Supporting Information for

Ti-Catalyzed Radical Alkylation of Secondary and Tertiary Alkyl Chlorides Using Michael Acceptors

Xiangyu Wu, Wei Hao, Ke-Yin Ye, Binyang Jiang, Gisselle Pombar, Zhidong Song, Song Lin*

correspondence to: songlin@cornell.edu

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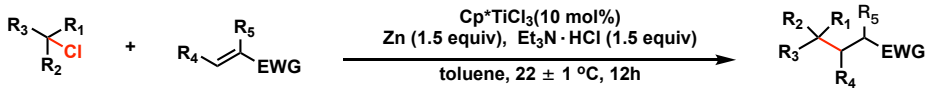
Section 1. General information

All reactions were conducted under a nitrogen atmosphere, unless otherwise noted. Flash chromatography was performed using silica gel 60 (230-400 mesh) from SiliCycle. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros, TCI, AK Scientific, and Oakwood and used as received with the following exceptions: toluene, dichloromethane, tetrahydrofuran, diethyl ether, and acetonitrile were dried by passing through columns of activated alumina; dimethylformamide was dried by passing through columns of activated molecular sieves; Toluene and ethyl acetate are dried over activated molecular sieves. Zinc powder is purchased form Fischer Scientific, catalog number is Z5-500. Triethylamine were distilled from CaH_2 at 760 torr. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Mercury-300 (300 MHz), Inova-400 (400 MHz) and Inova-500 (500 MHz) spectrometers. 2D NMR spectra were collected on Inova-600 (600 mHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0). Data are represented as follows: chemical shift, multiplicity (br. s = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using a Thermo Scientific Nicolet is10 FTIR spectrometer. Cyclic voltammetry data were measured with a BASi Epsilon potentiostat. The mass spectral data were obtained on a ThermoFisher Scientific Exactive series DART Mass Spectrometer. GC–MS data was collected on JMS-GC Mate II GCMS system.

Abbreviations: ^{t}Bu—*tert*-butyl, DMAP—4-dimethylaminopyridine, DCM—dichloromethane, Et_2O—diethyl ether, Et_3N—triethylamine, EtOAc—ethyl acetate, HOAc—acetic acid, K_2CO_3—potassium carbonate, mCPBA—m-chloroperbenzoic acid, MeCN—acetonitrile, MeOH—methanol, MsCl—methanesulfonyl chloride, PPh_3—triphenylphosphine, TBDMSCl—tert-butyldimethylsilyl chloride, TEMPO—(2,2,6,6-tetramethylpiperidin-1-yl)oxyl, THF—tetrahydrofuran, Ts—*p*-toluenesulfonyl, TMSCl—trimethylsilyl chloride.

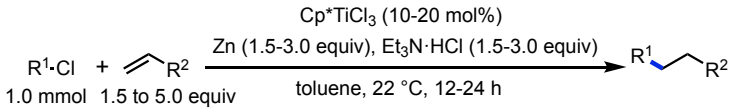
Section 2. General procedures for Ti-catalyzed radical alkylation of secondary and tertiary alkyl chlorides



Method A (0.1 mmol scale): In a N_2-filled glovebox, an oven-dried 8 mL culture tube equipped with a magnetic stir bar was charged with Zn (9.8 mg, 0.15 mmol, 1.5 equiv), $Et_3N{\cdot}HCl$ (20.6 mg, 0.15 mmol, 1.5 equiv) and a solution of Cp^*TiCl_3 in toluene (20 mM, 0.5 mL, 10 mol%). The mixture was stirred for 10 to 30 min till the color of solution changed from orange to green to allow reduction of the pre-catalyst. Subsequently, the alkene substrate (1.5 equiv) and alkyl chloride (0.10 mmol, 1.0 equiv) were added, and the resulting mixture was removed from the glovebox and stirred at room temperature (22 ± 1 °C) for 12 h. The reaction mixture was then all transferred onto a short silica gel column (1-1.5 cm in length, ca. 0.5 g) and flushed through with EtOAc (10 mL in total) to remove the inorganic salts and other insoluble solids. The product solution was concentration in vacuo and purified by flash chromatography on silica gel (5-6 cm in length, ca. 1.5 g) using hexanes/EtOAc to obtain the final product.

Note: For secondary alkyl chlorides, catalyst activation time is required to be longer than tertiary alkyl chlorides (ca. 30 to 60 mins). Besides, loading of reductant, proton source and catalyst also needs be modified accordingly. Detailed modification information is included in Table 3 in the main text and Section 4.

Figure S1. Pre-activation of the catalyst. Left: before pre-activation, showing red color from catalyst. Right: after pre-activation, showing green color of the Ti^{III} active catalyst.

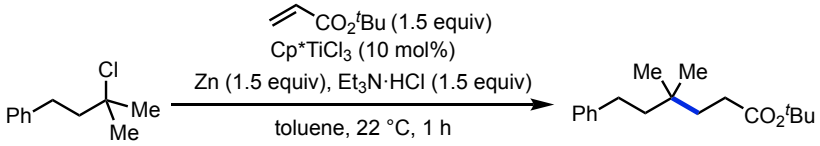


Method B (1.0 mmol scale): In a N_2-filled glovebox, an oven-dried 20 mL scintillation vial equipped with a magnetic stir bar was charged with Zn (1.5 to 3.0 equiv),

$Et_3N{\cdot}HCl$ (1.5 to 3.0 equiv) and a solution of Cp^*TiCl_3 in toluene (10 to 20 mol%). The mixture was stirred for 30 to 60 min till the color of solution changed from orange to green to allow full reduction of the pre-catalyst. Subsequently, the alkene (1.5 to 5.0 equiv) and alkyl chloride (1.0 mmol, 1.0 equiv) were added, and the resulting mixture was removed from the glovebox and stirred at room temperature (22 ± 1 °C) for 12 to 24 h. The reaction mixture was then flushed through a short pad of silica gel with EtOAc (200 mL in total) to remove the inorganic salts and other insoluble solids. The product solution was concentration in vacuo and purified by flash chromatography on silica gel using hexanes/EtOAc.

Reaction condition screening: Follow the general Method A, different reaction conditions were screened. Internal standard 1,3,5-trimethoxylbenzene was added before work-up, NMR yields were reported.

Table S1. Reaction Optimization.

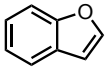
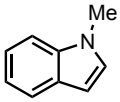
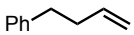
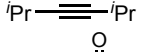
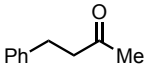
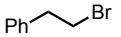
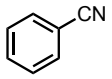


Entry	Variation from standard conditions	Yield (%)
1	None	70
2	$CpTiCl_3$ instead of Cp^*TiCl_3	10
3	Cp_2TiCl_2 instead of Cp^*TiCl_3	22
4	$Cp^*{}_2TiCl_2$ instead of Cp^*TiCl_3	21
5	**12 h reaction time**	**98**
6[a]	No Ti Catalyst	<5
7[a]	No Zn or $Et_3N \cdot HCl$	<5
8[a]	$Col \cdot HCl$ instead of $Et_3N \cdot HCl$	96
9[a]	Mn instead of Zn	<5
10[a]	DCM instead of Toluene	65
11[a]	EtOAc instead of Toluene	97
12[a]	MeCN or THF instead of Toluene	<5

All reactions were conducted on 0.1 mmol scale with NMR yields reported.
[a]Reaction time: 12 h.

Determination of functional compatibility using additive effect experiments

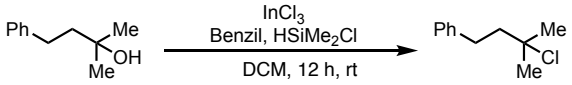
Procedure: In a N_2-filled glovebox, an oven-dried 8 mL culture tube equipped with a magnetic stir bar was charged with Zn (9.8mg, 0.15mmol, 1.5 equiv), $Et_3N{\cdot}HCl$ (20.6 mg, 0.15 mmol, 1.5 equiv) and a solution of Cp^*TiCl_3 in toluene (20 mM, 0.5mL, 10mol%). The mixture was stirred for 10 to 30 min till the color of solution changed from orange to green to allow reduction of the pre-catalyst. Subsequently, the additive (0.1 mmol, 1.0 equiv), the alkene substrate (1.5 equiv) and alkyl chloride (0.10 mmol, 1.0 equiv) were added sequentially. The resulting mixture was removed from the glovebox and stirred at room temperature (22 ± 1 °C) for 12 h. The reaction mixture was then all transferred onto a short silica gel column (1-1.5 cm in length, ca. 0.5 g) and flushed through with EtOAc (10mL in total) to remove the inorganic salts and other insoluble solids. The yields of **3** and recovery yields of **70**, **73**, **75**, and **77** were determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard. In another parallel reaction, a solution of a measured amount of *n*-dodecane standard in EtOAc was added to the reaction mixture after filtration through silica. After thoroughly mixing the resulting solutions, a ~1 mL aliquot was taken for each sample and analyzed by GC-flame ionization detection. The recovery of the additive was calculated based on a calibrated response factor (RF).

Additives	Area additive	Area internal standard	Recovery (%)	RF
	563.313	1023.8	98.26463668	1.78592248
	748.968	1212.8	95.05485131	1.53921828
	604.841	827.866	85.04321665	1.1640148
	555.351	904.089	84.18118758	1.37043574
	634.125	982.288	92.78763543	1.43732199
	355.596	633.939	87.86840288	1.56647452
	383.595	986.04	72.44644073	1.86225286
	398.138	766.403	83.71354576	1.61145916

Section 3. Preparation and characterization of substrates

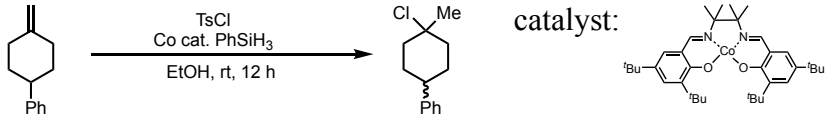
General information: Substrate **2**, **4**, **8**, **10**, **12**, **18**, **20**, **22**, **24**, **26**, **32, 46, 52, 56** were purchased from commercial sources and used as received. Other substrates are synthesized according literature procedures with minor modifications when necessary.

Synthetic procedures:



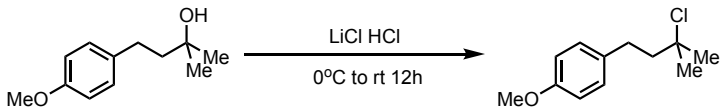
(3-chloro-3-methylbutyl)benzene (1). The synthesis of substrates followed literature with minor modification[1]. To a mixture of $InCl_3$ (0.2 mmol), benzil (2.0 mmol) and alcohol 1 (2.0 mmol) in dichloromethane (4.0 mL) was added chlorodimethylsilane ($HSiMe_2Cl$) (2.2 mmol) under nitrogen. The reaction mixture was stirred at room temperature for 12h. The resulting mixture was poured into aqueous $NaHCO_3$ (50 mL) and extracted with EtOAc (50 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified from the residue by flash column chromatography using hexanes. The product was separated from the residue by flash column chromatography using hexanes to afford **1** (310 mg, 92% yield) as a colorless liquid.

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 7.23-7.15 (m, 3H), 2.85-2.77 (m, 2H), 2.07-1.99 (m, 2H), 1.64 (s, 6H).



(4-chloro-4-methylcyclohexyl)benzene (34). Following literature with minor modification[2], cobalt catalyst (12 mg, 0.02 mmol, 2 mol %) was dissolved in EtOH (4 mL) at room temperature (RT) under argon. After 2 min, alkene (172 mg, 1.0 mmol)was added followed by TsCl (232 mg, 1.2 mmol, 1.2 equiv) and $PhSiH_3$ (1.0 mmol, 1.0 equiv). Another portion of EtOH (1 mL) was added. The resulting green solution was stirred at room temperature and the reaction was monitored by thin-layer chromatography (TLC). After completion the solvent was evaporated and the crude mixture purified by flash chromatography to afford the corresponding chloride **34** (117 mg, 56% yield), an 15:1 mixture of diastereomers, as a colorless liquid which matched literature spectra[2].

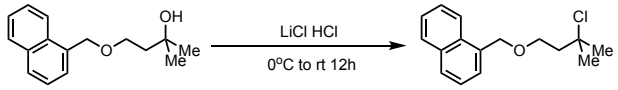
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.13 (m, 5H), 2.45 (tt, J = 12.3, 3.7 Hz, 1H), 2.17-2.03 (m, 2H), 1.98 (td, J = 12.9, 3.3 Hz, 2H), 1.76 (dd, J = 13.5, 3.6 Hz, 2H), 1.70-1.61 (m, 5H).



1-(3-chloro-3-methylbutyl)-4-methoxybenzene (40). Following literature with minor modification[3], an oven-dried flask was charged with LiCl (2.5 equiv), the solid was dissolved in concentrated HCl (0.5 M relative to substrate, v/v), capped with a rubber

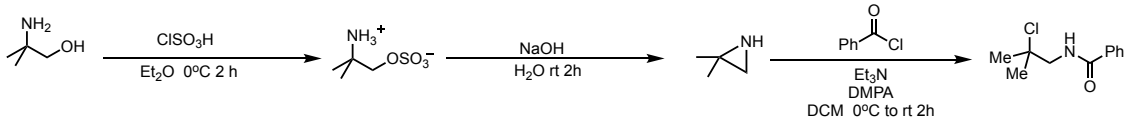
septum, and cooled to 0 °C. Alcohol was added to the flask, and the reaction was stirred at room temperature for 12 hours. The reaction mixture was extracted with DCM, washed once each with water, saturated $NaHCO_3$, and brine, dried with Na_2SO_4, and concentrated *in vacuo*, corresponding alkyl chloride was separated from the residue by flash column chromatography using EtOAc/hexanes to afford **40** (1.82 g, 82% yield) as colorless liquid which matched literature spectra[3].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 7.07 (m, 2H), 6.84-6.79 (m, 2H), 3.77 (s, 3H), 2.78-2.70 (m, 2H), 2.03-1.94 (m, 2H), 1.62 (s, 6H).



1-((3-chloro-3-methylbutoxy)methyl)naphthalene (36). An oven-dried round-bottom flask was charged with 3-methyl-1,3-butandiol (0.895 g, 8.6 mmol) and 5 mL DMF, and was placed in an ice bath. Sodium hydride (60% dispersion in mineral oil, 500 mg, 1.05 equiv) was carefully added to the solution in several portions, and the mixture was stirred for 10 minutes at 0 °C. Then 1-(bromomethyl)naphthalene (2.0 g, 1.05 equiv) was added to the mixture in several portions, then the ice bath was removed and resultant mixture was stirred at room temperature overnight. The reaction was quenched with saturated NH_4Cl solution, extracted with EtOAc, washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% EtOAc in hexanes) and subjected to next step without further purification. The alcohol product was further treated with chlorination conditons to afford **36** (149 mg, 14% yield) as colorless liquid.

IR (Film): 3055, 2959, 2924, 2867, 1602, 1509, 1454, 1370, 1343, 1271, 1124, 854, 815, 1100, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J=8.6, 1.9 Hz, 3H), 7.79 (d, J = 1.7 Hz, 1H), 7.53-7.45 (m, 3H), 4.69 (s, 2H), 3.77 (t, J = 6.7 Hz, 2H), 2.16 (t, J = 6.8 Hz, 2H), 1.64 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.94, 133.43, 133.11, 128.32, 128.02, 127.84, 126.47, 126.23, 125.98, 125.83, 77.41, 77.16, 76.91, 73.34, 69.65, 67.61, 45.33, 33.17; MS (DART) exact mass calculated for [$C_{16}H_{20}OCl^+$]: 263.1193, found 263.1194.



***N*-(2-chloro-2-methylpropyl)benzamide (38).**

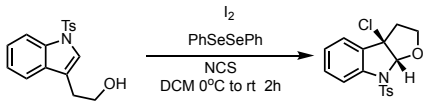
Note: This substrate was isolated as a byproduct from a previous project and its synthesis was not optimized.

The substrate was synthesized according to literature with minor modification[4,5]. An oven-dried two-necked round-bottom flask was fitted with a magnetic stirrer bar and an addition funnel. The flask was charged with a solution of 2-amino-2-methylpropan-1-ol (4.45 g, 50 mmol) in Et_2O (500 mL), the flask was cooled to 0 °C in an ice bath. Then, $ClSO_3H$ (5.82 g, 50 mmol) was slowly added under vigorous stirring; white solid was formed. The solution was stirred for 2 h at this temperature. The solid was collected via filtration and washed with Et_2O (3 × 50 mL). After drying under reduced pressure, the

amino alcohol hydrogen sulfate was obtained as colorless crystals. To an amino alcohol hydrogen sulfate (30 mmol) was added 6.2 M NaOH (24 mL), and the mixture was stirred at r.t. for 2 h, then distilled. The distillate was saturated with KOH pellets and the upper organic layer, which was separated, was extracted with DCM (3 × 20 mL). After drying over Na_2SO_4, the solution was subjected to next step without further purification.

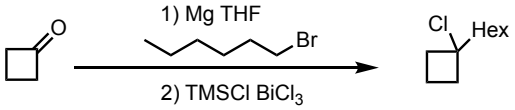
An oven-dried round-bottom flask was charged with 60 mL of 2,2-dimethylaziridine DCM solution (assume last step provided 80% yield), DMAP (292 mg, 0.1 equiv) and Et_3N (6.8 mL, 2.0 equiv). The mixture was placed in an ice bath, and benzoyl chloride (5.5 mL, 2.0 equiv) was added to the mixture dropwise. The reaction was stirred at room temperature overnight. The mixture was filtered through a short pad of silica gel, and concentrated *in vacuo*. The residue was purified by flash column chromatography using EtOAc/hexanes (2:3) and concentrated *in vacuo* to afford pale yellow solid. The solid was careful dissolved in a small amount DCM and recrystallized from hexanes to afford colorless needle-like crystals (541 mg, 8 % over 3 steps)

IR (Film): 3311, 2970, 2927, 1646, 1539, 1490, 1463, 1371, 1307, 1141, 1119, 710, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84-7.79 (m, 2H), 7.55-7.50 (m, 1H), 7.46 (dd, *J* = 8.3, 6.7 Hz, 2H), 6.59 (s, 1H), 3.72 (d, *J* = 6.2 Hz, 2H), 1.64 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.70, 134.38, 131.87, 128.83, 127.10, 77.41, 77.16, 76.91, 71.48, 51.65, 30.19; MS (DART) exact mass calculated for [$C_{11}H_{15}NOCl^+$]: 212.0834, found 212.0834.



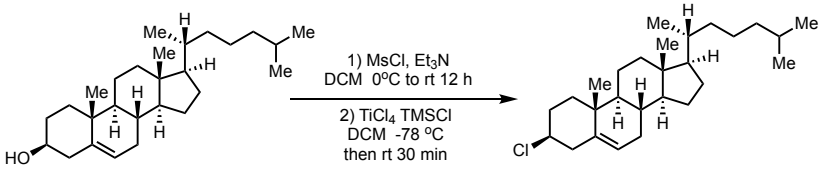
(3aR,8aS)-3a-chloro-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (44). The substrate was synthesized according to literature with minor modification[6,7]. An oven-dried pyrex Schlenk tube was charged with N-chlorosuccinimide (160 mg, 1.2 equiv), iodine (13 mg, 0.05 equiv), diphenyl diselenide (16 mg, 0.05 equiv) and DCM (5 mL) under nitrogen atmosphere. After being stirred for 10 min at room temperature, the mixture was cooled to 0 °C. 0.2 M solution of tryptamine derivative (315 mg, 1 mmol) in DCM (5 mL) was added to the mixture dropwise. After addition of tryptamine derivative, the ice bath was removed and stirred at room temperature for 1-2 h. After completion of the reaction (as monitored by TLC), the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ solution (5 mL). The organic phase was extracted with EtOAc (10 mL × 3), washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography using EtOAc/hexanes (30% EtOAc in hexanes) to afford the desired product **44** (281 mg, 81%) as pale yellow solid which matched literature spectra[7].

^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.50-7.44 (m, 1H), 7.35-7.26 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.11 (s, 1H), 4.08 (ddd, *J* = 9.1, 7.3, 1.6 Hz, 1H), 3.52-3.43 (m, 1H), 2.73 (td, *J* = 11.8, 7.4 Hz, 1H), 2.61 (dd, *J* = 12.5, 4.7 Hz, 1H), 2.35 (s, 3H).



1-(1-chlorocyclobutyl)hexan-1-one (48). An oven-dried three-neck flask equipped with a stir bar was fitted with condenser and backfilled with N2, activated Magnesium turnings (326 mg, 1.2 equiv) was charged in the flask. *n*-HexBr (12.1 mmol, 2.0g, 1.0 equiv) was dissolved in anhydrous THF, and a small portion of *n*-HexBr mixture was added to the flask. The mixture was heated gently until the color the solution started to change, then the rest of *n*-HexBr mixture was added dropwise to keep the mixture gently boiling. After addition, the mixture was refluxed for 2h. Freshly made Grignard reagent was added to a solution of cyclobutanone (10 mmol, 700mg) in anhydrous Et_2O dropwise at -78°C, the reaction mixture was warmed up gently to room temperature and was stirred at this temperature overnight. The mixture was quenched with water, extracted with DCM for 3 times, washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the crude product was purified with silica gel chromatography with 10% EtOAc in hexanes. The alcohol product (1 mmol, 156 mg) was subjected to a mixture of TMSCl (2.0 mmol, 216 mg, 2.0 equiv) and $BiCl_3$ (5mol%, 15.8 mg). The reaction mixture was stirred at 40 °C for 4h. The mixture was quenched with water, extracted with DCM for 3 times, washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the crude product was treated TBAF (1.5 mmol , 1.0 M solution, 1.5 mL) for 2h. The mixture was quenched with water and extracted with EtOAc for 3 times, washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the mixture was purified with silica gel chromatography with pure hexanes to afford final product (82% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.51 (tdd, J = 10.1, 7.6, 2.6 Hz, 2H), 2.36-2.27 (m, 2H), 2.17-2.05 (m, 1H), 1.91-1.83 (m, 2H), 1.83-1.74 (m, 1H), 1.53-1.41 (m, 2H), 1.40-1.23 (m, 6H), 0.94-0.90 (m,3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 72.54, 42.59, 38.71, 31.95, 29.37, 24.79, 22.76, 15.63, 14.23.

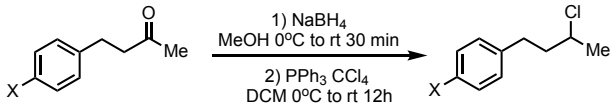


3β-Chloro-5-cholestene (66). The substrate was synthesized according to literature with minor modification[8]. To a solution of alcohol cholesterol (1 g, 2.6 mmol, 1.0 equiv) in anhydrous DCM (10 mL) at 0 °C was added freshly distilled Et_3N (0.54 mL, 1.5 equiv), followed by the addition of a solution of MsCl (0.213 mL, 1.05 equiv) in anhydrous DCM (1 mL) dropwise. The reaction was maintained at 0 °C for 30 min, warmed to room temperature, and stirred for 12 h. When the alcohol was consumed as evidenced by TLC (eluent: hexanes / EtOAc, 5:1), the reaction was concentrated in vacuo. The residue was purified by recrystallization from small amount of DCM and MeOH to afford corresponding methanesulfonate as a white solid.

To a solution of methanesulfonate (1.0 mmol, 1.0 equiv) in anhydrous DCM (10 mL) was added TMSCl (140 μL, 1.1 mmol). The reaction was cooled to -78 °C. $TiCl_4$ (1.0 M, 0.5 mL, 0.5 mmol) was added dropwise, the mixture was warmed up to room temperature. After 30 min, DCM (25 mL) and saturated $NaHCO_3$ aqueous solution (20 mL) were added

to quench the reaction. The organic phase was separated, and the aqueous phase was extracted with DCM (20 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified with silica gel column chromatography using pure hexanes followed by recrystallization using small amount of DCM and hexanes, to afford **66** (400 mg, 99%) as white solid which matched with literature spectra[8].

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (d, *J* = 5.1 Hz, 1H), 3.77 (td, *J* = 11.8, 6.0 Hz, 1H), 2.70-2.38 (m, 2H), 2.14-1.75 (m, 6H), 1.64-0.78 (m, 32H), 0.67 (s, 3H).



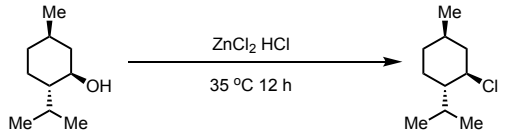
Method C. The substrate was synthesized according to literature with minor modification[3]. An oven-dried round-bottom flask equipped with a stir bar was fitted with a rubber septum and backfilled with N_2. $NaBH_4$ (4.0 equiv) and anhydrous MeOH (15 mL) were added before placing the flask in an ice bath. Corresponding ketone (1.0 equiv) was added dropwise at 0 °C to control the evolution of gas from the reaction flask. Once the addition was complete the ice bath was removed and the reaction was stirred at room temperature for 1.5 hours. After the ketone was fully consumed (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ (10 mL), diluted with water (10 mL) to dissolve the precipitate, extracted with DCM (15 mL× 3), dried with Na_2SO_4, and concentrated *in vacuo* to yield corresponding secondary alcohol. The crude product was used directly in the subsequent chlorination. An oven-dried flask equipped with a stir bar was charged with PPh_3 (2.0 equiv) and CCl_4 (2.1 equiv) under N_2. Anhydrous DCM (0.2 M) was added and the mixture was placed in an ice bath and stirred for 10 minutes at 0 °C. Alcohol (1 equiv), diluted in 1:5 in DCM (v/v), was added dropwise at 0 °C. Upon addition of the alcohol, the ice bath was removed and the reaction stirred for overnight at room temperature. TLC was used to monitor the process of reaction. After complete consumption of alcohol, the reaction was concentrated *in vacuo* and diluted with 25% EtOAc in hexanes and filtered through a plug of silica. The filtrate was concentrated *in vacuo* and purified by silica gel chromatography using EtOAc/hexanes.

(3-chlorobutyl)benzene (60). Following Method C, 4-phenylbutan-2-one (1.48 g, 10 mmol) was treated with reduction followed by chlorination of alcohol. The crude product was purified with silica gel column chromatography using gradient eluent of 0-10% EtOAc in hexanes to afford **60** (1.03 g, 61% yield) as colorless liquid which matched with literature spectra[3].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.04 (m, 5H), 4.06–3.93 (m, 1H), 2.97-2.62 (m, 2H), 2.13-1.90 (m, 2H), 1.54 (d, J = 6.5 Hz, 3H).

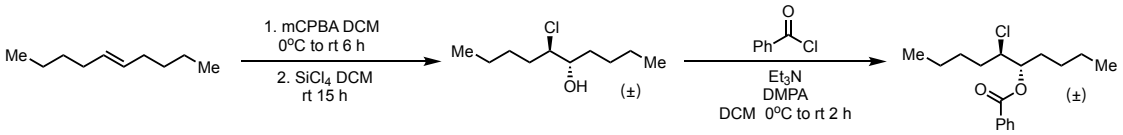
1-(3-chlorobutyl)-4-methoxybenzene (62). Following Method C, 4-(4-Methoxyphenyl)-2-butanol (1.00 g, 5.61 mmol) was treated with reduction followed by chlorination of alcohol. The crude product was purified with silica gel column chromatography using gradient eluent of 0-20% EtOAc in hexanes to afford **62** (867 g, 78% yield) as colorless liquid which matched with literature spectra[3].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.2 Hz, 2H), 4.03-3.93 (m, 1H), 3.79 (s, 3H), 2.84-2.74 (m, 1H), 2.73-2.64 (m, 1H), 1.97 (tt, J = 8.4, 4.9 Hz, 2H), 1.52 (dd, J = 6.5, 1.0 Hz, 3H).



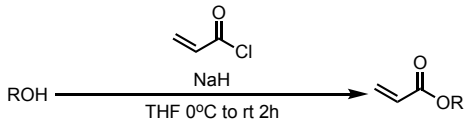
(1S,2R,4R)-2-chloro-1-isopropyl-4-methylcyclohexane (58). The substrate was synthesized according to literature with minor modification[9]. Lucas reagent was prepared by dissolving anhydrous zinc chloride (9.00 g, 66 mmol) in hydrochloric acid (37%, 73.2 mmol HCl) and the mixture was cooled to 0 °C. To the mixture, (-) menthol (3.125 g, 30 mmol) was added and was allowed to stir vigorously at 35 °C for 12 hours. The mixture was then cooled and extracted with Et_2O (50 ×3 mL), washed with water and then with sulfuric acid aqueous solution (2.0 M) until the latter was no longer discolored. The organic layer was then washed with water a few times and was dried with Na_2SO_4. The crude product was purified with silica gel column chromatography using gradient eluent of 0-10% EtOAc in hexanes to afford **58** (1.05 g, 30% yield) as colorless liquid which matched with literature spectra[10]. The synthesis of this substrate was not optimized.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (tdd, J = 11.1, 4.2, 2.0 Hz, 1H), 2.34 (dddt, J = 14.0, 6.9, 4.9, 2.5 Hz, 1H), 2.22 (ddq, J = 11.7, 4.8, 2.4 Hz, 1H), 1.77-1.66 (m, 2H), 1.47-1.32 (m, 2H), 1.09-0.95 (m, 2H), 0.94-0.86 (m, 8H), 0.77 (dd, J = 7.0, 2.0 Hz, 3H).



5-chlorononan-4-yl benzoate (64). An oven-dried round-bottom flask was charged with mCPBA (2.83 g, 1.2 equiv) in 50 mL of DCM and placed in an ice bath. A solution of trans-5-decene (1.40 g, 10 mmol) dissolved in 10 mL DCM was added to the mixture over 30 minutes. The ice bath was removed after addition, and the mixture was stirred at room temperature for 6 hours. After the reaction was complete (monitored by TLC) was quenched at room temperature, filtered, washed with 10% $NaHCO_3$, dried over anhydrous Na_2SO_4 and was concentrated *in vacuo*. The crude epoxide product was directly subjected to next step with further purification. In an oven-dried flask charged with a magnetic stir bar, a solution of crude epoxide product in DCM (10 mL) was treated with tetrachlorosilane (12 mL, 1.0 M in DCM). The mixture was stirred at room temperature for 15 hours, then was quenched with saturated KF solution (20 mL) and $NaHCO_3$ solution (10 mL). The solution was stirred vigorously for another 6 hours. Then the solution was extracted with Et_2O and concentrated *in vacuo*. The crude product was directly subjected to next step. In an oven-dried round-bottom flask was charged with crude alcohol product (578 mg, 3 mmol) in 30 mL DCM, DMAP (37 mg, 0.1 equiv) and Et_3N (0.834 mL, 2.0 equiv). The mixture was placed in an ice bath, and benzoyl chloride (0.417 mL, 1.2 equiv) was added to the mixture dropwise. The reaction was stirred at room temperature overnight. The mixture was filtered through a short pad of silica gel and concentrated *in vacuo*. The residue was purified by flash column chromatography using EtOAc/hexanes (1:4) and concentrated *in vacuo* to afford **64** (712 mg, 80% yield of acylation) as pale yellow oil.

IR (Film):2957, 2928, 2872, 1720, 1451, 1314, 1270, 1176, 1108, 1069, 1026, 710 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.10-8.04 (m, 2H), 7.62-7.54 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.26 (ddd, *J* = 9.4, 4.4, 3.3 Hz, 1H), 4.13 (dt, *J* = 9.9, 4.0 Hz, 1H), 1.97-1.58 (m, 2H), 1.46-1.25 (m, 4H), 0.91 (dt, *J* = 11.1, 7.2 Hz, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.23, 133.25, 130.25, 129.89, 128.58, 77.41, 77.16, 76.91, 76.52, 64.37, 33.82, 29.71, 28.91, 27.65, 22.68, 22.29, 14.09, 14.06; MS (DART) exact mass calculated for [$C_{17}H_{26}O_2Cl^+$]: 297.1610, found 297.1614.



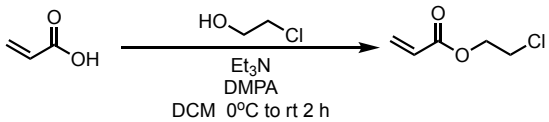
Method D. In an oven-dried round-bottom flask, to a solution of corresponding phenol (1.0 equiv) in THF (the concentration of substrate is 0.2 M to 0.5 M), NaH or was added at 0 °C. The mixture was stirred for 15 min, and a solution of acryloyl chloride (1.2 equiv) in THF was added dropwise, the reaction was stirred for another 2 hours and quenched with water. The mixture was extracted with EtOAc for 3 times and washed with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using EtOAc/hexanes.

4-bromophenyl acrylate (14). 4-Bromophenol (1.00 g, 5.78 mmol) was treated Method D using NaH and THF. EtOAc/hexanes (4:1) was used to purify the product, affording **14** (1.36 g, 86% yield) as pale-yellow liquid which matched with literature spectra[11].

^1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.47 (m, 2H), 7.09-6.97 (m, 2H), 6.61 (dd, *J* = 17.3, 1.2 Hz, 1H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.03 (dd, *J* = 10.4, 1.2 Hz, 1H).

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl acrylate (16). 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (850 mg, 3.86 mmol) was treated Method D using NaH and THF. EtOAc/hexanes (4:1) was used to purify the product, affording **16** (707 mg, 69% yield) as white solid.

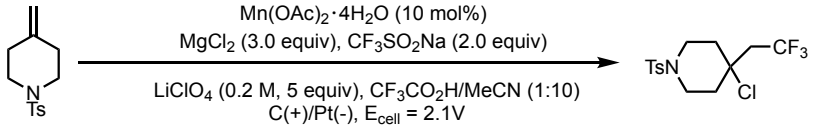
IR (Film): 2957, 2924, 1743, 1602, 1460, 1361, 1200, 1143, 1088, 1018, 859, 651 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.88-7.81 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.61 (dd, *J* = 17.3, 1.2 Hz, 1H), 6.32 (dd, *J* = 17.3, 10.5 Hz, 1H), 6.01 (dd, *J* = 10.5, 1.3 Hz, 1H), 1.34 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.46, 153.25, 136.34, 132.78, 128.07, 121.04, 84.05, 25.00; MS (DART) exact mass calculated for [$C_{15}H_{20}BO_4^+$]: 274.1480, found 274.1482.



2-chloroethyl acrylate (6). In an oven-dried round-bottom flask was charged with acrylic acid (3.0 g, mmol) in 30 mL DCM, DMAP (250 mg, 0.1 equiv) and DCC (0.834 mL, 2.0 equiv). The mixture was placed in an ice bath, and 2-chloroethan-1-ol (0.417 mL, 1.2 equiv) was added to the mixture dropwise. The reaction was stirred at room temperature overnight. The mixture was filtered through a short pad of celite and concentrated *in vacuo*.

The residue was firstly distilled to separate from polymerized impurities and subsequently purified by flash column chromatography using EtOAc/hexanes (1:9) and concentrated *in vacuo* to afford **6** (574 mg, 10% yield) as a pale-yellow oil which matched with literature spectra[12].

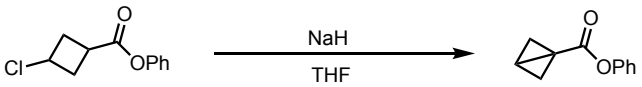
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.44 (dt, *J* = 17.3, 1.3 Hz, 1H), 6.13 (ddd, *J* = 17.3, 10.4, 1.0 Hz, 1H), 5.86 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.39 (td, *J* = 5.8, 1.1 Hz, 2H), 3.70 (td, *J* = 5.7, 0.9 Hz, 2H).



4-chloro-1-tosyl-4-(2,2,2-trifluoroethyl)piperidine (42). The substrate is synthesized according to literature[13]. An oven-dried, undivided electrochemical cell was equipped with a magnetic stir bar, a carbon felt anode (1×0.5×0.3 cm^3 connected to a 2B pencil lead), and a platinum plate cathode (0.5×1.0 cm^2). To this setup was added $Mn(OAc)_2$•$4H_2O$ (5.1 mg, 10 mol%), $MgCl_2$ (56.4 mg, 0.6 mmol, 3.0 equiv), and CF_3SO_2Na (62.4 mg, 0.4 mmol, 2.0 equiv). The cell was sealed using a rubber septum and flushed with nitrogen gas for 5 min, followed by the sequential addition via syringe of the electrolyte solution (0.2 M $LiClO_4$ in MeCN, 5.0 mL), olefin substrate (0.2 mmol, 1 equiv) and trifluoroacetic acid (0.5 mL). The reaction mixture was then purged with nitrogen gas for another 5 min. After piercing the septum with a nitrogen-filled balloon to sustain nitrogen atmosphere, electrolysis was initiated at a constant current of 15 mA at room temperature. The electrical input was removed after 4 h. The reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 15 mL). The aqueous layer was separated and extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield target product.

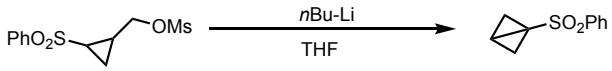
Followed modified above method from the corresponding olefin (50.2 mg, 0.20 mmol) using constant cell potential electrolysis (E_{cell} = 2.1V) for 4 h and purified using silica gel chromatography (hexanes/ethyl acetate = 10:1) to give 47.6 mg (67% yield) of **42** as a white solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.76-3.69 (m, 2H), 2.73 (ddd, *J* = 12.2, 10.3, 4.1 Hz, 2H), 2.65 (q, *J* = 10.5 Hz, 2H), 2.44 (s, 3H), 2.10-1.96 (m, 4H).



phenyl bicyclo[1.1.0]butane-1-carboxylate (28) The substrate is synthesized according literature[14].

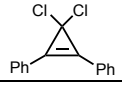
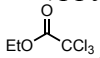
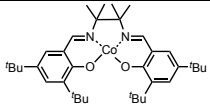
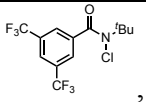
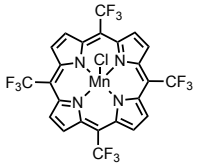
^{1}H NMR (400 MHz, $CDCl_3$ δ 7.40–7.31 (m, 2H), 7.21 (d, J=7.4 Hz, 1H), 7.10–7.04 (m, 2H), 2.51 (dt, J=3.5, 1.1 Hz, 2H), 2.32 (p, J=3.2 Hz, 1H), 1.29 (dt, J=3.0, 1.1 Hz, 2H).



1-(phenylsulfonyl)bicyclo[1.1.0]butane (30) The substrate is synthesized according literature[15].

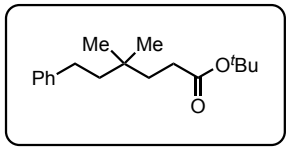
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.84 (m, 2H), 7.58-7.44 (m, 3H), 2.50 (t, J = 3.3 Hz, 1H), 2.45 (d, J = 3.7 Hz, 2H), 1.32 (d, J = 2.7 Hz, 2H).

Table S2. Summarized synthesis of alkyl chlorides from various functional groups

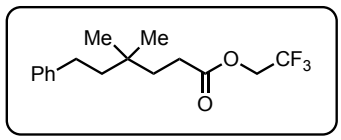
Entry	Substrate	Conditions	For the synthesis of	Reference
1	alcohol	$InCl_3$ (cat.), benzil, $HSiMe_2Cl$	2° and 3°	2
2	alcohol	$BiCl_3$ (cat.), TMSCl	2° and 3°	16
3	alcohol		2°	17
4	alcohol	PPh_3, CCl_4	2°	18
5	alcohol*	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (cat.),  , visible light	2° and 3°	19
6	alkene	 (ca.), TsCl, $PhSiH_3$	2° and 3°	3
7	alkene	PhSeSePh (cat.), $^nBu_4NCl$, TMSCl, *N*-fluoropyridinium tetrafluoroborate	2° and 3°	20
8	alkene	PhSeSePh (cat.), I_2, NCS	3°	6
9	alkene	$Mn(OTf)_2$ (cat.), $NaSO_2CF_3$, $MgCl_2$, electrolysis	2° and 3°	13
10	alkene	Acridinium catalyst, 2,6-lutidine-HCl, PhSH, visble light	2°	21
11	alkane	 , Cs_2CO_3, visble light	2° and 3°	22
12	alkane**	Visible light	2° and 3°	23
13	alkane	 , NaOCl	2°	24
14	alkane	$Ag(phen)_2OTf$ (cat), ^tBuOCl	2° and 3°	25
15	ketone	$In(OH)_3$ (cat.), $HSiMe_2Cl$	2°	26
16	ketone***	^tBuOCl, EtSH	2°	27

* Converting to cesium oxalates prior to chlorination.
** Directed intramolecular reaction using *N*-chlorosulfamate esters.
*** Converting to trityl hydrazones prior to chlorination.

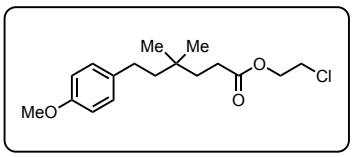
Section 4. Characterization of products



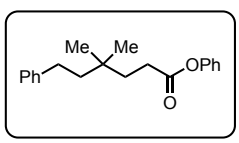
***tert*-butyl 4,4-dimethyl-6-phenylhexanoate (3).** Followed Method A with 1.5 equiv of alkene **2**, obtaining 26.6 mg (97% yield) of **3** as a pale-yellow oil. IR (Film): 2994, 2360, 1771, 1497, 1436, 1374, 1240, 1050, 913, 748, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.22-7.17 (m, 2H), 2.62-2.54 (m, 2H), 2.27-2.20 (m, 2H), 1.66-1.60 (m, 2H), 1.55-1.49 (m, 2H), 1.47 (s, 9H), 0.96 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.77, 143.26, 128.33, 128.29, 125.59, 80.05, 44.12, 36.48, 32.64, 30.84, 30.64, 28.12, 26.77; MS (DART) exact mass calculated for [$C_{18}H_{29}O_2^+$]: 271.2155, found 271.2152.



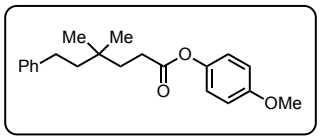
2,2,2-trifluoroethyl 4,4-dimethyl-6-phenylhexanoate (5). Followed Method A with 1.5 equiv of alkene **4**, obtaining 28.7 mg (95% yield) of **5** as a pale-yellow oil. IR (Film): 3027, 2959, 2869, 1759, 1497, 1412, 1278, 1075, 978, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (q, J = 9.9, 8.8 Hz, 2H), 7.25-7.19 (m, 3H), 4.50 (q, J = 8.5 Hz, 2H), 2.63-2.57 (m, 2H), 2.48-2.41 (m, 2H), 1.74-1.67 (m, 2H), 1.58-1.52 (m, 2H), 1.00 (s, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.78, 143.09, 128.52, 128.40, 125.83, 123.14 (q, J = 277.1 Hz), 60.40 (q, J = 36.5 Hz), 44.09, 36.30, 32.80, 30.73, 29.14, 26.74; ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.78, -73.80, -73.82; MS (DART) exact mass calculated for [$C_{16}H_{22}O_2F_3^+$]: 303.1561, found 303.1565.



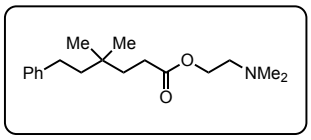
2-chloroethyl 6-(4-methoxyphenyl)-4,4-dimethylhexanoate (7). Followed Method A with 1.0 equiv of alkyl chloride **40** and 1.5 equiv of alkene **6**, and EtOAc as the solvent obtaining 29.8 mg (97% yield) of **7** as a pale-yellow oil. IR (Film): 2956, 1740, 1512, 1457, 1387, 1245, 1159, 1036, 913, 821, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.13-7.05 (m, 2H), 6.87-6.79 (m, 2H), 4.33 (dd, J = 6.3, 5.1 Hz, 2H), 3.79 (s, 3H), 3.68 (dd, J = 6.3, 5.1 Hz, 2H), 2.54-2.47 (m, 2H), 2.38-2.32 (m, 2H), 1.69-1.62 (m, 2H), 1.50-1.45 (m, 2H), 0.95 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.09, 157.78, 135.24, 129.24, 113.92, 64.06, 55.40, 44.35, 41.76, 36.46, 32.77, 29.76, 29.53, 26.83; MS (DART) exact mass calculated for [$C_{17}H_{26}O_3Cl^+$]: 313.1559, found 313.1561.



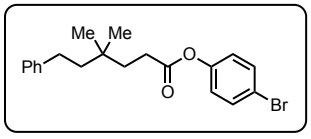
phenyl 4,4-dimethyl-6-phenylhexanoate (9). Followed Method A 1.5 equiv of alkene **8**, obtaining 18.3 mg (63% yield) of **9** as a pale-yellow oil. IR (Film): 2956, 1757, 1684, 1540, 1457, 1196, 1120, 1031, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.5, 7.4 Hz, 2H), 7.32-7.17 (m, 6H), 7.12-7.06 (m, 2H), 2.65-2.54 (m, 4H), 1.82-1.76 (m, 2H), 1.61-1.55 (m, 2H), 1.03 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.94, 150.91, 143.20, 129.55, 128.53, 128.45, 125.88, 125.82, 121.69, 44.19, 36.57, 32.94, 30.79, 29.94, 26.89; MS (DART) exact mass calculated for $[C_{20}H_{25}O_2^+]$: 297.1843, found 297.1838.



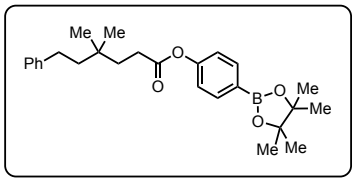
4-methoxyphenyl 4,4-dimethyl-6-phenylhexanoate (11). Followed Method A with 1.5 equiv of alkene **10**, obtaining 27.9 mg (86% yield) of **11** as a yellow oil. IR (Film): 2956, 1751, 1506, 1457, 1387, 1248, 1194, 1121, 1033, 911, 749, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 7.22-7.16 (m, 3H), 7.02-6.96 (m, 2H), 6.91-6.85 (m, 2H), 3.80 (s, 3H), 2.62-2.57 (m, 2H), 2.56-2.51 (m, 2H), 1.79-1.74 (m, 2H), 1.59-1.53 (m, 2H), 1.01 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.32, 157.31, 144.39, 143.20, 128.52, 128.44, 125.81, 122.41, 114.57, 55.72, 44.19, 36.59, 32.93, 30.79, 29.87, 26.89; MS (DART) exact mass calculated for $[C_{21}H_{27}O_3^+]$: 327.1948, found 327.1941.



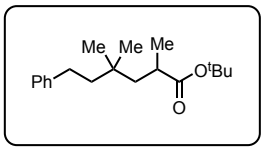
2-(dimethylamino)ethyl 4,4-dimethyl-6-phenylhexanoate (13). Followed Method A with 2 equiv of Zn, $Et_3N{\cdot}HCl$, and alkene **12**, at 40 °C, obtaining 22.7 mg (78% yield) of **13** as a yellow oil. IR (Film): 2955, 1734, 1647, 1521, 1457, 1374, 1241, 1164, 1033, 913, 747, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 7.20-7.14 (m, 3H), 4.17 (t, J = 5.8 Hz, 2H), 2.37-2.31 (m, 2H), 2.28 (s, 6H), 1.67-1.60 (m, 2H), 1.52-1.46 (m, 2H), 0.94 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.56, 143.27, 128.47, 128.41, 125.75, 62.30, 57.99, 45.88, 44.20, 36.44, 32.78, 30.75, 29.68, 26.86; MS (DART) exact mass calculated for $[C_{18}H_{30}NO_2^+]$: 292.2264, found 292.2257.



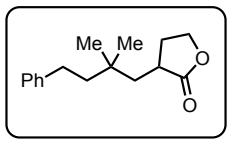
4-bromophenyl 4,4-dimethyl-6-phenylhexanoate (15). Followed Method A with 1.5 equiv of alkene **14**, obtaining 26.2 mg (70% yield) of **15** as a yellow oil, when cooled in fridge turned into solid. IR (Film): 3062, 3026, 2956, 2866, 1761, 1483, 1456, 1367, 1294, 1201, 1118, 1011, 941, 912, 843, 745, 721, 696, 501 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.31-7.24 (m, 2H), 7.22-7.16 (m, 3H), 6.99-6.94 (m, 2H), 2.62-2.57 (m, 2H), 2.57-2.52 (m, 2H), 1.80-1.72 (m, 2H), 1.59-1.52 (m, 2H), 1.01 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.60, 149.89, 143.12, 132.58, 128.53, 128.42, 125.84, 123.50, 118.94, 44.14, 36.52, 32.93, 30.78, 29.87, 26.86; MS (DART) exact mass calculated for $[C_{20}H_{24}O_2Br^+]$:375.9048, found 375.9050.



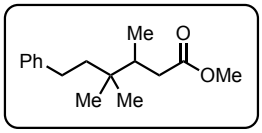
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl 4,4-dimethyl-6-phenylhexanoate (17). Followed Method A with 1.5 equiv of alkene **16**, obtaining 34.2 mg (81% yield) of **17** as a pale-yellow solid. Followed Method B with 1.5 equiv of Zn, $Et_3N{\cdot}HCl$, and alkene, obtaining 296 mg (70% yield) of **17** as a white solid. IR (Film): 2957, 1757, 1603, 1457, 1361, 1241, 1087, 1034, 913, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89-7.82 (m, 2H), 7.33-7.27 (m, 2H), 7.22 (dt, J = 8.0, 1.8 Hz, 3H), 7.14-7.08 (m, 2H), 2.66-2.54 (m, 4H), 1.83-1.76 (m, 2H), 1.62-1.55 (m, 2H), 1.37 (s, 12H), 1.03 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.67, 153.42, 143.18, 136.31, 128.52, 128.43, 125.81, 121.06, 84.02, 44.18, 36.52, 32.92, 30.79, 29.97, 26.89, 25.00; MS (DART) exact mass calculated for $[C_{26}H_{36}BO_4^+]$: 422.2728, found 422.2734.



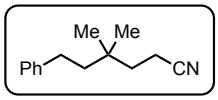
***tert*-butyl 2,4,4-trimethyl-6-phenylhexanoate (19).** Followed Method A with 1.5 equiv of alkene **18** and EtOAc as solvent, obtaining 28.4 mg (98% yield) of **19** as a pale-yellow oil. IR (Film): 2969, 1734, 1559, 1457, 1366, 1240, 1147, 1034, 913, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.13 (m, 3H), 2.55 (q, J = 8.0 Hz, 2H), 2.46-2.36 (m, 1H), 1.91 (dd, J = 14.2, 9.0 Hz, 1H), 1.50 (t, J = 8.8 Hz, 2H), 1.42 (s, 9H), 1.19 (dd, J = 14.2, 2.8 Hz, 1H), 1.14 (d, J = 7.1 Hz, 3H), 0.93 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.36, 143.49, 128.46, 128.43, 125.67, 79.86, 45.73, 44.83, 36.89, 33.60, 30.85, 28.10, 27.12, 27.00, 20.79; MS (DART) exact mass calculated for $[C_{19}H_{30}O_2^+]$: 291.2311, found 291.2315.



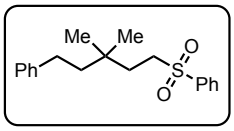
3-(2,2-dimethyl-4-phenylbutyl)dihydrofuran-2(3H)-one (21). Followed Method A with 2 equiv of Zn, $Et_3N{\cdot}HCl$, and alkene **20**, obtaining 9.8 mg (40% yield) of **21** as a pale-yellow oil. IR (Film): 2994, 1868, 1771, 1636, 1533, 1457,1374, 1241, 1049, 913, 743, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.18 (td, J = 6.0, 5.4, 2.3 Hz, 3H), 4.34 (td, J = 8.9, 1.6 Hz, 1H), 4.15 (ddd, J = 10.6, 9.0, 6.0 Hz, 1H), 2.66-2.46 (m, 4H), 2.15 (dd, J = 14.3, 2.0 Hz, 1H), 2.05-1.93 (m, 1H), 1.58-1.53 (m, 2H), 1.35 (dd, J = 14.4, 9.1 Hz, 1H), 1.01 (d, J = 2.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.38, 143.07, 128.54, 128.41, 125.85, 66.34, 44.75, 43.16, 36.24, 33.31, 31.94, 30.73, 27.48, 27.33; MS (DART) exact mass calculated for $[C_{16}H_{23}O_2^+]$: 247.1687, found: 247.1678.



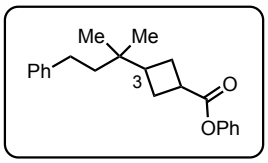
methyl 3,4,4-trimethyl-6-phenylhexanoate (23). Followed Method A with 1.5 equiv of alkene **22**, obtaining 12.5 mg (50% yield) of **23** as a pale-yellow oil. IR (Film): 2968, 1688, 1749, 1636, 1559, 1457, 1374, 1240, 1034, 913, 747, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.8 Hz, 2H), 7.20-7.15 (m, 3H), 3.68 (s, 3H), 2.62-2.53 (m, 2H), 2.50 (dd, *J* = 11.9, 7.5 Hz, 1H), 2.04-1.94 (m, 2H), 1.61-1.53 (m, 1H), 1.48 (ddd, *J* = 13.7, 10.3, 7.4 Hz, 1H), 0.95-0.85 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.77, 143.41, 128.50, 128.44, 125.77, 51.68, 42.89, 37.94, 37.08, 35.37, 30.47, 24.53, 24.33, 14.74; MS (DART) exact mass calculated for [$C_{16}H_{25}O_2^+$]: 249.1843, found: 249.1835.



4,4-dimethyl-6-phenylhexanenitrile (25). Followed Method A with 2 equiv of Zn, $Et_3N{\cdot}HCl$, and alkene **24**, obtaining 13.7 mg (68% yield) of **25** as a pale-yellow oil. IR (Film): 3026, 2958, 1717, 1653, 1559, 1457, 1368, 1275, 1031, 749, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2H), 7.22-7.15 (m, 3H), 2.60-2.53 (m, 2H), 2.33-2.27 (m, 2H), 1.73-1.68 (m, 2H), 1.54-1.49 (m, 2H), 0.98 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.64, 128.61, 128.38, 126.00, 120.60, 43.80, 37.39, 33.11, 30.65, 26.47, 12.52; MS (DART) exact mass calculated for [$C_{14}H_{20}N^+$]: 202.1586, found: 202.1589.

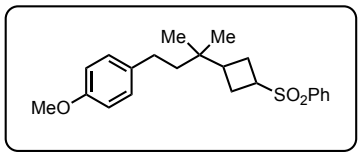


(3,3-dimethyl-5-(phenylsulfonyl)pentyl)benzene (27). Followed Method A with 2 equiv of Zn, $Et_3N{\cdot}HCl$, and alkene **26**, obtaining 28.1 mg (89% yield) of **27** as a pale yellow solid. Follow Method B with 1.5 equiv of Zn, $Et_3N{\cdot}HCl$, and alkene obtaining 267 mg (85% yield) of **27** as a white solid. IR (Film): 2955, 1735, 1446, 1368, 1304, 1149, 1087, 1031, 748, 699, 689, 562, 533 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96-7.89 (m, 2H), 7.70-7.64 (m, 1H), 7.58 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.30-7.24 (m, 2H), 7.21-7.15 (m, 1H), 7.14-7.07 (m, 2H), 3.10-3.03 (m, 2H), 2.50-2.43 (m, 2H), 1.73-1.66 (m, 2H), 1.48-1.41 (m, 2H), 0.92 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.63, 139.26, 133.81, 129.43, 128.55, 128.33, 128.17, 125.93, 52.64, 43.91, 33.72, 32.79, 30.55, 26.79; MS (DART) exact mass calculated for [$C_{19}H_{25}O_2S^+$]: 317.1564, found: 317.1568.

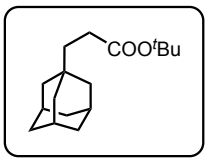


phenyl 3-(2-methyl-4-phenylbutan-2-yl)cyclobutane-1-carboxylate (29) Followed Method A with 1.5 equiv of alkene **28,** and using EtOAc as solvent, obtaining 28.9 mg (89% yield, 1.6:1 mixture of diastereomers, dr determinted by ^{13}C NMR using the ester carbon, major diastereomer could not be assigned using NMR) of **29** as a pale-yellow oil. IR (ATR):

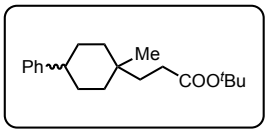
3063, 2973, 2925, 2890, 2864, 1721, 1439, 1153, 1118, 803, 740, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: the following resonances contain both major and minor diastereomers, which cannot be resolved: 7.46–7.36 (m, 2H), 7.35-7.17 (m, 6H), 7.16-7.08 (m, 2H), 3.16 (m, 1H), 2.58 (m, 2H), 2.41-2.20 (m, 4H), 1.54-1.44 (m, 2H); the following resonances can be tentatively assigned to the two diastereomeric products: 2.67-2.61 (m, minor diastereomer, H at C3), 2.30 (m, major diastereomers, H at C3), 0.96 (s, minor diastereomer, *gem*-Me), 0.95 (s, major diastereomer, *gem*-Me). ^{13}C NMR (126 MHz, $CDCl_3$) δ: the C resonances cannot be resolved using common techniques and are thus reported together: 175.08, 173.77, 151.05, 150.98, 143.45, 129.52, 129.50, 128.49, 128.42, 125.80, 125.78, 125.76, 121.66, 43.01, 42.55, 42.16, 41.62, 34.25, 34.19, 34.04, 33.43, 30.92, 30.83, 26.76, 25.78, 23.19, 22.85. MS (DART) exact mass calculated for [$C_{22}H_{27}O_2^+$]: 323.1999, found: 323.2006.



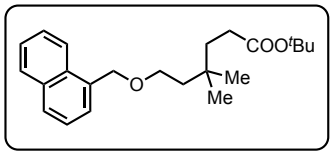
1-methoxy-4-(3-methyl-3-(3-(phenylsulfonyl)cyclobutyl)butyl)benzene (31) Followed Method A with 1 equiv of **40**, 1.0 equiv of $AlCl_3$ as Lewis additive, 1.5 equiv of alkene **30**, using EtOAc as solvent, obtaining 17.1 mg (46% yield, 3:1 mixture of diastereomers, dr determined by ^1H NMR using the MeO group), major diastereomer could not be assigned using NMR) of **31** as a white solid. IR (ATR): 2956, 2929, 2863, 1770, 1720, 1513, 1149, 1087, 822, 726 cm^{-1}. ^1H NMR (599 MHz, Chloroform-*d*) δ 7.95-7.77 (m, 2H), 7.65-7.59 (m, 1H), 7.56-7.50 (m, 2H), 7.03 (dd, J = 8.4, 6.1 Hz, 2H), 6.79 (dd, J = 8.6, 3.5 Hz, 2H), 3.78-3.79 (two singlets, each belong to one of the diastereomeric products, 3H), 3.55 (tt, J = 9.4, 7.7 Hz, 1H), 2.60-1.96 (m, this region contain 7H in total and the multiplicity cannot be resolved due to the two diastereomeric products with overlapping signal; they are thus reported together), 1.40-1.30 (m, 2H), 0.84 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: the C resonances cannot be resolved using common techniques and are thus reported together: 157.82, 138.36, 135.15, 133.68, 133.65, 129.35, 129.32, 129.23, 129.22, 128.48, 128.44, 113.96, 113.95, 55.42, 54.29, 52.70, 43.06, 42.45, 40.53, 39.92, 34.19, 34.14, 29.84, 29.73, 24.52, 23.42, 23.02, 22.63. MS (DART) exact mass calculated for [$C_{22}H_{29}O_3S^+$]: 373.1825, found: 373.1841.



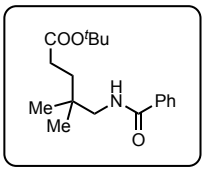
***tert*-butyl 3-((3r,5r,7r)-adamantan-1-yl)propanoate (33).** Followed Method A with 1 equiv of alkyl chloride **32** and 2 equiv of alkene **2**, obtaining 17.7 mg (67% yield) of **33** as a yellow oil. IR (Film): 2976, 2903, 2847, 1731, 1451, 1365, 1344, 1249, 1147, 1103, 1034, 952, 847, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.19-2.14 (m, 2H), 1.97-1.90 (m, 3H), 1.72-1.65 (m, 3H), 1.64-1.55 (m, 2H), 1.47-1.42 (m, 16H), 1.39-1.34 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.29, 80.01, 42.25, 39.18, 37.26, 32.05, 29.53, 28.77, 28.26; MS (DART) exact mass calculated for [$C_{17}H_{29}O_2^+$]: 265.2155, found: 265.2147.



***tert*-butyl 3-(1-methyl-4-phenylcyclohexyl)propanoate (35).** Followed Method A with 1 equiv of alkyl chloride **34** and 1.5 equiv of alkene **2**, obtaining 25.1 mg (83% yield, 2.6:1 mixture of diastereomers, in the major product, the acrylate is added on the same side as Ph) of **35** as a pale-yellow oil. The dr value was determined by ^{1}H NMR using the integral of methyl groups. The major product configuration was determined via analysis of COSY and ROSY. The 1.0 mmol scale reaction is conducted following Method B with 1.5 equiv of Zn, $Et_3N{\cdot}HCl$, and alkene obtaining 262 mg (87% yield) of **35** as a colorless oil. IR (Film): 2925, 2864, 1732, 1653, 1559, 1472, 1366, 1242, 1149, 1032, 913, 748, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.16 (m, 6H), 2.44 (ddt, *J* = 11.3, 7.9, 4.5 Hz, 1H), 2.28-2.22 (m, from minor diastereomer), 2.21-2.15 (m, from major diastereomer), 1.47 (two singlets, 9H, containing two overlapping diastereomers), 1.32 (m, 2H), 0.97 (s, from minor diastereomer), 0.90 (s, from major diastereomer); ^{13}C NMR (126 MHz, $CDCl_3$, diastereomeric resonances are reported together) δ 173.96, 173.90, 147.56, 147.46, 128.31, 128.29, 126.89, 126.82, 125.87, 80.07, 79.99, 44.66, 44.32, 40.64, 37.81, 37.67, 31.98, 31.69, 30.45, 30.37, 30.23, 29.76, 29.49, 29.16, 28.16, 28.14, 21.25; MS (DART) exact mass calculated for [$C_{20}H_{31}O_2^+$]: 303.2311, found: 303.2301.

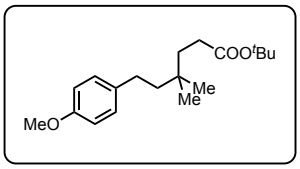


***tert*-butyl 4,4-dimethyl-6-(naphthalen-1-ylmethoxy)hexanoate (37).** Followed Method A with 1 equiv of alkyl chloride **36** and 1.5 equiv of alkene **2**, obtaining 27.4 mg (77% yield) of **37** as a pale-yellow oil. IR (Film): 2957, 2927, 2868, 1721, 1508, 1458, 1366, 1308, 1246, 1152, 1099, 913, 851, 815, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.80 (m, 3H), 7.78 (s, 1H), 7.49-7.44 (m, 2H), 4.66 (s, 2H), 3.58 (t, *J* = 7.4 Hz, 2H), 2.25-2.16 (m, 2H), 1.61 (t, *J* = 7.4 Hz, 2H), 1.58-1.51 (m, 2H), 1.43 (s, 9H), 0.90 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.82, 136.23, 133.45, 133.07, 128.24, 128.02, 127.81, 126.34, 126.14, 125.87, 125.84, 80.14, 73.25, 67.50, 40.97, 37.13, 32.01, 30.94, 28.23, 27.26; MS (DART) exact mass calculated for[$C_{23}H_{33}O_3^+$]: 357.2416, found: 357.2405.

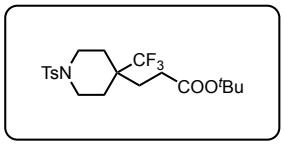


***tert*-butyl 5-benzamido-4,4-dimethylpentanoate (39).** Followed Method A with 1 equiv of alkyl chloride **38** and 1.5 equiv of alkene **2**, obtaining 27.8 mg (91% yield) of **39** as a white solid. IR (Film): 2964, 2930, 1729, 1646, 1540, 1367, 1307, 1152, 1032, 913, 846, 749, 695 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.51-7.38 (m, 3H), 6.69 (t, *J* = 6.5 Hz, 1H), 3.24 (d, *J* = 6.4 Hz, 2H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.60 (t, *J* = 7.4 Hz, 2H), 1.44 (s, 9H), 0.94 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.24, 167.57, 135.01,

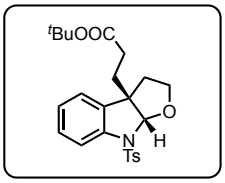
131.42, 128.68, 127.03, 80.78, 48.14, 34.77, 33.72, 30.41, 28.21, 25.36; MS (DART) exact mass calculated for [$C_{18}H_{28}NO_3^+$]:306.2057, found:306.2044.



***tert*-butyl 6-(4-methoxyphenyl)-4,4-dimethylhexanoate (41).** Followed Method A with 1 equiv of alkyl chloride **40** and 1.5 equiv of alkene **2**, obtaining 12.8 mg (42% yield) of **41** as a pale-yellow oil. IR (Film): 2956, 1733, 1653, 1540, 1457, 1364, 1246, 1150, 1037, 913, 746 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.07 (m, 2H), 6.84-6.80 (m, 2H), 3.78 (s, 3H), 2.55-2.46 (m, 2H), 2.23-2.17 (m, 2H), 1.62-1.55 (m, 2H), 1.45 (s, 11H), 0.93 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.92, 157.75, 135.45, 129.26, 113.91, 80.17, 55.42, 44.49, 36.62, 32.74, 30.98, 29.80, 28.26, 26.92; MS (DART) exact mass calculated for [$C_{19}H_{31}O_3^+$]: 307.2260, found:307.2263.

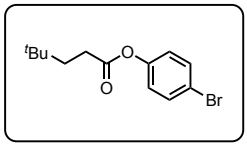


***tert*-butyl 3-(1-tosyl-4-(trifluoromethyl)piperidin-4-yl)propanoate (43).** Followed Method A with 1 equiv of alkyl chloride **42** and 1.5 equiv of alkene **2**, obtaining 15.7 mg (74% yield) of **43** as a colorless oil. The 1.0 mmol scale reaction is conducted following Method B with 2.0 equiv of Zn, $Et_3N{\cdot}HCl$, and 1.5 equiv of alkene obtaining 414 mg (93% yield) of **43** as a colorless oil. IR (Film): 2929, 2856, 1724, 1598, 1456, 1353, 1328, 1258, 1155, 1128, 1091, 1063, 934, 801, 724 cm^{-1}; ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.07 (ddd, J = 11.5, 6.8, 4.1 Hz, 2H), 2.99 (ddd, J = 12.1, 8.0, 3.9 Hz, 2H), 2.45 (s, 3H), 2.18-2.09 (m, 2H), 2.00 (q, J = 11.6 Hz, 2H), 1.74-1.60 (m, 6H), 1.41 (s, 9H); ^{13}C NMR: (126 MHz, $CDCl_3$) δ 172.3, 143.7, 133.2, 129.8, 127.6, 126.5 (q, J = 286.3 Hz), 80.7, 41.5, 39.3 (q, J = 26.4 Hz), 34.3, 32.3, 29.9, 29.4, 28.0, 21.6; ^{19}F NMR: (470 MHz, $CDCl_3$) δ –59.1 (t, J = 11.6 Hz); MS (EI) calculated for [$C_{21}H_{30}F_3NO_4S$]: 449.2, found 448.8.

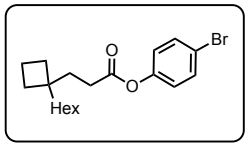


***tert*-butyl 3-((3aS,8aS)-8-tosyl-2,3,8,8a-tetrahydro-3aH-furo[2,3-b]indol-3a-yl)propanoate (45).** Followed Method A with 15 mol% catalyst loading, 1 equiv of alkyl chloride **44,** and 5 equiv of alkene **2**, obtaining 22.2 mg (50% yield, single diasteroisomer) of **45** as a pale yellow solid. The 1.0 mmol scale reaction is conducted following Method B with 15 mol% catalyst loading, 1.5 equiv of Zn, $Et_3N{\cdot}HCl$, and 5 equiv of alkene obtaining 414 mg (51% yield) of **45** as white solid after recrystallization. IR (Film): 2976, 2925, 1724, 1476, 1458, 1357, 1170, 1030, 1013, 751, 661 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91-7.85 (m, 2H), 7.42 (d, J = 8.2 Hz, 1H), 7.28-7.24 (m, 2H), 7.21 (td, J = 8.2,

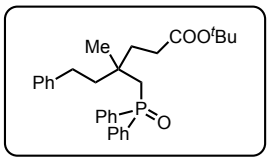
7.8, 1.4 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.02 (td, *J* = 7.5, 1.1 Hz, 1H), 5.81 (s, 1H), 3.96 (ddd, *J* = 8.6, 5.8, 2.4 Hz, 1H), 3.38-3.28 (m, 1H), 2.37 (s, 3H), 2.08 (ddd, *J* = 11.9, 9.0, 6.0 Hz, 3H), 1.95-1.66 (m, 3H), 1.39 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.05, 144.18, 141.87, 136.56, 133.24, 129.75, 128.93, 127.58, 124.06, 123.91, 113.16, 99.50, 67.55, 56.48, 40.30, 33.26, 31.39, 28.19, 21.73; MS (DART) exact mass calculated for [$C_{24}H_{29}NO_5S+NH_4^+$]: 461.2097, found: 461.2084.



***4*-bromophenyl 4,4-dimethylpentanoate (47).** Followed Method A with 4 equiv of alkyl chloride **46** and 1.0 equiv of alkene **14**, obtaining 21.4 mg (75% yield) of **47** as a colorless solid. IR (ATR): 3085, 3066, 2957, 2868, 1766, 1418, 1295, 1196, 1165, 1122, 1068, 961, 862 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.46 (m, 2H), 7.03-6.96 (m, 2H), 2.59-2.51 (m, 2H), 1.73-1.66 (m, 2H), 0.98 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.60, 149.81, 132.45, 123.39, 118.79, 38.46, 30.23, 30.20, 29.05. MS (DART) exact mass calculated for [$C_{13}H_{18}BrO_2^+$]: 285.0480, found: 285.0494.

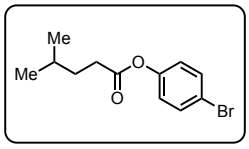


***4*-bromophenyl 3-(1-hexanoylcyclobutyl)propanoate (49).** Followed Method A with 1.0 equiv of alkyl chloride **48** and 1.5 equiv of alkene **14**, obtaining 21.4 mg (59% yield) of **49** as a pale-yellow oil. IR (ATR): 3062, 2958, 2928, 2858, 1766, 1724, 1486, 1251, 1165, 1128, 1068, 1011, 735 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 2.45-2.38 (m, 2H), 1.91-1.83 (m, 4H), 1.78-1.71 (m, 4H), 1.45-1.39 (m, 2H), 1.29 (q, J = 3.7, 3.1 Hz, 4H), 1.22-1.16 (m, 2H), 0.91-0.87 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.51, 149.81, 132.44, 123.39, 118.79, 40.93, 38.21, 33.16, 31.93, 31.40, 30.05, 29.60, 23.82, 22.72, 15.06, 14.13. MS (DART) exact mass calculated for [$C_{19}H_{27}BrO_2+NH_4^+$]:384.1525, found:384.1540.

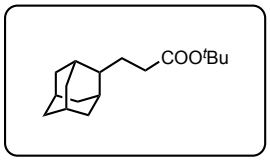


***tert*-butyl 4-((diphenylphosphoryl)methyl)-4-methyl-6-phenylhexanoate (51).** Followed Method A with 1.0 equiv of alkyl chloride **50** and 1.5 equiv of alkene **2**, obtaining 30.0 mg (63% yield) of **51** as a yellow oil. IR (ATR): 3062, 2973, 22925, 2890, 2864, 1721, 1439, 1152, 1118, 803, 740, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.70 (m, 4 H), 7.52 – 7.40 (m, 6 H), 7.22 (t, *J* = 7.4 Hz, 2 H), 7.14 (t, *J* = 7.3 Hz, 1 H), 7.08 (d, *J* = 7.3 Hz, 2 H), 2.55 (dd, *J* = 10.1, 7.2 Hz, 2 H), 2.37 (dd, *J* = 11.3, 5.0 Hz, 2 H), 2.17 (dd, *J* = 9.4, 7.0 Hz, 2 H), 1.79 – 1.74 (m, 4 H), 1.40 (s, 9 H), 1.06 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$)

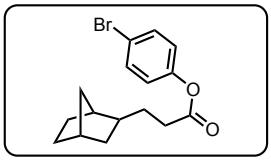
δ 173.16, 142.48, 135.74 (d, *J* = 15.0 Hz), 134.96 (d, *J* = 15.1 Hz), 131.54 (t, *J* = 2.8 Hz), 130.68 (dd, *J* = 9.0, 6.2 Hz), 128.75 (d, *J* = 11.5 Hz), 128.44 (d, *J* = 8.7 Hz), 125.79, 80.39, 42.43 (d, *J* = 6.2 Hz), 39.32, 38.76, 37.43 (d, *J* = 4.3 Hz), 36.07 (d, *J* = 8.6 Hz), 30.44 (d, *J* = 32.1 Hz), 28.20, 26.17 (d, *J* = 5.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.59. MS (DART) exact mass calculated for [$C_{30}H_{38}O_2P^+$]:477.2553, found: 477.2557.



***4*-bromophenyl 4-methylpentanoate (53).** Followed Method A with 20 mol% catalyst, 3.0 equiv of Zn and $Et_3N{\cdot}HCl$, 4.0 equiv of alkyl chloride **52** and 1.0 equiv of alkene **14**, and reaction time of 72 hours, obtaining 11.4 mg (42% yield) of **53** as a pale-yellow oil. IR (ATR): 2989, 2916, 2874, 1769, 1736, 1484, 1236, 1096, 1065, 1011, 848cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.33 (m, 2H), 7.10-6.85 (m, 2H), 2.75-2.30 (m, 2H), 1.65 (m, 3H), 1.03-0.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.22, 149.79, 132.44, 123.40, 118.78, 33.63, 32.43, 27.72, 22.24; MS (DART) exact mass calculated for [$C_{12}H_{16}O_2Br^+$]:271.0337, found:271.0324.

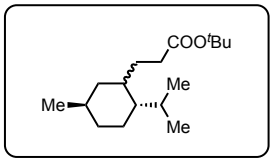


***tert*-butyl 3-((1r,3r,5r,7r)-adamantan-2-yl)propanoate (55).** Followed Method A with 1 equiv of alkyl chloride **46**, 3 equiv of Zn and $Et_3N{\cdot}HCl$, 1.5 equiv alkene **2**, obtaining 11.9 mg (45% yield) of **47** as a yellow oil. IR (Film): 2905, 2851, 1731, 1456, 1365, 1244, 1148, 1067, 848, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23-2.17 (m, 2H), 1.92-1.77 (m, 7H), 1.70 (d, *J* = 14.6 Hz, 6H), 1.65-1.46 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.82, 80.04, 44.18, 39.34, 38.51, 34.08, 31.80, 31.71, 28.41, 28.28, 28.19, 28.12; MS (DART) exact mass calculated for [$C_{17}H_{29}O_2^+$]: 265.2155, found: 265.2151.

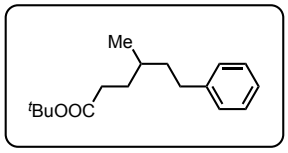


4-bromophenyl 3-((1S,4R)-bicyclo[2.2.1]heptan-2-yl)propanoate (57) Followed Method A with 20 mol% catalyst, 3.0 equiv of Zn and $Et_3N{\cdot}HCl$, 2.0 equiv of alkyl chloride **56** and 1.0 equiv of alkene **14**, and reaction time of 72 hours, obtaining 20.3mg (42% yield) of **57** as a pale-yellow solid. IR (ATR): 2946, 2868, 1758, 1480, 1354, 1279, 1201, 1163, 1126, 1064, 1007, 921, 843, 714cm^{-1}^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.36 (m, 2H), 7.13-6.82 (m, 2H), 2.51 (dd, J = 8.4, 7.0 Hz, 2H), 2.23 (t, J = 4.2 Hz, 1H), 2.01 (d, J = 3.6 Hz, 1H), 1.79-1.64 (m, 1H), 1.55-1.39 (m, 5H), 1.33 (dt, J = 9.8, 2.0 Hz, 1H), 1.20-0.96 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.27, 149.91, 132.56, 123.53, 118.90, 41.94,

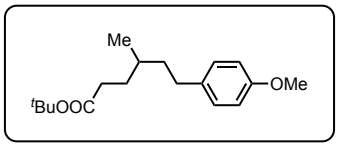
41.04, 38.04, 36.70, 35.40, 33.05, 31.82, 30.18, 28.84. MS (DART) exact mass calculated for [$C_{16}H_{20}O_2Br^+$]:323.0636, found: 323.0653.



***tert*-butyl 3-((2S,5R)-2-isopropyl-5-methylcyclohexyl)propanoate (59).** Followed Method A with 20 mol% catalyst, 3.0 equiv of Zn and $Et_3N{\cdot}HCl$, 1.0 equiv of alkyl chloride **58** and 1.0 equiv of alkene **2**, and reaction time of 72 hours, obtaining 20.1mg (74% yield, 1.8:1 mixture of diastereomers, alkyl chain containing *tert*-butyl group of major product is trans to *iso*-propyl group) of **59** as a pale-yellow oil. The dr value was determined by ^{13}C NMR using the ester carbon. The major product configuration was determined via analysis of HSQC, gCOSY and coupling constant. IR (Film): 1771, 1558, 1458, 1241, 1047, 913, 747 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$; number of H in each region is not assigned due to overlapping signal including two diastereomers) δ 2.33-2.20 (m), 2.18-1.95 (m), 1.82 (m), 1.74-1.55 (m), 1.45 (m, 9H, containing ^{t}Bu groups of two overlapping diastereomers), 1.37-1.19 (m), 1.14-0.78 (m), 0.72 (d, J = 6.9 Hz, 2H, tentatively assigned to Me of the major diastereomer), 0.62 (m); ^{13}C NMR (126 MHz, $CDCl_3$, two diastereomers are reported together) δ 173.92, 173.79, 80.11, 80.04, 48.42, 46.69, 40.99, 38.35, 38.03, 36.00, 35.45, 34.74, 34.10, 32.94, 32.45, 29.34, 28.29, 28.28, 28.05, 26.49, 25.98, 25.25, 24.42, 22.97, 22.94, 21.83, 21.75, 20.93, 20.60, 15.39; MS (DART) exact mass calculated for [$C_{17}H_{33}O_2^+$]: 269.2467, found: 269.2460.

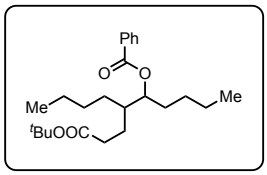


***tert*-butyl 4-methyl-6-phenylhexanoate (61).** Followed Method A with 1 equiv of alkyl chloride **60**, 3 equiv of Zn and $Et_3N{\cdot}HCl$, 3.0 equiv alkene **2**, obtaining 19.5 mg (41% yield) of **61** as colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.23 (m, 2H), 7.21-7.12 (m, 3H), 2.66 (ddd, J = 13.6, 10.4, 5.2 Hz, 1H), 2.61-2.53 (m, 1H), 2.22 (ddd, J = 15.4, 9.2, 6.1 Hz, 2H), 1.73-1.59 (m, 2H), 1.47 (td, J = 6.3, 4.9, 1.9 Hz, 3H), 1.43 (s, 9H), 0.94 (d, J = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.59, 142.96, 128.47, 128.43, 125.75, 80.14, 38.77, 33.49, 33.44, 32.21, 32.06, 28.25, 19.36. MS (DART) exact mass calculated for [$C_{17}H_{29}O_2^+$]: 265.2155, found: 265.2151.

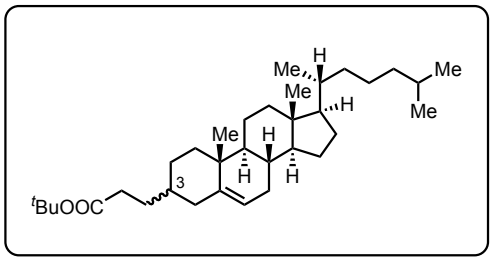


***tert*-butyl 6-(4-methoxyphenyl)-4-methylhexanoate (63).** Followed Method A with with 1 equiv of alkyl chloride **62** and 2 equiv of alkene **2**, obtaining 21.3 mg (73% yield) of **63** as a pale-yellow oil. IR (Film): 2994, 1884, 1771, 1647, 1533, 1241, 1050, 913, 749 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 3.78

(s, 3H), 2.56 (dddd, J = 40.6, 13.8, 10.0, 5.8 Hz, 2H), 2.22 (qdd, J = 15.4, 9.2, 6.2 Hz, 2H), 1.72-1.54 (m, 2H), 1.43 (m, 12H), 0.93 (d, J = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.59, 157.75, 135.02, 129.31, 113.85, 80.12, 55.40, 39.00, 33.44, 32.53, 32.12, 32.07, 28.25, 19.36; MS (DART) exact mass calculated for [$C_{18}H_{29}O_3^+$]: 293.2104, found: 293.2106.

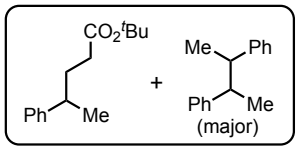


6-(3-(*tert*-butoxy)-3-oxopropyl)decan-5-yl benzoate (65). Followed Method A with 20 mol% catalyst, 1 equiv of alkyl chloride **64**, 3 equiv of Zn, $Et_3N{\cdot}HCl$ and alkene **2**, obtaining 20.7 mg (53% yield, 1.6:1 mixture of diastereomers, we were not able to determine the configuration of major product because of conformational flexibility of the main alkyl chain) of **65** as a pale-yellow oil. IR (Film): 2957, 2931, 2861, 1717, 1451, 1366, 1272, 1153, 1109, 1022, 711 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dt, J = 8.4, 1.4 Hz, 2H), 7.57-7.52 (m, 1H), 7.44 (t, J = 7.6 Hz, 2H), 5.20 (m, 1H), 2.41-2.32 (m, from minor product), 2.32-2.23 (m, 2H), 1.87-1.54 (m, 3H), 1.44 (s, from major product), 1.40 (s, from minor product), 1.37-1.22 (m, 10H), 0.88 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, two diastereomers are reported together) δ 173.26, 173.19, 166.42, 166.40, 132.87, 132.86, 130.84, 129.73, 129.71, 128.46, 80.28, 80.21, 76.41, 76.34, 40.94, 40.87, 33.71, 33.59, 31.07, 30.34, 29.82, 29.80, 29.65, 29.59, 28.29, 28.25, 28.20, 25.57, 25.06, 23.14, 23.05, 22.78, 22.74, 14.18, 14.14.; MS (DART) exact mass calculated for [$C_{24}H_{39}O_4^+$]:391.2833, found: 391.2827.

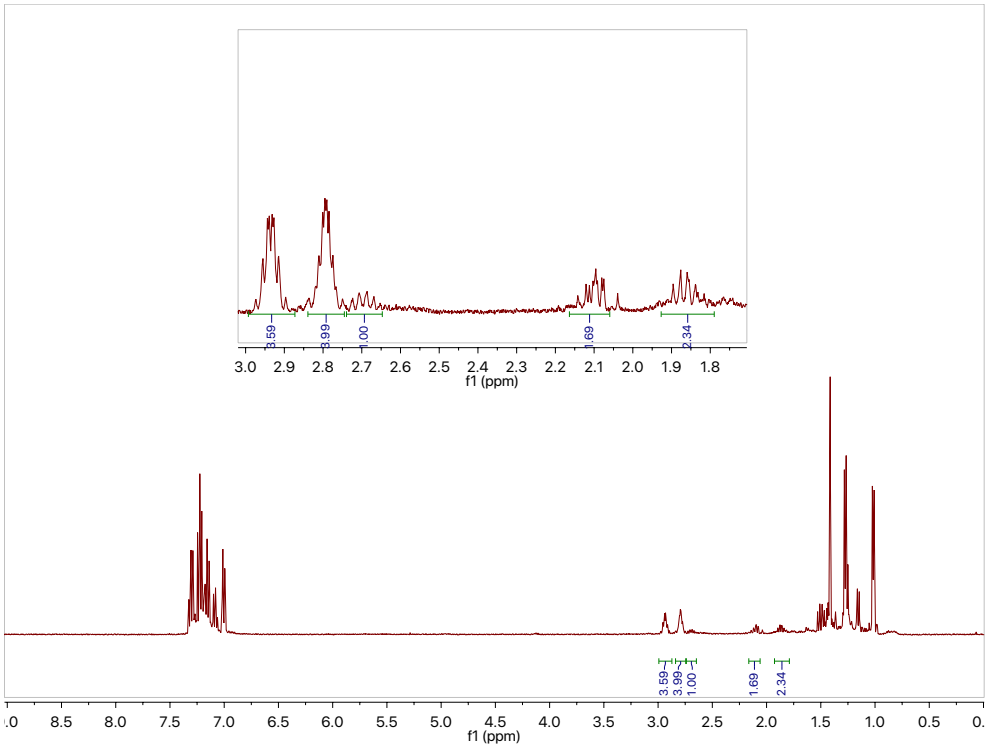


***tert*-butyl 3-((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)propanoate (67).** Followed Method A with 20 mol% catalyst, 1 equiv of alkyl chloride **66**, 3 equiv of Zn and $Et_3N{\cdot}HCl$, 4.0 equiv of alkene **2**, obtaining 23.0 mg (42% yield, the configuration of major product at 3 is *S*) of **67** as a yellow solid. The dr value was determined by ^{13}C NMR using the ester carbon. The major product configuration was determined via full series of 2D NMR. IR (Film): 2933, 2867, 1732, 1457, 1366, 1252,1147 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.26 (m, *J*, 1H), 2.47 (m, from major product), 2.26-2.10 (m, 2H), 2.05-1.63 (m, 4H), 1.62-0.77 (m, 18H), 1.45 (s, 9H from ^{t}Bu), 0.67 (two singlets, containing two overlapping diastereomers); ^{13}C NMR (126 MHz, $CDCl_3$, two diastereomers are reported together) δ 173.72, 173.59, 143.17, 140.37, 121.49, 119.63, 80.07, 80.03, 56.99, 56.31, 56.30, 50.59, 50.53, 42.45, 39.99, 39.68, 39.62, 39.44, 39.17, 37.54, 37.34, 36.88, 36.35, 35.97, 35.95, 34.06, 34.04, 33.82, 33.33, 32.39, 32.05, 32.04, 28.98, 28.41, 28.29, 28.27, 28.17, 26.13, 26.02, 24.44, 24.43, 24.00,

23.99, 22.98, 22.72, 21.07, 20.90, 19.62, 19.57, 18.87, 12.02, 12.00.; MS (DART) exact mass calculated for [$C_{34}H_{58}O_2$–$C_4H_9^+$]: 441.3715, found: 441.3722.



***tert*-butyl 4-phenylpentanoate** and **butane-2,3-diyldibenzene.** Followed Method A, obtaining 14.3 mg of a mixture of the alkylation and dimerization products. The ^{1}H NMR spectrum (see below) is consistent with literature[28, 29]. The peaks at 3.0-2.9 ppm correspond to the *d*,*l*-butane-2,3-diyldibenzene and those at 2.85-2.75 ppm correspond to *meso*-butane-2,3-diyldibenzene.[29] The peaks at 2.75-2.65, 2.15-2.05, and 1.9-1.8 correspond to *tert*-butyl 4-phenylpentanoate.[28]



Section 5. Cyclic voltammetry studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a $Ag/AgNO_3$ reference electrode, and a platinum wire counter electrode. The solution of interest was sparged with nitrogen for 3-5 minutes before data collection. Current was reported in μA, while all potentials were reported in mV against the $Fc^{+/0}$ redox couple. We did not apply iR compensation for these CV acquirements.

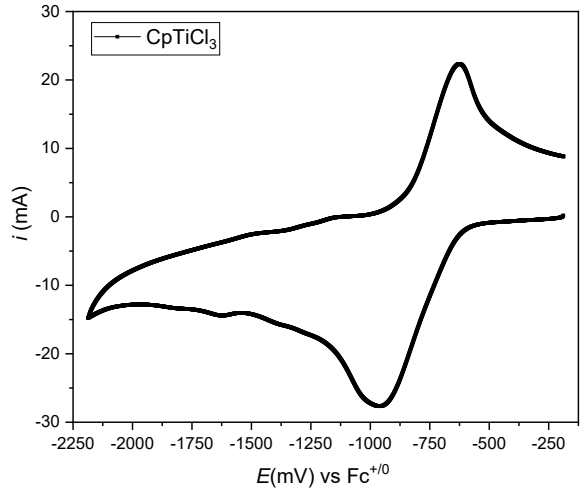


Figure S2. Cyclic voltammogram of $CpTiCl_3$ ($E_{1/2}$ = -0.79 V vs $Fc^{+/0}$). Conditions: $CpTiCl_3$ (2 mM), Bu_4NPF_6 (0.2 M) in DCM. Scan rate: 100 mV/s.

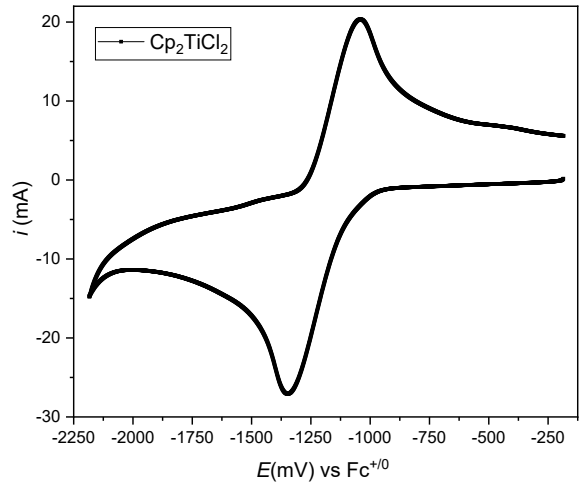


Figure S3. Cyclic voltammogram of Cp_2TiCl_2 ($E_{1/2}$ = -1.19 V vs $Fc^{+/0}$). Conditions: Cp_2TiCl_2 (2 mM), Bu_4NPF_6 (0.2 M) in DCM. Scan rate: 100 mV/s.

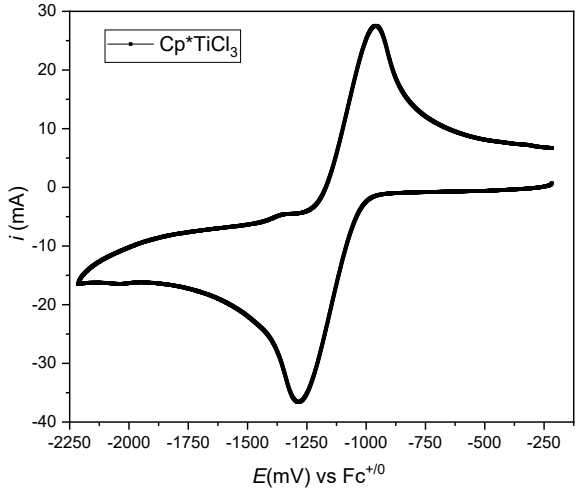


Figure S4. Cyclic voltammogram of Cp^*TiCl_3 ($E_{1/2}$ = -1.12 V vs $Fc^{+/0}$). Conditions: Cp^*TiCl_3 (2 mM), Bu_4NPF_6 (0.2 M) in DCM. Scan rate: 100 mV/s.

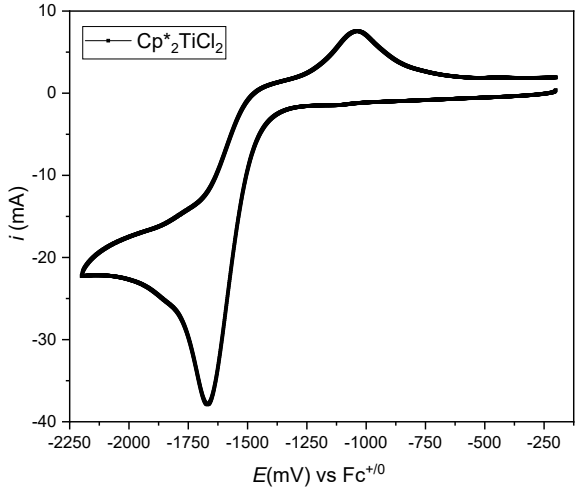


Figure S5. Cyclic voltammogram of $Cp^*_2TiCl_2$ ($E_{p/2}$ = -1.55 V vs $Fc^{+/0}$). Conditions: $Cp^*_2TiCl_2$ (2 mM), Bu_4NPF_6 (0.2 M) in DCM. Scan rate: 100 mV/s.

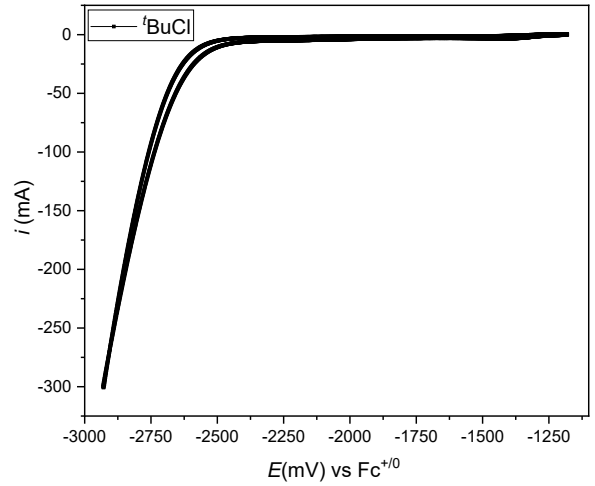


Figure S6. Cyclic voltammogram of ^{t}BuCl. Conditions: ^{t}BuCl (2 mM), Bu_4NPF_6 (0.2 M) in DCM. Scan rate: 100 mV/s.

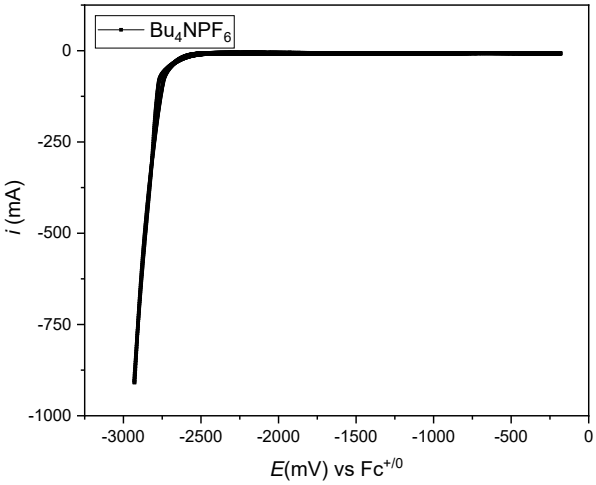
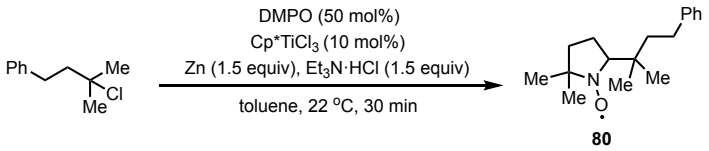


Figure S7. Cyclic voltammogram of Bu_4NPF_6 (0.2 M) in DCM. Scan rate: 100 mV/s.

Section 6. Mechanistic studies

General information: ESR spectra were recorded on a Bruker ELEXYS-II E500 spectrometer at National Biomedical Center for Advanced Electron Spin Resonance Technology(ACERT) at a microwave frequency of 9.32 GHz, microwave power of 0.63 mW, and modulation amplitude of 2 G. Samples were prepared in a N_2-filled glovebox.

Spin trapping with DMPO



In a N_2-filled glovebox, an oven-dried 8 mL culture tube equipped with a magnetic stir bar was charged with Zn (9.8 mg, 0.15 mmol, 1.5 equiv), $Et_3N{\cdot}HCl$ (20.6 mg, 0.15 mmol, 1.5 equiv) and a solution of Cp^*TiCl_3 in toluene (20 mM, 0.5 mL, 10 mol%). The mixture was stirred for 30 min until the color of solution changed from orange to green, to allow reduction of the pre-catalyst. Subsequently, 1 (18.2 mg, 0.1 mmol, 1 equiv), and DMPO (5.6 mg, 0.05 mmol, 50 mol%) were added, and the resulting mixture was stirred at room temperature (22 °C) for 0.5 h. Subsequently, the supernatant was analyzed by ESR and mass spectrometry (DART). ESR spectrum showed an average g value of 2.0061 with two hyperfine splittings of 14.8 G (assigned to the nitroxide nitrogen) and 20.5 G (assigned to the α-hydrogen). High-resolution mass spectrum showed a molecular weight (M_w) of 260.20081, corresponding to nitroxide product **80** (calculated for M^+: M_w=260.20025; ionization by losing an electron to form the oxoammonium ion).

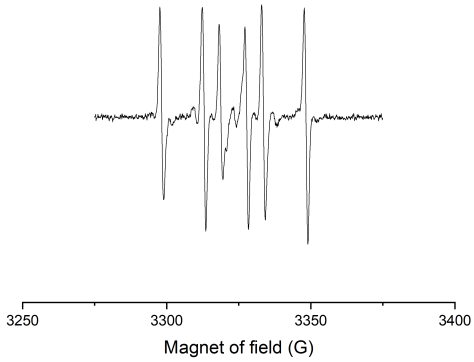
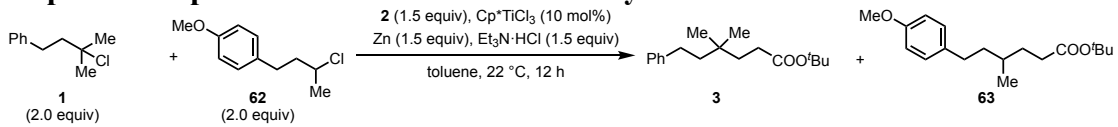


Figure S8. ESR spectrum of the reaction mixture in the presence of DMPO.

Competition experiments between different alkyl chlorides



In a N_2-filled glovebox, an oven-dried 8 mL culture tube equipped with a magnetic stir bar was charged with Zn (9.8 mg, 0.15 mmol, 1.5 equiv), $Et_3N{\cdot}HCl$ (20.6 mg, 0.15 mmol, 1.5 equiv) and a solution of Cp^*TiCl_3 in toluene (20 mM, 0.5 mL, 10 mol%). The mixture was stirred for 30 min until the color of solution changed from orange to green, to allow reduction of the pre-catalyst. Subsequently, two alkyl chlorides substrates (0.20 mmol, 2.0 equiv each) and **2** (19.2 mg, 0.15 mmol, 1.5 equiv) were added, and the resulting mixture was stirred at room temperature (22 ± 1 °C) for 12 h. The reaction mixture was then transferred onto a short silica gel column (1-1.5 cm in length, ca. 0.5 g) and flushed through with EtOAc (10 mL in total) to remove the inorganic salts and other insoluble solids. The product solution was concentrated *in vacuo* and analyzed by GC.

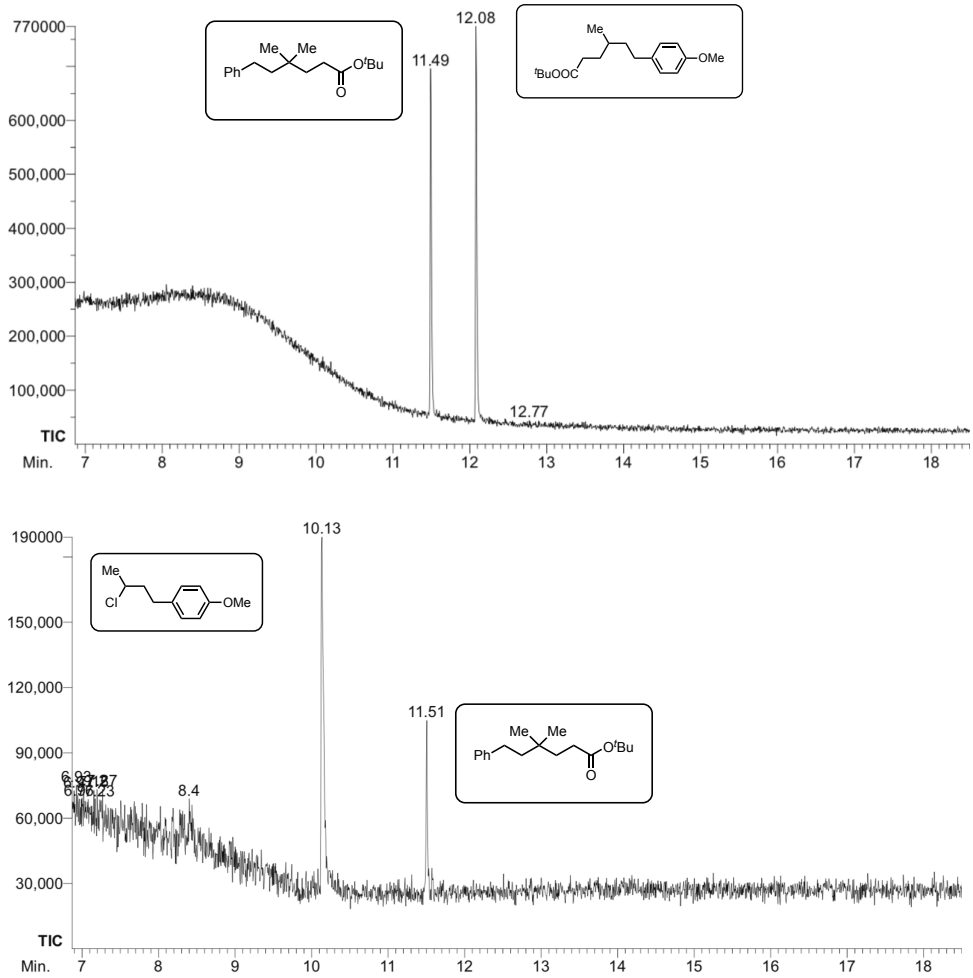
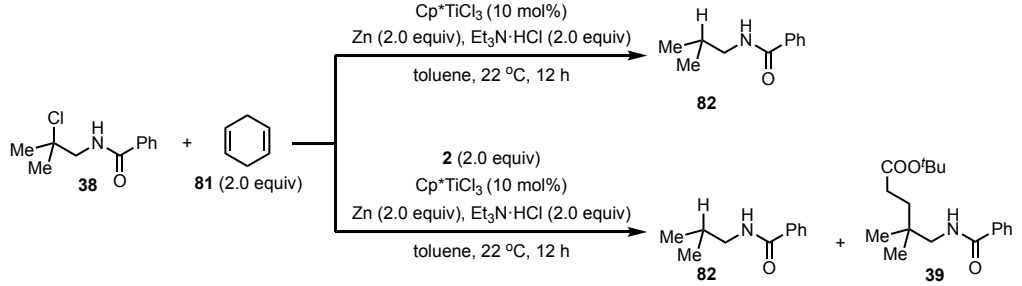


Figure S9. GC analysis of the competition experiment between **1** and **52**. Top: GC trace for a mixture of **3** (t_R = 11.49 min) and **53** (t_R = 12.08 min), made from pure products as a GC standard sample. Bottom: GC trace for the crude reaction mixture. The calculated molar ratio of the products is **3**:**53** > 19:1, secondary alkyl chloride remained unreacted.

Radical trapping with 1,4-cyclohexadiene and competition experiment between *tert*-butylacrylate and 1,4-cyclohexadiene



In a N_2-filled glovebox, an oven-dried 8 mL culture tube equipped with a magnetic stir bar was charged with Zn (13.0 mg, 0.2 mmol, 2.0 equiv), $Et_3N{\cdot}HCl$ (27.2 mg, 0.2 mmol, 2.0 equiv) and a solution of Cp^*TiCl_3 in toluene (20 mM, 0.5 mL, 10 mol%). The mixture was stirred for 30 min until the color of solution changed from orange to green, to allow reduction of the pre-catalyst. Subsequently, 1,4-cyclohexadiene (**81**) (16.0 mg, 0.20 mmol, 2.0 equiv) and alkyl chloride **38** (21.2 mg, 0.10 mmol, 1.0 equiv) were added, and the resulting mixture was stirred at room temperature (22 ± 1 °C) for 12 h. The reaction mixture was then transferred onto a short silica gel column (1-1.5 cm in length, ca. 0.5 g) and flushed through with EtOAc (10 mL in total) to remove the inorganic salts and other insoluble solids. The product solution was concentrated *in vacuo* and purified by flash chromatography on silica gel (5-6 cm in length, ca. 1.5 g) using hexanes/EtOAc to obtain product **60** (9.9 mg, 55% yield). The ^1H NMR spectrum is consistent with reported data.[18]

***N*-isobutylbenzamide (82).** ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.70 (m, 2H), 7.55-7.37 (m, 3H), 6.23 (s, 1H), 3.29 (td, J = 6.4, 6.0, 0.8 Hz, 2H), 1.90 (dt, J = 13.5, 6.7 Hz, 1H), 0.98 (dd, J = 6.7, 0.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.72, 135.11, 131.47, 128.72, 126.95, 77.41, 77.16, 76.91, 47.49, 28.80, 20.33; MS (DART) exact mass calculated for [$C_{11}H_{16}NO^+$]: 178.1223, found 178.1219.

In competition reaction, 1,4-cyclohexadiene **81**, *tert*-butylacrylate **2** (0.20 mmol, 2.0 equiv each), and alkyl chloride **38** (21.2 mg, 0.10 mmol, 1.0 equiv) were added, and the resulting mixture was stirred at room temperature (22 ± 1 °C) for 12 h. The reaction mixture was then transferred onto a short silica gel column (1-1.5 cm in length, ca. 0.5 g) and flushed through with EtOAc (10 mL in total) to remove the inorganic salts and other insoluble solids. The reaction mixture was analyzed by ^1H NMR.

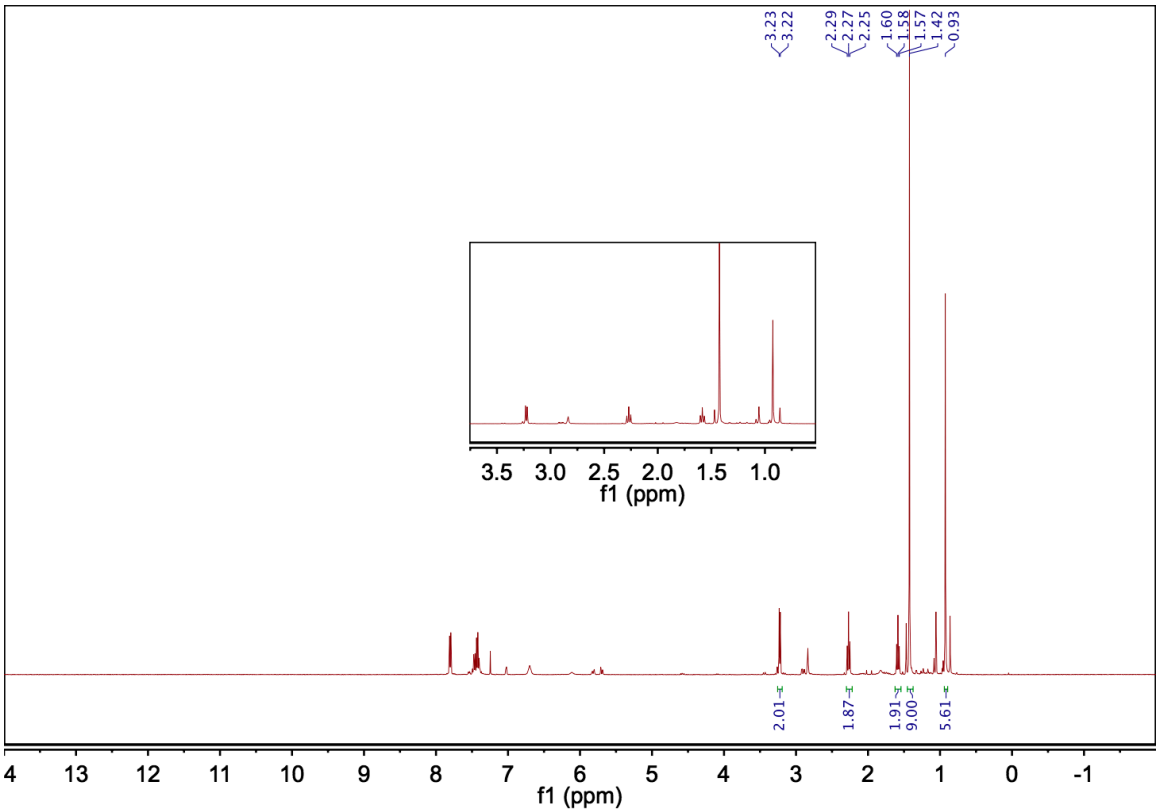


Figure S10. ^{1}H NMR of the crude mixture of the competition experiment between **2** and **59**. Peaks at 0.93 ppm (6H), 1.42 ppm (9H), 1.58 ppm (2H), 2.27 ppm (2H), 3.22 ppm (2H) belong to product **39**. The ratio of **39** to **82** is greater than 19:1.

NMR experiments of Ti catalyst and Lewis acid additive

In the NMR experiments, Cp*$TiCl_3$ (0.01 mmol, 2.9 mg) and $AlCl_3$ (0, 1 equiv, or 10 equiv) were added to an oven-dried 8 mL culture tube equipped with a magnetic stir bar. Subsequently, 1 mL of d^8-Toluene was added, and the mixture was stirred at room temperature for 30 min. NMR sample was prepared under N_2 protected environment.

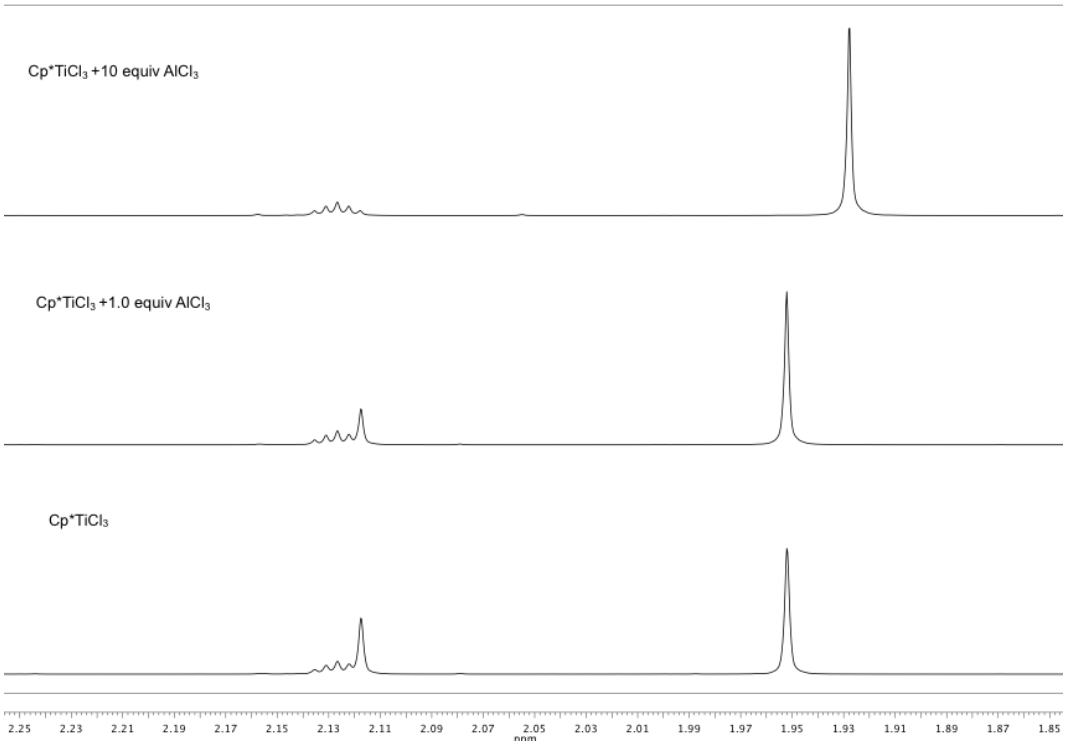


Figure S11. ^{1}H NMR of the crude mixture of different ratio of Ti catalyst and $AlCl_3$ in d_8-toluene (solvent peaks at 2.13 ppm).

Section 7. UV-vis study of Lewis acid effect

In a N_2-filled glovebox, an oven-dried 8 mL culture tube equipped with a magnetic stir bar was charged with reductant (0.8 mmol, 1.5 equiv), $Et_3N{\cdot}HCl$ (164.4 mg, 0.8 mmol, 1.5 equiv), $AlCl_3$ (106.4 mg, 0.8 mmol, 1.5 equiv) and a solution of Cp^*TiCl_3 in toluene (20 mM, 4.0 mL, 10 mol%). The mixture was stirred for 1 min until the catalyst is fully dissolved. In every 120 s (for Mn+$AlCl_3$) or 5 min (for Mn only), 0.1 mL of the reaction mixture is taken out and filtered through a plastic frit, subsequently diluted into 4.0 mL toluene. For each fraction, UV-Vis spectrum is taken from 280 to 600 nm to track the decay of absorbance at 450 nm.

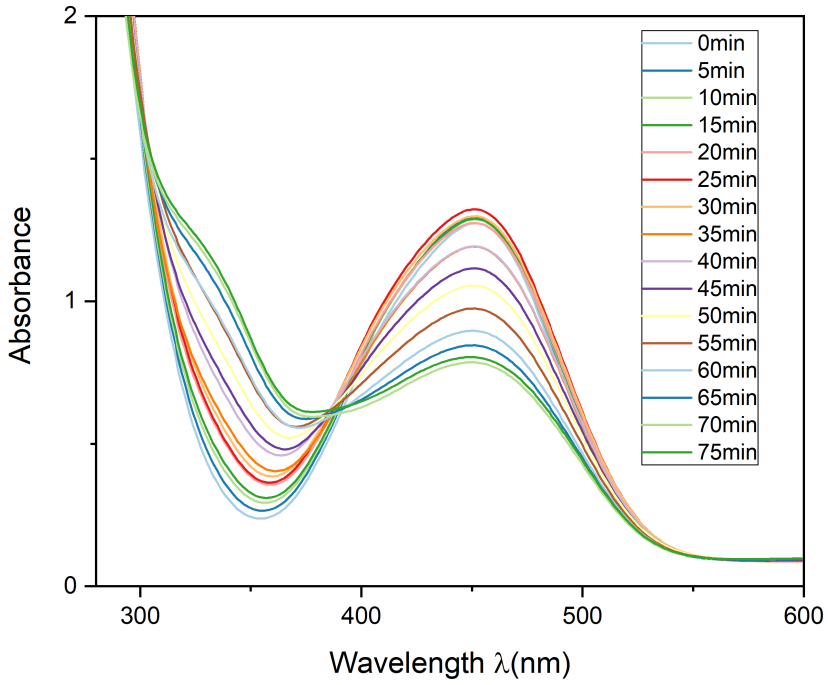


Figure S12. UV-Vis trace for detecting the decay of Ti^{IV} (450 nm). Only Mn was used as the reductant.

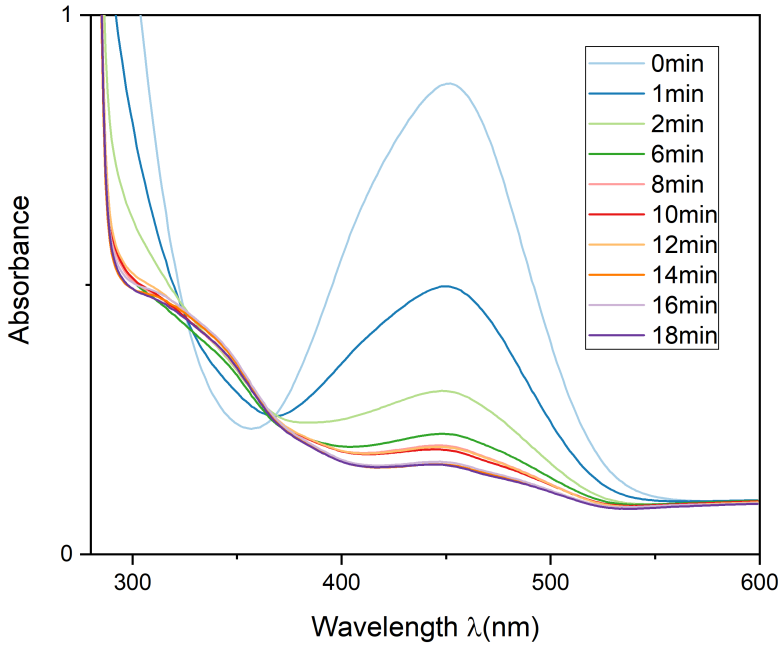


Figure S13. UV-Vis trace for detecting the decay of Ti^{IV} (450 nm). Mn and $AlCl_3$ were both added to activate catalyst.

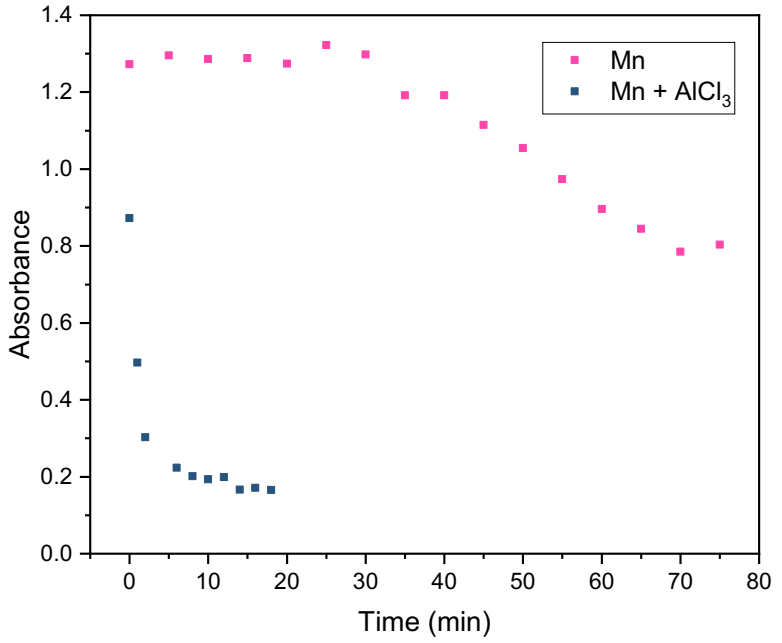


Figure S14. Absorbance versus time plot for three conditions. Lewis acid promoted activation of Ti catalyst can be observed.

Section 8. Computational studies

General information: Computational modeling was conducted using Gaussian 09. Both structural optimization and energy calculations were carried out using B3LYP/6-31+G(d) level of density functional theory (DFT).

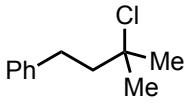
Bond dissociation energy calculation

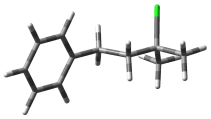
Table S3. Summary of calculated energies of homolysis 1 and its corresponding diradical and Ti complexes

Job #	*E*+ZPE	*G*	*H*	*S*
A	-888.203453	-888.24358	-888.19019	112.373
B	-427.949016	-427.98918	-427.93618	111.533
C	-2159.899439	-2159.9468	-2159.881	138.325
D	-2620.163166	-2620.2105	-2620.1435	140.982
E	-1312.465015	-1312.5206	-1312.440681	168.411
F	-852.229077	-852.283632	-852.205895	163.611
G	-460.1382991	N.A.*	N.A.*	N.A.*

*N.A.: Not applicable. Chlorine free radical does not have vibrational and rotational zero-point energy, translational zero-point energy is zero. Only electronic term is included.

(A) Substrate



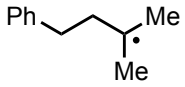


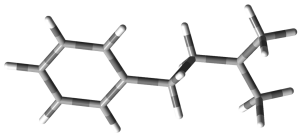
Charge: 0
Spin Multiplicity: 1

C	-2.11239400	1.18590800	-0.02899200
C	-3.45571700	1.28626500	0.34132800
C	-4.26485000	0.14620000	0.36474300
C	-3.71967900	-1.09128800	0.01251900
C	-2.37484400	-1.18527800	-0.35728900
C	-1.55050600	-0.05082000	-0.38187900
H	-1.49183800	2.07994500	-0.05098200
H	-3.87159100	2.25536900	0.60636900
H	-5.31109400	0.22278400	0.64973100
H	-4.34127700	-1.98348300	0.02039500
H	-1.96125800	-2.15275400	-0.63719200
C	-0.08417200	-0.15772400	-0.75078000
H	0.05856400	-1.01987900	-1.41285800
H	0.22345600	0.73173700	-1.31255500
C	0.81324300	-0.30022300	0.49488300
H	0.59774400	0.52072100	1.18924700

H	0.54505900	-1.22849400	1.02145100
C	2.33357300	-0.34931500	0.25921400
C	3.07404500	-0.49855200	1.59030800
H	4.15801000	-0.46779900	1.44266500
H	2.79705700	0.29718100	2.28890200
H	2.81472500	-1.46354500	2.04536400
C	2.76196000	-1.42866100	-0.73612100
H	2.43379700	-2.41066100	-0.36951100
H	2.32821700	-1.26731100	-1.72632200
H	3.85121200	-1.44828800	-0.84067200
Cl	2.86148700	1.29384700	-0.45656700

(B) Substrate radical

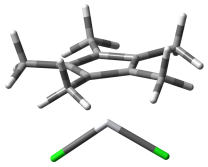




Charge: 0
Spin Multiplicity: 2

C	-3.01784800	1.20729200	-0.12016000
C	-1.65766000	1.20382100	0.19996600
C	-0.95524600	-0.00012600	0.36442300
C	-1.65786500	-1.20392500	0.19991000
C	-3.01806900	-1.20712600	-0.12022300
C	-3.70388900	0.00014200	-0.28230900
H	-3.54244500	2.15255900	-0.23781900
H	-1.13396600	2.14938100	0.33004300
H	-1.13437400	-2.14960200	0.32993500
H	-3.54282700	-2.15229800	-0.23793100
H	-4.76277100	0.00024400	-0.52829900
C	0.52593800	-0.00020200	0.66879400
H	0.78156700	-0.88165000	1.27040500
H	0.78157300	0.88100000	1.27075900
C	1.40969200	0.00003900	-0.62215600
H	1.13496500	-0.88207200	-1.21796600
H	1.13490600	0.88231200	-1.21769900
C	2.88386200	0.00003700	-0.34572500
C	3.57145600	1.28690400	-0.00150400
H	3.53801300	1.50426600	1.08370200
H	4.63598600	1.26091100	-0.27281100
H	3.11215700	2.14437800	-0.50965300
C	3.57147100	-1.28685100	-0.00160500
H	3.11237300	-2.14425600	-0.51006400
H	4.63606800	-1.26072600	-0.27260500
H	3.53771600	-1.50447800	1.08354200

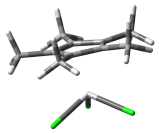
(C) $Cp^*Ti^{III}Cl_2$



Charge: 0
Spin Multiplicity: 2

C	1.02320600	1.13682000	-0.71284200
C	-0.33654700	1.15312500	-1.15908800
C	-1.17835700	1.18774200	-0.00139400
C	1.02159900	1.13694600	0.71496300
C	-0.33913200	1.15344400	1.15816300
Ti	-0.03795100	-0.86406900	-0.00002500
Cl	1.84880900	-2.12810000	0.00003800
Cl	-1.96947200	-2.05207100	0.00017100
C	-0.80878000	1.23077800	2.58669500
H	-0.94157300	2.27727300	2.89584900
H	-1.76904200	0.72471000	2.72735100
H	-0.09151500	0.77709900	3.27780800
C	2.23881200	1.16344800	1.59844000
H	2.54922800	2.19966100	1.79358900
H	2.05016600	0.69152200	2.56775500
H	3.08466500	0.64334600	1.14027200
C	-2.67563500	1.33060800	-0.00312500
H	-3.13119200	0.86756400	0.87668500
H	-2.95589100	2.39362300	-0.00413100
H	-3.12930900	0.86641400	-0.88331000
C	-0.80309200	1.23017300	-2.58865900
H	-1.76309300	0.72414300	-2.73126800
H	-0.93516900	2.27659900	-2.89836200
H	-0.08438000	0.77628000	-3.27812600
C	2.24240700	1.16348200	-1.59355100
H	3.08701300	0.64266900	-1.13389400
H	2.05574100	0.69238900	-2.56364800
H	2.55366200	2.19972700	-1.78718300

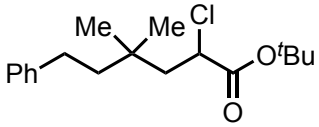
(D) $Cp^*Ti^{IV}Cl_3$

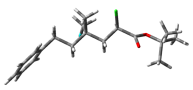


Charge: 0
Spin Multiplicity: 1

C	0.88196900	0.00776300	1.54134500
C	0.06047700	1.16494000	1.36090600
C	-1.25875600	0.72244100	1.04194200
C	0.05898000	-1.15018700	1.37367300
C	-1.25962700	-0.70938400	1.04941000
Ti	0.17273700	-0.00417100	-0.72511000
Cl	1.37781800	-1.77135600	-1.41688600
Cl	-1.59480400	0.00110200	-2.11881700
Cl	1.39957200	1.74252600	-1.43103200
C	-2.46129900	-1.59092700	0.86042200
H	-2.96109200	-1.76009000	1.82466700
H	-3.18930400	-1.14206800	0.18014700
H	-2.18899900	-2.56956800	0.45443400
C	0.47580400	-2.57044100	1.62286000
H	0.29457600	-2.83111200	2.67520000
H	-0.08372900	-3.27632000	1.00308600
H	1.53767600	-2.72443500	1.41695800
C	-2.45949200	1.60342200	0.84474000
H	-3.19006000	1.14680900	0.17247500
H	-2.95617500	1.78594900	1.80815300
H	-2.18693900	2.57621700	0.42508700
C	0.47946800	2.58729500	1.59405800
H	-0.07969800	3.28709000	0.96704900
H	0.29945700	2.85988500	2.64358900
H	1.54139000	2.73743700	1.38564100
C	2.33425100	0.00916600	1.92917700
H	2.85430500	-0.87731000	1.55495500
H	2.85620800	0.88844100	1.54086600
H	2.43758100	0.01769100	3.02341800

(E) Alpha-chloro ester





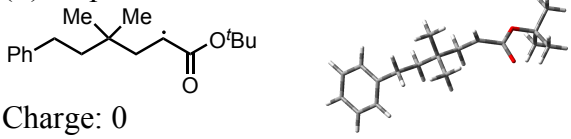
Charge: 0
Spin Multiplicity: 1

C	-2.80487818	0.33101045	0.00000000

C	-1.40971818	0.33101045	0.00000000
C	-0.71218018	1.53876145	0.00000000
C	-1.40983418	2.74727045	-0.00119900
C	-2.80465918	2.74719245	-0.00167800
C	-3.50226018	1.53898645	-0.00068200
H	-3.35463718	-0.62130655	0.00045000
H	-0.86021018	-0.62150255	0.00131500
H	-0.85963418	3.69941345	-0.00125800
H	-3.35478118	3.69947345	-0.00263100
H	-4.60186418	1.53916945	-0.00086200
C	0.82781956	1.53887348	0.00088786
H	1.18412578	2.40629082	0.51618683
H	1.18426576	0.65911992	0.49472972
C	1.34198807	1.55674039	-1.45063256
H	0.97609456	0.69531436	-1.96925297
H	0.99519247	2.44228395	-1.94098488
C	2.88189581	1.53989612	-1.44998600
C	3.38099144	0.26239324	-0.74963614
H	4.39002599	0.06443003	-1.04554128
H	3.34040857	0.39802144	0.31095710
H	2.75931382	-0.56288705	-1.02771775
C	3.40847144	2.77652809	-0.69828161
H	4.43922687	2.92948842	-0.94127625
H	2.84238255	3.63733786	-0.98715858
H	3.30967223	2.62197592	0.35587793
C	3.39613165	1.56392285	-2.90139367
H	3.03194406	0.70364045	-3.42310392
H	3.04765628	2.45053212	-3.38861941
C	4.93606908	1.55005862	-2.90068727
H	5.30040314	2.42539060	-2.40474915
Cl	5.50946213	0.11604505	-2.05663424
C	5.44991831	1.53113260	-4.35230732
O	4.88439405	0.61814424	-5.29651839
O	6.36575980	2.31633954	-4.71043441
C	6.77313624	1.99809202	-6.04372468
C	7.22052096	0.52583310	-6.10617943
H	6.42261045	-0.07332162	-6.49251145
H	8.07371175	0.43916511	-6.74606546
H	7.47608580	0.18872311	-5.12335520
C	7.94554894	2.90869305	-6.45342482
H	8.22472720	2.69751204	-7.46454404
H	7.64682916	3.93294892	-6.37239141
H	8.77968859	2.72830825	-5.80800065
C	5.59205174	2.21702188	-7.00742023
H	5.15411483	1.27270897	-7.25517895
H	4.85844652	2.83801171	-6.53721281

H	5.94297059	2.69245853	-7.89944935

(F) Alpha-chloro ester radical



Charge: 0
Spin Multiplicity: 2

C	-2.89192965	0.39079830	-0.26221806
C	-1.49165363	0.33397661	-0.27267416
C	-0.74151412	1.48636882	-0.00306950
C	-1.39157152	2.69540441	0.27803443
C	-2.79204775	2.75243880	0.28986234
C	-3.54222112	1.59966143	0.01983665
H	-3.46491074	-0.48881508	-0.46966010
H	-0.99486763	-0.58924500	-0.48677655
H	-0.81879566	3.57536116	0.48356997
H	-3.28808508	3.67563132	0.50444159
H	-4.61131203	1.64301227	0.02919444
C	0.79773082	1.42450616	-0.01484240
H	1.18901077	2.14750089	0.67055068
H	1.11765221	0.44678780	0.27733071
C	1.31322600	1.72976796	-1.43315263
H	0.92247906	1.00643597	-2.11779616
H	0.99315440	2.70747787	-1.72612794
C	2.85158603	1.66758633	-1.44501988
C	3.31233609	0.26015262	-1.02187839
H	4.38181171	0.21781312	-1.02994807
H	2.95386146	0.04906585	-0.03564766
H	2.92179694	-0.46348457	-1.70614650
C	3.41375981	2.70970895	-0.46118615
H	4.48203728	2.66867200	-0.46987972
H	3.09190938	3.68727573	-0.75469254
H	3.05620021	2.49828453	0.52464263
C	3.36685912	1.97088572	-2.86419038
H	2.97407784	1.24773362	-3.54860893
H	3.04882623	2.94882065	-3.15755467
C	4.90497399	1.90627678	-2.87751502
H	5.46009346	2.15704403	-1.99672617
C	5.64417521	1.47972290	-4.15976055
O	5.90036322	0.26472283	-4.36343952
O	5.99130073	2.34536754	-5.00381722
C	6.66507611	1.94551210	-6.20096009
C	7.48285201	0.66944247	-5.92982033
H	6.82609932	-0.11302929	-5.61112988
H	7.98633414	0.37040657	-6.82552601
H	8.20410812	0.86403064	-5.16364963

C	7.60989989	3.07199281	-6.65923761
H	8.11316681	2.77336927	-7.55546700
H	7.04180287	3.95842770	-6.84797048
H	8.33134593	3.26604751	-5.89387848
C	5.62749158	1.66425837	-7.30408042
H	4.97112599	0.88127763	-6.98518819
H	5.05964847	2.55133312	-7.49348332
H	6.13067281	1.36481479	-8.20038871

Transition state calculation

Table S4. Summary of calculated energies of ground state and transition state of ^{t}BuCl and Cp*$Ti^{III}Cl_2$

Job	***E***	***E*+ZPE**	***G***	***H***	***S***
GS	-2778.195149	-2777.845730	-2777.903081	-2777.818903	177.168
TS	-2778.185561	-2777.839716	-2777.897941	-2777.812842	179.107

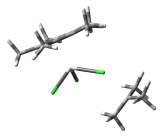
(**GS**) Ground state

Charge: 0
Spin Multiplicity: 2

C	-1.47305600	0.02254100	1.68504600
C	-1.68690400	1.26055500	0.99614900
C	-2.48266100	0.99578800	-0.16569600
C	-2.12285400	-1.00556000	0.93632400
C	-2.74634000	-0.40297600	-0.20458500
Ti	-0.37307500	-0.10081200	-0.39839300
Cl	-0.14641500	-2.06016100	-1.57645800
Cl	0.46462500	1.71775100	-1.60412800
C	-3.59456100	-1.12611400	-1.21380800
H	-4.62359800	-1.23663000	-0.84285500
H	-3.64402200	-0.58750800	-2.16475200
H	-3.20628100	-2.12696800	-1.42380700
C	-2.22284700	-2.45631700	1.32088700
H	-3.15341000	-2.64416800	1.87574200
H	-2.22099000	-3.10835500	0.44262600
H	-1.39222500	-2.76722200	1.96233100

C	-3.01215800	2.03267500	-1.11682400
H	-3.26973400	1.59906900	-2.08762400
H	-3.92146700	2.49868200	-0.71100100
H	-2.28025600	2.82479900	-1.29795400
C	-1.24813500	2.62258800	1.46296900
H	-1.04852300	3.29096600	0.62061600
H	-2.02752400	3.08793900	2.08358000
H	-0.33666900	2.57437400	2.06760000
C	-0.82056600	-0.14083700	3.03278100
H	-0.34324400	-1.11970000	3.14463600
H	-0.05520100	0.62007900	3.21311000
H	-1.56725300	-0.04888200	3.83447500
C	3.64911500	-0.04624100	0.04106700
C	4.64389000	-0.81944800	0.89897700
H	5.64601200	-0.68375600	0.47085300
H	4.66146200	-0.45111500	1.92934000
H	4.41911800	-1.89008600	0.90867000
C	3.52388800	-0.60314200	-1.36923300
H	3.27944300	-1.66895700	-1.36251400
H	2.76364900	-0.07048300	-1.94517600
H	4.49181300	-0.47274300	-1.87225100
C	3.87525800	1.45928400	0.07624900
H	3.09191000	1.99032800	-0.46983500
H	3.91498700	1.83404400	1.10390500
H	4.84027600	1.67331100	-0.40312800
Cl	1.94631800	-0.34323300	0.91036600

(**TS**) Transition state



Charge: 0
Spin Multiplicity: 2

C	-1.47810300	-0.03698700	1.71201300
C	-1.47556800	1.26594200	1.11789800
C	-2.27253200	1.21627900	-0.07105300
C	-2.24580100	-0.89558700	0.86917700
C	-2.73593200	-0.11985700	-0.23185100
Ti	-0.33521200	-0.17205600	-0.36146500
Cl	-0.42003000	-2.08491500	-1.60051800
Cl	0.45841300	1.47463200	-1.79123600
C	-3.65065000	-0.61900800	-1.31513800

H	-4.69917900	-0.56489400	-0.98882000
H	-3.55969800	-0.02401300	-2.22874600
H	-3.43542000	-1.65878100	-1.57715100
C	-2.57601200	-2.33698500	1.14000400
H	-3.52010000	-2.41514200	1.69822900
H	-2.68712100	-2.90624400	0.21304500
H	-1.80087400	-2.82835100	1.73611300
C	-2.64050000	2.38994700	-0.93328300
H	-2.81530600	2.09490000	-1.97181700
H	-3.56171100	2.85921700	-0.55911800
H	-1.85429000	3.14875600	-0.94123500
C	-0.83000600	2.49689200	1.69397700
H	-0.51136400	3.19037200	0.91010000
H	-1.53222600	3.03370700	2.34792600
H	0.05142800	2.24847000	2.29322400
C	-0.90059900	-0.40269500	3.05142900
H	-0.56877500	-1.44484900	3.08304800
H	-0.03981800	0.22078200	3.30759800
H	-1.65489000	-0.27035000	3.84028400
C	3.90117700	-0.03954500	0.01390000
C	4.66536900	-0.82464600	1.03663100
H	5.74352000	-0.75064700	0.80722900
H	4.51931300	-0.43382500	2.04853400
H	4.39996500	-1.88606600	1.02080700
C	3.78385100	-0.62493800	-1.35870900
H	3.55767400	-1.69483700	-1.33093200
H	3.02399300	-0.11398200	-1.95597600
H	4.75271000	-0.50264700	-1.87598800
C	3.94155300	1.45439900	0.12318200
H	3.18410000	1.92776500	-0.50650800
H	3.81832200	1.79375800	1.15641400
H	4.93152600	1.80498600	-0.22144900
Cl	1.65075800	-0.48278400	0.83636300

Section 9. X-ray crystallographic data

General information: Low-temperature X-ray diffraction data for **45** was collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with Cu Kα radiation (λ =1.54184 Å), from a Photon Jet micro-focus X-ray source at 100 K. The diffraction images were processed and scaled using the CrysAlisPro software.[30] The structures were solved through intrinsic phasing using SHELXT[31] and refined against F^2 on all data by full-matrix least squares with SHELXL[32] following established refinement strategies.[33] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the Ueq value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Tables S5.

The crystals of **45** was obtained via slow evaporation of a concentrated DCM and Hexanes solution of the corresponding compound at 4 °C.

Table S5. Crystal data and structure refinement for **45**.

Identification code	rxw3_abs	
Empirical formula	C24 H29 N O5 S	
Formula weight	443.54	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.98590(10) Å	a= 80.5240(10)°.
	b = 10.71110(10) Å	b= 74.4700(10)°.
	c = 12.6455(2) Å	g = 72.2380(10)°.
Volume	1112.21(3) $Å^3$	
Z	2	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	1.590 mm^{-1}	
F(000)	472	
Crystal size	0.176 x 0.119 x 0.091 mm^3	
Theta range for data collection	3.643 to 74.486°.	
Index ranges	-10<=h<=11, -13<=k<=13, -15<=l<=15	
Reflections collected	45739	
Independent reflections	4552 [R(int) = 0.0266]	
Completeness to theta = 67.684°	100.0 %	

Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.747
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4552 / 928 / 405
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0980
R indices (all data)	R1 = 0.0365, wR2 = 0.0991
Extinction coefficient	n/a
Largest diff. peak and hole	0.373 and -0.387 e.$Å^{-3}$

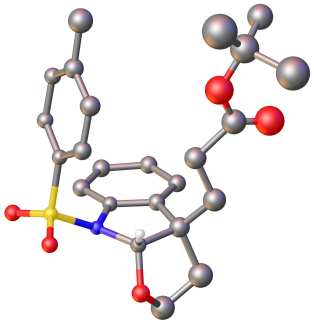


Figure S15. ORTEP drawing of **45** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Section 10. Reference

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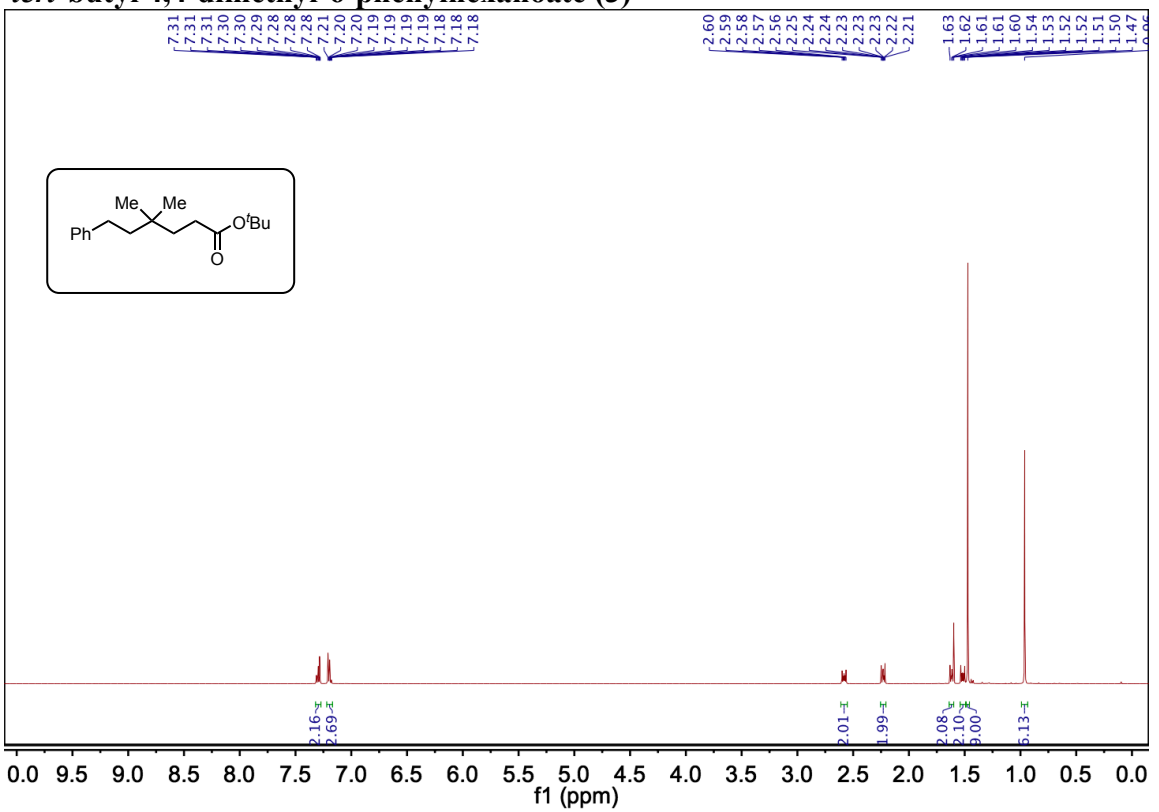
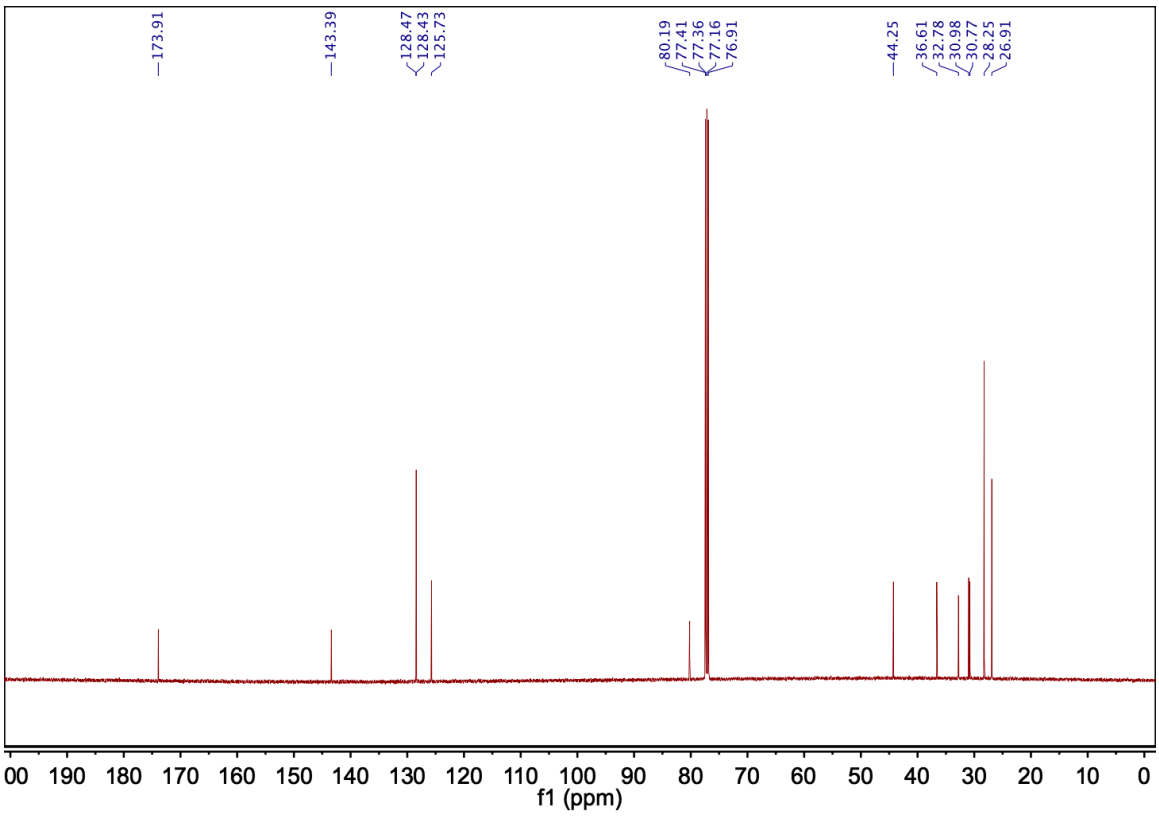
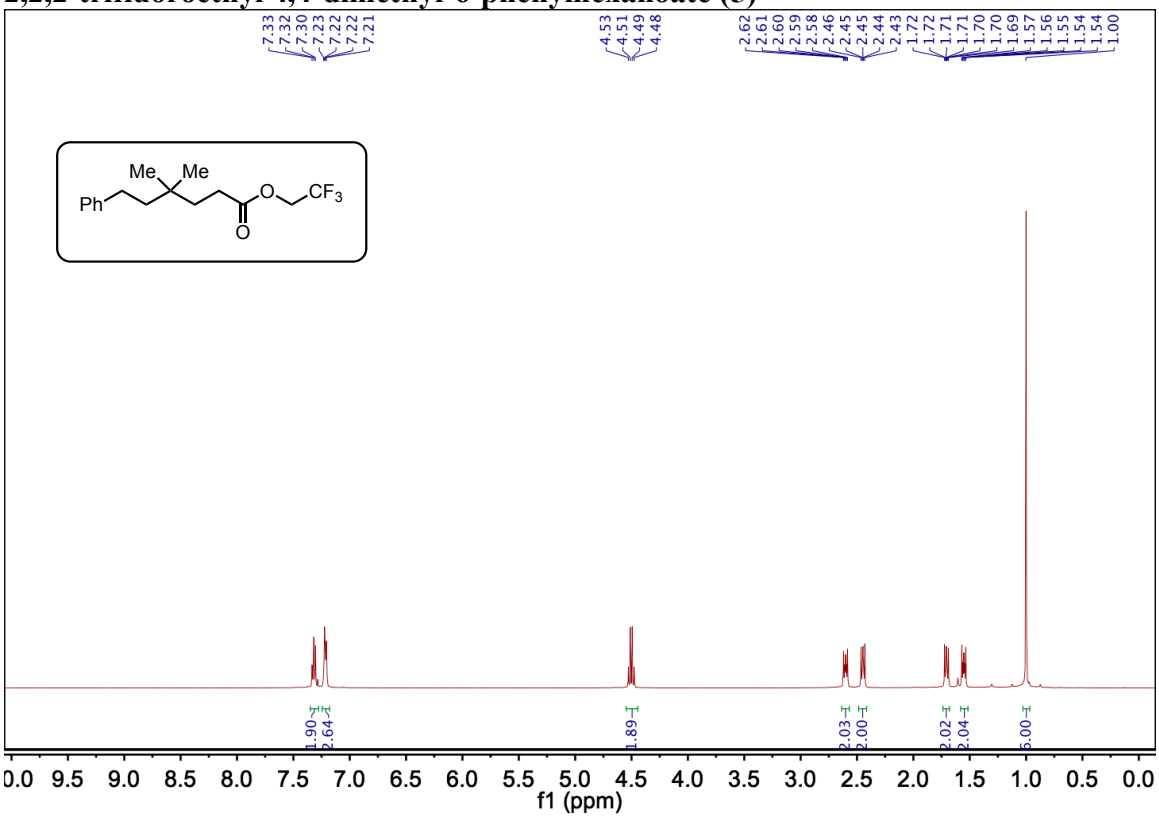
Section 11. Spectral data for products

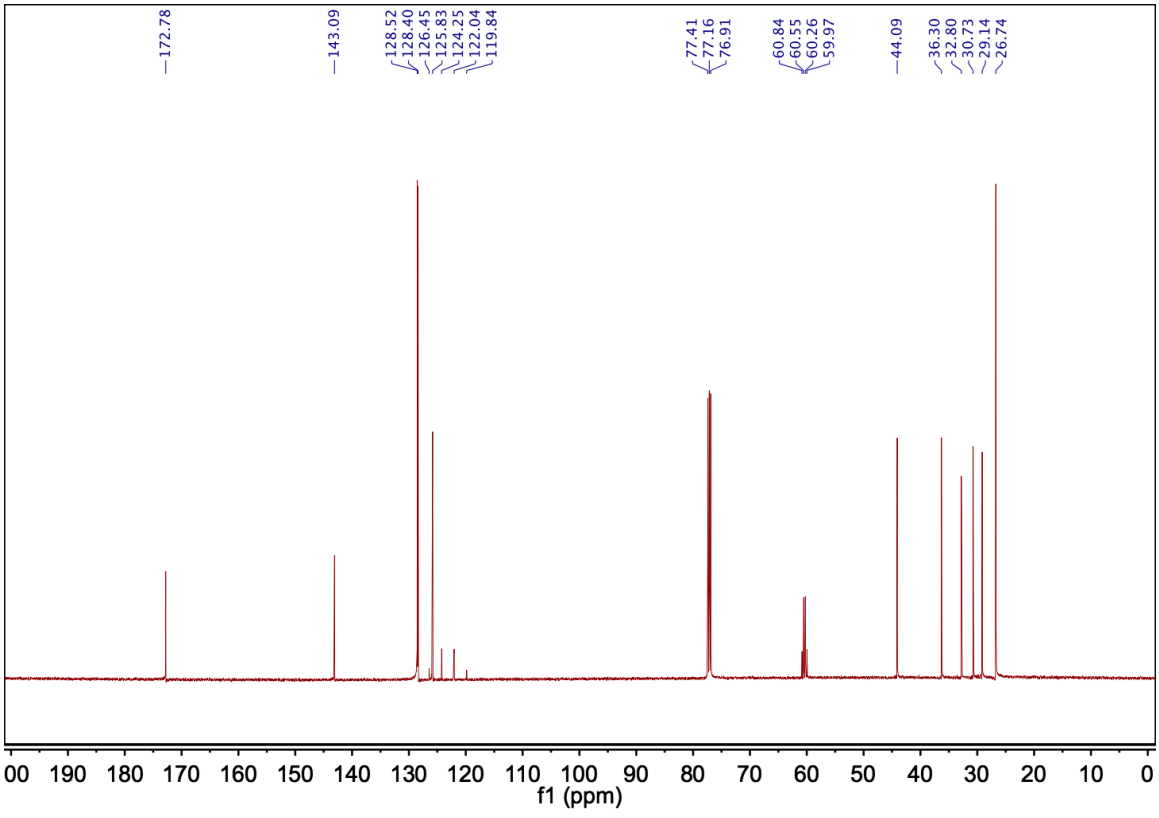
tert-butyl 4,4-dimethyl-6-phenylhexanoate (3)

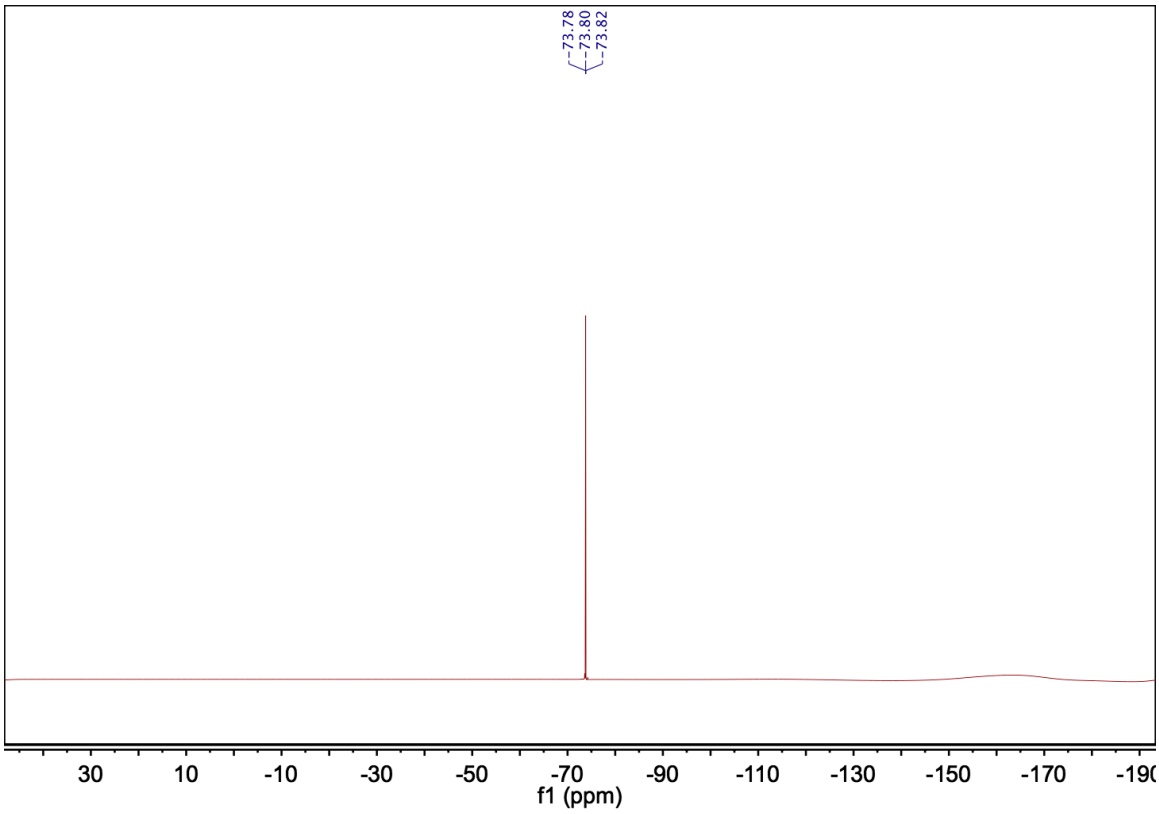




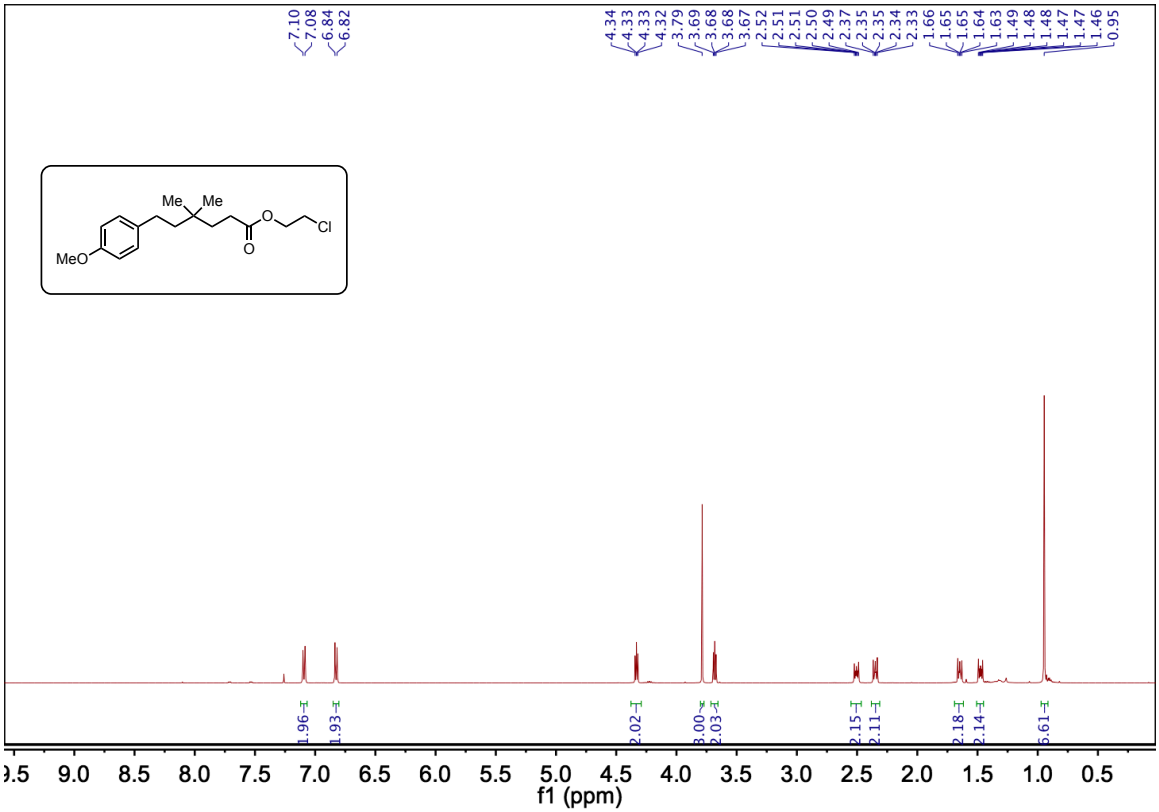
2,2,2-trifluoroethyl 4,4-dimethyl-6-phenylhexanoate (5)

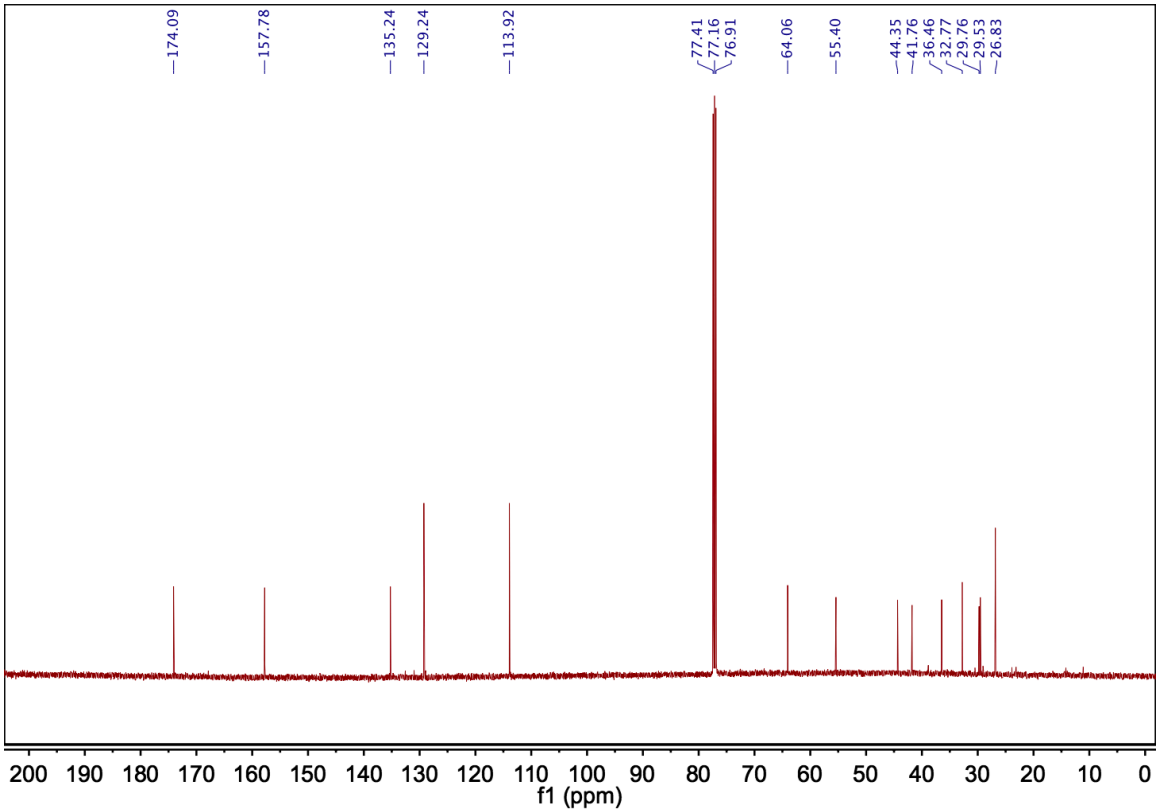




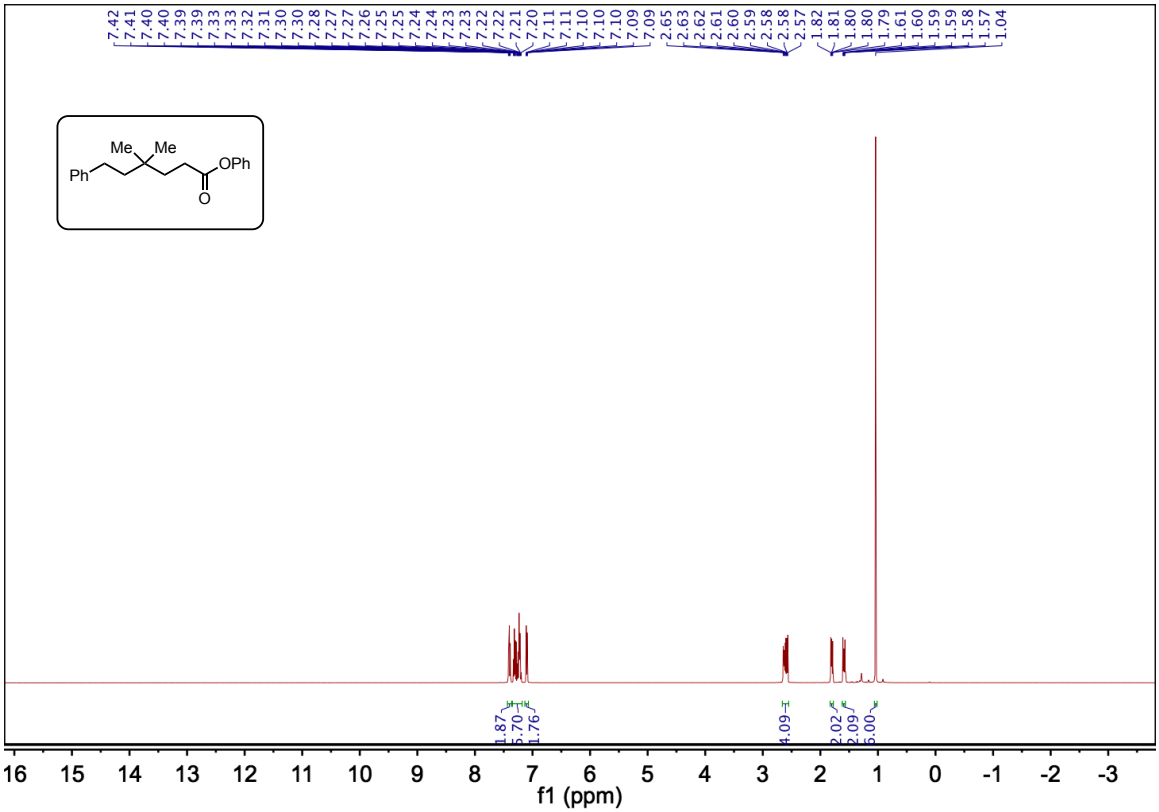

-73.78
-73.80
-73.82
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
f1 (ppm)

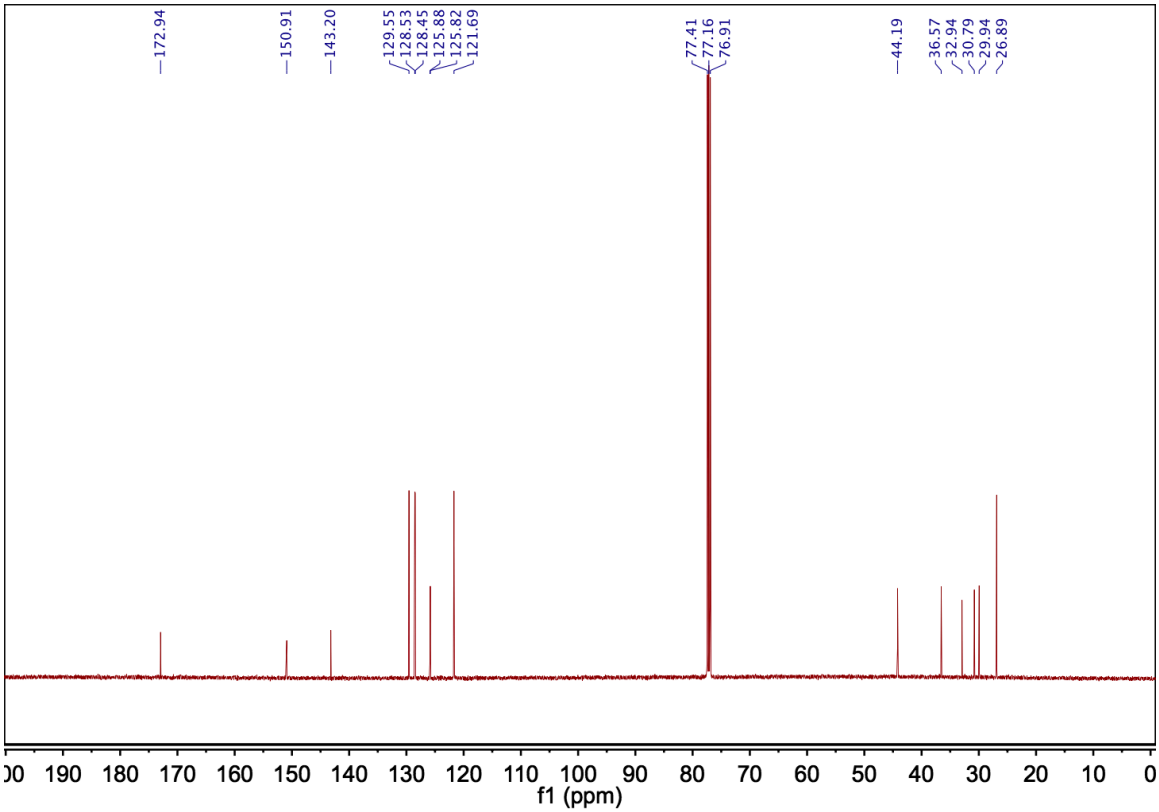
2-chloroethyl 6-(4-methoxyphenyl)-4,4-dimethylhexanoate (7)



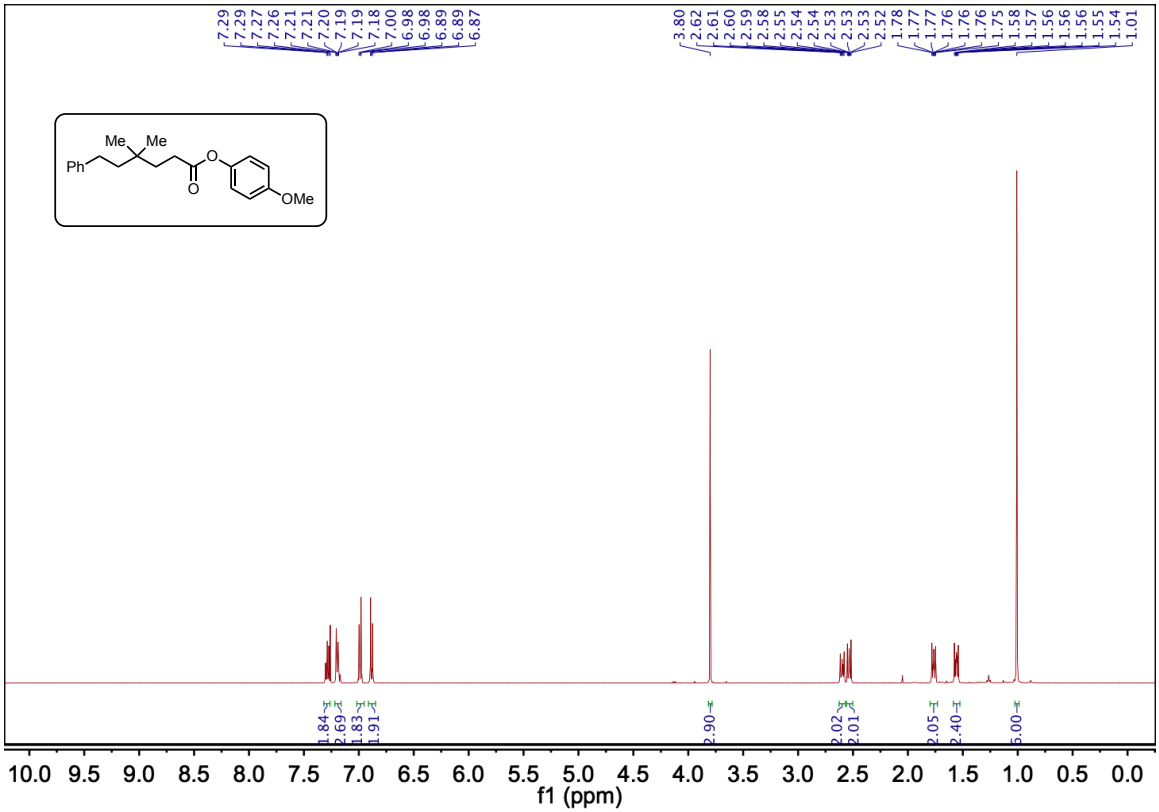


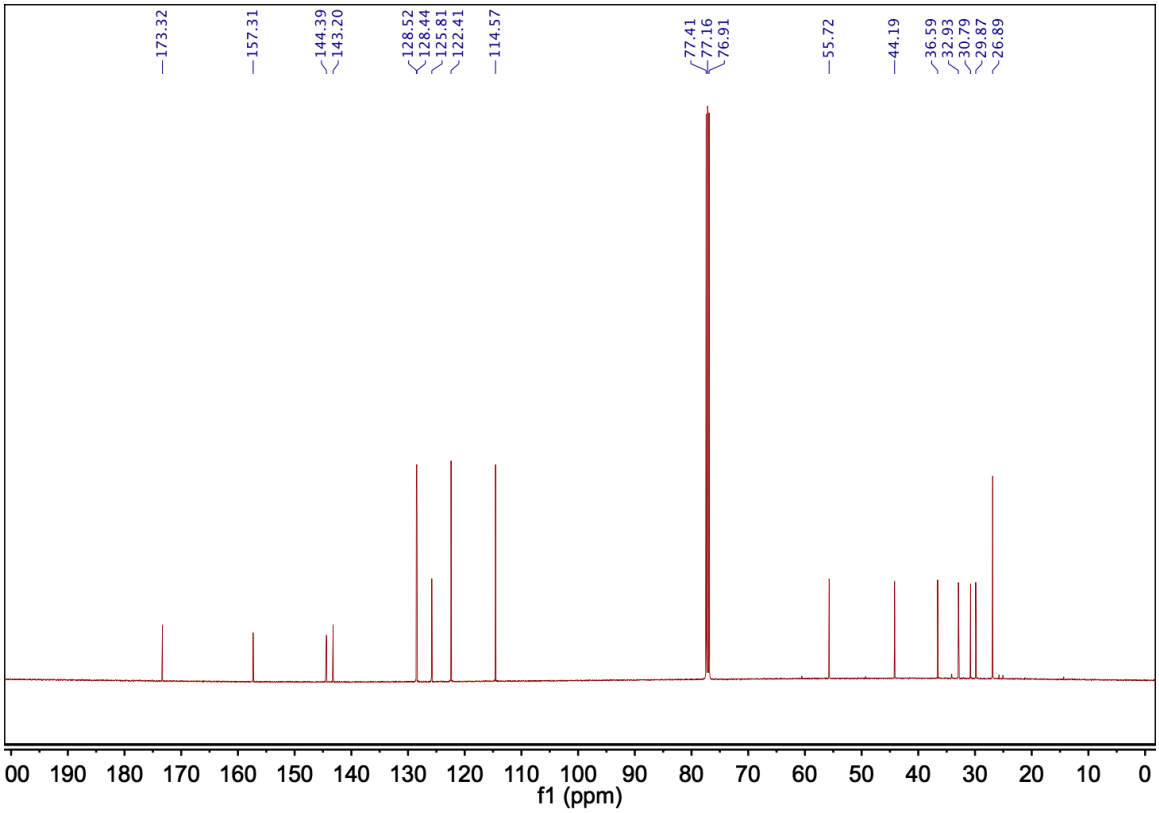
phenyl 4,4-dimethyl-6-phenylhexanoate (9)



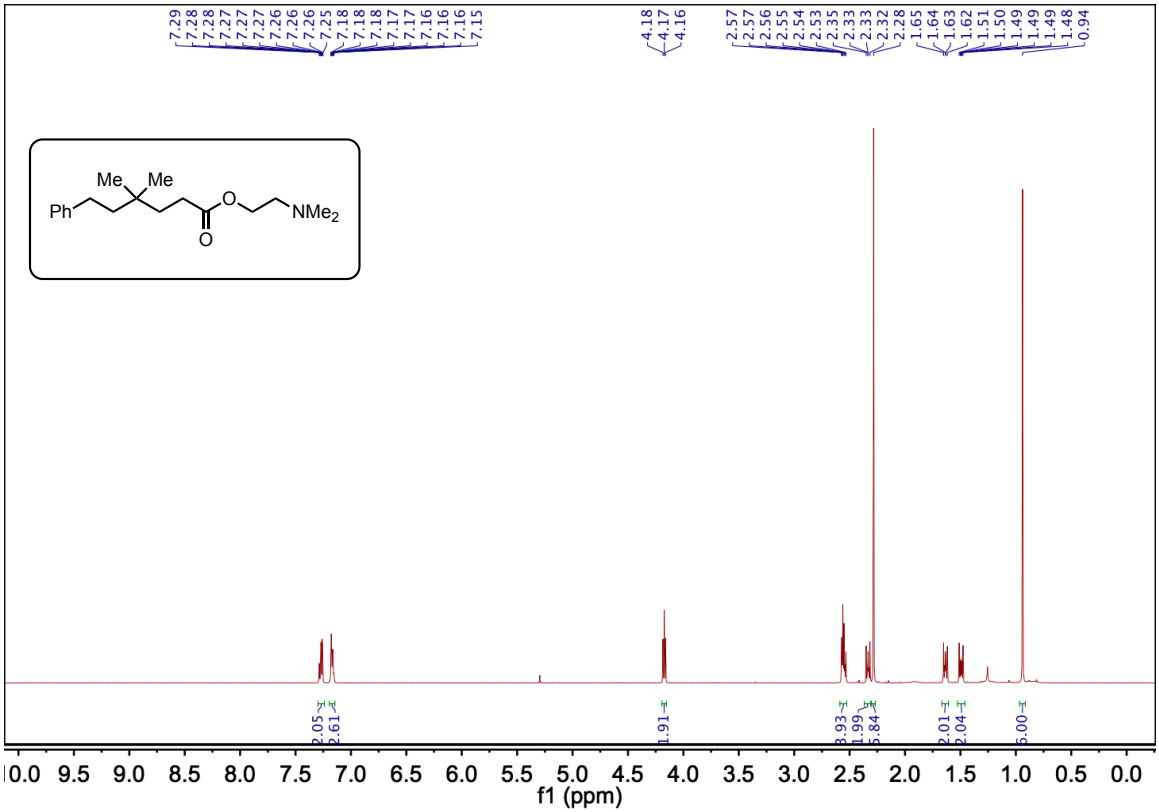


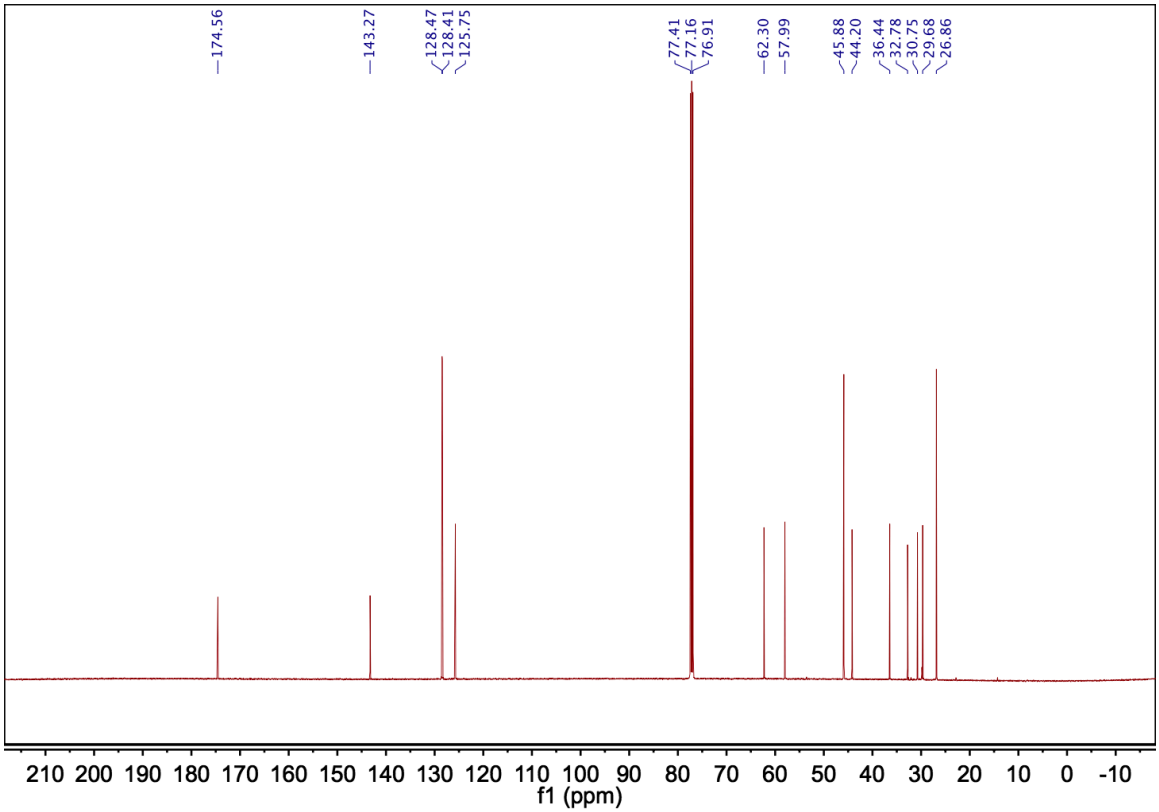
4-methoxyphenyl 4,4-dimethyl-6-phenylhexanoate (11)



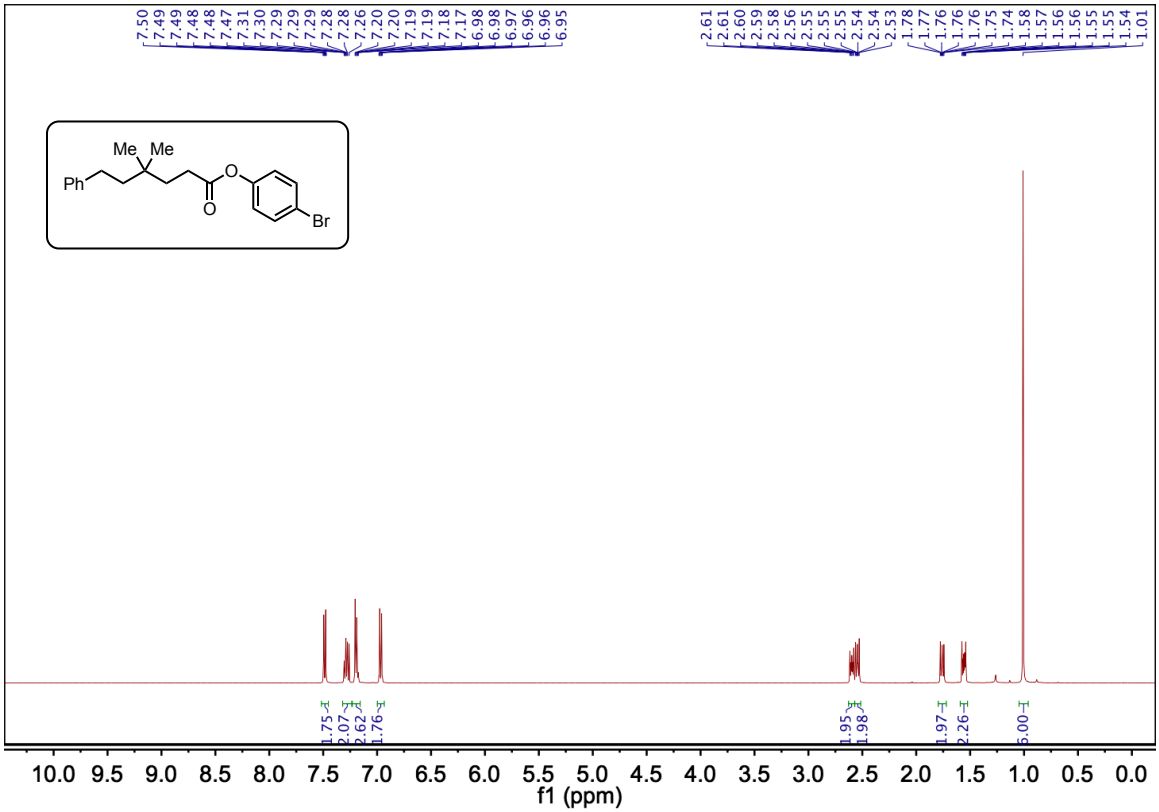


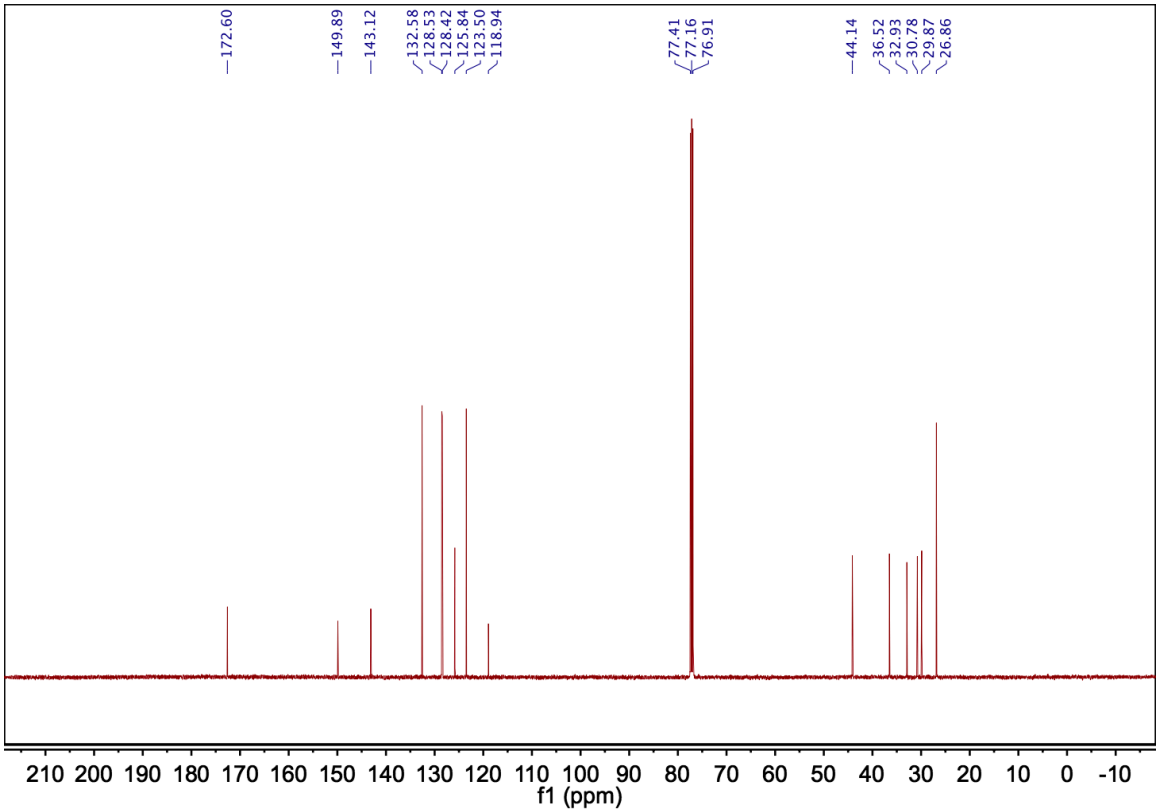
2-(dimethylamino)ethyl 4,4-dimethyl-6-phenylhexanoate (13)



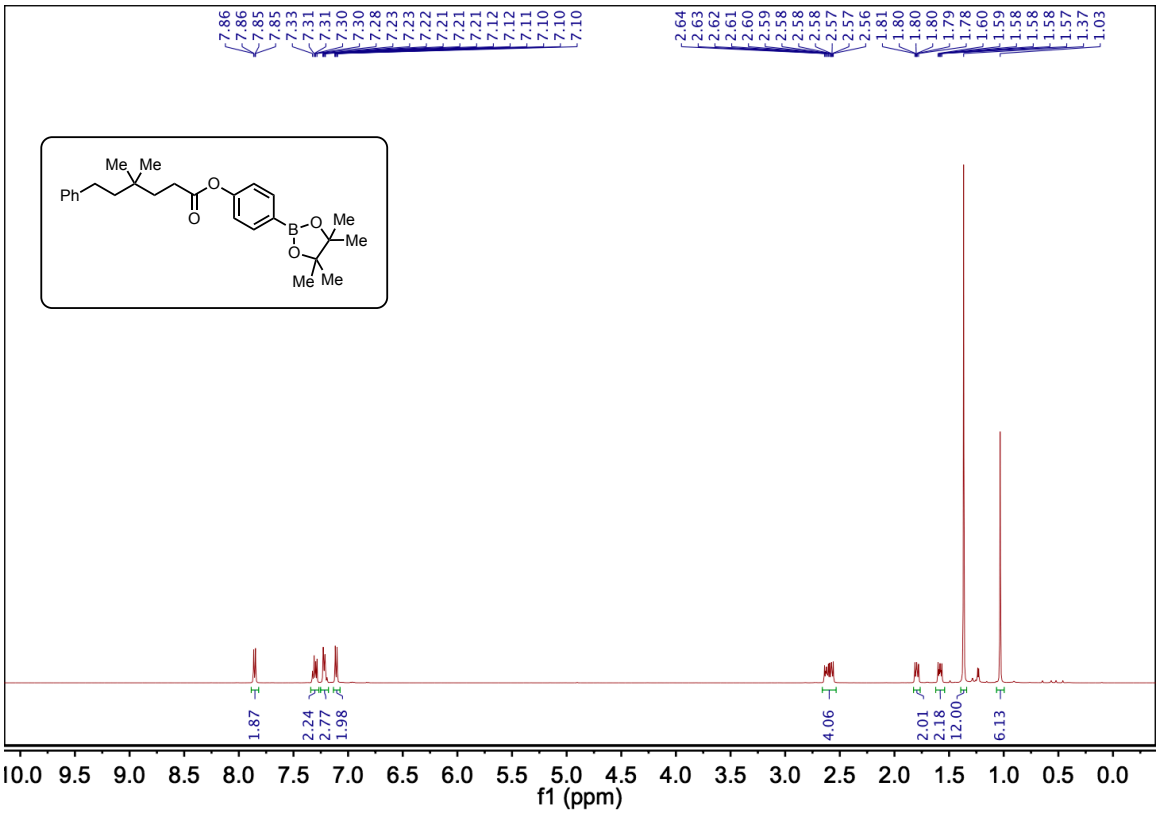


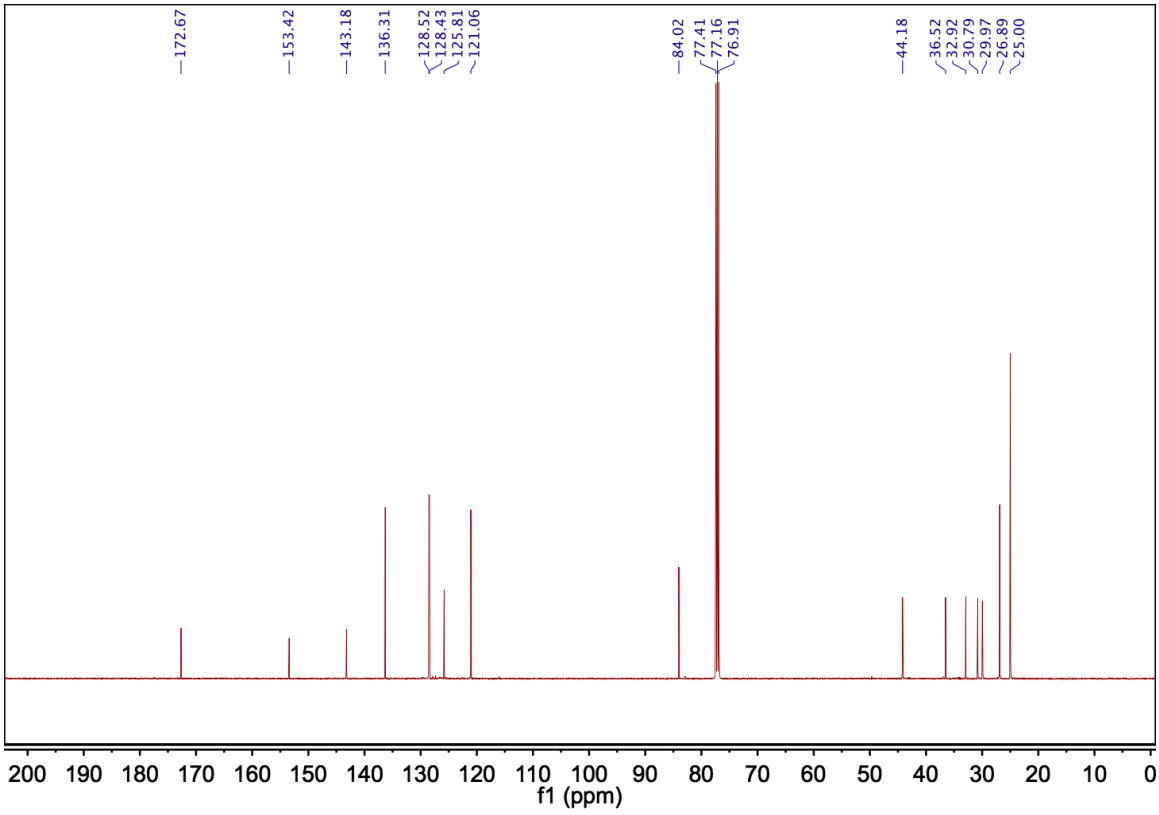
4-bromophenyl 4,4-dimethyl-6-phenylhexanoate (15)



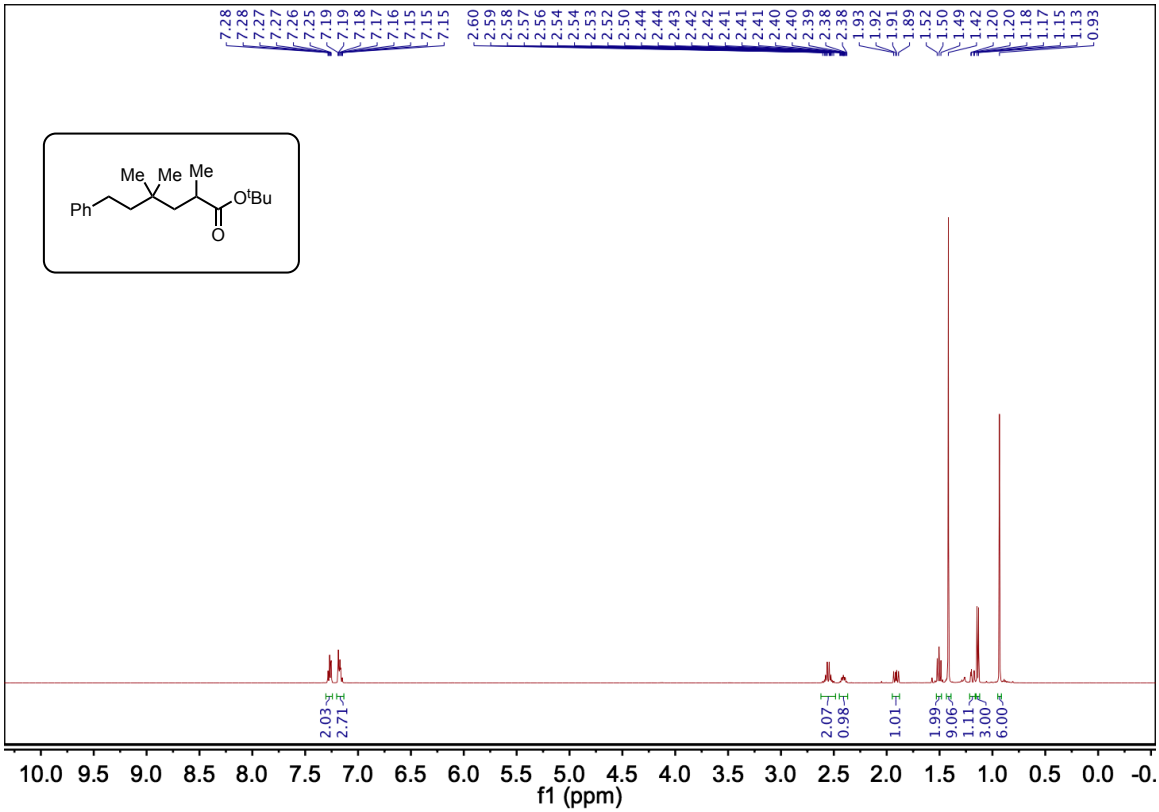


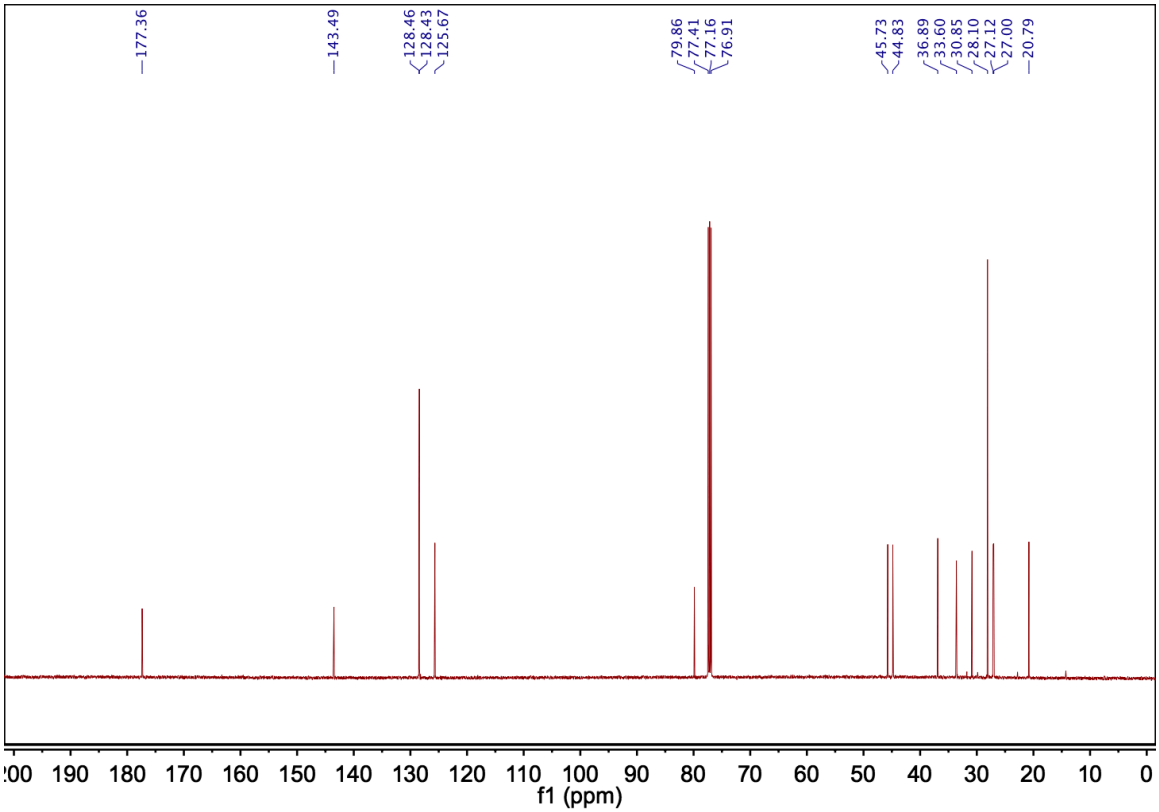
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl 4,4-dimethyl-6-phenylhexanoate (17)



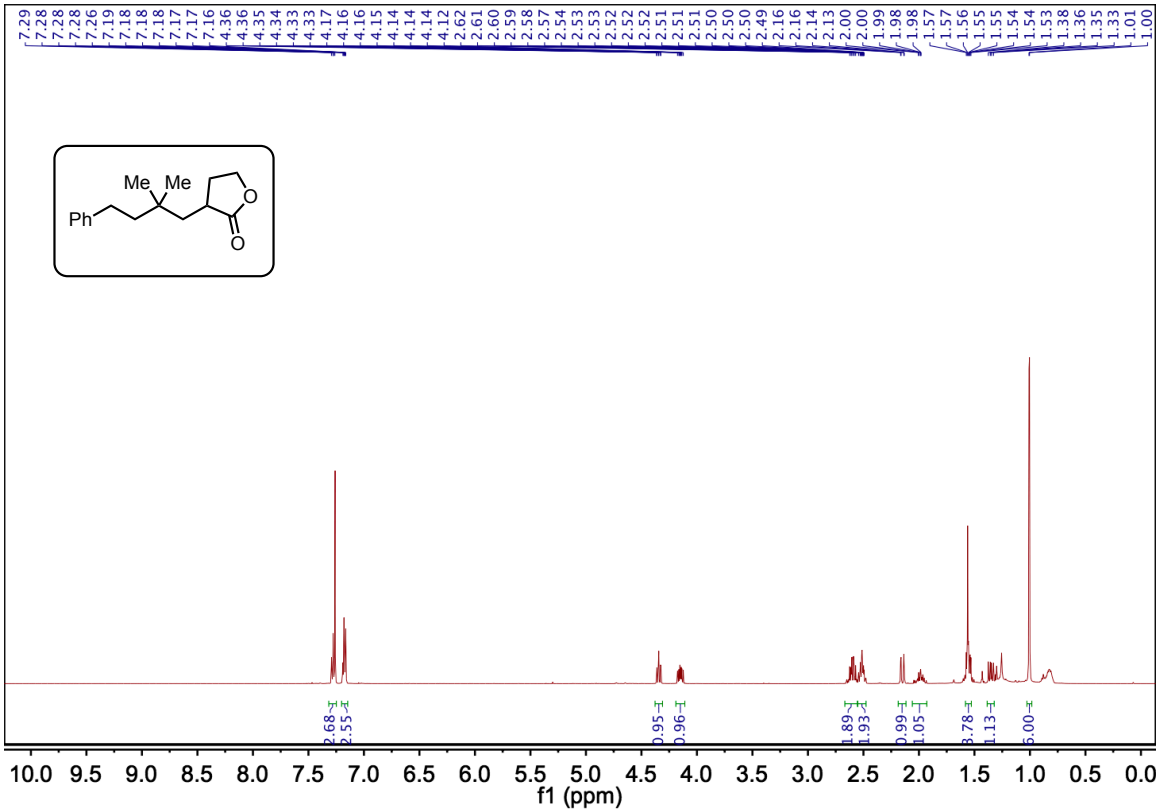


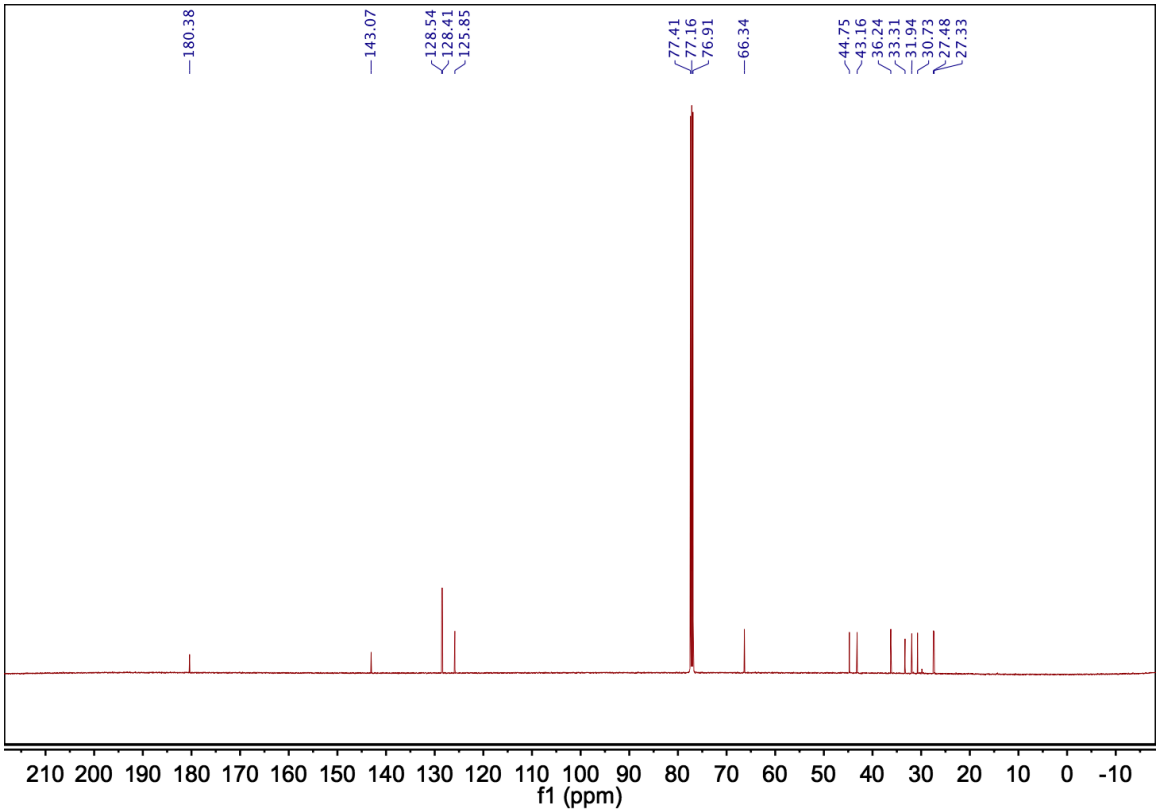
***tert*-butyl 2,4,4-trimethyl-6-phenylhexanoate (19)**



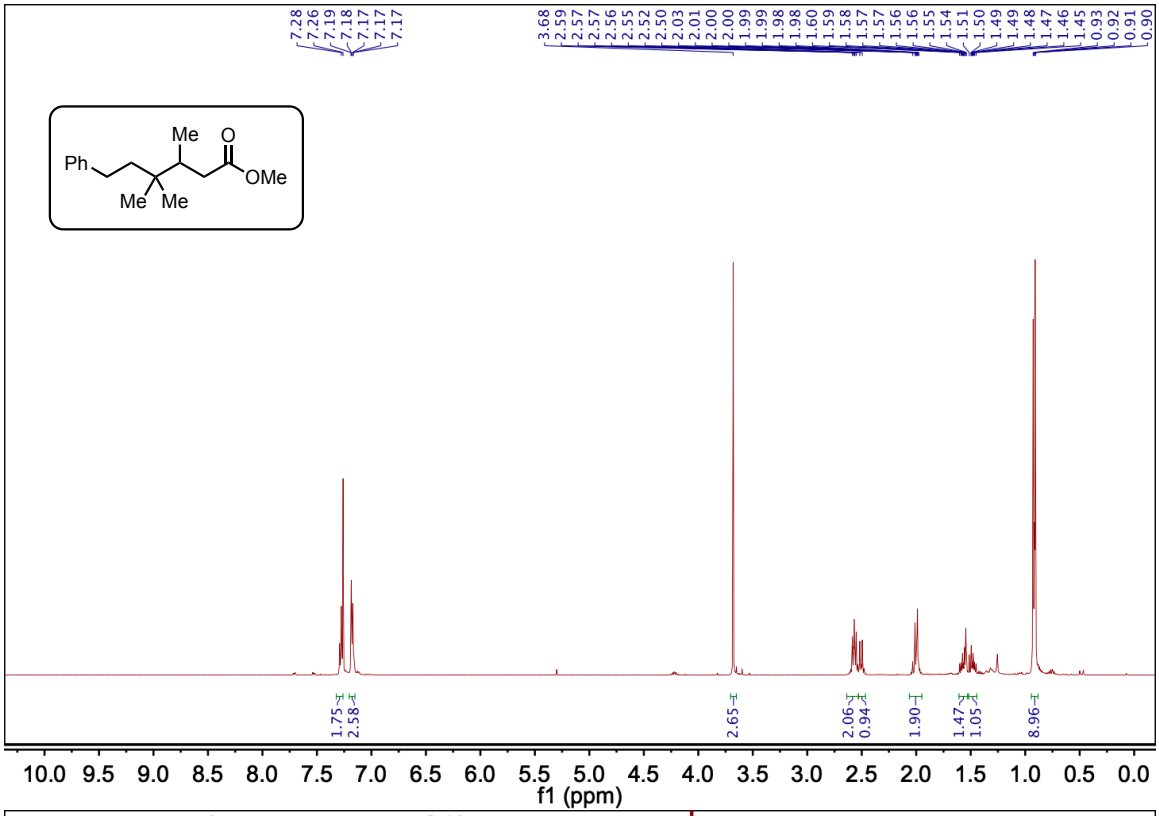


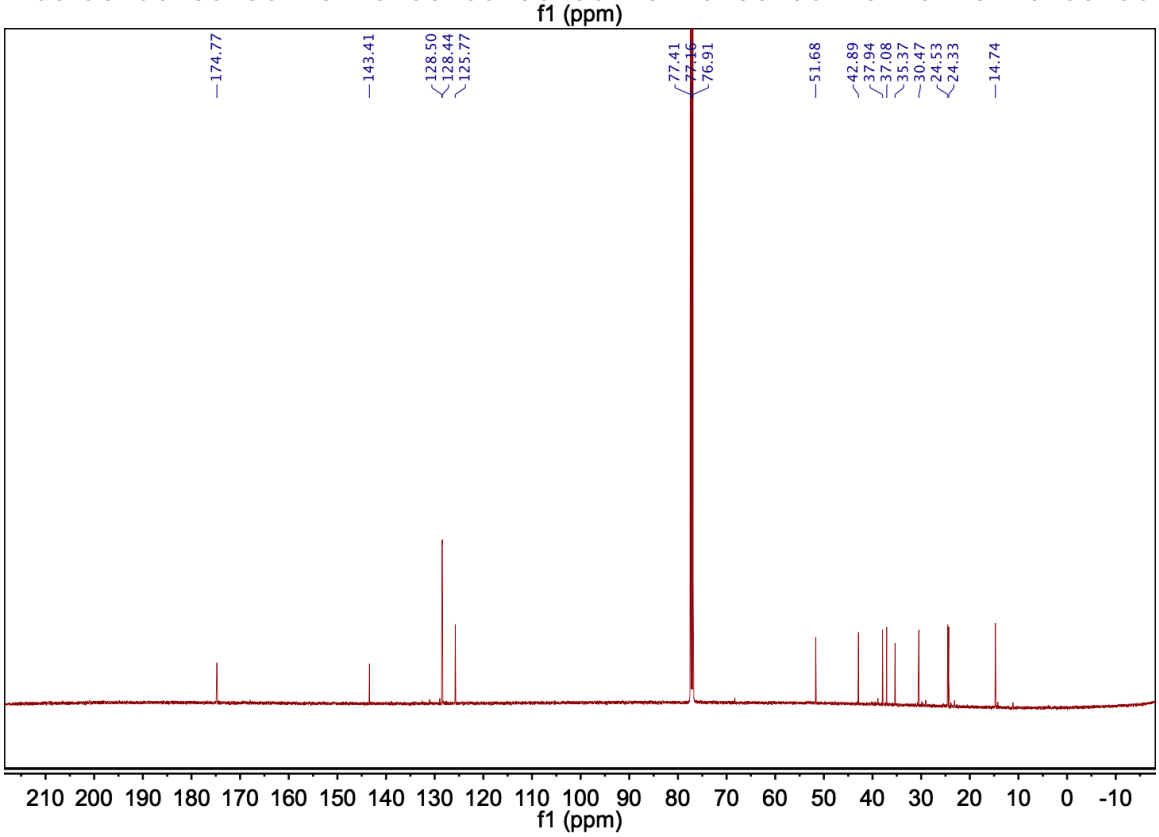
3-(2,2-dimethyl-4-phenylbutyl)dihydrofuran-2(3*H*)-one (21)



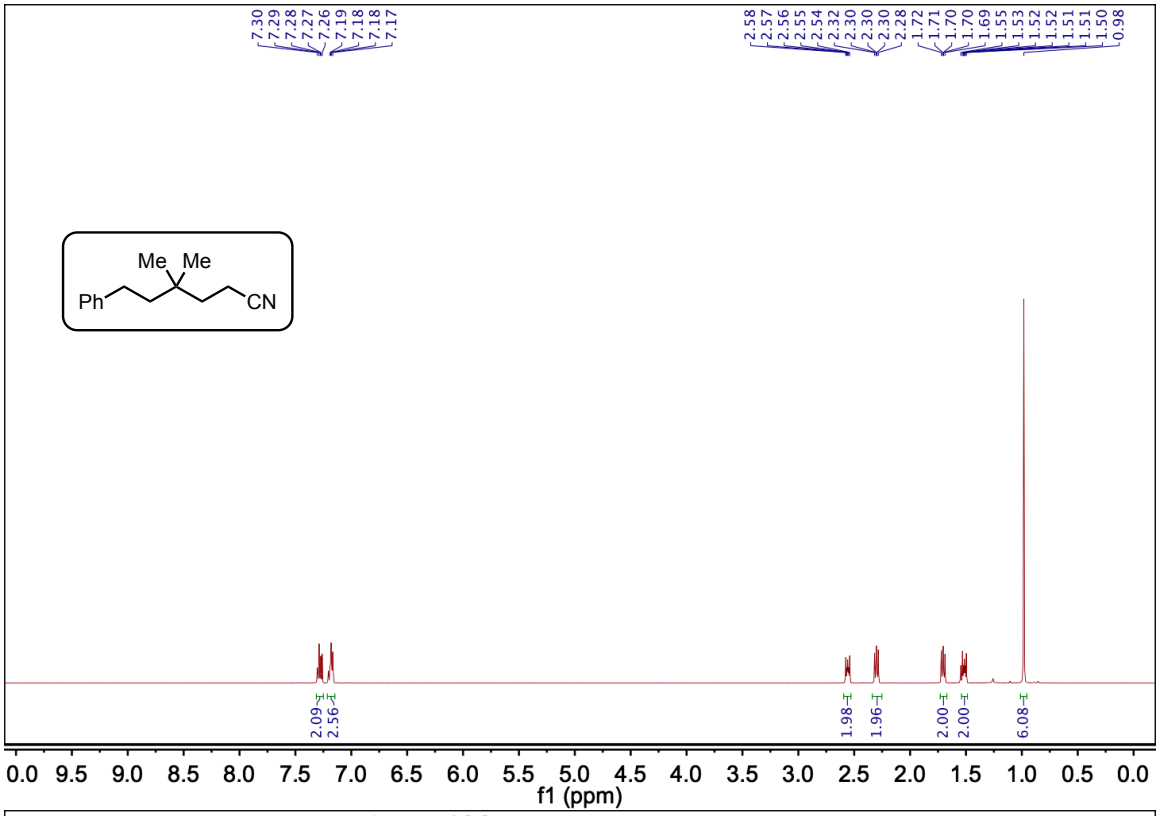


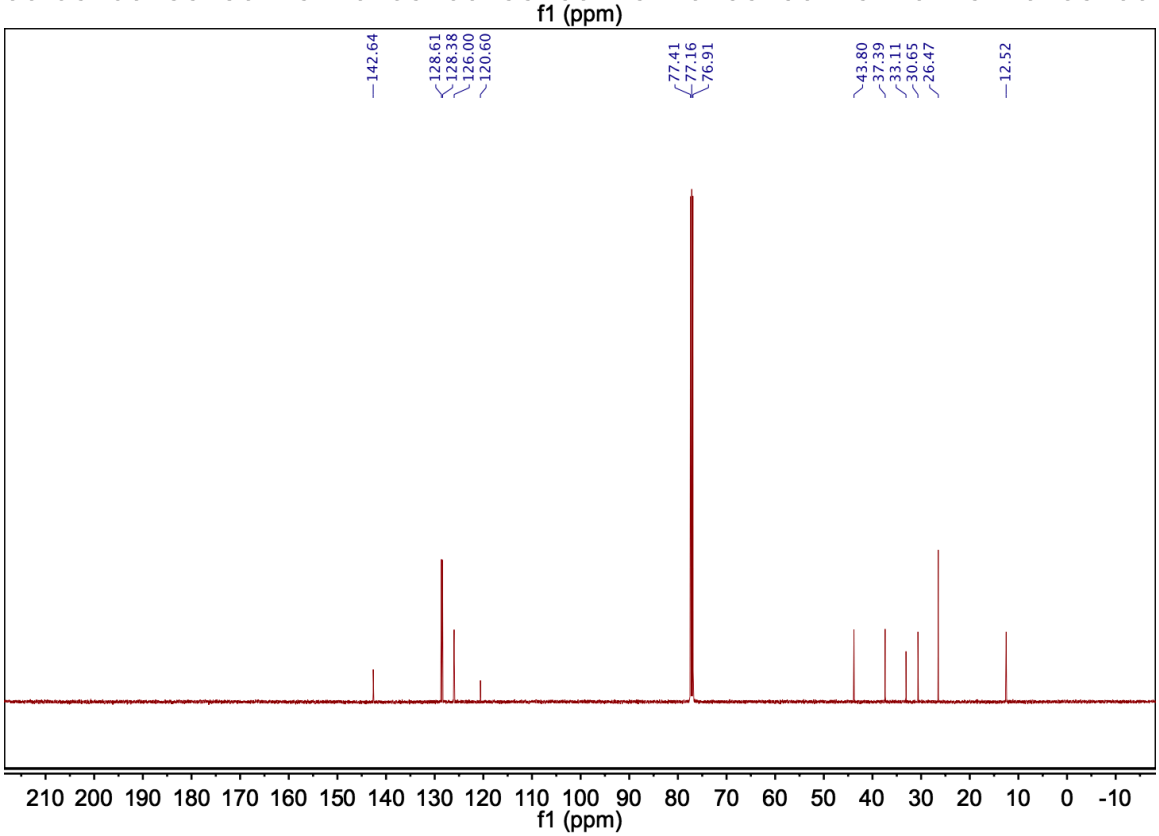
methyl 3,4,4-trimethyl-6-phenylhexanoate (23)



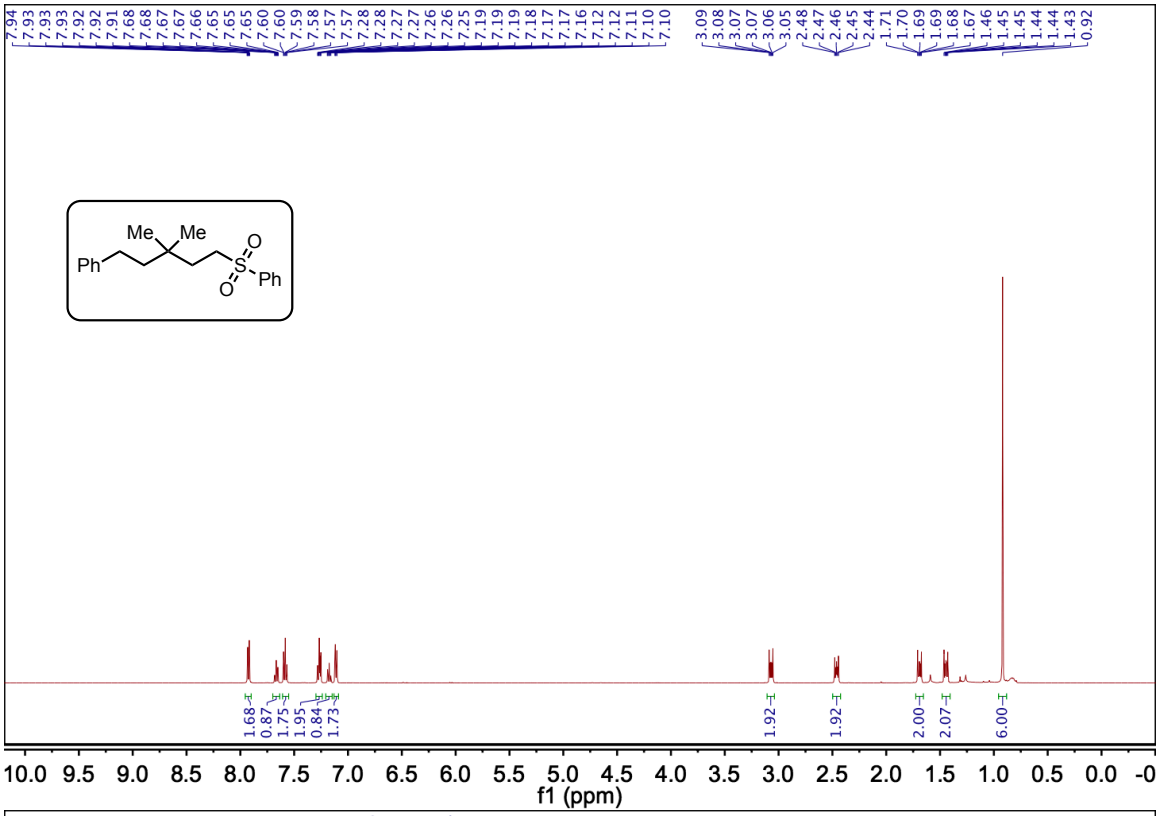


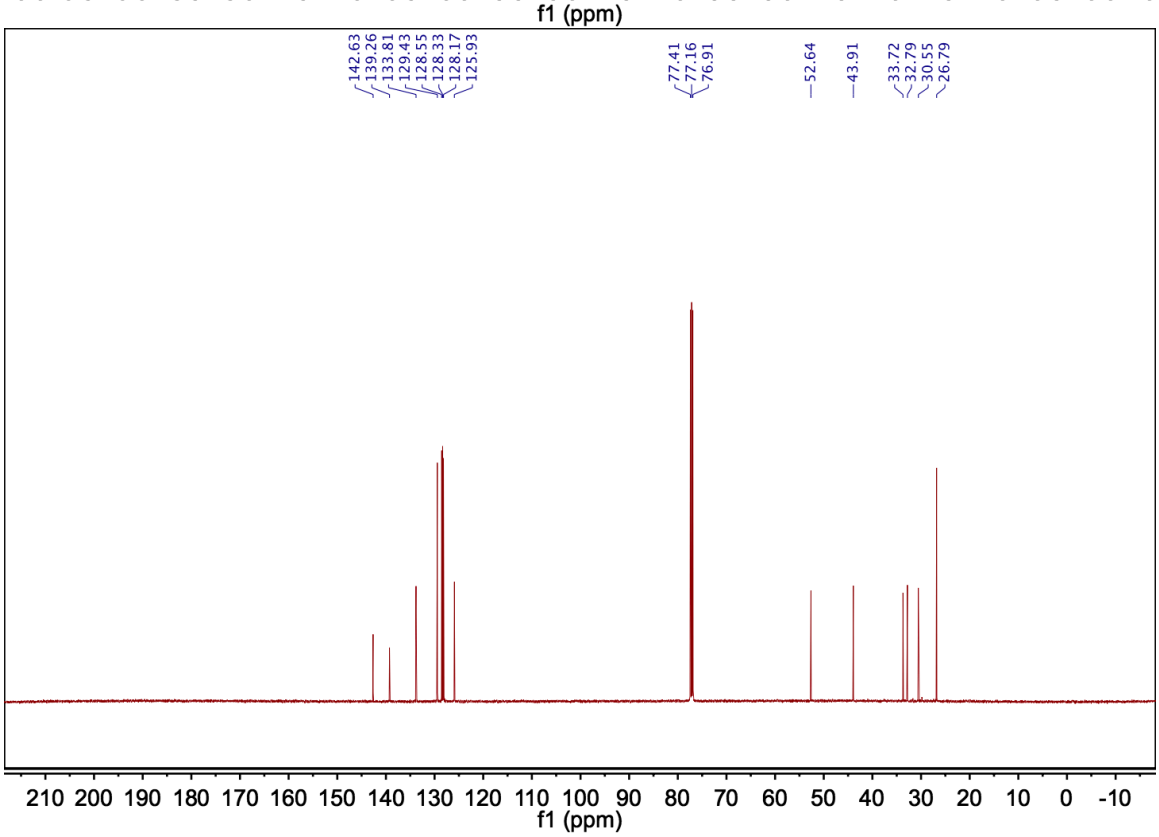
4,4-dimethyl-6-phenylhexanenitrile (25)



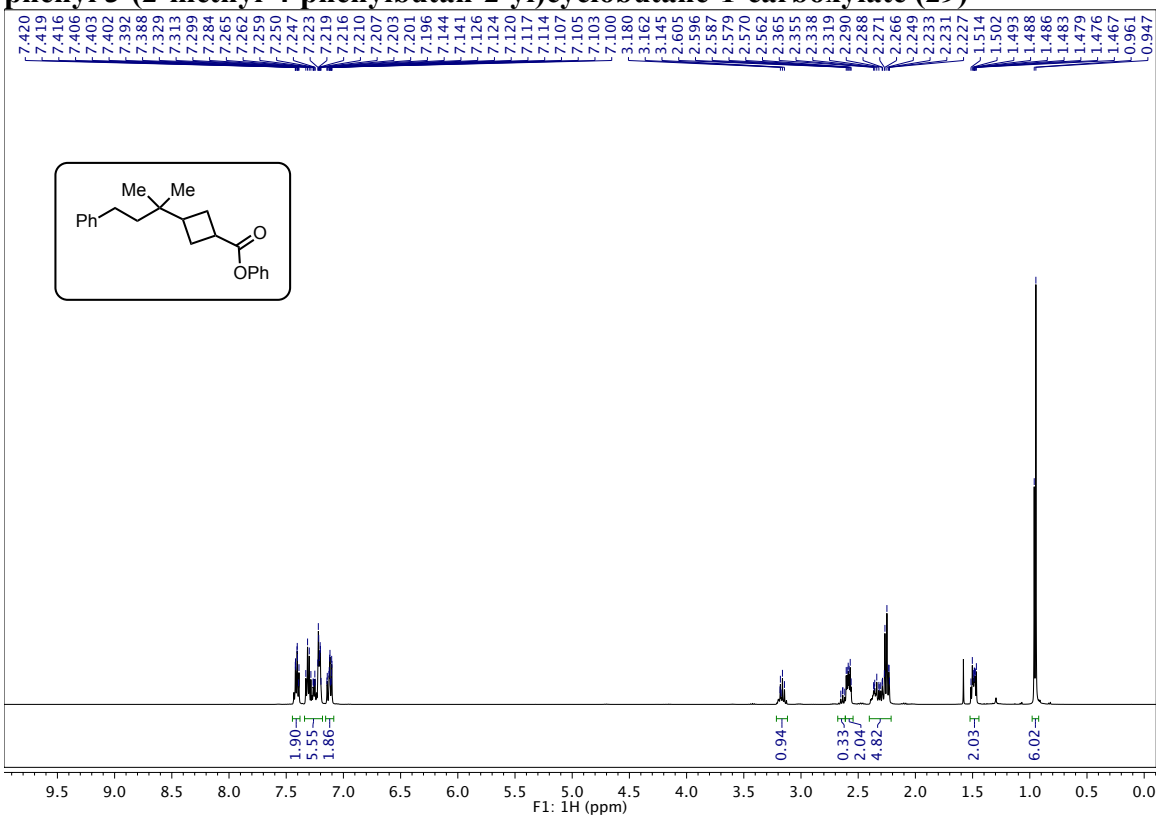


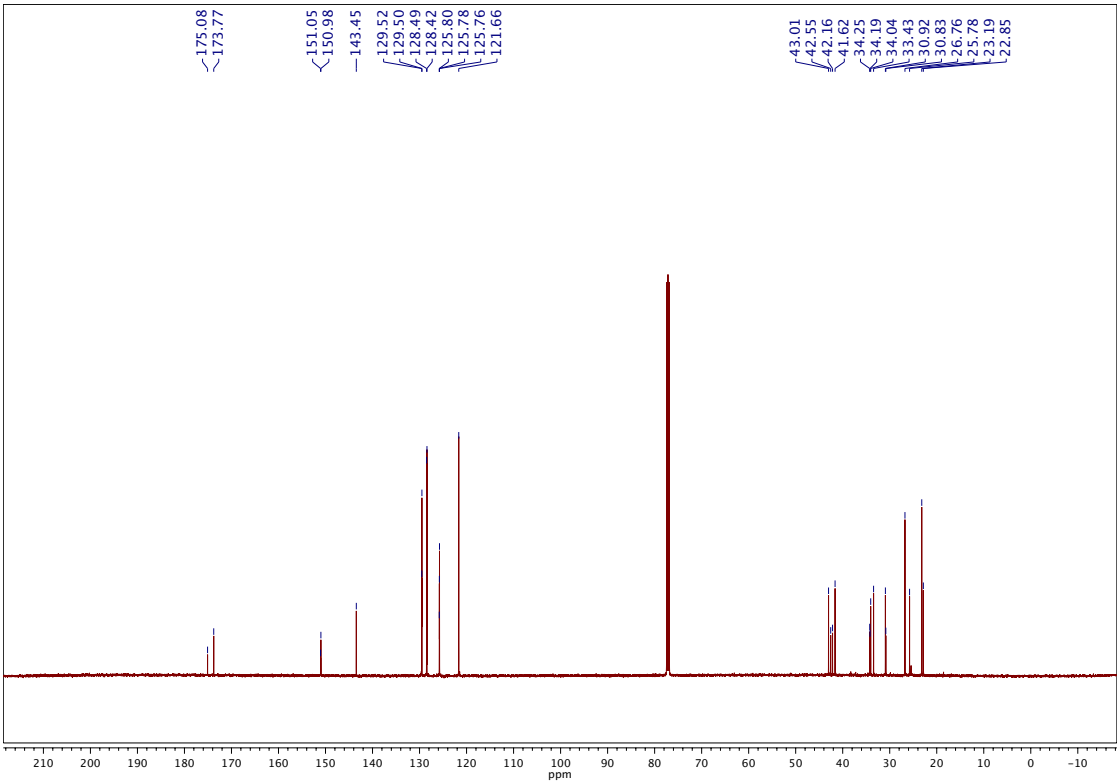
(3,3-dimethyl-5-(phenylsulfonyl)pentyl)benzene (27)





phenyl 3-(2-methyl-4-phenylbutan-2-yl)cyclobutane-1-carboxylate (29)





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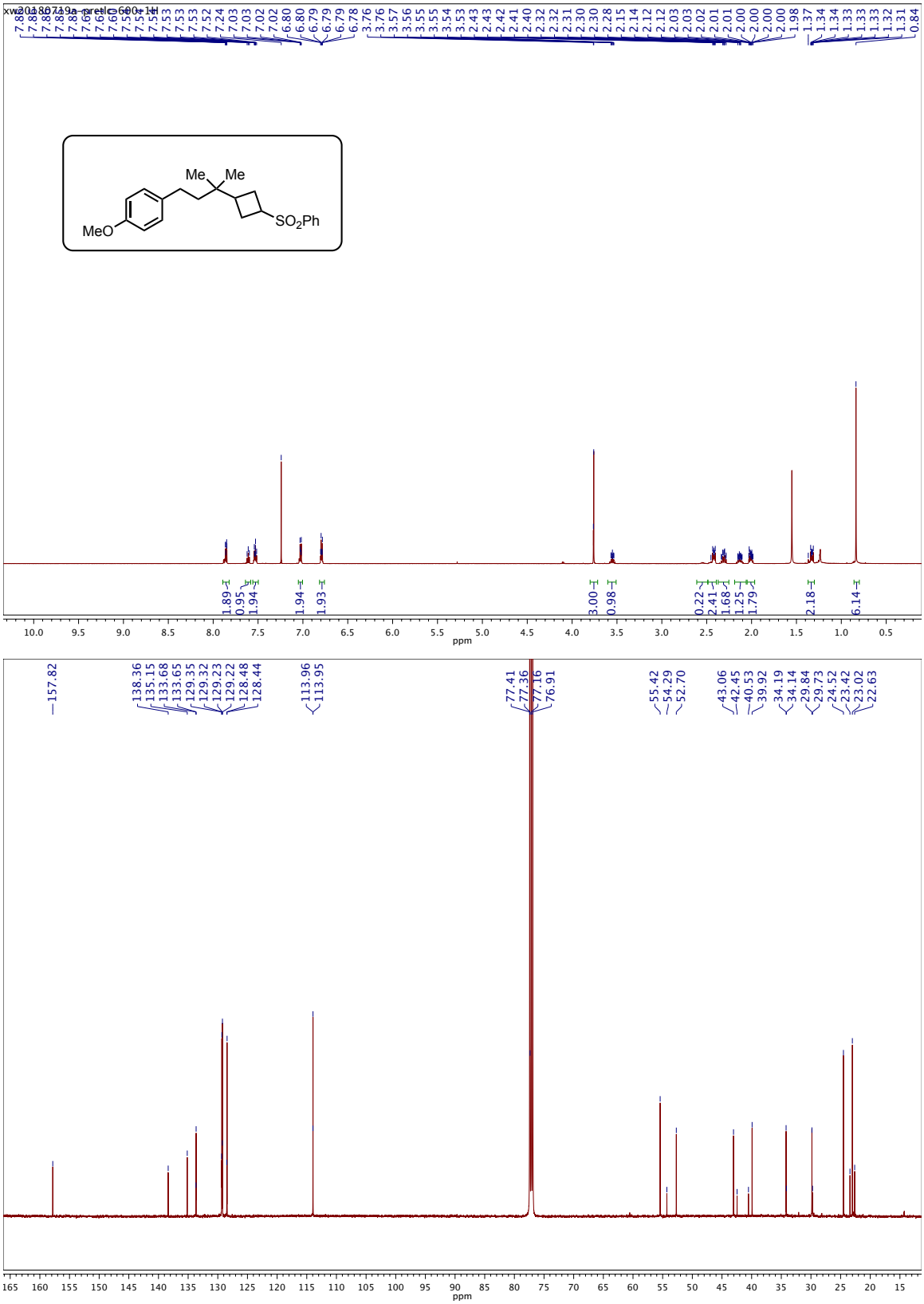
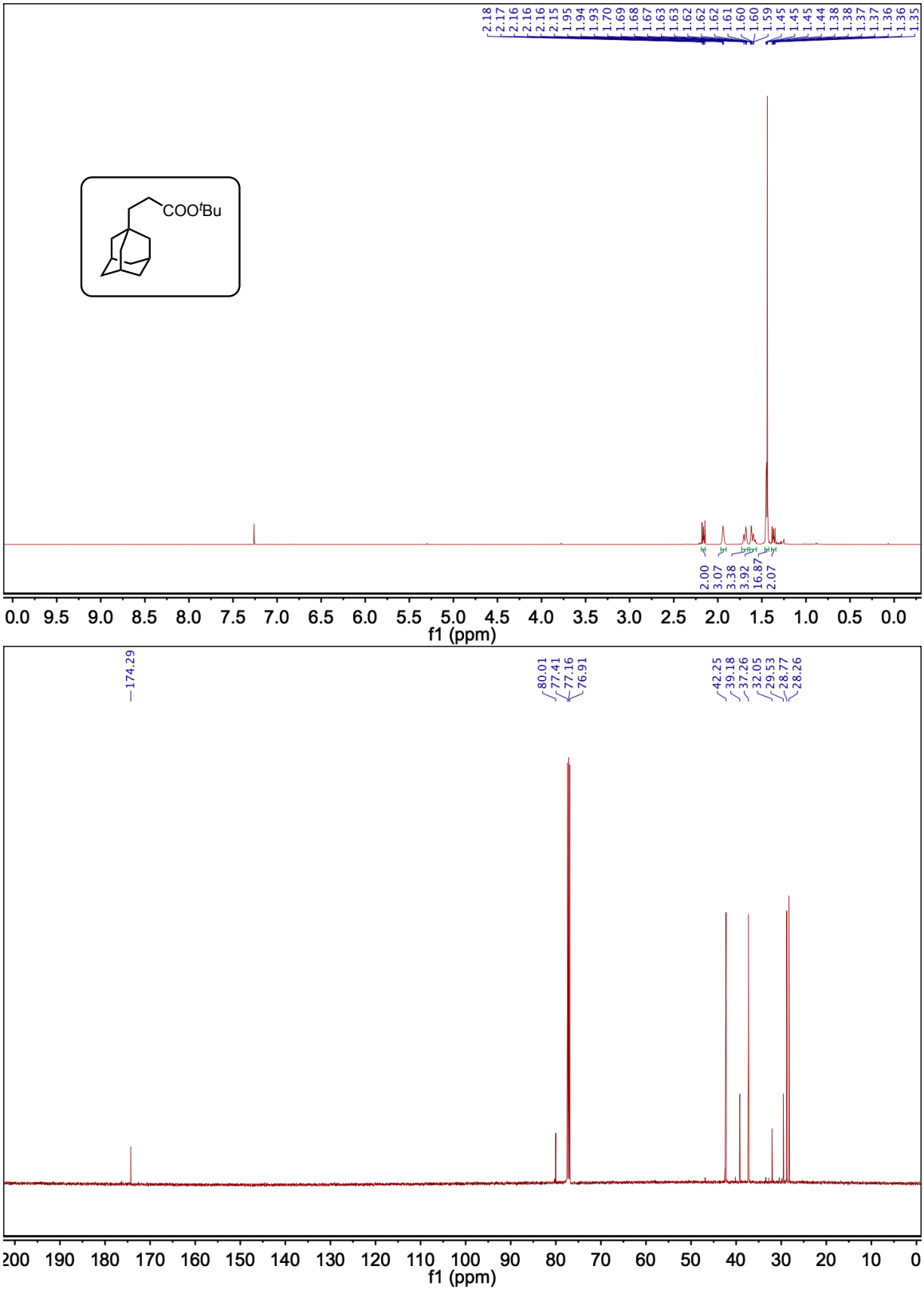


***tert*-butyl 3-((3*r*,5*r*,7*r*)-adamantan-1-yl)propanoate (33)**



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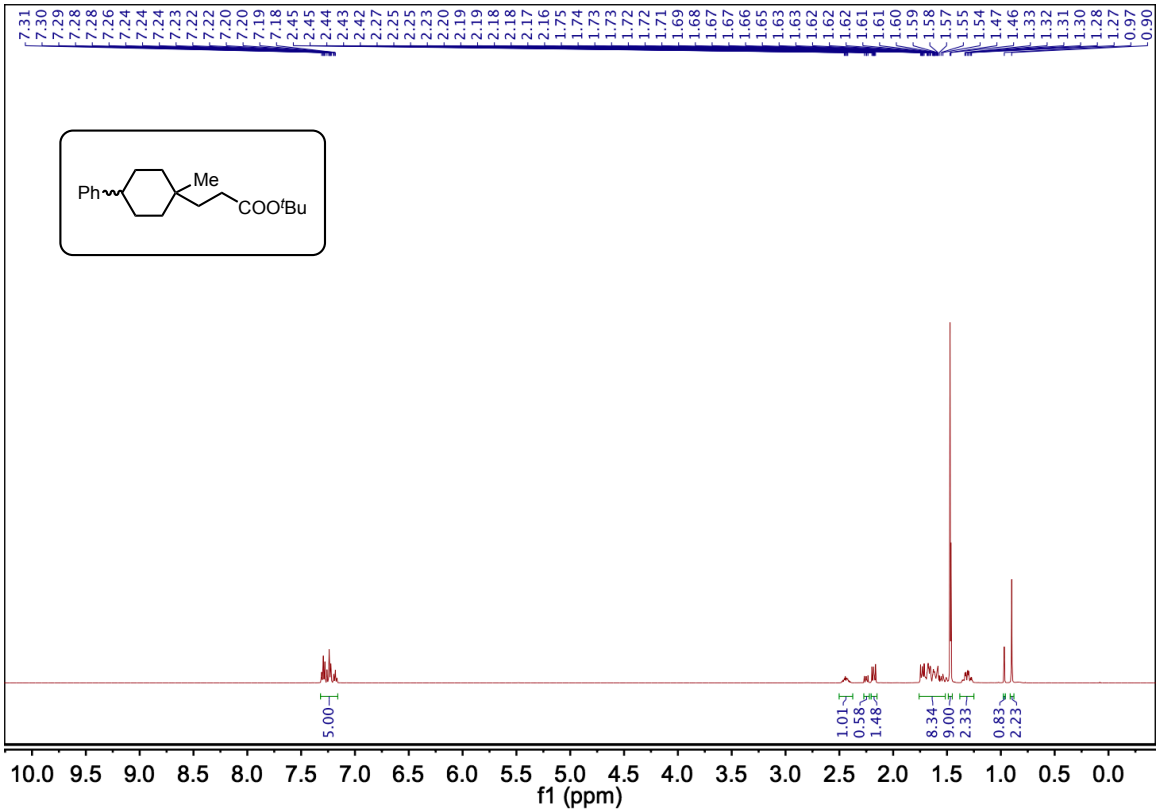
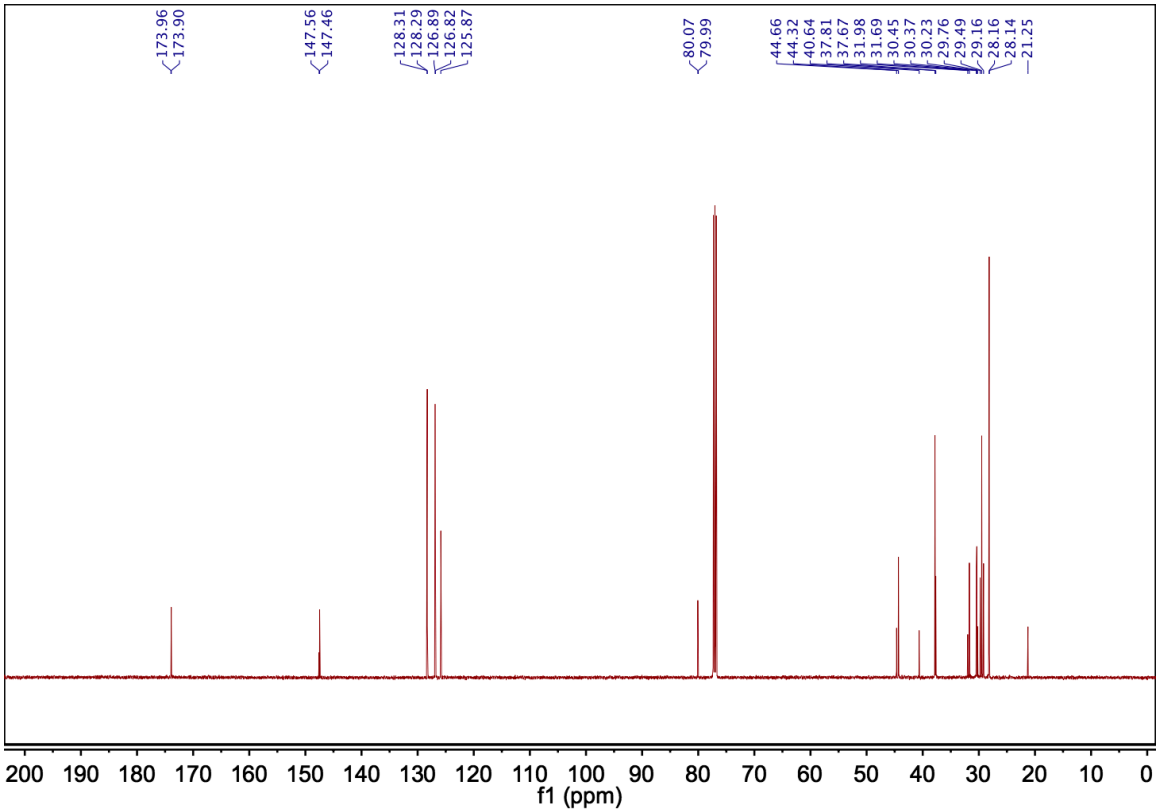
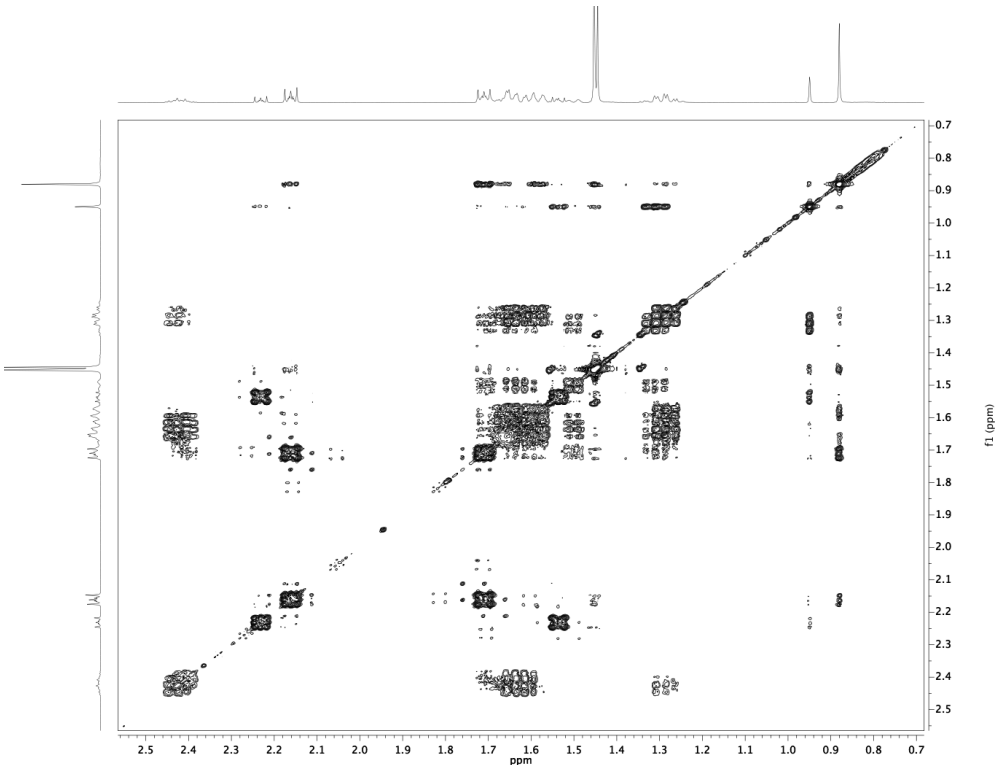
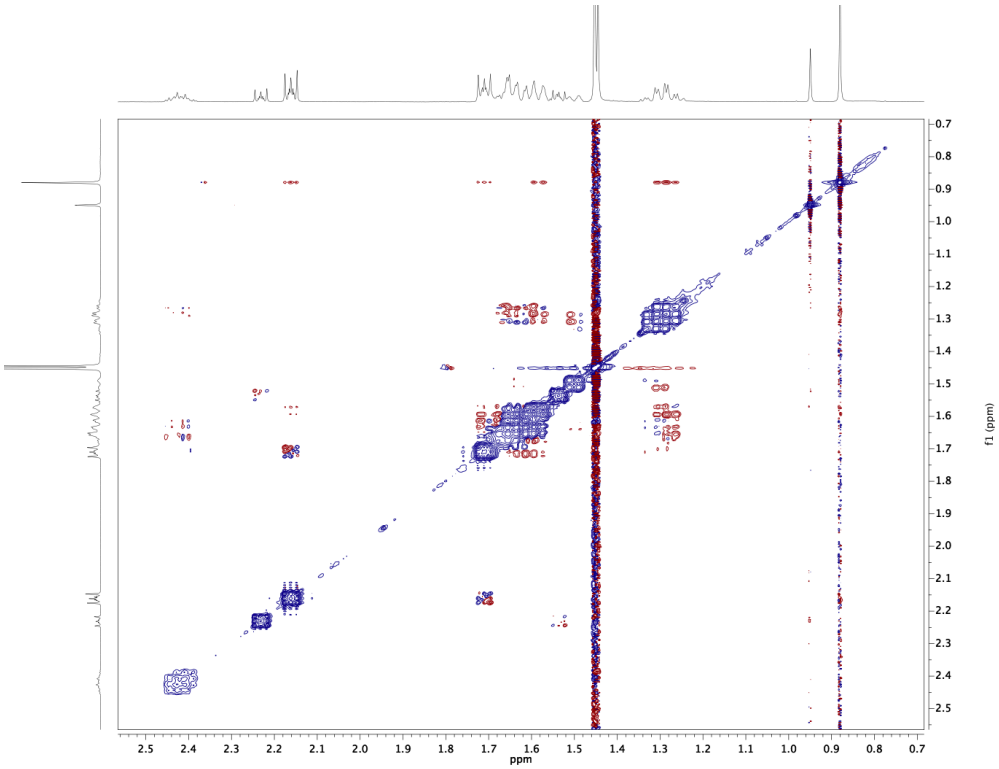




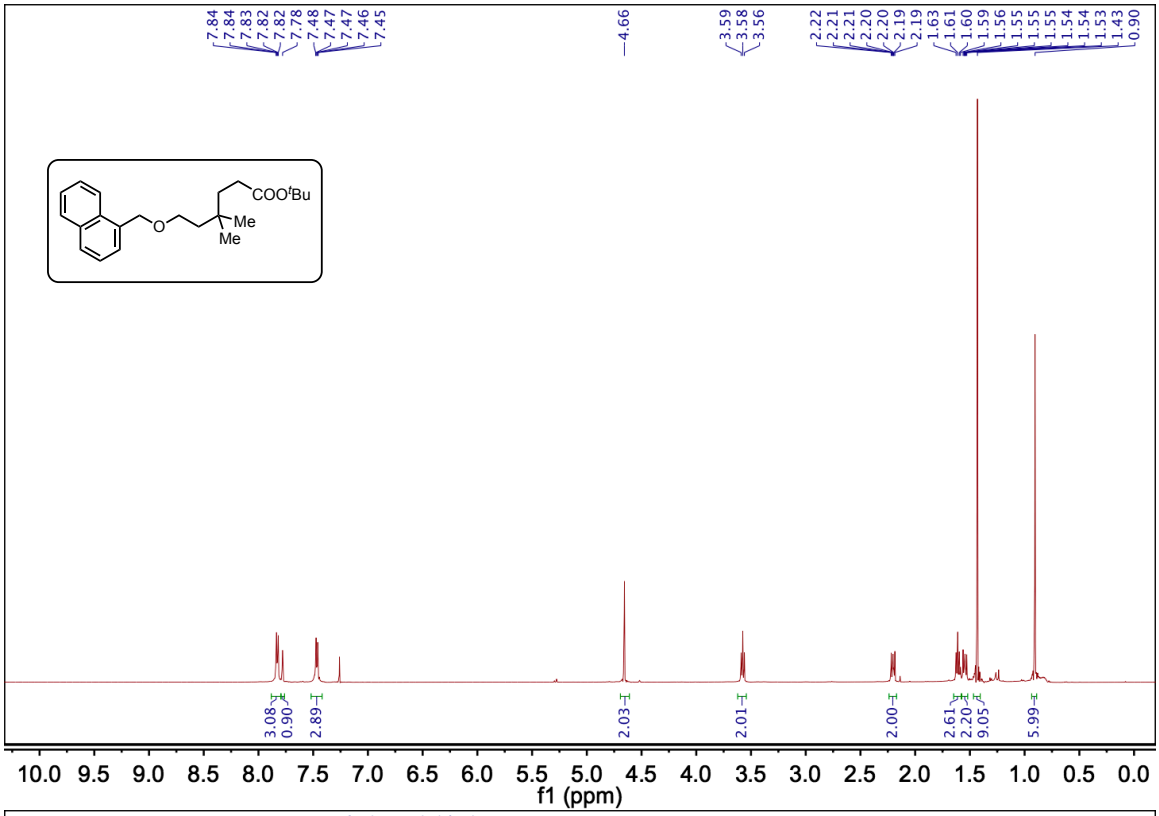
COSY

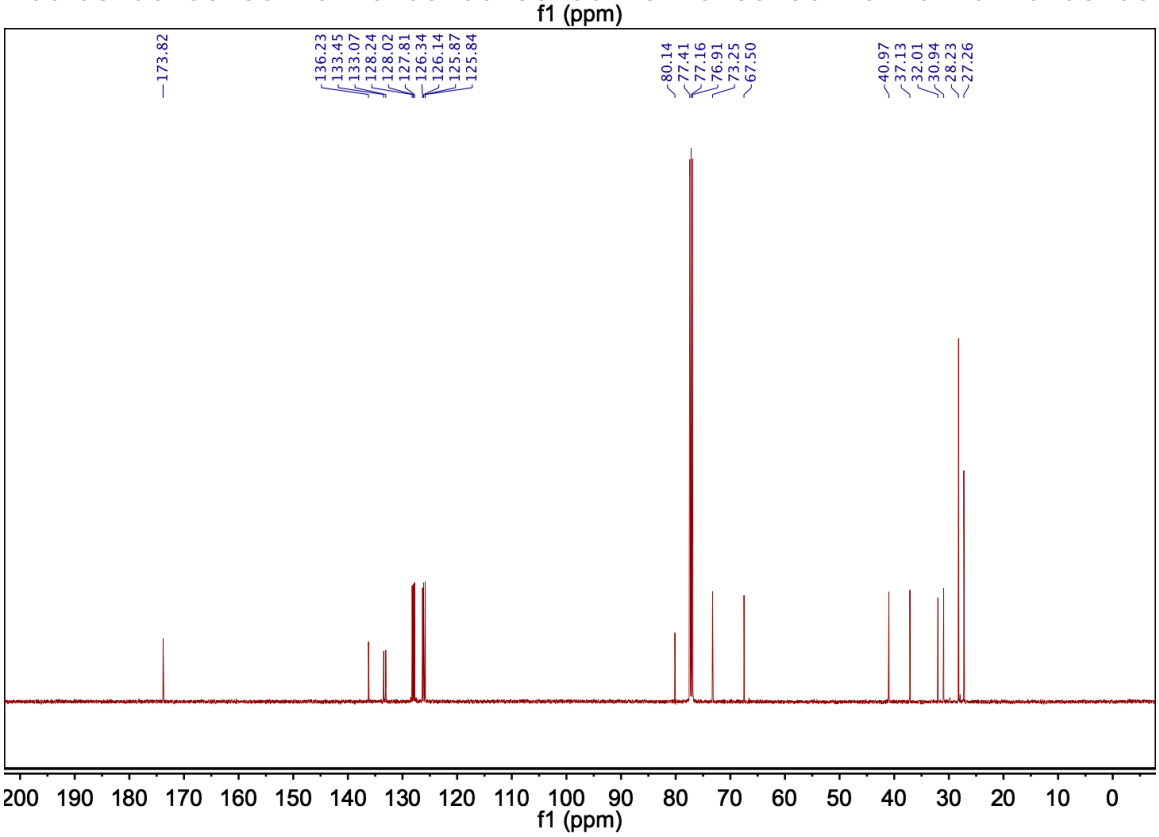

0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
f1 (ppm)
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7
ppm

ROSY

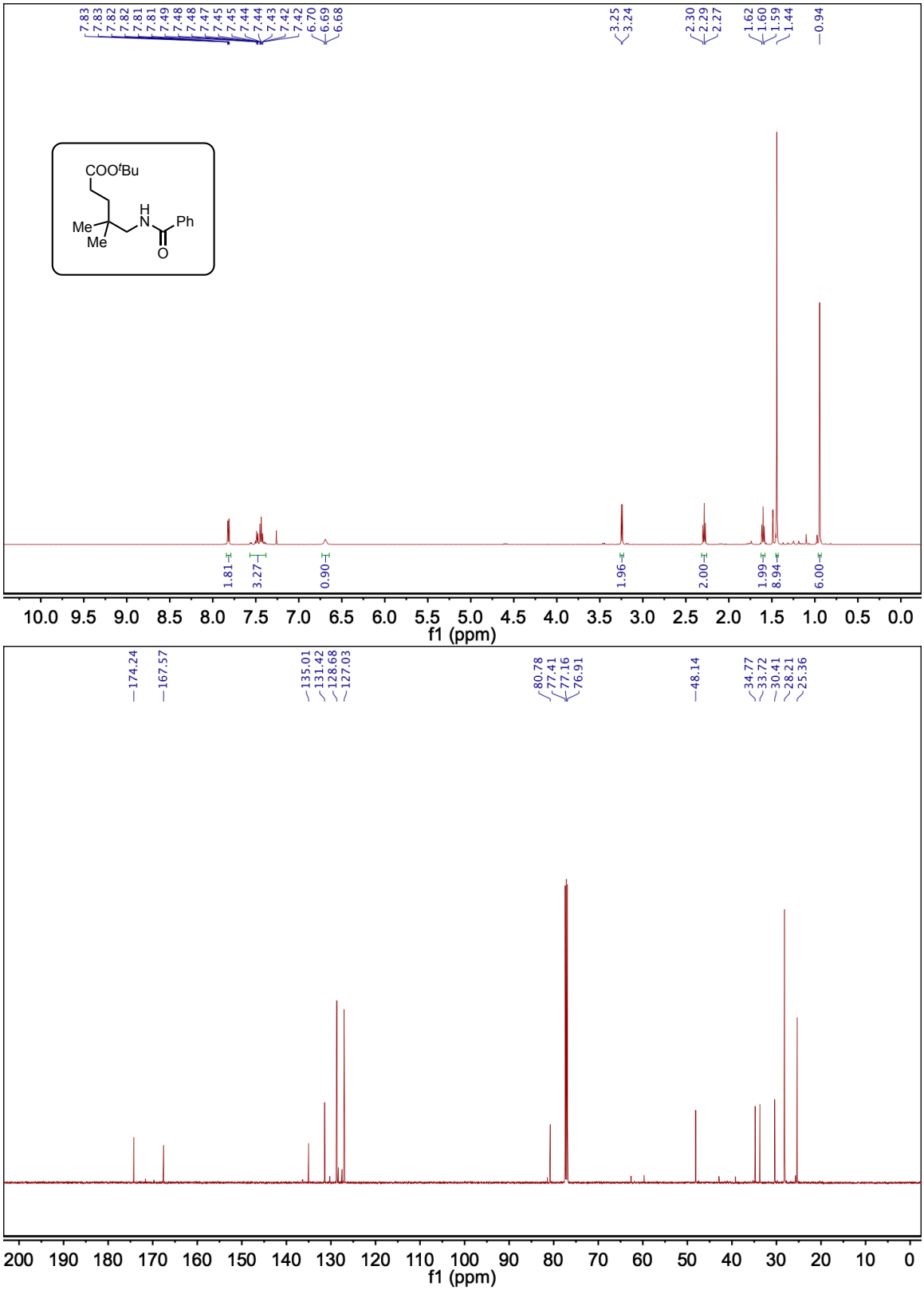

0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
f1 (ppm)
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7
ppm

tert-butyl 4,4-dimethyl-6-(naphthalen-1-ylmethoxy)hexanoate (37)

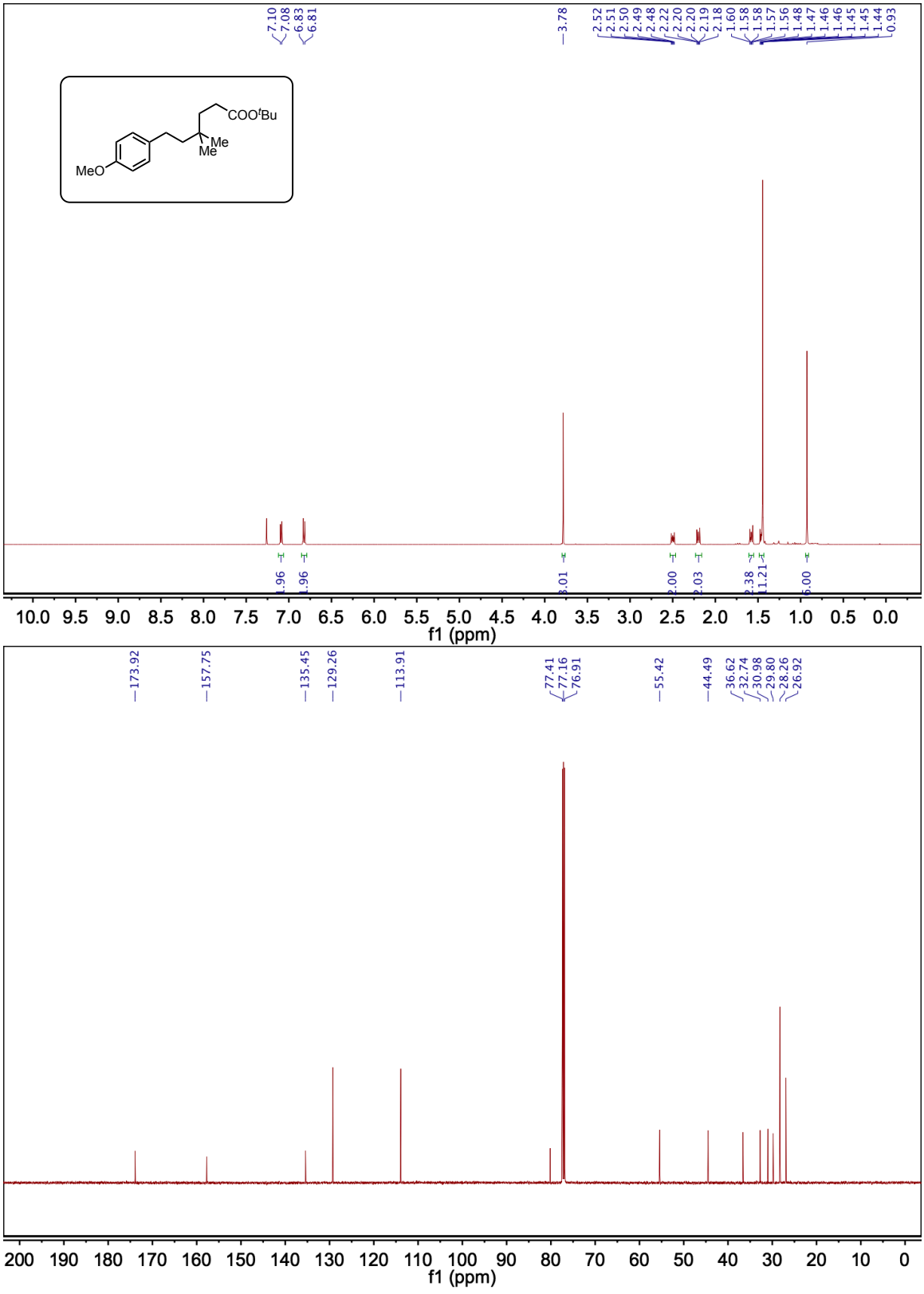




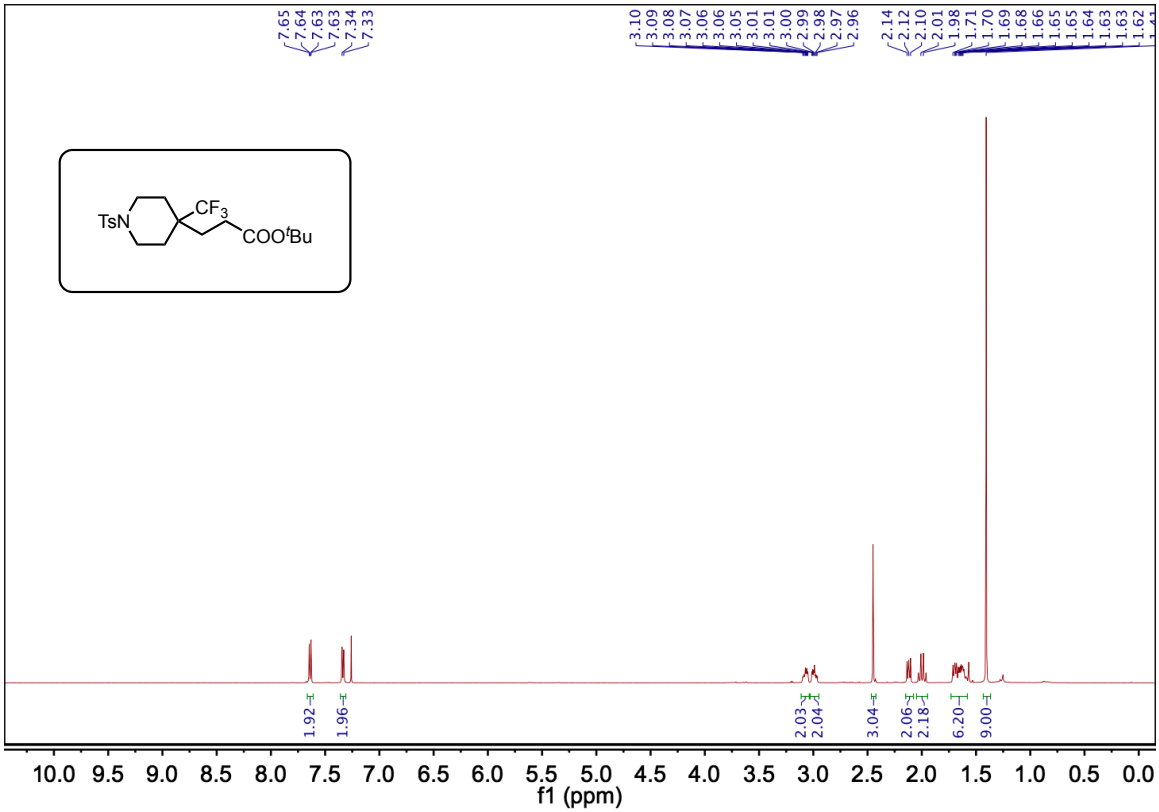
***tert*-butyl 5-benzamido-4,4-dimethylpentanoate (39)**

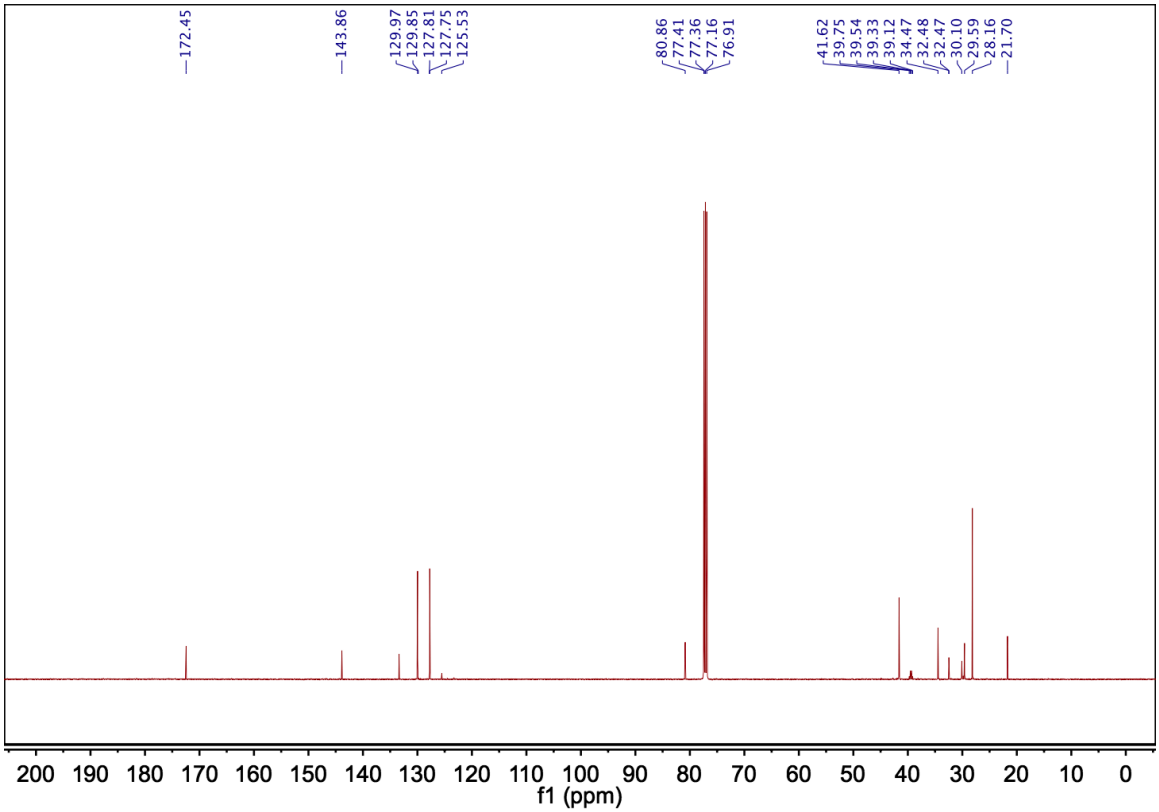


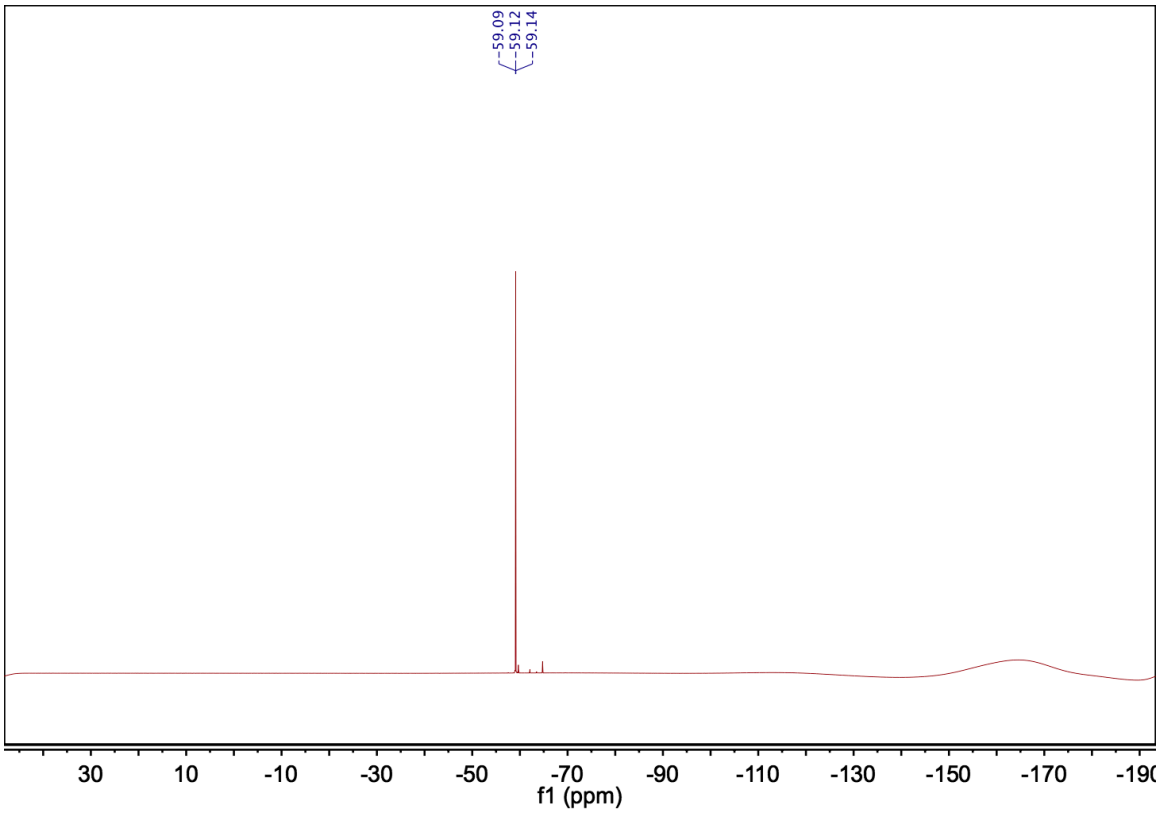
***tert*-butyl 6-(4-methoxyphenyl)-4,4-dimethylhexanoate (41)**



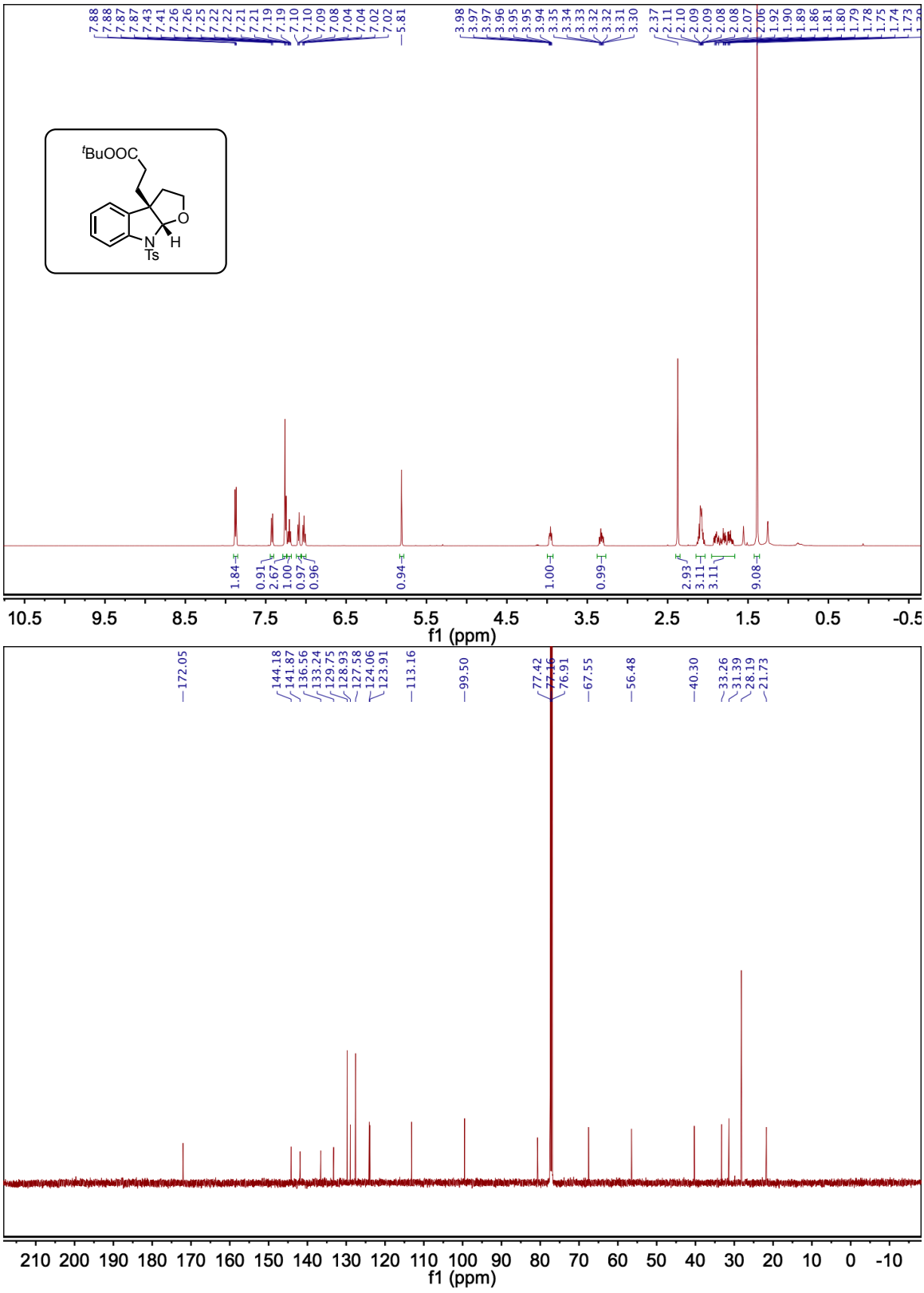
tert-butyl 3-(1-tosyl-4-(trifluoromethyl)piperidin-4-yl)propanoate (43)



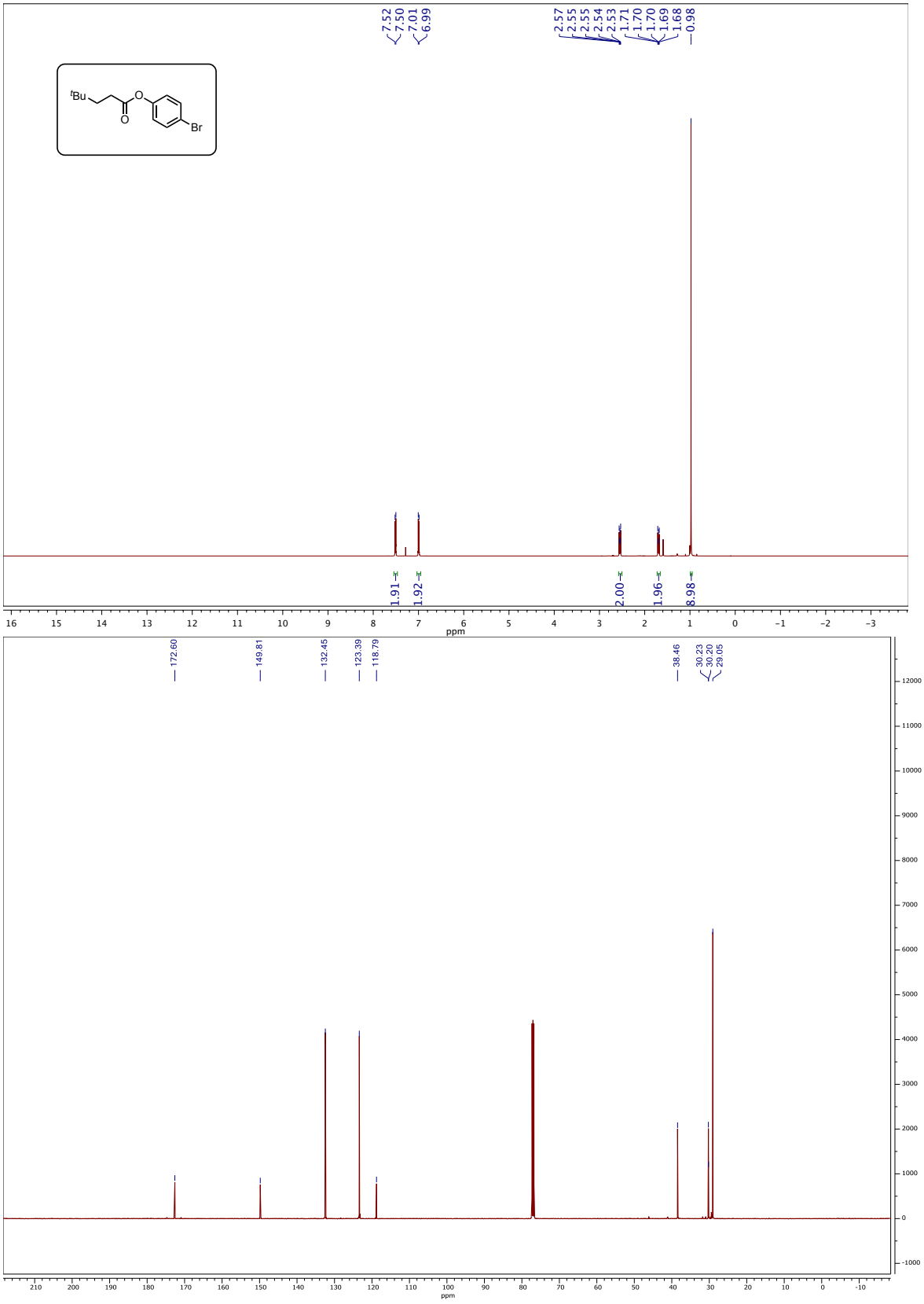



59.09
59.12
59.14
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
f1 (ppm)

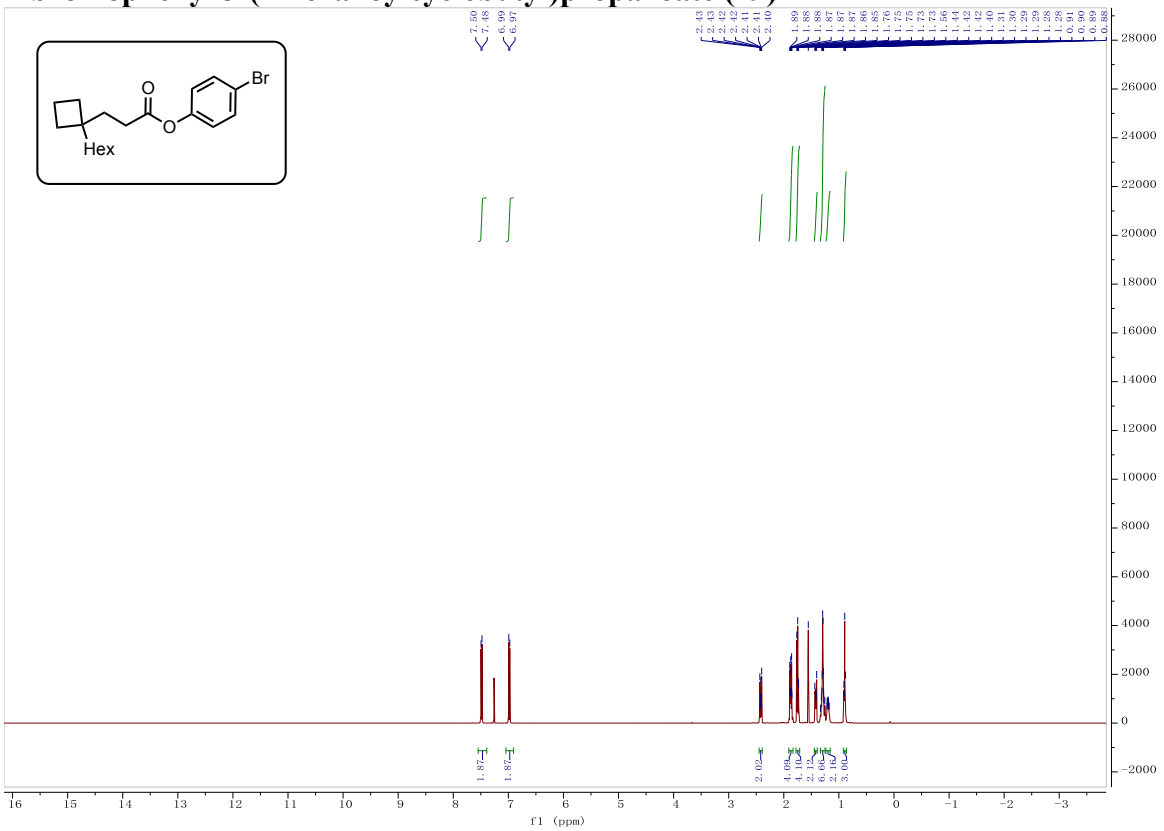
***tert*-butyl 3-((3a*S*,8a*S*)-8-tosyl-2,3,8,8a-tetrahydro-3a*H*-furo[2,3-*b*]indol-3a-yl)propanoate (45)**

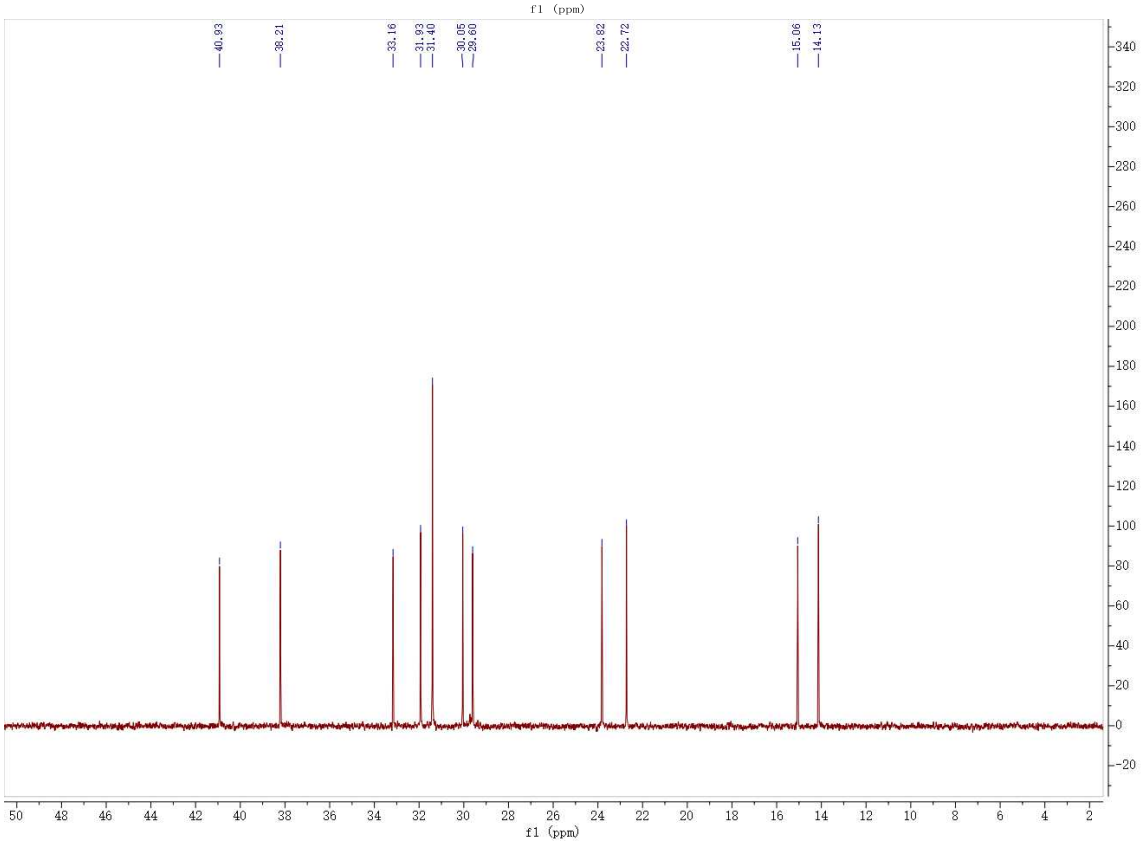


4-bromophenyl 4,4-dimethylpentanoate (47)

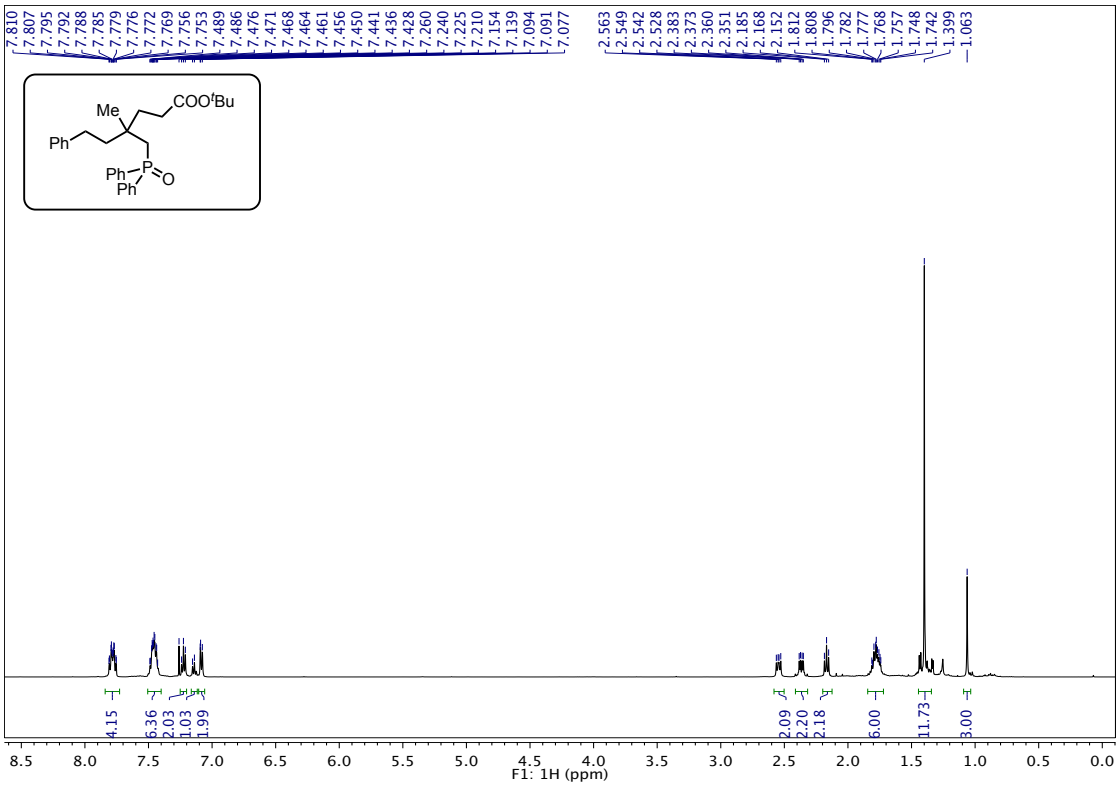


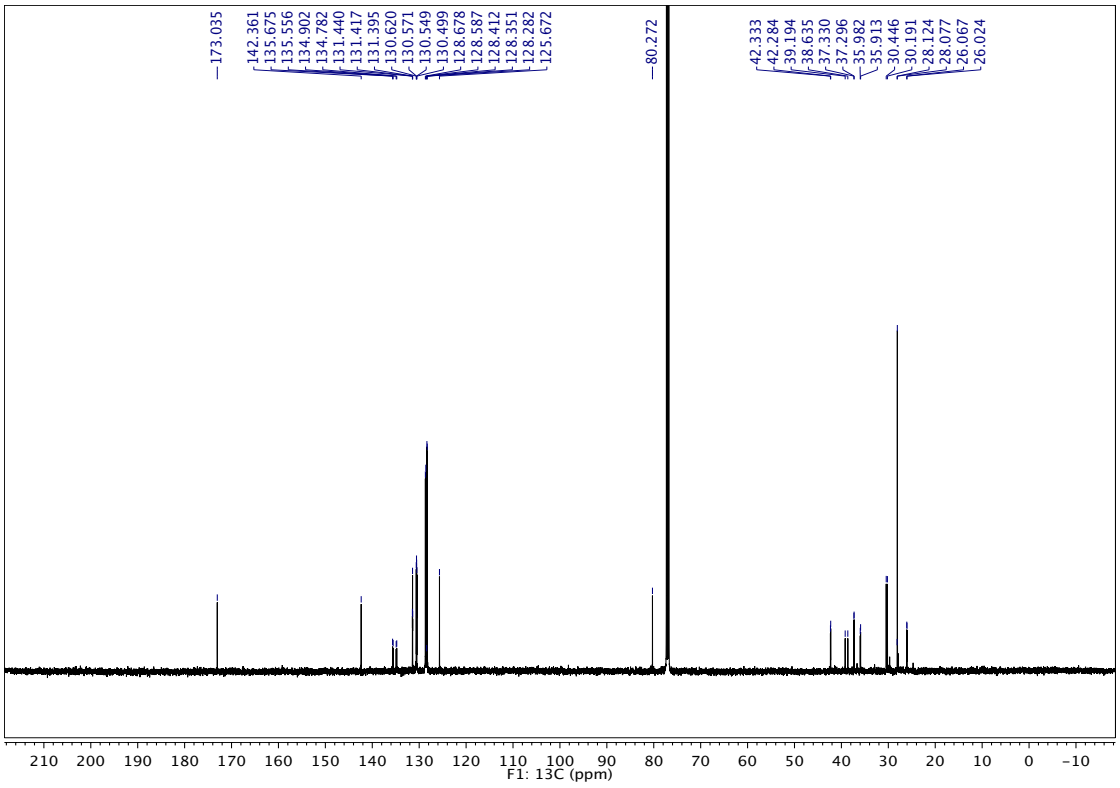
4-bromophenyl 3-(1-hexanoylcyclobutyl)propanoate (49)

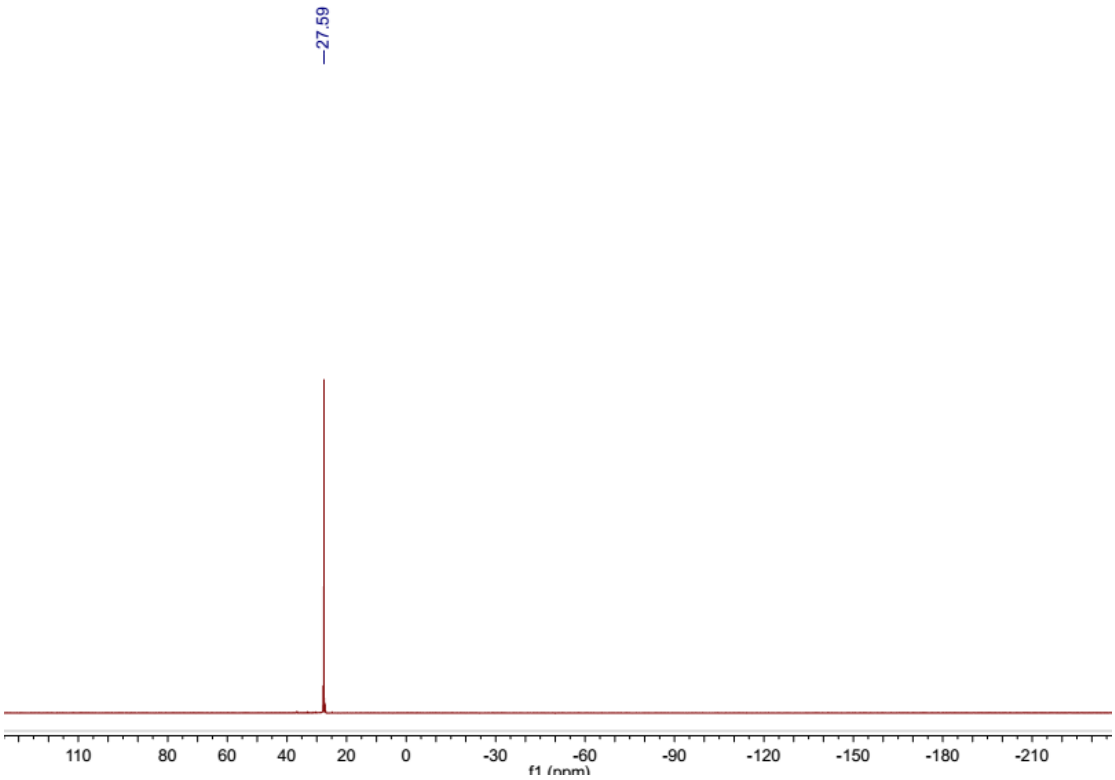




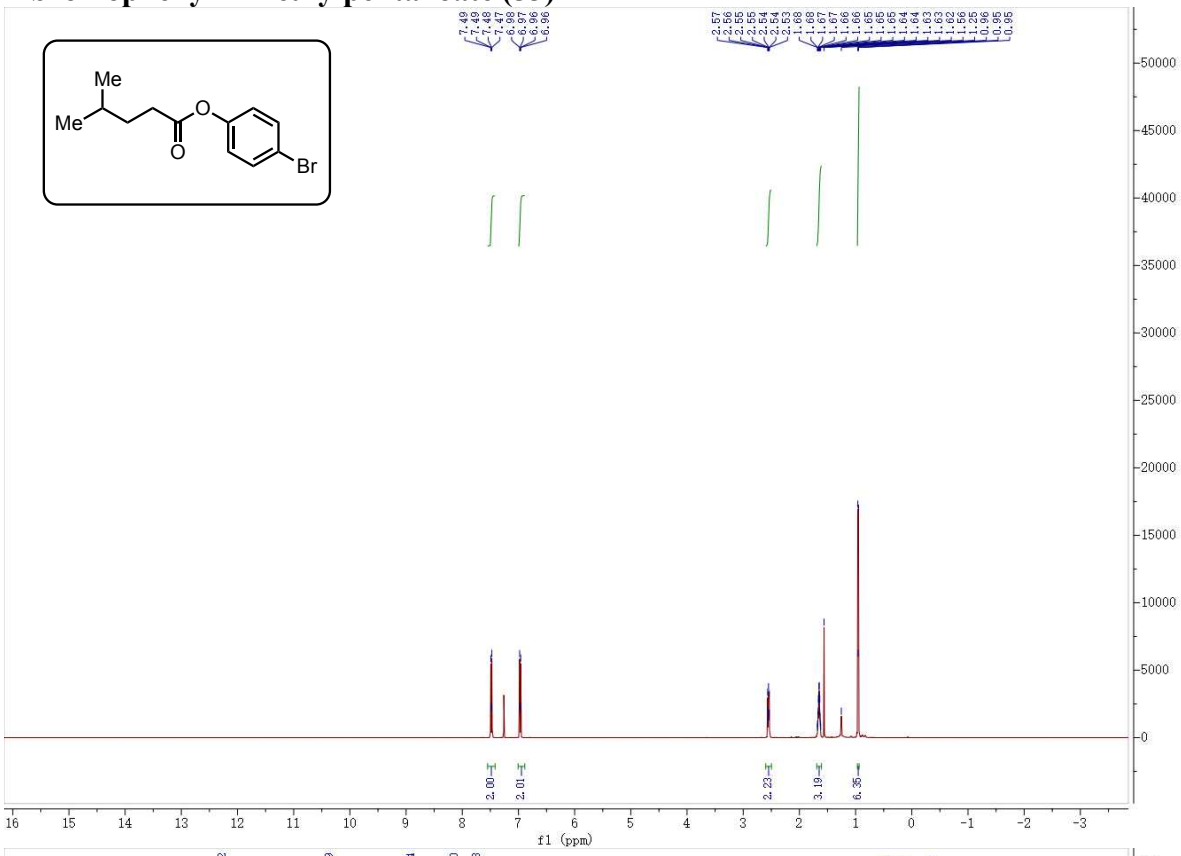
tert-butyl 4-((diphenylphosphoryl)methyl)-4-methyl-6-phenylhexanoate (51)

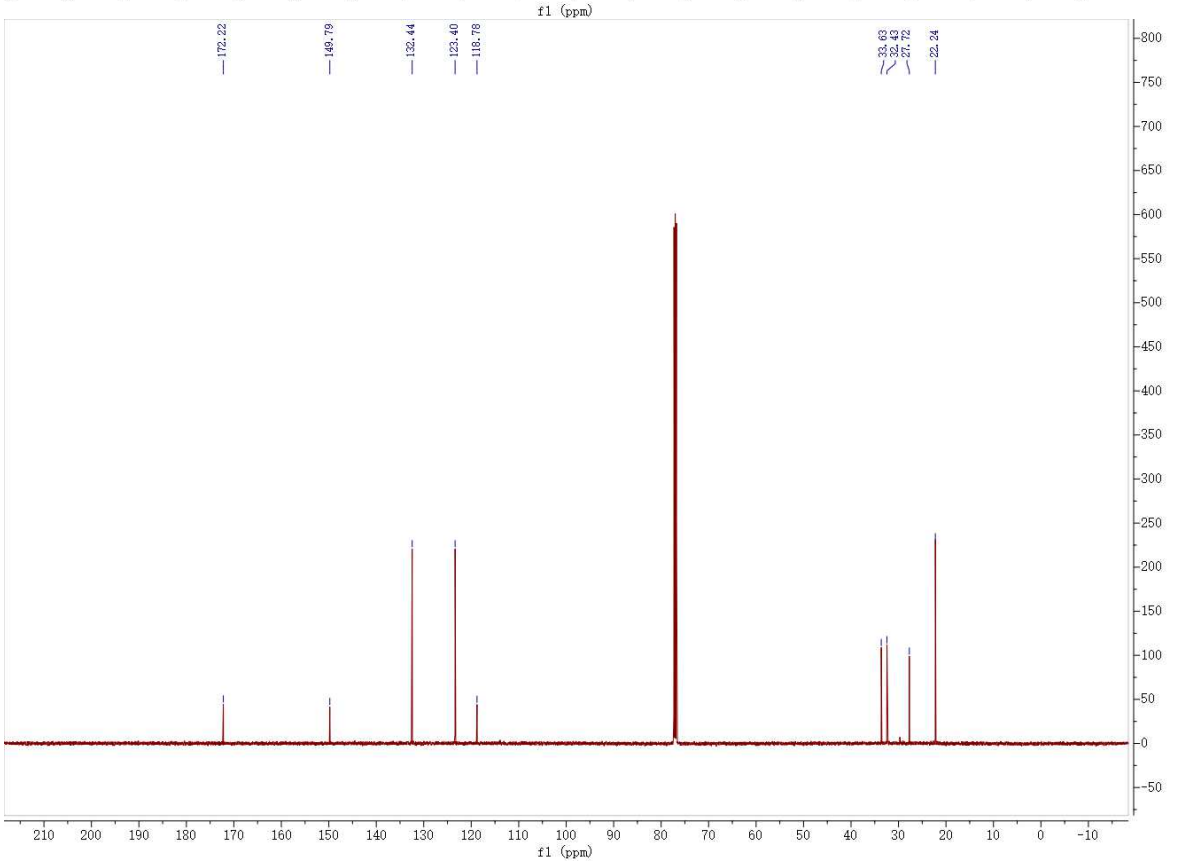




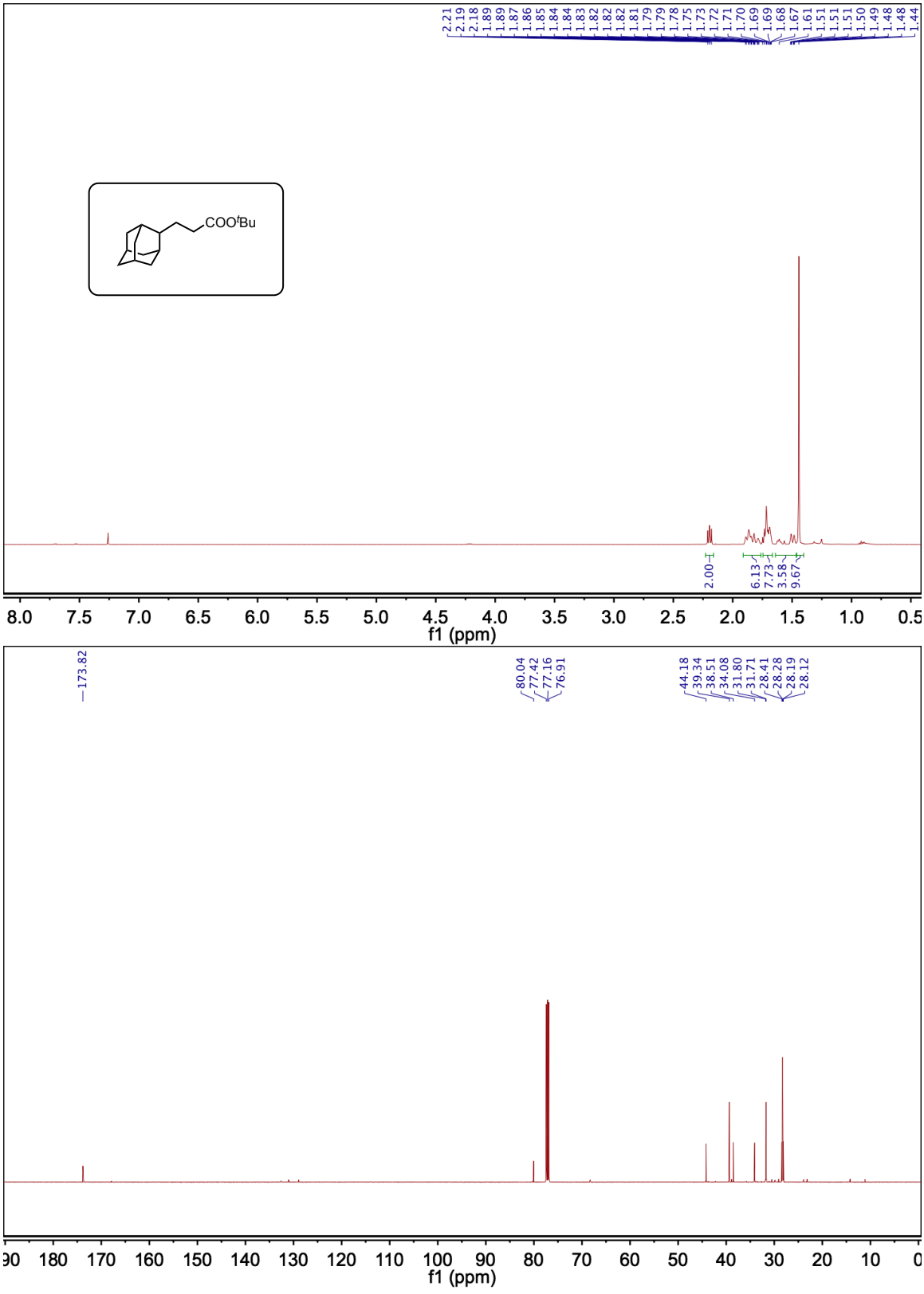

-27.59
110
80
60
40
20
0
-30
-60
-90
-120
-150
-180
-210
f1 (ppm)

4-bromophenyl 4-methylpentanoate (53)

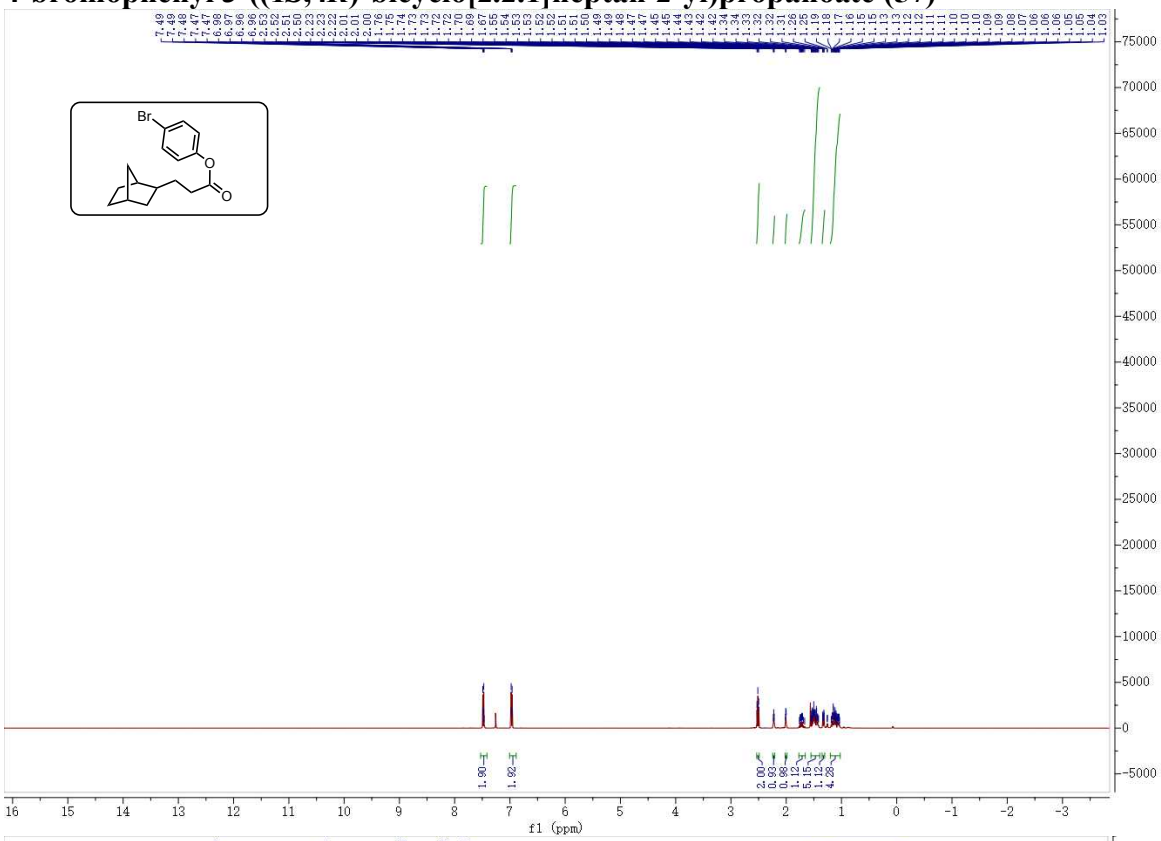


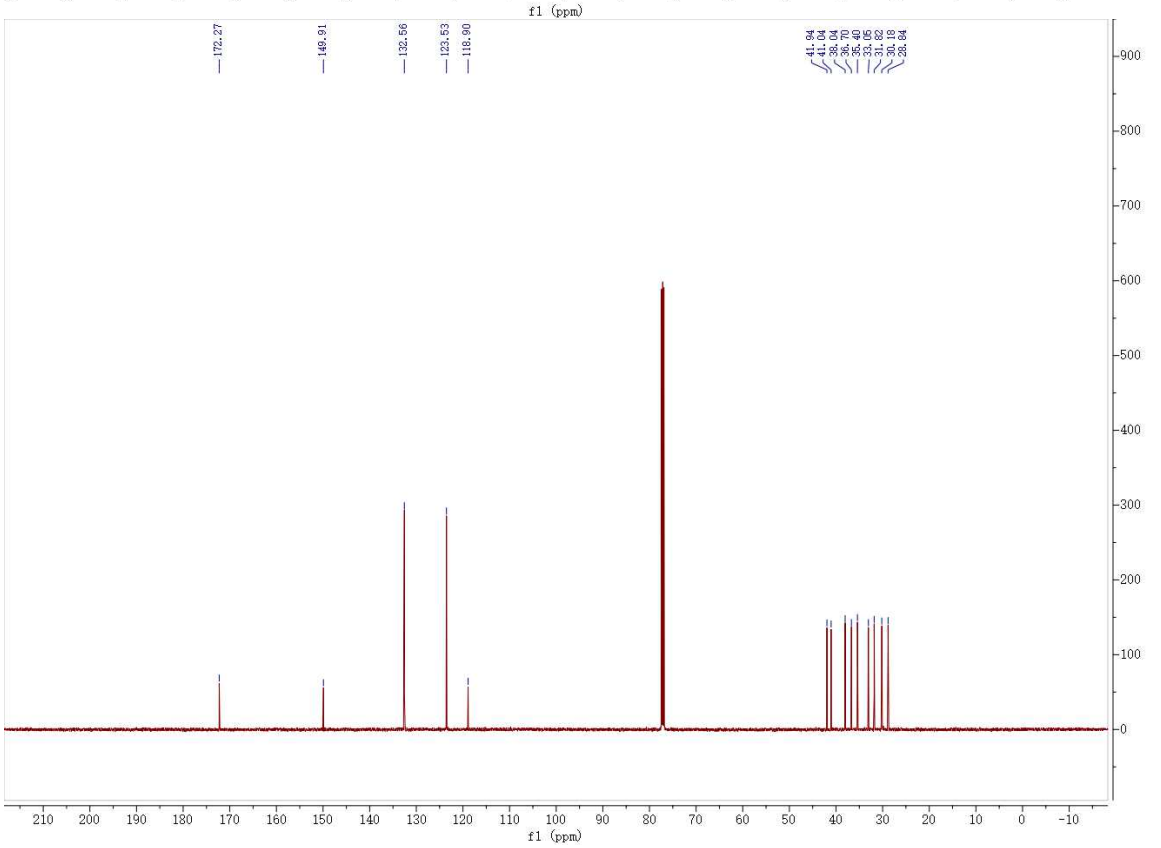


***tert*-butyl 3-((1*r*,3*r*,5*r*,7*r*)-adamantan-2-yl)propanoate (55)**



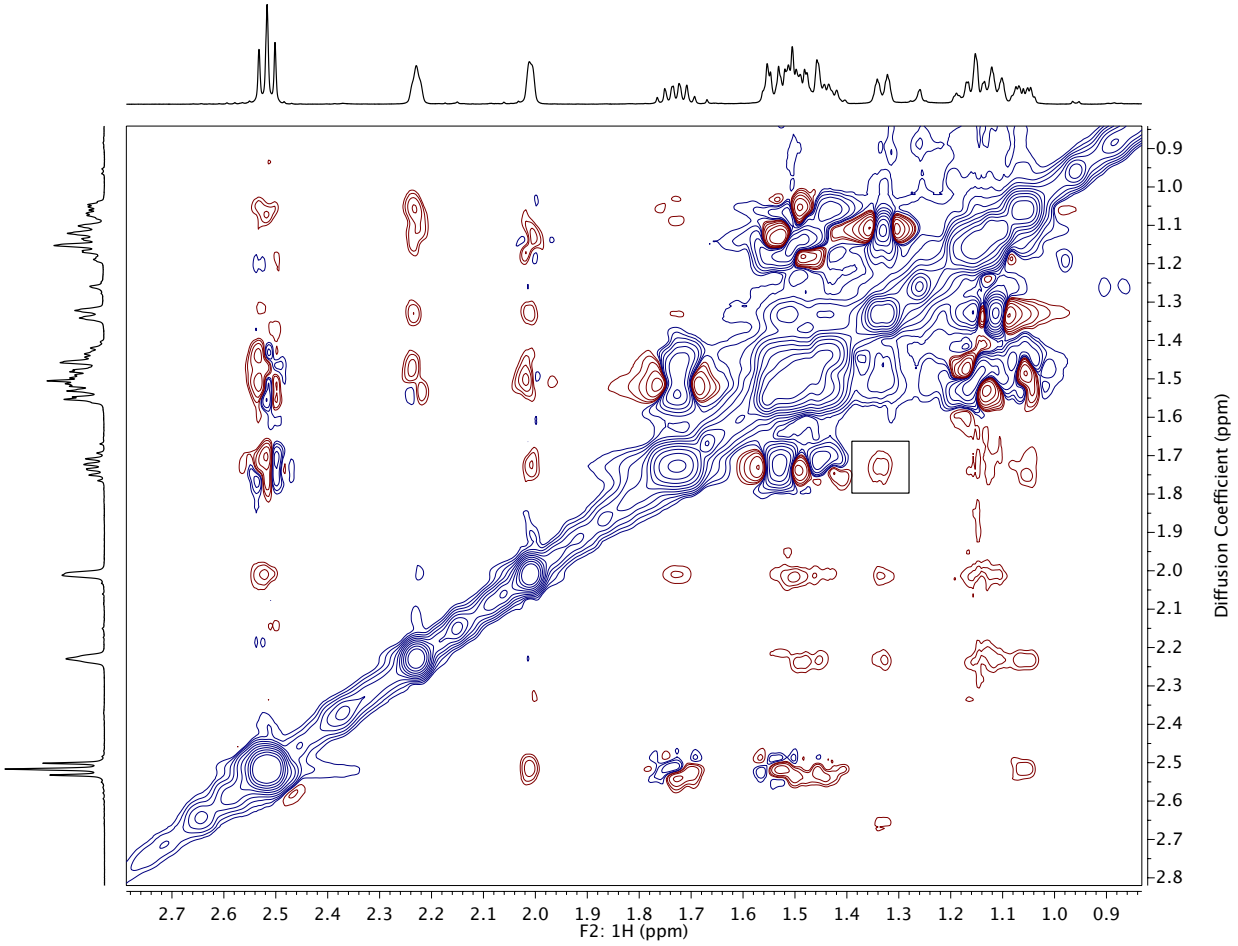
4-bromophenyl 3-((1*S*,4*R*)-bicyclo[2.2.1]heptan-2-yl)propanoate (57)



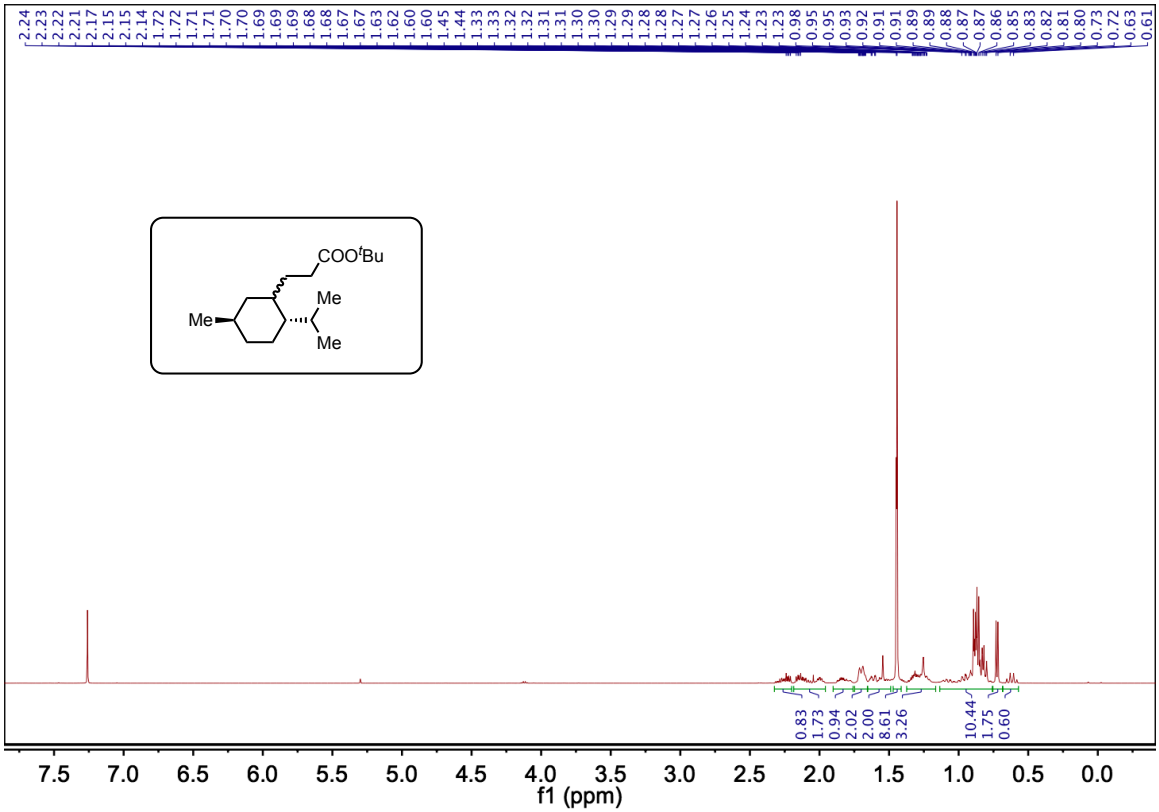


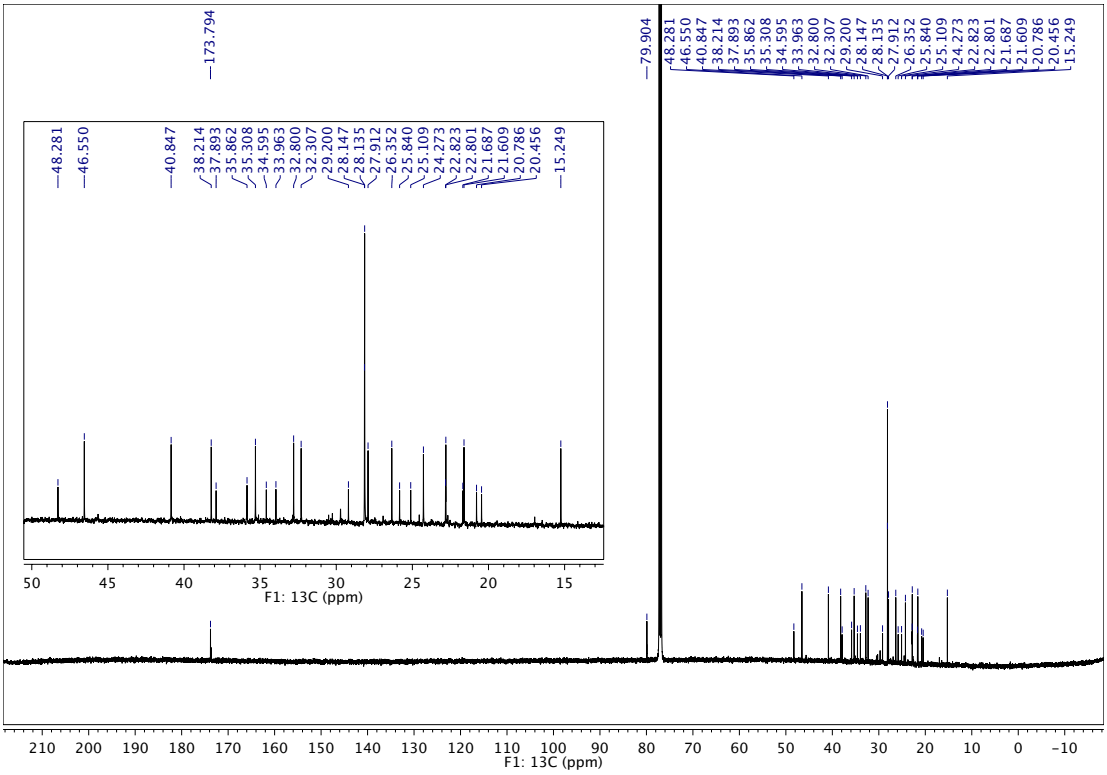
ROESY of **57**

The circled NOE correlation suggest that the product is more likely to be exo-configuration

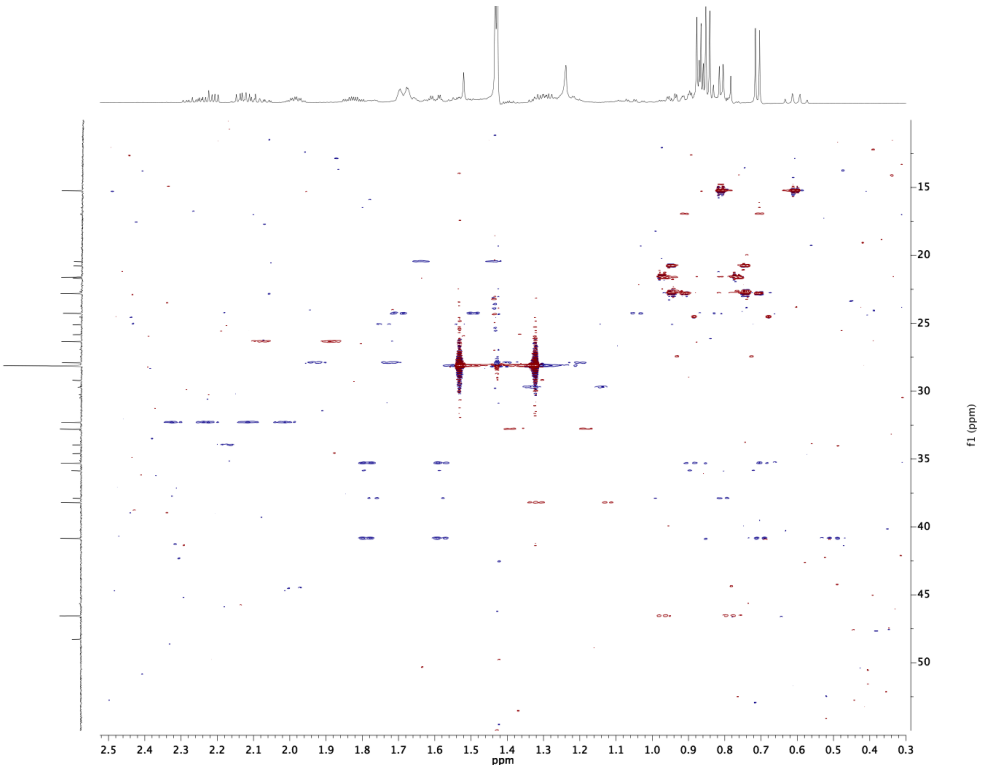


tert-butyl 3-((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)propanoate (59)

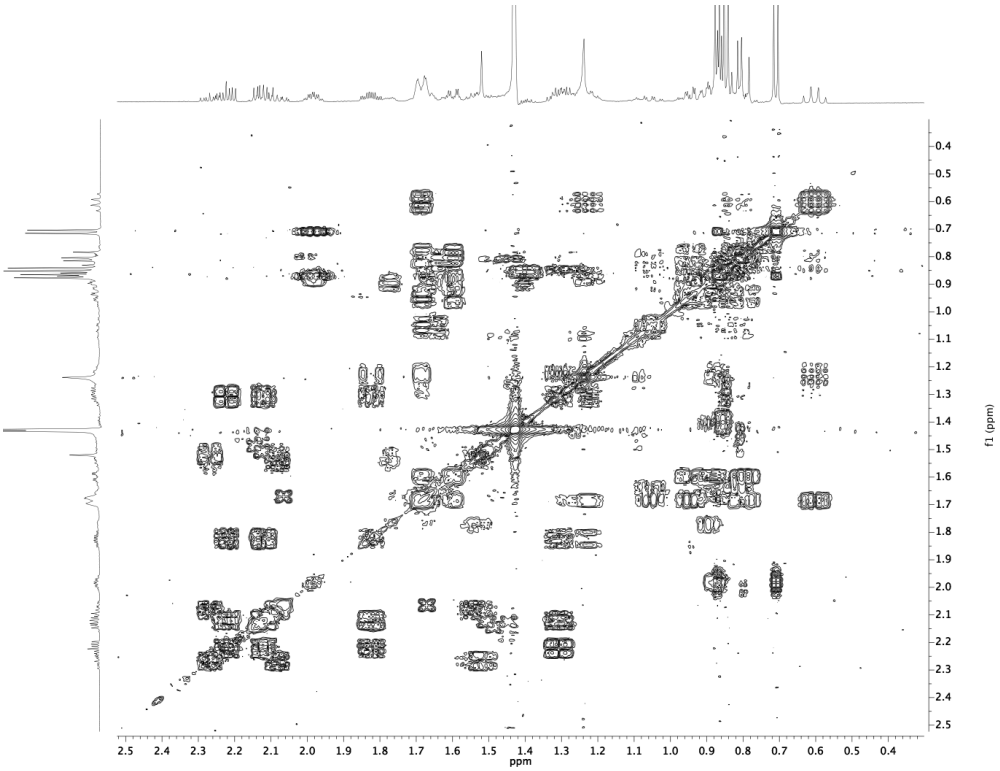




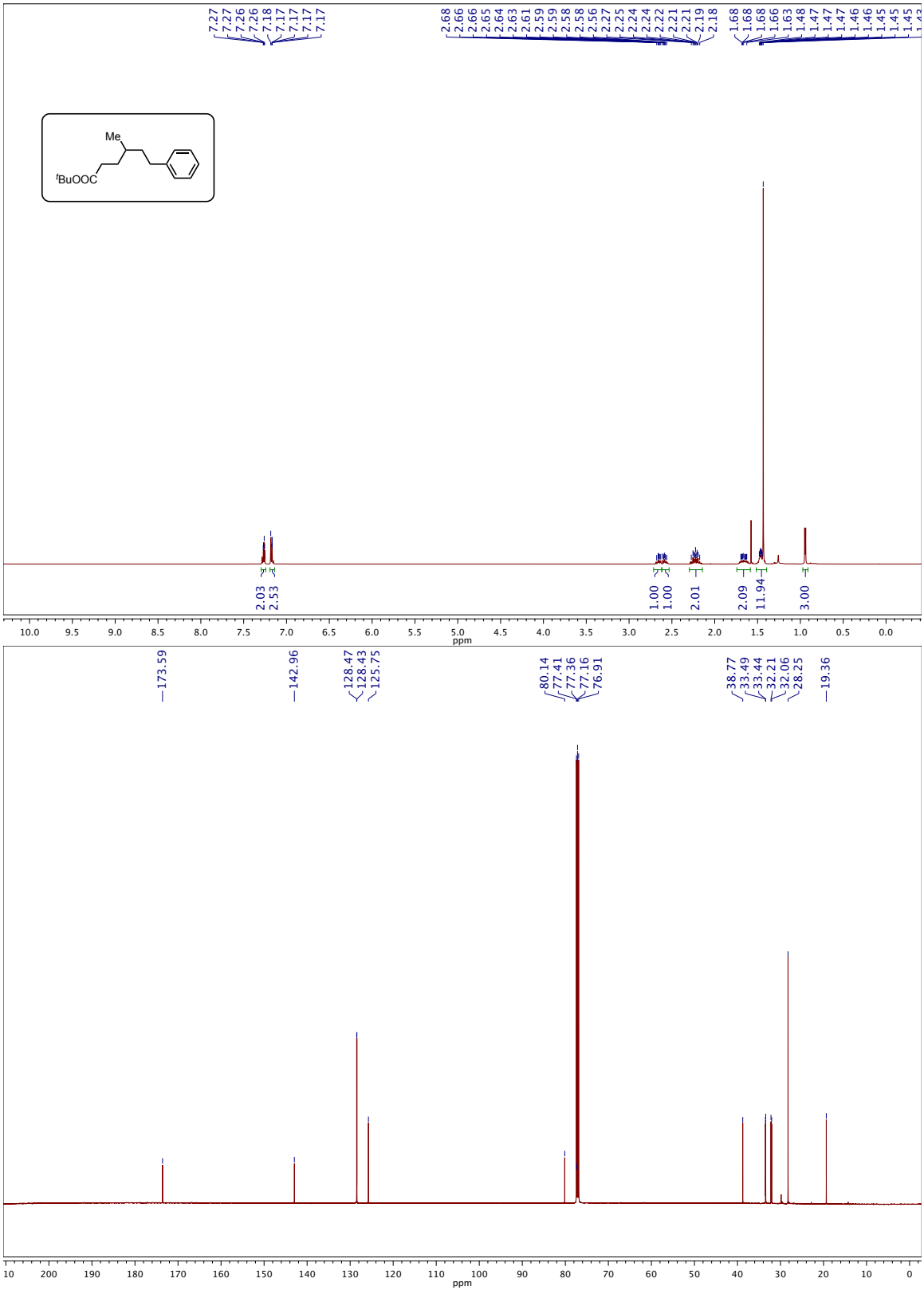
HSQC


15
20
25
30
35
40
45
50
f1 (ppm)
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3
ppm

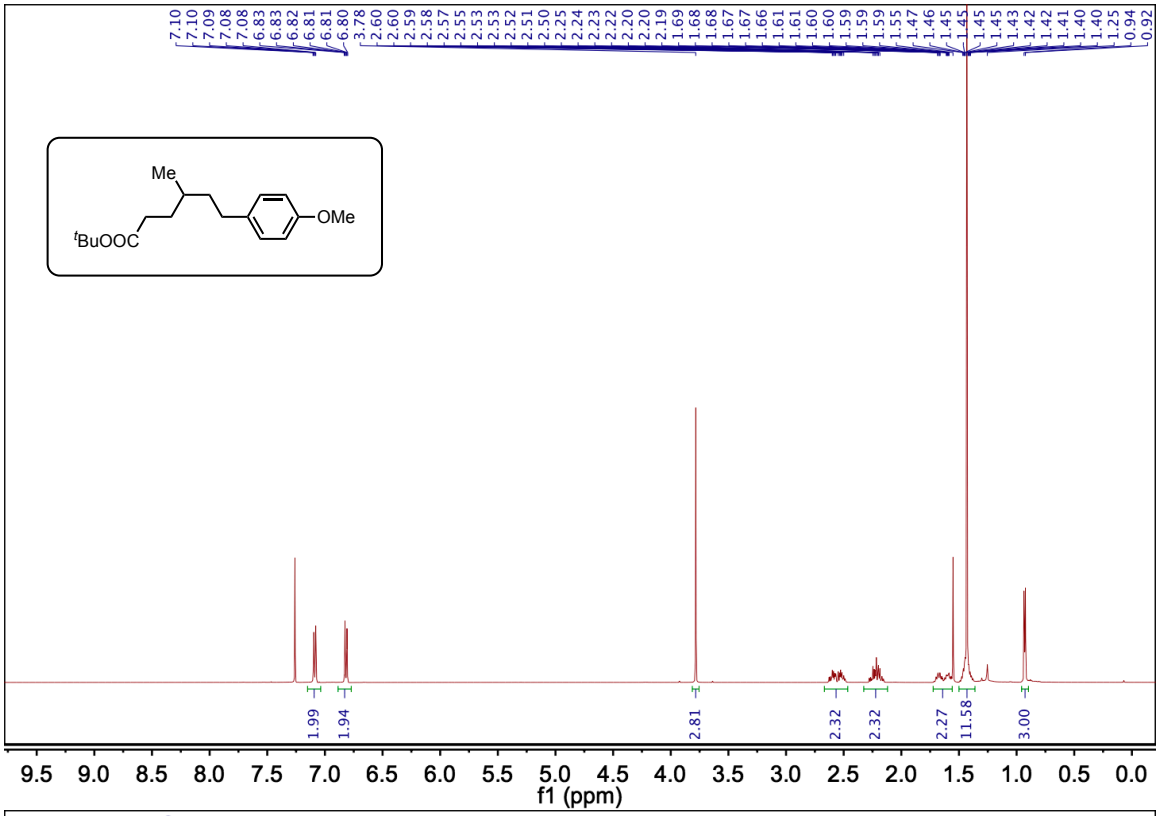
gCOSY

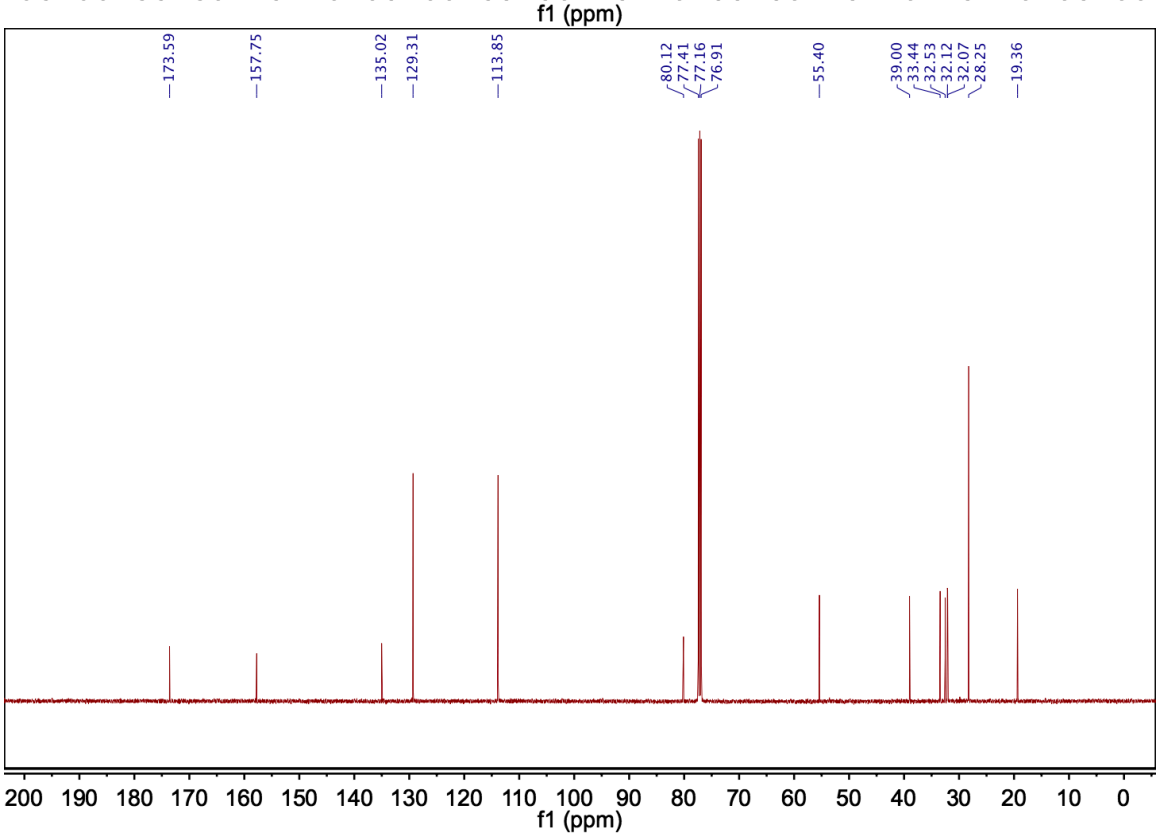

0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
f1 (ppm)
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4
ppm

tert-butyl 4-methyl-6-phenylhexanoate (61)

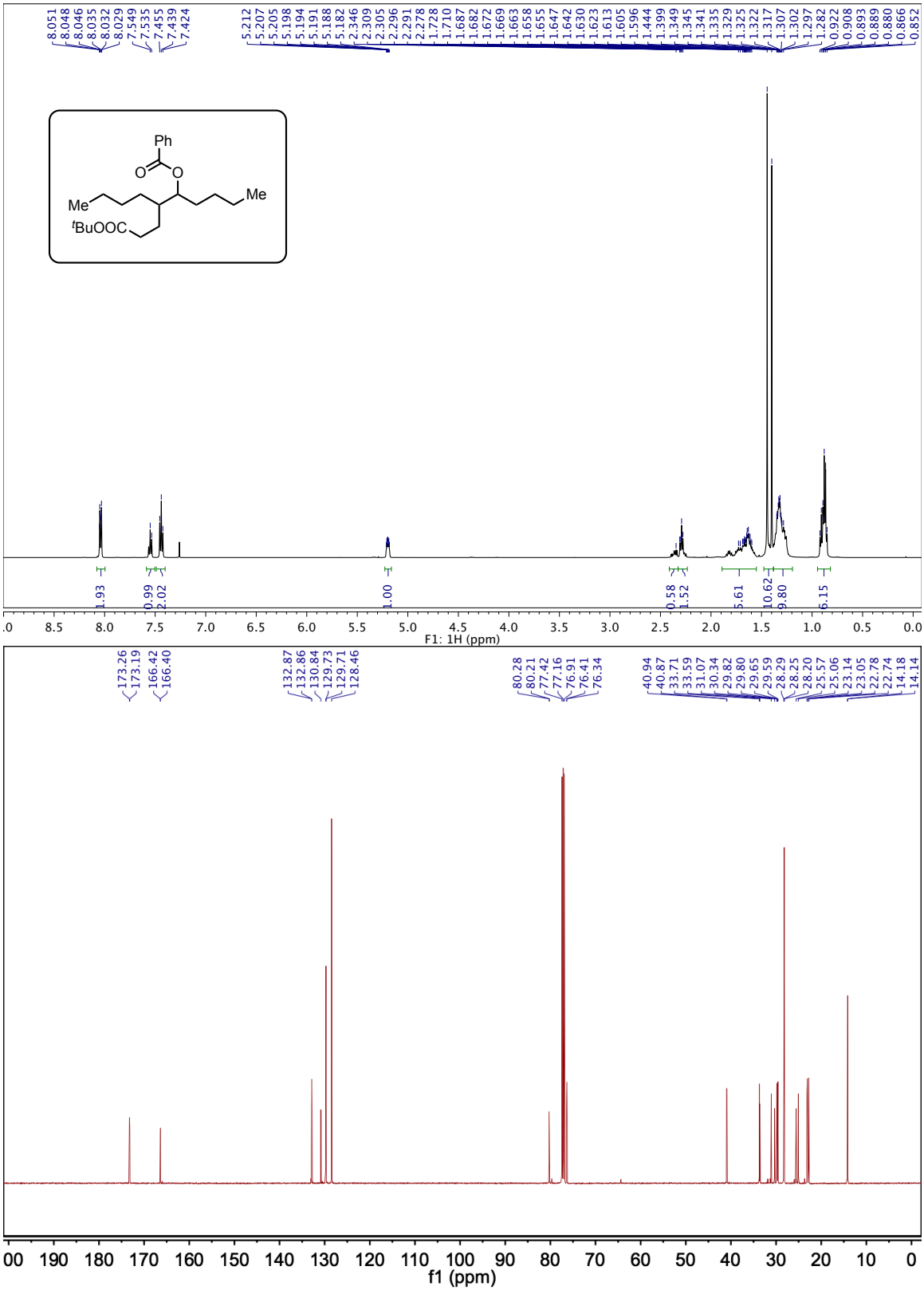


***tert*-butyl 6-(4-methoxyphenyl)-4-methylhexanoate (63)**

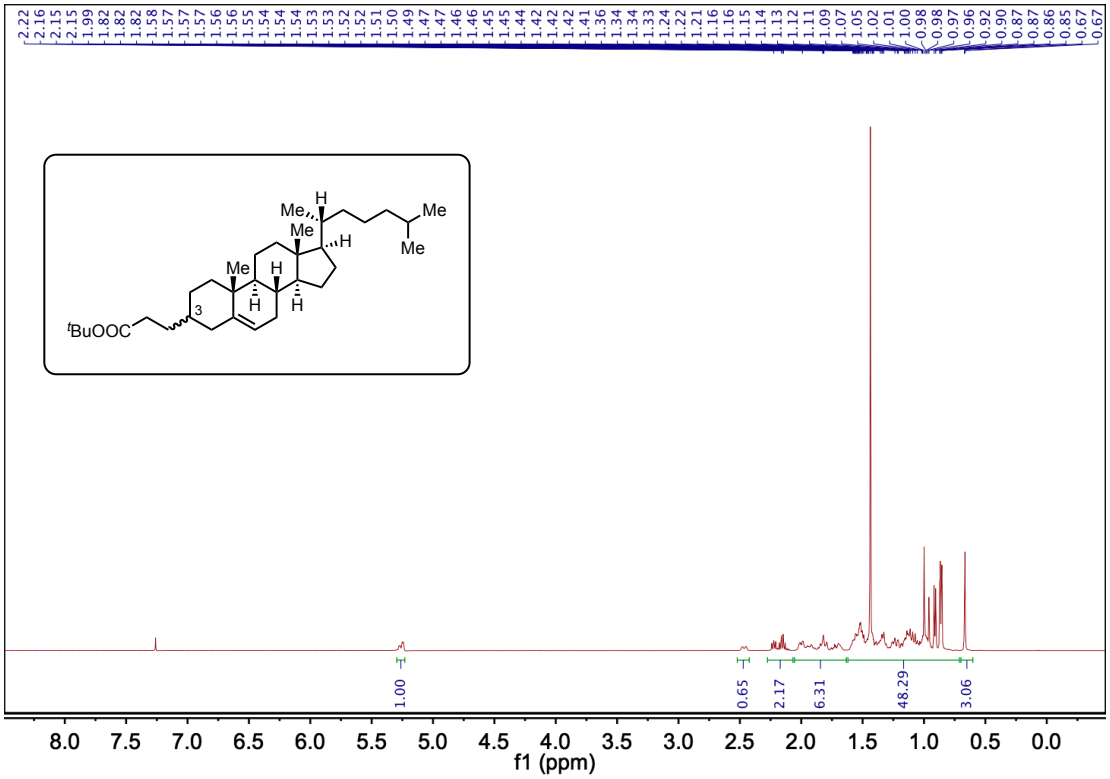


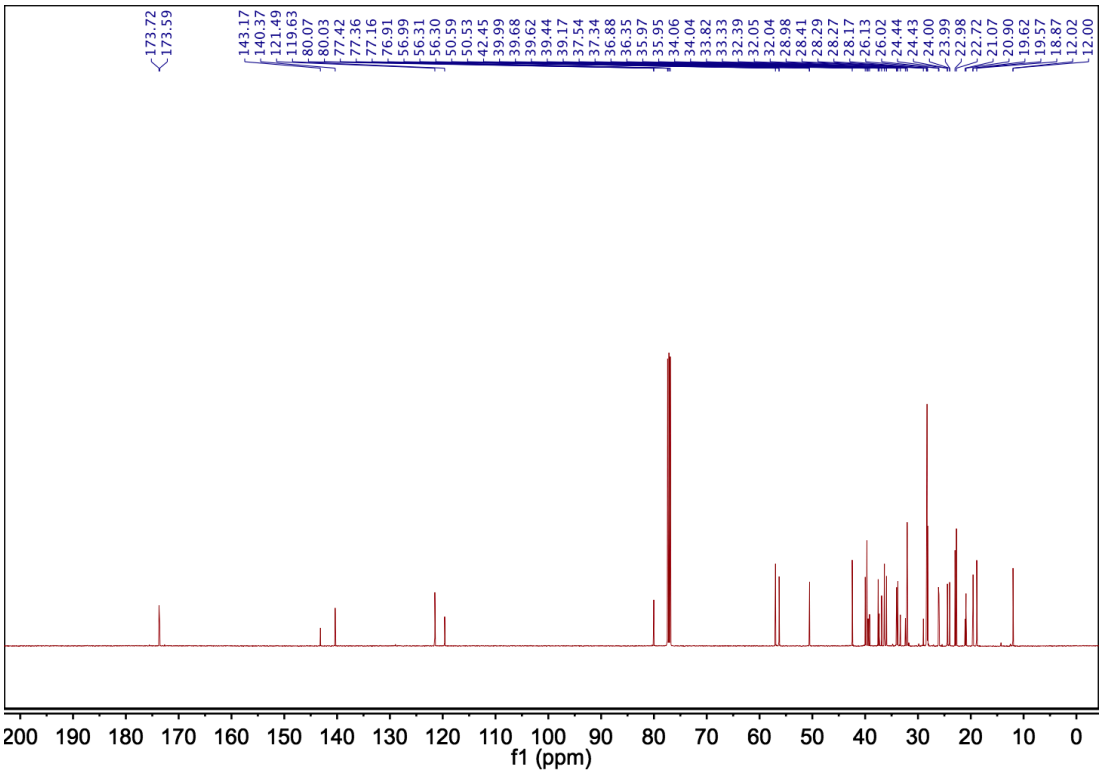


6-(3-(*tert*-butoxy)-3-oxopropyl)decan-5-yl benzoate (65)

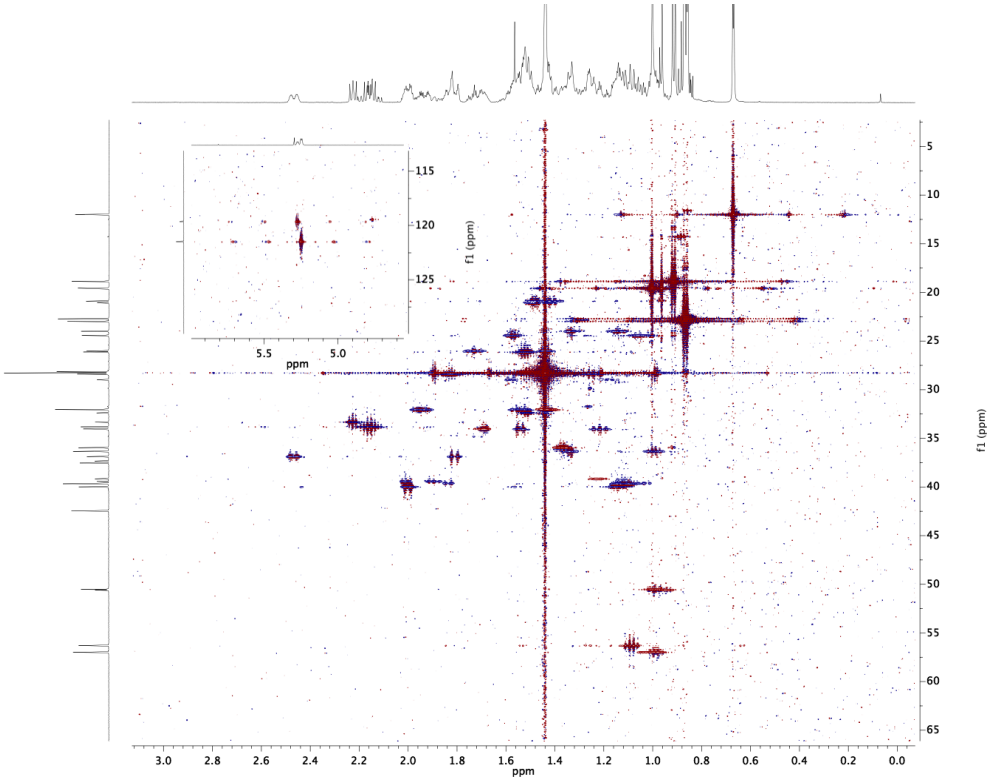


***tert*-butyl 3-((8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)propanoate (67)**

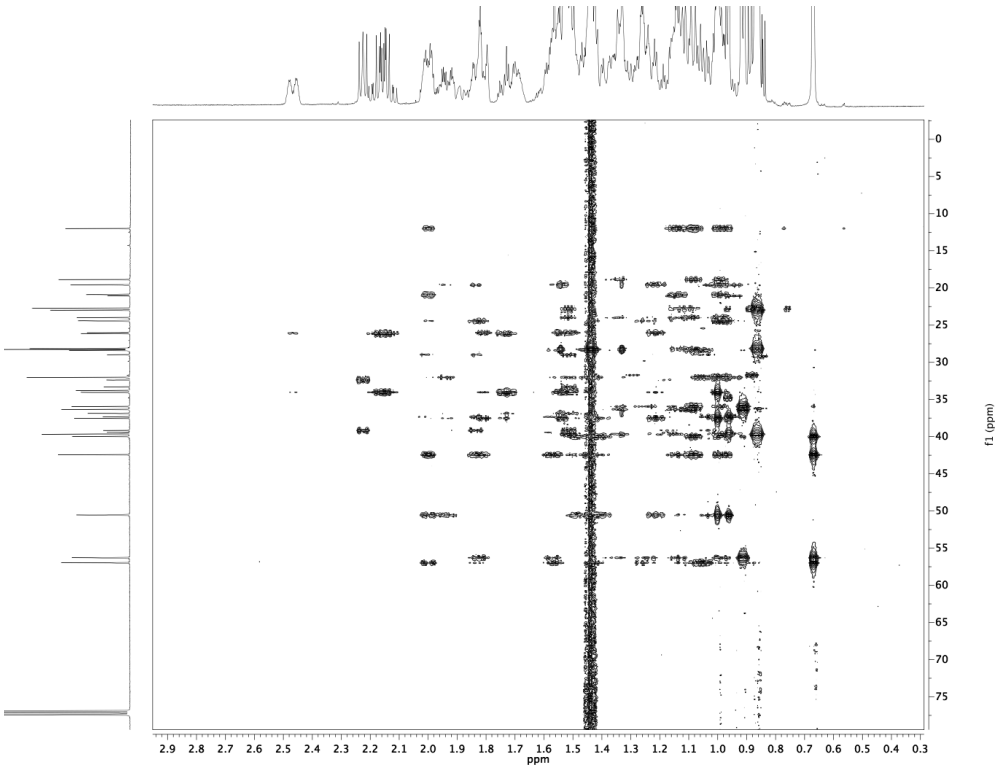




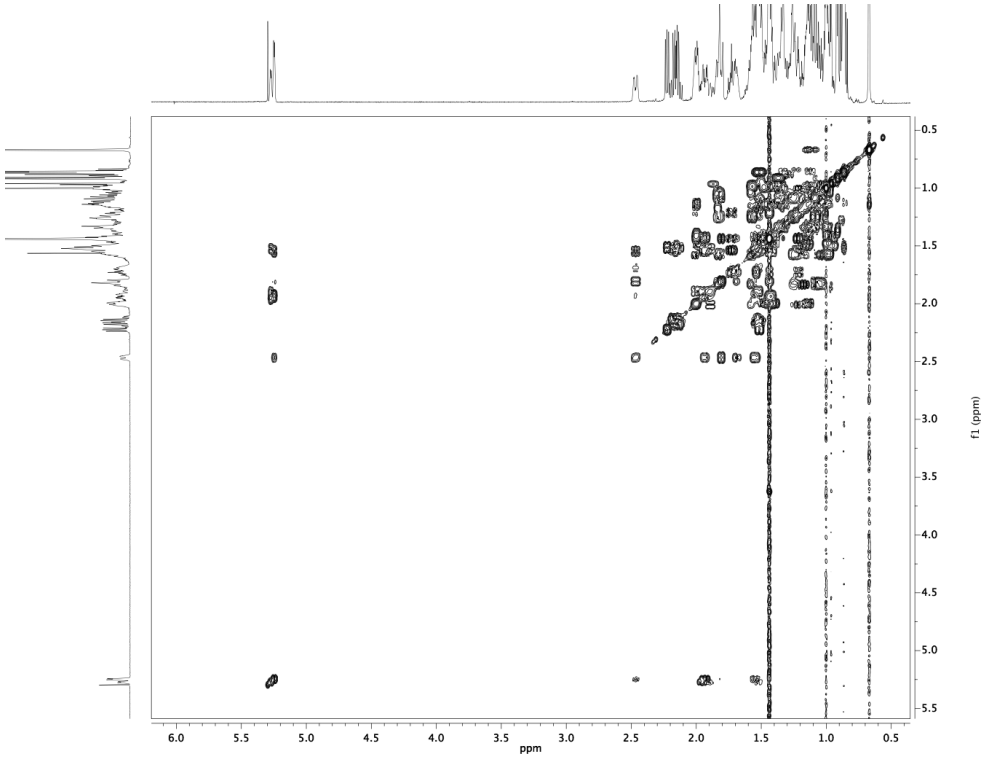
HSQC



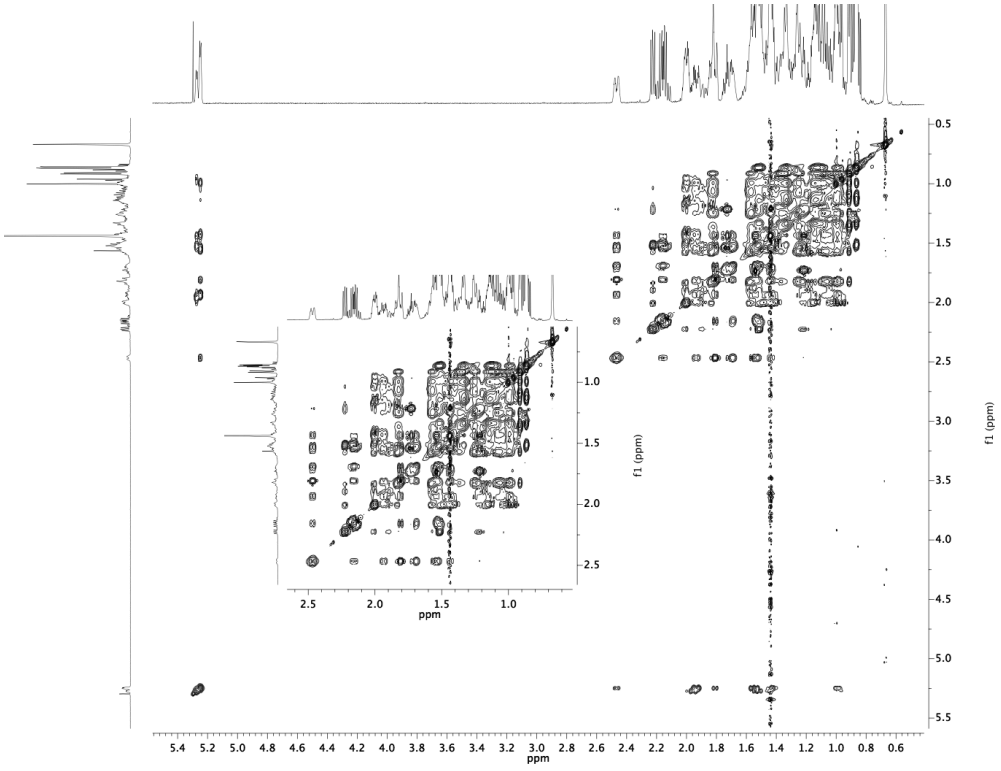
HMBC



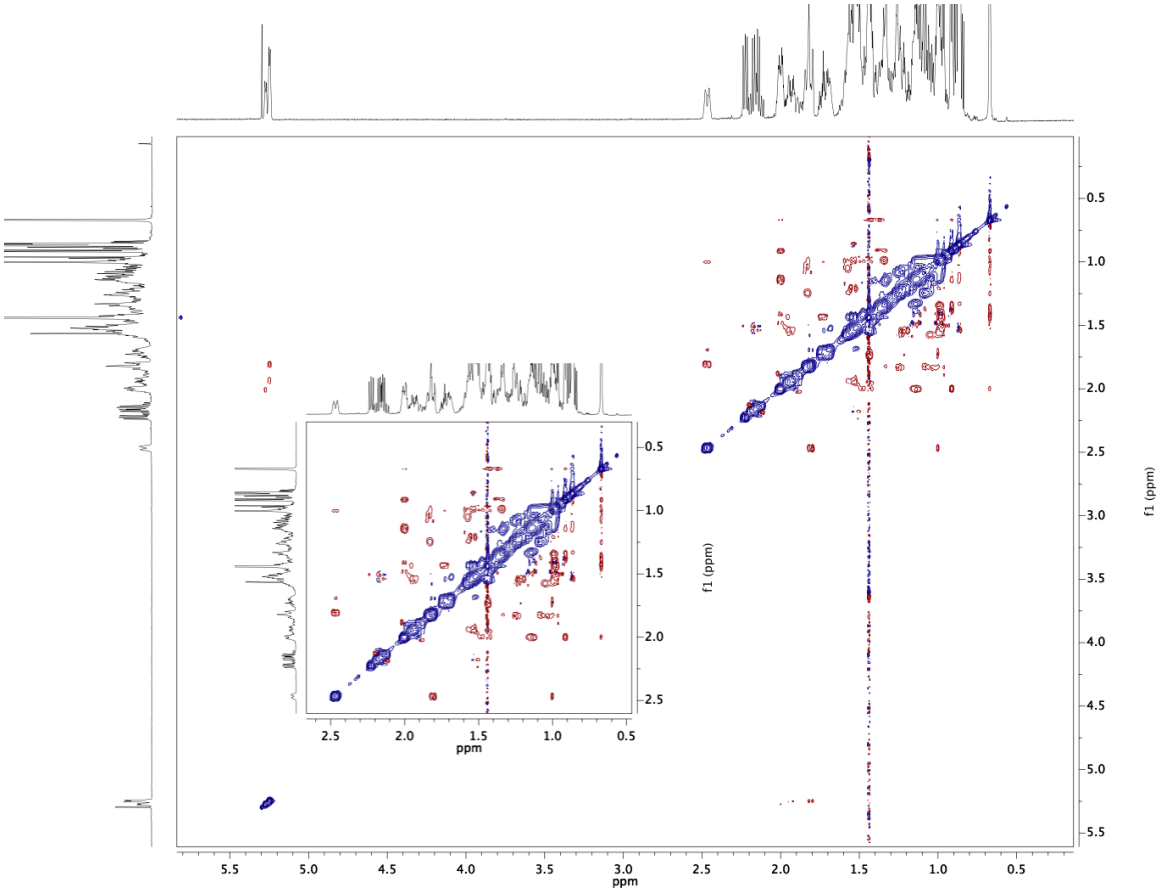
gCOSY


6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)

TOCSY


5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
ppm
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)
2.5 2.0 1.5 1.0
ppm
1.0 1.5 2.0 2.5
f1 (ppm)

ROSY


5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
f1 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5