Supporting information

Electrochemical Cross-Electrophile Coupling of Unactivated Tertiary Alkyl Bromides with Benzyl Chloride to Access Quaternary Stereocenters

Yun Yang [†a], Shaokun Tao[a], Li Chen[a], Yi Tan[a], Jiaqi Xu[a], Haiyan Fu[a], Ruixiang Li[a], Hua Chen[a], Weichao Xue*[a], Xueli Zheng*[a]

[a] Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China.
* Corresponding author: Xue-Li Zheng, Fax：(+86)-28-85412904;
E-mail address: weichaoxue@scu.edu.cn; zhengxueli@scu.edu.cn

Supporting Information

Table of Contents

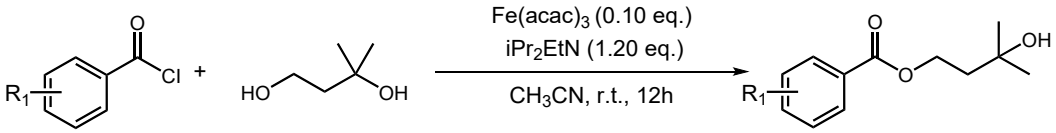
1. General Information

All reagents and starting materials were purchased from commercial suppliers without further purification, unless otherwise stated. All solvents were purified according to the established procedures. Column chromatography was performed with silica gel (300-400 mesh). ^{1}H NMR spectra were recorded on *Bruker* Avance 400 MHz spectrometers. Chemical shifts were reported in ppm referenced to 7.26 ppm of chloroform-*d.* ^{13}C NMR spectra were recorded on *Bruker* Avance 100 MHz spectrometers and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of chloroform-*d*. Data are reported as follows: chemical shift, multiplicity, coupling constants (Hz), and integration. HRMS was recorded on a *SCIEX* X500R QTOF (ESI). Electron paramagnetic resonance (EPR) was measured using a *Bruker* EMXplus X-band EPR spectrometer operated at 9.86 GHz with a microwave power of 2.00 mW. IKA RCT Basic was used as the heating source. The anodic electrode was stainless steel sheet (0.3 mm × 10.0 mm × 15.0 mm) and cathodic electrode was graphite felt (2.0 mm × 10.0 mm × 15.0 mm). *Maynuo* DC Source meter (M8831, 30V/1A) was used as power supply. Gas chromatography (GC) was performed on a *SHIMADZU* GC-2010 gas chromatograph equipped with a *SHIMADZU* SK-5MS column (30 m × 0.25 mm, 0.25 μm film thickness) using the following program: H_2, dry air, N_2 carrier gas, injection temperature 280 °C, detector temperature 260 °C, flow rate: 1.5 mL/min; temperature program: start temperature 40 °C, heating rate 20 °C/min, end temperature 280 °C for 5 min. Cyclic voltammetry tests were performed by using *CHI* 600E potentiostat equipped with the conventional three electrode system.

2. Experimental Details for the Preparation of Tertiary Alkyl Bromide

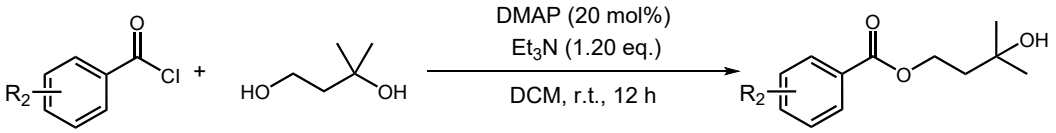
alkyl bromide substrates 1, **19a**, **20a**, **21a, 22a, 23a, 24a, 25a, 26a, 27a** were synthesized according to the reported procedure, and all spectroscopic data matched those reported.

2.1 Procedure 1 for the Preparation of Tertiary Alcohols (for the synthesis of 1, 23a, 24a, 25a)



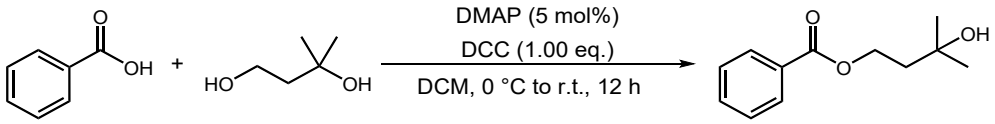
A pre-dried Schlenk flask was charged with 3-methyl-1,3-butanediol (24 mmol, 1.20 eq.), *N*,*N*-diisopropylethylamine (24 mmol, 1.20 eq.), benzoyl chloride (20 mmol, 1.00 eq.) and $Fe(acac)_3$ (2 mmol, 0.10 eq.). The flask was evacuated and backfilled with N_2 for 3 times, followed by the addition of dry acetonitrile (50 mL). The resulting mixture was quenched with 10 mL H_2O, and extracted with dichloromethane (DCM) (3 × 20 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to furnish the desired tertiary alcohol, R_f = 0.40 (PE/EtOAc = 75/25).[1]

2.2 Procedure 2 for the Preparation of Tertiary Alcohols (for the synthesis of 19a, 22a)



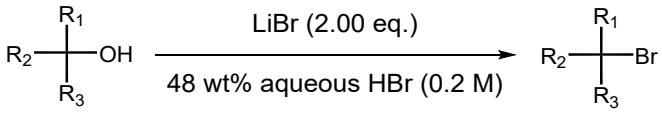
A pre-dried Schlenk flask was charged with 3-methyl-1,3-butanediol (24 mmol, 1.20 eq.), triethylamine (24 mmol, 1.20 eq.), benzyl chloride (20 mmol, 1.00 eq.) and 4-Dimethylaminopyridine (0.4 mmol, 0.02 eq.). The flask was evacuated and backfilled with N_2 for 3 times, followed by the addition of dry DCM (100 mL). The resulting mixture was quenched with 10 mL H_2O, and extracted with DCM (3 × 20 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to furnish the desired tertiary alcohol, R_f = 0.40 (PE/EtOAc = 80/20).[1]

2.3 Procedure 3 for the Preparation of Tertiary Alcohols (for the synthesis of 20a, 21a)

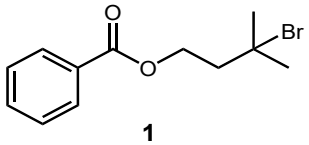


A Schlenk flask was charged with Benzoic acid (20 mmol, 1.00 eq.), *N,N*-diisopropylethylamine (1 mmol, 0.05 eq.), *N,N*-Dicyclohexylcarbodiimide (20 mmol, 1.00 eq.) and DCM (0.2 M) in an ice bath. Reacts at room temperature after addition of 3-methyl-1,3-butanediol (24 mmol, 1.20 eq.). The resulting mixture was quenched with 10 mL H_2O, and extracted with DCM (3 × 20 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to afford the product, R_f = 0.40 (PE/EtOAc = 80/20).

2.4 Procedure 4 for the Preparation of Tertiary Alkyl bromides



A pre-dried Schlenk flask was charged with tertiary alcohol precursor (10 mmol, 1.00 eq., neat or in a minimal amount of DCM). At 0 ºC, LiBr (20 mmol, 2.00 eq.) in 48 wt % aqueous HBr (0.2 M, 20 mL) was added dropwise. Then the reaction mixture was allowed to warm to r.t. and stirred for 12 h. The reaction mixture was diluted with ethyl acetate, and washed with water and saturated $NaHCO_3$. The organic layer was collected, washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography to afford the product.[2, 3]



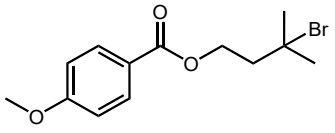
1

$C_{12}H_{15}BrO_2$

M = 270.03 g/mol

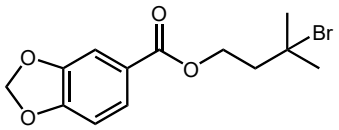
1: a colorless oil, 1.29 g, 48% yield, $\mathbf{R_f}$ = 0.65 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 – 8.00 (m, 2H), 7.61 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 4.58 (t, *J* = 6.7 Hz, 2H), 2.31 (t, *J* = 6.7 Hz, 2H), 1.86 (s, 6H). The characterization data is

consistent with those reported in the literature.[4]



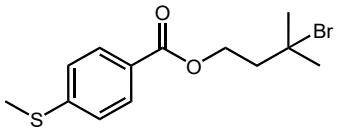
19a
$C_{13}H_{17}BrO_3$
M =300.04 g/mol

19a: a colorless oil, 1.45 g, 48% yield, $\mathbf{R_f}$ = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.0 – 7.9 (m, 2H), 7.0 – 6.9 (m, 2H), 4.5 (t, 2H), 3.9 – 3.8 (s, 3H), 2.3 (t, 2H), 1.9 – 1.8 (m, 6H).The characterization data is consistent with those reported in the literature.[4, 5]



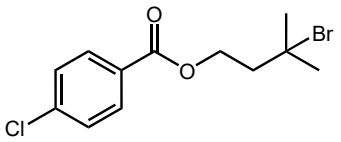
20a
$C_{13}H_{15}BrO_4$
M =314.02 g/mol

20a: a colorless oil, 0.75 g, 24% yield, $\mathbf{R_f}$ = 0.60 (PE/EtOAc = 10/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.57 (m, 1H), 7.46 – 7.43 (m, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.04 (s, 2H), 4.57 – 4.50 (t, *J* = 6.7 Hz, 2H), 2.29 (t, *J* = 6.7 Hz, 2H), 1.85 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.9, 151.8, 147.9, 125.5, 124.2, 109.6, 108.1, 102.0, 64.4, 63.2, 45.6, 34.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}BrO_4$: 315.0226; found: 315.0228.



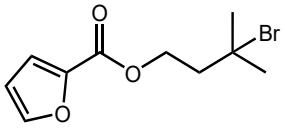
21a
$C_{13}H_{17}BrO_2S$
M =316.01 g/mol

21a: a colorless oil, 0.53 g, 17% yield, $\mathbf{R_f}$ = 0.5 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 4.55 (t, *J* = 6.7 Hz, 2H), 2.50 (s, 3H), 2.29 (t, *J* = 6.7 Hz, 2H), 1.85 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.3, 145.7, 130.0, 126.3, 125.0, 64.4, 63.1, 45.6, 34.8, 14.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}BrO_2S$: 317.0205; found: 317.0206.



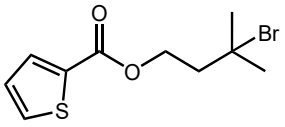
22a
$C_{12}H_{14}BrClO_2$
M =303.99 g/mol

22a: a colorless oil, 0.43 g, 14% yield, $\mathbf{R_f}$ = 0.60 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.58 (t, *J* = 6.8 Hz, 2H), 2.30 (t, *J* = 6.8 Hz, 2H), 1.85 (s, 6H). The characterization data is consistent with those reported in the literature.[4]



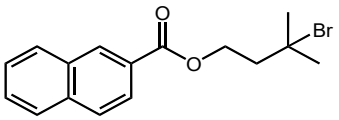
23a
$C_{10}H_{13}BrO_3$
M = 260.00 g/mol

23a: a colorless oil, 0.80 g, 30% yield, $\mathbf{R_f}$ =0.60 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 1H), 7.18 -7.12 (m, 1H), 6.53 – 6.45 (m, 1H), 4.54 (t, *J* = 6.8 Hz, 2H), 2.26 (t, *J* = 6.8 Hz, 2H), 1.82 (s, 6H). The characterization data is consistent with those reported in the literature.[4, 6]



24a
$C_{10}H_{13}BrO_2S$
M = 275.98 g/mol

24a: a colorless oil, 1.10 g, 40% yield, $\mathbf{R_f}$ = 0.60 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 1H), 7.56 – 7.50 (m, 1H), 7.11 – 7.02 (m, 1H), 4.52 (t, *J* = 6.7 Hz, 2H), 2.25 (t, *J* = 6.7 Hz, 2H), 1.82 (s, 6H). The characterization data is consistent with those reported in the literature.[2]

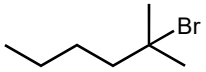


25a
$C_{16}H_{17}BrO_2$
M = 320.04 g/mol

25a: a colorless oil, 1.28 g, 40% yield, $\mathbf{R_f}$ = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, DMSO-*d*) δ 8.6 (s, 1H), 8.1 (d, *J* = 8.1 Hz, 1H), 8.1 – 8.0 (m, 3H), 7.71 – 7.57 (m, 2H), 4.6 (t, *J* = 6.7 Hz, 2H), 2.4 (t, *J* = 6.7 Hz, 2H), 1.9 (s, 6H). The characterization data is consistent with those reported in the literature.[7]

26a
$C_6H_{11}BrO$
M = 178.00 g/mol

26a: a colorless oil, 0.41 g, 23% yield, $\mathbf{R_f}$ = 0.60 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.88 – 3.63 (m, 4H), 2.00 – 1.95 (m, 1H), 1.95 – 1.92 (m, 1H), 1.85 (s, 3H), 1.79 – 1.62 (m, 2H). The characterization data is consistent with those reported in the literature.[3]



27a
$C_7H_{15}Br$
M = 178.04 g/mol

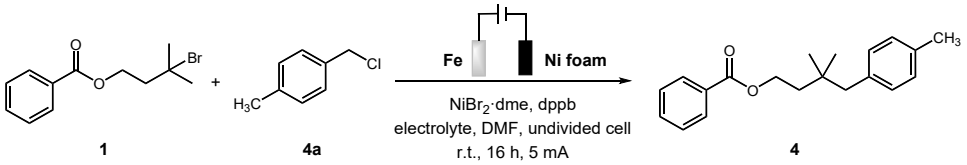
27a: a colorless oil,1.43 g, 80% yield, $\mathbf{R_f}$ = 0.60 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 1.83 – 1.67 (m, 8H), 1.53 – 1.41 (m, 2H), 1.41 – 1.26 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). The characterization data is consistent with those reported in the literature.[4]

3. Optimization Studies

3.1 Optimization Study Using Alkyl Bromides and benzyl Chlorides

General procedure for the optimization of electroreductive cross-electrophile coupling using tertiary alkyl bromide and benzyl chloride: Electrochemical reactions were carried out in an undivided cell using pre-dried Schlenk tube with electrodes. The pre-dried Schlenk tube equipped with a stir bar is evacuated and backfilled with N_2 for 3 times. Subsequently, the tube was charged with metal catalyst, ligand, electrolyte, additive, 3-bromo-3-methylbutyl benzoate **1** (0.20 mmol, 1.00 eq.) and 4-methylbenzyl chloride **4a** (0.40 mmol, 2.00 eq.). Then the tube was sealed, evacuated and backfilled with N_2 for 3 times, followed by the addition of solvent (4 mL) through syringe. The tube was stirred at r.t. with a constant current maintained for 16 h. After that, the electrodes were washed with DCM (3 × 5 mL). H_2O (20 mL) was added to the reaction tube, and the resulting mixture was extracted with DCM (2 × 20 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to furnish the desired product.

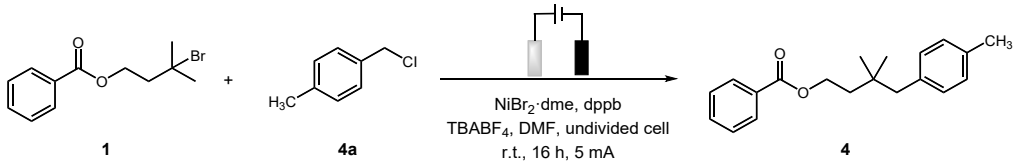
Table S1. Screening of electrolytes.



entry	electrolyte	yield [%][a]
1	$TBABF_4$	30
2	Et_4NBF_4	21
3	$Zn(BF_4)_2$	17
4	$NaBF_4$	11
5	$Mg(OTf)_2$	29
6	Et_4NOTf	28
7	LiOTf	24
8	TBAOTf	22
9	NaOTf	18

[a]Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme (0.02 mmol), dppb (0.04 mmol), electrolyte (0.40 mmol), DMF (4 mL) under 5 mA constant current at room temperature for 16 h with an iron plate as the anode and nickel foam as the cathode. [a]GC yield.

Table S2. Screening of electrodes.

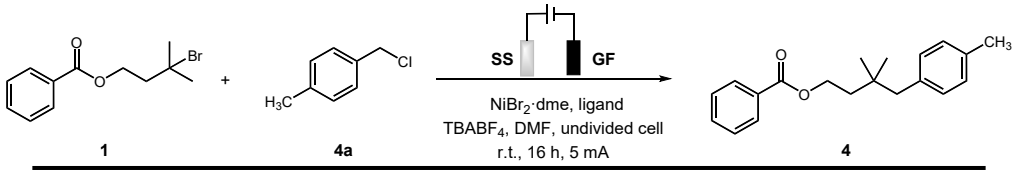


1 **4a** **4**

entry	electrode	yield [%][a]
1	SS (+)|GF (-)	35
2	Zn (+)|GF (-)	27
3	Fe (+)|GF (-)	21
4	Al (+)|GF (-)	16
5	Mg (+)|GF (-)	N.D.
6	SS (+)|Ni foam (-)	22
7	Mg (+)|Ni foam (-)	5
8	Zn (+)|Ni foam (-)	3
9	Al (+)|Ni foam (-)	3

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme (0.02 mmol), dppb (0.04 mmol), $TBABF_4$ (0.40 mmol), DMF (4 mL) under 5 mA constant current at room temperature for 16 h with different materials. [a]GC yield.

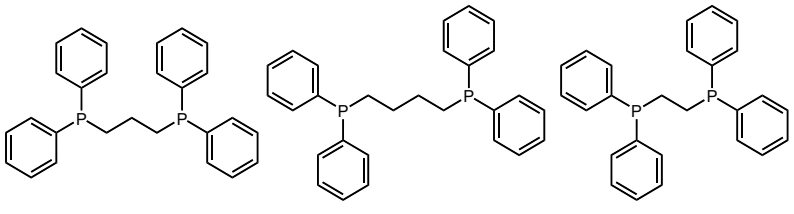
Table S3. Screening of ligands.



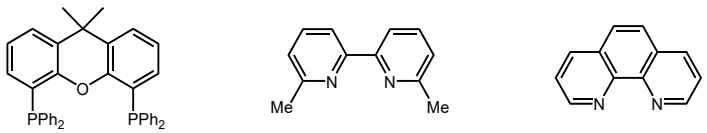
1 **4a** **4**

entry	ligand	yield [%][a]
1	L1 (dppp)	44
2	L2	35
3	L3	33
4	L4	13
5	L5	21
6	L6	6

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme (0.02 mmol), ligand (0.04 mmol), $TBABF_4$ (0.40 mmol), DMF (4 mL), under 5 mA constant current at room temperature for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode. [a]GC yield.

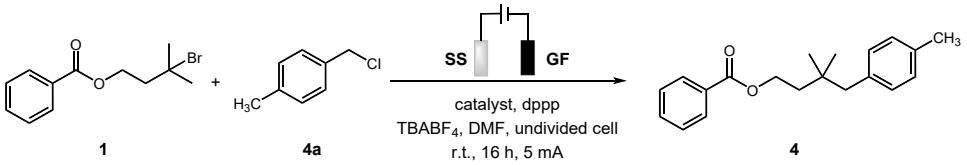


L1 **L2** **L3**



L4 **L5** **L6**

Table S4. Screening of catalysts.

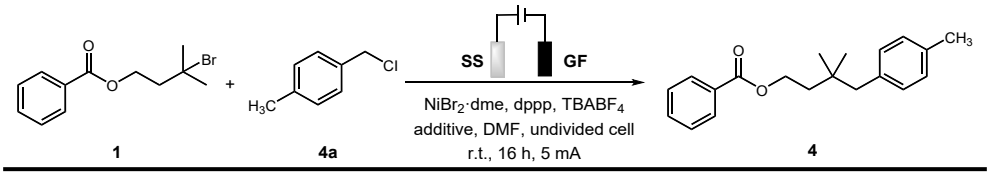


1 4a 4

entry	catalyst	yield [%][a]
1	$NiBr_2$·dme	44
2	NiI_2	37
3	$NiBr_2$	34
4	$Ni(cod)_2$	30
4	$NiBr_2$·diglyme	29
5	$NiCl_2$·$(PPh_3)_2$	22
6	$NiCl_2$·dme	20
7	Ni_2SO_4	14
8	$Ni(ClO_4)_2$·$6H_2O$	14
9	$Ni(OAc)_2$·$4H_2O$	7
10	$Ni(OTf)_2$	3
11	$NiCl_2$·$6H_2O$	N.D.

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), [Cat] (0.02 mmol), dppp (0.04 mmol), $TBABF_4$ (0.40 mmol), DMF (4 mL) under 5 mA constant current at room temperature for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode. [a]GC yield.

Table S5. Screening of additive.

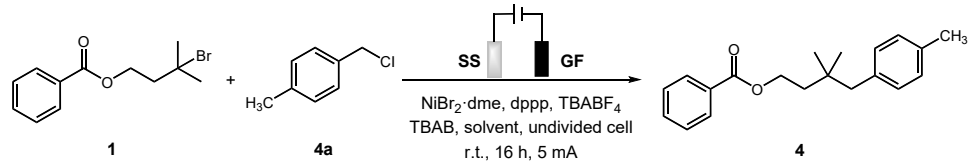


1 **4a** **4**

entry	additive	yield [%][a]
1	TBAB	64
2	TBAOTf	46
3	LiOTf	45
4	NaBr	41
5	$Mg(OTf)_2$	39
6	KI	34
7	TBAI	30
8	LiBr	19

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme (0.02 mmol), dppp (0.04 mmol), $TBABF_4$ (0.40 mmol), additive (0.20 mmol), DMF (4 mL) under 5 mA constant current at room temperature for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode. [a]GC yield.

Table S6. Screening of solvents.

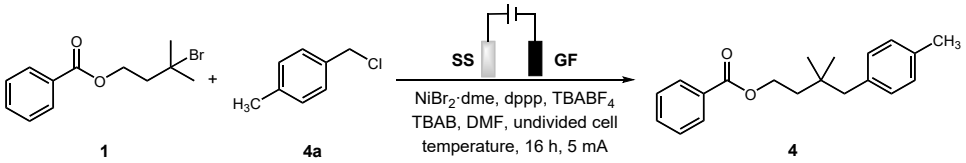


1 **4a** **4**

entry	solvent	yield [%][a]
1	DMF	64
2	DMA	51
3	DMSO	40
4	NMP	15
5	MeCN	10

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme (0.02 mmol), dppp (0.04 mmol), $TBABF_4$ (0.40 mmol), TBAB (0.20 mmol), solvent (4 mL) under 5 mA constant current for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode. [a]GC yield.

Table S7. Screening of temperature.

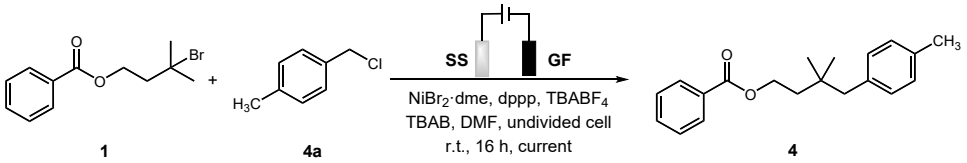


1 **4a** **4**

entry	temperature	yield [%][a]
1	r.t.	64
2	15 ºC	57
3	40 ºC	48
4	60 ºC	21
5	80 ºC	N.D.

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme (0.02 mmol), dppp (0.04 mmol), $TBABF_4$ (0.40 mmol), TBAB (0.20 mmol), DMF (4 mL) under 5 mA constant current for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode. [a]GC yield.

Table S8. Screening of currents.

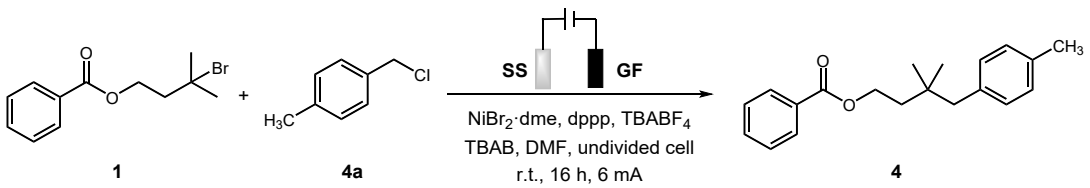


1 **4a** **4**

entry	current	yield [%][a]
1	1 mA	N.D.
2	4 mA	57
3	5 mA	64
4	6 mA	68
5	7 mA	52
6	8 mA	62

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme (0.02 mmol), dppp (0.04 mmol), $TBABF_4$ (0.40 mmol), TBAB (0.20 mmol), DMF (4 mL) under constant current for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode. [a]GC yield.

Table S9. Screening of catalysts and ligand loadings.

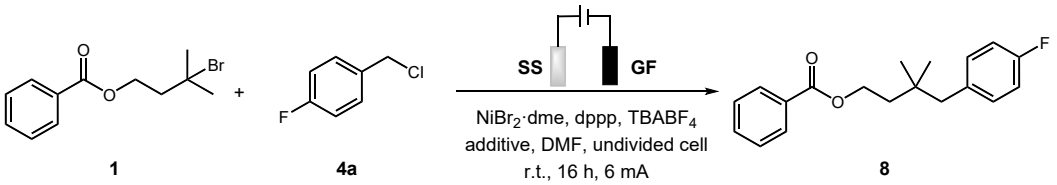


1 **4a** **4**

entry	catalyst, ligand	yield [%][a]
1	10 mol% $NiBr_2$·dme, 20 mol% dppp	68
2	10 mol% $NiBr_2$·dme, 25 mol% dppp	55
3	10 mol% $NiBr_2$·dme, 30 mol% dppp	56
4	20 mol% $NiBr_2$·dme, 20 mol% dppp	53
5	20 mol% $NiBr_2$·dme, 30 mol% dppp	61
6	20 mol% $NiBr_2$·dme, 40 mol% dppp	73

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme, dppp, $TBABF_4$ (0.40 mmol), TBAB (0.20 mmol), DMF (4 mL) under 6 mA constant current at room temperature for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode. [a]GC yield.

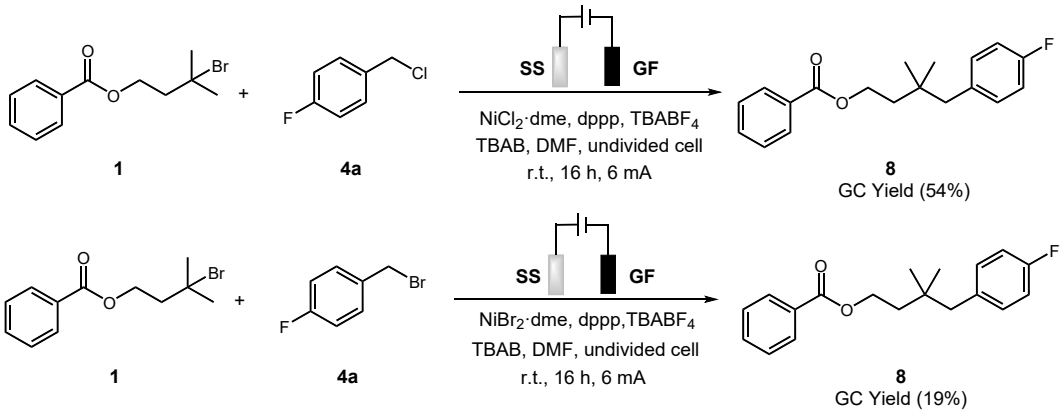
Table S10. Control experiments for probing the function of TBAB



1 **4a** **8**

entry	additive	yield [%][a]
1	TBAB	71
2	$MgBr_2$	69
3	TPAB	59
4	LiBr	55
5	TBAC	54
6	TEAC	45
7	LiCl	31

Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), $NiBr_2$·dme (0.04 mmol), dppp (0.08 mmol), $TBABF_4$ (0.40 mmol), additive (0.20 mmol), DMF (4 mL) under 5 mA constant current at room temperature for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode. [a]GC yield.



1 **4a** **8** GC Yield (54%)

1 **4a** **8** GC Yield (19%)

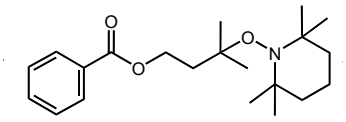
Reaction conditions: undivided cell, **1** (0.20 mmol), **4a** (0.40 mmol), catalyst (0.04 mmol), dppp (0.08 mmol), $TBABF_4$ (0.40 mmol), TBAB (0.20 mmol), DMF (4 mL) under 6 mA constant current at room temperature for 16 h with a stainless steel sheet as the anode and graphite felt as the cathode.

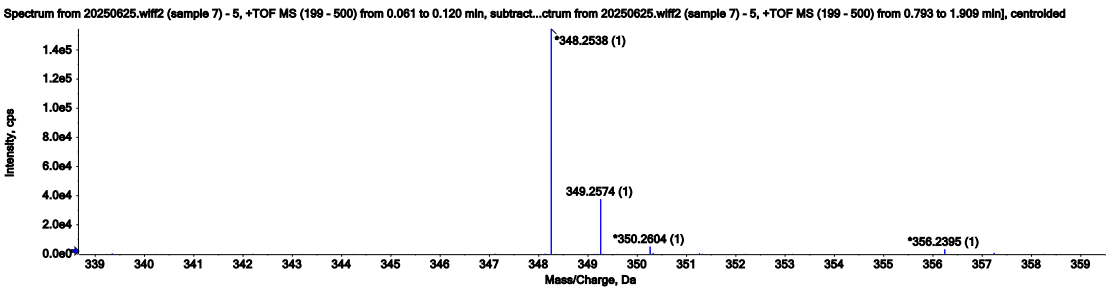
4. Experimental Details for the Mechanism Study

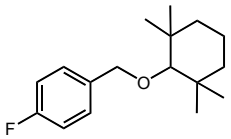
4.1 Procedure for Radical Trapping Experiments

$NiBr_2$·dme (0.04 mmol), dppp (0.08 mmol), $TBABF_4$ (0.40 mmol), TBAB (0.20 mmol), 3-bromo-3-methylbutyl benzoate **1** (0.20 mmol, 1.00 eq.), 4-fluorobenzyl chloride **2** (0.50 mmol, 2.00 eq.) and radical scavenger (0.8 mmol) were placed in a 15 mL pre-dried Schlenk tube with a magnetic stirring bar. The Schlenk tube was equipped with a stainless steel sheet (0.3 mm × 10.0 mm × 15.0 mm) and graphite felt (2.0 mm × 10.0 mm × 15.0 mm). And then the tube was evacuated and backfilled with N_2 (3 times), followed by the addition of DMF (4 mL). The tube was stirred at r.t. with a constant current at 6 mA maintained for 16 h. The electrodes were washed with DCM (3 × 5 mL). H_2O (20 mL) was added to the system, and the resulting mixture was extracted with DCM (2 × 20 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered through celite and then analyzed by HRMS.

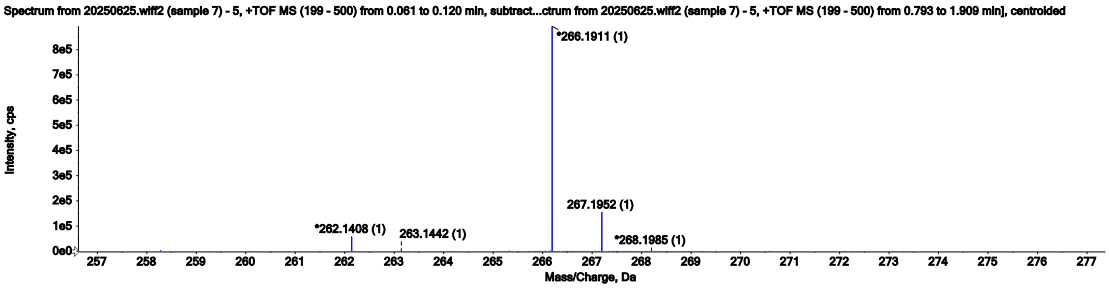
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{33}NO_3$: 348.2533; found: 348.2538.







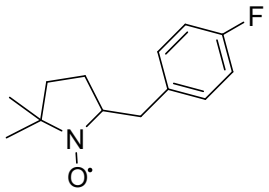
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{24}FNO_3$: 266.1915; found: 266.1911.


Spectrum from 20250625.wiff2 (sample 7) - 5, +TOF MS (199 - 500) from 0.061 to 0.120 min, subtract...ctrum from 20250625.wiff2 (sample 7) - 5, +TOF MS (199 - 500) from 0.793 to 1.909 min], centroided
Intensity, cps
8e5
7e5
6e5
5e5
4e5
3e5
2e5
1e5
0e0
*266.1911 (1)
267.1952 (1)
*262.1408 (1)
263.1442 (1)
*268.1985 (1)
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
Mass/Charge, Da

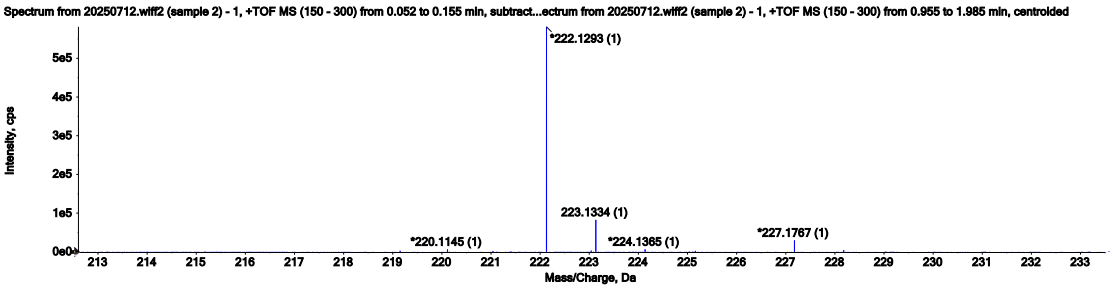
4.2 EPR study

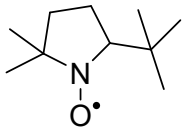
To a pre-dried Schlenk flask (15 mL) equipped with a magnetic stir bar is added $NiBr_2$·dme (0.040 mmol, 20 mol%), dppp (0.080 mmol, 40 mol%), $TBABF_4$ (0.40 mmol, 2.00 eq.), TBAB (0.20 mmol, 1.00 eq.), 2-bromo-2-methylpropane (0.20 mmol, 1 eq.), 4-fluorobenzyl chloride (0.40 mmol, 2.00 eq.) and DMF (4 mL). A stainless steel electrode and a graphite felt electrode were installed as the anode and cathode, respectively. The cell was sealed with a rubber septum and flushed with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA at r.t. for 30 minutes. *N*-tert-butyl-α-phenylnitrone (PBN) (142 mg, 2.00 eq.) was added into the reaction mixture and was continued stirring for 1 minute to trap any transient radical species. Upon completion, the mixture was directly analyzed by electron paramagnetic resonance (EPR) spectroscopy. The EPR spectrum exhibited a strong radical signal, the simulation of which was consistent with the PBN-adduct of a tertiary alkyl radical (fitting result: g =2.006, a_N = 14.6 G, a_H = 2.5 G).[2]

To a pre-dried Schlenk flask (15 mL) equipped with a magnetic stirring bar is added $NiBr_2$·dme (0.040 mmol, 20 mol%), dppp (0.080 mmol, 40 mol%), $TBABF_4$ (0.40 mmol, 2.00 eq.), TBAB (0.20 mmol, 1.00 eq.), 2-bromo-2-methylpropane (0.20 mmol, 1 eq.), 4-fluorobenzyl chloride (0.40 mmol, 2.00 eq.), and DMF (4 mL). A stainless steel electrode and a graphite felt electrode were installed as the anode and cathode, respectively. The cell was sealed with a rubber septum and flushed with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA at r.t. for 30 minutes. A spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (89 μL) was added into the reaction mixture and was continued stirring for 1 minute to detect transient radical species. Upon completion, the mixture was directly analyzed by EPR spectroscopy. The EPR spectrum exhibited a strong radical signal, the simulation of which was consistent with the DMPO-adduct of a benzyl radical (fitting result: g =2.006, a_N = 14.3 G, a_H = 20.7 G).[9]

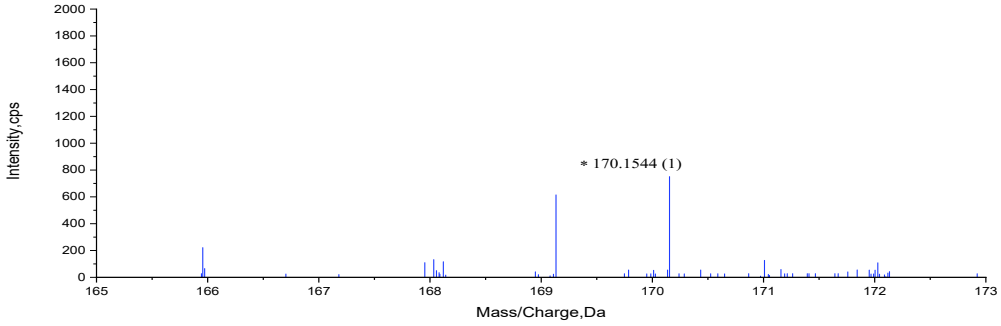


HRMS (ESI-TOF) m/z: $[M]^+$: Calcd for $C_{13}H_{17}FNO$•: 222.1294; found: 222.1293.





HRMS (ESI-TOF) m/z: $[M]^+$: Calcd for $C_{10}H_{20}NO$•: 170.1545; found: 170.1544.



5. Experimental Details for the Electrochemical Coupling Reaction

General procedure (**GP**) for electrochemical cross-coupling of tertiary alkyl bromides and benzyl chlorides was follow: the reaction was carried out in undivided cell using pre-dried Schlenk tube with a stainless steel sheet (0.3 mm × 10.0 mm × 15.0 mm) and graphite felt (2.0 mm × 10.0 mm × 15.0 mm). The pre-dried Schlenk tube equipped with a stir bar was evacuated and backfilled with N_2 (3 times). After that, the tube was charged with $NiBr_2$·dme (0.040 mmol), dppp (0.080 mmol), $TBABF_4$ (0.40 mmol), tertiary alkyl bromide (0.40 mmol, 1.00 eq.) and benzyl chloride (0.40 mmol, 2.00 eq.). Then the tube was evacuated and backfilled with N_2 (3 times), followed by the addition of DMF (4 mL). The tube was sealed and stirred at r.t. with a constant current at 6 mA maintained for 16 h. The electrodes were washed with DCM (3 × 5 mL). H_2O (20 mL) was added to the system, and the resulting mixture was extracted with DCM (2 × 20 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to furnish the desired product.

6. Experimental Details for Cyclic Voltammetry Tests

Cyclic voltammetry tests of alkyl bromide or 4-fluorobenzyl chloride were performed in a three-electrode cell at r.t. under N_2 atmosphere. A steady carbon glass disk electrode was used as working electrode and a platinum plate acted as counter electrode. The reference was an Ag/AgCl (3.0 M KCl_{aq}) electrode. 20 mL DMF containing 0.10 M $TBABF_4$ was poured into the electrochemical cell in this experiment. The concentration of all substrates was 0.01 M at measuring. The scan rate was 0.10 V/s, and the range was 0 V ~ -3.0 V.

Figure S1. Cyclic voltammetry tests under N_2, $NiBr_2$·dme (0.01 M), dppp (0.02 M), $TBABF_4$ (0.10 M), DMF (20 mL).

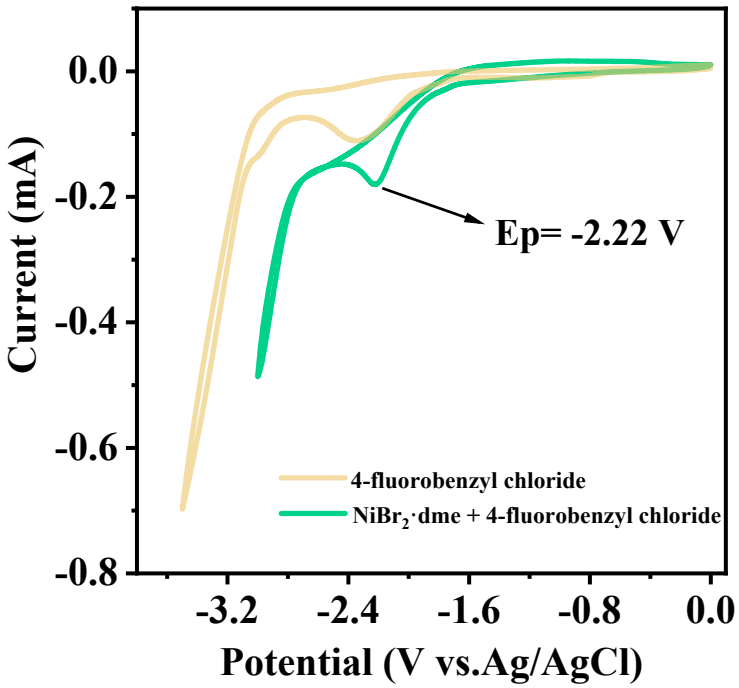


Figure S2. Cyclic voltammetry tests under N_2: 4-fluorobenzyl chloride (0.01M), $NiBr_2$·dme (0.01 M), dppp (0.02 M), $TBABF_4$ (0.1 M), DMF (20 mL).

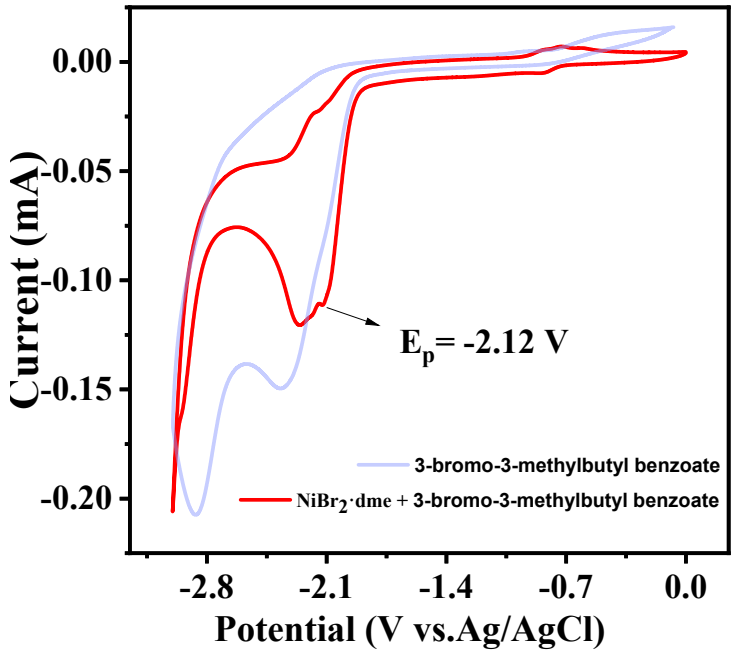


Figure S3. Cyclic voltammetry tests under N_2: 3-bromo-3-methylbutyl benzoate (0.01M), $NiBr_2$·dme (0.01 M), dppp (0.02 M), $TBABF_4$ (0.1 M), DMF (20 mL).

7. Proposed Alternative Mechanism[8]

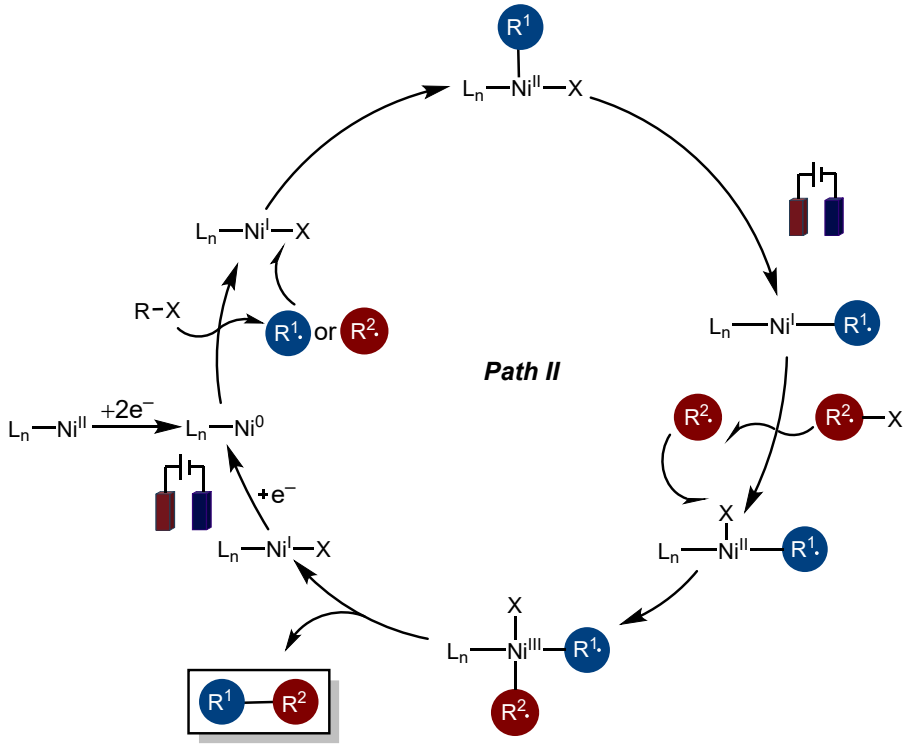
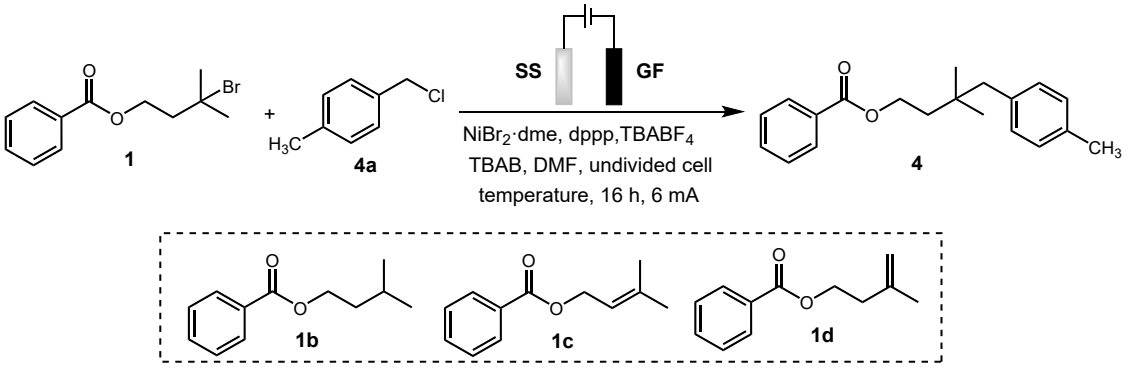


Figure S4. Alternative Nickel catalytic cycle.

8. Mass Balance of Selected Examples

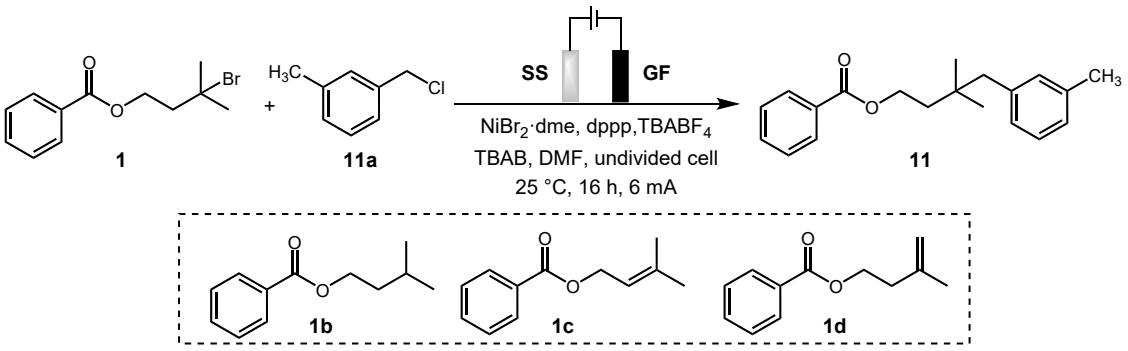


r.t.

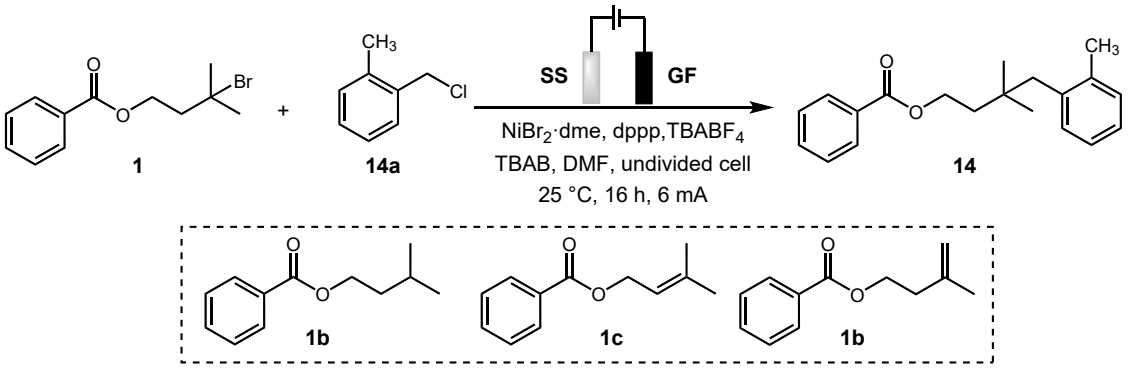
Mass balance	**1**	**1b**	**1c+1d**	**4**
Yield (%)[a]	0	12	29	59

40 ℃

Mass balance	**1**	**1b**	**1c+1d**	**4**
Yield (%)[a]	0	18	38	44



Mass balance	**1**	**1b**	**1c+1d**	**11**
Yield (%)[a]	0	21	27	52



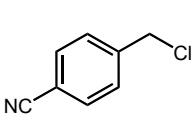
Mass balance	**1**	**1b**	**1c+1d**	**14**

Yield (%)[a]	0	22	42	36

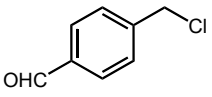
[a]Yield was determined by GC.

9. Characterization and Examples

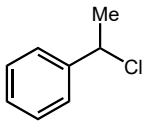
9.1 Failed examples



n.d.

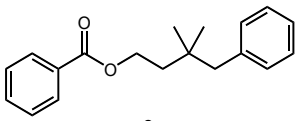


n.d.



n.d.

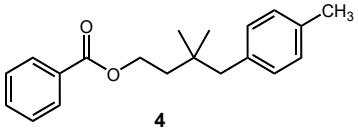
9.2 Characterization Data of the product



3
$C_{19}H_{22}O_2$
M = 282.16 g/mol

3,3-dimethyl-4-phenylbutyl benzoate (**3**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with benzyl chloride (**3a**, 50.6 mg, 0.4 mmol) at room temperature. Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **3** as a colorless oil (31.0 mg, 55% yield).

R_f = 0.50 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 2H), 7.59 – 7.49 (m, 1H), 7.47 – 7.39 (m, 2H), 7.32 – 7.11 (m, 5H), 4.44 (t, *J* = 7.3 Hz, 2H), 2.60 (s, 2H), 1.74 (t, *J* = 7.3 Hz, 2H), 0.98 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 138.8, 133.0, 130.8, 130.6, 129.7, 128.5, 127.9, 126.1, 62.5, 49.1, 40.1, 33.8, 27.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}O_2$: 283.1693; found: 283.1691.

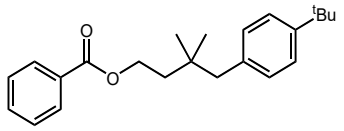


4
$C_{20}H_{24}O_2$
M = 296.18 g/mol

3,3-dimethyl-4-(p-tolyl)butyl benzoate (**4**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(chloromethyl)-4-methylbenzene (**4a**, 56.2 mg, 0.4 mmol) at room temperature**.** Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **4** as a colorless oil (32.6 mg, 55% yield).

R_f = 0.50 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.48 – 7.39 (m, 2H), 7.13 – 7.01 (m, 4H), 4.44 (t, *J* = 7.3 Hz, 2H), 2.57 (s, 2H), 2.33 (s, 3H), 1.74 (t, *J* = 7.3 Hz, 2H), 0.98 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 135.7, 135.6, 133.0, 130.7, 130.6, 129.7, 128.6, 128.5, 62.6,

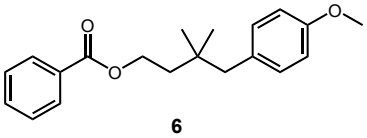
48.6, 40.0, 33.7, 27.1, 21.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}O_2$: 297.1849; found: 297.1853.



5
$C_{23}H_{30}O_2$
M = 338.22 g/mol

4-(4-(tert-butyl)phenyl)-3,3-dimethylbutyl benzoate (**5**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(tert-butyl)-4-(chloroMethyl)benzene (**5a**, 73.0 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **5** as a colorless oil (35.9 mg, 53% yield).

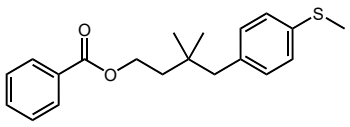
$\mathbf{R_f}$ = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.44 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.12 – 7.05 (m, 2H), 4.45 (t, *J* = 7.3 Hz, 2H), 2.57 (s, 2H), 1.74 (t, *J* = 7.3 Hz, 2H), 1.31 (s, 9H), 0.98 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 148.9, 135.7, 133.0, 130.6, 130.5, 129.7, 128.5, 124.8, 62.6, 48.6, 40.1, 34.5, 33.8, 31.6, 27.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{30}O_2$: 339.2319; found: 339.2322.



6
$C_{20}H_{24}O_3$
M = 312.17 g/mol

4-(4-methoxyphenyl)-3,3-dimethylbutyl benzoate (**6**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(chloromethyl)-4-methoxybenzene (**6a**, 62.6 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **6** as a colorless oil (32.5 mg, 40% yield).

$\mathbf{R_f}$ = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 2H), 7.60 – 7.50 (m, 1H), 7.50 – 7.39 (m, 2H), 7.11 – 7.01 (m, 2H), 6.87 – 6.79 (m, 2H), 4.44 (t, *J* = 7.3 Hz, 2H), 3.80 (s, 3H), 2.54 (s, 2H), 1.72 (t, *J* = 7.3 Hz, 2H), 0.97 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 158.1, 133.0, 131.6, 130.8, 130.6, 129.7, 128.5, 113.3, 62.6, 55.3, 48.2, 40.0, 33.8, 27.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}O_3$: 313.1804; found: 313.1805.

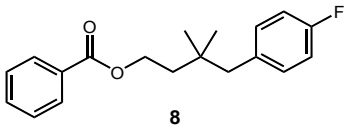


7

$C_{20}H_{24}O_2S$
M = 328.15 g/mol

3,3-dimethyl-4-(4-(methylthio)phenyl)butyl benzoate (**7**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with (4-(chloromethyl)phenyl)(methyl)sulfane (**7a**, 69.1 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **7** as a colorless oil (23.0 mg, 35% yield).

R_f = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 2H), 7.60 – 7.51 (m, 2H), 7.48 - 7.40 (m, 2H), 7.23 – 7.15 (m, 2H), 7.12 – 7.04 (m, 1H), 4.44 (t, *J* = 7.3 Hz, 2H), 2.56 (s, 2H), 2.48 (s, 3H), 1.72 (t, *J* = 7.3 Hz, 2H), 0.97(s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.8, 135.8, 133.0, 131.2, 130.6, 129.7, 128.5, 126.5, 62.5, 48.5, 40.0, 33.8, 27.0, 16.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}O_2S$: 329.1575; found: 329.1570.

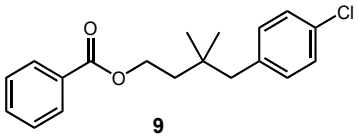


8

$C_{19}H_{21}FO_2$
M = 300.15 g/mol

4-(4-fluorophenyl)-3,3-dimethylbutyl benzoate (**8**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(chloromethyl)-4-fluorobenzene (**2**, 57.8 mg, 0.4 mmol) at room temperature. Purification by flash column chromatography on silica gel using using PE/EtOAc = 99/1 afforded **8** as a colorless oil (39.0 mg, 65 % yield).

R_f = 0.50 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 2H), 7.60 – 7.50 (m, 1H), 7.48-7.40 (m, 2H), 7.15 – 7.05 (m, 2H), 7.02 – 6.92 (m, 2H), 4.44 (t, *J* = 7.3 Hz, 2H), 2.57 (s, 2H), 1.72 (t, *J* = 7.3 Hz, 2H), 0.96 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 161.7 (d, *J* = 243.8 Hz), 134.3, 133.0, 132.0 (d, *J* = 8.0 Hz), 130.5, 129.7, 128.5, 114.7 (d, *J* = 21.1 Hz), 62.4, 48.2, 40.0, 33.7, 26.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}FO_2$: 301.1604; found: 301.1597.



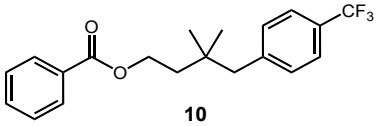
9

$C_{19}H_{21}ClO_2$

M = 316.12 g/mol

4-(4-chlorophenyl)-3,3-dimethylbutyl benzoate (**9**): Prepared from 3-bromo-3-methylbutyl benzoate **1**, according to **GP** with 1-chloro-4-(chloromethyl)benzene (**9a**, 64.4 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc =99/1 afforded **9** as a colorless oil (43.0 mg, 68% yield).

$\mathbf{R_f}$ = 0.60 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 – 8.02 (m, 2H), 7.62 – 7.53 (m, 1H), 7.48 – 7.42 (m, 2H), 7.30 – 7.24 (m, 2H), 7.14 – 7.06 (m, 2H), 4.45 (t, *J* = 7.3 Hz, 2H), 2.59 (s, 2H), 1.74 (t, *J* = 7.3 Hz, 2H), 0.99 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.0, 139.5, 134.3, 132.0, 132.0, 131.1, 128.9, 114.8, 114.6, 62.7, 48.2, 40.0, 33.7, 26.9. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}ClO_2$: 339.1128; found: 339.1122.



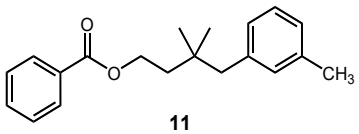
10

$C_{20}H_{21}F_3O_2$

M = 350.15 g/mol

3,3-dimethyl-4-(4-(trifluoromethyl)phenyl)butyl benzoate (**10**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(chloromethyl)-4-(trifluoromethyl)benzene (**10a**, 77.8 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **9** as a colorless oil (32.2 mg, 46% yield).

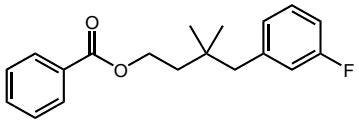
$\mathbf{R_f}$ = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 2H), 7.61 – 7.51 (m, 3H), 7.48 – 7.40 (m, 2H), 7.28 – 7.22 (m, 2H), 4.45 (t, *J* = 7.3 Hz, 2H), 2.66 (s, 2H), 1.74 (t, *J* = 7.3 Hz, 2H), 0.99 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.8, 142.9, 133.1, 131.0, 130.5, 129.7, 128.7, 128.5, 124.9 (q, *J* = 3.7 Hz), 124.6 (d, *J* = 270 Hz), 62.3, 48.8, 40.2, 33.9, 27.0. **HRMS** (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}F_3O_2$: 351.1572; found: 351.1572.



11
$C_{20}H_{24}O_2$
M = 296.18 g/mol

3,3-dimethyl-4-(m-tolyl)butyl benzoate (**11**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(chloromethyl)-3-methylbenzene (**11a**, 56.2mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **11** as a colorless oil (24.9 mg, 42% yield).

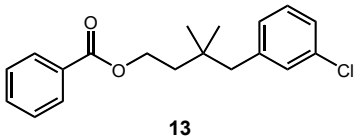
R_f = 0.50 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.50 – 7.42 (m, 2H), 7.23 – 7.12 (m, 1H), 7.13 – 7.06 (m, 1H), 6.98 – 6.90 (m, 2H), 4.44 (t, *J* = 7.3 Hz, 2H), 2.56 (s, 2H), 2.34 (s, 3H), 1.74 (t, *J* = 7.3 Hz, 2H), 0.98 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 138.7, 137.4, 133.0, 131.6, 130.6, 129.7, 128.5, 127.8, 127.8, 126.9, 62.5, 49.0, 40.2, 33.7, 27.1, 21.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}O_2$: 297.1849; found: 297.1853.



12
$C_{19}H_{21}FO_2$
M = 300.15 g/mol

4-(3-fluorophenyl)-3,3-dimethylbutyl benzoate (**12**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(chloromethyl)-3-fluorobenzene (**12a**, 57.8 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **12** as a colorless oil (37.2 mg, 62% yield).

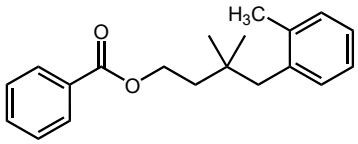
R_f = 0.50 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 – 7.93 (m, 2H), 7.53 – 7.44 (m, 1H), 7.41 – 7.33 (m, 2H), 7.21 – 7.11 (m, 1H), 6.90 – 6.75 (m, 3H), 4.37 (t, *J* = 7.3 Hz, 2H), 2.52 (s, 2H), 1.67 (t, *J* = 7.3 Hz, 2H), 0.91 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.8, 162.6 (d, *J* = 245.1 Hz), 141.3 (d, *J* = 7.2 Hz), 133.0, 130.5, 129.7, 129.3 (d, *J* = 8.3 Hz), 128.5, 126.4 (d, *J* = 2.9 Hz), 117.5 (d, *J* = 20.7 Hz), 113.1 (d, *J* = 21.0 Hz), 62.4, 48.8, 40.1, 33.8, 27.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}FO_2$: 301.1604; found: 301.1609.



13
$C_{19}H_{21}ClO_2$
M = 316.12 g/mol

4-(3-chlorophenyl)-3,3-dimethylbutyl benzoate (**13**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-chloro-3-(chloromethyl)benzene (**13a**, 64.4 mg, 0.2 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc =99/1 afforded **13** as a colorless oil (28.5 mg, 45% yield).

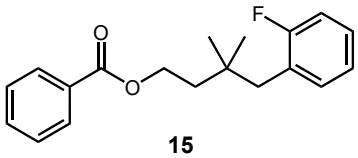
R_f = 0.60 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.39 (m, 2H), 7.26 – 7.17 (m, 2H), 7.17 – 7.12 (m, 1H), 7.07 – 7.00 (m, 1H), 4.44 (t, *J* = 7.2 Hz, 2H), 2.58 (s, 2H), 1.74 (t, *J* = 7.2 Hz, 2H), 0.99 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.8, 140.8, 133.8, 133.0, 130.7, 130.5, 129.7, 129.2, 128.9, 128.5, 126.4, 62.3, 48.7, 40.2, 33.8, 27.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}ClO_2$: 317.1308; found: 317.1309.



14
$C_{20}H_{24}O_2$
M = 296.18 g/mol

3,3-dimethyl-4-(*o*-tolyl)butyl benzoate (**14**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(chloromethyl)-2-methylbenzene (**14a**, 56.2 mg, 0.4 mmol)**.** Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **14** as a colorless oil (18.4 mg, 31% yield).

R_f = 0.50 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 2H), 7.61 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 7.19 – 7.07 (m, 4H), 4.46 (t, *J* = 7.2 Hz, 2H), 2.67 (s, 2H), 2.34 (s, 3H), 1.83 (t, *J* = 7.2 Hz, 2H), 1.00 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) 166.9, 137.3, 133.0, 131.8, 130.6, 130.6, 129.7, 128.5, 128.5, 126.3, 125.3, 62.5, 44.8, 41.0, 35.2, 27.0, 20.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}O_2$: 297.1849; found: 297.1853.

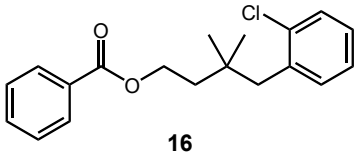


15

$C_{19}H_{21}FO_2$
M = 300.15 g/mol

4-(2-fluorophenyl)-3,3-dimethylbutyl benzoate (**15**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-(chloromethyl)-2-fluorobenzene (**15a**, 57.8 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **15** as a colorless oil (31.8 mg, 53 % yield).

$\mathbf{R_f}$ = 0.50 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 - 8.00 (m, 2H), 7.60 – 7.51 (m, 1H), 7.48 – 7.48 (m, 2H), 7.25 – 7.12 (m, 2H), 7.10 – 6.98 (m, 2H), 4.46 (t, *J* = 7.2 Hz, 2H), 2.65 (s, 2H), 1.78 (t, *J* = 7.2 Hz, 2H), 1.00 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 161.7 (d, *J* = 244.6 Hz), 133.1 (d, *J* = 4.9 Hz), 133.0, 130.6, 129.7, 128.5, 128.1 (d, *J* = 8.2 Hz), 125.8 (d, *J* = 16.1 Hz), 123.5 (d, *J* = 3.6 Hz), 115.4 (d, *J* = 23.4 Hz), 62.5, 41.4, 40.2, 34.3, 26.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}FO_2$: 301.1604; found: 301.1604.

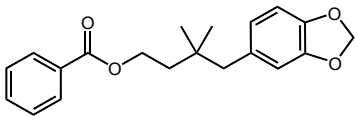


16

$C_{19}H_{21}ClO_2$
M = 316.12 g/mol

4-(2-chlorophenyl)-3,3-dimethylbutyl benzoate (**16**): Prepared from 3-bromo-3-methylbutyl benzoate **1** according to **GP** with 1-chloro-2-(chloromethyl)benzene (**16a**, 64.4 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **16** as colorless oil (27.2 mg, 43% yield).

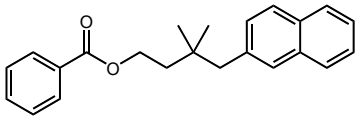
$\mathbf{R_f}$ = 0.60 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 2H), 7.60 – 7.51 (m, 1H), 7.48 – 7.40 (m, 2H), 7.39 – 7.33 (m, 1H), 7.26 – 7.11 (m, 3H), 4.46 (t, *J* = 7.2 Hz, 2H), 2.82 (s, 2H), 1.84 (t, *J* = 7.2 Hz, 2H), 1.03 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.9, 136.8, 135.4, 133.0, 132.8, 130.6, 129.9, 129.7, 128.5, 127.7, 126.2, 62.5, 44.7, 40.6, 35.2, 26.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}ClO_2$: 317.1308; found: 317.1303.



17
$C_{20}H_{22}O_4$
M = 326.15 g/mol

4-(benzo[d][1,3]dioxol-5-yl)-3,3-dimethylbutyl benzoate (**17**): Prepared from 3-bromo-3-methylbutyl benzoate **1**, according to **GP** with 5-(chloromethyl)benzo[d][1,3]dioxole (**17a**, 55.2 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **17** as a colorless oil (27.4 mg, 42% yield).

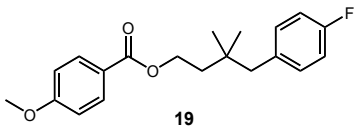
R_f = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 – 8.00 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 6.85 – 6.44 (m, 3H), 5.93 (s, 2H), 4.43 (t, *J* = 7.3 Hz, 2H), 2.52 (s, 2H), 1.72 (t, *J* = 7.3 Hz, 2H), 0.97 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.8, 147.2, 146.0, 133.0, 132.5, 130.6, 129.7, 128.5, 123.6, 111.1, 107.8, 100.9, 62.5, 48.9, 40.0, 33.8, 27.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}O_4$: 327.1596; found: 327.1591.



18
$C_{23}H_{24}O_2$
M = 332.18 g/mol

3,3-dimethyl-4-(naphthalen-2-yl)butyl benzoate (**18**): Prepared from 3-bromo-3-methylbutyl benzoate **1**, according to **GP** with 2-(chloromethyl)naphthalene (**18a**, 78.4 mg, 0.4 mmol). Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **18** as a colorless oil (28.6 mg, 43% yield).

R_f = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 2H), 7.86 – 7.73 (m, 3H), 7.62 – 7.51 (m, 2H), 7.51 – 7.39 (m, 4H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.49 (t, *J* = 7.2 Hz, 2H), 2.78 (s, 2H), 1.80 (t, *J* = 7.3 Hz, 2H), 1.04 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.8, 147.2, 146.0, 133.0, 132.5, 130.6, 129.7, 128.5, 123.6, 111.1, 107.8, 100.9, 62.5, 48.9, 40.0, 33.8, 27.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}O_2$: 333.1849; found: 333.1852.



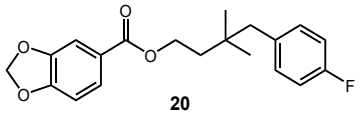
19

$C_{20}H_{23}FO_3$

M = 330.16 g/mol

4-(4-fluorophenyl)-3,3-dimethylbutyl 4-methoxybenzoate (**19**): Prepared from 3-bromo-3-methylbutyl 4-methoxybenzoate (**19a**, 60 mg, 0.20 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**. Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **19** as a colorless oil (35.0 mg, 53% yield). $\mathbf{R_f}$ = 0.40 (PE/EtOAc = 95/5).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.94 (m, 2H), 7.15 – 7.05 (m, 2H), 7.02 – 6.86 (m, 4H), 4.41 (t, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 2.57 (s, 2H), 1.71 (t, *J* = 7.3 Hz, 2H), 0.96 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.6, 163.4, 161.7 (d, *J* = 243.8 Hz), 134.4 (d, *J* = 3.3 Hz), 132.0 (d, *J* = 7.7 Hz), 131.7, 123.0, 114.7 (d, *J* = 21.0 Hz), 113.7, 62.1, 55.6, 48.2, 40.1, 33.7, 27.0. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}FO_3$: 331.1709; found: 331.1710.



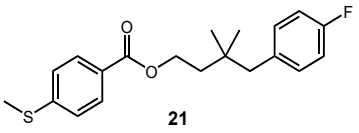
20

$C_{20}H_{21}FO_4$

M = 344.14 g/mol

4-(4-fluorophenyl)-3,3-dimethylbutyl benzo[d][1,3]dioxole-5-carboxylate (**20**): Prepared from 3-bromo-3-methylbutyl benzo[d][1,3]dioxole-5-carboxylate (**20a**, 62.8 mg, 0.2 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**. Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **20** a colorless oil (31.0 mg,45 % yield).

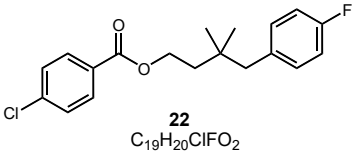
$\mathbf{R_f}$ = 0.30 (PE/EtOAc = 98/2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.13 – 7.05 (m, 2H), 7.01 – 6.91 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.03 (s, 2H), 4.39 (t, *J* = 7.3 Hz, 2H), 2.56 (s, 2H), 1.70 (t, *J* = 7.3 Hz, 2H), 0.95 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.2, 161.7 (d, *J* = 243.9 Hz), 151.7, 147.9, 134.4 (d, *J* = 3.3 Hz), 132.0 (d, *J* = 7.7 Hz), 125.4, 124.6, 114.7 (d, *J* = 20.9 Hz), 109.6, 108.1, 101.9, 62.3, 48.2, 40.1, 33.7, 26.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}FO_4$: 345.1502; found: 345.1498.



21
$C_{20}H_{23}FO_2S$
M = 346.14 g/mol

4-(4-fluorophenyl)-3,3-dimethylbutyl 4-(methylthio)benzoate (**21**): Prepared from 3-bromo-3-methylbutyl 4-(methylthio)benzoate (**21a**, 63.2 mg, 0.2 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**. Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **21** as a colorless oil (32.5 mg, 47% yield).

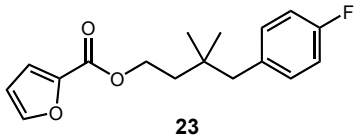
$\mathbf{R_f}$ = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 – 7.91 (m, 2H), 7.30 – 7.23 (m, 2H), 7.17 – 7.07 (m, 2H), 7.04 – 6.94 (m, 2H), 4.44 (t, *J* = 7.3 Hz, 2H), 2.59 (s, 2H), 2.54 (s, 3H), 1.73 (t, *J* = 7.3 Hz, 2H), 0.98 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.6, 161.7 (d, *J* = 243.9 Hz), 145.5, 134.4(d, *J* = 3.3 Hz), 132.0 (d, *J* = 7.7 Hz), 130.0, 126.7, 125.1, 114.7 (d, *J* = 21.0 Hz), 62.3, 48.2, 40.0, 33.7, 27.0, 15.0. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{20}H_{23}FO_2S$: 347.1481; found: 347.1476



22
$C_{19}H_{20}ClFO_2$
M = 334.11 g/mol

3,3-dimethyl-4-phenylbutyl 4-chlorobenzoate (**22**): Prepared from 3-bromo-3-methylbutyl 4-chlorobenzoate (**22a**, 60.8 mg, 0.20 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**. Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **22** as a colorless oil (26.7 mg, 40% yield).

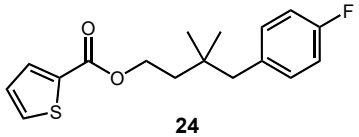
$\mathbf{R_f}$ = 0.60 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.92 (m, 2H), 7.46 – 7.37 (m, 2H), 7.14 – 7.05 (m, 2H), 7.02 – 6.92 (m, 2H), 4.42 (t, *J* = 7.3 Hz, 2H), 2.56 (s, 2H), 1.71 (t, *J* = 7.3 Hz, 2H), 0.96 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.8, 161.6 (d, *J* = 243.9 Hz), 139.4, 134.1, 131.9 (d, *J* = 7.7 Hz), 130.9, 128.8, 128.7, 114.6 (d, *J* = 21.0 Hz), 62.5, 48.1, 39.9, 33.6, 26.8. **HRMS** (ESI-TOF) m/z:$[M+Na]^+$ Calcd for $C_{19}H_{20}ClFO_2$: 357.1028; found: 357.1034



23
$C_{17}H_{19}FO_3$
M = 290.13 g/mol

4-(4-fluorophenyl)-3,3-dimethylbutyl furan-2-carboxylate (**23**): Prepared from 3-bromo-3-methylbutyl furan-2-carboxylate (**23a**, 52.0 mg, 0.20 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**. Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **23** a colorless oil (30.2 mg, 52% yield).

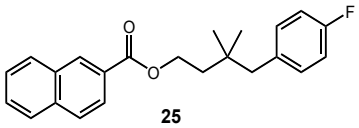
R_f = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 1H), 7.20 – 7.04 (m, 3H), 7.01 – 6.91 (m, 2H), 6.52 – 6.48 (m, 1H), 4.4 (t, *J* = 7.4 Hz, 2H), 2.6 (s, 2H), 1.7 (t, *J* = 7.4 Hz, 2H), 0.9 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.7 (d, *J* = 243.8 Hz), 159.0, 146.4, 144.9, 134.3 (d, *J* = 3.2 Hz), 132.0 (d, *J* = 7.8 Hz), 118.0, 114.7 (d, *J* = 21.0 Hz), 112.0, 62.4, 48.1, 39.8, 33.7, 26.9. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{17}H_{19}FO_3$: 291.1396; found: 291.1404.



24
$C_{17}H_{19}FO_2S$
M = 306.11 g/mol

4-(4-fluorophenyl)-3,3-dimethylbutyl thiophene-2-carboxylate (**24**): Prepared from 3-bromo-3-methylbutyl thiophene-2-carboxylate (**24a**, 55.2 mg, 0.20 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**. Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **24** as a colorless oil (31.8 mg, 52% yield).

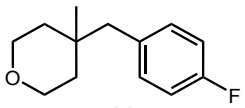
R_f = 0.40 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.15 – 7.05 (m, 3H), 7.01 – 6.92 (m, 2H), 4.41 (t, *J* = 7.2 Hz, 2H), 2.56 (s, 2H), 1.70 (t, *J* = 7.2 Hz, 2H), 0.95 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 162.5, 161.7 (d, *J* = 243 Hz), 134.3 (d, *J* = 3.3 Hz), 134.1, 133.5, 132.4, 132.0 (d, *J* = 7.8 Hz), 127.9, 114.7 (d, *J* = 21.0 Hz), 62.6, 48.1, 39.9, 33.7, 26.9. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{17}H_{19}FO_2S$: 307.1168; found: 307.1165.



25
$C_{23}H_{23}FO_2$
M = 350.17 g/mol

4-(4-fluorophenyl)-3,3-dimethylbutyl 2-naphthoate (**25**): Prepared from 3-bromo-3-methylbutyl 2-naphthoate (**25a**, 64.0 mg, 0.20 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**. Purification by flash column chromatography on silica gel using PE/EtOAc = 99/1 afforded **25** a white solid (32.9 mg, 47% yield).

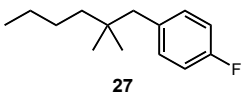
R_f = 0.50 (PE/EtOAc = 95/5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.50 (m, 2H), 7.16 – 7.07 (m, 2H), 7.03 – 6.92 (m, 2H), 4.50 (t, *J* = 7.4 Hz, 2H), 2.60 (s, 2H), 1.78 (t, *J* = 7.4 Hz, 2H), 0.99 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.0, 161.7 (d, *J* = 243.6 Hz), 135.6, 134.4 (d, *J* = 3.2 Hz), 132.6, 132.0 (d, *J* = 7.7 Hz), 131.1, 129.5, 128.4, 128.3, 127.9, 127.8, 126.8, 125.3, 114.7 (d, *J* = 21.0 Hz), 62.6, 48.2, 40.1, 33.8, 27.0. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{23}H_{23}FO_2$: 351.1760; found: 351.1770.



26
$C_{13}H_{17}FO$
M = 208.13 g/mol

4-(4-fluorobenzyl)-4-methyltetrahydro-2H-pyran (**26**): Prepared from 4-bromo-4-methyltetrahydro-2H-pyran (**26a**, 35.6 mg, 0.20 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**. Purification by flash column chromatography on silica gel using PE afforded **26** as a colorless oil (20.0 mg, 48% yield).

R_f = 0.65 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.11 – 7.03 (m, 2H), 7.01 – 6.90 (m, 2H), 3.82 – 3.72 (m, 2H), 3.65 – 3.56 (m, 2H), 2.56 (s, 2H), 1.63 – 1.51 (m, 3H), 1.32–1.21 (m, 1H), 0.94 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.7 (d, *J* = 244.0 Hz), 133.7 (d, *J* = 3.3 Hz), 132.1 (d, *J* = 7.8 Hz), 114.7 (d, *J* = 21.0 Hz), 64.1, 48.5, 37.5, 32.0, 23.2. **HRMS** (ESI-TOF) m/z: $[M+OCH_3]^+$ Calcd for $C_{13}H_{17}FO$: 239.1447; found: 239.1442.



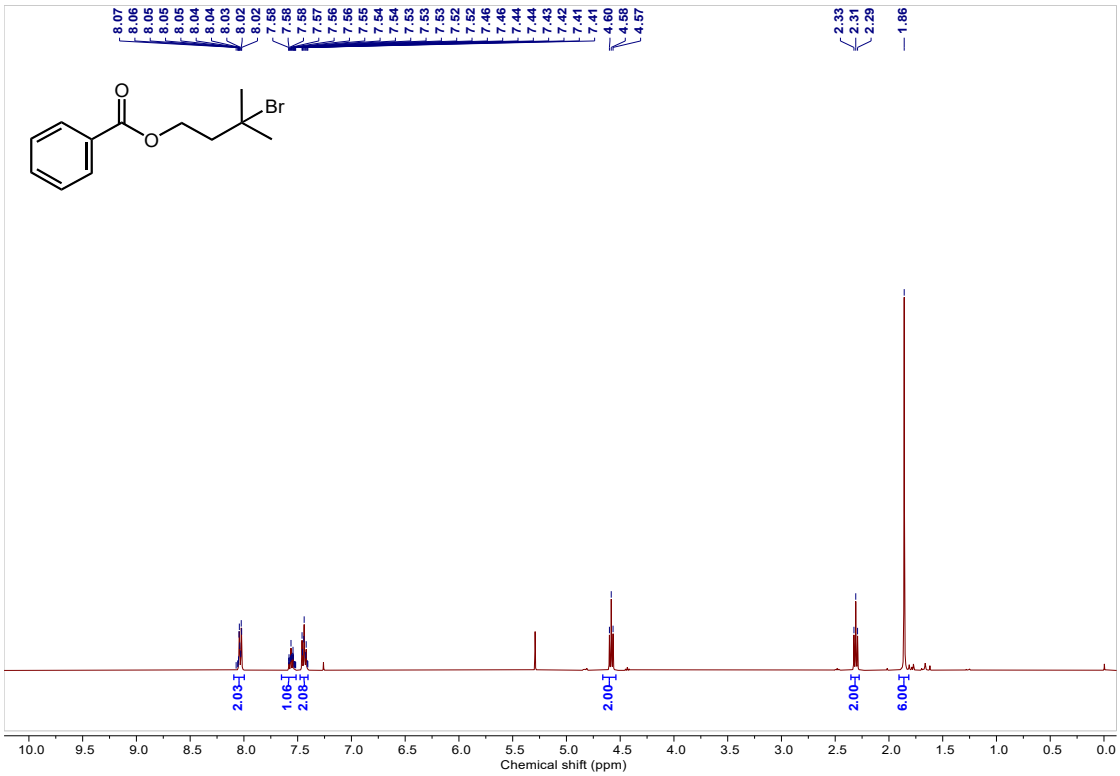
27
$C_{14}H_{21}F$
M = 208.16 g/mol

1-(2,2-dimethylhexyl)-4-fluorobenzene (**27**): Prepared from 2-bromo-2-methylhexane (**27a**, 35.6 mg, 0.20 mmol) according to **GP** with 1-(chloromethyl)-4-fluorobenzene **2**.Purification by flash column chromatography on silica gel using PE afforded **27** as a colorless oil (16.7 mg, 40% yield).

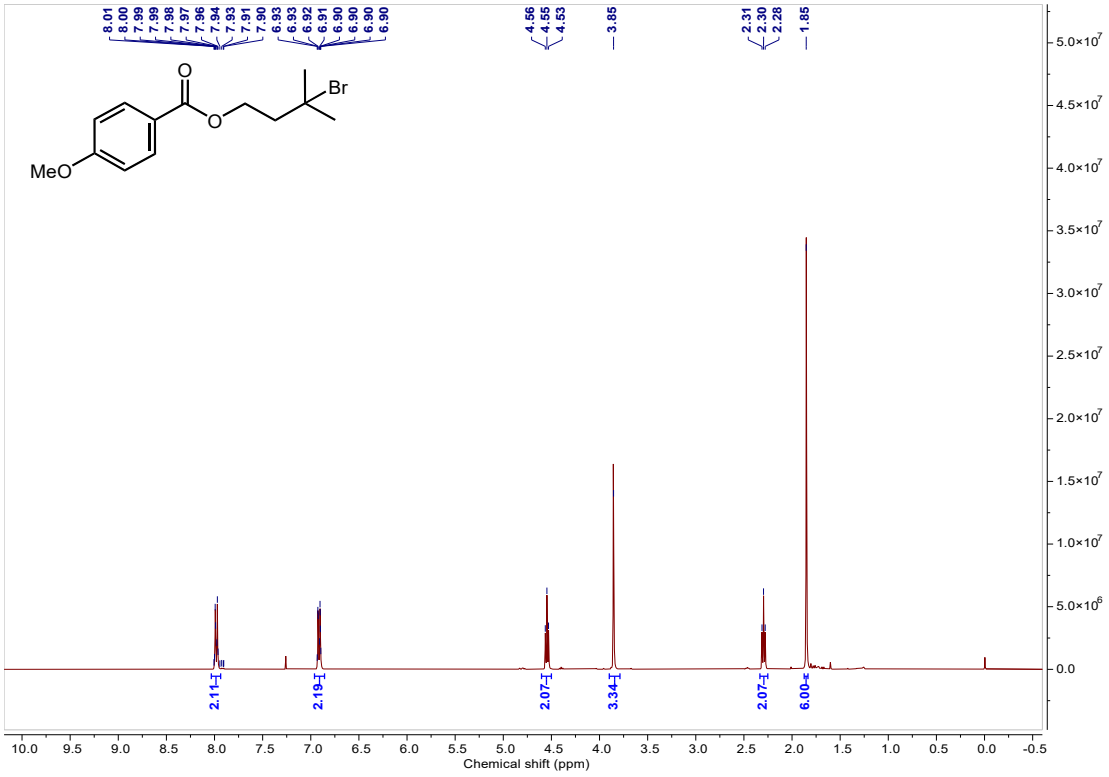
R_f = 0.65 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.10 – 7.02 (m, 2H), 6.99 – 6.90 (m, 2H), 2.46 (s, 2H), 1.36 – 1.22 (m, 6H), 0.96 – 0.88 (m, 3H), 0.82 (s, 6H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.5 (d, *J* = 243.3 Hz), 135.3 (d, *J* = 3.3 Hz), 131.9 (d, *J* = 7.6 Hz), 114.5 (d, *J* = 21.0 Hz), 47.6, 41.9, 34.2, 26.9, 26.5, 23.7, 14.4. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ Calcd for $C_{13}H_{17}FO$: 209.1706; found: 209.1709.

10. NMR Spectra

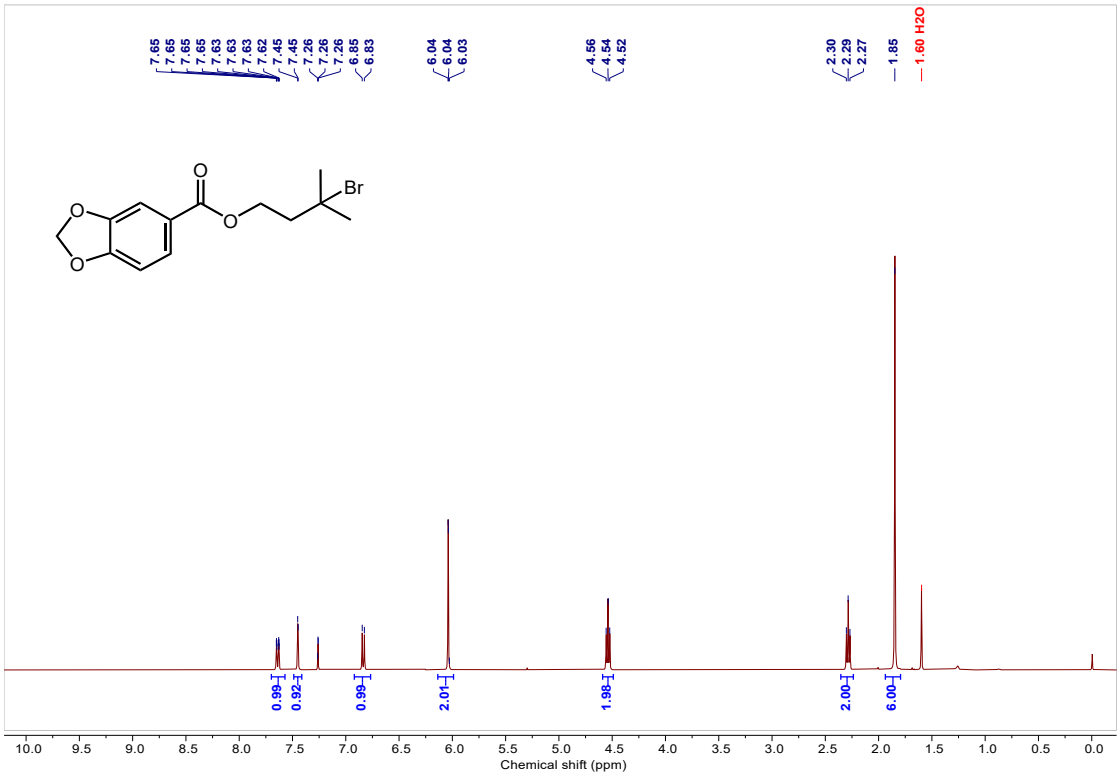
1: ^{1}H NMR (400 MHz, Chloroform-*d*)



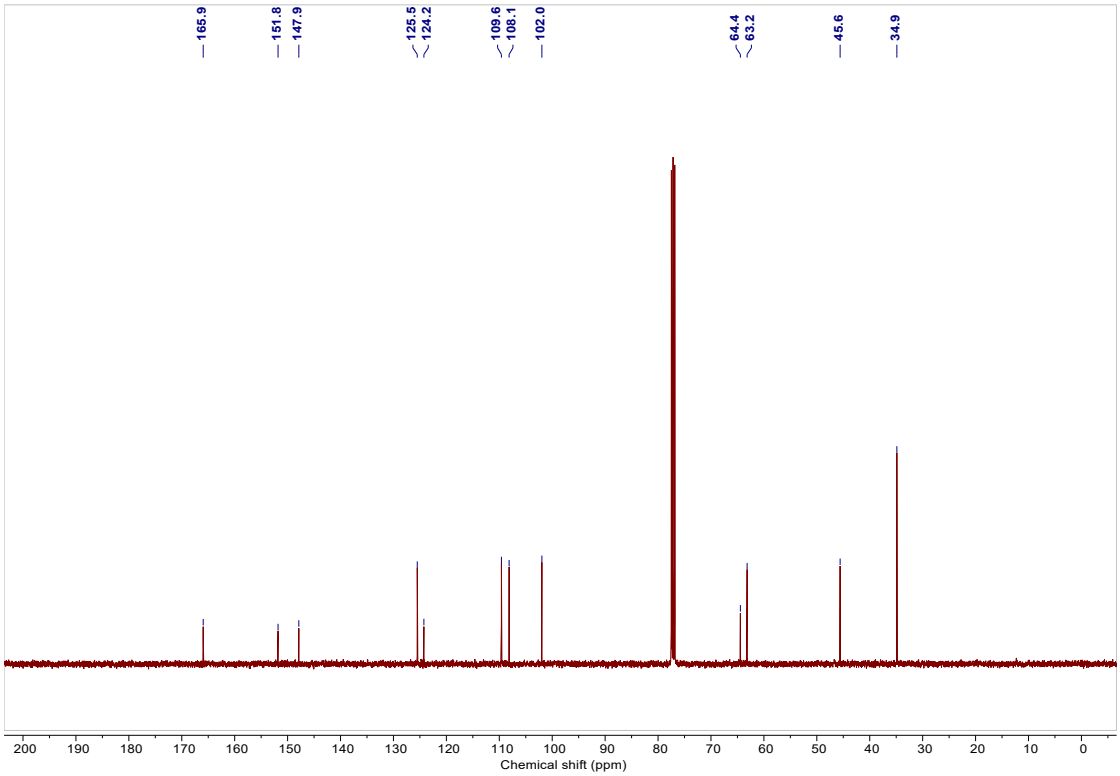
19a: ^{1}H NMR (400 MHz, Chloroform-*d*)



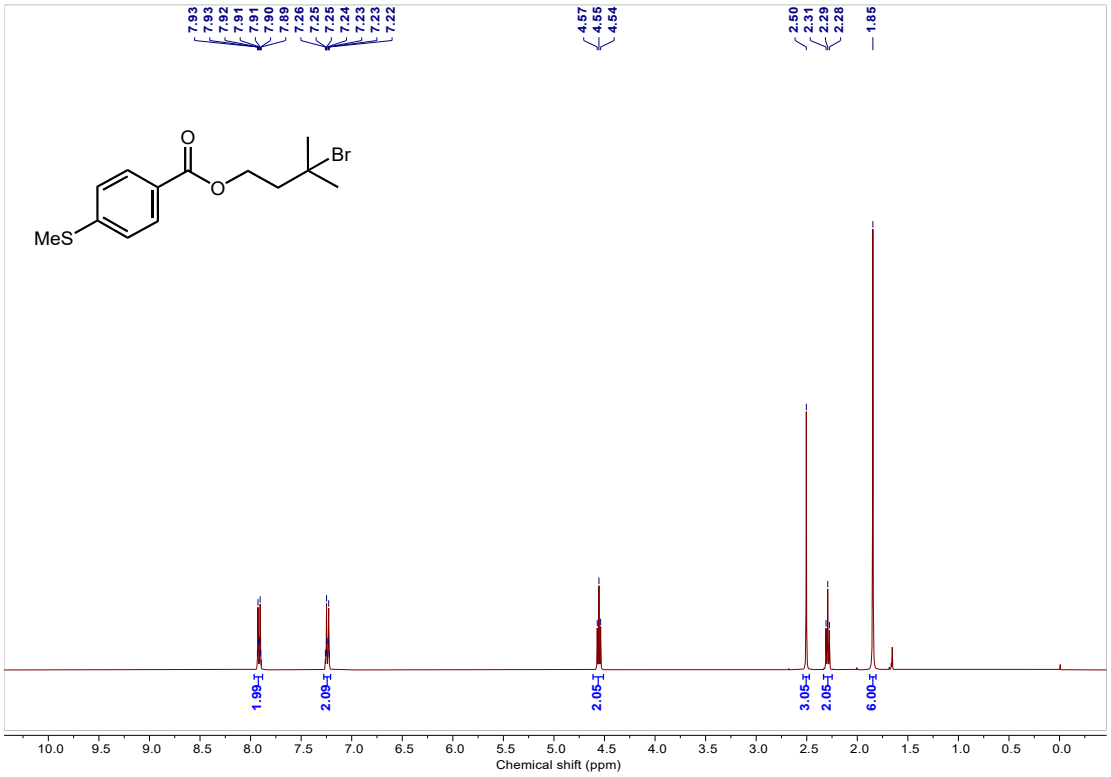
20a: ^{1}H NMR (400 MHz, Chloroform-*d*)



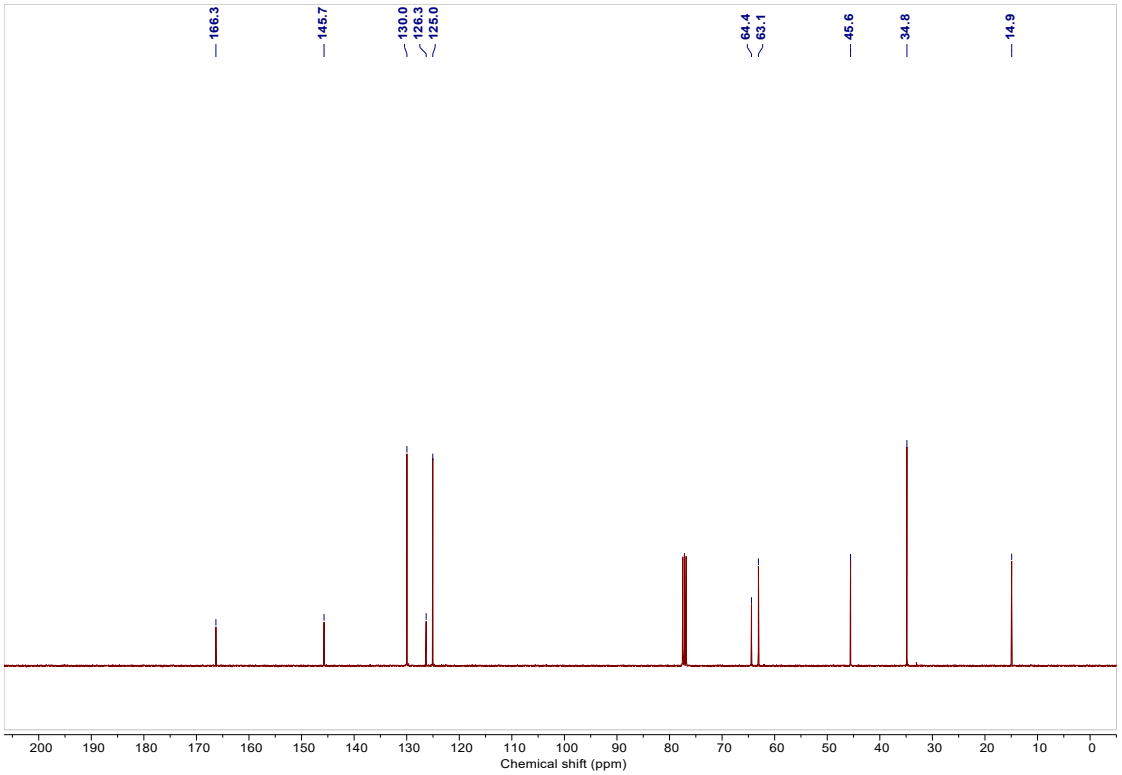
20a: ^{13}C NMR (100 MHz, Chloroform-*d*)



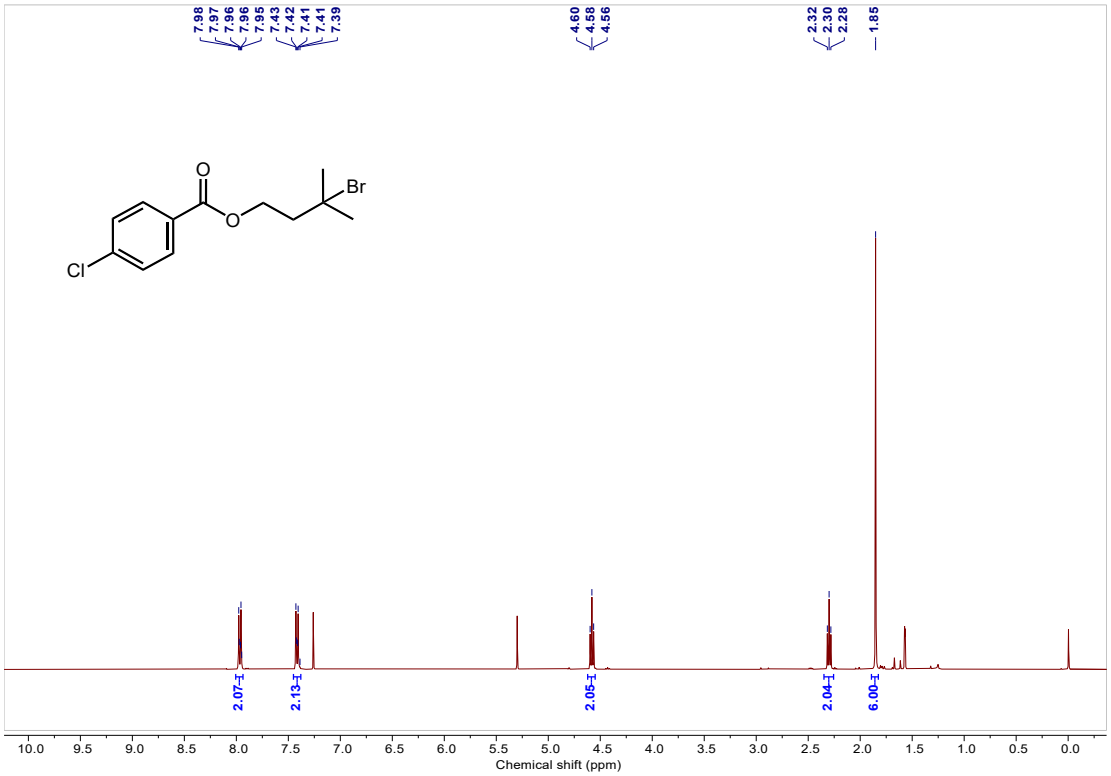
21a: ^{1}H NMR (400 MHz, Chloroform-*d*)



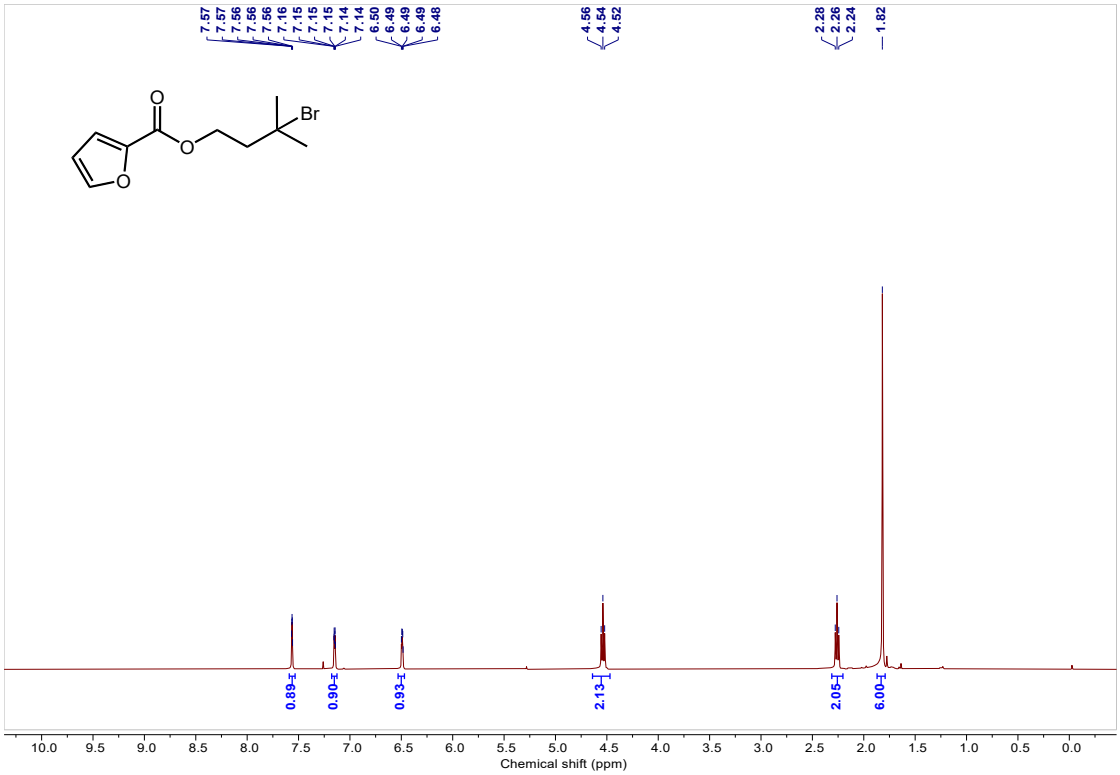
21a: ^{13}C NMR (100 MHz, Chloroform-*d*)



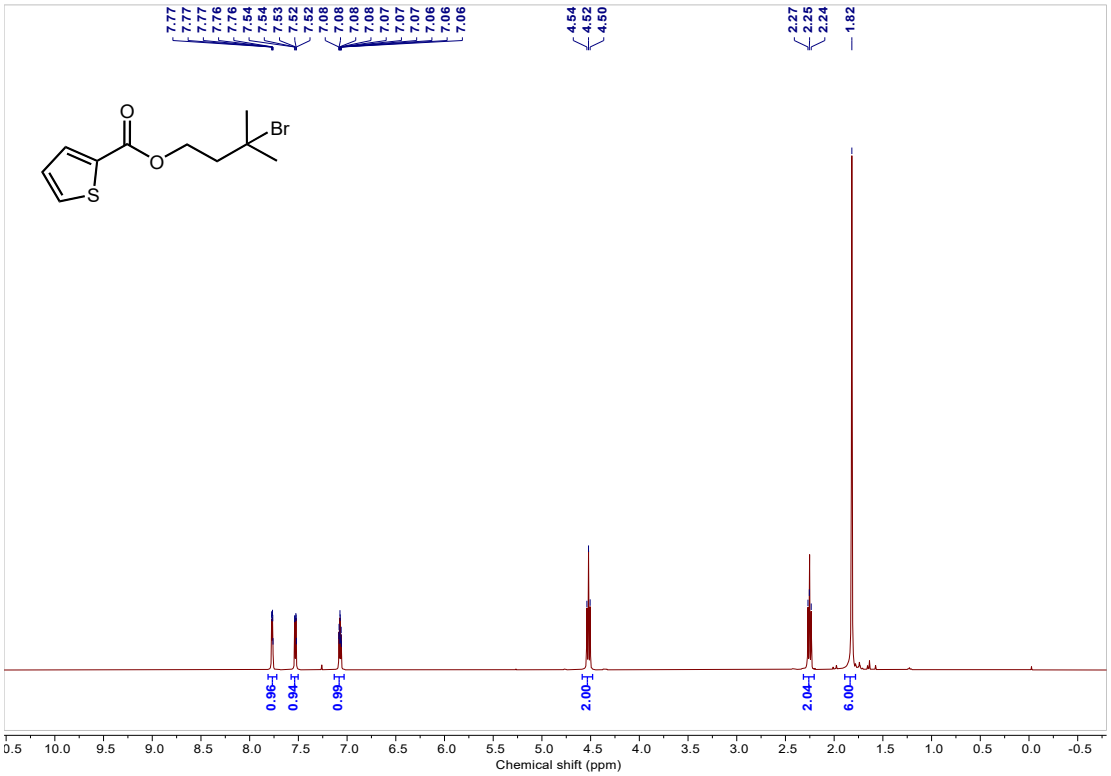
22a: ^{1}H NMR (400 MHz, Chloroform-*d*)



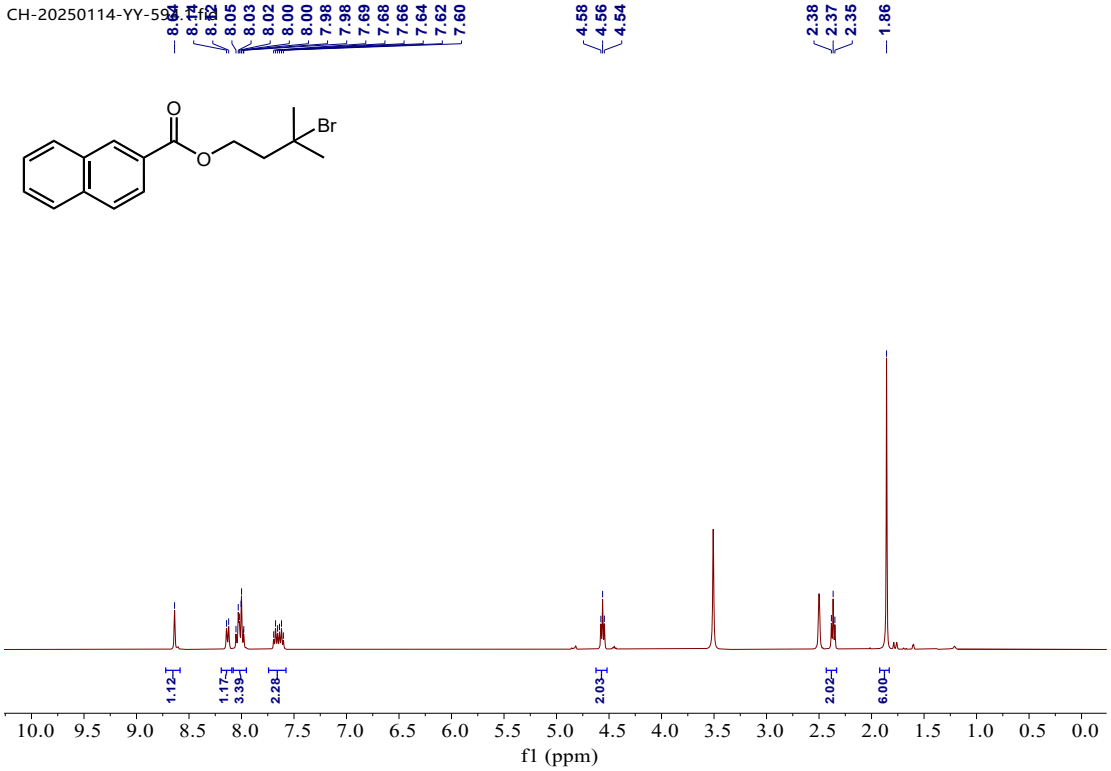
23a: ^{1}H NMR (400 MHz, Chloroform-*d*)



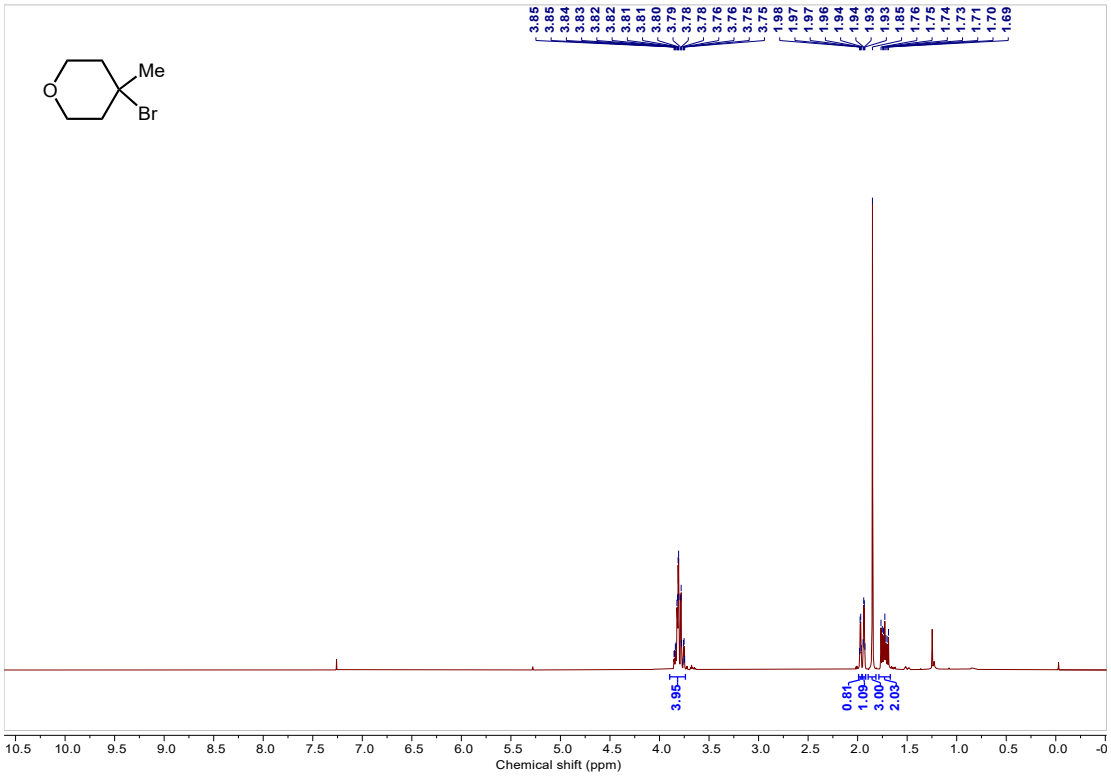
24a: ^{1}H NMR (400 MHz, Chloroform-*d*)



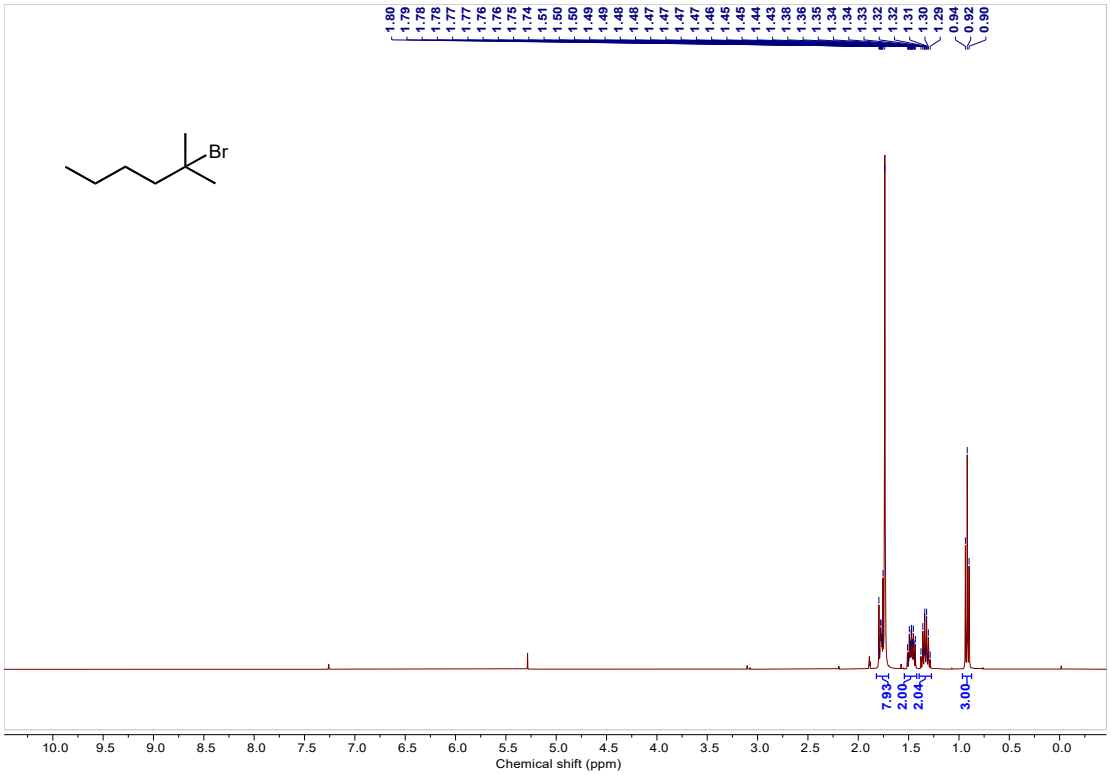
25a: ^{1}H NMR (400 MHz, DMSO-d_6)



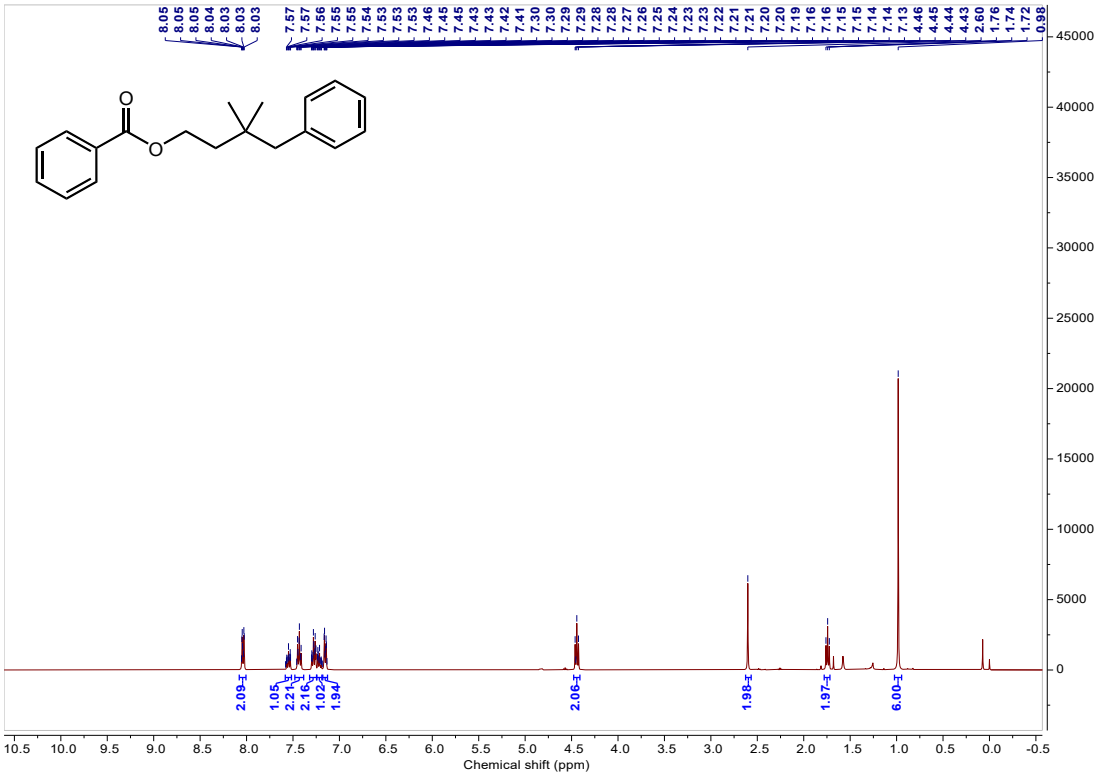
26a: ^{1}H NMR (400 MHz, Chloroform-*d*)



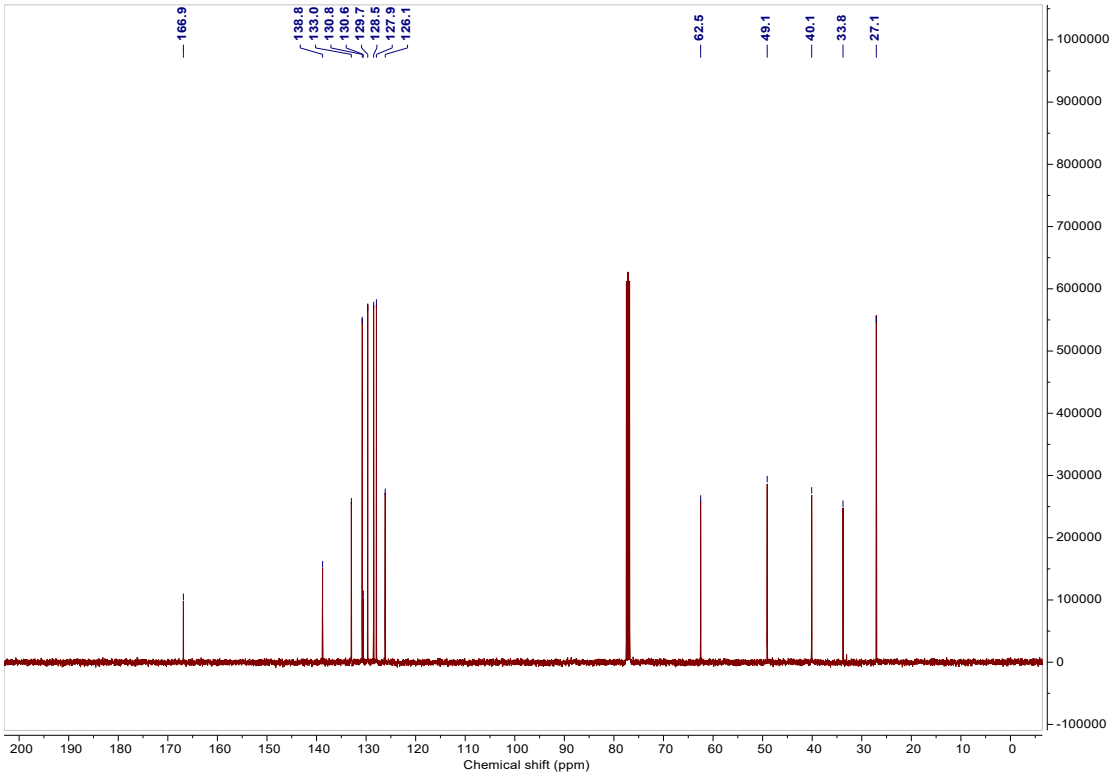
27a: ^{1}H NMR (400 MHz, Chloroform-d)



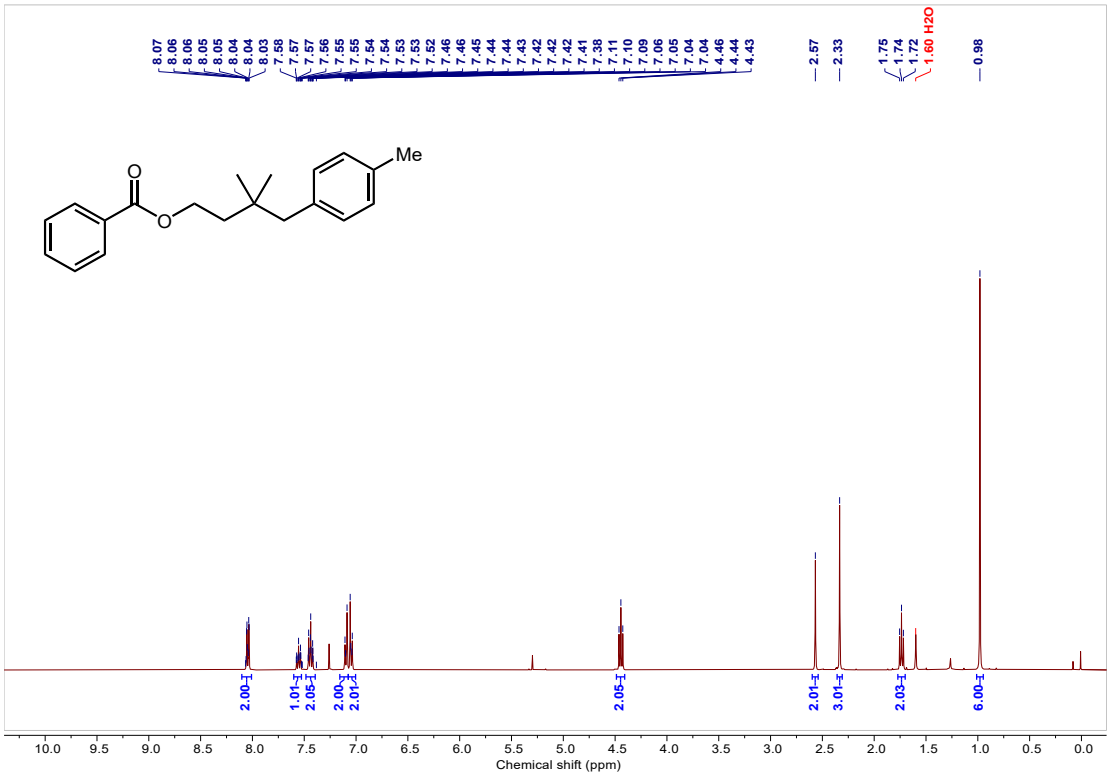
3: ^{1}H NMR (400 MHz, Chloroform-*d*)



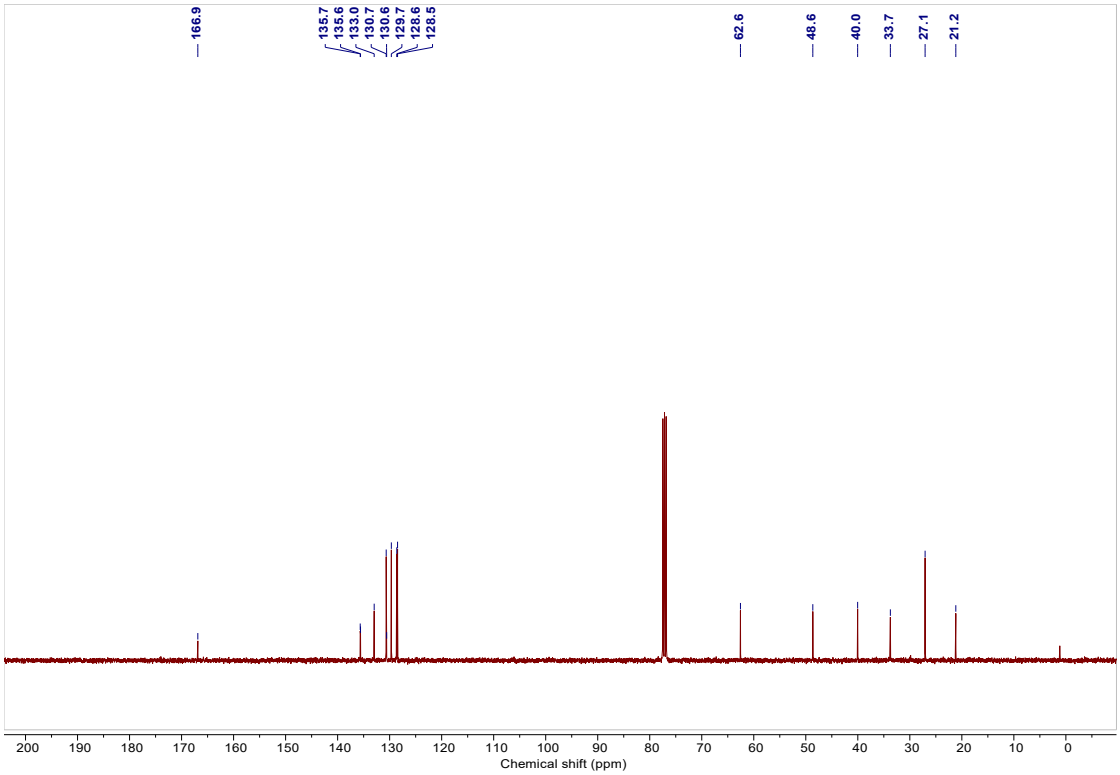
3: ^{13}C NMR (100 MHz, Chloroform-*d*)



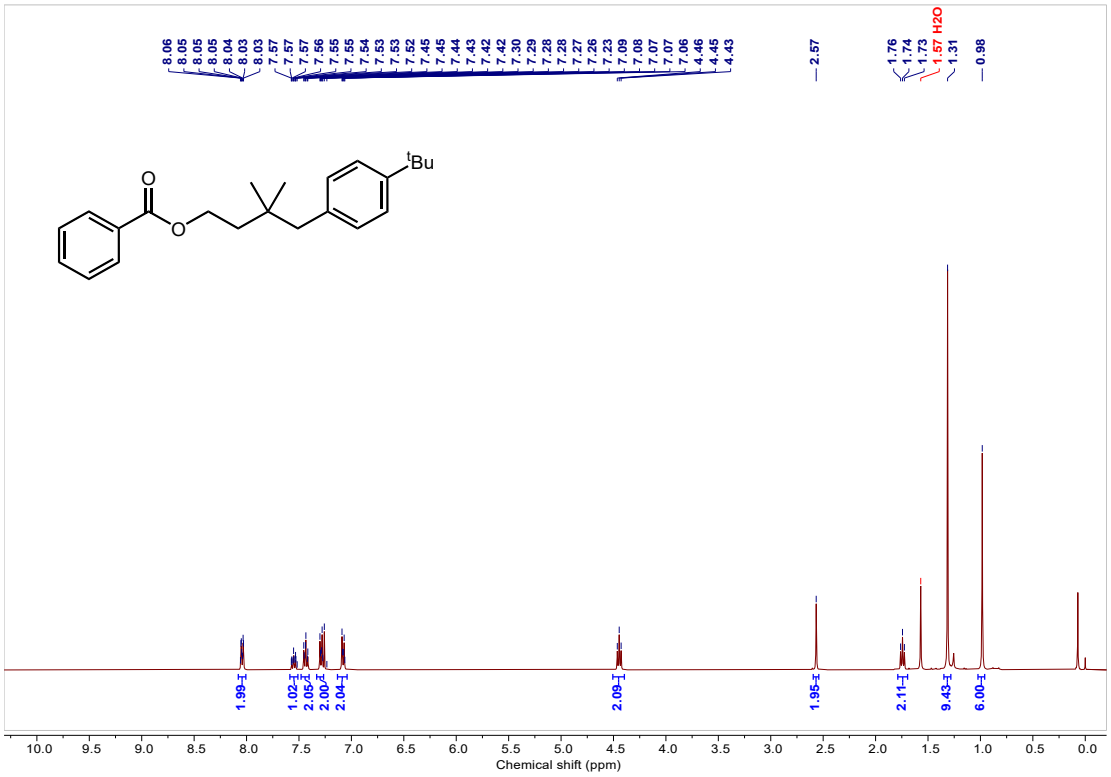
4: ^{1}H NMR (400 MHz, Chloroform-*d*)



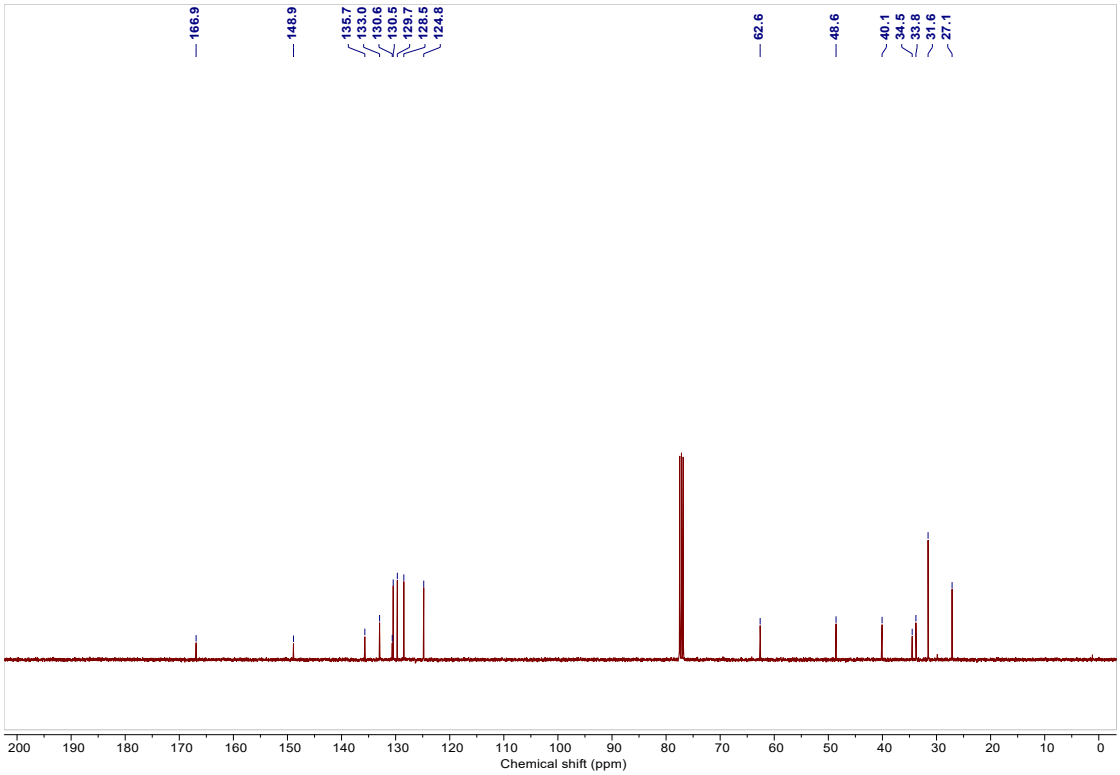
4: ^{13}C NMR (100 MHz, Chloroform-*d*)



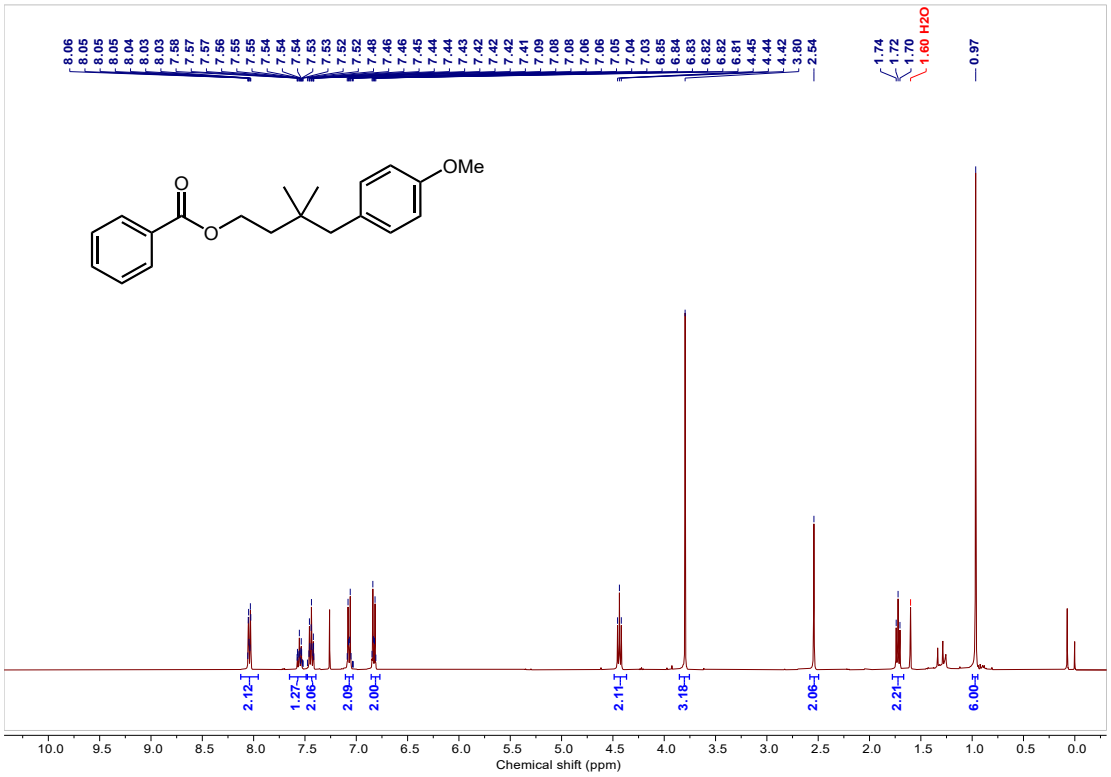
5: ^{1}H NMR (400 MHz, Chloroform-*d*)



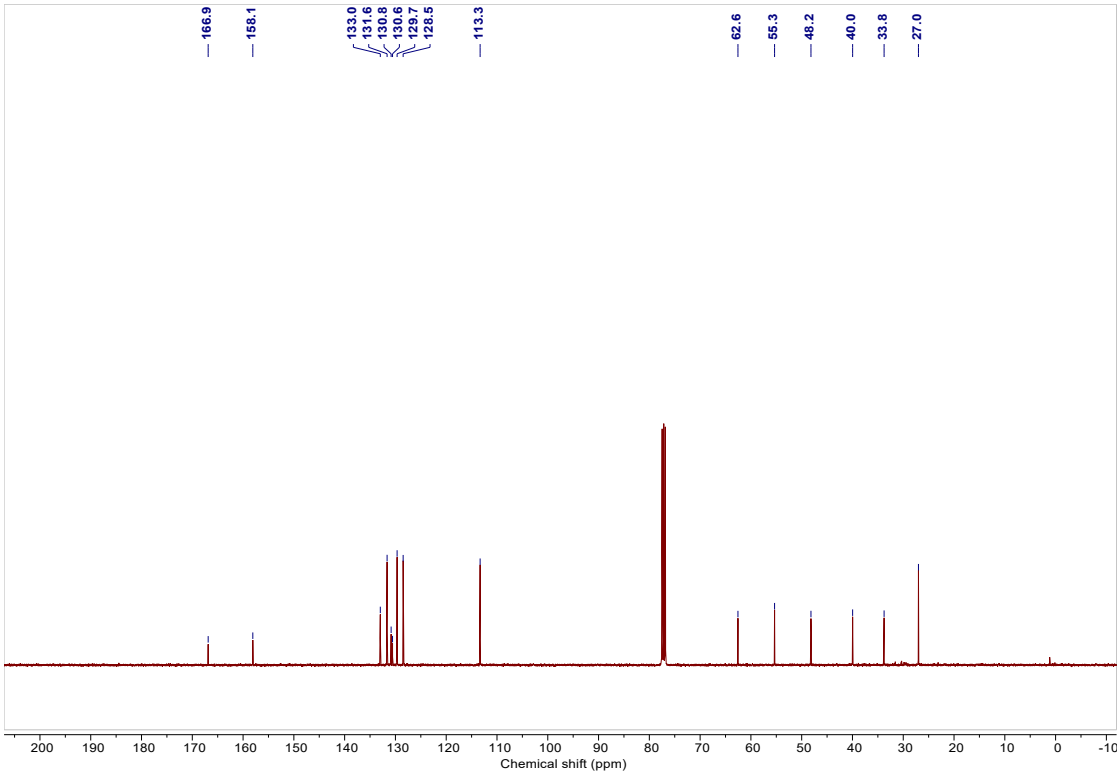
5: ^{13}C NMR (100 MHz, Chloroform-*d*)



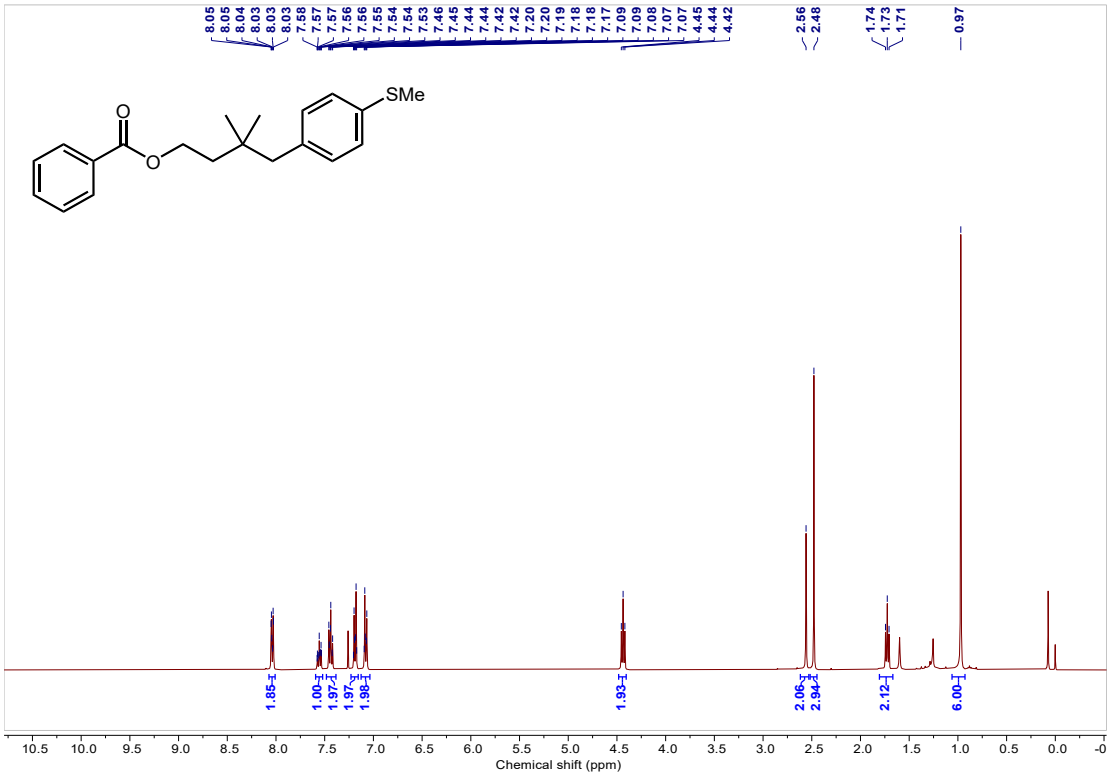
6: ^{1}H NMR (400 MHz, Chloroform-*d*)



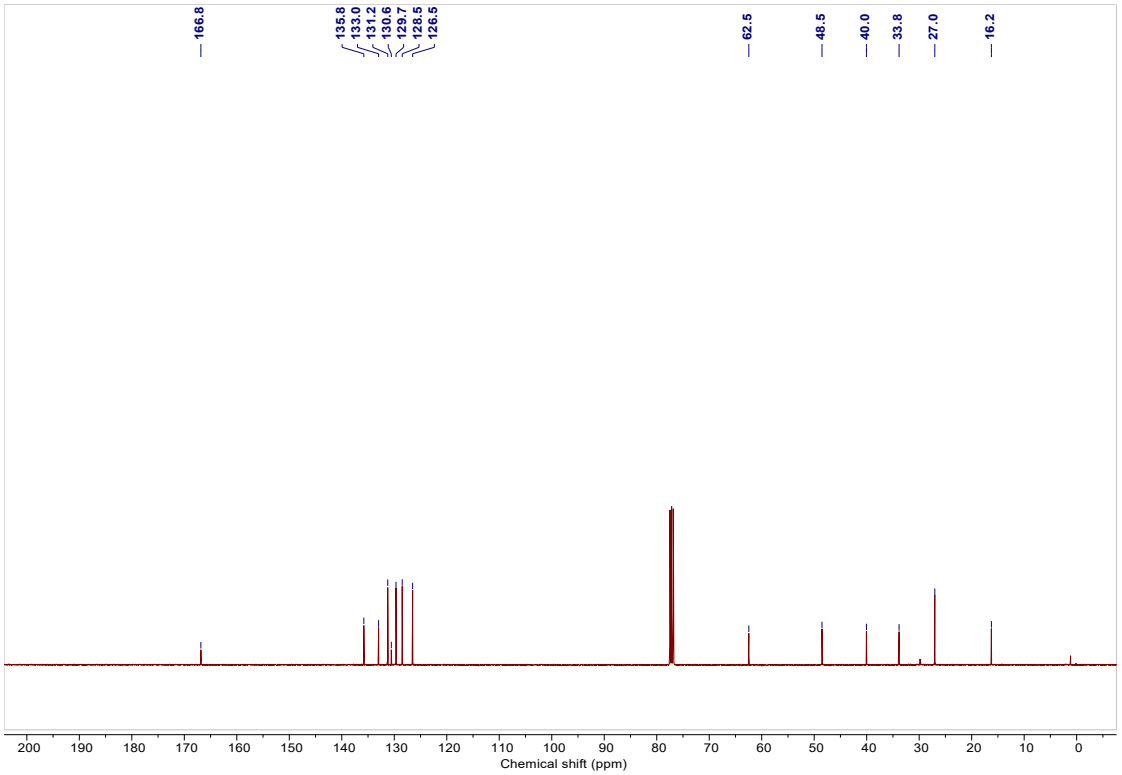
6: ^{13}C NMR (100 MHz, Chloroform-*d*)



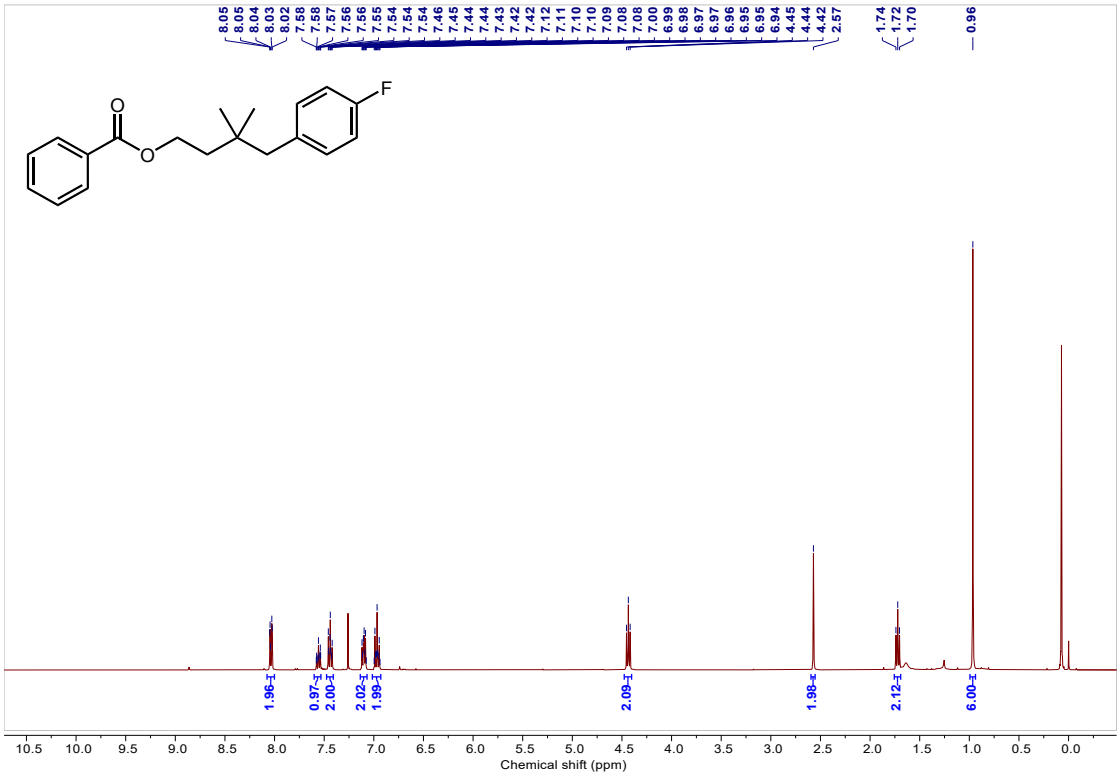
7: ^{1}H NMR (400 MHz, Chloroform-*d*)



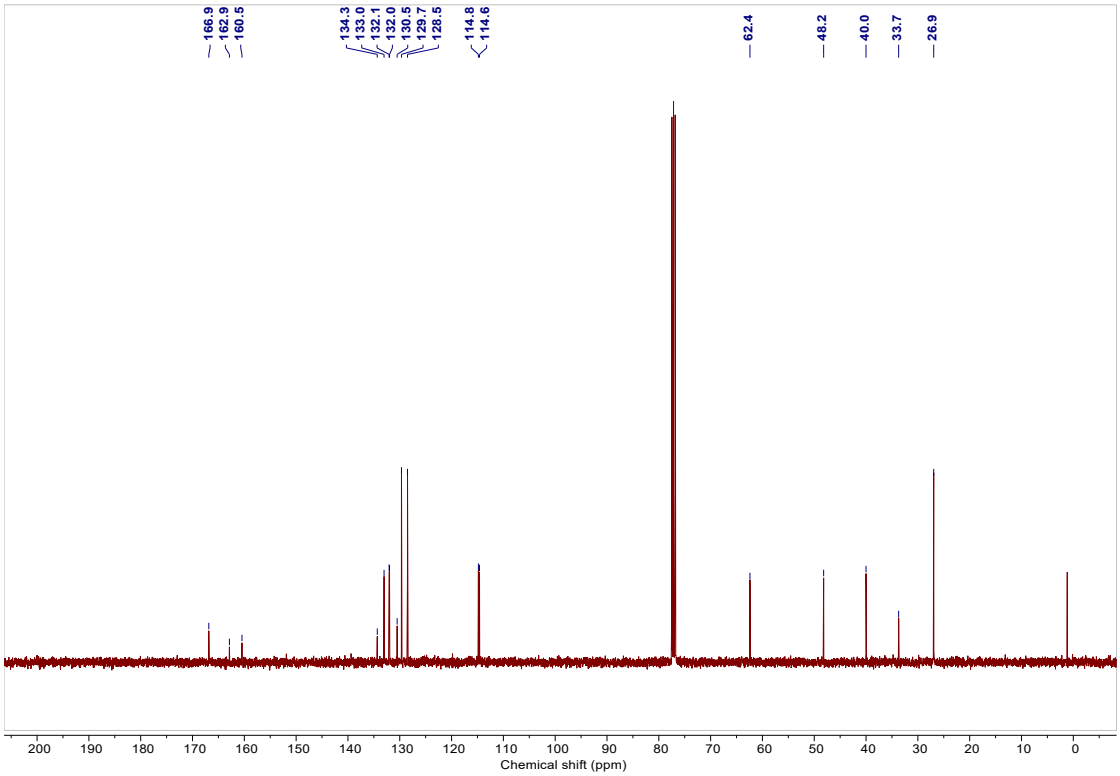
7: ^{13}C NMR (100 MHz, Chloroform-*d*)



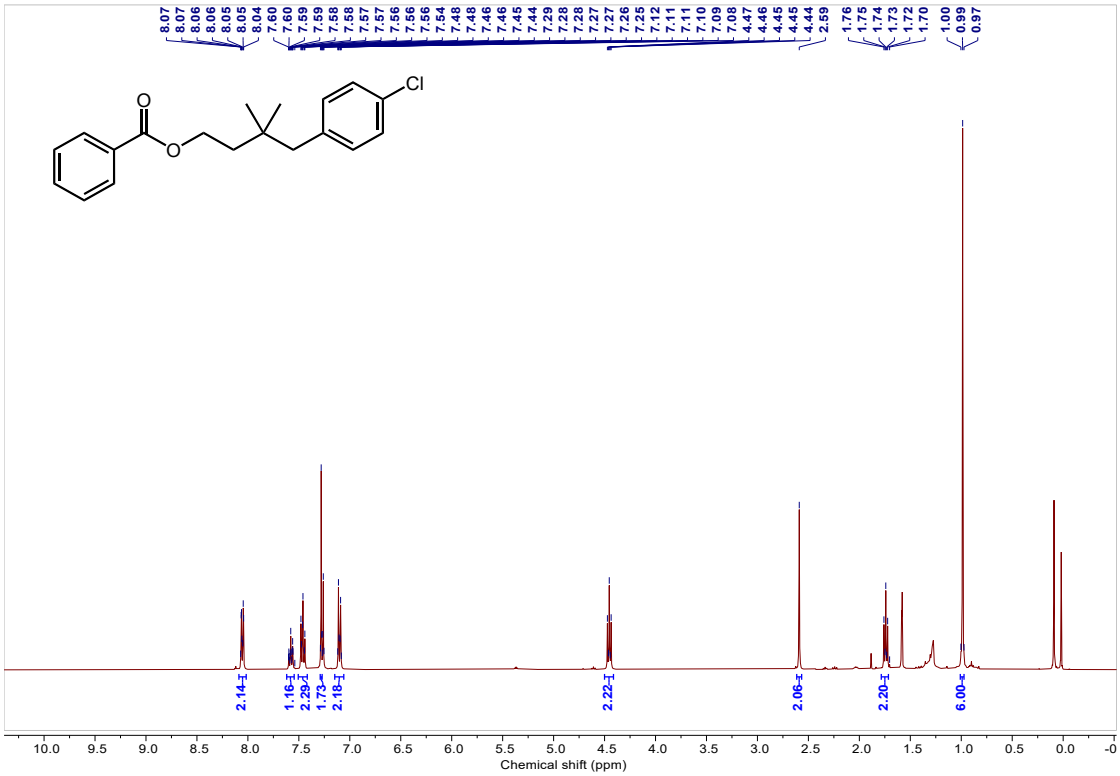
8: ^{1}H NMR (400 MHz, Chloroform-*d*)



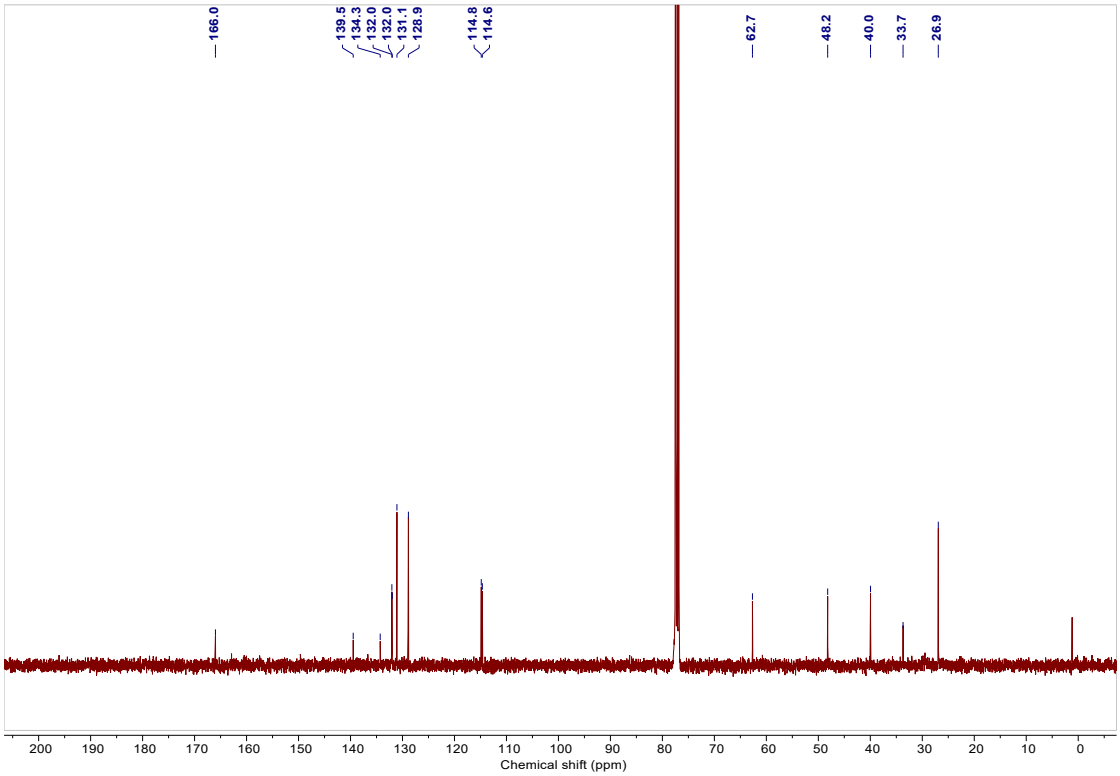
8: ^{13}C NMR (100 MHz, Chloroform-*d*)



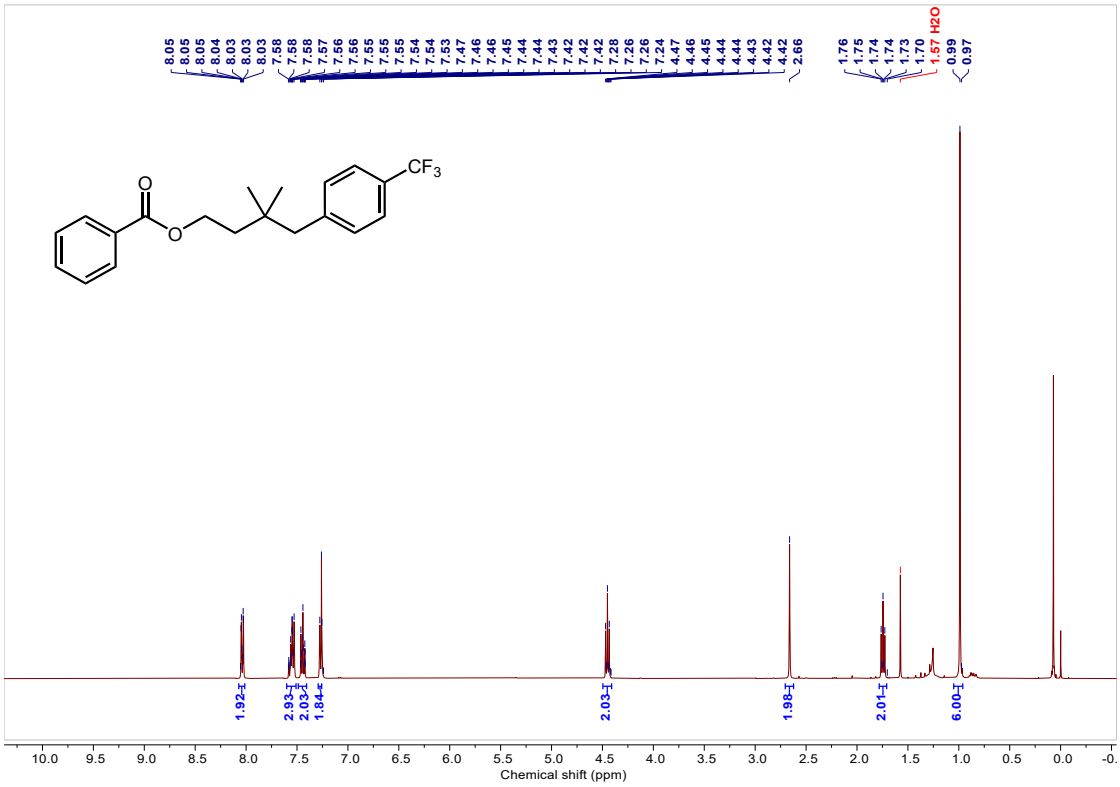
9: ^{1}H NMR (400 MHz, Chloroform-*d*)



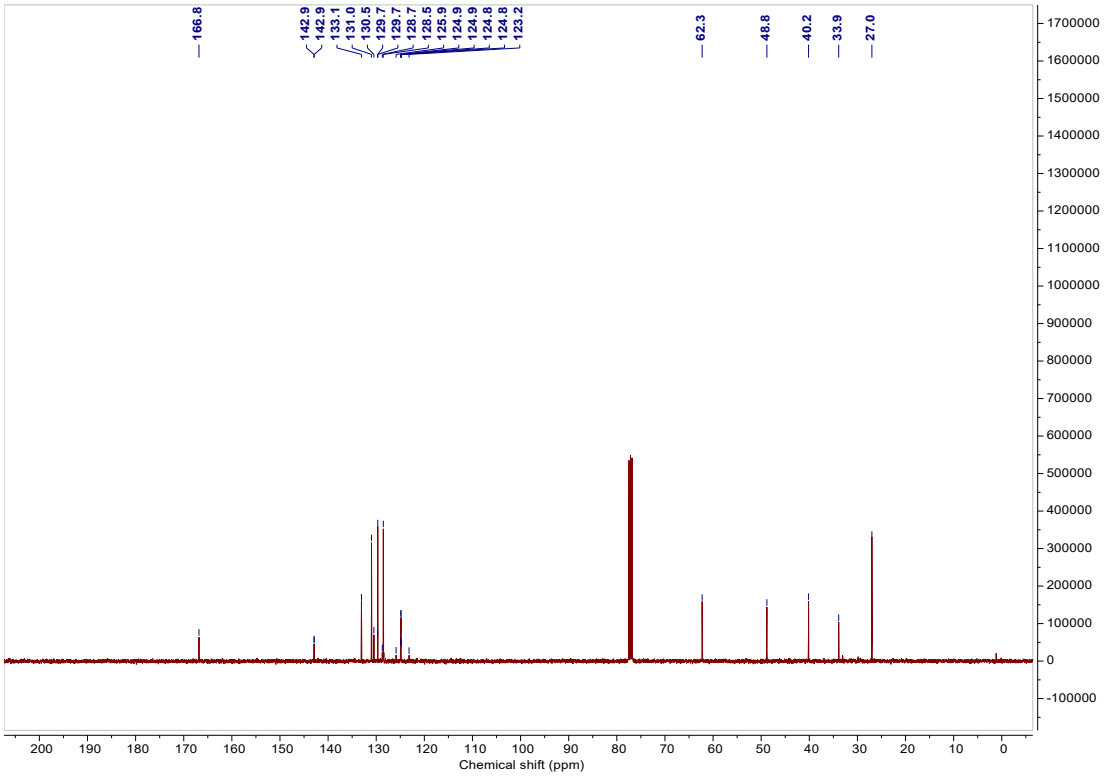
9: ^{13}C NMR (100 MHz, Chloroform-*d*)



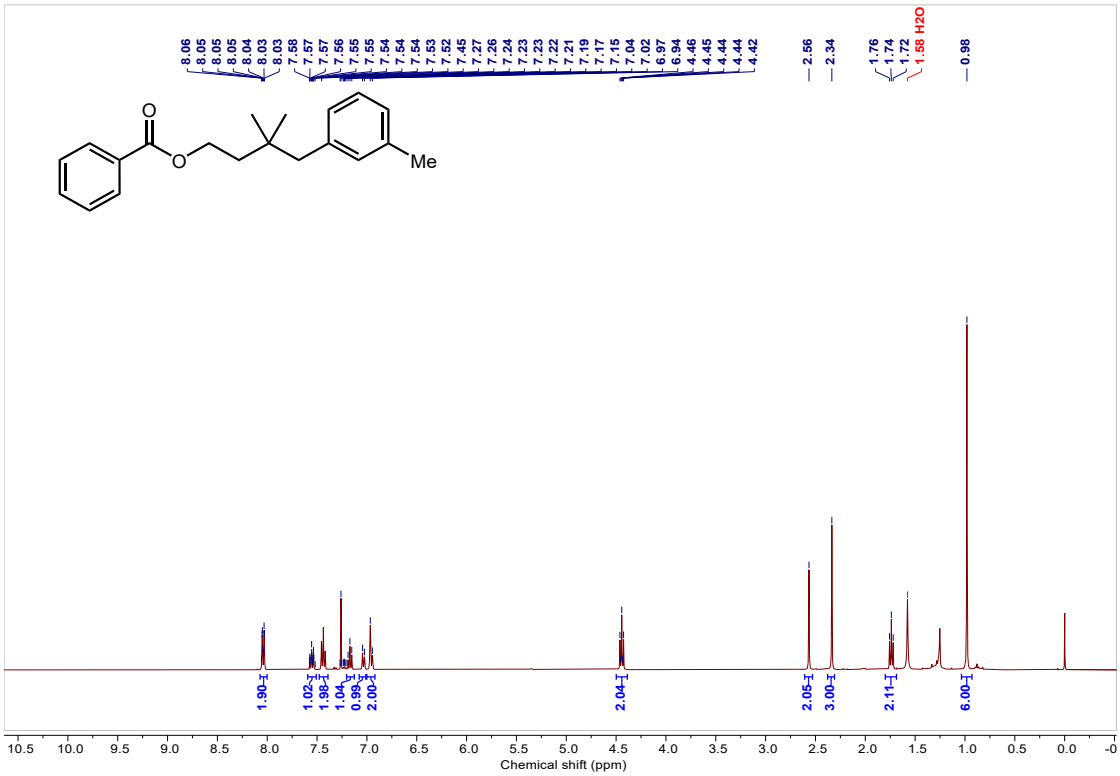
10: ^{1}H NMR (400 MHz, Chloroform-*d*)



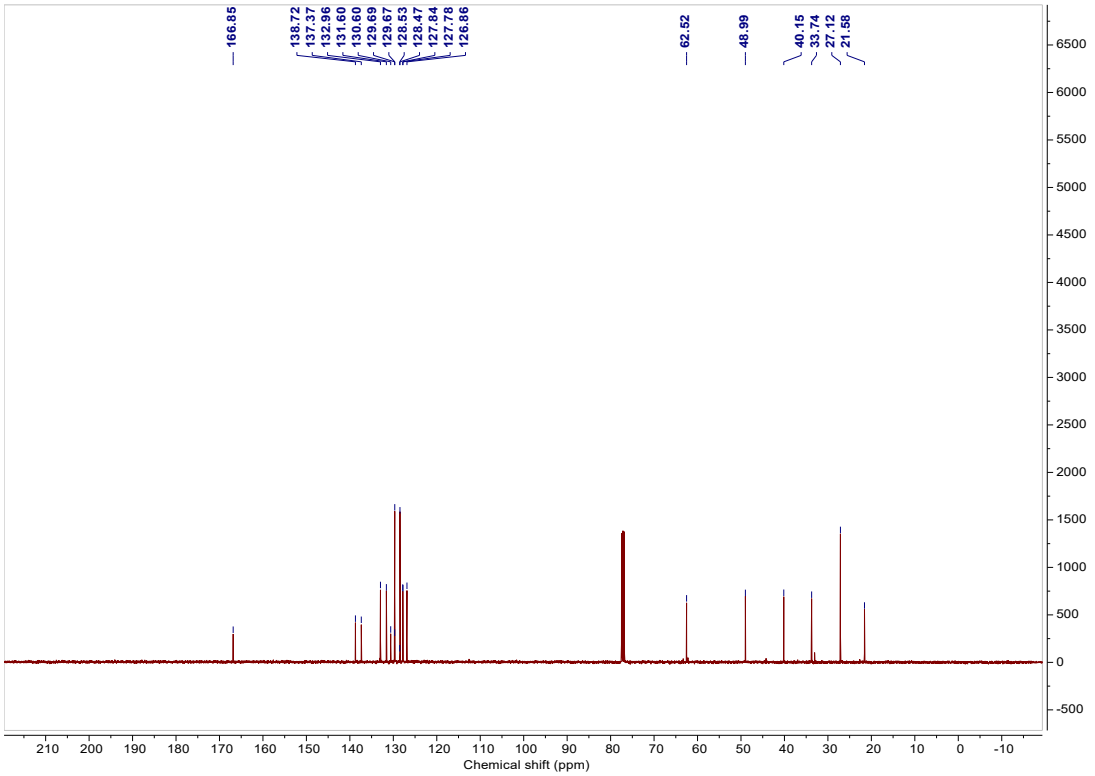
10: ^{13}C NMR (100 MHz, Chloroform-*d*)



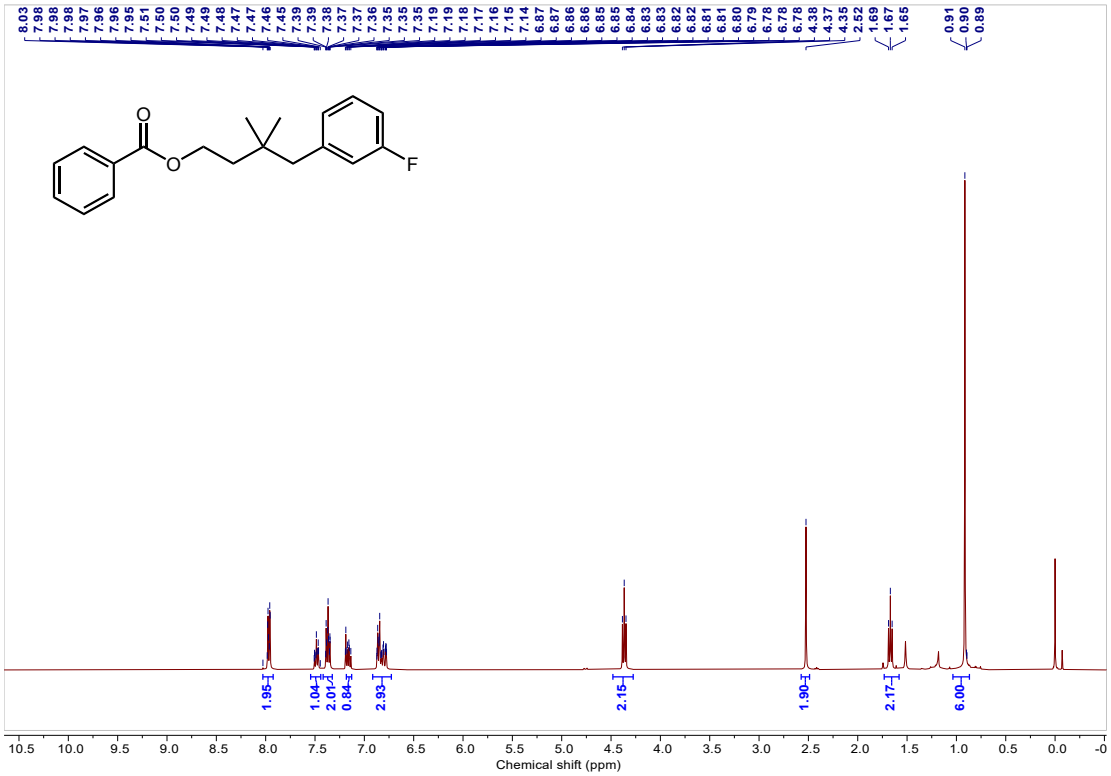
11: ^{1}H NMR (400 MHz, Chloroform-*d*)



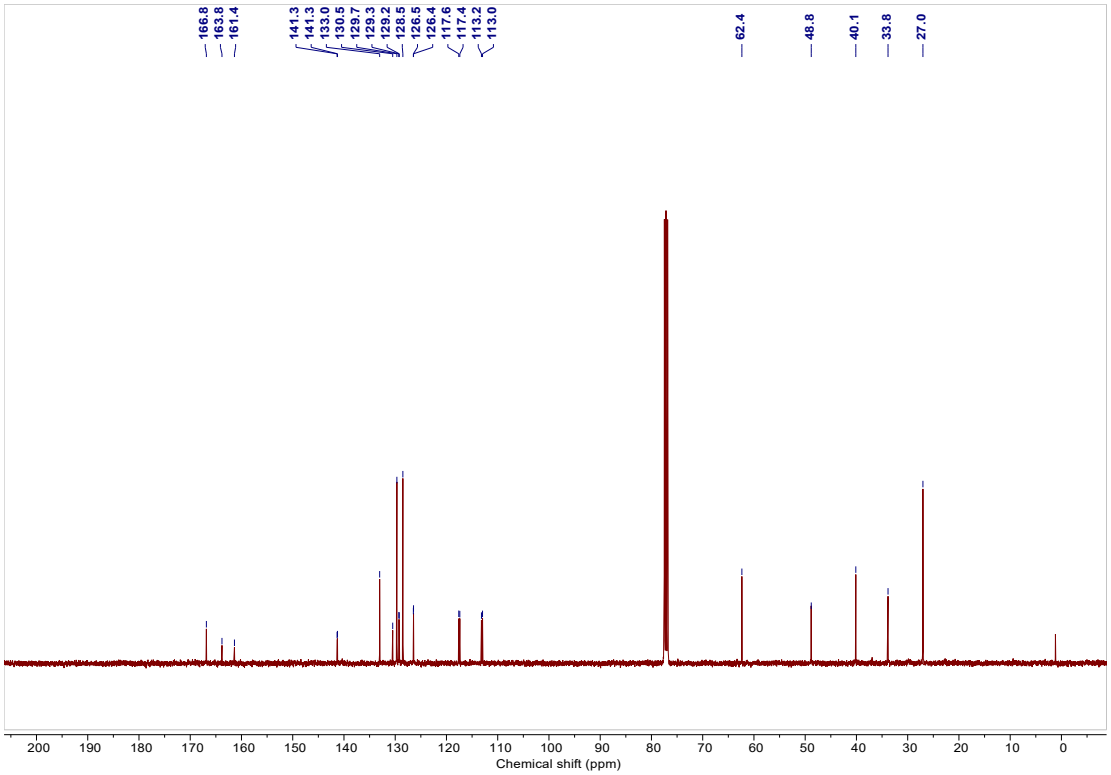
11: ^{13}C NMR (100 MHz, Chloroform-*d*)



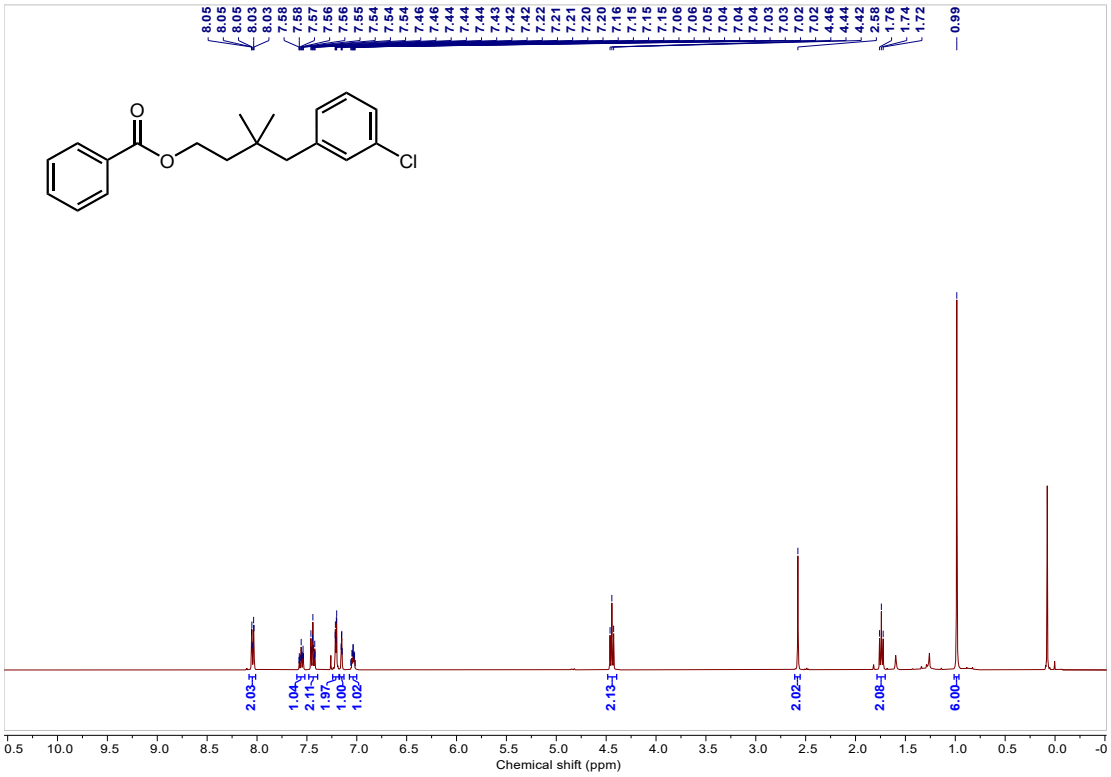
12: ^{1}H NMR (400 MHz, Chloroform-*d*)



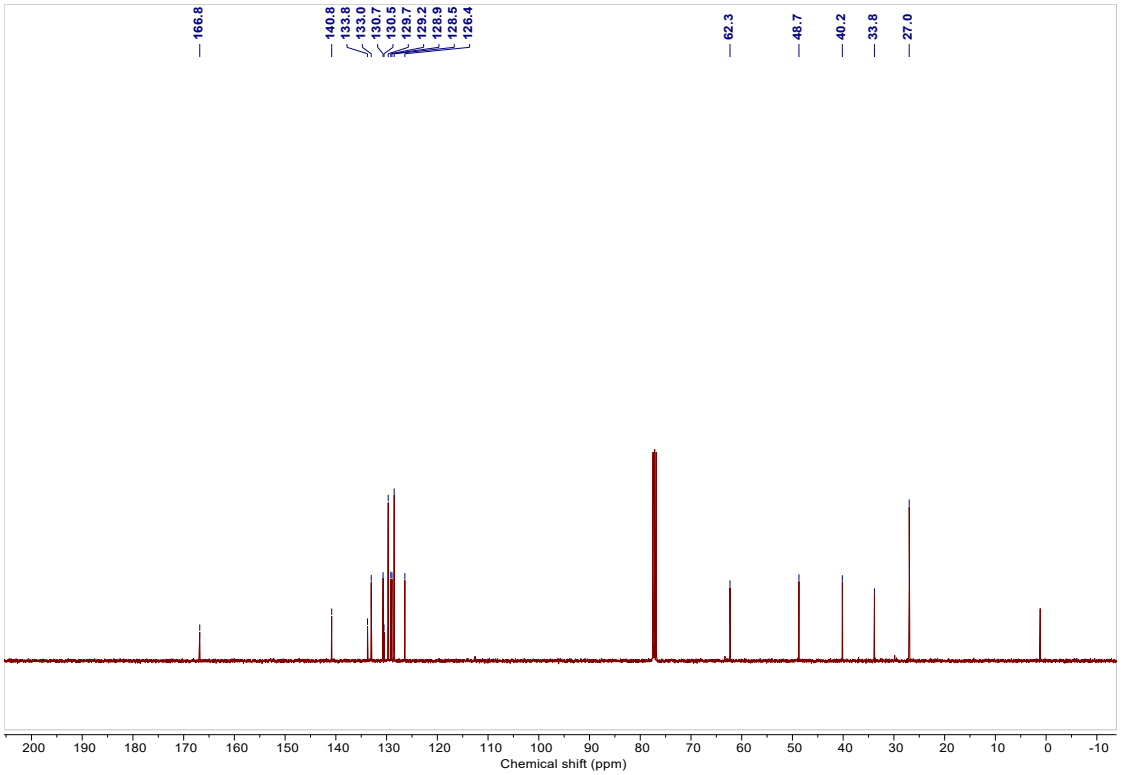
12: ^{13}C NMR (100 MHz, Chloroform-*d*)



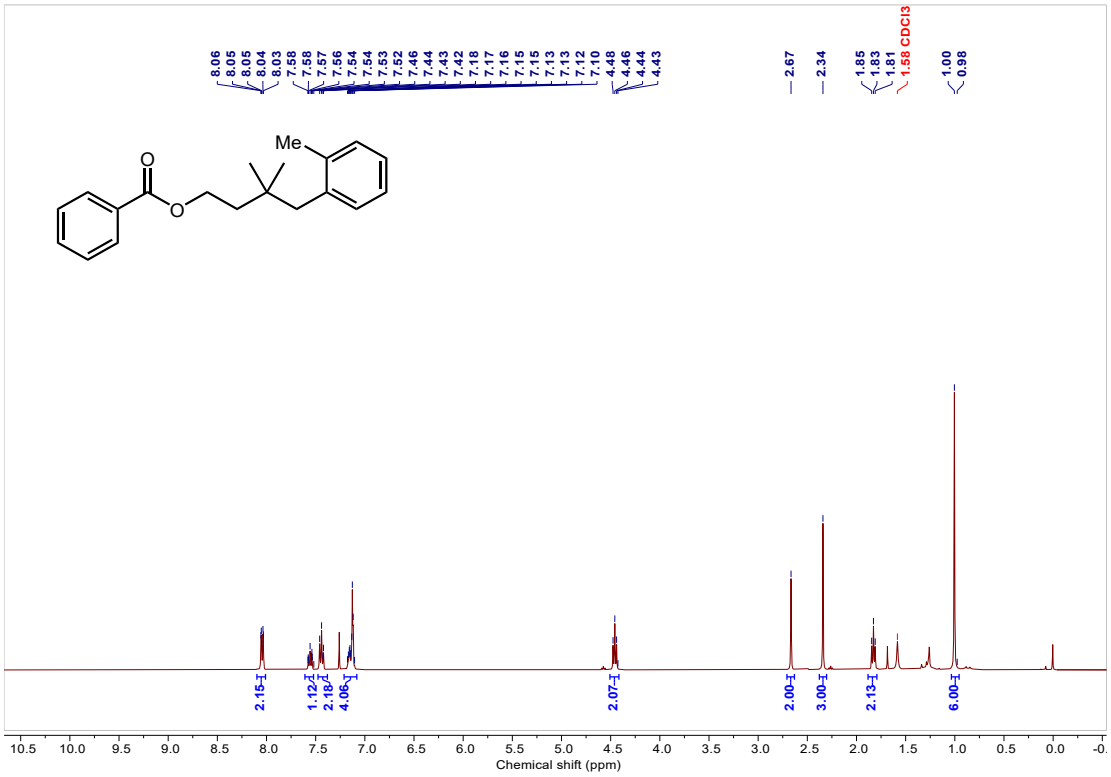
13: ^{1}H NMR (400 MHz, Chloroform-*d*)



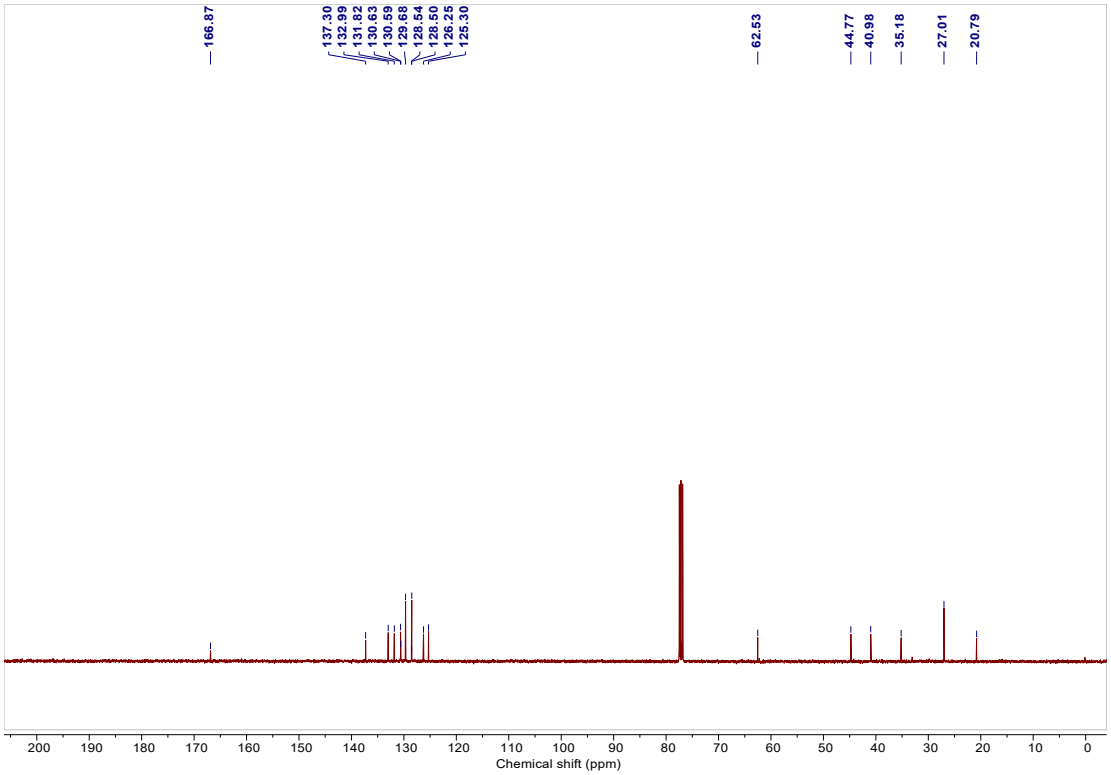
13: ^{13}C NMR (100 MHz, Chloroform-*d*)



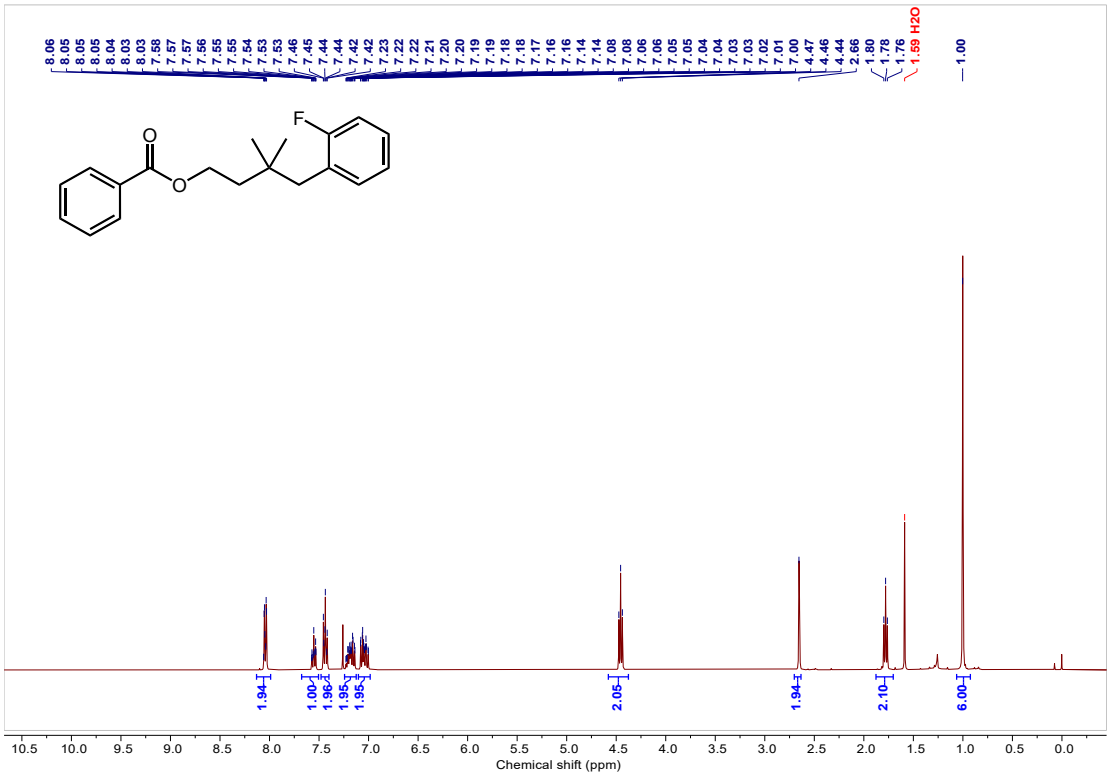
14: ^{1}H NMR (400 MHz, Chloroform-*d*)



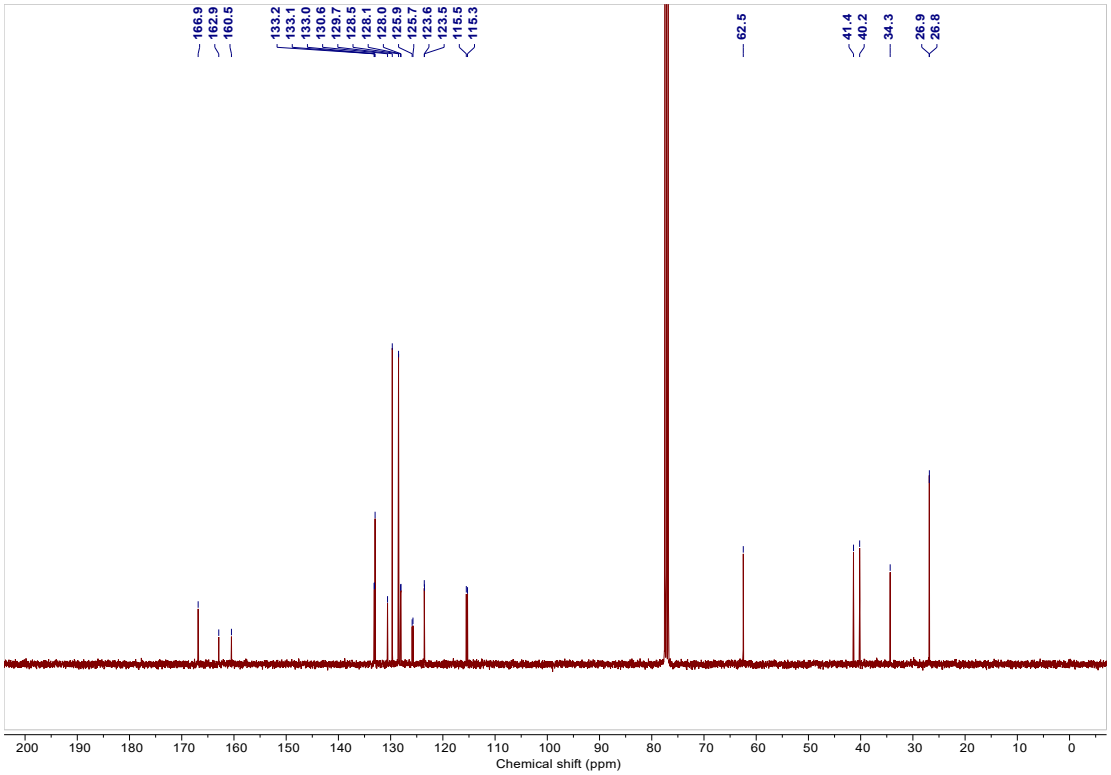
14: ^{13}C NMR (100 MHz, Chloroform-*d*)



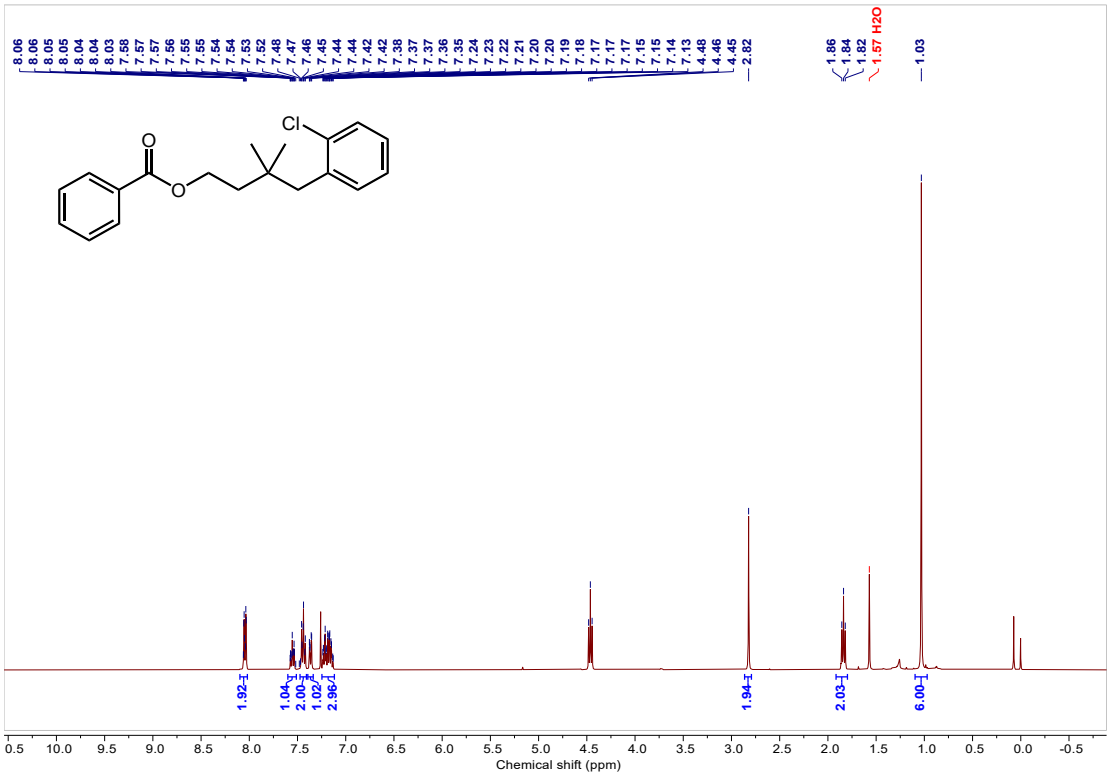
15: ^{1}H NMR (400 MHz, Chloroform-*d*)



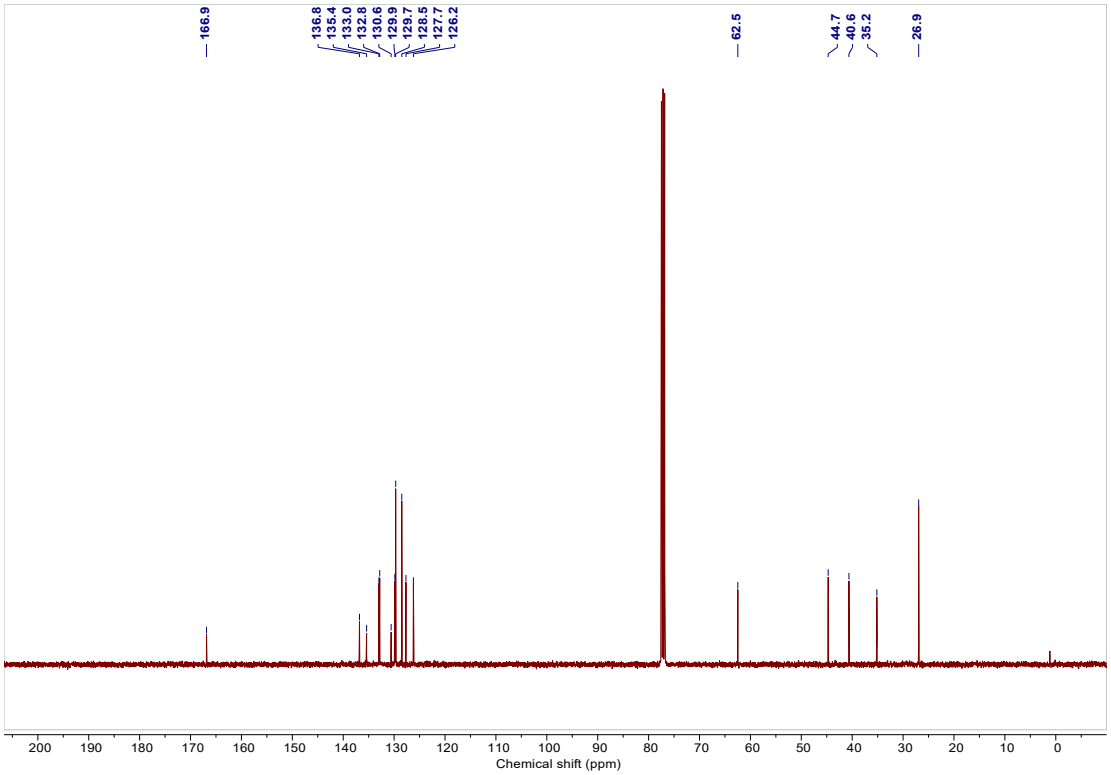
15: ^{13}C NMR (100 MHz, Chloroform-*d*)



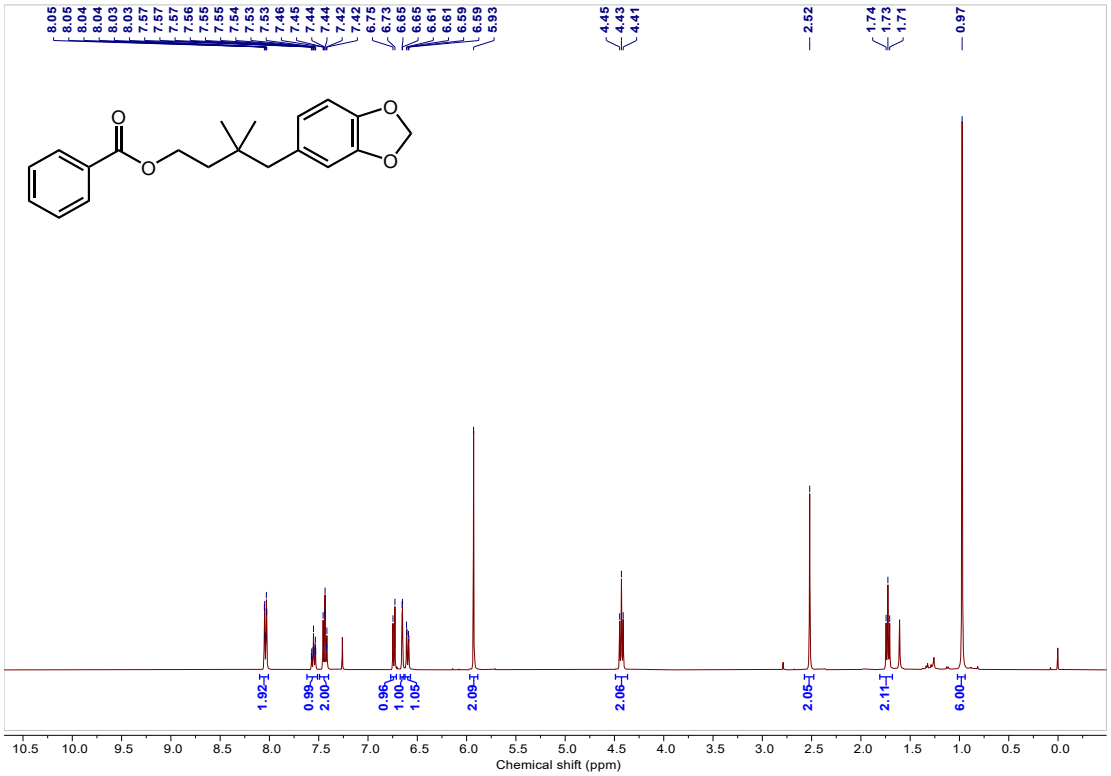
16: ^{1}H NMR (400 MHz, Chloroform-*d*)



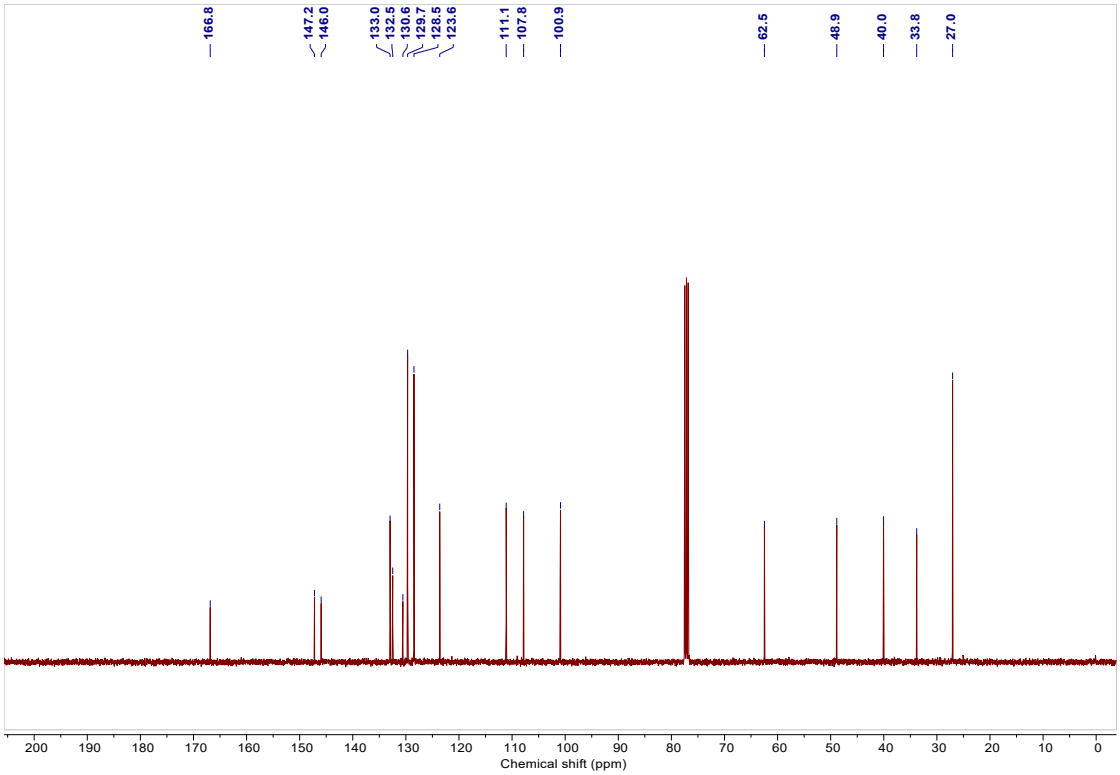
16: ^{13}C NMR (100 MHz, Chloroform-*d*)



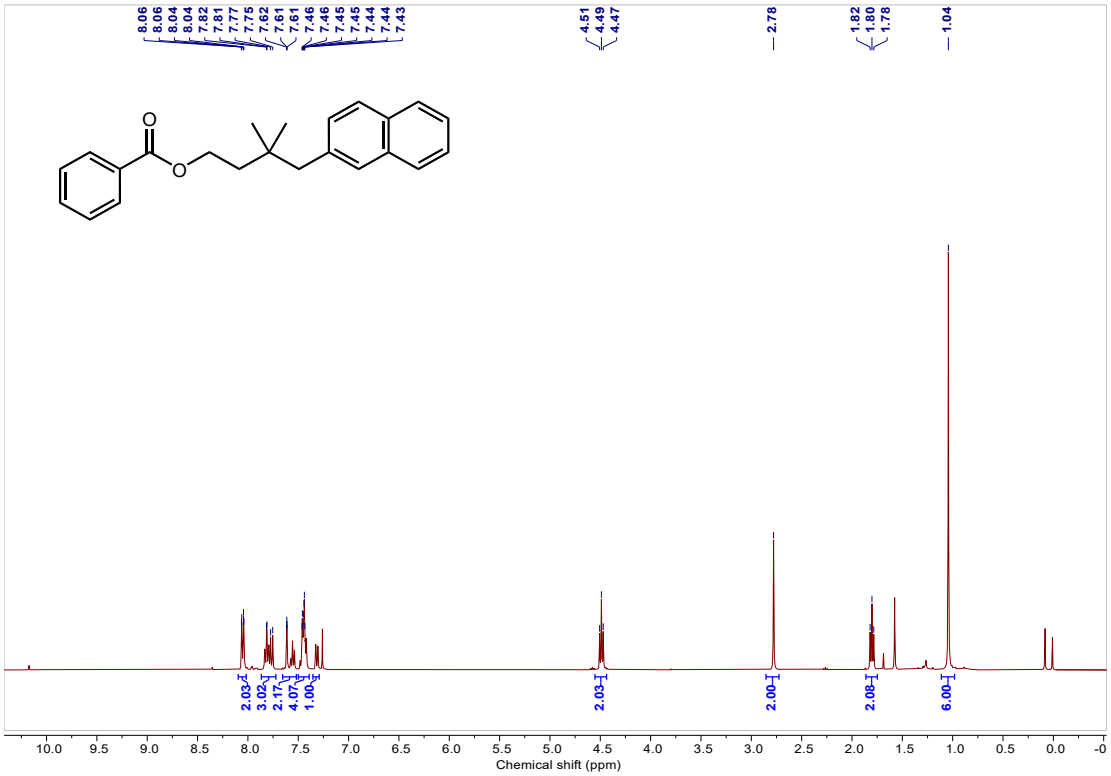
17: ^{1}H NMR (400 MHz, Chloroform-*d*)



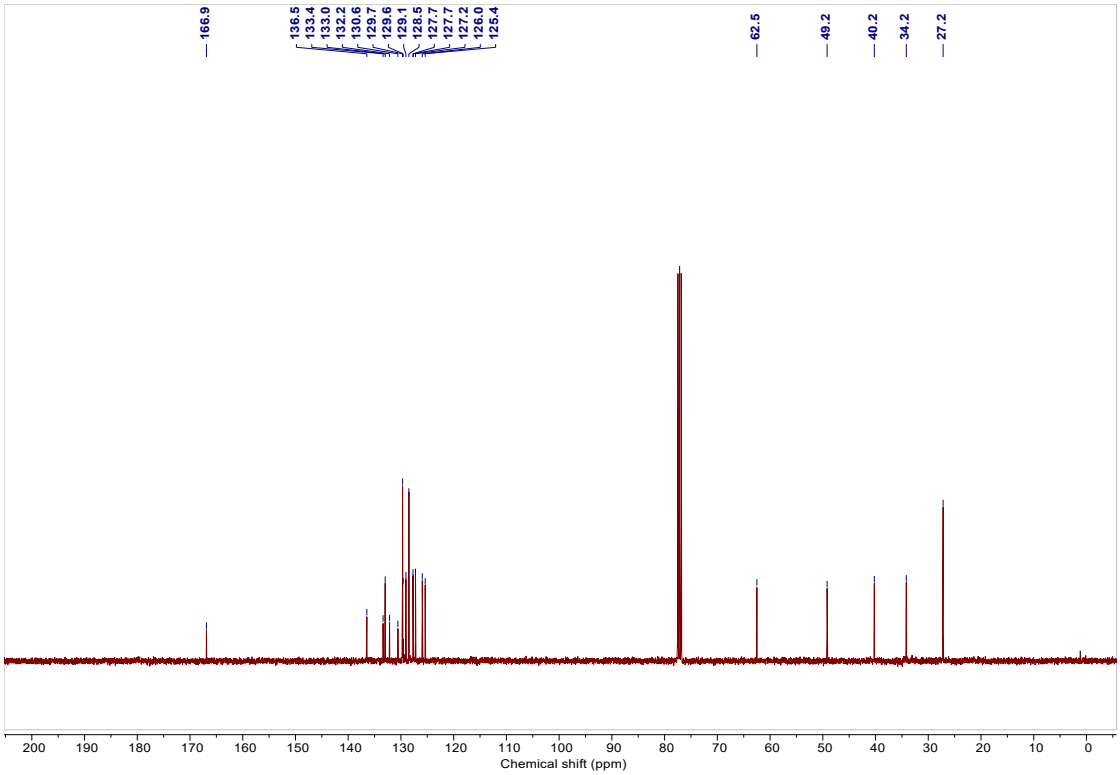
17: ^{13}C NMR (100 MHz, Chloroform-*d*)



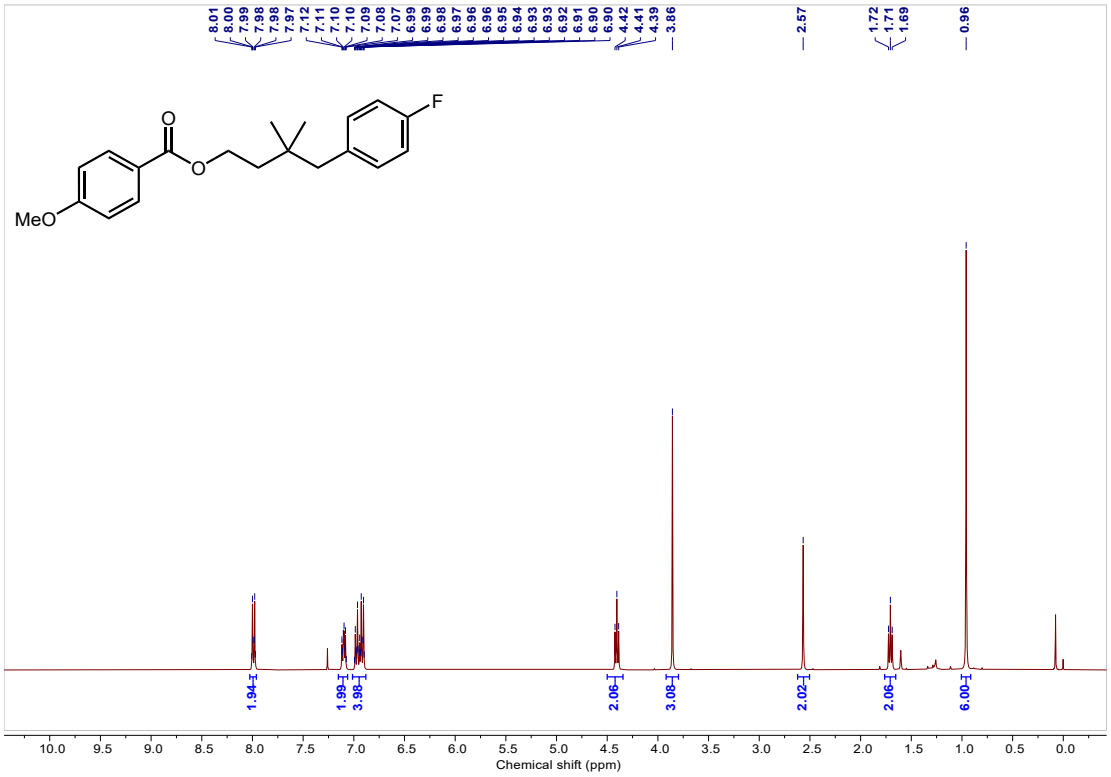
18: ^{1}H NMR (400 MHz, Chloroform-*d*)



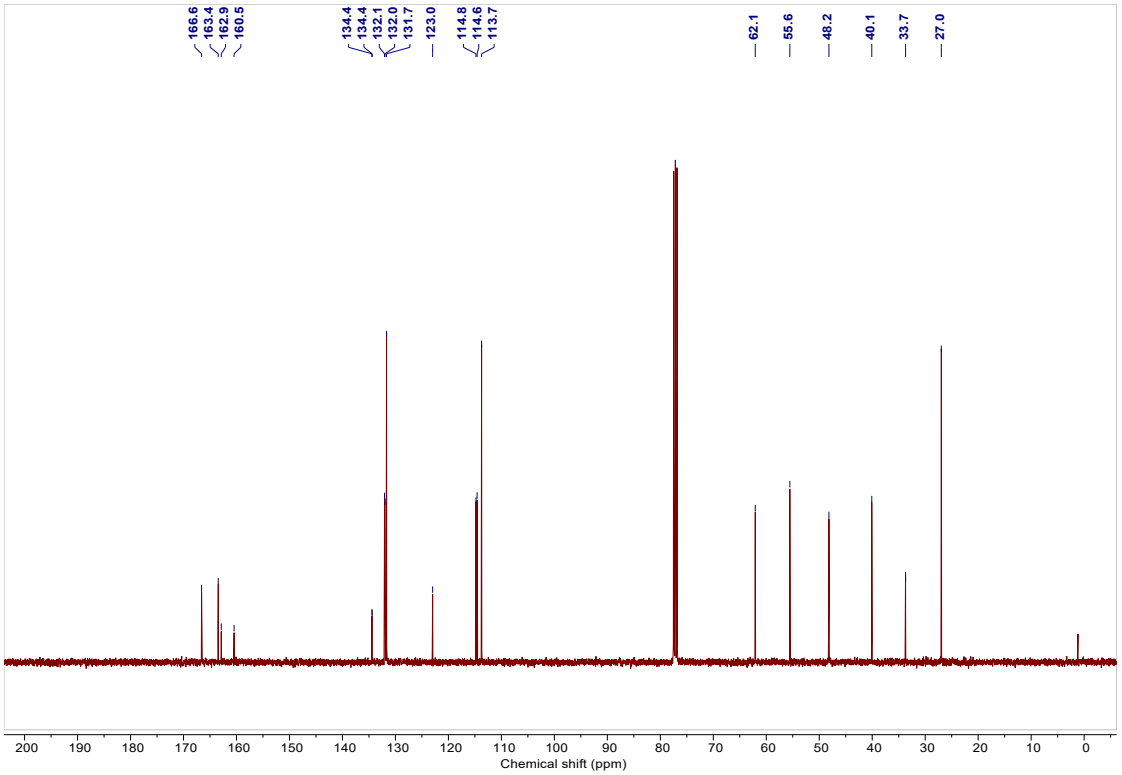
18: ^{13}C NMR (100 MHz, Chloroform-*d*)



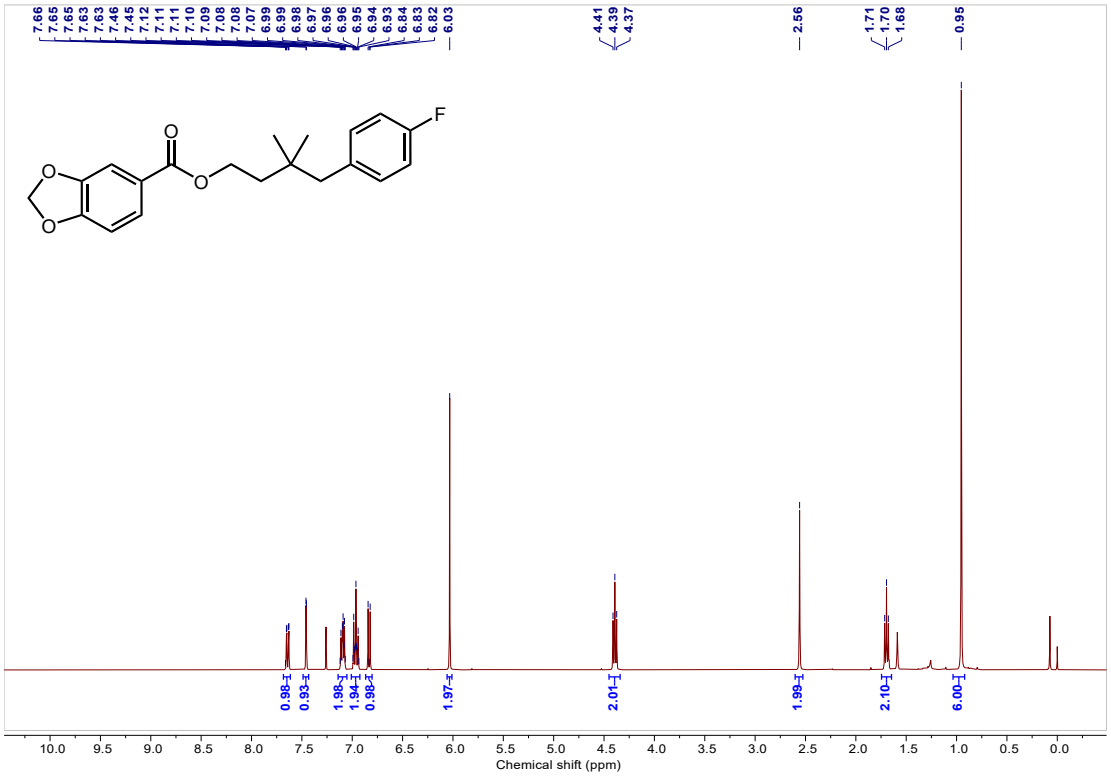
19: ^{1}H NMR (400 MHz, Chloroform-d)



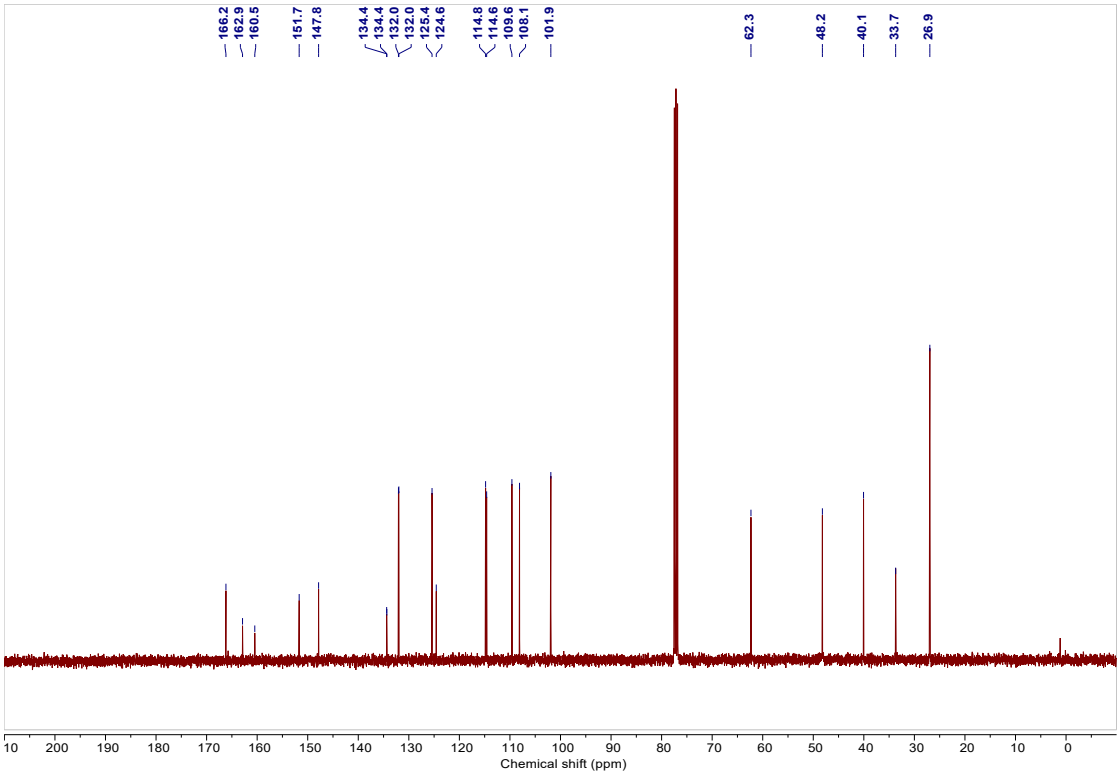
19: ^{13}C NMR (100 MHz, Chloroform-*d*)



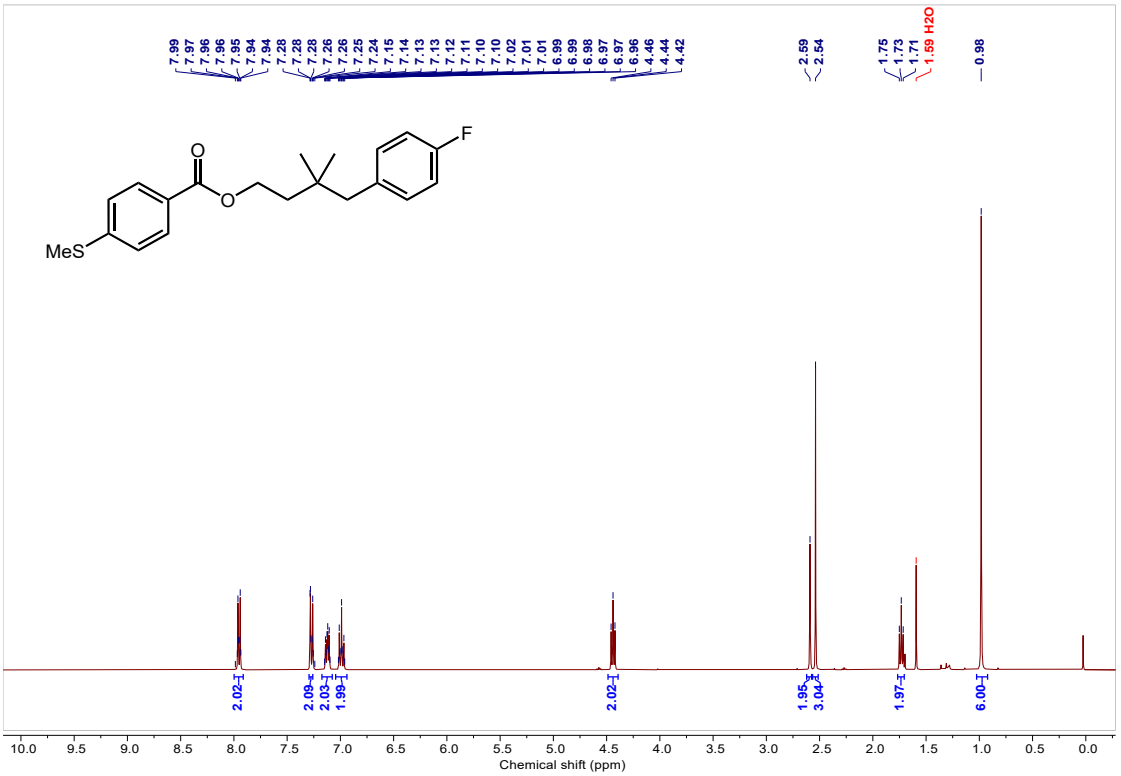
20: ^{1}H NMR (400 MHz, Chloroform-*d*)



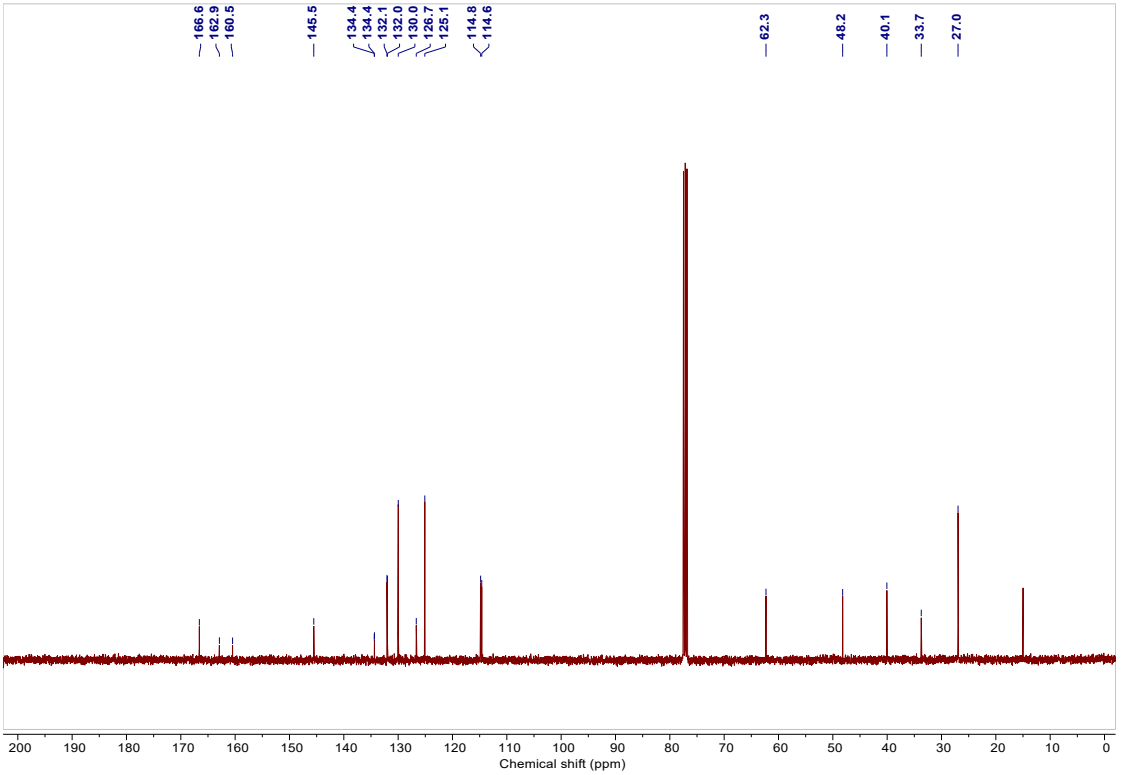
20: ^{13}C NMR (100 MHz, Chloroform-*d*)



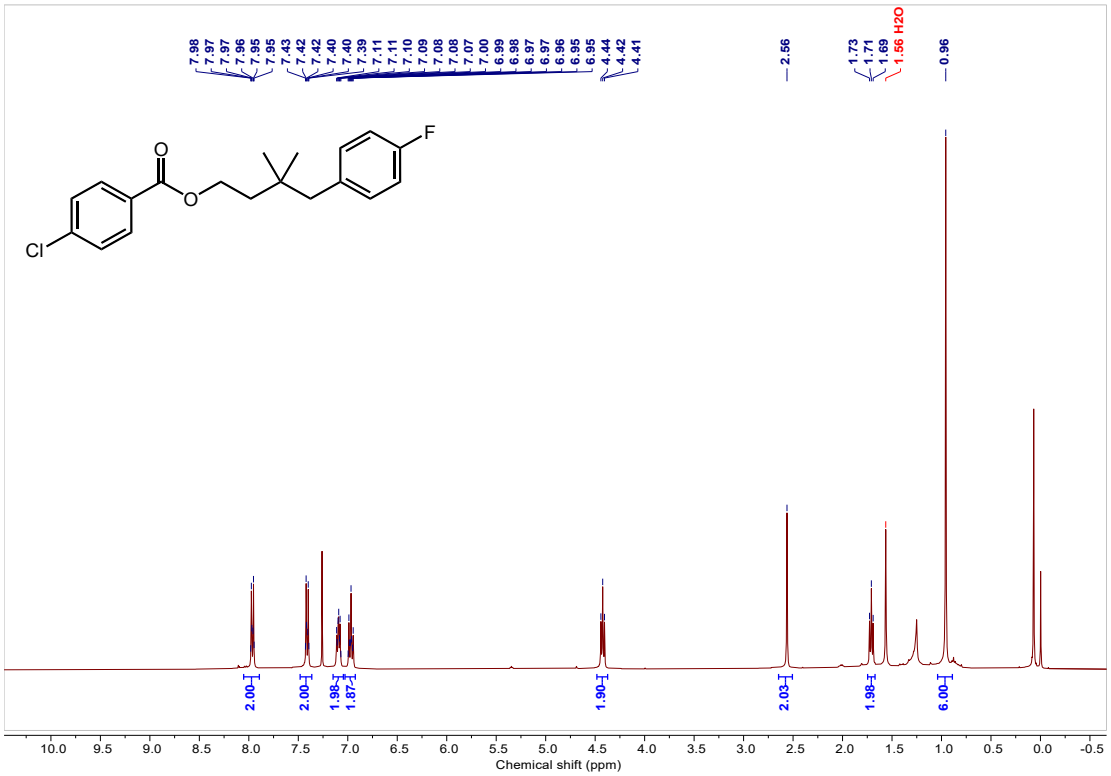
21: 1H NMR (400 MHz, Chloroform-*d*)



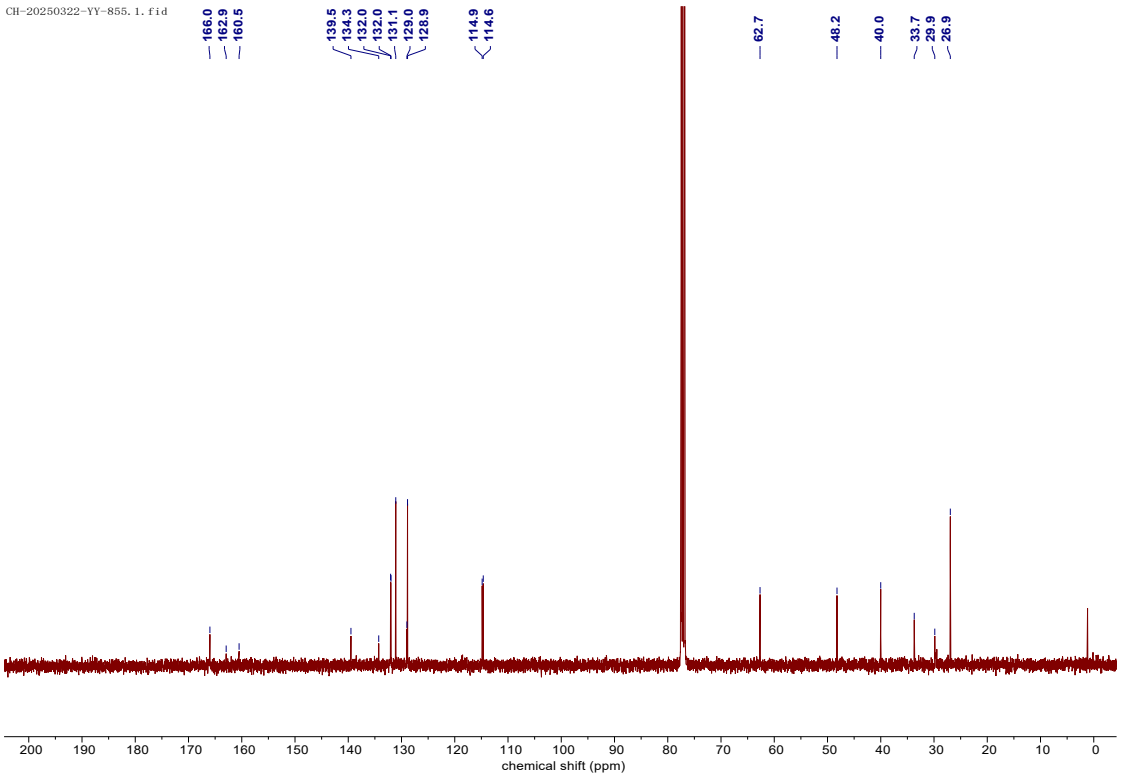
21: ^{13}C NMR (100 MHz, Chloroform-*d*)



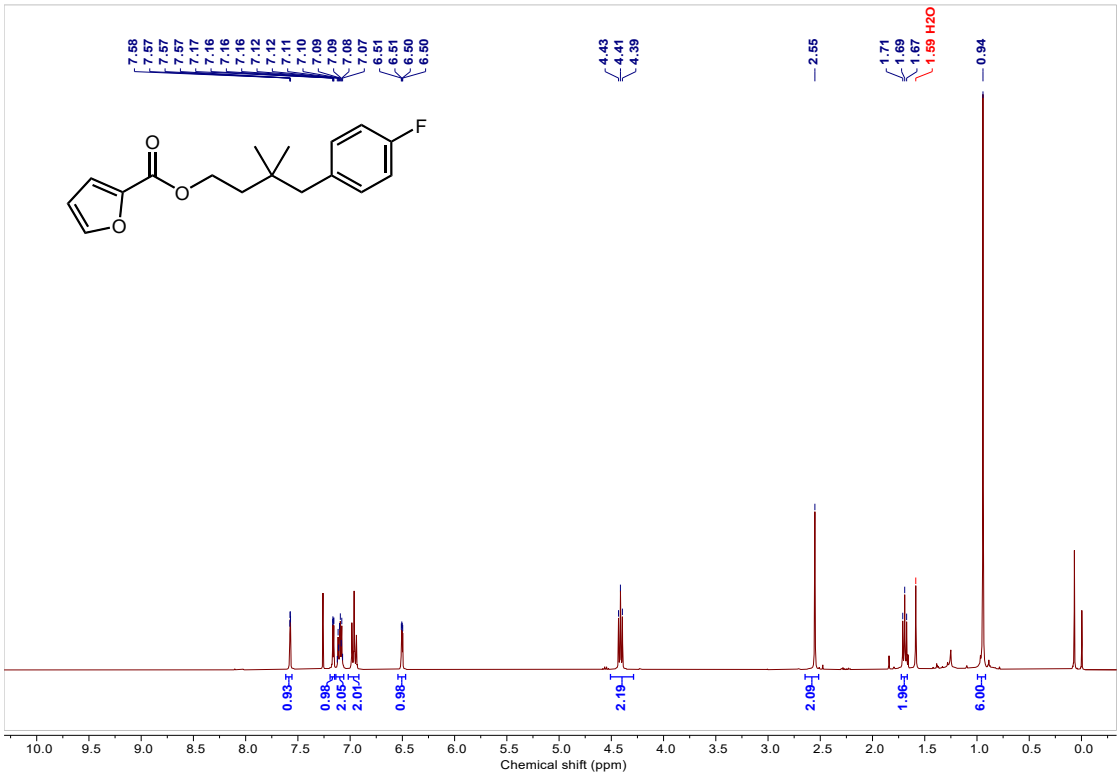
22: ^{1}H NMR (400 MHz, Chloroform-*d*)



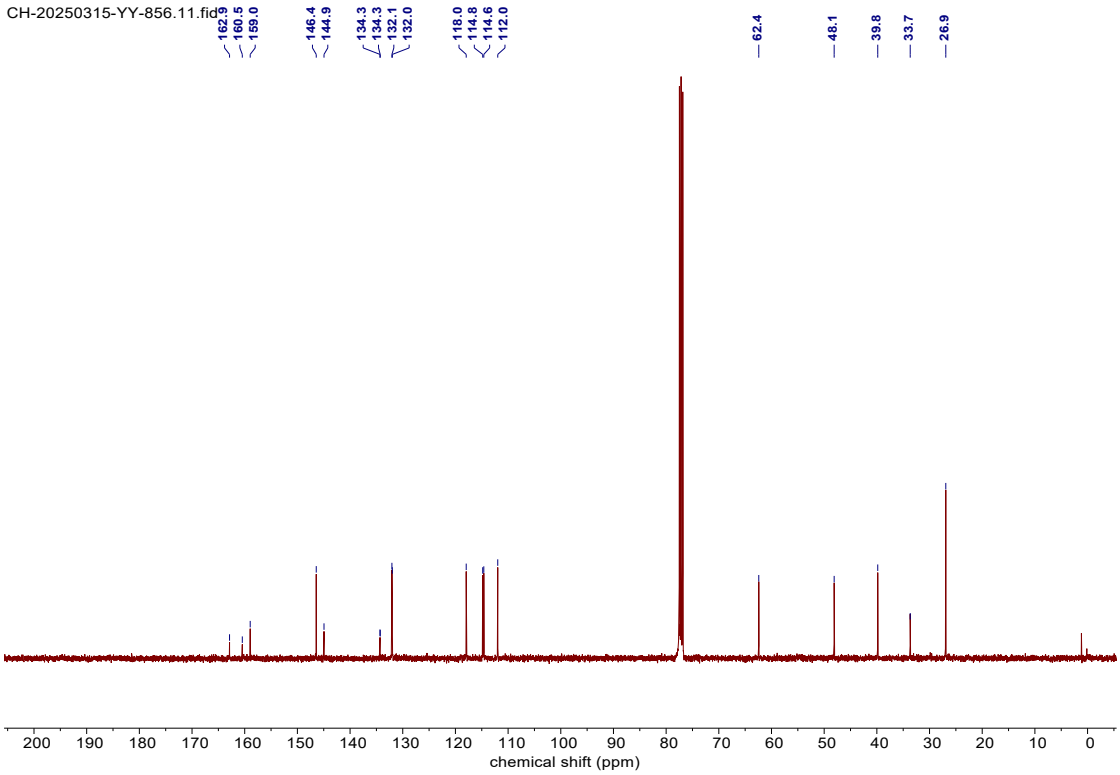
22: ^{13}C NMR (100 MHz, Chloroform-*d*)



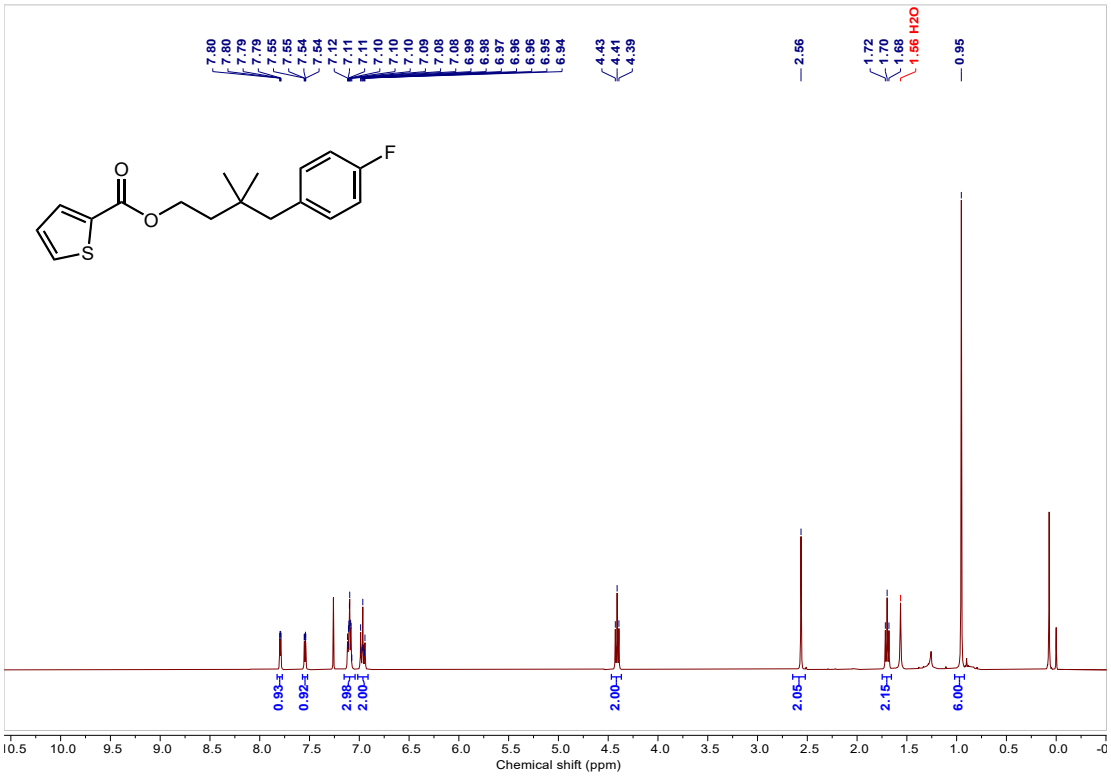
23: ^{1}H NMR (400 MHz, Chloroform-*d*)



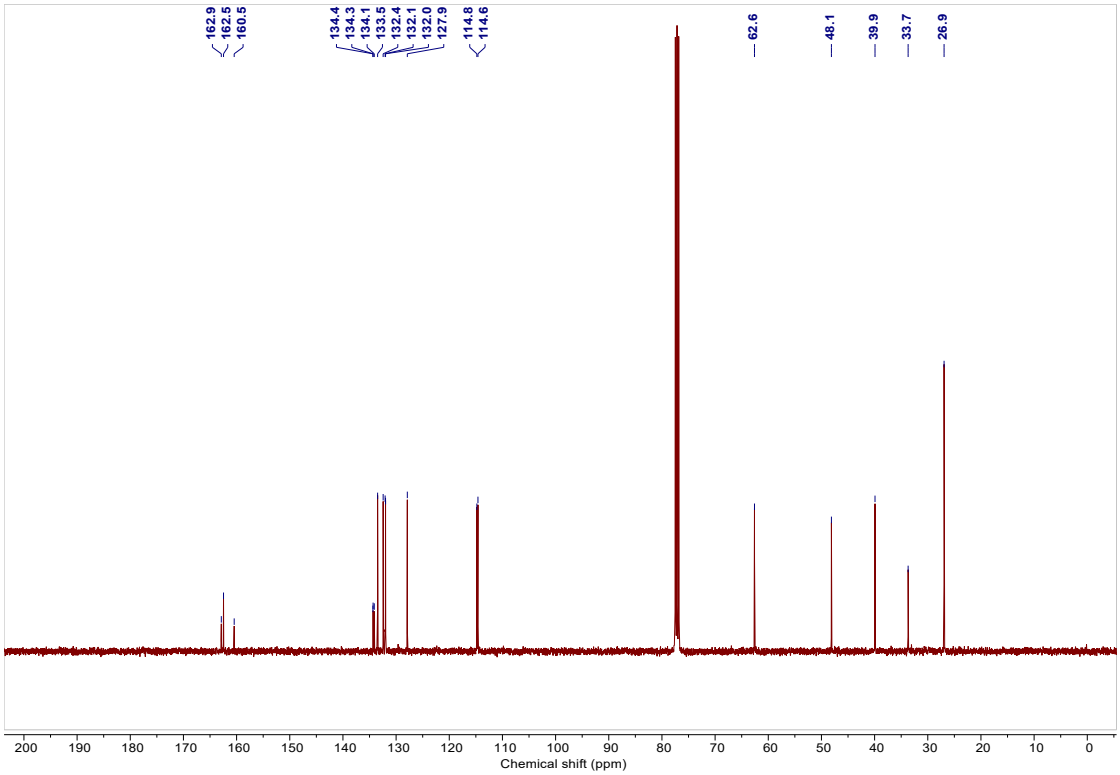
23: ^{13}C NMR (100 MHz, Chloroform-*d*)



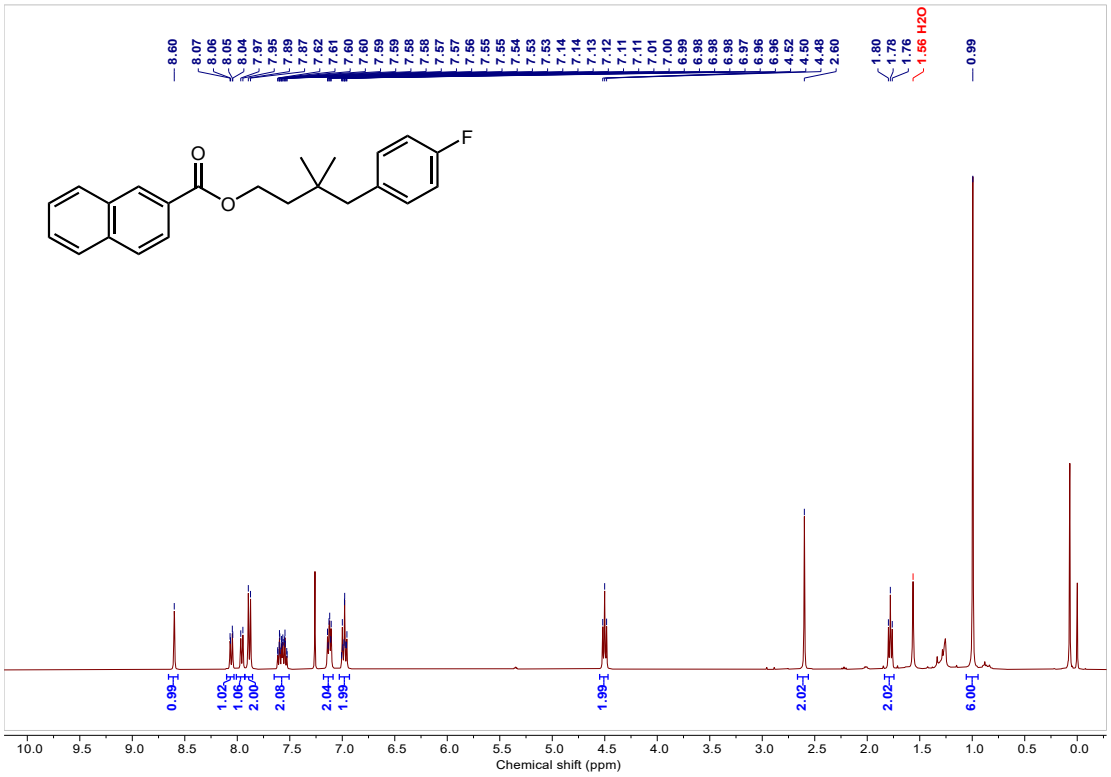
24: ^{1}H NMR (400 MHz, Chloroform-*d*)



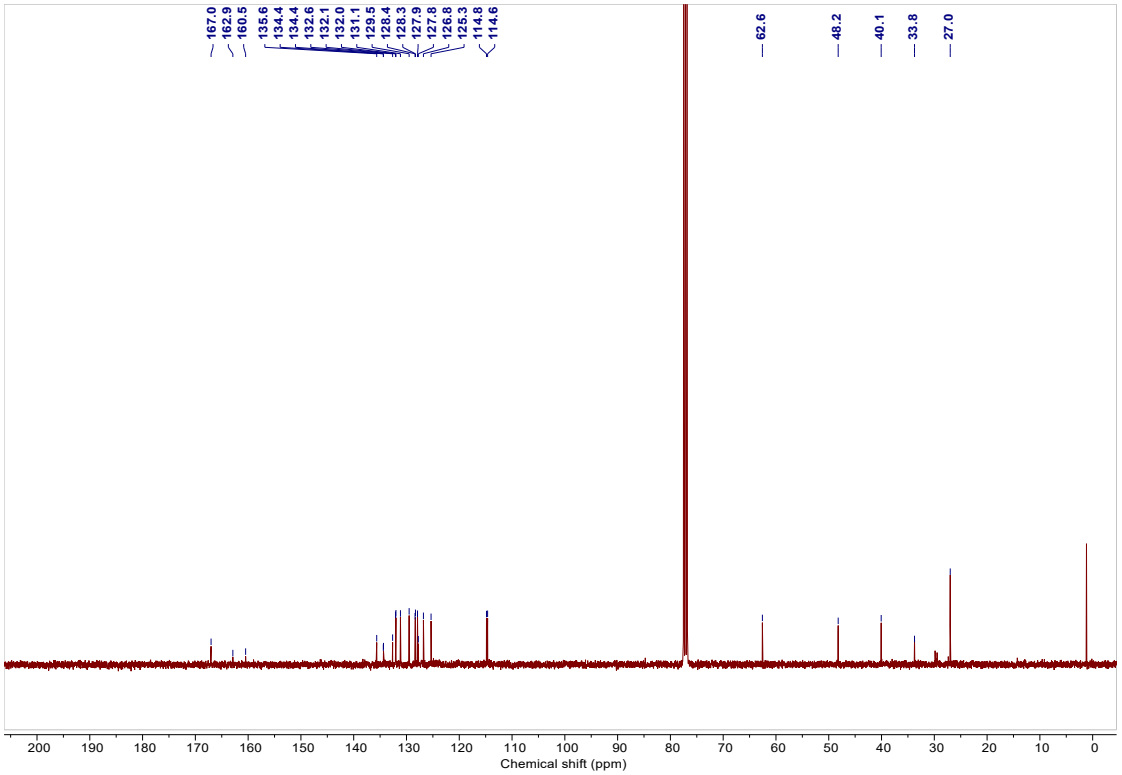
24: ^{13}C NMR (100 MHz, Chloroform-*d*)



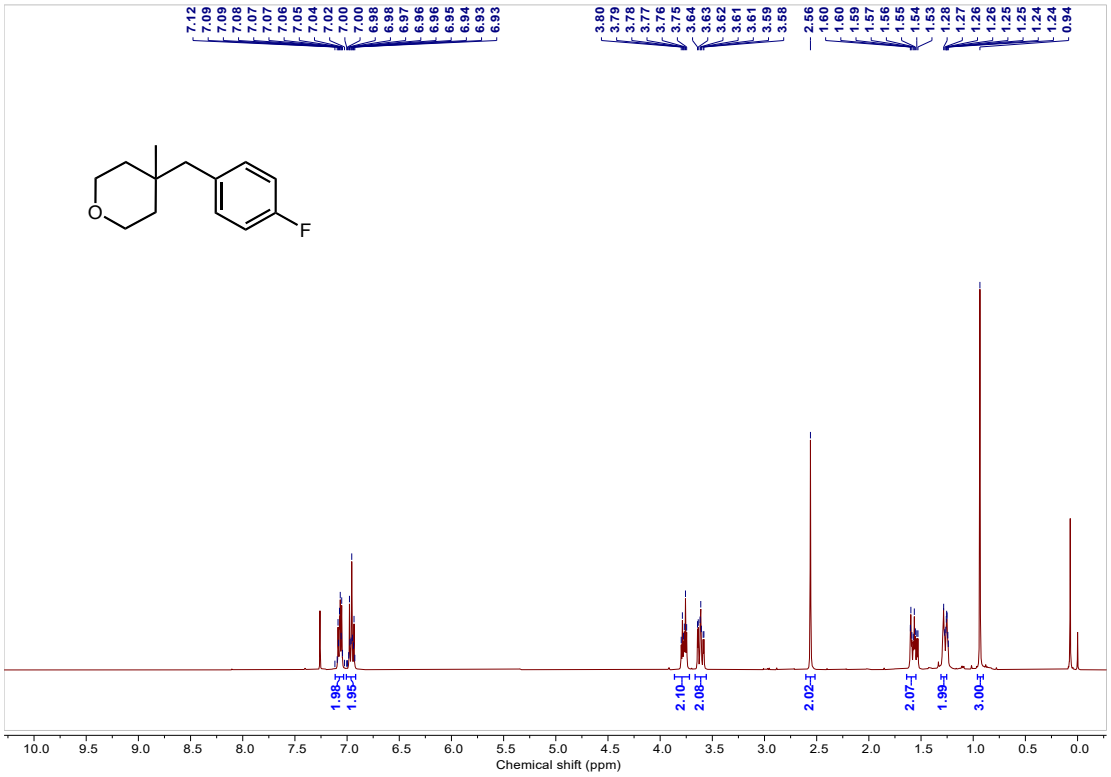
25: ^{1}H NMR (400 MHz, Chloroform-*d*)



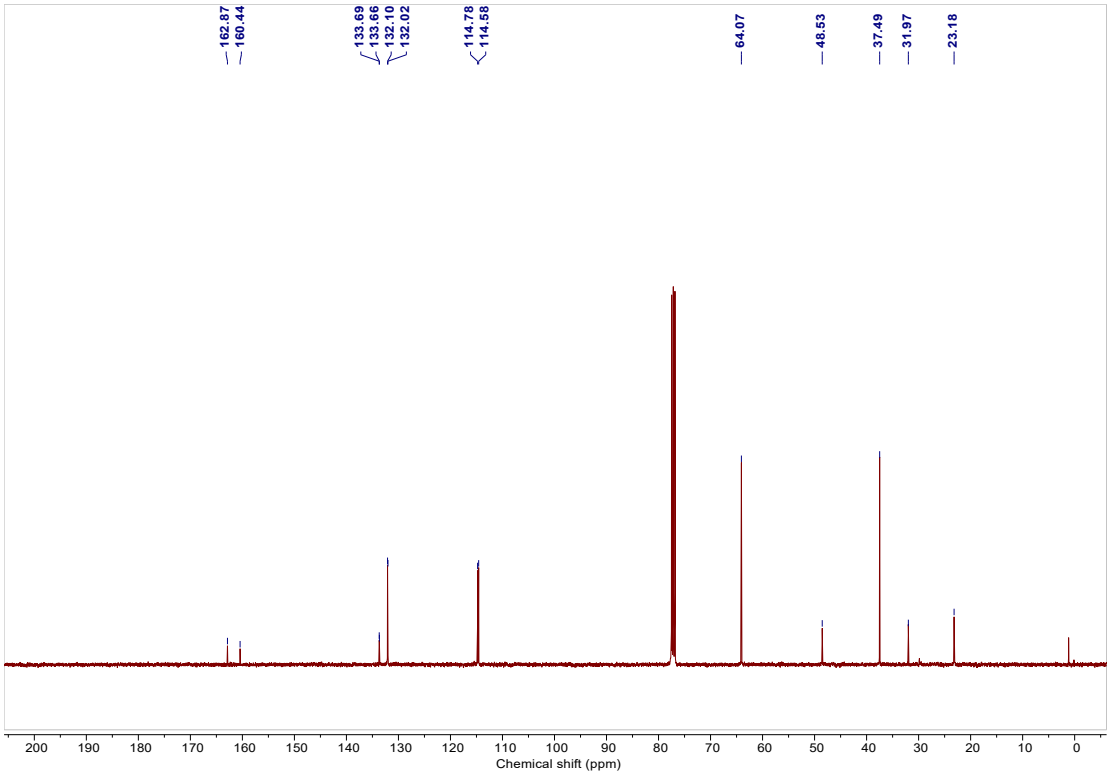
25: ^{13}C NMR (100 MHz, Chloroform-*d*)



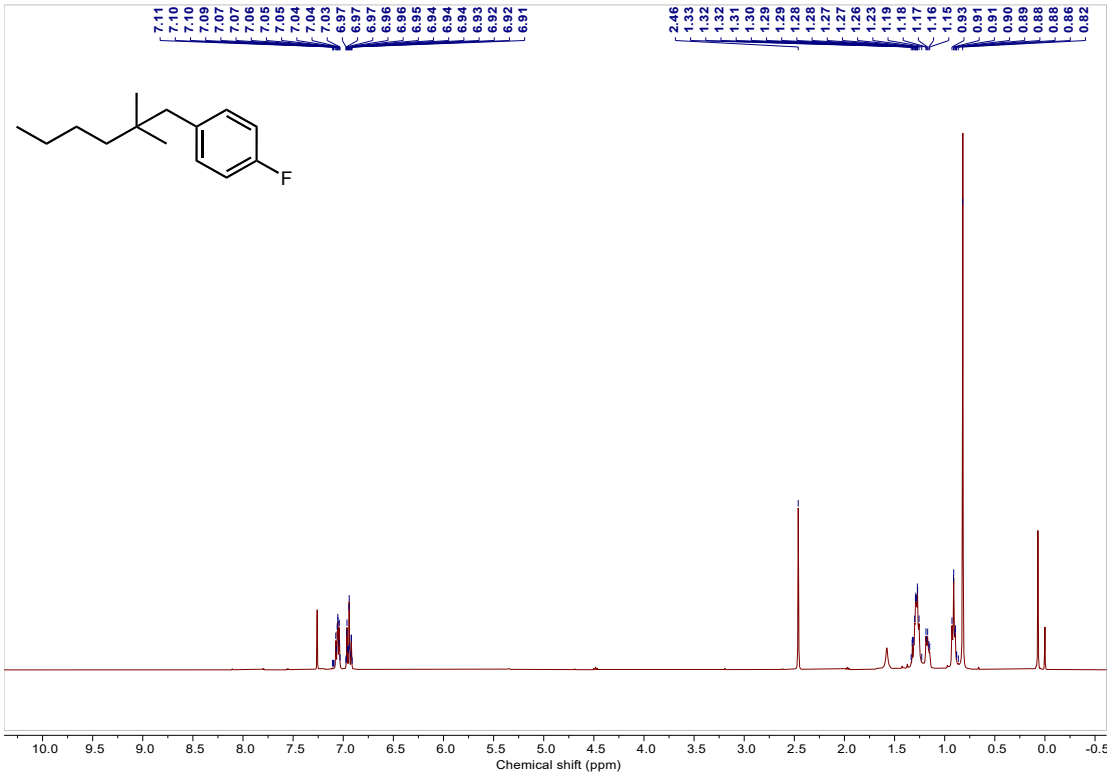
26: ^{1}H NMR (400 MHz, Chloroform-*d*)



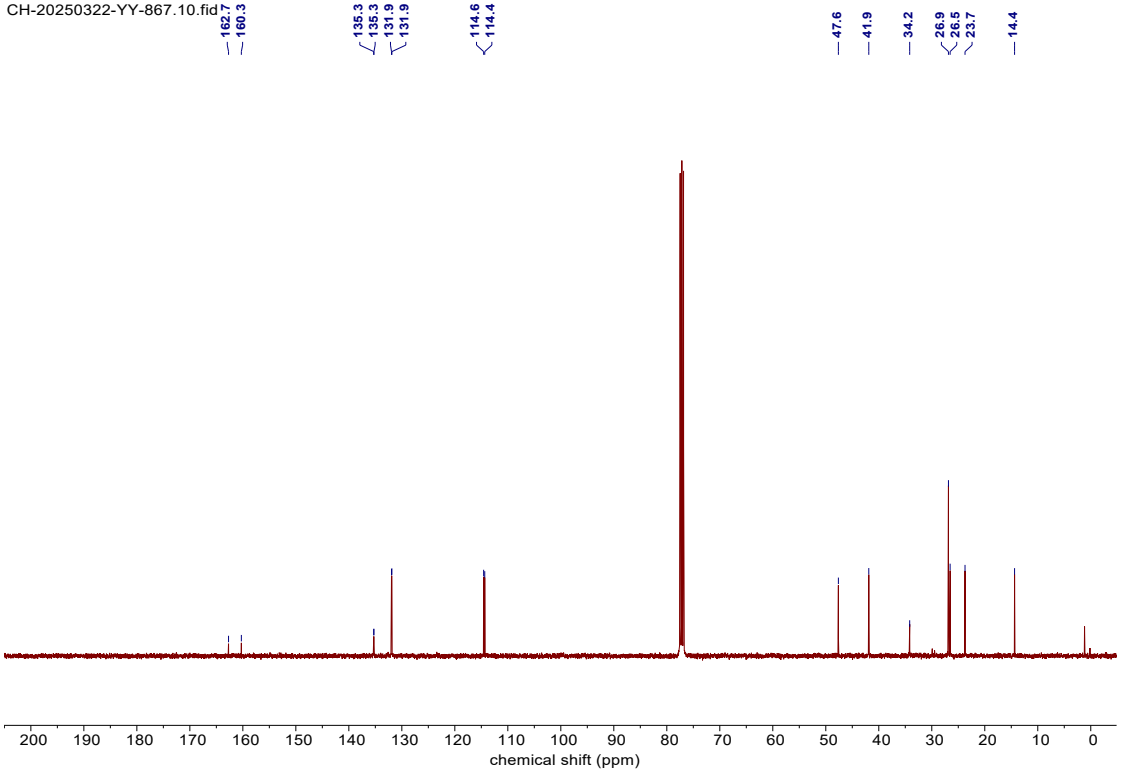
26: ^{13}C NMR (100 MHz, Chloroform-*d*)



27: ^{1}H NMR (400 MHz, Chloroform-*d*)



27: ^{13}C NMR (100 MHz, Chloroform-*d*)



11. References

(1) Zhang, W.; Gu, Y. C.; Lin, J. H.; Xiao, J. C. Dehydroxylative Fluorination of Tertiary Alcohols. *Org. Lett.* **2020**, *22*, 6642-6646.

(2) Huang, H. M.; Bellotti, P.; Pflüger, P. M.; Schwarz, J. L.; Heidrich, B.; Glorius, F. Three-Component, Interrupted Radical Heck/Allylic Substitution Cascade Involving Unactivated Alkyl Bromides. *J. Am. Chem. Soc.* **2020**, *142*, 10173-10183.

(3) Dudnik, A. S.; Fu, G. C. Nickel-Catalyzed Coupling Reactions of Alkyl Electrophiles, Including Unactivated Tertiary Halides, To Generate Carbon–Boron Bonds. *J. Am. Chem. Soc.* **2012**, *134*, 10693-10697.

(4) Chen, H.; Jia, X.; Yu, Y.; Qian, Q.; Gong, H. Nickel-Catalyzed Reductive Allylation of Tertiary Alkyl Halides with Allylic Carbonates. *Angew. Chem. Int. Ed.* **2017**, *56*, 13103-13106.

(5) Zhou, W. J.; Cao, G. M.; Shen, G.; Zhu, X. Y.; Gui, Y. Y.; Ye, J. H.; Sun, L.; Liao, L. L.; Li, J.; Yu, D. G. Visible-Light-Driven Palladium-Catalyzed Radical Alkylation of C-H Bonds with Unactivated Alkyl Bromides. *Angew. Chem. Int. Ed.* **2017**, *56*, 15683-15687.

(6) Wang, Z. Y.; Freas, D. J.; Fu, G. C. Phosphine Catalysis of the Fluorination of Unactivated Tertiary Alkyl Chlorides under Mild and Convenient Conditions. *J. Am. Chem. Soc.* **2023**, *145*, 25093-25097.

(7) Chen, H.; Liu, Z.; Lv, Y.; Tan, X.; Shen, H.; Yu, H. Z.; Li, C. Selective Radical Fluorination of Tertiary Alkyl Halides at Room Temperature. *Angew. Chem. Int. Ed.* **2017**, *56*, 15411-15415.

(8) Buettner , G. R. Spin trapping: ESR parameters of spin adducts. *Free Radical Biol. Med*. **1987**, *3*, 259–303.

(9) Li, P.; Zhu, Z.; Guo, C.; Kou, G.; Wang, S.; Xie, P.; Ma, D.; Feng, T.; Wang, Y.; Qiu, Y. Nickel-electrocatalysed C(sp^3)–C(sp^3) cross-coupling of unactivated alkyl halides. *Nat. Catal.* **2024**, *7*, 412-421.