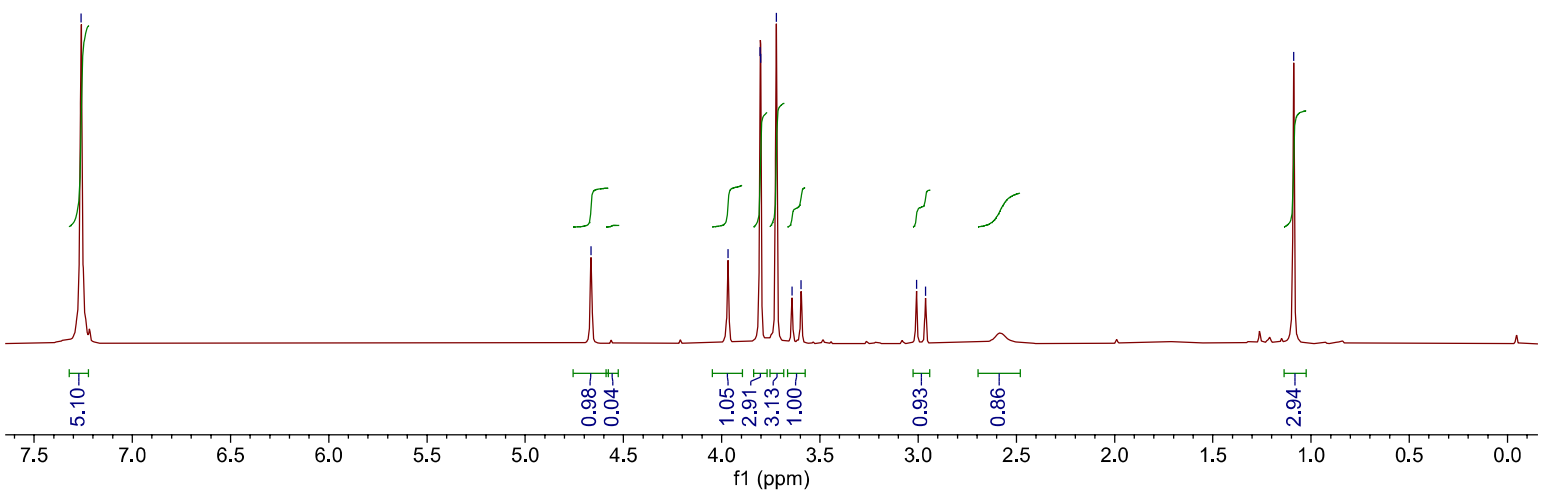
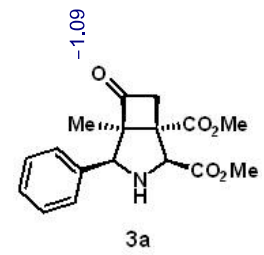
3.60

3.01

2.96

1.09

Parameter	Value
1 Title	LLC-1-30-AC.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	301.5
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2021-07-29T22:09:27
8 Spectrometer Frequency	400.13



207.04

171.27

170.42

136.02

128.43

128.18

127.43

79.23

70.93

64.53

52.52

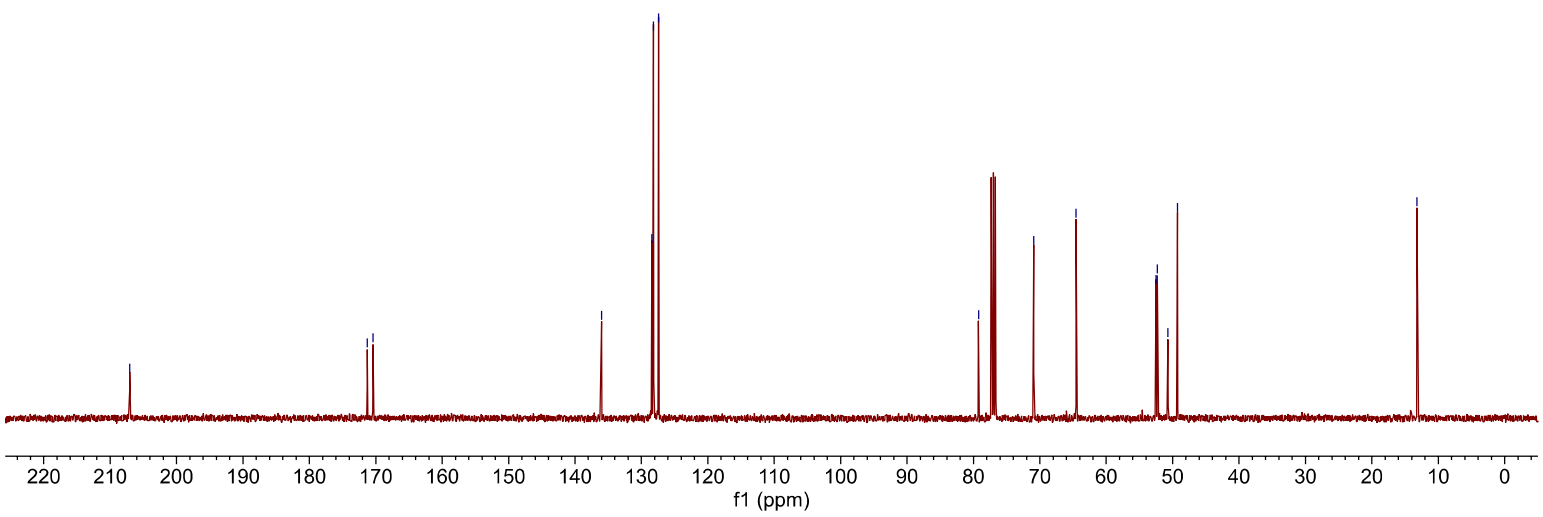
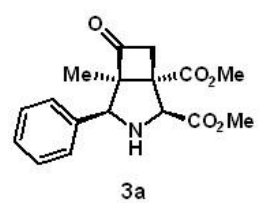
52.30

50.70

49.29

13.21

Parameter	Value
1 Title	llc-1-30-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	302.0
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-07-30T00:31:28
8 Spectrometer Frequency	100.62



7.57
7.55
7.43
7.41

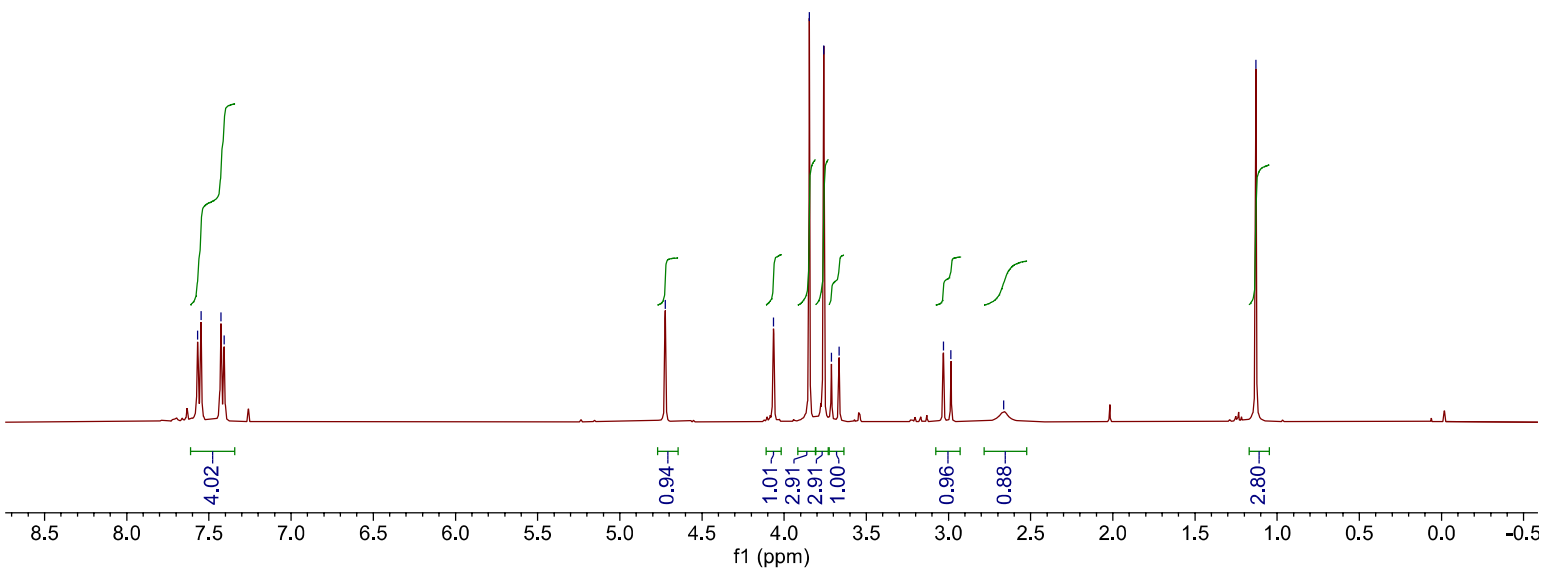
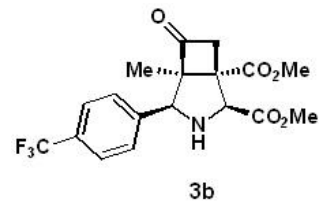
4.72

4.06
3.85
3.76
3.71
3.67

3.03
2.98
2.66

1.13

Parameter	Value
1 Title	LLC-1-89.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.3
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2021-11-27T22:37:27
8 Spectrometer	400.13
Frequency	



206.83

171.03
170.20

140.20
130.96
130.64
130.31
130.31
129.99
127.82
125.34
125.18
125.14
125.11
125.07
122.63

78.71

70.11

64.51

52.66

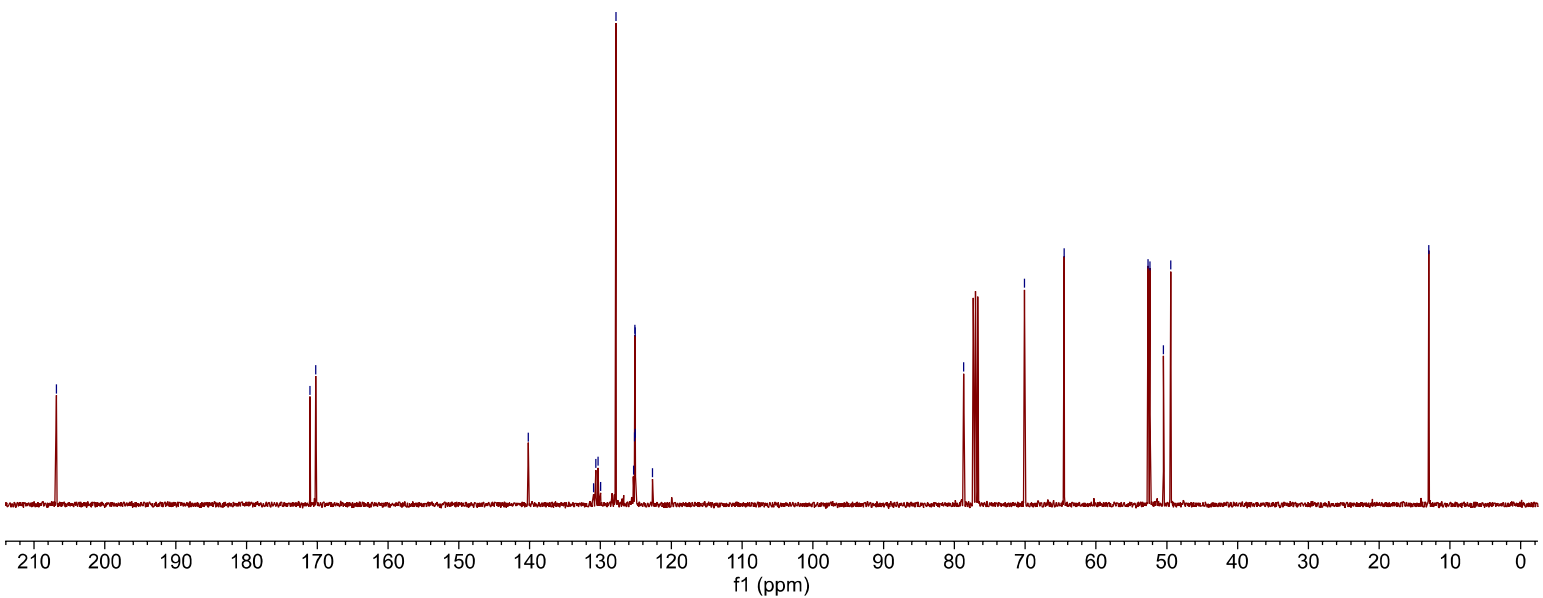
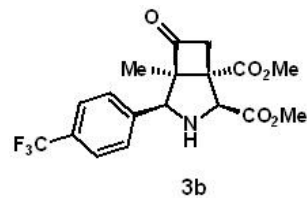
52.40

50.46

49.42

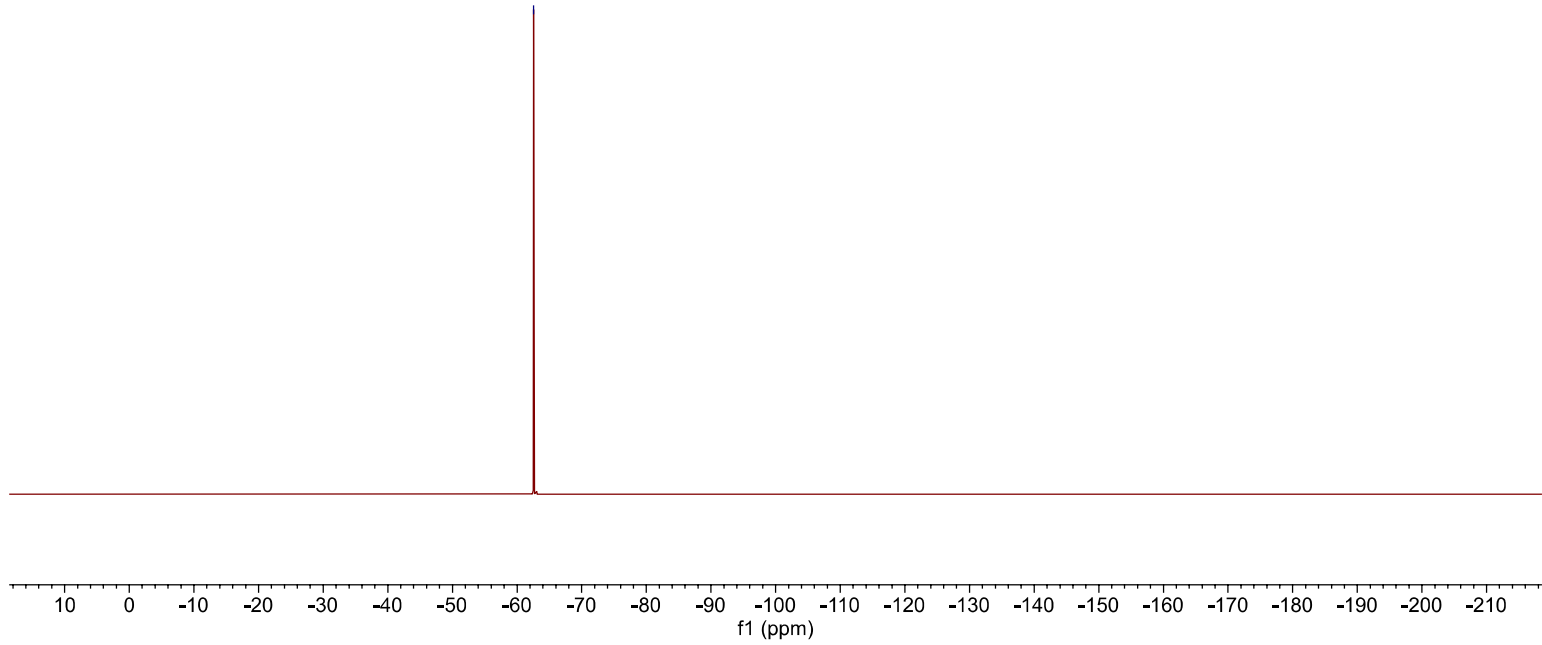
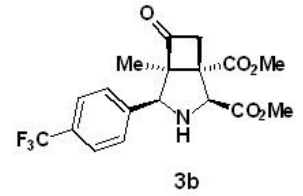
13.00

Parameter	Value
1 Title	llc-1-89-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.9
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-11-27T23:46:35
8 Spectrometer	Frequency 100.62

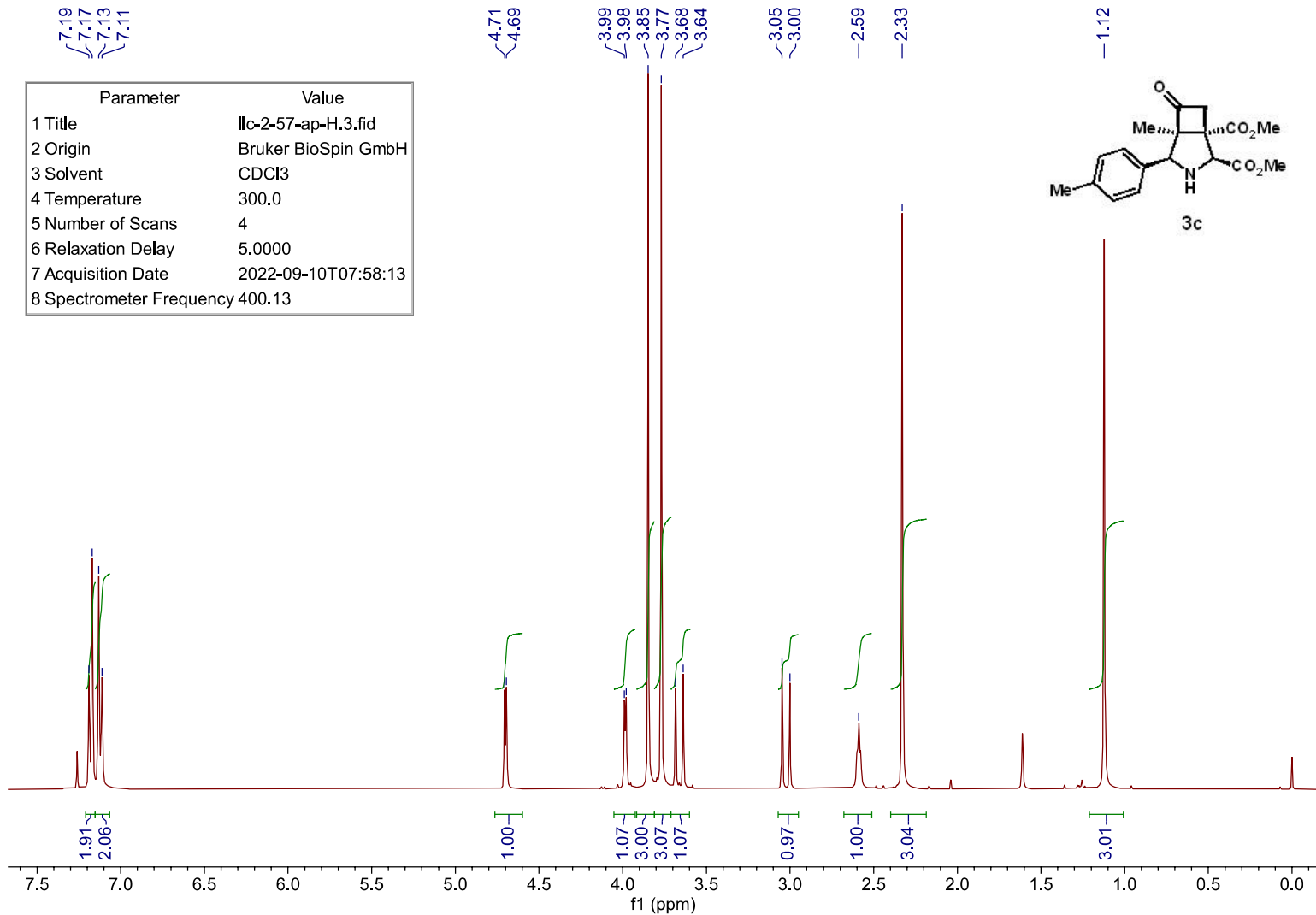
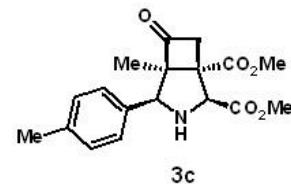


Parameter	Value
1 Title	llc-1-90-n-F.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.4
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-11-30T20:53:06
8 Spectrometer Frequency	376.46

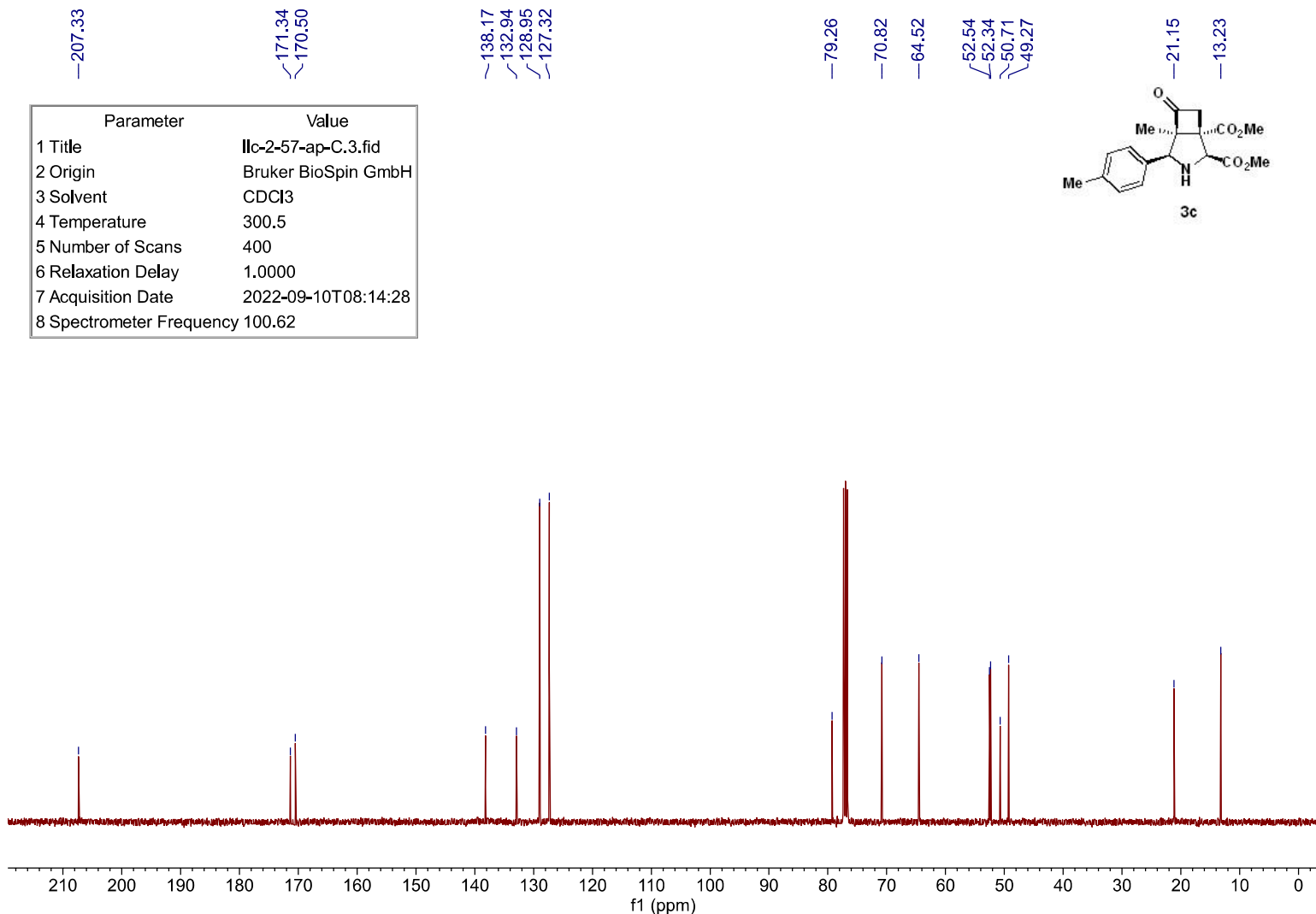
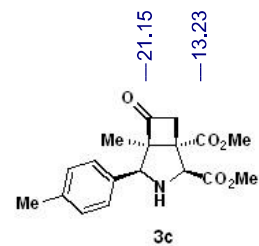
—62.54



Parameter	Value
1 Title	llc-2-57-ap-H.3.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300,0
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-10T07:58:13
8 Spectrometer Frequency	400.13



Parameter	Value
1 Title	llc-2-57-ap-C.3.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300,5
5 Number of Scans	400
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-10T08:14:28
8 Spectrometer Frequency	100.62



7.22
7.20
7.18
7.12
7.10
7.08

4.71
4.70

3.98
3.97
3.85
3.77
3.68
3.64

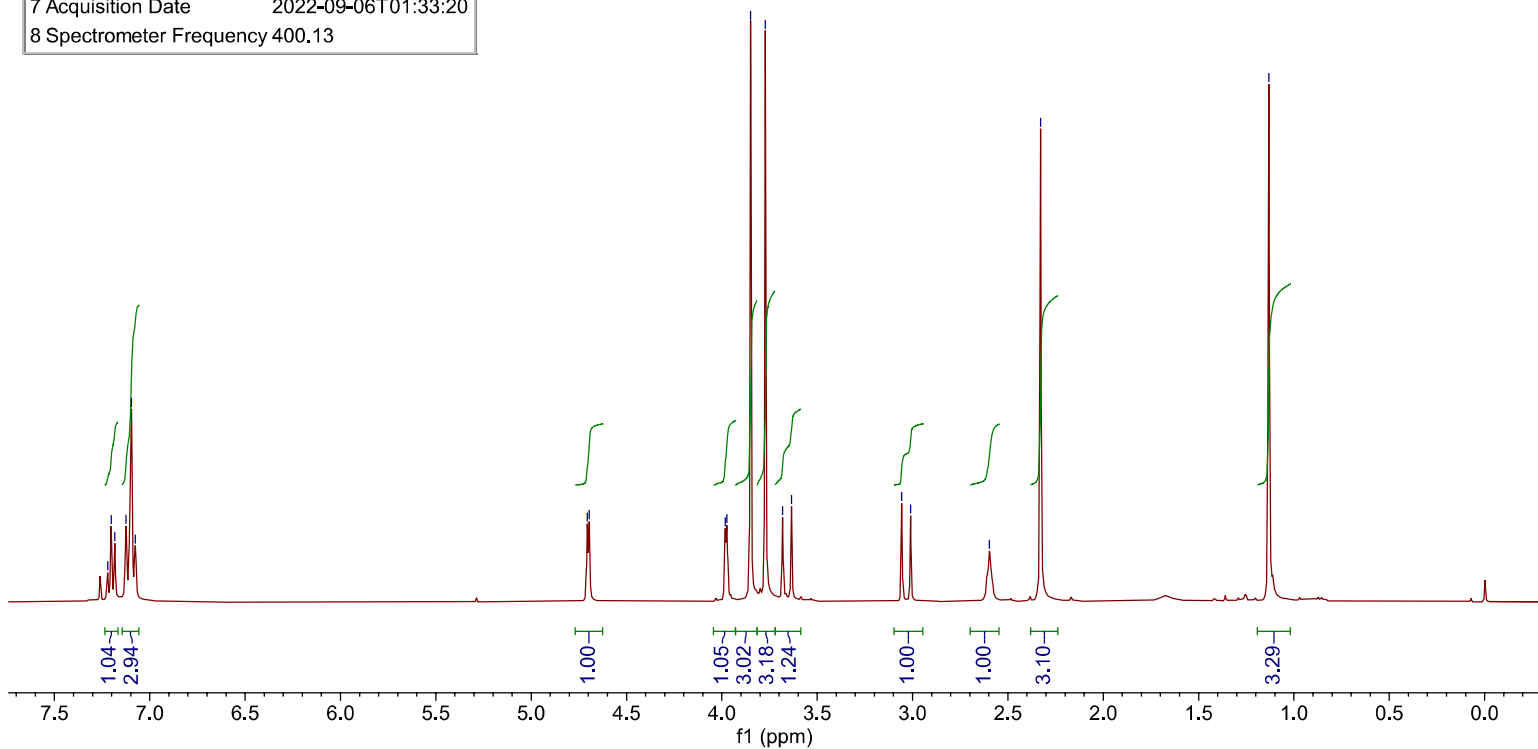
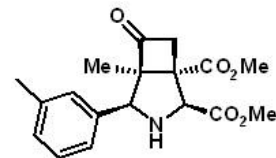
3.06
3.01

2.60

2.33

1.13

Parameter	Value
1 Title	c-2-54-ap-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-06T01:33:20
8 Spectrometer Frequency	400.13



207.09

171.29
170.47

137.76
135.90
129.22
128.03
124.53

79.23

70.90

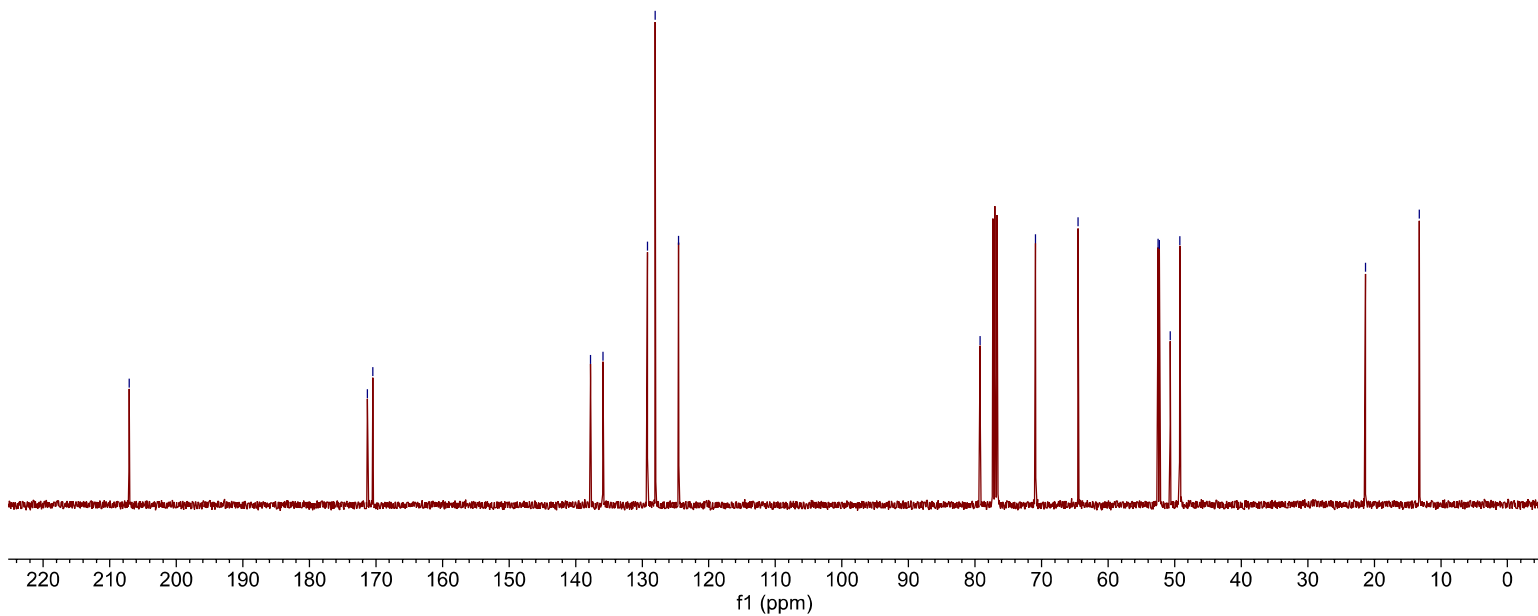
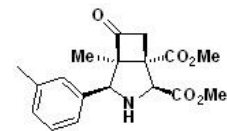
64.50

52.51
52.31
50.67
49.23

21.35

13.24

Parameter	Value
1 Title	c-2-55-b-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.5
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-06T01:54:24
8 Spectrometer Frequency	100.62



7.41
7.41
7.40
7.39
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.13
7.12

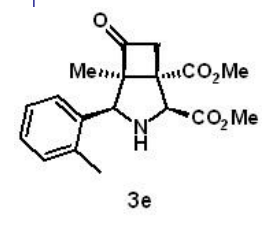
4.73
4.73
4.72
4.41

3.86
3.77
3.71
3.67

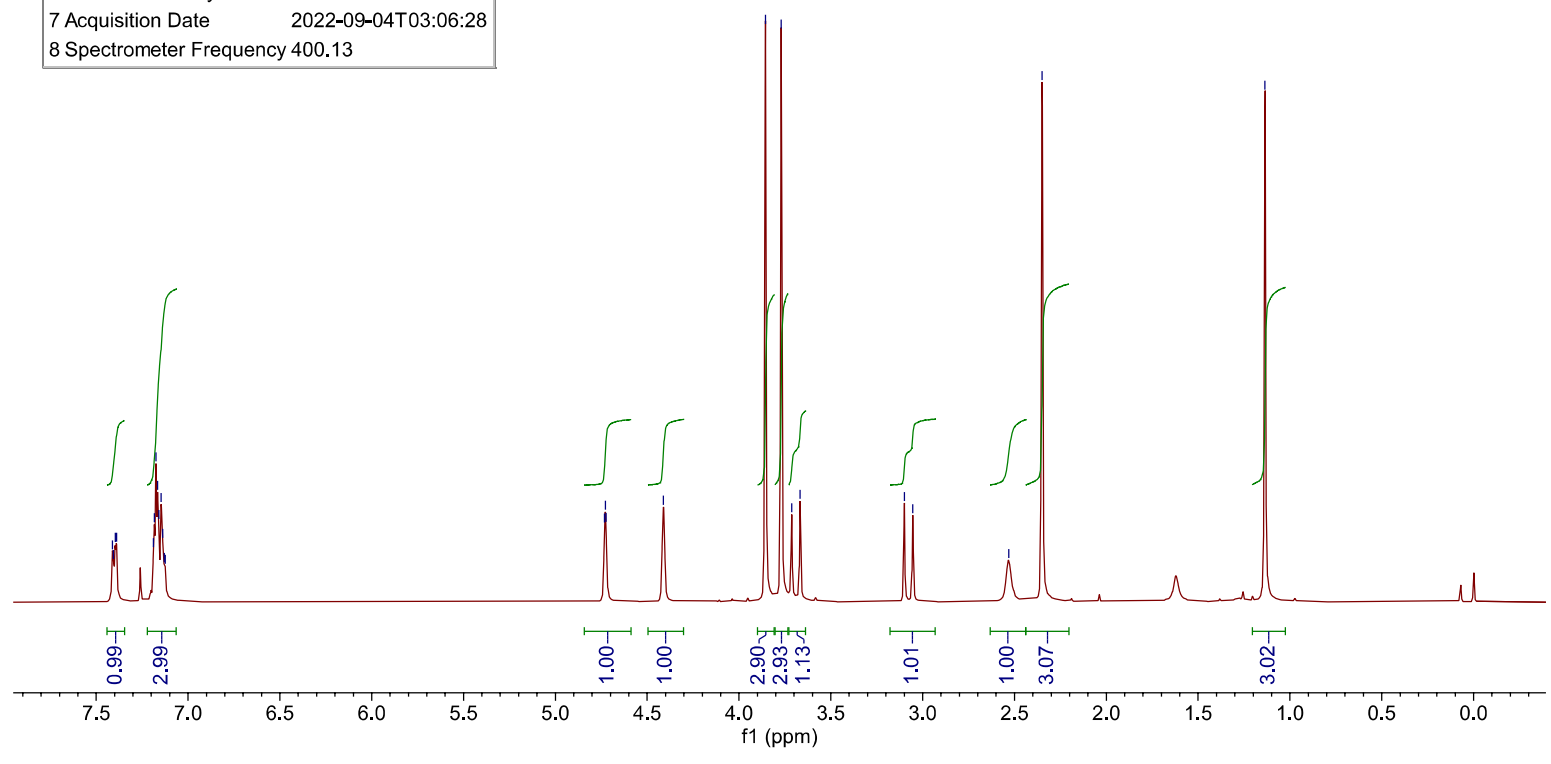
3.10
3.05

2.53
2.35

1.14



Parameter	Value
1 Title	LLC-2-52.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.2
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-04T03:06:28
8 Spectrometer Frequency	400.13



207.34

171.33
170.45

135.77
133.91
130.54
128.17
127.99
125.83

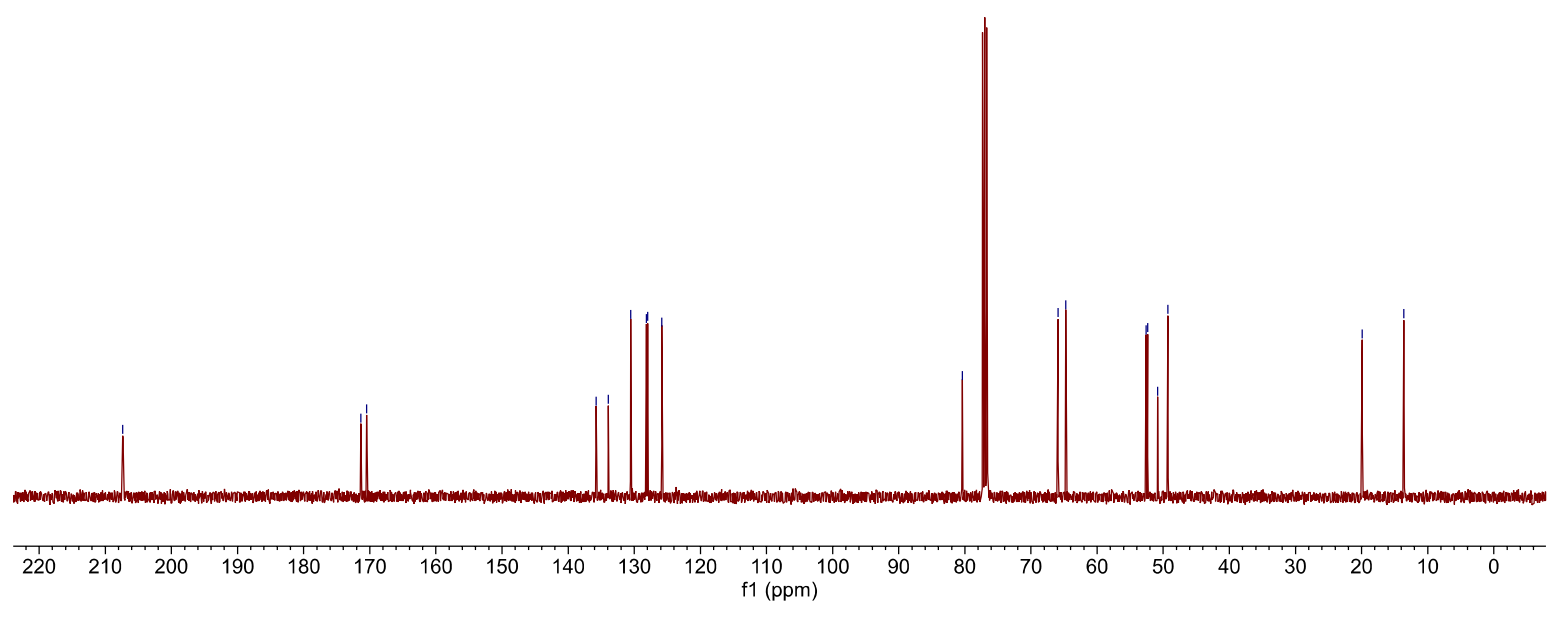
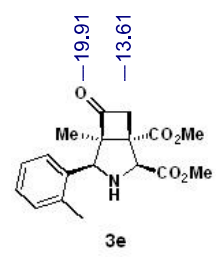
80.38

65.91
64.75

52.58
52.36
50.84
49.29

19.91
13.61

Parameter	Value
1 Title	LLC-2-52-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.7
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-04T04:15:03
8 Spectrometer Frequency	100.62



7.26
7.08
7.06
7.04
7.03
7.02
7.01
7.00

4.69
4.68

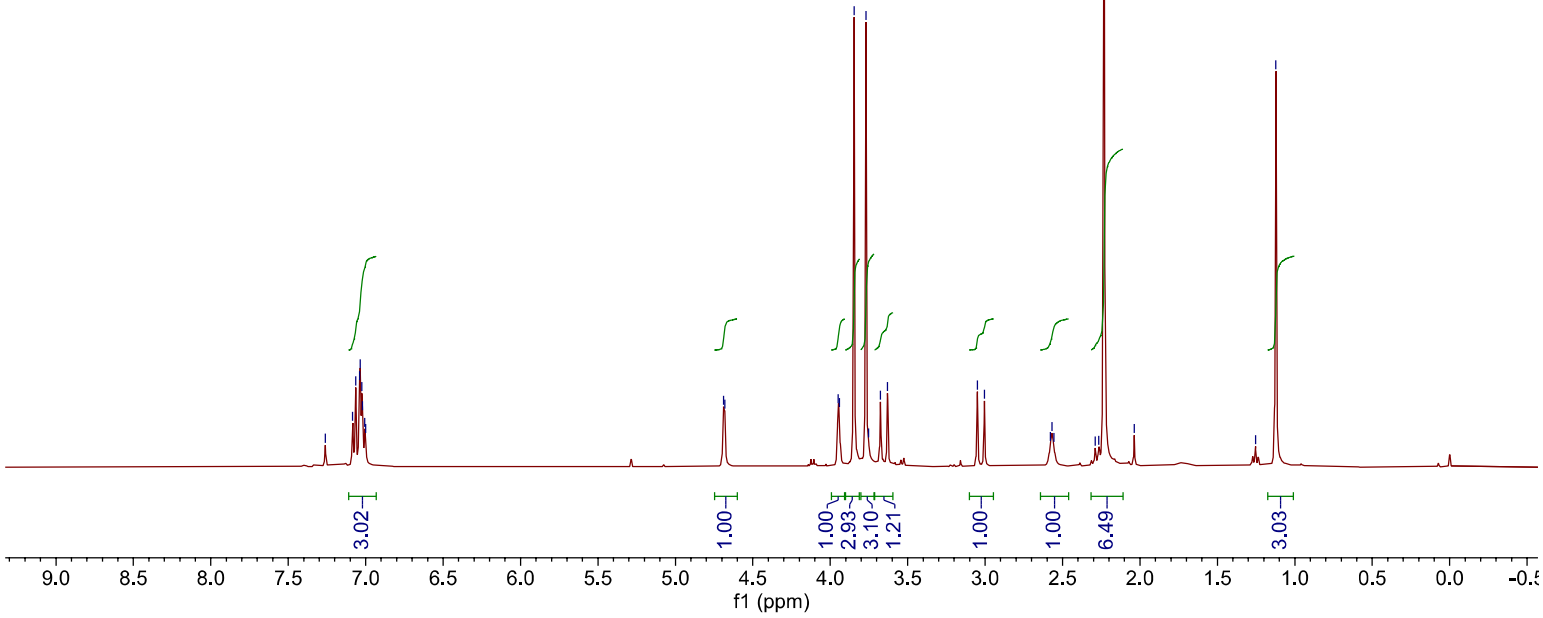
3.95
3.94
3.85
3.77
3.75
3.68
3.63

3.05
3.00

2.58
2.57
2.56
2.29
2.27
2.23
2.04

1.25
1.12

Parameter	Value
1 Title	llc-1-171.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.8
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-07-22T01:51:02
8 Spectrometer Frequency	400.13



207.37

171.34
170.53

136.78
136.35
133.30
129.47
128.58
124.83

79.27

70.82

64.49

52.51

52.32

50.70

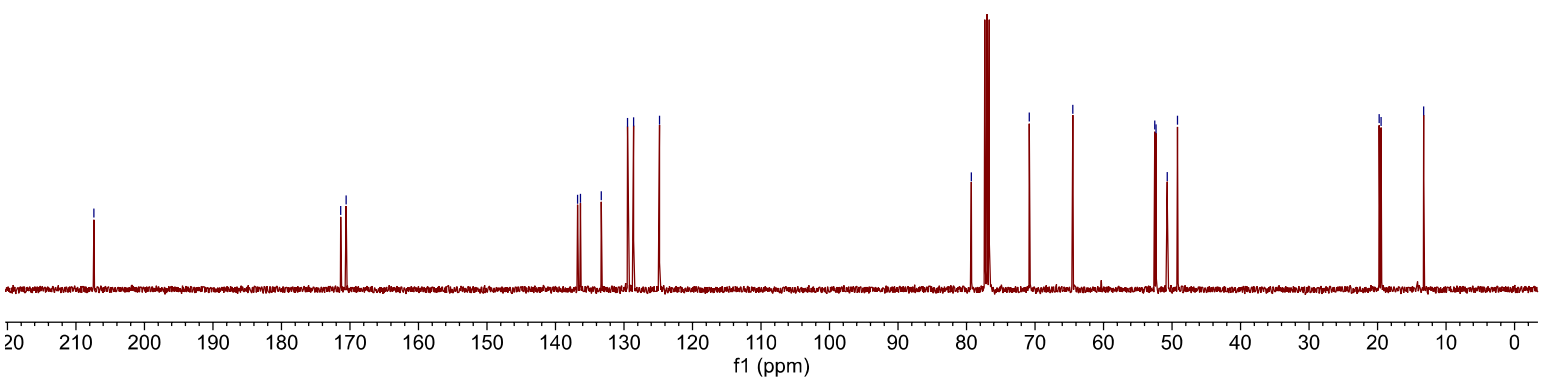
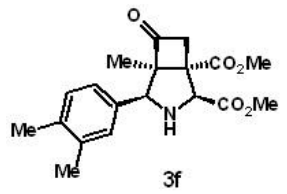
49.18

19.73

19.46

13.25

Parameter	Value
1 Title	llc-1-171-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.3
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-07-22T02:38:43
8 Spectrometer Frequency	100.62



7.39
7.38
7.36
7.15
7.14
7.13
7.12

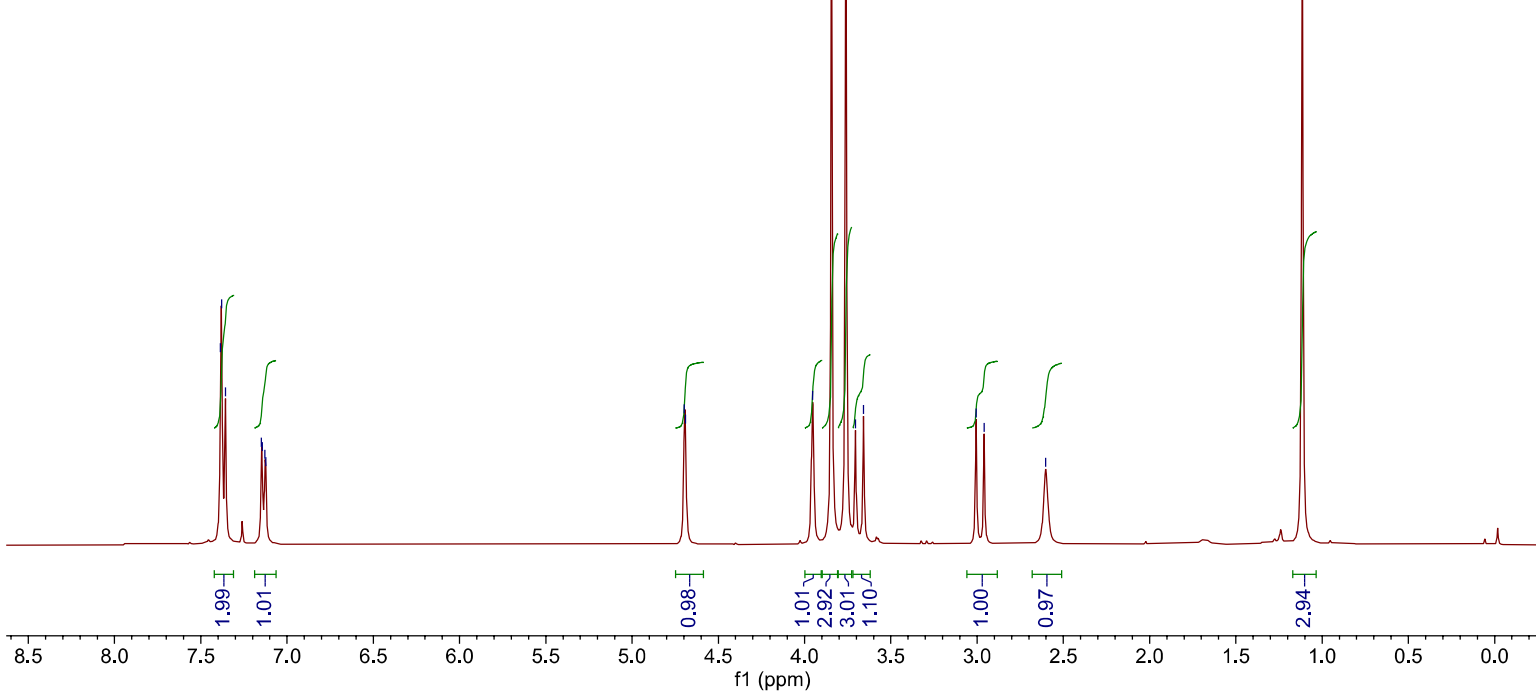
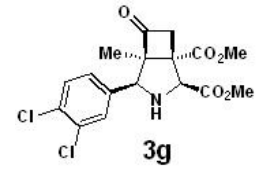
4.70
4.69

3.95
3.84
3.76
3.71
3.66

3.01
2.96
2.60

1.12

Parameter	Value
1 Title	LLC-1-94-2,1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.0
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2021-12-14T16:28:17
8 Spectrometer Frequency	400.13



206.74

170.96
170.11

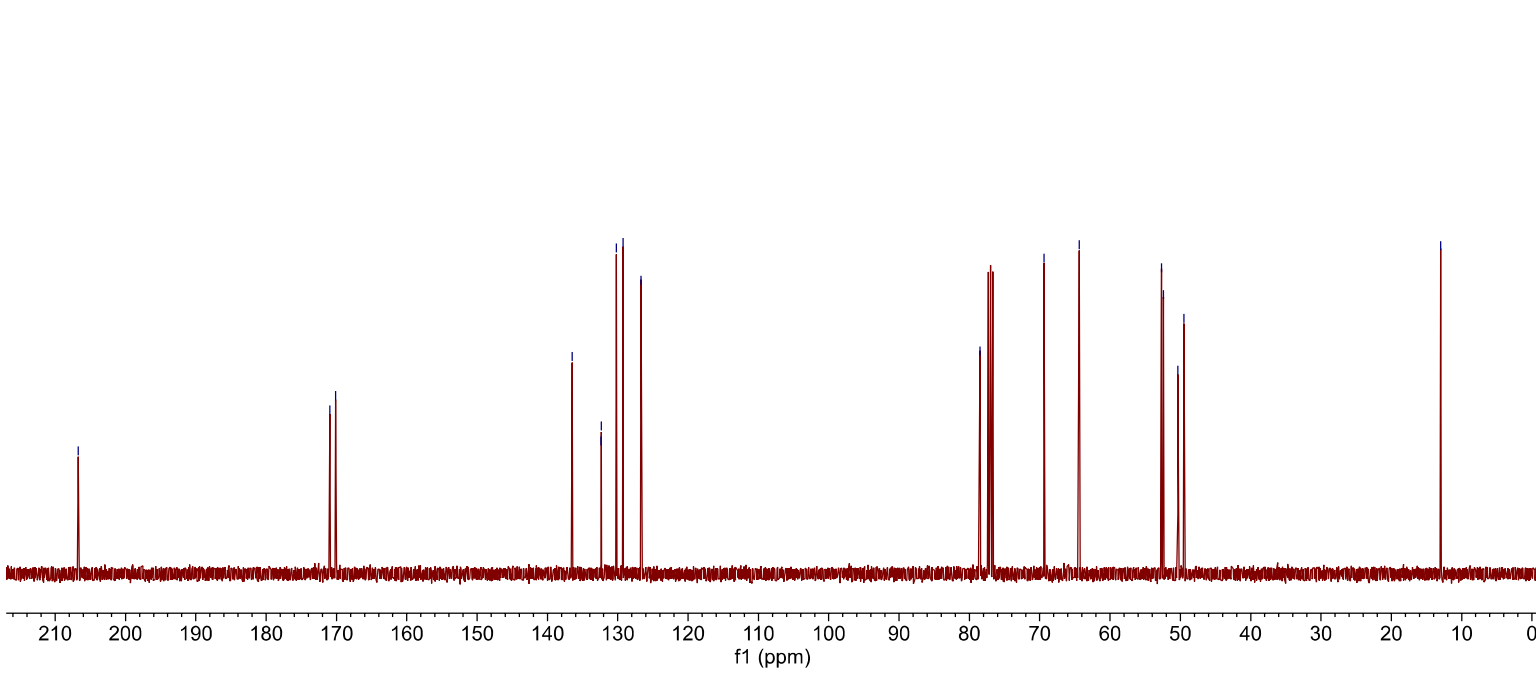
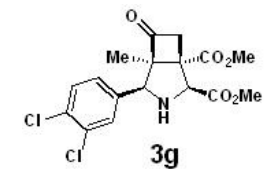
136.48
132.39
132.36
130.18
129.26
126.68

78.50
69.39
64.39

52.68
52.43
50.36
49.47

13.01

Parameter	Value
1 Title	LLC-1-94-2-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.6
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-12-14T16:40:45
8 Spectrometer Frequency	100.62



6.94
6.89

4.69

3.94
3.86
3.85
3.77
3.68
3.63

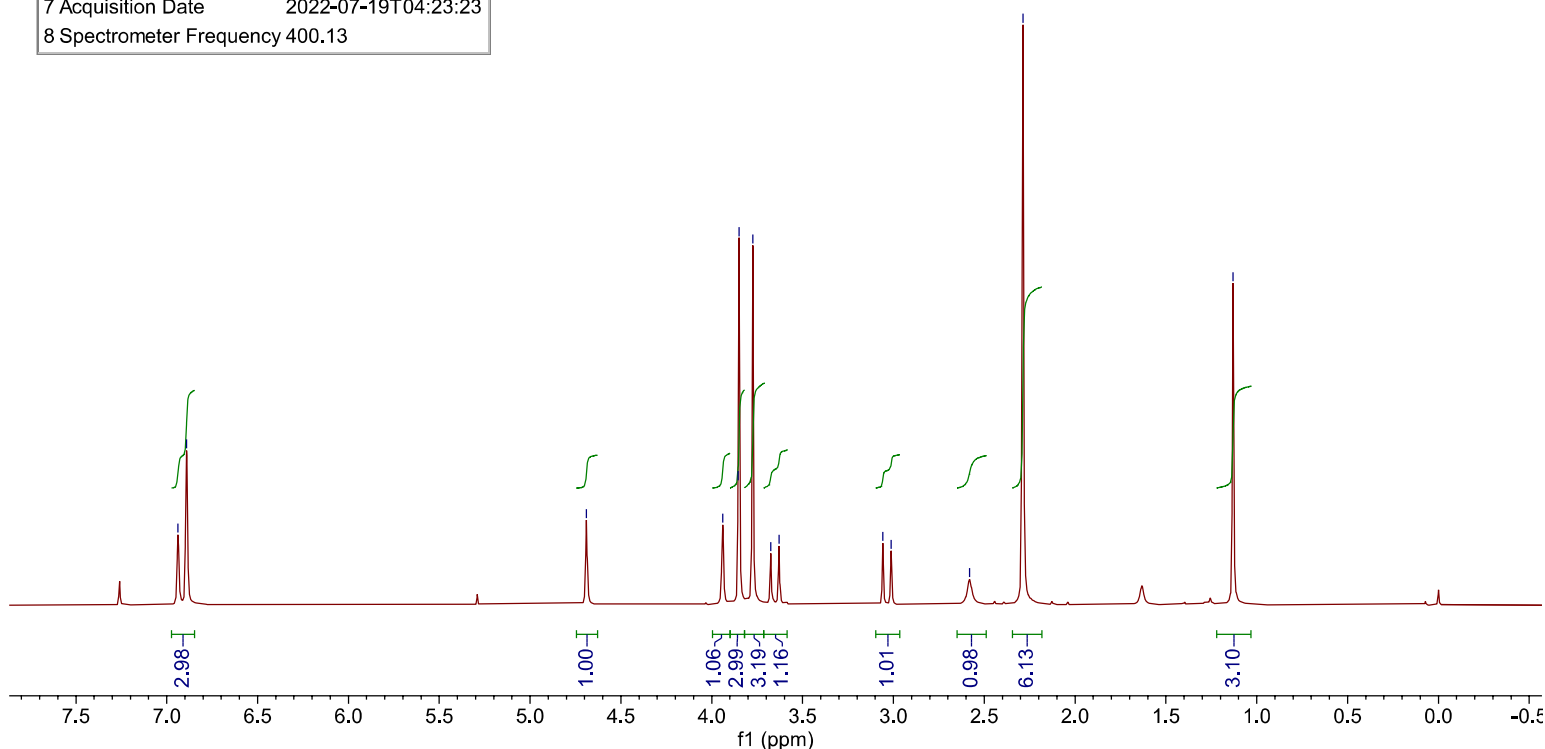
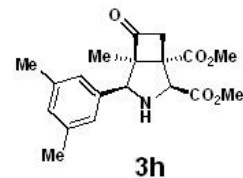
3.06
3.01

2.58

2.29

1.13

Parameter	Value
1 Title	llc-1-154-ap.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.6
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-07-19T04:23:23
8 Spectrometer Frequency	400.13



207.18

171.35
170.56

137.66
135.84
130.22
125.21

79.31

70.95

64.52

52.54

52.36

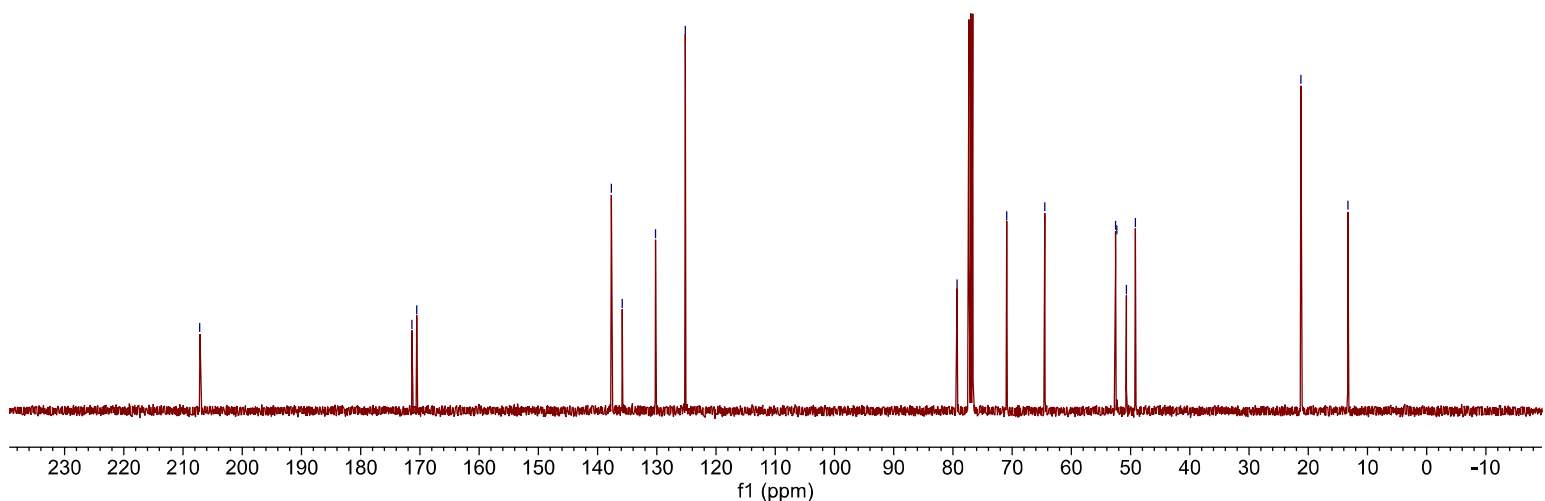
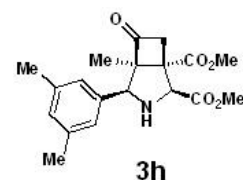
50.72

49.22

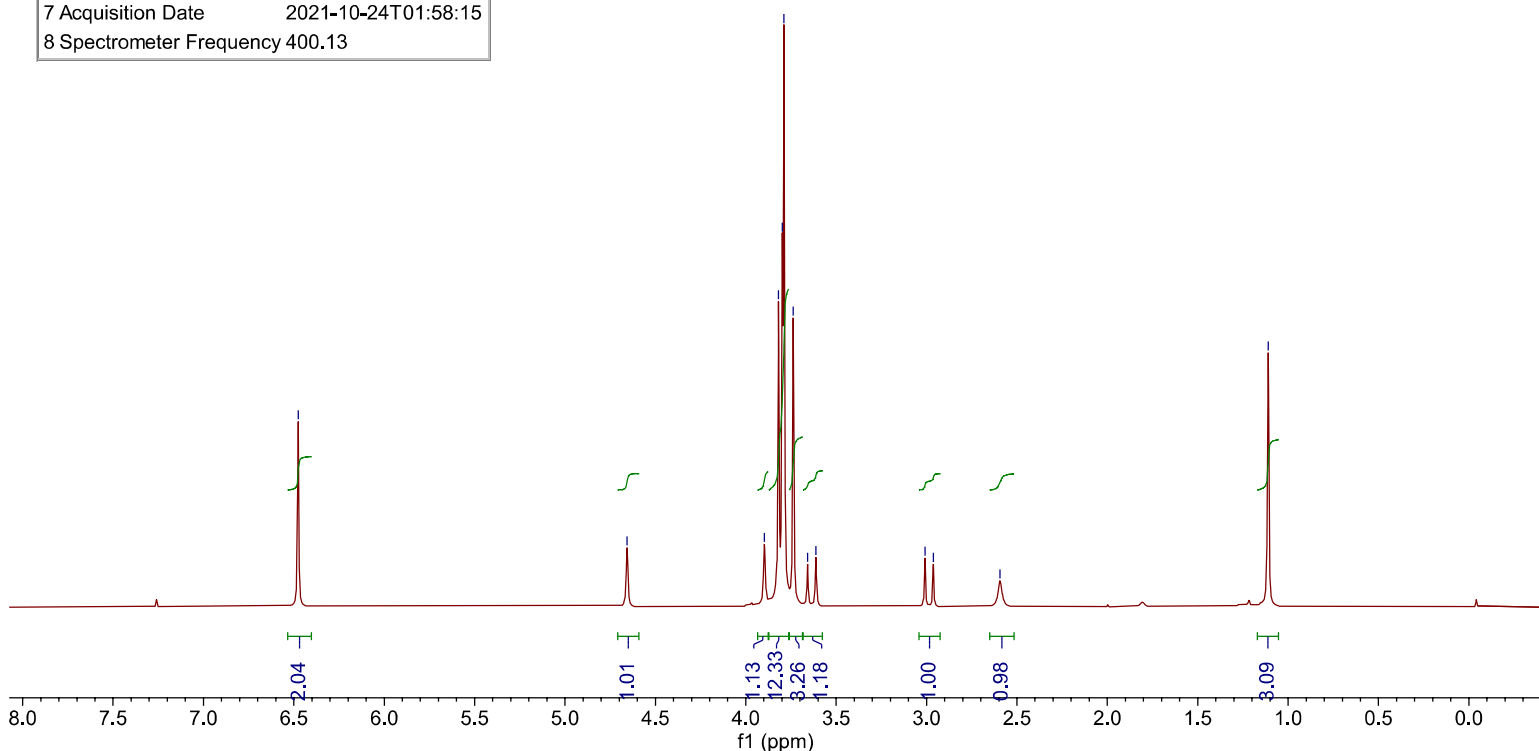
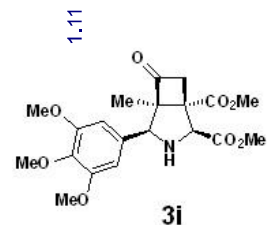
21.26

13.32

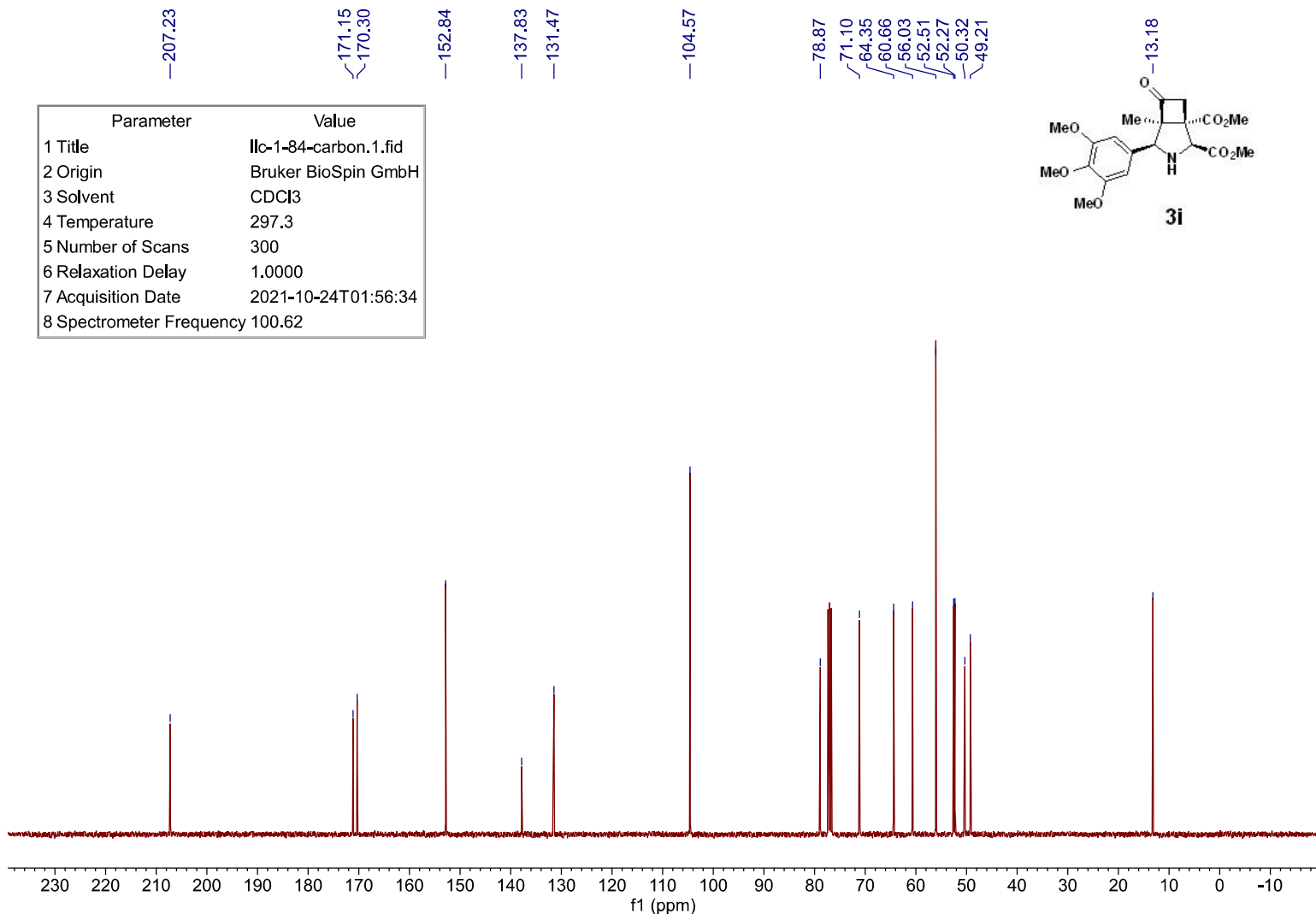
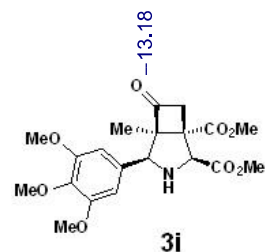
Parameter	Value
1 Title	llc-1-154-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.4
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-07-19T15:13:01
8 Spectrometer Frequency	100.62

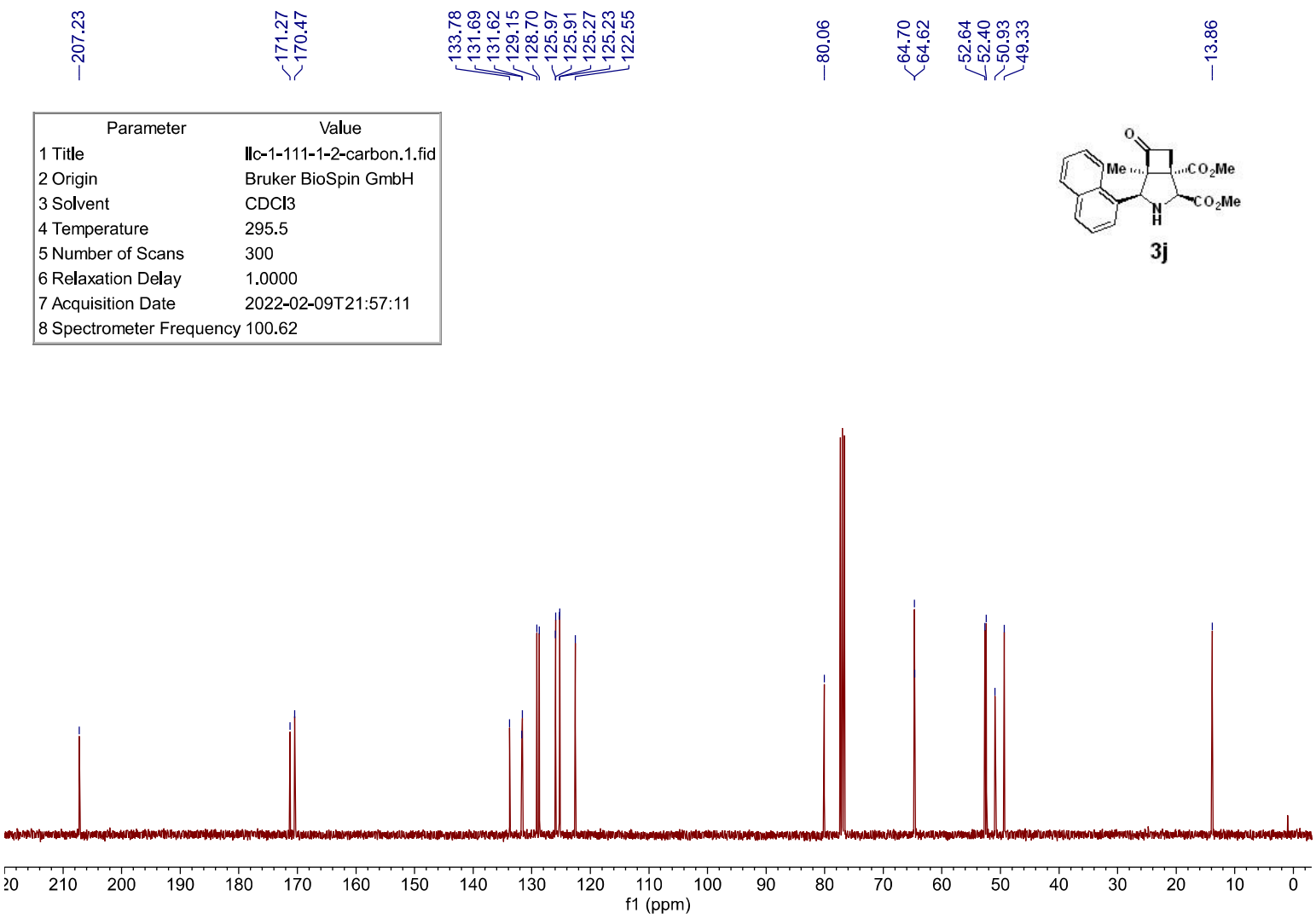
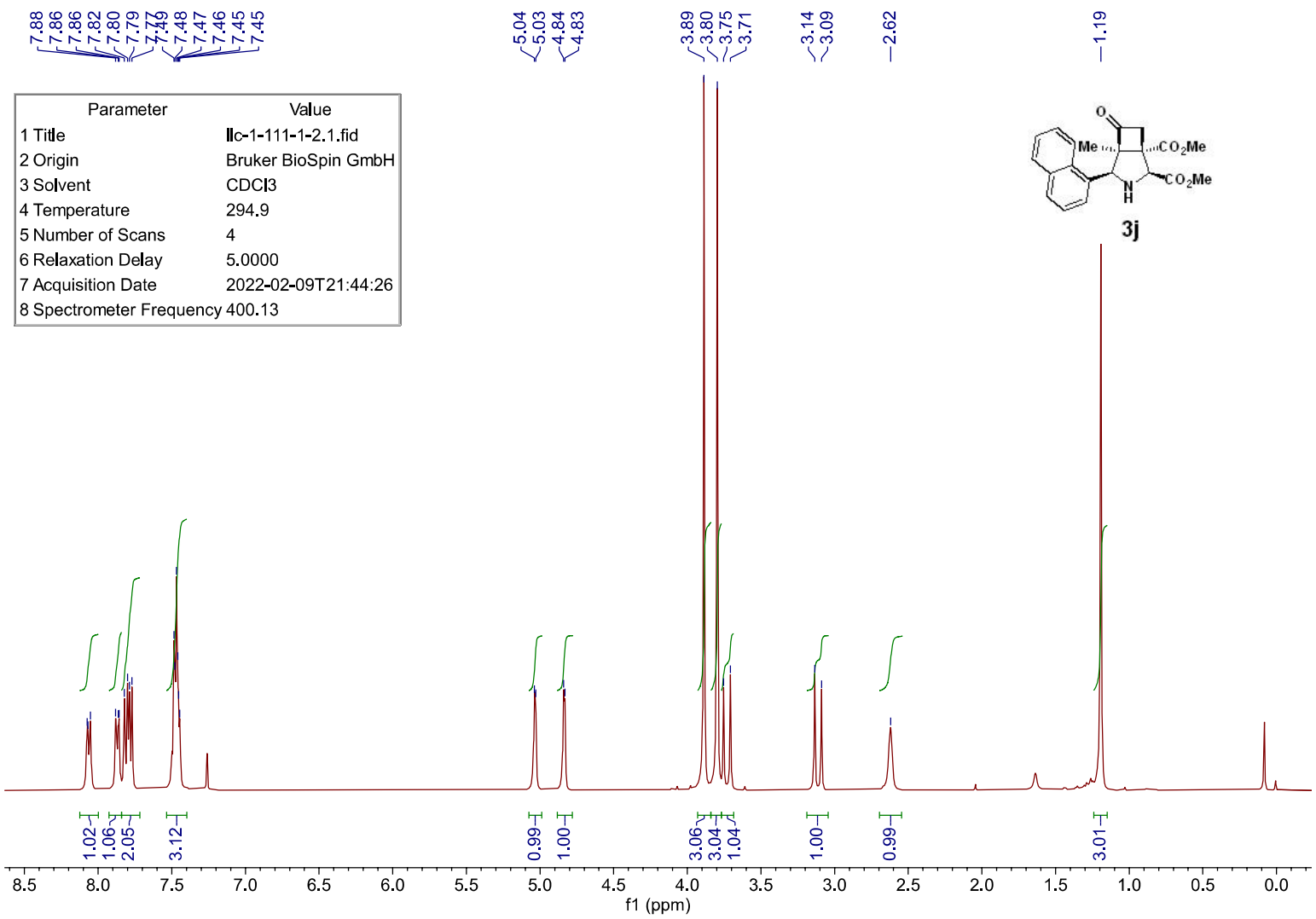


Parameter	Value
1 Title	llc-1-84-r2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.8
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2021-10-24T01:58:15
8 Spectrometer Frequency	400.13



Parameter	Value
1 Title	llc-1-84-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.3
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-24T01:56:34
8 Spectrometer Frequency	100.62





7.38
7.37
7.37
7.26

6.35
6.34
6.33
6.33

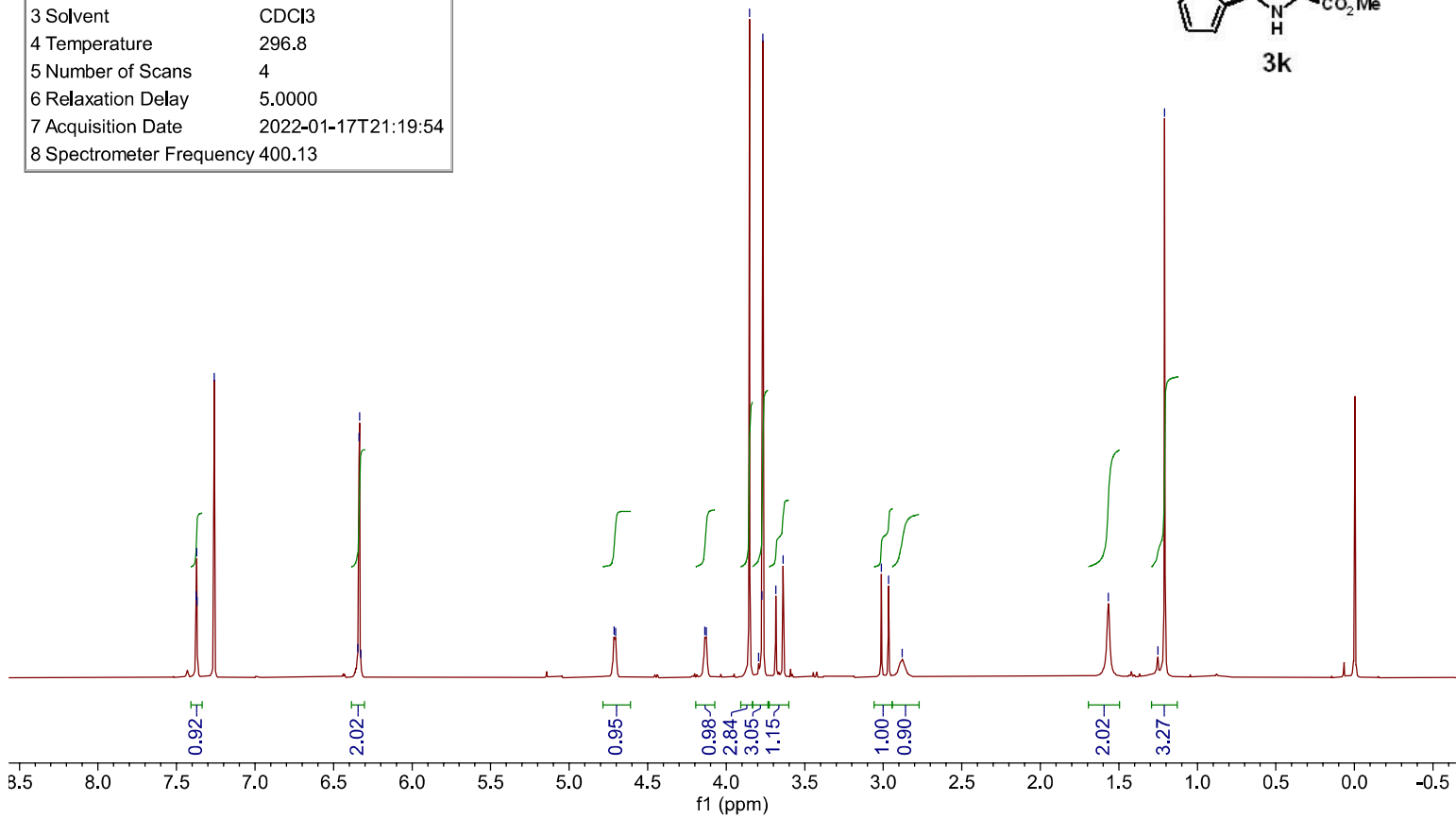
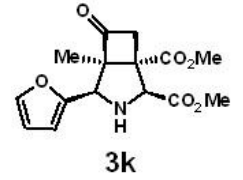
4.71
4.70

4.14
4.13
3.85
3.79
3.77
3.77
3.68
3.64
3.01
2.97
2.88

1.57

1.25
1.21

Parameter	Value
1 Title	llc-1-100-p2-1.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.8
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-01-17T21:19:54
8 Spectrometer Frequency	400.13



206.02

170.94
170.13

149.57

142.57

110.35
107.72

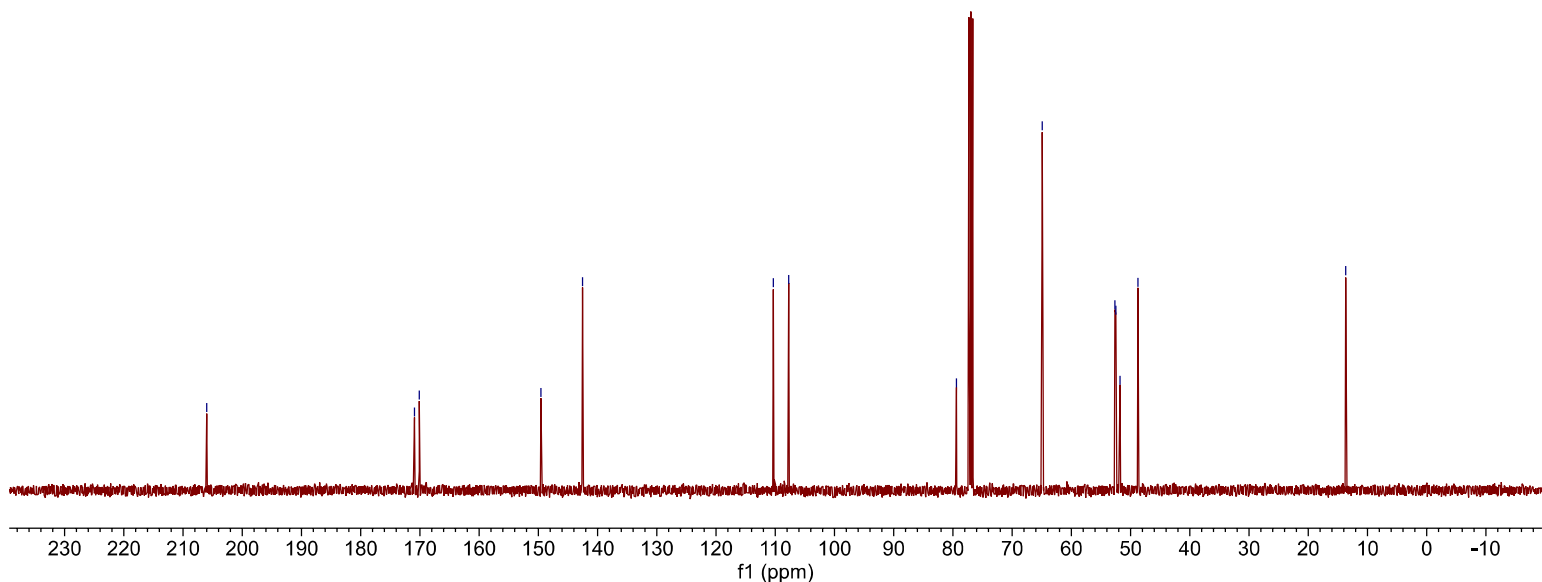
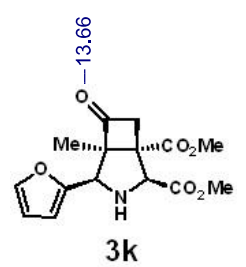
79.40

64.92

52.67
52.50
51.79
48.78

13.66

Parameter	Value
1 Title	llc-1-100-p1-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.7
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-01-16T01:26:42
8 Spectrometer Frequency	100.62



7.26
7.24
7.24
7.23
7.23
7.02
7.01
7.01
7.00
7.00
6.99
6.98
6.97

4.70
4.69

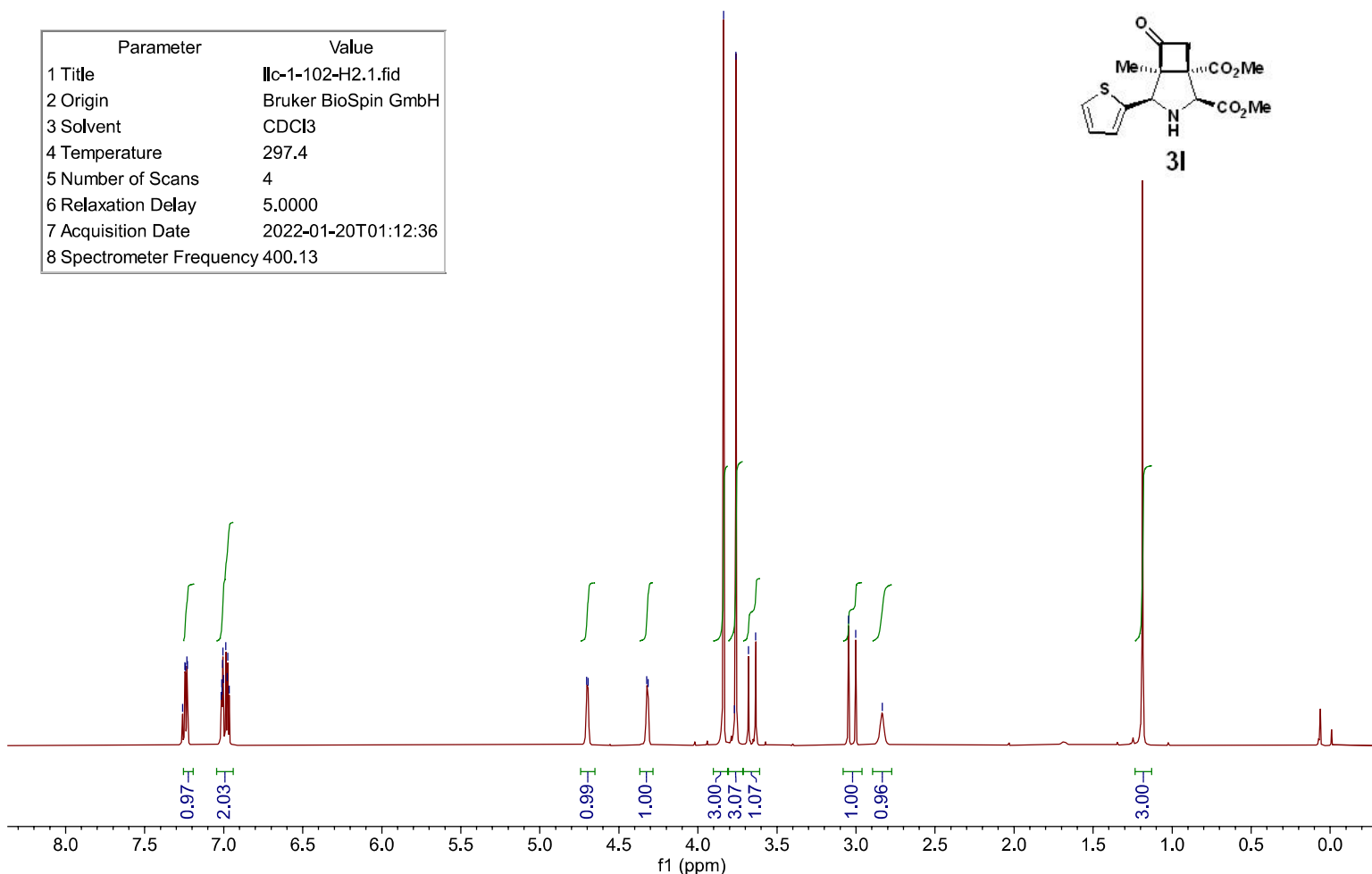
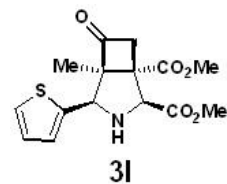
4.32
4.32

3.84
3.77
3.76
3.68
3.63

3.05
3.00
2.83

1.19

Parameter	Value
1 Title	llc-1-102-H2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.4
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-01-20T01:12:36
8 Spectrometer Frequency	400.13



206.45

171.03
170.01

139.54

126.77
125.05
124.88

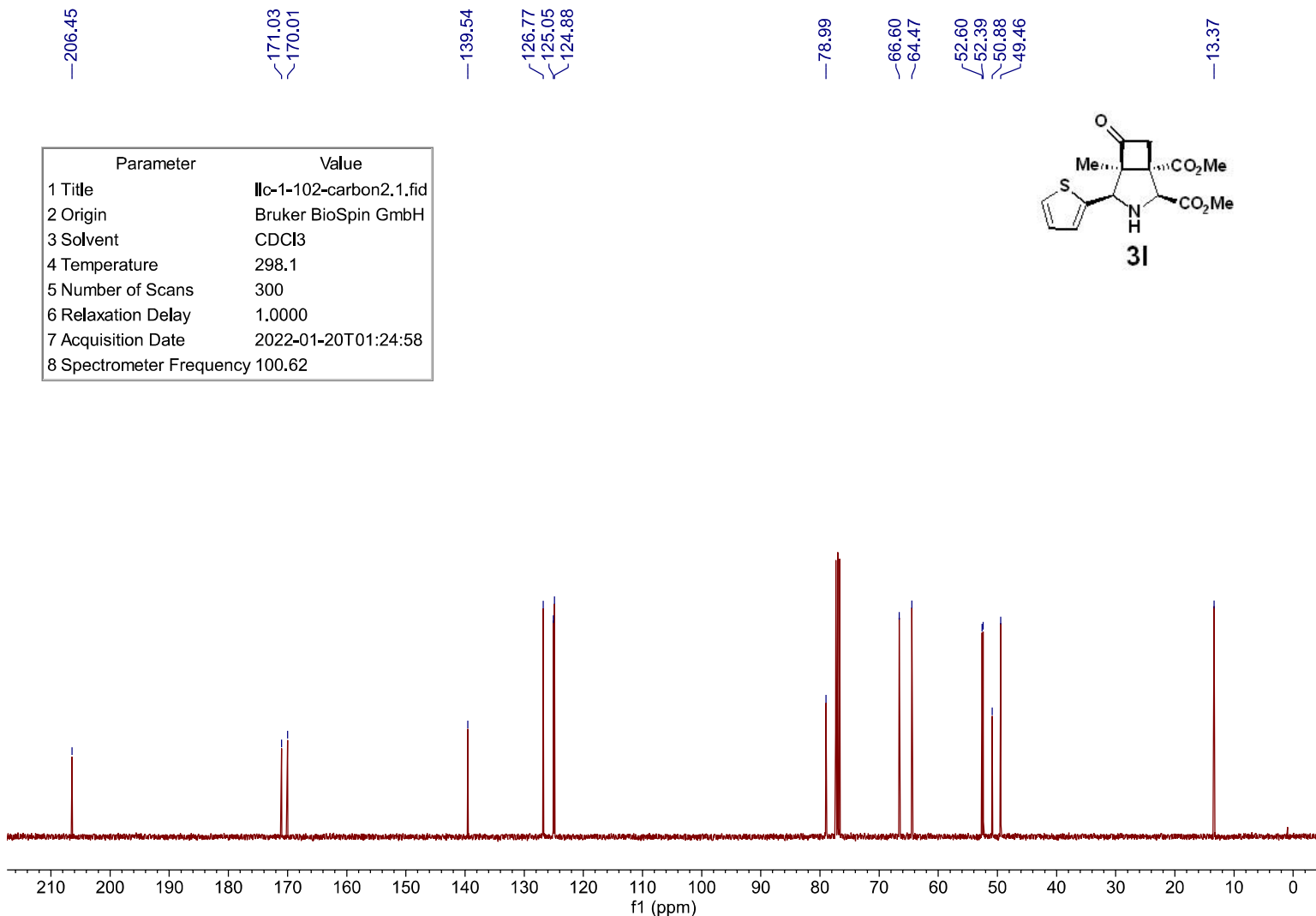
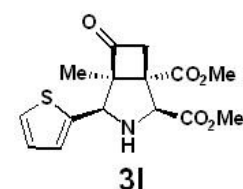
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66.60
64.47

52.60
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50.88
49.46

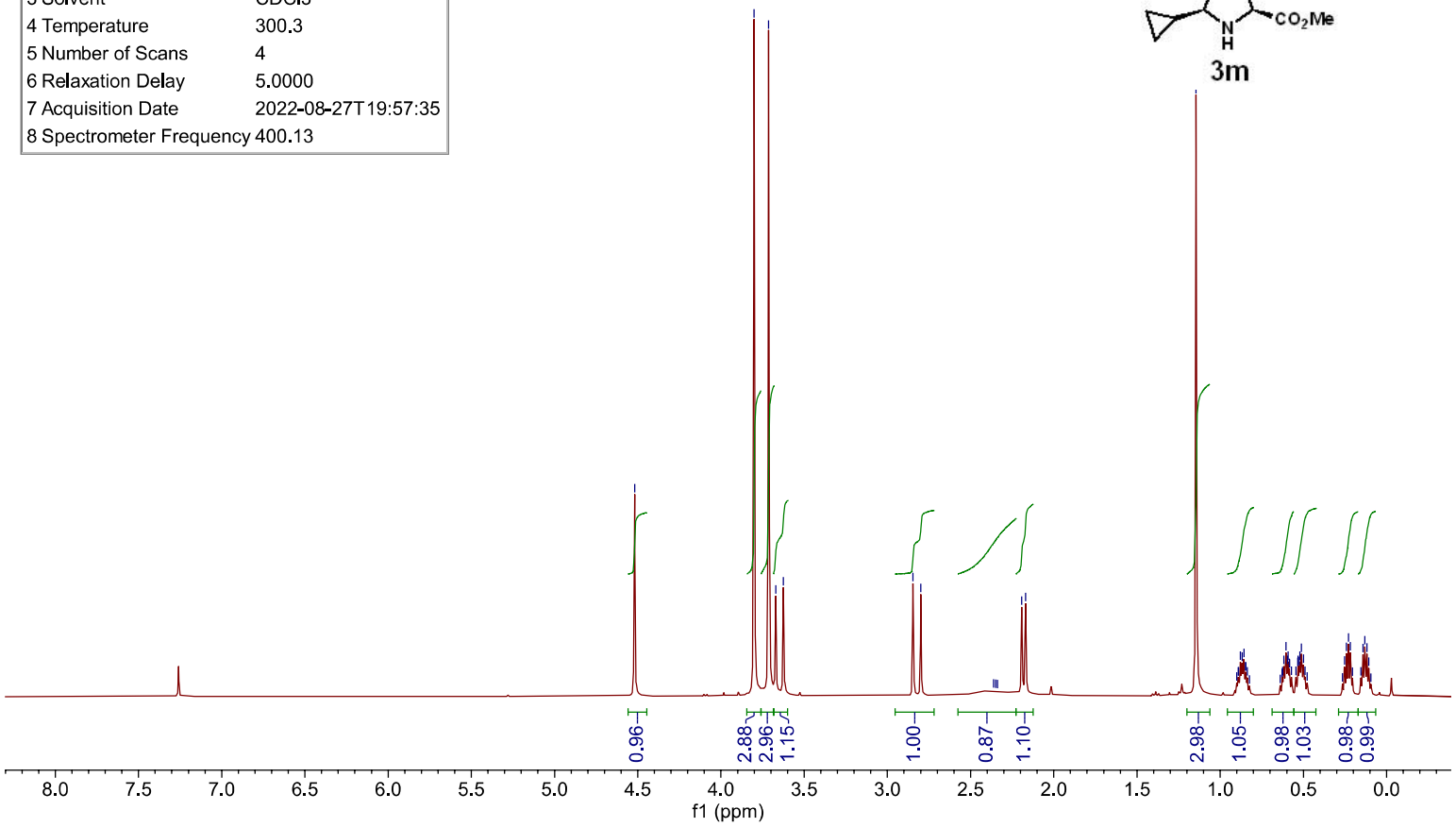
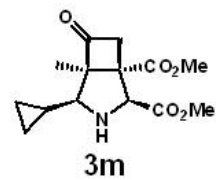
13.37

Parameter	Value
1 Title	llc-1-102-carbon2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.1
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-01-20T01:24:58
8 Spectrometer Frequency	100.62



4.52
3.80
3.71
3.67
3.62
2.85
2.80
2.36
2.35
2.34
2.19
2.17
1.15
0.90
0.89
0.89
0.88
0.87
0.86
0.85
0.85
0.84
0.82
0.64
0.63
0.62
0.60
0.60
0.59
0.58
0.57
0.54
0.53
0.53
0.52
0.51
0.50
0.49
0.48
0.27
0.25
0.24
0.23
0.22
0.20
0.15
0.14
0.13
0.12
0.11
0.09

Parameter	Value
1 Title	llc-2-38-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.3
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-08-27T19:57:35
8 Spectrometer Frequency	400.13



208.82

171.27
170.55

79.10

72.48

64.53

52.50

52.32

52.07

48.57

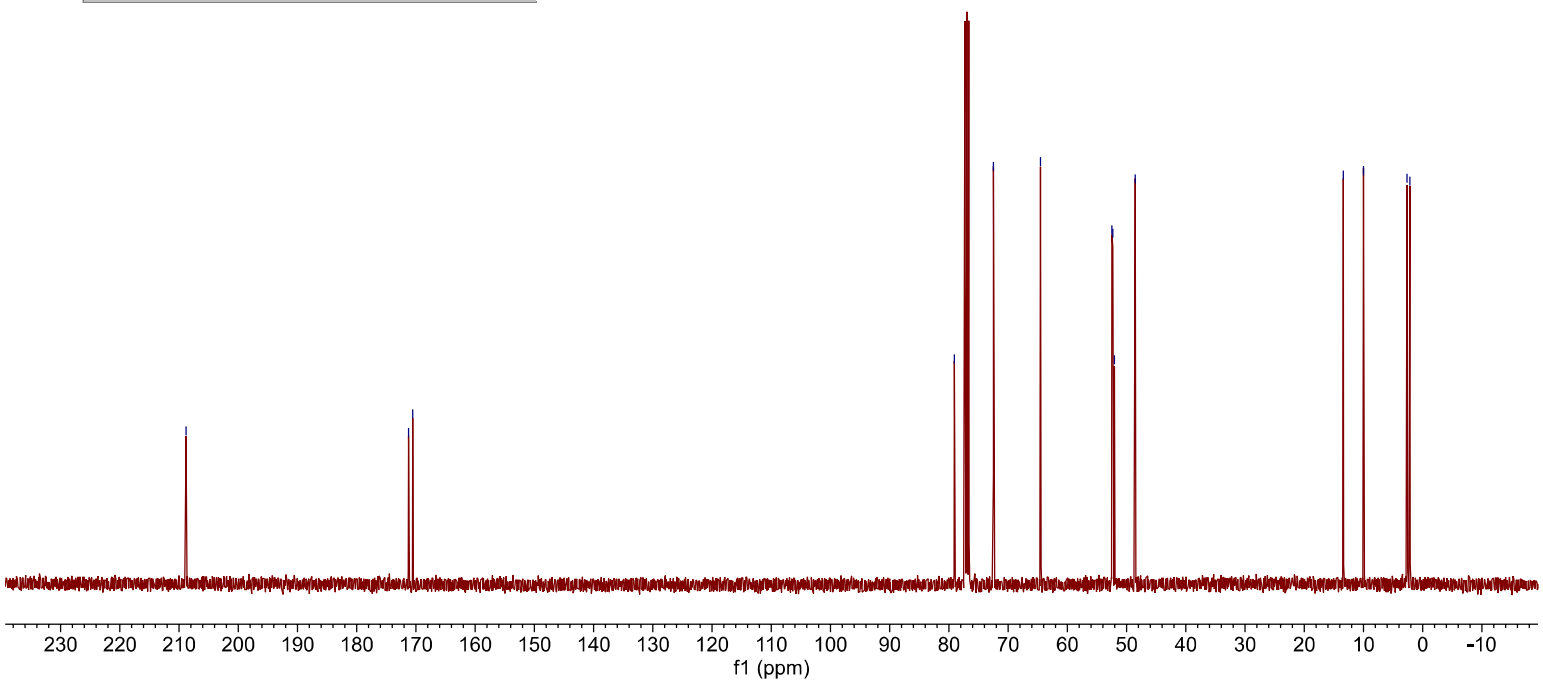
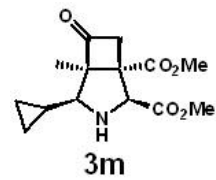
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10.03

2.65

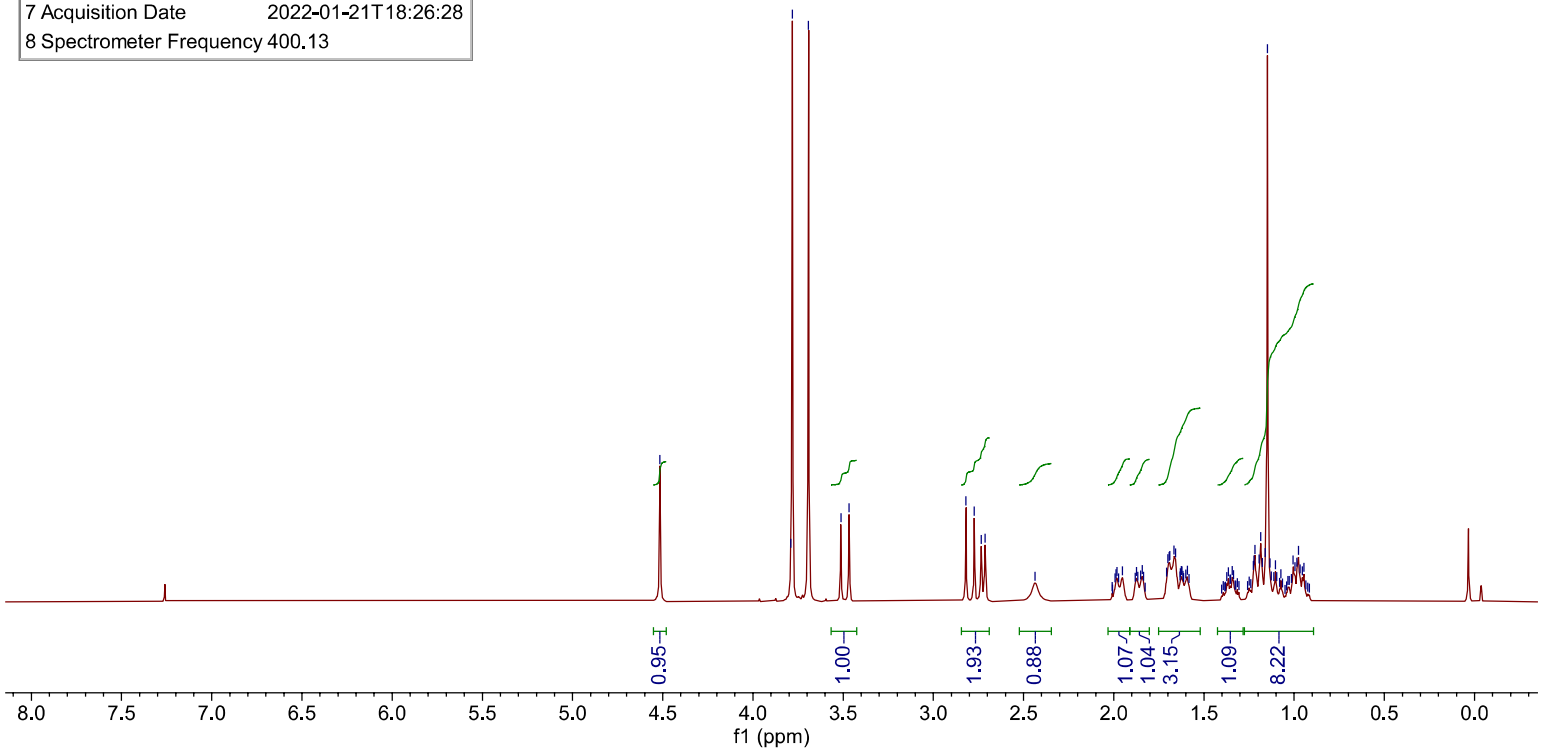
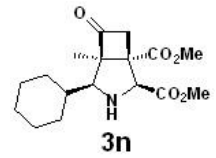
2.17

Parameter	Value
1 Title	llc-2-38-Carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.8
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-08-27T20:52:07
8 Spectrometer Frequency	100.62



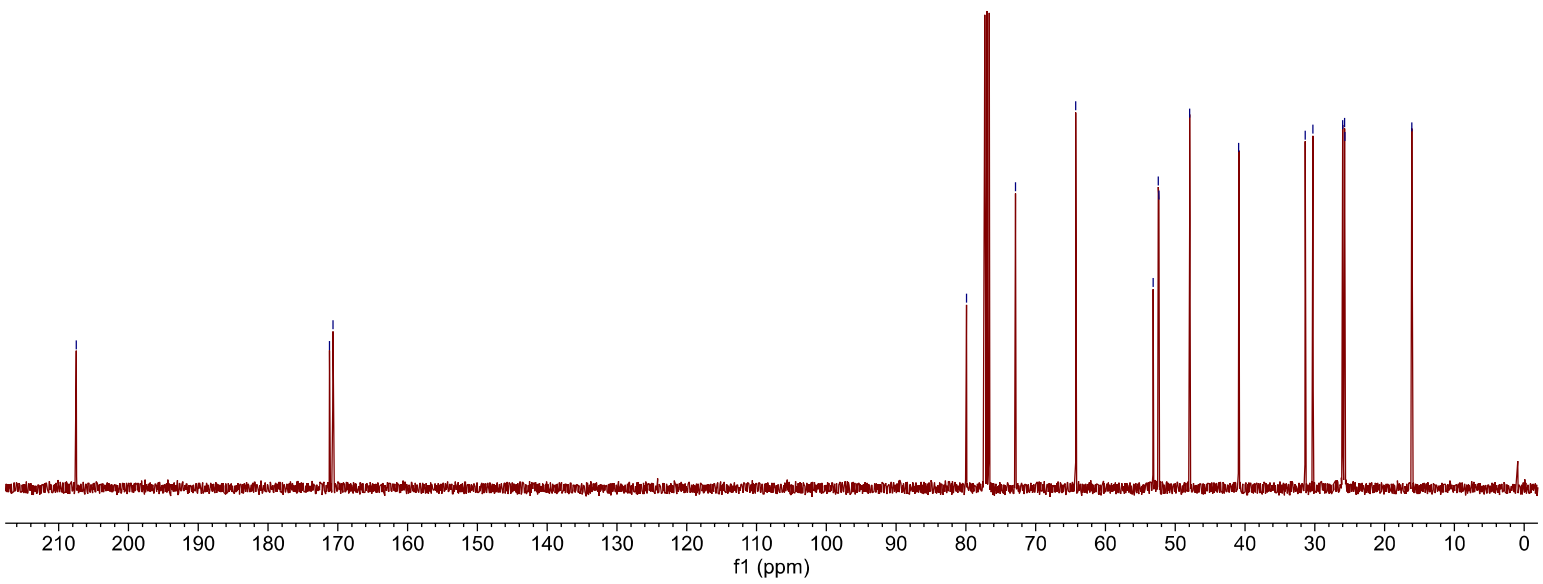
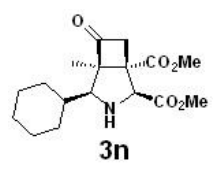
4.52
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3.47
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2.77
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2.71
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2.44
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1.99
1.98
1.97
1.95
1.88
1.87
1.87
1.85
1.84
1.83
1.71
1.70
1.69
1.69
1.67
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1.63
1.63
1.62
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1.22
1.19
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1.18
1.18
1.16
1.15
1.13
1.13
1.11
1.10
1.10
1.07
1.07
1.03
1.03
1.01
1.01
1.00
1.00
0.98
0.98
0.97
0.95

Parameter	Value
1 Title	llc-1-108-H2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.2
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-01-21T18:26:28
8 Spectrometer Frequency	400.13

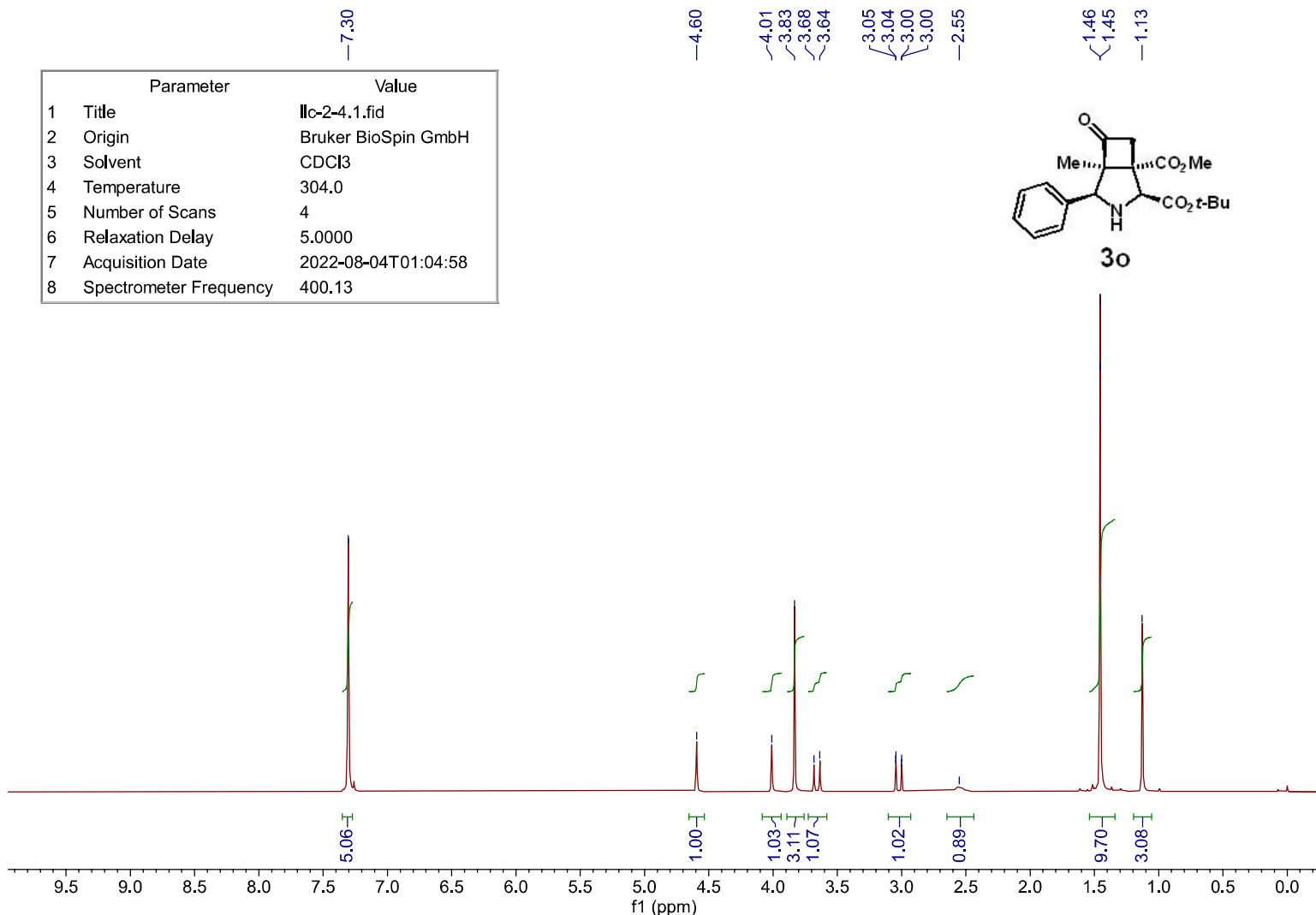
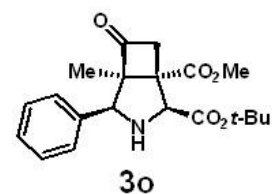


207.48
171.20
170.69
79.93
72.91
64.26
53.17
52.45
47.95
40.91
31.38
30.27
26.00
25.75
25.69
16.11

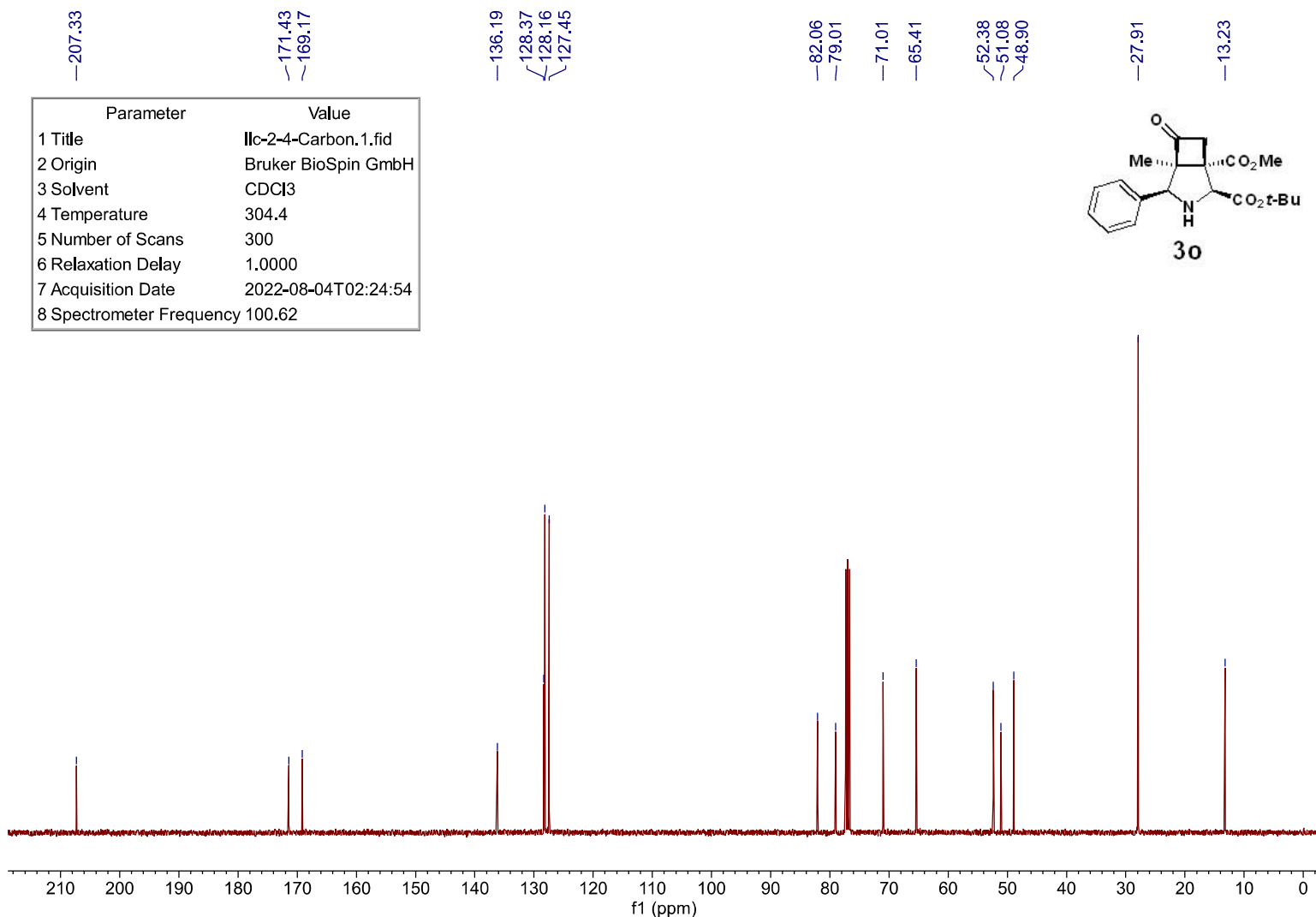
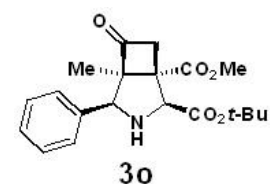
Parameter	Value
1 Title	llc-1-107-CARBON.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.7
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-01-21T18:21:54
8 Spectrometer Frequency	100.62



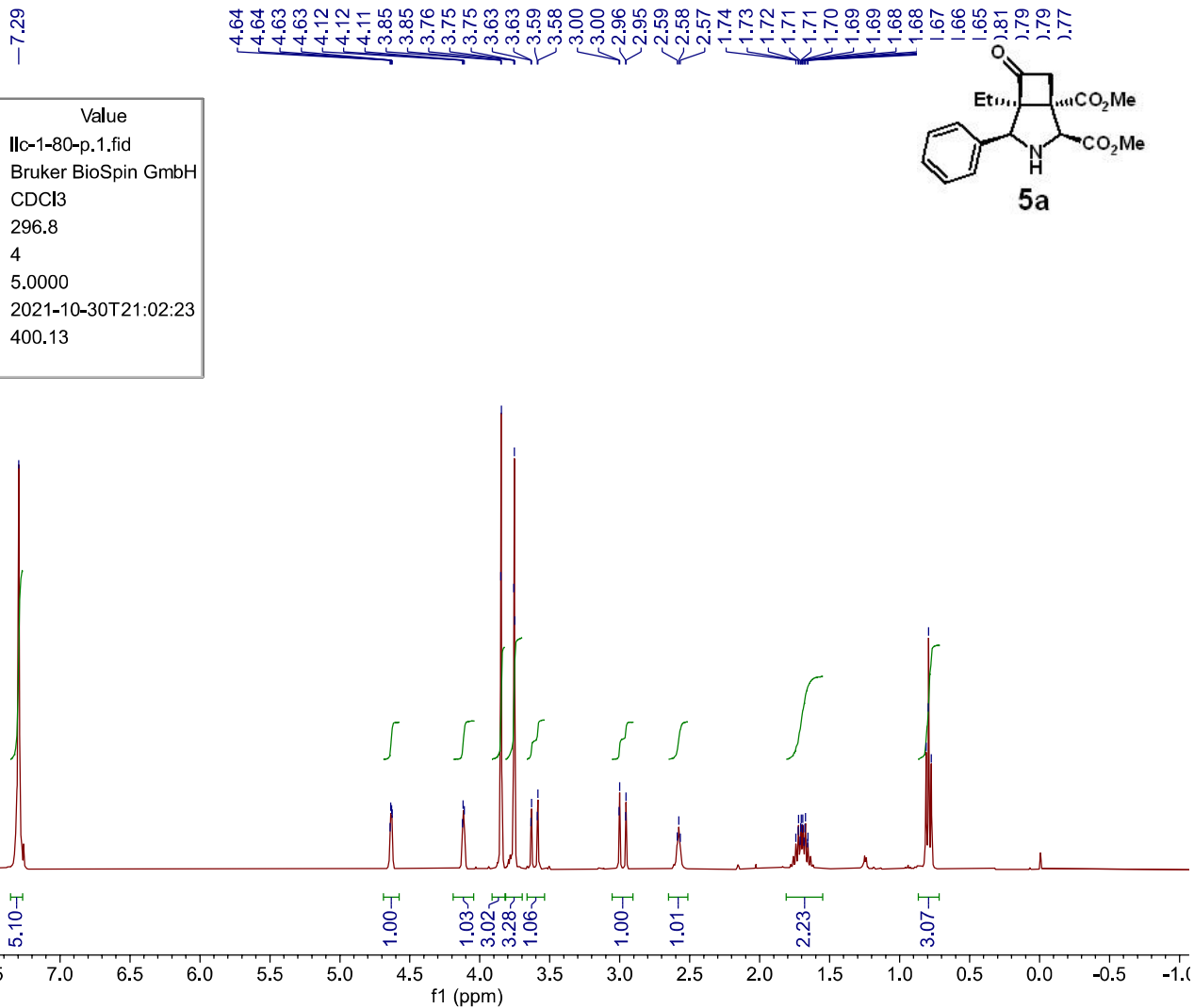
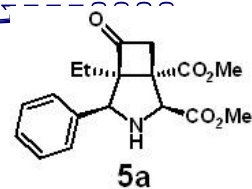
Parameter	Value
1 Title	llc-2-4.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	304.0
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-08-04T01:04:58
8 Spectrometer Frequency	400.13



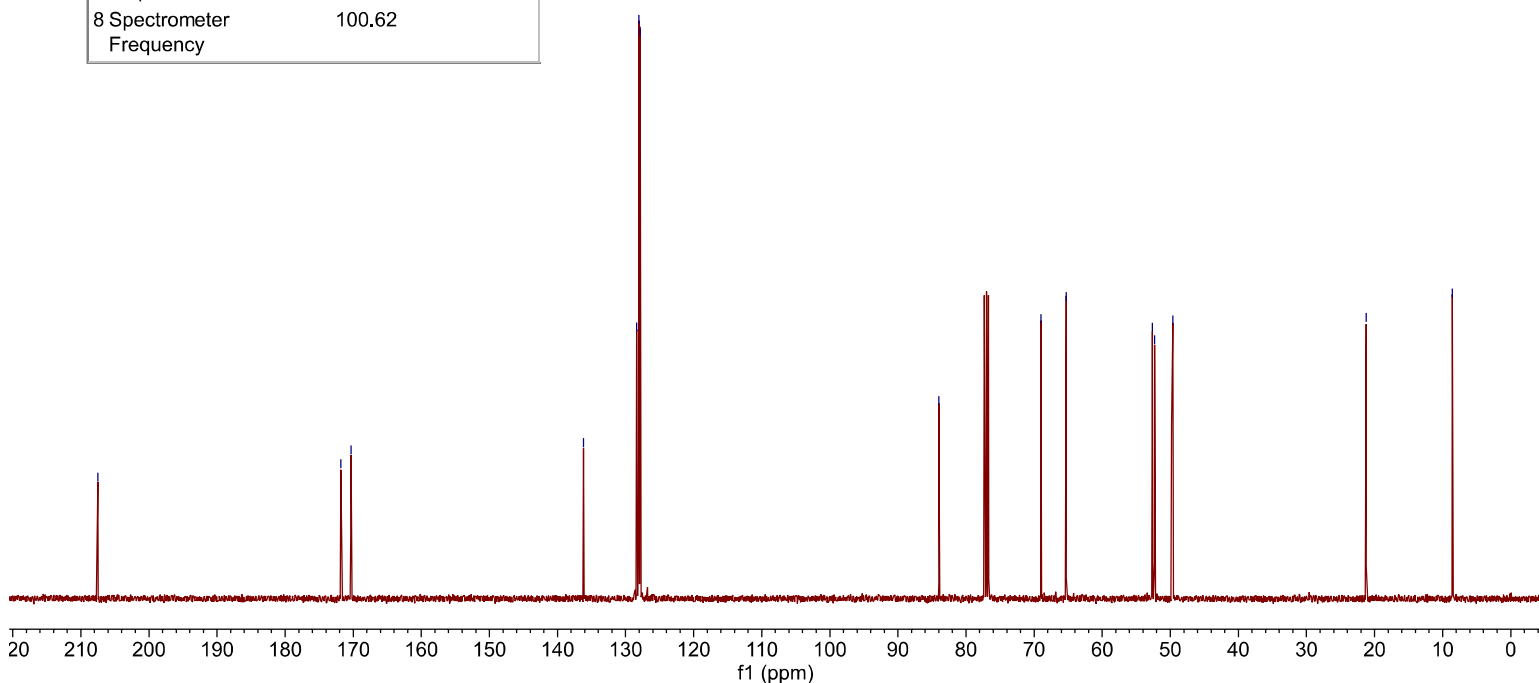
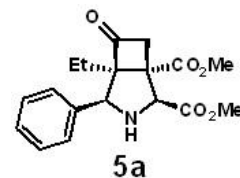
Parameter	Value
1 Title	llc-2-4-Carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	304.4
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-08-04T02:24:54
8 Spectrometer Frequency	100.62



Parameter	Value
1 Title	llc-1-80-p.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.8
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2021-10-30T21:02:23
8 Spectrometer	400.13
Frequency	



Parameter	Value
1 Title	llc-1-80-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.3
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2021-10-31T00:57:09
8 Spectrometer	100.62
Frequency	

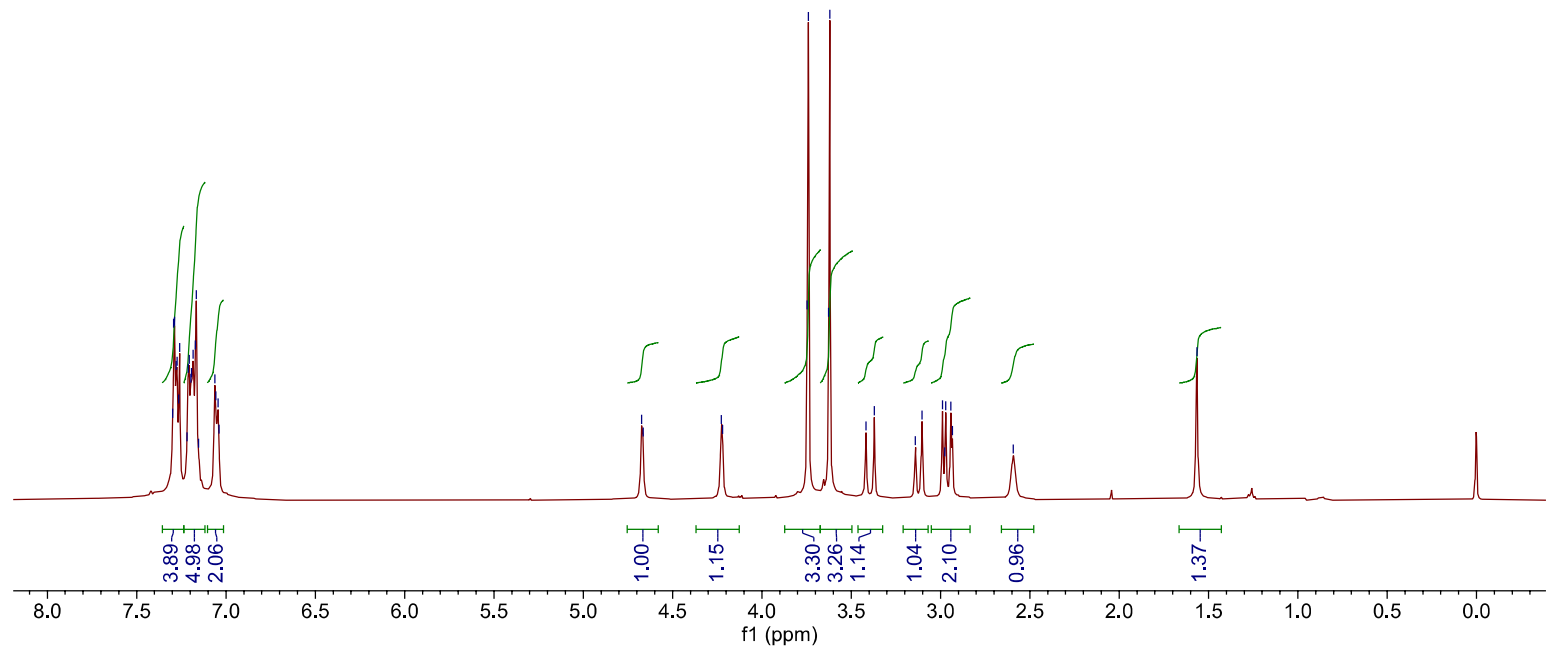
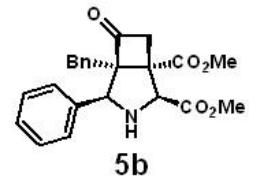


7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.22
7.21
7.21
7.20
7.19
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7.17
7.17
7.15
7.06
7.06
7.04
7.04

4.67
4.66
4.23
4.22
3.75
3.74
3.63
3.62
3.42
3.37
3.14
3.10
2.99
2.97
2.94
2.93
2.59

1.56

Parameter	Value
1 Title	llc-2-23-ap2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.4
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-08-29T21:16:15
8 Spectrometer Frequency	400.13



207.36

171.58
170.24

136.01
135.31
130.37
128.39
128.21
128.04
128.02
126.77

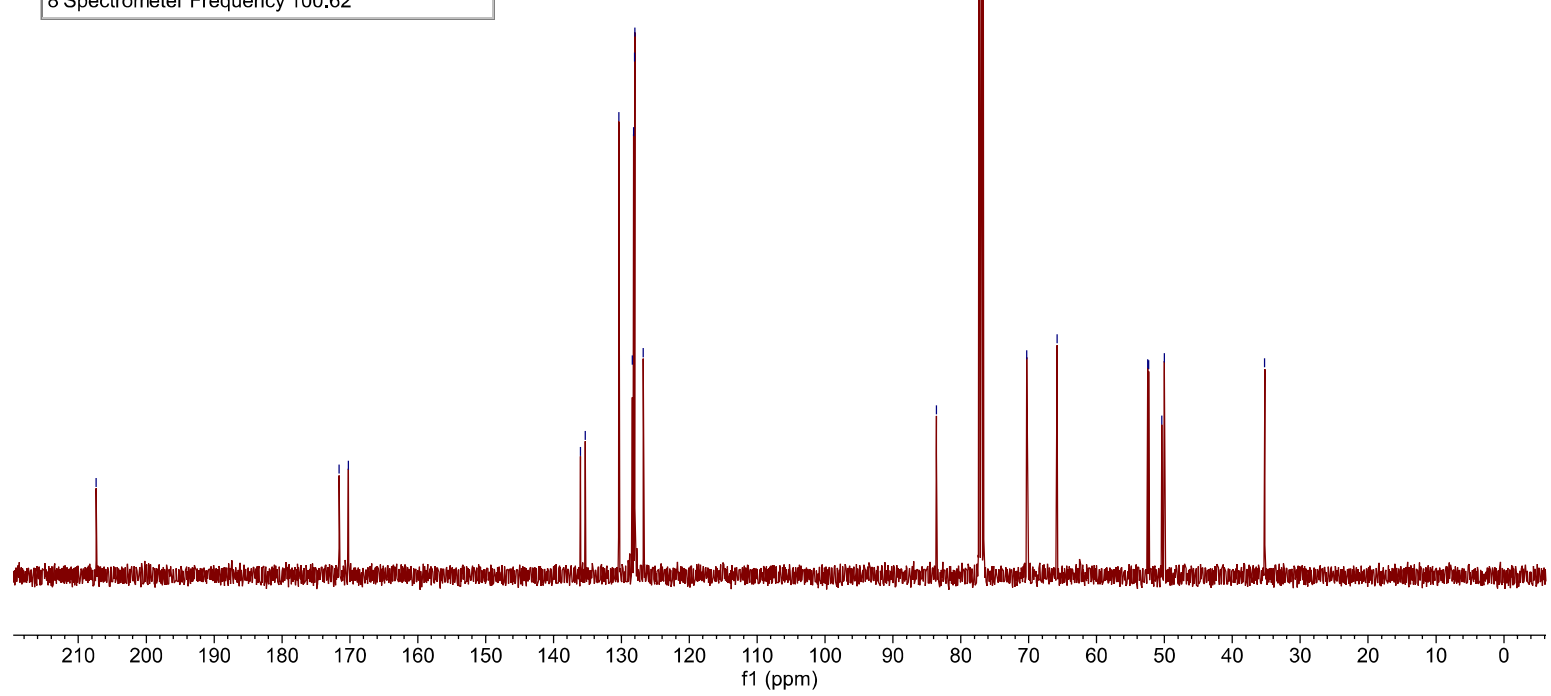
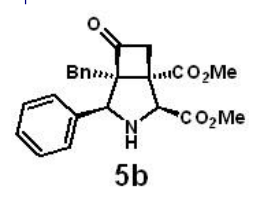
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70.28
65.80

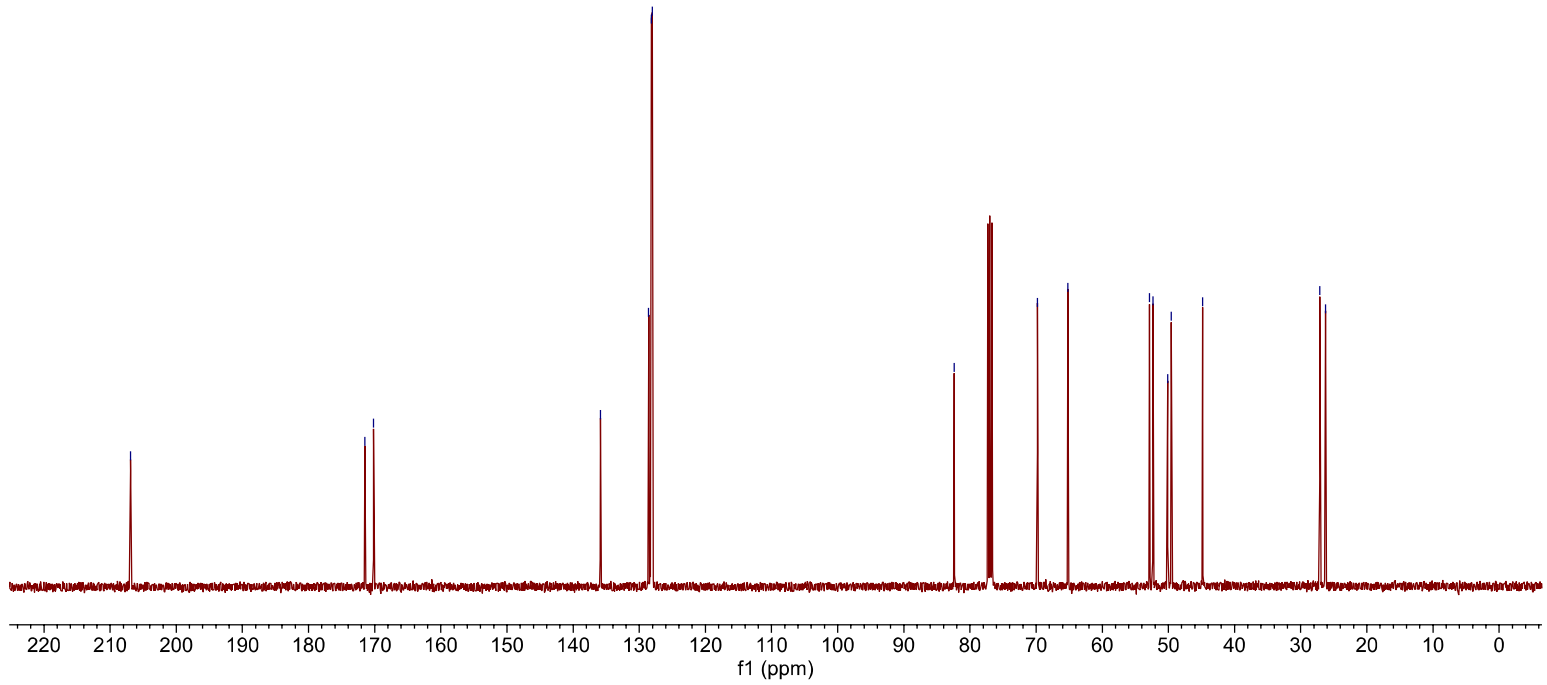
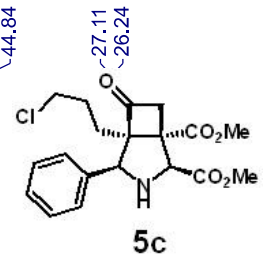
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35.23

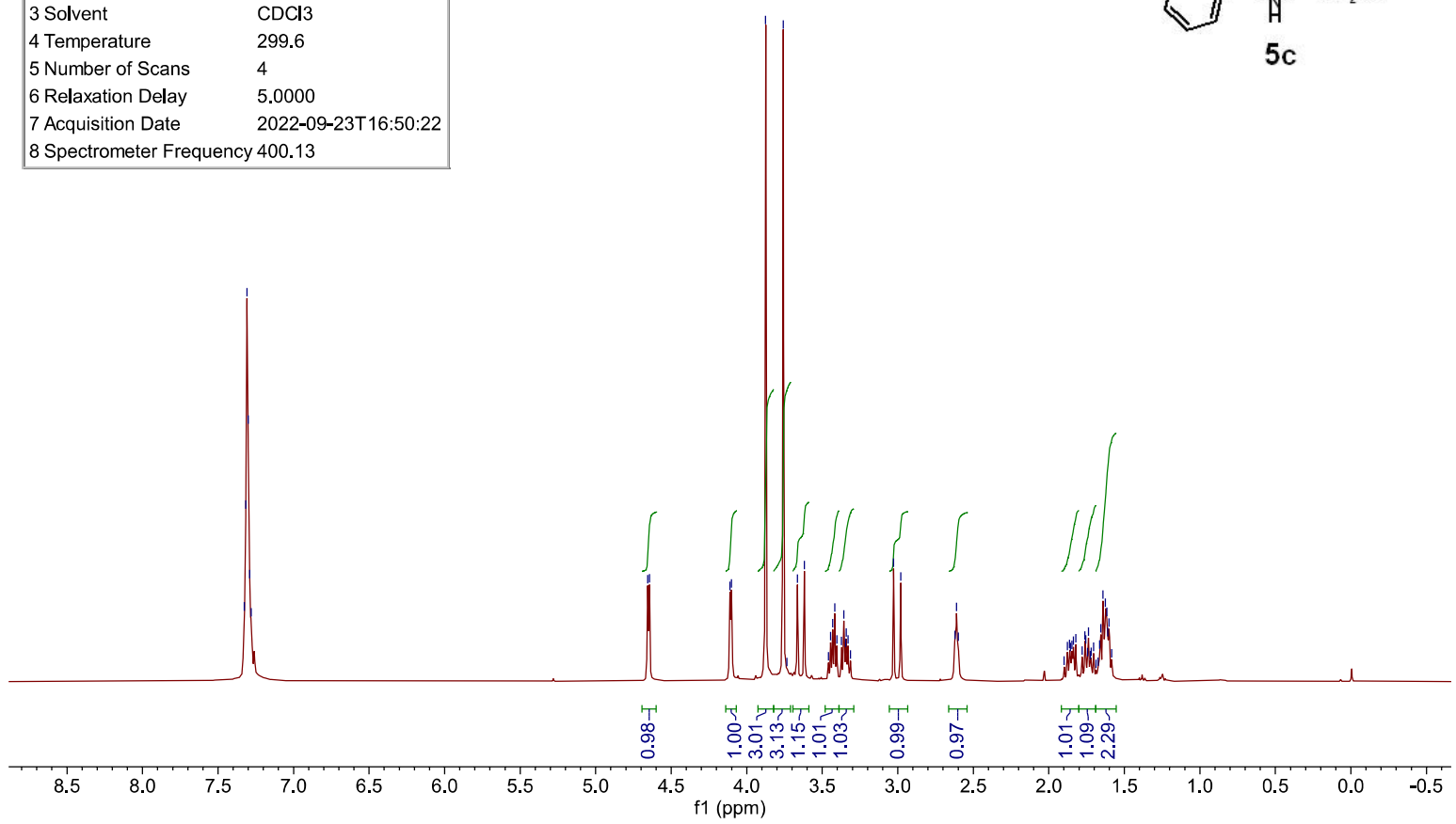
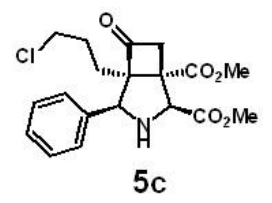
Parameter	Value
1 Title	llc-2-24-ap2.2.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.6
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-08-29T21:40:52
8 Spectrometer Frequency	100.62



Parameter	Value
1 Title	LLC-2-75-ap-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.1
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-23T17:02:44
8 Spectrometer Frequency	100.62

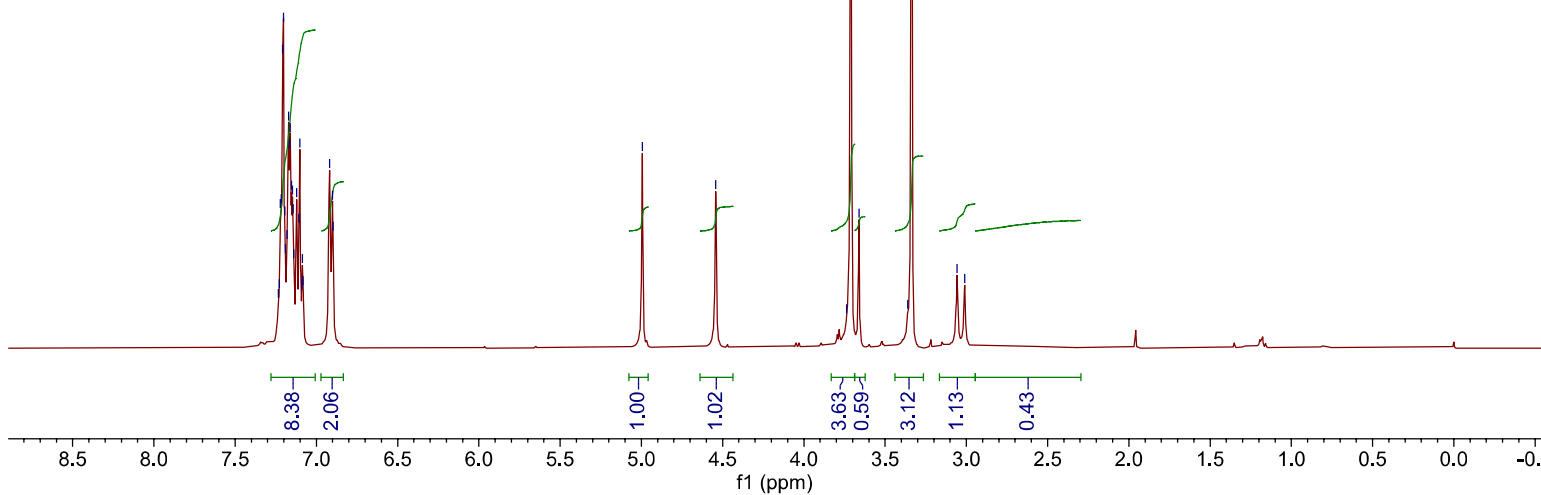
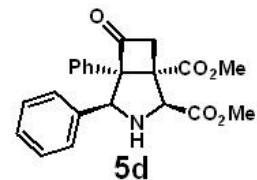


Parameter	Value
1 Title	LLC-2-75-ap.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.6
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-23T16:50:22
8 Spectrometer Frequency	400.13



7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.12
7.11
7.10
7.09
7.09
7.08
6.92
6.90

Parameter	Value
1 Title	llc-1-138-p-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	301.5
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-03-13T00:49:23
8 Spectrometer Frequency	400.13



204.47

170.69
170.08

135.11
134.29
128.41
128.23
127.87
127.84
126.95
126.50

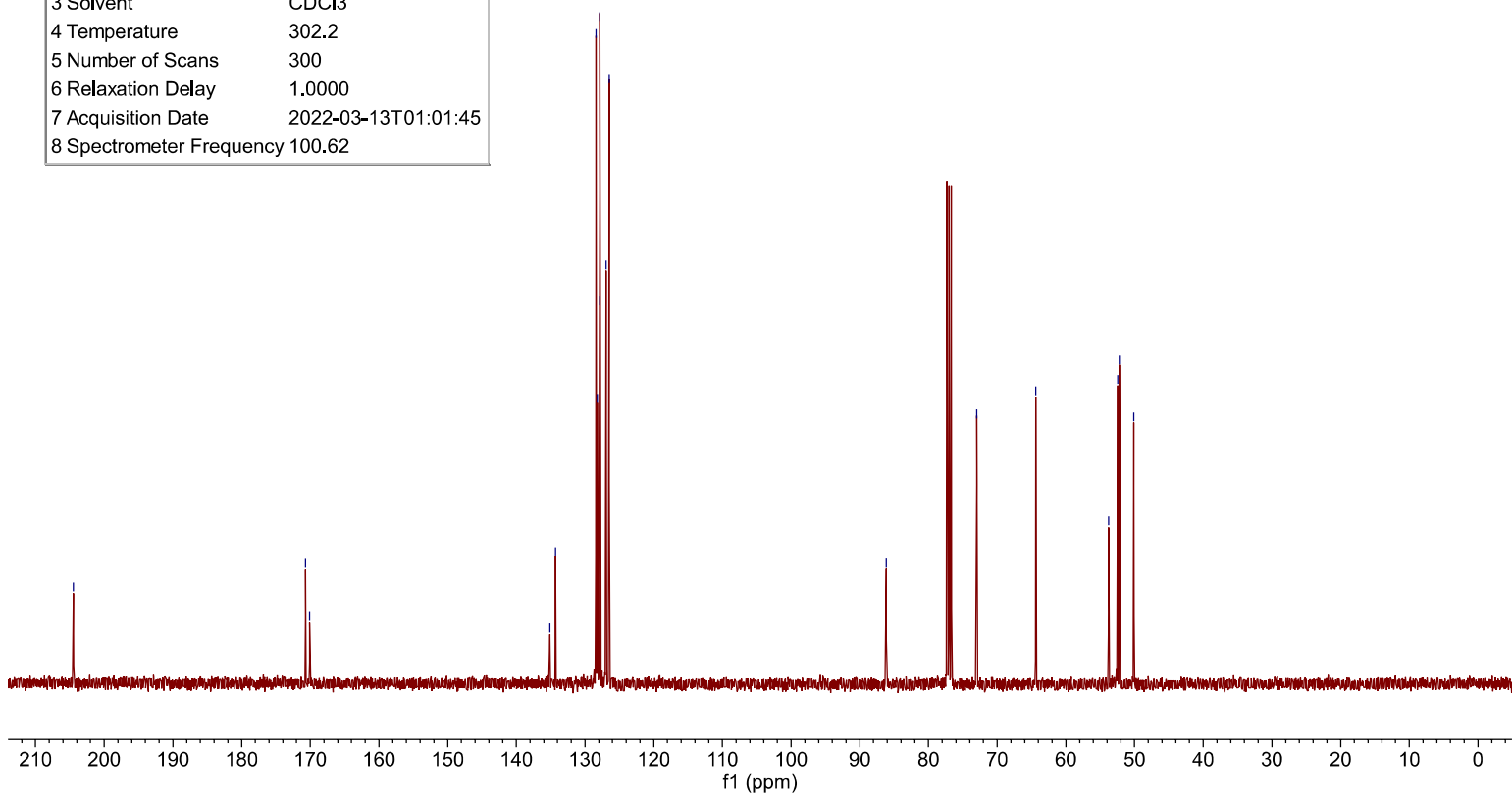
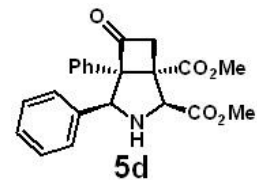
86.17

72.96

64.39

53.76
52.43
52.21
50.10

Parameter	Value
1 Title	llc-1-138-p-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	302.2
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-03-13T01:01:45
8 Spectrometer Frequency	100.62



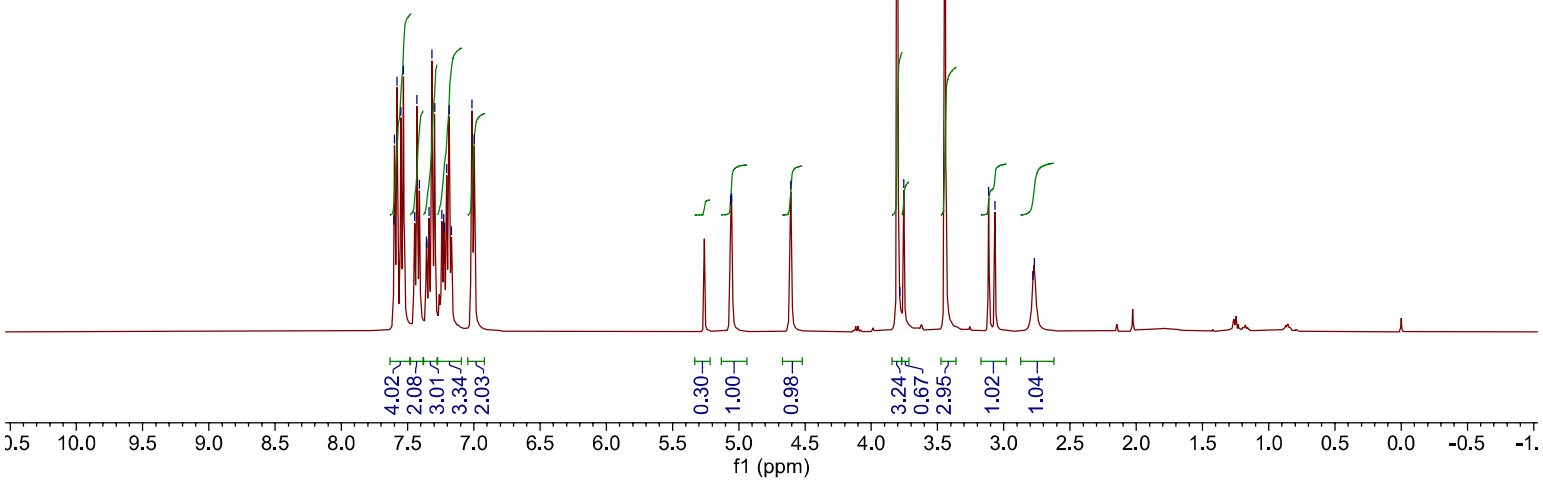
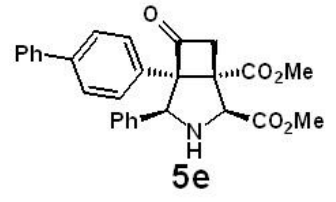
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7.36
7.35
7.34
7.32
7.30
7.24
7.23
7.22
7.21
7.19
7.17
7.02
7.00

5.06
5.05

4.61

3.80
3.78
3.75
3.44
3.11
3.07
2.78
2.77

Parameter	Value
1 Title	LLC-2-60-ap-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.3
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-13T20:42:36
8 Spectrometer Frequency	400.13



204.62

170.81
170.28

140.41
140.11
135.37
133.32
128.80
128.25
127.89
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126.91
126.88

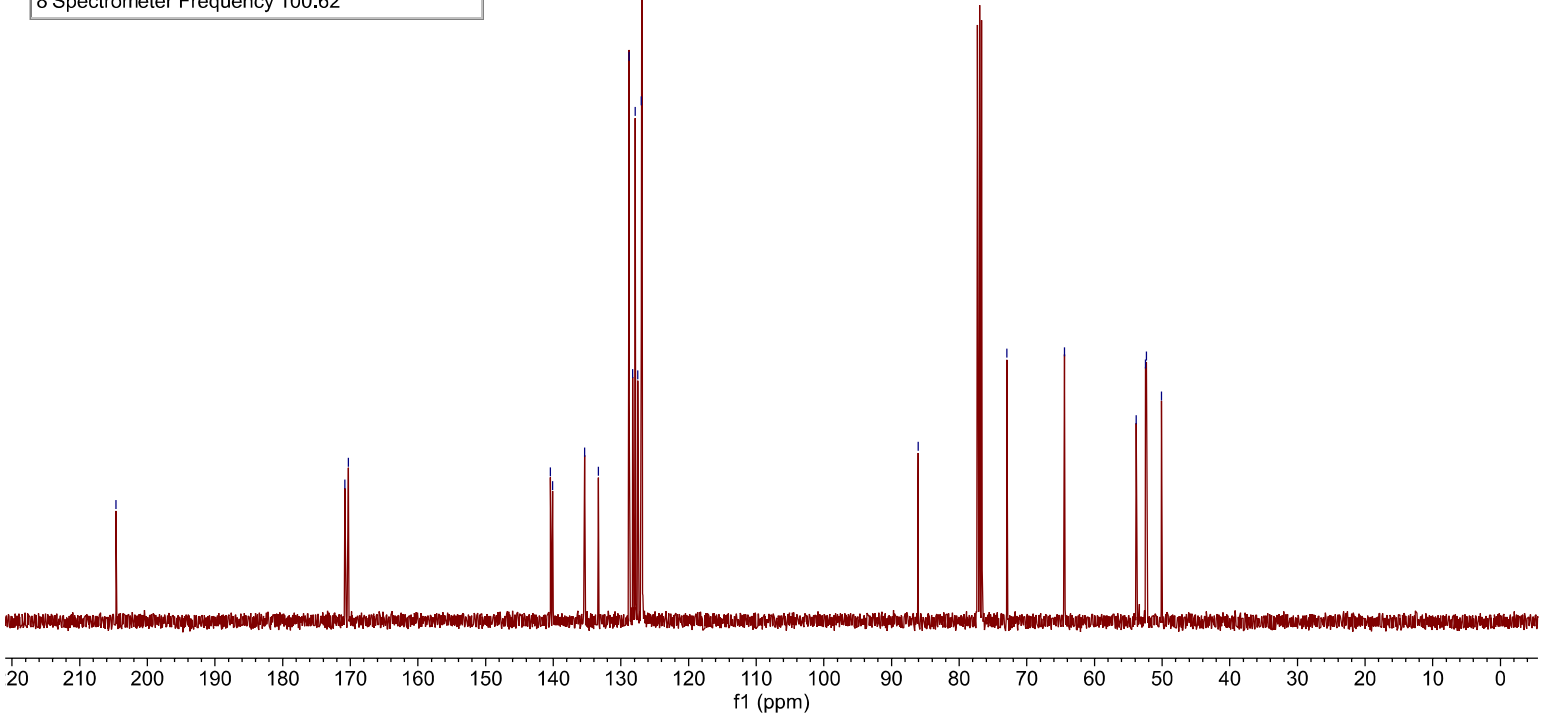
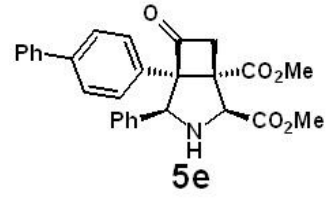
86.08

72.97

64.46

53.85
52.45
52.31
50.09

Parameter	Value
1 Title	LLC-2-59-ap-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.6
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-13T20:38:46
8 Spectrometer Frequency	100.62



7.32
7.31

4.29

3.79

3.78

3.57

3.52

3.25

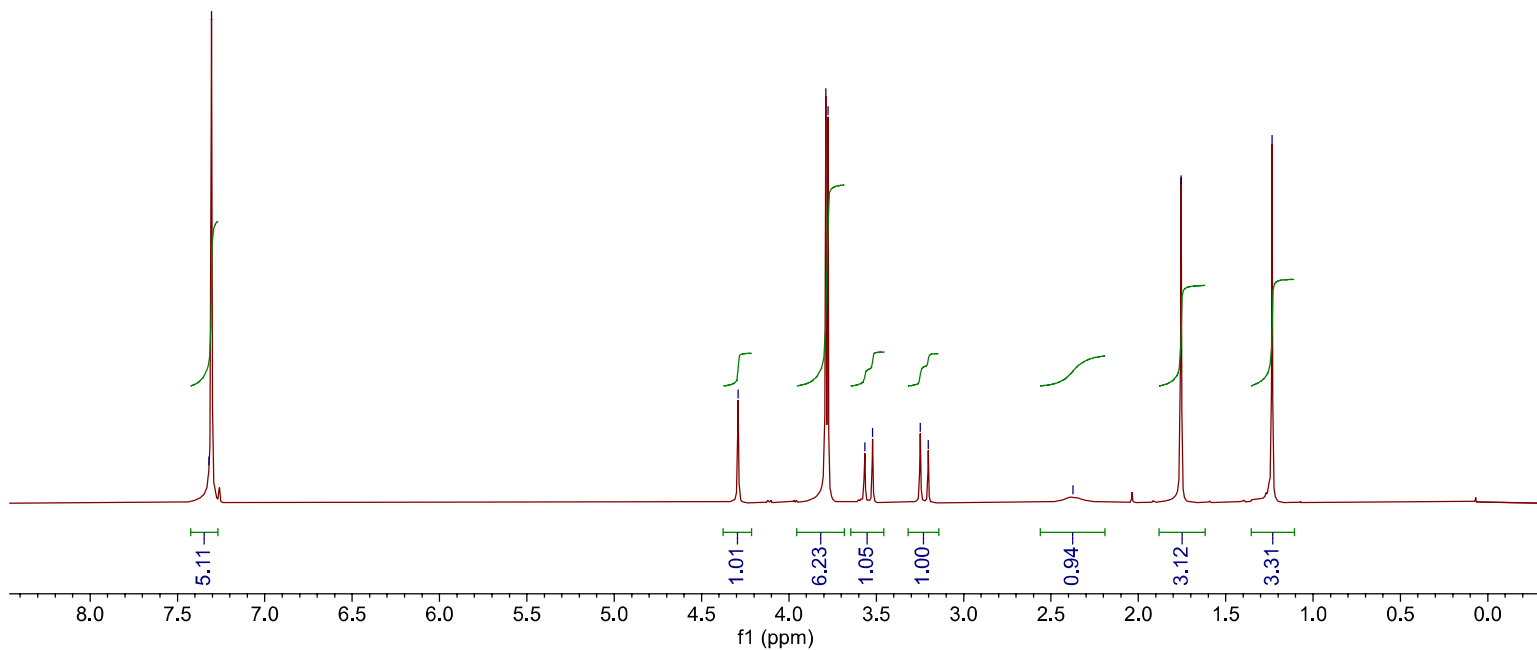
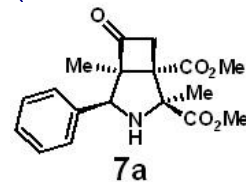
3.20

2.37

1.76

1.23

Parameter	Value
1 Title	llc-1-114.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.4
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-02-11T00:46:52
8 Spectrometer Frequency	400.13



206.83

173.22

170.53

136.57

128.43

128.26

127.18

78.47

69.93

68.31

53.56

53.22

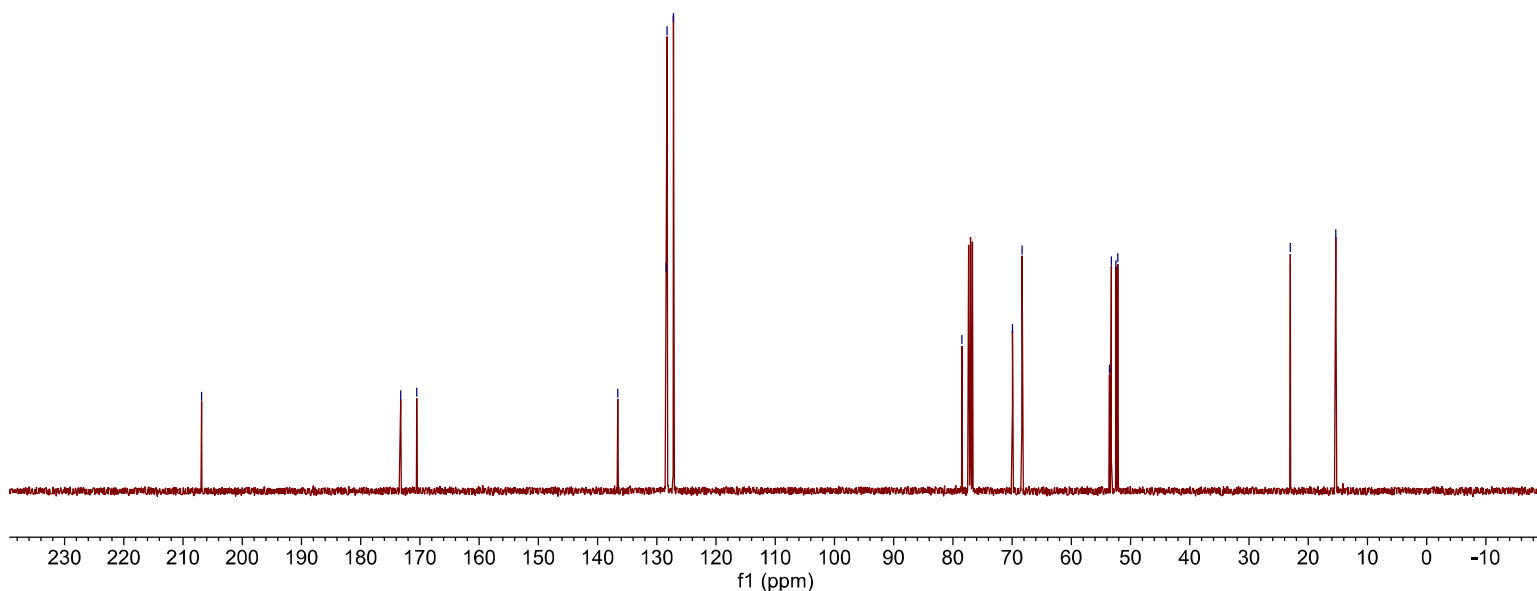
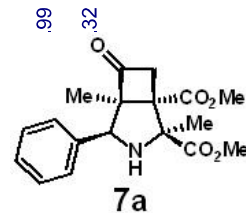
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52.13

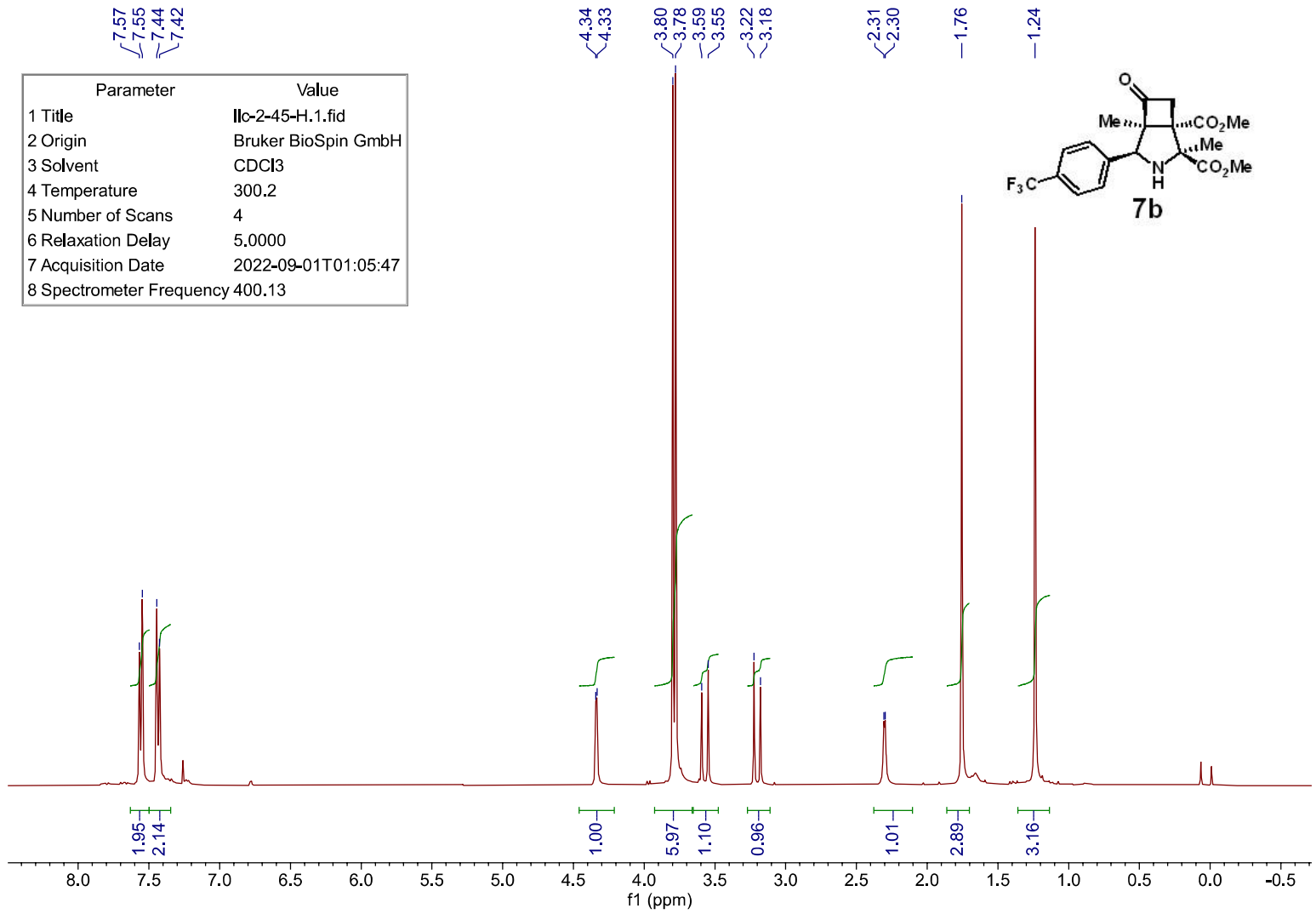
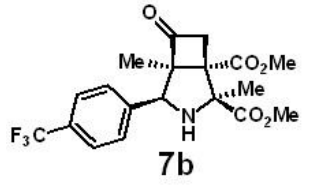
99

32

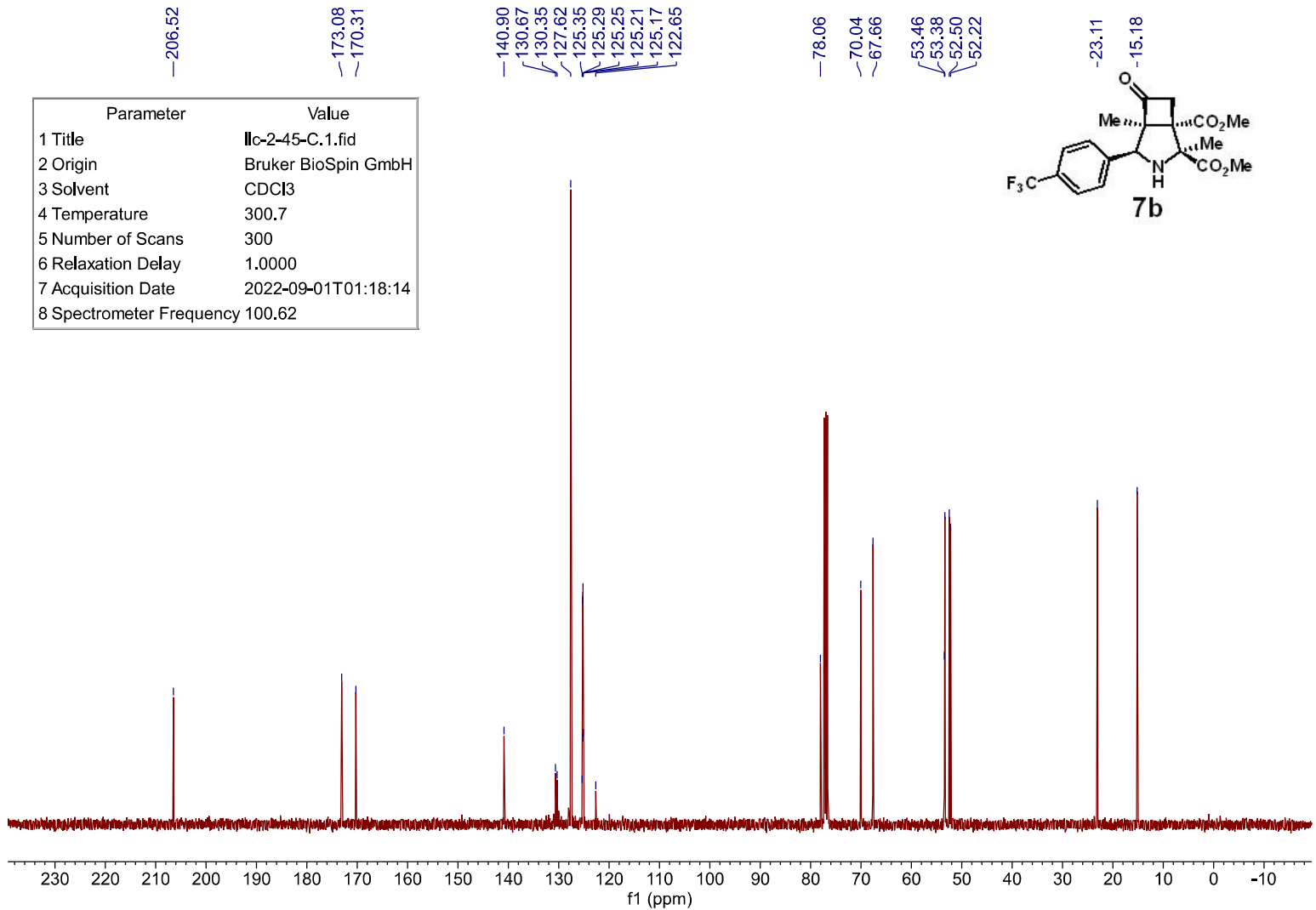
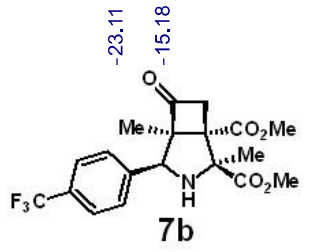
Parameter	Value
1 Title	llc-1-114-carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.0
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-02-11T01:30:54
8 Spectrometer Frequency	100.62



Parameter	Value
1 Title	llc-2-45-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.2
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-01T01:05:47
8 Spectrometer Frequency	400.13

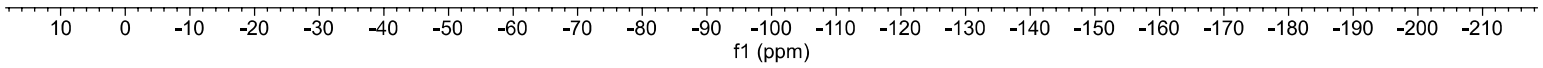
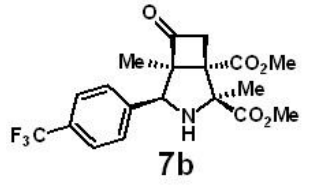


Parameter	Value
1 Title	llc-2-45-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.7
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-01T01:18:14
8 Spectrometer Frequency	100.62

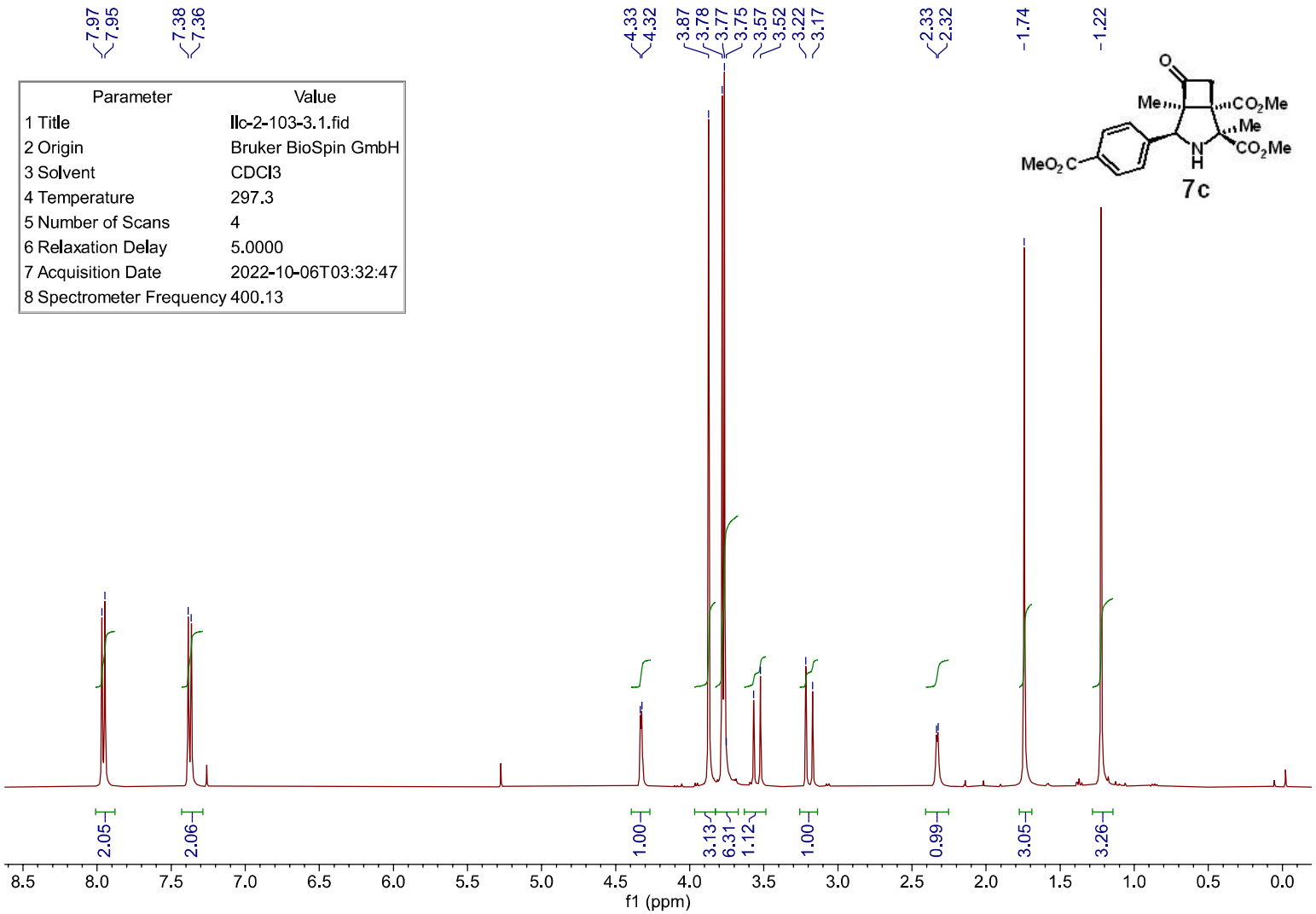
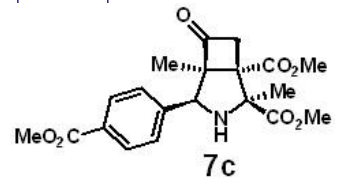


Parameter	Value
1 Title	llc-2-46-F.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.4
5 Number of Scans	16
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-01T02:50:25
8 Spectrometer Frequency	376.46

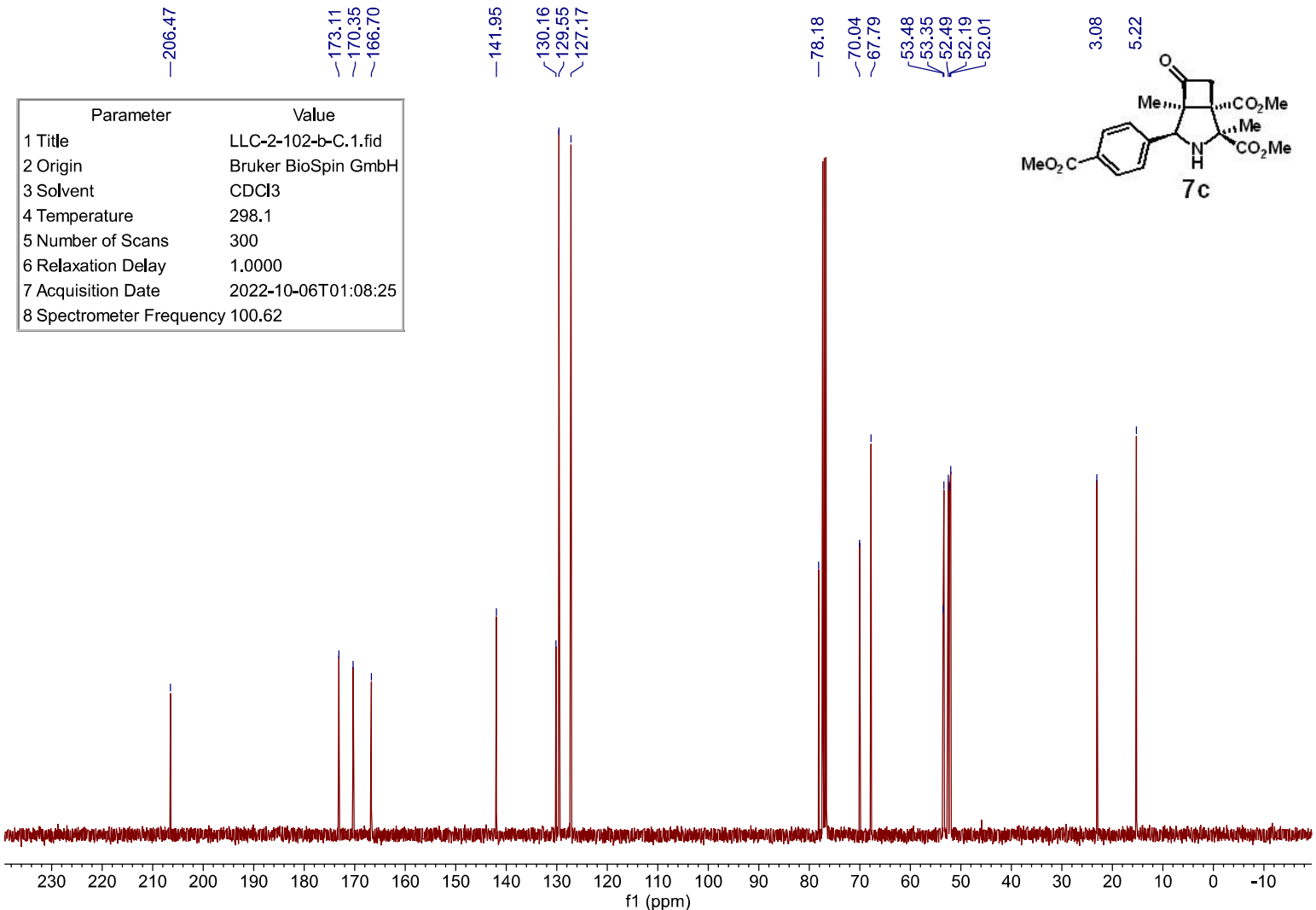
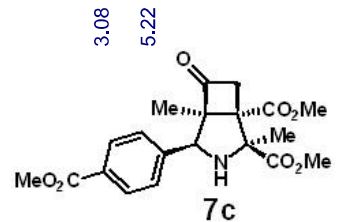
-62.54



Parameter	Value
1 Title	llc-2-103-3.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.3
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-10-06T03:32:47
8 Spectrometer Frequency	400.13



Parameter	Value
1 Title	LLC-2-102-b-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.1
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-10-06T01:08:25
8 Spectrometer Frequency	100.62



7.41
7.41
7.38
7.36
7.17
7.16
7.15
7.14

4.24
4.23

3.80
3.78
3.60
3.55

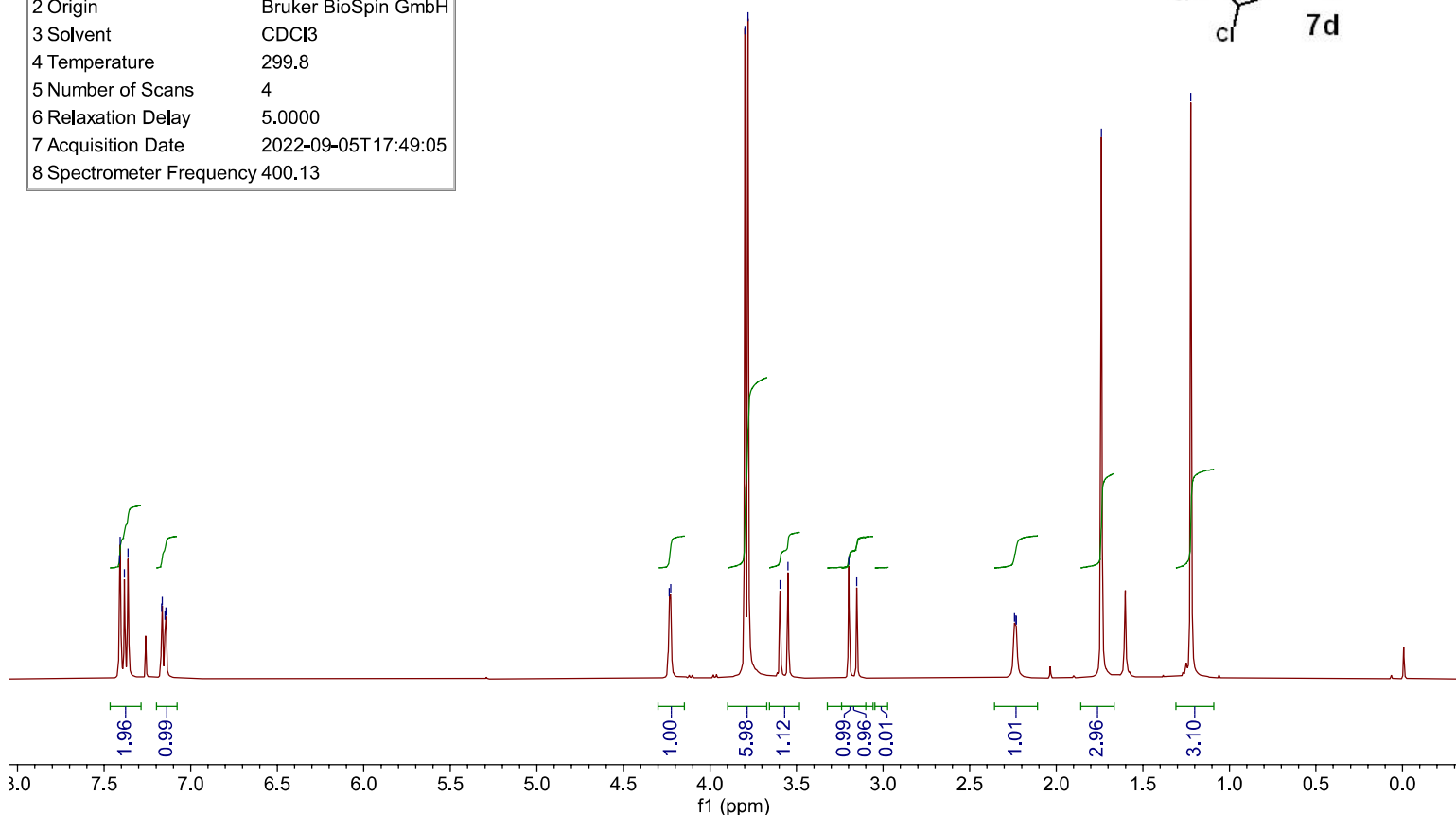
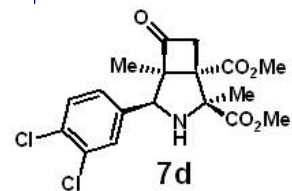
3.20
3.15

2.24
2.23
2.23

1.74

1.22

Parameter	Value
1 Title	llc-2-48-ap-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-05T17:49:05
8 Spectrometer Frequency	400.13



206.48

173.01
170.24

137.20
132.48
132.31
130.25
129.09
126.49

77.82

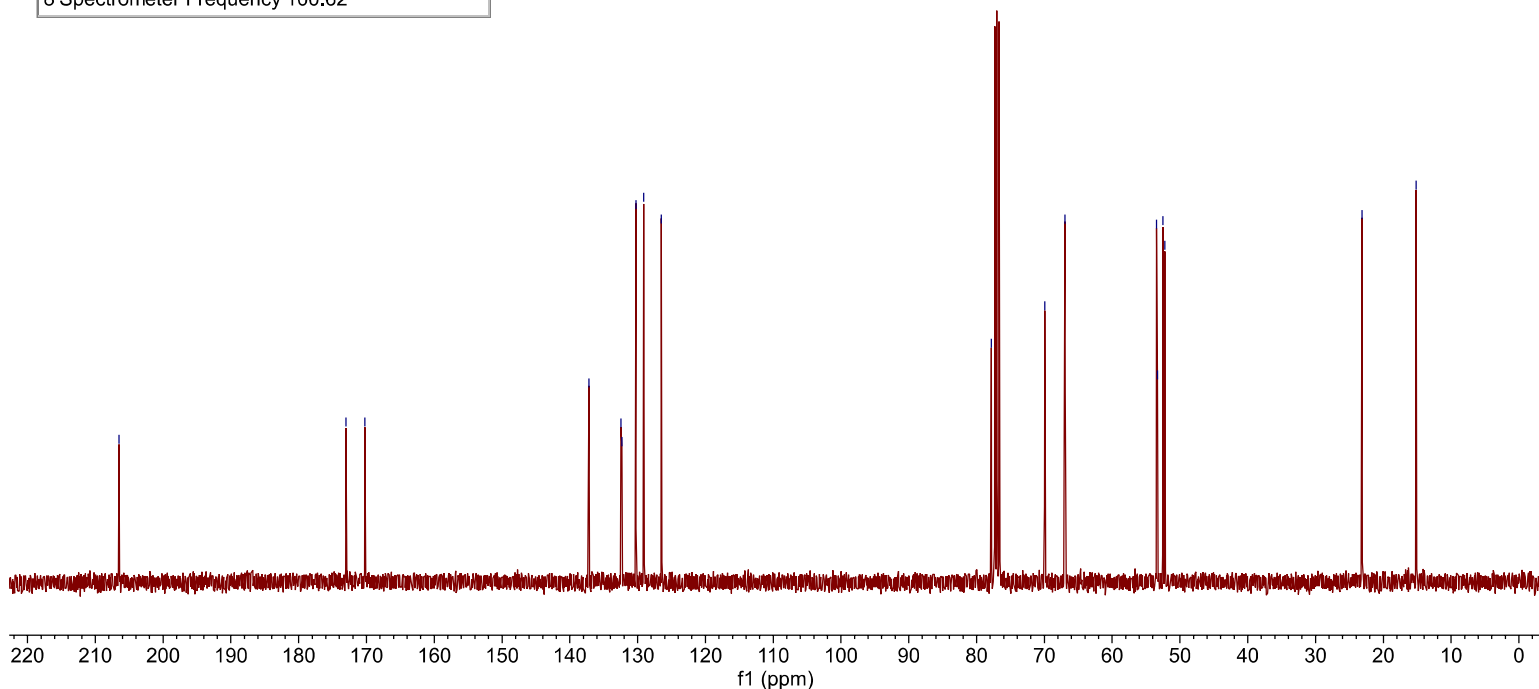
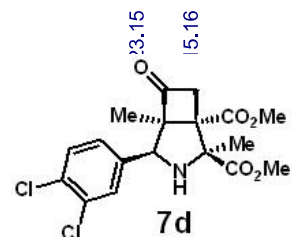
69.95
66.96

53.44
53.33
52.51
52.24

3.15

15.16

Parameter	Value
1 Title	llc-2-49-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.4
5 Number of Scans	194
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-01T22:33:43
8 Spectrometer Frequency	100.62



8.13
8.11
7.88
7.86
7.86
7.81
7.79
7.78
7.77
7.52
7.51
7.50
7.48
7.48
7.47
7.46
7.45
7.43

5.36
5.35

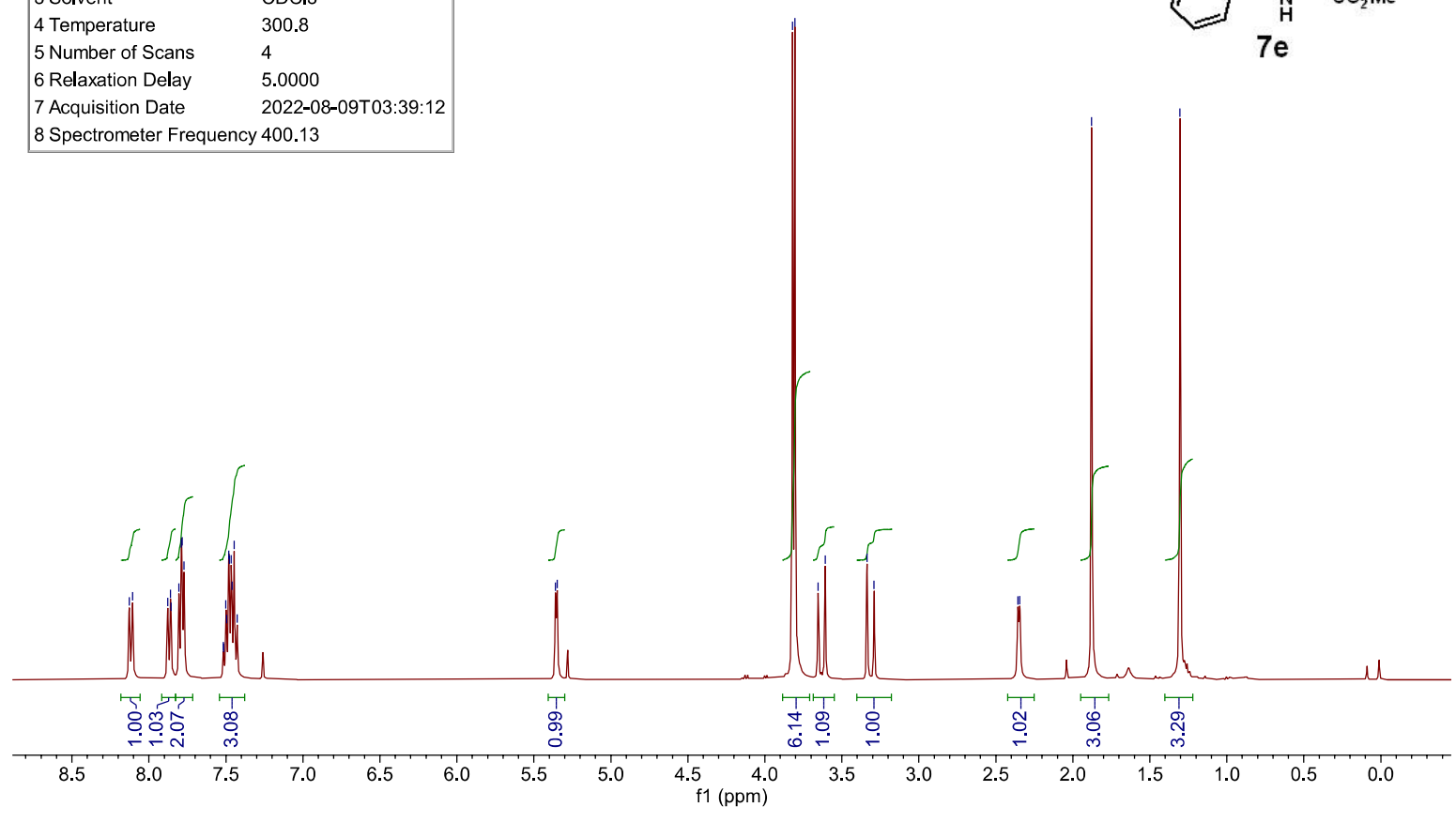
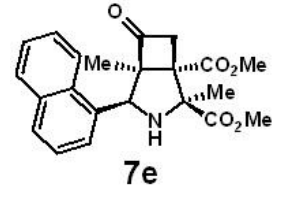
3.82
3.80
3.65
3.61
3.34
3.29

2.36
2.34

1.88

1.30

Parameter	Value
1 Title	llc-2-17.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.8
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-08-09T03:39:12
8 Spectrometer Frequency	400.13



207.00

173.34
170.47

133.87
132.43
131.84
129.18
128.67
125.89
125.49
125.28
125.22
122.53

79.42

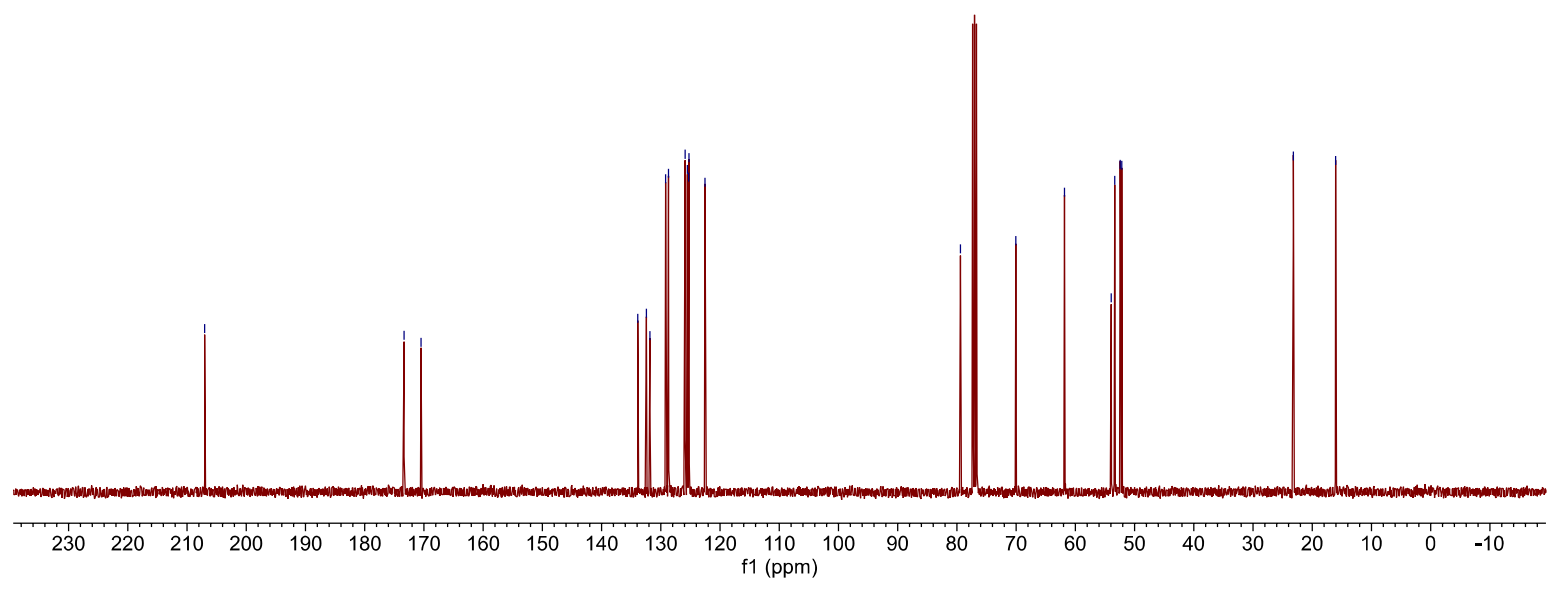
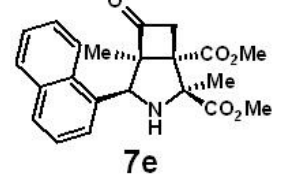
70.02

61.83
53.95
53.33
52.44
52.13

23.18

16.03

Parameter	Value
1 Title	llc-2-17-Carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	303.5
5 Number of Scans	400
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-08-09T12:09:16
8 Spectrometer Frequency	100.62



7.35
7.34

6.30
6.30
6.29

4.33
4.31

3.78
3.77
3.75

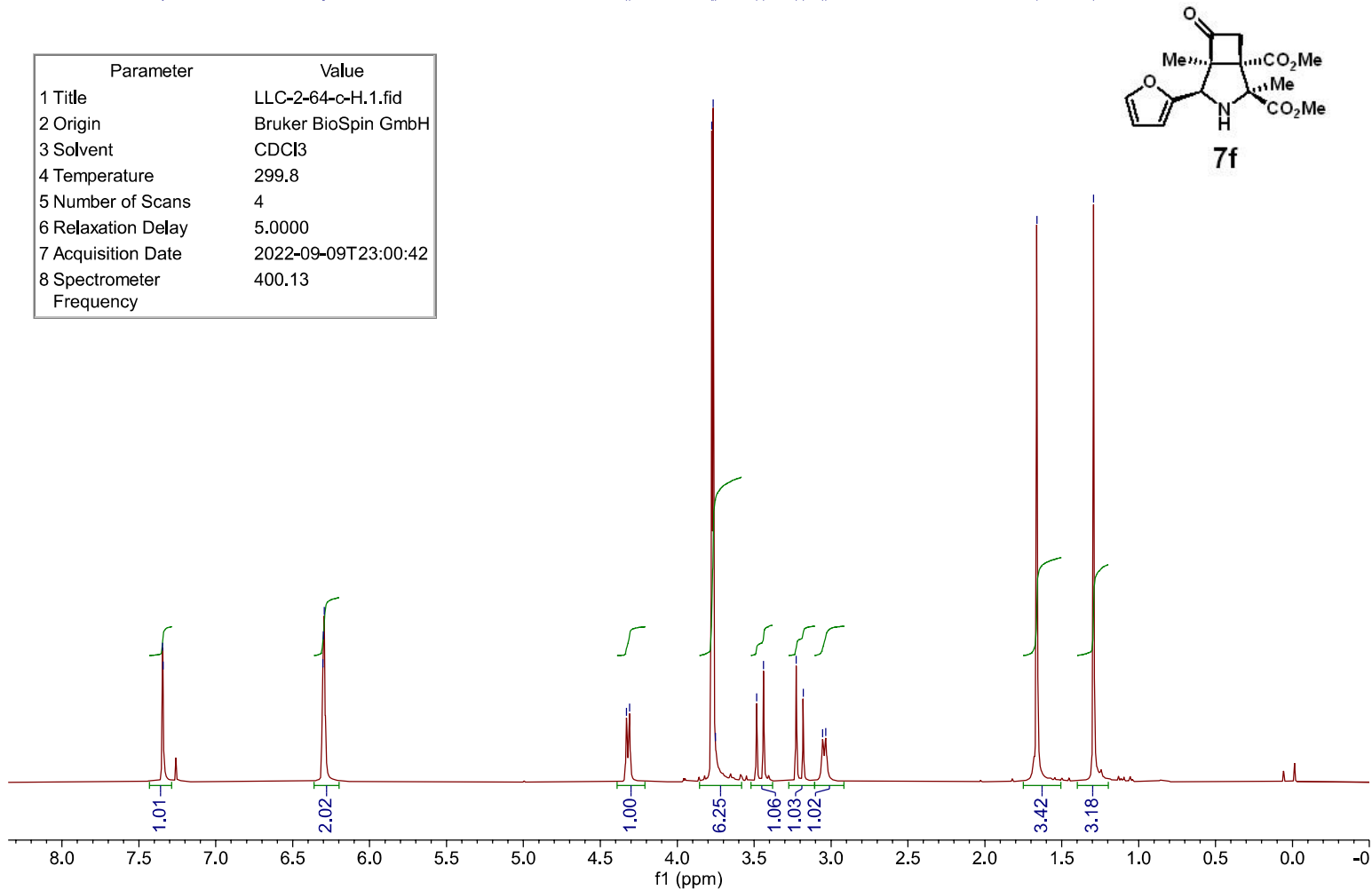
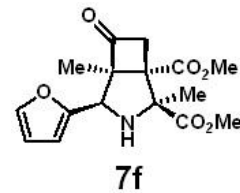
3.48
3.44

3.23
3.18
3.05
3.03

1.66

1.29

Parameter	Value
1 Title	LLC-2-64-c-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-09T23:00:42
8 Spectrometer	400.13
Frequency	



205.56

172.61
170.29

149.85

142.61

110.29
107.62

78.69

70.48

63.48

55.02

52.63

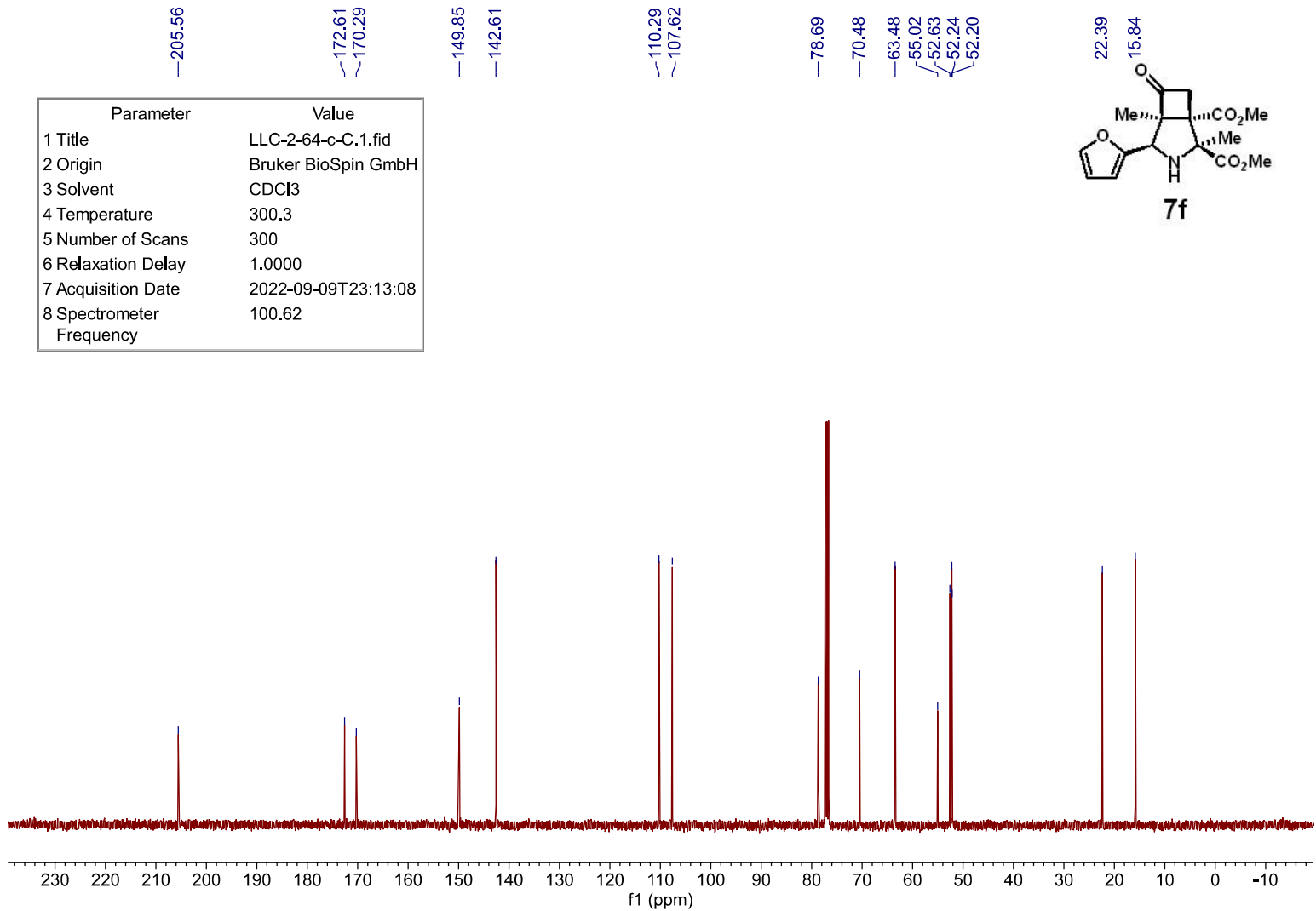
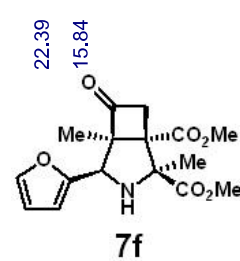
52.24

52.20

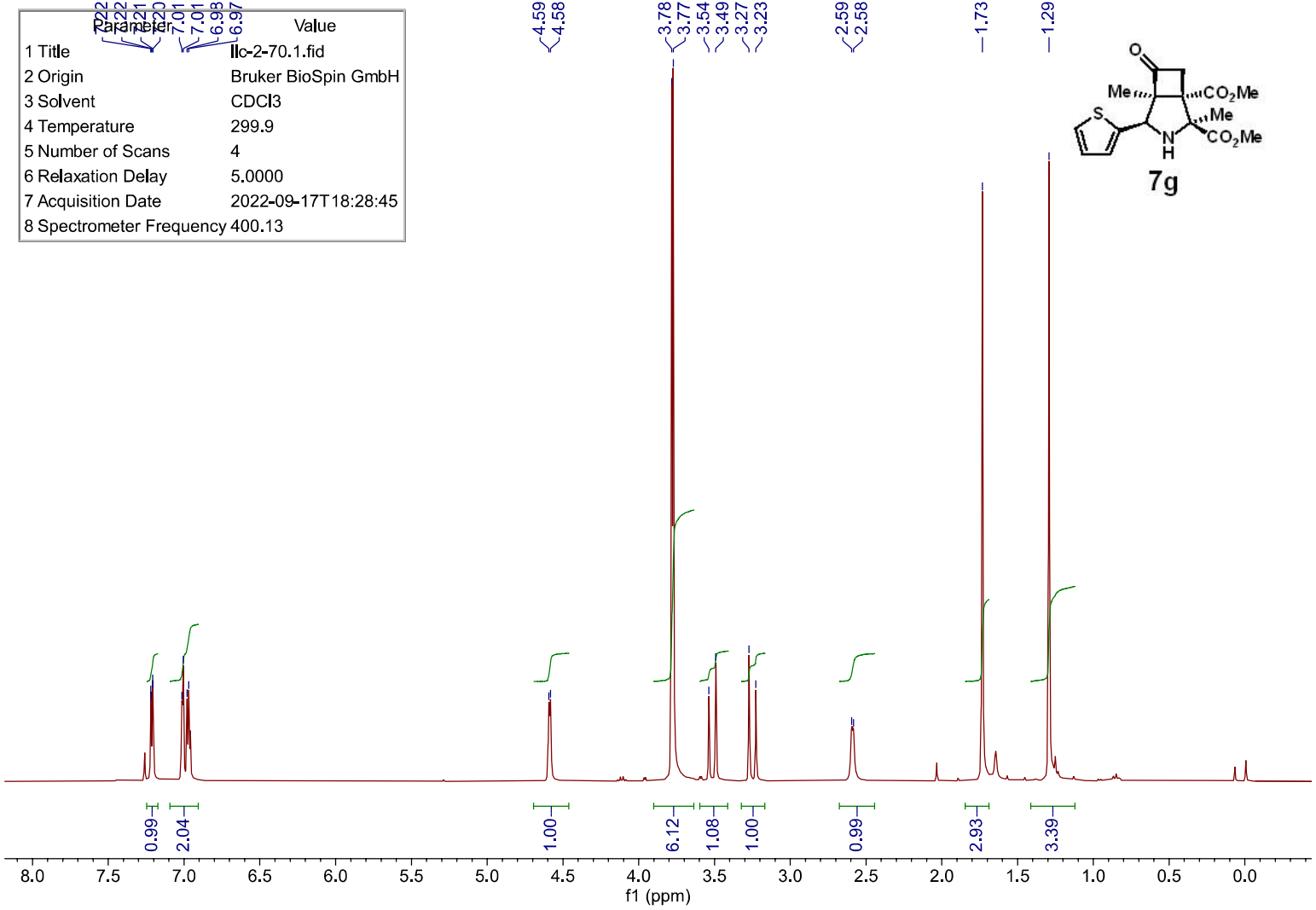
22.39

15.84

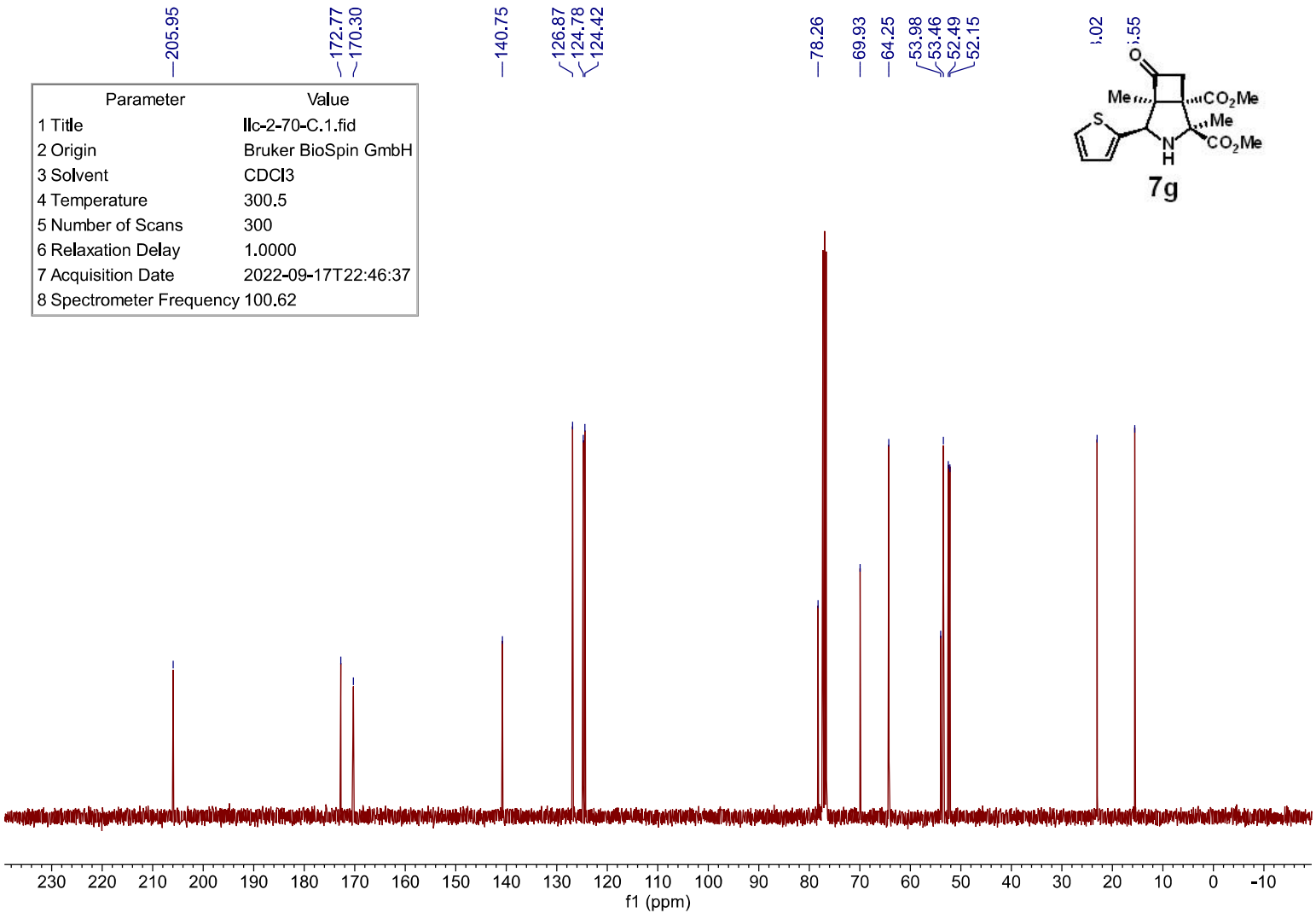
Parameter	Value
1 Title	LLC-2-64-c-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.3
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-09T23:13:08
8 Spectrometer	100.62
Frequency	

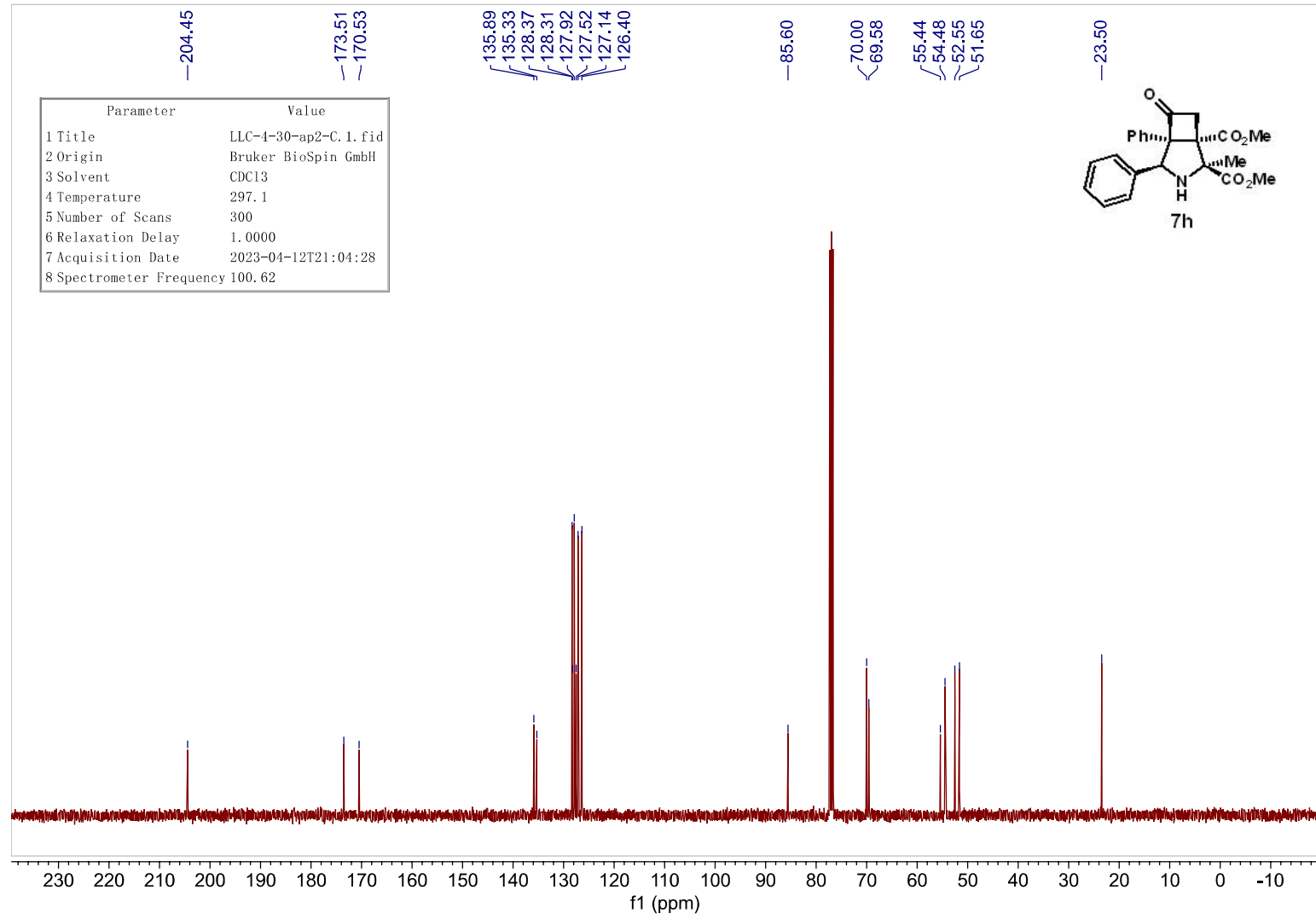
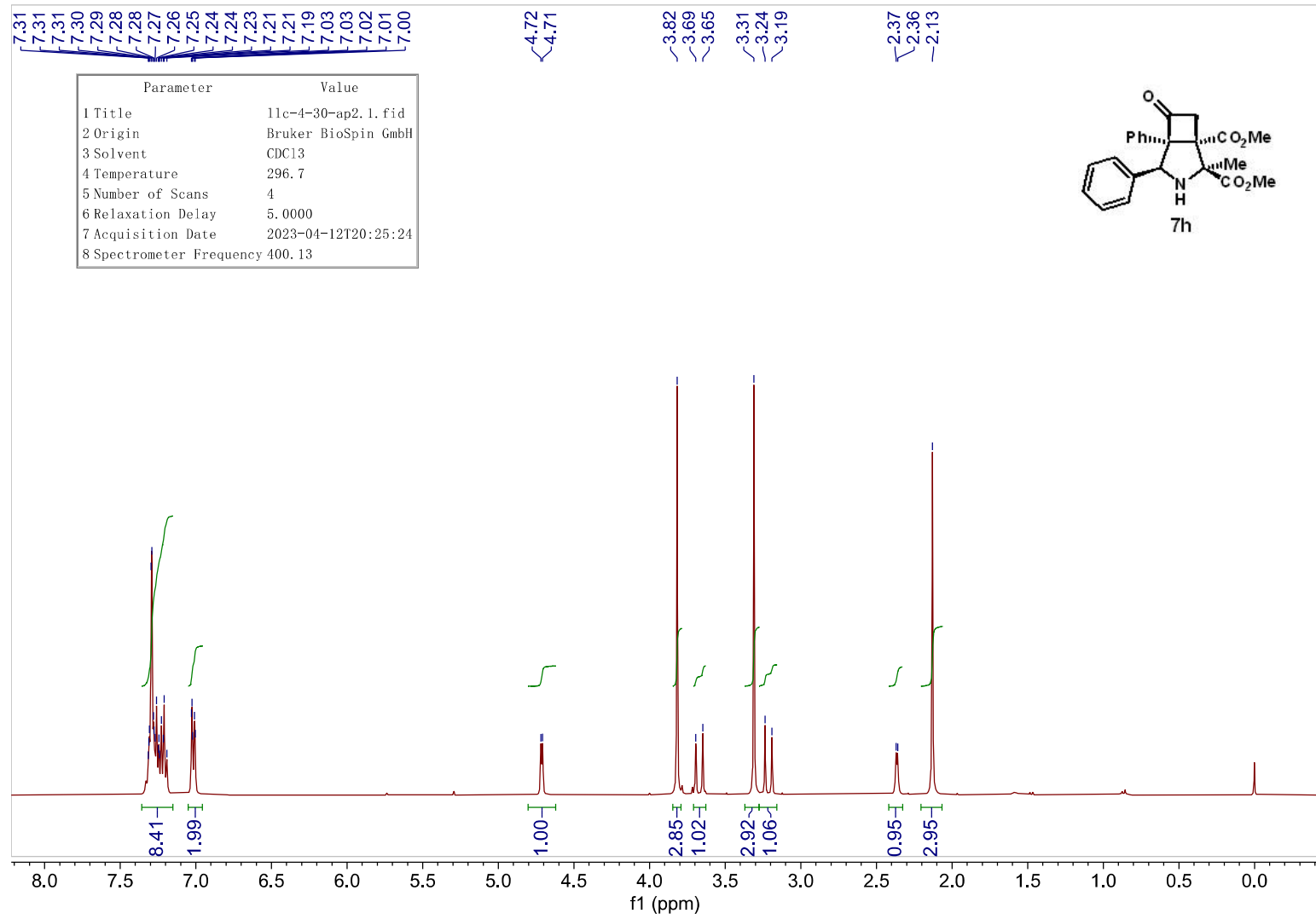


Parameter	Value
1 Title	llc-2-70.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.9
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-17T 18:28:45
8 Spectrometer Frequency	400.13



Parameter	Value
1 Title	llc-2-70-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.5
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-17T 22:46:37
8 Spectrometer Frequency	100.62

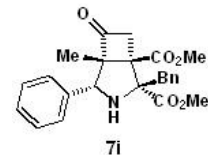




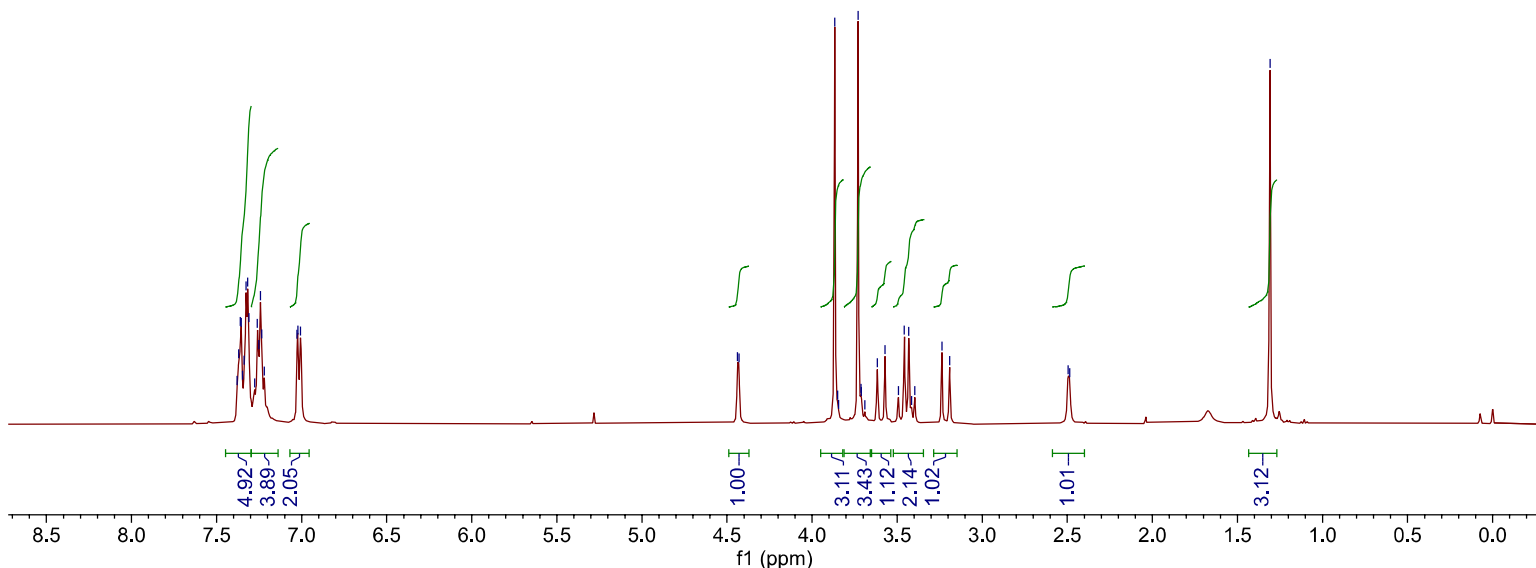
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.28
7.26
7.25
7.24
7.23
7.22
7.03
7.02
7.01

4.44
4.43
3.87
3.85
3.84
3.73
3.71
3.71
3.69
3.62
3.57
3.49
3.46
3.43
3.42
3.40
3.24
3.19
2.50
2.49

1.31



Parameter	Value
1 Title	11c-1-168.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.7
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-07-20T02:46:12
8 Spectrometer Frequency	400.13



206.81

171.99
170.22

136.60
135.82
129.45
128.84
128.56
128.30
127.30
127.29

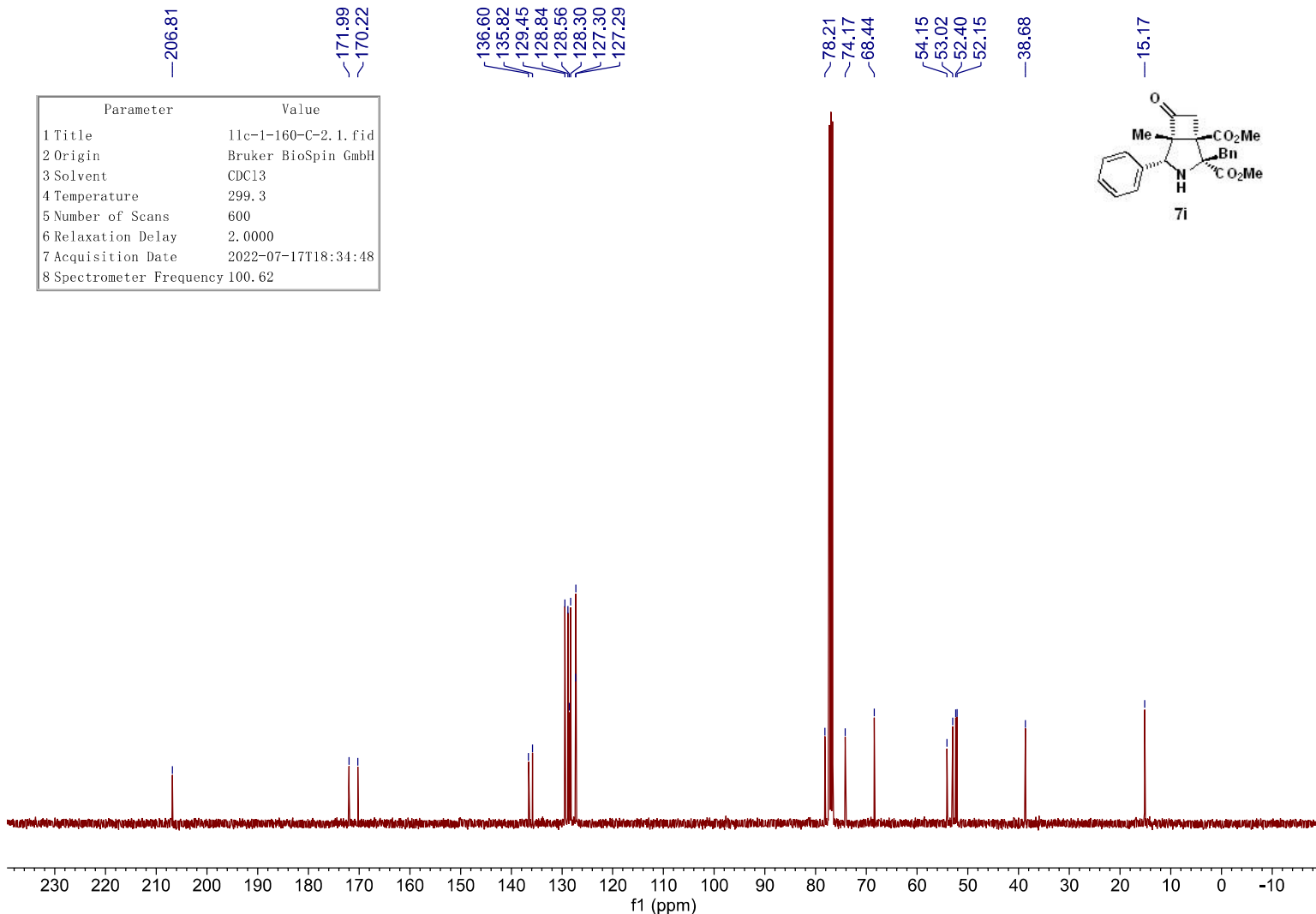
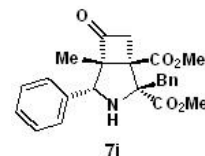
78.21
74.17
68.44

54.15
53.02
52.40
52.15

38.68

15.17

Parameter	Value
1 Title	11c-1-160-C-2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.3
5 Number of Scans	600
6 Relaxation Delay	2.0000
7 Acquisition Date	2022-07-17T18:34:48
8 Spectrometer Frequency	100.62



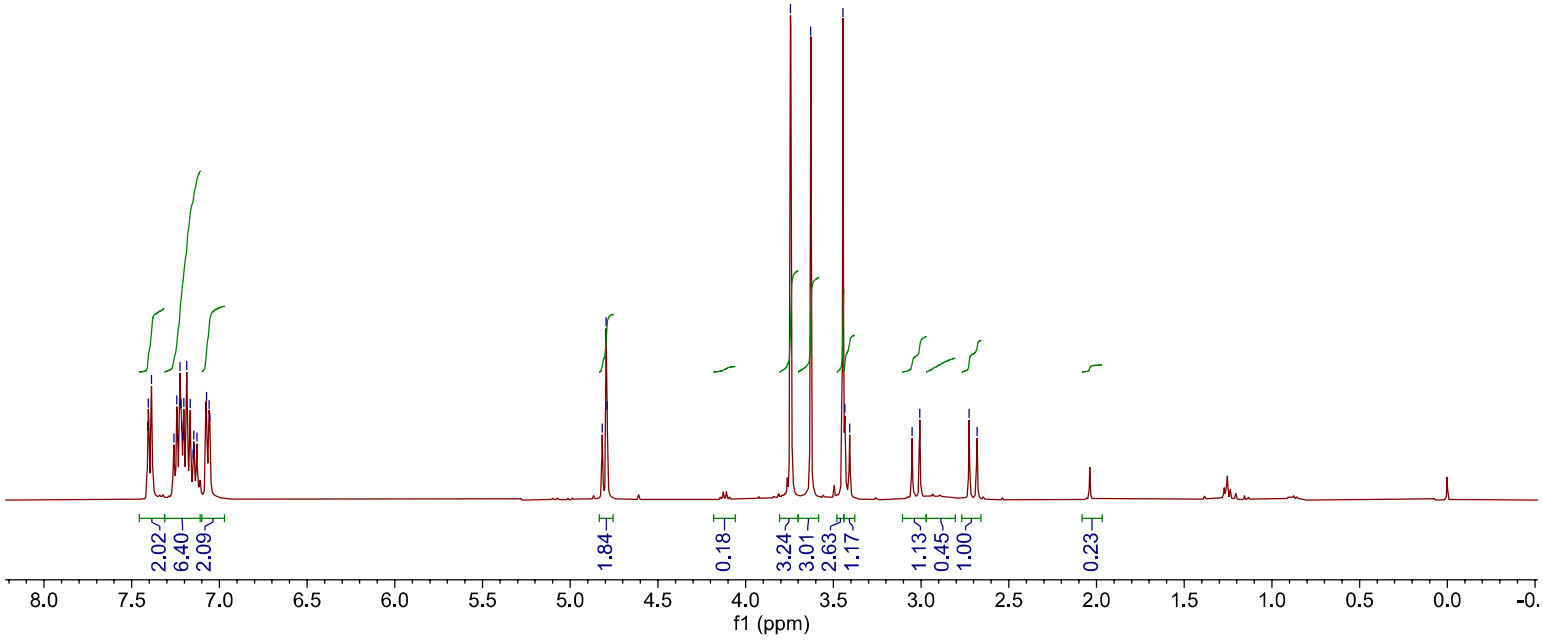
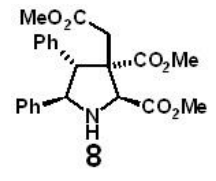
7.41
7.40
7.39
7.26
7.24
7.22
7.22
7.21
7.20
7.19
7.17
7.15
7.14
7.13
7.08
7.07
7.06

4.82
4.80
4.79

3.74
3.63
3.45
3.43
3.41

3.05
3.01
2.73
2.68

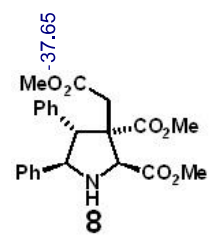
Parameter	Value
1 Title	llc-2-66-b2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-13T15:25:09
8 Spectrometer Frequency	400.13



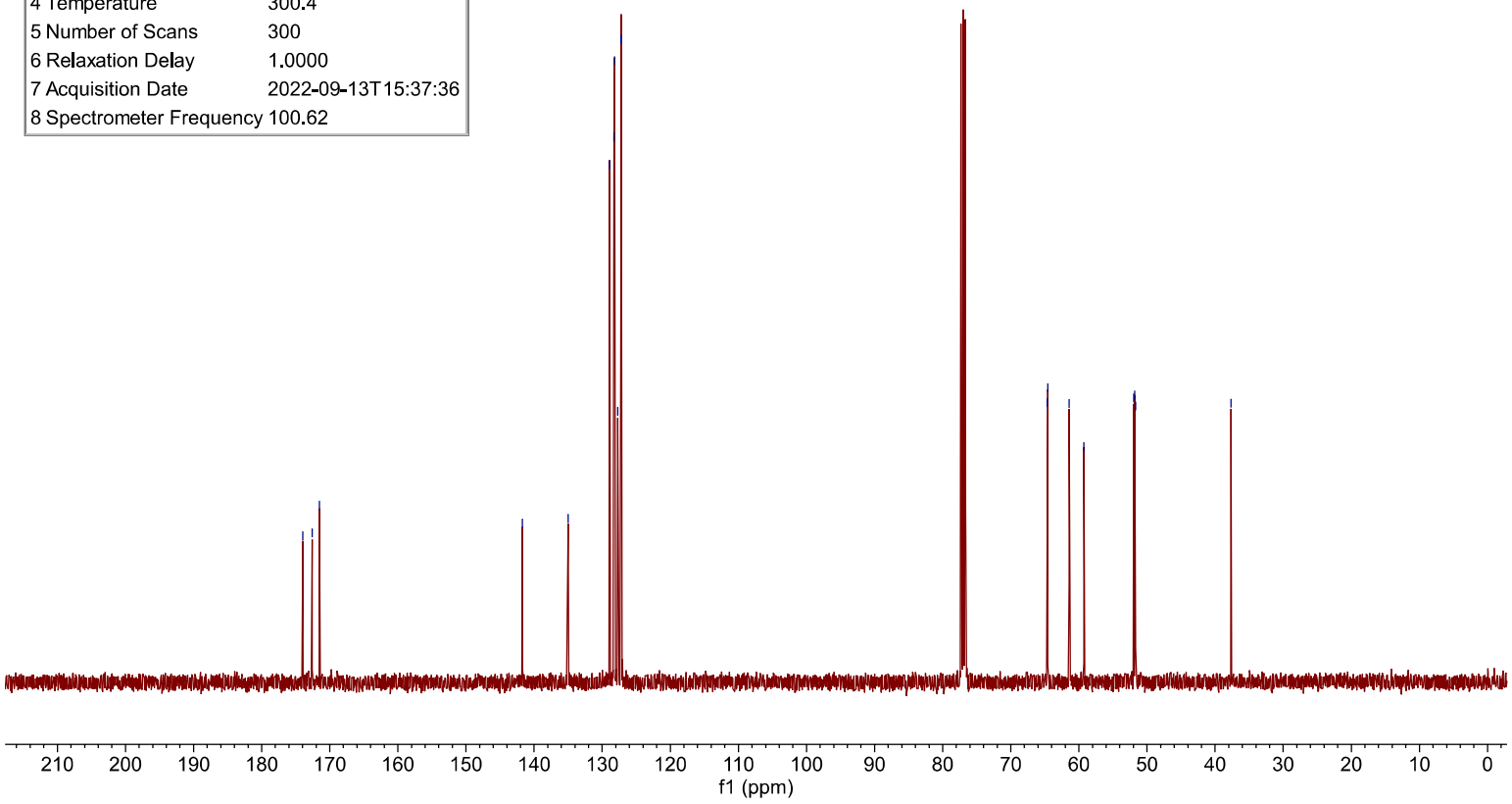
173.97
172.59
171.51

141.74
134.98
128.92
128.26
128.18
127.74
127.24

64.67
64.59
61.42
59.25
51.94
51.79
51.68



Parameter	Value
1 Title	llc-2-66-b2-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.4
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-13T15:37:36
8 Spectrometer Frequency	100.62



7.28
7.26
7.25
7.08
7.07
7.06
7.04
7.04
7.03
7.02
7.01
7.01
7.00
6.99
6.99
6.98
6.97
6.96
6.94
6.92
5.65
5.63

4.51
4.49

4.10
4.07

3.78
3.75
3.74

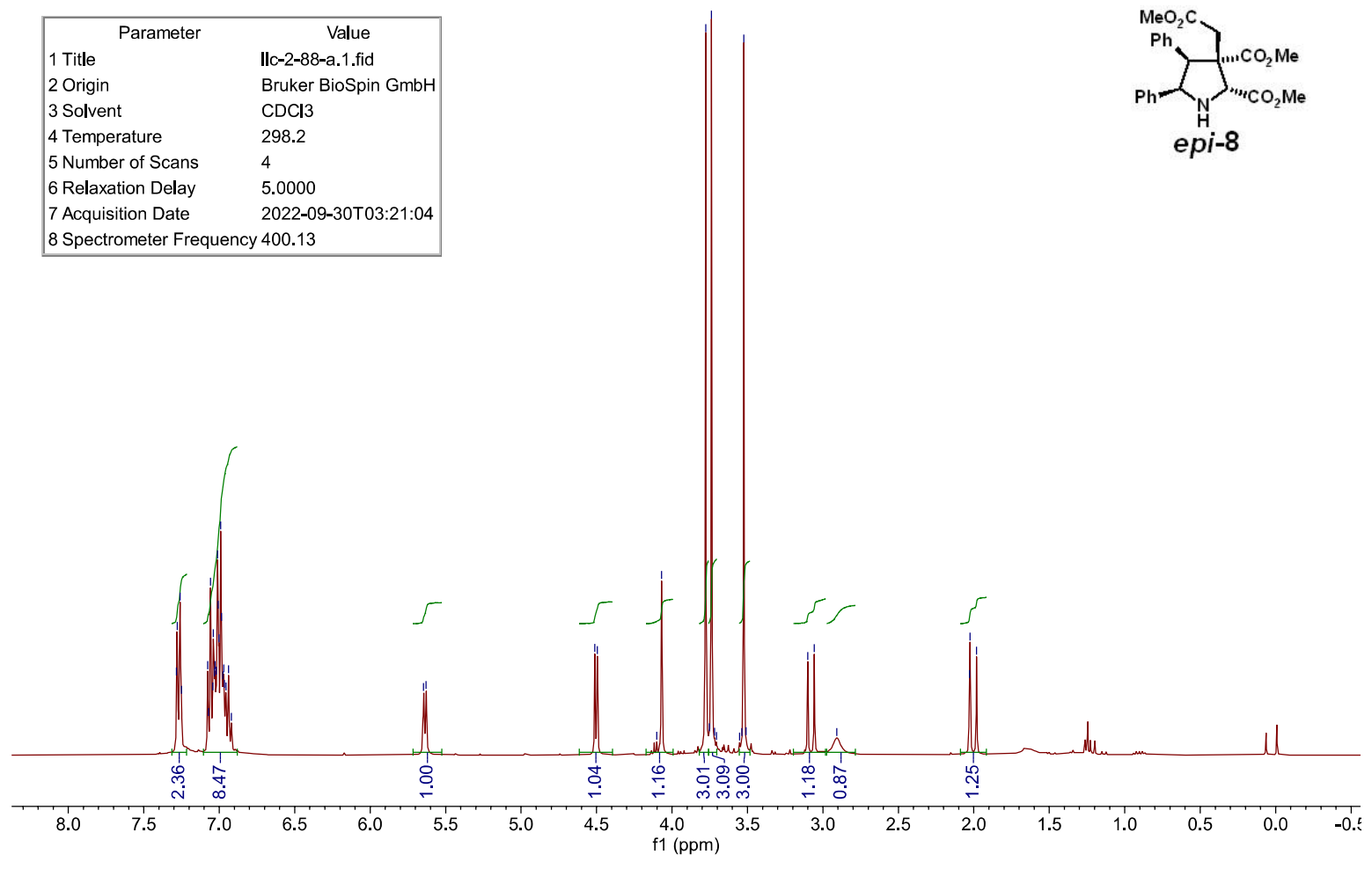
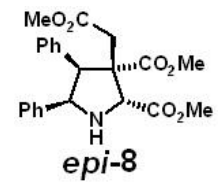
3.72
3.71

3.55
3.54
3.52
3.51

3.10
3.06
2.91

2.03
2.03
1.98

Parameter	Value
1 Title	llc-2-88-a.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.2
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-09-30T03:21:04
8 Spectrometer Frequency	400.13



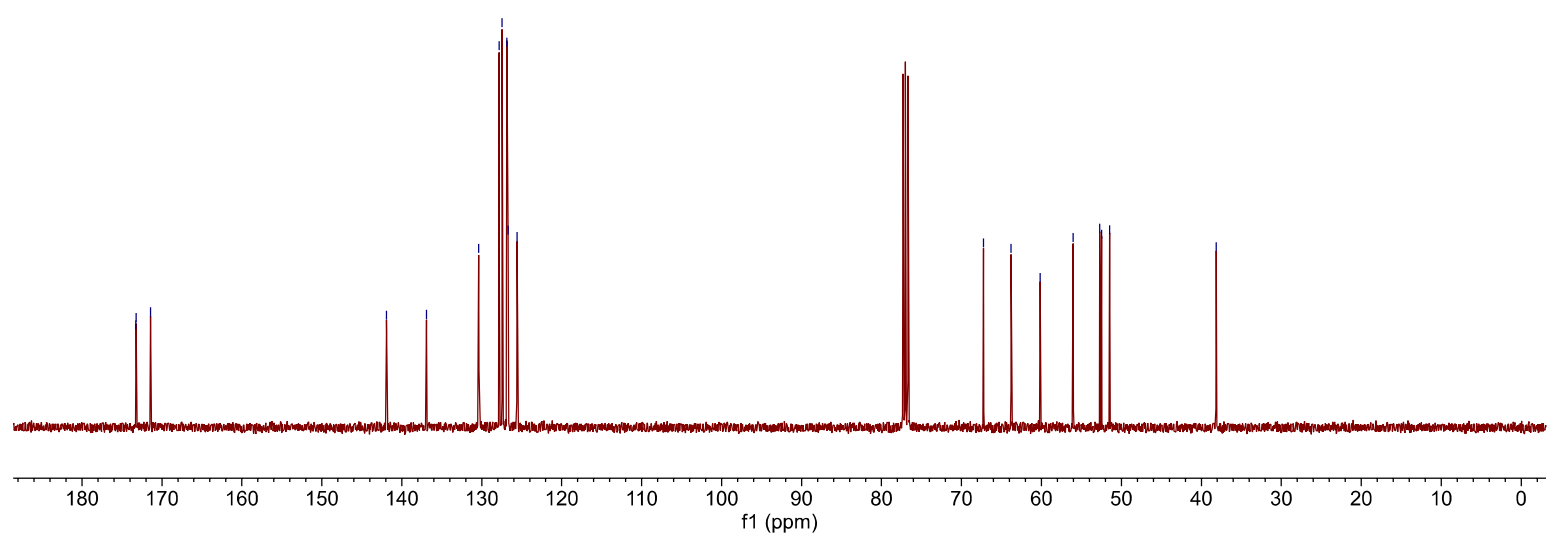
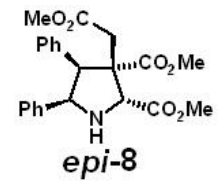
173.26
173.21
171.42

141.91
136.91
130.39
127.82
127.45
126.87
126.70
125.59

67.23
63.79
60.17
56.03
52.70
51.49

38.14

Parameter	Value
1 Title	llc-2-88-a-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.9
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-09-30T14:25:20
8 Spectrometer Frequency	100.62



7.30
7.28
7.26
7.21
7.20
7.19
7.06
7.05
7.04
7.03
7.01
6.99
6.97
6.96
6.95

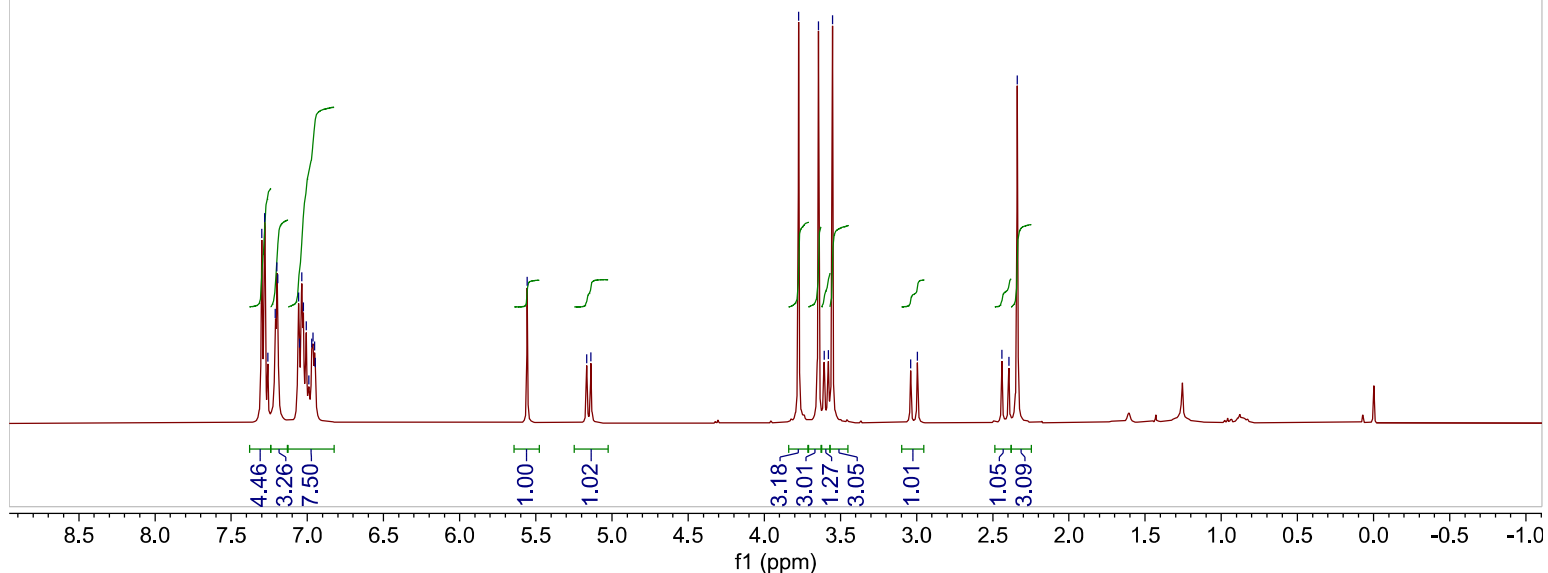
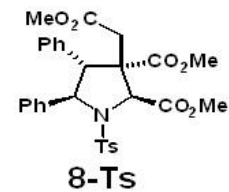
5.56
5.17
5.14

3.77
3.64
3.61
3.58
3.55

3.04
2.99

2.44
2.39
2.34

Parameter	Value
1 Title	LLC-3-102-2-ap2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	295.8
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2023-02-17T04:51:02
8 Spectrometer Frequency	400.13

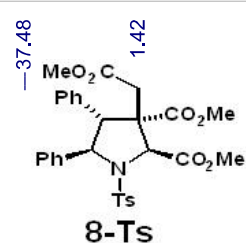


171.85
170.59
170.49

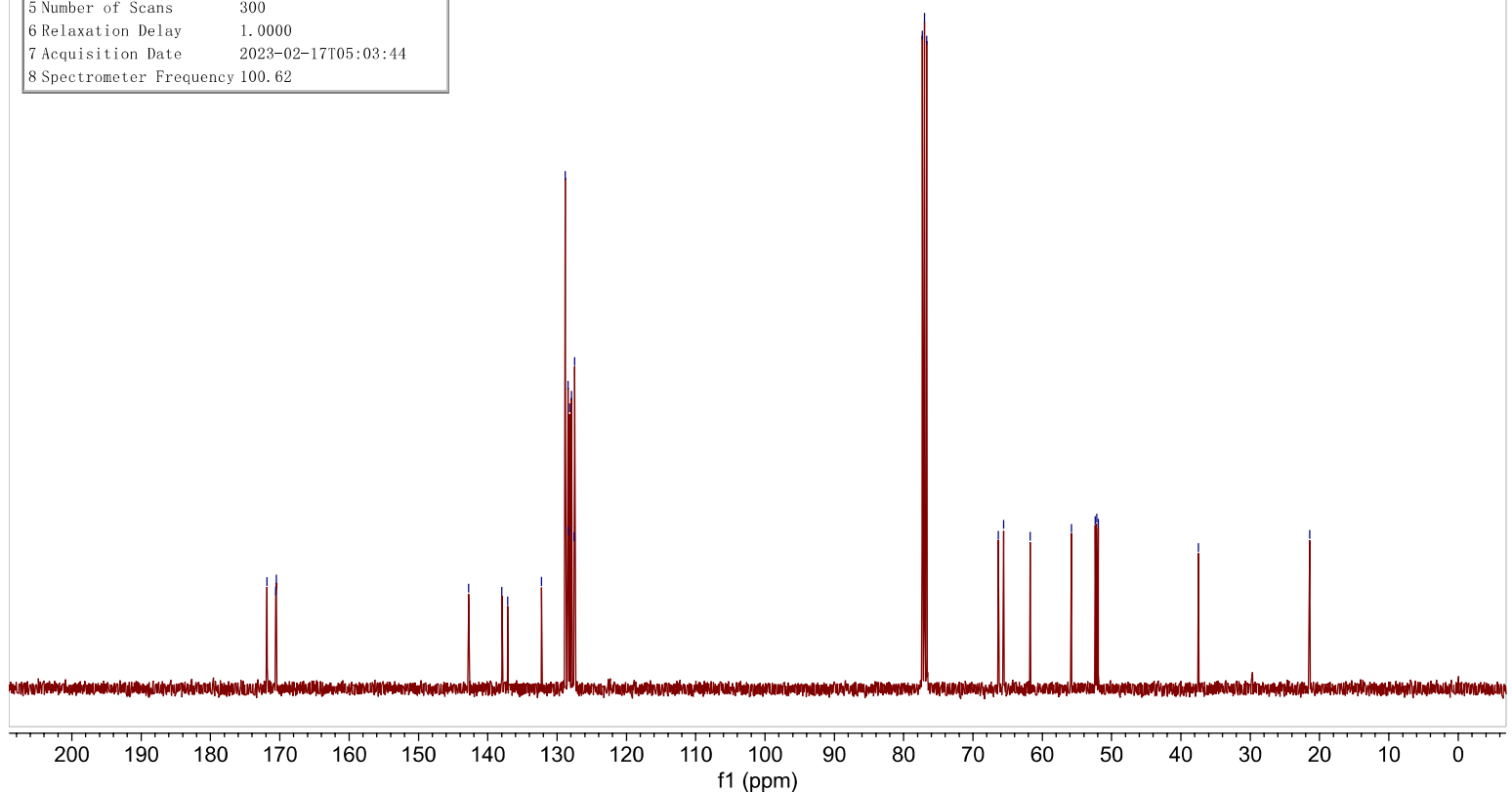
142.76
137.96
137.12
132.24
128.81
128.44
128.36
128.20
127.91
127.54
127.46

77.32
77.00
76.68

66.33
65.59
61.77
55.81
52.96
52.16
51.93



Parameter	Value
1 Title	LLC-3-102-2-ap2-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.4
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2023-02-17T05:03:44
8 Spectrometer Frequency	100.62



7.49
7.49
7.47
7.26
7.24
7.22
7.21
7.20
7.18
7.16
7.13
7.12
7.11
7.10

5.14
5.12

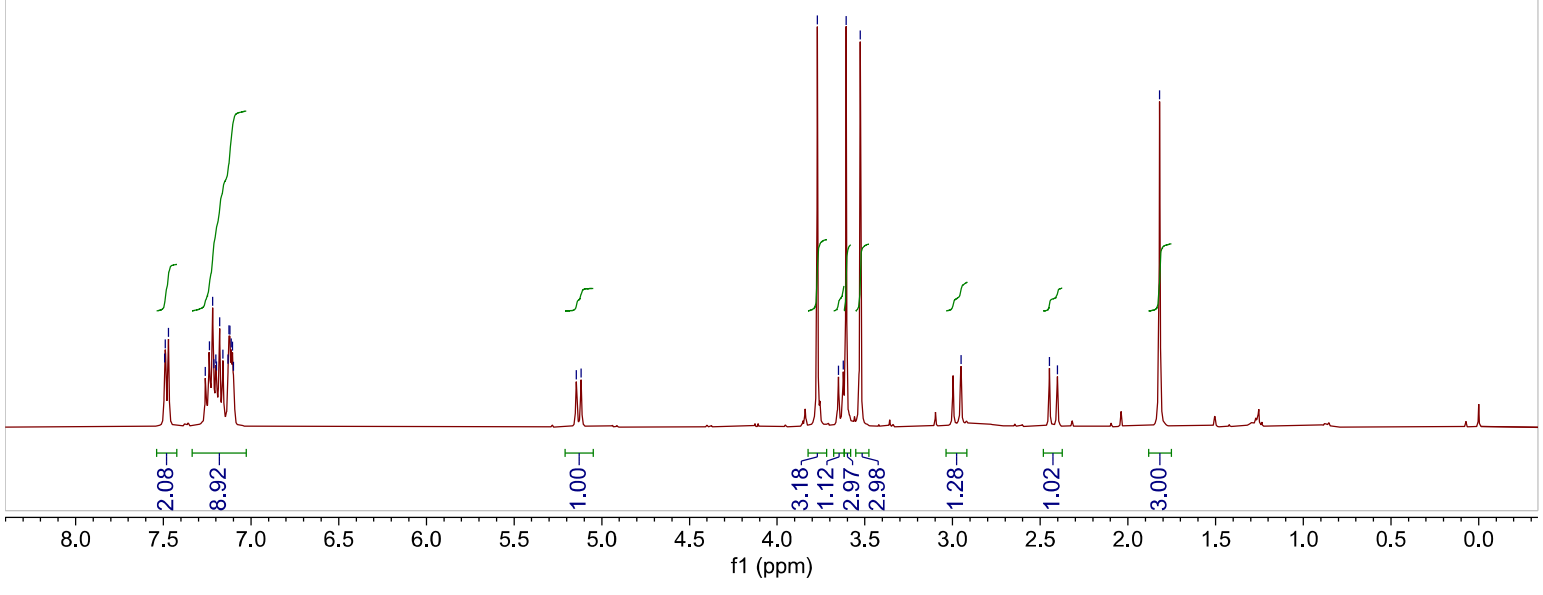
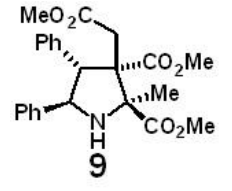
3.77
3.65
3.62
3.61
3.53

2.95

2.45
2.40

1.82

Parameter	Value
1 Title	LLC-4-63-p1B2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	296.4
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2023-04-25T23:09:40
8 Spectrometer	400.13
Frequency	



175.99
170.76
170.54

142.53
134.87
129.17
128.34
128.10
127.88
127.42
126.96

71.54

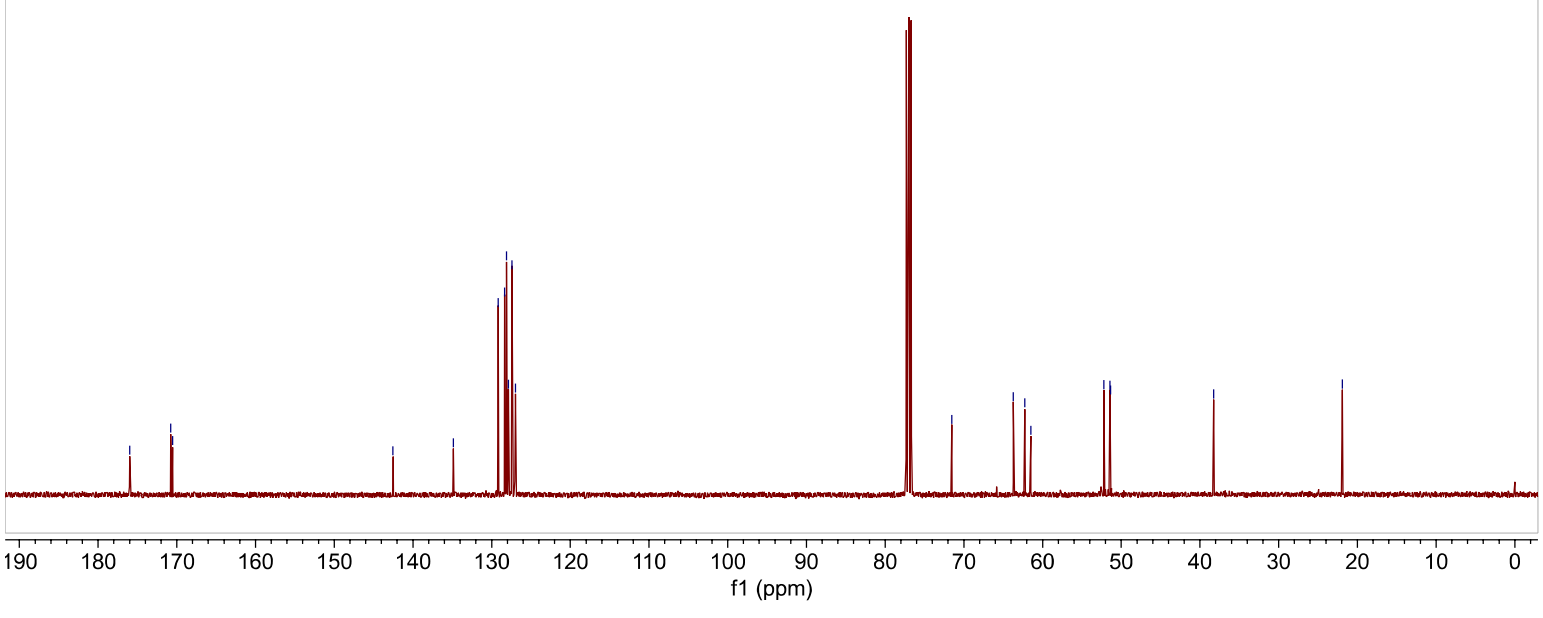
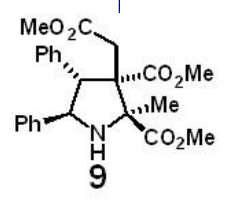
63.71
62.27
61.50

52.20
51.44
51.38

38.27

21.91

Parameter	Value
1 Title	LLC-4-34-b-C
2 Origin	Varian
3 Solvent	cdcl3
4 Temperature	25.0
5 Number of Scans	2000
6 Relaxation Delay	1.0000
7 Acquisition Date	2023-04-14T01:51:49
8 Spectrometer	100.56
Frequency	



7.19
7.18
7.17
7.08
7.06
7.04
7.00
6.98
6.96
6.95

5.09
5.07

4.52
4.50

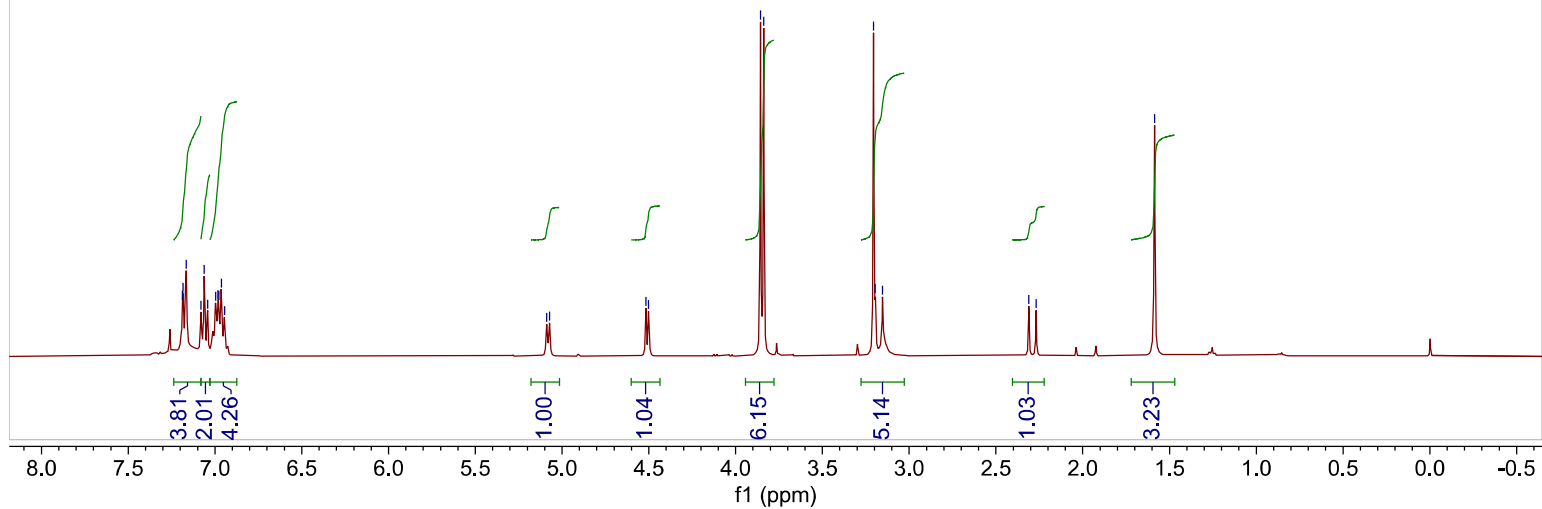
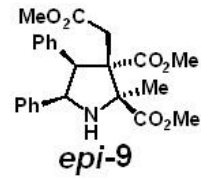
3.86
3.84

3.21
3.20
3.15

2.31
2.27

1.59

Parameter	Value
1 Title	LLC-4-63-p1A2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.4
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2023-04-25T23:05:53
8 Spectrometer Frequency	400.13

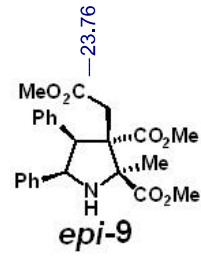


174.31
174.23
171.53

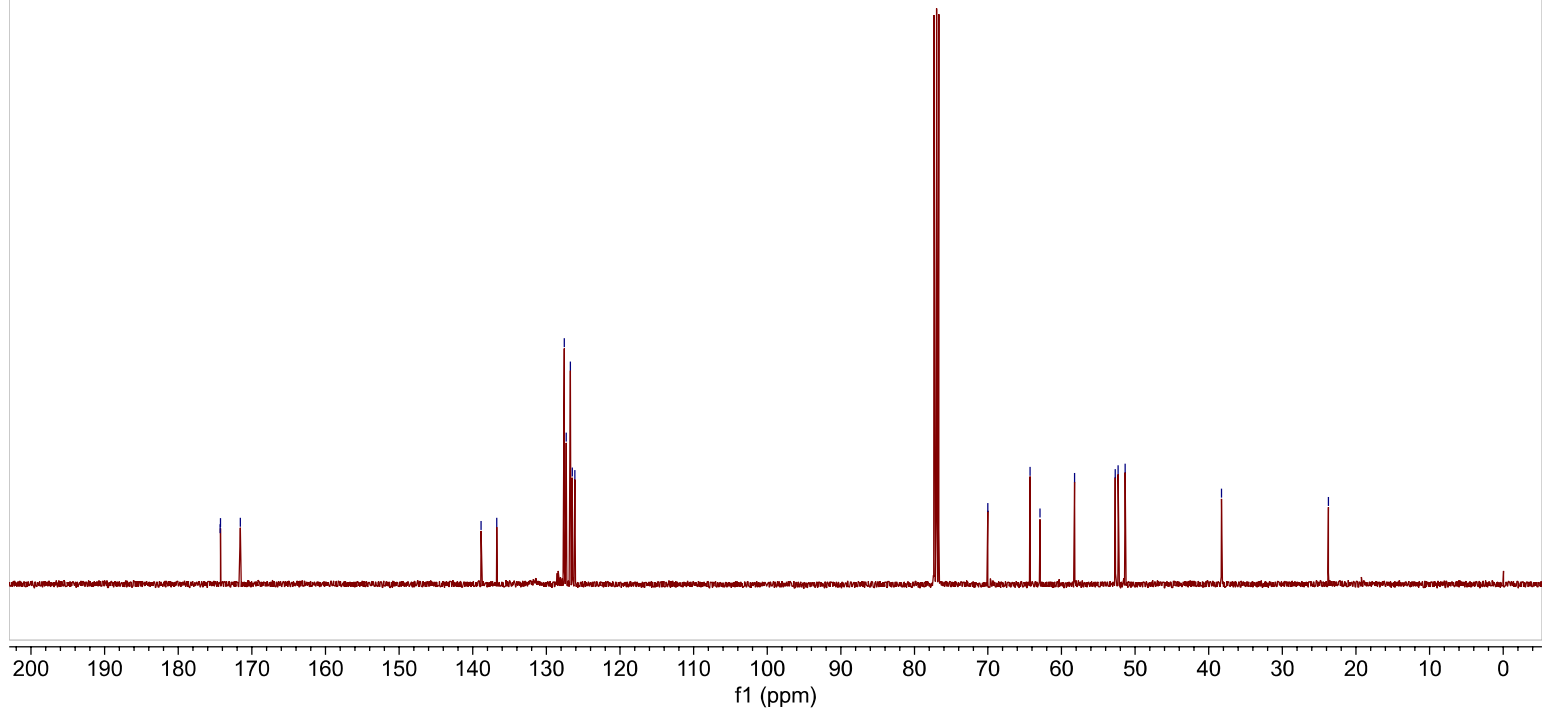
138.84
136.70
127.57
127.31
126.74
126.46
126.12

70.04
64.30
62.95
58.26
52.70
52.31
51.35

38.28



Parameter	Value
1 Title	LLC-4-34-a-C
2 Origin	Varian
3 Solvent	cdcl3
4 Temperature	25.0
5 Number of Scans	2000
6 Relaxation Delay	1.0000
7 Acquisition Date	2023-04-14T00:32:20
8 Spectrometer Frequency	100.56



7.92
7.91
7.90
7.89
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.00
7.00
6.99
6.98

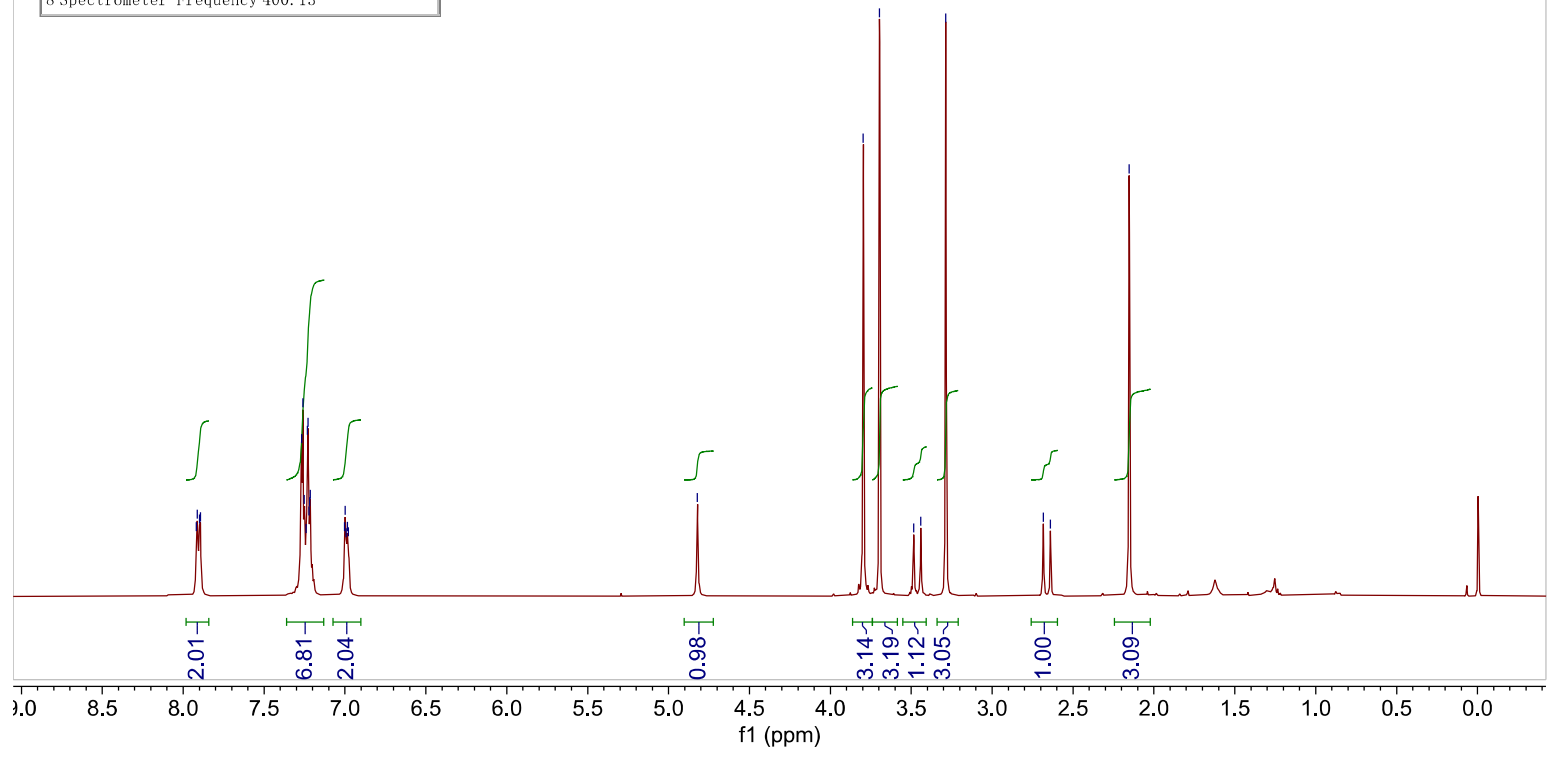
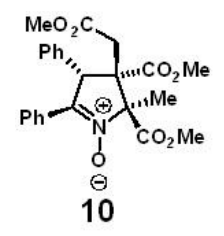
4.82

3.80
3.70
3.48
3.44
3.29

2.68
2.64

2.15

Parameter	Value
1 Title	LLC-3-39-5B.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.5
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2023-04-14T03:57:32
8 Spectrometer Frequency	400.13



169.82
169.61
168.17

141.29
134.45
129.84
129.62
128.50
128.48
128.30
128.15
127.88

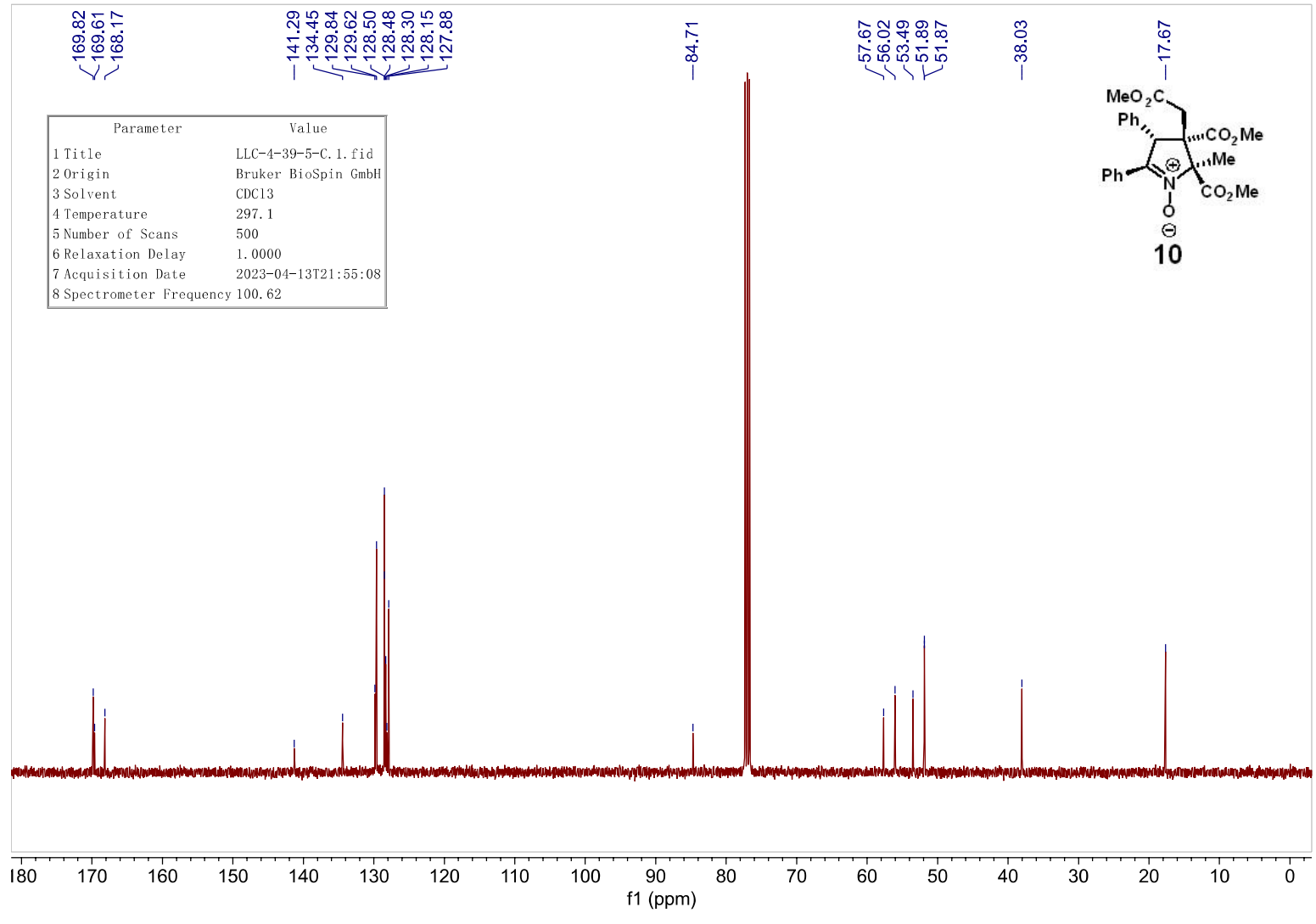
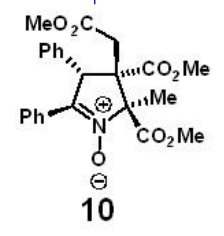
84.71

57.67
56.02
53.49
51.89
51.87

38.03

17.67

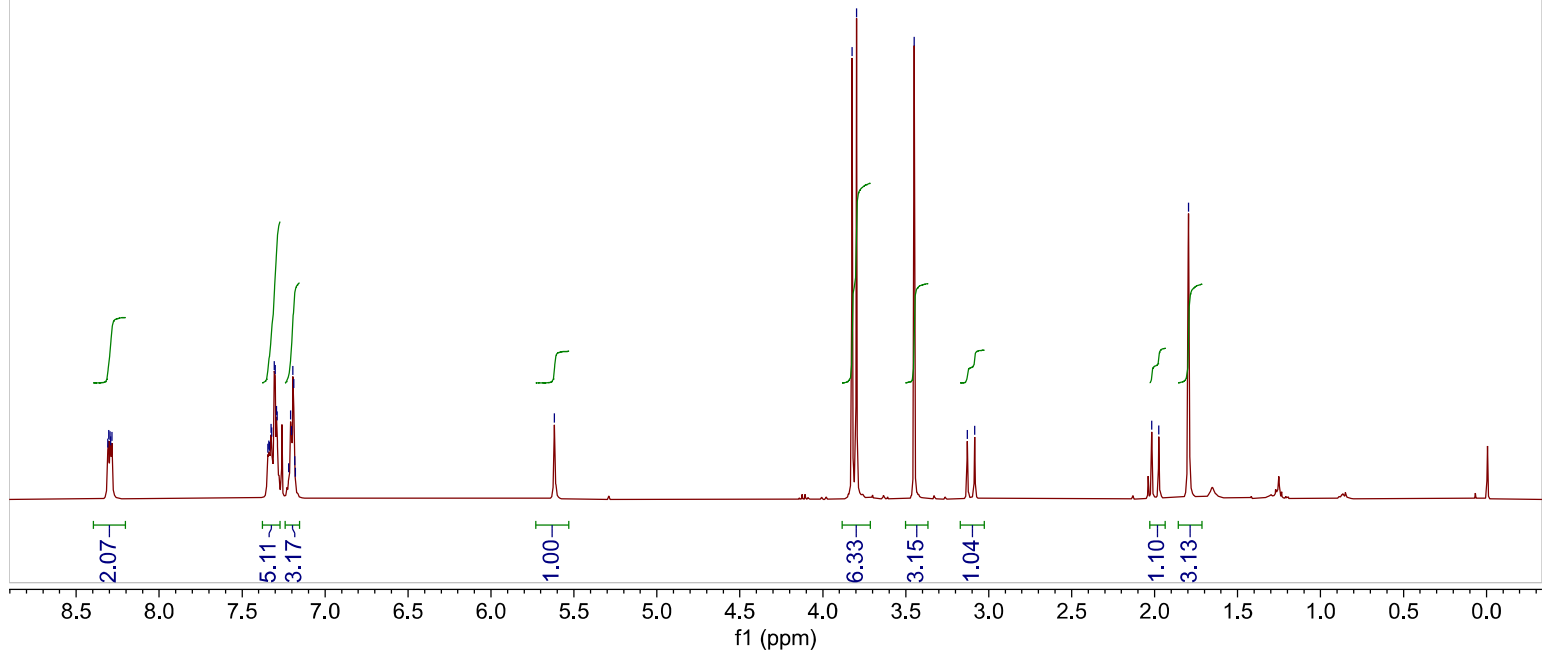
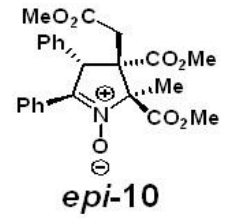
Parameter	Value
1 Title	LLC-4-39-5-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.1
5 Number of Scans	500
6 Relaxation Delay	1.0000
7 Acquisition Date	2023-04-13T21:55:08
8 Spectrometer Frequency	100.62



8.31
8.30
8.30
8.29
8.28
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.29
7.22
7.21
7.20
7.19
7.19
7.18
7.18
-5.62

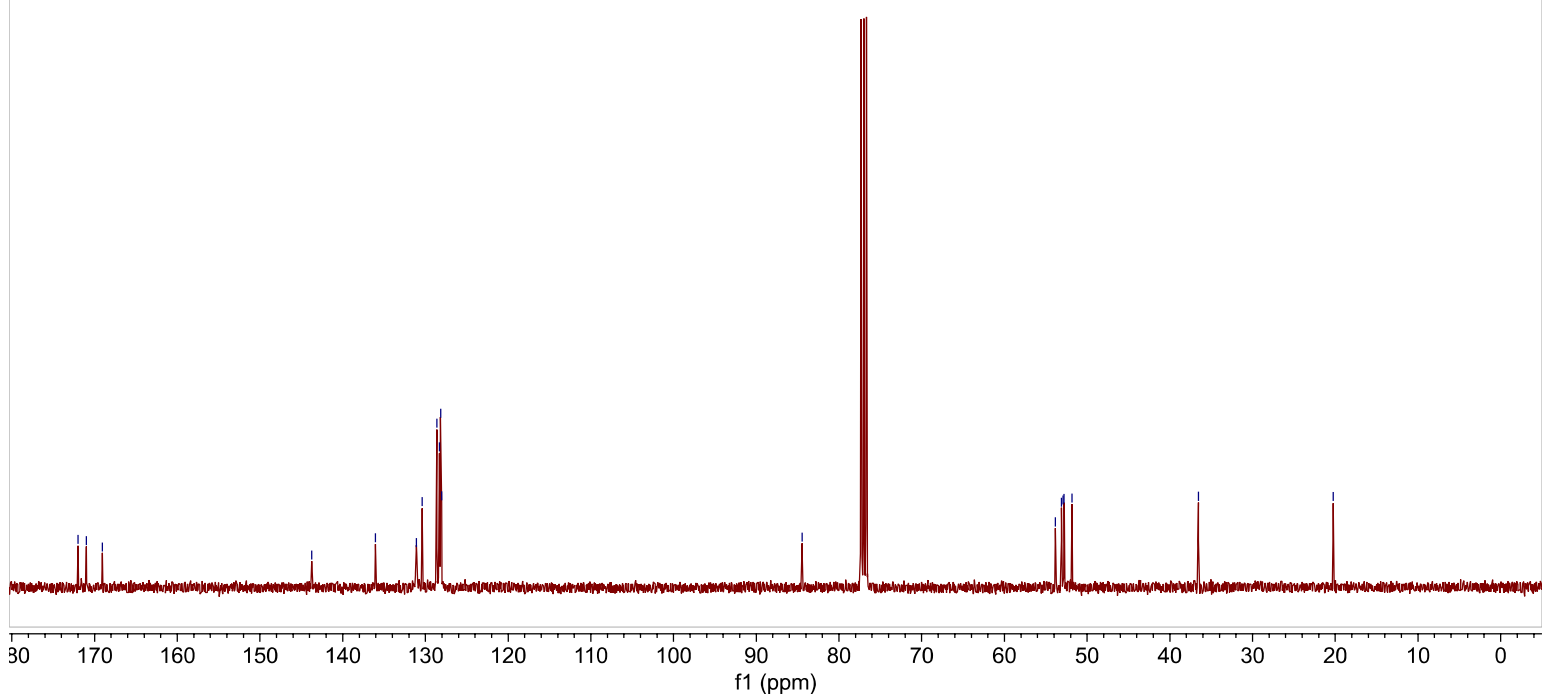
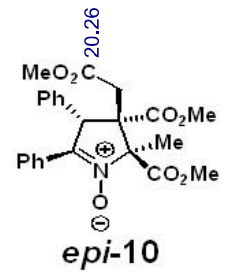
3.82
3.80
3.45
3.13
3.09
2.02
1.97
1.80

Parameter	Value
1 Title	LLC-4-39-4-B. 1. fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.6
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2023-04-14T01:52:43
8 Spectrometer Frequency	400.13



171.99
171.00
169.07
143.76
136.05
131.09
130.40
128.63
128.32
128.17
128.04
84.46
53.84
53.09
52.91
52.79
51.84
36.55

Parameter	Value
1 Title	LLC-4-39-4B-C. 1. fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.2
5 Number of Scans	1000
6 Relaxation Delay	1.0000
7 Acquisition Date	2023-04-14T08:28:05
8 Spectrometer Frequency	100.62



7.69
7.68
7.67
7.66
7.21
7.21
7.20
7.19
7.16
7.15
7.14
7.13
7.12
7.11

5.59

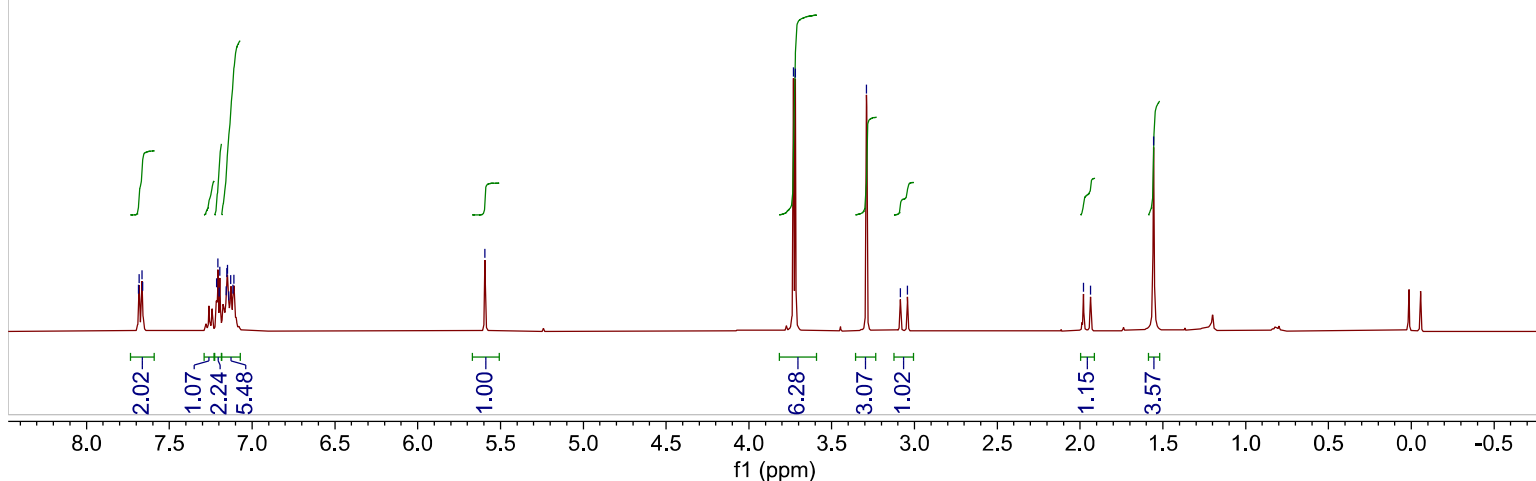
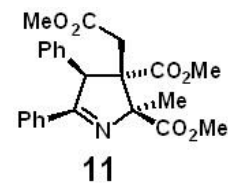
3.73
3.72

3.29
3.09
3.04

1.98
1.94

1.56

Parameter	Value
1 Title	LLC-4-66-H2.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	296.7
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2023-04-26T20:58:40
8 Spectrometer Frequency	400.13



174.25
173.38
172.65
171.49

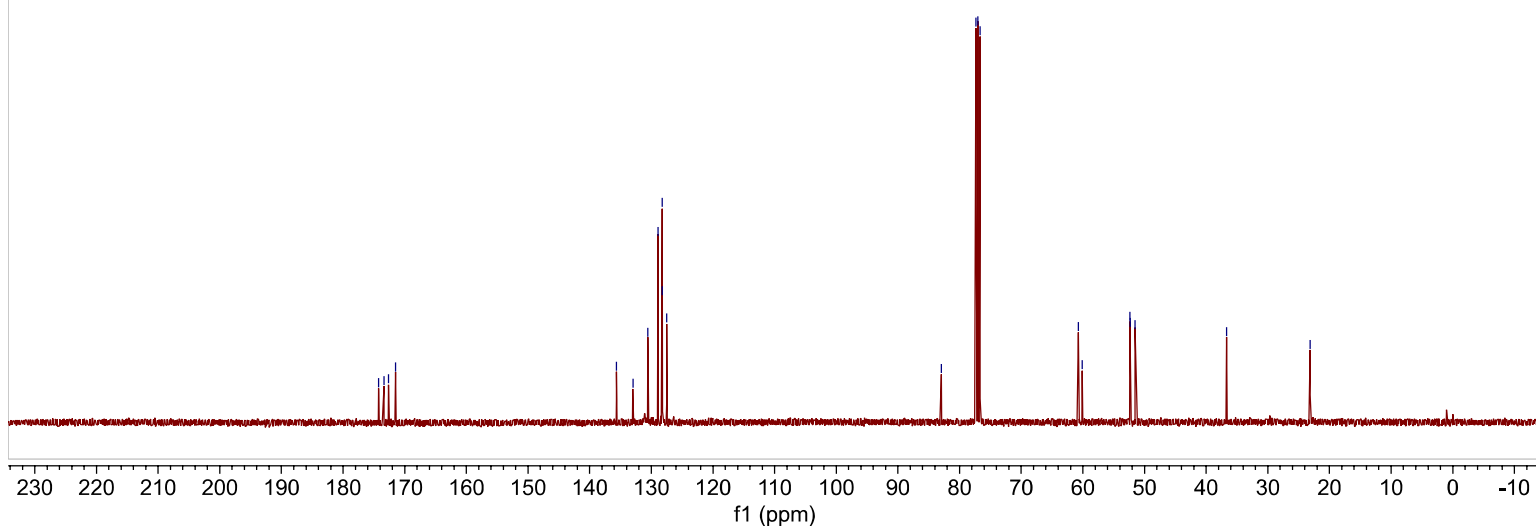
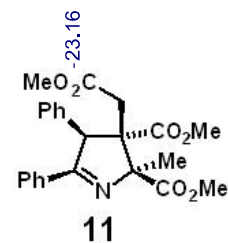
135.67
132.98
130.56
128.89
128.23
128.21
127.51

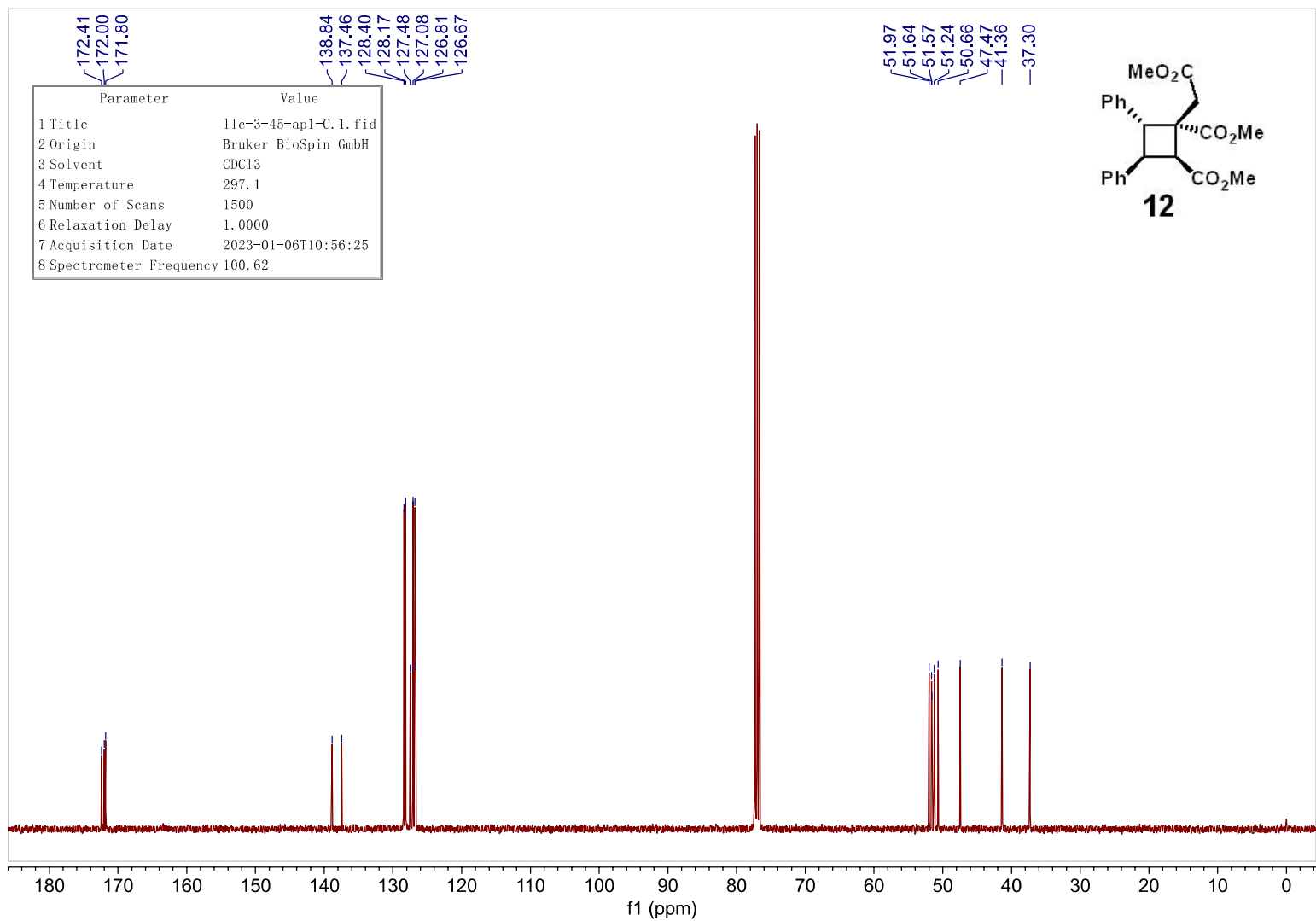
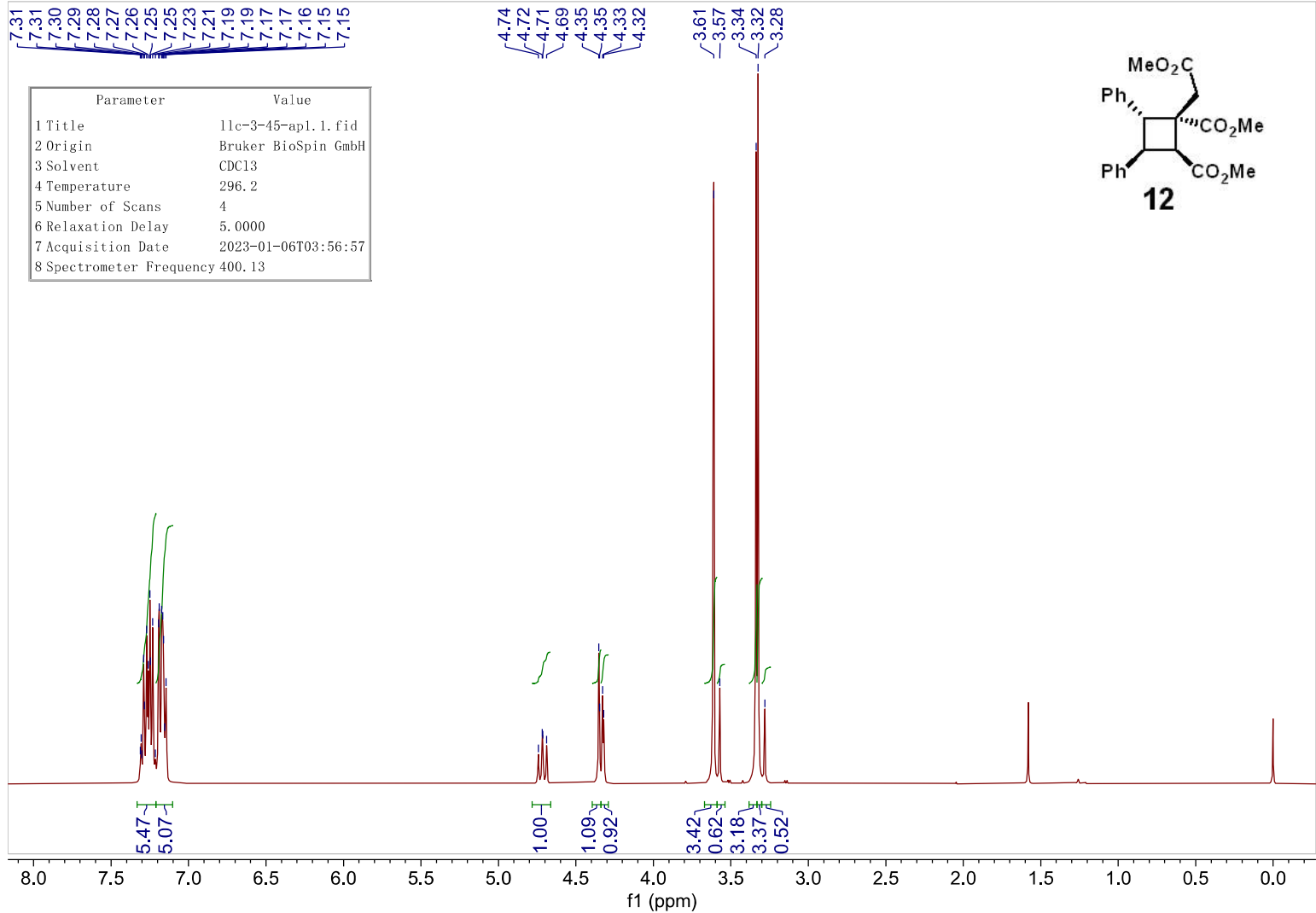
82.94
77.33
77.01
76.69

60.75
60.11
52.35
52.33
51.52

36.67

Parameter	Value
1 Title	LLC-4-66-C
2 Origin	Varian
3 Solvent	cdcl3
4 Temperature	25.0
5 Number of Scans	1000
6 Relaxation Delay	1.0000
7 Acquisition Date	2023-04-26T17:02:44
8 Spectrometer Frequency	100.56



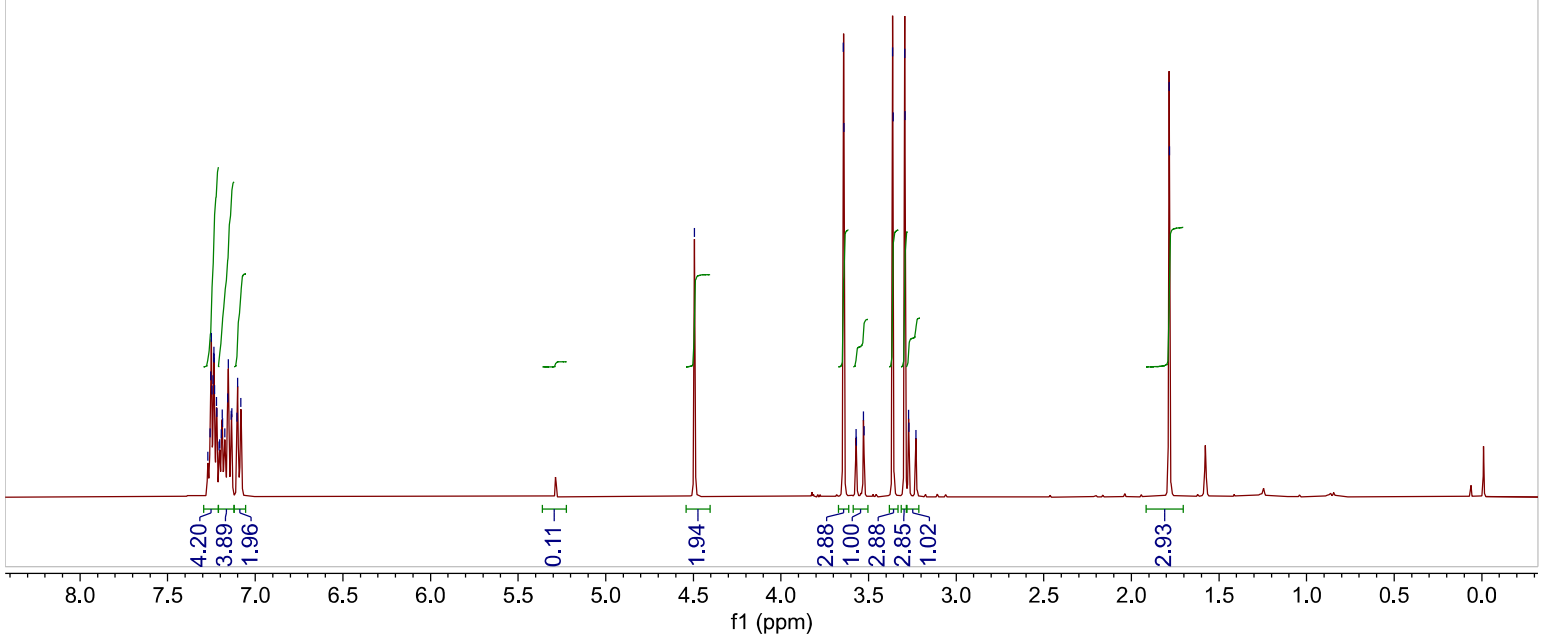
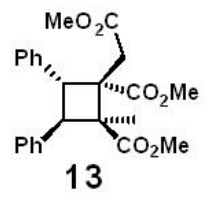


7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.20
7.19
7.19
7.17
7.16
7.15
7.14
7.13
7.10
7.10
7.08

4.49
3.64
3.64
3.57
3.57
3.53
3.53
3.36
3.36
3.29
3.29
3.27
3.27
3.23

1.78
1.78

Parameter	Value
1 Title	LLC-4-78-1-H
2 Origin	Varian
3 Solvent	cdcl3
4 Temperature	25.0
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2023-05-01T06:09:07
8 Spectrometer Frequency	399.89

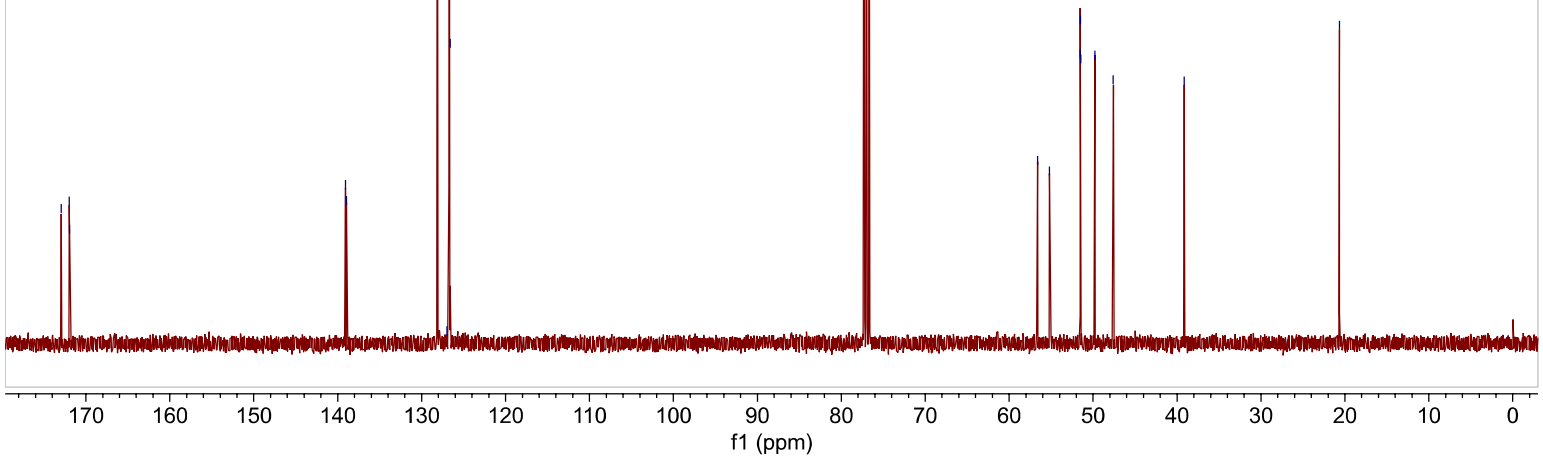
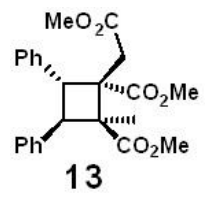


172.95
171.97
171.94
139.08
138.94
128.13
128.12
127.00
126.74
126.70
126.59

56.61
55.20
51.53
51.51
49.80
47.60
39.15

20.67

Parameter	Value
1 Title	LLC-4-78-1-C
2 Origin	Varian
3 Solvent	cdcl3
4 Temperature	25.0
5 Number of Scans	512
6 Relaxation Delay	1.0000
7 Acquisition Date	2023-05-01T06:09:55
8 Spectrometer Frequency	100.56

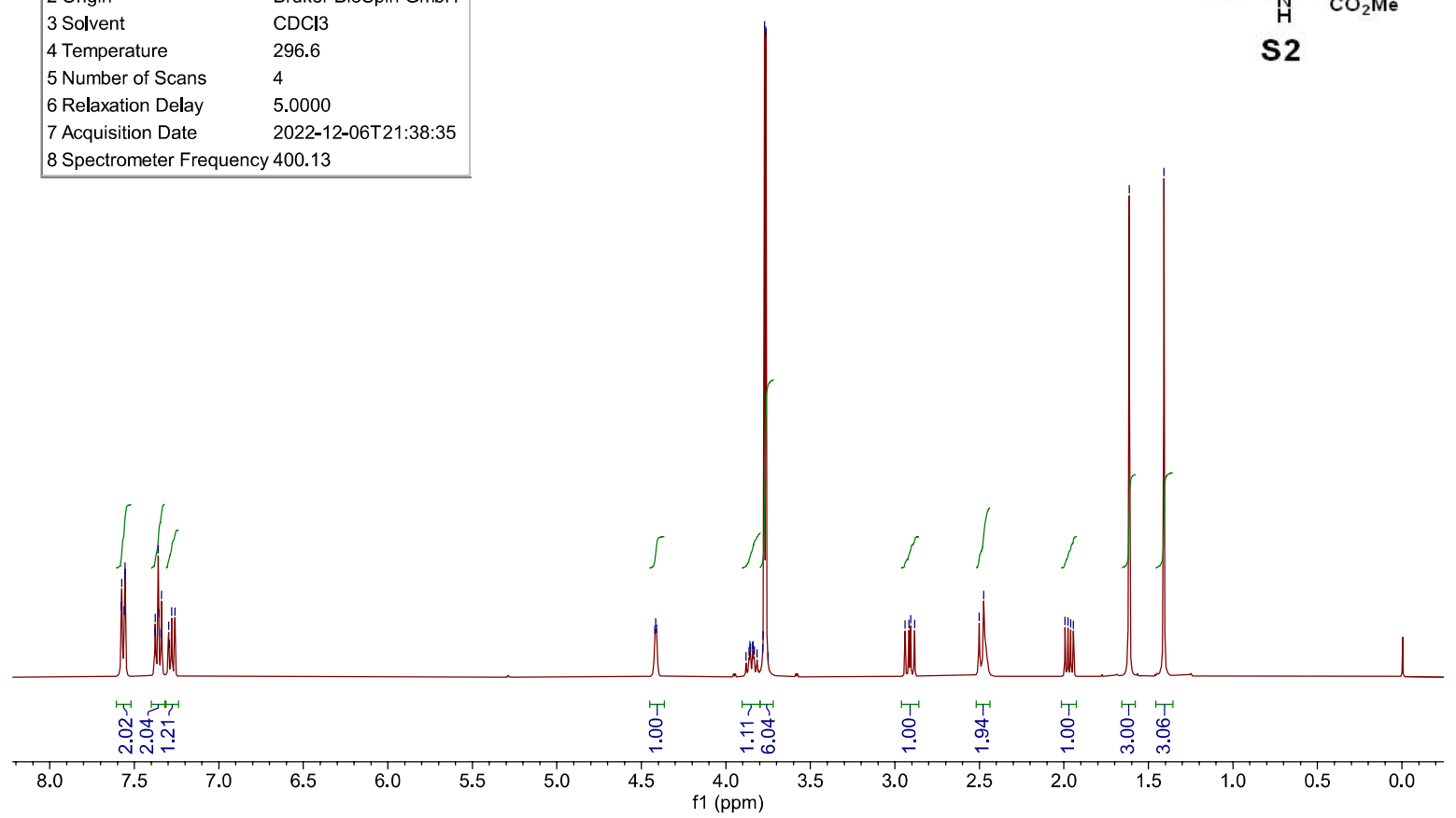
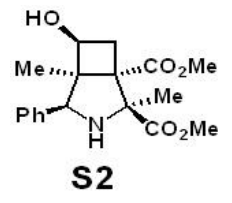


7.58
7.57
7.56
7.55
7.38
7.36
7.35
7.34
7.34
7.30
7.29
7.28
7.26

4.42
4.41
4.41
3.88
3.86
3.85
3.84
3.84
3.83
3.82
3.78
3.78
3.77
3.76
3.75
2.94
2.92
2.91
2.88
2.50
2.48

1.99
1.98
1.96
1.94
1.61
1.41

Parameter	Value
1 Title	llc-2-195-3-Bruker.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.6
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-12-06T21:38:35
8 Spectrometer Frequency	400.13



173.85
171.80

138.32

128.61
127.59
126.79

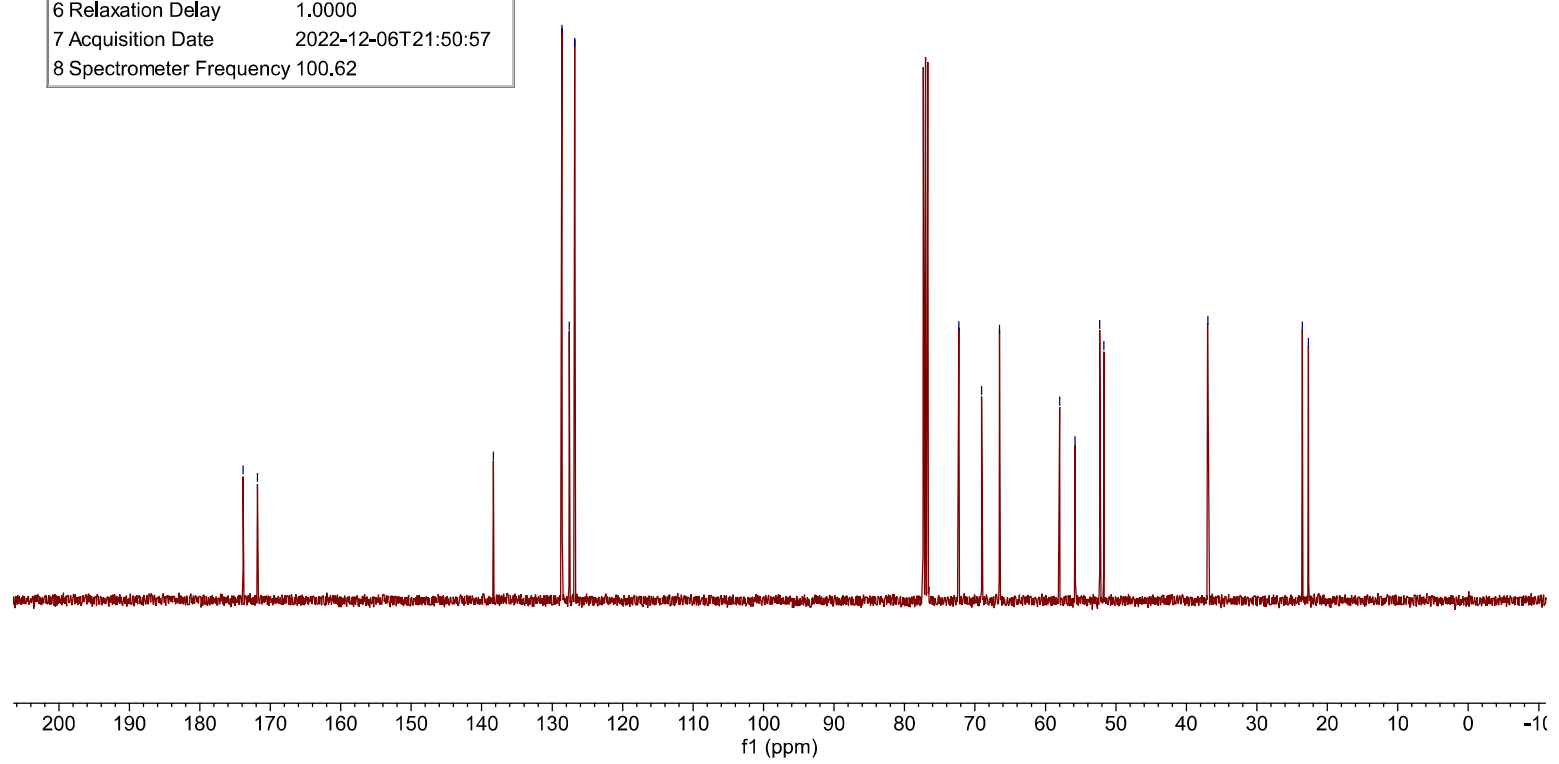
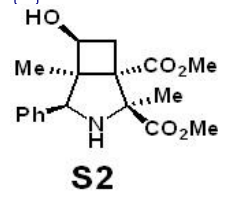
72.27
69.05
66.54

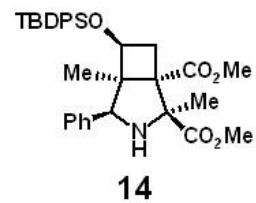
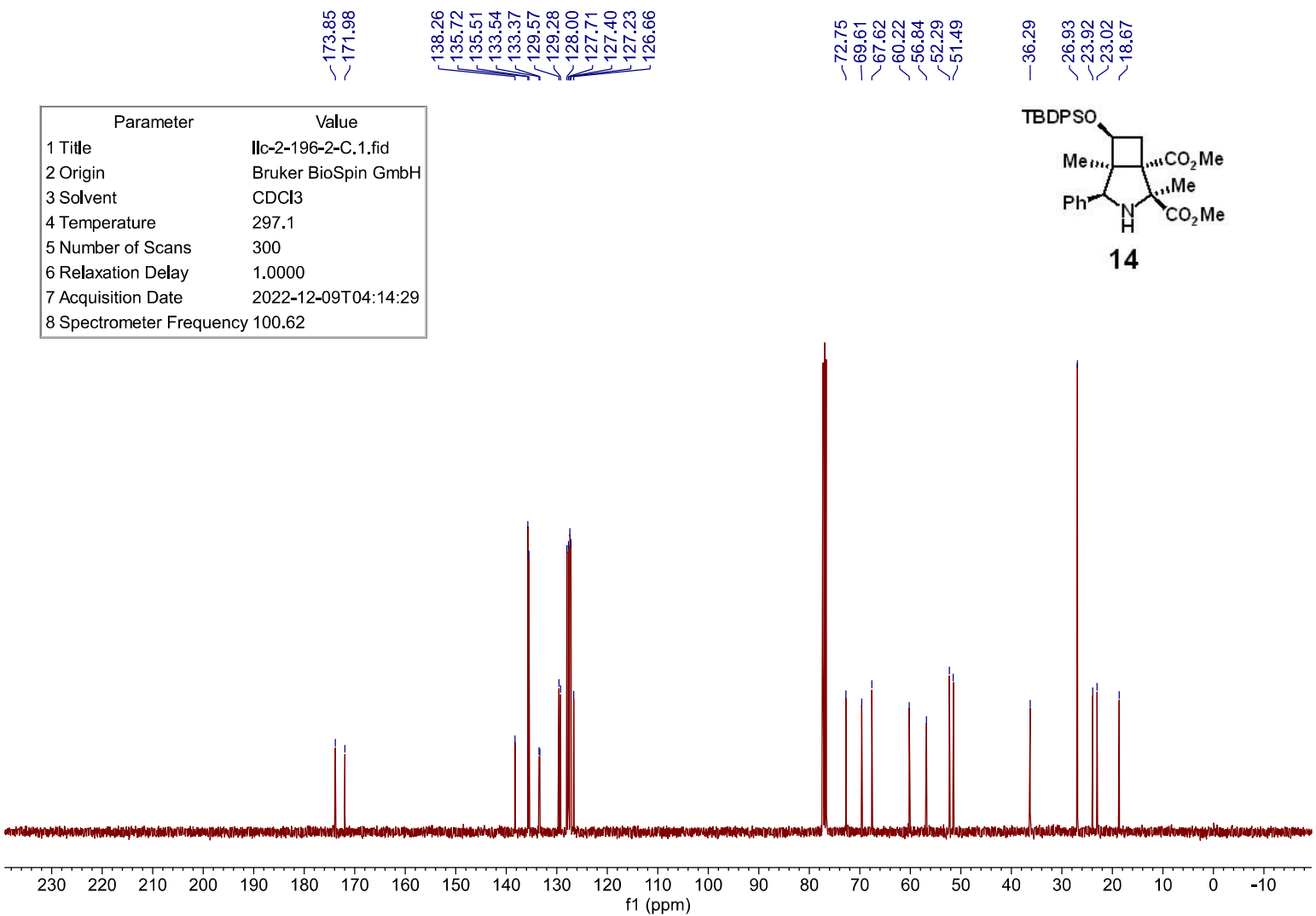
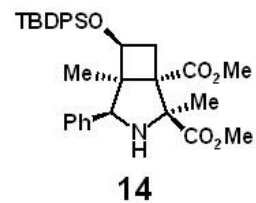
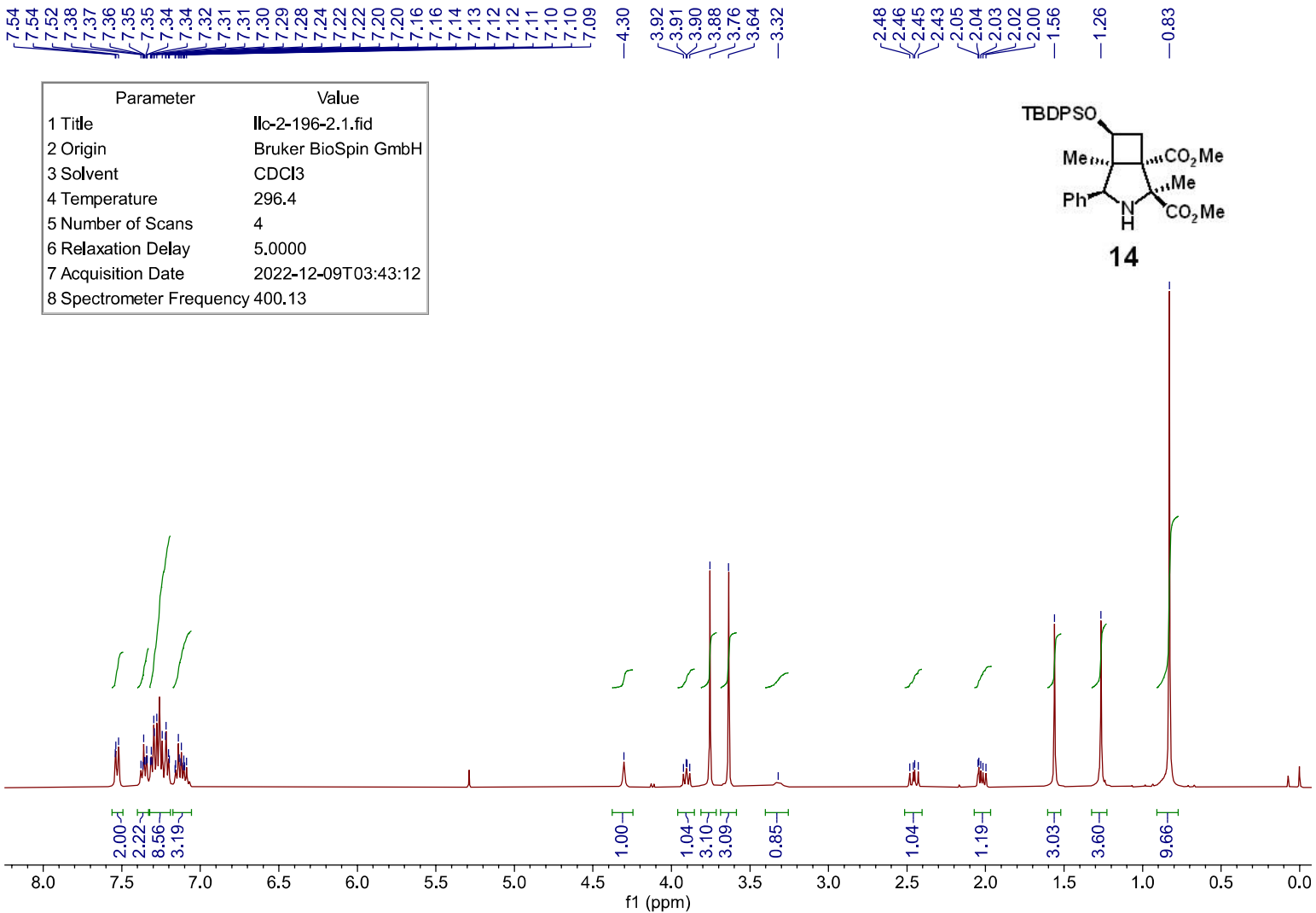
58.00
55.79
52.29
51.71

36.97

23.55
22.67

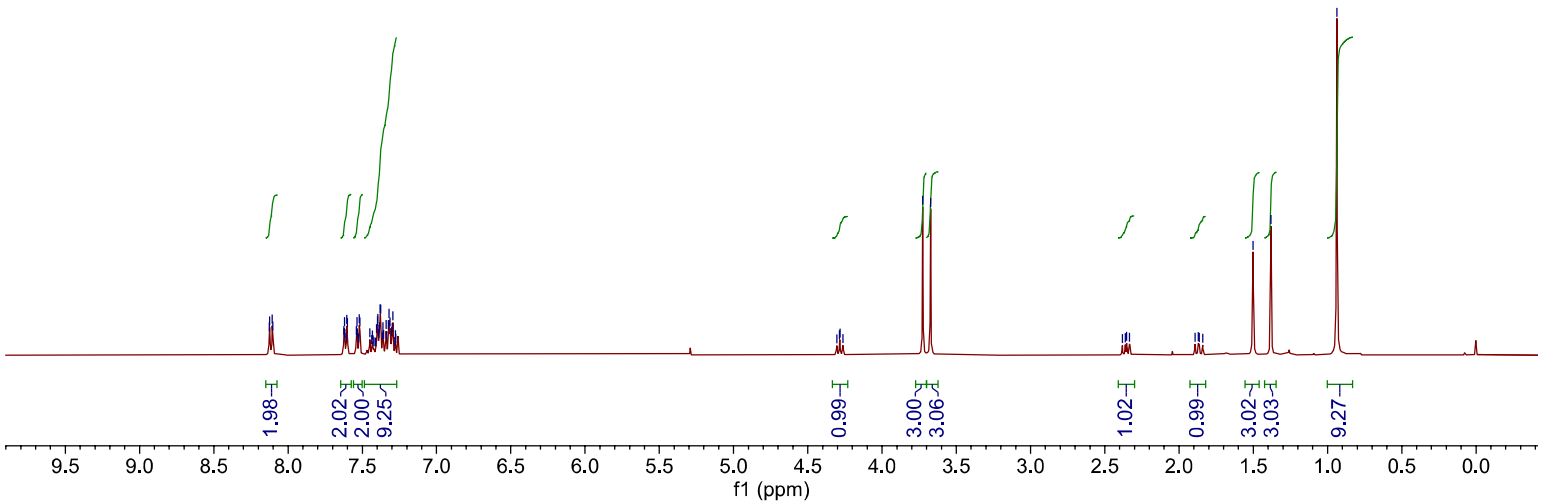
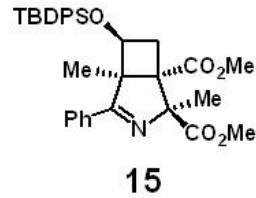
Parameter	Value
1 Title	llc-2-195-3-Carbon.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.2
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-12-06T21:50:57
8 Spectrometer Frequency	100.62



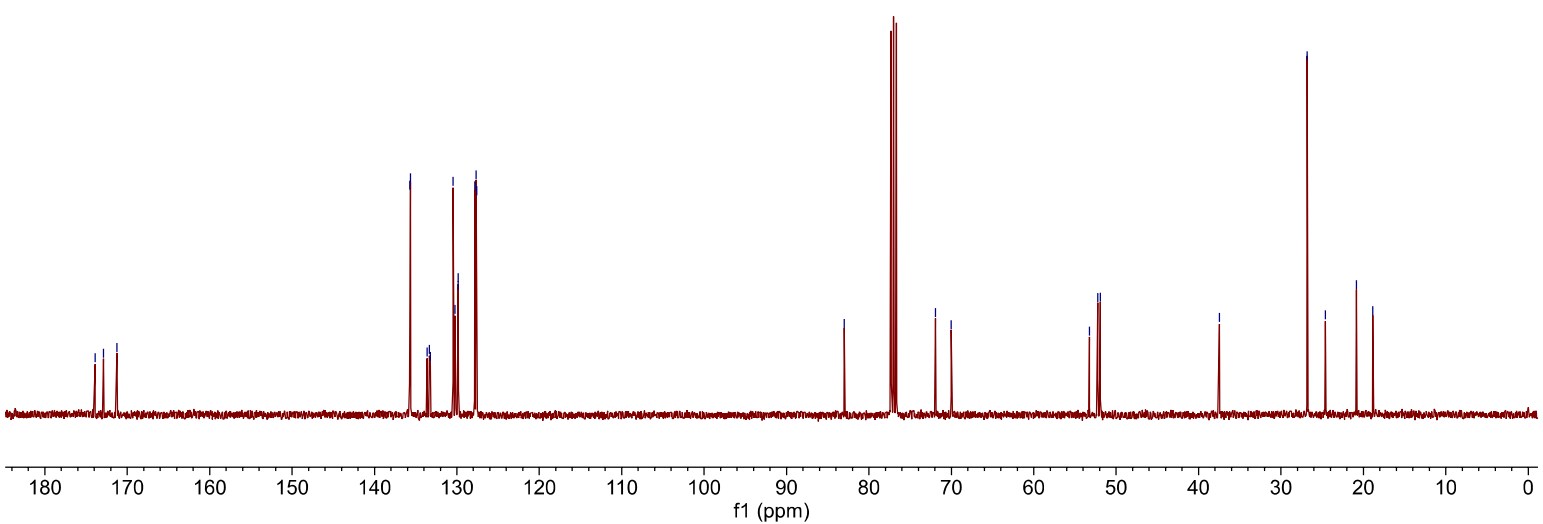
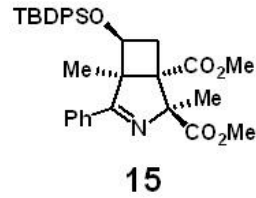


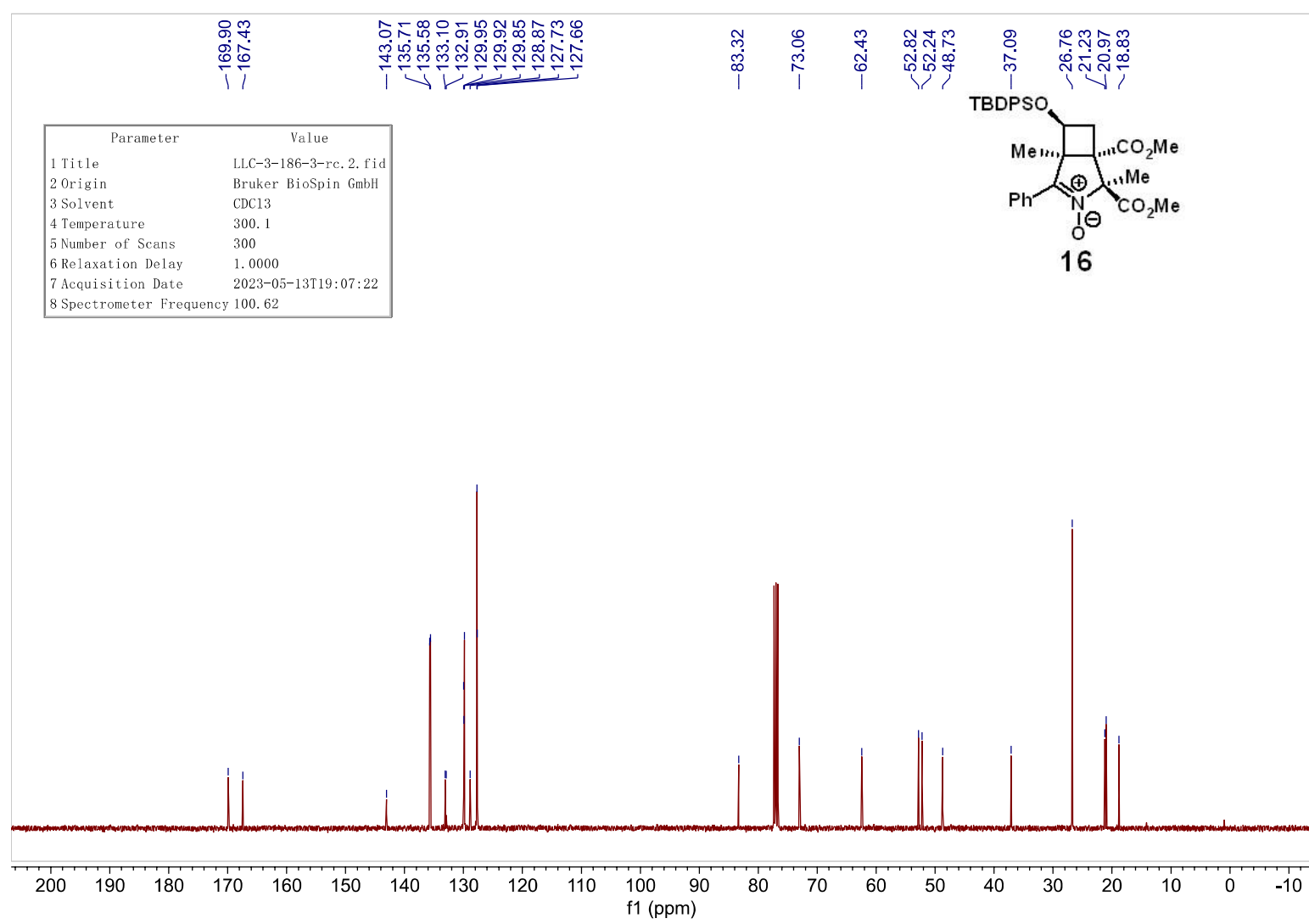
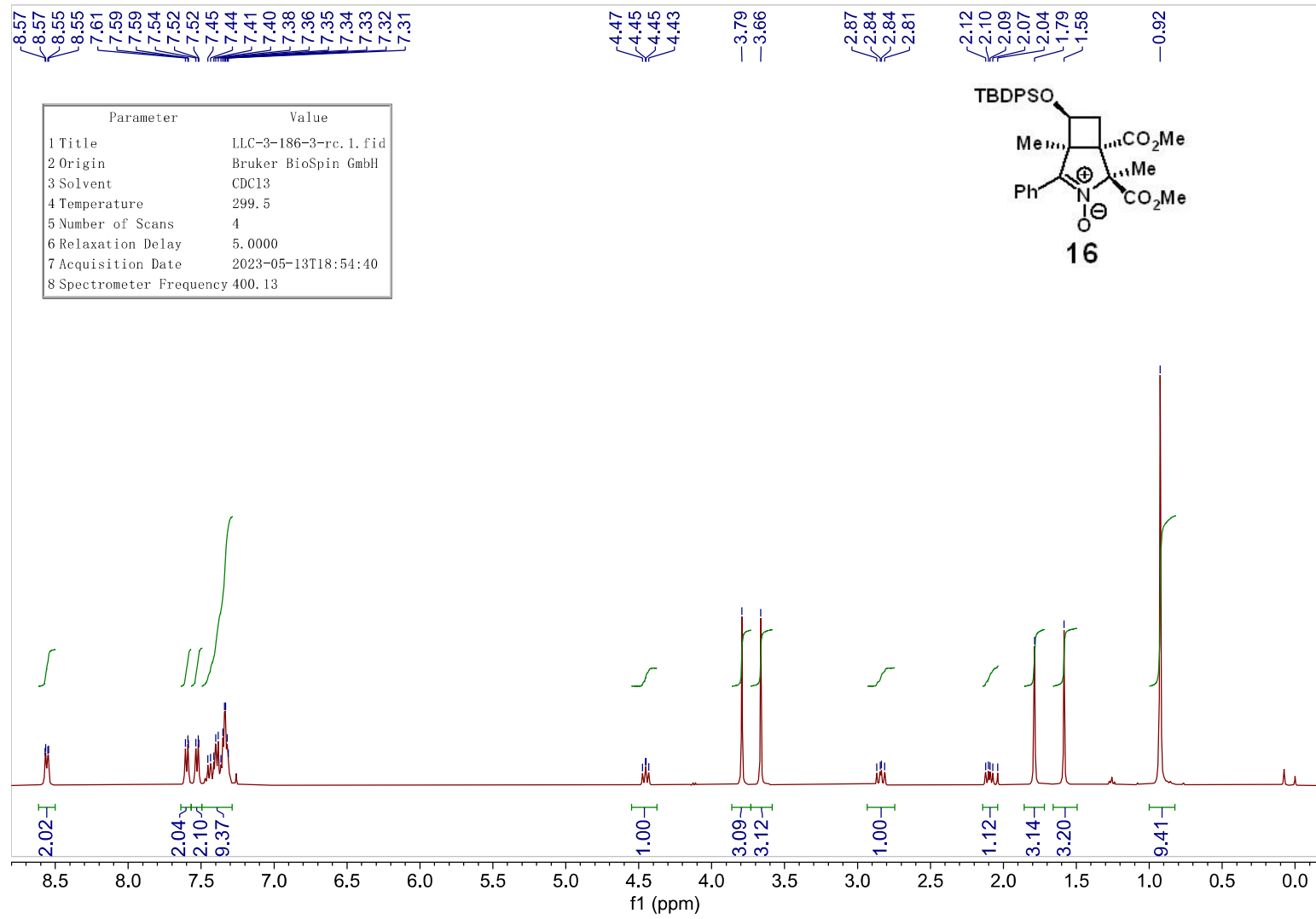


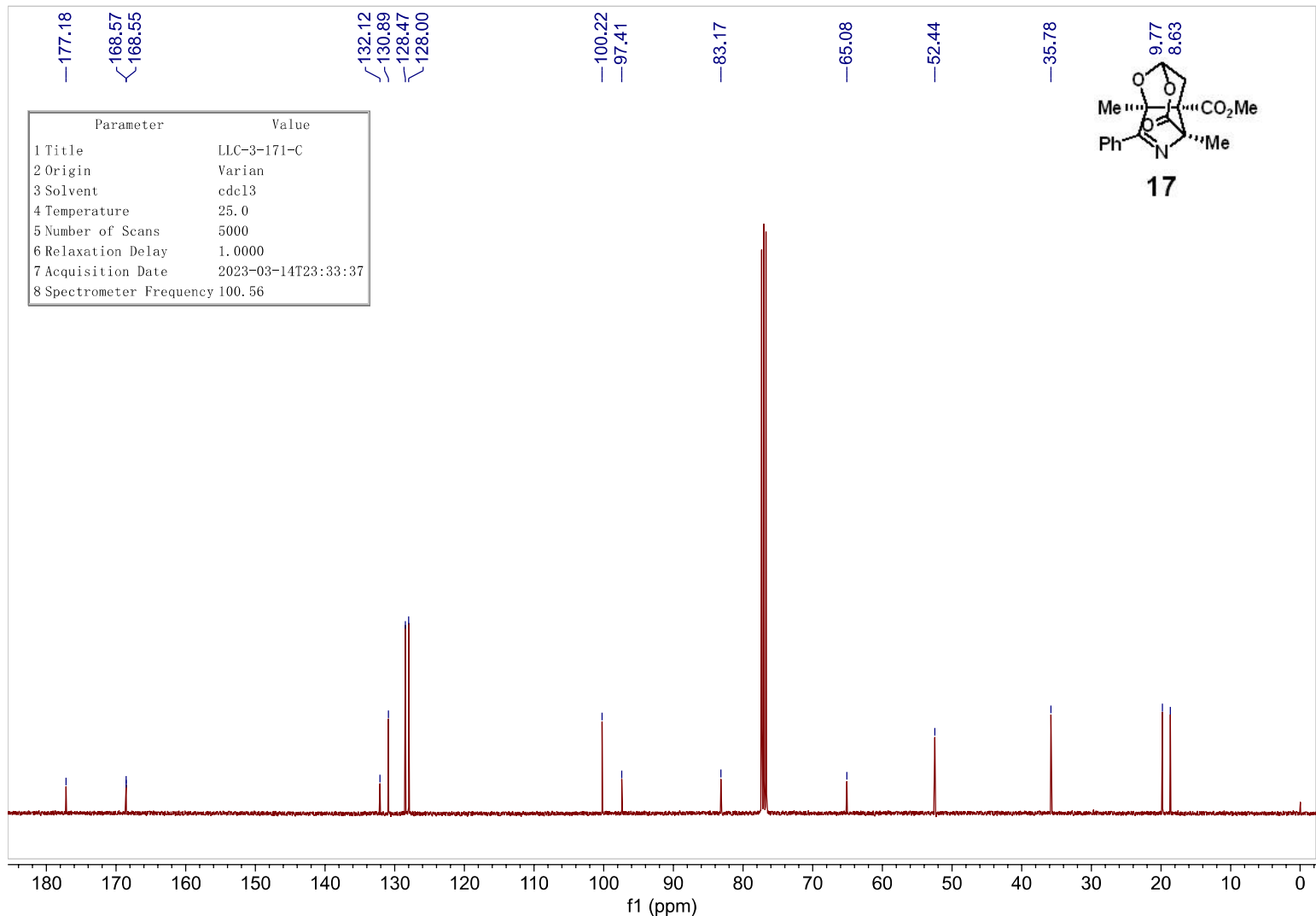
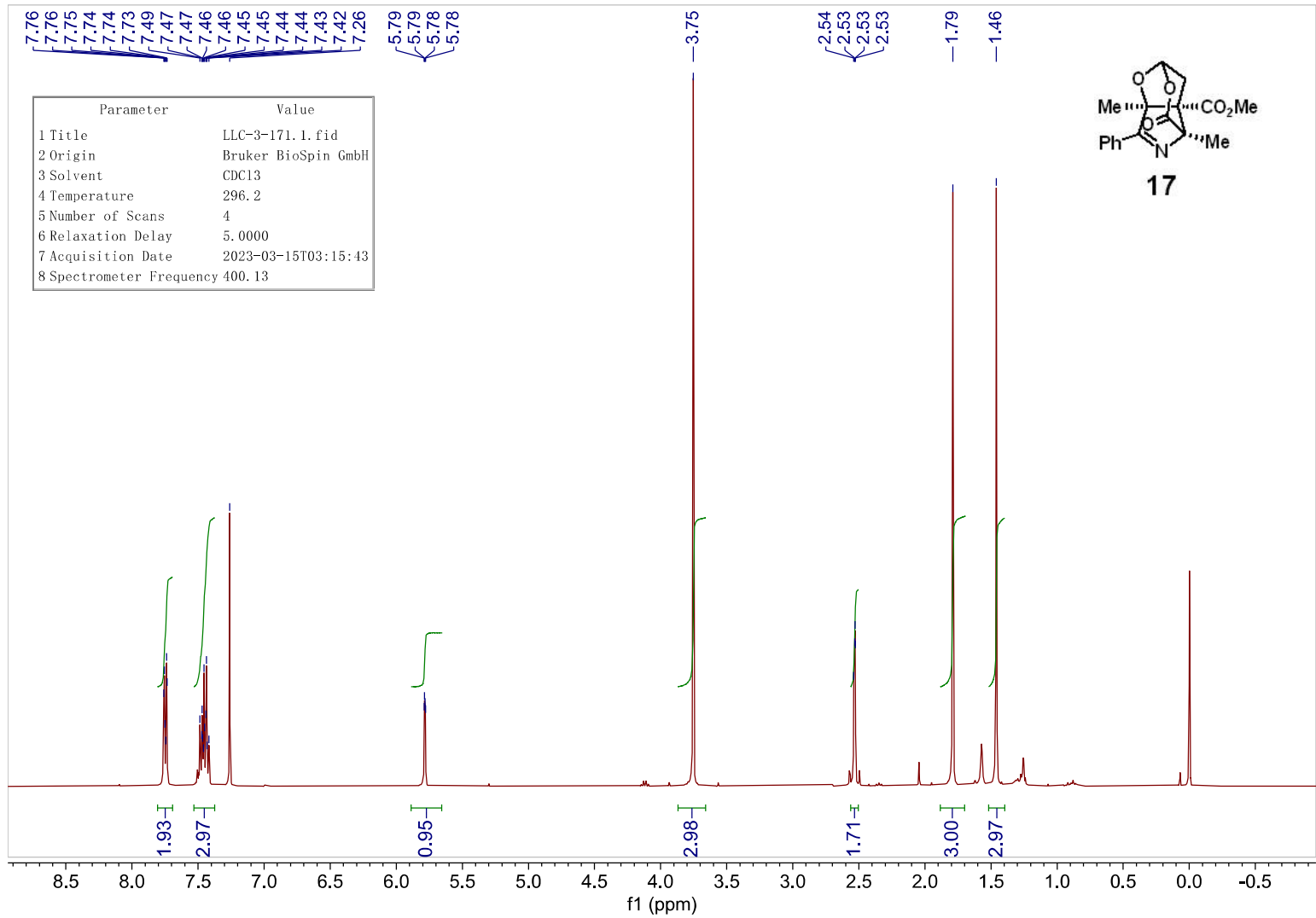
Parameter	Value
1 Title	llc-2-199-Bruker-H.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	296.7
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2022-12-10T02:29:10
8 Spectrometer Frequency	400.13

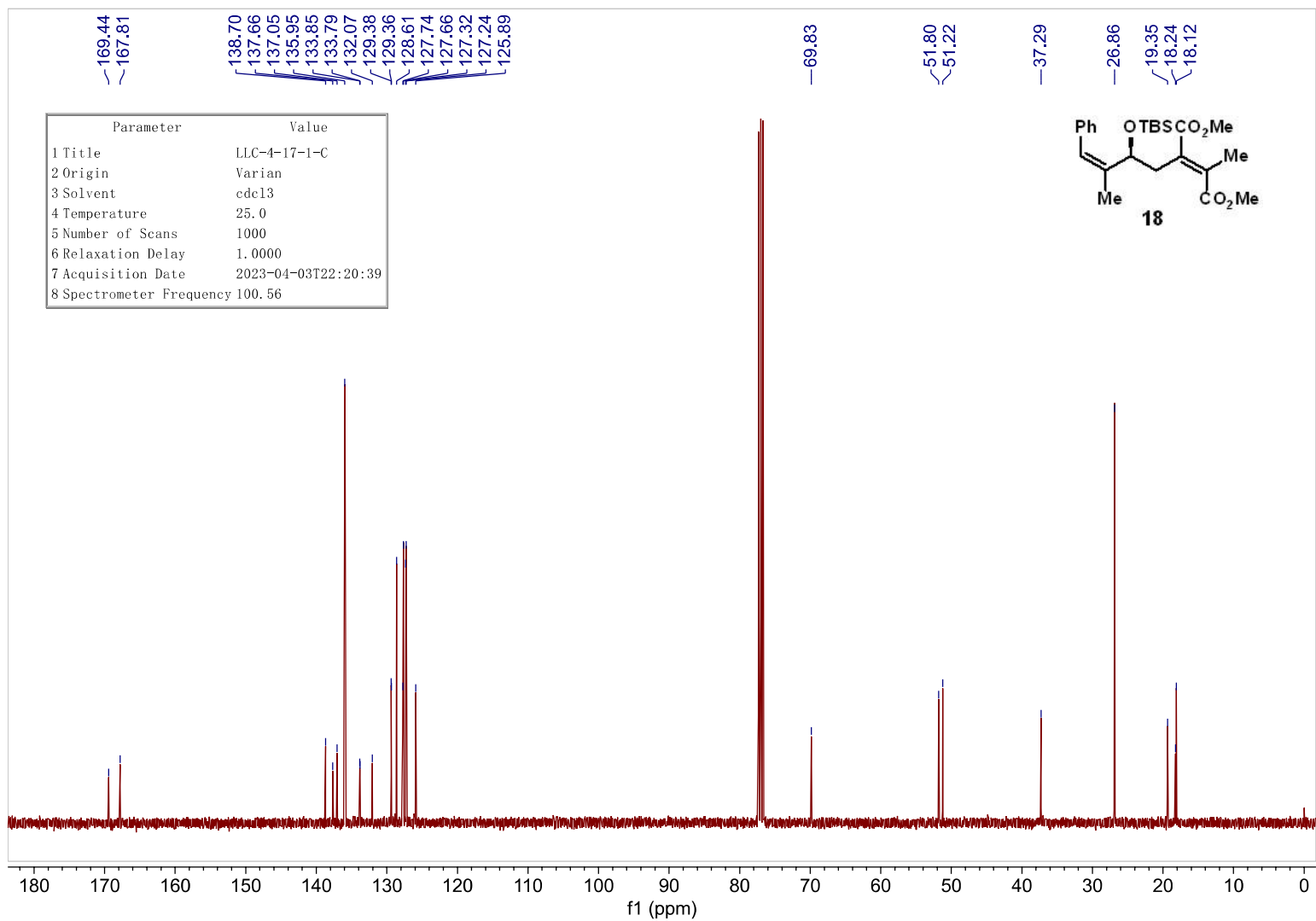
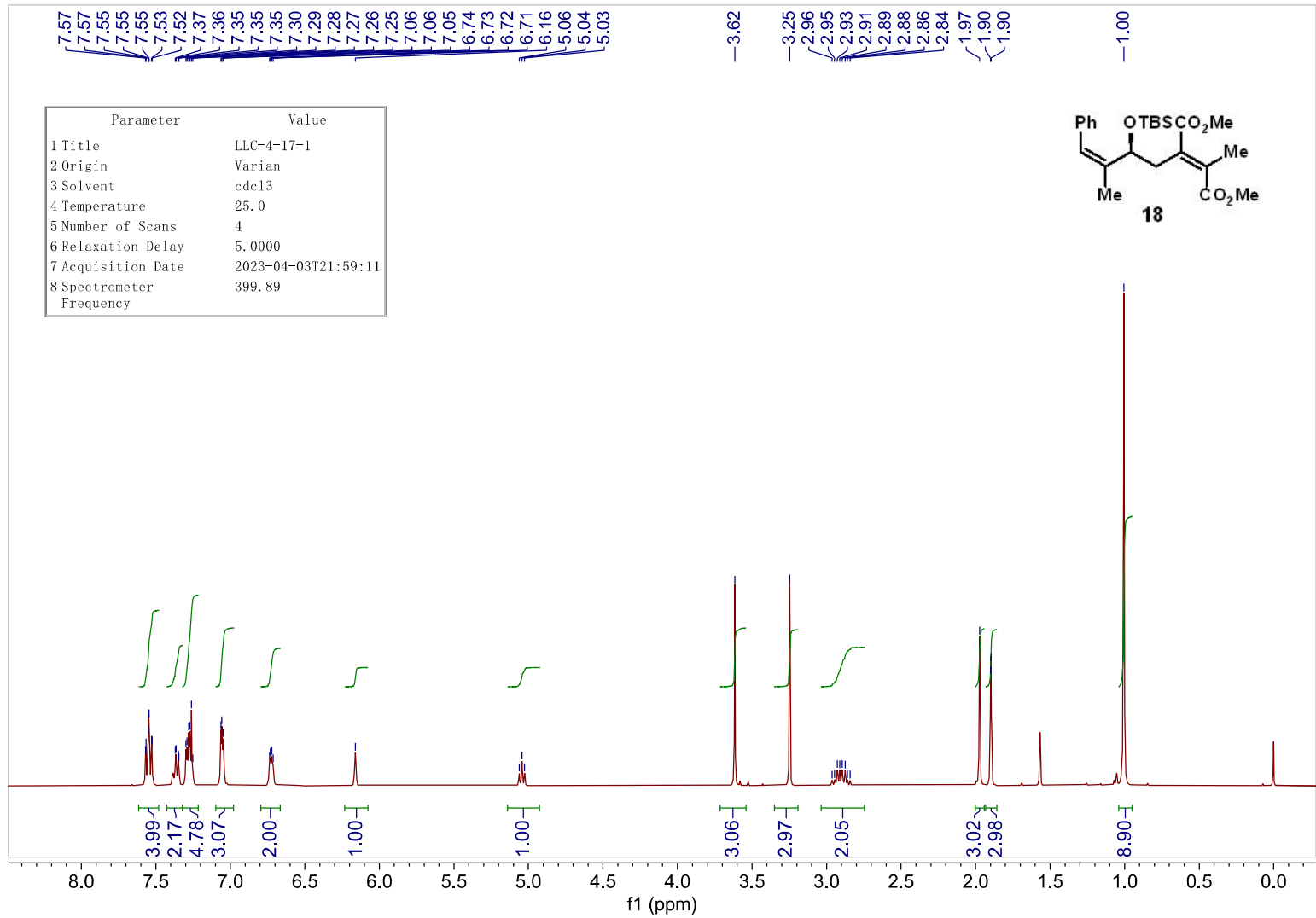


Parameter	Value
1 Title	llc-2-199-Bruker-C.1.fid
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.3
5 Number of Scans	300
6 Relaxation Delay	1.0000
7 Acquisition Date	2022-12-10T02:42:01
8 Spectrometer Frequency	100.62

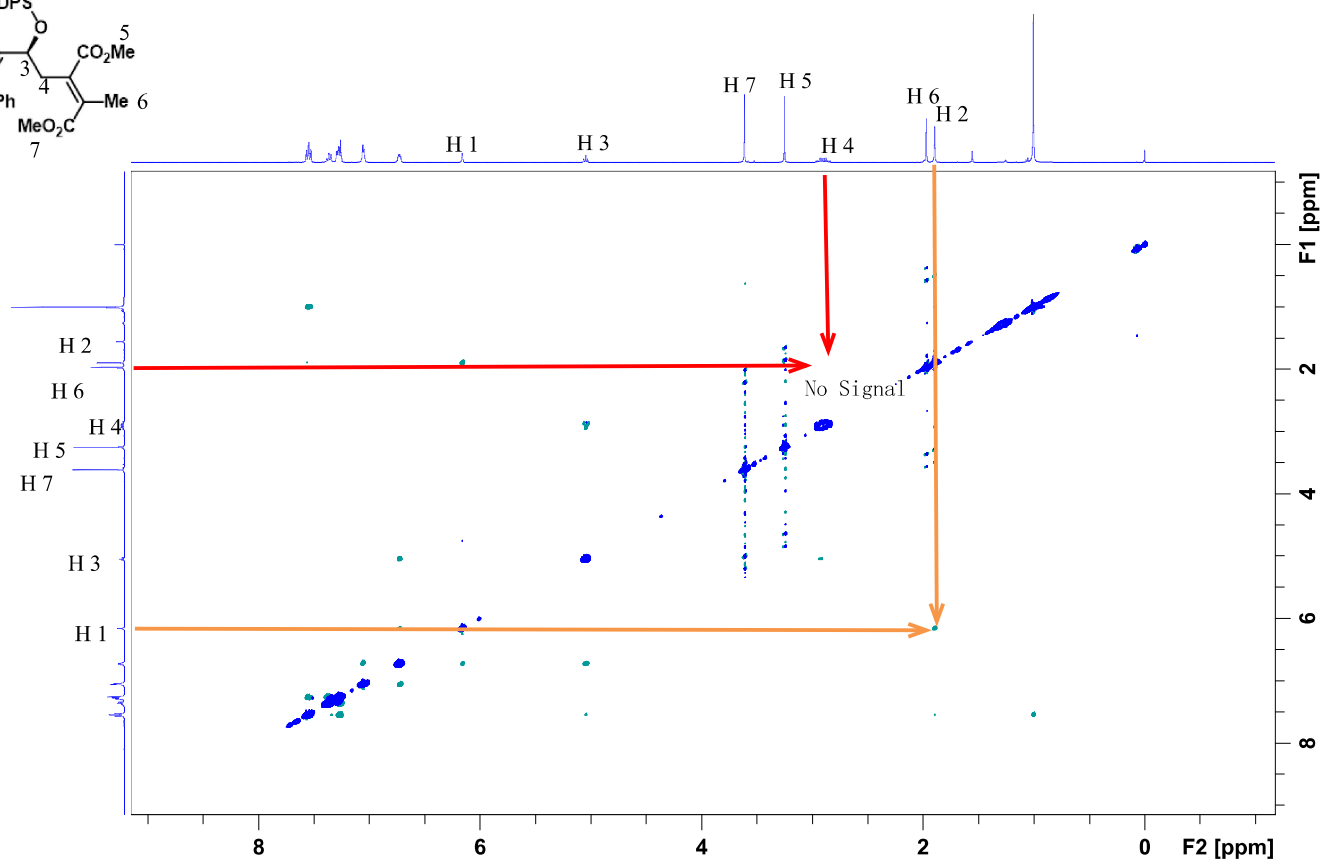
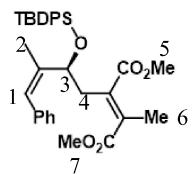


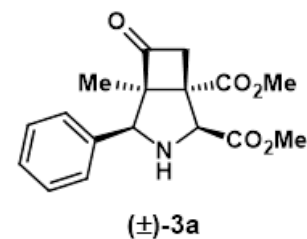






NOESY NMR spectrum of dimethyl 2-((*S,Z*)-2-((*tert*-butyldiphenylsilyl)oxy)-3-methyl-4-phenylbut-3-en-1-yl)-3-methylfumarate (18)





<Sample Information>

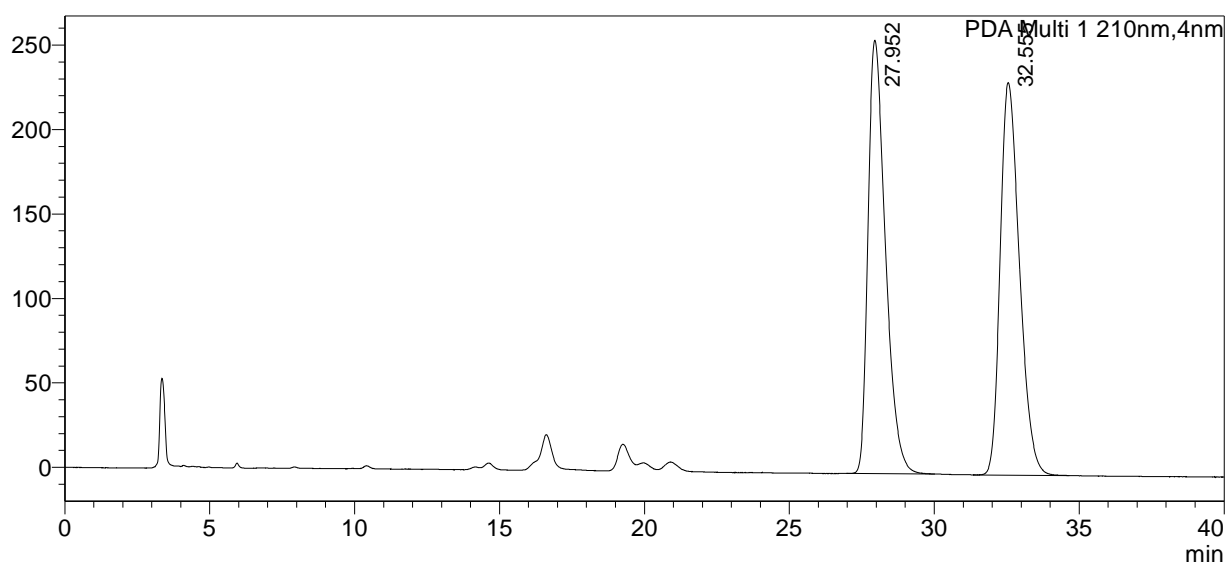
Sample Name : LLC-1-30-0514
 Sample ID :
 Data Filename : LLC-1-30-0514.lcd

Method Filename : IC,1ml 10%IPA in Hex;40min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-93
 Injection Volume : 10 uL
 Date Acquired : 5/14/2023 2:53:36 PM
 Date Processed : 5/14/2023 3:33:39 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

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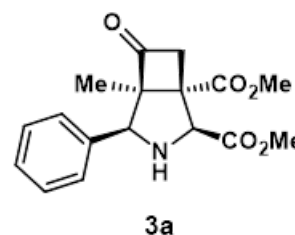
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.952	10735921	256539	49.940			
2	32.555	10761597	232453	50.060			
Total		21497518	488991				



<Sample Information>

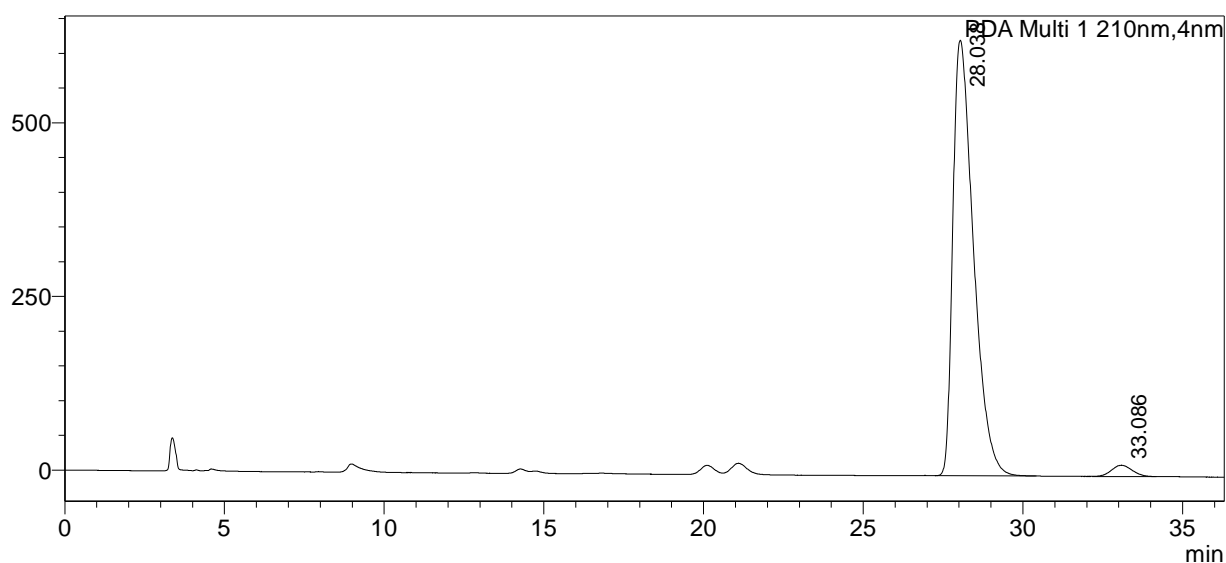
Sample Name : LLC-4-95 IC-10%
 Sample ID :
 Data Filename : LLC-4-95 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-92
 Injection Volume : 10 uL
 Date Acquired : 5/14/2023 2:16:46 PM
 Date Processed : 5/14/2023 2:53:06 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 210nm

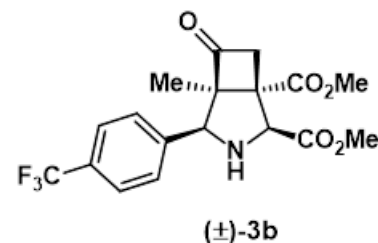
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.038	28165494	626777	97.457			
2	33.086	734853	16282	2.543		V	
Total		28900348	643059				

<Sample Information>

Sample Name : LLC-1-89 ADH 5%
 Sample ID :
 Data Filename : LLC-1-89 ADH 5%.lcd

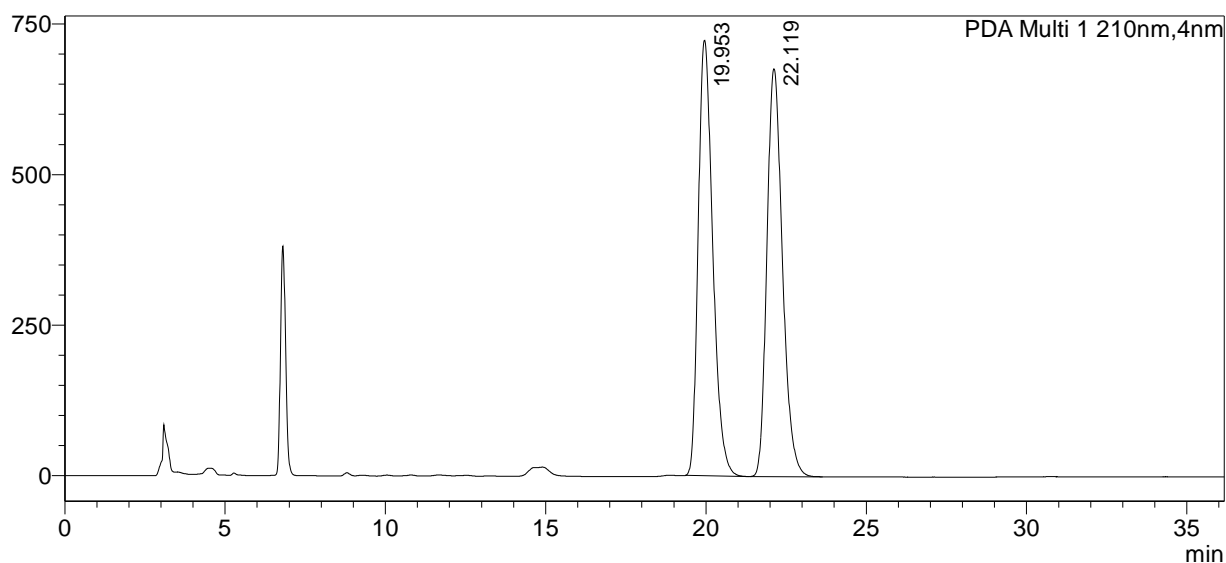
Method Filename : AD-H; 1 ml; 5%IPA in Hex; 60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-50
 Injection Volume : 10 uL
 Date Acquired : 12/1/2021 7:50:02 PM
 Date Processed : 12/1/2021 8:26:14 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator



<Chromatogram>

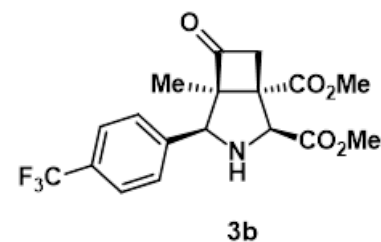
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.953	22762604	722863	49.912			
2	22.119	22842913	676979	50.088			
Total		45605517	1399843				



<Sample Information>

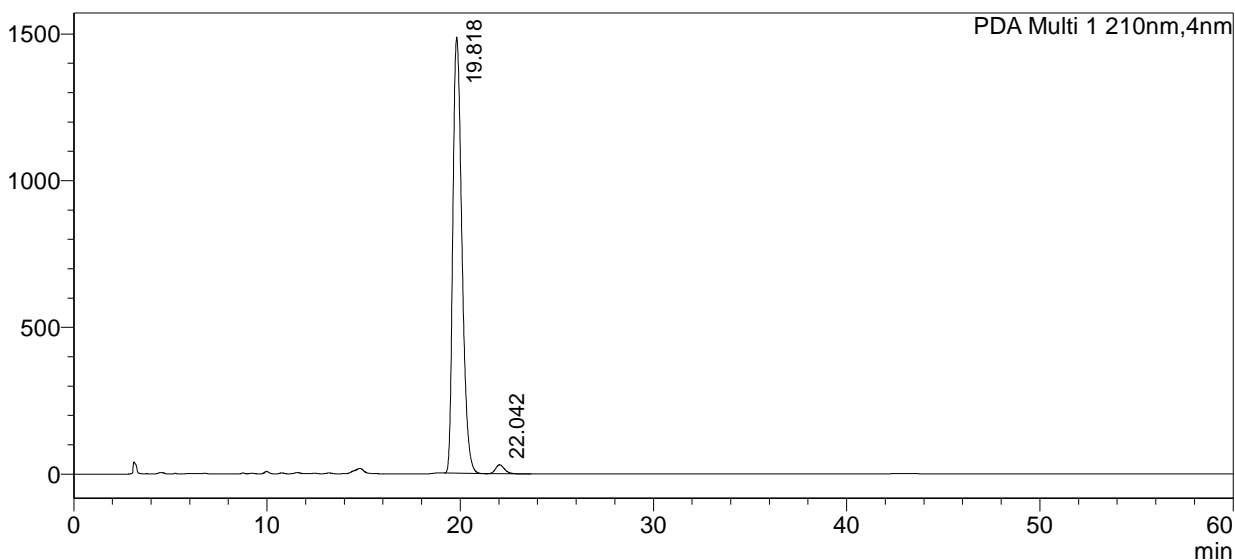
Sample Name : LLC-1-90 ADH 5%
 Sample ID :
 Data Filename : LLC-1-90 ADH 5%.lcd

Method Filename : AD-H; 1 ml; 5%IPA in Hex; 60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-51
 Injection Volume : 10 uL
 Date Acquired : 12/1/2021 8:26:44 PM
 Date Processed : 12/1/2021 9:26:47 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

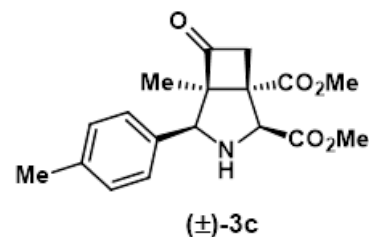
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.818	48544582	1485194	98.009			
2	22.042	986092	30757	1.991			
Total		49530674	1515951				



<Sample Information>

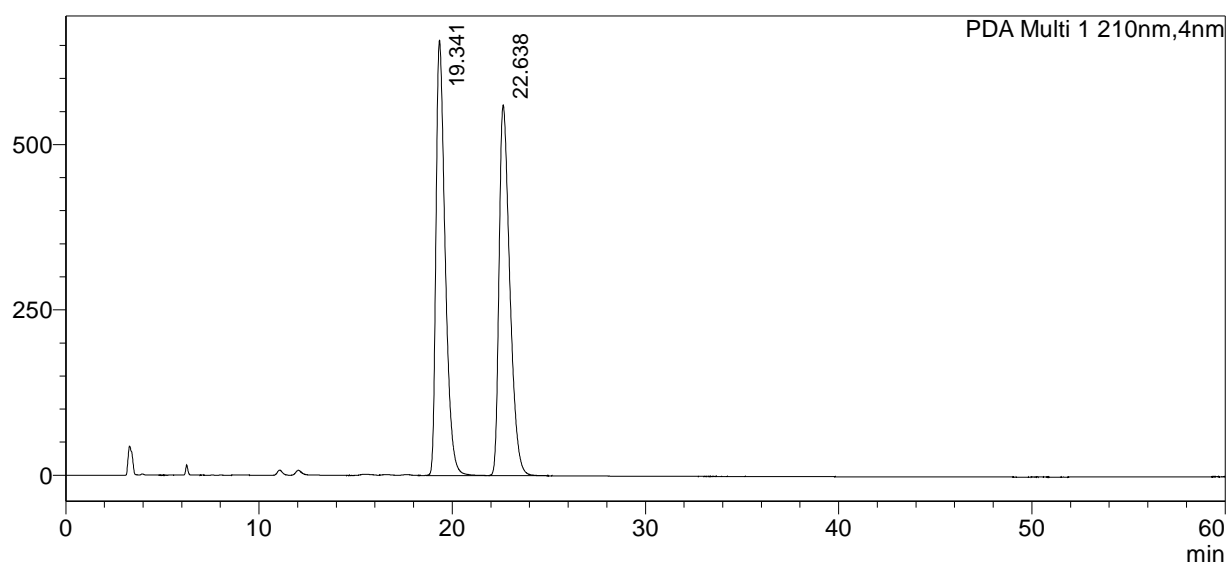
Sample Name : LLC-2-57 ap IC-20%
 Sample ID :
 Data Filename : LLC-2-57 IC-20%.lcd

Method Filename : IC,1ml 20%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-31
 Injection Volume : 10 uL
 Date Acquired : 9/19/2022 1:26:28 PM
 Date Processed : 9/19/2022 2:26:30 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

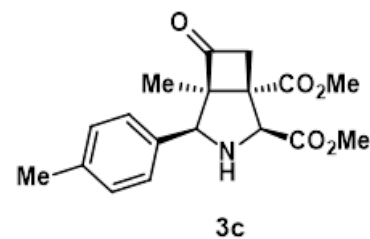
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.341	21768662	658149	50.167		SV	
2	22.638	21623437	560762	49.833			
Total		43392099	1218910				



<Sample Information>

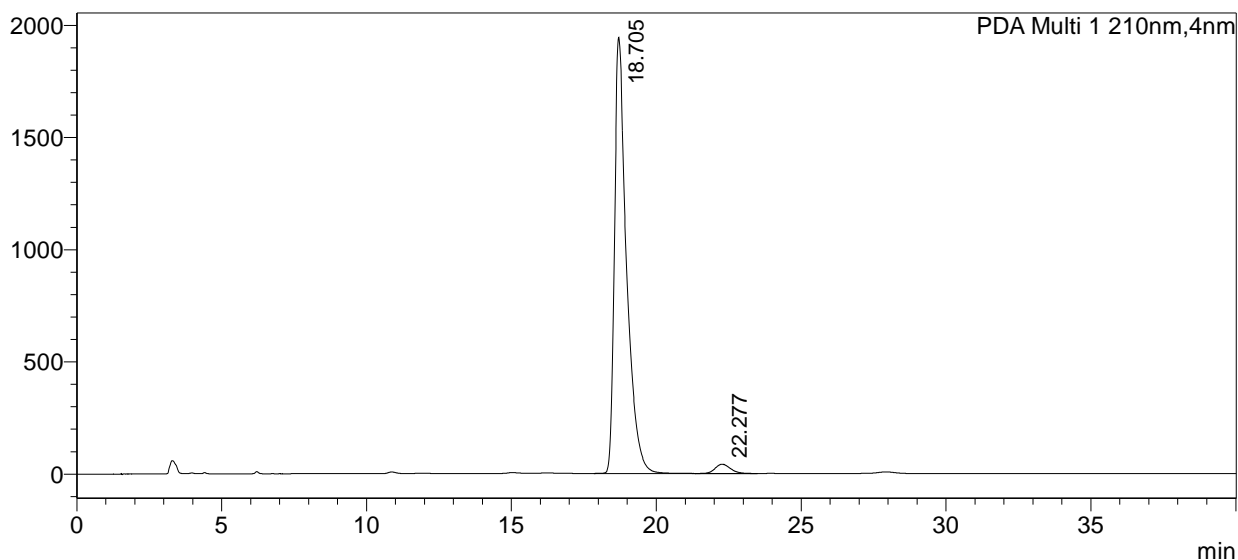
Sample Name : LLC-2-58 ap IC-20%
 Sample ID :
 Data Filename : LLC-2-58 IC-20%.lcd

Method Filename : IC,1ml 20%IPA in Hex;40min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-32
 Injection Volume : 10 uL
 Date Acquired : 9/19/2022 2:27:00 PM
 Date Processed : 9/19/2022 3:07:04 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

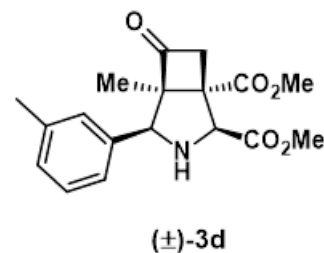
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.705	56228324	1943318	97.385		S	
2	22.277	1509783	41398	2.615		T	
Total		57738108	1984716				



<Sample Information>

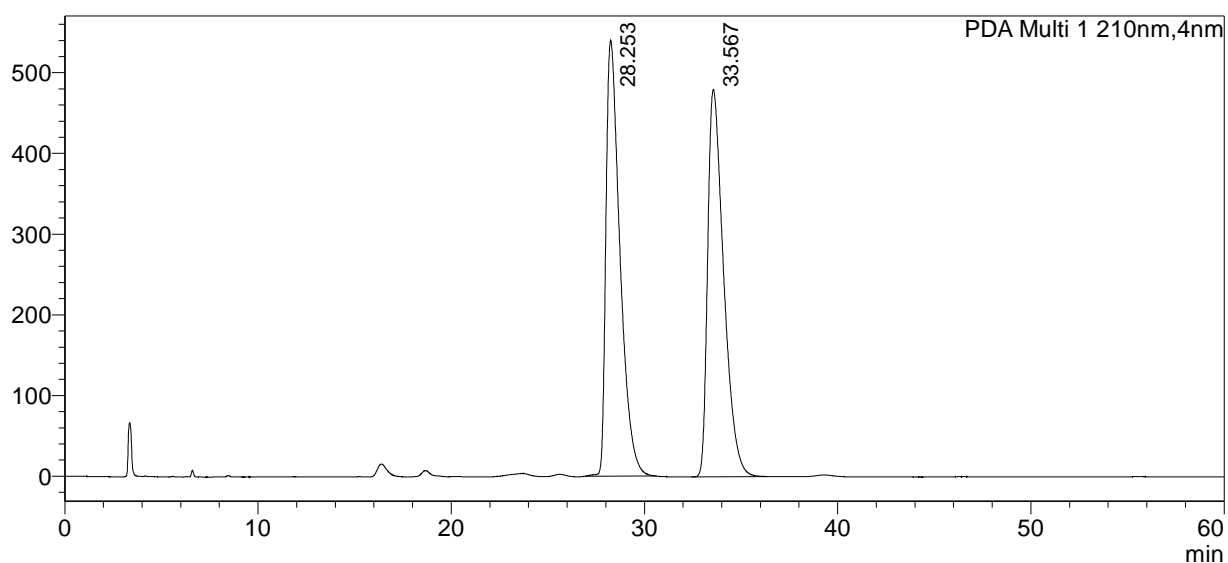
Sample Name : LLC-2-54 IC-10%B
 Sample ID :
 Data Filename : LLC-2-54 IC-10%B.lcd

 Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-61
 Injection Volume : 10 uL
 Date Acquired : 9/6/2022 7:44:21 PM
 Date Processed : 9/6/2022 8:44:23 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

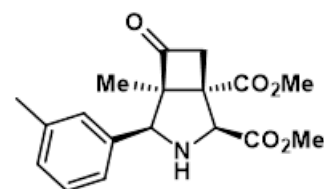
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.253	27302509	539929	49.704			
2	33.567	27627344	480182	50.296			
Total		54929853	1020111				



3d

<Sample Information>

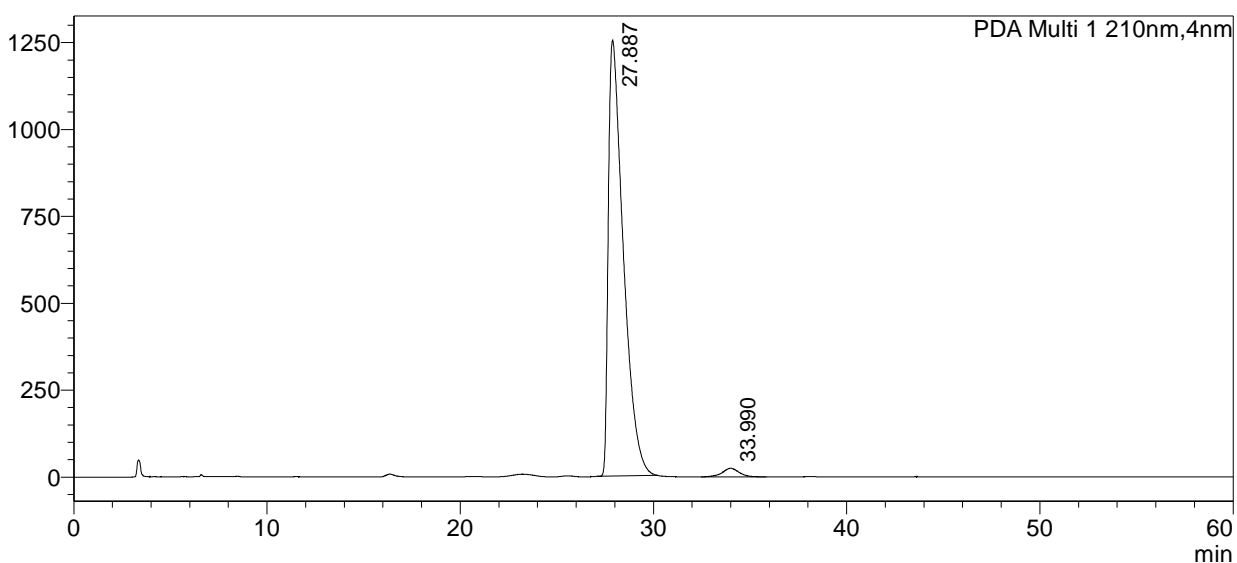
Sample Name : LLC-2-55 IC-10%B
 Sample ID :
 Data Filename : LLC-2-55 IC-10%B.lcd

 Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-62
 Injection Volume : 10 uL
 Date Acquired : 9/6/2022 8:44:54 PM
 Date Processed : 9/6/2022 9:44:56 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

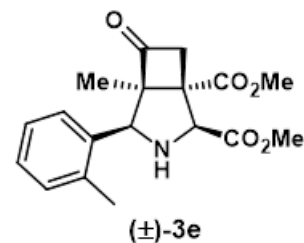
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.887	67759575	1253614	97.826			
2	33.990	1505975	24656	2.174		V	
Total		69265550	1278270				



<Sample Information>

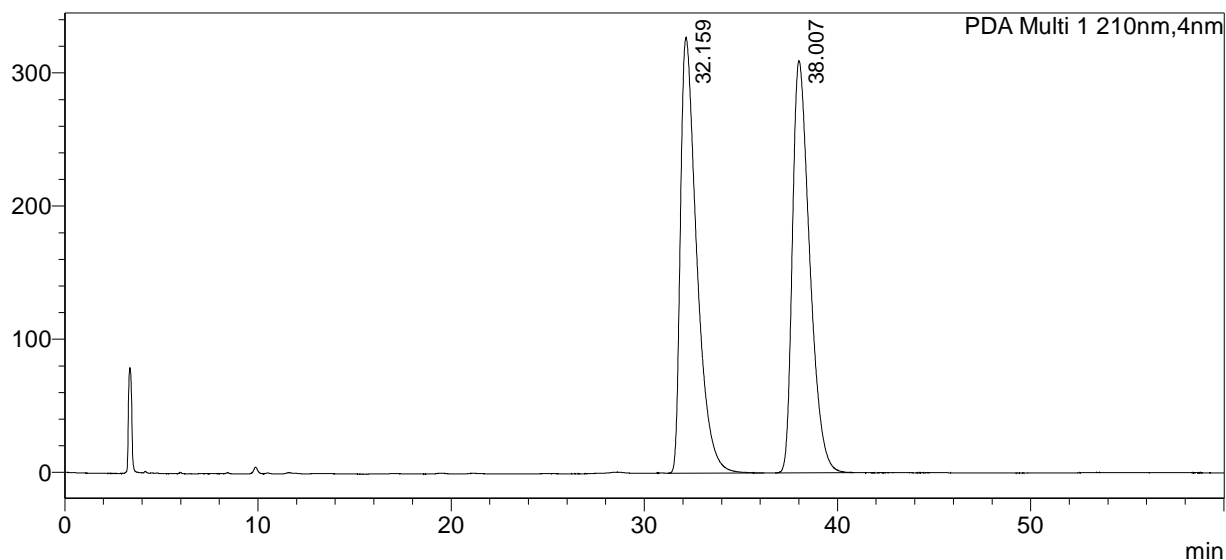
Sample Name : LLC-2-52 IC-10%
 Sample ID :
 Data Filename : LLC-2-52 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-93
 Injection Volume : 10 uL
 Date Acquired : 9/4/2022 2:52:17 AM
 Date Processed : 9/4/2022 3:52:20 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

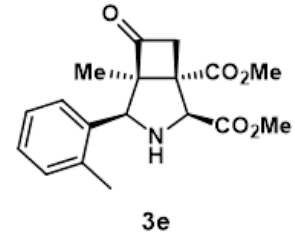
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	32.159	19245123	327259	49.967		S	
2	38.007	19270623	309471	50.033			
Total		38515745	636730				



<Sample Information>

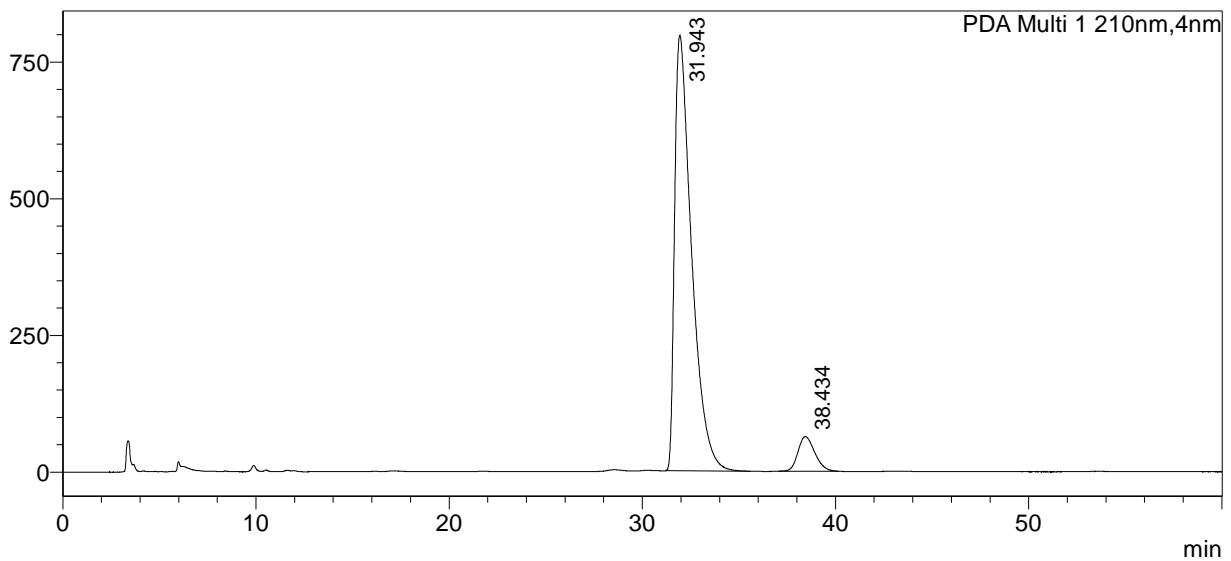
Sample Name : LLC-2-53 IC-10%
 Sample ID :
 Data Filename : LLC-2-53 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-94
 Injection Volume : 10 uL
 Date Acquired : 9/4/2022 3:52:49 AM
 Date Processed : 9/4/2022 4:52:52 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

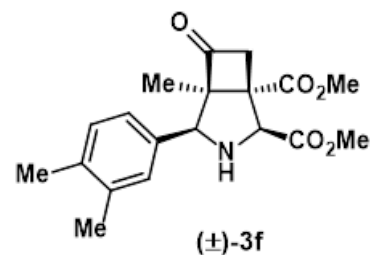
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.943	48624086	796509	92.675			
2	38.434	3843069	63491	7.325			
Total		52467155	860000				



<Sample Information>

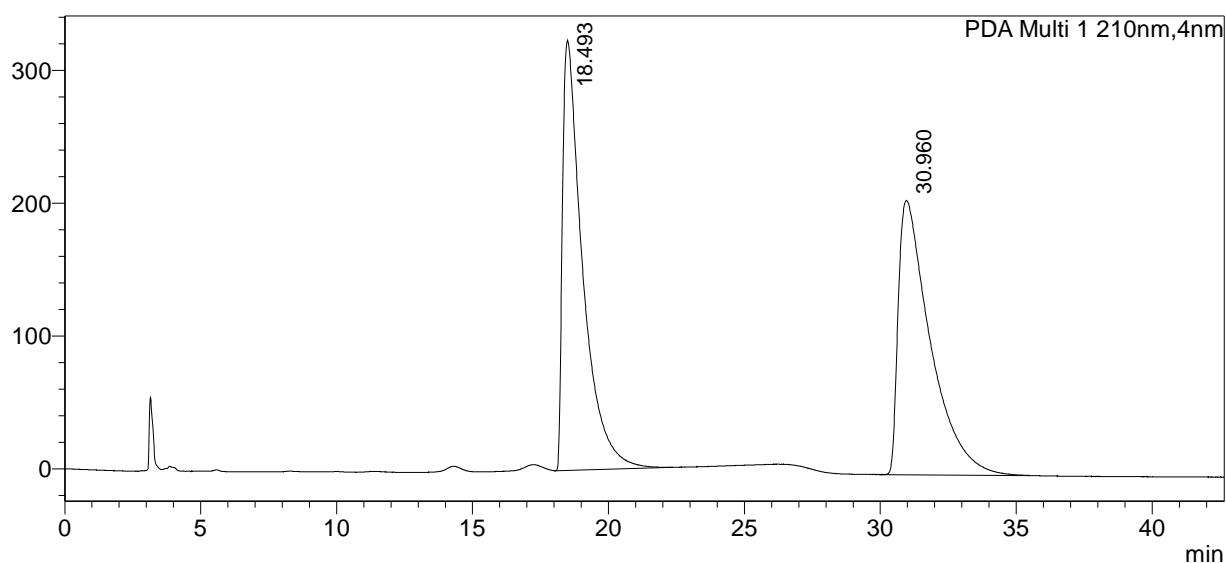
Sample Name : LLC-1-170-ap2 ODH-5%
 Sample ID :
 Data Filename : LLC-1-170-ap2 ODH-5%.lcd

Method Filename : OD-H,1ml 5%IPA in Hex;60min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-26
 Injection Volume : 10 uL
 Date Acquired : 5/12/2023 10:07:55 AM
 Date Processed : 5/12/2023 10:50:36 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

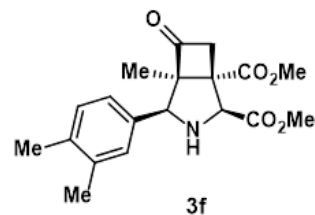
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.493	16677421	323660	49.625			
2	30.960	16929696	206493	50.375			
Total		33607117	530152				



<Sample Information>

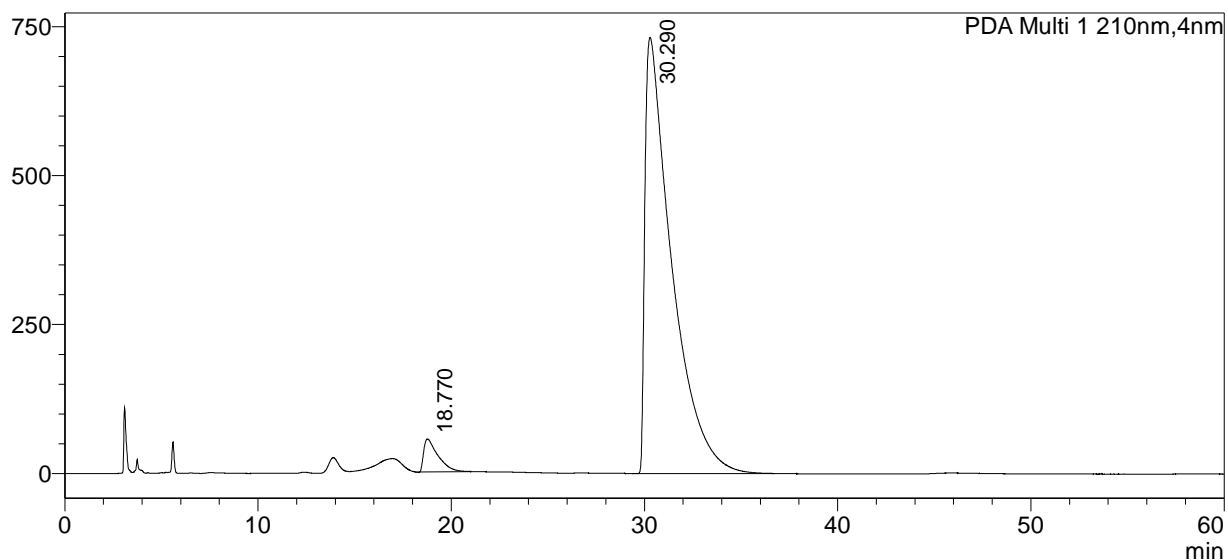
Sample Name : LLC-1-171 ODH-5%
 Sample ID :
 Data Filename : LLC-1-171 ODH-5%.lcd

Method Filename : OD-H,1ml 5%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-65
 Injection Volume : 10 uL
 Date Acquired : 7/28/2022 1:44:06 PM
 Date Processed : 7/28/2022 2:44:08 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

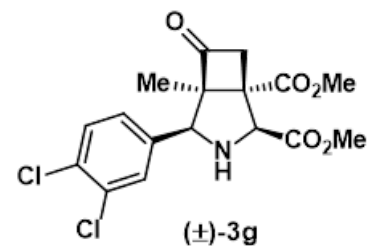
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.770	2796603	55091	3.816			
2	30.290	70493162	732078	96.184			
Total		73289765	787169				



<Sample Information>

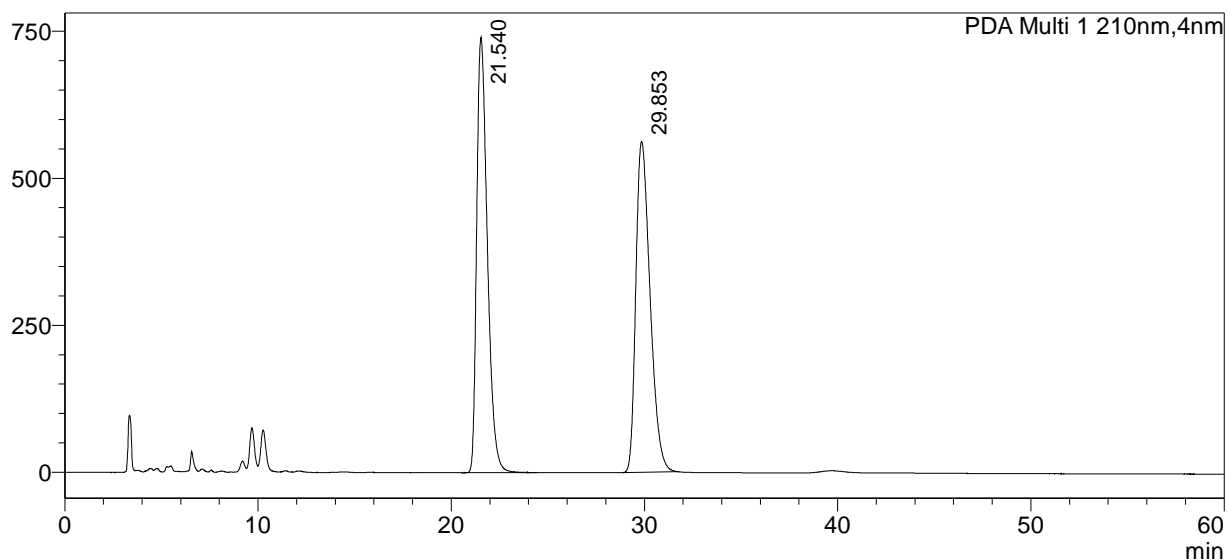
Sample Name : LLC-1-93 IC-10%
 Sample ID :
 Data Filename : LLC-1-93 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-16
 Injection Volume : 10 uL
 Date Acquired : 12/14/2021 3:03:23 PM
 Date Processed : 12/14/2021 4:03:26 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 210nm

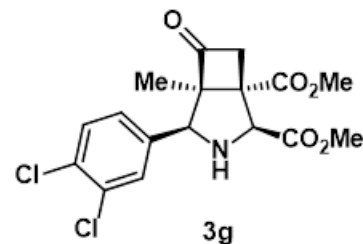
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.540	28404089	740508	49.642			
2	29.853	28813705	563123	50.358			
Total		57217794	1303631				

<Sample Information>

Sample Name : LLC-1-94 IC-10%
 Sample ID :
 Data Filename : LLC-1-94 IC-10%.lcd

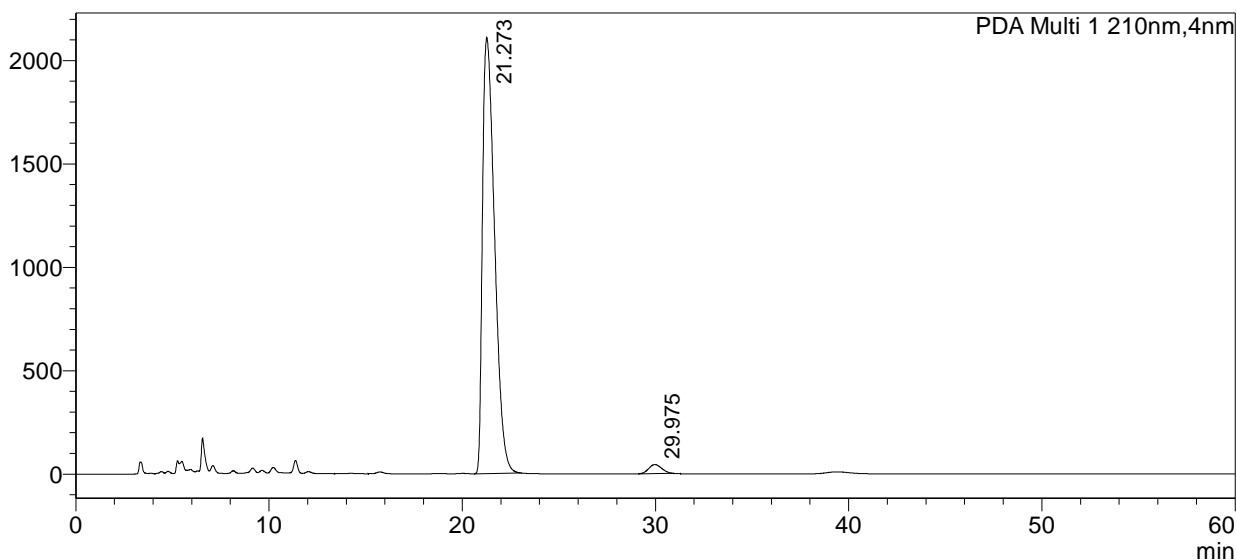
Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-32
 Injection Volume : 10 uL
 Date Acquired : 12/14/2021 5:24:57 PM
 Date Processed : 12/14/2021 6:25:00 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator



<Chromatogram>

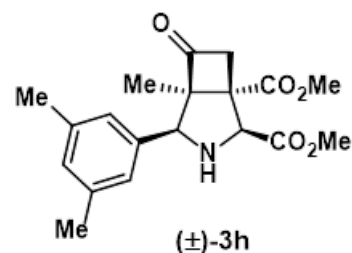
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.273	91863325	2109956	97.823			
2	29.975	2044415	43677	2.177			
Total		93907740	2153633				



<Sample Information>

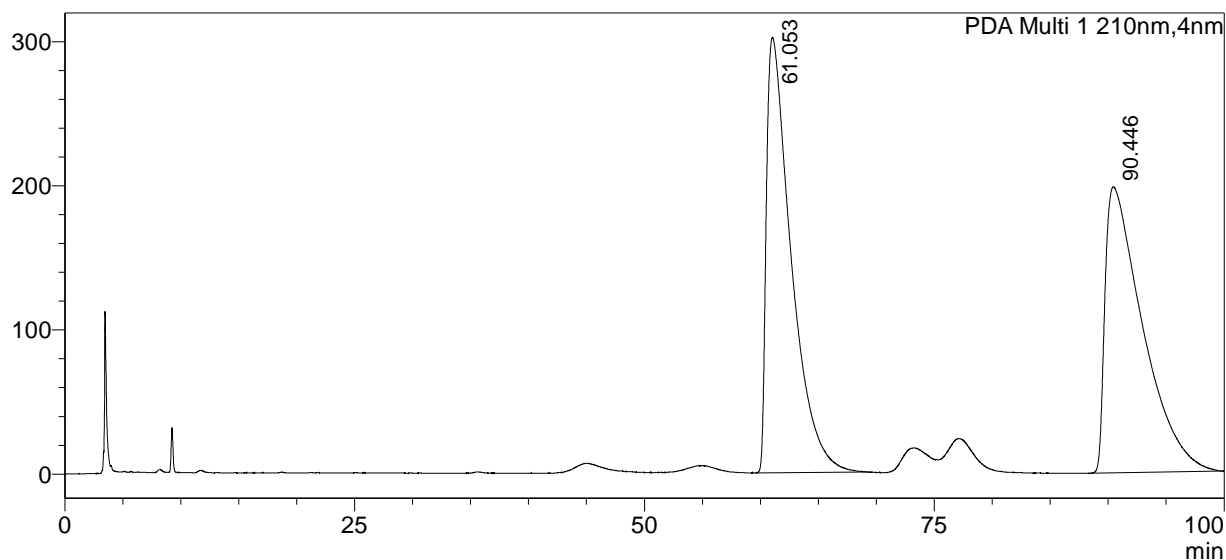
Sample Name : LLC-1-54 IC-2.5%
 Sample ID :
 Data Filename : LLC-1-154 IC-2.5%.lcd

Method Filename : IC,1ml 2.5%IPA in Hex;100min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-4
 Injection Volume : 10 uL
 Date Acquired : 7/16/2022 11:51:25 AM
 Date Processed : 7/16/2022 1:31:28 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 210nm

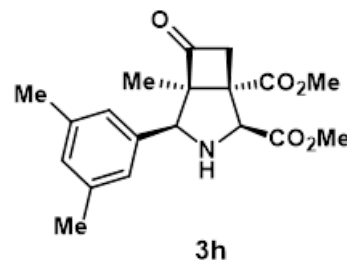
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	61.053	44887480	301975	50.105			
2	90.446	44699635	198417	49.895			
Total		89587115	500392				

<Sample Information>

Sample Name : LLC-1-55 IC-2.5%
 Sample ID :
 Data Filename : LLC-1-155 IC-2.5%.lcd

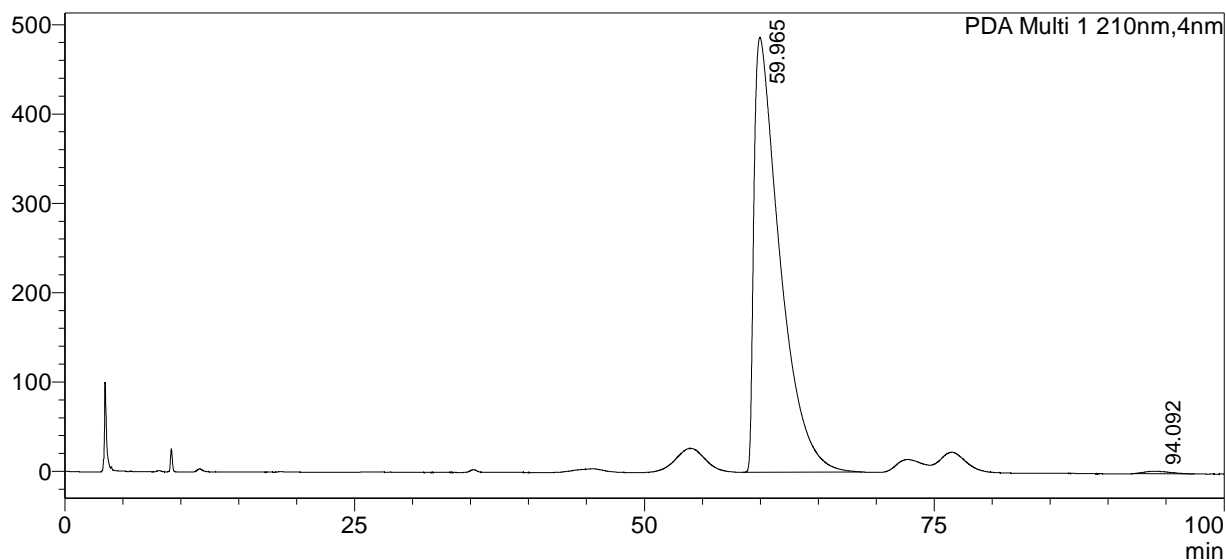
Method Filename : IC,1ml 2.5%IPA in Hex;100min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-5
 Injection Volume : 10 uL
 Date Acquired : 7/16/2022 1:31:52 PM
 Date Processed : 7/16/2022 3:11:55 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator



<Chromatogram>

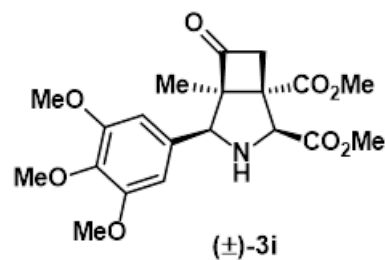
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	59.965	75526879	486732	99.424			
2	94.092	437241	2896	0.576			
Total		75964121	489628				



<Sample Information>

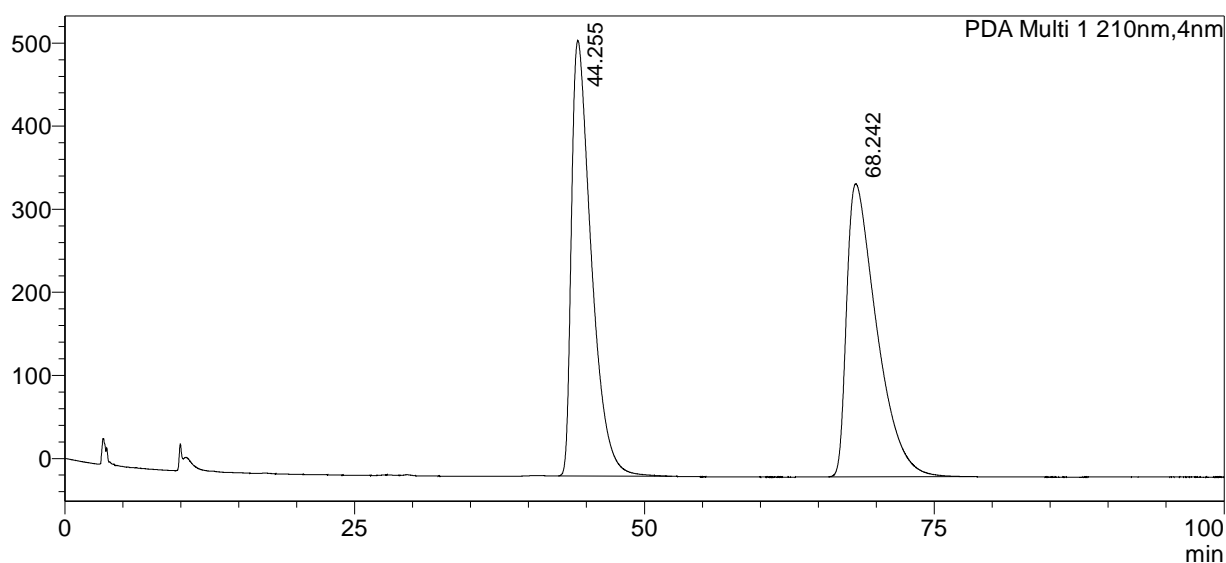
Sample Name : LLC-1-83-2 IC-30%
 Sample ID :
 Data Filename : LLC-1-83-2 IC-30%.lcd

Method Filename : IC,1ml 30%IPA in Hex;100min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-47
 Injection Volume : 10 uL
 Date Acquired : 10/31/2021 1:02:28 AM
 Date Processed : 10/31/2021 2:42:30 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU

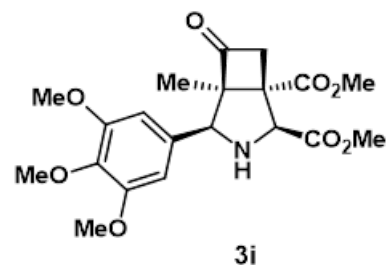


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	44.255	62416499	524224	49.606			
2	68.242	63408654	352680	50.394			
Total		125825153	876904				

Analysis Report



<Sample Information>

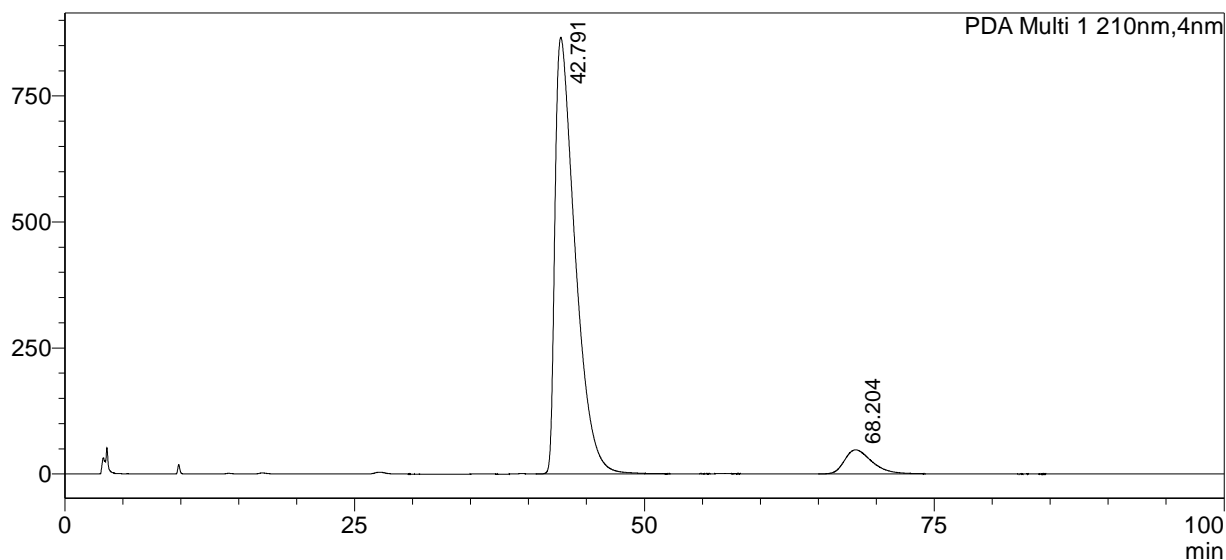
Sample Name : LLC-1-84 IC-30% 100min
 Sample ID :
 Data Filename : LLC-1-84 IC-30% 100min.lcd

Method Filename : IC,1ml 30%IPA in Hex;100min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-3
 Injection Volume : 10 uL
 Date Acquired : 10/30/2021 3:35:43 PM
 Date Processed : 10/30/2021 5:15:45 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

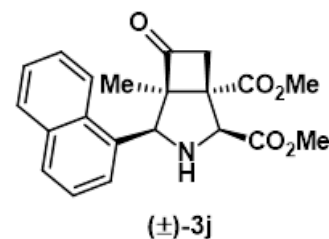
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	42.791	104671953	866210	93.053			
2	68.204	7814533	47679	6.947			
Total		112486486	913889				



<Sample Information>

Sample Name : LLC-1-110 ADH-10%-N
 Sample ID :
 Data Filename : LLC-1-110 ADH-10%-N.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 40min.lcm

Batch Filename : 1.lcb

Vial # : 1-63

Injection Volume : 10 uL

Date Acquired : 3/5/2023 10:42:41 PM

Date Processed : 3/6/2023 8:45:41 AM

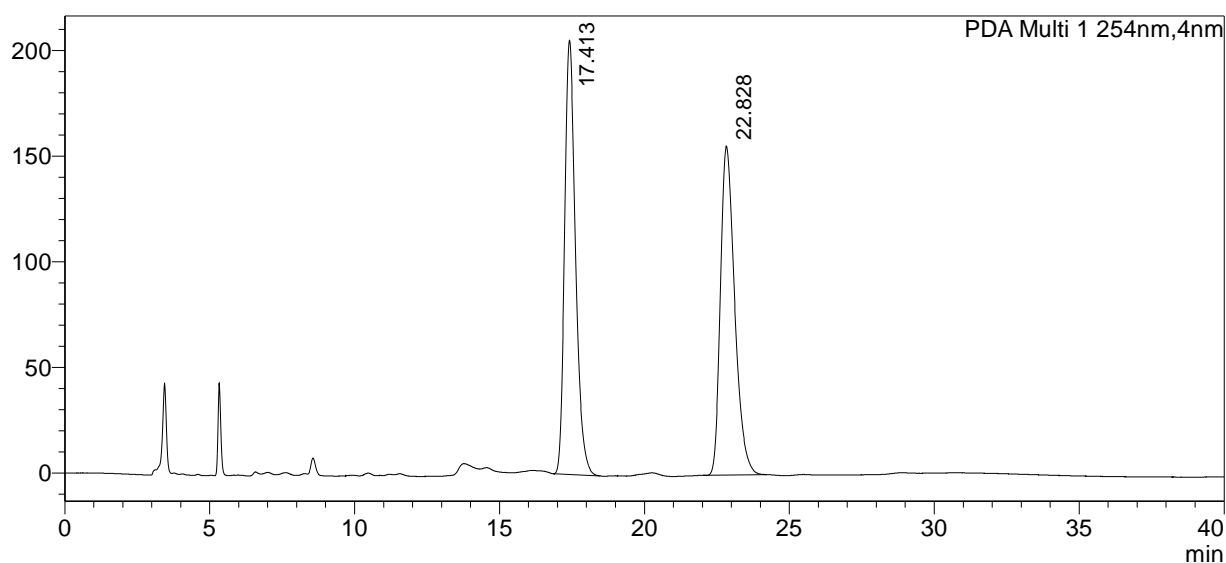
Sample Type : Unknown

Acquired by : System Administrator

Processed by : System Administrator

<Chromatogram>

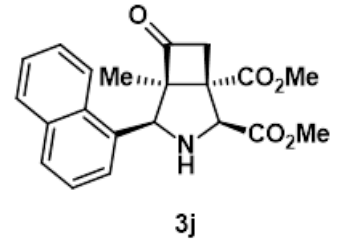
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.413	5372714	205568	50.189			
2	22.828	5332352	155840	49.811			
Total		10705066	361409				



<Sample Information>

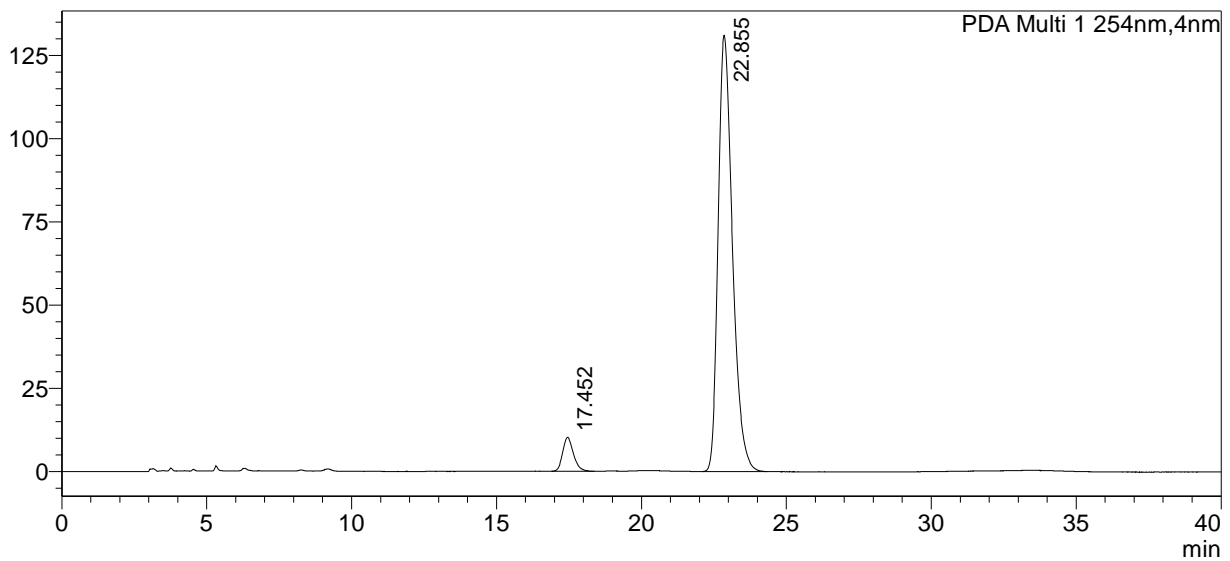
Sample Name : LLC-3-121 ADH-10%-N
 Sample ID :
 Data Filename : LLC-3-121 ADH-10%-N.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 40min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-62
 Injection Volume : 10 uL
 Date Acquired : 3/5/2023 11:23:14 PM
 Date Processed : 3/6/2023 12:03:17 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 254nm

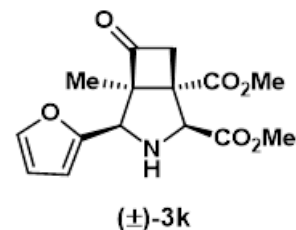
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.452	263963	10181	5.530			
2	22.855	4509062	131011	94.470			
Total		4773024	141192				

Analysis Report

<Sample Information>

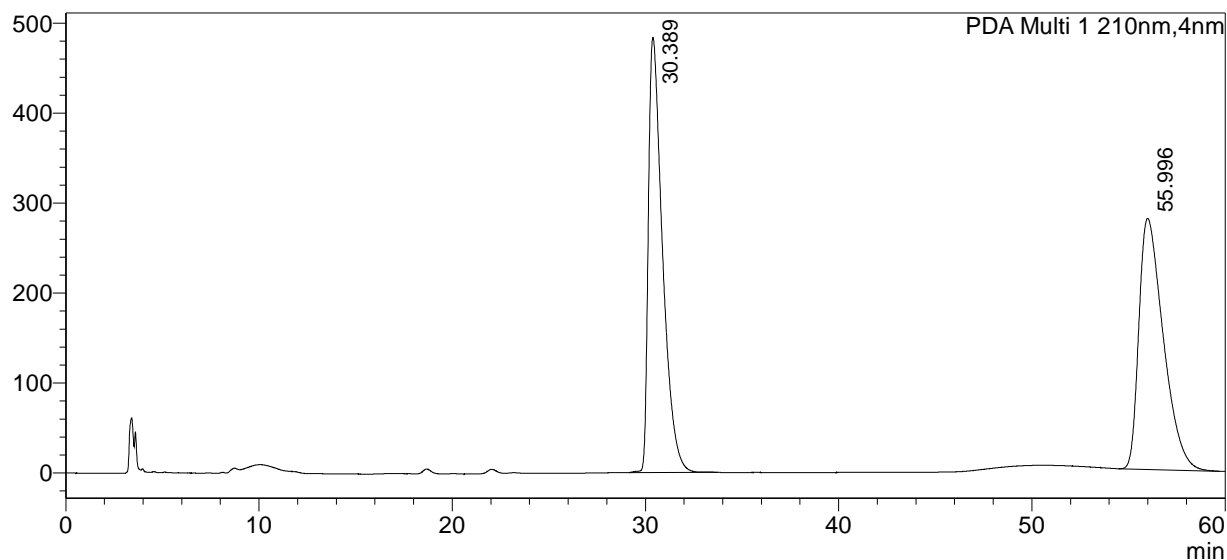
Sample Name : LLC-1-100 IC-10%
 Sample ID :
 Data Filename : LLC-1-100 IC-10%.lcd
 Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-2
 Injection Volume : 10 uL
 Date Acquired : 1/17/2022 9:49:38 AM
 Date Processed : 1/17/2022 10:49:41 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator



<Chromatogram>

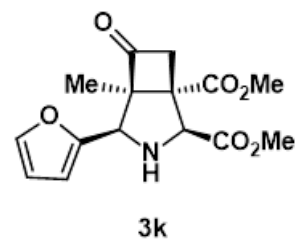
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.389	24664741	483605	50.144			
2	55.996	24522894	279137	49.856			
Total		49187635	762742				



<Sample Information>

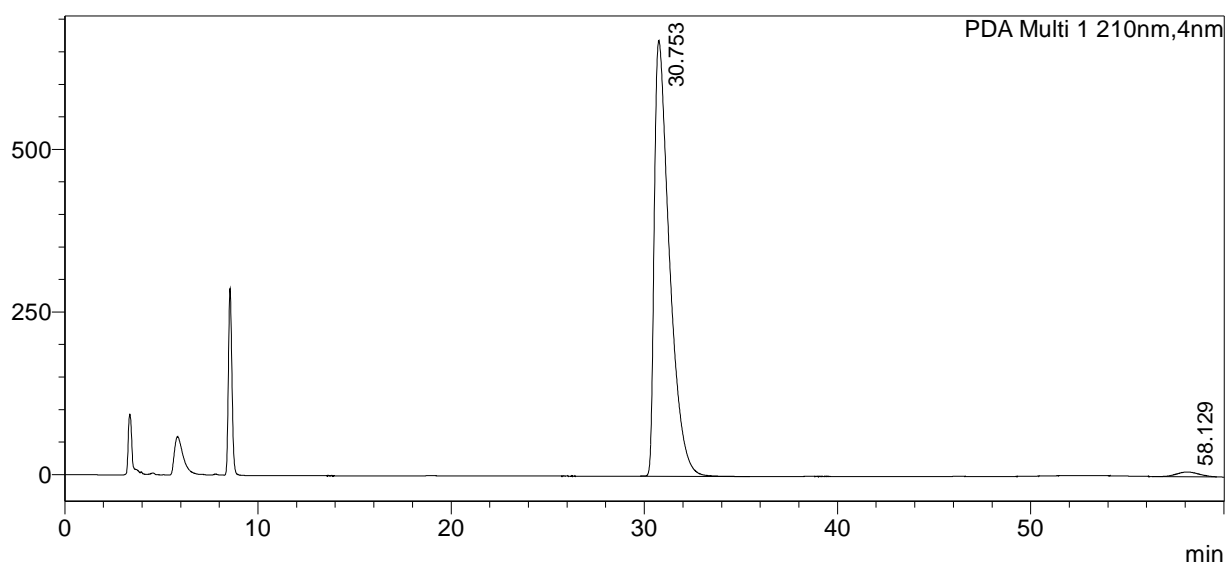
Sample Name : LLC-1-99 IC-10%
 Sample ID :
 Data Filename : LLC-1-99 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-1
 Injection Volume : 10 uL
 Date Acquired : 1/17/2022 8:49:04 AM
 Date Processed : 1/17/2022 1:09:39 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 210nm

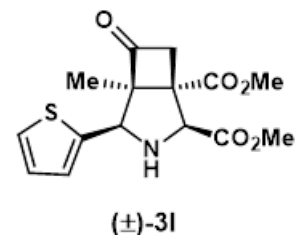
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.753	36503657	670039	98.474			
2	58.129	565649	7142	1.526			
Total		37069305	677182				

<Sample Information>

Sample Name : LLC-1-102 IC-10%
 Sample ID :
 Data Filename : LLC-1-102 IC-10%.lcd

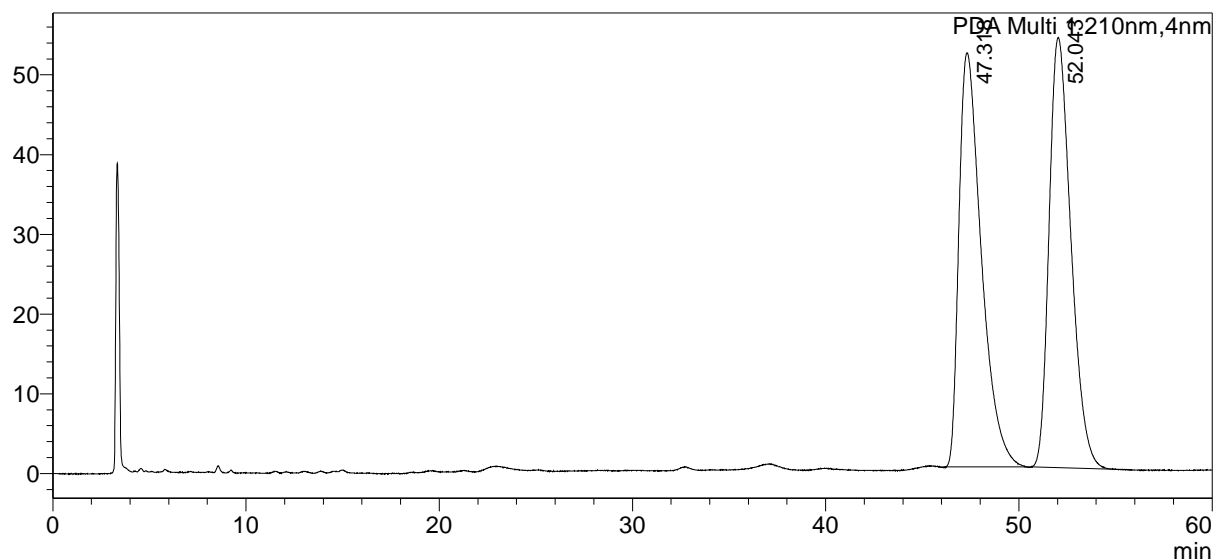
Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-61
 Injection Volume : 10 uL
 Date Acquired : 1/19/2022 10:13:14 PM
 Date Processed : 1/19/2022 11:13:16 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator



<Chromatogram>

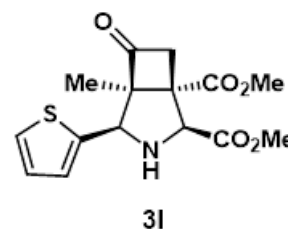
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	47.318	4186296	51905	49.719			
2	52.043	4233688	53967	50.281			
Total		8419984	105871				



<Sample Information>

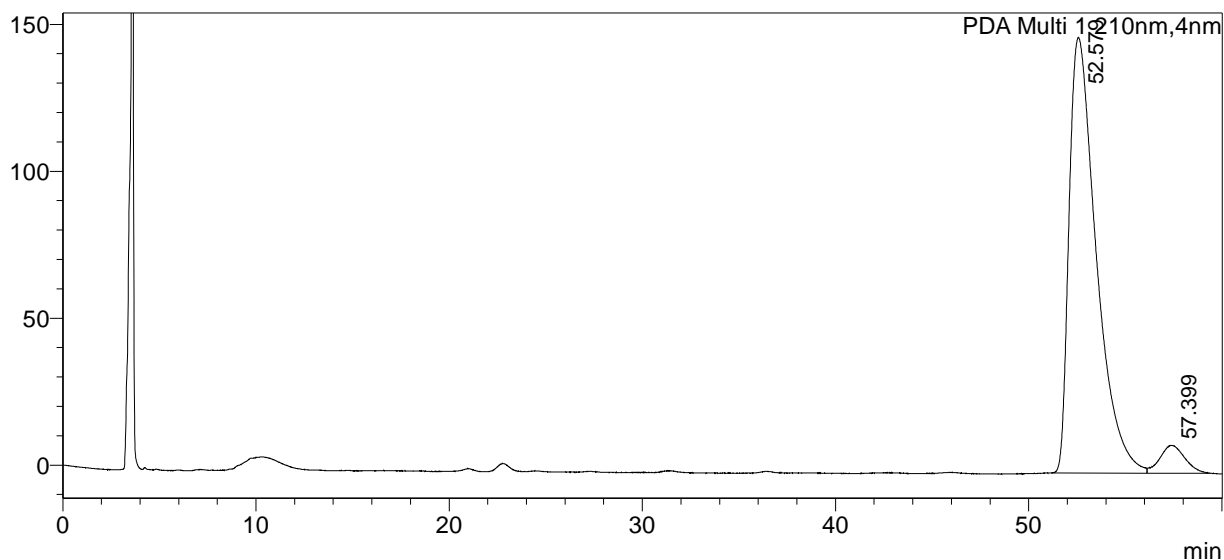
Sample Name : LLC-3-120--2 IC-10%
 Sample ID :
 Data Filename : LLC-3-120--2 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-65
 Injection Volume : 10 uL
 Date Acquired : 2/23/2023 4:36:43 PM
 Date Processed : 2/23/2023 5:36:46 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

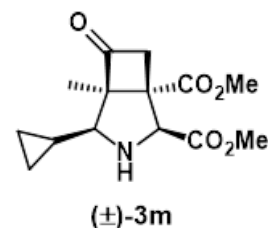
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	52.579	14488884	148268	94.459			
2	57.399	849882	9458	5.541		V	
Total		15338766	157726				



<Sample Information>

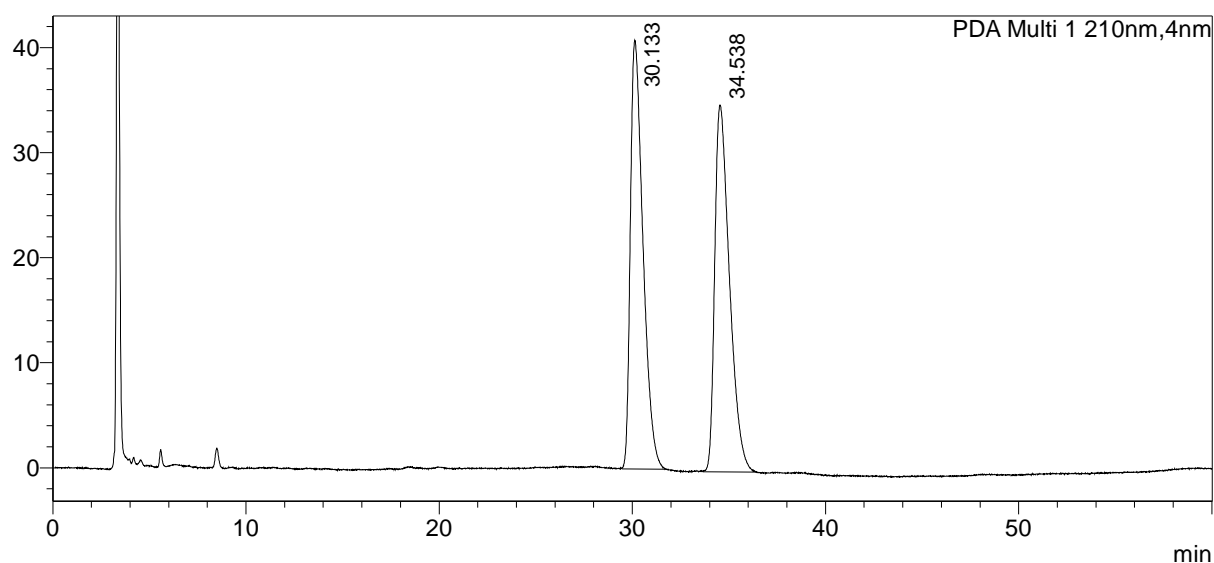
Sample Name : LLC-2-38 IC-10%2
 Sample ID :
 Data Filename : LLC-2-38 IC-10%2.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-62
 Injection Volume : 10 uL
 Date Acquired : 8/27/2022 10:50:44 PM
 Date Processed : 8/27/2022 11:50:47 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

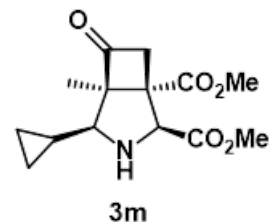
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.133	1850288	40800	49.977		V	
2	34.538	1851982	34933	50.023		V	
Total		3702270	75734				



<Sample Information>

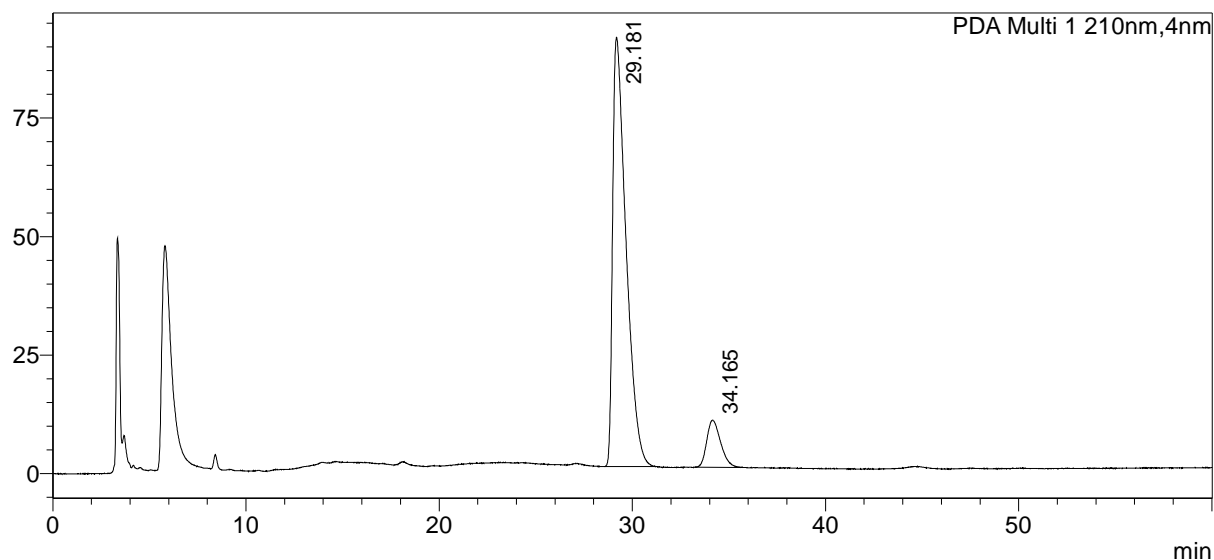
Sample Name : LLC-2-39 IC-10%2
 Sample ID :
 Data Filename : LLC-2-39 IC-10%2.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-63
 Injection Volume : 10 uL
 Date Acquired : 8/27/2022 11:51:17 PM
 Date Processed : 8/28/2022 12:51:21 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

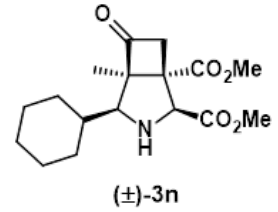
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.181	4358917	90510	89.779			
2	34.165	496243	9969	10.221		S	
Total		4855161	100479				



<Sample Information>

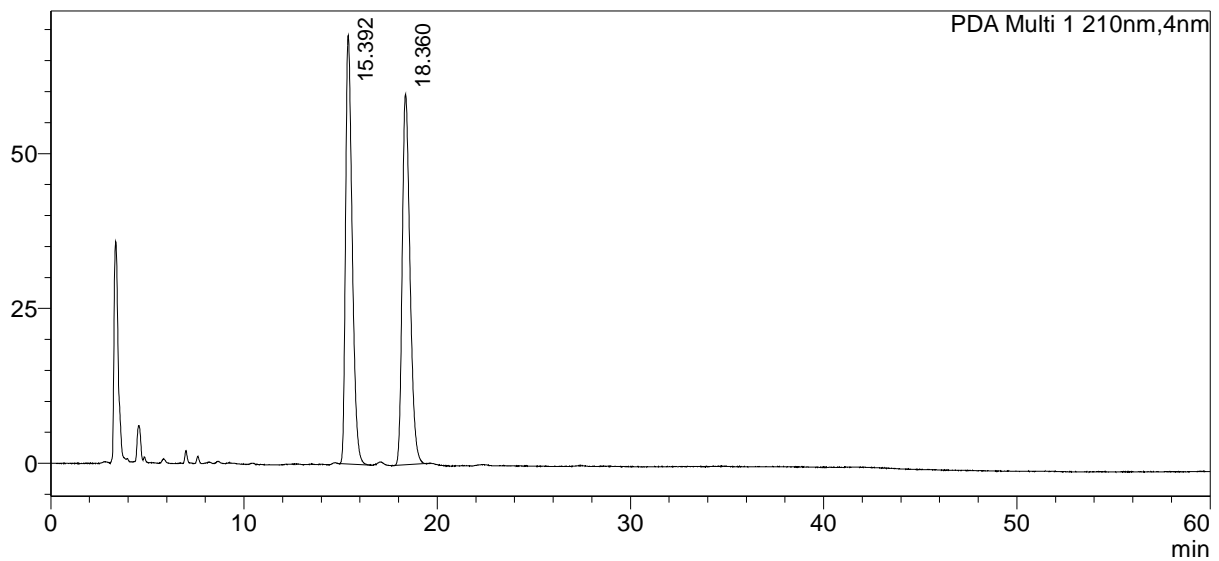
Sample Name : LLC-1-107 IC-10%
 Sample ID :
 Data Filename : LLC-1-107 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-46
 Injection Volume : 10 uL
 Date Acquired : 1/20/2022 9:24:16 PM
 Date Processed : 1/20/2022 10:24:18 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

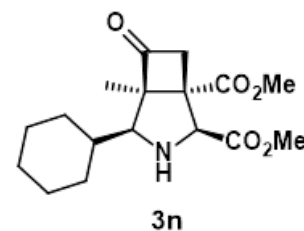
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.392	1655463	69196	49.715			
2	18.360	1674413	59825	50.285			
Total		3329877	129021				



<Sample Information>

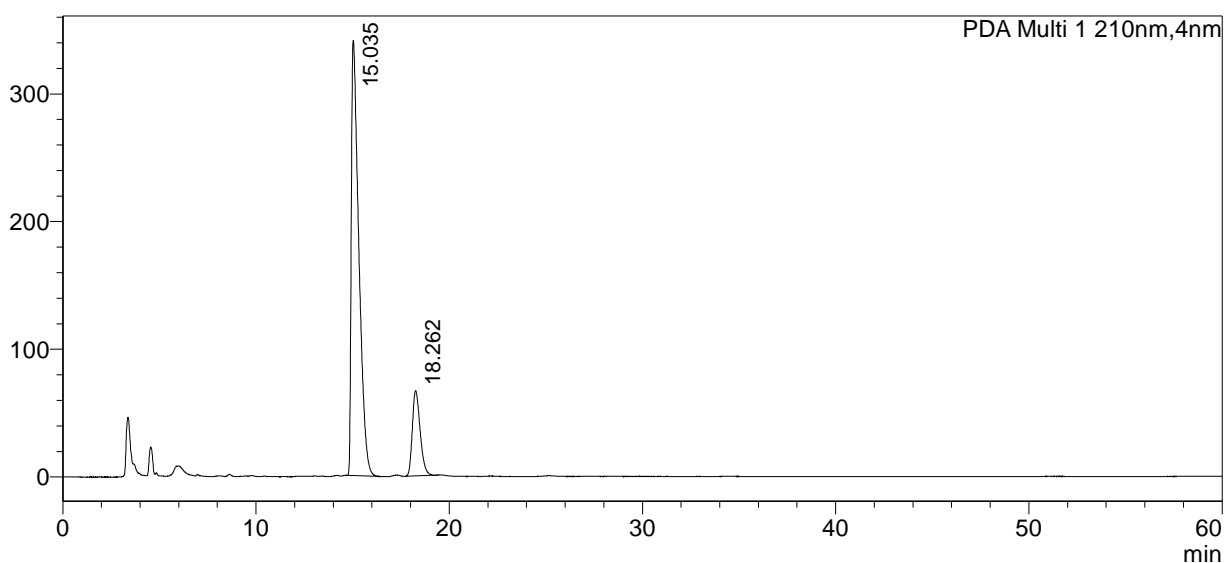
Sample Name : LLC-1-108 IC-10%
 Sample ID :
 Data Filename : LLC-1-108 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-47
 Injection Volume : 10 uL
 Date Acquired : 1/20/2022 10:24:48 PM
 Date Processed : 1/20/2022 11:24:51 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

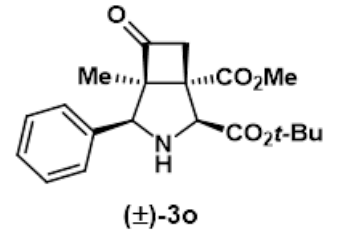
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.035	9249613	340856	83.173			
2	18.262	1871282	66708	16.827			
Total		11120895	407564				



<Sample Information>

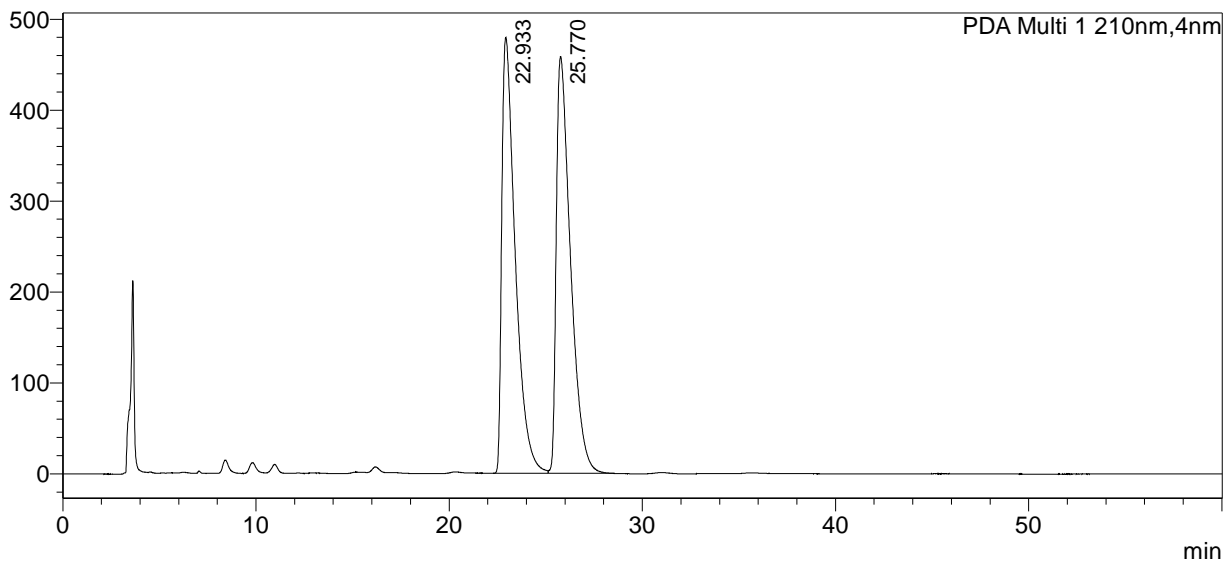
Sample Name : LLC-2-4 IC-5%
 Sample ID :
 Data Filename : LLC-2-4 IC-5%.lcd

Method Filename : IC,1ml 5%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-46
 Injection Volume : 10 uL
 Date Acquired : 8/4/2022 9:55:16 AM
 Date Processed : 8/4/2022 10:55:18 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

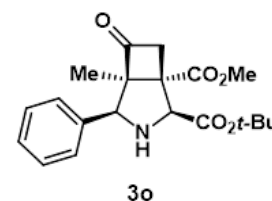
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.933	23268923	479529	49.770			
2	25.770	23483857	458690	50.230		V	
Total		46752780	938219				



<Sample Information>

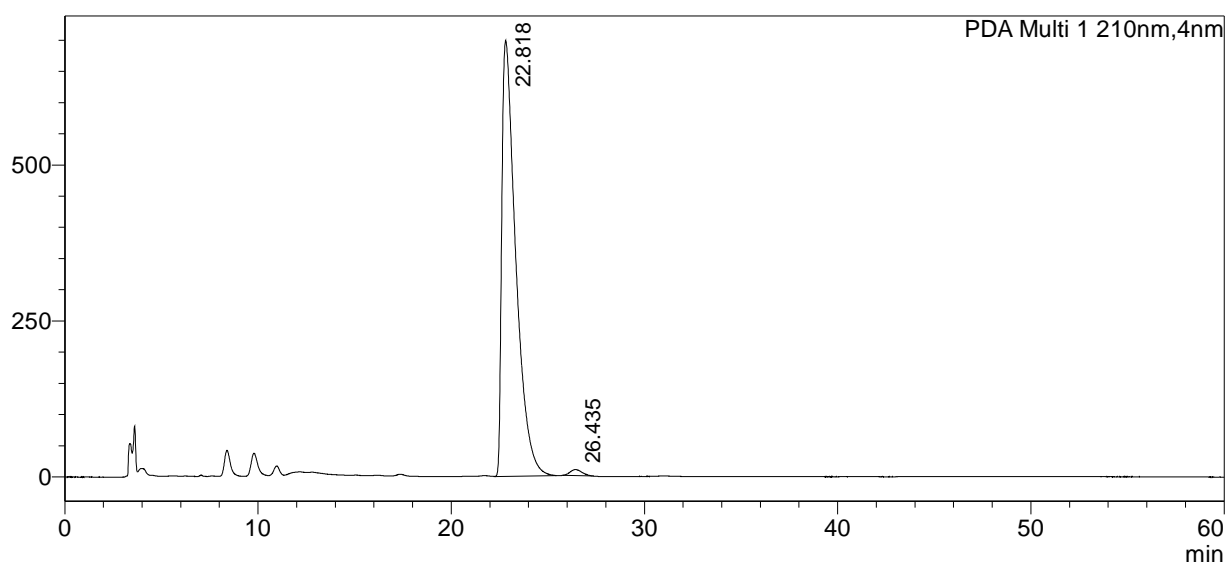
Sample Name : LLC-2-5 IC-5%
 Sample ID :
 Data Filename : LLC-2-5 IC-5%.lcd

Method Filename : IC,1ml 5%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-47
 Injection Volume : 10 uL
 Date Acquired : 8/4/2022 10:55:49 AM
 Date Processed : 8/4/2022 11:55:52 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

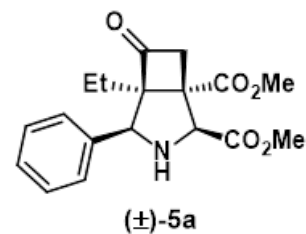
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.818	35104539	698324	98.811			
2	26.435	422274	9764	1.189			
Total		35526813	708088				



<Sample Information>

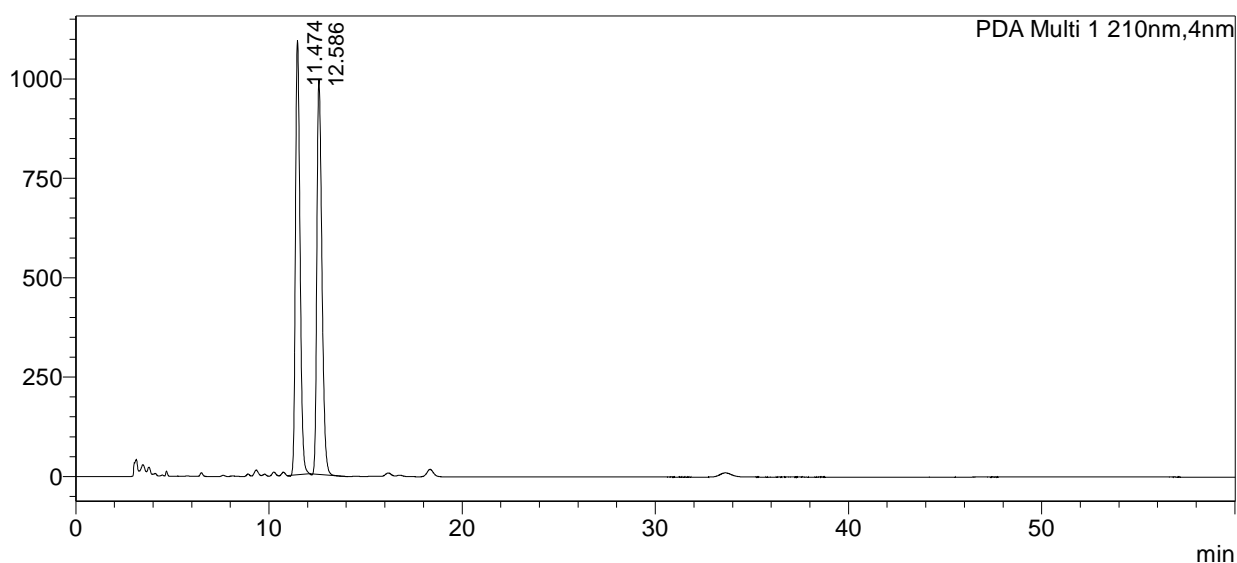
Sample Name : LLC-1-81 IA-10%
 Sample ID :
 Data Filename : LLC-1-81 IA-10%.lcd

Method Filename : IA,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-1
 Injection Volume : 10 uL
 Date Acquired : 11/6/2021 2:22:12 AM
 Date Processed : 11/6/2021 3:22:15 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 210nm

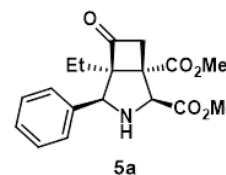
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.474	17922943	1092624	49.770			
2	12.586	18088520	994517	50.230			
Total		36011463	2087142				

<Sample Information>

Sample Name : LLC-1-80 IA-10%
 Sample ID :
 Data Filename : LLC-1-80 IA-10%.lcd

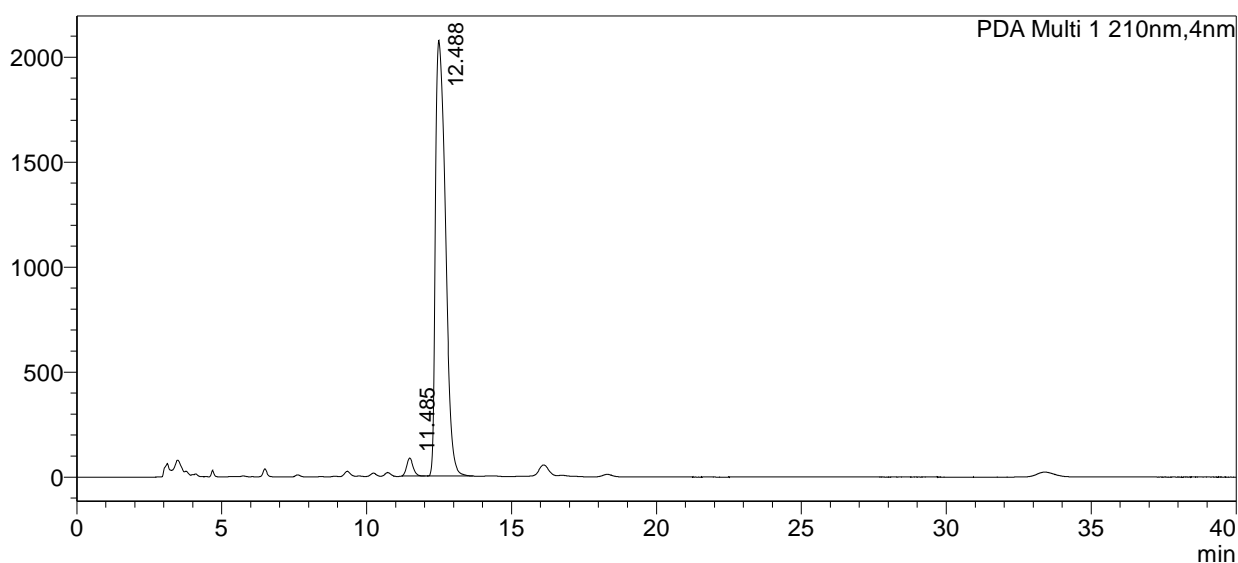
Method Filename : IA,1ml 10%IPA in Hex;40min.lcm
 Batch Filename : 20210901.lcb
 Vial # : 1-3
 Injection Volume : 10 uL
 Date Acquired : 11/6/2021 8:20:35 PM
 Date Processed : 11/15/2021 5:31:03 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator



<Chromatogram>

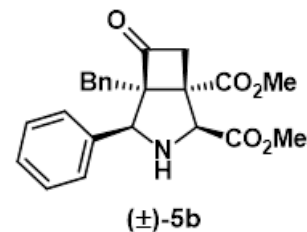
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.485	1307374	85384	2.544			
2	12.488	50090269	2075107	97.456			
Total		51397643	2160491				



<Sample Information>

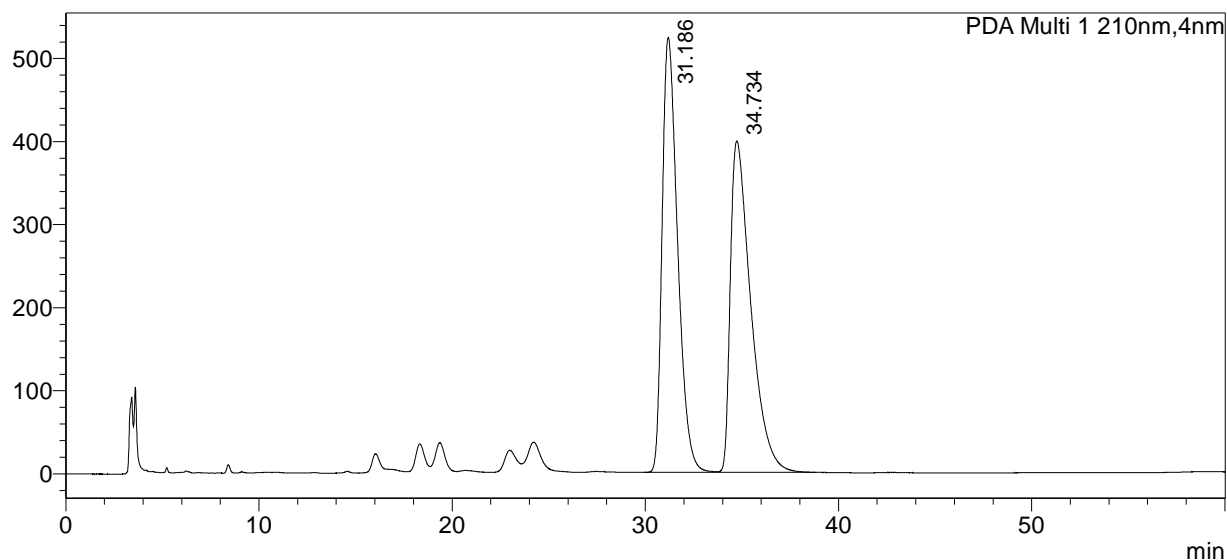
Sample Name : LLC-2-23 IC-10%
 Sample ID :
 Data Filename : LLC-2-23 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-16
 Injection Volume : 10 uL
 Date Acquired : 8/10/2022 10:20:53 PM
 Date Processed : 8/10/2022 11:20:55 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU

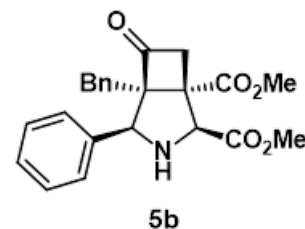


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.186	29232174	523663	49.905		V	
2	34.734	29343295	399046	50.095		V	
Total		58575469	922709				

<Sample Information>



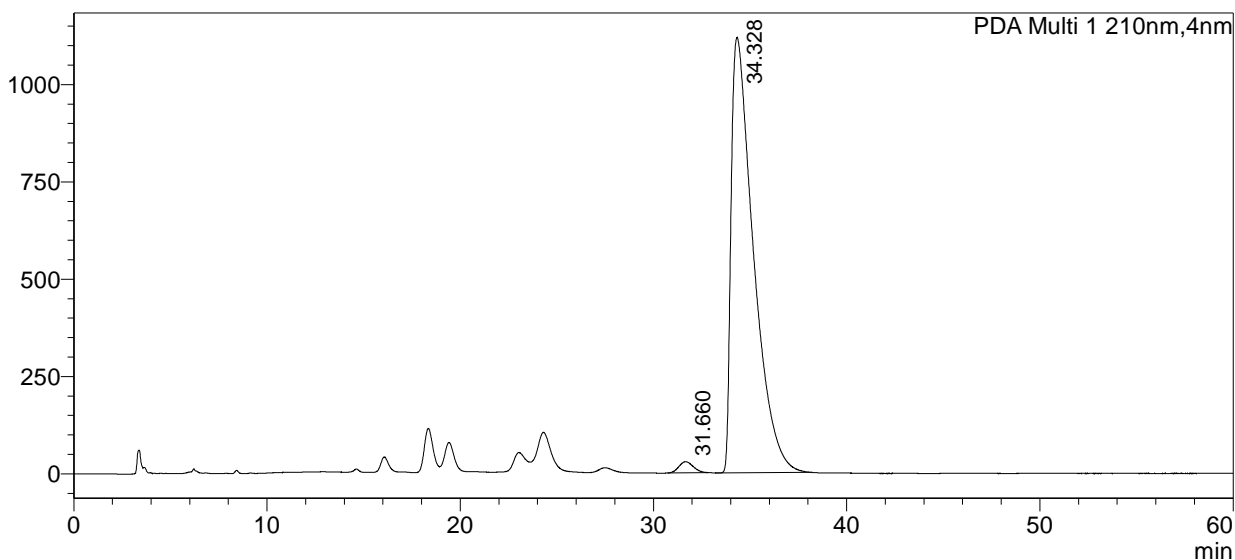
Sample Name : LLC-2-24 IC-10%
 Sample ID :
 Data Filename : LLC-2-24 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-17
 Injection Volume : 10 uL
 Date Acquired : 8/10/2022 11:21:25 PM
 Date Processed : 8/11/2022 12:21:28 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

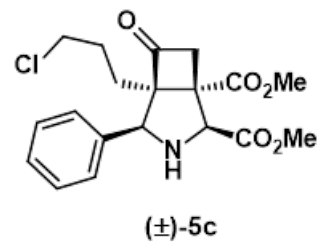
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.660	1471370	28537	1.611			
2	34.328	89871237	1118491	98.389			
Total		91342607	1147028				



<Sample Information>

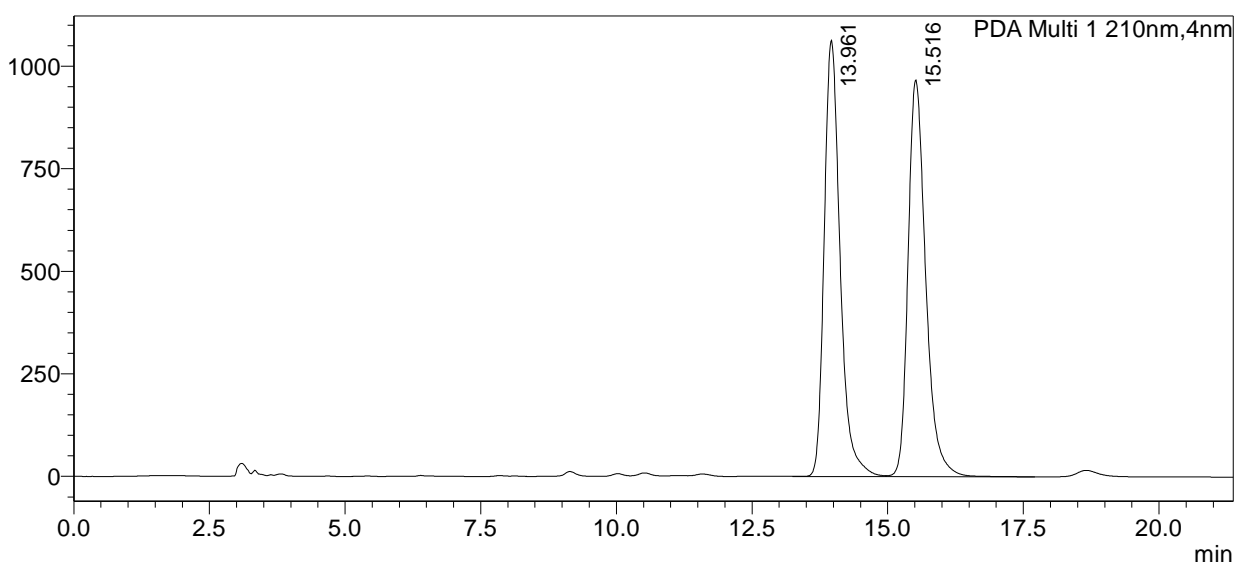
Sample Name : LLC-2-75 IA-10%
 Sample ID :
 Data Filename : LLC-2-75 IA-10%.lcd

Method Filename : IA,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-61
 Injection Volume : 10 uL
 Date Acquired : 9/23/2022 9:56:27 PM
 Date Processed : 9/23/2022 10:17:53 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

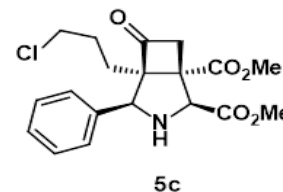
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.961	21715669	1063353	49.784			
2	15.516	21904059	967078	50.216		V	
Total		43619727	2030431				



<Sample Information>

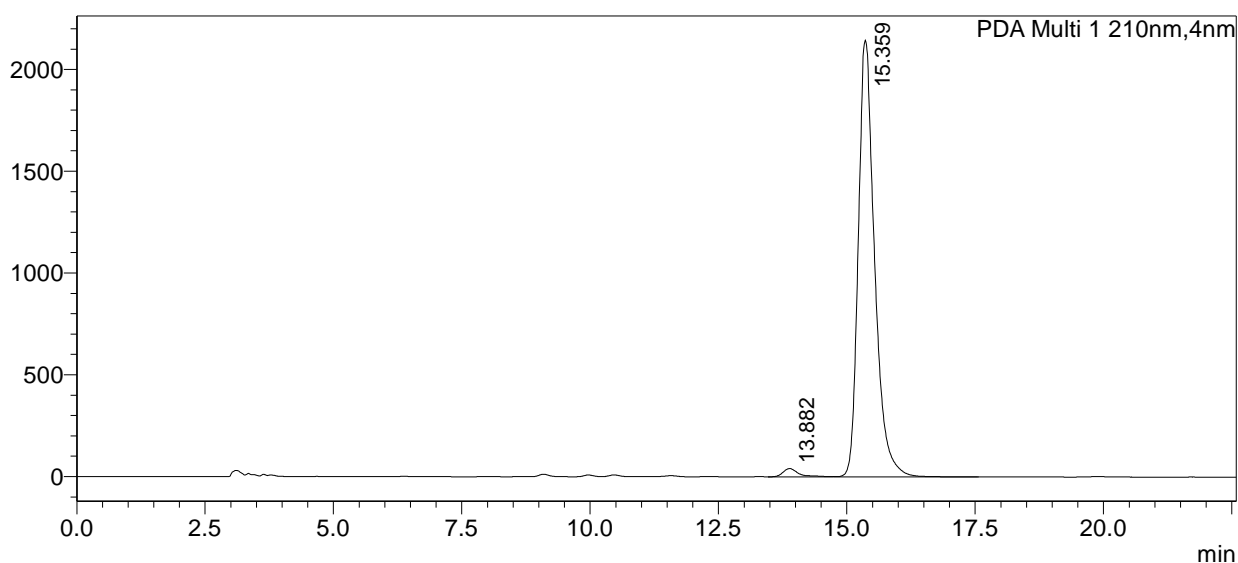
Sample Name : LLC-2-76 IA-10%
 Sample ID :
 Data Filename : LLC-2-76 IA-10%.lcd

Method Filename : IA,1ml 10%IPA in Hex;30min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-62
 Injection Volume : 10 uL
 Date Acquired : 9/23/2022 10:44:47 PM
 Date Processed : 9/23/2022 11:07:26 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU

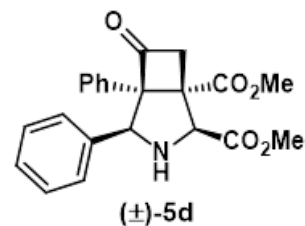


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.882	876836	40758	1.817			
2	15.359	47380312	2144500	98.183		V	
Total		48257148	2185258				

Analysis Report



<Sample Information>

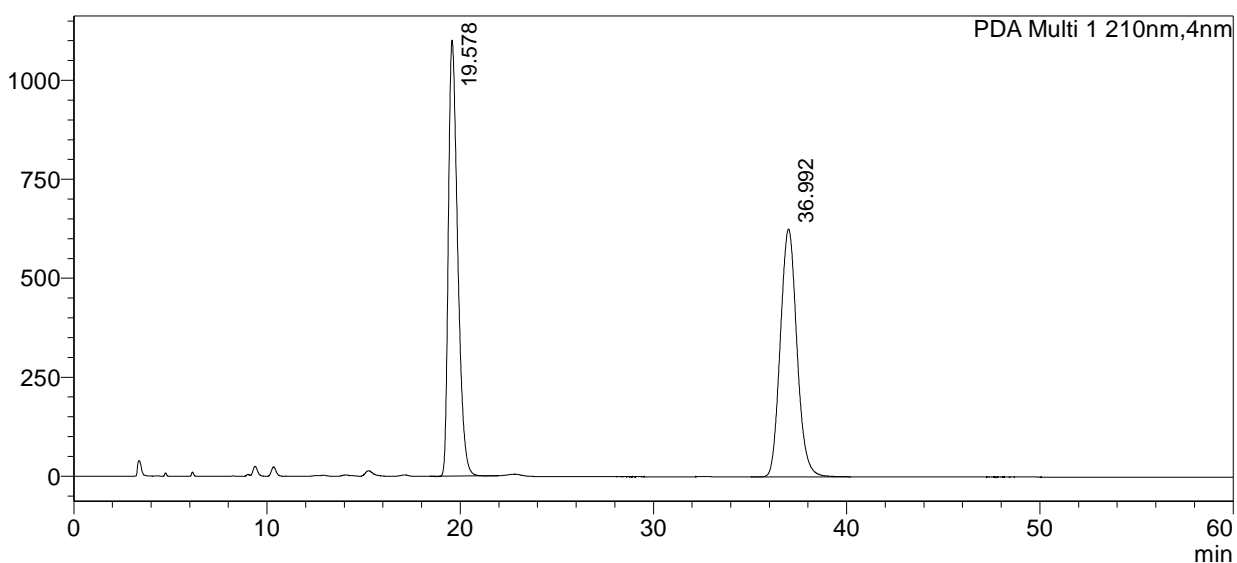
Sample Name : LLC-1-137 IC-10%
 Sample ID :
 Data Filename : LLC-1-137 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-4
 Injection Volume : 10 uL
 Date Acquired : 3/12/2022 6:04:05 PM
 Date Processed : 3/12/2022 7:04:08 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

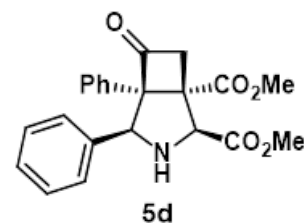
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.578	36821226	1100670	49.689			
2	36.992	37281797	625784	50.311			
Total		74103022	1726454				



<Sample Information>

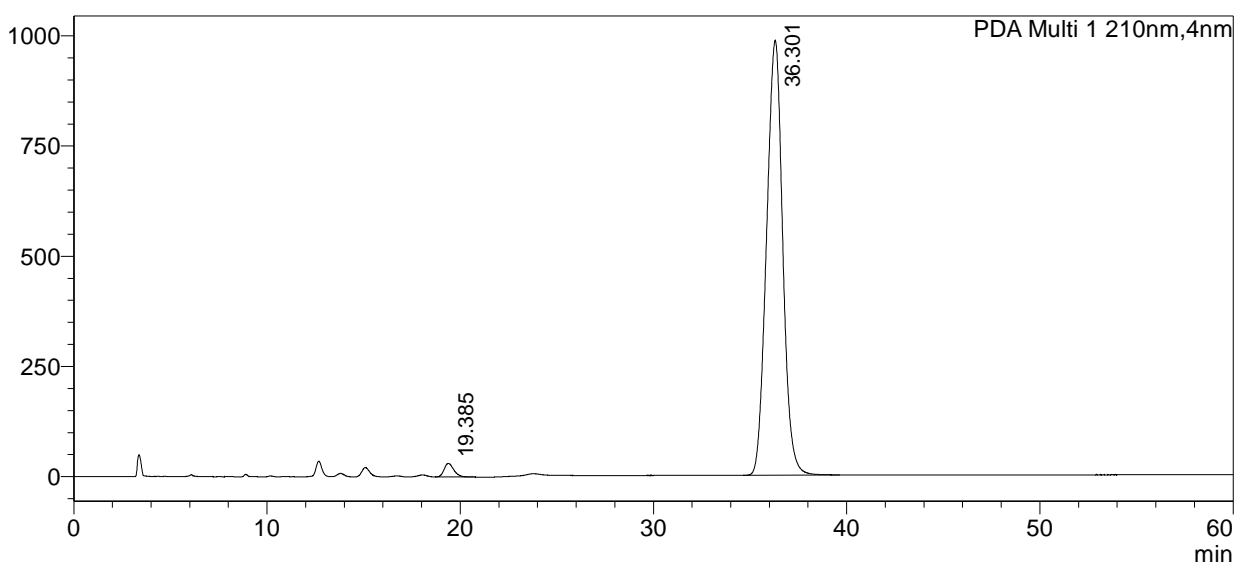
Sample Name : LLC-1-138 IC-10%
 Sample ID :
 Data Filename : LLC-1-138 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-5
 Injection Volume : 10 uL
 Date Acquired : 3/12/2022 7:34:23 PM
 Date Processed : 3/12/2022 8:34:25 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

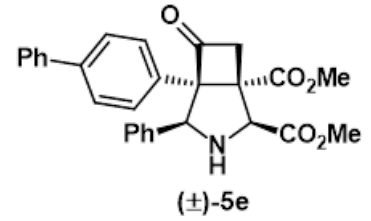
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.385	1075111	30953	1.841			
2	36.301	57312066	986146	98.159		S	
Total		58387177	1017100				



<Sample Information>

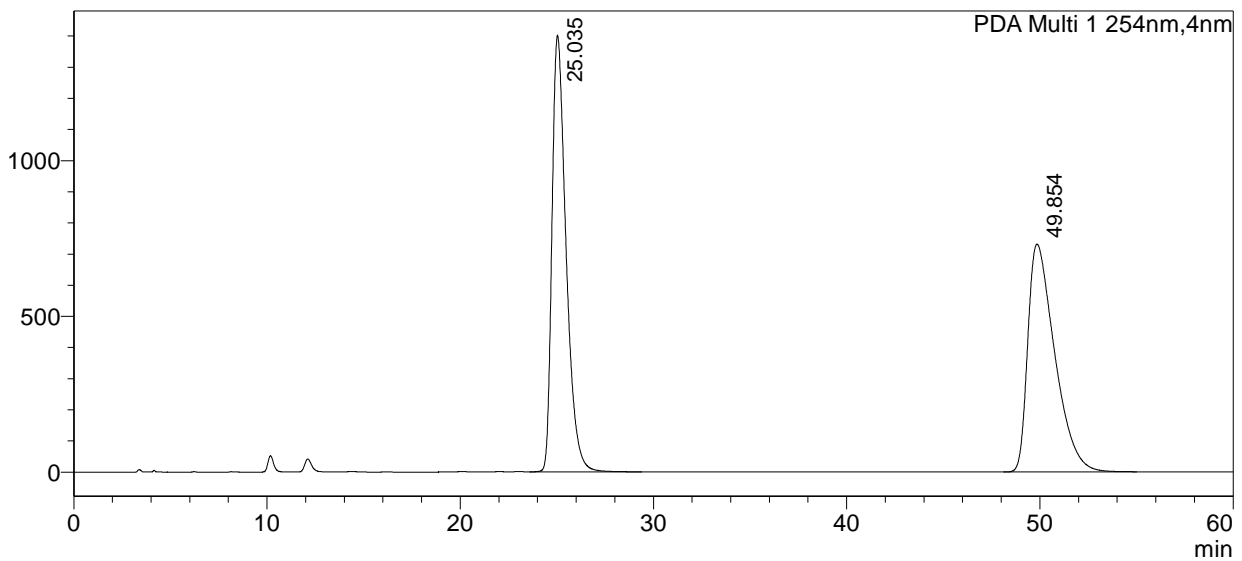
Sample Name : LLC-2-59 IC-10%
 Sample ID :
 Data Filename : LLC-2-59 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-76
 Injection Volume : 10 uL
 Date Acquired : 9/8/2022 1:12:59 AM
 Date Processed : 9/8/2022 2:13:02 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

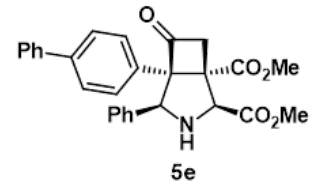
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.035	71216461	1401547	50.167			
2	49.854	70742046	731471	49.833			
Total		141958506	2133018				



<Sample Information>

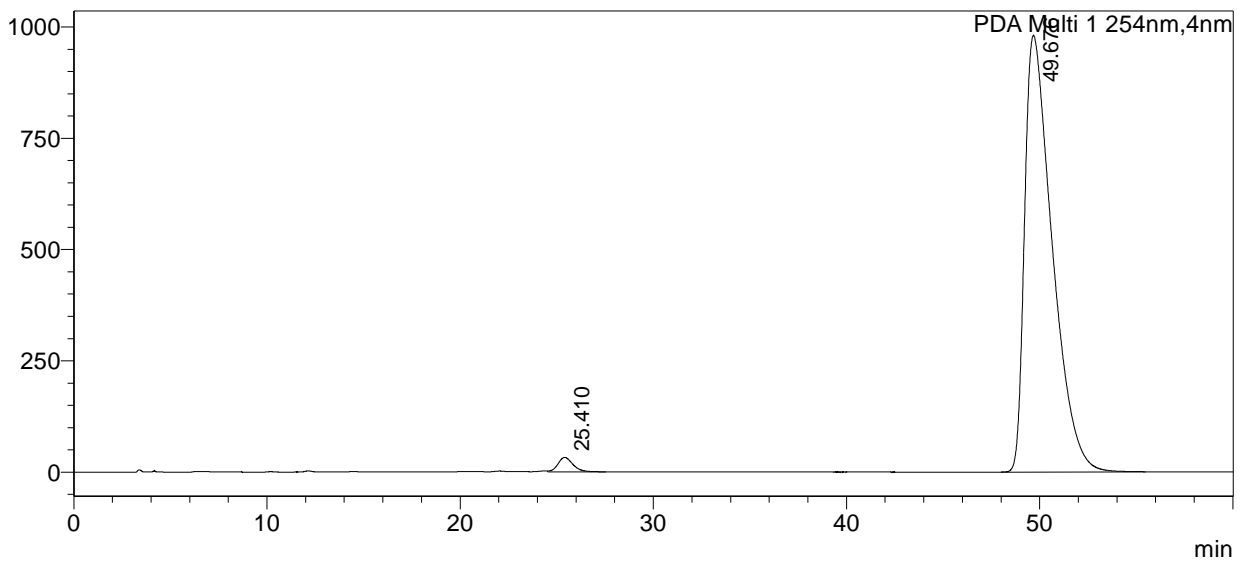
Sample Name : LLC-2-60 IC-10%
 Sample ID :
 Data Filename : LLC-2-60 IC-10%.lcd

Method Filename : IC,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-77
 Injection Volume : 10 uL
 Date Acquired : 9/8/2022 2:13:33 AM
 Date Processed : 9/8/2022 3:13:36 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

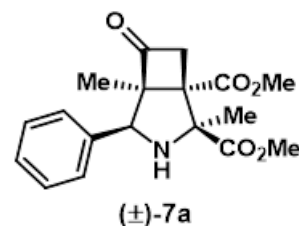
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.410	1760805	32479	1.775			
2	49.676	97421139	981089	98.225			
Total		99181944	1013568				



<Sample Information>

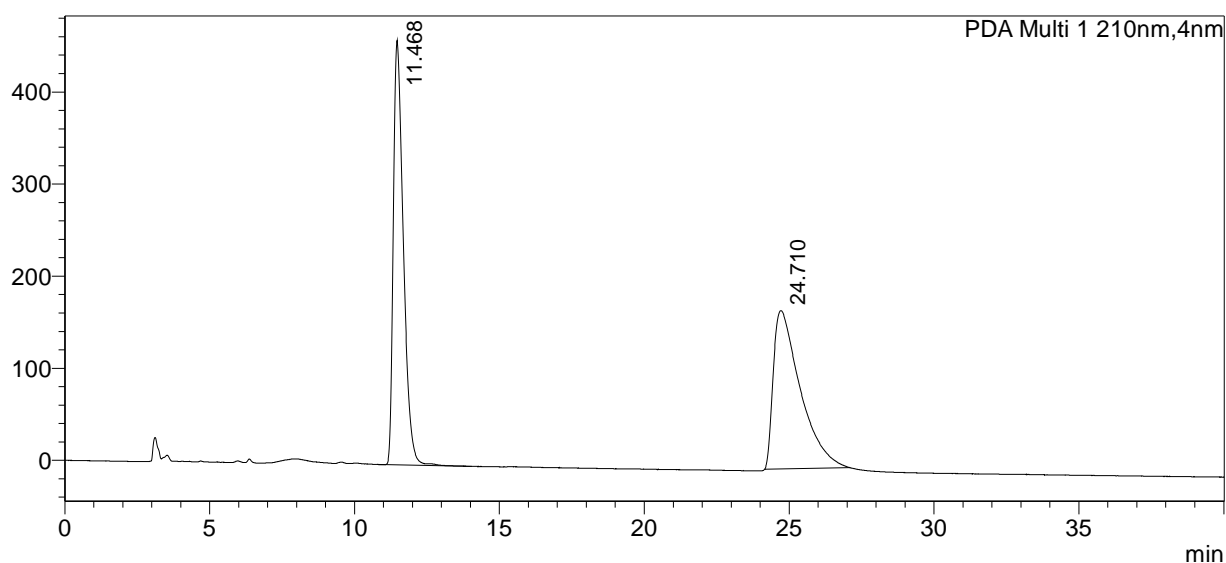
Sample Name : LLC-1-113 ODH-10%-320-2
 Sample ID :
 Data Filename : LLC-1-113 ODH-10%-320-2.lcd

Method Filename : OD-H,1ml 10%IPA in Hex;40min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-62
 Injection Volume : 10 uL
 Date Acquired : 3/20/2023 11:17:52 AM
 Date Processed : 3/20/2023 11:57:55 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

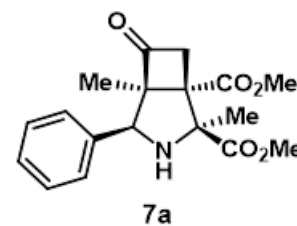
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.468	11133698	460956	49.979			
2	24.710	11143216	171943	50.021			
Total		22276914	632899				



<Sample Information>

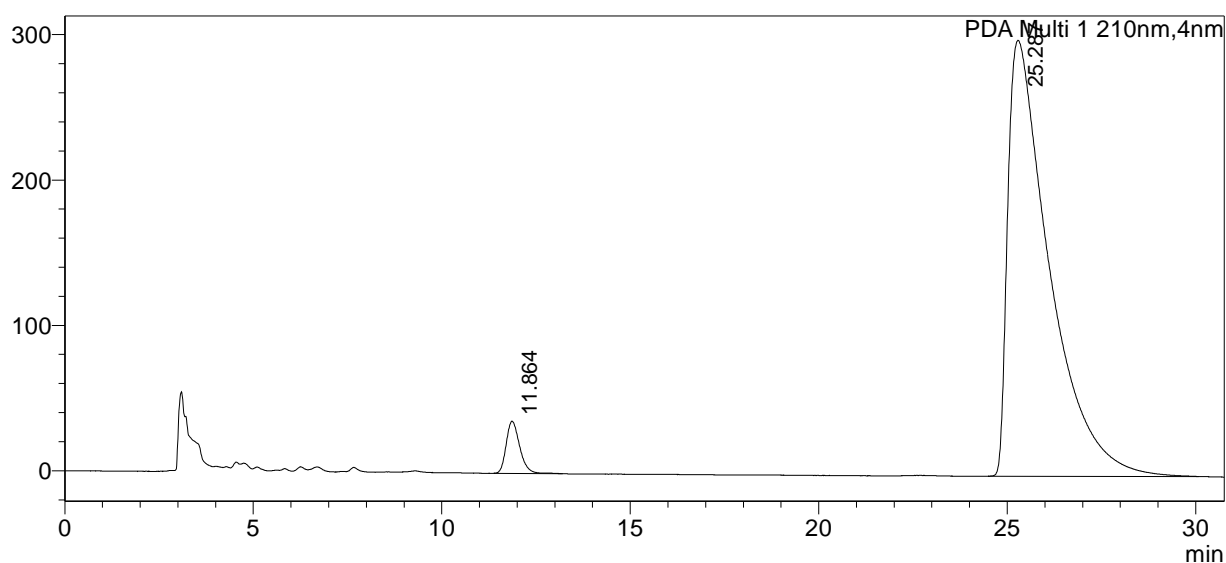
Sample Name : LLC-3-178 ODH-10%
 Sample ID :
 Data Filename : LLC-3-178 ODH-10%.lcd

Method Filename : OD-H,1ml 10%IPA in Hex;40min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-61
 Injection Volume : 10 uL
 Date Acquired : 3/19/2023 7:06:18 PM
 Date Processed : 3/19/2023 7:37:06 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

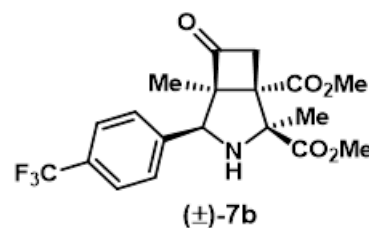
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.864	893825	35892	3.740			
2	25.287	23003828	299957	96.260		SV	
Total		23897653	335849				



<Sample Information>

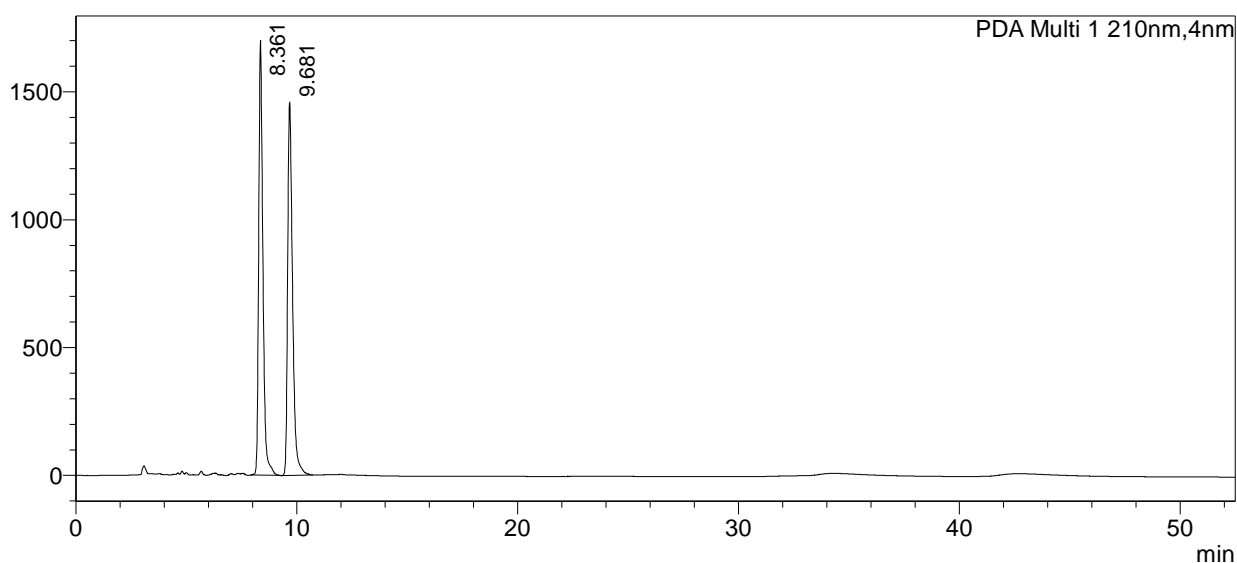
Sample Name : LLC-2-45 IA-10%
 Sample ID :
 Data Filename : LLC-2-45 IA-10%.lcd

Method Filename : IA,1ml 10%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-2
 Injection Volume : 10 uL
 Date Acquired : 9/1/2022 9:46:41 AM
 Date Processed : 9/1/2022 10:39:13 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

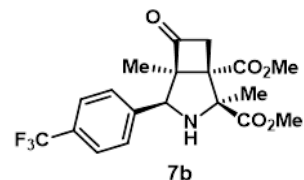
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.361	22439592	1699987	49.948			
2	9.681	22486251	1457177	50.052			
Total		44925843	3157165				



<Sample Information>

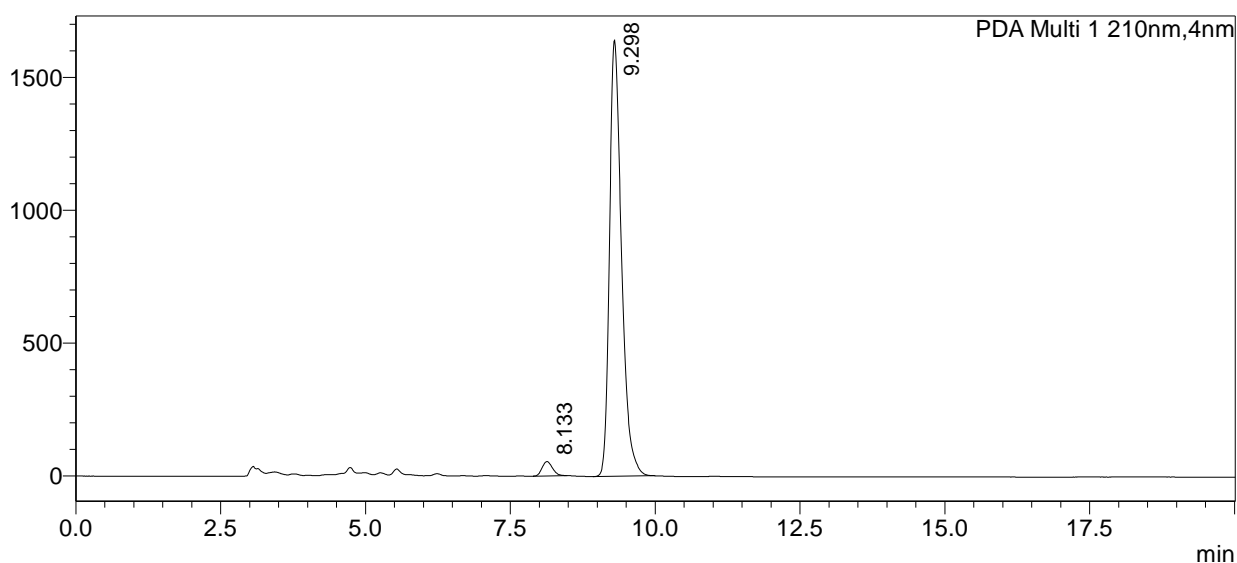
Sample Name : LLC-4-4 IA-10%
 Sample ID :
 Data Filename : LLC-4-4 IA-10%.lcd

Method Filename : IA,1ml 10%IPA in Hex;20min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-61
 Injection Volume : 10 uL
 Date Acquired : 3/30/2023 10:01:19 AM
 Date Processed : 3/30/2023 10:21:22 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

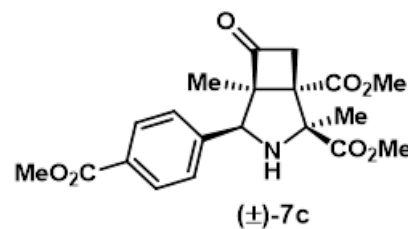
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.133	680263	54299	2.794			
2	9.298	23665173	1640510	97.206			
Total		24345436	1694809				



<Sample Information>

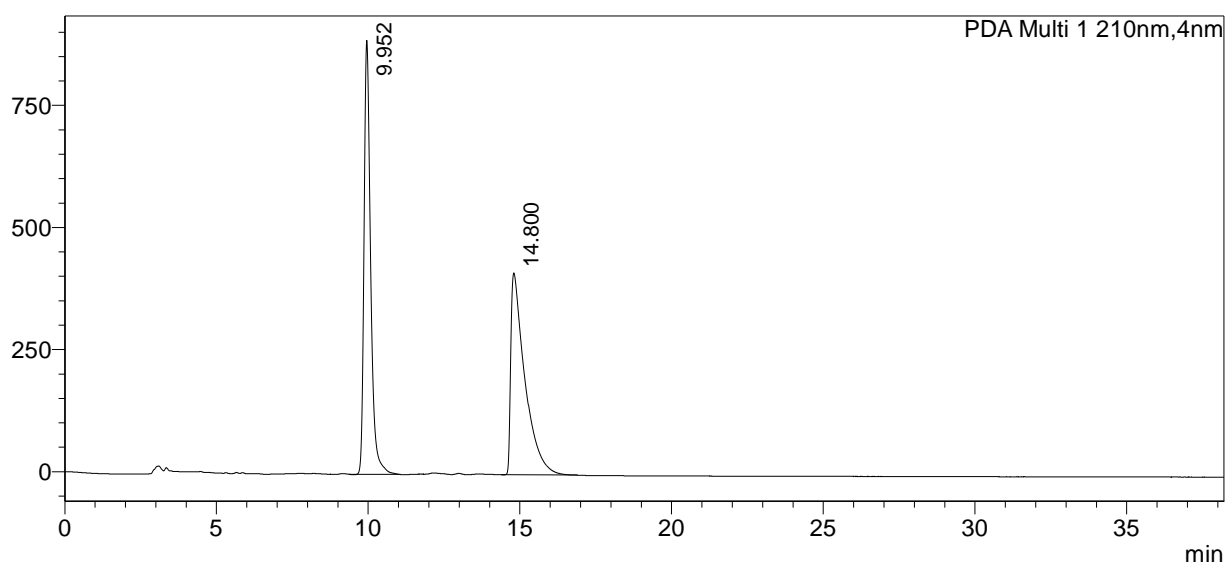
Sample Name : LLC-2-102 IA-20%
 Sample ID :
 Data Filename : LLC-2-102 IA-20%.lcd

Method Filename : IA,1ml 20%IPA in Hex;60min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-91
 Injection Volume : 10 uL
 Date Acquired : 10/6/2022 9:53:17 AM
 Date Processed : 10/6/2022 10:31:33 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

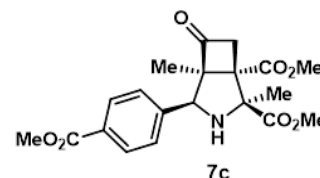
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.952	13589822	888535	50.325			
2	14.800	13414527	413153	49.675			
Total		27004349	1301688				



<Sample Information>

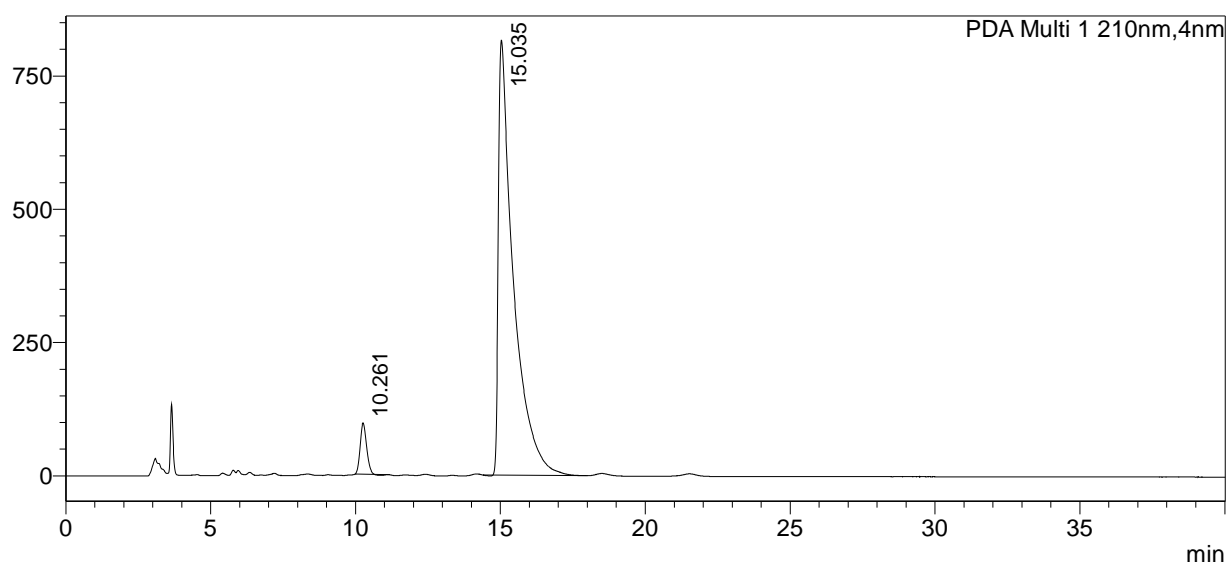
Sample Name : LLC-3-195 IA-20%
 Sample ID :
 Data Filename : LLC-3-195 IA-20%.lcd

Method Filename : IA,1ml 20%IPA in Hex;40min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-79
 Injection Volume : 10 uL
 Date Acquired : 3/25/2023 12:52:03 AM
 Date Processed : 3/25/2023 1:32:05 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

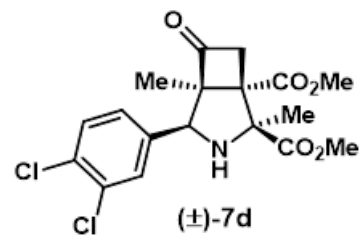
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.261	1453879	96216	4.718			
2	15.035	29361922	815549	95.282			
Total		30815800	911765				



<Sample Information>

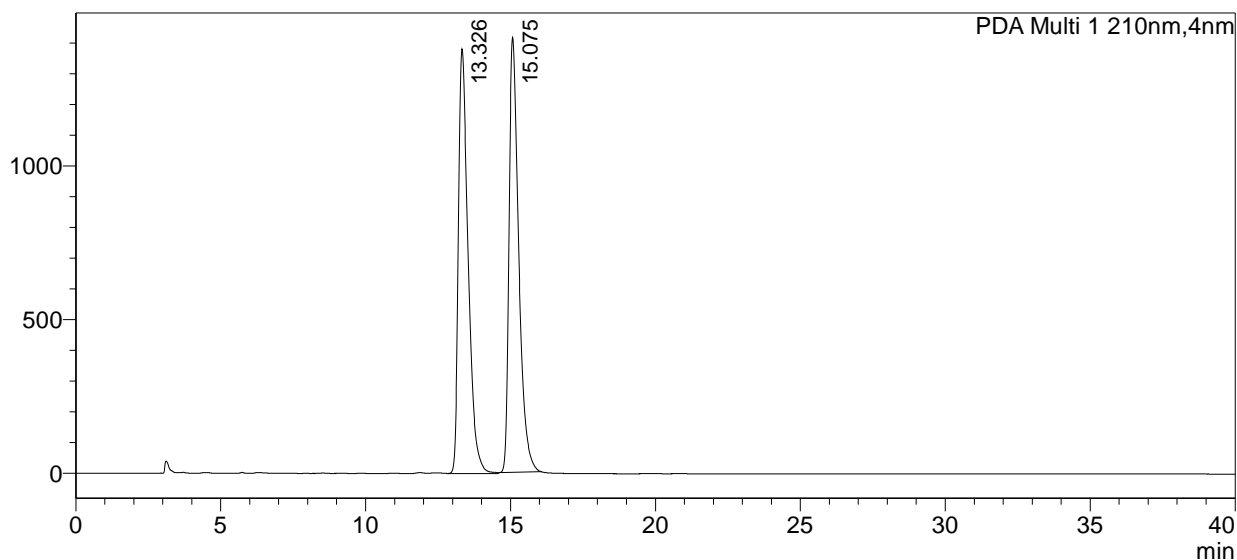
Sample Name : LLC-2-48 IA-5%
 Sample ID :
 Data Filename : LLC-2-48 IA-5%.lcd

Method Filename : IA,1ml 5%IPA in Hex;40min.lcm
 Batch Filename : 0825.lcb
 Vial # : 1-16
 Injection Volume : 10 uL
 Date Acquired : 9/5/2022 4:47:05 PM
 Date Processed : 9/5/2022 5:27:07 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

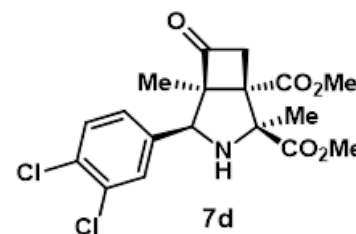
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.326	32359148	1381499	49.654			
2	15.075	32809892	1414584	50.346			
Total		65169040	2796082				



<Sample Information>

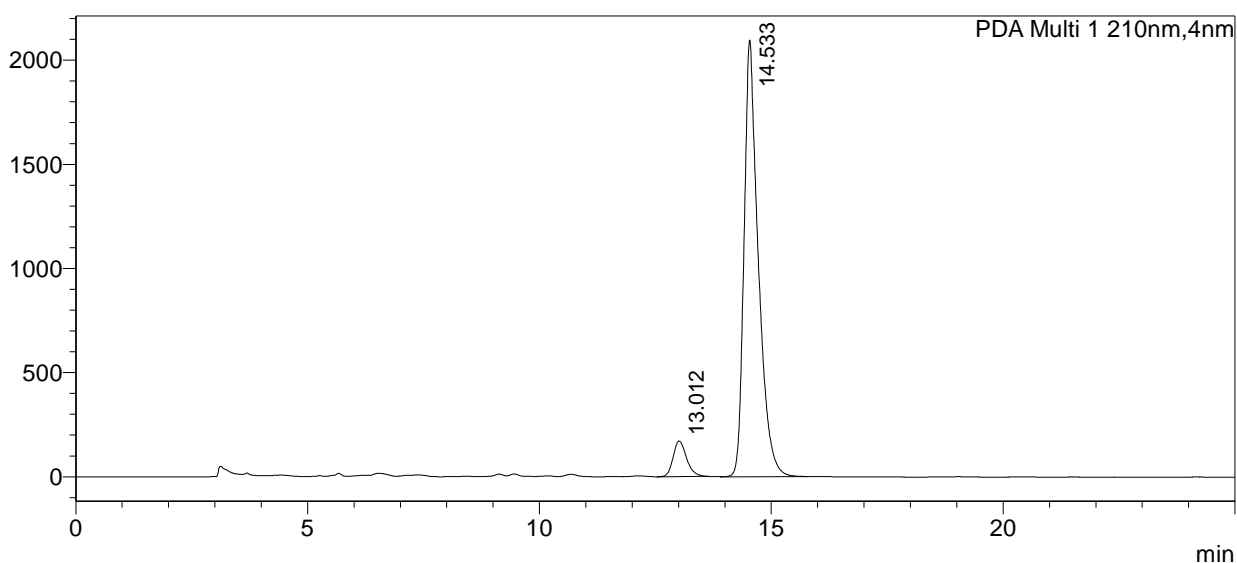
Sample Name : LLC-4-8 IA-5%
 Sample ID :
 Data Filename : LLC-4-8 IA-5%.lcd

Method Filename : IA,1ml 5%IPA in Hex;25min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-92
 Injection Volume : 10 uL
 Date Acquired : 3/31/2023 12:39:20 PM
 Date Processed : 3/31/2023 1:04:23 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

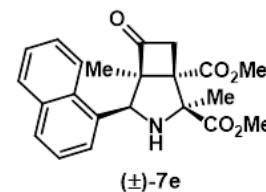
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.012	3438268	170740	7.143			
2	14.533	44699355	2094589	92.857			
Total		48137623	2265329				



<Sample Information>

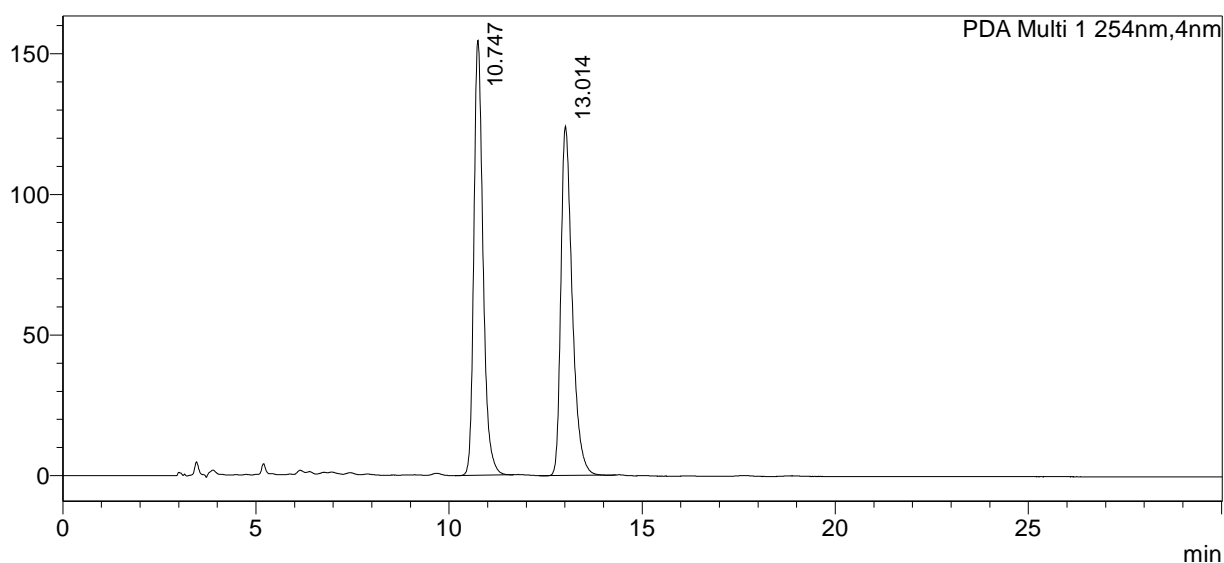
Sample Name : LLC-3-198 IA-10%
 Sample ID :
 Data Filename : LLC-3-198 IA-10%.lcd

Method Filename : IA,1ml 10%IPA in Hex;30min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-63
 Injection Volume : 10 uL
 Date Acquired : 3/27/2023 9:19:35 PM
 Date Processed : 3/27/2023 9:49:37 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

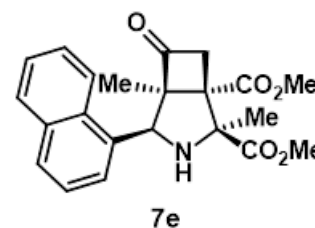
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.747	2549616	154644	50.203			
2	13.014	2528948	124232	49.797			
Total		5078564	278876				



<Sample Information>

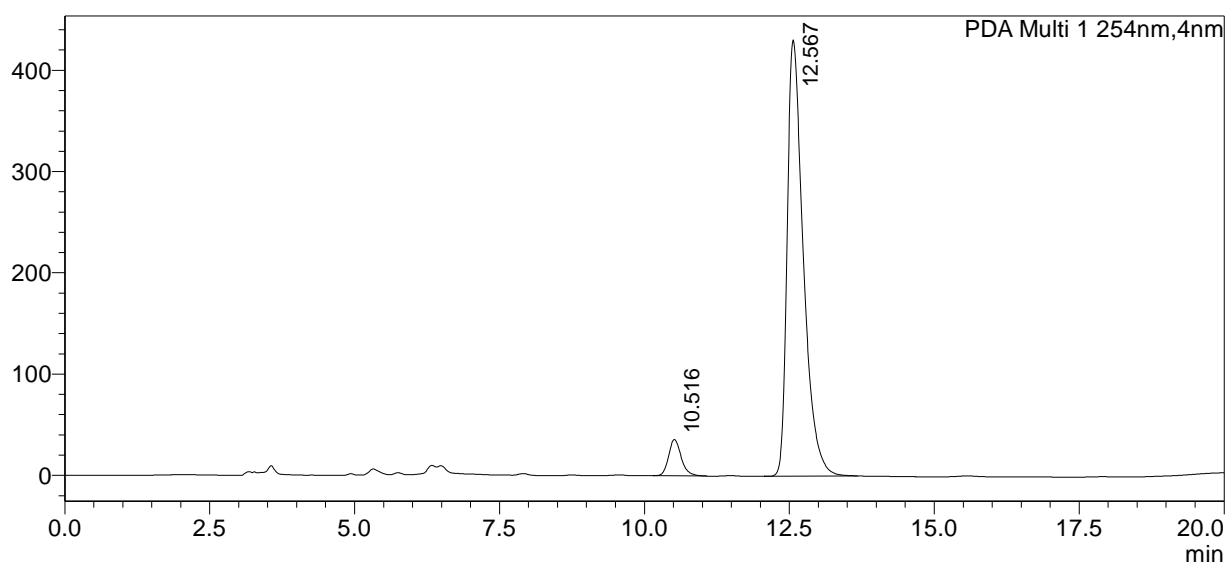
Sample Name : LLC-3-190 IA-10%
 Sample ID :
 Data Filename : LLC-3-190 IA-10%.lcd

Method Filename : IA,1ml 10%IPA in Hex;20min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-61
 Injection Volume : 10 uL
 Date Acquired : 3/23/2023 4:18:26 PM
 Date Processed : 3/23/2023 4:38:28 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

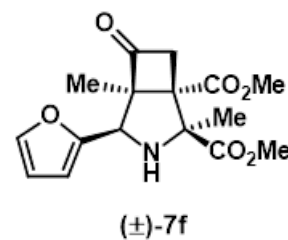
mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.516	545880	35877	6.141			
2	12.567	8343756	430348	93.859			
Total		8889636	466225				



<Sample Information>

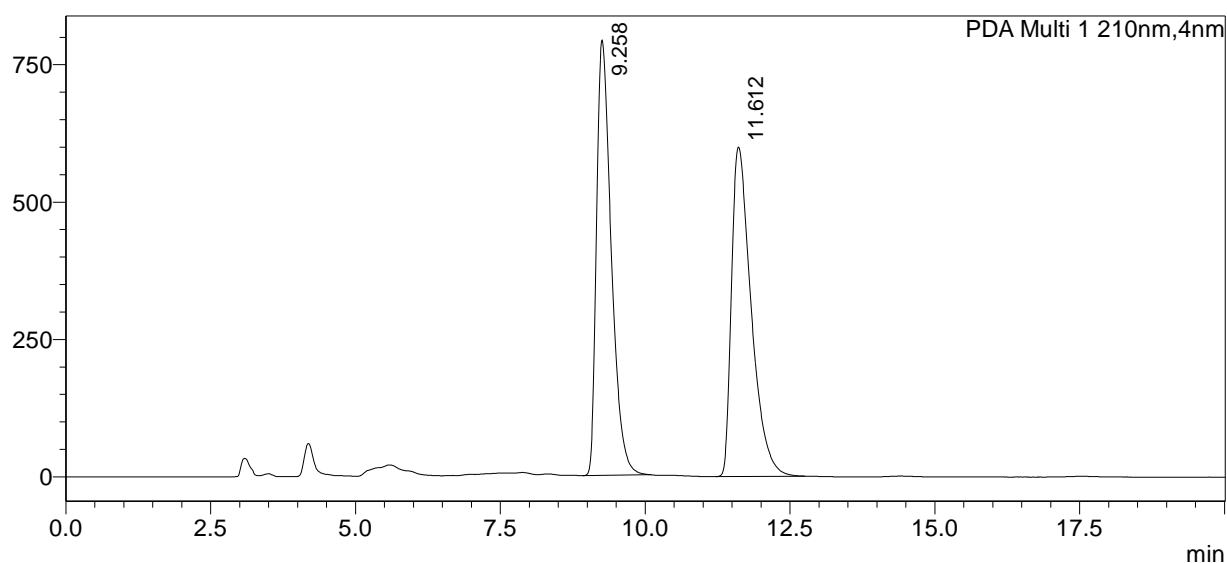
Sample Name : LLC-4-9-1 ODH-10%
 Sample ID :
 Data Filename : LLC-4-9-1 ODH-10%.lcd

Method Filename : OD-H,1ml 10%IPA in Hex;20min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-1
 Injection Volume : 10 uL
 Date Acquired : 4/1/2023 7:14:05 PM
 Date Processed : 4/1/2023 7:34:07 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

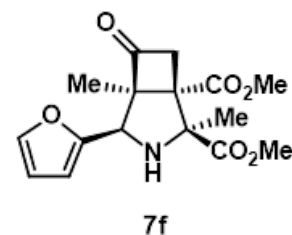
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.258	14053348	791625	49.828			
2	11.612	14150518	599360	50.172			
Total		28203866	1390985				



<Sample Information>

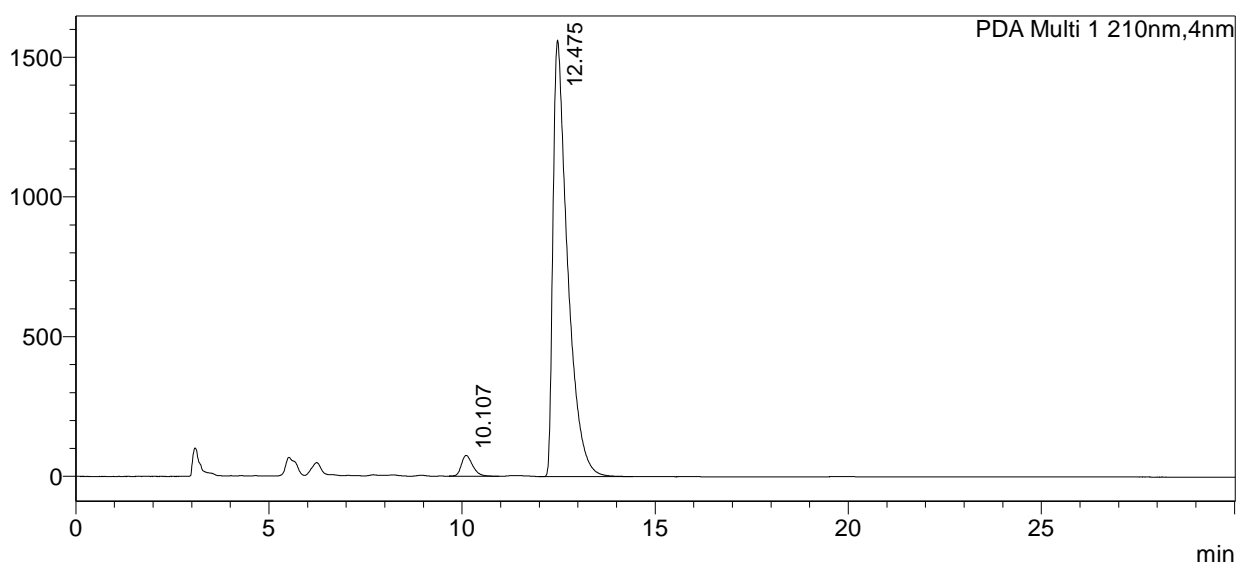
Sample Name : LLC-3-194 ODH-10%
 Sample ID :
 Data Filename : LLC-3-194 ODH-10%.lcd

Method Filename : OD-H,1ml 10%IPA in Hex;30min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-78
 Injection Volume : 10 uL
 Date Acquired : 3/25/2023 12:01:17 AM
 Date Processed : 3/25/2023 12:31:19 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

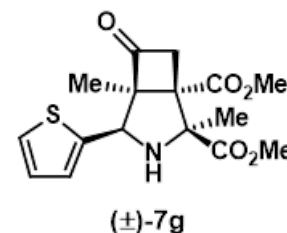
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.107	1514600	74389	3.550			
2	12.475	41145555	1560903	96.450			
Total		42660156	1635292				



<Sample Information>

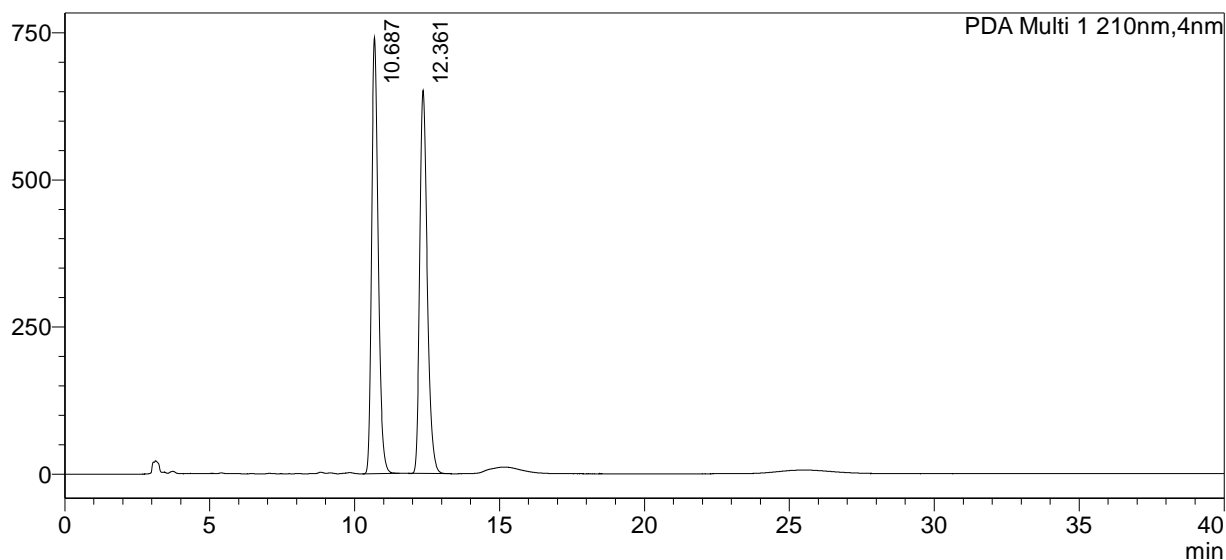
Sample Name : LLC-2-183 ADH-10%
 Sample ID :
 Data Filename : LLC-2-183 ADH-10%.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 40min.lcm
 Batch Filename : 20221007.lcb
 Vial # : 1-61
 Injection Volume : 10 uL
 Date Acquired : 11/27/2022 9:50:00 PM
 Date Processed : 11/27/2022 10:30:03 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

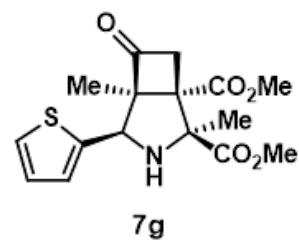
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.687	11784639	741482	50.070			
2	12.361	11751538	650983	49.930			
Total		23536178	1392466				



<Sample Information>

Sample Name : LLC-3-185 ADH-10%
 Sample ID :
 Data Filename : LLC-3-185 ADH-10%.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex;20 min.lcm

Batch Filename : 1.lcb

Vial # : 1-47

Injection Volume : 10 uL

Date Acquired : 3/21/2023 8:00:51 PM

Date Processed : 3/21/2023 8:17:34 PM

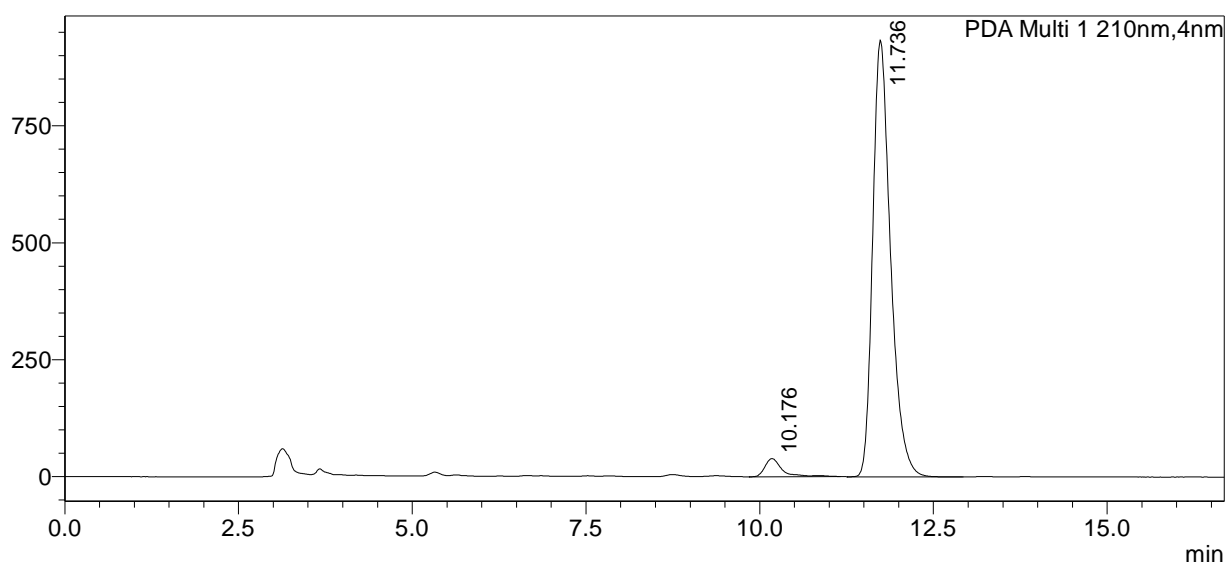
Sample Type : Unknown

Acquired by : System Administrator

Processed by : System Administrator

<Chromatogram>

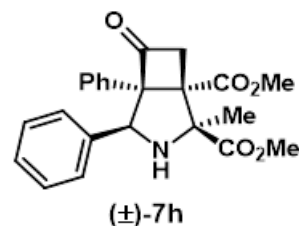
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.176	669787	38889	3.861			
2	11.736	16676599	932666	96.139			
Total		17346386	971555				



<Sample Information>

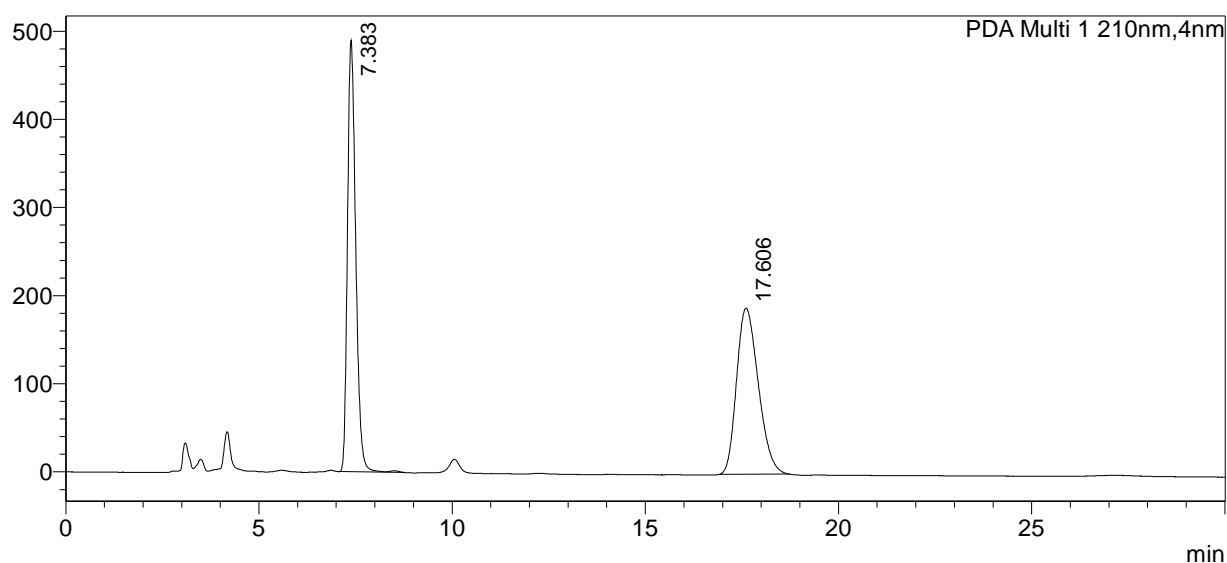
Sample Name : LLC-4-43 ODH-10%
 Sample ID :
 Data Filename : LLC-4-43 ODH-10%.lcd

Method Filename : OD-H,1ml 10%IPA in Hex;30min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-31
 Injection Volume : 10 uL
 Date Acquired : 4/16/2023 2:38:38 PM
 Date Processed : 4/16/2023 3:08:41 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

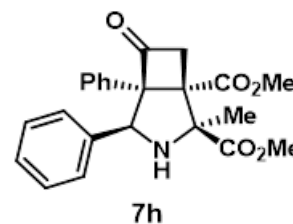
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.383	7294455	489348	49.795			
2	17.606	7354485	188379	50.205			
Total		14648940	677726				



<Sample Information>

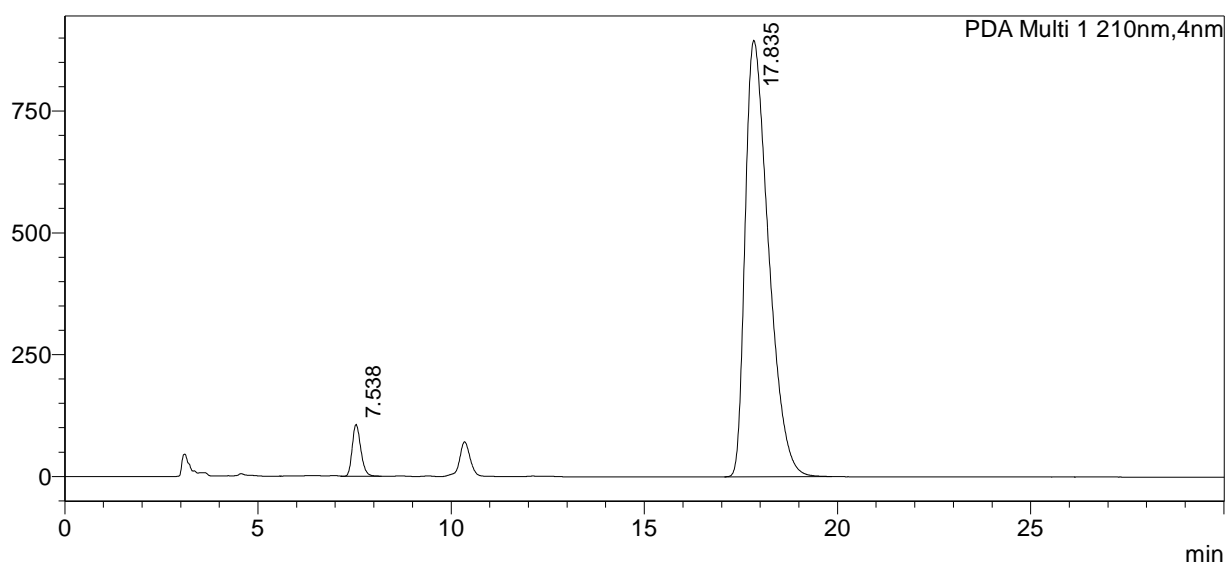
Sample Name : LLC-4-30-ap ODH-10%
 Sample ID :
 Data Filename : LLC-4-30-ap ODH-10%.lcd

Method Filename : OD-H,1ml 10%IPA in Hex;30min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-33
 Injection Volume : 10 uL
 Date Acquired : 4/12/2023 12:30:17 AM
 Date Processed : 4/12/2023 1:00:20 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

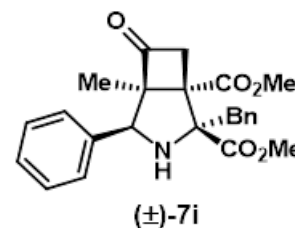
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.538	1637990	106033	4.176			
2	17.835	37590084	895540	95.824			
Total		39228074	1001573				



<Sample Information>

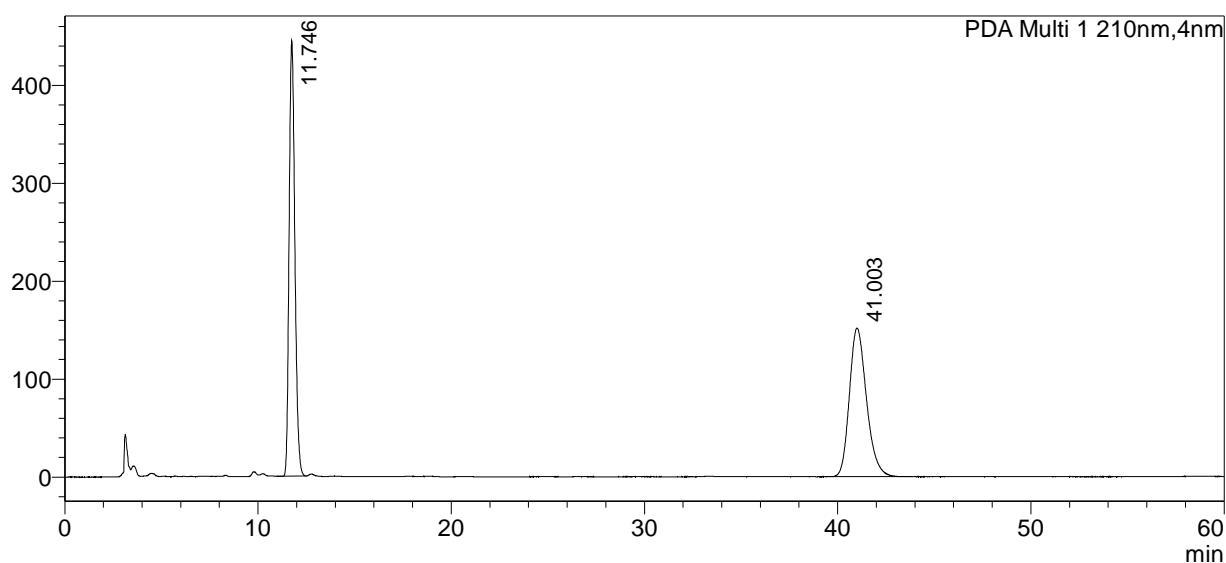
Sample Name : LLC-3-96 ADH-5%
 Sample ID :
 Data Filename : LLC-3-96 ADH-5%001.lcd

Method Filename : AD-H; 1 ml; 5%IPA in Hex; 60min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-19
 Injection Volume : 10 uL
 Date Acquired : 4/29/2023 12:56:27 AM
 Date Processed : 4/29/2023 1:56:30 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

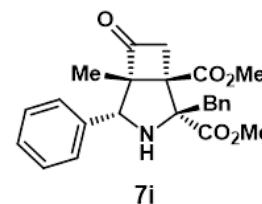
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.746	9204295	444954	49.629			
2	41.003	9341726	151797	50.371			
Total		18546021	596751				



<Sample Information>

Sample Name : LLC-4-70 ADH-5%
 Sample ID :
 Data Filename : LLC-4-70 ADH-5%.lcd

Method Filename : AD-H; 1 ml; 5%IPA in Hex; 60min.lcm

Batch Filename : 1.lcb

Vial # : 1-18

Injection Volume : 10 uL

Date Acquired : 4/28/2023 11:55:54 PM

Date Processed : 4/29/2023 12:55:56 AM

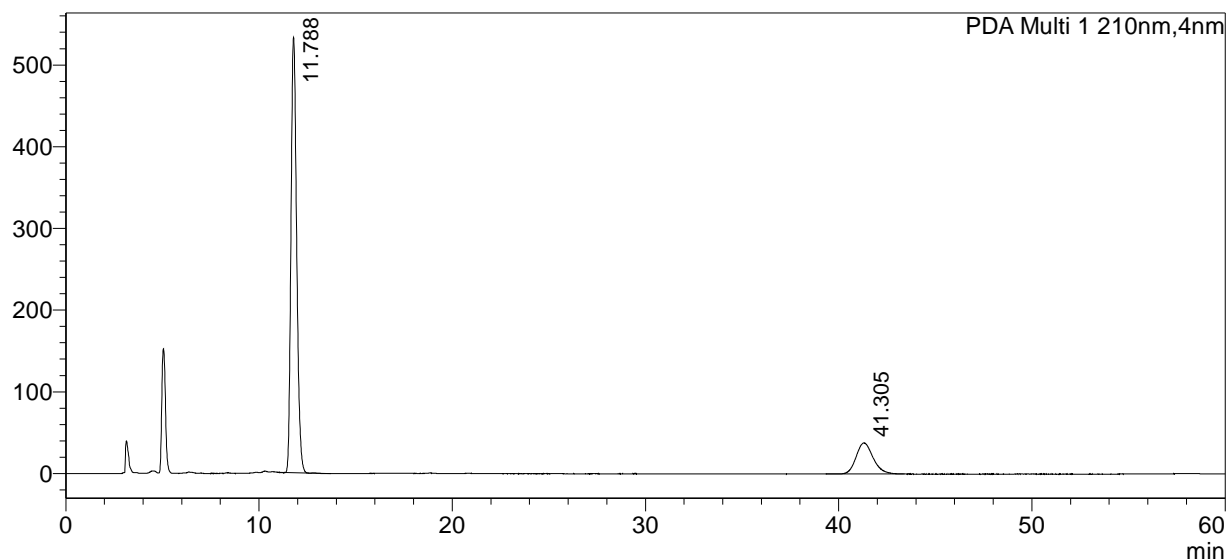
Sample Type : Unknown

Acquired by : System Administrator

Processed by : System Administrator

<Chromatogram>

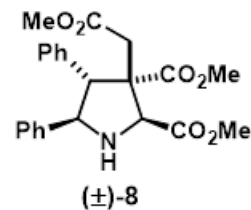
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.788	10860778	532674	82.337			
2	41.305	2329866	37981	17.663			
Total		13190644	570655				



<Sample Information>

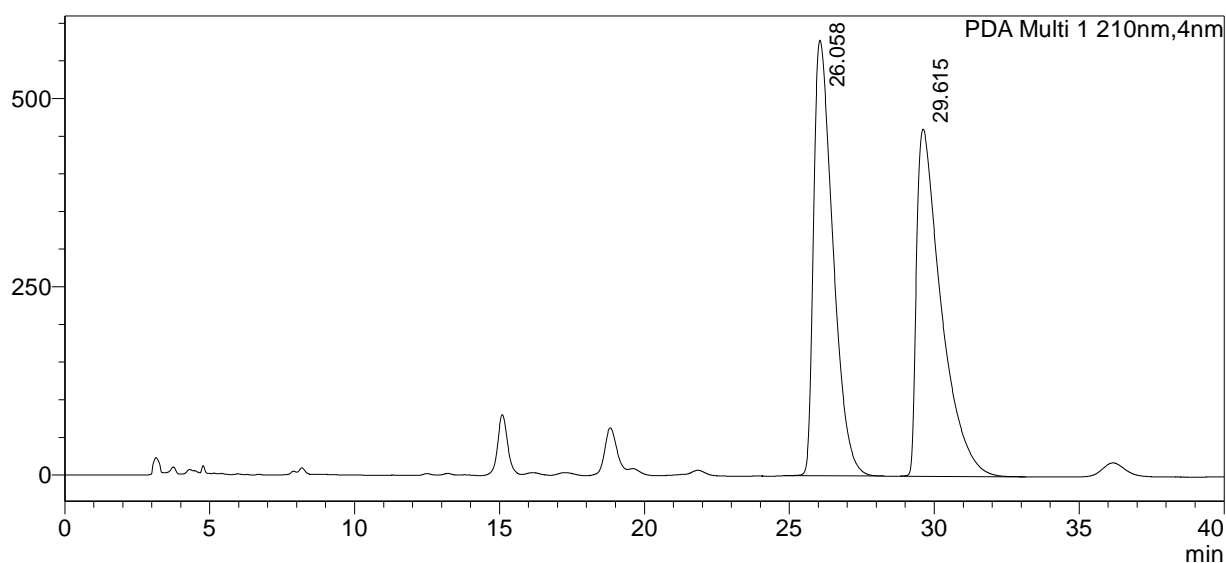
Sample Name : LLC-2-88 ADH-10%-2
 Sample ID :
 Data Filename : LLC-2-88 ADH-10%-3.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 40min.lcm
 Batch Filename : 20221007.lcb
 Vial # : 1-33
 Injection Volume : 10 uL
 Date Acquired : 1/3/2023 2:52:08 PM
 Date Processed : 1/3/2023 3:32:10 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

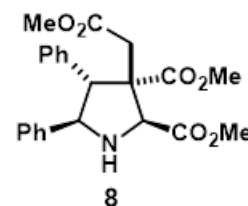
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	26.058	26888427	578281	49.720			
2	29.615	27191681	460860	50.280			
Total		54080108	1039141				



<Sample Information>

Sample Name : LLC-3-40-4 ADH-10%
 Sample ID :
 Data Filename : LLC-3-40-4 ADH-10%.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 40min.lcm

Batch Filename : 20221007.lcb

Vial # : 1-32

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 1/3/2023 1:45:26 PM

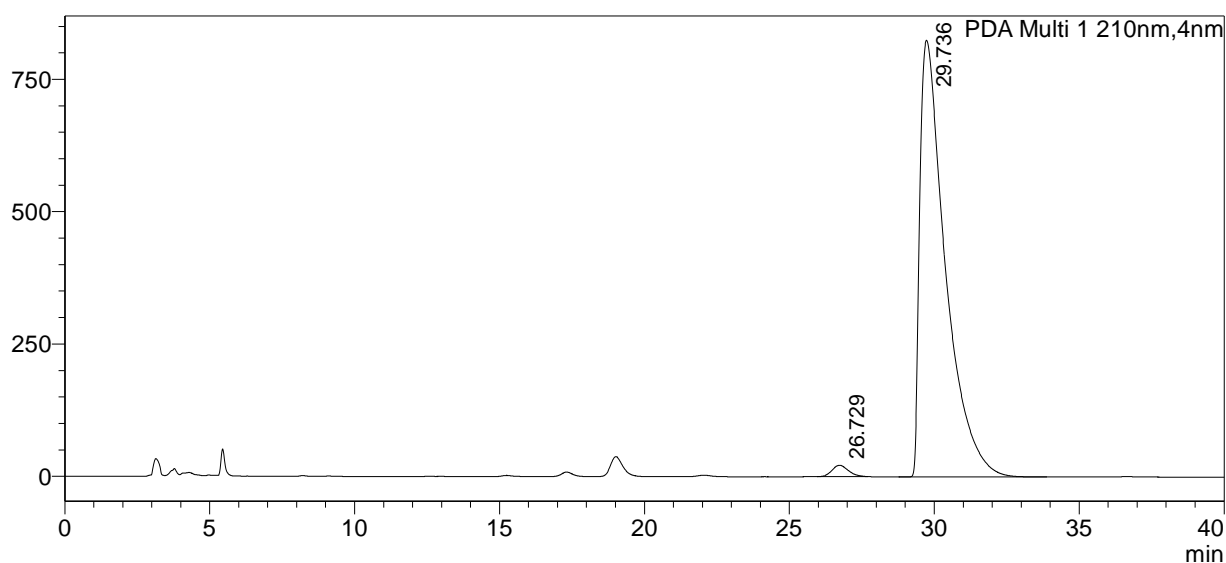
Acquired by : System Administrator

Date Processed : 1/3/2023 2:25:29 PM

Processed by : System Administrator

<Chromatogram>

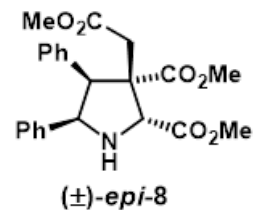
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	26.729	836079	21366	1.626			
2	29.736	50589539	824582	98.374			
Total		51425618	845948				



<Sample Information>

Sample Name : LLC-2-88-a ADH-10%
 Sample ID :
 Data Filename : LLC-2-88-a ADH-10%.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 60min.lcm

Batch Filename : 20221007.lcb

Vial # : 1-31

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 1/31/2023 10:07:24 AM

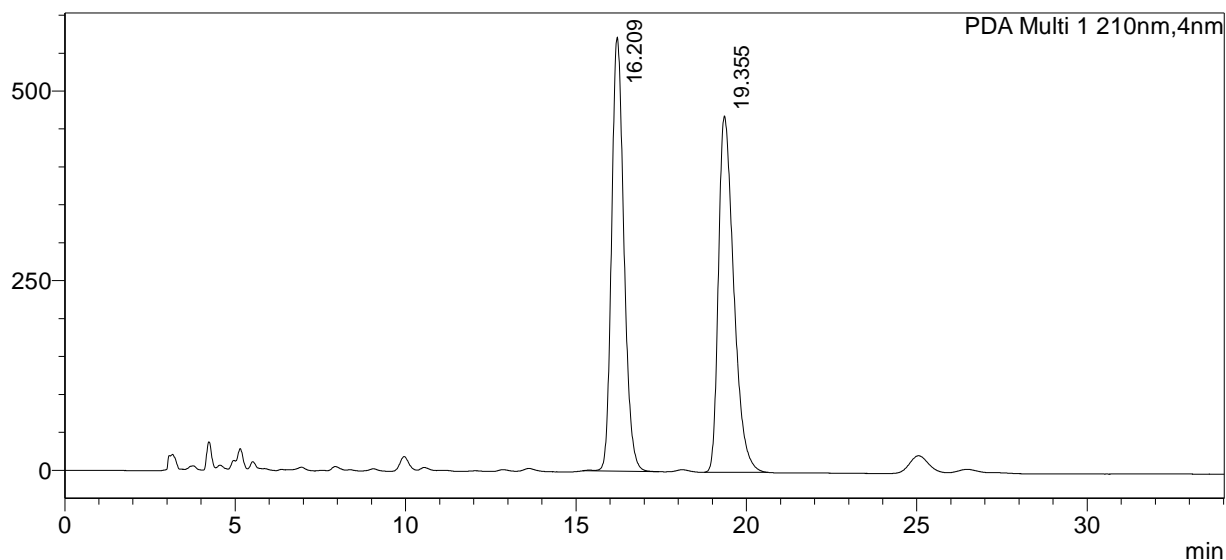
Acquired by : System Administrator

Date Processed : 1/31/2023 10:41:28 AM

Processed by : System Administrator

<Chromatogram>

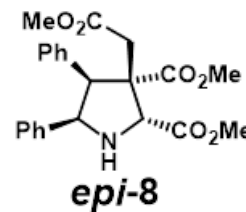
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.209	14410223	572086	49.583			
2	19.355	14652413	469640	50.417			
Total		29062635	1041727				



<Sample Information>

Sample Name : LLC-3-40-1-ap ADH-10%
 Sample ID :
 Data Filename : LLC-3-40-1-ap ADH-10%.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 40min.lcm

Batch Filename : 1.lcb

Vial # : 1-61

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 2/4/2023 6:49:35 PM

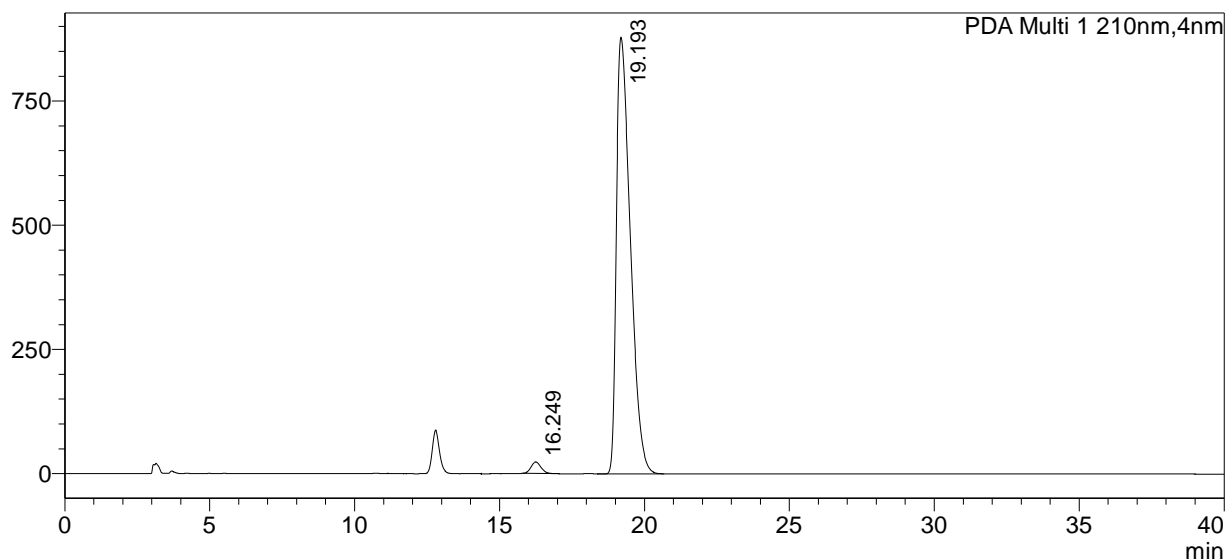
Acquired by : System Administrator

Date Processed : 2/4/2023 7:29:37 PM

Processed by : System Administrator

<Chromatogram>

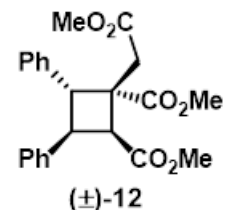
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.249	556426	23397	1.855			
2	19.193	29447624	878579	98.145			
Total		30004050	901976				



<Sample Information>

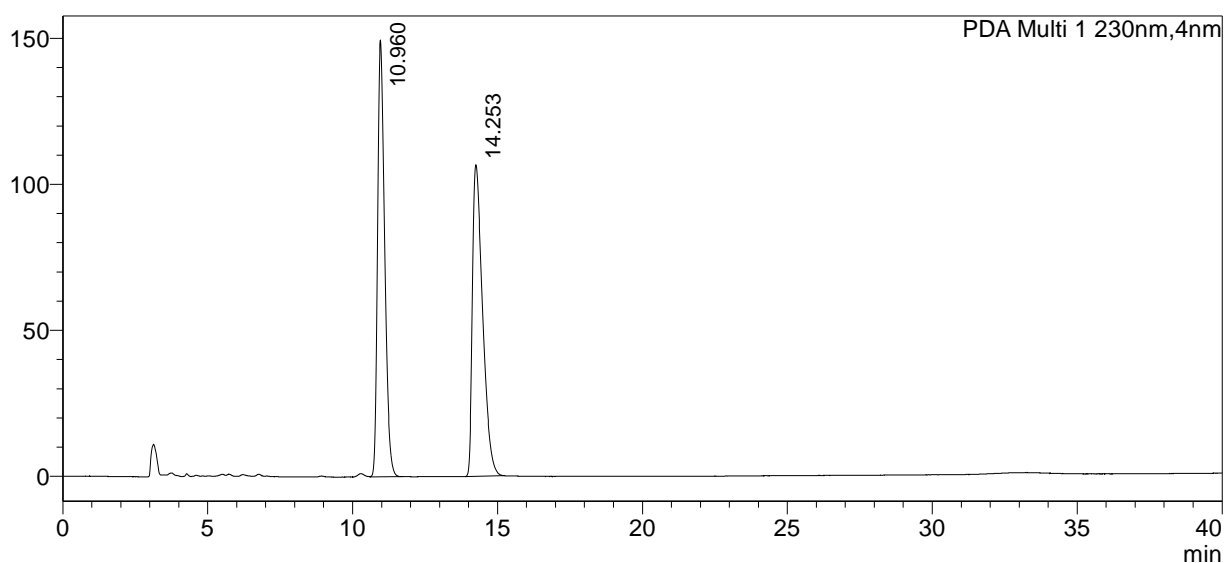
Sample Name : LLC-2-106-a ADH-10%2
 Sample ID :
 Data Filename : LLC-2-106-a ADH-10%2.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 40min.lcm
 Batch Filename : 20221007.lcb
 Vial # : 1-16
 Injection Volume : 10 uL
 Date Acquired : 1/11/2023 1:52:54 PM
 Date Processed : 1/11/2023 2:32:57 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

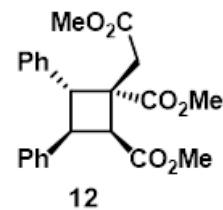
mAU



<Peak Table>

PDA Ch1 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.960	2561822	149401	49.534			
2	14.253	2610019	106702	50.466			
Total		5171841	256104				



<Sample Information>

Sample Name : LLC-3-45-ap1 ADH-10%
 Sample ID :
 Data Filename : LLC-3-45-ap1 ADH-10%.lcd

Method Filename : AD-H; 1 ml; 10%IPA in Hex; 30min.lcm

Batch Filename : 20221007.lcb

Vial # : 1-17

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 1/12/2023 8:07:53 PM

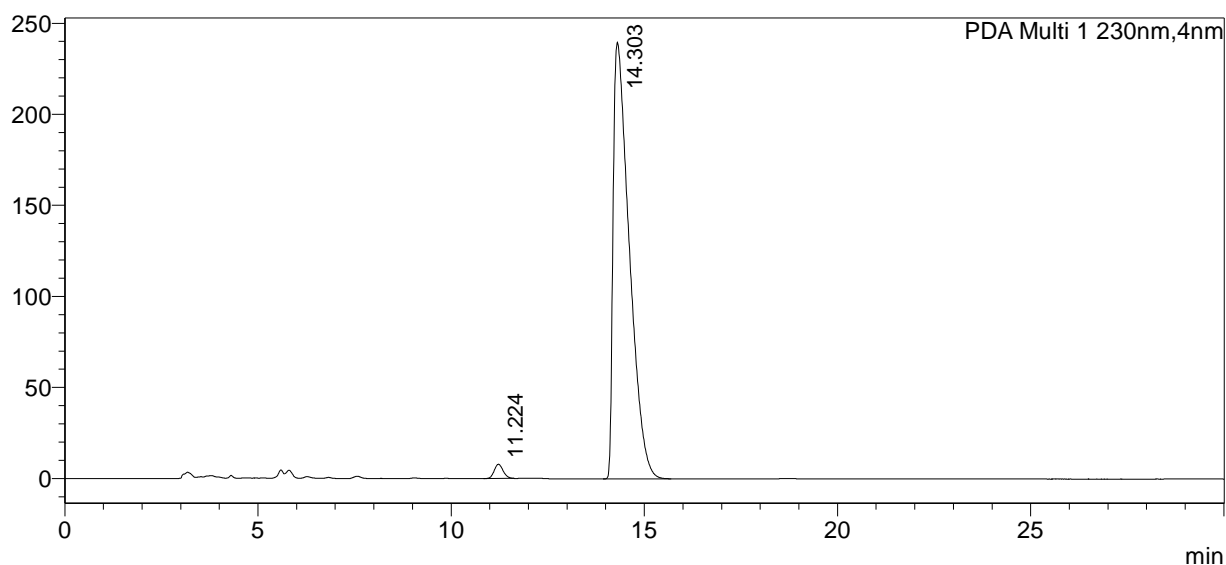
Acquired by : System Administrator

Date Processed : 1/12/2023 8:37:55 PM

Processed by : System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 230nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.224	124529	7814	1.753			
2	14.303	6980772	239705	98.247			
Total		7105301	247519				