

Supporting Information

Photoinduced Copper-Catalyzed Alkoxy carbonylation of Alkyl Fluorides

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1. General information

Reagents and solvents: Unless otherwise noted, reagents were ordered from *Sigma-Aldrich*, *TCI*, *ABCR*, *Alfa Aesar* or *BLD pharm*, and used without purification. Pure solvents was available from *Thermo Fisher*, and degassed (3 times) under argon atmosphere, then store under standard Schlenk technique (anhydrous and under inert atmosphere).

Purification: Analytical thin layer chromatography was performed using *MACHERY-NAGEL Gmbn & Co. KG* silica gel plates (Silica gel 60 UV₂₅₄). Visualization was by ultraviolet fluorescence ($\lambda = 254$ nm) and/or staining with potassium permanganate (KMnO₄). The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck). Gradient flash chromatography was conducted eluting with PE/EA, PE refers to pentane and EA refers to ethyl acetate, they were listed as volume/volume ratios.

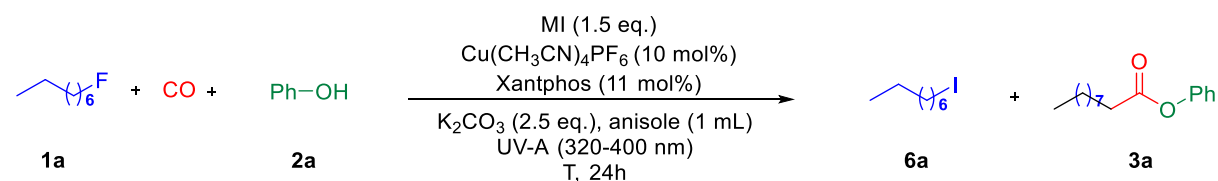
Irradiation: The light source was placed ca. 23 cm from the reaction vial on top of a manufactured autoclave (see Figure S1). In every reaction the strong light source Portable Lumatec SUPERLITE S 04^[1] was used with different set filters: UV-A ($\lambda = 320 - 400$ nm) at maximum intensity (100% power). Figures S2, S3 illustrate relevant photophysical properties of the lamps.

Data collection: GC analysis was performed on an Agilent HP-7890A instrument with FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μ m film thickness) using argon as carrier gas. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). The data are given as mass units per charge (m/z). NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Multiplets were assigned as s(singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). Chemical shifts (ppm) are given relative to solvent: references for CDCl₃ were 7.26 ppm (¹H NMR) and 77.00 ppm (¹³C NMR). All measurements were carried out at room temperature unless otherwise stated.

NOTE: Because of the high toxicity of carbon monoxide, all the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.

2. Additional Optimization Information

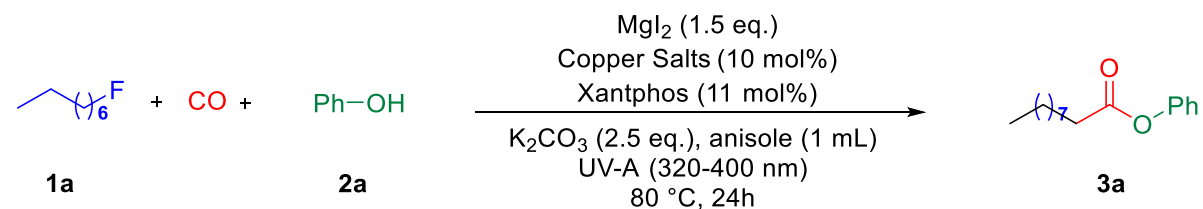
Table S1. Optimization of metal iodides.



Entry	Metal iodide	T (°C)	Conv. 6a (%)	Yield 3a (%)
1	MgI ₂	25	0	0
2	MgI ₂	60	61	42
3	MgI ₂	80	89	95
4	LiI (3 eq.)	80	75	0
5	NaI (3 eq.)	80	trace	0
6	KI (3 eq.)	80	trace	0
7	AgI (3 eq.)	80	60	0
8	CaI ₂	80	71	0

Reaction conditions: 1a (0.2 mmol), 2a (0.1 mmol), **Metal iodide** (1.5 eq.), Cu(CH₃CN)₄PF₆ (10 mol%), Xantphos (11 mol%), K₂CO₃ (2.5 eq.), CO (40 atm), anisole (1 mL), stirred at 80 °C for 24 h under UV-A (320-400 nm). Determined by GC with hexadecane as internal standard.

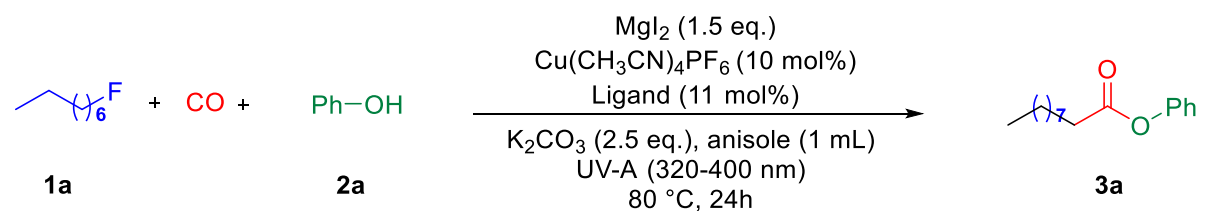
Table S2. Optimization of copper salts.



Entry	Copper Salts	Yield (%)
1	Cu(CH ₃ CN) ₄ PF ₆	95
2	CuBr	5
3	CuI	15
4	CuCN	trace
5	Cu(OAc) ₂	0
6	CuCl ₂	0
7	Cu(OTf) ₂	0
8	IMesCuCl	8
9	CuBr(Me ₂ S)	trace

Reaction conditions: 1a (0.2 mmol), 2a (0.1 mmol), MgI₂ (1.5 eq.), **Copper salts** (10 mol%), Xantphos (11 mol%), K₂CO₃ (2.5 eq.), CO (40 atm), anisole (1 mL), stirred at 80 °C for 24 h under UV-A (320-400 nm). NMR yield.

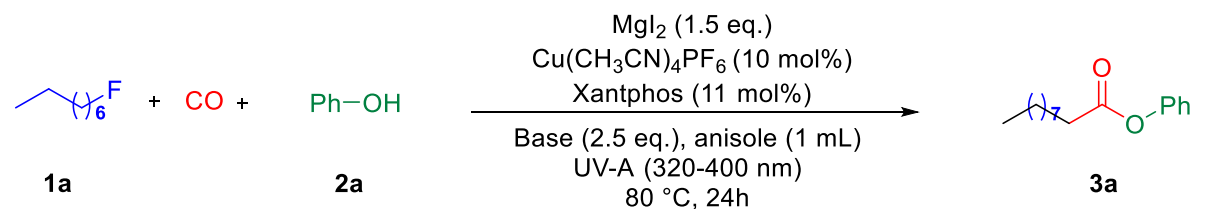
Table S3. Optimization of ligands.



Entry	Ligand	Yield (%)
1	Xantphos	95
2	Nixantphos	16
3	Sixantphos	20
4	BNIAP	<5
5	DPEphos	0
6	DPPBz	0
7	DPPE	0
8	DPPP	0
9	DCyPE	0
10	BuPAd ₂	0
11	Pyridine	0
12	Bipyridine	0
13	1,10-phen	0

Reaction conditions: 1a (0.2 mmol), 2a (0.1 mmol), MgI₂ (1.5 eq.), Cu(CH₃CN)₄PF₆ (10 mol%), **Ligand** (11 mol%), K₂CO₃ (2.5 eq.), CO (40 atm), anisole (1 mL), stirred at 80 °C for 24 h under UV-A (320-400 nm). NMR yield.

Table S4. Optimization of ligands.



Entry	Base	Yield (%)
1	K ₂ CO ₃	95
2	Li ₂ CO ₃	0
3	Na ₂ CO ₃	<5
4	Rb ₂ CO ₃	62
5	Cs ₂ CO ₃	33
6	KHCO ₃	0
7	KOH	0
8	KO ^t Bu	0
9	DBU	0
10	DABCO	0

Reaction conditions: 1a (0.2 mmol), 2a (0.1 mmol), MgI₂ (1.5 eq.), Cu(CH₃CN)₄PF₆ (10 mol%), Xantphos (11 mol%), **Base** (2.5 eq.), CO (40 atm), anisole (1 mL), stirred at 80 °C for 24 h under UV-A (320-400 nm). NMR yield.

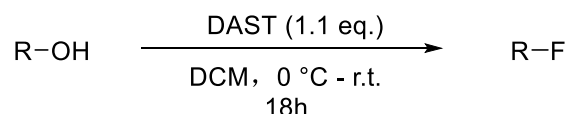
Table S5. Optimization of solvent.

1a	2a		3a
Entry	Solvent	Yield (%)	
1	Anisole	95	
2	4-Methylanisole	80	
3	Toluene	40	
4	Fluorobenzene	26	
5	Chlorobenzene	17	
6	Benzotrifluoride	trace	
7	<i>p</i> -Xylene	trace	
8	Cumene	trace	
9	DCE	0	
10	CH ₃ CN	0	
11	THF	0	
12	1,4-Dioxane	0	
13	DME	0	
14	DMF	0	
15	DMSO	0	
16	EtOH	0	
17	HFIP	0	

Reaction conditions: 1a (0.2 mmol), 2a (0.1 mmol), MgI₂ (1.5 eq.), Cu(CH₃CN)₄PF₆ (10 mol%), Xantphos (11 mol%), K₂CO₃ (2.5 eq.), CO (40 atm), **solvent** (1 mL), stirred at 80 °C for 24 h under UV-A (320-400 nm). NMR yield.

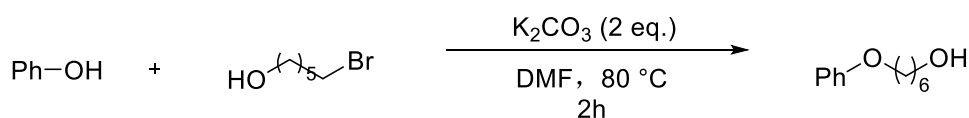
3. Preparation of Substrates

General Procedure A^[2]:



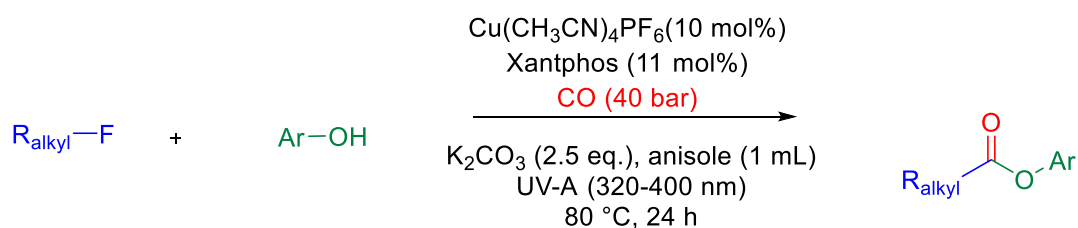
A round-bottom flask containing a stirring bar was charged DAST (1.1 eq.) and DCM (4 mL), a solution of alcohol (3 mmol) in DCM (4 mL) was slowly added at 0 °C followed by stirring at the temperature for 18 h. The reaction mixture was quenched by addition of mixture of ice and water and extracted with DCM (15 mL×3). Combined organic layer was dried over MgSO₄, concentrated, and purified by flash column chromatography on silica gel to obtain corresponding fluorides.

General Procedure ^[3]:



A round-bottom flask containing a stirring bar was charged with the phenol (8.0 eq.), 6-bromo-1-hexanol (5 mmol), and DMF (10 mL). Then K₂CO₃ (2.0 eq.) was added. The reaction mixture was stirred at 80 °C for 2 h. After the reaction was completed, the reaction mixture was diluted with AcOEt and washed with water and brine. Combined organic layer was dried over MgSO₄, concentrated, and purified by flash column chromatography on silica gel to obtain corresponding fluorides.

4. General procedure



A 4 mL screw-cap vial was charged with Phenol (9.4 mg, 1 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (3.7 mg, 10 mol%), Xantphos (6.4 mg, 11 mol%), MgI_2 (41.7 mg, 1.5 eq.), K_2CO_3 (34.5 mg, 2.5 eq.), and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After anisole (1.0 mL), and alkyl fluoride (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to a cannula and transferred into a 300 mL photoautoclave, manufactured by Parr instrument company®, under an argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar of CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was reacted at 80 °C under UV-A (320-400 nm) for 24h. After the reaction was complete, the pressure of the autoclave was released carefully. Then the reaction was extracted with EA (3 x 3 mL). The Combined organic layer was dried over MgSO_4 , concentrated, and purified by flash column chromatography on silica gel to obtain the corresponding product.



Figure S1. Photoautoclave and photoreactor used in this research.

Note: All photos in this material were taken by the first author Peng Yang.

SPEKTRUM

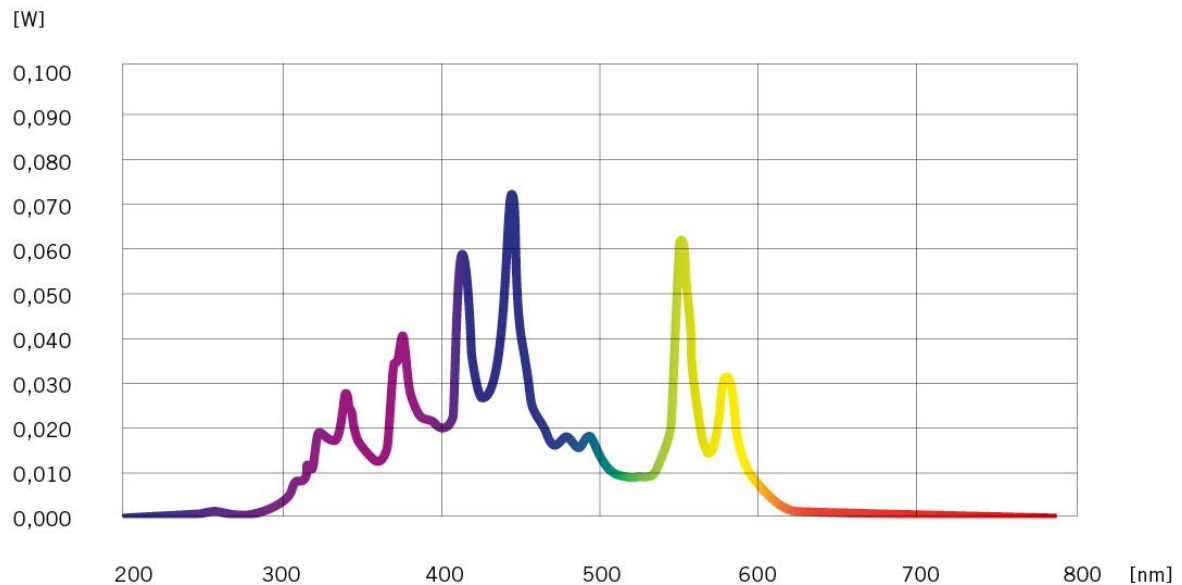


Figure S2. Emission spectrums of the Portable Lumatec SUPERLITE S 04.

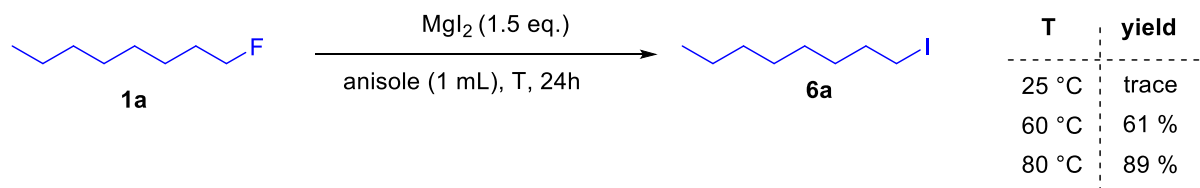
OPTISCHE LEISTUNG

	Spektrum	Leistung	Intensität
UVA	320–400 nm	2.100 mW	10.500 mW/cm ²
UVA + Blau	320–500 nm	6.900 mW	34.500 mW/cm ²
Blau	400–500 nm	4.800 mW	24.000 mW/cm ²
Weiß	400–700 nm	9.700 mW	48.500 mW/cm ²
Violett	415 nm	2.000 mW	10.000 mW/cm ²
Blau 440	440 nm	2.300 mW	11.500 mW/cm ²
Blau 460	460 nm	2.000 mW	10.000 mW/cm ²
Türkis	490 nm	1.200 mW	6.000 mW/cm ²
Grün	550 nm	1.400 mW	7.000 mW/cm ²
Gelb	570 nm	1.800 mW	9.000 mW/cm ²

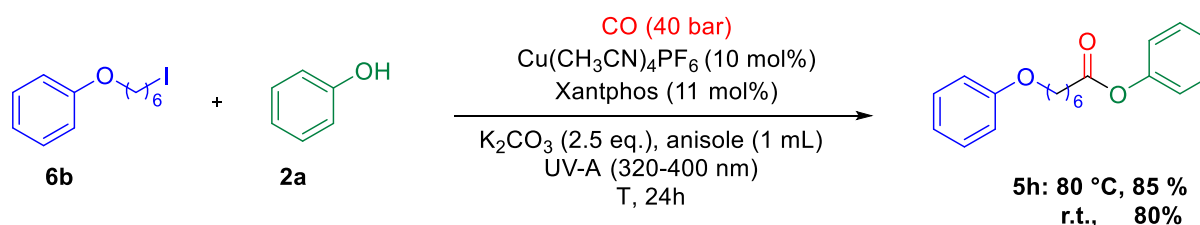
Figure S3. Technical specifications of the Portable Lumatec SUPERLITE S 04

5. Mechanism studies.

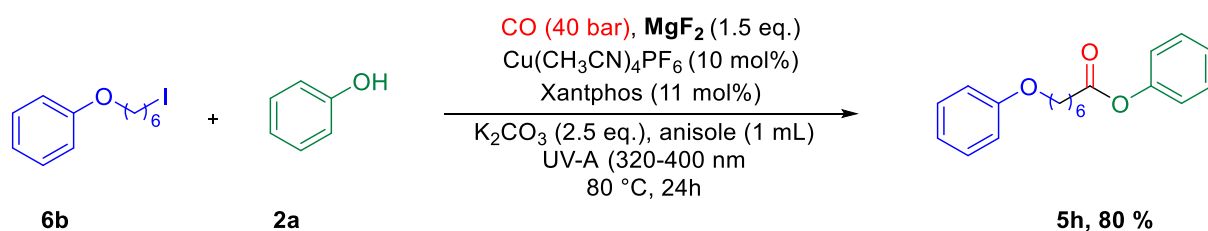
5.1 Control experiments



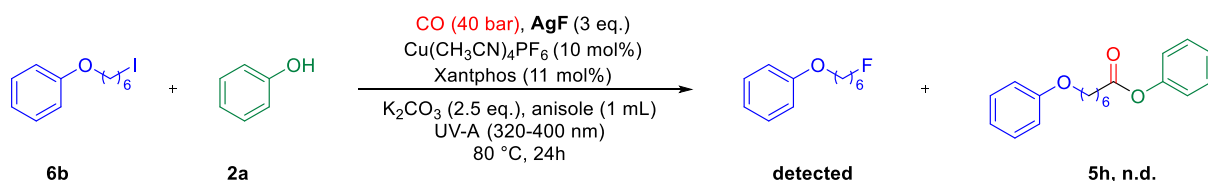
In a flame-dried 10 mL Schlenk tube equipped with oven-dried stir added MgI_2 (41.7 mg, 1.5 eq.), and 1-fluorooctane (0.2 mmol), followed by the addition of DCM (4.0 mL). Then the mixture was stirred at established temperature for 24 h. After the reaction was complete, 10 μL of hexadecane was added to the tube. And a proper amount of solvent was taken for GC analysis. The result is shown above.



A 4 mL screw-cap vial was charged with Phenol (9.4 mg, 1 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (3.7 mg, 10 mol%), Xantphos (6.4 mg, 11 mol%), K_2CO_3 (34.5 mg, 2.5 eq.), and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After anisole (1.0 mL), and **6b** (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to a cannula and transferred into a 300 mL photoautoclave, manufactured by Parr instrument company®, under an argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar of CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was reacted at established temperature under UV-A (320-400 nm) for 24h. After the reaction was complete, the pressure of the autoclave was released carefully. Then, 8.4 mg 1,3,5-trimethoxybenzene was added to the vials. A proper amount of solvent was dried under high vacuum and dissolved in CDCl_3 taken for NMR analysis.

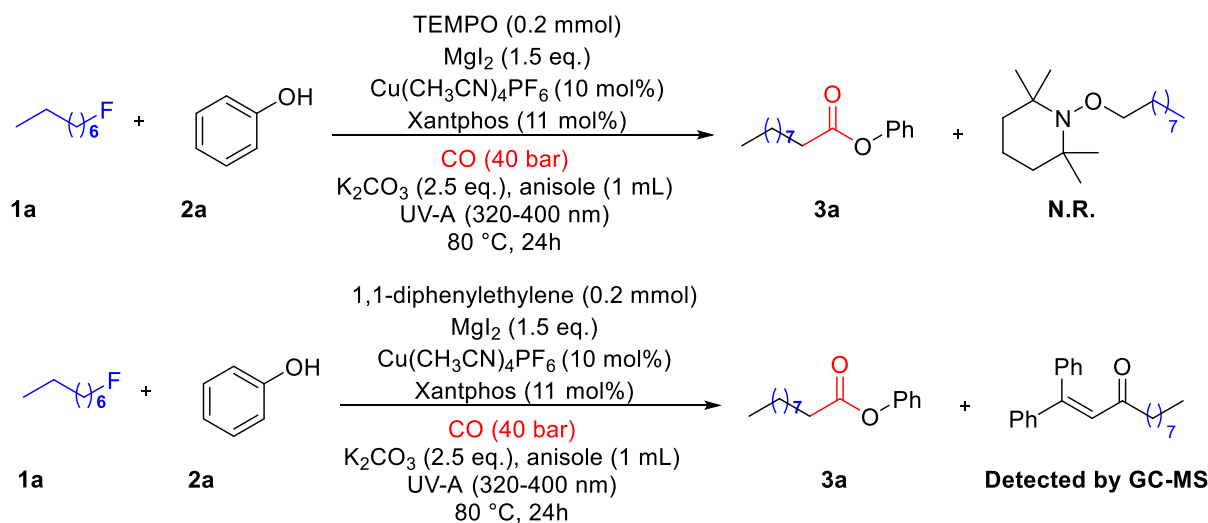


A 4 mL screw-cap vial was charged with Phenol (9.4 mg, 1 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (3.7 mg, 10 mol%), Xantphos (6.4 mg, 11 mol%), MgF_2 (9.4 mg, 1.5 eq.), K_2CO_3 (34.5 mg, 2.5 eq.), and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After anisole (1.0 mL), and **6b** (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to a cannula and transferred into a 300 mL photoautoclave, manufactured by Parr instrument company®, under an argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar of CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was reacted at 80°C under UV-A (320-400 nm) for 24h. After the reaction was complete, the pressure of the autoclave was released carefully. Then, 8.4 mg 1,3,5-trimethoxybenzene was added to the vials. A proper amount of solvent was dried under high vacuum and dissolved in CDCl_3 taken for NMR analysis.



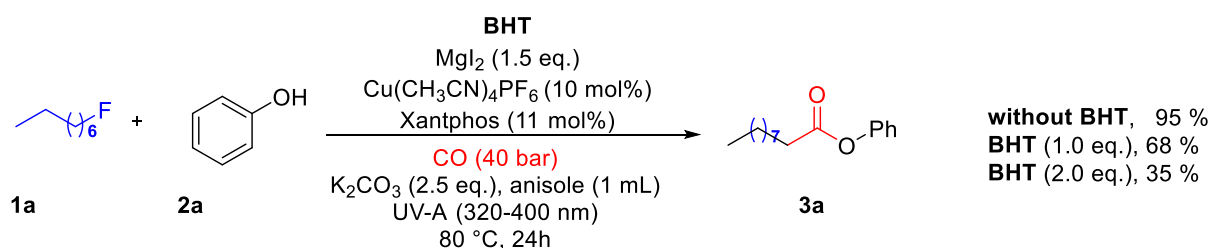
A 4 mL screw-cap vial was charged with Phenol (9.4 mg, 1 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (3.7 mg, 10 mol%), Xantphos (6.4 mg, 11 mol%), AgF_2 (38.1 mg, 3 eq.), K_2CO_3 (34.5 mg, 2.5 eq.), and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After anisole (1.0 mL), and **6b** (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to a cannula and transferred into a 300 mL photoautoclave, manufactured by Parr instrument company®, under an argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar of CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was reacted at 80°C under UV-A (320-400 nm) for 24h. After the reaction was complete, the pressure of the autoclave was released carefully. Then, a proper amount of solvent was taken for GC-MS analysis.

5.2 Radical capture experiments



A 4 mL screw-cap vial was charged with Phenol (9.4 mg, 1 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (3.7 mg, 10 mol%), Xantphos (6.4 mg, 11 mol%), MgI_2 (41.7 mg, 1.5 eq.), K_2CO_3 (34.5 mg, 2.5 eq.), radical scavenger (1.5 eq.), and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After anisole (1.0 mL), and 1-fluorooctane (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to a cannula and transferred into a 300 mL photoautoclave, manufactured by Parr instrument company®, under an argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar of CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was reacted at 80 °C under UV-A (320-400 nm) for 24h. After the reaction was complete, the pressure of the autoclave was released carefully. Then, a proper amount of solvent was taken for GC-MS analysis. The result is shown in Figure S2.

5.2 Radical inhibition experiments



A 4 mL screw-cap vial was charged with Phenol (9.4 mg, 1 mmol), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (3.7 mg, 10 mol%), Xantphos (6.4 mg, 11 mol%), MgI_2 (41.7 mg, 1.5 eq.), K_2CO_3 (34.5 mg, 2.5 eq.), 2,6-di-tert-butyl-4-methylphenol (0-2 eq) and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After anisole (1.0 mL), and 1-fluorooctane (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to a cannula and transferred into a 300 mL photoautoclave, manufactured by Parr instrument company®, under an argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar of CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was reacted at 80 °C under UV-A (320-400 nm) for 24h. After the reaction was complete, the pressure of the autoclave was released carefully. Then, 8.4 mg 1,3,5-trimethoxybenzene was added to the vials. A proper amount of solvent was dried under high vacuum and dissolved in CDCl_3 taken for NMR analysis.

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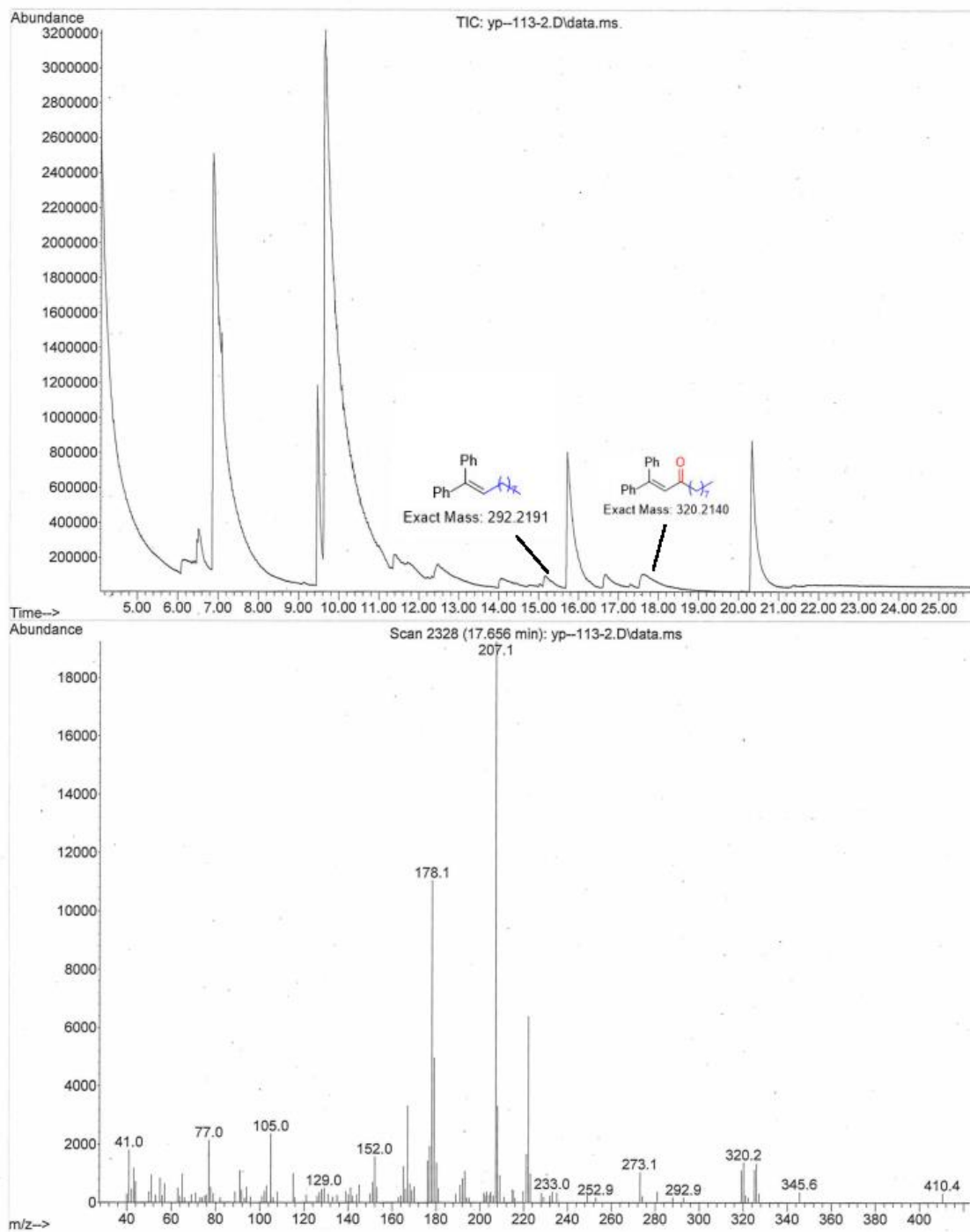
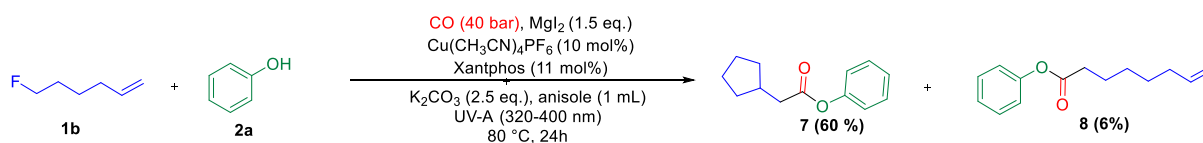
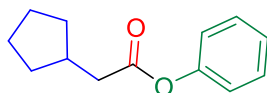


Figure S2 GC-MS of the reaction solvent

5.2 Radical clock experiments



A 4 mL screw-cap vial was charged with Phenol (9.4 mg, 1 mmol), Cu(CH₃CN)₄PF₆ (3.7 mg, 10 mol%), Xantphos (6.4 mg, 11 mol%), MgI₂ (41.7 mg, 1.5 eq.), K₂CO₃ (34.5 mg, 2.5 eq.), and an oven-dried stir bar. The vial was closed with a Teflon septum and cap and connected to the atmosphere via a needle. After anisole (1.0 mL), and 6-fluorohex-1-ene (0.2 mmol) were added with a syringe under argon atmosphere, the vial was moved to a cannula and transferred into a 300 mL photoautoclave, manufactured by Parr instrument company®, under an argon atmosphere. At room temperature, the autoclave was flushed with CO three times and charged with 40 bar of CO. The autoclave was placed on a heating plate equipped with a magnetic stirrer and an aluminum block. The reaction mixture was reacted at 80 °C under UV-A (320-400 nm) for 24h. After the reaction was complete, the pressure of the autoclave was released carefully. Then, a proper amount of solvent was taken for GC-MS analysis. And the crude residue was purified by silica gel chromatography (pentane/EA = 200:1) to afford a mixture of 7 and 8.



Phenyl 2-cyclopentylacetate (7) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA =100:1) to afford the title compound as a colorless oil (12.3 mg, 60% yield)

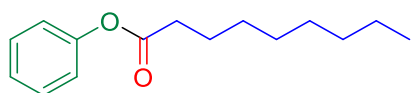
¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 7.10 – 7.06 (m, 2H), 2.57 (d, J = 7.59 Hz, 2H), 2.45 – 2.29 (m, 1H), 1.97 – 1.88 (m, 2H), 1.78 – 1.59 (m, 4H), 1.31 – 1.24 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): δ 171.88, 150.78, 129.40, 125.71, 121.62, 40.46, 36.62, 32.47, 25.05.

6. References

1. <http://www.lumatec.de/de/produkte/uv-lichtquelle-superlite-s04/>
2. T. Iwasaki, R. Shimizu, R. Imanishi, H. Kuniyasu, N. Kambe, *Angew. Chem. Int. Ed.* **2015**, 54, 9347-9350.
3. T. Suzuki, Y. Nagano, A. Kouketsu, A. Matsuura, S. Maruyama, M. Kurotaki, H. Nakagawa, N. Miyata, *J. Med. Chem.* **2005**, 48, 1019-1032.
4. P. Wang, Y. Wang, H. Neumann, M. Beller, *Chem. Sci.* **2022**, 13, 13459-13465.
5. H.-J. Ai, C.-L. Li, H. Wang, X.-F. Wu, *ACS Catal.* **2020**, 10, 5147-5152.

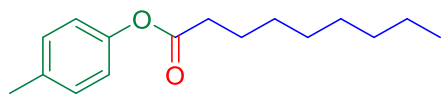
7. Spectroscopic data of products



Phenyl nonanoate (3a) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (21.5 mg, 92% yield)^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.35 (m, 2H), 7.26 – 7.20 (m, 1H), 7.11 – 7.06 (m, 2H), 2.56 (t, J = 7.35 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.49 – 1.27 (m, 10H), 0.92 – 0.85 (m, 3H).

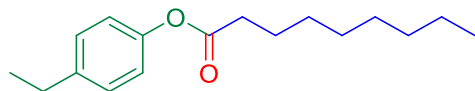
¹³C NMR (75 MHz, CDCl₃): δ 172.35, 150.80, 129.40, 125.71, 121.61, 34.44, 31.83, 29.25, 29.15, 29.14, 24.98, 22.67.



p-Tolyl nonanoate (3b) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (21.3 mg, 86% yield)^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.18 – 7.15 (m, 2H), 6.97 – 6.93 (m, 2H), 2.54 (t, J = 7.32 Hz, 2H), 2.34 (s, 3H), 1.80 – 1.70 (m, 2H), 1.44 – 1.28 (m, 10H), 0.91 – 0.87 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.54, 148.55, 135.31, 129.90, 121.25, 34.43, 31.81, 29.23, 29.13, 25.00, 22.65, 20.86, 14.10.

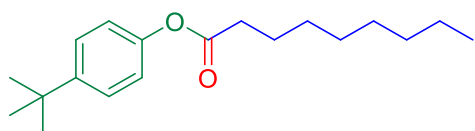


4-Ethylphenyl nonanoate (3c) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (21.5 mg, 82% yield)

¹H NMR (300 MHz, CDCl₃): δ 7.22 – 7.17 (m, 2H), 7.00 – 6.96 (m, 2H), 2.65 (q, J = 7.59 Hz, 2H), 2.55 (t, J = 7.41 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.43 – 1.27 (m, 10H), 1.24 (t, J = 7.59 Hz, 3H), 0.92 – 0.88 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.55, 148.69, 141.63, 128.72, 121.29, 34.44, 31.83, 29.25, 29.15, 28.30, 25.01, 22.67, 15.58, 14.11.

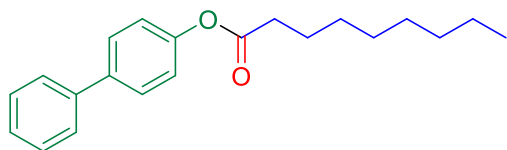
HRMS-El(m/z): calcd for C₁₇H₂₆O₂⁺ [M⁺] 262.19273, found 262.19315.



4-(tert-Butyl)phenyl nonanoate (3d) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (23.2 mg, 80% yield)^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.40 – 7.35 (m, 2H), 7.02 – 6.97 (m, 2H), 2.54 (t, J = 7.32 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.43 – 1.27 (m, 19H), 0.92 – 0.87 (m, 3H).

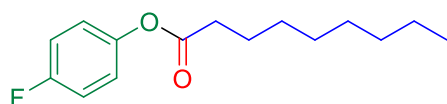
¹³C NMR (75 MHz, CDCl₃): δ 172.56, 148.49, 148.41, 126.29, 120.88, 34.46, 31.83, 31.43, 29.25, 29.15, 29.14, 25.01, 22.66, 14.12.



[1,1'-Biphenyl]-4-yl nonanoate (3e) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (25.1 mg, 81% yield) ^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.61 – 7.54 (m, 4H), 7.47 – 7.41 (m, 2H), 7.38 – 7.32 (m, 1H), 7.18 – 7.13 (m, 2H), 2.58 (t, *J* = 7.32 Hz, 2H), 1.83 – 1.73 (m, 2H), 1.46 – 1.26 (m, 10H), 0.92 – 0.88 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.44, 150.20, 140.44, 138.89, 128.80, 128.16, 127.33, 127.14, 121.87, 34.47, 31.83, 29.25, 29.15, 24.99, 22.67, 14.12.



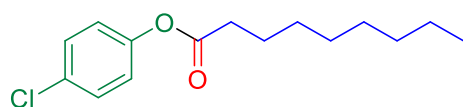
4-Fluorophenyl nonanoate (3f) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 400:1) to afford the title compound as a colorless oil (23.2 mg, 92% yield)

¹H NMR (300 MHz, CDCl₃): δ 7.15– 7.03 (m, 4H), 2.54 (t, *J* = 7.32 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.37 – 1.26 (m, 10H), 0.91 – 0.87 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.38, 160.17(d, *J* = 242.51 Hz), 146.59 (d, *J* = 3.01 Hz), 122.96 (d, *J* = 8.36 Hz), 116.03 (d, *J* = 23.42 Hz), 34.31, 31.81, 29.22, 29.13, 29.11, 24.92, 22.66, 14.11.

¹⁹F NMR (300 MHz, CDCl₃): δ -117.25 (p, *J* = 6.5 Hz),

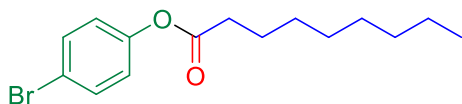
HRMS-EI(m/z): calcd for C₁₅H₂₁O₂F₁⁺ [M⁺] 252.15201, found 252.15273.



4-Chlorophenyl nonanoate (3g) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (26.2 mg, 98% yield) ^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.36 – 7.31 (m, 2H), 7.05 – 7.00 (m, 2H), 2.54 (t, *J* = 7.32 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.43 – 1.28 (m, 10H), 0.92 – 0.87 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): δ 172.06, 149.26, 131.06, 129.44, 122.96, 34.33, 31.81, 29.21, 29.10, 24.89, 22.65, 14.10.

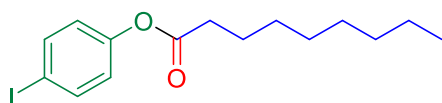


4-Bromophenyl nonanoate (3h) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (28.5 mg, 91% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.51 – 7.46 (m, 2H), 7.00 – 6.95 (m, 2H), 2.54 (t, *J* = 7.32 Hz, 2H), 1.80 – 1.69 (m, 2H), 1.43 – 1.26 (m, 10H), 0.92 – 0.87 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 171.98, 149.80, 132.43, 123.41, 114.87, 34.34, 31.82, 29.22, 29.13, 29.10, 24.89, 22.66, 14.12.

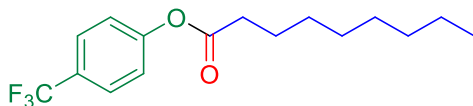
HRMS-EI(*m/z*): calcd. for C₁₅H₂₁BrO₂⁺ [*M*+][•] 312.07194, found 312.07260.



4-Iodophenyl nonanoate (3i) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (25.2 mg, 70% yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.70– 7.65 (m, 2H), 6.87 – 6.82 (m, 2H), 2.54 (t, *J* = 7.35 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.42 – 1.25 (m, 10H), 0.91 – 0.86 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 171.98, 150.61, 138.44, 123.82, 89.69, 34.36, 31.81, 29.21, 29.12, 29.10, 24.88, 22.66, 14.12.



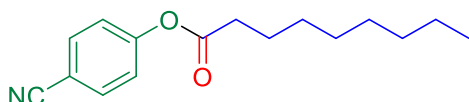
4-(Trifluoromethyl)phenyl nonanoate (3j) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (19.3 mg, 64% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.67– 7.62 (m, 2H), 7.23 – 7.18 (m, 2H), 2.58 (t, *J* = 7.35 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.44 – 1.26 (m, 22H), 0.91 – 0.87 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 171.80, 153.26, 127.99 (q, *J* = 32.44 Hz), 126.76 (q, *J* = 3.67 Hz), 124.02 (q, *J* = 315.01 Hz), 122.10, 34.36, 31.80, 29.21, 29.12, 29.09, 24.84, 22.65, 14.10.

¹⁹F NMR (300 MHz, CDCl₃): δ -62.23

HRMS-EI(*m/z*): calcd for C₁₆H₂₁F₃O₂⁺ [*M*+][•] 302.14882, found 302.14927

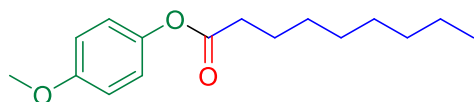


4-Cyanophenyl nonanoate (3k) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (12.4 mg, 48% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.71 – 7.66 (m, 2H), 7.24 – 7.20 (m, 2H), 2.58 (t, *J* = 7.35 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.43 – 1.25 (m, 10H), 0.91 – 0.86 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 171.43, 154.07, 133.65, 122.75, 118.28, 109.63, 34.34, 31.79, 29.18, 29.10, 29.06, 24.77, 22.64, 14.09.

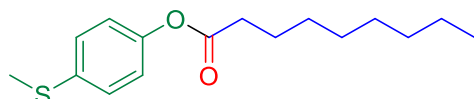
HRMS-El(m/z): calcd for C₁₆H₂₁NO₂⁺ [M⁺] 259.15668, found 259.15631.



4-Methoxyphenyl nonanoate (3l) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (14.5 mg, 55% yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.02 – 6.96 (m, 2H), 6.91 – 6.85 (m, 2H), 3.80 (s, 3H), 2.53 (t, *J* = 7.32 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.43 – 1.26 (m, 10H), 0.91 – 0.86 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.73, 157.17, 144.29, 122.32, 114.44, 55.60, 34.37, 31.81, 29.23, 29.13, 24.99, 22.65, 14.10.

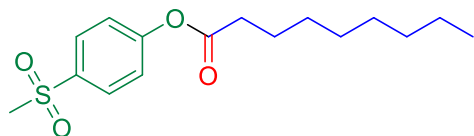


4-(Methylthio)phenyl nonanoate (3m) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a yellow oil (19.8 mg, 71% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.29 – 7.25 (m, 2H), 7.03 – 6.99 (m, 2H), 2.54 (t, *J* = 7.32 Hz, 2H), 2.48 (s, 3H), 1.79 – 1.69 (m, 2H), 1.43 – 1.26 (m, 10H), 0.91 – 0.87 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.37, 148.52, 135.49, 128.06, 122.08, 34.39, 31.82, 29.23, 29.13, 29.12, 24.94, 22.66, 16.56, 14.11.

HRMS-El(m/z): calcd for C₁₆H₂₄O₃⁺ [M⁺] 280.14915, found 280.14924.

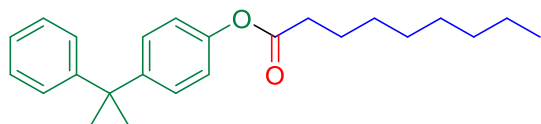


4-(Methylsulfonyl)phenyl nonanoate (3n) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 5:1) to afford the title compound as a yellow oil (16.2 mg, 52% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.99 – 7.95 (m, 2H), 7.32 – 7.27 (m, 2H), 3.06 (s, 3H), 2.59 (t, *J* = 7.41 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.37 – 1.25 (m, 10H), 0.91 – 0.86 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 171.59, 154.85, 137.70, 129.19, 122.71, 44.68, 34.36, 31.79, 29.70, 29.19, 29.10, 29.06, 24.79, 22.64, 14.10.

HRMS-El(m/z): calcd for C₁₆H₂₄O₄S⁺ [M⁺] 312.13898, found 312.13893.

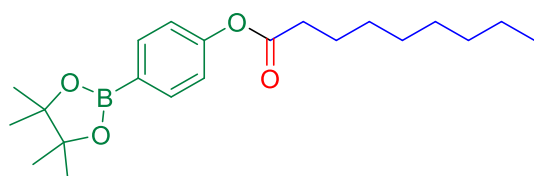


4-(2-Phenylpropan-2-yl)phenyl nonanoate (3o) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (31.0 mg, 88% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.30 – 7.27 (m, 1H), 7.25 – 7.15 (m, 6H), 6.99 – 6.94 (m, 2H), 2.54 (t, *J* = 7.32 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.68 (m, 6H) 1.43 – 1.27 (m, 10H), 0.91 – 0.87 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.47, 150.38, 148.57, 148.07, 128.05, 127.81, 126.79, 125.72, 120.88, 42.72, 34.45, 31.82, 30.84, 29.24, 29.15, 29.12, 24.99, 22.66, 14.11.

HRMS-El(m/z): calcd for C₂₄H₃₂O₂+ [M⁺] 352.23968, found 352.23959.



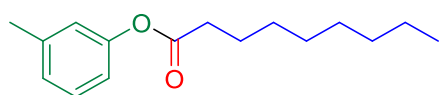
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl nonanoate (3p) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a colorless oil (28.4 mg, 79% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.85– 7.80 (m, 2H), 7.10 – 7.05 (m, 2H), 2.55 (t, *J* = 7.32 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.38 – 1.27 (m, 22H), 0.91 – 0.86 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.10, 153.31, 136.17, 120.97, 83.89, 34.47, 31.82, 29.72, 29.23, 29.13, 24.93, 24.86, 22.66, 14.11.

¹¹B NMR (300 MHz, CDCl₃): δ 29.60.

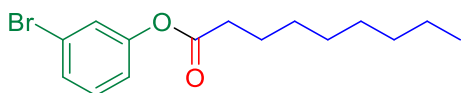
HRMS-El(m/z): calcd for C₂₁H₃₃BO₄+ [M⁺] 360.24664, found 360.24675.



***m*-Tolyl nonanoate (3q)** Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (18.9 mg, 76% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.27 – 7.22 (m, 1H), 7.05 – 7.01 (m, 1H), 6.89 – 6.85 (m, 2H), 2.54 (t, *J* = 7.41 Hz, 2H), 2.36 (s, 3H), 1.80 – 1.70 (m, 2H), 1.41 – 1.26 (m, 10H), 0.91 – 0.87 (m, 3H).

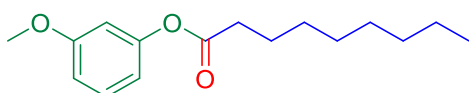
¹³C NMR (75 MHz, CDCl₃): δ 172.49, 150.72, 139.58, 129.12, 126.53, 122.20, 118.53, 34.45, 31.83, 29.24, 29.14, 25.00, 22.66, 21.32, 14.11.



3-Bromophenyl nonanoate (3r) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (24.4 mg, 78% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.38 – 7.34 (m, 1H), 7.28 – 7.21 (m, 2H), 7.05 – 7.02 (m, 1H), 2.54 (t, *J* = 7.41 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.41 – 1.26 (m, 10H), 0.91 – 0.87 (m, 3H).

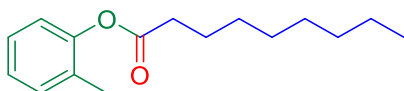
¹³C NMR (75 MHz, CDCl₃): δ 171.89, 151.30, 130.43, 128.90, 125.14, 122.35, 120.50, 34.31, 31.81, 29.20, 29.11, 29.09, 24.87, 22.65, 14.10.



3-Methoxyphenyl nonanoate (3s) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (23.8 mg, 90% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.27 (t, *J* = 8.15 Hz, 1H), 6.79 – 6.76 (m, 1H), 6.70 – 6.66 (m, 1H), 6.63 (t, *J* = 2.31 Hz, 1H), 3.80 (s, 3H), 2.54 (t, *J* = 7.41 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.41 – 1.26 (m, 10H), 0.91 – 0.87 (m, 3H).

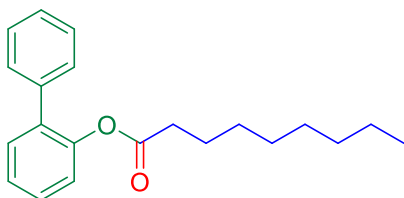
¹³C NMR (75 MHz, CDCl₃): δ 172.24, 160.49, 151.76, 129.78, 113.83, 111.56, 107.63, 55.40, 34.44, 31.82, 29.23, 29.13, 24.96, 22.66, 14.10.



o-Tolyl nonanoate (3t) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (17.4 mg, 70% yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.25 – 7.11 (m, 3H), 7.01 – 6.98 (m, 1H), 2.58 (t, *J* = 7.32 Hz, 2H), 2.18 (s, 3H), 1.83 – 1.73 (m, 2H), 1.43 – 1.26 (m, 10H), 0.92 – 0.87 (m, 3H).

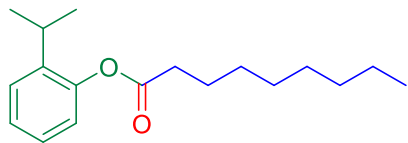
¹³C NMR (75 MHz, CDCl₃): δ 172.08, 149.40, 131.11, 130.11, 126.90, 125.93, 121.91, 34.30, 31.82, 29.24, 29.21, 29.15, 25.11, 22.66, 16.22, 14.11.



[1,1'-Biphenyl]-2-yl nonanoate (3u) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a colorless oil (27.3 mg, 88% yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.44 – 7.29 (m, 8H), 7.15 – 7.12 (m, 1H), 2.35 (t, *J* = 7.32 Hz, 2H), 1.58 – 1.48 (m, 2H), 1.36 – 1.24 (m, 10H), 0.93 – 0.88 (m, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 172.20, 147.90, 137.69, 135.08, 130.88, 129.02, 128.49, 128.21, 127.42, 126.24, 122.88, 34.24, 31.82, 29.19, 29.08, 28.97, 24.71, 22.68, 14.13.

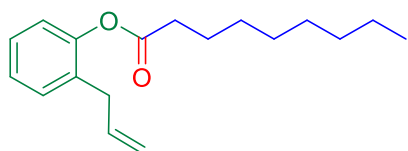


2-Isopropylphenyl nonanoate (3v) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (17.9 mg, 65% yield).

^1H NMR (300 MHz, CDCl_3): δ 7.33 – 7.29 (m, 1H), 7.21 – 7.16 (m, 2H), 7.00 – 6.96 (m, 1H), 3.07 – 2.98 (m, 1H), 2.58 (t, J = 7.32 Hz, 2H), 1.83 – 1.73 (m, 2H), 1.43 – 1.26 (m, 10H), 1.21 (d, J = 6.96 Hz, 6H), 0.92 – 0.87 (m, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 172.50, 148.14, 140.15, 126.62, 126.60, 126.20, 122.29, 34.42, 31.82, 29.25, 29.21, 29.16, 27.33, 25.06, 22.96, 22.67, 14.12.

HRMS-El(m/z): calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2$ + $[\text{M}]^+$ 276.20838, found 276.20793.

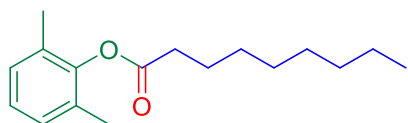


2-Allylphenyl nonanoate (3w) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (14.0 mg, 65% yield).

^1H NMR (300 MHz, CDCl_3): δ 7.25 – 7.15 (m, 3H), 7.04 – 7.01 (m, 1H), 5.97 – 5.84 (m, 1H), 5.09 – 5.02 (m, 2H), 3.31 – 3.28 (m, 2H), 2.56 (t, J = 7.35 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.39 – 1.26 (m, 10H), 0.91 – 0.87 (m, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 172.19, 148.99, 135.93, 131.91, 130.34, 127.38, 126.05, 122.38, 116.20, 34.56, 34.34, 31.82, 29.24, 29.20, 29.14, 24.99, 22.66, 14.10.

HRMS-El(m/z): calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2$ + $[\text{M}]^+$ 274.19273, found 274.19272.

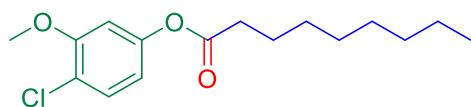


2,6-Dimethylphenyl nonanoate (3x) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (14.7 mg, 56% yield).

^1H NMR (300 MHz, CDCl_3): δ 7.09 – 7.04 (m, 3H), 2.60 (t, J = 7.35 Hz, 2H), 2.14 (s, 6H), 1.85 – 1.75 (m, 2H), 1.37 – 1.26 (m, 10H), 0.92 – 0.87 (m, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 171.55, 148.24, 130.12, 128.55, 125.73, 34.10, 31.45, 29.30, 29.24, 29.15, 25.17, 22.65, 16.37, 14.10.

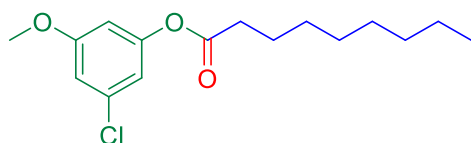
HRMS-El(m/z): calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$ + $[\text{M}]^+$ 262.19273, found 262.19332.



4-Chloro-3-methoxyphenyl nonanoate (3y) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (27.4 mg, 92% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.34 (d, *J* = 8.52 Hz, 1H), 6.69 – 6.63 (m, 2H), 3.88 (s, 3H), 2.55 (t, *J* = 7.32 Hz, 2H), 1.80 – 1.70 (m, 2H), 1.44 – 1.25 (m, 10H), 0.91 – 0.86 (m, 3H).

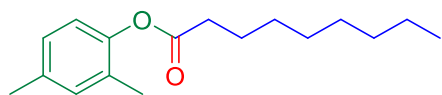
¹³C NMR (75 MHz, CDCl₃): δ 172.10, 155.47, 150.16, 130.20, 119.43, 114.21, 106.30, 56.24, 34.36, 31.81, 29.22, 29.12, 24.87, 22.66, 14.11.



3-Chloro-5-methoxyphenyl nonanoate (3z) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (27.4 mg, 92% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 6.78 – 6.76 (m, 1H), 6.72 (t, *J* = 1.92 Hz, 1H), 6.54 (t, *J* = 2.22 Hz, 1H), 3.78 (s, 3H), 2.53 (t, *J* = 7.32 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.41 – 1.29 (m, 10H), 0.91 – 0.87 (m, 3H).

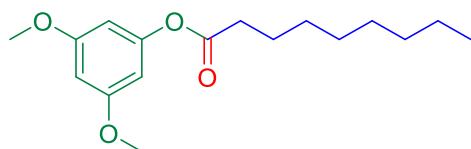
¹³C NMR (75 MHz, CDCl₃): δ 171.80, 160.75, 151.89, 135.02, 114.64, 112.03, 106.60, 55.68, 34.32, 31.81, 29.20, 29.12, 29.08, 24.86, 22.65, 14.09.



2,4-Dimethylphenyl nonanoate (4a) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (21.2 mg, 81% yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.04 – 6.98 (m, 2H), 6.87 (d, *J* = 8.07 Hz, 1H), 2.56 (t, *J* = 7.32 Hz, 2H), 2.31 (s, 3H), 2.14 (s, 3H), 1.82 – 1.72 (m, 2H), 1.45 – 1.27 (m, 10H), 0.92 – 0.87 (m, 3H).

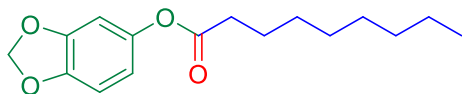
¹³C NMR (75 MHz, CDCl₃): δ 172.27, 147.16, 135.46, 131.74, 129.64, 127.43, 121.55, 34.31, 31.82, 29.24, 29.22, 29.15, 25.13, 22.66, 20.81, 16.14, 14.10.



3,5-Dimethoxyphenyl nonanoate (4b) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (27.6 mg, 94% yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 6.33 (t, *J* = 2.28 Hz, 1H), 6.25 (t, *J* = 2.9 Hz, 1H), 3.77 (s, 6H), 2.53 (t, *J* = 7.32 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.41 – 1.27 (m, 10H), 0.91 – 0.87 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.13, 161.13, 152.34, 100.23, 98.17, 55.46, 34.43, 31.82, 29.22, 29.13, 24.93, 22.65, 14.09.

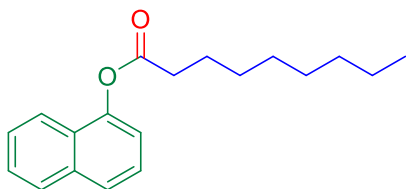


Benzo[d][1,3]dioxol-5-yl nonanoate (4c) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (17.2 mg, 62% yield).

¹H NMR (300 MHz, CDCl₃): δ 6.76 (d, *J* = 8.07 Hz, 1H), 6.59 – 6.49 (m, 2H), 5.97 (s, 2H), 2.52 (t, *J* = 7.32 Hz, 2H), 1.78 – 1.68 (m, 2H), 1.38 – 1.25 (m, 10H), 0.91 – 0.86 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.67, 147.98, 145.08, 113.92, 107.97, 103.78, 101.68, 34.32, 31.82, 29.22, 29.14, 29.13, 24.96, 22.66, 14.1. HRMS-ESI(*m/z*): calcd for C₁₆H₂₃O₄⁺ [*M*+H]⁺ 279.1591, found

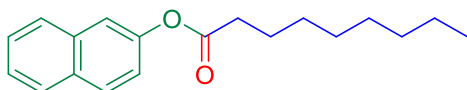
HRMS-EI(*m/z*): calcd for C₁₆H₂₂O₄⁺ [*M*+]⁺ 278.15126, found 278.15149.



Naphthalen-2-yl nonanoate (4d) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (13.7 mg, 48% yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.91 – 7.86 (m, 2H), 7.75 (d, *J* = 8.25 Hz, 2H), 7.56 – 7.45 (m, 3H),), 7.29 – 7.23 (m, 1H), 2.75 (t, *J* = 732 Hz, 2H), 1.91 – 1.84 (m, 2H), 1.46 – 1.28 (m, 10H), 0.94 – 0.90 (m, 3H).

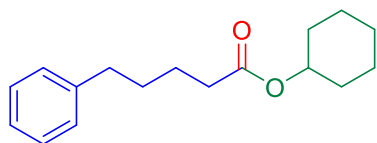
¹³C NMR (75 MHz, CDCl₃): δ 172.33, 146.68, 134.68, 128.05, 126.91, 126.40, 125.90, 125.43, 121.17, 118.10, 34.47, 31.84, 29.28, 29.26, 29.18, 25.15, 22.68, 14.12.



Naphthalen-2-yl nonanoate (4e) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (19.9 mg, 70% yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.87 – 7.79 (m, 3H), 7.57– 7.43 (m, 3H), 7.26 – 7.21 (m, 1H), 2.62 (t, *J* = 7.44 Hz, 2H), 1.86 – 1.76 (m, 2H), 1.47 – 1.30 (m, 10H), 0.94 – 0.89 (m, 3H).

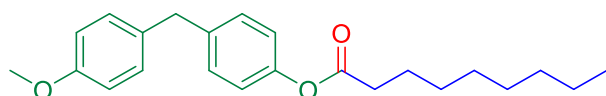
¹³C NMR (75 MHz, CDCl₃): δ 172.53, 148.45, 133.81, 131.44, 129.37, 127.78, 127.64, 126.54, 125.65, 121.24, 118.52, 34.51, 31.85, 29.27, 29.17, 25.02, 22.69, 14.13.



Cyclohexyl 5-phenylpentanoate (4f) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (5.8 mg, 22% yield). ^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.31– 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 4.80 – 4.71 (m, 1H), 2.65 – 2.61 (m, 2H), 2.33 – 2.29 (m, 2H), 1.86 – 1.80 (m, 2H), 1.72 – 1.62 (m, 6H), 1.42 – 1.26 (m, 3H).

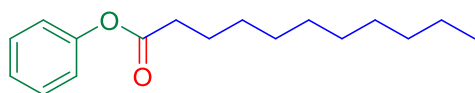
¹³C NMR (75 MHz, CDCl₃): δ 173.14, 142.24, 128.40, 128.32, 125.76, 72.42, 35.62, 34.60, 31.67, 30.92, 25.41, 24.75, 23.77.



4-(4-Methoxybenzyl)phenyl nonanoate (4g) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (28.3 mg, 80% yield). ^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.18 – 7.07 (m, 4H), 7.00 – 6.95 (m, 2H), 6.86 – 6.81 (m, 2H), 3.91 (s, 2H), 3.79 (s, 3H), 2.53 (t, *J* = 7.35 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.42 – 1.26 (m, 10H), 0.91 – 0.86 (m, 3H).

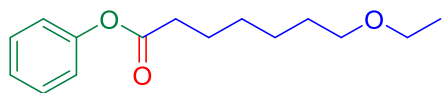
¹³C NMR (75 MHz, CDCl₃): δ 172.49, 158.05, 148.98, 139.02, 132.93, 129.91, 129.68, 121.45, 113.92, 55.28, 40.38, 34.43, 31.82, 29.23, 29.14, 24.98, 22.66, 14.11.



Phenyl undecanoate (5a) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (23.3 mg, 89% yield). ^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.41– 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 7.10 – 7.05 (m, 2H), 2.56 (t, *J* = 7.35 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.41 – 1.28 (m, 12H), 0.91 – 0.87 (m, 3H).

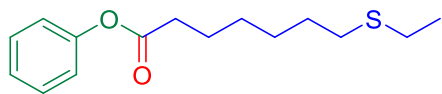
¹³C NMR (75 MHz, CDCl₃): δ 172.35, 150.80, 129.39, 125.71, 121.60, 34.44, 31.92, 29.57, 29.49, 29.33, 29.28, 29.13, 24.98, 22.70, 14.13.



Phenyl 7-ethoxyheptanoate (5b) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (20.7 mg, 83% yield). ^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.41– 7.34 (m, 2H), 7.24 – 7.19 (m, 1H), 7.09 – 7.05 (m, 2H), 3.51 – 3.40 (m, 2H), 2.56 (t, *J* = 7.35 Hz, 2H), 1.82 – 1.72 (m, 2H), 1.66 – 1.56 (m, 2H), 1.46 – 1.41 (m, 4H), 1.20 (t, *J* = 6.96 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.25, 150.77, 129.39, 125.72, 121.58, 70.57, 66.12, 34.34, 29.65, 28.97, 25.93, 24.91, 15.25.

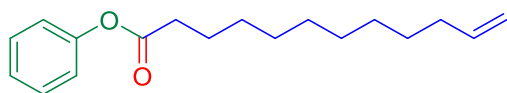


Phenyl 7-(ethylthio)heptanoate (5c) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a yellow oil (21.5 mg, 81% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 7.09 – 7.05 (m, 2H), 2.59 – 2.54 (m, 6H), 1.82 – 1.72 (m, 2H), 1.65 – 1.58 (m, 2H), 1.65 – 1.58 (m, 4H), 1.26 (t, *J* = 7.44 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 172.23, 150.74, 129.42, 125.75, 121.58, 34.31, 31.45, 29.48, 28.72, 28.55, 25.92, 24.82, 14.85.

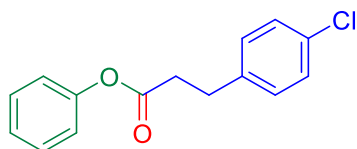
HRMS-El(m/z): calcd for C₁₅H₂₂O₄S₁⁺ [M⁺] 266.13350, found 266.13306.



Phenyl dodec-11-enoate (5d) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 400:1) to afford the title compound as a colorless oil (12.9 mg, 47% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 7.09 – 7.05 (m, 2H), 5.88 – 7.75 (m, 1H), 5.03 – 4.91 (m, 2H), 2.55 (t, *J* = 7.35 Hz, 2H), 2.01 – 2.00 (m, 2H), 1.82 – 1.70 (m, 2H), 1.40 – 1.25 (m, 12H).

¹³C NMR (75 MHz, CDCl₃): δ 172.33, 150.80, 139.22, 129.39, 125.71, 121.60, 121.56, 114.15, 34.43, 33.82, 29.43, 29.41, 29.25, 29.12, 28.94, 24.97.

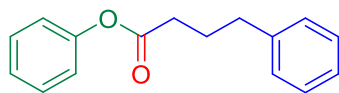


phenyl 3-(4-chlorophenyl)propanoate (5e) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (19.3 mg, 74% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.40 – 7.33 (m, 2H), 7.32 – 7.19 (m, 5H), 7.03 – 6.99 (m, 2H), 3.05 (t, *J* = 7.41 Hz, 2H), 2.30 – 2.84 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): δ 171.13, 150.58, 138.59, 132.28, 129.82, 129.45, 128.72, 125.89, 121.48, 35.81, 30.27.

HRMS-El(m/z): calcd for C₁₅H₁₃O₂Cl₁⁺ [M⁺] 260.05986, found 260.05836.

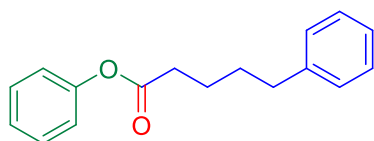


Phenyl 4-phenylbutanoate (5f) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (18.1 mg, 75% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.29 (m, 4H), 7.26 – 7.19 (m, 4H), 7.10 – 7.05 (m, 2H), 2.76 (t, *J* = 7.23 Hz, 2H), 2.59 (t, *J* = 7.41 Hz, 2H), 2.14 – 2.05 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): δ 172.01, 150.74, 141.24, 129.44, 128.57, 128.51, 126.14, 125.80, 121.59, 35.11, 33.69, 26.53.

HRMS-EI(*m/z*): calcd for C₁₆H₁₆O₂+ [*M*+][•] 240.11448, found 240.11612.

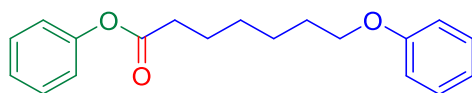


Phenyl 5-phenylpentanoate (5g) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (18.3 mg, 72% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.17 (m, 8H), 7.09 – 7.04 (m, 2H), 2.69 (t, *J* = 7.32 Hz, 2H), 2.59 (t, *J* = 7.05 Hz, 2H), 1.87 – 1.72 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ 172.12, 150.73, 142.04, 129.42, 128.43, 128.39, 125.87, 125.77, 121.59, 35.59, 34.26, 30.88, 24.57.

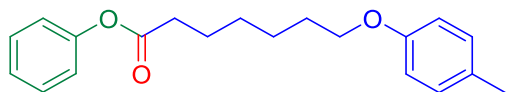
HRMS-EI(*m/z*): calcd for C₁₇H₁₈O₂+ [*M*+][•] 254.13013, found 254.13047.



Phenyl 7-phenoxyheptanoate (5h) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (24.1 mg, 81% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.40 – 7.19 (m, 5H), 7.10 – 7.05 (m, 2H), 6.96 – 6.88 (m, 3H), 3.97 (t, *J* = 6.42 Hz, 2H), 2.58 (t, *J* = 7.38 Hz, 2H), 1.87 – 1.75 (m, 4H), 1.60 – 1.44 (m, 4H).

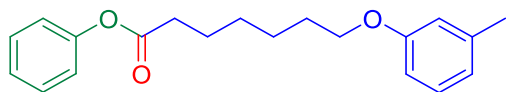
¹³C NMR (75 MHz, CDCl₃): δ 172.22, 159.08, 150.76, 129.44, 129.42, 125.75, 121.59, 120.55, 114.51, 67.66, 34.32, 29.14, 28.86, 25.81, 24.87.



Phenyl 7-(*p*-tolylloxy)heptanoate (5i) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (25.2 mg, 81% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 7.09 – 7.05 (m, 4H), 6.82 – 6.77 (m, 2H), 3.95 (t, *J* = 6.39 Hz, 2H), 2.58 (t, *J* = 7.51 Hz, 2H), 2.29 (s, 3H), 1.85 – 1.75 (m, 4H), 1.52 – 1.50 (m, 4H).

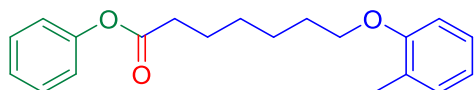
¹³C NMR (75 MHz, CDCl₃): δ 172.21, 156.96, 150.76, 129.87, 129.74, 129.41, 125.73, 121.58, 114.38, 67.85, 34.32, 29.17, 28.86, 25.79, 24.87, 20.46.



Phenyl 7-(*m*-tolylloxy)heptanoate (5j) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (25.3 mg, 81% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.34 (m, 2H), 7.25 – 7.16 (m, 2H), 7.10 – 7.06 (m, 2H), 6.77 – 6.69 (m, 3H), 3.96 (t, *J* = 6.39 Hz, 2H), 2.58 (t, *J* = 7.38 Hz, 2H), 2.33 (s, 3H), 1.87 – 1.76 (m, 4H), 1.56 – 1.50 (m, 4H).

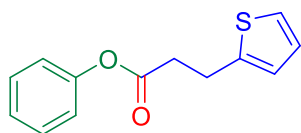
¹³C NMR (75 MHz, CDCl₃): δ 172.22, 159.11, 150.77, 139.45, 129.41, 129.18, 125.74, 121.59, 121.39, 115.40, 111.37, 67.62, 34.32, 29.17, 28.86, 25.81, 24.88, 21.54.



Phenyl 7-(*o*-tolylloxy)heptanoate (5k) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (25.9 mg, 83% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.34 (m, 2H), 7.26 – 7.06 (m, 5H), 6.88 – 6.80 (m, 2H), 3.98 (t, *J* = 6.24 Hz, 2H), 2.59 (t, *J* = 7.38 Hz, 2H), 2.24 (s, 3H), 1.90 – 1.77 (m, 4H), 1.63 – 1.46 (m, 4H).

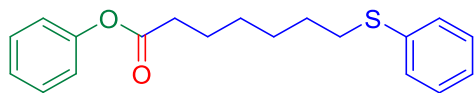
¹³C NMR (75 MHz, CDCl₃): δ 172.22, 157.20, 150.77, 130.60, 129.41, 126.84, 126.73, 125.74, 121.58, 120.14, 110.93, 67.67, 34.33, 29.22, 28.86, 25.90, 24.90, 16.25.



Phenyl 3-(thiophen-2-yl)propanoate (5l) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (14.0 mg, 60% yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.20 (m, 4H), 7.08 – 7.00 (m, 4H), 3.11 (t, *J* = 7.77 Hz, 2H), 2.92 – 2.87 (m, 2H).

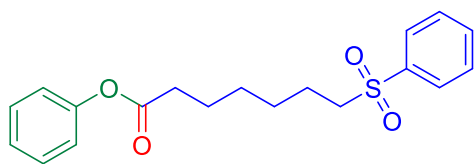
¹³C NMR (75 MHz, CDCl₃): δ 171.41, 150.67, 140.44, 129.44, 128.03, 125.85, 125.81, 121.54, 120.96, 35.30, 25.51.



Phenyl 7-(phenylthio)heptanoate (5m) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a yellow oil (26.7 mg, 85% yield). ^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.14 (m, 8H), 7.09 – 7.05 (m, 2H), 2.94 (t, *J* = 7.14 Hz, 2H), 2.55 (t, *J* = 7.44 Hz, 2H), 1.81 – 1.64 (m, 4H), 1.53 – 1.38 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ 172.17, 150.74, 136.84, 129.42, 129.02, 128.87, 125.77, 125.75, 121.57, 34.28, 33.55, 28.94, 28.62, 28.41, 24.78.

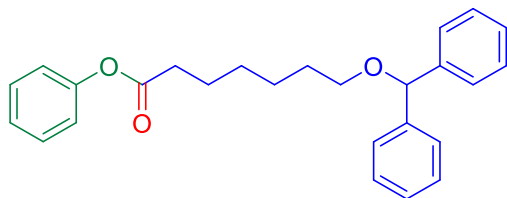


Phenyl 7-(phenylsulfonyl)heptanoate (5n) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 5:1) to afford the title compound as a yellow oil (24.9 mg, 72% yield).

¹H NMR (300 MHz, CDCl₃): δ 7.93 – 7.89 (m, 2H), 7.68 – 7.54 (m, 3H), 7.40 – 7.33 (m, 2H), 7.24 – 7.18 (m, 1H), 7.07 – 7.03 (m, 2H), 3.12 – 3.07 (m, 2H), 2.53 (t, *J* = 7.35 Hz, 2H), 1.80 – 1.66 (m, 4H), 1.49 – 1.37 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ 171.97, 150.67, 139.18, 133.69, 129.43, 129.31, 128.05, 125.80, 121.53, 56.17, 34.11, 28.48, 27.96, 24.48, 22.52.

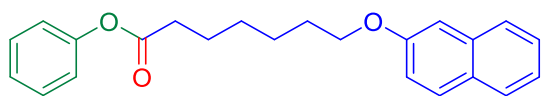
HRMS-EI(*m/z*): calcd for C₁₉H₂₂O₄S₁⁺ [*M*⁺] 346.12333, found 346.12433.



Phenyl 7-(benzhydryloxy)heptanoate (5o) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a colorless oil (15.5 mg, 40 % yield). ^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.42 – 7.20 (m, 13H), 7.10 – 7.06 (m, 2H), 5.35 (s, 1H), 3.48 (t, *J* = 6.42 Hz, 2H), 2.56 (t, *J* = 7.32 Hz, 2H), 1.83 – 1.65 (m, 4H), 1.53 – 1.42 (m, 4H).

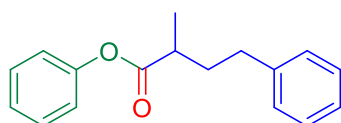
¹³C NMR (75 MHz, CDCl₃): δ 172.27, 150.77, 142.61, 129.41, 128.36, 127.36, 126.97, 125.73, 121.60, 83.66, 69.04, 34.36, 29.72, 28.95, 25.97, 24.91.



Phenyl 7-(naphthalen-2-yloxy)heptanoate (5p) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a colorless oil (13.8 mg, 42 % yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.78 – 7.71 (m, 3H), 7.46 – 7.30 (m, 4H), 7.25 – 7.05 (m, 5H), 4.10 (t, *J* = 6.42 Hz, 2H), 2.60 (t, *J* = 7.38 Hz, 2H), 1.94 – 1.78 (m, 4H), 1.63 – 1.53 (m, 4H).

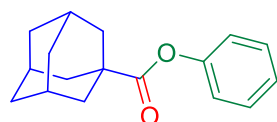
¹³C NMR (75 MHz, CDCl₃): δ 172.21, 157.06, 150.76, 134.63, 129.41, 129.35, 128.93, 127.65, 126.71, 126.31, 125.74, 123.51, 121.58, 119.01, 106.60, 67.80, 34.33, 29.09, 28.87, 25.85, 24.88.



Phenyl 2-methyl-4-phenylbutanoate (5q) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a colorless oil (13.8 mg, 42 % yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.17 (m, 8H), 7.09 – 7.05 (m, 2H), 2.77 – 2.69 (m, 3H), 2.23 – 2.11 (m, 1H), 1.92 – 1.80 (m, 1H), 1.35 (d, *J* = 6.96 Hz, 3H).

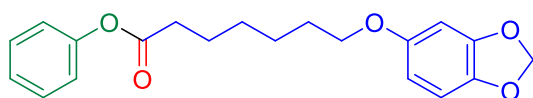
¹³C NMR (75 MHz, CDCl₃): δ 175.04, 150.82, 141.52, 129.45, 128.51, 126.07, 125.78, 121.56, 39.17, 35.45, 33.53, 17.16.



Phenyl (3r,5r,7r)-adamantane-1-carboxylate (5r) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 400:1) to afford the title compound as a colorless oil (22.8 mg, 89 % yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.40 – 7.34 (m, 2H), 7.24 – 7.18 (m, 1H), 7.07 – 7.03 (m, 2H), 2.09 – 2.07 (m, 9H), 1.82 – 1.78 (m, 6H).

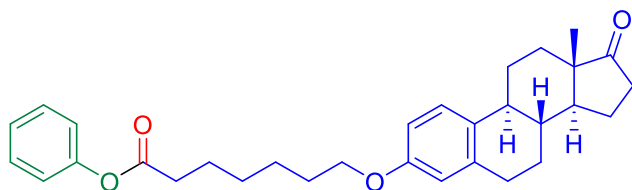
¹³C NMR (75 MHz, CDCl₃): δ 175.04, 150.82, 141.52, 129.45, 128.51, 126.07, 125.78, 121.56, 39.17, 35.45, 33.53, 17.16.



Phenyl 7-(benzo[d][1,3]dioxol-5-yloxy)heptanoate (5s) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a white oil (27.5 mg, 85 % yield).^[4]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 7.10 – 7.06 (m, 2H), 6.70 (d, *J* = 8.43 Hz, 1H), 6.50 (d, *J* = 2.46 Hz, 1H), 6.32 (dd, *J* = 8.43, 2.46 Hz, 1H), 5.91 (s, 2H), 3.89 (t, *J* = 6.42 Hz, 2H), 2.58 (t, *J* = 7.35 Hz, 2H), 1.84 – 1.74 (m, 4H), 1.54 – 1.47 (m, 4H).

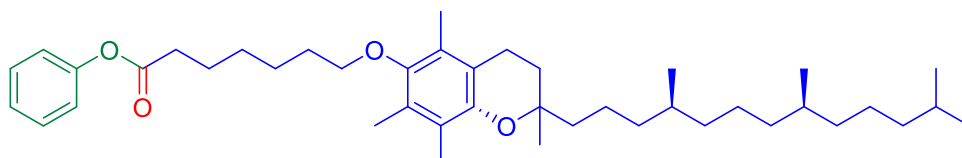
¹³C NMR (75 MHz, CDCl₃): δ 172.21, 154.63, 150.76, 148.24, 141.51, 129.42, 125.75, 121.59, 107.95, 105.68, 101.09, 98.07, 68.74, 34.31, 29.14, 28.84, 25.77, 24.86.



Phenyl 7-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)heptanoate (5t) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a colorless oil (37.9 mg, 80 % yield).^[5]

¹H NMR (300 MHz, CDCl₃): δ 7.41 – 7.34 (m, 2H), 7.26 – 7.18 (m, 2H), 7.10 – 7.06 (m, 2H), 6.74 – 6.65 (m, 2H), 3.95 (t, *J* = 6.42 Hz, 2H), 2.93 – 2.88 (m, 2H), 2.58 (t, *J* = 7.32 Hz, 2H), 2.53 – 1.27 (m, 21H), 0.92 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 220.96, 172.21, 157.13, 150.77, 137.73, 131.93, 129.42, 126.33, 125.75, 121.60, 114.59, 112.15, 67.71, 50.44, 48.04, 44.02, 38.42, 35.90, 34.32, 31.63, 29.69, 29.18, 28.85, 26.60, 25.96, 25.81, 24.88, 21.62, 13.89.



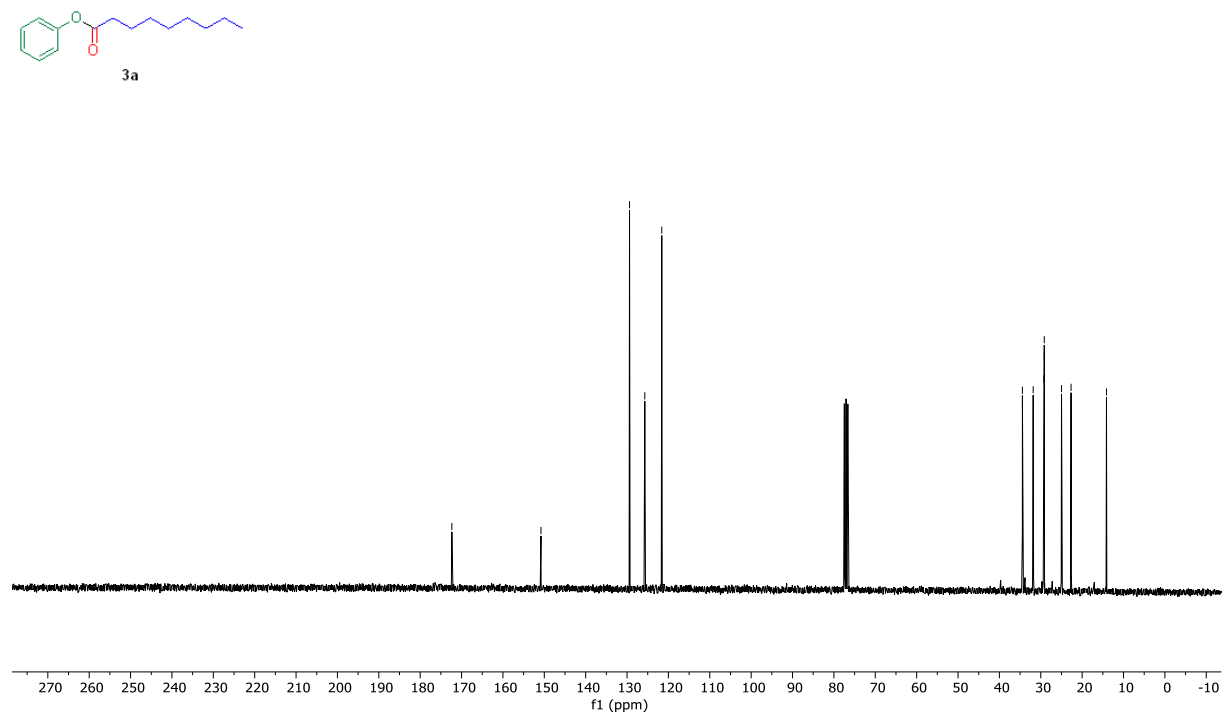
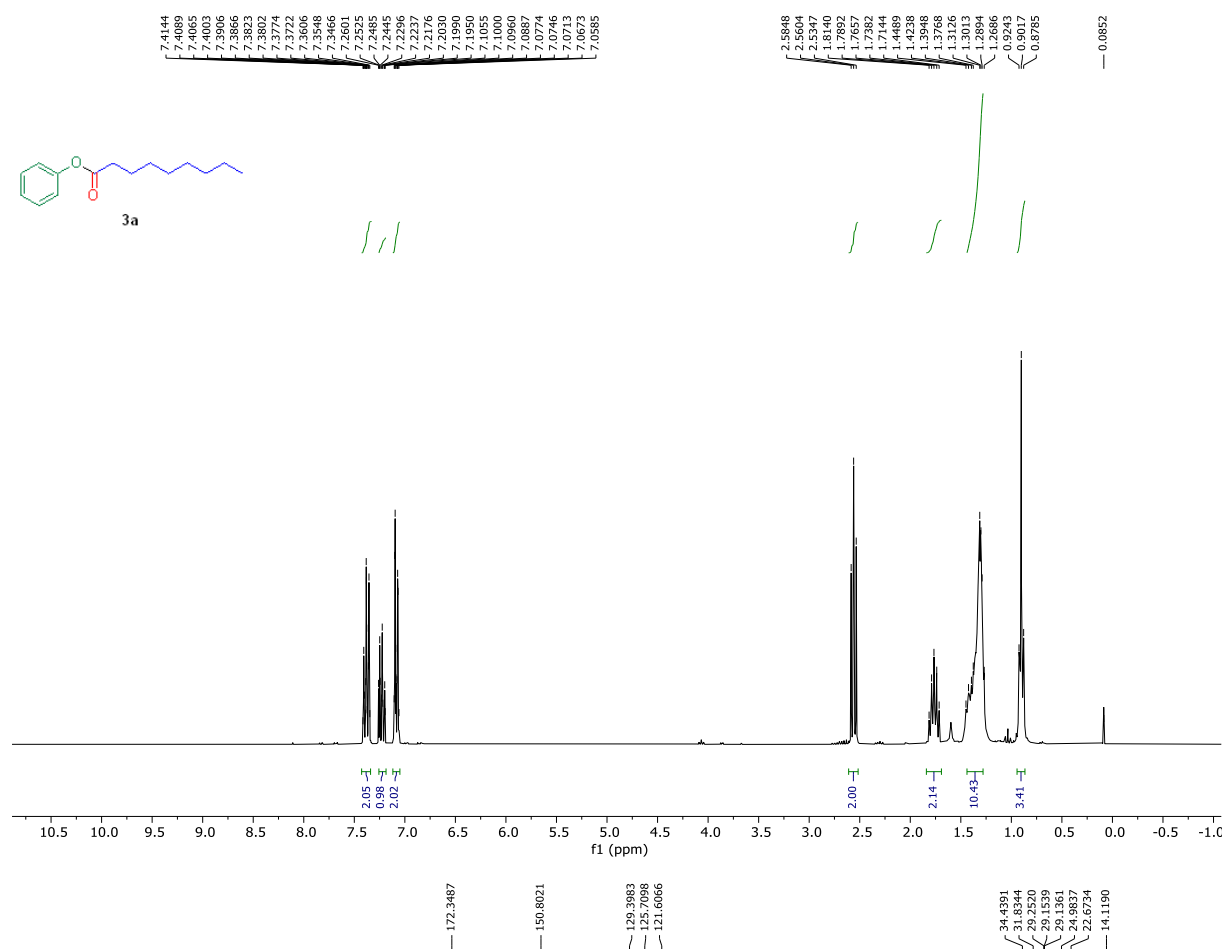
Phenyl 7-((2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)heptanoate (5u) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a colorless oil (38.1 mg, 60% yield).

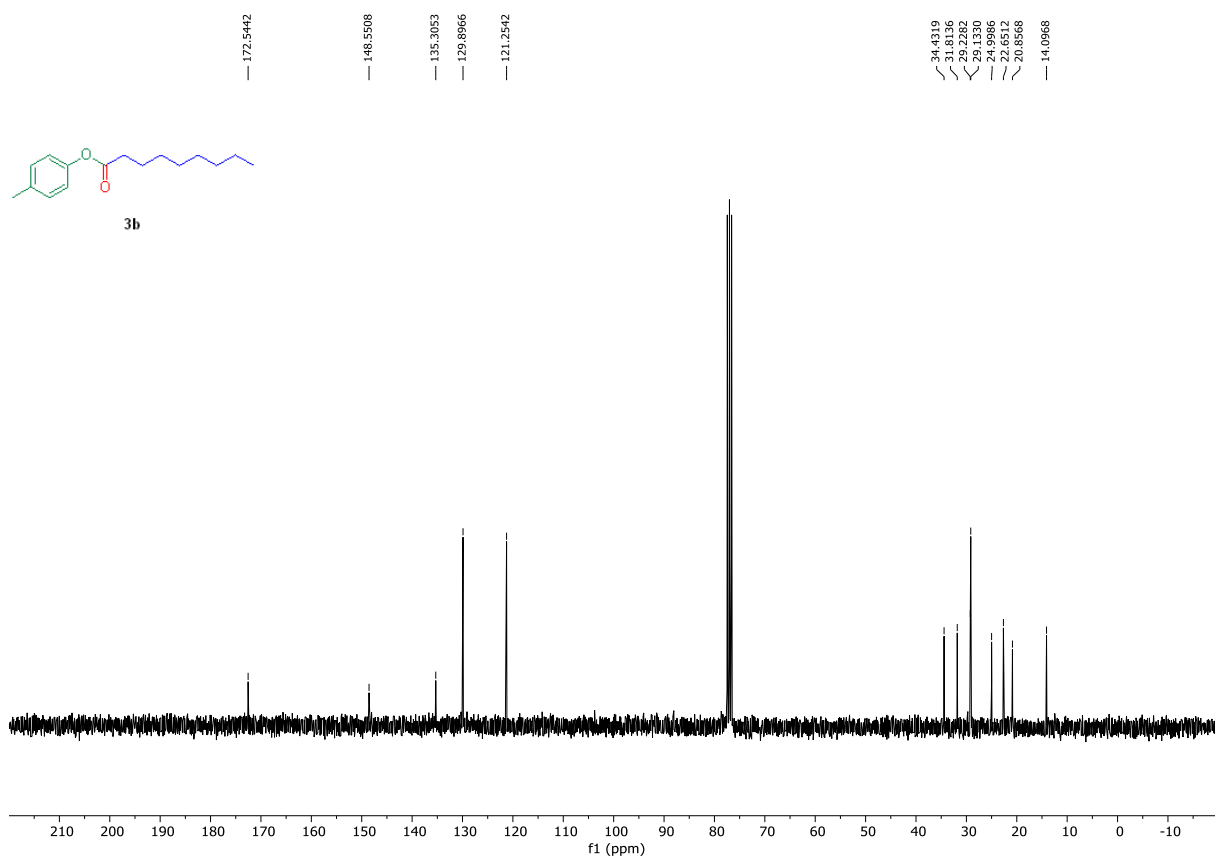
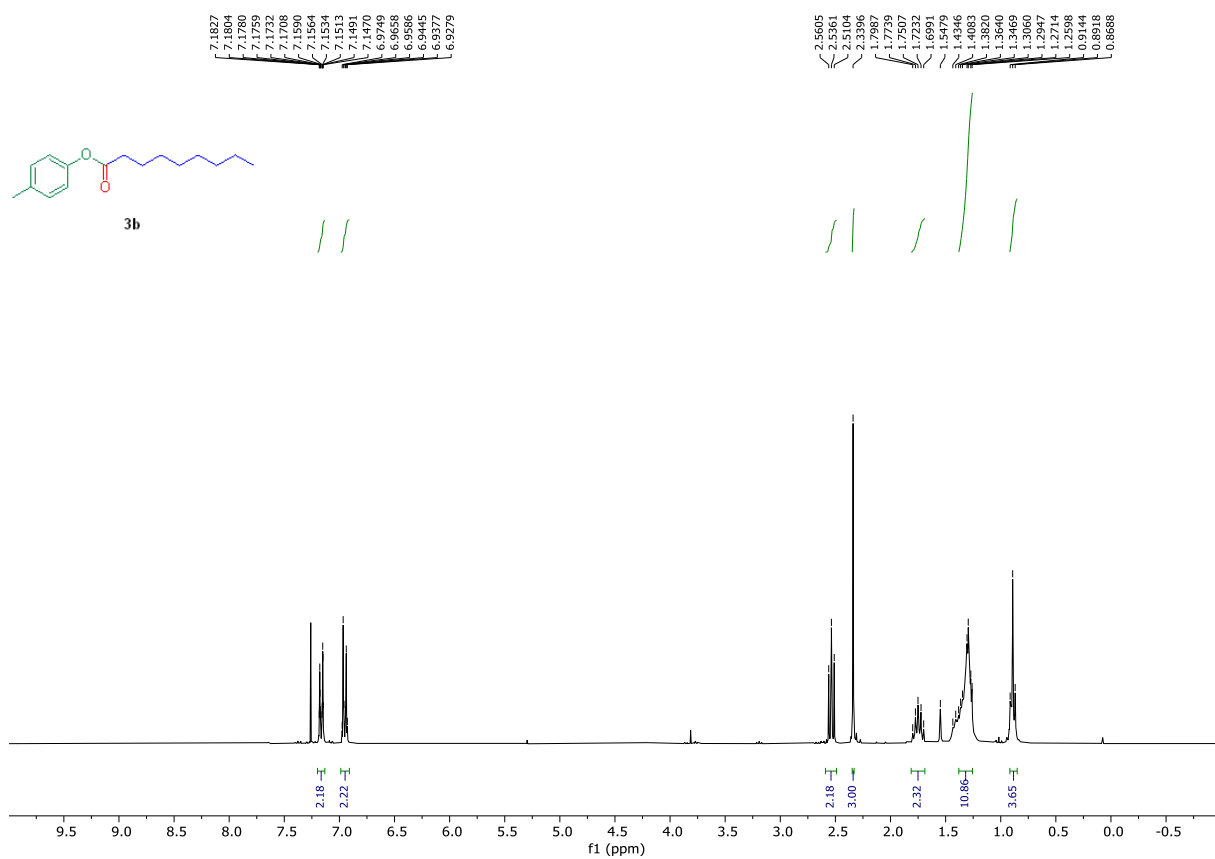
¹H NMR (300 MHz, CDCl₃): δ 7.42 – 7.36 (m, 2H), 7.26 – 7.21 (m, 1H), 7.12 – 7.07 (m, 2H), 3.67 (t, *J* = 6.51 Hz, 2H), 2.63 – 2.56 (m, 4H), 2.19 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 1.88 – 1.76 (m, 4H), 1.64 – 1.09 (m, 28H), 0.90 – 0.85 (m, 12H).

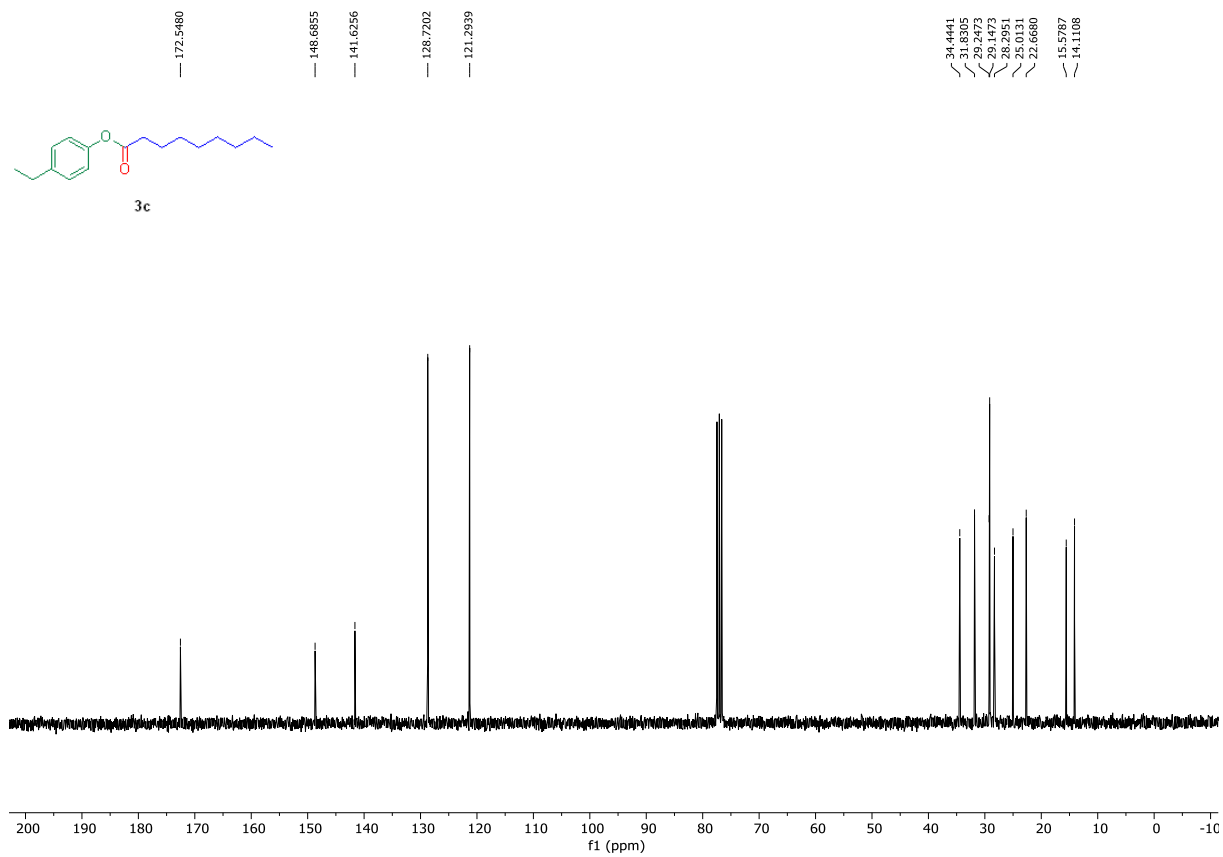
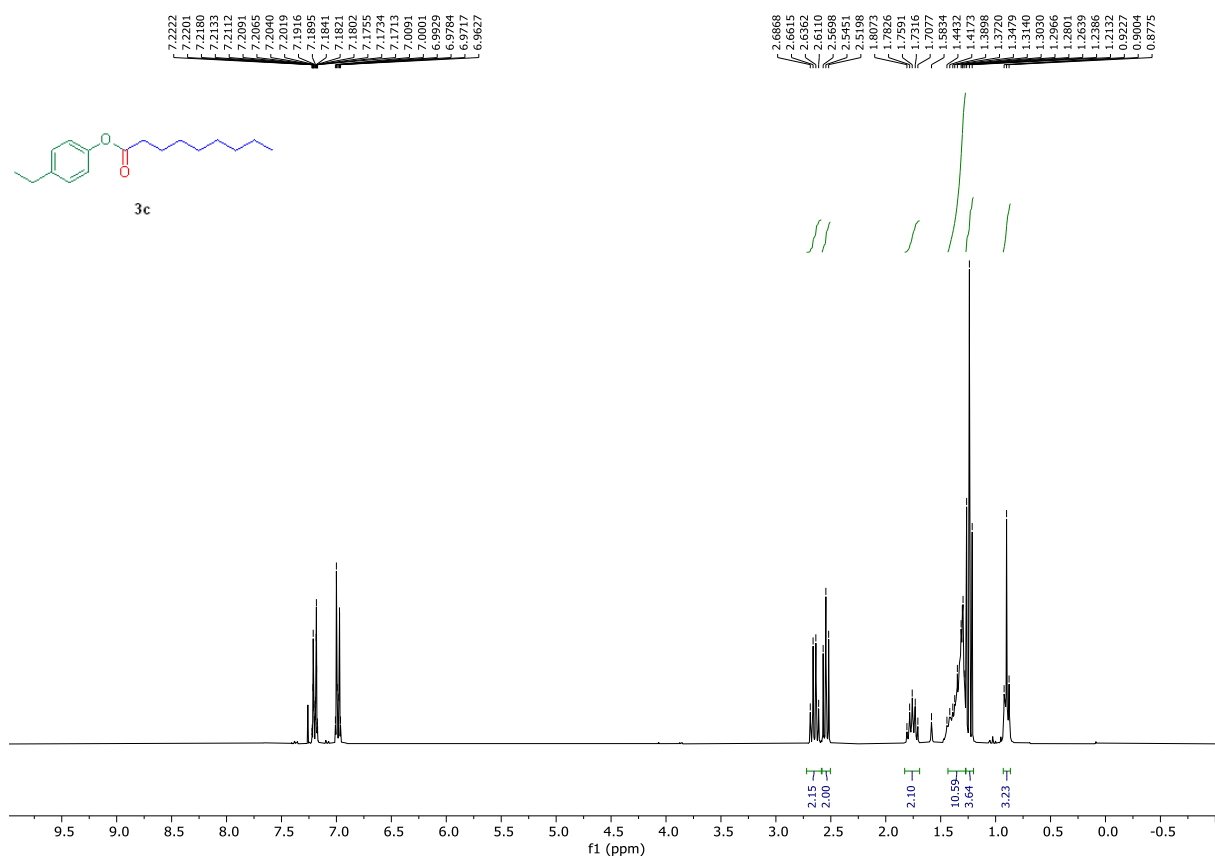
¹³C NMR (75 MHz, CDCl₃): δ 172.26, 150.78, 148.35, 147.69, 129.42, 127.84, 125.82, 125.75, 122.80, 121.62, 117.50, 74.77, 72.90, 40.13, 39.41, 37.61, 37.50, 37.43, 37.32, 34.39, 32.83, 32.81, 32.74, 32.71, 31.34, 31.29, 30.22, 29.14, 28.02, 26.01, 24.96, 24.85, 24.48, 23.93, 22.77, 22.67, 21.09, 20.70, 19.80, 19.73, 19.67, 19.64, 12.79, 11.92, 11.84.

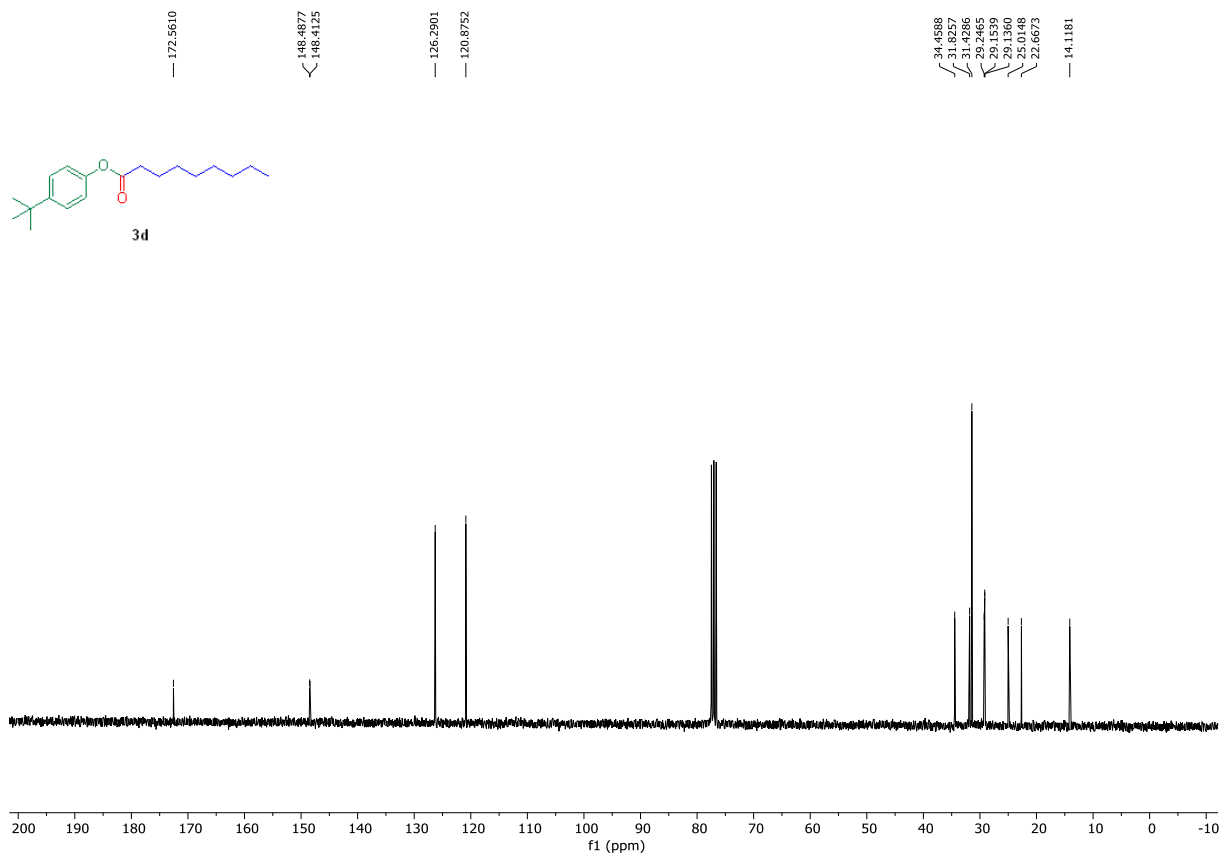
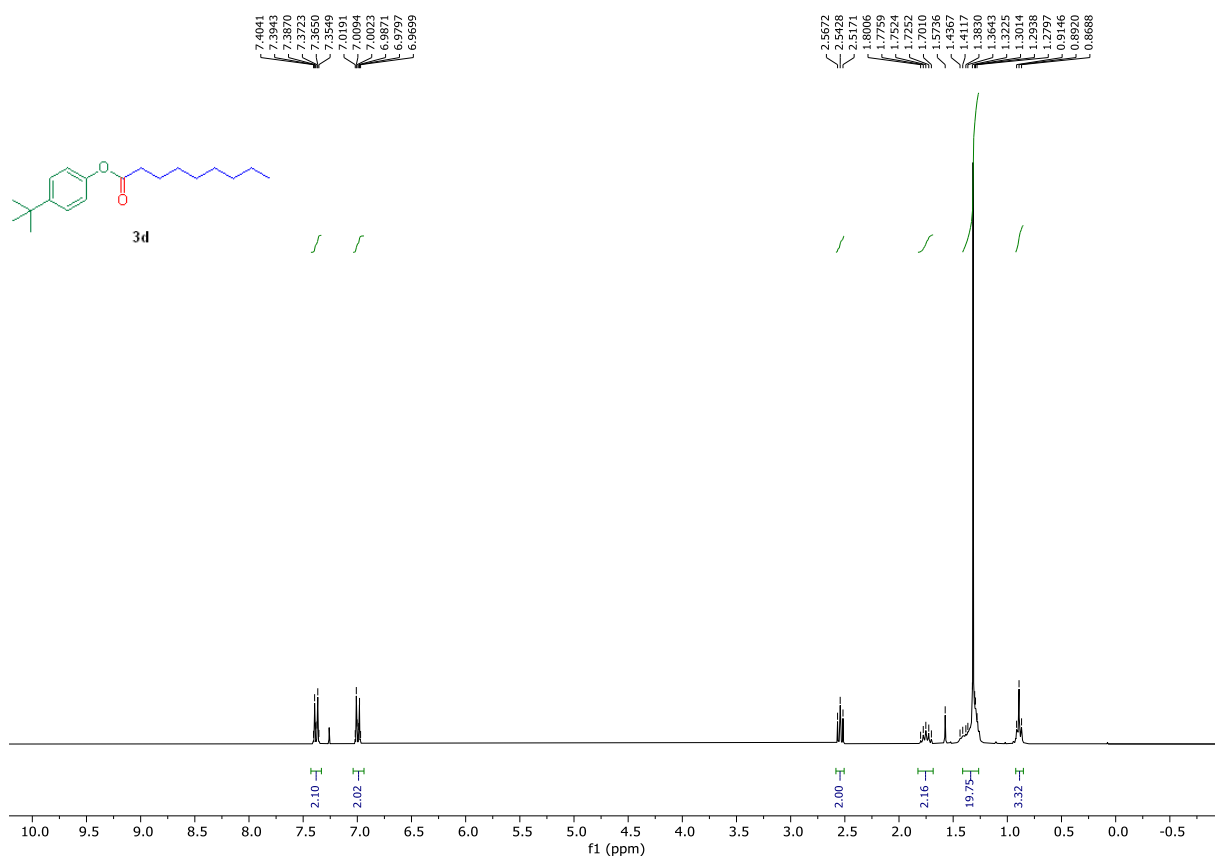
HRMS-EI(*m/z*): calcd for C₄₂H₆₆O₄⁺ [*M*⁺] 634.49556, found 634.49454.

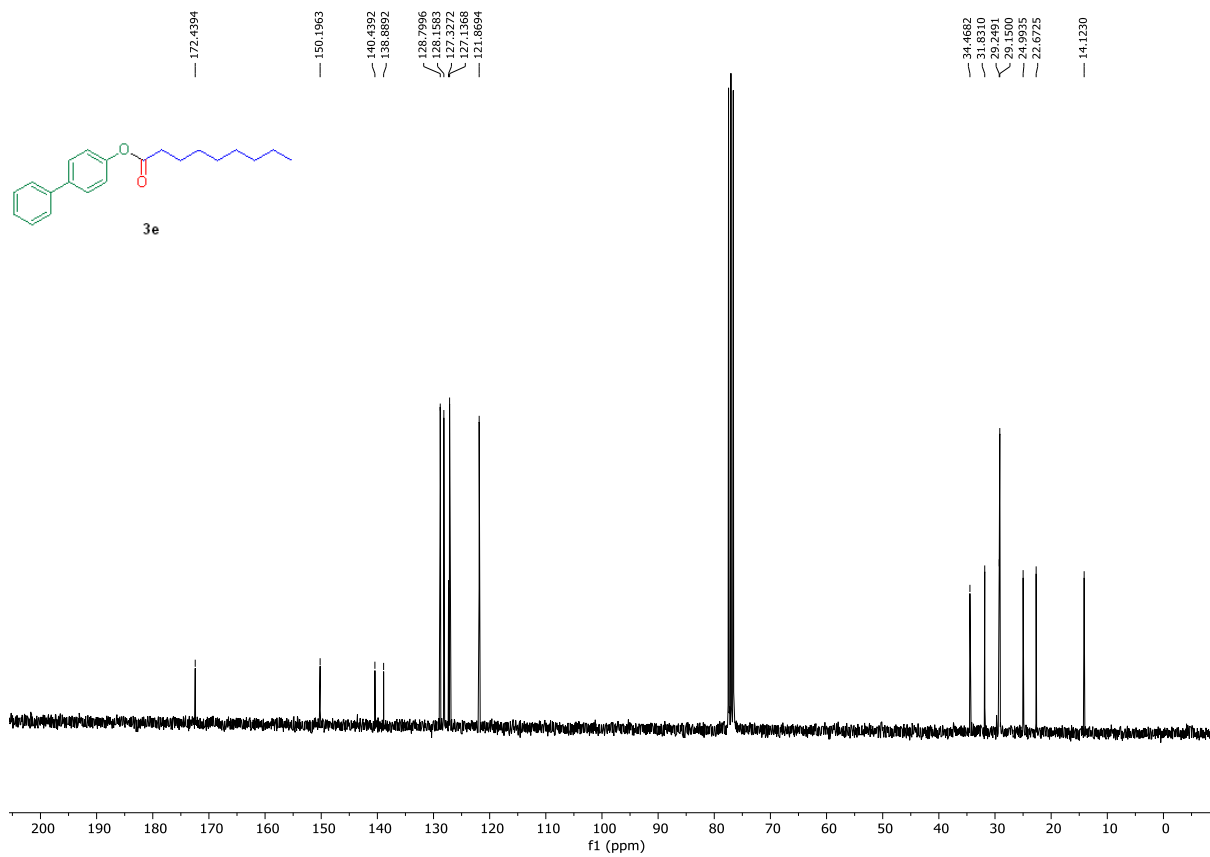
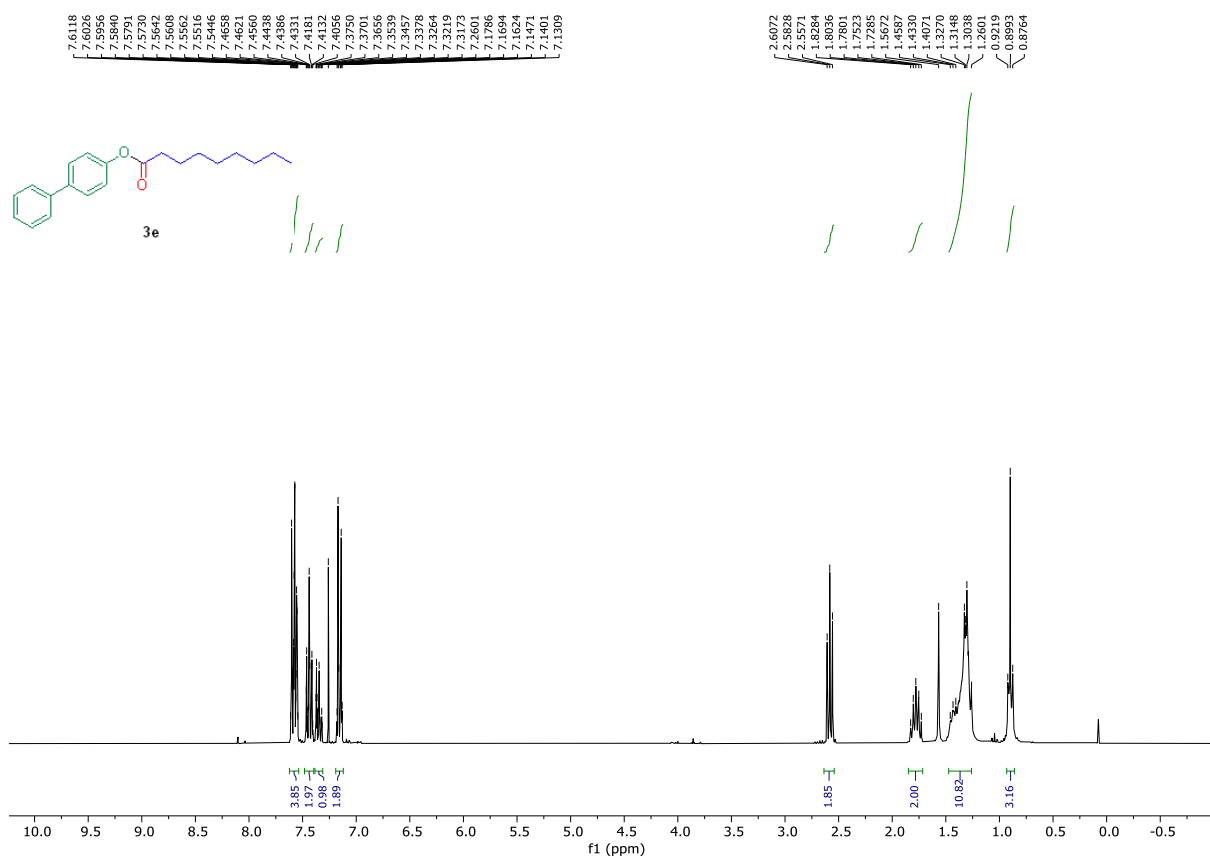
8. NMR spectra of the products

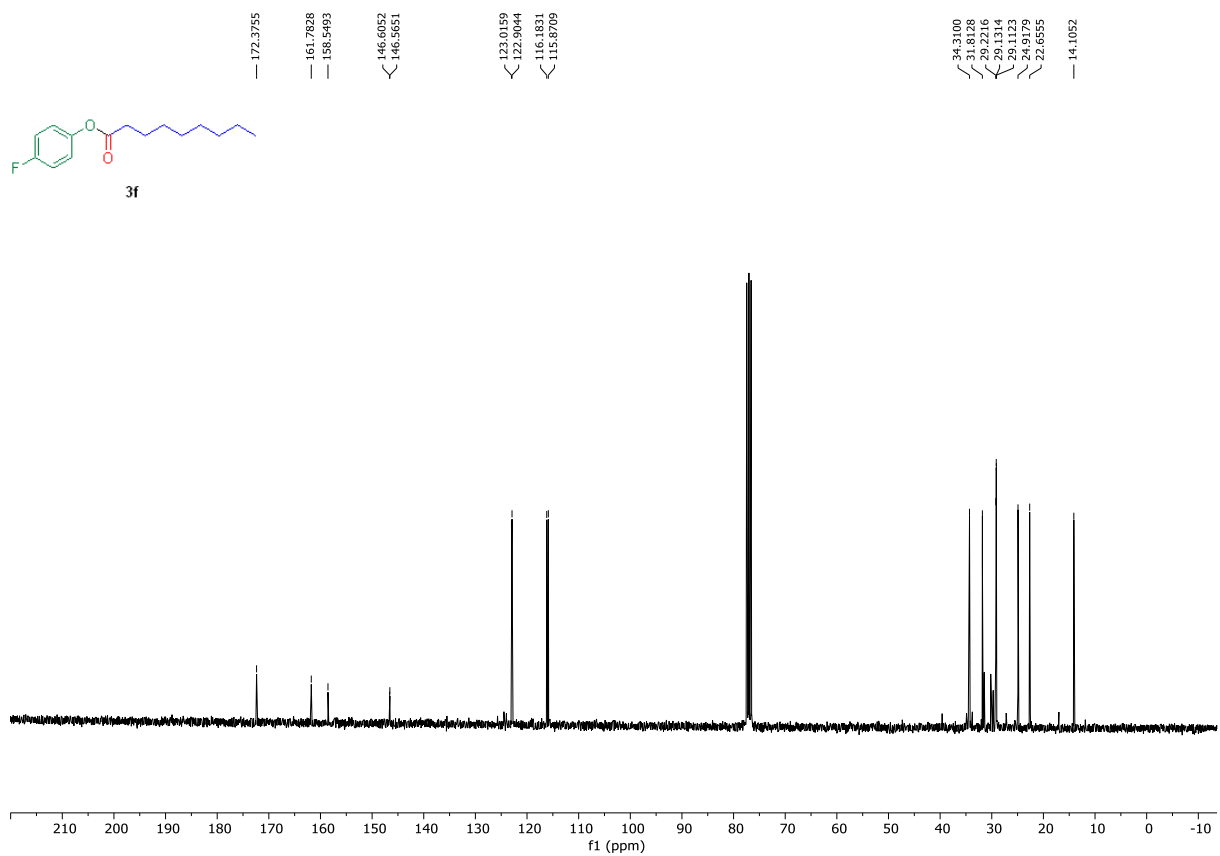
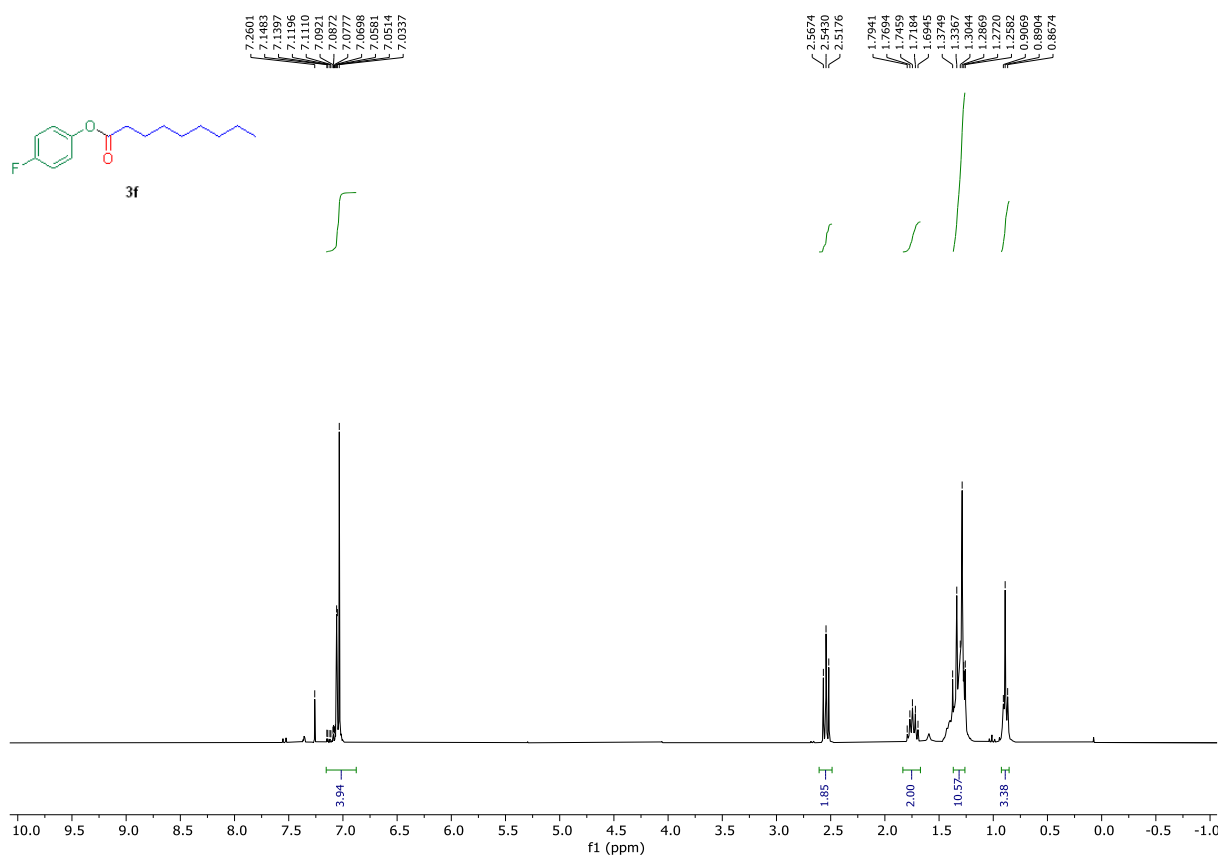


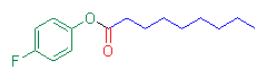












3f

-117.2043
-117.2286
-117.2502
-117.2719
-117.2935

