Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Synthesis of Cyclobutane-fused Chromanones via Gold-mediated Photocatalysis

Vladislav A. Voloshkin[a], Marco Villa[b], Ekaterina A. Martynova[a], Marek Beliš[a], Kristof Van Hecke[a], Paola Ceroni*[b] and Steven P. Nolan*[a]

Table of Contents

General information

Unless otherwise noted all reactions were performed in anhydrous/dried over molecular sieves and degassed solvents. All organic reagents were purchased and used as received without further purification unless otherwise stated.

^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300, 400 or 500 MHz spectrometers at 298 K. Chemical shifts (ppm) in ^{1}H and ^{13}C are referenced to the residual solvent peak ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). Coupling constants (J) are given in hertz. Abbreviations used in the designation of the signals: s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, dd = doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, m = multiplet, q = quadruplet, br q = broad quadruplet, dq = doublet of quadruplets.

All [Au(NHC)(Cbz)] complexes were synthesized according to previously reported procedure.[1]

Absorption spectra were recorded on Perkin Elmer LAMBDA^{TM} 950 spectrophotometer using quartz cuvettes.

Photocatalytic experiments were performed in EvoluChem^{TM} PhotoRedOx Box or EvoluChem^{TM} PhotoRedOx Duo Box by HepatoChem. EvoluChem^{TM} LED. 365PF (365 nm, 18 W, 9 mW/cm²), 365DX (365 nm, 30 W, 25 mW/cm²), 380PF (380 nm, 18 W, 8 mW/cm²) and 405PF (405 nm, 18W, 28 mW/cm^{2}) lamps were used as light sources. In case of PhotoRedOx Duo setup two lamps 18W and 30W were used together. For both setups the built-in fans were used for cooling.

Position of the vials: for optimization of the reaction conditions we always used the first row (closer to the lamp) in PhotoRedOx Box for a fair comparison.

For the reaction scope, the same first row was used in PhotoRedOx Box with one lamp, and 2 rows which are closer to the more powerful lamp in PhotoRedOx Duo Box with 2 lamps.

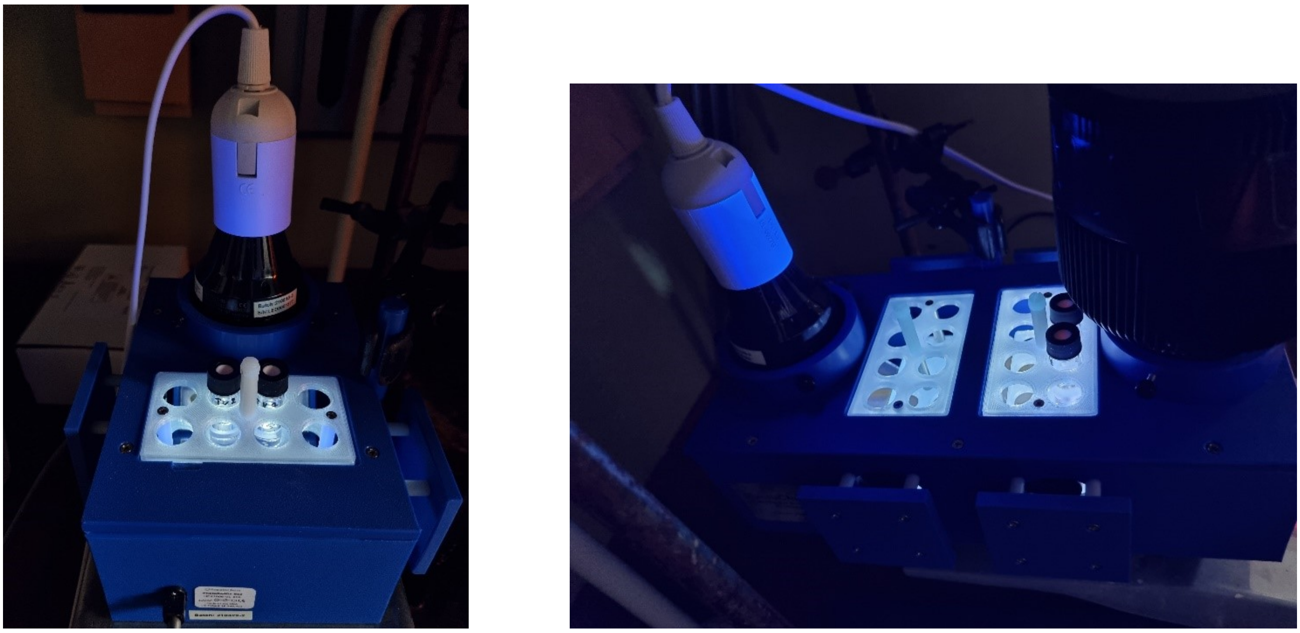


Figure S1. The photocatalytic setups with one lamp (left) and with two lamps (right).

Photophysical measurements. Optically dilute solutions of concentrations on the order of 10^{-5} or 10^{-6} M of the photocatalysts were prepared in spectroscopic or HPLC grade solvents for absorption and emission analysis. Absorption spectra were recorded at room temperature on a Varian Cary 50 BIO spectrophotometer with a 1 cm quartz cuvette. Degassed solutions were prepared via four freeze-pump-thaw cycles and spectra were taken using home-made Schlenk quartz cuvette. Steady-state emission, excitation spectra and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980 or a Edinburgh Instruments FS5, equipped with a Hamamatsu R928 phototube. Samples were excited at 370 nm for steady-state measurements and at 340 nm for time-resolved measurements. Photochemical reactions were performed at room temperature on thoroughly stirred air equilibrated solutions by using a Helios Italquartz Polymer 125 medium pressure Hg lamp (125 W). The selection of the desired irradiation wavelength (365 or 313 nm) was accomplished by the use of an appropriate interference filter. The number of incident photons in the solution experiments, determined by ferrioxalate actinometry in its micro version. Photoreaction quantum yield (λ_{irr}= 365 nm) was determined from the disappearance of the absorption band of the coumarin at low conversion percentages (<10%, extrapolation to t=0 was made) in presence and absence of TEMPO (0.5 mM). The fraction of light transmitted at the irradiation wavelength was taken into account in the calculation of the yields. The estimated experimental errors are 2 nm on the band maximum, 5% on the molar absorption coefficient and luminescence lifetime and 10% on the quantum yield.

Fitting of time-resolved luminescence measurements: Time-resolved PL measurements were fitted to a sum of exponentials decay model, with chi-squared (χ^2) values between 1 and 2, using the EI FLS980 or Edinburgh FLS920 software. Each component of the decay is assigned a weight, (w_i), which is the contribution of the emission from each component to the total emission.

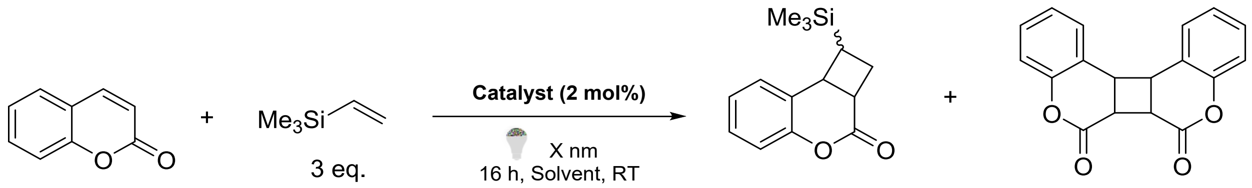
Electrochemical experiments were conducted in argon-filled glovebox using a Metrohm Autolab M204 potentiostat and screen-printed DRP-550 electrodes with a platinum working electrode, platinum auxiliary electrode and silver reference-electrode. Data was recorded using Autolab NOVA software.

Optimization of photocatalytic conditions

Coumarin **1a** (0.1-0.3 mmol) and the catalyst were weighted and transferred in a 4 mL vial equipped with a stirring bar. Ethyl acetate (1 mL) was added via syringe and the mixture was degassed by bubbling inert gas through it for 3 minutes. Under the flow of inert gas vinyltrimethylsilane was added to reaction mixture via syringe and the vial was closed with a screw cap. The vial was placed into the photoreactor for the indicated time. After the reaction, the conversion of coumarin and yields of **2a** and **3** were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. Each reaction was performed twice, and the average conversion and yields are reported.

Table S1. Optimization of reaction conditions

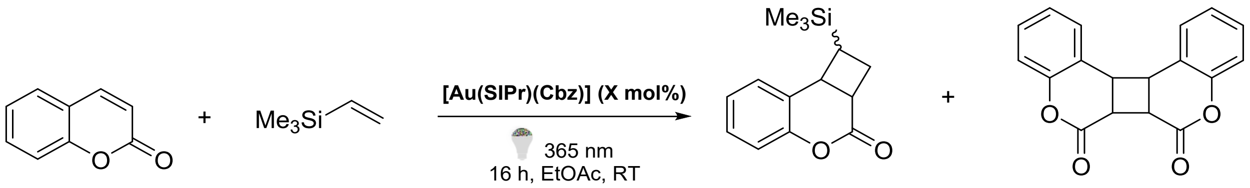
Entry	Cat.loading mol%	Alkene, eq.	Concentration, M	Time, h	NMR yield of product, %	NMR yield of dimer, %
1	2	3	0.1	1	35	64
2	1	3	0.1	1	21	72
3	2	3	0.2	1	35	64
4	2	3	0.3	1	34	60
5	2	5	0.1	1	36	62
6	2	10	0.1	1	43	46
7	2	10	0.3	1	56	32
8	2	3	0.1	4	71	<10
9	2	3	0.1	16	88	-



Coumarin **1a** (14.6 mg, 0.1 mmol) and the catalyst (2 mol%) were weighted and transferred in a 4 mL vial equipped with a stirring bar. Solvent (1 mL) was added via syringe and the mixture was degassed by bubbling inert gas through it for 3 minutes. Under the flow of the inert gas, alkene (3 eq., 44 µL) was added via syringe to reaction mixture and the vial was closed with a screw cap. The vial was placed into the photoreactor for 16 hours. After the reaction, conversion of coumarin and yields of **2a** and **3** were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. Each reaction was performed twice, and the average conversion and yields are reported.

Table S2. Catalyst screening

Entry	Catalyst	Wavelength, nm	Solvent	E_T, kcal/mol	NMR yield of product	NMR yield of dimer
1	[Au(SIPr)(Cbz)]	365	EtOAc	67.9	88	-
2	[Au(IMes)(Cbz)]	365	EtOAc	ND	85	-
3	[Au(IPr)(Cbz)]	365	EtOAc	67.6	83	-
4	[Au(SIMes)(Cbz)]	365	EtOAc	ND	84	-
5	[Au(ICy)(Cbz)]	365	EtOAc	ND	59	-
6	Thioxanthone	405	EtOAc	65.5	29	69
7	Thioxanthone	365	EtOAc	65.5	28	70
8	[Ir(dF(CF$_3$)ppy)$_2$(dtppy)]PF$_6$	405	EtOAc	61.8	29	70
9	[Ir(dF(CF$_3$)ppy)$_2$(dtppy)]PF$_6$	365	EtOAc	61.8	27	71
10	[Au(SIPr)(Cbz)]	380	EtOAc	67.9	67	32
11	Thioxanthone	365	MeCN	65.5	37	62
12	[Ir(dF(CF$_3$)ppy)$_2$(dtppy)]PF$_6$	365	MeCN	61.8	38	62
13	Thioxanthone	405	MeCN	65.5	36	59
14	[Ir(dF(CF$_3$)ppy)$_2$(dtppy)]PF$_6$	405	MeCN	61.8	38	61
15	Benzophenone (4 mol%)	365	EtOAc	68.6	26	74

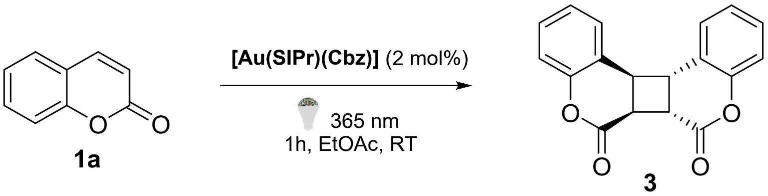


Coumarin **1a** (0.1-0.3 mmol) and [Au(SIPr)(Cbz)] were weighted and transferred in a 4 mL vial equipped with a stirring bar. Ethyl acetate (1 mL) was added via syringe and the mixture was degassed by bubbling inert gas through it for 3 minutes. Under the flow of inert gas, the alkene was added to reaction mixture and the vial was closed with a screw cap. The vial was placed into the photoreactor for 16 hours. After reaction, the conversion of coumarin and yields of **2a** and **3** were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. Each reaction was performed twice, and the average conversion and yields are reported.

Table S3. Conditions screening

Entry	Alkene, eq	Catalyst, mol%	Concentration, M	NMR yield of product	NMR yield of dimer
1	1	2	0.1	64	10
2	2	2	0.1	80	-
3	3	2	0.1	88	-
4	3	2	0.2	86	-
5	3	1	0.2	87	-
6	3	0.5	0.2	87	-
7	3	0.1	0.3	-	50

Reaction without alkene



Full conversion to dimer

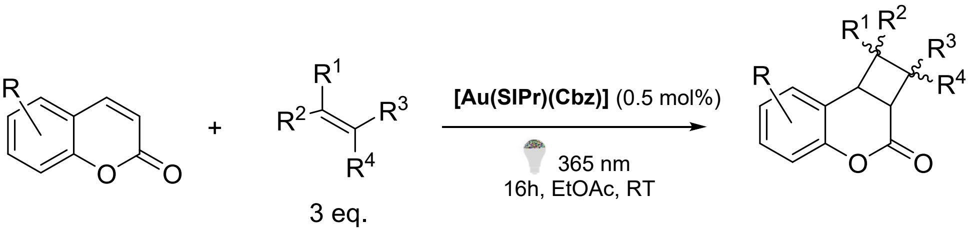
Scheme S1. Reaction without alkene present in reaction mixture

Coumarin **1a** (0.2 mmol) and [Au(SIPr)(Cbz)] (2 mol%) were weighted and transferred into a 4 mL vial equipped with a stirring bar. Ethyl acetate (2 mL) was added via syringe and the mixture was degassed by bubbling inert gas through it for 3 minutes. The vial was placed into the photoreactor for 16 hours. After the reaction was deemed complete, the conversion of coumarin and yield of **3** were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.41 – 7.32 (m, 4H), 7.27 – 7.18 (m, 2H), 7.16 – 7.08 (m, 2H), 3.97 – 3.82 (m, 4H).

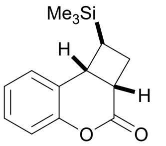
Analytical data is consistent with previously reported values.[2]

General procedure for photocatalytic [2+2] cycloaddition of coumarins and alkenes



Coumarin (0.4 mmol), [Au(SIPr)(Cbz)] (0.5 mol%, 1.5 mg) and alkene (If solid) (3 eq.) were weighted and transferred into a 4 mL vial equipped with a stirring bar. Ethyl acetate (2 mL) was added via syringe and the mixture was degassed by bubbling inert gas through it for 3 minutes. Under flow of inert gas, alkene (if a liquid) was added to reaction mixture via syringe and the vial was closed with a screw cap. The vial was placed into the photoreactor for the indicated time. After completion, the volatiles from the reaction mixture were evaporated and the product was purified using column chromatography. Each reaction was performed twice, and the average yield of two runs is presented. The combined yield of all diastereomers is presented. Diastereomeric ratios were determined using ^{1}H NMR spectroscopic analysis of the reaction crude. Structures of diastereomers were determined using ^{1}H, DEPT ^{13}C NMR spectra with combination with COSY, HSQC, HMBC and NOESY 2D NMR spectra. In the case where isolation of pure minor diastereomer proved possible, their spectra are also provided.

2a



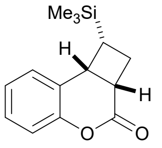
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (15:1). Oil, 160 mg (d.r. 10:1) (Average yield of two runs – 81%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 1H), 7.09 (td, *J* = 7.4, 1.3 Hz, 1H), 7.06 – 6.97 (m, 2H), 3.59 (t, *J* = 7.6 Hz, 1H, C**H**-C^{Ar}), 3.54 – 3.43 (m, 1H, C**H**-CO), 2.65 – 2.52 (m, 1H, CH_2), 2.52 – 2.37 (m, 1H, CH_2), 1.98 – 1.74 (m, 1H, C**H**-$SiMe_3$), 0.10 (s, 9H, CH_3).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.8 (C=O), 151.15 (C^{Ar}-O), 128.35 (CH^{Ar}), 128.0 (CH^{Ar}), 125.0 (CH^{Ar}), 124.9 (C^{Ar}(IV)), 117.5 (**C**H^{Ar}—C^{Ar}-O), 36.4 (**C**H-CO), 36.0 (**C**H-C^{Ar}), 32.25 (**C**H-$SiMe_3$), 26.7 (CH_2), -3.3 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{14}H_{19}O_2Si^+$ $[M+H]^+$ 247.1149; found 247.1138.

2a'



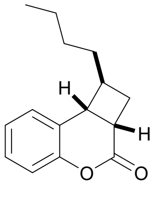
Minor diastereomer.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.26 – 7.18 (m, 1H), 7.08 (d, *J* = 4.1 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 4.22 – 3.96 (m, 1H), 3.77 – 3.50 (m, 1H), 3.00 – 2.66 (m, 1H, CH_2), 2.50 – 2.26 (m, 2H, CH_2 and CH), -0.24 (s, 9H, CH_3).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.9 (C=O), 151.5 (C^{Ar}-O), 129.4 (CH^{Ar}), 128.7 (CH^{Ar}), 124.5 (CH^{Ar}), 122.5 (C^{Ar}(IV)), 117.5 (**C**H^{Ar}—C^{Ar}-O), 35.9, 35.6, 29.4 (**C**H-$SiMe_3$), 27.1 (CH_2), -2.75 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{14}H_{19}O_2Si^+$ $[M+H]^+$ 247.1149; found 247.1141.

2b



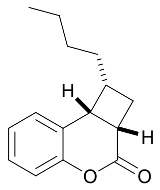
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (25:1). Oil, 113 mg (d.r. 4:1) (Average yield of two runs – 62%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 1H), 7.11 – 7.06 (m, 2H), 7.06 – 7.00 (m, 1H), 3.50 – 3.37 (m, 1H, C**H**-CO)), 3.37 – 3.25 (m, 1H, C**H**-C^{Ar}), 2.65 – 2.50 (m, 1H, CH_2), 2.50 – 2.32 (m, 1H, CH-Bu), 2.32 – 2.18 (m, 1H, CH_2), 1.80 – 1.60 (m, 1H, CH_2-Pr), 1.60 – 1.46 (m, 1H, CH_2-Pr), 1.42 – 1.20 (m, 4H, CH_2-CH_2), 0.97 – 0.77 (m, 3H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6 (C=O), 151.4 (C^{Ar}-O), 128.3, 127.8, 124.7, 123.5 (C^{Ar}(IV)), 117.3 (**C**H^{Ar}—C^{Ar}-O), 44.5 (**C**H-Bu), 41.1 (**C**H-C^{Ar}), 35.3 (CH_2-Pr), 33.5 (**C**H-CO), 32.3 (CH_2), 29.0 (CH$_2^{Hex}$), 22.6 (CH$_2^{Hex}$), 14.0 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{15}H_{19}O_2^+$ $[M+H]^+$ 231.1380; found 231.1372.

2b'



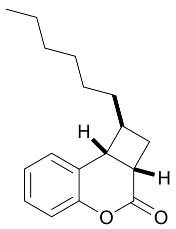
Minor diastereomer.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.29 – 7.21 (m, 1H), 7.10 (td, *J* = 7.3, 1.4 Hz, 1H), 7.07 – 7.02 (m, 2H), 3.90 – 3.74 (m, 1H, CH), 3.56 – 3.35 (m, 1H, CH), 2.88 – 2.53 (m, 2H, CH and CH_2), 2.13 – 1.94 (m, 1H, CH_2), 1.42 – 0.89 (m, 6H, CH_2), 0.81 (t, *J* = 7.0 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.8 (C=O), 152.0 (C^{Ar}-O), 130.0, 128.5, 124.3, 119.5, 117.5, 39.3, 38.0, 33.4, 32.7, 31.6 (CH_2), 28.8(CH_2^{Hex}), 22.7(CH_2^{Hex}), 14.1(CH_3).

HRMS (ESI-TOF): Calcd for $C_{15}H_{19}O_2^+$ $[M+H]^+$ 231.1380; found 231.1369.

2c



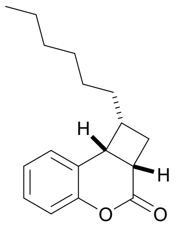
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (25:1). Oil, 154 mg (d.r. 4:1) (Average yield of two runs – 75%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 1H), 7.11 – 7.06 (m, 2H), 7.06 – 7.00 (m, 1H), 3.49 – 3.36 (m, 1H, CH), 3.36 – 3.23 (m, 1H, CH), 2.65 – 2.49 (m, 1H, CH_2), 2.49 – 2.32 (m, 1H, CH-Hex), 2.32 – 2.13 (m, 1H, CH_2), 1.78 – 1.59 (m, 1H, CH_2-Pent), 1.59 – 1.44 (m, 1H, CH_2-Pent), 1.27 (br s, 8H, CH_2), 0.91 – 0.84 (m, 3H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7 (C=O), 151.5 (C^{Ar}-O), 128.4, 127.9, 124.8, 123.6 (C^{Ar}(IV)), 117.4 (**C**H^{Ar}—C^{Ar}-O), 44.6 (**C**H-Hex), 41.2, 35.8 (CH), 33.6 (CH), 32.4, 31.9, 29.3, 26.9, 22.7, 14.2 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{17}H_{23}O_2^+$ $[M+H]^+$ 259.1693; found 259.1684.

2c'



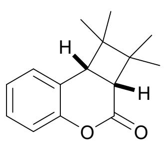
Minor diastereomer

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.29 – 7.21 (m, 1H), 7.10 (td, *J* = 7.3, 1.3 Hz, 1H), 7.06 – 6.99 (m, 2H), 3.91 – 3.74 (m, 1H, CH), 3.58 – 3.35 (m, 1H, CH), 2.87 – 2.59 (m, 2H, CH and CH_2), 2.24 – 1.92 (m, 1H, CH_2), 1.44 – 1.03 (m, 10H, CH_2), 0.84 (t, *J* = 6.8 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9 (C=O), 150.2 (C^{Ar}-O), 130.0 , 128.5, 124.3, 119.5 (C^{Ar}(IV)), 117.5 (**C**H^{Ar}—C^{Ar}-O), 39.3 (CH), 38.0 (CH), 33.4 (CH), 32.7, 32.0, 31.9, 29.3, 26.6, 22.7, 14.2 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{17}H_{23}O_2^+$ $[M+H]^+$ 259.1693; found 259.1692.

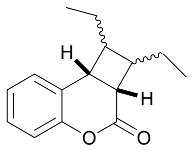
2d[3]



Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (4:1). Oil, 148 mg. (Average yield of two runs – 81%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.17 (m, 1H), 7.08 (td, *J* = 7.4, 1.3 Hz, 1H), 7.04 – 6.95 (m, 2H), 3.38 (d, *J* = 9.7 Hz, 1H), 3.20 (d, *J* = 9.7 Hz, 1H), 1.27 (s, 3H), 1.22 (s, 3H), 1.02 (s, 3H), 0.75 (s, 3H).

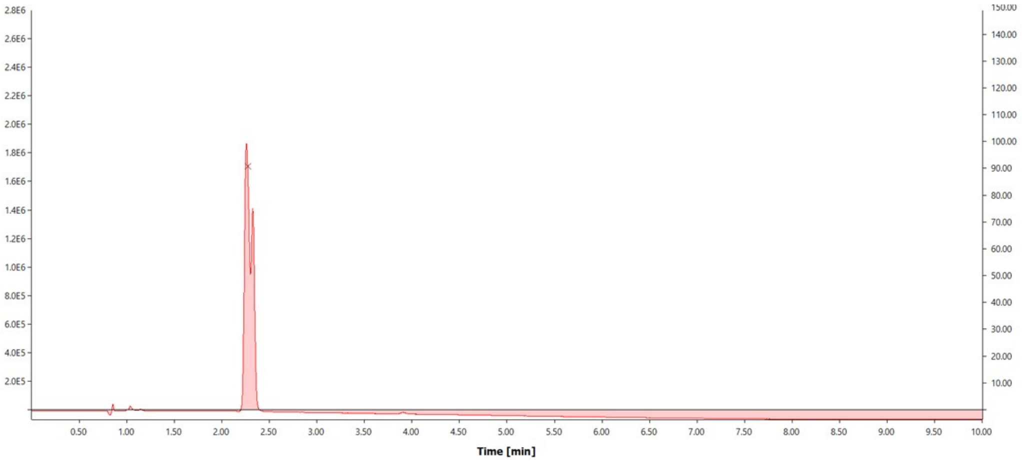
2e



Was synthesized according to the general procedure. Irradiation time 32 h, LEDs 30W+18W. Eluent PE-EtOAc (20:1). Was isolated as mixture of 3 diastereomers. Attempts to separate them failed. Oil, 153 mg (d.r. 1:2:2) (Average yield of two runs – 90%).

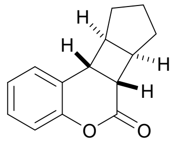
^{1}H and ^{13}C NMR of the mixture of 3 diastereomers can be found in NMR spectra section

LC-MS chromatogram of mixture of diastereomers



LC-MS: t = 2.260 min, m/z: 231, 147; t = 2.327 min, m/z: 231, 147
HRMS (ESI-TOF): Calcd for $C_{15}H_{19}O_2^+$ $[M+H]^+$ 231.1380; found 231.1370.

2f

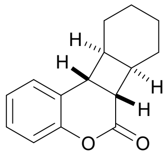


Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (15:1). Solid, 149 mg (d.r. 2.2:1) (Average yield of two runs – 87%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.18 (m, 1H, CH^{Ar}), 7.13 – 7.04 (m, 2H, CH^{Ar}), 7.01 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.19 (dd, *J* = 9.4, 3.9 Hz, 1H, C**H**-C^{Ar}(IV)), 3.16 – 3.09 (m, 1H), 3.04 (ddd, *J* = 9.4, 5.1, 1.2 Hz, 1H, C**H**-C=O), 2.74 – 2.64 (m, 1H, CH), 2.05 – 1.81 (m, 4H, CH_2), 1.70 – 1.52 (m, 2H, CH_2).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3 (C=O), 150.5 (C^{Ar}-O), 128.25, 128.1, 125.1, 123.8 (C^{Ar}(IV)), 117.5, 47.6, 44.1, 38.5, 37.6, 33.1 (CH_2), 32.8 (CH_2), 24.7 (CH_2).
HRMS (ESI-TOF): Calcd for $C_{14}H_{15}O_2^+$ $[M+H]^+$ 215.1067; found 215.1066

2g



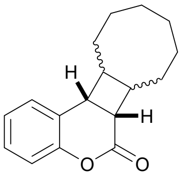
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (15:1). Solid, 165 mg (d.r. 3.6:2:1) (Average yield of two runs – 90%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.20 (m, 1H), 7.10 – 7.05 (m, 2H), 7.05 – 7.00 (m, 1H), 3.83 (t, *J* = 8.9 Hz, 1H, C**H**-C^{Ar}(IV)), 3.53 (t, *J* = 9.6 Hz, 1H, C**H**-C=O), 3.14 – 2.98 (m, 1H, CH), 2.92 – 2.76 (m, 1H, CH), 1.78 – 1.55 (m, 2H), 1.46 – 1.05 (m, 6H, CH_2).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1 (C=O), 152.2 (C^{Ar}-O), 128.7, 128.4, 124.5, 121.2, 117.3, 37.85 (CH), 37.8 (CH), 36.6 (CH), 36.4 (CH), 23.8 (CH_2), 23.7 (CH_2), 22.0 (CH_2), 21.7 (CH_2).
HRMS (ESI-TOF): Calcd for $C_{15}H_{17}O_2^+$ $[M+H]^+$ 229.1223; found 229.1222

Second isolated fraction contained two different diastereomers, the ^{1}H and ^{13}C NMR spectra of the mixture can be found in NMR spectra section

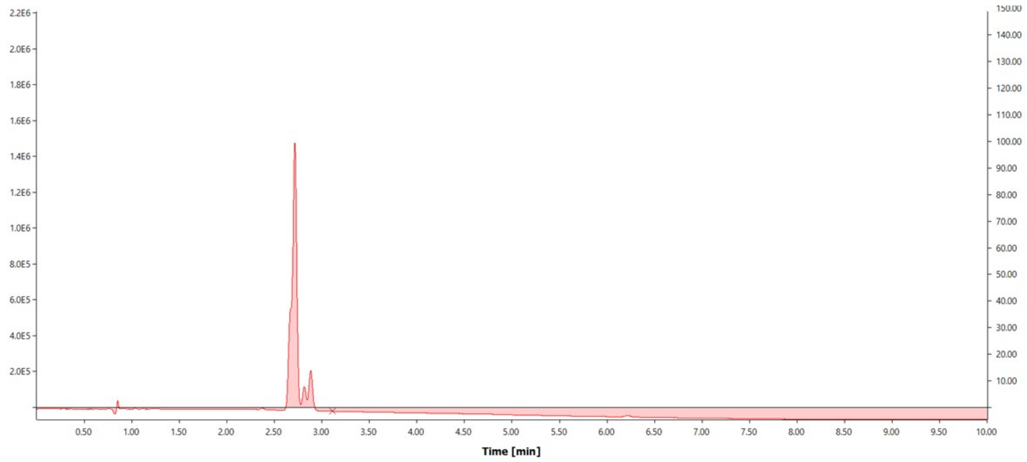
2h



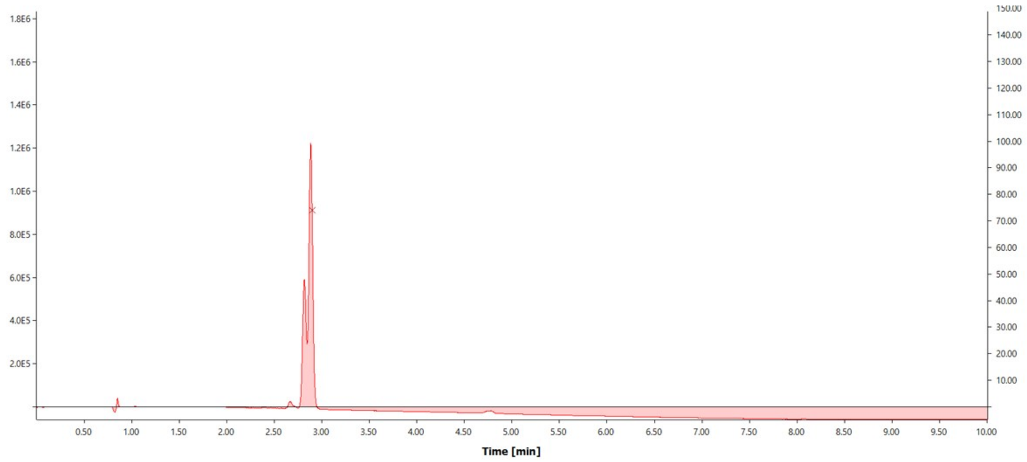
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (15:1). Was isolated as two pairs of diastereomers. Attempts to separate them failed. White solid, 153 mg (d.r. 1:3:4:6) (Average yield of two runs – 81%)

^{1}H and ^{13}C NMR of the mixtures of two pairs of diastereomers can be found in NMR spectra section

LC-MS chromatogram of first pair of diastereomers

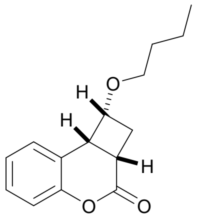


LC-MS chromatogram of second pair of diastereomers



LC-MS: t = 2.717 min, m/z: 257, 147; t = 2.817 min, m/z: 257, 147; t = 2.884, m/z: 257, 147
HRMS (ESI-TOF): Calcd for $C_{17}H_{21}O_2^+$ $[M+H]^+$ 257.1536; found 257.1539.

2i

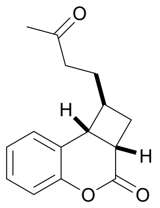


Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (8:1). White solid, 104 mg (Average yield of two runs – 53%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 1H), 7.20 – 7.09 (m, 2H), 7.07 – 7.01 (m, 1H), 4.36 – 4.11 (m, 1H, CH-O), 3.94 (td, *J* = 7.3, 3.5 Hz, 1H, CH), 3.51 – 3.30 (m, 2H, CH_2-O), 3.29 – 3.05 (m, 1H, CH), 2.87 – 2.64 (m, 1H, C$\mathbf{H_2}$-CH), 2.47 – 2.28 (m, 1H, C$\mathbf{H_2}$-CH), 1.53 – 1.38 (m, 2H, CH_2), 1.38 – 1.18 (m, 2H, CH_2), 0.85 (t, *J* = 7.3 Hz, 3H, CH_3).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.6 (C=O), 152.0, 131.2, 128.7, 124.1, 117.2, 117.1, 73.8 (CH-O), 69.2 (CH_2-O), 41.6, 35.6 (**C**H_2-CH), 31.8, 29.6, 19.4, 14.0.

HRMS (ESI-TOF): Calcd for $C_{15}H_{19}O_4^-$ $[M+OH]^-$ 263.1289; found 263.1323.

2j



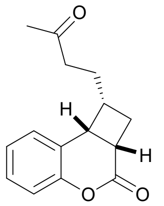
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (2:1). Oil, 182 mg (d.r. 6:1) (Average yield of two runs – 93%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (ddd, *J* = 8.1, 6.6, 2.4 Hz, 1H), 7.13 – 7.05 (m, 2H), 7.02 (dd, *J* = 8.0, 1.0 Hz, 1H), 3.48 – 3.38 (m, 1H, CH-CO), 3.37 – 3.26 (m, 1H, CH-C^{Ar}(IV)), 2.61 – 2.49 (m, 1H, $CH_2^{cyclobutane}$), 2.46 – 2.34 (m, 3H, **C**H-$(CH_2)_2$ and CH_2), 2.31 – 2.20 (m, 1H, $CH_2^{cyclobutane}$), 2.13 (s, 3H, CH_3), 2.03 – 1.88 (m, 1H, CH_2), 1.88 – 1.73 (m, 1H, CH_2).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.1 (C=O), 170.4 (C=O), 151.5 (C^{Ar}-O), 128.7, 127.8, 124.9, 123.0, 117.5, 43.9 (**C**H-(CH$_2$)$_2$), 41.3 (**C**H-CO), 40.8, 33.5 (**C**H-C^{Ar}(IV)), 32.1, 30.2 (CH$_3$), 29.2.

HRMS (ESI-TOF): Calcd for $C_{15}H_{17}O_3$ [M+H]$^+$ 245.1172; found 245.1170.

2j’

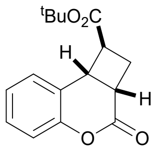


Minor diastereomer

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.22 (m, 1H), 7.11 (td, *J* = 7.4, 1.3 Hz, 1H), 7.08 – 7.01 (m, 2H), 3.95 – 3.75 (m, 1H, C**H**-CO), 3.47 (q, *J* = 8.6 Hz, 1H, C**H**-C^{Ar}(IV)), 2.84 – 2.72 (m, 1H, CH), 2.72 – 2.61 (m, 1H, CH$_2$^{cyclobtane}), 2.36 – 2.18 (m, 2H, CH$_2$), 2.07 (s, 3H, CH$_3$), 2.05 – 1.94 (m, 1H, CH$_2$^{cyclobtane}), 1.75 – 1.61 (m, 1H, CH$_2$), 1.31 – 1.11 (m, 1H, CH$_2$).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.1 (C=O), 168.4 (C=O), 151.9 (C^{Ar}-O), 130.0, 128.7, 124.5, 118.8, 117.6, 40.1 (CH$_2$), 38.2 (CH), 37.8 (CH), 33.1 (CH), 32.0 (CH$_2$^{cyclobtane}), 30.1 (CH$_3$), 25.8 (CH$_2$).

HRMS (ESI-TOF): Calcd for $C_{15}H_{17}O_3$ [M+H]$^+$ 245.1172; found 245.1171.

2k

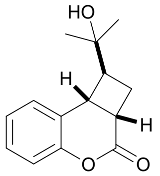


Was synthesized according to the general procedure. Irradiation time 16 h, LEDs 30W+18W. Eluent PE-EtOAc (10:1). White solid, 164 mg (d.r. 3:1) (Average yield of two runs – 75%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 1H), 7.19 – 7.08 (m, 2H), 7.04 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.92 (t, *J* = 8.3 Hz, 1H, C**H**-C^{Ar}(IV)), 3.53 – 3.42 (m, 1H, C**H**-CO), 3.18 – 3.09 (m, 1H, CH, C**H**-CO$_2$^{t}Bu), 2.93 – 2.80 (m, 1H, CH$_2$^{cyclobutane}), 2.67 – 2.52 (m, 1H, CH$_2$^{cyclobutane}), 1.49 (s, 9H, CH$_3$).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3 (**C**O$_2$^{t}Bu), 169.5 (C=O), 151.5 (C^{Ar}-O), 129.2, 128.2, 125.1, 121.9 (C^{Ar}(IV)), 117.5, 81.5 (**C**-(CH$_3$)$_3$), 46.6 (**C**H-CO), 38.5 (**C**H-C^{Ar}(IV)), 33.2 (CH), 28.8 (CH$_2$), 28.2 (CH$_3$).

2l

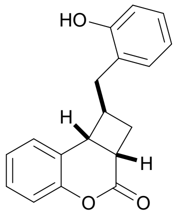
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (1.5:1). Oil, 104 mg (Average yield of two runs – 51%)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 1H), 7.15 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.12 – 7.06 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 3.85 – 3.67 (m, 1H, CH), 3.45 – 3.26 (m, 1H, CH), 2.69 – 2.53 (m, 1H, CH$_2$), 2.53 – 2.29 (m, 2H, CH$_2$ and CH), 1.47 (br s, OH), 1.26 (s, 3H, CH$_3$), 1.17 (s, 3H, CH$_3$).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9 (C=O), 151.9 (C^{Ar}-O), 128.5 (CH^{Ar}), 128.3 (CH^{Ar}), 124.8 (CH^{Ar}), 123.8 (C^{Ar}(IV)), 117.5 (**C**H^{Ar}—C^{Ar}-O), 70.8 (**C**-OH), 53.5 (**C**H-C-OH), 36.1 (CH), 32.7 (CH), 27.8 (CH$_3$), 27.2 (CH$_2$), 27.0 (CH$_3$).

HRMS (ESI-TOF): Calcd for $C_{14}H_{17}O_3^+$ [M+H]$^+$ 233.1172; found 233.1162.

2m

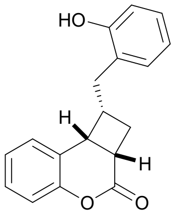


Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (5:1). Oil, 145 mg (d.r. 8:1) (Average yield of two runs – 65%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.20 – 7.07 (m, 3H), 7.00 – 6.83 (m, 3H), 6.77 – 6.71 (m, 1H), 6.63 (dd, *J* = 7.5, 1.7 Hz, 1H), 5.00 (br s, 1H, OH), 3.55 – 3.21 (m, 2H, CH), 3.07 – 2.71 (m, 3H, CH$_2$Ph and CH-Bn), 2.71 – 2.50 (m, 1H, CH$_2$), 2.50 – 2.28 (m, 1H, CH$_2$).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.9 (C=O), 153.8 (C^{Ar}-OH), 151.4 (C^{Ar}-O), 131.2, 128.3, 128.0, 127.9, 125.5 (C^{Ar}-CH$_2$), 124.7, 123.3 (C^{Ar}(IV)), 121.0, 117.2, 115.5, 44.0 (**C**H-Bn), 40.1, 35.4 (CH$_2$), 33.3, 32.1 (CH$_2$).

HRMS (ESI-TOF): Calcd for $C_{18}H_{17}O_3^+$ [M+H]$^+$ 281.1172; found 281.1179.

2m’



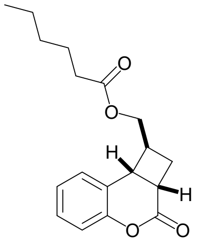
Minor diastereomer

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 – 7.23 (m, 1H), 7.17 – 7.00 (m, 4H), 6.94 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.81 (td, *J* = 7.4, 1.0 Hz, 1H), 6.75 – 6.66 (m, 1H), 4.95 (br s, 1H, OH), 3.94 (td, *J* = 8.5, 2.0 Hz, 1H, CH-C^{Ar}), 3.49 (q, *J* = 8.6 Hz, 1H, CH-CO), 3.36 – 3.07 (m, 1H, CH-Bn), 2.74 (dd, *J* = 13.9, 5.3 Hz, 1H, CH_2-Ph), 2.68 – 2.45 (m, 1H, CH_2), 2.33 – 2.13 (m, 2H, CH_2—Bn and CH_2).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.9 (C=O), 153.6 (C^{Ar}-OH), 152.0 (C^{Ar}-O), 130.5, 130.1, 128.7, 127.6, 125.4 (**C**^{Ar}-CH_2), 124.5, 120.9, 119.15 (C^{Ar}), 117.6, 115.3, 38.4 (CH-Bn), 38.2 (CH-C^{Ar}), 33.2 (**C**H-CO), 32.5 (CH_2), 32.4 (CH_2).

HRMS (ESI-TOF): Calcd for $C_{18}H_{15}O_3^-$ [M-H]$^-$ 279.1027; found 279.1020.

2n



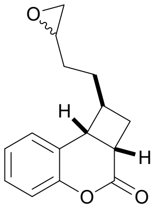
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (5:1). Oil, 155 mg (d.r. 9:1) (Average yield of two runs – 64%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 1H), 7.17 – 7.07 (m, 2H), 7.04 (dd, *J* = 7.9, 1.0 Hz, 1H), 4.36 – 4.05 (m, 2H, CH_2-O), 3.69 – 3.40 (m, 2H, CH^{cyclobutane} x2), 2.89 – 2.65 (m, 1H, C**H**-CH_2O), 2.65 – 2.40 (m, 2H, $CH_2^{cyclobutane}$), 2.35 (t, *J* = 7.5 Hz, 2H, CH_2-CO), 1.80 – 1.55 (m, 2H, CH_2), 1.45 – 1.18 (m, 4H, CH_2), 0.98 – 0.73 (m, 3H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9 (C=O), 169.75 (C=O), 151.5 (C^{Ar}-O), 128.9, 127.9, 124.95, 122.35, 117.5, 65.6 (CH_2-O), 42.5 (**C**H-CH_2O), 38.1 (CH^{cyclobutane}), 34.3 (**C**H_2-CO), 33.4 (CH^{cyclobutane}), 31.4 (CH_2), 28.5 ($CH_2^{cyclobutane}$), 24.75 (CH_2), 22.4 (CH_2), 14.0 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{18}H_{23}O_4^+$ [M+H]$^+$ 303.1591; found 303.1591.

2o



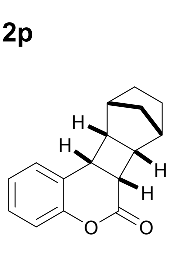
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (3:1). Oil, 74 mg (d.r. 3:1). Was obtained as mixture 1:1 stereoisomers (R and S oxirane), therefore all resonances in ^{13}C NMR are doubled. (Average yield of two runs – 38%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.26 – 7.20 (m, 1H), 7.11 – 7.05 (m, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 3.53 – 3.38 (m, 1H, CH-CO), 3.38 – 3.27 (m, 1H, CH-C^{Ar}), 2.95 – 2.82 (m, 1H, CH-O), 2.82 – 2.71 (m, 1H, CH_2-O), 2.69 – 2.52 (m, 1H, $CH_2^{cyclobutane}$), 2.52 – 2.37 (m, 2H, CH^{cyclobutane} and CH_2-O), 2.37 – 2.19 (m, 1H, $CH_2^{cyclobutane}$), 1.99 – 1.33 (m, 4H, CH_2).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.4 (C=O), 170.35, 151.6 (C^{Ar}-O), 151.5, 128.65, 127.9, 127.8, 124.9, 124.85, 123.2 (C^{Ar}(IV)), 123.1, 117.5 (**C**H^{Ar}—C^{Ar}-O), 117.48, 51.99 (CH-O), 51.90, 47.21 (CH_2-O), 47.10, 44.26 (CH-O), 44.13, 41.38 (**C**H-C^{Ar}), 41.25, 33.58 (**C**H-CO), 33.55, 32.38 ($CH_2^{cyclobutane}$), 32.16, 31.98 (CH_2), 31.79, 30.02 (CH_2), 29.83.

HRMS (ESI-TOF): Calcd for $C_{15}H_{17}O_3^+$ [M+H]$^+$ 245.1172; found 245.1162.

2p



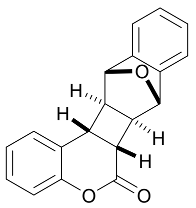
Was synthesized according to the general procedure with 1 mol% [Au(SIPr)(Cbz)]. Irradiation time 32 h. Eluent PE-EtOAc (5:1). Oil, 159 mg (d.r. >10:1) (Average yield of two runs – 83%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 1H), 7.09 (td, *J* = 7.4, 1.4 Hz, 1H), 7.05 – 6.96 (m, 2H), 3.26 (dd, *J* = 9.5, 3.7 Hz, 1H, CH-C^{Ar}), 3.17 – 3.04 (m, 1H, CH-CO), 2.67 – 2.58 (m, 1H, C**H**-CHCO), 2.46 – 2.29 (m, 2H, C**H**-CH_2), 2.27 – 2.17 (m, 1H, C**H**-CHC^{Ar}), 2.01 – 1.88 (m, 1H, CH_2^{bridge}), 1.55 – 1.40 (m, 3H, CH_2^{bridge} and CH_2), 1.13 – 0.93 (m, 2H, CH_2).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.0 (C=O), 150.5 (C^{Ar}-O), 128.2, 127.9, 125.2, 123.5, 117.5 (C^{Ar}(IV)), 51.2 (**C**H-CHC^{Ar}), 47.4 (**C**H-CHCO), 39.3 (CH-CH_2), 39.2 (CH-CH_2), 37.9 (**C**H-CO), 36.5 (**C**H-C^{Ar}), 32.6 (CH_2^{bridge}), 27.3 (CH_2), 27.3 (CH_2).

HRMS (ESI-TOF): Calcd for $C_{16}H_{17}O_2^+$ [M+H]$^+$ 241.1223; found 241.1212.

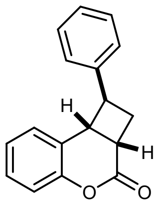
2q



Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (5:1). Oil, 146 mg (d.r. 6:1). (Average yield of two runs – 63%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.29 – 7.10 (m, 7H), 7.05 – 6.94 (m, 1H), 5.46 (d, *J* = 13.0 Hz, 2H), 3.56 (dd, *J* = 9.5, 3.6 Hz, 1H, C**H**-C^{Ar}(IV)), 3.38 (ddd, *J* = 9.5, 4.2, 0.8 Hz, 1H, C**H**-CO), 2.72 (dd, *J* = 6.5, 4.4 Hz, 1H, C**H**-CH-CO), 2.43 – 2.25 (m, 1H, C**H**-CH-C^{Ar}(IV)).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.6, 150.5, 142.9, 142.4, 128.7, 128.2, 127.5, 125.4, 122.2, 120.0, 119.6, 117.6, 81.4, 48.0, 44.3, 35.6, 34.6.

2r

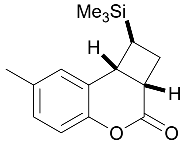


Was synthesized according to the general procedure. Irradiation time 16 h, LEDs 30W+18W. Eluent PE-EtOAc (5:1). White solid, 179 mg (d.r. 8:1). (Average yield of two runs – 90%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (t, *J* = 7.5 Hz, 2H, CH^{Ar}), 7.30 – 7.22 (m, 4H, CH^{Ar}), 7.12 – 7.01 (m, 3H, CH^{Ar}), 3.72 (dq, *J* = 17.7, 8.7 Hz, 2H), 3.50 (td, *J* = 9.4, 8.8, 3.3 Hz, 1H), 3.03 – 2.72 (m, 2H, CH$_2$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8 (C=O), 151.8 (**C**^{Ar}-O), 142.0 (**C**(IV)^{Ar}), 128.9, 128.9, 127.7, 127.1, 126.4, 124.9, 122.8 (**C**(IV)^{Ar}), 48.4, 43.6, 33.6, 33.0 (**C**H$_2$).

2s



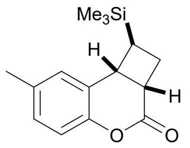
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (15:1). White solid, 160 mg, (d.r. 9.5:1). (Average yield of two runs – 77%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.01 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.78 (d, *J* = 2.1 Hz, 1H), 3.61 – 3.32 (m, 2H, CH), 2.71 – 2.50 (m, 1H, CH$_2$), 2.50 – 2.35 (m, 1H, CH$_2$), 2.29 (s, 3H, CH$_3$), 1.95 – 1.76 (m, 1H, CH-Si), 0.10 (s, 9H, (CH$_3$)$_3$Si).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.9 (C=O), 149.0, 134.5, 128.9, 128.3, 124.5, 117.2, 36.3, 36.0, 32.1 (CH-Si), 26.6, 20.9 (CH$_3$), -3.3. ((CH$_3$)$_3$Si)

HRMS (ESI-TOF): Calcd for $C_{16}H_{17}O_2^+$ [M+H]$^+$ 261.1305; found 261.1309.

2s'

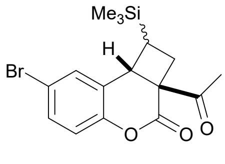


Minor diastereomer.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.06 – 6.96 (m, 1H), 6.95 – 6.82 (m, 2H), 4.10 – 3.95 (m, 1H), 3.76 – 3.55 (m, 1H), 2.91 – 2.67 (m, 1H), 2.44 – 2.23 (m, 5H), -0.24 (s, 9H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.0, 149.4, 134.0, 129.7, 129.2, 122.1, 117.2, 35.9, 35.5, 29.4, 27.1, 20.7, -2.75.

HRMS (ESI-TOF): Calcd for $C_{16}H_{17}O_2^+$ [M+H]$^+$ 261.1305; found 261.1317.

2t



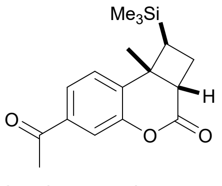
Was synthesized according to the general procedure. Irradiation time 16 h. Eluent PE-EtOAc (15:1). White solid, 248 mg, (d.r. 5:1). (Average yield of two runs – 85%) *The exact structure of major diastereomer was not determined due to dispersive peaks in 2D NOESY spectrum, caused by incomplete suppression of COSY crosspeaks.*

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.17 (d, *J* = 2.3 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 3.73 (d, *J* = 10.6 Hz, 1H, CH), 2.72 – 2.53 (m, 2H, CH$_2$), 2.21 (s, 3H, CH$_3$CO), 1.96 – 1.79 (m, 1H, CHSi), 0.04 (s, 9H, (CH$_3$)$_3$Si).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 200.8 (C=O), 168.0 (C=O), 150.3, 131.8, 130.4, 125.4, 119.1, 117.6, 58.7, 39.6, 32.3 (CH_2), 28.2, 26.1, -3.2.

HRMS (ESI-TOF): Calcd for $C_{16}H_{20}BrO_3Si^+$ $[M+H]^+$ 367.0360; found 367.0375.

2u

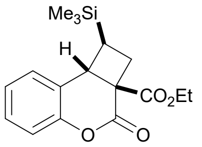


Was synthesized according to the general procedure with 1 mol% of [Au(SIPr)(Cbz)]. Irradiation time 32h, LEDs 30W+18W. Eluent PE-EtOAc (5:1). White solid, 231 mg. (Average yield of two runs – 96%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.5 Hz, 1H), 6.91 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 3.25 – 3.08 (m, 1H, C**H**-CO), 2.45 (ddd, *J* = 11.4, 10.6, 8.8 Hz, 1H, CH_2), 2.30 (s, 3H, CH_3CO), 2.30 – 2.19 (m, 1H, CH_2), 1.79 (ddd, *J* = 10.6, 4.8, 1.0 Hz, 1H, CH-Si), 1.48 (s, 3H, CH_3), 0.14 (s, 9H, $(CH_3)_3Si$).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.3 (C=O), 168.0 (C=O), 150.0, 149.95, 128.5 (C^{Ar}(IV)), 128.0, 118.8, 110.7, 42.7 (C**H**-CO), 42.1 (**C**-CH_3), 36.4 (CH-Si), 27.5 (CH_3CO), 23.5 (CH_2), 21.2 (CH_3), -1.7 $(CH_3)_3Si$)

HRMS (ESI-TOF): Calcd for $C_{17}H_{23}O_4Si^-$ $[M+OH]^-$ 319.1371; found 319.1357.

2v

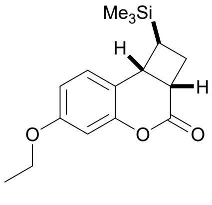


Was synthesized according to the general procedure. Irradiation time 16h. Eluent PE-EtOAc (15:1). White solid, 216 mg (d.r. 6:1). (Average yield of two runs – 85%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.29 – 7.21 (m, 1H), 7.13 – 7.05 (m, 2H), 7.05 – 6.98 (m, 1H), 4.31 – 3.96 (m, 2H, C**H$_2$**-CO), 3.70 (d, *J* = 10.5 Hz, 1H, C**H**-C^{Ar}), 2.84 (t, *J* = 11.9 Hz, 1H, CH_2), 2.57 (ddd, *J* = 11.8, 9.2, 0.9 Hz, 1H, CH_2), 1.89 (ddd, *J* = 12.1, 10.5, 9.2 Hz, 1H, C**H**-Si), 1.19 (t, *J* = 7.1 Hz, 3H, C**H$_3$**-CH_2), 0.06 (s, 9H, $(CH_3)_3$-Si).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.9 (C=O), 168.1 (C=O), 151.5 (C^{Ar}-O), 128.9 (CH^{Ar}), 127.4 (CH^{Ar}), 124.9 (CH^{Ar}), 122.9 (C^{Ar}(IV)), 117.5 (CH^{Ar}), 62.2, 52.1 (**C**-CO_2Et), 42.15, 30.25 (CH_2), 29.1, 14.05, -3.2 (CH_3-Si).

HRMS (ESI-TOF): Calcd for $C_{17}H_{23}O_4^+$ $[M+H]^+$ 319.1360; found 319.1363.

2w

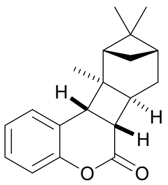


Was synthesized according to the general procedure with 1 mol% of [Au(SIPr)(Cbz)]. Irradiation time 16h, LEDs 30W+18W. Eluent PE-EtOAc (10:1). White solid, 193 mg (d.r. 7.5:1). (Average yield of two runs – 83%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.88 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.65 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 4.00 (q, *J* = 7.0 Hz, 2H, C**H$_2$**CH_3), 3.62 – 3.31 (m, 2H, CH), 2.63 – 2.31 (m, 2H, CH_2), 1.89 – 1.72 (m, 1H, CH-Si), 1.41 (t, *J* = 7.0 Hz, 3H CH_3), 0.08 (s, 9H, $(CH_3)_3Si$).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.0 (C=O), 159.0 (C^{Ar}-OEt), 151.8 (C^{Ar}-O), 128.5 (CH^{Ar}), 116.7 (C^{Ar}(IV)), 112.1 (CH^{Ar}), 102.9 (CH^{Ar}), 63.9 (CH_2-O), 36.4 (CH), 35.5 (CH), 32.3 (CH-Si), 26.6 (CH_2), 14.8 (CH_3), -3.3 (CH_3Si).

HRMS (ESI-TOF): Calcd for $C_{16}H_{23}O_3Si^+$ $[M+H]^+$ 291.1411; found 291.1421.

2x



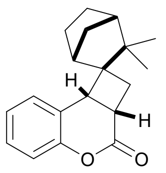
Was synthesized according to the general procedure with 1 mol% of [Au(SIPr)(Cbz)]. Irradiation time 16h, LEDs 30W+18W. Eluent PE-EtOAc (15:1). White solid, 164 mg. (Average yield of two runs – 73%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.17 (m, 1H), 7.11 – 6.97 (m, 2H), 6.90 – 6.77 (m, 1H), 3.68 (d, *J* = 10.6 Hz, 1H, CH-C^{Ar}(IV)), 3.22 (dd, *J* = 10.6, 6.2 Hz, 1H, CH-CO), 2.62 – 2.53 (m, 1H, C**H**-CHCO), 2.53 – 2.41 (m, 1H, CH_2^{bridge}), 2.39 – 2.23 (m, 1H, CH_2), 2.07 – 1.94 (m, 2H, C**H**-CH_2 and CH_2), 1.89 (dd, *J* = 6.4, 4.4 Hz, 1H, C**H**-CCH_3), 1.80 (d, *J* = 11.0 Hz, 1H, CH_2^{bridge}), 1.30 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 0.80 (s, 3H, CH_3).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.8 (C=O), 151.9 (C^{Ar}-O), 129.7, 128.3, 124.4, 120.8 (C^{Ar}(IV)), 117.3, 51.3 (CH), 46.2 (C^{IV}-$(CH_3)_2$), 42.8 (**C**H-CHCO), 41.5 (**C**H-CO), 41.2 (CH), 40.1 (**C**H-C^{Ar}(IV)), 38.8 (C^{IV}-CH_3), 33.9 (CH_2), 27.6 (CH_3), 27.5 (CH_2^{bridge}), 24.3 (CH_3), 24.0 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{20}H_{29}O_3Si^+$ $[M+H]^+$ 283.1693; found 283.1692.

2y



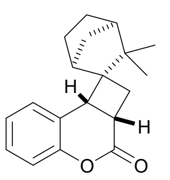
Was synthesized according to the general procedure. Irradiation time 16h. Eluent PE-EtOAc (10:1). White solid, 202 mg (d.r. 3:1). (Average yield of two runs – 90%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.28 – 7.14 (m, 2H), 7.14 – 6.98 (m, 2H), 3.79 (d, *J* = 9.4 Hz, 1H, C**H**-C^{Ar}), 3.13 (td, *J* = 9.7, 2.8 Hz, 1H, C**H**-CO), 2.53 (dd, *J* = 12.4, 10.0 Hz, 1H, $CH_2^{cyclobutane}$), 2.30 (ddd, *J* = 12.4, 2.8, 0.9 Hz, 1H, $CH_2^{cyclobutane}$), 2.18 – 2.02 (m, 1H, CH^{bottom}), 1.67 (dd, *J* = 3.3, 1.6 Hz, 1H, CH^{top}), 1.60 – 1.44 (m, 1H), 1.43 – 1.19 (m, 4H), 1.17 (s, 3H, CH_3), 0.88 (s, 3H, CH_3).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.8(C=O), 153.24 (C^{Ar}-O), 129.33, 128.66, 124.35, 120.70, 117.41, 58.8 (C(IV)), 48.7 (CH^{top}), 43.8 (CH^{bottom}), 41.02, 40.6 (C**H**-C^{Ar}), 35.28, 31.2 (**C**H-CO), 30.9 ($CH_2^{cyclobutane}$), 28.30, 24.83, 24.62, 22.14.

HRMS (ESI-TOF): Calcd for $C_{19}H_{23}O_2^+$ $[M+H]^+$ 283.1693; found 283.1704.

2y'



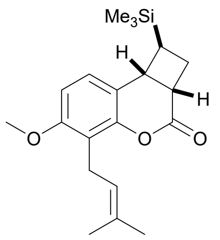
Minor diastereomer.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.16 (m, 2H), 7.05 (td, *J* = 7.4, 1.3 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.72 (d, *J* = 10.0 Hz, 1H, C**H**-C^{Ar}), 3.21 (ddd, *J* = 10.0, 8.7, 4.4 Hz, 1H, C**H**-CO), 2.55 – 2.46 (m, 2H, $CH_2^{cyclobutane}$), 2.28 – 2.18 (m, 1H, CH^{bottom}), 1.83 – 1.73 (m, 1H), 1.69 – 1.14 (m, 6H), 0.85 (s, 3H, CH_3), 0.55 (s, 3H, CH_3).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.4 (C=O), 152.6 (C^{Ar}-O), 129.6, 128.7, 124.4, 124.0 (C^{Ar}(IV)), 117.1, 60.1, 56.0 (CH^{bottom}), 51.3, 49.3 (**C**H-C^{Ar}), 42.0, 34.8, 32.0 (**C**H-CO), 31.1 (CH_2), 28.6 (CH_3), 26.5 (CH_3), 24.6, 22.1.

HRMS (ESI-TOF): Calcd for $C_{19}H_{23}O_2^+$ $[M+H]^+$ 283.1693; found 283.1696.

2z



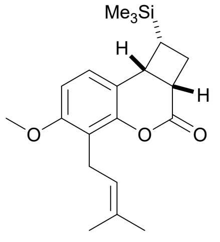
Was synthesized according to the general procedure. Irradiation time 16h. Eluent PE-EtOAc (15:1). White solid, 96 mg (d.r. 6:1). (Average yield of two runs – 35%)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.78 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 5.32 – 5.13 (m, 1H, CH^{alkene}), 3.82 (s, 3H, CH_3O), 3.59 – 3.46 (m, 1H, CH), 3.47 – 3.34 (m, 3H, C**H**$_2$$C^{Ar}$ and CH), 2.61 – 2.30 (m, 2H, $CH_2^{cyclobutane}$), 1.91 – 1.74 (m, 1H, CH-Si), 1.81 (d, *J* = 1.3 Hz, 3H, CH_3), 1.67 (d, *J* = 1.3 Hz, 3H, CH_3), 0.07 (s, 9H, $(CH_3)_3Si$).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.3 (C=O), 157.2 (**C**^{Ar}-OCH_3), 149.6 (C^{Ar}-O), 132.13, 125.29, 122.0 (CH^{alkene}), 118.70, 117.27, 107.07, 56.0 (CH_3O), 36.6 (CH), 36.0 (CH), 32.4 (**C**H-Si), 26.8 ($CH_2^{cyclobutane}$), 26.0 (CH_3), 22.5 (**C**H$_2$$C^{Ar}$), 18.0 ($CH_3$), -3.3 ($(CH_3)_3Si$).

HRMS (ESI-TOF): Calcd for $C_{20}H_{29}O_3Si^+$ $[M+H]^+$ 345.1881; found 345.1881.

2z'



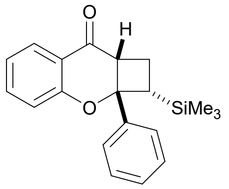
Minor diastereomer

^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.84 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 5.17 (tdd, *J* = 5.8, 2.8, 1.4 Hz, 1H), 4.05 (t, *J* = 9.6 Hz, 1H), 3.83 (s, 3H), 3.60 (dd, *J* = 4.9, 1.6 Hz, 1H), 3.41 (d, *J* = 7.2 Hz, 2H), 3.01 – 2.69 (m, 1H), 2.40 – 2.17 (m, 2H), 1.80 (d, *J* = 1.3 Hz, 3H), 1.65 (q, *J* = 1.3 Hz, 3H), -0.25 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.4, 157.4, 149.9, 132.1, 126.6, 122.0, 118.7, 114.9, 106.7, 56.0, 35.5, 35.4, 29.4, 27.0, 25.9, 22.4, 18.0, -2.7.

HRMS (ESI-TOF): Calcd for $C_{20}H_{29}O_3Si^+$ [M+H]$^+$ 345.1881; found 345.1891.

2aa

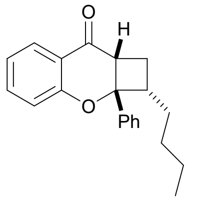


Was synthesized according to the general procedure with 1 mol% of [Au(SIPr)(Cbz)] and 6 eq. of vinyltrimerhylsilane. Irradiation time 32h, LEDs 30W+18W. Eluent PE-EtOAc (12:1). White solid, 147 mg (d.r. 5:1). (Average yield of two runs – 57%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 1H), 7.50 (ddd, *J* = 8.3, 7.2, 1.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.22 (m, 1H), 7.07 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.99 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 3.95 – 3.74 (m, 1H, C**H**-CO), 2.77 – 2.31 (m, 3H, CH_2 and CH-Si), 0.06 (s, 9H, CH_3).
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.70 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.60 (ddd, *J* = 8.9, 7.2, 1.8 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.39 – 7.30 (m, 2H), 7.30 – 7.22 (m, 1H), 7.21 – 7.15 (m, 1H), 7.08 – 6.99 (m, 1H), 4.08 – 3.82 (m, 1H), 2.65 – 2.41 (m, 2H), 2.41 – 2.24 (m, 1H), 0.01 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.6, 161.5, 143.6, 136.5, 128.6, 127.8, 127.3, 125.0, 121.3, 119.7, 118.4, 89.1 (C(**IV**)-Ph), 49.3 (**C**H-CO), 38.4 (CH-Si), 24.2 (CH_2), -1.5 (CH_3).
^{13}C NMR (75 MHz, DMSO-d_6) δ 191.6, 160.8, 143.3, 136.7, 128.4, 127.6, 126.4, 124.8, 121.4, 119.3, 118.3, 88.7, 48.4, 37.5, 23.5, -1.7.

HRMS (ESI-TOF): Calcd for $C_{20}H_{23}O_2Si^+$ [M+H]$^+$ 323.1462; found 323.1460

2ab



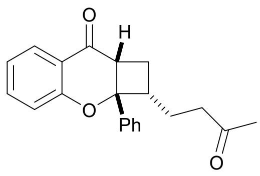
Was synthesized according to the general procedure with 1 mol% of [Au(SIPr)(Cbz)] and 6 eq. of hex-1-ene. Irradiation time 32h, LEDs 30W+18W. Eluent PE-EtOAc (15:1). Oil, 195 mg (d.r. 1.7:1) (Average yield of two runs – 80%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.21 (m, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 3.55 (t, *J* = 9.7 Hz, 1H, C**H**-C=O), 2.86 – 2.71 (m, 1H, C**H**-Bu), 2.69 – 2.51 (m, 1H, CH**H**-CPh), 2.22 (q, *J* = 10.2 Hz, 1H, C**H**H-CPh), 1.88 – 1.62 (m, 2H, CH_2^{Bu}), 1.38 – 1.10 (m, 4H, CH_2^{Bu}), 0.86 (t, *J* = 7.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.1 (C=O), 161.7 (C^{Ar}-O), 142.5, 136.4, 128.7, 128.0, 127.3, 125.1, 121.4, 119.8, 118.6, 87.4 (C(IV)-Ph), 47.8 (CH_2), 45.7 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 27.9 (CH_2), 22.9 (CH_2), 14.2 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{21}H_{23}O_2^+$ [M+H]$^+$ 307.1693; found 307.1693

2ac

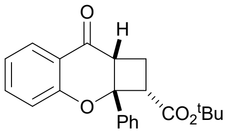


Was synthesized according to the general procedure with 1 mol% of [Au(SIPr)(Cbz)] and 6 eq. of hex-5-en-2-one. Irradiation time 32h, LEDs 30W+18W. Eluent PE-EtOAc (4:1). Isolated as mixture of two diastereomers, which were not separated. Oil, 106 mg (d.r. 2:1) (Average yield of two runs – 42%)

The ^{1}H and ^{13}C NMR spectra of the mixure of the diastereoisomers can be found in NMR spectra section.

HRMS (ESI-TOF): Calcd for $C_{21}H_{21}O_3^+$ [M+H]$^+$ 321.1485; found 321.1483

2ad



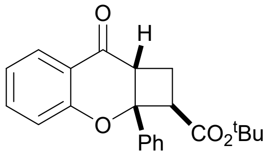
Was synthesized according to the general procedure with 1 mol% of [Au(SIPr)(Cbz)] and 6 eq. of *tert*-butylacrylate. Irradiation time 32h, LEDs 30W+18W. Eluent PE-EtOAc (15:1). Oil, 199 mg (d.r. 1.3:1) (Average yield of two runs – 71%)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.54 – 7.47 (m, 1H), 7.44 – 7.35 (m, 2H), 7.35 – 7.28 (m, 1H), 7.11 – 7.01 (m, 2H), 3.93 (ddd, *J* = 10.6, 6.1, 1.2 Hz, 1H, C**H**-C=O), 3.79 (ddd, *J* = 9.4, 7.1, 1.2 Hz, 1H, CH-CO$_2$^{t}Bu), 2.84 (ddd, *J* = 12.2, 10.6, 7.1 Hz, 1H, CH**H**), 2.50 (ddd, *J* = 12.2, 9.4, 6.1 Hz, 1H, C**H**H), 1.07 (s, 9H, CH$_3$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.1 (C^{Ar}-**C**=O), 169.4 (**C**O-O^{t}Bu), 159.3 (C^{Ar}-O), 138.7, 136.7, 128.6, 128.4, 127.3, 125.8, 122.2, 119.9, 119.2, 85.0 (C(IV)-Ph), 81.3 (**C**-(CH$_3$)$_3$), 51.0 (**C**H-CO$_2$^{t}Bu), 46.3 (**C**H-CO), 27.6 (CH$_3$), 24.3 (CH$_2$).

HRMS (ESI-TOF): Calcd for $C_{22}H_{23}O_4^+$ [M+H]$^+$ 351.1591; found 351.1590

2ad’

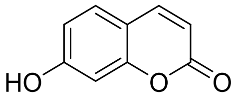


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.50 – 7.42 (m, 1H), 7.41 – 7.28 (m, 3H), 7.03 – 6.97 (m, 1H), 6.94 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.78 – 3.57 (m, 2H, C**H**-C=O and C**H**-CO$_2$^{t}Bu), 3.07 – 2.88 (m, 1H, CH**H**), 2.65 – 2.51 (m, 1H, C**H**H), 1.50 (s, 9H, CH$_3$).

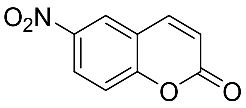
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.3 (C^{Ar}-**C**=O), 168.6 (**C**O-O^{t}Bu), 160.7 (C^{Ar}-O), 141.2, 136.5, 128.70, 128.67, 127.2, 125.6, 121.8, 119.4, 118.5, 86.9 (C(IV)-Ph), 81.7 (C-(CH$_3$)$_3$), 50.1 (CH), 44.3 (CH), 28.3 (CH$_3$), 24.7 (CH$_2$).

HRMS (ESI-TOF): Calcd for $C_{22}H_{22}O_4Na^+$ [M+Na]$^+$ 373.1410; found 373.1410

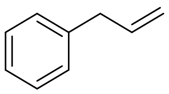
Substrates which failed to react

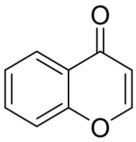


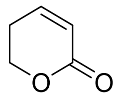
Solubility issues
No reaction in
EtOAc, DCM or
MeOH

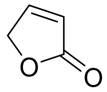


(photo)decomposition



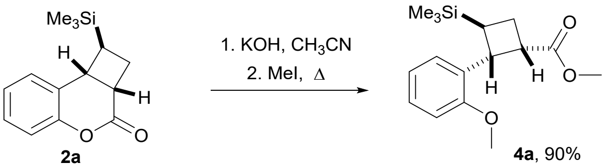






E_T of substrates is too high to be accesible for EnT

Functionalization of chromanone 2a



KOH (5 eq., 140 mg) was suspended in CH_3CN (5 mL) and **2a** (0.5 mmol, 123 mg) was added to the suspension and the reaction mixture was stirred at room temperature for 1 hour. Then methyliodide (4.8 mmol, 0.3 mL) was added and the reaction mixture was refluxed for 16 hours. After this time, water (20 mL) was added to the reaction mixture and it was extracted with EtOAc (3 x 20mL). Organic layers were combined, dried over $MgSO_4$ and volatiles were evaporated. Product **4a** was isolated using column chromatography with PE-EtOAc (20:1) as eluent. Oil, 131 mg, yield – 90%.

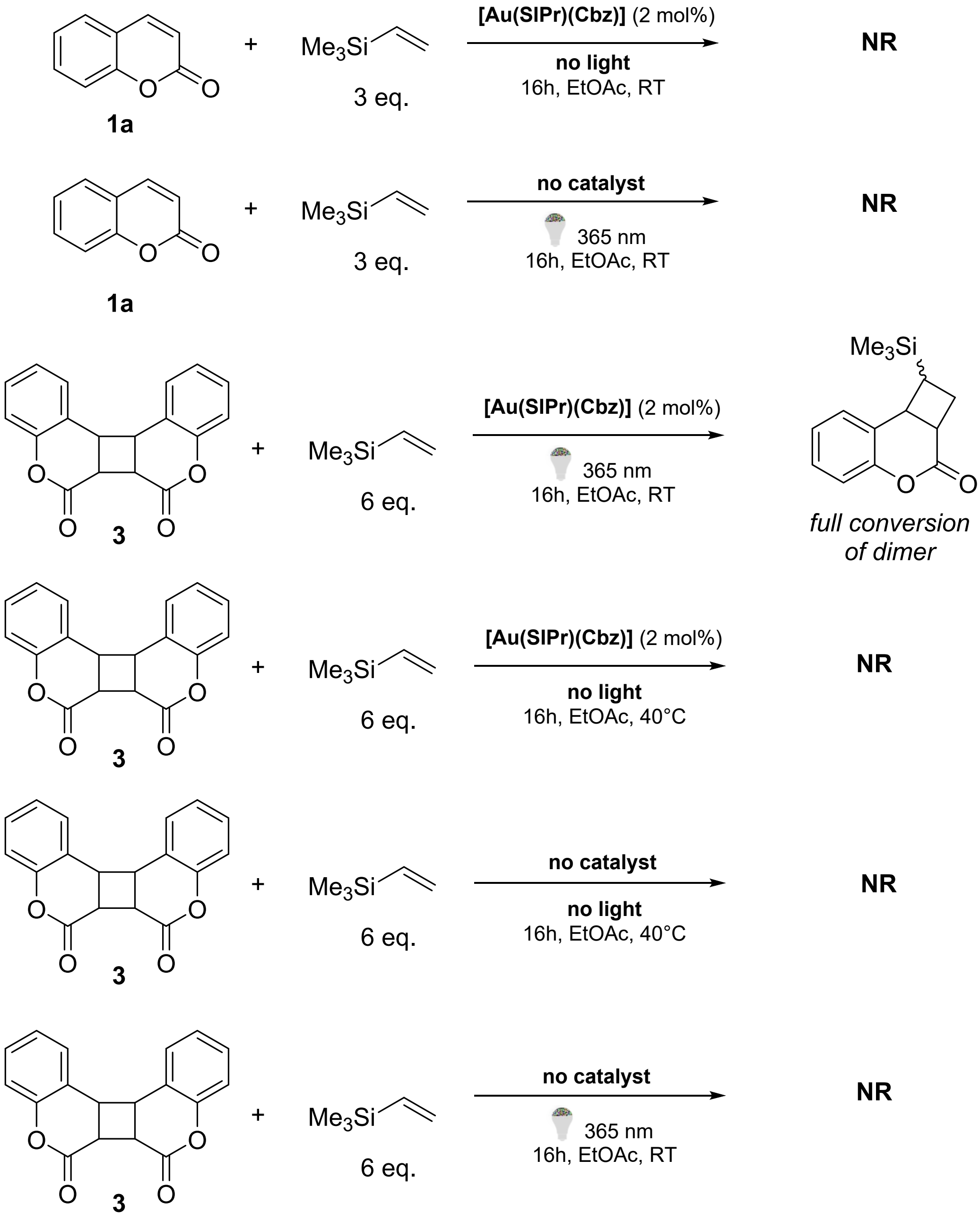
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.21 – 7.09 (m, 2H), 6.95 – 6.84 (m, 1H), 6.78 (dd, J = 8.1, 1.1 Hz, 1H), 4.21 – 4.01 (m, 1H, CH-Ar), 3.81 (s, 3H, CH_3), 3.62 – 3.48 (m, 1H, C**H**-CO_2Me), 3.19 (s, 3H, CH_3), 2.64 – 2.41 (m, 1H), 2.30 (dddd, J = 10.9, 9.8, 3.2, 0.9 Hz, 1H, CH_2), 2.04 (ddd, J = 11.2, 10.1, 7.9 Hz, 1H, CH_2), -0.01 (s, 9H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 174.43, 157.42, 129.84, 127.47 (d, J = 3.8 Hz), 120.22, 109.68, 55.5 (CH_3), 51.0 (CH_3), 45.59, 38.31, 23.92, 21.6 (CH_2), -3.1 (CH_3).

HRMS (ESI-TOF): Calcd for $C_{16}H_{25}O_3Si^+$ $[M+H]^+$ 293.1568; found 293.1559.

Mechanistic studies

Control experiments

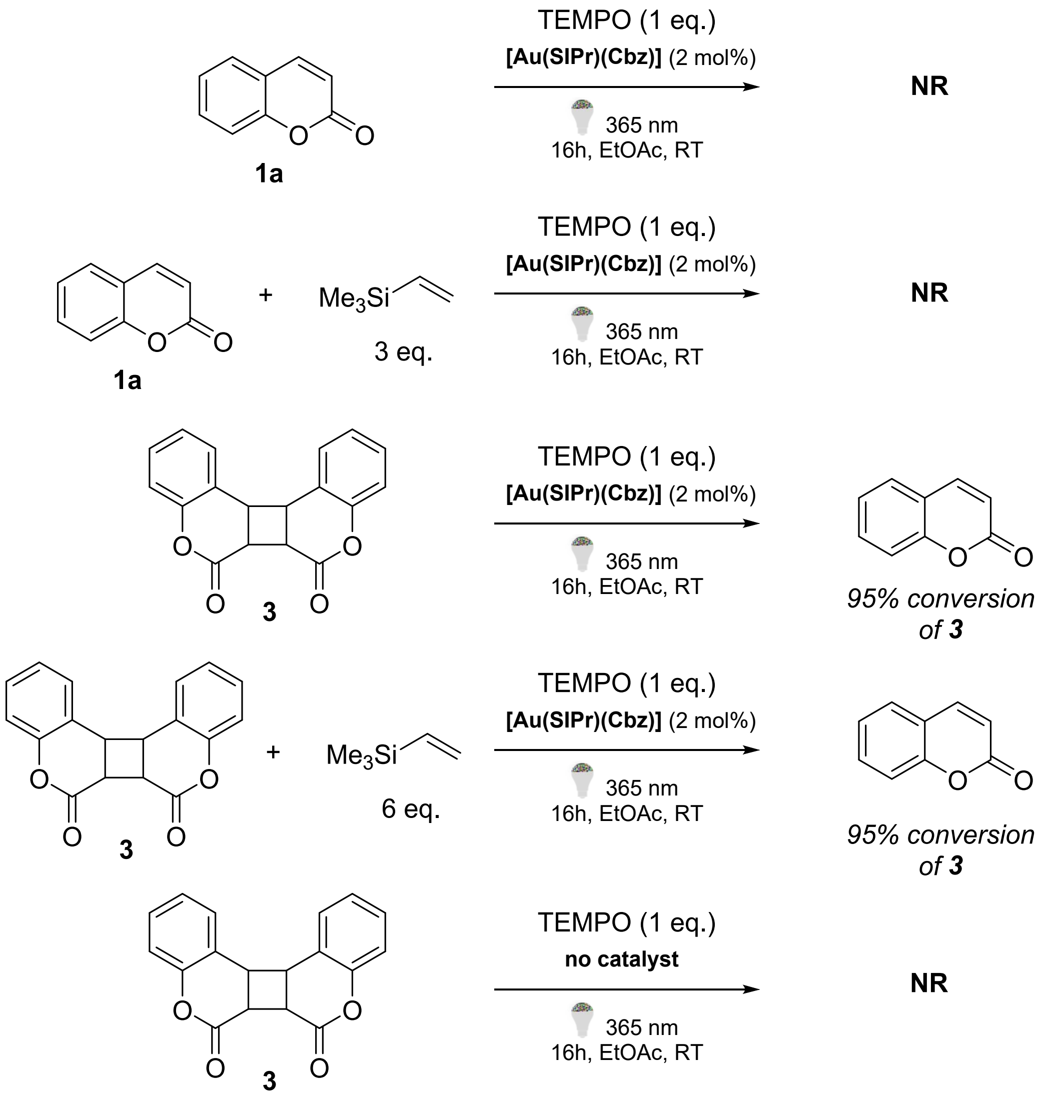
Coumarin **1a** (14.6 mg, 0.1 mmol) or coumarin dimer **3** (14.6 mg, 0.05 mmol) and [Au(SIPr)(Cbz)] (if present) (2 mol%) were weighted and transferred into a 4 mL vial equipped with a stirring bar. Ethyl acetate (1 mL) was added to the reaction mixture which was degassed by bubbling inert gas through it for 3 minutes. Under flow of inert gas, the alkene (if present) was added to the reaction mixture and the vial was closed with a screw cap. The vial was placed into the photoreactor or covered with foil and stirred for 16 hours. After the reaction, the conversion was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.



Scheme S2. Control experiments with coumarin **1a** and coumarin dimer **3**

Reactions with TEMPO

Coumarin **1a** (14.6 mg, 0.1 mmol) or coumarin dimer **3** (14.6 mg, 0.05 mmol), TEMPO (1 eq.) and [Au(SIPr)(Cbz)] (if present) (2 mol%) were weighted and transferred into a 4 mL vial equipped with a stirring bar. Ethyl acetate (1 mL) was added to the reaction mixture which was degassed by bubbling inert gas through it for 3 minutes. Under flow of inert gas, alkene (if present) was added to reaction mixture and the vial was closed with a screw cap. The vial was placed into the photoreactor and stirred for 16 hours. After reaction, the conversion was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.



Scheme S3. Experiments with coumarin **1a** and coumarin dimer **3** in the presence of TEMPO

Absorption spectra

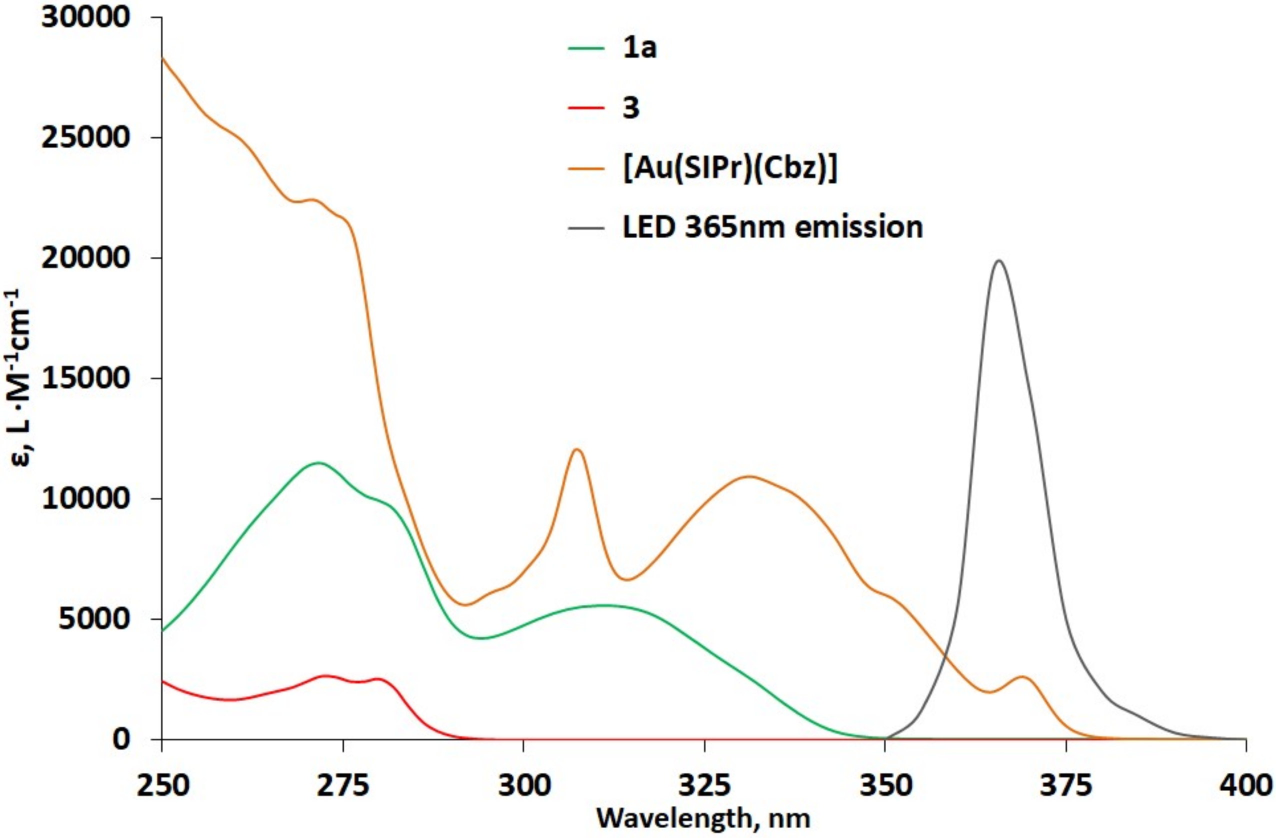


Figure S2. Absorption spectra of **1a, 3,** and **[Au(SIPr)Cbz]**. For clarity emission spectrum of the LED lamp 365 nm is included in the graph.

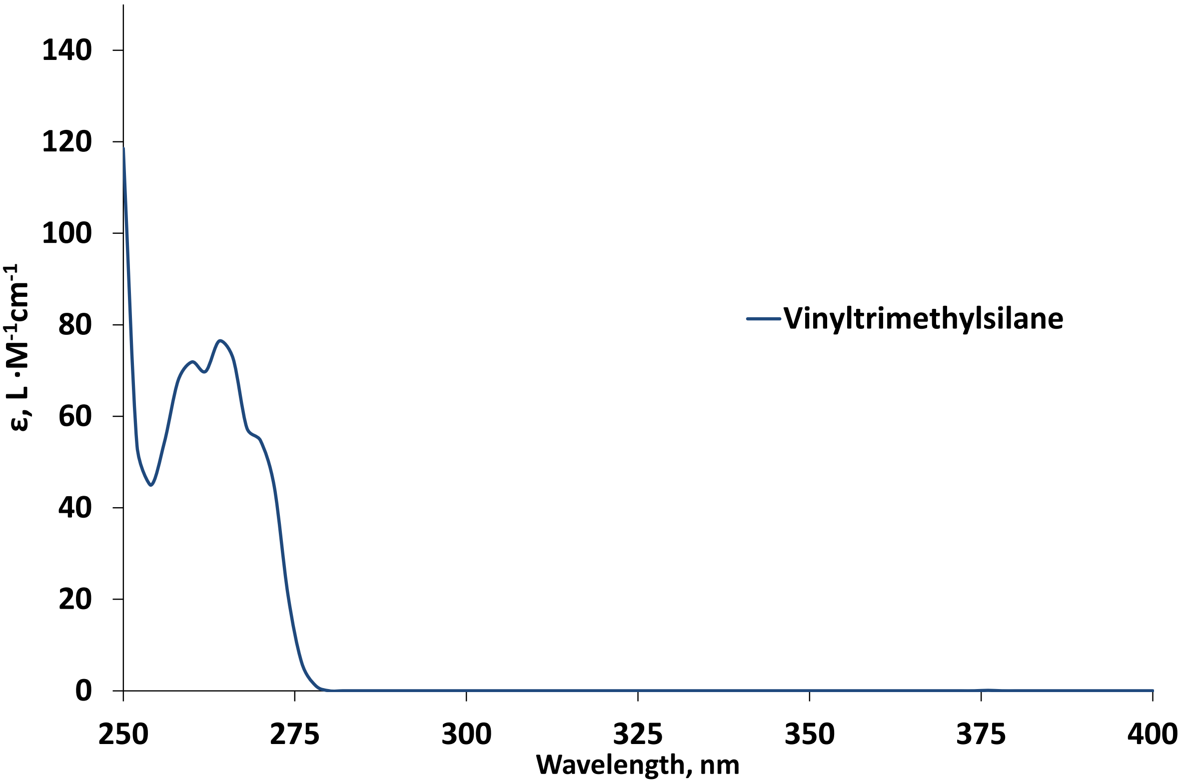
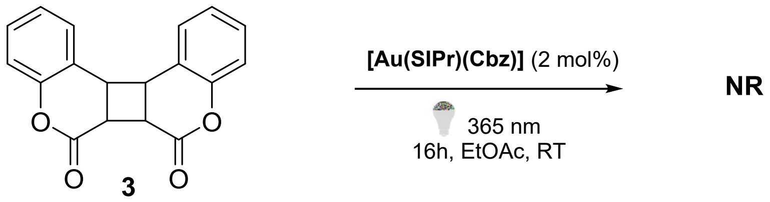


Figure S3. Absorption spectra of vinyltrimethylsilane.

Dimer cleavage tests

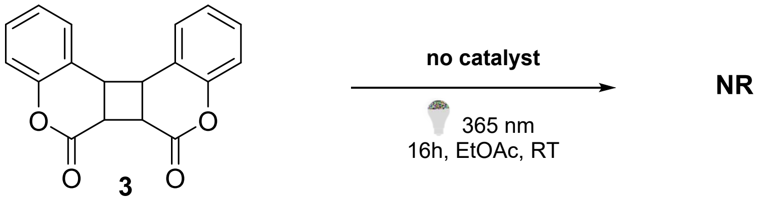
Coumarin dimer **3** (14.6 mg, 0.05 mmol) and [Au(SIPr)(Cbz)] (2 mol%) were weighted and transferred into a 4 mL vial equipped with a stirring bar. Ethyl acetate (1 mL) was added to the reaction mixture which was degassed by bubbling inert gas through it for 3 minutes. The vial was placed into the photoreactor and stirred for 16 hours. After reaction, the conversion was determined by ^{1}H NMR spectroscopy.



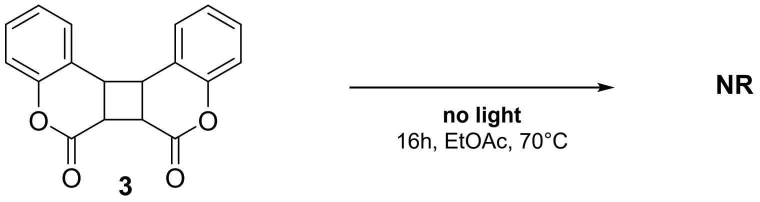
Scheme S4. Dimer cleavage test under irradiation and in the presence of [Au(SIPr)(Cbz)]

Coumarin dimer **3** (14.6 mg, 0.05 mmol) was weighted and transferred into a 4 mL vial equipped with a stirring bar. Ethyl acetate (1 mL) was added to the reaction mixture which was degassed by bubbling inert gas through it for 3 minutes. The vial was placed into the photoreactor or covered with foil and placed to a stirring plate at 70°C and stirred for 16 hours. After reaction, the conversion was determined by ^{1}H NMR and absorption spectra of an aliquot of the reaction mixture was recorded.

3 + hv



3 + 70°C



Scheme S5. Dimer cleavage test under direct irradiation (**3+hv**) or upon heating (**3+70°C**)

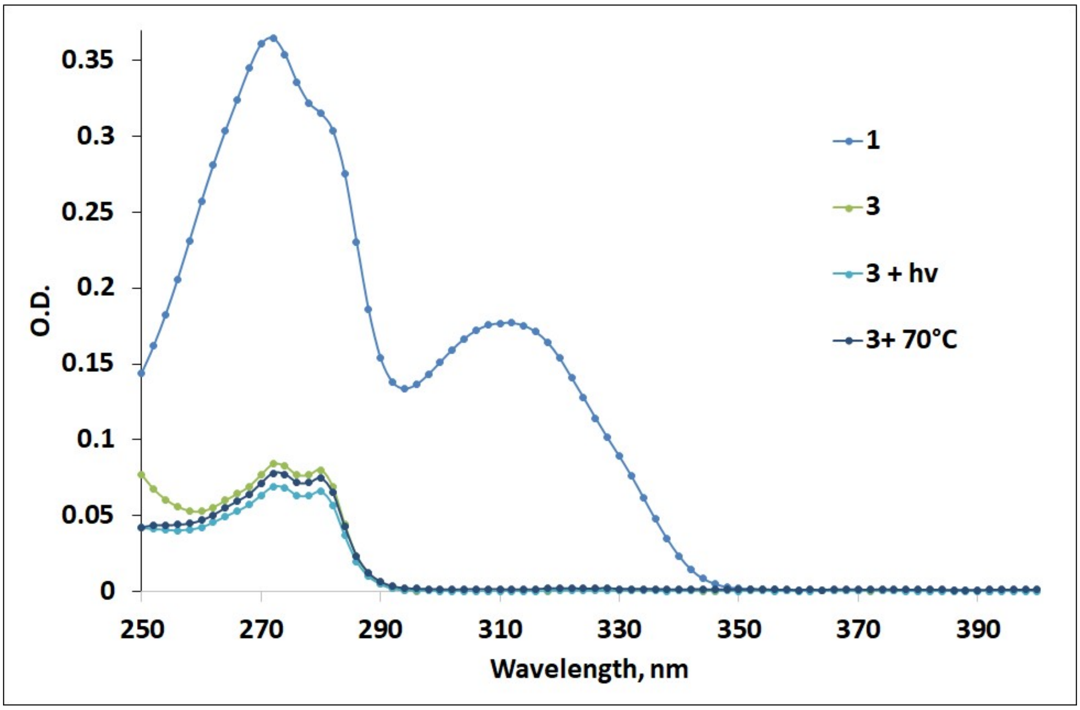


Figure S4. Absorption spectra of coumarin **1a**, coumarin dimer **3** solutions and diluted to same concentration reaction mixtures.

Quenching studies

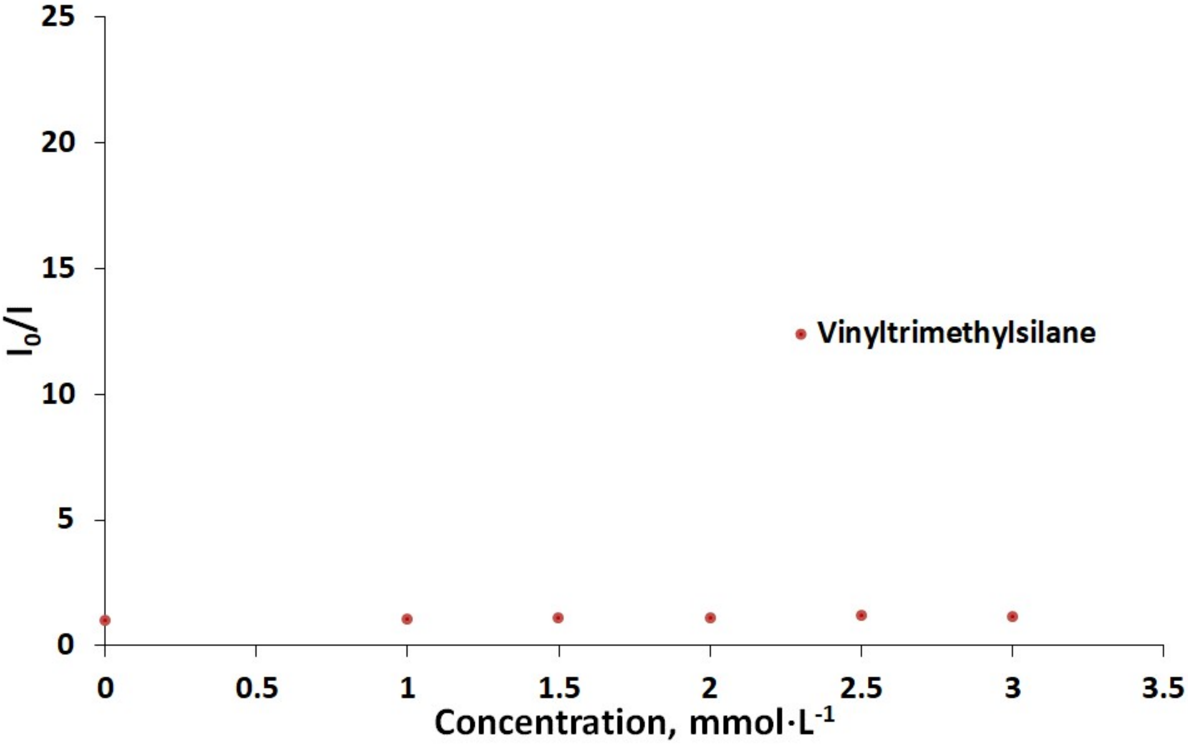


Figure S5. Stern-Volmer plot for **Vinyltrimethylsilane**

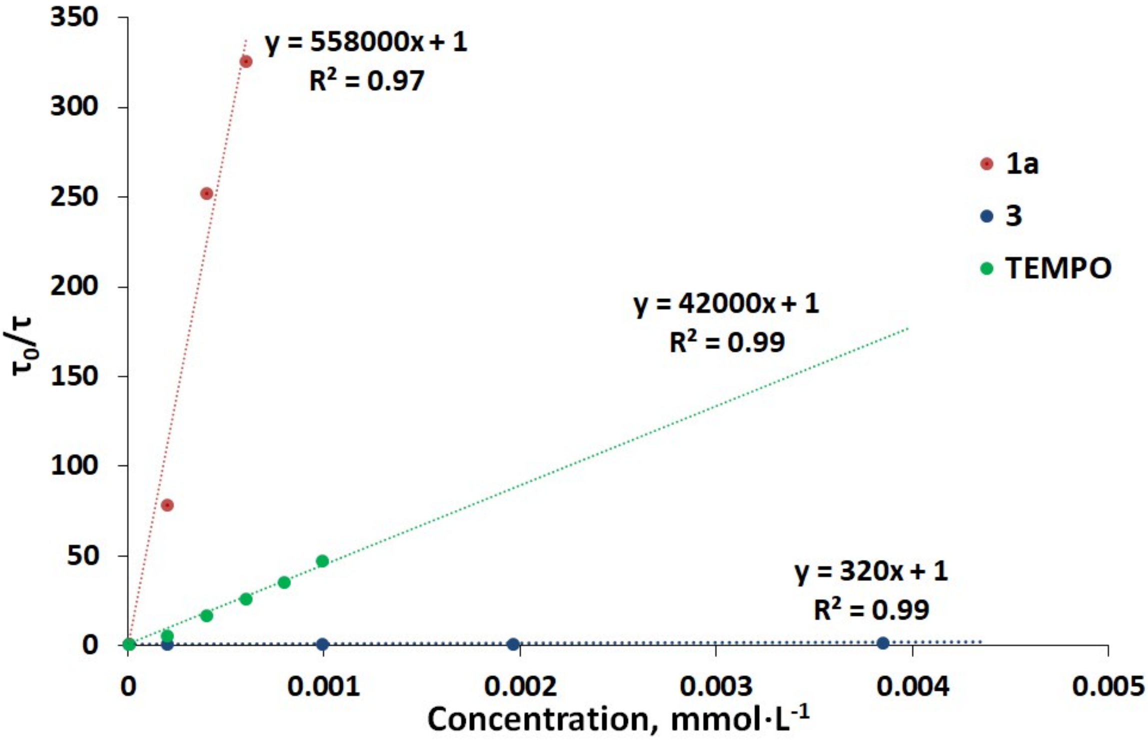


Figure S6. Stern-Volmer plots for **1a, 3** and TEMPO

It is possible to determine quenching rate constant $\mathbf{k_q}$ using the known intrinsic lifetime of **[Au(SIPr)Cbz]** and obtained Stern-Volmer quenching constant K_V from equation:

$$\frac{\Phi^0}{\Phi} = \frac{\tau^0}{\tau} = 1 + k_q \tau^0 [Q]$$

Where Φ^0 is the emission quantum yield without quencher, Φ is the emission quantum yield after addition of the quencher, τ^0 is the lifetime without quencher, τ is the lifetime after the addition of the quencher, k_q is the quenching constant, [Q] is the concentration of the quencher.

The quenching rate constants $\mathbf{k_q}$ were detmined as: $\mathbf{k_q}^{\mathbf{1a}} = 1.64 \cdot 10^{10}$ $M^{-1} \cdot s^{-1}$and $\mathbf{k_q}^{\mathbf{3}} = 8.76 \cdot 10^{6}$ $M^{-1} \cdot s^{-1}$. The quenching constant for TEMPO was determined as $\mathbf{k_q}^{\mathbf{TEMPO}} = 1.05 \cdot 10^{9}$ $M^{-1} \cdot s^{-1}$ under experiment conditions.

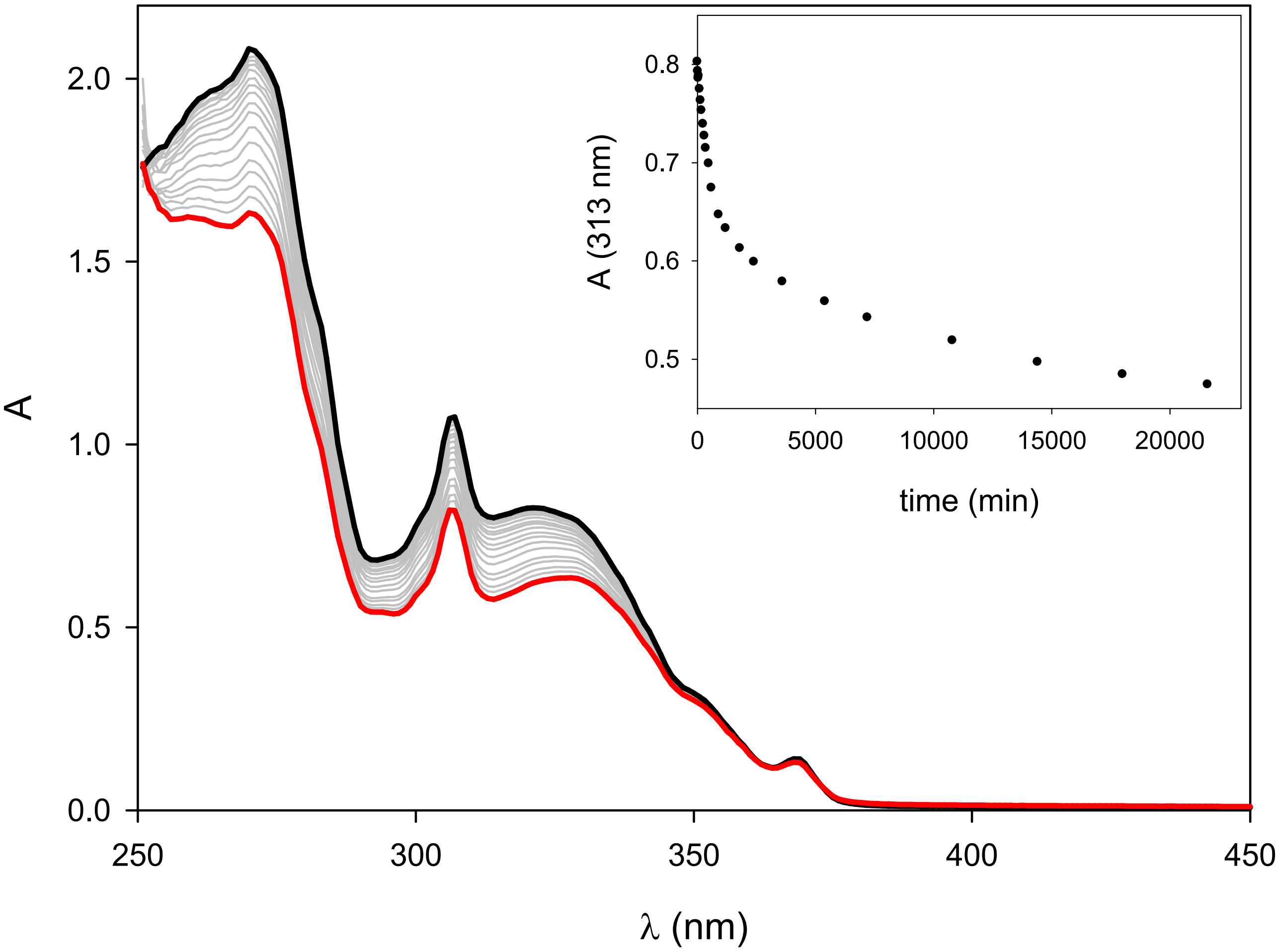


Figure S7. Absorption spectra of a solution of **[Au(SIPr)Cbz]** in AcOEt and Coumarin 0.12 mM before (black line) and after irradiation at 365 nm. Inset: Absorbance changes at 313 nm after irradiation at 365 nm.

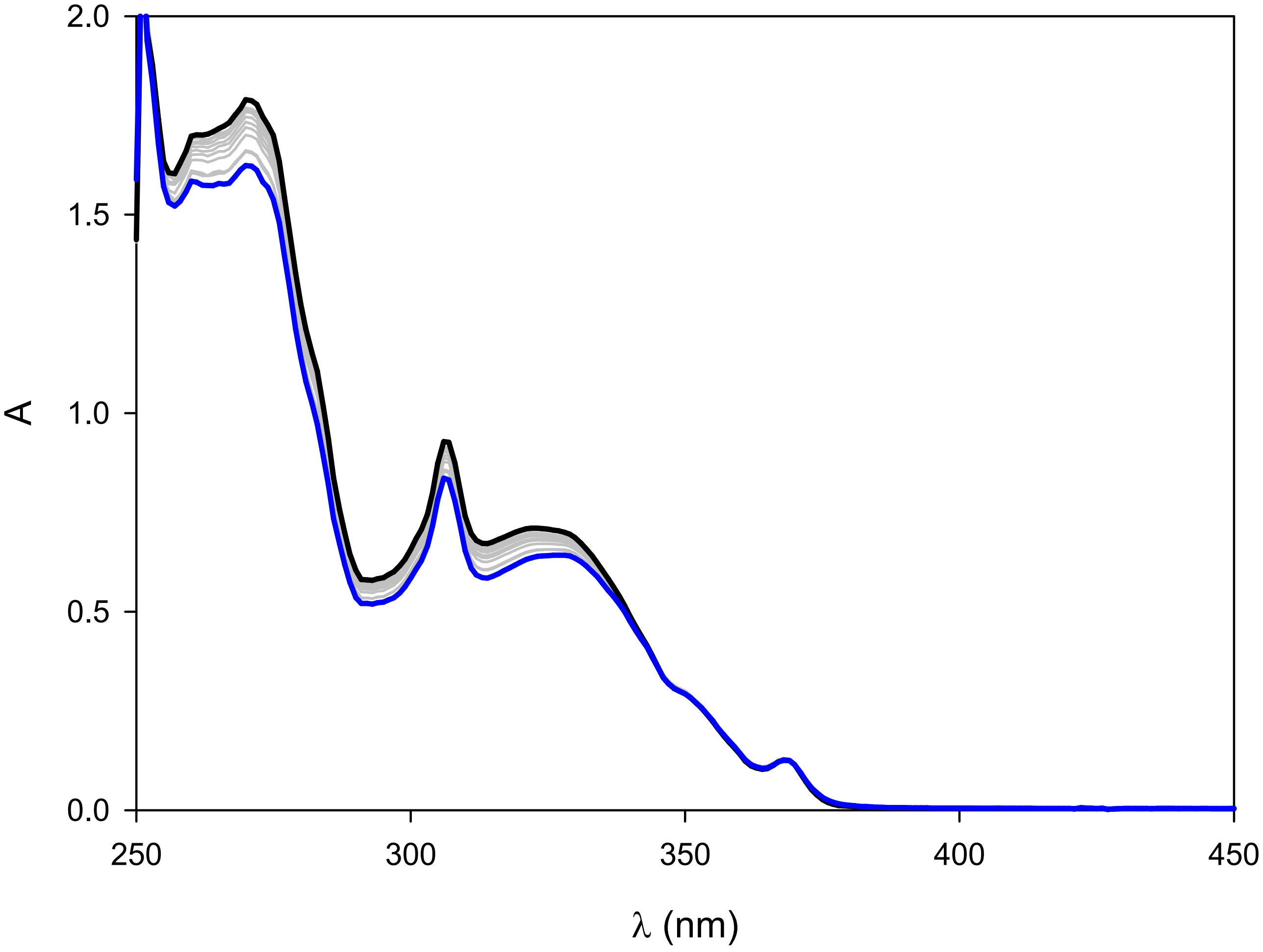


Figure S8. Absorption spectra of a solution of **[Au(SIPr)Cbz]**, **TEMPO** (0.5 mM) and Coumarin (0.12 mM) in AcOEt before (black line) and after irradiation at 365 nm.

Table S4. Quenching constants (k_q) of the phosphorescent excited state of the [Au(SIPr)Cbz] photocatalyst and corresponding quenching efficiency (η).

Compound	**k_q ($M^{-1}\cdot s^{-1}$)**	?.^{a} **(%)**	?.^{b} **(%)**	?.^{c} **(%)**
1a	$1.64\cdot10^{10}$	>99.9	95	94
3	$8.76\cdot10^{6}$	<0.01	5	<0.1
TEMPO	$1.05\cdot10^{9}$			6
Alkene	-	-	-	-

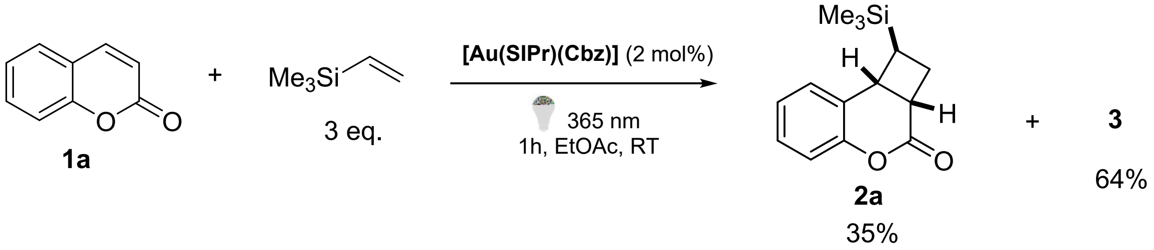
[a] Concentration of **1a** and **3** at 0.1 M. [b] Concentration of **1a** (0.001 M) and **3** (0.1 M). [c] Concentration of **1a**, **TEMPO** and **3** at 0.1 M.

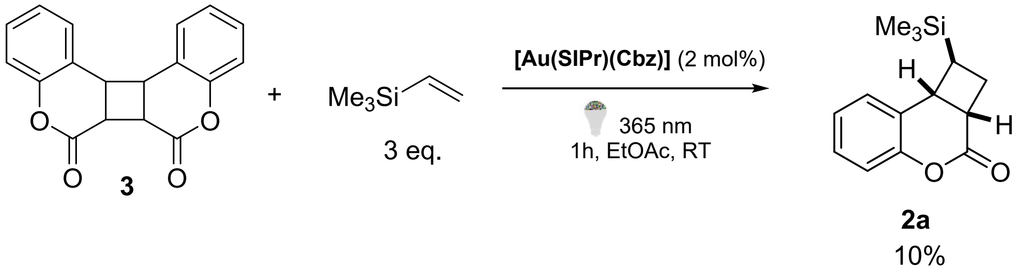
Table S5. Quenching constants ($\mathbf{k_q}$) of **1a**, efficiency of quenching (η^{i}) of **1a** and photodimerization quantum yield (Φ_d).

Compound	**k_q ($M^{-1}\cdot s^{-1}$)**	?.^{i} **(%)**^{a}	**Φ_d**^{b}
1a	$3.5\cdot10^{8}$ ^{c}	33	0.083
TEMPO	$7.4\cdot10^{8}$	67	0.059

^{a} Quenching efficiency in the presence of coumarin **1a** and TEMPO 0.1 M. ^{b}Photosensitized dimerization quantum yield of **1a** (0.12 mM) upon selective excitation of the [Au(SIPr)Cbz] photocatalyst at 365 nm. ^{c}From ref.: J. Org. Chem. 1971, 36, 1, 102–108.

Comparison of initial rate of product formation





Coumarin **1a** (0.1 mmol) and coumarin dimer (0.1 mmol) were weighted in a two separate 4 mL vials equipped with a stirring bar. [Au(SIPr)(Cbz)] (2 mol%) were added in each vial. Ethyl acetate (2 mL) was added via syringe to each vial and the mixtures were degassed by bubbling inert gas through them for 3 minutes. 3 equivalents of vinyltrimethylsilane were added to each vial under the flow of argon and vials were closed with a screw cap. The vials were placed into the photoreactor simultaneously for 1 hour. The yield of **2a** in each vial was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Experiments have been performed twice and the average yields are reported.

Results: In case of the reaction of coumarin **1a** we observed full conversion of coumarin after 1 hour. 35% yield of chromanone **2a** and 64% yield of coumarin dimer **3** were observed in the reaction mixture.

In case of the reaction of coumarin dimer **3**, we observed only 10% yield of chromanone **2a** after 1 hour of irradiation. We also did not observe any traces of coumarin **1a**.

Triplet energy determination

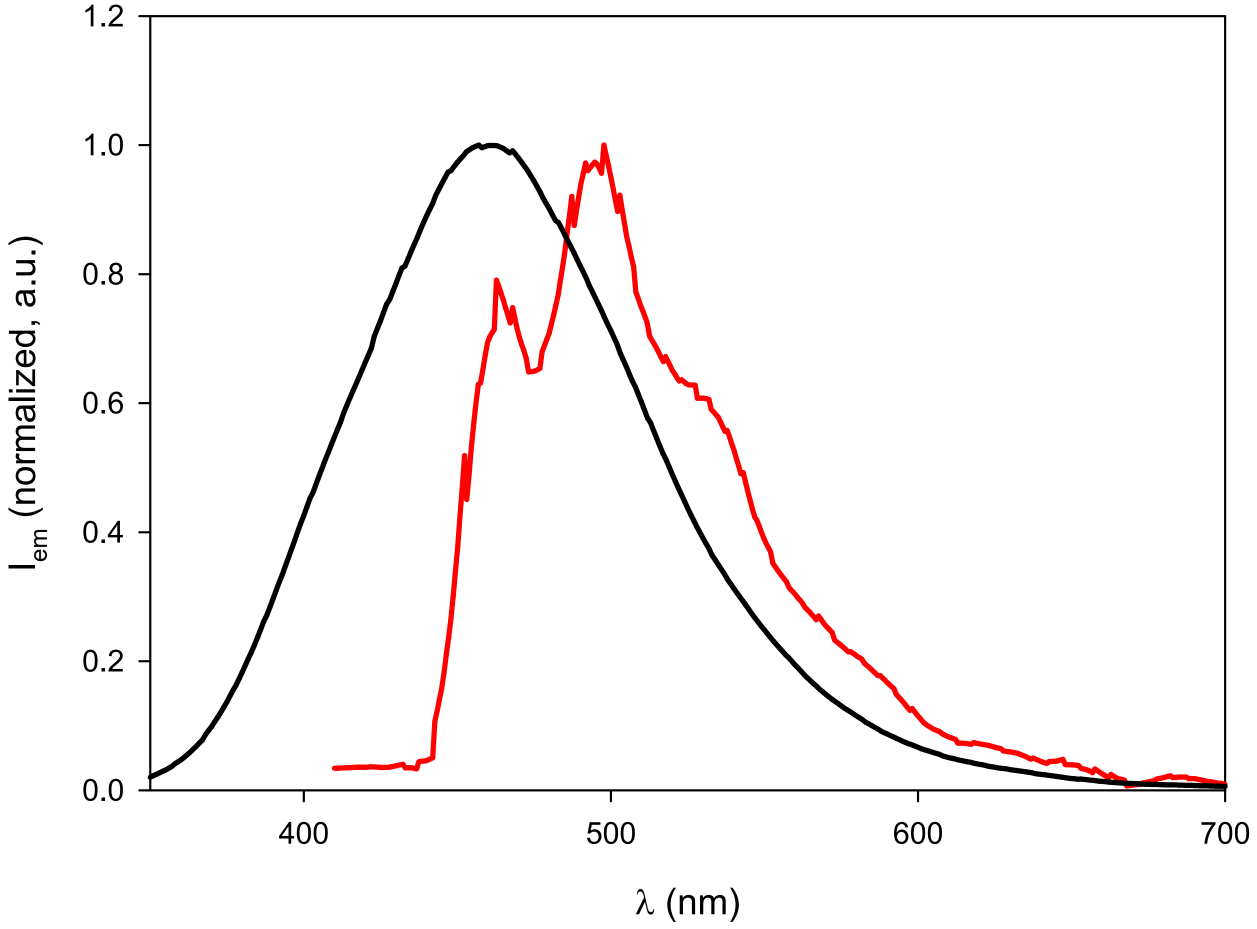


Figure S9. Emission spectra of Coumarin (red line) and Coumarin dimer (black line) in a MeOH/DCM 1:1 rigid matrix at 77 K. Dealy 50 ms, gate 500 ms, λ_{exc} =280 nm for Coumarin dimer **3** and , λ_{exc} =280 nm for Coumarin **1a**.

Table S6. Triplet energy for the investigated compounds[a]

Compound	E_T (Kcal/mol)	E_T (eV)
1a	63.2	2.74
3	74.6	3.24
[Au(SIPr)Cbz]	67.9	2.94

[a] Triplet energies were determined as energy corresponding to the wavelength at 20% height of phosphorescence peaks.

Electrochemical studies

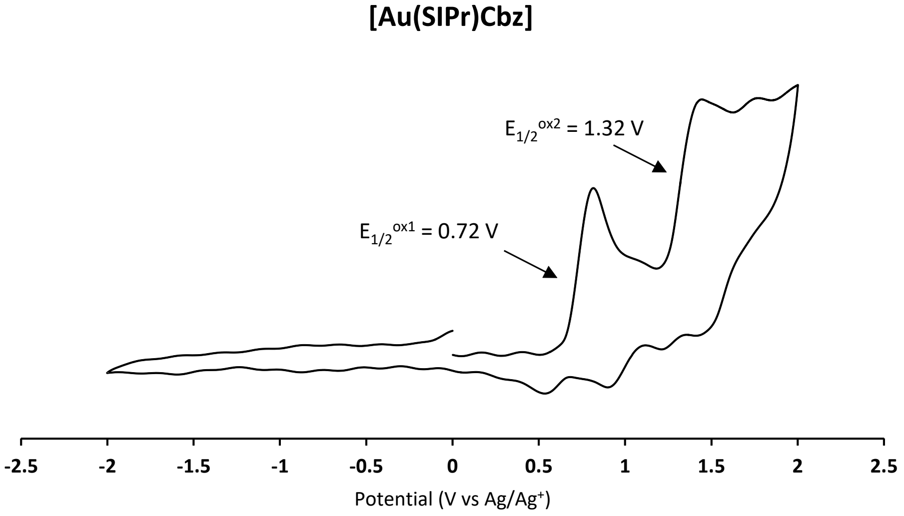


Figure S10. Cyclic voltammogram of **[Au(SIPr)(Cbz)]**

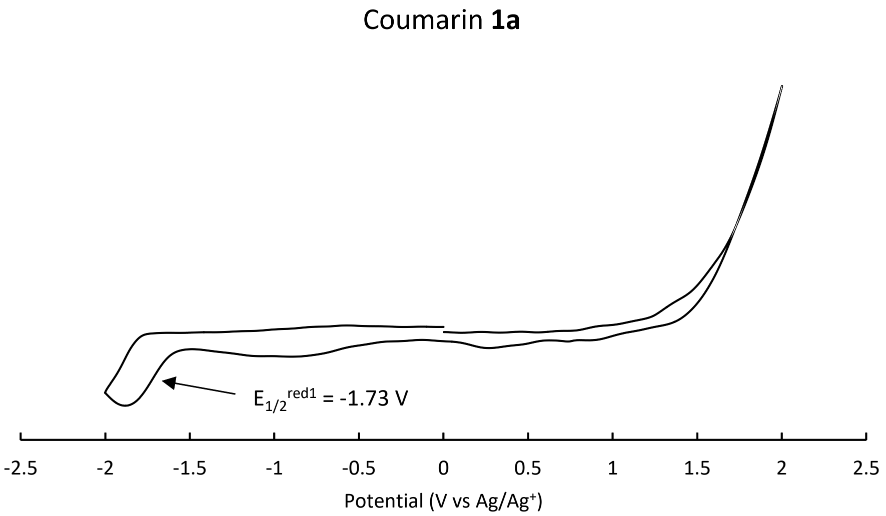


Figure S11 Cyclic voltammogram of coumarin **1a**

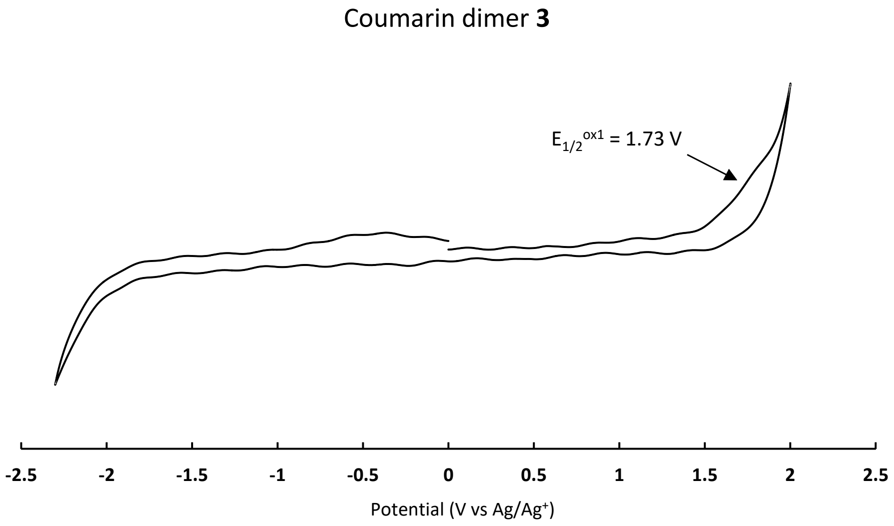


Figure S12. Cyclic voltammogram of coumarin dimer **3**

Table S7. Measured redox potentials

Potential	**V, vs Ag/AgCl**	**V, vs SCE**
E([Au(SIPr)(Cbz)]$^{\bullet+}$/[Au(SIPr)(Cbz)])	0.72	0.67
E([Au(SIPr)(Cbz)]/[Au(SIPr)(Cbz)]$^{\bullet-}$)	< - 2.0	< -2.05
E([Au(SIPr)(Cbz)]$^{\bullet+}$/[Au(SIPr)(Cbz)]*)	-2.22	-2.27
E([Au(SIPr)(Cbz)]*/[Au(SIPr)(Cbz)]$^{\bullet-}$)	< 0.94	< 0.89
E(**1a**$^{\bullet+}$**/1a**)	> 2.0	> 1.95
E(**1a/1a**$^{\bullet-}$)	-1.73	-1.79
E(**3**$^{\bullet+}$**/3**)	1.73	1.68
E(**3/3**$^{\bullet-}$)	< -2.3	< - 2.35

Excited state redox potentials of [Au(SIPr)(Cbz)] were estimated using Rehm-Weller equation.

Table S8. Known redox potentials[4,5]

Potential	V, vs SCE
E([Ir(dF(CF$_3$)ppy)$_2$(dtppy)] $^{\bullet+}$/[Ir(dF(CF$_3$)ppy)$_2$(dtppy)]*)	-0.89
E([Ir(dF(CF$_3$)ppy)$_2$(dtppy)]*/[Ir(dF(CF$_3$)ppy)$_2$(dtppy)]$^{\bullet-}$)	1.21
E(TXT$^{\bullet+}$/TXT*)	-1.11
E(TXT*/TXT$^{\bullet-}$)	1.18
E(Benzophenone$^{\bullet+}$/ Benzophenone*)	-0.61
E(Benzophenone*/ Benzophenone$^{\bullet-}$)	1.28

Considered EnT-eT-BeT mechanisms

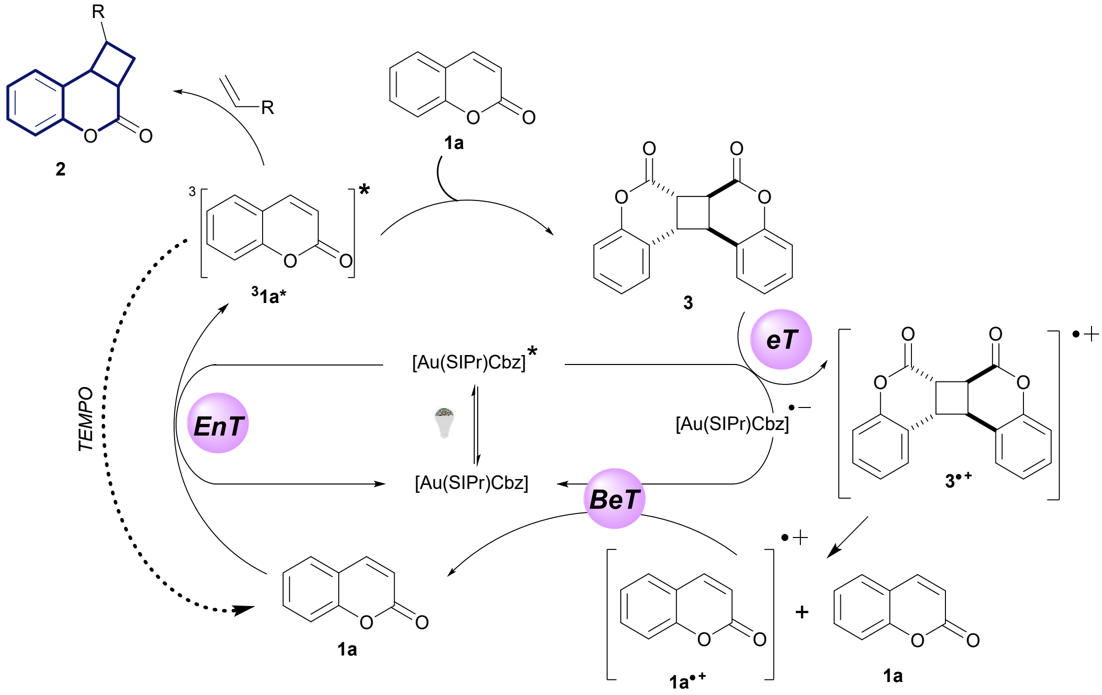


Figure S13. Possible EnT-eT-BeT mechanism with reductive quenching cycle

According to **table S7** excited state [Au(SIPr)(Cbz)] cannot oxidize coumarin dimer **3**, as EMF of this reaction will be < - 0.79 V. Interestingly, according to table S8 all other examined photocatalysts are not able to oxidize **3** as well, making this pathway not thermodynamically feasible.

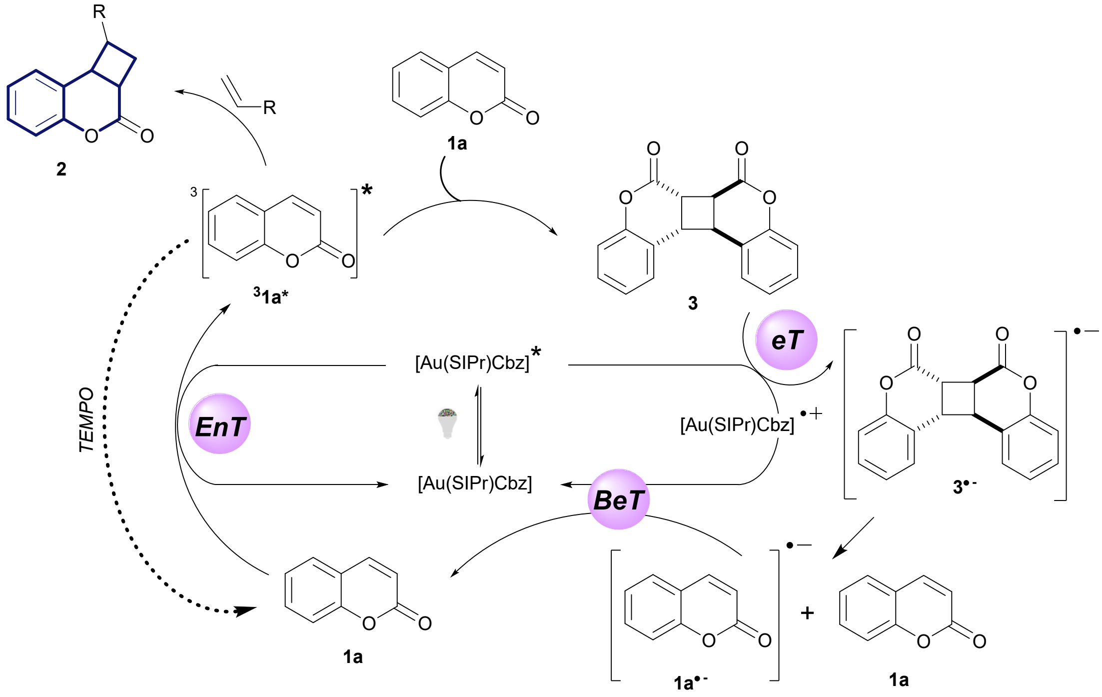


Figure S14. Possible EnT-eT-BeT mechanism with oxidative quenching cycle

According to the **table S7** EMF of the reduction of coumarin dimer **3** by excited state [Au(SIPr)(Cbz)] will be at least < - 0.08 V, which corresponds to 1.85 kcal/mol endergonic process. Nevertheless, we did not observe reduction of coumarin dimer **3** while performing cyclic voltammetry in the THF solvent window. It means that E(**3/3**$^{\bullet-}$) potential is even lower than -2.35 V, leading to much more endergonic oxidative quenching of the photocatalyst. Moreover, for all other studied photocatalysts such oxidative quenching would be endergonic by at least – 1.0 V (See **Table S8**), making this pathway for them thermodynamically not feasible.

X-Ray crystal data

Figure S15. X-Ray structure of **2v**

Crystals of **2v** suitable for XRD analysis were obtained by slow evaporation of acetone/hexane solution. *CCDC 2283605 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.*

Table S4. Crystal data and structure refinement for **2v**

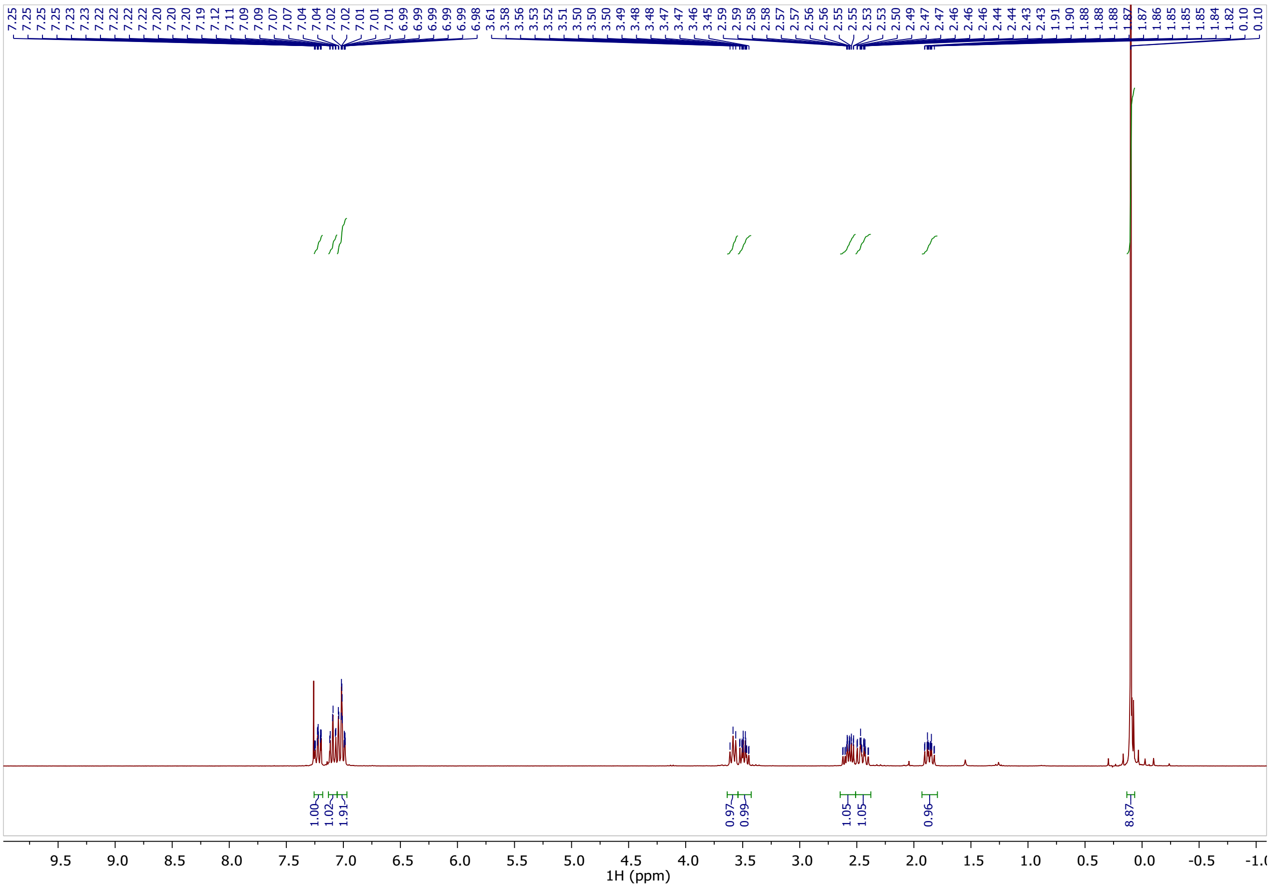
Empirical formula	$C_{19}H_{22}O_2$
Formula weight	282.37
Temperature/K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	11.8092(3)
b/Å	6.61169(13)
c/Å	18.3462(4)
α/°	90
β/°	92.755(2)
γ/°	90
Volume/Å^3	1430.79(6)
Z	4
ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	0.652
F(000)	608.0
Crystal size/mm^3	0.348 × 0.16 × 0.112
Radiation	CuK_α (λ = 1.54184)
2Θ range for data collection/°	8.718 to 147.804
Index ranges	$-14 \le h \le 14$, $-8 \le k \le 8$, $-21 \le l \le 22$
Reflections collected	13957
Independent reflections	2868 [R_{int} = 0.0383, R_{sigma} = 0.0241]
Data/restraints/parameters	2868/0/193
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0405, wR_2 =0.1073
Final R indexes [all data]	R_1 = 0.0441, wR_2 = 0.1118
Largest diff. peak/hole / e Å^{-3}	0.35/-0.21

References

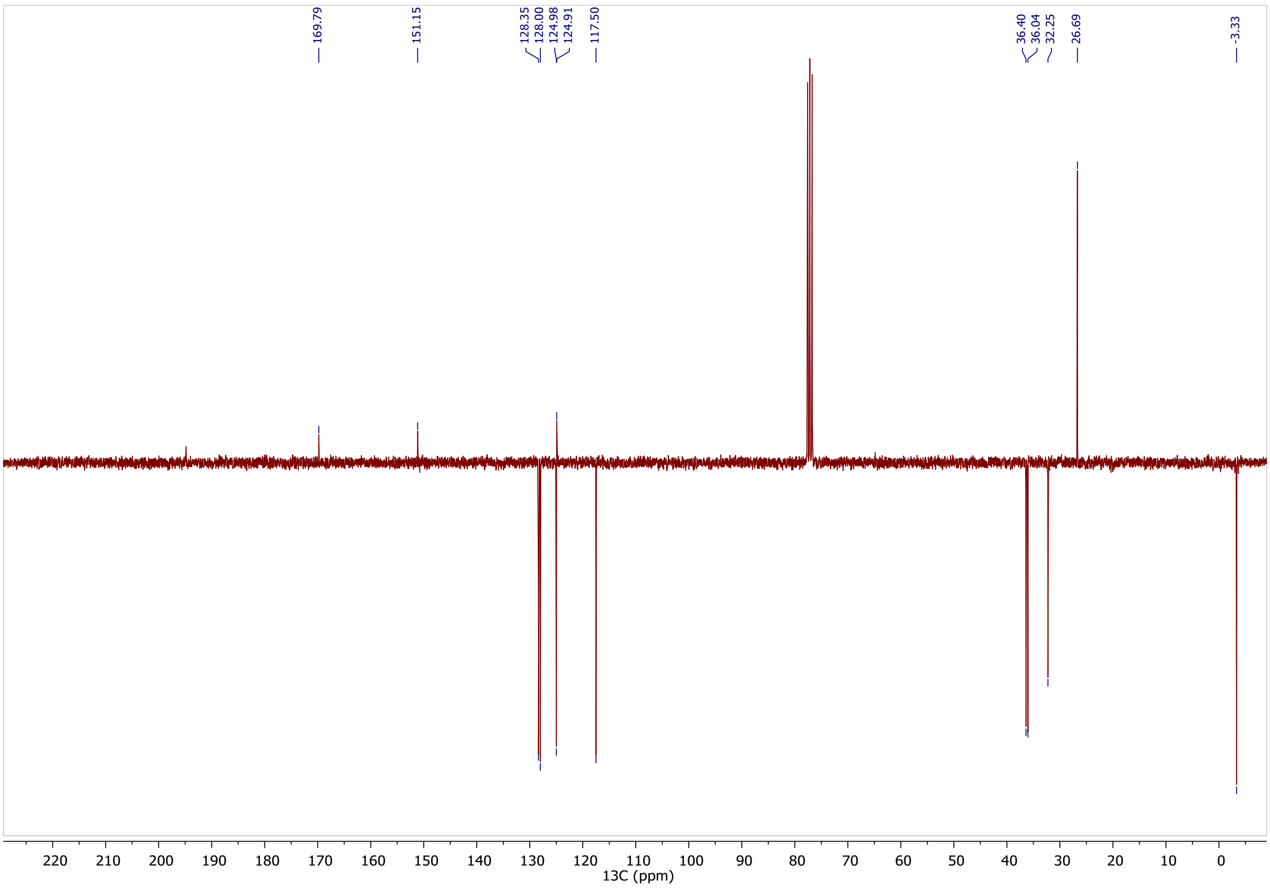
[1] N. V. Tzouras, E. A. Martynova, X. Ma, T. Scattolin, B. Hupp, H. Busen, M. Saab, Z. Zhang, L. Falivene, G. Pisanò, K. Van Hecke, L. Cavallo, C. S. J. Cazin, A. Steffen, S. P. Nolan, *Chem. – Eur. J.* **2021**, *27*, 11904–11911.
[2] M. Jiang, N. Paul, N. Bieniek, T. Buckup, N. Hampp, M. Motzkus, *Phys. Chem. Chem. Phys.* **2017**, *19*, 4597–4606.
[3] T. Hartman, R. Cibulka, *Org. Lett.* **2016**, *18*, 3710–3713.
[4] R. Bevernaegie, S. A. M. Wehlin, B. Elias, L. Troian-Gautier, *ChemPhotoChem* **2021**, *5*, 217–234.
[5] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166.

NMR spectra

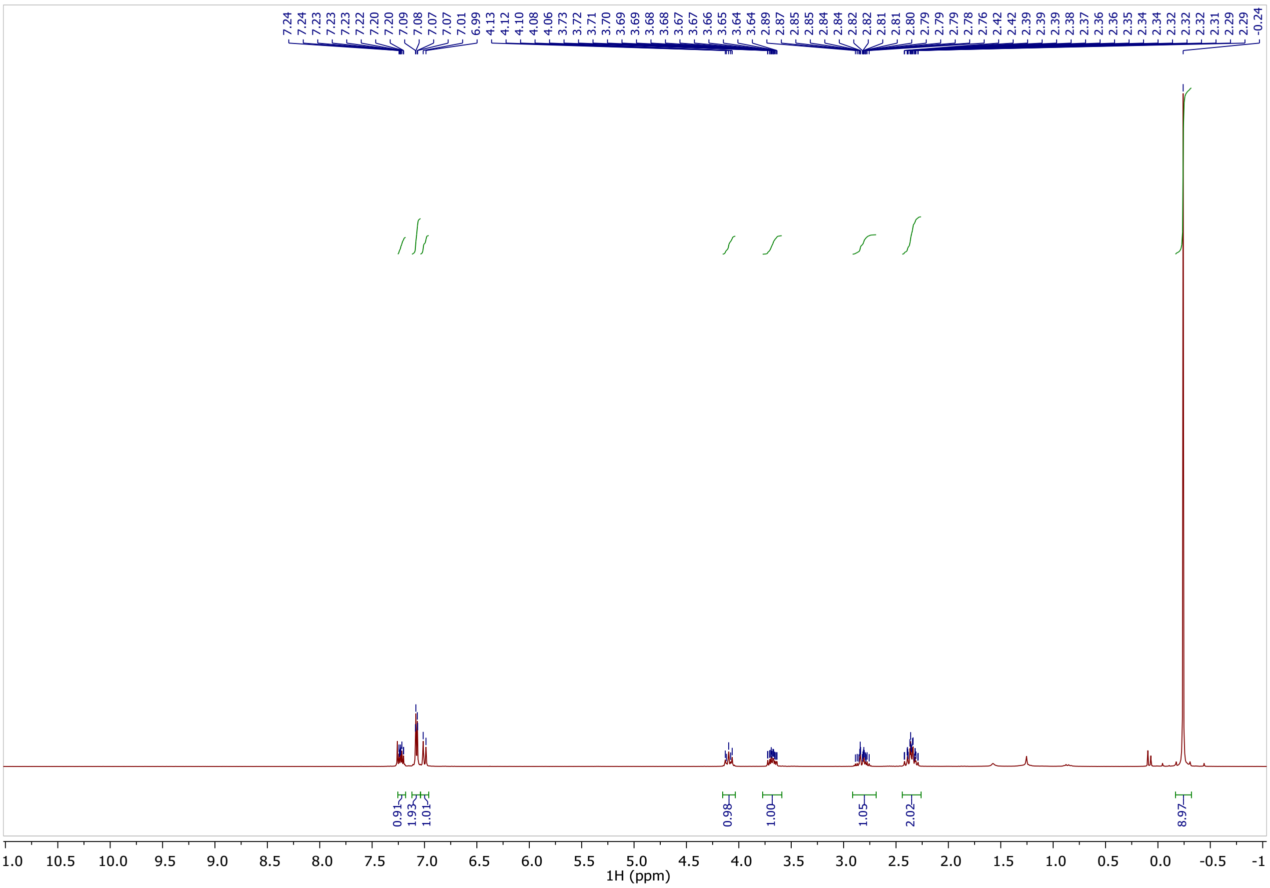
^{1}H NMR (300 MHz, CDCl$_3$) of **2a**



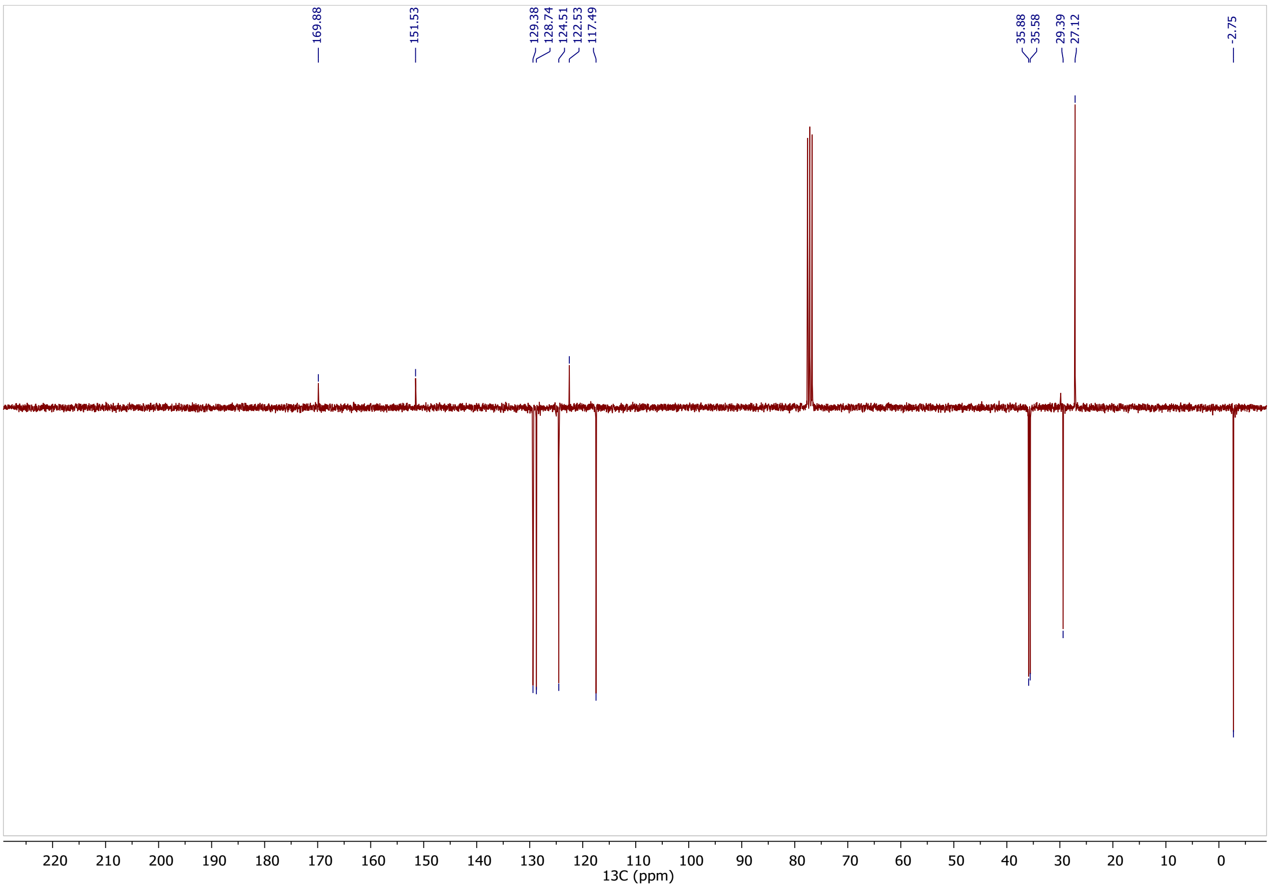
^{13}C NMR (101 MHz, CDCl$_3$) of **2a**



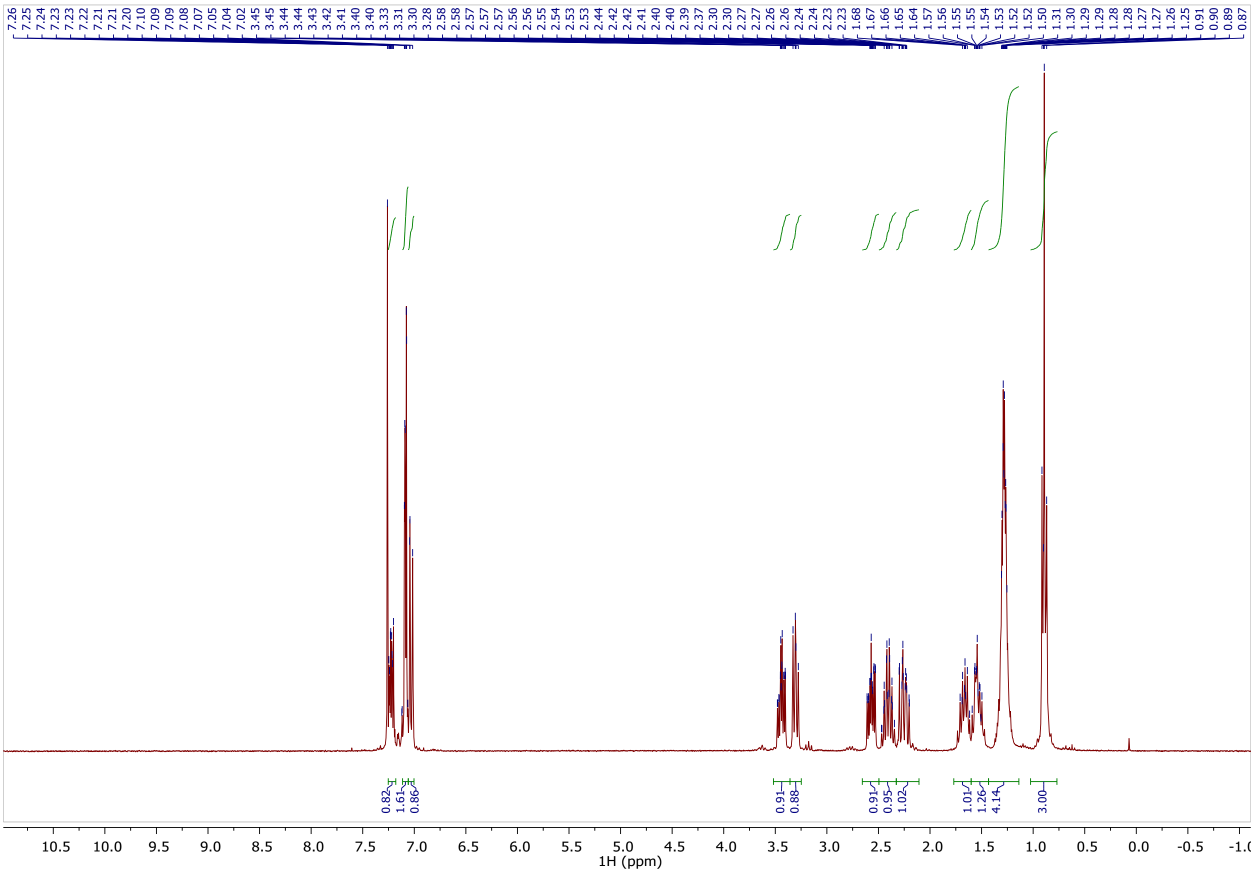
^{1}H NMR (300 MHz, CDCl$_3$) of **2a'**



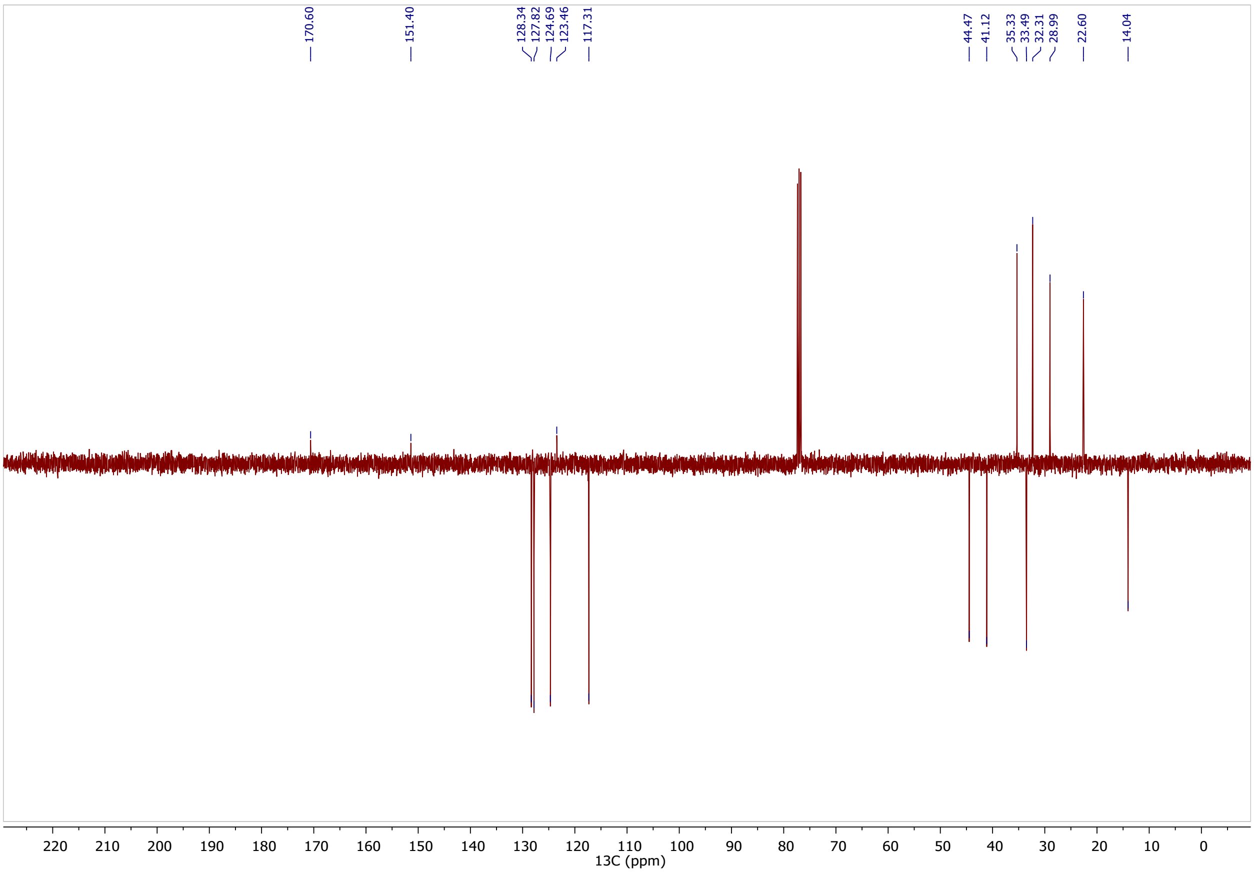
^{13}C NMR (101 MHz, CDCl$_3$) of **2a’**



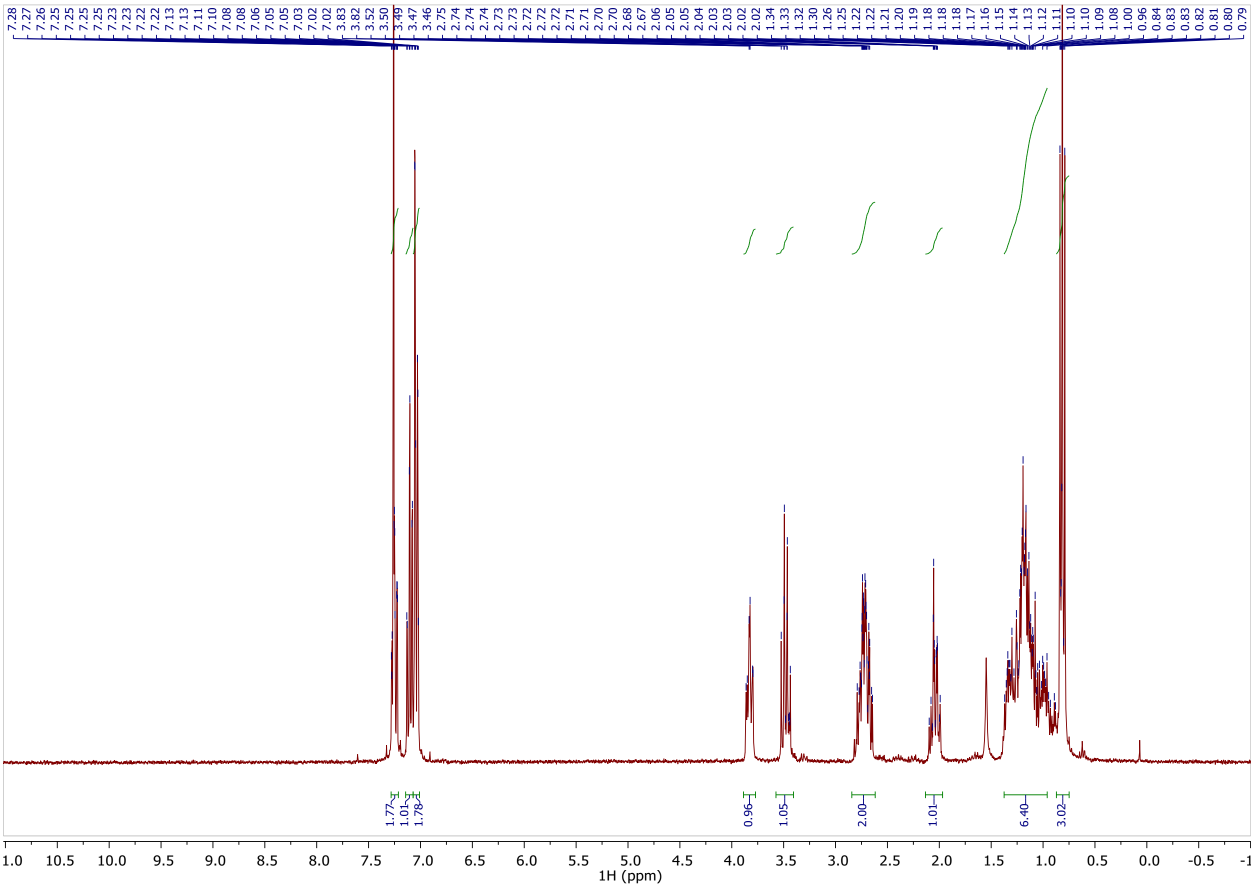
^{1}H NMR (300 MHz, CDCl$_3$) of **2b**



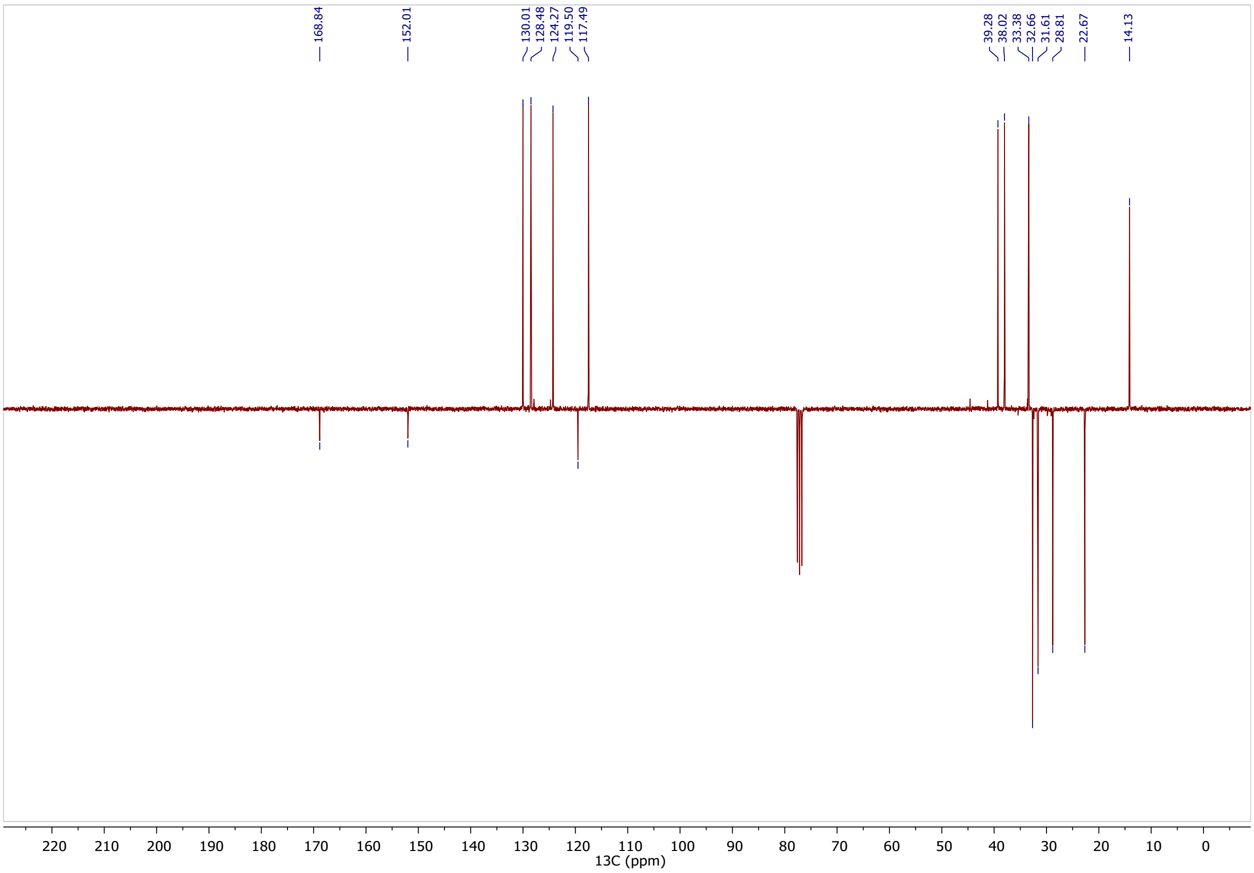
^{13}C NMR (101 MHz, $CDCl_3$) of **2b**



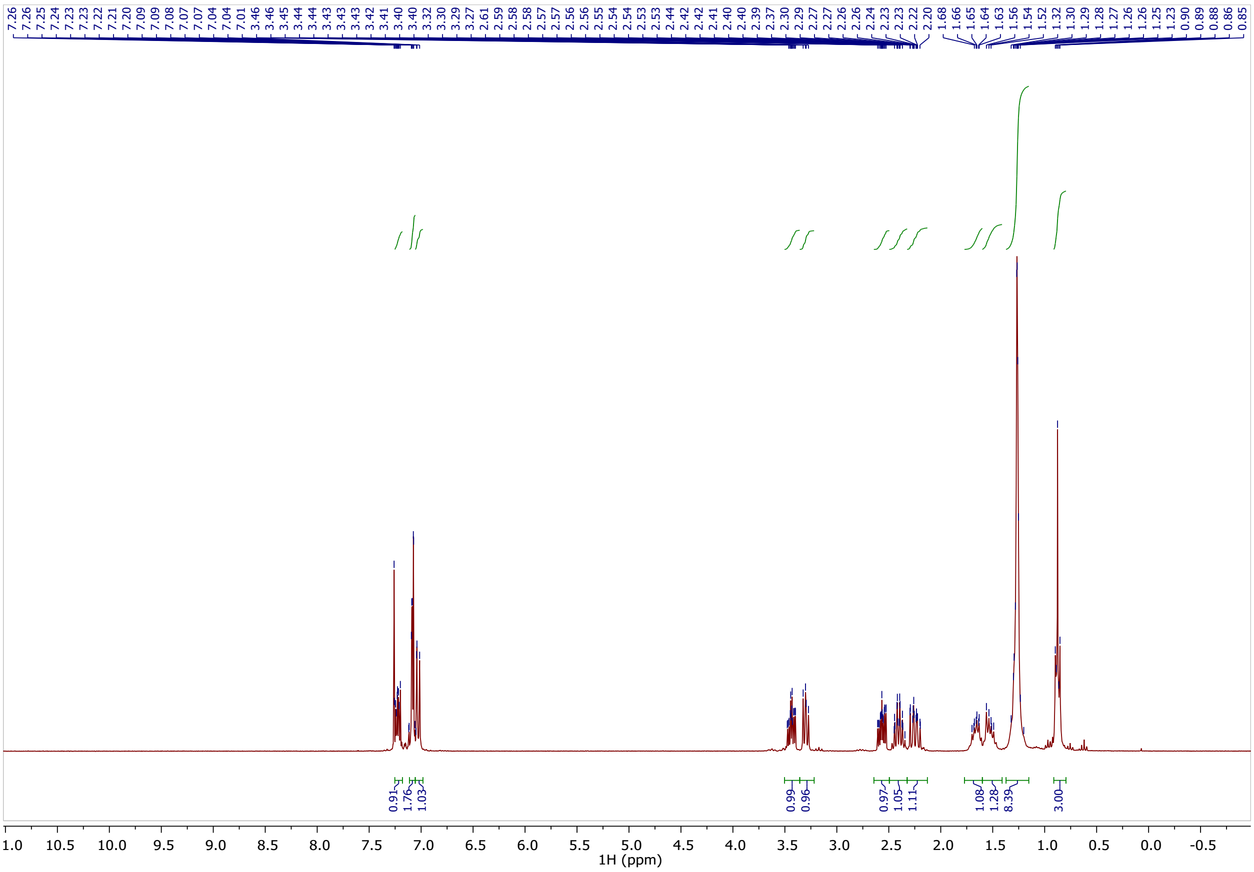
^{1}H NMR (300 MHz, $CDCl_3$) of **2b'**



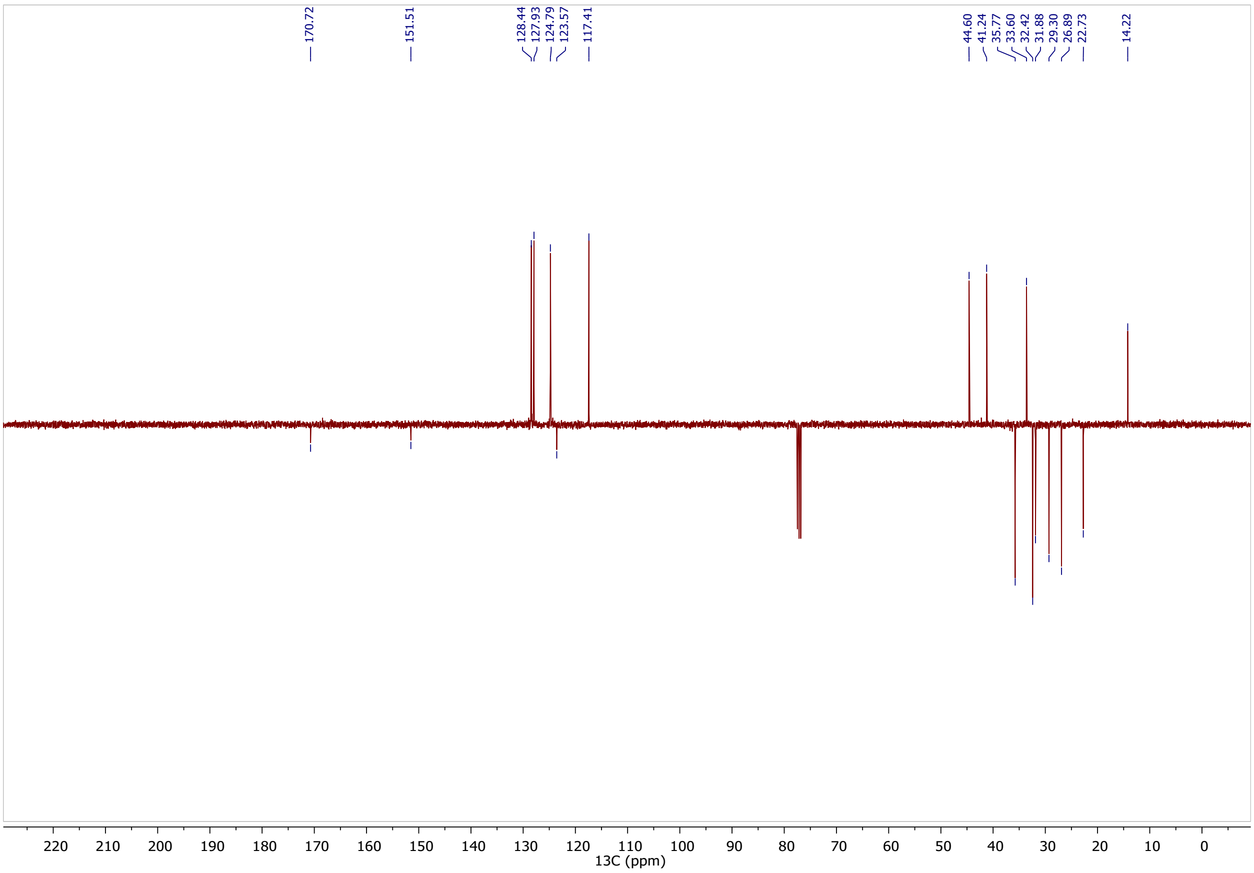
^{13}C NMR (101 MHz, CDCl$_3$) of **2b'**



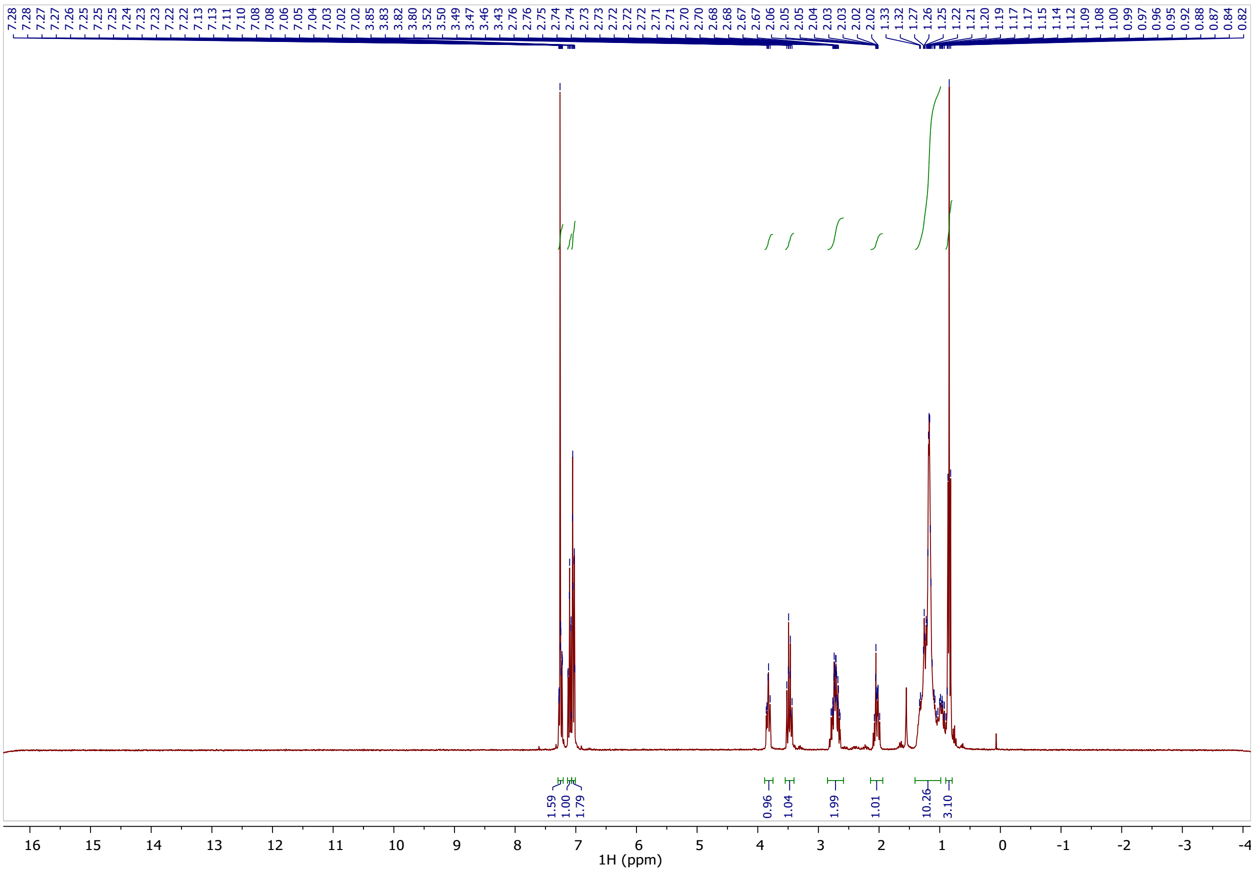
^{1}H NMR (300 MHz, CDCl$_3$) of **2c**



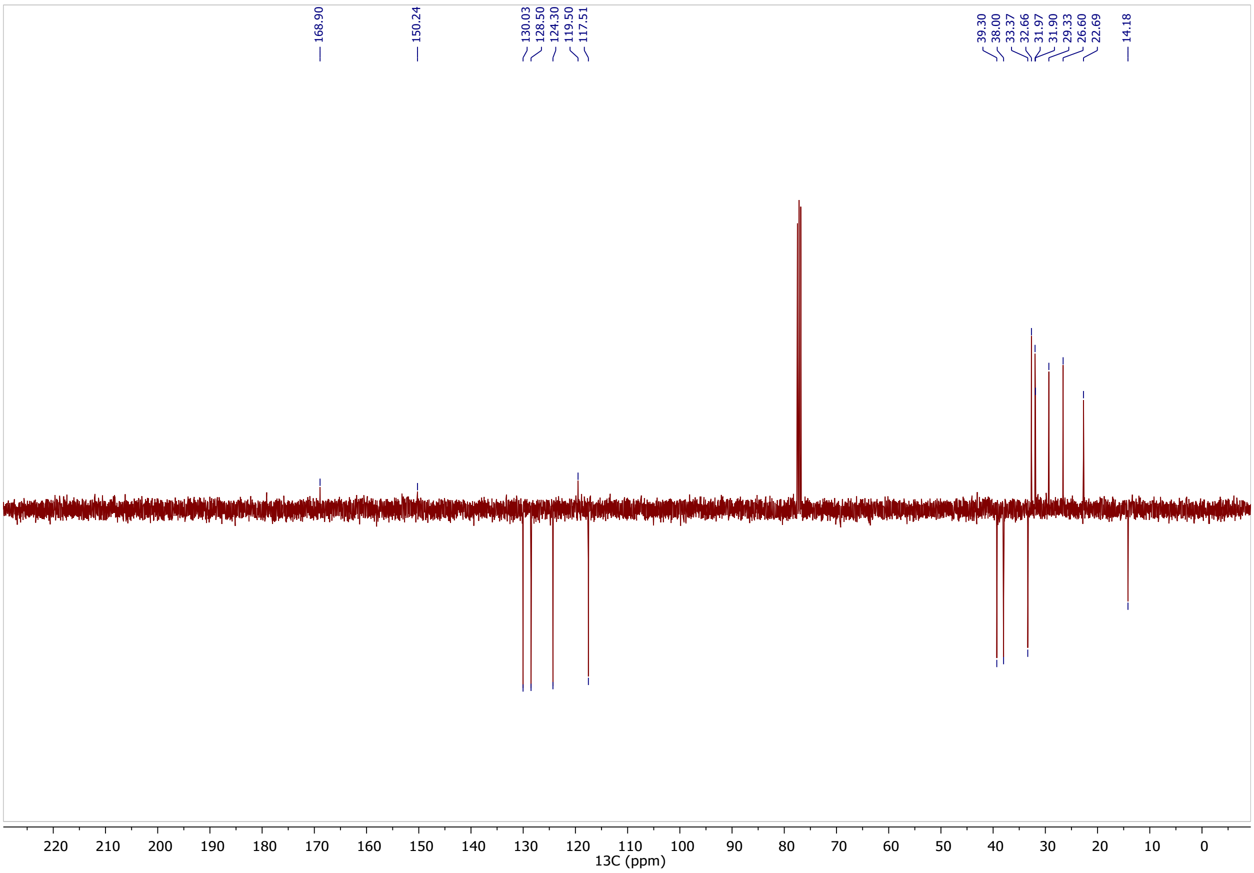
^{13}C NMR (101 MHz, $CDCl_3$) of **2c**



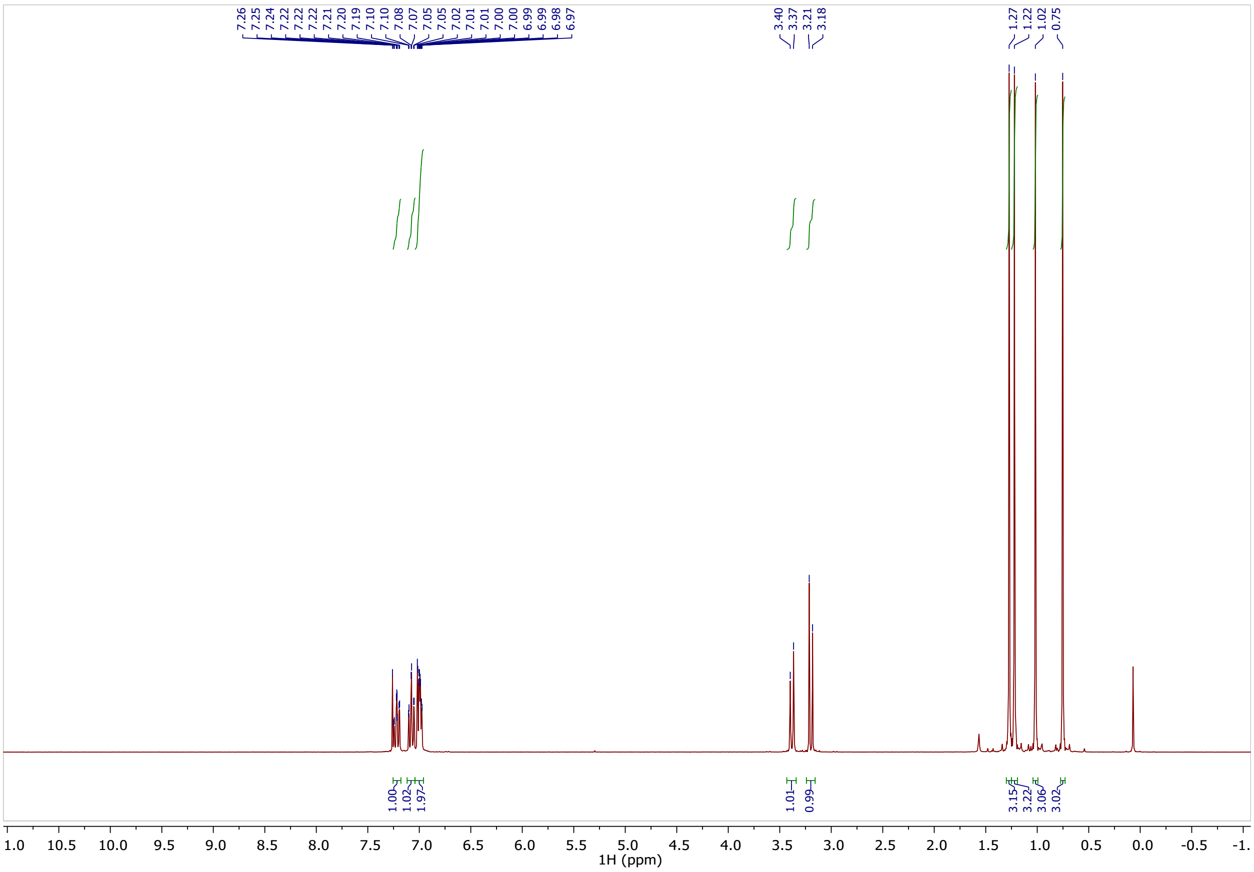
^{1}H NMR (300 MHz, $CDCl_3$) of **2c'**



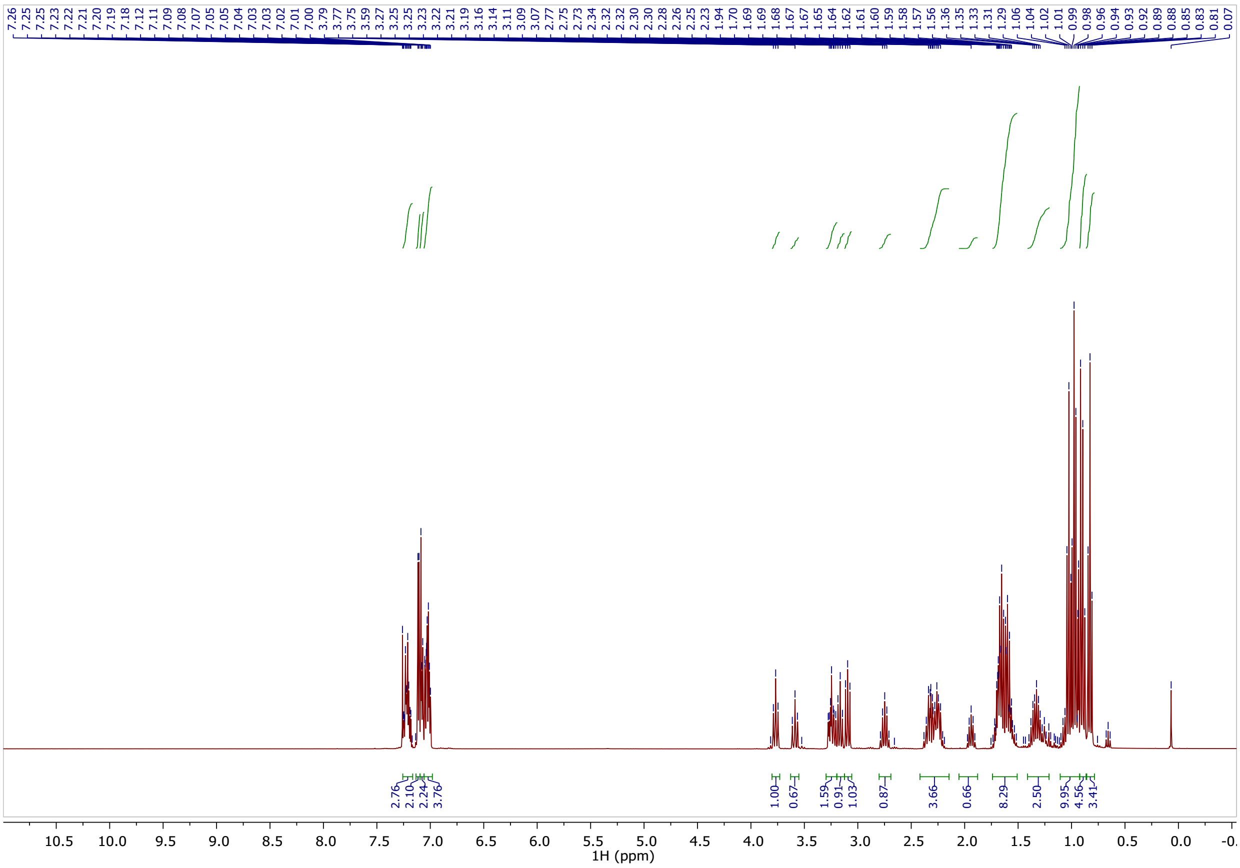
^{13}C NMR (101 MHz, CDCl$_3$) of **2c'**



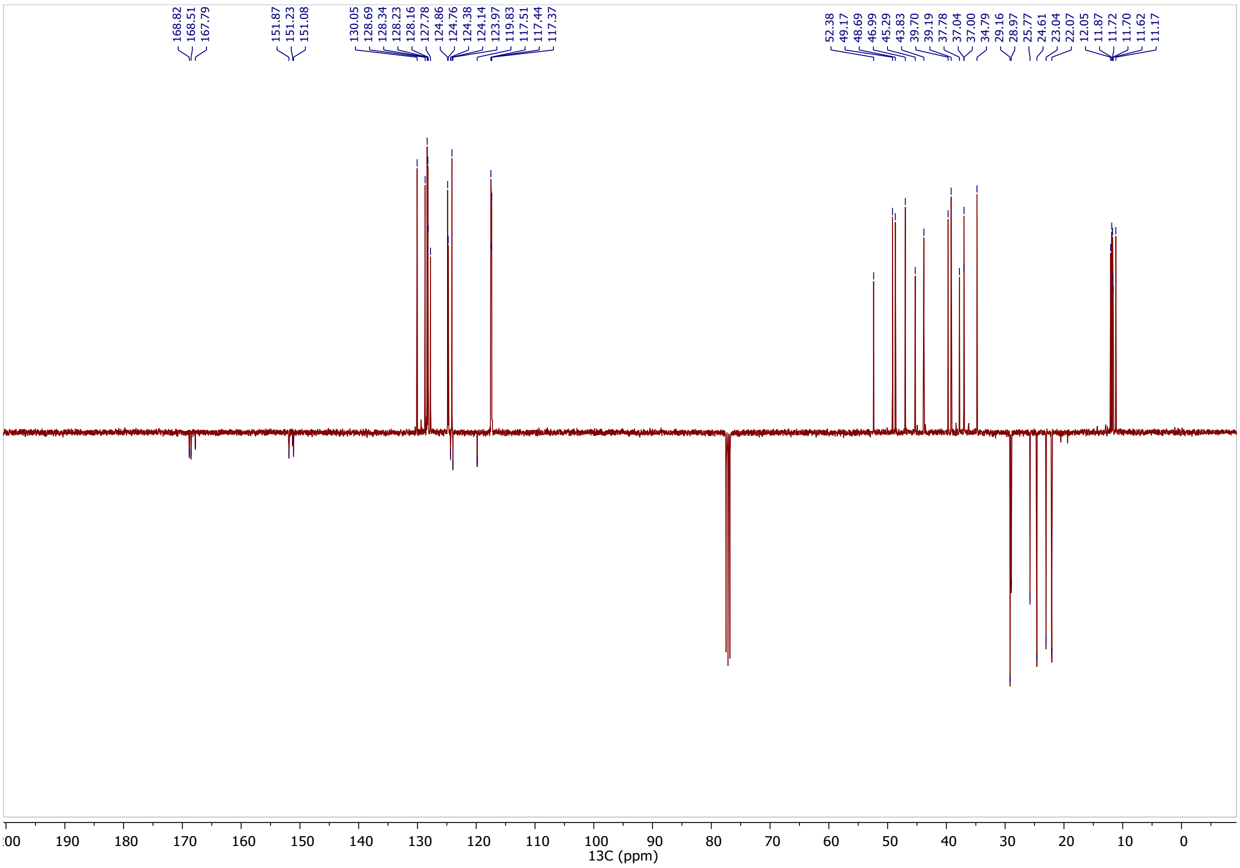
^{1}H NMR (300 MHz, CDCl$_3$) of **2d**



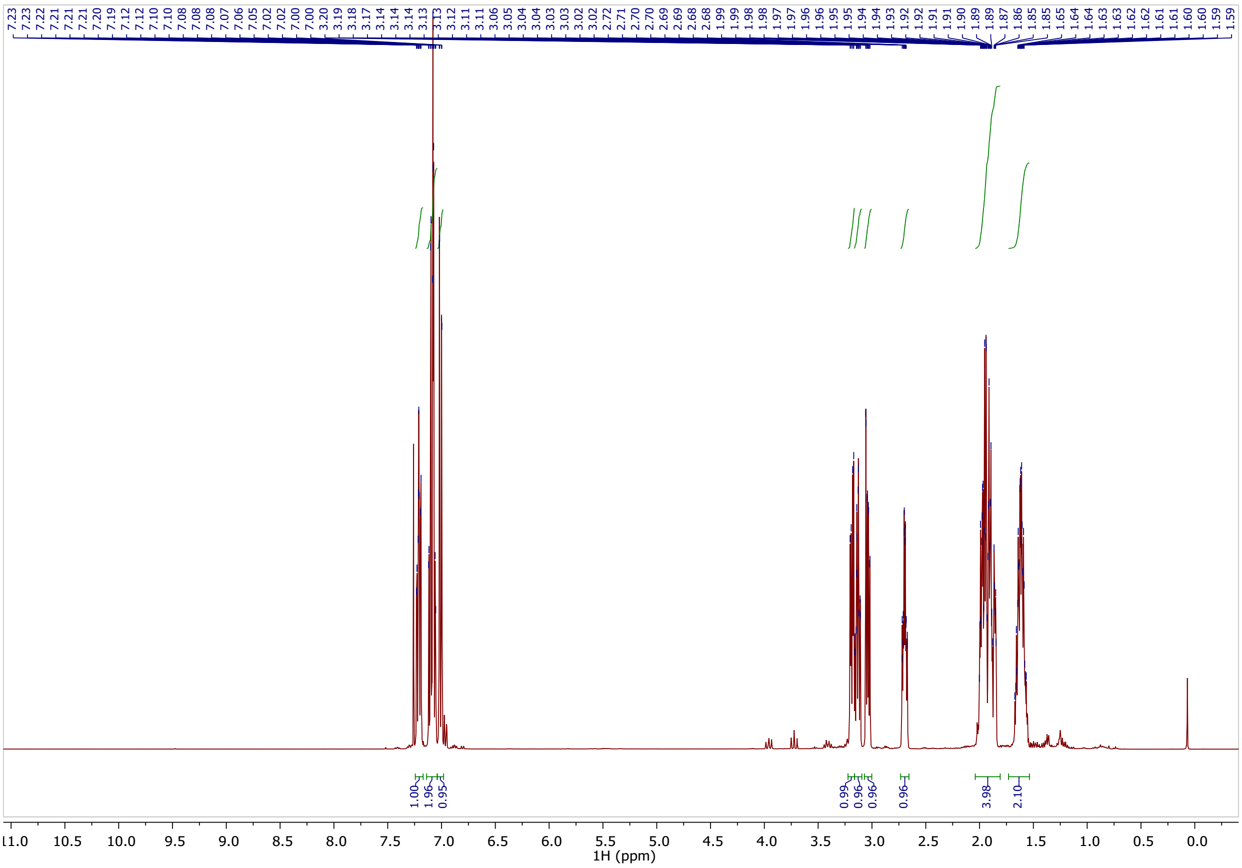
^{1}H NMR (300 MHz, CDCl$_3$) of **2e** (*mixture of diastereomers*)



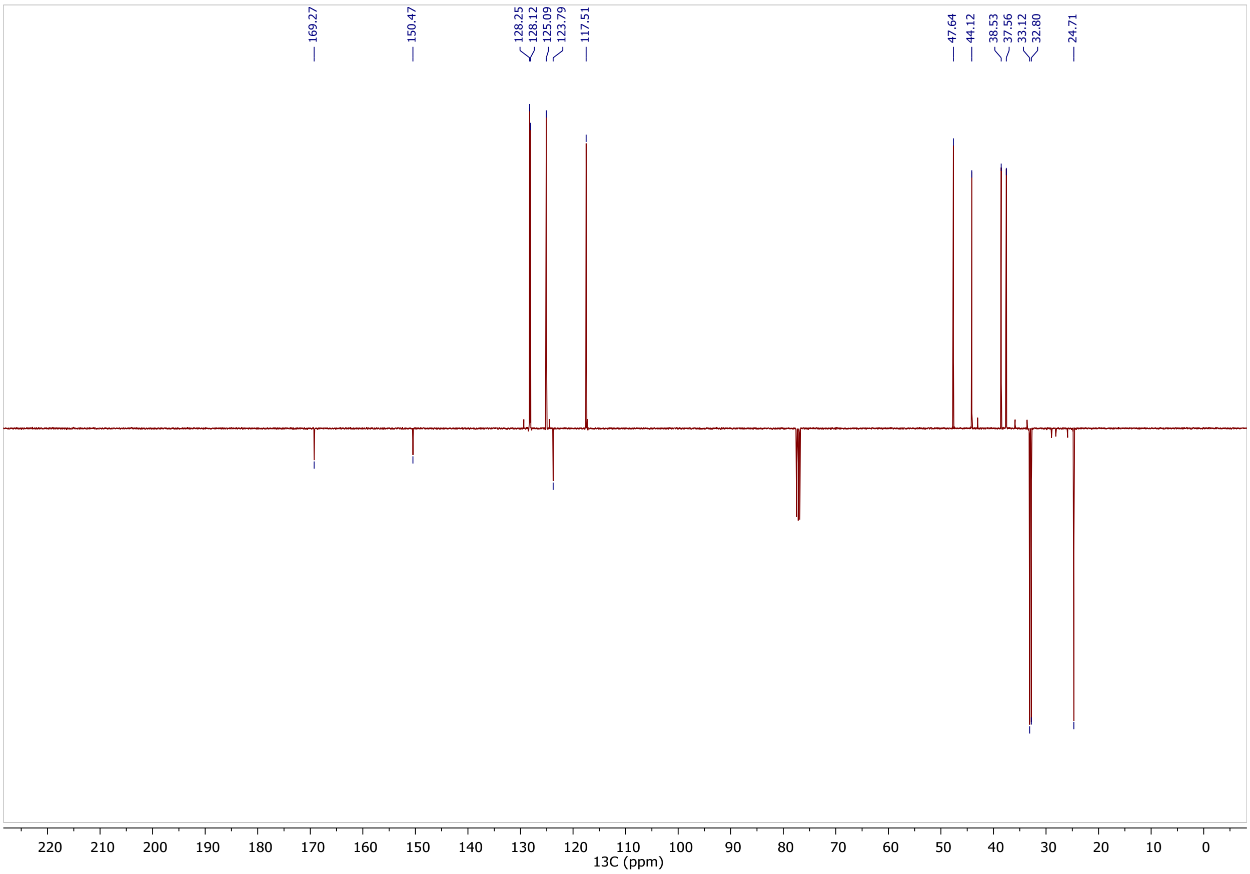
^{13}C NMR (101 MHz, CDCl$_3$) of **2e** (*mixture of diastereomers*)



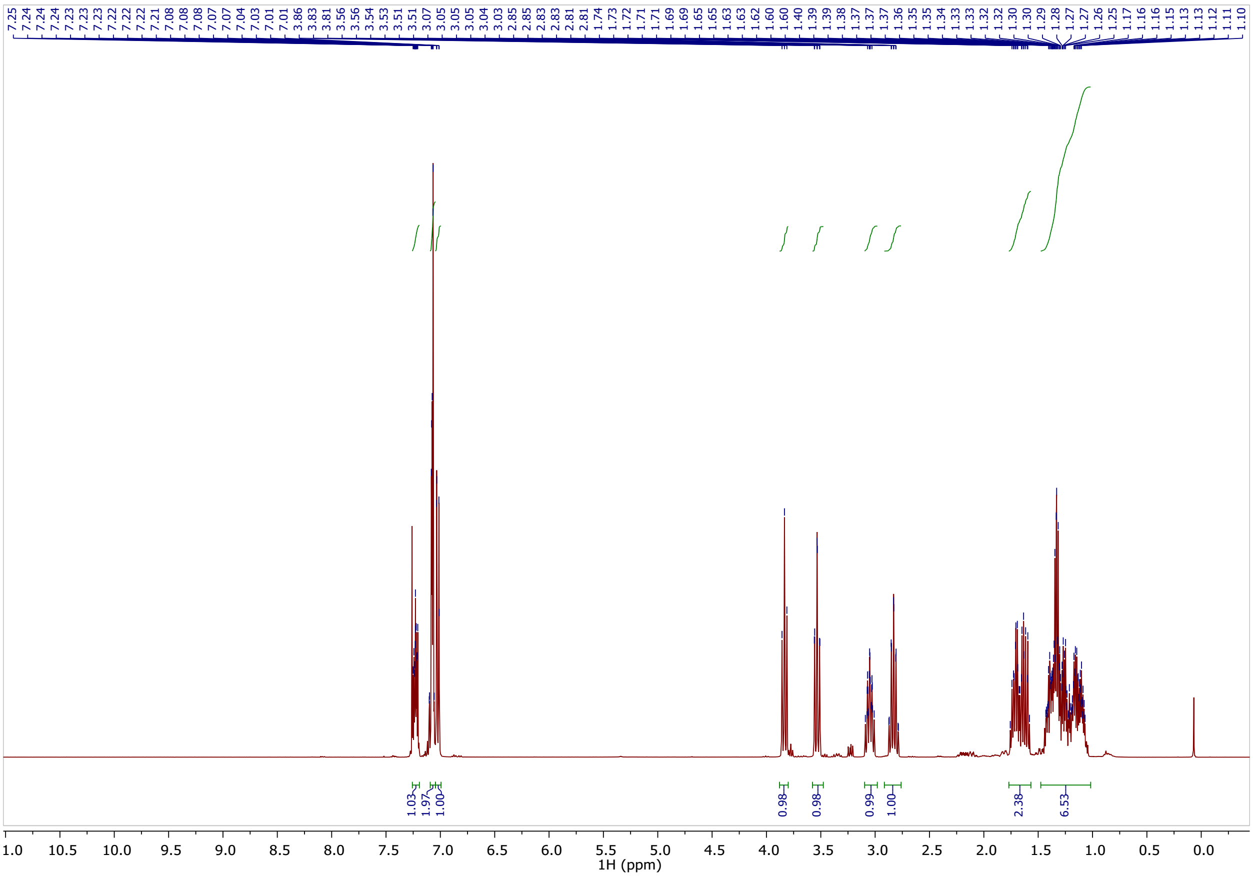
^{1}H NMR (300 MHz, CDCl$_3$) of **2f**



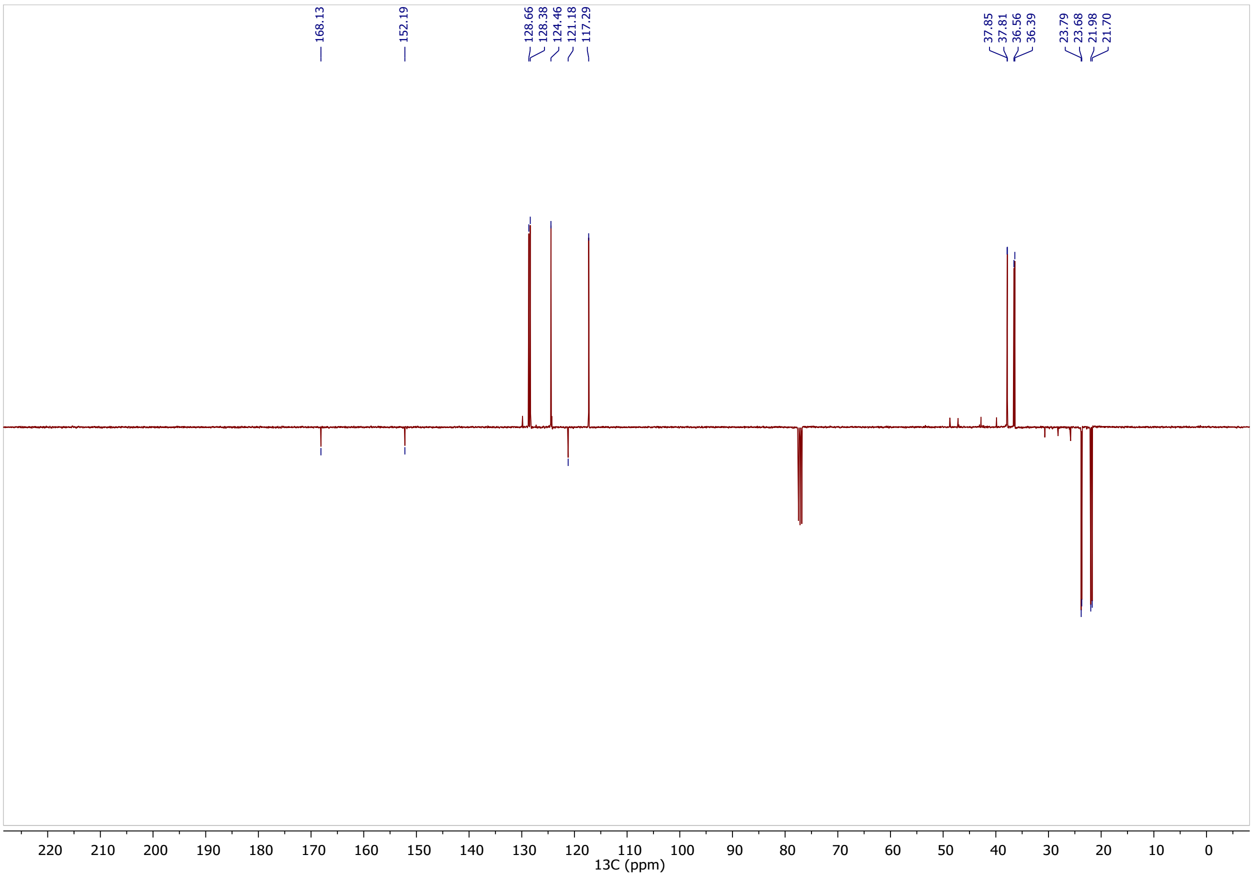
^{13}C NMR (101 MHz, CDCl$_3$) of **2f**



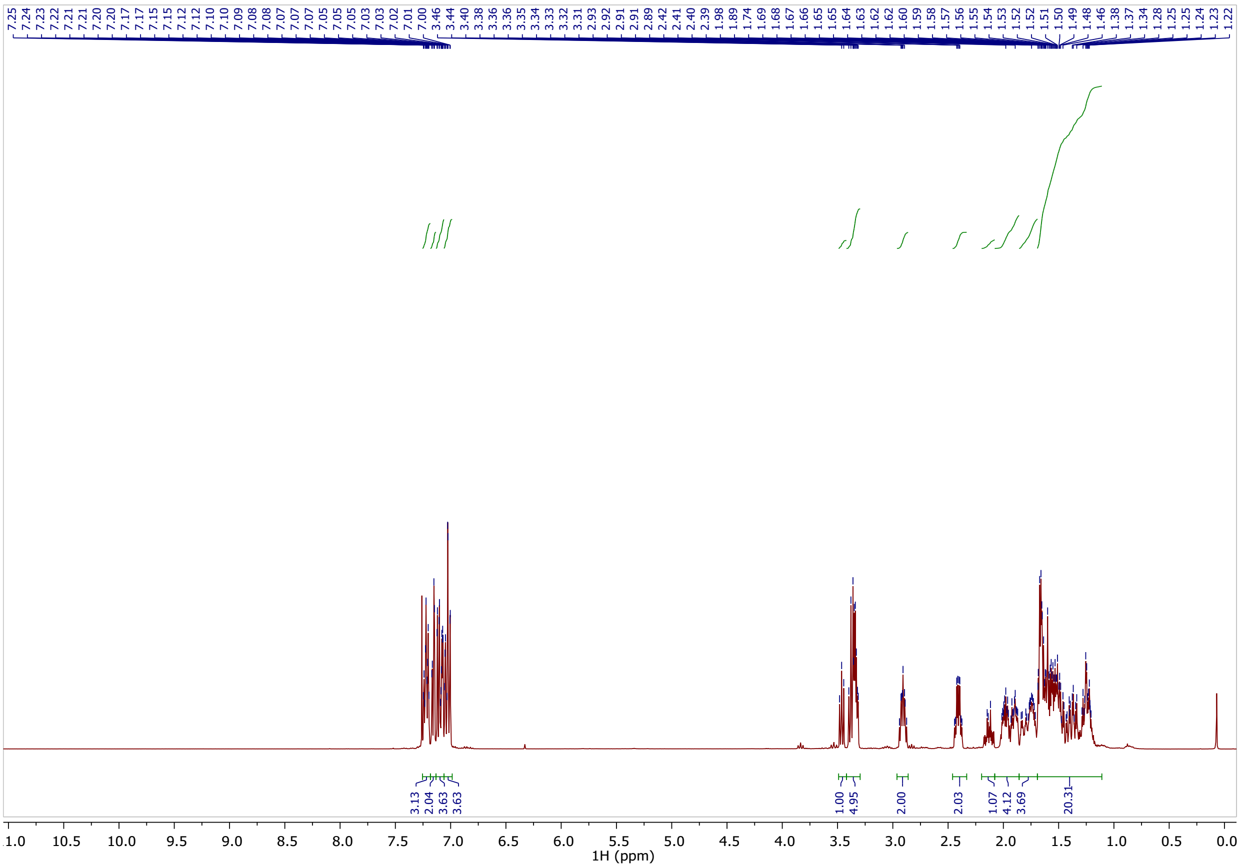
^{1}H NMR (300 MHz, $CDCl_3$) of **2g**



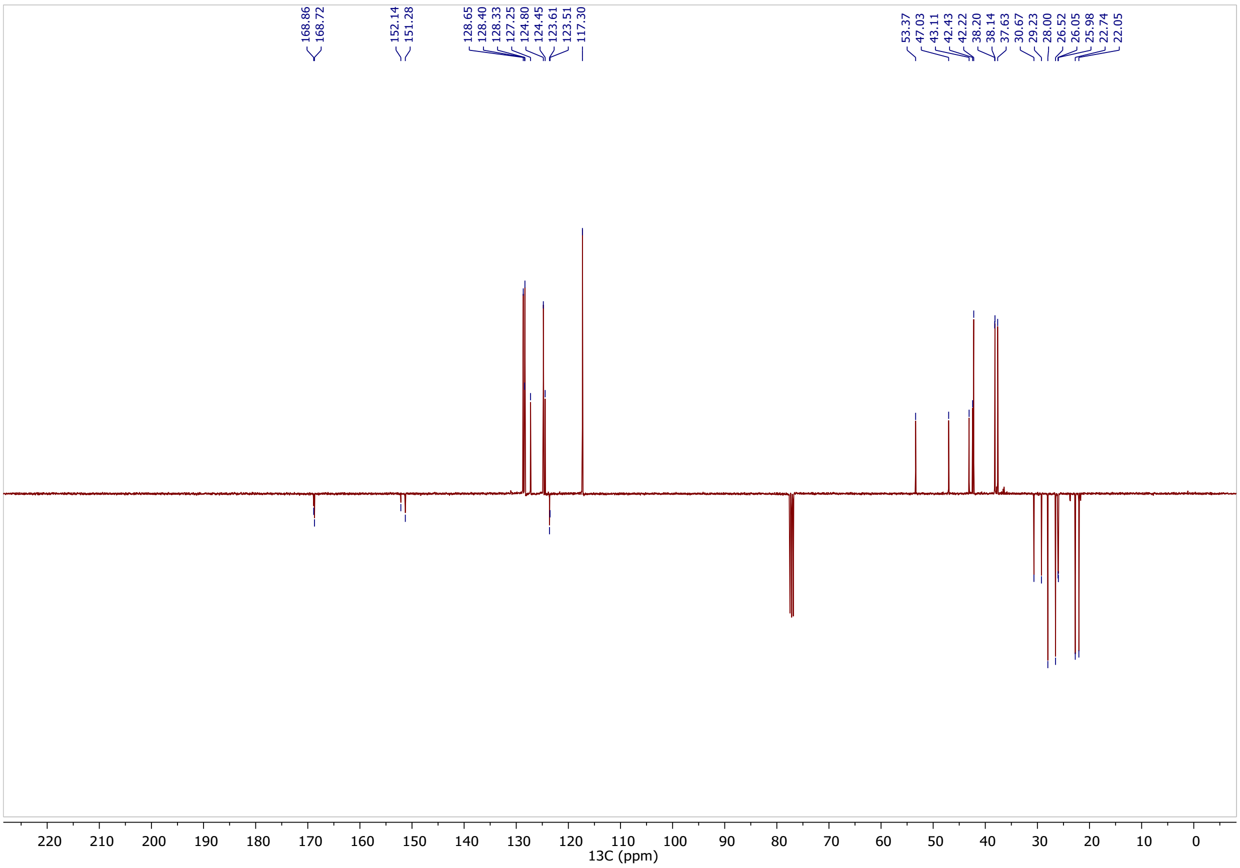
^{13}C NMR (101 MHz, $CDCl_3$) of **2g**



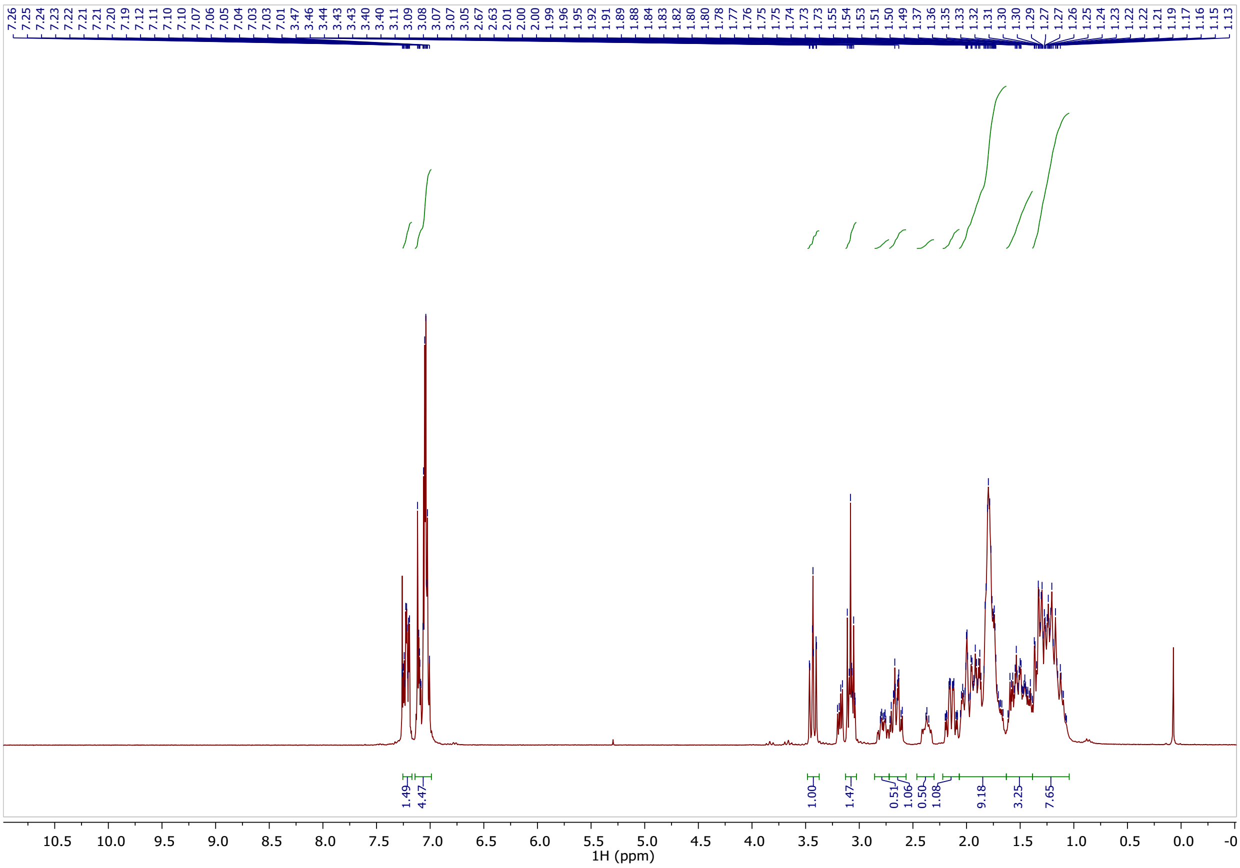
^{1}H NMR (300 MHz, $CDCl_3$) of **2g** (*mixture of two minor diastereomers*)



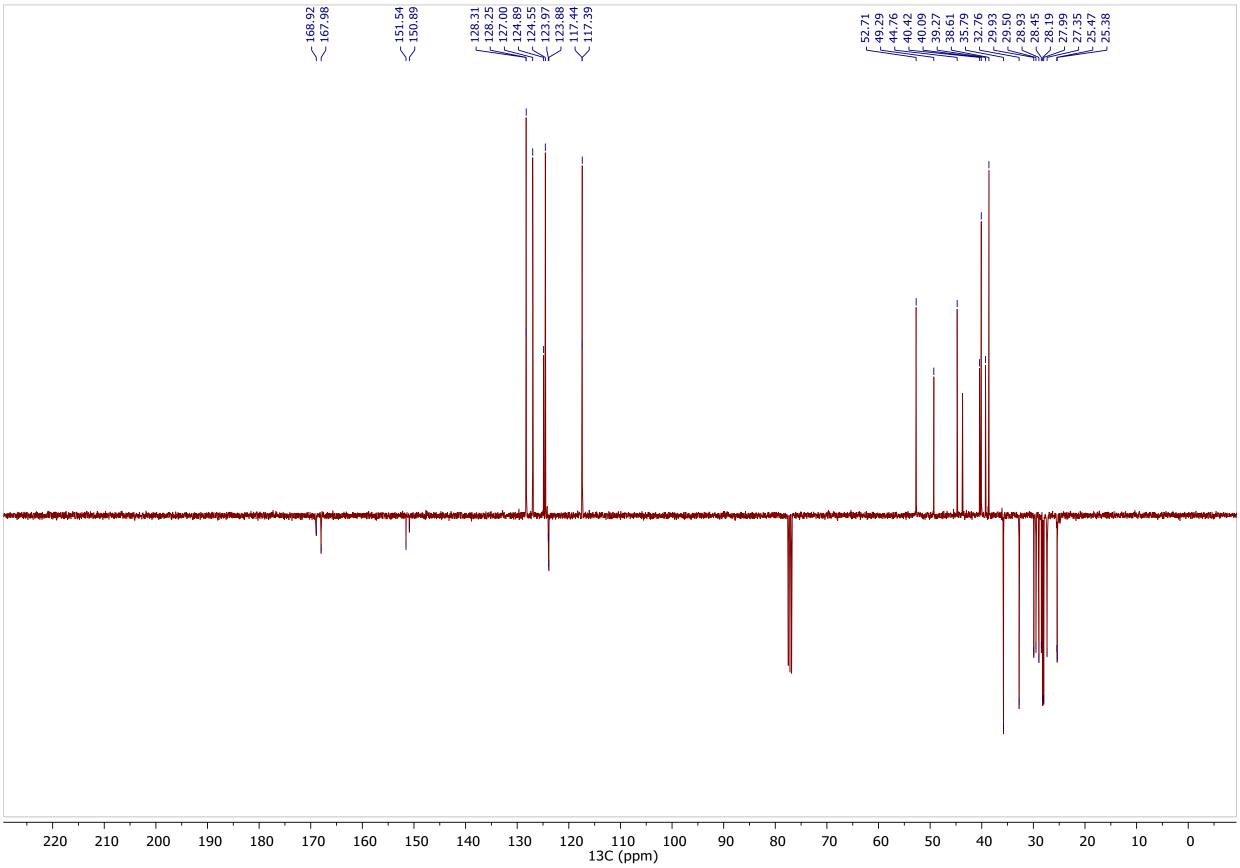
^{13}C NMR (101 MHz, $CDCl_3$) of **2g** (*mixture of two minor diastereomers*)



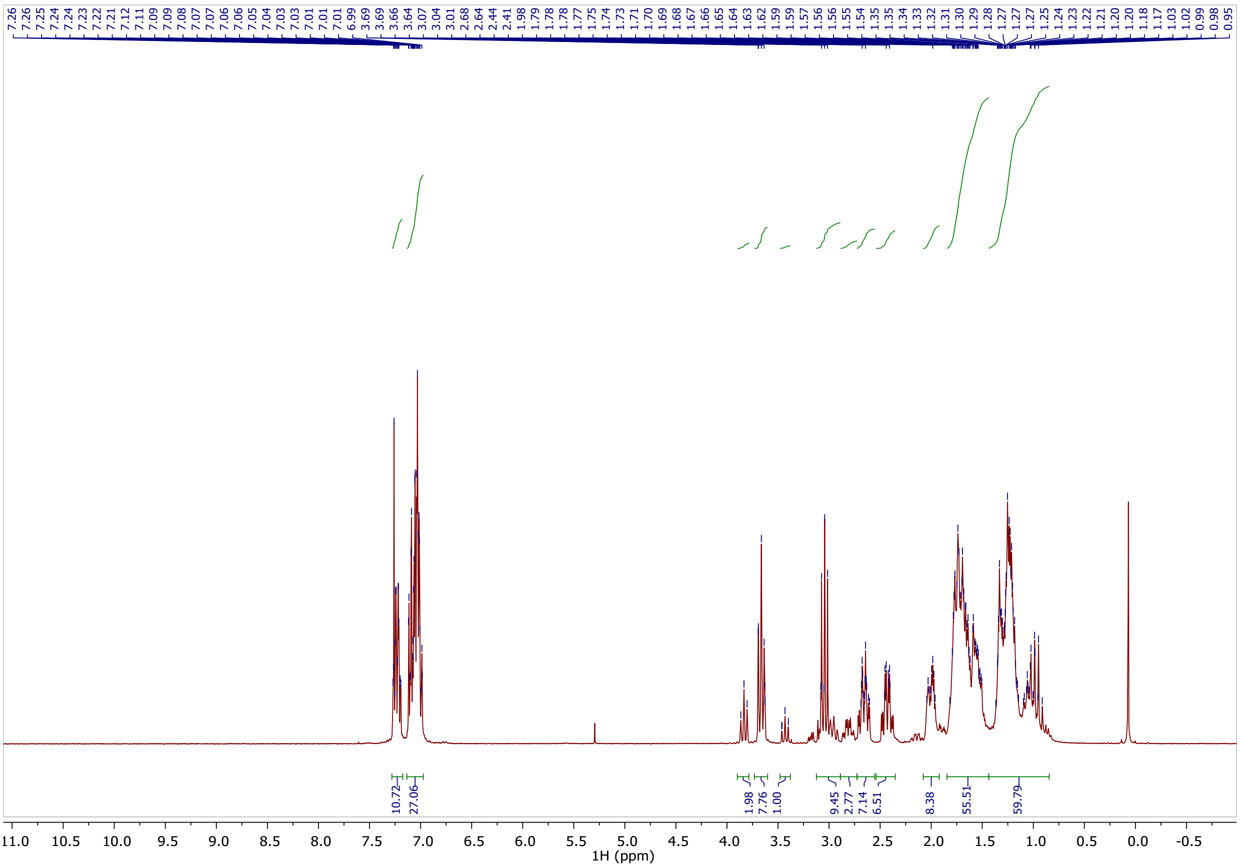
^{1}H NMR (300 MHz, CDCl$_3$) of **2h** (*mixture of first pair of diastereomers*)



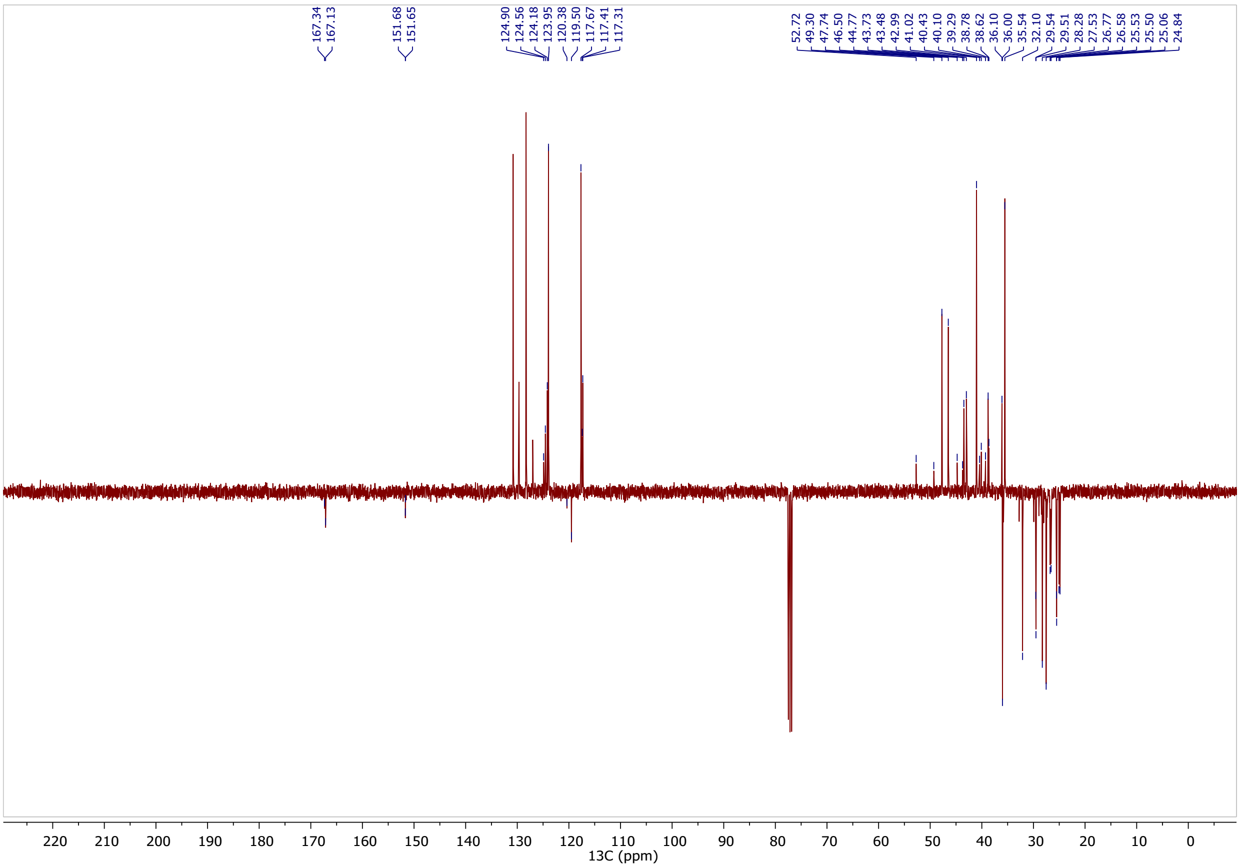
^{13}C NMR (101 MHz, CDCl$_3$) of **2g** (*mixture of first pair of diastereomers*)



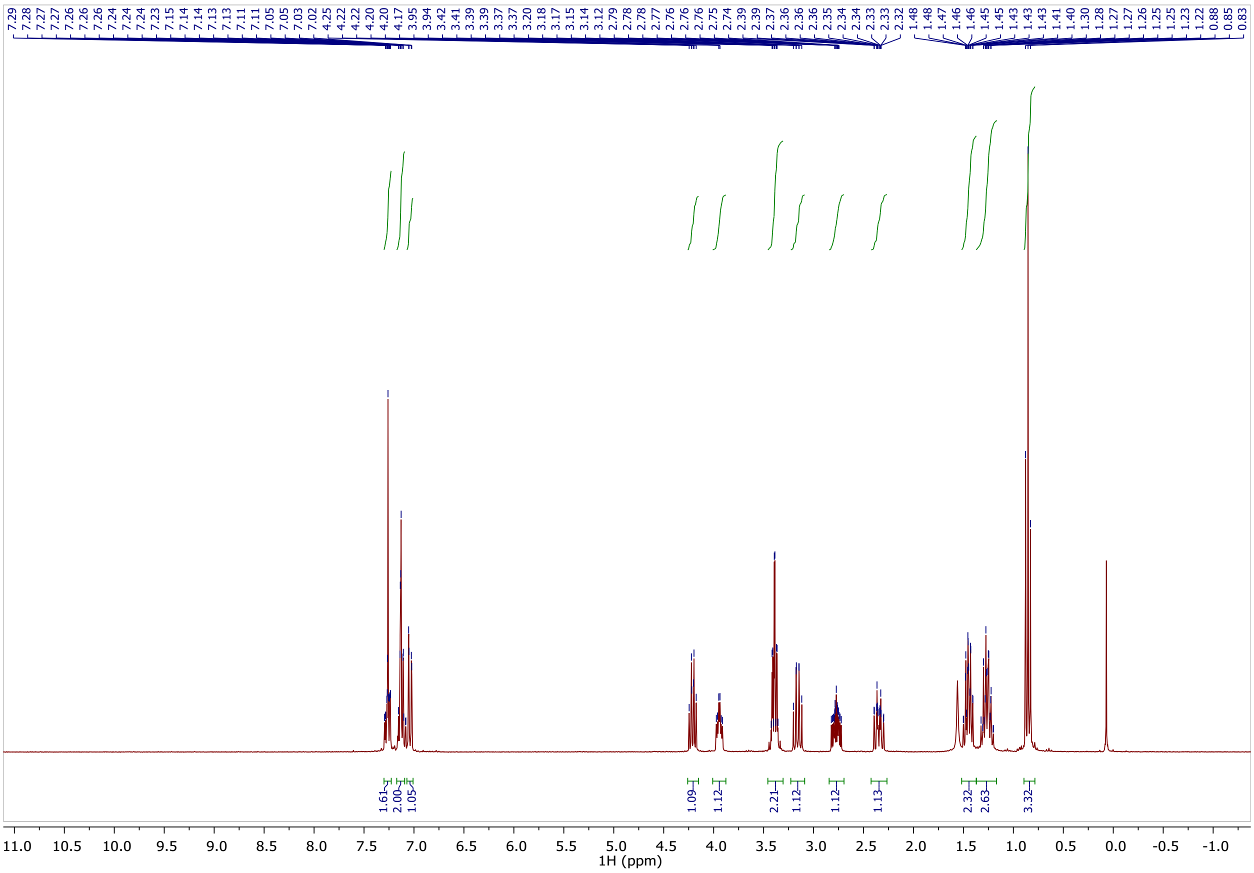
^{1}H NMR (300 MHz, CDCl$_3$) of **2h** (*mixture of second pair of diastereomers*)



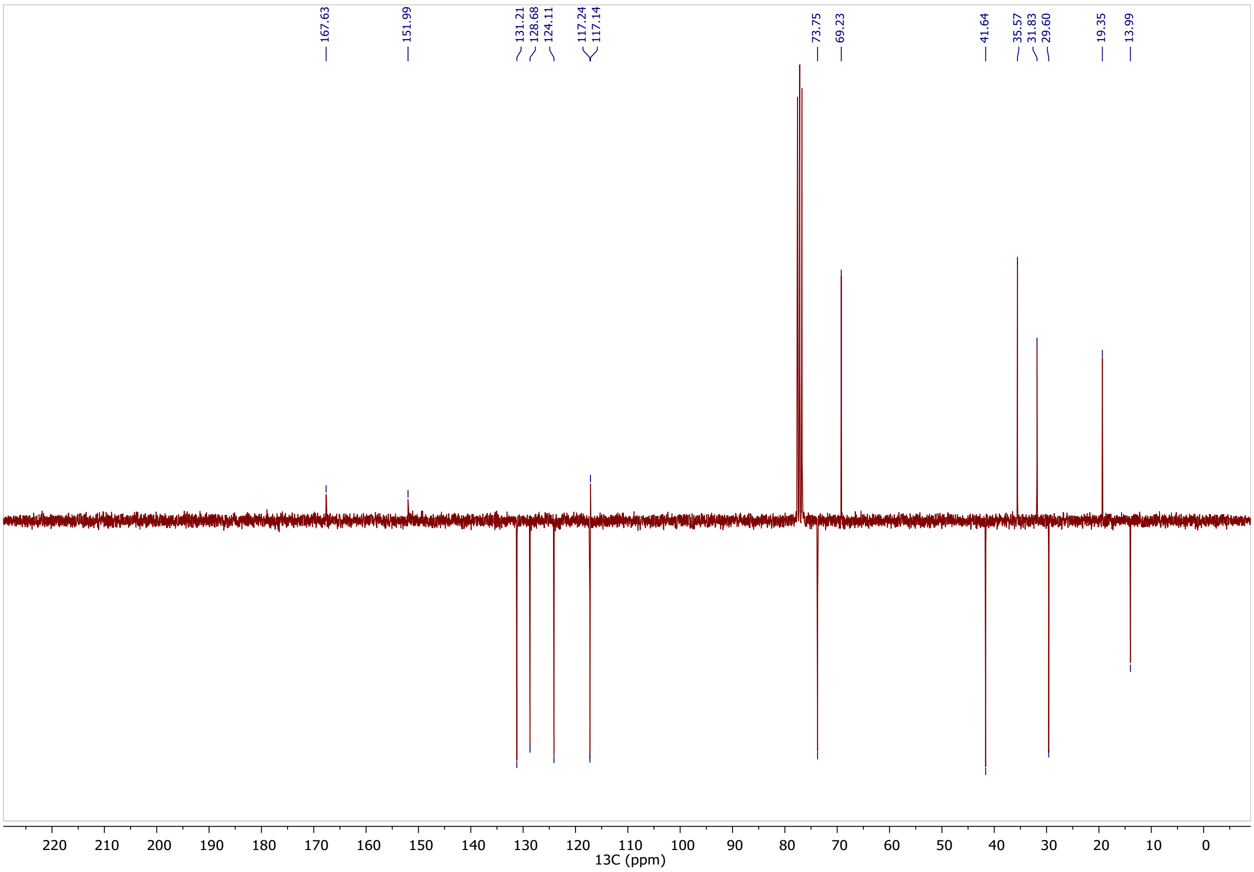
^{13}C NMR (101 MHz, CDCl$_3$) of **2h** (*mixture of first pair of diastereomers*)



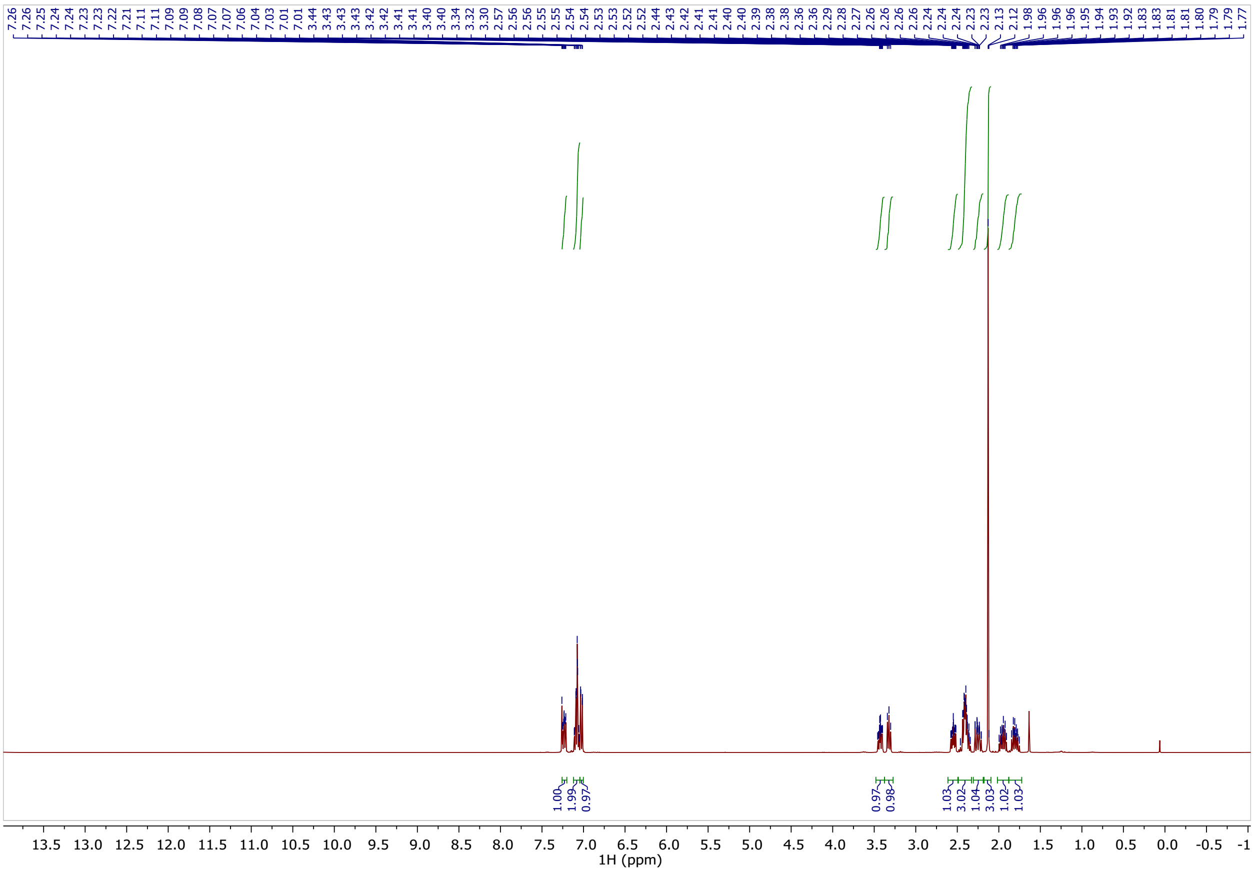
^{1}H NMR (300 MHz, $CDCl_3$) of **2i**



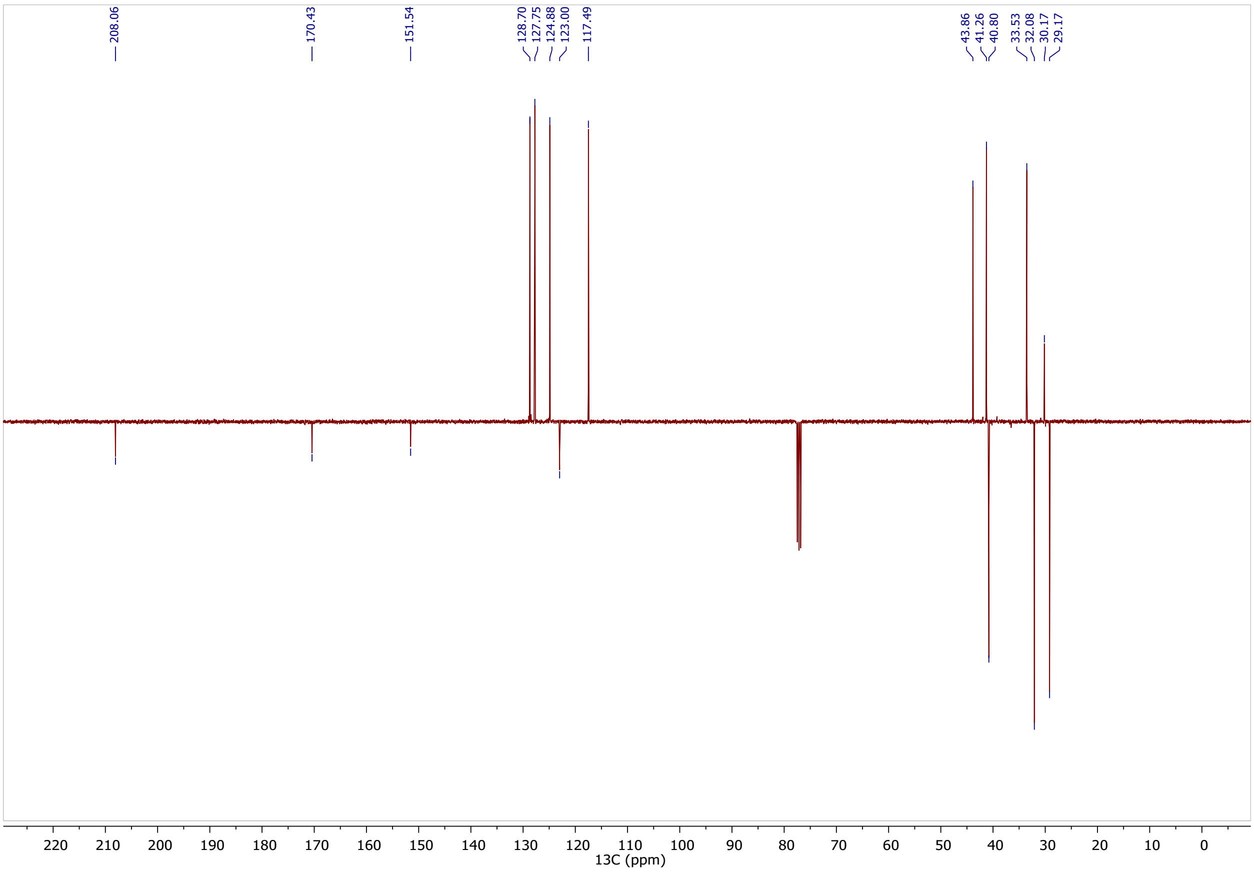
^{13}C NMR (101 MHz, $CDCl_3$) of **2i**



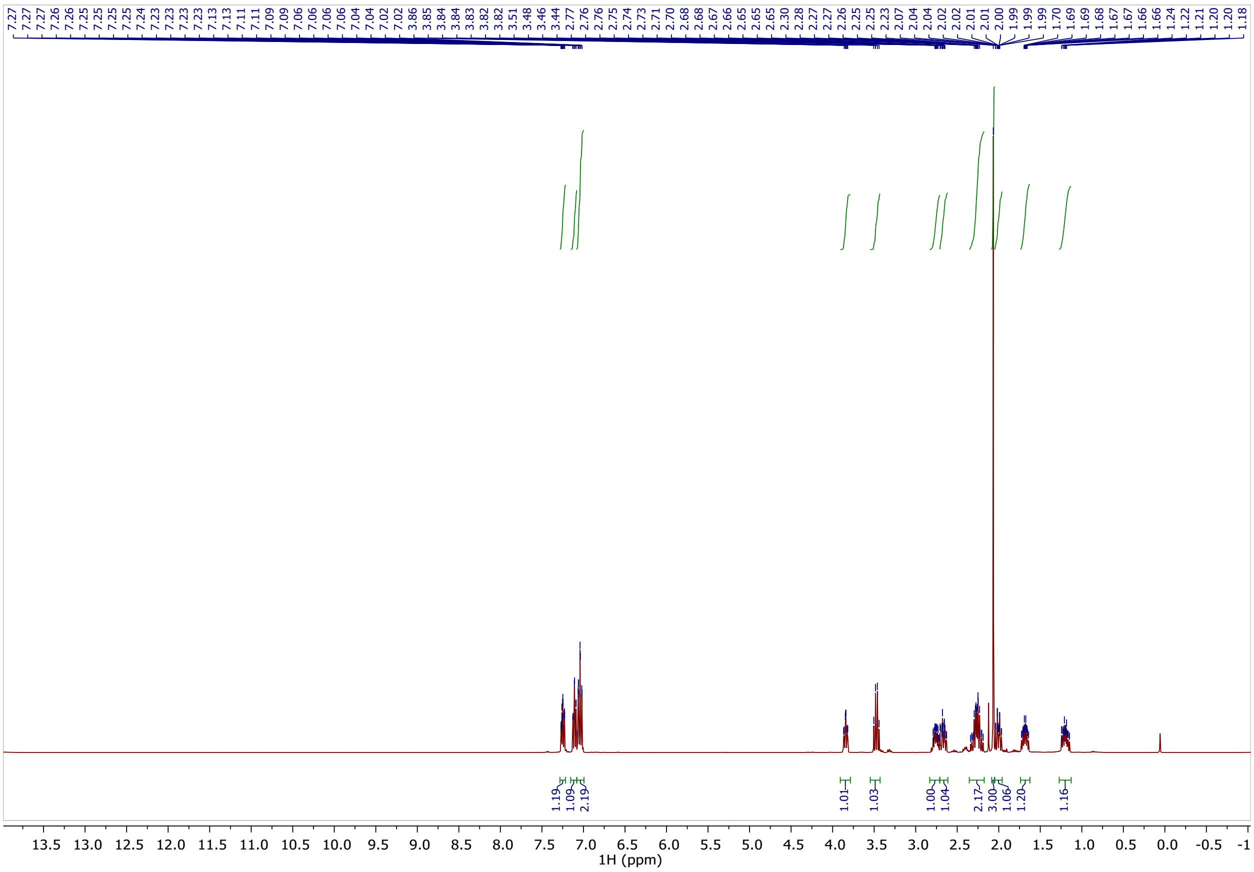
^{1}H NMR (300 MHz, CDCl$_3$) of **2j**



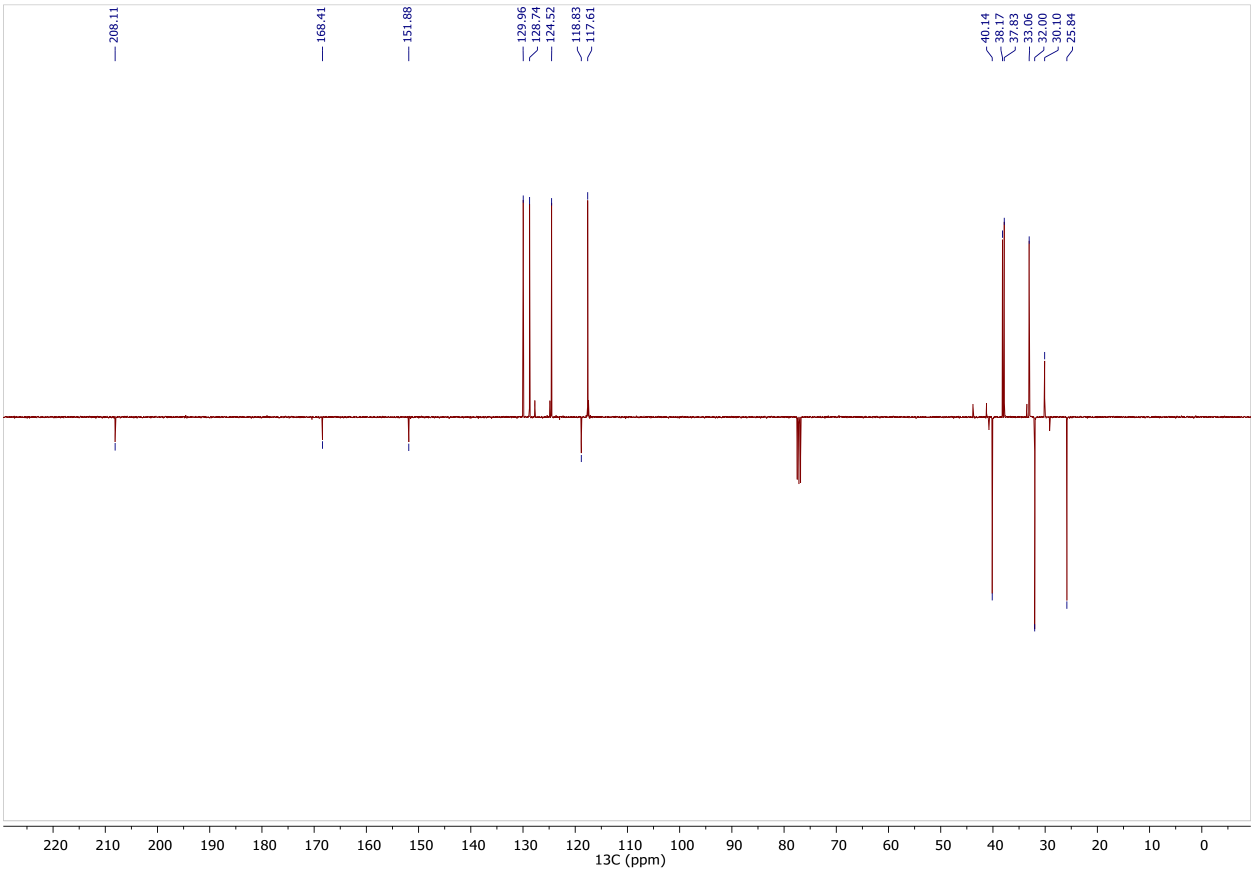
^{13}C NMR (101 MHz, CDCl$_3$) of **2j**



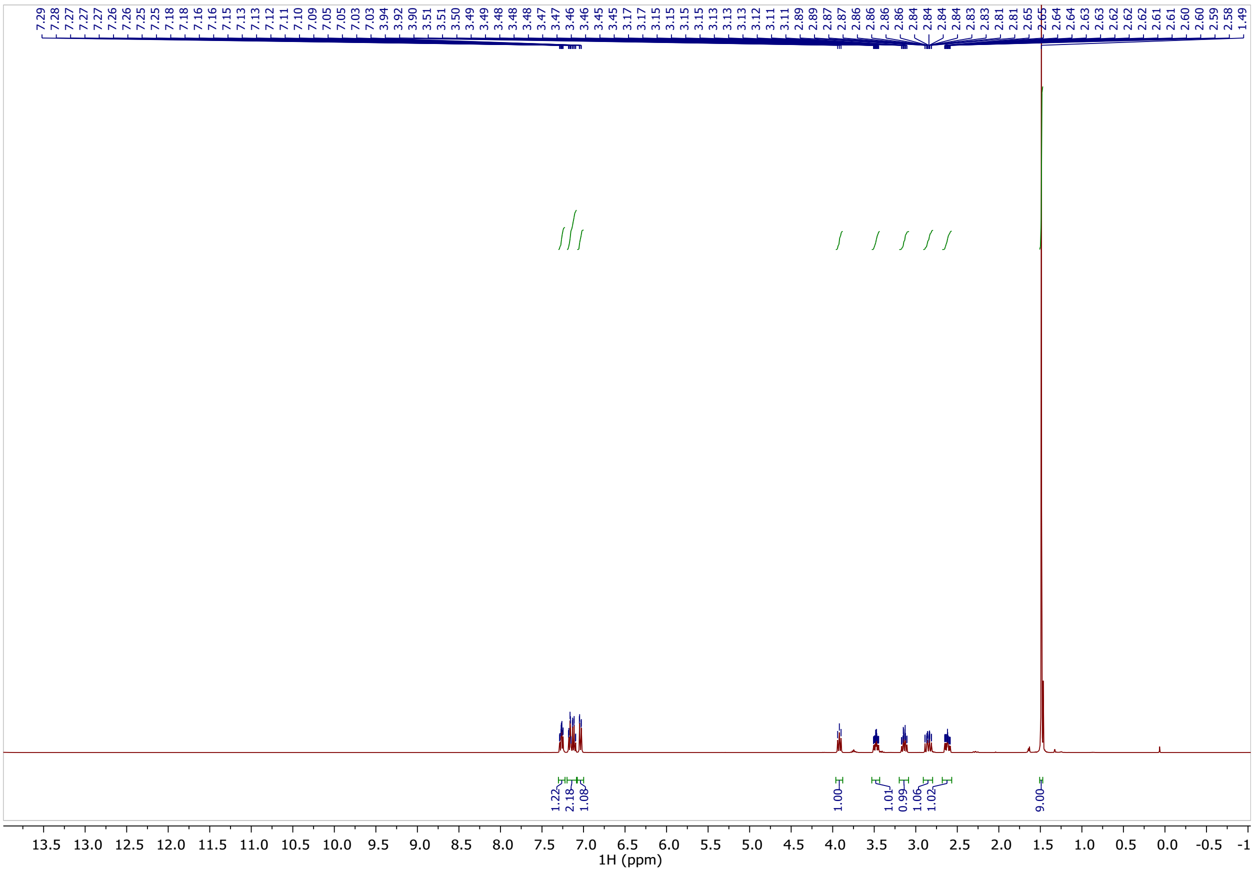
^{1}H NMR (300 MHz, $CDCl_3$) of **2j'**



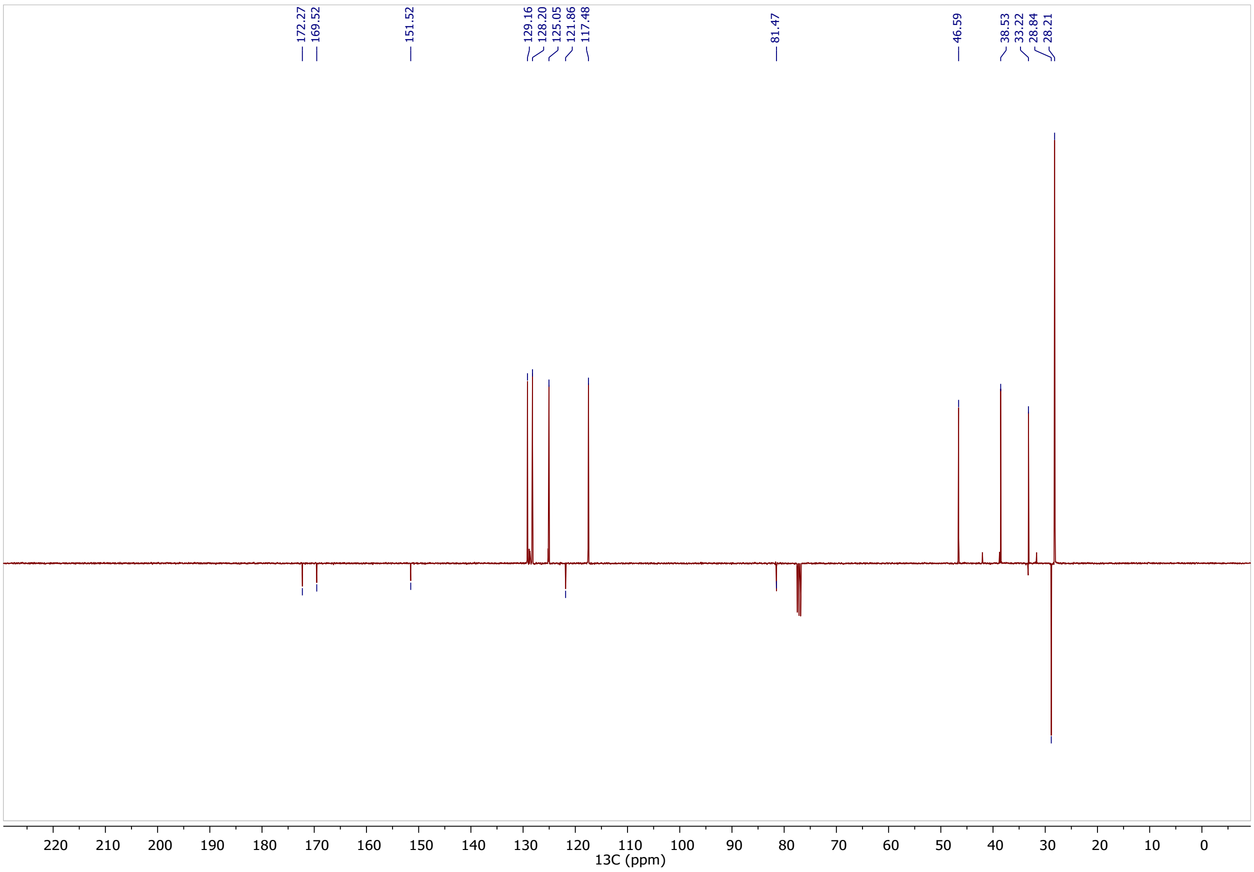
^{13}C NMR (101 MHz, $CDCl_3$) of **2j'**



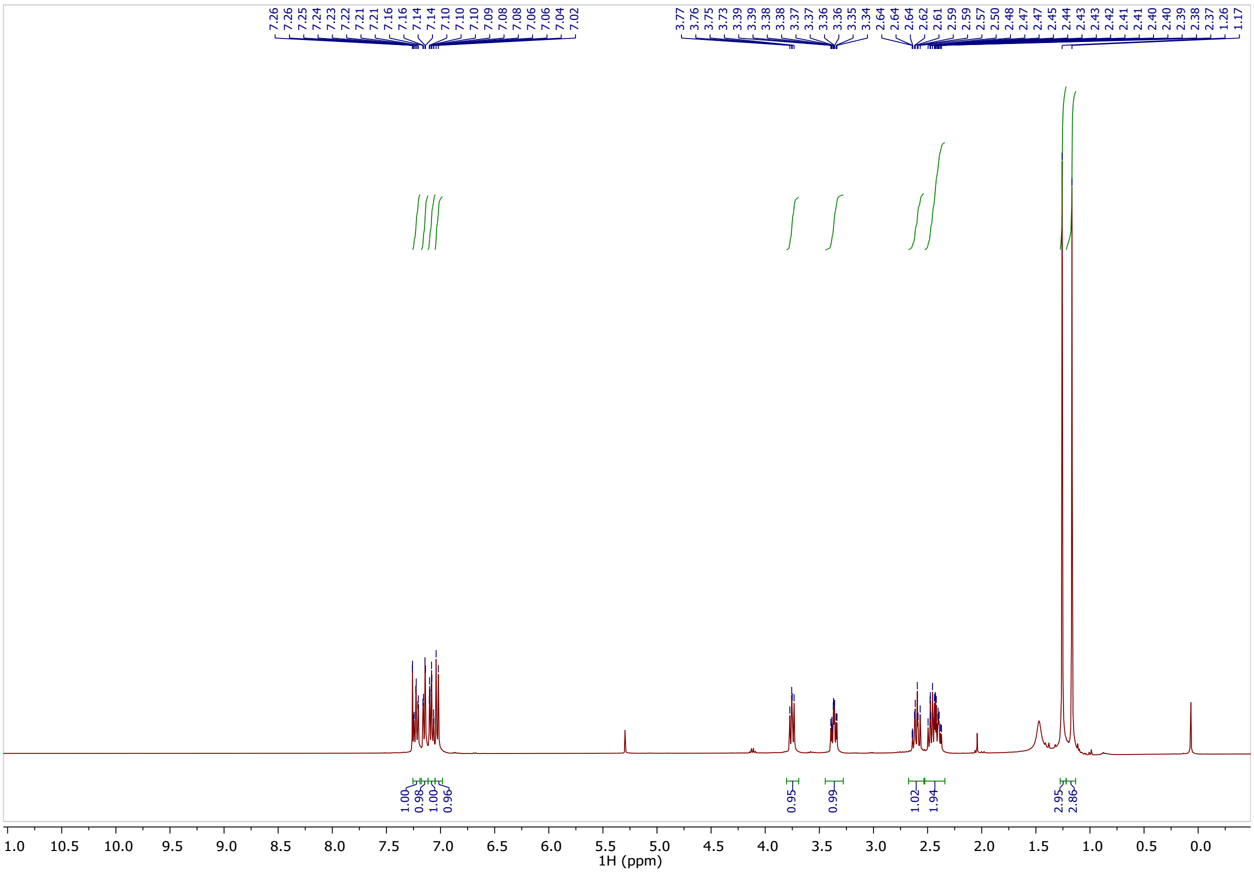
^1H NMR (300 MHz, $CDCl_3$) of **2k**



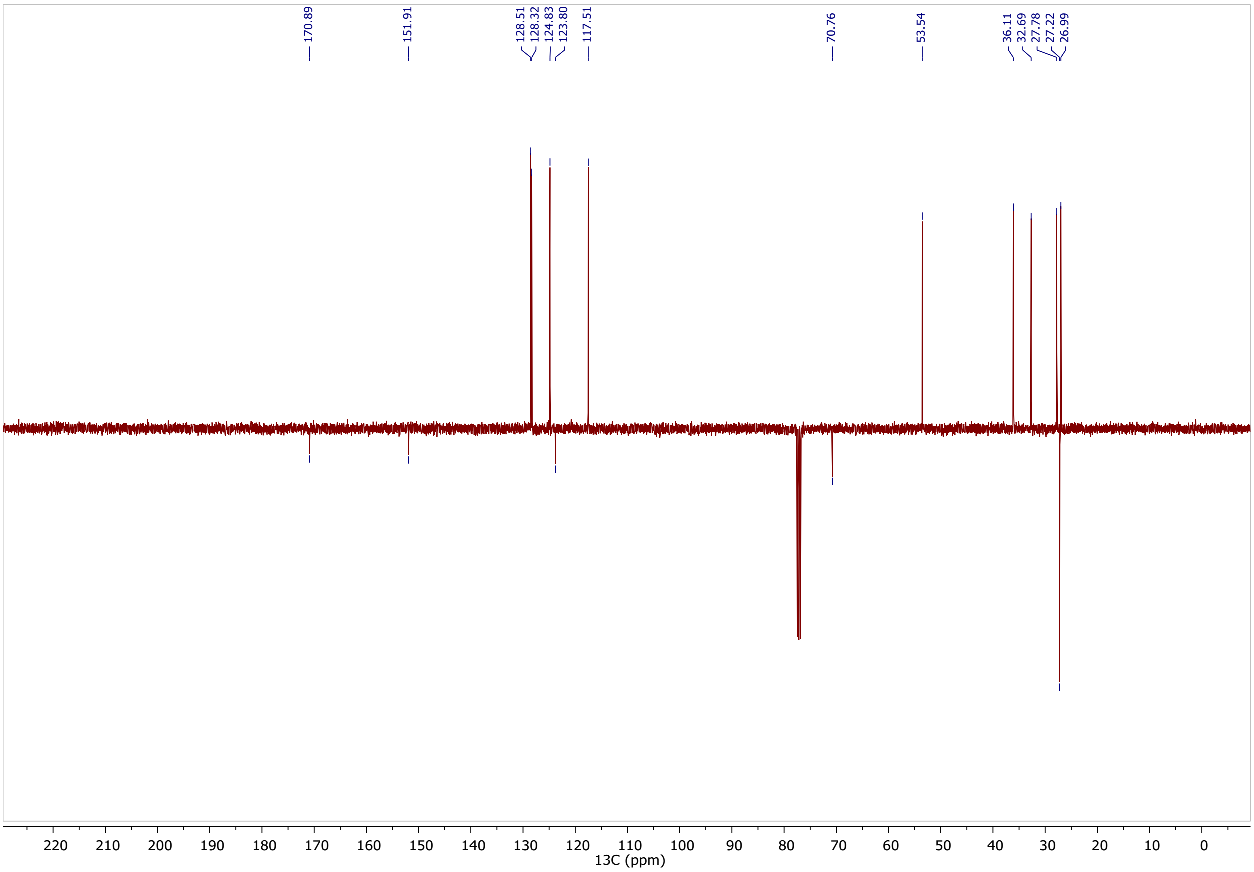
^{13}C NMR (101 MHz, $CDCl_3$) of **2k**



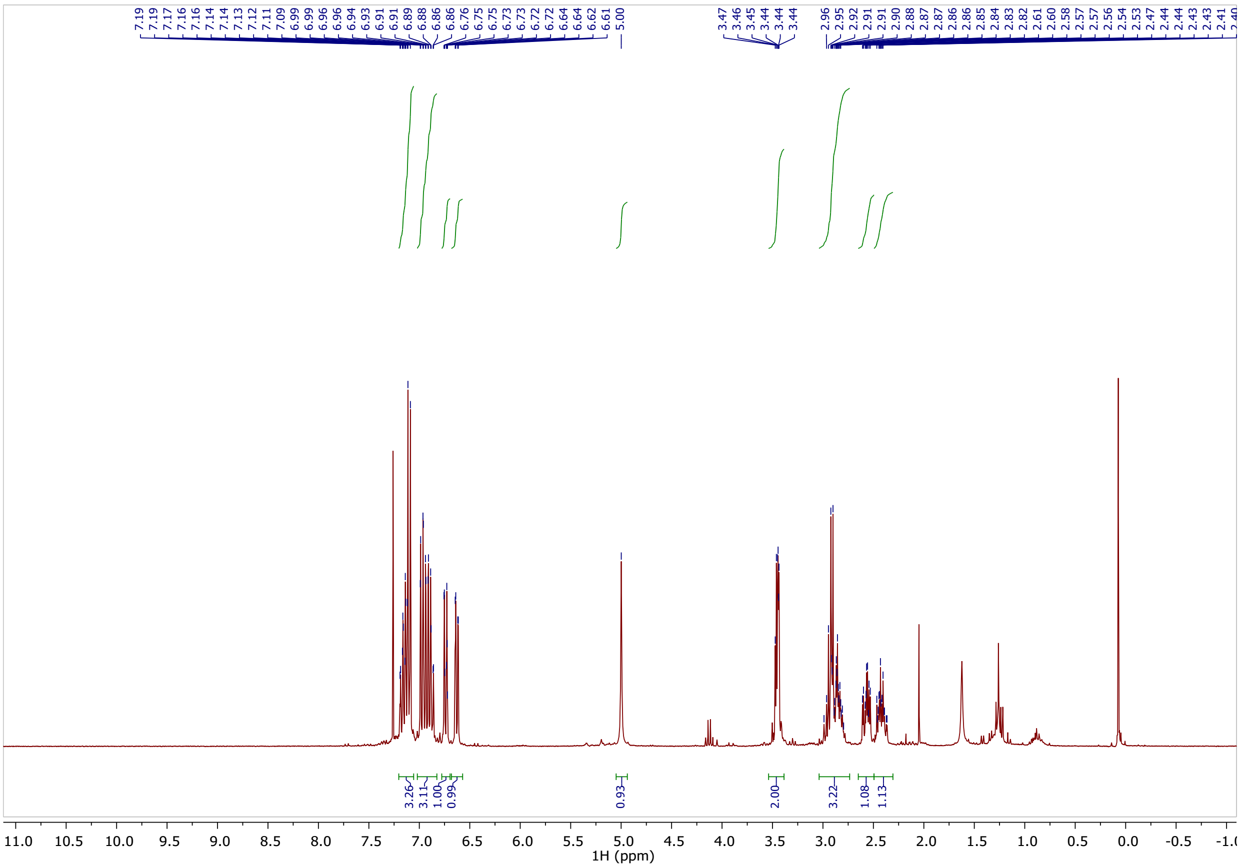
^{1}H NMR (300 MHz, CDCl$_3$) of **2l**



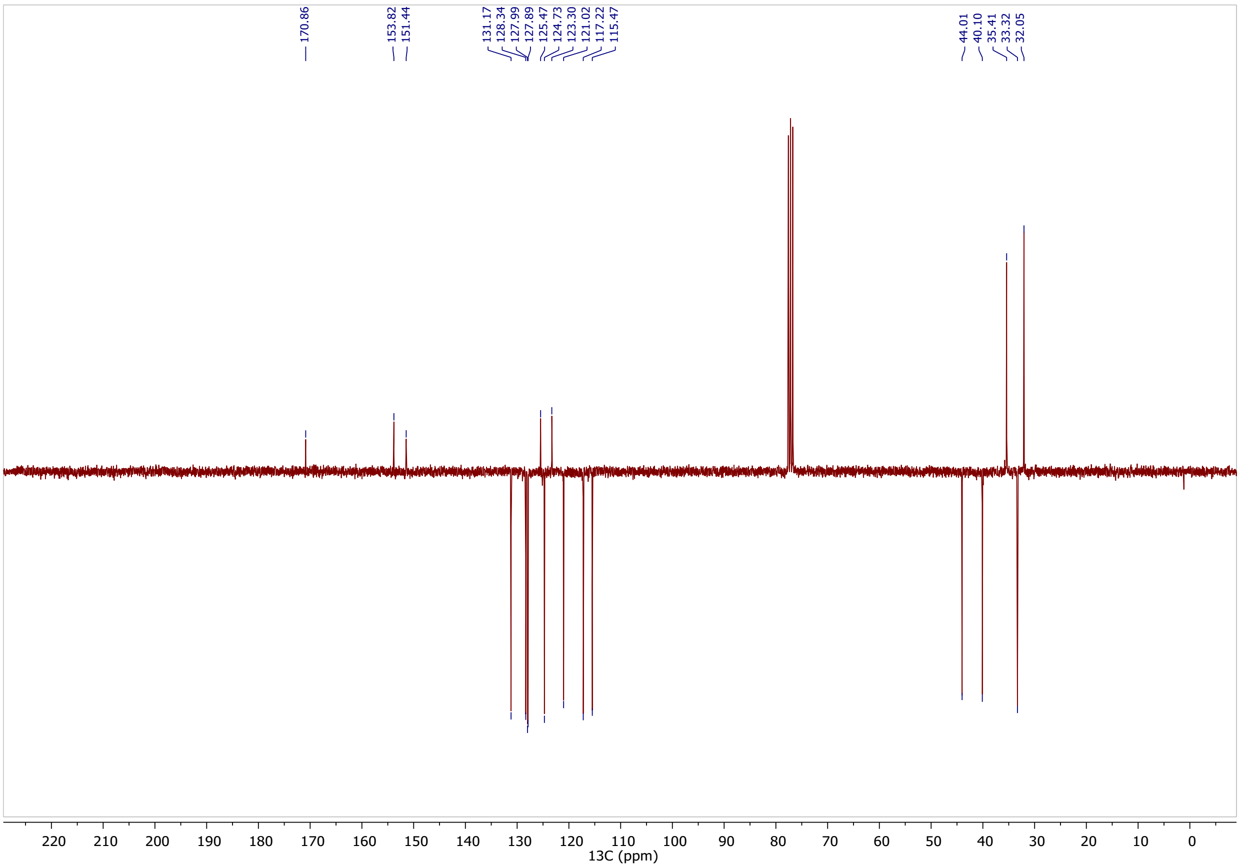
^{13}C NMR (101 MHz, CDCl$_3$) of **2l**



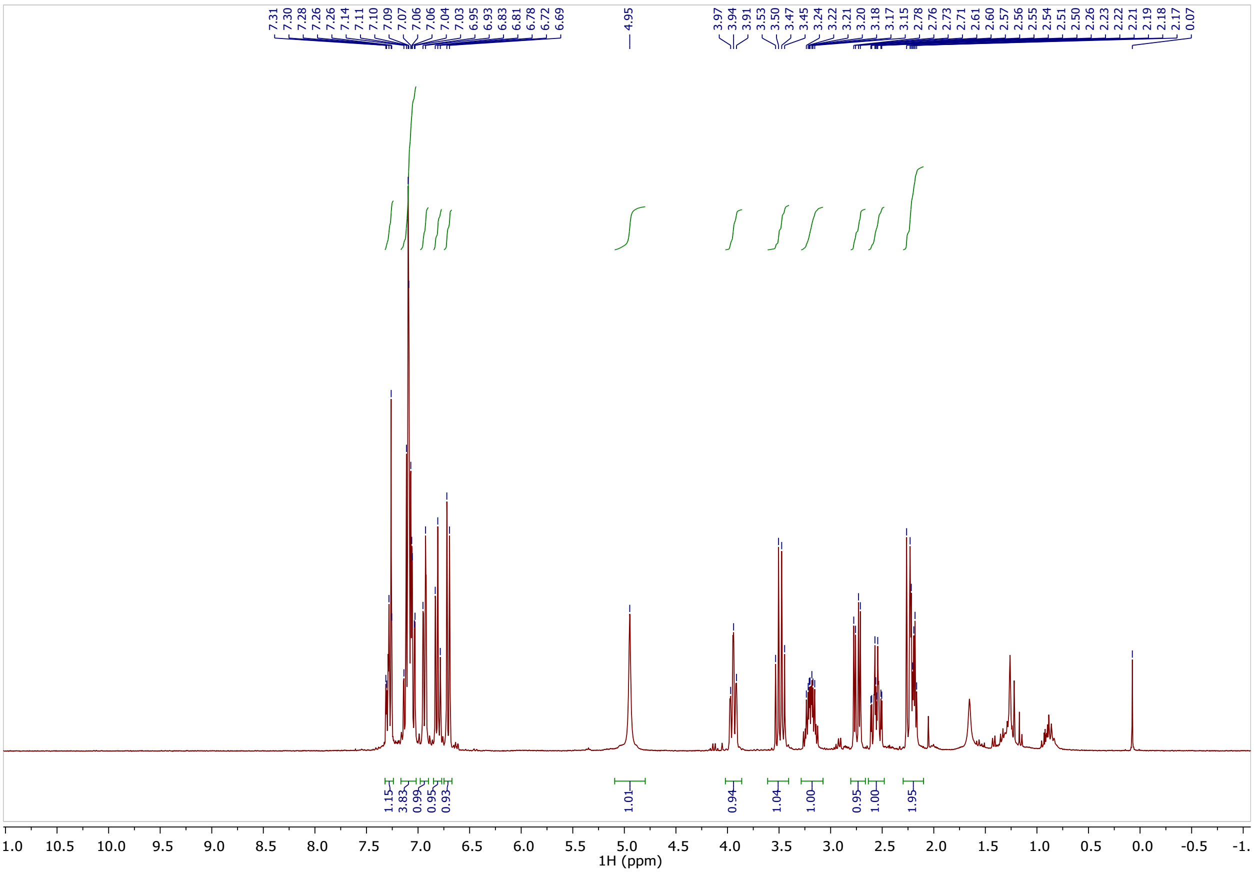
^{1}H NMR (300 MHz, $CDCl_3$) of **2m**



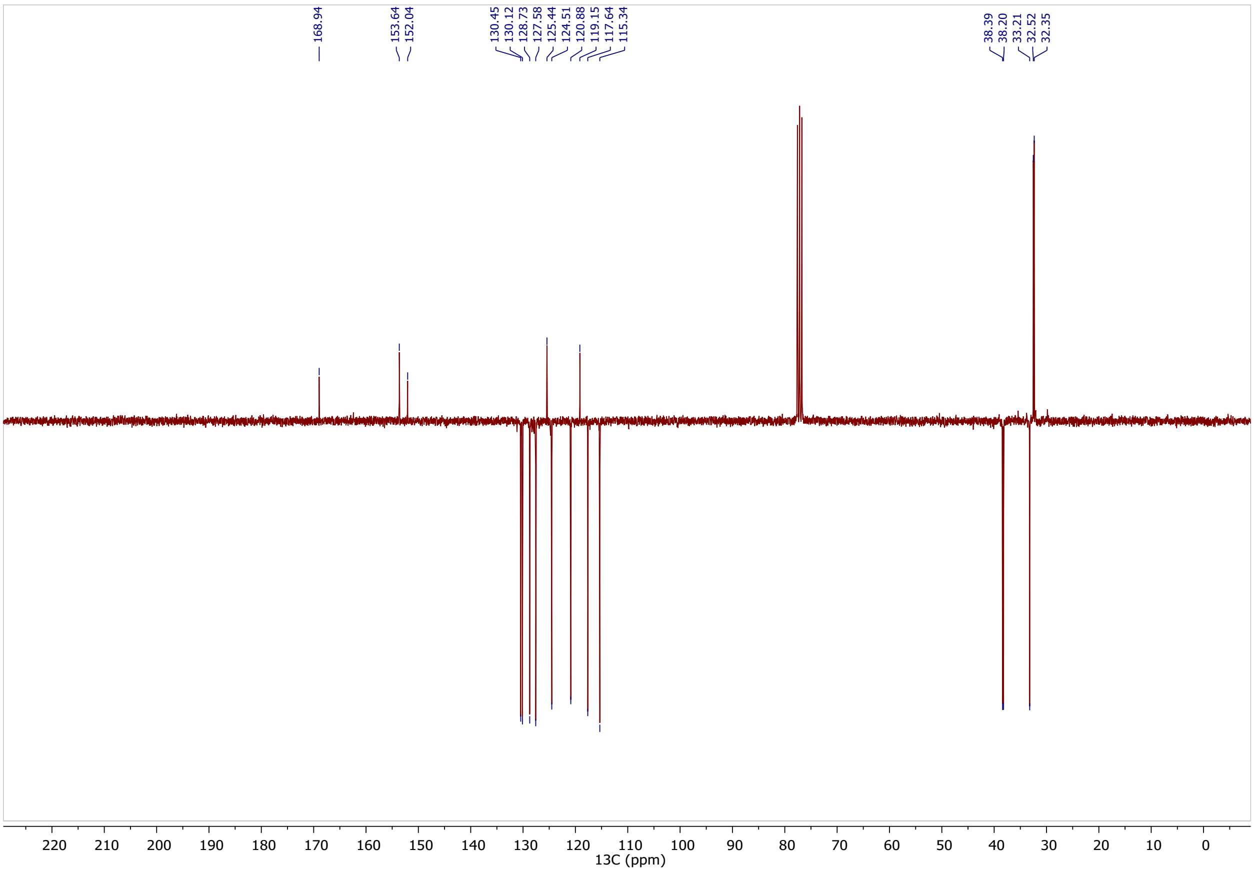
^{13}C NMR (101 MHz, $CDCl_3$) of **2m**



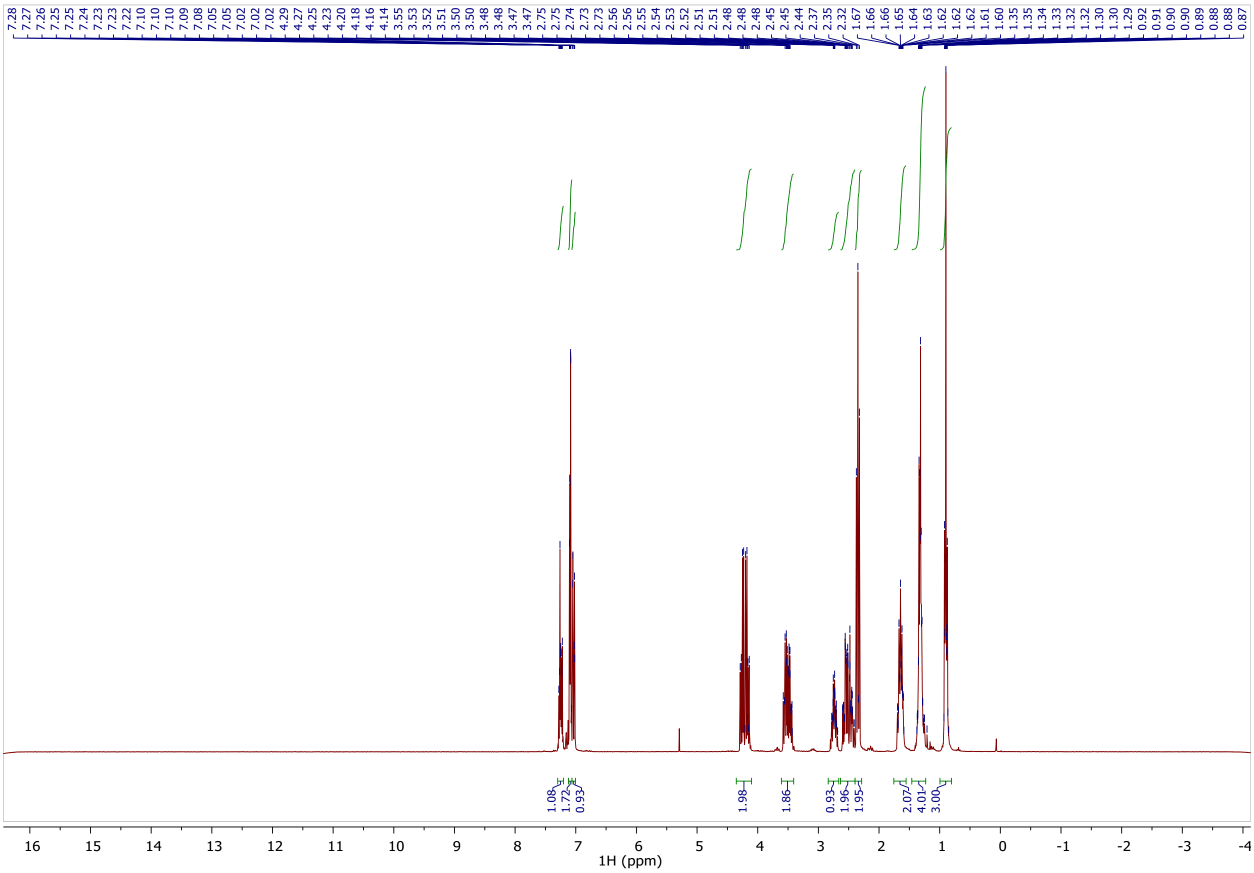
^{1}H NMR (300 MHz, CDCl$_3$) of **2m’**



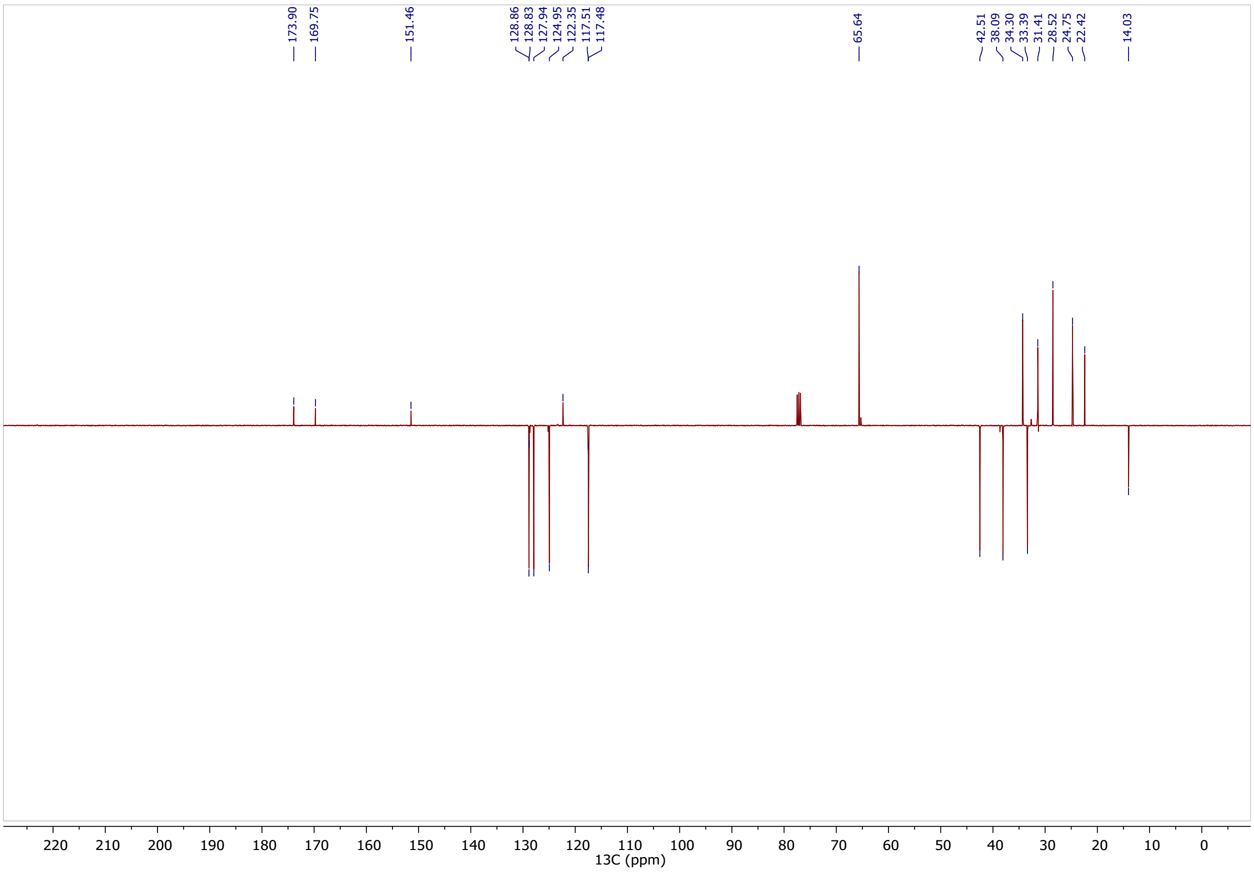
^{13}C NMR (101 MHz, CDCl$_3$) of **2m’**



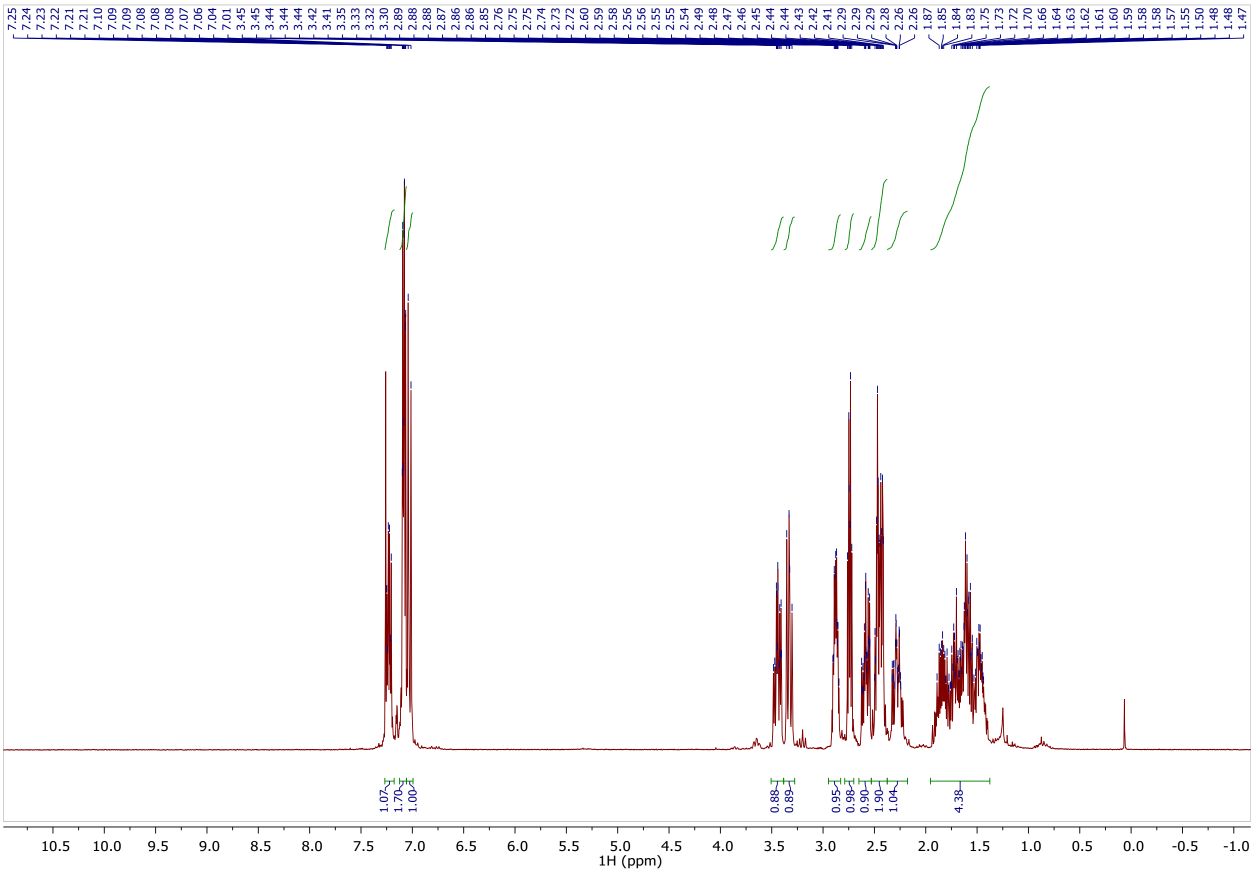
^{1}H NMR (300 MHz, CDCl$_3$) of **2n**



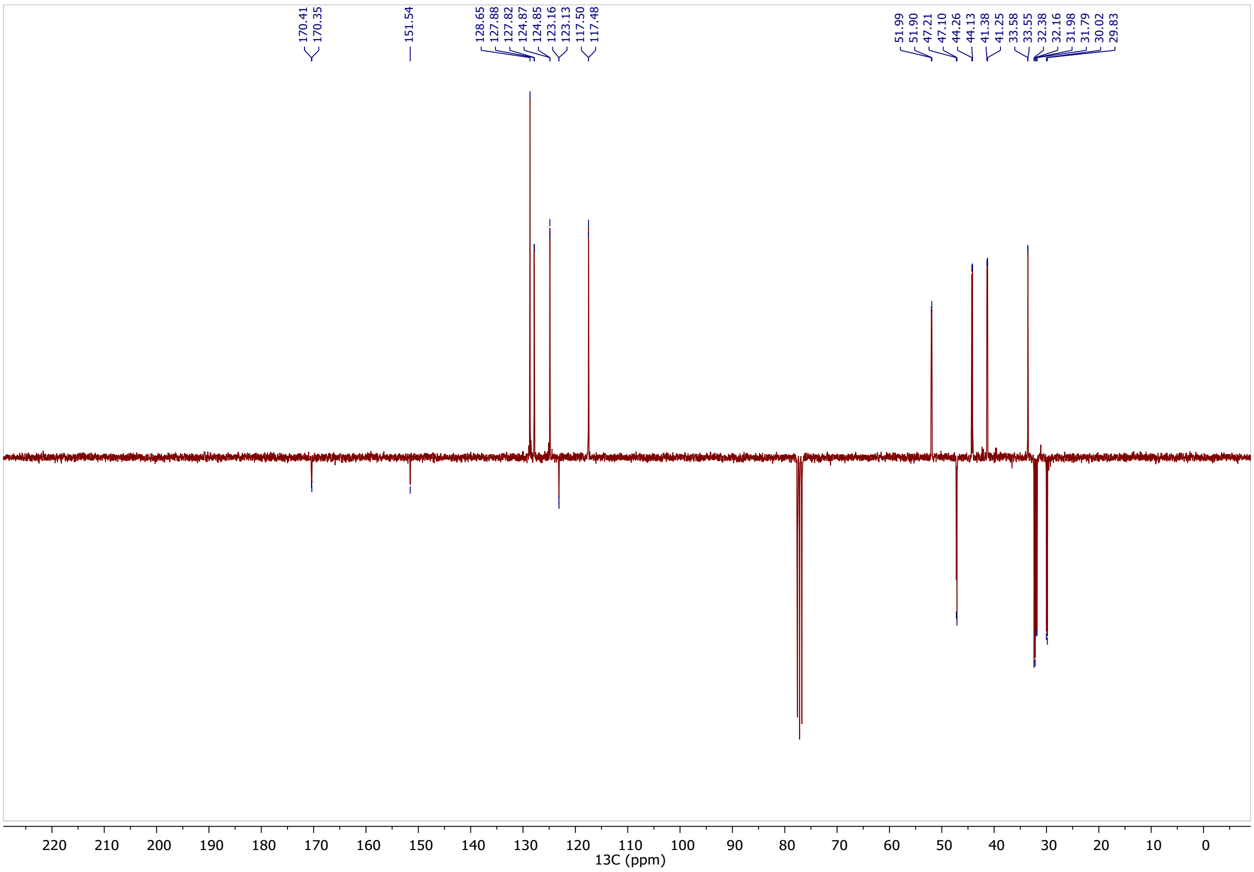
^{13}C NMR (101 MHz, CDCl$_3$) of **2n**



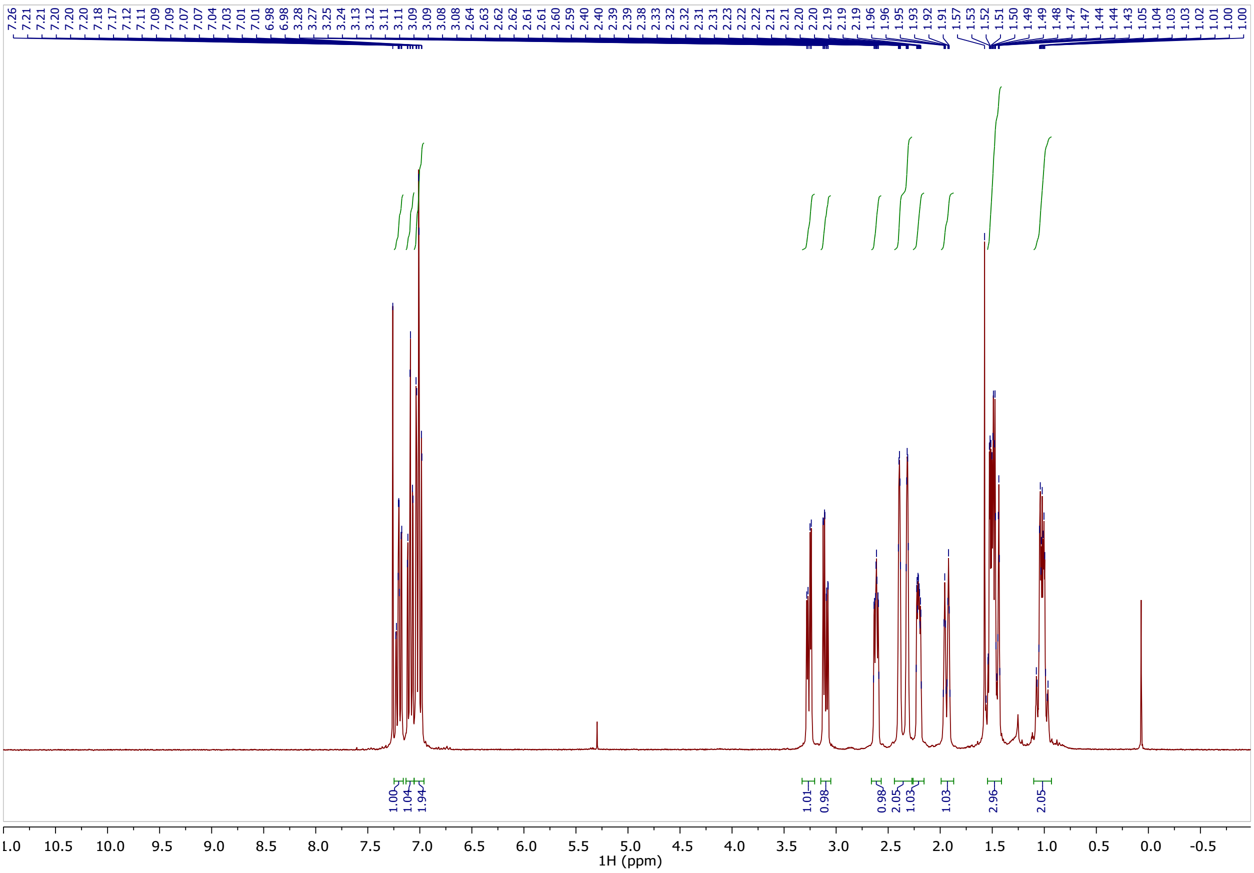
^{1}H NMR (300 MHz, CDCl$_3$) of **2o**



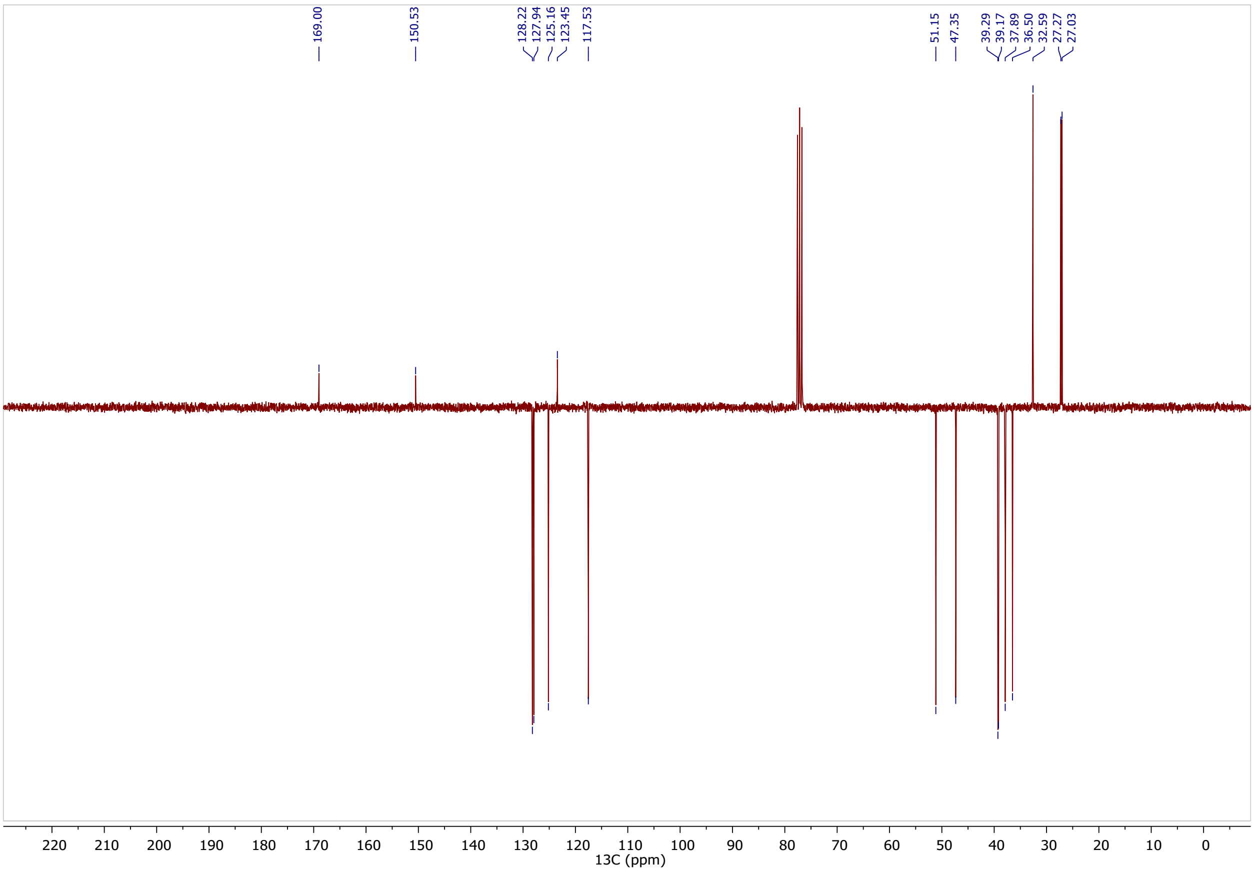
^{13}C NMR (101 MHz, CDCl$_3$) of **2o**



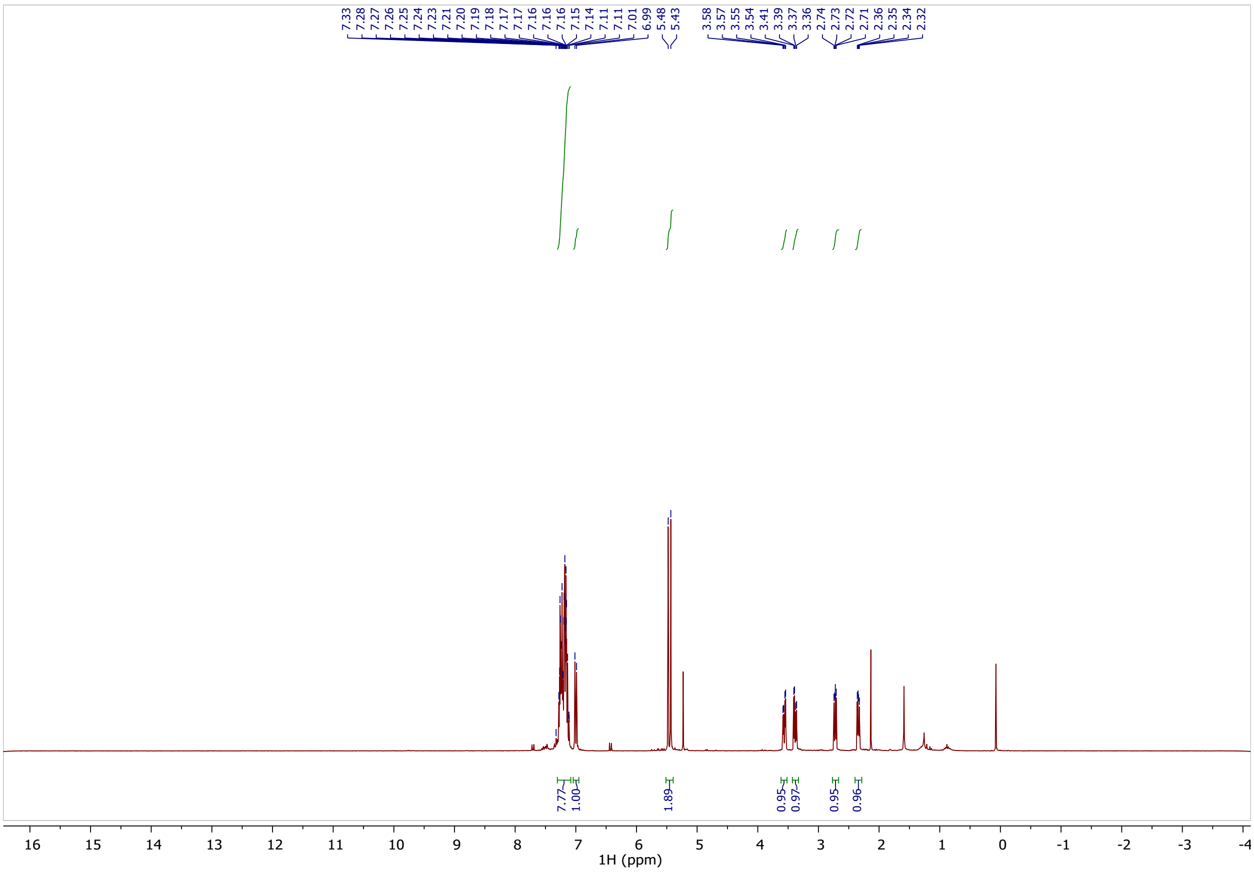
^{1}H NMR (300 MHz, CDCl$_3$) of **2p**



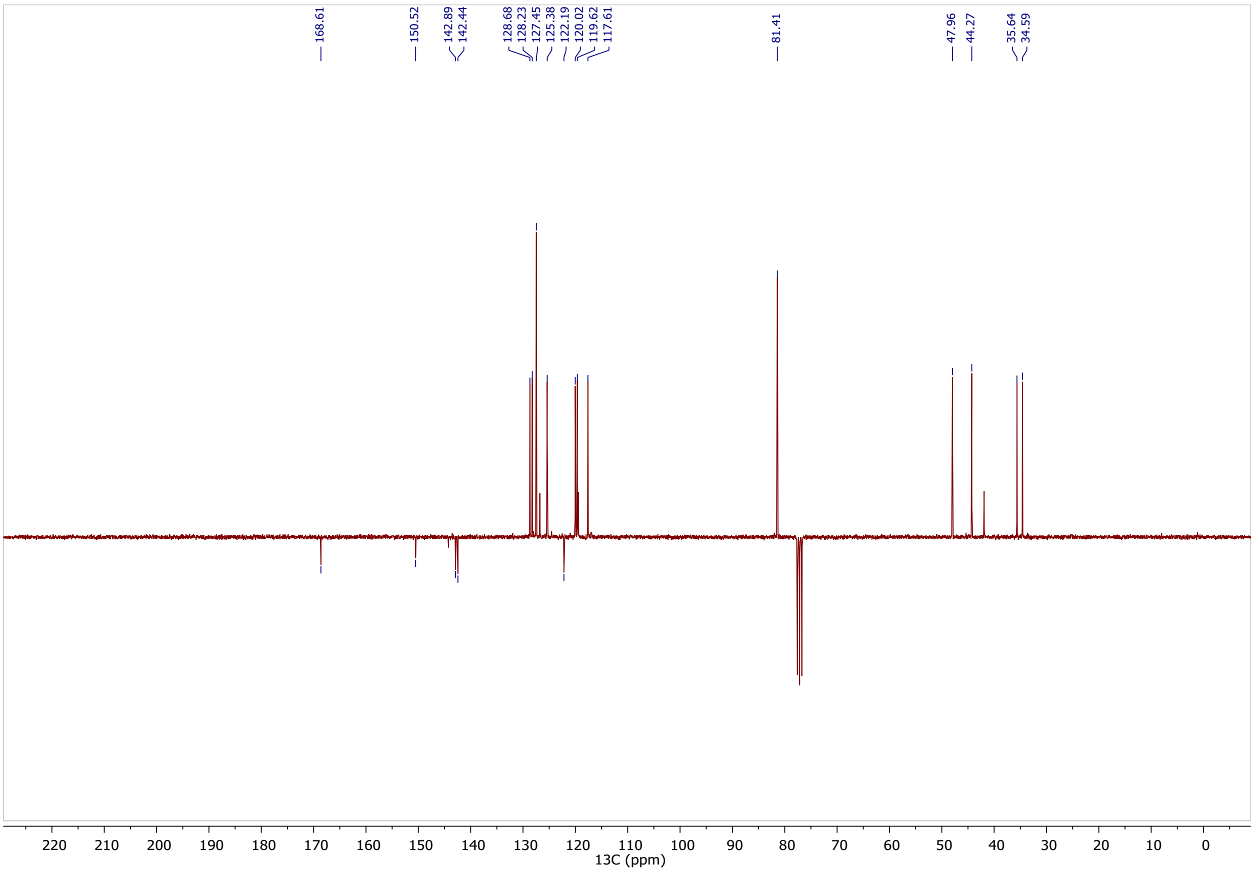
^{13}C NMR (101 MHz, CDCl$_3$) of **2p**



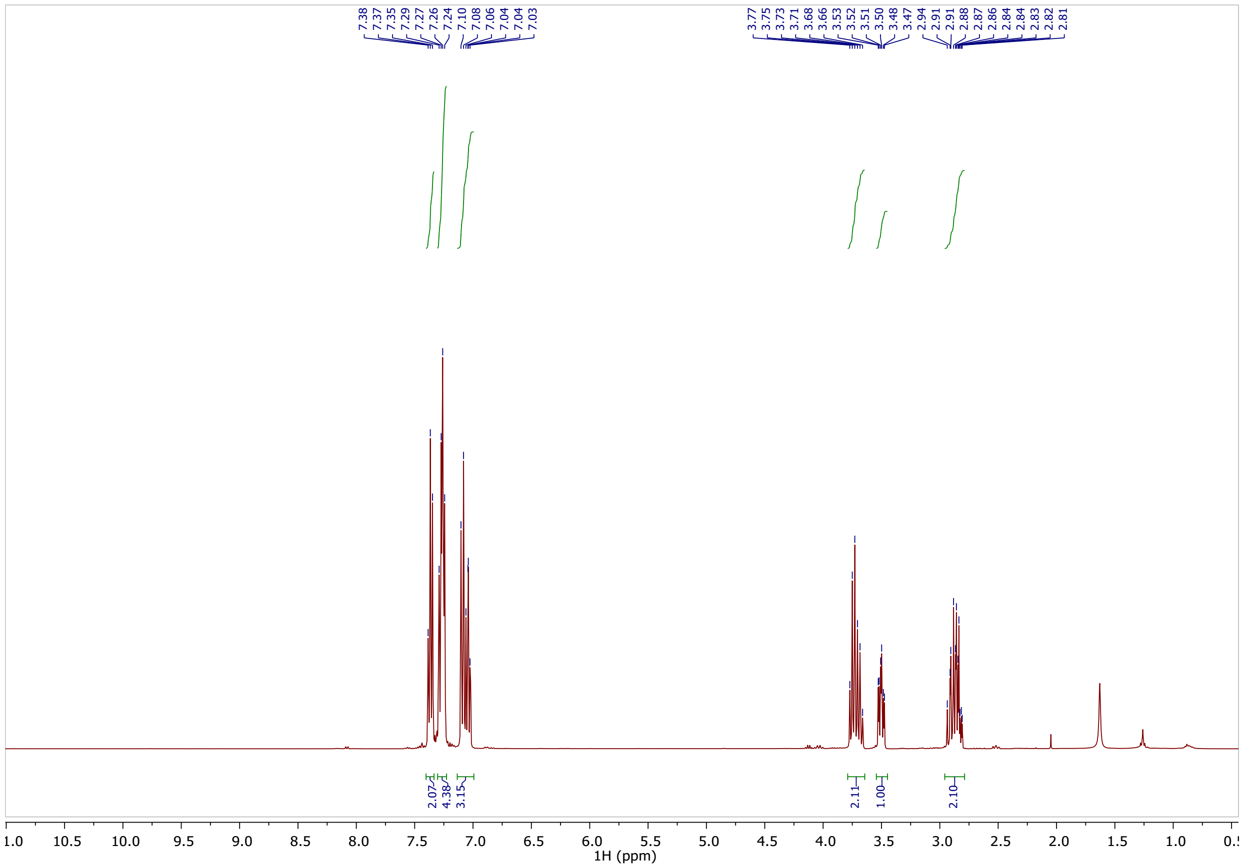
^{1}H NMR (300 MHz, $CDCl_3$) of **2q**



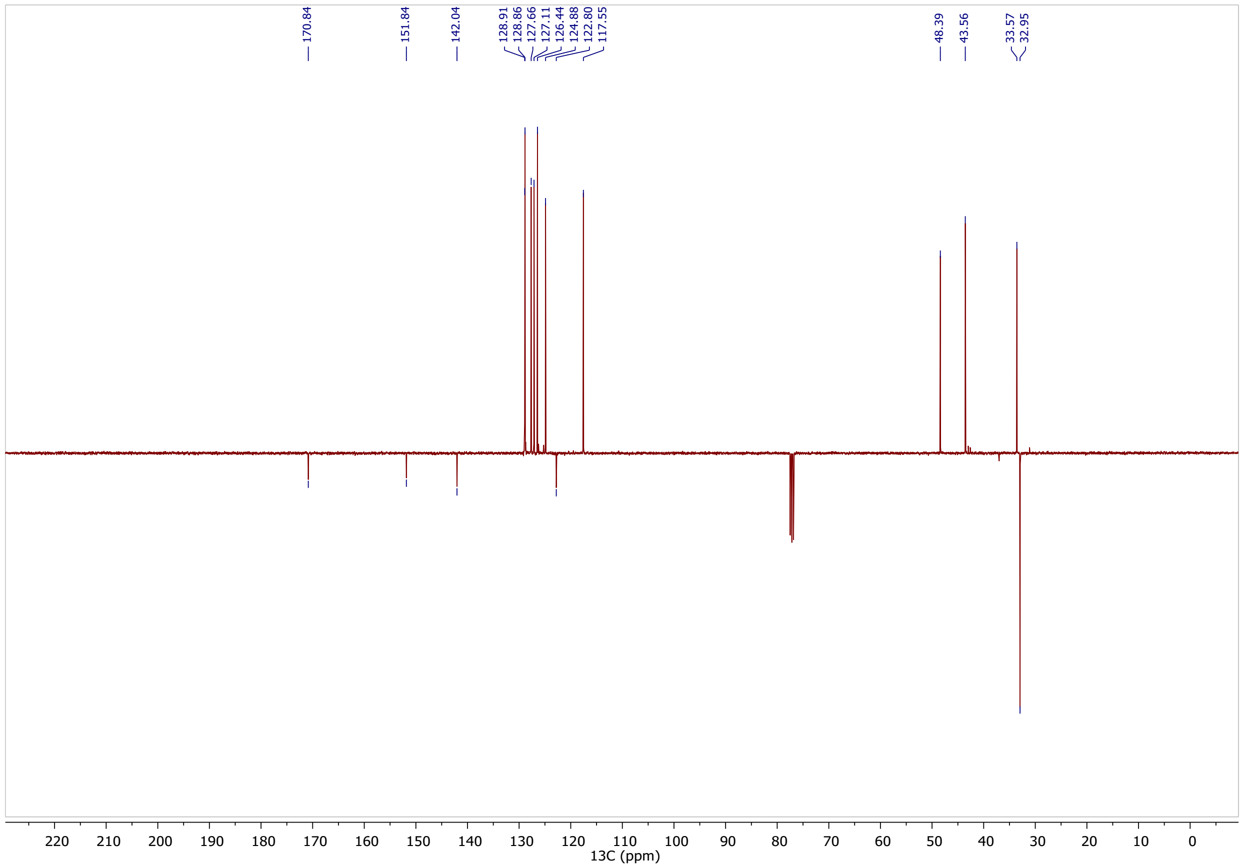
^{13}C NMR (101 MHz, $CDCl_3$) of **2q**



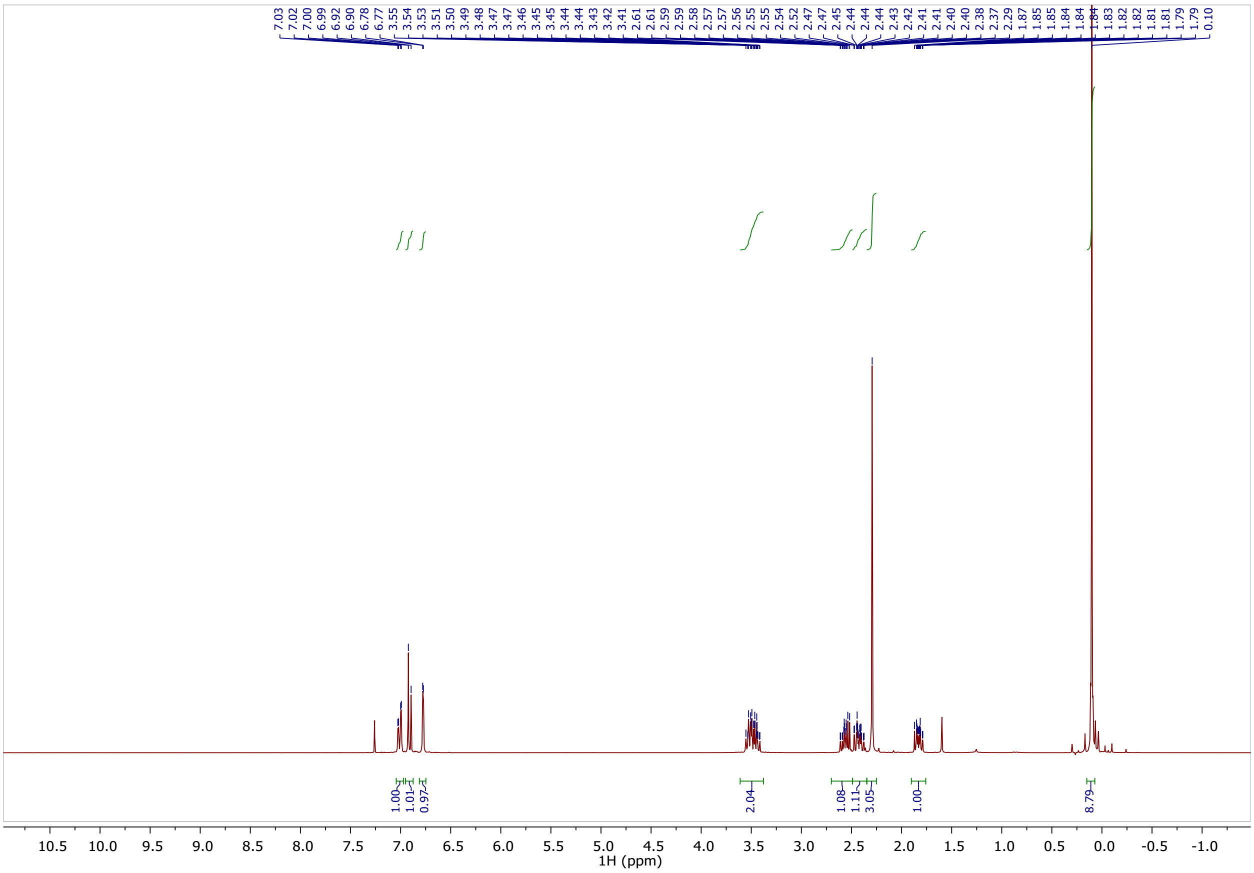
^{1}H NMR (300 MHz, $CDCl_3$) of **2r**



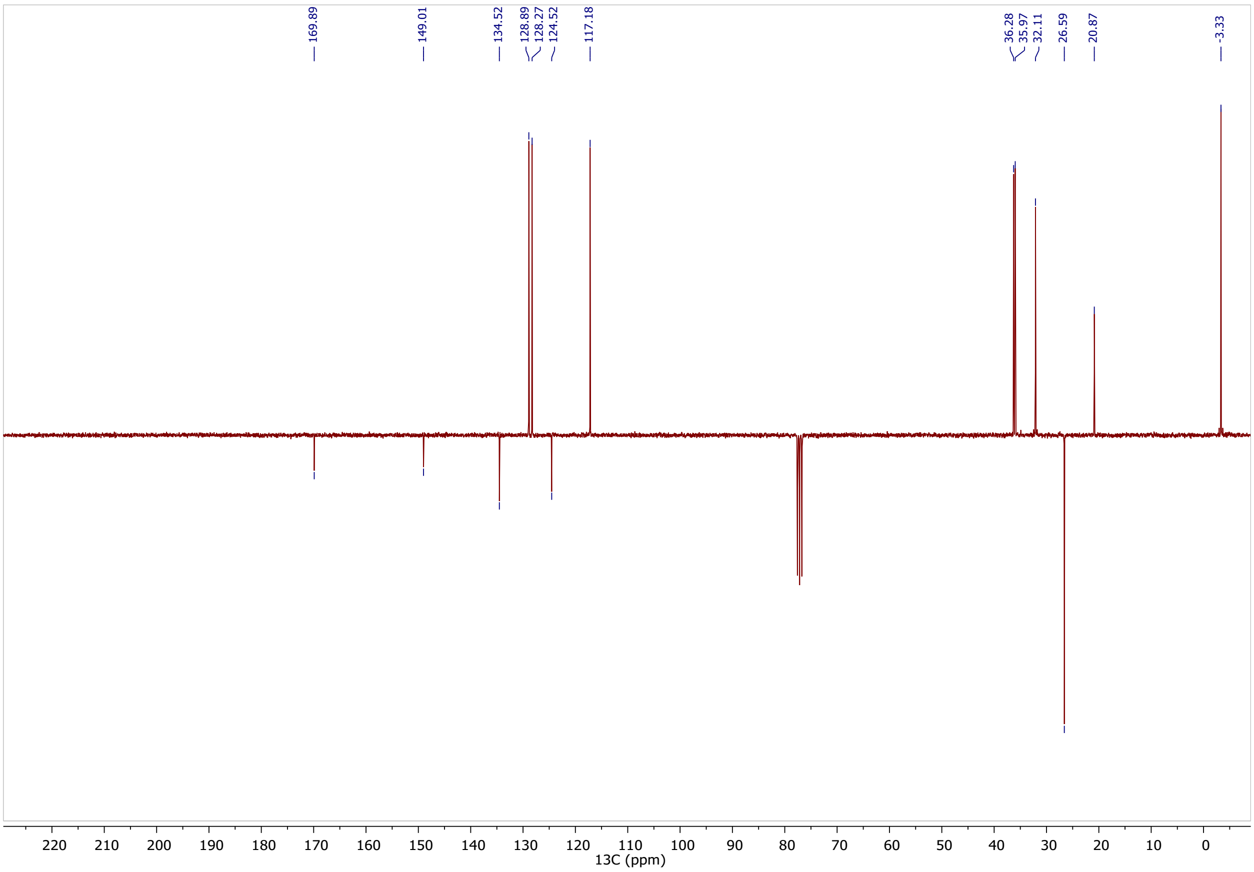
^{13}C NMR (101 MHz, $CDCl_3$) of **2r**



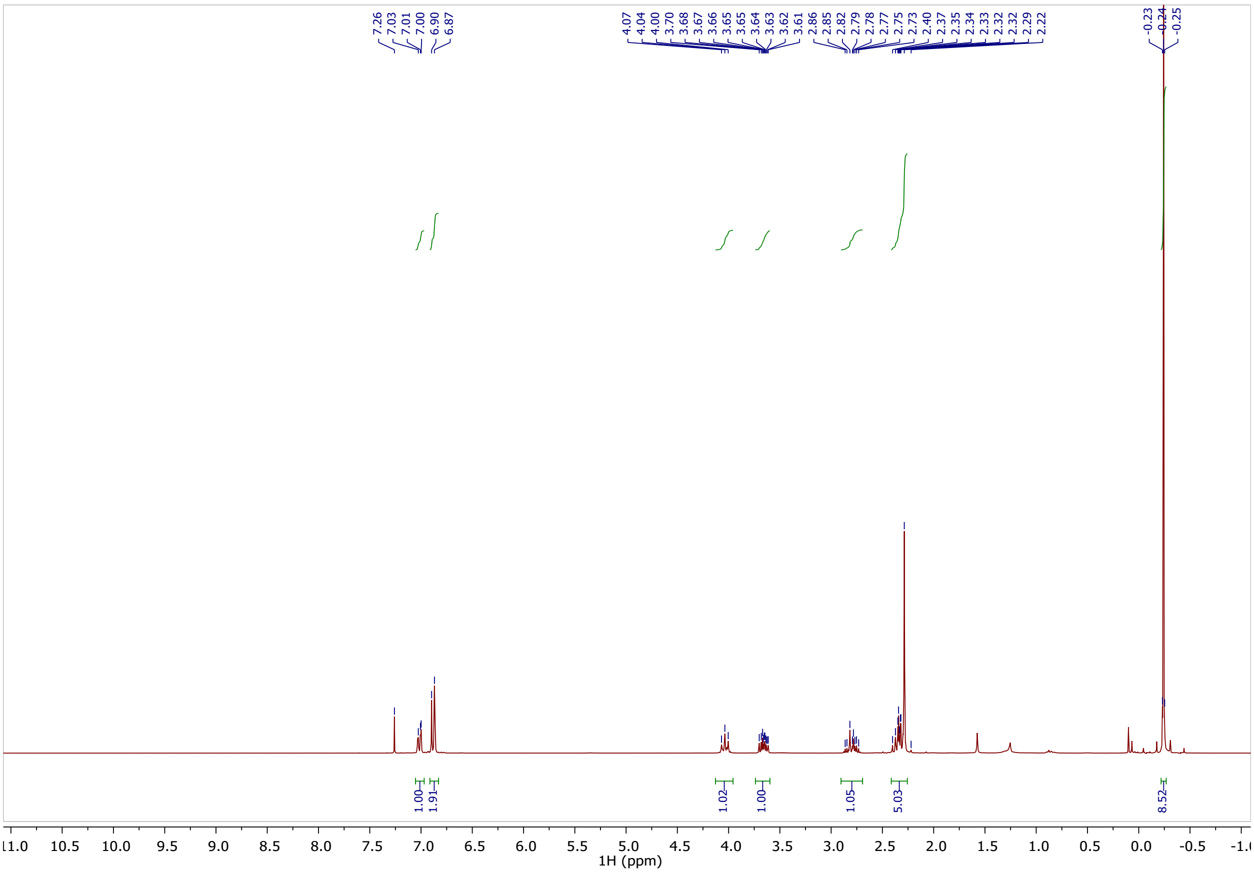
^{1}H NMR (300 MHz, CDCl$_3$) of **2s**



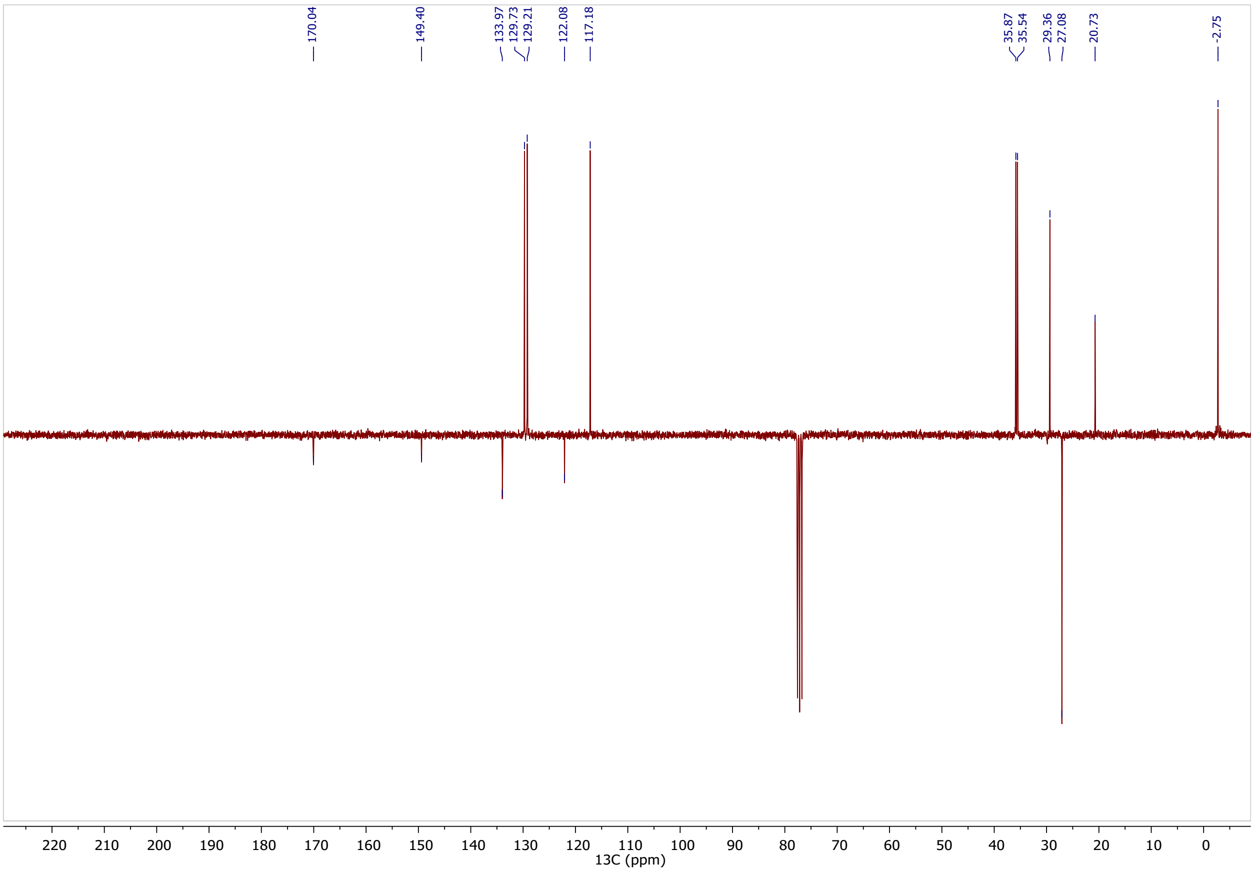
^{13}C NMR (101 MHz, CDCl$_3$) of **2s**



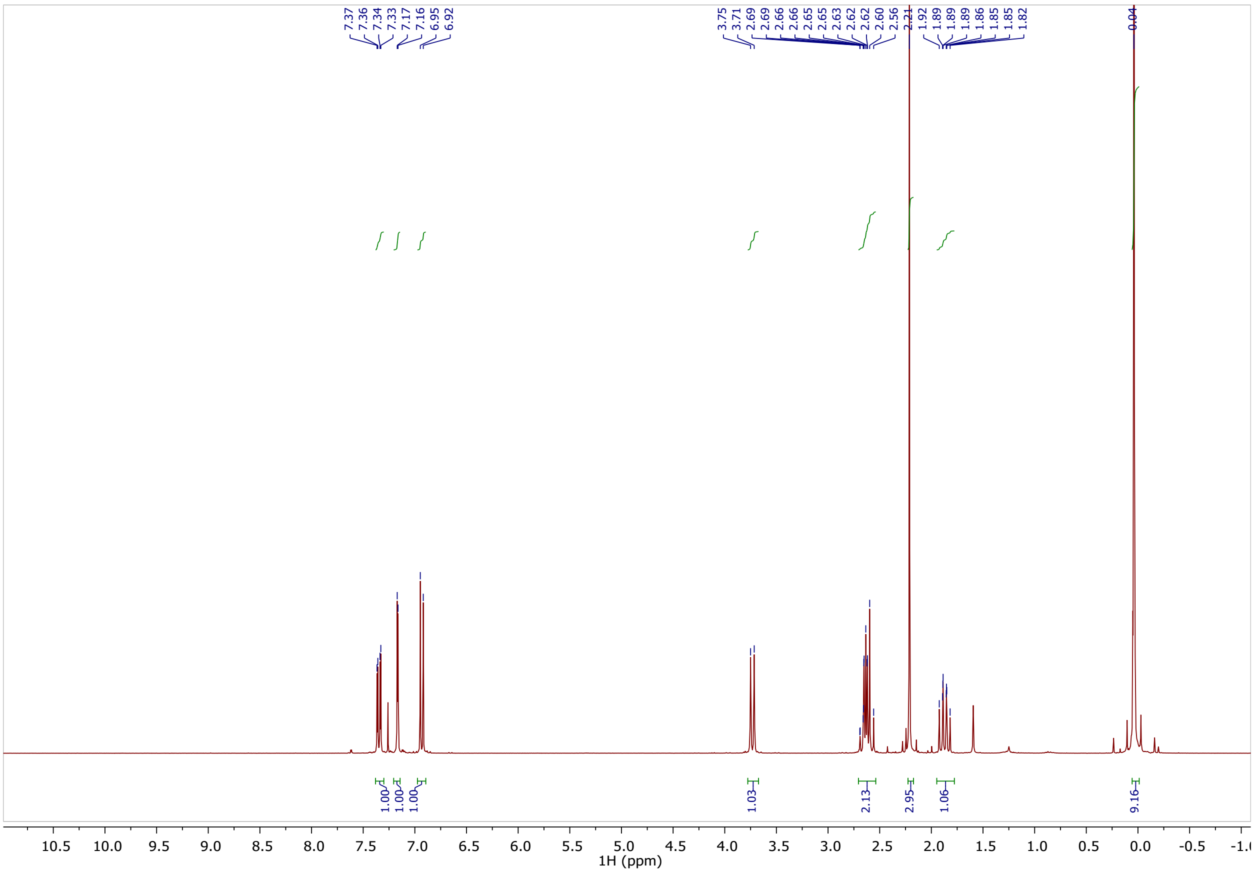
^{1}H NMR (300 MHz, CDCl$_3$) of **2s'**



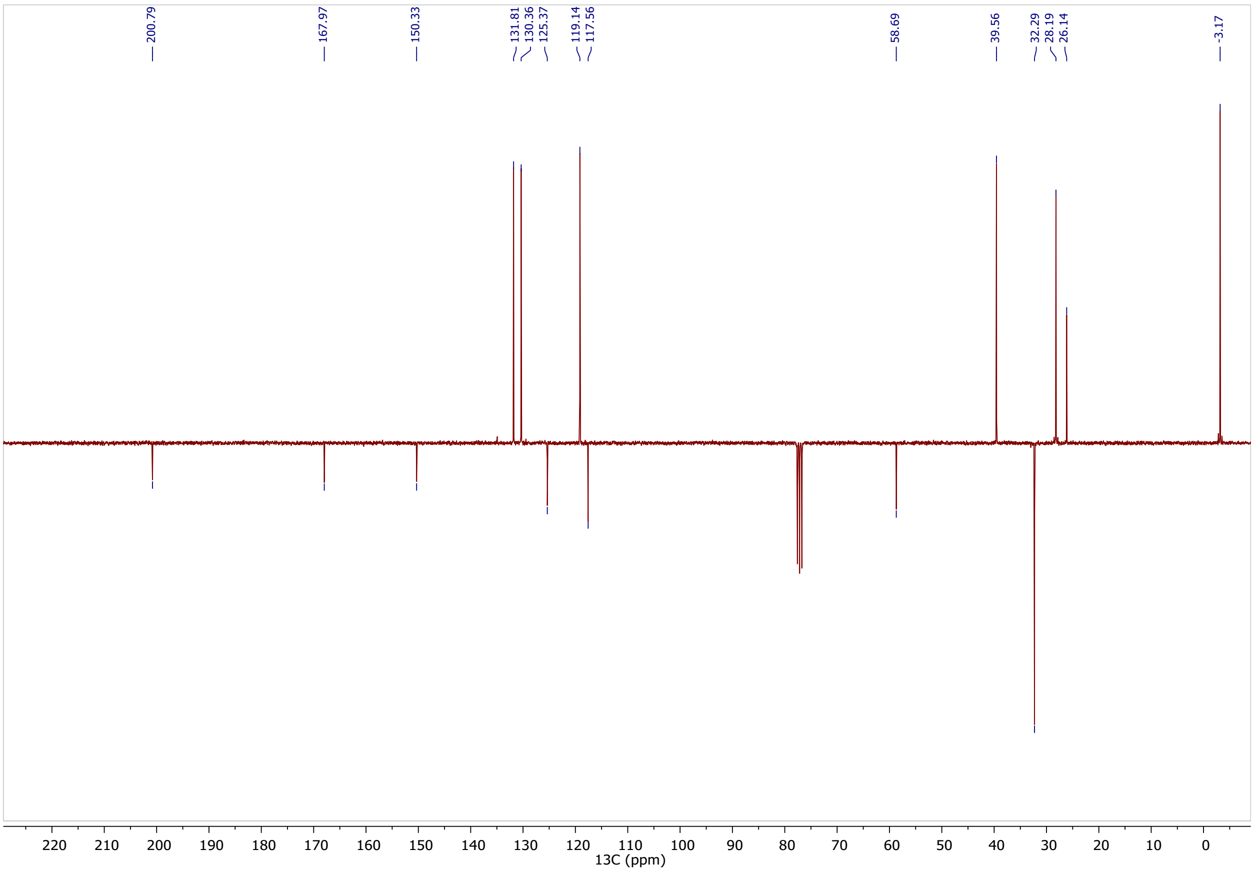
^{13}C NMR (101 MHz, CDCl$_3$) of **2s'**



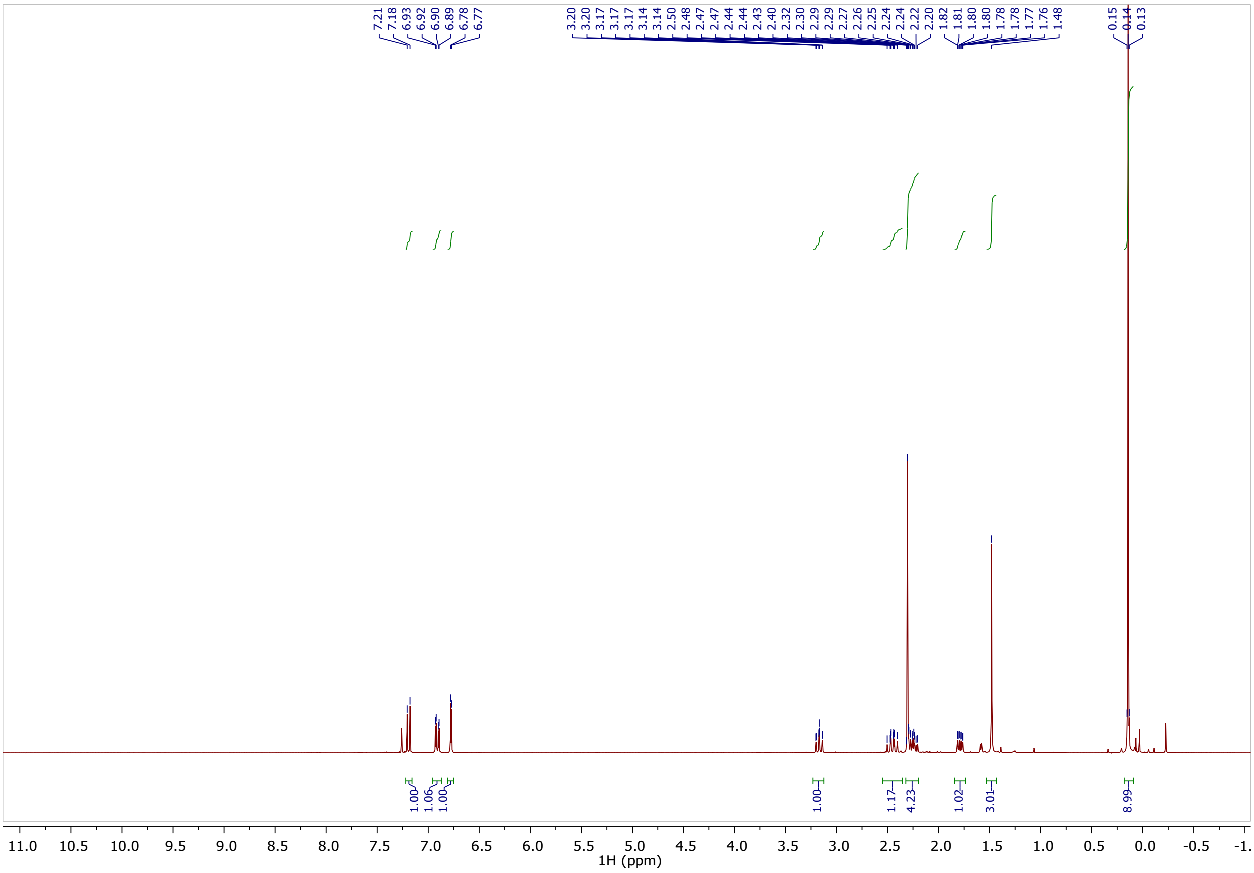
^{1}H NMR (300 MHz, CDCl$_3$) of **2t**



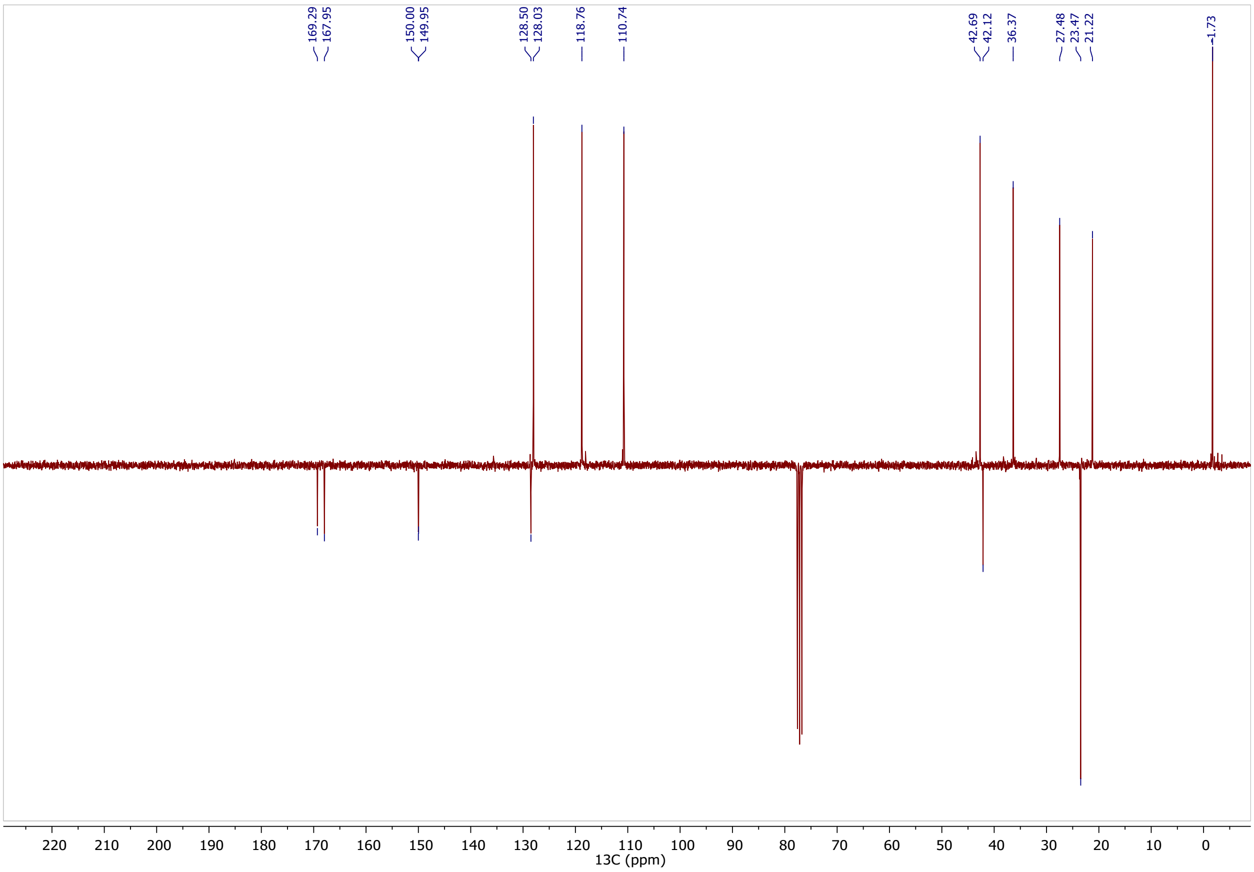
^{13}C NMR (101 MHz, CDCl$_3$) of **2t**



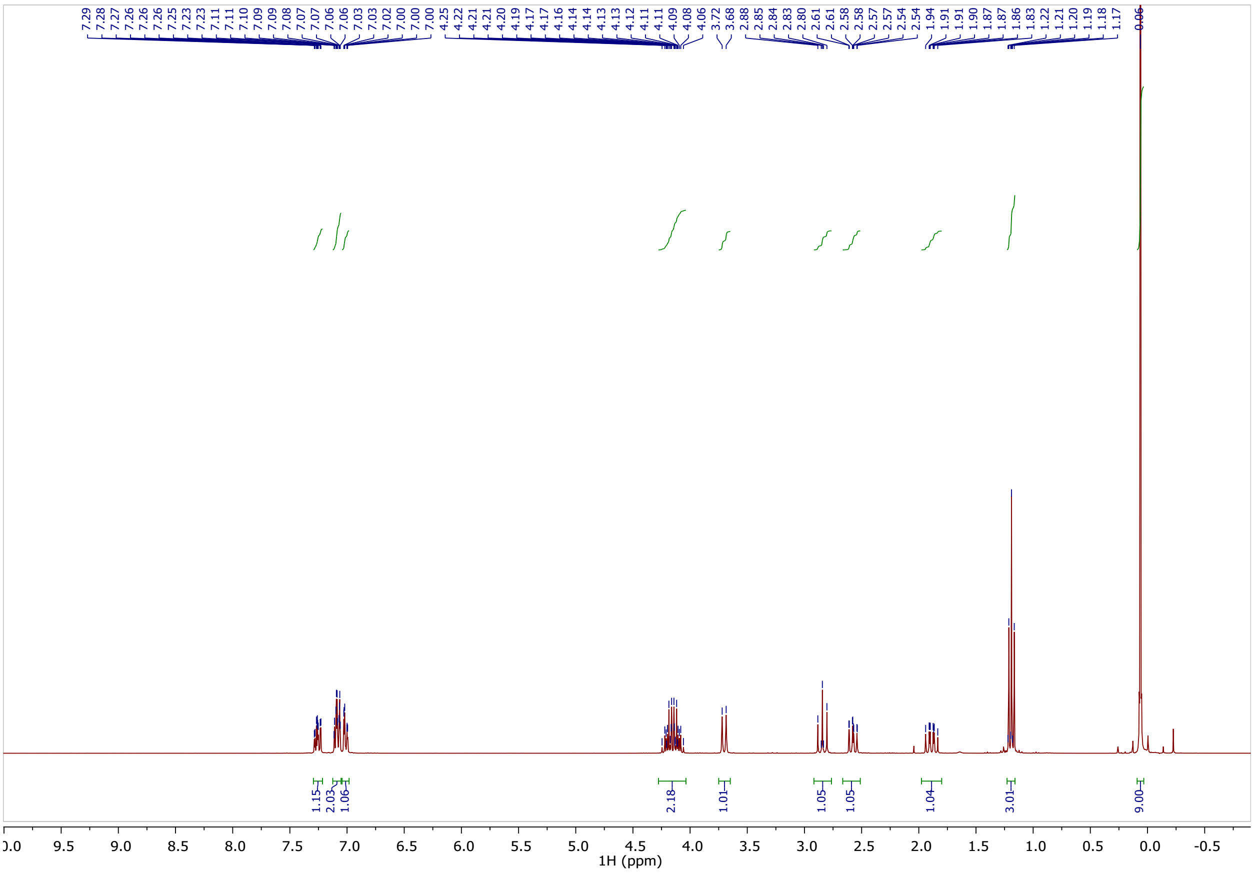
^{1}H NMR (300 MHz, CDCl$_3$) of **2u**



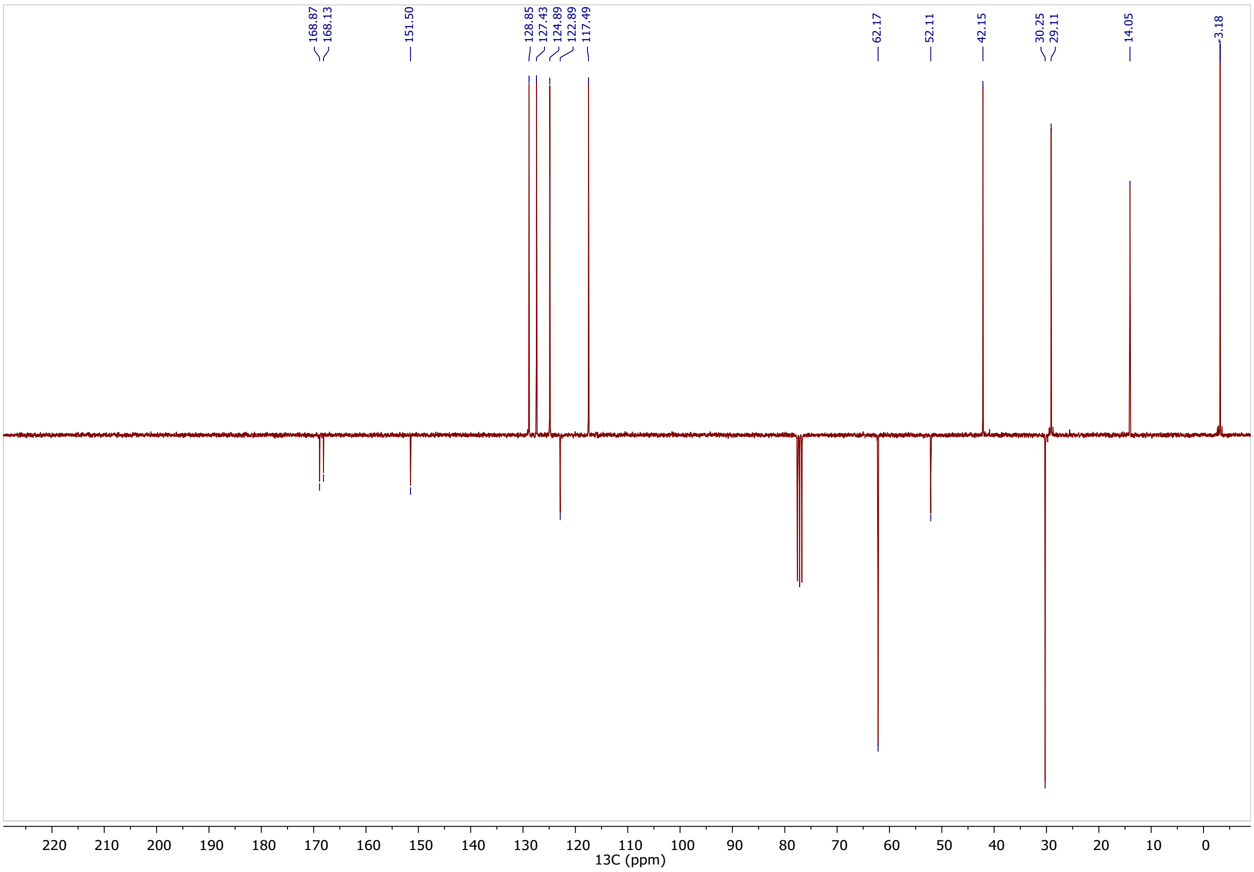
^{13}C NMR (101 MHz, CDCl$_3$) of **2u**



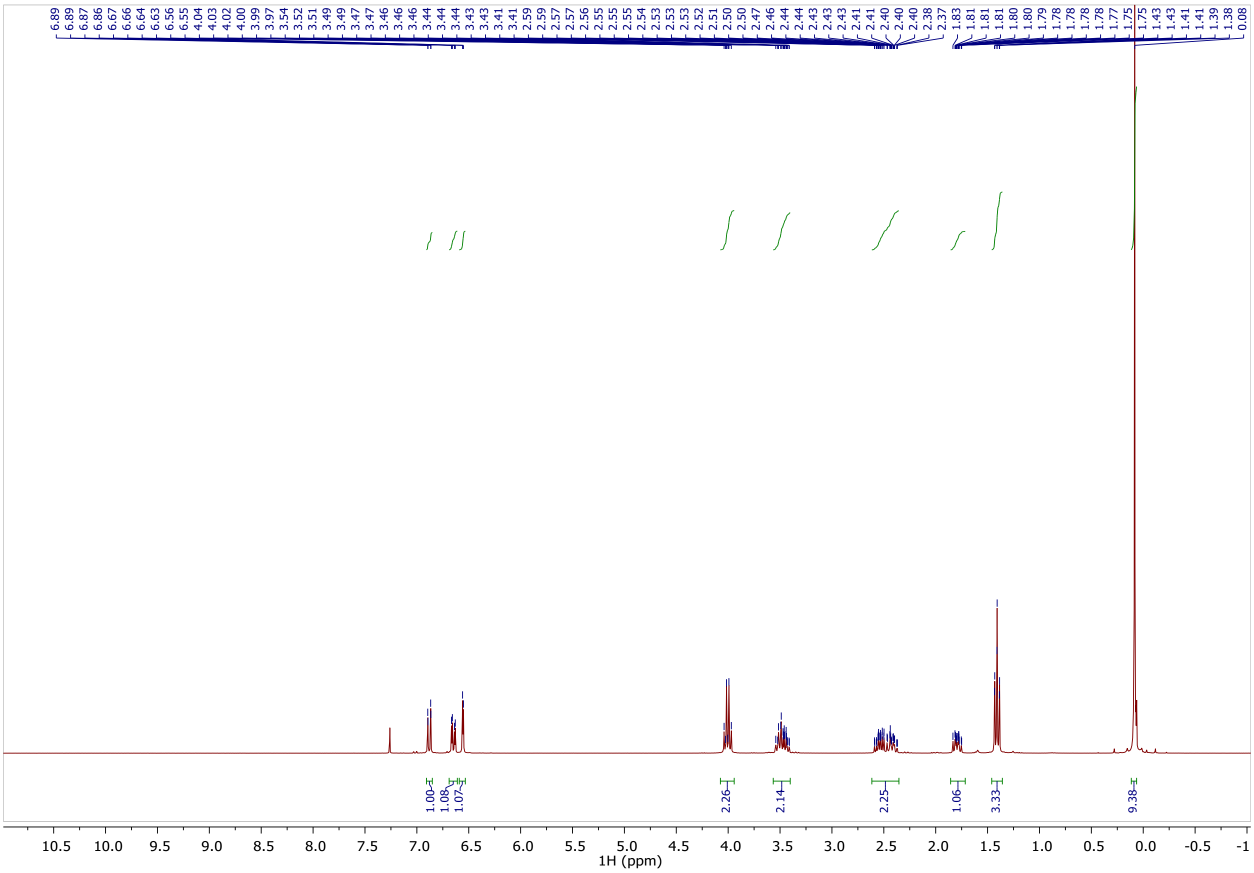
^{1}H NMR (300 MHz, CDCl$_3$) of **2v**



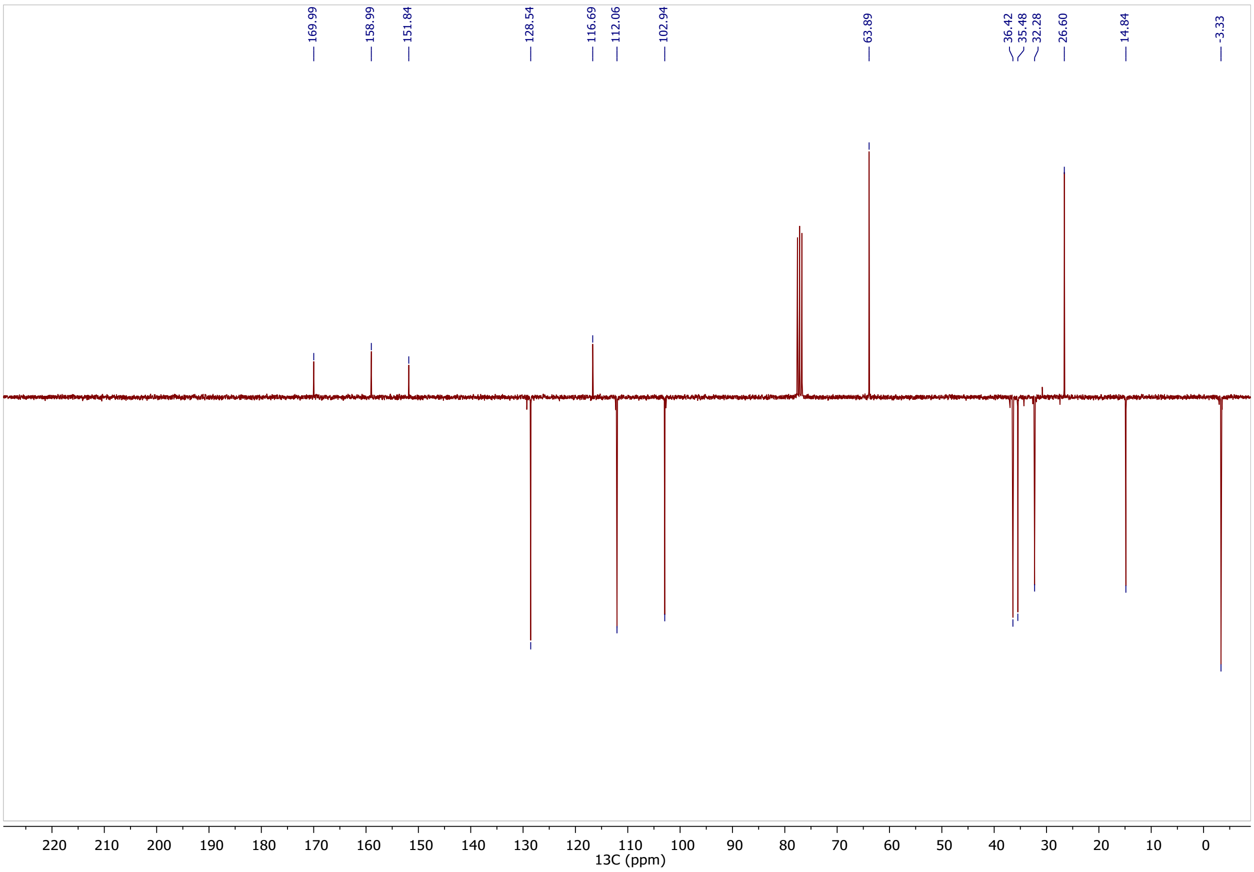
^{13}C NMR (101 MHz, CDCl$_3$) of **2v**



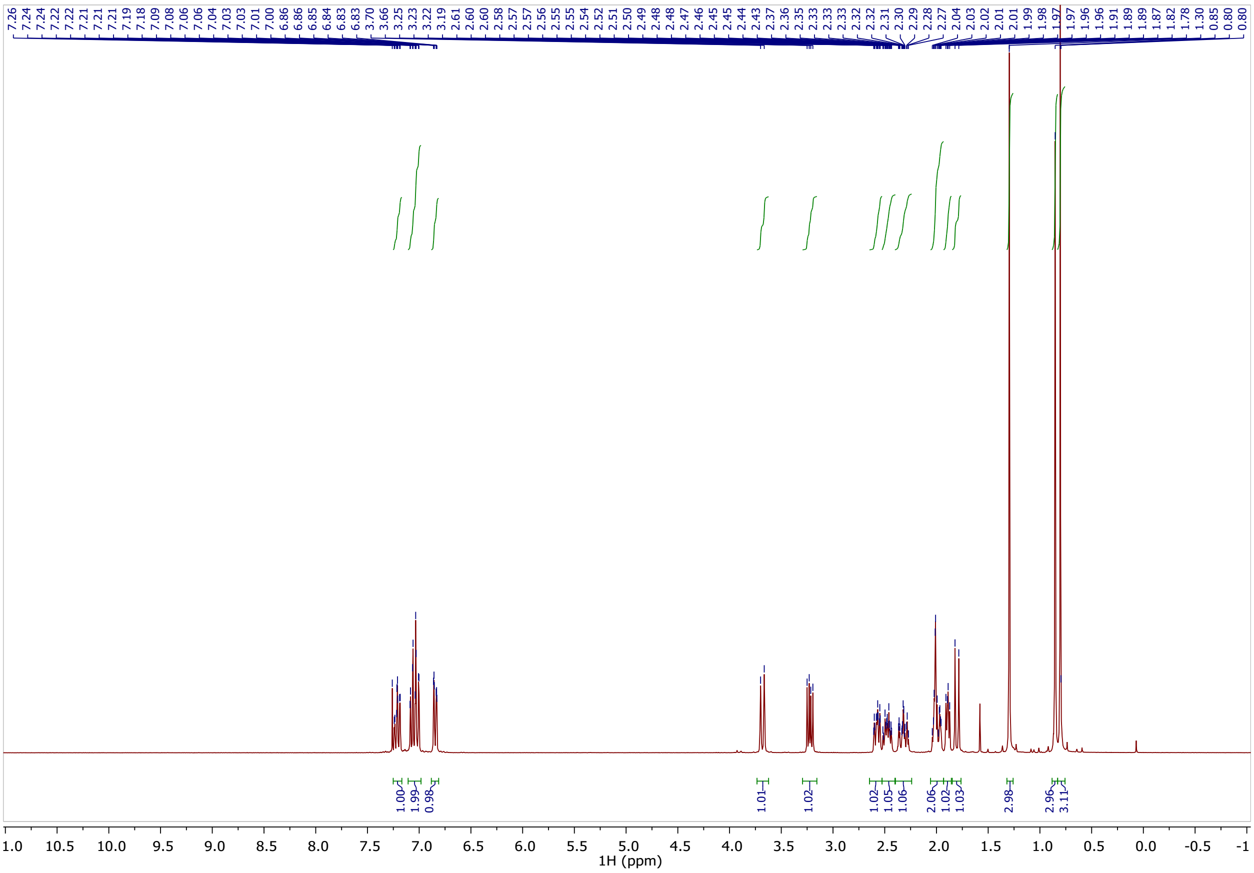
^{1}H NMR (300 MHz, $CDCl_3$) of **2w**



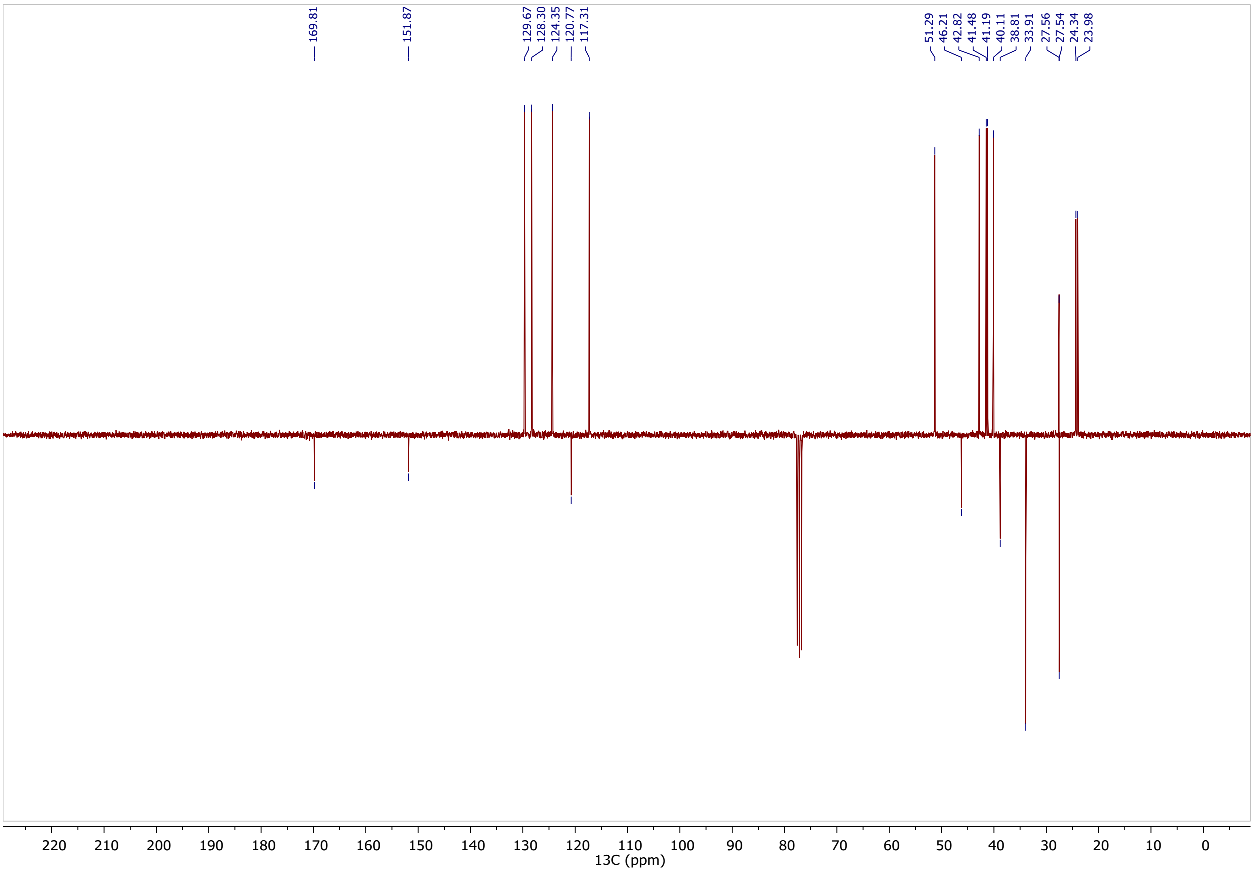
^{13}C NMR (101 MHz, $CDCl_3$) of **2w**



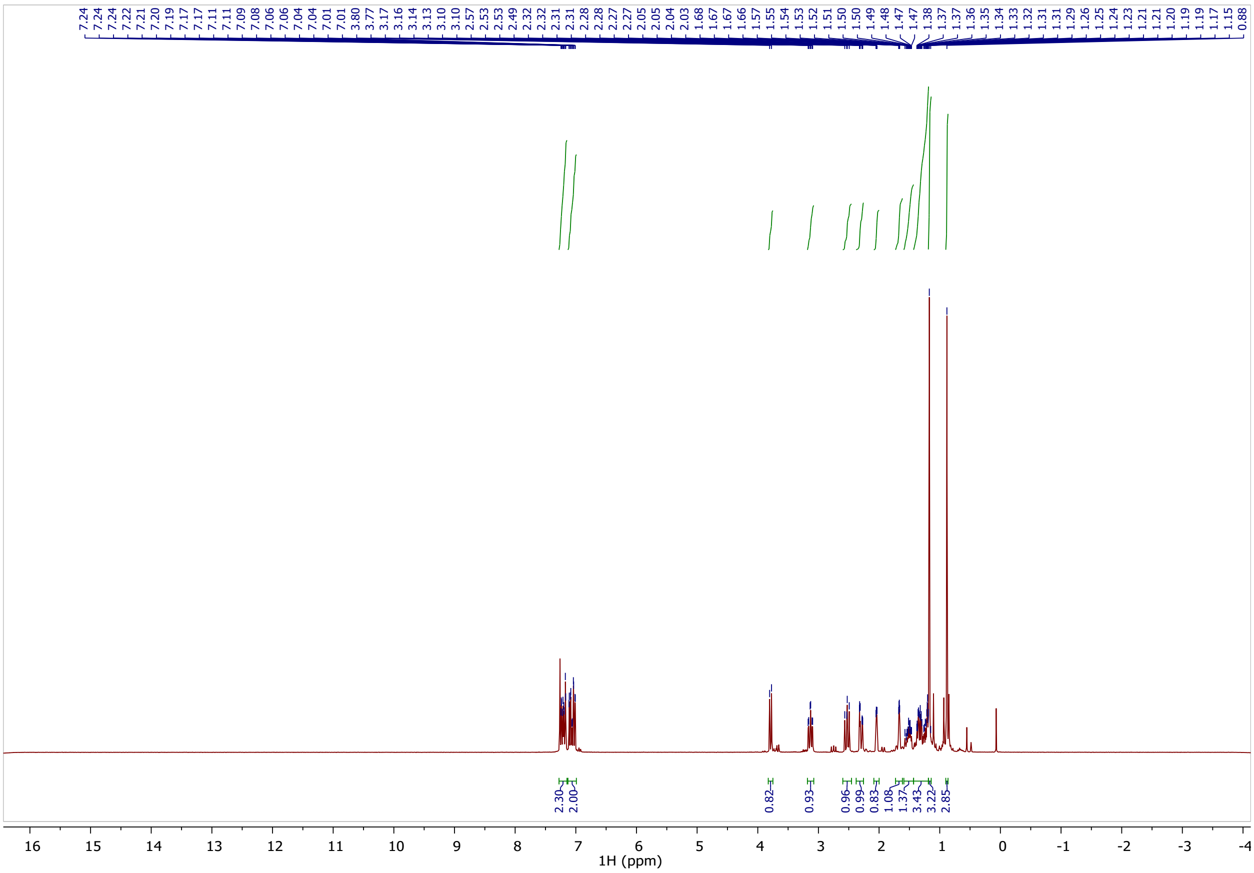
^{1}H NMR (300 MHz, CDCl$_3$) of **2x**



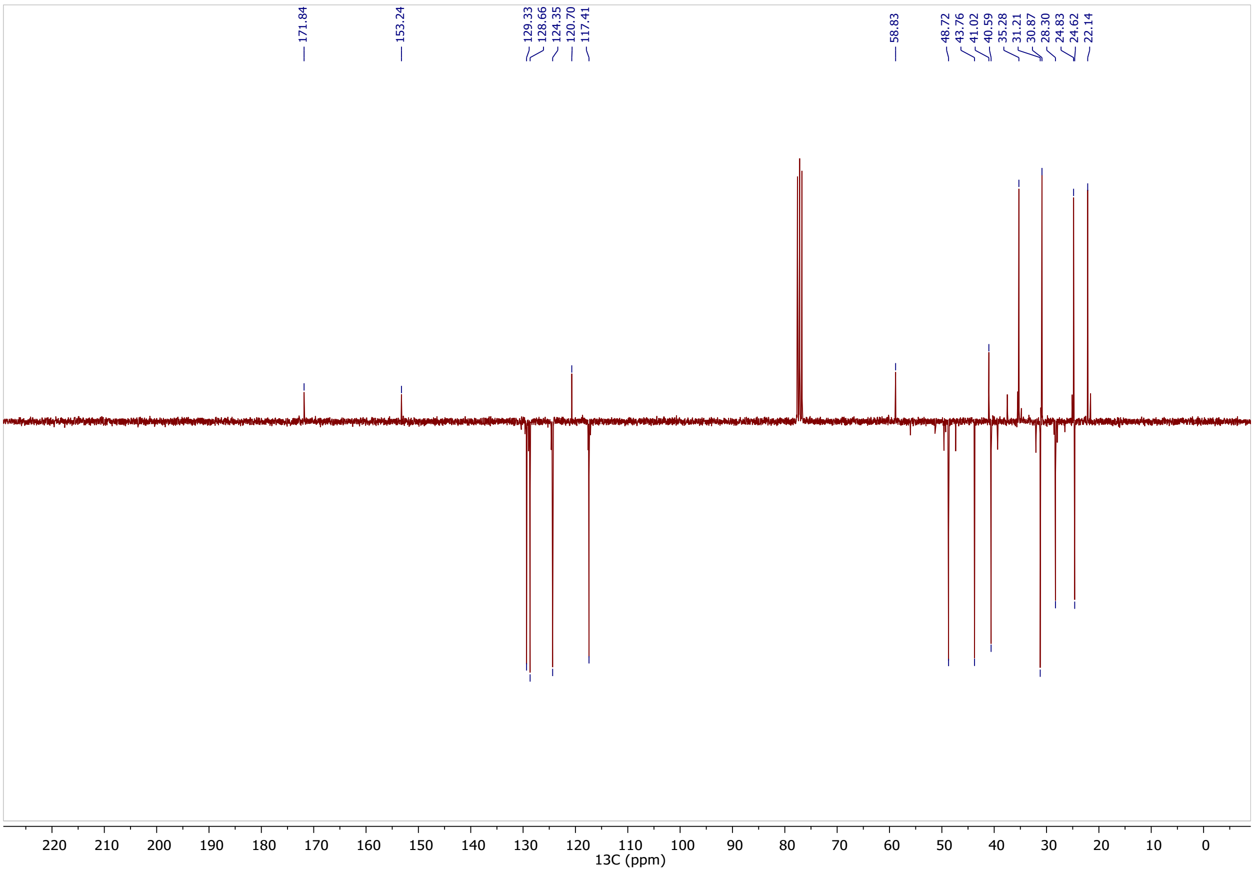
^{13}C NMR (101 MHz, CDCl$_3$) of **2x**



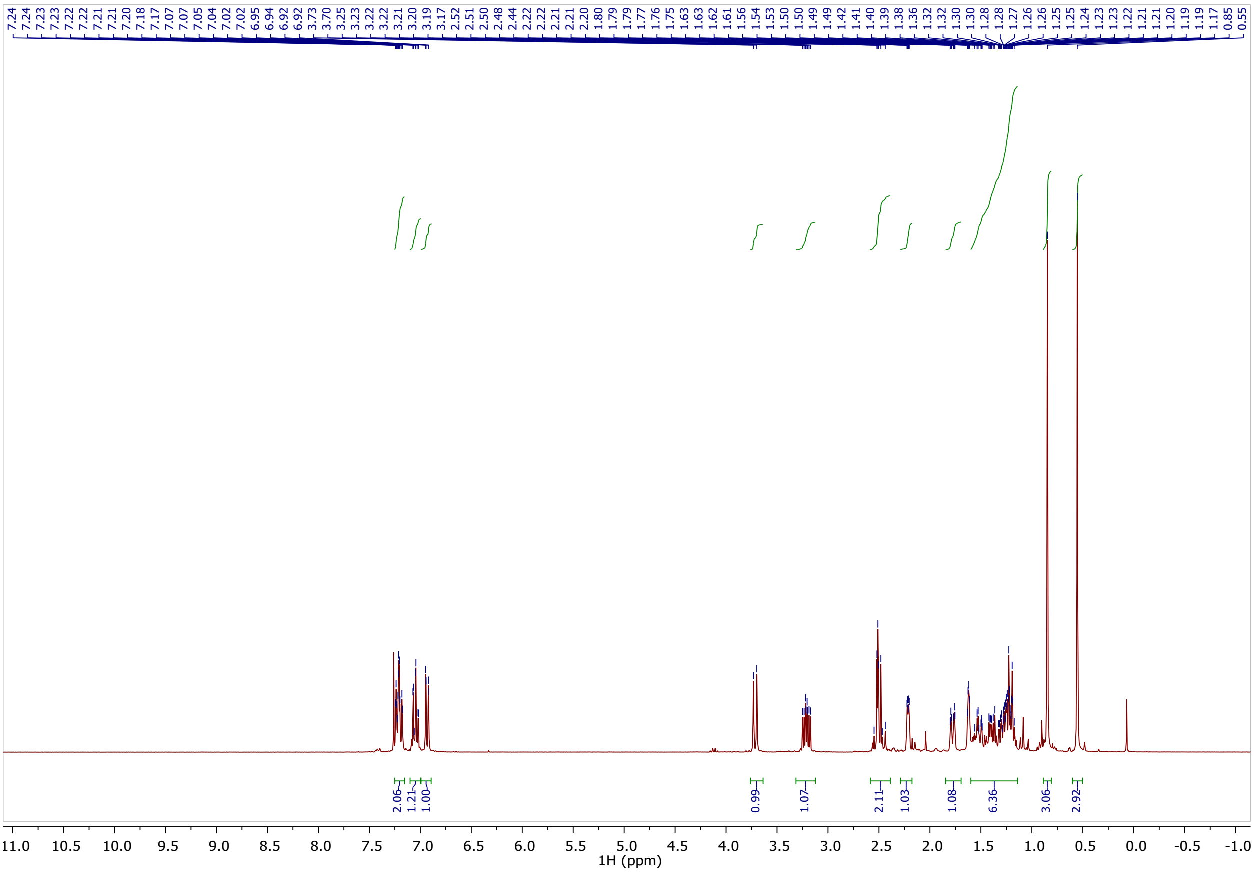
^{1}H NMR (300 MHz, $CDCl_3$) of **2y**



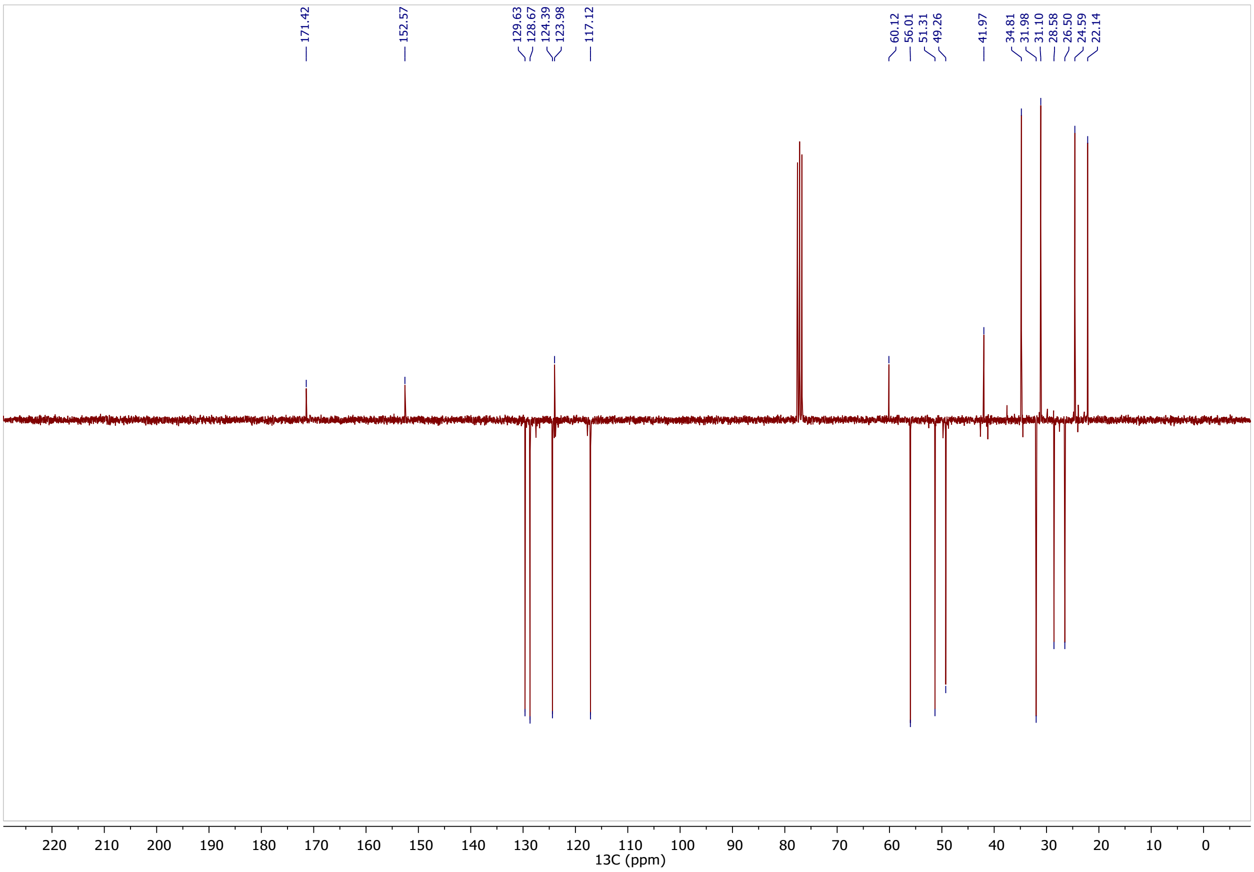
^{13}C NMR (101 MHz, $CDCl_3$) of **2y**



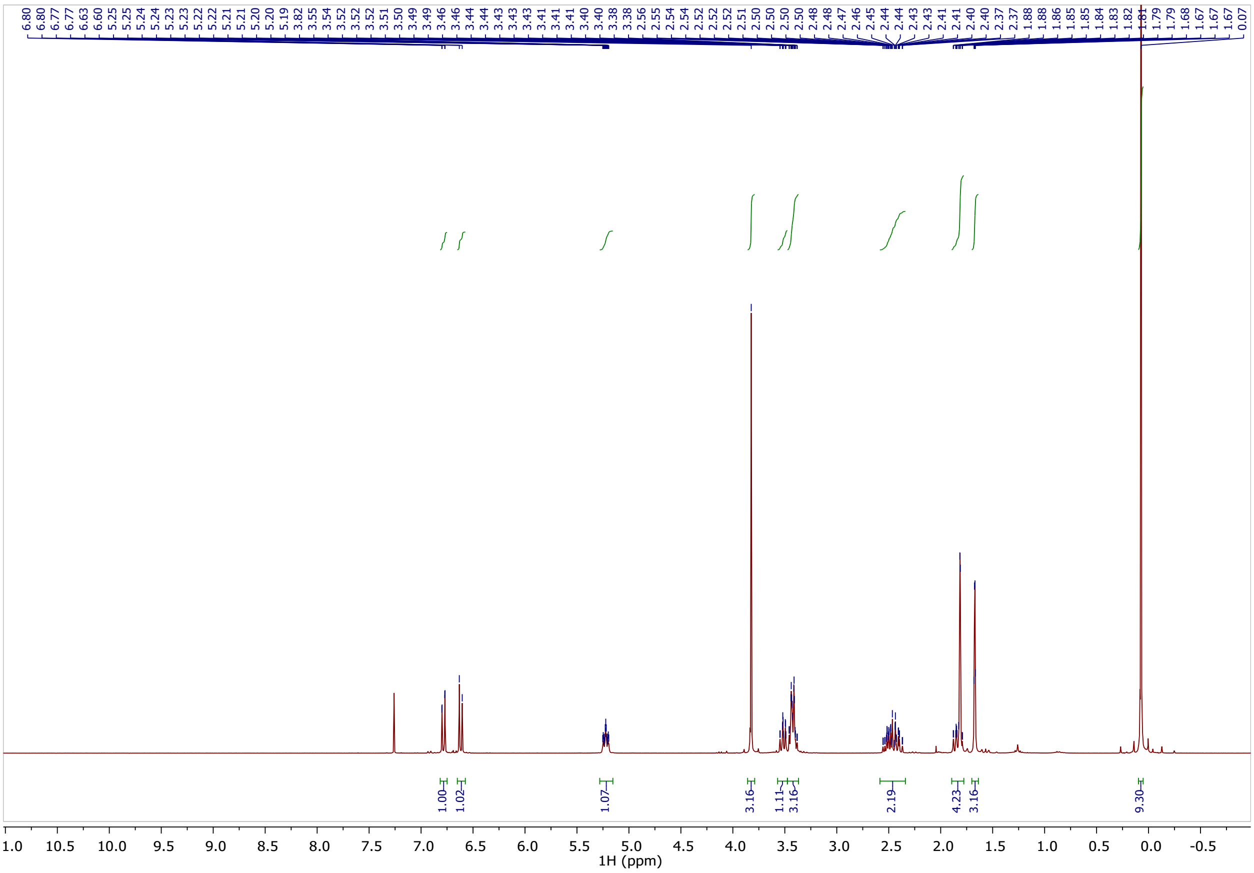
^{1}H NMR (300 MHz, CDCl$_3$) of **2y'**



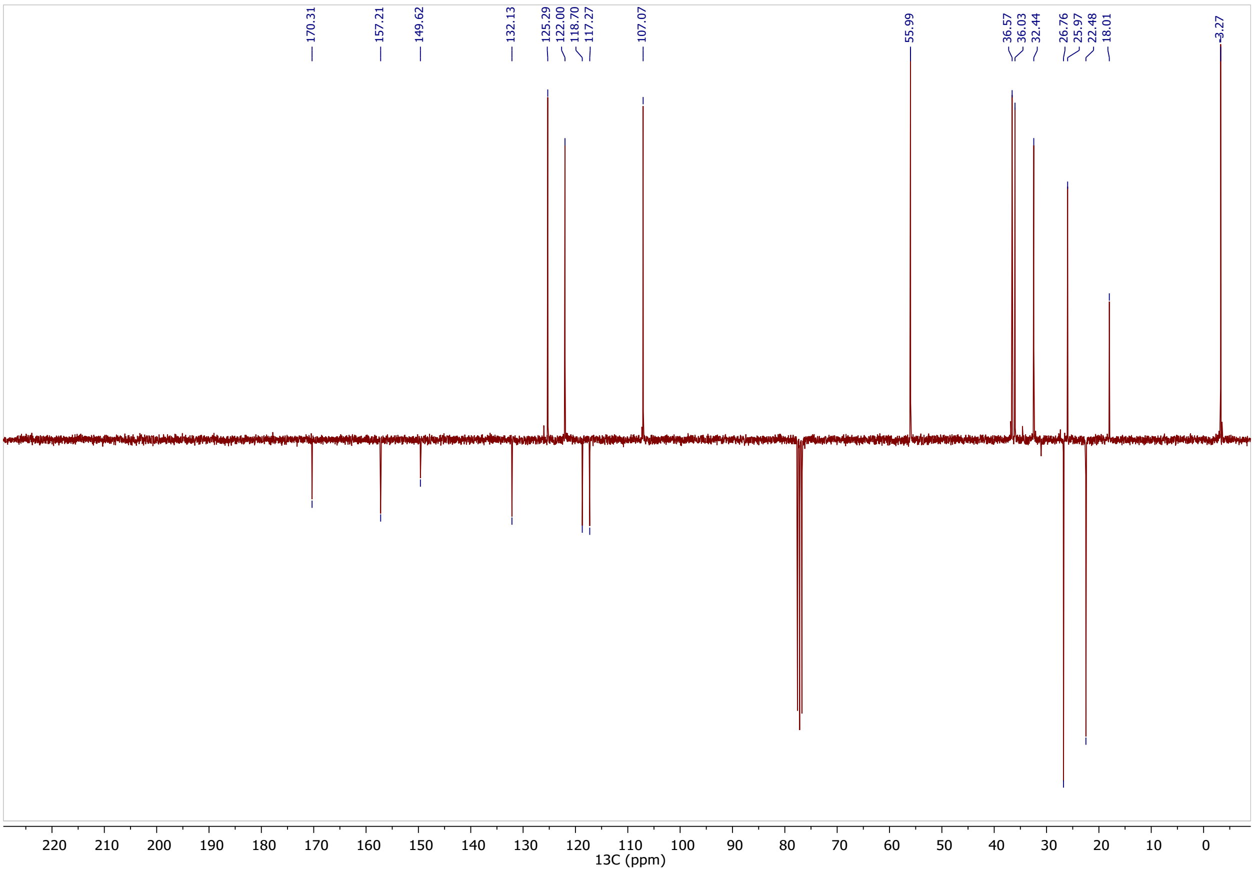
^{13}C NMR (101 MHz, CDCl$_3$) of **2y'**



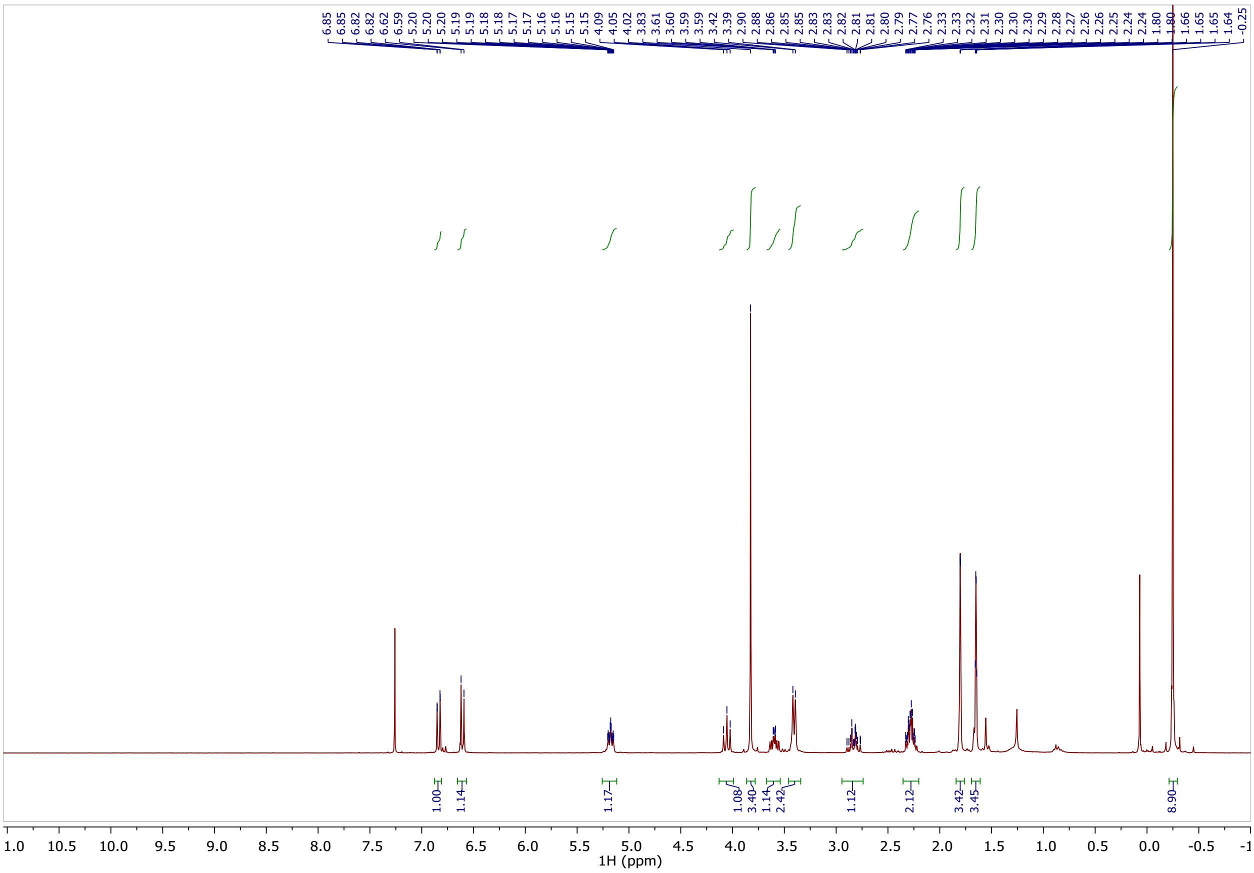
^{1}H NMR (300 MHz, CDCl$_3$) of **2z**



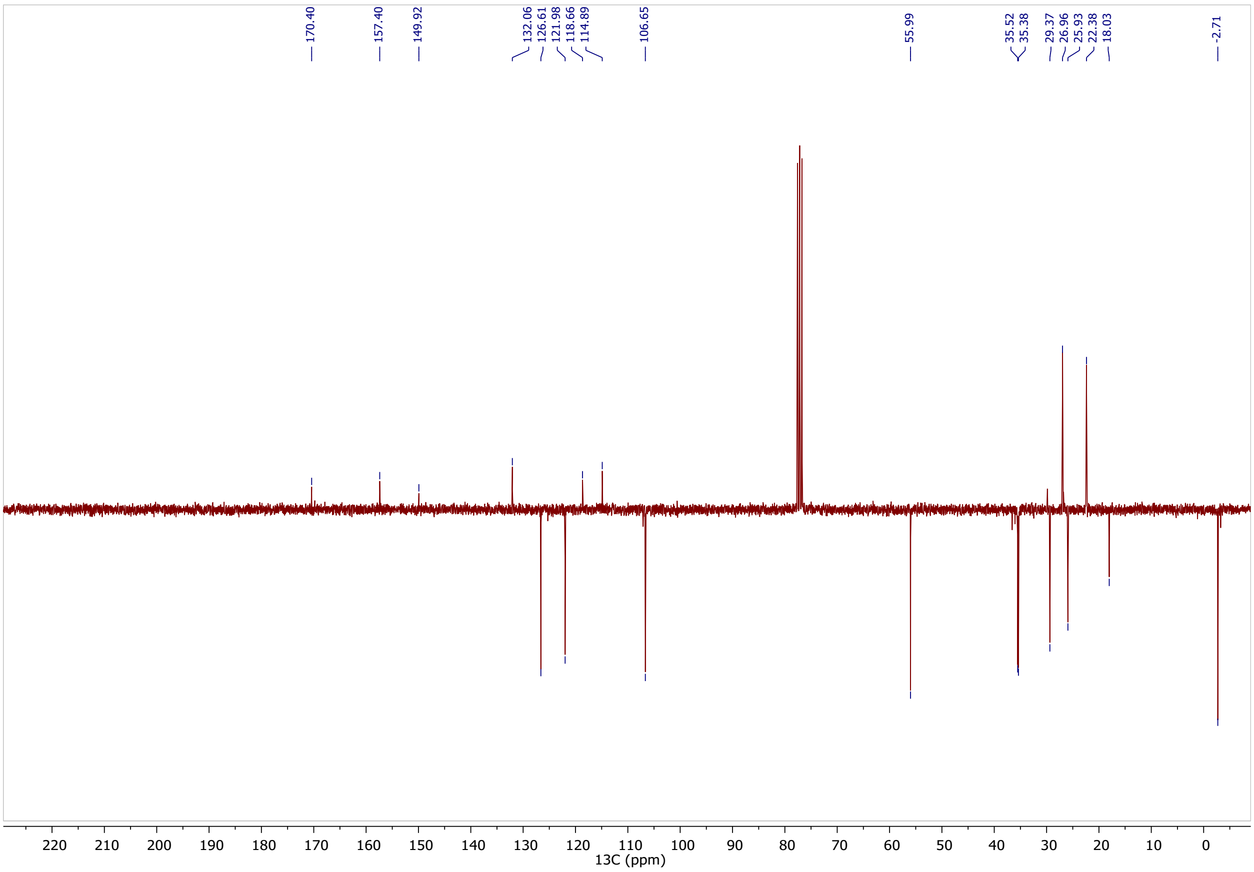
^{13}C NMR (101 MHz, CDCl$_3$) of **2z**



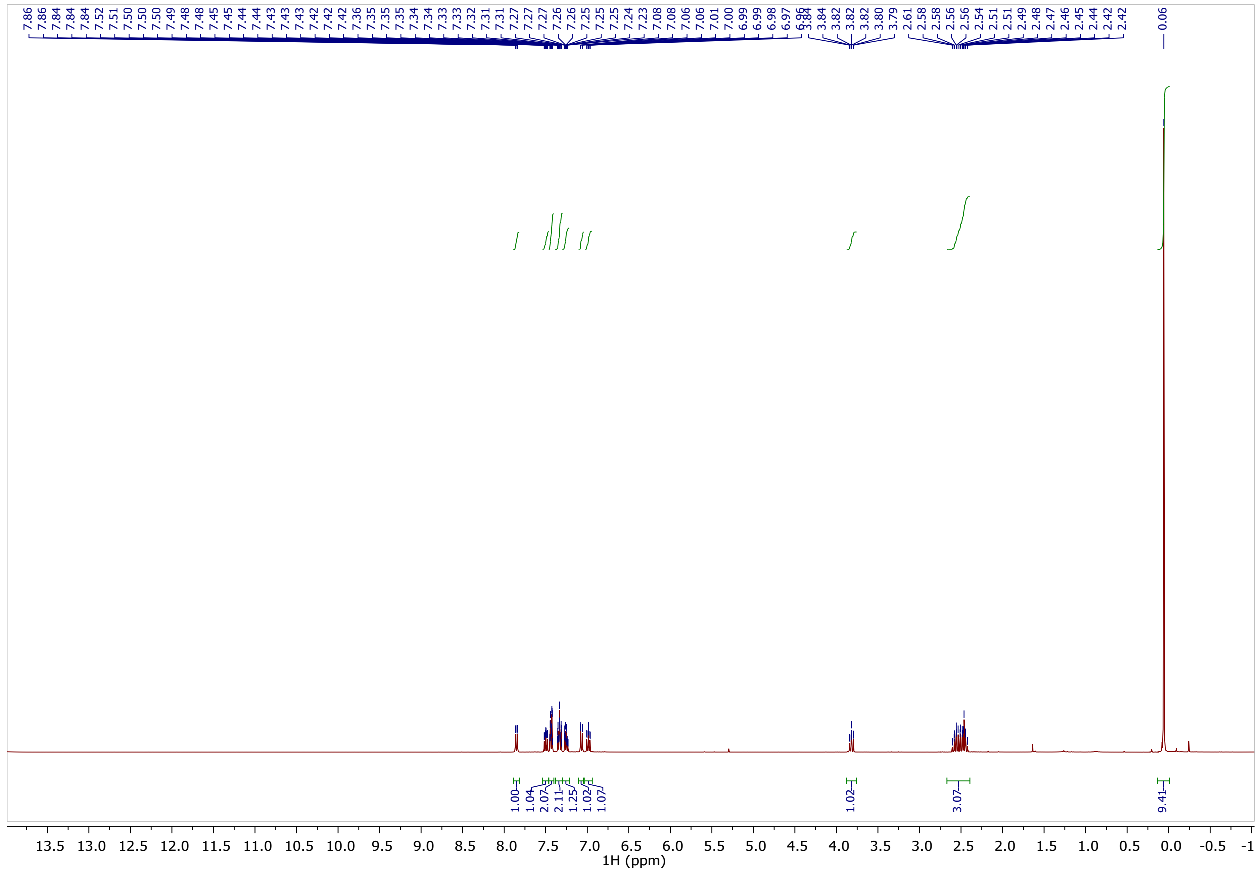
^{1}H NMR (300 MHz, CDCl$_3$) of **2z'**



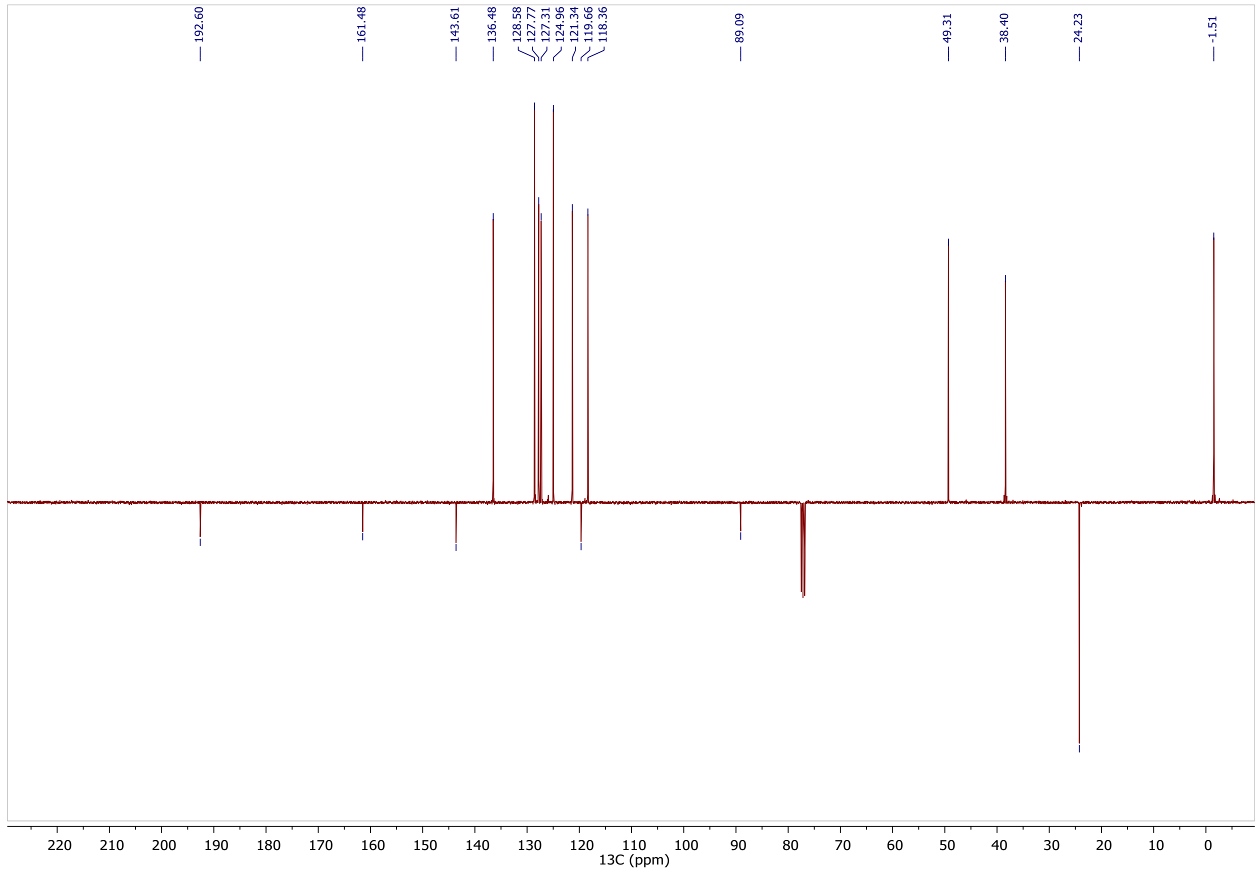
^{13}C NMR (101 MHz, CDCl$_3$) of **2z'**



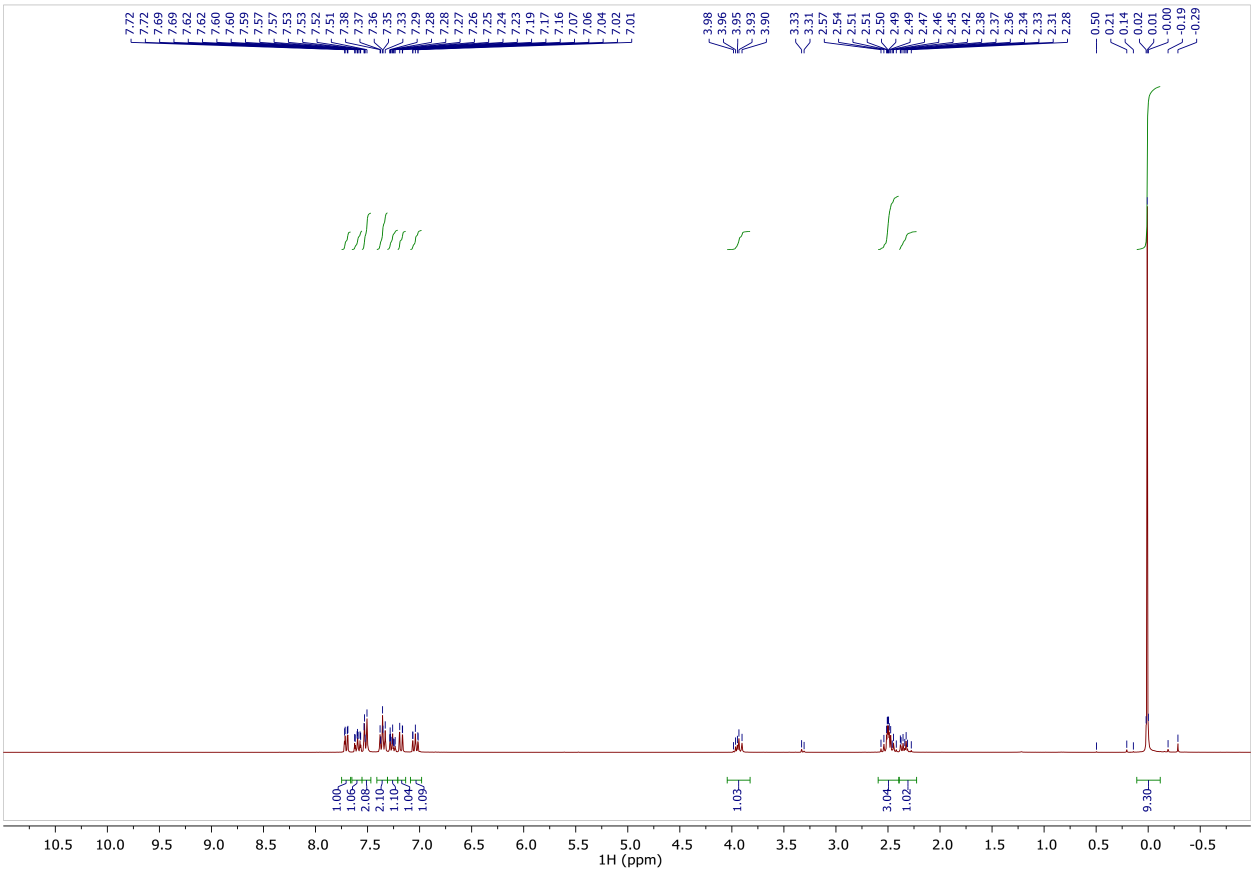
^{1}H NMR (300 MHz, CDCl$_3$) of **2aa**



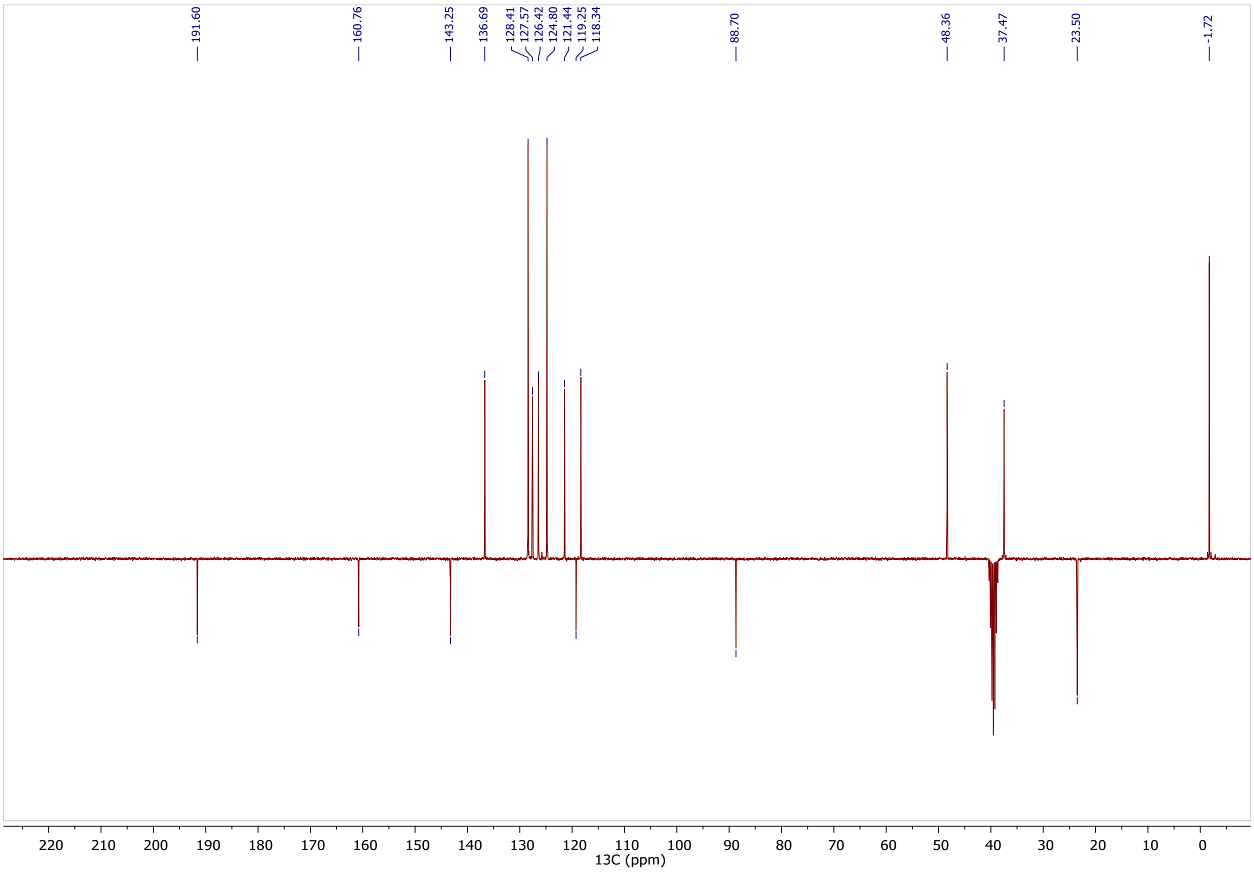
^{13}C NMR (101 MHz, CDCl$_3$) of **2aa**



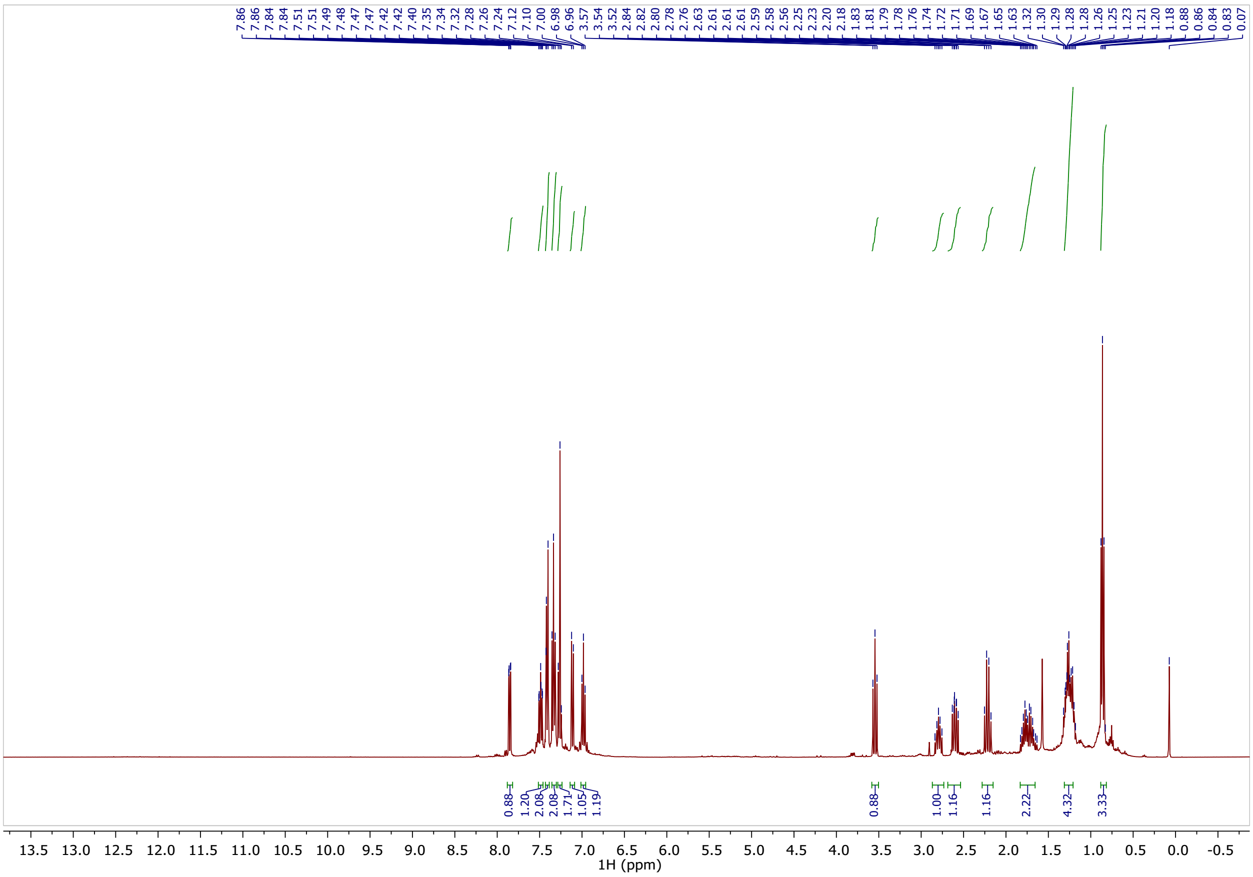
^{1}H NMR (300 MHz, DMSO-d_6) of **2aa**



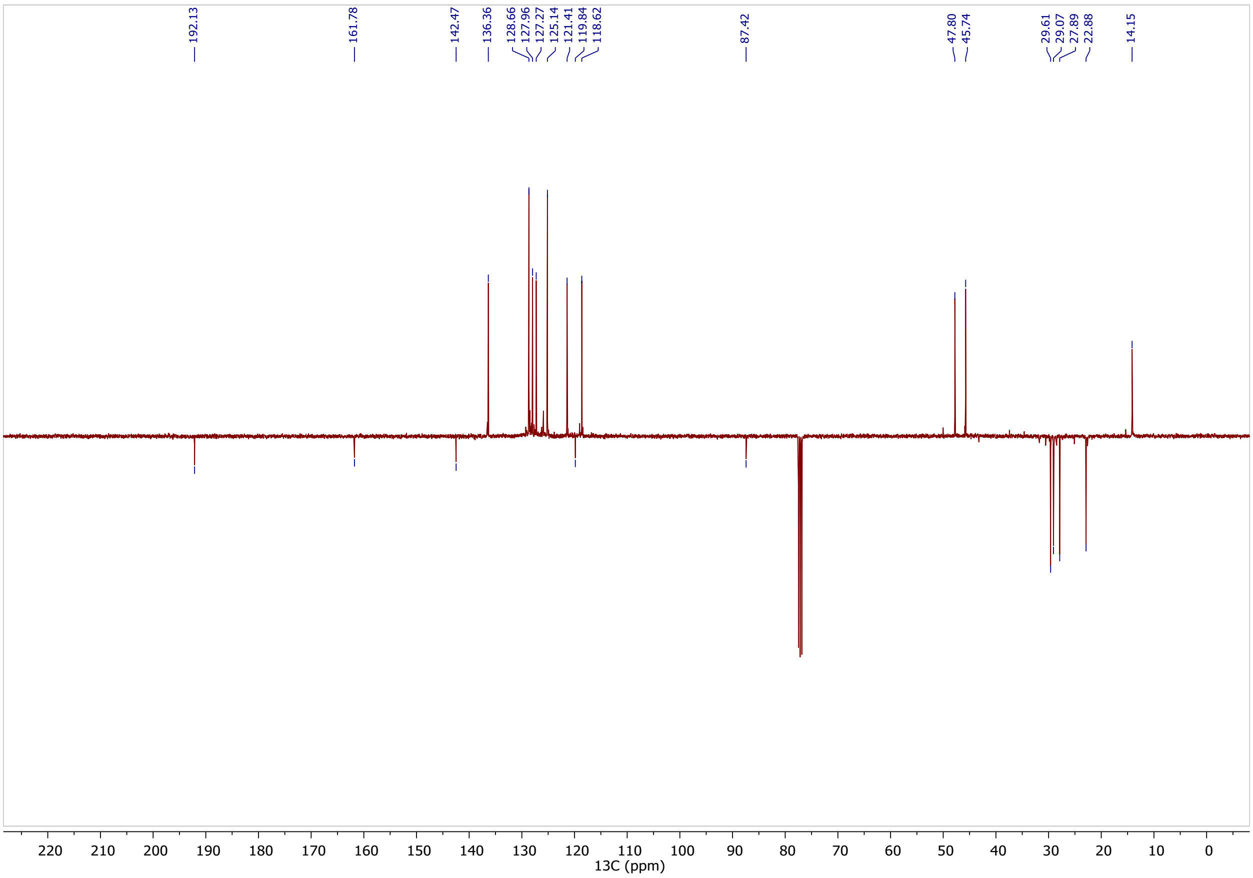
^{13}C NMR (101 MHz, DMSO-d_6) of **2aa**



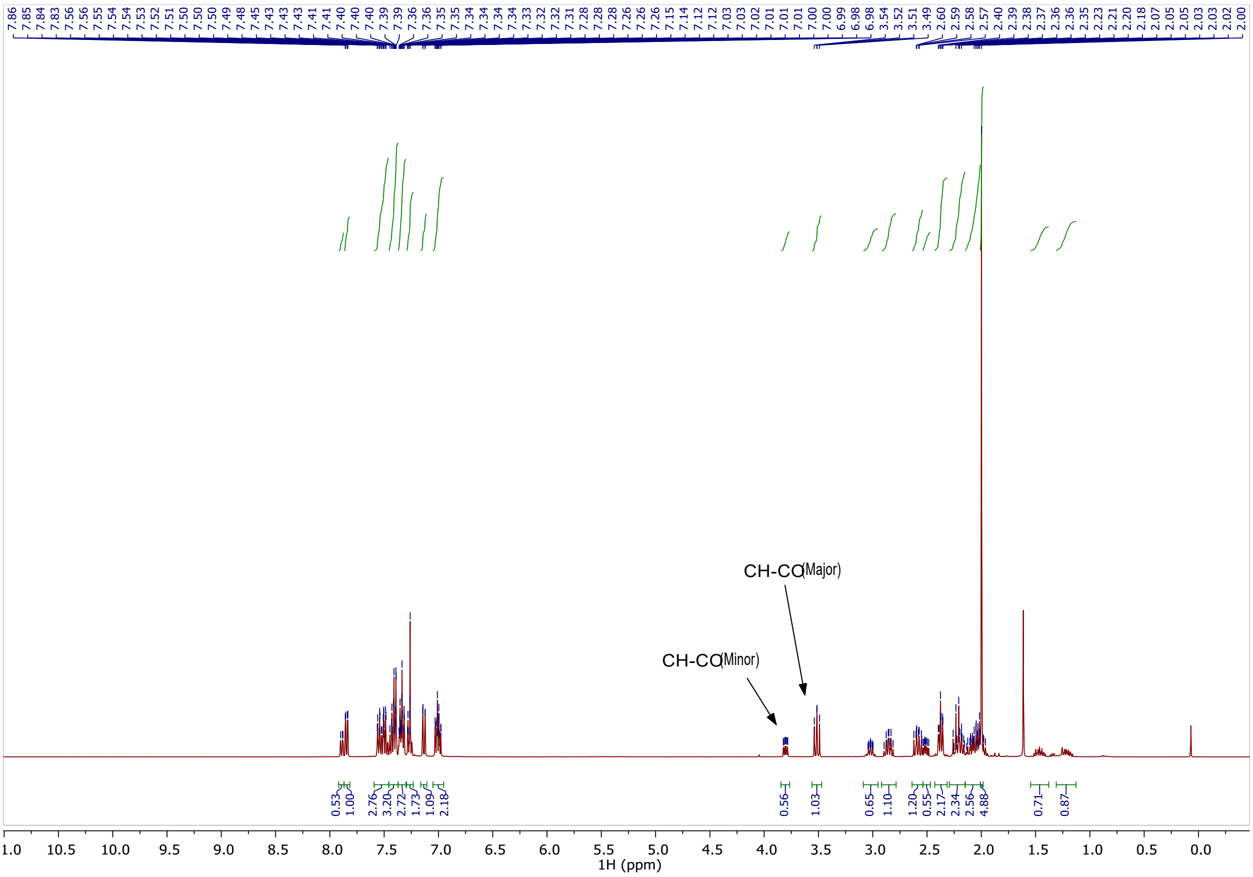
^{1}H NMR (300 MHz, CDCl$_3$) of **2ab**



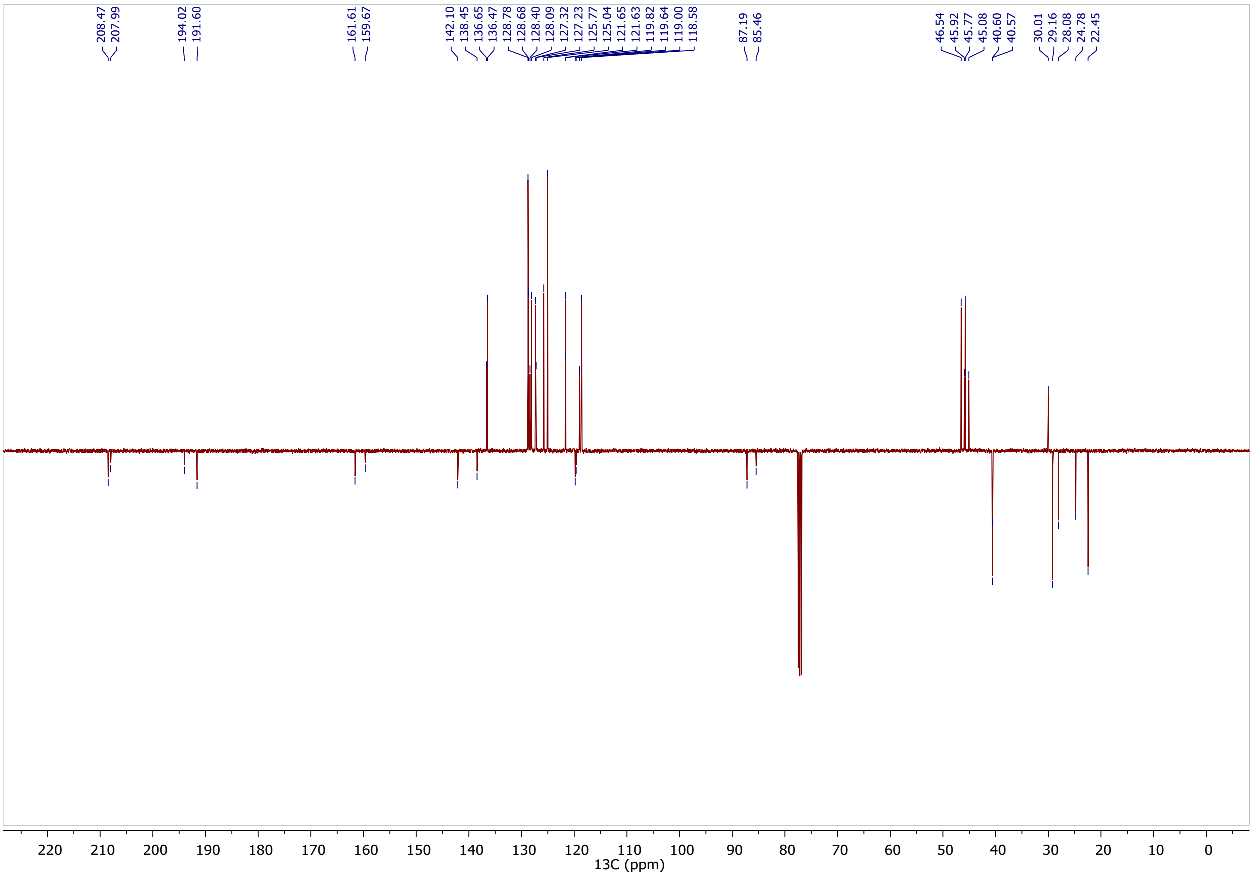
^{13}C NMR (101 MHz, CDCl$_3$) of **2ab**



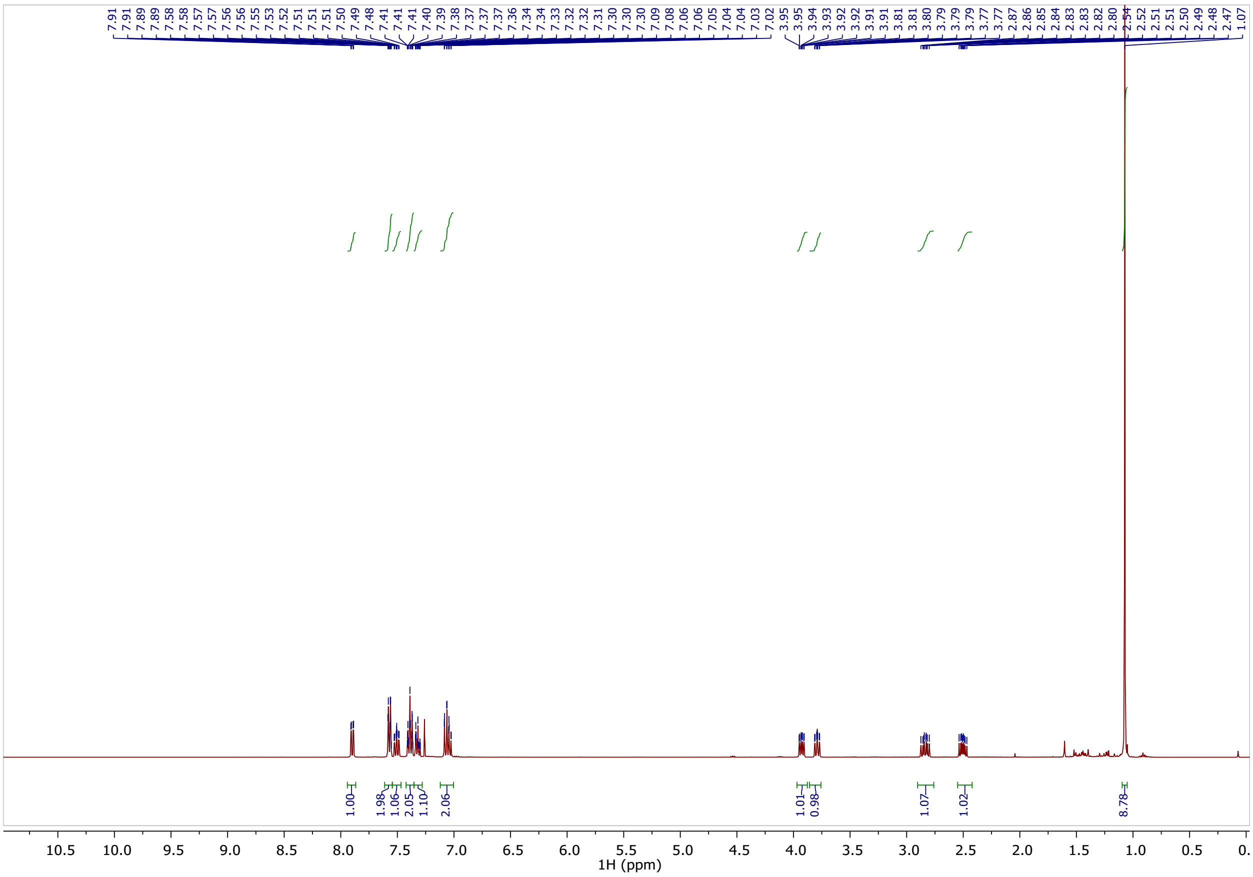
^{1}H NMR (300 MHz, $CDCl_3$) of **2ac** (*mixture of diastereomers*)



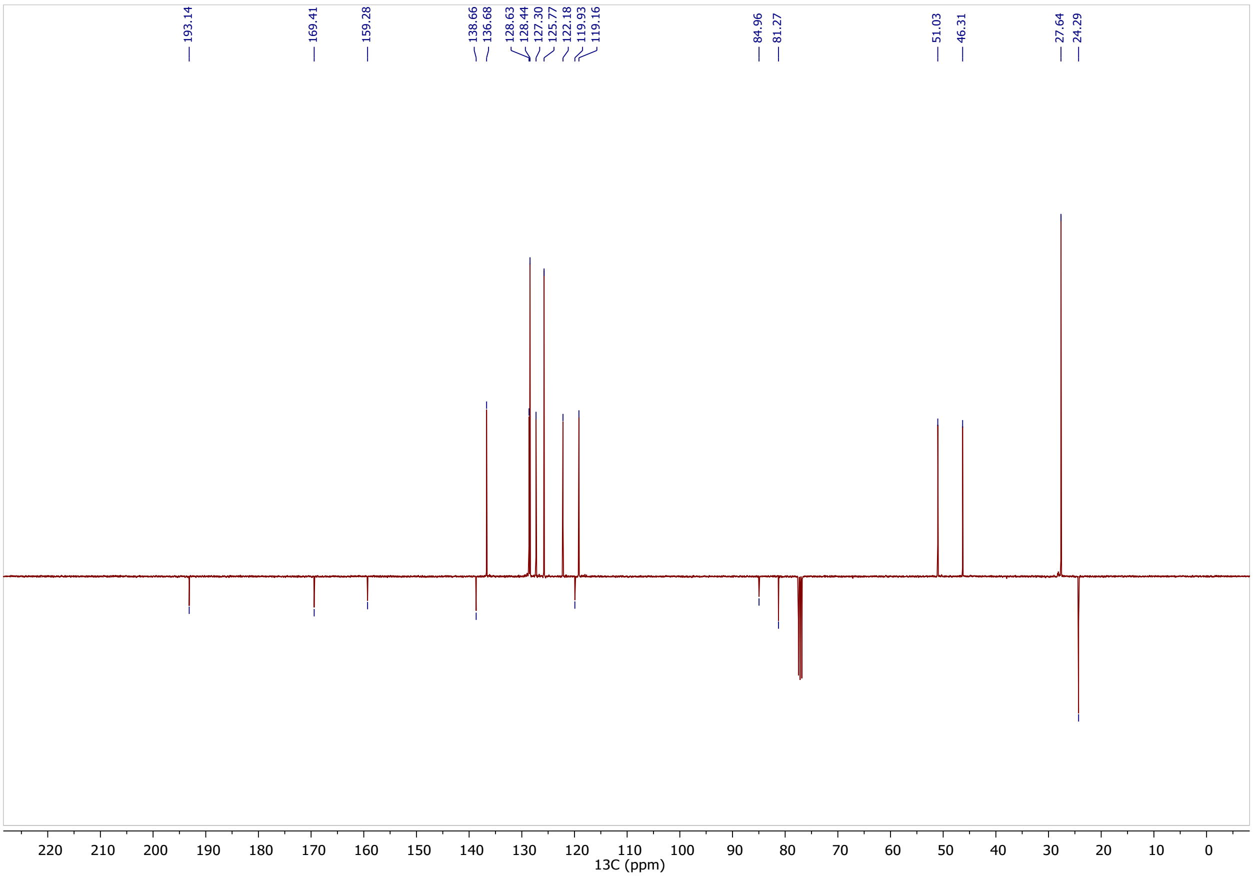
^{13}C NMR (101 MHz, $CDCl_3$) of **2ac** (*mixture of diastereomers*)



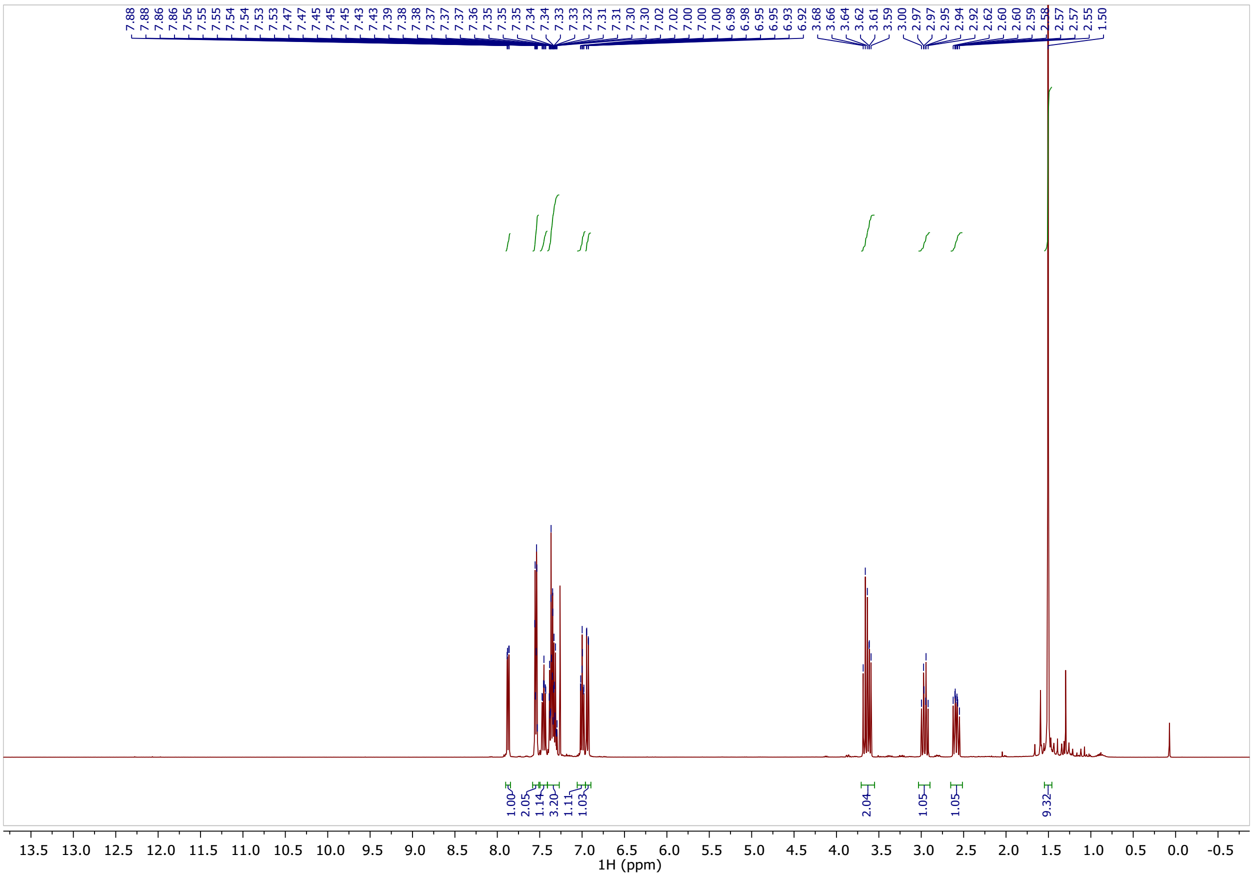
^{1}H NMR (300 MHz, CDCl$_3$) of **2ad**



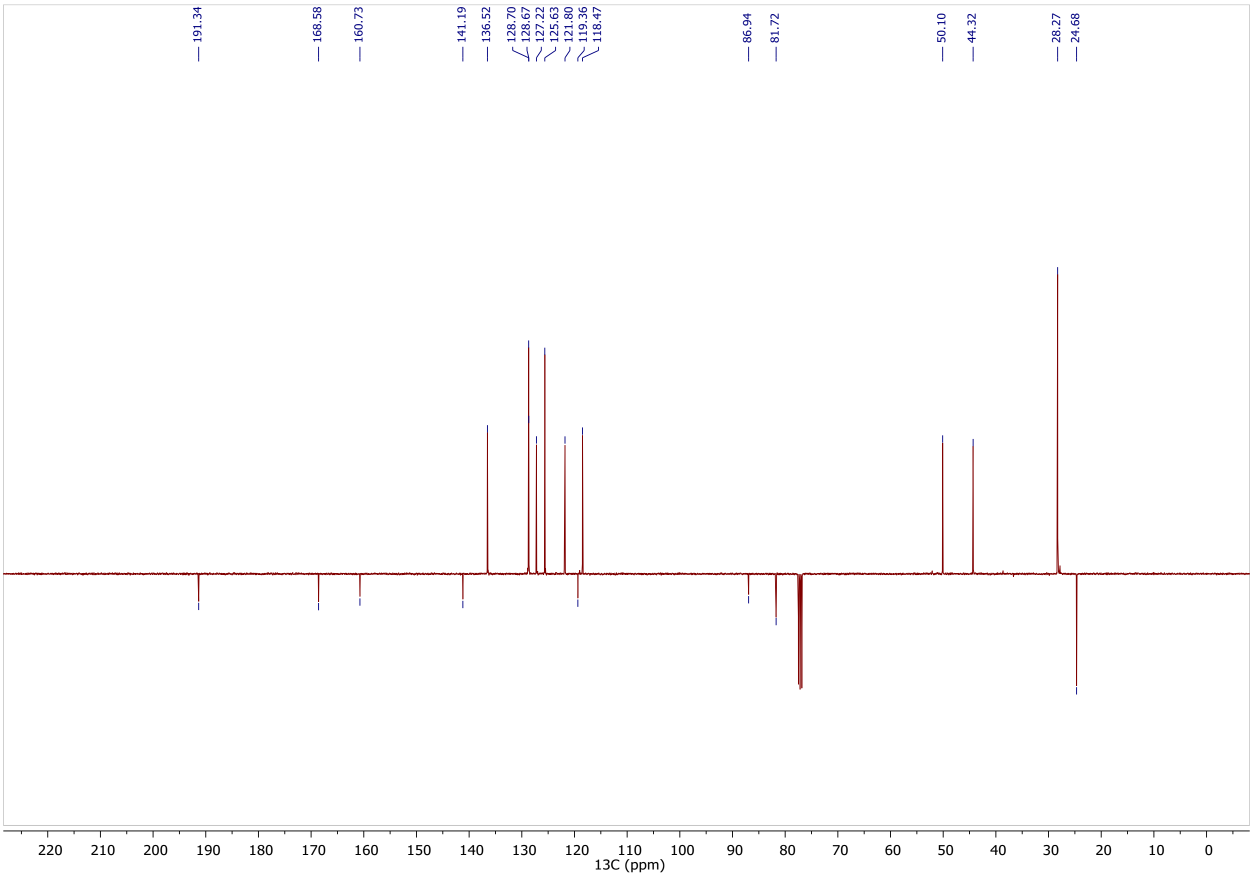
^{13}C NMR (101 MHz, CDCl$_3$) of **2ad**



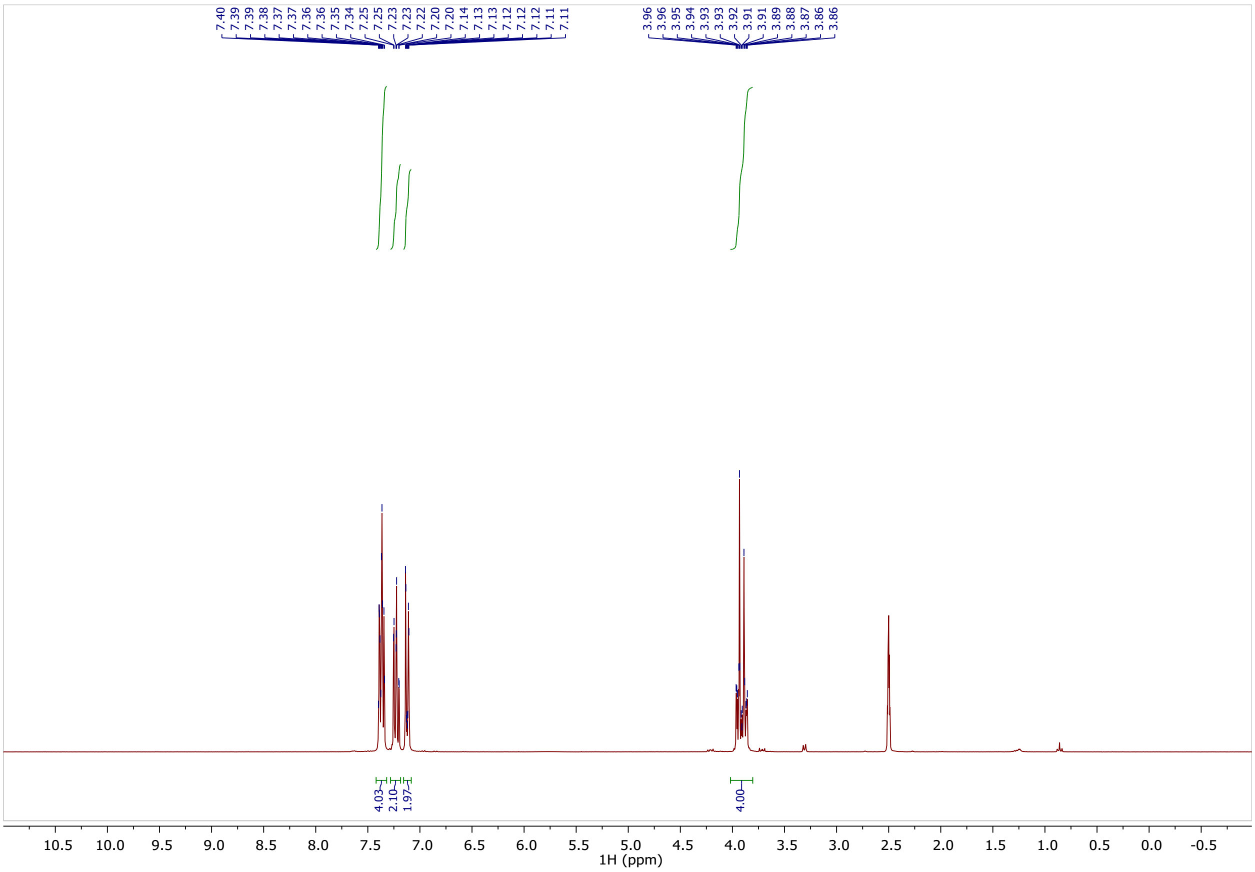
^{1}H NMR (300 MHz, CDCl$_3$) of **2ad’**



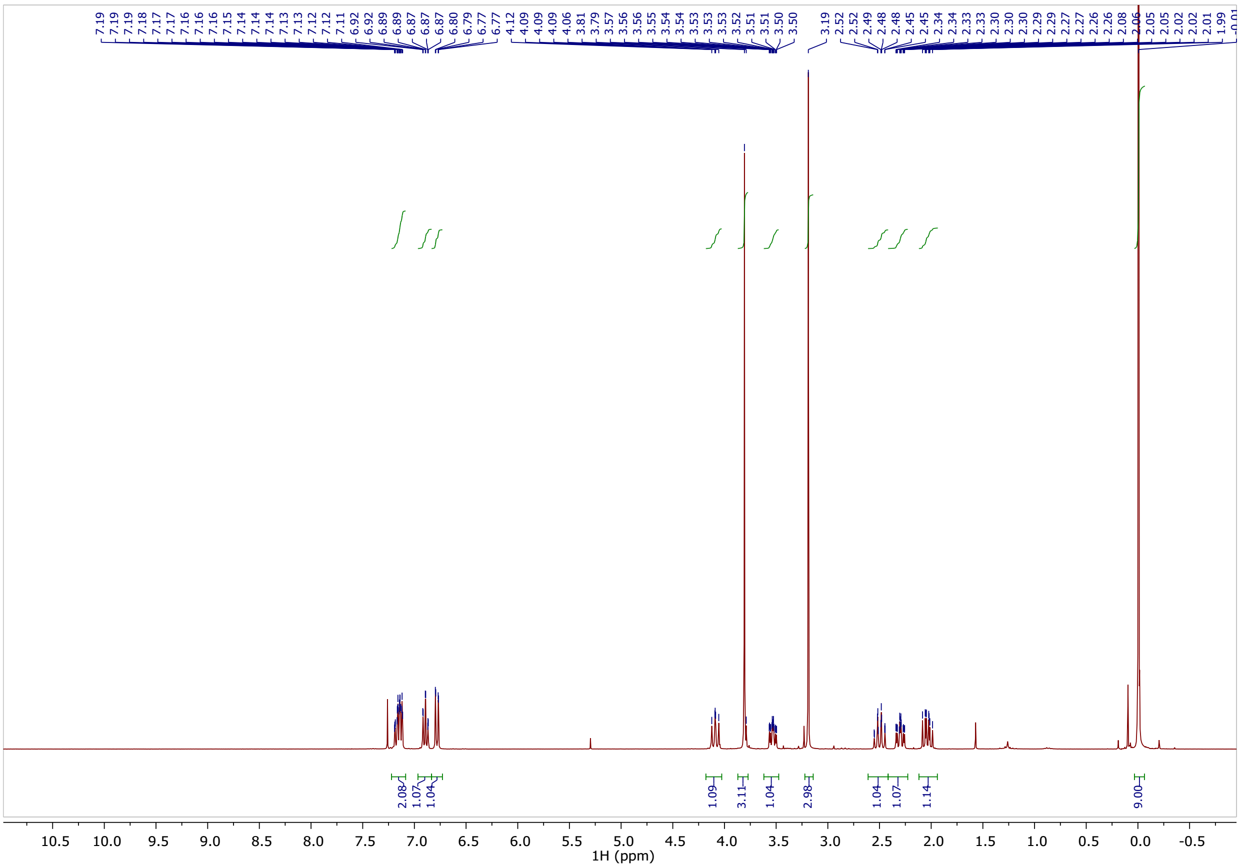
^{13}C NMR (101 MHz, CDCl$_3$) of **2ad’**



^{1}H NMR (300 MHz, DMSO-d_6) of **3**



^{1}H NMR (300 MHz, CDCl$_3$) of **4a**



^{13}C NMR (101 MHz, $CDCl_3$) of **4a**