Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Rhodium-Catalyzed Isomerization of Homoallylic Alcohols with a Tethered Carbonyl Group: Pathway to 1,6-Diketones

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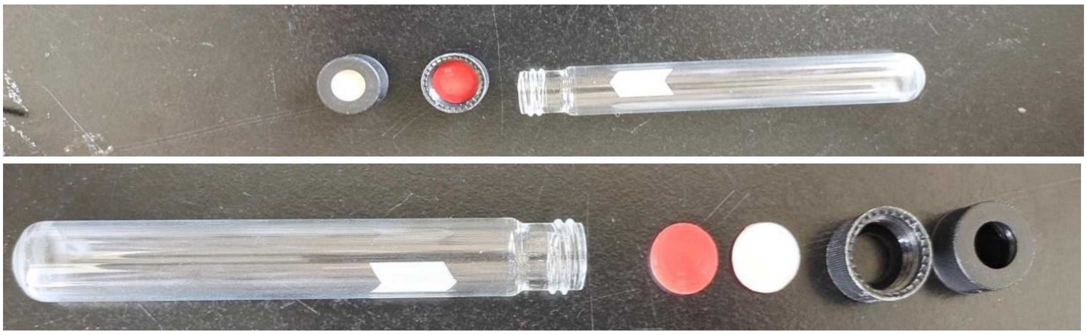
I. General Information

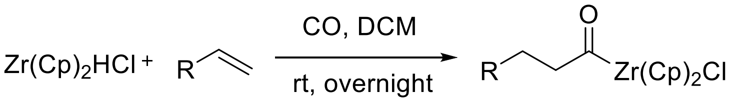
All solvents used in reactions were dried and distilled in appropriate method. Solvents employed for column chromatography were purchased in technical grade quality without distillation before using. The experimental reagent section uses $[Rh(cod)Cl]_2$, $[Rh(cod)_2]BF_4$, Cp_2ZrHCl, $Ni(cod)_2$ purchased from Laajoo, and all the above reagents are stored under nitrogen in glovebox. Bis(cyclopentadienyl)zirconium dichloride, Isoprene 99% (stabilized with TBC), Benzaldehyde, Cesium carbonate, Styrene, benezylmagnesium bromide (1.0 M in THF) and Xanthhos purchased from Energy Chemical. THF, Tol., DCM, Na_2SO_4, purchased from Chengdu Kelong Chemical Reagent Factory, and other commercial reagents purchased from Alfa Aesar, Aladdin, TCI, J&K, Energy Chemical, and Bide Pharmatech Co., Ltd. Column chromatography was performed using glass columns with Silica Gel (Haiyang, 300-400 mesh). Ethyl acetate purchased from Shanghai Exploration Platform. The deuterated reagents used in nuclear magnetic testing are $CDCl_3$ with a purity of 99.8% using Energy and Leyan Chemical.

All unknown compounds starting materials and products were characterized by ^1H NMR, ^{13}C NMR, and high-resolution mass spectrometry, IR. The known desired products were characterized by ^1H NMR, ^{13}C NMR. NMR spectra were obtained on a Bruker 600 MHz spectrometer (operating at 600 MHz for ^1H NMR, 151 MHz for ^{13}C NMR, 564 MHz for ^{19}F NMR) or Varian 400 MHz spectrometer (operating at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR). Data for ^1H, ^{13}C, ^{19}F are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiple, br = broad), integration, and coupling constant (Hz). High-resolution mass spectra (HRMS) were obtained using a quadrupole time-of-flight (Q-TOF) mass spectrometer with an electronspray ionization (ESI) or Electron Impact ionization (EI) resource. Melting points were determined using a melting point apparatus. Single-crystal Xray diffraction data of the compound was collected at room temperature on Japan Rigku xtalab synergy diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.54 nm). Using Olex2, the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXH-1997 refinement package using Least Squares minimisation. Melting points range were determined in a X-4 micromelting point instrument (made in Shanghai, China). Medium-sized screw-cap test tubes (8 mL) were used for all catalytic reaction: Fisher 13 × 100 mm tubes.



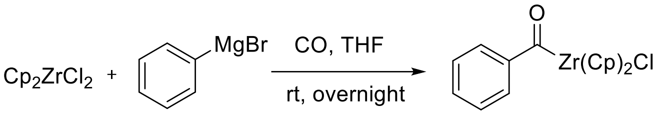
II. Preparation of substrates

Preparation of alkyl acyl zirconium[1]:



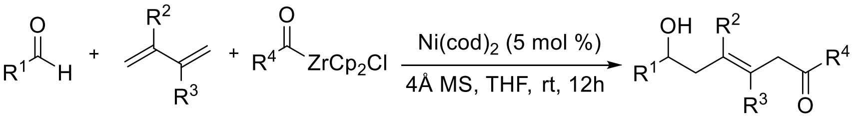
Under an argon atmosphere, to a suspension of Cp_2ZrHCl (1.0 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (4 mL) was added alkene (2 mmol, 2.0 equiv) and the mixture was stirred for 0.5 h at ambient temperature. After that, the mixture was stirred under CO atmosphere (CO balloon) for 2 h, the solution was concentrated under vacuum to dryness to give the desired Acylzirconocene chloride as a solid. (The acylzirconocene chloride (solid) was stable at low temperature under argon atmosphere) (This method was not applied to prepare benzoylzirconocene chloride.

Preparation of phenyl acyl zirconium[2]:



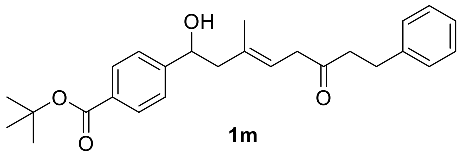
A flame-dried Schlenk tube was charged with Cp_2ZrCl_2 (365 mg, 1.25 mmol, 1.25 equiv), evacuated, and backfilled with CO and added anhydrous THF (3 mL) at ambient temperature, and the phenylmagnesium bromide (1.0 mmol, 1.0 equiv) was added slowly to the suspension under a CO atmosphere (CO balloon). The reaction mixture was then stirred at ambient temperature for 4 h, after that, the solution was concentrated under vacuum to dryness to give product as a viscous solid.

Synthesis of ε-hydroxyl-β, γ-unsaturated ketone[3]:



In the glovebox, to a dry vial with a magnetic stir bar was added Ni(cod)$_2$ (5 mol %, 0.01 mmol, 2.7 mg) and 1 mL THF, then the solution was added 1,3-diene (1.0 mmol, 5.0 equiv), aldehyde (0.2 mmol, 1.0 equiv), 4Å molecular sieve (50 mg) and acylzirconocene chloride (0.4 mmol, 2.0 equiv) successively (Note:1,3-diene must be added firstly, acylzirconocene chlorideshould be added in solid phase). The vial was sealed, removed from the gloveboxand stirred at ambient temperature for 12 hours. The reaction was quenched by 5 mL HCl aqueoussolution (2 M), then extracted with EtOAc (3 x 10 mL), the combined organic solvents was removed under vacuo, and the residue was purified by column chromatography on silica gel to give the product.(TLC monitored by staining with phophomolibdic acid solution in ethanol)

tert-butyl (E)-4-(1-hydroxy-3-methyl-6-oxo-8-phenyloct-3-en-1-yl)benzoate (1m)



1m

According to the general procedure, the homoallylic alcohol **1m** was isolated (petroleum ether/EtOAc = 5 : 1 v/v as the eluent solvent) as a colorless liquid (69.3 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 6.9 Hz, 2H), 7.18 (t, *J* = 8.4 Hz, 3H), 5.39 (t, *J* = 6.9 Hz, 1H), 4.81 (dd, *J* = 8.9, 4.1 Hz, 1H), 3.13 (d, *J* = 7.1 Hz, 2H), 2.88 (d, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.46 – 2.33 (m, 2H), 1.61 (s, 3H), 1.59 (s, 9H).

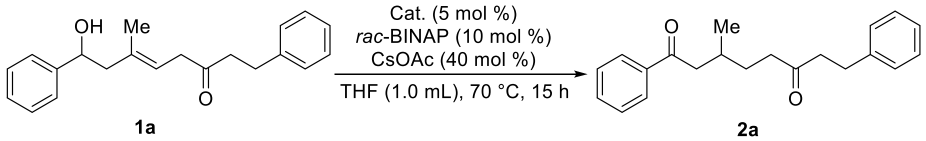
^{13}C NMR (151 MHz, $CDCl_3$) δ 208.0, 165.7, 148.9, 140.9, 135.9, 131.0, 129.5, 128.5, 128.4, 126.2, 125.5, 120.3, 81.0, 77.3, 77.1, 76.9, 71.0, 50.1, 43.9, 42.5, 29.8, 28.2, 16.5.

HRMS-ESI (m/z): Calcd for $C_{26}H_{32}O_4Na$ $[M+Na]^+$: 431.2193; found: 431.2198.

IR (KBr): υ 3475, 2976,2928, 1708, 1610, 1489, 1373, 1113, 1020, 853 cm^{-1}.

III. Optimization of Reaction Conditions

Table S1: Optimization of Catalyst[a]

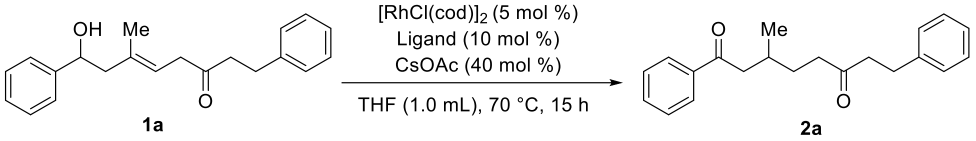


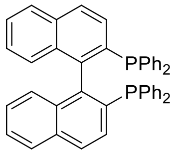
entry	cat.	yield of **2a** (%)[b]
1	**$[RhCl(cod)]_2$**	**22**
2	$[Rh(cod)_2]BF_4$	trace
3	$[IrCl(cod)]_2$	N.R.
4	$Pd(OAc)_2$	N.R.
5	$Pd(PPh_3)_4$	N.R.

6	$NiBr_2(DME)$	N.R.
7	$Ni(cod)_2$	N.R.
8	$RuCl_2(cod)$	N.R.
9	$[RuCl_2(p\text{-}cymene)]_2$	N.R.
10	$Cu(CN)_4(PF_6)$	N.R.

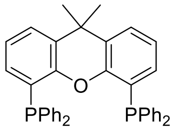
[a]All the reactions were performed with **1a** (0.1 mmol), Cat. (5 mol %), *rac*-BINAP (10 mol %) and CsOAc (40 mol %) in THF (1.0 mL) at 70 °C under N_2 atmosphere for 15 h. [b]The yield was determined by ^1H NMR by using dimethyl terephthalate as internal standard.

Table S2: Optimization of Ligand[a]

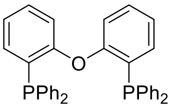




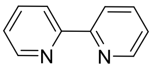
L1
17%



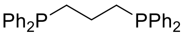
L2[a]
22%[b]



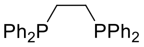
L3
20%



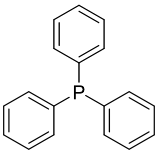
L4
N.R.



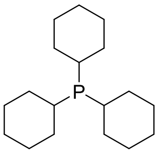
L5
13%



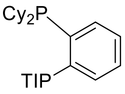
L6
trace



L7
N.R.



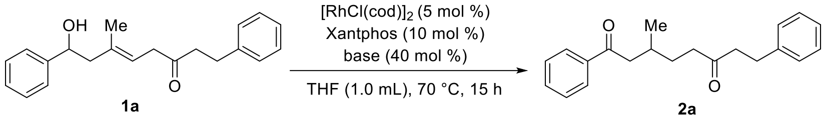
L8
N.R



L9
N.R.

[a]All the reactions were performed with **1a** (0.1 mmol), $[Rh(cod)Cl]_2$ (5 mol %), Ligand (10 mol %) and CsOAc (40 mol %) in THF (1.0 mL) at 70 °C under N_2 atmosphere for 15 h. [b]The yield was determined by ^1H NMR by using dimethyl terephthalate as internal standard.

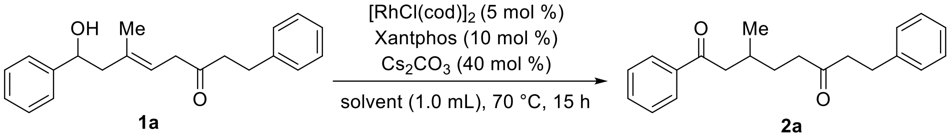
Table S3: Optimization of Base[a]



entry	base	yield of 2a (%) b
1	CsOAc	19
2	**Cs_2CO_3**	**50**
3	K_2CO_3	31
4	Na_2CO_3	33
5	Ag_2CO_3	15
6	NaO*t*Bu	N.D.
7	KO*t*Bu	N.D.
8	KOMe	N.D.
9	LiOMe	38
10	NaOH	N.D.
11	KOH	N.D.
12	DBU	trace

[a]All the reactions were performed with **1a** (0.1 mmol), $[Rh(cod)Cl]_2$ (5 mol %), Xantphos (10 mol %) and base (40 mol %) in THF (1.0 mL) at 70 °C under N_2 atmosphere for 15 h. [b]The yield was determined by ^1H NMR by using dimethyl terephthalate as internal standard.

Table S4: Optimization of Solvent[a]

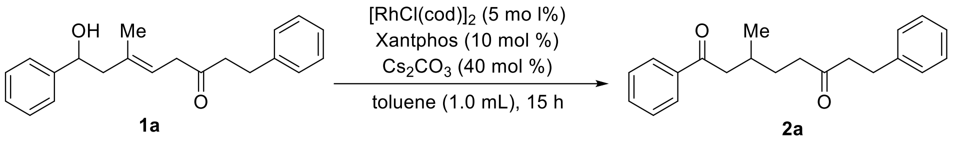


entry	solvent	yield of **2a** (%) [b]
1	THF	48
2	MTBE	52
3	MeCN	35
4	**toluene**	**55**

5	xylene	40
6	DME	49
7	1,4-Dioxane	45
8	DMF	24
9	DCE	37

[a]All the reactions were performed with **1a** (0.1 mmol), $[Rh(cod)Cl]_2$ (5 mol %), Xantphos (10 mol %) and Cs_2CO_3 (40 mol %) in solvent (1.0 mL) at 70 °C under N_2 atmosphere for 15 h. [b]The yield was determined by ^1H NMR by using dimethyl terephthalate as internal standard.

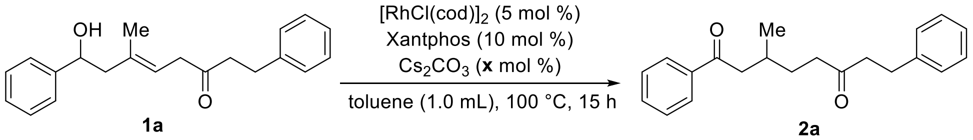
Table S5: Optimization of Temperature[a]



entry	temp (°C)	yield of **2a** (%) [b]
1	60	trace
2	70	51
3	80	72
4	90	80
5	**100**	**86**
6	110	69

[a]All the reactions were performed with **1a** (0.1 mmol), $[Rh(cod)Cl]_2$ (5 mol %), Xantphos (10 mol %) and Cs_2CO_3 (40 mol %) in toluene (1.0 mL) under N_2 atmosphere for 15 h. [b]The yield was determined by ^1H NMR by using dimethyl terephthalate as internal standard.

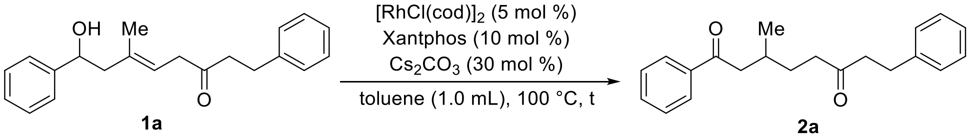
Table S6: Optimization of the Amount of Base[a]



entry[a]	X	yield of **2a** (%) [b]
1	10	36
2	20	80
3	**30**	**95**
4	40	86
5	50	84
6	60	72

[a]All the reactions were performed with **1a** (0.1 mmol), $[Rh(cod)Cl]_2$ (5 mol %), Xantphos (10 mol %) and Cs_2CO_3 (**x** mol %) in toluene (1.0 mL) at 100 °C under N_2 atmosphere for 15 h. [b]The yield was determined by ^1H NMR by using dimethyl terephthalate as internal standard.

Table S7: Optimization of Time[a]

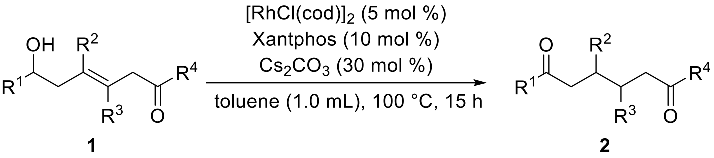


entry[a]	time (h)	yield of **2a** (%) [b]
1	12	88
2	**15**	**97**
3	18	96
4	21	97

[a]All the reactions were performed with **1a** (0.1 mmol), $[Rh(cod)Cl]_2$ (5 mol %), Xantphos (10 mol %) and Cs_2CO_3 (30 mol %) in toluene (1.0 mL) at 100 °C under N_2 atmosphere. [b]The yield was determined by ^1H NMR by using dimethyl terephthalate as internal standard.

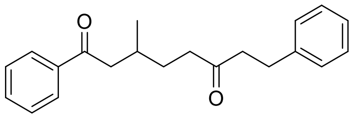
Ⅳ.General Procedure for the Catalytic Reaction

Rhodium-Catalyzed Isomerization of Homoallylic Alcohols with a Tethered Carbonyl Group: Pathway to 1,6-Diketones



General procedures: In the glovebox, to a dry vial with a magnetic stir bar was added $[Rh(cod)Cl]_2$ (0.005 mmol, 2.4 mg, 0.05 equiv), Xantphos (0.01 mmol, 5.8 mg, 0.1 equiv), and homoallylic alcohol (0.1 mmol, 1.0 equiv) and 1 mL of toluene was added, then was added Cs_2CO_3 (0.03 mmol, 9.8 mg, 0.3 equiv). the vial was sealed by a cap stopper, removed from the glovebox and stirred at 100 ºC for 15 hours. After the reaction is completed, the solvent was removed under vacuum, and the residue was purified by column chromatography to give 1,6-diketone.

3-methyl-1,8-diphenyloctane-1,6-dione (2a)



2a

According to the general procedure, the 1,6-dione **2a** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a white solid (28.7 mg, 93% yield, mp = 41.2 °C – 41.8 °C.).

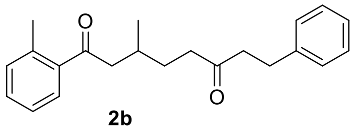
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.54 (m, 1H), 7.48 – 7.45 (m, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.19 (m, 3H), 2.93 – 2.88 (m, 3H), 2.76 – 2.72 (m, 3H), 2.50 – 2.38 (m, 2H), 2.17 – 2.14 (m, 1H), 1.73 – 1.68 (m, 1H), 1.55 – 1.49 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.0, 199.8, 141.1, 137.2, 133.0, 128.63, 128.56, 128.51, 128.4, 128.3, 128.1 126.1, 45.7, 44.3, 40.8, 30.7, 29.9, 29.2, 19.9.

HRMS-ESI (m/z): Calcd for $C_{21}H_{24}O_2Na$ $[M+Na]^+$: 331.1669; found: 331.1680.

IR (KBr): υ 3435, 3191,1715, 1682, 1600, 1371, 1261, 1011 cm^{-1}.

3-methyl-8-phenyl-1-(o-tolyl)octane-1,6-dione (2b)



2b

According to the general procedure, the 1,6-dione **2b** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (21.6 mg, 67% yield).

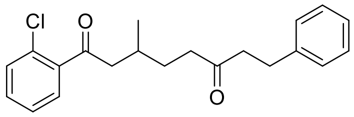
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.28 (m, 1H), 7.26 – 7.19 (m, 4H), 7.18 – 7.08 (m, 3H), 2.88 – 2.81 (m, 3H), 2.77 – 2.66 (m, 3H), 2.52 – 2.22 (m, 5H), 2.15 – 2.05 (m, 1H), 1.68 – 1.55 (m, 1H), 1.49 – 1.42 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 208.9, 203.1, 140.0, 137.4, 136.8, 130.9, 130.1, 127.5, 127.3, 125.1, 124.6, 47.8, 43.2, 39.7, 29.6, 28.8, 28.3, 20.2, 18.7.

HRMS-ESI (m/z): Calcd for $C_{22}H_{26}O_2Na$ $[M+Na]^+$: 345.1825; found: 345.1832.

IR (KBr):υ 3803, 3306, 2962, 2366, 1709, 1675, 1447 cm^{-1}.

1-(2-chlorophenyl)-3-methyl-8-phenyloctane-1,6-dione (2c)



2c

According to the general procedure, the 1,6-dione **2c** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (26.1 mg, 76% yield).

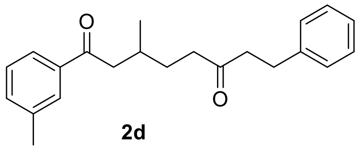
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.24 (m, 6H), 7.21 – 7.12 (m, 3H), 2.94 – 2.83 (m, 3H), 2.78 – 2.71 (m, 3H), 2.48 – 2.35 (m, 2H), 2.12 – 2.09 (m, 1H), 1.71 – 1.61 (m, 1H), 1.55 – 1.43 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 209.9, 203.1, 141.1, 139.8, 131.6, 130.6, 128.8, 128.5, 128.3, 127.0, 126.1, 50.1, 44.3, 40.7, 30.4, 29.8, 29.2, 19.7.

HRMS-ESI (m/z): Calcd for $C_{21}H_{23}O_2ClNa$ $[M+Na]^+$: 365.1279; found: 365.1305.

IR (KBr):υ 3067, 1709, 1595, 1502, 1368, 1069 cm^{-1}.

3-methyl-8-phenyl-1-(m-tolyl)octane-1,6-dione (2d)



2d

According to the general procedure, the 1,6-dione **2d** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (23.2 mg, 72% yield).

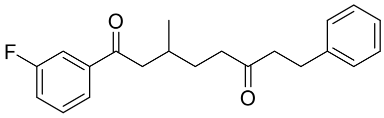
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.67 (m, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.22 (m, 2H), 7.20 – 7.11 (m, 3H), 2.93 – 2.85 (m, 3H), 2.77 – 7.67 (m, 3H), 2.52 – 2.35 (m, 5H), 2.15 – 2.08 (m, 1H), 1.71 – 1.63 (m, 1H), 1.56 – 1.44 (m, 1H), 0.94 (d, J = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.0, 200.1, 141.1, 138.4, 137.3, 133.8, 128.6, 128.5, 128.3, 126.1, 125.3, 45.8, 44.3, 40.8, 30.7, 29.8, 29.2, 21.4, 19.9.

HRMS-ESI (m/z): Calcd for $C_{22}H_{26}O_2Na$ $[M+Na]^+$: 345.1825; found: 345.1832.

IR (KBr):υ 3823, 3061, 2922, 1953, 1715, 1677, 1494 cm^{-1}.

1-(3-fluorophenyl)-3-methyl-8-phenyloctane-1,6-dione (2e)



2e

According to the general procedure, the 1,6-dione **2e** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (25.5 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 1H), 7.63 – 7.54 (m, 1H), 7.45 – 7.37 (m, 1H), 7.28 – 7.19 (m, 3H), 7.18 – 7.09 (m, 3H), 2.91 – 2.82 (m, 3H), 2.77 – 2.67

(m, 3H), 2.51 – 2.35 (m, 2H), 2.15 – 2.10 (m, 1H), 1.71 – 1.63 (m, 1H), 1.55 – 1.42 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H).

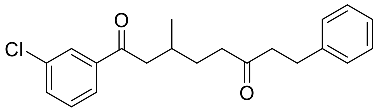
^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 198.5, 163.7, 162.1, 141.1, 139.3, 130.3, 128.4 (d, *J* = 15.2 Hz), 126.1, 123.8, 120.1, 120.0, 114.9, 114.8, 45.9, 44.3, 40.8, 30.6, 29.8, 29.1, 19.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -111.81.

HRMS-ESI (m/z): Calcd for $C_{21}H_{23}FO_2Na$ $[M+Na]^+$: 349.1574; found: 349.1584.

IR (KBr):υ 3407, 3073, 2966, 1953, 1715, 1682, 1490 cm^{-1}.

1-(3-chlorophenyl)-3-methyl-8-phenyloctane-1,6-dione (2f)



2f

According to the general procedure, the 1,6-dione **2f** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (29.1 mg, 85% yield).

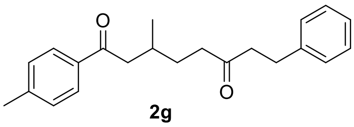
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.28 – 7.24 (m, 2H), 7.19 – 7.16 (m, 3H), 2.93 – 2.87 (m, 3H), 2.77 – 2.73 (m, 3H), 2.49 – 2.36 (m, 2H), 2.15 – 2.10 (m, 1H), 1.72 – 1.61 (m, 1H), 1.54 – 1.40 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 198.4, 141.1, 138.8, 135.0, 133.0, 130.0, 128.5, 128.3, 128.2, 126.2, 126.1, 45.8, 44.3, 40.7, 30.6, 29.9, 29.1, 19.8.

HRMS-ESI (m/z): Calcd for $C_{21}H_{23}O_2ClNa$ $[M+Na]^+$: 365.1279; found: 365.1305.

IR (KBr):υ 3845, 3673, 2963, 1714, 1683, 1571, 1212 cm^{-1}.

3-methyl-8-phenyl-1-(p-tolyl)octane-1,6-dione (2g)



2g

According to the general procedure, the 1,6-dione **2g** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (23.2 mg, 72% yield).

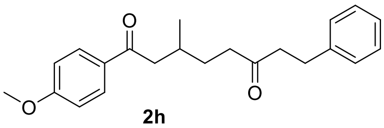
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.24 (m, 4H), 7.22 – 7.17 (m, 3H), 2.94 – 2.83 (m, 3H), 2.81 – 2.63 (m, 3H), 2.50 – 2.38 (m, 5H), 2.15 – 2.06 (m, 1H), 1.73 – 1.60 (m, 1H), 1.55 – 1.42 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 210.1, 199.6, 143.8, 141.1, 134.8, 129.3, 128.5, 128.3, 128.2, 126.1, 53.5, 45.6, 44.3, 40.8, 30.7, 29.8, 29.3, 21.6, 19.9.

HRMS-ESI (m/z): Calcd for $C_{22}H_{26}O_2Na$ $[M+Na]^+$: 345.1825; found: 345.1832.

IR (KBr):υ 3883, 3844, 3371, 3028, 2862, 1714, 1675, 1410 cm^{-1}.

1-(4-methoxyphenyl)-3-methyl-8-phenyloctane-1,6-dione (2h)



2h

According to the general procedure, the 1,6-dione **2h** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (18.6 mg, 55% yield).

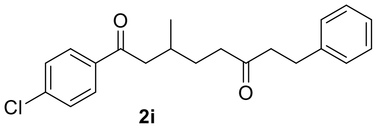
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.18 – 7.07 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.94 – 2.81 (m, 3H), 2.73 – 2.60 (m, 3H), 2.47 – 2.23 (m, 2H), 2.13 – 1.98 (m, 1H), 1.72 – 1.51 (m, 1H), 1.50 – 1.32 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 210.1, 198.4, 163.4, 141.1, 130.4, 128.5, 128.3, 126.1, 113.7, 55.5, 45.4, 44.3, 40.8, 30.8, 29.8, 29.4, 19.9.

HRMS-ESI (m/z): Calcd for $C_{22}H_{26}O_3Na$ $[M+Na]^+$: 361.1774; found: 361.1779.

IR (KBr):υ 3881, 3782, 2961, 1709, 1668, 1593, 1252 cm^{-1}.

1-(4-chlorophenyl)-3-methyl-8-phenyloctane-1,6-dione (2i)



2i

According to the general procedure, the 1,6-dione **2i** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (32.6 mg, 95% yield).

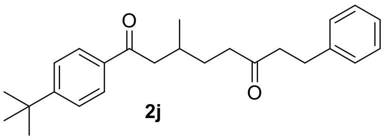
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.27 – 7.19 (m, 2H), 7.18 – 7.06 (m, 3H), 2.88 – 2.76 (m, 3H), 2.74 – 2.64 (m, 3H), 2.52 – 2.33 (m, 2H), 2.13 – 1.97 (m, 1H), 1.70 – 1.51 (m, 1H), 1.49 – 1.30 (m, 1H), 0.93 (d, J = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 198.5, 141.1, 139.5, 135.5, 129.5, 128.9, 128.5, 128.3, 126.1, 45.7, 44.3, 40.8, 30.6, 29.8, 29.2, 19.8.

HRMS-ESI (m/z): Calcd for $C_{21}H_{23}O_2ClNa$ $[M+Na]^+$: 365.1279; found: 365.1305.

IR (KBr):υ 3863, 3759, 3025, 2362, 1710, 1678 cm^{-1}.

1-(4-(tert-butyl)phenyl)-3-methyl-8-phenyloctane-1,6-dione (2j)



2j

According to the general procedure, the 1,6-dione **2j** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (31.7 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.28 –

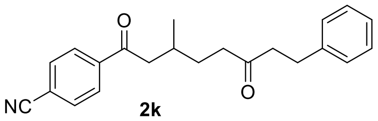
7.25 (m, 2H), 7.19 – 7.18 (m, 3H), 2.93 – 2.87 (m, 3H), 2.79 – 2.73 (m, 3H), 2.50 – 2.38 (m, 2H), 2.17 – 2.13 (m, 1H), 1.69 – 1.68 (m, 1H), 1.51 – 1.50 (m, 1H), 1.35 (s, 9H), 0.94 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, CDCl3) δ 210.1, 199.5, 156.7, 141.1, 134.7, 128.5, 128.3, 128.1, 126.1, 125.6, 45.6, 44.3, 40.8, 35.1, 31.4, 31.1, 30.8, 29.8, 29.3, 19.9.

HRMS-ESI (m/z): Calcd for $C_{25}H_{32}O_2K$ [M+K]$^+$: 403.2034; found: 403.2030.

IR (KBr):υ 3813, 3664, 2960, 1713, 1674, 1602, 1018 cm^{-1}.

4-(3-methyl-6-oxo-8-phenyloctanoyl)benzonitrile (2k)



2k

According to the general procedure, the 1,6-dione **2k** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless solid (23.3 mg, 70% yield, mp = 79.4 °C – 80.2 °C.).

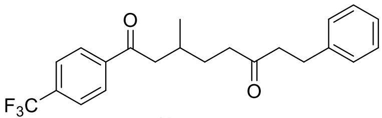
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.19 (m, 2H), 7.18 – 7.08 (m, 3H), 2.96 – 2.85 (m, 3H), 2.76 – 2.58 (m, 3H), 2.53 – 2.35 (m, 2H), 2.13 – 1.99 (m, 1H), 1.72 – 1.63 (m, 1H), 1.55 – 1.40 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.8, 198.3, 141.0, 140.1, 132.6, 128.5, 128.3, 126.1, 118.0, 116.3, 46.0, 44.3, 40.7, 30.5, 29.8, 29.0, 19.7.

HRMS-ESI (m/z): Calcd for $C_{22}H_{23}NO_2Na$ [M+Na]$^+$: 356.1621; found: 356.1611.

IR (KBr):υ 3063, 2965, 1947, 1714, 1685, 1499, 1284 cm^{-1}.

3-methyl-8-phenyl-1-(4-(trifluoromethyl)phenyl)octane-1,6-dione (2l)



2l

According to the general procedure, the 1,6-dione **2l** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (31.2 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.19 – 7.16 (m, 3H), 2.98 – 2.86 (m, 3H), 2.84 – 2.71 (m, 3H), 2.52 – 2.36 (m, 2H), 2.14 – 2.11 (m, 1H), 1.70 – 1.69 (m, 1H), 1.55 – 1.44 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H).

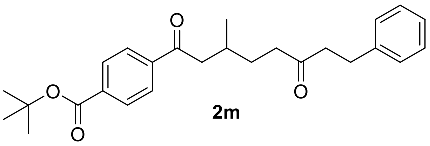
^{13}C NMR (151 MHz, $CDCl_3$) δ 209.8, 198.8, 141.0, 139.8, 128.5, 128.45, 128.41, 128.34, 128.27, 126.14, 126.07, 125.72, 125.67, 46.0, 44.3, 40.7, 30.6, 29.8, 29.1, 19.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.08.

HRMS-ESI (m/z): Calcd for $C_{22}H_{23}F_3O_2Na$ $[M+Na]^+$: 399.1542; found: 399.1551.

IR (KBr):υ 3838, 3005, 1703, 1687, 1367, 1124, 832 cm^{-1}.

tert-butyl 4-(3-methyl-6-oxo-8-phenyloctanoyl)benzoate(2m)



2m

According to the general procedure, the 1,6-dione **2m** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (30.2 mg, 74% yield).

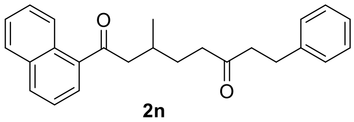
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 2.96 – 2.85 (m, 3H), 2.77 (dt, *J* = 24.3, 7.2 Hz, 3H), 2.52 – 2.35 (m, 2H), 2.13 (d, *J* = 6.4 Hz, 1H), 1.69 (dd, *J* = 14.3, 8.4 Hz, 1H), 1.61 (s, 9H), 1.54 – 1.44 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 208.83, 198.36, 163.83, 140.01, 138.97, 134.70, 128.63, 127.46, 127.29, 126.79, 125.07, 80.75, 45.02, 43.23, 39.71, 29.57, 28.79, 28.08, 27.11, 18.75.

HRMS-ESI (m/z): Calcd for $C_{26}H_{33}O_4Na$ $[M+Na]^+$: 431.2193; found: 431.2198.

IR (KBr):υ 2963, 2963, 2357, 1703, 1260, 1092, 800, 688 cm^{-1}.

3-methyl-1-(naphthalen-1-yl)-8-phenyloctane-1,6-dione (2n)



2n

According to the general procedure, the 1,6-dione **2n** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (24.7 mg, 69% yield).

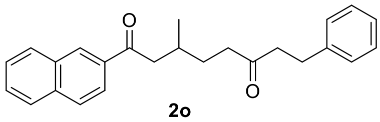
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 6.6 Hz, 1H), 7.62 – 7.47 (m, 3H), 7.28 – 7.26 (m, 2H), 7.20 – 7.17 (m, 3H), 3.03 (dd, *J* = 16.0, 5.8 Hz, 1H), 2.93 – 2.82 (m, 3H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.53 – 2.36 (m, 2H), 2.20 – 2.19 (m, 1H), 1.74 – 1.73 (m, 1H), 1.59 – 1.49 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 204.3, 141.1, 136.5, 134.0, 132.5, 130.1, 128.5, 128.4, 127.9, 127.4, 126.5, 126.1, 125.7, 124.4, 49.4, 44.2, 40.8, 30.7, 29.9, 29.8, 19.9.

HRMS-ESI (m/z): Calcd for $C_{25}H_{26}O_2Na$ $[M+Na]^+$: 381.1825; found: 381.1831.

IR (KBr):υ 3057, 2963, 2862, 1949, 1717, 1668, 1367 cm^{-1}.

3-methyl-1-(naphthalen-2-yl)-8-phenyloctane-1,6-dione (2o)



2o

According to the general procedure, the 1,6-dione **2o** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (26.5 mg, 74% yield).

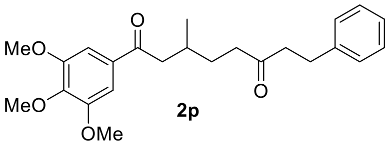
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.06 – 7.97 (m, 2H), 7.95 – 7.83 (m, 2H), 7.63 – 7.50 (m, 2H), 7.28 – 7.24 (m, 2H), 7.20 – 7.16 (m, 3H), 3.05 (dd, *J* = 16.1, 5.8 Hz, 1H), 2.98 – 2.84 (m, 3H), 2.80 – 2.69 (m, 2H), 2.51 – 2.30 (m, 2H), 2.24 – 2.09 (m, 1H), 1.77 – 1.63 (m, 1H), 1.59 – 1.49 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.0, 199.8, 141.1, 135.6, 134.6, 132.6, 129.7, 129.6, 128.50, 128.49,128.46, 128.3, 127.8, 126.8, 126.1, 123.9, 45.8, 44.3, 40.6, 30.8, 29.8, 29.4, 19.9.

HRMS-ESI (m/z): Calcd for $C_{25}H_{26}O_2Na$ $[M+Na]^+$: 381.1825; found: 381.1831.

IR (KBr):υ 3748, 3026, 2922, 2369, 1712, 1673, 1589, 1408 cm^{-1}.

3-methyl-8-phenyl-1-(3,4,5-trimethoxyphenyl)octane-1,6-dione (2p)



2p

According to the general procedure, the 1,6-dione **2p** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (14.3 mg, 36% yield).

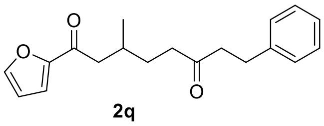
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.22 – 7.13 (m, 5H), 3.92 (s, 9H), 2.92 – 2.86 (m, 3H), 2.73 (dd, *J* = 15.7, 8.3 Hz, 3H), 2.52 – 2.37 (m, 2H), 2.14 (m, 1H), 1.74 – 1.66 (m, 1H), 1.54 – 1.44 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 208.9, 197.5, 152.1, 141.5, 140.0, 131.5, 127.5, 127.3, 125.1, 104.6, 59.9, 55.3, 44.5, 43.2, 39.8, 29.8, 28.8, 28.3, 18.8.

HRMS-ESI (m/z): Calcd for $C_{24}H_{30}O_5Na$ $[M+Na]^+$: 421.1985; found:421.1969 .

IR (KBr):υ 2935, 2358, 1709, 1583, 1411, 1124, 1003, 703 cm^{-1}.

1-(furan-2-yl)-3-methyl-8-phenyloctane-1,6-dione (2q)



2q

According to the general procedure, the 1,6-dione **2q** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (19.4 mg, 65% yield).

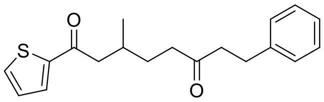
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.56 (m, 1H), 7.28 – 7.24 (m, 2H), 7.17 – 7.16 (m, 4H), 6.55 – 6.50 (m, 1H), 2.90 – 2.87 (m, 2H), 2.75 – 2.71 (m, 3H), 2.66 – 2.60 (m, 1H), 2.49 – 2.37 (m, 2H), 2.12 – 2.07 (m, 1H), 1.72 – 1.64 (m, 1H), 1.57 – 1.51 (m, 1H), 0.93 (d, J = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 189.0, 153.1, 146.4, 141.1, 128.5, 128.3, 126.1, 117.1, 112.2, 45.5, 44.3, 40.7, 30.7, 29.8, 29.4, 19.8.

HRMS-ESI (m/z): Calcd for $C_{19}H_{22}O_3Na$ $[M+Na]^+$: 321.1461; found: 321.1459.

IR (KBr):υ 3733, 3027, 2868, 1712, 1668, 1459, 811 cm^{-1}.

3-methyl-8-phenyl-1-(thiophen-2-yl)octane-1,6-dione (2r)



2r

According to the general procedure, the 1,6-dione **2r** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (22.3 mg, 71%

yield).

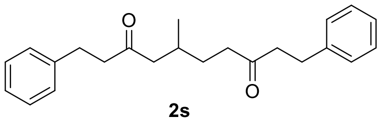
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 3.8 Hz, 1H), 7.63 (d, *J* = 4.7 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.19 – 7.16 (m, 3H), 7.14 – 7.11 (m, 1H), 2.92 – 2.82 (m, 3H), 2.73 – 2.67 (m, 3H), 2.44 – 2.36 (m, 2H), 2.20 – 2.09 (m, 1H), 1.73 – 1.65 (m, 1H), 1.56 – 1.47 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 192.7, 144.8, 141.1, 133.7, 131.9, 128.5, 128.3, 128.1, 126.1, 46.5, 44.3, 40.8, 30.7, 29.83, 29.76, 19.8.

HRMS-ESI (m/z): Calcd for $C_{19}H_{22}O_2SNa$ $[M+Na]^+$: 337.1233; found: 337.1245.

IR (KBr):υ 3863, 2960, 1709, 1657, 1409, 751 cm^{-1}.

5-methyl-1,10-diphenyldecane-3,8-dione (2s)



2s

According to the general procedure, the 1,6-dione **2s** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (29.6 mg, 88% yield).

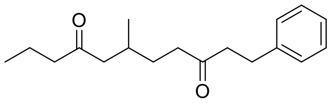
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.27 (m, 4H), 7.26 (m, 6H), 2.89 – 2.87 (m, 4H), 2.74 – 2.68 (m, 4H), 2.41 – 2.29 (m, 3H), 2.20 (dd, *J* = 16.3, 7.7 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.58 – 1.51 (m, 1H), 1.41 – 1.34 (m, 1H), 0.83 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 209.6, 141.1, 128.5, 128.3, 126.1, 50.2, 44.8, 44.3, 40.7, 30.4, 29.8, 29.7, 28.6, 19.7.

HRMS-ESI (m/z): Calcd for $C_{23}H_{28}O_2Na$ $[M+Na]^+$: 359.1982; found: 359.1980.

IR (KBr):υ 3882, 3732, 2920, 1951, 1710, 1451 cm^{-1}.

6-methyl-1-phenylundecane-3,8-dione (2t)



2t

According to the general procedure, the 1,6-dione **2t** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (15.4 mg, 56% yield).

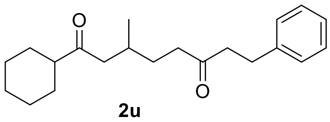
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.19 – 7.16 (m, 3H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.39 – 2.30 (m, 4H), 2.21 (dd, *J* = 16.2, 7.7 Hz, 1H), 1.97 – 1.94 (m, 1H), 1.62 – 1.53 (m, 4H), 1.44 – 1.35 (m, 1H), 0.96 – 0.82 (m, 6H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.7, 210.0, 141.1, 128.5, 128.3, 126.1, 50.0, 45.3, 44.3, 40.7, 30.5, 29.8, 28.7, 19.7, 17.2, 13.8.

HRMS-ESI (m/z): Calcd for $C_{18}H_{26}O_2Na$ $[M+Na]^+$: 297.1825; found: 297.1828.

IR (KBr):υ 3784, 3335, 3027, 2868, 1712, 1501 cm^{-1}.

1-cyclohexyl-3-methyl-8-phenyloctane-1,6-dione (2u)



2u

According to the general procedure, the 1,6-dione **2u** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (17.6 mg, 56% yield).

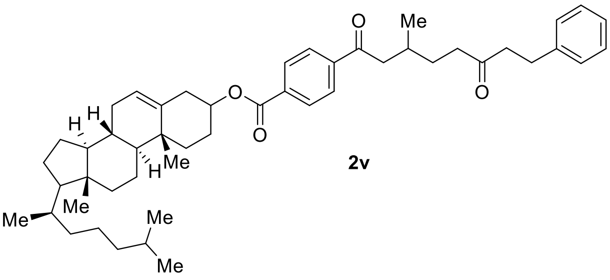
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.20 – 7.16 (m, 3H), 2.90 – 2.86 (m, 2H), 2.75 – 2.70 (m, 2H), 2.42 – 2.22 (m, 5H), 2.00 – 1.92 (m, 1H), 1.84 – 1.74 (m, 4H), 1.61 – 1.50 (m, 1H), 1.44 – 1.36 (m, 1H), 1.34 – 1.11 (m, 6H), 0.83 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 212.6, 209.0, 140.1, 127.5, 127.3, 125.1, 50.2, 46.9, 43.2, 39.8, 29.5, 28.8, 27.39, 27.37, 27.31, 24.8, 24.7, 24.6, 18.7.

HRMS-ESI (m/z): Calcd for $C_{21}H_{30}O_2Na$ $[M+Na]^+$: 337.2138; found: 337.2146.

IR (KBr):υ 3027, 2963, 2851, 1707, 1603, 1495, 1409, 1095 cm^{-1}.

(8S,9S,10R,13R,14S)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(1-hydroxy-3-methyl-6-oxo-8-phenyloctyl)benzoate (2v)



2v

According to the general procedure, the 1,6-dione **2v** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless solid (30.3 mg, 42% yield, mp = 80.2 °C – 80.8 °C).

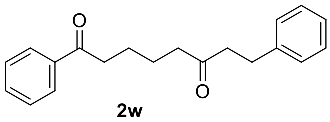
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.95 – 7.81 (m, 2H), 7.21 – 7.19 (m, 2H), 7.12 – 7.09 (m, 3H), 5.35 – 5.35 (m, 1H), 4.86 – 4.74 (m, 1H), 2.90 – 2.78 (m, 3H), 2.69 – 2.64 (m, 3H), 2.38 – 2.35 (m, 3H), 1.99 – 1.40 (m, 16H), 1.26 – 1.21 (m, 3H), 1.17 – 0.90 (m, 15H), 0.86 – 0.84 (m, 5H), 0.82 – 0.77 (m, 6H), 0.62 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.8, 199.3, 165.1, 141.1, 140.3, 139.5, 134.5, 129.8, 128.5, 128.3, 127.9, 126.1, 123.0, 75.2, 56.7, 56.2, 50.1, 46.1, 44.3, 42.3, 40.8, 39.8, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 32.0, 30.6, 29.8, 29.1, 28.3, 28.1, 28.0, 24.3, 23.9, 22.9, 22.6, 21.1, 19.8, 19.4, 18.7, 11.9.

HRMS-ESI (m/z):Calcd for $C_{49}H_{68}O_4Na$ $[M+Na]^+$: 743.5010; found: 743.5015.

IR (KBr):υ 3851, 3070, 2965, 1718, 1682, 1460, 1112 cm^{-1}.

1,8-diphenyloctane-1,6-dione (2w)



2w

According to the general procedure, the 1,6-dione **2w** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless solid (25.9 mg, 88% yield, mp = 79.2 °C – 80.0 °C).

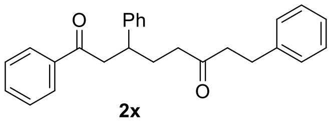
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.51 – 7.46 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 2.97 (t, *J* = 5.5 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.45 (t, *J* = 5.5 Hz, 2H), 1.76 – 1.62 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.9, 200.0, 141.1, 137.0, 133.0, 128.6, 128.5, 128.3, 128.0, 126.1, 44.3, 42.8, 38.3, 29.8, 23.7, 23.4.

HRMS-ESI (m/z): Calcd for $C_{20}H_{22}O_2Na$ [M+Na]$^+$: 317.1512; found: 317.1515.

IR (KBr):υ 3747, 2932, 1715, 1679, 1499, 1449, 1027 cm^{-1}.

1,3,8-triphenyloctane-1,6-dione (2x)



2x

According to the general procedure, the 1,6-dione **2x** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless solid (26.7 mg, 72% yield, mp = 45.2 °C – 46.0 °C).

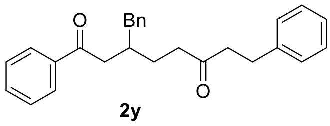
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.3 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.45 – 7.41 (m, 2H), 7.30 – 7.11 (m, 10H), 3.35 – 3.20 (m, 3H), 2.85 – 2.75 (m, 2H), 2.65 – 2.55 (m, 2H), 2.37 – 2.26 (m, 1H), 2.25 – 2.15 (m, 1H), 2.10 – 2.01 (m, 1H), 1.93 – 18.4(m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 208.6, 197.6, 142.7, 140.0, 136.0, 132.0, 127.6, 127.5, 127.4, 127.3, 127.0, 126.6, 125.6, 125.0, 44.9, 43.2, 40.0, 39.5, 28.8, 28.7.

HRMS-ESI (m/z): Calcd for $C_{26}H_{27}O_2Na$ $[M+Na]^+$: 393.1825; found: 393.1831.

IR (KBr):υ 3435, 3069, 3024, 2923,2857, 2358, 1678, 1492,1085, 800, 689 cm^{-1}.

3-benzyl-1,8-diphenyloctane-1,6-dione (2y)



2y

According to the general procedure, the 1,6-dione **2y** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless solid (29.6 mg, 77% yield, mp = 45.3 °C – 45.9 °C).

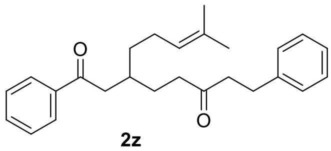
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.57 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 7.29 – 7.23 (m, 4H), 7.21 – 7.12 (m, 6H), 2.97 – 2.78 (m, 4H), 2.72 – 2.55 (m, 4H), 2.44 – 2.35 (m, 2H), 1.82 – 1.68 (m, 1H), 1.68 – 1.61 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 208.2, 198.2, 139.5, 138.4, 135.5, 131.4, 127.7, 127.0, 126.9, 126.8, 126.7, 126.4, 124.6, 124.5, 42.5, 40.9, 39.1, 39.0, 34.1, 28.2, 26.4.

HRMS-ESI (m/z): Calcd for $C_{27}H_{28}O_2Na$ $[M+Na]^+$: 407.1982; found: 407.2012.

IR (KBr):υ 3884, 3736, 2919, 1710,1677, 1558, 802 cm^{-1}.

3-(4-methylpent-3-en-1-yl)-1,8-diphenyloctane-1,6-dione (2z)



2z

According to the general procedure, the 1,6-dione **2z** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (34.3 mg, 91% yield).

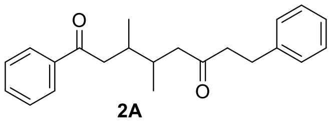
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.43 (m, 2H), 7.28 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 5.06 (t, *J* = 7.0 Hz, 1H), 3.00 – 2.80 (m, 4H), 2.76 – 2.69 (m, 2H), 2.45 – 2.35 (m, 2H), 2.16 – 2.03 (m, 1H), 2.00 – 1.93 (m, 2H), 1.71 – 1.57 (m, 8H), 1.41 – 1.30 (m, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 210.0, 200.0, 141.1, 137.3, 133.0, 131.8, 128.6, 128.4, 128.3, 128.1, 126.1, 124.1, 44.2, 43.1, 40.5, 34.2, 33.4, 29.8, 28.0, 25.7, 25.2, 17.7.

HRMS-ESI (m/z): Calcd for $C_{26}H_{32}O_2Na$ $[M+Na]^+$: 399.2295; found: 399.2287.

IR (KBr):υ 3065, 2967, 1716,1679, 1495, 1369, 1215 cm^{-1}.

3,4-dimethyl-1,8-diphenyloctane-1,6-dione (2A)



2A

According to the general procedure, the 1,6-dione **2A** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (16.4 mg, 51% yield).

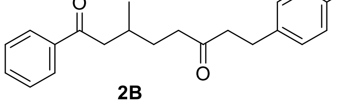
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 – 7.87 (m, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 7.28 – 7.25 (m, 2H), 7.21 – 7.16 (m, 3H), 2.98 – 2.86 (m, 3H), 2.80 – 2.67 (m, 3H), 2.49 – 2.39 (m, 1H), 2.31 – 2.09 (m, 3H), 0.96 – 0.79 (m, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 209.8, 200.1, 141.1, 137.3, 133.0, 128.6, 128.5, 128.4, 128.1, 126.1, 48.3, 47.0, 44.8, 44.7, 43.6, 42.4, 34.0, 33.6, 33.5, 33.2, 29.8, 17.0, 15.2.

HRMS-ESI (m/z): Calcd for $C_{22}H_{26}O_2Na$ $[M+Na]^+$: 345.1825; found: 345.1832.

IR (KBr):υ 3856, 3070, 2863, 1956, 1713, 1674, 1499 cm^{-1}.

8-(4-fluorophenyl)-3-methyl-1-phenyloctane-1,6-dione (2B)



2B

According to the general procedure, the 1,6-dione **2B** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless solid (27.7 mg, 85% yield, mp = 70.2 °C – 70.8 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.41 (m, 2H), 7.15 – 7.10 (m, 2H), 6.98 – 6.92 (m, 2H), 2.98 – 2.64 (m, 6H), 2.48 – 2.32 (m, 2H), 2.17 – 2.06 (m, 1H), 1.71 – 1.65 (m, 1H), 1.52 – 1.40 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H).

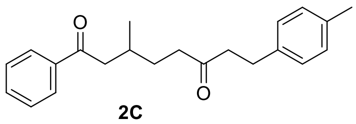
^{13}C NMR (151 MHz, $CDCl_3$) δ 209.7, 199.8, 162.2, 160.6, 137.3, 136.7 (d, *J* = 3.2 Hz), 133.0, 129.7 (d, *J* = 7.7 Hz), 128.6, 128.1, 115.3, 115.1, 45.7, 44.3, 40.8, 30.7, 29.2, 28.9, 19.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.29.

HRMS-ESI (m/z): Calcd for $C_{21}H_{23}O_2FNa$ $[M+Na]^+$: 349.1574; found: 349.1584.

IR (KBr):υ 3733, 3063, 2964, 1887, 1715, 1674, 1508 cm^{-1}.

3-methyl-1-phenyl-8-(p-tolyl)octane-1,6-dione (2C)



2C

According to the general procedure, the 1,6-dione **2C** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (21.3 mg, 66% yield).

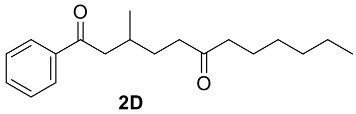
^{1}H NMR (400 MHz,$CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.56 (m, 1H), 7.47-7.46 (m, 2H), 7.10 – 7.03 (m, 4H), 2.95 – 2.78 (m, 4H), 2.72 (m, 2H), 2.50 – 2.36 (m, 2H), 2.30 (s, 3H), 2.14 (m, 1H), 1.68 (m, 1H), 1.51 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 210.1, 199.8, 138.0, 137.3, 135.6, 133.0, 129.2, 128.6, 128.2, 128.1, 45.7, 44.4, 40.8, 30.7, 29.4, 29.2, 21.0, 19.8.

HRMS-ESI (m/z): Calcd for $C_{22}H_{26}O_2Na$ $[M+Na]^+$: 345.1825; found: 345.1837.

IR (KBr):υ 3686, 2956, 2365, 1714, 1678, 1590, 1509 cm^{-1}.

3-methyl-1-phenyldodecane-1,6-dione (2D)



2D

According to the general procedure, the 1,6-dione **2D** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (6.4 mg, 57% yield).

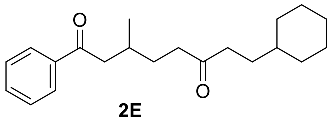
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.59 – 7.53 (m, 1H), 7.48 – 7.42 (m, 2H), 2.94 (dd, *J* = 16.2, 5.7 Hz, 1H), 2.79 (dd, *J* = 16.2, 7.7 Hz, 1H), 2.61 – 2.24 (m, 4H), 2.23 – 2.08 (m, 1H), 1.75 – 1.65 (m, 1H), 1.59 – 1.42 (m, 3H), 1.38 – 1.09 (m, 6H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.3, 199.9, 137.3, 133.0, 128.6, 128.1, 45.8, 42.9, 40.5, 31.6, 30.8, 29.3, 28.9, 23.9, 22.5, 19.9, 14.0

HRMS-ESI (m/z): Calcd for $C_{19}H_{28}O_2Na$ $[M+Na]^+$: 311.1982; found: 311.1985.

IR (KBr):υ 3845, 2963, 2859, 1717, 1679, 1590, 1456 cm^{-1}.

8-cyclohexyl-3-methyl-1-phenyloctane-1,6-dione (2E)



2E

According to the general procedure, the 1,6-dione **2E** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (21.1 mg, 67% yield).

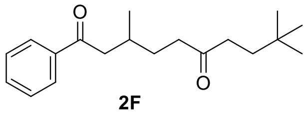
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.42 (m, 2H), 2.94 (dd, *J* = 16.1, 5.7 Hz, 1H), 2.79 (dd, *J* = 16.2, 7.7 Hz, 1H), 2.58 – 2.32 (m, 4H), 2.16 (m, 1H), 1.73 – 1.59 (m, 6H), 1.54 – 1.41 (m, 3H), 1.25 – 1.08 (m, 4H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.90 – 0.79 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.5, 199.9, 137.3, 133.0, 128.6, 128.1, 45.8, 40.5, 40.4, 37.3, 33.1, 31.3, 30.9, 29.3, 26.6, 26.3, 19.9.

HRMS-ESI (m/z): Calcd for $C_{21}H_{30}O_2Na$ $[M+Na]^+$: 337.2138; found: 337.2146.

IR (KBr):υ 3797, 2962, 2850, 1713, 1684, 1448 cm^{-1}.

3,9,9-trimethyl-1-phenyldecane-1,6-dione (2F)



2F

According to the general procedure, the 1,6-dione **2F** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (19.9 mg, 69% yield).

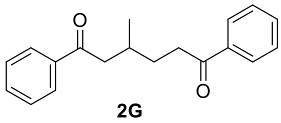
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 2.94 (dd, J = 15.3, 6.3 Hz, 1H), 2.79 (dd, J = 16.2, 9.5 Hz, 1H), 2.52 – 2.44 (m, 2H), 2.39 – 2.31 (m, 2H), 2.18 – 2.11 (m, 1H), 1.73 – 1.65 (m, 1H), 1.56 – 1.41 (m, 3H), 0.95 (d, J = 6.6 Hz, 3H), 0.87 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.5, 199.9, 137.3, 133.0, 128.6, 128.1, 45.8, 40.5, 38.5, 37.4, 30.9, 29.9, 29.3, 29.1, 19.9.

HRMS-ESI (m/z): Calcd for $C_{19}H_{28}O_2Na$ $[M+Na]^+$: 311.1982; found: 311.1985.

IR (KBr):υ 3850, 2960, 1716, 1459, 1368, 1175 cm^{-1}.

3-methyl-1,6-diphenylhexane-1,6-dione (2G)



2G

According to the general procedure, the 1,6-dione **2G** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (21.0 mg, 75% yield).

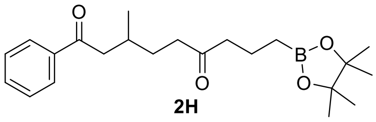
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 4H), 7.57 – 7.52 (m, 2H), 7.50 – 7.44 (m, 4H), 3.12 – 2.93 (m, 3H), 2.85 (dd, *J* = 16.2, 7.8 Hz, 1H), 2.33 – 2.23 (m, 1H), 1.92 – 1.81 (m, 1H), 1.75 – 1.65 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.2, 198.9, 136.2, 135.9, 132.0, 127.6, 127.1, 127.0, 44.8, 35.4, 30.3, 28.4, 18.9.

HRMS-ESI (m/z): Calcd for $C_{19}H_{20}O_2Na$ $[M+Na]^+$: 303.1356; found: 303.1358.

IR (KBr):υ 3738, 1681, 1589, 1449, 1268, 800 cm^{-1}.

3-methyl-1-phenyl-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonane-1,6-dione (2H)



2H

According to the general procedure, the 1,6-dione **2H** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (17.9 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.56 – 7.52 (m, 1H), 7.46 – 7.43 (m, 2H), 2.95 (dd, *J* = 16.1, 5.6 Hz, 1H), 2.77 (dd, *J* = 16.1, 7.9 Hz, 1H), 2.49 – 2.36 (m, 4H), 2.14 – 2.09 (m, 1H), 1.71 – 1.67 (m, 3H), 1.55 – 1.44 (m, 1H), 1.22 (s, 12H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.76 (t, *J* = 7.8 Hz, 2H).

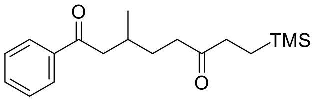
^{13}C NMR (151 MHz, $CDCl_3$) δ 211.1, 199.9, 137.3, 133.0, 128.6, 128.1, 83.1, 45.8, 45.1, 40.5, 30.8, 29.3, 24.8, 19.8, 18.6.

^{11}B NMR (193 MHz, $CDCl_3$) δ 33.76.

HRMS-ESI (m/z): Calcd for $C_{22}H_{33}BO_4Na$ $[M+Na]^+$: 395.2364; found: 395.2374.

IR (KBr):υ 3856, 3748, 3061, 2969, 2877, 1608, 1588 cm^{-1}.

3-methyl-1-phenyl-9-(trimethylsilyl)nonane-1,6-dione (2I)



2I

According to the general procedure, the 1,6-dione **2I** was isolated (petroleum ether/EtOAc = 10 : 1 v/v as the eluent solvent) as a colorless liquid (22.2 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.55 – 7.51 (m, 1H), 7.46 – 7.42 (m, 2H), 2.93 (dd, *J* = 16.2, 5.7 Hz, 1H), 2.78 (dd, *J* = 16.2, 7.7 Hz, 1H), 2.49 – 2.42 (m, 2H), 2.37 – 2.31 (m, 2H), 2.19 – 2.11 (m, 1H), 1.74 – 1.64 (m, 1H), 1.54 – 1.45 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.76 – 0.69 (m, 2H), -0.03 (s, 9H).

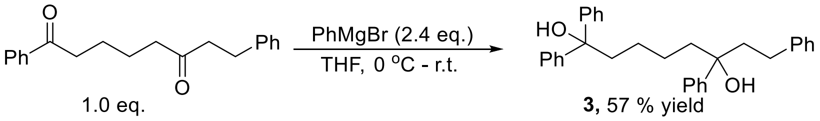
^{13}C NMR (151 MHz, $CDCl_3$) δ 213.8, 201.7, 139.1, 134.8, 130.4, 129.9, 47.6, 41.6, 39.1, 32.8, 31.2, 21.7, 12.2, 0.

HRMS-ESI (m/z): Calcd for $C_{18}H_{29}O_2SiNa$ $[M+H]^+$: 305.1931; found: 305.1933.

IR (KBr):υ 3064, 2953, 2358, 1685, 1592, 1685, 1252, 852, 754, 693, 589 cm^{-1}.

Ⅴ. The Utility of 1,6-Diketone

a) The synthesis of 1,1,6,8-tetraphenyloctane-1,6-diol[4]



At 0 ℃, PhMgBr (0.24 ml, 0.24 mmol, 1 M in THF) was aded in a dry reaction tube under Ar atmosphere, then 1,6-diketone(29.4 mg, 0.1 mmol, 1.0 equiv) was dissolved in 0.5 ml dry THF and slowly added to the reaction tube. Next, the reaction temperature was changed to room temperature and reacted overnight. The reaction was quenched with sat. NH_4Cl (aq.), and extracted with ethyl acetate three times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (elution: ethylacetate/hexanes 1 : 10–1 : 3) to afford **3** (25.5 mg) in 57% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 8H), 7.33 – 7.14 (m, 10H), 7.11 – 7.09 (m, 2H), 2.64 – 2.56 (m, 1H), 2.39 – 2.29 (m, 1H), 2.24 – 2.16 (m, 2H), 2.15 – 2.10 (m, 2H), 1.83 – 1.75 (m, 2H), 1.37 – 1.29 (m, 1H), 1.27 – 1.17 (m, 2H), 1.15 – 1.02 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.1, 147.0, 145.8, 142.4, 128.43, 128.36, 128.2, 128.2, 126.8, 126.5, 126.1, 125.8, 125.3, 78.2, 44.9, 43.2, 41.9, 30.0, 24.1, 23.9.

HRMS-ESI (m/z): Calcd for $C_{32}H_{34}NaO_2$ $[M+Na]^+$: 473.2451; found: 473.2447.

IR (KBr):υ 3562, 3467, 3059, 3027, 2937, 2859, 2357, 1599, 1493, 1449, 973 cm^{-1}.

b) The synthesis of 3-phenyl-1-(2-phenylcyclopent-2-en-1-yl)propan-1-one[5]

In the glovebox, to a dry vial with a magnetic stir bar was added 1,6-dione (29.4 mg, 0.1 mmol, 1.0 equiv), $AlCl_3$ (13.3 mg, 0.1 mmol, 1.0 equiv) and DCM (1.0 mL) was added. The resulting mixture reacted at room temperature overnight. The progress of the reaction was monitored by TLC (eluent: ethyl acetate/hexanes 1:5 v/v). After the reaction is complete, the solvent is removed under vacuum. The crude product was purified by flash chromatography on silica gel (elution: ethylacetate/hexanes 1:5) to afford **4** (21.0 mg) in 76% yield as a colorless oil.

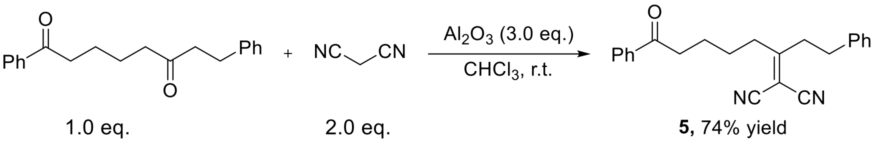
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.24 – 7.18 (m, 3H), 7.18 – 7.13 (m, 1H), 7.10 – 7.03 (m, 2H), 6.38 – 6.36 (m, 1H), 4.05 – 3.99 (m, 1H), 2.85 – 2.72 (m, 3H), 2.63 – 2.56 (m, 3H), 2.36 – 2.25 (m, 1H), 1.98 – 1.89 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.9, 141.4, 141.3, 135.4, 130.6, 128.6, 128.40, 128.36, 127.5, 126.0, 125.8, 59.6, 40.6, 32.6, 29.7, 27.9.

HRMS-ESI (m/z): Calcd for $C_{20}H_{21}O$ $[M+H]^+$: 277.1587; found: 277.1587.

IR (KBr):υ 2929, 2851, 2358, 1704, 1493, 1448, 1083, 752, 695 cm^{-1}.

c) The synthesis of 2-(8-oxo-1,8-diphenyloctan-3-ylidene)malononitrile[6]



In the glovebox, in a dry reaction tube, 1,6-dione (29.4 mg, 0.1 mmol, 1.0 equiv), malononitrile (15.4 mg, 0.2 mmol, 2.0 equiv), and $CHCl_3$ (1.0 ml) were added. Then Al_2O_3 (30.6 mg, 0.3 mmol, 3.0 equiv) was slowly added to the reaction tube and reacted overnight at room temperature. The reaction progress was monitored by TLC (developing solvent: ethyl acetate/hexane 1:8 v/v). The crude product was purified by flash chromatography on silica gel (elution: ethylacetate/hexanes 1 : 8) to afford **5** (20.8 mg) in 74% yield.

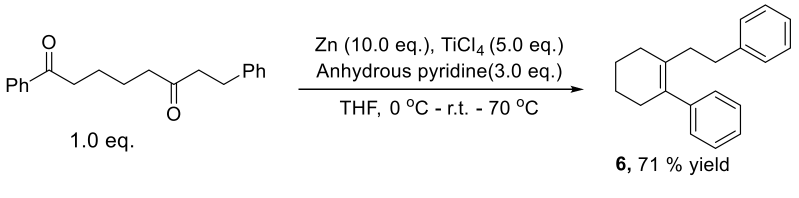
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.95 (m, 2H), 7.60 – 7.56 (m, 1H), 7.50 – 7.46 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 3.03 (t, *J* = 6.8 Hz, 2H), 2.89 (br, 4H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.70 – 1.62 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.3, 184.8, 138.6, 136.8, 133.3, 128.9, 128.7, 128.3, 128.0, 127.1, 111.8, 111.7, 86.7, 37.5, 37.4, 35.9, 34.1, 27.3, 23.6.

HRMS-ESI (m/z): Calcd for $C_{23}H_{23}N_2O$ $[M+H]^+$: 343.1805; found: 343.1804.

IR (KBr):υ 3738, 3064, 3029, 2930, 2865, 2358, 1683, 1589, 1452, 747, 693 cm^{-1}.

d) The synthesis of 6-phenethyl-2,3,4,5-tetrahydro-1,1'-biphenyl[7]



At Ar atmosphere, Zn (1.0 g, 1.5 mmol, 10.0 equiv) and dry THF (2.5 mL) were placed in a dry reaction tube and cooled to 0 °C. Then, $TiCl_4$ (60 uL, 0.5 mmol, 5.0 equiv) was added. The reaction was carried out at room temperature for 0.5 hours and then heated to 70 °C for 2.5 hours. Next, anhydrous pyridine (26 uL, 0.3 mmol, 3.0 equiv) was added at 0 °C and stirred for 10 minutes, added 1,6-diketone (29.4 mg, 0.1 mmol, 1.0 equiv). Finally, the reaction mixture was refluxed at 70 °C overnight. The progress of the reaction was monitored by TLC (eluent: ethyl acetate/hexane 1 : 10 v/v). The reaction was quenched with sat. K_2CO_3 (aq.) and extracted three times with ethyl acetate. The combined organics were washed with brine, dried over Na_2SO_4, filtered, and then concentrated. The crude product was purified by flash chromatography on silica gel (elution: ethylacetate/hexanes 1 : 50 – 1 : 10) to afford **6** (19.5 mg) in 71% yield as a colorless oil.

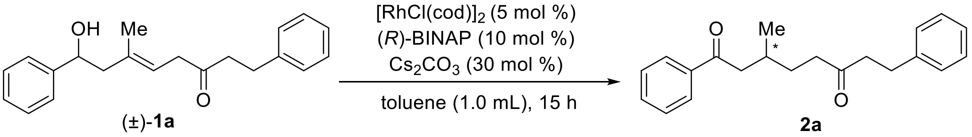
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.21 – 7.17 (m, 3H), 7.14 – 7.10 (m, 1H), 7.03 – 6.95 (m, 4H), 2.64 – 2.60 (m, 2H), 2.21 (br, 2H), 2.17 – 2.13 (t, *J* = 7.8 Hz, 4H), 1.73 – 1.69 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 142.4, 134.0, 132.2, 128.4, 128.21, 128.16, 128.0, 125.9, 125.6, 36.5, 34.9, 32.5, 29.0, 23.5, 23.2.

IR (KBr):υ 2923, 2856, 1668, 1452, 1261, 1081, 1023, 802, 752,699 cm^{-1}.

Ⅵ. Preliminary Asymmetric Studies

Table S8: Optimization of Temperature[a]

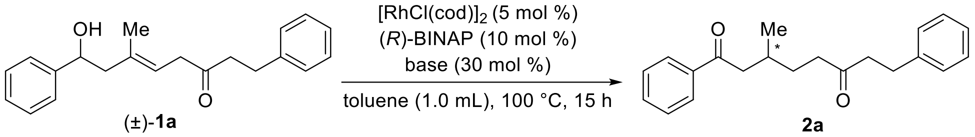


entry	temp (°C)	yield of **2a** (%) [b]	ee% of **2a** (%) [c]
1	60	13	6
2	80	34	4

3	**100**	**65**	**28**
4	110	61	28

[a]All the reactions were performed with **1a** (0.1 mmol), [Rh(cod)Cl]$_2$ (5 mol %), (*R*)-BINAP (10 mol %) and Cs_2CO_3 (30 mol %) in toluene (1.0 mL) under N_2 atmosphere for 15 h. [b]Isolated yield. [c]Enantiomeric excess was determined by chiral HPLC (Daicel Chiralcel OJ-H, hexane/isopropyl alcohol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm), t^1 = 27.9 min (major), t^2 = 34.2 min (minor).

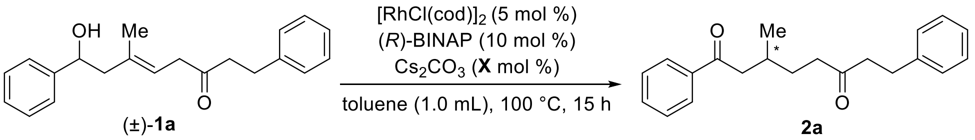
Table S9: Optimization of Base[a]



entry[a]	base	yield of **2a** (%) [b]	ee% of **2a** (%) [c]
1	CsOAc	13	28
2	**Cs_2CO_3**	**71**	**29**
3	K_2CO_3	25	29
4	Ag_2CO_3	61	28
5	AgOTf	N.R.	-
6	DBU	36	26

[a]All the reactions were performed with **1a** (0.1 mmol), [Rh(cod)Cl]$_2$ (5 mol %), (*R*)-BINAP (10 mol %) and base (30 mol %) in toluene (1.0 mL) at 100 ℃ under N_2 atmosphere for 15 h.[b]Isolated yield.[c]Enantiomeric excess was determined by chiral HPLC (Daicel Chiralcel OJ-H, hexane/isopropyl alcohol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm), t^1 = 27.9 min (major), t^2 = 34.2 min (minor)

Table S10: Optimization of the amount of Base[a]

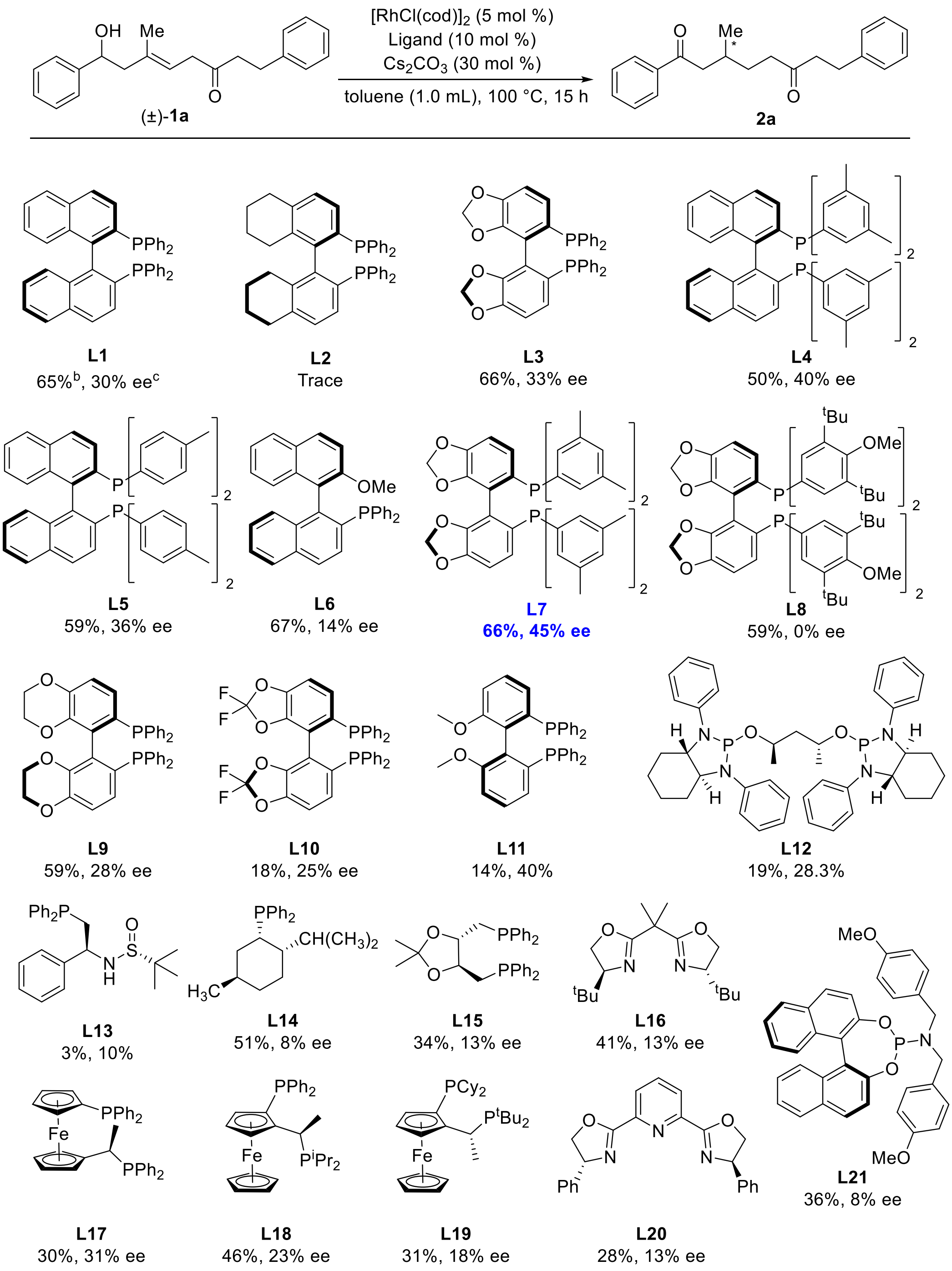


entry[a]	X	yield of **2a** (%) [b]	ee% of **2a** (%) [c]

1	10	23	12
2	**30**	**71**	**33**
3	100	65	30
4	200	69	31

[a]All the reactions were performed with **1a** (0.1 mmol), $[Rh(cod)Cl]_2$ (5 mol %), (*R*)-BINAP (10 mol %) and Cs_2CO_3 (X mol %) in toluene (1.0 mL) at 100 °C under N_2 atmosphere for 15 h. [b]Isolated yield. [c]Enantiomeric excess was determined by chiral HPLC (Daicel Chiralcel OJ-H, hexane/isopropyl alcohol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm), t^1 = 27.9 min (major), t^2 = 34.2 min (minor).

Table S11: Optimization of Ligand[a]



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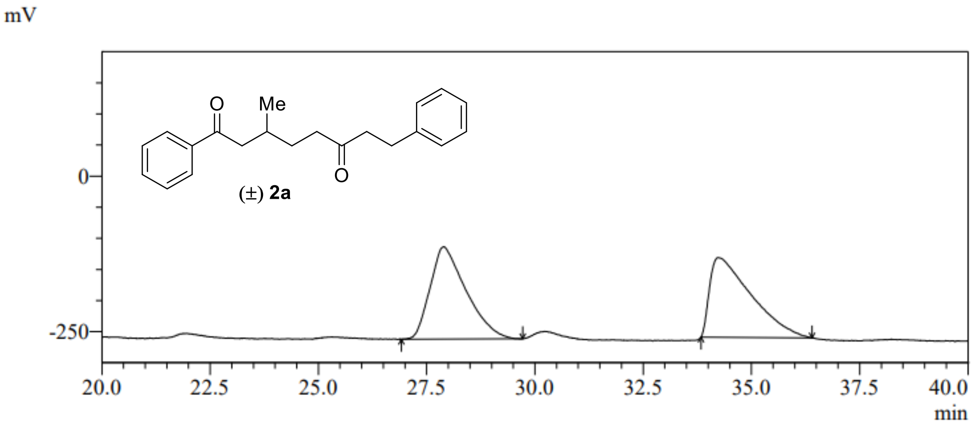
[a]All the reactions were performed with **1a** (0.1 mmol), $[Rh(cod)Cl]_2$ (5 mol %), Ligand (10 mol %) and Cs_2CO_3 (30 mol %) in toluene (1.0 mL) at 100 °C under N_2 atmosphere for 15 h. [b]Isolated yield.[c]Enantiomeric excess was determined by chiral HPLC (Daicel Chiralcel OJ-H, hexane/isopropyl alcohol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm), t^1 = 26.0 min (major), t^2 = 34.8 min (minor).

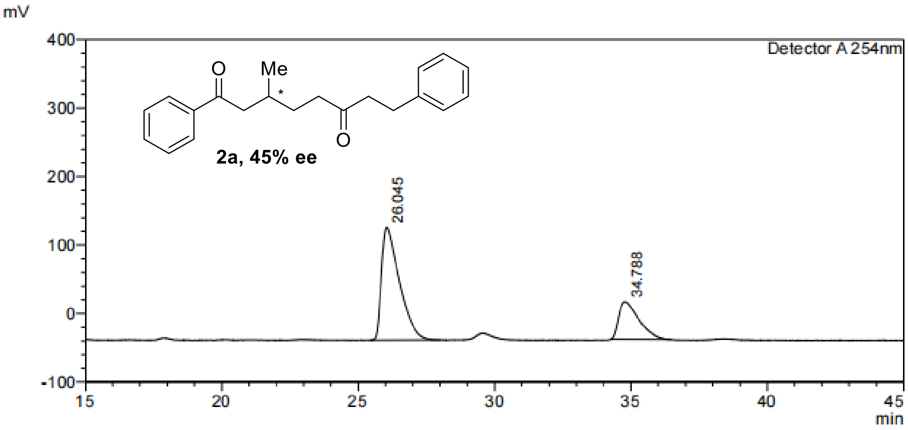


Peak Table

Detector A 254nm

Peak#	Ret. Time	S/N	Noise	Area	Height	Area%
1	27.897	127.25	1165.76	8577323	148338	50.087
2	34.229	110.04	1165.76	8547681	128282	49.913
Total				17125004	276620	100.000

<Chromatogram>



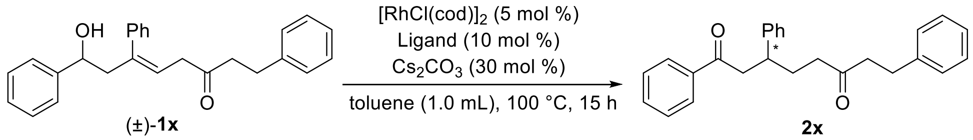
<Peak Table>

Detector A 254nm

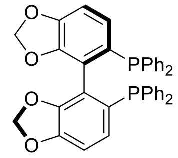
Peak#	Ret. Time	Area	Height	Area%
1	26.045	7509624	164438	72.714
2	34.788	2817932	54401	27.286
Total		10327555	218839	100.000

Figure 3. The HPLC data of **2a** using L7 as chiral ligand

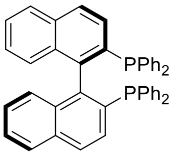
Table S12: Optimization of Ligand using **1x** as starting material[a]



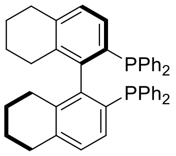
(±)-**1x** **2x**



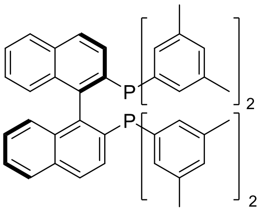
L1
33%, 77% ee



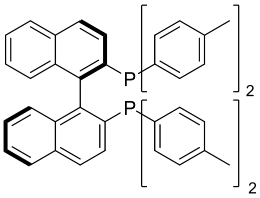
L2
33%[b], 85% ee[c,d]



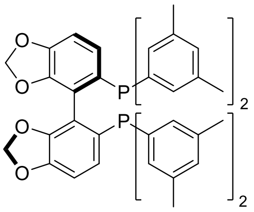
L3
Trace



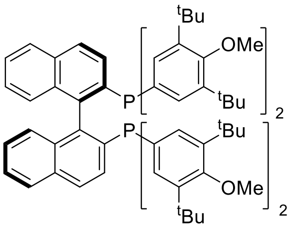
L4
39%, 64% ee



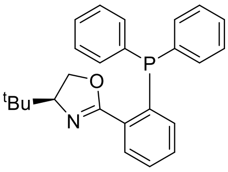
L5
18%, 67% ee



L7
30%, 78% ee



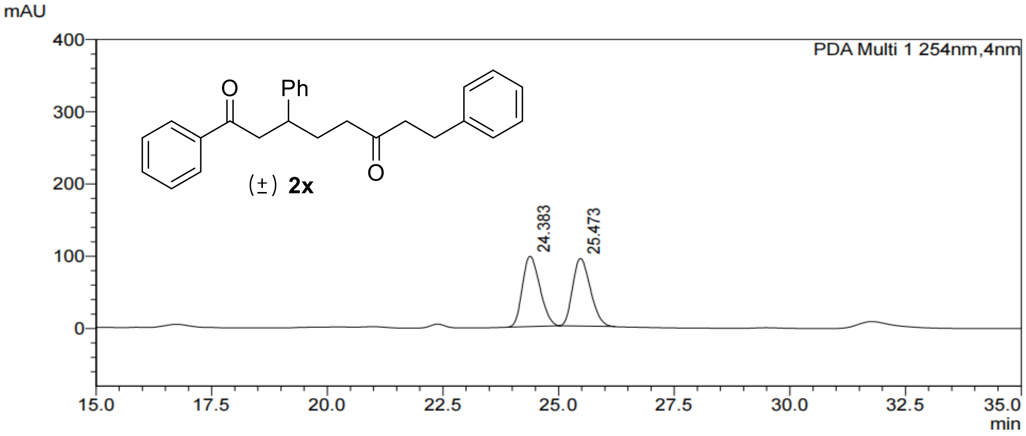
L8
33%, 77% ee



L22
10%, 10% ee

[a]All the reactions were performed with **1x** (0.1 mmol), [Rh(cod)Cl]$_2$ (5 mol %), Ligand (10 mol %) and CsCO$_3$ (30 mol %) in toluene (1.0 mL) at 100 °C under N$_2$ atmosphere for 15 h.[b]Isolated yield.[c]Enantiomeric excess was determined by chiral HPLC (Daicel Chiralcel IH, hexane/isopropyl alcohol = 91/9, flow rate = 0.5 mL/min, λ = 254 nm), t^1 = 24.1 min (major), t^2 = 25.4 min (minor).[d]Optical rotation: $[\alpha]_D^{22}$ = -2 (C = 0.1, CH$_2$Cl$_2$)

<Chromatogram>

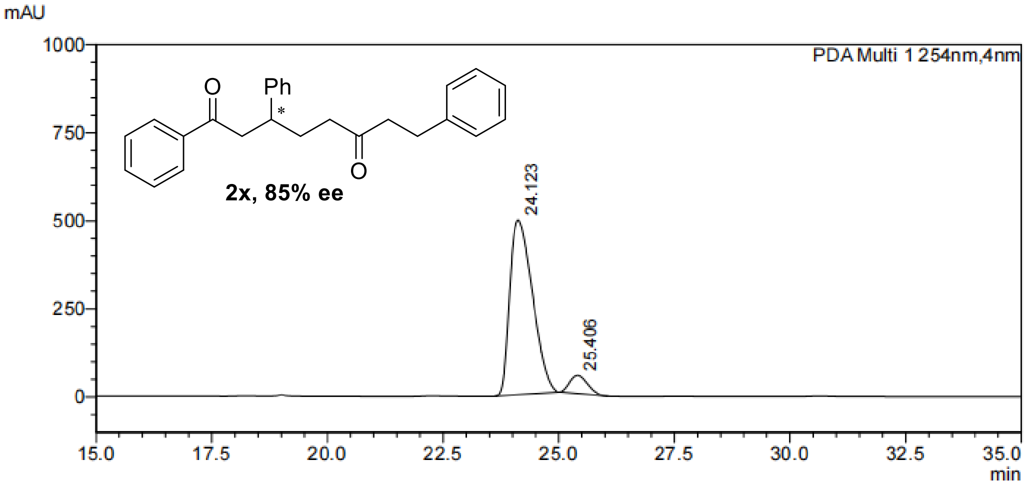


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Peak Start	Peak End	Area	Height	Area%
1	24.383	23.904	25.003	2551014	97205	50.491
2	25.473	25.013	26.197	2501395	93613	49.509
Total				5052409	190818	100.000

<Chromatogram>



<Peak Table>

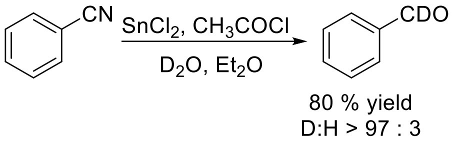
PDA Ch1 254nm

Peak#	Ret. Time	Peak Start	Peak End	Height	Area	Area%
1	24.123	23.637	25.024	495763	16984248	92.519
2	25.406	25.035	26.037	51453	1373255	7.481
Total				547216	18357503	100.000

Figure 4. The HPLC data of **2x** using (*R*)-BINAP as chiral ligand

Ⅶ. Mechanism Studies

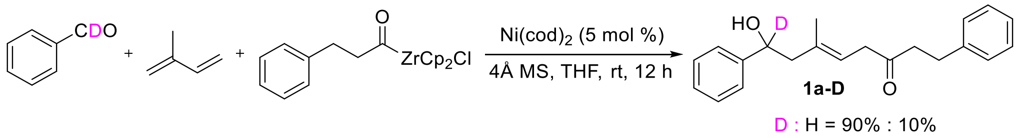
Synthesis of Benzaldehyde-D[8]



To a solution of anhydrous diethyl ether (10 mL), anhydrous stannous chloride (3.7g, 20 mmol) and acetyl chloride (6.28 g, 80 mmol) at –10 °C was added deuterium oxide (1.5 g, 75 mmol) slowly dropwise such that the temperature did not rise above 10 °C. To the homogeneous solution was added benzonitrile (1.03 g, 10 mmol), and stirring was continued for 12 h at room temperature. The precipitated crystalline stannic chloride complex was filtered away from the solution, washed with ether, dried in the dark. Hydrolysis of the complex to benzaldehyde-D was accomplished upon addition to hot water. Then the aqueous layer was extracted with EA for three times, the combined organic layers were dried and concentrated under reduced pressure, the residue was purified by column chromatography to furnish the Benzaldehyde-D (0.85 g, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 2H), 7.68 – 7.61 (m, 1H), 7.57 – 7.50 (m, 2H).

Synthesis of 8-hydroxy-6-methyl-1,8-diphenyloct-5-en-3-one-8-d[3](1a-D)



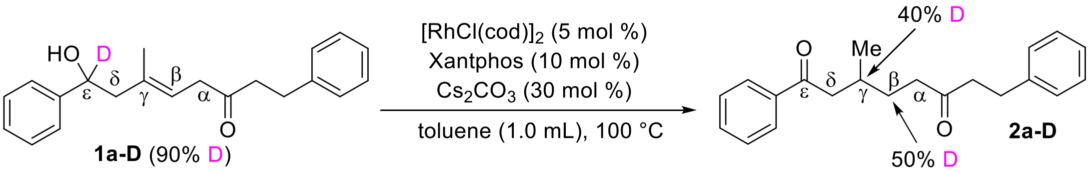
In the glovebox, to a dry vial with a magnetic stir bar was added $Ni(cod)_2$ (5 mol %, 0.01 mmol,2.7 mg) and 1 mL THF, then the solution was added 1,3-diene (1.0 mmol, 5.0 eq.), benzaldehyde-d (0.2 mmol, 1.0 eq.), 4Å molecular sieve (50 mg) and acylzirconocene chloride(0.4 mmol, 2.0 eq.) successively (Note:1,3-diene must be added firstly, acylzirconocene chlorideshould be added in solid phase). The vial was sealed by a rubber stopper, removed from the gloveboxand stirred at ambient temperature for 12 hours. The reaction was quenched by 5 mL HCl aqueoussolution (2 M), then extracted with EtOAc (3 x 10 mL), the combined organic solvents was removedunder vacuo, and the residue was purified by column chromatography on silica gel to give the product **1a-D** as a yellow oil liquid in 80% yield. (TLC monitored by staining with phophomolibdic acid solution in ethanol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 10H), 5.41 (t, *J* = 7.2 Hz, 1H), 3.14 (d, *J* = 3.6 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.61 (br, 1H), 2.44 (s, 2H), 1.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 208.1, 144.2, 141.0, 136.3, 128.6, 128.4, 127.4, 126.2, 125.8, 119.8, 50.0, 43.8, 42.7, 29.8, 16.5.

HRMS-ESI (m/z): Calcd for $C_{21}H_{23}DO_2Na$ $[M+Na]^+$: 332.1731; found: 332.1737.

Synthesis of 3-methyl-1,8-diphenyloctane-1,6-dione(**2a-D**)



In a glove box, [Rh(cod)Cl]$_2$ (0.005 mmol, 2.4 mg, 0.05 equiv.), Xantphos (0.01 mmol, 5.8 mg, 0.1 equiv.), homoallylic alcohol **1a-D** (0.1 mmol, 1.0 equiv.) and toluene (1 mL) was added to a reaction tube sequentially, the Cs_2CO_3 (0.03 mmol, 9.75 mg, 0.3 equiv.) was added at last. The reaction tube's stopper was sealed and wrapped with a sealing film before removing it from the glove box. The reaction mixture was stirred at 100 °C for 15 h. After the reaction was completed, the solvent was concentrated under vacuum, and the crude product was purified by column chromatography. Compound **2a-D** was obtained as a white solid in 64% yield (19.9 mg, eluent: petroleum ether/EtOAc = 10/1, mp = 41.2 °C – 41.8 °C.)

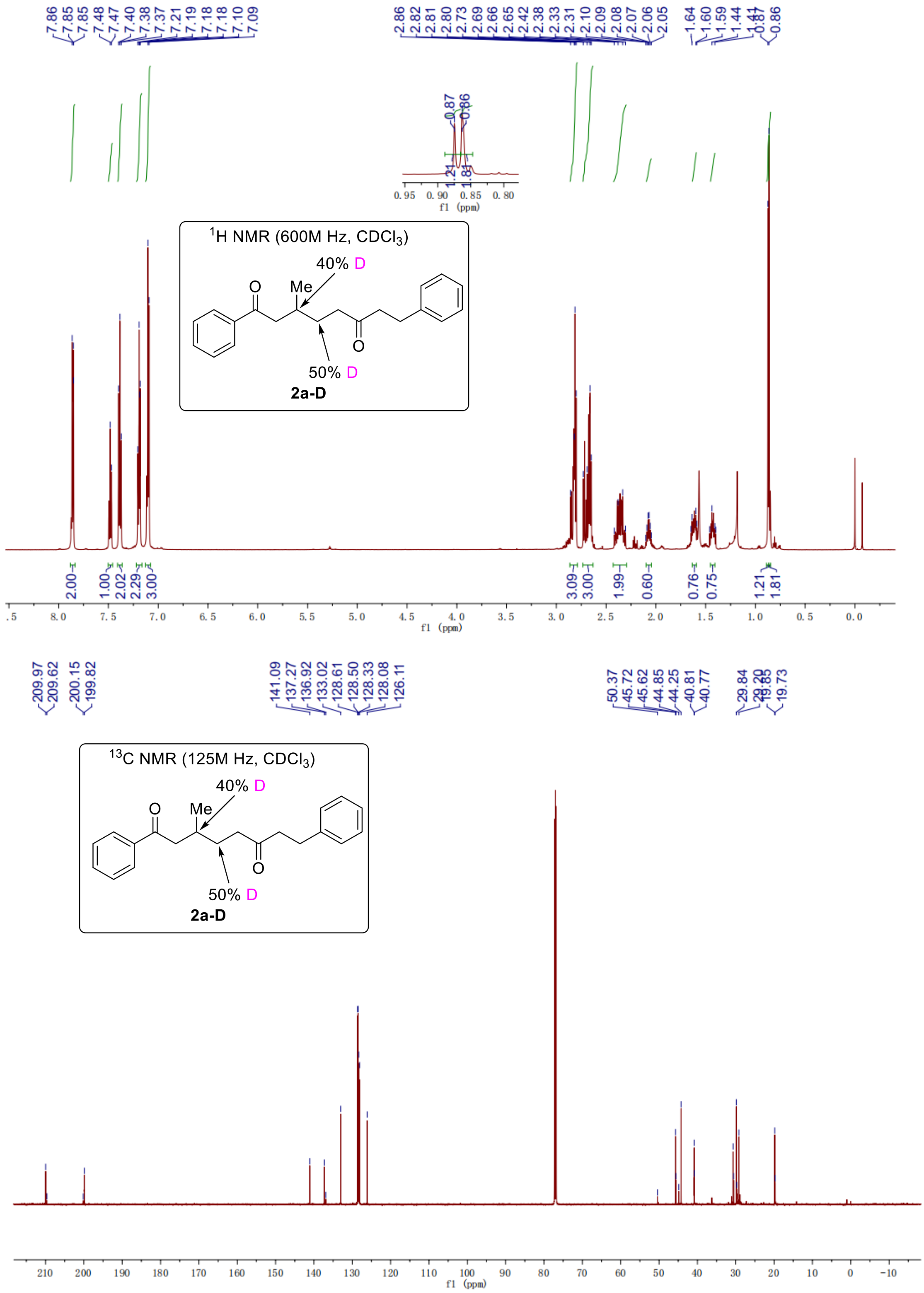
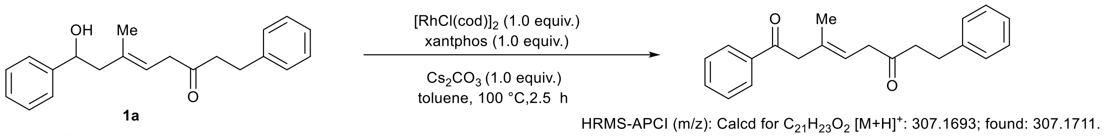


Figure 1. ^{1}H NMR and ^{13}C NMR of 2**a-D.**

The stoichiometric reaction of 1a with [RhCl(cod)]₂, xantphos, and Cs₂CO₃



1a

(0.1 mmol, 1.0 equiv.)

HRMS-APCI (m/z): Calcd for $C_{21}H_{23}O_2$ $[M+H]^+$: 307.1693; found: 307.1711.

In a glovebox, a dry reaction tube was charged with [Rh(cod)Cl]$_2$ (24 mg, 0.05 mmol, 0.5 equiv.), xantphos (58 mg, 0.1 mmol, 1.0 equiv.), and toluene (1.5 mL). The mixture was stirred for 30 min at room temperature. Subsequently, Cs_2CO_3 (32.6 mg, 0.1 mmol, 1.0 equiv.) was added, and stirring was continued for an additional 30 min. A solution of **1a** (30.8 mg, 0.1 mmol, 1.0 equiv.) in toluene (0.5 mL) was then introduced into the reaction mixture. The tube was sealed with a stopper, wrapped with parafilm, and removed from the glovebox. The reaction was stirred at 100 °C for 2.5 h. Then, the mixture was filtered through a Celite pad, and the solvent was concentrated under reduced pressure. The crude product was analyzed by HRMS. The unsaturated 1,6-dione was detected. This observation suggests the presence of an alkoxy rhodium intermediate in the catalytic cycle, with the first (xantphos)Rh–H species being generated via β-H elimination of this intermediate.

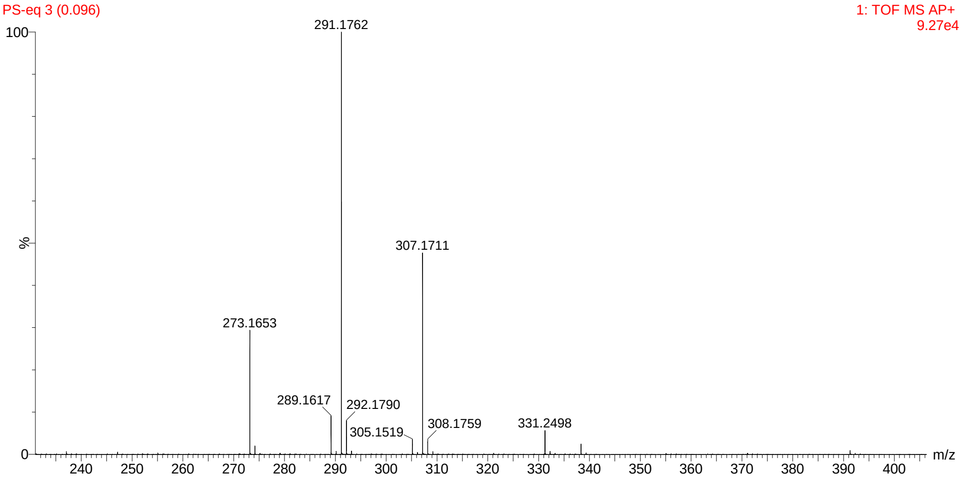
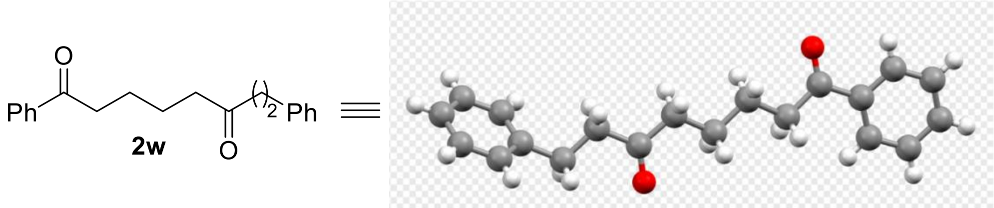


Figure 2. HMRS spectrum of the stoichiometric reaction of **1a** with [RhCl(cod)]$_2$, xantphos, and Cs_2CO_3**.**

Ⅷ.Crystal data of 2w

Single crystal of compound **2w** [$C_{19}H_{20}O_2$] was obtained in hexane and EtOAc using gas phase diffusion method. The CCDC of **2w** is 2390628 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/



Displacement ellipsoids of image are drawn at the 50% probability level.

Identification code	exp_5700_auto
Empirical formula	$C_{20}H_{22}O_2$
Formula weight	294.37
Temperature/K	295.70(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.3649(4)
b/Å	5.54250(10)
c/Å	17.0356(4)
α/°	90
β/°	116.075(2)
γ/°	90
Volume/Å3	1642.33(6)
Z	4
ρcalcg/cm3	1.191

μ/mm-1	0.590
F(000)	632.0
Crystal size/mm3	0.2 × 0.18 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.08 to 153.854
Index ranges	-24 ≤ h ≤ 22, -6 ≤ k ≤ 5, -21 ≤ l ≤ 21
Reflections collected	18261
Independent reflections	3382 [Rint = 0.0313, Rsigma = 0.0209]
Data/restraints/parameters	3382/0/200
Goodness-of-fit on F2	1.088
Final R indexes [I>=2σ (I)]	R1 = 0.0450, wR2 = 0.1271
Final R indexes [all data]	R1 = 0.0512, wR2 = 0.1322
Largest diff. peak/hole / e Å-3	0.19/-0.14

Ⅸ. References

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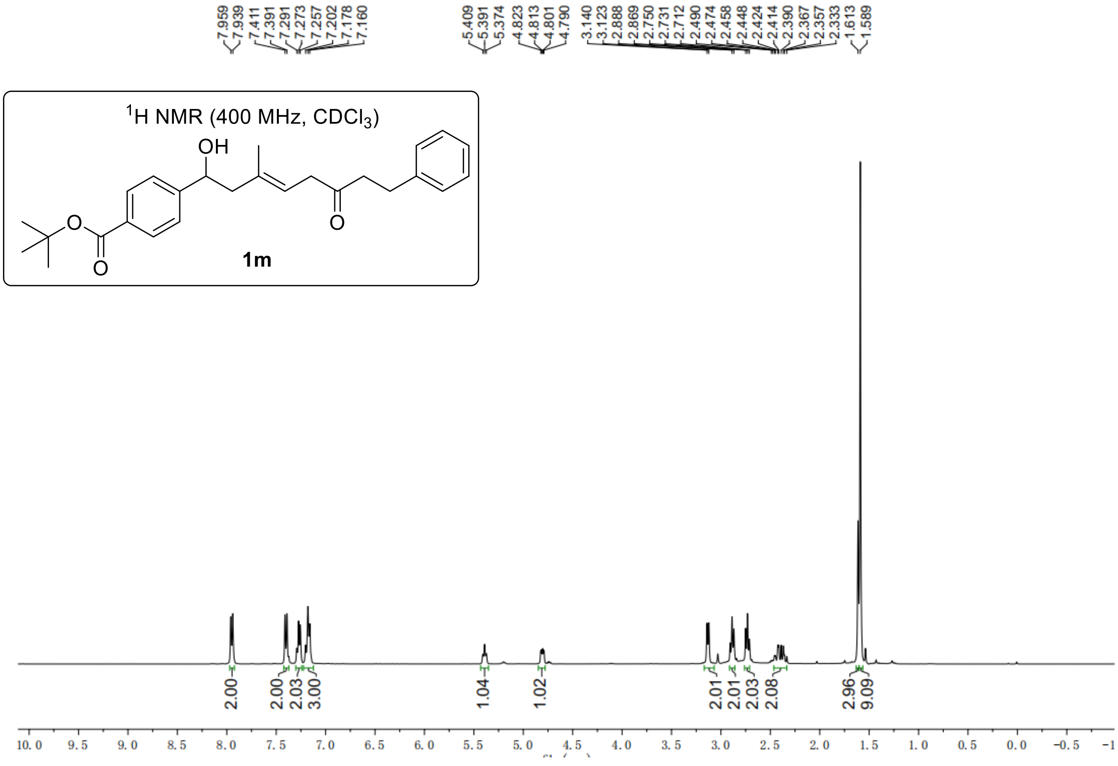
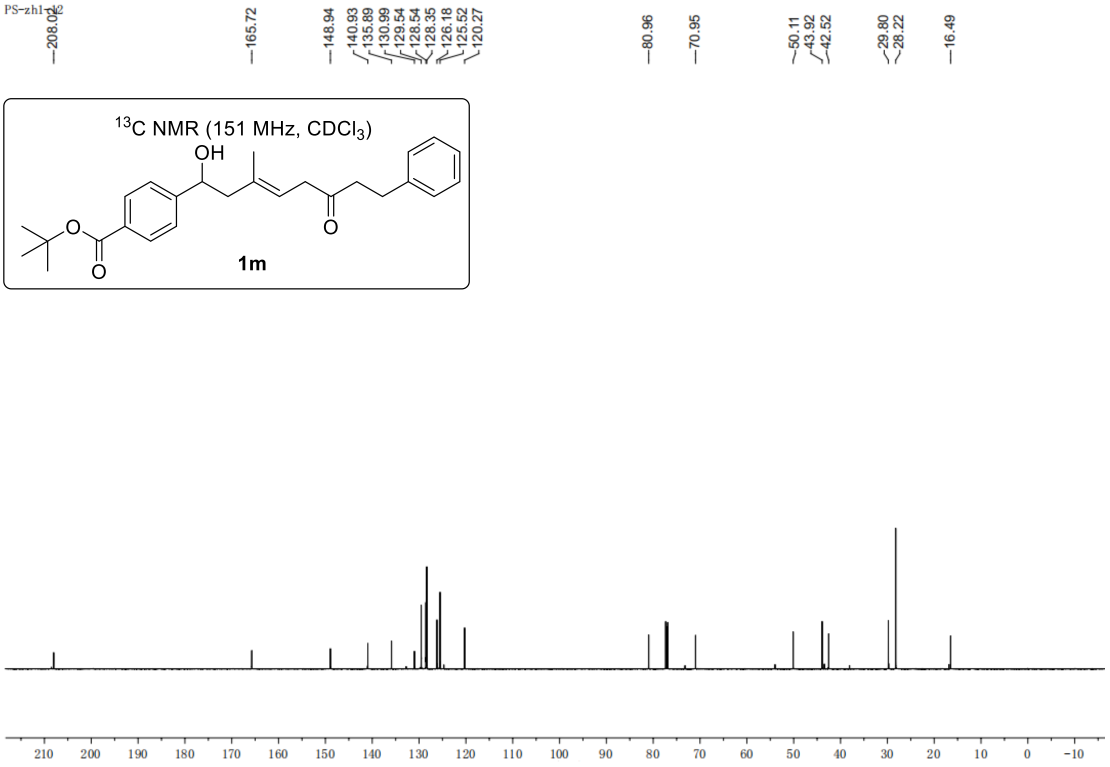
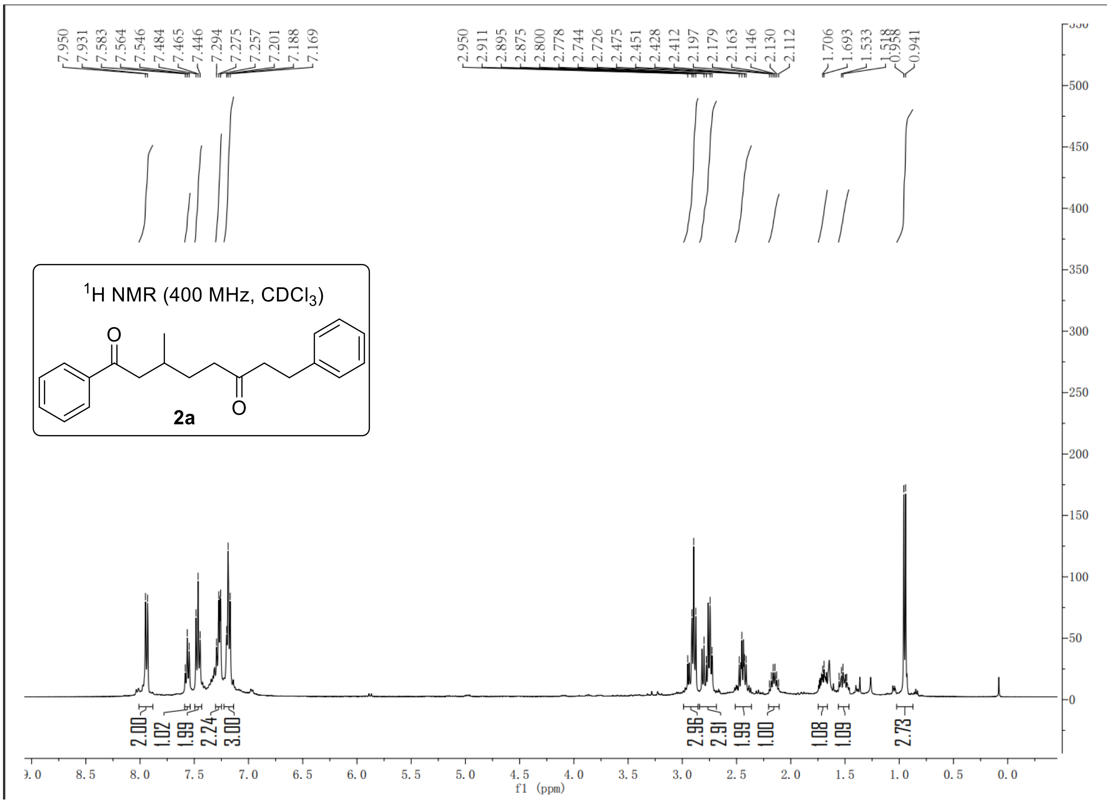
Spectroscopic Data (NMR Spectrum)



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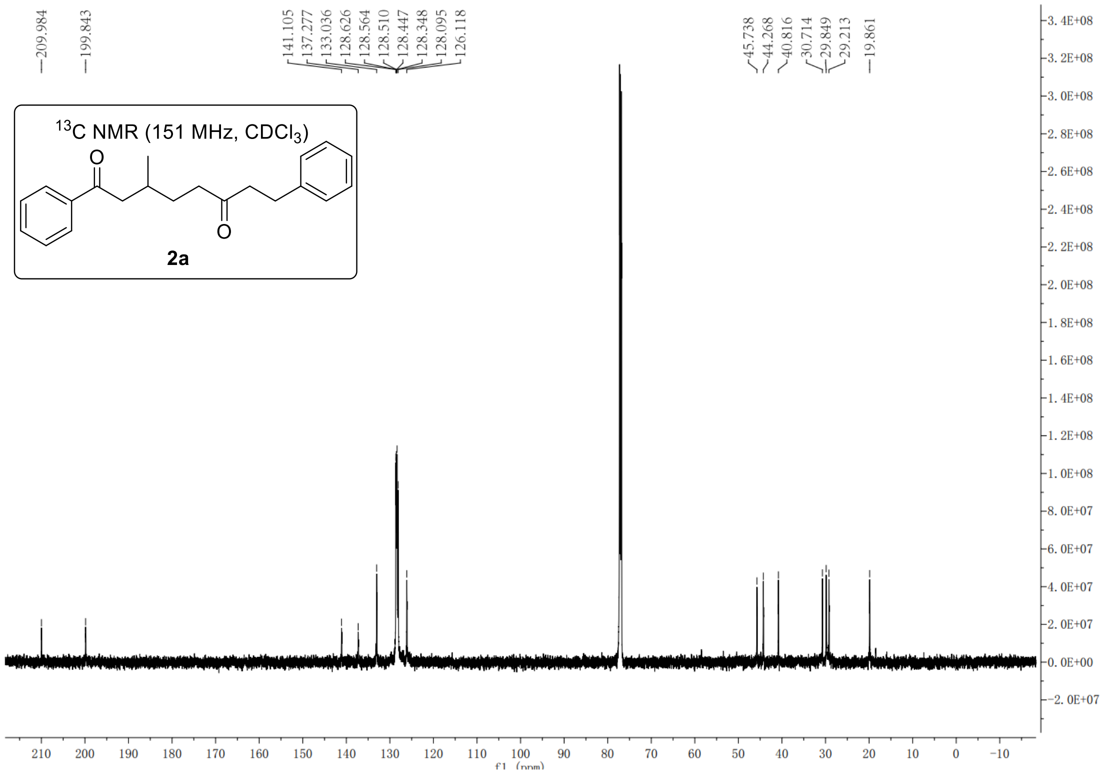
7.583
7.564
7.546
7.484
7.465
7.446
7.294
7.275
7.257
7.201
7.188
7.169
2.950
2.911
2.895
2.875
2.800
2.778
2.744
2.726
2.475
2.451
2.428
2.412
2.197
2.179
2.163
2.146
2.130
2.112
1.706
1.693
1.533
1.518
0.958
0.941
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2a
2.00
1.02
1.99
2.24
3.00
2.96
2.91
1.99
1.00
1.08
1.09
2.73
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0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126.118
45.738
44.268
40.816
30.714
29.849
29.213
19.861
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
3.4E+08
3.2E+08
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
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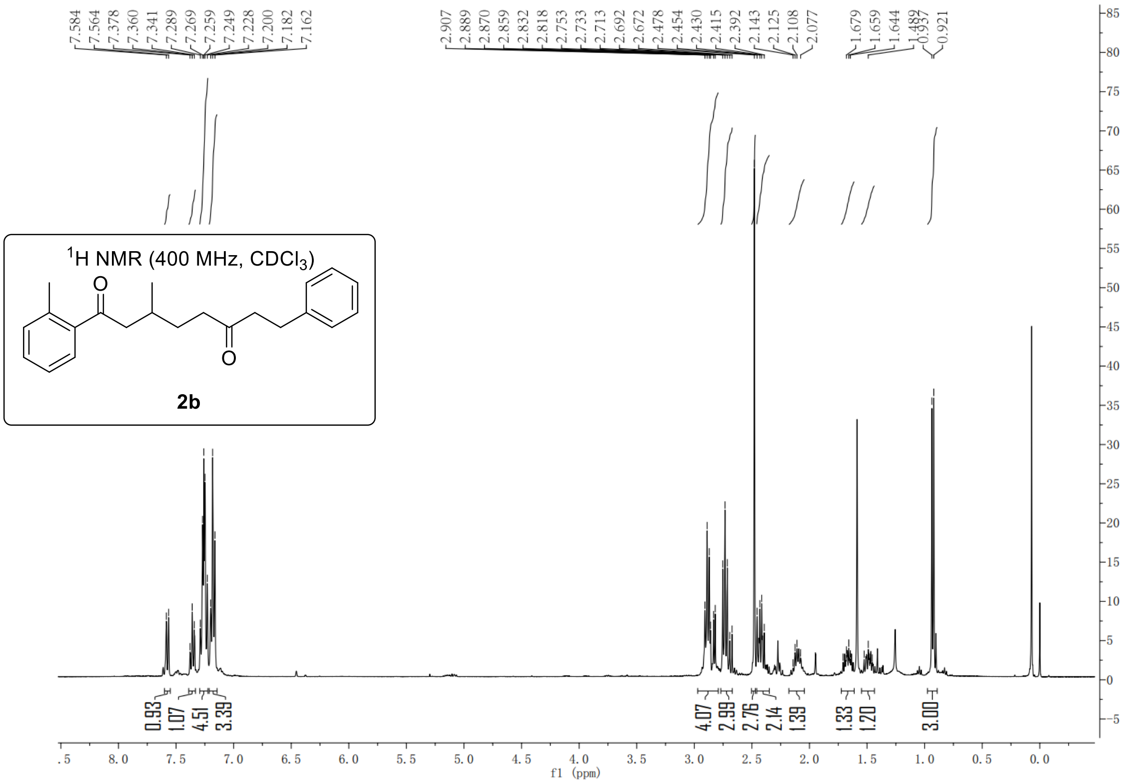

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7.360
7.341
7.289
7.269
7.259
7.249
7.228
7.200
7.182
7.162
2.907
2.889
2.870
2.859
2.832
2.818
2.753
2.733
2.713
2.692
2.672
2.478
2.454
2.430
2.415
2.392
2.143
2.125
2.108
2.077
1.679
1.659
1.644
1.489
0.937
0.921
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2b
0.93
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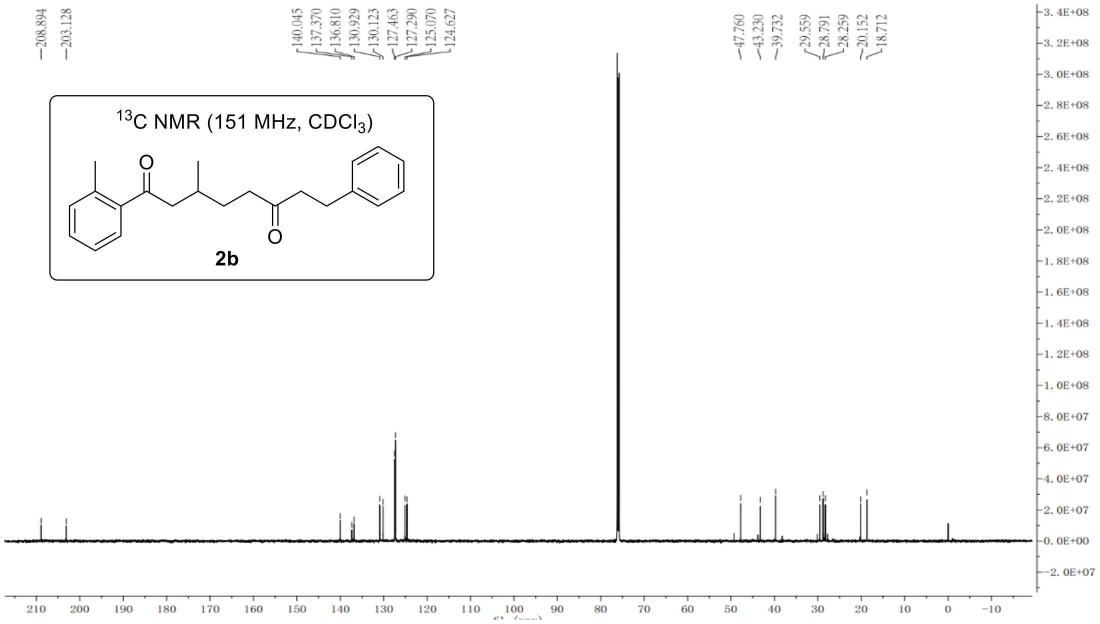
4.51
3.39
4.07
2.99
2.76
2.14
1.39
1.33
1.20
3.00
f1 (ppm)



208.894
203.128
140.045
137.370
136.810
130.929
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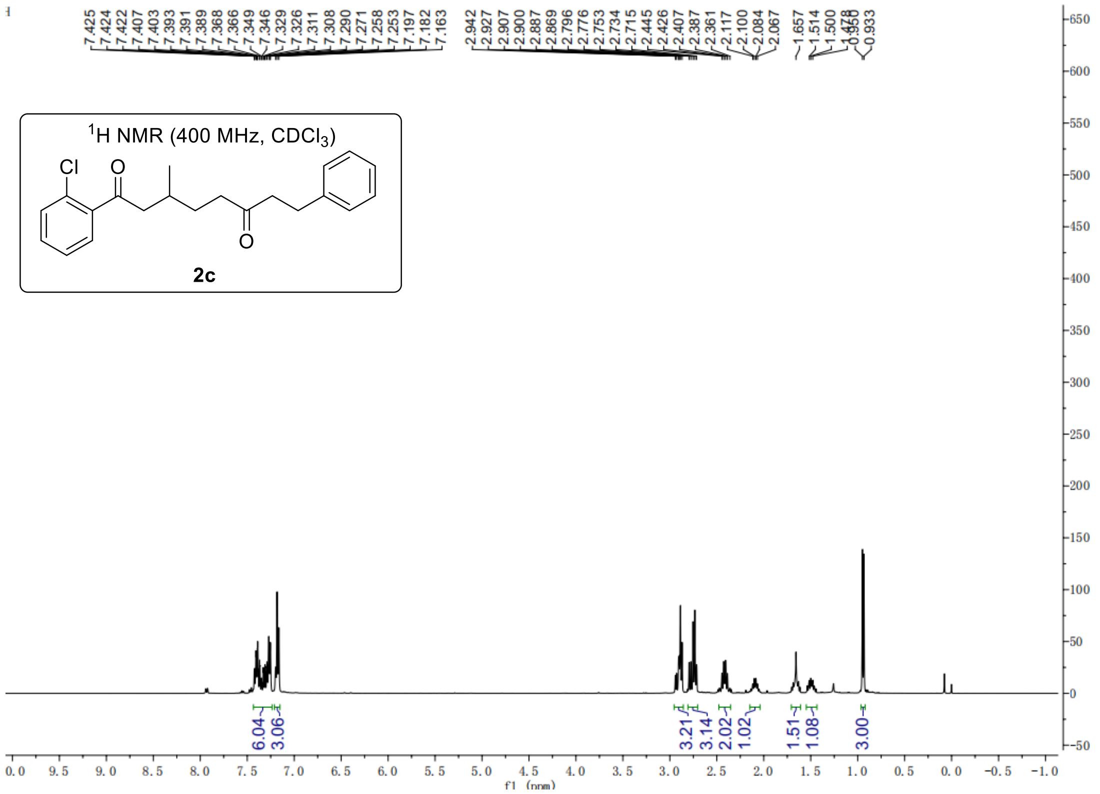
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2b



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7.403
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7.391
7.389
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7.366
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7.346
7.329
7.326
7.311
7.308
7.290
7.271
7.258
7.253
7.197
7.182
7.163
2.942
2.927
2.907
2.900
2.887
2.869
2.796
2.776
2.753
2.734
2.715
2.445
2.426
2.407
2.387
2.361
2.117
2.100
2.084
2.067
1.657
1.514
1.500
1.478
0.950
0.933
^{1}H NMR (400 MHz, CDCl$_3$)
Cl
O
O
2c
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3.06
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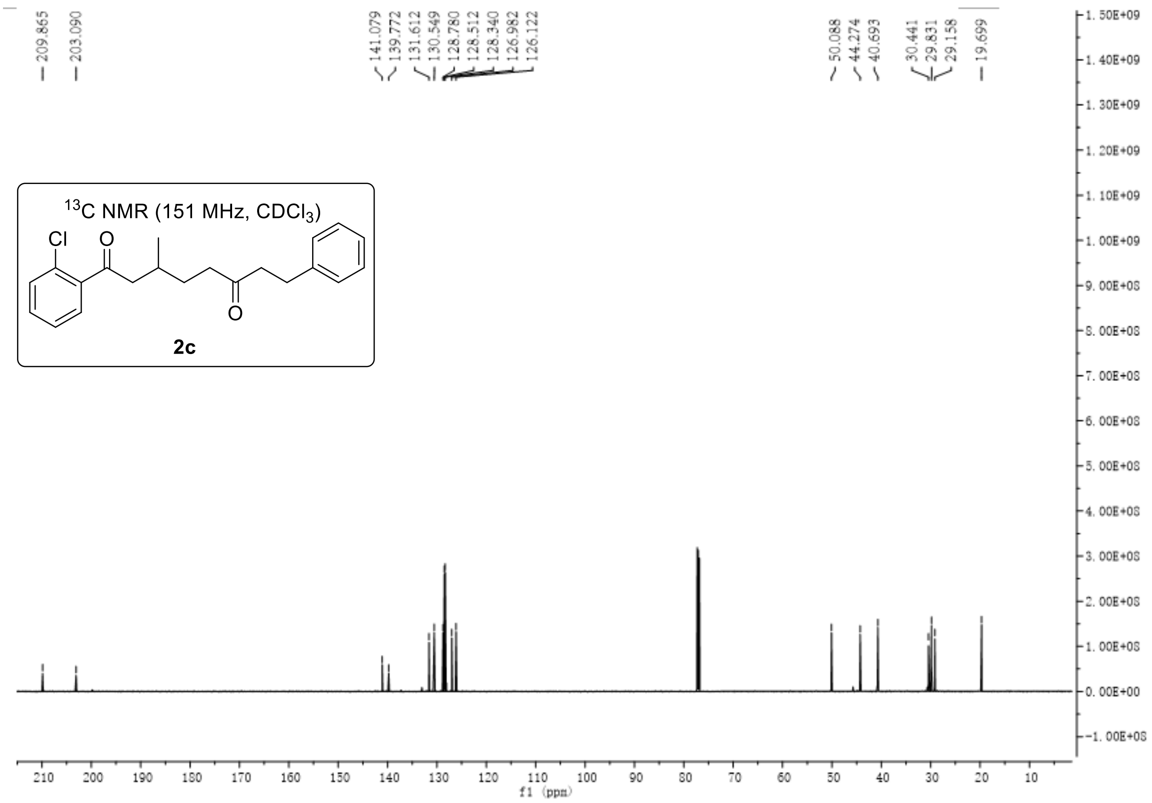
3.14
2.02
1.02
1.51
1.08
3.00
f1 (ppm)



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44.274
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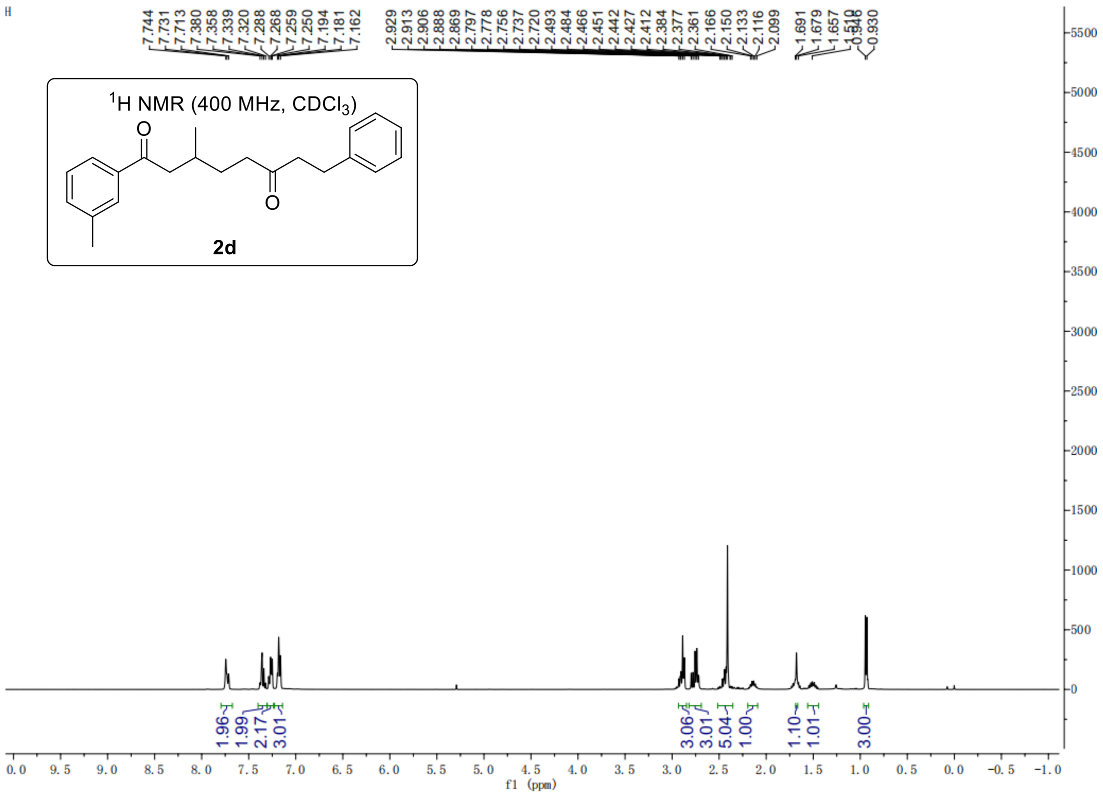
Cl
O
O
2c
f1 (ppm)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7.250
7.194
7.181
7.162
2.929
2.913
2.906
2.888
2.869
2.797
2.778
2.756
2.737
2.720
2.493
2.484
2.466
2.451
2.442
2.427
2.412
2.384
2.377
2.361
2.166
2.150
2.133
2.116
2.099
1.691
1.679
1.657
0.946
0.930
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2d
1.96
1.99
2.17
3.01
3.06
3.01
5.04
1.00
1.10
1.01
3.00
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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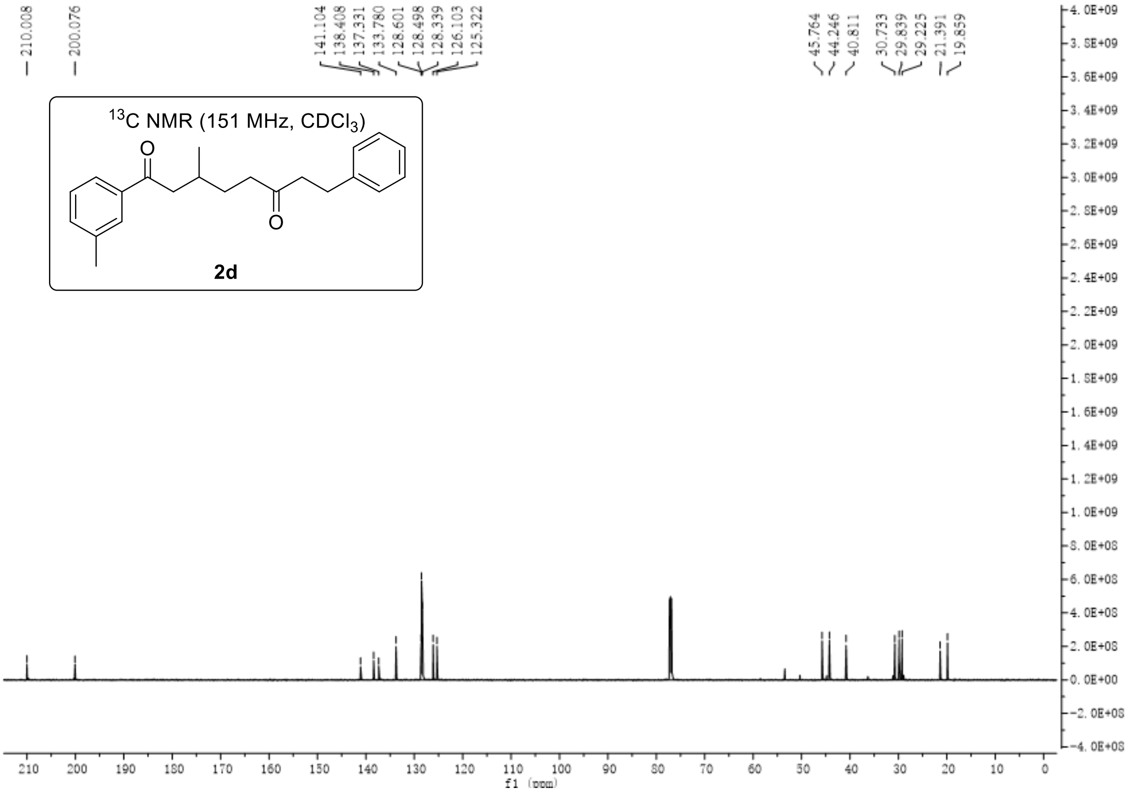
f1 (ppm)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40.811
30.733
29.839
29.225
21.391
19.859
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O
O
2d
4.0E+09
3.8E+09
3.6E+09
3.4E+09
3.2E+09
3.0E+09
2.8E+09
2.6E+09
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2.0E+09
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1.4E+09
1.2E+09
1.0E+09
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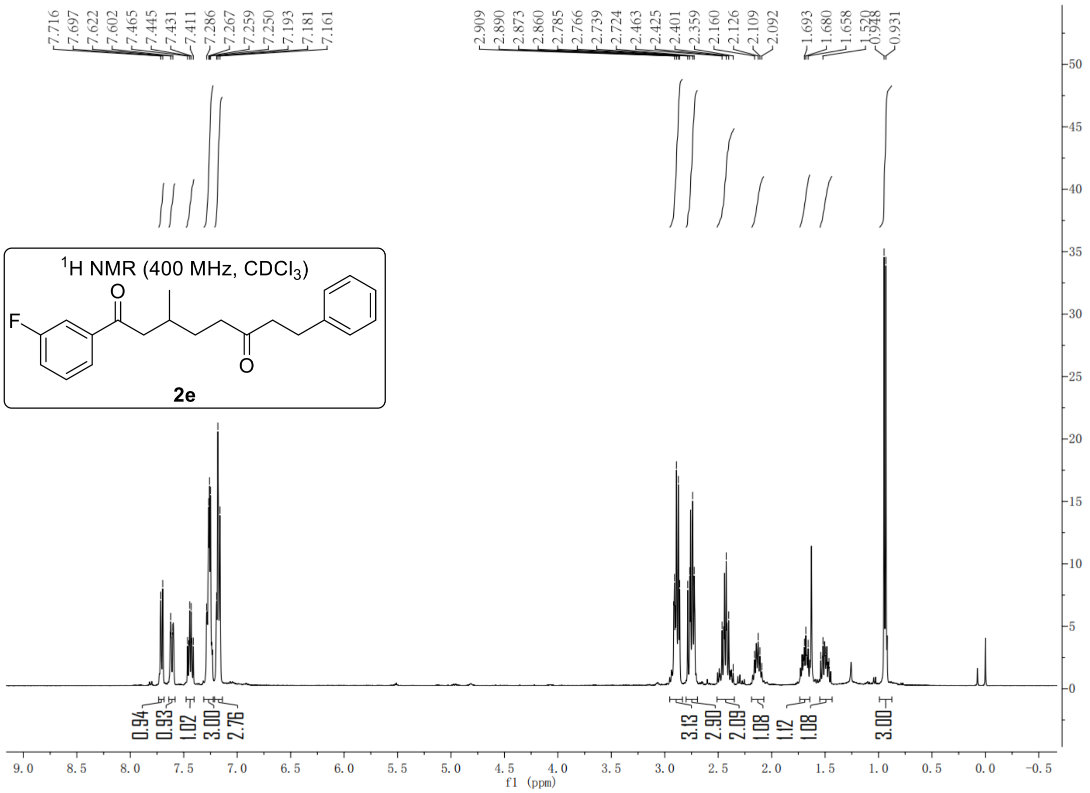
6.0E+08
4.0E+08
2.0E+08
0.0E+00
-2.0E+08
-4.0E+08
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.267
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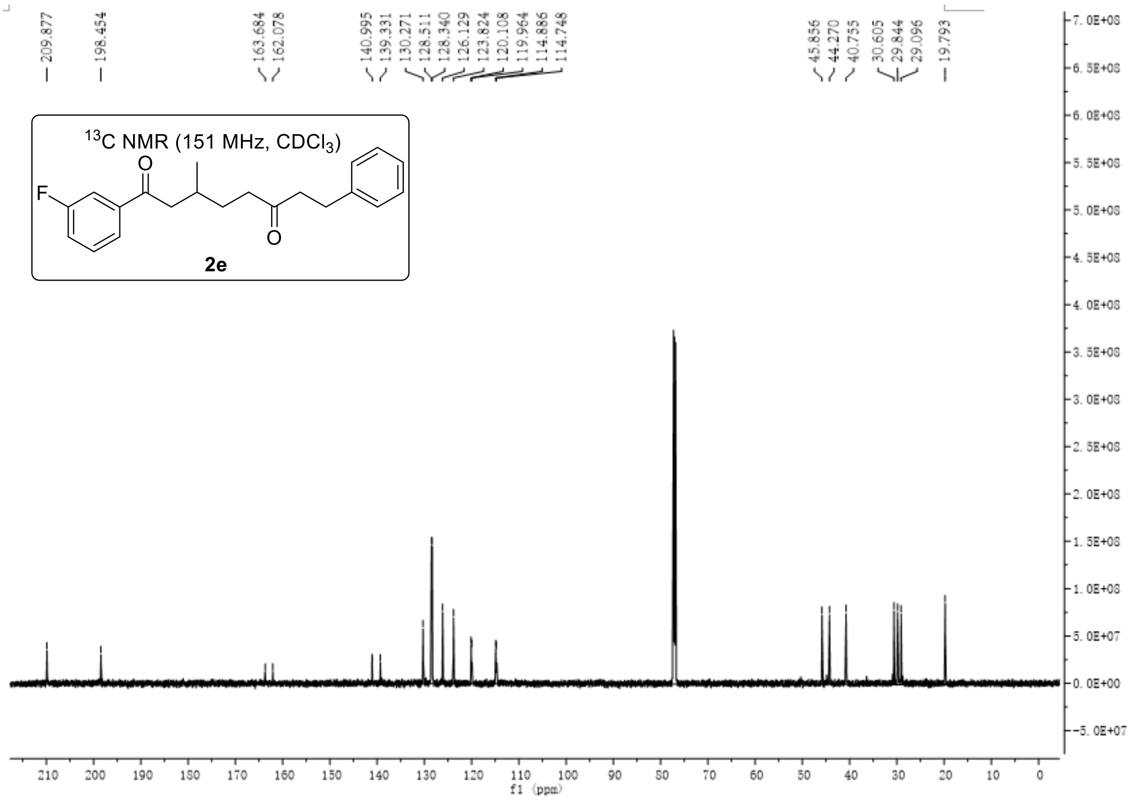
7.250
7.193
7.181
7.161
2.909
2.890
2.873
2.860
2.785
2.766
2.739
2.724
2.463
2.425
2.401
2.359
2.160
2.126
2.109
2.092
1.693
1.680
1.658
1.520
0.948
0.931
^{1}H NMR (400 MHz, CDCl$_3$)
F
O
O
2e
0.94
0.93
1.02
3.00
2.76
3.13
2.90
2.09
1.08
1.12
1.08
3.00
f1 (ppm)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126.129
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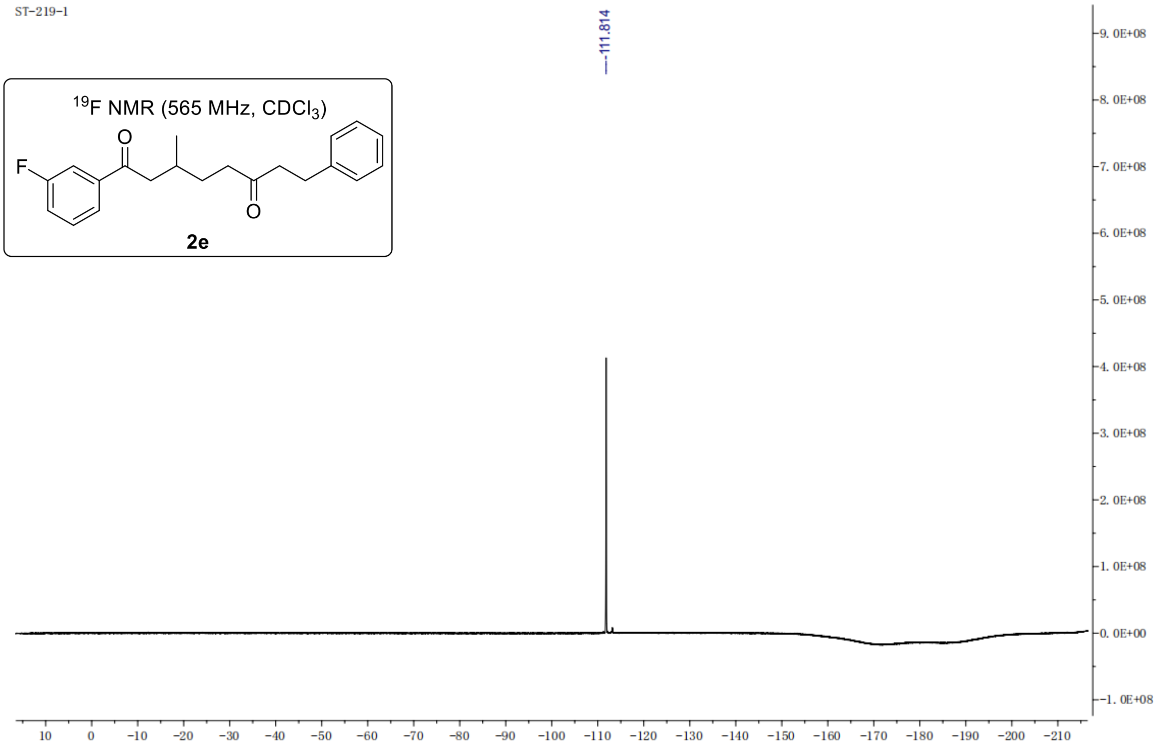
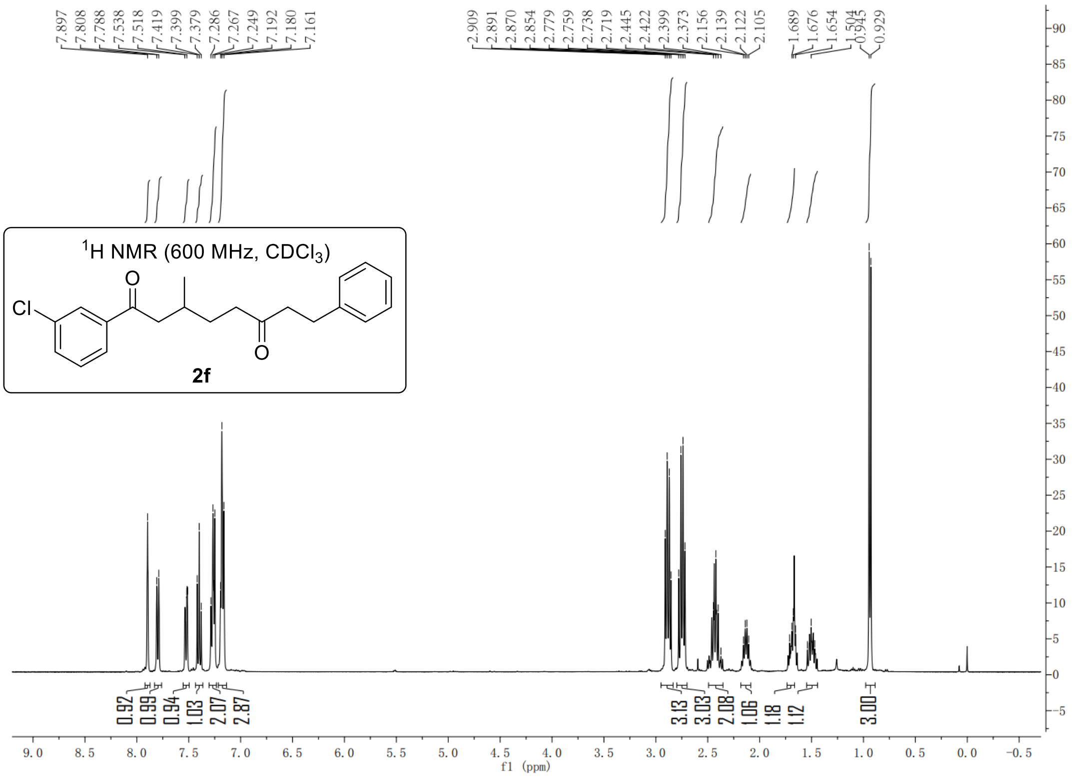
114.885
114.748
45.856
44.270
40.755
30.605
29.844
29.096
19.793
^{13}C NMR (151 MHz, CDCl$_3$)
F
O
O
2e
f1 (ppm)



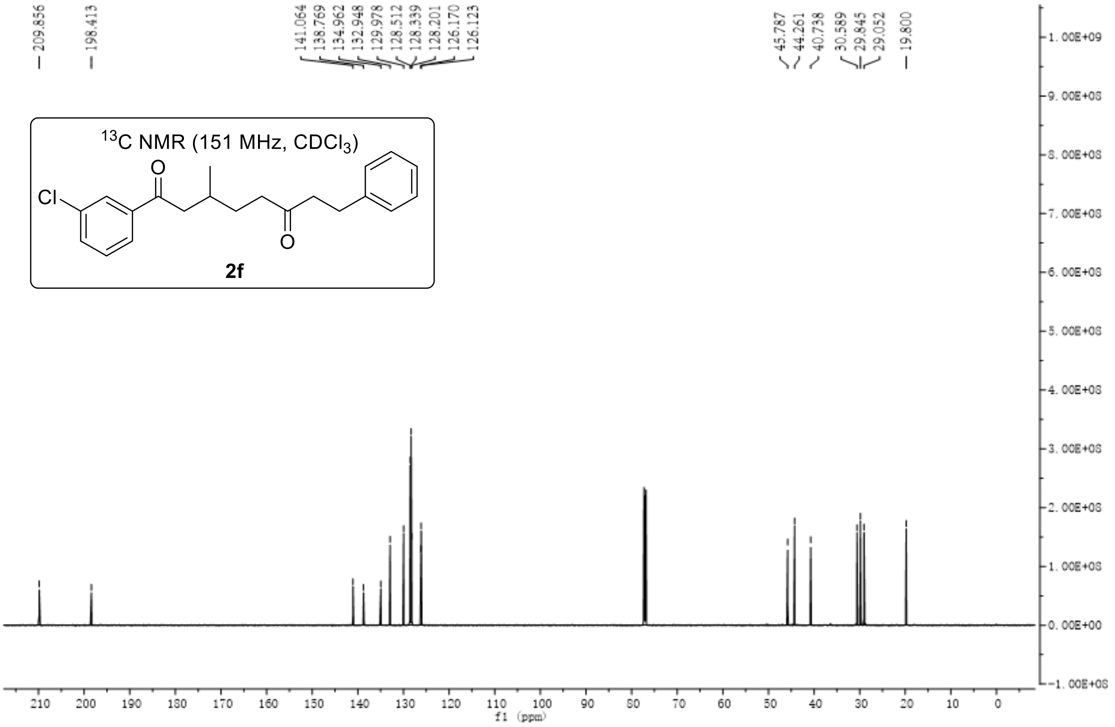
^{19}F NMR (565 MHz, CDCl$_3$)

2e



^{1}H NMR (600 MHz, CDCl$_3$)

2f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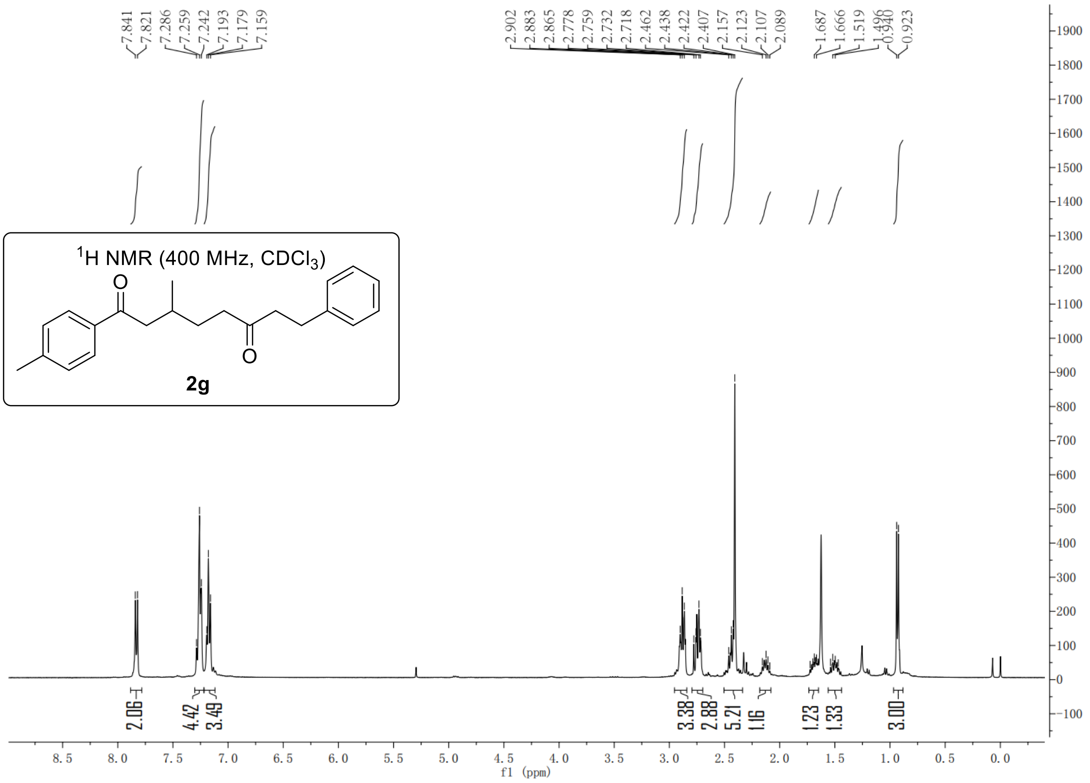
126.123
45.787
44.261
40.738
30.589
29.845
29.052
19.800
^{13}C NMR (151 MHz, CDCl$_3$)
Cl
O
O
2f
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.242
7.193
7.179
7.159
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2.883
2.865
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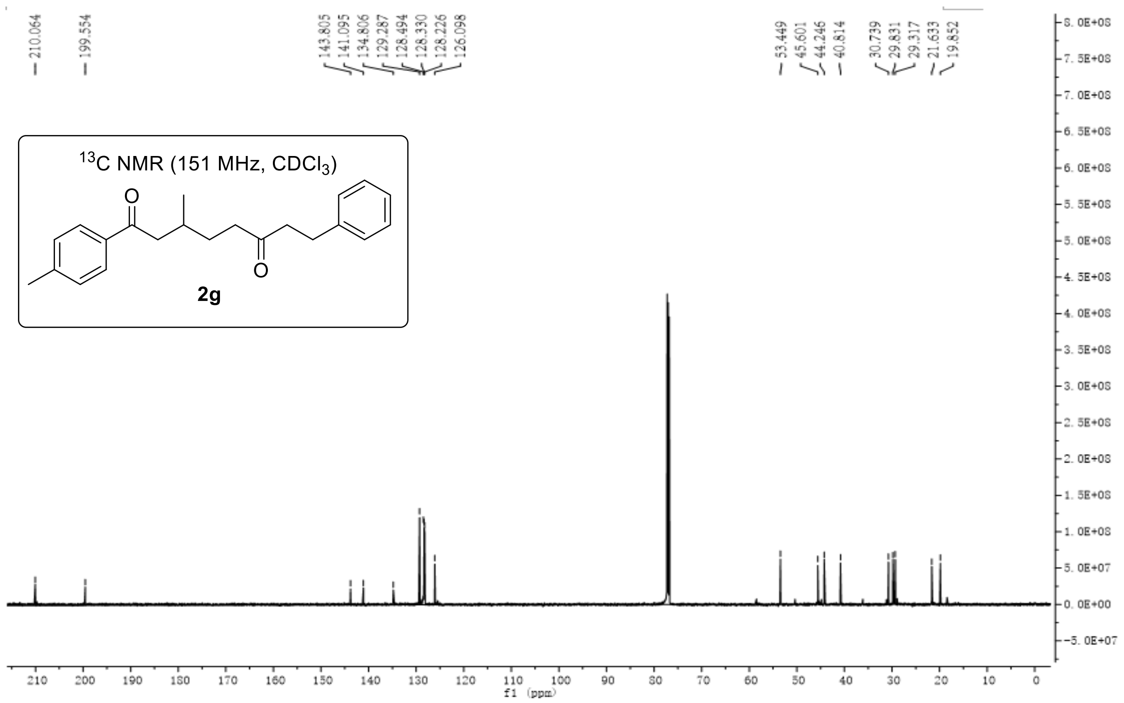
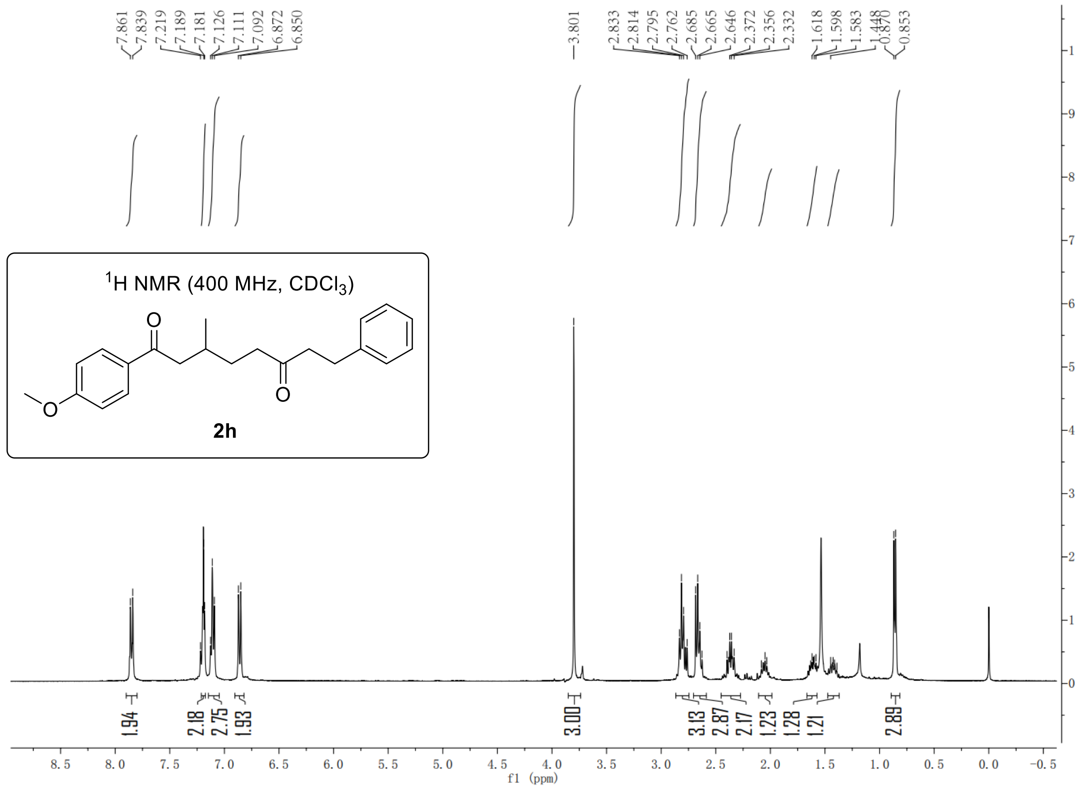
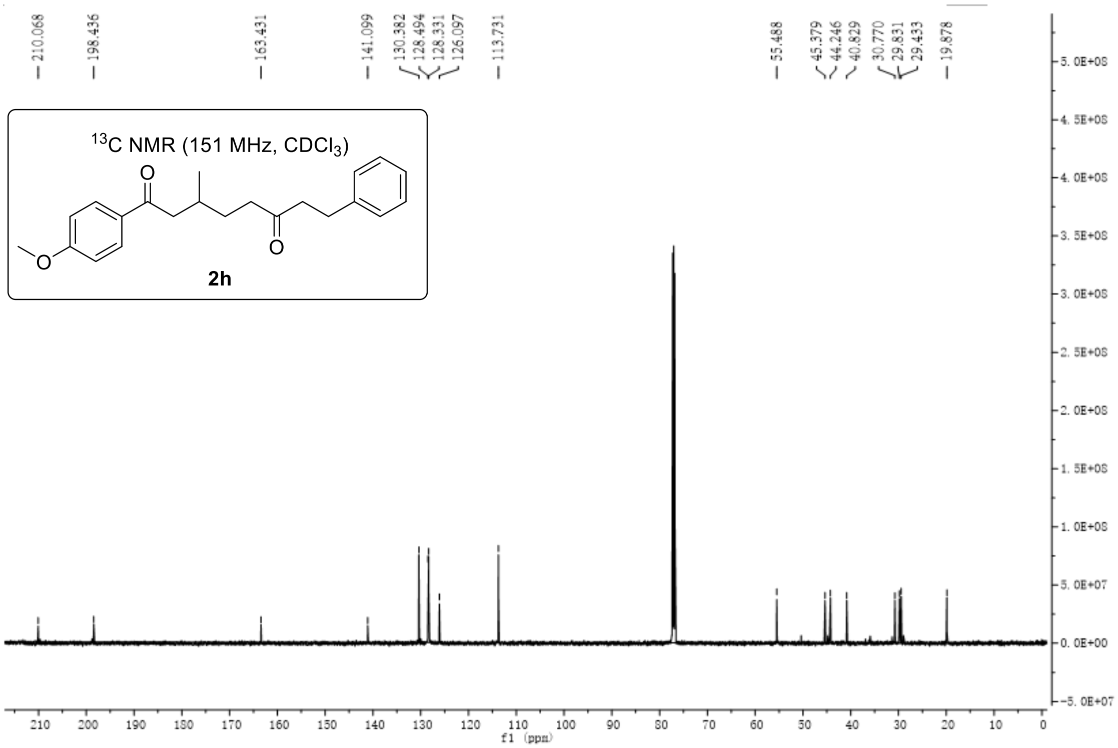
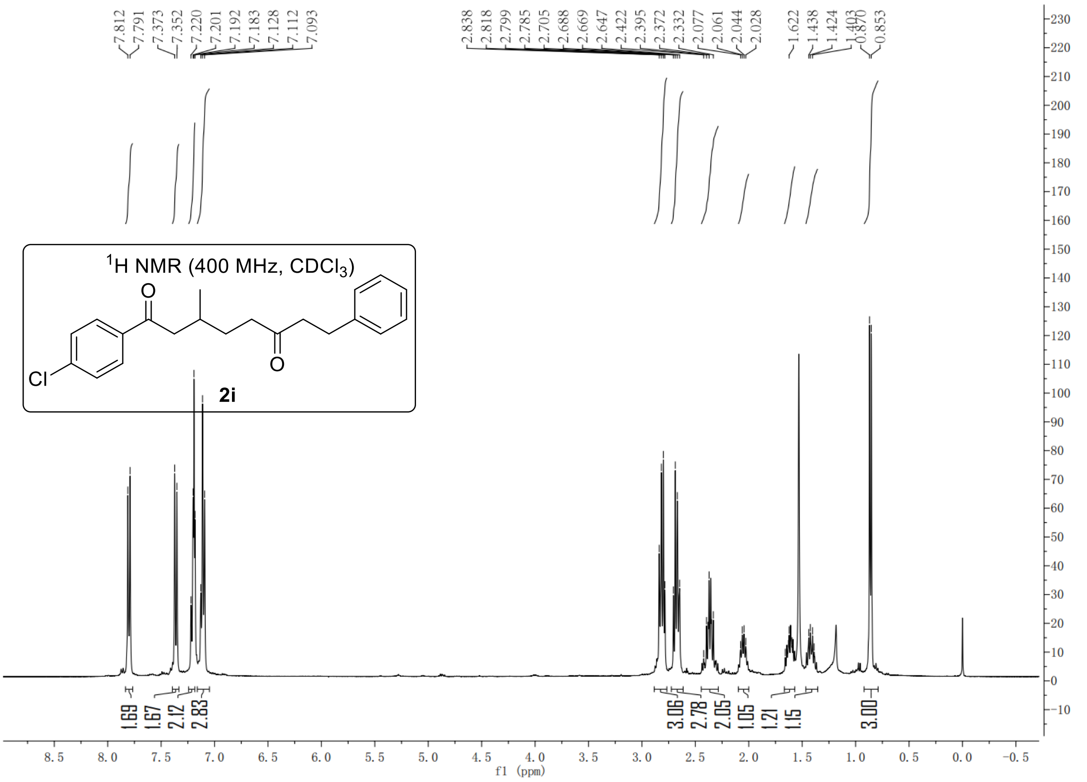
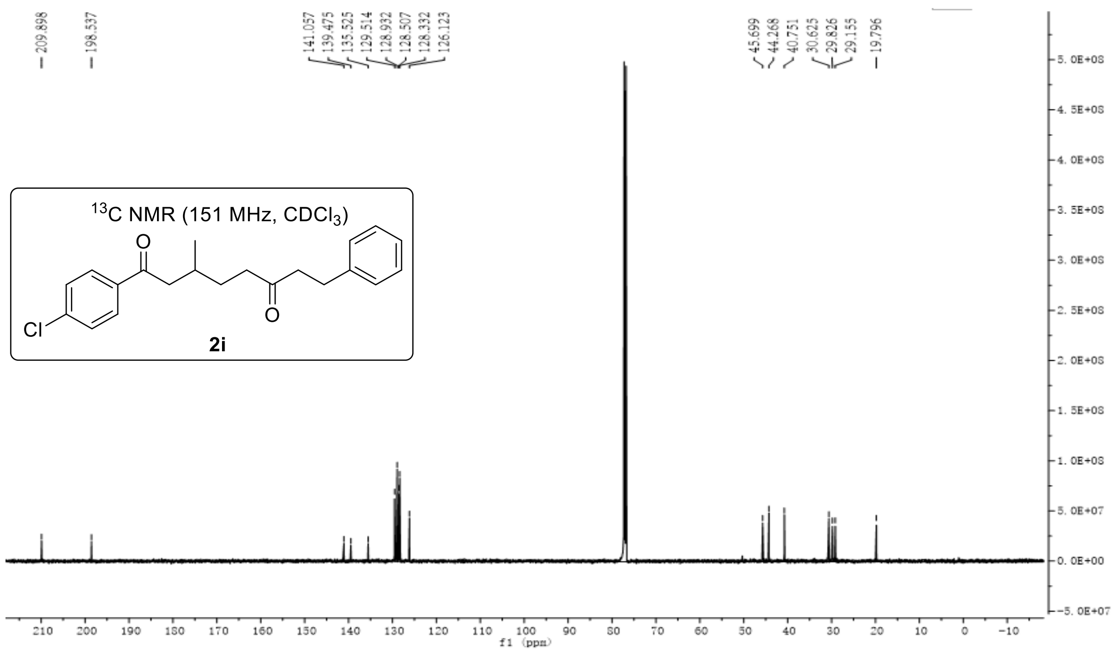
2.732
2.718
2.462
2.438
2.422
2.407
2.157
2.123
2.107
2.089
1.687
1.666
1.519
1.496
0.940
0.923
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2g
2.06
4.42
3.49
3.38
2.88
5.21
1.16
1.23
1.33
3.00
1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


210.064
199.554
143.805
141.095
134.806
129.287
128.494
128.330
128.226
126.098
53.449
45.601
44.246
40.814
30.739
29.831
29.317
21.633
19.852
13C NMR (151 MHz, CDCl3)
O
O
2g
8.0E+08
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

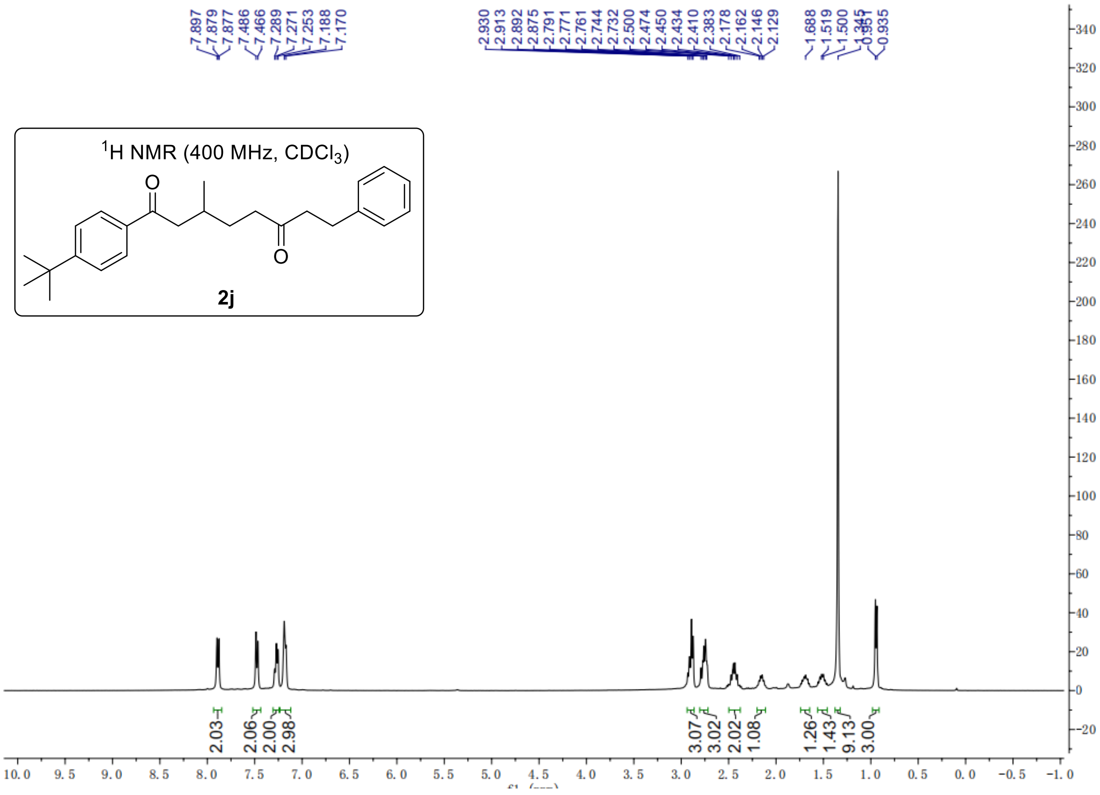

7.861
7.839
7.219
7.189
7.181
7.126
7.111
7.092
6.872
6.850
3.801
2.833
2.814
2.795
2.762
2.685
2.665
2.646
2.372
2.356
2.332
1.618
1.598
1.583
1.448
0.870
0.853
1H NMR (400 MHz, CDCl3)
O
O
O
2h
1.94
2.18
2.75
1.93
3.00
3.13
2.87
2.17
1.23
1.28
1.21
2.89
100
90
80
70
60
50
40
30
20
10
0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


210.068
198.436
163.431
141.099
130.382
128.494
128.331
126.097
113.731
55.488
45.379
44.246
40.829
30.770
29.831
29.433
19.878
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
O
2h
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

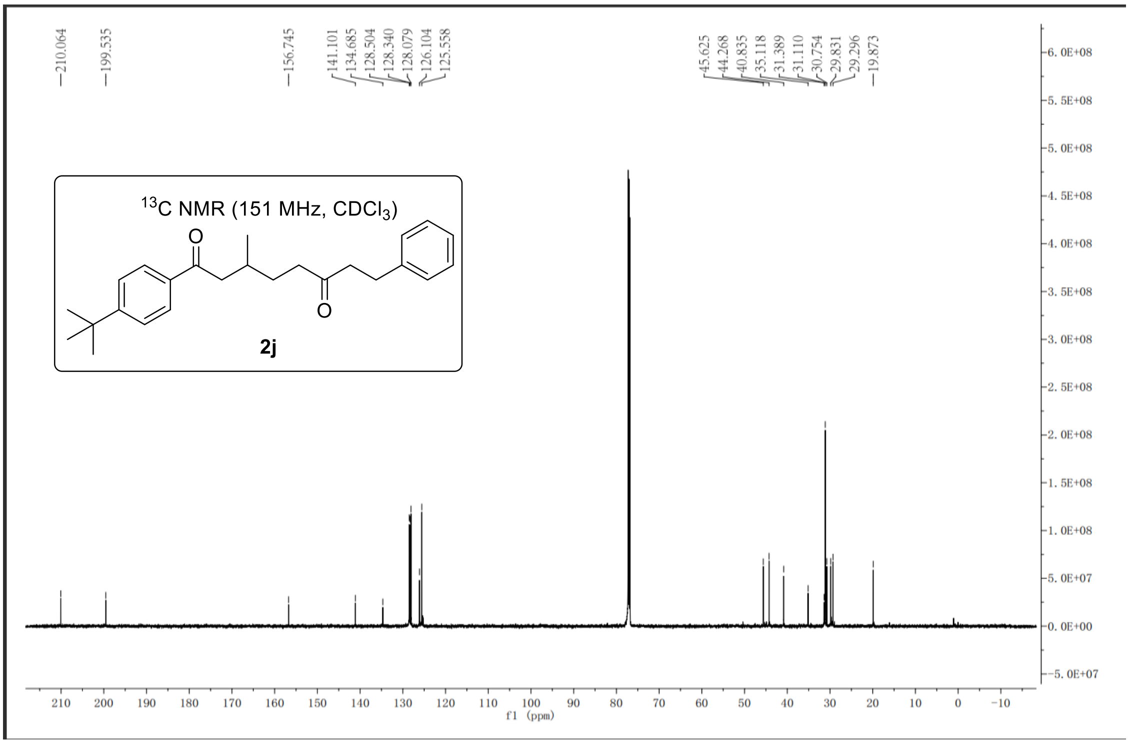

7.812
7.791
7.373
7.352
7.220
7.201
7.192
7.183
7.128
7.112
7.093
2.838
2.818
2.799
2.785
2.705
2.688
2.669
2.647
2.422
2.395
2.372
2.332
2.077
2.061
2.044
2.028
1.622
1.438
1.424
1.403
0.870
0.853
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
Cl
2i
1.69
1.67
2.12
2.83
3.06
2.78
2.05
1.05
1.21
1.15
3.00
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


209.898
198.537
141.057
139.475
135.525
129.514
128.932
128.507
128.332
126.123
45.699
44.268
40.751
30.625
29.826
29.155
19.796
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
Cl
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

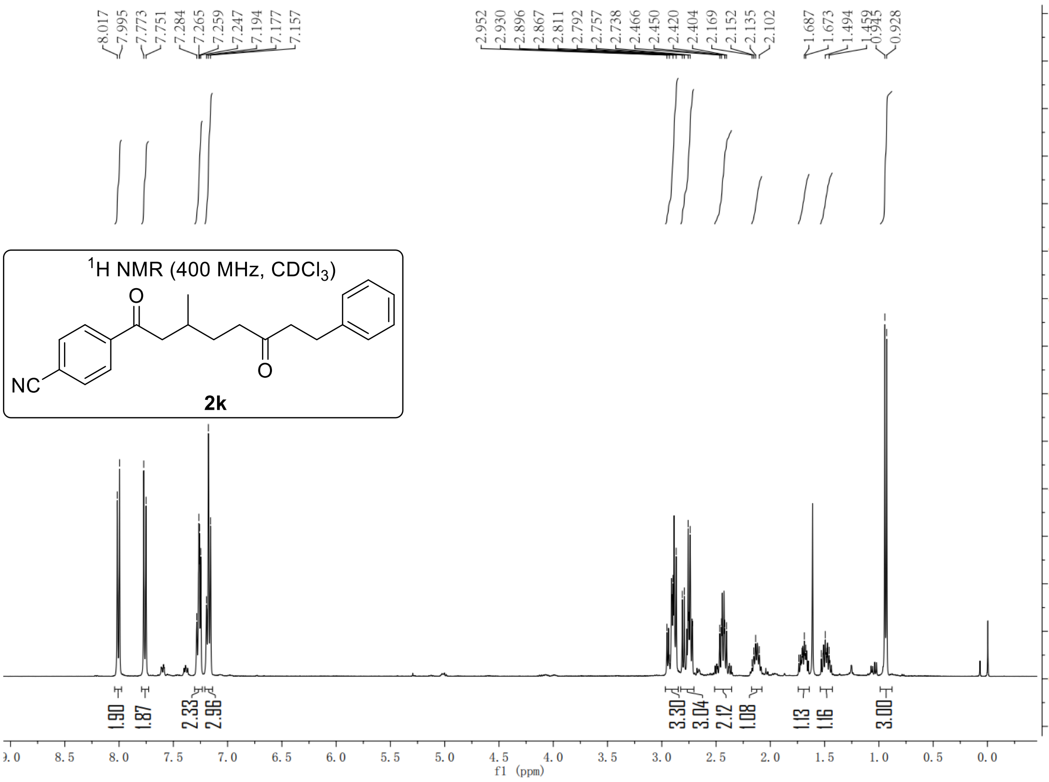
2i


7.897
7.879
7.877
7.486
7.466
7.289
7.271
7.253
7.188
7.170
2.930
2.913
2.892
2.875
2.791
2.771
2.761
2.744
2.732
2.500
2.474
2.450
2.434
2.410
2.383
2.178
2.162
2.146
2.129
1.688
1.519
1.500
1.345
0.951
0.935
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2.03
2.06
2.00
2.98
3.07
3.02
2.02
1.08
1.26
1.43
9.13
3.00
340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

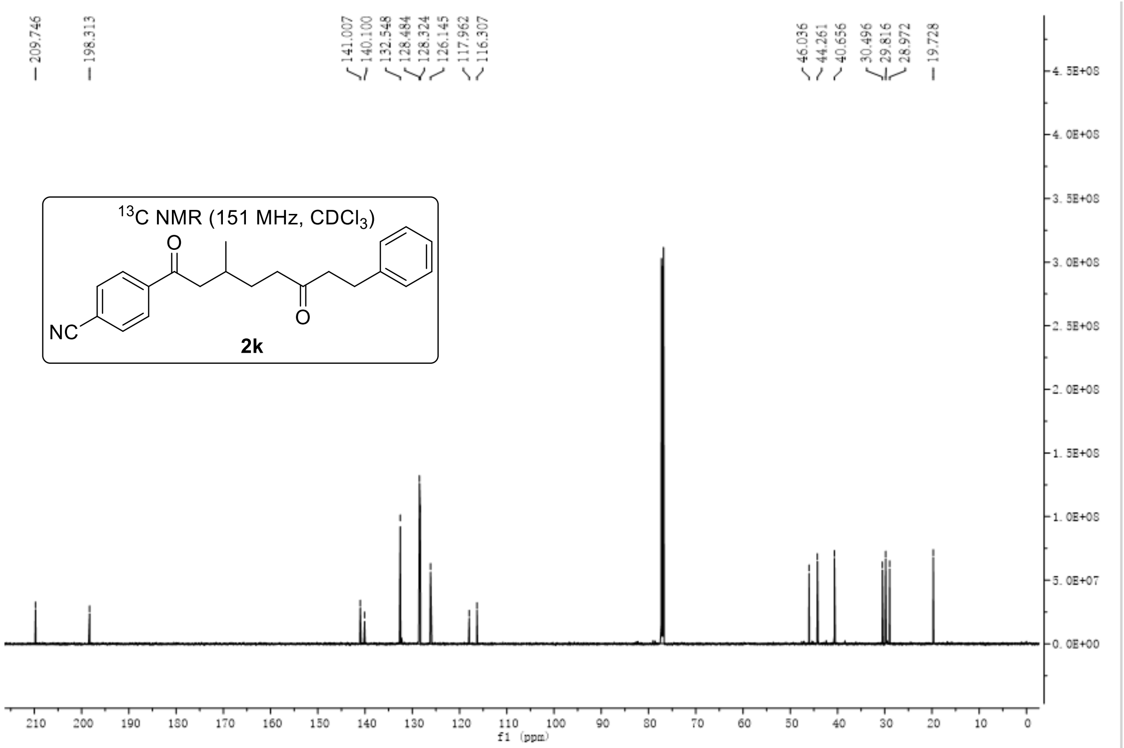
2j



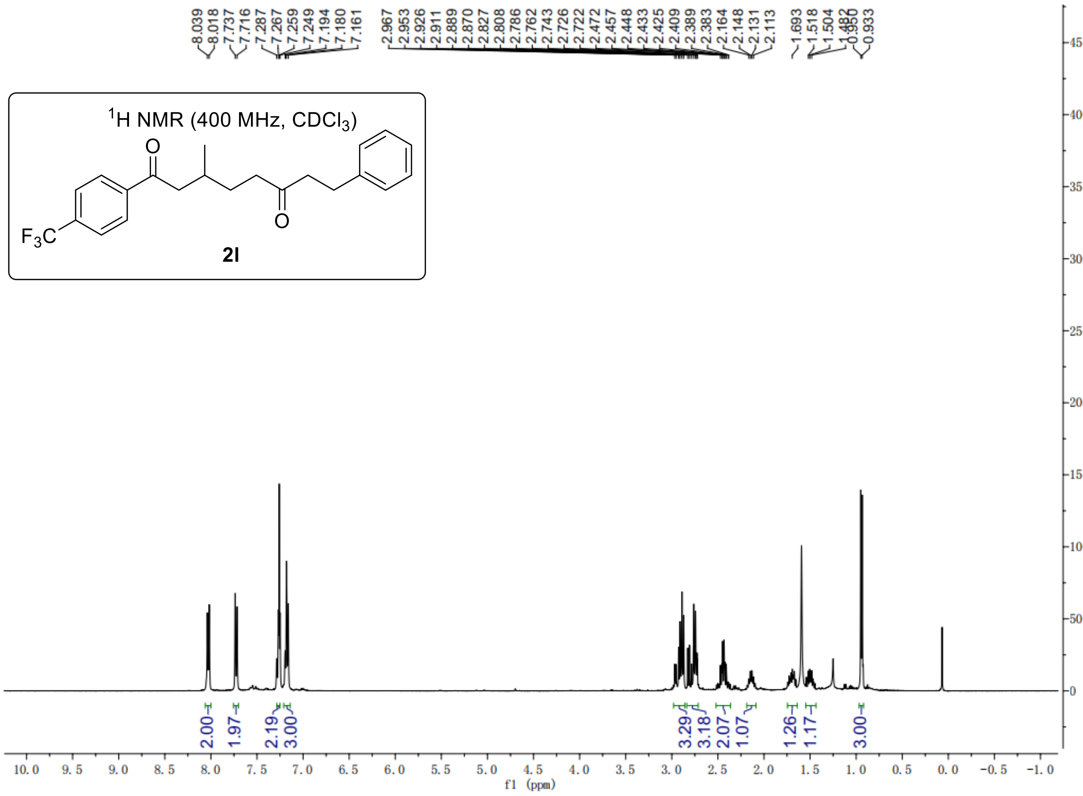
210.064
199.535
156.745
141.101
134.685
128.504
128.340
128.079
126.104
125.558
45.625
44.268
40.835
35.118
31.389
31.110
30.754
29.831
29.296
19.873
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2j
6. 0E+08
5. 5E+08
5. 0E+08
4. 5E+08
4. 0E+08
3. 5E+08
3. 0E+08
2. 5E+08
2. 0E+08
1. 5E+08
1. 0E+08
5. 0E+07
0. 0E+00
-5. 0E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



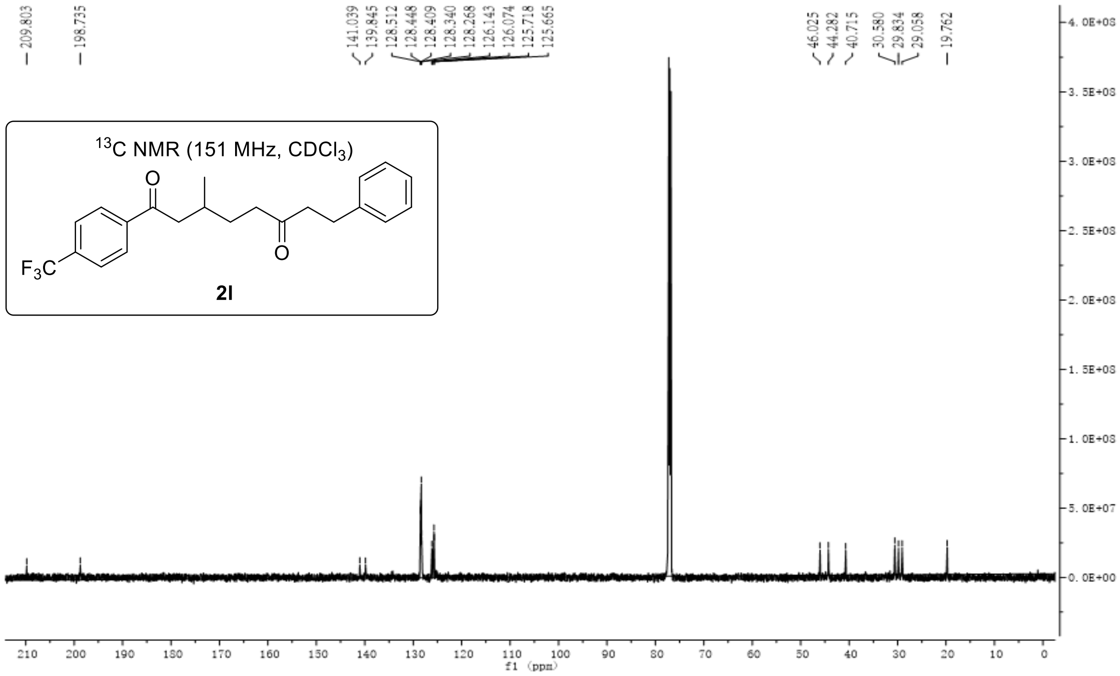
8.017
7.995
7.773
7.751
7.284
7.265
7.259
7.247
7.194
7.177
7.157
2.952
2.930
2.896
2.867
2.811
2.792
2.757
2.738
2.466
2.450
2.420
2.404
2.169
2.152
2.135
2.102
1.687
1.673
1.494
1.459
0.945
0.928
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
NC
2k
1.90
1.87
2.33
2.96
3.30
3.04
2.12
1.08
1.13
1.16
3.00
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

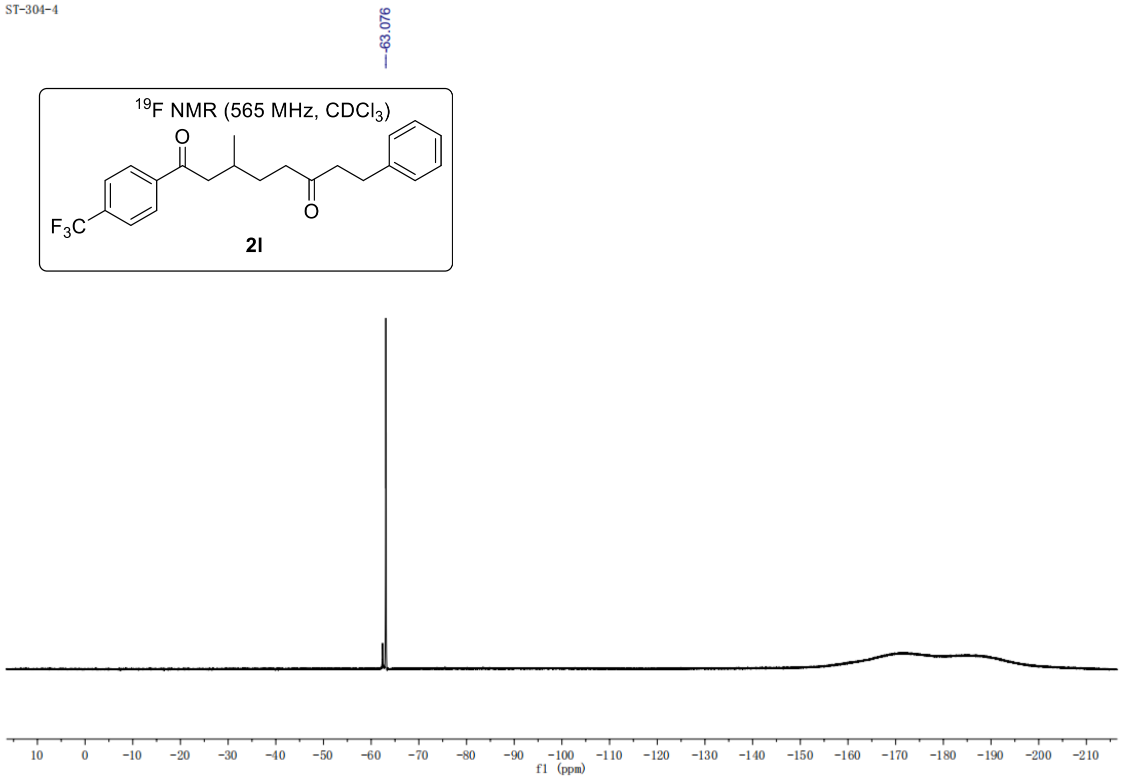


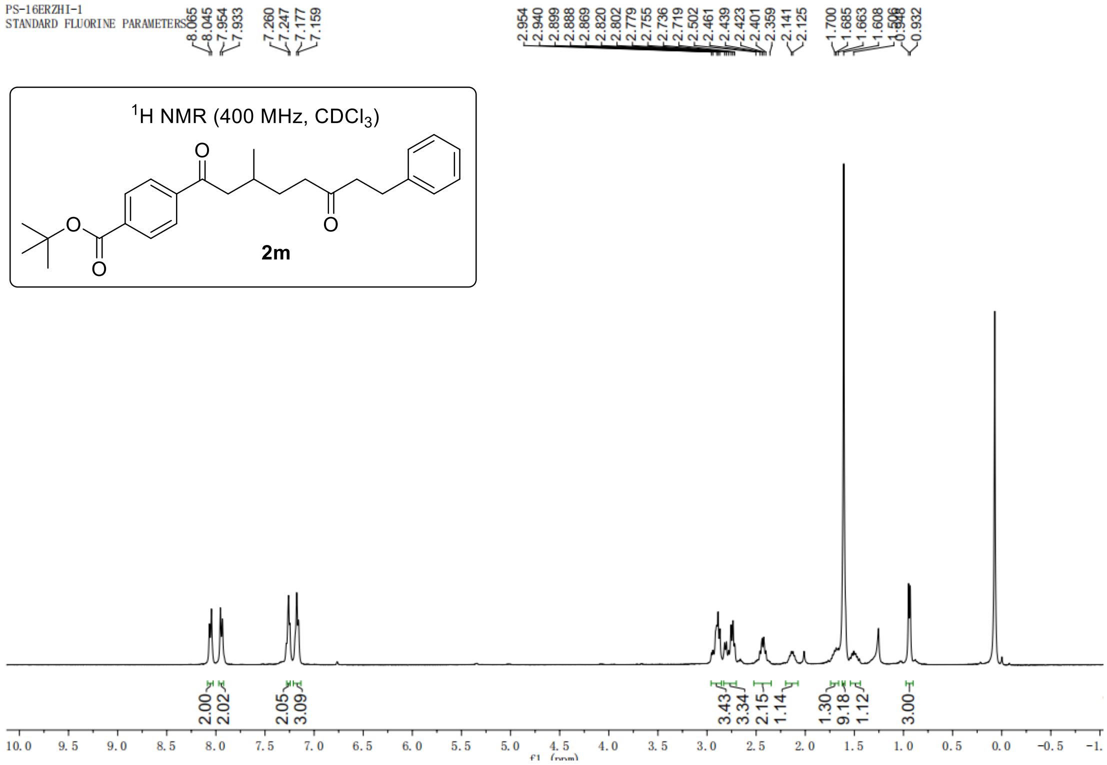
209.746
198.313
141.007
140.100
132.548
128.484
128.324
126.145
117.962
116.307
46.036
44.261
40.656
30.496
29.816
28.972
19.728
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
NC
2k
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

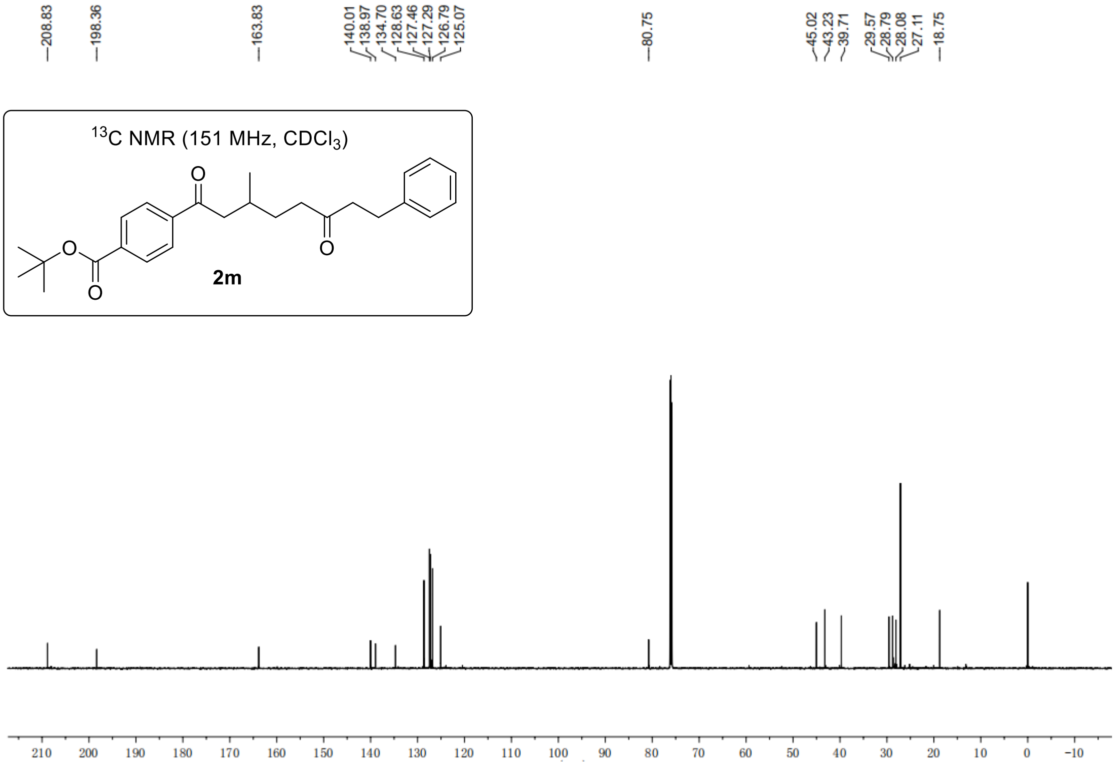


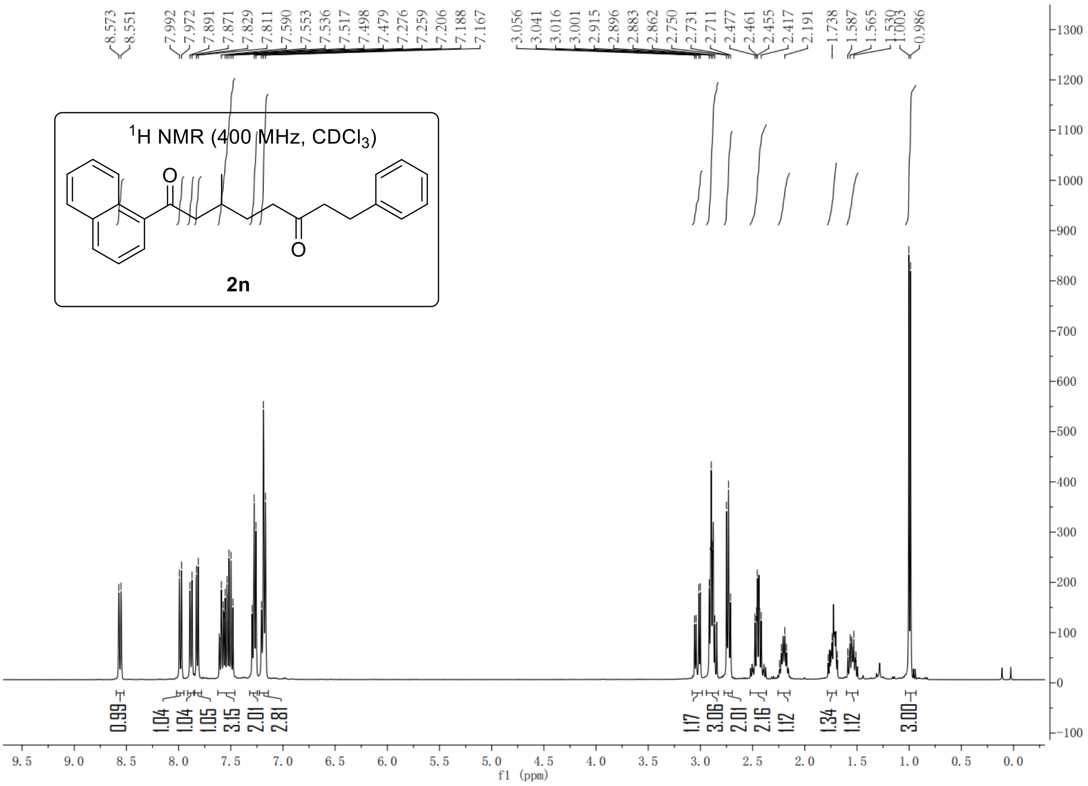
8.039
8.018
7.737
7.716
7.287
7.267
7.259
7.249
7.194
7.180
7.161
2.967
2.953
2.926
2.911
2.889
2.870
2.827
2.808
2.786
2.762
2.743
2.726
2.722
2.472
2.457
2.448
2.433
2.425
2.409
2.389
2.383
2.164
2.148
2.131
2.113
1.693
1.518
1.504
1.482
0.950
0.933
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
F$_3$C
2l
450
400
350
300
250
200
150
100
50
0
2.00
1.97
2.19
3.00
3.29
3.18
2.07
1.07
1.26
1.17
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

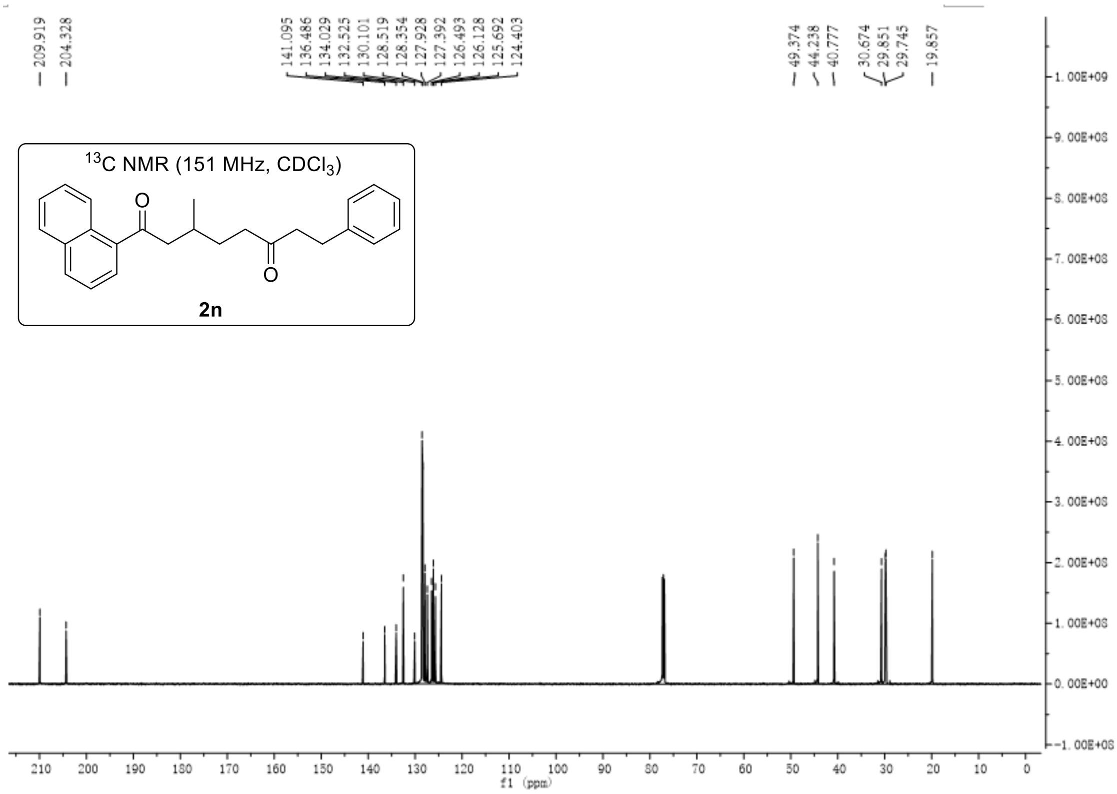

209.803
198.735
141.039
139.845
128.512
128.448
128.409
128.340
128.268
126.143
126.074
125.718
125.665
46.025
44.282
40.715
30.580
29.834
29.058
19.762
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
F$_3$C
2l
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

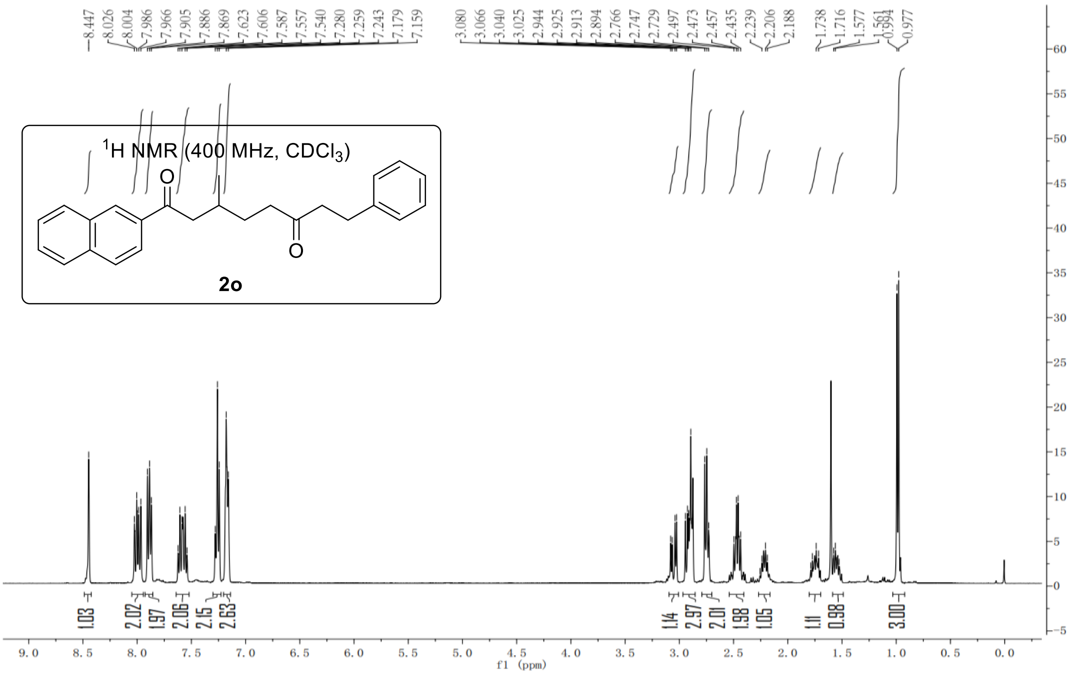

ST-304-4
-63.076
^{19}F NMR (565 MHz, CDCl$_3$)
O
O
F$_3$C
2l
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

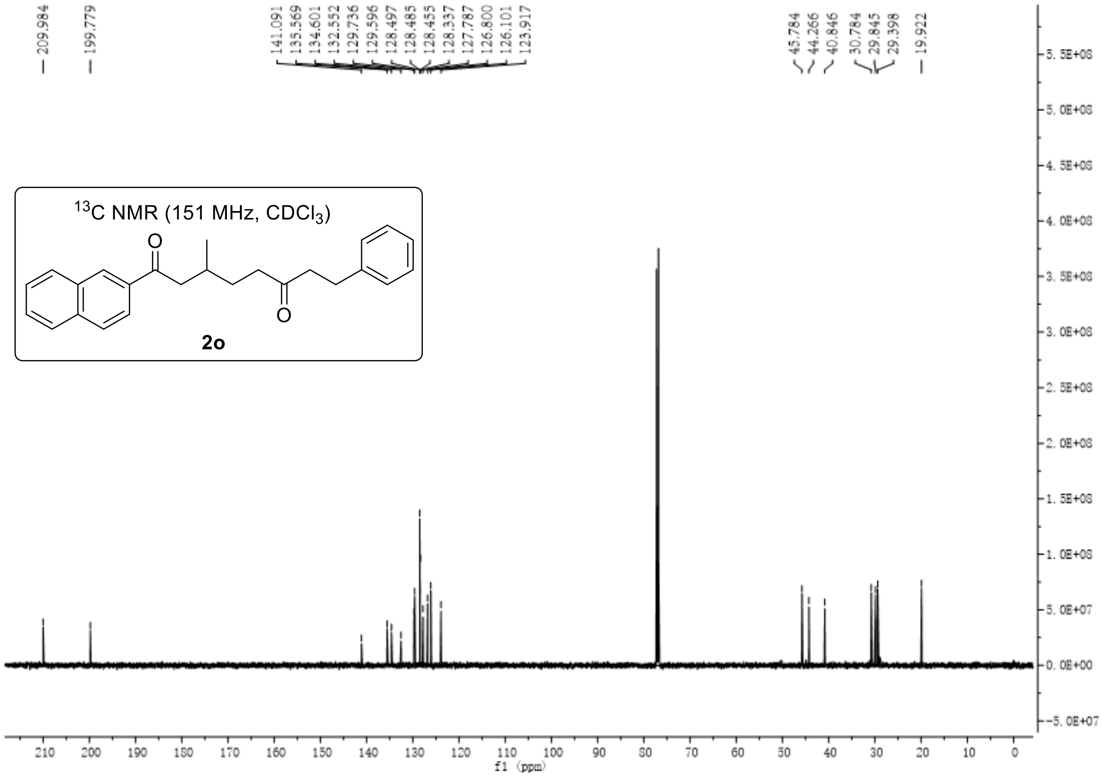

PS-16ERZHI-1
STANDARD FLUORINE PARAMETERS
8.065
8.045
7.954
7.933
7.260
7.247
7.177
7.159
2.954
2.940
2.899
2.888
2.869
2.820
2.802
2.779
2.755
2.736
2.719
2.502
2.461
2.439
2.423
2.401
2.359
2.141
2.125
1.700
1.685
1.663
1.608
1.598
0.948
0.932
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
O
O
2m
2.00
2.02
2.05
3.09
3.43
3.34
2.15
1.14
1.30
9.18
1.12
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

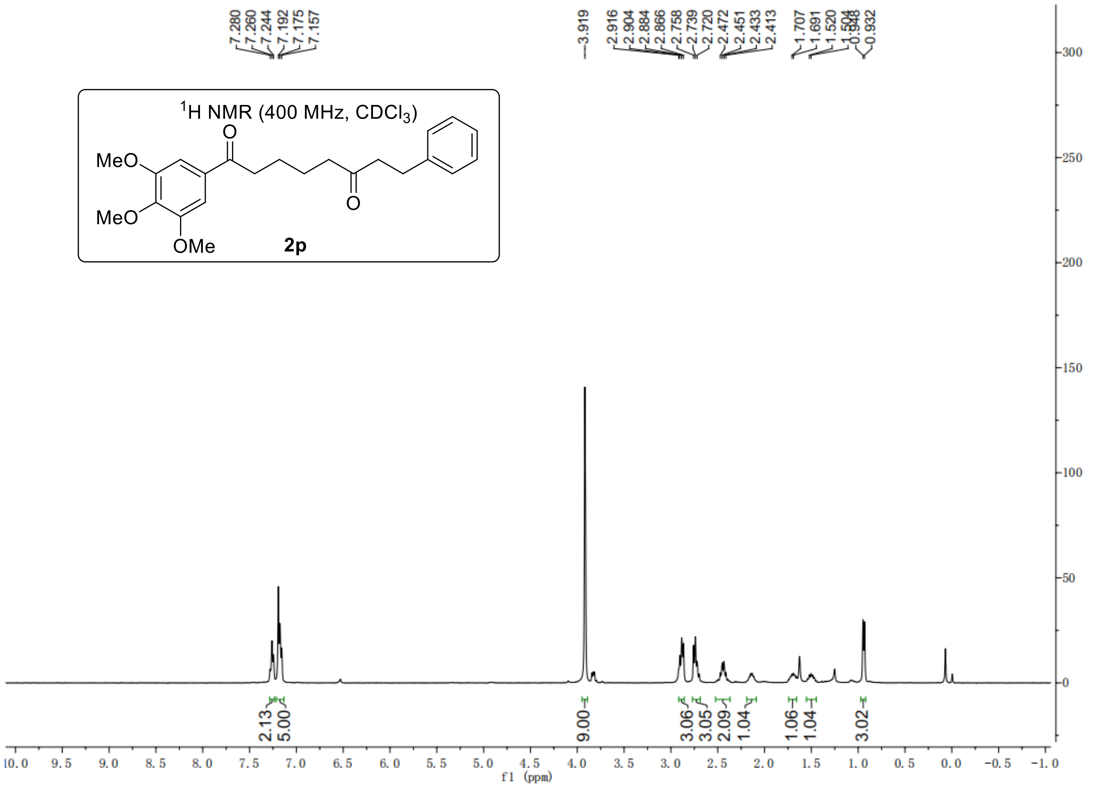

208.83
198.36
163.83
140.01
138.97
134.70
128.63
127.46
127.29
126.79
125.07
80.75
45.02
43.23
39.71
29.57
28.79
28.08
27.11
18.75
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
O
O
2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

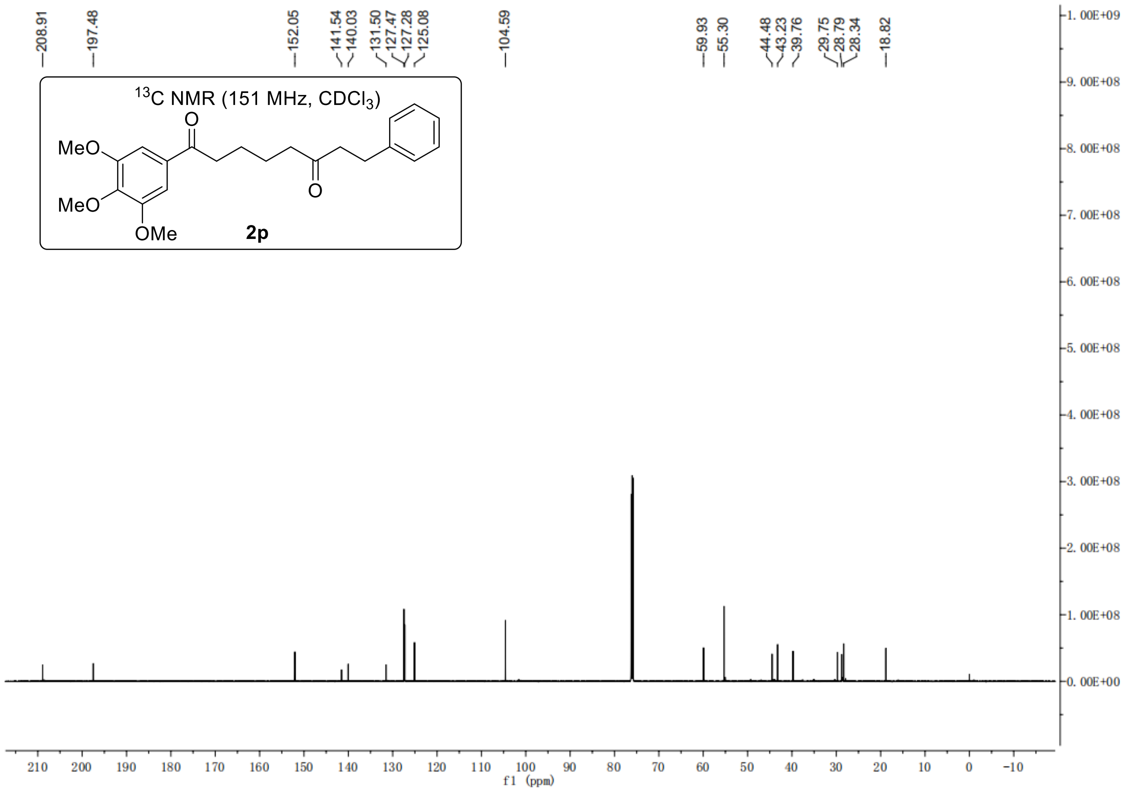

8.573
8.551
7.992
7.972
7.891
7.871
7.829
7.811
7.590
7.553
7.536
7.517
7.498
7.479
7.276
7.259
7.206
7.188
7.167
3.056
3.041
3.016
3.001
2.915
2.896
2.883
2.862
2.750
2.731
2.711
2.477
2.461
2.455
2.417
2.191
1.738
1.587
1.565
1.530
1.003
0.986
1H NMR (400 MHz, CDCl3)
O
O
2n
0.99
1.04
1.04
1.05
3.15
2.01
2.81
1.17
3.06
2.01
2.16
1.12
1.34
1.12
3.00
f1 (ppm)

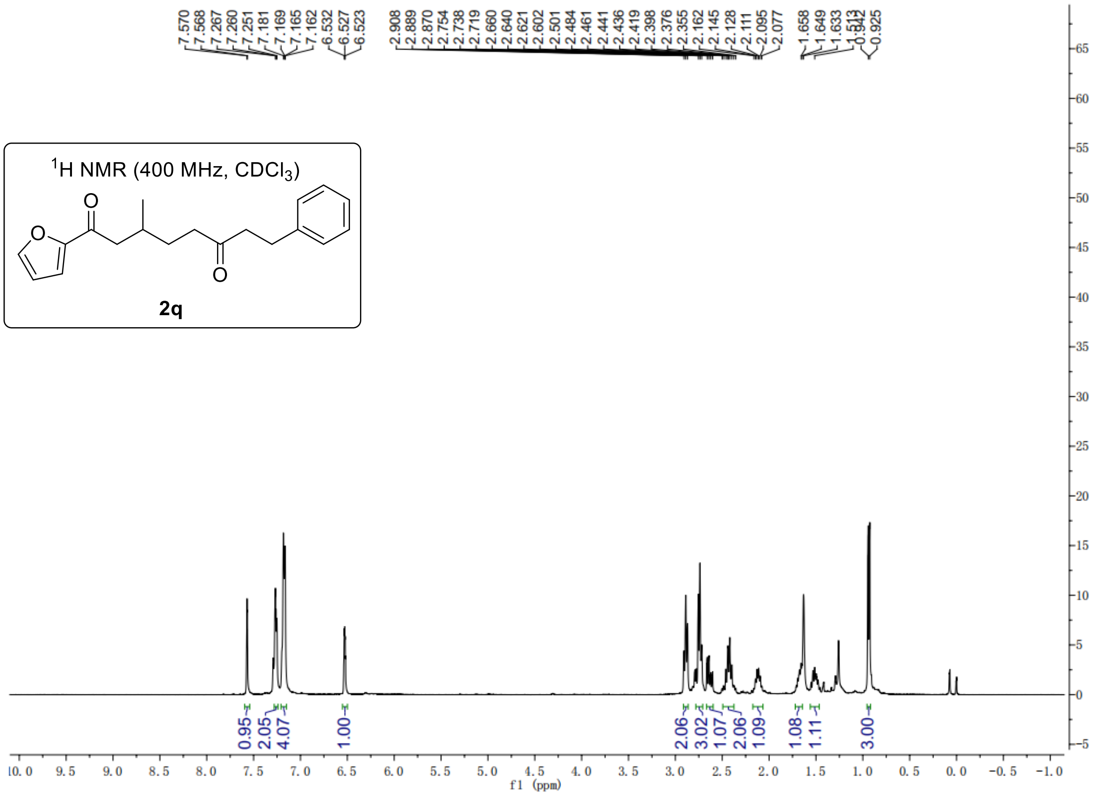

209.919
204.328
141.095
136.486
134.029
132.525
130.101
128.519
128.354
127.928
127.392
126.493
126.128
125.692
124.403
49.374
44.238
40.777
30.674
29.851
29.745
19.857
13C NMR (151 MHz, CDCl3)
O
O
2n
f1 (ppm)

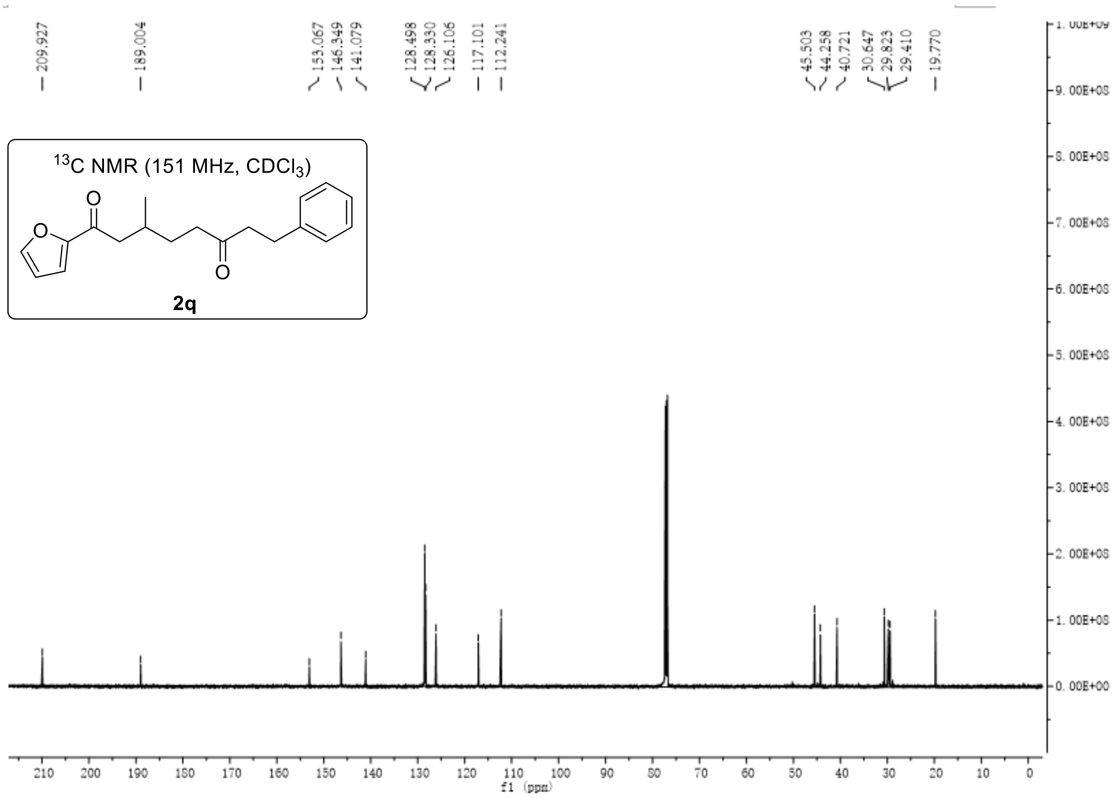

8.447
8.026
8.004
7.986
7.966
7.905
7.886
7.869
7.623
7.606
7.587
7.557
7.540
7.280
7.259
7.243
7.179
7.159
3.080
3.066
3.040
3.025
2.944
2.925
2.913
2.894
2.766
2.747
2.729
2.497
2.473
2.457
2.435
2.239
2.206
2.188
1.738
1.716
1.577
1.561
0.994
0.977
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2o
1.03
2.02
1.97
2.06
2.15
2.63
1.14
2.97
2.01
1.98
1.05
1.11
0.98
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
-60 -55 -50 -45 -40 -35 -30 -25 -20 -15 -10 -5 -0 -−5

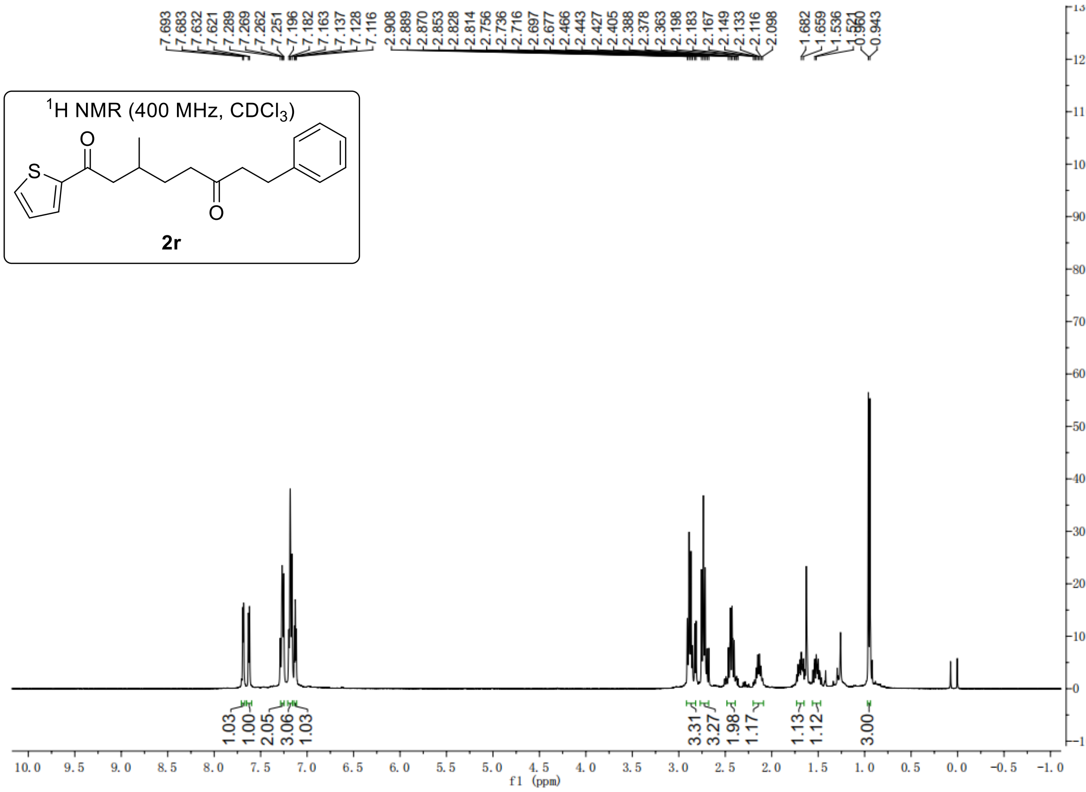

209.984
199.779
141.091
135.569
134.601
132.552
129.736
129.596
128.497
128.485
128.455
128.337
127.787
126.800
126.101
123.917
45.784
44.266
40.846
30.784
29.845
29.398
19.922
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
5.5E+08 5.0E+08 4.5E+08 4.0E+08 3.5E+08 3.0E+08 2.5E+08 2.0E+08 1.5E+08 1.0E+08 5.0E+07 0.0E+00 −5.0E+07

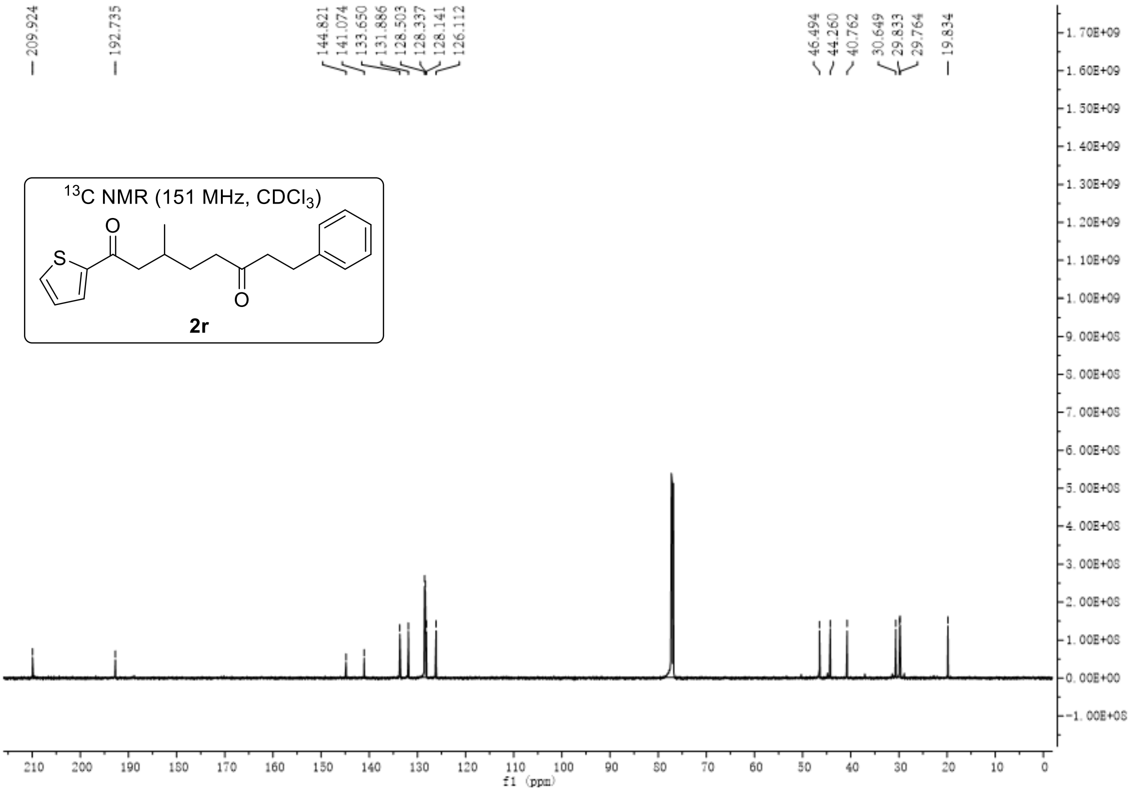

7.280
7.260
7.244
7.192
7.175
7.157
3.919
2.916
2.904
2.884
2.866
2.758
2.739
2.720
2.472
2.451
2.433
2.413
1.707
1.691
1.520
1.504
0.948
0.932
^{1}H NMR (400 MHz, CDCl$_3$)
O
MeO
MeO
OMe
O
2p
2.13
5.00
9.00
3.06
3.05
2.09
1.04
1.06
1.04
3.02
300
250
200
150
100
50
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

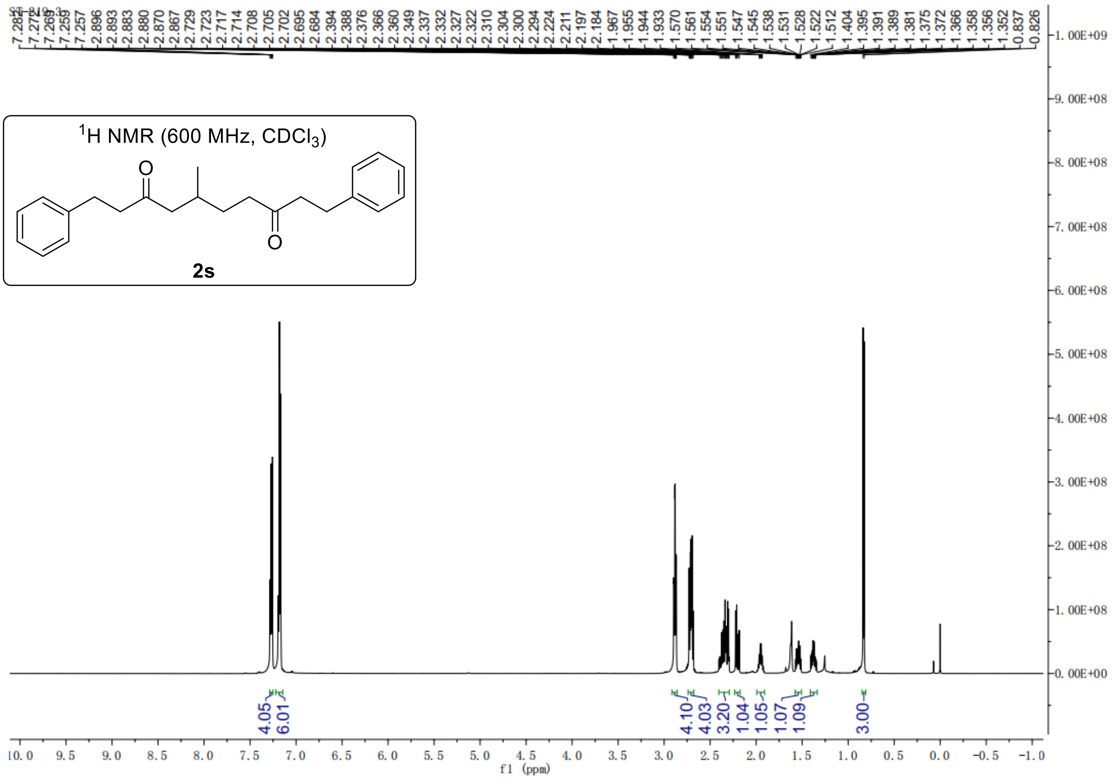

208.91
197.48
152.05
141.54
140.03
131.50
127.47
127.28
125.08
104.59
59.93
55.30
44.48
43.23
39.76
29.75
28.79
28.34
18.82
^{13}C NMR (151 MHz, CDCl$_3$)
O
MeO
MeO
OMe
O
2p
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


^{1}H NMR (400 MHz, CDCl$_3$)
O
O
O
2q
7.570
7.568
7.267
7.260
7.251
7.181
7.169
7.165
7.162
6.532
6.527
6.523
2.908
2.889
2.870
2.754
2.738
2.719
2.660
2.640
2.621
2.602
2.501
2.484
2.461
2.441
2.436
2.419
2.398
2.376
2.355
2.162
2.145
2.128
2.111
2.095
2.077
1.658
1.649
1.633
1.513
0.942
0.925
0.95
2.05
4.07
1.00
2.06
3.02
1.07
2.06
1.09
1.08
1.11
3.00
f1 (ppm)


^{13}C NMR (151 MHz, CDCl$_3$)
O
O
O
2q
209.927
189.004
153.067
146.349
141.079
128.498
128.330
126.106
117.101
112.241
45.503
44.258
40.721
30.647
29.823
29.410
19.770
f1 (ppm)

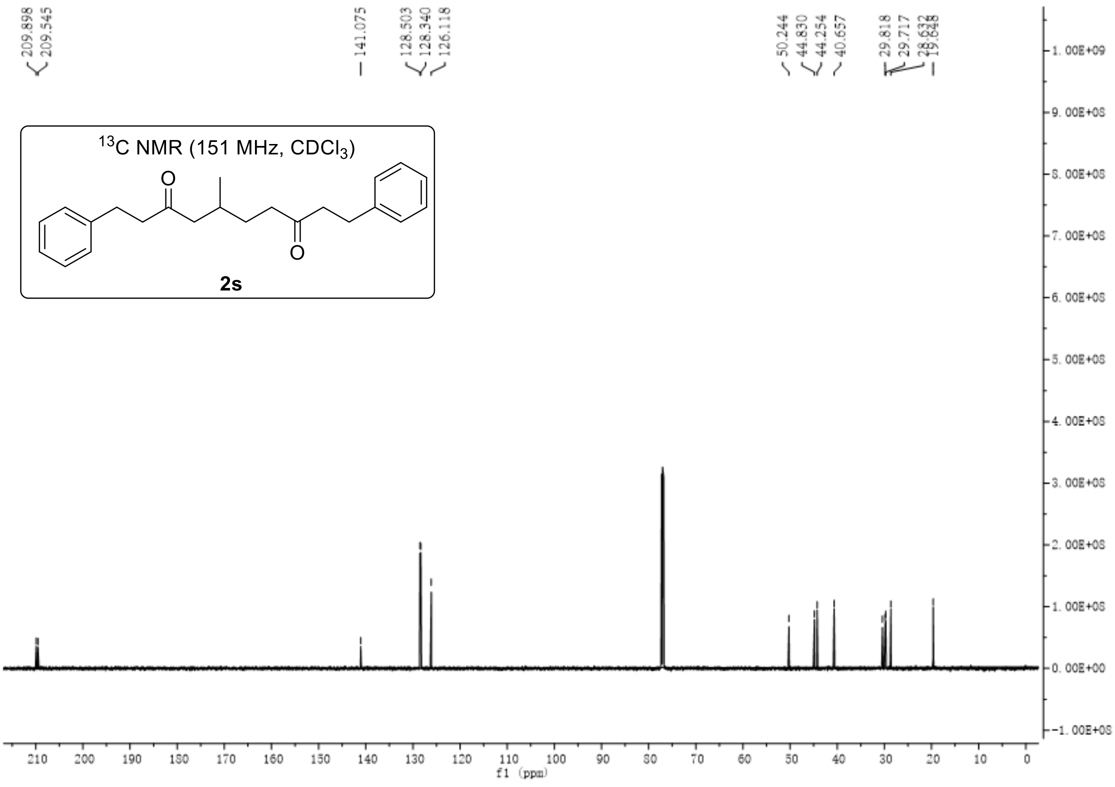

7.693
7.683
7.632
7.621
7.289
7.269
7.262
7.251
7.196
7.182
7.163
7.137
7.128
7.116
2.908
2.889
2.870
2.853
2.828
2.814
2.756
2.736
2.716
2.697
2.677
2.466
2.443
2.427
2.405
2.388
2.378
2.363
2.198
2.183
2.167
2.149
2.133
2.116
2.098
1.682
1.659
1.536
1.521
0.960
0.943
^{1}H NMR (400 MHz, CDCl$_3$)
O
S
O
2r
1.03
1.00
2.05
3.06
1.03
3.31
3.27
1.98
1.17
1.13
1.12
3.00
f1 (ppm)


209.924
192.735
144.821
141.074
133.650
131.886
128.503
128.337
128.141
126.112
46.494
44.260
40.762
30.649
29.833
29.764
19.834
^{13}C NMR (151 MHz, CDCl$_3$)
O
S
O
2r
f1 (ppm)



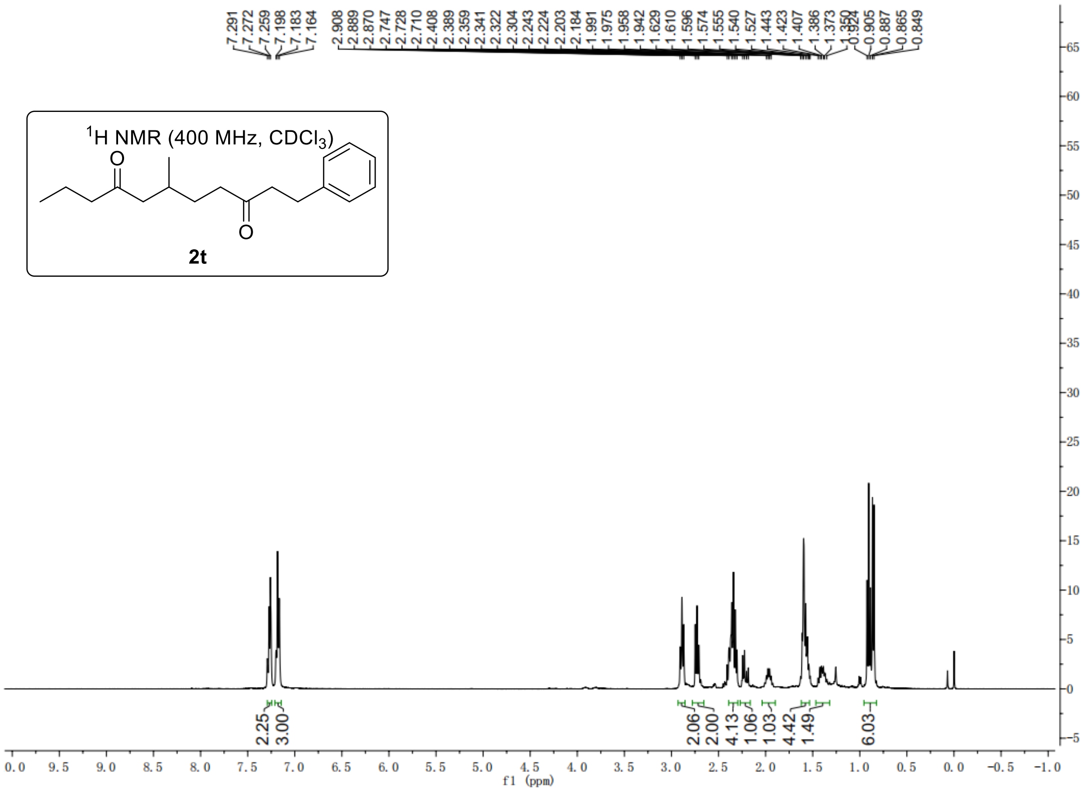
^{1}H NMR (600 MHz, CDCl$_3$)

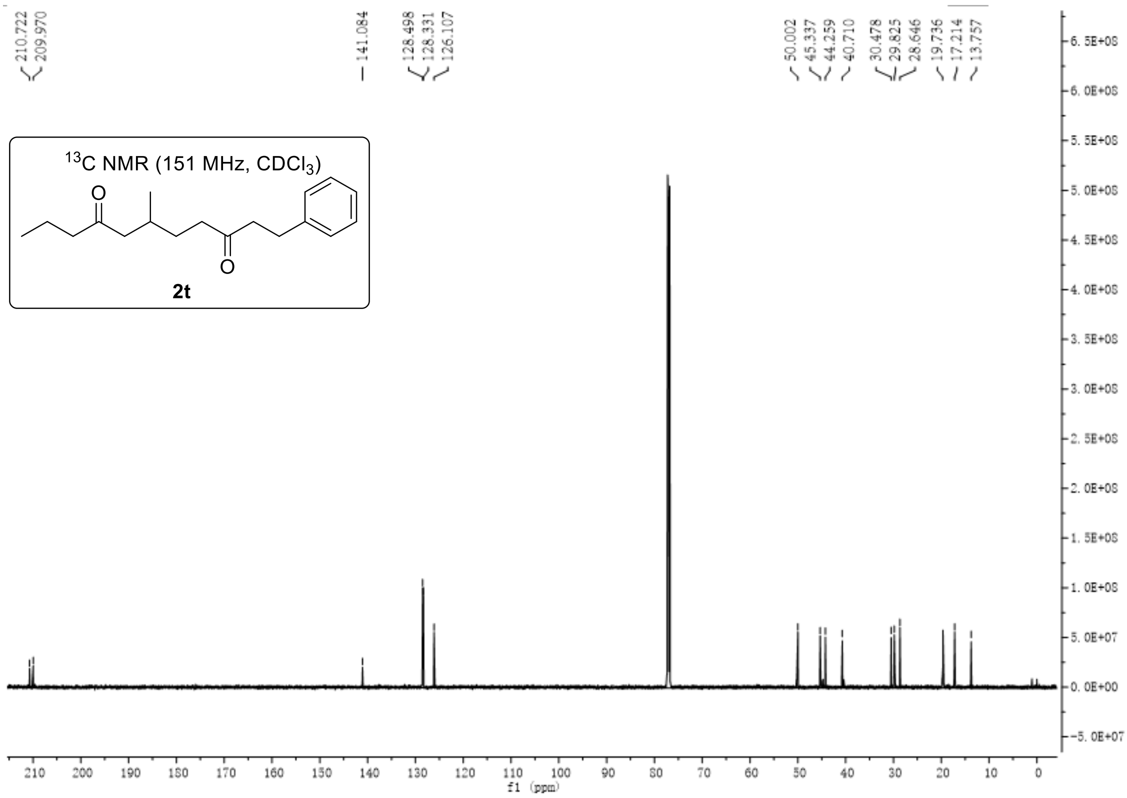
2s

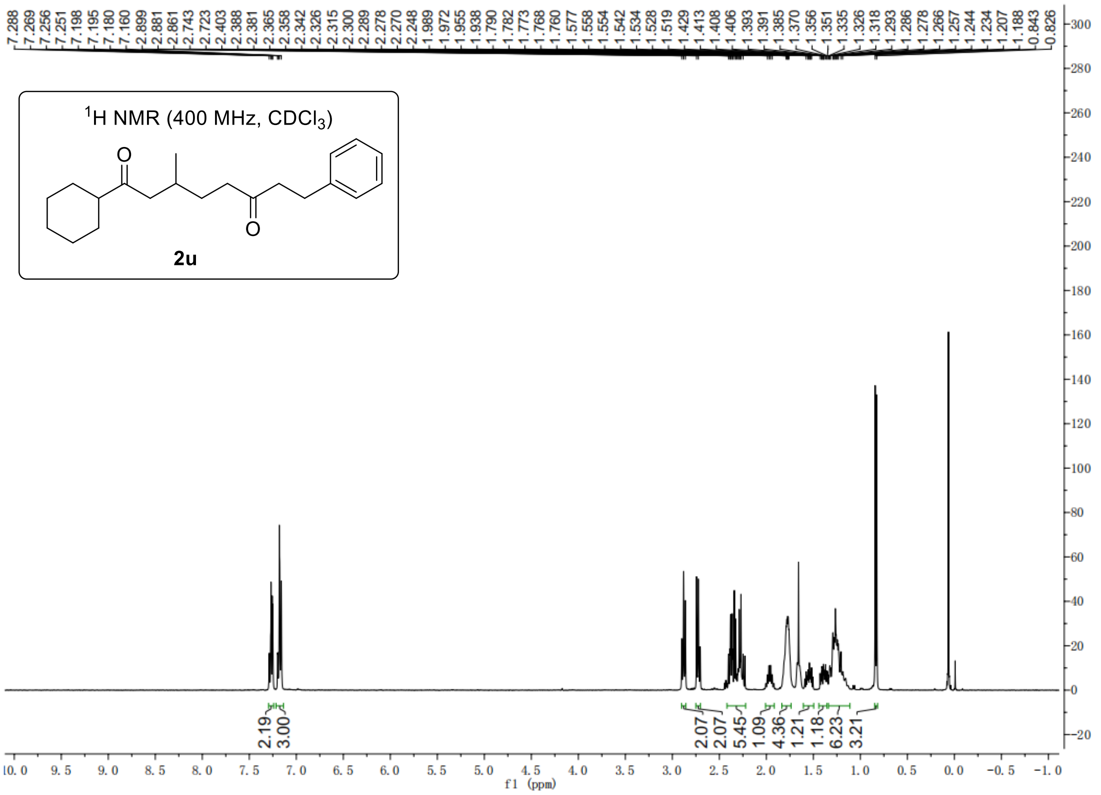


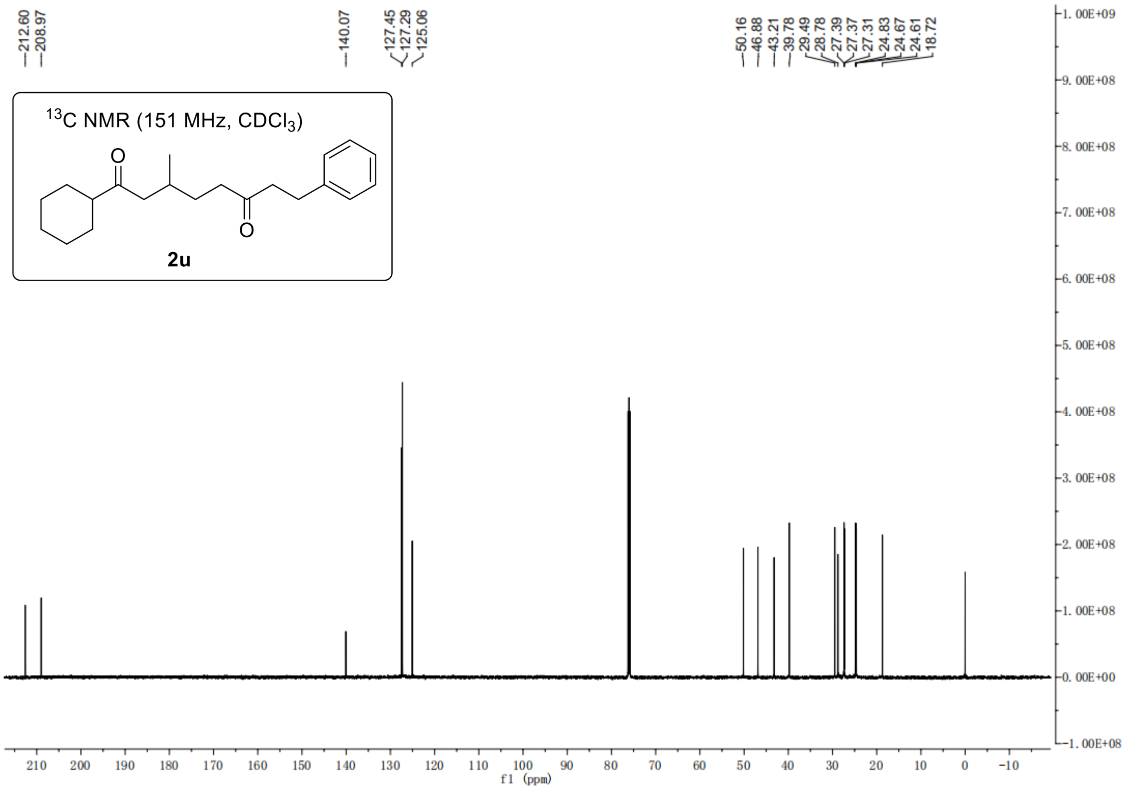
^{13}C NMR (151 MHz, CDCl$_3$)

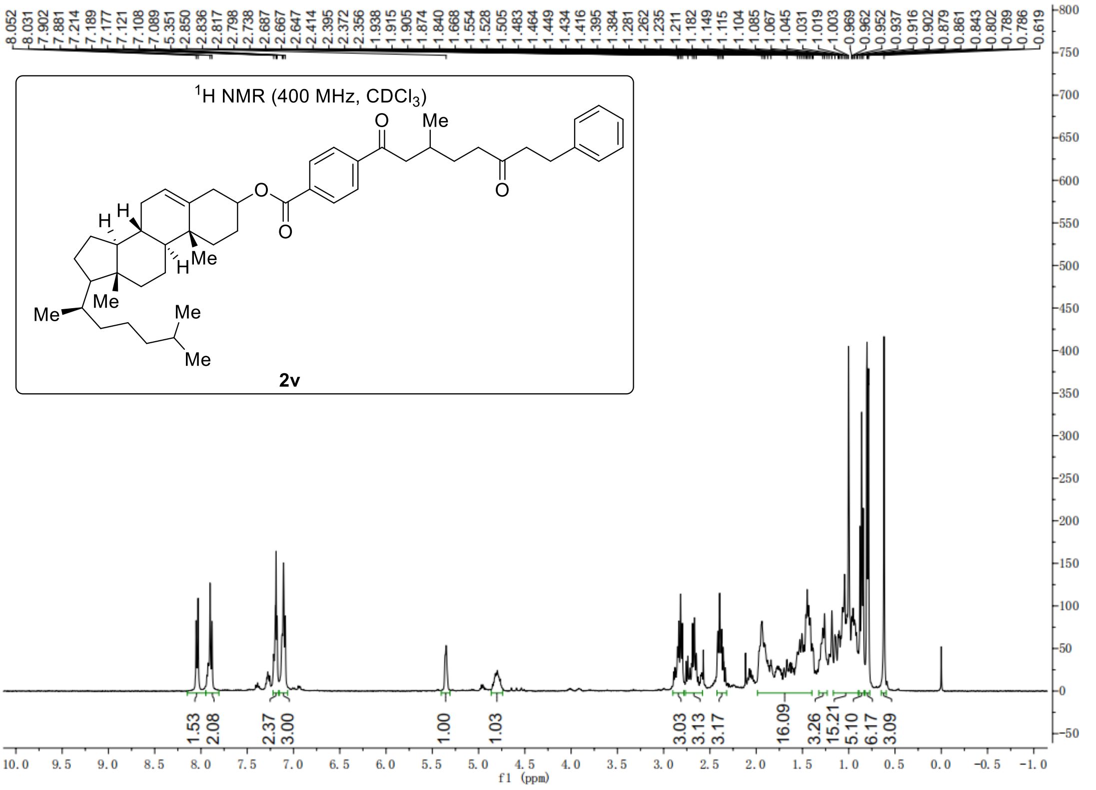
2s

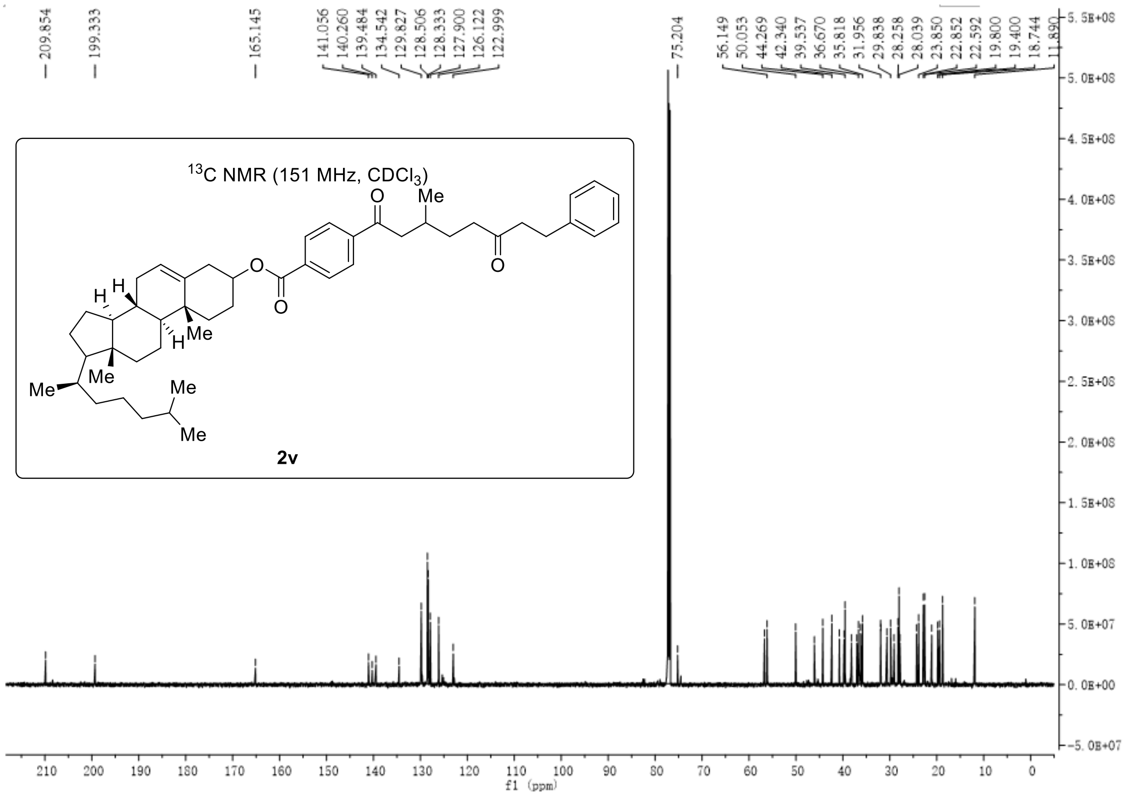

7.291
7.272
7.259
7.198
7.183
7.164
2.908
2.889
2.870
2.747
2.728
2.710
2.408
2.389
2.359
2.341
2.322
2.304
2.243
2.224
2.203
2.184
1.991
1.975
1.958
1.942
1.629
1.610
1.596
1.574
1.555
1.540
1.527
1.443
1.423
1.407
1.386
1.373
1.350
0.924
0.905
0.887
0.865
0.849
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2t
2.25
3.00
2.06
2.00
4.13
1.06
1.03
4.42
1.49
6.03
f1 (ppm)

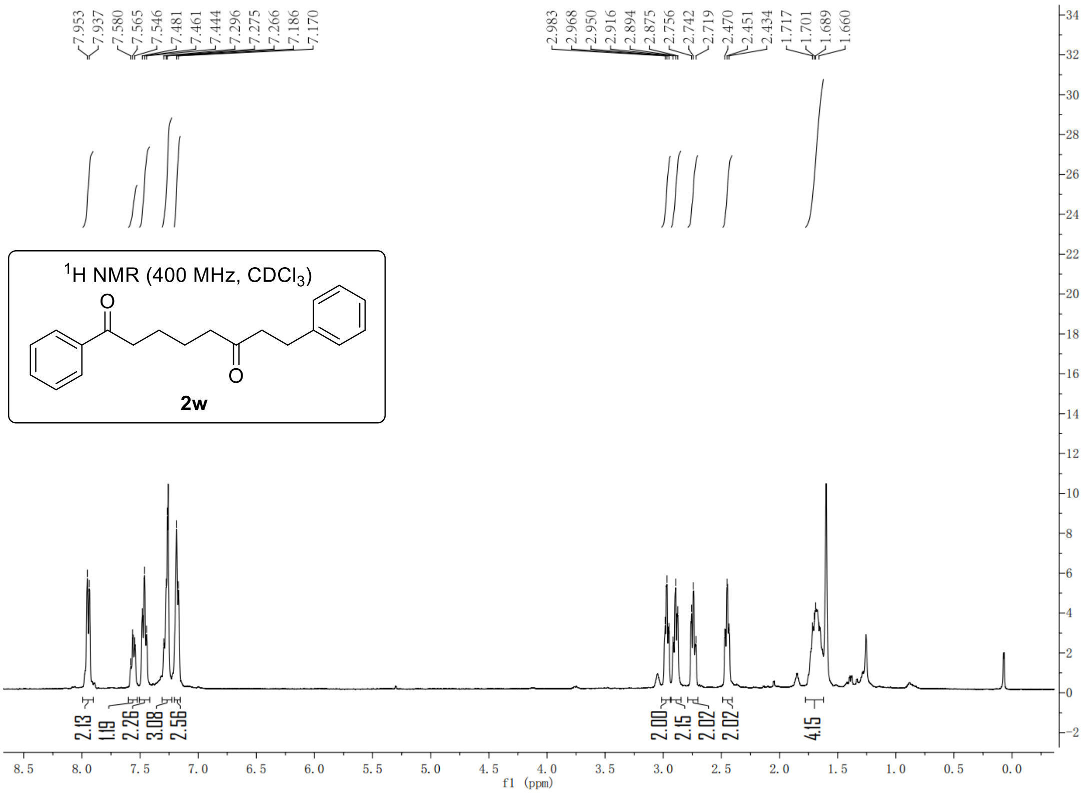

210.722
209.970
141.084
128.498
128.331
126.107
50.002
45.337
44.259
40.710
30.478
29.825
28.646
19.736
17.214
13.757
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2t
f1 (ppm)

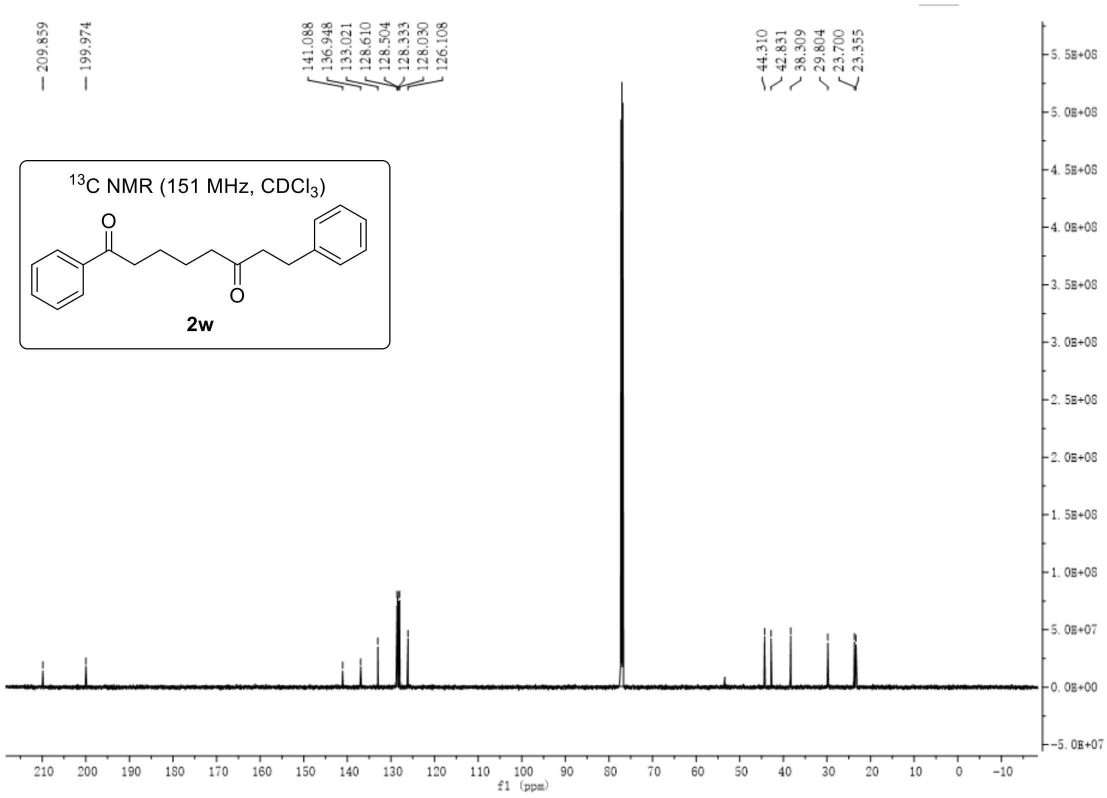

7.288
7.269
7.256
7.251
7.198
7.195
7.180
7.160
2.899
2.881
2.861
2.743
2.723
2.403
2.388
2.381
2.365
2.358
2.342
2.326
2.315
2.300
2.289
2.278
2.270
2.248
1.989
1.972
1.955
1.938
1.790
1.782
1.773
1.768
1.760
1.577
1.558
1.554
1.542
1.534
1.528
1.519
1.429
1.413
1.408
1.406
1.393
1.391
1.385
1.370
1.356
1.351
1.335
1.326
1.318
1.293
1.286
1.278
1.266
1.257
1.244
1.234
1.207
1.188
0.843
0.826
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2u
2.19
3.00
2.07
2.07
5.45
1.09
4.36
1.21
1.18
6.23
3.21
f1 (ppm)

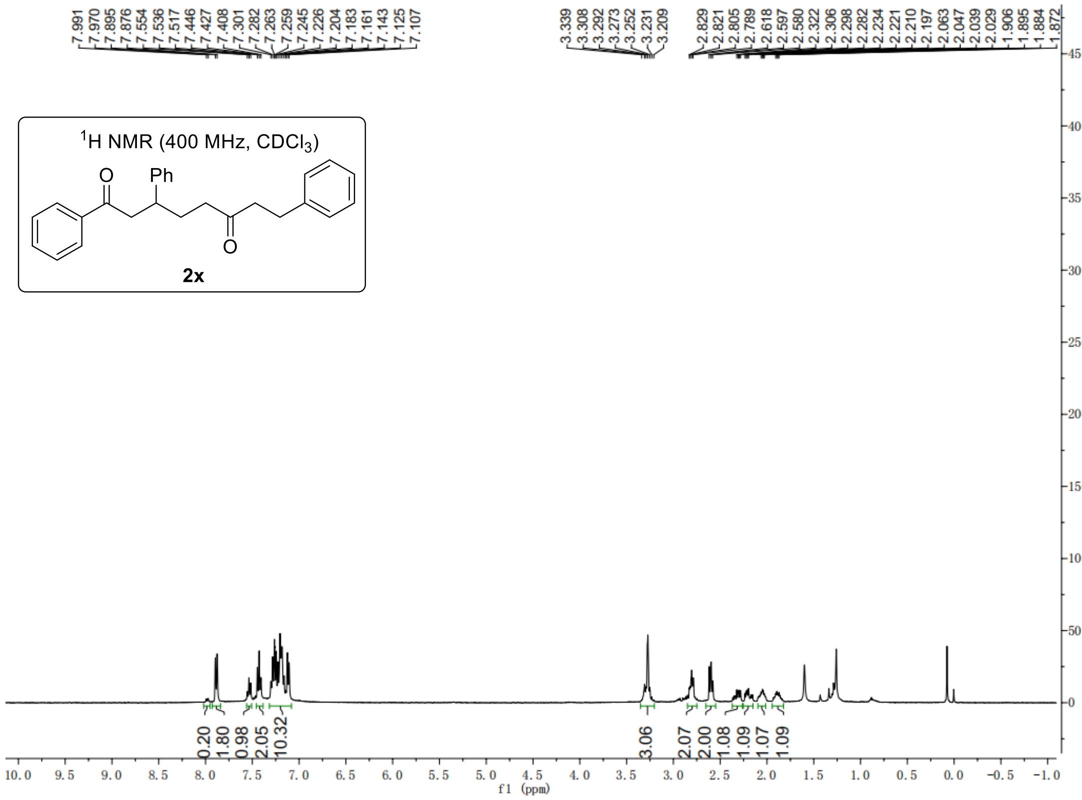

212.60
208.97
140.07
127.45
127.29
125.06
50.16
46.88
43.21
39.78
29.49
28.78
27.39
27.37
27.31
24.83
24.67
24.61
18.72
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2u
f1 (ppm)

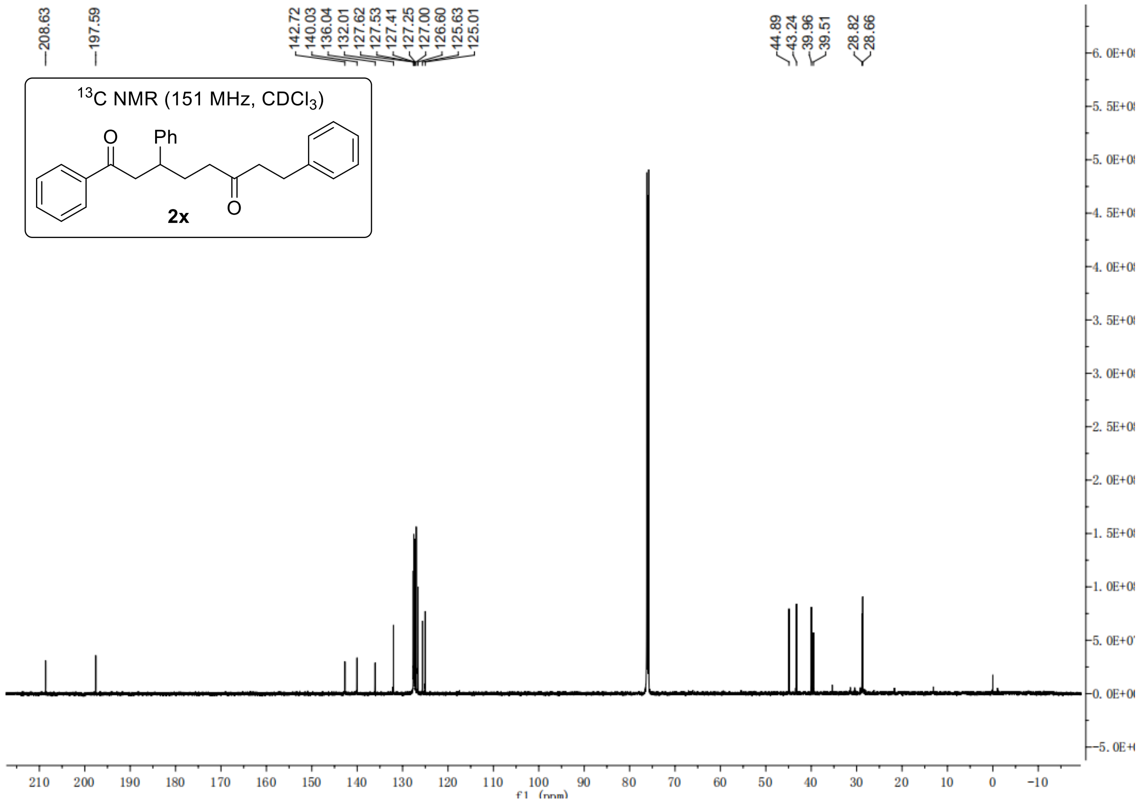

8.052
8.031
7.902
7.881
7.214
7.189
7.177
7.121
7.108
7.089
5.351
2.850
2.836
2.817
2.798
2.738
2.687
2.667
2.647
2.414
2.395
2.372
2.356
1.938
1.915
1.905
1.874
1.840
1.668
1.554
1.528
1.505
1.483
1.464
1.449
1.434
1.416
1.395
1.384
1.281
1.262
1.235
1.211
1.182
1.149
1.115
1.104
1.085
1.067
1.045
1.031
1.019
1.003
0.969
0.962
0.952
0.937
0.916
0.902
0.879
0.861
0.843
0.802
0.789
0.786
0.619
1H NMR (400 MHz, CDCl3)
O
Me
O
O
O
H
H
H
Me
Me
Me
Me
Me
2v
1.53
2.08
2.37
3.00
1.00
1.03
3.03
3.13
3.17
16.09
3.26
15.21
5.10
6.17
3.09
f1 (ppm)

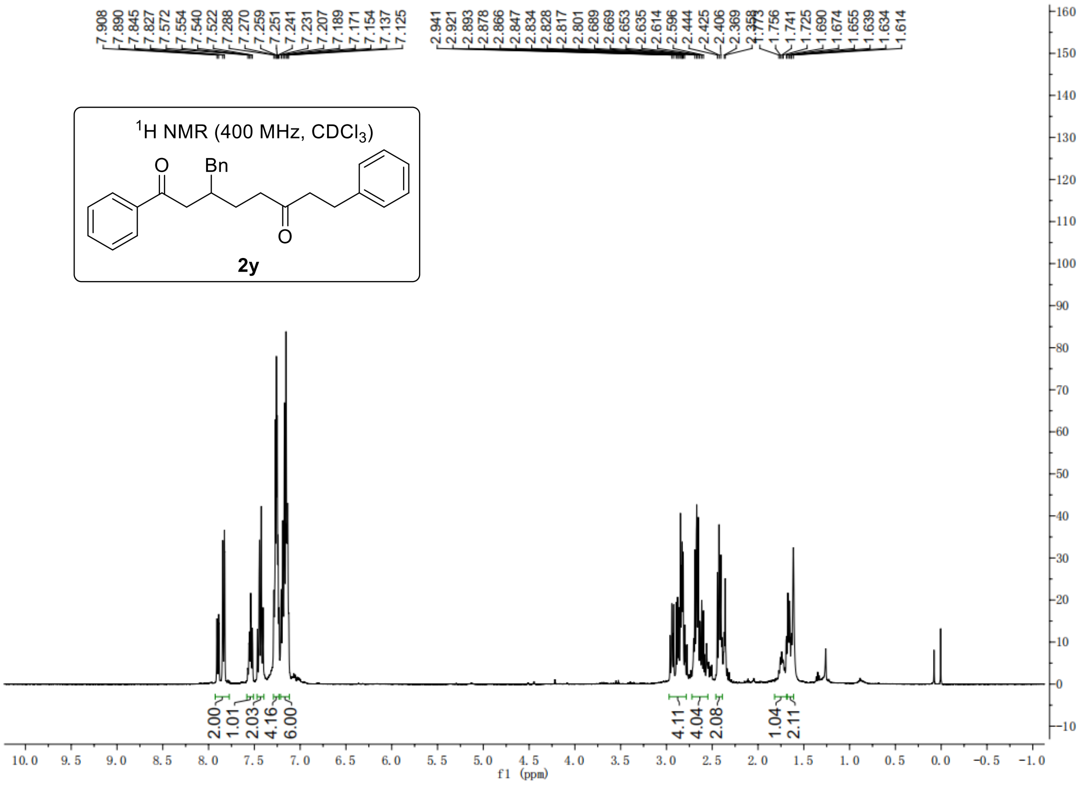

209.854
199.333
165.145
141.056
140.260
139.484
134.542
129.827
128.506
128.333
127.900
126.122
122.999
75.204
56.149
50.053
44.269
42.340
39.537
36.670
35.818
31.956
29.838
28.258
28.039
23.850
22.852
22.592
19.800
19.400
18.744
11.890
13C NMR (151 MHz, CDCl3)
O
Me
O
O
O
H
H
H
Me
Me
Me
Me
Me
2v
f1 (ppm)

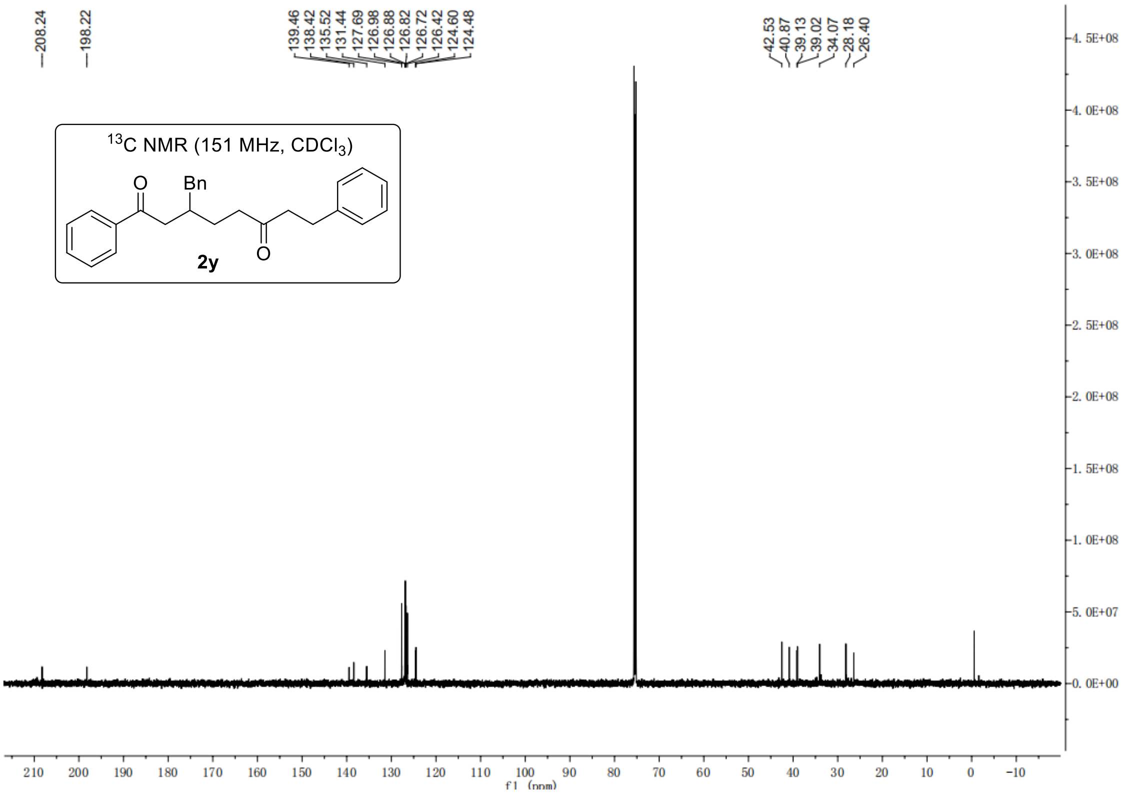

7.953
7.937
7.580
7.565
7.546
7.481
7.461
7.444
7.296
7.275
7.266
7.186
7.170
2.983
2.968
2.950
2.916
2.894
2.875
2.756
2.742
2.719
2.470
2.451
2.434
1.717
1.701
1.689
1.660
1H NMR (400 MHz, CDCl3)
O
O
2w
2.13
1.19
2.26
3.08
2.56
2.00
2.15
2.02
2.02
4.15
f1 (ppm)

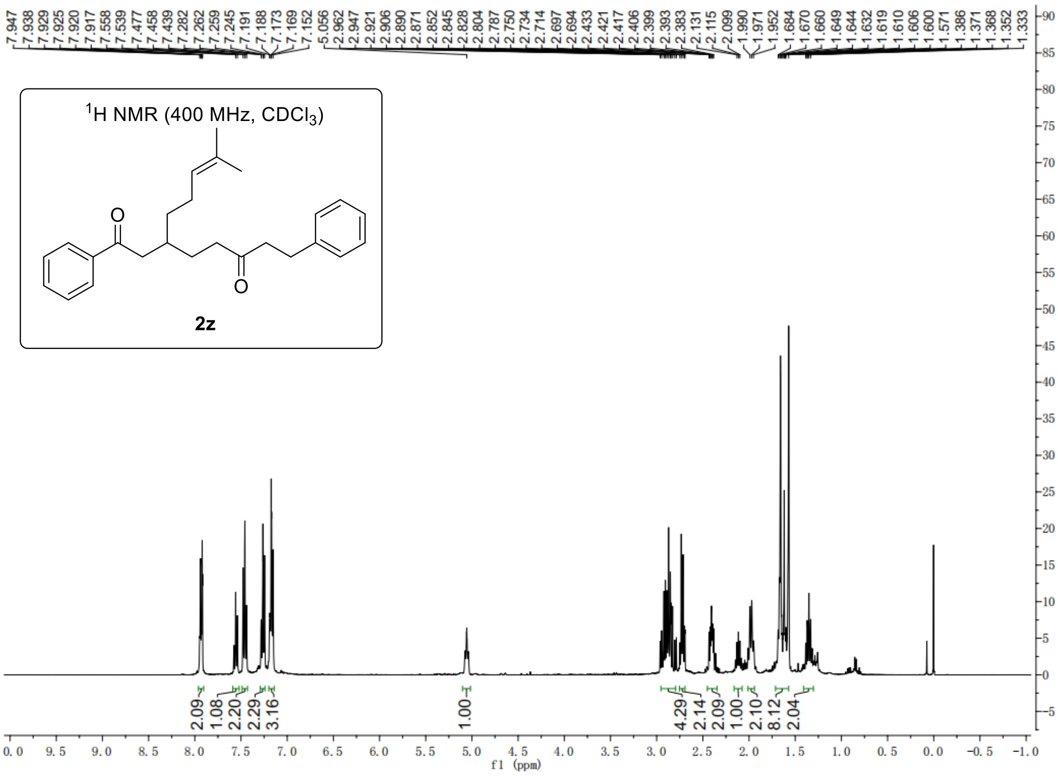

209.859
199.974
141.088
136.948
133.021
128.610
128.504
128.333
128.030
126.108
44.310
42.831
38.309
29.804
23.700
23.355
13C NMR (151 MHz, CDCl3)
O
O
2w
f1 (ppm)


7.991
7.970
7.895
7.876
7.554
7.536
7.517
7.446
7.427
7.408
7.301
7.282
7.263
7.259
7.245
7.226
7.204
7.183
7.161
7.143
7.125
7.107
3.339
3.308
3.292
3.273
3.252
3.231
3.209
2.829
2.821
2.805
2.789
2.618
2.597
2.580
2.322
2.306
2.298
2.282
2.234
2.221
2.210
2.197
2.063
2.047
2.039
2.029
1.906
1.895
1.884
1.872
1H NMR (400 MHz, CDCl3)
O
Ph
O
2x
0.20
1.80
0.98
2.05
10.32
3.06
2.07
2.00
1.08
1.09
1.07
1.09
f1 (ppm)

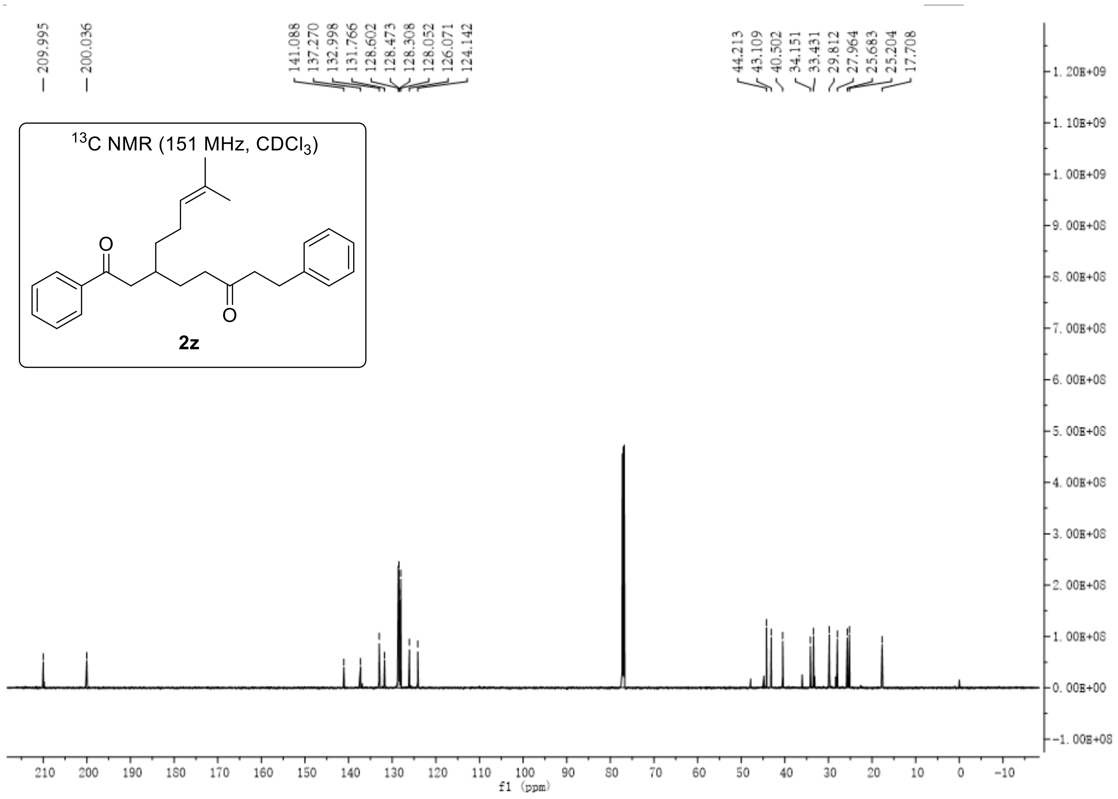

208.63
197.59
142.72
140.03
136.04
132.01
127.62
127.53
127.41
127.25
127.00
126.60
125.63
125.01
44.89
43.24
39.96
39.51
28.82
28.66
13C NMR (151 MHz, CDCl3)
O
Ph
O
2x
f1 (ppm)


7.908
7.890
7.845
7.827
7.572
7.554
7.540
7.522
7.288
7.270
7.259
7.251
7.241
7.231
7.207
7.189
7.171
7.154
7.137
7.125
2.941
2.921
2.893
2.878
2.866
2.847
2.834
2.828
2.817
2.801
2.689
2.669
2.653
2.635
2.614
2.596
2.444
2.425
2.406
2.369
2.358
1.773
1.756
1.741
1.725
1.690
1.674
1.655
1.639
1.634
1.614
1H NMR (400 MHz, CDCl3)
O
Bn
O
2y
2.00
1.01
2.03
4.16
6.00
4.11
4.04
2.08
1.04
2.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

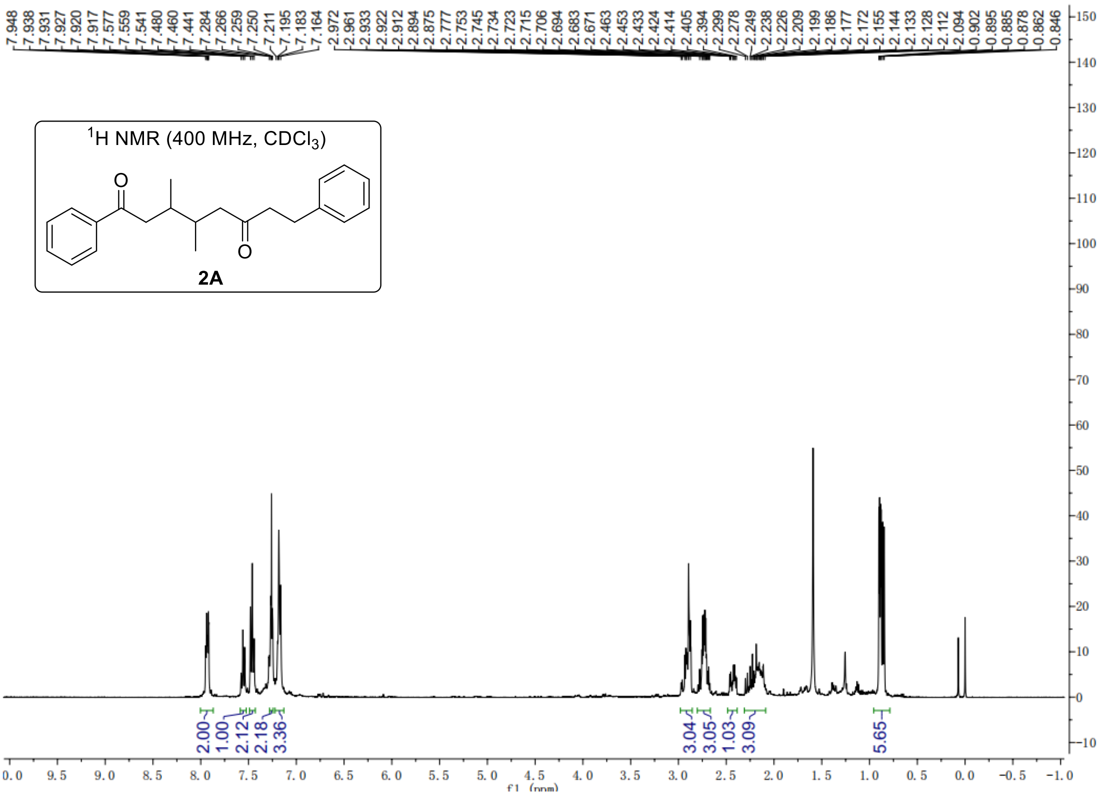

208.24
198.22
139.46
138.42
135.52
131.44
127.69
126.98
126.88
126.82
126.72
126.42
124.60
124.48
42.53
40.87
39.13
39.02
34.07
28.18
26.40
13C NMR (151 MHz, CDCl3)
O
Bn
O
2y
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

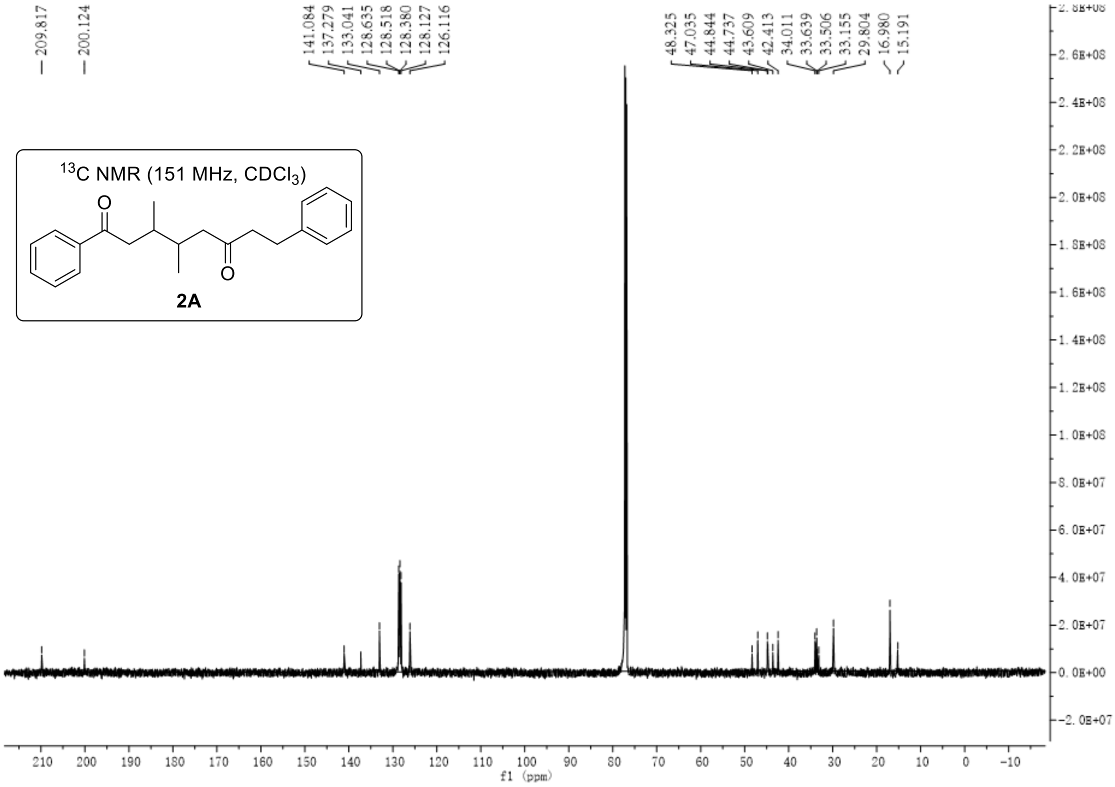


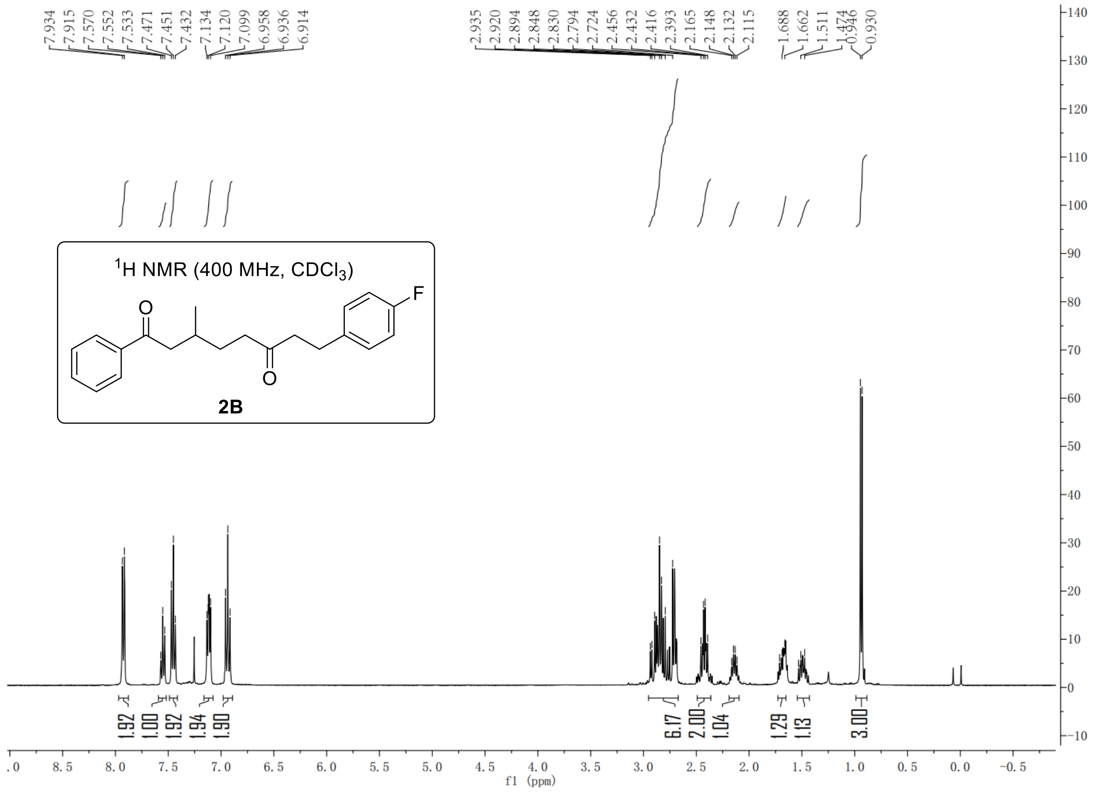
7.947
7.938
7.929
7.925
7.920
7.917
7.558
7.539
7.477
7.458
7.439
7.282
7.262
7.259
7.245
7.191
7.188
7.173
7.169
7.152
5.056
2.962
2.947
2.921
2.906
2.890
2.871
2.852
2.845
2.828
2.804
2.787
2.750
2.734
2.714
2.697
2.694
2.433
2.421
2.417
2.406
2.399
2.393
2.383
2.131
2.115
2.099
1.990
1.971
1.952
1.684
1.670
1.660
1.649
1.644
1.632
1.619
1.610
1.606
1.600
1.571
1.386
1.371
1.368
1.352
1.333
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2z
2.09
1.08
2.20
2.29
3.16
1.00
4.29
2.14
2.09
1.00
2.10
8.12
2.04
f1 (ppm)

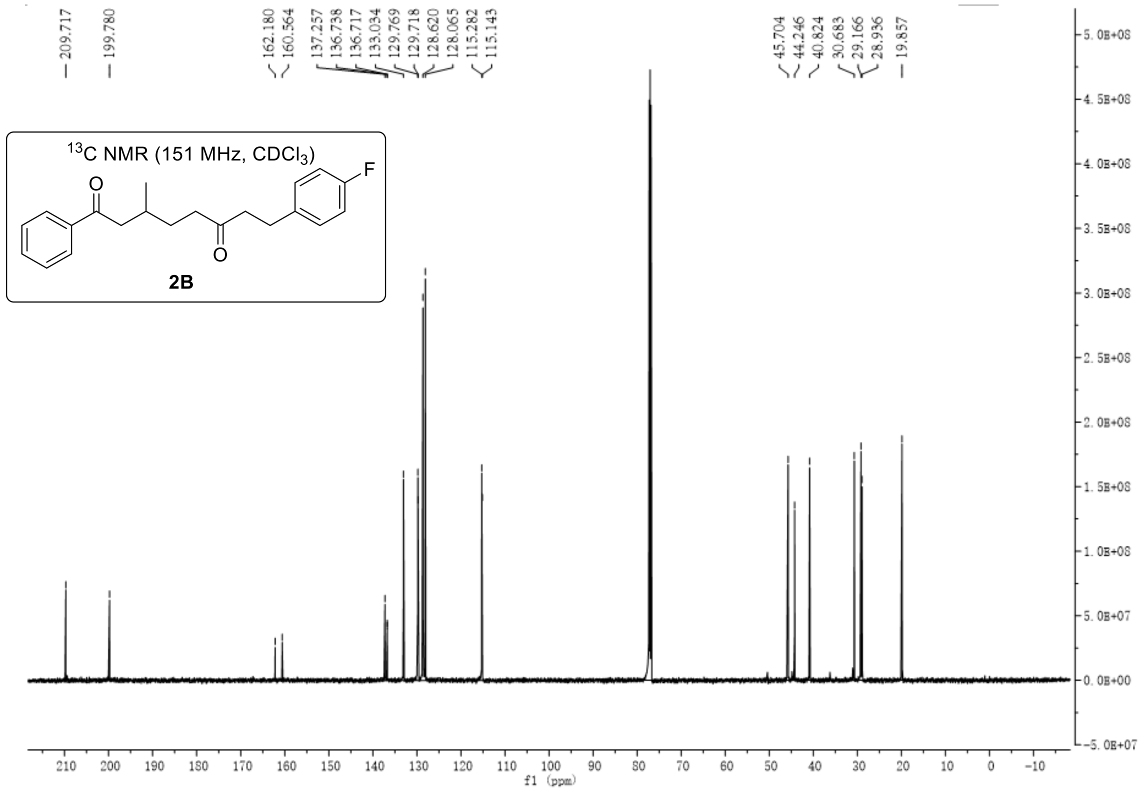


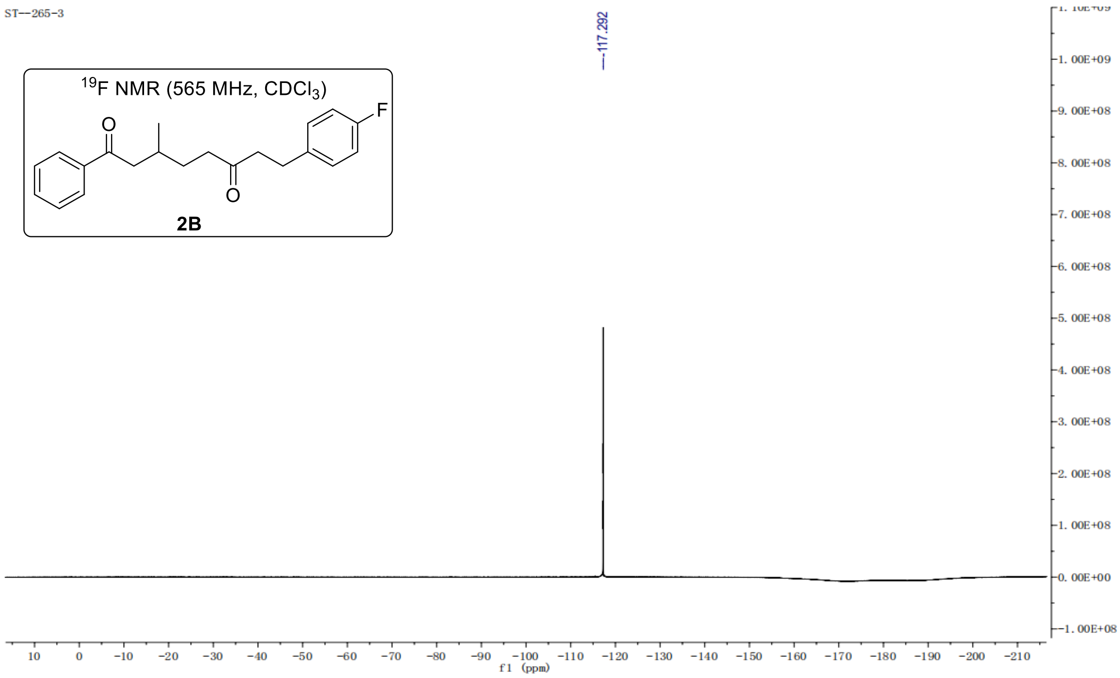
209.995
200.036
141.088
137.270
132.998
131.766
128.602
128.473
128.308
128.052
126.071
124.142
44.213
43.109
40.502
34.151
33.431
29.812
27.964
25.683
25.204
17.708
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2z
f1 (ppm)

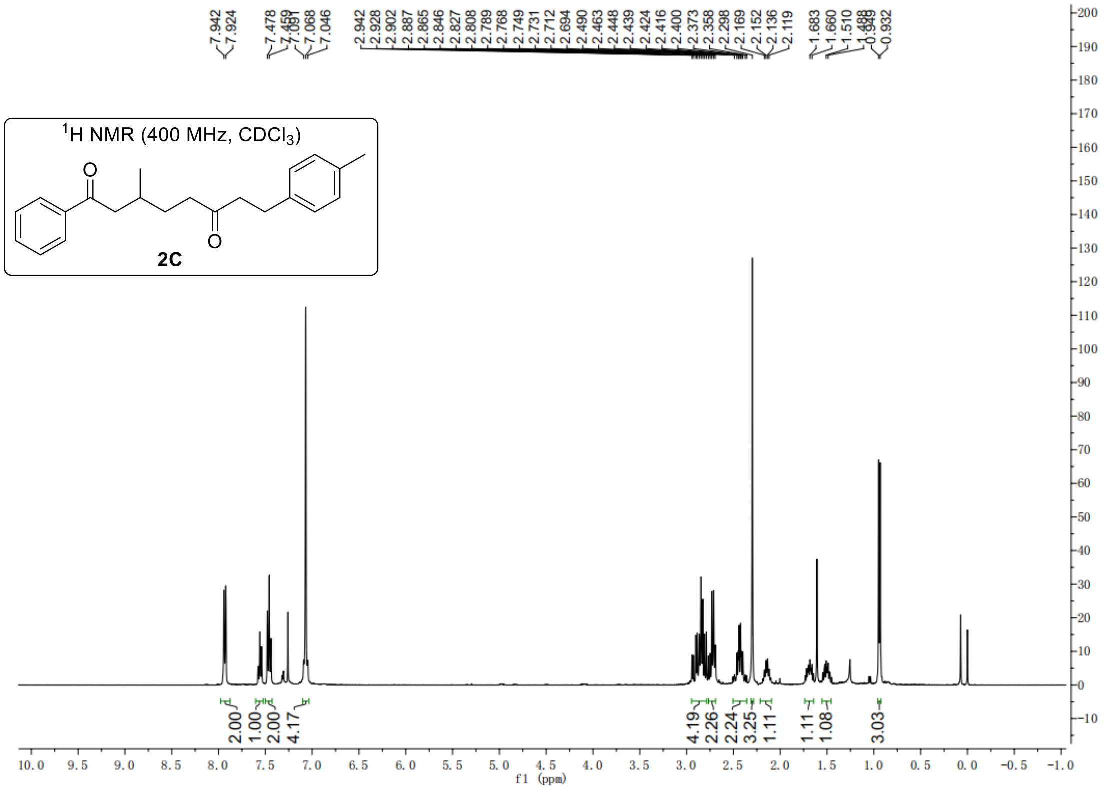

7.948 7.938 7.931 7.927 7.920 7.917 7.577 7.559 7.541 7.480 7.460 7.441 7.284 7.266 7.259 7.250 7.211 7.195 7.183 7.164 2.972 2.961 2.933 2.922 2.912 2.894 2.875 2.777 2.753 2.745 2.734 2.723 2.715 2.706 2.694 2.683 2.671 2.463 2.453 2.433 2.424 2.414 2.405 2.394 2.299 2.278 2.249 2.238 2.226 2.209 2.199 2.186 2.177 2.172 2.155 2.144 2.133 2.128 2.112 2.094 0.902 0.895 0.885 0.878 0.862 0.846
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2A
2.00
1.00
2.12
2.18
3.36
3.04
3.05
1.03
3.09
5.65
f1 (ppm)

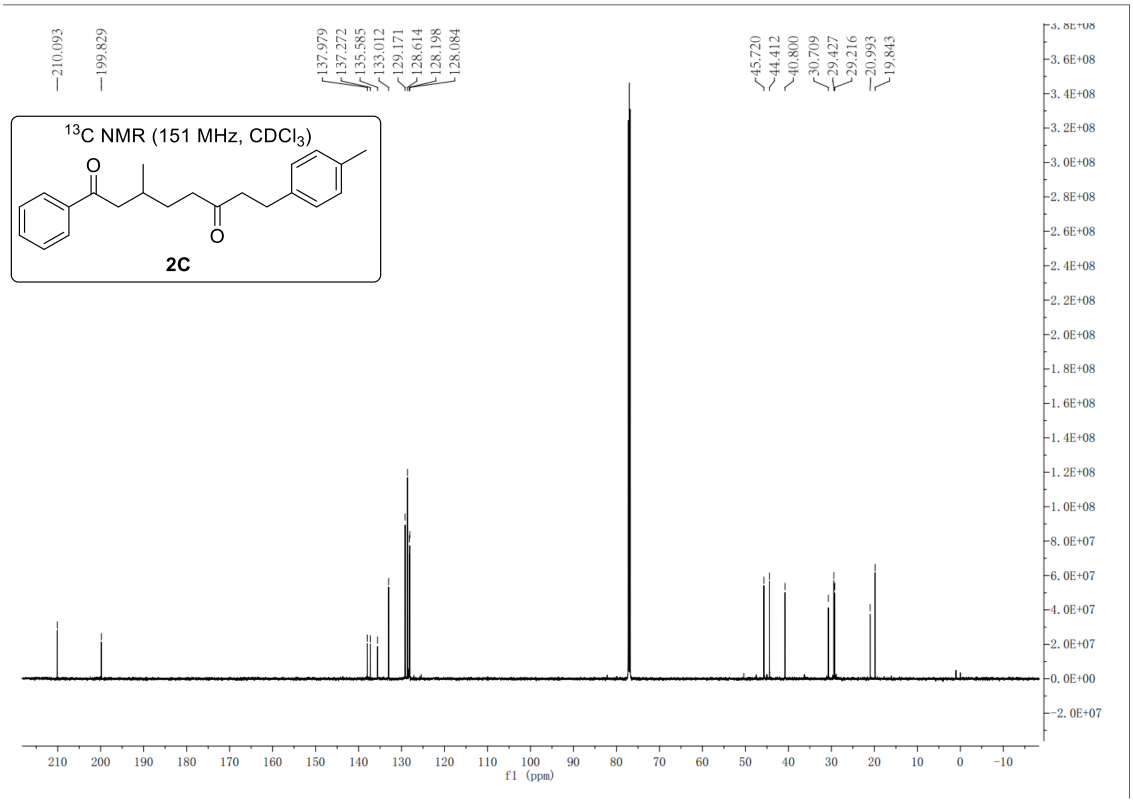

209.817
200.124
141.084 137.279 133.041 128.635 128.518 128.380 128.127 126.116
48.325 47.035 44.844 44.737 43.609 42.413 34.011 33.639 33.506 33.155 29.804 16.980 15.191
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2A
f1 (ppm)

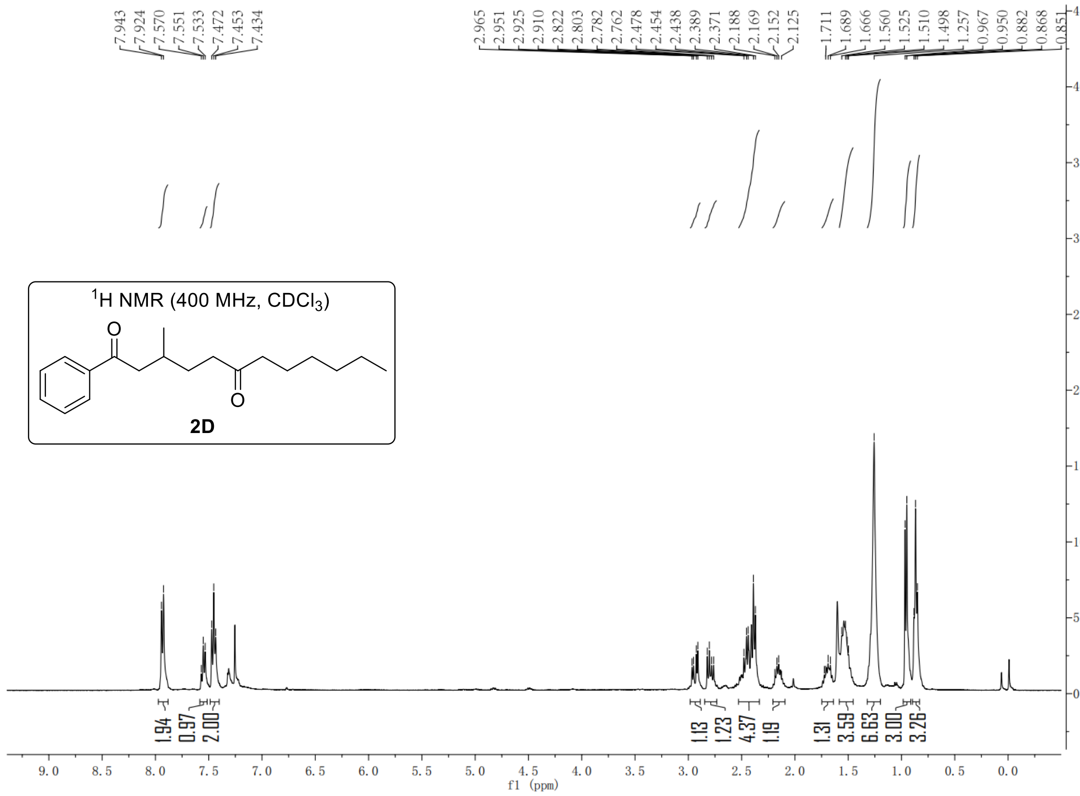

7.934
7.915
7.570
7.552
7.533
7.471
7.451
7.432
7.134
7.120
7.099
6.958
6.936
6.914
2.935
2.920
2.894
2.848
2.830
2.794
2.724
2.456
2.432
2.416
2.393
2.165
2.148
2.132
2.115
1.688
1.662
1.511
1.474
0.946
0.930
^{1}H NMR (400 MHz, CDCl$_3$)
O
F
O
2B
1.92
1.00
1.92
1.94
1.90
6.17
2.00
1.04
1.29
1.13
3.00
f1 (ppm)

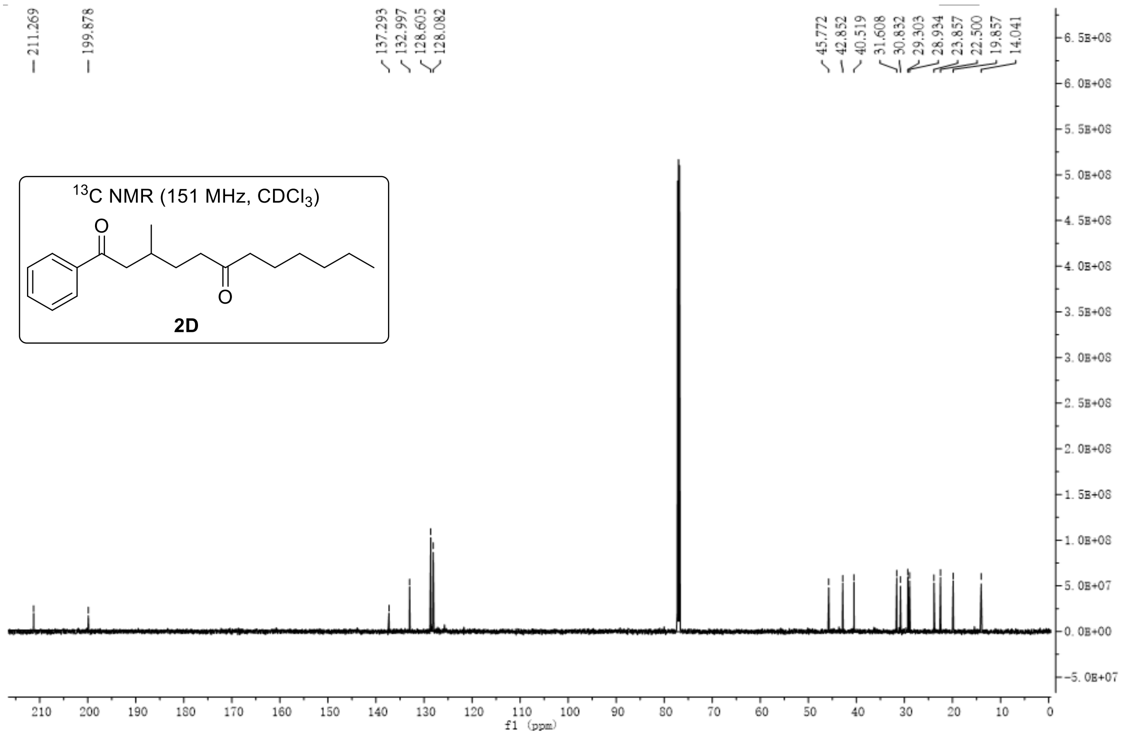

209.717
199.780
162.180
160.564
137.257
136.738
136.717
133.034
129.769
129.718
128.620
128.065
115.282
115.143
45.704
44.246
40.824
30.683
29.166
28.936
19.857
^{13}C NMR (151 MHz, CDCl$_3$)
O
F
O
2B
f1 (ppm)


ST—265-3
-117.292
19F NMR (565 MHz, CDCl3)
O
F
O
2B
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.942
7.924
7.478
7.459
7.091
7.068
7.046
2.942
2.928
2.902
2.887
2.865
2.846
2.827
2.808
2.789
2.768
2.749
2.731
2.712
2.694
2.490
2.463
2.448
2.439
2.424
2.416
2.400
2.373
2.358
2.298
2.169
2.152
2.136
2.119
1.683
1.660
1.510
1.488
0.949
0.932
1H NMR (400 MHz, CDCl3)
O
O
2C
2.00
1.00
2.00
4.17
4.19
2.26
2.24
3.25
1.11
1.11
1.08
3.03
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

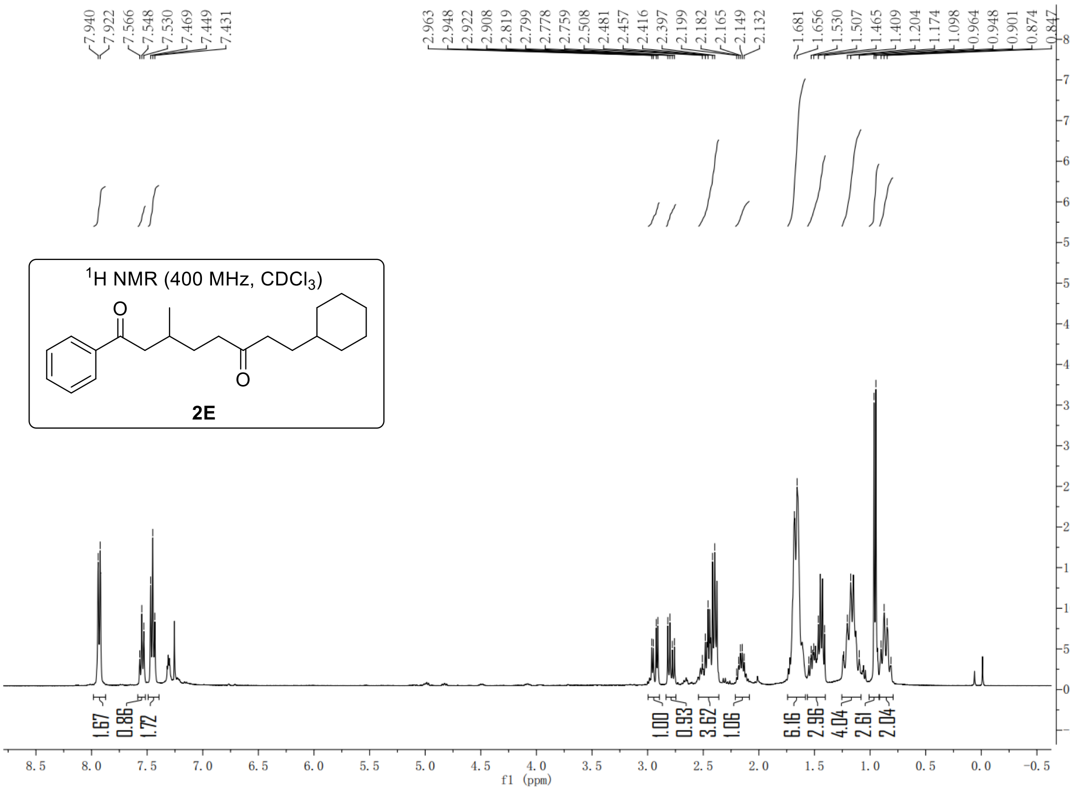

210.093
199.829
137.979
137.272
135.585
133.012
129.171
128.614
128.198
128.084
45.720
44.412
40.800
30.709
29.427
29.216
20.993
19.843
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2C
3.6E+08
3.4E+08
3.2E+08
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.943
7.924
7.570
7.551
7.533
7.472
7.453
7.434
2.965
2.951
2.925
2.910
2.822
2.803
2.782
2.762
2.478
2.454
2.438
2.389
2.371
2.188
2.169
2.152
2.125
1.711
1.689
1.666
1.560
1.525
1.510
1.498
1.257
0.967
0.950
0.882
0.868
0.851
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
2D
1.94
0.97
2.00
1.13
1.23
4.37
1.19
1.31
3.59
6.63
3.00
3.26
45
40
35
30
25
20
15
10
5
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



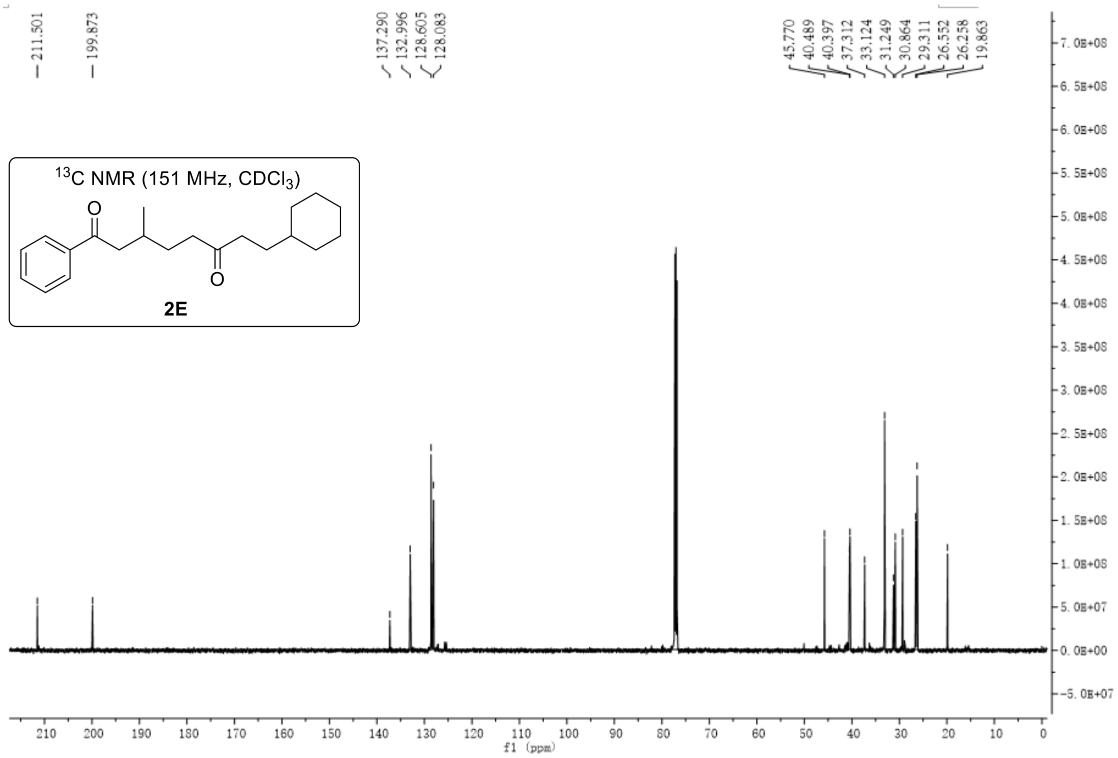
211.269
199.878
137.293
132.997
128.605
128.082
45.772
42.852
40.519
31.608
30.832
29.303
28.934
23.857
22.500
19.857
14.041
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

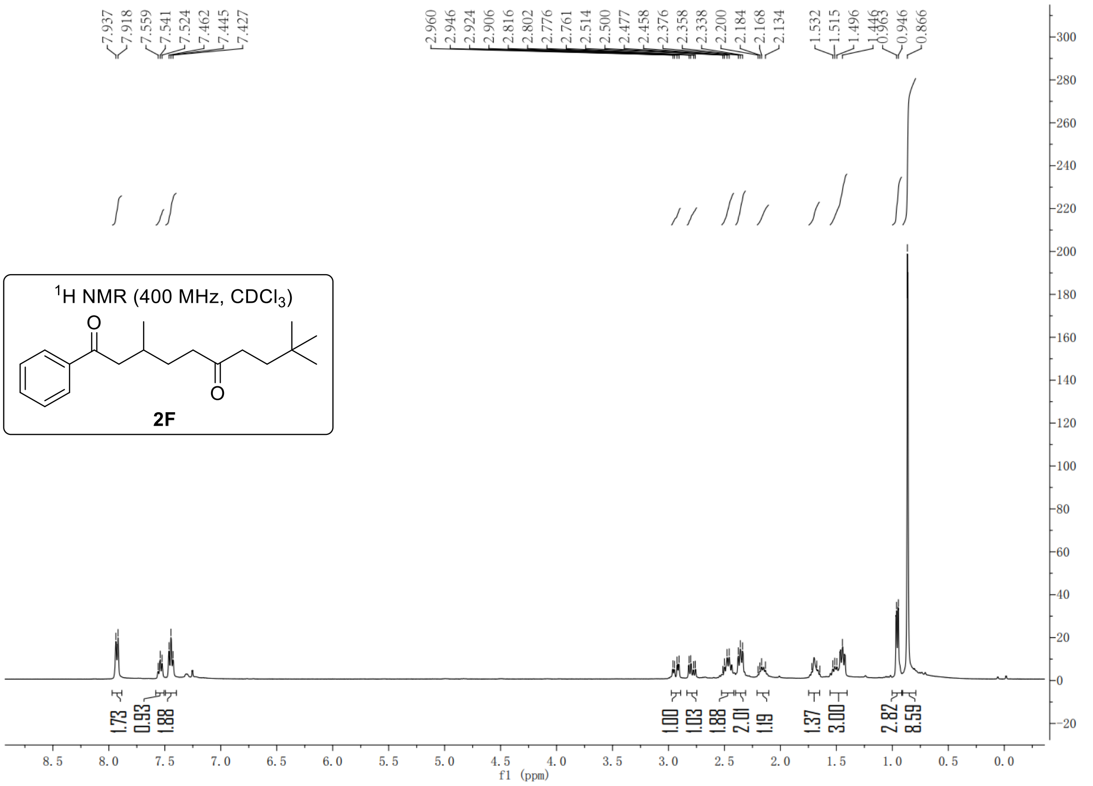
2D

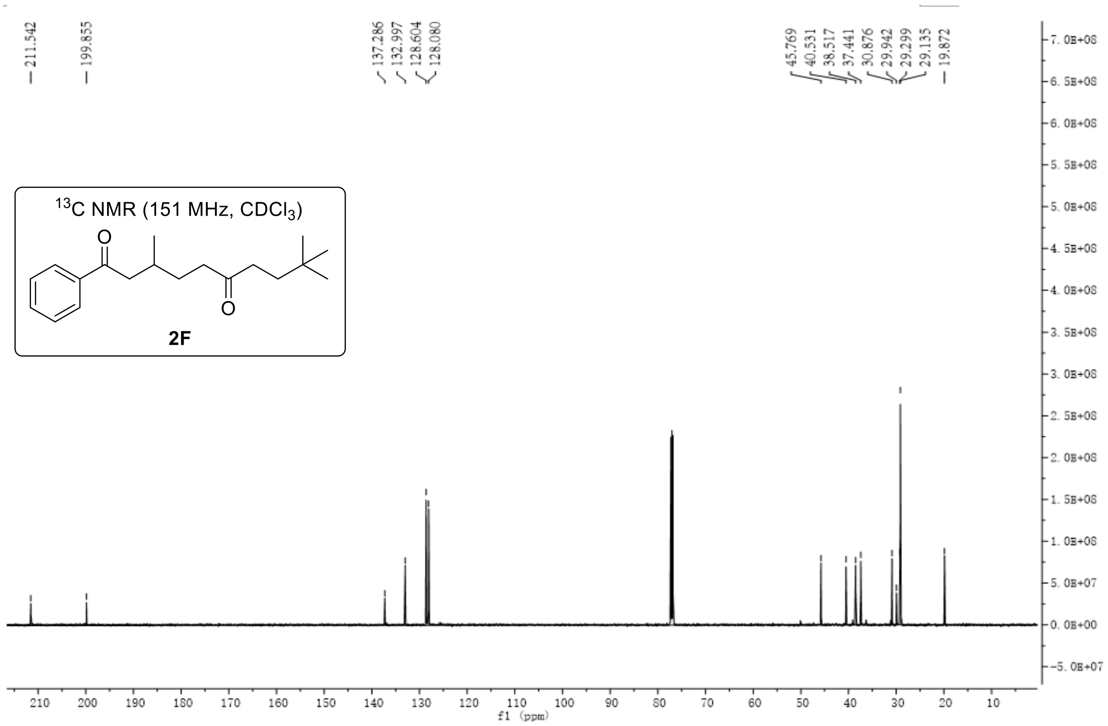


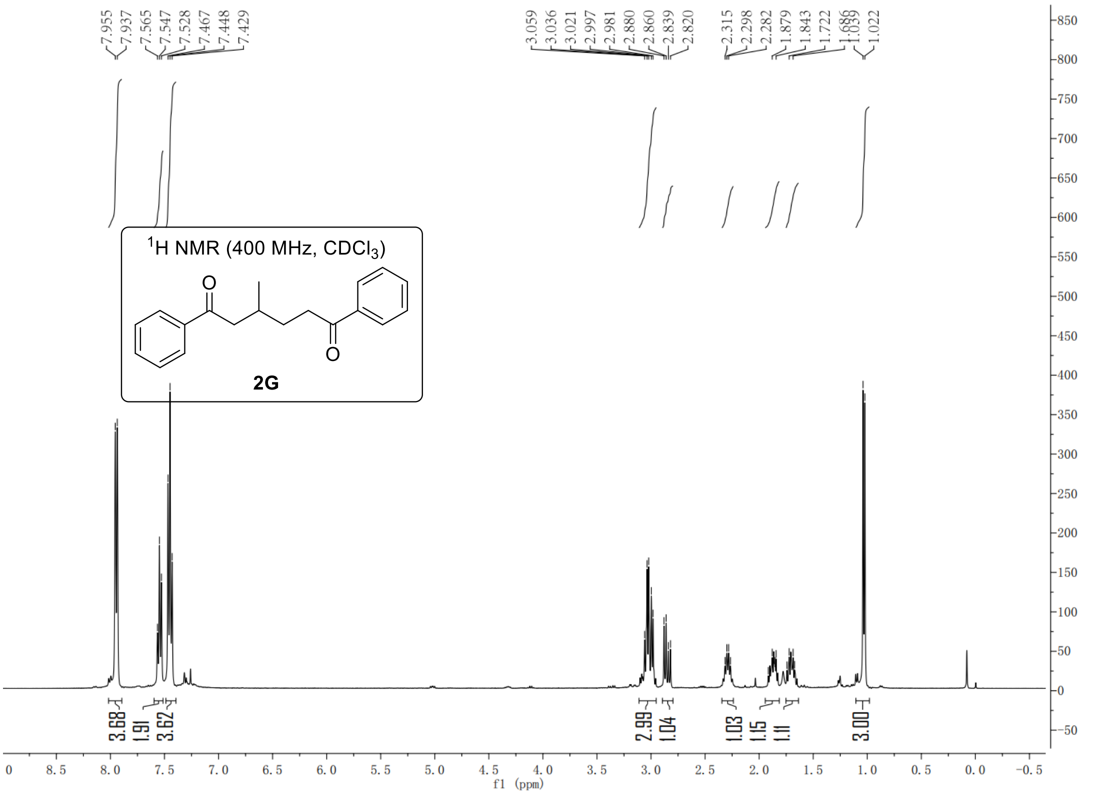
7.940
7.922
7.566
7.548
7.530
7.469
7.449
7.431
2.963
2.948
2.922
2.908
2.819
2.799
2.778
2.759
2.508
2.481
2.457
2.416
2.397
2.199
2.182
2.165
2.149
2.132
1.681
1.656
1.530
1.507
1.465
1.409
1.204
1.174
1.098
0.964
0.948
0.901
0.874
0.847
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
1.67
0.86
1.72
1.00
0.93
3.62
1.06
6.16
2.96
4.04
2.61
2.04
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

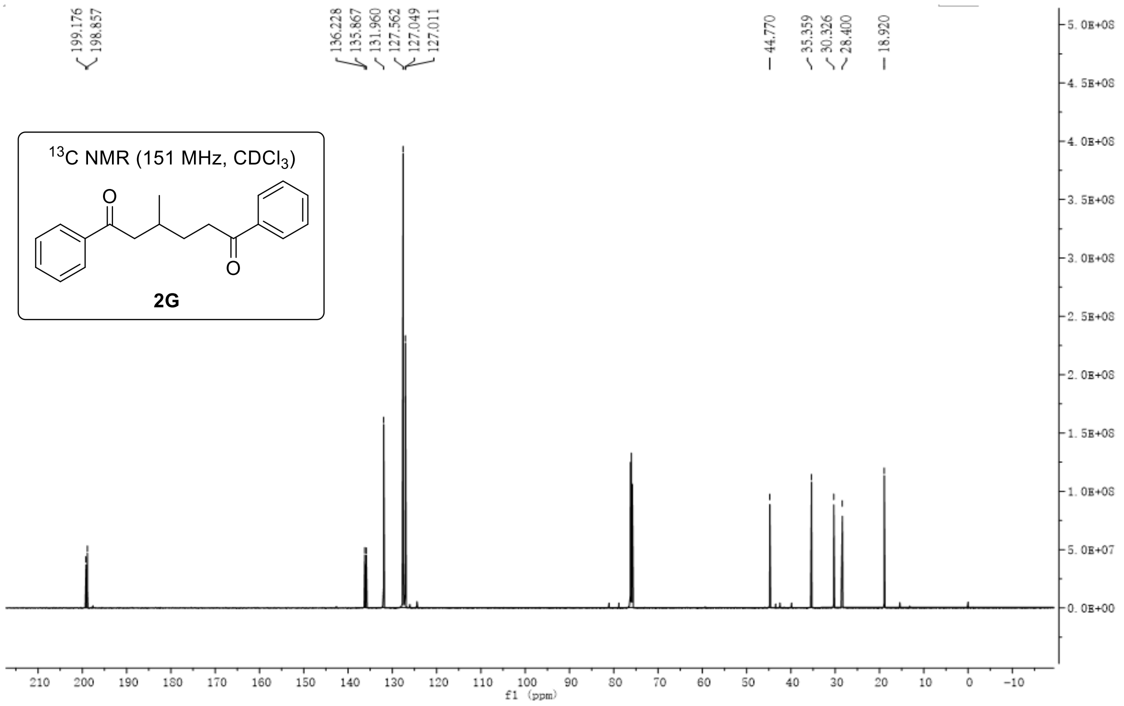
2E

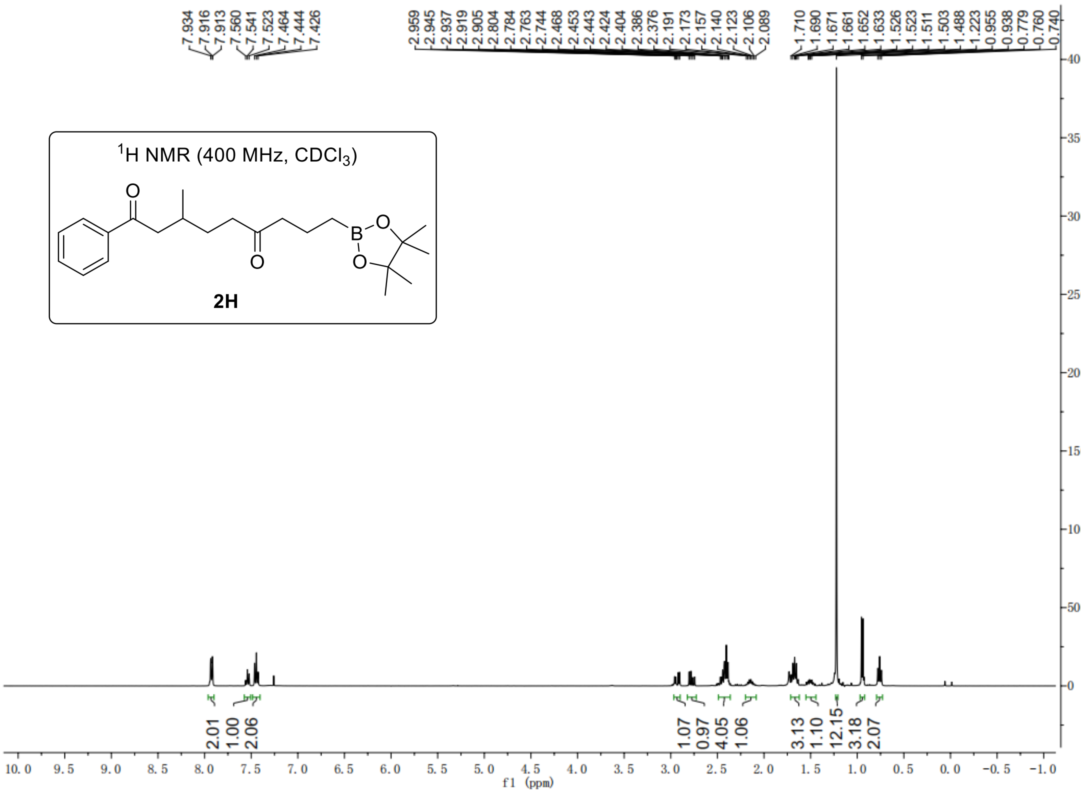

211.501
199.873
137.290
132.996
128.605
128.083
45.770
40.489
40.397
37.312
33.124
31.249
30.864
29.311
26.552
26.258
19.863
13C NMR (151 MHz, CDCl3)
O
O
2E
f1 (ppm)

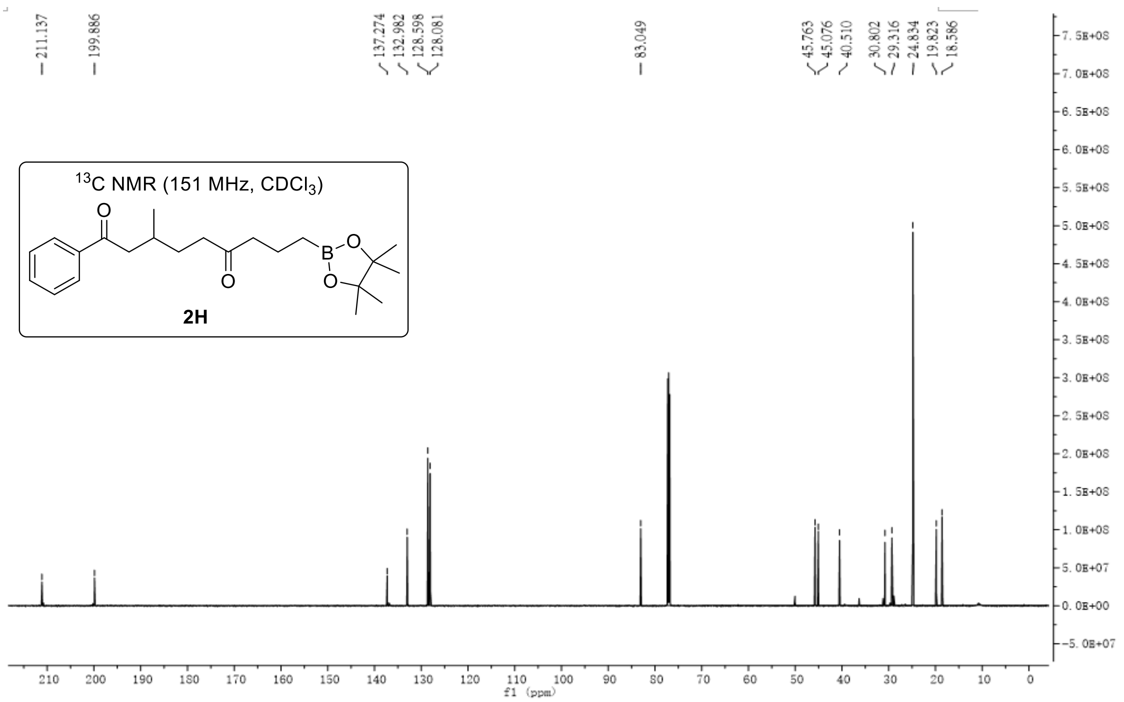

7.937
7.918
7.559
7.541
7.524
7.462
7.445
7.427
2.960
2.946
2.924
2.906
2.816
2.802
2.776
2.761
2.514
2.500
2.477
2.458
2.376
2.358
2.338
2.200
2.184
2.168
2.134
1.532
1.515
1.496
1.446
0.963
0.946
0.866
1H NMR (400 MHz, CDCl3)
O
O
2F
1.73
0.93
1.88
1.00
1.03
1.88
2.01
1.19
1.37
3.00
2.82
8.59
f1 (ppm)


211.542
199.855
137.286
132.997
128.604
128.080
45.769
40.531
38.517
37.441
30.876
29.942
29.299
29.135
19.872
13C NMR (151 MHz, CDCl3)
2F
f1 (ppm)

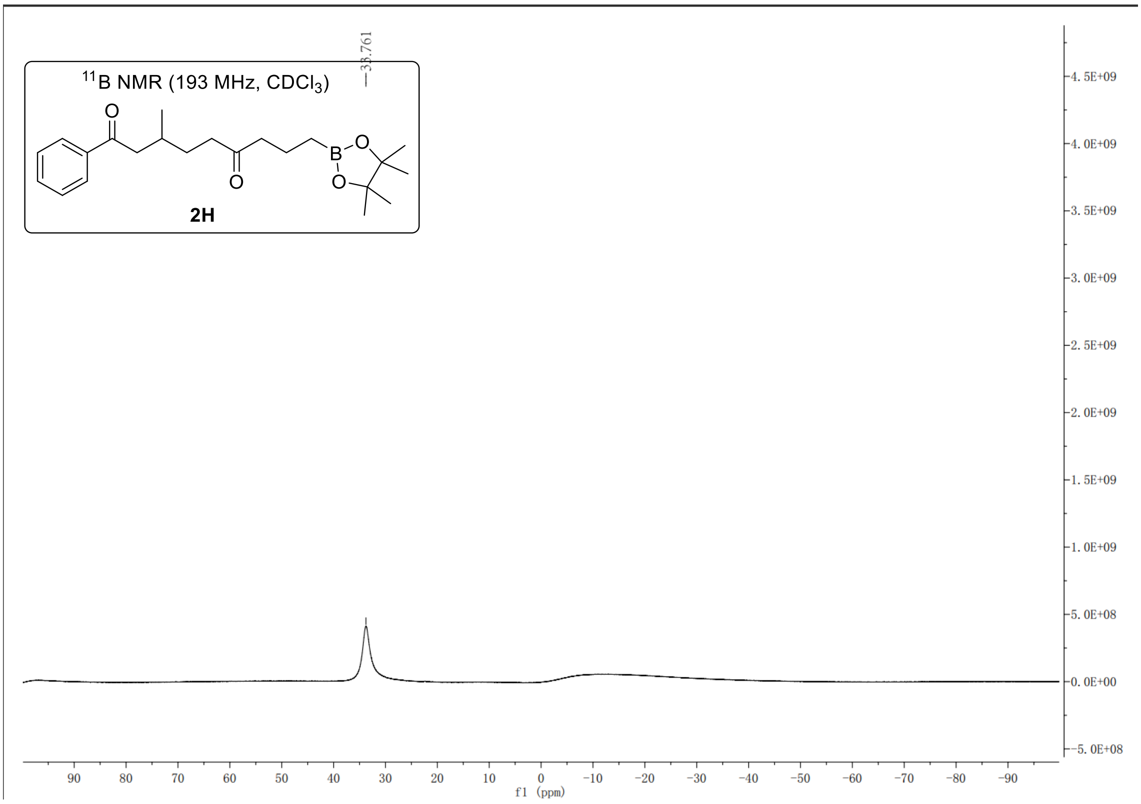

7.955
7.937
7.565
7.547
7.528
7.467
7.448
7.429
3.059
3.036
3.021
2.997
2.981
2.880
2.860
2.839
2.820
2.315
2.298
2.282
1.879
1.843
1.722
1.686
1.039
1.022
1H NMR (400 MHz, CDCl3)
2G
3.68
1.91
3.62
2.99
1.04
1.03
1.15
1.11
3.00
f1 (ppm)


199.176
198.857
136.228
135.867
131.960
127.562
127.049
127.011
44.770
35.359
30.326
28.400
18.920
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
2G
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

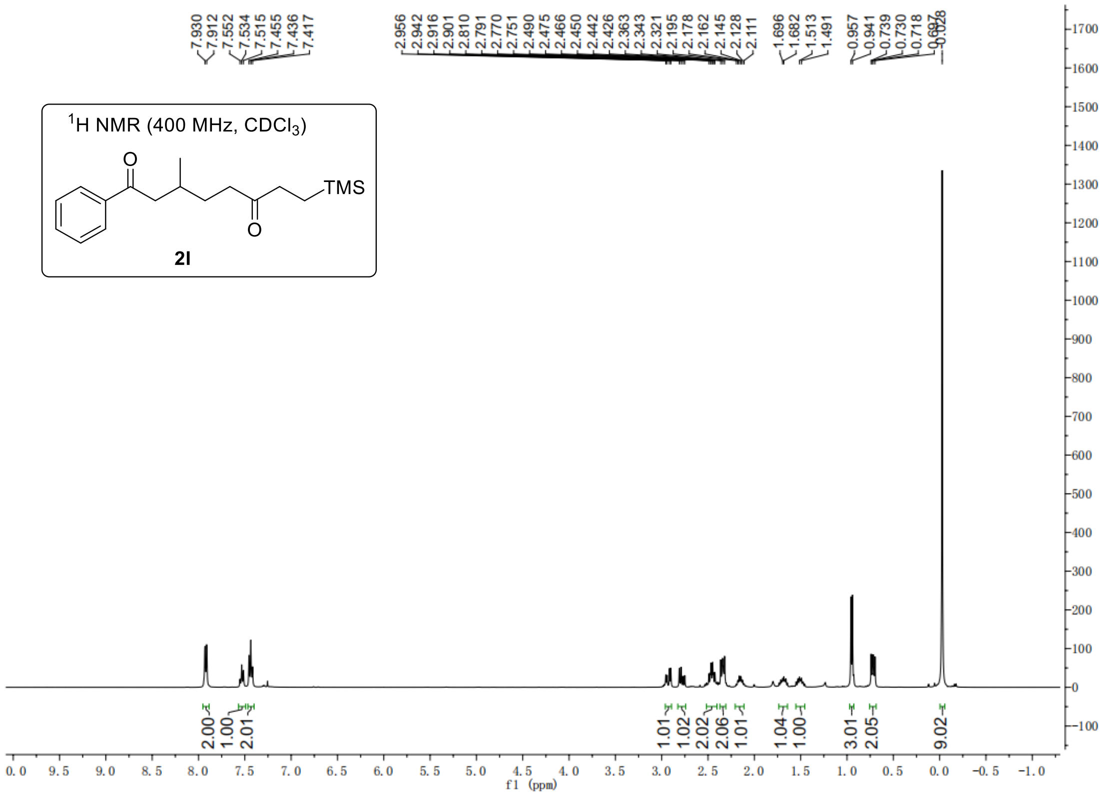

7.934
7.916
7.913
7.560
7.541
7.523
7.464
7.444
7.426
2.959
2.945
2.937
2.919
2.905
2.804
2.784
2.763
2.744
2.468
2.453
2.443
2.424
2.404
2.386
2.376
2.191
2.173
2.157
2.140
2.123
2.106
2.089
1.710
1.690
1.671
1.661
1.652
1.633
1.526
1.523
1.511
1.503
1.488
1.223
0.955
0.938
0.779
0.760
0.740
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
B
O
O
2H
2.01
1.00
2.06
1.07
0.97
4.05
1.06
3.13
1.10
12.15
3.18
2.07
400
350
300
250
200
150
100
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



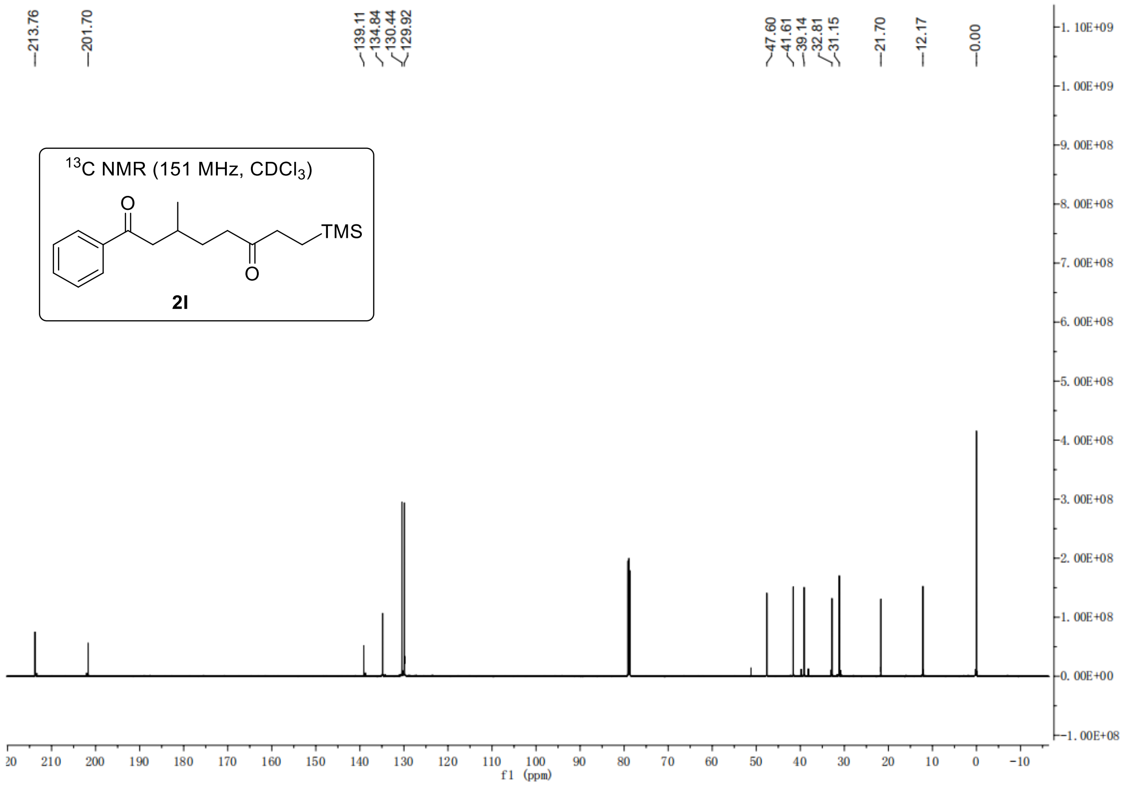
211.137
199.886
137.274
132.982
128.598
128.081
83.049
45.763
45.076
40.510
30.802
29.316
24.834
19.823
18.586
^{13}C NMR (151 MHz, CDCl$_3$)
O
O
B
O
O
2H
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
−5.0E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



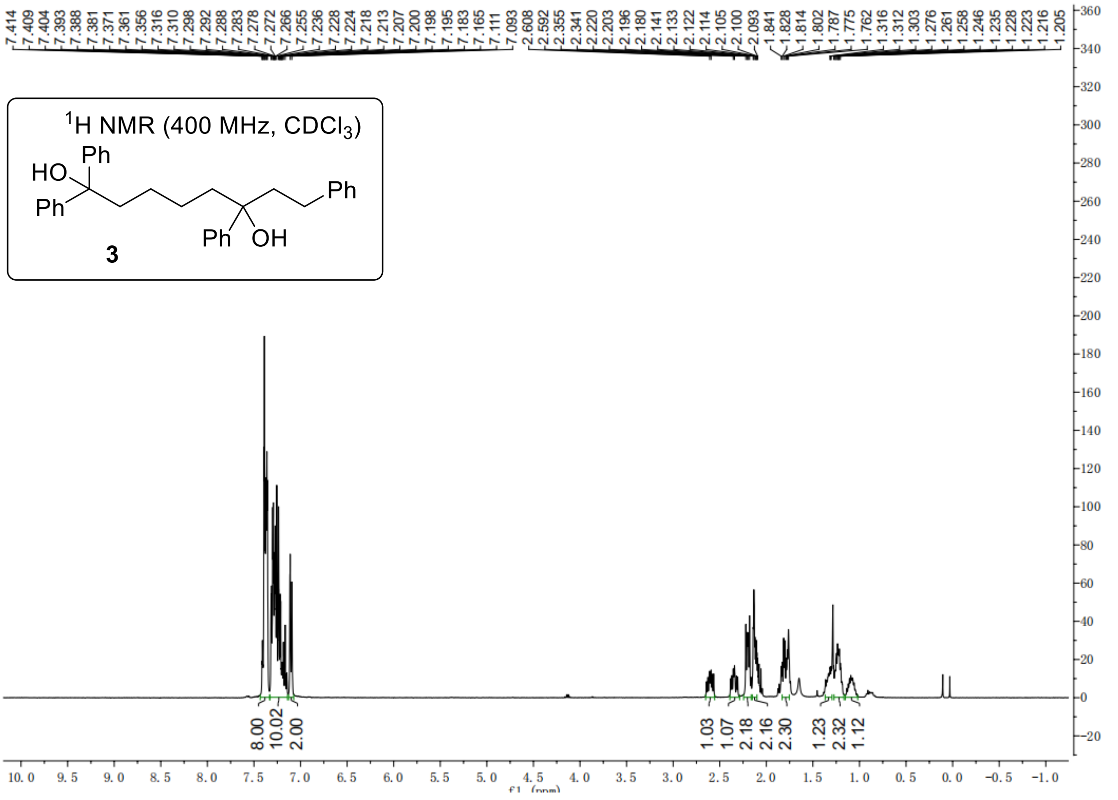
33.761
^{11}B NMR (193 MHz, CDCl$_3$)
O
O
B
O
O
2H
4.5E+09
4.0E+09
3.5E+09
3.0E+09
2.5E+09
2.0E+09
1.5E+09
1.0E+09
5.0E+08
0.0E+00
−5.0E+08
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

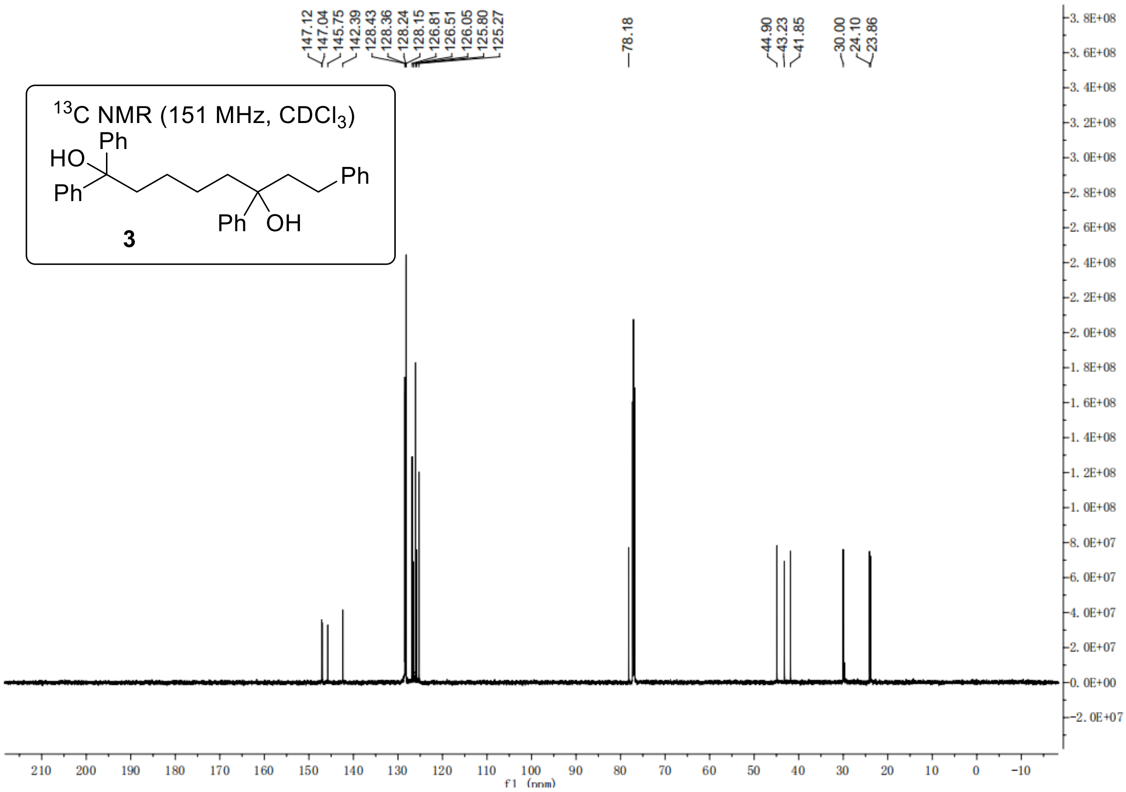


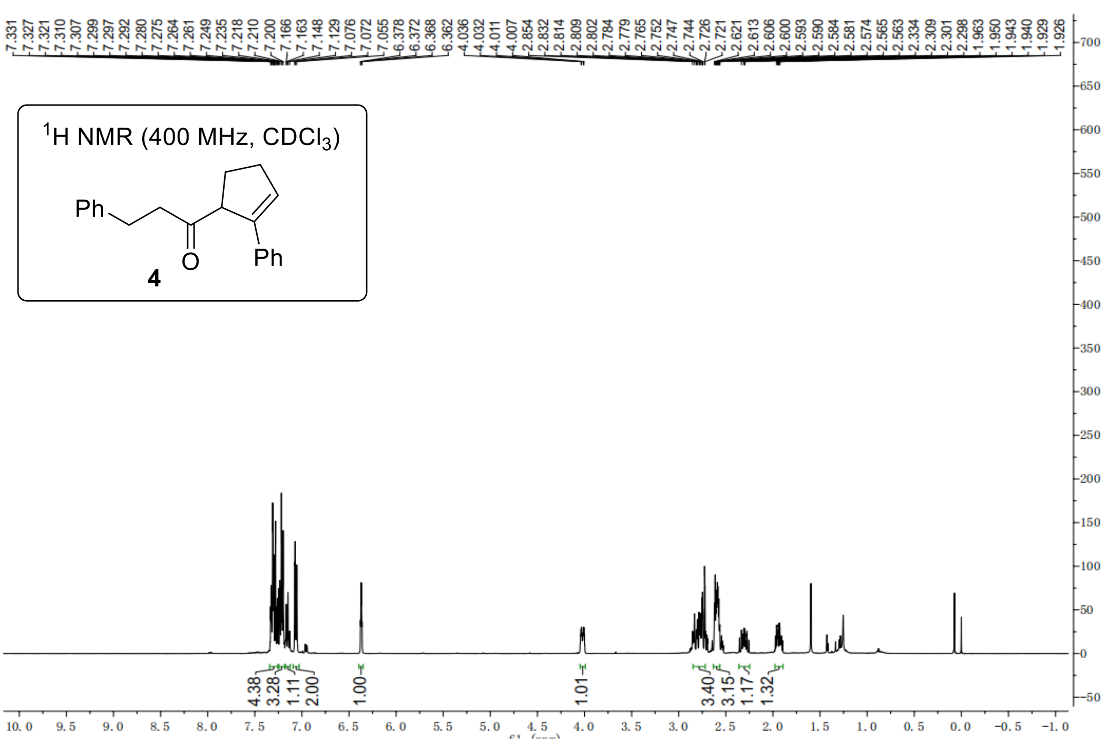
7.930
7.912
7.552
7.534
7.515
7.455
7.436
7.417
2.956
2.942
2.916
2.901
2.810
2.791
2.770
2.751
2.490
2.475
2.466
2.450
2.442
2.426
2.363
2.343
2.321
2.195
2.178
2.162
2.145
2.128
2.111
1.696
1.682
1.513
1.491
0.957
0.941
0.739
0.730
0.718
0.697
0.028
^{1}H NMR (400 MHz, CDCl$_3$)
O
TMS
O
2l
2.00
1.00
2.01
1.01
1.02
2.02
2.06
1.01
1.04
1.00
3.01
2.05
9.02
f1 (ppm)

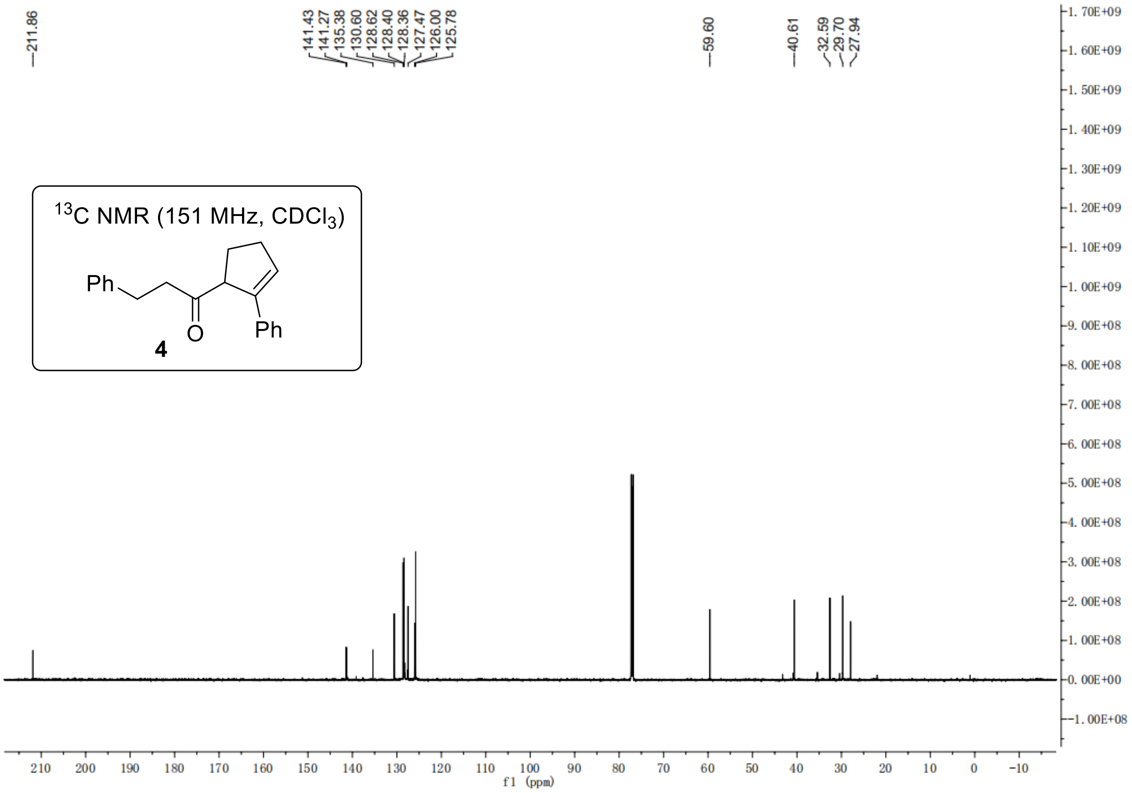


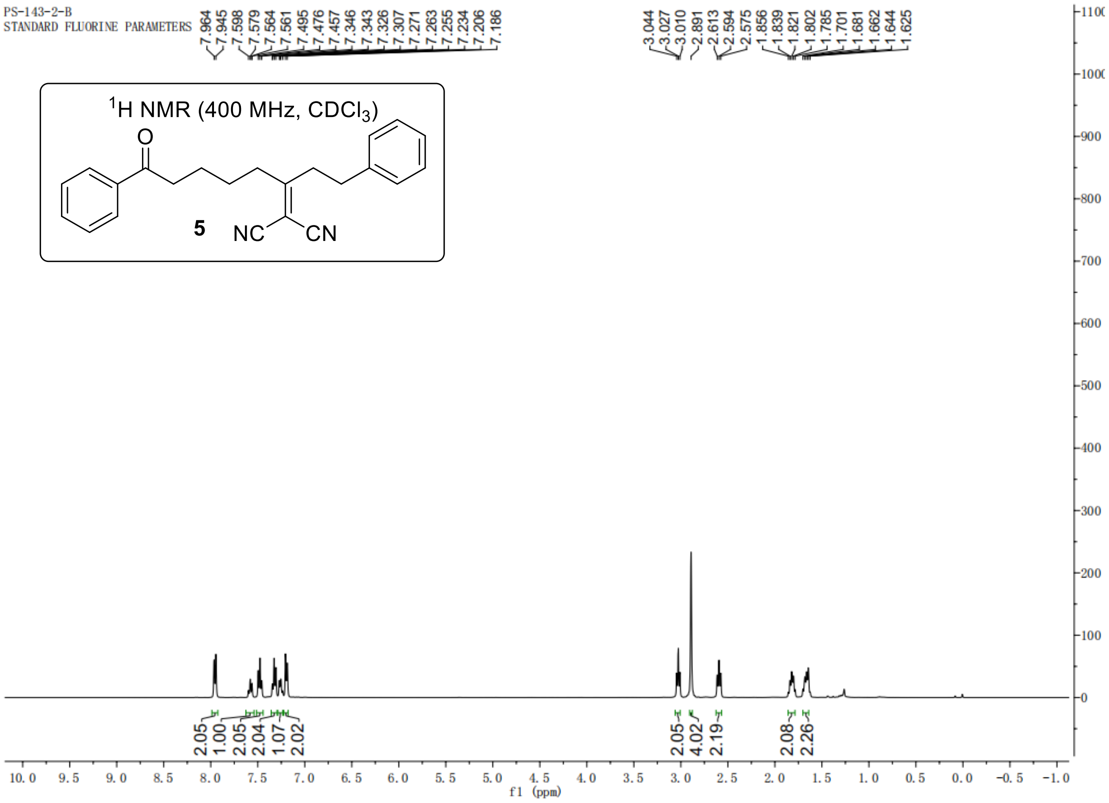
213.76
201.70
139.11
134.84
130.44
129.92
47.60
41.61
39.14
32.81
31.15
21.70
12.17
0.00
^{13}C NMR (151 MHz, CDCl$_3$)
O
TMS
O
2l
f1 (ppm)

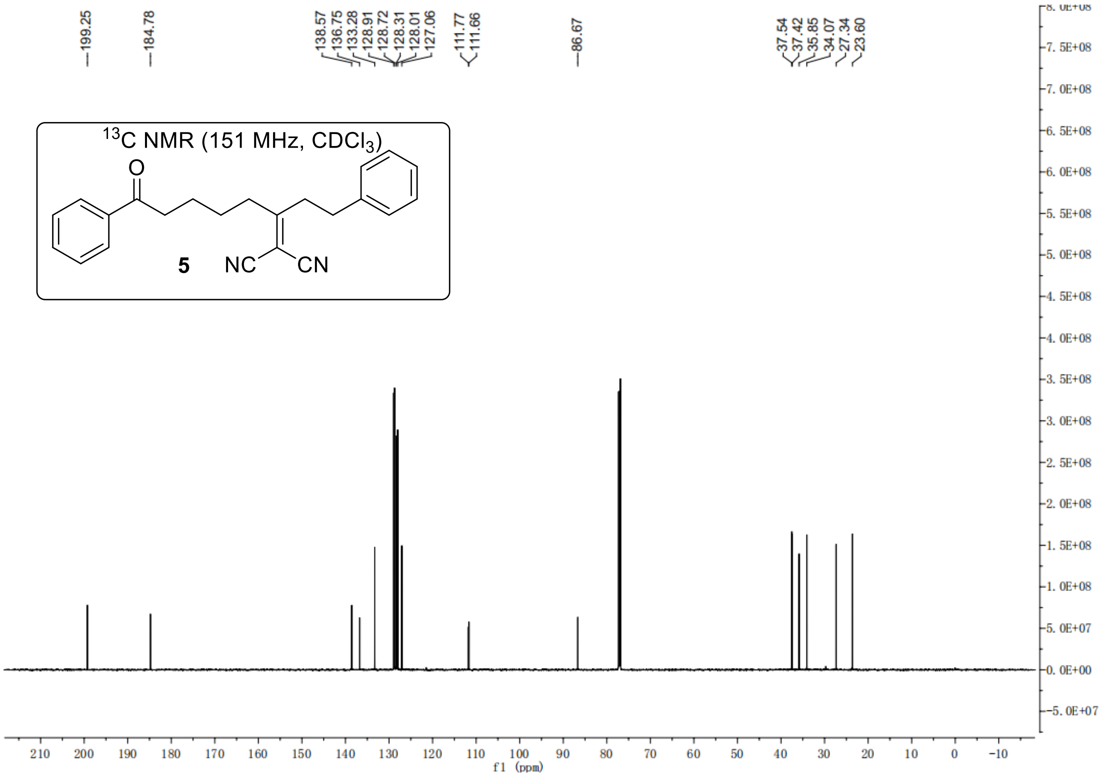

7.414
7.409
7.404
7.393
7.388
7.381
7.371
7.361
7.356
7.316
7.310
7.298
7.292
7.288
7.283
7.278
7.272
7.266
7.255
7.236
7.228
7.224
7.218
7.213
7.207
7.200
7.198
7.195
7.183
7.165
7.111
7.093
2.608
2.592
2.355
2.341
2.220
2.203
2.196
2.180
2.141
2.133
2.122
2.114
2.105
2.100
2.093
1.841
1.828
1.814
1.802
1.787
1.775
1.762
1.316
1.312
1.303
1.276
1.261
1.258
1.246
1.235
1.228
1.223
1.216
1.205
1H NMR (400 MHz, CDCl3)
HO
Ph
Ph
Ph
Ph
OH
3
8.00
10.02
2.00
1.03
1.07
2.18
2.16
2.30
1.23
2.32
1.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 −20

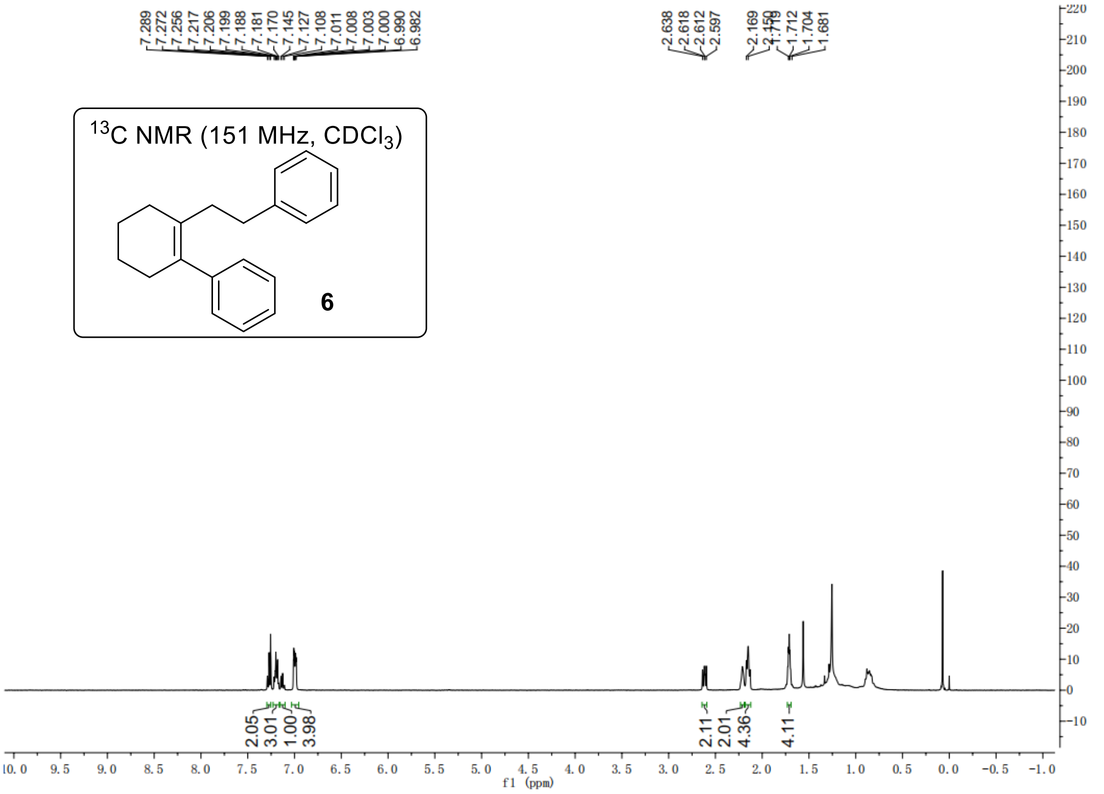

147.12
147.04
145.75
142.39
128.43
128.36
128.24
128.15
126.81
126.51
126.05
125.80
125.27
78.18
44.90
43.23
41.85
30.00
24.10
23.86
13C NMR (151 MHz, CDCl3)
HO
Ph
Ph
Ph
Ph
OH
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
3.8E+08 3.6E+08 3.4E+08 3.2E+08 3.0E+08 2.8E+08 2.6E+08 2.4E+08 2.2E+08 2.0E+08 1.8E+08 1.6E+08 1.4E+08 1.2E+08 1.0E+08 8.0E+07 6.0E+07 4.0E+07 2.0E+07 0.0E+00 −2.0E+07

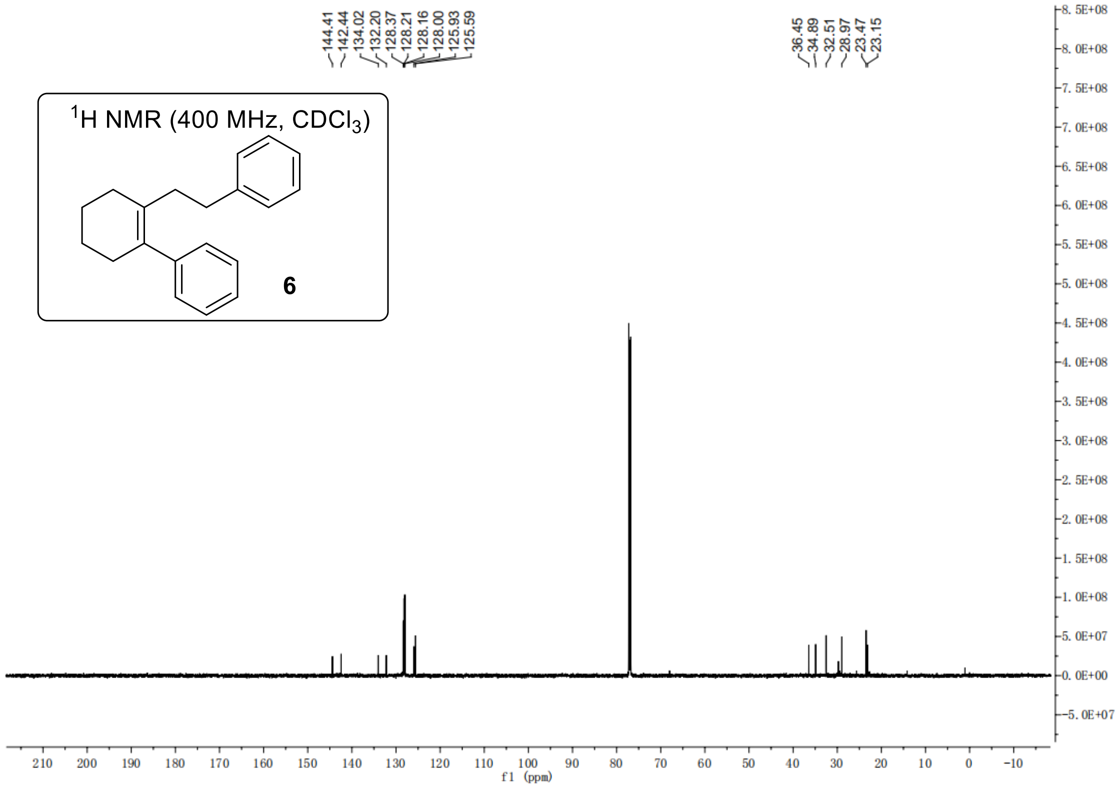

7.331
7.327
7.321
7.310
7.307
7.299
7.297
7.292
7.280
7.275
7.264
7.261
7.249
7.235
7.218
7.210
7.200
7.166
7.163
7.148
7.129
7.076
7.072
7.055
6.378
6.372
6.368
6.362
4.036
4.032
4.011
4.007
2.854
2.832
2.814
2.809
2.802
2.784
2.779
2.765
2.752
2.747
2.744
2.726
2.721
2.621
2.613
2.606
2.600
2.593
2.590
2.584
2.581
2.574
2.565
2.563
2.334
2.309
2.301
2.298
1.963
1.950
1.943
1.940
1.929
1.926
1H NMR (400 MHz, CDCl3)
Ph
O
Ph
4
4.38
3.28
1.11
2.00
1.00
1.01
3.40
3.15
1.17
1.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

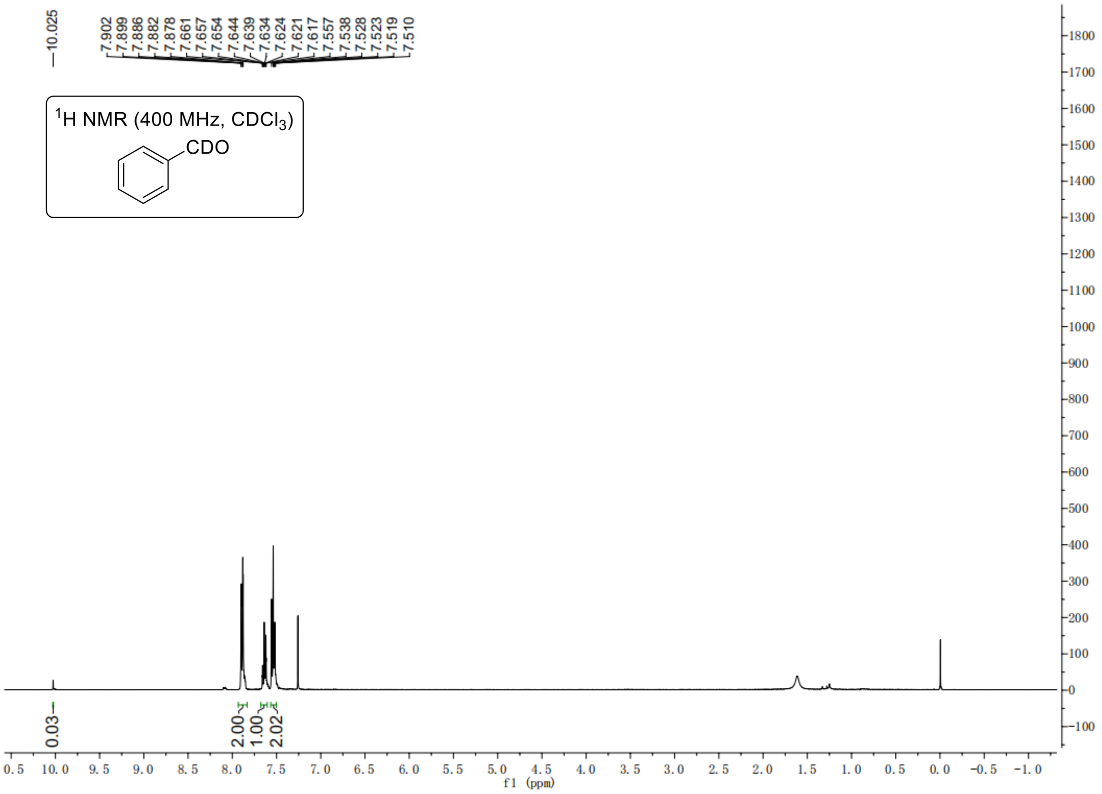

211.86
141.43
141.27
135.38
130.60
128.62
128.40
128.36
127.47
126.00
125.78
59.60
40.61
32.59
29.70
27.94
13C NMR (151 MHz, CDCl3)
Ph
O
Ph
4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1.70E+09
1.60E+09
1.50E+09
1.40E+09
1.30E+09
1.20E+09
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08

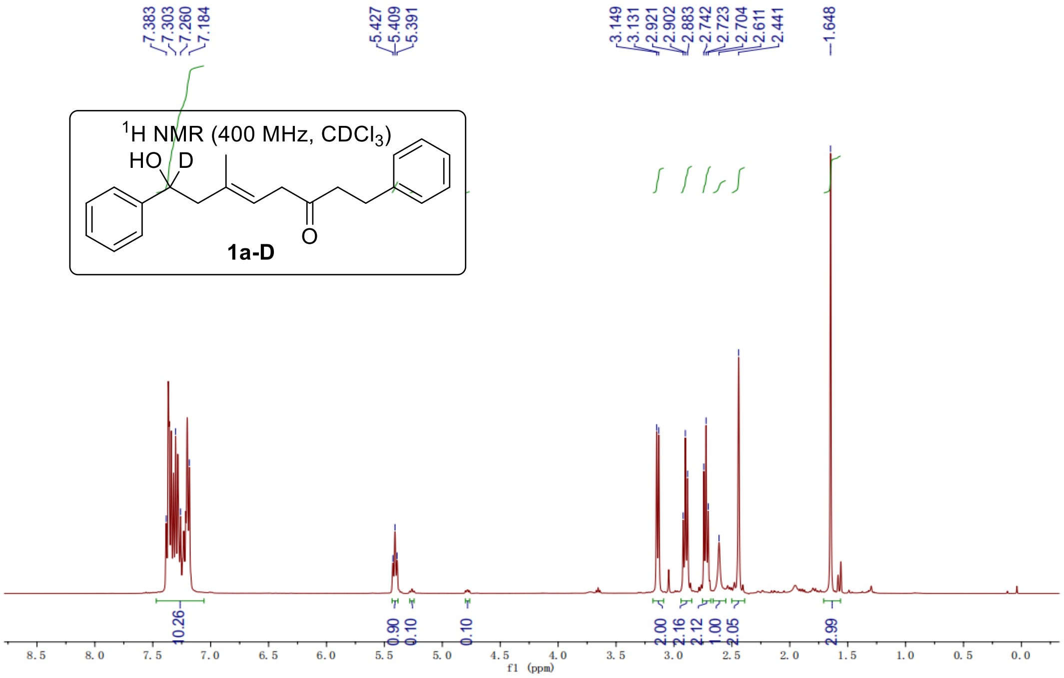

PS-143-2-B
STANDARD FLUORINE PARAMETERS
7.964
7.945
7.598
7.579
7.564
7.561
7.495
7.476
7.457
7.346
7.343
7.326
7.307
7.271
7.263
7.255
7.234
7.206
7.186
3.044
3.027
3.010
2.891
2.613
2.594
2.575
1.856
1.839
1.821
1.802
1.785
1.701
1.681
1.662
1.644
1.625
¹H NMR (400 MHz, CDCl₃)
O
5
NC
CN
2.05
1.00
2.05
2.04
1.07
2.02
2.05
4.02
2.19
2.08
2.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
1100 1000 900 800 700 600 500 400 300 200 100 0


199.25
184.78
138.57
136.75
133.28
128.91
128.72
128.31
128.01
127.06
111.77
111.66
86.67
37.54
37.42
35.85
34.07
27.34
23.60
¹³C NMR (151 MHz, CDCl₃)
O
5
NC
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
8.0E+08 7.5E+08 7.0E+08 6.5E+08 6.0E+08 5.5E+08 5.0E+08 4.5E+08 4.0E+08 3.5E+08 3.0E+08 2.5E+08 2.0E+08 1.5E+08 1.0E+08 5.0E+07 0.0E+00 −5.0E+07

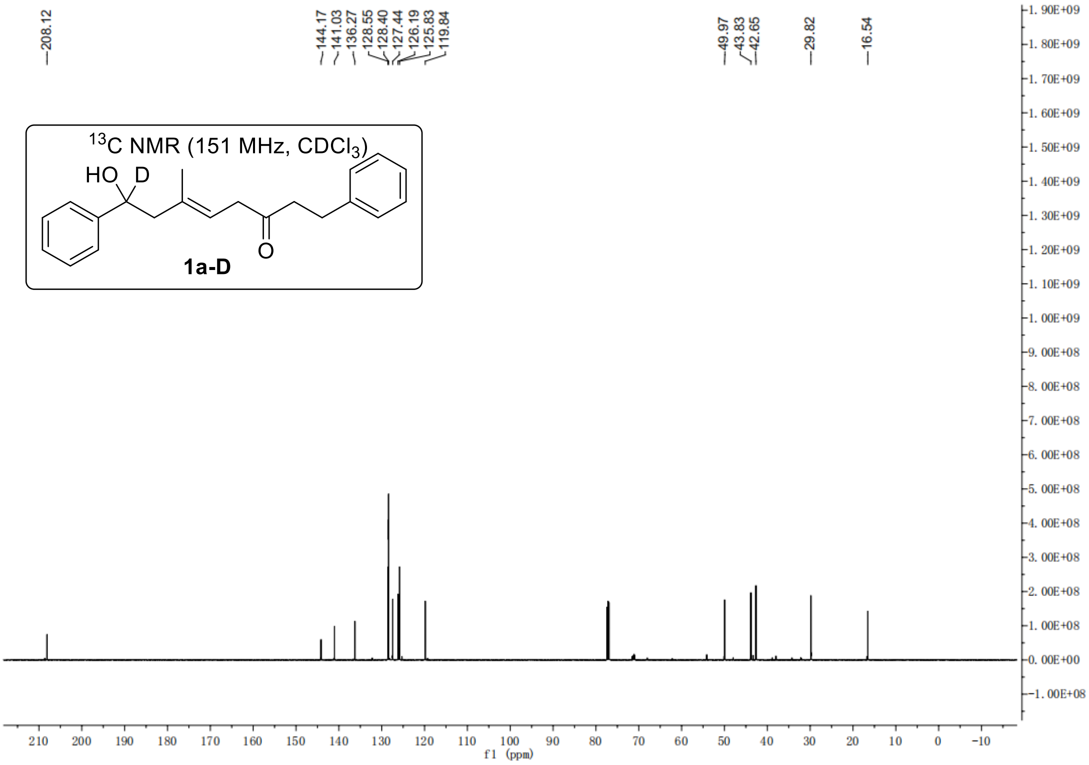

7.289
7.272
7.256
7.217
7.206
7.199
7.188
7.181
7.170
7.145
7.127
7.108
7.011
7.008
7.003
7.000
6.990
6.982
2.638
2.618
2.612
2.597
2.169
2.159
1.719
1.712
1.704
1.681
^{13}C NMR (151 MHz, CDCl$_3$)
6
2.05
3.01
1.00
3.98
2.11
2.01
4.36
4.11
f1 (ppm)


144.41
142.44
134.02
132.20
128.37
128.21
128.16
128.00
125.93
125.59
36.45
34.89
32.51
28.97
23.47
23.15
^{1}H NMR (400 MHz, CDCl$_3$)
6
f1 (ppm)


1H NMR (400 MHz, CDCl3)
CDO
10.025
7.902
7.899
7.886
7.882
7.878
7.661
7.657
7.654
7.644
7.639
7.634
7.624
7.621
7.617
7.557
7.538
7.528
7.523
7.519
7.510
0.03
2.00
1.00
2.02
f1 (ppm)


1H NMR (400 MHz, CDCl3)
HO D
O
7.383
7.303
7.260
7.184
5.427
5.409
5.391
3.149
3.131
2.921
2.902
2.883
2.742
2.723
2.704
2.611
2.441
1.648
10.26
0.90
0.10
0.10
2.00
2.16
2.12
1.00
2.05
2.99
f1 (ppm)

1a-D


208.12
144.17
141.03
136.27
128.55
128.40
127.44
126.19
125.83
119.84
49.97
43.83
42.65
29.82
16.54
^{13}C NMR (151 MHz, CDCl$_3$)
HO
D
O
1a-D
1.90E+09
1.80E+09
1.70E+09
1.60E+09
1.50E+09
1.40E+09
1.30E+09
1.20E+09
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)