Supplementary information

for

Desaturative arylaldehyde synthesis by synergistic carbocatalysis and organocatalysis

Naokatsu Kannari[a, b*], Ivan Curic[b], Nina Place[b], Lukas Enders[b], Shotaro Kawasaki[a], Anna Lenarda[b*] and Juho Helaja[b*]

a) Division of Environmental Engineering Science, Graduate School of Science and Technology, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515, Japan.
b) Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, P.O. Box 55, 000014, Helsinki (Finland).

Corresponding authors:
Juho Helaja: juho.helaja@helsinki.fi
Naokatsu Kannari: nkannari@gunma-u.ac.jp
Anna Lenarda: anna.lenarda@helsinki.fi

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General remarks

If not described differently, all reactions were performed under air and at RT (18 - 20 °C). Reactions sensitive to water or oxygen were kept under an inert atmosphere of dry argon, handling them with Schlenk-technique with syringe and septum in absolute and degassed solvents dried on 3Å molecular sieves prior use. All HPLC-grade solvents were used without further purification as obtained from the supplier (Honeywell, VWR, Merck, Sigma Aldrich). Distilled water was produced with an Aquatron AS4 (Bibby). All commercially available reagents were used without further purification as obtained from the supplier. Column chromatography was executed with pressurized air and at RT over silica gel (pore size 40 - 63 µm, VWR). All NMR spectra were measured at a sample temperature of 293 K. The following devices were used: Avance Neo 500 (Bruker, 500 MHz), Avance Neo 400 (Bruker, 400 Mhz). The chemical shift δ in parts per million (ppm) is relative to the shift of tetramethylsilane (δ = 0 ppm) in both ^{1}H and ^{13}C NMR spectra. The spectra were calibrated to the residual proton or carbon shifts of the corresponding deuterated solvents (^{1}H-NMR: $CDCl_3$ 7.26 ppm, DMSO-d_6: 2.50, ^{13}C-NMR: $CDCl_3$ 77.16 ppm, DMSO-d_6: 39.52). NMR yields were determined with 1,3,5-trimethoxybenzene as an internal standard using a pulse-width of pw = 3.33 µs and a relaxation delay of d1 = 35 s. High-resolution mass spectra (HRMS) were obtained using a JEOL MStation JMS-700 (EI) instrument.

Preparation of oxidized activated carbon materials

Activated carbon (AC, DARCO ~100 mesh particle size, powder) was oxidized with concentrated HNO_3 according to a previously reported procedure. [1] To remove residual metal impurities, AC was first washed with 12 M HCl to obtain demetallized AC (AC_{dm}). Then, AC_{dm} was then added to the concentrated HNO_3, and the mixture was stirred for 140 °C for 3 h. Subsequently, the mixture was dried in vacuum at 140 °C for 6 h. The oxidized AC was denoted as oAC_{HNO3}.

To prepare reference materials with reduced oxygen functionalities, AC_{dm} and oAC_{HNO3} were further heat-treated at 1000 °C under a N_2 stream without holding the temperature to obtain HT-AC_{dm} and HT-oAC_{HNO3}, respectively.

XPS analysis

The surface composition and chemical states of the carbon samples were evaluated by X-ray photoelectron spectroscopy (XPS; Kratos AXIS NOVA, Shimadzu Corp.) using Al Kα radiation (15 kV, 10 mA). The samples were fixed to an aluminum plate with conductive carbon tape. The charge-up shift correction of the binding energy was performed using the C1s binding energy at 284.5 eV. The O1s spectra were deconvoluted into the five peaks according to reported procedure.[2]

Table S1 XPS analysis of AC and oAC_{HNO3}: Atomic concentrations (%)

Sample	Atomic concentration (%)		O/C
	C	O	
AC	93.1	6.9	0.074
oAC_{HNO3}	82.2	17.8	0.217

Table S2 XPS analysis of AC and oAC$_{HNO3}$: summary of O1s deconvolutions.

Sample	Ratio (%)				
	C=O	C-OH	C-O esters, anhydrides	O-C=O	H_2O
	531.5±0.5 eV	532.3±0.5 eV	533.3±0.5 eV	534.2±0.5 eV	535.9±0.5 eV
AC	7.7	34.7	28.9	20.7	8.0
oAC$_{HNO3}$	14.9	31.1	26.8	19.2	8.1

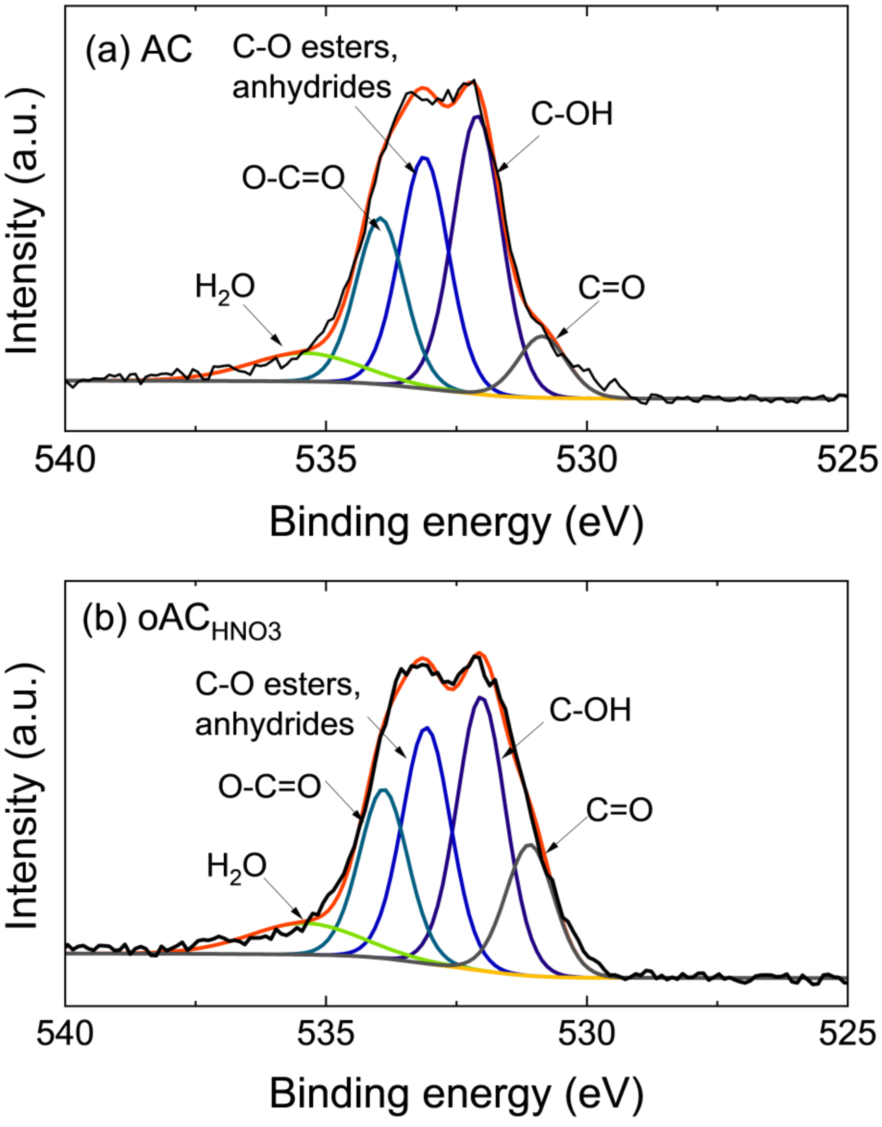


Fig. S1 O1s XPS scan of (a) AC and (b) oAC$_{HNO3}$

TPD measurements

Temperature programmed desorption (TPD) measurement was conducted by heating the carbons from rt to 1000 °C in a He stream. During the heat treatment, desorbed CO and CO_2 (m/z = 28 and 44) were detected by a quadrupole mass spectrometer (Pfeiffer Vacuum, QMG250 PrismaPro) and collected in a gas bag for off-line GC analysis to determine the CO and CO_2 amounts.

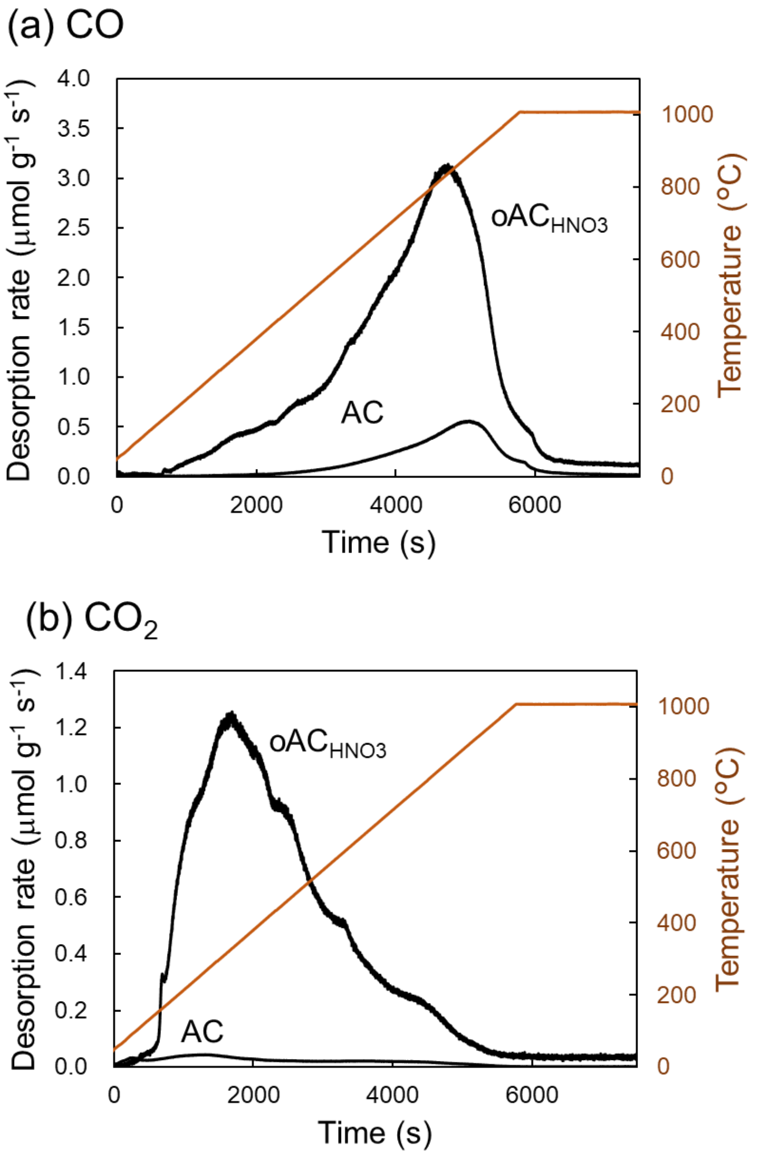


Fig. S2 TPD profiles of (a) CO and (b) CO_2

Table S3 Desorption amounts of CO and CO_2

Sample	**TPD**	
	CO (mmol g^{-1})	**CO_2 (mmol g^{-1})**
AC	0.96	0.13
oAC_{HNO3}	6.83	2.87

Optimization of reaction conditions

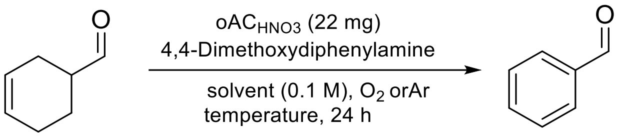


Table S4 Screening of reaction conditions

T (°C)	Amine amount (%)	Solvent	Atmosphere	Product yield[1)] (%)	SM conversion[1)] (%)
60	30	Toluene	O_2	26	48
90	30	Toluene	O_2	70	90
110	30	Toluene	O_2	90	>99
90	10	Toluene	O_2	49	77
90	20	Toluene	O_2	60	87
90	60	Toluene	O_2	71	>99
90	100	Toluene	O_2	74	>99
90	30	Toluene	Ar	36	55
90	30	Toluene	air	43	65
60	30	Acetonitrile	O_2	22	42
60	30	o-Dichlorobenzene	O_2	21	37
60	30	N,N-Dimethylformamide	O_2	10	15

1) determined by GC

Chemical blocking of functional groups

Carbonyl groups were converted to phenylhydrazones with phenyl hydrazine.[3] Phenyl hydrazine (0.4 g, 3.7 mmol) was dissolved to deoxygenated chloroform (20 mL). oAC$_{HNO3}$ (0.2 g) was added to the solution and mixture was stirred at room temperature for 72 h. To remove unreacted phenyl hydrazine, modified carbocatalyst was Soxhlet extracted for 20 h. Product was dried at 60 °C under vacuum for 24 h.

Phenolic hydroxyl groups were esterified with benzoic anhydride.[3] Benzoic anhydride (1.0 g, 4.4 mmol) was dissolved to deoxygenated chloroform (10 mL), after which oAC$_{HNO3}$ (0.2 g) was added. Mixture was stirred at 60 °C for 24 hours. Modified carbocatalyst was filtered and washed with chloroform (400 mL). Product was dried at 60 °C under vacuum for 24 hours.

Carboxylic acids were esterified with 2-bromo-1-phenylethanone.[3] oAC$_{HNO3}$ (0.2 g) and 2-bromo-1-phenylethanone (0.4 g, 2.0 mmol) were mixed in deoxygenated chloroform (10 mL). Mixture was stirred for 5 hours protected from light. Modified carbocatalyst was filtered and washed with chloroform (400 mL). Product was dried at 60 °C under vacuum for 24 h.

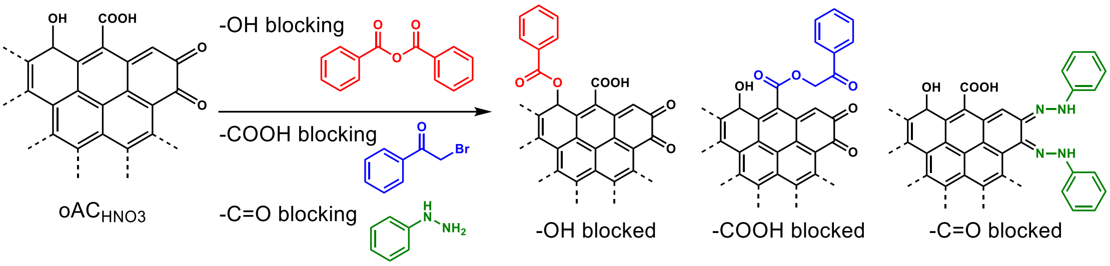


Fig. S3 Selective blocking of oxygen functionalities on oAC$_{HNO3}$

Table S5 XPS analysis of blocked carbons: summary of O1s deconvolutions

Sample	**Ratio (%)**				
	C=O	**C-OH**	**C-O esters, anhydrides**	**O-C=O**	**H_2O**
	531.5±0.5 eV	532.3±0.5 eV	533.3±0.5 eV	534.2±0.5 eV	535.9±0.5 eV
oAC$_{HNO3}$	14.9	31.0	26.8	19.2	8.1
OH blocked-oAC$_{HNO3}$	13.1	27.1	30.1	18.9	10.8
COOH blocked-HNO_3- oAC$_{HNO3}$	16.3	27.8	28.6	16.3	11.0
C=O blocked- oAC$_{HNO3}$	10.7	28.5	28.7	22.6	9.5

Table S6 XPS analysis of blocked carbons: atomic XPS concentrations

Sample	**Atomic concentration (%)**		
	C	O	N
oAC$_{HNO3}$	82.6	17.4	–$^{1)}$
OH blocked-oAC$_{HNO3}$	82.8	17.3	–$^{1)}$
COOH blocked-oAC$_{HNO3}$	83.8	16.2	–$^{1)}$
C=O blocked-oAC$_{HNO3}$	84.2	13.8	1.91

1) Not measured

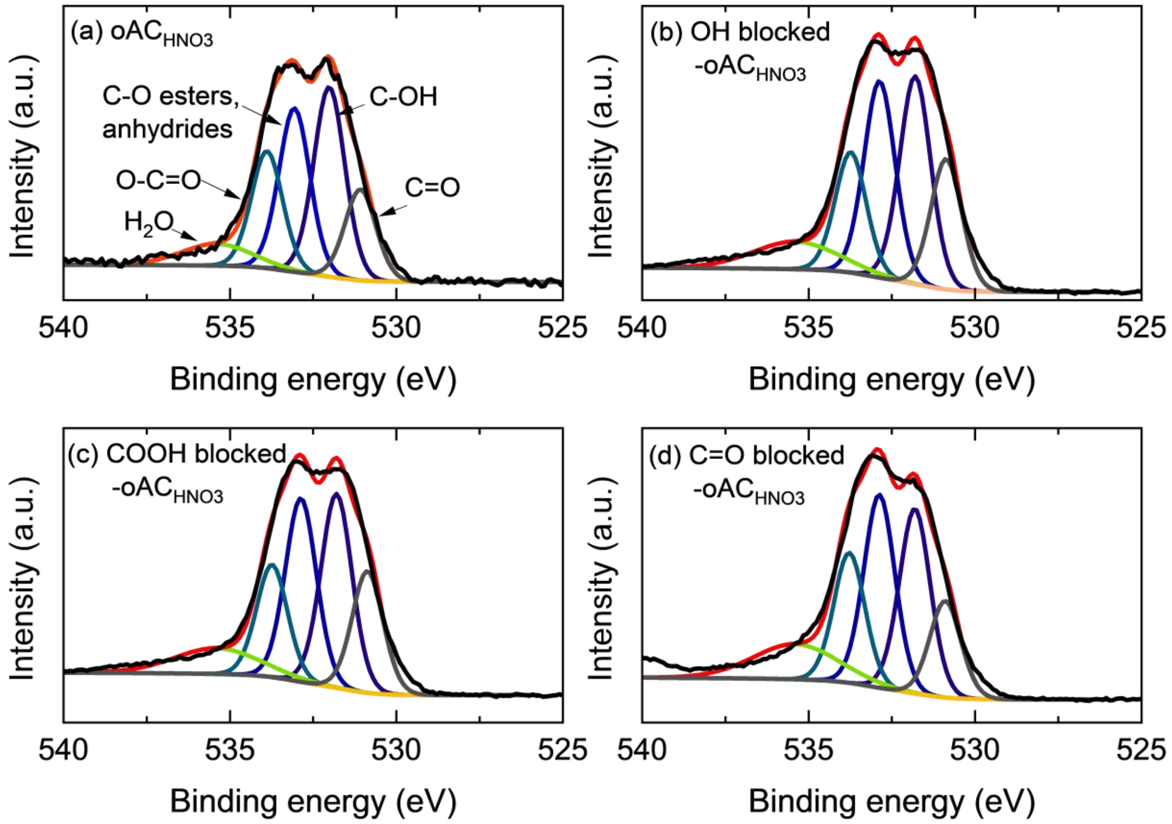


Fig. S4 O1s XPS scan of (a) oAC$_{HNO3}$, (b) OH blocked-oAC$_{HNO3}$, (c) COOH blocked oAC$_{HNO3}$ and (d) C=O blocked-oAC$_{HNO3}$

Catalytic tests

General method

In a typical procedure, carbon catalyst (22 mg), cyclohexene aldehyde (0.1 mmol), secondary amine (30 mol%), and solvent (1 ml, 0.1 M) were added to a glass vial. Atmosphere was exchanged to O_2 and the reaction mixture was stirred at 90 °C for 24 hours. After the reaction, the solid catalyst was separated using a Celite pad or a PTFE membrane and subsequently washed with approximately 40 ml of dichloromethane. Solvent was removed under reduced pressure, and the crude was analyzed using ^{1}H NMR or gas chromatography-flame ionization detector (GC-FID), with 1,3,5-trimethoxybenzene serving as the internal standard to calculate the yield of the reaction

Radical-trapping experiments were conducted by adding TEMPO or 4-oxo-TEMPO (0.05 mmol) to the standard reaction mixture (oAC$_{HNO3}$ (22 mg), **1a** (0.1 mmol), and **A6** (30 mol%) in 1 ml toluene) and following the general method.

Recycling test

oAC_{HNO3} (22 mg), Cyclohex-3-ene-1-carbaldehyde (**1a**, 0.1 mmol), bis(4-methoxyphenyl)amine (**A6**, 30 mol%), and toluene (1 mL, 0.1 M) were added to a test tube. The atmosphere in the tube was then exchanged to O_2, and the reaction mixture was stirred at 90°C for 24 hours. After the reaction, the solid catalyst was recovered by filtration through a PTFE membrane and washed with dichloromethane (40 mL). The recovered catalyst was reused for subsequent runs following the same procedure. This recycling process was repeated for five cycles. The yields were determined by gas chromatography using 1,3,5-trimethoxybenzene as an internal standard. In addition to the yield, the amine recovery (%) was calculated based on the amount of recovered amine relative to the initial amount. To investigate the influence of adsorbed amines on the activity and pore structure, a separate experiment was conducted where the catalyst recovered after 1st cycle was washed with acetic acid (AcOH) before being reused for the 2nd run.

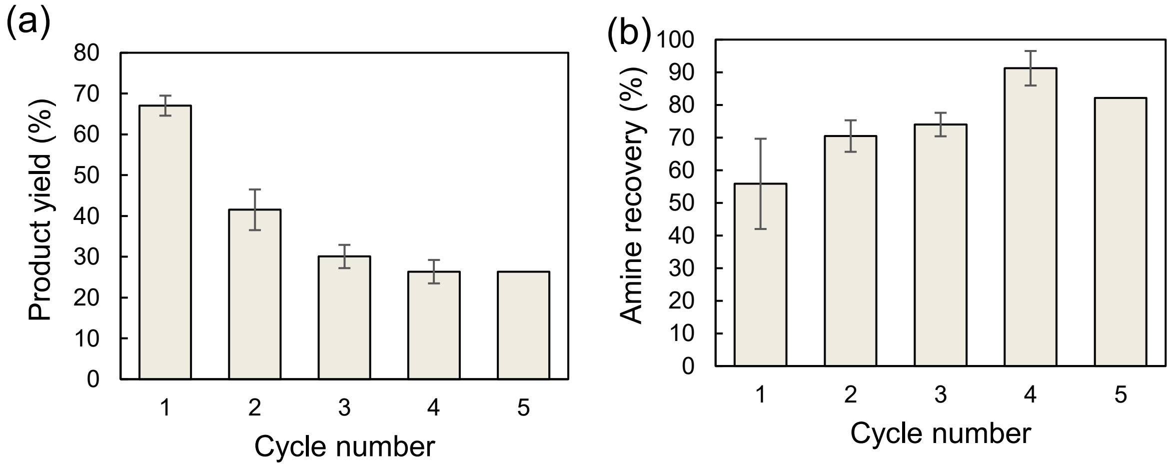


Fig. S5 Results of recycling test, (a) product yield and (b) amine recovery.

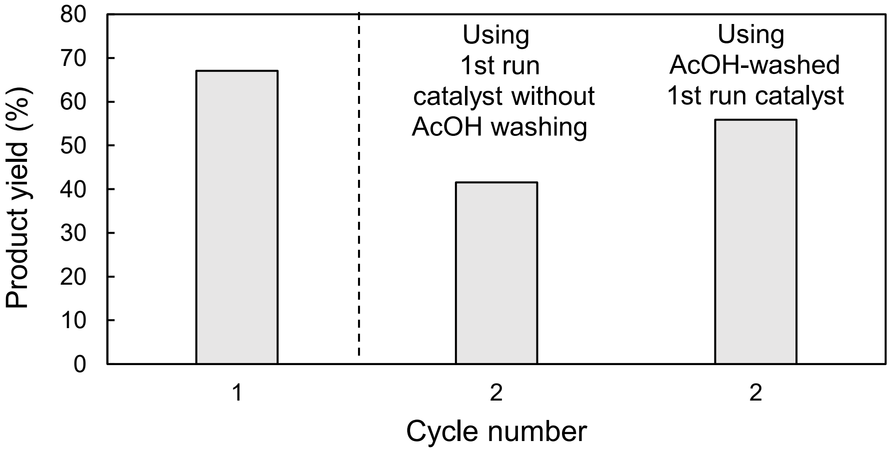


Fig. S6 Effect of acetic acid (AcOH) washing of the used oAC_{HNO3} on the product yield.

Table S7 XPS analysis of oAC_{HNO3} before and after one catalytic cycle: Atomic concentrations (%).

Sample	Atomic concentration (%)		O/C
	C	O	
oAC_{HNO3}	82.6	17.4	0.211
oAC_{HNO3} after 1st cycle	83.2	16.8	0.202

Table S8 XPS analysis of oAC_{HNO3} before and after one catalytic cycle: summary of O1s deconvolutions

Sample	Component (%)				
	C=O	C-OH	C-O esters, anhydrides	O-C=O	H_2O
	531.5±0.5 eV	532.3±0.5 eV	533.3±0.5 eV	534.2±0.5 eV	535.9±0.5 eV
oAC_{HNO3}	14.9	31.0	26.8	19.2	8.1
oAC_{HNO3} after 1st cycle	10.3	28.6	28.6	25.0	7.6

BET and pore volume analysis of fresh and used oAC_{HNO3}

Specific surface area (S_{BET}), mesopore volume (V_{meso}) and micropore volume (V_{micro}) of oAC_{HNO3} both before and after the catalytic tests were determined from N_2 adsorption isotherms at 77 K (BELSORP MAX, MicrotracBell corp.). Prior to the measurement, the samples were pretreated at 200 °C for 2 h under vacuum to remove adsorbed water. S_{BET}, V_{meso} and V_{micro} were calculated using Brunauer - Emmett – Teller, Barrett-Joyner-Halenda(BJH) and Dubinin-Astakhov (DA) methods, respectively.

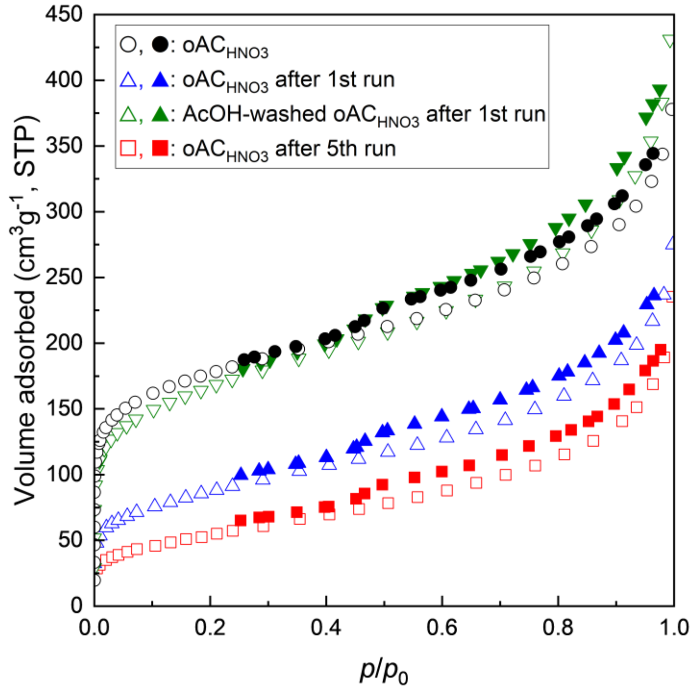


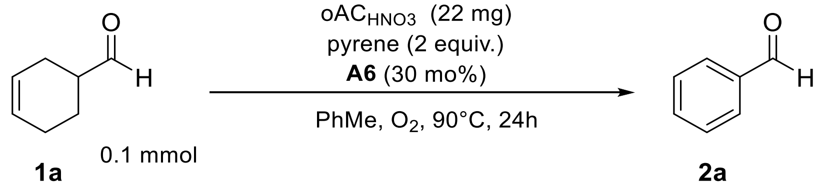
Fig. S7 Adsorption-desorption isotherms of fresh oAC$_{HNO3}$ and the recovered oAC$_{HNO3}$ samples. Open and filled symbols represent the adsorption and desorption branches, respectively.

Table S9 S_{BET}, V_{micro} and V_{meso} of the fresh oAC$_{HNO3}$ and used oAC$_{HNO3}$

	S_{BET} (m^2 g^{-1})	$V_{micro}$$^{2)}$ (cm^3 g^{-1})	$V_{meso}$$^{3)}$ (cm^3 g^{-1})
oAC$_{HNO3}$	635	0.24	0.30
oAC$_{HNO3}$ after 1st cycle	313	0.11	0.26
oAC$_{HNO3}$ after 1st cycle washed with AcOH	598	0.22	0.38
oAC$_{HNO3}$ after 5th cycle$^{1)}$	194	0.07	0.22

1) Sample was heat-treated at 300 °C for 3h between 4th and 5th cycles
2) Calculated by DA method
3) Calculated by BJH method

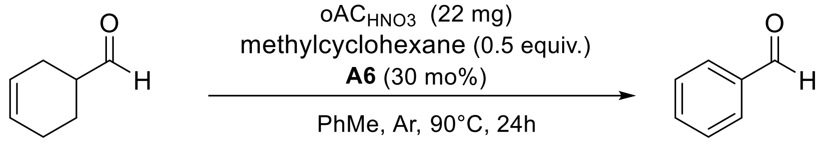
Pore blocking tests



1a
[110.15]

2a
[110.15]

Cyclohex-3-ene-1-carbaldehyde (**1a,** 11 mg, 0.1 mmol, 1.0 equiv.), bis(4-methoxyphenyl)amine (**A6**, 6.8 mg, 0.03 mmol, 30 mol%) and oAC$_{HNO3}$ (22.0 mg) were added to a glass vial together with pyrene (2.0 equiv.). Toluene (1 mL) and a magnetic stir bar were added. The atmosphere was exchanged to pure oxygen, and the mixture was stirred at 90 °C for 24 h. The mixture was cooled down and filtered, then the solid was washed with 40 ml of DCM. The yield was determined by gas chromatography-flame ionization detector (GC-FID) using 1,3,5-trimethoxybenzene as an internal standard.



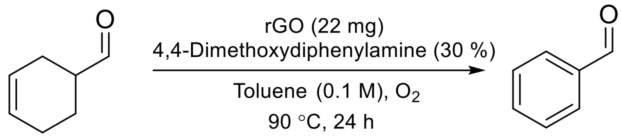
1a
[110.15]

2a
[110.15]

Cyclohex-3-ene-1-carbaldehyde (**1a,** 11 mg, 0.1 mmol, 1.0 equiv.), bis(4-methoxyphenyl)amine (**A6**, 6.8 mg, 0.03 mmol, 30 mol%) and oAC_{HNO3} (22.0 mg) were added to a glass vial together with methylcyclohexane (0,5 equiv.). Toluene (1 mL) and a magnetic stir bar were added. The atmosphere was exchanged to argon, and the mixture was stirred at 90 °C for 24 h. The mixture was cooled down and filtered, then the solid was washed with 100 ml of DCM. The yield was determined by NMR, obtained yield was 32% **2a** (50% conversion).

With the same procedure, using decalin instead of methylcyclohexane, the yield obtained was 24% **2a** and 60% **1a**, while using betulin for the same purpose the reaction yielded 25% **2a** (41% conversion). Reference test under Ar in the absence of additives yielded 36% **2a** and 55% conversion (see Table S4) indicating substantial pore blocking with nonaromatic compounds.

Reaction with reduced graphene oxide



1a
[110.15]

2a
[106.12]

Reaction was conducted in 10 ml glass tubes, capped with Biotage cap with septa, reduced graphen oxide was (rGO) was purchased from Nanografi (Purity: 99%, S.A:1562 m2/g, 2-5 layers). Cyclohex-3-ene-1-carbaldehyde (11 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (6.9 mg, 0.03 mmol, 0.3 eq), rGO (22 mg) were measured, to which was added 1 ml of PhMe and a stir bar. Tube was capped and sonicated for 5 minutes, the atmosphere was exchanged with pure oxygen from a prefilled ballon. Tube was lowered in a 90 ^{0}C oil bath and the contents were stirred for 24 h. Filtration of the cooled reaction mixture through a celite pad was performed to remove the carbon as well as washing with 100 ml of DCM. Volatiles were removed under reduced pressure. NMR yield showed 1% 2a and 80% 1a.

Effect of radical inhibitor and catalyst regeneration

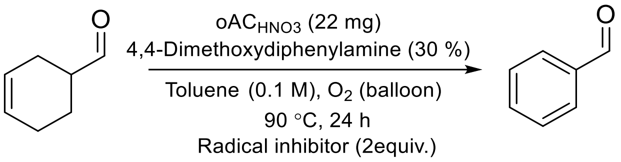
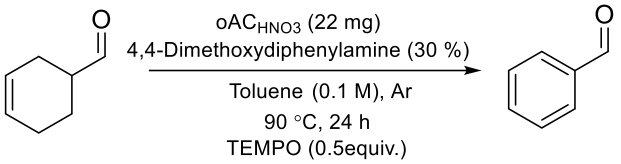


Table S10 Effect of radical inhibitor

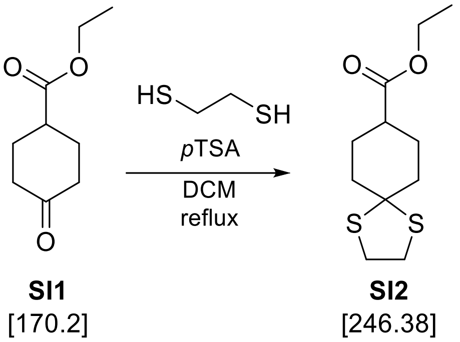
Radical inhibitor	**Product yield (%)**	**SM conversion (%)**
None	70	90
TEMPO	44	78
2-Oxo-TEMPO	39	88



Cyclohex-3-ene-1-carbaldehyde (**1a,** 11 mg, 0.1 mmol, 1.0 equiv.), bis(4-methoxyphenyl)amine (**A6**, 6.8 mg, 0.03 mmol, 30 mol%) and oAC$_{HNO3}$ (22.0 mg) were added to a glass vial together with TEMPO (0,5 equiv.). Toluene (1 mL) and a magnetic stir bar were added. The atmosphere was exchanged to argon, and the mixture was stirred at 90 °C for 24 h. The mixture was cooled down and filtered, then the solid was washed with 100 ml of DCM. The yield was determined by NMR, obtained yield was 16% **2a** and 56% **1a**.

Synthesis of starting materials

ethyl 1,4-dithiaspiro[4.5]decane-8-carboxylate (SI2)[4]

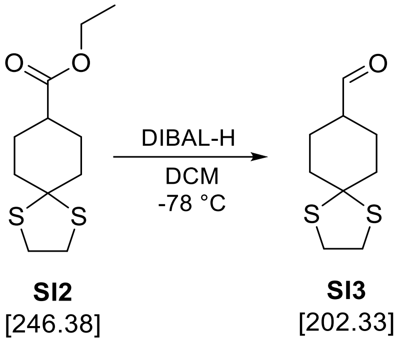


Ethyl 4-oxocyclohexane-1-carboxylate **(SI1)** (936 µL ,1 g, 5.88 mmol, 1 eq), pTSA (280 mg, 1.47 mmol, 0.25 eq) and ethane-1,2-dithiol (591 µL, 664 mg, 7.05 mmol, 1.2 eq) were dissolved in 90 ml CH_2Cl_2 and refluxed for 24 hours. Mixture was neutralized with 2 M KOH (50 ml) and extracted with EtOAc (100 ml). Organic phase was washed with brine (20 ml) and dried over $MgSO_4$. Crude was purified by flash column chromatography (Hex/EtOAc 98/2 → 9/1) providing ethyl 1,4-dithiaspiro[4.5]decane-8-carboxylate **(SI2)** (1.2559 g, 5.1 mmol, 87%)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.13 (q, *J* = 7.1 Hz, 2H), 3.34 – 3.25 (m, 4H), 2.30 (m, 1H), 2.22 – 2.13 (m, 2H), 2.03 – 1.90 (m, 4H), 1.86 – 1.73 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.2, 67.8, 60.5, 41.5, 39.0, 38.4, 28.5, 14.4.

1,4-dithiaspiro[4.5]decane-8-carbaldehyde (SI3)[5]



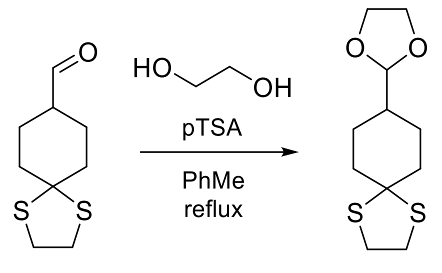
All the glassware used was oven dried overnight, dry DCM was from the VAC solvent purifier system, the reaction was carried out under argon and cooled with acetone/dry-ice bath. Ethyl 1,4-dithiaspiro[4.5]decane-8-carboxylate **(SI2)** (1.15 g, 4.67 mmol, 1 eq) was dissolved in DCM and cooled to -78 °C. 1.2 M DIBAL-H in toluene (4.08 ml, 4.9 mmol, 1.05 eq) was added dropwise with a syringe. After the addition the mixture was left to stir at -78 °C for 2 hours. 1 ml of dry EtOAc was added dropwise and the reaction was lifted from the dry-ice bath and left to heat up to 0 °C. Saturated solution of sodium potassium tartrate (50 ml) was slowly added at 0 °C after which the reaction was stirred for additional 30 minutes. Extraction was performed with 300 ml of DCM followed by 100 ml brine wash and drying over $MgSO_4$. Crude was purified by flash column chromatography (Hex/EtOAc 95/5 → 8/2) providing a colorless oil 1,4-dithiaspiro[4.5]decane-8-carbaldehyde **(SI3)** (601.6 mg, 2.97 mmol, 64%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.64 (s, 1H), 3.30 (m, 4H), 2.30 – 2.13 (m, 3H), 2.03 – 1.92 (m, 4H), 1.81 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 203.9, 67.7, 48.2, 41.0, 38.9, 38.5, 25.5.

HRMS (**ESI$^+$**): Exact mass calculated for $C_9H_{14}OS_2$ (M)$^+$: 202.0486, found: 202.0478

2-(1,4-dithiaspiro[4.5]decan-8-yl)-1,3-dioxolane (SI4)[6]



SI3 [202.33] **SI4** [246.38]

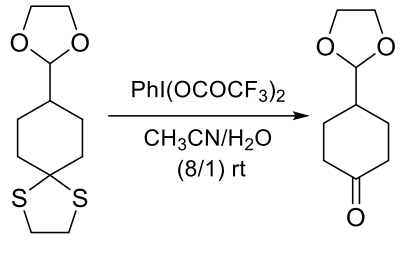
1,4-dithiaspiro[4.5]decane-8-carbaldehyde **(SI3)** (4.98 g, 24.61 mmol, 1 eq), 1,2-ethanediol (27.40 ml, 30.55 g, 492.2 mmol, 20 eq) and *p*TSA (230 mg, 1.23 mmol, 0.05 eq) were dissolved in 200 ml of toluene. The mixture was refluxed with a Dean-Stark trap attached for 5 hours. Reaction was quenched with a saturated solution of $NaHCO_3$ (150 ml) followed by extractions with DCM (300 ml). The organic phase was first washed with water (200 ml) and brine (50 ml) then dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 9/1 → 8/2) providing a colourless oil 2-(1,4-dithiaspiro[4.5]decan-8-yl)-1,3-dioxolane **(SI4)** (5.5962 g, 22.71 mmol, 92%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.61 (d, *J* = 4.9 Hz, 1H), 3.98 – 3.77 (m, 4H), 3.34 – 3.21 (m, 4H), 2.17 (d, *J* = 13.5 Hz, 2H), 1.97 – 1.76 (m, 1H), 1.59 – 1.35 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 106.95, 68.40, 65.09, 41.89, 40.43, 38.91, 38.18, 26.91.

HRMS (**ESI$^+$**): Exact mass calculated for $C_{11}H_{18}O_2S_2$ (M)$^+$: 246.0748, found: 246.0753

4-(1,3-dioxolan-2-yl)cyclohexan-1-one (SI5)[4]



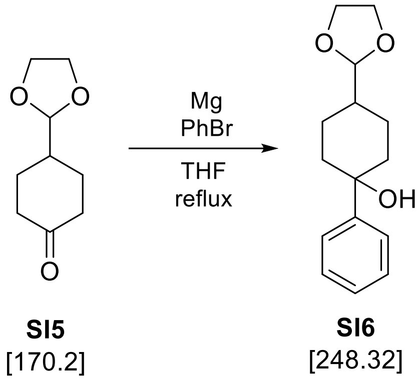
SI4 [246.38] **SI5** [170.2]

1,4-dithiaspiro[4.5]decane-8-carbaldehyde **(SI4)** (5.5 g, 22.3 mmol, 1 eq) was dissolved in a mixture of CH_3CN (120 ml) a water (15 ml). Phenyl iodine bis(trifluoroacetate) (22.1 g, 51.3 mmol, 2.3 eq) was added at once, the reaction was stirred for a minute and then quenched with saturated solution of $NaHCO_3$ (150 ml). Aqueous phase was extracted with EtOAc (750 ml), combined organic phases were washed with brine (100 ml) and dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 9/1 → 6/4) providing a pale-yellow oil 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** (3.1842 g, 18.7 mmol, 84%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.74 (d, *J* = 4.8 Hz, 1H), 4.03 – 3.82 (m, 4H), 2.51 – 2.39 (m, 2H), 2.39 – 2.26 (m, 2H), 2.19 – 2.07 (m, 2H), 2.07 – 1.94 (m, 1H), 1.69 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 211.63, 106.29, 65.27, 40.39, 39.99, 26.98.

4-(1,3-dioxolan-2-yl)-1-phenylcyclohexan-1-ol (SI6)

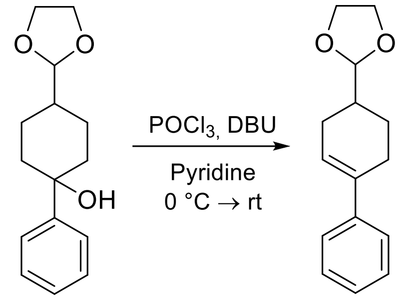


All the glassware used was oven dried overnight, dry THF was from the VAC solvent purifier system, and the reaction was carried out under argon. Magnesium turnings (189 mg, 7.76 mmol, 2.2 eq) were added to a round bottom flask along with 12 ml of THF. Bromobenzene (389 µL, 581mg, 3.7 mmol, 1.05 eq) was slowly added with a syringe, and an iodine crystal was added to start the reaction. Reaction was refluxed for 30 minutes and then the 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** (600 mg, 3.53 mmol, 1 eq) was added slowly and reflux was continued for additional 4 hours. Reaction was cooled to room temperature and quenched with 30 ml of NH$_4$Cl saturated solution. Extraction was performed three times with 30 ml EtOAc, combined organic layers were then neutralized with 30 ml 1 M NaOH, washed with brine and dried with MgSO$_4$. Crude product was purified by flash chromatography (Hex/EtOAc 8/2 → 1/1) providing 4-(1,3-dioxolan-2-yl)-1-phenylcyclohexan-1-ol **(SI6)** (328 mg, 1.32 mmol, 37%).

^{1}H NMR (400 MHz, CDCl3): δ = 7.49 – 7.39 (m, 2H), 7.28 (q, J = 7.6 Hz, 2H), 7.24 – 7.13 (m, 1H), 4.66 – 4.60 (m, 1H), 3.96 – 3.69 (m, 4H), 2.39 – 2.28 (m, 1H), 1.88 – 1.52 (m, 8H), 1.38 – 1.25 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 149.4, 128.6, 128.4, 127.4, 126.9, 125.8, 124.6, 107.4, 106.6, 73.4, 72.9, 65.1, 65.0, 41.1, 39.5, 38.1, 36.7, 24.0, 22.8.

2-(2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-yl)-1,3-dioxolane (SI7)[7]



SI6
[248.32]

SI7
[230.3]

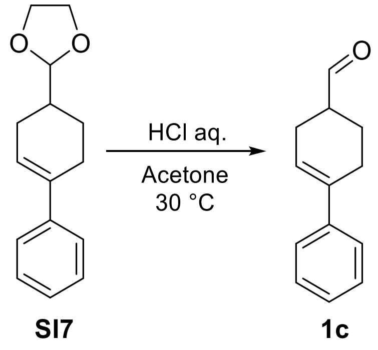
All the glassware used was oven dried overnight, pyridine was dried with molecular sieves (4Å) and the reaction was carried out under argon. 4-(1,3-dioxolan-2-yl)-1-phenylcyclohexan-1-ol **(SI6)** (328 mg, 1.32 mmol, 1 eq) was dissolved in 5 ml of pyridine. $POCl_3$ (492 µL, 810 mg, 5.28 mmol, 4 eq) was added with a syringe at 0 °C followed by the addition of DBU (197 µL, 201 mg, 1.32 mmol, 1 eq). The reaction mixture was stirred at room temperature for 5 h. Quenching was performed with 20 ml of water and extraction with 50 ml of EtOAc, followed by three water washings (90 ml) and a brine wash (30 ml). Organic layer was dried with $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 75/25) providing 2-(2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-yl)-1,3-dioxolane **(SI7)** (213.8 mg, 0.93 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.5 Hz , 2H), 7.30 (t, *J* = 6.8 Hz, 2H), 7.22 (t, *J* = 7.3 Hz , 1H), 6.16 – 6.08 (m, 1H), 4.77 (d, *J* = 5.3 Hz, 1H), 4.05 – 3.83 (m, 4H), 2.58 – 2.40 (m, 2H), 2.41 – 2.30 (m, 1H), 2.19 – 1.99 (m, 2H), 1.90 (m, 1H), 1.62 – 1.47 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.24, 136.65, 128.36, 126.81, 125.12, 123.45, 107.25, 65.15, 37.63, 26.99, 26.91, 24.06.

HRMS (**ESI$^+$**): Exact mass calculated for $C_{15}H_{18}O_2$ $(M)^+$: 230.1307, found: 230.1298

4-Phenyl-3-cyclohexene-1-carboxaldehyde (1c)



SI7
[230.3]

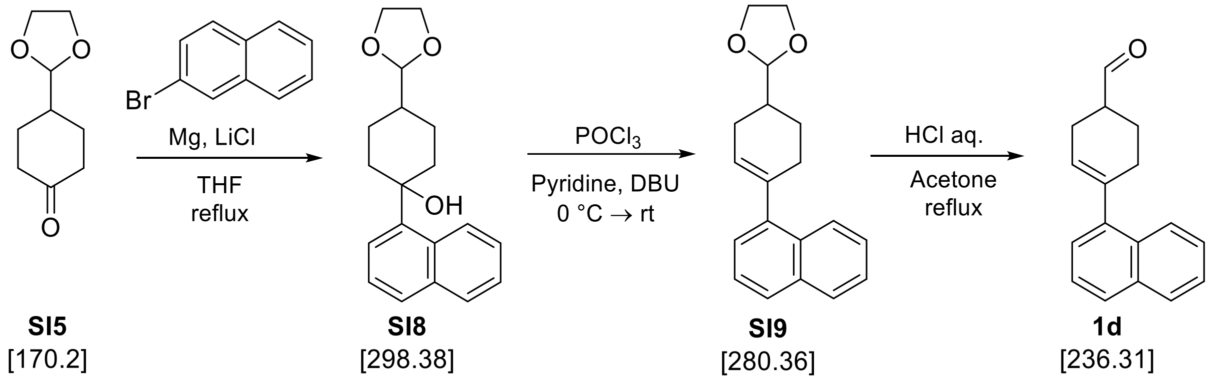
1c
[186.25]

2-(2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-yl)-1,3-dioxolane **(SI7)** (100mg, 0.434 mmol) was dissolved in acetone (3 ml). Mixture of water (1.5 ml) and concentrated HCl (0.5 ml) were added as well. Reaction was stirred for 24 h at 30 °C. Quenching was performed with saturated solution of $NaHCO_3$ (30 ml), the aqueous layer was extracted three times with a total of 90 ml EtOAc. Organic phases were combined then washed with brine and dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 9/1) providing 4-Phenyl-3-cyclohexene-1-carboxaldehyde **(1c)** (78.7 mg, 0.27 mmol, 75%)

^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.77 (s, 1H), 7.37-7.22 (m, 5H), 6.13 (m, 1H), 2.62-2.46 (m, 5H), 2.20-2.15 (m, 1H), 1.88-1.80 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$): δ = 204.4, 141.8, 137.0, 128.4, 127.1, 125.2, 122.2, 45.9, 26.2, 25.2, 22.8.

4-(naphthalen-1-yl)cyclohex-3-ene-1-carbaldehyde (1d)



The product 4-(naphthalen-1-yl)cyclohex-3-ene-1-carbaldehyde **(1d)** was obtained from 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** without isolation of the intermediary products in steps 1 and 2. In steps 2 and 3 reagents were used in excess based on the theoretical yield from the previous steps.

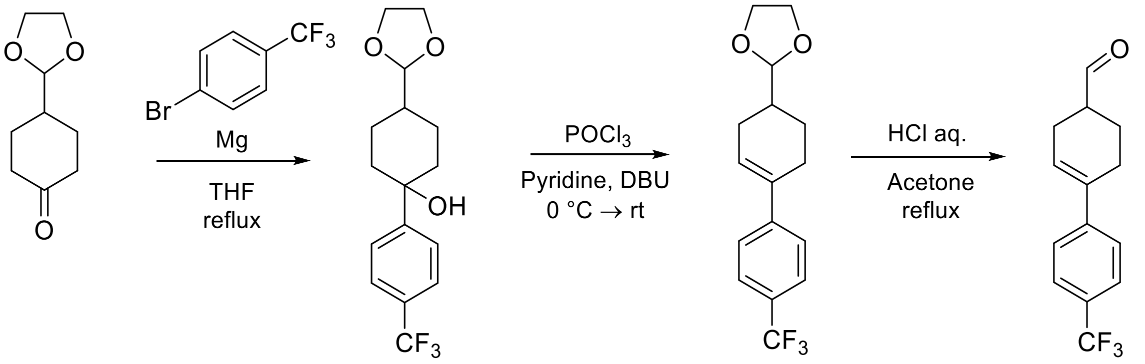
1. **Step:** All the glassware used was oven-dried overnight, dry THF was from the VAC solvent purifier system and the reaction was carried out under argon. Lithium chloride was dried under vacuum at 110 ^{0}C. Magnesium turnings (106.9 mg, 4.4 mmol, 1.15 eq) and lithium-chloride (169.5 mg, 4.0 mmol, 1.05 eq) were added to a round bottom flask along with 5 ml of THF. 2-bromonaphthalene (560 µL, 828.2 mg, 4.0 mmol, 1.05 eq) was slowly added with a syringe, and an iodine crystal was added to start the reaction. Reaction was stirred for 30 minutes at room temperature and then the 4-(1,3-dioxolan-2-yl)cyclohexan-1-one (646.9 mg, 3.8 mmol, 1 eq) was added slowly and refluxed for further 3 hours. Reaction was cooled down to room temperature and quenched with 30 ml of NH_4Cl saturated solution. Extraction was performed three times with 50 ml EtOAc, combined organic layers were washed with brine (50 ml) and dried with $MgSO_4$.
2. **Step:** All the glassware used was oven dried overnight, pyridine was dried with molecular sieves (4Å) and the reaction was carried out under argon. Crude (1 eq) from the previous step was dissolved in 20 ml of pyridine. $POCl_3$ (1.25 ml, 2.0570 g, 13.4 mmol, 4 eq) was added with a syringe at 0 °C followed by the addition of DBU (500 µL, 510 mg, 3.35 mmol, 1 eq). The reaction mixture was stirred at room temperature for 6 h. Quenching was performed with 50 ml of water and extraction with 150 ml EtOAc, followed by three water washings (150 ml) and a brine wash (50 ml). Organic layer was dried with $MgSO_4$.
3. **Step:** Crude (1 eq) was dissolved in acetone (28 ml). A mixture of water (15 ml) and concentrated HCl (4 ml) was added, and the reaction was refluxed for 24 h. Quenching was performed with saturated solution of $NaHCO_3$ (30 ml), the aqueous layer was extracted three times with a total of 150 ml EtOAc. Combined organic phases were then washed with brine and dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 95/5) providing a colorless oil 4-(naphthalen-1-yl)cyclohex-3-ene-1-carbaldehyde **(1d)** (275 mg, 1.16 mmol, 30%)

^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.85 (s, 1H), 7.92-7.90 (m, 1H), 7.86-7.84 (m, 1H), 7.75 (d, *J*=8.2 Hz, 1H), 7.47-7.46 (m, 2H), 7.42 (t, *J*=15.3 Hz, 2H), 7.24 (d, J=7 Hz, 1H), 5.81 (m, 1H), 2.76-2.70 (m, 1H), 2.54-2.49 (m, 4H), 2.24-2.18 (m, 1H), 2.01-1.94 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$): δ = 204.4, 142.0, 138.1, 133.9, 131.4, 128.5, 127.3, 125.9, 125.8, 125.6, 125.5, 125.1, 124.9, 45.9, 29.7, 24.8, 22.9.

HRMS (**ESI$^+$**): Exact mass calculated for $C_{17}H_{16}O$ (M)$^+$: 236.1201, found: 236.1201

4'-(trifluoromethyl)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde (1e)



SI5 [170.2] **SI10** [316.32] **SI11** [298.3] **1e** [254.25]

The product 4'-(trifluoromethyl)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1e)** was obtained from 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** without isolation of the intermediary products in steps one and two. In steps 2 and 3 reagents were used in excess based on the theoretical yield from the previous steps.

1. **Step:** All the glassware used was oven-dried overnight, dry THF was from the VAC solvent purifier system and the reaction was carried out under argon. Magnesium turnings (97.2 mg, 4.0 mmol, 2.2 eq) were added to a round bottom flask along with 12 ml of THF. 1-bromo-4-(trifluoromethyl)benzene (280 µL, 450 mg, 2.0 mmol, 1.1 eq) was slowly added with a syringe, and an iodine crystal was added to start the reaction. Reaction was refluxed for 5 h and then the 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** (309 mg, 1.81 mmol, 1 eq) was added slowly and reflux was continued for additional 4 hours. Reaction was cooled to room temperature and quenched with 30 ml of NH_4Cl saturated solution. Extraction was performed three times with 30 ml EtOAc, combined organic layers were then neutralized with 30 ml 1 M NaOH, washed with brine and dried with $MgSO_4$.
2. **Step:** All the glassware used was oven dried overnight, pyridine was dried with molecular sieves (4Å) and the reaction was carried out under argon. Crude (1 eq) from the previous step was dissolved in 8 ml of pyridine. $POCl_3$ (398 µL, 655 mg, 4.27 mmol, 4 eq) was added with a syringe at 0 ^{o}C followed by the addition of DBU (160 µL, 162.2 mg, 1.06 mmol, 1 eq). The reaction mixture was stirred at room temperature for 5 h. Quenching was performed with 20 ml of water and extraction with 50 ml of EtOAc, followed by three water washings (90 ml) and a brine wash (30 ml). Organic layer was dried with $MgSO_4$.
3. **Step:** Crude (1 eq) was dissolved in acetone (7 ml). A mixture of water (3.5 ml) and concentrated HCl (1 ml) was added, and the reaction was refluxed for 24 h. Quenching was performed with saturated solution of $NaHCO_3$ (30 ml), the aqueous layer was extracted three times with a total of 90 ml EtOAc. Combined organic phases were then washed with brine and dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc

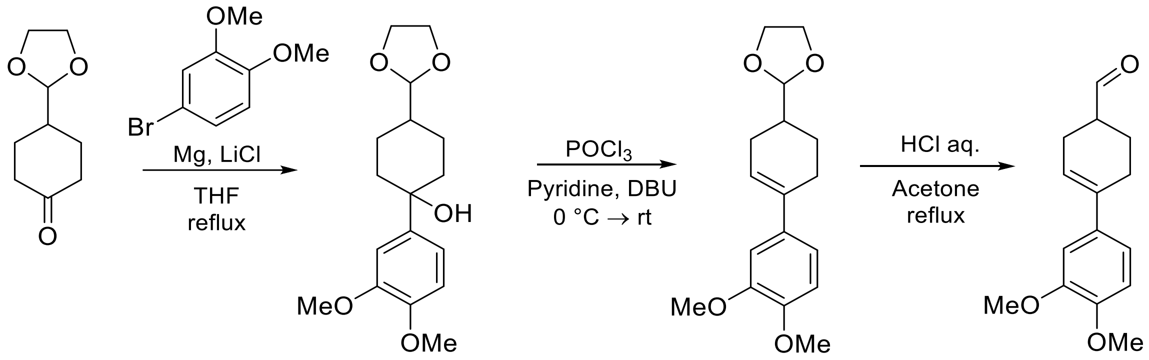
9/1) providing 4'-(trifluoromethyl)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1e)** (221 mg, 0.87 mmol, 48%)

^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.77 (s, 1H), 7.56 (d, *J*=8.2 Hz, 2H), 7.45 (d, *J*=8.4 Hz, 2H), 6.21 (m, 1H), 2.64-2.58 (m, 1H), 2.52-2.49 (m, 4H), 2.22-2.17 (m, 1H), 1.90-1.82 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$): δ = 204.0, 145.2, 136.1, 129.2, 129.0, 125.4-125.3 (m, 2C), 124.5, 45.6, 26.1, 25.2, 22.6.

^{19}F NMR (377 MHz, CDCl3): δ = -62.43.

3',4'-dimethoxy-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde (1f)



SI5 [170.2] **SI12** [308.37] **SI13** [290.35] **1f** [246.3]

'The product 3',4'-dimethoxy-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1f)** was obtained from 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** without isolation of the intermediary products in steps one and two. In steps 2 and 3 reagents were used in excess based on the theoretical yield from the previous steps.

1. **Step:** All the glassware used was oven-dried overnight, dry THF was from the VAC solvent purifier system and the reaction was carried out under argon. Lithium chloride was dried under vacuum at 110 °C. Magnesium turnings (106.9 mg, 4.4 mmol, 1.15 eq) and lithium-chloride (169.5 mg, 4.0 mmol, 1.05 eq) were added to a round bottom flask along with 5 ml of THF. 2-bromoveratrole (520 µL, 784 mg, 4.0 mmol, 1.05 eq) was slowly added with a syringe, and an iodine crystal was added to start the reaction. Reaction was refluxed for 3 hours and then 4-(1,3-dioxolan-2-yl) cyclohexan-1-one **(SI5)** (637 mg, 3.8 mmol, 1 eq) dissolved in 5 ml of THF was added slowly and refluxed for 1 hour. Reaction was cooled down to room temperature and quenched with 30 ml of NH$_4$Cl saturated solution. Extraction was performed three times with 50 ml EtOAc, combined organic layers were washed with brine (50 ml) and dried with MgSO$_4$.
2. **Step:** All the glassware used was oven dried overnight, pyridine was dried with molecular sieves (4Å) and the reaction was carried out under argon. Crude (1 eq) from the previous step was dissolved in 15 ml of pyridine. POCl$_3$ (1.42 ml, 2.3359 g, 15.2 mmol, 4 eq) was added with a syringe at 0 °C followed by the addition of DBU (570 µL, 580.2 mg, 3.8 mmol, 1 eq). The reaction mixture was stirred at room temperature for 6 h. Quenching was performed with 50 ml of water and extraction with 150 ml EtOAc, followed by three water washings (150 ml) and a brine wash (50 ml). Organic layer was dried with MgSO$_4$.
3. **Step:** Crude (1 eq) was dissolved in acetone (28 ml). A mixture of water (15 ml) and concentrated HCl (4 ml) was added, and the reaction was refluxed for 24 h. Quenching was

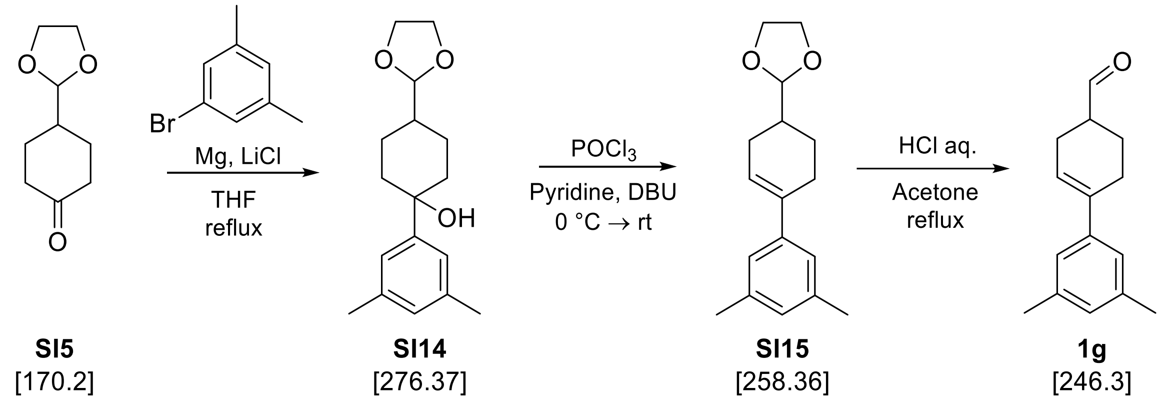
performed with saturated solution of $NaHCO_3$ (30 ml), the aqueous layer was extracted three times with a total of 150 ml EtOAc. Combined organic phases were then washed with brine and dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 9/1) providing a colorless oil 3',4'-dimethoxy-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1f)** (207.6 mg, 0.84 mmol, 23%)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 6.90 (sex, *J*=2.4, 2H), 6.83-6.80 (m, 1H), 6.04 (m, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.61-2.57 (m, 1H), 2.54-2.43 (m, 4H), 2.19-2.12 (m, 1H), 1.88-1.78 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 204.4, 148.8, 148.3, 136.6, 134.8, 120.9, 117.5, 111.0, 108.6, 56.0, 56.0, 45.9, 26.3, 25.1, 22.8.

HRMS (**ESI$^+$**): Exact mass calculated for $C_{15}H_{18}O_3$ $(M)^+$: 246.1256, found: 246.1251

3',5'-dimethyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde (1g)



The product 3',5'-dimethyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1g)** was obtained from 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** without isolation of the intermediary products in steps one and two. In steps 2 and 3 reagents were used in excess based on the theoretical yield from the previous steps.

1. **Step:** All the glassware used was oven-dried overnight, dry THF was from the VAC solvent purifier system and the reaction was carried out under argon. Lithium chloride was dried under vacuum at 110 °C. Magnesium turnings (106.9 mg, 4.4 mmol, 1.15 eq) and lithium-chloride (169.5 mg, 4.0 mmol, 1.05 eq) were added to a round bottom flask along with 5 ml of THF. 5-Bromo-*m*-xylene (540 µL, 735.5 mg, 4.0 mmol, 1.05 eq) was slowly added with a syringe, and an iodine crystal was added to start the reaction. Reaction was refluxed for 2 hours and then 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** (638.1 mg, 3.8 mmol, 1 eq) was added slowly and refluxed for 2 hours. Reaction was cooled to room temperature and quenched with 30 ml of NH_4Cl saturated solution. Extraction was performed three times with 50 ml EtOAc, combined organic layers were washed with brine (50 ml) and dried with $MgSO_4$.
2. **Step:** All the glassware used was oven dried overnight, pyridine was dried with molecular sieves (4Å) and the reaction was done under argon. Crude (1 eq) from the previous step was dissolved in 15 ml of pyridine. $POCl_3$ (1.42 ml, 2.3359 g, 15.2 mmol, 4 eq) was added with a syringe at 0 °C followed by the addition of DBU (570 µL, 580.2 mg, 3.8 mmol, 1 eq). The reaction mixture was stirred at room temperature for 6 h. Quenching was performed with 50 ml of water and extraction with 150 ml EtOAc, followed by three water washings (150 ml) and a brine wash (50 ml). Organic layer was dried with $MgSO_4$.
3. **Step:** Crude (1 eq) was dissolved in acetone (28 ml). A mixture of water (15 ml) and concentrated HCl (4 ml) was added, and the reaction was refluxed for 24 h. Quenching was performed with saturated solution of $NaHCO_3$ (30 ml), the aqueous layer was extracted three

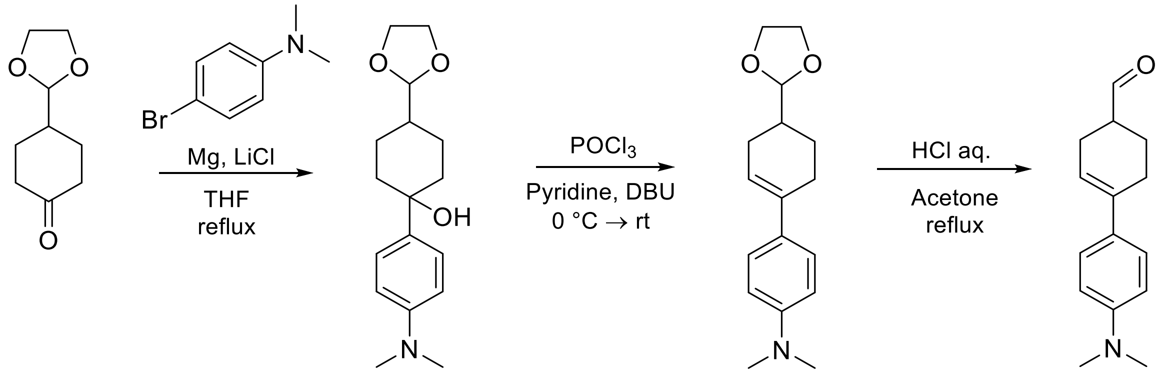
times with a total of 150 ml EtOAc. Combined organic phases were then washed with brine and dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 95/5) providing overall a colorless oil 3',5'-dimethyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1g)** (240.3 mg, 1.12 mmol, 30%)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 6.98 (s, 2H), 6.89 (s, 1H), 6.08 (m, 1H), 2.60-2.44 (m, 5H), 2.31 (s, 6H), 2.19-2.13 (m, 1H), 1.85-1.78(m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 204.5, 141.9, 137.9, 137.2, 128.8, 123.2, 121.8, 46.0, 26.4, 25.2, 22.9, 21.5.

HRMS (**ESI$^+$**): Exact mass calculated for $C_{15}H_{18}O$ $(M)^+$: 214.1358, found: 214.1359

4'-(dimethylamino)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde (1h)



SI5 [170.2] **SI16** [291.39] **SI17** [273.37] **1h** [229.32]

The product 4'-(dimethylamino)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1h)** was obtained from 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** without isolation of the intermediary products in steps one and two. In steps 2 and 3 reagents were used in excess based on the theoretical yield from the previous steps.

1. **Step:** All the glassware used was oven-dried overnight, dry THF was from the VAC solvent purifier system and the reaction was carried out under argon. Lithium chloride was dried under vacuum at 110 °C . Magnesium turnings (106.9 mg, 4.4 mmol, 1.15 eq) and lithium-chloride (169.5 mg, 4.0 mmol, 1.05 eq) were added to a round bottom flask along with 5 ml of THF. 4-bromo-*N,N*-dimethylaniline (802 mg, 4.0 mmol, 1.05 eq) was slowly added with a syringe, and an iodine crystal was added to start the reaction. Reaction was refluxed for 2 hours and then the 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** (639 mg, 3.8 mmol, 1 eq) was added slowly and refluxed overnight. Reaction was cooled to room temperature and quenched with 30 ml of NH_4Cl saturated solution. Extraction was performed three times with 50 ml EtOAc, combined organic layers were washed with brine (50 ml) and dried with $MgSO_4$.
2. **Step:** All the glassware used was oven dried overnight, pyridine was dried with molecular sieves (4Å) and the reaction was carried out under argon. Crude (1 eq) from the previous step was dissolved in 15 ml of pyridine. $POCl_3$ (1.42 ml, 2.3359 g, 15.2 mmol, 4 eq) was added with a syringe at 0 °C followed by the addition of DBU (570 µL, 580.2 mg, 3.8 mmol, 1 eq). The reaction mixture was stirred at room temperature for 6 h. Quenching was performed with 50 ml of water and extraction with 150 ml of EtOAc, followed by three water washings (150 ml) and a brine wash (50 ml). Organic layer was dried with $MgSO_4$.
3. **Step:** Crude (1 eq) was dissolved in acetone (28 ml). A mixture of water (15 ml) and concentrated HCl (4 ml) was added, and the reaction was refluxed for 24 h. Quenching was performed with saturated solution of $NaHCO_3$ (30 ml), the aqueous layer was extracted three

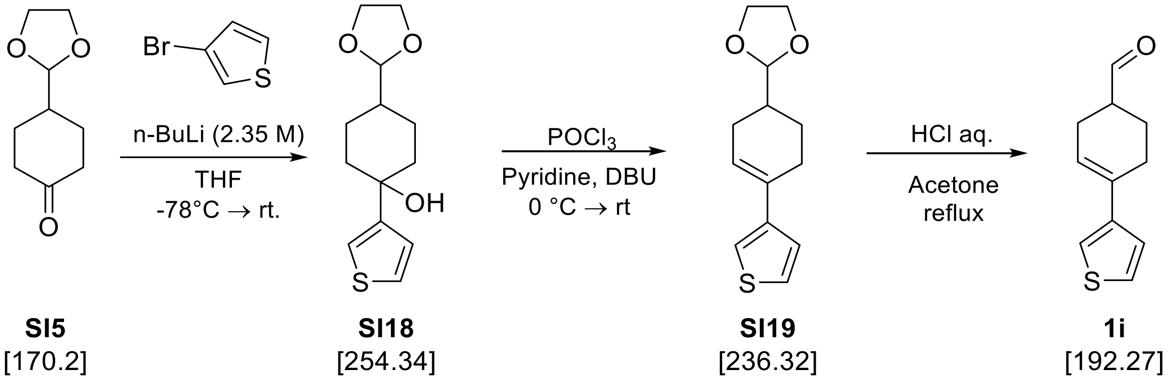
times with a total of 150 ml EtOAc. Combined organic phases were then washed with brine and dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 95/5) providing a yellow solid 4'-(dimethylamino)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1h)** (248 mg, 1.08 mmol, 28%)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (d, *J*=1.36 Hz, 1H), 7.28 (d, *J*=9 Hz, 2H), 6.69 (d, *J*=9 Hz, 2H), 6.00 (m, 1H), 2.95 (s, 6H), 2.59-2.40 (m, 5H), 2.19-2.12 (m, 1H), 1.86-1.76 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 204.80, 149.90, 136.42, 130.02, 125.79, 118.76, 112.51, 46.09, 40.75, 26.11, 25.26, 22.95.

HRMS (**ESI$^+$**): Exact mass calculated for $C_{15}H_{19}NO$ $(M)^+$: 229.1467, found: 229.1476

4-(thiophen-3-yl)cyclohex-3-ene-1-carbaldehyde (1i)



The product 4-(thiophen-3-yl)cyclohex-3-ene-1-carbaldehyde **(1i)** was obtained from 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** without isolation of the intermediary products in steps one and two. In steps 2 and 3 reagents were used in excess based on the theoretical yield from the previous steps.

1. **Step:** All the glassware used was oven-dried overnight, dry THF was from the VAC solvent purifier system and the reaction was carried out under argon. 3-bromothiophene (330 µL, 574 mg, 3.52 mmol, 1 eq) was dissolved in 4 ml of THF and cooled to -78 °C. n-Butyllithium 2.35 M solution in hexane (1.65 ml, 3.87 mmol, 1.1 eq) was added and left to stir for 2 hours. 4-(1,3-dioxolan-2-yl)cyclohexan-1-one **(SI5)** (600 mg, 3.52 mmol, 1 eq) dissolved in 2 ml of THF was added to the mixture at -78 °C. The mixture was warmed to rt after which the reaction was quenched with 40 ml of saturated NH_4Cl, extracted with 3 portions of 30 ml EtOAc. Combined organic phases were then washed with brine and dried over $MgSO_4$.
2. **Step:** All the glassware used was oven-dried overnight, pyridine was dried with molecular sieves (4Å) and the reaction was carried out under argon. Crude (1 eq) from the previous step was dissolved in 5 ml of pyridine. $POCl_3$ (813 µL, 1.34 g, 8.72 mmol, 4 eq) was added with a syringe at 0 ^{o}C followed by the addition of DBU (325 µL, 332 mg, 2.18 mmol, 1 eq). The reaction mixture was stirred at room temperature for 5 h. Quenching was performed with 20 ml of water and extraction with 50 ml of EtOAc, followed by three water washings (90 ml) and a brine wash (30 ml). Organic layer was dried with $MgSO_4$.
3. **Step:** Crude (1 eq) was dissolved in acetone (7 ml). A mixture of water (3.5 ml) and concentrated HCl (1 ml) was added, and the reaction was refluxed for 24 h. Quenching was performed with saturated solution of $NaHCO_3$ (30 ml), the aqueous layer was extracted three times with a total of 90 ml EtOAc. Combined organic phases were then washed with brine and dried over $MgSO_4$. Crude product was purified by flash column chromatography (Hex/EtOAc 9/1) providing 4-(thiophen-3-yl)cyclohex-3-ene-1-carbaldehyde **(1i)** (187.9 mg, 0.97 mmol, 28%)

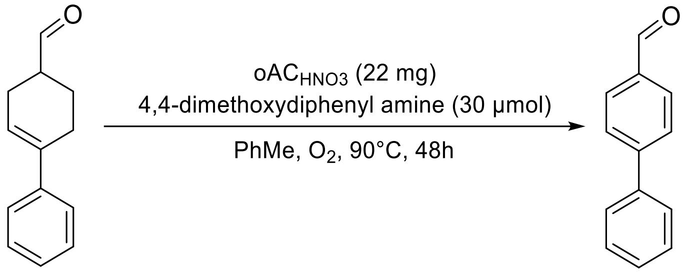
^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.75 (s, 1H), 7.24 – 6.91 (m, 3H), 6.18 (s, 1H), 2.63 – 2.40 (m, 5H), 2.20 – 2.11 (m, 1H), 1.88 – 1.77 (m, 1H).

^{13}C NMR (126 MHz, CDCl$_3$): δ = 204.3, 143.1, 132.2, 125.6, 124.8, 121.2, 118.7, 45.9, 26.1, 24.9, 22.6.

HRMS (**ESI$^+$**): Exact mass calculated for $C_{11}H_{12}OS$ (M)$^+$: 192.0609, found: 192.0612

Synthesis of aryl aldehydes (2c-i)

[1,1'-biphenyl]-4-carbaldehyde (2c)



1c
[186.25]

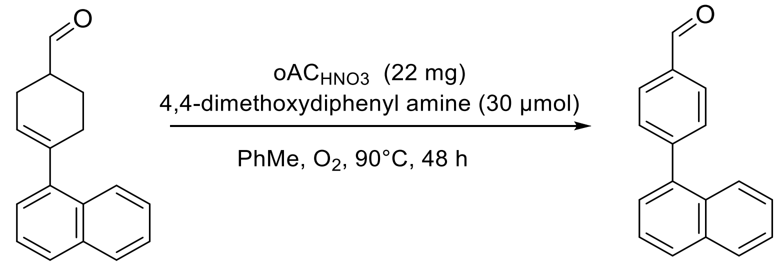
2c
[182.22]

4-Phenyl-3-cyclohexene-1-carboxaldehyde **(1c)** (17.5 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (6.9 mg, 0.03 mmol, 0.3 eq) and oAC$_{HNO3}$ (21.5 mg) were mixed in 1 ml of toluene and sonicated for 5 minutes. The atmosphere was exchanged to pure oxygen and the mixture was stirred at 90 °C for 48 h. Mixture was cooled down and filtered through Celite, then washed with 100 ml of DCM, and solvent was removed under reduced pressure. Flash chromatography purification (Hex/EtOAc 95/5 → 9/1) provided [1,1'-biphenyl]-4-carbaldehyde **(2c)** (15.3 mg, 0.08 mmol, 89%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.06 (s, 1H), 7.96 (d, *J*=8.6 Hz, 2H), 7.76 (d, *J*=8.2 Hz, 2H), 7.65 (d, *J*=7.0 Hz, 2H), 7.49 (t, *J*=7.0 Hz, 2H), 7.42 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 192.0, 147.3, 139.9, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5.

4-(naphthalen-1-yl) benzaldehyde (2d)



1d
[236.31]

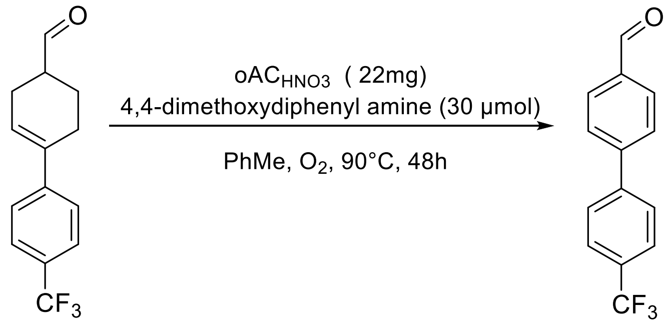
2d
[232.28]

4-(naphthalen-1-yl)cyclohex-3-ene-1-carbaldehyde **(1d)** (22.6 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (9.2 mg, 0.03 mmol, 0.3 eq), oAC$_{HNO3}$ (25.2 mg) were mixed in 1 ml of toluene and sonicated for 5 minutes; the atmosphere was exchanged to pure oxygen and stirred at 90 °C for 48 h. Mixture was cooled down and filtered through Celite, then washed with 100 ml of DCM, and solvent was removed under reduced pressure. Flash chromatography purification (Hex/EtOAc 95/5 → 9/1) provided 4-(naphthalen-1-yl) benzaldehyde **(2d)** (17.7 mg, 0.08 mmol, 79%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.13 (s, 1H), 8.02 (d, *J*=8.5 Hz, 2H), 7.93 (t, *J*=8.0 Hz, 2H), 7.84 (d, *J*=9.0 Hz, 1H), 7.68 (d, *J*=8.1 Hz, 2H), 7.57-7.43 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 192.2, 147.4, 139.0, 135.5, 133.9, 131.3, 130.9, 129.9, 128.7, 128.6, 127.1, 126.6, 126.2, 125.6, 125.5.

4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbaldehyde (2e)



1e
[254.25]

2e
[250.22]

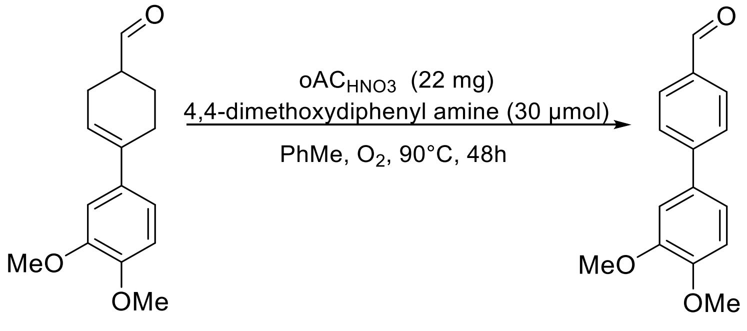
4'-(trifluoromethyl)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1e)** (26.6 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (9.0 mg, 0.03 mmol, 0.3 eq), oAC$_{HNO3}$ (23.7 mg)) were mixed in 1 ml of toluene and sonicated for 5 minutes; the atmosphere was exchanged to pure oxygen and stirred at 90 °C for 48 h. Mixture was cooled down and filtered through Celite, then washed with 100 ml of DCM, and solvent was removed under reduced pressure. Flash chromatography purification (Hex/EtOAc 95/5 → 9/1) provided 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbaldehyde **(2e)** (20.0 mg, 0.08 mmol, 77%) as a pale-yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.08 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.78-7.74 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 191.86, 145.70, 143.40, 136.01, 130.61 (q, *J* = 32.7 Hz, CCF$_3$), 130.51, 128.07, 127.86, 126.10 (q, *J* = 3.8 Hz, CH), 124.22 (q, *J* = 272.1 Hz, CF$_3$).

^{19}F NMR (470 MHz, CDCl3): δ = -62.58.

3',4'-dimethoxy-[1,1'-biphenyl]-4-carbaldehyde (2f)



1f
[246.3]

2f
[242.27]

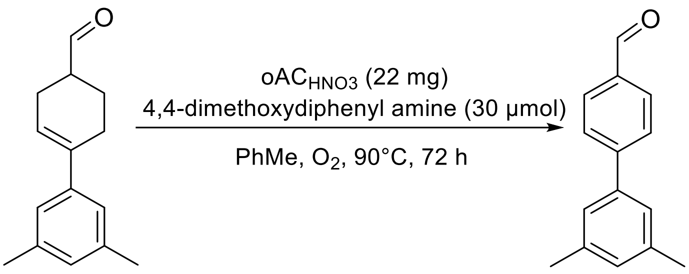
3',4'-dimethoxy-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1f)** (25.9 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (6.4 mg, 0.03 mmol, 0.3 eq), oAC$_{HNO3}$ (21.7 mg) were mixed in 1 ml of toluene and sonicated for 5 minutes; the atmosphere was exchanged to pure oxygen and stirred at 90 °C for

48 h. Mixture was cooled down and filtered through Celite, then washed with 100 ml of DCM, and solvent was removed under reduced pressure. Flash chromatography purification (Hex/EtOAc 95/5 → 8/2) provided 3',4'-dimethoxy-[1,1'-biphenyl]-4-carbaldehyde **(2f)** (22,7 mg, 0.09 mmol, 89%) as a pale-yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10,04 (s, 1H), 7.93 (d, *J*=8.5 Hz, 2H), 7.72 (d, *J*=8.4 Hz, 2H), 7.22 (dd, *J*=8.3, 2.1 Hz, 1H), 7.15 (d, *J*=2.3 Hz, 1H), 6.98 (d, *J*=8.4 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 192.0, 149.8, 149.5, 147.2, 135.0, 132.7, 130.4, 127.4, 120.1, 111.7, 110.6, 56.2 (m, 2C).

3',5'-dimethyl-[1,1'-biphenyl]-4-carbaldehyde (2g)



1g
[214.3]

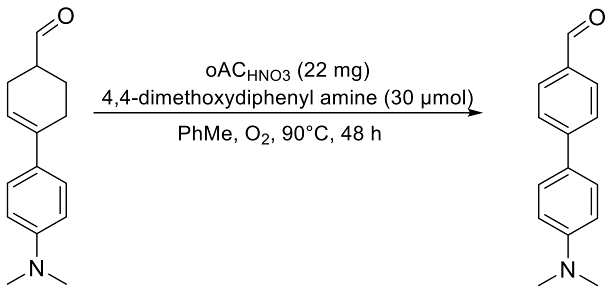
2g
[210.27]

3',5'-dimethyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1g)** (22.8 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (6.5 mg, 0.03 mmol, 0.3 eq), oAC$_{HNO3}$ (21.0 mg) were mixed in 1 ml of toluene and sonicated for 5 minutes; the atmosphere was exchanged to pure oxygen and stirred at 90 °C for 72 h. Mixture was cooled down and filtered through Celite, then washed with 100 ml of DCM, and solvent was removed under reduced pressure. Flash chromatography purification (Hex/EtOAc 95/5 → 9/1) provided 3',5'-dimethyl-[1,1'-biphenyl]-4-carbaldehyde **(2g)** (10.3 mg, 0.05 mmol, 49%) as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.06 (s, 1H), 7.94 (d, *J*=8.6 Hz, 1H), 7.74 (d, *J*=8.3 Hz, 1H), 7.26 (s, 2H), 7.07 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 192.10, 147.66, 139.86, 138.73, 135.21, 130.32, 130.25, 127.83, 125.41, 21.52.

4'-(dimethylamino)-[1,1'-biphenyl]-4-carbaldehyde (2h)

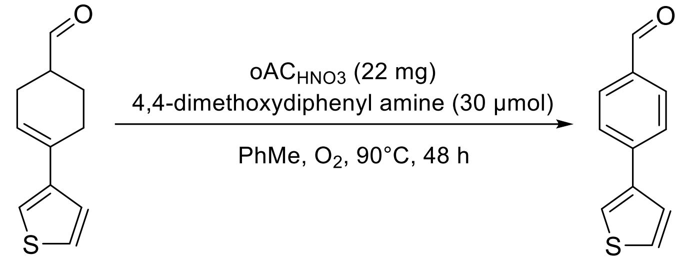


1h
[229.32]

2h
[225.39]

4'-(dimethylamino)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde **(1h)** (22.9 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (7.7 mg, 0.03 mmol, 0.3 eq), oAC_{HNO3} (21.5 mg) were mixed in 1 ml of toluene and sonicated for 5 minutes; the atmosphere was exchanged to pure oxygen and stirred at 90 °C for 48 h. Mixture was cooled down and filtered through Celite, then washed with 100 ml of DCM, and solvent was removed under reduced pressure. NMR yield of 4'-(dimethylamino)-[1,1'-biphenyl]-4-carbaldehyde **(2h)** was 49%.

4-(thiophen-3-yl)benzaldehyde (2i)

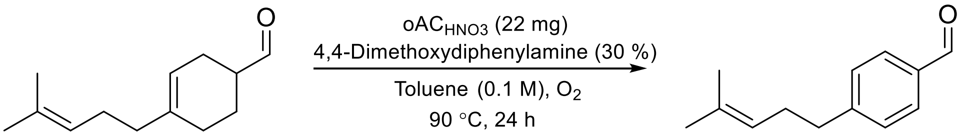


1i
[192.27]

2i
[188.24]

4-(thiophen-3-yl)cyclohex-3-ene-1-carbaldehyde **(1i)** (19.2 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (7.7 mg, 0.03 mmol, 0.3 eq), oAC_{HNO3} (21.0 mg) were mixed in 1 ml of toluene and sonicated for 5 minutes; the atmosphere was exchanged to pure oxygen and stirred at 90 °C for 48 h. Mixture was cooled down and filtered through Celite, then washed with 100 ml of DCM, and solvent was removed under reduced pressure. NMR yield of 4-(thiophen-3-yl)benzaldehyde **(2i)** was 53%.

4-(4-methylpent-3-en-1-yl)benzaldehyde (SI21)



SI20
[192.3]

SI21
[188.22]

4-(4-methylpent-3-en-1-yl)cyclohex-3-ene-1-carbaldehyde (19.2 mg, 0.1 mmol, 1 eq), 4,4'-Dimethoxydiphenylamine (6.9 mg, 0.03 mmol, 0.3 eq), oAC_{HNO3} (21.0 mg) were mixed in 1 ml of toluene and sonicated for 5 minutes; the atmosphere was exchanged to pure oxygen and stirred at 90 °C for 24 h. Mixture was cooled down and filtered through Celite, then washed with 100 ml of DCM, and solvent was removed under reduced pressure. NMR yield of **SI21** was 13% with 45% leftover starting material and about 15% of aldol condensation products.

Computational supplementary information

All geometry optimizations were performed using the M06-2X functional[8] with Grimme's D3 dispersion correction (emp=GD3)[9] and the 6-31+G(d,p) basis set and the CPCM solvation model for toluene, as implemented in the *Gaussian 16* program package.[10] Transition-state (TS) structures were located using the Berny algorithm (calculated force constants), with initial guesses obtained from saddle-point distance scans. Intrinsic reaction coordinate (IRC) calculations were carried out for TS structures (one imaginary frequency) to verify their connectivity between reactants and products. Single-point energy and frequency calculations were performed at the same level of theory and solvation model using the larger 6-311++G(d,p) basis set. Cartesian coordinates (XYZ) of optimized structures are provided in separate files along with their free energies and, where applicable, imaginary frequencies for TS structures.

Phenanthrenequinone (PQ) was initially employed as an alternative quinoid model compound to evaluate oAC-driven dehydrogenative aromatization of enamines **1a-A4**, **1a-A6**, and **1a**-morpholine (Figs S5 and S6). Formation of the initial van der Waals encounter complex is computed to be slightly endergonic (ΔG = +1.9 to +3.7 kcal mol^{-1}). The calculated reaction profile indicates that the first transition state (TS1), corresponding to hydride abstraction by a quinone oxygen from the doubly allylic C2 position of the enamine, represents the highest free-energy barrier along an overall exergonic dehydrogenation pathway.

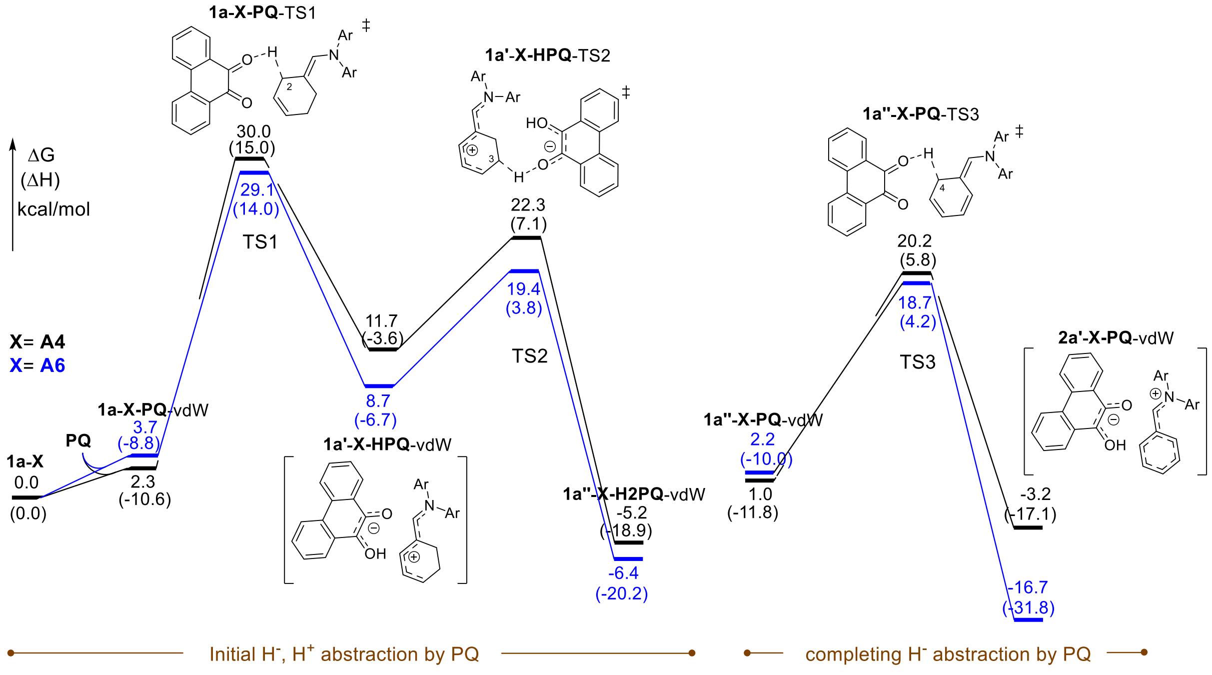


Fig S8. Aromatization energy profiles of enamines **1a-A4** and **1a-A6** via consecutive dehydrogenation and hydride-abstraction steps mediated by PQ. M062x/6-311++g(d,p)//M062x/6-31+g(d,p) CPCM(toluene) emp=gd3

Table S11. List of computed free energies (Δ*G*) and enthalpies (Δ*H*) M06-2x/6-311++(d,p)//M06-2x/6-31G+(d,p) GD3 CPCM(toluene).

entry	Structure / complex	*ΔG* (in a.u.)	*ΔH* (in a.u.)	i-freq	name (XYZ)
1	1a-A4	-789.761092	-789.699541		1a-A4
2	PQ	-688.523883	-688.474401		PQ
3	1a-A4-PQ-vdW	-1478.281247	-1478.190800		1a-A4-PQ-vdW
4	1a-A4-PQ-TS1	-1478.237161	-1478.150077	-1287.24	1a-A4-PQ-TS1
5	1a’-A4-HPQ-vdW	-1478.266319	-1478.179753		1a’-A4-HPQ-vdW
6	1a’-A4-HPQ-TS2	-1478.249453	-1478.162581	-423.29	1a’-A4-HPQ-TS2
7	1a”-A4-H$_2$PQ-vdW	-1478.293307	-1478.204117		1a”-A4-H$_2$PQ-vdW
8	1a”-A4-PQ-vdW	-1477.087278	-1476.997218		1a”-A4-PQ-vdW
9	1a”-A4-PQ-TS3	-1477.056739	-1476.969112	-1502.39	1a”-A4-PQ-TS3
10	2a’-A4-HPQ-vdW	-1477.094002	-1477.005499		2a’-A4-PQ-vdW
11	1a-A6	-1018.72699	-1018.653808		1a-A6
12	1a-A6-PQ-vdW	-1707.24495	-1707.142194		1a-A6-PQ-vdW
13	1a-A6-PQ-TS1	-1707.204463	-1707.105892	-1312.48	1a-A6-PQ-TS1
14	1a’-A6-HPQ-vdW	-1707.236962	-1707.138846		1a’-A6-HPQ-vdW
15	1a’-A6-HPQ-TS2	-1707.219905	-1707.122213	-1331.04	1a’-A6-HPQ-TS2
16	1a”-A6-H$_2$PQ-vdW	-1707.260995	-1707.160347		1a”-A6-H$_2$PQ-vdW
17	1a”-A6-PQ-vdW	-1706.051775	-1705.949302		1a”-A6-PQ-vdW
18	1a”-A6-PQ-TS3	-1706.025408	-1705.926542	-1528.53	1a”-A6-PQ-TS3
19	2a’-A6-PQ-vdW	-1706.081888	-1705.984045		2a’-A6-PQ-vdW
20	Morpholine (Morp)	-559.007374	-558.957254		Morp
21	1a-Morp-PQ-vdW	-1247.528236	-1247.449295		1a-Morp-PQ-vdW
22	1a-Morp-PQ-TS1	-1247.483286	-1247.406613	-1286.42	1a-Morp-PQ-TS1
23	1a’-Morp-HPQ-vdW	-1247.519094	-1247.441718		1a’-Morp-HPQ-vdW
24	1a’-Morp-HPQ-TS2	-1247.503221	-1247.427235	-1455.29	1a’-Morp-HPQ-TS2
25	1a”-Morp-H$_2$PQ-vdW	-1247.539611	-1247.460600		1a”-Morp-H$_2$PQ-vdW
26	1a”-Morp-PQ-vdW	-1246.332813	-1246.252921		1a”-Morp-PQ-vdW
27	1a”-Morp-PQ-TS3	-1246.302952	-1246.225914	-1477.57	1a”-Morp-PQ-TS3
28	2a’-Morp-HPQ-vdW	-1246.371144	-1246.295268		2a’-Morp-PQ-vdW

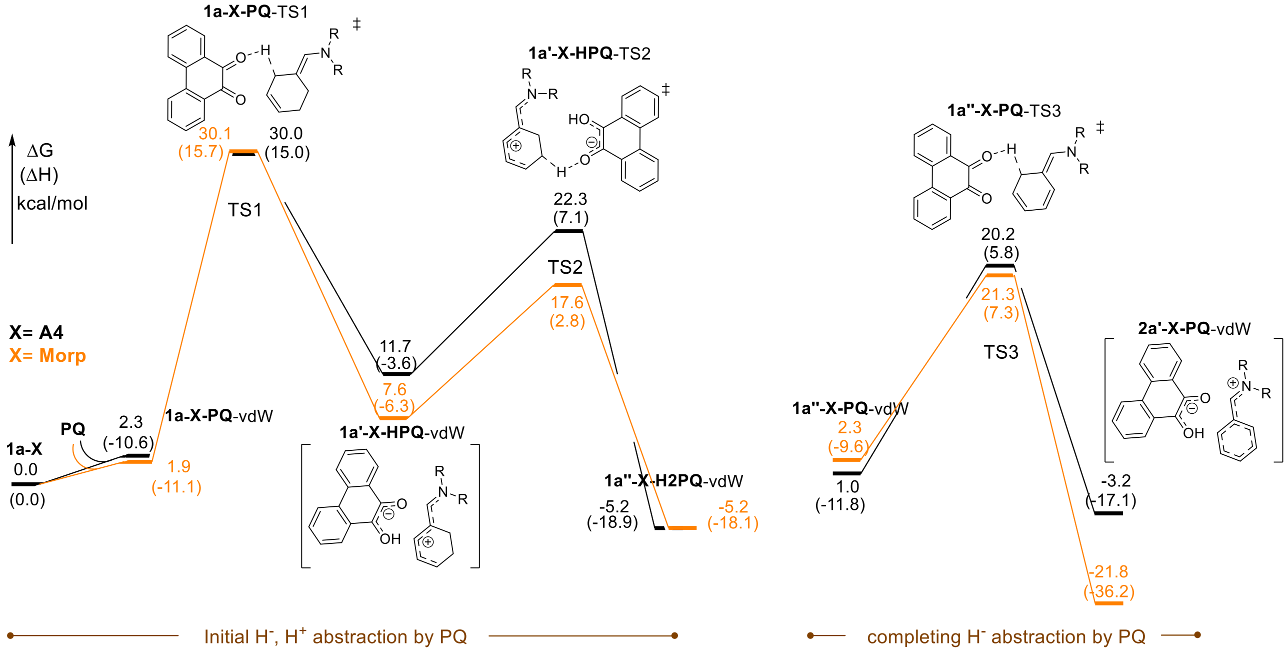


Fig S9. Aromatization energy profiles of enamines **1a-A4** and **1a-Morp** via consecutive dehydrogenation and hydride-abstraction steps mediated by PQ. M062x/6-311++g(d,p)//M062x/6-31+g(d,p) CPCM(toluene) emp=gd3

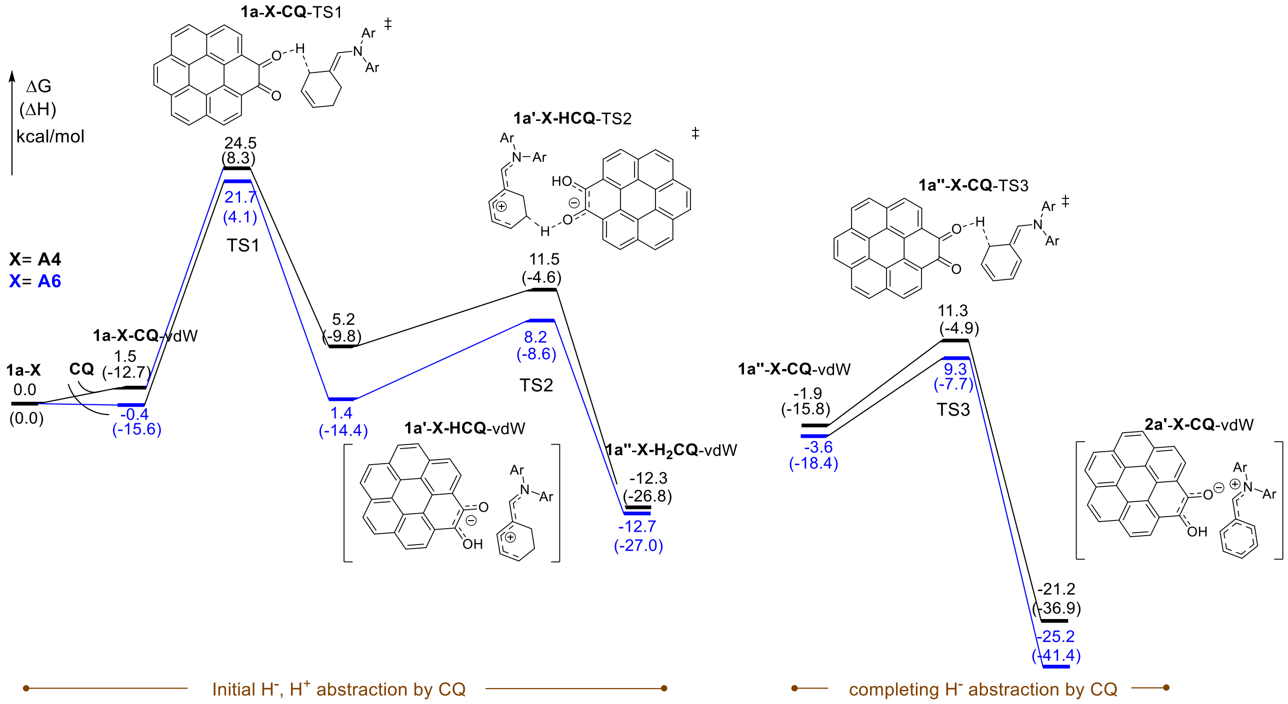


Fig S10. Aromatization energy profiles of enamines **1a-A4** and **1a-A6** via consecutive dehydrogenation and hydride-abstraction steps mediated by CQ. M062x/6-311++g(d,p)//M062x/6-31+g(d,p) CPCM(toluene) emp=gd3

Table S12. List of computed free energies (Δ*G*) and enthalpies (Δ*H*) M06-2x/6-311++(d,p)//M06-2x/6-31G+(d,p) GD3 CPCM(toluene).

entry	Structure / complex	*ΔG* (in a.u.)	*ΔH* (in a.u.)	i-freq	name (XYZ)
1	CQ	-1070.742663	-1070.68342		CQ
2	1a-A4-CQ-vdW	-1860.501289	-1860.403127		1a-A4-CQ-vdW
3	1a-A4-CQ-TS1	-1860.464669	-1860.369655	-1456.62	1a-A4-CQ-TS1
4	1a'-A4-HCQ-vdW	-1860.495473	-1860.398623		1a'-A4-HCQ-vdW
5	1a'-A4-HCQ-TS2	-1860.485421	-1860.39024	-1336.96	1a'-A4-HCQ-TS2
6	1a''-A4-H_2CQ-vdW	-1860.523306	-1860.425718		1a''-A4-H_2CQ-vdW
7	1a''-A4-CQ-vdW	-1859.310739	-1859.212509		1a''-A4-CQ-vdW
8	1a''-A4-CQ-TS3	-1859.289747	-1859.195294	-1356.40	1a''-A4-CQ-TS3
9	2a'-A4-HCQ-vdW	-1859.341489	-1859.246269		2a'-A4-HCQ-vdW
10	1a-A6-CQ-vdW	-2089.470307	-2089.362039		1a-A6-CQ-vdW
11	1a-A6-CQ-TS1	-2089.43509	-2089.330631	-1490.09	1a-A6-CQ-TS1
12	1a'-A6-HCQ-vdW	-2089.467378	-2089.360191		1a'-A6-HCQ-vdW
13	1a'-A6-HCQ-TS2	-2089.45666	-2089.350863	-1391.46	1a'-A6-HCQ-TS2
14	1a''-A6-H_2CQ-vdW	-2089.48994	-2089.38032		1a''-A6-H_2CQ-vdW
15	1a''-A6-CQ-vdW	-2088.279847	-2088.171626		1a''-A6-CQ-vdW
16	1a''-A6-CQ-TS3	-2088.259241	-2088.154591	-1321.56	1a''-A6-CQ-TS3
17	2a'-A6-HCQ-vdW	-2088.314121	-2088.208251		2a'-A6-HCQ-vdW
18	CQCA	-1259.302572	-1259.236757		CQCA
19	1a-A4-CQCA-vdW	-2049.062207	-2048.957115		1a-A4-CQCA-vdW
20	1a-A4-CQCA-TS1	-2049.026076	-2048.925382	-1492.79	1a-A4-CQCA-TS1
21	1a'-A4-HCQCA-vdW	-2049.05789	-2048.954228		1a'-A4-HCQCA-vdW
22	1a'-A4-HCQCA-TS2	-2049.049101	-2048.946846	-1341.97	1a'-A4-HCQCA-TS2
23	1a''-A4-H_2CQCA-vdW	-2049.086005	-2048.981232		1a''-A4-H_2CQCA-vdW
24	1a''-A4-CQCA-vdW	-2047.871969	-2047.766492		1a''-A4-CQCA-vdW

25	1a’’-A4-CQCA-TS3	-2047.851029	-2047.749957	-1278.72	1a’’-A4-CQCA-TS3
26	2a’-A4-HCQCA-vdW	-2047.904525	-2047.802139		2a’-A4-HCQCA-vdW
27	1a-A6-CQCA-vdW	-2278.031144	-2277.916496		1a-A6-CQCA-vdW
28	1a-A6-CQCA-TS1	-2277.99791	-2277.887575	-1495.67	1a-A6-CQCA-TS1
29	1a’-A6-HCQCA-vdW	-2278.032028	-2277.918503		1a’-A6-HCQCA-vdW
30	1a’-A6-HCQCA-TS2	-2278.021323	-2277.909795	-1404.84	1a’-A6-HCQCA-TS2
31	1a’’-A6-H_2CQCA-vdW	-2278.053124	-2277.938996		1a’’-A6-H_2CQCA-vdW
32	1a’’-A6-CQCA-vdW	-2276.842163	-2276.725097		1a’’-A6-CQCA-vdW
33	1a’’-A6-CQCA-TS3	-2276.825936	-2276.716496	-1232.08	1a’’-A6-CQCA-TS3
34	2a’-A6-HCQCA-vdW	-2276.877428	-2276.765767		2a’-A6-HCQCA-vdW
35	1a-Morp-CQ-vdW	-1629.749572	-1629.662616		1a-Morp-CQ-vdW
36	1a-Morp-CQ-TS1	-1629.714742	-1629.630423	-1473.16	1a-Morp-CQ-TS1
37	1a’-Morp-HCQ-vdW	-1629.74598	-1629.6596		1a’-Morp-HCQ-vdW
38	1a’-Morp-HCQ-TS2	-1629.734666	-1629.648723	-1390.29	1a’-Morp-HCQ-TS2
39	1a’’-Morp-H_2CQ-vdW	-1629.768577	-1629.68094		1a’’-Morp-H_2CQ-vdW
40	1a’’-Morp-CQ-vdW	-1628.558037	-1628.47197		1a’’-Morp-CQ-vdW
41	1a’’-Morp-CQ-TS3	-1628.543403	-1628.46022	-1226.60	1a’’-Morp-CQ-TS3
42	2a’-Morp-HCQ-vdW	-1628.594144	-1628.509837		2a’-Morp-HCQ-vdW
43	1a-Morp-CQCA-vdW	-1818.309944	-1818.216339		1a-Morp-CQCA-vdW
44	1a-Morp-CQCA-TS1	-1818.275571	-1818.184454	-1474.20	1a-Morp-CQCA-TS1
45	1a’-Morp-HCQCA-vdW	-1818.307666	-1818.214559		1a’-Morp-HCQCA-vdW
46	1a’-Morp-HCQCA-TS2	-1818.295689	-1818.203476	-1398.93	1a’-Morp-HCQCA-TS2
47	1a’’-Morp-H_2CQCA-vdW	-1818.330024	-1818.235631		1a’’-Morp-H_2CQCA-vdW
48	1a’’-Morp-CQCA-vdW	-1817.118242	-1817.02556		1a’’-Morp-CQCA-vdW
49	1a’’-Morp-CQCA-TS3	-1817.104173	-1817.014387	-1190.89	1a’’-Morp-CQCA-TS3
50	2a’-Morp-HCQCA-vdW	-1817.155903	-1817.06492		2a’-Morp-HCQCA-vdW

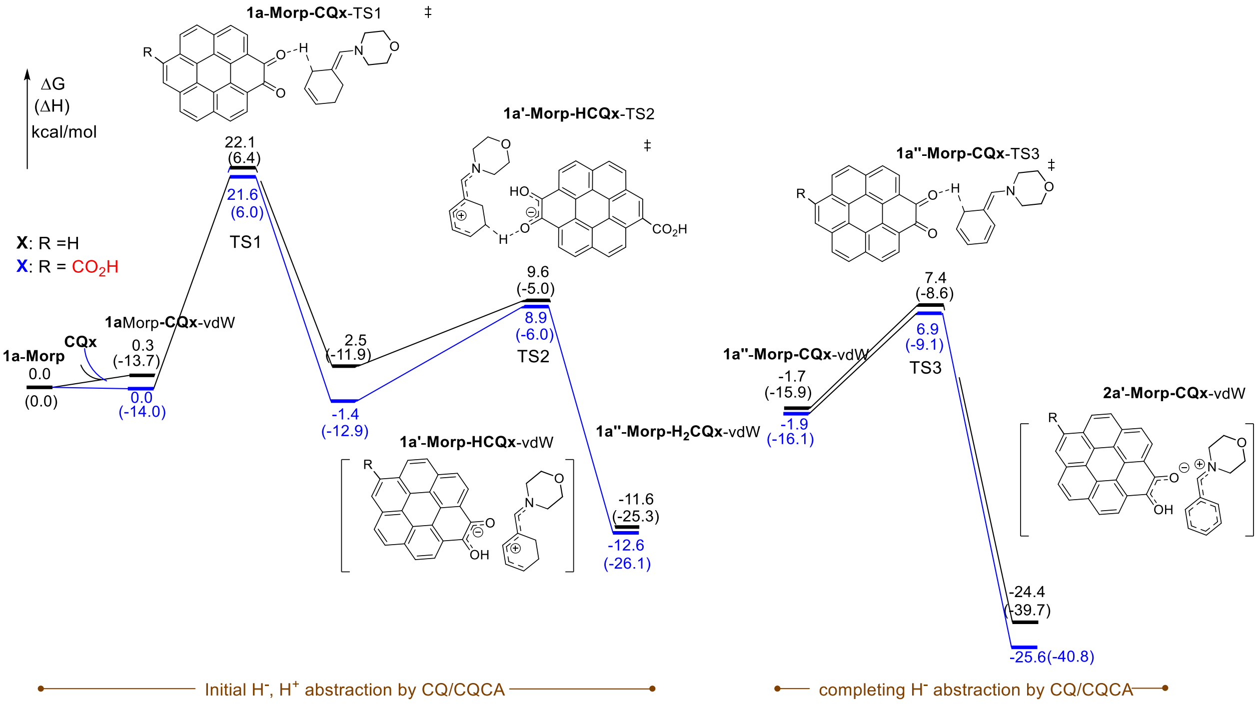
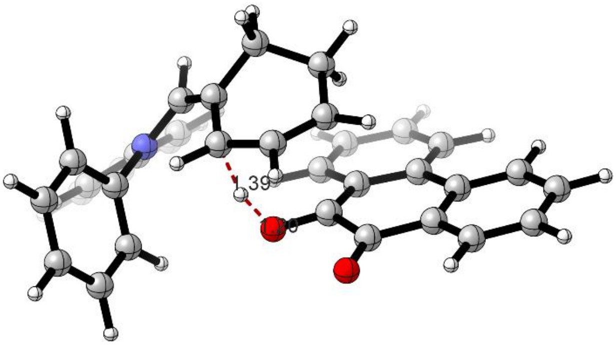
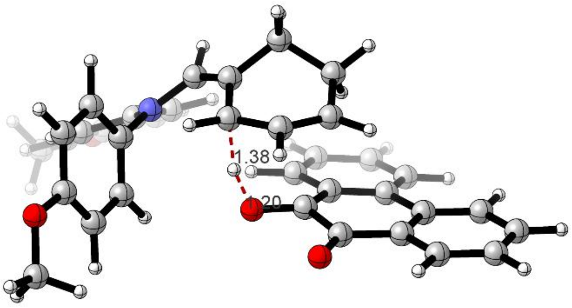


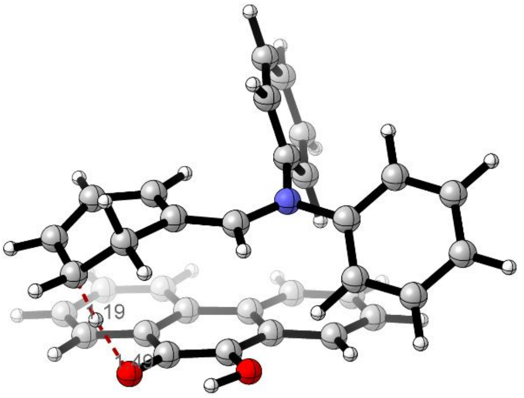
Fig S11. Aromatization energy profiles of enamine **1a-Morp** via consecutive dehydrogenation and hydride-abstraction steps mediated by CQ or COCA. M062x/6-311++g(d,p)//M062x/6-31+g(d,p) CPCM(toluene) emp=gd3



1a-A4-PQ-TS1



1a-A6-PQ-TS1



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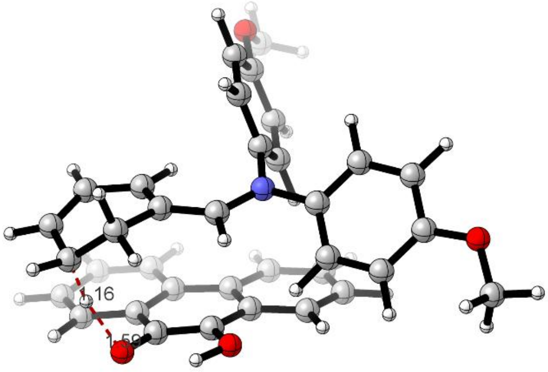

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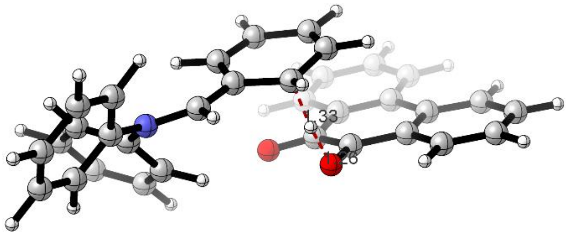
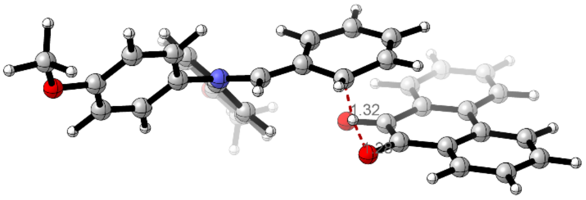


1a-A4-PQ-TS3

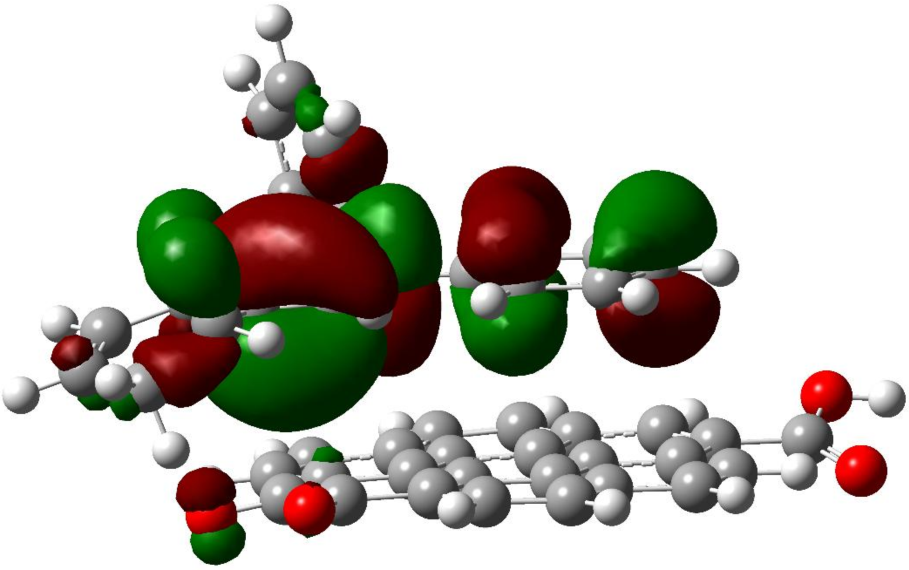


1a-A6-PQ-TS3

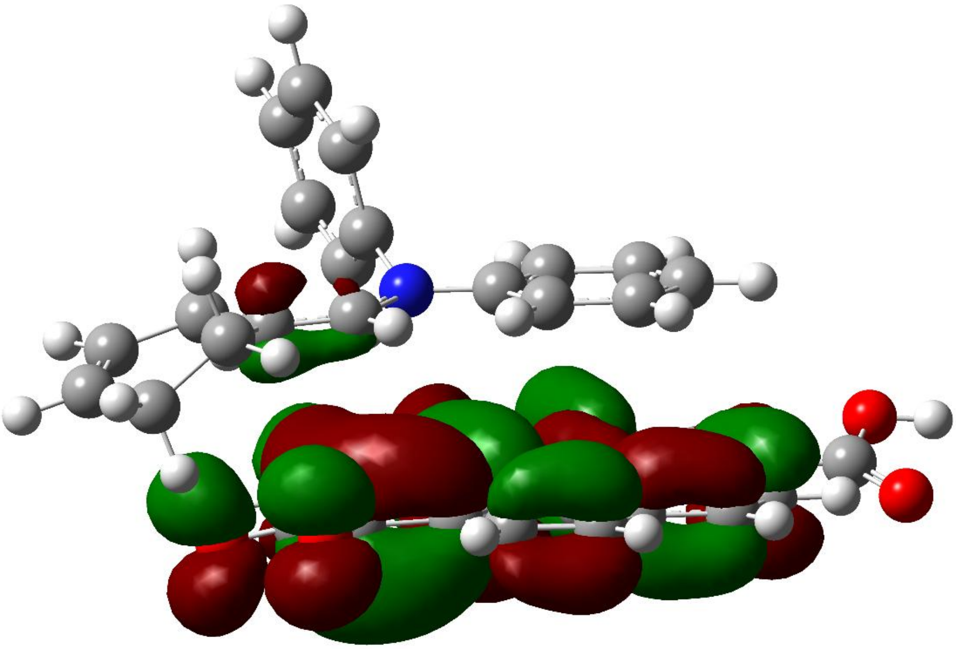
Frontier molecular orbitals of van der Waals complexes

Enamine on CQCA

A) **1a-A4-CQCA**



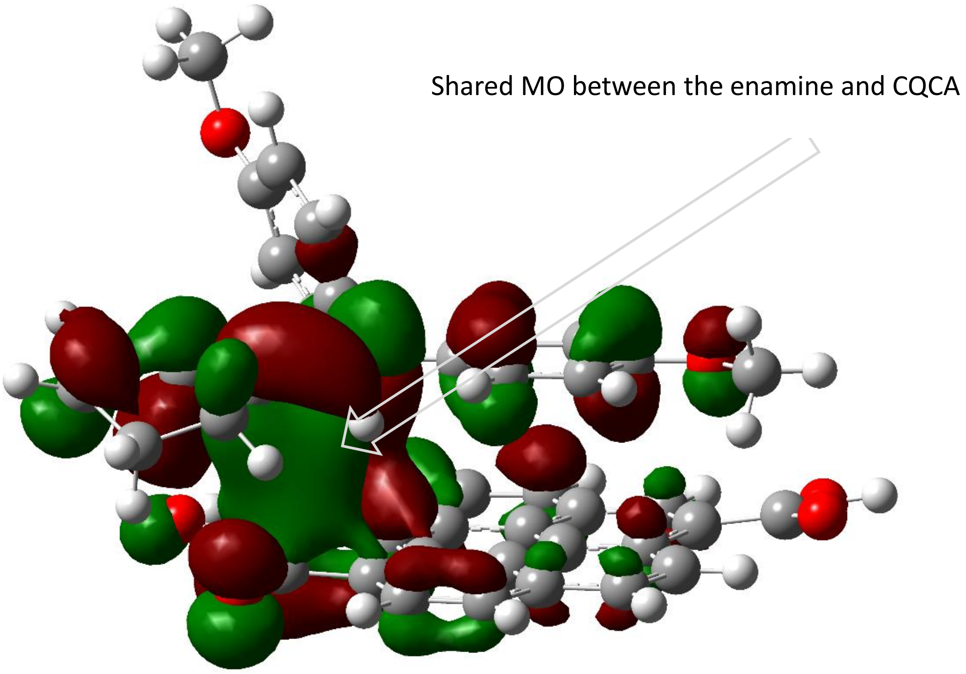
HOMO -6.472 eV



LUMO -2.667 eV MO gap= 3.805

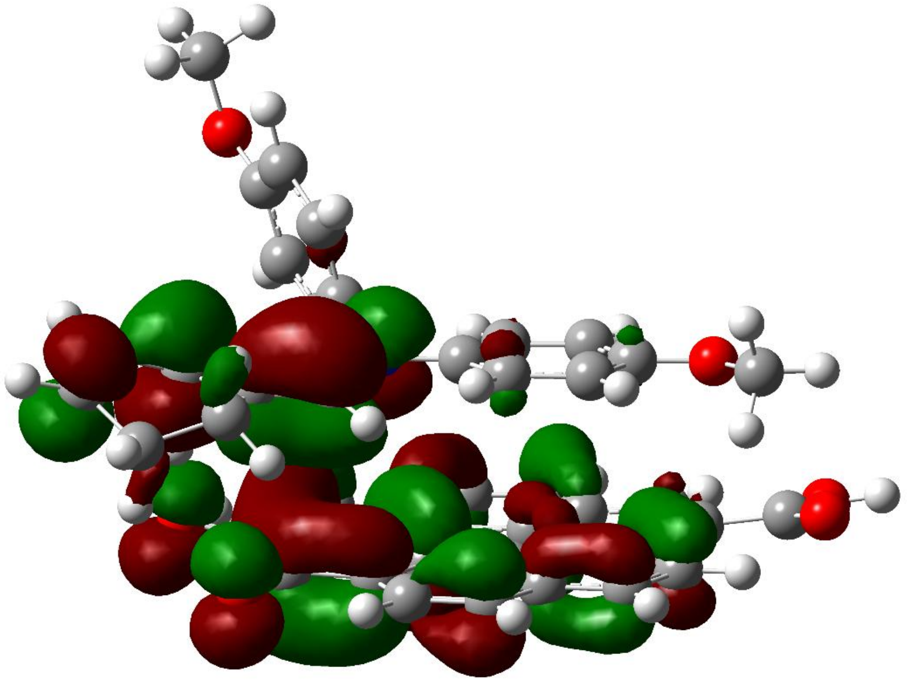
NBO charge -0.0150 CQCA +0.015 enamine

B) **1a-A6-CQCA**



Shared MO between the enamine and CQCA

HOMO -6.264 eV



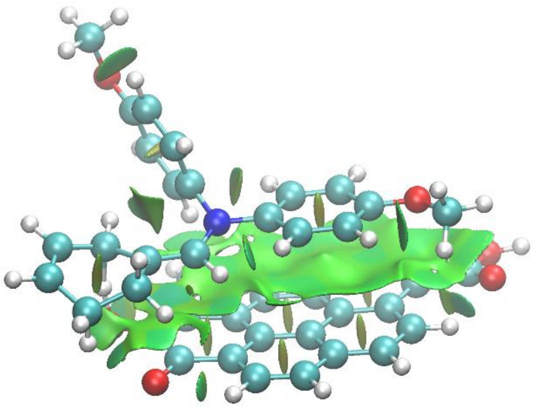
LUMO -2.631 eV MO gap= 3.633

NBO charge -0.03539 CQCA +0.03539 enamine

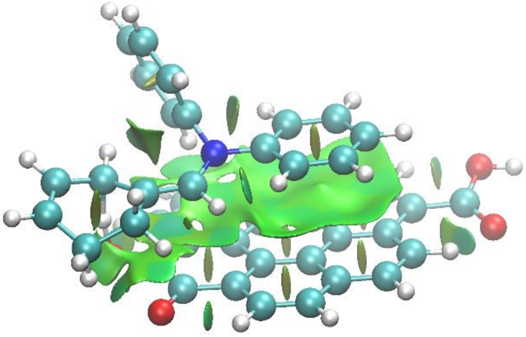
-Strong ground state electronic coupling: π-π-stacking with some charge transfer character

NCI plots

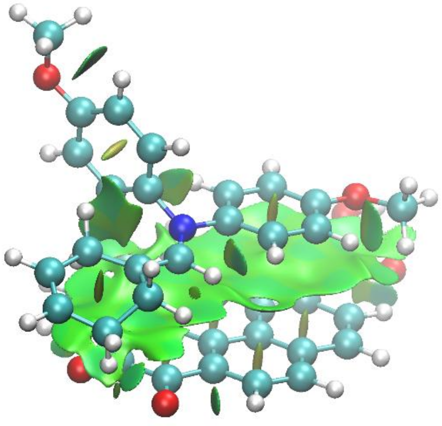
NCI plot visualization (with VMD) of TS1 and vdW structures of **1a**-**A4** and **1a**-**A6** with CQCA. In G16 optimizations a name.wfx output file was requested the in-keyword list (output.wfx). Fine resolution was used in the NCI plot software[11] to generate name-grad-cube, name-dens.cube and name.vmd files. These files were used in VMD[12] visualization software for plotting of noncovalent interactions (with default graphical presentation parameters).



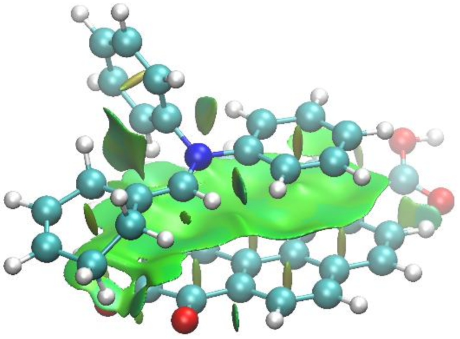
1a-**A6**-CQCA-TS1



1a-**A4**- CQCA TS1



1a-**A6**- CQCA vdW



1a-**A4**-CQCA vdW

SET and HAT study

For comparison, the Gibbs free energies of single-electron transfer (SET) and hydrogen atom transfer (HAT) processes were calculated between enamines (**1a-A4**, **1a-A6**, and **A1**-Morp) and quinonoid models (PQ, CQ, and CQCA) (Table S8). The SET processes were found to be highly endergonic, with energies ranging from 56.0 to 67.1 kcal/mol, depending on the enamine and quinone model employed. The corresponding HAT processes were also endergonic, though significantly less so, with energies in the range of 10.7–13.8 kcal/mol. In contrast, the thermodynamically favorable pathway proceeds via ionic complexes formed between cationic intermediates and hydroquinone anions, which were calculated to be exergonic (Figs. 4 and S8).

Table S13. Enamine SET and HAT reaction Gibbs free energies by PQ, CQ, CQCA, respectively. (kcal/mol (M06-2x/6-311++g(d,p)//M062x/6-31+g(d,p) CPCM(toluene) emp=gd3))

SET	HAT
$\mathbf{PQ} + \mathbf{1a\text{-}A4} \xrightarrow{\Delta G = 67.1} \mathbf{PQ}^{\bullet-} + \mathbf{1a\text{-}A4}^{\bullet+}$	$\mathbf{PQ} + \mathbf{1a\text{-}A4} \xrightarrow{\Delta G = 13.8} \mathbf{HPQ}^{\bullet} + \mathbf{1a\text{-}A4}^{\bullet}$
$\mathbf{PQ} + \mathbf{1a\text{-}A6} \xrightarrow{\Delta G = 57.5} \mathbf{PQ}^{\bullet-} + \mathbf{1a\text{-}A6}^{\bullet+}$	$\mathbf{PQ} + \mathbf{1a\text{-}A6} \xrightarrow{\Delta G = 13.4} \mathbf{HPQ}^{\bullet} + \mathbf{1a\text{-}A6}^{\bullet}$
$\mathbf{PQ} + \mathbf{1a\text{-}Morp} \xrightarrow{\Delta G = 63.3} \mathbf{PQ}^{\bullet-} + \mathbf{1a\text{-}Morp}^{\bullet+}$	$\mathbf{PQ} + \mathbf{1a\text{-}Morp} \xrightarrow{\Delta G = 13.2} \mathbf{HPQ}^{\bullet} + \mathbf{1a\text{-}Morp}^{\bullet}$
$\mathbf{CQ} + \mathbf{1a\text{-}A4} \xrightarrow{\Delta G = 61.9} \mathbf{CQ}^{\bullet-} + \mathbf{1a\text{-}A4}^{\bullet+}$	$\mathbf{CQ} + \mathbf{1a\text{-}A4} \xrightarrow{\Delta G = 11.5} \mathbf{HCQ}^{\bullet} + \mathbf{1a\text{-}A4}^{\bullet}$
$\mathbf{CQ} + \mathbf{1a\text{-}A6} \xrightarrow{\Delta G = 52.3} \mathbf{CQ}^{\bullet-} + \mathbf{1a\text{-}A6}^{\bullet+}$	$\mathbf{CQ} + \mathbf{1a\text{-}A6} \xrightarrow{\Delta G = 11.0} \mathbf{HCQ}^{\bullet} + \mathbf{1a\text{-}A6}^{\bullet}$
$\mathbf{CQ} + \mathbf{1a\text{-}Morp} \xrightarrow{\Delta G = 58.1} \mathbf{CQ}^{\bullet-} + \mathbf{1a\text{-}Morp}^{\bullet+}$	$\mathbf{CQ} + \mathbf{1a\text{-}Morp} \xrightarrow{\Delta G = 10.9} \mathbf{HCQ}^{\bullet} + \mathbf{1a\text{-}Morp}^{\bullet}$
$\mathbf{CQCA} + \mathbf{1a\text{-}A4} \xrightarrow{\Delta G = 59.8} \mathbf{CQCA}^{\bullet-} + \mathbf{1a\text{-}A4}^{\bullet+}$	$\mathbf{CQCA} + \mathbf{1a\text{-}A4} \xrightarrow{\Delta G = 11.2} \mathbf{HCQCA}^{\bullet} + \mathbf{1a\text{-}A4}^{\bullet}$
$\mathbf{CQCA} + \mathbf{1a\text{-}A6} \xrightarrow{\Delta G = 50.2} \mathbf{CQCA}^{\bullet-} + \mathbf{1a\text{-}A6}^{\bullet+}$	$\mathbf{CQCA} + \mathbf{1a\text{-}A6} \xrightarrow{\Delta G = 10.8} \mathbf{HCQCA}^{\bullet} + \mathbf{1a\text{-}A6}^{\bullet}$
$\mathbf{CQCA} + \mathbf{1a\text{-}Morp} \xrightarrow{\Delta G = 56.0} \mathbf{CQCA}^{\bullet-} + \mathbf{1a\text{-}Morp}^{\bullet+}$	$\mathbf{CQCA} + \mathbf{1a\text{-}Morp} \xrightarrow{\Delta G = 10.7} \mathbf{HCQCA}^{\bullet} + \mathbf{1a\text{-}Morp}^{\bullet}$

Table S14. Calculated energetics of open-shell intermediates associated with SET and HAT processes (Table S8). (M06-2x/6-311++g(d,p)//M062x/6-31+g(d,p) CPCM(toluene) emp=gd3))

Entry	Structure	*ΔG* (in a.u.)	*ΔH* (in a.u.)	name (XYZ)*
1	$PQ^{\bullet-}$	-688.638873	-688.588594	PQ-rA
2	$CQ^{\bullet-}$	-1070.865864	-1070.806099	CQ-rA
3	$CQCA^{\bullet-}$	-1259.42918	-1259.362903	CQCA-rA
4	$1a\text{-}A4^{\bullet+}$	-789.539215	-789.476859	1a-A4-rK
5	$1a\text{-}A6^{\bullet+}$	-1018.52044	-1018.447441	1a-A6-rK
6	$1a\text{-}Morp^{\bullet+}$	-558.791537	-558.740493	1a-Morp-rK
7	$HPQ^{\bullet}$	-689.117983	-689.067954	HPQ-r
8	$HCQ^{\bullet}$	-1071.340471	-1071.28087	HCQ-r
9	$HCQCA^{\bullet}$	-1259.900761	-1259.834573	HCQCA-r
10	$1a\text{-}A4^{\bullet}$	-789.145005	-789.083088	1a-A4-r
11	$1a\text{-}A6^{\bullet}$	-1018.111584	-1018.038255	1a-A6-r
12	$1a\text{-}Morp^{\bullet}$	-558.3922	-558.341652	1a-Morp-r

*rA= radical anion, rK= radical cation, r=neutral radical

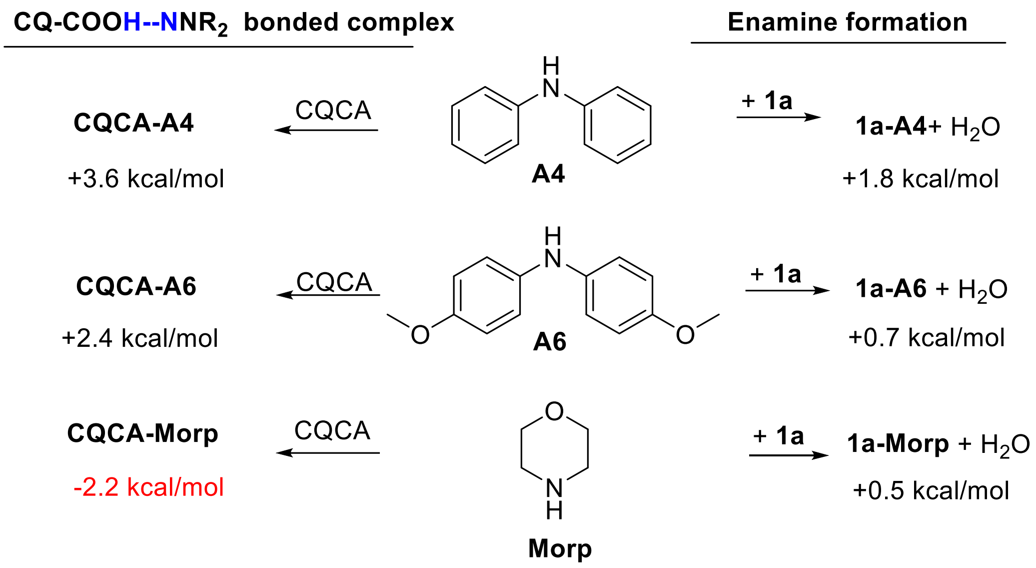


Figure S12. Free energies comparing enamine formation and competing H-bonded acid–side-complex formation with CQCA (Table S10).

Thermodynamics for amine organo-co-catalysis (with **A4**, **A6** and morpholine) were computed, both for enamine formation with **1a** and for H-bonded acid complex formation with **CQCA** (Figure S9, Table S10). Strikingly, the latter is exergonic only for morpholine ($\Delta G = -2.2$ kcal mol^{-1}), whereas it is endergonic for the diarylamines ($\Delta G = +3.6$ and $+2.4$ kcal mol^{-1} for **A4** and **A6**, respectively). This suggests that morpholine is prone to act as a Brønsted base under the reaction conditions, which may explain its sluggish catalytic performance.

Table S15. Calculated energetics enamine formation and the competing H-bonded acid–side-complex formation with CQCA for Figure S9.

Entry	Structure	ΔG (in a.u.)	ΔH (in a.u.)	name (XYZ)*
1	morpholine	-287.647312	-287.612854	Morp
2	A4 (NHPh$_2$)	-518.403060	-518.355531	A4
3	A6 (NH(4-OMePh)$_2$)	-747.367221	-747.308515	A6
4	1a	-347.782434	-347.742450	1a
5	H$_2$O	-76.42156	-76.4001	H$_2$O
6	Morp-CQCA-H-bond	-1546.953461	-1546.87163	Morph-CQCA-H-bond
7	A4-CQCA-H-bond	-1777.699844	-1777.60555	A4-CQCA-H-bond
8	A6-CQCA-H-bond	-2006.665963	-2006.56057	A6-CQCA-H-bond

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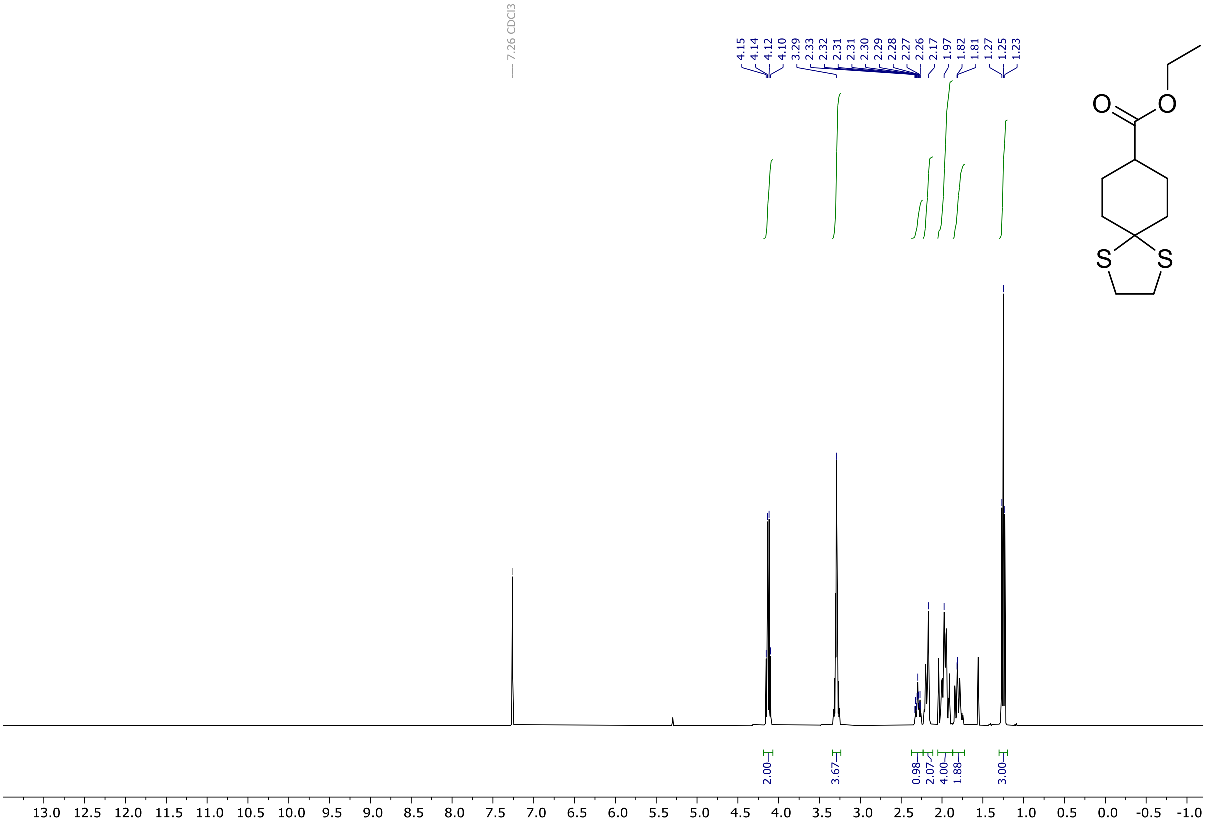
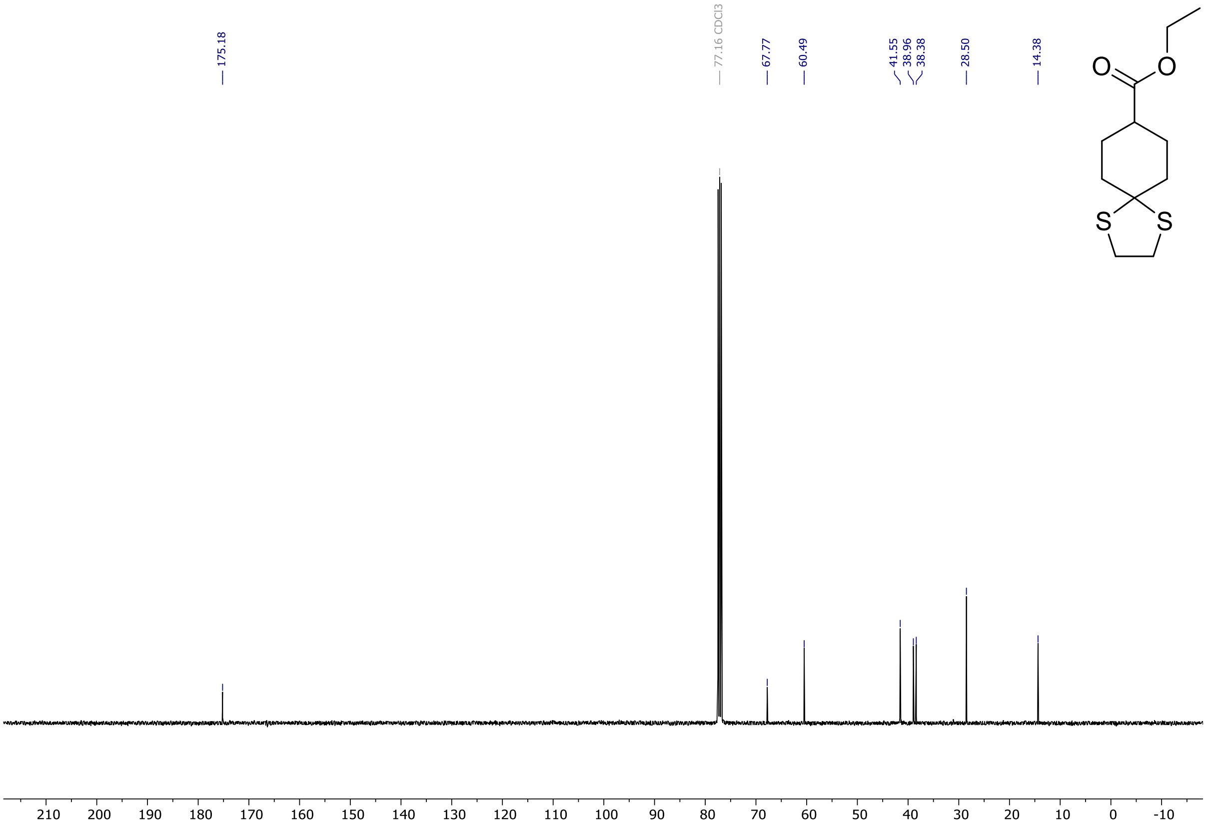
Copies of NMR spectra

^{1}H NMR (400 MHz, CDCl$_3$): SI2



^{13}C NMR (101 MHz, CDCl$_3$): SI2



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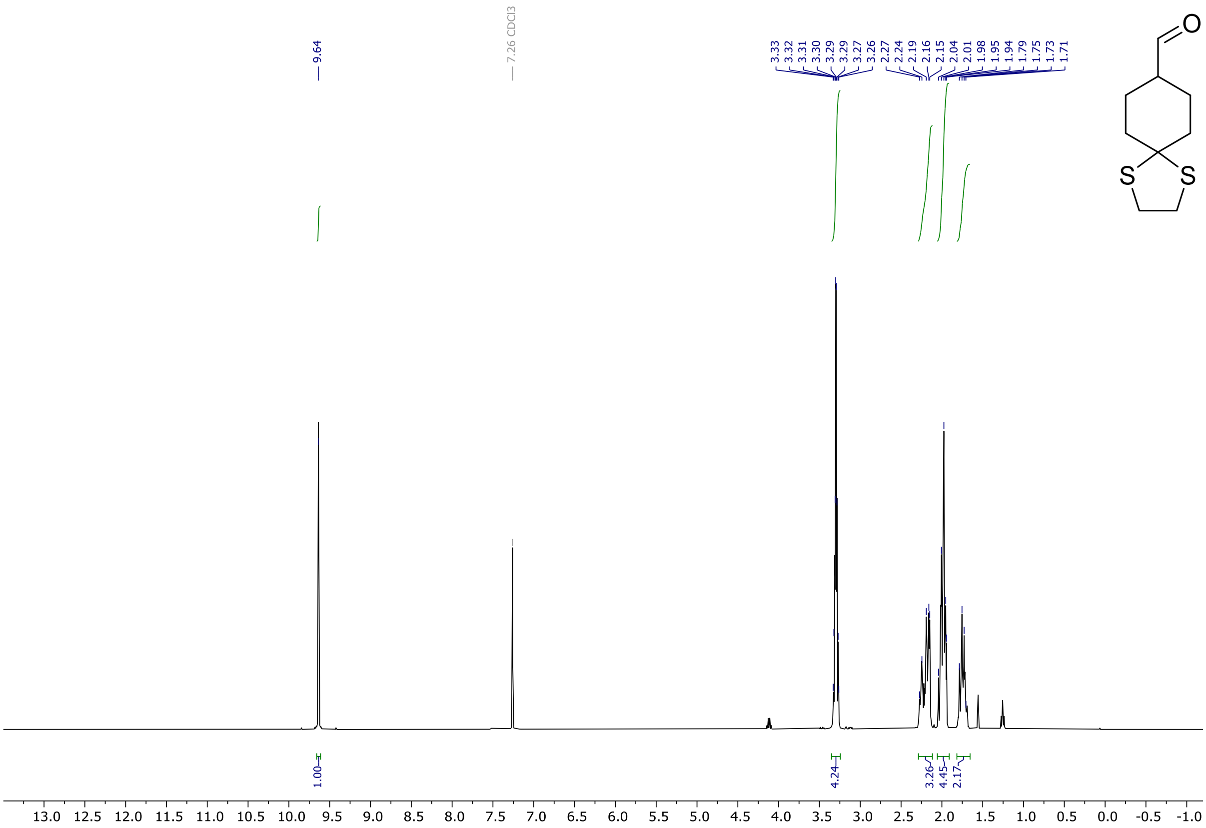

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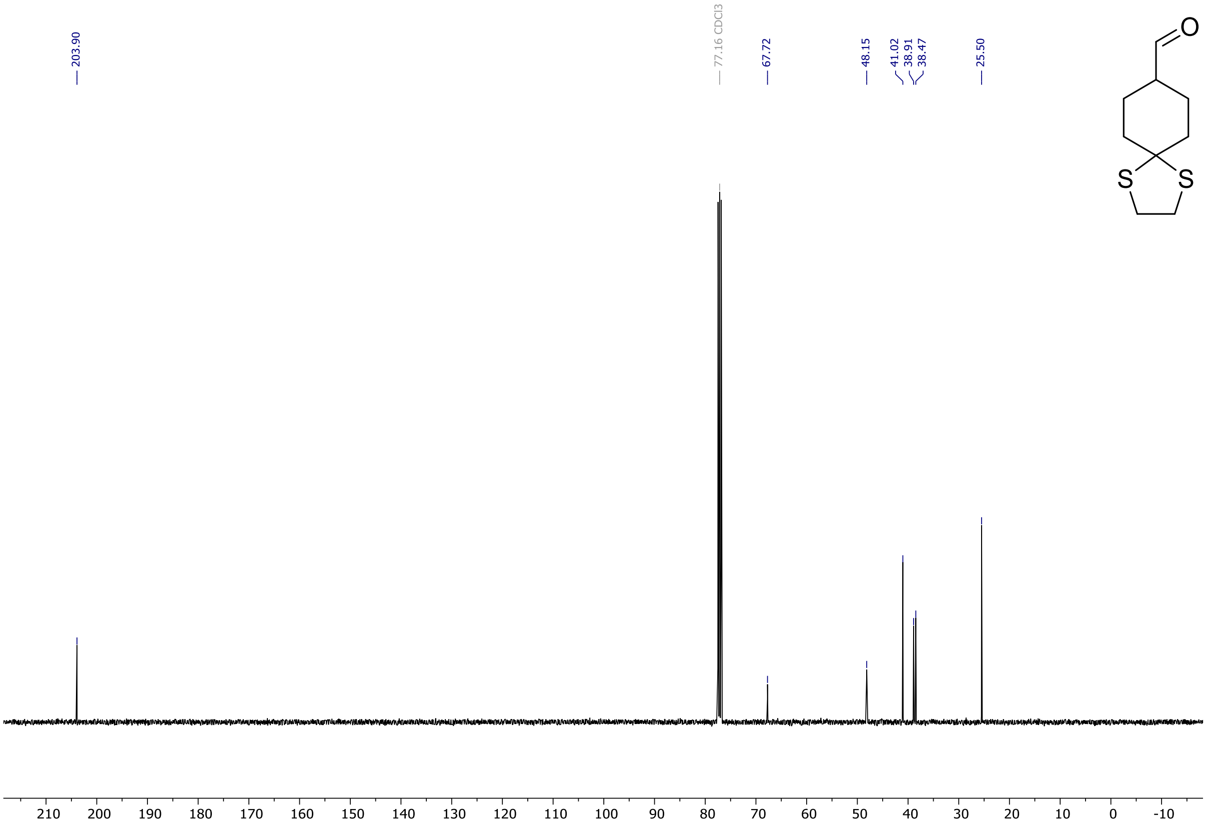

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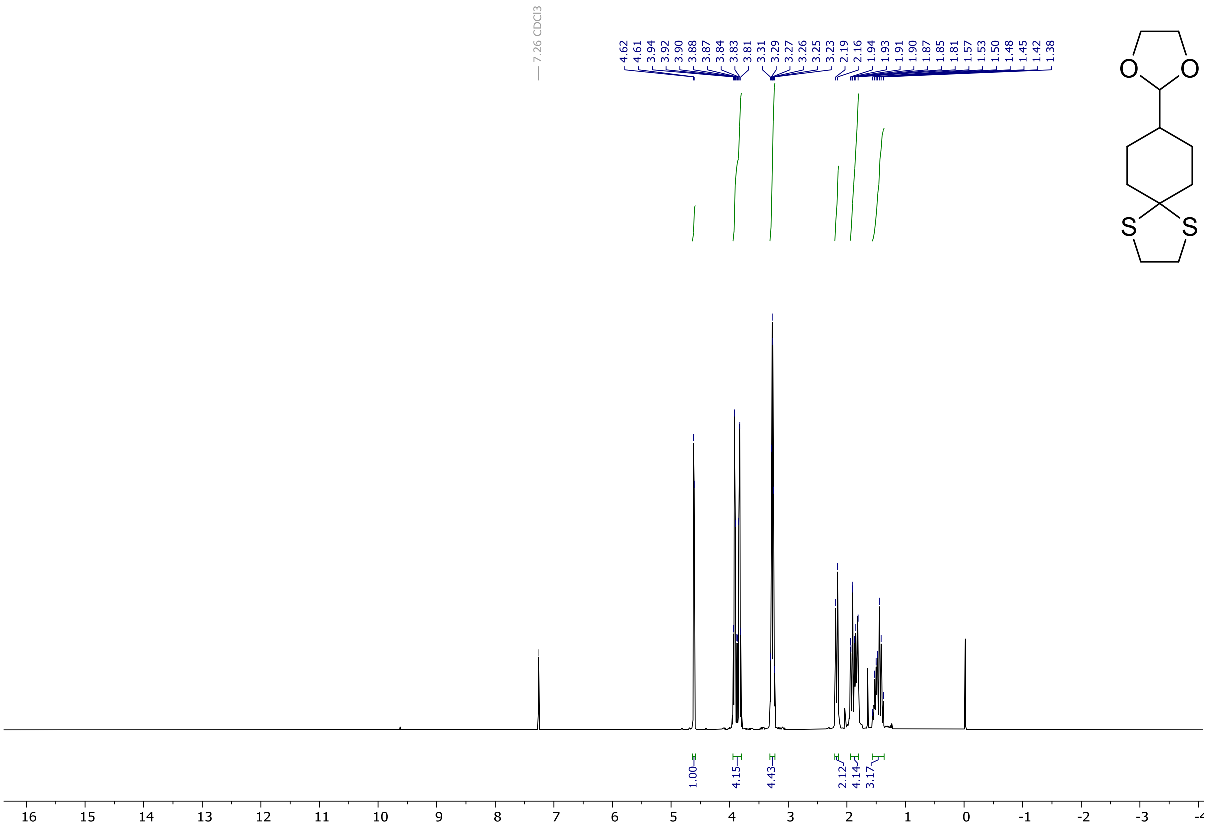

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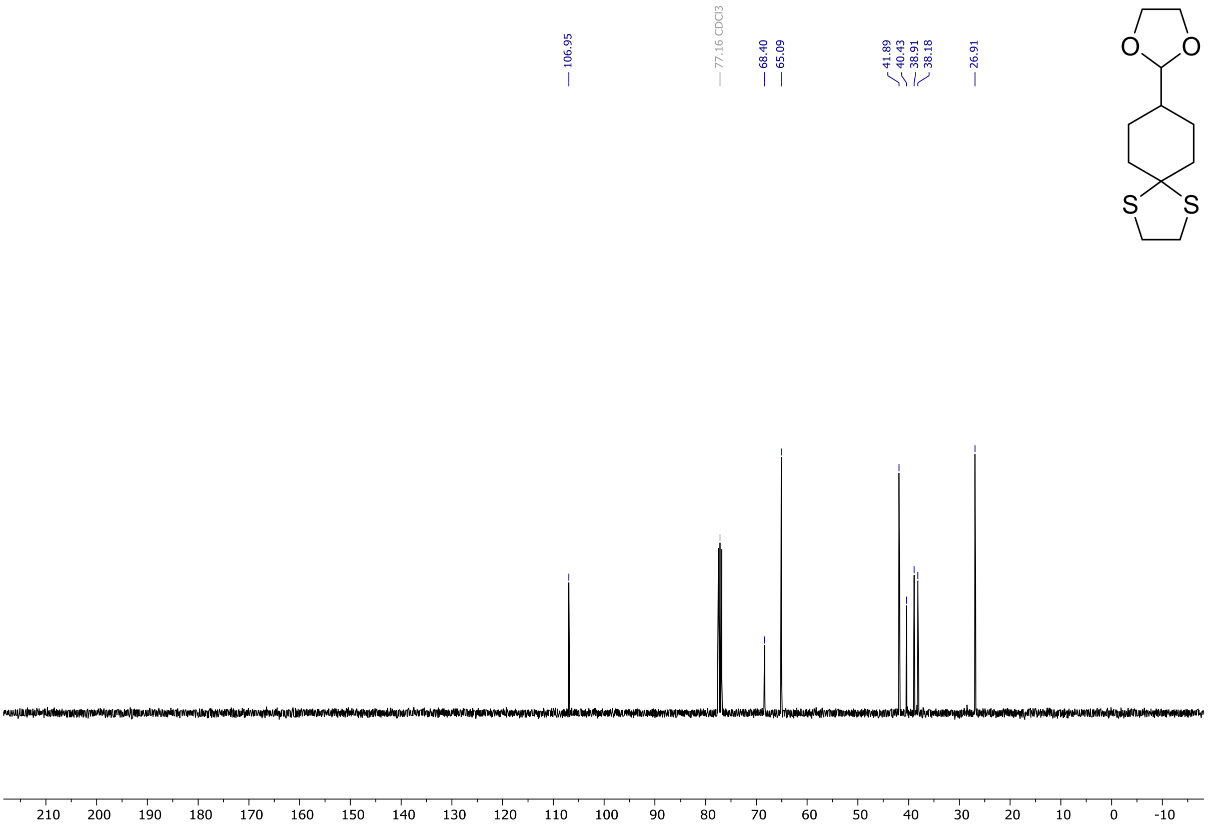

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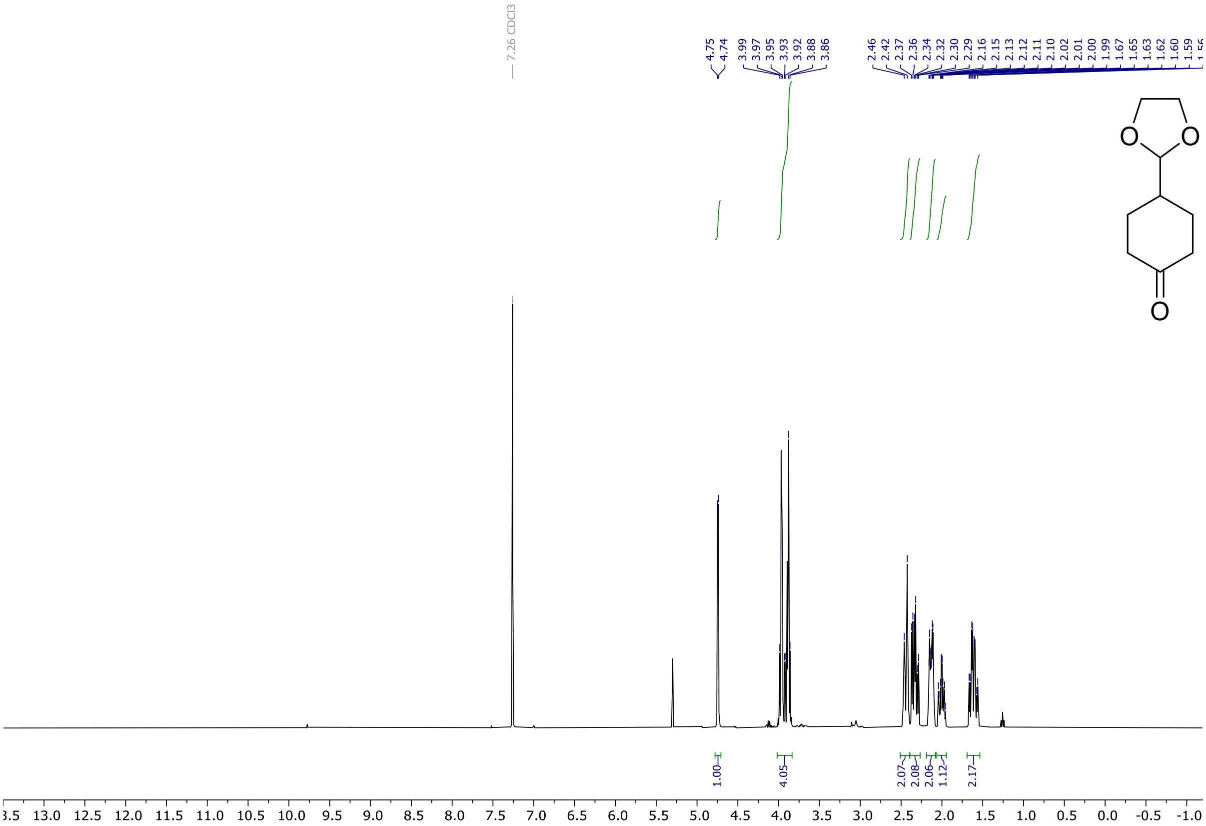

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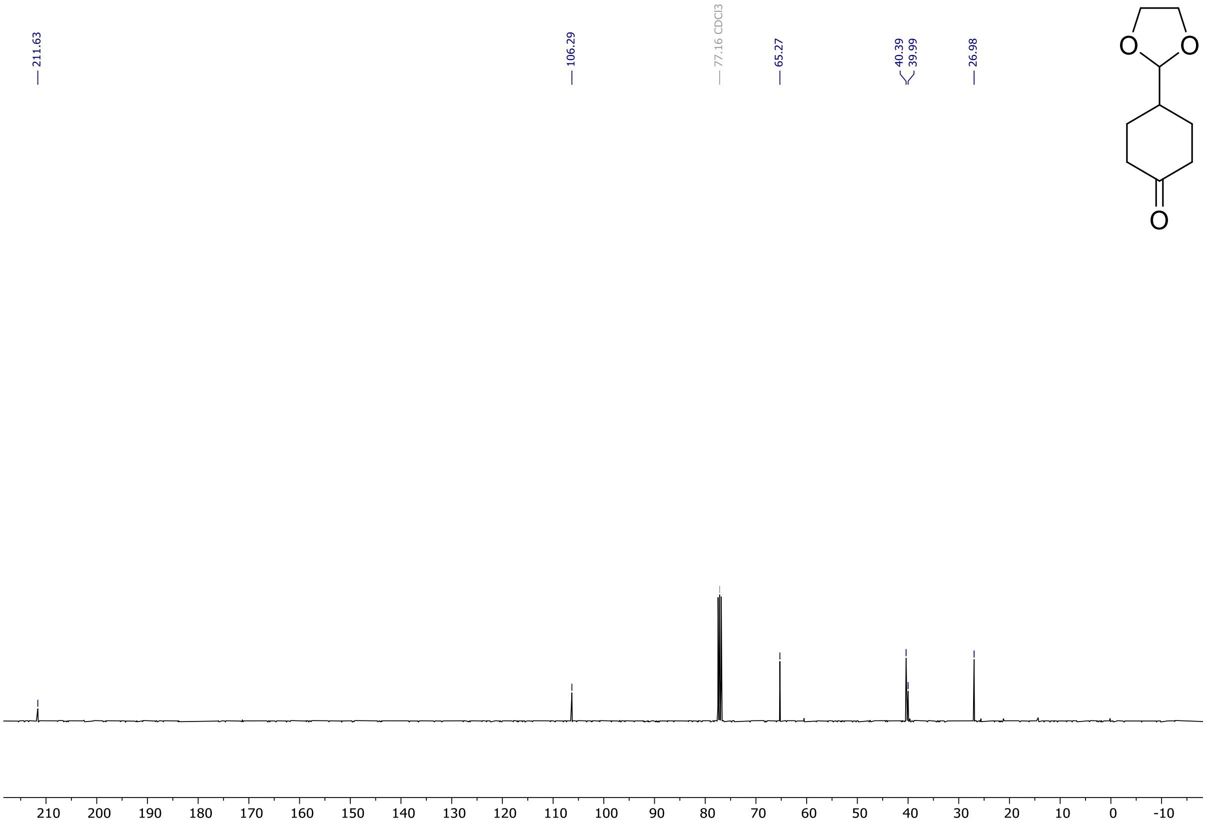

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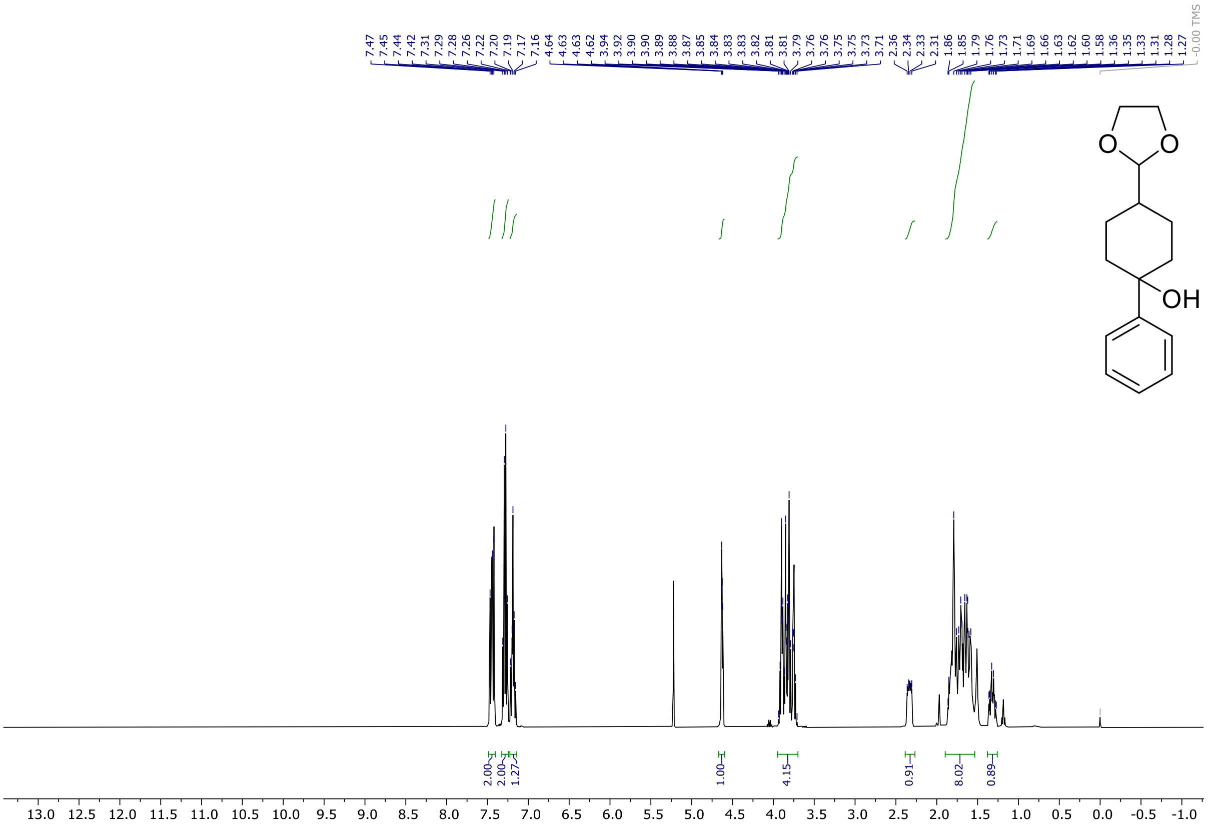
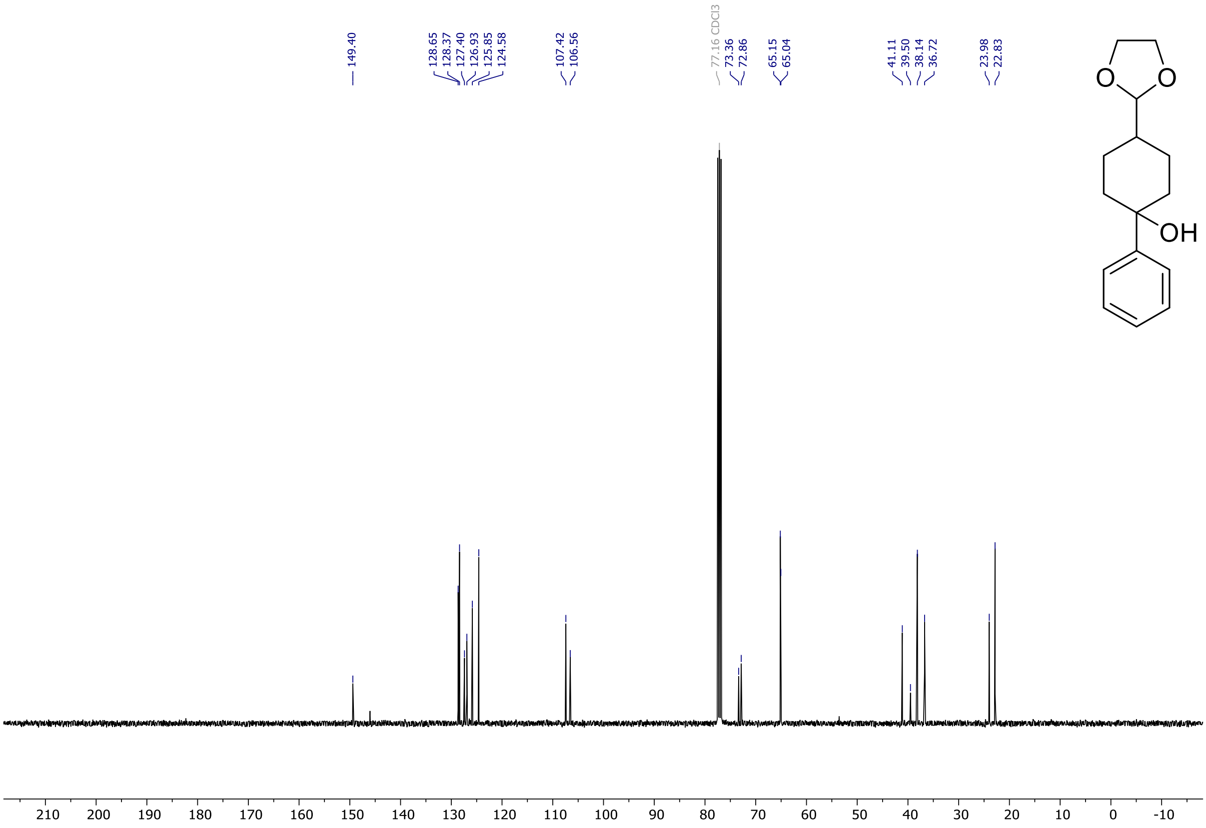
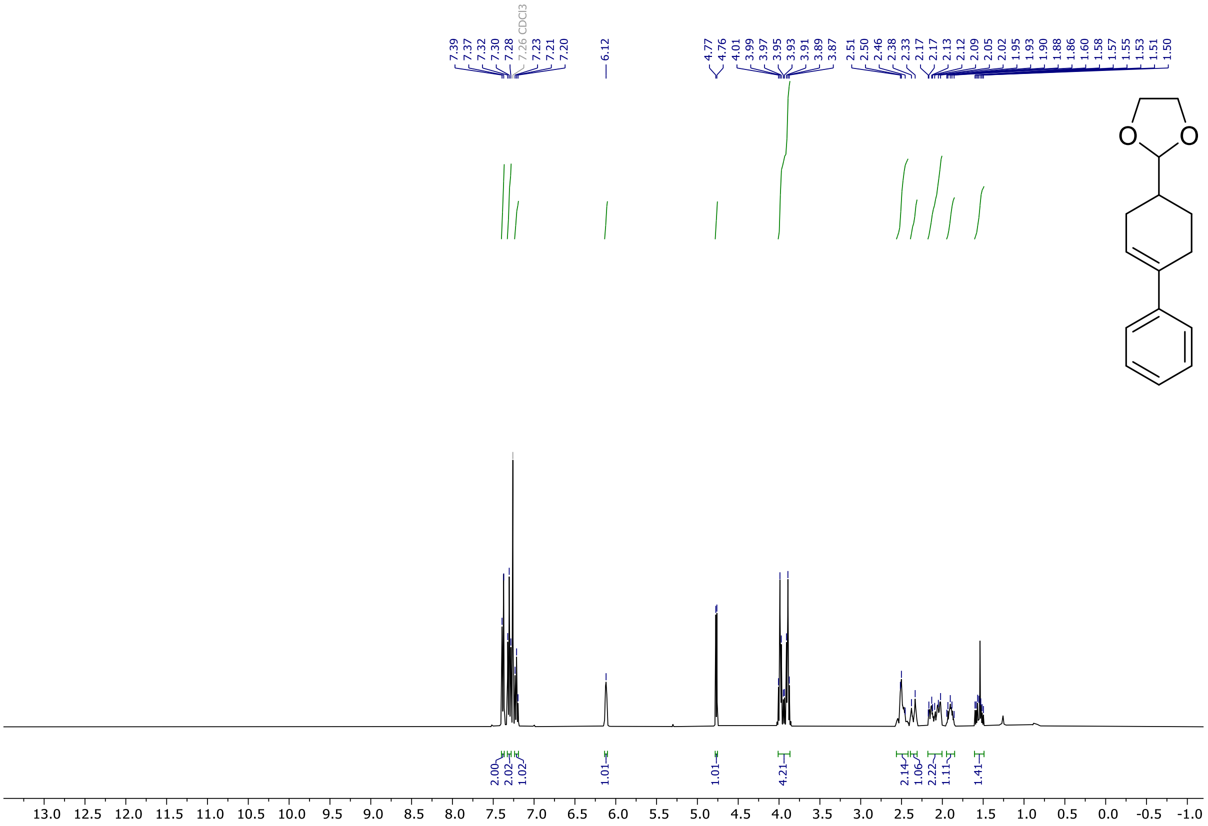


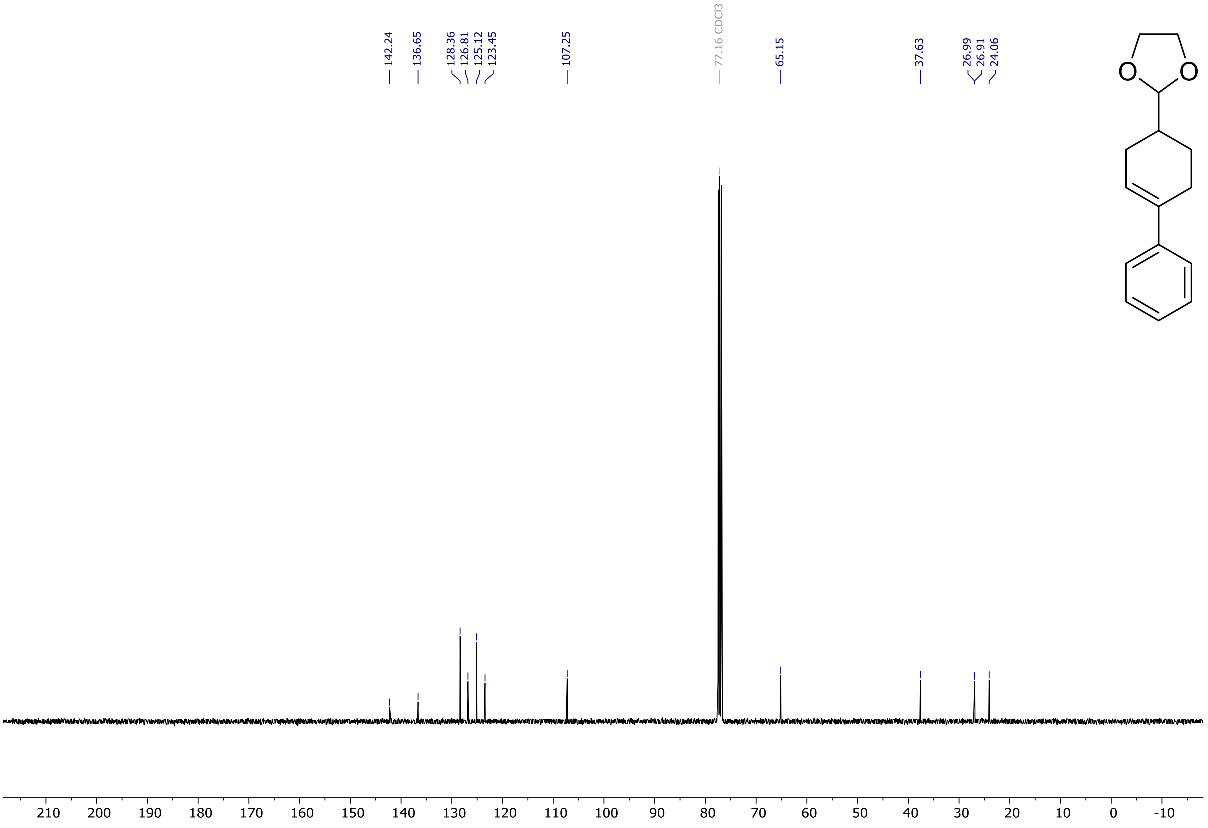
^{13}C NMR (101 MHz, CDCl$_3$): SI6



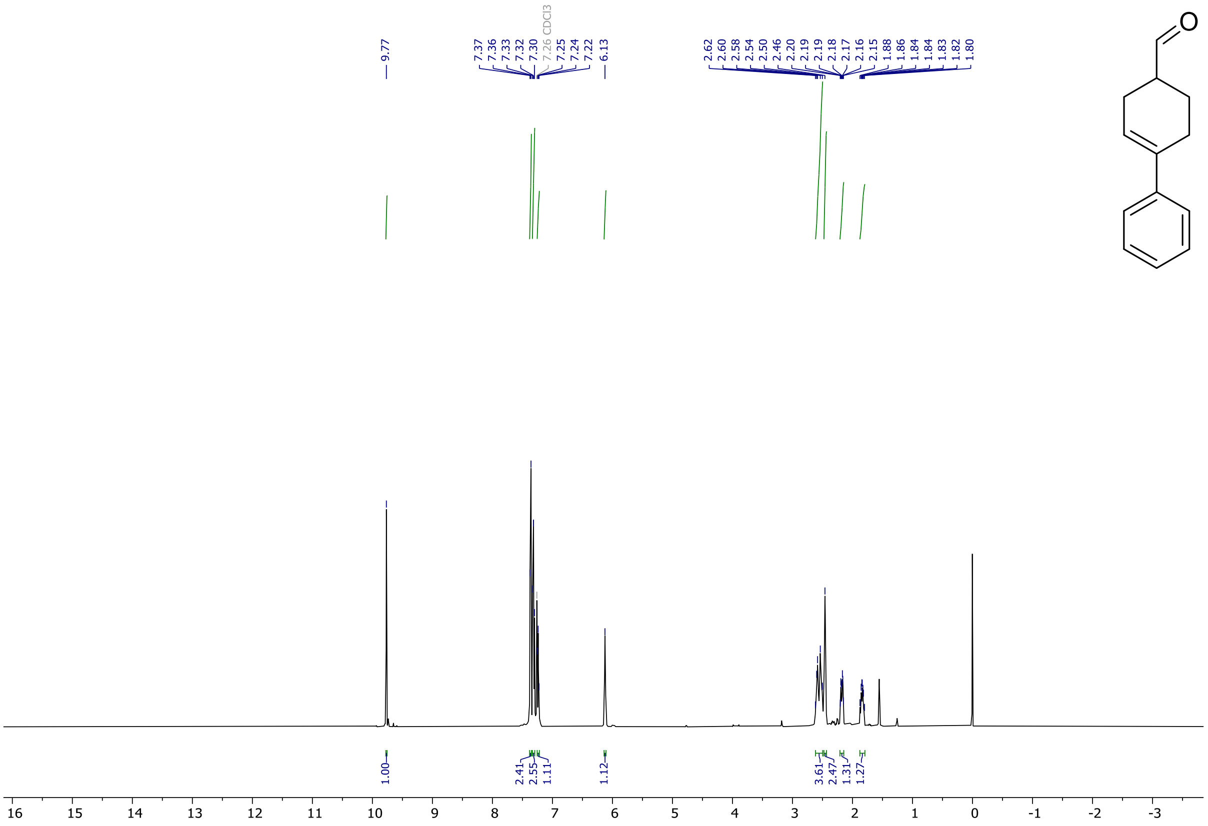
^{1}H NMR (400 MHz, CDCl$_3$): SI7



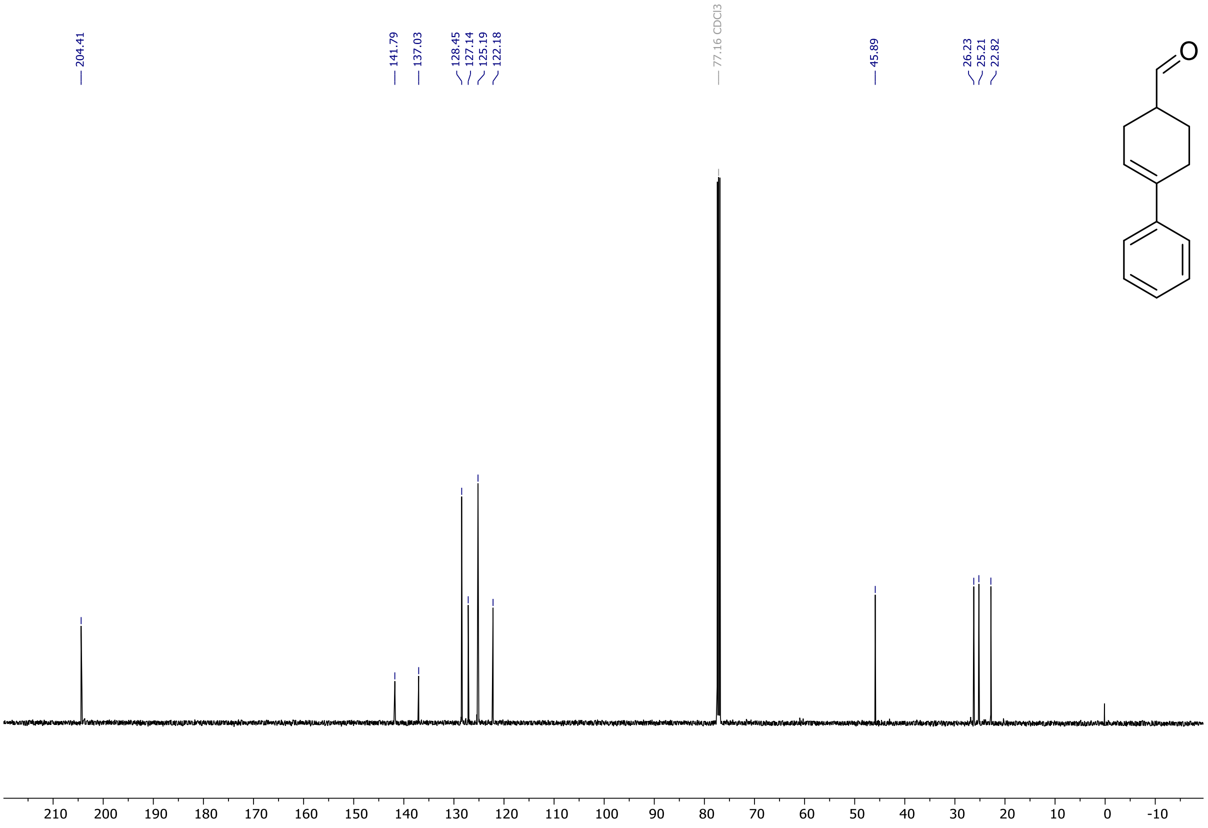
^{13}C NMR (101 MHz, CDCl$_3$): SI7



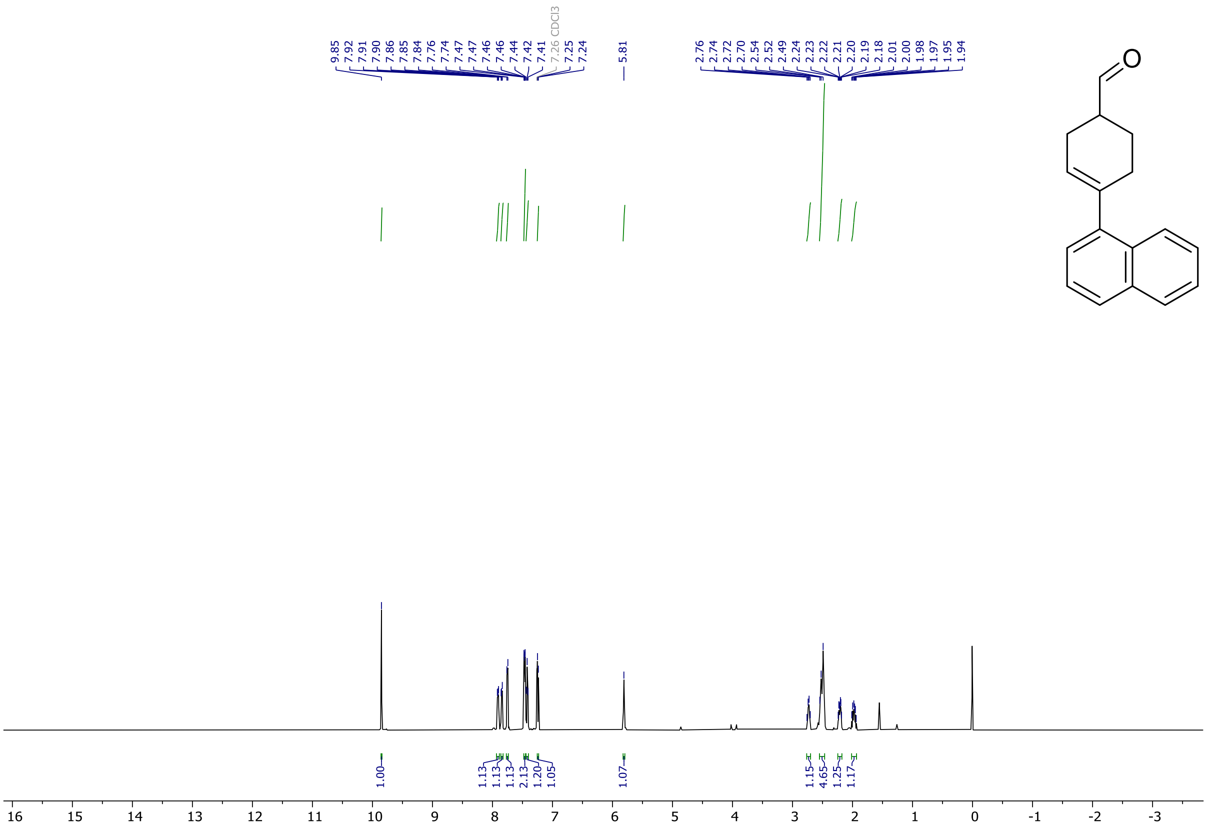
^{1}H NMR (500 MHz, CDCl$_3$): 1c



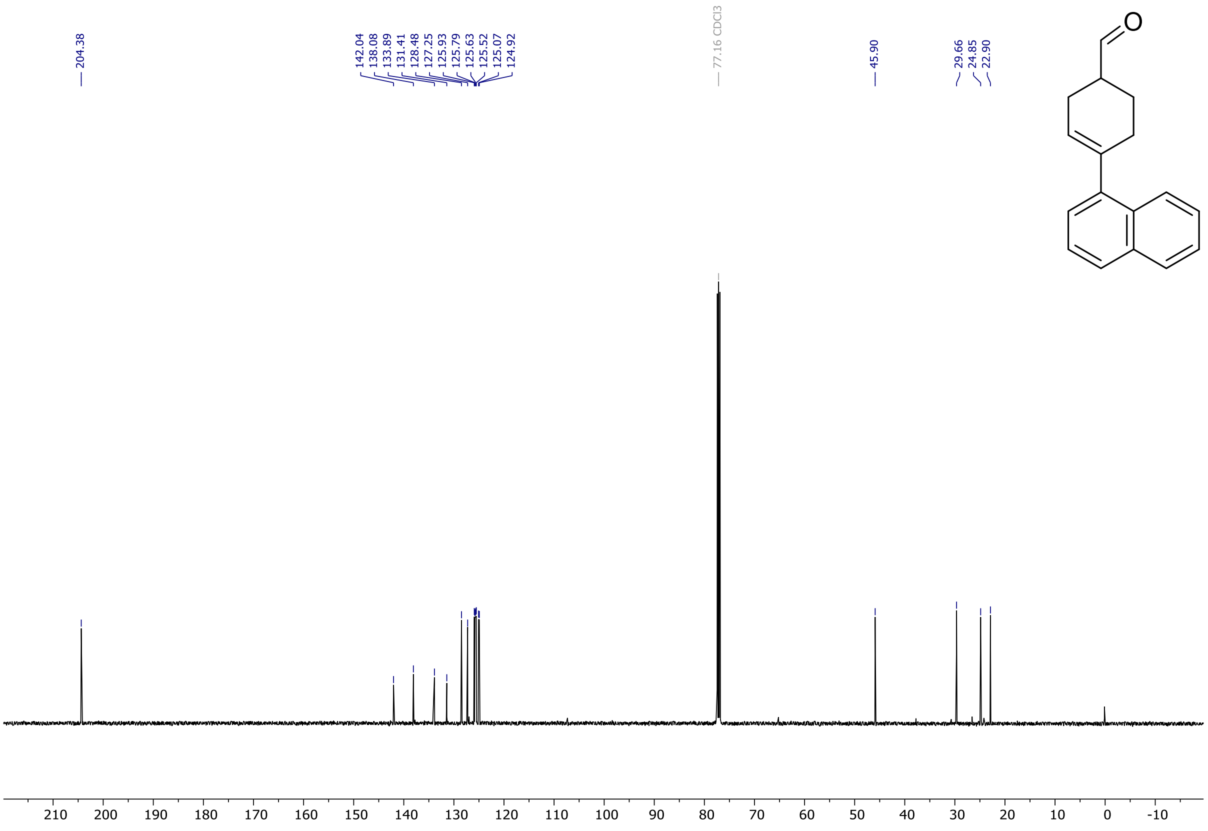
^{13}C NMR (126 MHz, CDCl$_3$): 1c



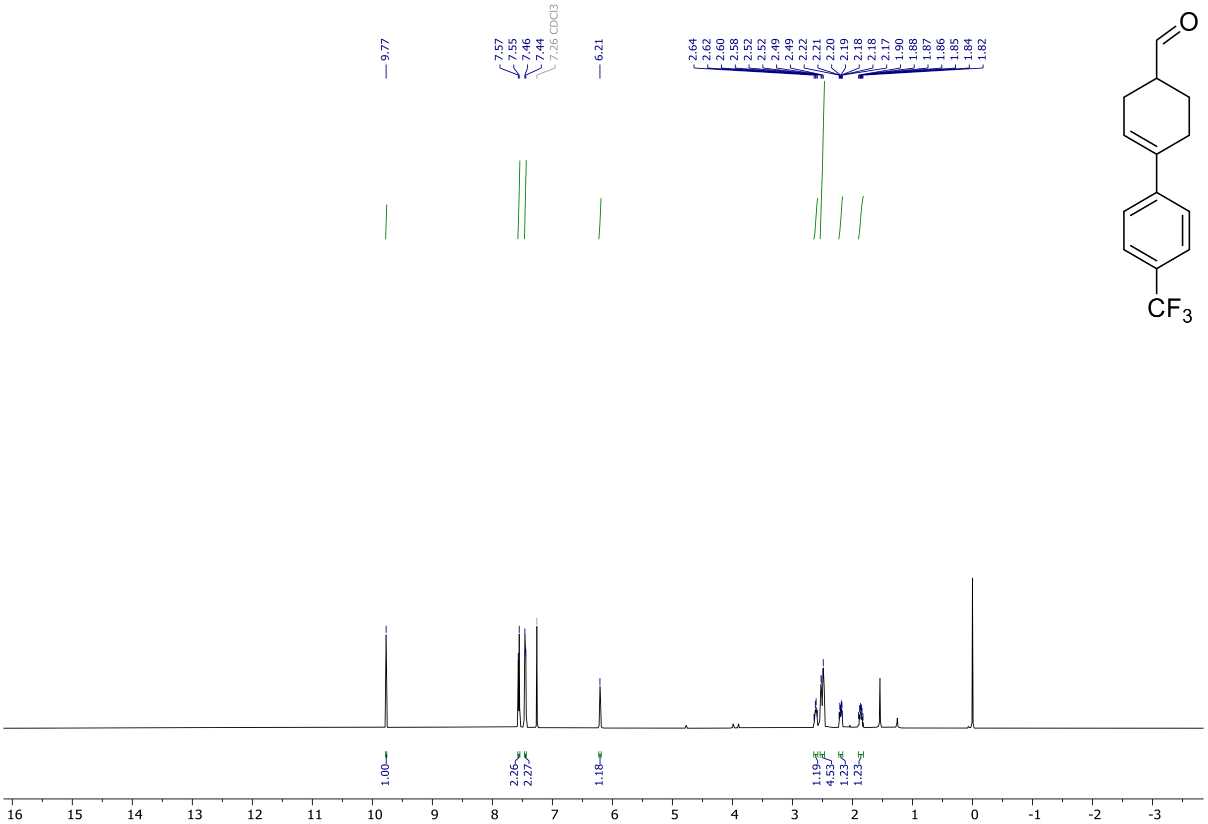
^{1}H NMR (500 MHz, CDCl$_3$): 1d



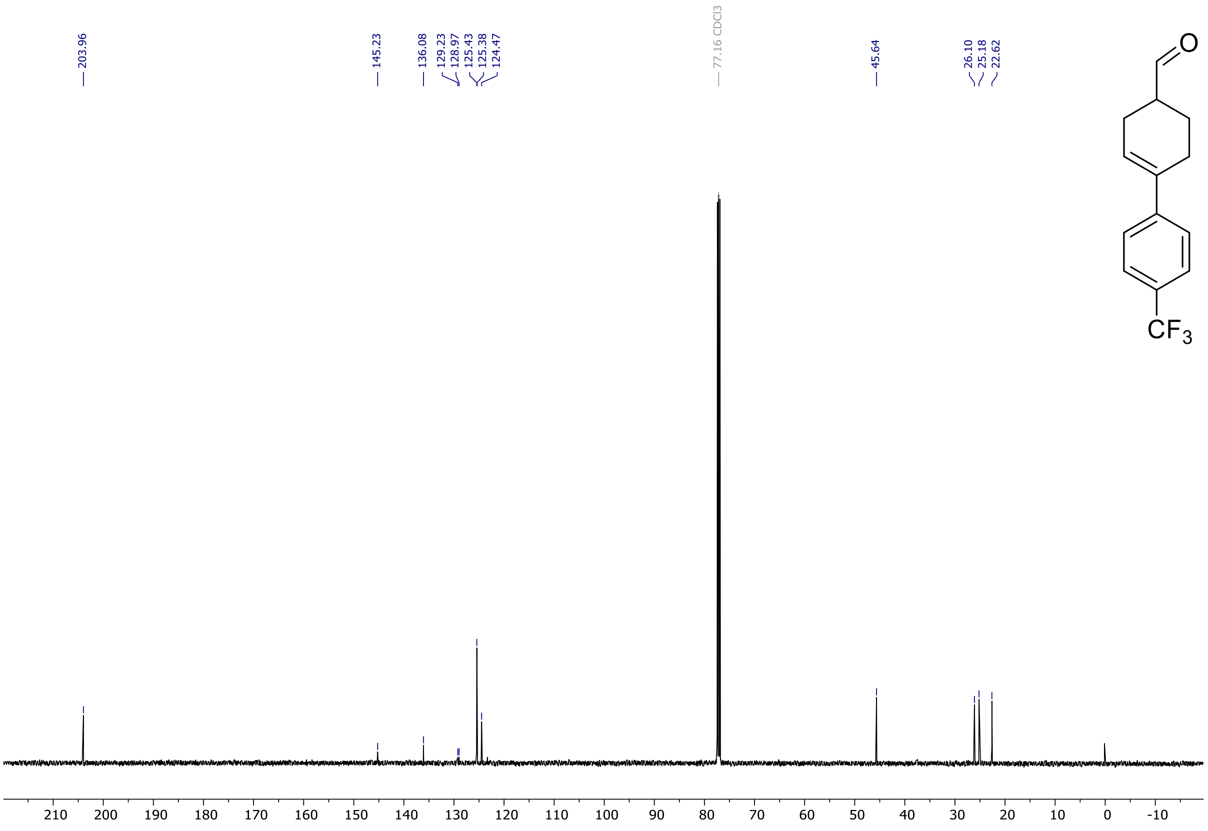
^{13}C NMR (126 MHz, CDCl$_3$): 1d



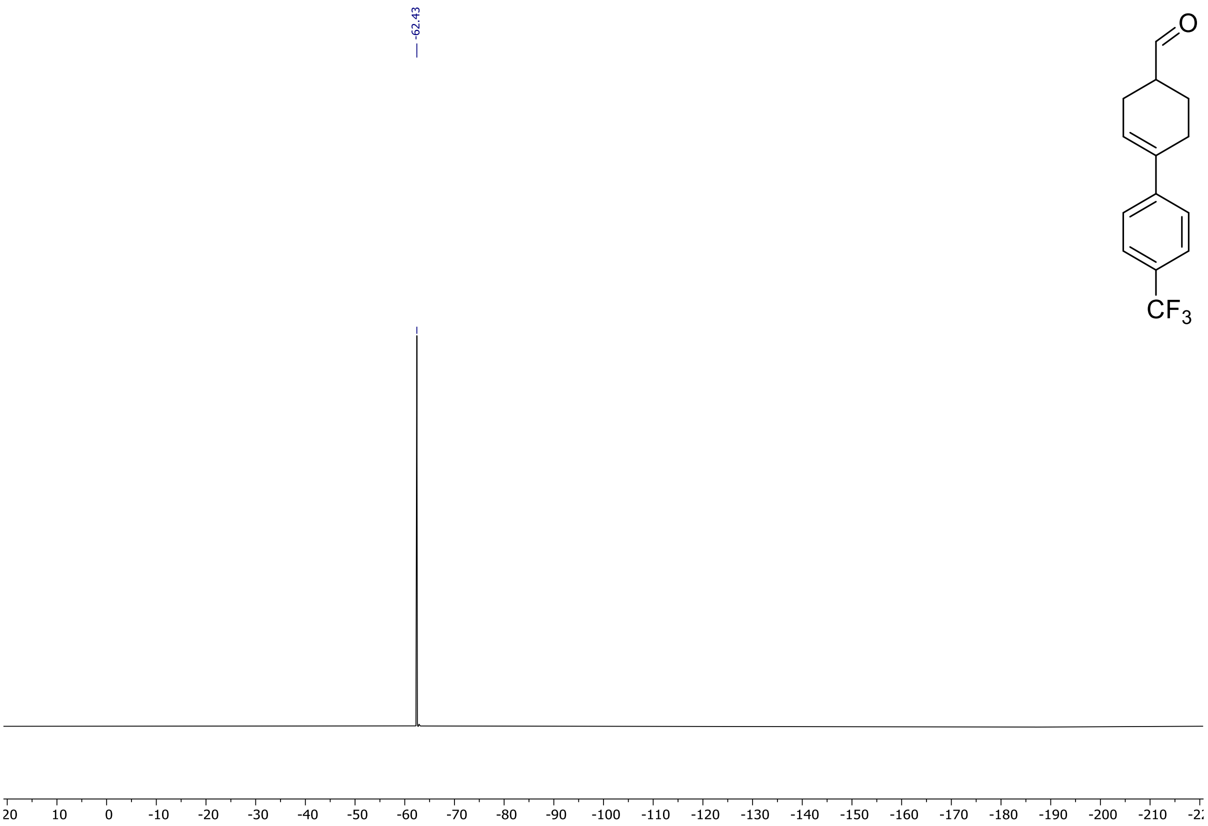
^{1}H NMR (500 MHz, CDCl$_3$): 1e



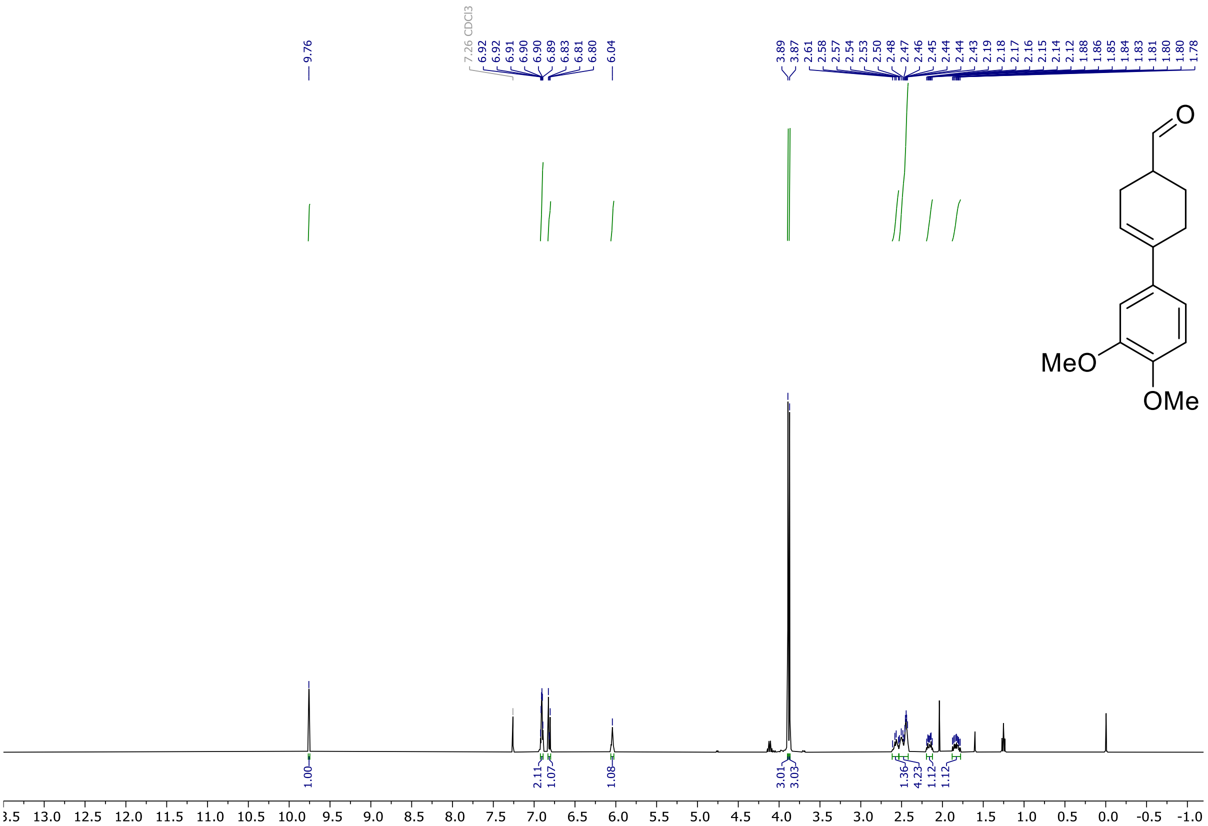
^{13}C NMR (126 MHz, CDCl$_3$): 1e



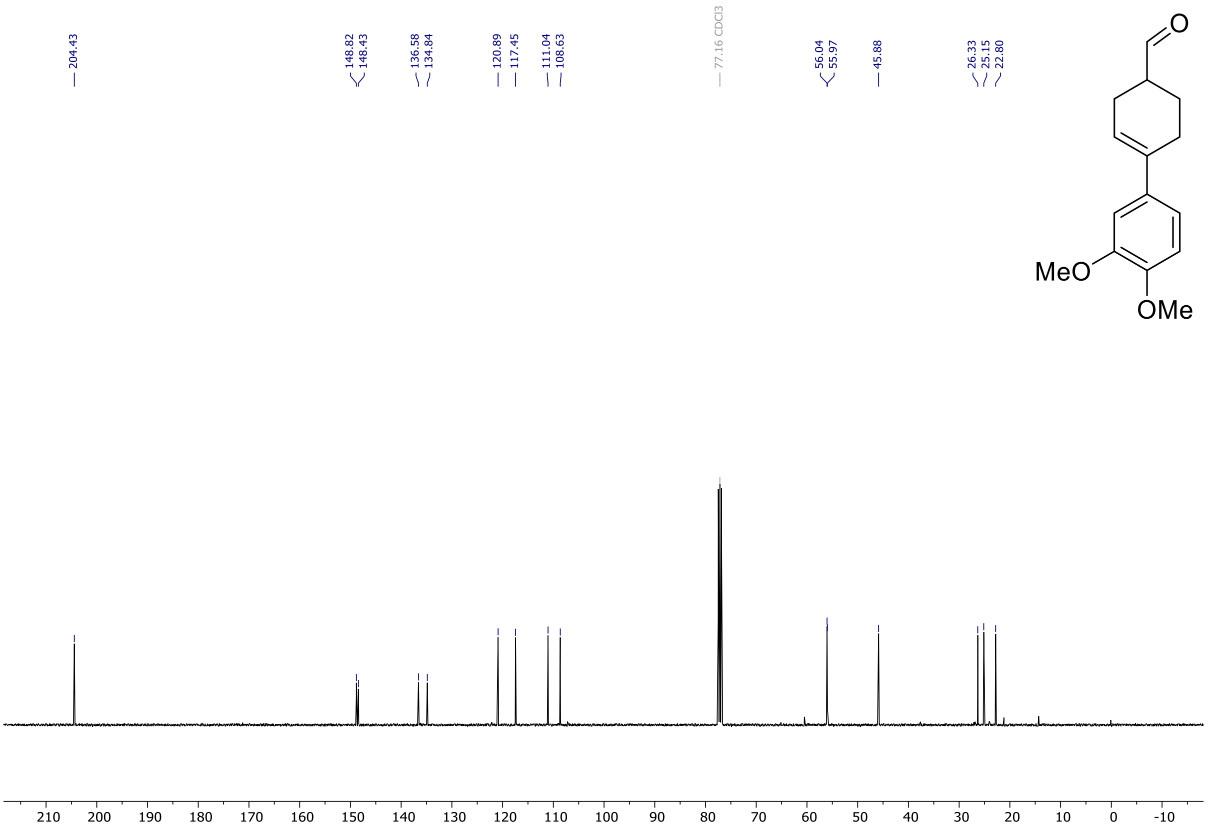
^{19}F NMR (377 MHz, CDCl3): 1e



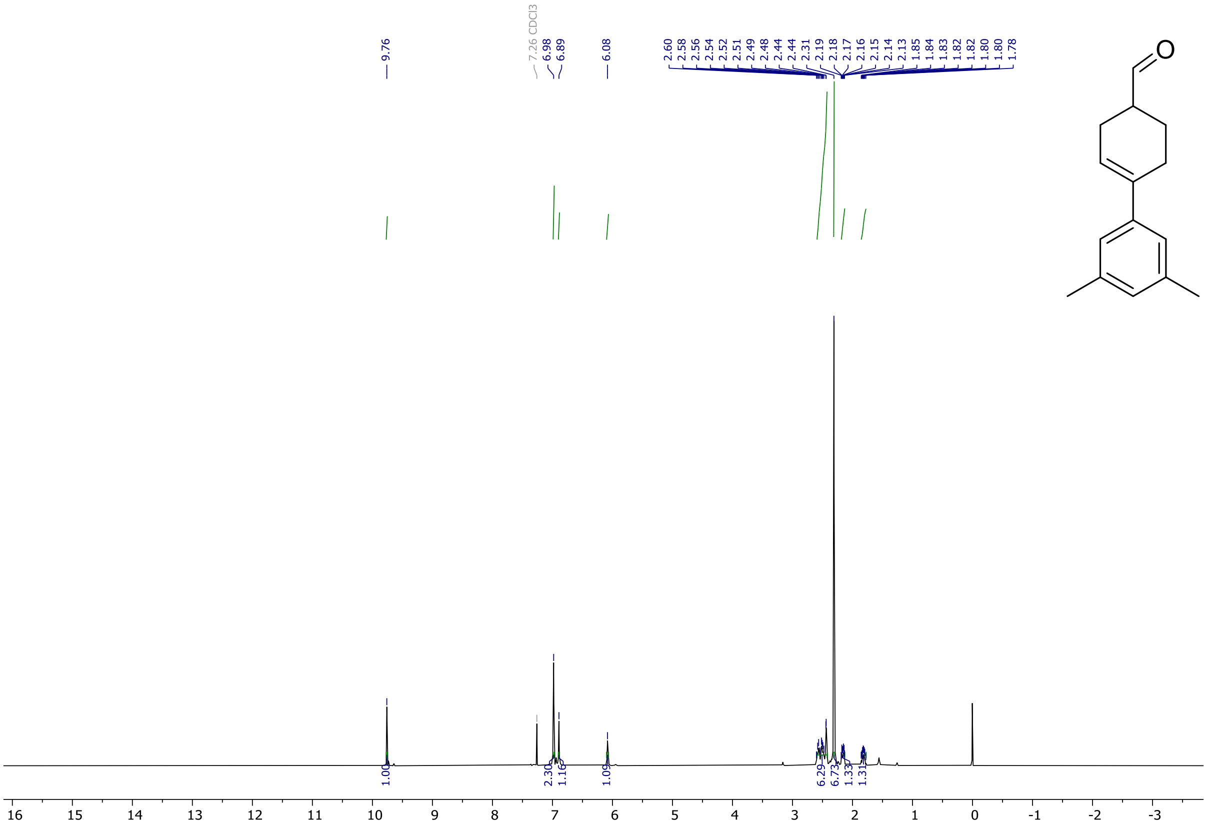
^{1}H NMR (400 MHz, CDCl$_3$): 1f



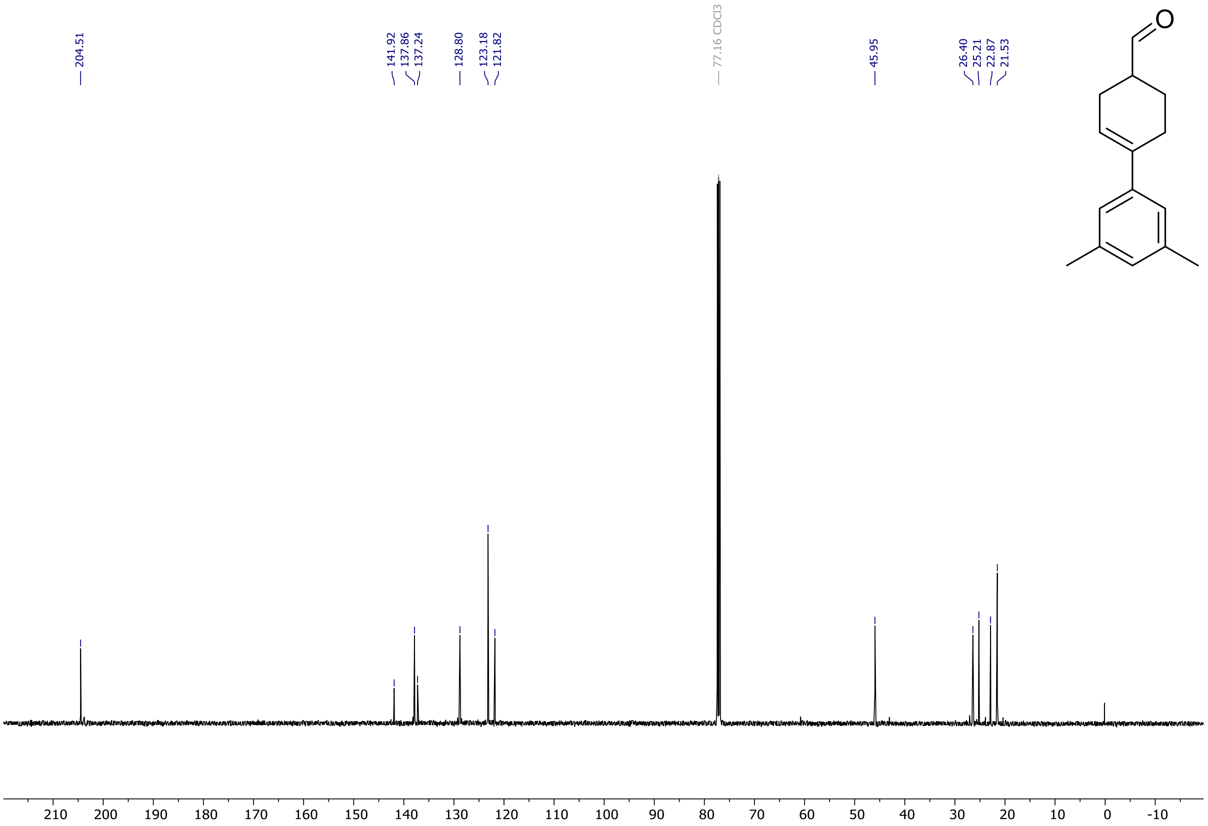
^{13}C NMR (101 MHz, $CDCl_3$): 1f



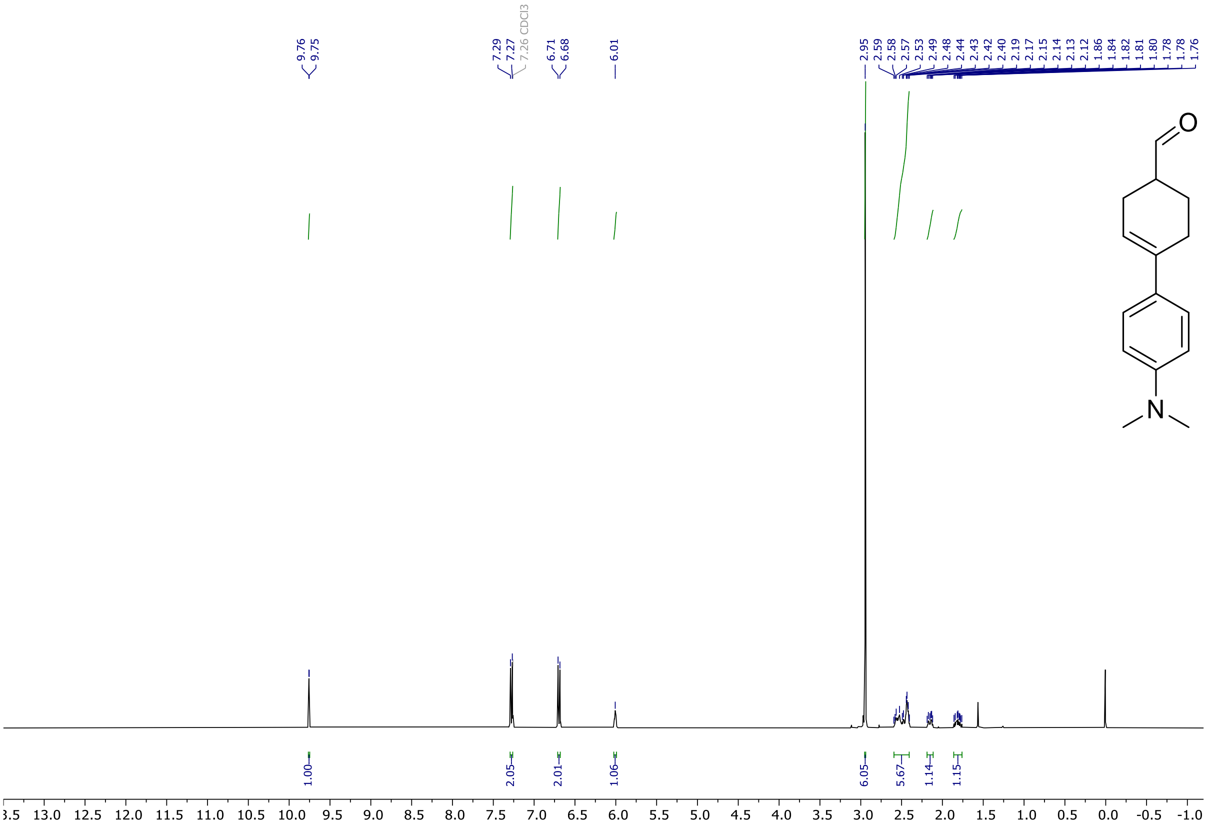
^{1}H NMR (500 MHz, $CDCl_3$): 1g



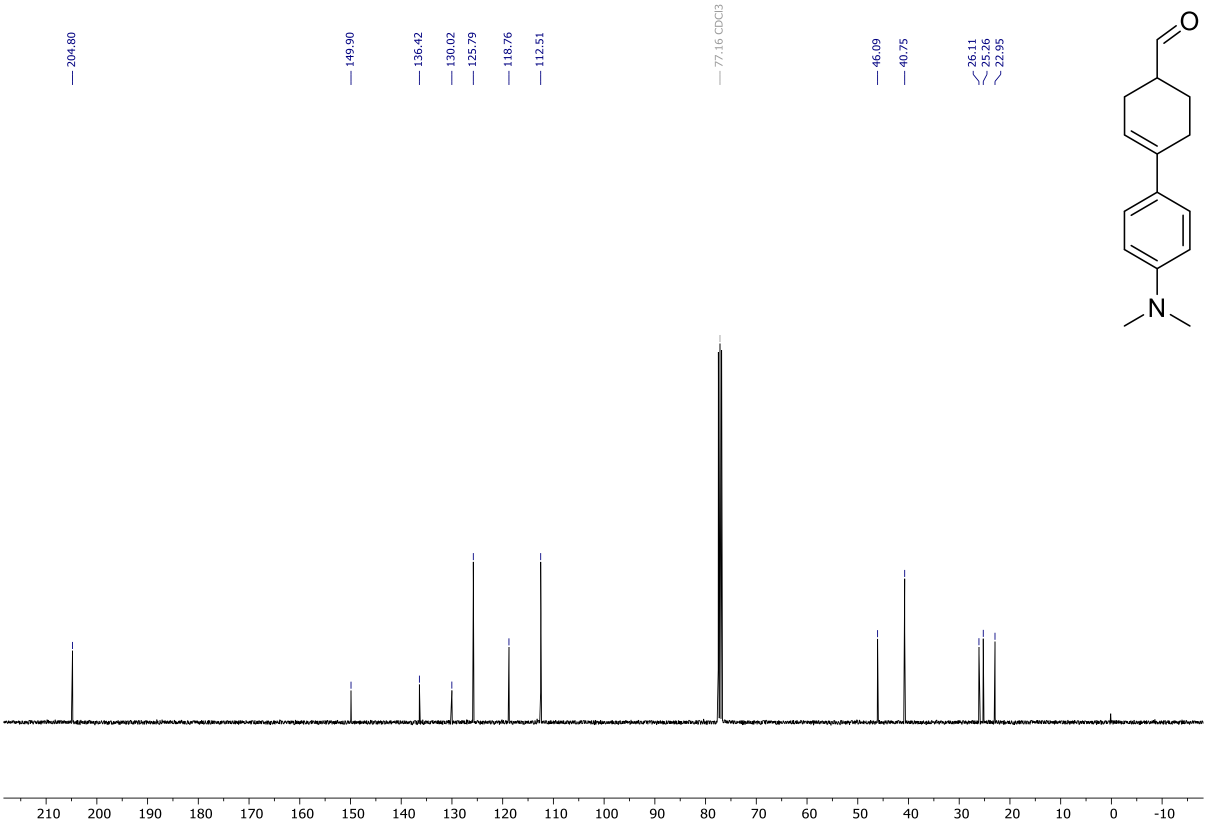
^{13}C NMR (126 MHz, CDCl$_3$): 1g



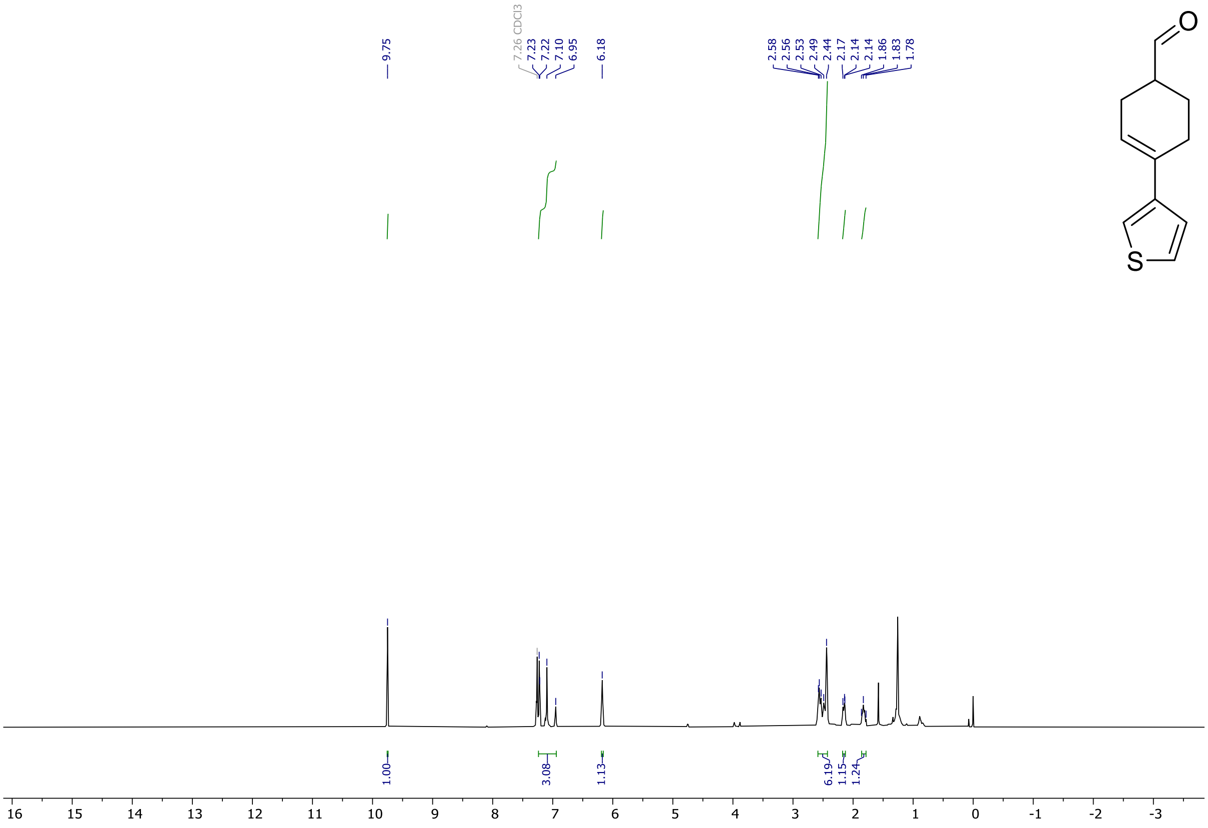
^{1}H NMR (400 MHz, CDCl$_3$): 1h



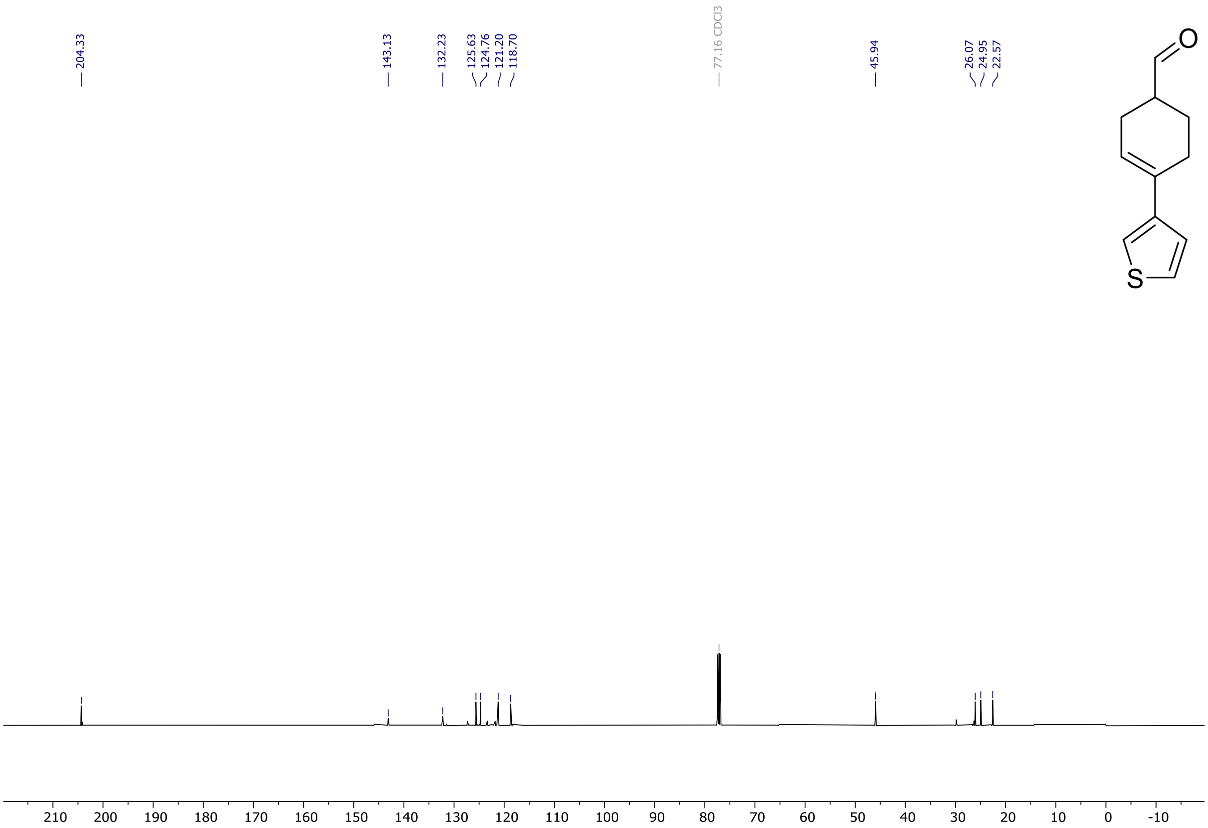
^{13}C NMR (101 MHz, CDCl$_3$): 1h



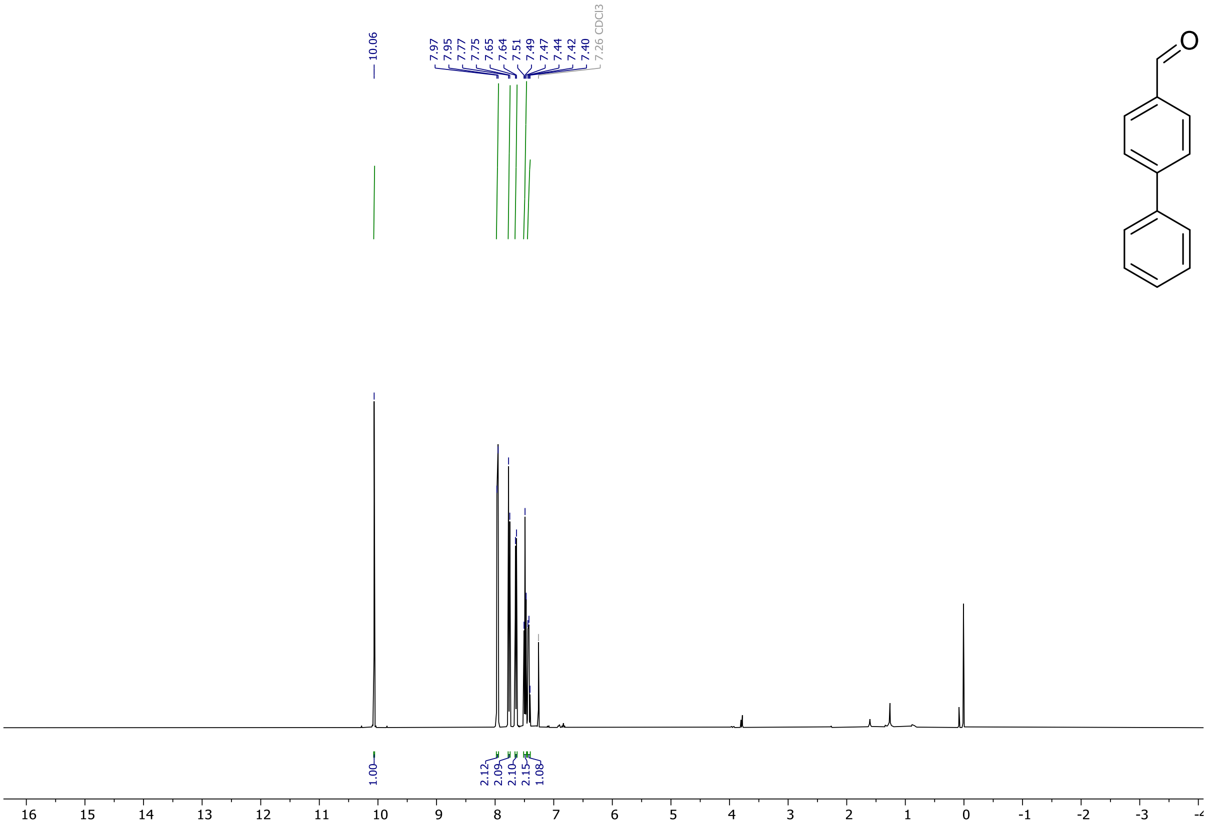
^{1}H NMR (500 MHz, CDCl$_3$): 1i



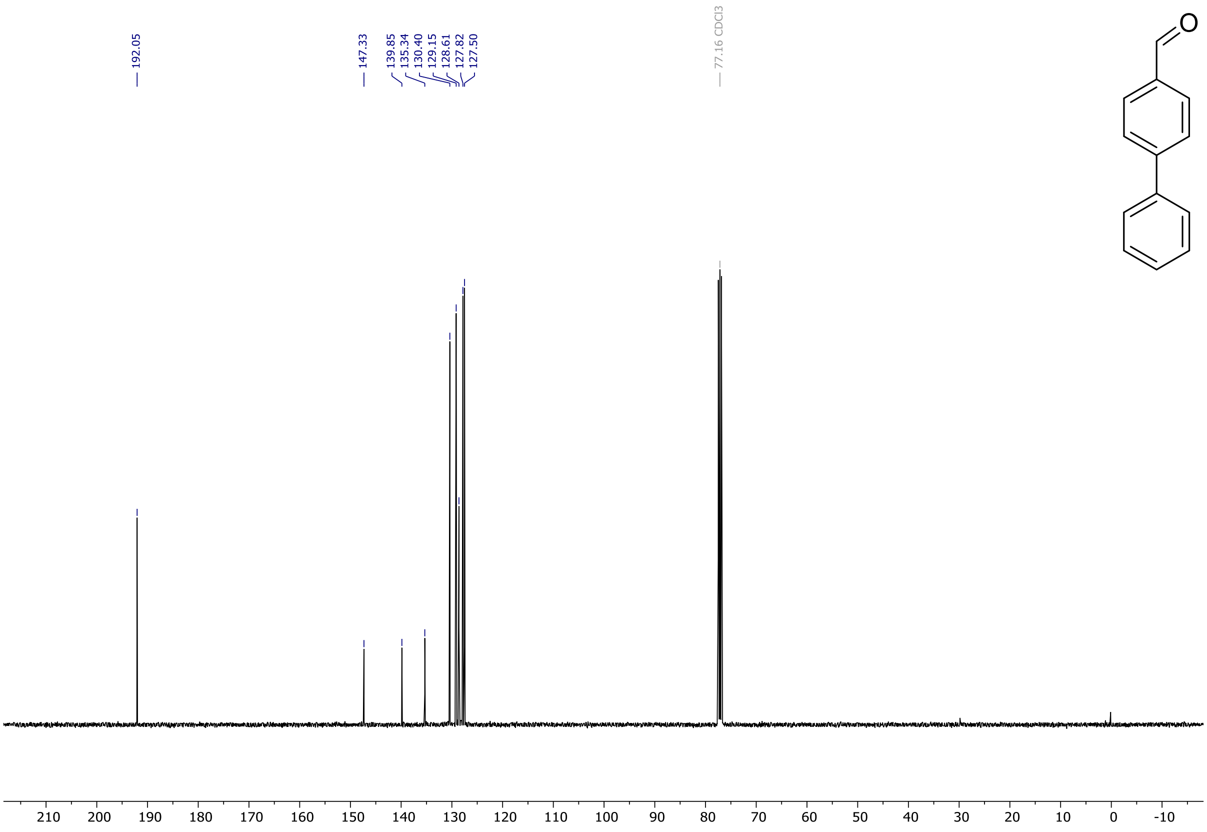
^{13}C NMR (126 MHz, $CDCl_3$): 1i



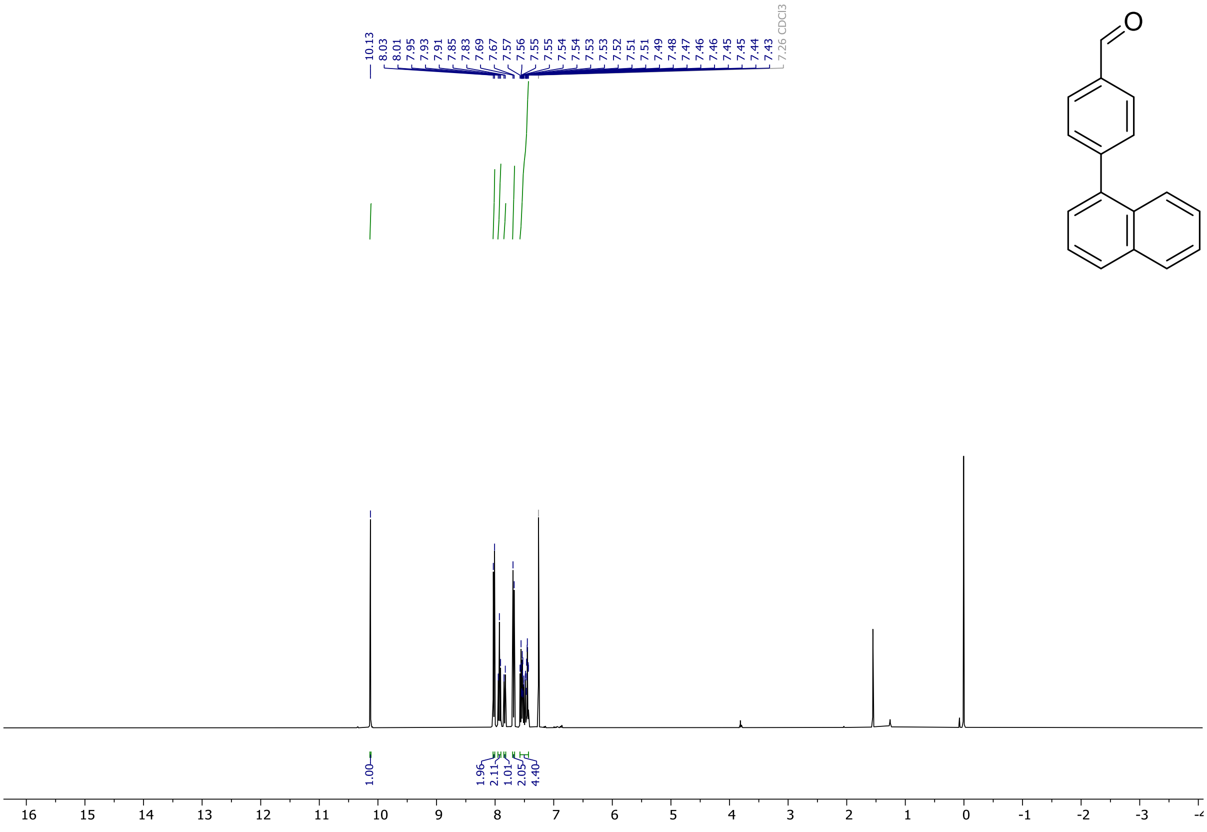
^{1}H NMR (400 MHz, $CDCl_3$): 2c



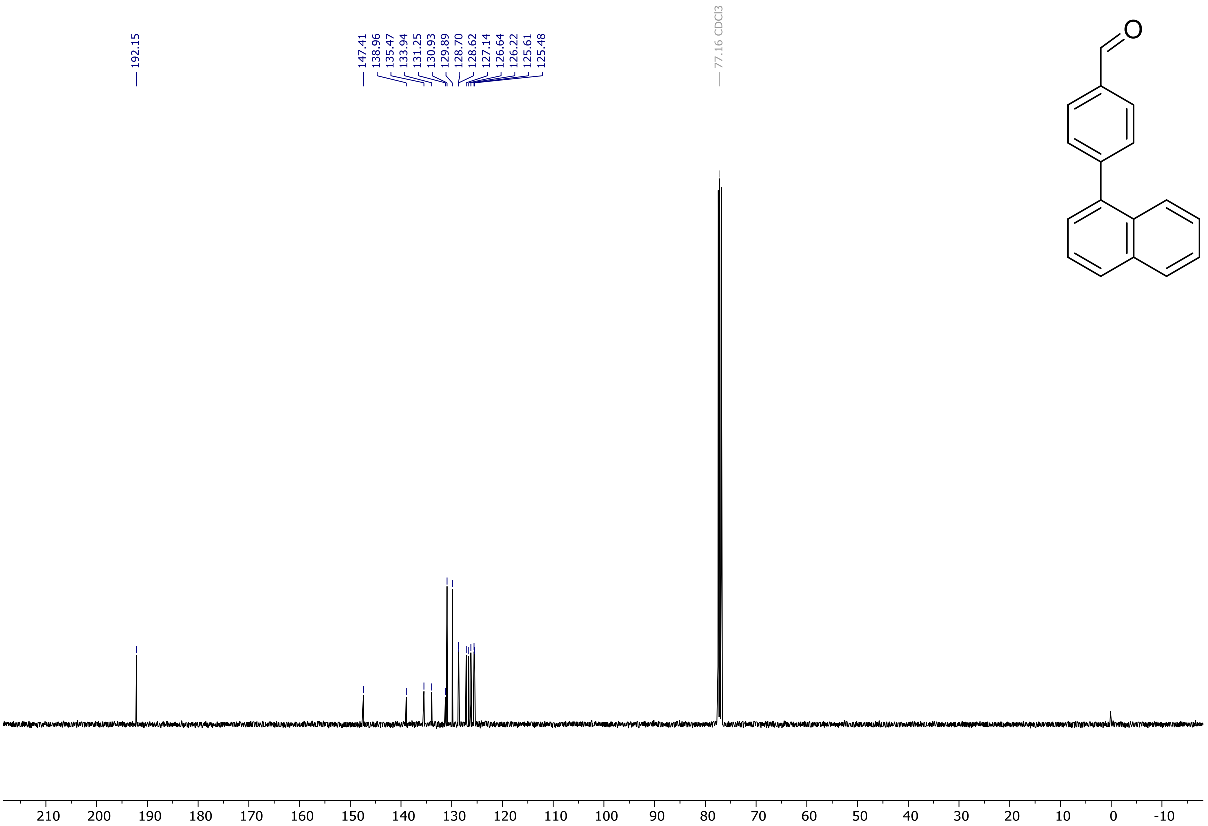
^{13}C NMR (101 MHz, CDCl$_3$): 2c



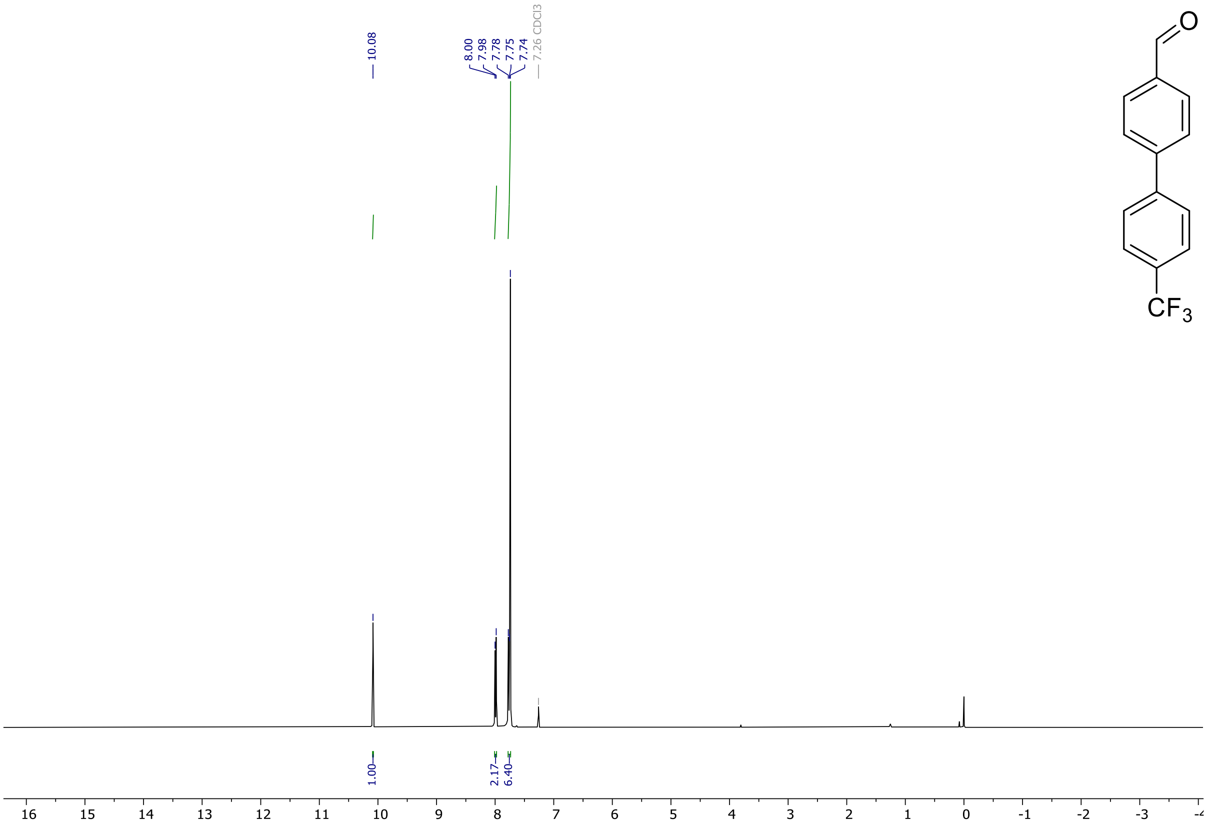
^{1}H NMR (400 MHz, CDCl$_3$): 2d



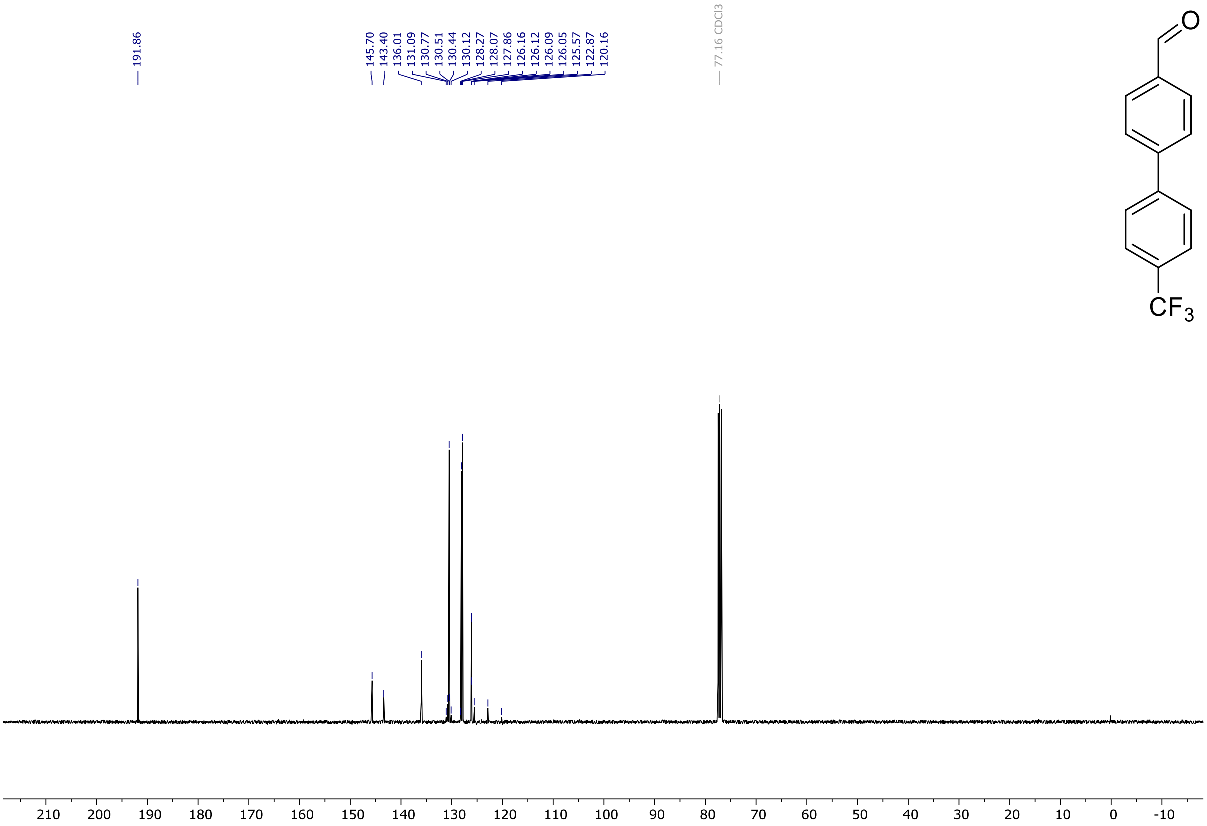
^{13}C NMR (101 MHz, CDCl$_3$): 2d



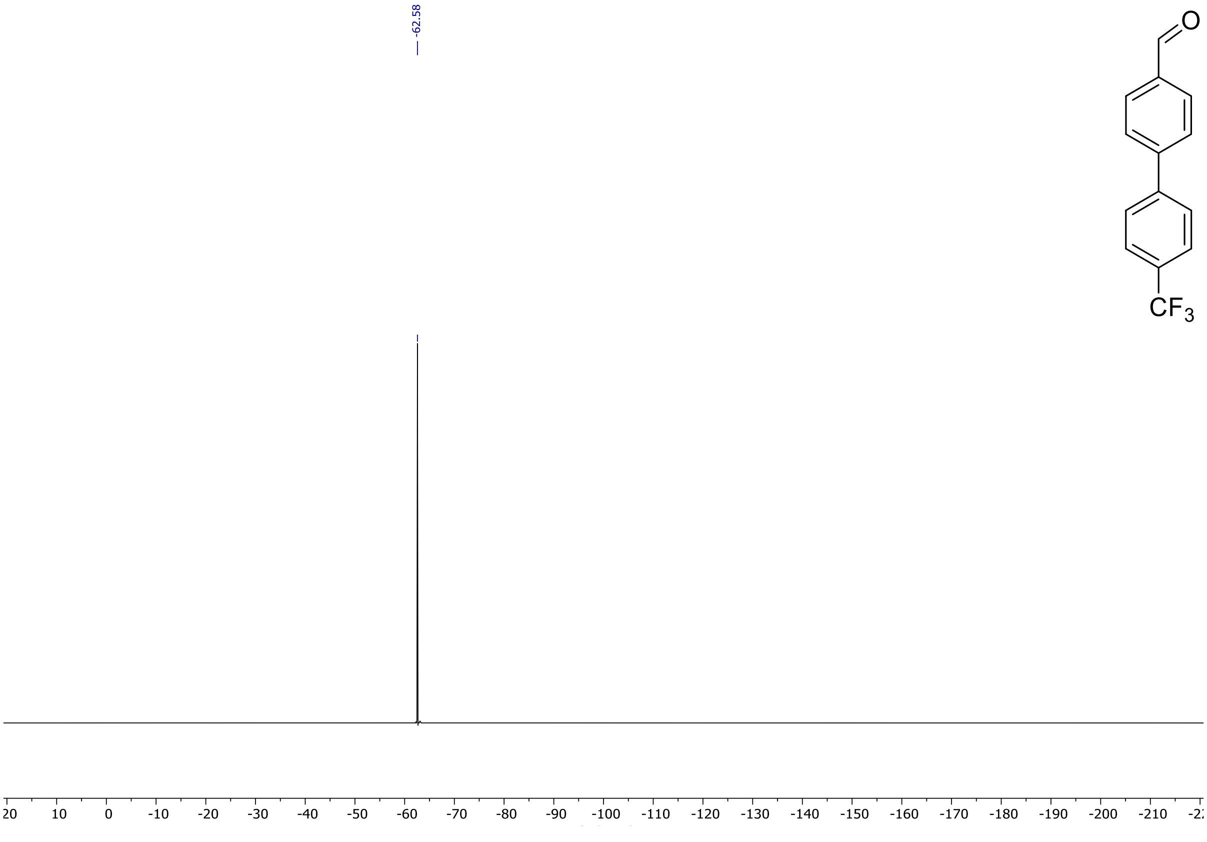
^{1}H NMR (400 MHz, CDCl$_3$): 2e



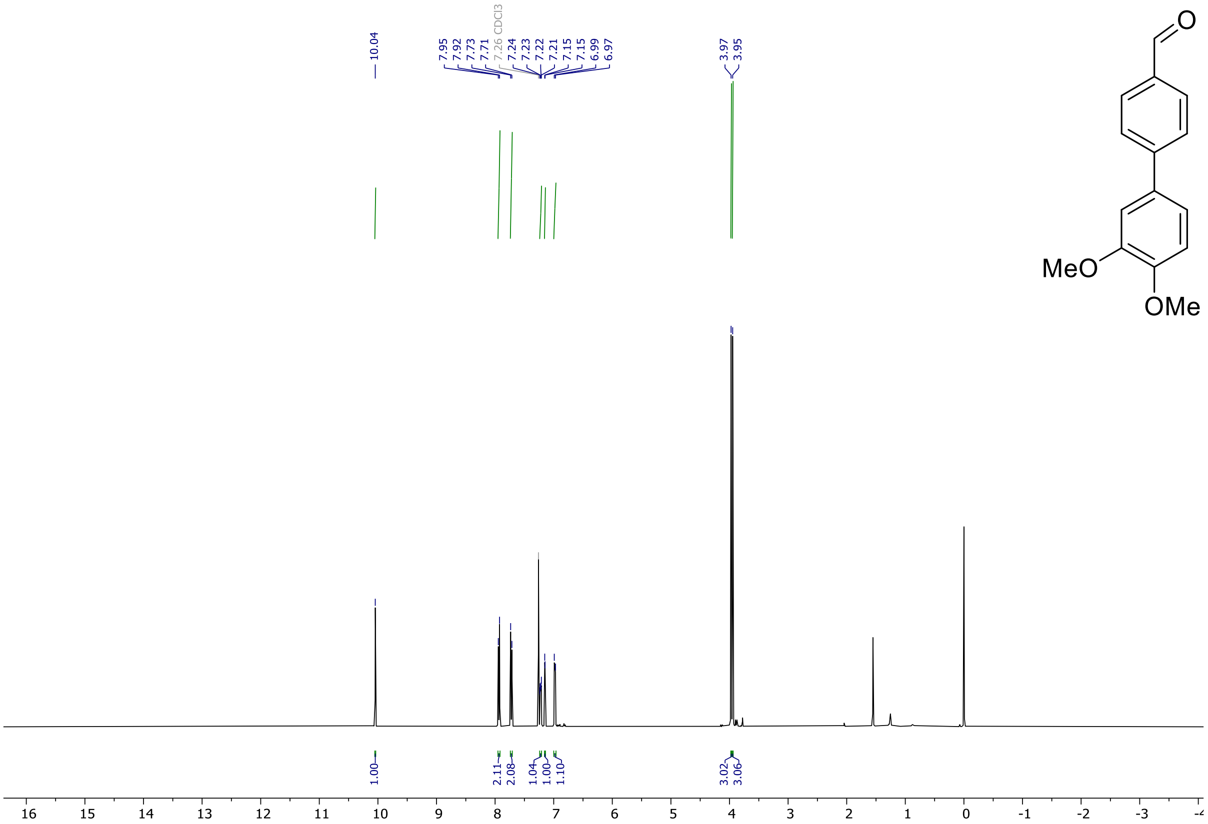
^{13}C NMR (101 MHz, CDCl$_3$): 2e



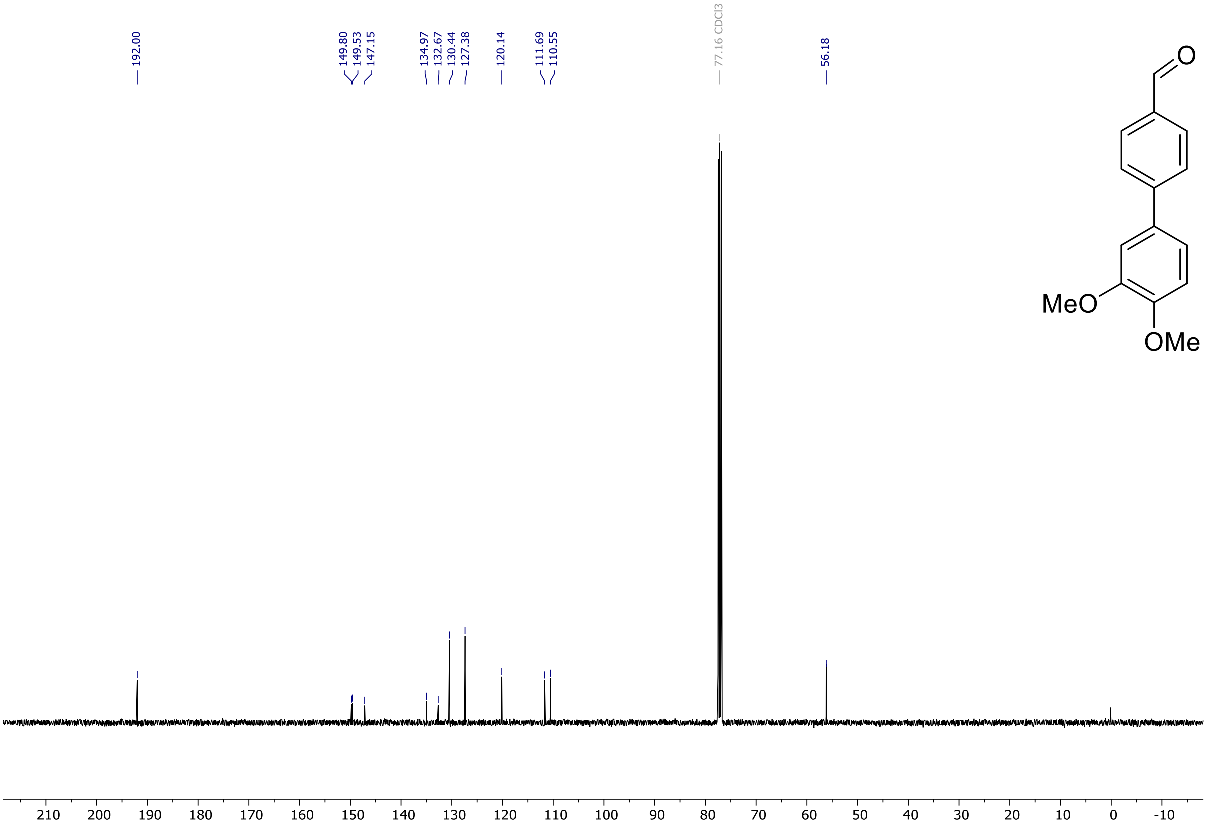
^{19}F NMR (470 MHz, CDCl3): 2e



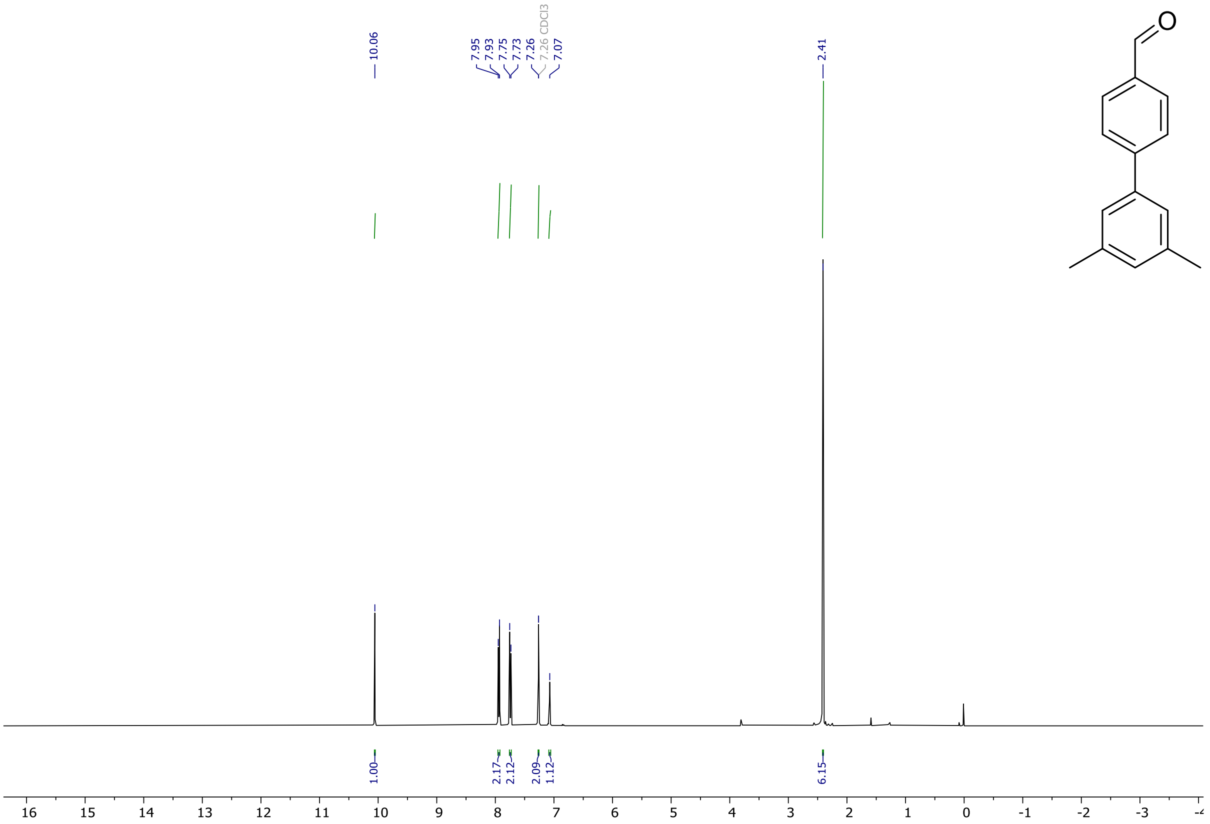
^{1}H NMR (400 MHz, CDCl$_3$): 2f



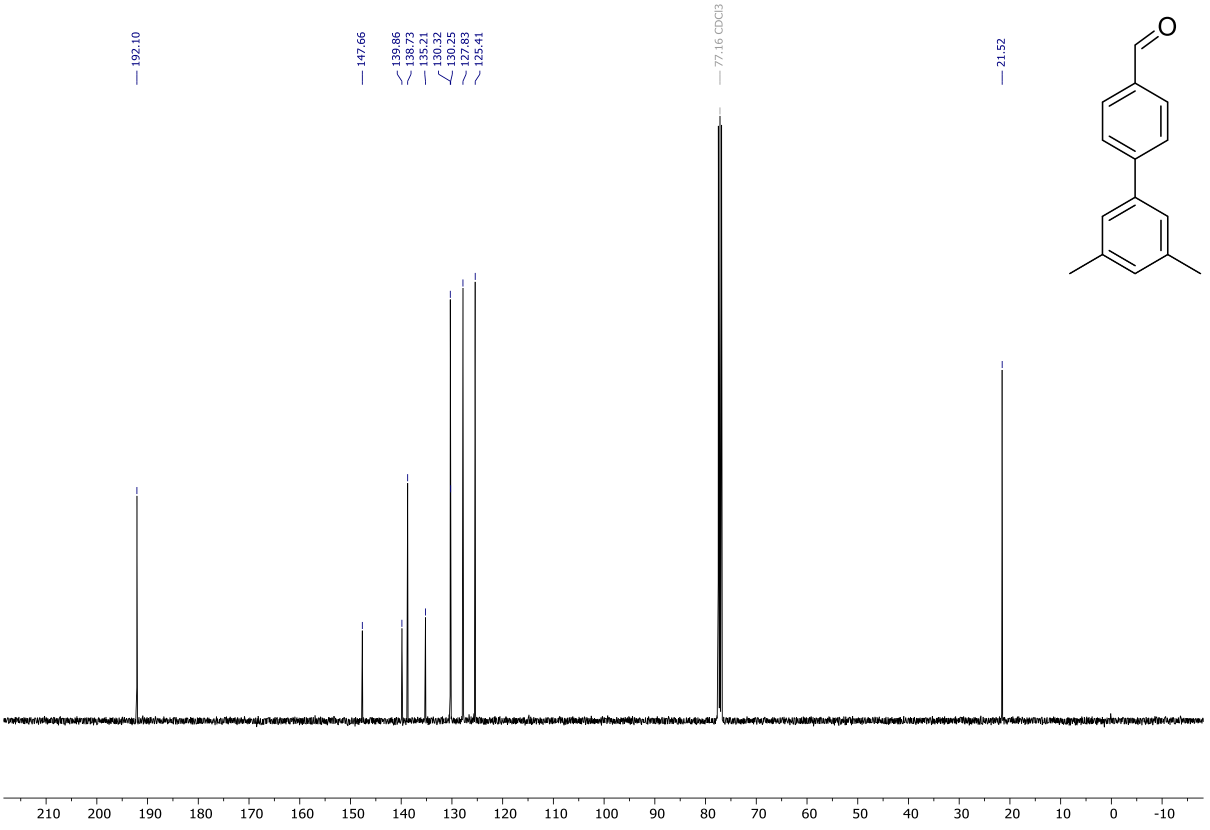
^{13}C NMR (101 MHz, CDCl$_3$): 2f



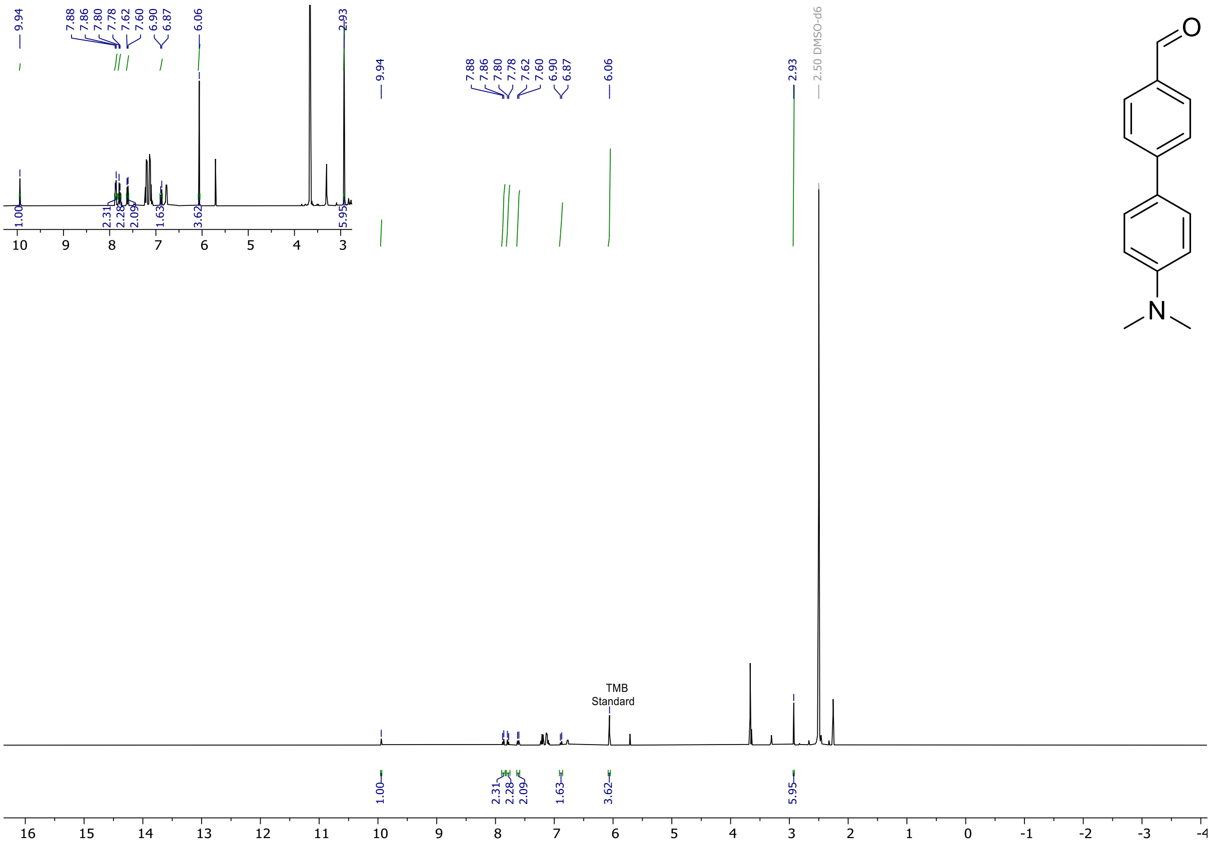
^{1}H NMR (400 MHz, CDCl$_3$): 2g



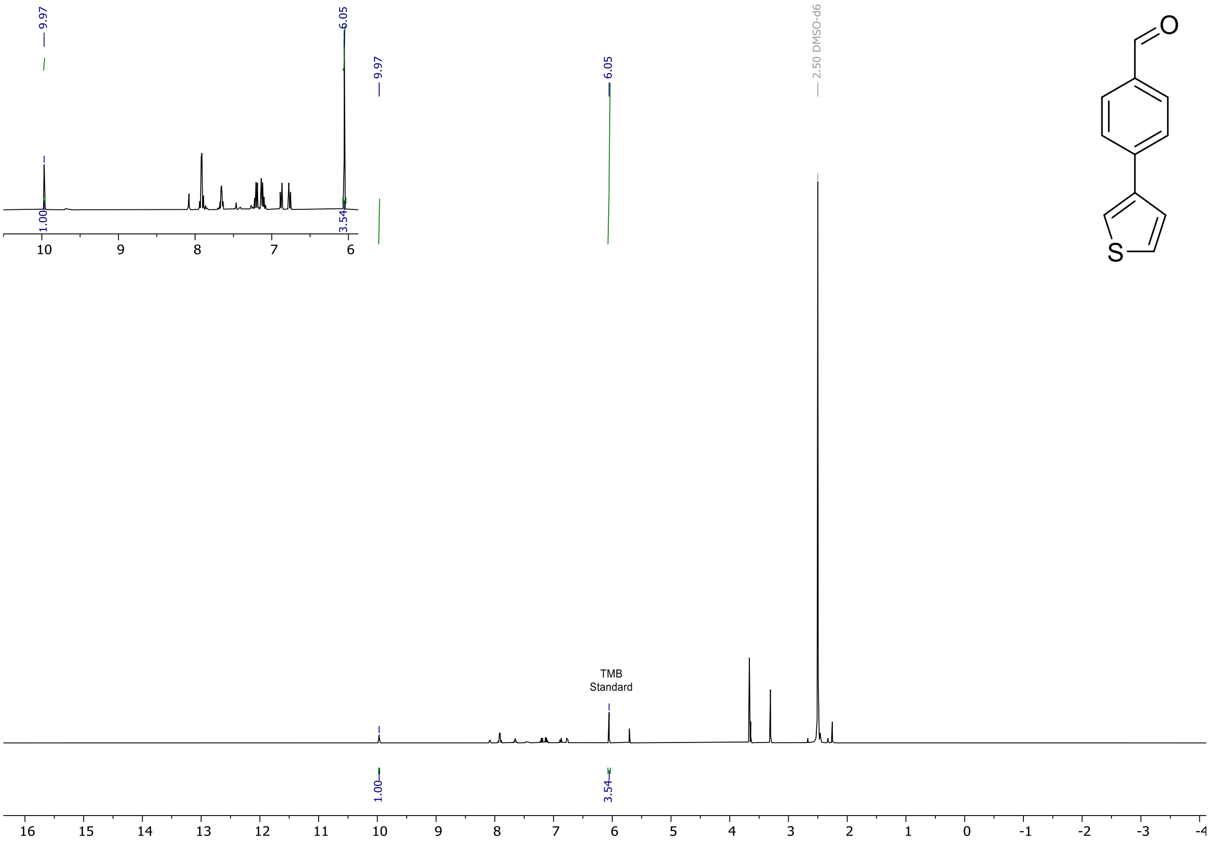
^{13}C NMR (101 MHz, CDCl$_3$): 2g



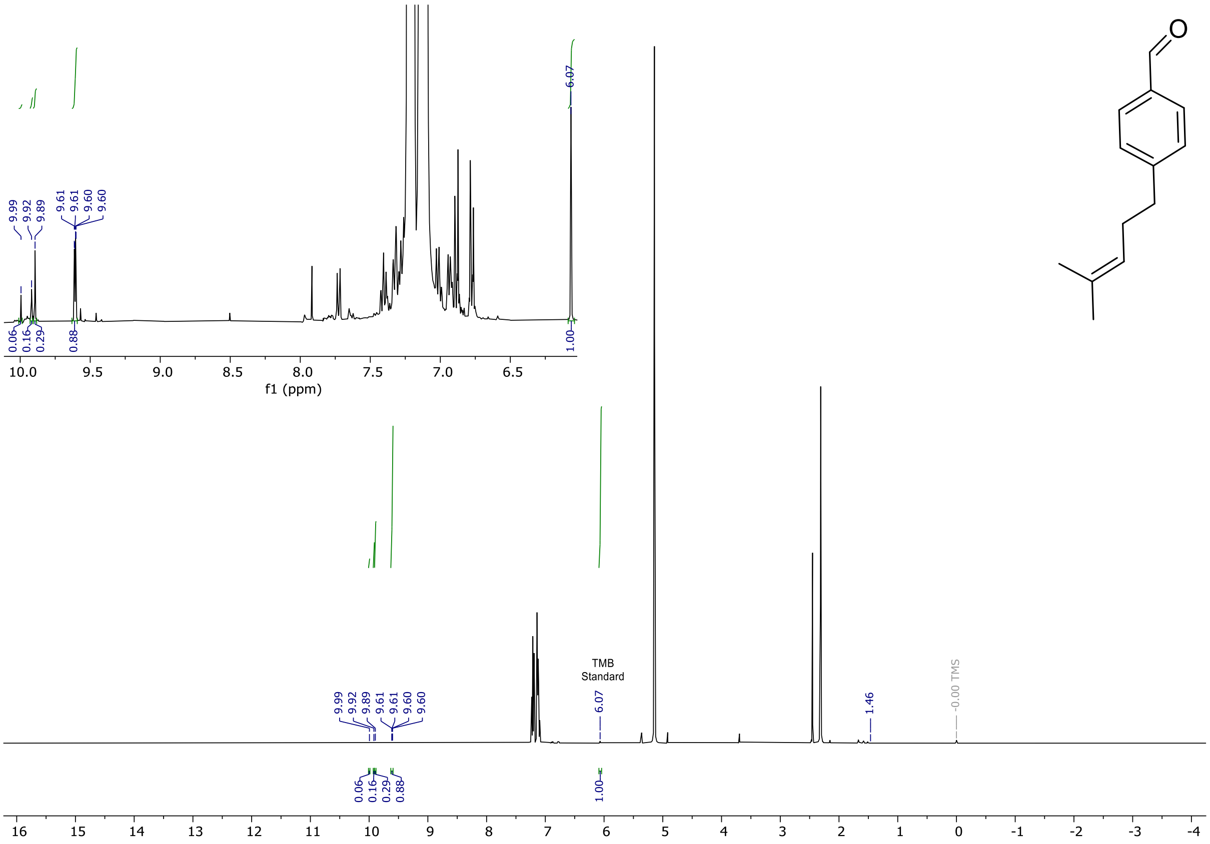
^{1}H NMR (400 MHz, DMSO): reaction mixture 2h



^{1}H NMR (400 MHz, DMSO): reaction mixture 2i



^{1}H NMR (400 MHz, $CDCl_3$): reaction mixture SI21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0.16
0.29
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1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
f1 (ppm)
TMB
Standard
1.46
-0.00 TMS
16
15
14
13
12
11
10
9
8
7
6
5
4
3
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1
0
-1
-2
-3
-4
O