Bisphosphonium-Catalyzed Ring-Opening of Cycloalkenes under Visible-light Irradiation

Kaining Zhang [a†], Jiazhao Wang [b†], Wenlong Chen [c], Mingfeng Li [c], Shengfei Jin*[b], and Zhiwei Zuo*[c]

[a] *School of Chemistry and Materials Science, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou, 310024, China.*

[b] *Wuya College of Innovation, Shenyang Pharmaceutical University, Shenyang, 110016, China*

[c] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China*

Contents

1. General information.

Reagents were purchased from Aldrich, TCI, Energy Chemical and J&K chemical, and were used as received. All reactions were carried out in glassware under an atmosphere of argon unless otherwise noted. Purification of products were accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz), Bruker 400 (400 and 100 MHz) and Varian 400 (400 MHz and 100 MHz) and are internally referenced to residual protio solvent signals ($CDCl_3$, δ 7.26 and 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. GC analyses were carried out on Agilent 7890B Infinity system. High Resolution Mass spectra were obtained from Thermo Fisher Q-Exactive High-resolution MS, Thermo Fisher Scientific LTQ FTICR-MS and JEOL-AccuTOF-GCv4G-GCT MS.

2. The continuous-flow reaction set-up

A homemade flow-photoreactor was used for each single photoredox reactions. The reaction mixture was fed into a FEP coil (1/32’ - 1/16’, 36 m) by a persistalic pump. The LED chips were cooled with continuous water flow, the heating effect of the high power LEDs can be offset and the reaction temperature can be maintained at ambient temperature. Through this design, identical irradiation intensity and ambient temperature can be guaranteed for each reaction to ensure data consistency.

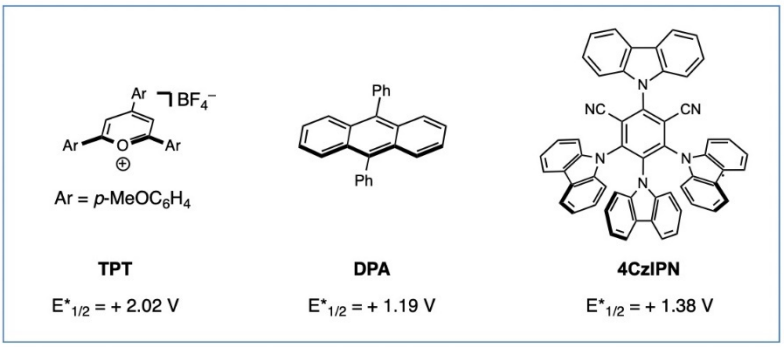
Figure S1. The continuous-flow reaction set-up.

3. Reaction optimization

Table S1. Optimization of the Reaction Conditions[a]

1 **2**

entry	variations from the "standard" conditions	yield[b] (%)
1	with 5 mol% $CeCl_3$, 15 mol% TBACl, 5 mol% DPA	35
2	*trans*-2-phenylcyclohexanol instead of **1**	89
3	4CzIPN instead of BPP	0
4	DPA instead of BPP	0
5	$TPT^+BF_4^-$ instead of BPP	0



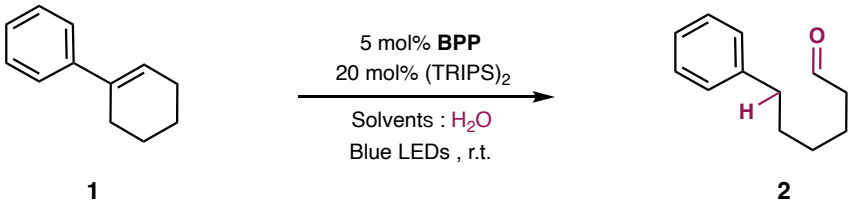
TPT $E^*_{1/2} = +2.02$ V

DPA $E^*_{1/2} = +1.19$ V

4CzIPN $E^*_{1/2} = +1.38$ V

[a] Reaction conditions: A solution of 1-phenylcyclohexene **1** (0.2 mmol), **BPP** (5 mol%) and $(TRIPS)_2$ (20 mol%) and H_2O in MeCN (2.0 mL) was irradiated in blue LEDs for 48 h at room temperature under argon atmosphere. [b] Yields were determined by GC-FID analysis of the crude mixture using PhOMe as internal standard, and the recovered 2-phenylcyclohexanol intermediate is shown in parentheses.

Table S2. Optimization of the Solvents[a]

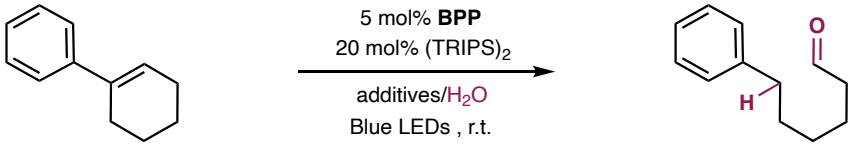


1 **2**

entry	Solvents : H_2O	conversion (%)	alcohol intermediate (%)	yield (%)
1	MeCN : H_2O = 40:1	100	24	49
2	MeCN : H_2O = 20:1	100	3	75
3	MeCN : H_2O = 10:1	100	0	80
4	MeCN : H_2O = 4:1	100	0	74
5	MeCN : H_2O = 1:1	100	0	62
6	Acetone : H_2O = 10:1	100	0	77
7	EA : H_2O = 10:1	100	15	63
8	THF : H_2O = 10:1	100	20	60
9	CPME : H_2O = 10:1	49	39	1
10	^{t}BuOH : H_2O = 10:1	100	0	64
11	DMSO : H_2O = 10:1	99	29	6

[a] Reaction conditions: 1-Phenylcyclohexene **1** (0.2 mmol), **BPP** (5 mol%), and $(TRIPS)_2$ (20 mol%), were dissolved in a 2.0 mL mixture of H_2O and organic solvents. The solution was then irradiated with blue LEDs for 48 hours at room temperature under an argon atmosphere. [b] Yields were determined by GC-FID analysis of the crude mixture using PhOMe as internal standard.

Table S3. Water as the reaction solvent with the aid of surfactants and phase transfer agents[a]

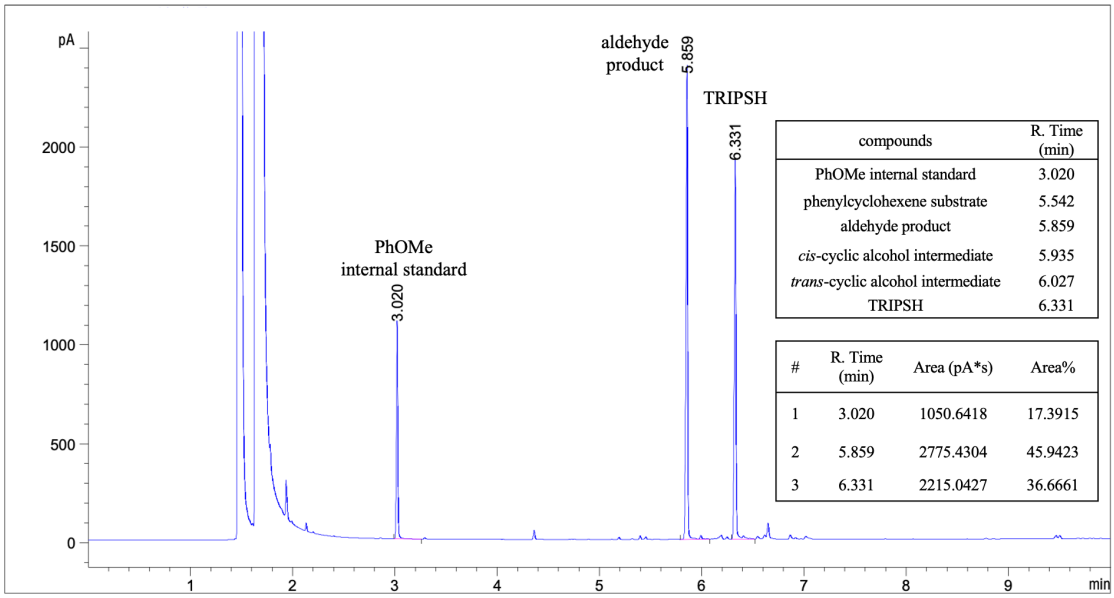


1 **2**

entry	additives	conversion (%)	alcohol intermediate (%)	yield (%)
1	–	89	16	22
2	5 wt% Brij C20/H_2O	97	4	13
3	5 wt% Polidocanol	96	2	21
4	4.5 wt% PEGMOE	99	0	20
5	4.5 wt% TPGS-750-M	94	7	28
6	0.5 equiv. NP-9	97	4	16
7	0.5 equiv. TBACl	91	30	3
8	0.5 equiv. 18-crown-6	96	4	4
9	0.5 equiv. SDS	92	10	9

[a] Reaction conditions: A solution of 1-phenylcyclohexene **1** (0.2 mmol), **BPP** (5 mol%), $(TRIPS)_2$ (20 mol%) and surfactant or phase transfer agent in H_2O (2.0 mL) was irradiated in blue LEDs for 48 h at room temperature under argon atmosphere. [b] Yields were determined by GC-FID analysis of the crude mixture using PhOMe as internal standard.

Scheme S1. GC trace for the crude reaction mixture of photocatalytic ring-opening of model substrate **1** under the optimal reaction conditions



compounds	R. Time (min)
PhOMe internal standard	3.020
phenylcyclohexene substrate	5.542
aldehyde product	5.859
cis-cyclic alcohol intermediate	5.935
trans-cyclic alcohol intermediate	6.027
TRIPSH	6.331

#	R. Time (min)	Area (pA*s)	Area%
1	3.020	1050.6418	17.3915
2	5.859	2775.4304	45.9423
3	6.331	2215.0427	36.6661

GC conditions: Agilent HP-5 column, split ratio 10:1, carrier gas N_2, injection temperature 300°C, detector: Flame Ionization Detector (FID), detector temperature 300°C, flow rate 3 mL/min, oven temperature program: 60°C hold for 1 min, then 30°C/min to 300°C.

4. Experimental procedures and spectral characterization

Synthesis of bisphosphonium: According to the literature.[1] A solution of $Cu(OTf)_2$ (3.62 g, 10.0 mmol, 1.0 equiv.) and 1.1'-Binaphthyl-2.2'-diphemyl phosphine (6.23 g, 10.0 mmol, 1.0 equiv.) in acetonitrile (200 mL) was stirred at room temperature for 15 minutes. The solvent was then evaporated, and the crude mixture was purified by silica gel chromatography (20% acetone in dichloromethane). The yellow band eluted was collected. The resulting solution was concentrated under *vacuo* to a volume of 10 mL. Diethyl ether diffused slowly into the concentrated solution, resulting in the formation of a microcrystalline solid. The solid was washed with Et_2O (2 × 20 mL), and afforded a yellow crystal (1.96 g, 20% yield).

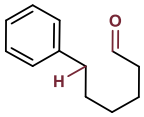
4.1. Experimental procedures and spectral characterization of the products

General procedure A: An 8-mL vial was charged with 2,3,4,5-tetrahydro-1,1'-biphenyl (31.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL). The vial was sealed with a polytetrafluoroethylene-lined cap, the reaction mixture was degassed by Argon sparging for 5 min, then irradiated with Blue LED. The reaction was stirred under irradiation at ambient temperature for the indicated time, then concentrated in *vacuo*. Purification by flash chromatography on silica gel (5% ethyl acetate in hexanes) provided the desired product.

General procedure B: An 8-mL vial was charged with 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (37.6 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL). The vial was sealed with a polytetrafluoroethylene-lined cap, the reaction mixture was degassed by Argon sparging for 5 min, then irradiated with Blue LED. After 24 hours of irradiation, a solution of collidine (3.0 equiv., 80 μL) in DCM (2 mL) was added. The reaction was stirred under irradiation at ambient temperature for the indicated time, then concentrated in *vacuo.* Purification by flash

chromatography on silica gel (5% ethyl acetate in hexanes) provided the desired product.

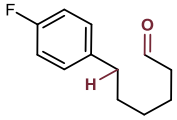
6-Phenylhexanal (2)



According to the general procedure A, 2,3,4,5-tetrahydro-1,1'-biphenyl (31.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (26.1 mg, 74%). The spectral data is consistent with the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 2.0 Hz, 1H), 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.43 (dt, *J* = 2.0, 7.2 Hz, 2H), 1.71-1.59 (m, 4H), 1.42-1.32 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.4, 142.1, 128.1, 128.0, 125.5, 43.5, 35.5, 31.0, 28.5, 21.6; **HRMS (EI+):** calcd. for $C_{12}H_{16}O^+$ $(M)^+$ 176.1196, found 176.1196.

6-(4-fluorophenyl)hexanal (3)

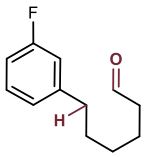


According to the general procedure A, 4'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (25.6 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 2.0 Hz, 1H), 7.16-7.06 (m, 2H), 6.99-6.90 (m, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.43 (td, *J* = 7.2, 2.0 Hz, 2H), 1.75-1.55 (m, 4H), 1.40-1.30 (m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.7, 161.1 (d, *J* = 193 Hz), 137.9 (d, *J* = 3 Hz), 129.6 (d, *J* = 6 Hz), 115.0 (d, *J* = 17 Hz), 43.8, 34.8, 31.3, 28.6, 21.8. **^{19}F**

NMR (376 MHz, $CDCl_3$): δ -117.90. **HRMS (EI+):** calcd. for $C_{12}H_{15}FO^+$ $(M)^+$ 194.1101, found 194.1102.

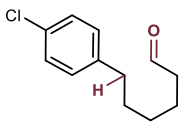
6-(3-fluorophenyl)hexanal (4)



According to the general procedure A, 3'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (25.2 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 1.6 Hz, 1H), 7.25-7.19 (m, 1H), 6.93 (d, *J* = 6.0 Hz, 1H), 6.90-6.84 (m, 2H), 2,61 (t, *J* = 6.4 Hz, 2H), 2.43 (td, *J* = 5.6, 1.6 Hz, 2H), 1.70-1.60 (m, 4H), 1.40-1.30 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.6, 162.9 (d, *J* = 174 Hz), 144.9 (d, *J* = 5 Hz), 129.6 (d, *J* = 6 Hz), 124.0 (d, *J* = 3 Hz), 115.1 (d, *J* = 17 Hz), 112.6 (d, *J* = 17 Hz), 43.8, 35.4, 30.9, 28.6, 21.8. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -114.08 (m). **HRMS (FI+):** calcd. for $C_{12}H_{15}FO^+$ $(M)^+$ 194.1101, found 194.1099.

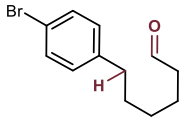
6-(4-chlorophenyl)hexanal (5)



According to the general procedure A, 4'- chloro-2,3,4,5-tetrahydro-1,1'-biphenyl (38.5 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (33.7 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 2.0 Hz, 1H), 7.26-7.20 (m, 2H), 7.12-7.06 (m, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.42 (td , *J* = 7.2, 2.0 Hz, 2H), 1.72-1.56 (m , 4H), 1.42-1.30 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.6, 140.8, 131.4, 129.7, 128.4, 43.8, 35.0, 31.0, 28.6, 21.8. **HRMS (EI+):** calcd. for $C_{12}H_{15}ClO^+$ $(M)^+$ 210.0806, found 210.0807.

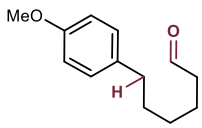
6-(4-bromophenyl)hexanal (6)



According to the general procedure A, 4'-bromo-2,3,4,5-tetrahydro-1,1'-biphenyl (47.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (32.6 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.03, (d, *J* = 8.0 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 1.72-1.55 (m, 4H), 1.43-1.30 (m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.6, 141.3, 131.3, 130.1, 119.4, 43.7, 35.0, 31.0, 28.6, 21.8. **HRMS (FI+):** calcd. for $C_{12}H_{15}BrO^+$ $(M)^+$ 254.0301, found 254.0295.

6-(4-methoxyphenyl)hexanal (7)

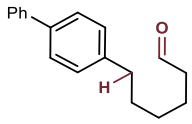


According to the general procedure B, 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (37.6 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL), collidine (80 μL, 3.0 equiv.), and 2 mL DCM were used. After 48 h, the product

was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (35.0 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (t, *J* = 1.6 Hz, 1H), 7.08 (d, *J* = 6.8 Hz, 2H), 6.82 (d , *J* = 6.8 Hz, 2H), 3.79 (s, 3H), 2.55 (t, *J* = 6.0 Hz, 2H), 2.42 (td, *J* = 6.0, 1.6 Hz, 2H), 1.70-1.55 (m, 4H), 1.41-1.30 (m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.8, 157.6, 134.4, 129.2, 113.7, 55.2, 43.8, 34.7, 31.4, 28.7, 21.9. **HRMS (EI+):** calcd. for $C_{13}H_{18}O_2^+$ $(M)^+$ 206.1301, found 206.1303.

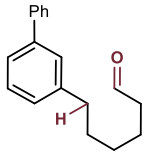
6-([1,1'-biphenyl]-3-yl)hexanal (8)



According to the general procedure B, 2,3,4,5-tetrahydro-1,1':4',1"-terphenyl (46.8 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL), collidine (80 µL, 3.0 equiv.), and 2 mL DCM were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (22.7 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (t, *J* = 1.6 Hz, 1H), 7.63-7.57 (m, 2H), 7.56-7.50 (m, 2H), 7.48-7.39 (m, 2H), 7.37-7.31 (m, 1H,), 7.29-7.23 (m, 2H), 2.68 (t, *J* = 8.8 Hz, 2H), 2.45 (td, *J* = 8.0, 1.6 Hz, 2H), 1.76-1.61 (m, 4H), 1.49-1.36 (m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.72, 141.47, 141.02, 138.63, 128.75, 128.66, 126.99, 126.95, 126.92, 43.78, 35.26, 31.12, 28.73, 21.87. **HRMS (ESI+):** calcd. for $C_{18}H_{20}ONa^+$ $(M+Na)^+$ 275.1406, found 275.1402.

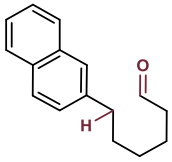
6-([1,1'-biphenyl]-3-yl)hexanal (9)



According to the general procedure B, 2,3,4,5-tetrahydro-1,1':3',1"-terphenyl (46.8 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL), collidine (80 μL, 3.0 equiv.), and 2 mL DCM were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (31.8 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (t, *J* = 1.6 Hz, 1H), 7.63-7.57 (m, 2H), 7.49-7.31(m, 6H), 7.19-7.15 (m,1H), 2.70 (t, *J* = 8.0 Hz, 2H) 2.44 (td, *J* = 8.0, 1.6 Hz, 2H), 1.78-1.60 (m, 4H), 1.48-1.35 (m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.72, 142.83, 141.30, 141.22, 128.67, 127.30, 127.26, 127.14, 124.62, 43.79, 35.76, 31.22, 28.76, 21.88. **HRMS (FI+):** calcd. for $C_{18}H_{20}O^+$ $(M)^+$ 252.1509, found 252.1511.

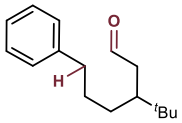
6-(naphthalen-2-yl)hexanal (10)



According to the general procedure B, 2-(cyclohex-1-en-1-yl)naphthalene (41.6 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL), collidine (80 μL, 3.0 equiv.), and 2 mL DCM were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (20.3 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.85-7.74 (m, 3H), 7.61 (s, 1H), 7.49-7.39, (m, 2H), 7.36-7.30 (m, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.80-1.64(m, 4H), 1.47-1.36(m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.7, 139.9, 133.6, 131.9, 127.8, 127.6, 127.4, 127.3, 126.3, 125.9, 125.1, 43.8, 35.8, 31.0, 28.7, 21.9. **HRMS (ESI+):** calcd. for $C_{16}H_{18}ONa^+$ $(M+Na)^+$ 249.1250, found 249.1245.

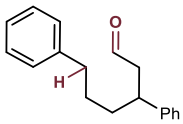
3-(tert-butyl)-6-phenylhexanal (11)



According to the general procedure A, 4-(tert-butyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (42.8 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (38.5 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (t, *J* = 2.0 Hz, 1H), 7.27-7.21 (m, 2H), 7.18-7.11 (m, 3H), 2.67-2.58 (m, 1H), 2.57-2.45 (m, 2H), 2.21-2.12 (m, 1H), 1.82-1.72 (m, 1H), 1.66-1.57 (m, 2H), 1.53-1.43 (m, 1H), 1.12-1.02 (m, 1H), 0.83 (s, 9H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.34, 142.24, 128.32, 128.27, 125.71, 46.04, 42.62, 36.12, 33.48, 30.69, 30.61, 27.55. **HRMS (ESI+):** calcd. for $C_{16}H_{24}ONa^+$ $(M+Na)^+$ 255.1719, found 255.1715.

3,6-diphenylhexanal (12)

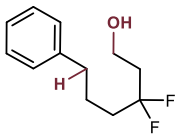


According to the general procedure A, 1',2',3',6'-tetrahydro-1,1':4',1''-terphenyl (46.8 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (31.2 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (t, *J* = 2.0 Hz, 1H), 7.33-7.28 (m, 2H), 7.28-7.20 (m, 3H), 7.20-7.13 (m, 3H), 7.13-7.07 (m, 2H), 3.25-3.15 (m, 1H), 2.80-2.65 (m, 2H), 2.65-2.47 (m, 2H), 1.77-1.64 (m, 2H), 1.64-1.40 (m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.87, 143.59, 142.09, 128.64, 128.30, 128.25, 127.43, 126.62, 125.71, 50.61, 39.94,

36.04, 35.65, 28.99. **HRMS (ESI+):** calcd. for $C_{18}H_{20}ONa^+$ $(M+Na)^+$ 275.1406, found 275.1402.

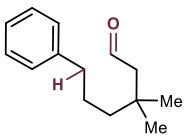
3,3-difluoro-6-phenylhexan-1-ol (13-alcohol)



According to the general procedure A, 4,4-difluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (38.8 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, 3 equiv. $NaBH_4$ were added to reduce the unstable aldehyde to an alcohol, followed by stirring for 1 hour. The alcohol product was isolated by flash chromatography (25% ethyl acetate in hexanes) as a colorless oil (26.6 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m, 2H), 7.24-7.15 (m, 3H), 3.84 (t, *J* = 4.8 Hz, 2H), 2.67 (t, *J* = 5.2 Hz, 2H), 2.19-2.04 (m, 2H), 1.97-1.78 (m, 4H), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 141.4, 128.4, 126.9, 126.0, 125.0 (t, J = 238.8 Hz), 57.0 (t, *J* = 5.0 Hz), 38.9 (t, *J* = 25.0 Hz), 36.4 (t, *J* = 5.0 Hz), 35.3, 23.8 (t, *J* = 5.0 Hz). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -97.96, **HRMS (ESI+):** calcd. for $C_{12}H_{16}F_2ONa^+$ $(M+Na)^+$ 237.1061, found 237.1066.

3,3-dimethyl-6-phenylhexanal (14)

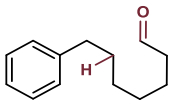


According to the general procedure A, 4,4-dimethyl-2,3,4,5-tetrahydro-1,1'-biphenyl (37.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1,

2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (26.5 mg, 65% yield). The spectral data is ,Lconsistent with the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (t, *J* = 3.2 Hz, 1H), 7.37-7.22 (m, 2H), 7.22-7.12, (m, 3H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.24 (d, *J* = 3.2 Hz, 2H), 1.69-1.55 (m, 2H), 1.43-1.33 (m, 2H), 1.03 (s, 6H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.6, 142.3, 128.3, 125.8, 54.7, 42.3, 36.4, 33.4, 27.4, 26.0. **HRMS (ESI+):** calcd. for $C_{14}H_{20}ONa^+$ $(M+Na)^+$ 227.1406, found 227.1410.

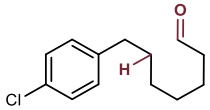
7-Phenylheptanal (15)



According to the general procedure A, (cyclohex-1-en-1-ylmethyl)benzene (34.4 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL) and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (28.1 mg, 74% yield). The spectral data is consistent with the literature [4].

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 1.6 Hz, 1H), 7.30-7.26 (m, 2H), 7.20-7.13 (m, 3H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.42 (dt, *J* = 7.6, 1.6 Hz, 2H), 1.67-1.59 (m, 4H), 1.38-1.32 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.9, 142.7, 128.4, 128.2, 125.6, 43.9, 35.9, 31.3, 29.1, 29.0, 22.0. **HRMS (EI+):** calcd. for $C_{13}H_{18}O^+$ $(M)^+$ 190.1352, found 190.1348.

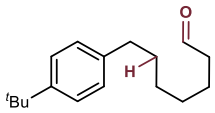
7-(4-Chlorophenyl)heptanal (16)



According to the general procedure A, 1-chloro-4-(cyclohex-1-en-1-ylmethyl)benzene (41.3 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL) and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (30.6 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (t, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 2.57 (t, *J* = 8.0 Hz, 2H), 2.42 (td, *J* = 7.0, 2.0 Hz, 2H), 1.66-1.55 (m, 4H), 1.39-1.31 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.8, 141.0, 131.3, 129.7, 128.3, 43.8, 35.1, 31.1, 28.9, 28.8, 21.9. **HRMS (EI+):** calcd. for $C_{13}H_{17}ClO^+$ $(M)^+$ 224.0962, found 224.0963.

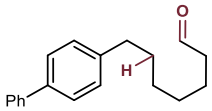
7-(4-(*Tert*-butyl)phenyl)heptanal (17)



According to the general procedure A, 1-(tert-butyl)-4-(cyclohex-1-en-1-ylmethyl)benzene (91.2 mg, 0.4 mmol, 1.0 equiv.), **BPP** (18.4 mg, 0.02 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (37.6 mg, 0.08 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 4.0 mL) and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (76.8 mg, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 2.57 (t, *J* = 8.0 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.68-1.56 (m, 4H), 1.40-1.34 (m, 4H), 1.31 (s, 9H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.9, 148.4, 139.5, 128.0, 125.1, 43.9, 35.3, 34.3, 31.4, 31.2, 29.1, 29.0, 22.0. **HRMS (ESI+):** calcd. for $C_{17}H_{27}O^+$ $(M+H)^+$ 247.2056, found 247.2048.

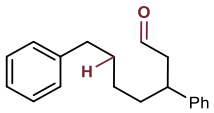
7-([1,1'-Biphenyl]-4-yl)heptanal (18)



According to the general procedure A, 4-(cyclohex-1-en-1-ylmethyl)-1,1'-biphenyl (49.6 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL) and 2 mL DCM and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (40.4 mg, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26-7.23 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 1.70-1.55 (m, 4H), 1.45-1.35 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.83, 141.73, 141.10, 138.61, 128.77, 128.68, 126.99, 126.95, 43.84, 35.45, 31.19, 28.99 (2C), 21.97; **HRMS (EI+):** calcd. for $C_{19}H_{22}O^+$ $(M)^+$ 266.1665, found 266.1660.

3,7-Diphenylheptanal (19)

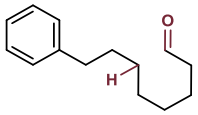


According to the general procedure A, 4-benzyl-1,2,3,6-tetrahydro-1,1'-biphenyl (49.6 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (30.9 mg, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.33-7.28 (m, 2H), 7.27-7.20 (m, 3H), 7.20-7.09 (m, 5H), 3.25-3.10 (m, 1H), 2.78-2.66 (m 2H), 2.61-2.47 (m, 2H), 1.74-1.49 (m, 5H), 1.23-1.13 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.00, 143.79, 142.49,

128.63, 128.31, 128.23, 127.43, 126.58, 125.62, 50.54, 39.98, 36.38, 35.68, 31.29, 26.91; **HRMS (EI+):** calcd. for $C_{19}H_{22}O^+$ $(M)^+$ 266.1665, found 266.1661.

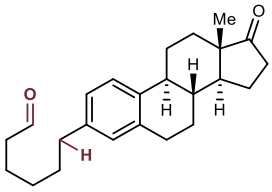
8-phenyloctanal (20)



According to the general procedure A, (2-(cyclohex-1-en-1-yl)ethyl)benzene (37.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the yield was determined by NMR (8% yield). The spectral data is consistent with the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 1.6 Hz, 1H), 7.31-7.25 (m, 2H), 7.21-7.15, (m, 3H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.42 (td, *J* = 6.0, 1.6 Hz, 2H),1.68-1.56 (m, 4H), 1.38-1.31 (m, 6H), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.9, 142.7, 128.4, 128.2, 125.6, 43.9, 35.9, 31.4, 29.2, 29.1, 29.0, 22.0. **HRMS (EI+):** calcd. for $C_{14}H_{20}O^+$ $(M)^+$ 204.1509, found 204.1507.

6-((13S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)hexanal (21)

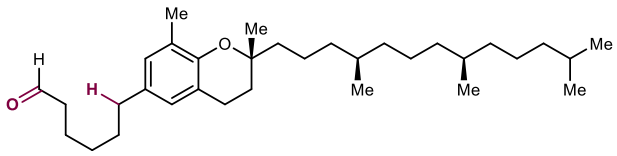


According to the general procedure A, 3-(cyclohex-1-en-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta [a]phenanthren-17-one (33.4mg, 0.1 mmol, 1.0 equiv.), **BPP** (4,6 mg, 0.005 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (9.4 mg, 0.02 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1,

1.0 mL) were used. After 48 h, the product was isolated by flash chromatography (25% ethyl acetate in hexanes) as a colorless oil (27.1 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.25-7.18 (m, 1H), 7.00-6.85 (m, 2H), 2.55 (t, *J* = 6.0 Hz, 2H), 2.61-2.52 (m, 2H), 2.52-2.46 (m, 1H), 2.46-2.41 (m, 2H), 2.35-2.24 (m, 1H), 2.22-1.85 (m, 5H), 1.70-1.35 (m, 12H), 0.91 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 220.9, 202.7, 139.8, 137.0, 136.3, 128.9, 125.8, 125.2, 50.4, 48.0, 44.2, 43.8, 38.2, 35.8, 35.1, 31.6, 31.1, 29.3, 28.8, 26.5, 25.7, 21.9, 21.5, 13.8. **HRMS (ESI+):** calcd. for $C_{24}H_{33}O_2^+$ $(M+H)^+$ 353.2475, found 353.2471.

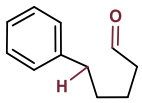
6-(2,8-dimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)hexanal (22)



According to the general procedure B, 2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (46.7 mg, 0.1 mmol, 1.0 equiv.), **BPP** (4.6 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 1.0 mL), collidine (40 μL, 3.0 equiv.), and 1 mL DCM were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (21.2 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 2.0 Hz, 1H), 6.75 (s, 1H), 6.68 (s, 1H), 2.78 - 2.64 (m, 2H), 2.51-2.36 (m, 4H), 2.13 (s, 3H), 1.87-1.71 (m, 2H), 1.71-1.63 (m, 2H), 1.63-1.59 (m, 1H), 1.55-1.48 (m, 2H), 1.41-1.32 (m, 6H), 1.32-1.18 (m, 12H), 1.18-0.98 (m, 7H), 0.91-0.80 (m, 12H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.90, 150.09, 132.44, 128.30, 126.43, 125.91, 120.10, 75.75, 43.85, 40.22, 39.35, 37.43, 37.40, 37.26, 34.86, 32.78, 32.68, 31.53, 31.25, 29.69, 28.89, 27.97, 24.79, 24.43, 24.25, 22.71, 22.62, 22.33, 21.97, 20.98, 19.74, 19.65, 16.04. **HRMS (ESI+):** calcd. for $C_{33}H_{57}O_2^+$ $(M+H)^+$ 485.4353, found 485.4360.

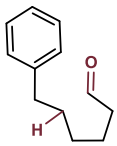
5-phenylpentanal (23)



According to the general procedure A, cyclopent-1-en-1-ylbenzene (28.8 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (16.2 mg, 50% yield). The spectral data is consistent with the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (t, *J* = 2.0 Hz, 1H), 7.31-7.26 (m, 2H), 7.22-7.15, (m, 3H), 2.64 (t, *J* = 6.5 Hz, 2H), 2.49-2.40 (m, 2H), 1.72-1.63 (m, 4H), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.5, 141.9, 128.4, 128.3, 125.8, 43.7, 35.6, 30.9, 21.7. **HRMS (FI+):** calcd. for $C_{11}H_{14}O^+$ $(M)^+$ 162.1039, found 162.1038.

6-Phenylhexanal (2)

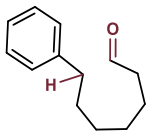


According to the general procedure A, 2,3,4,5-tetrahydro-1,1'-biphenyl (31.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (19:1, 2.0 mL) and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (23.6 mg, 67% yield). The spectral data is consistent with the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 2.0 Hz, 1H), 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.43 (dt, *J* = 2.0, 7.2 Hz, 2H), 1.71-1.59 (m, 4H), 1.42-1.32 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.4, 142.1, 128.1, 128.0, 125.5,

43.5, 35.5, 31.0, 28.5, 21.6; **HRMS (EI+):** calcd. for $C_{12}H_{16}O^+$ $(M)^+$ 176.1196, found 176.1196.

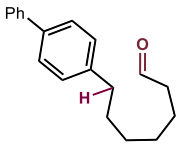
7-Phenylheptanal (15)



According to the general procedure A, 1-phenylcyclohept-1-ene (34.4 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (30.8 mg, 81% yield). The spectral data is consistent with the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 1.6 Hz, 1H), 7.30-7.26 (m, 2H), 7.20-7.13 (m, 3H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.42 (dt, *J* = 7.6, 1.6 Hz, 2H), 1.67-1.59 (m, 4H), 1.38-1.32 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.9, 142.7, 128.4, 128.2, 125.6, 43.9, 35.9, 29.2, 29.1, 29.0, 22.0. **HRMS (EI+):** calcd. for $C_{13}H_{18}O^+$ $(M)^+$ 190.1352, found 190.1348.

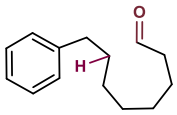
7-([1,1'-Biphenyl]-4-yl)heptanal (18)



According to the general procedure B, 4-(cyclohept-1-en-1-yl)-1,1'-biphenyl, **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.), CH_3CN/H_2O (10:1, 2.0 mL), collidine (80 μL, 3.0 equiv.), and 2 mL

DCM and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (25.6 mg, 48% yield). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.77 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26-7.23 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 1.70-1.55 (m, 4H), 1.45-1.35 (m, 4H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.83, 141.73, 141.10, 138.61, 128.77, 128.68, 126.99, 126.95, 43.84, 35.45, 31.19, 28.99 (2C), 21.97; **HRMS (EI+):** calcd. for $C_{19}H_{22}O^+$ $(M)^+$ 266.1665, found 266.1660.

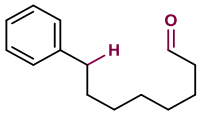
8-phenyloctanal (20)



According to the general procedure A, 1-phenylcyclooct-1-ene (37.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (29.0 mg, 71% yield). The spectral data is consistent with the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 1.6 Hz, 1H), 7.31-7.25 (m, 2H), 7.21-7.15, (m, 3H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.42 (td, *J* = 6.0, 1.6 Hz, 2H), 1.68-1.56 (m, 4H), 1.38-1.31 (m, 6H), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.9, 142.7, 128.4, 128.2, 125.6, 43.9, 35.9, 31.4, 29.2, 29.1, 29.0, 22.0. **HRMS (EI+):** calcd. for $C_{14}H_{20}O^+$ $(M)^+$ 204.1509, found 204.1507.

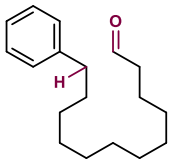
8-phenyloctanal (20)



According to the general procedure A, 1-benzylcyclohept-1-ene (37.2 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) , CH_3CN/H_2O (10:1, 2.0 mL) and 400 nm LEDs were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (24.2 mg, 59% yield). The spectral data is consistent with the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 1.6 Hz, 1H), 7.31-7.25 (m, 2H), 7.21-7.15, (m, 3H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.42 (td, *J* = 6.0, 1.6 Hz, 2H), 1.68-1.56 (m, 4H), 1.38-1.31 (m, 6H), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 202.9, 142.7, 128.4, 128.2, 125.6, 43.9, 35.9, 31.4, 29.2, 29.1, 29.0, 22.0. **HRMS (EI+):** calcd. for $C_{14}H_{20}O^+$ $(M)^+$ 204.1509, found 204.1507.

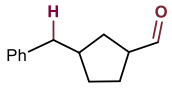
12-phenyldodecanal (24)



According to the general procedure A, 1-phenylcyclododec-1-ene (48.4 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (32.2 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (t, *J* = 2.0 Hz, 1H), 7.30-7.22 (m, 2H), 7.19-7.12, (m, 3H), 2.59 (t, *J* = 6.4 Hz, 2H), 2.41 (td, *J* =5.6, 2.0 Hz, 2H), 1.68-1.54 (m, 4H), 1.36-1.19 (m, 14H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.94, 142.88, 128.34, 128.16, 125.50, 43.87, 35.94, 31.49, 29.51, 29.50, 29.45, 29.36, 29.30, 29.28, 29.11, 22.04. **HRMS (FI+):** calcd. for $C_{18}H_{28}O^+$ $(M)^+$ 260.2142, found 260.2139.

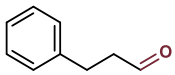
3-benzylcyclopentane-1-carbaldehyde (25)



According to the general procedure A, 2-phenylbicyclo[2.2.1]hept-2-ene (34.0 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) were used. After 48 h, the product was isolated by flash chromatography (5% ethyl acetate in hexanes) as a colorless oil (16.7 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (d, *J* = 2.0 Hz, 1H), 7.30-7.24 (m, 2H), 7.22-7.15 (m, 3H), 2.83-2.73 (m, 1H), 2.70-2.59 (m, 2H), 2.26-2.16 (m, 1H), 2.02-1.90 (m, 2H), 1.85-1.73 (m, 2H), 1.53-1.45 (m, 1H), 1.31-1.25 (m, 1H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.7, 141.4, 128.7, 128.3, 125.9, 51.3, 42.5, 41.4, 32.8, 32.0, 25.5. **HRMS (FI+):** calcd. for $C_{13}H_{16}O^+$ $(M)^+$ 188.1195, found 188.1191.

3-phenylpropanal (26)



According to the general procedure A, (4-methylpent-3-en-1-yl)benzene (32.0 mg, 0.2 mmol, 1.0 equiv.), **BPP** (9.2 mg, 0.01 mmol, 0.05 equiv.), 1,2-bis(2,4,6-triisopropylphenyl)disulfane (18.8 mg, 0.04 mmol, 0.2 equiv.) and CH_3CN/H_2O (10:1, 2.0 mL) and 400 nm LEDs were used. After 48 h, the yield was determined by GC-FID (64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (t, *J* = 1.2 Hz, 1H), 7.33-7.27 (m, 2H), 7.24-7.17 (m, 3H), 2.97 (t, J = 6.0 Hz, 2H), 2.83-2.76 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.3, 141.0, 128.3, 128.0, 126.0, 45.0, 27.8.

4.2. Experimental procedures and spectral characterization of the starting materials

General procedure for synthesis of phenylcycloalkene derivatives

To an arylmagnesium bromide THF solution (2.0 equiv.) was added cyclohexanone derivatives (1.0 equiv.) in THF (0.8 M) slowly at 0 ℃. When cyclohexanone derivatives were consumed, the reaction was quenched by 3 M HCl and water. The organic phase was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified with crude silica gel chromatography to afford the crude alcohol. The alcohol was dissolved in DCM (0.5 M), and 2 equiv. DMAP (4-Dimethylaminopyridine) was added. Then 0.5 equiv. triphosgene was added in small baches slowly under 0 ℃. The reaction was stirred overnight and quenched by 3 M HCl and water, the organic phase was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified with silica gel chromatography, and afforded the phenylcyclohexene derivatives.

General procedure A for synthesis of benzylcycloalkene derivatives

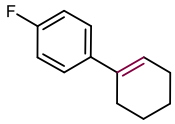
According to the literature.[7] A 25-mL flask charged with cut zinc powder (6.0 equiv.) and a stirring bar was flame-dried and flushed with argon. THF and 1,2-dibromoethane were added, and the zinc was activated by heating to reflux, then allowing to cool. This procedure was repeated until foam no longer occurred as a result of heating. The mixture was cooled to 0 °C before adding benzyl bromide derivatives (1.5 equiv.) in THF (5 mL) dropwise (0.1 drop/s). The mixture was kept at 0 °C until the reaction had completed to afford the organozinc halide.

The cyclohexenyl triflate or its derivaties (1 equiv.), $Pd(dppf)Cl_2$ (0.07 equiv.), Bu_4NI (3.0 equiv.) were dissolved in THF/NMP (1.5 mL, 1:1). To this mixture, the organozinc halide prepared in the previous procedure was added, and the mixture was stirred at 60 ℃ for 4 hours. The mixture was cooled to room temperature and quenched as usual. The crude product was purified by chromatography (100% petroleum ether) .

General procedure B for synthesis of benzylcycloalkene derivatives

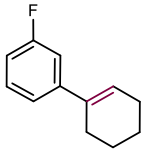
According to the literature.[7] A 25-mL seal tube charged with cyclohexenyl triflate or its derivaties (1 equiv.), Grignard reagent (3 equiv.), $Ni(OAc)_2$ (0.1 equiv.), ICy·HCl (1,3-dicyclohexyl-imidazolium chloride, 0.2 equiv.) were dissolved in toluene (0.25 M). Then the tube was sealed and heated to 100 ℃ and stirred for 4 h. The mixture was cooled to room temperature and quenched with water. The crude product was purified by chromatography (100% petroleum ether).

4'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (S1)



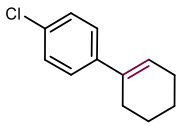
According to the general procedure for synthesis of phenylcyclohexene derivatives. 4'-fluoro phenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), cyclohexanone (1960 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 4'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl as colorless oil (2.26 g, 64% yield). The spectral data is consistent with the literature.[8]

3'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (S2)



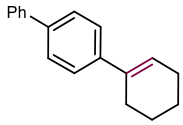
According to the general procedure for synthesis of phenylcyclohexene derivatives. 3'-fluorophenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), cyclohexanone (1960 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 3'-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl as colorless oil (2.89 g, 82% yield). The spectral data is consistent with the literature.[9]

4'-chloro-2,3,4,5-tetrahydro-1,1'-biphenyl (S3)



According to the general procedure for synthesis of phenylcyclohexene derivatives. 3'-chlorophenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), cyclohexanone (1960 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 4'-chloro-2,3,4,5-tetrahydro-1,1'-biphenyl as colorless oil (2.06 g, 54% yield). The spectral data is consistent with the literature.[10]

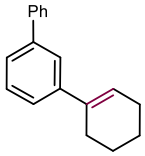
2,3,4,5-tetrahydro-1,1':4',1''-terphenyl (S4)



According to the general procedure for synthesis of phenylcyclohexene derivatives. 4-biphenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), cyclohexanone (1960 mg, 1.0 equiv.). DMAP (9760 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 2,3,4,5-tetrahydro-1,1':3',1''-terphenyl as white solid (2.33 g, 50% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64-7.59 (m, 2H), 7.59-7.52 (m, 2H), 7.50-7.45 (m, 2H), 7.45-7.40 (m, 2H), 7.37-7.30 (m, 1H), 6.29-6.12 (m, 1H), 2.52-2.41 (m, 2H), 2.28-2.20 (m, 2H), 1.85-1.77 (m, 2H), 1.74-1.64 (m, 2H), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 141.57, 140.90, 139.21, 136.04, 128.70, 127.05, 126.90, 126.86, 125.24, 124.92, 27.31, 25.92, 23.04, 22.14. **HRMS (ESI+):** calcd. for $C_{18}H_{19}^{+}$ $(M+H)^{+}$ 235.1481, found 235.1480.

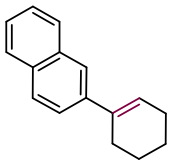
2,3,4,5-tetrahydro-1,1':3',1''-terphenyl (S5)



According to the general procedure for synthesis of phenylcyclohexene derivatives. 3-biphenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), cyclohexanone (1960 mg, 1.0 equiv.). DMAP (9760 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 2,3,4,5-tetrahydro-1,1':3',1''-terphenyl as colorless oil (2.31 g, 50% yield).

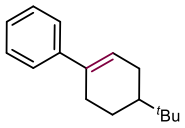
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.58 (m, 3H), 7.49-7.42 (m, 3H), 7.42-7.31 (m, 3H), 6.22-6.16 (m, 1H), 2.52-2.44 (m, 2H), 2.29-2.20 (m, 2H), 1.87-1.78 (m, 2H), 1.74-1.64 (m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.22, 141.54, 141.13, 136.61, 128.66, 128.56, 127.21, 127.15, 125.40, 125.14, 123.99, 123.94, 27.51, 25.88, 23.05, 22.14. **HRMS (EI+):** calcd. for $C_{18}H_{18}^{+}$ $(M)^{+}$ 234.1403, found 234.1408.

2-(cyclohex-1-en-1-yl)naphthalene (S6)



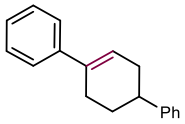
According to the general procedure for synthesis of phenylcyclohexene derivatives. Naphthalen-2-ylmagnesium bromide bromide THF solution (0.5 M, 90 mL, 1.5 equiv.), cyclohexanone (2940 mg, 1.0 equiv.). DMAP (7320 mg, 2.0 equiv.) and triphosgene (4455 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 2-(cyclohex-1-en-1-yl)naphthalene as colorless oil (5.14 g, 82% yield). The spectral data is consistent with the literature.[8]

4-(tert-butyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (S7)



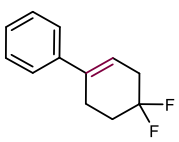
According to the general procedure for synthesis of phenylcyclohexene derivatives. 4-(tert-butyl)-phenylmagnesium bromide THF solution (1.0 M, 20 mL, 2.0 equiv.), cyclohexanone (980 mg, 1.0 equiv.). DMAP (2440 mg, 2.0 equiv.) and triphosgene (1485 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 4-(tert-butyl)-2,3,4,5-tetrahydro-1,1'-biphenylas colorless oil (1.86 g, 87% yield). The spectral data is consistent with the literature.[11]

1',2',3',6'-tetrahydro-1,1':4',1''-terphenyl (S8)



According to the general procedure for synthesis of phenylcyclohexene derivatives. phenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), 4-phenylcyclohexan-1-one (3485 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 1',2',3',6'-tetrahydro-1,1':4',1''-terphenyl as white solid (3.06 g, 65% yield). The spectral data is consistent with the literature.[12]

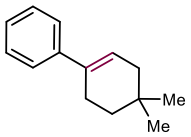
4,4-difluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (S9)



According to the general procedure for synthesis of phenylcyclohexene derivatives. phenylmagnesium bromide THF solution (1.0 M, 12 mL, 2.0 equiv.), 4,4-difluorocyclohexan-1-one (800 mg, 1.0 equiv.). DMAP (1464 mg, 2.0 equiv.) and triphosgene (1782 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 4,4-difluoro-2,3,4,5-tetrahydro-1,1'-biphenyl as colorless oil (621 mg, 53% yield).

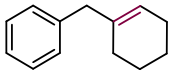
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.30 (m, 4H), 7.30-7.22 (m, 1H), 5.96-5.86 (m, 1H), 2.79-2.64 (m, 4H), 2.28-2.10 (m, 2H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.7, 136.3, 128.4, 127.3, 125.3, 122.7 (t, J = 191 Hz), 119.0 (t, J = 4 Hz), 35.0 (t, J = 21 Hz), 30.6 (t, J = 19 Hz), 25.9 (t, J = 4 Hz), **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.91. **HRMS (EI+):** calcd. for $C_{12}H_{12}F_2^+$ $(M)^+$ 194.0902, found 194.0905.

4,4-dimethyl-2,3,4,5-tetrahydro-1,1'-biphenyl (S10)



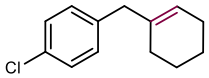
According to the general procedure for synthesis of phenylcyclohexene derivatives. phenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), 4,4-dimethylcyclohexan-1-one (2520 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 4,4-dimethyl-2,3,4,5-tetrahydro-1,1'-biphenyl as colorless oil (2.38 g, 64% yield). The spectral data is consistent with the literature.[13]

Benzylcyclohexene (S11)



Accroding to General procedure B for synthesis of benzylcycloalkene derivatives, 1-cyclohexenyl triflate (921 mg, 1.0 equiv.), BnMgBr in THF (1 M in THF, 12 mL), $Ni(OAc)_2$ (70.8 mg, 0.1 equiv.), ICy·HCl (215 mg, 0.2 equiv.) and toluene (16 mL) were used. The reaction was purified by chromatography (100% petroleum ether) to afford desired product as colorless oil (656 mg, 95% yield). The spectral data is consistent with the literature.[14]

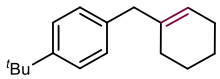
Chloro-4-(cyclohex-1-en-1-ylmethyl)benzene (S12)



Accroding to General procedure A for synthesis of benzylcycloalkene derivatives, zinc powder (1.5 g), 1-(bromomethyl)-4-chlorobenzene (1315 mg, 1.6 equiv.), 1-cyclohexenyl triflate (921 mg, 1.0 equiv.), TBAI (4438 mg, 3.0 equiv.) and $Pd(dppf)Cl_2$ (205 mg, 0.07 equiv.) were used. The reaction was purified by chromatography (100% Petroleum Ether) to afford desired product as colorless oil (412 mg, 50% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.21 (m, 2H), 7.13-7.07 (m, 2H), 5.49-5.42 (m, 1H), 3.20 (m, 2H), 2.07-1.97 (m, 2H), 1.89-1.78(m, 2H), 1.64-1.49 (m, 4H), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 138.9, 136.8, 131.5, 130.2, 128.2, 123.3, 44.0, 28.0, 25.3, 22.8, 22.3. **HRMS (EI+):** calcd. for $C_{13}H_{15}Cl^+$ $(M)^+$ 206.0857, found 206.0863.

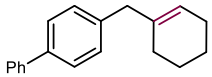
1-(tert-butyl)-4-(cyclohex-1-en-1-ylmethyl)benzene (S13)



Accroding to General procedure A for synthesis of benzylcycloalkene derivatives, zinc powder (1.3 g), 1-(bromomethyl)-4-(tert-butyl)benzene (1362 mg, 3 equiv.), 1-cyclohexenyl triflate (460 mg, 1.0 equiv.), TBAI (2.22 g, 3.0 equiv.) and $Pd(dppf)Cl_2$ (103 mg, 0.07 equiv.) were used. The reaction was purified by chromatography (100% petroleum ether) to afford desired product as colorless oil (441 mg, 97% yield).

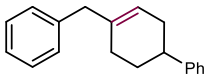
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.28 (m, 2H), 7.16-7.07 (m, 2H), 5.52-5.43 (m, 1H), 3.22 (s, 2H), 2.09-1.98 (m, 2H), 1.94-1.83 (m, 2H), 1.64-1.51 (m, 4H), 1.32 (s, 9H), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 148.5, 137.3, 128.5, 125.0, 122.7, 44.1, 34.3, 31.4 (3C), 28.1, 25.3, 22.9, 22.4. **HRMS (EI+):** calcd. for $C_{17}H_{24}^+$ $(M)^+$ 228.1873, found 228.1876.

4-(cyclohex-1-en-1-ylmethyl)-1,1'-biphenyl (S14)



Accroding to General procedure A for synthesis of benzylcycloalkene derivatives, zinc powder (1.5 g), 4-(bromomethyl)-1,1'-biphenyl (1581 mg, 1.6 equiv.), 1-cyclohexenyl triflate (921 mg, 1.0 equiv.), TBAI (4438 mg, 3.0 equiv.) and $Pd(dppf)Cl_2$ (205 mg, 0.07 equiv.) were used. The reaction was purified by chromatography (100% petroleum ether) to afford desired product as colorless oil (694 mg, 70% yield). The spectral data is consistent with the literature.[15]

4-benzyl-1,2,3,6-tetrahydro-1,1'-biphenyl (S15)

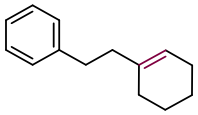


Accroding to General procedure B for synthesis of benzylcycloalkene derivatives, 1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (1530 mg, 1.0 equiv.), BnMgBr in toluene (1 M in THF, 15 mL, 3.0 equiv.), $Ni(OAc)_2$ (88 mg, 0.1 equiv.), ICy·HCl (269 mg, 0.2 equiv.) and toluene (15 mL) were used. The reaction was purified by chromatography (100% petroleum ether) to afford desired product as colorless oil (897 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.28 (m, 4H), 7.26-7.18 (m, 6H), 5.62-5.55 (m, 1H), 3.34 (s, 2H), 2.83-2.73 (m, 1H), 2.41-2.30 (m, 1H), 2.28-1.89 (m, 4H), 1.84-1.70 (m, 1H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.1, 140.2, 137.2, 128.9, 128.3, 128.2,

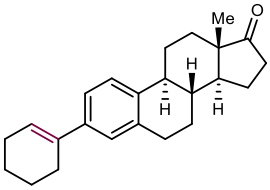
126.9, 125.9, 122.5, 44.3, 40.1, 33.6, 30.0, 28.7. **HRMS (EI+):** calcd. for $C_{19}H_{20}^{+}$ $(M)^{+}$ 248.1560, found 248.1557.

(2-(cyclohex-1-en-1-yl)ethyl)benzene (S16)



According to the general procedure for synthesis of phenylcyclohexene derivatives. phenethylmagnesium bromide THF solution (0.5 M, 40 mL, 2.0 equiv.), cyclohexanone (980 mg, 1.0 equiv.). DMAP (2440 mg, 2.0 equiv.) and triphosgene (1485 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded (2-(cyclohex-1-en-1-yl)ethyl)benzene as colorless oil (1.03 g, 60% yield). The spectral data is consistent with the literature.[16]

3-(cyclohex-1-en-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (S17)

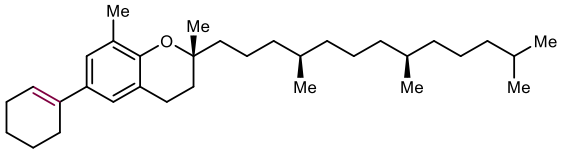


A 100 mL flask charged with estrone (5.0g, 1.0 equiv.), Et_3N (7.7 mL, 3 equiv.), and dry DCM 100 mL, then Tf_2O (3.4 mL, 1.1 eqiuv.) in DCM was added slowly under 0 ℃. The solution was stirred for 24 h and quenched with water. The mixture was extracted with ethyl acetate, the organic extracts were dried over Na_2SO_4, and concentrated in *vacuo*. The residue is chromatographed through silica gel (PE/EA = 10:1) afforded the corresponding phenyl trifluoromethanesulfonate derivatives.

To a 100 mL flask charged with the phenyl trifluoromethanesulfonate derivatives (2000 mg, 1.0 equiv.), 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1611 mg, 1.5 equiv.), $Pd(PPh_3)_4$ (288.8 mg, 0.05 equiv.) and Cs_2CO_3 (2781 mg, 3.0 equiv.)

in Toluene/Methanol (4:1, 50 mL). Then the mixture was refluxed overnight under nitrogen atmosphere. The reaction was quenched with water and extracted with ethyl acetate, the organic phase was dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified with chromatography (100% petroleum ether) as white solid (924 mg, 55% yield). The spectral data is consistent with the literature.[17]

6-(cyclohex-1-en-1-yl)-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl) chromane (S18)



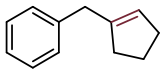
A 100 mL flask charged with D-delta-Tocopherol (2.0 g, 1.0 equiv.), DMAP (111.2 mg, 0.2 equiv.), Et_3N (1.4 mL, 2.0 equiv.) and dry DCM 20 mL, then N, N-bis-(trifluoromethanesulphonyl)-aniline (2129 mg, 1.2 equiv.) in DCM was added slowly under 0 ℃. The solution was stirred until D-delta-Tocopherol was consumed and quenched with water. The mixture was extracted with ethyl acetate, the organic extracts were dried over Na_2SO_4, and concentrated in *vacuo*. The residue is chromatographed through silica gel (PE/EA=20:1) afforded the corresponding phenyl trifluoromethanesulfonate derivatives.

To a 100 mL flask charged with the phenyl trifluoromethanesulfonate derivatives (2500 mg, 1.0 equiv.), 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1947 mg, 2.0 equiv.), $Pd(PPh_3)_4$ (270 mg, 0.05 equiv.) and Cs_2CO_3 (4574 mg, 3.0 equiv.) in Toluene/Methanol (3:1, 20 mL). Then the mixture was refluxed overnight under nitrogen atmosphere. The reaction was quenched with water and extracted with ethyl acetate, the organic phase was dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified with chromatography (100% petroleum ether) as colorless oil (781 mg, 36% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03-7.00 (m, 1H), 6.95-6.91 (m, 1H), 6.06-5.93 (m, 1H), 2.84-2.64 (m, 2H), 2.43-2.33 (m, 2H), 2.24-2.10 (m, 5H), 1.90-1.69 (m, 4H), 1.69-

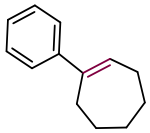
1.61 (m, 2H), 1.61-1.49 (m, 3H), 1.49-1.34 (m, 4H), 1.34-1.20 (m, 11H), 1.18-1.13 (m, 2H), 1.20-1.01 (m, 4H), 0.93-0.81 (m, 12H), **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.1, 136.3, 133.4, 125.8, 125.1, 123.3, 122.3, 119.9, 40.1, 39.4, 37.5, 37.3, 32.8, 32.7, 31.4, 28.0, 27.5, 25.8, 24.8, 24.5, 24.3, 23.2, 22.7, 22.6, 22.5, 22.3, 21.0, 19.8, 19.7, 16.2. **HRMS (ESI+):** calcd. for $C_{33}H_{55}O^+$ $(M+H)^+$ 467.4247, found 467.4240.

(cyclopent-1-en-1-ylmethyl)benzene (S19)



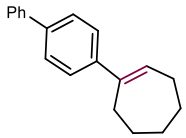
Accroding to General procedure B for synthesis of Benzylcycloalkene derivatives, 1-cyclopentenyl triflate (235 mg, 1.0 equiv.), BnMgBr in THF (1 M in THF, 3 mL. 3.0 equiv.) $Ni(OAc)_2$ (18 mg, 0.1 equiv.), ICy·HCl (54 mg, 0.2 equiv.) and toluene (3 mL) were used. The reaction was purified by chromatography (100% petroleum ether) to afford desired product as colorless oil (128 mg, 73% yield). The spectral data is consistent with the literature.[18]

1-phenylcyclohept-1-ene (S20)



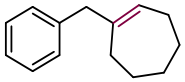
According to the general procedure for synthesis of phenylcyclohexene derivatives. phenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), cycloheptanone (2244 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 1-phenylcyclohept-1-ene as colorless oil (2.93 g, 85% yield). The spectral data is consistent with the literature.[19]

4-(cyclohept-1-en-1-yl)-1,1'-biphenyl (S21)



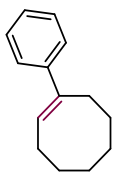
According to the general procedure for synthesis of phenylcyclohexene derivatives. 4-biphenylmagnesium bromide THF solution (1.0 M, 20 mL, 2.0 equiv.), cycloheptanone (980 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (1485 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 4-(cyclohept-1-en-1-yl)-1,1'-biphenyl as colorless oil (1.78 g, 82% yield). The spectral data is consistent with the literature.[20]

1-benzylcyclohept-1-ene (S22)



Accroding to General procedure B for synthesis of benzylcycloalkene derivatives, 1-cyclohexenyl triflate (976 mg, 1.0 equiv.), BnMgBr in THF (1 M in THF, 12 mL) $Ni(OAc)_2$ (70.8 mg, 0.1 equiv.), ICy·HCl (215 mg, 0.2 equiv.) and toluene (16 mL) were used. The reaction was purified by chromatography (100% petroleum ether) to afford desired product as colorless oil (762 mg, quant.). The spectral data is consistent with the literature.[21]

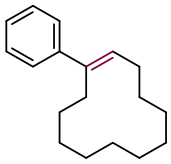
1-phenylcyclooct-1-ene (S23)



According to the general procedure for synthesis of phenylcyclohexene derivatives. phenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), cyclooctanone (2524 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5

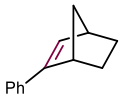
equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 1-phenylcyclooct-1-ene as colorless oil (1.55 g, 42% yield). The spectral data is consistent with the literature.[22]

1-phenylcyclododec-1-ene (S24)



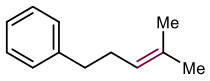
According to the general procedure for synthesis of phenylcyclohexene derivatives. phenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), cyclododecanone (3646 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 1-phenylcyclooct-1-ene as colorless oil (2.57 g, 53% yield). The spectral data is consistent with the literature.[23]

2-phenylbicyclo[2.2.1]hept-2-ene (S25)



According to the general procedure for synthesis of phenylcyclohexene derivatives. phenylmagnesium bromide THF solution (1.0 M, 40 mL, 2.0 equiv.), bicyclo[2.2.1]heptan-2-one (2203 mg, 1.0 equiv.). DMAP (4880 mg, 2.0 equiv.) and triphosgene (2970 mg, 0.5 equiv.) were used. The reaction was purified with silica gel chromatography (100% petroleum ether) afforded 2-phenylbicyclo[2.2.1]hept-2-ene as light yellow oil (2.37 g, 70% yield). The spectral data is consistent with the literature.[24]

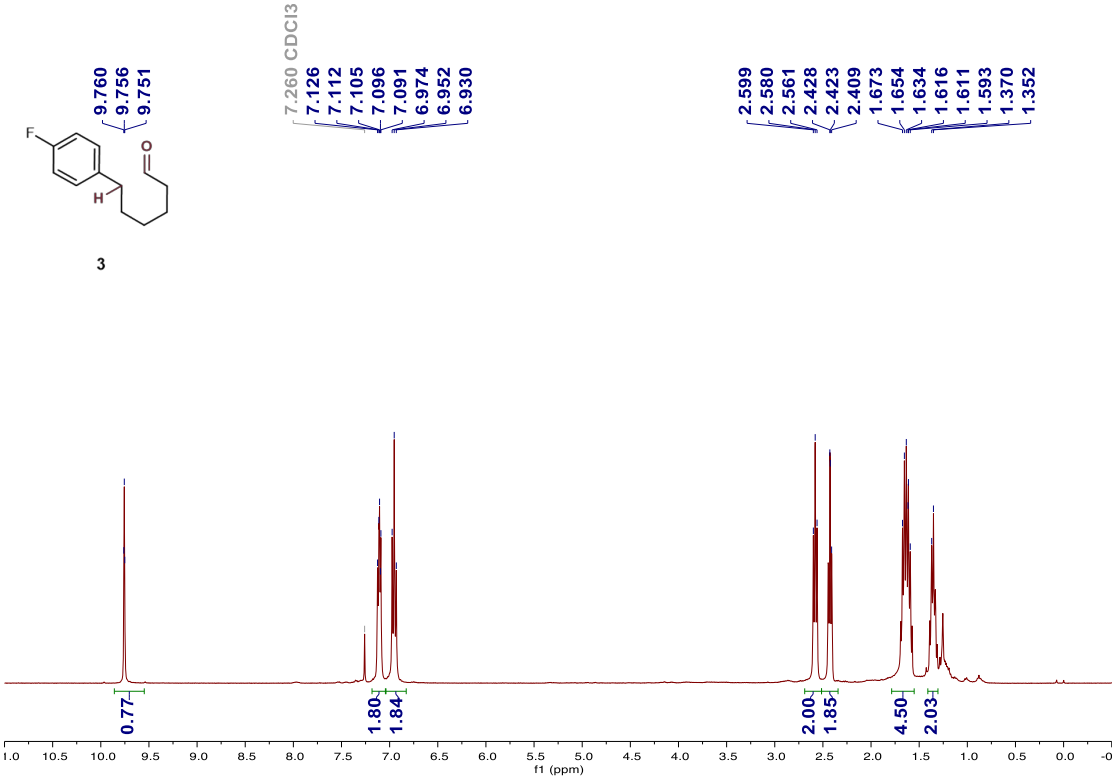
(4-methylpent-3-en-1-yl)benzene (S26)



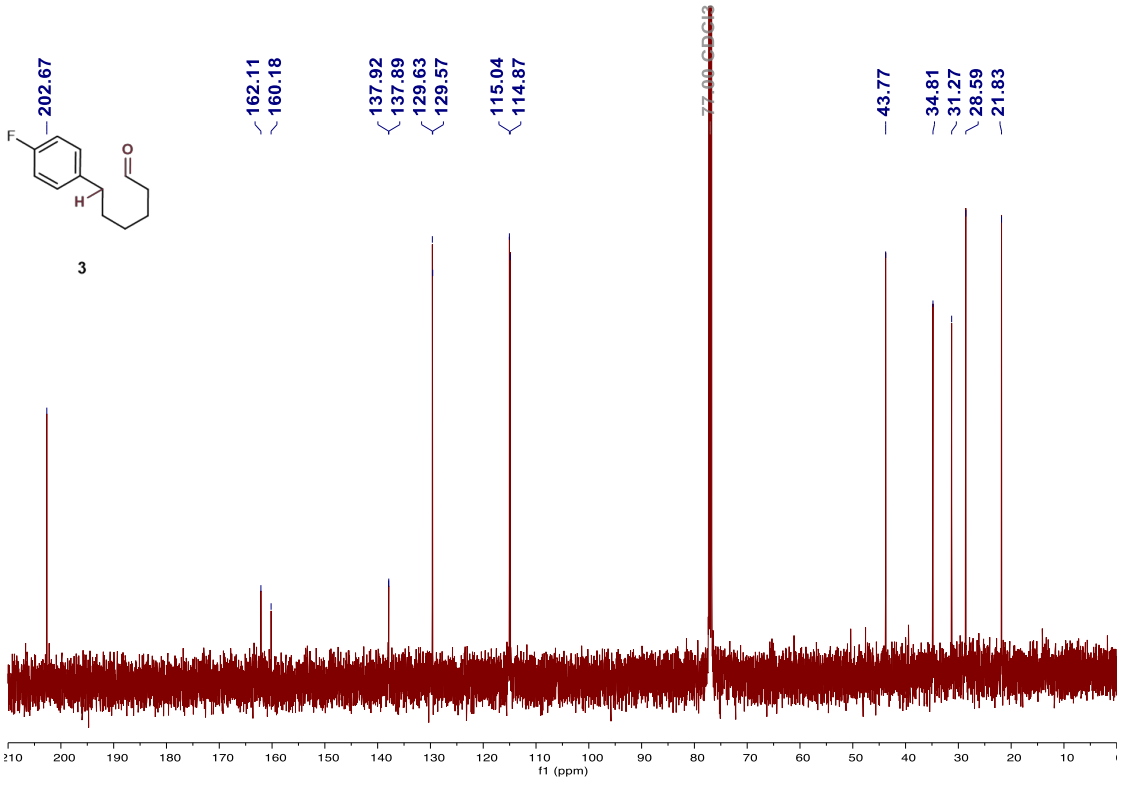
To a dried 100 mL flask, isopropyltriphenylphosphonium bromide (7706 mg, 2.0 equiv.) and THF (40 mL) were added. Then, n-butyllithium (2.5 M, 8 mL, 2.0 equiv.) was added slowly under -78 ℃, and the mixture was stirred for 1 hour. Once the white solid of isopropyltriphenylphosphonium bromide was consumed, the mixture was warmed to 0 ℃, and a solution of 3-phenylpropanal (1340 mg, 1.0 equiv.) in THF was added. The mixture was then allowed to warm slowly to room temperature. After 1 hour, the reaction was quenched with 3 M HCl and water, and the product was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed in *vacuo*. The residue was purified by flash chromatography (eluting with 100% petroleum ether) to yield the desired product as a colorless oil (481 mg, 30% yield). The spectral data is consistent with the literature.[25]

5. Spectral data

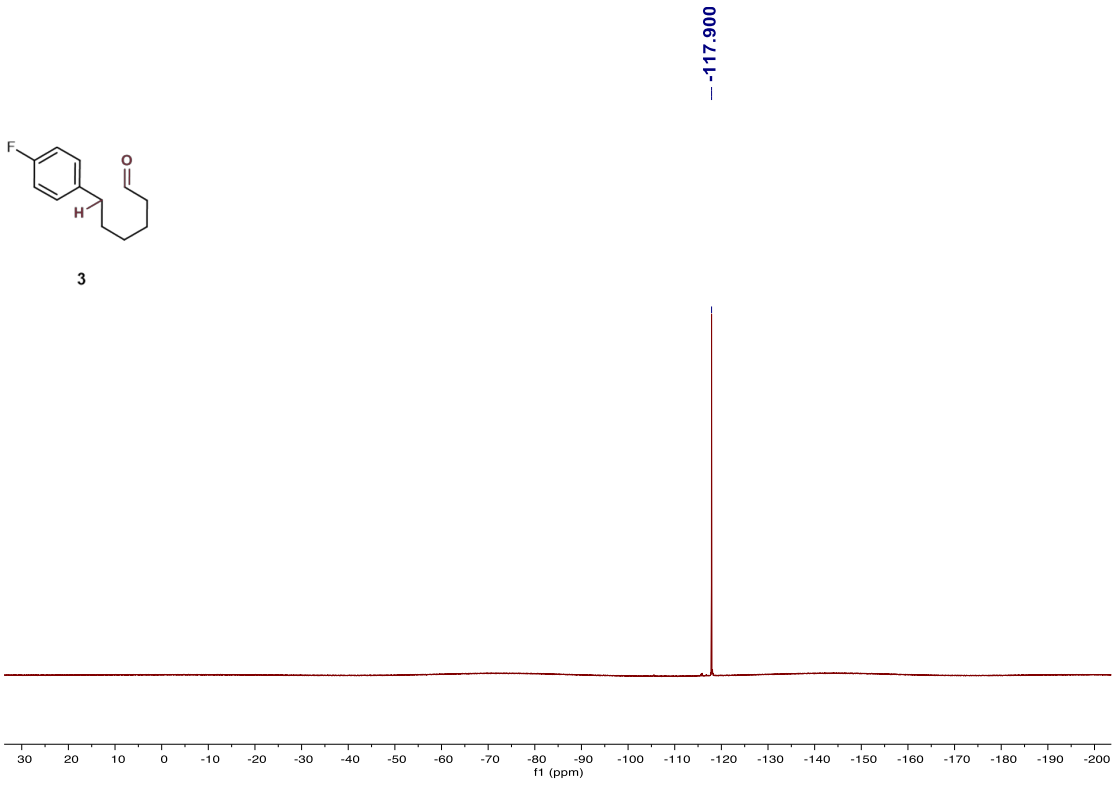
^{1}H NMR (400 MHz, $CDCl_3$)



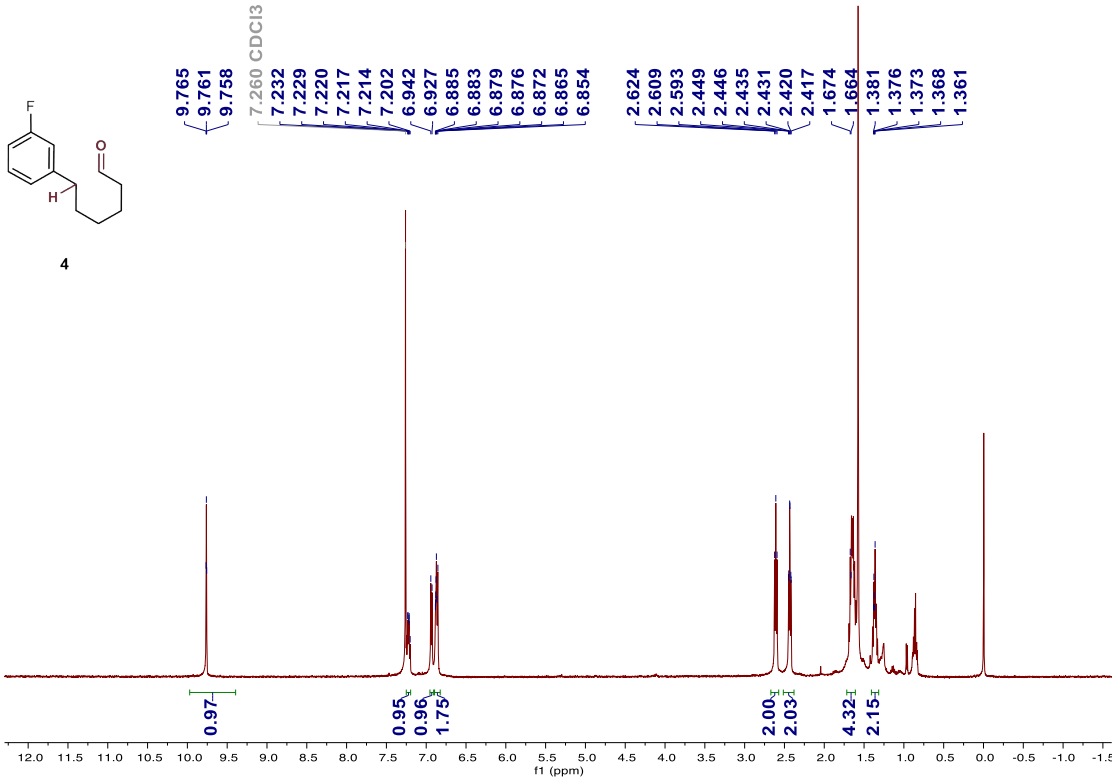
^{13}C NMR (100 MHz, $CDCl_3$)



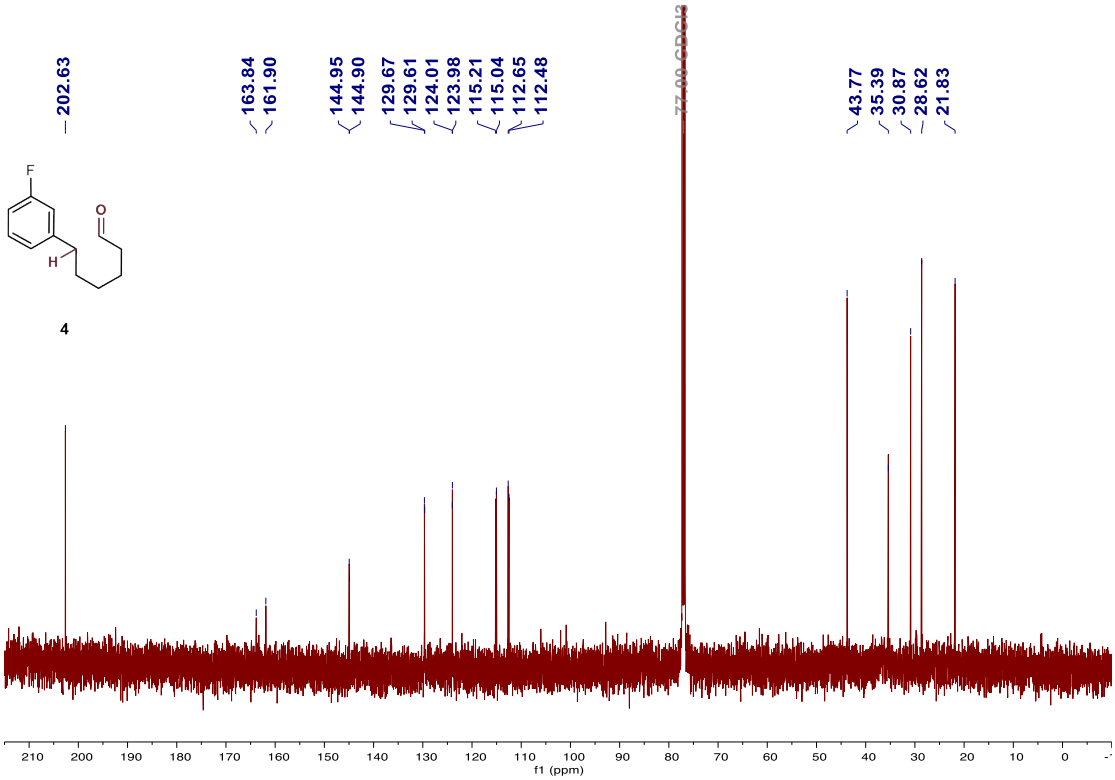
^{19}F NMR (376 MHz, $CDCl_3$)



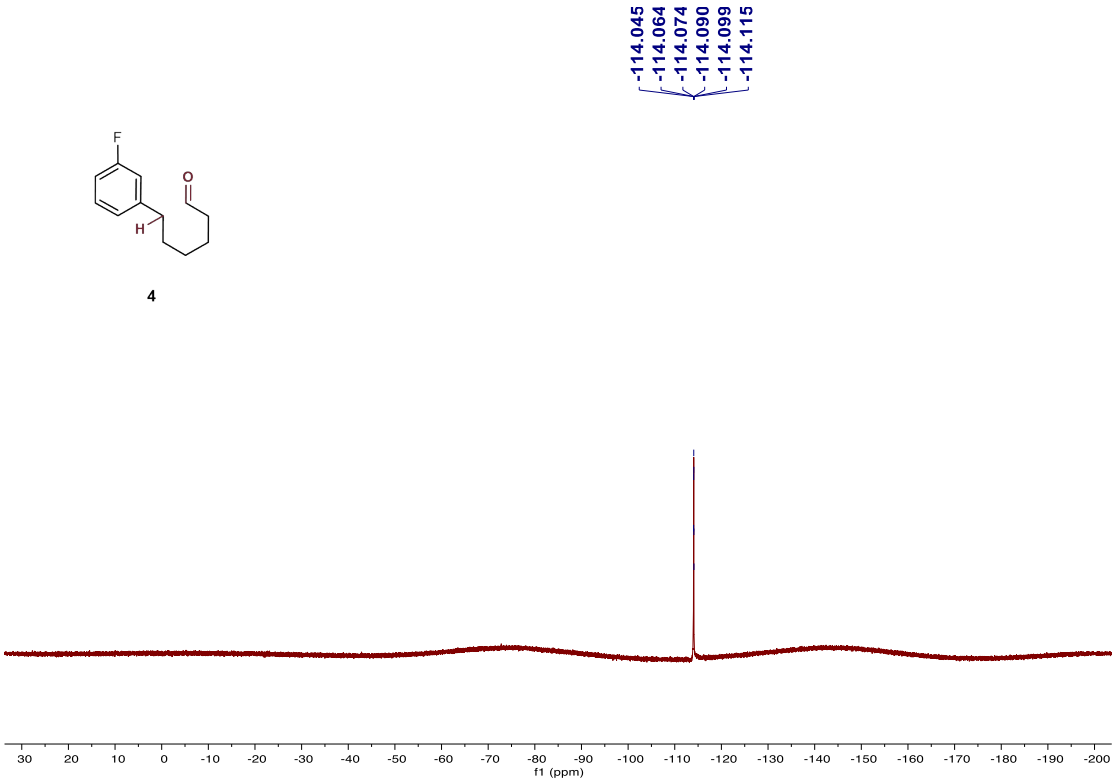
^{1}H NMR (400 MHz, $CDCl_3$)



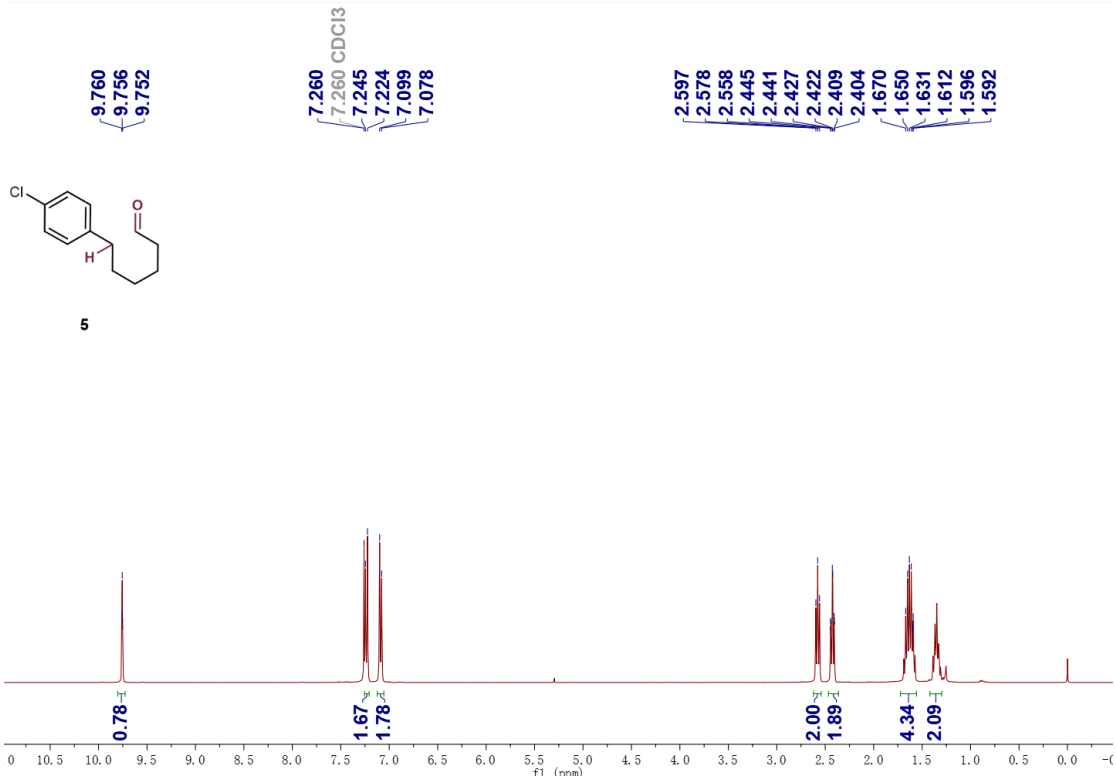
^{13}C NMR (100 MHz, $CDCl_3$)



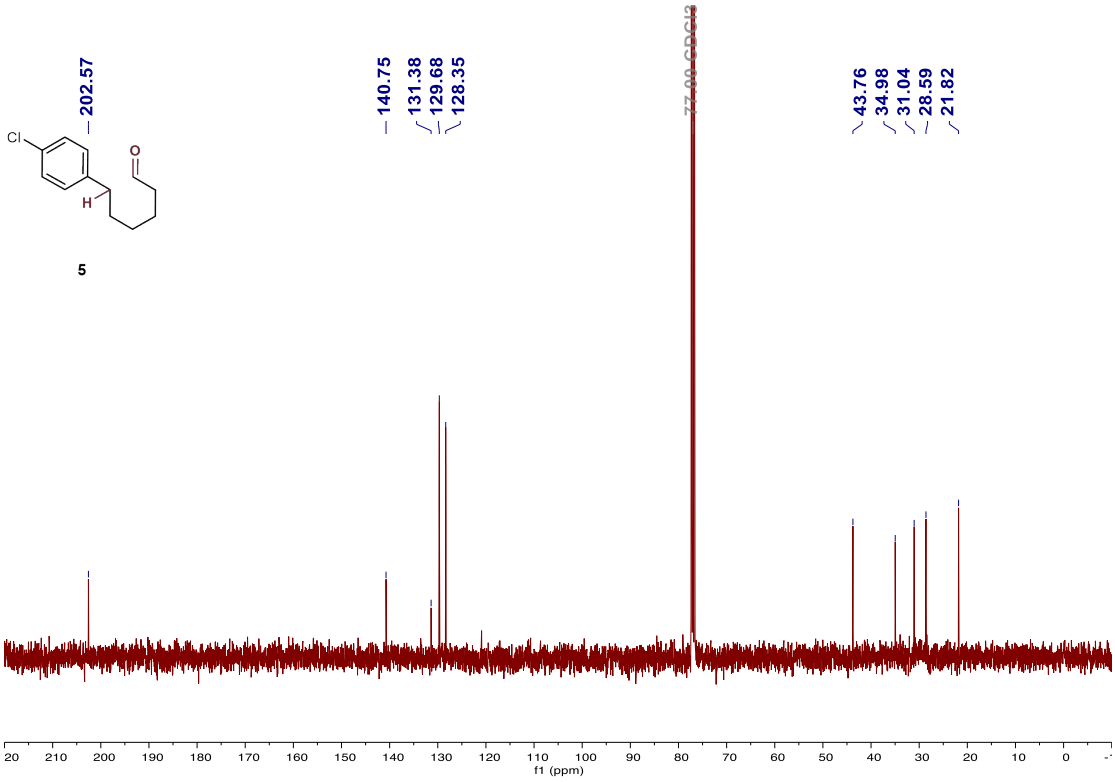
^{19}F NMR (376 MHz, $CDCl_3$)



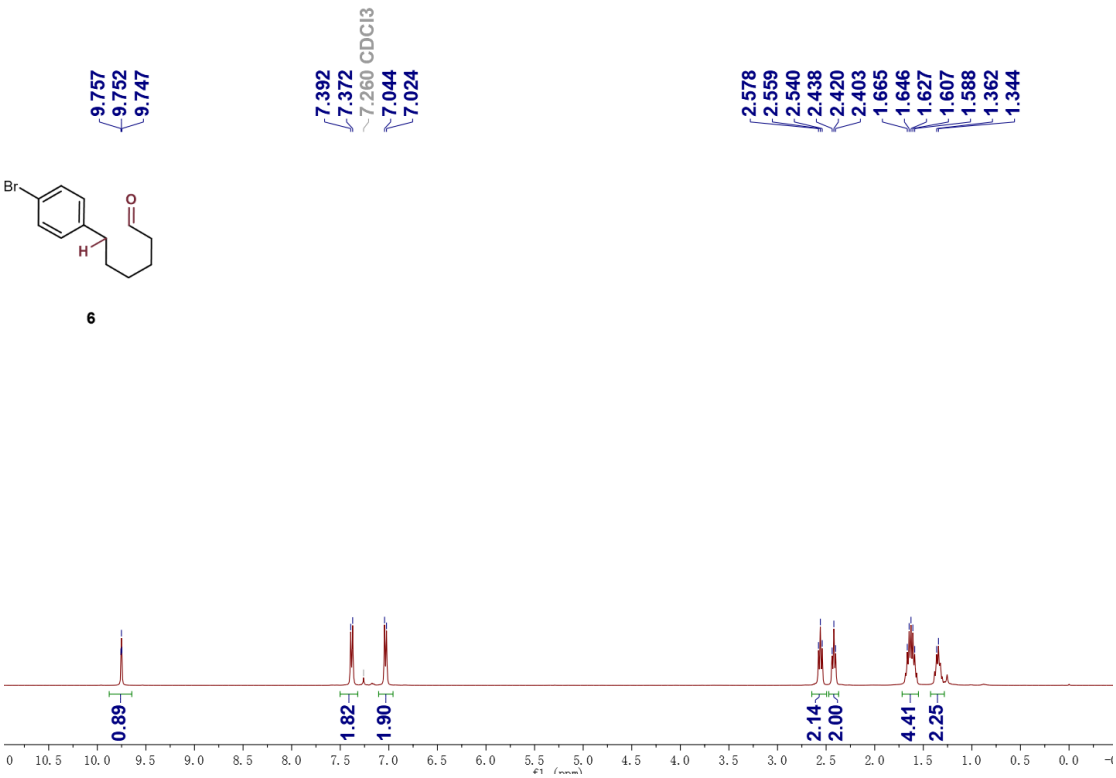
^{1}H NMR (400 MHz, $CDCl_3$)



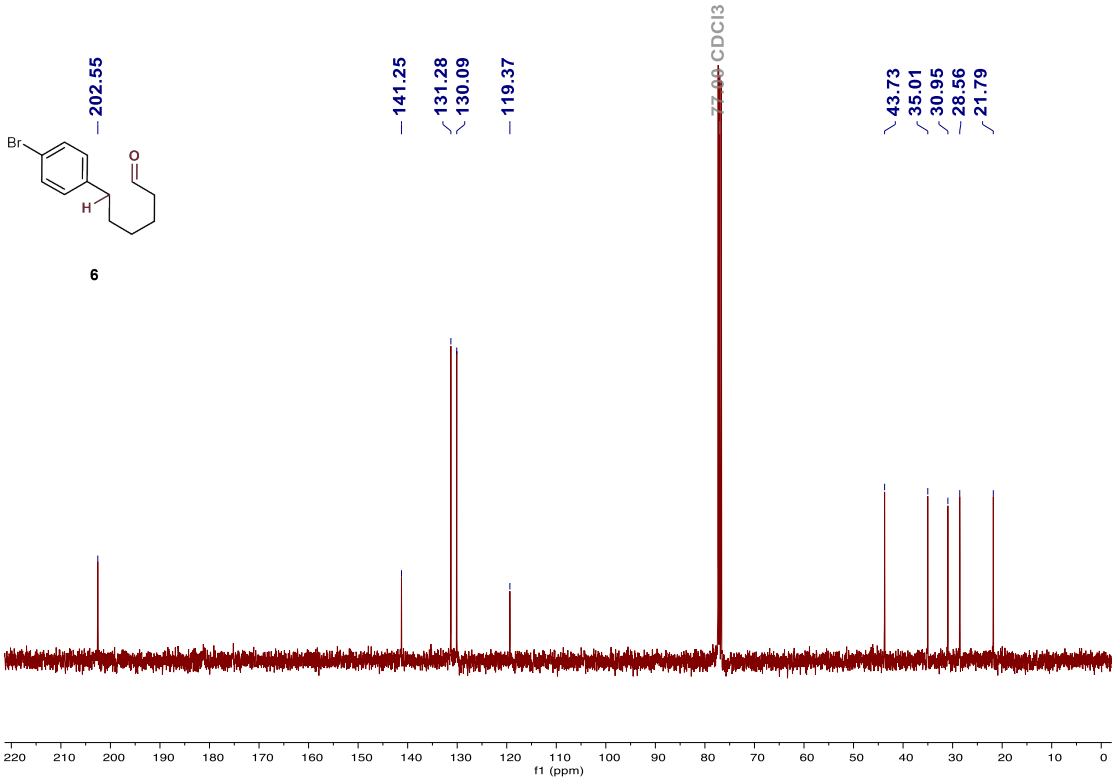
^{13}C NMR (100 MHz, $CDCl_3$)



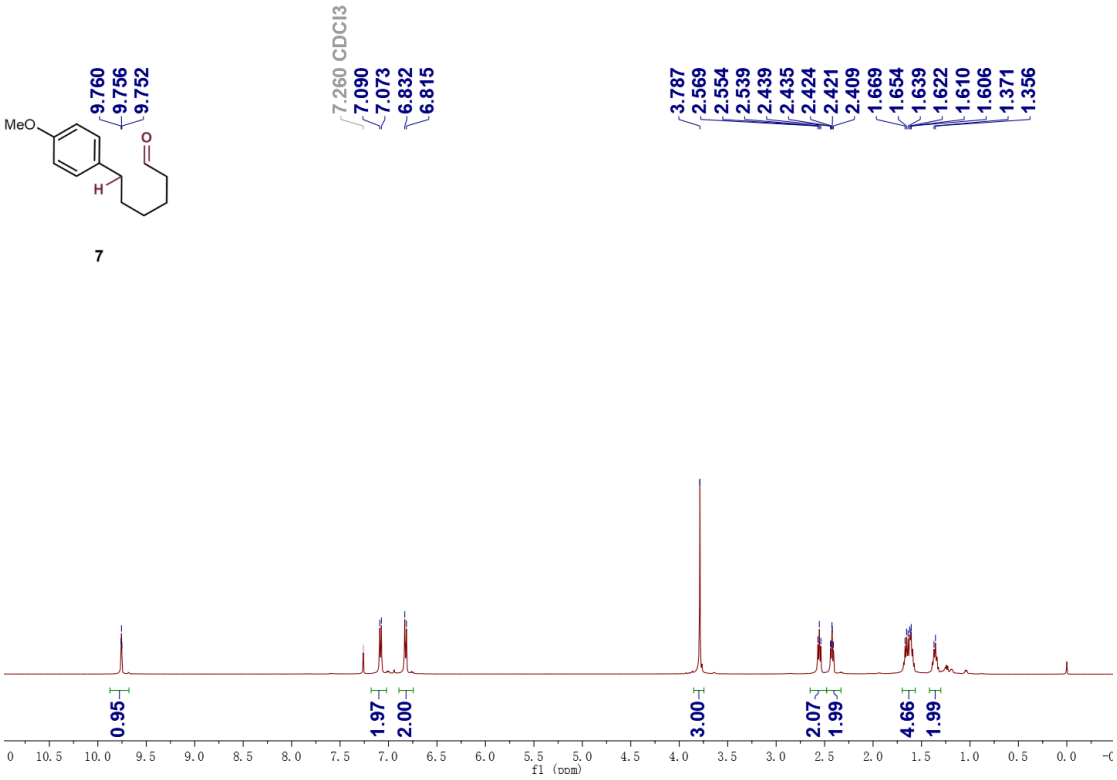
^{1}H NMR (400 MHz, $CDCl_3$)



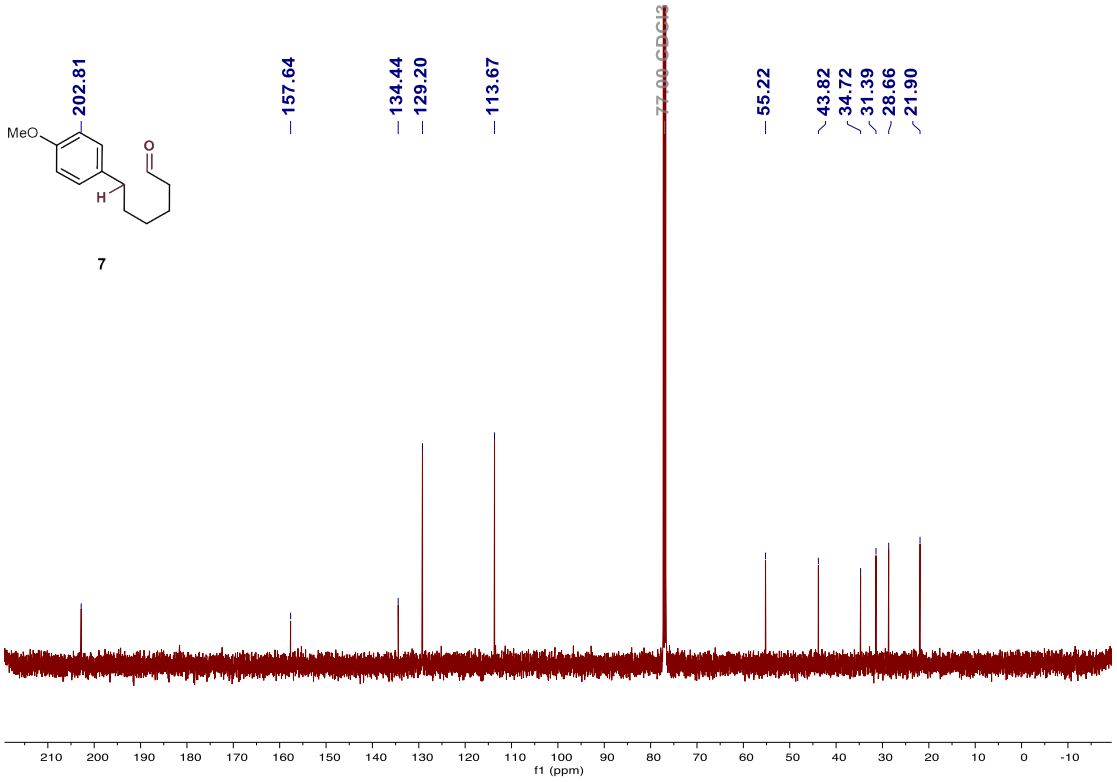
^{13}C NMR (100 MHz, $CDCl_3$)



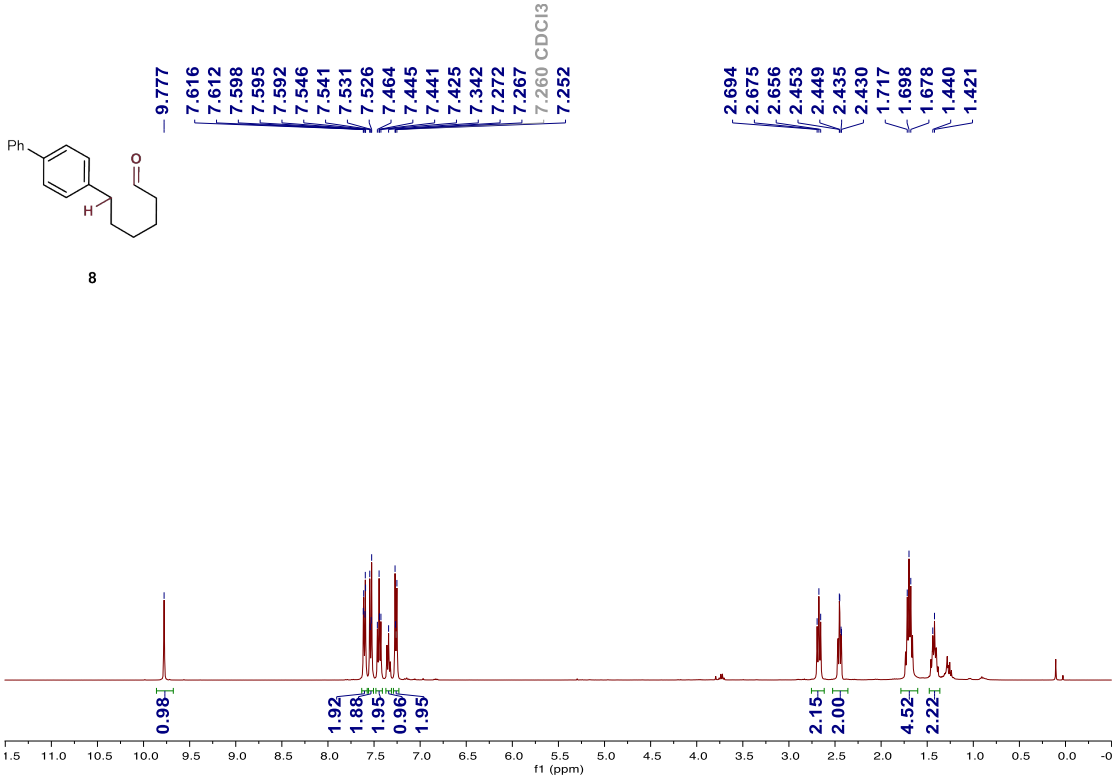
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

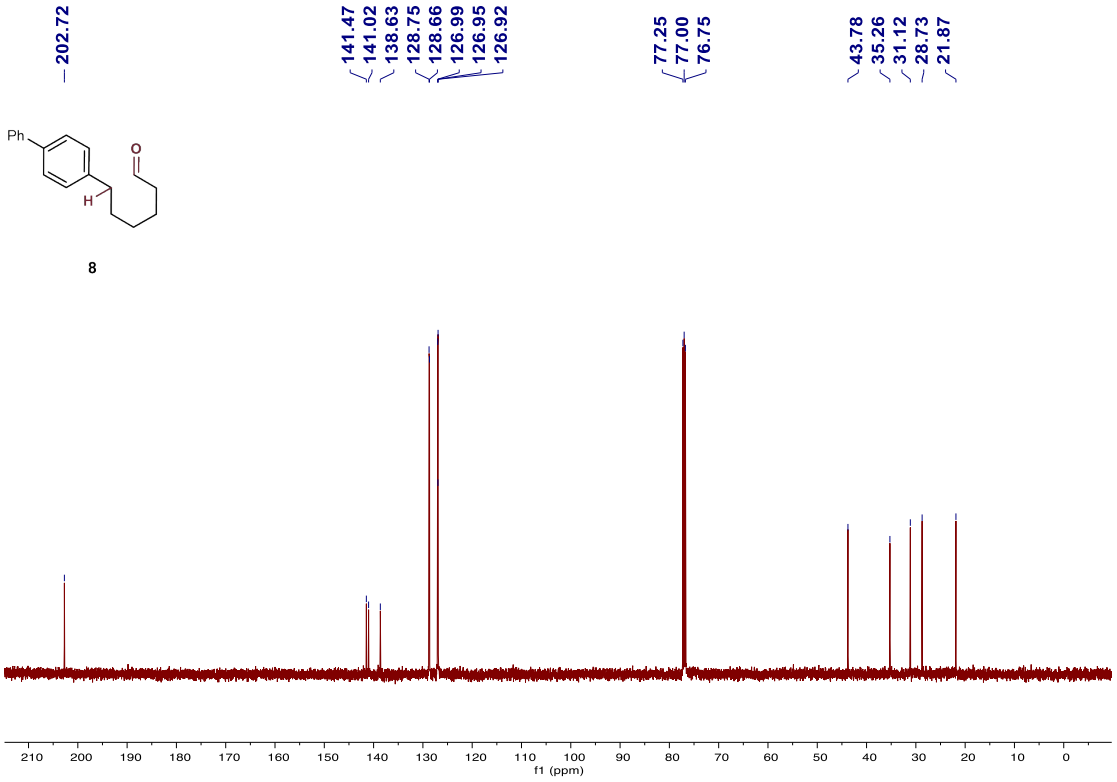


^{1}H NMR (400 MHz, $CDCl_3$)



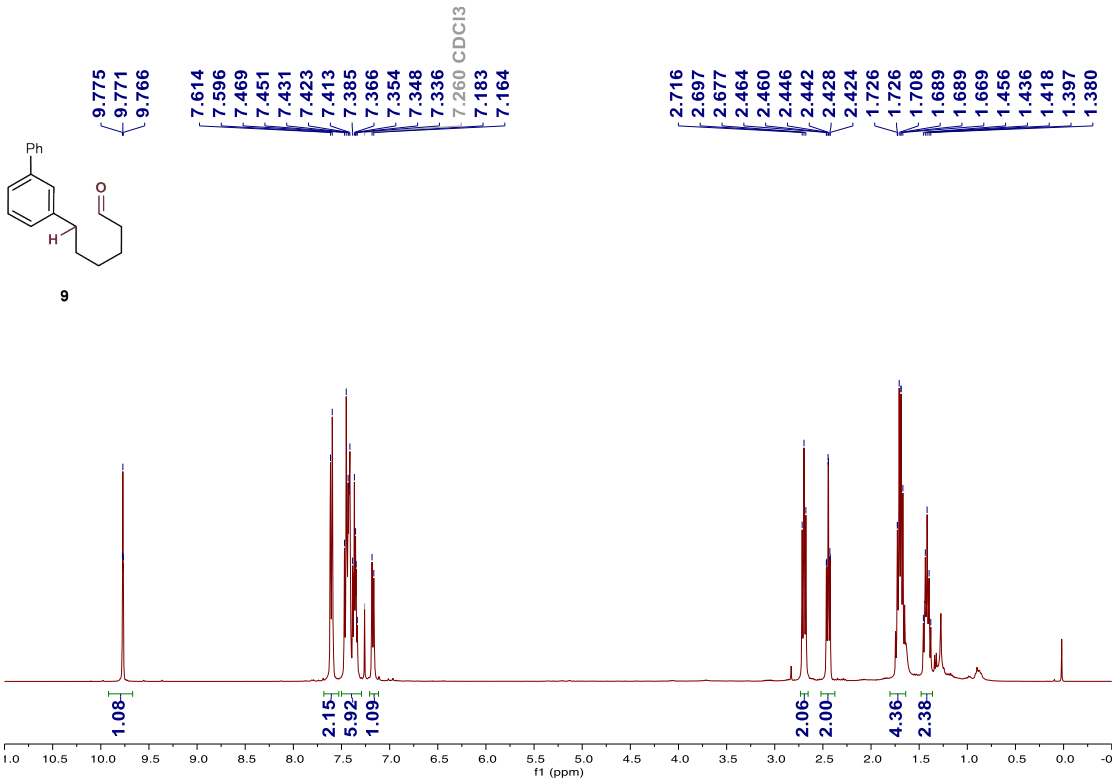
8

^{13}C NMR (100 MHz, $CDCl_3$)

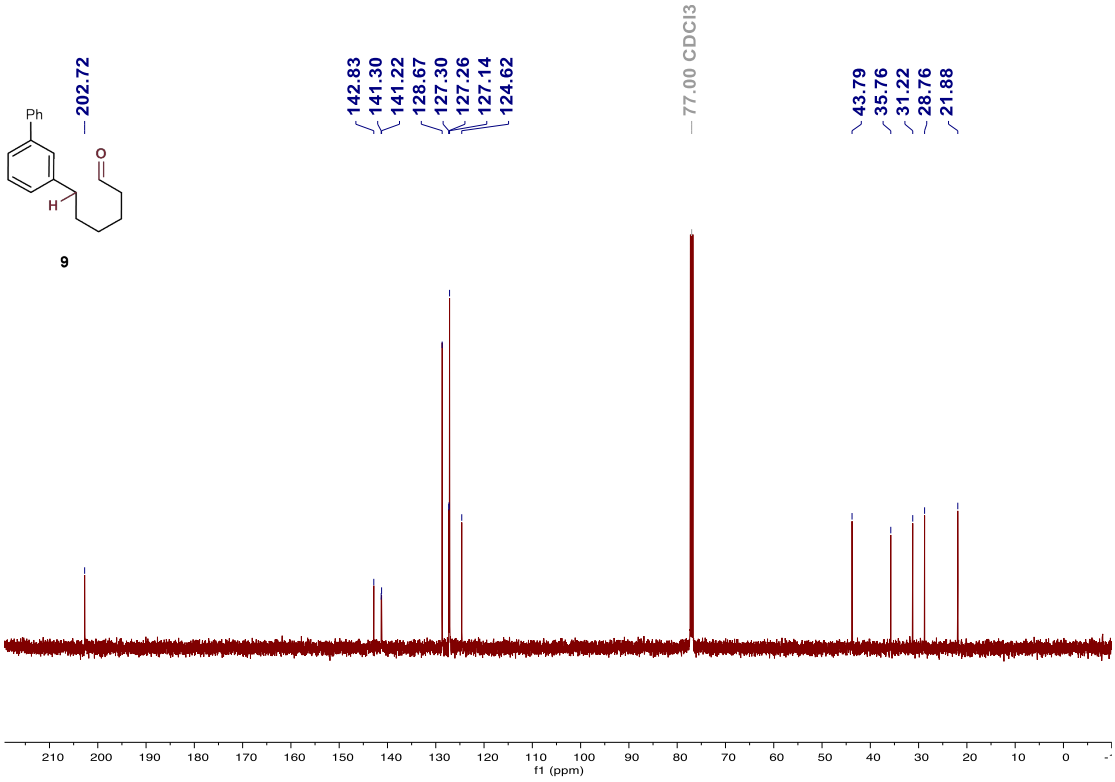


8

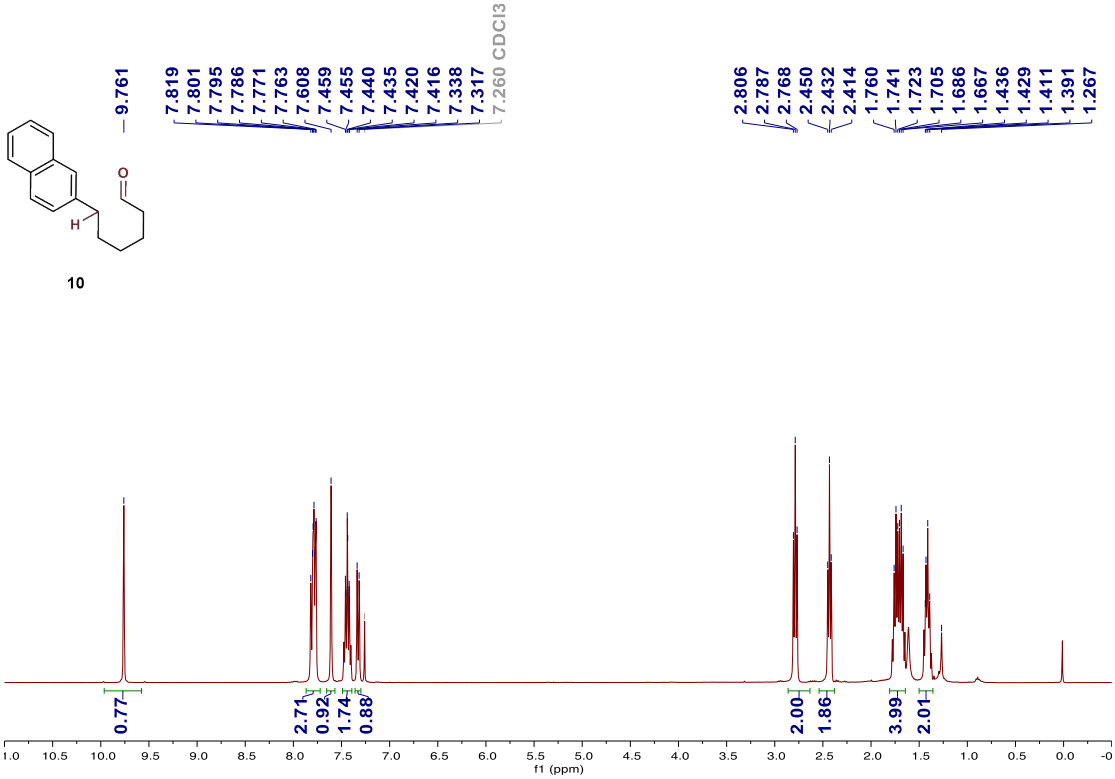
^{1}H NMR (400 MHz, $CDCl_3$)



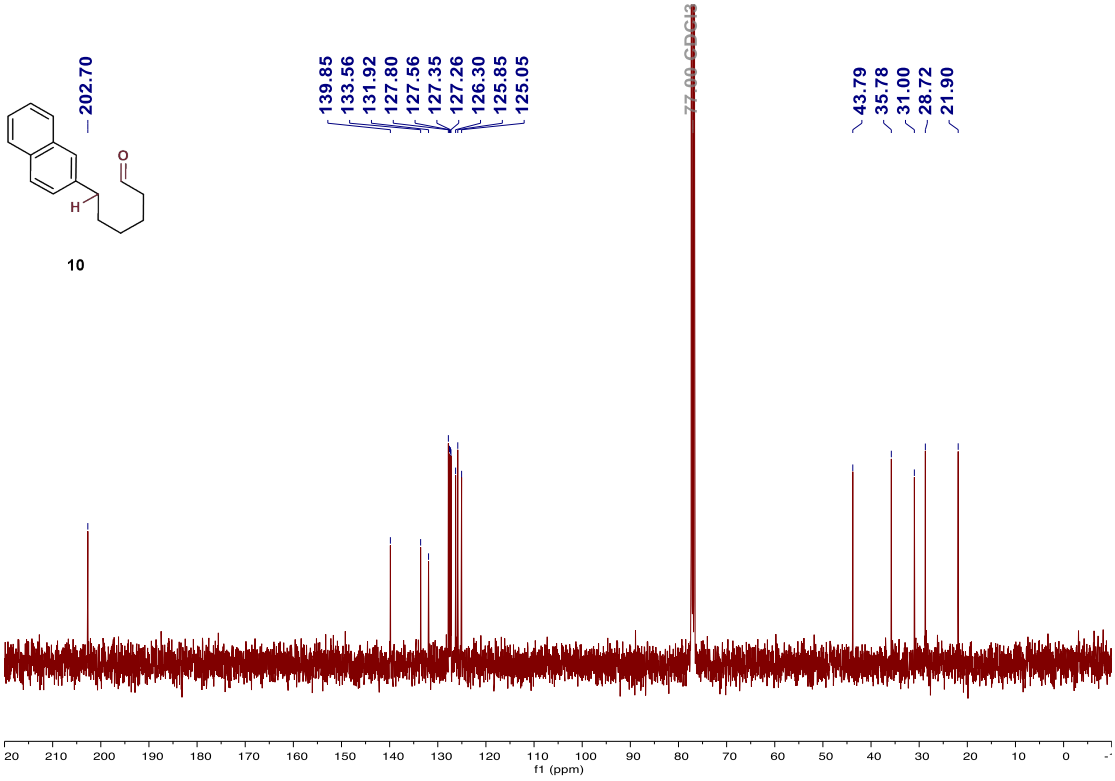
^{13}C NMR (100 MHz, $CDCl_3$)



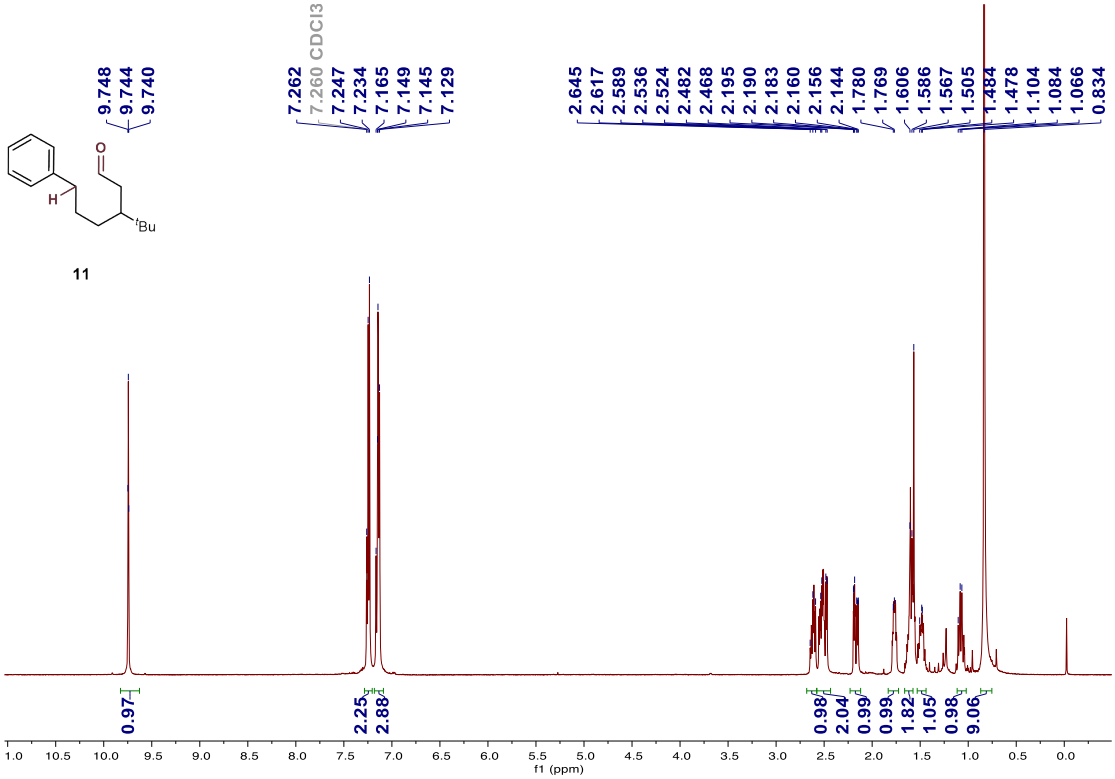
^{1}H NMR (400 MHz, $CDCl_3$)



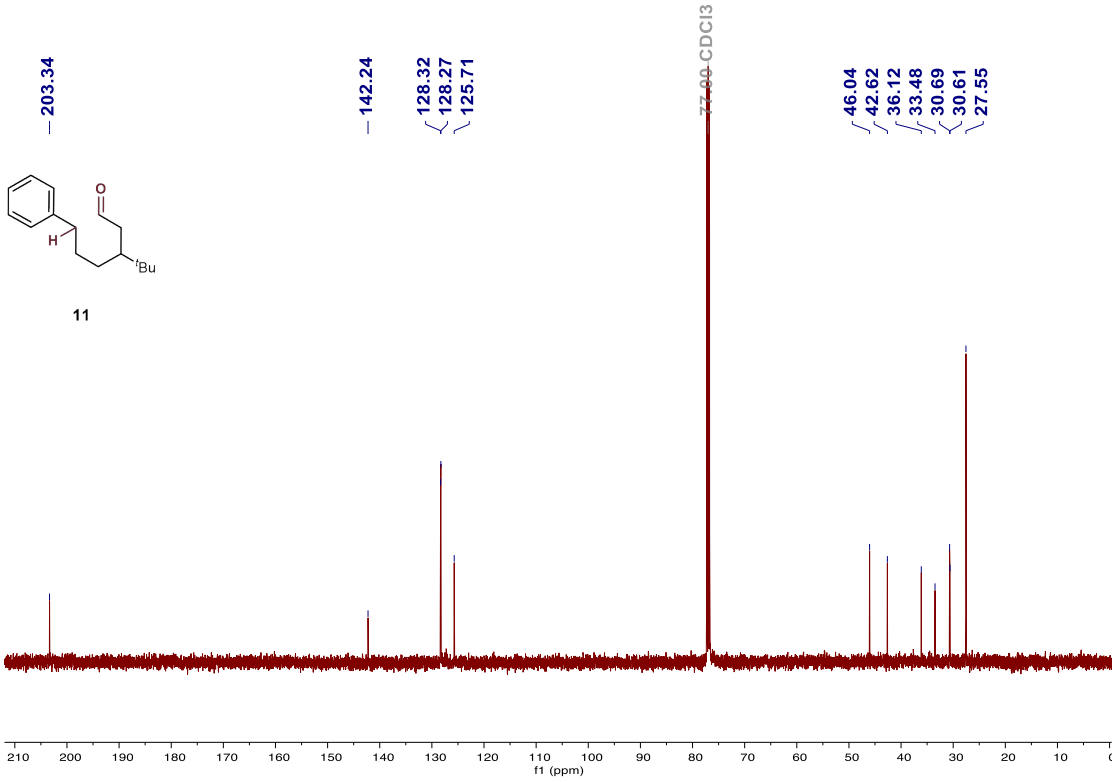
^{13}C NMR (100 MHz, $CDCl_3$)



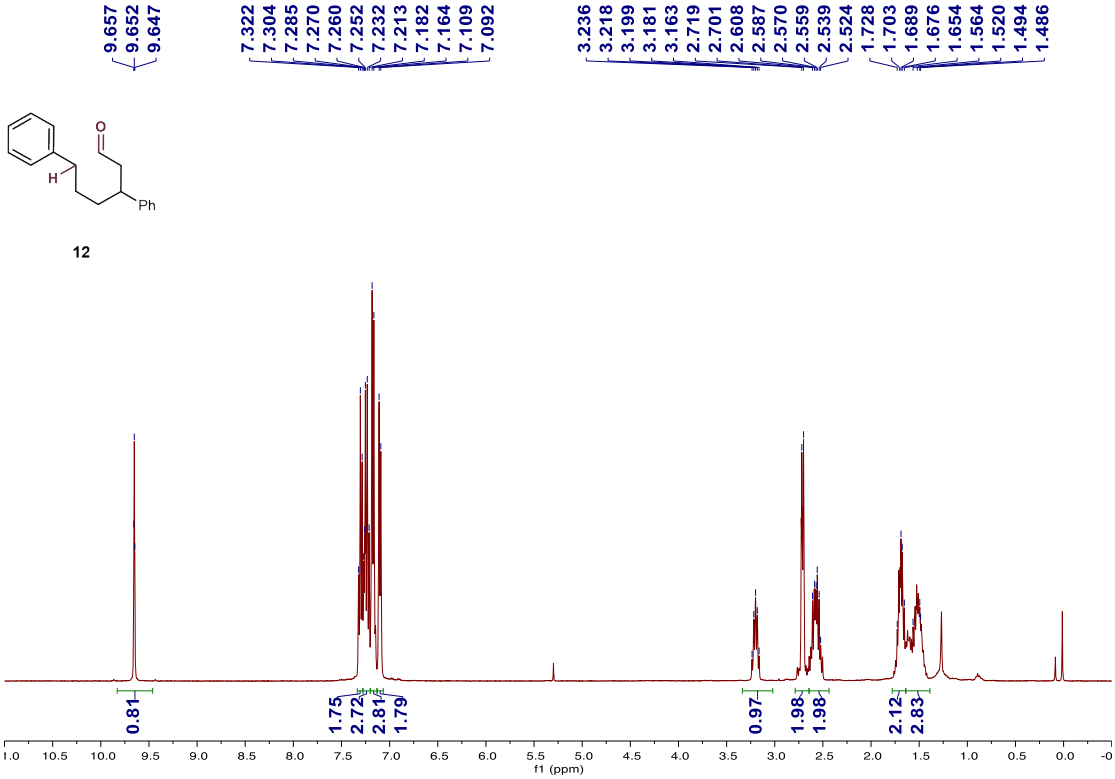
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

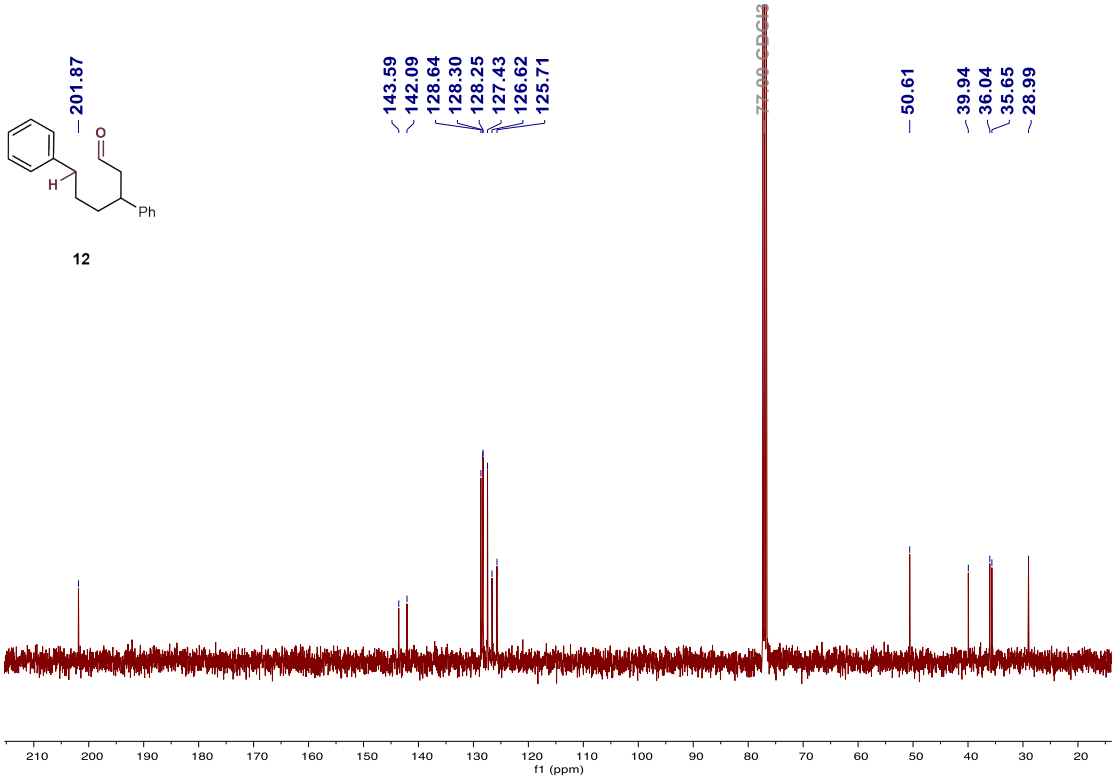


^{1}H NMR (400 MHz, $CDCl_3$)



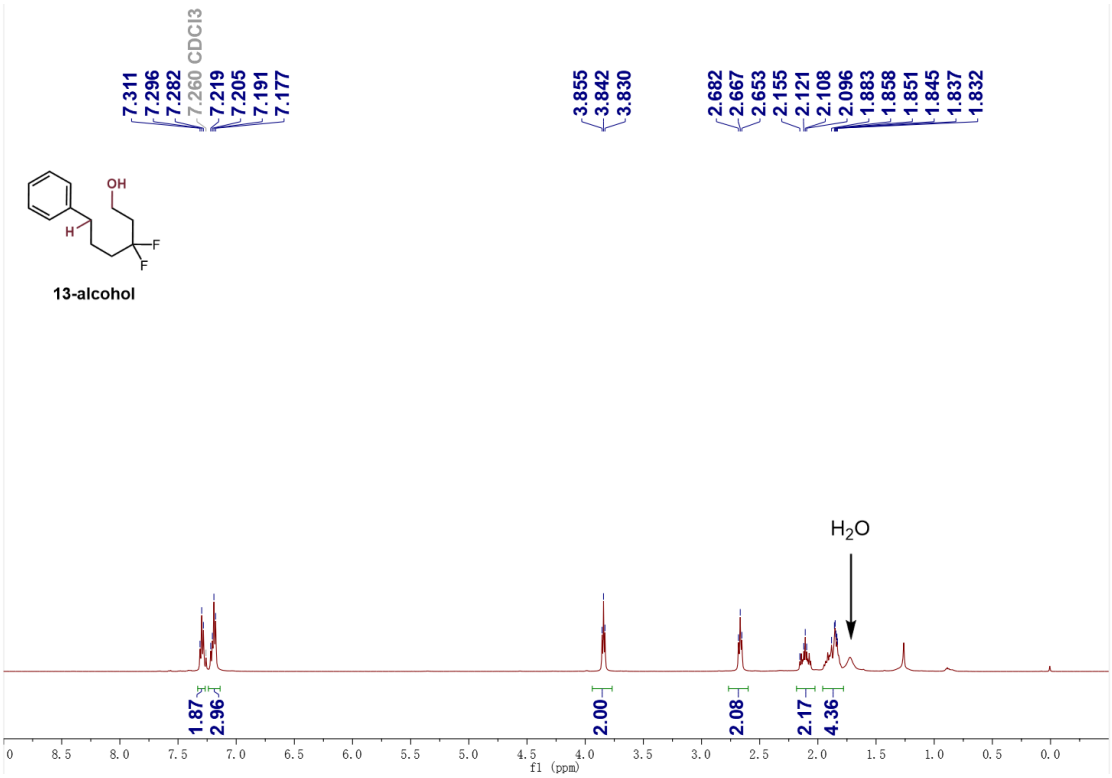
12

^{13}C NMR (100 MHz, $CDCl_3$)

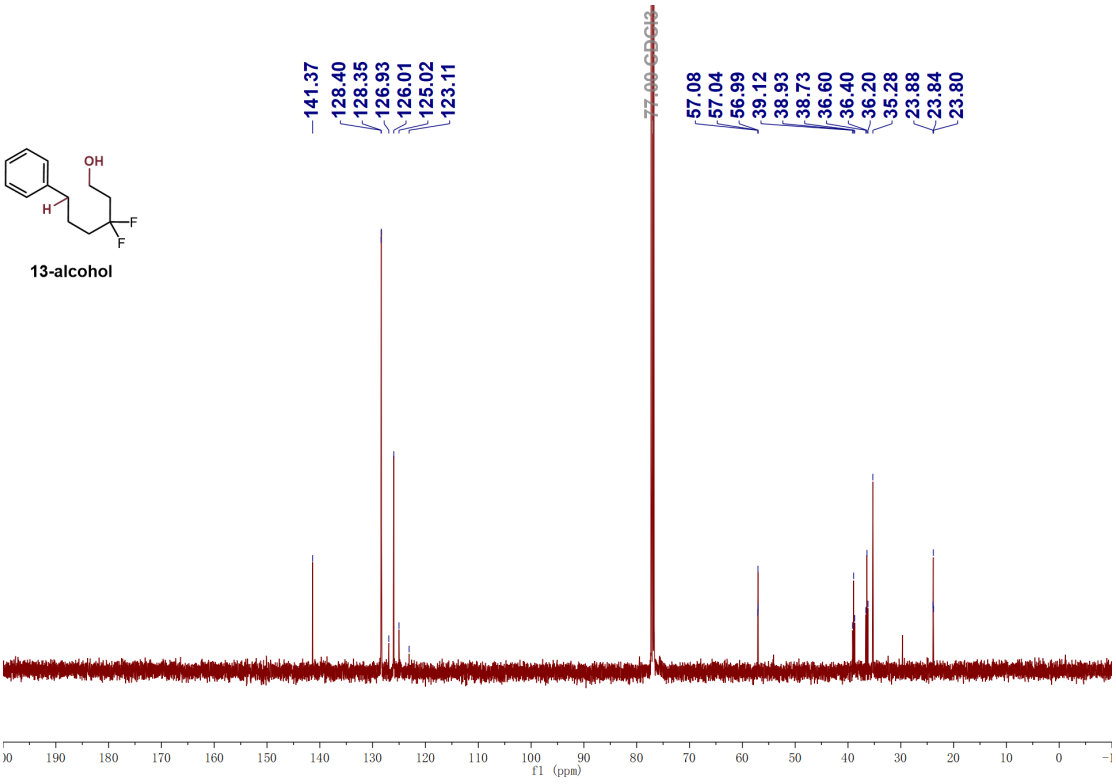


12

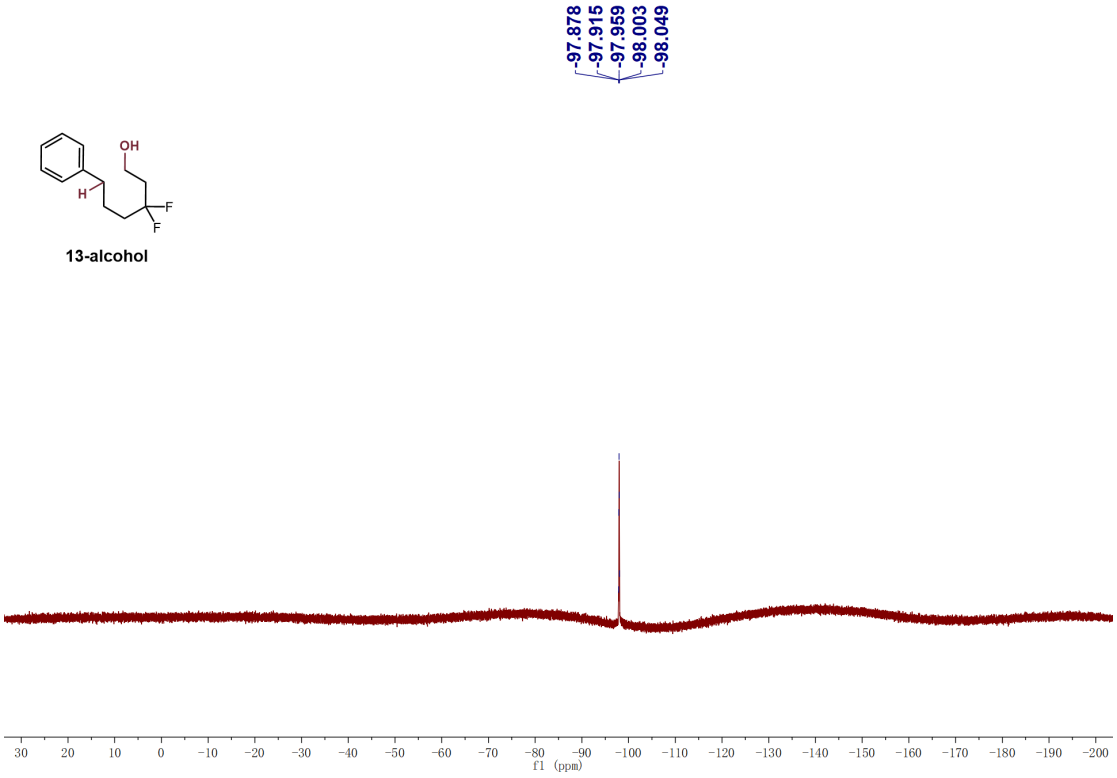
^{1}H NMR (400 MHz, $CDCl_3$)



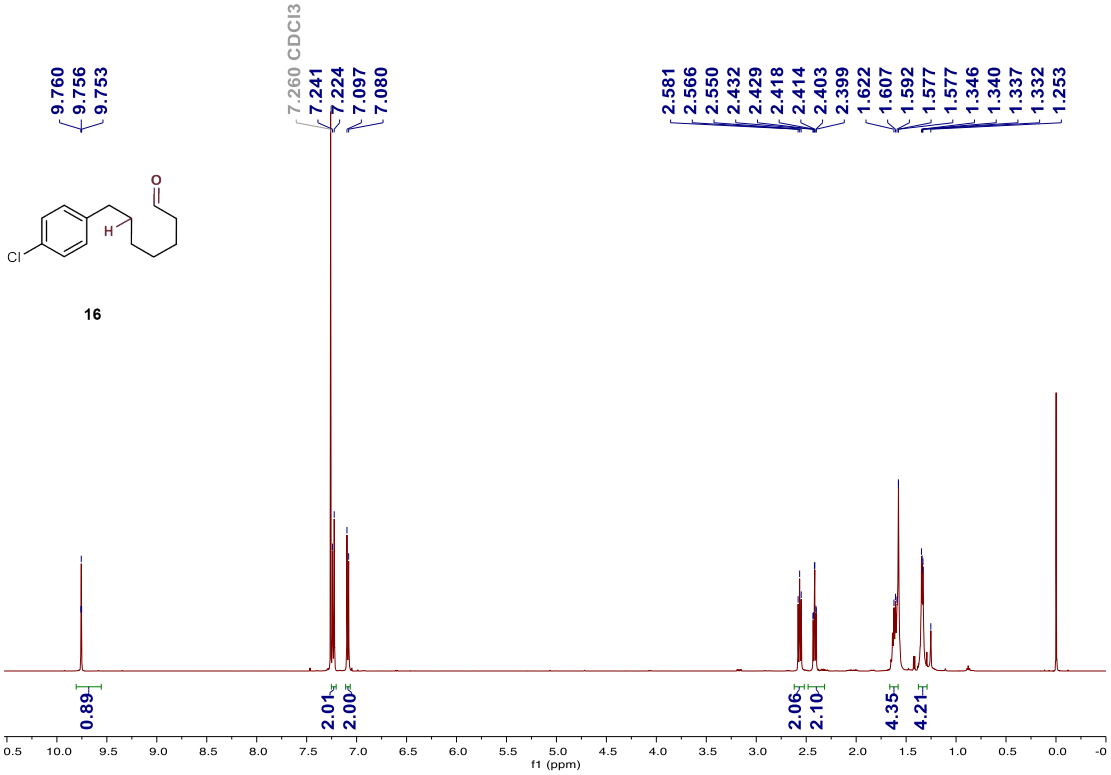
^{13}C NMR (125 MHz, $CDCl_3$)



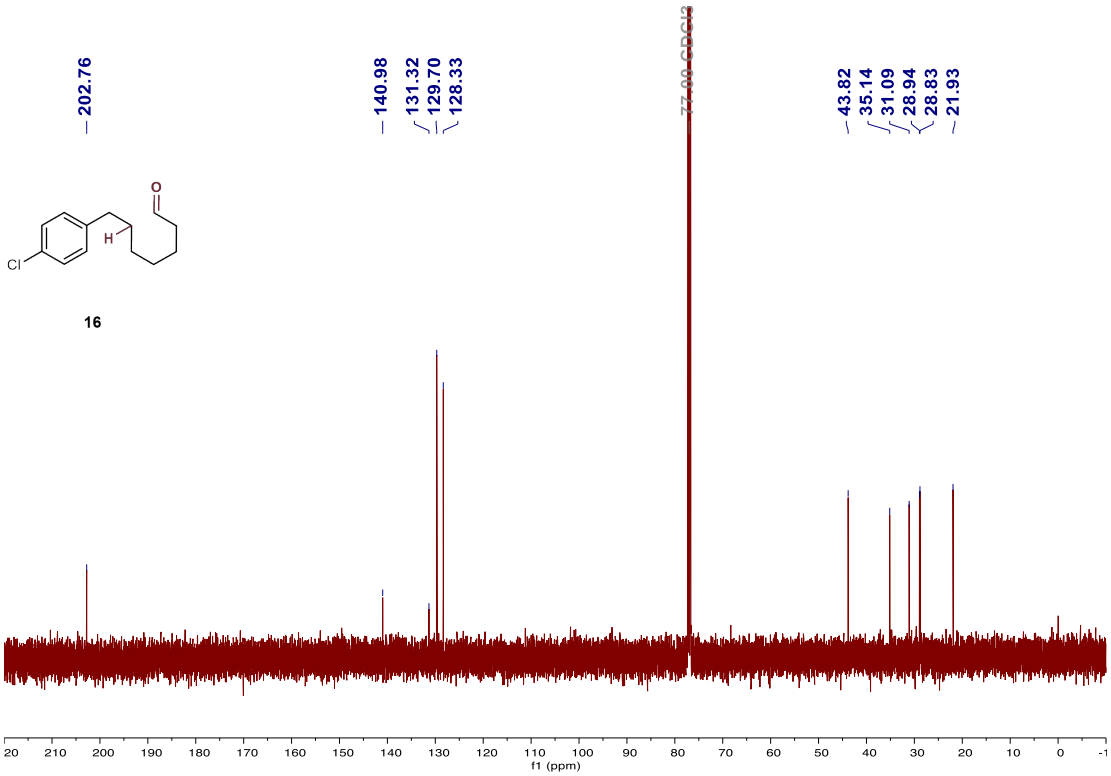
^{19}F NMR (376 MHz, $CDCl_3$)



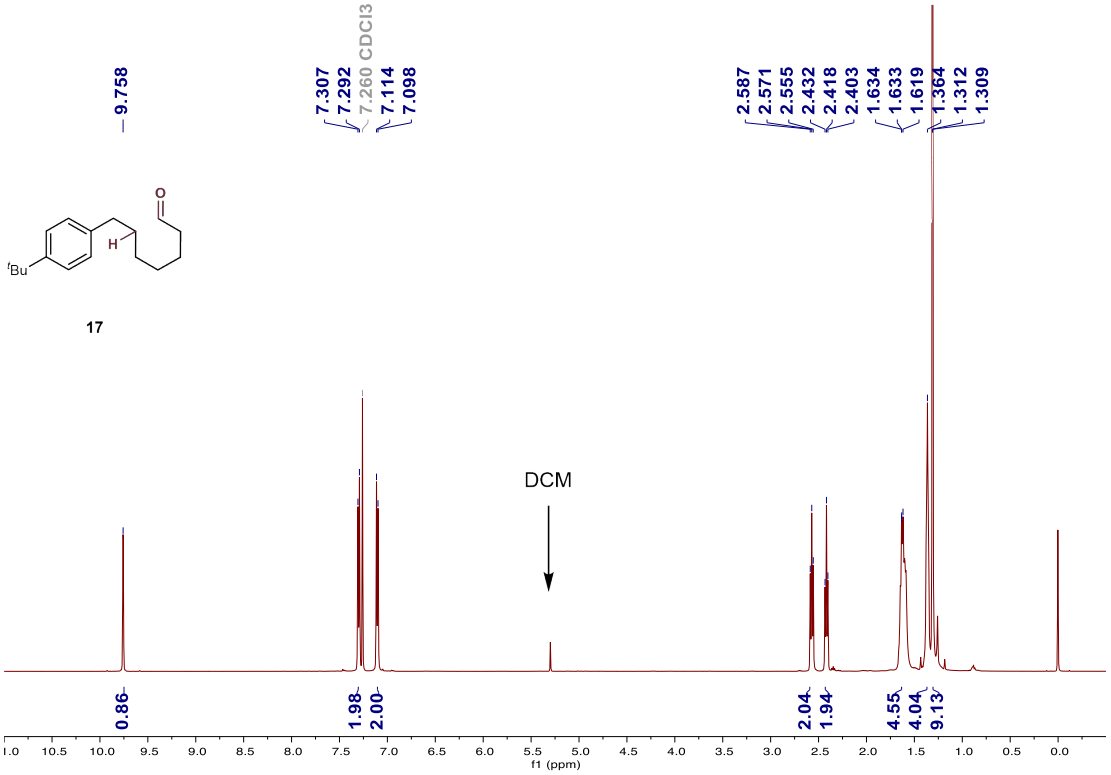
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

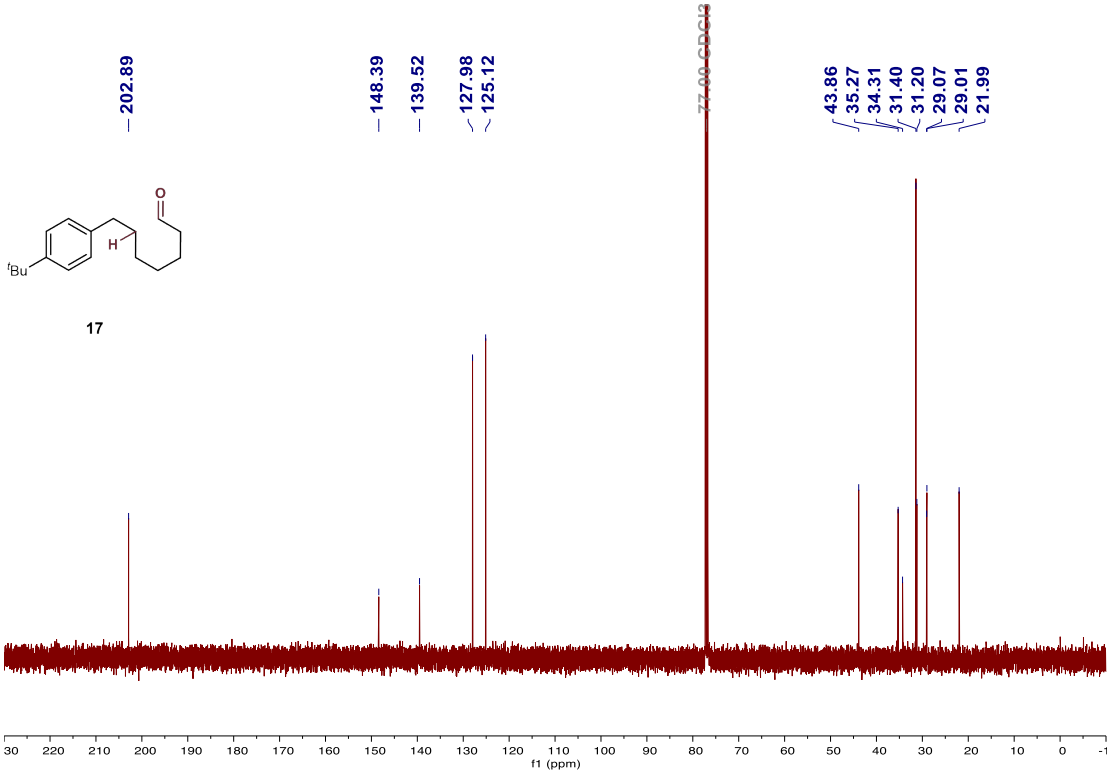


^{1}H NMR (500 MHz, $CDCl_3$)



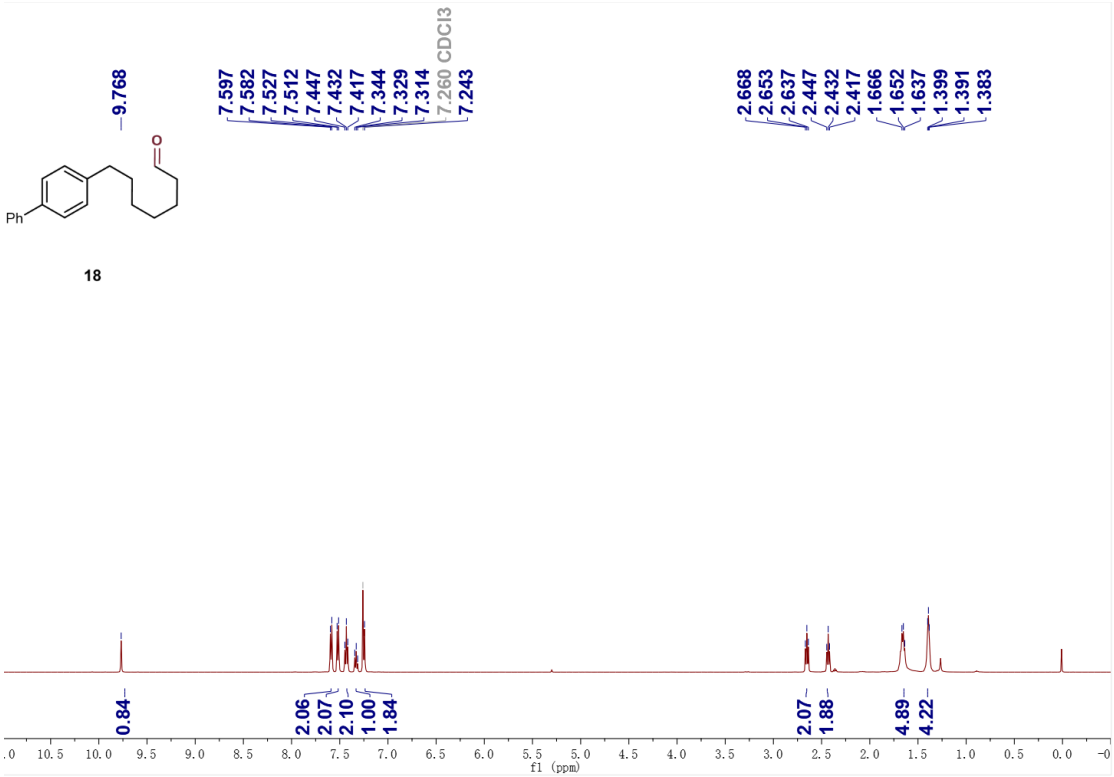
17

^{13}C NMR (125 MHz, $CDCl_3$)

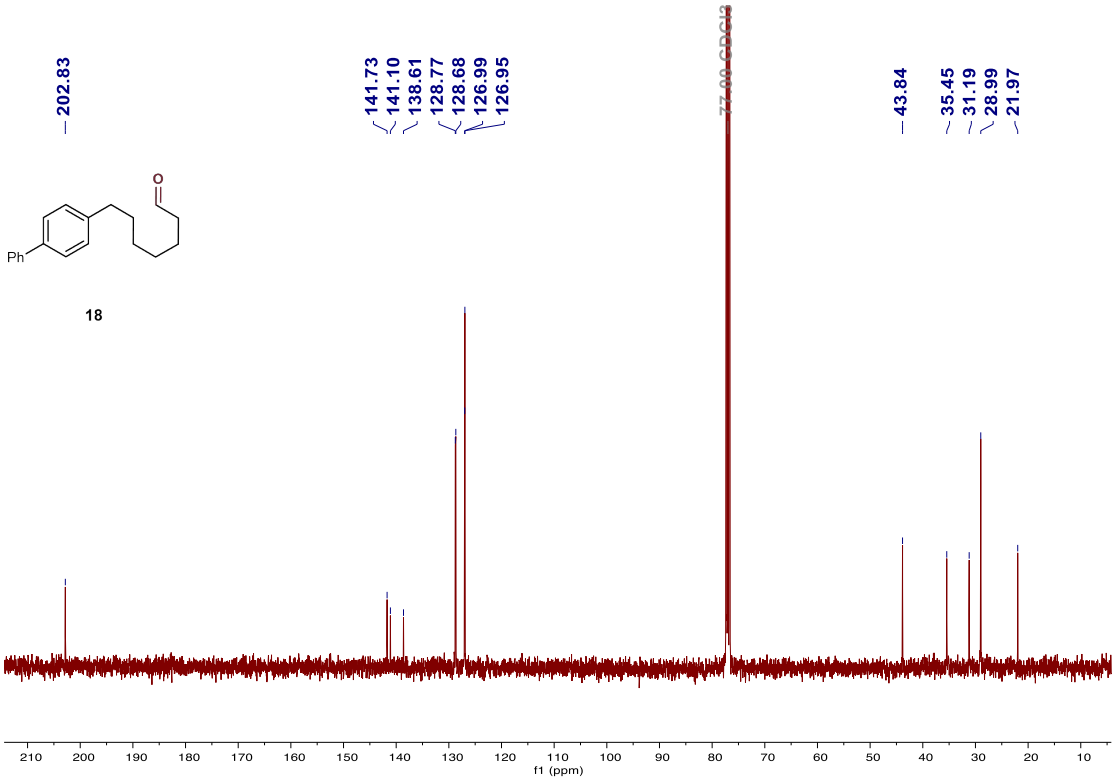


17

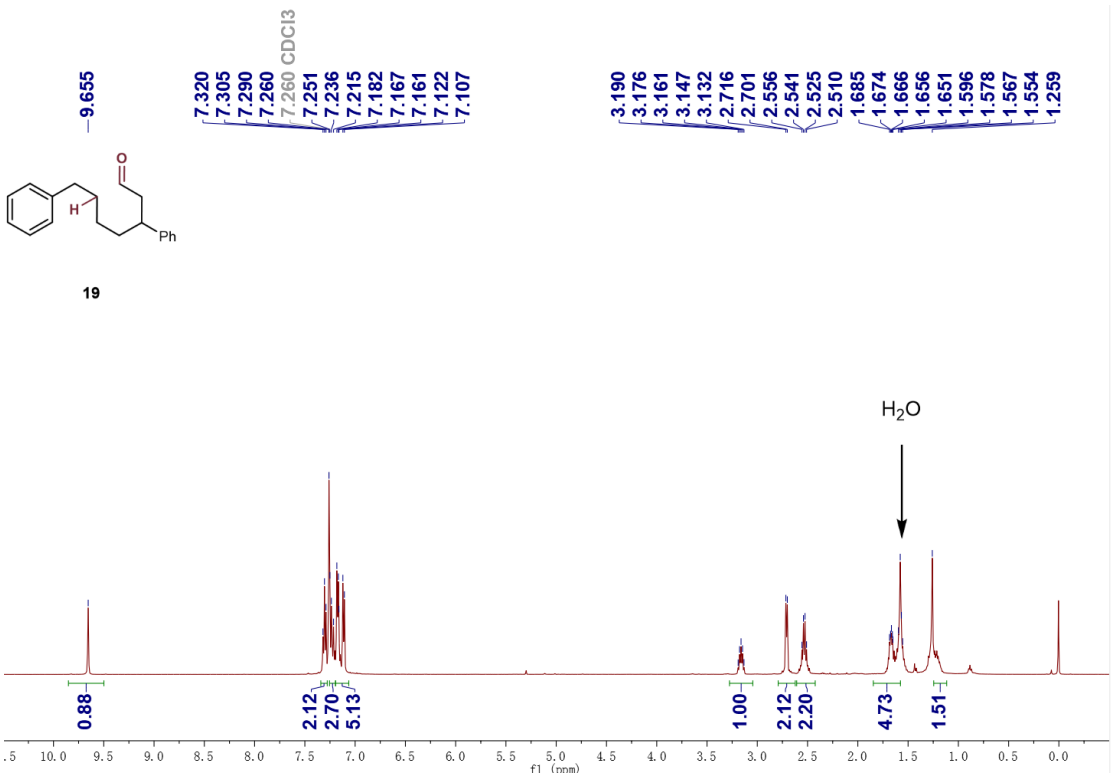
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

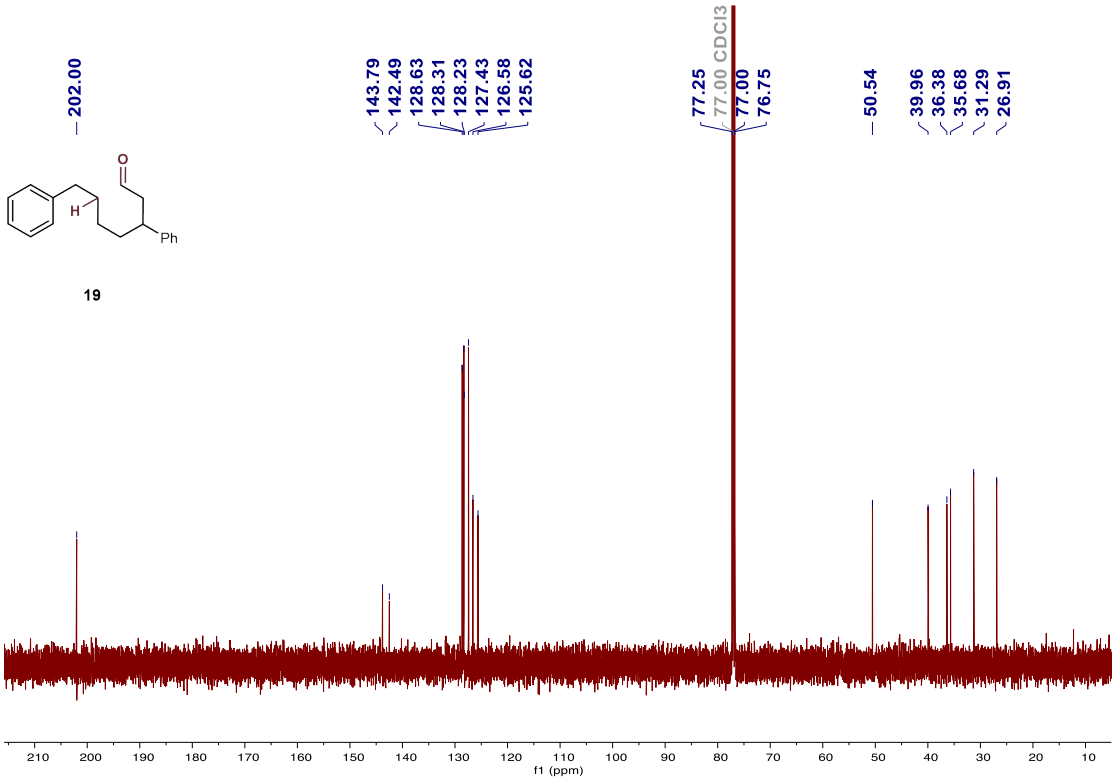


^{1}H NMR (500 MHz, $CDCl_3$)



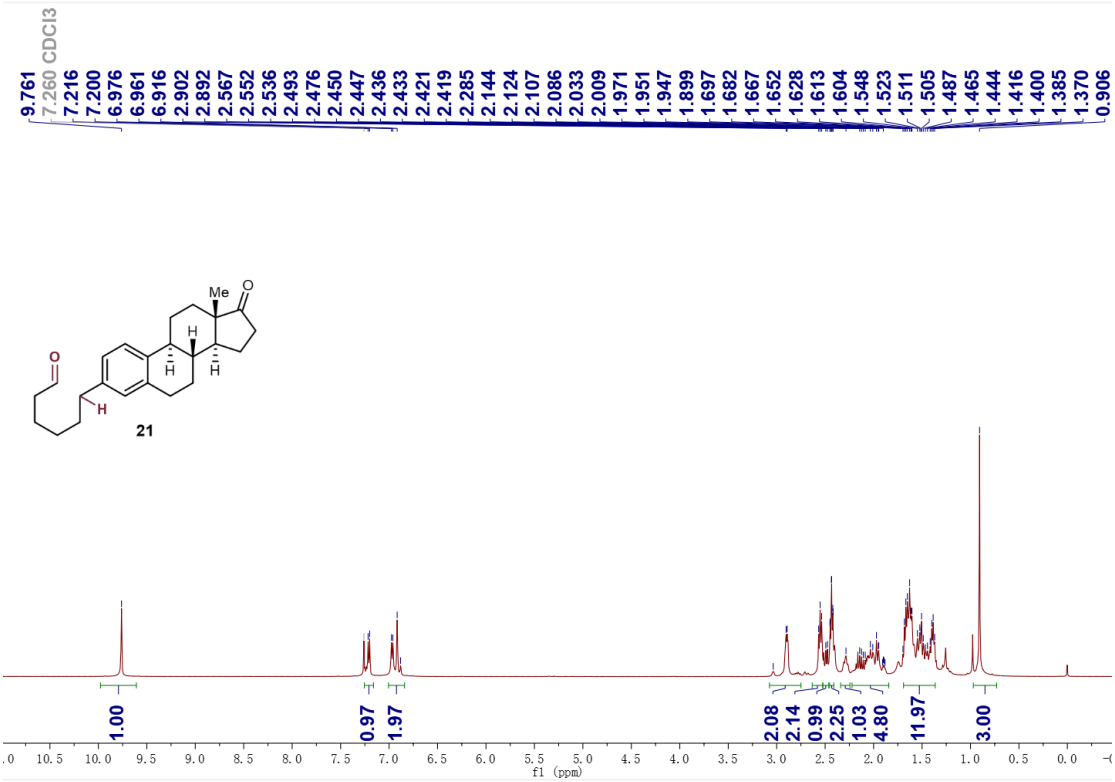
19

^{13}C NMR (100 MHz, $CDCl_3$)

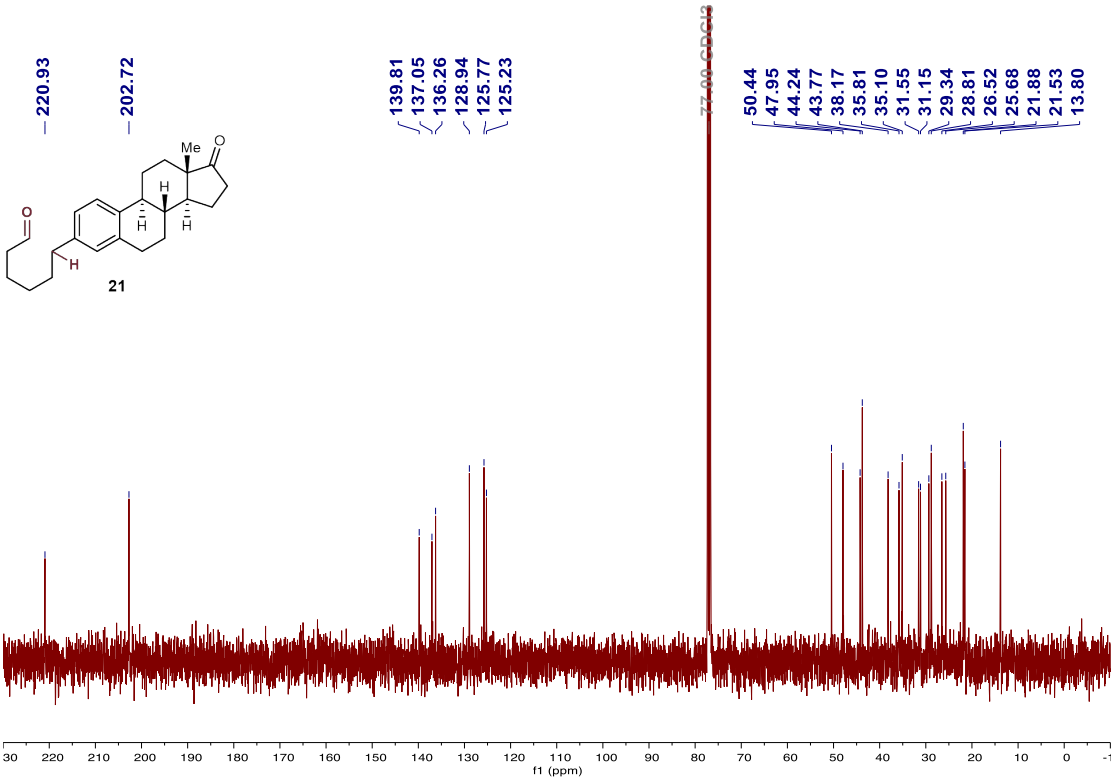


19

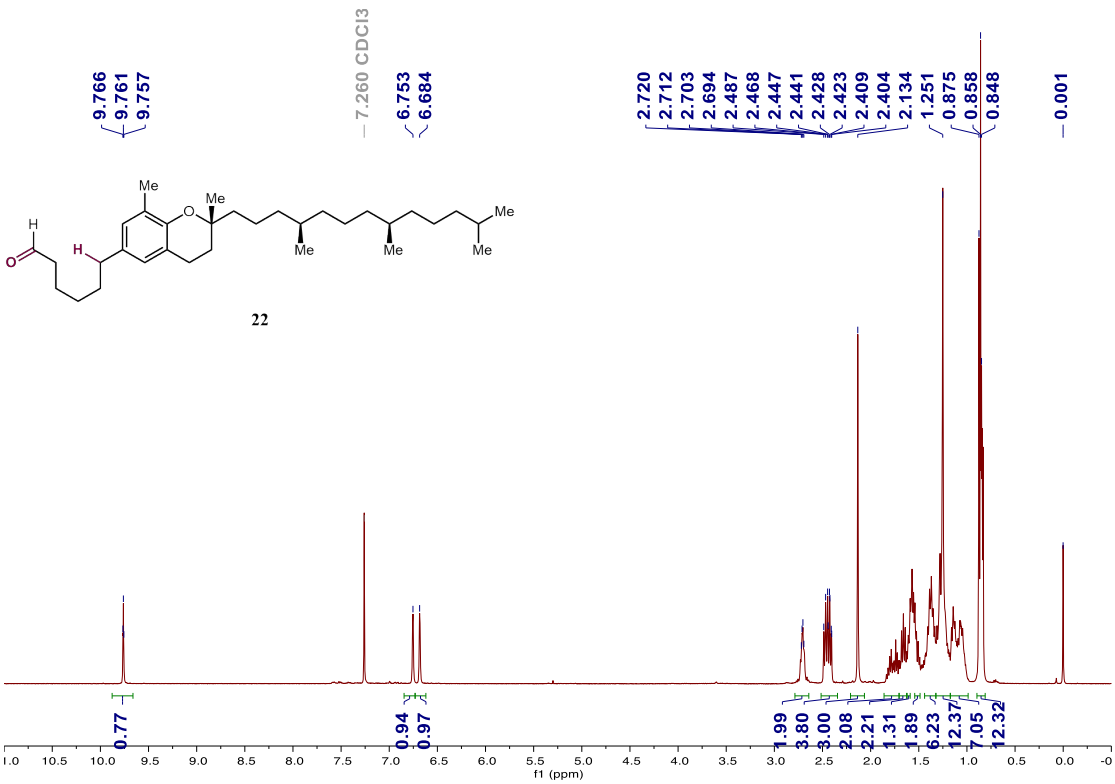
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

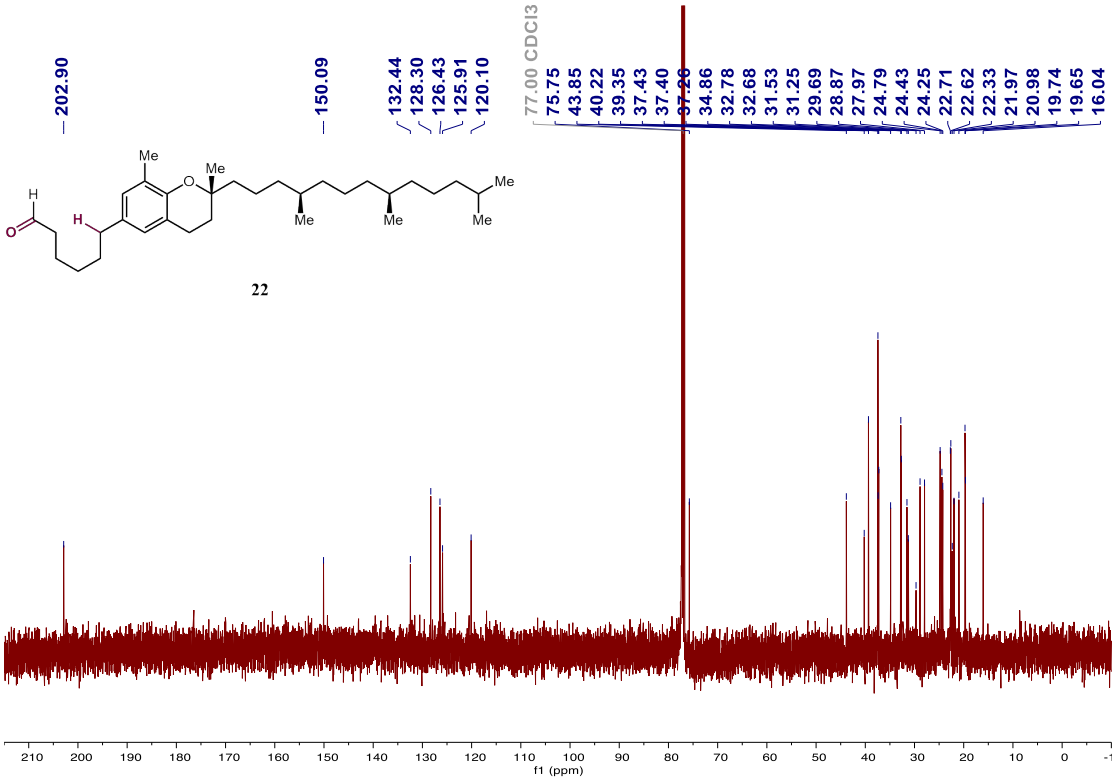


^{1}H NMR (400 MHz, $CDCl_3$)



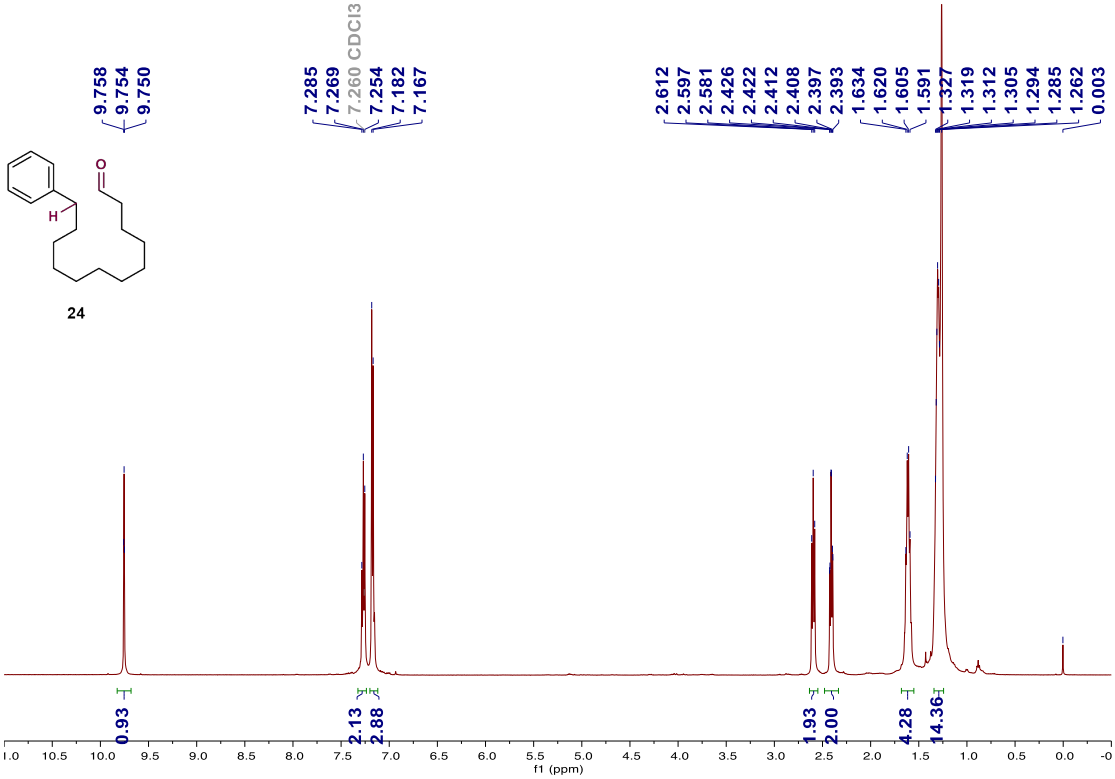
22

^{13}C NMR (100 MHz, $CDCl_3$)

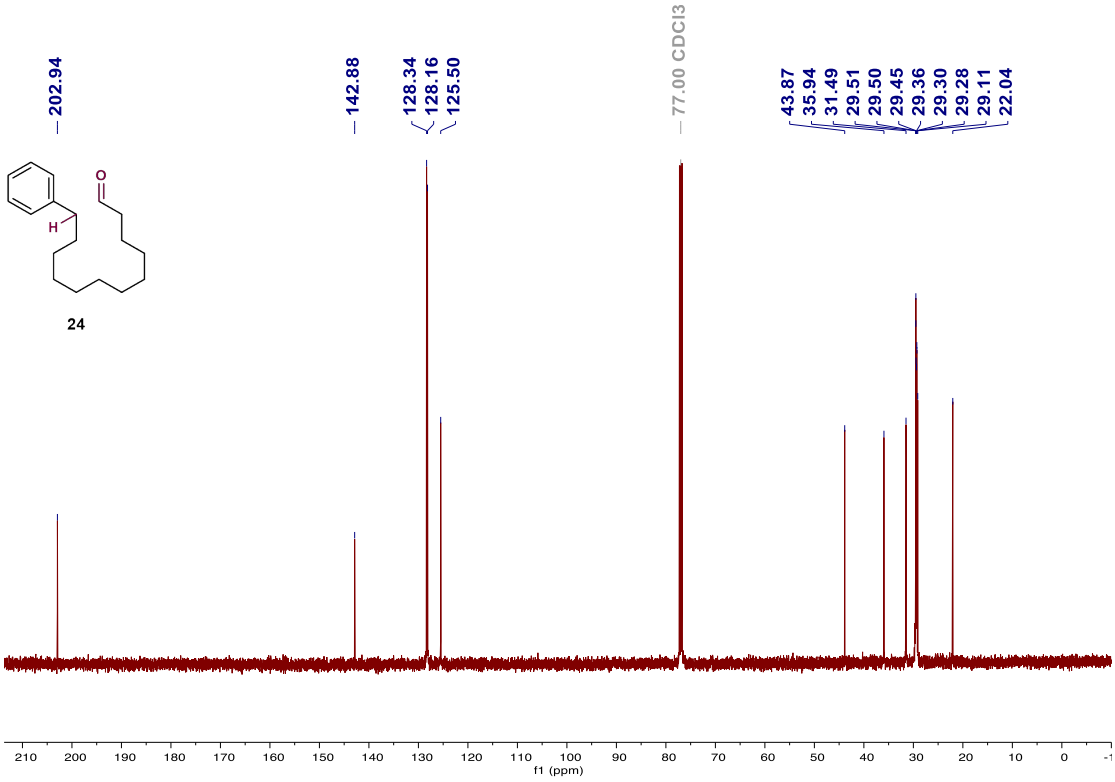


22

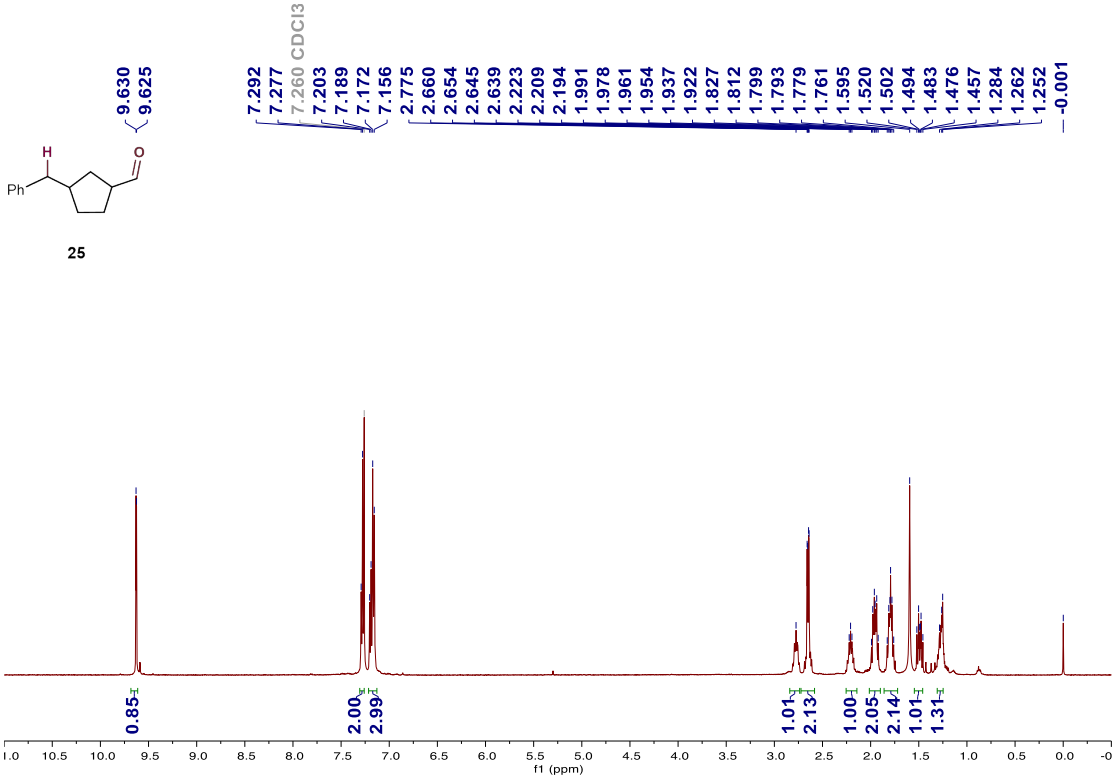
^{1}H NMR (400 MHz, $CDCl_3$)



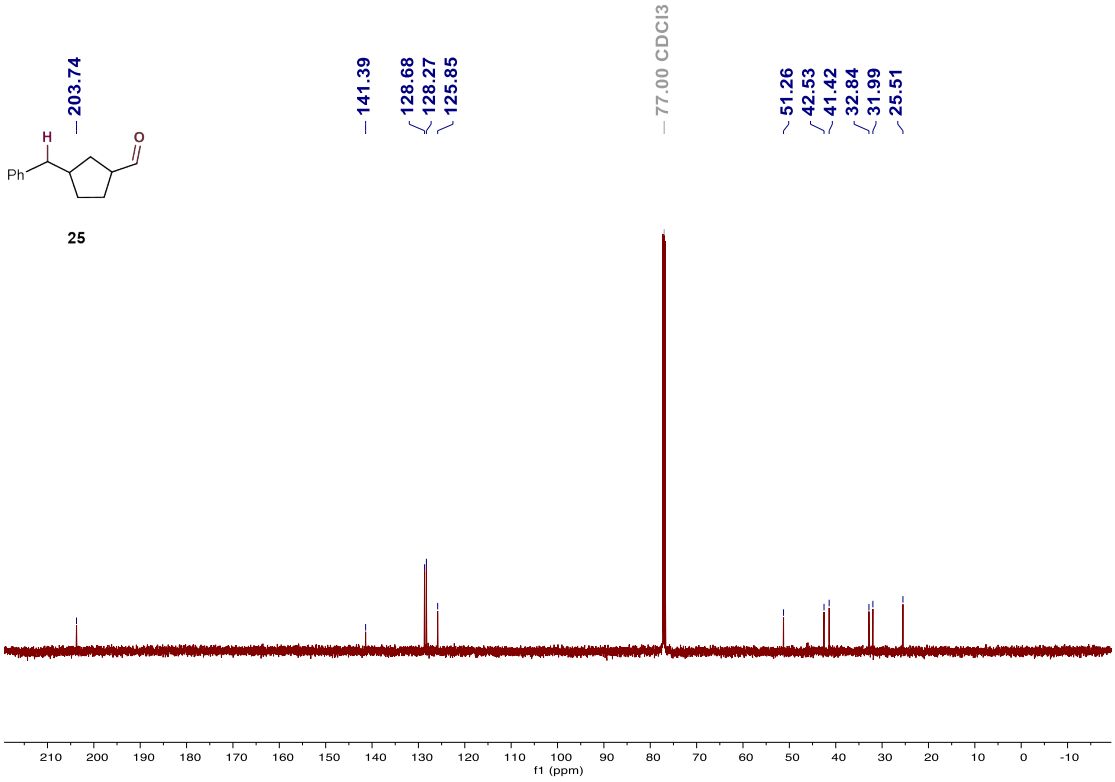
^{13}C NMR (100 MHz, $CDCl_3$)



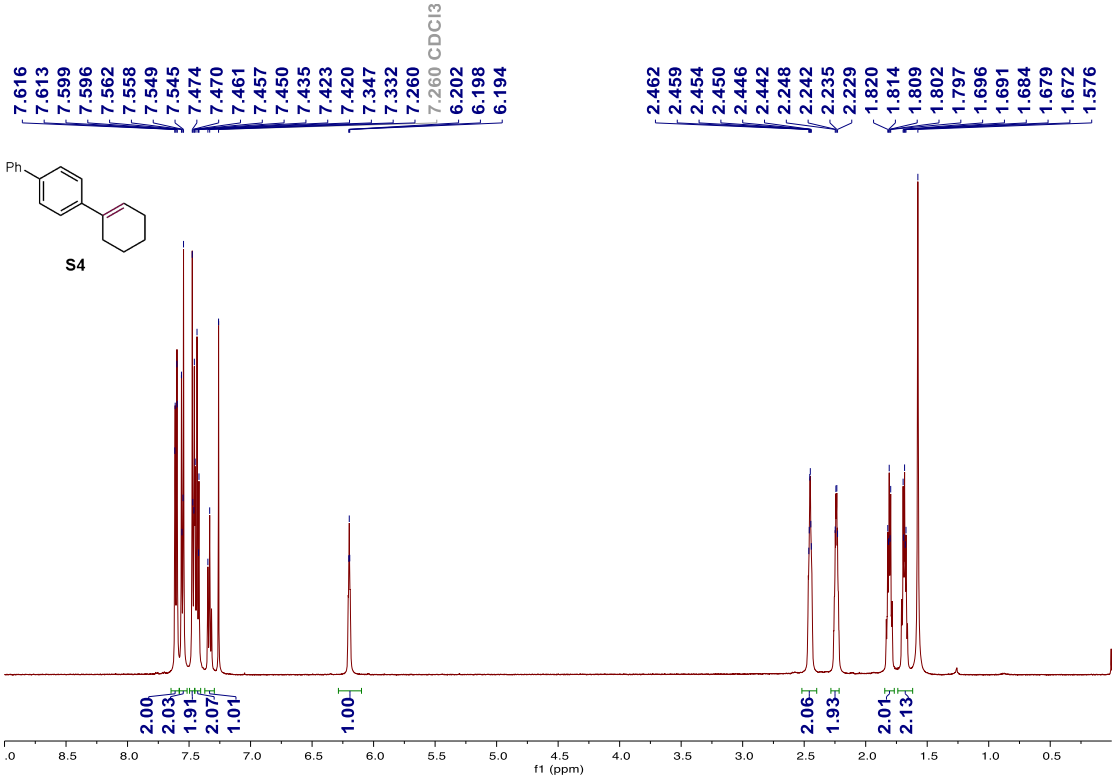
^{1}H NMR (400 MHz, $CDCl_3$)



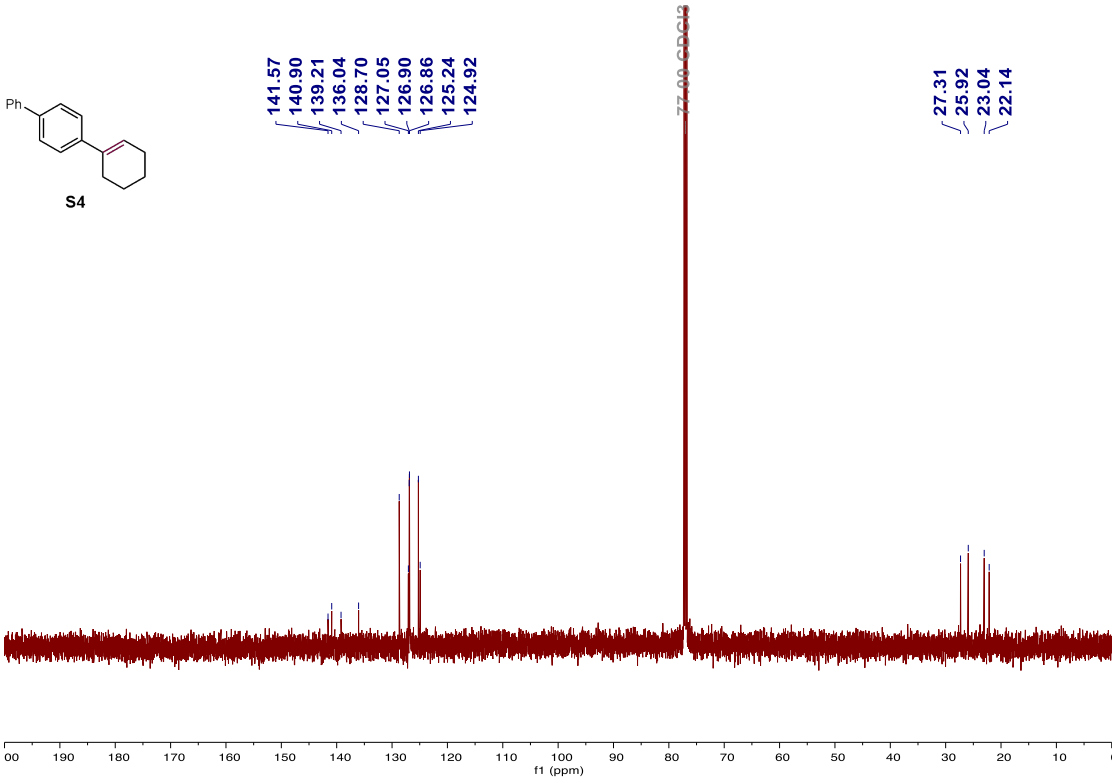
^{13}C NMR (100 MHz, $CDCl_3$)



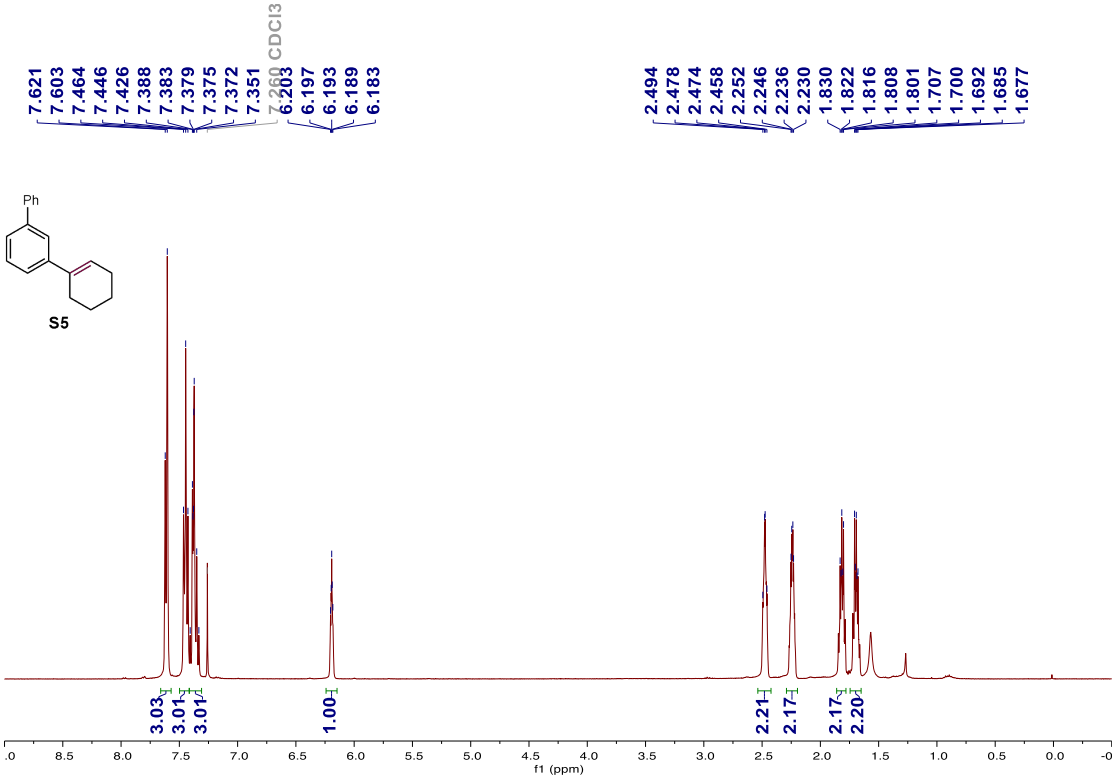
^{1}H NMR (500 MHz, $CDCl_3$)



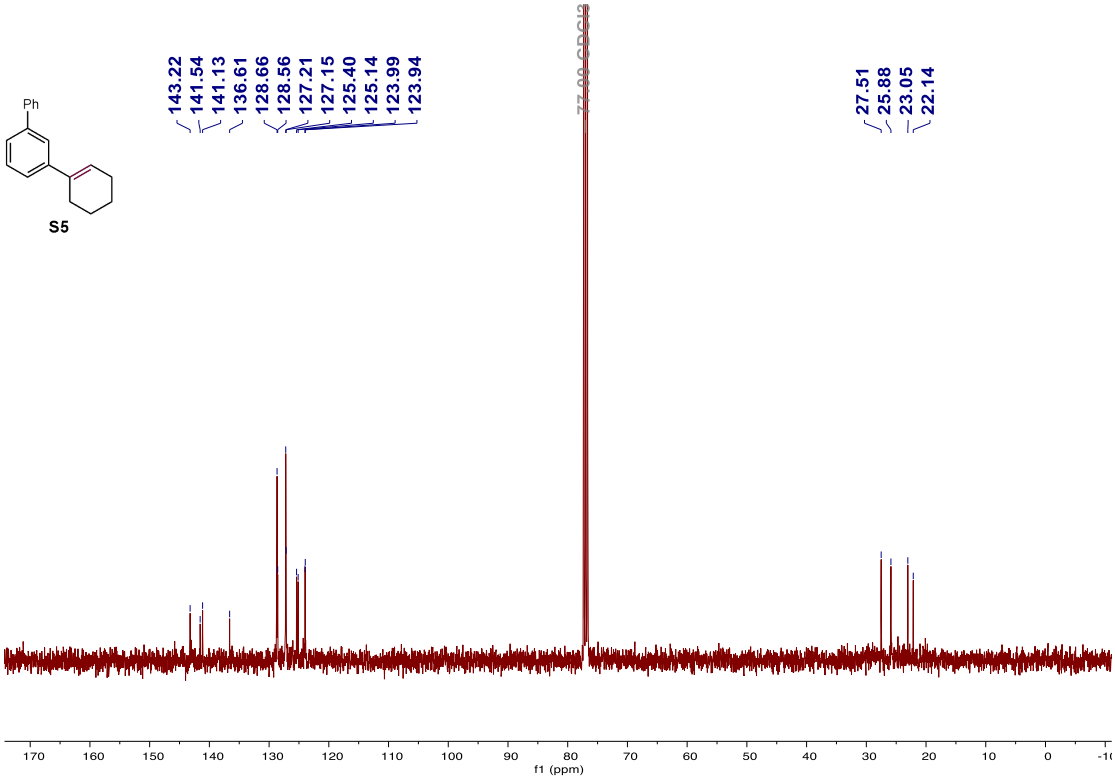
^{13}C NMR (125 MHz, $CDCl_3$)



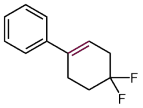
^{1}H NMR (400 MHz, $CDCl_3$)



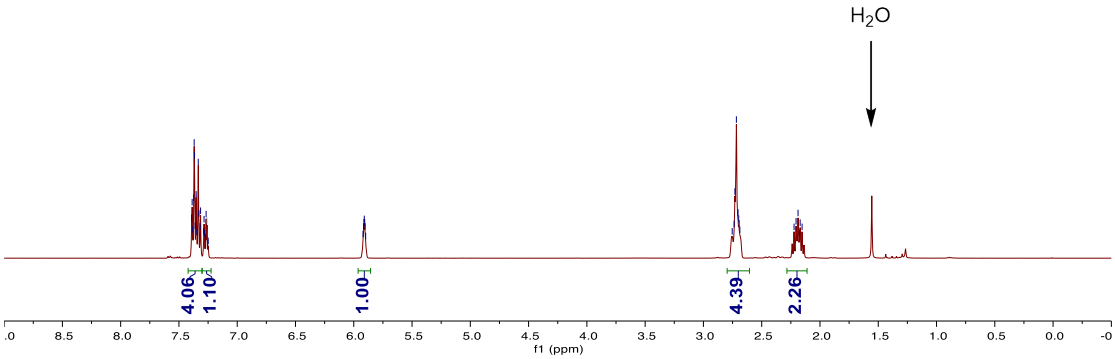
^{13}C NMR (100 MHz, $CDCl_3$)



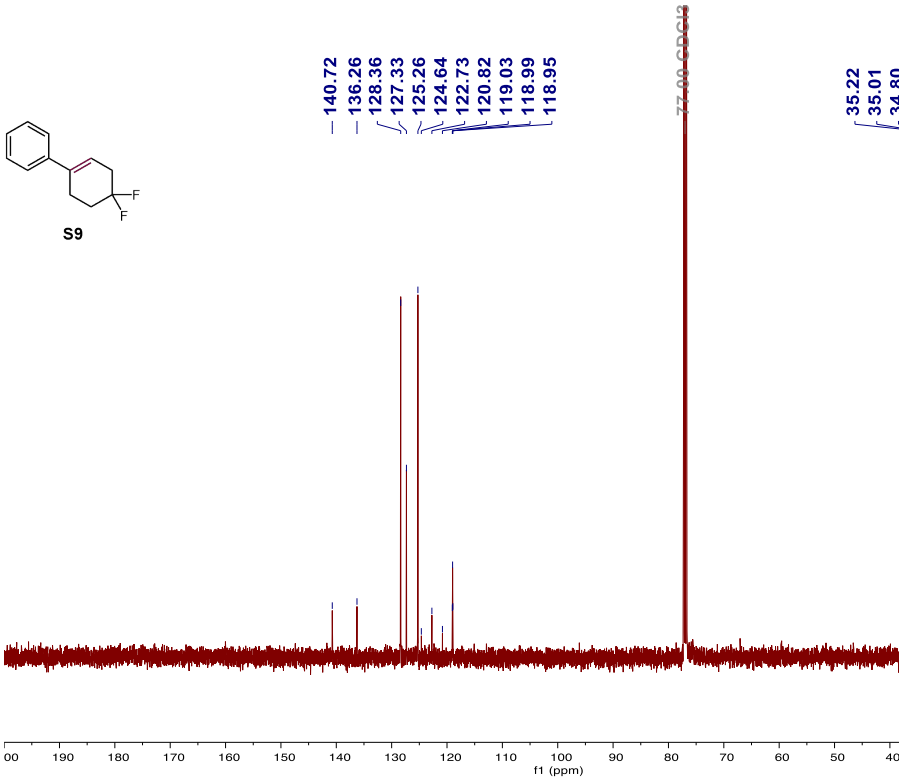
^{1}H NMR (400 MHz, $CDCl_3$)



S9

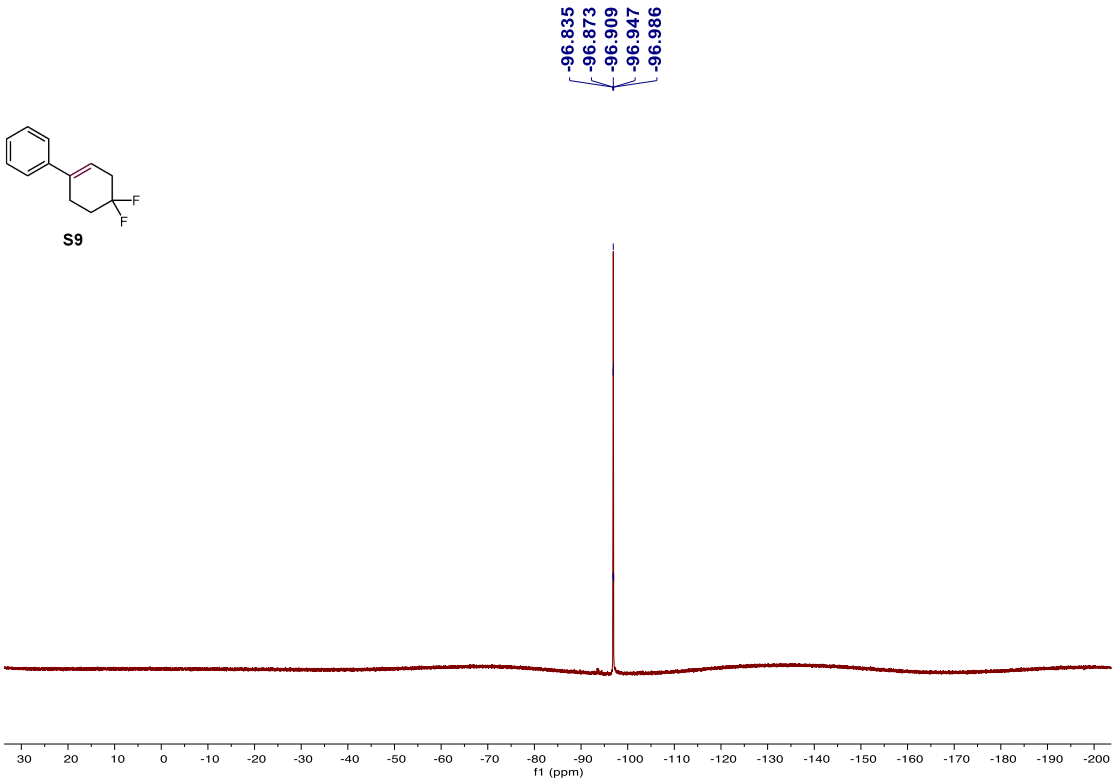


^{13}C NMR (100 MHz, $CDCl_3$)

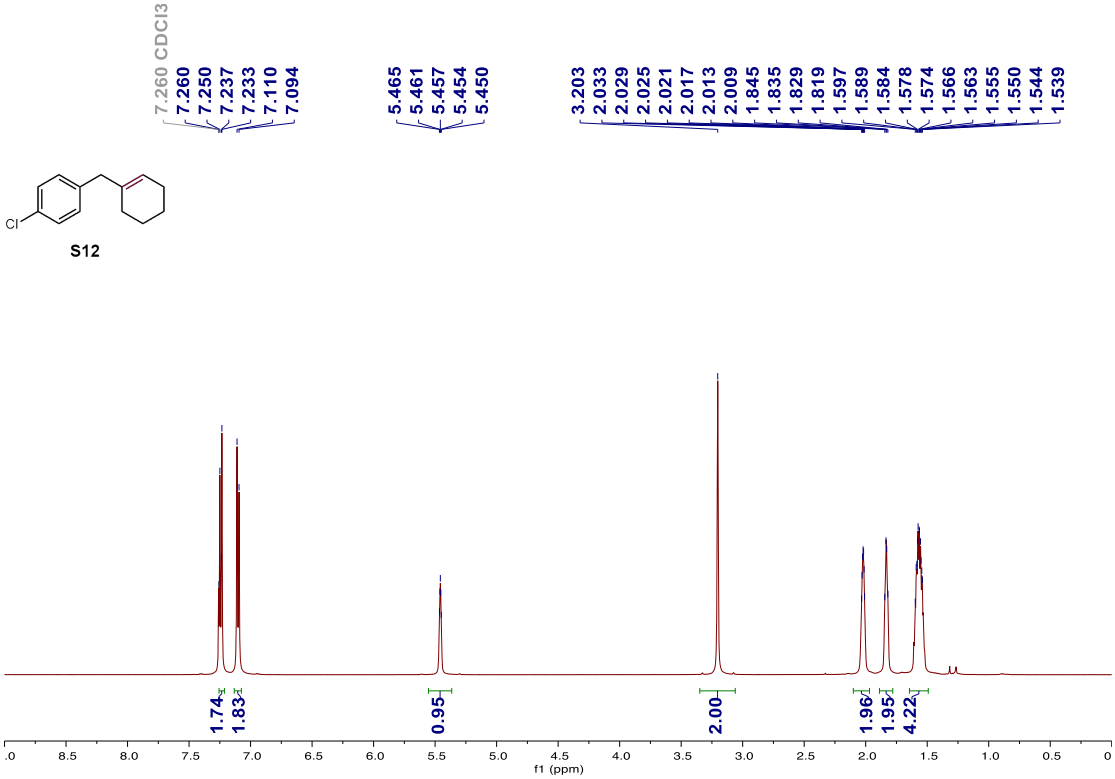


S9

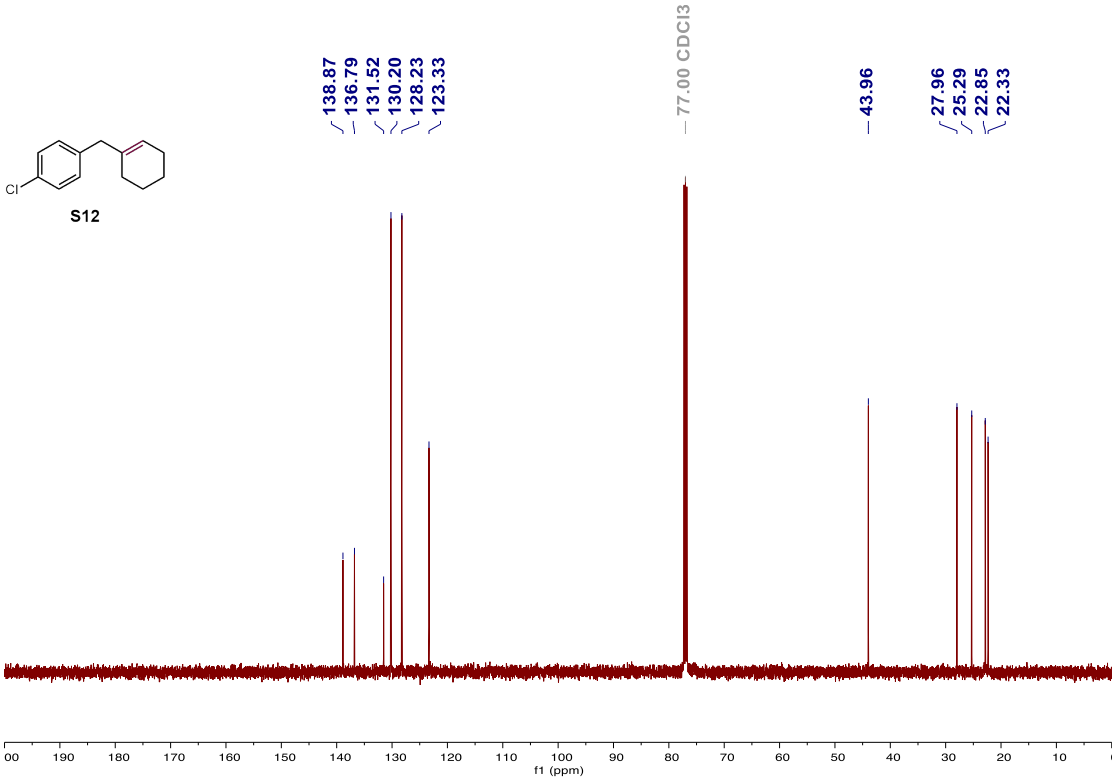
^{19}F NMR (376 MHz, $CDCl_3$)



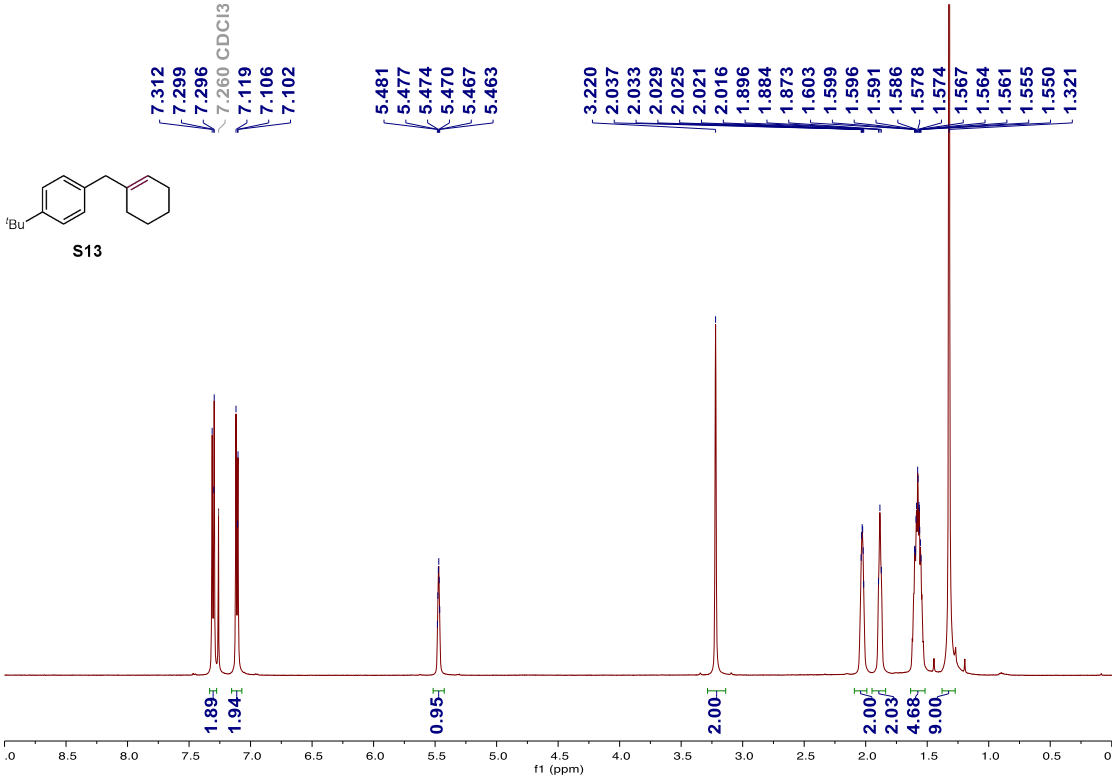
^{1}H NMR (500 MHz, $CDCl_3$)



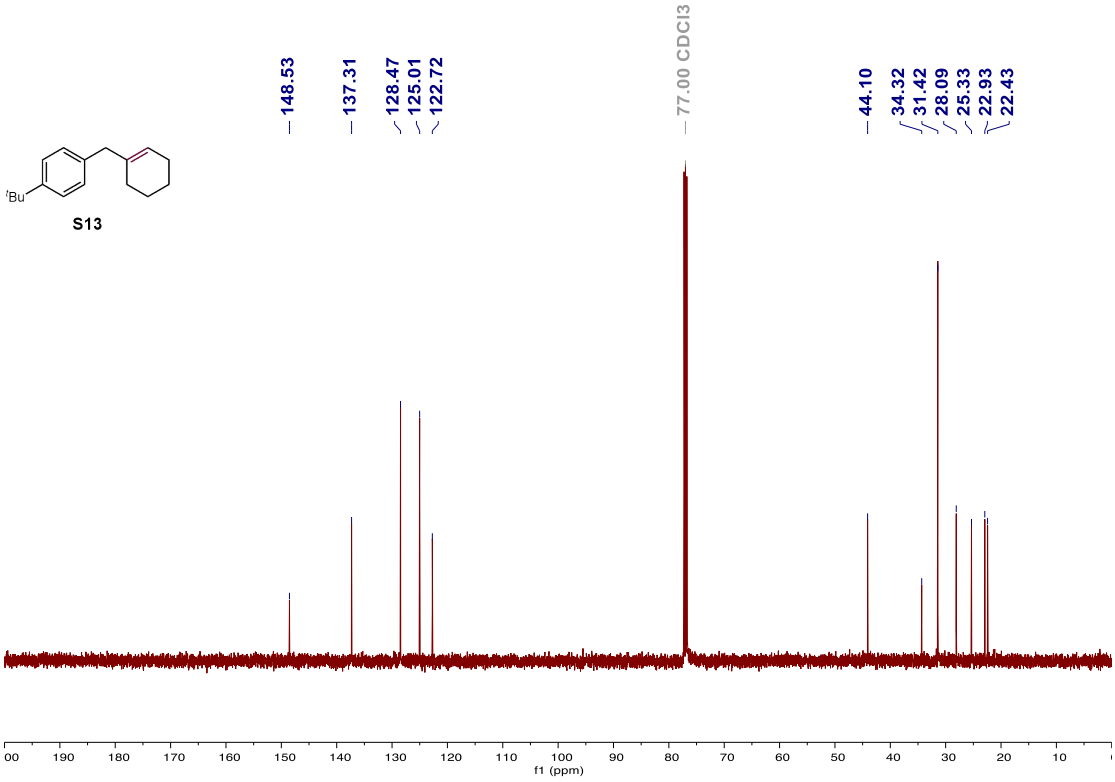
^{13}C NMR (125 MHz, $CDCl_3$)



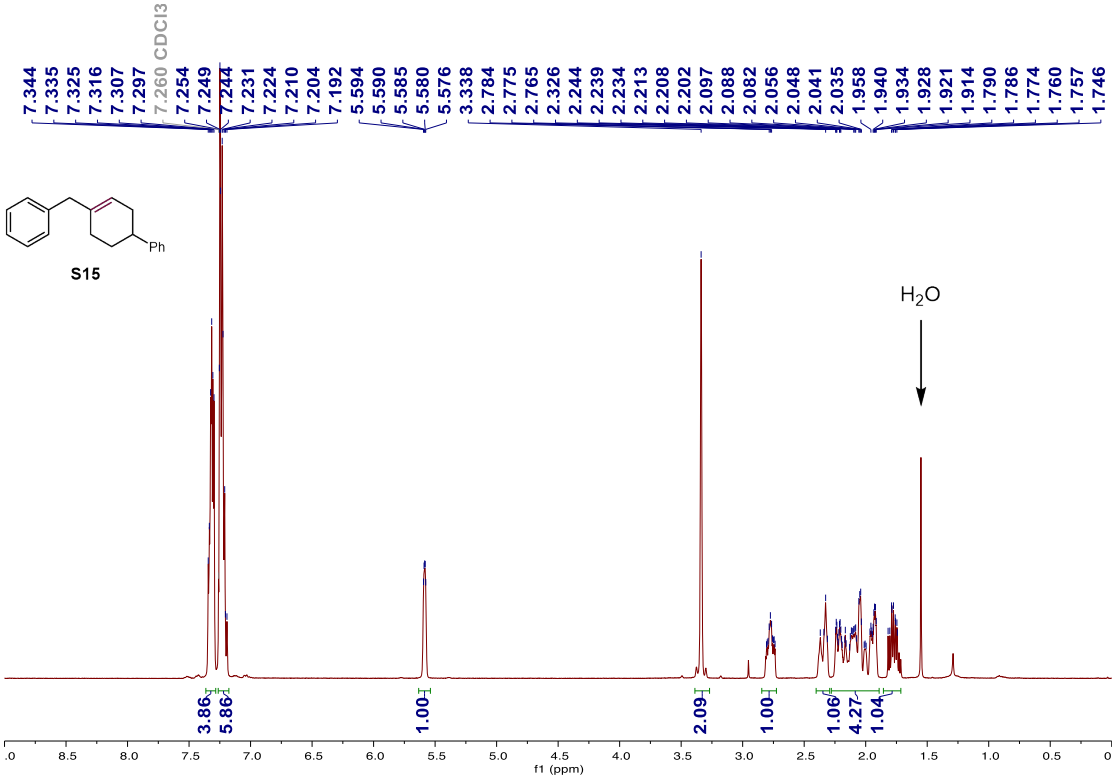
^{1}H NMR (500 MHz, $CDCl_3$)



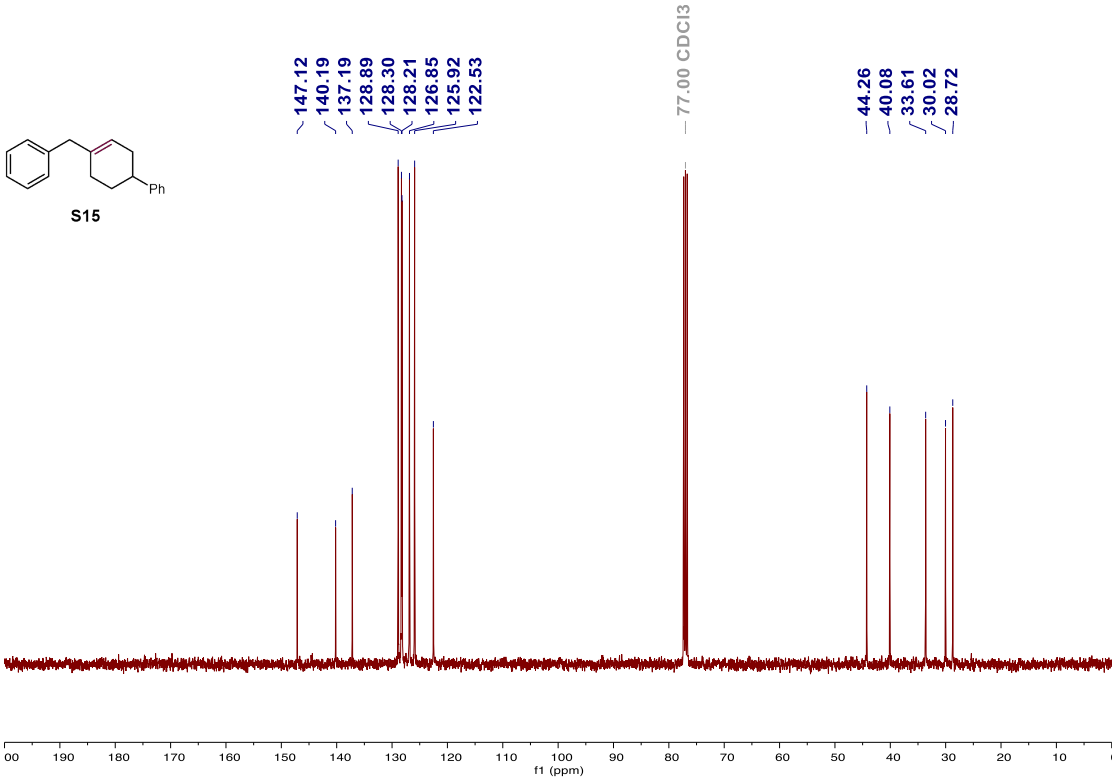
^{13}C NMR (125 MHz, $CDCl_3$)



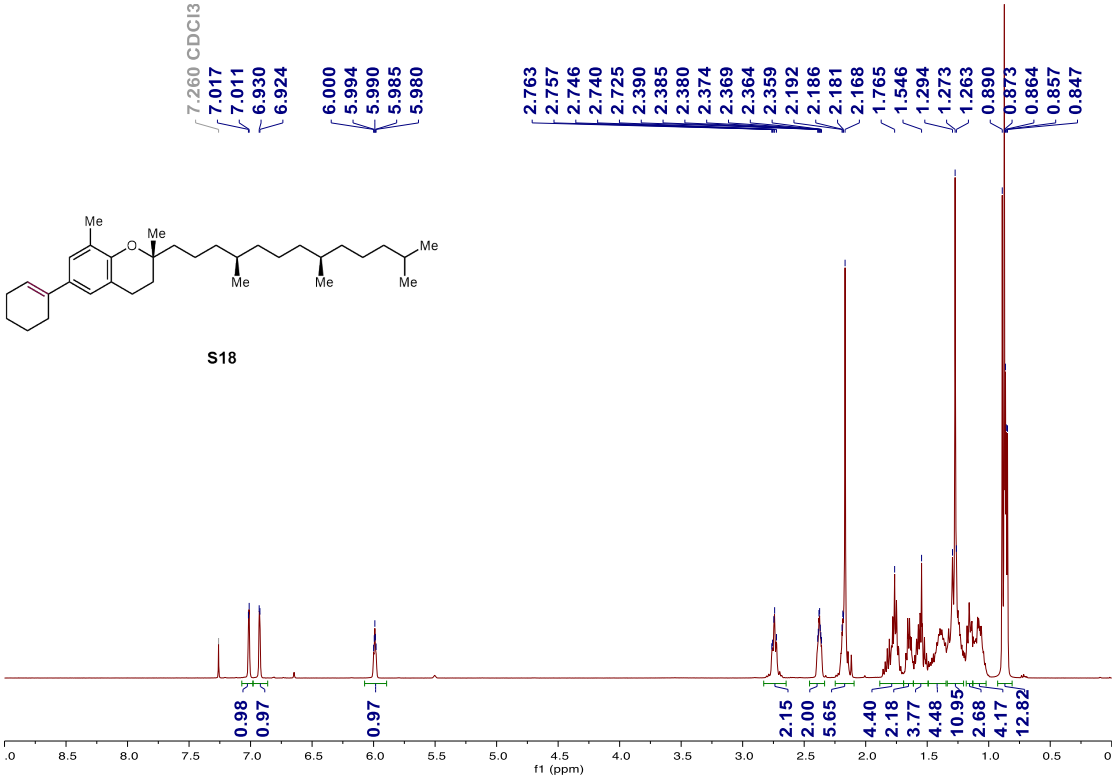
^{1}H NMR (400 MHz, $CDCl_3$)



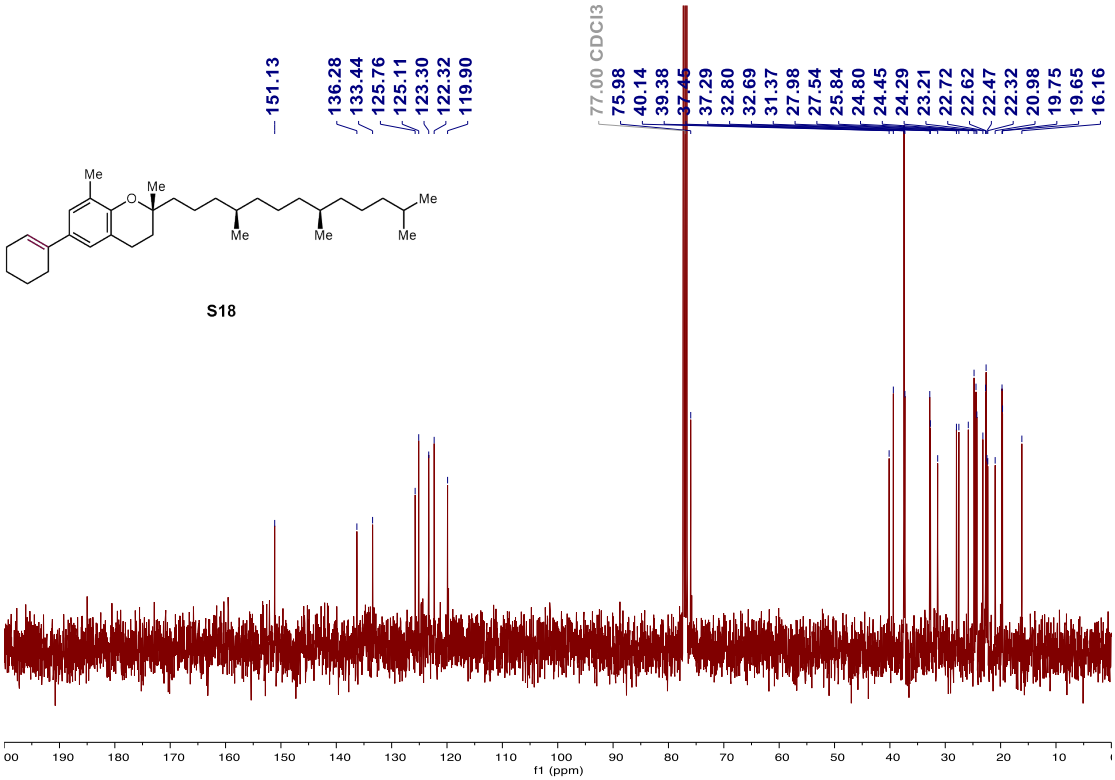
^{13}C NMR (100 MHz, $CDCl_3$)



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



^{13}C NMR (100 MHz, $CDCl_3$)



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