Supplementary Materials for

Integrating hydroformylations into a methanol economy

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General Considerations

All chemicals were purchased from Sigma-Aldrich, Doug Discovery, Tokyo Chemical Industry (TCI), or Strem, and were used as received without further purification. Unless otherwise stated, all non-aqueous reactions were performed in either oven-dried or flame-dried apparatus under an atmosphere of argon. Solvents used in the argon-filled glovebox were dried according to standard procedures and degassed with argon.

Flash column chromatography (FCC) was conducted using silica gel (230-400 mesh particle size, 60 Å pore size) as the stationary phase. Automated flash column chromatography (AFCC) was conducted with Interchim PuriFlash XS520Plus with 30 µm prepacked columns.

NMR spectroscopy data were recorded on a Bruker 400 MHz Ascend spectrometer. Chemical shifts are reported in ppm relative to the solvent residual peak. NMR spectra are reported as: chemical shift (peak multiplicity; *J*-coupling constant(s) in Hz; integration). Peak multiplicities are abbreviated as: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, oct = octet, m = multiplet.

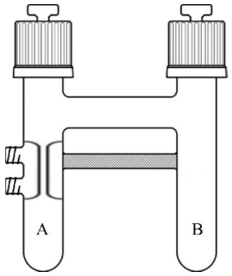
GC-MS spectra of solutions were recorded on an Agilent 8890 GC System equipped with Agilent5977B GC/MSD detector.

GC spectra of gases were recorded on an SRI 8610C Multiple Gas Analyzer #5 (MG#5) (TCD-FID-Methanizer) using a 0.5-meter Hayesep D pre-column and 1.5 meter Molesieve 5A column with argon as carrier gas at 90 °C.

HRMS spectral analysis was measured with a Bruker Maxis Impact Spectrometer using ESI.

Pressure measurements were performed using a Keller Druckmesstechnik Leo Record apparatus.

All hydroformylation reactions were performed in a modified two-chamber system composed of two glass cylinders (chambers A (refluxing chamber) and B (non-refluxing chamber)) connected with a glass bridge allowing for gas diffusion between the chambers. Chamber A contains a 3.0 cm long reflux condenser with an inner diameter of 3.2 mm and two outlets for connecting to a cooling system. Total volume = 22 mL. The chambers were sealed with screw caps and PTEF H-caps fitted with two O-rings (NBR70, 7.1 × 1.6 mm).

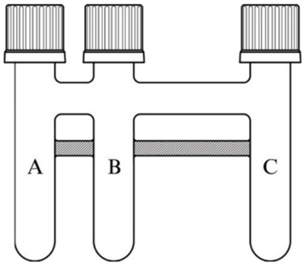


Glassware under pressure - Warning!

- Glass equipment should always be examined for damage to its surface, which may weaken its strength.
- One must abide by all laboratory safety procedures and always work behind a shield when working with glass equipment under pressure.
- COware® is pressure tested to 224 psi (15 bar). However, under no circumstances the COware® should be operated above 60 psi (5 bar).

Optimization reactions

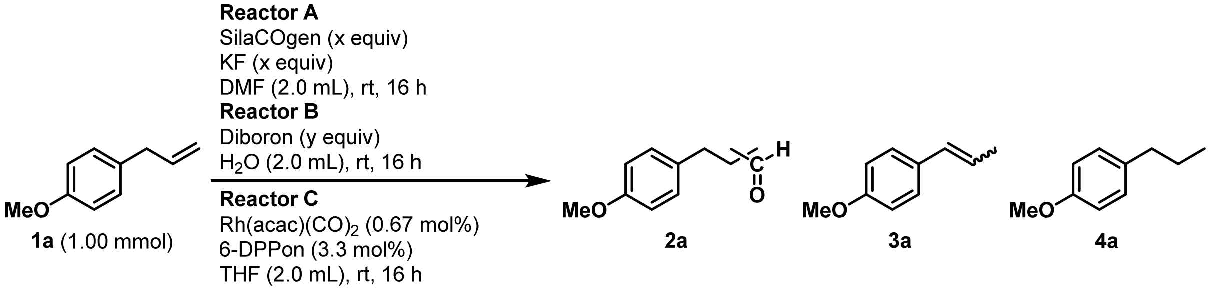
Selectivity of low-pressure hydroformylation



In an argon-filled glovebox, a fresh [Rh]-stock solution was prepared by Rh(acac)$(CO)_2$ (0.67 mol%) and 6-DPPon (3.3 mol%) in THF (0.3 mL/µmol catalyst). The catalyst solution was stirred for at least 5 minutes before use.

To a three-chamber reactor equipped with stir bars, reactor A (CO release) was charged with SilaCOgen (x equiv) and KF (x equiv). Reactor B (H_2 release) was charged with 2,2'-bi(1,3,6,2-dioxazaborocane) (Diboron) (y equiv). Reactor C was charged with estragole (154 µL, 1.00 mmol, 1.0 equiv) via Hamilton syringe and [Rh]-solution (2.0 mL) via syringe and the reactor was capped. At last, reactor B was added water (2 mL) via syringe and quickly the reactor immediately capped, followed by reactor A added DMF (2 mL) via syringe and the reactor immediately capped. The three-reactor was removed from the glovebox, placed in a heating block, and stirred (1000 rpm) for 16 h at room temperature. The hydroformylation reaction mixture was transferred to a round-bottomed flask using DCM, concentrated under reduced pressure, and the obtained crude mixture was analysed by ^{1}H-NMR spectroscopy using mesitylene as the internal standard (100 µL) added via Hamilton syringe.

Table S1. Selectivity of low-pressure hydroformylation. Presented yields of 2a are combined yields of the linear and branched aldehydes along linear-to-branched ratio (*l*:*b*). Presented yields of 3a are combined yields of E/Z-olefins.



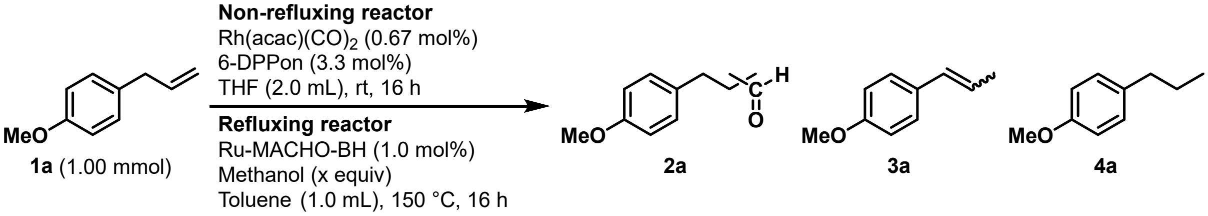
Entry	SilaCOgen/KF (x equiv) Diboron (y equiv)	Yield [%]			
		1a	**2a (*l*:*b*)**	**3a**	**4a**
1	0.00:3.00	-	-	12	89
2	0.75:3.00	-	71 (16:1)	6	26
3	1.50:3.00	5	94 (7:1)	2	Trace
4	2.25:3.00	17	81 (6:1)	3	Trace
5	3.00:3.00	35	66 (5:1)	2	Trace
6	3.00:2.25	32	67 (5:1)	Trace	Trace
7	3.00:1.50	41	62 (5:1)	Trace	Trace
8	3.00:0.75	52	49 (5:1)	Trace	Trace
9	3.00:0.00	100	-	-	-

Methanol concentration

In an argon-filled glovebox, fresh catalyst stock solutions were prepared; a [Ru]-solution of Ru-MACHO-BH (1.0 mol%) in toluene (0.1 mL/µmol catalyst), followed by a [Rh]-solution of $Rh(acac)(CO)_2$ (0.67 mol%) and 6-DPPon (3.3 mol%) in THF (0.3 mL/µmol catalyst). Both catalyst solutions were stirred for at least 5 minutes before use.

To a two-reactor system equipped with magnetic stir bars, the non-refluxing reactor was charged with estragole (154 µL, 1.00 mmol, 1.0 equiv) via Hamilton syringe and [Rh]-solution (2.0 mL) via syringe. The refluxing reactor was charged with [Ru]-solution (1.0 mL) via syringe and methanol (x equiv) via Hamilton syringe. Both reactors were sealed immediately, and the two-reactor system was removed from the glovebox. The refluxing reactor was placed in a heating block at room temperature and the condenser was connected to a water-cooling system (~ 8 °C). The condenser was allowed to cool for at least 5 minutes before heating the refluxing reactor to 150 °C while the non-refluxing reactor remained at room temperature. Both reactors were stirred vigorously (1000 rpm) for 16 h. The hydroformylation reaction mixture was transferred to a round-bottomed flask using DCM, concentrated under reduced pressure, and the obtained crude mixture was analysed by ^{1}H-NMR spectroscopy using mesitylene as the internal standard (100 µL) added via Hamilton syringe.

Table S2. Methanol concentration. Presented yields of 2a are combined yields of the linear and branched aldehydes along linear-to-branched ratio (*l*:*b*). Presented yields of 3a are combined yields of E/Z-olefins. Yield reported in brackets is isolated yield. [a]Without toluene as solvent in the refluxing reactor.



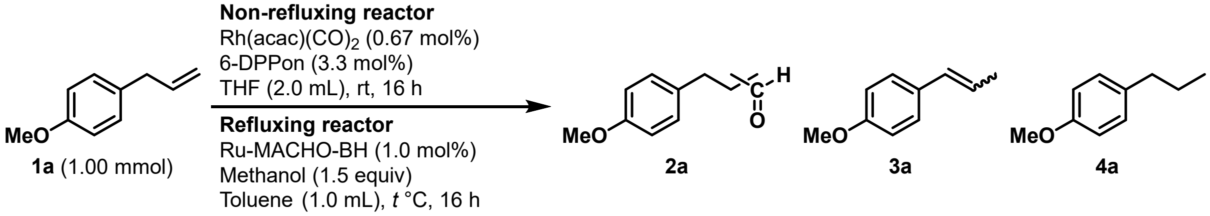
Entry	Methanol (x equiv)	Yield [%]			
		1a	2a (*l*:*b*)	3a	4a
1	20	-	14 (>20:1)	28	58
2	10	-	28 (>20:1)	32	39
3	10	13	42 (15:1)	12	34
4	5.0	5	62 (19:1)	19	15
5	2.5	7	89 (7:1)	3	Trace
6	2.0	4	95 (7:1)	Trace	Trace
7	1.5	-	98 [98] (9:1)	Trace	Trace
8	1.1	-	83 (>20:1)	7	10

Temperature

In an argon-filled glovebox, fresh catalyst stock solutions were prepared; a [Ru]-solution of Ru-MACHO-BH (1.0 mol%) in toluene (0.1 mL/µmol catalyst), followed by a [Rh]-solution of Rh(acac)(CO)$_2$ (0.67 mol%) and 6-DPPon (3.3 mol%) in THF (0.3 mL/µmol catalyst). Both catalyst solutions were stirred for at least 5 minutes before use.

To a two-reactor system equipped with magnetic stir bars, the non-refluxing reactor was charged with estragole (154 µL, 1.00 mmol, 1.0 equiv) via Hamilton syringe and [Rh]-solution (2.0 mL) via syringe. The refluxing reactor was charged with [Ru]-solution (1.0 mL) via syringe and methanol (61 µL, 1.5 mmol, 1.5 equiv equiv) via Hamilton syringe. Both reactors were sealed immediately, and the two-reactor system was removed from the glovebox. The refluxing reactor was placed in a heating block at room temperature and the condenser was connected to a water-cooling system (~ 8 °C). The condenser was allowed to cool for at least 5 minutes before heating the refluxing reactor to the stated temperature while the non-refluxing reactor remained at room temperature. Both reactors were stirred vigorously (1000 rpm) for 16 h. The hydroformylation reaction mixture was transferred to a round-bottomed flask using DCM, concentrated under reduced pressure, and the obtained crude mixture was analysed by ^{1}H-NMR spectroscopy using mesitylene as the internal standard (100 µL) added via Hamilton syringe.

Table S3. Temperature of refluxing reactor. Presented yields of 2a are combined yields of the linear and branched aldehydes along linear-to-branched ratio (*l*:*b*). Presented yields of 3a are combined yields of E/Z-olefins.



Entry	Temperature [°C]	Yield [%]			
		1a	**2a (*l*:*b*)**	**3a**	**4a**
1	170	Trace	97 (7:1)	2	Trace
2	150	Trace	98 [98] (9:1)	Trace	Trace
3	130	-	77 (>20:1)	9	12
4	110	28	39 (>20:1)	14	15

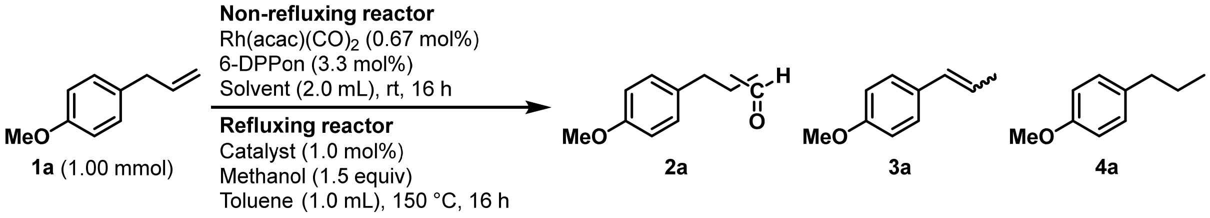
Hydroformylation solvent

In an argon-filled glovebox, fresh catalyst stock solutions were prepared; a [Ru]-solution of Ru-MACHO-BH (1.0 mol%) in toluene (0.1 mL/µmol catalyst), followed by a [Rh]-solution of Rh(acac)(CO)$_2$ (0.67 mol%) and 6-DPPon (3.3 mol%) in solvent (0.3 mL/µmol catalyst). Both catalyst solutions were stirred for at least 5 minutes before use.

To a two-reactor system equipped with magnetic stir bars, the non-refluxing reactor was charged with estragole (154 µL, 1.00 mmol, 1.0 equiv) via Hamilton syringe and [Rh]-solution (2.0 mL) via syringe. The refluxing reactor was charged with [Ru]-solution (1.0 mL) via syringe and methanol (61 µL, 1.5 mmol, 1.5 equiv) via Hamilton syringe. Both reactors were sealed immediately, and the two-reactor system was removed from the glovebox. The refluxing reactor was placed in a heating block at room temperature and the condenser was connected to a water-cooling system (~ 8 °C). The condenser was allowed to cool for at least 5 minutes before heating the refluxing reactor to 150 °C while the non-refluxing reactor remained at room temperature. Both reactors were stirred vigorously (1000 rpm) for 16 h. The hydroformylation reaction mixture was transferred to a round-bottomed flask using

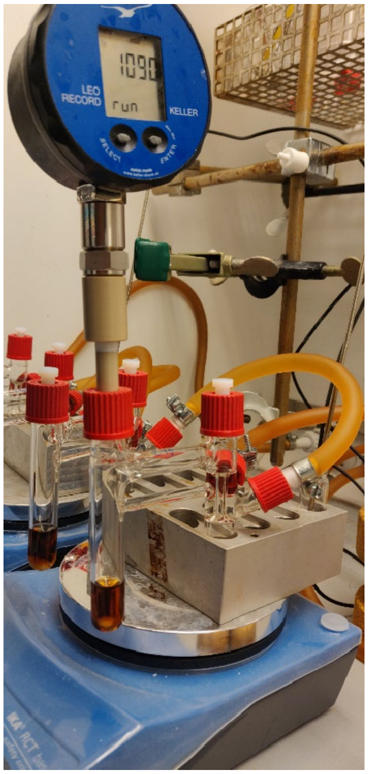
DCM, concentrated under reduced pressure, and the obtained crude mixture was analysed by ^{1}H-NMR spectroscopy using mesitylene as the internal standard (100 µL) added via Hamilton syringe.

Table S4. Hydroformylation solvent screening. Presented yields of 2a are combined yields of the linear and branched aldehydes along linear-to-branched ratio (*l*:*b*). Presented yields of 3a are combined yields of E/Z-olefins.



Entry	Solvent, solubility	Yield [%]			
		1a	**2a (*l*:*b*)**	**3a**	**4a**
1	THF, fully	-	98 [98] (9:1)	Trace	Trace
2	2-MeTHF, partially	Trace	96 (9:1)	3	Trace
3	Acetone, fully	25	75 (8:1)	Trace	Trace
4	MeOH, fully	Trace	91 (12:1)	3	Trace
5	PhMe, fully	17	79 (14:1)	3	Trace
6	CPME, fully	12	87 (14:1)	Trace	Trace
7	1,4-Dioxane	-	74 (>20:1)	11	15

Gas Pressure Studies



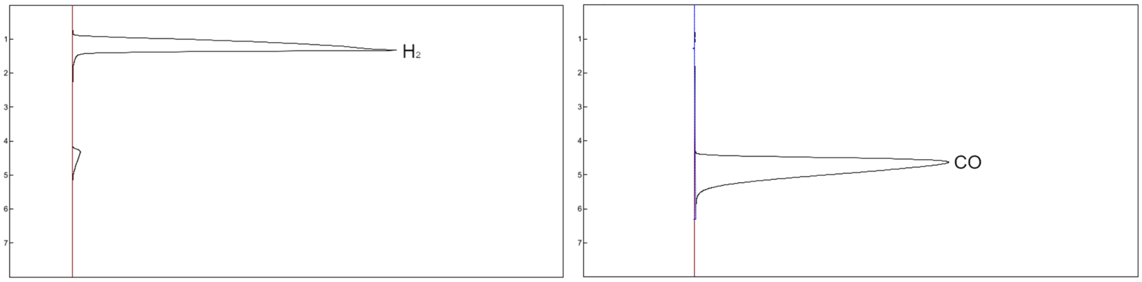
In an argon-filled glovebox, fresh catalyst stock solution was prepared; a [Ru]-solution of Ru-MACHO-BH (5.86 mg, 10 µmol) in toluene (1.0 mL), catalyst solution was stirred for at least 5 minutes before use.

To a two-reactor system equipped with magnetic stir bars, the non-refluxing reactor was charged with THF (2.0 mL) via syringe. The refluxing reactor was charged with [Ru]-solution (1.0 mL) via syringe and syngas surrogate (1.5 equiv). Immediately, the non-refluxing reactor was sealed with a Keller manometer and the refluxing reactor with an H-cap, and the two-reactor system was removed from the glovebox. The refluxing reactor was placed in a heating block at room temperature and the condenser was connected to a water-cooling system (~ 8 °C). The condenser was allowed to cool for at least 5 minutes before heating the refluxing reactor to 150 °C while the non-refluxing reactor remained at room temperature. Both reactors were stirred vigorously (1000 rpm) for 16 h. Data from the Keller manometer was extracted via KOLIBRI software and plotted in Excel.

Syngas composition measurements

In an argon-filled glovebox, fresh catalyst stock solution was prepared; a [Ru]-solution of Ru-MACHO-BH (5.86 mg, 10 µmol) in toluene (1.0 mL), catalyst solution was stirred for at least 5 minutes before use.

To a two-reactor system equipped with magnetic stir bars, the non-refluxing reactor was charged with THF (2.0 mL) via syringe. The refluxing reactor was charged with [Ru]-solution (1.0 mL) via syringe and syngas surrogate (1.5 equiv). Both reactors were sealed immediately using natural rubber stoppers (14.5/10.5 x 20 mm) allowing for gas-tight sampling, and the two-reactor system was removed from the glovebox. The refluxing reactor was placed in a heating block at room temperature and the condenser was connected to a water-cooling system (~ 8 °C). The condenser was allowed to cool for at least 5 minutes before heating the refluxing reactor to 150 °C while the non-refluxing reactor remained at room temperature. Both reactors were stirred vigorously (1000 rpm) for stated number of hours. The two-reactor was cooled to room temperature and gas samples measured by GC using gas-tight syringes.



Scheme S5. General example of FID and TCD measurements for methanol after 1 h of reaction time.

Dehydrogenation Catalyst Screening

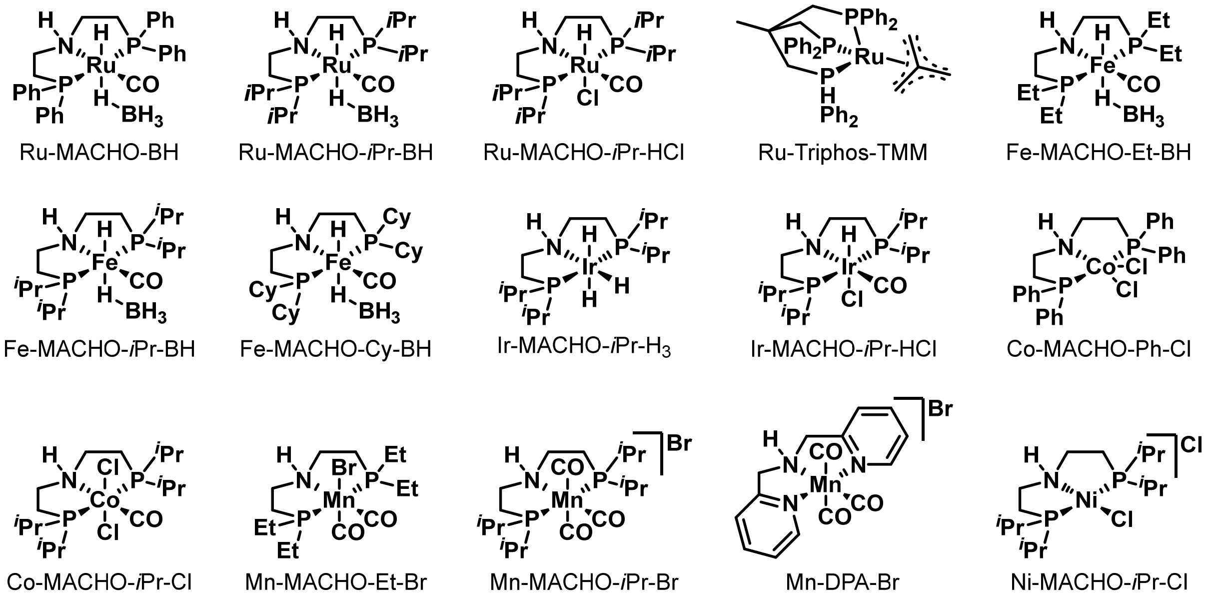
In an argon-filled glovebox, fresh catalyst stock solutions were prepared; a [M]-solution of catalyst (1.0 mol%) in toluene (0.1 mL/μmol catalyst), followed by a [Rh]-solution of $Rh(acac)(CO)_2$ (0.67 mol%) and 6-DPPon (3.3 mol%) in THF (0.3 mL/μmol catalyst). Both catalyst solutions were stirred for at least 5 minutes before use.

To a two-reactor system equipped with magnetic stir bars, the non-refluxing reactor was charged with estragole (154 μL, 1.00 mmol, 1.0 equiv) via Hamilton syringe and [Rh]-solution (2.0 mL) via syringe. The refluxing reactor was charged with [Ru]-solution (1.0 mL) via syringe and methanol (61 μL, 1.5 mmol, 1.5 equiv) via Hamilton syringe. Both reactors were sealed immediately, and the two-reactor system was removed from the glovebox. The refluxing reactor was placed in a heating block at room temperature and the condenser was connected to a water-cooling system (~ 8 °C). The condenser was allowed to cool for at least 5 minutes before heating the refluxing reactor to 150 °C while the non-refluxing reactor remained at room temperature. Both reactors were stirred vigorously (1000 rpm) for 16 h. The hydroformylation reaction mixture was transferred to a round-bottomed flask using DCM, concentrated under reduced pressure, and the obtained crude mixture was analysed by ^{1}H-NMR spectroscopy using mesitylene as the internal standard (100 μL) added via Hamilton syringe.

Table S6. Dehydrogenation catalyst screening. Presented yields of 2a are combined yields of the linear and branched aldehydes along linear-to-branched ratio (*l*:*b*). Presented yields of 3a are combined yields of E/Z-olefins. [a] Added *t*BuOK (2 mol%) as activator.

Entry	Catalyst	Yield [%]

		1a	**2a (*l*:*b*)**	**3a**	**4a**
1	Ru-MACHO-BH	-	98 [98] (9:1)	Trace	Trace
2	Ru-MACHO-*i*Pr-BH	-	97 (9:1)	Trace	Trace
3	Ru-MACHO-*i*Pr-HCl[a]	12	72 (>20:1)	7	9
4	Ru-Triphos-TMM	100	-	-	-
5	Fe-MACHO-Et-BH	6	Trace	47	47
6	Fe-MACHO-*i*Pr-BH	11	Trace	30	58
7	Fe-MACHO-Cy-BH	6	Trace	38	55
8	Ir-MACHO-*i*Pr-H_3	17	4 (>20:1)	33	46
9	Ir-MACHO-*i*Pr-HCl[a]	45	5 (>20:1)	43	7
10	Co-MACHO-Ph-Cl[a]	100	-	-	-
11	Co-MACHO-*i*Pr-Cl[a]	100	-	-	-
12	Mn-MACHO-Et-Br[a]	20	6 (>20:1)	29	45
13	Mn-MACHO-*i*Pr-Br[a]	4	71 (>20:1)	15	10
14	Mn-DPA-Br[a]	100	-	-	-
15	Ni-MACHO-*i*Pr-Cl[a]	100	-	-	-



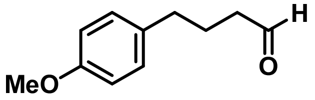
Scheme S7. Overview of dehydrogenation catalyst used in the screening.

General Procedure

In an argon-filled glovebox, fresh catalyst stock solutions were prepared; a [Ru]-solution of Ru-MACHO-BH (1.0 mol%) in toluene (0.1 mL/µmol catalyst), followed by a [Rh]-solution of Rh(acac)$(CO)_2$ (0.67 mol%) and 6-DPPon (3.3 mol%) in THF (0.3 mL/µmol catalyst). Both catalyst solutions were stirred for at least 5 minutes before use.

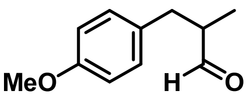
To a two-reactor system equipped with magnetic stir bars, the non-refluxing reactor was charged with estragole (154 µL, 1.00 mmol, 1.0 equiv) via Hamilton syringe and [Rh]-solution (2.0 mL) via syringe. The refluxing reactor was charged with [Ru]-solution (1.0 mL) via syringe and methanol (61 µL, 1.5 mmol, 1.5 equiv) via Hamilton syringe. Both reactors were sealed immediately, and the two-reactor system was removed from the glovebox. The refluxing reactor was placed in a heating block at room temperature and the condenser was connected to a water-cooling system (~ 8 °C). The condenser was allowed to cool for at least 5 minutes before heating the refluxing reactor to 150 °C while the non-refluxing reactor remained at room temperature. Both reactors were stirred vigorously (1000 rpm) for 16 h. The hydroformylation reaction mixture was transferred to a round-bottomed flask using DCM, concentrated under reduced pressure, and the obtained crude mixture was analysed by ^{1}H-NMR spectroscopy using mesitylene as the internal standard (100 µL) added via Hamilton syringe.

4-(4-Methoxyphenyl)butanal (Linear) and 3-(4-methoxyphenyl)-2-methylpropanal (Branched) (1)



Linear

and



Branched

The title compounds **1** were prepared using the General Procedure with estragole (148 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **1** as a colourless oil (173 mg, 0.972 mmol, 97%, *l*:*b* = 9:1).

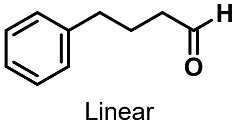
Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.75 (t, *J* = 1.6 Hz, 1.0H), 9.71 (d, *J* = 1.5 Hz, 0.1H), 7.10 – 7.08 (m, 2.2H), 6.85 – 6.82 (m, 2.2H), 3.79 (s, 3.3H), 3.02 (dd, *J* = 13.3, 5.6 Hz, 0.1H), 2.66 – 2.54 (m, 2.2H), 2.44 (td, *J* = 7.3, 1.7 Hz, 2.0H), 1.93 (quin, *J* = 7.3 Hz, 2.0H), 1.08 (d, *J* = 6.8 Hz, 0.3H).

Linear (major): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 202.4, 157.9, 133.2, 129.3, 113.8, 55.2, 43.1, 34.1, 23.9.

Branched (minor): ^{13}**C NMR** (101 MHz, CDCl$_3$) δ_C 204.6, 158.2, 130.7, 129.9, 113.9, 55.2, 48.2, 35.7, 13.1.

Linear and branched in accordance with literature.[1, 2]

4-Phenylbutanal (Linear) and 2-methyl-3-phenylpropanal (Branched) (2)



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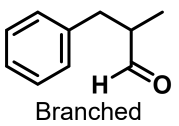


The title compounds **2** were prepared using the General Procedure with allylbenzene (118 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to pentane/DCM 1:1) afforded **2** as a colourless oil (144 mg, 0.970 mmol, 97%, *l*:*b* = 9:1).

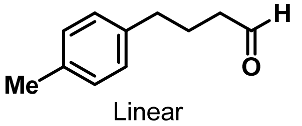
Linear (major) and Branched (minor): ^{1}**H NMR** (400 MHz, CDCl$_3$) δ_H 9.76 (t, *J* = 1.6 Hz, 0.9H), 9.73 (d, *J* = 1.5 Hz, 0.1H), 7.32 – 7.28 (m, 2.2H), 7.24 – 7.17 (m, 3.3H), 3.10 (dd, *J* = 13.3, 5.6 Hz, 0.1H), 2.73 – 2.58 (m, 2.3H), 2.46 (td, *J* = 7.3, 1.6 Hz, 2.0H), 1.97 (quin, *J* = 7.4 Hz, 2.0H), 1.10 (d, *J* = 6.8 Hz, 0.4H).

Linear (major): ^{13}**C NMR** (101 MHz, CDCl$_3$) δ_C 202.3, 141.3, 128.5, 128.5, 126.1, 43.2, 35.0, 23.7.

Branched (minor): ^{13}**C NMR** (101 MHz, CDCl$_3$) δ_C 204.4, 138.9, 129.1, 128.6, 126.4, 48.1, 36.7, 13.2.

Linear and branched in accordance with literature.[3, 4]

4-(4-Methylphenyl)butanal (Linear) and 3-(4-methylphenyl)-2-methylpropanal (Branched) (3)



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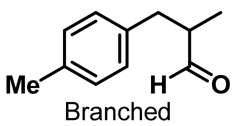


The title compounds **3** were prepared using the General Procedure with *p*-allyltoluene (132 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to pentane/DCM 1:1) afforded **3** as a colourless oil (159 mg, 0.982 mmol, 98%, *l*:*b* = 7:1).

Linear (major) and Branched (minor): ^{1}**H NMR** (400 MHz, CDCl$_3$) δ_H 9.76 (t, *J* = 1.7 Hz, 1.0H), 9.72 (d, *J* = 1.5 Hz, 0.1H), 7.12 – 7.06 (m, 4.6H), 3.05 (dd, *J* = 13.4, 5.7 Hz, 0.1H), 2.70 – 2.55 (m, 2.3H), 2.45 (td, *J* = 7.3, 1.7 Hz, 2.0H), 2.33 (s, 3.4H), 1.95 (quin, *J* = 7.4 Hz, 2.0H), 1.09 (d, *J* = 6.8 Hz, 0.4H).

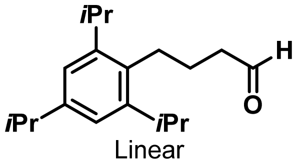
Linear (major): ^{13}**C NMR** (101 MHz, CDCl$_3$) δ_C 202.6, 138.2, 135.7, 129.3, 128.5, 43.3, 34.7, 23.9, 21.1.

Branched (minor): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 204.7, 136.1, 135.8, 129.3, 129.0, 48.3, 36.4, 21.1, 13.3.

HRMS (ESI$^+$) *m/z* calcd. for $C_{11}H_{14}ONa$ [M+Na]$^+$: 185.0937, found: 185.0931.

Linear in accordance with literature.[5]

4-(2,4,6-Triisopropylphenyl)butanal (Linear) (4)

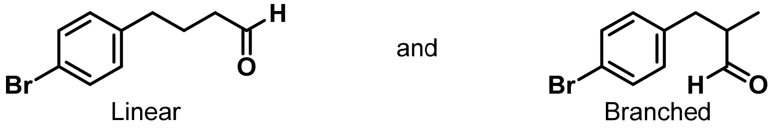


The title compound **4** was prepared using the General Procedure with 2-allyl-1,3-5-triisopropylbenzene (244 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to pentane/DCM 1:1) afforded **4** as a white solid (271 mg, 0.988 mmol, 99%, *l*:*b* = >20:1).

Linear (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.83 (t, *J* = 1.7 Hz, 1H), 6.98 (s, 2H), 3.15 (sept, *J* = 6.8 Hz, 2H), 2.86 (sept, *J* = 6.9 Hz, 1H), 2.69 – 2.64 (m, 2H), 2.58 (td, *J* = 7.1, 1.7 Hz, 2H), 1.84 – 1.76 (m, 2H), 1.25 (d, *J* = 6.9 Hz, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 202.4, 146.6, 146.6, 132.7, 121.1, 44.3, 34.2, 29.3, 27.3, 24.7, 24.4, 24.2.

Linear in accordance with literature.[6]

4-(4-Bromophenyl)butanal (Linear) and 3-(4-bromophenyl)-2-methylpropanal (Branched) (5)



The title compounds **5** were prepared using the General Procedure with *p*-bromoallylbenzene (197 mg, 1.00 mmol). Purification via FCC (pentane to pentane/DCM 1:1) afforded **5** as a colourless oil (224 mg, 0.987 mmol, 99%, *l*:*b* = 6:1).

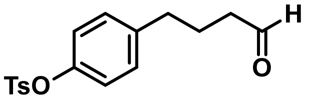
Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.76 (t, *J* = 1.5 Hz, 0.9H), 9.70 (d, *J* = 1.4 Hz, 0.1H), 7.42 – 7.39 (m, 2.3H), 7.06 – 7.04 (m, 2.3H), 3.04 (dd, *J* = 13.6, 5.8 Hz, 0.2H), 2.68 – 2.53 (m, 2.4H), 2.45 (td, *J* = 7.2, 1.5 Hz, 2.0H), 1.93 (quin, *J* = 7.4 Hz, 2.0H), 1.09 (d, *J* = 7.0 Hz, 0.5H).

Linear (major): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 202.1, 140.3, 131.6, 130.3, 120.0, 43.1, 34.5, 23.5.

Branched (minor): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 204.0, 138.0, 131.7, 130.9, 120.4, 48.0, 36.0, 13.3.

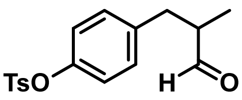
Linear and branched in accordance with literature.[7, 8]

4-(4-Phenyl tosylate)butanal (Linear) and 3-(4-phenyl tosylate)-2-methylpropanal (Branched) (6)



Linear

and



Branched

The title compounds **6** were prepared using the General Procedure with *p*-bromoallylbenzene (197 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **6** as a colourless oil (286 mg, 0.900 mmol, 90%, *l*:*b* = 8:1).

Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, CDCl$_3$) δ$_H$ 9.75 (t, *J* = 1.6 Hz, 1.0H), 9.68 (d, *J* = 1.4 Hz, 0.1H), 7.71 – 7.69 (m, 2.2H), 7.32 – 7.30 (m, 2.2H), 7.09 – 7.06 (m, 2.2H), 6.90 – 6.88 (m, 2.2H), 3.05 (dd, *J* = 13.4, 5.6 Hz, 0.1H), 2.65 – 2.55 (m, 2.3H), 2.50 – 2.42 (m, 5.4H), 1.91 (quin, *J* = 7.3 Hz, 2.0H), 1.06 (d, *J* = 6.8 Hz, 0.4H).

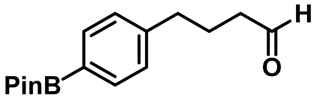
Linear (major): ^{13}C NMR (101 MHz, CDCl$_3$) δ$_C$ 202.0, 147.8, 145.4, 140.4, 132.3, 129.7, 129.5, 128.4, 122.2, 43.0, 34.3, 23.4, 21.7.

Branched (minor): ^{13}C NMR (101 MHz, CDCl$_3$) δ$_C$ 203.8, 148.1, 145.4, 138.0, 132.2, 130.1, 129.7, 129.5, 122.3, 47.7, 35.7, 21.7, 13.1.

HRMS (ESI$^+$) *m/z* calcd. for C$_{17}$H$_{18}$O$_4$SNa [M+Na]$^+$: 341.0818, found: 341.0821.

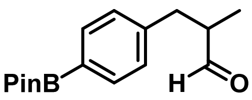
Linear in accordance with literature.[9]

4-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]butanal (Linear) and 3-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-2-methylpropanal (Branched) (7)



Linear

and



Branched

The title compounds **7** were prepared using the General Procedure with *p*-allylphenylboronic acid pinacol ester (244 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM/acetone 19:1) afforded **7** as a colourless oil (222 mg, 0.809 mmol, 81%, *l*:*b* = 6:1).

Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, CDCl$_3$) δ$_H$ 9.75 (t, *J* = 1.6 Hz, 1.0H), 9.71 (d, *J* = 1.4 Hz, 0.2H), 7.75 – 7.73 (m, 2.4H), 7.20 – 7.18 (m, 2.4H), 3.11 (dd, *J* = 13.2, 5.5 Hz, 0.2H), 2.71 – 2.57 (m, 2.4H), 2.44 (td, *J* = 7.3, 1.5 Hz, 2.0H), 1.96 (quin, *J* = 7.4 Hz, 2.0H), 1.34 (s, 14.4H), 1.07 (d, *J* = 6.8 Hz, 0.6H).

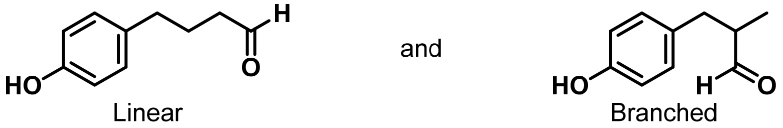
Linear (major): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 202.4, 144.7, 135.1, 128.1, 83.8, 43.2, 35.3, 25.0, 23.6.

Branched (minor): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 204.3, 142.3, 135.2, 128.6, 83.9, 48.1, 36.9, 25.0, 13.3.

GC-MS (EI) 274.1 ([M], 4%), 259.1 (9%), 231.1 (15%), 229.2 (28%), 215.1 (36%), 214.1 (10%), 157 (15%), 146 (12%), 145 (48%), 144.1 (95%), 131 (71%), 130 (77%), 129 (34%), 118 (14%), 117 (30%), 116 (10%), 103.9 (10%), 90.9 (11%), 85 (15%).

It was not possible to obtain useful HRMS or LCMS data, thus GC-MS was conducted instead.

4-(4-Hydroxyphenyl)butanal (Linear) and 3-(4-hydroxyphenyl)-2-methylpropanal (Branched) (8)



The title compounds **8** were prepared using the General Procedure with *p*-allylphenol (134 mg, 1.00 mmol). Purification via FCC (DCM to DCM/acetone 19:1) afforded **8** as a colourless oil (161 mg, 0.981 mmol, 98%, *l*:*b* = 9:1).

Linear (major) and Branched (minor): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.75 (t, *J* = 1.7 Hz, 1.0H), 9.70 (d, *J* = 1.6 Hz, 0.1H), 7.05 – 7.01 (m, 2.2H), 6.78 – 6.74 (m, 2.2H), 5.01 – 4.72 (m, 1.1H), 3.00 (dd, *J* = 13.4, 5.8 Hz, 0.1H), 2.66 – 2.55 (m, 2.2H), 2.45 (td, *J* = 7.3, 1.7 Hz, 2.0H), 1.92 (quin, *J* = 7.4 Hz, 2.0H), 1.08 (d, *J* = 6.8 Hz, 0.3H).

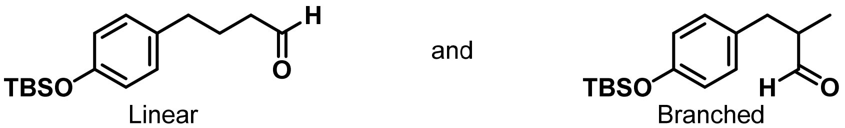
Linear (major): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 204.4, 154.1, 132.9, 129.5, 115.3, 43.0, 34.0, 23.8.

Branched (minor): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 206.4, 154.4, 130.2, 130.1, 115.4, 48.2, 35.7, 13.0.

HRMS (ESI^+) *m/z* calcd. for $C_{10}H_{13}O_2$ $[M+H]^+$: 165.0910, found: 165.0913.

Linear in accordance with literature.[10]

4-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)butanal (Linear) and 3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-2-methylpropanal (Branched) (9)



The title compounds **9** were prepared using the General Procedure with *p*-allylphenoxy(*tert*-butyl)dimethylsilane (248 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to pentane/DCM 1:1) afforded **9** as a colourless oil (267 mg, 0.959 mmol, 96%, *l*:*b* = 8:1).

Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.75 (t, *J* = 1.7 Hz, 1.0H), 9.71 (d, *J* = 1.5 Hz, 0.1H), 7.03 – 7.00 (m, 2.2H), 6.77 – 6.74 (m, 2.2H), 3.01 (dd, *J* = 13.5, 5.8 Hz, 0.1H), 2.65 – 2.52 (m, 2.2H), 2.43 (td, *J* = 7.3, 1.7 Hz, 2.0H), 1.92 (quin, *J* = 7.5 Hz, 2.0H), 1.07 (d, *J* = 6.8 Hz, 0.4H), 0.98 (s, 10.1H), 0.18 (s, 6.7H).

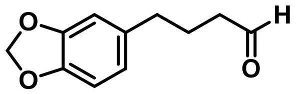
Linear (major): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 202.6, 154.0, 134.0, 129.4, 120.1, 43.3, 34.3, 25.8, 24.0, 18.3, -4.3.

Branched (minor): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 204.8, 154.3, 131.5, 130.0, 120.2, 48.3, 36.1, 25.8, 18.3, 13.3, -4.3.

HRMS (ESI$^+$) *m/z* calcd. for $C_{16}H_{27}O_2Si$ $[M+H]^+$: 279.1775, found: 279.1777.

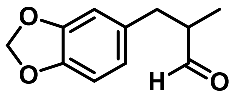
Linear in accordance with literature.[11]

4-(3,4-Methylenedioxyphenyl)butanal (Linear) and 2-methyl-3-(3,4-methylenedioxyphenyl)propanal (Branched) (10)



Linear

and



Branched

The title compounds **10** were prepared using the General Procedure with safrole (162 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **10** as a colourless oil (189 mg, 0.982 mmol, 98%, *l*:*b* = 7:1).

Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.75 (t, *J* = 1.6 Hz, 1.0H), 9.70 (d, *J* = 1.6 Hz, 0.1H), 6.75 – 6.71 (m, 1.1H), 6.67 – 6.65 (m, 1.1H), 6.62 – 6.60 (m, 1.1H), 5.93 – 5.92 (m, 2.3H), 2.99 (dd, *J* = 13.5, 5.8 Hz, 0.1H), 2.64 – 2.51 (m, 2.3H), 2.44 (td, *J* = 7.3, 1.6 Hz, 2.0H), 1.91 (quin, *J* = 7.4 Hz, 2.0H), 1.08 (d, *J* = 6.9 Hz, 0.4H).

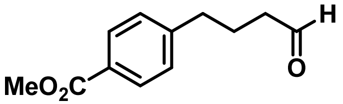
Linear (major): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 202.2, 147.7, 145.8, 135.0, 121.2, 108.8, 108.1, 100.8, 43.0, 34.7, 23.8.

Branched (minor): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 204.3, 147.7, 146.1, 132.5, 121.9, 109.3, 108.2, 100.9, 48.2, 36.3, 13.1.

HRMS (ESI$^+$) *m/z* calcd. for $C_{11}H_{13}O_3$ $[M+H]^+$: 193.0859, found: 193.0845.

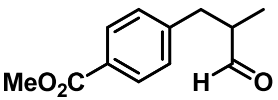
Linear and branched in accordance with literature.[12, 13]

4-(4-Carbomethoxyphenyl)butanal (Linear) and 2-methyl-3-(4-carbomethoxyphenyl)propanal (Branched) (11)



Linear

and



Branched

The title compounds **11** were prepared using the General Procedure with methyl 4-allylbenzoate (176 mg, 1.00 mmol). Purification via FCC (pentane/DCM 3:1 to DCM/acetone 19:1) afforded **11** as a colourless oil (204 mg, 0.991 mmol, 99%, *l*:*b* = 5:1).

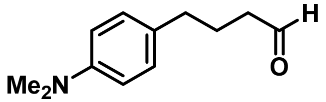
Linear (major) and Branched (minor): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.76 (t, *J* = 1.5 Hz, 1.0H), 9.71 (d, *J* = 1.3 Hz, 0.2H), 7.97 – 7.95 (m, 2.4H), 7.25 – 7.23 (m, 2.4H), 3.90 (s, 3.6H), 3.15 (dd, *J* = 12.9, 5.2 Hz, 0.2H), 2.73 – 2.61 (m, 2.4H), 2.46 (td, *J* = 7.3, 1.5 Hz, 2.0H), 1.97 (quin, *J* = 7.4 Hz, 2.0H), 1.09 (d, *J* = 6.8 Hz, 0.6H).

Linear (major): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 201.7, 166.8, 146.7, 129.6, 128.4, 128.0, 51.8, 42.9, 34.8, 23.1.

Branched (minor): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 203.5, 166.7, 144.4, 129.6, 128.9, 128.3, 51.9, 47.5, 36.3, 13.0.

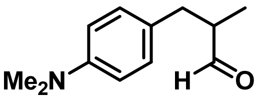
Linear and branched in accordance with literature.[14, 15]

4-(4-Dimethylaminophenyl)butanal (Linear) and 3-(4-dimethylaminophenyl)-2-methylpropanal (Branched) (12)



Linear

and



Branched

The title compounds **12** were prepared using the General Procedure with *p*-allyl-*N*,*N*-dimethylaniline (161 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM/acetone 19:1) afforded **12** as a colourless oil (185 mg, 0.968 mmol, 97%, *l*:*b* = 12:1).

Linear (major) and Branched (minor): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.77 (t, *J* = 1.8 Hz, 1.0H), 9.75 (d, *J* = 1.7 Hz, 0.1H), 7.10 – 7.05 (m, 2.2H), 6.75 – 6.71 (m, 2.2H), 2.95 (s, 6.4H), 2.68 – 2.52 (m, 2.2H), 2.47 (td, *J* = 7.3, 1.7 Hz, 2.0H), 1.95 (quin, *J* = 7.4 Hz, 2.0H), 1.11 (d, *J* = 6.8 Hz, 0.2H).

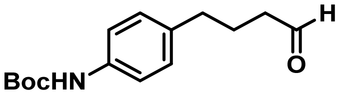
Linear (major): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 202.8, 149.3, 129.3, 129.2, 113.1, 43.3, 41.0, 34.1, 24.1.

Branched (minor): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 205.2, 149.4, 129.8, 126.7, 113.0, 48.5, 40.9, 35.9, 13.3.

HRMS (ESI$^+$) *m/z* calcd. for $C_{12}H_{18}NO$ [M+H]$^+$: 192.1383, found: 192.1387.

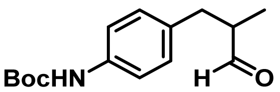
Branched in accordance with literature.[16]

tert-Butyl (4-(4-oxobutyl)phenyl)carbamate (Linear) and *tert*-butyl (4-(2-methyl-3-oxopropyl)phenyl)carbamate (Branched) (13)



Linear

and



Branched

The title compounds **13** were prepared using the General Procedure with *tert*-butyl 4-allylphenylcarbamate (233 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM/acetone 19:1) afforded **13** as a colourless oil (257 mg, 0.974 mmol, 97%, *l*:*b* = 12:1).

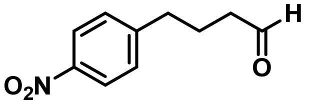
Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.74 (t, *J* = 1.6 Hz, 1.0H), 9.70 (d, *J* = 1.5 Hz, 0.1H), 7.29 – 7.26 (m, 2.2H), 7.10 – 7.08 (m, 2.2H), 6.44 (bs, 1.1H), 3.03 (dd, *J* = 13.4, 5.7 Hz, 0.1H), 2.65 – 2.56 (m, 2.2H), 2.43 (td, *J* = 7.3, 1.6 Hz, 2.0H), 1.92 (quin, *J* = 7.4 Hz, 2.0H), 1.51 (s, 10.1H), 1.07 (d, *J* = 6.8 Hz, 0.4H).

Linear (major): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 202.5, 153.0, 136.5, 135.5, 128.7, 118.7, 80.0, 42.9, 34.1, 28.2, 23.5.

Branched (minor): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 204.6, 153.0, 136.8, 133.0, 129.3, 118.7, 80.0, 47.9, 35.8, 28.2, 12.9.

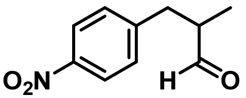
HRMS (ESI$^+$) *m/z* calcd. for $C_{15}H_{21}NO_3Na$ [M+Na]$^+$: 286.1414, found: 286.1417.

4-(4-Nitrophenyl)butanal (Linear) and 3-(4-nitrophenyl)-2-methylpropanal (Branched) (14)



Linear

and



Branched

The title compounds **14** were prepared using the General Procedure with *p*-allylnitrobenzene (163 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **14** as a pale yellow oil (184 mg, 0.950 mmol, 95%, *l*:*b* = 4:1).

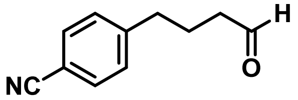
Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.79 (t, *J* = 1.3 Hz, 1.0H), 9.71 (d, *J* = 1.1 Hz, 0.2H), 8.16 – 8.14 (m, 2.5H), 7.35 – 7.33 (m, 2.5H), 3.24 – 3.17 (m, 0.2H), 2.78 – 2.67 (m, 2.5H), 2.51 (td, *J* = 7.1, 1.3 Hz, 2.0H), 1.99 (quin, *J* = 7.2 Hz, 2.0H), 1.13 (d, *J* = 6.9 Hz, 0.7H).

Linear (major): ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 201.6, 149.3, 146.2, 129.1, 123.5, 42.7, 34.6, 22.9.

Branched (minor): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 203.1, 147.0, 146.4, 129.8, 123.4, 47.4, 35.9, 13.1.

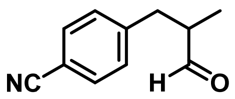
Linear and branched in accordance with literature.[17, 18]

4-(4-Cyanophenyl)butanal (Linear) and 3-(4-cyanophenyl)-2-methylpropanal (Branched) (15)



Linear

and



Branched

The title compounds **15** were prepared using the General Procedure with *p*-allylbenzonitrile (143 mg, 1.00 mmol). Purification via FCC (pentane/DCM 3:1 to DCM) afforded **15** as a colourless oil (166 mg, 0.958 mmol, 96%, *l*:*b* = 5:1).

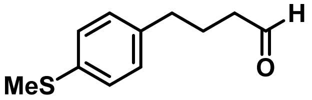
Linear (major) and Branched (minor): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.78 (t, *J* = 1.5 Hz, 1.0H), 9.70 (d, *J* = 1.2 Hz, 0.2H), 7.59 – 7.57 (m, 2.3H), 7.29 – 7.27 (m, 2.3H), 3.15 (dd, *J* = 12.9, 5.3 Hz, 0.2H), 2.73 – 2.62 (m, 2.3H), 2.49 (td, *J* = 7.2, 1.4 Hz, 2.0H), 1.96 (quin, *J* = 7.3 Hz, 2.0H), 1.11 (d, *J* = 6.8 Hz, 0.5H).

Linear (major): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 201.6, 147.1, 132.4, 129.3, 119.1, 110.2, 43.0, 35.2, 23.2.

Branched (minor): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 203.2, 144.8, 132.4, 130.0, 118.9, 110.2, 47.7, 36.5, 13.4.

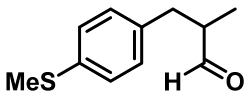
Linear and branched in accordance with literature.[9, 19]

4-(4-Methylsufanylphenyl)butanal (Linear) and 3-(4-methylsufanylphenyl)-2-methylpropanal (Branched) (16)



Linear

and



Branched

The title compounds **16** were prepared using the General Procedure with *p*-allylthioanisole (164 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **16** as a colourless oil (178 mg, 0.917 mmol, 92%, *l*:*b* = 8:1).

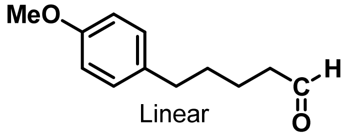
Linear (major) and Branched (minor): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.76 (t, *J* = 1.6 Hz, 1.0H), 9.71 (d, *J* = 1.5 Hz, 0.1H), 7.21 – 7.19 (m, 2.3H), 7.11 – 7.08 (m, 2.3H), 3.04 (dd, *J* = 13.4, 5.7 Hz, 0.1H), 2.68 – 2.54 (m, 2.3H), 2.47 – 2.42 (m, 5.4H), 1.93 (quin, *J* = 7.4 Hz, 2.0H), 1.08 (d, *J* = 7.0 Hz, 0.4H).

Linear (major): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 202.3, 138.4, 135.9, 129.1, 127.3, 43.2, 34.6, 23.7, 16.4.

Branched (minor): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 204.4, 136.3, 135.9, 129.7, 127.1, 48.1, 36.2, 16.2, 13.3.

HRMS (ESI$^+$) *m/z* calcd. for $C_{11}H_{15}OS$ $[M+H]^+$: 195.0838, found: 195.0833.

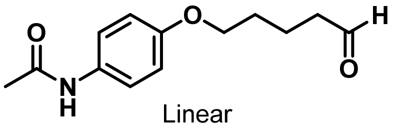
5-(4-Methoxyphenyl)pentanal (Linear) (17)



The title compound **17** was prepared using the General Procedure with 4-(*p*-methoxyphenyl)but-1-ene (162 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **17** as a colourless oil (187 mg, 0.972 mmol, 93%, *l*:*b* = >20:1).

Linear (major): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.75 (t, *J* = 1.8 Hz, 1H), 7.10 – 7.07 (m, 2H), 6.84 – 6.81 (m, 2H), 3.79 (s, 3H), 2.58 (t, *J* = 7.1 Hz, 2H), 2.44 (td, *J* = 7.1, 1.8 Hz, 2H), 1.70 – 1.58 (m, 4H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 202.7, 157.9, 134.1, 129.4, 113.9, 55.4, 43.9, 34.8, 31.2, 21.7. Linear in accordance with literature.[20]

N-(4-((5-Oxopentyl)oxy)phenyl)acetamide (Linear) (18)

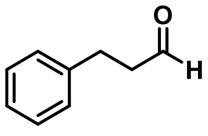


The title compound **18** was prepared using the General Procedure with *N*-(4-(but-3-en-1-yloxy)phenyl)acetamide (205 mg, 1.00 mmol). Purification via FCC (DCM to DCM/Acetone 6:1) afforded **18** as a white solid (220 mg, 0.935 mmol, 94%, *l*:*b* = >20:1).

Linear (major): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.79 (t, *J* = 1.6 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.14 (bs, 1H), 6.85 – 6.81 (m, 2H), 3.96 – 3.93 (m, 2H), 2.54 – 2.51 (m, 2H), 2.15 (s, 3H), 1.84 – 1.80 (m, 4H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 202.4, 168.3, 155.9, 131.1, 122.0, 114.9, 67.7, 43.6, 28.8, 24.5, 18.9.

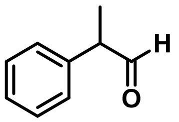
HRMS (ESI$^+$) *m/z* calcd. for $C_{13}H_{17}NO_3Na$ $[M+Na]^+$: 258.1101, found: 258.1105.

3-Phenylpropanal (Linear) and 2-phenylpropanal (Branched) (19)



Linear

and



Branched

The title compounds **19** were prepared using the General Procedure with styrene (104 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **19** as a colourless oil (107 mg, 0.797 mmol, 80%, *l*:*b* = 1:3).

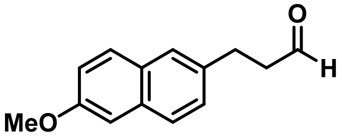
Linear (minor) and Branched (major): ^{1}H NMR (400 MHz, CDCl$_3$) δ_H 9.83 (t, *J* = 1.4 Hz, 0.3H), 9.69 (d, *J* = 1.5 Hz, 1.0H), 7.41 – 7.28 (m, 3.6H), 7.23 – 7.19 (m, 2.9H), 3.64 (dq, *J* = 7.1, 1.4 Hz, 1.0H), 2.97 (t, *J* = 7.6 Hz, 0.6H), 2.81 – 2.77 (m, 0.6H), 1.45 (d, *J* = 7.1 Hz, 3.0H).

Linear (minor): ^{13}C NMR (101 MHz, CDCl$_3$) δ_C 201.7, 140.4, 128.7, 128.4, 126.4, 45.4, 28.2.

Branched (major): ^{13}C NMR (101 MHz, CDCl$_3$) δ_C 201.3, 137.8, 129.2, 128.4, 127.7, 53.1, 14.7.

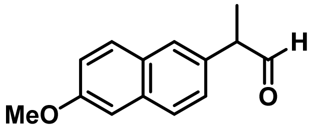
Linear and branched in accordance with literature.[21, 22]

3-(6-Methoxynaphthalen-2-yl)propanal (Linear) and 2-(6-methoxynaphthalen-2-yl)propanal (Branched) (20)



Linear

and



Branched

The title compounds **20** were prepared using the General Procedure with 2-methoxy-6-vinylnapthalene (184 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to pentane/DCM 1:1) afforded **20** as a white solid (198 mg, 0.926 mmol, 93%, *l*:*b* = 1:3).

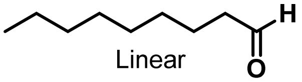
Linear (minor) and Branched (major): ^{1}H NMR (400 MHz, CDCl$_3$) δ_H 9.86 (t, *J* = 1.5 Hz, 0.3H), 9.75 (d, *J* = 1.4 Hz, 1.0H), 7.76 (d, *J* = 8.5 Hz, 1.0H), 7.72 (d, *J* = 8.9 Hz, 1.0H), 7.69 – 7.66 (m, 0.6H), 7.60 (bs, 1.0H), 7.56 (bs, 0.3H), 7.30 – 7.27 (m, 1.3H), 7.18 – 7.11 (m, 2.6H), 3.93 (s, 3.0H), 3.91 (s, 0.9H), 3.77 (qd, *J* = 7.1, 1.4 Hz, 1.0H), 3.09 (t, *J* = 7.5 Hz, 0.6H), 2.86 (td, *J* = 7.5, 1.4 Hz, 0.6H), 1.52 (d, *J* = 7.1 Hz, 3.0H).

Linear (minor): ^{13}C NMR (101 MHz, CDCl$_3$) δ_C 201.8, 157.5, 135.6, 133.3, 129.2, 129.1, 127.5, 127.3, 126.4, 119.1, 105.8, 55.4, 45.4, 28.2.

Branched (major): ^{13}C NMR (101 MHz, CDCl$_3$) δ_C 201.3, 158.0, 134.0, 132.8, 129.3, 129.3, 127.8, 127.2, 126.9, 119.5, 105.7, 55.5, 53.1, 14.8.

Linear and branched in accordance with literature.[23, 24]

Nonanal (Linear) (21)

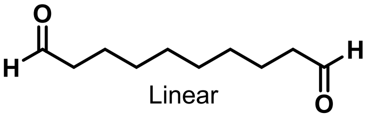


The title compound **21** was prepared using the General Procedure with 1-octene (112 mg, 1.00 mmol). Purification via FCC (pentane/DCM 9:1 to pentane/DCM 1:1) afforded **21** as a colourless oil (123.8 mg, 0.870 mmol, 87%, *l*:*b* = >20:1).

Linear (major): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.75 (t, *J* = 1.9 Hz, 1H), 2.41 (td, *J* = 7.4, 1.9 Hz, 2H), 1.61 (quin, *J* = 7.3 Hz, 2H), 1.32 – 1.24 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 203.1, 44.0, 31.9, 29.4, 29.3, 29.2, 22.8, 22.2, 14.2.

Linear in accordance with literature.[25]

Decanedial (Linear) (22)

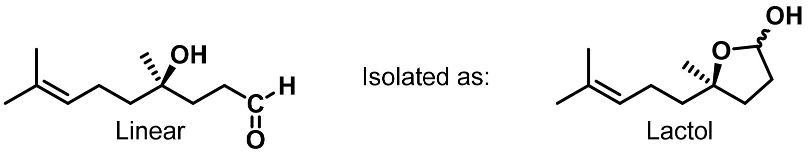


The title compound **22** was prepared using the General Procedure with 1,7-octadiene (55.1 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **22** as a colourless oil (81.3 mg, 0.478 mmol, 96%, *l*:*b* = >20:1).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.76 (t, *J* = 1.8 Hz, 2H), 2.42 (td, *J* = 7.3, 1.8 Hz, 4H), 1.65 – 1.58 (m, 4H), 1.33 – 1.30 (m, 8H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 202.7, 43.7, 28.9, 28.9, 21.8.

Linear in accordance with literature.[26]

(*R*)-4-Hydroxy-4,8-dimethylnon-7-enal (Linear) isolated as (5*R*)-5-methyl-5-(4-methylpent-3-en-1-yl)tetrahydrofuran-2-ol (Lactol) (23)

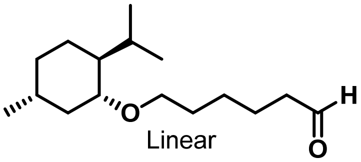


The title compound **23** was prepared using the General Procedure with L-linalool (154 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **23** as a colourless oil (183 mg, 0.993 mmol, 99%, *l*:*b* = >20:1).

Linear/Lactol (major): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 5.51 – 5.48 (m, 1H), 5.13 – 5.06 (m, 1H), 3.37 – 3.36 (m, 0.5H), 3.18 – 3.18 (m, 0.5H), 2.12 – 1.64 (m, 10H), 1.61 – 1.59 (m, 3H), 1.52 – 1.40 (m, 1H), 1.38 (s, 1.5H), 1.15 (s, 1.5H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 131.5, 131.3, 124.5, 124.4, 98.6, 98.2, 85.2, 84.8, 43.0, 41.7, 34.7, 34.5, 33.7, 33.2, 28.2, 25.7, 25.7, 23.8, 23.3, 17.7, 17.6.

Linear in accordance with literature.[27]

6-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)hexanal (Linear) (24)

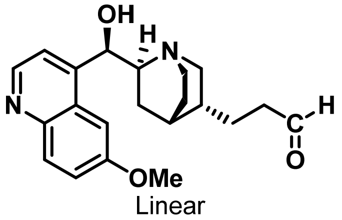


The title compound **24** was prepared using the General Procedure with (1*S*,2*R*,4*R*)-1-isopropyl-4-methyl-2-(pent-4-en-1-yloxy)cyclohexane (224 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM) afforded **24** as a colourless oil (240 mg, 0.944 mmol, 94%, *l*:*b* = >20:1).

Linear (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.76 (t, *J* = 1.8 Hz, 1H), 3.61 (dt, *J* = 9.0, 6.1 Hz, 1H), 3.25 (dt, *J* = 9.1, 6.6 Hz, 1H), 2.97 (dt, *J* = 10.6, 4.2 Hz, 1H), 2.43 (dt, *J* = 7.4, 1.8 Hz, 2H), 2.18 (septd, *J* = 7.0, 2.6 Hz, 1H), 2.09 – 2-04 (m, 1H), 1.68 – 1.50 (m, 6H), 1.44 – 1.27 (m, 3H), 1.23 – 1.16 (m, 1H), 1.00 – 0.80 (m, 9H), 0.75 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 202.4, 79.1, 68.0, 48.3, 43.8, 40.4, 34.6, 31.5, 30.0, 25.9, 25.6, 23.3, 22.3, 21.9, 20.9, 16.2.

HRMS (ESI$^+$) *m/z* calcd. for $C_{16}H_{31}O_2$ $[M+H]^+$: 255.2319, found: 255.2316.

10,11-Dihydroquinine-11-carbaldehyde (Linear) (25)

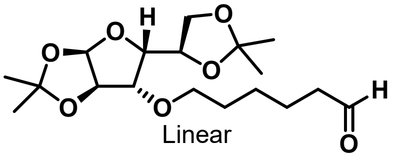


The title compound **25** was prepared using the General Procedure with quinine (324 mg, 1.00 mmol). Purification via FCC (Al_2O_3, DCM to DCM/MeOH 97:3) afforded **25** as a white solid (299.6 mg, 0.850 mmol, 85%, *l*:*b* = >20:1).

Linear (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.71 (t, *J* = 1.6 Hz, 1H), 8.66 (d, *J* = 4.5 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.49 (d, *J* = 4.5 Hz, 1H), 7.33 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.23 (d, *J* = 2.7 Hz, 1H), 5.51 (d, *J* = 4.3 Hz, 1H), 3.89 (s, 3H), 3.47 – 3.38 (m, 1H), 3.32 (bs, 1H), 3.12 – 3.03 (m, 2H), 2.65 – 2.59 (m, 1H), 2.38 – 2.34 (m, 3H), 1.78 – 1.70 (m, 3H), 1.59 – 1.44 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 202.3, 157.8, 148.2, 147.5, 144.1, 131.5, 126.7, 121.5, 118.5, 101.5, 72.0, 59.9, 58.4, 55.8, 43.3, 42.0, 35.1, 28.2, 26.9, 25.7, 21.3.

Linear in accordance with literature.[28]

1,2:5,6-Di-*O*-isopropylidene-3-*O*-hexanal-α-D-glucofuranose (Linear) (26)

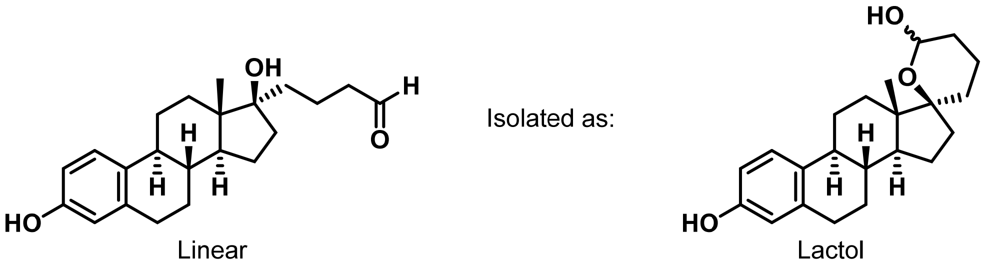


The title compound **26** was prepared using the General Procedure with 1,2:5,6-di-*O*-isopropylidene-3-*O*-pentenyl-α-D-glucofuranose (324 mg, 1.00 mmol). Purification via FCC (DCM to DCM/acetone 19:1) afforded **26** as a colourless oil (343 mg, 0.956 mmol, 96%, *l*:*b* = >20:1).

Linear (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.76 (t, *J* = 1.7 Hz, 1H), 5.86 (d, *J* = 3.7 Hz, 1H), 4.51 (d, *J* = 3.7 Hz, 1H), 4.28 (dt, *J* = 7.7, 6.0 Hz, 1H), 4.11 – 4.05 (m, 2H), 3.97 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.83 (d, *J* = 3.1 Hz, 1H), 3.60 (t, *J* = 9.3, 6.3 Hz, 1H), 3.51 (dt, *J* = 9.3, 6.3 Hz, 1H), 2.43 (td, *J* = 7.3 Hz, 1.7 Hz, 2H), 1.68 – 1.54 (m, 4H), 1.48 (s, 3H), 1.43 – 1.37 (m, 5H), 1.33 (s, 3H), 1.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 202.6, 111.9, 109.1, 105.4, 82.6, 82.3, 81.3, 72.6, 70.3, 67.4, 43.9, 29.6, 27.0, 26.9, 26.4, 25.8, 25.6, 21.9.

HRMS (ESI$^+$) *m/z* calcd. for $C_{18}H_{31}O_7$ $[M+H]^+$: 359.2064, found: 359.2072.

4-(Estra-1,3,5(10)-trien-3,17β-diol-17α-yl)butanal (Linear) isolated as 3-hydroxy-17β-estra-1,3,5(10)-trien-21,17-carbolactol (Lactol) (27)

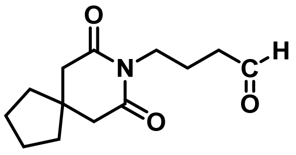


The title compound **27** was prepared using the General Procedure with 17α-allyl-estra-1,3,5(10)-trien-3,17β-diol (312 mg, 1.00 mmol). Purification via FCC (DCM/acetone 9:1 to DCM/acetone 7:3) afforded **27** as a white solid (290.6 mg, 0.849 mmol, 85%, *l*:*b* = >20:1).

Linear/Lactol (major): ^{1}H NMR (400 MHz, methanol-*d*$_4$) δ_H 7.02 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 8.7 Hz, 1H), 6.43 (s, 1H), 4.69 (d, *J* = 9.7 Hz, 1H), 3.27 (s, 1H), 2.79 – 2.67 (m, 2H), 2.26 – 2.23 (m, 1H), 2.08 – 2.02 (m, 1H), 1.96 – 1.12 (m, 18H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, methanol-*d*$_4$) δ_C 155.9, 138.8, 132.6, 127.2, 116.0, 113.7, 94.4, 87.4, 49.8, 49.7, 48.1, 45.3, 41.0, 34.2, 33.0, 31.3, 30.7, 30.1, 28.9, 27.6, 24.6, 19.9, 14.6.

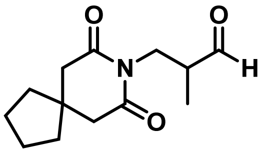
HRMS (ESI$^+$) *m/z* calcd. for $C_{22}H_{30}O_3Na$ $[M+Na]^+$: 365.2087, found: 365.2086.

4-(7,9-Dioxo-8-azaspiro[4.5]decan-8-yl)butanal (Linear) and 3-(7,9-dioxo-8-azaspiro[4.5]decan-8-yl)-2-methylpropanal (Branched) (28)



Linear

and



Branched

The title compounds **28** were prepared using the General Procedure with 8-allyl-8-azaspiro[4.5]decane-7,9-dione (207 mg, 1.00 mmol). Purification via FCC (pentane/DCM 4:1 to DCM/acetone 19:1) afforded **28** as a colourless oil (217 mg, 0.915 mmol, 92%, *l*:*b* = 5:1).

Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, CDCl$_3$) δ_H 9.75 (t, *J* = 1.3 Hz, 1.0H), 9.58 (d, *J* = 3.0 Hz, 0.2H), 4.10 (dd, *J* = 13.3, 8.6 Hz, 0.2H), 3.87 (dd, *J* = 13.4, 5.6 Hz, 0.2H), 3.80 (t, *J* = 7.1 Hz, 2.0H), 2.68 – 2.64 (m, 0.2H), 2.59 (s, 4.8H), 2.46 (td, *J* = 7.3, 1.4 Hz, 2.0H), 1.86 (quin, *J* = 7.3 Hz, 2.0H), 1.73 – 1.69 (m, 4.8H), 1.51 – 1.48 (m, 4.8H), 1.11 (d, *J* = 7.1 Hz, 0.6H).

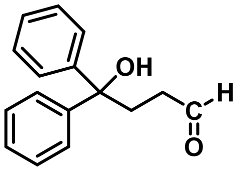
Linear (major): ^{13}C NMR (101 MHz, CDCl$_3$) δ_C 201.4, 172.4, 44.9, 41.4, 39.6, 38.8, 37.7, 24.3, 20.6.

Branched (minor): ^{13}C NMR (101 MHz, CDCl$_3$) δ_C 203.0, 172.5, 45.9, 44.8, 39.9, 39.5, 37.7, 24.3, 11.8.

HRMS (ESI$^+$) *m/z* calcd. for $C_{13}H_{19}O_3Na$ [M+Na]$^+$: 260.1257, found: 260.1251.

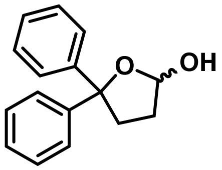
Linear in accordance with literature.[29]

4-Hydroxy-4,4-diphenylbutanal (Linear) isolated as 5,5-diphenyltetrahydrofuran-2-ol (Lactol) (29)



Linear

Isolated as:



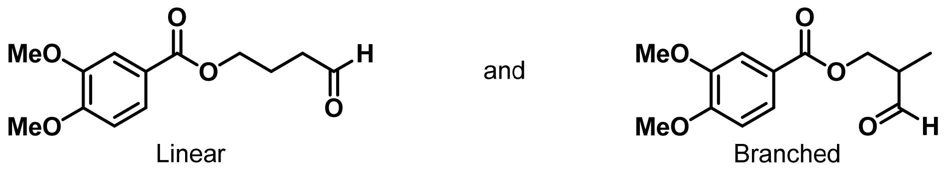
Lactol

The title compound **29** was prepared using the General Procedure with 1,1-diphenylpropenol (210 mg, 1.00 mmol). Purification via FCC (pentane/DCM 1:1 to DCM/acetone 19:1) afforded **29** as a white solid (239 mg, 0.994 mmol, 99%, *l*:*b* = >20:1).

Linear/Lactol (major): ^{1}H NMR (400 MHz, CDCl$_3$) δ_H 7.48 – 7.45 (m, 2H), 7.42 – 7.39 (m, 2H), 7.32 – 7.27 (m, 4H), 7.23 – 7.18 (m, 2H), 5.75 (td, *J* = 4.6, 1.7 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.65 – 2.58 (m, 2H), 2.09 – 1.95 (m, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ_C 146.7, 146.0, 128.2, 127.0, 126.9, 126.4, 125.8, 98.9, 89.8, 36.9, 33.4.

HRMS (ESI$^+$) *m/z* calcd. for $C_{16}H_{16}O_2Na$ [M+Na]$^+$: 263.1043, found: 263.1042.

4-Oxobutyl 3,4-dimethoxybenzoate (Linear) and 2-methyl-3-oxopropyl 3,4-dimethoxybenzoate (Branched) (30)



The title compounds **30** were prepared using the General Procedure with allyl 3,4-dimethoxybenzoate (222 mg, 1.00 mmol). Purification via FCC (pentane/DCM 1:1 to DCM/acetone 19:1) afforded **30** as a colourless oil (242 mg, 0.960 mmol, 96%, *l*:*b* = 1.1:1).

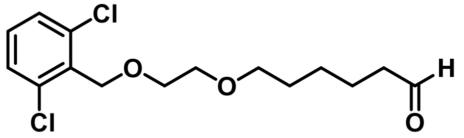
Linear (major) and Branched (minor): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.83 (t, *J* = 1.4, 1.0H), 9.79 (d, *J* = 1.4 Hz, 0.9H), 7.66 – 7.61 (m, 1.9H), 7.51 (d, *J* = 2.0 Hz, 1.0H), 7.49 (d, *J* = 2.0 Hz, 0.9H), 6.89 – 6.86 (m, 1.9H), 4.56 – 4.48 (m, 1.8H), 4.34 (t, *J* = 6.3 Hz, 2.0H), 3.93 – 3.91 (m, 11.4H), 2.89 – 2.81 (m, 0.9H), 2.62 (td, *J* = 7.1, 1.3 Hz, 2.0H), 2.12 (quin, *J* = 6.7 Hz, 2.0H), 1.24 (d, *J* = 7.2 Hz, 2.7H).

Linear (major): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 201.4, 166.4, 153.2, 148.8, 123.7, 122.6, 112.1, 110.4, 64.0, 56.1, 56.1, 40.8, 21.7.

Branched (minor): ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 202.2, 166.2, 153.3, 148.8, 123.8, 122.2, 112.1, 110.4, 64.0, 56.1, 56.1, 46.1, 10.8.

HRMS (ESI$^+$) *m/z* calcd. for $C_{13}H_{16}O_5Na$ [M+Na]$^+$: 275.0890, found: 275.0891.

6-(2-((2,6-Dichlorobenzyl)oxy)ethoxy)hexanal (Linear) (31)

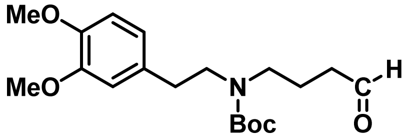


The title compound **31** was prepared using the General Procedure with 1,3-dichloro-2-((2-(pent-4-en-1-yloxy)ethoxy)methyl)benzene (289 mg, 1.00 mmol). Purification via FCC (pentane/DCM 1:1 to DCM/Acetone 19:1) afforded **31** as a colourless oil (307 mg, 0.962 mmol, 96%, *l*:*b* = >20:1).

Linear (major): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ_H 9.75 (t, *J* = 1.8 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.19 – 7.15 (m, 1H), 4.82 (s, 2H), 3.70 – 3.68 (m, 2H), 3.61 – 3.59 (m, 2H), 3.46 (t, *J* = 6.5 Hz, 2H), 2.42 (td, *J* = 7.4, 1.8 Hz, 2H), 1.68 – 1.56 (m, 4H), 1.42 – 1.35 (m, 2H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ_C 202.9, 137.1, 133.5, 130.0, 128.5, 71.1, 70.2, 70.1, 67.7, 44.0, 29.6, 25.9, 22.0.

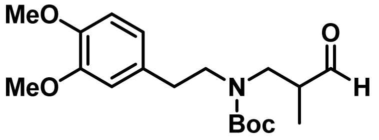
Linear in accordance with literature.[29]

tert-Butyl (3,4-dimethoxyphenethyl)(4-oxobutyl)carbamate (Linear) and *tert*-butyl (3,4-dimethoxyphenethyl)(2-methyl-3-oxopropyl)carbamate (Branched) (32)



Linear

and

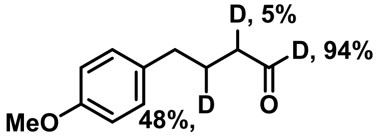


Branched

The title compounds **32** were prepared using the General Procedure with *tert*-butyl allyl(3,4-dimethoxyphenethyl)carbamate (321 mg, 1.00 mmol). Purification via FCC (DCM to DCM/acetone 19:1) afforded **32** as a colourless oil (339.8 mg, 0.967 mmol, 97%, *l*:*b* = 10:1).

Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, $CDCl_3$) [rotameric mixture] δ_H 9.76 – 9.75 (m, 1.0H), 9.65 – 9.64 (m, 0.1H), 6.80 – 6.68 (m, 3.3H), 3.87 – 3.85 (m, 6.6H), 3.49 – 3.29 (m, 2.3H), 3.24 – 3.07 (m, 2.2H), 2.82 – 2.70 (m, 2.2H), 2.48 – 2.38 (m, 2.0H), 1.87 – 1.75 (m, 2.0H), 1.45 (s, 9.9H), 1.07 (dd, J = 7.2, 1.7 Hz, 0.3H). **^{13}C NMR** (101 MHz, $CDCl_3$) [rotameric mixture] δ_C 203.5, 203.3, 201.7, 201.4, 155.5, 155.3, 148.8, 147.5, 131.7, 131.6, 120.7, 112.0, 111.3, 79.5, 79.4, 55.9, 55.8, 50.5, 49.3, 49.2, 48.4, 46.7, 46.4, 41.0, 40.8, 34.7, 34.0, 28.4, 28.3, 21.0, 20.8, 11.7. **HRMS** (ESI$^+$) *m/z* calcd. for $C_{19}H_{29}O_5NNa$ $[M+Na]^+$: 374.1938, found: 374.1942.
Linear in accordance with literature.[29]

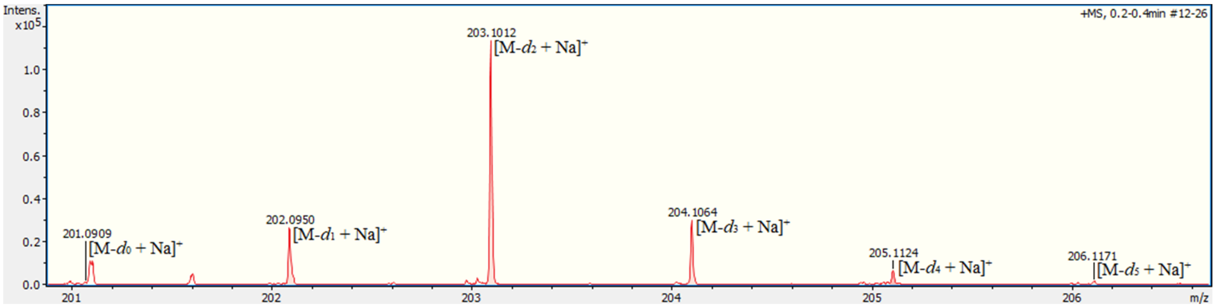
4-(4-Methoxyphenyl)butanal-1,3-d_2 (Linear) (33)



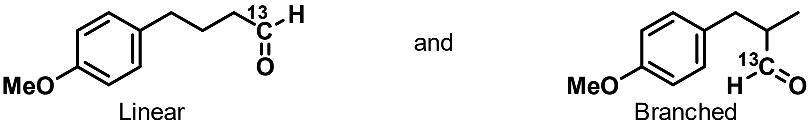
Linear

The title compound **33** were prepared using the General Procedure with *p*-allylanisole (148 mg, 1.00 mmol) and methanol-d_4 (61 µL) in the syngas-releasing chamber. Purification via FCC (pentane/DCM 4:1 to DCM) afforded **33** as a colourless oil (166.1 mg, 0.922 mmol, 92%, *l*:*b* = >20:1, 1.99 D-incorporation).

Linear (major): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.75 (t, J = 1.6 Hz, 0.06H, 94% D), 7.11 – 7.07 (m, 2.0H), 6.85 – 6.82 (m, 2.0H), 3.79 (s, 3.0H), 2.62 – 2.59 (m, 2.0H), 2.45 – 2.42 (m, 1.9H, 5% D), 1.97 – 1.88 (m, 1.05H, 48% D). **^{2}H NMR** (61 MHz, $CDCl_3$) δ_D 9.79 (bs, 1.00D), 2.43 (bs, 0.08D), 1.93 (0.88D). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 202.5 – 202.0 (m, D), 158.1, 133.4, 129.5, 114.0, 55.4, 43.0 – 42.9 (m, D), 34.1, 24.0 – 23.4 (m, D). **HRMS** (ESI$^+$) *m/z* calcd. for $C_{11}H_{12}{}^2H_2O_2Na$ $[M+Na]^+$: 203.1012, found: 203.1012.



4-(4-Methoxyphenyl)butanal-1-^{13}C (Linear) and 3-(4-methoxyphenyl)-2-methylpropanal-1-^{13}C (Branched) (34)



The title compounds **34** were prepared using the General Procedure with *p*-allylanisole (148 mg, 1.00 mmol) and methanol-^{13}C (61 μL) in the syngas-releasing chamber. Purification via FCC (pentane/DCM 4:1 to DCM) afforded **34** as a colourless oil (175.6 mg, 0.980 mmol, 98%, *l*:*b* = 10:1).

Linear (major) and Branched (minor): ^{1}H NMR (400 MHz, CDCl$_3$) δ_H 9.75 (dt, *J* = 170.7, 1.5 Hz, 1.0H), 9.71 (dd, *J* = 169.9, 1.5 Hz, 0.1H), 7.11 – 7.07 (m, 2.2H), 6.85 – 6.82 (m, 2.2H), 3.79 (s, 3.3H), 3.05 – 2.99 (m, 0.1H), 2.66 – 2.53 (m, 2.2H), 2.44 (tdd, *J* = 7.5, 6.1, 1.7 Hz, 2.0H), 1.93 (quind, *J* = 7.4, 4.5 Hz, 2.0H), 1.08 (dd, *J* = 6.8, 5.3 Hz, 0.3H).

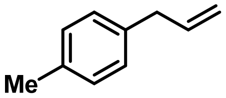
Linear (major): ^{13}C NMR (101 MHz, CDCl$_3$) δ_C 202.2 (^{13}C), 157.9, 133.2. 129.3, 113.8, 55.1, 43.0 (d, *J* = 38.6 Hz), 34.0 (d, *J* = 3.6 Hz), 23.8 (d, *J* = 1.5 Hz).

Branched (minor): ^{13}C NMR (101 MHz, CDCl$_3$) δ_C 204.4 (^{13}C), 158.1, 130.7 (d, *J* = 3.2 Hz), 129.9, 113.8, 55.1, 48.1 (d, *J* = 38.7 Hz), 35.7, 13.0.

HRMS (ESI$^+$) *m/z* calcd. for $C_{10}{}^{13}CH_{14}O_2Na$ [M+Na]$^+$: 202.0920, found: 202.0918.

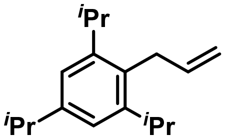
Starting materials

p-Allyltoluene (35)



To a COtube was added *p*-bromotoluene (3.42 g, 20.0 mmol), magnesium turnings (583 mg, 24.0 mmol), and anhydrous THF (20 mL) followed by stirring for 1 h. The resulting suspension was added a solution of allyl bromide (2.0 mL, 24 mmol) in anhydrous THF (10 mL). The reaction mixture was refluxed overnight followed by quenching with water (20 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL) and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via FCC (pentane) afforded **35** as a colourless oil (841 mg, 6.36 mmol, 32%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H 7.13 – 7.08 (m, 4H), 5.97 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.11 – 5.04 (m, 2H), 3.36 (d, *J* = 6.7 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 137.9, 137.1, 135.7, 129.2, 128.6, 115.7, 40.0, 21.2.
In accordance with literature.[30]

2-Allyl-1,3-5-triisopropylbenzene (36)

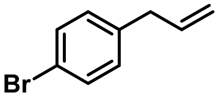


Using Schlenk technique; a three-necked 50-mL round-bottom flask fitted with a reflux condenser, a rubber septum, and a stopcock attached to the Schlenk line was added magnesium turnings (583 mg, 24.0 mmol), anhydrous THF (20 mL), and 1,2-dibromoethane (2 drops) at room temperature. The solution was slowly added 2,4,6-triisopropylbromobenzene (5.0 mL, 20 mmol) while the temperature was increased to reflux. After addition, the reaction mixture was stirred at reflux for 2 h and then allowed to cool to room temperature. A separate three-necked 100-mL round-bottom flask fitted with a reflux condenser, a rubber septum, and a stopcock attached to the Schlenk line was added anhydrous THF (20 mL) and allyl bromide (16.9 mL, 200 mmol) at room temperature. The Grignard solution was slowly cannulated into the allyl bromide solution. After addition, the reaction mixture was stirred at reflux overnight. The reaction mixture was allowed to cool to room temperature and quenched with water (20 mL). The solution was transferred to a separatory funnel, diluted with heptane (200 mL), and the organic phase was washed with brine (2 x 100 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via FCC (pentane) followed by distillation afforded **36** as a colourless oil (2.52 g, 10.3 mmol, 52%).

^{1}H NMR (400 MHz, CDCl$_3$) δ_H 7.01 (s, 2H), 5.99 (ddt, *J* = 17.1, 10.7, 5.4 Hz, 1H), 5.01 (dq, *J* = 10.2, 1.9 Hz, 1H), 4.86 (dq, *J* = 17.1, 2.0 Hz, 1H), 3.47 (dt, *J* = 5.4, 2.0 Hz, 2H), 3.14 (sept, *J* = 6.8 Hz, 2H), 2.89 (sept, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.23 (d, *J* = 6.8 Hz, 12H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ_C 147.1, 146.8, 138.1, 130.5, 121.0, 115.1, 34.3, 31.7, 29.4, 24.4, 24.2.

In accordance with literature.[31]

p-Allylbromobenzene (37)

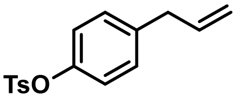


To a COtube was added copper(I) iodide (1.19 g, 6.25 mmol) and anhydrous THF (115 mL), followed by dropwise addition of vinylmagnesium bromide (1.0 M in THF, 37.5 mL, 37.5 mmol) at -50 °C. After stirring for 10 min, a solution of benzyl bromide (6.25 g, 25.0 mmol) in anhydrous THF (30 mL) was added slowly. The resulting reaction mixture was stirred at -50 °C for 1 h and then allowed to warm to room temperature followed by stirring overnight. The reaction mixture was filtered through Celite®, quenched with water (50 mL), followed by evaporation of bulk THF in vacuo. The resulting suspension was transferred to a separatory funnel and the aqueous phase was acidified with 4 M HCl. The aqueous phase was extracted with DCM (3 x 50 mL) and the combined organic phases were dried over MgSO$_4$, filtered, and concentrated in vacuo. Purification via FCC (pentane) afforded **37** as a colourless oil (4.29 g, 21.8 mmol, 87%).

^{1}H NMR (400 MHz, CDCl$_3$) δ_H 7.41 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 5.93 (ddt, *J* = 17.0, 10.5, 6.7 Hz, 1H), 5.11 – 5.04 (m, 2H), 3.34 (d, *J* = 6.6 Hz, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ_C 139.1, 136.9, 131.6, 130.1, 120.0, 116.4, 39.7.

In accordance with literature.[32]

p-Allylphenol tosylate (38)

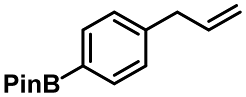


To a COtube was added *p*-allylphenol (671 mg, 5.00 mmol), DCM (10 mL), tosyl chloride (1.43 g, 7.50 mmol), followed by triethylamine (1.4 mL, 10 mmol) at room temperature. The reaction mixture was stirred for 1 h at the same temperature. The solution was transferred to a separatory funnel, diluted with DCM (40 mL), and the organic phase was washed with 1 M NaOH (3 x 20 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by AFCC (heptane to heptane/EtOAc 15%) afforded **38** as a white solid (1.33 g, 4.60 mmol, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.70 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 5.91 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.15 – 4.86 (m, 2H), 3.34 (d, J = 6.7 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 148.1, 145.4, 139.2, 136.9, 132.6, 129.9, 129.8, 128.7, 122.4, 116.5, 39.6, 21.9.

In accordance with literature.[9]

p-Allylphenylboronic acid pinacol ester (39)

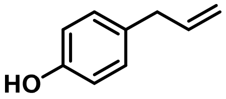


Using Schlenk technique; a Schlenk tube was added *p*-allylbromobenzene (985 mg, 5.00 mmol) and dry THF (5 mL) followed by cooling to -78 °C. *n*-BuLi (2.5 M in hexanes, 2.4 mL, 6.0 mmol) was added dropwise and the reaction mixture was stirred for 1 h at -78 °C. Isopropyl pinacol borate (1.1 mL, 5.5 mmol) was added dropwise and the reaction mixture was stirred for an additional 30 min at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with water (15 mL) and the aqueous phase was extracted with DCM (3 x 15 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification via FCC (pentane to pentane/Et_2O 19:1) afforded **39** as a colourless oil (879 mg, 3.60 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.75 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.96 (ddt, J = 15.8, 10.4, 6.7 Hz, 1H), 5.11 – 5.06 (m, 2H), 3.41 (d, J = 6.7 Hz, 2H), 1.34 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 143.6, 137.3, 135.1, 128.2, 116.1, 83.8, 40.5, 25.0.

In accordance with literature.[33]

p-Allylphenol (40)

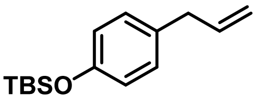


To a COtube was added 4-allylanisole (741 mg, 5.00 mmol) and anhydrous DCM (5 mL), followed by dropwise addition of BBr_3 (0.52 mL, 5.5 mmol) at 0 °C. The reaction mixture was stirred for 1 h at the same temperature. The reaction mixture was carefully quenched with water (10 mL) followed by extraction with DCM (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by AFCC (heptane to heptane/EtOAc 1:3) afforded **40** as a colourless oil (408 mg, 3.04 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.06 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.00 – 5.90 (m, 1H), 5.09 – 5.03 (m, 2H), 4.64 – 4.62 (m, 1H), 3.32 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 153.9, 138.0, 132.4, 129.9, 115.6, 115.4, 39.5.

In accordance with literature.[34]

p-Allylphenoxy(*tert*-butyl)dimethylsilane (41)

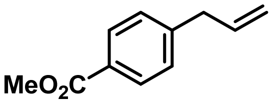


To a COtube was added *p*-allylphenol (671 mg, 5.00 mmol), DMF (5 mL), imidazole (681 mg, 10.0 mmol), and TBSCl (1.13 g, 7.50 mmol). The reaction mixture was stirred at room temperature for 4 h followed by quenching with water (5 mL). The aqueous phase was extracted with DCM (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification via FCC (pentane to pentane/EtOAc 9:1) afforded **41** as a colourless oil (1.11 g, 4.46 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.05 – 7.02 (m, 2H), 6.78 – 6.75 (m, 2H), 5.96 (ddt, *J* = 15.7, 10.7, 6.7 Hz, 1H), 5.08 – 5.03 (m, 2H), 3.32 (d, *J* = 6.7 Hz, 2H), 0.98 (s, 9H), 0.19 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 154.0, 138.1, 132.8, 129.6, 120.1, 115.5, 39.6, 25.8, 18.3, -4.3.

In accordance with literature.[35]

Methyl 4-allylbenzoate (42)

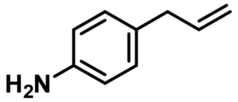


A COtube charged with 4-methoxycarbonylphenylboronic acid (1.80 g, 10.0 mmol) and K_2CO_3 (3.46 g, 25.0 mmol) was transferred to a glovebox, where $Pd(PPh_3)_4$ (578 mg, 0.5 mmol), DME (20 mL), and water (10 mL) was added. Outside the glovebox, allyl bromide was added via syringe (1.3 mL, 15 mmol). The reaction mixture was heated to 90 °C and stirred overnight. The mixture was diluted with brine (50 mL) followed by extraction with Et_2O (3 x 50 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 49:1) afforded the **42** as a colourless oil (1.24 g, 7.01 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.98 – 7.95 (m, 2H), 7.27 – 2.25 (m, 2H), 5.96 (ddt, *J* = 17.0, 10.5, 6.7 Hz, 1H), 5.12 – 5.07 (m, 2H), 3.90 (s, 3H), 3.44 (d, *J* = 6.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 167.2, 145.6, 136.5, 129.9, 128.8, 128.2, 116.7, 52.1, 40.3.

In accordance with literature.[36]

p-Allylaniline (43)

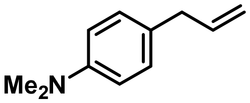


To a COtube was added Cu_2O (286 mg, 2.00 mmol), *p*-allylbromobenzene (1.97 g, 10.0 mmol), *N*-methyl-2-pyrrolidone (6.5 mL), and NH_4OH (25% in water, 6.5 mL) followed by stirring for 2 d at 80 °C. The reaction mixture was transferred to a separatory funnel and diluted with water (25 mL). The aqueous phase was acidified with 4 M HCl and extracted with DCM (3 x 25 mL). The combined organic phases were discarded. The aqueous phase was basified with 4 M NaOH and extracted with DCM (3 x 25 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via FCC (pentane to pentane/acetone 19:1) afforded **43** as a colourless oil (853 mg, 6.40 mmol, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.00 – 6.97 (m, 2H), 6.66 – 6.63 (m, 2H), 5.95 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.08 – 5.01 (m, 2H), 3.57 (bs, 2H), 3.29 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 144.6, 138.3, 130.2, 129.5, 115.4, 115.3, 39.5.

In accordance with literature.[37]

p-Allyl-*N*,*N*-dimethylaniline (44)

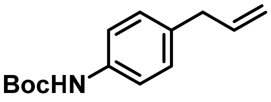


To a round-bottomed flask was added *p*-allylaniline (400 mg, 3.00 mmol), acetic acid (10 mL), paraformaldehyde (901 mg, 30.0 mmol), and $NaBH_3CN$ (943 mg, 15.0 mmol) followed by stirring at room temperature overnight. The reaction mixture was quenched and basified with 1 M NaOH, and the aqueous phase was extracted with $CHCl_3$ (3 x 25 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 19:1) afforded **44** as a colourless oil (352 mg, 2.18 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.10 – 7.07 (m, 2H), 6.74 – 6.72 (m, 2H), 5.98 (ddt, *J* = 16.7, 10.0, 6.7 Hz, 1H), 5.10 – 5.02 (m, 2H), 3.32 (d, *J* = 6.7 Hz, 2H), 2.93 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 149.4, 138.5, 129.3, 128.3, 115.1, 113.2, 41.0, 39.4.

In accordance with literature.[38]

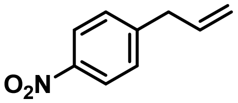
tert-Butyl 4-allylphenylcarbamate (45)



To a round-bottomed flask was added *p*-allylaniline (400 mg, 3.00 mmol), triethylamine (2 mL), methanol (8 mL), and Boc_2O followed by stirring at room temperature overnight. The reaction mixture was diluted with EtOAc (30 mL) and the organic phase was washed with 0.5 M HCl (15 mL) and saturated NaOH aqueous solution (3 x 15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 9:1) afforded **45** as a white solid (519 mg, 2.23 mmol, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.29 – 7.27 (m, 2H), 7.11 – 7.09 (m, 2H), 6.40 (bs, 1H), 5.94 (ddt, *J* = 16.0, 10.6, 6.7 Hz, 1H), 5.08 – 5.03 (m, 2H), 3.33 (d, *J* = 6.7 Hz, 2H), 1.51 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 153.0, 137.7, 136.5, 134.8, 129.2, 118.9, 115.8, 80.5, 39.7, 28.5. **HRMS** (ESI$^+$) *m/z* calcd. for $C_{14}H_{19}NO_2Na$ $[M+Na]^+$: 256.1308, found: 256.1307.

p-Allylnitrobenzene (46)

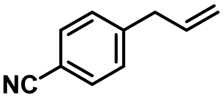


A three-necked round-bottomed flask was charged with 1-bromo-4-nitrobenzene (2.02 g, 10.0 mmol) and dioxane (110 mL), and the mixture was degassed with argon for 10 minutes. $Pd(PPh_3)_4$ (289 mg, 0.250 mmol, 2.5 mol%), a solution of K_2CO_3 (2.76 g, 20.0 mmol) in degassed water (20 mL), and allylboronic acid pinacol ester (1.85 g, 11.0 mmol) was added to the reaction mixture. The reaction mixture was brought to reflux and allowed to stir overnight. After cooling to room temperature, the reaction mixture was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification via AFCC (heptane) afforded **46** as a pale-yellow oil (475 mg, 2.91 mmol, 29%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.17 – 8.14 (m, 2H), 7.36 – 7.33 (m, 2H), 5.94 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.18 – 5.10 (m, 2H), 3.49 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 147.9, 146.7, 135.6, 129.5, 123.8, 117.6, 40.0.

In accordance with literature.[39]

p-Allylbenzonitrile (47)

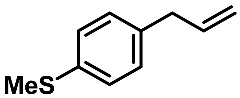


A round-bottomed flask was charged with 4-cyanophenylboronic acid (2.94 g, 20.0 mmol), Na_2CO_3 (3.82 g, 36.0 mmol), THF (80 mL), and water (20 mL). The mixture was degassed with argon for 10 min, followed by the addition of $Pd(PPh_3)_4$ (462 mg, 0.400 mmol) and allyl bromide (2.5 mL, 30 mmol). The flask was fitted with a reflux condenser and the reaction mixture was stirred at reflux overnight. The reaction mixture was cooled to room temperature, diluted with brine (10 mL), and extracted by Et_2O (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification via AFCC (pentane to pentane/Et_2O 49:1) afforded **47** as a colourless oil (564 mg, 3.94 mmol, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.59 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.92 (ddt, J = 16.8, 10.1, 6.7 Hz, 1H), 5.19 – 5.06 (m, 2H), 3.44 (d, J = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 145.8, 135.8, 132.4, 129.5, 119.2, 117.4, 110.2, 40.3.

In accordance with literature.[40]

p-Allylthioanisole (48)

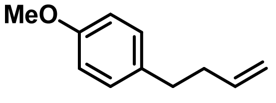


In a glovebox; to a round-bottomed flask was added 4-(methylthio)phenylboronic acid (1.68 g, 10.0 mmol), $Pd(PPh_3)_4$ (231 mg, 0.200 mmol), K_2CO_3 (3.46 g, 25.0 mmol), THF (20 mL), water (5 mL), and allyl bromide (1.3 mL, 15 mmol). Outside the glovebox, the reaction mixture was heated to reflux followed by stirring overnight. The reaction mixture was cooled to room temperature followed by quenching with brine (25 mL). The aqueous phase was extracted with Et_2O (3 x 25 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 99:1) afforded **48** as a colourless oil (782 mg, 4.76 mmol, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.23 – 7.20 (m, 2H), 7.14 – 7.10 (m, 2H), 5.95 (ddt, J = 17.8, 9.2, 6.6 Hz, 1H), 5.10 – 5.05 (m, 2H), 3.35 (d, J = 6.7 Hz, 2H), 2.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 137.4, 137.3, 135.8, 129.3, 127.3, 116.0, 39.8, 16.4.

In accordance with literature.[41]

4-(*p*-Methoxyphenyl)but-1-ene (49)

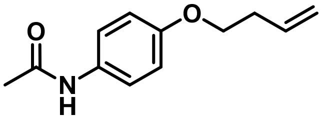


To a COtube was added 4-methoxybenzyl chloride (3.92 g, 25.0 mmol) in dry THF (50 mL) followed by slow addition of allylmagnesium bromide (1 M in THF, 50 mL, 50 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature followed by stirring for 4 h. The reaction mixture was quenched with a saturated NH_4Cl aqueous solution (50 mL). The aqueous phase was extracted with Et_2O (3 x 50 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 99:1) afforded **49** as a colourless oil (3.36 g, 20.7 mmol, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.13 – 7.10 (m, 2H), 6.85 – 6.82 (m, 2H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.04 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.00 – 4.96 (m, 1H), 3.79 (s, 3H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.38 – 2.32 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 157.9, 138.3, 134.1, 129.4, 115.0, 113.8, 55.4, 35.9, 34.6.

In accordance with literature.[42]

N-(4-(But-3-en-1-yloxy)phenyl)acetamide (50)

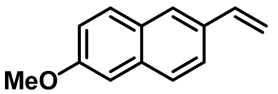


To a COtube was added 4-acetamidophenol (1.51 g, 10.0 mmol), potassium carbonate (2.76 g, 20.0 mmol), and acetonitrile (50 ml). The mixture was refluxed for 1 h before being added 1-bromo-3-butene (1.2 mL, 12 mmol). The reaction mixture was stirred overnight at reflux. The resultant suspension was filtered through Celite® followed by concentration in vacuo. The residue was redissolved in EtOAc (100 mL) and the organic phase was washed with a saturated solution of sodium carbonate (2 x 25 mL) and brine (25 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 1:4) afforded **50** as a white solid (1.35 g, 6.59 mmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.41 (bs, 1H), 7.39 – 7.35 (m, 2H), 6.85 – 6.81 (m, 2H), 5.89 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.18 – 5.09 (m, 2H), 3.98 (t, *J* = 6.7 Hz, 2H), 2.4 – 2.49 (m, 2H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 168.5, 155.9, 134.5, 131.2, 122.0, 117.2, 115.0, 67.6, 33.8, 24.4.

In accordance with literature.[43]

2-Methoxy-6-vinylnaphthalene (51)



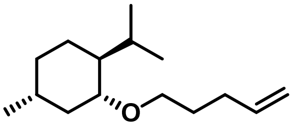
To a round-bottomed flask was added methyltriphenylphosphonium bromide (7.15 g, 20.0 mmol), potassium *tert*-butoxide (2.24 g, 20.0 mmol), and dry THF (40 mL). The mixture was stirred for 30 min at room temperature before being added 6-methoxy-2-naphthaldehyde (1.86 g, 10.0 mmol) followed by stirring overnight at the same temperature. The reaction mixture was quenched with a saturated NH_4Cl aqueous solution (30 mL) and the aqueous phase was extracted with Et_2O (3 x 30 mL).

The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 19:1) afforded **51** as a white solid (1.78 g, 9.68 mmol, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.72 – 7.69 (m, 3H), 7.61 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.15 – 7.12 (m, 2H), 6.85 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.82 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.28 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 157.9, 137.1, 134.4, 133.1, 129.7, 129.1, 127.1, 126.3, 123.9, 119.1, 113.2, 106.0, 55.5.

In accordance with literature.[29]

(1*S*,2*R*,4*R*)-1-Isopropyl-4-methyl-2-(pent-4-en-1-yloxy)cyclohexane (52)

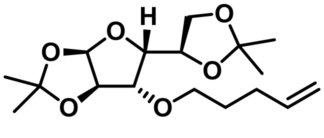


In a COtube, a stirring solution of (-)-menthol (1.56 g, 10.0 mmol) in dry DMF (20 mL) was added NaH (60%, 800 mg, 20.0 mmol) at 0 °C. After stirring for 30 min, 5-bromopentene (1.8 mL, 15 mmol) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred overnight followed by quenching with a saturated NH_4Cl aqueous solution (20 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via FCC (pentane to pentane/Et_2O 19:1) afforded **52** as a colourless oil (706 mg, 3.15 mmol, 32%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 – 4.94 (m, 2H), 3.63 (dt, *J* = 9.1, 6.2 Hz, 1H), 3.27 (dt, *J* = 9.1, 6.8 Hz, 1H), 2.99 (td, *J* = 10.5, 4.1 Hz, 1H), 2.28 – 2.06 (m, 4H), 1.73 – 1.56 (m, 4H), 1.40 – 1.27 (m, 1H), 1.25 – 1.18 (m, 1H), 1.01 – 0.82 (m, 9H), 0.77 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 138.7, 114.7, 79.3, 67.9, 48.5, 40.7, 34.8, 31.7, 30.6, 29.6, 25.7, 23.5, 22.5, 21.1, 16.4.

In accordance with literature.[44]

1,2:5,6-Di-*O*-isopropylidene-3-*O*-pentenyl-α-D-glucofuranose (53)

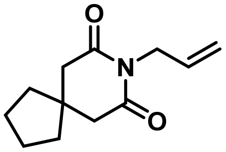


In a COtube, a stirring solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2.60 g, 10.0 mmol) in dry DMF (20 mL) was added NaH (60%, 800 mg, 20.0 mmol) at 0 °C. After stirring for 30 min, 5-bromopentene (1.8 mL, 15 mmol) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred overnight followed by quenching with a saturated NH_4Cl aqueous solution (20 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via FCC (pentane to pentane/EtOAc 9:1) afforded **53** as a colourless oil (2.92 g, 8.89 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.87 (d, J = 3.7 Hz, 1H), 5.79 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.05 – 4.95 (m, 2H), 4.52 (d, J = 3.7 Hz, 1H), 4.33 – 4.28 (m, 1H), 4.12 – 4.06 (m, 2H), 3.98 (dd, J = 8.5, 5.9 Hz, 1H), 3.85 (d, J = 3.1 Hz, 1H), 3.64 – 3.59 (m, 1H), 3.54 – 3.49 (m, 1H), 2.15 – 2.10 (m, 2H), 1.66 (quin, J = 6.6 Hz, 2H), 1.49 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 138.2, 115.1, 111.9, 109.0, 105.4, 82.6, 82.2, 81.3, 72.6, 69.8, 67.4, 30.3, 29.0, 27.0, 26.9, 26.4, 25.5.

In accordance with literature.[45]

8-Allyl-8-azaspiro[4.5]decane-7,9-dione (54)

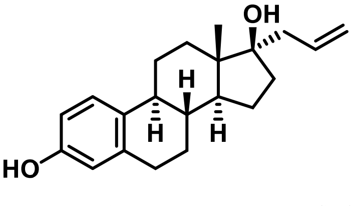


To a COtube was added 8-azaspiro[4.5]decane-7,9-dione (3.34 g, 20.0 mmol), K_2CO_3 (5.53 g, 40.0 mmol), acetone (40 mL), and allyl bromide (8.5 mL, 100 mmol). The reaction mixture was stirred at reflux overnight. The reaction mixture was filtered through Celite® and the filtrate was concentrated in vacuo. Purification via FCC (pentane to pentane/EtOAc 9:1) afforded **54** as a colourless oil (1.35 g, 6.49 mmol, 32%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.78 (ddt, J = 17.1, 10.2, 5.8 Hz, 1H), 5.19 – 5.11 (m, 2H), 4.37 (dt, J = 5.7, 1.4 Hz, 2H), 2.61 (s, 4H), 1.73 – 1.69 (m, 4H), 1.53 – 1.49 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 172.0, 132.2, 117.5, 45.0, 41.7, 39.7, 37.8, 24.3.

In accordance with literature.[29]

17α-Allyl-estra-1,3,5(10)-trien-3,17β-diol (55)



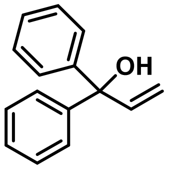
In a COtube, a stirring solution of estrone (1.35 g, 5.0 mmol) in dry THF (40 mL) was added allylmagnesium bromide (0.7 M in Et_2O, 21 mL, 15 mmol) dropwise at -78 °C. The reaction mixture was allowed to slowly warm to room temperature over 4 h before being stirred at room temperature for 2 h. The reaction mixture was quenched with a saturated NH_4Cl aqueous solution (50 mL). The aqueous phase was extracted with Et_2O (3 x 50 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 1:1) afforded almost pure **55**. Recrystallization from heptane/methanol afforded **55** as a white solid (1.00 g, 3.21 mmol, 64%).

^{1}H NMR (400 MHz, methanol-*d*$_4$) δ_H 7.16 (d, *J* = 8.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.56 (d, *J* = 2.7 Hz, 1H), 6.02 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.23 – 5.16 (m, 2H), 4.60 (s, 1H), 2.89 – 2.77 (m, 2H), 2.40 – 2.24 (m, 3H), 2.18 – 2.12 (m, 1H), 2.04 – 1.97 (m, 1H), 1.91 – 1.86 (m, 1H), 1.69 – 1.58 (m, 4H), 1.54 – 1.27 (m, 6H), 0.93 (s, 3H). **^{13}C NMR** (101 MHz, methanol-*d*$_4$) δ_C 155.9, 138.8, 136.9, 132.6, 127.2, 117.8, 116.0, 113.7, 83.9, 51.0, 48.0, 45.2, 42.8, 41.3, 34.1, 32.7, 30.7, 28.8, 27.6, 24.4, 15.1.

HRMS (ESI$^+$) *m/z* calcd. for $C_{21}H_{28}O_2Na$ $[M+Na]^+$: 335.1982, found: 335.1981.

In accordance with literature.[46]

1,1-Diphenylpropenol (56)

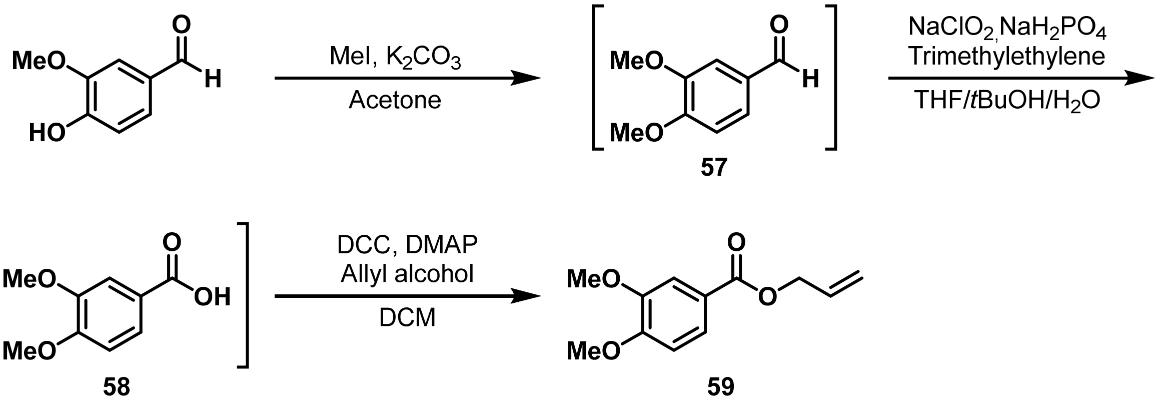


In a COtube, a stirring solution of benzophenone (1.82 g, 10.0 mmol) in dry THF (10 mL) was added vinylmagnesium bromide (1 M in THF, 15 mL, 15 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature followed by stirring for 2 h. The reaction mixture was quenched with water (20 mL) and bulk THF evaporated under reduced pressure. The suspension was transferred to a separatory funnel, acidified with 1 M HCl, and extracted with DCM (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via FCC (pentane to pentane/Et_2O 7:1) afforded **56** as a colourless oil (2.02 g, 9.61 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.41 – 7.39 (m, 4H), 7.36 – 7.33 (m, 4H), 7.30 – 7.27 (m, 2H), 6.57 – 6.50 (m, 1H), 5.37 – 5.35 (m, 1H), 5.32 (bs, 1H), 2.30 (bs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 145.9, 143.6, 128.3, 127.4, 127.0, 114.2, 79.5.

In accordance with literature.[29]

Allyl 3,4-dimethoxybenzoate (59)

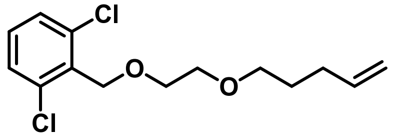


To a COtube was added vanillin (2.28 g, 15.0 mmol), K_2CO_3 (3.11 g, 22.5 mmol), acetone (60 mL), and MeI (1.4 mL, 23 mmol) at room temperature and the reaction mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature and the suspension filtered through celite® using acetone. The filtrate was concentrated in vacuo and the resultant oil was filtered through a short silica plug using Et_2O. The filtrate was concentration in vacuo to afford crude **57** as a colourless oil that was used in the next step without further purification. The crude **57** was added THF (80 mL), *tert*-butanol (20 mL), and 2-methyl-2-butene (12.7 mL, 120 mmol). In a separate flask, sodium chlorite (6.78 g, 75.0 mmol) and sodium dihydrogen phosphate monohydrate (16.6 g, 120 mmol) were dissolved in water (50 mL). Once fully dissolved, the aqueous solution was poured into the stirring organic solution and the resultant reaction mixture was stirred for 4 h. The solution was transferred to a separatory funnel and diluted with EtOAc (250 mL). The aqueous phase was made acidic with 4 M HCl and the organic phase was washed with 1 M HCl (2 x 100 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The obtained off-white solid was briefly sonicated in Et_2O (10 mL) and crude **58** (2.46 g, ~13.5 mmol, ~90% over two steps) was collected as a white solid by vacuum filtration. The crude **58** was dissolved in dry DCM (45 mL) followed by the addition of DCC (3.34 g, 16.2 mmol), DMAP (165 mg, 1.35 mmol), and allyl alcohol (1.4 mL, 20 mmol). The reaction mixture was stirred overnight at room temperature. The suspension was filtered through Celite® using DCM and the filtrate was concentrated in vacuo. Purification via FCC (pentane/DCM 1:1 to DCM) afforded **59** as a colourless oil (2.06 g, 9.27 mmol, 62% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.71 (dd, J = 8.4, 2.0 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.04 (ddt, J = 17.3, 10.5, 5.6 Hz, 1H), 5.40 (dq, J = 17.3, 1.6 Hz, 1H), 5.28 (dq, J = 10.4, 1.3 Hz, 1H), 4.81 (d, J = 5.6 Hz, 2H), 3.95 – 3.92 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 166.2, 153.2, 148.7, 132.6, 123.8, 122.8, 118.2, 112.1, 110.4, 65.6, 56.2, 56.1.

In accordance with literature.[47]

1,3-Dichloro-2-((2-(pent-4-en-1-yloxy)ethoxy)methyl)benzene (60)

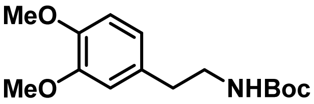


To a COtube was added NaH (90%, 413 mg, 15.5 mmol), dry THF (25 mL), and ethylene glycol (7.2 mL, 0.13 mol) dropwise at 0 °C. The mixture was allowed to reach room temperature followed by stirring for 30 minutes. The mixture was then cooled to 0 °C and 2,6-dichlorobenzyl bromide (3.10 g, 12.9 mmol) was added dropwise using dry THF (5 mL). The reaction mixture was heated to reflux and stirred overnight. After cooling to room temperature, the reaction mixture was quenched with a saturated NH_4Cl aqueous solution (30 mL) and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. The resultant residue was filtered through a short silica plug (heptane/EtOAc 7:3) to afford crude 2-((2,6-dichlorobenzyl)oxy)ethan-1-ol as a colourless oil (2.70 g, ~12.2 mmol, ~95%) which was used in the next step without further purification. A COtube charged with crude 2-((2,6-dichlorobenzyl)oxy)ethan-1-ol (2.67 g, ~12.1 mmol) was added dry DMF (15 mL) followed by NaH (90%, 436 mg, 18.2 mmol) using DMF (5 mL) at room temperature. The mixture was stirred for 30 min before being added 5-bromopentene (2.9 mL, 24 mmol) at room temperature. The reaction mixture was stirred overnight before being quenched with a saturated NH_4Cl aqueous solution (25 mL). The aqueous phase was extracted with Et_2O (3 x 25 mL) and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 9:1) afforded **60** as a colourless oil (2.60 g, 8.99 mmol, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.32 – 7.30 (m, 2H), 7.19 – 7.15 (m, 1H), 5.81 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.04 – 4.93 (m, 2H), 4.83 (s, 2H), 3.72 – 3.69 (m, 2H), 3.62 – 3.60 (m, 2H), 3.47 (t, J = 6.6 Hz, 2H), 2.14 – 2.08 (m, 2H), 1.71 – 1.64 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 138.3, 136.9, 133.4, 129.8, 128.3, 114.6, 70.6, 70.1, 70.0, 67.5, 30.2, 28.9.

In accordance with literature.[29]

tert-Butyl (3,4-dimethoxyphenethyl)carbamate (61)

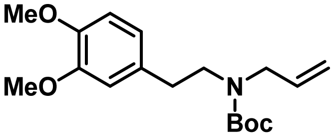


To a round-bottomed flask was added 3,4-dimethoxyphenethylamine (1.82 g, 10.0 mmol), dry THF (20 mL), Boc_2O (2.40 g, 11.0 mmol), and triethylamine (4.2 mL, 30 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature followed by stirring for 2 h. The reaction mixture was diluted with EtOAc (50 mL) and the organic phase was washed with 1 M HCl (3 x 25 mL), saturated $NaHCO_3$ (25 mL), and brine (25 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 1:1) afforded **61** as a white solid (2.67 g, 9.50 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.80 (d, *J* = 8.0 Hz, 1H), 6.73 – 6.70 (m, 2H), 4.56 (bs, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.34 (q, *J* = 6.8 Hz, 2H), 2.73 (t, *J* = 7.1 Hz, 2H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C 156.0, 149.1, 147.7, 131.6, 120.8, 112.1, 111.4, 79.3, 56.0, 55.9, 42.0, 35.9, 28.5.

In accordance with literature.[29]

tert-Butyl allyl(3,4-dimethoxyphenethyl)carbamate (62)



A round-bottomed flask was added *tert*-butyl (3,4-dimethoxyphenethyl)carbamate (2.67 g, 9.50 mmol), toluene (40 mL), allyl bromide (2.4 mL, 29 mmol), K_2CO_3 (1.71 g, 12.4 mmol), KOH (1.60 g, 28.5 mmol), and TBAB (306 mg, 0.950 mmol). The reaction mixture was stirred at 80 °C for 6 h. After cooling to room temperature, the reaction mixture was diluted with water (40 mL) and neutralized with 4 M HCl. The aqueous phase was extracted with toluene (3 x 40 mL) and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification via AFCC (heptane to heptane/EtOAc 4:1) afforded **62** as a colourless oil (2.66 g, 8.28 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) [rotameric mixture] δ_H 6.79 (d, *J* = 8.1 Hz, 1H), 6.75 – 6.64 (m, 2H), 5.82 – 5.68 (m, 1H), 5.16 – 5.03 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.82 – 3.68 (m, 2H), 3.43 – 3.28 (m, 2H), 2.82 – 2.68 (m, 2H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) [rotameric mixture] δ_C 155.5, 149.0, 147.6, 134.4, 132.1, 120.9, 116.5, 116.0, 112.2, 111.4, 79.6, 56.0, 55.9, 50.4, 49.7, 48.8, 34.8, 34.3, 28.5.

In accordance with literature.[29]

References

(1) Lima, F.; Sharma, U. K.; Grunenberg, L.; Saha, D.; Johannsen, S.; Sedelmeier, J.; Van der Eycken, E. V.; Ley, S. V. A Lewis Base Catalysis Approach for the Photoredox Activation of Boronic Acids and Esters. *Angew. Chem. Int. Ed.* **2017**, *56* (47), 15136–15140.

(2) Hofmann, M.; Hampel, N.; Kanzian, T.; Mayr, H. Electrophilic Alkylations in Neutral Aqueous or Alcoholic Solutions. *Angew. Chem. Int. Ed.* **2004**, *43* (40), 5402–5405.

(3) Tyler, J. L.; Noble, A.; Aggarwal, V. K. Strain-Release-Driven Friedel–Crafts Spirocyclization of Azabicyclo[1.1.0]butanes. *Angew. Chem. Int. Ed.* **2021**, *61* (3), e202114235.

(4) Knaus, T.; Mutti, F. G.; Humphreys, L. D.; Turner, N. J.; Scrutton, N. S. Systematic methodology for the development of biocatalytic hydrogen-borrowing cascades: application to the synthesis of chiral α-substituted carboxylic acids from α-substituted α,β-unsaturated aldehydes. *Org. Biomol. Chem.* **2015**, *13* (1), 223–233.

(5) Jefferies, L. R.; Cook, S. P. Iron-Catalyzed Arene Alkylation Reactions with Unactivated Secondary Alcohols. *Org. Lett.* **2014**, *16* (7), 2026–2029.

(6) Berthiol, F.; Doucet, H.; Santelli, M. Heck Reaction of Protected Alk-1-en-3-ol, -4-ols, -5-ol or -6-ol with Aryl Bromides Catalysed by a Palladium Complex Derived from a Tetraphosphine. *Synthesis* **2006**, *9*, 1518–1536.

(7) Rodríguez-Alvarado, M.; Russo, R.; Connell, N. D.; Brenner-Moyer, S. E. Design, organocatalytic synthesis, and bioactivity evaluation of enantiopure fluorinated LpxC inhibitors. *Org. Biomol. Chem.* **2020**, *18* (30), 5867–5878.

(8) Chowdari, N. S.; Barbas, C. F. Total Synthesis of LFA-1 Antagonist BIRT-377 via Organocatalytic Asymmetric Construction of a Quaternary Stereocenter. *Org. Lett.* **2005**, *7* (5), 867–870.

(9) Wu, F.-P.; Li, D.; Peng, J.-B.; Wu, X.-F. Carbonylative Transformation of Allylarenes with CO Surrogates: Tunable Synthesis of 4-Arylbutanoic Acids, 2-Arylbutanoic Acids, and 4-Arylbutanals. *Org. Lett.* **2019**, *21* (14), 5699–5703.

(10) Reddy, R. R.; Gudup, S. S.; Ghorai, P. Organocatalytic, Enantioselective Synthesis of Cyclohexadienone Containing Hindered Spirocyclic Ethers through an Oxidative Dearomatization/Oxa-Michael Addition Sequence. *Angew. Chem. Int. Ed.* **2016**, *55* (48), 15115–15119.

(11) Niermann, A.; Reissig, H.-U. 7-Siloxy-Substituted Hexahydronaphthalene Derivatives: Samarium Diiodide Promoted Synthesis and Typical Reactions. *Synthesis*, **2020**, *52* (18), 2721–2730.

(12) Vilches-Herrera, M.; Concha-Puelles, M.; Carvajal, N.; Molina, J.; Santander, R.; Rezende, M. C.; Lühr, S. Influence of the bite natural angle of bidentate diphosphine ligands in the syngas-

free branched hydroformylation of β-functionalized olefins. *Catal. Commun.* **2018**, *116*, 62–66.

(13) Stueckler, C.; Mueller, N. J.; Winkler, C. K.; Glueck, S. M.; Gruber, K.; Steinkellner, G.; Faber, K. Bioreduction of α-methylcinnamaldehyde derivatives: chemo-enzymatic asymmetric synthesis of Lilial™ and Helional™. *Dalton Trans.* **2010**, *39* (36), 8472–8576.

(14) Li, Y.-H.; Ouyang, Y.; Chekshin, N.; Yu, J.-Q. $\mathrm{Pd}^{\mathrm{II}}$–Catalyzed Site-selective β- and γ-C(sp^3)–H Arylation of Primary Aldehydes Controlled by Transient Directing Groups. *J. Am. Chem. Soc.* **2022**, *144* (11), 4727–4733.

(15) Liu, K.; Studer, A. Formal β-C−H Arylation of Aldehydes and Ketones by Cooperative Nickel and Photoredox Catalysis. *Angew. Chem. Int. Ed.* **2022**, *61* (31), e202206533.

(16) Liu, Z.; Vidović, D. Michael Additions Catalyzed by a β-Diketiminate-Supported Aluminum Complex. *J. Org. Chem.* **2018**, *83* (9), 5295–5300.

(17) Xu, B.; Lumb, J.-P.; Arndtsen, B. A. A TEMPO-Free Copper-Catalyzed Aerobic Oxidation of Alcohols. *Angew. Chem. Int. Ed.* **2015**, *54* (14), 4208–4211.

(18) Tuokko, S.; Pihko, P. M. Palladium on Charcoal as a Catalyst for Stoichiometric Chemo- and Stereoselective Hydrosilylations and Hydrogenations with Triethylsilane. *Org. Process Res. Dev.* **2014**, *18* (14), 1740–1751.

(19) Littke, A. F.; Fu, G. C. A Versatile Catalyst for Heck Reactions of Aryl Chlorides and Aryl Bromides under Mild Conditions. *J. Am. Chem. Soc.* **2001**, *123* (29), 6989–7000.

(20) Xiong, N.; Li, Y.; Zeng, R. Merging Photoinduced Iron-Catalyzed Decarboxylation with Copper Catalysis for C–N and C–C Couplings. *ACS Catal.* **2023**, *13* (3), 1678–1685.

(21) Cheng, C.; Brookhart, M. Efficient Reduction of Esters to Aldehydes through Iridium-Catalyzed Hydrosilylation. *Angew. Chem. Int. Ed.* **2012**, *51* (37), 9422–9424.

(22) Vyas, D. J.; Larionov, E.; Besnard, C.; Guénée, L.; Mazet, C. Isomerization of Terminal Epoxides by a [Pd–H] Catalyst: A Combined Experimental and Theoretical Mechanistic Study. *J. Am. Chem. Soc.* **2013**, *135* (16), 6177–6183.

(23) Morimoto, T.; Fujii, T.; Miyoshi, K.; Makado, G.; Tanimoto, H.; Nishiyama, Y.; Kakiuchi, K. Accessible protocol for asymmetric hydroformylation of vinylarenes using formaldehyde. *Org. Biomol. Chem.* **2015**, *13* (16), 4632–4636.

(24) Friest, J. A.; Maezato, Y.; Broussy, S.; Blum, P.; Berkowitz, D. B. Use of a Robust Dehydrogenase from an Archael Hyperthermophile in Asymmetric Catalysis−Dynamic Reductive Kinetic Resolution Entry into (S)-Profens. *J. Am. Chem. Soc.* **2010**, *132* (17), 5930–5931.

(25) Ren, W.; Chang, W.; Dai, J.; Shi, Y.; Li, J.; Shi, Y. An Effective Pd-Catalyzed Regioselective Hydroformylation of Olefins with Formic Acid. *J. Am. Chem. Soc.* **2016**, *138* (45), 14864–14867.

(26) Straub, A. T.; Otto, M.; Usui, I.; Breit, B. Room Temperature Ambient Pressure (RTAP)-Hydroformylation in Water Using a Self-Assembling Ligand. *Adv. Synth. Catal.* **2013**, *355* (10), 2071–2075.

(27) da Silva, J. G.; Barros, H. J. V.; dos Santos, E. N.; Gusevskaya, E. V. Rhodium catalyzed hydroformylation of linalool. *Appl. Catal. A: Gen.* **2006**, *309* (2), 169–176.

(28) Lambers, M.; Beijer, F. H.; Padron, J. M.; Toth, I.; de Vries, J. G. Highly Selective Hydroformylation of the Cinchona Alkaloids. *J. Org. Chem.* **2002**, *67* (14), 5022–5024.

(29) Pedersen, S. K.; Gudmundsson, H. G.; Nielsen, D. U.; Donslund, B. S.; Hammershøj, H. C. D.; Daasbjerg, K.; Skrydstrup, T. Main element chemistry enables gas-cylinder-free hydroformylations. *Nat. Catal.* **2020**, *3*, 843–850.

(30) Zhang, S.; Ullah, A.; Yamamoto, Y.; Bao, M. Palladium-Catalyzed Regioselective Allylation of Chloromethyl(hetero)arenes with Allyl Pinacolborate. *Adv. Synth. Catal.* **2017**, *359* (16), 2723–2728.

(31) Levin, M. D.; Toste, F. D. Gold-Catalyzed Allylation of Aryl Boronic Acids: Accessing Cross-Coupling Reactivity with Gold. *Angew. Chem. Int. Ed.* **2014**, *53* (24), 6211–6215.

(32) Occhialini, G.; Palani, V.; Wendlandt, A. E. Catalytic, *contra*-Thermodynamic Positional Alkene Isomerization. *J. Am. Chem. Soc.* **2022**, *144* (1), 145–152.

(33) Baron, O.; Knochel, P. Preparation and Selective Reactions of Mixed Bimetallic Aromatic and Heteroaromatic Boron–Magnesium Reagents. *Angew. Chem. Int. Ed.* **2005**, *44* (20), 3133–3135.

(34) Byatt, B. J.; Kato, A.; Pyne, S. G. Synthesis and Structural Revision of Glyphaeaside C. *Org. Lett.* **2021**, *23* (10), 4029–4033.

(35) Guérard, K. C.; Guérinot, A.; Bouchard-Aubin, C.; Ménard, M.-A.; Lepage, M.; Beaulieu, M. A.; Canesi, S. Oxidative 1,2- and 1,3-Alkyl Shift Processes: Developments and Applications in Synthesis. *J. Org. Chem.* **2012**, *77* (5), 2121–2133.

(36) Min, G. K.; Bjerglund, K.; Kramer, S.; Gøgsig, T. M.; Lindhardt, A. T.; Skrydstrup, T. Generation of Stoichiometric Ethylene and Isotopic Derivatives and Application in Transition-Metal-Catalyzed Vinylation and Enyne Metathesis. *Chem. Eur. J.* **2013**, *19* (51), 17603–17607.

(37) Bergami, M.; Protti, S.; Ravelli, D.; Fagnoni, M. Flow Metal-Free Ar–C Bond Formation *via* Photogenerated Phenyl Cations. *Adv. Synth. Catal.* **2016**, *358* (7), 1164–1172.

(38) Doobary, S.; Sedikides, A. T.; Caldora, H. P.; Poole, D. L.; Lennox, A. J. J. Electrochemical Vicinal Difluorination of Alkenes: Scalable and Amenable to Electron-Rich Substrates. *Angew. Chem. Int. Ed.* **2019**, *59* (3), 1155–1160.

(39) Albarrán-Velo, J.; Gotor-Fernández, V.; Lavandera, I. Markovnikov Wacker-Tsuji Oxidation of Allyl(hetero)arenes and Application in a One-Pot Photo-Metal-Biocatalytic Approach to Enantioenriched Amines and Alcohols. *Adv. Synth. Catal.* **2021**, *363* (16), 4096–4108.

(40) Corcé, V.; Chamoreau, L.-M.; Derat, E.; Goddard, J.-P.; Ollivier, C.; Fensterbank, L. Silicates as Latent Alkyl Radical Precursors: Visible-Light Photocatalytic Oxidation of Hypervalent Bis-Catecholato Silicon Compounds. *Angew. Chem. Int. Ed.* **2015**, *54* (39), 11414–11418.

(41) Lazzaroni, S.; Dondi, D.; Fagnoni, M.; Albini, A. Photochemical Arylation Reactions by 4-Chlorothioanisole. *Eur. J. Org. Chem.* **2007**, *2007* (26), 4360–4365.

(42) Nagasawa, S.; Sasano, Y.; Iwabuchi, Y. Catalytic Oxygenative Allylic Transposition of Alkenes into Enones with an Azaadamantane-Type Oxoammonium Salt Catalyst. *Chem. Eur. J.* **2017**, *23* (43), 10276–10279.

(43) Oh, H.; Park, A.; Jeong, K.-S.; Han, S. B.; Lee, H. Copper-Catalyzed 1,2-Bistrifluoromethylation of Terminal Alkenes. *Adv. Synth. Catal.* **2019**, *361* (9), 2136–2140.

(44) Falk, E.; Makai, S.; Delcaillau, T.; Gürtler, L.; Morandi, B. Design and Scalable Synthesis of *N*-Alkylhydroxylamine Reagents for the Direct Iron-Catalyzed Installation of Medicinally Relevant Amines. *Angew. Chem. Int. Ed.* **2020**, *59* (47), 21064–21071.

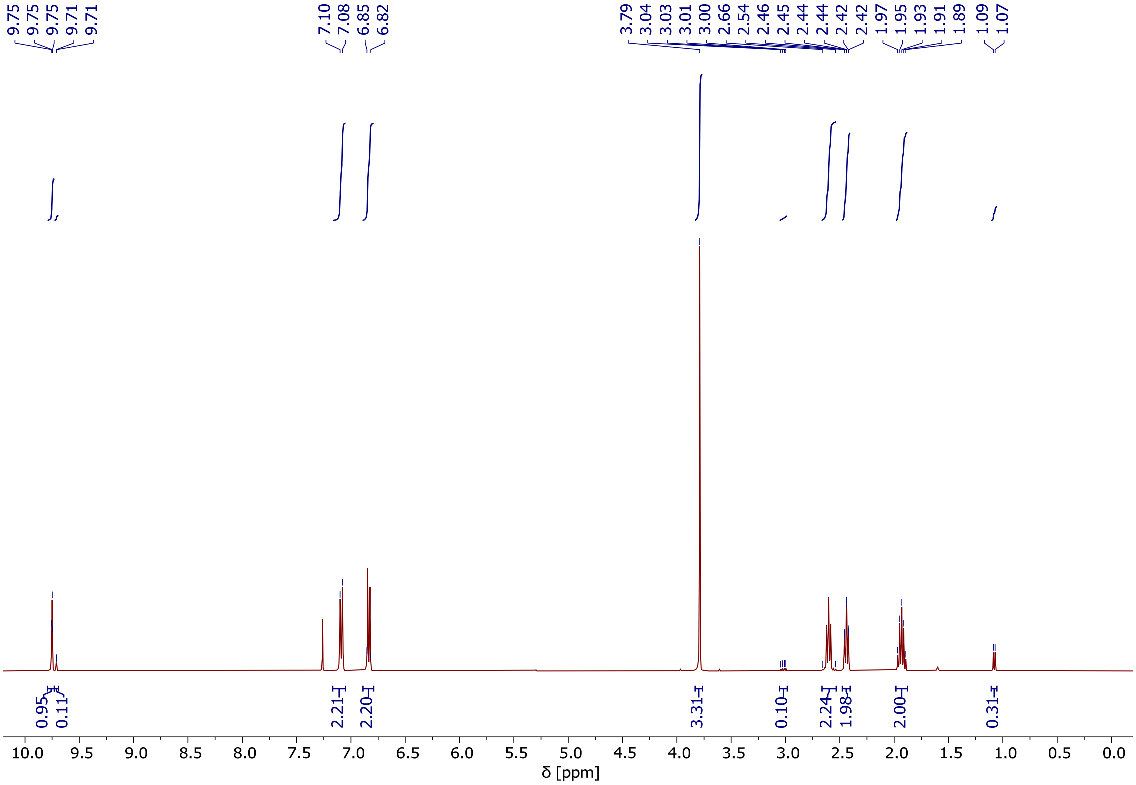
(45) Bianchini, R.; Catelani, G.; Cecconi, R.; D'Andrea, F.; Guazzelli, L.; Isaad, J.; Rolla, M. Ethereal Glycoconjugated Azodyes (GADs): A New Group of Water-Soluble, Naturalised Dyes. *Eur. J. Org. Chem.* **2008**, *2008* (3), 444–454.

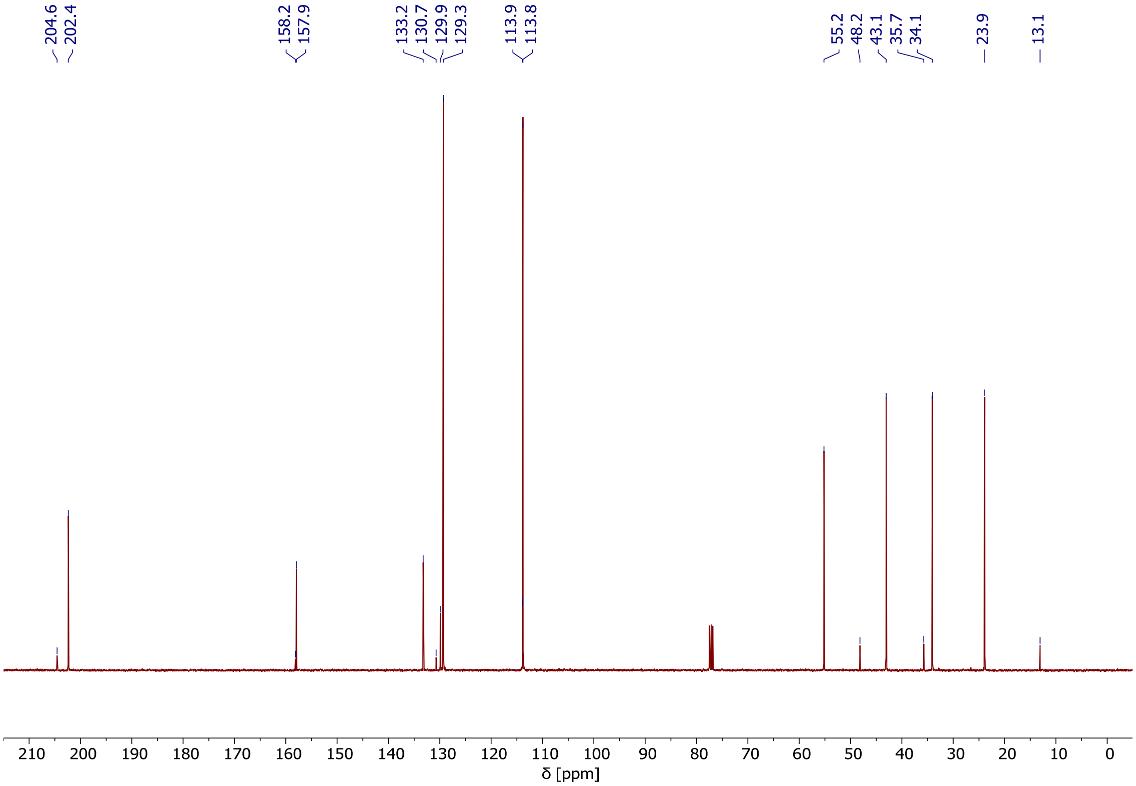
(46) Dionne, P.; Ngatcha, B. T.; Poirier, D. D-ring allyl derivatives of 17β- and 17α-estradiols: Chemical synthesis and ^{13}C NMR data. *Steroids* **1997**, *62* (10), 674–681.

(47) Tu, H.-Y.; Wang, F.; Huo, L.; Li, Y.; Zhu, S.; Zhao, X.; Li, H.; Qing, F.-L.; Chu, L. Enantioselective Three-Component Fluoroalkylarylation of Unactivated Olefins through Nickel-Catalyzed Cross-Electrophile Coupling. *J. Am. Chem. Soc.* **2020**, *142* (21), 9604–9611.

NMR Spectra

1 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]





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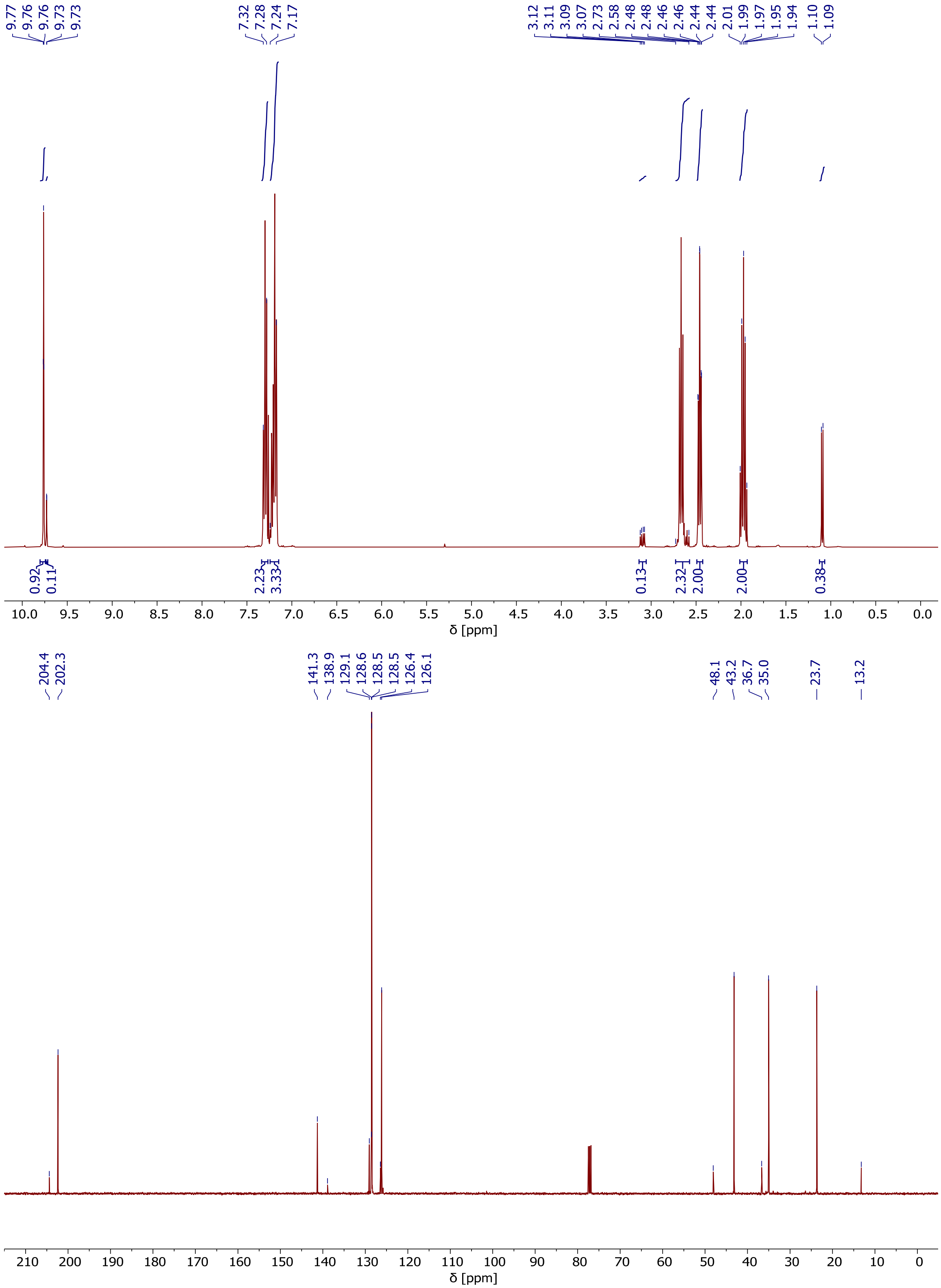

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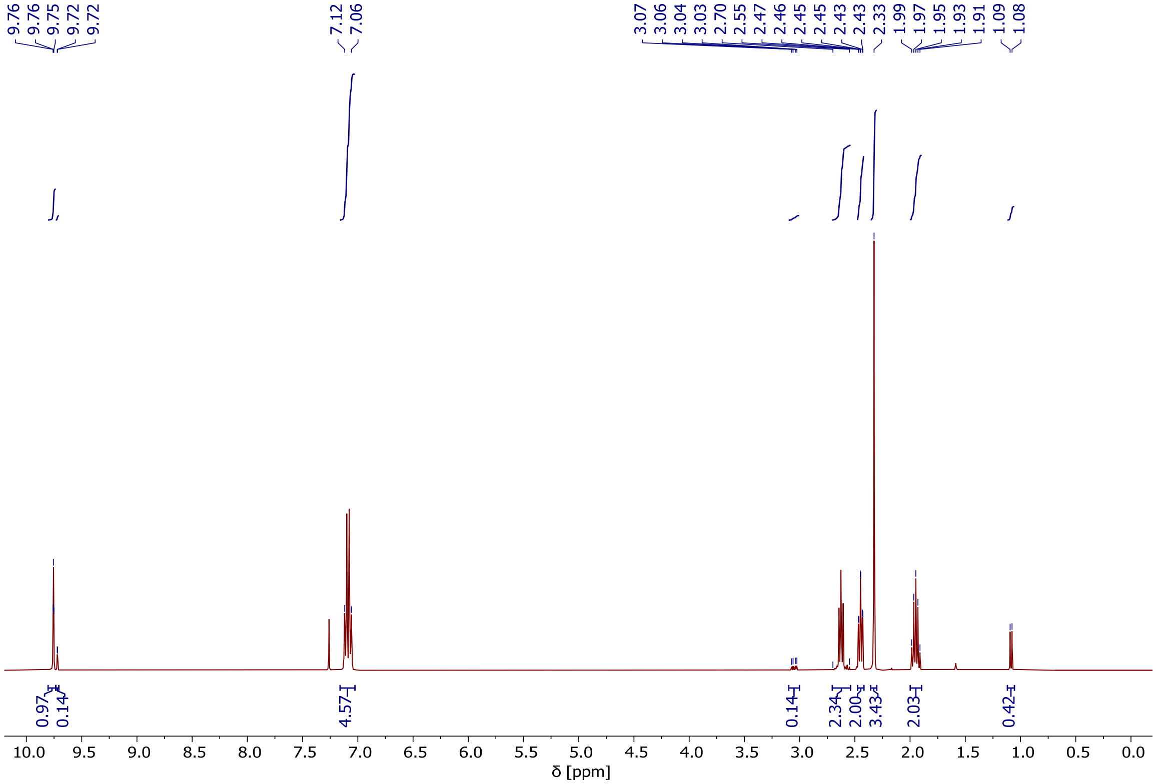
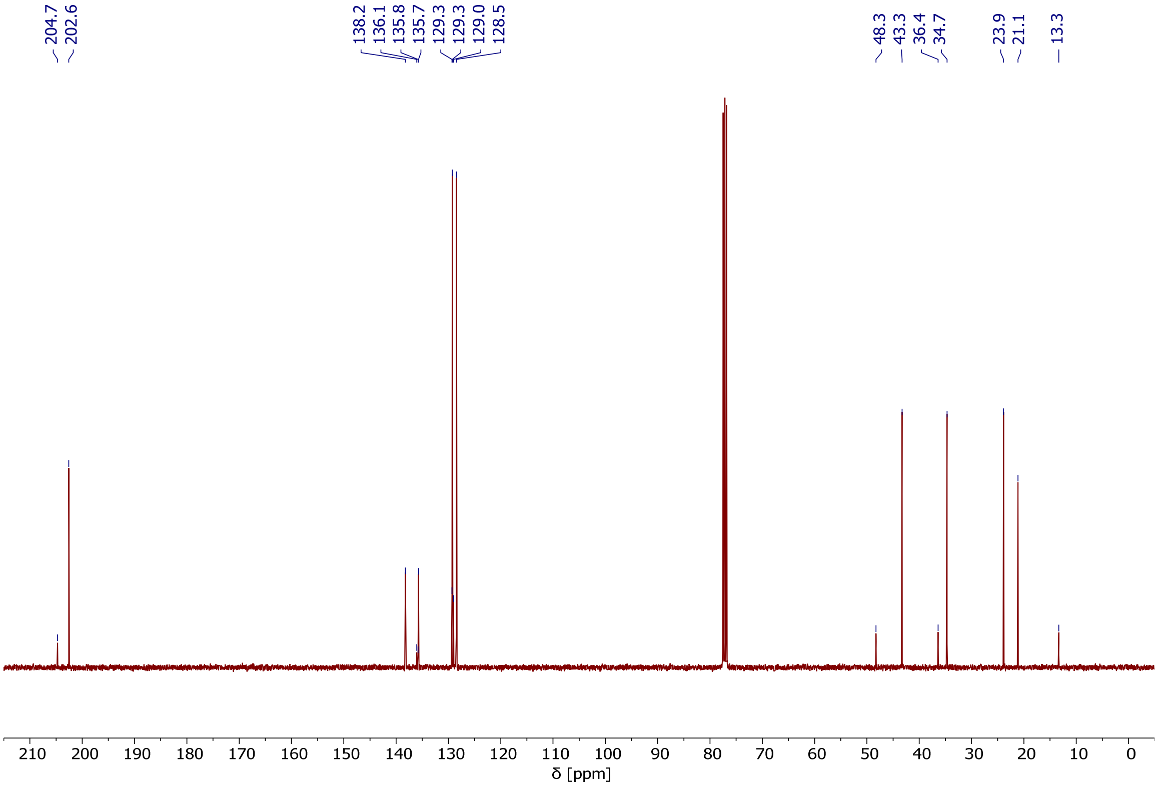
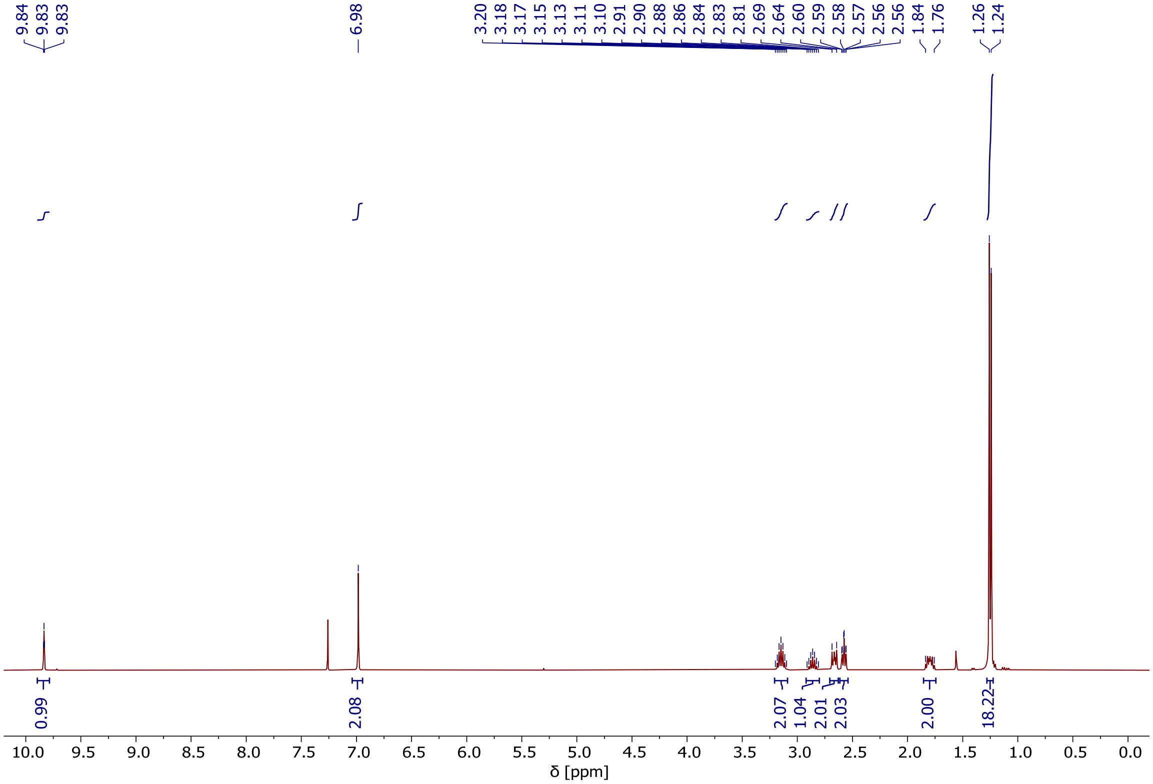
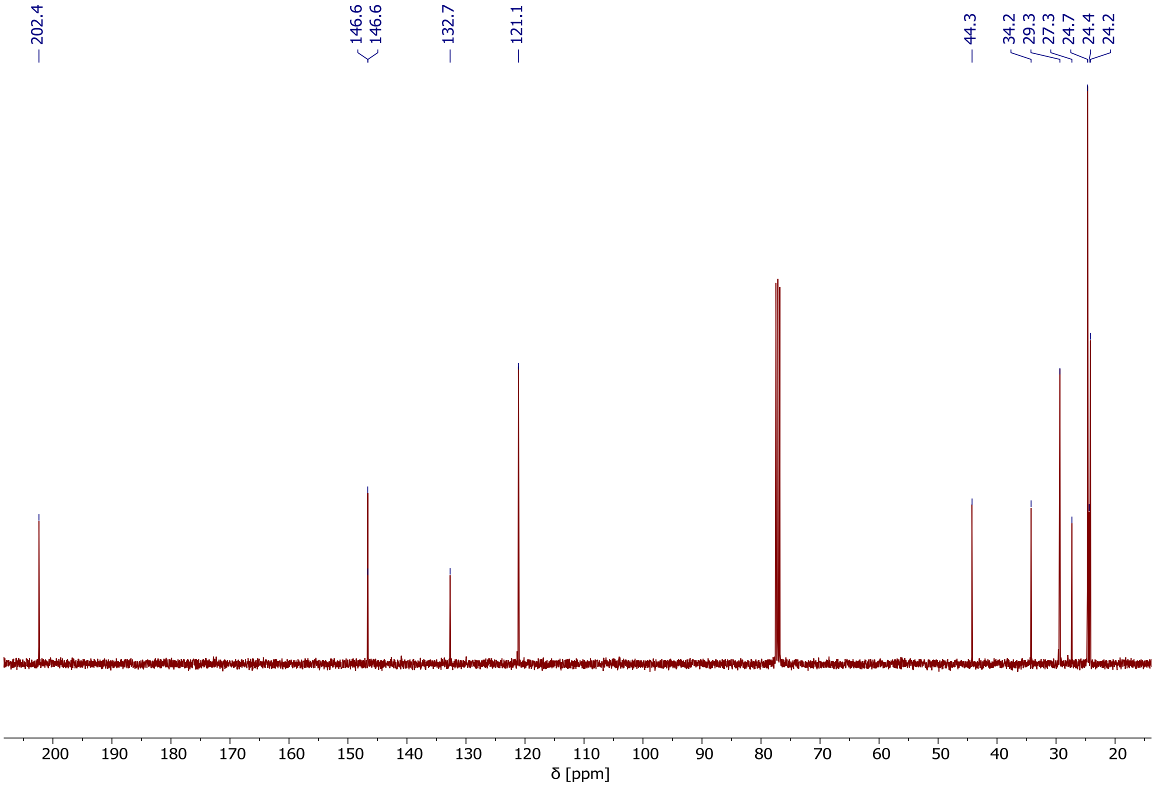
3 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



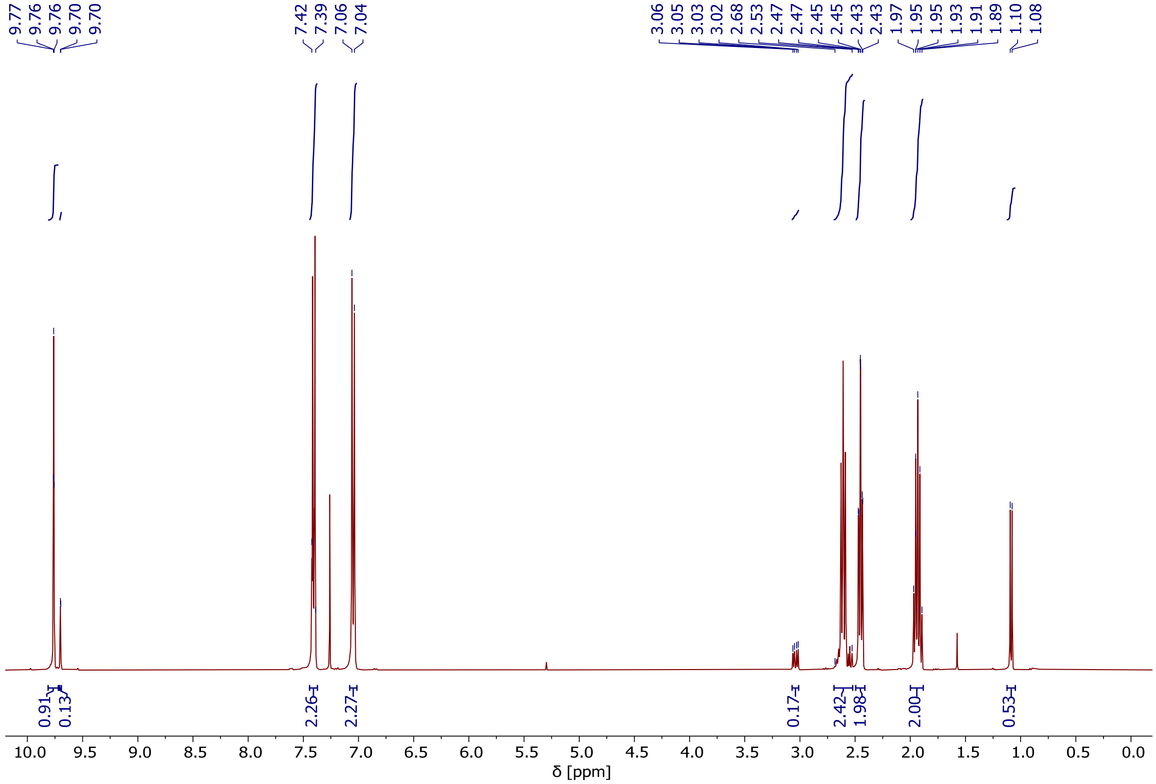


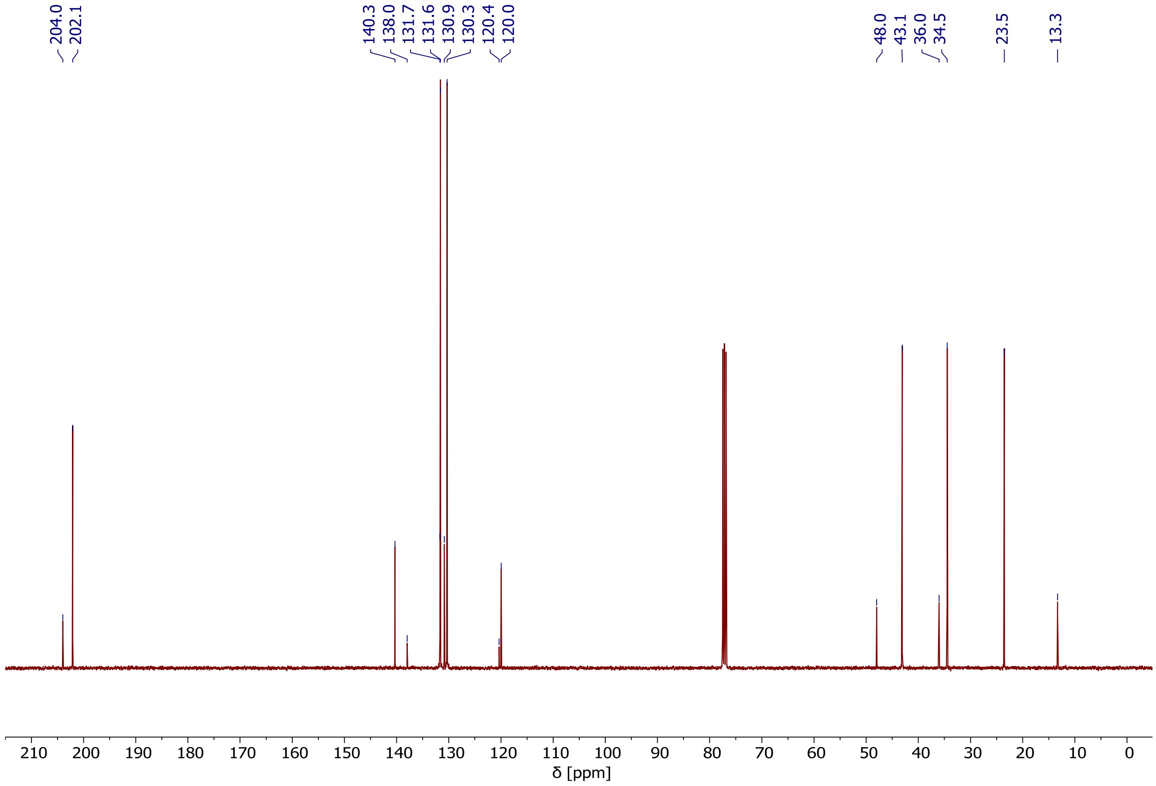
4 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



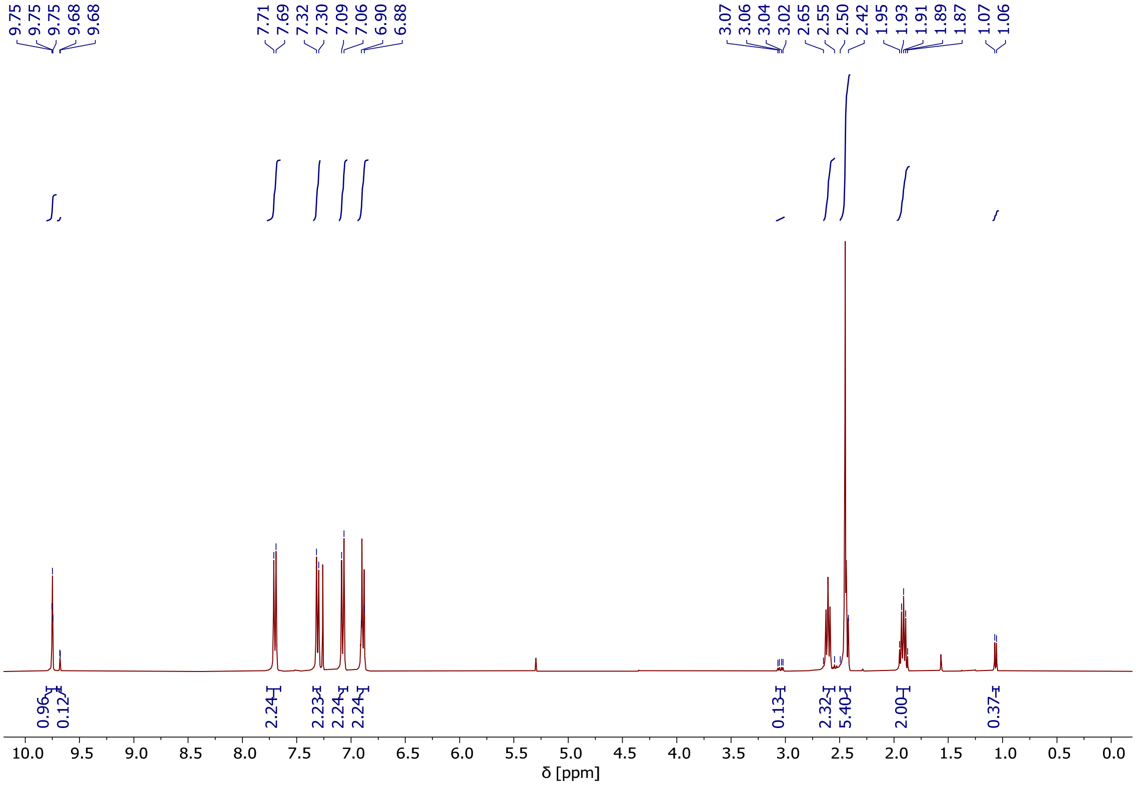


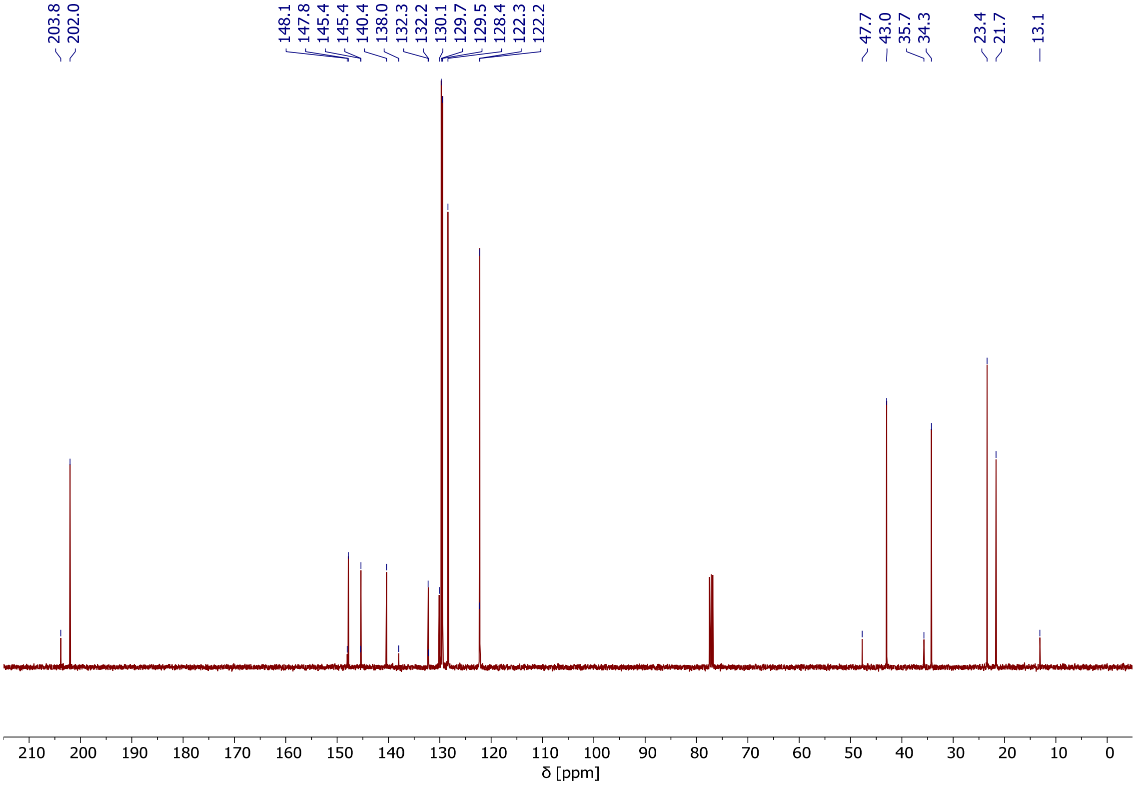
5 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



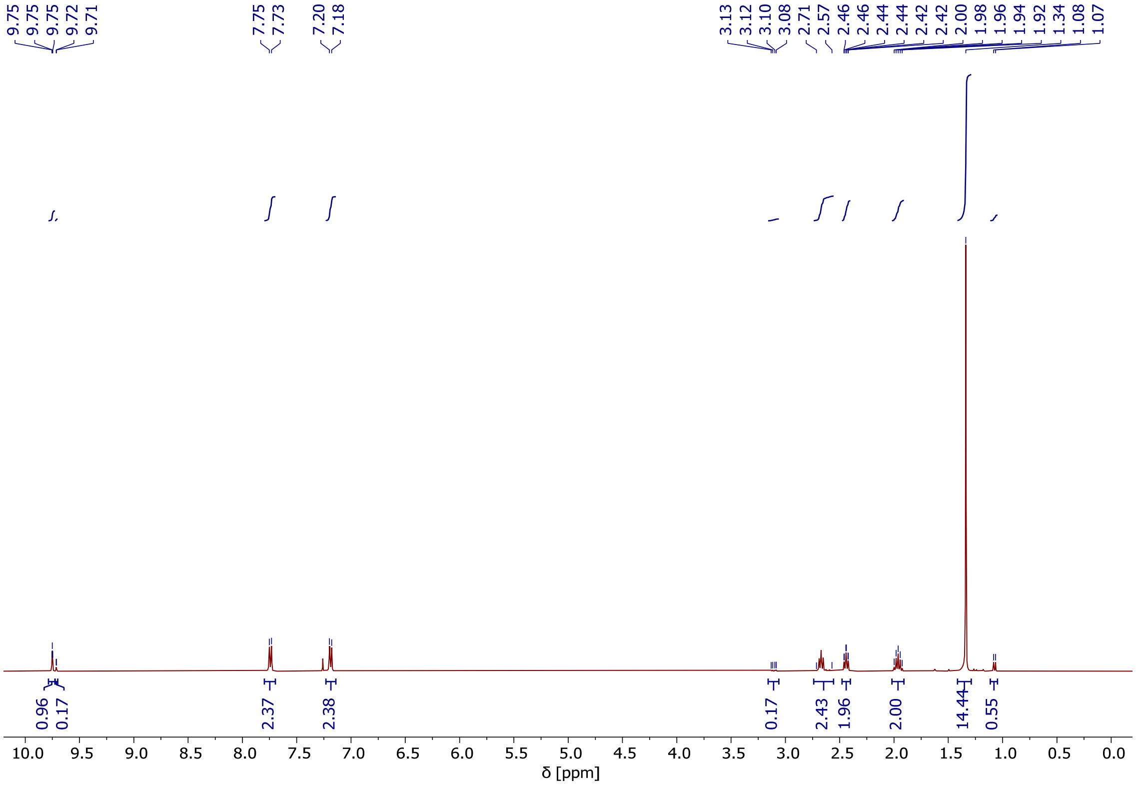


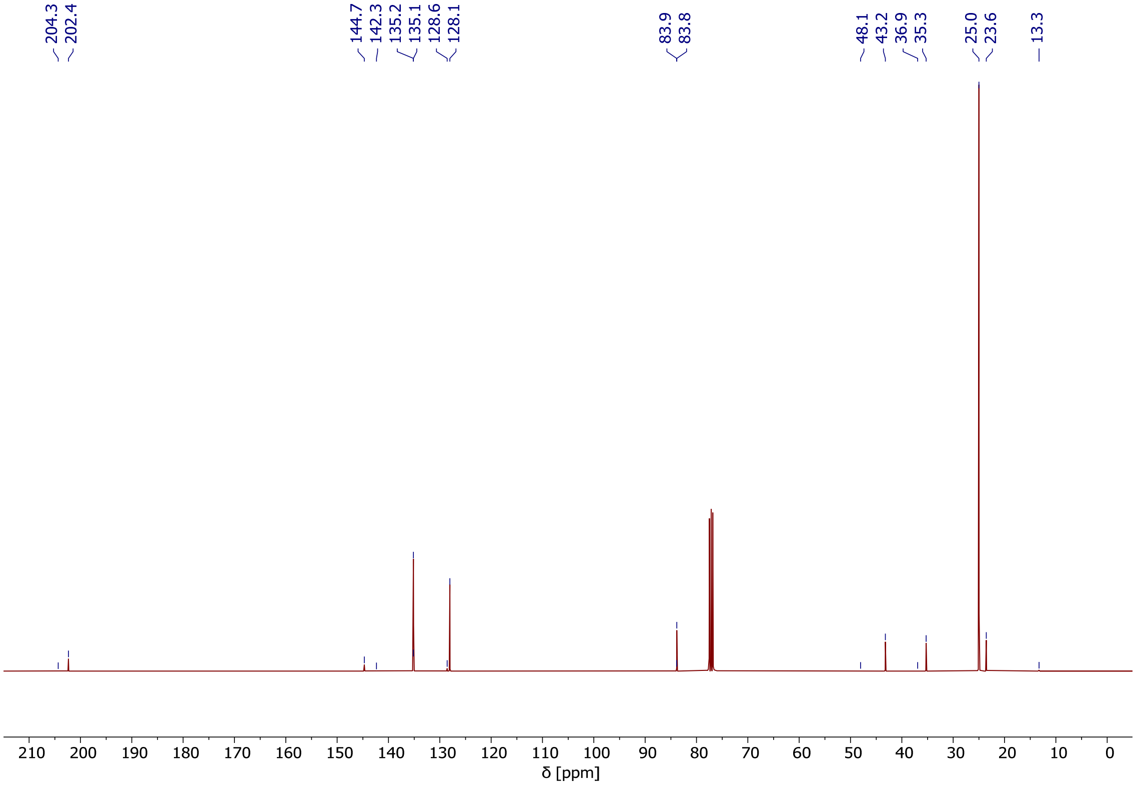
6 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



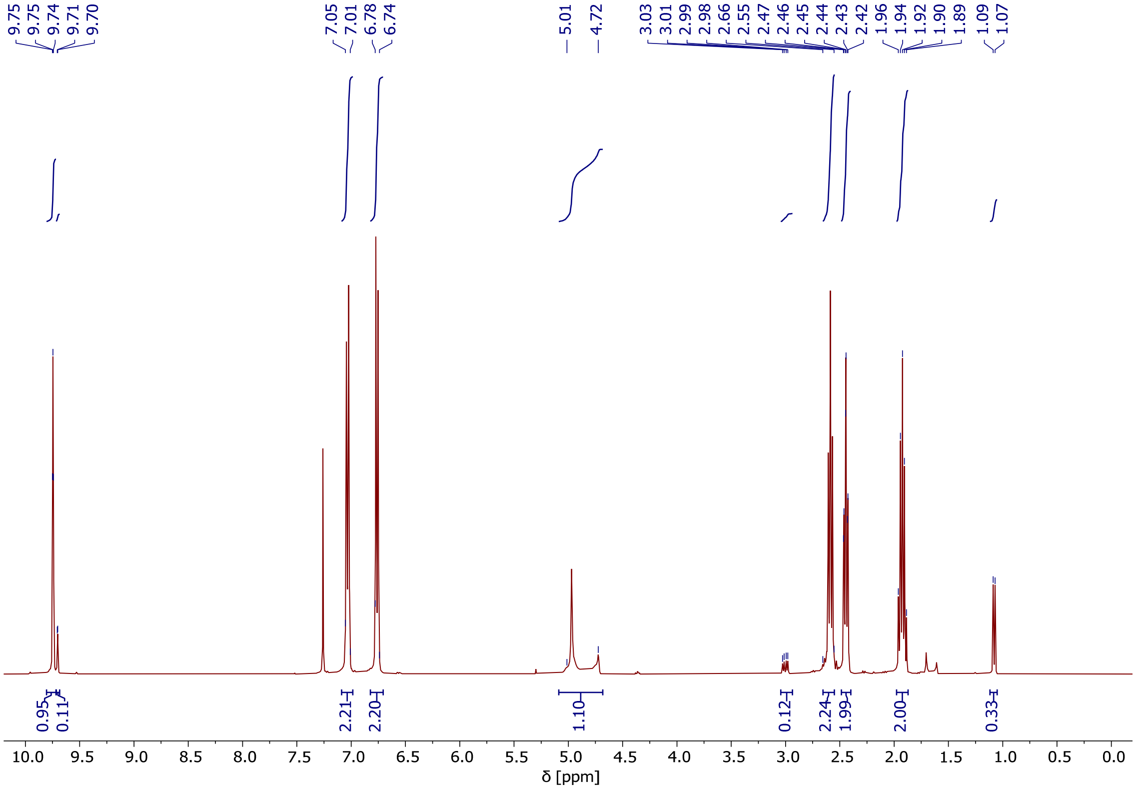


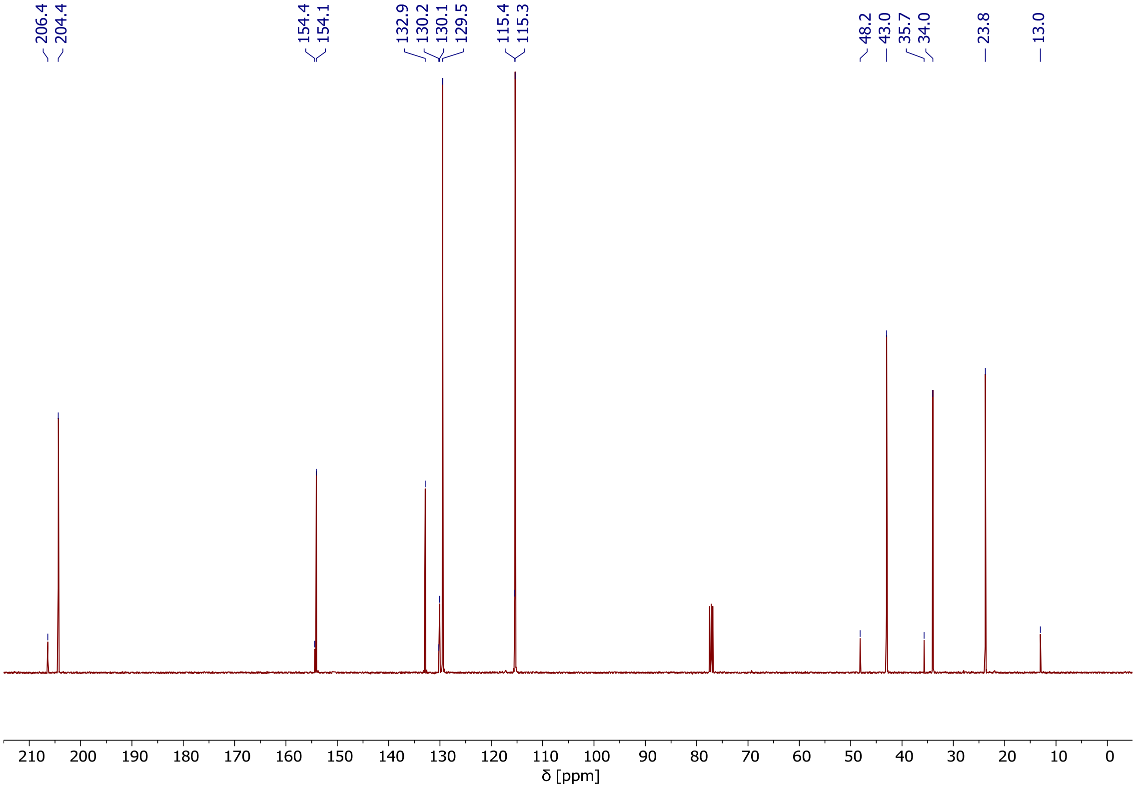
7 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



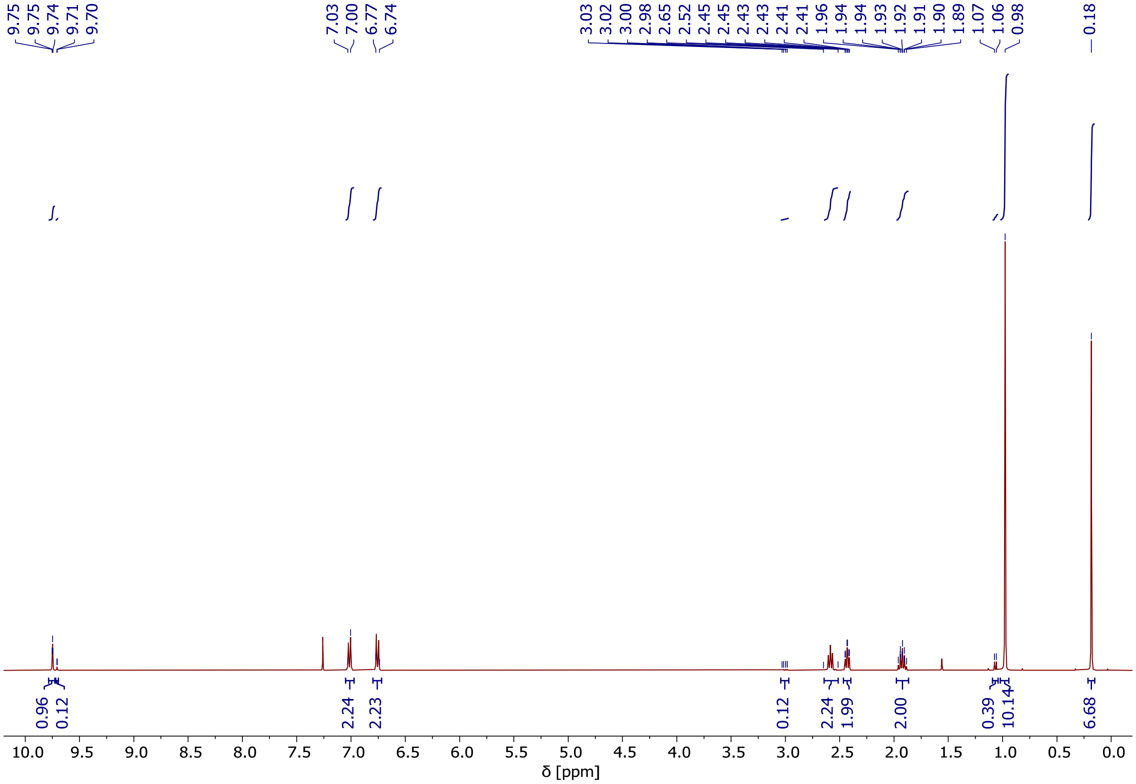


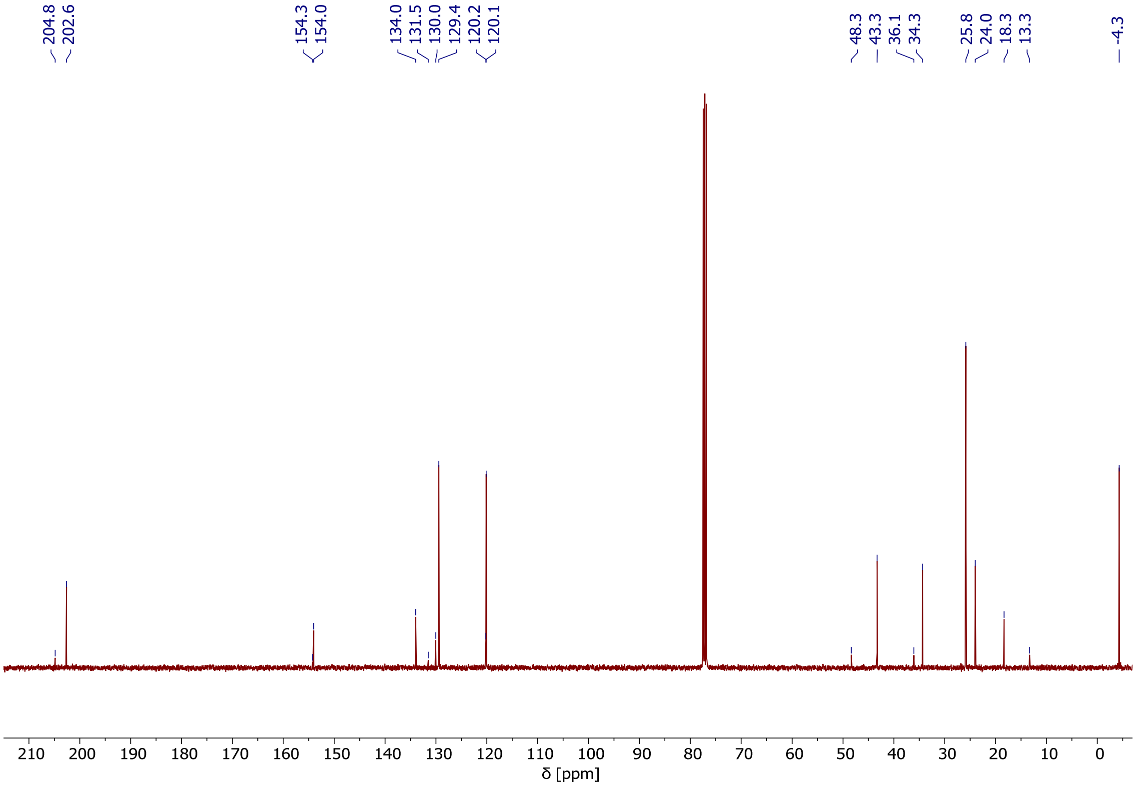
8 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



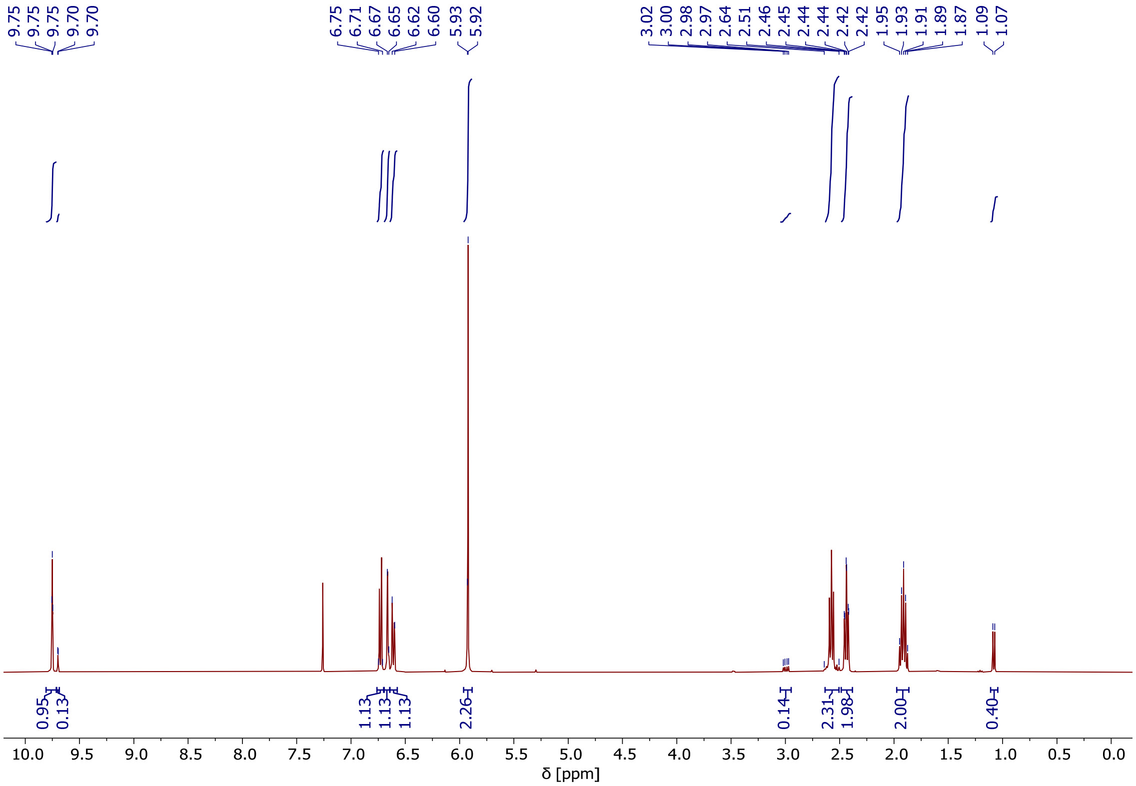


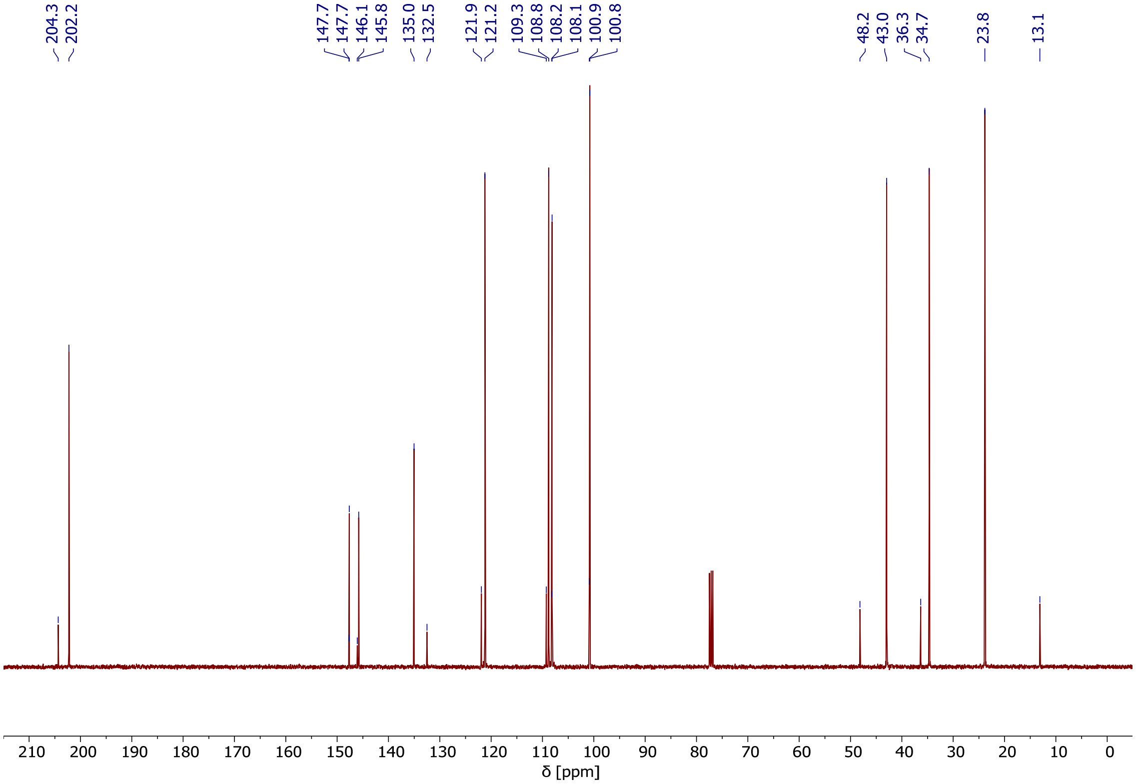
9 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



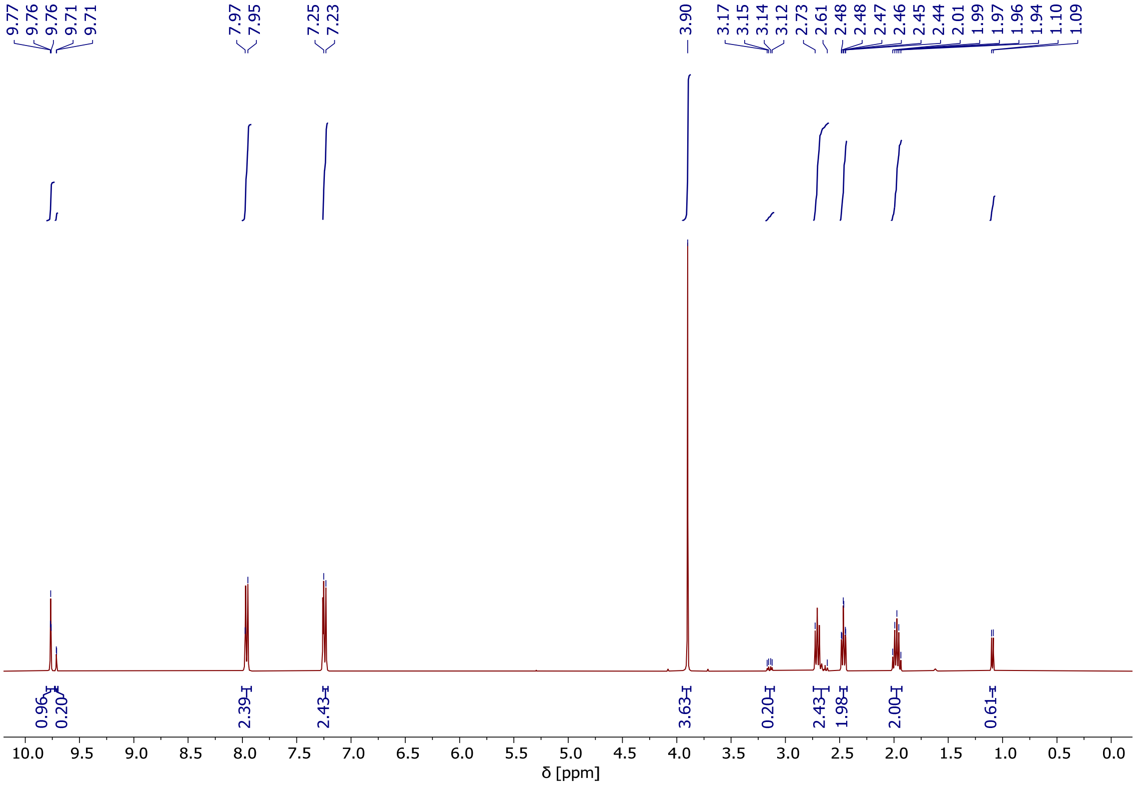


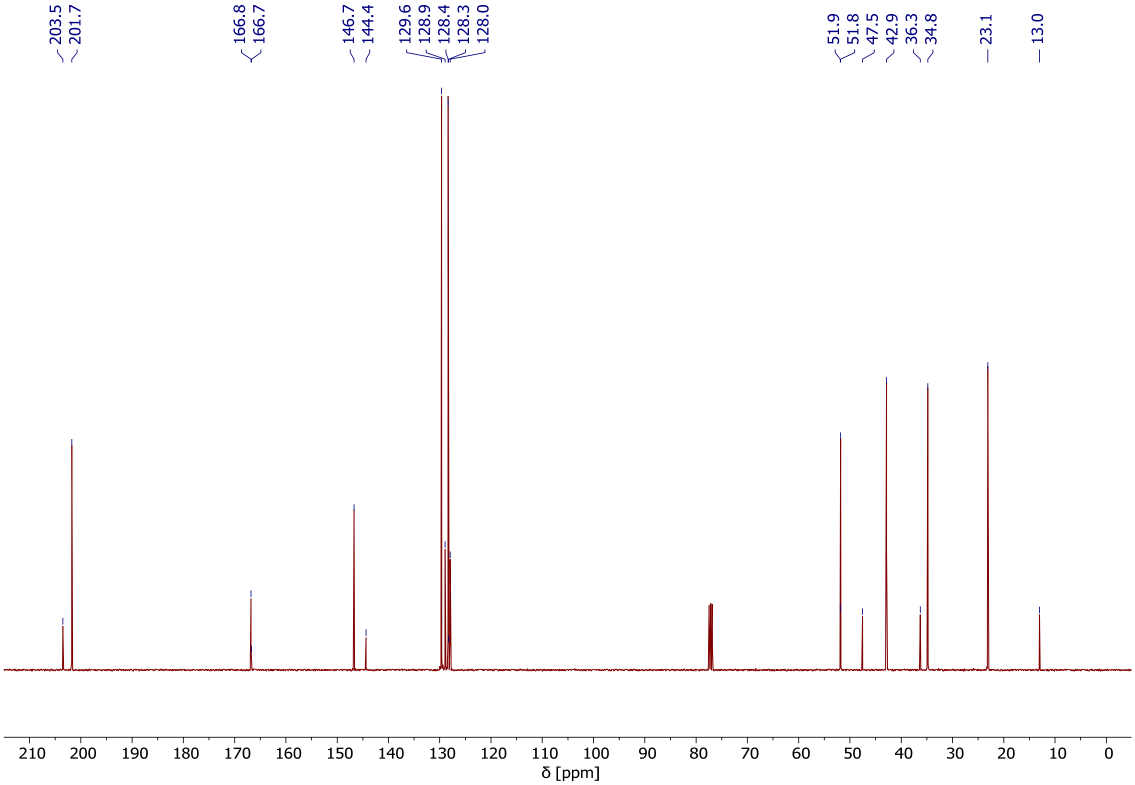
10 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



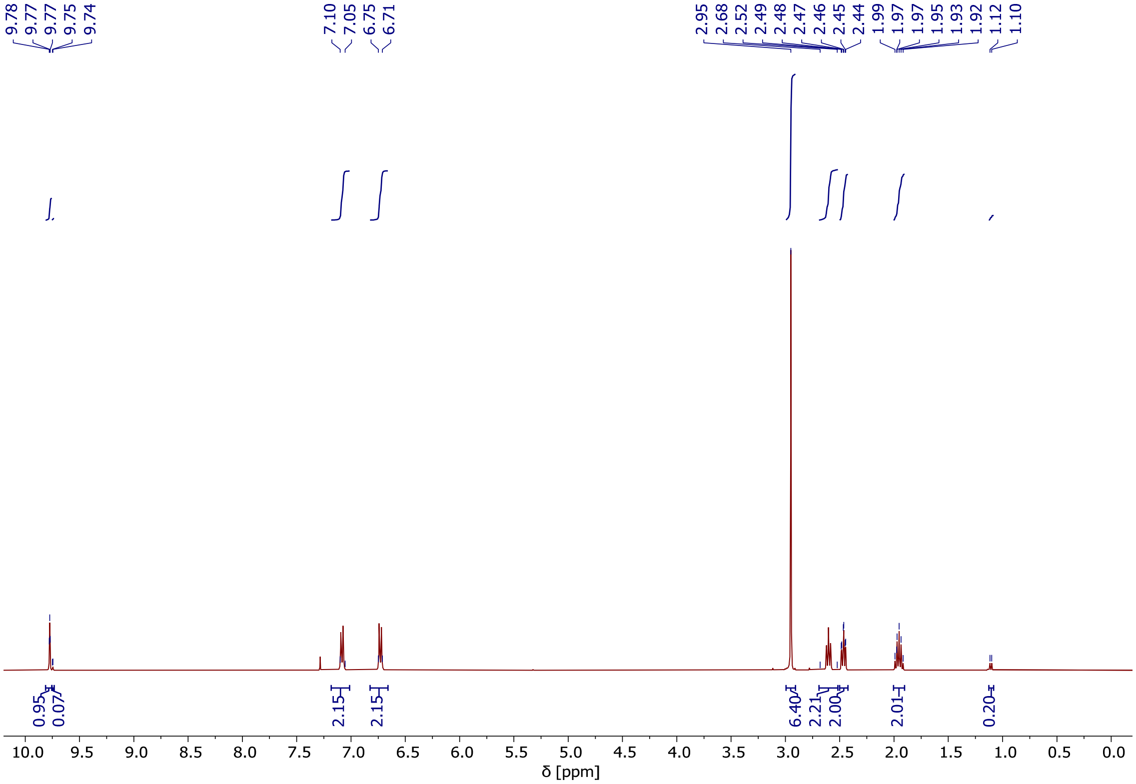


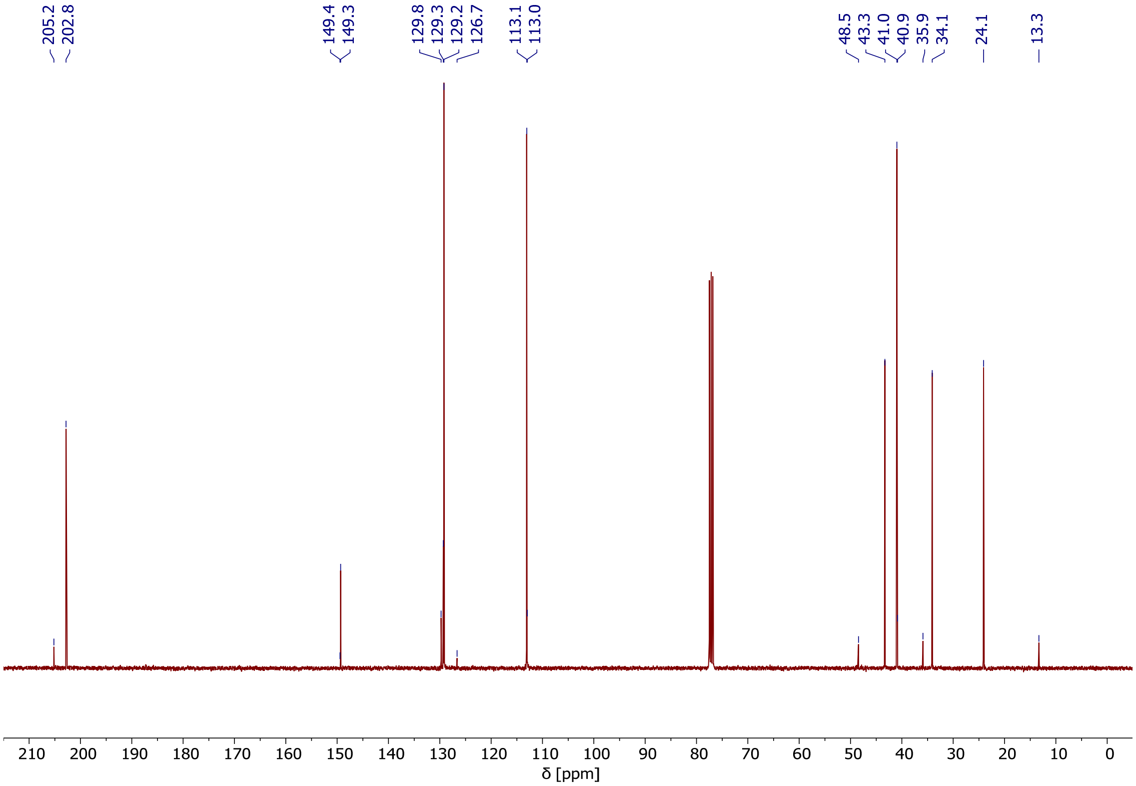
11 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



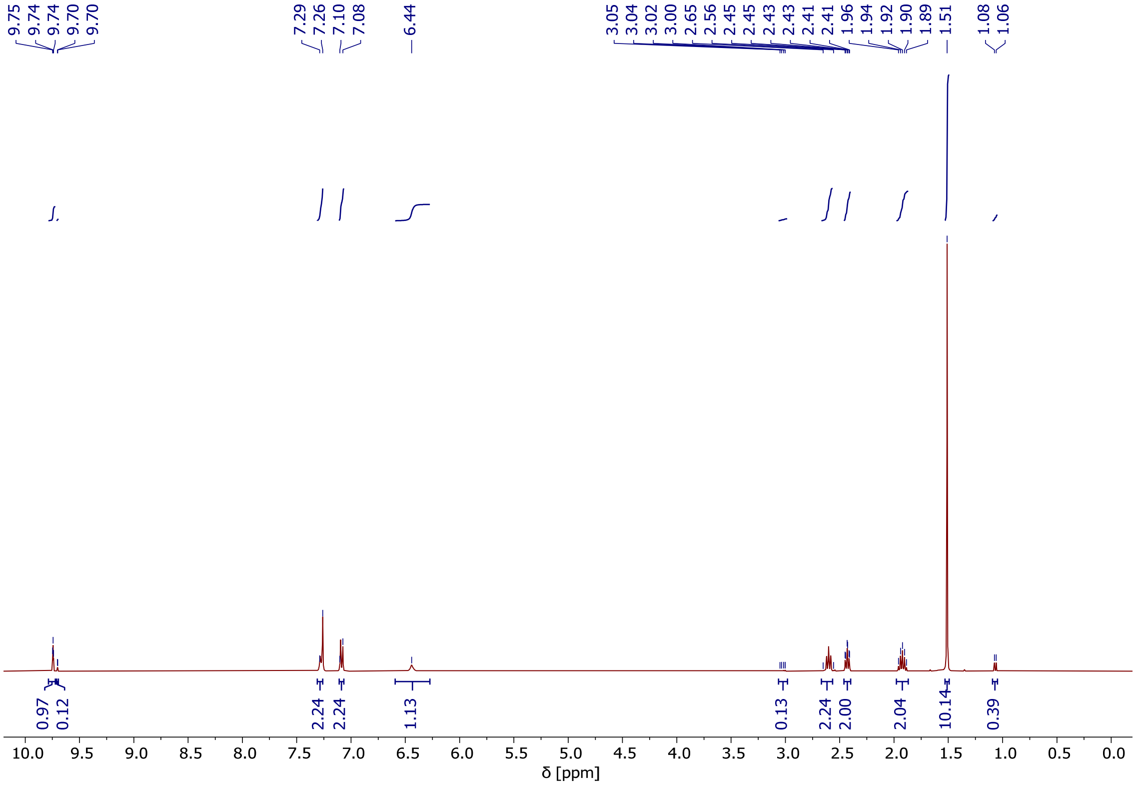


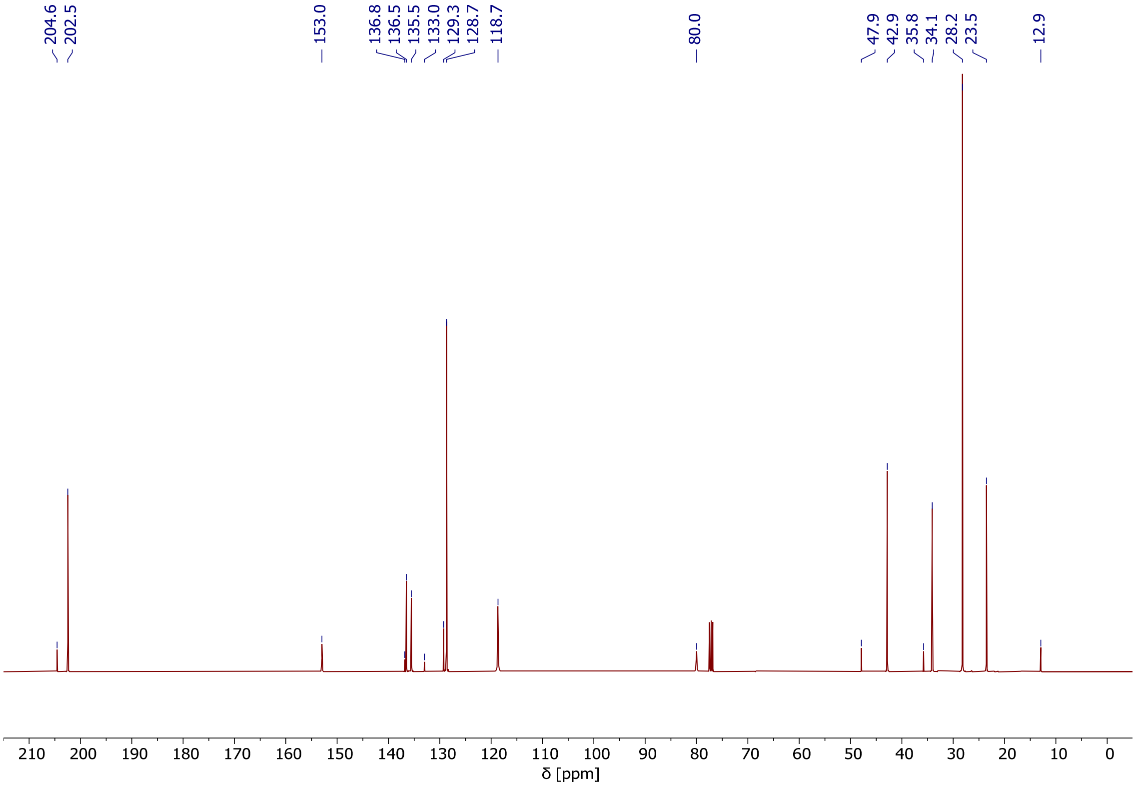
12 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



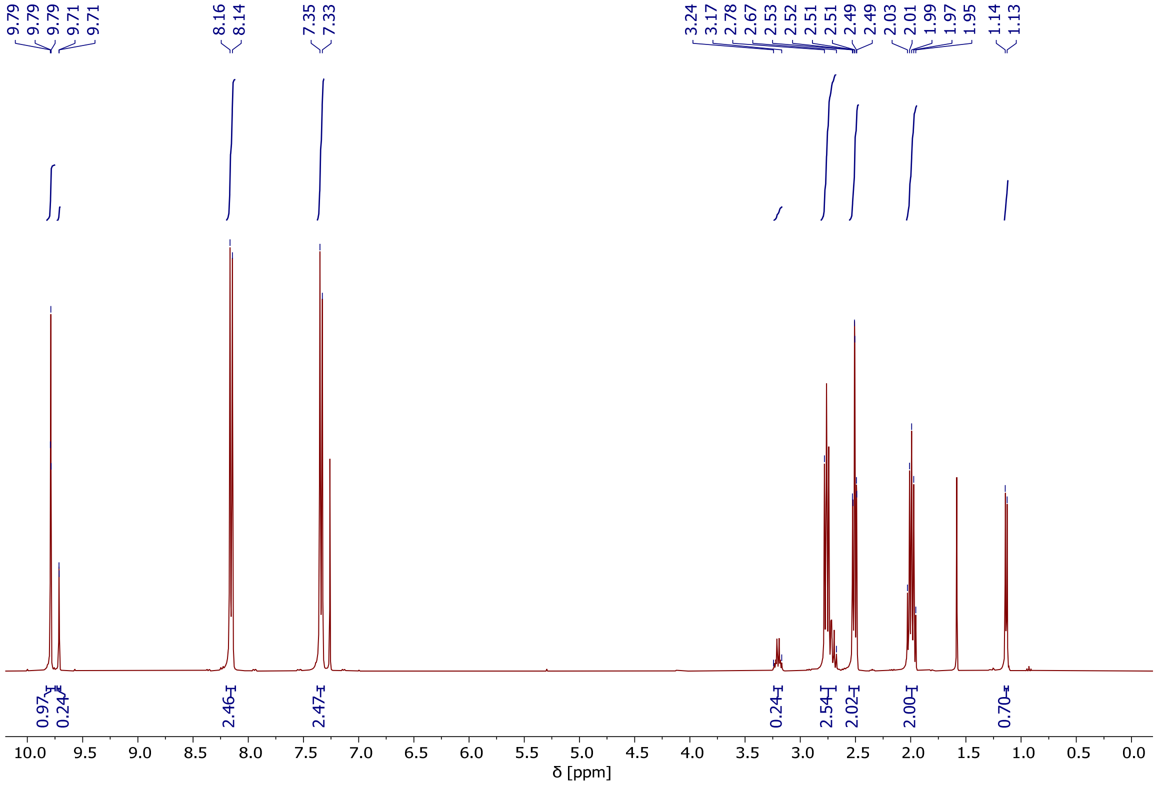


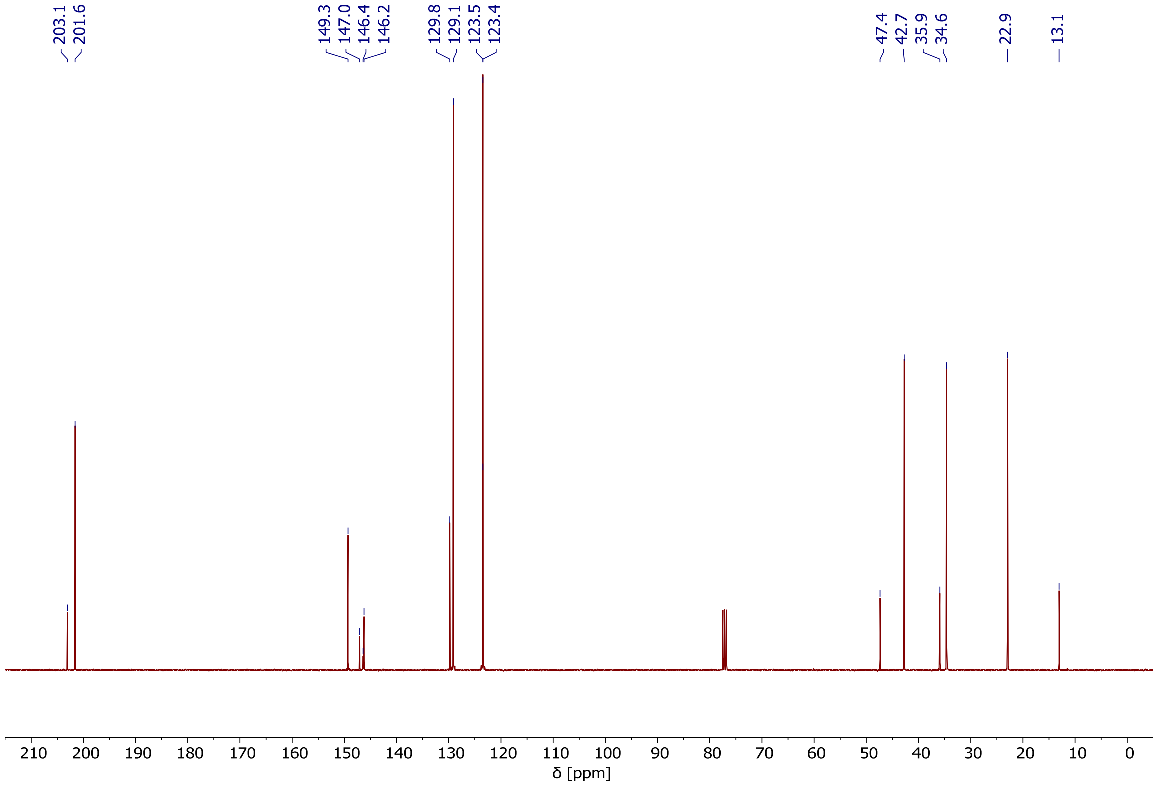
13 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



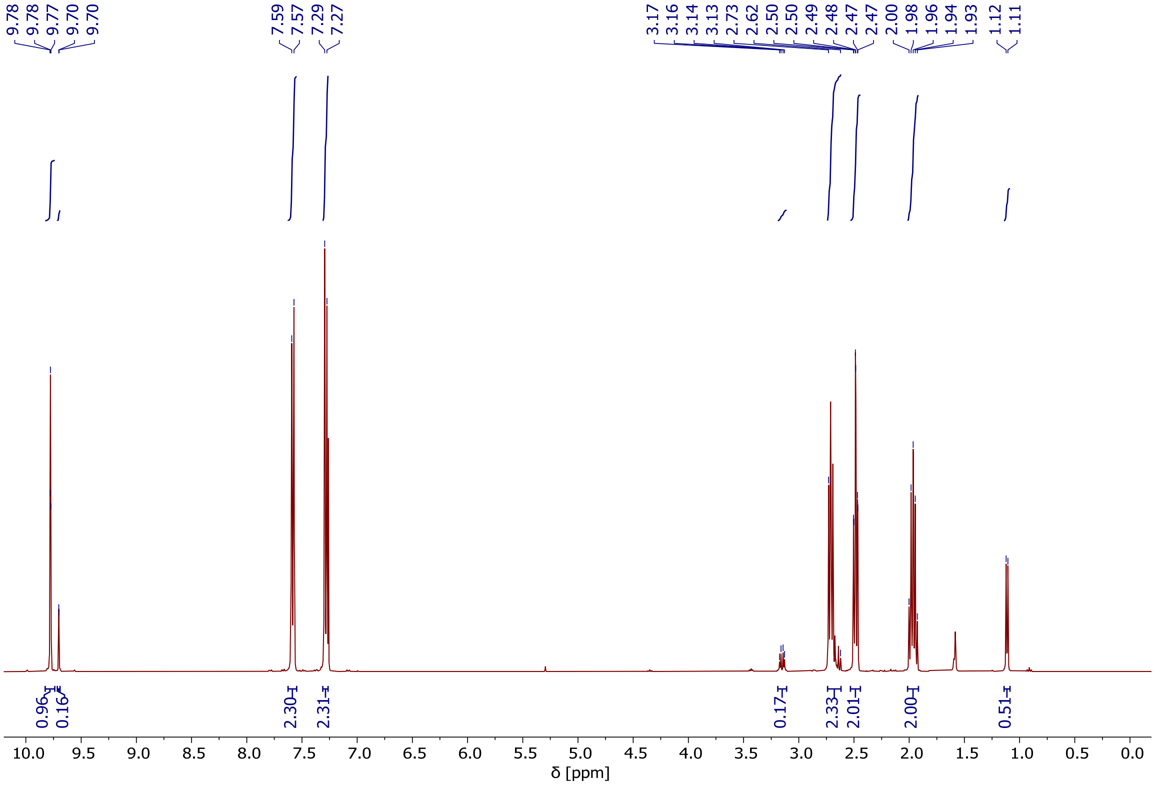


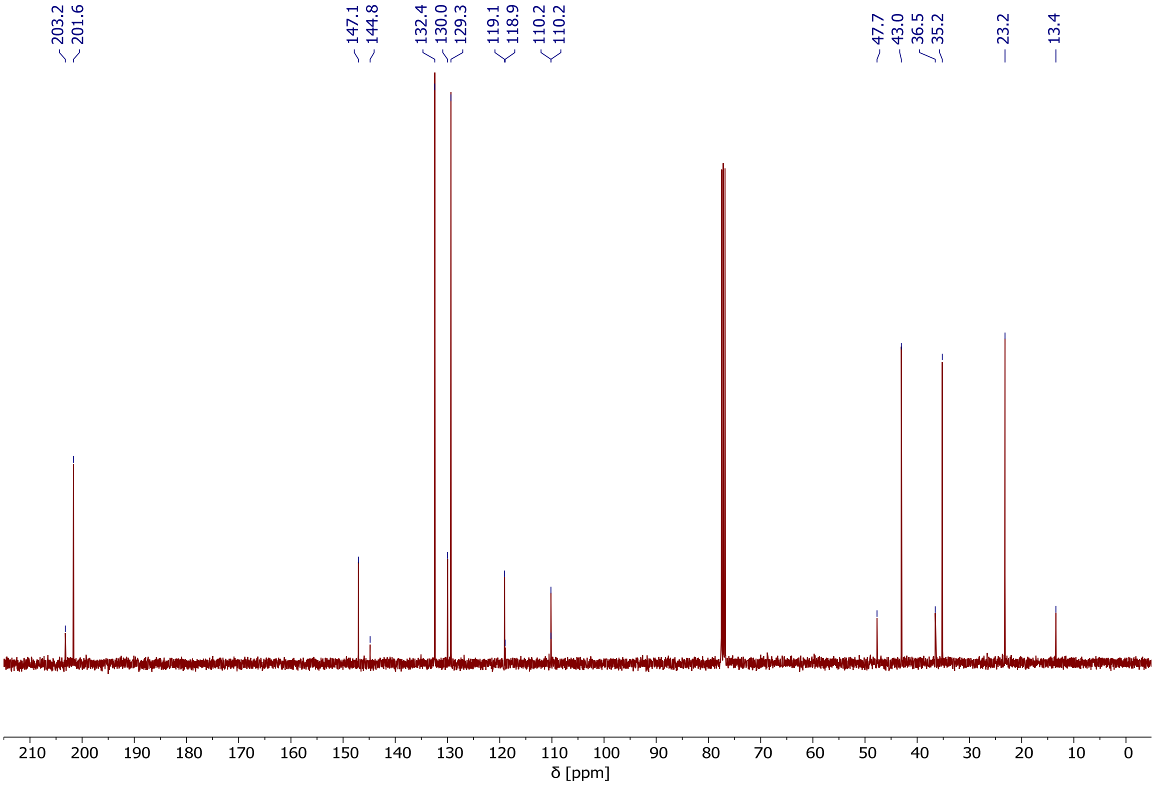
14 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]s



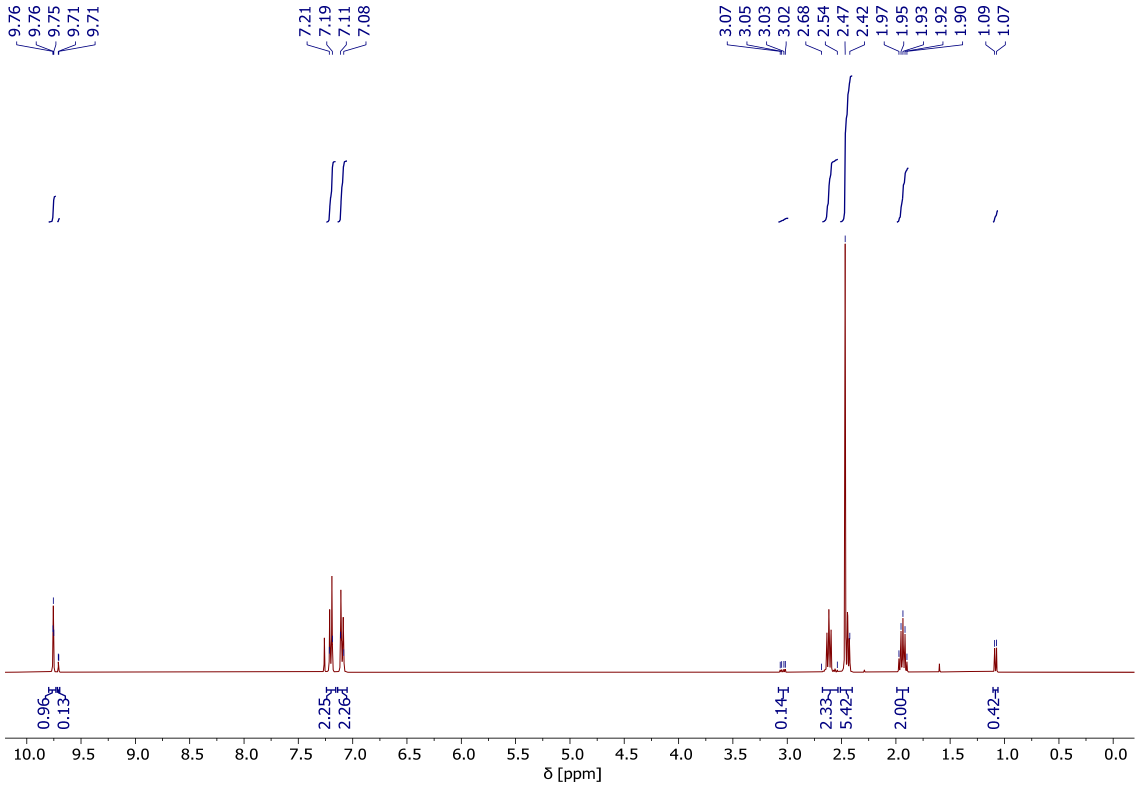


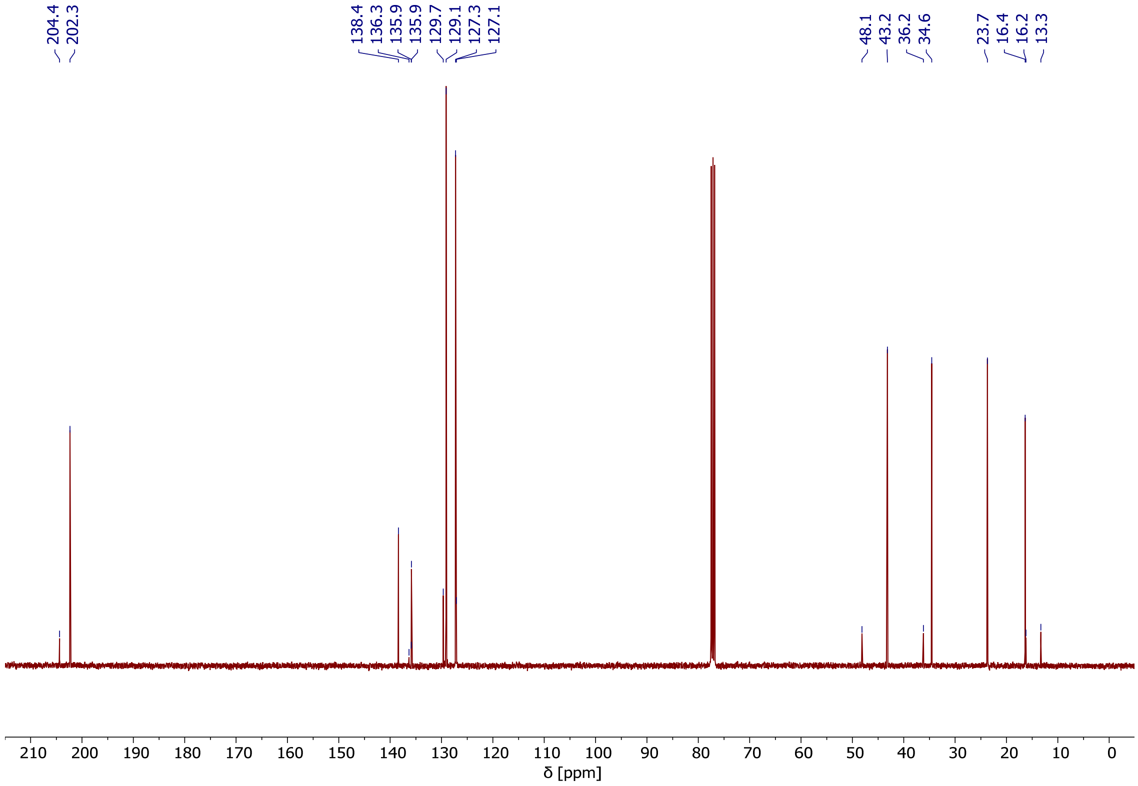
15 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



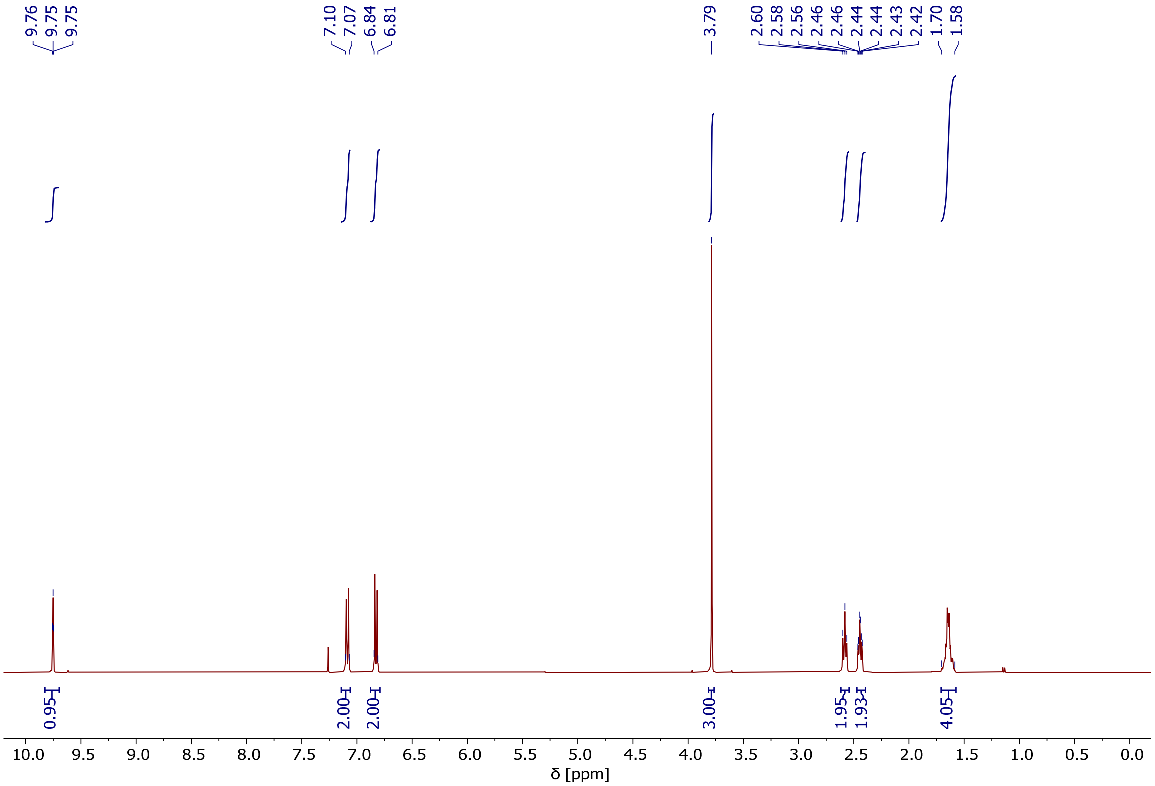


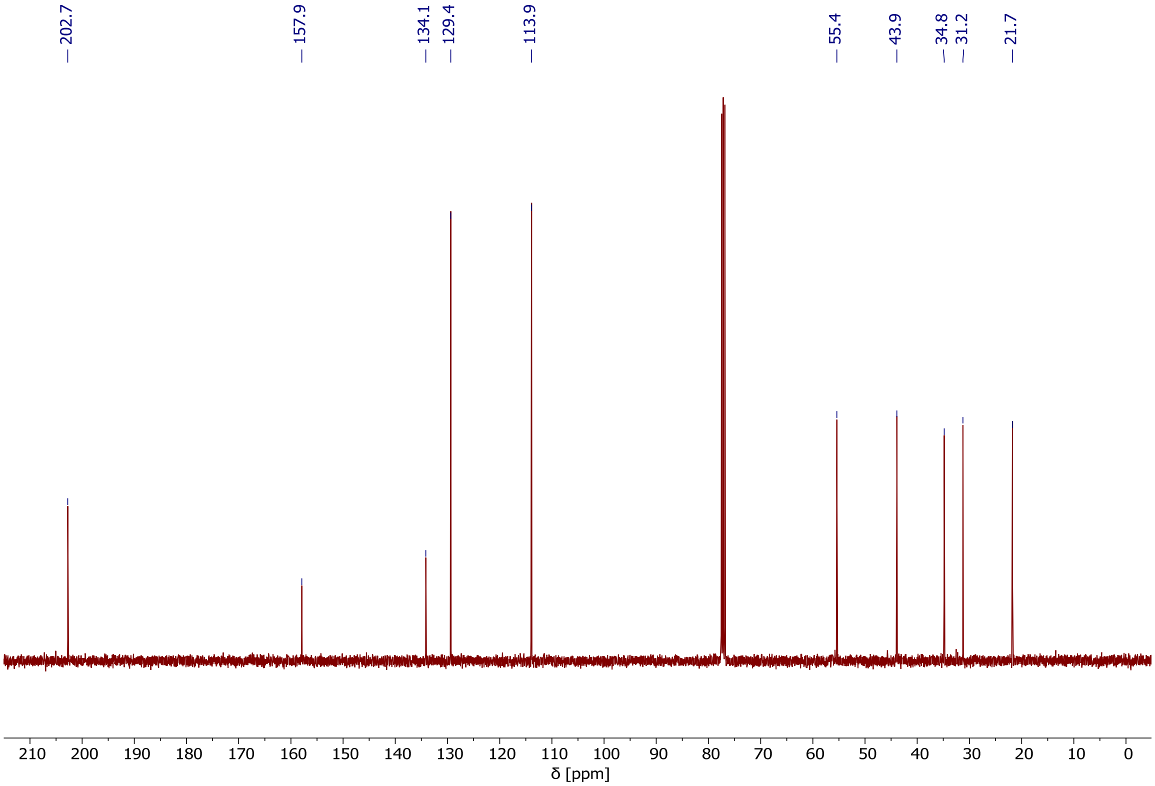
16 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



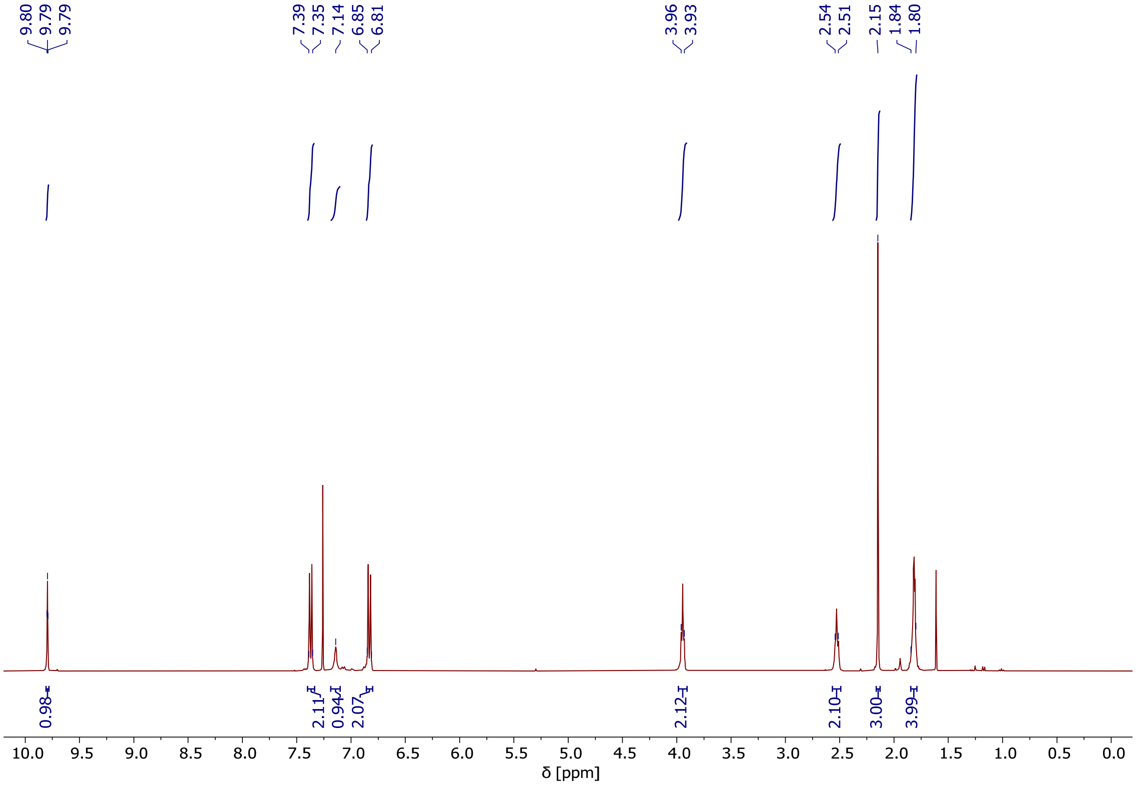


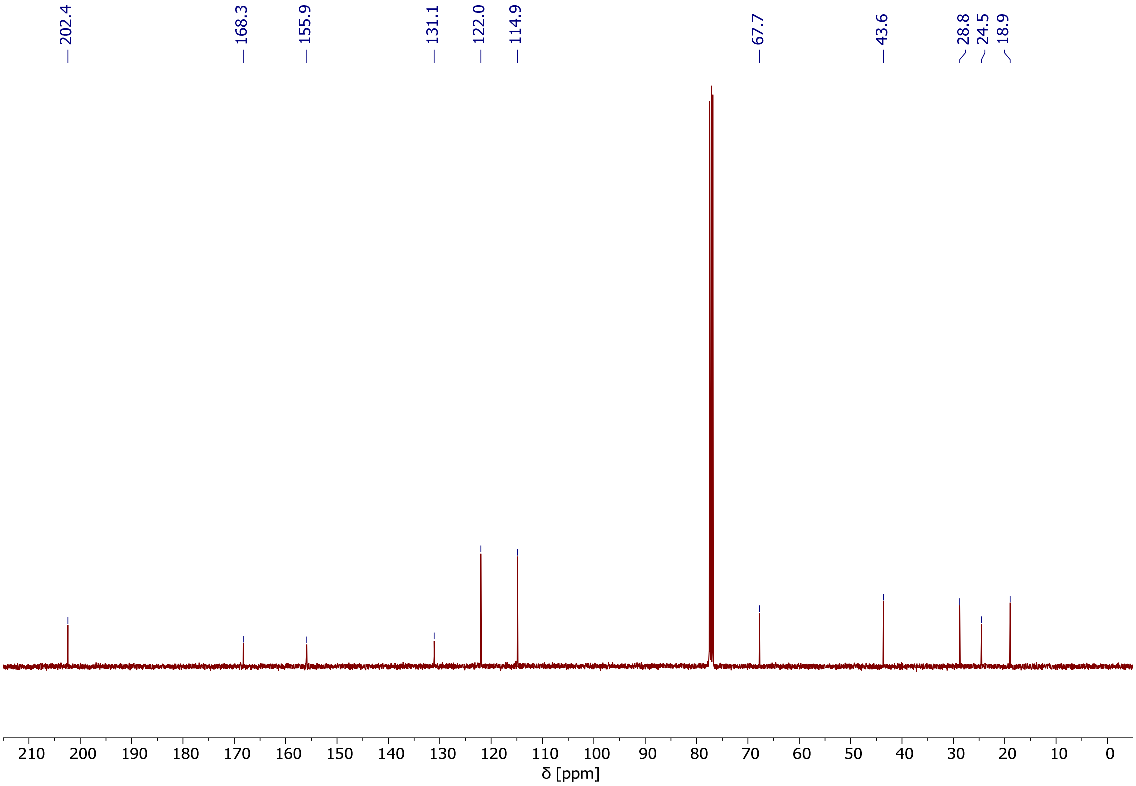
17 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



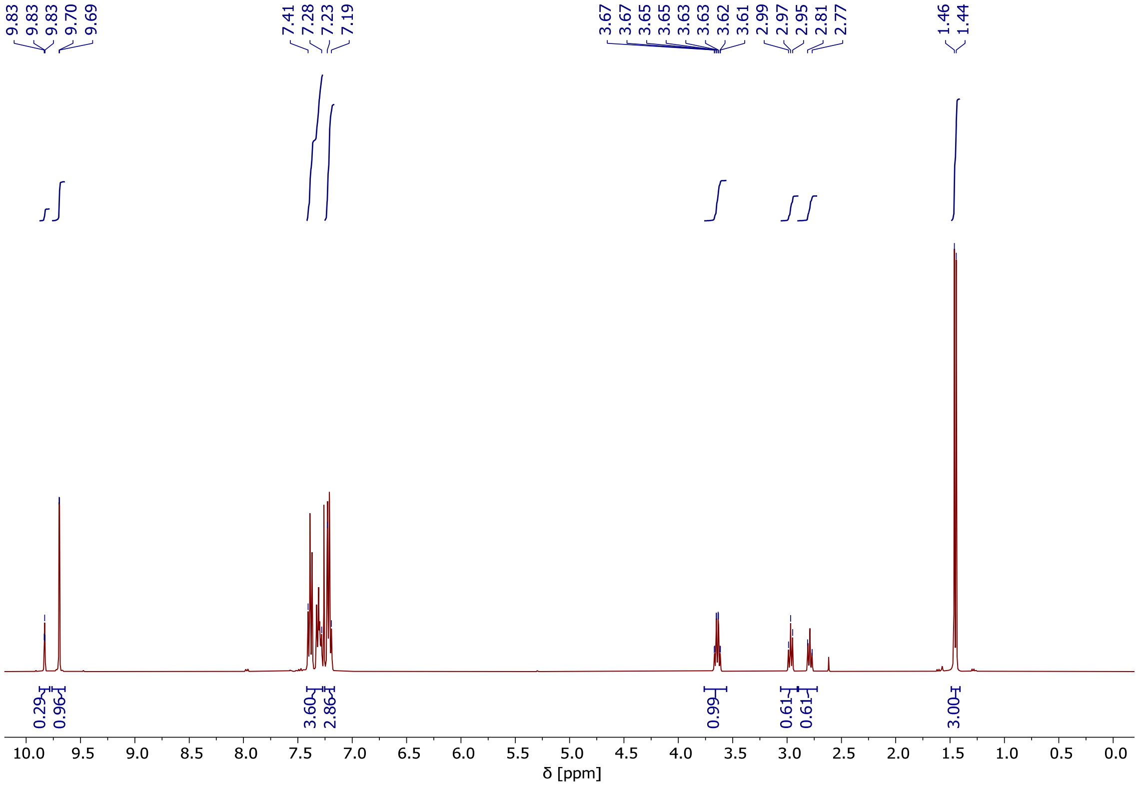


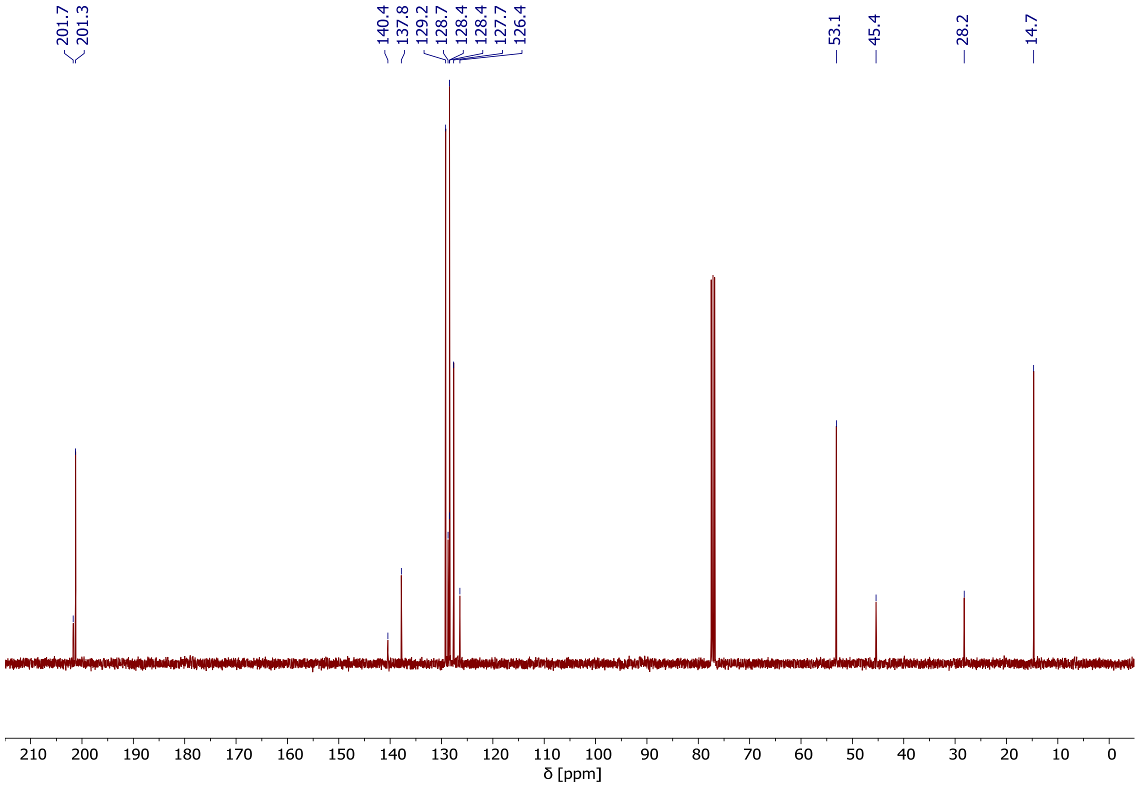
18 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



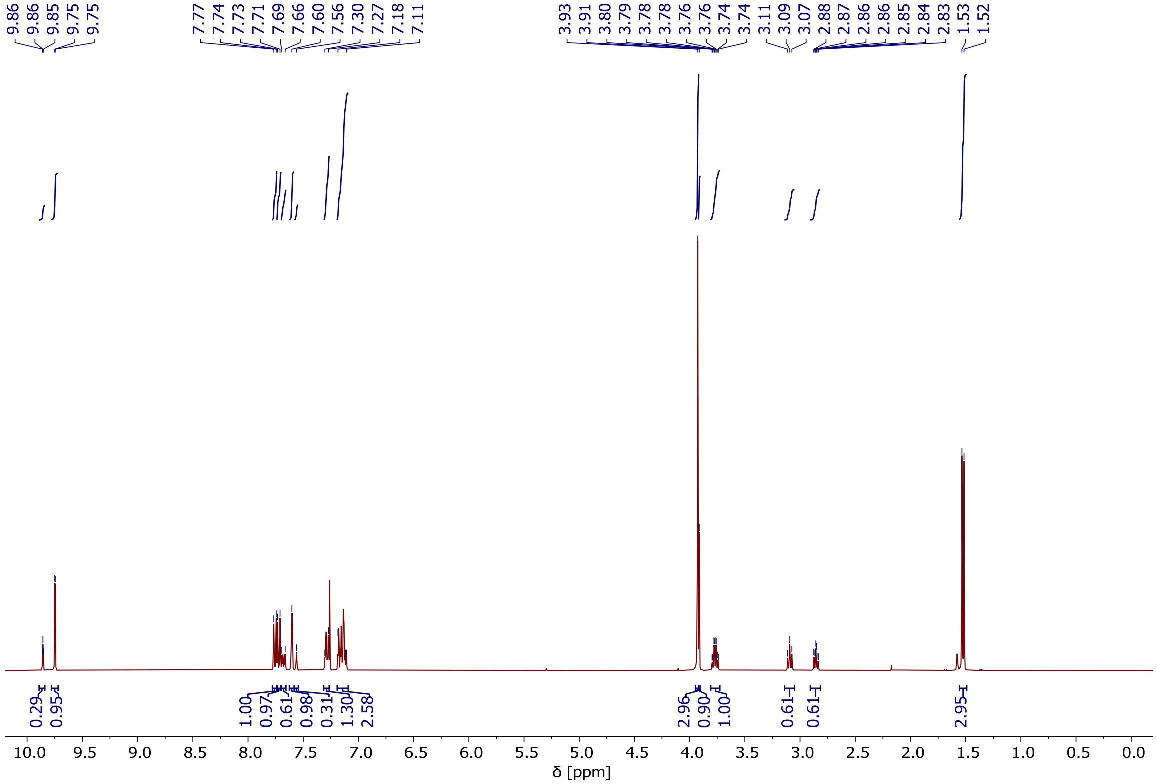


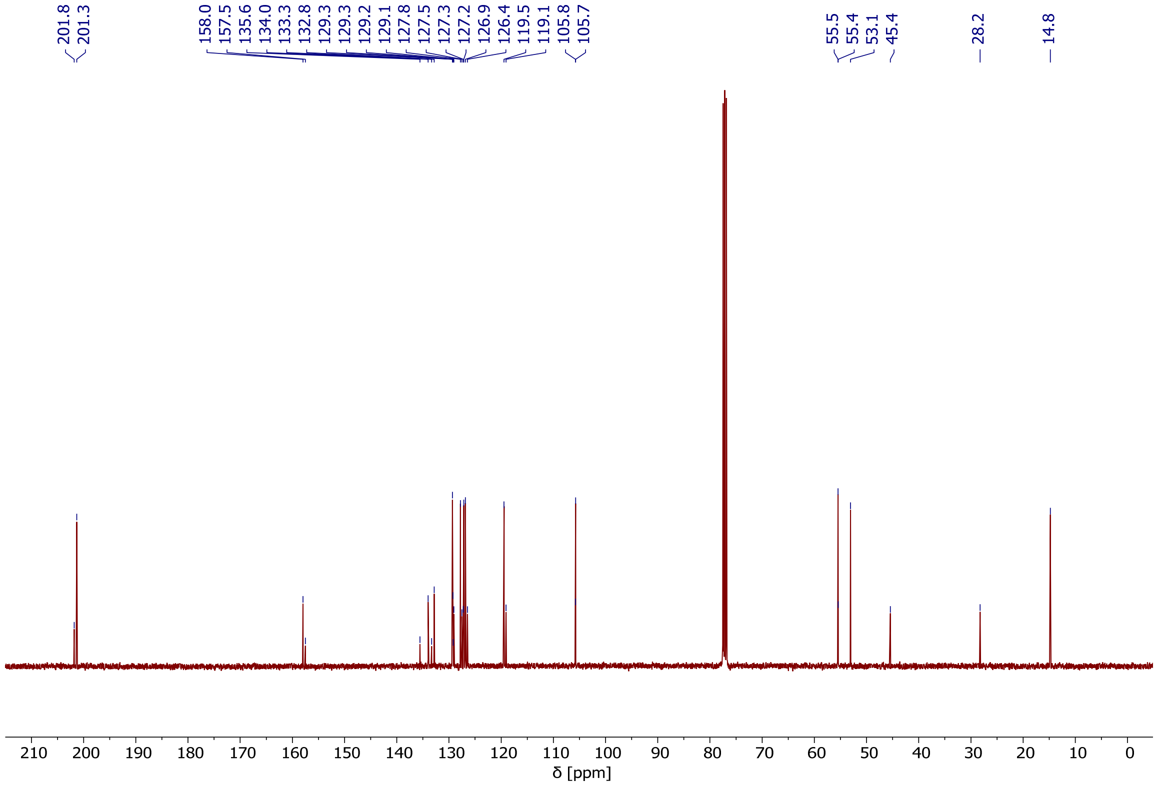
19 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



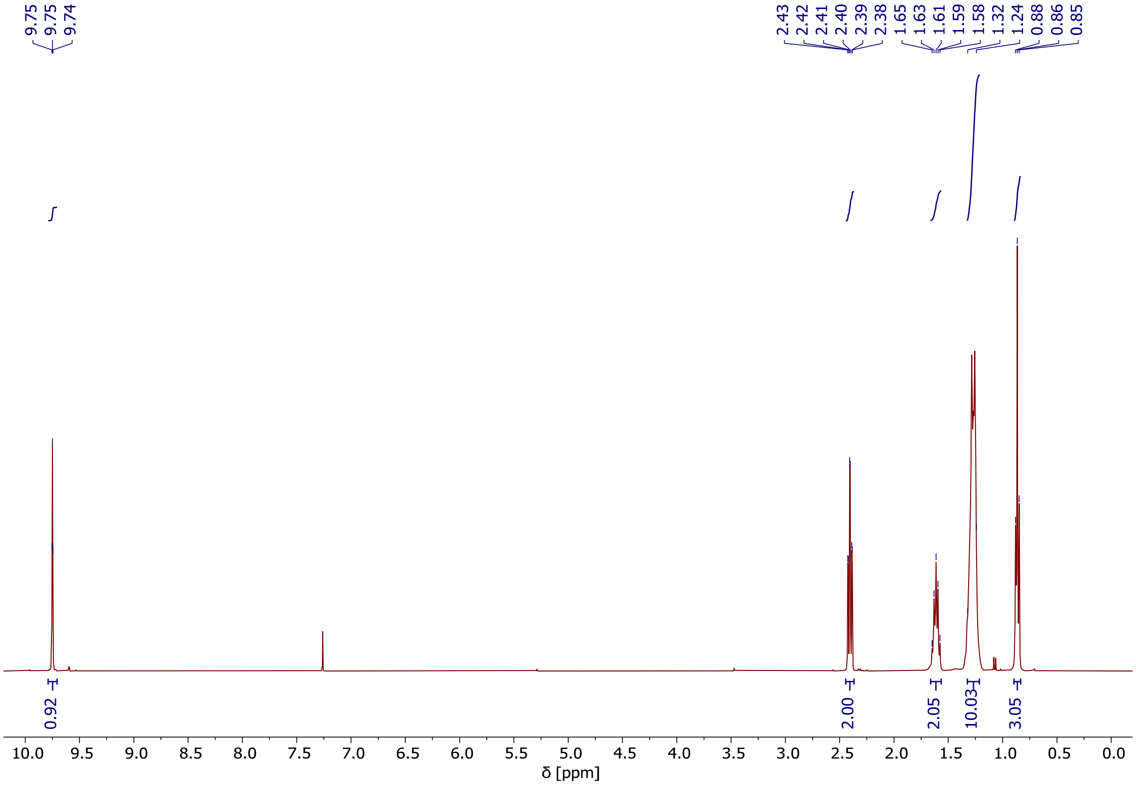


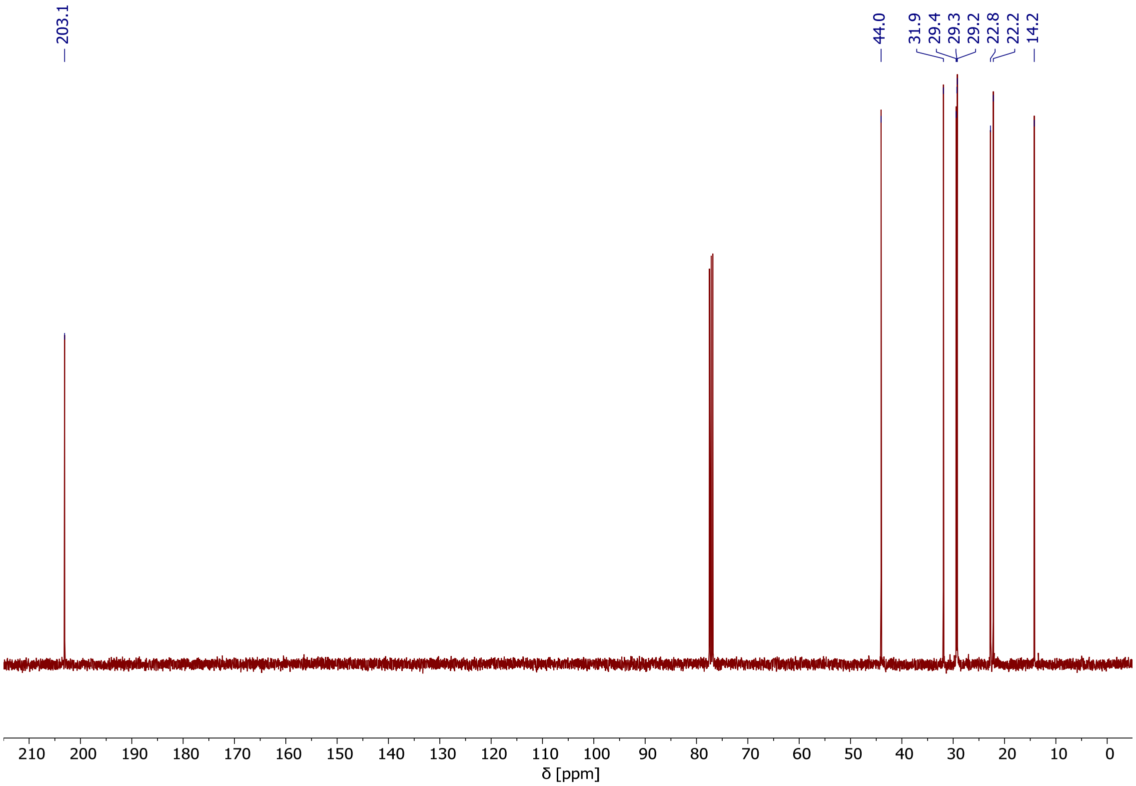
20 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



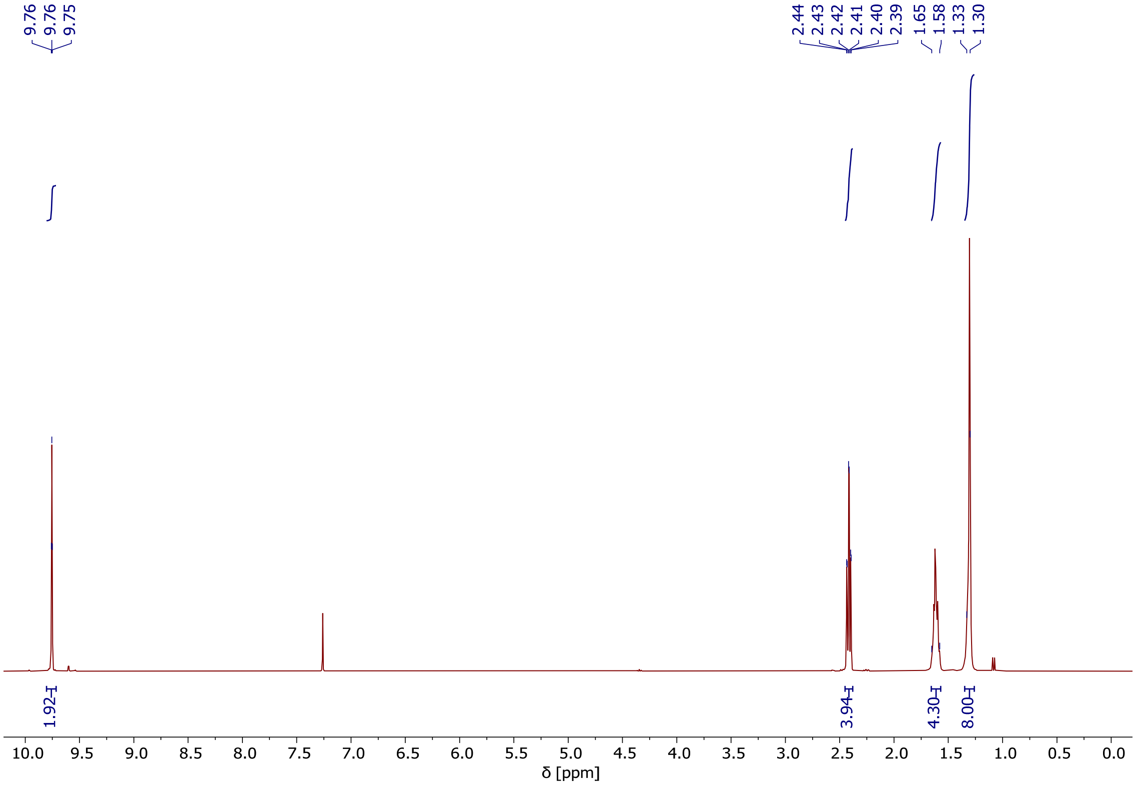


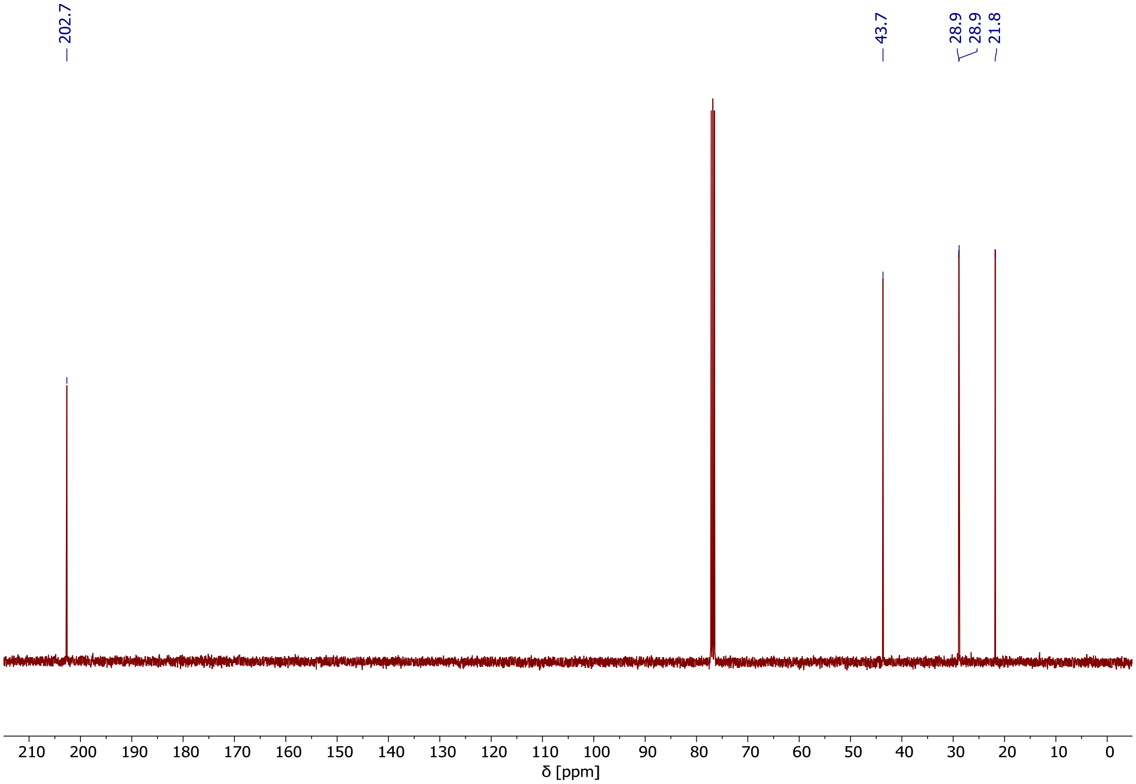
21 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



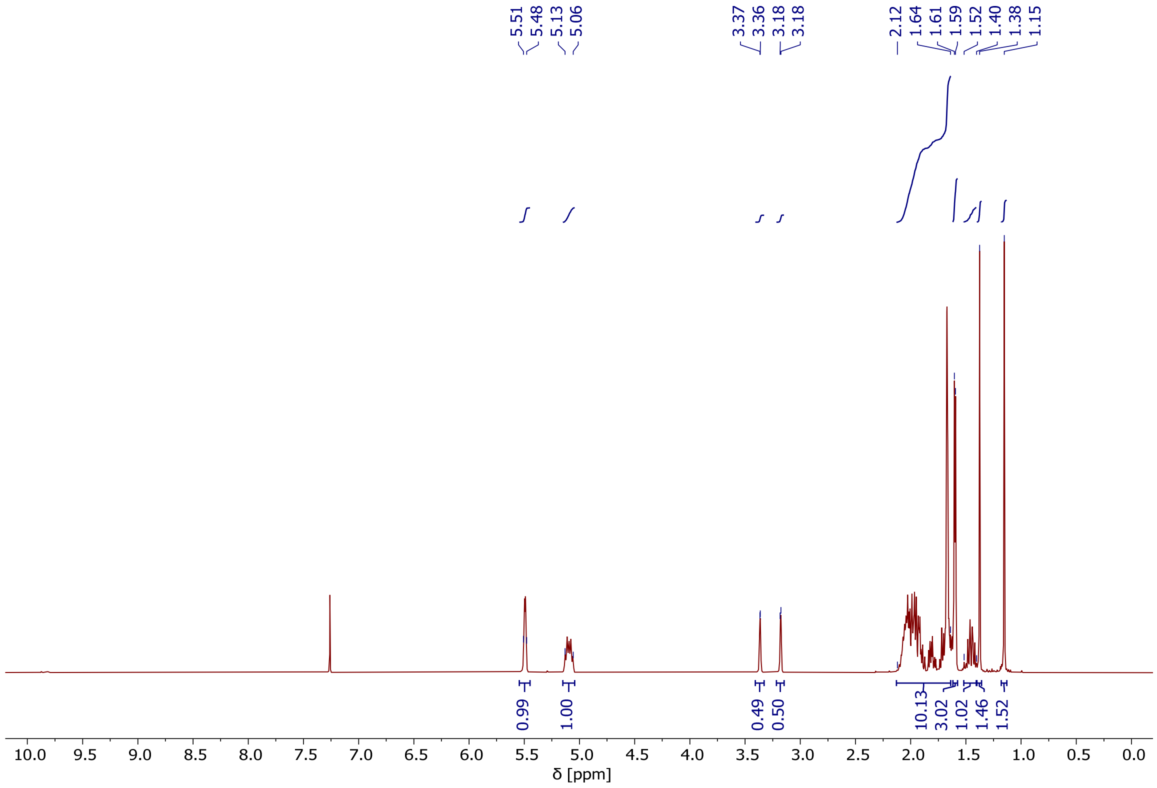


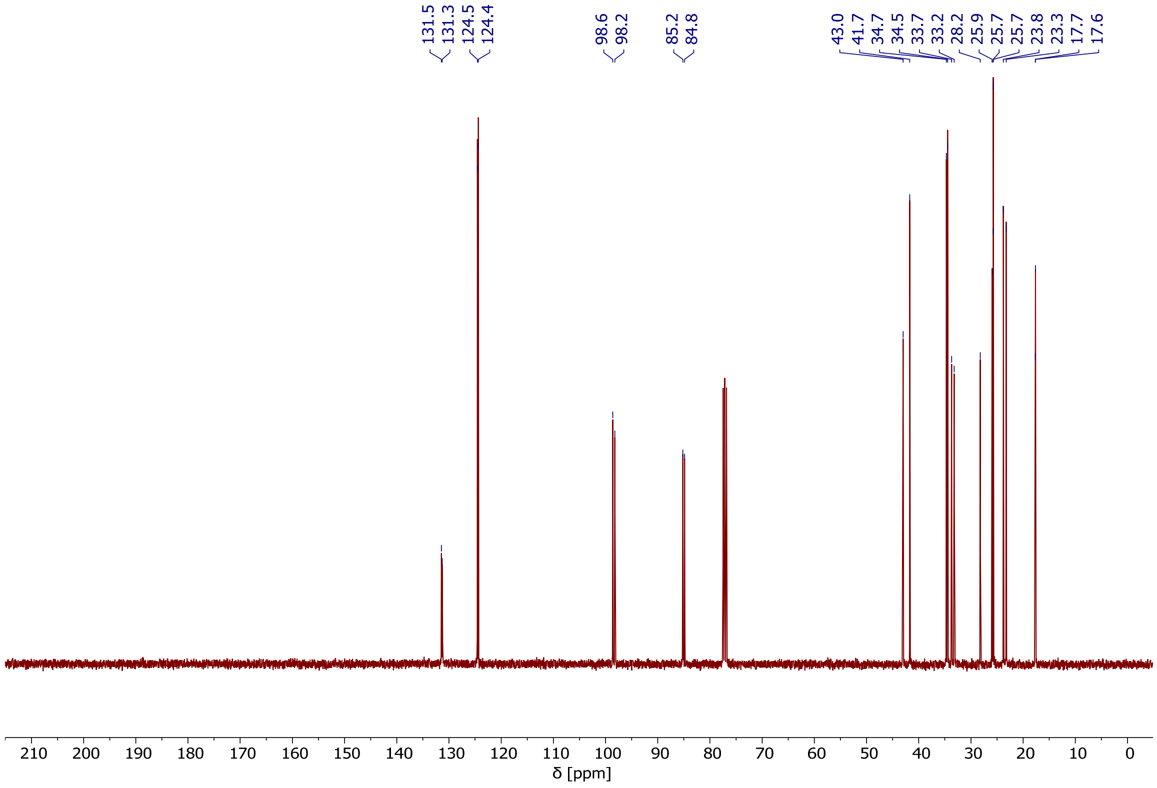
22 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



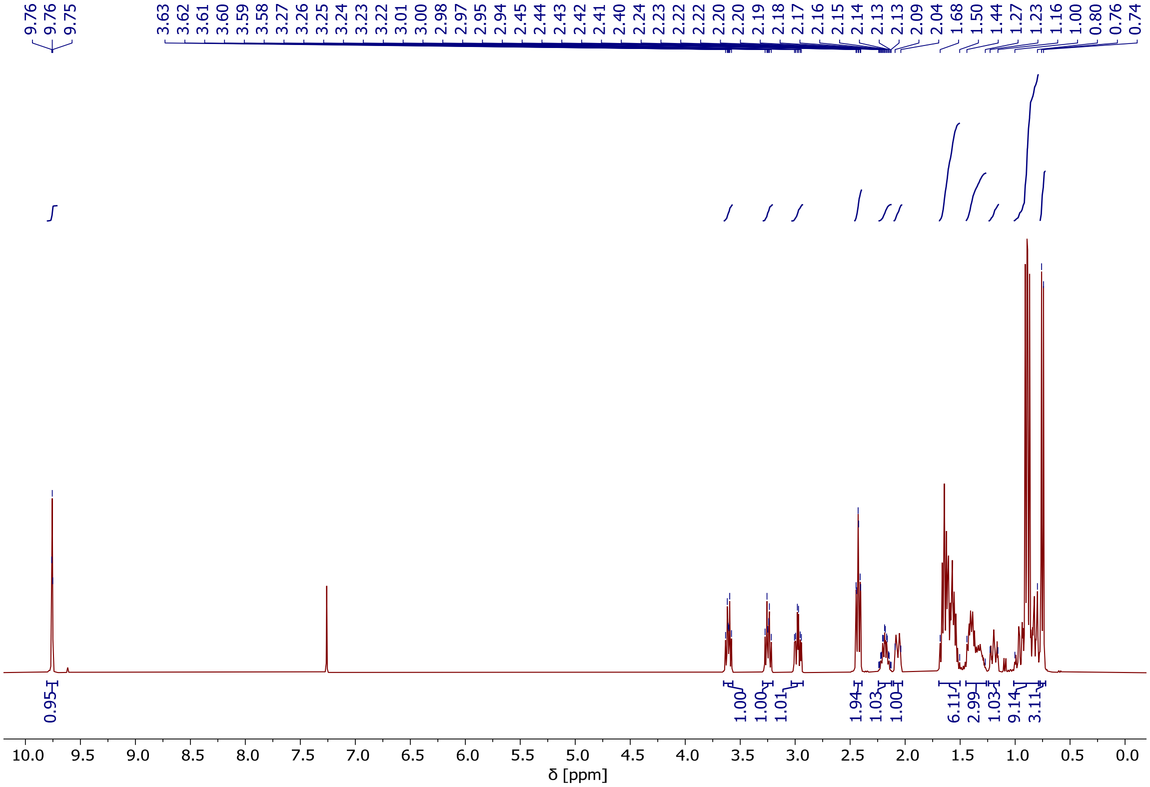


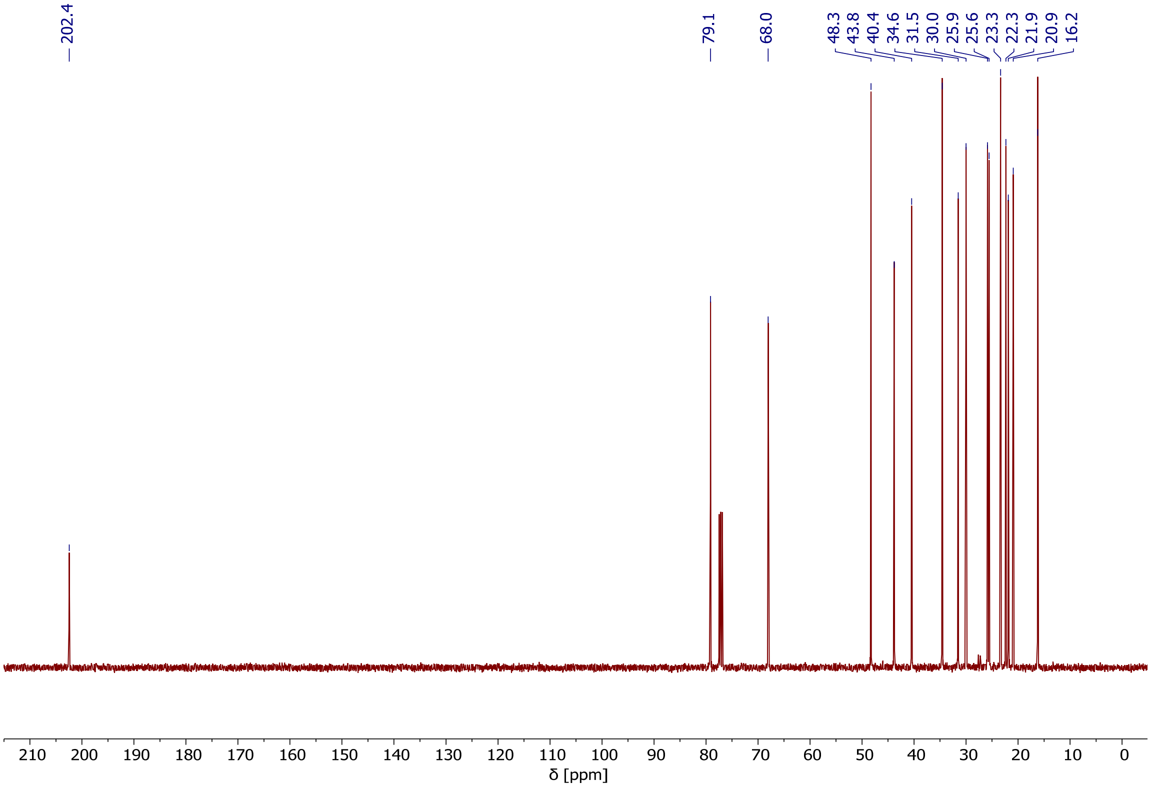
23 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



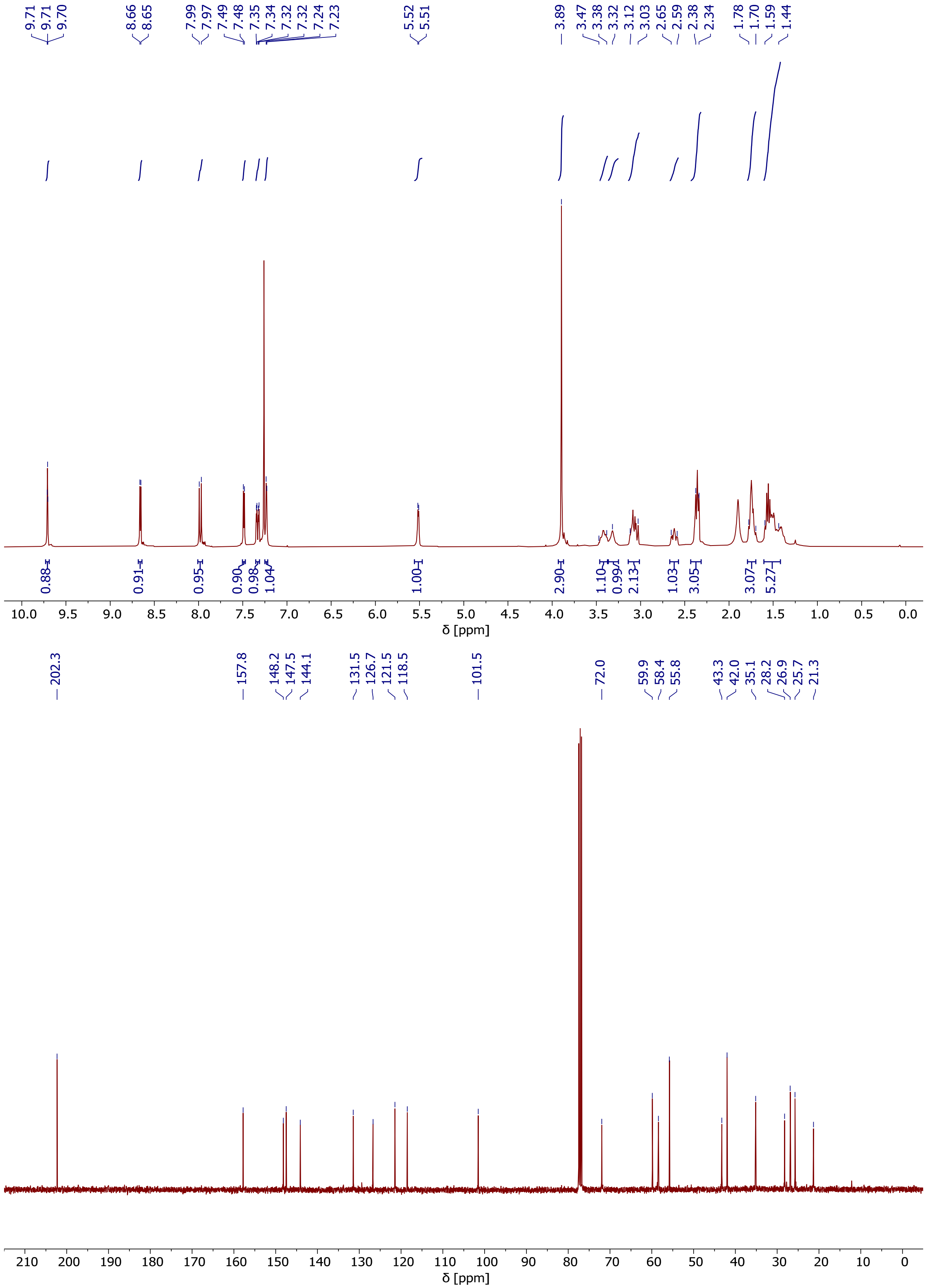


24 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]

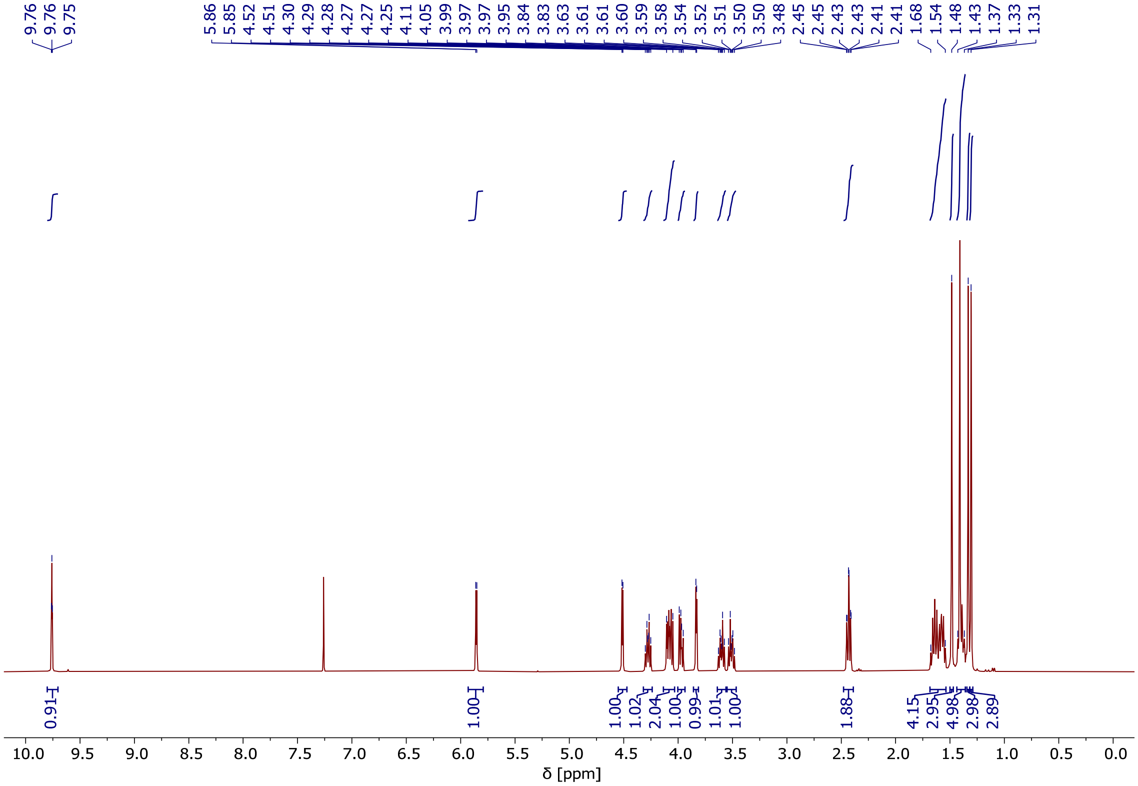


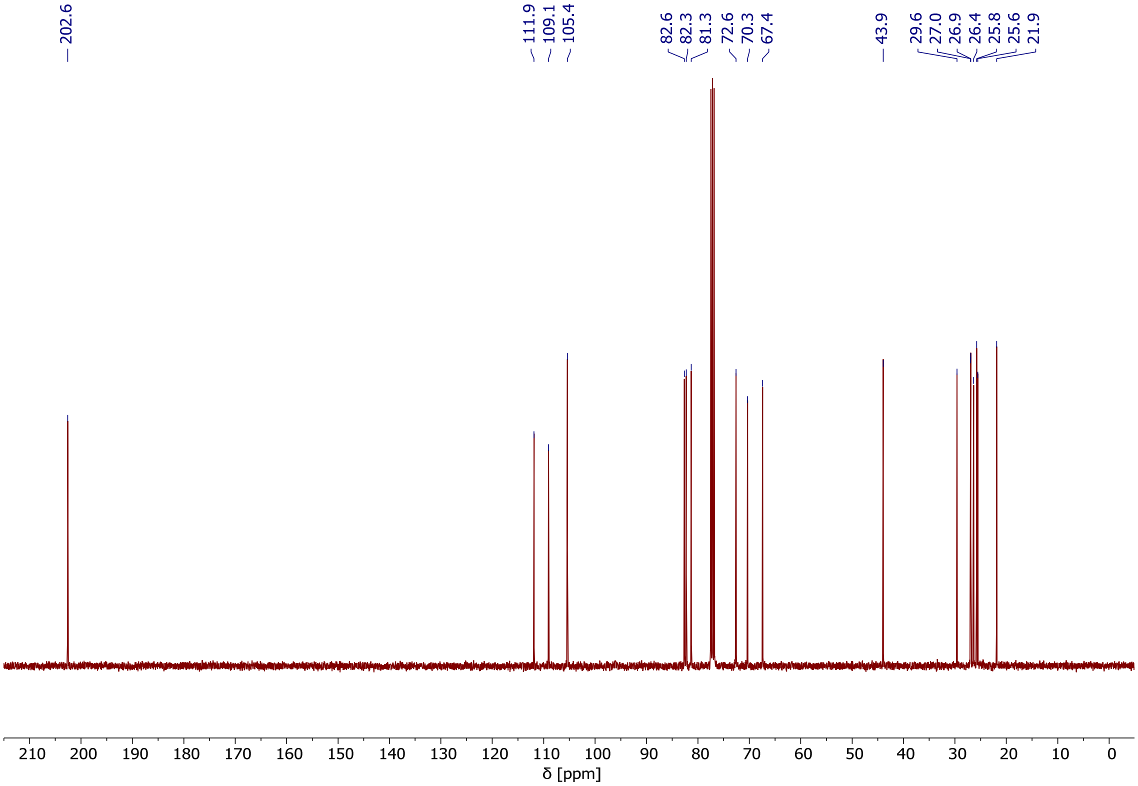


25 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]

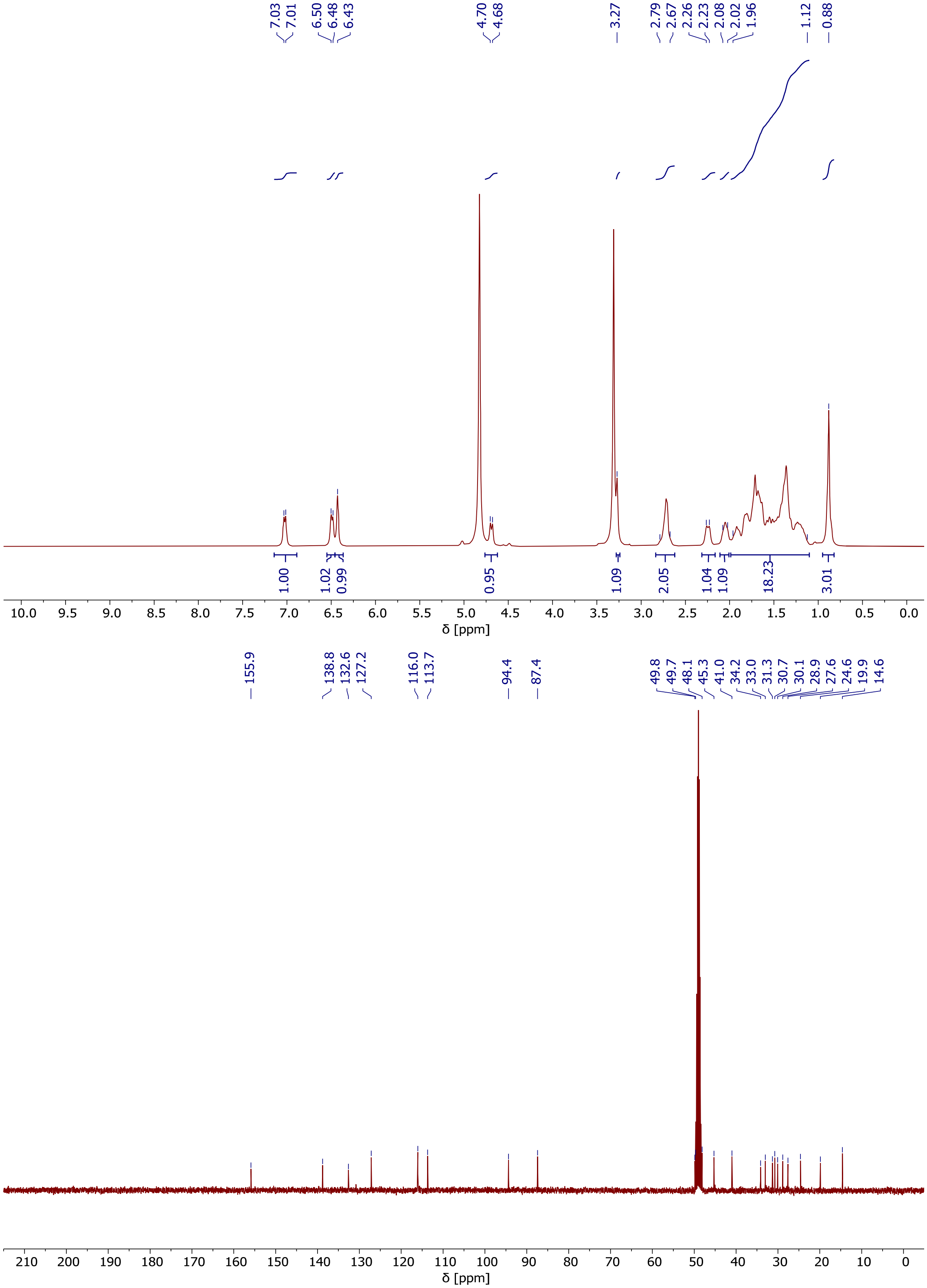


26 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]

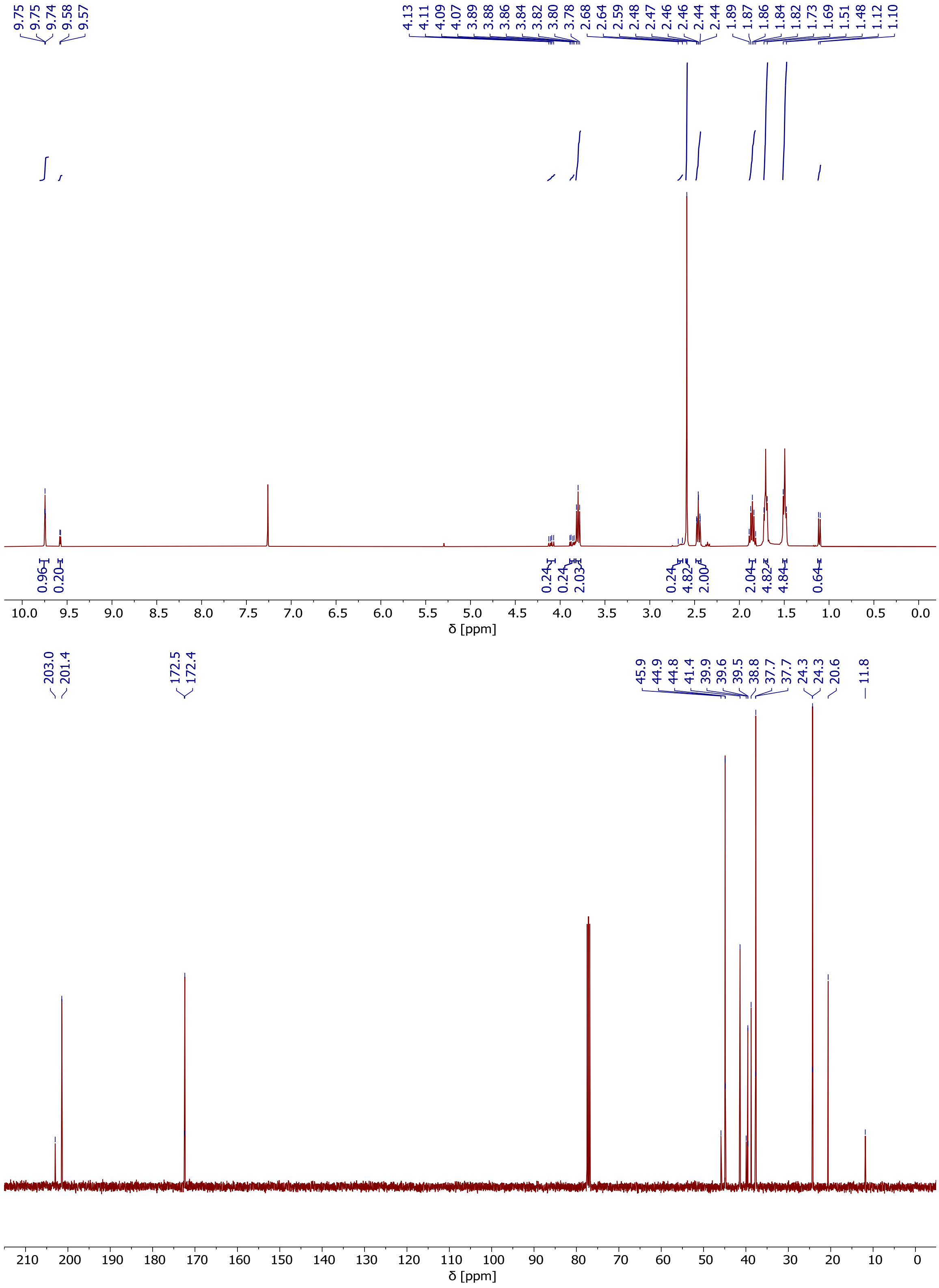




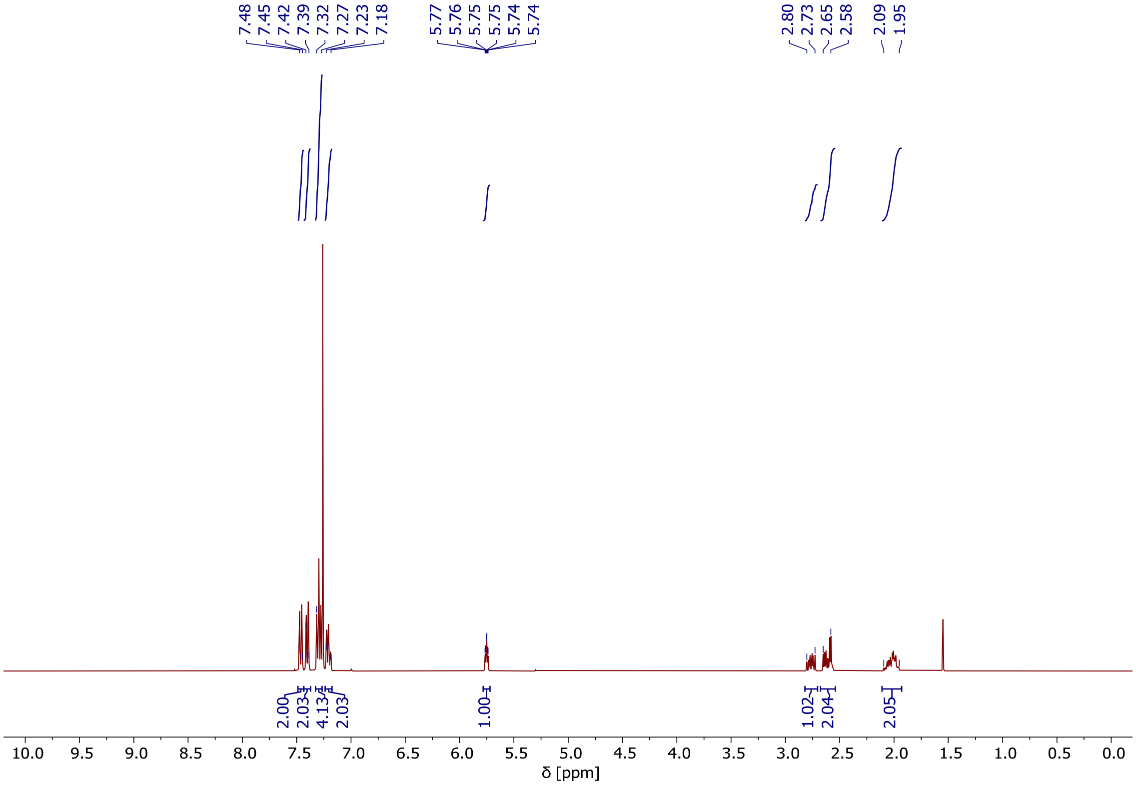
27 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in methanol-d_4]

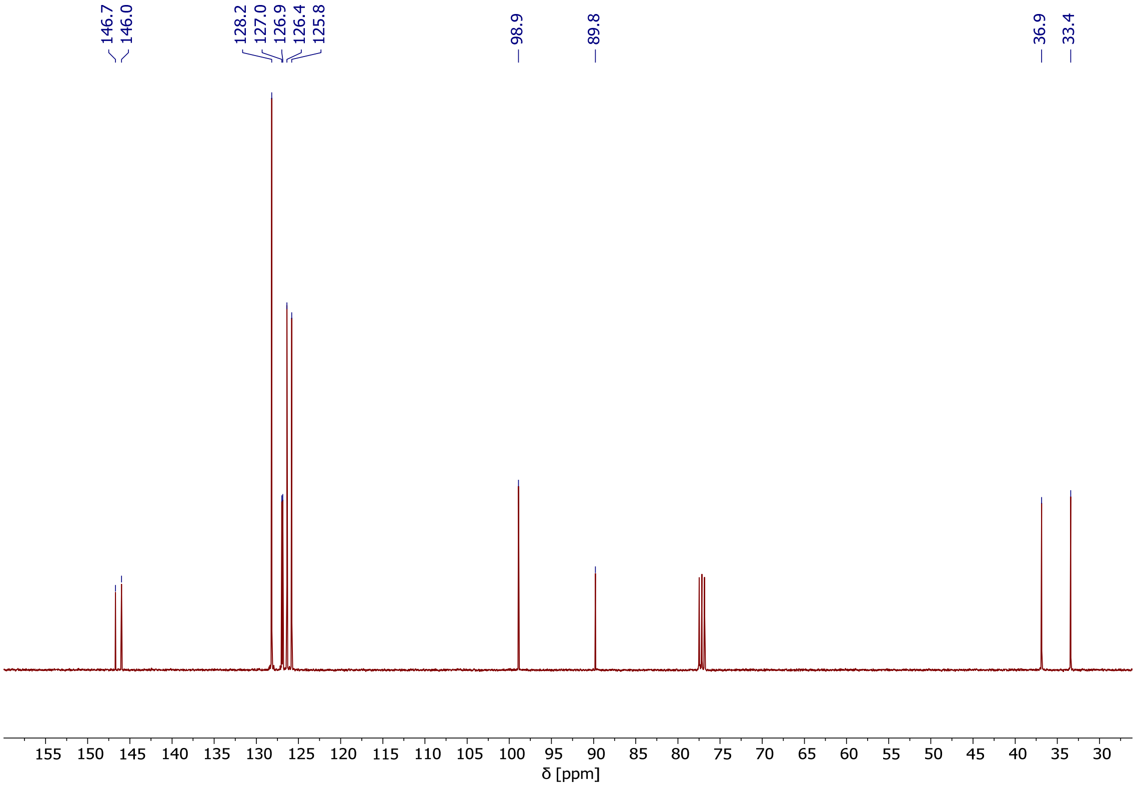


28 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]

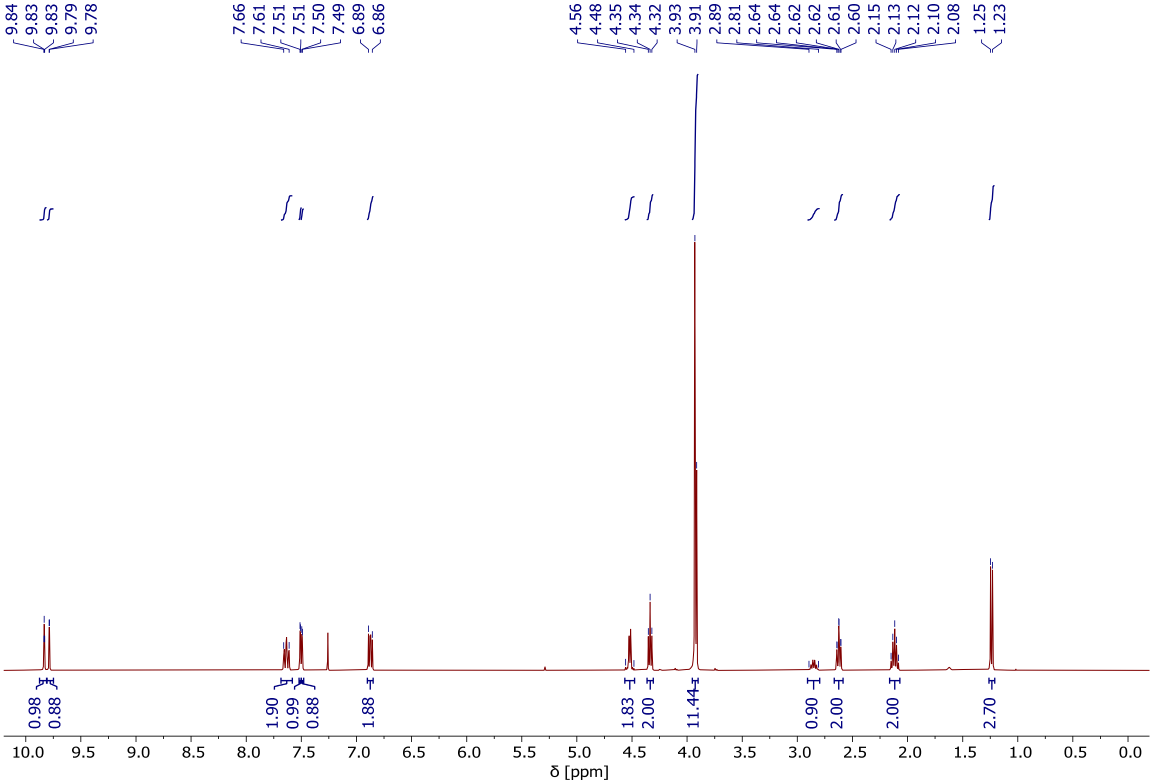


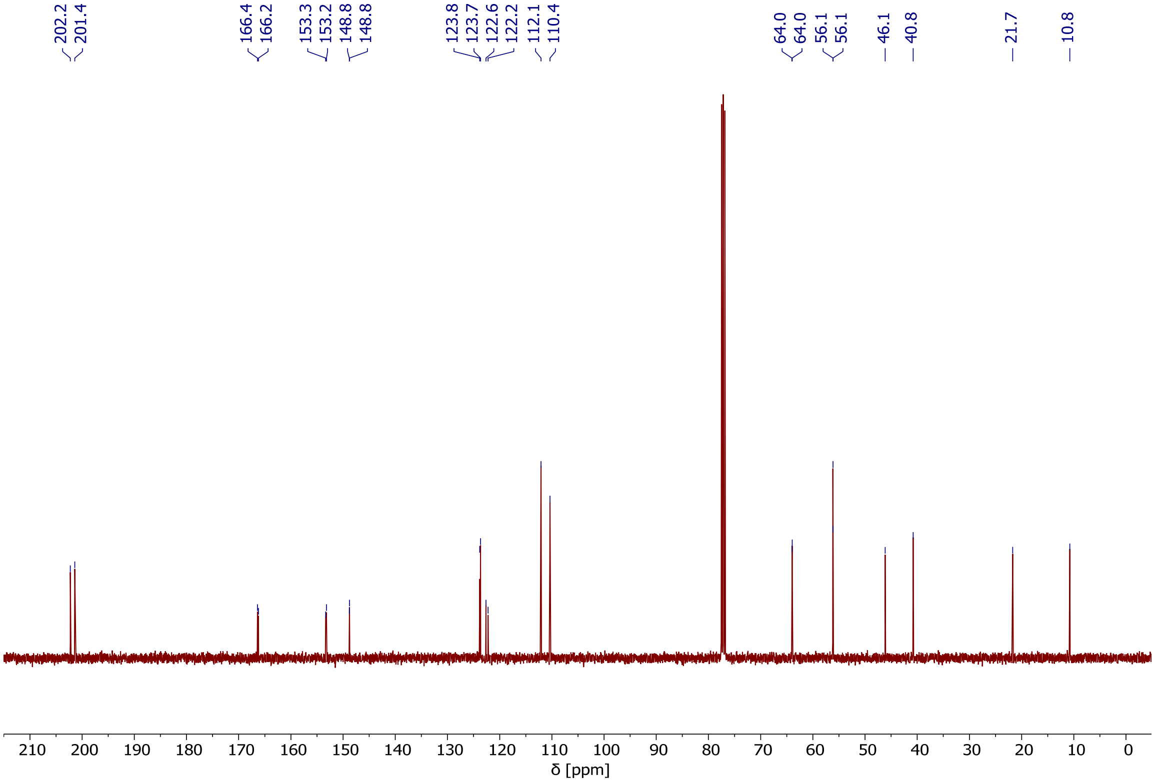
29 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



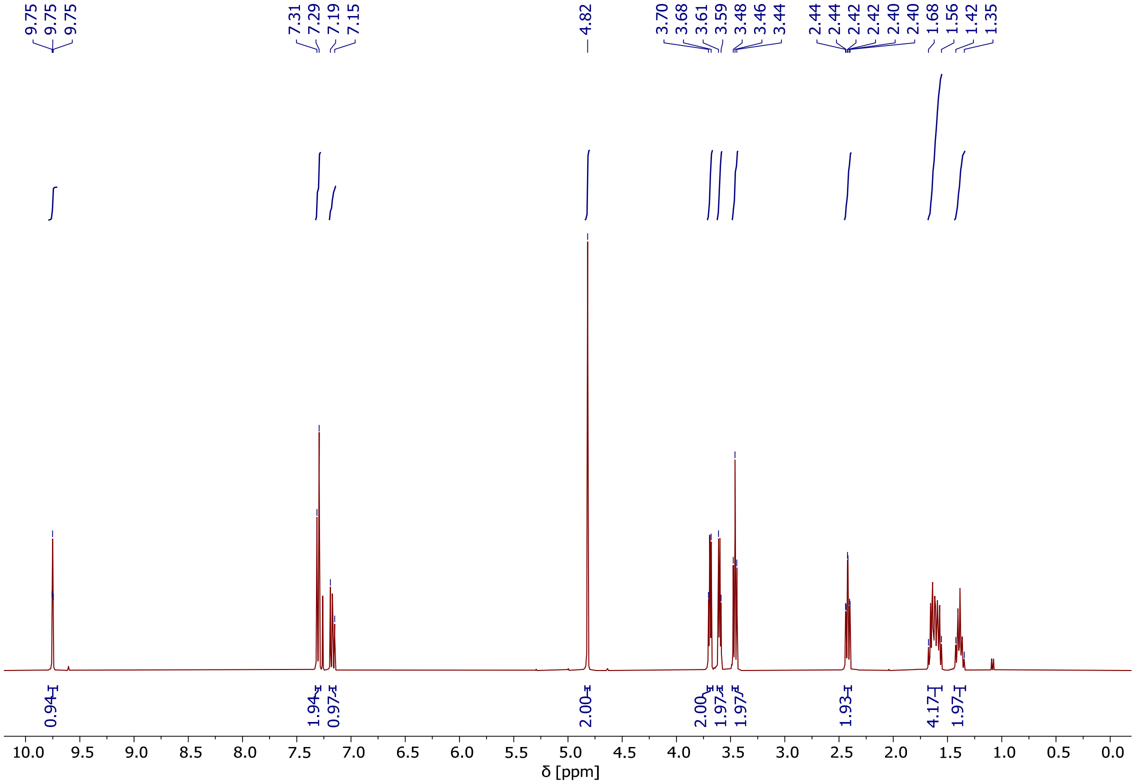


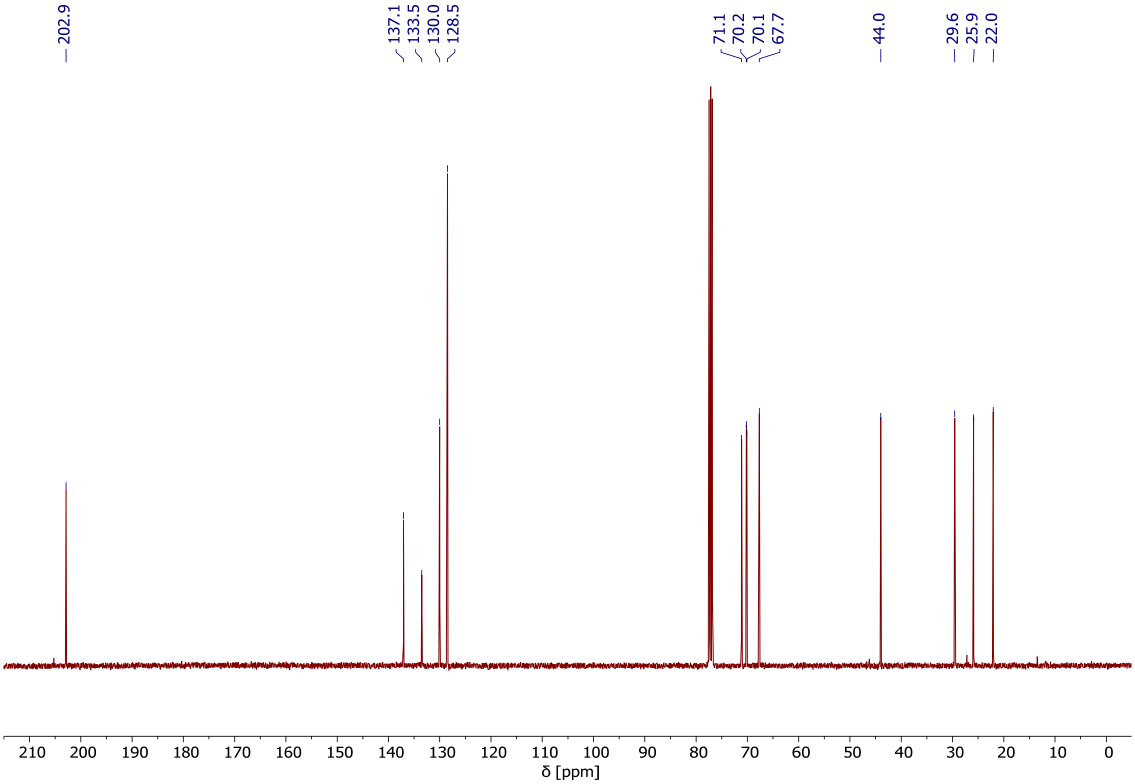
30 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]



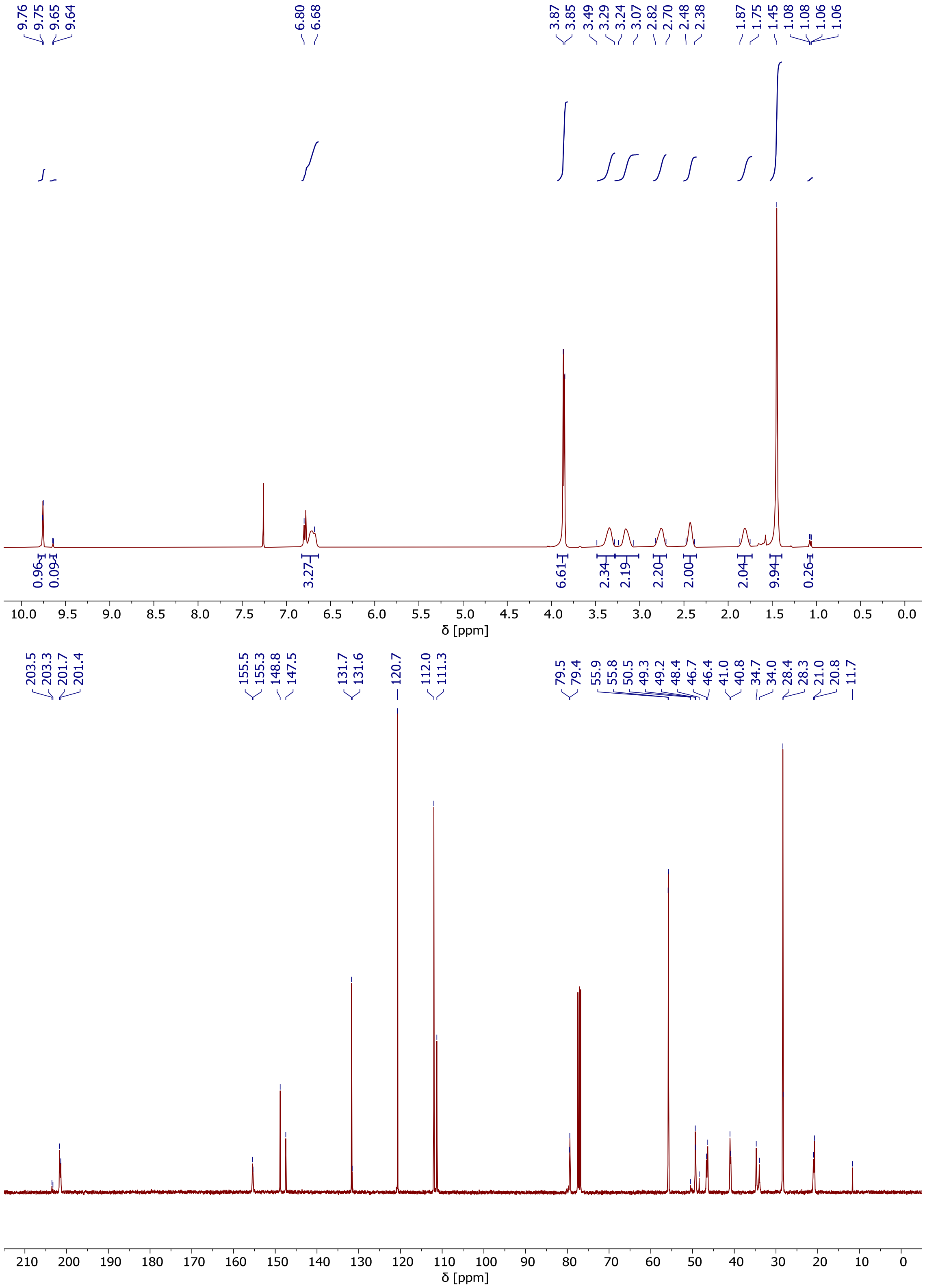


31 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]

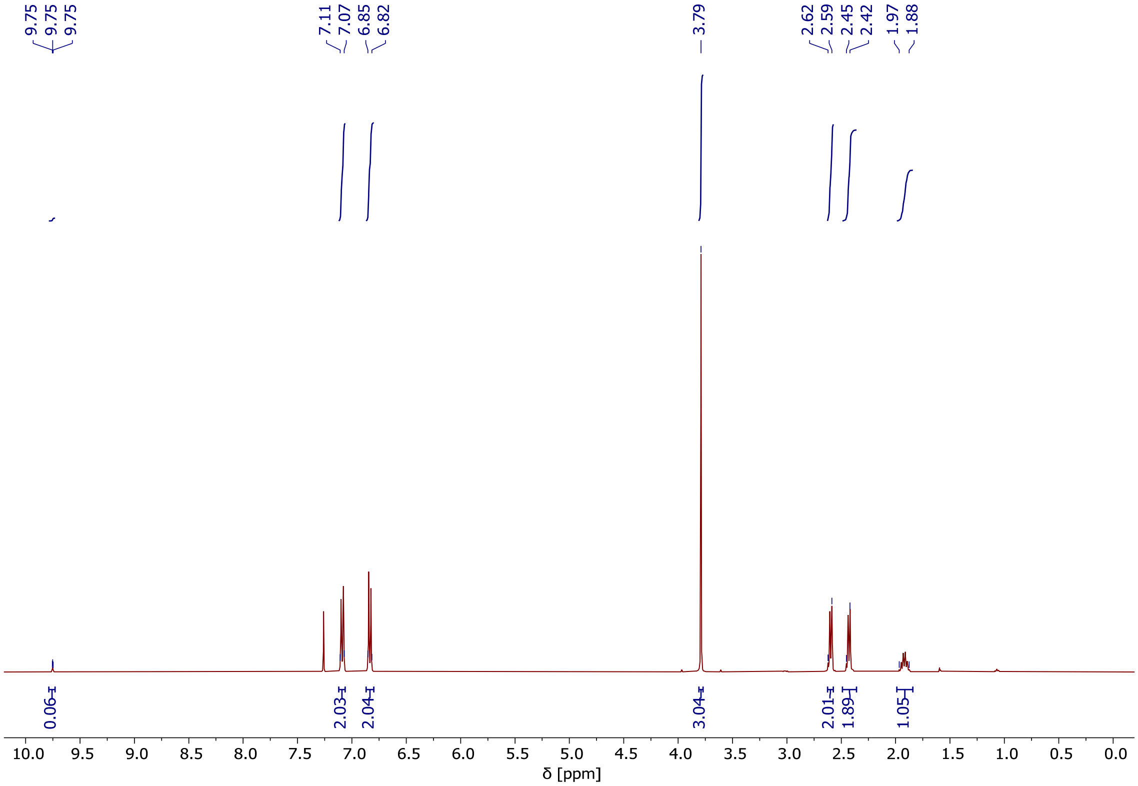


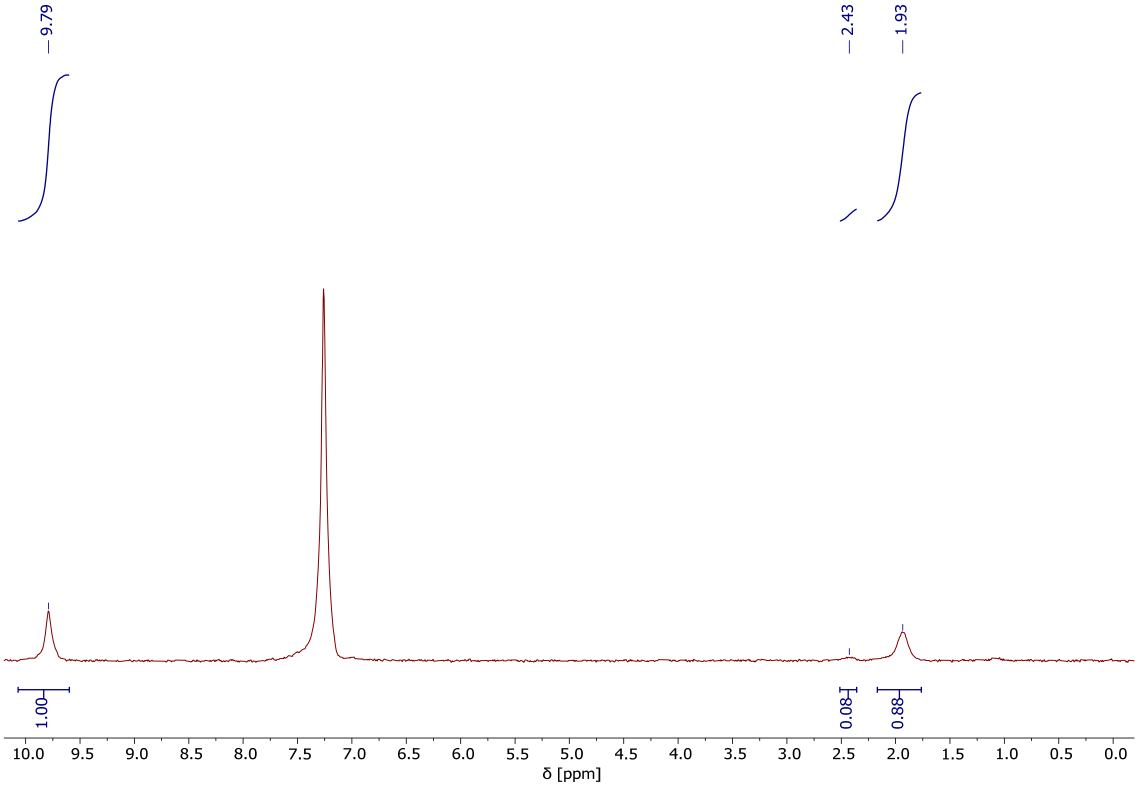


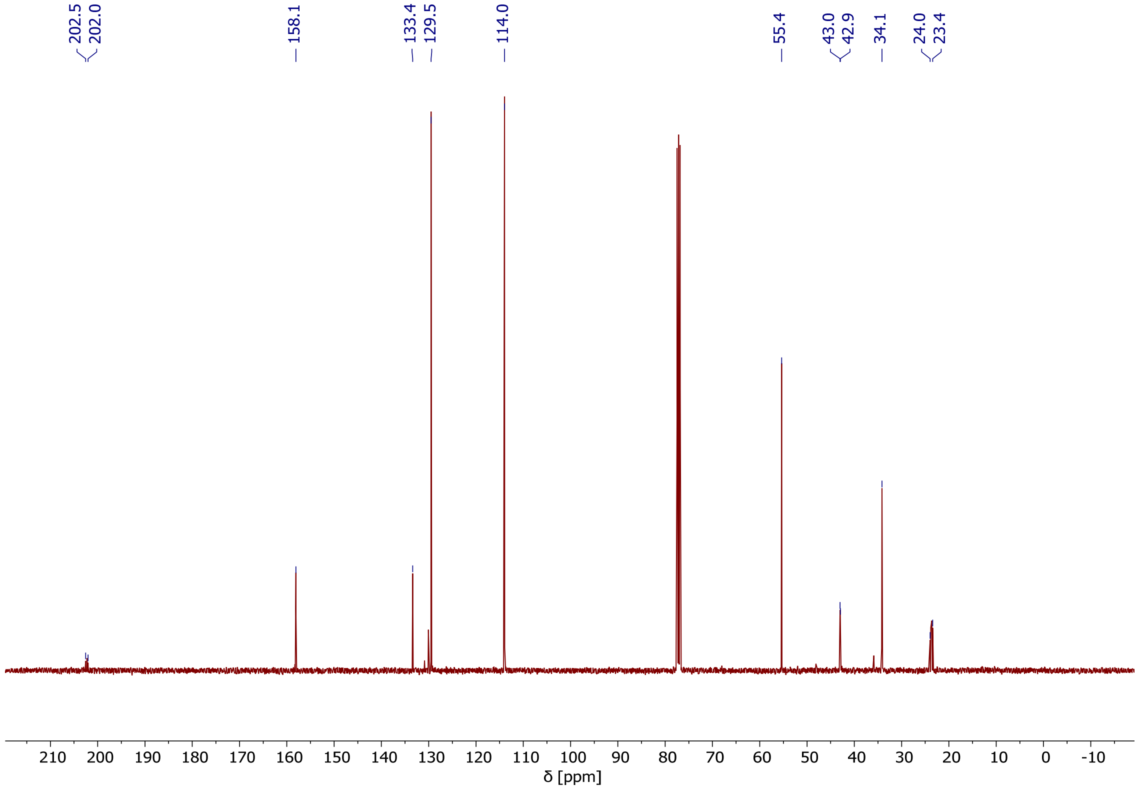
32 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in $CDCl_3$]



33 [^{1}H NMR (400 MHz), ^{2}H NMR (61 MHz), and ^{13}C NMR (101 MHz) in CDCl$_3$]






202.5
202.0
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43.0
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
δ [ppm]

34 [^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) in CDCl$_3$]