SUPPORTING INFORMATION

Palladium-Catalyzed Synthesis of Mixed Anhydrides via Carbonylative Telomerization

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S 1. Experimental Procedures

S 1.1. General

Solvents and Chemicals: All Solvents and chemicals were purchased from ABCR, Acros Organics, TCI, Sigma Aldrich, VWR or UMICORE. Dioxane was dried over 3 Å molecular sieves for at least 24 h and distilled before use. All precursors and ligands were stored in Schlenk flasks under an argon atmosphere.

Autoclaves: The catalytic experiments were performed in 25 mL stainless steel autoclaves (Figure S1). The autoclaves were equipped with a quick-fit adapter for a simple and safe connection to the pressure station.

Figure S1: 25 mL autoclave for high-pressure catalytic experiments

Carbonylative telomerization (DoE): First, the acid (nucleophile) was weighed into the 25 mL stainless steel vessel of the autoclave containing a stirring bar. The reactor was closed and then evacuated and purged with argon. $Pd(OAc)_2$ (6.74 mg, 0.03 mmol, 1 mol%) and PCy_2Ph (17.3 mg, 0.06 mmol, 2 mol%) were weighed in a 20 mL headspace vial. The vial was sealed with a crimp cap, then alternately evacuated and purged with argon using a needle connected to the Schlenk-line. 3 mL of dioxane and the internal standard *n*-decane (75 mg, 0.527 mmol) were added *via* syringe through the septum of the crimp cap. The mixture was placed in an ultrasonic bath until a homogeneous solution was observed and then transferred to the reactor *via* syringe under argon counter flow. Liquid 1,3-butadiene was added to the reactor from the cylinder *via* a pressure resistant and transparent pipe. The exact amount was determined by differential weighing. The reactor was pressurized with carbon monoxide to the desired temperature and placed in a pre-heated heating block, magnetically stirred for 20 h.

Derivatization: After 20 h, the reactor was cooled using a water/ice bath, carefully depressurized and purged with argon. Piperidine (1032 mg, 12 mmol, 4 eq.) was added to the reaction mixture

via syringe under argon counter flow. The solution was stirred for another 5 h at 50 °C in a heating block. Finally, the autoclave was cooled again and an aliquot was taken for GC-FID analysis.

Carbonylative telomerization (isolated yield amides): The reaction was performed as described above without the addition of the internal standard. After completion of the derivatization step, the reaction mixture was concentrated in reduced pressure and dissolved in 10 mL dichloromethane (DCM). This solution was extracted with 15 mL of aqueous sulfuric acid solution (5 wt%). The aqueous phase was extracted two more times with 10 mL DCM. Afterwards, the organic phases were combined and extracted with a 0.1M NaOH (3x 20 mL) solution. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was adsorbed to celite and further purified by column chromatography using a 40 g silica gel cartridge (ethyl acetate: cyclohexane, 1% to 10% in 2 CV, 10% until eluted).

Carbonylative telomerization (isolated yield anhydrides): The reaction was carried out as described above without the addition of an internal standard and no amine was added for derivatization. The reaction solution was concentrated under reduced pressure. The crude product was then purified by "Dry Column Vacuum Chromatography" using a gradient of 1% to 10% of dry ethyl acetate in dry cyclohexane.[1]

S 1.2. Synthesis of 3,8-Nonadienoic acid 1c

First methyl 3,8-nonadienoate was synthesized as previously reported.[2] Then 30 mL of a 1M NaOH solution were added to a flask equipped with a Teflon-coated stirring bar. To the solution methyl 3,8-nonadienoate (2.00 g, 11.9 mmol) was added. The mixture was heated to 90 °C and stirred for 3 h. During the reaction the turbid reaction mixture turned clear, and no phase separation could be observed. The mixture was neutralized with a 5wt% H_2SO_4 afterwards the aqueous phase was extracted with diethyl ether (3 x 20 mL). Removing the solvent under reduced pressure yielded 3,8-Nonadienoic acid (1.76 g, 96%) as a light-yellow liquid.

S 1.3. Exclusion of alternative pathways

3,8-nonadienoic acid (467 mg, 3 mmol, 1 eq.) was weighed into a 25 mL stainless steel reactor containing a stirring bar. The reactor was closed, then evacuated and purged with argon. The palladium precursor $Pd(OAc)_2$ (6.74 mg, 0.03 mmol, 1 mol%) and PCy_2Ph (17.3 mg, 0.06 mmol, 2 mol%) were weighed into a 20 mL headspace vial and sealed with a crimp cap. The vial was then alternately evacuated and purged with argon. The corresponding amount of dioxane (3 mL) was added to the vial via syringe. The mixture was placed in an ultrasonic bath until a homogeneous solution was obtained and then transferred to the reactor *via* syringe under argon counter flow. Piperidine (1032 mg, 3 mmol, 4 eq.) and 75 mg of the internal standard *n*-decane were also added to the reactor *via* syringe und argon counter flow. The reactor was stirred for 5 h at 50 °C. Afterwards the reaction was stopped by an ice bath and the reaction mixture analyzed *via* GC.

S 1.4. Screening of the derivatization step

The procedure for the carbonylative telomerization was carried out as stated above, except for the ligand being P(*n*-Bu)$_3$. In the derivatization step, different conditions were compared. Triethylamine, tributylamine and piperidine were tested at low to medium temperatures at reaction times of 2 h or 22 h (Table S1). Highest yields were achieved after 22 h using piperidine at 50 °C. However, lowering the reaction time for derivatization to 2 h reduced the amide yield by only 3%. To compensate for the lower yield, a four-fold excess of piperidine was chosen at a reaction time of 5 h.

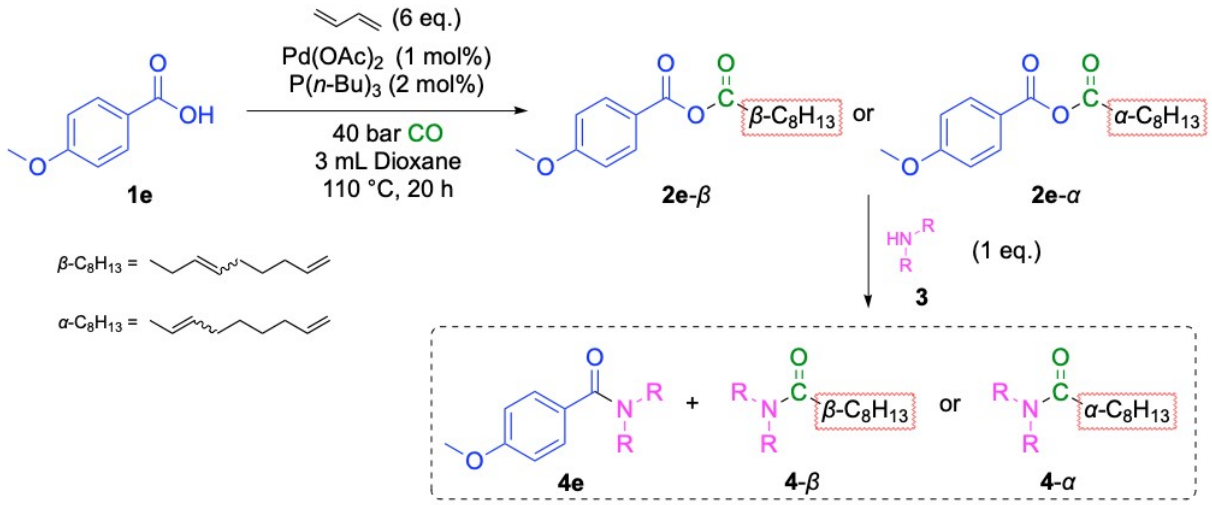


Figure S2: Screening of the derivatization conditions.

Table S1: Parameter screening for derivatization.

Entry	Amine	T [°C]	T [h]	Combined Amide Yield [%]
1	Diethylamine **3c**	50	22	58
2	Diethylamine **3c**	25	22	53
3	Diethylamine **3c**	25	2	51
4	di-*n*-butylamine **3d**	50	22	59
5	di-*n*-butylamine **3d**	25	22	57
6	di-*n*-butylamine **3d**	25	2	57
7[a]	di-*n*-butylamine **3d**	50	22	56
8[a]	di-*n*-butylamine **3d**	25	23	55
9[a]	di-*n*-butylamine **3d**	25	3	55
10	piperidine **3b**	50	22	68
11	piperidine **3b**	25	22	67
12	piperidine **3b**	25	2	65

Conditions: carbonylative telomerization: 3 mmol anisic acid, 18 mmol 1,3-butadiene, 1 mol% Pd(OAc)2, 2 mol% P(*n*-Bu)$_3$, 3 mL dioxane, 40 bar CO, 110 °C, 20 h, 600 rpm, internal standard: 75 mg *n*-decane. Derivatization: 3 mmol amine, 600 rpm. a = 1 eq. pyridine added. Yield related to acid determined *via* GC-FID analysis.

S 1.5. Optimization of Anhydride Formation via DoE

The reaction parameters and results are displayed below (Table S2), and the experiments were carried out as stated above. The yield is an average value resulting from two separate runs.

Table S2: Series of performed experiments for the DoE.

Entry	Temperature [°C]	CO pressure [bar]	1,3-Butadiene equivalents [-]	TOLMAN angle [°]	Yield [%]
1	80	40	9	163.5	71
2	100	30	6.5	163.5	77
3	120	20	4	163.5	50
4	120	20	4	132	41
5	80	30	6.5	147.75	62
6	100	30	6.5	147.75	57
7	80	20	4	132	20
8	80	20	4	163.5	56
9	80	40	9	132	45
10	120	40	4	163.5	45
11	100	30	6.5	147.75	60
12	120	40	9	132	59
13	80	40	4	132	23
14	120	40	9	163.5	61
15	80	20	9	163.5	69
16	100	30	6.5	132	55
17	100	30	4	147.75	43
18	120	40	4	132	41
19	80	40	4	163.5	41
20	100	20	6.5	147.75	59
21	120	20	9	163.5	57
22	80	20	9	132	40
23	120	20	9	132	48
24	100	30	6.5	147.75	57
25	120	30	6.5	147.75	42
26	100	30	9	147.75	62
27	100	40	6.5	147.75	55

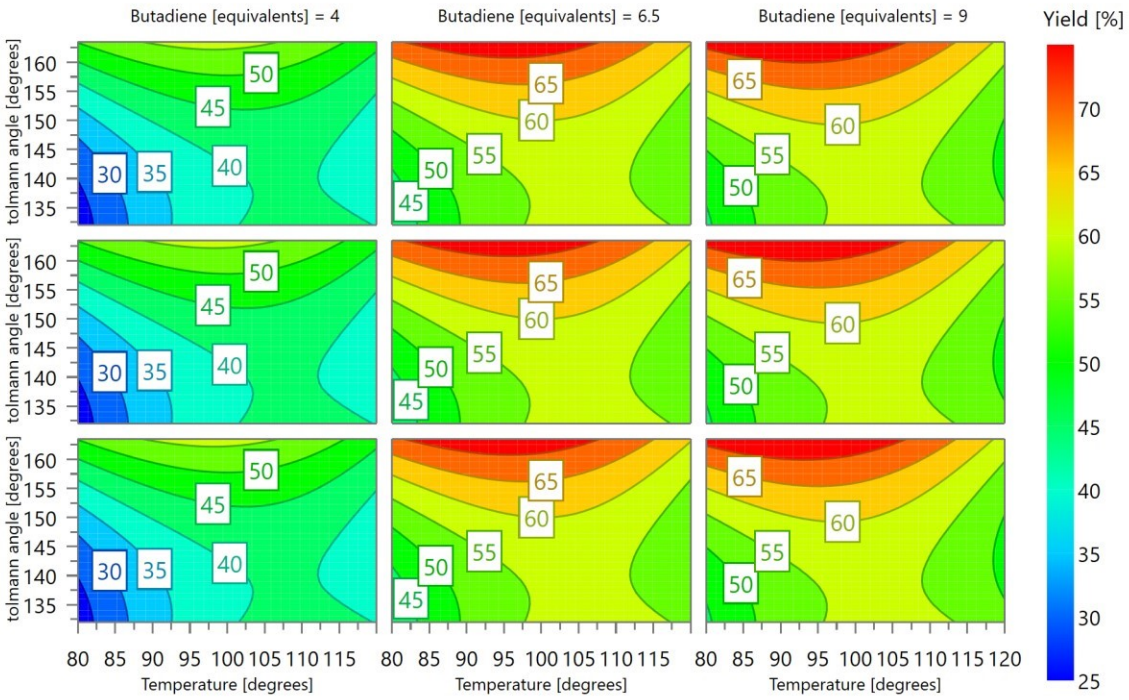


Figure S3: DoE results in contour plot.

S 2. Analytics

S 2.1. General

NMR-Spectroscopy: ^{1}H- and ^{13}C-NMR-spectra were recorded using Bruker Avance III HD NanoBay - 400 MHz, Bruker Avance NEO – 500 MHz or Bruker Avance III HD – 600 MHz spectrometers at ambient temperature with the frequency and solvent noted. Chemical shifts δ are given in ppm relative to tetramethylsilane (0 ppm) and were referenced to residual solvent signals (^{1}H: $CDCl_3$ 7.26 ppm, ^{13}C: $CDCl_3$ 77.16 ppm).

Gas chromatography (GC): Conversion and yield of the reactions were determined *via* GC on an Agilent Technologies INC. chromatograph of the type 7890B with a flame ionization detector (FID). A HP-5 column was used (30 m long, 0.32 mm diameter, 0.25 µm thickness of the layer, 5 minutes at 50 °C, heating rate 15 °C/min to 290°C, heating rate 40 °C/min to 320 °C, holding for 10 minutes). The split was set to 1:75. *n*-Dodecane was chosen as internal standard and response factors of the substrates and products were obtained experimentally by analyzing known quantities of the substances (calibration) or were calculated form literature known methods.[3]

Mass Spectrometry (MS): Qualitative mass analysis was performed *via* GC. A HP-5MS UI (30 m long, 0.25 mm diameter, 0.25 µm thickness of the layer) column was used. The carrier gas was Helium, and the detector was of the Type 5977A MSD of Agilent Technologies INC.

High Resolution Mass Spectrometry (HR-MS):

Samples for HRMS were diluted with acetonitrile or methanol to a concentration of 100 µg/mL and measured with an LTQ-Orbitrap (Thermo Scientific).

IR Spectroscopy:

All IR-Spectra were acquired using a Bruker Alpha FT-IR with Diamond-ATR.

Flash Chromatography:

For isolation of individual substances, a Büchi Flash Pure C-815 was used with cyclohexane and ethyl acetate as eluents. Cartridge size and solvent gradient were used as stated.

S 2.2. Degree of Isomerization

The degree of isomerization was determined *via* NMR. Both isomers were isolated in the same fraction and the degree of isomerization was determined *via* integration of specific signals as the example shows (Figure 3). The molar ratio of the isomers **4b-β**:**4b-α** = 2.68.

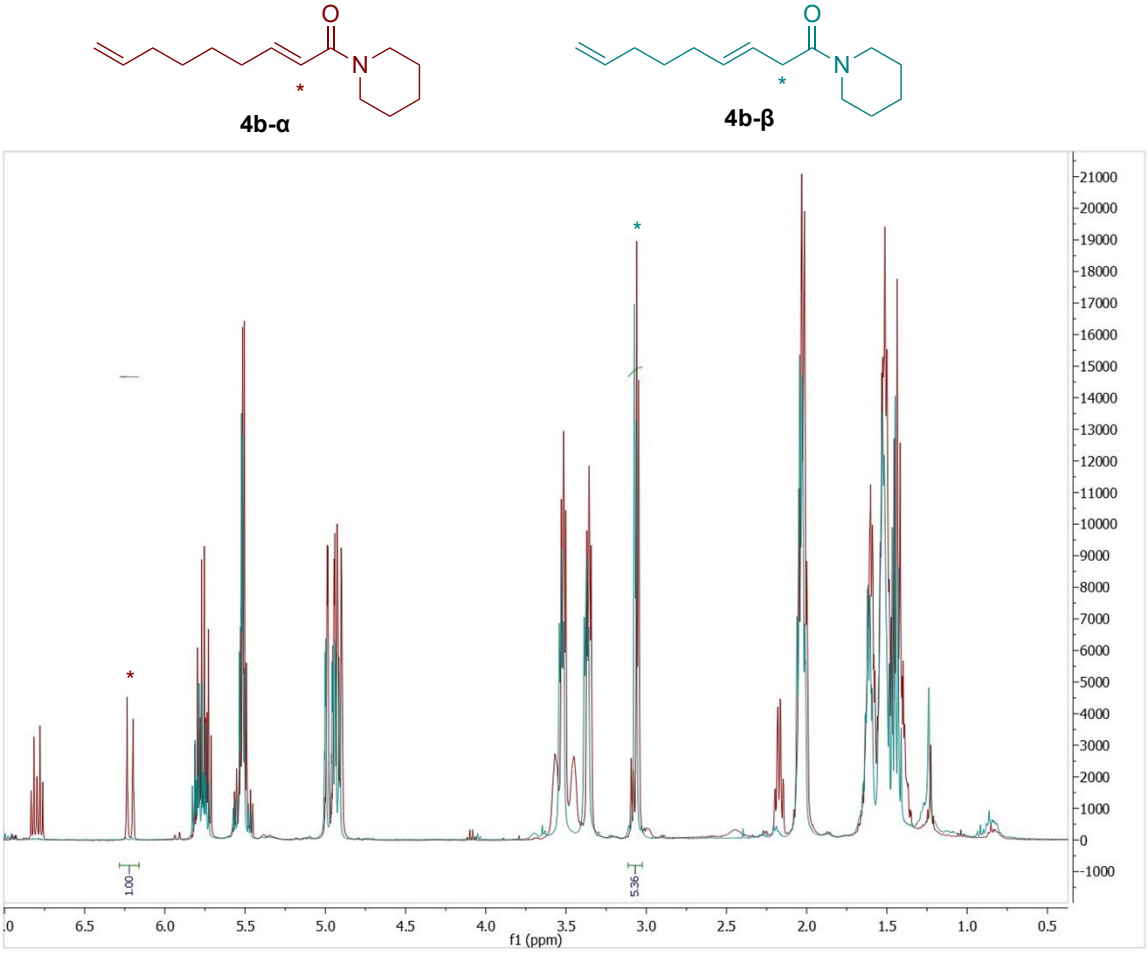


Figure S4: Determination of isomerization *via* NMR. (Red: ^{1}H (400MHz, $CDCl_3$) Spectrum of a mixture of isomers **4b** and **4'b**; teal: ^{1}H (400MHz, $CDCl_3$) Spectrum of **4b** for comparison.

S 2.3. GC-MS determination of 3,8-nonadienoic acetic anhydride 2a

Carbonylative telomerization of acetic acid yields 3,8-nonadienoic acetic anhydride **2a**. Figure S2 shows an example chromatogram of the reaction and below it shows the mass-spectrum of the chromatographic peak.

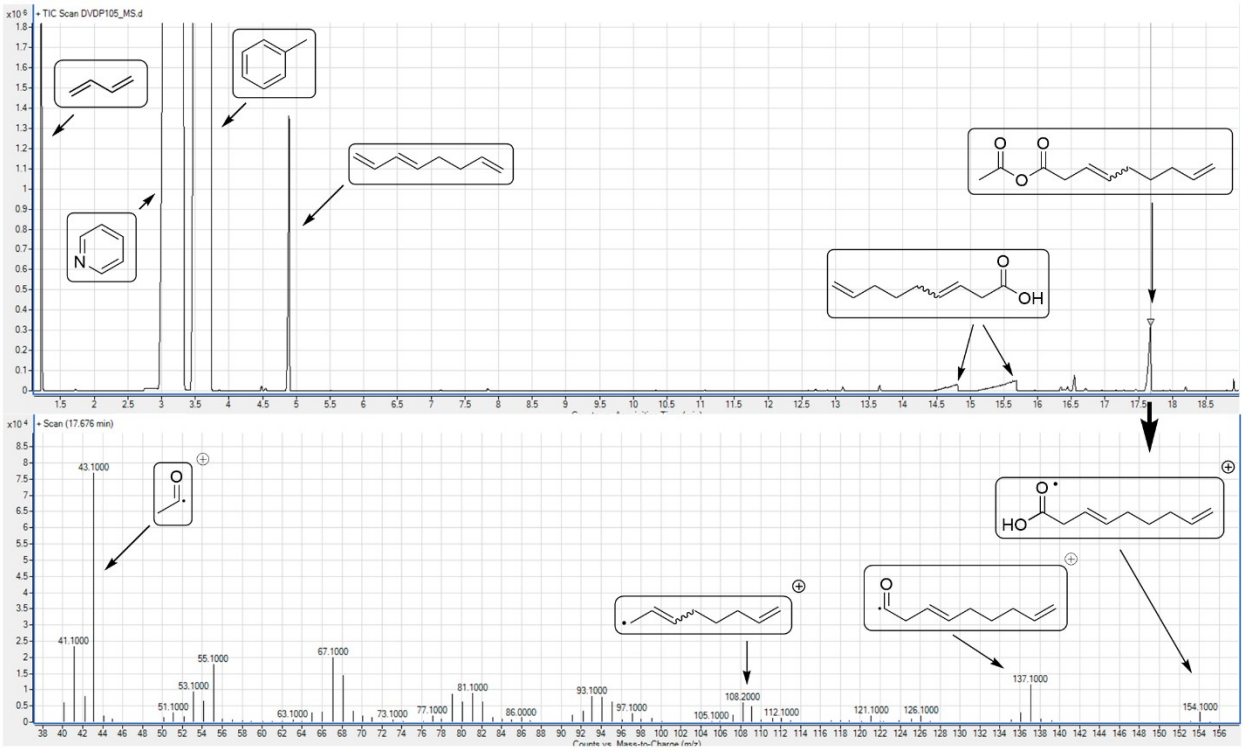


Figure S5: Exemplary chromatogram of the carbonylative telomerization of acetic acid.

The molecule-ion could of the anhydride could not be observed, however the mass-spectrum contains a large signal at a m/z of 43.1 which can be assigned to the acetyl-cation resulting from the cleavage of the one of the anhydride bonds. The anhydride can also be cleaved at the opposite side of the anhydride oxygen and yield the 3,8-nonadienal ion with a corresponding m/z value of 137.1. These signals strongly indicate the presence of 3,8-nonadienoic acetic anhydride **2a** as they include the main fragments of the compound.

S 2.4. GC-MS determination of 3,8-nonadienoic benzoic anhydride 2b

The chromatogram of the reaction mixture with benzoic acid shows similar features to one of 3,8-nonadienoic acetic anhydride (Figure S3). However, benzoic acid has a higher boiling point and is separated from the solvents. Additionally, the MS-spectrums of the peaks suggest the presence of two symmetric anhydrides, which presumably form in the GC injector block at elevated temperatures.

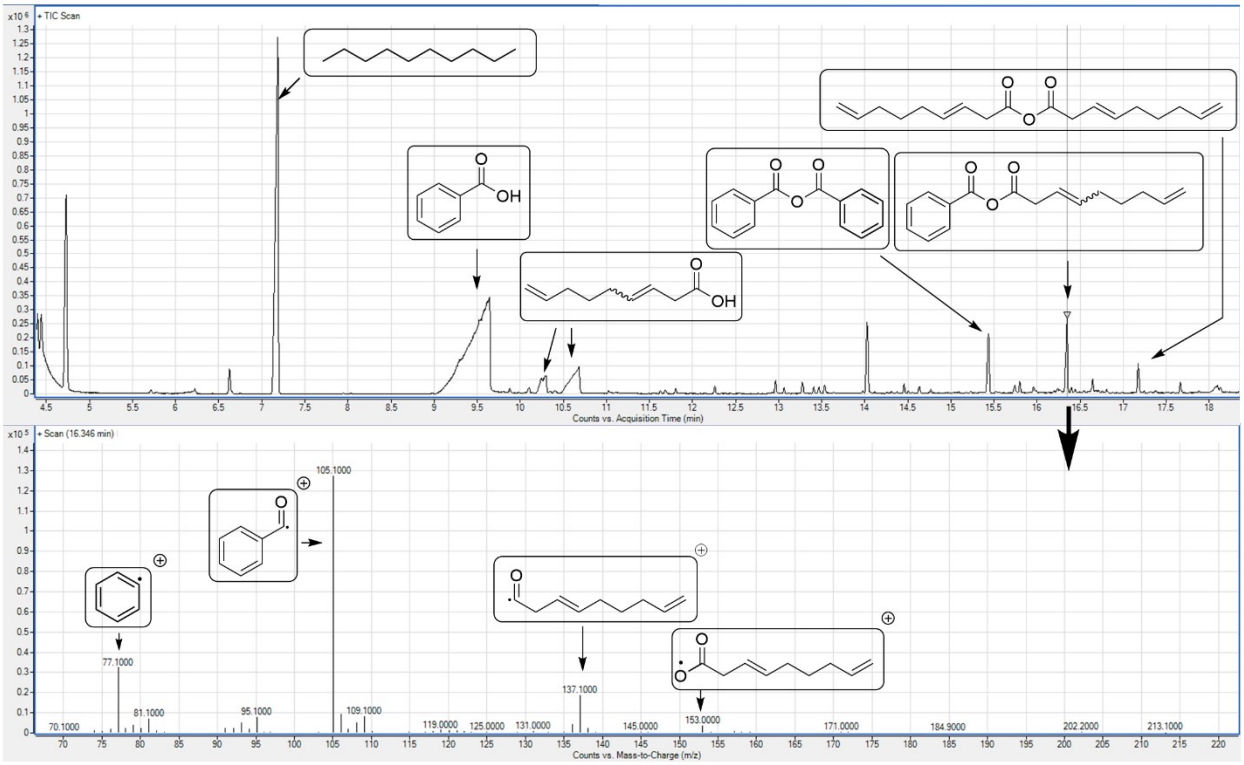
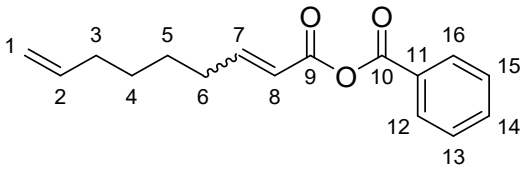


Figure S6: Exemplary GC-chromatogram of the carbonylative telomerization of benzoic acid.

The MS-spectrum of 3,8-nonadienoic benzoic anhydride 2b (Figure S3) again does not show the molecular ion, due to the poor stability of the compound. It is very likely to form fragments at the anhydride bond, which can all be observed in the spectrum.

S 2.5. Product Characterization

2,8-Nonadienoic benzoic anhydride (2b)



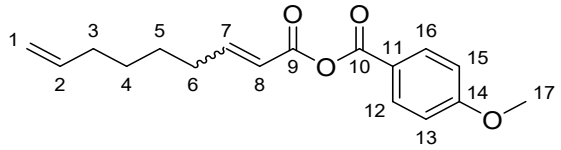
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 – 8.05 (12/16, m, 2H), 7.71 – 7.60 (14, m, 1H), 7.52 (13/15, ddd, J = 15.5, 9.2, 4.6 Hz, 2H), 7.25 – 6.99 (7, m, 1H), 6.08 – 5.95 (8, m, 1H), 5.85 – 5.74 (2, m, 2H), 5.05 – 4.94 (1, m, 2H), 2.38 – 2.21 (6, m, 2H), 2.14 – 1.99 (3m, 2H), 1.57 – 1.40 (4/5, m, 4H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 162.48 (9, q), 161.98 (10, q), 154.72 (7, t), 138.46 (2, t), 134.67 (14, t), 134.44 (11, q), 130.71 (12/16, t), 129.01 (13/15, t), 120.66(8, t), 114.96 (1, s), 33.34 (3, s), 32.58 (6, s), 28.52 (4, s), 28.48 (5, s) ppm.

FTIR: ν = 2928 (C-H, alkane stretch), 1787 (C=O, anhydride stretch), 1728 (C=O, conjugated anhydride stretch), 1641 (C=C, disubstituted (cis) or monosubstituted alkene stretch), 1452 (C-H, bending), 1038 (OC-O-CO, anhydride stretch), 993 (C=C, monosubstituted alkene bend), 909 (C=C, monosubstituted alkene bend), 704 (C=C, disubstituded(cis) alkene bend) cm-1.

LR-MS: m/z (%) = 153(1), 138(1), 137(13), 119(1), 109(6), 108(4), 106(8), 105(100), 95(6), 81(6), 77(23).

2,8-Nonadienoic 4-methoxybenzoic anhydride (2e)

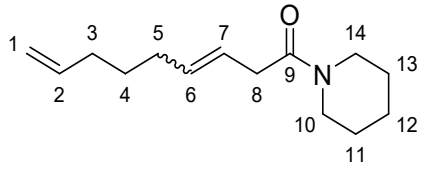


^{1}H NMR (400 MHz, $CDCl_3$): $\boldsymbol{\delta}$ = 8.15 – 7.92 (12/16, m, 2H), 7.23 – 7.04 (7, m, 1H), 6.99 – 6.89 (13/15, m, 2H), 6.00 – 5.83 (8, m, 1H), 5.83 – 5.72 (2, m, 1H), 5.03 – 4.97 (1, m, 1H), 4.97 – 4.92 (1, m, 1H), 3.91 – 3.82 (17, m, 3H), 2.33 – 2.21 (6, m, 2H), 2.10 – 2.02 (3 ,m, 2H), 1.54 – 1.39 (4/5, m, 4H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): $\boldsymbol{\delta}$ = 164.59 (9, q), 162.26 (14, q) 162.19 (10, q), 154.18 (7, t), 138.39(2, t), 132.79 (12/16, t), 121.13 (11, q), 120.70 (8, t), 114.84 (1, s), 114.11 (13/15, t), 55.62 (17, p), 33.45 (3, s), 32.43 (6, s), 28.38 (4, s), 27.23 (5, s) ppm.

LR-MS: m/z (%) = 288(1), 244(1), 214(1), 187(1), 152(6), 136(10), 135(100), 119(1), 109(2), 108(1), 107(7), 95(3), 93(3), 92(12), 81(4), 77(12), 74(1).

1-(Piperidin-1-yl) nona-3,8-dien-1-one (4b)

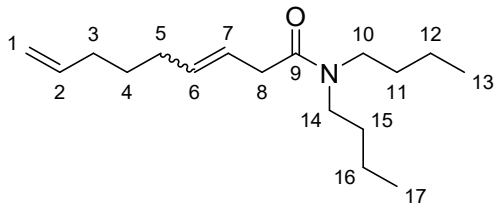


^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 – 5.70 (2, m, 1H), 5.60 – 5.44 (6/7, m, 2H), 5.06 – 4.87 (1, m, 2H), 3.59 – 3.46 (10, m, 2H), 3.46 – 3.29 (14, m, 2H), 3.07 (8, d, J = 4.8 Hz, 2H), 2.09 – 1.98 (3/5, m, 4H), 1.65 – 1.57 (4, m, 2H), 1.57 – 1.49 (m, 4H), 1.49 – 1.40 (m, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 169.90 (9, q), 138.79 (2, t), 133.47 (7, t), 123.41 (6, t), 114.63 (1, s), 47.01 (10, s), 42.81 (14, s), 38.03 (8, s), 33.31 (5, s), 32.07 (3, s), 28.57(4, s), 26.59 (10/14, s), 25.65 (11/13, s), 24.62 (12, s) ppm

HR-MS (APCI): calcd. $[M+H]^+$ = 222.1852, found $[M+H]^+$ = 222.18546.

Di-butylnona-3,8-dienamide (3d)

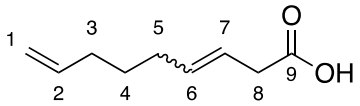


^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.81 – 5.72 (2, m, 1H), 5.62 – 5.44 (6/7, m, 2H), 5.01 – 4.94 (1, m, 1H), 4.94 – 4.90 (1, m, 1H), 3.32 – 3.24 (10, m, 2H), 3.22 – 3.15 (14, m, 2H), 3.10 – 3.01 (8, m, 2H), 2.07 – 1.96 (3/5, m, 4H), 1.57 – 1.39 (4/10/14, m, 6H), 1.35 – 1.22 (12/16, m, 4H), 0.97 – 0.85 (13/17, m, 6H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ = 171.23 (9, q), 138.80 (2, t), 133.27 (7, t), 123.78 (6, t), 114.58 (1, s), 47.91 (10, s), 45.73 (14, s), 37.70 (8, s), 33.29 (5, s), 32.03 (3, s), 31.30 (10/14, s), 29.92 (11/15, s), 28.51 (4, s), 20.34 (12, s), 20.20 (16, s), 13.99 (13, p), 13.94 (17, p) ppm.

LR-MS m/z (%): 265 (35), 224 (22), 210 (15), 182 (23), 156 (95), 137 (2), 128 (30), 109 (7), 86 (100)

3,8-Nonadienoic acid (1c)



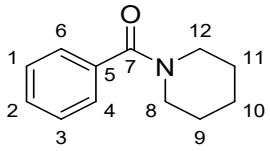
^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.78 (OH, s, 1H), 5.84 – 5.72 (m, 1H), 5.63 – 5.47 (m, 2H), 5.03 – 4.97 (m, 1H), 4.96 – 4.91 (m, 1H), 3.09 (m, 2H), 2.10 – 2.01 (m, 4H), 1.52 – 1.42 (m, 2H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 178.75 (9, q), 138.72 (2, t), 135.15 (7, t), 121.3 (6, t), 114.88 (1, s), 38 (8, s), 33.3 (5, s), 31.96 (3, s), 28.52 (4, s) ppm.

HR-MS (ESI): calcd. $[M+H]^+$ = 155.1072, found $[M+H]^+$ = 155.1067.

LR-MS m/z (%): 154 (1), 137 (3), 136 (21), 126 (4), 125 (6), 118 (6), 113 (16), 112 (100), 109 (9), 108 (36).

N-benzoyl-piperidine (4bb)

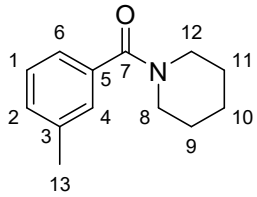


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (1/2/3/4/6, s, 5H), 3.70 (8, br s, 2H), 3.33 (12, bs s, 2H), 1.67 (9/11, br s, 4H), 1.51 (10, br s, 3H)

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 170.44 (7), 136.61 (5), 129.45 (2), 128.50 (4/6), 126.89 (1/3), 48.86 (8), 43.25 (12), 26.62 (9), 25.68 (11), 24.70 (10).

HR-MS (APCI): calcd. $[M+H]^+$ = 190.1226, found $[M+H]^+$ = 190.12279.

N-*3*-methylbenzoly-piperidine (4db)



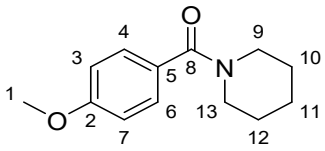
Was isolated as a mixture with **4b.**

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27 – 7.23 (m, 1H), 7.19 – 7.17 (m, 2H), 7.15 – 7.12 (m, 1H), 3.68 (br s, 2H), 3.32 (br s, 2H), 2.35 (s, 3H), 1.69 – 1.64 (m, overlapping with **4b**), 1.64 – 1.59 (m, overlapping with **4b**) ppm.

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 170.64 (7, q), 138.34 (3, q), 136.47 (5, q), 130.14 (2, t), 128.28 (1, t), 127.48 (4, t), 123.75(6, t), 48.85 (12, s), 43.20 (8, s), 26.63 (11, s), 25.70 (9, s), 24.70 (10, s), 21.45 (13, p) ppm.

HR-MS (APCI): calcd. $[M+H]^+$ = 204.1383, found $[M+H]^+$ = 204.13847.

N-*p*-methoxybenzoyl-piperidine (4eb)



^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (4/6, d, *J* = 8.8 Hz, 2H), 6.88 (3/7, d, *J* = 8.8 Hz, 2H), 3.80 (1, s, 3H), 3.53 (9/13s, 4H), 1.65 (11, d, *J* = 4.2 Hz, 2H), 1.57 (10/12, s, 4H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 170.44 (8), 160.61 (2), 128.92 (4/6), 128.21 (5), 113.66 (3/7), 55.33 (9/13), 48.94 (9, broad), 43.72 (13, broad), 26.17 (10/12), 24.60 (11, broad).

HR-MS (APCI): calcd. $[M+H]^+$ = 220.1332, found $[M+H]^+$ = 220.13340.

Broad signals were received for the ^{1}H and ^{13}C signals of the piperidinyl ring due to rotation of the amide bond, which aligns with other literature reports of the compound.[4]

S 3. Appendix

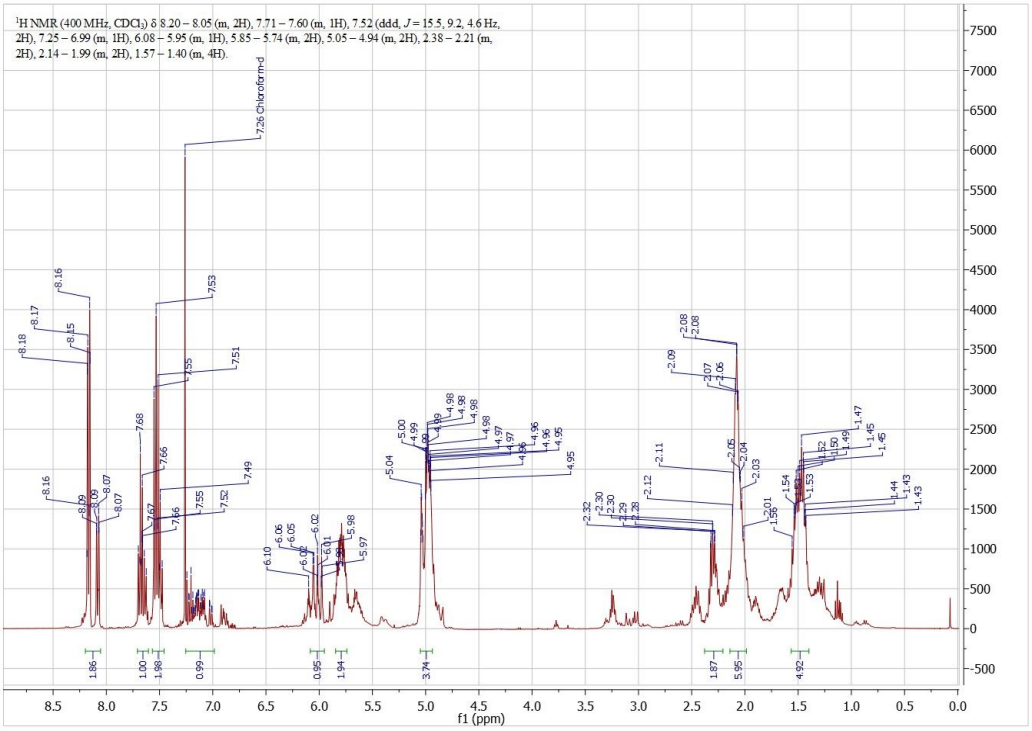


Figure S7: ^{1}H NMR spectrum of 3,8-Nonadienoic benzoic acid anhydride (**2b**)

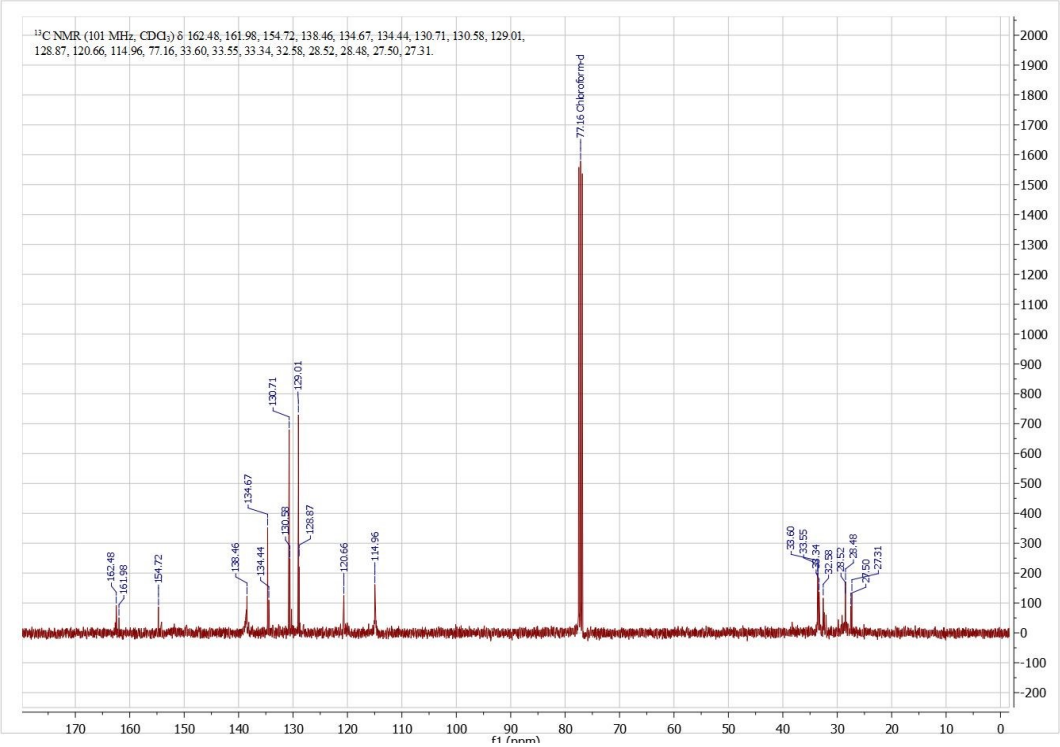


Figure S8: ^{13}C NMR spectrum of 3,8-Nonadienoic benzoic acid anhydride (**2b**).

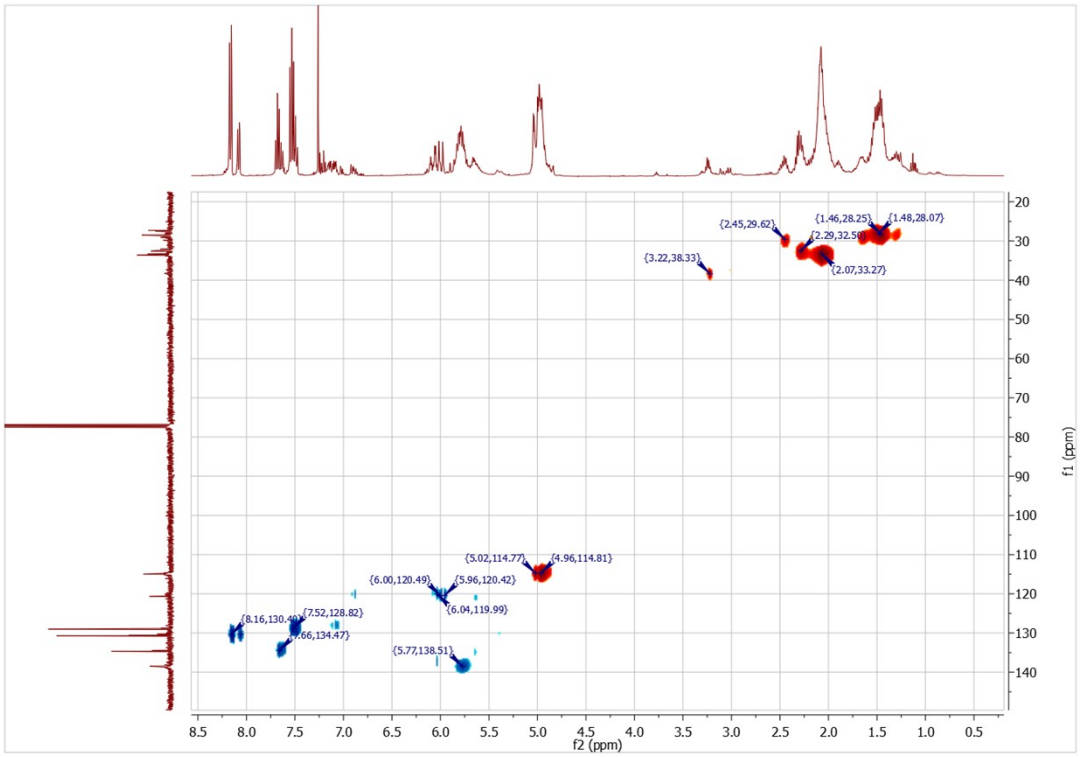


Figure S9: HSQC 2D- NMR spectrum of 3,8-Nonadienoic benzoic acid anhydride (**2b**).

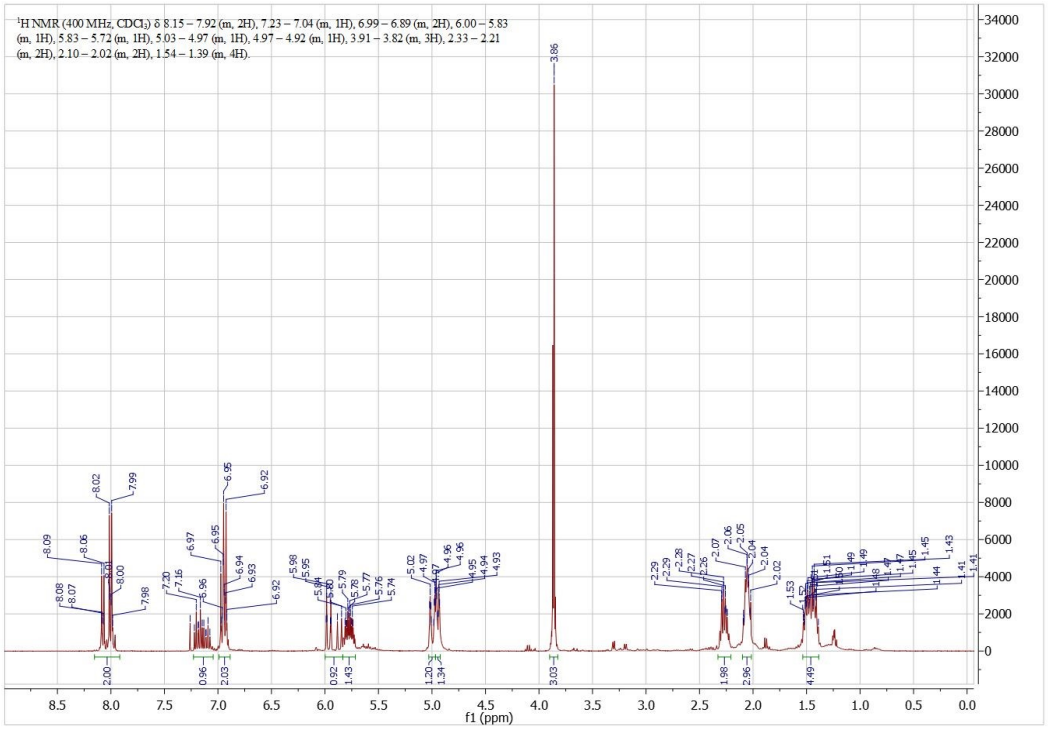


Figure S10: ^{1}H NMR spectrum of 3,8-Nonadienoic anisic anhydride (**2e**).

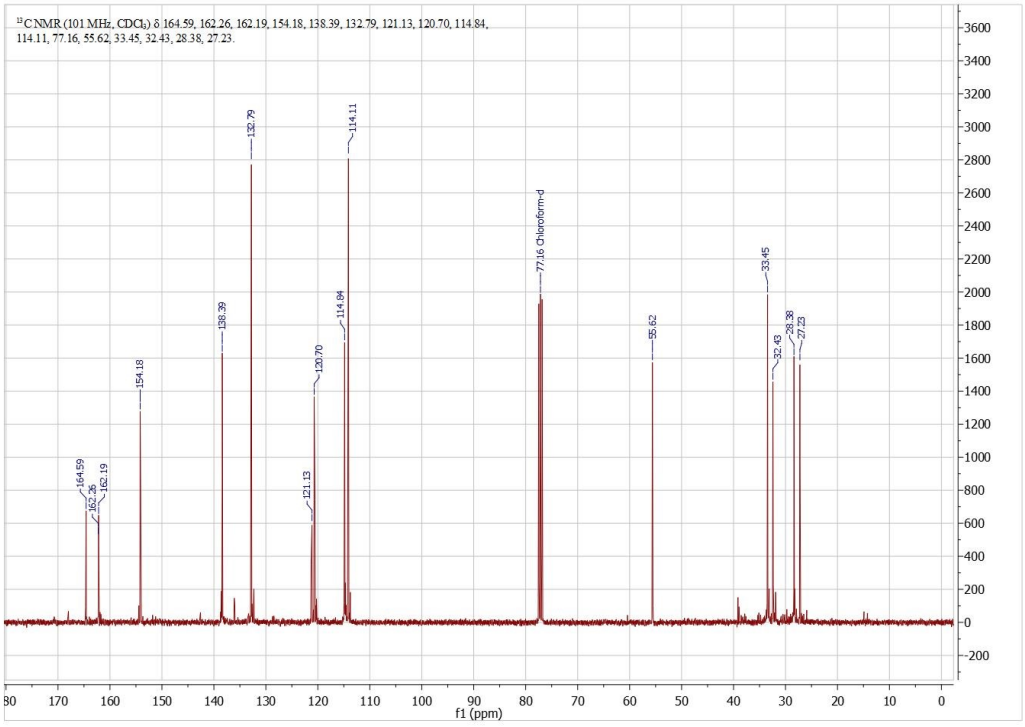


Figure S11: ^{13}C NMR spectrum of 3,8-Nonadienoic anisic anhydride (**2e**).

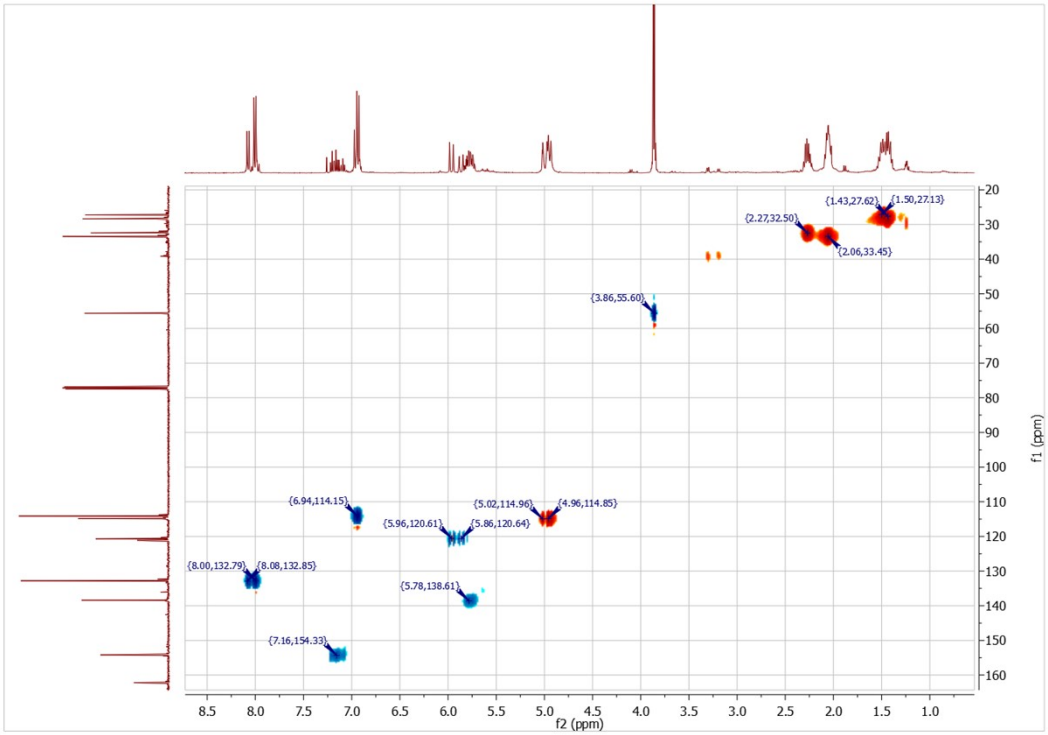


Figure S12: HSQC 2D-NMR spectrum of 3,8-Nonadienoic anisic anhydride (**2e**).

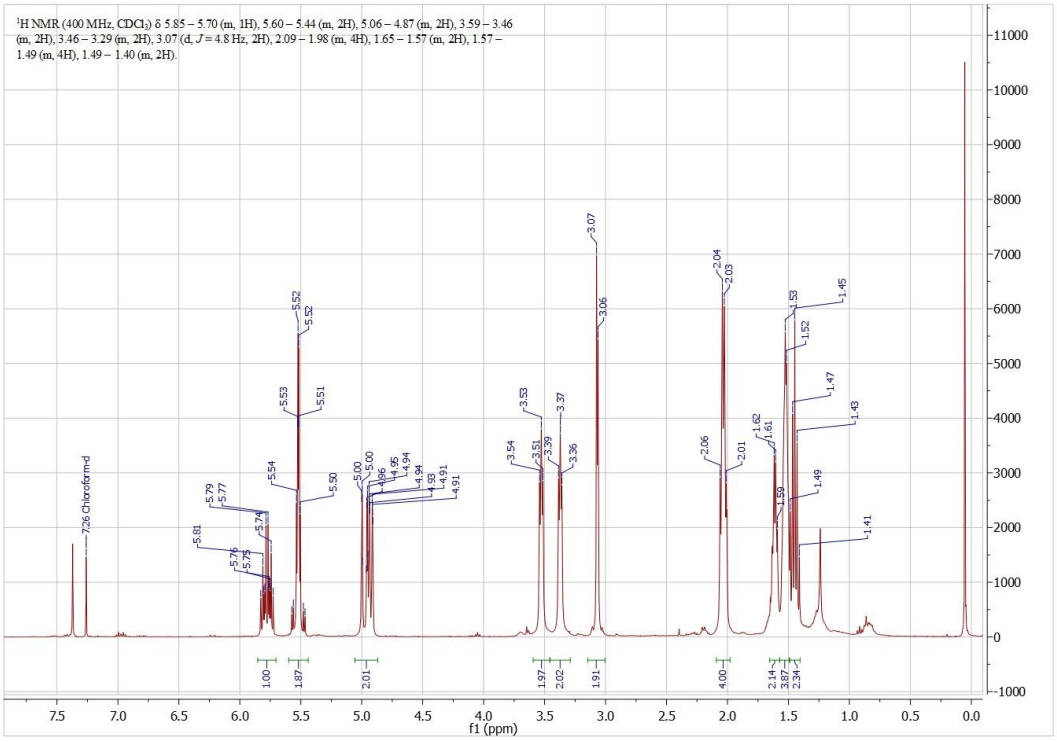


Figure S13: ¹H NMR spectrum of Spectrum 1-(piperidin-1-yl) nona-3,8-dien-1-one (**4b**).

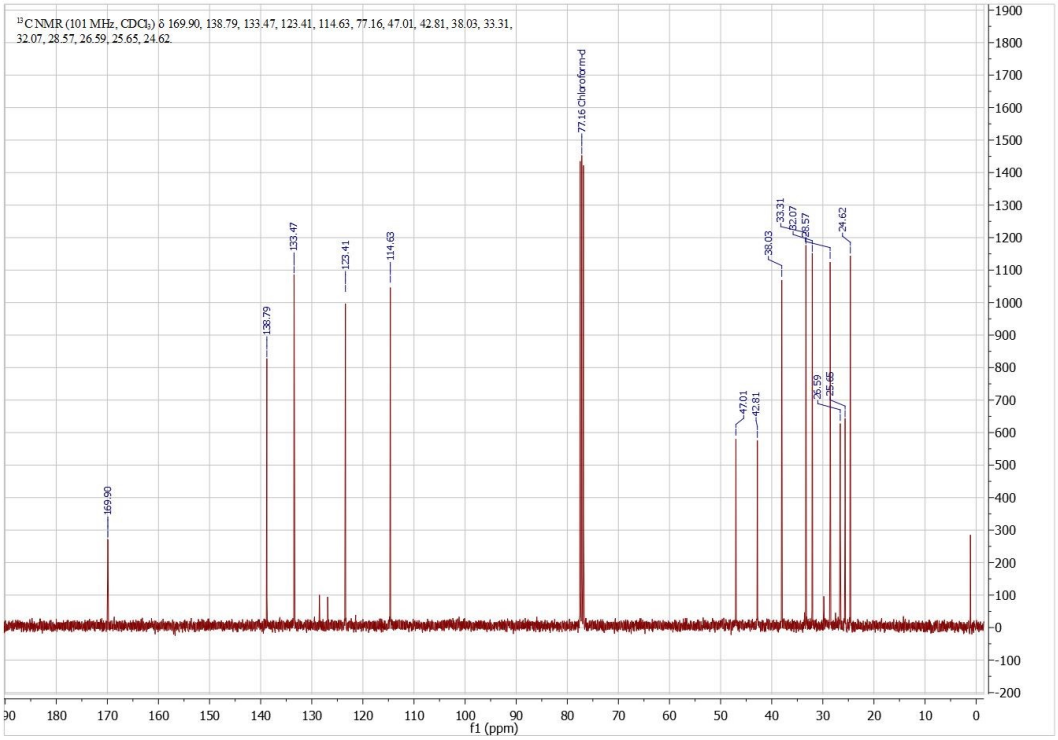


Figure S14: ^{13}C NMR spectrum of Spectrum 1-(piperidin-1-yl) nona-3,8-dien-1-one (**4b**).

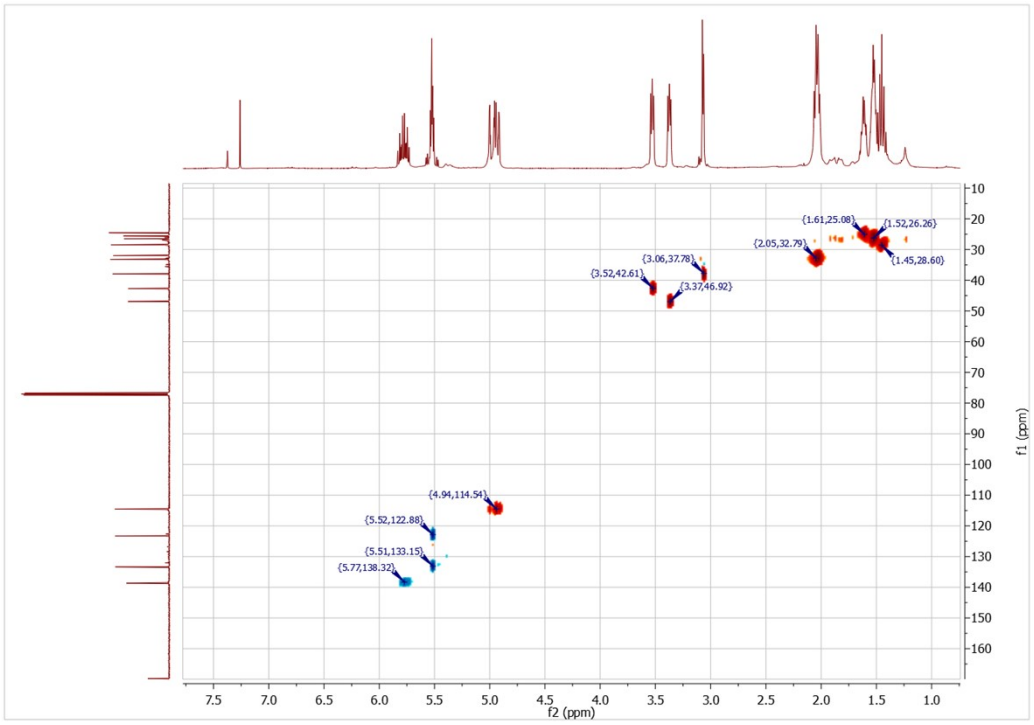


Figure S15: HSQC 2D-NMR spectrum of Spectrum 1-(piperidin-1-yl) nona-3,8-dien-1-one (**4b**).

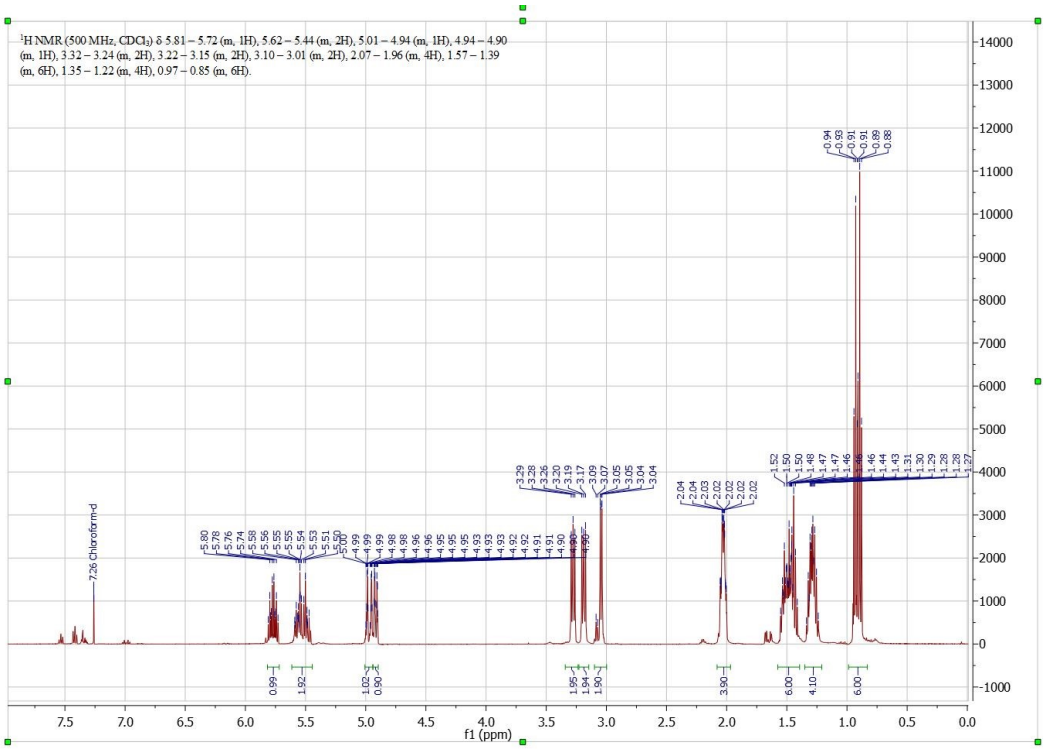


Figure S16: ^{1}H NMR Spectrum N,N-dibutylnona-3,8-dienamide **4d**.

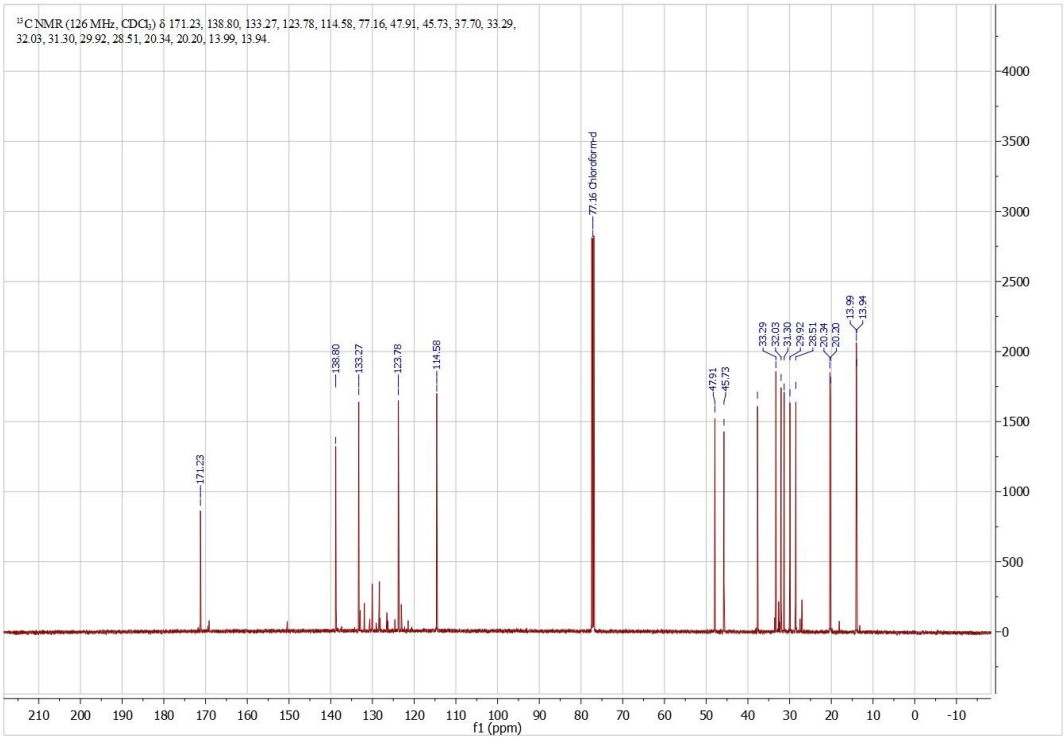


Figure S17: ^{13}C NMR Spectrum N,N-dibutylnona-3,8-dienamide **4d**.

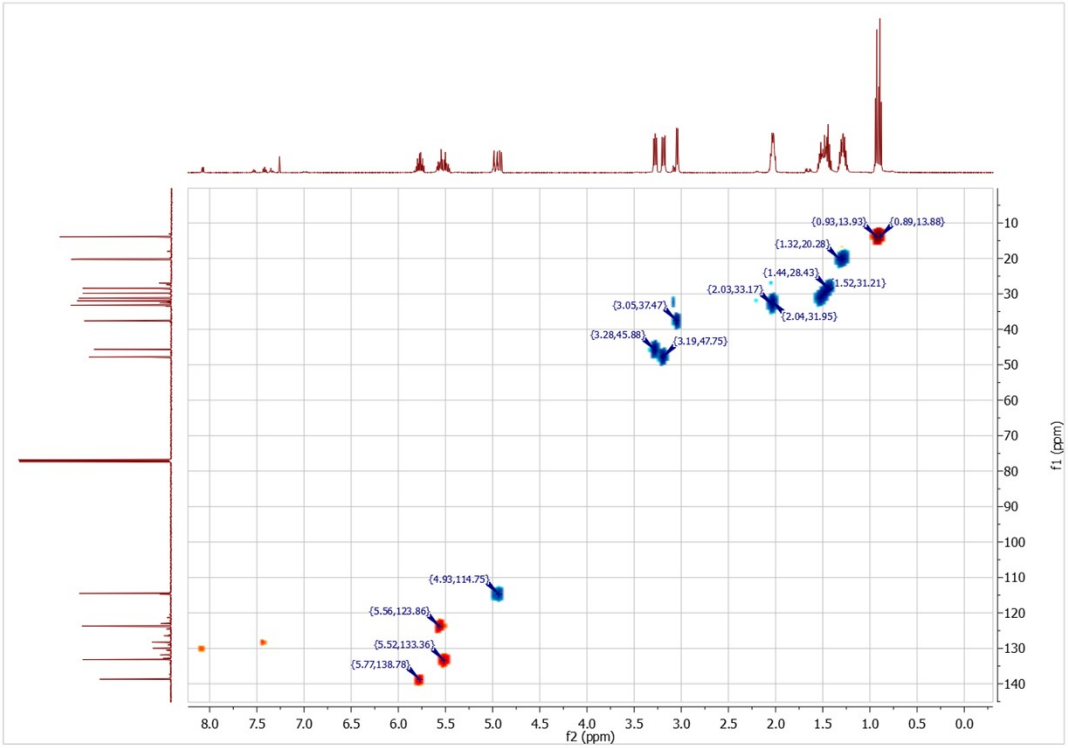


Figure S18: HSQC 2D-NMR Spectrum N,N-dibutylnona-3,8-dienamide **4d**.

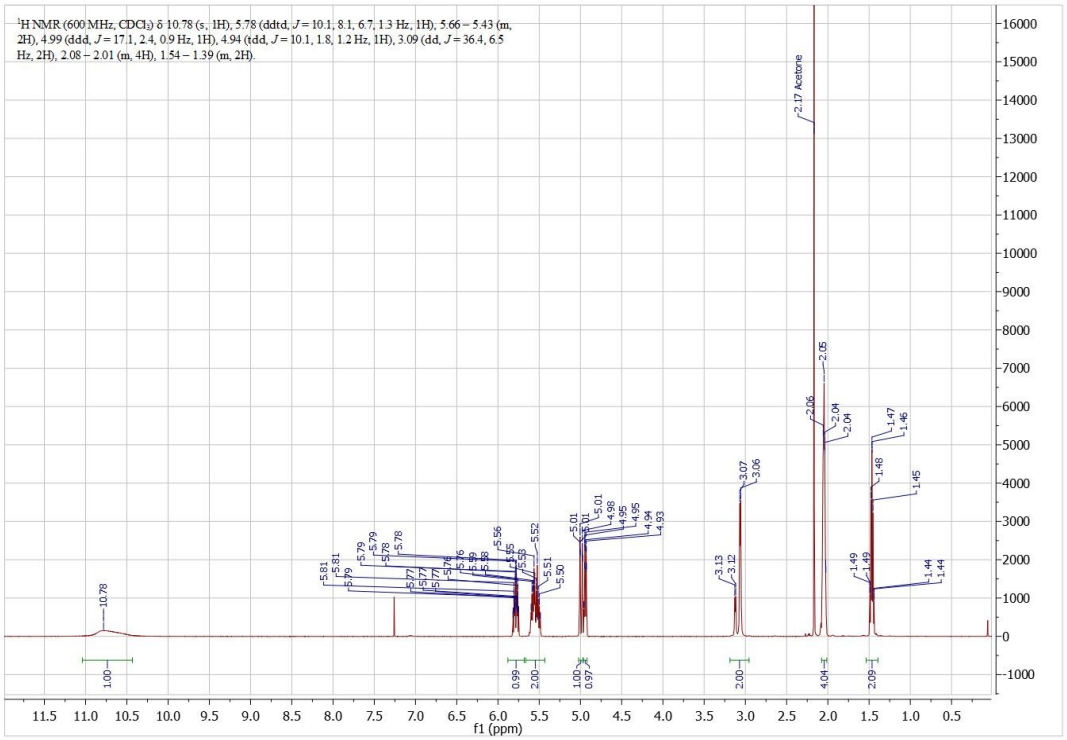


Figure S19: ^{1}H NMR spectrum of 3,8-nonadienoic acid (**1c**).

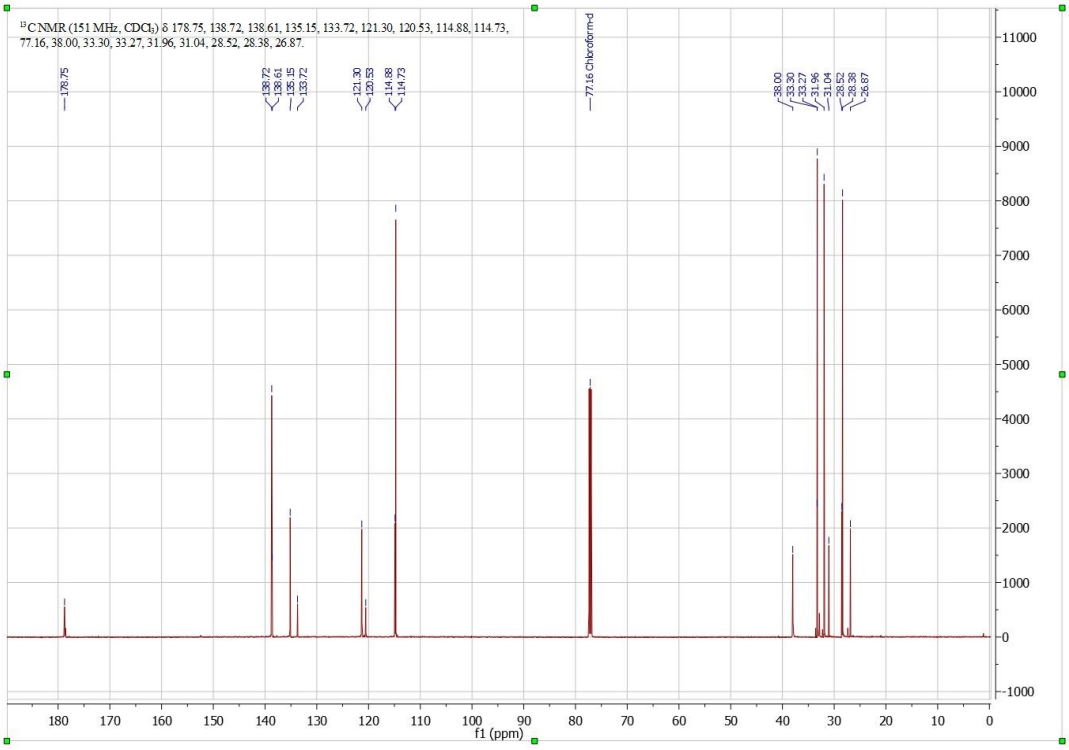


Figure S20: ^{13}C {^{1}H} NMR spectrum of 3,8-nonadienoic acid (**1c**).

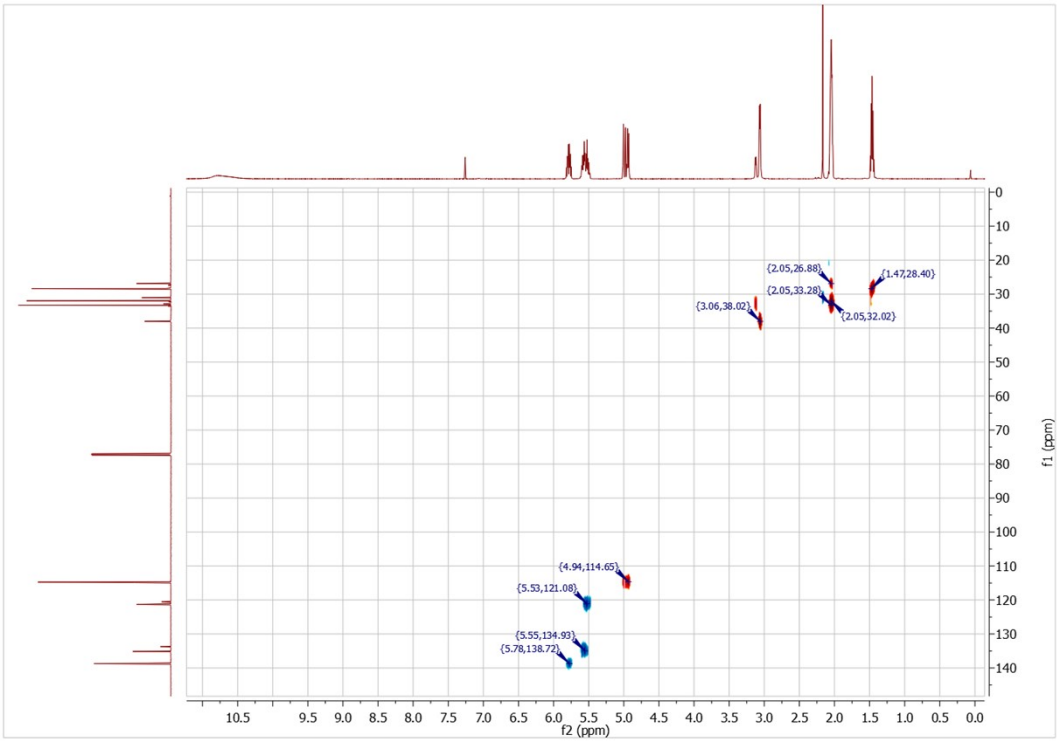


Figure S21: HSQC 2D-NMR spectrum of 3,8-nonadienoic acid (**1c**).

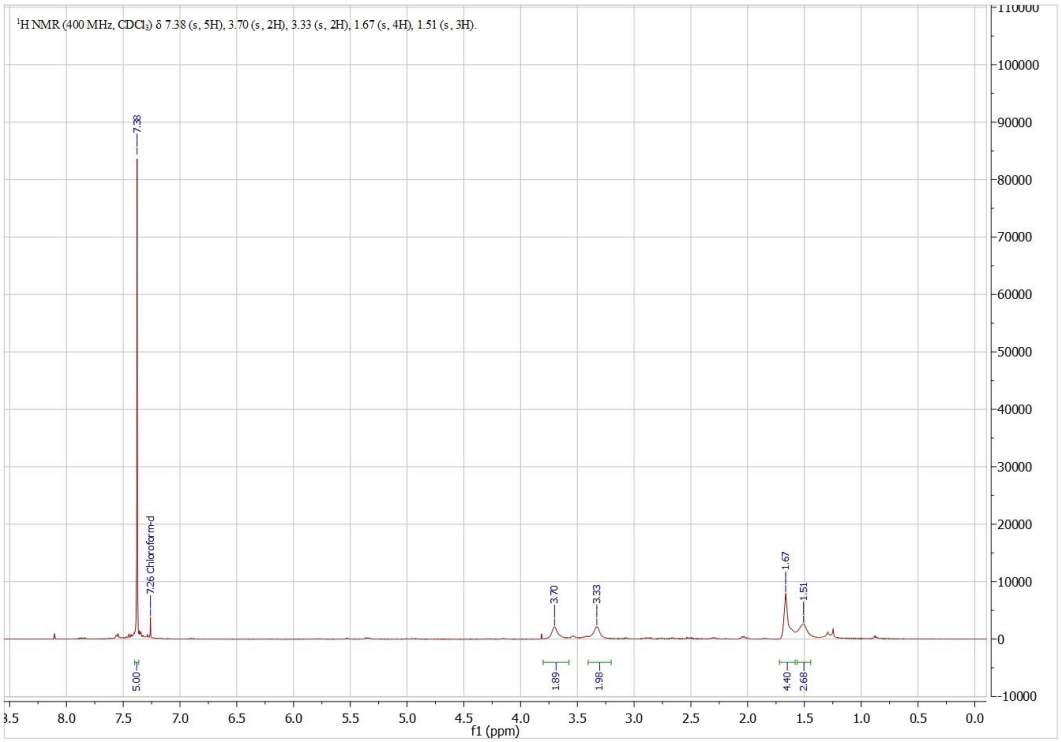


Figure S22 : ^{1}H NMR spectrum of N-benzoyl-piperidine (**4bb**)

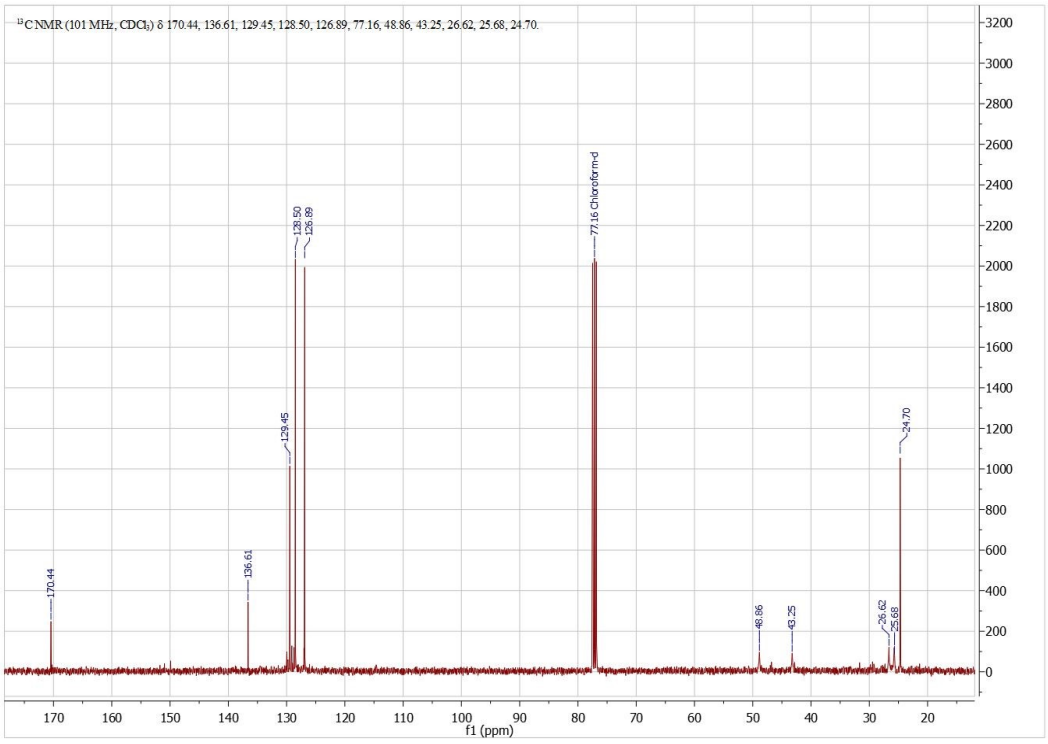


Figure S23: ^{13}C {^{1}H} NMR spectrum of N-benzoyl-piperidine (**4bb**)

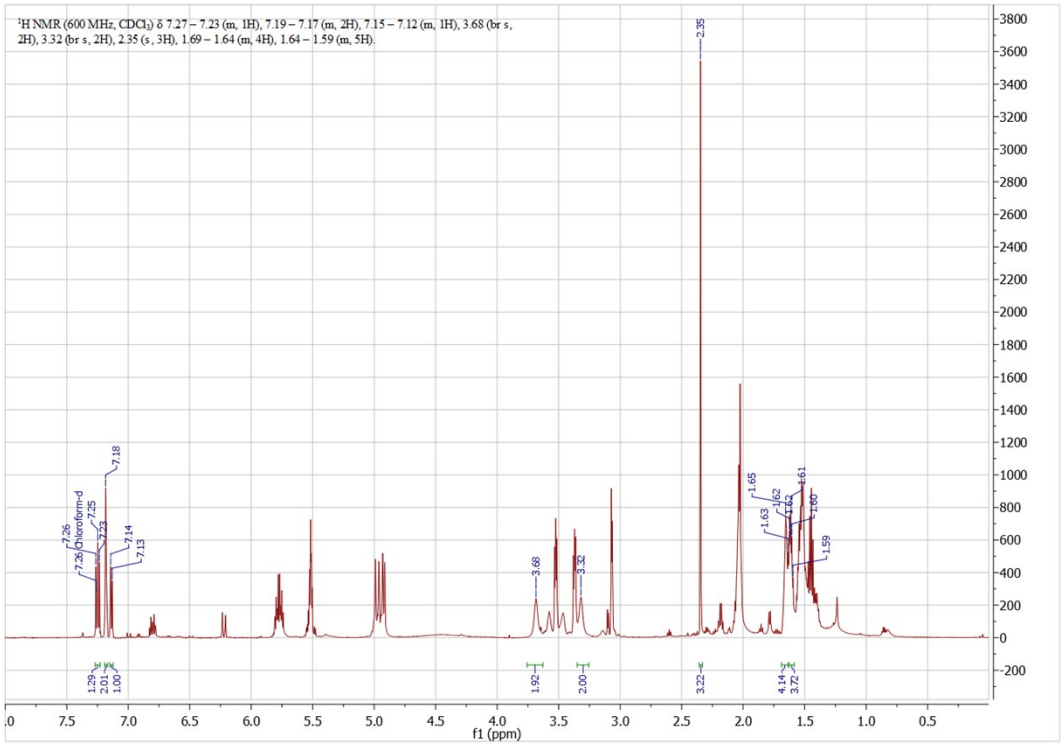


Figure S24: ^{1}H NMR spectrum of N-(3-methylbenzoyl)-piperidine (**4db**) as a mixture with **4b**.

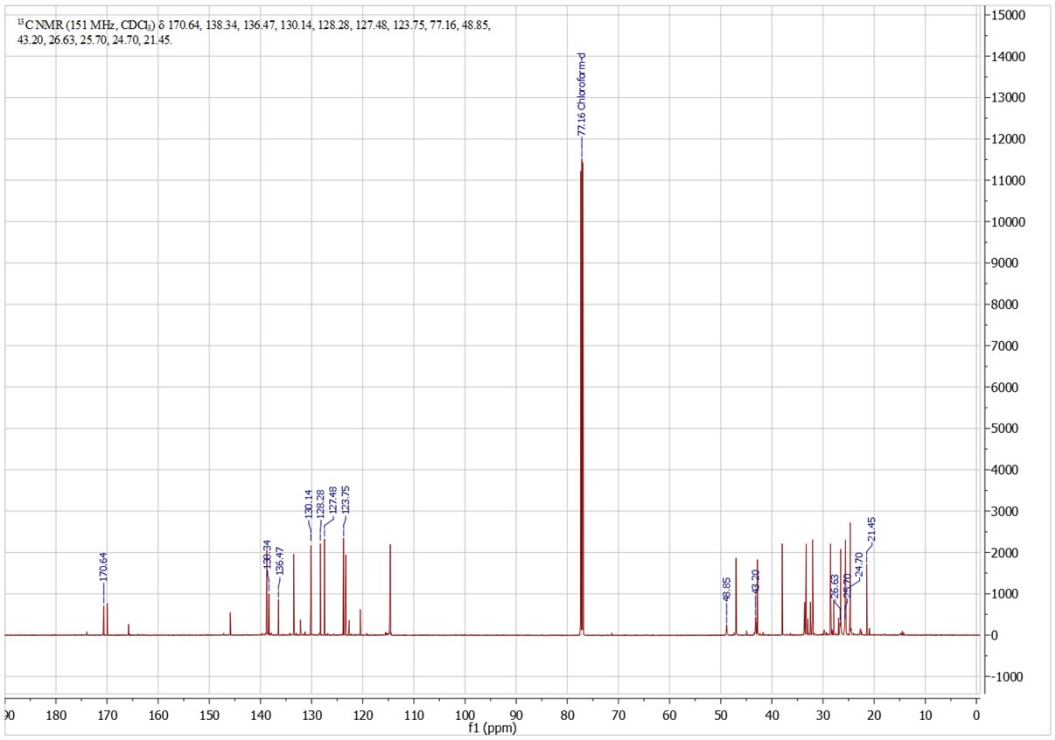


Figure S25: ^{13}C {^{1}H} NMR spectrum of N-(3-methylbenzoyl)-piperidine (**4db**) as a mixture with **4b.**

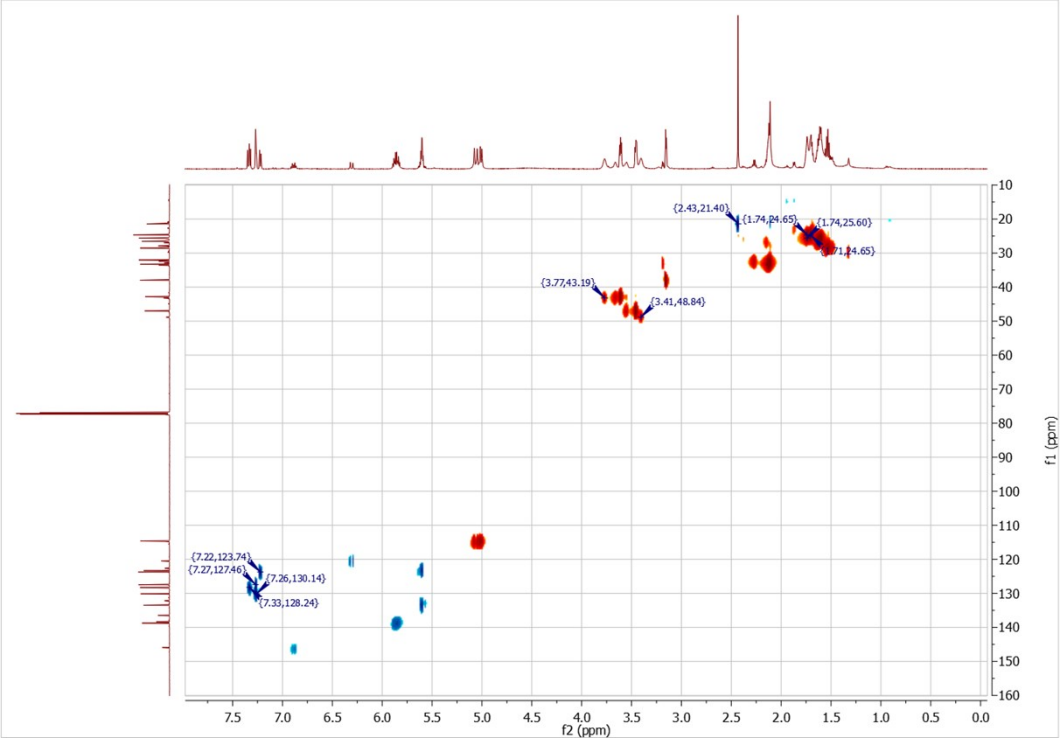


Figure S26: HSQC 2D-NMR spectrum of N-(3-methylbenzoyl)-piperidine (**4db**) as a mixture with **4b.**

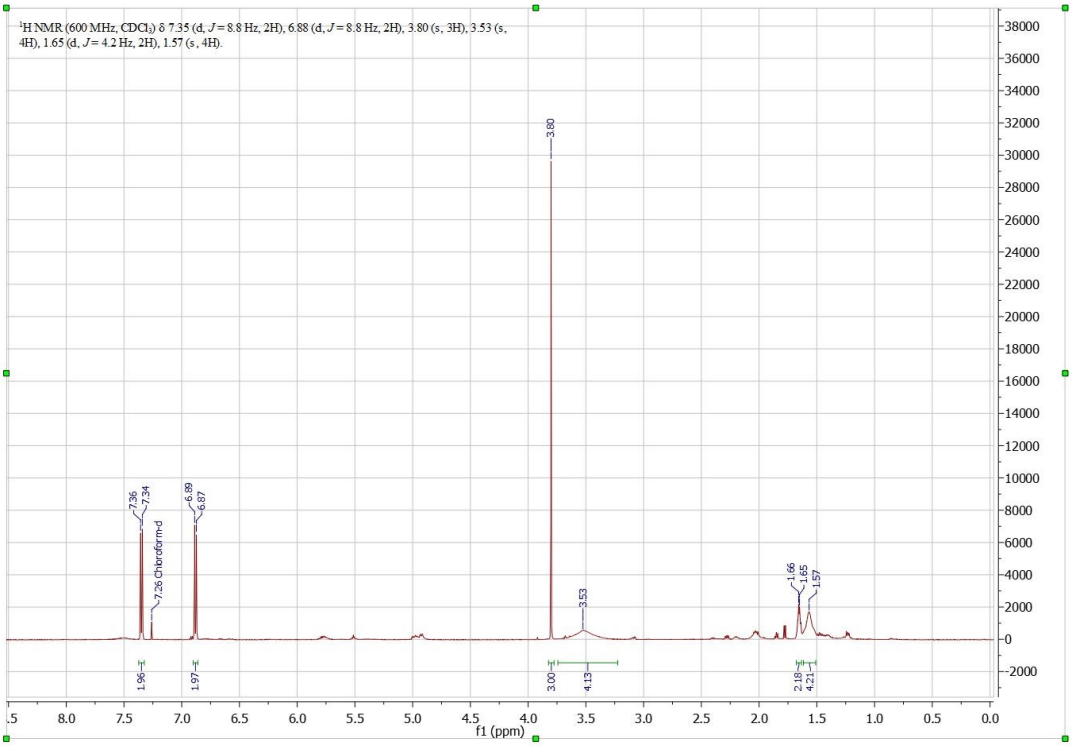


Figure S27: ^{1}H-NMR spectrum of N-(4-methoxybenzoyl)-piperidine

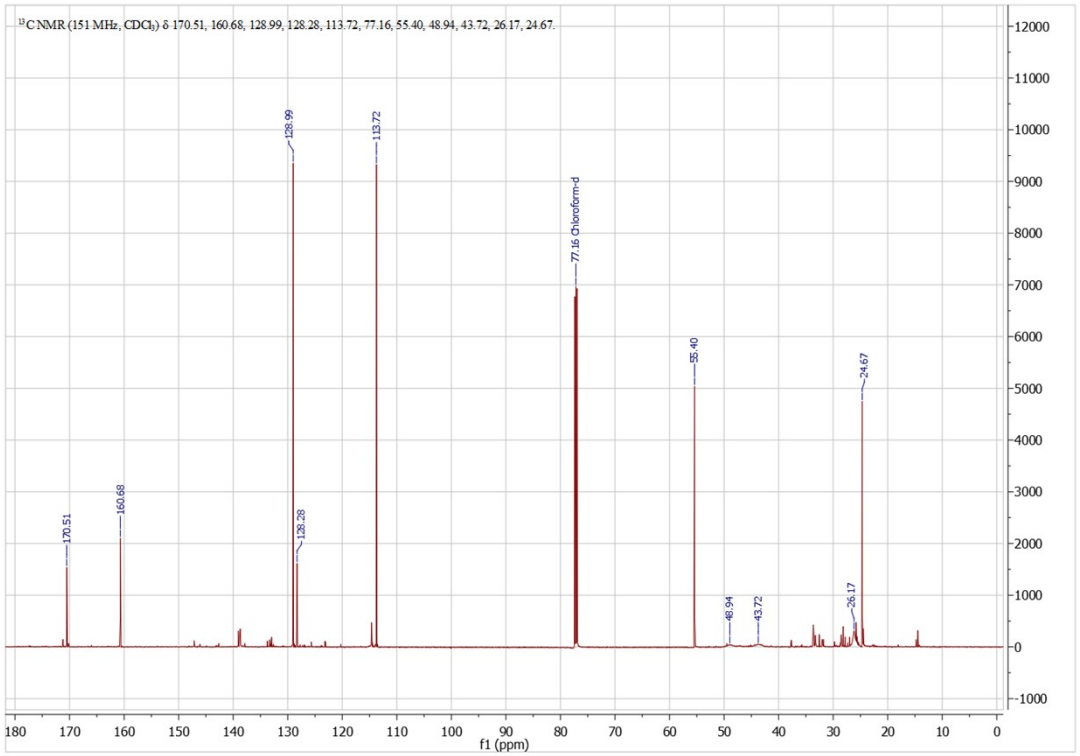


Figure S28: $^{13}C\{^{1}H\}$ NMR- spectrum of N-(4-methoxybenzoyl)-piperidine.

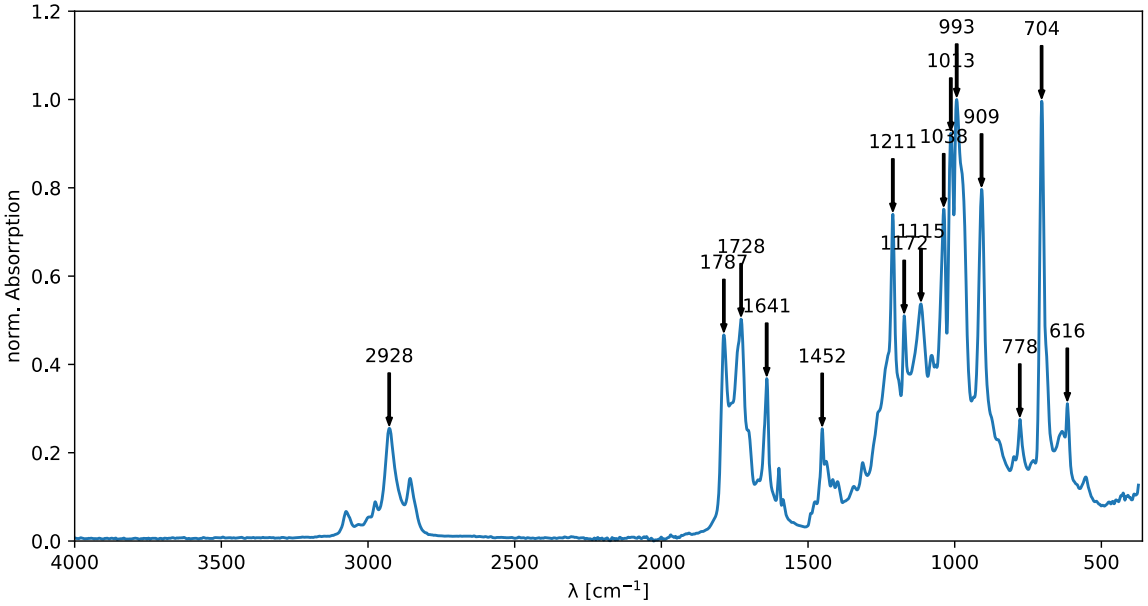


Figure S29: FTIR spectrum for 3,8-nonadienoic benzoic anhydride.

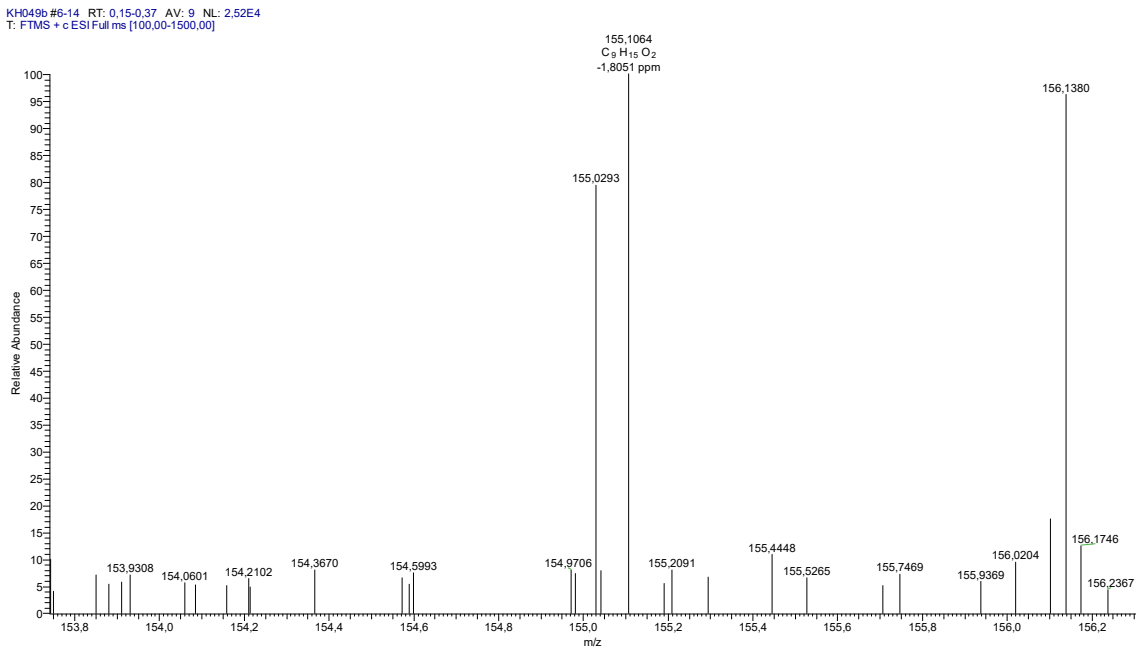


Figure S30: ESI-MS spectrum of 3,8-nonadienoic acid **1c**.

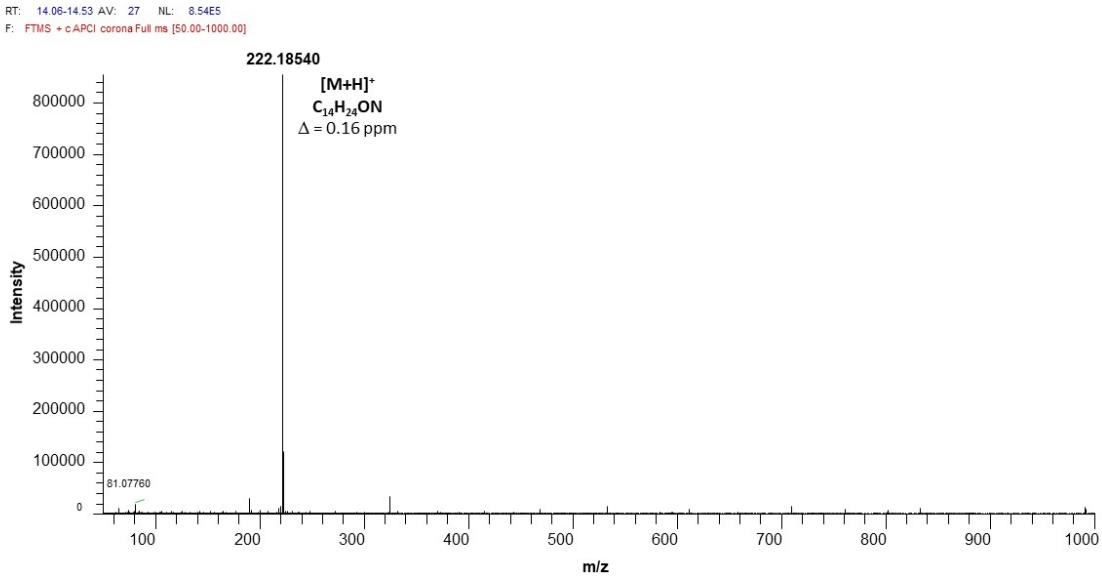


Figure S31: HR-MS(APCI) spectrum of 1-(piperidin-1-yl) nona-3,8-dien-1-one (**4b**)

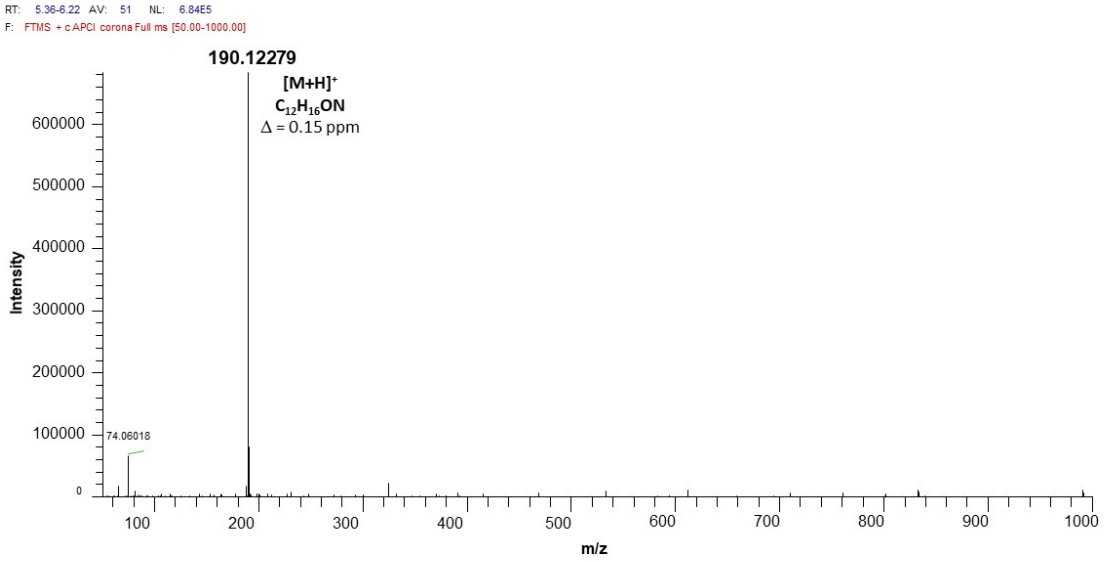


Figure S32: HR-MS(APCI) spectrum of N-benzoyl-piperidine (**4bb**)

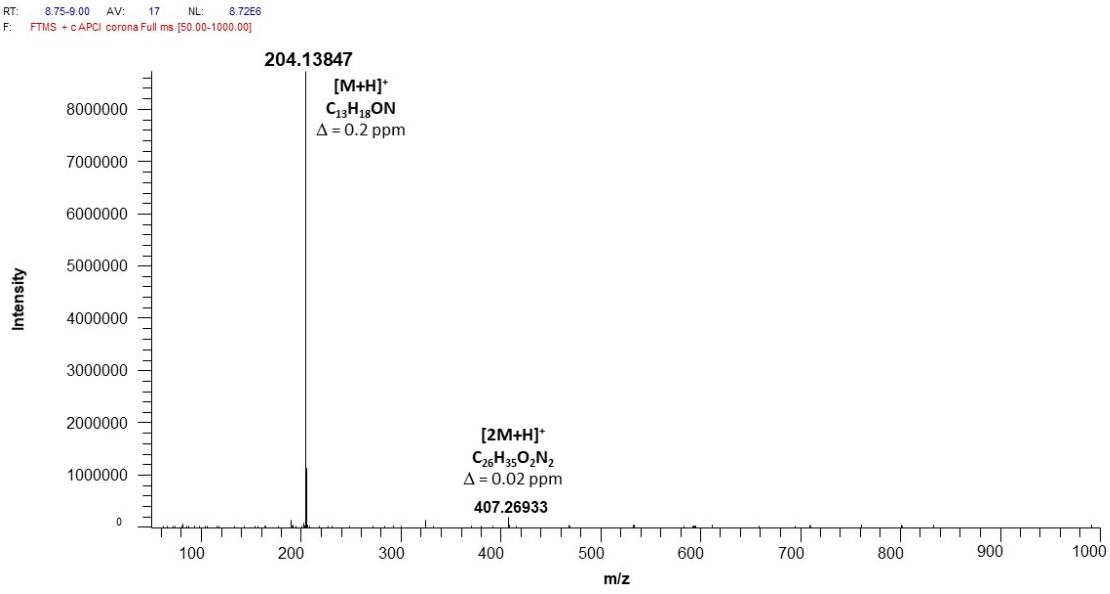


Figure S33: HR-MS(APCI) spectrum of N-(3-methylbenzoyl)-piperidine (**4db**)

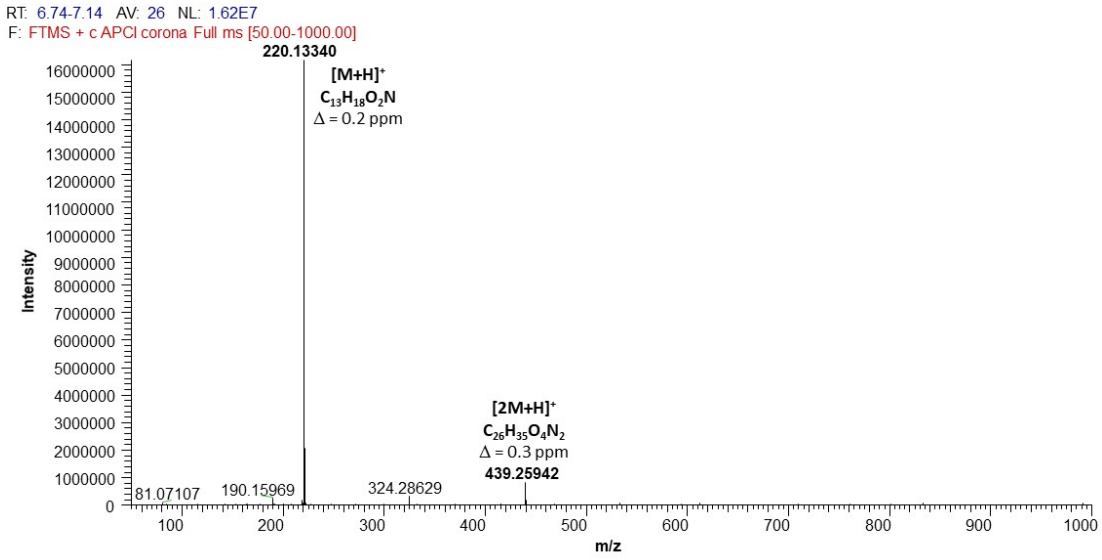


Figure S34: HR-MS(APCI) spectrum of N-(4-methoxybenzoyl)-piperidine (**4eb**)

S 4. Literature

1 D. Pedersen and C. Rosenbohm, *Synthesis (Stuttg).*, 2004, **2001**, 2431–2434.

2 D. Vogelsang, J. Vondran, K. Hares, K. Schäfer, T. Seidensticker and A. J. Vorholt, *Adv. Synth. Catal.*, 2020, **362**, 679–687.

3 A. D. Jorgensen, K. C. Picel and V. C. Stamoudis, *Anal. Chem.*, 1990, **62**, 683–689.

4 H. Neumann, A. Brennführer, P. Groß, T. Riermeier, J. Almena and M. Beller, *Adv. Synth. Catal.*, 2006, **348**, 1255–1261.