

Supplementary Information

Switchable Chlorine Atom Transfer Radical Reactions

Huang et al.

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1. General Information

All reactions are conducted in oven-dried 4 mL vials under nitrogen atmosphere unless otherwise noted. Unless otherwise noted, all reagents are used as received and handled in air. Chloroform-*d*1 is purchased from J & K Scientific Ltd.

NMR spectra are recorded on a Bruker Ultra-shield 400, 500 or 600 MHz spectrometer. ¹H NMR, ¹³C NMR, ¹⁹F NMR and ³¹P NMR are recorded on an NMR spectrometer with CDCl₃ as solvent. Chemical shifts of ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra are reported in parts per million (ppm). The ¹⁹F NMR spectra are {¹H} decoupled and the ¹³C NMR spectra are {¹H} decoupled. The residual solvent signals are used as standard, and the chemical shifts are converted to the corresponding scale (CDCl₃: δ H = 7.26 ppm, δ C = 77.00 ppm). All coupling constants (*J* values) are reported in hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), quintet (quint), and multiplet (m). Gas chromatographic (GC) analyses are performed on a GC equipped with a flame-ionization detector and an Rtx@-65 (30 m × 0.32 mm ID × 0.25 μm df) column. GC-MS analyses are performed on a GC-MS with an EI mode. EI-HRMS and ESI-HRMS spectra were obtained on a Waters Premier GC-TOF MS and a Thermo Scientific Q Exactive HF Orbitrap-FTMS, respectively. FI-HRMS spectra were obtained on a JEOLAccuTOF-GCv4G-GCT MS. The EPR experiments are conducted on a Bruker EMXplus electron paramagnetic resonance spectrometer. The X-ray experiments are conducted on a Bruker D8 Venture with TXS. The IR spectra are recorded on a Bruker Alpha FT/IR instrument. Luminescence quenching experiment were performed with F-7000 FL Spectrophotometer (Hitachi, Japan). The PR160L-370 nm Gen 2 LEDs (40 W, λ = 350-400 nm, λ_{max} = 370 nm) are purchased from Kessil. The compound names are generated by the computer program ChemDraw according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC).

All reagents are purchased from commercial suppliers, Aladdin, Adamas-beta®, TCI (Shanghai) Development Co., Ltd, Energy Chemical, J & K scientific Ltd., Bide Pharmatech Ltd, Alfa-Aesar and Sigma-Aldrich unless otherwise noted.

2. Optimization of the Reaction Conditions

2.1 Reaction conditions of ATRA reaction of alkyl chlorides

Supplementary Table 1. Screening of solvents^a

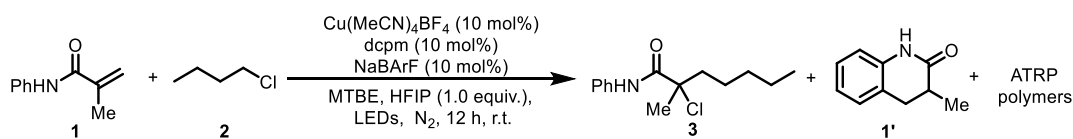
Entry	solvent	Yield (3 , %) ^b	Yield (1' , %) ^b
1	MTBE	18	trace
2	THF	trace	5
3	Tol	trace	8
4	MeCN	NR	NR
5	DMSO	NR	NR
6	DMA	NR	NR

^aReaction conditions: **1** (0.1 mmol), **2** (0.5 mmol), Cu(MeCN)₄BF₄ (10 mol%), dcpm (10 mol%), solvent (1 mL), 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

Supplementary Table 2. Screening of additives^a

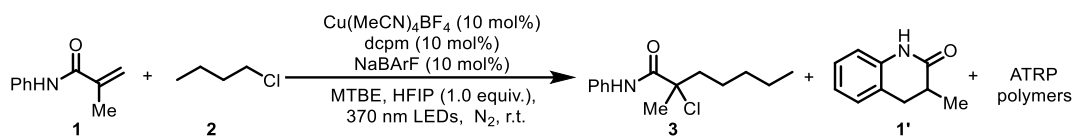
Entry	Additive	Yield (3 , %) ^b	Yield (1' , %) ^b
1	LiCl	9	trace
2	TBACl	14	trace
3	Zn	12	trace
4	Mn	8	trace
5	NEt ₃	8	trace
6	HOAc	23	trace
7	NaBARF (10 mol%)	34	trace
8	HFIP	28	trace
9	NaBARF (10 mol%) + HFIP	38	trace

^aReaction conditions: **1** (0.1 mmol), **2** (0.5 mmol), Cu(MeCN)₄BF₄ (10 mol%), dcpm (10 mol%), additive (0.1 mmol), MTBE (1 mL), 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

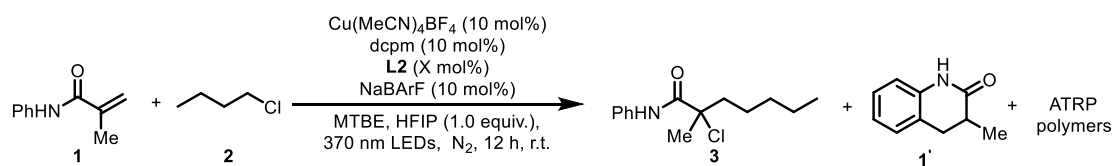
Supplementary Table 3. Screening of LEDs source^a

Entry	LEDs source	Yield (3 , %) ^b	Yield (1' , %) ^b
1	370 nm LEDs	38	trace
2	390 nm LEDs	14	trace
3	440 nm LEDs	trace	ND
4	Blue LEDs	ND	ND
5	White LEDs	ND	ND
6	Without light	ND	ND

^aReaction conditions: **1** (0.1 mmol), **2** (0.5 mmol), Cu(MeCN)₄BF₄ (10 mol%), dcpm (10 mol%), NaBArF (10 mol%), HFIP (0.1 mmol), MTBE (1 mL), LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

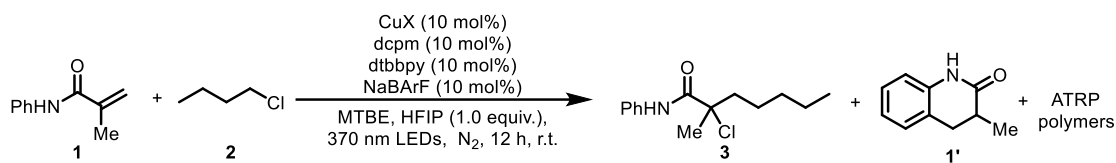


Discussion: **1'** was consistently detected in the reaction mixture (< 10%), presumably arising from energy transfer (EnT) between **1** and the catalyst. Given that the primary side products resulted from chlorine-transfer polymerization, we attempted to introduce additional ligands to accelerate desired C-Cl bond forming process.

Supplementary Table 4. Screening of additional ligands^{a,b}

20 mol%, 12%	20 mol%, n.d.	10 mol%, n.d.	10 mol%, n.d.	10 mol%, 4%
10 mol%, 38%	10 mol%, 42%	10 mol%, 24%	10 mol%, 8%	10 mol%, n.d.

^aReaction conditions: **1** (0.1 mmol), **2** (0.5 mmol), Cu(MeCN)₄BF₄ (10 mol%), dcpm (10 mol%), **L2** (x mol%), NaBArF (10 mol%), HFIP (0.1 mmol), MTBE (1 mL), 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

Supplementary Table 5. Screening of Cu salts^a

Entry	Cu salts	Yield (3 , %) ^b	Yield (1' , %) ^b
1	CuCl	49	6
2	CuBr	49	5
3	CuI	47	5
4	CuCN	37	trace
5	CuTc	33	trace
6	Cu(MeCN) ₄ PF ₆	41	trace

^aReaction conditions: **1** (0.1 mmol), **2** (0.5 mmol), CuX (10 mol%), dcpm (10 mol%), dtbbpy (10 mol%), NaBARF (10 mol%), HFIP (0.1 mmol), MTBE (1 mL), 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

Discussion: A new dinuclear Cu catalyst **cat.A1** was obtained with CuCl, dcpm and NaBARF in the mixed solvent of MTBE-HFIP. Subsequent optimizations of the reaction conditions were based on this complex.

Supplementary Table 6. Screening of mixed solvents^a

Reaction scheme showing the ATRP of **1** and **2** to form **3** using catalysts **cat.A1** and **cat.B**. Reagents: **cat.A1** (5.0 mol%), **cat.B** (2.5 mol%), solvent (1 mL), 370 nm LEDs, N₂, 12 h, r.t.

Entry	MTBE/HFIP	Yield (3 , %) ^b
1	MTBE (1mL), HFIP (1.0 equiv.)	49
2	MTBE (1mL), HFIP (5.0 equiv.)	56
3	8:2	61
4	7:3	72
5	6:4	74
6	5:5	68

^aReaction conditions: **1** (0.1 mmol), **2** (0.5 mmol), **cat.A1** (5 mol%), **cat.B** (2.5 mol%), solvent (1 mL), 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

Supplementary Table 7. Screening of ratio of substrates and catalysts^a

cat.A1

cat.B

Entry	1/2	cat.A1/cat.B	Yield (3, %) ^b
1	1:5	5mol%:5mol%	72
2	1:5	5mol%:2.5mol%	74
3	3:1	5mol%:2.5mol%	17
4	1:1	5mol%:2.5mol%	47
5	1:3	5mol%:2.5mol%	74
6	1:10	5mol%:2.5mol%	68

^aReaction conditions: **1** (x mmol), **2** (y mmol), **cat.A1** (a mol%), **cat.B** (b mol%), MTBE/HFIP = 3/2, 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

Supplementary Table 8. Screening of the reaction time^a

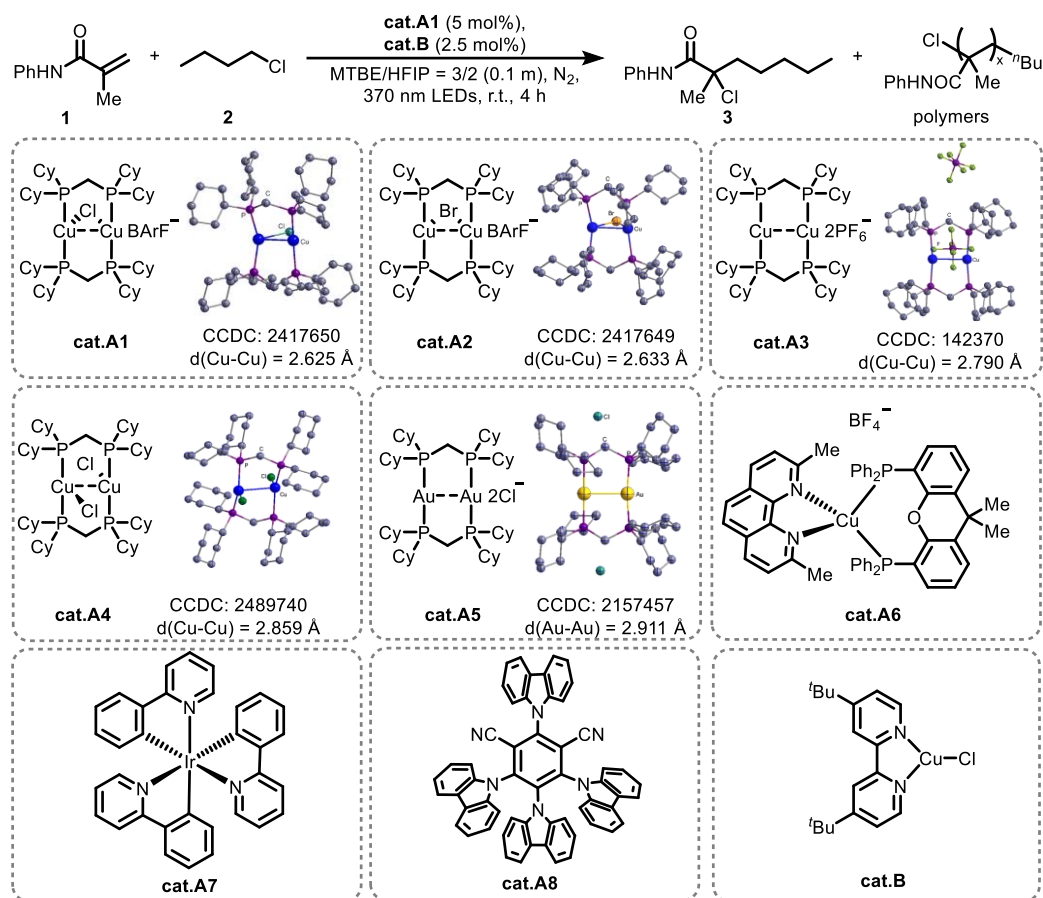
cat.A1

cat.B

Entry	Reaction time	Yield (3, %) ^b
1	1 h	54
2	2 h	73
3	4 h	75 (71 ^c)
4	6 h	74
5	12 h	74

^aReaction conditions: **1** (0.1 mmol), **2** (0.3 mmol), **cat.A1** (5 mol%), **cat.B** (2.5 mol%), MTBE/HFIP = 3/2, 370 nm LEDs, r.t., x h. ^bGC yield with dodecane as an internal standard. ^cIsolated yield.

Supplementary Table 9. Control experiment^a



Entry	Variation of standard conditions	Yield (%) ^b
1	none	75 (71) ^c
2	cat. A2 instead of cat. A1	67
3	cat. A3 instead of cat. A1	63
4	cat. A4 instead of cat. A1	60
5	cat. A5 instead of cat. A1	NR
6	cat. A6 instead of cat. A1	NR
7	cat. A7 instead of cat. A1	NR
8	cat. A8 instead of cat. A1	NR
9	solvent = MeCN	NR
10	without cat. A1	ND
11	without cat. B	36
12	without light irradiation	ND

^aStandard conditions: **cat.A1** (5 mol%), **cat.B** (2.5 mol%), **1** (0.1 mmol), **2** (0.3 mmol, 3 equiv.), MTBE/HFIP (0.6/0.4 mL), 40 W 370 nm LEDs, room temperature (r.t.), 4 h; ^bGC yield using dodecane as an internal standard; ^cIsolated yields; MTBE, methyl tert-butyl ether; HFIP, 1,1,1,3,3,3-hexafluoro-2-propanol; BARF, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; NR, no reaction; ND, not detected.

2.2 Reaction conditions of ATRA reaction of aryl chlorides

Supplementary Table 10. Screening of solvents^a

cat.A1

cat.B

Entry	Solvent	Yield (%) ^b
1	MTBE	NR
2	THF	NR
3	MeCN	NR
4	toluene	NR
5	DMSO	23
6	DMA	trace

^aReaction conditions: **1** (0.1 mmol), methyl 4-chlorobenzoate (0.2 mmol), **cat.A1** (5 mol%), **cat.B** (5 mol%), solvent (1 mL), 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

Supplementary Table 11. Screening of mixed solvents^a

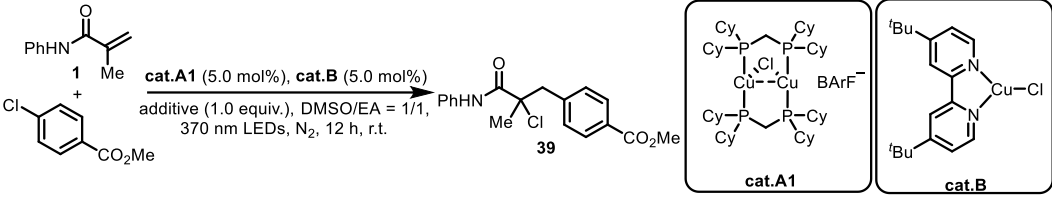
cat.A1

cat.B

Entry	Mixed solvent	Yield (%) ^b
1	DMSO/HFIP = 8/2	NR
2	DMSO/DMA = 8/2	trace
3	DMSO/EA = 8/2	40
4	DMSO/EA = 5/5	46
5	DMSO/EA = 2/8	46
6	DMSO/EA = 1/9	33

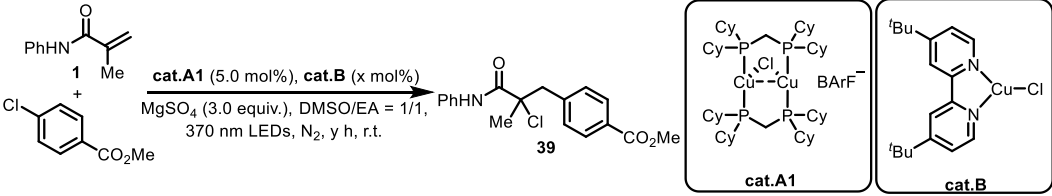
^aReaction conditions: **1** (0.1 mmol), methyl 4-chlorobenzoate (0.2 mmol), **cat.A1** (5 mol%), **cat.B** (5 mol%), solvent (1 mL), 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

Supplementary Table 12. Screening of additives^a

		
Entry	Additive (1.0 equiv.)	Yield (%) ^b
1	HCO ₂ Na	16
2	NEt ₃	19
3	HOAc	44
4	4Å molecular sieves (20 mg)	48
5	Na ₂ SO ₄	50
6	MgSO ₄	55
7	MgSO ₄ (3.0 equiv.)	61

^aReaction conditions: **1** (0.1 mmol), methyl 4-chlorobenzoate (0.2 mmol), **cat.A1** (5 mol%), **cat.B** (5 mol%), additive (1.0 equiv.), DMSO/EA = 1/1, 370 nm LEDs, r.t., 12 h. ^bGC yield with dodecane as an internal standard.

Supplementary Table 13. Screening of the reaction time and loading of **cat.B**^a

			
Entry	Loading of cat.B	Reaction time	Yield (%) ^b
1	2.5 mol%	12 h	62
2	2.5 mol%	24 h	64
3	5.0 mol%	12 h	64
4	5.0 mol%	24 h	66 (64 ^c)

^aReaction conditions: **1** (0.1 mmol), methyl 4-chlorobenzoate (0.2 mmol), **cat.A1** (5 mol%), **cat.B** (x mol%), MgSO₄ (3.0 equiv.), DMSO/EA = 1/1, 370 nm LEDs, r.t., y h. ^bGC yield with dodecane as an internal standard. ^cIsolated yield.

2.3 Reaction conditions of ATRP-type reaction of alkyl chlorides

Supplementary Table 14. Screening of catalysts and solvents^a

Entry	Catalyst	Solvent	Conv. (%) ^b	<i>M_n</i> (kDa)	<i>Đ</i>
1	cat.A4	MTBE/HFIP	> 98%	6.6	1.50
2	cat.A4	THF	> 98%	ω-terminal is mostly hydrogenated	
3	cat.A4	DMSO	> 98%	peaks of alkenes are not observed	
4	cat.A4	DMA	> 98%	peaks of alkenes are not observed	
5	cat.A1	MTBE/HFIP	74%	-	-

^aReaction conditions: **76** (0.3 mmol), **83** (1.5 mmol), cat (0.2 mol%), solvent (1 mL), 370 nm LEDs, r.t., 1 h. ^b Conversion was calculated by integration of ¹H NMR of the crude reaction mixture.

Supplementary Table 15. Control experiment^a

Entry	Variation of standard conditions	Conv. (%) ^b	<i>M_n</i> (kDa)	<i>Đ</i>
1	none	> 98%	6.6	1.50
2	without cat.A4	< 1%	-	-
3	without light irradiation	< 1%	-	-

^aReaction conditions: **76** (0.3 mmol), **83** (1.5 mmol), **cat.A4** (0.2 mol%), MTBE/HFIP (0.6/0.4 mL), 40 W 370 nm LEDs, r.t., 1 h. ^b Conversion was calculated by integration of ¹H NMR of the crude reaction mixture.

2.4 Reaction conditions of hydrogenation of PVC

Supplementary Table 16. Screening of solvents and H sources^a

PVC (M_n - 106.1 kDa, $\bar{D}$ - 1.63) + H source $\xrightarrow[\text{solvent, 370 nm LEDs, r.t., 1 h}]{\text{cat.A4 (2 mol\%)}}$ 105

cat.A4 structure:

Entry	Solvent	H source	Dehal (%) ^b	M_n (kDa)	$\bar{D}$
1	THF	γ -terpinene	4.8%	104.0	1.65
2	THF	(ⁱ Pr) ₃ SiH	< 1%	-	-
3	THF	HEH	< 1%	-	-
4	THF	2,4,6-triisopropylbenzenethiol	< 1%	-	-
5	DMSO	γ -terpinene	reaction gelled	-	-
6	DMA	γ -terpinene	reaction gelled	-	-

^aReaction conditions: PVC (100 mg), H source (6.4 mmol), **cat.A4** (2.0 mol%), solvent (16 mL), 370 nm LEDs, r.t., 1 h. ^b Dehalogenative hydrogenation ratio was calculated by integration of ¹H NMR of the product.

2.5 Reaction conditions of grafting modification of PVC

Supplementary Table 17. Screening of solvents and additives^a

PVC (M_n - 106.1 kDa, $\bar{D}$ - 1.63) + $\text{CH}_2=\text{CHCO}_2\text{Et}$ $\xrightarrow[\text{solvent, DIPEA, 370 nm LEDs, r.t., 1 h}]{\text{cat.A4 (2 mol\%)}}$ 108

cat.A4 structure:

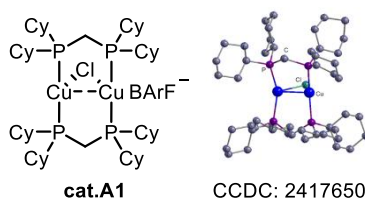
Entry	Solvent	Additive	Grafting (%) ^b	Dehal (%) ^b	M_n (kDa)	$\bar{D}$
1	THF	-	reaction gelled	-	-	-
2	DMSO	-	reaction gelled	-	-	-
3	DMA	-	reaction gelled	-	-	-
4	THF	DIPEA (0.2 equiv.)	9.9%	< 1%	113.7	1.71
5	THF	DIPEA (1.0 equiv.)	9.6%	2.3%	112.8	1.68
6	THF	HEH (1.0 equiv.)	< 1%	< 1%	-	-

^aReaction conditions: PVC (100 mg), ethyl acrylate (4.8 mmol), DIPEA (0.32 mmol), **cat.A4** (2.0 mol%), solvent (16 mL), 370 nm LEDs, r.t., 1 h. ^b Grafting ratio and dehalogenative hydrogenation ratio were calculated by integration of ¹H NMR of the product.

3. Synthesis of Starting Materials

Procedure for the synthesis of photocatalyst cat.A1

An oven-dried 25 mL round-bottom flask equipped with a magnetic stir bar is charged with CuCl (0.5 mmol, 1.0 equiv., 50 mg), dcpm (0.5 mmol, 1.0 equiv., 204 mg), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (0.5 mmol, 1.0 equiv., 443 mg) under N₂ atmosphere. Dry MTBE (12 mL) and HFIP (3 mL) are successively added and the solution is allowed to stir at r.t. for 4 h. The solvent is then mostly evaporated and petroleum ether is added to yield a white solid (391 mg, 85%). Crystals suitable for single-crystal X-ray diffraction were obtained by recrystallization from MTBE and hexane at -20 °C.



IR: ν = 2933, 2856, 1611, 1448, 1354, 1274, 1118, 886, 681, 669 cm⁻¹.

¹H NMR (500 MHz, Chloroform-d) δ 7.79 – 7.65 (m, 8H), 7.53 (s, 4H), 2.20 – 1.67 (m, 52H), 1.51 – 1.07 (m, 40H).

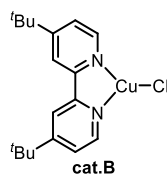
³¹P NMR (202 MHz, Chloroform-d) δ 12.43 (s).

¹³C NMR (126 MHz, Chloroform-d) δ 162.6 – 160.6 (m), 134.8, 129.4 – 128.2 (m), 128.0 – 121.0 (m), 117.8 – 116.9 (m), 35.1 – 34.8 (m), 34.8, 30.5, 30.1 – 29.9 (m), 29.3, 28.8, 27.3 – 27.1 (m), 27.1, 27.1 – 26.9 (m), 25.9, 25.8.

HRMS (ESI) calcd. for C₅₀H₉₂ClCu₂P₄ [M-BArF]⁺: 977.4425, found: 977.4417.

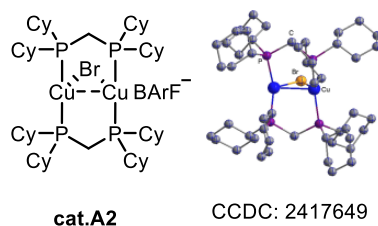
Procedure for the synthesis of catalyst cat.B

An oven-dried 25 mL round-bottom flask equipped with a magnetic stir bar is charged with CuCl (1.0 mmol, 1.0 equiv., 99 mg), dtbbpy (1.0 mmol, 1.0 equiv., 268 mg) under N₂ atmosphere. Dry DCM (10 mL) is successively added and the solution is allowed to stir at r.t. for 2 h. The solvent is then evaporated to yield a brown solid (338 mg, 92%).

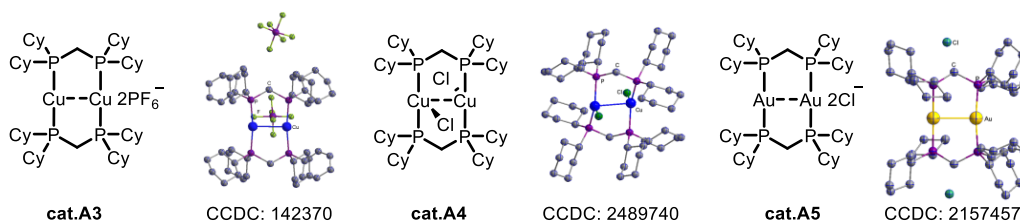


Procedure for the synthesis of photocatalyst cat.A2

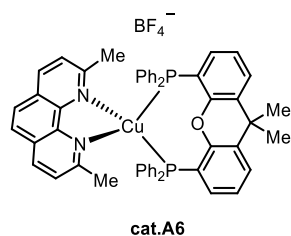
An oven-dried 25 mL round-bottom flask equipped with a magnetic stir bar is charged with CuBr (0.5 mmol, 1.0 equiv., 71mg), dcpm (0.5 mmol, 1.0 equiv., 204 mg), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (0.5 mmol, 1.0 equiv., 443 mg) under N₂ atmosphere. Dry MTBE (12 mL) and HFIP (3 mL) are successively added and the solution is allowed to stir at r.t. for 4 h. The solvent is then mostly evaporated and petroleum ether is added to yield a white solid (387 mg, 82%). Crystals suitable for single-crystal X-ray diffraction were obtained by recrystallization from MTBE and hexane at -20 °C.



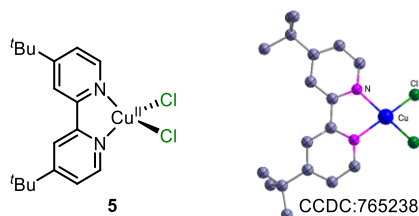
Catalysts **cat.A3**¹, **cat.A4**¹, **cat.A5**² were synthesized using literature procedures.



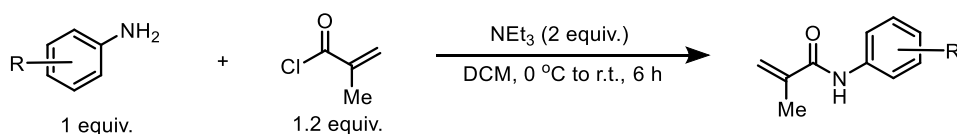
Catalyst **cat.A6**³ was synthesized using literature procedures.



5⁴ was synthesized using literature procedures.



General procedure for the synthesis of *N*-aryl methacrylamides⁵⁻⁸



To a solution of aniline (10 mmol) and Et₃N (2.8 mL, 20 mmol) in CH₂Cl₂ (20 mL), methacryloyl chloride (1.16 mL, 12 mmol) is added dropwise at 0 °C. The resulting solution is then stirred at rt for 6 h. Subsequently, the reaction mixture is poured into water and the aqueous layer is extracted with CH₂Cl₂ (3×15 mL). The combined organic layers are dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude product is purified by column chromatography (silica) to provide products.

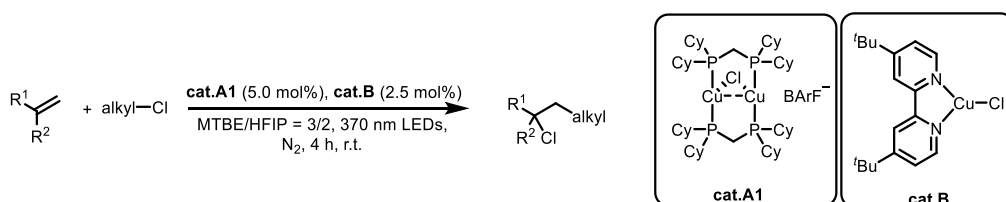
4. General Procedures



Supplementary Figure 1. Reaction set-up (Left: 40 W LEDs, Right: 40 W LEDs; $\lambda_{\text{max}} = 370 \text{ nm}$).
(The fan is used to keep the reaction temperature being around room temperature $\sim 25^\circ\text{C}$)

4.1 General procedures of ATRA reaction of alkyl chlorides

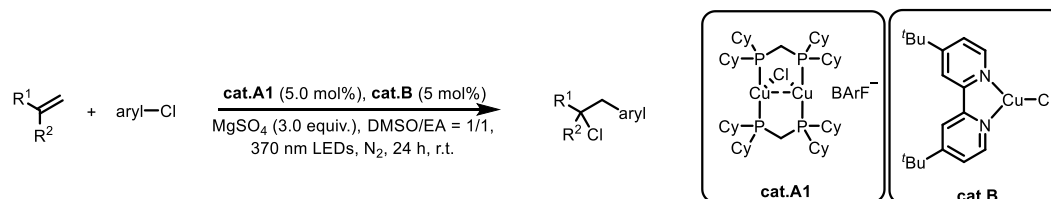
General procedure A



In N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar is charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), alkene (0.1 mmol, 1.0 equiv.) and alkyl chlorides (0.3 mmol, 3 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) are added into the vial. The vial is sealed, removed from the glove-box and is irradiated under 370 nm LEDs (40 W $\times$ 2) for 4 h at room temperature with vigorous stirring. After completion of the reaction, the solvent is removed under vacuum and the resulting residue is purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford the desired ATRA products.

4.2 General procedures of ATRA reaction of aryl chlorides

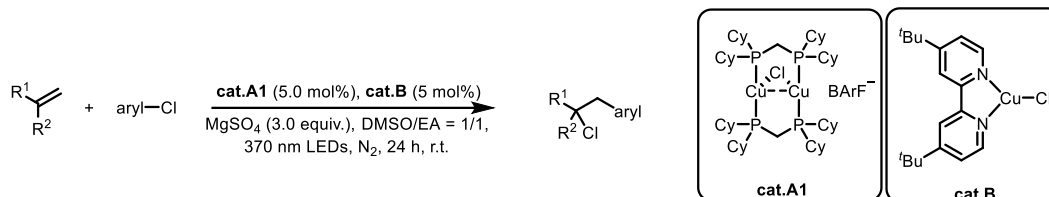
General procedure B (for electron-deficient alkenes)



In N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar is charged with

cat.A1 (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (1.8 mg, 0.005 mmol, 5.0 mol%), alkene (0.1 mmol, 1.0 equiv.), aryl chlorides (0.2 mmol, 2 equiv.) and MgSO_4 (36 mg, 0.3 mmol, 3.0 equiv.). Then, DMSO (0.5 mL) and EA (0.5 mL) are added into the vial. The vial is sealed, removed from the glove-box and is irradiated under 370 nm LEDs ($40\text{ W} \times 2$) for 24 h at room temperature with vigorous stirring. After completion of the reaction, the solvent is removed under vacuum and the resulting residue is purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford the desired ATRA products.

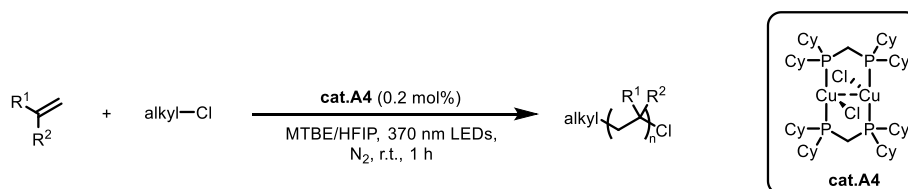
General procedure C (for unactivated alkenes)



In N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar is charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (1.8 mg, 0.005 mmol, 5.0 mol%), alkene (0.5 mmol, 5.0 equiv.), aryl chlorides (0.1 mmol, 1 equiv.) and MgSO_4 (36 mg, 0.3 mmol, 3.0 equiv.). Then, DMSO (0.5 mL) and EA (0.5 mL) are added into the vial. The vial is sealed, removed from the glove-box and is irradiated under 370 nm LEDs ($40\text{ W} \times 2$) for 24 h at room temperature with vigorous stirring. After completion of the reaction, the solvent is removed under vacuum and the resulting residue is purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford the desired ATRA products.

4.3 General procedures of ATRP-type reaction of alkyl chlorides

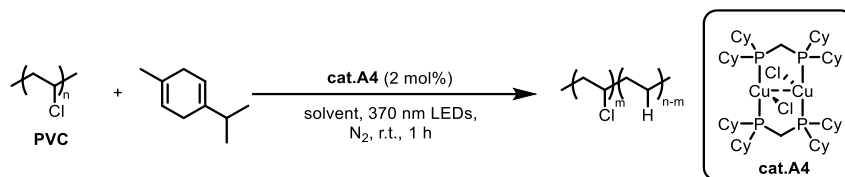
General procedure D



In N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar is charged with **cat.A4** (3.0 mg, 0.003 mmol, 0.2 mol%), alkenes (1.5 mmol, 1.0 equiv.) and alkyl chlorides (0.3 mmol, 0.2 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) are added into the vial. The vial is sealed, removed from the glove-box and is irradiated under 370 nm LEDs ($40\text{ W} \times 2$) for 1 h at room temperature with vigorous stirring. After completion of the reaction, the mixture is added dropwise into 20 mL of a mixed solvent system consisting of pentane and methanol ($v/v = 40:1$), leading to precipitation of the polymer as a waxy solid. The solid is then washed five times with the same mixed solvent system, followed by decantation to remove the solvent, and dried under reduced pressure to afford the desired chlorine-transfer polymerization products.

4.4 General procedures of hydrogenation of PVC

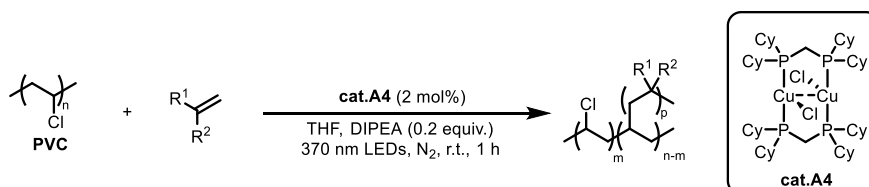
General procedure E



In N₂-filled glove-box, an oven-dried vial (20 mL) equipped with a magnetic stir bar is charged with **cat.A4** (32.5 mg, 0.032 mmol, 2.0 mol%), PVC (100 mg, 1.6 mmol of vinyl chloride repeat units, 1.0 equiv.) and γ -terpinene (1.0 mL, 6.4 mmol, 4.0 equiv.). Then, THF (16 mL) is added into the vial. The vial is sealed, removed from the glove-box and is irradiated under 370 nm LEDs (40 W $\times$ 2) for 1 h at room temperature with vigorous stirring. After completion of the reaction, the mixture is poured into 80 mL methanol, causing the polymer to precipitate. After 1 hour of stirring, the precipitate is collected via vacuum filtration and dried under reduced pressure.

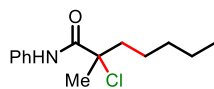
4.5 General procedures of grafting modification of PVC

General procedure F



In N₂-filled glove-box, an oven-dried vial (20 mL) equipped with a magnetic stir bar is charged with **cat.A4** (32.5 mg, 0.032 mmol, 2.0 mol%), PVC (100 mg, 1.6 mmol of vinyl chloride repeat units, 1.0 equiv.), alkenes (4.8 mmol, 3.0 equiv.) and DIPEA (56 μ L, 0.32 mmol, 0.2 equiv.). Then, THF (16 mL) is added into the vial. The vial is sealed, removed from the glove-box and is irradiated under 370 nm LEDs (40 W $\times$ 2) for 1 h at room temperature with vigorous stirring. After completion of the reaction, the mixture is poured into 80 mL methanol, causing the polymer to precipitate. After 1 hour of stirring, the precipitate is collected via vacuum filtration and dried under reduced pressure.

5. Characterization of Products



2-chloro-2-methyl-*N*-phenylheptanamide (3)

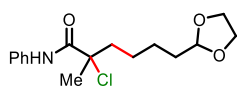
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 18.1 mg, 71%). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

^1H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.56 (d, J = 7.4 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.16 (t, J = 7.5 Hz, 1H), 2.23 (ddd, J = 14.1, 11.9, 4.3 Hz, 1H), 1.90 (ddd, J = 14.0, 11.9, 4.3 Hz, 1H), 1.85 (s, 3H), 1.63 – 1.51 (m, 1H), 1.46 – 1.34 (m, 1H), 1.37 – 1.25 (m, 4H), 0.91 – 0.85 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 137.1, 129.0, 124.9, 120.0, 75.0, 43.0, 31.4, 30.0, 24.6, 22.4, 13.9.

IR (ATR): ν = 3402, 2931, 2857, 1671, 1529, 1276, 1123, 886, 682, 670 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{21}\text{ClNO}$ $[\text{M}+\text{H}]^+$: 254.1306, found: 254.1296.



2-chloro-6-(1,3-dioxolan-2-yl)-2-methyl-*N*-phenylhexanamide (13)

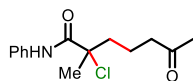
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 19.4 mg, 62%). R_f = 0.4 (PE/EA = 5:1). Colorless oil.

^1H NMR (500 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.59 – 7.50 (m, 2H), 7.39 – 7.30 (m, 2H), 7.18 – 7.10 (m, 1H), 4.83 (t, J = 4.7 Hz, 1H), 3.99 – 3.89 (m, 2H), 3.88 – 3.77 (m, 2H), 2.24 (ddd, J = 14.0, 11.9, 4.0 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.85 (s, 3H), 1.69 – 1.55 (m, 3H), 1.49 – 1.39 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.5, 137.1, 129.0, 124.9, 120.0, 104.3, 74.7, 64.8, 42.9, 33.6, 30.0, 24.9, 23.6.

IR (ATR): ν = 3399, 2947, 2866, 1678, 1597, 1525, 1142, 1032, 754, 691 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{23}\text{ClNO}_3$ $[\text{M}+\text{H}]^+$: 312.1361, found: 312.1357.



2-chloro-2-methyl-6-oxo-*N*-phenylheptanamide (14)

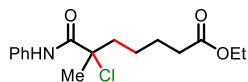
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 18.8 mg, 70%). R_f = 0.3 (PE/EA = 5:1). Colorless oil.

^1H NMR (500 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 7.63 – 7.51 (m, 2H), 7.38 – 7.31 (m, 2H), 7.20 – 7.12 (m, 1H), 2.54 – 2.40 (m, 2H), 2.25 – 2.16 (m, 1H), 2.12 (s, 3H), 1.96 – 1.87 (m, 2H), 1.85 (s, 3H), 1.70 – 1.59 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.0, 169.3, 137.0, 129.0, 125.0, 120.0, 74.1, 42.9, 41.9, 30.0, 29.8, 19.3.

IR (ATR): ν = 3351, 2934, 1713, 1680, 1529, 1441, 1240, 1165, 757, 693 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{19}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$: 268.1099, found: 268.1092.



ethyl 6-chloro-6-methyl-7-oxo-7-(phenylamino)heptanoate (15)

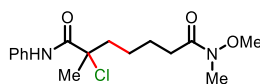
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 22.4 mg, 72%). R_f = 0.3 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.61 – 7.51 (m, 2H), 7.40 – 7.31 (m, 2H), 7.19 – 7.09 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.34 – 2.27 (m, 2H), 2.27 – 2.20 (m, 1H), 1.97 – 1.88 (m, 1H), 1.85 (s, 3H), 1.70 – 1.56 (m, 3H), 1.47 – 1.35 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 173.3, 169.4, 137.0, 129.0, 124.9, 120.0, 74.5, 60.2, 42.5, 34.0, 30.0, 24.6, 24.5, 14.2.

IR (ATR): ν = 3355, 2933, 1731, 1680, 1527, 1441, 1241, 1158, 754, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₆H₂₃ClNO₃ [M+H]⁺: 312.1361, found: 312.1353.



2-chloro-*N'*-methoxy-*N'*,2-dimethyl-*N*¹-phenylheptanediamide (16)

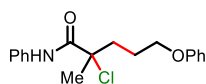
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1). (0.1 mmol scale, 23.0 mg, 70%). R_f = 0.2 (PE/EA = 3:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.59 – 7.53 (m, 2H), 7.40 – 7.30 (m, 2H), 7.20 – 7.07 (m, 1H), 3.65 (s, 3H), 3.15 (s, 3H), 2.47 – 2.38 (m, 2H), 2.31 – 2.21 (m, 1H), 1.99 – 1.90 (m, 1H), 1.85 (s, 3H), 1.69 – 1.59 (m, 3H), 1.47 – 1.36 (m, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.5, 137.1, 129.0, 124.9, 120.0, 74.6, 61.2, 42.7, 32.1, 31.6, 30.0, 24.8, 24.2.

IR (ATR): ν = 3323, 2935, 1651, 1579, 1526, 1440, 1385, 994, 754, 692 cm⁻¹.

HRMS (ESI) calcd. for C₁₆H₂₄ClN₂O₃ [M+H]⁺: 327.1470, found: 327.1463.



2-chloro-2-methyl-5-phenoxy-*N*-phenylpentanamide (17)

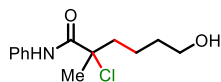
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 23.7 mg, 75%). R_f = 0.6 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 7.61 – 7.55 (m, 2H), 7.40 – 7.34 (m, 2H), 7.30 – 7.24 (m, 2H), 7.21 – 7.13 (m, 1H), 6.97 – 6.92 (m, 1H), 6.91 – 6.85 (m, 2H), 4.04 – 3.94 (m, 2H), 2.52 – 2.38 (m, 1H), 2.19 – 2.05 (m, 2H), 1.96 – 1.86 (m, 4H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.3, 158.8, 137.0, 129.4, 129.0, 125.0, 120.7, 120.0, 114.4, 74.3, 67.0, 39.6, 30.0, 25.1.

IR (ATR): ν = 3397, 2929, 1678, 1597, 1525, 1495, 1441, 1239, 751, 690 cm⁻¹.

HRMS (ESI) calcd. for C₁₈H₂₁ClNO₂ [M+H]⁺: 318.1255, found: 318.1249.



2-chloro-6-hydroxy-2-methyl-N-phenylhexanamide (18)

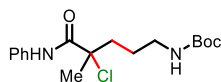
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). (0.1 mmol scale, 10.6 mg, 41%). R_f = 0.2 (PE/EA = 3:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.60 – 7.53 (m, 2H), 7.39 – 7.31 (m, 2H), 7.19 – 7.11 (m, 1H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.35 – 2.23 (m, 1H), 1.97 – 1.88 (m, 1H), 1.86 (s, 3H), 1.72 – 1.63 (m, 1H), 1.63 – 1.55 (m, 2H), 1.50 – 1.40 (m, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.6, 137.0, 129.1, 125.0, 120.0, 74.7, 62.4, 42.5, 32.2, 30.1, 21.4.

IR (ATR): ν = 3396, 3339, 2933, 2868, 1668, 1597, 1528, 1442, 754, 692 cm⁻¹.

HRMS (ESI) calcd. for C₁₃H₁₉ClNO₂ [M+H]⁺: 256.1099, found: 256.1092.



tert-butyl (4-chloro-4-methyl-5-oxo-5-(phenylamino)pentyl)carbamate (19)

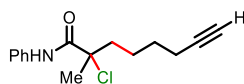
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, with 1% NEt₃). (0.1 mmol scale, 25.2 mg, 74%). R_f = 0.6 (PE/EA = 3:1). White solid. **m.p.** 68.5–71.9 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.59 – 7.51 (m, 2H), 7.40 – 7.32 (m, 2H), 7.20 – 7.12 (m, 1H), 4.58 (s, 1H), 3.19 – 3.02 (m, 2H), 2.35 – 2.24 (m, 1H), 1.97 – 1.89 (m, 1H), 1.86 (s, 3H), 1.82 – 1.74 (m, 1H), 1.60 – 1.50 (m, 1H), 1.43 (s, 9H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.3, 155.9, 137.0, 129.0, 125.0, 120.0, 79.2, 74.2, 39.9, 30.2, 28.4, 25.7.

IR (ATR): ν = 3391, 3349, 2930, 1680, 1523, 1441, 1245, 1164, 753, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₇H₂₆ClN₂O₃ [M+H]⁺: 341.1626, found: 341.1619.



2-chloro-2-methyl-N-phenyloct-7-ynamide (20)

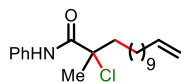
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 18.6 mg, 71%). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.60 – 7.52 (m, 2H), 7.41 – 7.32 (m, 2H), 7.22 – 7.12 (m, 1H), 2.31 – 2.17 (m, 3H), 1.98 – 1.90 (m, 2H), 1.86 (s, 3H), 1.76 – 1.66 (m, 1H), 1.63 – 1.45 (m, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.5, 137.1, 129.0, 125.0, 120.0, 84.0, 74.6, 68.5, 42.4, 30.0, 28.1, 24.1, 18.2.

IR (ATR): ν = 3400, 3302, 2933, 2117, 1679, 1598, 1526, 1441, 755, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₅H₁₉ClNO [M+H]⁺: 264.1150, found: 264.1140.



2-chloro-2-methyl-N-phenyltetradec-13-enamide (21)

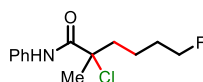
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 23.5 mg, 67%). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.63 – 7.49 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.24 – 7.12 (m, 1H), 5.90 – 5.73 (m, 1H), 5.04 – 4.87 (m, 2H), 2.28 – 2.19 (m, 1H), 2.08 – 1.99 (m, 2H), 1.94 – 1.86 (m, 1H), 1.85 (s, 3H), 1.59 – 1.51 (m, 1H), 1.37 – 1.25 (m, 15H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.6, 139.2, 137.1, 129.0, 124.9, 120.0, 114.1, 75.0, 43.0, 33.8, 30.0, 29.5, 29.5, 29.4, 29.3, 29.3, 29.1, 28.9, 24.9.

IR (ATR): ν = 3405, 2924, 2853, 1683, 1598, 1526, 1441, 1313, 753, 690 cm⁻¹.

HRMS (ESI) calcd. for C₂₁H₃₃ClNO [M+H]⁺: 350.2245, found: 350.2237.



2-chloro-6-fluoro-2-methyl-N-phenylhexanamide (22)

According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 14.1 mg, 55%). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

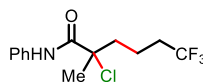
¹H NMR (500 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 7.61 – 7.53 (m, 2H), 7.39 – 7.31 (m, 2H), 7.20 – 7.12 (m, 1H), 4.54 – 4.45 (m, 1H), 4.43 – 4.35 (m, 1H), 2.34 – 2.25 (m, 1H), 2.01 – 1.90 (m, 1H), 1.87 (s, 3H), 1.78 – 1.66 (m, 3H), 1.58 – 1.45 (m, 1H).

¹⁹F NMR (471 MHz, Chloroform-*d*) δ -218.4.

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.4, 137.0, 129.1, 125.0, 120.0, 83.7 (d, *J* = 164.8 Hz), 74.5, 42.5, 30.1 (d, *J* = 2.9 Hz), 30.0, 21.0 (d, *J* = 5.2 Hz).

IR (ATR): ν = 3397, 2961, 1677, 1597, 1525, 1441, 1240, 830, 755, 692 cm⁻¹.

HRMS (ESI) calcd. for C₁₃H₁₈ClFNO [M+H]⁺: 258.1055, found: 258.1047.



2-chloro-6,6,6-trifluoro-2-methyl-N-phenylhexanamide (23)

According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 21.9 mg, 75%). R_f = 0.6 (PE/EA = 10:1). Colorless oil.

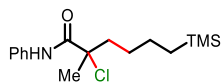
¹H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.60 – 7.51 (m, 2H), 7.42 – 7.34 (m, 2H), 7.23 – 7.13 (m, 1H), 2.40 – 2.30 (m, 1H), 2.21 – 2.06 (m, 2H), 2.01 – 1.93 (m, 1H), 1.92 – 1.81 (m, 4H), 1.74 – 1.62 (m, 1H).

¹⁹F NMR (471 MHz, Chloroform-*d*) δ -66.3.

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.0, 136.9, 129.1, 126.8 (q, *J* = 277.2 Hz), 125.2, 120.1, 73.9, 41.5, 33.4 (q, *J* = 28.9 Hz), 30.2, 17.8 (q, *J* = 3.1 Hz).

IR (ATR): ν = 3404, 2935, 1677, 1598, 1527, 1442, 1253, 1010, 755, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₃H₁₆ClF₃NO [M+H]⁺: 294.0867, found: 294.0858.



2-chloro-2-methyl-N-phenyl-6-(trimethylsilyl)hexanamide (24)

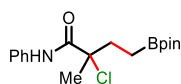
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 21.9 mg, 70%). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.59 – 7.52 (m, 2H), 7.42 – 7.32 (m, 2H), 7.19 – 7.12 (m, 1H), 2.28 – 2.18 (m, 1H), 1.96 – 1.87 (m, 1H), 1.86 (s, 3H), 1.64 – 1.53 (m, 1H), 1.47 – 1.38 (m, 1H), 1.36 – 1.28 (m, 2H), 0.55 – 0.46 (m, 2H), -0.04 (s, 9H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.7, 137.1, 129.0, 124.9, 120.0, 74.9, 42.8, 30.0, 28.7, 23.7, 16.5, -1.7.

IR (ATR): ν = 3405, 2950, 1683, 1598, 1527, 1441, 1247, 862, 753, 690 cm⁻¹.

HRMS (ESI) calcd. for C₁₆H₂₇ClNOSi [M+H]⁺: 312.1545, found: 312.1536.



2-chloro-2-methyl-N-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (25)

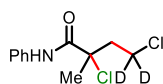
According to the general procedure A for 24 h, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). (0.1 mmol scale, 25.4 mg, 75%). R_f = 0.4 (PE/EA = 10:1). White solid. **m.p.** 81.4–85.5 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.59 – 7.51 (m, 2H), 7.39 – 7.29 (m, 2H), 7.19 – 7.10 (m, 1H), 2.41 – 2.29 (m, 1H), 2.08 – 1.98 (m, 1H), 1.84 (s, 3H), 1.23 (d, *J* = 2.3 Hz, 12H), 1.09 – 1.01 (m, 1H), 0.92 – 0.82 (m, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.6, 137.1, 129.0, 124.9, 120.0, 83.3, 76.2, 37.6, 29.3, 24.8, 24.8.

IR (ATR): ν = 3403, 2978, 2929, 1679, 1526, 1370, 1317, 885, 755, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₇H₂₆BClNO₃ [M+H]⁺: 338.1689, found: 338.1682.



2,4-dichloro-2-methyl-N-phenylbutanamide-4,4-d2 (26)

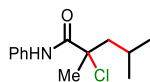
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 17.1 mg, 69%). R_f = 0.6 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.59 – 7.51 (m, 2H), 7.41 – 7.32 (m, 2H), 7.22 – 7.12 (m, 1H), 2.79 (d, *J* = 14.3 Hz, 1H), 2.39 (d, *J* = 14.3 Hz, 1H), 1.90 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 168.4, 136.8, 129.1, 125.2, 120.1, 72.1, 44.8, 30.4.

IR (ATR): ν = 3364, 2922, 2853, 1683, 1653, 1599, 1066, 754, 690, 436 cm⁻¹.

HRMS (ESI) calcd. for C₁₁H₁₂D₂Cl₂NO [M+H]⁺: 248.0572, found: 248.0551.



2-chloro-2,4-dimethyl-N-phenylpentanamide (27)

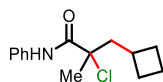
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 14.3 mg, 60%). R_f = 0.7 (PE/EA = 10:1). White solid. **m.p.** 44.7-46.8 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 7.62 – 7.51 (m, 2H), 7.40 – 7.32 (m, 2H), 7.22 – 7.10 (m, 1H), 2.25 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.90 – 1.82 (m, 4H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.7, 137.2, 129.1, 124.9, 120.0, 74.5, 50.8, 31.4, 25.7, 24.3, 22.7.

IR (ATR): ν = 3403, 2958, 2932, 1676, 1598, 1524, 1441, 1240, 752, 690 cm⁻¹.

HRMS (ESI) calcd. for C₁₃H₁₉ClNO [M+H]⁺: 240.1150, found: 240.1142.



2-chloro-3-cyclobutyl-2-methyl-N-phenylpropanamide (28)

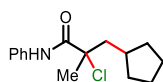
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 14.7 mg, 58%). R_f = 0.7 (PE/EA = 10:1). White solid. **m.p.** 48.1-50.0 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.57 – 7.50 (m, 2H), 7.39 – 7.31 (m, 2H), 7.19 – 7.12 (m, 1H), 2.67 – 2.52 (m, 1H), 2.34 (dd, *J* = 14.4, 7.1 Hz, 1H), 2.14 – 2.03 (m, 2H), 2.03 – 1.96 (m, 1H), 1.88 – 1.81 (m, 4H), 1.80 – 1.70 (m, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.5, 137.2, 129.0, 124.9, 119.9, 74.2, 49.6, 32.9, 30.0, 29.7, 29.0, 19.1.

IR (ATR): ν = 3402, 2972, 2934, 1677, 1597, 1525, 1312, 1241, 754, 690 cm⁻¹.

HRMS (ESI) calcd. for C₁₄H₁₉ClNO [M+H]⁺: 252.1150, found: 252.1142.



2-chloro-3-cyclopentyl-2-methyl-N-phenylpropanamide (29)

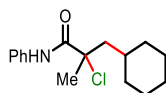
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 18.5 mg, 70%). R_f = 0.7 (PE/EA = 10:1). White solid. **m.p.** 67.2-69.1 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 7.60 – 7.51 (m, 2H), 7.40 – 7.32 (m, 2H), 7.21 – 7.12 (m, 1H), 2.39 – 2.29 (m, 1H), 2.10 – 1.98 (m, 2H), 1.92 – 1.83 (m, 4H), 1.81 – 1.72 (m, 1H), 1.64 – 1.54 (m, 2H), 1.53 – 1.41 (m, 2H), 1.24 – 1.09 (m, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.8, 137.2, 129.1, 124.9, 120.0, 74.8, 48.7, 37.2, 34.0, 32.8, 30.9, 25.1, 24.7.

IR (ATR): ν = 3324, 2953, 2868, 1667, 1560, 1530, 1440, 1314, 750, 690 cm⁻¹.

HRMS (ESI) calcd. for C₁₅H₂₁ClNO [M+H]⁺: 266.1306, found: 266.1298.



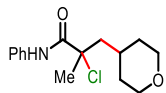
2-chloro-3-cyclohexyl-2-methyl-N-phenylpropanamide (30)

According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 14.5 mg, 52%). R_f = 0.7 (PE/EA = 10:1). White solid. **m.p.** 81.0-83.8 °C.

^1H NMR (500 MHz, Chloroform- d) δ 8.66 (s, 1H), 7.63 – 7.46 (m, 2H), 7.42 – 7.31 (m, 2H), 7.23 – 7.11 (m, 1H), 2.24 (dd, J = 14.5, 6.9 Hz, 1H), 1.88 – 1.80 (m, 4H), 1.79 – 1.55 (m, 6H), 1.32 – 0.96 (m, 5H). **^{13}C NMR** (126 MHz, Chloroform- d) δ 169.8, 137.2, 129.1, 124.9, 120.1, 74.4, 49.6, 35.0, 34.6, 33.3, 31.2, 26.3, 26.2, 26.1.

IR (ATR): ν = 3402, 2921, 2850, 1676, 1598, 1523, 1440, 1240, 752, 690 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{23}\text{ClNO}$ $[\text{M}+\text{H}]^+$: 280.1463, found: 280.1455.



2-chloro-2-methyl-N-phenyl-3-(tetrahydro-2H-pyran-4-yl)propanamide (31)

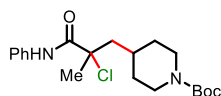
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 16.9 mg, 60%). R_f = 0.4 (PE/EA = 10:1). White solid. **m.p.** 66.0-68.5 °C.

^1H NMR (400 MHz, Chloroform- d) δ 8.67 (s, 1H), 7.60 – 7.50 (m, 2H), 7.41 – 7.32 (m, 2H), 7.24 – 7.13 (m, 1H), 3.99 – 3.82 (m, 2H), 3.45 – 3.26 (m, 2H), 2.41 – 2.26 (m, 1H), 1.91 – 1.80 (m, 5H), 1.71 – 1.56 (m, 2H), 1.49 – 1.30 (m, 2H).

^{13}C NMR (126 MHz, Chloroform- d) δ 169.5, 137.0, 129.1, 125.0, 120.0, 73.9, 67.8, 67.8, 49.0, 34.1, 33.1, 32.4, 31.5.

IR (ATR): ν = 3401, 2930, 2843, 1681, 1598, 1527, 1441, 1140, 755, 692 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{21}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$: 282.1255, found: 282.1246.



tert-butyl 4-(2-chloro-2-methyl-3-oxo-3-(phenylamino)propyl)piperidine-1-carboxylate (32)

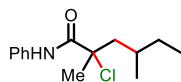
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, with 1% NEt_3). (0.1 mmol scale, 23.7 mg, 62%). R_f = 0.5 (PE/EA = 5:1). Colorless oil.

^1H NMR (500 MHz, Chloroform- d) δ 8.66 (s, 1H), 7.58 – 7.49 (m, 2H), 7.40 – 7.32 (m, 2H), 7.19 – 7.13 (m, 1H), 4.19 – 3.81 (m, 2H), 2.78 – 2.56 (m, 2H), 2.32 (dd, J = 14.7, 6.7 Hz, 1H), 1.90 – 1.82 (m, 4H), 1.81 – 1.72 (m, 2H), 1.68 – 1.60 (m, 1H), 1.43 (s, 9H), 1.29 – 1.13 (m, 2H).

^{13}C NMR (126 MHz, Chloroform- d) δ 169.5, 154.7, 137.0, 129.1, 125.0, 120.0, 79.2, 73.9, 48.5, 33.4, 33.2, 32.1, 31.5, 28.4.

IR (ATR): ν = 3322, 2976, 2929, 1683, 1528, 1441, 1169, 865, 756, 692 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{30}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 381.1939, found: 381.1931.



2-chloro-2,4-dimethyl-N-phenylhexanamide (33)

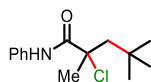
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 14.2 mg, 56%, d.r. = 1.1:1). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.77 – 8.56 (m, 1H), 7.60 – 7.47 (m, 2H), 7.40 – 7.32 (m, 2H), 7.19 – 7.13 (m, 1H), 2.34 – 2.14 (m, 1H), 1.96 – 1.78 (m, 4H), 1.75 – 1.65 (m, 1H), 1.45 – 1.34 (m, 1H), 1.30 – 1.14 (m, 1H), 1.02 – 0.81 (m, 6H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.8, 169.8, 137.2, 137.2, 129.1, 124.9, 124.9, 120.0, 120.0, 74.7, 74.6, 49.2, 48.9, 31.8, 31.8, 31.4, 30.8, 30.8, 29.8, 20.8, 19.4, 11.2, 11.1.

IR (ATR): ν = 3403, 2962, 2931, 1680, 1598, 1526, 1441, 1240, 754, 690 cm⁻¹.

HRMS (ESI) calcd. for C₁₄H₂₁ClNO [M+H]⁺: 254.1306, found: 254.1297.



2-chloro-2,4,4-trimethyl-N-phenylpentanamide (34)

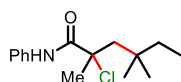
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 17.0 mg, 67%). R_f = 0.7 (PE/EA = 10:1). White solid. **m.p.** 48.7-50.5 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.31 (m, 2H), 7.21 – 7.13 (m, 1H), 2.52 (d, *J* = 15.0 Hz, 1H), 1.90 (d, *J* = 15.0 Hz, 1H), 1.86 (s, 3H), 1.04 (s, 9H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.8, 137.3, 129.1, 124.9, 120.0, 73.5, 54.0, 33.6, 32.0, 30.7.

IR (ATR): ν = 3404, 2980, 2955, 1680, 1599, 1526, 1442, 1367, 753, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₄H₂₁ClNO [M+H]⁺: 254.1306, found: 254.1296.



2-chloro-2,4,4-trimethyl-N-phenylhexanamide (35)

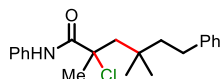
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 18.8 mg, 70%). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.62 – 7.50 (m, 2H), 7.39 – 7.30 (m, 2H), 7.20 – 7.10 (m, 1H), 2.48 (d, *J* = 15.1 Hz, 1H), 1.90 (d, *J* = 15.1 Hz, 1H), 1.86 (s, 3H), 1.45 – 1.27 (m, 2H), 1.03 (s, 3H), 0.95 (s, 3H), 0.84 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 170.0, 137.3, 129.1, 124.9, 120.0, 73.6, 51.5, 36.4, 34.5, 33.8, 27.6, 26.8, 8.4.

IR (ATR): ν = 3405, 2967, 1684, 1599, 1527, 1441, 1312, 1241, 752, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₅H₂₃ClNO [M+H]⁺: 268.1463, found: 268.1454.



2-chloro-2,4,4-trimethyl-N,6-diphenylhexanamide (36)

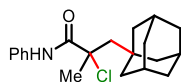
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 15.8 mg, 46%). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 7.59 – 7.49 (m, 2H), 7.38 – 7.31 (m, 2H), 7.28 – 7.22 (m, 2H), 7.21 – 7.08 (m, 4H), 2.72 – 2.53 (m, 3H), 1.99 (d, *J* = 15.1 Hz, 1H), 1.89 (s, 3H), 1.78 – 1.67 (m, 1H), 1.65 – 1.58 (m, 1H), 1.13 (s, 3H), 1.08 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.8, 143.0, 137.2, 129.1, 128.3, 128.3, 125.5, 124.9, 120.1, 73.4, 51.5, 46.0, 34.6, 34.0, 30.5, 28.1, 27.5.

IR (ATR): ν = 3401, 2934, 1682, 1599, 1526, 1441, 1312, 881, 752, 691 cm⁻¹.

HRMS (ESI) calcd. for C₂₁H₂₇ClNO [M+H]⁺: 344.1776, found: 344.1768.



3-((3r,5r,7r)-adamantan-1-yl)-2-chloro-2-methyl-N-phenylpropanamide (37)

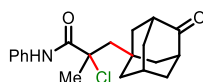
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 19.8 mg, 60%). R_f = 0.7 (PE/EA = 10:1). Off white solid. **m.p.** 101.3–103.1 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 7.59 – 7.52 (m, 2H), 7.42 – 7.33 (m, 2H), 7.22 – 7.11 (m, 1H), 2.36 (d, *J* = 15.1 Hz, 1H), 1.94 – 1.89 (m, 3H), 1.84 (s, 3H), 1.82 – 1.77 (m, 3H), 1.69 – 1.56 (m, 10H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.9, 137.3, 129.1, 124.9, 120.1, 72.9, 55.4, 42.9, 36.8, 34.1, 33.9, 28.7.

IR (ATR): ν = 3402, 2899, 2847, 1677, 1597, 1523, 1440, 1310, 749, 689 cm⁻¹.

HRMS (ESI) calcd. for C₂₀H₂₇ClNO [M+H]⁺: 332.1776, found: 332.1768.



2-chloro-2-methyl-3-(4-oxo-1-adamantan-1-yl)-N-phenylpropanamide (38)

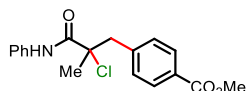
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 20.0 mg, 58%). R_f = 0.4 (PE/EA = 5:1). White solid. **m.p.** 119.5–120.6 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 7.59 – 7.49 (m, 2H), 7.40 – 7.32 (m, 2H), 7.22 – 7.11 (m, 1H), 2.55 – 2.46 (m, 3H), 2.21 – 2.12 (m, 2H), 2.10 – 2.05 (m, 1H), 2.01 – 1.87 (m, 7H), 1.87 – 1.78 (m, 5H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 217.8, 169.5, 137.0, 129.1, 125.1, 120.1, 72.3, 52.9, 46.5, 46.4, 44.4, 43.3, 41.4, 38.5, 38.4, 34.1, 33.9, 27.8.

IR (ATR): ν = 3348, 2924, 2856, 1720, 1681, 1526, 1441, 1240, 752, 691 cm⁻¹.

HRMS (ESI) calcd. for C₂₀H₂₅ClNO₂ [M+H]⁺: 346.1568, found: 346.1559.



methyl 4-(2-chloro-2-methyl-3-oxo-3-(phenylamino)propyl)benzoate (39)

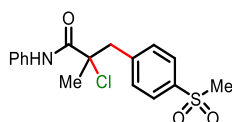
According to the general procedure B, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 21.3 mg, 64%). R_f = 0.6 (PE/EA = 5:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.00 – 7.90 (m, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.30 (m, 4H), 7.17 – 7.12 (m, 1H), 3.89 (s, 3H), 3.64 (d, *J* = 13.8 Hz, 1H), 3.19 (d, *J* = 13.9 Hz, 1H), 1.94 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 168.6, 166.9, 140.6, 136.6, 130.7, 129.3, 129.2, 129.0, 125.2, 120.3, 73.8, 52.1, 48.0, 30.2.

IR (ATR): ν = 3399, 2951, 1719, 1680, 1527, 1441, 1279, 1109, 756, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₈H₁₉ClNO₃ [M+H]⁺: 332.1048, found: 332.1038.



2-chloro-2-methyl-3-(4-(methylsulfonyl)phenyl)-N-phenylpropanamide (40)

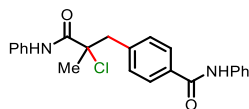
According to the general procedure B, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). (0.1 mmol scale, 25.7 mg, 73%). R_f = 0.3 (PE/EA = 3:1). White solid. **m.p.** 159.8–163.2 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.90 – 7.79 (m, 2H), 7.53 – 7.46 (m, 2H), 7.43 – 7.39 (m, 2H), 7.36 – 7.30 (m, 2H), 7.20 – 7.10 (m, 1H), 3.70 (d, *J* = 13.8 Hz, 1H), 3.22 (d, *J* = 13.8 Hz, 1H), 3.01 (s, 3H), 1.96 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 168.3, 141.8, 139.5, 136.5, 131.7, 129.1, 127.0, 125.3, 120.2, 73.5, 47.6, 44.4, 30.4.

IR (ATR): ν = 3354, 2986, 2927, 1678, 1598, 1529, 1303, 1149, 758, 692 cm⁻¹.

HRMS (ESI) calcd. for C₁₇H₁₉ClNO₃S [M+H]⁺: 352.0769, found: 352.0763.



4-(2-chloro-2-methyl-3-oxo-3-(phenylamino)propyl)-N-phenylbenzamide (41)

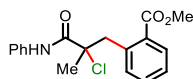
According to the general procedure B, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). (0.1 mmol scale, 17.7 mg, 45%). R_f = 0.2 (PE/EA = 5:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.84 (s, 1H), 7.80 – 7.74 (m, 2H), 7.65 – 7.57 (m, 2H), 7.46 – 7.27 (m, 8H), 7.19 – 7.10 (m, 2H), 3.66 (d, *J* = 13.8 Hz, 1H), 3.20 (d, *J* = 13.8 Hz, 1H), 1.95 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 168.7, 165.4, 139.5, 137.9, 136.7, 133.9, 131.1, 129.1, 129.0, 126.8, 125.2, 124.5, 120.3, 120.2, 73.8, 47.9, 30.2.

IR (ATR): ν = 3350, 3323, 2986, 1674, 1578, 1509, 1333, 1145, 744, 687 cm⁻¹.

HRMS (ESI) calcd. for C₂₃H₂₂ClN₂O₂ [M+H]⁺: 393.1364, found: 393.1358.



methyl 2-(2-chloro-2-methyl-3-oxo-3-(phenylamino)propyl)benzoate (42)

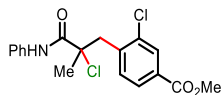
According to the general procedure B, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 16.6 mg, 50%). R_f = 0.4 (PE/EA = 10:1). White solid. **m.p.** 78.4-80.4 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.88 – 7.81 (m, 1H), 7.43 – 7.39 (m, 2H), 7.38 – 7.34 (m, 1H), 7.34 – 7.28 (m, 4H), 7.16 – 7.10 (m, 1H), 4.10 (d, *J* = 14.1 Hz, 1H), 3.86 (s, 3H), 3.84 (d, *J* = 14.1 Hz, 1H), 1.91 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 168.9, 168.7, 136.9, 136.1, 132.5, 132.0, 131.3, 130.3, 128.9, 127.3, 124.9, 120.2, 74.4, 52.1, 43.6, 29.8.

IR (ATR): ν = 3399, 2987, 2950, 1720, 1682, 1527, 1442, 1296, 1083, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₈H₁₉ClNO₃ [M+H]⁺: 332.1048, found: 332.1041.



methyl 3-chloro-4-(2-chloro-2-methyl-3-oxo-3-(phenylamino)propyl)benzoate (43)

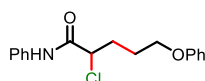
According to the general procedure B, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 23.2 mg, 63%, r.r. > 20:1). R_f = 0.5 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.06 (d, *J* = 1.8 Hz, 1H), 7.81 (m, 1H), 7.50 – 7.47 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.21 – 7.13 (m, 1H), 3.90 (s, 3H), 3.72 (d, *J* = 14.3 Hz, 1H), 3.64 (d, *J* = 14.2 Hz, 1H), 1.95 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 168.7, 165.7, 138.6, 136.8, 135.9, 132.0, 130.8, 130.7, 129.1, 127.4, 125.2, 120.2, 73.5, 52.4, 43.7, 29.9.

IR (ATR): ν = 3399, 2973, 2934, 1698, 1656, 1545, 1434, 1256, 1083, 692 cm⁻¹.

HRMS (ESI) calcd. for C₁₈H₁₈Cl₂NO₃ [M+H]⁺: 366.0658, found: 366.0652.



2-chloro-5-phenoxy-N-phenylpentanamide (44)

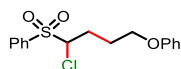
According to the modified procedure A, loading of **cat.B** was increased to 5 mol%. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 17.0 mg, 56%). R_f = 0.4 (PE/EA = 5:1). White solid. **m.p.** 103.7-105.2 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.59 – 7.52 (m, 2H), 7.40 – 7.33 (m, 2H), 7.31 – 7.26 (m, 2H), 7.20 – 7.13 (m, 1H), 6.98 – 6.93 (m, 1H), 6.92 – 6.85 (m, 2H), 4.57 (dd, *J* = 8.3, 4.5 Hz, 1H), 4.08 – 3.95 (m, 2H), 2.54 – 2.39 (m, 1H), 2.30 – 2.18 (m, 1H), 2.13 – 1.97 (m, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 166.6, 158.7, 136.8, 129.4, 129.1, 125.1, 120.8, 120.1, 114.4, 66.8, 61.1, 32.6, 25.9.

IR (ATR): ν = 3293, 2957, 2928, 1669, 1601, 1542, 1445, 1313, 754, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₇H₁₉ClNO₂ [M+H]⁺: 304.1099, found: 304.1091.



(4-chloro-4-(phenylsulfonyl)butoxy)benzene (45)

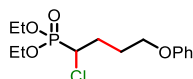
According to the general procedure A for 24 h, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 18.8 mg, 58%). R_f = 0.4 (PE/EA = 5:1). White solid. **m.p.** 115.3–117.5 °C.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.90 (m, 2H), 7.74 – 7.66 (m, 1H), 7.61 – 7.53 (m, 2H), 7.31 – 7.23 (m, 2H), 6.97 – 6.90 (m, 1H), 6.87 – 6.79 (m, 2H), 4.75 (dd, J = 10.3, 3.1 Hz, 1H), 4.04 – 3.93 (m, 2H), 2.69 – 2.61 (m, 1H), 2.17 – 2.07 (m, 1H), 2.05 – 1.93 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.5, 135.1, 134.5, 130.0, 129.5, 129.1, 120.9, 114.4, 74.6, 66.4, 28.1, 25.8.

IR (ATR): ν = 3064, 2928, 1599, 1586, 1496, 1447, 1243, 1151, 688, 587 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{18}\text{ClO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 325.0660, found: 325.0657.



diethyl (1-chloro-4-phenoxybutyl)phosphonate (46)

According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). (0.1 mmol scale, 21.7 mg, 68%). R_f = 0.2 (PE/EA = 5:1). Colorless oil.

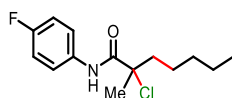
^1H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 6.98 – 6.92 (m, 1H), 6.91 – 6.85 (m, 2H), 4.28 – 4.18 (m, 4H), 4.06 – 3.98 (m, 2H), 3.96 – 3.90 (m, 1H), 2.40 – 2.29 (m, 1H), 2.22 – 2.12 (m, 1H), 2.07 – 1.89 (m, 2H), 1.36 (t, J = 7.0 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.7, 129.4, 120.7, 114.4, 66.6, 63.7 (d, J = 6.9 Hz), 63.3 (d, J = 6.9 Hz), 52.1 (d, J = 160.3 Hz), 29.2, 26.3 (d, J = 12.3 Hz), 16.5 (d, J = 4.3 Hz), 16.4 (d, J = 4.3 Hz).

^{31}P NMR (202 MHz, Chloroform-*d*) δ 20.2.

IR (ATR): ν = 2980, 2931, 1600, 1497, 1391, 1243, 1020, 967, 753, 692 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{23}\text{ClO}_4\text{P}$ $[\text{M}+\text{H}]^+$: 321.1017, found: 321.1008.



2-chloro-N-(4-fluorophenyl)-2-methylheptanamide (47)

According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 16.4 mg, 60%). R_f = 0.6 (PE/EA = 10:1). Colorless oil.

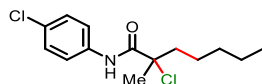
^1H NMR (500 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.56 – 7.48 (m, 2H), 7.04 (t, J = 8.6 Hz, 2H), 2.28 – 2.16 (m, 1H), 1.95 – 1.85 (m, 1H), 1.84 (s, 3H), 1.59 – 1.51 (m, 1H), 1.44 – 1.28 (m, 5H), 0.92 – 0.85 (m, 3H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -117.1.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.7, 159.7 (d, J = 244.5 Hz), 133.1 (d, J = 3.0 Hz), 121.9 (d, J = 7.7 Hz), 115.7 (d, J = 22.6 Hz), 74.9, 42.9, 31.4, 29.9, 24.6, 22.4, 13.9.

IR (ATR): ν = 3404, 2956, 2931, 1673, 1510, 1408, 1213, 1158, 832, 516 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{20}\text{ClFNO}$ $[\text{M}+\text{H}]^+$: 272.1212, found: 272.1203.



2-chloro-*N*-(4-chlorophenyl)-2-methylheptanamide (48)

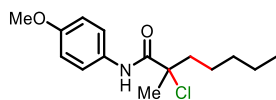
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 17.8 mg, 62%). *R*_f = 0.6 (PE/EA = 10:1). White solid. **m.p.** 40.8–42.1 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.55 – 7.48 (m, 2H), 7.37 – 7.28 (m, 2H), 2.29 – 2.16 (m, 1H), 1.94 – 1.82 (m, 4H), 1.58 – 1.51 (m, 1H), 1.40 – 1.28 (m, 5H), 0.88 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.8, 135.7, 129.9, 129.1, 121.2, 74.9, 42.9, 31.4, 29.9, 24.6, 22.4, 13.9.

IR (ATR): ν = 3399, 2955, 2928, 1678, 1593, 1519, 1493, 1091, 826, 508 cm⁻¹.

HRMS (ESI) calcd. for C₁₄H₂₀Cl₂NO [M+H]⁺: 288.0916, found: 288.0906.



2-chloro-*N*-(4-methoxyphenyl)-2-methylheptanamide (49)

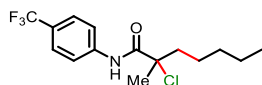
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1). (0.1 mmol scale, 19.5 mg, 69%). *R*_f = 0.5 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 7.49 – 7.41 (m, 2H), 6.93 – 6.83 (m, 2H), 3.80 (s, 3H), 2.29 – 2.16 (m, 1H), 1.95 – 1.82 (m, 4H), 1.59 – 1.51 (m, 1H), 1.42 – 1.28 (m, 5H), 0.91 – 0.83 (m, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.5, 156.8, 130.3, 121.8, 114.2, 75.0, 55.5, 43.0, 31.4, 30.0, 24.6, 22.4, 14.0.

IR (ATR): ν = 3405, 2954, 2931, 1671, 1512, 1301, 1247, 1036, 827, 523 cm⁻¹.

HRMS (ESI) calcd. for C₁₅H₂₃ClNO₂ [M+H]⁺: 284.1412, found: 284.1403.



2-chloro-2-methyl-*N*-(4-(trifluoromethyl)phenyl)heptanamide (50)

According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1). (0.1 mmol scale, 21.1 mg, 66%). *R*_f = 0.6 (PE/EA = 10:1). White solid. **m.p.** 58.7–61.2 °C.

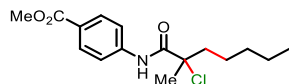
¹H NMR (500 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 2.29 – 2.17 (m, 1H), 1.96 – 1.82 (m, 4H), 1.59 – 1.51 (m, 1H), 1.42 – 1.27 (m, 5H), 0.93 – 0.85 (m, 3H).

¹⁹F NMR (471 MHz, Chloroform-*d*) δ -62.2.

¹³C NMR (126 MHz, Chloroform-*d*) δ 170.1, 140.1, 126.7 (q, *J* = 32.8 Hz), 126.3 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 271.6 Hz), 119.6, 74.8, 42.9, 31.4, 29.9, 24.6, 22.4, 13.9.

IR (ATR): ν = 3400, 2932, 2864, 1684, 1527, 1409, 1322, 1114, 1067, 841 cm⁻¹.

HRMS (ESI) calcd. for C₁₅H₂₀ClF₃NO [M+H]⁺: 322.1180, found: 322.1173.



methyl 4-(2-chloro-2-methylheptanamido)benzoate (**51**)

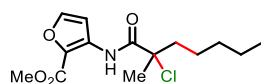
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 19.1 mg, 61%). *R*_f = 0.5 (PE/EA = 10:1). White solid. **m.p.** 56.1–57.3 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H), 2.26 – 2.17 (m, 1H), 1.94 – 1.83 (m, 4H), 1.59 – 1.50 (m, 1H), 1.42 – 1.28 (m, 5H), 0.90 – 0.83 (m, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 170.0, 166.4, 141.2, 130.8, 126.3, 119.1, 74.8, 52.0, 42.9, 31.4, 29.8, 24.6, 22.4, 13.9.

IR (ATR): ν = 3395, 2953, 2930, 1720, 1519, 1407, 1276, 1176, 1109, 770 cm⁻¹.

HRMS (ESI) calcd. for C₁₆H₂₃ClNO₃ [M+H]⁺: 312.1361, found: 312.1354.



methyl 3-(2-chloro-2-methylheptanamido)furan-2-carboxylate (**52**)

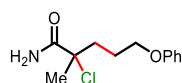
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 13.3 mg, 44%). *R*_f = 0.7 (PE/EA = 5:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 10.49 – 10.19 (m, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 3.96 (s, 3H), 2.28 – 2.13 (m, 1H), 1.96 – 1.87 (m, 1H), 1.83 (s, 3H), 1.57 – 1.50 (m, 1H), 1.41 – 1.29 (m, 5H), 0.87 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 170.3, 160.3, 145.7, 134.4, 129.7, 106.9, 73.7, 52.0, 42.9, 31.4, 29.7, 24.5, 22.4, 13.9.

IR (ATR): ν = 3332, 2956, 2931, 1683, 1614, 1488, 1307, 1204, 1090, 884 cm⁻¹.

HRMS (ESI) calcd. for C₁₄H₂₁ClNO₄ [M+H]⁺: 302.1154, found: 302.1148.



2-chloro-2-methyl-5-phenoxy-pentanamide (**53**)

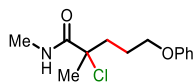
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1). (0.1 mmol scale, 17.2 mg, 71%). *R*_f = 0.1 (PE/EA = 5:1). White solid. **m.p.** 59.6–61.3 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 6.97 – 6.91 (m, 1H), 6.91 – 6.86 (m, 2H), 6.77 (s, 1H), 6.05 (s, 1H), 4.07 – 3.91 (m, 2H), 2.39 – 2.26 (m, 1H), 2.12 – 2.01 (m, 2H), 1.92 – 1.85 (m, 1H), 1.82 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 174.3, 158.8, 129.4, 120.7, 114.4, 73.0, 67.1, 39.3, 29.9, 25.1.

IR (ATR): ν = 3475, 3337, 2960, 2931, 1671, 1496, 1240, 1030, 752, 691 cm⁻¹.

HRMS (ESI) calcd. for C₁₂H₁₇ClNO₂ [M+H]⁺: 242.0942, found: 242.0936.



2-chloro-N,2-dimethyl-5-phenoxy-pentanamide (**54**)

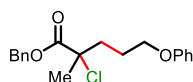
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 4:1). (0.1 mmol scale, 19.0 mg, 74%). R_f = 0.2 (PE/EA = 5:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 6.98 – 6.83 (m, 4H), 4.01 – 3.88 (m, 2H), 2.86 (d, *J* = 4.8 Hz, 3H), 2.37 – 2.28 (m, 1H), 2.09 – 1.96 (m, 2H), 1.87 – 1.73 (m, 4H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 171.8, 158.8, 129.4, 120.6, 114.4, 74.3, 67.1, 39.4, 30.1, 26.9, 25.1.

IR (ATR): ν = 3365, 2931, 2875, 1653, 1525, 1241, 1172, 1038, 753, 692 cm⁻¹.

HRMS (ESI) calcd. for C₁₃H₁₉ClNO₂ [M+H]⁺: 256.1099, found: 256.1089.



benzyl 2-chloro-2-methyl-5-phenoxy-pentanoate (**55**)

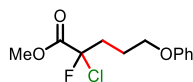
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 13.5 mg, 41%). R_f = 0.5 (PE/EA = 20:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 5H), 7.31 – 7.26 (m, 2H), 6.98 – 6.92 (m, 1H), 6.89 – 6.82 (m, 2H), 5.21 (s, 2H), 3.95 (t, *J* = 6.2 Hz, 2H), 2.28 (ddd, *J* = 14.0, 10.3, 6.1 Hz, 1H), 2.19 (ddd, *J* = 13.9, 10.4, 5.8 Hz, 1H), 1.94 – 1.85 (m, 2H), 1.81 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 171.0, 158.8, 135.3, 129.4, 128.6, 128.4, 128.0, 120.7, 114.4, 68.7, 67.7, 67.1, 38.8, 27.8, 25.0.

IR (ATR): ν = 2965, 2935, 1738, 1600, 1497, 1456, 1244, 1048, 753, 693 cm⁻¹.

HRMS (FI) calcd. for C₁₉H₂₁ClO₃ [M]⁺: 332.1174, found: 332.1171.



methyl 2-chloro-2-fluoro-5-phenoxy-pentanoate (**56**)

According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 11.0 mg, 42%). R_f = 0.4 (PE/EA = 20:1). Colorless oil.

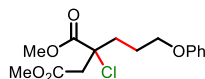
¹H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 6.98 – 6.92 (m, 1H), 6.91 – 6.86 (m, 2H), 4.02 (t, *J* = 6.0 Hz, 2H), 3.89 (s, 3H), 2.60 – 2.48 (m, 2H), 2.18 – 2.05 (m, 1H), 2.03 – 1.92 (m, 1H).

¹⁹F NMR (471 MHz, Chloroform-*d*) δ -116.6.

¹³C NMR (126 MHz, Chloroform-*d*) δ 166.0, 158.6, 129.5, 120.9, 114.4, 105.5 (d, *J* = 255.5 Hz), 66.3, 53.8, 37.2 (d, *J* = 21.6 Hz), 23.4 (d, *J* = 2.4 Hz).

IR (ATR): ν = 2957, 2926, 1762, 1600, 1497, 1244, 1035, 961, 755, 692 cm⁻¹.

HRMS (FI) calcd. for C₁₂H₁₄ClFO₃ [M]⁺: 260.0610, found: 260.0607.



dimethyl 2-chloro-2-(3-phenoxypropyl)succinate (57)

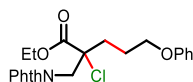
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1). (0.1 mmol scale, 26.0 mg, 83%). R_f = 0.2 (PE/EA = 20:1). Colorless oil.

^1H NMR (500 MHz, Chloroform- d) δ 7.31 – 7.25 (m, 2H), 6.98 – 6.92 (m, 1H), 6.90 – 6.84 (m, 2H), 3.98 (t, J = 6.1 Hz, 2H), 3.82 (s, 3H), 3.70 (s, 3H), 3.22 (d, J = 16.5 Hz, 1H), 3.11 (d, J = 16.5 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.27 – 2.17 (m, 1H), 2.06 – 1.95 (m, 1H), 1.94 – 1.83 (m, 1H).

^{13}C NMR (126 MHz, Chloroform- d) δ 170.4, 169.3, 158.7, 129.4, 120.8, 114.4, 68.7, 66.9, 53.4, 52.0, 45.0, 37.0, 24.4.

IR (ATR): ν = 2954, 1741, 1600, 1497, 1473, 1355, 1244, 1046, 755, 693 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{20}\text{ClO}_5$ $[\text{M}+\text{H}]^+$: 315.0994, found: 315.0990.



ethyl 2-chloro-2-((1,3-dioxoisindolin-2-yl)methyl)-5-phenoxy-pentanoate (58)

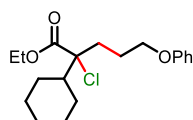
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1). (0.1 mmol scale, 30.3 mg, 73%). R_f = 0.3 (PE/EA = 5:1). Colorless oil.

^1H NMR (500 MHz, Chloroform- d) δ 7.89 – 7.83 (m, 2H), 7.79 – 7.70 (m, 2H), 7.30 – 7.19 (m, 2H), 6.92 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.1 Hz, 2H), 4.32 – 4.24 (m, 4H), 3.99 (t, J = 6.1 Hz, 2H), 2.46 – 2.35 (m, 1H), 2.20 – 2.05 (m, 2H), 1.94 – 1.82 (m, 1H), 1.32 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform- d) δ 168.9, 167.8, 158.7, 134.2, 131.7, 129.4, 123.6, 120.6, 114.4, 72.1, 66.9, 63.1, 45.9, 35.8, 24.8, 13.9.

IR (ATR): ν = 2979, 2937, 1778, 1718, 1422, 1390, 1243, 1029, 755, 692 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{23}\text{ClNO}_5$ $[\text{M}+\text{H}]^+$: 416.1259, found: 416.1253.



ethyl 2-chloro-2-cyclohexyl-5-phenoxy-pentanoate (59)

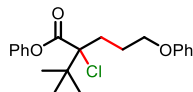
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 24.3 mg, 72%). R_f = 0.4 (PE/EA = 20:1). Colorless oil.

^1H NMR (500 MHz, Chloroform- d) δ 7.31 – 7.26 (m, 2H), 6.97 – 6.91 (m, 1H), 6.91 – 6.85 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 4.06 – 3.90 (m, 2H), 2.26 – 2.17 (m, 1H), 2.15 – 2.02 (m, 2H), 2.02 – 1.94 (m, 1H), 1.89 – 1.75 (m, 3H), 1.75 – 1.65 (m, 2H), 1.59 – 1.51 (m, 1H), 1.42 – 1.27 (m, 5H), 1.26 – 1.17 (m, 3H).

^{13}C NMR (126 MHz, Chloroform- d) δ 170.8, 158.8, 129.4, 120.6, 114.4, 80.0, 67.3, 62.1, 47.3, 36.0, 28.4, 27.0, 26.2, 26.1, 26.1, 25.1, 14.2.

IR (ATR): ν = 2971, 2932, 2857, 1749, 1718, 1497, 1245, 1184, 754, 692 cm^{-1} .

HRMS (FI) calcd. for $\text{C}_{19}\text{H}_{27}\text{ClO}_3$ $[\text{M}]^+$: 338.1643, found: 338.1638.



phenyl 2-(*tert*-butyl)-2-chloro-5-phenoxy-pentanoate (60)

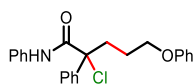
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 31.3 mg, 87%). R_f = 0.4 (PE/EA = 20:1). Colorless oil.

^1H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.37 (m, 2H), 7.33 – 7.24 (m, 3H), 7.12 – 7.07 (m, 2H), 6.98 – 6.94 (m, 1H), 6.93 – 6.90 (m, 2H), 4.12 – 4.00 (m, 2H), 2.67 – 2.58 (m, 1H), 2.36 – 2.22 (m, 1H), 2.17 – 2.05 (m, 1H), 1.98 – 1.84 (m, 1H), 1.28 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.9, 158.8, 150.6, 129.5, 129.4, 126.2, 121.3, 120.7, 114.5, 83.7, 67.4, 40.0, 33.2, 26.7, 26.1.

IR (ATR): ν = 2975, 1765, 1742, 1600, 1493, 1243, 1187, 1165, 752, 722 cm^{-1} .

HRMS (DART) calcd. for $\text{C}_{21}\text{H}_{26}\text{ClO}_3$ $[\text{M}+\text{H}]^+$: 361.1565, found: 361.1565.



2-chloro-5-phenoxy-N,2-diphenylpentanamide (61)

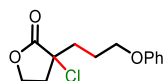
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 12.6 mg, 33%). R_f = 0.6 (PE/EA = 10:1). Colorless oil.

^1H NMR (500 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.68 – 7.61 (m, 2H), 7.56 – 7.51 (m, 2H), 7.42 – 7.33 (m, 5H), 7.29 – 7.25 (m, 2H), 7.19 – 7.12 (m, 1H), 6.96 – 6.91 (m, 1H), 6.89 – 6.85 (m, 2H), 4.08 – 3.94 (m, 2H), 2.83 – 2.73 (m, 1H), 2.69 – 2.57 (m, 1H), 2.07 – 1.94 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.8, 158.9, 140.1, 137.1, 129.4, 129.1, 128.7, 128.7, 126.3, 125.0, 120.7, 120.0, 114.5, 78.2, 67.2, 38.7, 25.3.

IR (ATR): ν = 3393, 3028, 2926, 1671, 1598, 1525, 1495, 1241, 752, 691 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{23}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$: 380.1412, found: 380.1406.



3-chloro-3-(3-phenoxypropyl)dihydrofuran-2(3H)-one (62)

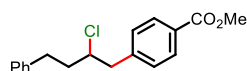
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1). (0.1 mmol scale, 16.0 mg, 63%). R_f = 0.2 (PE/EA = 20:1). White solid. **m.p.** 57.5-59.4 $^{\circ}\text{C}$.

^1H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 2H), 6.98 – 6.93 (m, 1H), 6.92 – 6.85 (m, 2H), 4.53 – 4.45 (m, 1H), 4.43 – 4.37 (m, 1H), 4.10 – 3.98 (m, 2H), 2.62 – 2.55 (m, 1H), 2.54 – 2.45 (m, 1H), 2.41 – 2.31 (m, 1H), 2.25 – 2.16 (m, 1H), 2.15 – 2.06 (m, 1H), 1.97 – 1.86 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.6, 158.6, 129.5, 120.9, 114.4, 66.8, 65.7, 65.5, 37.9, 34.7, 24.6.

IR (ATR): ν = 2924, 1778, 1600, 1497, 1293, 1175, 1080, 1022, 755, 692 cm^{-1} .

HRMS (FI) calcd. for $\text{C}_{13}\text{H}_{15}\text{ClO}_3$ $[\text{M}]^+$: 254.0704, found: 254.0702.



methyl 4-(2-chloro-4-phenylbutyl)benzoate (63)

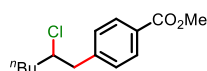
According to the general procedure C, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 15.0 mg, 50%). R_f = 0.5 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.92 (m, 2H), 7.34 – 7.26 (m, 3H), 7.26 – 7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 7.19 – 7.14 (m, 2H), 4.13 – 4.05 (m, 1H), 3.91 (s, 3H), 3.15 – 3.04 (m, 2H), 2.97 – 2.89 (m, 1H), 2.82 – 2.71 (m, 1H), 2.14 – 1.94 (m, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 166.9, 143.0, 140.7, 129.7, 129.4, 128.7, 128.5, 128.5, 126.1, 62.2, 52.0, 44.8, 39.4, 32.6.

IR (ATR): ν = 2952, 2924, 1719, 1435, 1279, 1180, 1105, 1067, 751, 701 cm⁻¹.

HRMS (FI) calcd. for C₁₈H₁₉ClO₂ [M]⁺: 302.1068, found: 302.1062.



methyl 4-(2-chlorohexyl)benzoate (64)

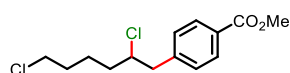
According to the general procedure C, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 11.5 mg, 45%). R_f = 0.5 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.04 – 7.93 (m, 2H), 7.34 – 7.27 (m, 2H), 4.15 – 4.04 (m, 1H), 3.91 (s, 3H), 3.17 – 3.01 (m, 2H), 1.82 – 1.66 (m, 2H), 1.59 – 1.51 (m, 1H), 1.48 – 1.38 (m, 1H), 1.37 – 1.25 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 167.0, 143.4, 129.7, 129.4, 128.7, 63.3, 52.0, 44.8, 37.6, 28.6, 22.1, 13.9.

IR (ATR): ν = 2954, 2931, 2861, 1719, 1435, 1275, 1180, 1108, 762, 706 cm⁻¹.

HRMS (FI) calcd. for C₁₄H₁₉ClO₂ [M]⁺: 254.1068, found: 254.1065.



methyl 4-(2,6-dichlorohexyl)benzoate (65)

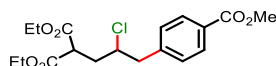
According to the general procedure C, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 16.3 mg, 56%). R_f = 0.5 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.96 (m, 2H), 7.34 – 7.27 (m, 2H), 4.10 (m, 1H), 3.91 (s, 3H), 3.53 (t, *J* = 6.2 Hz, 2H), 3.18 – 3.03 (m, 2H), 1.85 – 1.70 (m, 5H), 1.61 – 1.54 (m, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 166.9, 143.0, 129.7, 129.4, 128.8, 62.8, 52.1, 44.8, 44.6, 37.0, 31.9, 23.8.

IR (ATR): ν = 2952, 1719, 1611, 1435, 1278, 1180, 1105, 1021, 764, 707 cm⁻¹.

HRMS (FI) calcd. for C₁₄H₁₈Cl₂O₂ [M]⁺: 288.0678, found: 288.0676.



diethyl 2-(2-chloro-3-(4-(methoxycarbonyl)phenyl)propyl)malonate (66)

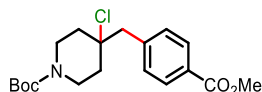
According to the general procedure C, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 23.2 mg, 63%). R_f = 0.1 (PE/EA = 20:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 7.96 (m, 2H), 7.34 – 7.27 (m, 2H), 4.23 – 4.14 (m, 5H), 3.90 (s, 3H), 3.76 (dd, *J* = 10.4, 4.1 Hz, 1H), 3.20 – 3.06 (m, 2H), 2.53 – 2.41 (m, 1H), 2.22 – 2.09 (m, 1H), 1.30 – 1.22 (m, 6H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 168.9, 168.6, 166.9, 142.3, 129.7, 129.4, 128.9, 61.7, 61.6, 60.3, 52.0, 49.3, 44.9, 36.8, 14.0, 14.0.

IR (ATR): ν = 2984, 1722, 1611, 1435, 1278, 1180, 1105, 1021, 859, 765 cm⁻¹.

HRMS (ESI) calcd. for C₁₈H₂₄ClO₆ [M+H]⁺: 371.1256, found: 371.1248.



tert-butyl 4-chloro-4-(4-(methoxycarbonyl)benzyl)piperidine-1-carboxylate (67)

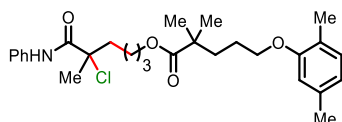
According to the general procedure C, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). (0.1 mmol scale, 19.5 mg, 53%). R_f = 0.6 (PE/EA = 5:1). White solid. **m.p.** 93.0–94.9 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 2H), 7.41 – 7.30 (m, 2H), 4.12 – 3.88 (m, 5H), 3.22 – 3.03 (m, 4H), 1.89 – 1.71 (m, 4H), 1.44 (s, 9H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 166.9, 154.6, 140.5, 131.1, 129.2, 129.0, 79.7, 71.9, 71.9, 52.1, 51.2, 38.5, 28.4.

IR (ATR): ν = 2975, 2952, 2921, 1721, 1689, 1417, 1278, 1104, 765, 710 cm⁻¹.

HRMS (ESI) calcd. for C₁₉H₂₇ClNO₄ [M+H]⁺: 368.1623, found: 368.1620.



5-chloro-5-methyl-6-oxo-6-(phenylamino)hexyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (68)

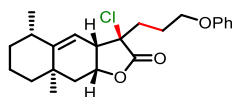
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 31.0 mg, 64%). R_f = 0.7 (PE/EA = 10:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.57 – 7.50 (m, 2H), 7.40 – 7.30 (m, 2H), 7.19 – 7.11 (m, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.71 – 6.63 (m, 1H), 6.60 (d, *J* = 1.5 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.89 (t, *J* = 5.6 Hz, 2H), 2.31 (s, 3H), 2.29 – 2.24 (m, 1H), 2.17 (s, 3H), 1.99 – 1.90 (m, 1H), 1.86 (s, 3H), 1.76 – 1.63 (m, 7H), 1.52 – 1.41 (m, 1H), 1.19 (s, 6H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 177.7, 169.3, 156.9, 137.0, 136.4, 130.2, 129.0, 125.0, 123.5, 120.6, 120.0, 111.9, 74.5, 67.9, 63.8, 42.4, 42.0, 37.0, 30.0, 28.3, 25.1, 25.1, 21.5, 21.4, 15.8.

IR (ATR): ν = 2954, 2924, 1725, 1684, 1528, 1509, 1313, 1130, 755, 692 cm⁻¹.

HRMS (ESI) calcd. for C₂₈H₃₉ClNO₄ [M+H]⁺: 488.2562, found: 488.2551.



(3R,3aS,5S,8aR,9aR)-3-chloro-5,8a-dimethyl-3-(3-phenoxypropyl)-3a,5,6,7,8,8a,9,9a-octahydronaphtho[2,3-b]furan-2(3H)-one (69)

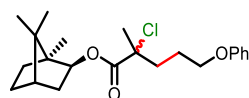
According to the general procedure A for 12 h, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 26.8 mg, 69%, d.r. > 20:1). R_f = 0.4 (PE/EA = 20:1). White solid. **m.p.** 70.0–74.8 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.00 – 6.93 (m, 1H), 6.92 – 6.87 (m, 2H), 5.21 (d, *J* = 3.2 Hz, 1H), 5.13 – 5.06 (m, 1H), 4.23 – 4.13 (m, 1H), 4.06 – 3.95 (m, 1H), 3.27 – 3.12 (m, 1H), 2.55 – 2.43 (m, 1H), 2.38 – 2.23 (m, 2H), 2.21 – 2.11 (m, 2H), 2.05 – 1.95 (m, 1H), 1.89 – 1.77 (m, 1H), 1.67 – 1.53 (m, 4H), 1.49 – 1.42 (m, 1H), 1.24 (s, 3H), 1.18 – 1.07 (m, 4H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 173.1, 158.6, 153.3, 129.5, 120.8, 114.3, 113.3, 76.3, 71.6, 66.8, 47.7, 42.4, 42.2, 38.6, 33.1, 32.8, 30.6, 28.4, 24.3, 22.7, 16.7.

IR (ATR): ν = 2929, 1776, 1599, 1497, 1244, 1184, 994, 955, 754, 692 cm⁻¹.

HRMS (ESI) calcd. for C₂₃H₃₀ClO₃ [M+H]⁺: 389.1878, found: 389.1871.



1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-chloro-2-methyl-5-phenoxy-pentanoate (70)

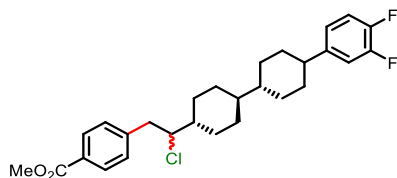
According to the general procedure A, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 24.7 mg, 65%, d.r. = 1:1). R_f = 0.4 (PE/EA = 20:1). Colorless oil.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 6.96 – 6.92 (m, 1H), 6.90 – 6.85 (m, 2H), 4.74 – 4.67 (m, 1H), 3.98 (t, *J* = 6.2 Hz, 2H), 2.28 – 2.12 (m, 2H), 1.95 – 1.80 (m, 3H), 1.79 – 1.67 (m, 6H), 1.62 – 1.53 (m, 1H), 1.19 – 1.06 (m, 2H), 1.02 (s, 3H), 0.90 (d, *J* = 2.3 Hz, 3H), 0.86 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 170.5, 170.5, 158.8, 129.4, 120.7, 114.4, 82.9, 82.9, 69.0, 68.8, 67.2, 67.1, 49.0, 48.9, 47.0, 45.0, 38.8, 38.6, 33.6, 33.6, 27.8, 27.7, 27.0, 25.1, 25.1, 20.1, 19.9, 11.5, 11.4.

IR (ATR): ν = 2957, 2883, 1734, 1558, 1541, 1498, 1245, 1051, 753, 691 cm⁻¹.

HRMS (DART) calcd. for C₂₂H₃₅ClNO₃ [M+NH₄]⁺: 396.2300, found: 396.2296.



methyl 4-(2-chloro-2-((1R,4R)-4'-(3,4-difluorophenyl)-[1,1'-bi(cyclohexan)]-4-yl)ethyl)benzoate (71)

According to the general procedure C, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). (0.1 mmol scale, 26.8 mg, 57%, d.r. = 1.4:1). R_f = 0.5 (PE/EA = 20:1). White solid. **m.p.** 110.0–113.4 °C.

¹H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.96 (m, 2H), 7.34 – 7.27 (m, 2H), 7.09 – 7.01 (m, 1H), 7.01 – 6.96 (m, 1H), 6.92 – 6.86 (m, 1H), 4.09 – 3.99 (m, 1H), 3.91 (s, 3H), 3.16 (dd, *J* = 14.2, 4.9 Hz,

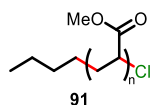
1H), 3.01 (dd, $J = 14.2, 9.2$ Hz, 1H), 2.45 – 2.36 (m, 1H), 2.01 – 1.77 (m, 9H), 1.41 – 1.24 (m, 5H), 1.21 – 1.04 (m, 5H).

^{19}F NMR (376 MHz, Chloroform- d) δ -138.67 (d, $J = 21.1$ Hz), -142.53 (d, $J = 21.4$ Hz)

^{13}C NMR (126 MHz, Chloroform- d) δ 167.0, 150.1 (dd, $J = 247.0, 12.6$ Hz), 148.5 (dd, $J = 245.0, 12.9$ Hz), 144.7 (q, $J = 5.0$ Hz), 144.0, 129.7, 129.2, 128.6, 122.5 (dd, $J = 6.0, 3.2$ Hz), 116.7 (d, $J = 16.8$ Hz), 115.4 (d, $J = 16.7$ Hz), 68.9, 52.0, 43.8, 43.6, 42.9, 42.5, 41.9, 34.5, 30.4, 30.1, 30.1, 29.5, 29.4, 27.6.

IR (ATR): $\nu = 2921, 2852, 1716, 1517, 1276, 1105, 1019, 818, 737, 704\text{ cm}^{-1}$.

HRMS (FI) calcd. for $\text{C}_{28}\text{H}_{33}\text{ClF}_2\text{O}_2$ $[\text{M}]^+$: 474.2132, found: 474.2133.



α -*n*-butyl-poly(methyl acrylate) (91)

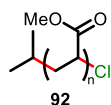
According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** = 98%, 91.4 mg).

^1H NMR (500 MHz, Chloroform- d) δ 4.30 – 4.18 (m, 1H), 3.67 – 3.49 (m, 238H), 2.40 – 2.15 (m, 79H), 1.98 – 1.32 (m, 161H).

^{13}C NMR (126 MHz, Chloroform- d) δ [174.9, 174.8], [51.8, 51.7], [41.3, 41.2, 41.1], [35.6, 35.1, 34.9, 34.2], 31.5, 26.7, 22.3, 13.9.

IR (ATR): $\nu = 2954, 1730, 1436, 1266, 1196, 1161, 1118, 827, 732, 702\text{ cm}^{-1}$.

M_n - 4.3 kDa, **$\bar{D}$** - 1.51



α -*iso*-propyl-poly(methyl acrylate) (92)

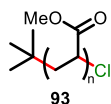
According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** = 97%, 93.1 mg).

^1H NMR (500 MHz, Chloroform- d) δ 4.29 – 4.16 (m, 1H), 3.61 (m, 240H), 2.43 – 2.17 (m, 80H), 1.99 – 1.33 (m, 165H).

^{13}C NMR (126 MHz, Chloroform- d) δ [174.9, 174.8], [51.7, 51.6], [41.3, 41.2, 41.0], [35.9, 35.0, 34.8, 34.2], 25.8, 22.1.

IR (ATR): $\nu = 2954, 1728, 1436, 1266, 1195, 1158, 1119, 827, 734, 702\text{ cm}^{-1}$.

M_n - 4.7 kDa, **$\bar{D}$** - 1.64



α -*tert*-butyl-poly(methyl acrylate) (93)

According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** = 98%, 103.9 mg).

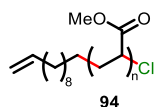
^1H NMR (500 MHz, Chloroform- d) δ 4.29 – 4.16 (m, 1H), 3.68 – 3.51 (m, 241H), 2.39 – 2.13 (m, 81H), 1.96 – 1.31 (m, 162H), 0.78 – 0.76 (m, 9H).

^{13}C NMR (126 MHz, Chloroform- d) δ [174.9, 174.8], [51.7, 51.6], [41.2, 41.2, 41.0], [35.9, 35.0, 34.8,

34.2], 30.7, 29.2.

IR (ATR): $\nu = 2953, 1727, 1436, 1380, 1195, 1157, 1119, 827, 734, 702 \text{ cm}^{-1}$.

Mn - 3.8 kDa, **D** - 1.57



α -undec-10-en-1-yl-poly(methyl acrylate) (94)

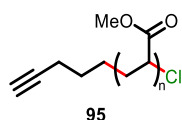
According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** > 98%, 90.5 mg).

^1H NMR (500 MHz, Chloroform-*d*) δ 5.78 – 5.67 (m, 1H), 4.94 – 4.81 (m, 2H), 4.37 – 4.07 (m, 1H), 3.59 (m, 360H), 2.42 – 2.12 (m, 120H), 1.97 – 1.30 (m, 268H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ [174.9, 174.9], 139.2, 114.0, [51.8, 51.7], [45.1, 41.3, 41.2], 41.1, [36.0, 35.1, 34.9, 34.2], 32.6, 29.5, 29.4, 29.1, 28.9, 28.8, 26.8, 22.6.

IR (ATR): $\nu = 2952, 1728, 1436, 1379, 1194, 1157, 974, 827, 734, 703 \text{ cm}^{-1}$.

Mn - 6.6 kDa, **D** - 1.50



α -pent-4-yn-1-yl-poly(methyl acrylate) (95)

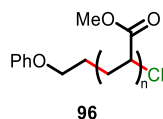
According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** = 97%, 89.2 mg).

^1H NMR (500 MHz, Chloroform-*d*) δ 4.28 – 4.18 (m, 1H), 3.69 – 3.51 (m, 371H), 2.38 – 2.17 (m, 126H), 1.93 – 1.33 (m, 256H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ [174.9, 174.8], 84.1, 73.9, [51.7, 51.6], [41.2, 41.1, 41.0], [35.9, 35.4, 34.8, 34.1], 26.1, 25.0, 16.8.

IR (ATR): $\nu = 2953, 1727, 1436, 1380, 1195, 1158, 1118, 827, 733, 702 \text{ cm}^{-1}$.

Mn - 6.4 kDa, **D** - 1.68



α -2-phenoxyethyl-poly(methyl acrylate) (96)

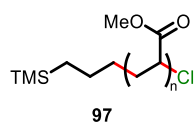
According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** = 98%, 100.7 mg).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 2H), 6.90 – 6.84 (m, 1H), 6.84 – 6.77 (m, 2H), 4.28 – 4.18 (m, 1H), 3.92 – 3.82 (m, 2H), 3.68 – 3.53 (m, 180H), 2.43 – 2.17 (m, 60H), 1.97 – 1.33 (m, 124H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ [174.8, 174.7], 158.7, 129.3, 120.5, 114.3, 67.0, [51.7, 51.6], [41.2, 41.1, 41.0], [35.8, 35.0, 34.7, 34.1], 26.7.

IR (ATR): $\nu = 2953, 1729, 1436, 1381, 1195, 1160, 1057, 827, 733, 702 \text{ cm}^{-1}$.

Mn - 3.1 kDa, **D** - 1.67



α -3-(trimethylsilyl)propyl-poly(methyl acrylate) (97)

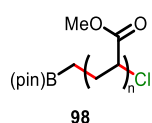
According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** > 98%, 85.2 mg).

^1H NMR (500 MHz, Chloroform-*d*) δ 4.29 – 4.18 (m, 1H), 3.66 – 3.55 (m, 219H), 2.37 – 2.17 (m, 73H), 1.94 – 1.36 (m, 147H), -0.14 – -0.20 (m, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ [174.9, 174.8], [51.8, 51.7], [41.3, 41.2, 41.1], [36.0, 35.1, 34.9, 34.2], 23.7, 22.6, 16.4, -1.8.

IR (ATR): ν = 2953, 1731, 1437, 1380, 1196, 1161, 1119, 828, 734, 702 cm^{-1} .

M_n - 4.1 kDa, **$\bar{D}$** - 1.51



α -(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl-poly(methyl acrylate) (98)

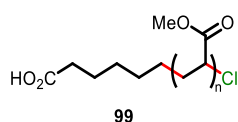
According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** = 95%, 106.0 mg).

^1H NMR (400 MHz, Chloroform-*d*) δ 4.28 – 4.18 (m, 1H), 3.65 – 3.52 (m, 354H), 2.36 – 2.14 (m, 116H), 1.96 – 1.35 (m, 238H), 1.15 (m, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ [174.9, 174.8], 83.0, [51.7, 51.6], [41.2, 41.2, 41.0], [35.9, 35.0, 34.8, 34.1], 24.7, 24.4.

IR (ATR): ν = 2953, 1728, 1436, 1379, 1195, 1158, 1057, 827, 734, 702 cm^{-1} .

M_n - 5.0 kDa, **$\bar{D}$** - 1.45



α -5-carboxy-1-*n*-pentyl -poly(methyl acrylate) (99)

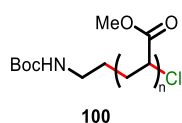
According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** = 97%, 97.7 mg).

^1H NMR (500 MHz, Chloroform-*d*) δ 4.28 – 4.16 (m, 1H), 3.68 – 3.49 (m, 212H), 2.36 – 2.15 (m, 73H), 1.95 – 1.30 (m, 147H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.7, [174.9, 174.8], [51.8, 51.7], [41.3, 41.2, 41.1], [36.0, 35.1, 34.9, 34.2], 29.6, 28.9, 28.7, 26.8, 24.6.

IR (ATR): ν = 2953, 1727, 1436, 1380, 1194, 1157, 1119, 973, 827, 734 cm^{-1} .

M_n - 3.7 kDa, **$\bar{D}$** - 2.15



α -2-((tert-butoxycarbonyl)amino)ethyl-poly(methyl acrylate) (100)

According to the general procedure D, the product was obtained as a waxy solid (conv. of **83** = 97%,

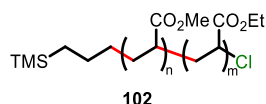
91.6 mg).

¹H NMR (500 MHz, Chloroform-*d*) δ 4.64 – 4.46 (m, 1H), 4.29 – 4.21 (m, 1H), 3.69 – 3.54 (m, 200H), 2.40 – 2.19 (m, 66H), 1.97 – 1.40 (m, 132H), 1.40 – 1.38 (m, 9H).

¹³C NMR (126 MHz, Chloroform-*d*) δ [174.9, 174.8], 155.9, [51.8, 51.7], [41.3, 41.2, 41.1], [36.0, 35.1, 34.9, 34.2], 29.6, 28.4, 14.1.

IR (ATR): ν = 2953, 1727, 1436, 1380, 1195, 1157, 1119, 827, 734, 702 cm⁻¹.

M_n - 4.0 kDa, *D* - 1.57



α -3-(trimethylsilyl)propyl-poly(methyl acrylate) – b- poly(ethyl acrylate) (102)

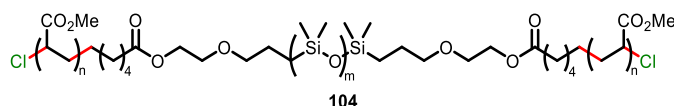
According to the general procedure D, in an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A4** (3.0 mg, 0.003 mmol), ethyl acrylate (1.5 mmol) and **97** (98.2 mg). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) for 1 h at room temperature with vigorous stirring. After completion of the reaction, the mixture was added dropwise into 20 mL of a mixed solvent system consisting of pentane and methanol (v/v = 40:1), leading to precipitation of the polymer as a waxy solid. The solid was then washed five times with the same mixed solvent system, followed by decantation to remove the solvent, and dried under reduced pressure to afford **102** (153.6 mg).

¹H NMR (500 MHz, Chloroform-*d*) δ 4.15 – 3.94 (m, 190H), 3.68 – 3.50 (m, 222H), 2.45 – 2.09 (m, 172H), 1.97 – 1.33 (m, 351H), 1.31 – 1.09 (m, 297H), -0.08 – -0.14 (m, 9H).

¹³C NMR (126 MHz, Chloroform-*d*) δ [174.9, 174.8], [174.5, 174.4, 174.4], [60.6, 60.4, 60.3], [51.7, 51.6], [41.3, 41.2, 41.0], [36.0, 35.2, 35.0, 34.2], 23.6, 16.4, [14.1, 14.0], -1.8.

IR (ATR): ν = 2954, 1726, 1445, 1379, 1155, 1114, 1023, 852, 828, 735 cm⁻¹.

M_n - 6.5 kDa, *D* - 1.48



poly(methyl acrylate)-b-polydimethylsiloxane-b-poly(methyl acrylate) (104)

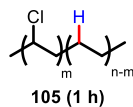
An oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **99** (118.1 mg), PDMS (15 mg, purchased from Aladdin, *M_n* - 1.3 kDa, *D* - 1.48), DMAP (1.0 mg) and EDC (7.4 mg), anhydrous DCM (2.0 mL) was added. The mixture was stirred at r.t. for 12 h. After completion of the reaction, the mixture was added dropwise into 20 mL of a mixed solvent system consisting of pentane and methanol (v/v = 40:1), leading to precipitation of the polymer as a waxy solid. The solid was then washed five times with the same mixed solvent system, followed by decantation to remove the solvent, and dried under reduced pressure to afford **104** (125.3 mg).

¹H NMR (500 MHz, Chloroform-*d*) δ 4.29 – 4.21 (m, 2H), 3.69 – 3.51 (m, 420H), 2.40 – 2.18 (m, 142H), 1.93 – 1.34 (m, 296H), 0.05 – -0.04 (m, 118H).

¹³C NMR (126 MHz, Chloroform-*d*) δ [174.9, 174.8], 173.7, 74.0, 68.4, 63.4, [51.7, 51.6], [41.3, 41.2, 41.0], [35.9, 35.1, 34.9, 34.0], 28.8, 26.9, 24.7, 23.2, 14.0, 1.1, 0.9, 0.0.

IR (ATR): ν = 2954, 1729, 1436, 1381, 1195, 1160, 1023, 802, 735, 702 cm⁻¹.

Mn - 8.1 kDa, **Đ** - 1.59



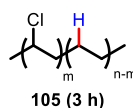
Hydrogenated PVC (105 (1 h))

According to the general procedure E for 1 h, the product was obtained as an off-white solid (97.0 mg, 4.8% dehalogenation).

¹H NMR (500 MHz, Pyridine-*d*5) δ 4.96 – 4.23 (m, 1H), 2.67 – 1.67 (m, 2.19H), 1.53 – 1.17 (m, 0.13H), 0.60 – 0.47 (m, 0.10H).

IR (ATR): ν = 2908, 1425, 1328, 1257, 1091, 1018, 958, 801, 680, 607 cm⁻¹.

Mn - 104.0 kDa, **Đ** - 1.65



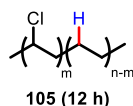
Hydrogenated PVC (105 (3 h))

According to the general procedure E for 3 h, the product was obtained as an off-white solid (91.4 mg, 8.7% dehalogenation).

¹H NMR (500 MHz, Pyridine-*d*5) δ 4.90 – 3.97 (m, 1H), 2.67 – 1.54 (m, 3.31H), 1.49 – 1.19 (m, 0.19H), 0.59 – 0.48 (m, 0.19H).

IR (ATR): ν = 2908, 1426, 1328, 1257, 1090, 1015, 959, 802, 681, 609 cm⁻¹.

Mn - 101.0 kDa, **Đ** - 1.62



Hydrogenated PVC (105 (12 h))

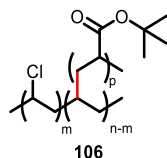
According to the general procedure E for 12 h, the product was obtained as an off-white solid (89.3 mg, 10.7% dehalogenation).

¹H NMR (500 MHz, Pyridine-*d*5) δ 4.79 – 4.02 (m, 1H), 2.64 – 1.56 (m, 4.34H), 1.51 – 1.20 (m, 0.46H), 0.54 (m, 0.24H).

¹³C NMR (126 MHz, Pyridine-*d*5) δ 61.6, 59.2, 58.9, 57.9, 47.3, 46.3, 38.6, 27.1, 24.1, 1.8.

IR (ATR): ν = 2907, 1432, 1325, 1259, 1092, 1018, 955, 802, 679, 607 cm⁻¹.

Mn - 99.3 kDa, **Đ** - 1.63



Poly(*tert*-butyl acrylate) grafted PVC (106)

According to the general procedure F for 1 h, the product was obtained as an off-white solid (113.5 mg, 13.0% grafting ratio).

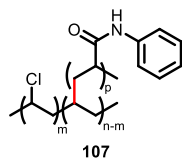
¹H NMR (500 MHz, Pyridine-*d*5) δ 4.96 – 4.54 (m, 1H), 2.84 – 2.65 (m, 0.13H), 2.61 – 1.80 (m,

2.05H), 1.79 – 1.43 (m, 1.38H), 0.57 – 0.51 (m, 0.05H).

^{13}C NMR (126 MHz, Pyridine-*d*5) δ 174.4, 58.8, 57.8, 56.8, 47.2, 46.4, 28.5, 1.8.

IR (ATR): ν = 2931, 1723, 1426, 1392, 1255, 1146, 1098, 844, 685, 609 cm^{-1} .

Mn - 116.2 kDa, *D* - 1.74



Poly(*N*-phenyl acrylamide) grafted PVC (107)

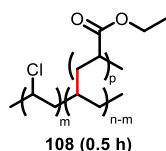
According to the general procedure F for 1 h, the product was obtained as an off-white solid (115.2 mg, 8.0% grafting ratio).

^1H NMR (500 MHz, Pyridine-*d*5) δ 8.09 – 7.70 (m, 0.13H), 7.43 – 7.32 (m, 0.09H), 7.17 – 6.98 (m, 0.11H), 4.96 – 4.49 (m, 1H), 3.20 – 2.89 (m, 0.08H), 2.66 – 1.96 (m, 1.81H), 0.61 – 0.42 (m, 0.05H).

^{13}C NMR (126 MHz, Pyridine-*d*5) δ 136.2, 129.4, 124.2, 121.4, 58.8, 57.8, 56.9, 47.2, 46.3.

IR (ATR): ν = 2910, 1665, 1599, 1533, 1499, 1254, 962, 753, 691, 610 cm^{-1} .

Mn - 116.1 kDa, *D* - 1.51



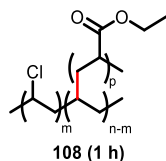
Poly(ethyl acrylate) grafted PVC (108 (0.5 h))

According to the general procedure F for 0.5 h, the product was obtained as an off-white solid (104.8 mg, 4.8% grafting ratio).

^1H NMR (500 MHz, Pyridine-*d*5) δ 4.94 – 4.50 (m, 1H), 4.38 – 4.12 (m, 0.10H), 2.91 – 2.71 (m, 0.05H), 2.68 – 1.73 (m, 2.04H), 1.48 – 1.12 (m, 0.21H).

IR (ATR): ν = 2909, 1728, 1425, 1328, 1252, 1176, 1095, 960, 688, 608 cm^{-1} .

Mn - 109.0 kDa, *D* - 1.63



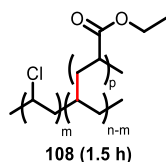
Poly(ethyl acrylate) grafted PVC (108 (1 h))

According to the general procedure F for 1 h, the product was obtained as an off-white solid (106.3 mg, 9.9% grafting ratio).

^1H NMR (500 MHz, Pyridine-*d*5) δ 4.94 – 4.51 (m, 1H), 4.33 – 4.19 (m, 0.22H), 2.87 – 2.75 (m, 0.10H), 2.62 – 1.71 (m, 2.12H), 1.48 – 1.09 (m, 0.41H), 0.58 – 0.50 (m, 0.01H).

IR (ATR): ν = 2909, 1726, 1426, 1328, 1243, 1159, 1094, 958, 680, 608 cm^{-1} .

Mn - 113.7 kDa, *D* - 1.71



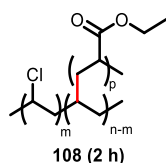
Poly(ethyl acrylate) grafted PVC (108 (1.5 h))

According to the general procedure F for 1.5 h, the product was obtained as an off-white solid (108.7 mg, 13.4% grafting ratio).

¹H NMR (500 MHz, Pyridine-*d*₅) δ 4.96 – 4.48 (m, 1H), 4.37 – 4.08 (m, 0.31H), 2.92 – 2.72 (m, 0.13H), 2.63 – 1.68 (m, 2.23H), 1.46 – 1.11 (m, 0.55H), 0.54 (m, 0.01H).

IR (ATR): ν = 2906, 1724, 1426, 1326, 1254, 1158, 1092, 961, 682, 611 cm⁻¹.

Mn - 118.0 kDa, **Đ** - 1.63



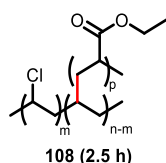
Poly(ethyl acrylate) grafted PVC (108 (2 h))

According to the general procedure F for 2 h, the product was obtained as an off-white solid (111.9 mg, 16.2% grafting ratio).

¹H NMR (500 MHz, Pyridine-*d*₅) δ 4.94 – 4.50 (m, 1H), 4.37 – 4.07 (m, 0.39H), 2.96 – 2.69 (m, 0.17H), 2.62 – 1.68 (m, 2.47H), 1.45 – 1.07 (m, 0.62H), 0.60 – 0.50 (m, 0.02H).

IR (ATR): ν = 2908, 1726, 1427, 1330, 1253, 1159, 1096, 961, 682, 608 cm⁻¹.

Mn - 120.2 kDa, **Đ** - 1.66



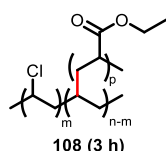
Poly(ethyl acrylate) grafted PVC (108 (2.5 h))

According to the general procedure F for 2.5 h, the product was obtained as an off-white solid (115.5 mg, 18.6% grafting ratio).

¹H NMR (500 MHz, Pyridine-*d*₅) δ 4.97 – 4.49 (m, 1H), 4.39 – 4.03 (m, 0.46H), 3.01 – 2.64 (m, 0.19H), 2.62 – 1.65 (m, 2.33H), 1.45 – 1.04 (m, 0.78H), 0.59 – 0.39 (m, 0.01H).

IR (ATR): ν = 2909, 1725, 1427, 1328, 1253, 1158, 1095, 963, 682, 610 cm⁻¹.

Mn - 127.7 kDa, **Đ** - 1.60



Poly(ethyl acrylate) grafted PVC (108 (3 h))

According to the general procedure F for 3 h, the product was obtained as an off-white solid (120.6 mg, 21.8% grafting ratio).

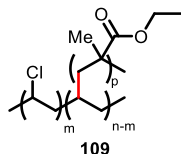
¹H NMR (500 MHz, Pyridine-*d*₅) δ 4.93 – 4.51 (m, 1H), 4.41 – 4.08 (m, 0.56H), 2.93 – 2.68 (m, 0.22H),

2.64 – 1.68 (m, 2.60H), 1.45 – 1.11 (m, 0.90H), 0.59 – 0.45 (m, 0.01H).

^{13}C NMR (126 MHz, Pyridine-*d*5) δ 175.2, 61.2, 58.8, 57.8, 56.9, 47.2, 46.3, 42.4, 14.7.

IR (ATR): ν = 2906, 1725, 1427, 1329, 1254, 1157, 1095, 963, 680, 609 cm^{-1} .

M_n - 136.0 kDa, $\bar{D}$ - 1.70



Poly(ethyl methacrylate) grafted PVC (109)

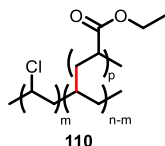
According to the general procedure F for 1 h, the product was obtained as an off-white solid (120.4 mg, 16.5% grafting ratio).

^1H NMR (500 MHz, Pyridine-*d*5) δ 4.98 – 4.48 (m, 1H), 4.41 – 4.09 (m, 0.40H), 2.66 – 2.04 (m, 1.35H), 1.63 – 1.12 (m, 1.31H), 0.66 – 0.46 (m, 0.02H).

^{13}C NMR (126 MHz, Pyridine-*d*5) δ 178.1, 61.4, 58.8, 57.8, 56.8, 47.2, 46.0, 17.8, 14.3.

IR (ATR): ν = 2906, 1721, 1428, 1386, 1258, 1144, 1023, 963, 678, 611 cm^{-1} .

M_n - 130.3 kDa, $\bar{D}$ - 1.78



Poly(ethyl acrylate) grafted PVC (110)

According to the general procedure F for 0.5 h, the PVC substrate comes from shredded wire casing, packaging bags, and piping, the product was obtained as an off-white solid (105.2 mg, 4.3% grafting ratio).

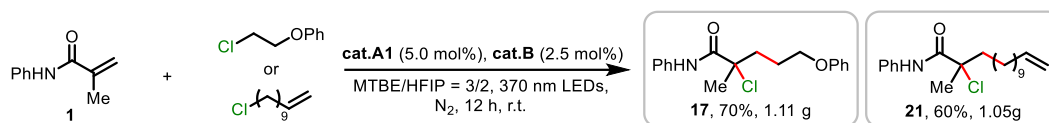
^1H NMR (500 MHz, Pyridine-*d*5) δ 4.95 – 4.50 (m, 1H), 4.32 – 4.21 (m, 0.09H), 2.85 – 2.75 (m, 0.05H), 2.64 – 1.97 (m, 1.80H), 1.51 – 1.02 (m, 0.31H), 0.64 – 0.48 (m, 0.01H).

^{13}C NMR (126 MHz, Pyridine-*d*5) δ 175.2, 61.2, 58.8, 57.8, 56.9, 47.2, 46.3, 42.3, 14.7.

IR (ATR): ν = 2907, 1728, 1425, 1329, 1254, 1094, 1022, 962, 679, 609 cm^{-1} .

6. Transformation of Products

6.1 Gram-scale reaction

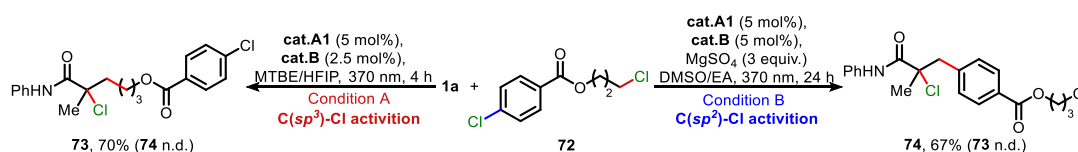


Supplementary Figure 2. Gram-scale reaction

In an N₂-filled glove-box, an oven-dried flask (48 mL) equipped with a magnetic stir bar was charged with **cat.A1** (276 mg, 0.15 mmol, 3.0 mol%), **cat.B** (27.6 mg, 0.075 mmol, 1.5 mol%), alkene **1** (806 mg, 5.0 mmol, 1.0 equiv.), 2-phenoxyethyl chloride (2.1 mL, 15 mmol, 3 equiv.), MTBE (18 mL) and HFIP (12 mL). Then the flask was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W × 2) for 12 h at 25 °C with vigorous stirring. When the reaction was completed, the mixture was then concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford **17** (1.11 g, 70%).

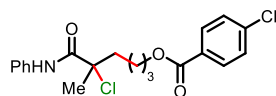
In an N₂-filled glove-box, an oven-dried flask (48 mL) equipped with a magnetic stir bar was charged with **cat.A1** (276 mg, 0.15 mmol, 3.0 mol%), **cat.B** (27.6 mg, 0.075 mmol, 1.5 mol%), alkene **1** (806 mg, 5.0 mmol, 1.0 equiv.), 11-chloro-1-undecene (2.85 mL, 15 mmol, 3 equiv.), MTBE (18 mL) and HFIP (12 mL). Then the flask was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W × 2) for 12 h at 25 °C with vigorous stirring. When the reaction was completed, the mixture was then concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford **21** (1.05g, 60%).

6.2 Activation of C(sp³)-Cl bond vs. C(sp²)-Cl bond



In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 5.0 mol%), **cat.B** (0.9 mg, 2.5 mol%), **1** (16.2 mg, 0.1 mmol, 1.0 equiv.) and

72 (69.9 mg, 0.3 mmol, 3 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) for 4 h at room temperature with vigorous stirring. After completion of the reaction, the solvent was removed under vacuum and purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford the desired **73** (27.4 mg, 70%).



5-chloro-5-methyl-6-oxo-6-(phenylamino)hexyl 4-chlorobenzoate (73) (colorless oil)

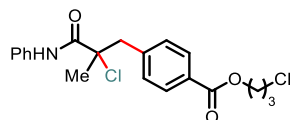
¹H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.01 – 7.90 (m, 2H), 7.53 (d, J = 7.9 Hz, 2H), 7.42 – 7.31 (m, 4H), 7.22 – 7.12 (m, 1H), 4.40 – 4.26 (m, 2H), 2.40 – 2.28 (m, 1H), 2.03 – 1.92 (m, 1H), 1.87 (d, J = 1.6 Hz, 3H), 1.84 – 1.77 (m, 2H), 1.76 – 1.68 (m, 1H), 1.60 – 1.48 (m, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.4, 165.7, 139.3, 136.9, 130.9, 129.1, 128.7, 128.6, 125.1, 120.0, 74.5, 64.6, 42.4, 30.1, 28.3, 21.6.

IR (ATR): ν = 3401, 2954, 1719, 1680, 1597, 1529, 1273, 1015, 758, 691 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$: 394.0971, found: 394.0969.

In an N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 5.0 mol%), **cat.B** (1.8 mg, 5.0 mol%), **1** (16.2 mg, 0.1 mmol, 1.0 equiv.), **72** (46.6 mg, 0.2 mmol, 2 equiv.) and MgSO_4 (36 mg, 0.3 mmol, 3.0 equiv.). Then, DMSO (0.5 mL) and EA (0.5 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) for 24 h at room temperature with vigorous stirring. After completion of the reaction, the solvent was removed under vacuum and was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford **74** (26.3 mg, 67%).



3-chloropropyl 4-(2-chloro-2-methyl-3-oxo-3-(phenylamino)propyl)benzoate (74) (colorless oil)

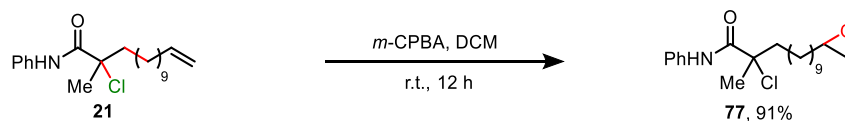
¹H NMR (500 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.20 – 7.11 (m, 1H), 4.45 (t, J = 6.0 Hz, 2H), 3.70 – 3.62 (m, 3H), 3.20 (d, J = 13.9 Hz, 1H), 2.27 – 2.15 (m, 2H), 1.95 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 168.6, 166.2, 140.8, 136.7, 130.8, 129.3, 129.0, 125.2, 120.3, 73.8, 61.6, 48.0, 41.2, 31.7, 30.2.

IR (ATR): ν = 3394, 2966, 1718, 1680, 1529, 1443, 1275, 1111, 750, 692 cm^{-1} .

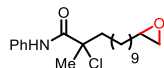
HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$: 394.0971, found: 394.0970.

6.3 Downstream transformations



Following the literature procedures⁹, an oven-dried vial (8 mL) equipped with a magnetic stir bar was charged with **21** (35.0 mg, 0.1 mmol, 1.0 equiv.) and *m*-CPBA (34.5 mg, 0.2 mmol, 2 equiv.). Anhydrous DCM (1.0 mL) was added. The mixture was then stirred at r.t. for 12 h. The crude

product was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford **77** (33.3 mg, 91%).



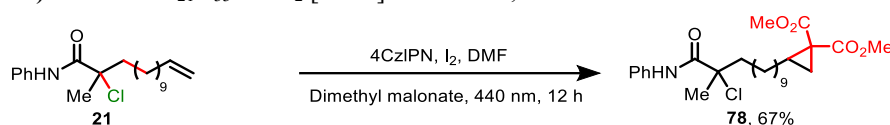
2-chloro-2-methyl-12-(oxiran-2-yl)-N-phenyldodecanamide (77) (colorless oil)

¹H NMR (500 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.59 – 7.51 (m, 2H), 7.38 – 7.31 (m, 2H), 7.21 – 7.10 (m, 1H), 2.95 – 2.83 (m, 1H), 2.73 (dd, J = 5.1, 4.0 Hz, 1H), 2.45 (dd, J = 5.0, 2.7 Hz, 1H), 2.22 (ddd, J = 14.1, 11.9, 4.2 Hz, 1H), 1.89 (ddd, J = 14.2, 11.8, 4.3 Hz, 1H), 1.84 (s, 3H), 1.60 – 1.35 (m, 6H), 1.33 – 1.23 (m, 12H).

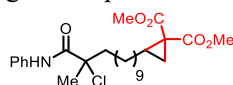
¹³C NMR (126 MHz, Chloroform-*d*) δ 169.6, 137.1, 129.0, 124.9, 120.0, 74.9, 52.4, 47.1, 43.0, 32.4, 29.9, 29.4, 29.4, 29.4, 29.4, 29.3, 29.2, 25.9, 24.9.

IR (ATR): ν = 3350, 2924, 1681, 1598, 1528, 1441, 1315, 753, 692, 508 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{33}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$: 366.2194, found: 366.2191.



Following the literature procedures¹⁰, an oven-dried vial (8 mL) was charged with a magnetic stir bar and photocatalyst (4CzIPN, 1.6 mg, 2 mol%). **21** (35.0 mg, 0.1 mmol, 1 eq), dimethyl malonate (23 μL , 0.2 mmol, 2 equiv.), I_2 (1.3 mg, 5 mol%), and anhydrous DMF (1 mL) were added to the vial in air. The resulting mixture was then irradiated with 440 nm KESSIL blue LEDs under O_2 atmosphere. After 12 h, the crude product was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford **78** (32.2 mg, 67%).



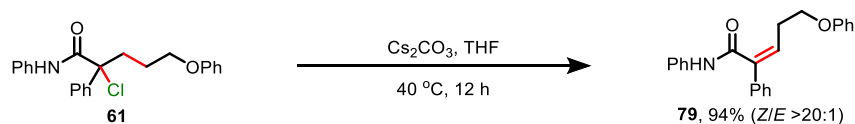
Dimethyl-2-(11-chloro-11-methyl-12-oxo-12-(phenylamino)dodecyl)cyclopropane-1,1-dicarboxylate (78) (colorless oil)

¹H NMR (500 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.61 – 7.49 (m, 2H), 7.39 – 7.30 (m, 2H), 7.20 – 7.07 (m, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.21 (ddd, J = 14.0, 11.9, 4.1 Hz, 1H), 1.93 – 1.86 (m, 2H), 1.84 (s, 3H), 1.58 – 1.51 (m, 1H), 1.45 – 1.34 (m, 6H), 1.32 – 1.21 (m, 12H), 1.18 – 1.08 (m, 1H).

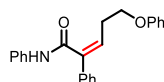
¹³C NMR (126 MHz, Chloroform-*d*) δ 170.9, 169.6, 168.7, 137.1, 129.0, 124.9, 120.0, 74.9, 52.5, 52.4, 43.0, 33.9, 29.9, 29.4, 29.4, 29.3, 29.2, 28.8, 28.8, 28.6, 24.9, 21.4.

IR (ATR): ν = 3364, 2927, 2855, 1727, 1684, 1530, 1440, 1276, 751, 693 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{39}\text{ClNO}_5$ $[\text{M}+\text{H}]^+$: 480.2511, found: 480.2506.



Following the literature procedures¹¹, an oven-dried vial (8 mL) was charged with a magnetic stir bar and **61** (19.0 mg, 0.05 mmol, 1 eq), Cs_2CO_3 (32.6 mg, 0.1 mmol, 2 equiv.) and anhydrous THF (1 mL) were added to the vial. The resulting mixture was stirred at 40 $^\circ\text{C}$ for 12 h. The crude product was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford **79** (16.1 mg, 94%, Z/E >20:1).



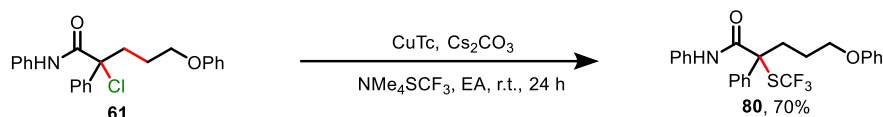
(Z)-5-phenoxy-N,2-diphenylpent-2-enamide (79) (white solid, m.p. 86.0-88.3 °C)

¹H NMR (500 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.66 – 7.59 (m, 2H), 7.53 – 7.47 (m, 2H), 7.39 – 7.28 (m, 7H), 7.17 – 7.10 (m, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.23 (t, *J* = 8.1 Hz, 1H), 4.22 (t, *J* = 5.8 Hz, 2H), 2.96 (dt, *J* = 7.9, 5.8 Hz, 2H).

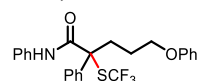
¹³C NMR (126 MHz, Chloroform-*d*) δ 166.6, 158.4, 140.8, 137.8, 137.3, 130.0, 129.7, 129.1, 128.7, 128.2, 127.0, 124.5, 121.4, 119.8, 114.6, 67.2, 30.2.

IR (ATR): ν = 3284, 3027, 1659, 1598, 1532, 1440, 1243, 1037, 751, 691 cm⁻¹.

HRMS (ESI) calcd. for C₂₃H₂₂NO₂ [M+H]⁺: 344.1645, found: 344.1639.



Following the literature procedures¹², an oven-dried vial (8 mL) was charged with a magnetic stir bar and **61** (19.0 mg, 0.05 mmol, 1 equiv.), (Me₄N)SCF₃ (13.1 mg, 0.075 mmol, 1.5 equiv.), CuTc (1.43 mg, 0.0075 mmol, 15 mol%), Cs₂CO₃ (32.6 mg, 0.10 mmol, 2.0 equiv.), and EA (1.0 mL). Then the reaction mixture was stirred at r.t. for 24 h. The crude product was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford **80** (15.7 mg, 70%).



5-phenoxy-N,2-diphenyl-2-((trifluoromethylthio)thio)pentanamide (80) (colorless oil)

¹H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.47 (m, 3H), 7.45 – 7.36 (m, 5H), 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 2H), 4.08 – 3.93 (m, 2H), 2.89 – 2.73 (m, 1H), 2.69 – 2.57 (m, 1H), 2.06 – 1.86 (m, 2H).

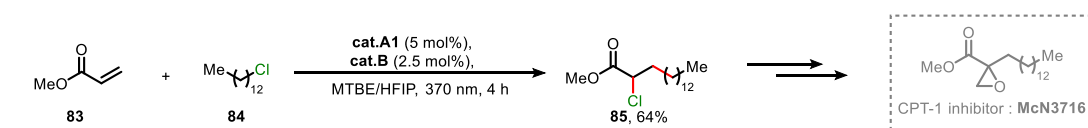
¹⁹F NMR (376 MHz, Chloroform-*d*) δ -37.06.

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.1, 158.7, 138.0, 137.0, 129.6 (q, *J* = 309.7 Hz), 129.4, 129.1, 129.1, 128.9, 127.0, 125.0, 120.7, 120.2, 114.4, 67.1, 66.3, 34.6, 25.0.

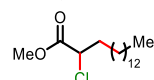
IR (ATR): ν = 3318, 2931, 1667, 1599, 1526, 1498, 1244, 1112, 751, 692 cm⁻¹.

HRMS (ESI) calcd. for C₂₄H₂₃F₃NO₂S [M+H]⁺: 446.1396, found: 446.1388.

6.4 Formal synthesis of McN3716



According to the general procedure A, the crude product is purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford **85** (0.1 mmol scale, 19.5 mg, 64%).



methyl 2-chlorohexadecanoate (85) (colorless oil)

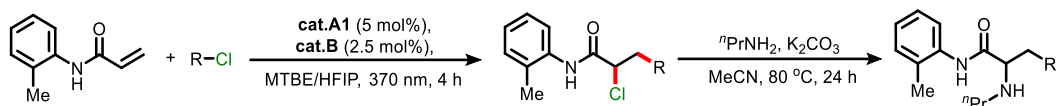
¹H NMR (500 MHz, Chloroform-*d*) δ 4.27 (dd, *J* = 7.9, 6.2 Hz, 1H), 3.78 (s, 3H), 2.09 – 1.96 (m, 1H), 1.97 – 1.85 (m, 1H), 1.50 – 1.36 (m, 2H), 1.34 – 1.23 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 170.3, 57.3, 52.8, 34.9, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 28.8, 26.0, 22.7, 14.1.

IR (ATR): ν = 2923, 2853, 1748, 1465, 1437, 1276, 1195, 1167, 750, 722 cm^{-1} .

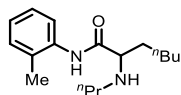
HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{34}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 305.2242, found: 305.2224.

6.5 Synthesis of Prilocaine analogues



According to the general procedure A, the crude product is purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford ATRA product.

An oven-dried vial (8 mL) was charged with a magnetic stir bar and ATRA product (0.1 mmol, 1 equiv.), $n\text{PrNH}_2$ (41 μL , 0.5 mmol, 5 equiv.), K_2CO_3 (27.6 mg, 0.2 mmol, 2 equiv.) and anhydrous MeCN (1 mL) was added to the vial. The resulting mixture was stirred at 80 $^\circ\text{C}$ for 24 h. The crude product was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford product.



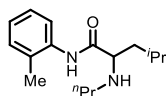
2-(propylamino)-*N*-(*o*-tolyl)heptanamide (87) (colorless oil)

^1H NMR (500 MHz, Chloroform- d) δ 9.52 (s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 3.23 – 3.12 (m, 1H), 2.71 – 2.56 (m, 2H), 2.28 (s, 3H), 1.92 – 1.80 (m, 1H), 1.69 – 1.49 (m, 4H), 1.48 – 1.38 (m, 2H), 1.37 – 1.28 (m, 4H), 0.96 (t, J = 7.4 Hz, 3H), 0.93 – 0.84 (m, 3H).

^{13}C NMR (126 MHz, Chloroform- d) δ 172.6, 136.0, 130.3, 127.3, 126.8, 124.1, 121.0, 64.0, 51.2, 33.9, 31.7, 25.7, 23.4, 22.4, 17.7, 14.0, 11.7.

IR (ATR): ν = 3304, 2956, 2927, 1680, 1587, 1522, 1454, 1250, 1046, 752 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{29}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 277.2274, found: 277.2266.



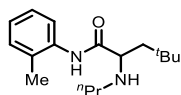
4-methyl-2-(propylamino)-*N*-(*o*-tolyl)pentanamide (88) (colorless oil)

^1H NMR (500 MHz, Chloroform- d) δ 9.53 (s, 1H), 8.16 – 8.09 (m, 1H), 7.25 – 7.19 (m, 1H), 7.18 – 7.15 (m, 1H), 7.06 – 6.99 (m, 1H), 3.29 – 3.20 (m, 1H), 2.72 – 2.57 (m, 2H), 2.28 (s, 3H), 1.79 – 1.69 (m, 3H), 1.61 – 1.52 (m, 2H), 1.52 – 1.45 (m, 1H), 1.02 – 0.97 (m, 6H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform- d) δ 173.0, 136.1, 130.3, 127.3, 126.8, 124.1, 121.0, 62.4, 51.1, 43.1, 25.3, 23.4, 23.2, 21.9, 17.7, 11.7.

IR (ATR): ν = 3303, 2957, 2929, 1680, 1587, 1522, 1454, 1137, 1047, 742 cm^{-1} .

HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{27}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 263.2118, found: 263.2099.



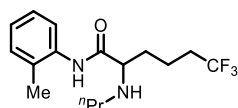
4,4-dimethyl-2-(propylamino)-*N*-(*o*-tolyl)pentanamide (89) (colorless oil)

¹H NMR (500 MHz, Chloroform-*d*) δ 9.60 (s, 1H), 8.17 (d, $J = 8.2$ Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.16 (d, $J = 7.5$ Hz, 1H), 7.02 (t, $J = 7.5$ Hz, 1H), 3.15 (dd, $J = 8.5, 2.0$ Hz, 1H), 2.71 – 2.62 (m, 1H), 2.63 – 2.53 (m, 1H), 2.28 (s, 3H), 1.86 (dd, $J = 14.5, 2.0$ Hz, 1H), 1.57 – 1.51 (m, 3H), 1.37 – 1.30 (m, 1H), 1.03 (s, 9H), 0.95 (t, $J = 7.4$ Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 173.7, 136.2, 130.2, 126.9, 126.9, 123.9, 120.7, 62.2, 51.1, 48.6, 31.1, 29.9, 23.6, 17.7, 11.7.

IR (ATR): $\nu = 3244, 2989, 1690, 1660, 1588, 1528, 1276, 1261, 764, 750$ cm⁻¹.

HRMS (ESI) calcd. for C₁₇H₂₉N₂O [M+H]⁺: 277.2274, found: 277.2271.



6,6,6-trifluoro-2-(propylamino)-*N*-(*o*-tolyl)hexanamide (90) (colorless oil)

¹H NMR (500 MHz, Chloroform-*d*) δ 9.47 (s, 1H), 8.13 – 8.06 (m, 1H), 7.25 – 7.20 (m, 1H), 7.18 (d, $J = 7.5$ Hz, 1H), 7.09 – 7.02 (m, 1H), 3.20 (t, $J = 5.9$ Hz, 1H), 2.74 – 2.57 (m, 2H), 2.28 (s, 3H), 2.20 – 2.07 (m, 2H), 1.97 – 1.86 (m, 1H), 1.82 – 1.67 (m, 3H), 1.63 – 1.48 (m, 3H), 0.97 (t, $J = 7.4$ Hz, 3H).

¹⁹F NMR (471 MHz, CDCl₃) δ -66.22.

¹³C NMR (126 MHz, Chloroform-*d*) δ 171.7, 135.8, 130.3, 127.4, 126.9 (q, $J = 276.3$ Hz), 126.9, 124.4, 121.1, 63.3, 51.1, 33.6 (q, $J = 28.8$ Hz), 32.9, 23.5, 18.6 (q, $J = 3.1$ Hz), 17.6, 11.6.

IR (ATR): $\nu = 3294, 2960, 2932, 1678, 1587, 1521, 1455, 1253, 1135, 752$ cm⁻¹.

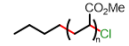
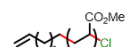
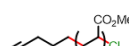
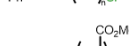
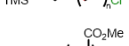
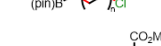
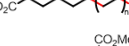
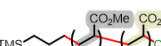
HRMS (ESI) calcd. for C₁₆H₂₄F₃N₂O [M+H]⁺: 317.1835, found: 317.1830.

7. Characterization of Polymer

7.1 Measurement of chlorine-transfer polymerization products

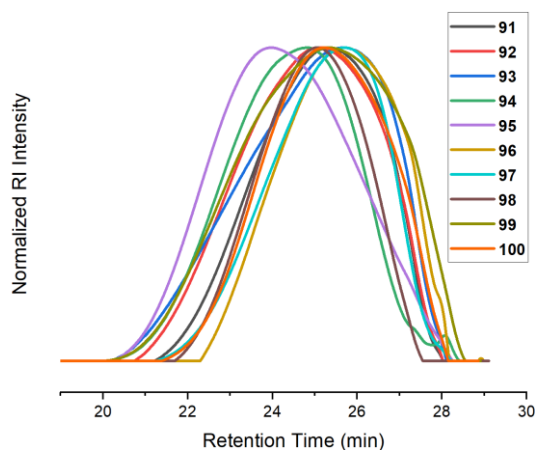
A series of measurements were carried out on the chlorine-transfer polymerization products. The detailed data are shown in the **Supplementary Table 18**.

Supplementary Table 18. Data of chlorine-transfer polymerization products

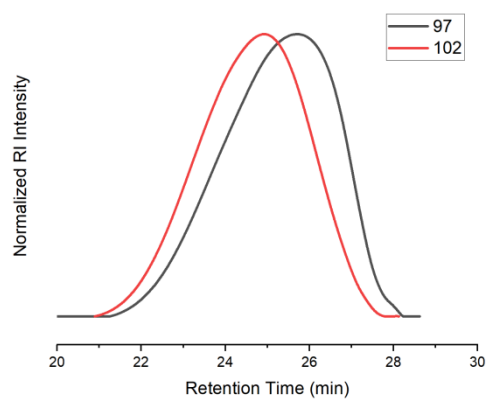
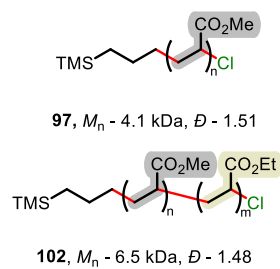
Structure	Polymer	conv. of 83	M_n	D
	91	98%	4.3 kDa	1.51
	92	97%	4.7 kDa	1.64
	93	98%	3.8 kDa	1.57
	94	> 98%	6.6 kDa	1.50
	95	97%	6.4 kDa	1.68
	96	98%	3.1 kDa	1.67
	97	> 98%	4.1 kDa	1.51
	98	95%	5.0 kDa	1.45
	99	97%	3.7 kDa	2.15
	100	97%	4.0 kDa	1.57
	102	-	6.5 kDa	1.48
	104	-	8.1 kDa	1.59

1) GPC

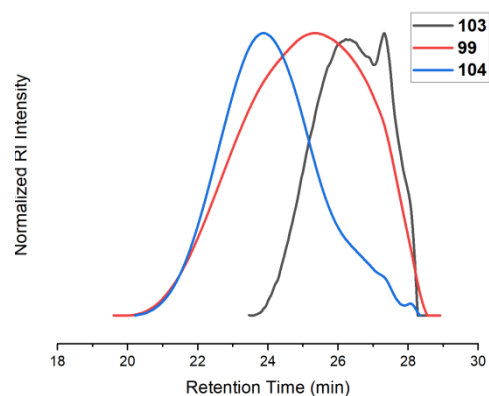
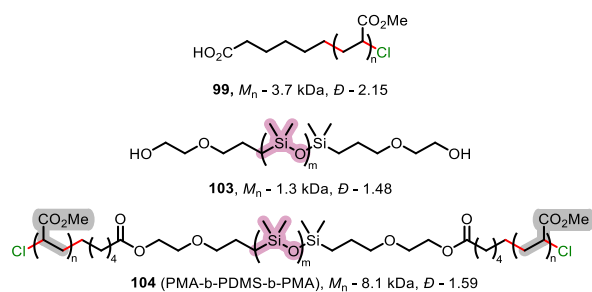
Polymer samples were made by dissolving 2 mg of product in 1 mL of unstabilized THF while stirring and heating at 40 °C. All samples were filtered through a 0.22 µm nylon syringe filter. All GPC traces were normalized to the same intensity.



Supplementary Figure 3. GPC of 91 - 100



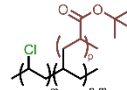
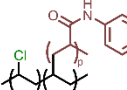
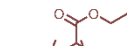
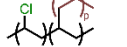
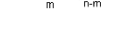
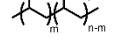
Supplementary Figure 4. GPC of 97 and 102



Supplementary Figure 5. GPC of 99, 103 and 104

7.2 Measurement of modified PVC

Supplementary Table 19. Data of modified PVC

Structure	Polymer	Dehalogenation ratio	Grafting ratio	M_n	$\bar{D}$	T_g	T_{d5}
	PVC	-	-	106.1 kDa	1.63	84.7 °C	288.2 °C
	105 (1 h)	4.8%	-	104.0 kDa	1.65	72.6 °C	288.4 °C
	105 (3 h)	8.7%	-	101.0 kDa	1.62	63.0 °C	289.8 °C
	105 (12 h)	10.7%	-	99.3 kDa	1.63	48.2 °C	295.0 °C
	106	-	13.0%	116.2 kDa	1.74	80.5 °C	242.9 °C
	107	-	8.0%	116.1 kDa	1.51	92.2 °C	274.2 °C
	108 (0.5 h)	-	4.8%	109.0 kDa	1.63	76.9 °C	284.7 °C
	108 (1 h)	-	9.9%	113.7 kDa	1.71	64.0 °C	288.0 °C
	108 (1.5 h)	-	13.4%	118.0 kDa	1.63	59.3 °C	289.7 °C
	108 (2 h)	-	16.2%	120.2 kDa	1.66	55.7 °C	291.8 °C
	108 (2.5 h)	-	18.6%	127.7 kDa	1.60	52.0 °C	294.4 °C
	108 (3 h)	-	21.8%	136.0 kDa	1.70	49.9 °C	296.1 °C
	109	-	16.5%	130.3 kDa	1.78	84.6 °C	279.4 °C

A series of measurements were carried out on the PVC used and the modified PVC. The detailed data are shown in **Supplementary Table 19**. Regarding the thermal properties, we found that hydrogenation of PVC significantly lowers its T_g, which may facilitate processing. In contrast, the effect of graft modification depends on the nature of the grafted monomer: acrylate-based grafting also reduces the T_g of PVC, whereas acrylamide-based modification increases it. Furthermore, the polymer dispersities (Đ) remained similar to that of pristine PVC, indicating that no significant chain-scission side reactions occurred during the modification process.

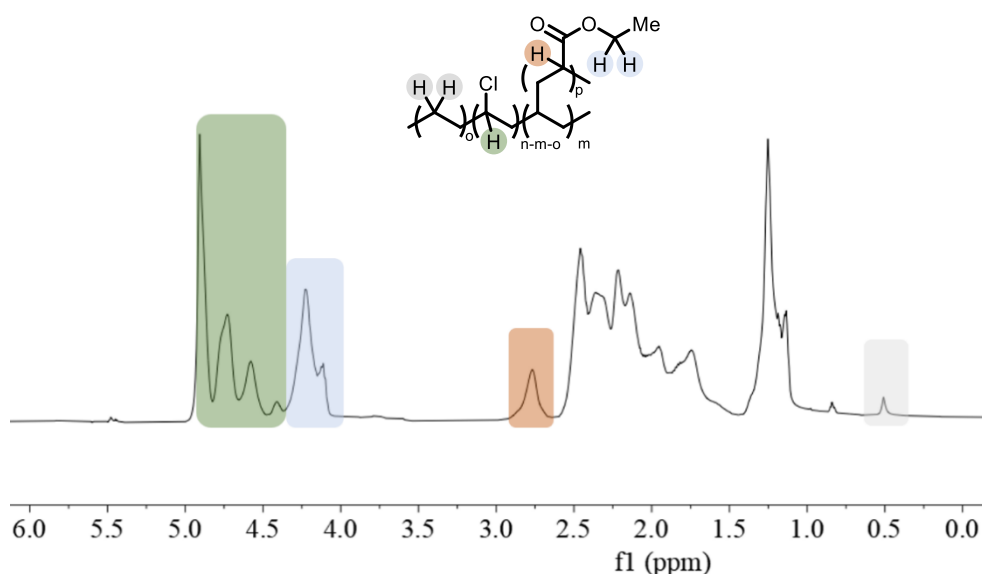
1) Calculation of dehalogenation ratios and grafting ratios

The ratio of dehalogenation was determined using the following equation:

$$\text{dehalogenation ratio \%} = \frac{A_H}{A_{\text{graft}} + 2 \times A_{\text{Cl}} + A_H} \times 100\% \quad (\text{Eq.1})$$

The ratio of grafting was determined using the following equation:

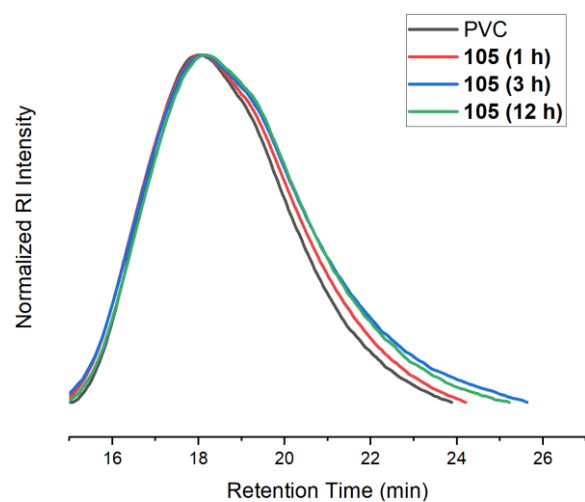
$$\text{grafting ratio \%} = \frac{A_{\text{graft}}}{A_{\text{graft}} + 2 \times A_{\text{Cl}} + A_H} \times 100\% \quad (\text{Eq.2})$$



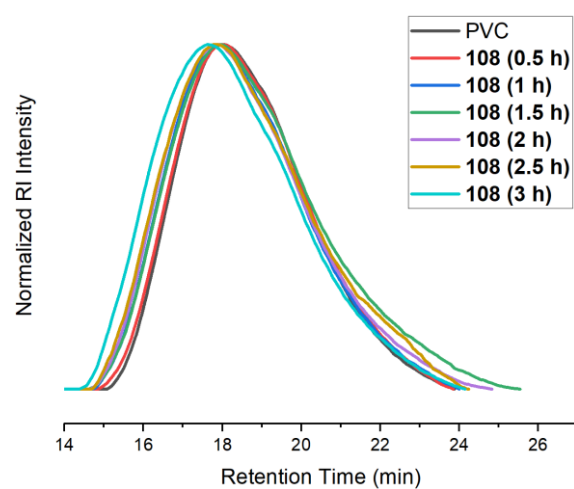
Supplementary Figure 6. ¹H NMR spectra showing highlighted regions for ratio calculations

2) GPC Chromatograms

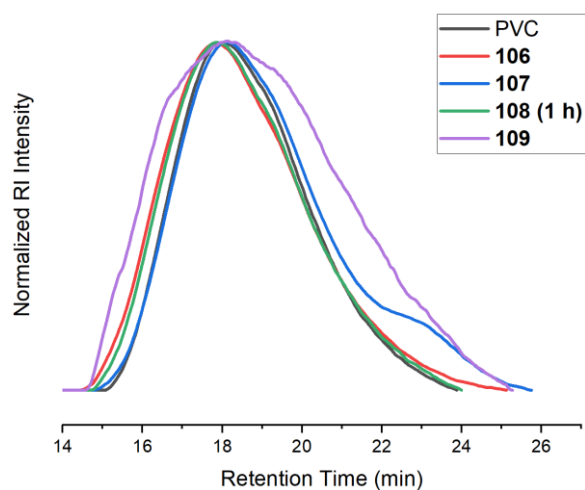
Polymer samples were made by dissolving 2 mg of solid in 1 mL of unstabilized THF with stirring and heating at 40 °C. All samples were filtered through a 0.22 μm nylon syringe filter. All GPC traces were normalized to the same intensity.



Supplementary Figure 7. GPC of hydrogenated PVC

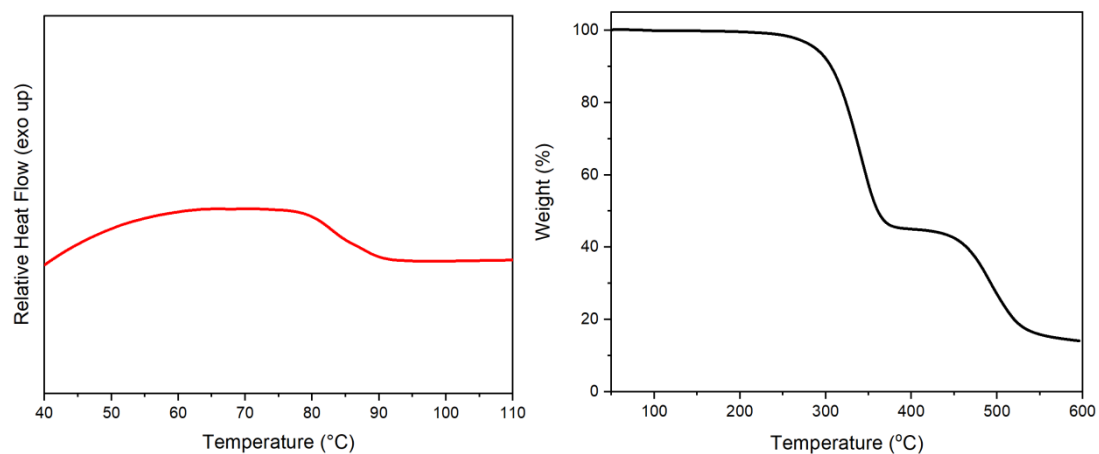


Supplementary Figure 8. GPC of PVC of different grafting ratios

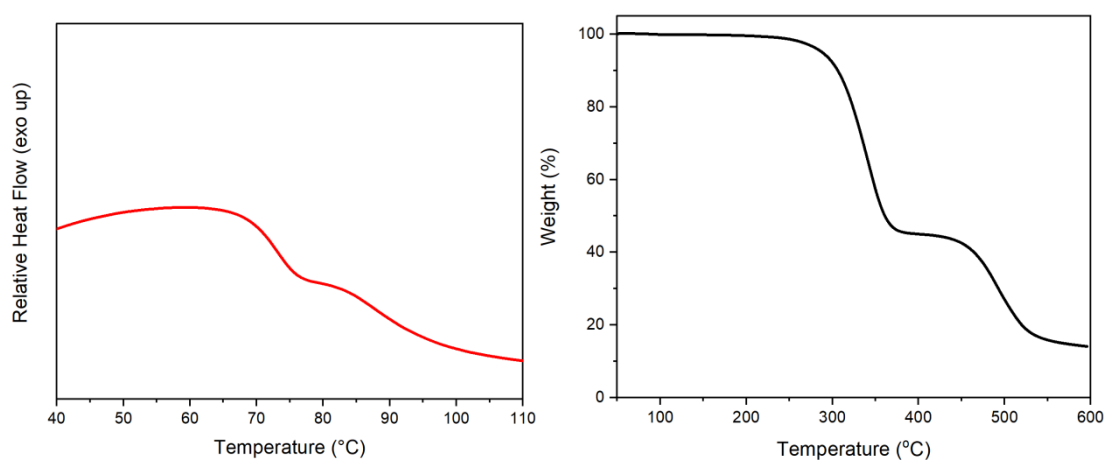


Supplementary Figure 9. GPC of PVC of different grafting groups

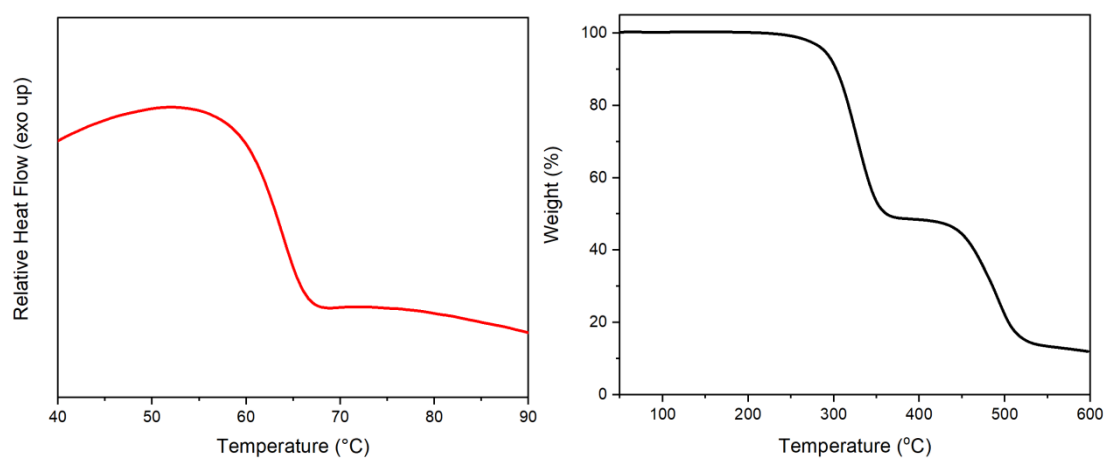
3) DSC and TGA Spectra



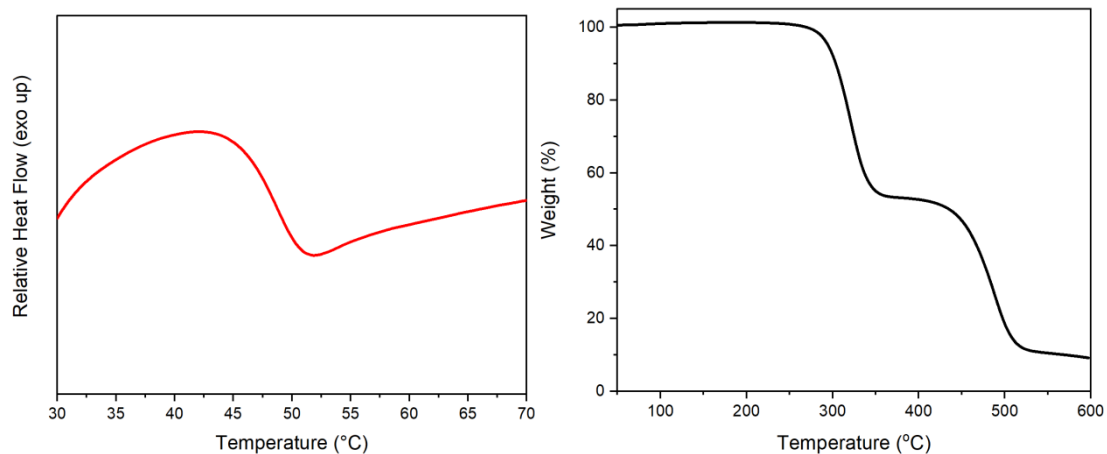
Supplementary Figure 10. DSC and TGA Spectra of PVC



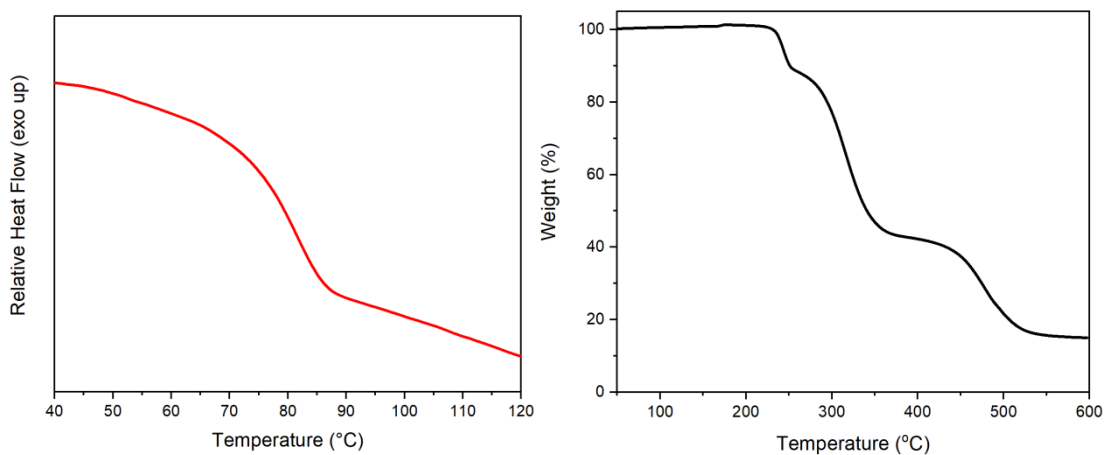
Supplementary Figure 11. DSC and TGA Spectra of 105 (1 h)



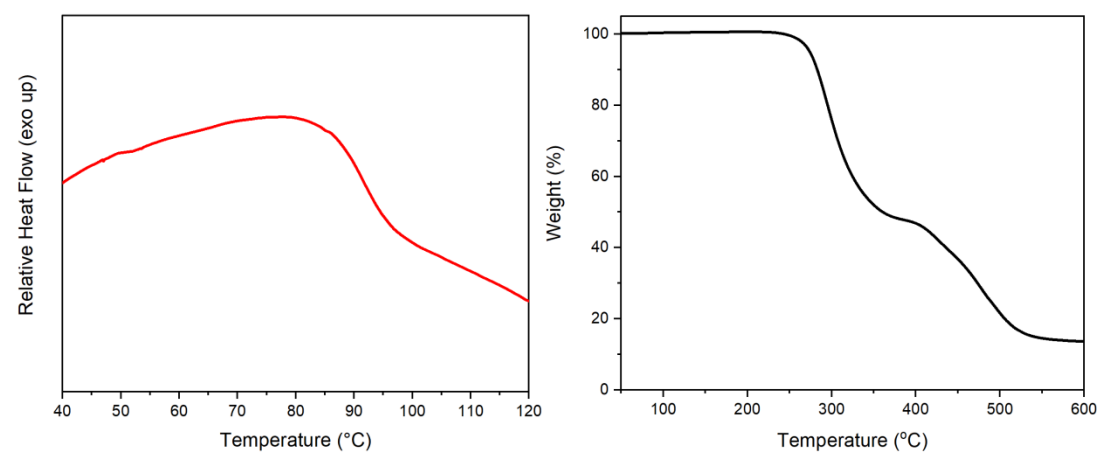
Supplementary Figure 12. DSC and TGA Spectra of 105 (3 h)



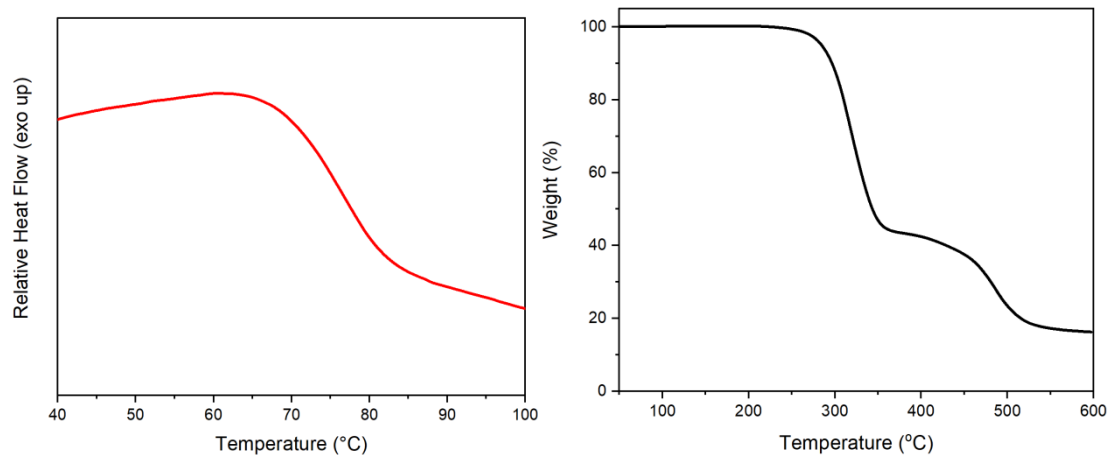
Supplementary Figure 13. DSC and TGA Spectra of 105 (12 h)



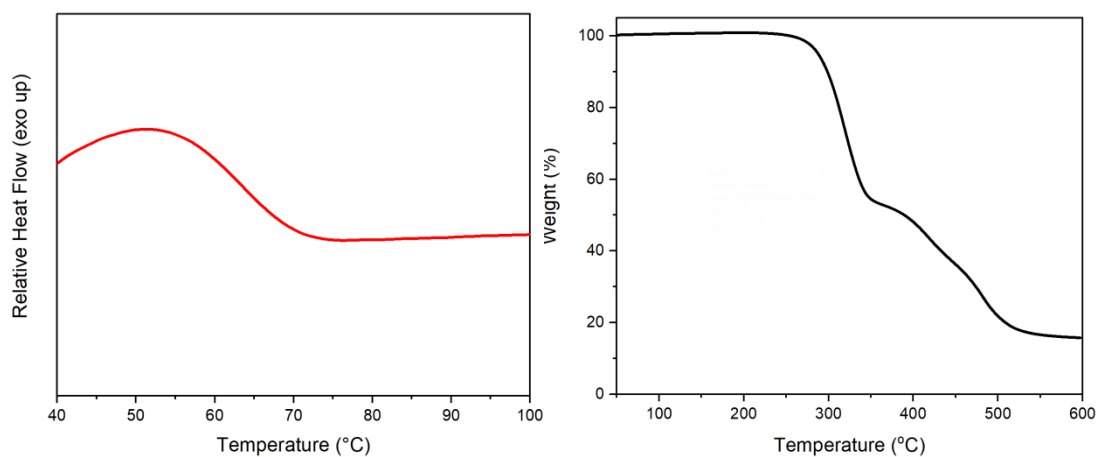
Supplementary Figure 14. DSC and TGA Spectra of 106



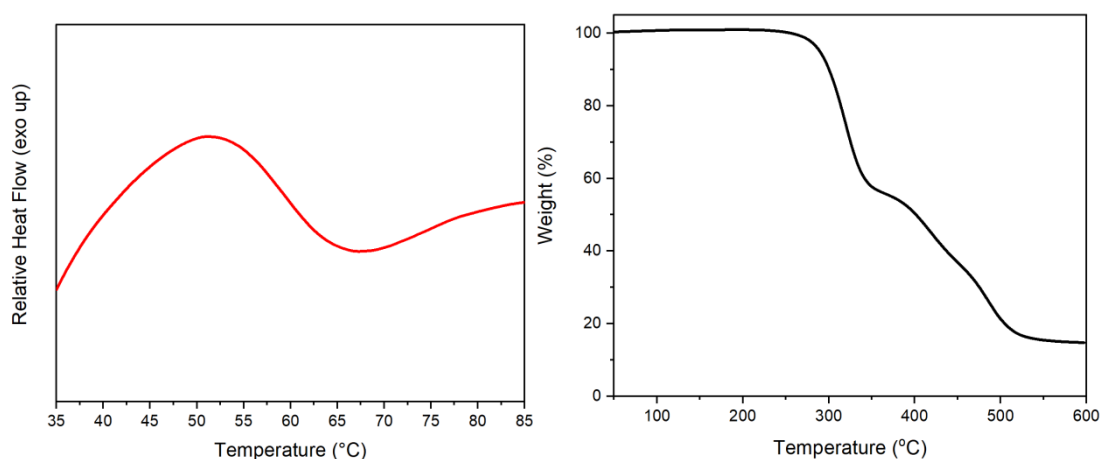
Supplementary Figure 15. DSC and TGA Spectra of 107



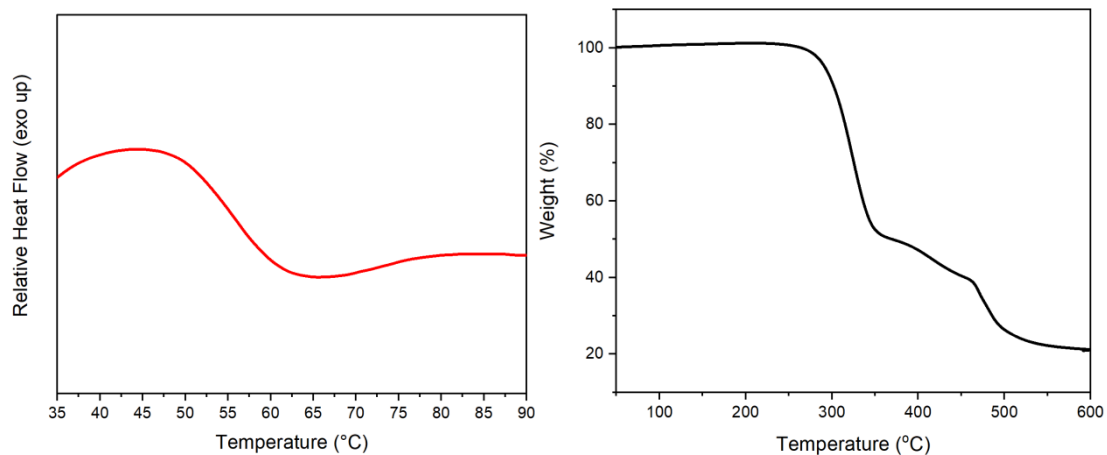
Supplementary Figure 16. DSC and TGA Spectra of 108 (0.5 h)



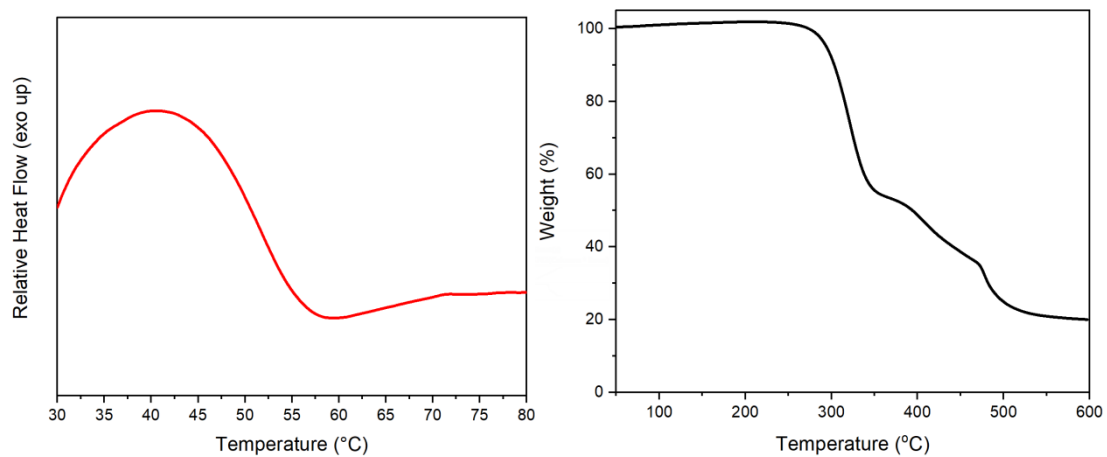
Supplementary Figure 17. DSC and TGA Spectra of 108 (1 h)



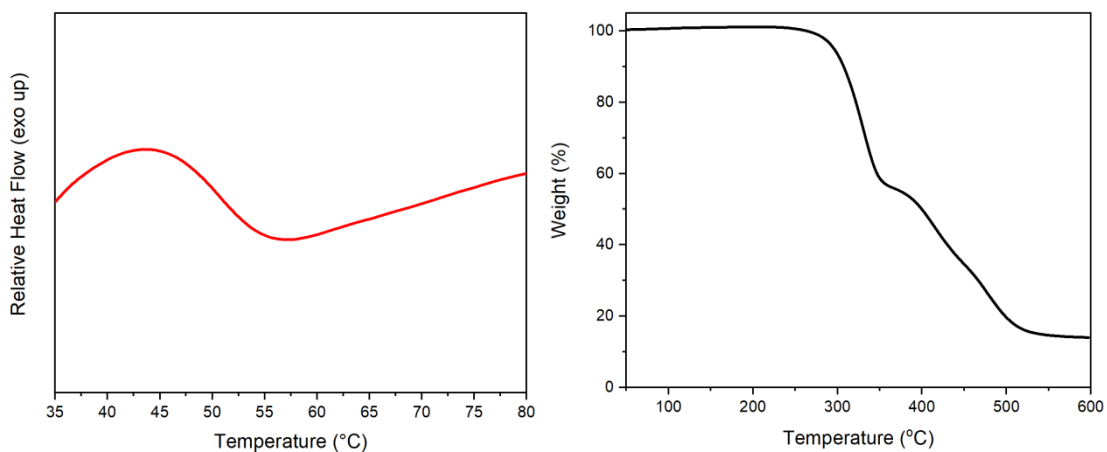
Supplementary Figure 18. DSC and TGA Spectra of 108 (1.5 h)



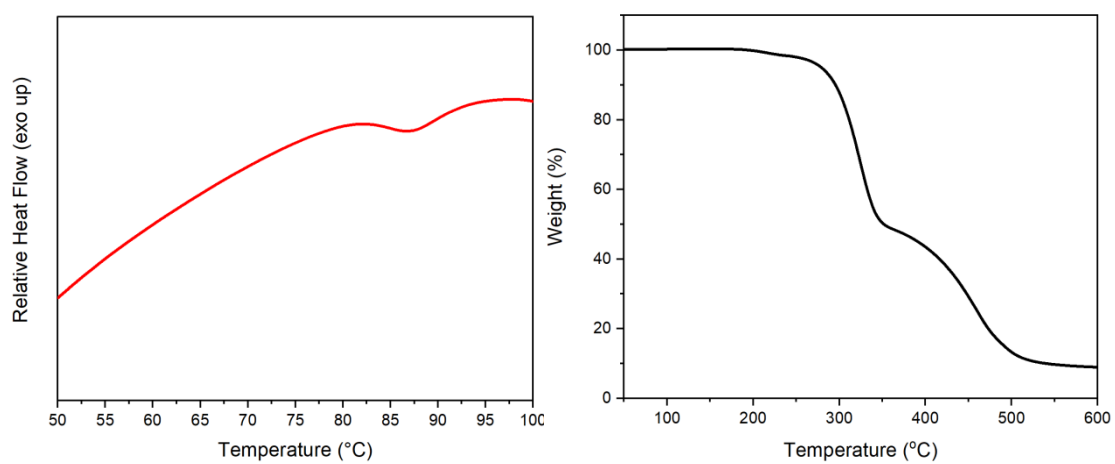
Supplementary Figure 19. DSC and TGA Spectra of 108 (2 h)



Supplementary Figure 20. DSC and TGA Spectra of 108 (2.5 h)



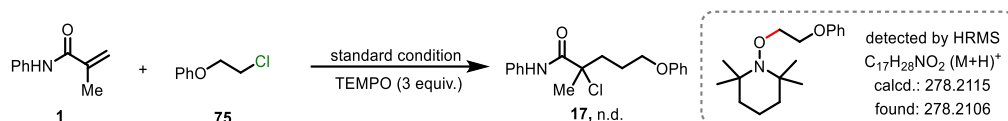
Supplementary Figure 21. DSC and TGA Spectra of 108 (3 h)



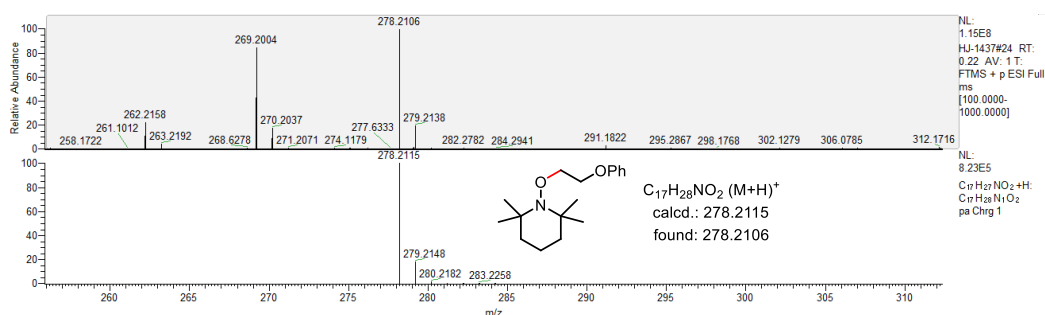
Supplementary Figure 22. DSC and TGA Spectra of 109

8. Mechanistic Studies

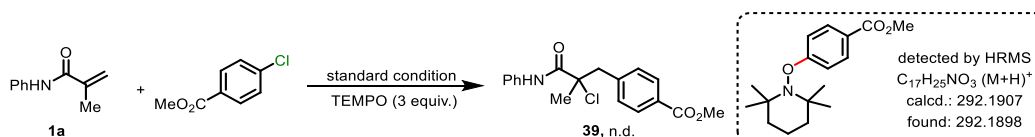
8.1 Radical trapping experiments



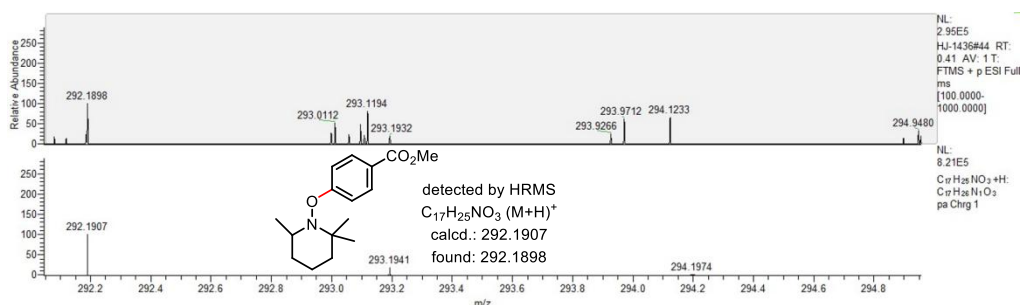
In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), **1** (0.1 mmol, 1.0 equiv.), TEMPO (46.6 mg, 0.3 mmol, 3.0 equiv.), and alkyl chloride **75** (0.3 mmol, 3 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W × 2) for 4 h at room temperature with vigorous stirring. After the reaction finished, the reaction mixture was analyzed by GC-MS. **17** was not detected, and the TEMPO-trapped radical adduct was detected by HRMS.



Supplementary Figure 23. The HRMS result for radical trapping with TEMPO (alkyl)

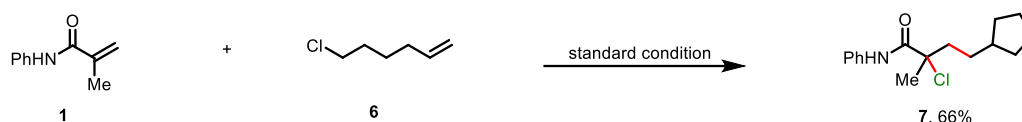


In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (1.8 mg, 0.005 mmol, 5.0 mol%), **1** (0.1 mmol, 1.0 equiv.), the aryl chloride (0.2 mmol, 2 equiv.), TEMPO (46.6 mg, 0.3 mmol, 3.0 equiv.), and MgSO₄ (36 mg, 0.3 mmol, 3.0 equiv.). Then, DMSO (0.5 mL) and EA (0.5 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W × 2) for 24 h at room temperature with vigorous stirring. After the reaction finished, the reaction mixture was analyzed by GC-MS. **39** was not detected, and the TEMPO-trapped radical adduct was detected by HRMS.

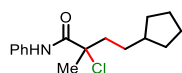


Supplementary Figure 24. The HRMS result for radical trapping with TEMPO (aryl)

8.2 Radical clock experiments



According to the general procedure A, in an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), **1** (0.1 mmol, 1.0 equiv.) and **6** (0.3 mmol, 3 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W × 2) for 4 h at room temperature with vigorous stirring. After completion of the reaction, the solvent was removed under vacuum and the resulting residue was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford only 5-exo-trig cyclization product **7** (18.3 mg, 66%).



2-chloro-4-cyclopentyl-2-methyl-N-phenylbutanamide (**7**, colorless oil)

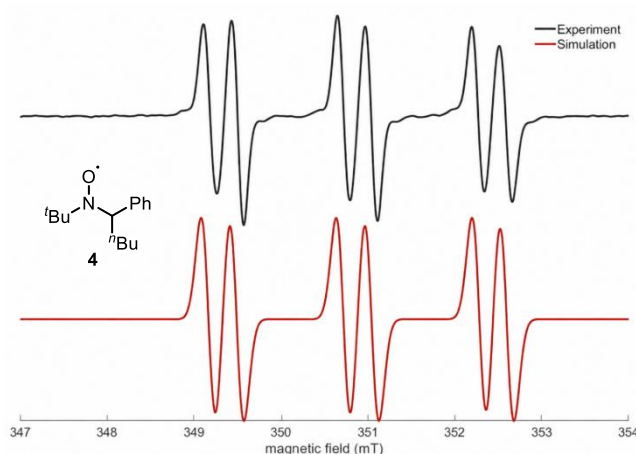
¹H NMR (500 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.62 – 7.51 (m, 2H), 7.42 – 7.31 (m, 2H), 7.21 – 7.11 (m, 1H), 2.32 – 2.21 (m, 1H), 1.97 – 1.89 (m, 1H), 1.85 (s, 3H), 1.80 – 1.71 (m, 3H), 1.64 – 1.55 (m, 3H), 1.53 – 1.45 (m, 2H), 1.44 – 1.35 (m, 1H), 1.14 – 1.02 (m, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 169.7, 137.2, 129.0, 124.9, 120.0, 75.0, 42.2, 39.8, 32.6, 32.5, 31.2, 30.0, 25.2, 25.2.

IR: ν = 2921, 1671, 1502, 1370, 1124, 1056, 1052, 916, 829, 690 cm⁻¹.

HRMS (ESI) calcd. for C₁₆H₂₃ClNO [M+H]⁺: 280.1463, found: 280.1455.

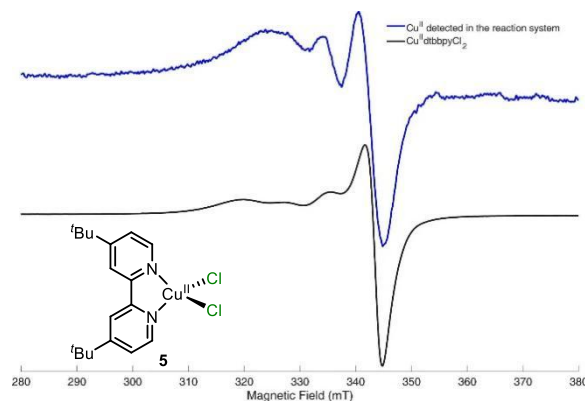
8.3 EPR experiments



Supplementary Figure 25. EPR spectrum of trapped *n*Bu radical by PBN. The continuous wave X-band EPR spectrum was obtained at 9.8526 GHz

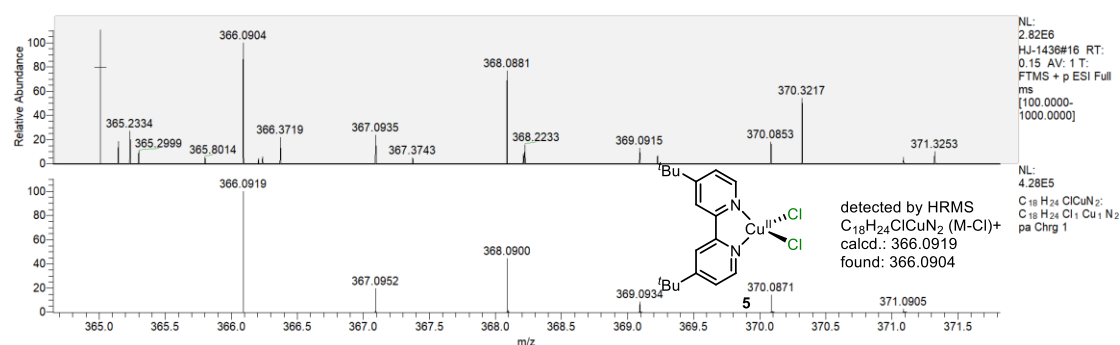
In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), **1** (0.1 mmol, 1.0 equiv.), **2** (31.2 μL, 0.3 mmol, 3 equiv.) and *N*-tert-butyl-α-phenylnitron (PBN) (35 mg, 0.2 mmol, 2 equiv.). Then, MTBE (0.3 mL) and HFIP (0.2 mL) were added into the vial. The vial was

sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W × 2) for 1 h at room temperature with vigorous stirring. After the reaction finished, the electron paramagnetic resonance (EPR) analysis of the reaction mixture revealed a strong radical signal (Supplementary Figure 25), which would be assigned to the PBN-trapped *n*-butyl radical according to the simulated spectrum (fitting result: $g = 2.006$, $A_N = 15.6$ G, $A_H = 3.2$ G).



Supplementary Figure 26. EPR spectrum of Cu^{II} species and **5**. The continuous wave X-band EPR spectra were obtained at 9.8545 GHz (Cu^{II} detected in the reaction system) and 9.8526 GHz (**5**)

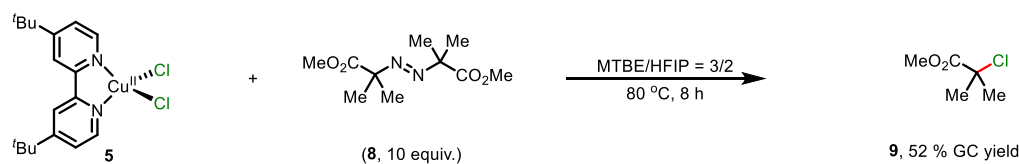
What's more, a Cu^{II} EPR signal was also detected in the above reaction system. To assign the EPR signal of this Cu^{II} species ($g_{\perp} = 2.01$, $g_{\parallel} = 2.32$, $A_{\perp} = 20$ G, $A_{\parallel} = 100$ G), we synthesized **5** according to reported procedures⁴. Its EPR spectrum in MTBE/HFIP mixed solvent (1.8 mg **5** in 0.3 mL MTBE & 0.2 mL HFIP) exhibited close alignment with the signal observed in our catalytic system ($g_{\perp} = 2.01$, $g_{\parallel} = 2.32$, $A_{\perp} = 25$ G, $A_{\parallel} = 104$ G).



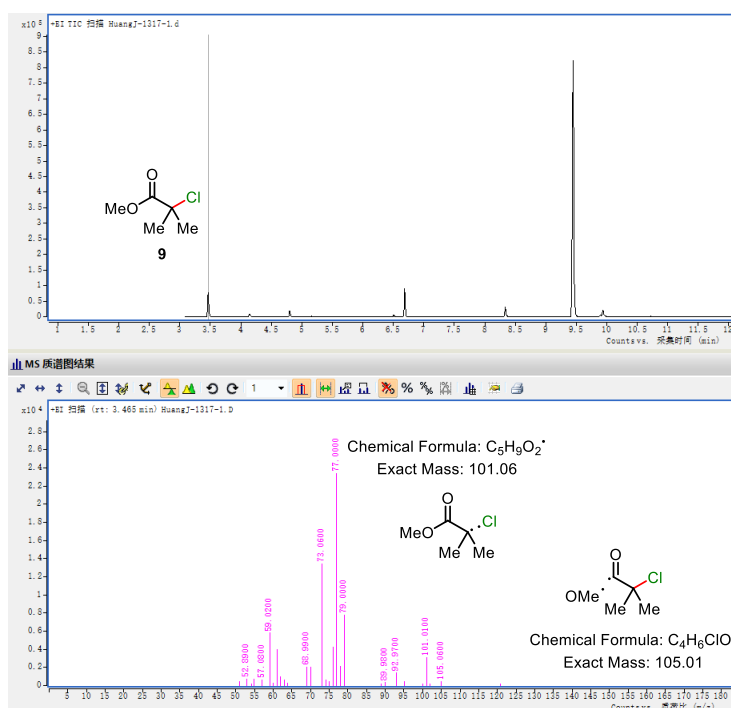
Supplementary Figure 27. **5** detected by HRMS in the model reaction

Furthermore, HRMS analysis of the model reaction mixture confirmed the presence of **5**, providing additional verification.

8.4 Cl transfer experiments



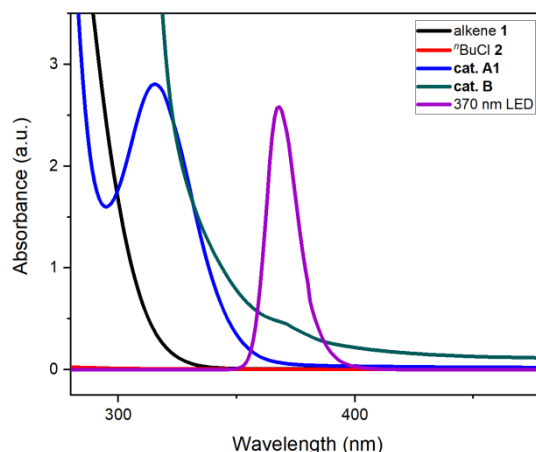
In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **5** (20.1 mg, 0.05 mmol, 1 equiv.) and **8** (109 μ L, 0.5 mmol, 10 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was stirred at 80 °C for 8 h. After the reaction finished, the reaction mixture was analyzed by GC-MS and GC.



Supplementary Figure 28. **9** detected by GC-MS

8.5 UV-vis absorption spectroscopic measurement

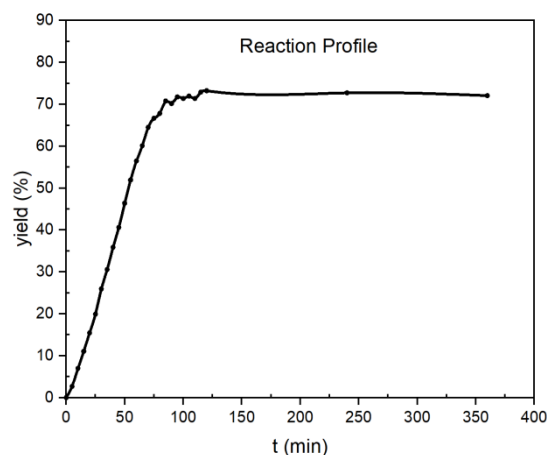
The UV-vis experiments were performed on F-7000 FL Spectrophotometer (Hitachi, Japan) with a quartz cuvette (10 mm path length). All of the samples were measured in the mixed solvent of MTBE/HFIP (3:2, degassed with a stream of N₂ for 1 h) with 100 μ M concentration.



Supplementary Figure 29. UV-vis spectroscopic absorption

8.6 The total reaction profile

In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), **1** (0.1 mmol, 1.0 equiv.), **2** (31.2 μ L, 0.3 mmol, 3 equiv.) and dodecane (23 μ L, 0.1 mmol, 1.0 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature with vigorous stirring. At 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 240, 360 min, 20 μ L the reaction mixture was carefully taken out by micro-syringe into 2.0 mL vial. Then 1.0 mL EA was added into the vial. The reaction mixture was analyzed by GC after filtration.



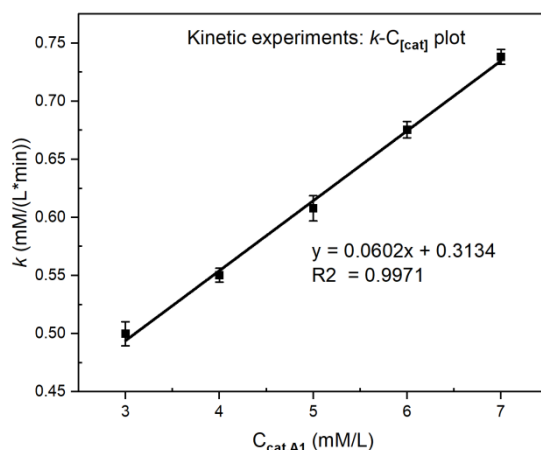
Supplementary Figure 30. The total reaction profile

8.7 Kinetic experiments

Dependence of the reaction rate on concentration of [cat.A1 + cat.B]

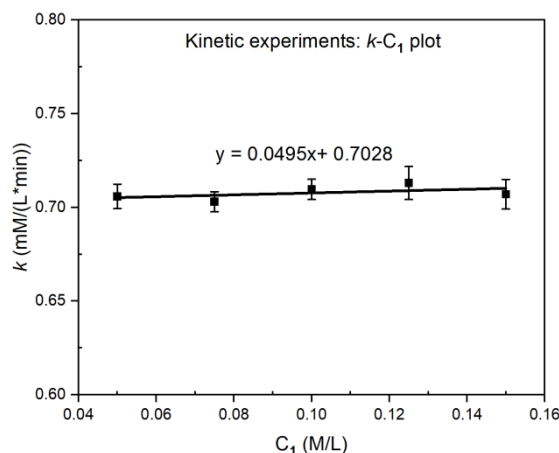
In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (3/4/5/6/7 mol%), **cat.B** (1.5/2/2.5/3/3.5 mol%), **1** (0.1 mmol, 1.0 equiv.), **2** (31.2 μ L, 0.3 mmol, 3 equiv.) and dodecane (23 μ L, 0.1 mmol, 1.0 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature with vigorous stirring. At 0, 5, 10, 15, 20, 25, 30 min, 20 μ L the reaction mixture was carefully taken out by micro-syringe into 2.0 mL

vial. Then 1.0 mL EA was added into the vial. The reaction mixture was analyzed by GC.



Supplementary Figure 31. Dependence of the reaction rate on concentration of [cat.A1 + cat.B]
Dependence of the reaction rate on concentration of 1

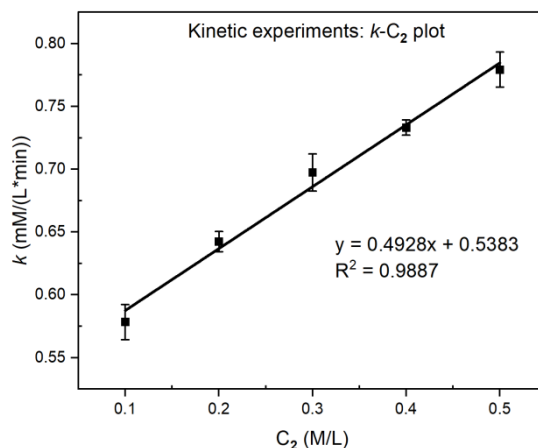
In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol), **cat.B** (0.9 mg, 0.0025 mmol), **1** (0.05/0.075/0.10/0.125/0.15 mmol), **2** (31.2 μL, 0.3 mmol) and dodecane (23 μL, 0.1 mmol, 1.0 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W × 2) at room temperature with vigorous stirring. At 0, 5, 10, 15, 20, 25, 30 min, 20 μL the reaction mixture was carefully taken out by micro-syringe into 2.0 mL vial. Then 1.0 mL EA was added into the vial. The reaction mixture was analyzed by GC.



Supplementary Figure 32. Dependence of the reaction rate on concentration of **1**

Dependence of the reaction rate on concentration of 2

In an N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol), **cat.B** (0.9 mg, 0.0025 mmol), **1** (16.1 mg, 0.10 mmol), **2** (0.1/0.2/0.3/0.4/0.5 mmol) and dodecane (23 μL, 0.1 mmol, 1.0 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W × 2) at room temperature with vigorous stirring. At 0, 5, 10, 15, 20, 25, 30 min, 20 μL the reaction mixture was carefully taken out by micro-syringe into 2.0 mL vial. Then 1.0 mL EA was added into the vial. The reaction mixture was analyzed by GC.

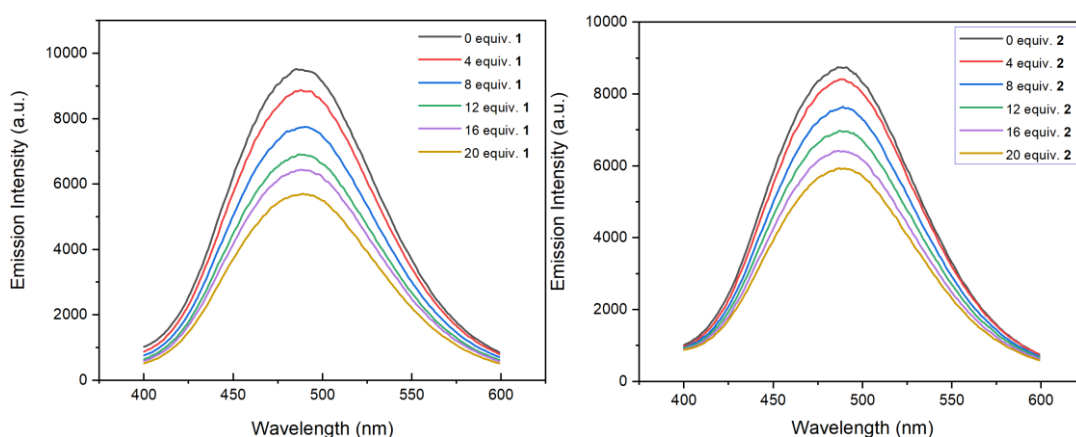


Supplementary Figure 33. Dependence of the reaction rate on concentration of **2**

The plots of K_{obs} suggest a zero-order kinetic dependence in **1**, and a first-order kinetic dependence in [**cat.A1** + **cat.B**] and **2**. Kinetic studies excluded radical addition as the rate-determining step, but either C–Cl bond activation or reformation may be possible.

8.8 Luminescence quenching experiment

The luminescence quenching experiment was performed using a F-7000 FL Spectrophotometer (Hitachi, Japan). The experiments were carried out in 2×10^{-4} mol/L of **cat.A1** in MTBE/HFIP at 25 °C. The excitation wavelength was 320 nm and the emission intensity was collected at 488 nm. Luminescence quenching of **cat.A1** was observed with both components. However, the detection of isomerized product **1'** during condition screening indicates energy transfer between **cat.A1** and **1**. Thus, the primary reaction pathway remains initiated through single-electron reduction of 1-chlorobutane (**2**).

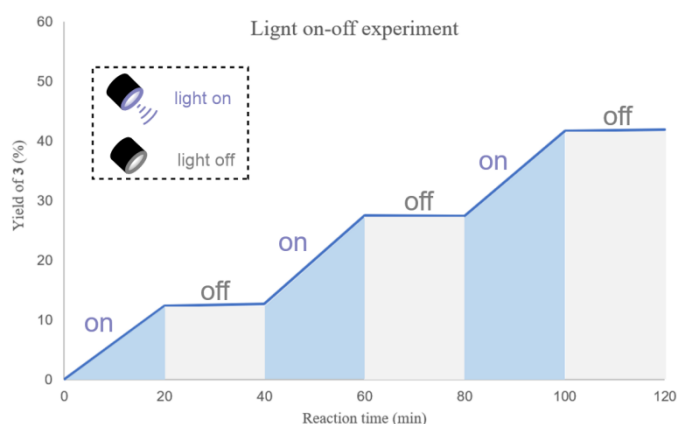


Supplementary Figure 34. Luminescence quenching experiment

8.9 Light on/off experiment

In an N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), **1** (16.1 mg, 0.1 mmol, 1.0 equiv.), **2** (31.2 μ L, 0.3 mmol, 3 equiv.) and dodecane (23 μ L, 0.1 mmol, 1.0 equiv.).

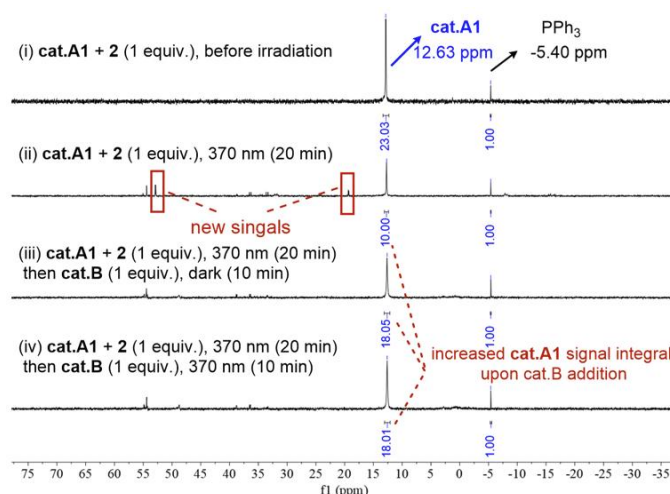
Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature with vigorous stirring. The process of photocatalytic reaction with and without light was monitored by GC. It was found that the formation of **3** needed continuous irradiation of light.



Supplementary Figure 35. Light on/off experiment

8.10 ^{31}P NMR monitoring experiments

To verify the relay process between dinuclear and mononuclear copper catalysts, we performed stepwise catalyst addition experiments. Initial irradiation of dinuclear catalyst **cat.A1** with **2** generated multiple distinct ^{31}P NMR signals. Subsequent addition of mononuclear catalyst **cat.B**, followed by stirring under both light and dark conditions, resulted in partial restoration of the original **cat.A1** phosphine signature as quantified by signal integration. This observation demonstrates that **cat.B** engages in a light-independent relay with the oxidized dinuclear species to regenerate catalytically active **cat.A1**.



Supplementary Figure 36. ^{31}P NMR monitoring experiments

The detailed operating steps are as follows (For ^{31}P NMR testing, the reaction solution (~ 0.5 mL) was drawn into an NMR tube inside a glovebox under N_2 atmosphere. A capillary tube containing the internal standard solution—triphenylphosphine in deuterated chloroform (0.02 M)—was sealed and placed inside the NMR tube. The NMR tube was then capped, and the rim of the cap was sealed with laboratory film. Finally, the NMR tube was removed from the glovebox and the phosphorus spectrum was monitored as soon as possible.):

Vial 1 (i): In N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (18.4 mg, 0.01 mmol, 1 equiv.), **2** (1.0 μ L, 0.01 mmol, 1 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature for 20 min with vigorous stirring. ³¹P NMR of the mixture was tested.

Vial 2 (ii): In N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (18.4 mg, 0.01 mmol, 1 equiv.), **2** (1.0 μ L, 0.01 mmol, 1 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature for 20 min with vigorous stirring. Subsequently, the vial was transferred back into the glovebox, where **cat. B** (3.7 mg, 0.01 mmol, 1 equiv.) was added. After sealing the vial, it was removed from the glovebox and stirred in the dark for 10 min. ³¹P NMR of the mixture was tested.

Vial 3 (iii): In N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (18.4 mg, 0.01 mmol, 1 equiv.), **2** (1.0 μ L, 0.01 mmol, 1 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature for 20 min with vigorous stirring. Subsequently, the vial was transferred back into the glovebox, where **cat. B** (3.7 mg, 0.01 mmol, 1 equiv.) was added. After sealing the vial, it was removed from the glovebox and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature for 10 min with vigorous stirring. ³¹P NMR of the mixture was tested.

8.11 Time-yield profiles and corresponding ³¹P NMR monitoring experiments.

Time-yield profiling of the model reaction revealed distinct catalytic behaviors: When only **cat.A1** was employed, the reaction reached completion within 80 minutes but afforded **3** in diminished yield (~ 30%) with substantial polymeric precipitate formation. In contrast, inclusion of **cat.B** significantly enhanced the yield to 74% - consistent with our design rationale that accelerating the C–Cl bond formation outcompetes polymerization side reactions. Complementary ³¹P NMR monitoring further demonstrated sustained high concentrations of photoactivated **cat.A1** throughout the reaction when **cat.B** was present. Conversely, the **cat.A1**-only system exhibited multiple phosphorous species. We attribute this degradation to radical interception by polymerization-depleted alkenes, ultimately triggering deleterious side reactions including hydrogen atom abstraction between alkyl radicals and oxidized copper species.

The detailed operating steps are as follows (For ³¹P NMR testing, the reaction solution (~ 0.5 mL) was drawn into an NMR tube inside a glovebox under N₂ atmosphere. A capillary tube containing the internal standard solution—triphenylphosphine in deuterated chloroform (0.01 M)—was sealed and placed inside the NMR tube. The NMR tube was then capped, and the rim of the cap was sealed with laboratory film. Finally, the NMR tube was removed from the glovebox and the phosphorus spectrum was monitored as soon as possible.):

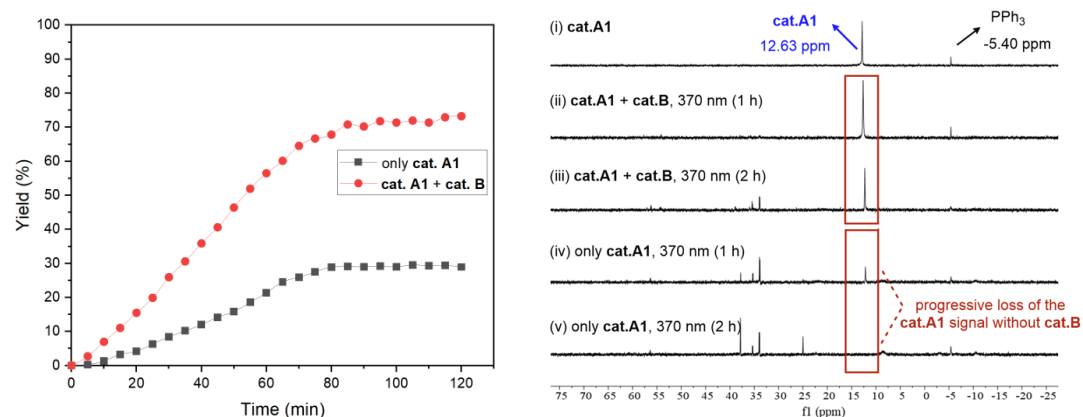
Vial 1: In N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **1** (16.1 mg, 0.1 mmol, 1.0 equiv.), **2** (31.2 μ L, 0.3 mmol, 3 equiv.) and dodecane (23 μ L, 0.1 mmol, 1.0 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) for 2 h at room temperature with vigorous stirring. At 5,

10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120 min, 20 μL the reaction mixture was carefully taken out by micro-syringe into 2.0 mL vial. Then 1.0 mL EA was added into the vial. The reaction mixture was analyzed by GC after filtration.

Vial 1': In N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **1** (16.1 mg, 0.1 mmol, 1.0 equiv.) and **2** (31.2 μL , 0.3 mmol, 3 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature with vigorous stirring. At 1, 2 h, ^{31}P NMR of the mixture was tested.

Vial 2: In N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), **1** (16.1 mg, 0.1 mmol, 1.0 equiv.), **2** (31.2 μL , 0.3 mmol, 3 equiv.) and dodecane (23 μL , 0.1 mmol, 1.0 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) for 2 h at room temperature with vigorous stirring. At 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120 min, 20 μL the reaction mixture was carefully taken out by micro-syringe into 2.0 mL vial. Then 1.0 mL EA was added into the vial. The reaction mixture was analyzed by GC after filtration.

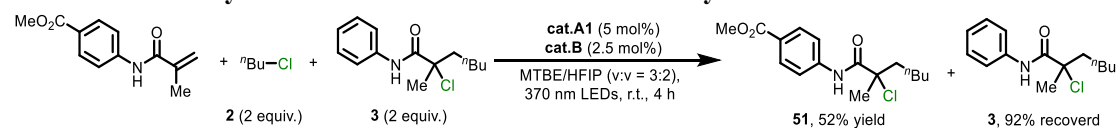
Vial 2': In N_2 -filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), **1** (16.1 mg, 0.1 mmol, 1.0 equiv.) and **2** (31.2 μL , 0.3 mmol, 3 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) at room temperature with vigorous stirring. At 1, 2 h, ^{31}P NMR of the mixture was tested.



Supplementary Figure 37. Time-yield profiles and corresponding ^{31}P NMR monitoring experiments

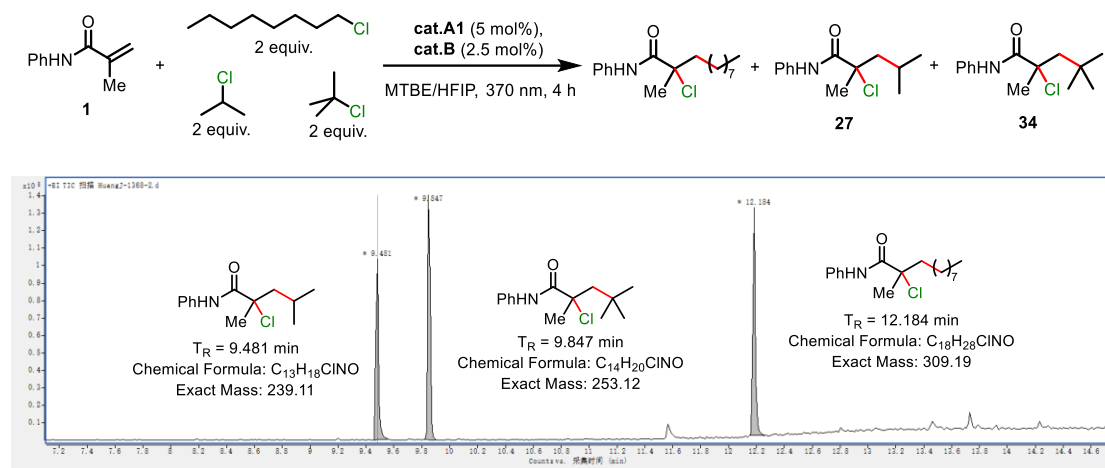
8.12 The issues of selectivity in ATRA reactions

• Chemoselectivity between activated and unactivated alkyl chlorides



In N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), methyl 4-methacrylamidobenzoate (21.9 mg, 0.1 mmol, 1.0 equiv.), **2** (21.7 μ L, 0.2 mmol, 2.0 equiv.) and **3** (50.6 mg, 0.2 mmol, 2.0 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) for 4 h at room temperature with vigorous stirring. After the reaction finished, the reaction mixture was analyzed by GC-MS (**3**: 93% recovery by GC; **51**: did not elute as a peak in GC, its GC yield could not be calculated). The solvent was then removed under vacuum and the resulting residue was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as eluent to afford ATRA product **51** in 52% isolated yield (16.3 mg), while compound **3** was recovered in 92% isolated yield (46.4 mg).

● **Chemoselectivity between differently hindered unactivated alkyl chlorides**



Supplementary Figure 38. Competitive experiments with differently hindered chloroalkanes

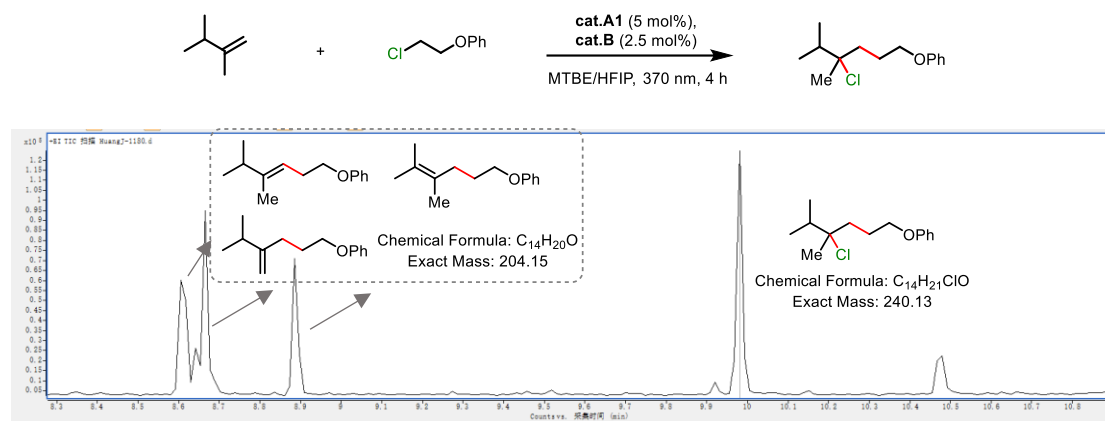
In N₂-filled glove-box, an oven-dried vial (4 mL) equipped with a magnetic stir bar was charged with **cat.A1** (9.2 mg, 0.005 mmol, 5.0 mol%), **cat.B** (0.9 mg, 0.0025 mmol, 2.5 mol%), **1** (16.1 mg, 0.1 mmol, 1.0 equiv.), 1-chlorooctane (34.0 μ L, 0.2 mmol, 2.0 equiv.), 2-chloropropane (18.3 μ L, 0.2 mmol, 2.0 equiv.), and tert-butyl chloride (21.8 μ L, 0.2 mmol, 2.0 equiv.). Then, MTBE (0.6 mL) and HFIP (0.4 mL) were added into the vial. The vial was sealed, removed from the glove-box and was irradiated under 370 nm LEDs (40 W $\times$ 2) for 4 h at room temperature with vigorous stirring. After the reaction finished, the reaction mixture was analyzed by GC-MS.

Supplementary Table 20. Competitive Experiments with differently hindered chloroalkanes

Alkyl Chlorides	BDE (kcal/mol)	T _R (min)	Peak area	ratio
1-chlorooctane	84.5	12.184	161606	1.13
2-chloropropane	84.6	9.481	143439	1
tert-butyl chloride	84.1	9.847	181664	1.27

Subsequently, we added equimolar amounts of 1-chlorooctane, 2-chloropropane, and tert-butyl chloride to the reaction, and found that the product yields were comparable. This further demonstrates that our ATRA reaction is insensitive to the steric hindrance of chloroalkanes.

• Chemoselectivity with unactivated alkenes



Supplementary Figure 39. ATRA reactions between alkyl chlorides and unactivated alkenes
 We further investigated ATRA reactions between alkyl chlorides and unactivated alkenes. Given the electronic incompatibility between nucleophilic alkyl radicals and electron-rich olefins, 2,3-dimethylbut-1-ene was strategically selected as the radical acceptor to leverage the thermodynamic stability of the tertiary radical intermediate. However, GC-MS analysis revealed multiple olefinic isomers arising from elimination pathways coexisting with the desired product.

9. DFT Studies

All density functional theory (DFT) calculations were performed using ORCA 5.0.3.^{13,14} All geometry optimizations were conducted with the PBE functional¹⁵, utilizing the D3 version of Grimme's dispersion correction¹⁶. The def2-TZVP¹⁷ basis set was employed to describe the copper atom, and all other atoms were described by the def2-SVP¹⁷ basis set. To incorporate solvation effects of methyl tert-butyl ether (MTBE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), the Conductor-like Polarizable Continuum Model (CPCM)^{18,19} was employed. Vibrational frequency analyses were subsequently performed at the same level of theory to characterize the optimized structures as local minima (zero imaginary frequencies) or transition states (one imaginary frequency). Thermal corrections to the Gibbs free energies at 298.15 K were evaluated using the Shermo 2.6.2²⁰. Low-frequency vibrational contributions to the entropy were treated using Grimme's entropy interpolation scheme. Intrinsic reaction coordinate (IRC) calculations^{21,22} were performed to confirm the connectivity of each transition state structure to its corresponding reactant and product minima. Critically, ^{BS}TS3 and ^{BS}TS3' both adopt broken-symmetry configurations, as their respective T₁ or S₀ states exhibit higher energies than the broken-symmetry counterparts. These broken-symmetry transition states represent energetically favored pathways.

Single-point energy calculations were carried out with the M06L functional²³ and the def2-TZVP basis set¹⁷ on all atoms at the optimized geometries. These single-point calculations also incorporated CPCM^{18,19} to account for solvent (MTBE/HFIP) effects and refine the electronic energies. The reported Gibbs free energies were obtained by combining the solution-phase electronic energies with the thermal corrections derived from frequency calculations performed at the corresponding CPCM-solvated level. All thermodynamic quantities were evaluated at 298.15 K and are reported in kcal mol⁻¹ using a standard state of 1 atm. All optimized molecular structures and the inter-fragment interactions derived from the independent gradient model based on Hirshfeld partition (IGMH) analyses were rendered using the VMD 1.9.3²⁴. IGMH analyses were computed using Multiwfn 3.8 dev²⁵. Steric maps were computed using SambVca 2.0^{26,27}.

The outer-sphere pathway was modeled as a concerted dissociative electron transfer (DET) from the triplet excited dinuclear copper catalyst (³cat.A1*) to 1-chlorobutane, in which electron transfer and C–Cl bond cleavage occur in a single elementary step. Following electron transfer to 1-chlorobutane, C–Cl bond cleavage occurs, necessitating consideration of the bond dissociation free energy (BDFE) at this site. The energy barrier of the outer-sphere SET ($\Delta G^\ddagger$)^{28,29} can be estimated by:

$$\Delta G^\ddagger = \frac{(\Delta G_0 + \lambda)^2}{4\lambda} = \frac{\lambda}{4} \left(1 + \frac{\Delta G_0}{\lambda}\right)^2 \quad (\text{S1})$$

$$\lambda = \lambda_i + \lambda_0 + D_R \quad (\text{S2})$$

where ΔG_0 is the Gibbs free energy change, λ is total reorganization energy, comprising the internal energy (λ_i), solvent external energy (λ_0) and bond dissociation free energy (D_R). And the internal reorganization energy λ_i was estimated by the 4-point rule, according to Marcus theory:

$$\lambda_{i1} = [E^{D^*}(Q_P) + E^A(Q_P)] - [E^{D^*}(Q_R) + E^A(Q_R)] \quad (\text{S3})$$

$$\lambda_{12} = [E^{D^+}(Q_R) + E^{A^-}(Q_R)] - [E^{D^+}(Q_P) + E^{A^-}(Q_P)] \quad (\text{S4})$$

$$\lambda_i = \frac{\lambda_{i1} + \lambda_{i2}}{2} \quad (\text{S5})$$

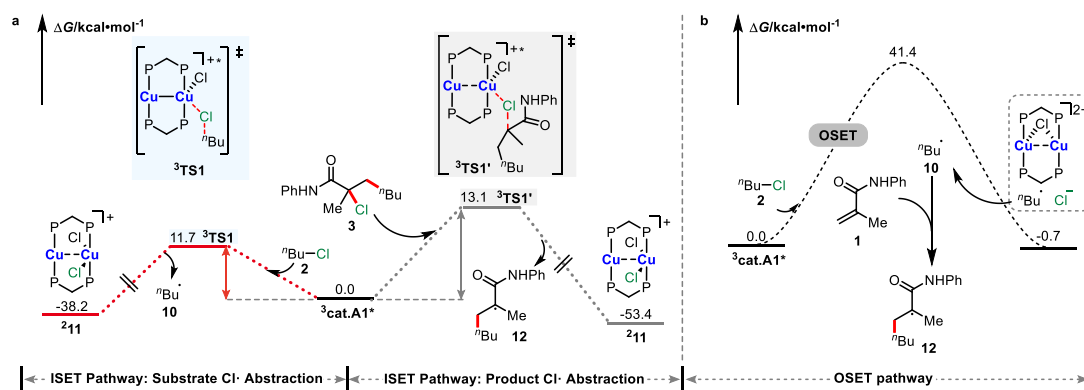
Here, Q_R and Q_P denote the equilibrium geometries of the reactant-state (D^*+A) and electron-transfer product-state (D^++A^-) configurations, respectively. λ_{i1} is the energy required to distort the reactant-state species from Q_R to Q_P while retaining the D^*+A electronic configuration. In the reverse construction, λ_{i2} is the energy required to distort the electron-transfer product-state species from Q_P to Q_R while retaining the D^++A^- electronic configuration. The internal reorganization energy, λ_i , was taken as the average of these two contributions.

The external reorganization energy can be approximated as:

$$\lambda_0 = 332 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon} \right) \quad (\text{S6})$$

$$R = a_1 + a_2 \quad (\text{S7})$$

Here, a_1 and a_2 represent the effective radii of the electron donor and acceptor, respectively. R denotes the center-to-center separation between the donor and acceptor; under the contact-sphere approximation employed here, R was taken as $a_1 + a_2$. ϵ_{op} and ϵ denote the optical and static dielectric constants of the solvent medium, respectively. For the MTBE/HFIP solvent system used in this work, $\epsilon_{op} = 1.78$ and $\epsilon = 9.90$.

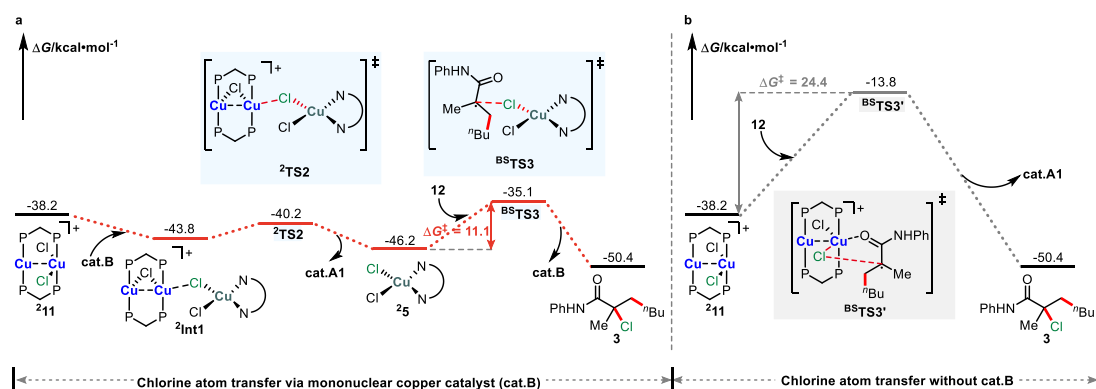


Supplementary Figure 40. DFT calculation results. Free energy profiles (in kcal mol⁻¹) for the C–Cl bond activation step, computed at the M06L/def2-TZVP/CPCM(MTBE-HFIP)//PBE(D3)/def2-SVP/def2-TZVP/CPCM(MTBE-HFIP) level of theory. **a**, Inner-sphere electron transfer (ISET)-Enabled C–Cl Activation via Cl· Abstraction: Substrate vs Product Capture. **b**, Outer-sphere electron transfer (OSET) pathway.

Building upon prior studies^{2,30,31} and experimental evidence, computations were initiated from the photoexcited state of the dinuclear copper catalyst (³cat.A1*), with primary focus on the C–Cl bond activation step that commences the catalytic cycle. At this entry stage, we evaluated inner-sphere electron transfer (ISET) versus outer-sphere electron transfer (OSET) scenarios. The OSET pathway

is kinetically inaccessible, with a prohibitively high barrier ($\Delta G^\ddagger = 41.4 \text{ kcal mol}^{-1}$), thereby supporting an ISET-enabled chlorine-atom abstraction (Cl abstraction/XAT) manifold for radical generation. Within the ISET framework, we next examined two competing Cl $\cdot$ -capture channels: chlorine-atom abstraction from the substrate alkyl chloride via $^3\text{TS1}$ ($\Delta G^\ddagger = 11.7 \text{ kcal mol}^{-1}$) versus chlorine-atom back-abstraction from the product via $^3\text{TS1}'$ ($\Delta G^\ddagger = 13.1 \text{ kcal mol}^{-1}$) (Supplementary Figure 40). Although the barrier difference is modest ($\Delta\Delta G^\ddagger = 1.4 \text{ kcal mol}^{-1}$), it establishes a clear kinetic bias toward the substrate-derived pathway. Notably, despite the lower C–Cl bond dissociation energy (BDE) of the product, the product-derived channel remains higher in energy barrier.

Subsequent investigations focused on the chlorine-atom transfer step to elucidate the role of the mononuclear copper catalyst (**cat.B**) within the tiered system. The Cl-bound binuclear Cu species ^2II , generated post C–Cl cleavage, transfers its chlorine atom to **cat.B** via a low-barrier transition state $^2\text{TS2}$ ($\Delta G^\ddagger = 3.6 \text{ kcal mol}^{-1}$), yielding the Cl–Cu(II) complex $^2\text{5}$ while regenerating the dinuclear catalyst **cat.A1**. The low barrier associated with $^2\text{TS2}$ underscores the kinetic feasibility and efficiency of the catalyst relay process between binuclear and mononuclear copper species. To probe the final halogenation step, two distinct pathways for chlorine atom transfer to radical intermediate **12** were evaluated: (i) via the mononuclear intermediate $^2\text{5}$ (transition state $^{\text{BS}}\text{TS3}$, Supplementary Figure 41a), and (ii) via the binuclear intermediate ^2II (transition state $^{\text{BS}}\text{TS3}'$, Supplementary Figure 41b). The mononuclear pathway proceeds with a barrier of $\Delta G^\ddagger = 11.1 \text{ kcal mol}^{-1}$, whereas direct transfer from the binuclear species requires a substantially higher barrier ($\Delta G^\ddagger = 24.4 \text{ kcal mol}^{-1}$). This energy difference ($\Delta\Delta G^\ddagger = 13.3 \text{ kcal mol}^{-1}$) supports the kinetic superiority of the tiered copper relay system for halogen-atom transfer.



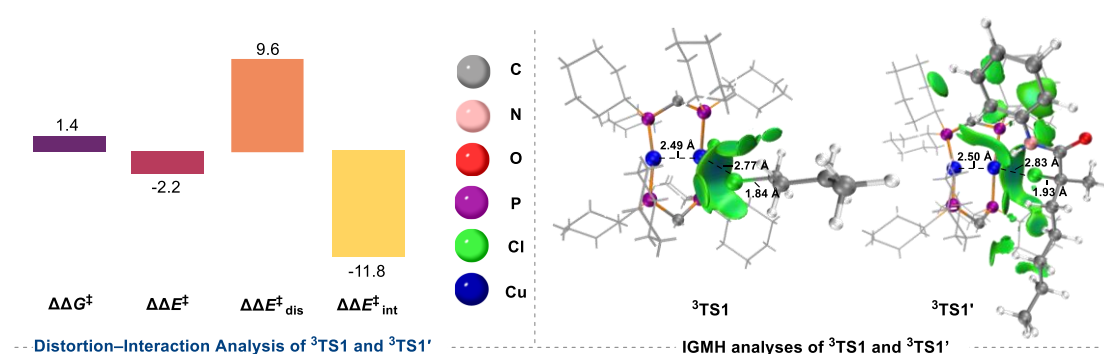
Supplementary Figure 41. DFT calculations results. Free energy profiles (in kcal mol⁻¹) for the chlorine-atom transfer step, computed at the M06L/def2-TZVP/CPCM(MTBE-HFIP)/PBE(D3)/def2-SVP/def2-TZVP/CPCM(MTBE-HFIP) level of theory. **a**, Chlorine atom transfer via mononuclear copper catalyst (**cat.B**). **b**, Chlorine atom transfer without mononuclear copper catalyst (**cat.B**).

As described in the distortion-interaction energy model^{32,33}, the electronic energy barriers $\Delta E^\ddagger$ can be decomposed into the distortion energy ΔE_{dist} and the interaction energy ΔE_{int} ($\Delta E^\ddagger = \Delta E_{\text{dist}} + \Delta E_{\text{int}}$). First, we investigated the counterintuitive selectivity during the C–Cl bond activation step by comparing transition states $^3\text{TS1}$ and $^3\text{TS1}'$ (Supplementary Figure 42, 44). The photoexcited dinuclear copper catalyst ($^3\text{cat.A1}^*$) was defined as Fragment 1 (Frag-1), and the corresponding reactant—either substrate **2** (for $^3\text{TS1}$) or product **3** (for $^3\text{TS1}'$) was defined as Fragment 2 (Frag-

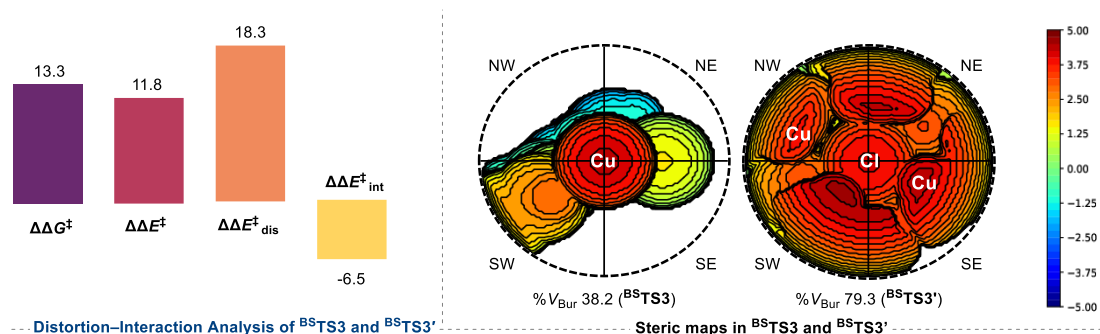
2). The results demonstrate that the substrate-derived pathway ($^3\text{TS1}$) exhibits a lower free-energy barrier primarily because its distortion energy is significantly lower than that of the product-derived pathway ($^3\text{TS1}'$) ($\Delta\Delta E_{\text{dist}}^\ddagger = 9.6 \text{ kcal mol}^{-1}$). This substantial advantage in distortion energy dictates the overall barrier trend, allowing $^3\text{TS1}$ to overcome its relative disadvantage in interaction energy ($\Delta\Delta E_{\text{int}}^\ddagger = -11.8 \text{ kcal mol}^{-1}$). The pronounced geometric strain in the product-derived pathway arises from the greater steric congestion between product **3** and the dinuclear copper catalyst. To attain the transition-state geometry for C–Cl activation, the reacting fragments must therefore undergo more extensive structural distortion than in the substrate-derived pathway ($^3\text{TS1}$). The resulting increase in distortion energy contributes to the higher free-energy barrier associated with $^3\text{TS1}'$. Furthermore, we applied the model to analyze the substantial difference in the barriers between the tiered copper synergy catalytic pathway ($^{\text{BS}}\text{TS3}$) and the single-catalyst pathway ($^{\text{BS}}\text{TS3}'$) (Supplementary Figure 43, 44). For transition states $^{\text{BS}}\text{TS3}$ and $^{\text{BS}}\text{TS3}'$, the radical intermediate **12** was defined as Fragment 2, and the rest of the system as Fragment 1. The results, presented in **Supplementary Table 21**, demonstrate that the difference in energy barriers between $^{\text{BS}}\text{TS3}$ and $^{\text{BS}}\text{TS3}'$ is primarily attributed to distortion energy. Specifically, the higher distortion energy of $^{\text{BS}}\text{TS3}'$ is associated with the larger buried volume^{26,27} at its copper center, which reflects a more sterically congested reactive environment. This congestion imposes greater geometric constraints on the reacting fragments, requiring more extensive structural distortion to attain a geometry suitable for chlorine transfer to radical intermediate **12**.

Supplementary Table 21. Distortion–interaction analysis results for $^3\text{TS1}$, $^3\text{TS1}'$, $^{\text{BS}}\text{TS3}$ and $^{\text{BS}}\text{TS3}'$ (energies in kcal mol^{-1}).

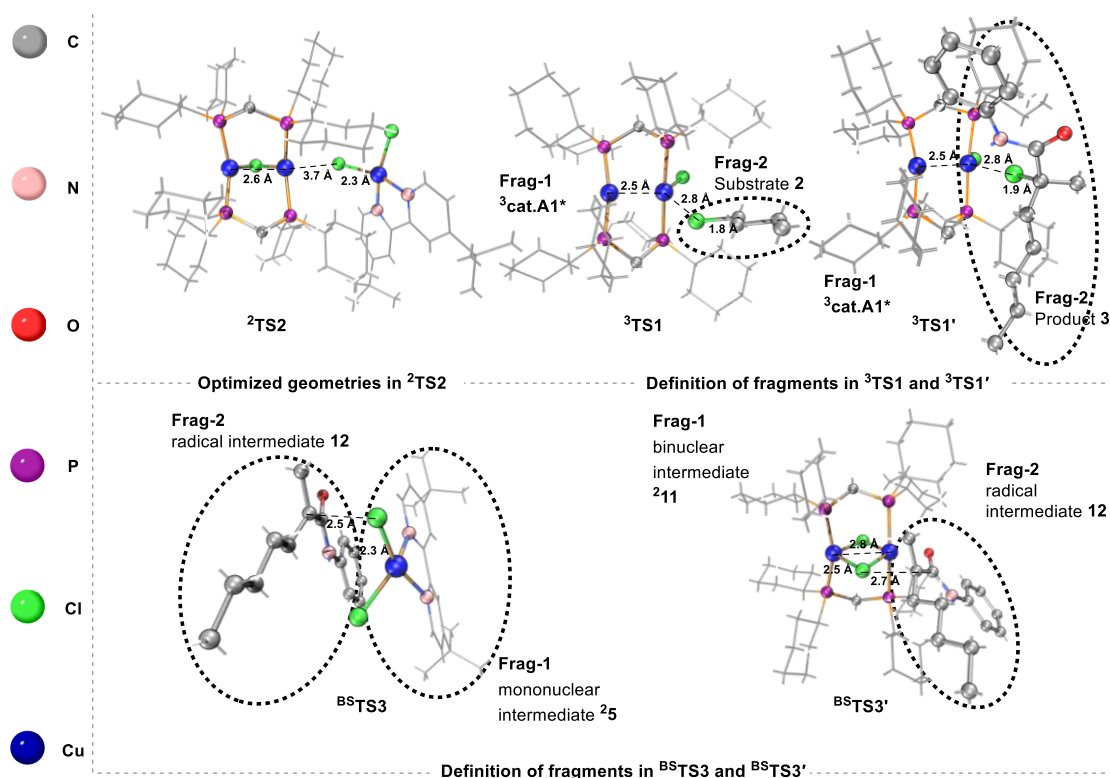
Transition State	$\Delta G^\ddagger$	$\Delta E^\ddagger$	ΔE_{dist}	ΔE_{int}
$^3\text{TS1}$	11.70	-5.16	3.58	-8.74
$^3\text{TS1}'$	13.10	-7.38	13.15	-20.53
$^{\text{BS}}\text{TS3}$	11.10	-6.80	7.10	-13.90
$^{\text{BS}}\text{TS3}'$	24.40	4.99	25.43	-20.44



Supplementary Figure 42. Distortion–interaction analyses comparing $^3\text{TS1}$ and $^3\text{TS1}'$, and IGMH analysis of $^3\text{TS1}$ and $^3\text{TS1}'$.



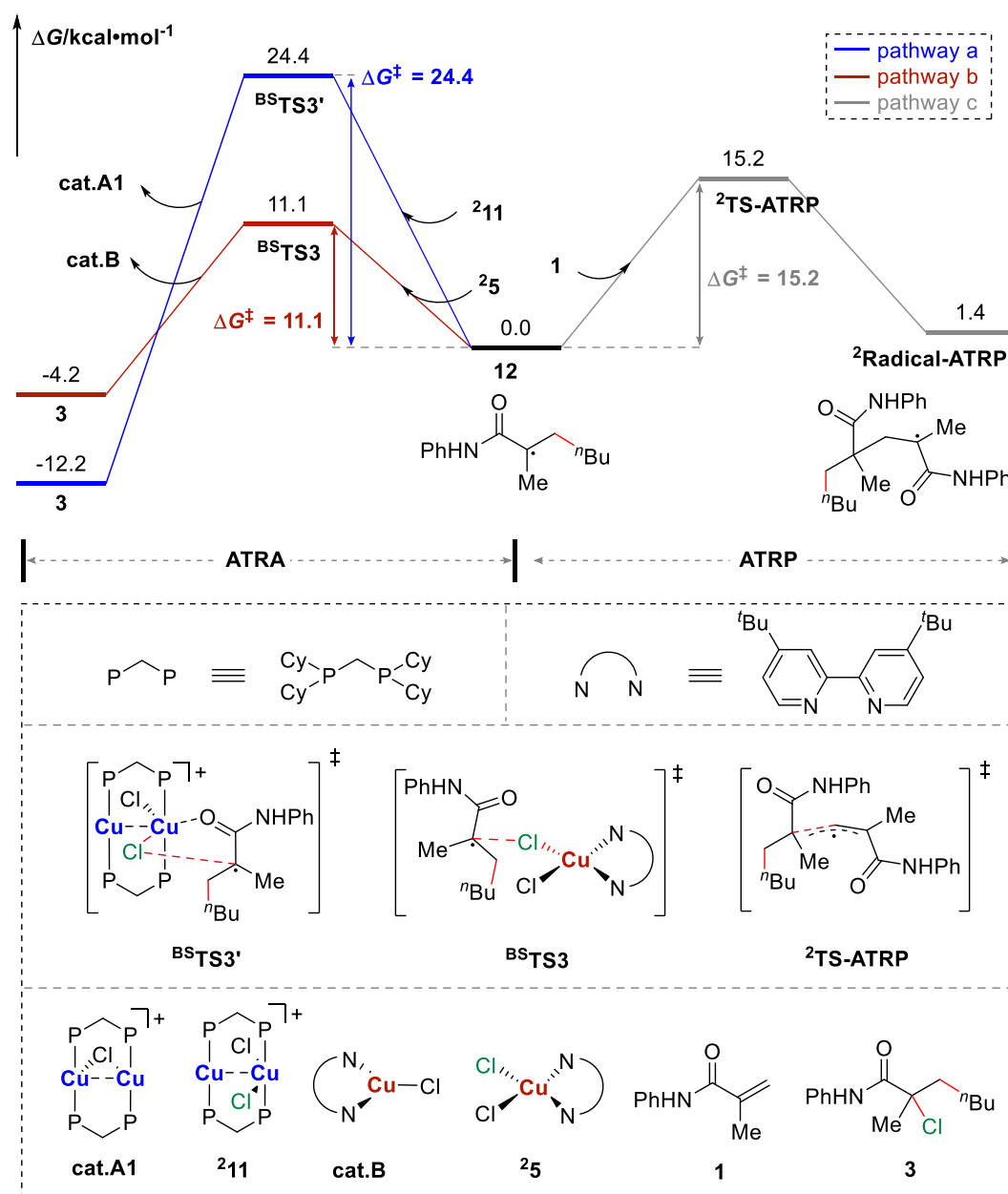
Supplementary Figure 43. Distortion-interaction analyses comparing $B^S TS3$ and $B^S TS3'$, and steric maps of $B^S TS3$ and $B^S TS3'$.



Supplementary Figure 44. Optimized geometries in 2^TS2 , and definition of fragments in 3^TS1 , $3^TS1'$, $B^S TS3$ and $B^S TS3'$.

To further elucidate how the tiered copper system enables switchable selectivity between ATRA and ATRP, we compared two ATRA pathways and one ATRP pathway starting from the common radical intermediate **12**. After C–Cl bond cleavage mediated by the photoexcited dinuclear copper catalyst $3^{cat}.A1^*$ and subsequent radical addition, **12** emerges as the key branching intermediate that determines the reaction outcome. In the presence of the mononuclear relay component **cat.B**, the Cl-bound dinuclear copper species 2^{11} first transfers its chlorine atom to **cat.B** through a low-barrier relay process, generating the cat.B-derived Cl–Cu(II) species 2^5 . **12** then receives a chlorine atom from 2^5 via $B^S TS3$ to afford the ATRA product **3**, with an activation barrier of only 11.1 kcal mol^{–1}. In contrast, direct chlorine-atom transfer from the dinuclear copper species 2^{11} to **12** via $B^S TS3'$ requires a much higher barrier of 24.4 kcal mol^{–1}, indicating that the dinuclear copper species alone is not an efficient terminal chlorine-atom donor.

Importantly, in the absence of the cat.B-mediated mononuclear chlorine-transfer channel, the reaction pathway of **12** is switched. Rather than undergoing direct chlorine-atom transfer from **211** to form the ATRA product, **12** preferentially adds to another molecule of alkene **1** through the ATRP-type transition state **²TS-ATRP**, with a barrier of 15.2 kcal mol⁻¹, which is substantially lower than that of direct chlorine transfer from the dinuclear copper species. Thus, **cat.B** does not merely enhance the overall efficiency of the transformation; instead, it provides a kinetically preferred Cl-atom transfer channel that redirects **12** from ATRP chain propagation toward productive ATRA termination.



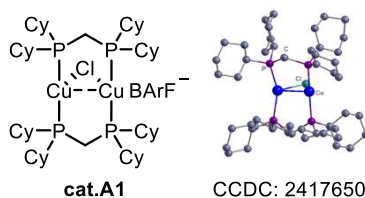
Supplementary Figure 45. DFT calculations results for switchable ATRA/ATRP selectivity. Free energy profiles, in kcal mol⁻¹, for the competing ATRA and ATRP pathways from the common radical intermediate **12**, computed at the M06L/def2-TZVP/CPCM(MTBE-HFIP)//PBE(D3)/def2-SVP/def2-TZVP/CPCM(MTBE-HFIP) level of theory. **Pathway a**, direct chlorine-atom transfer from the Cl-bound dinuclear copper species **211** to **12** to afford the ATRA product **3**. **Pathway b**,

chlorine-atom transfer from the cat.B-derived Cl–Cu(II) species **25** to **12** to afford the ATRA product **3**. **Pathway c**, addition of **12** to another molecule of alkene **1** to enter the ATRP-type chain-growth pathway.

These computational results reveal that the tiered copper catalytic system assigns C–Cl bond activation and C–Cl bond reconstruction to distinct copper components: the dinuclear copper catalyst enables efficient radical generation, whereas the mononuclear copper catalyst ensures rapid and selective chlorine-atom return. By controlling the participation of **cat.B**, the fate of radical intermediate **12** can therefore be switched between ATRA and ATRP-type pathways, enabling switchable chlorine atom transfer reactivity. This mechanistic picture not only rationalizes the experimentally observed selectivity divergence, but also provides theoretical support for the central concept of "Switchable Chlorine Atom Transfer Reactions": programmable conversion of unactivated organochlorides between small-molecule ATRA synthesis and polymer-forming ATRP-type through catalyst-defined chlorine-atom transfer pathways.

2. X-Ray Crystal Data

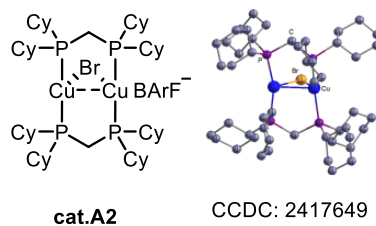
Compound **cat.A1** was crystallized as a colorless crystal via vaporization of a hexane/MTBE solution by x-ray structure analysis. CCDC 2417650 contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Supplementary Figure 46. X-Ray Crystal of cat.A1

Identification code	CCDC 2417650
Empirical formula	C ₈₂ H ₁₀₄ BClCu ₂ F ₂₄ P ₄
Formula weight	1842.87
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	13.1975(7)
b/Å	18.6722(11)
c/Å	19.0732(9)
α/°	67.298(2)
β/°	83.819(2)
γ/°	89.122(2)
Volume/Å ³	4309.0(4)
Z	2
ρ _{calc} /cm ³	1.420
μ/mm ⁻¹	0.693
F(000)	1904.0
Crystal size/mm ³	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.67 to 55.094
Index ranges	-14 ≤ h ≤ 17, -24 ≤ k ≤ 23, -24 ≤ l ≤ 24
Reflections collected	40575
Independent reflections	19716 [R _{int} = 0.0786, R _{sigma} = 0.1282]
Data/restraints/parameters	19716/858/1271
Goodness-of-fit on F ²	1.070
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0840, wR ₂ = 0.1598
Final R indexes [all data]	R ₁ = 0.1567, wR ₂ = 0.1972
Largest diff. peak/hole / e Å ⁻³	1.27/-0.67

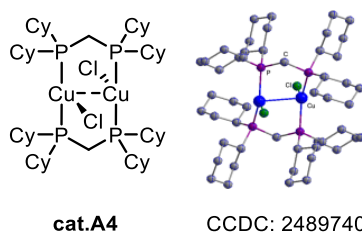
Compound **cat.A2** was crystallized as a colorless crystal via vaporization of a hexane/MTBE solution by x-ray structure analysis. CCDC 2417649 contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Supplementary Figure 47. X-Ray Crystal of cat.A2

Identification code	CCDC 2417649
Empirical formula	C ₈₂ H ₁₀₄ BBrCu ₂ F ₂₄ P ₄
Formula weight	1887.33
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	13.7702(11)
b/Å	15.3477(12)
c/Å	22.2981(18)
α/°	70.420(2)
β/°	80.559(3)
γ/°	89.165(3)
Volume/Å ³	4375.7(6)
Z	2
ρ _{calc} /cm ³	1.432
μ/mm ⁻¹	3.958
F(000)	1940.0
Crystal size/mm ³	0.13 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	3.712 to 108.246
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -26 ≤ l ≤ 26
Reflections collected	64833
Independent reflections	15927 [R _{int} = 0.0501, R _{sigma} = 0.0453]
Data/restraints/parameters	15927/268/1190
Goodness-of-fit on F ²	1.055
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0415, wR ₂ = 0.1011
Final R indexes [all data]	R ₁ = 0.0589, wR ₂ = 0.1106
Largest diff. peak/hole / e Å ⁻³	0.56/-0.39

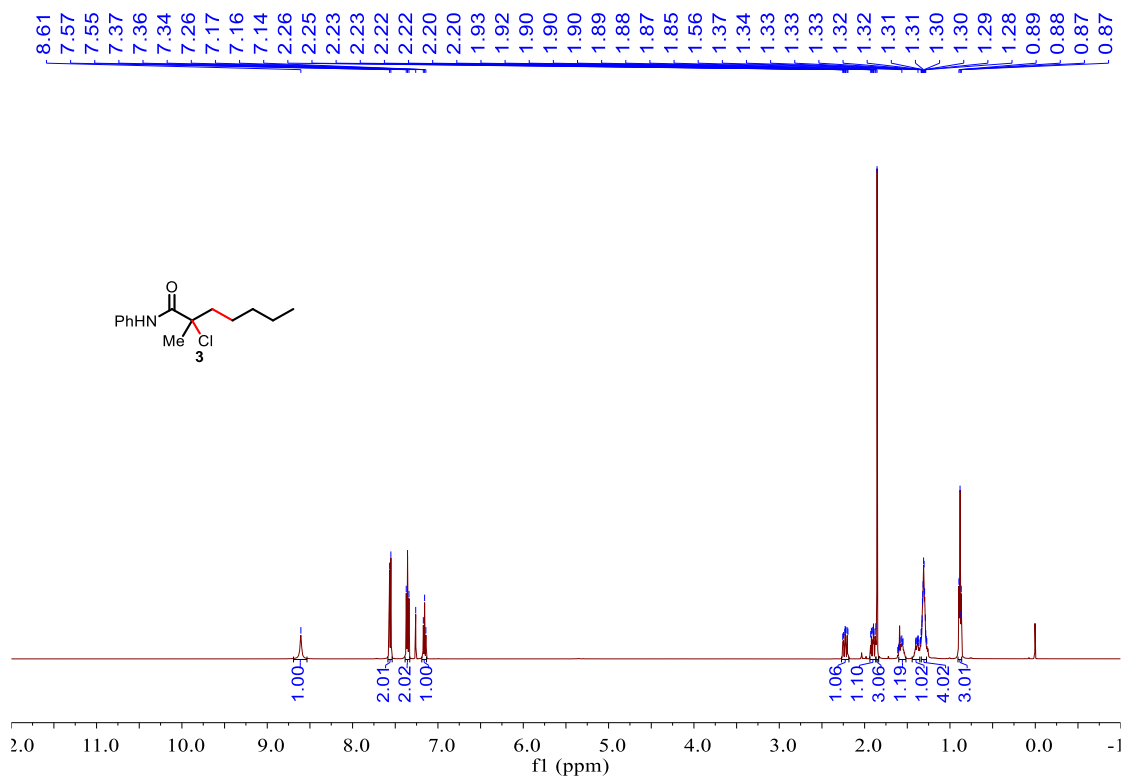
Compound **cat.A4** was crystallized as a colorless crystal via vaporization of a hexane/DCM solution by x-ray structure analysis. CCDC 2489740 contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



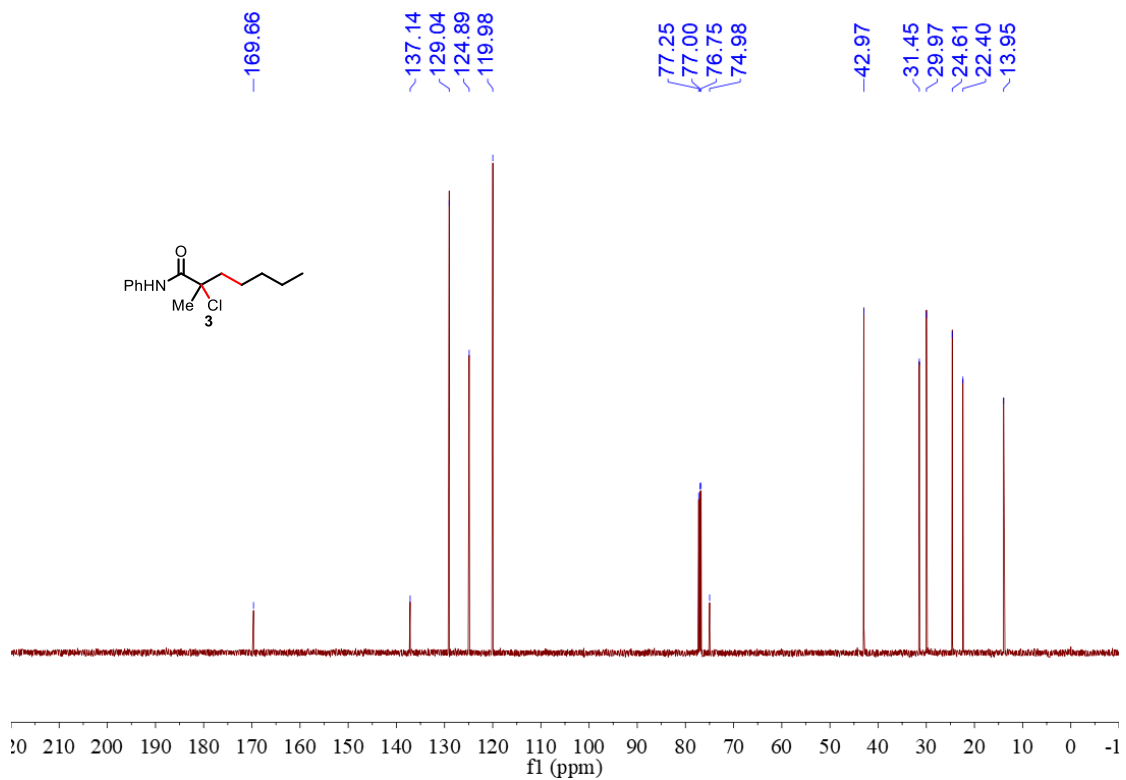
Supplementary Figure 48. X-Ray Crystal of cat.A4

Identification code	2489740
Empirical formula	C ₅₂ H ₉₆ C ₁₆ Cu ₂ P ₄
Formula weight	1184.94
Temperature/K	223.00
Crystal system	triclinic
Space group	P-1
a/Å	10.7773(19)
b/Å	12.977(3)
c/Å	13.355(3)
α/°	115.123(7)
β/°	111.842(6)
γ/°	94.835(7)
Volume/Å ³	1503.1(5)
Z	1
ρ _{calc} /cm ³	1.309
μ/mm-1	1.113
F(000)	628.0
Crystal size/mm ³	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.724 to 55.162
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 12, -15 ≤ l ≤ 17
Reflections collected	13865
Independent reflections	6838 [R _{int} = 0.0401, R _{sigma} = 0.0581]
Data/restraints/parameters	6838/64/315
Goodness-of-fit on F ²	1.020
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0427, wR ₂ = 0.0943
Final R indexes [all data]	R ₁ = 0.0592, wR ₂ = 0.1055
Largest diff. peak/hole / e Å ⁻³	0.49/-0.53

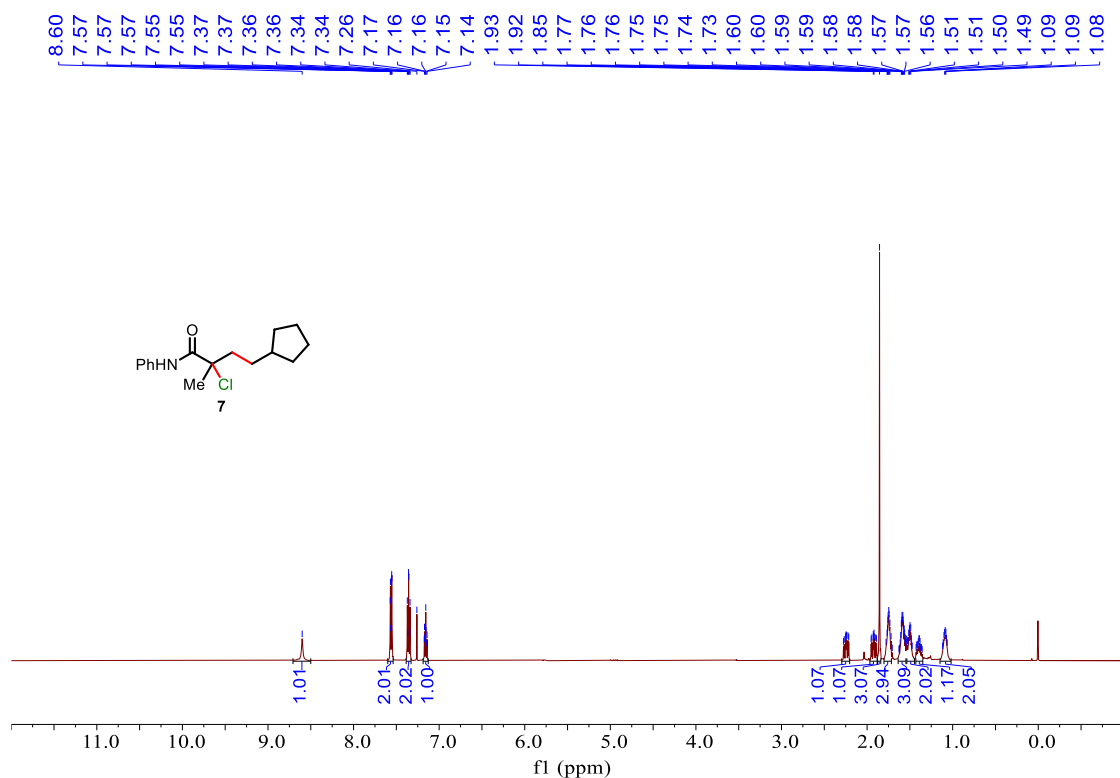
11. Copies of NMR Spectra



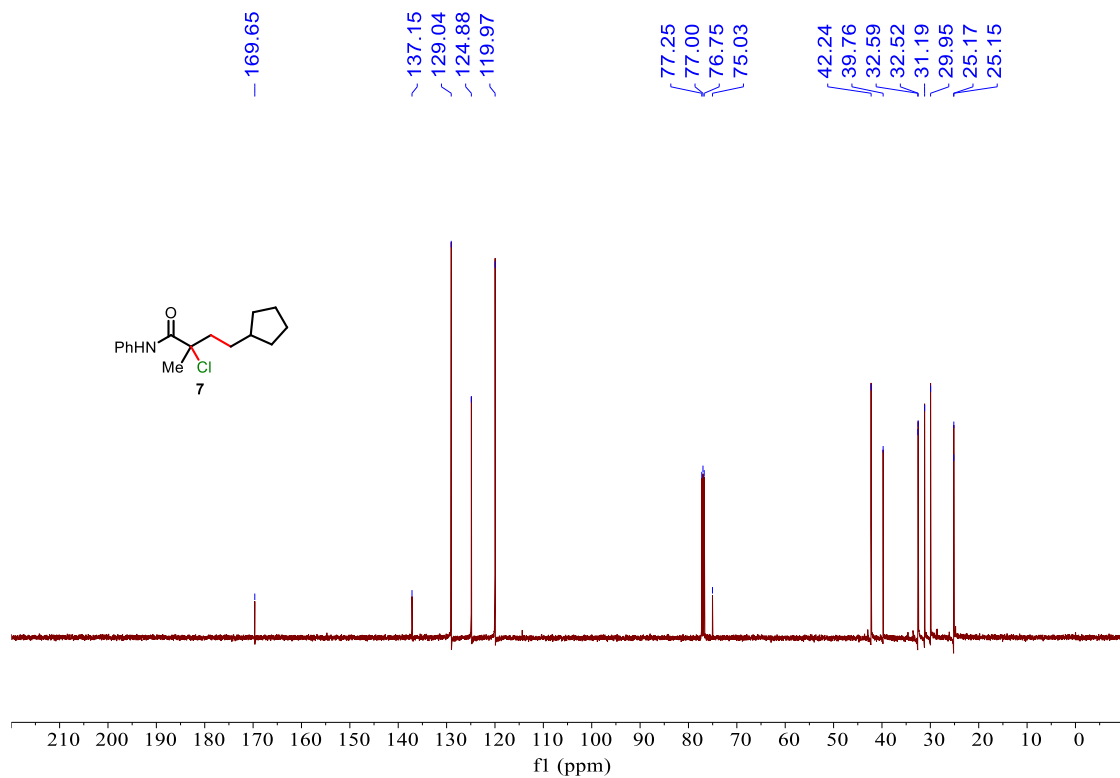
Supplementary Figure 49. ¹H NMR (500 MHz, CDCl₃) spectrum for compound 3



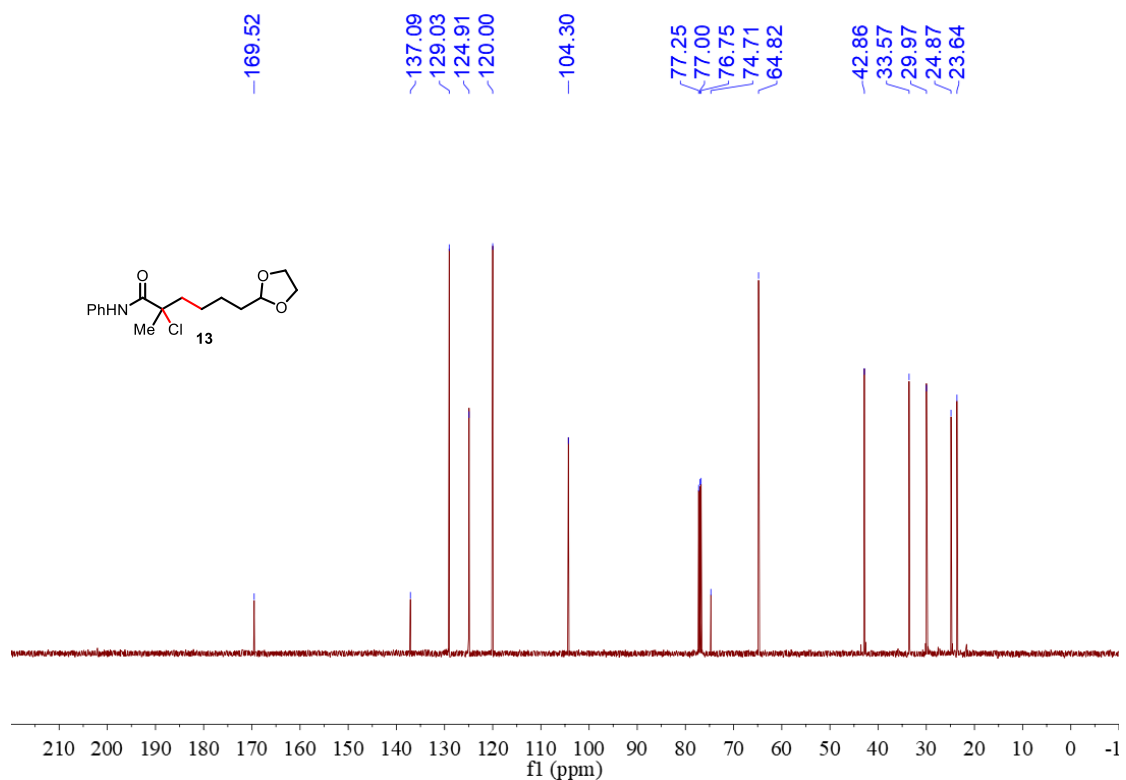
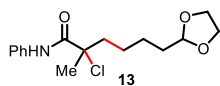
Supplementary Figure 50. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound 3

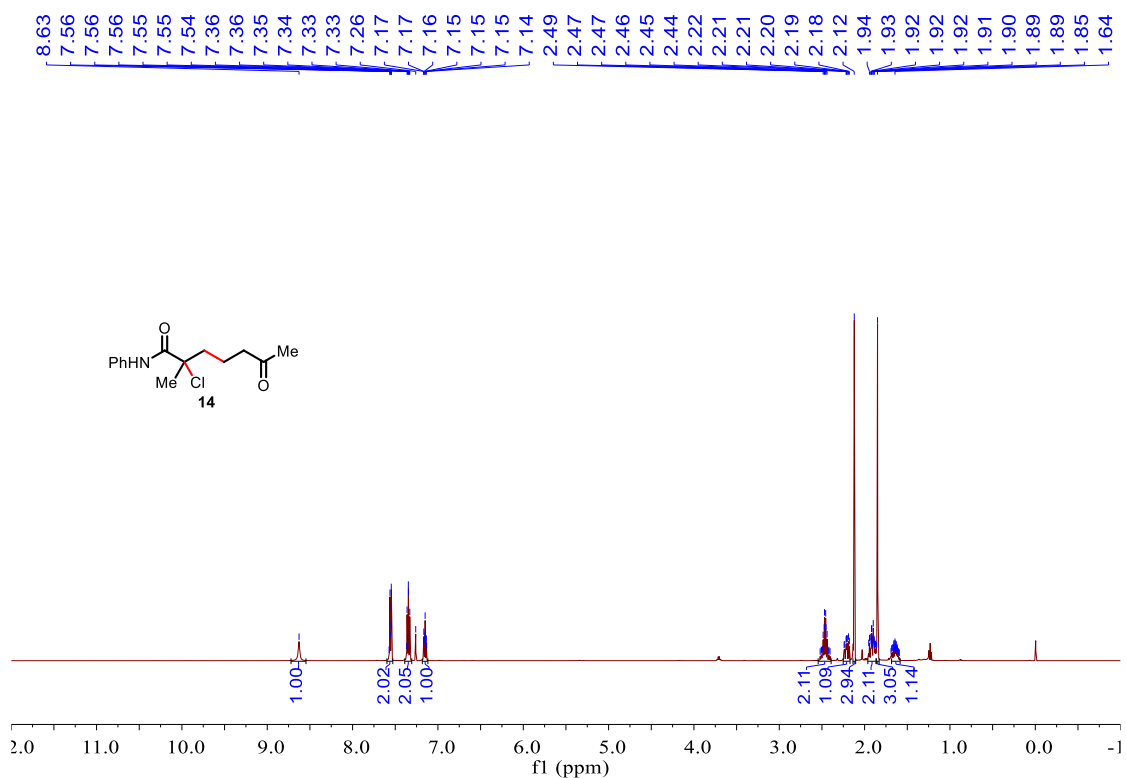


Supplementary Figure 51. ¹H NMR (500 MHz, CDCl₃) spectrum for compound 7

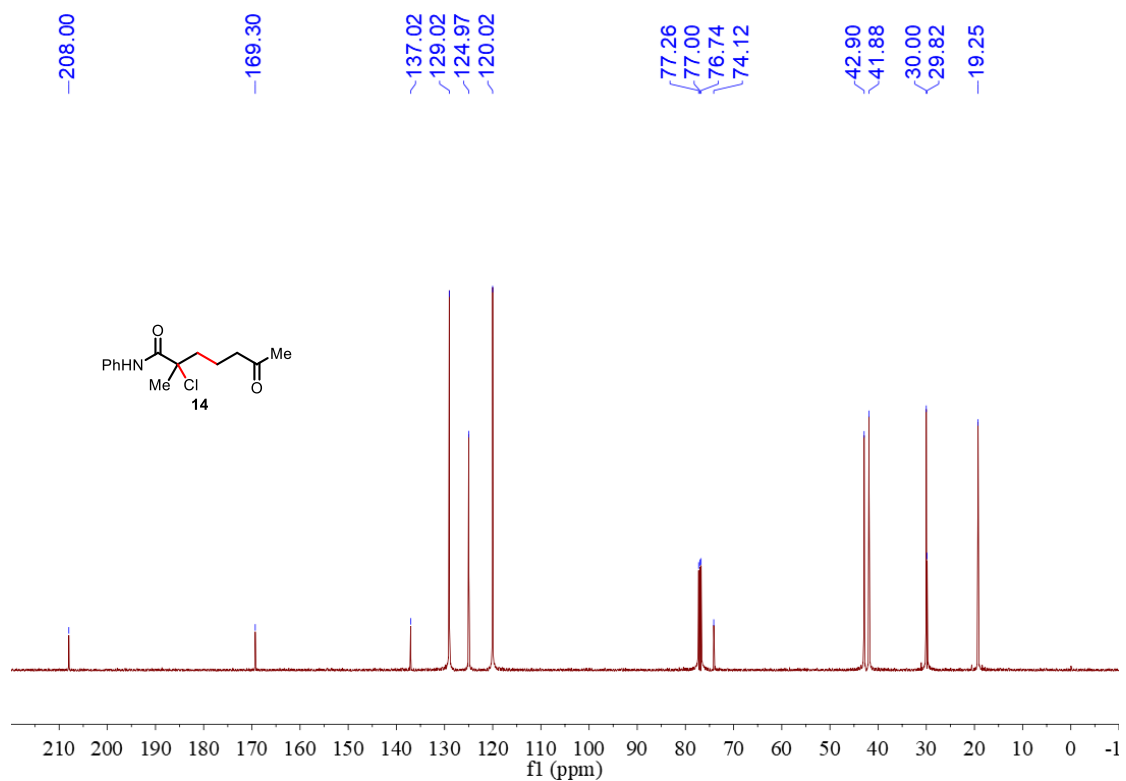


Supplementary Figure 52. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound 7

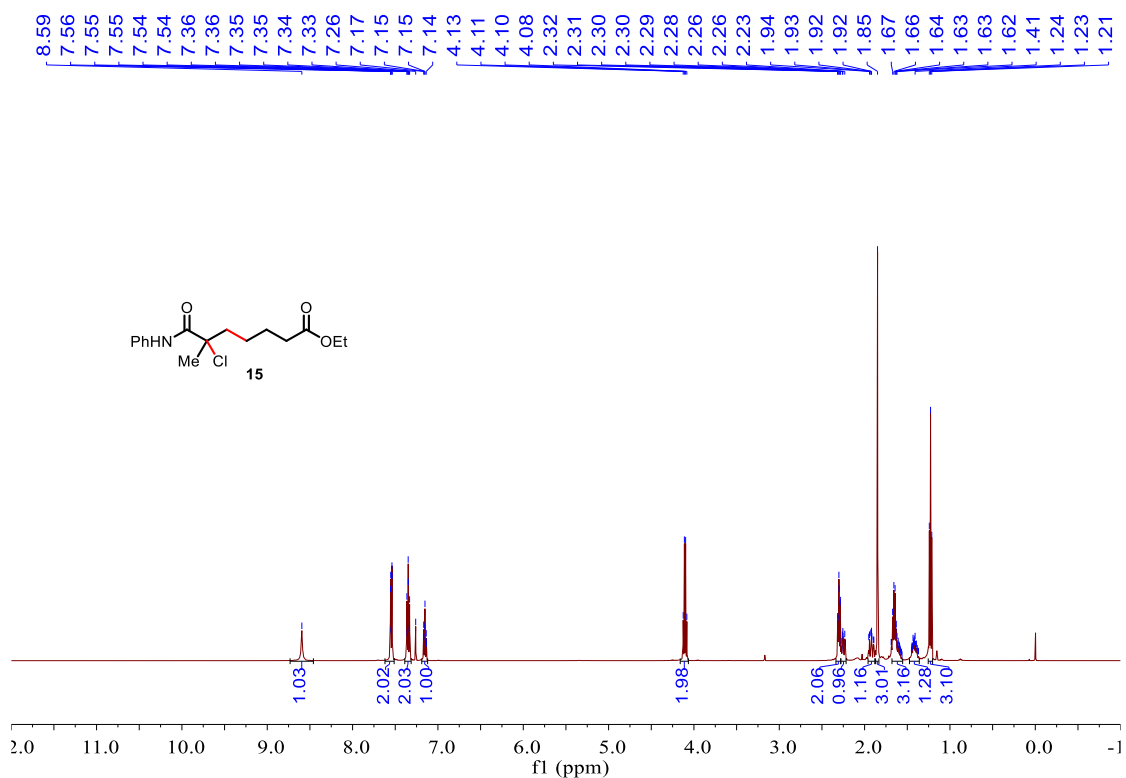




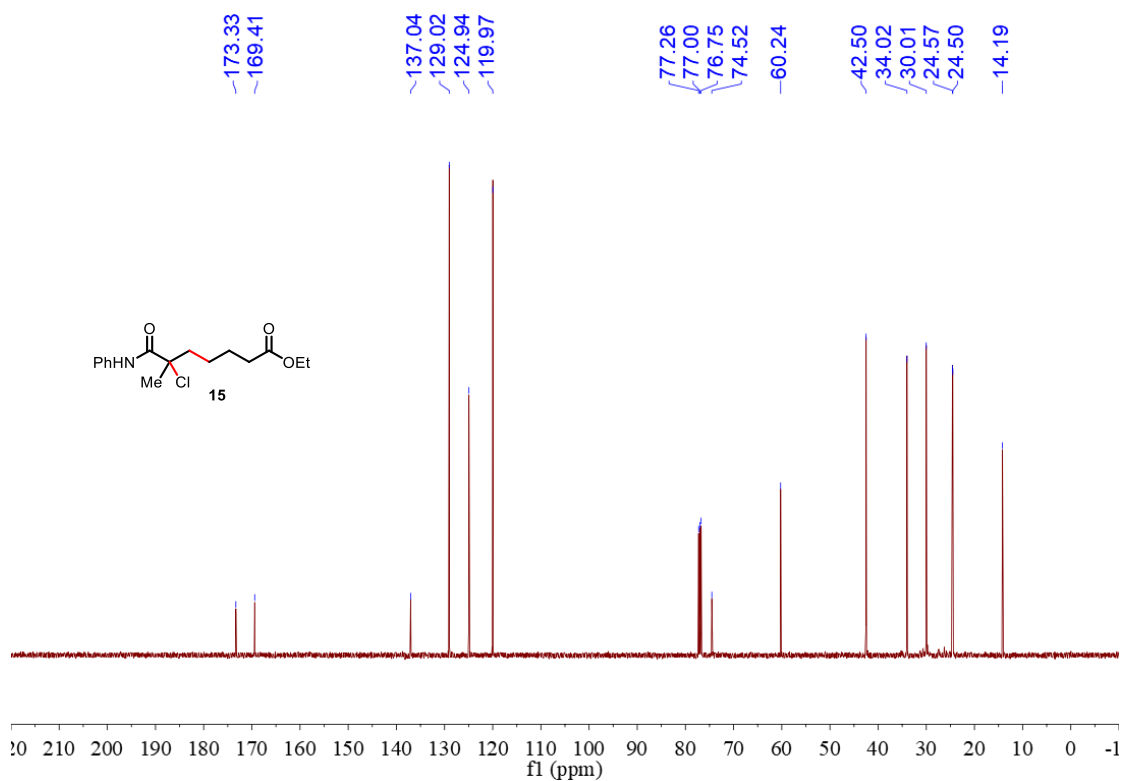
Supplementary Figure 55. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **14**



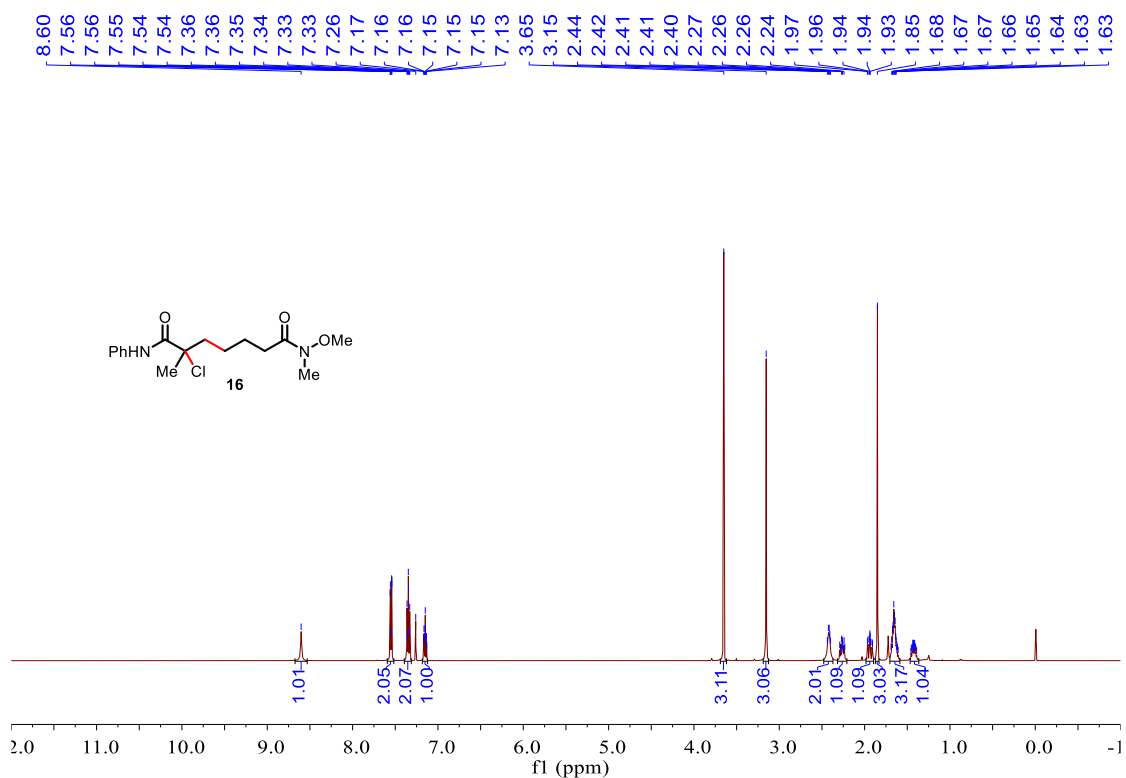
Supplementary Figure 56. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **14**



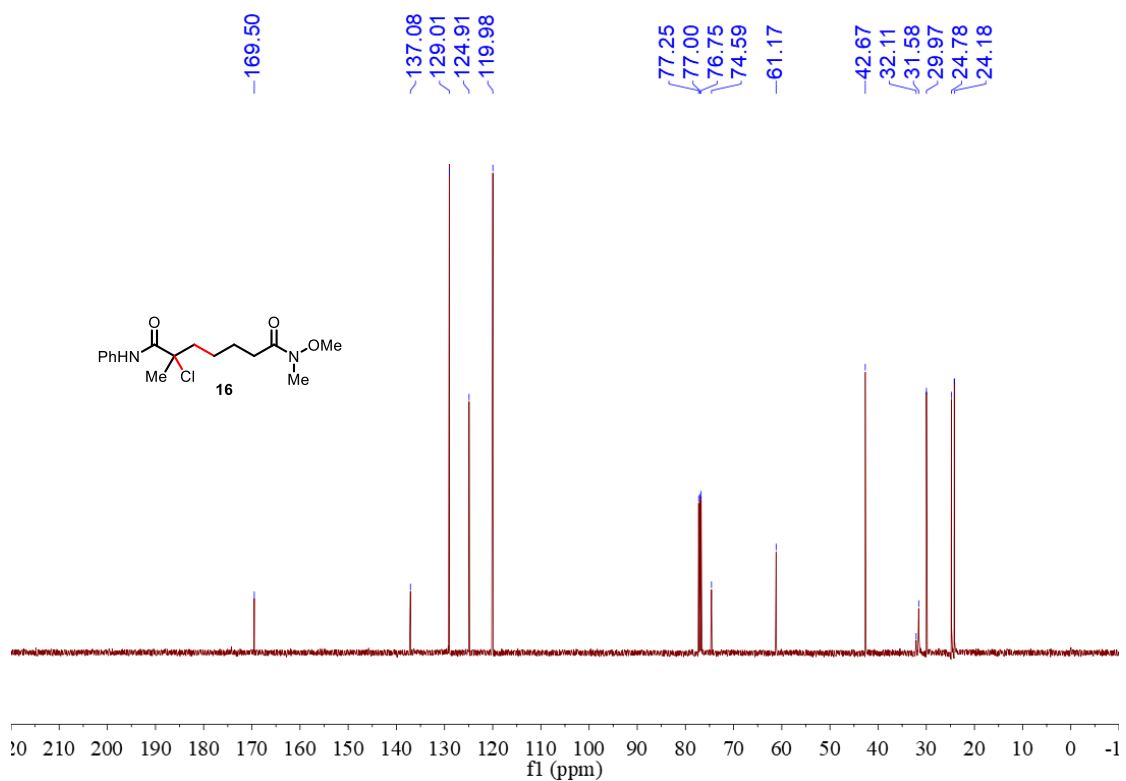
Supplementary Figure 57. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **15**



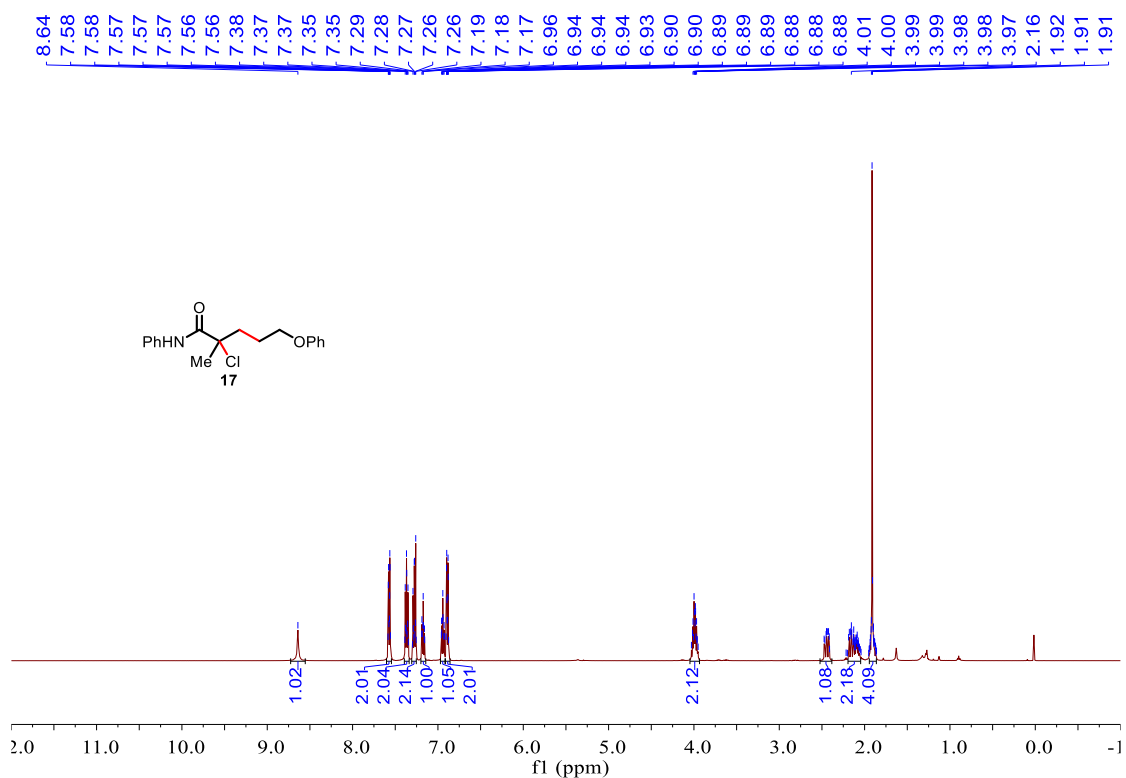
Supplementary Figure 58. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **15**



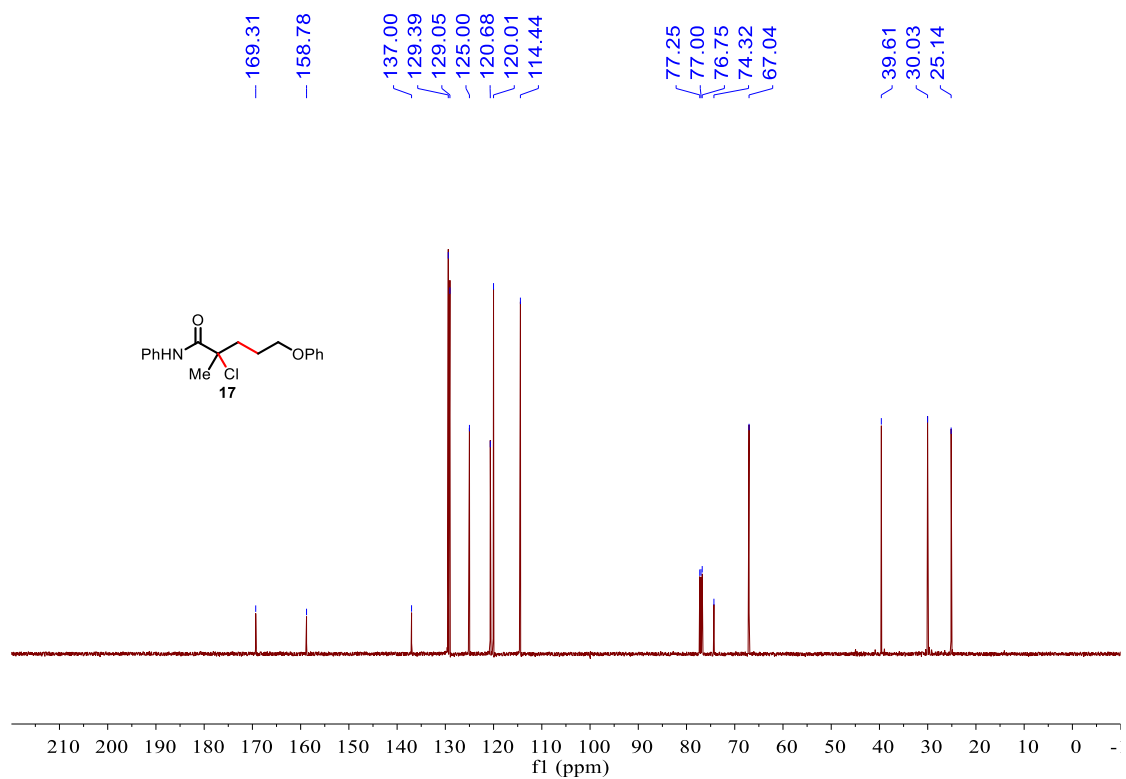
Supplementary Figure 59. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **16**



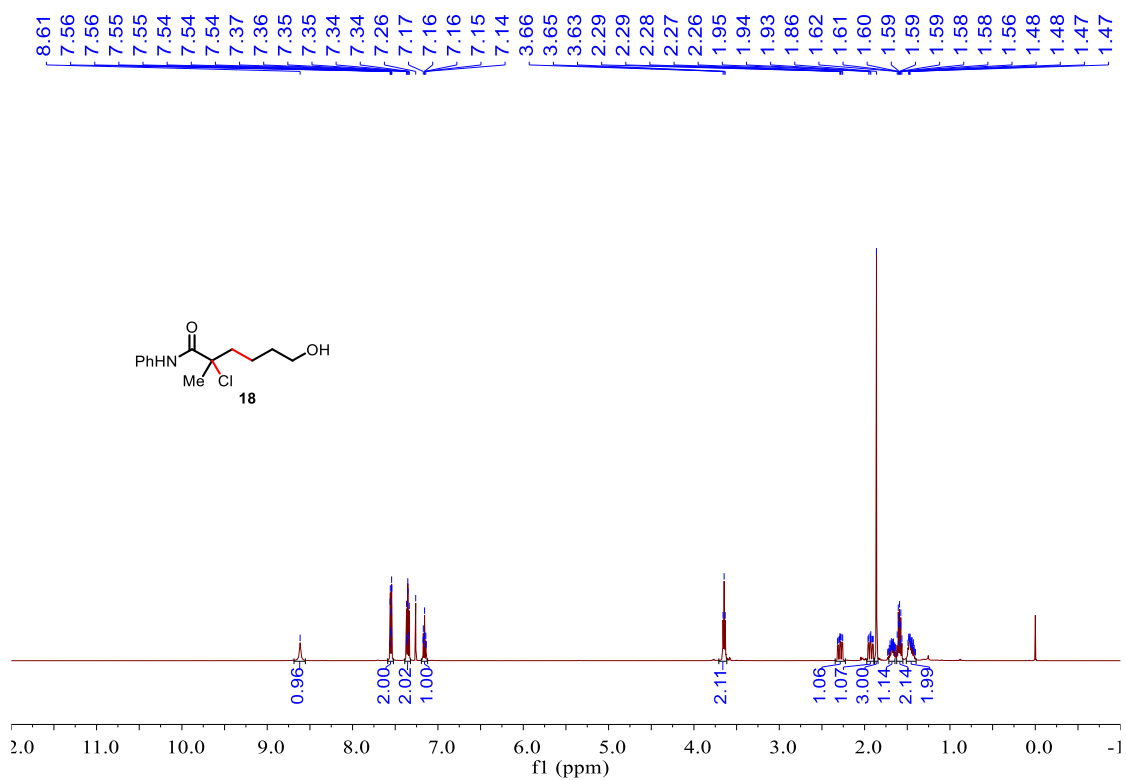
Supplementary Figure 60. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **16**



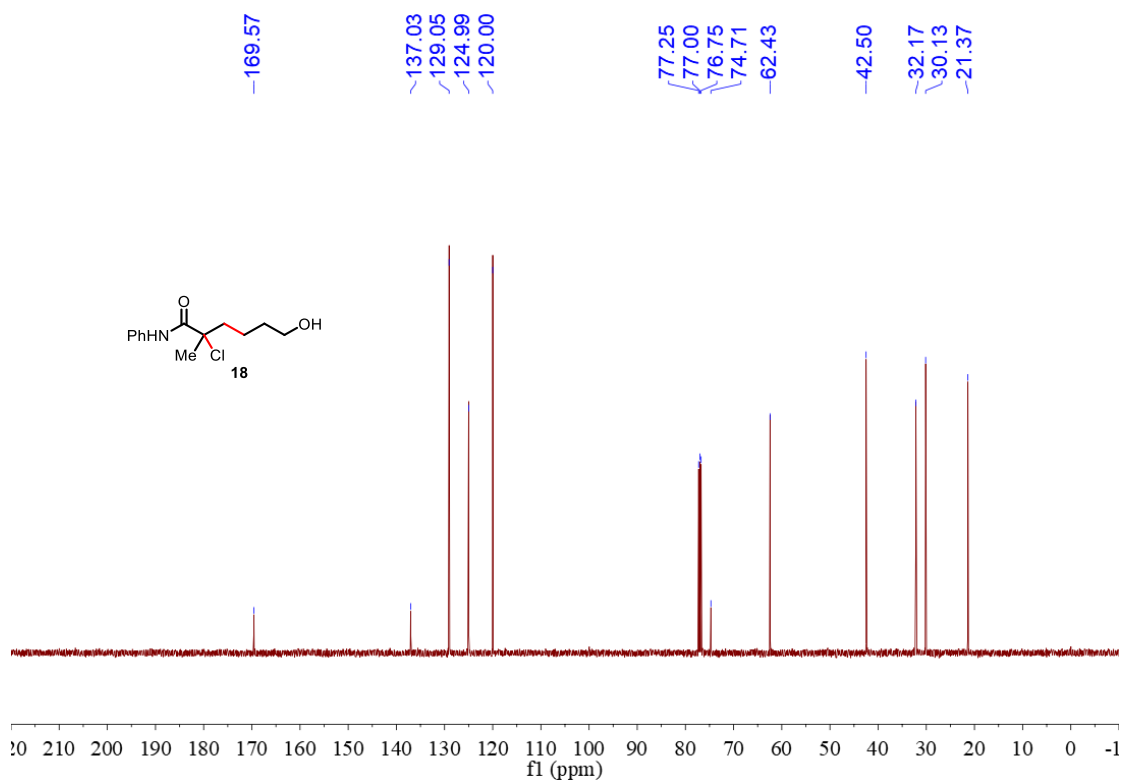
Supplementary Figure 61. ¹H NMR (500 MHz, CDCl₃) spectrum for compound 17



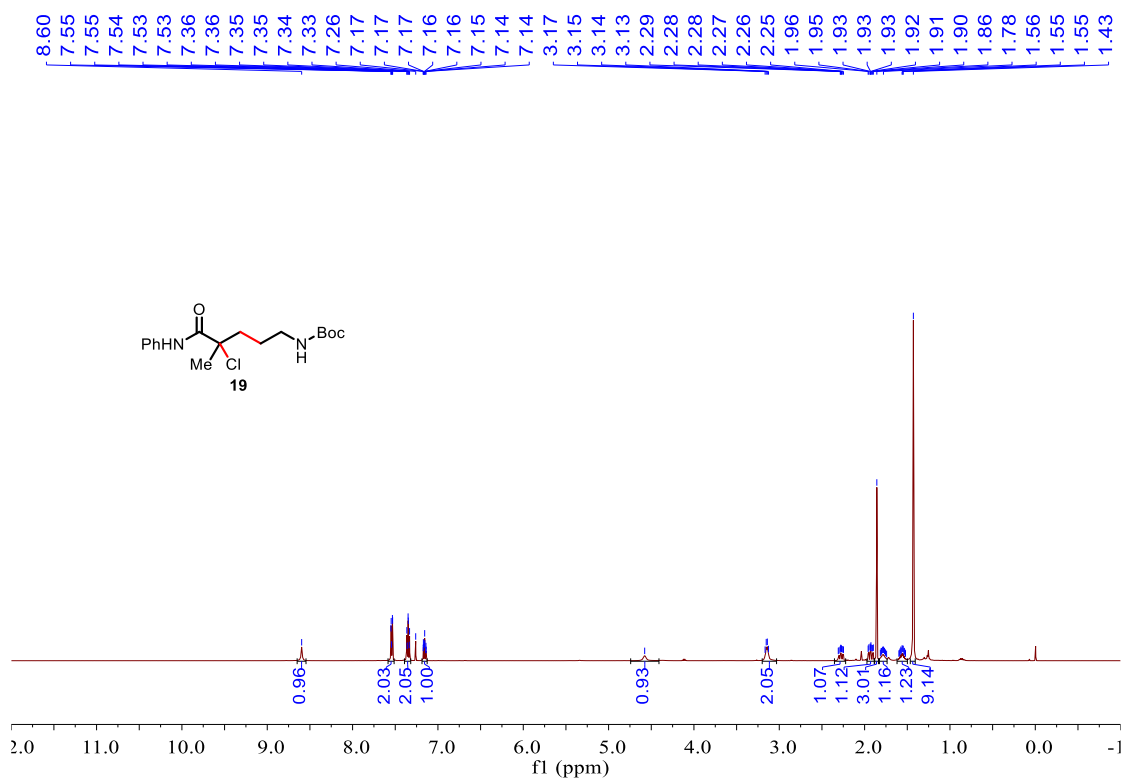
Supplementary Figure 62. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound 17



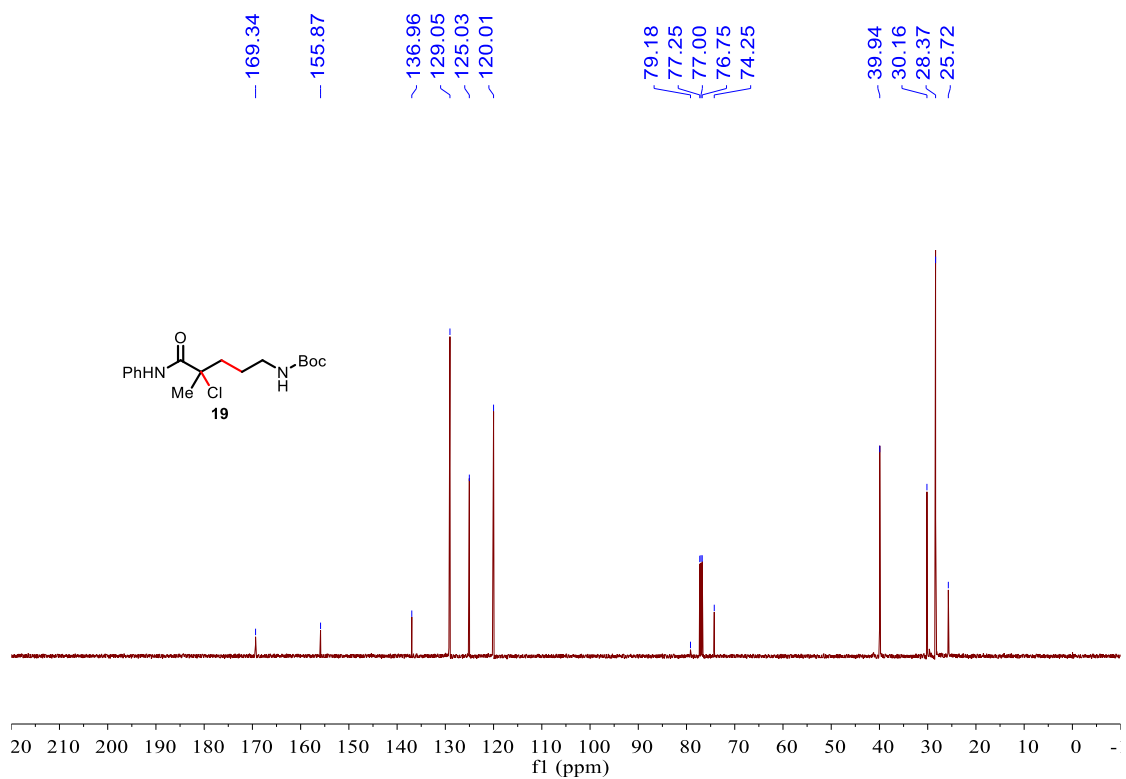
Supplementary Figure 63. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **18**



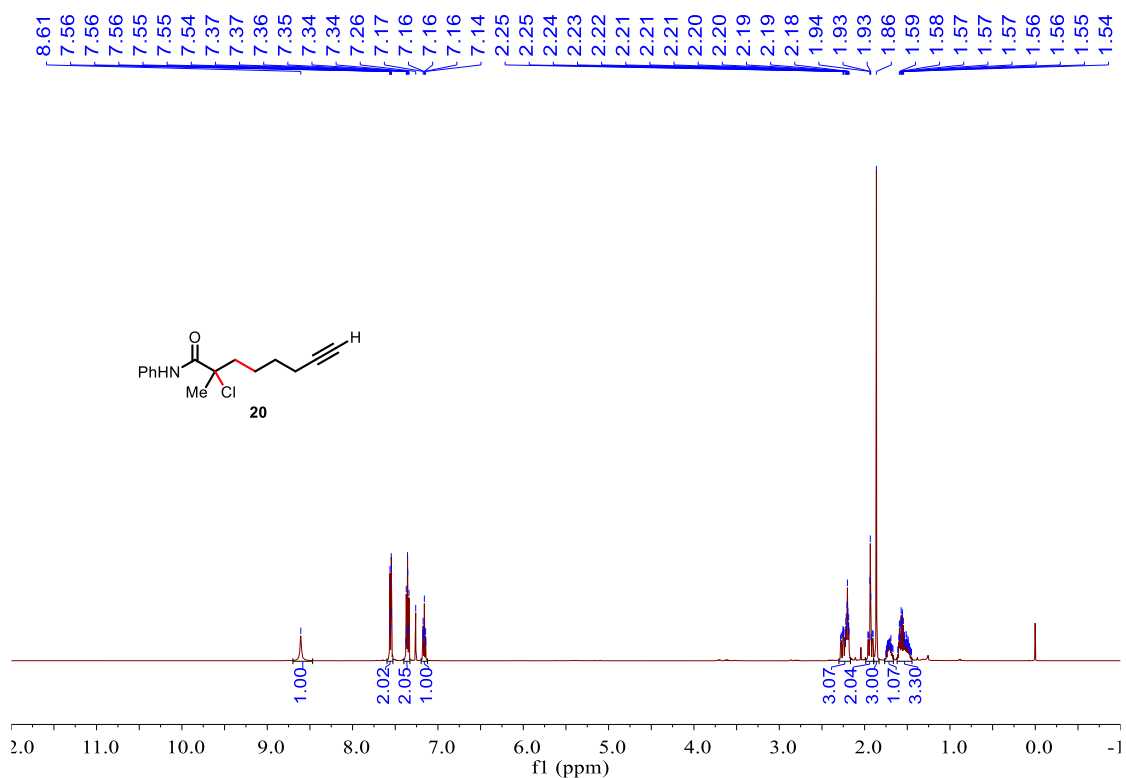
Supplementary Figure 64. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **18**



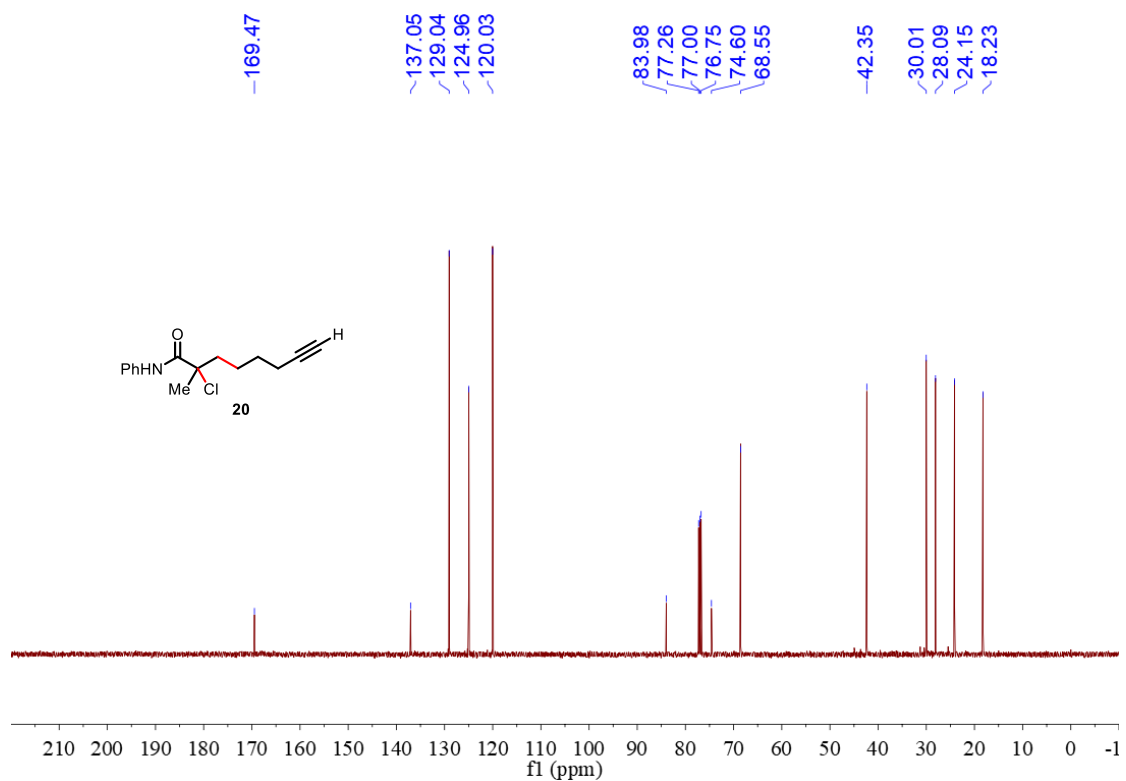
Supplementary Figure 65. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **19**



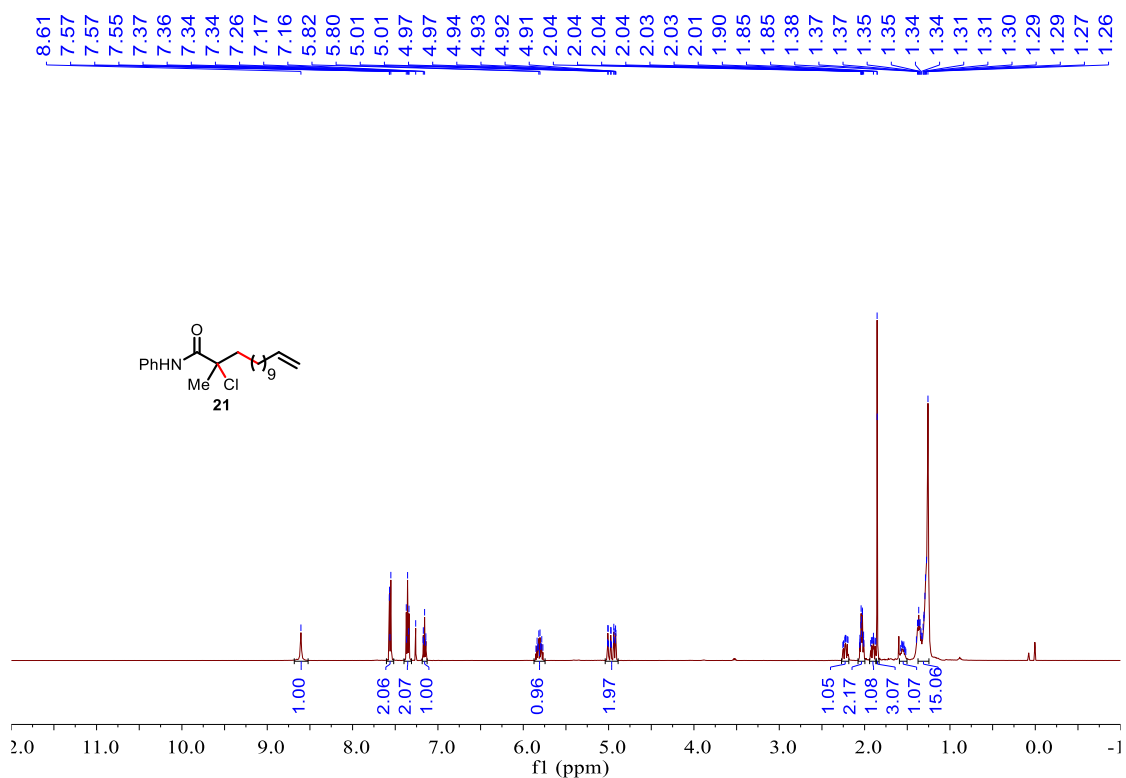
Supplementary Figure 66. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **19**



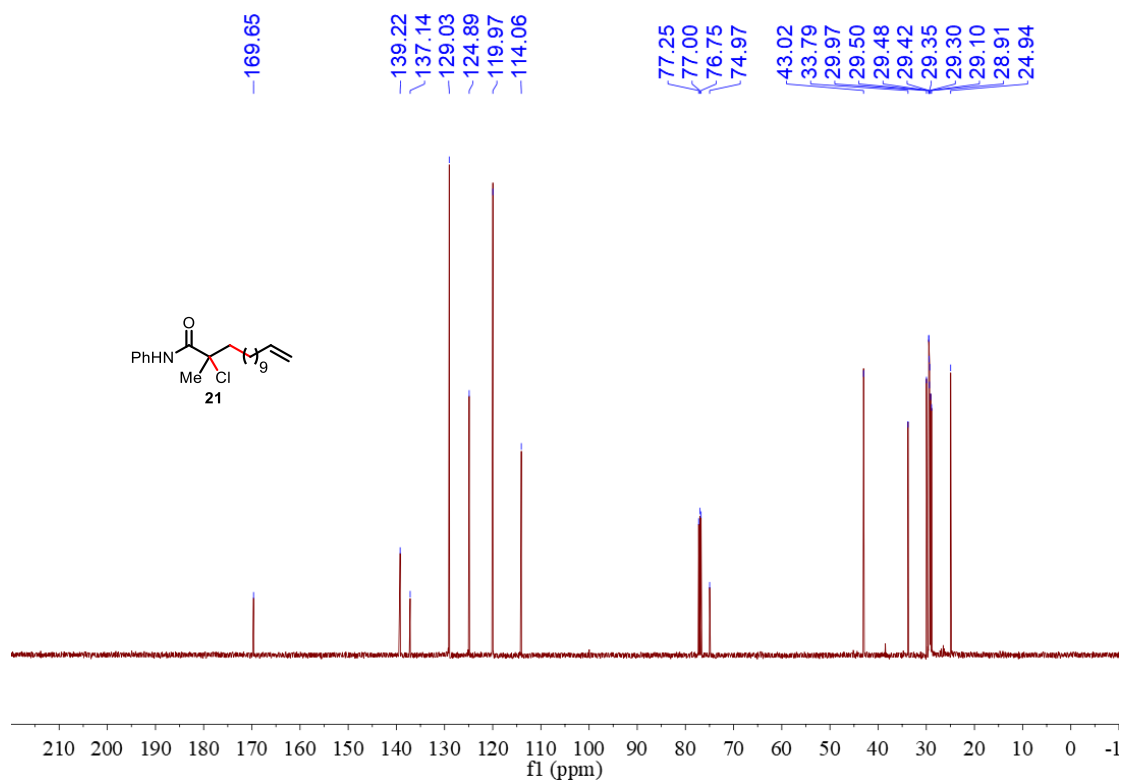
Supplementary Figure 67. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **20**



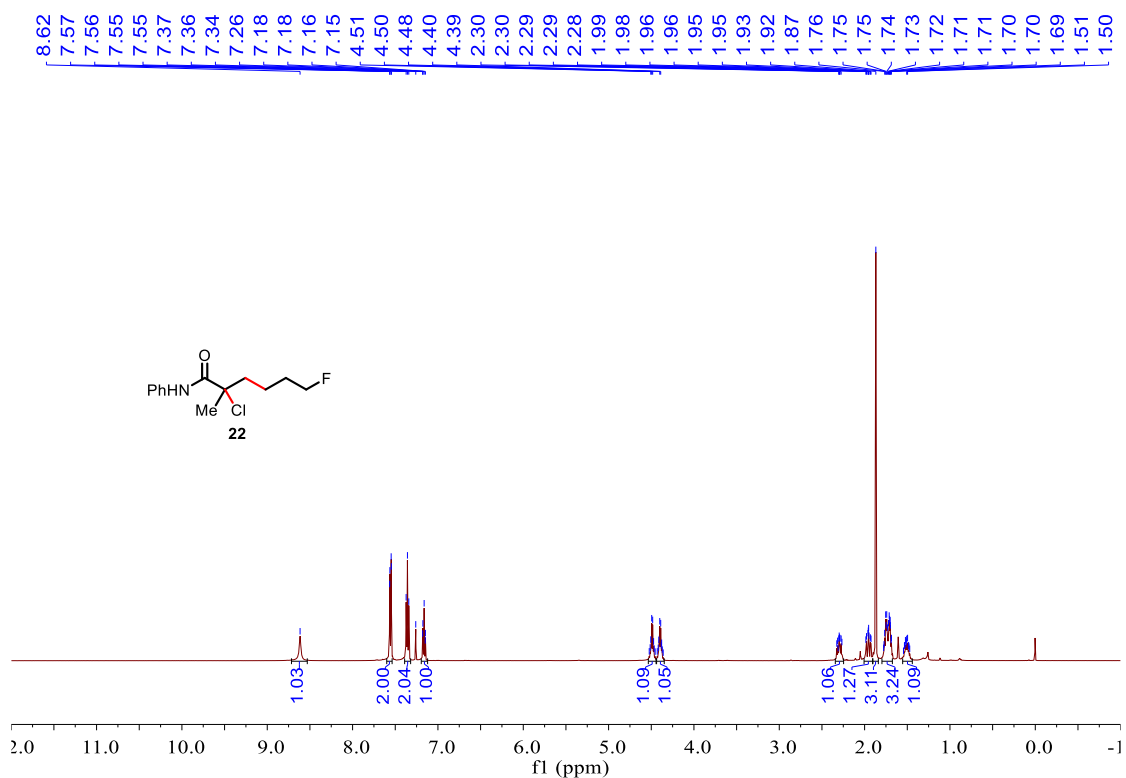
Supplementary Figure 68. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **20**



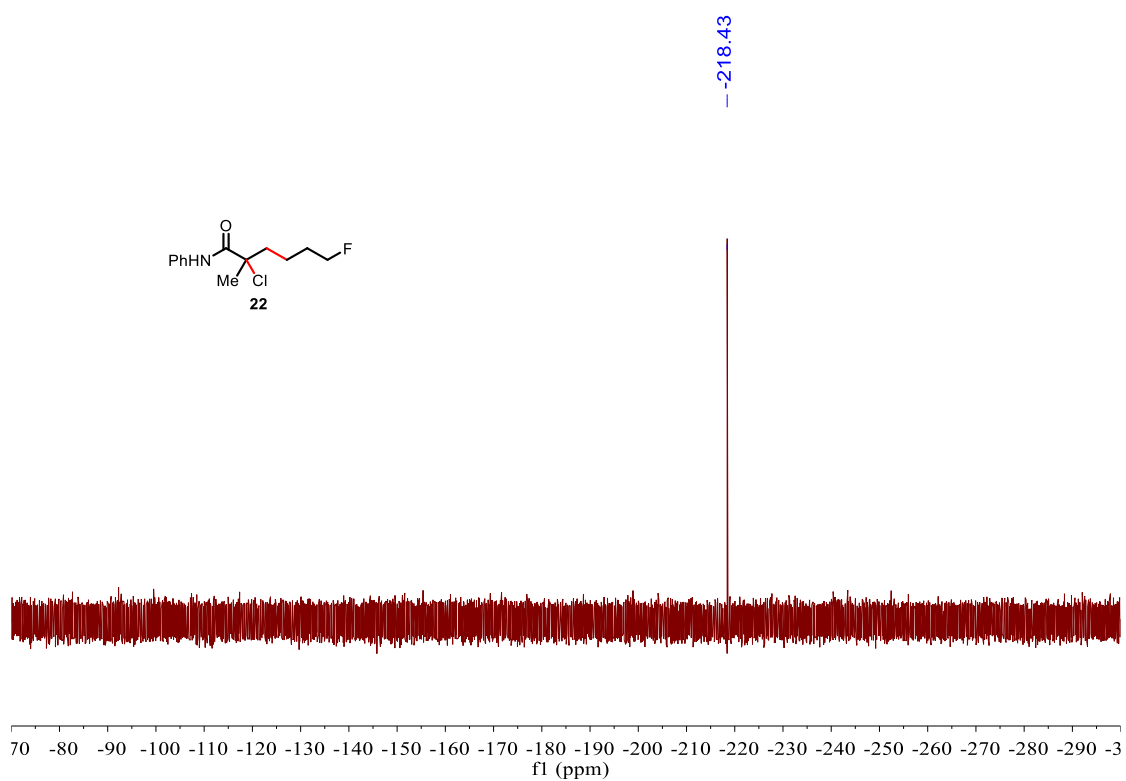
Supplementary Figure 69. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **21**



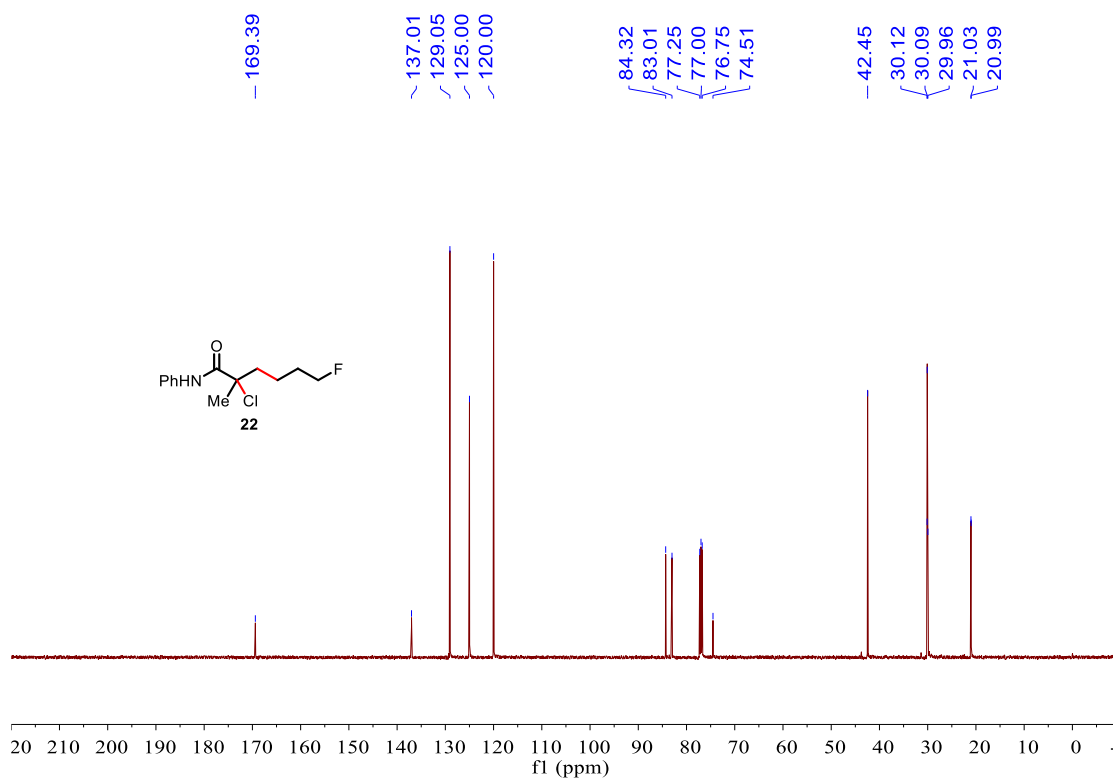
Supplementary Figure 70. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **21**



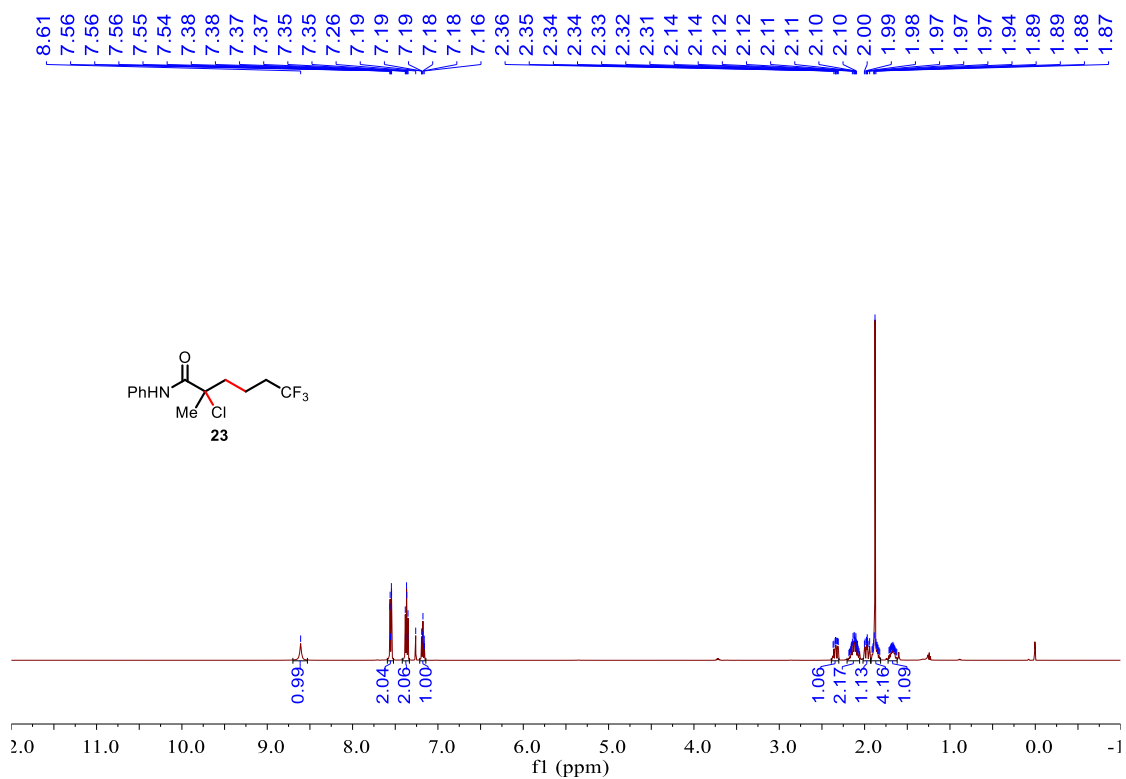
Supplementary Figure 71. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **22**



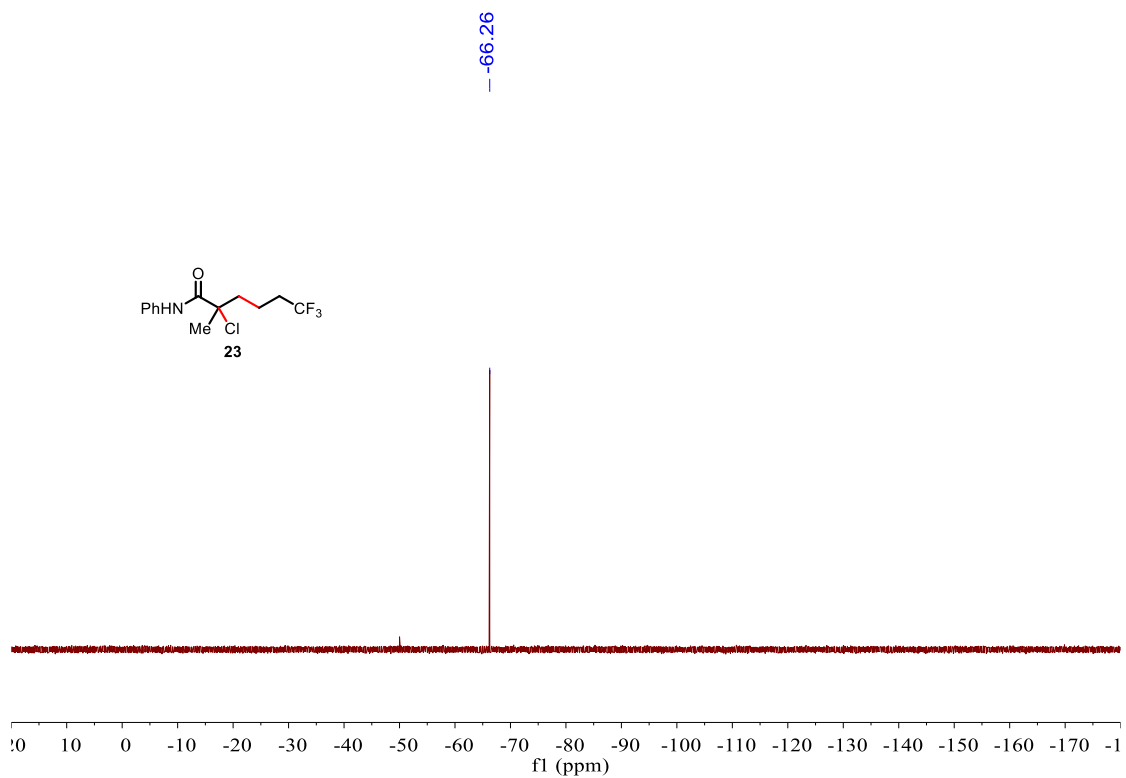
Supplementary Figure 72. ¹⁹F NMR (471 MHz, CDCl₃) spectrum for compound **22**



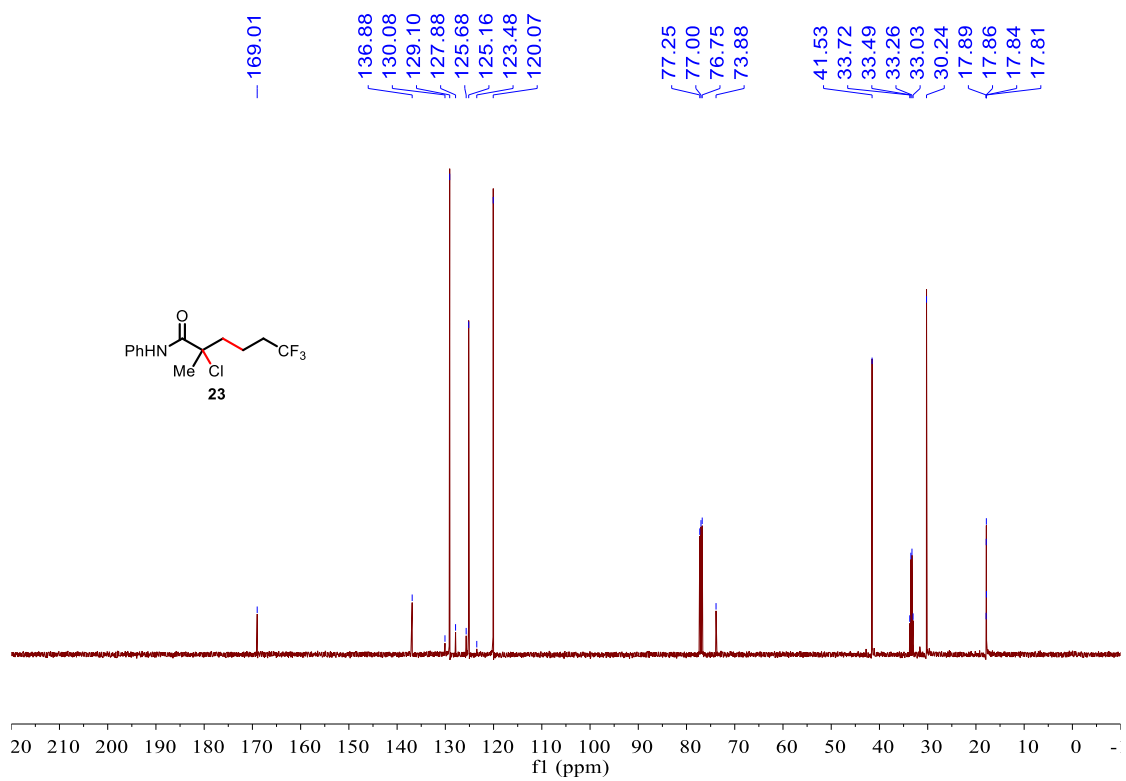
Supplementary Figure 73. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **22**



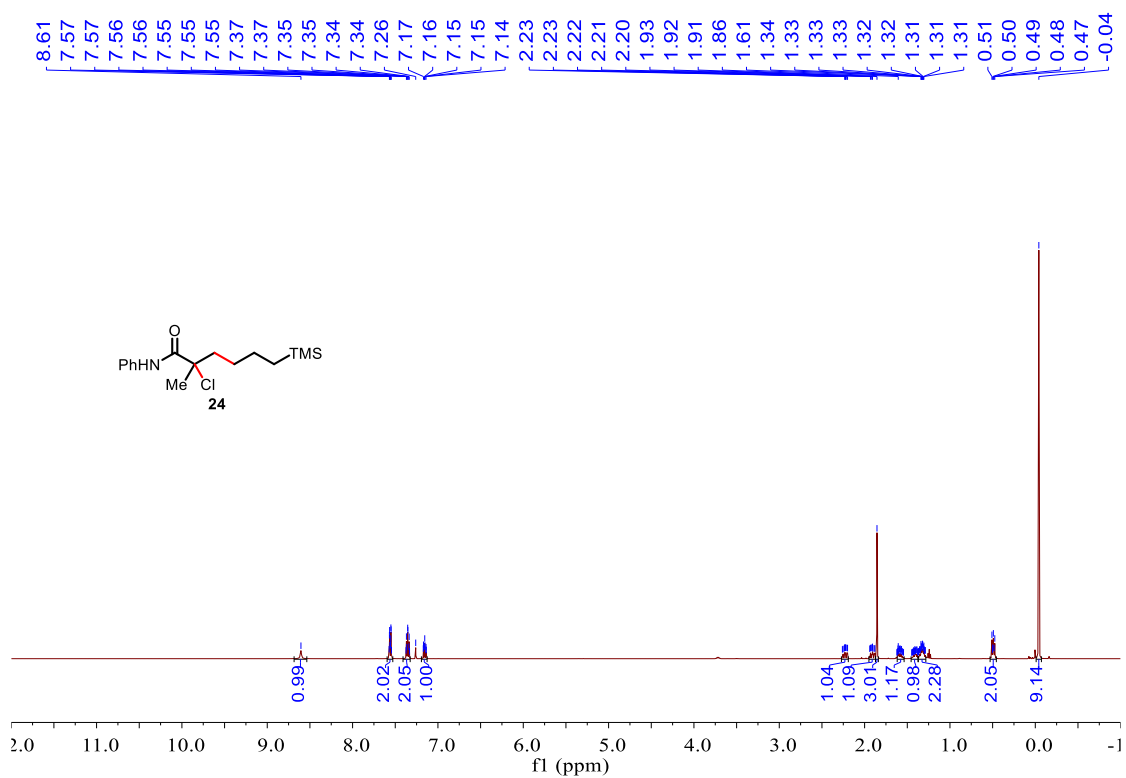
Supplementary Figure 74. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **23**



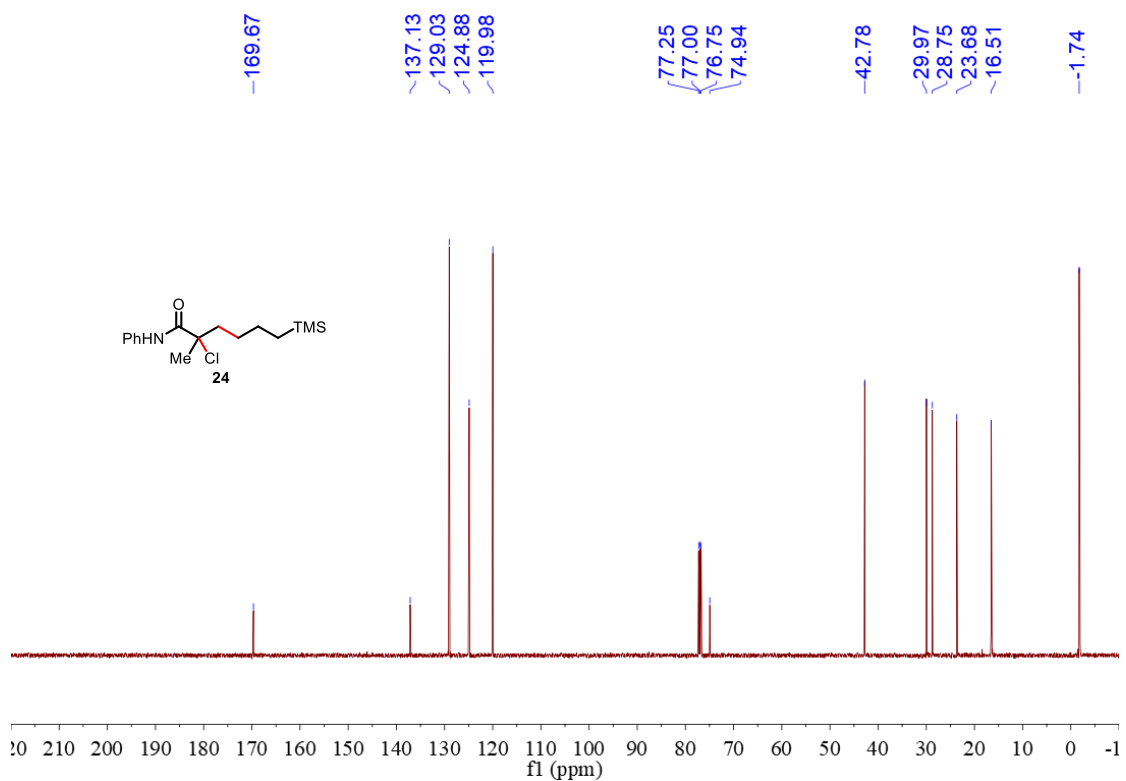
Supplementary Figure 75. ¹⁹F NMR (471 MHz, CDCl₃) spectrum for compound **23**



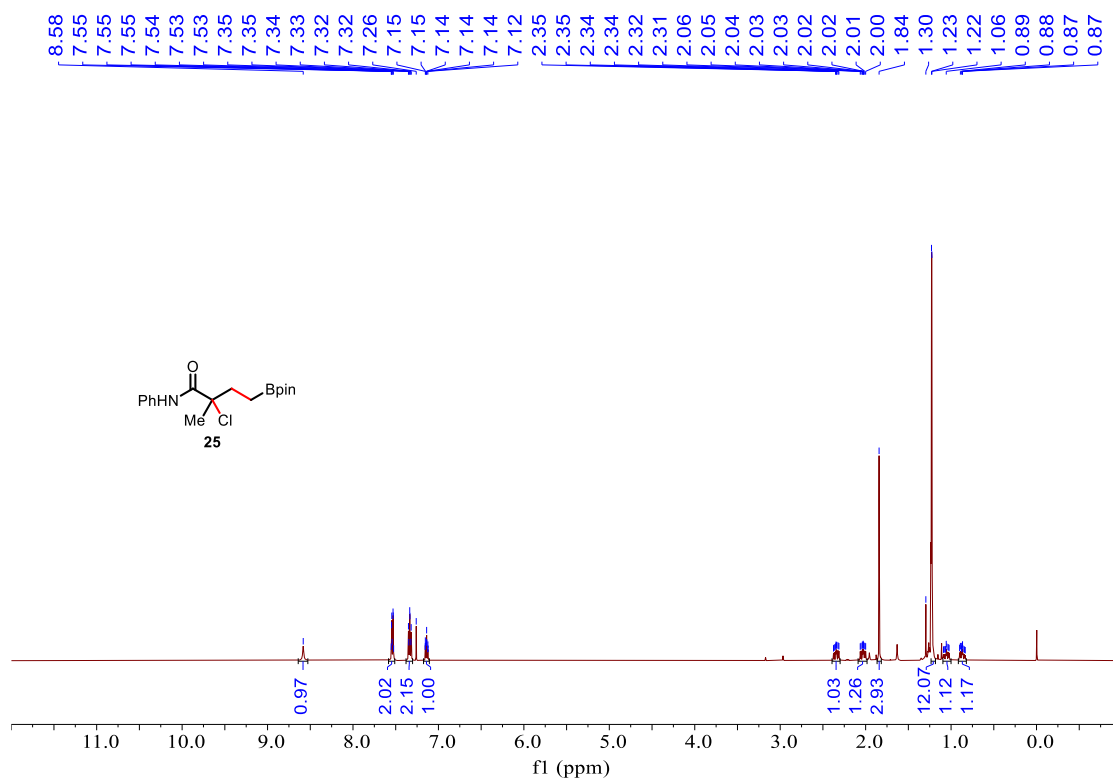
Supplementary Figure 76. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **23**



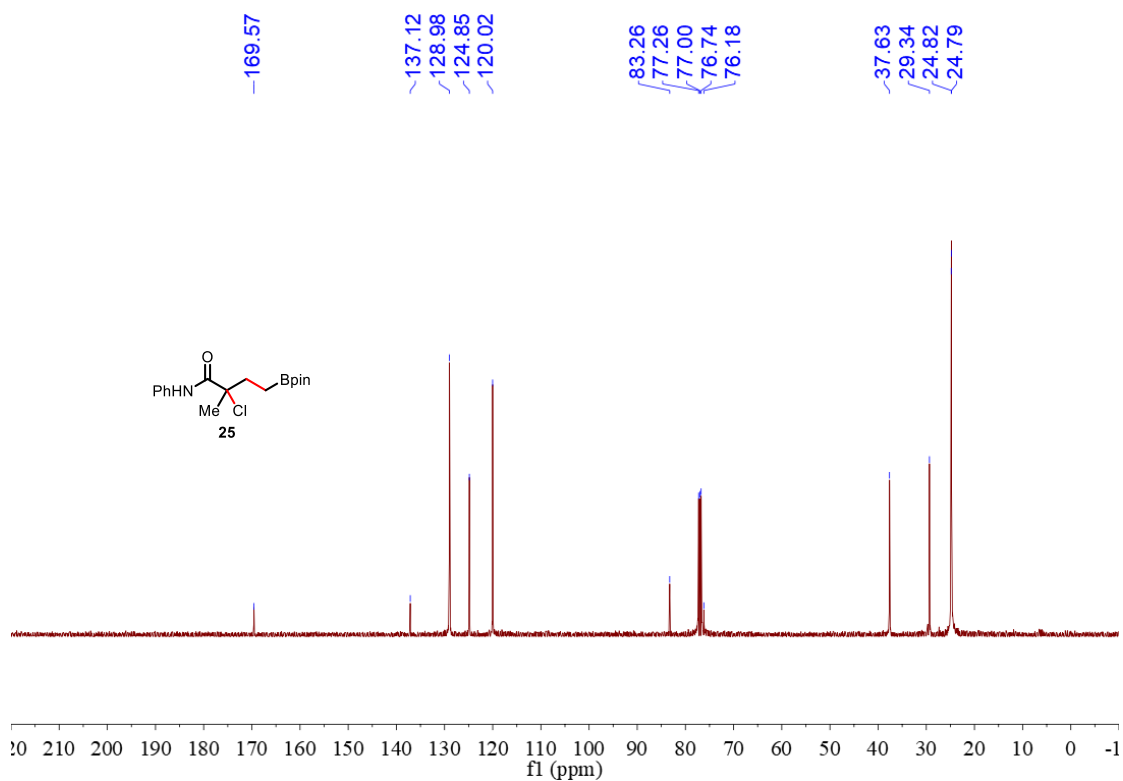
Supplementary Figure 77. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **24**



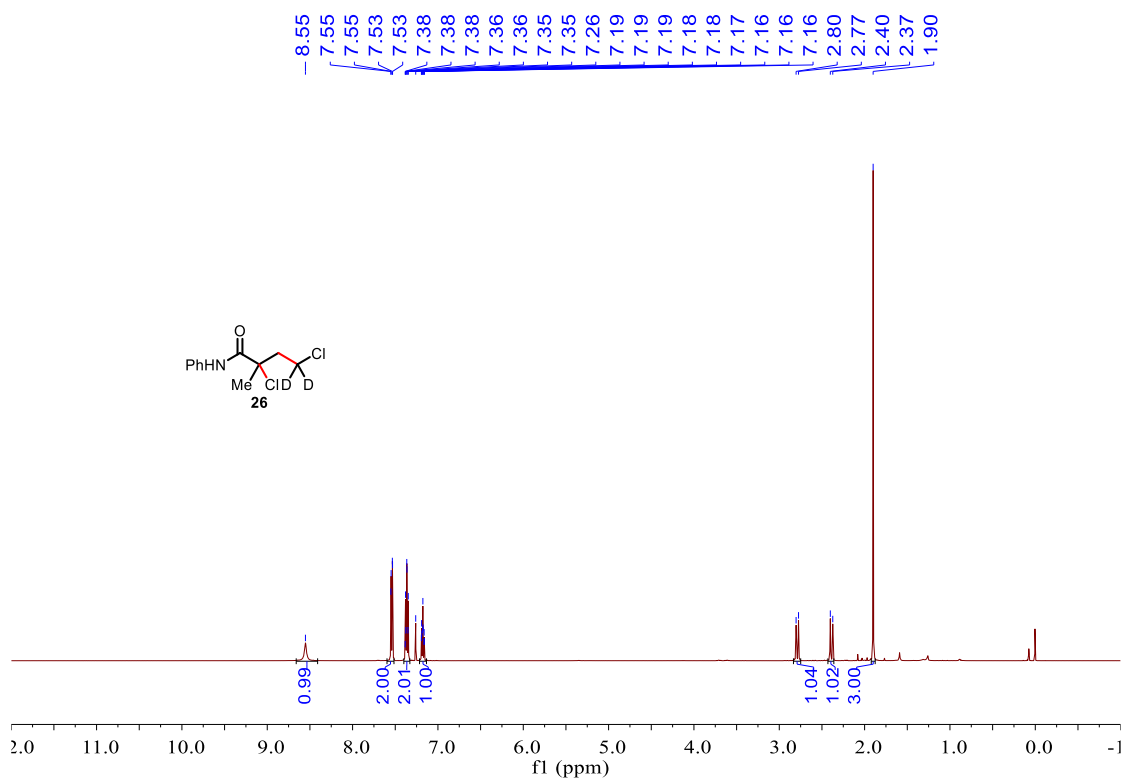
Supplementary Figure 78. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **24**



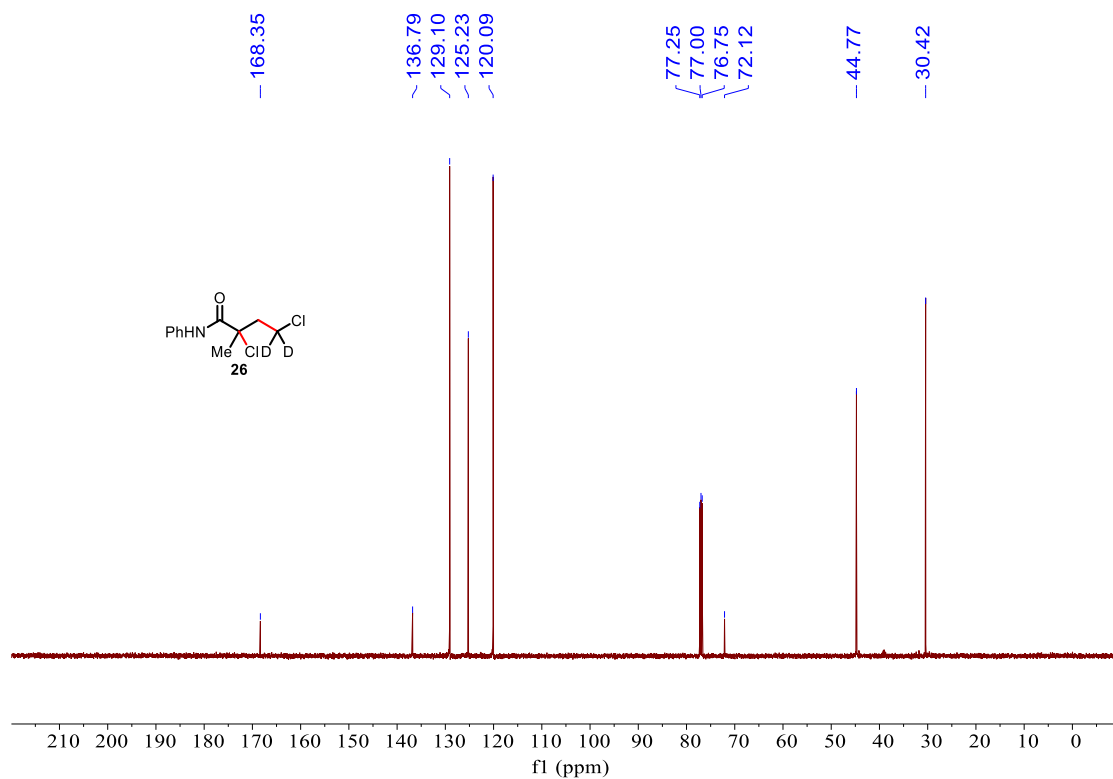
Supplementary Figure 79. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **25**



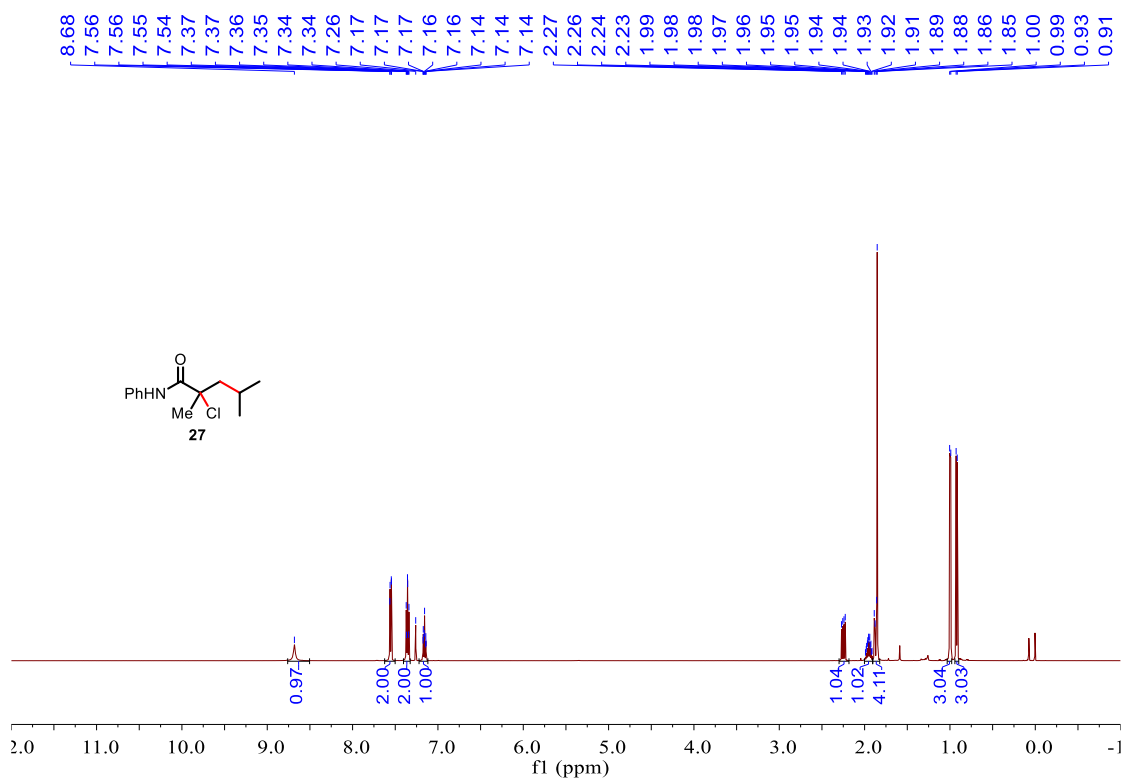
Supplementary Figure 80. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **25**



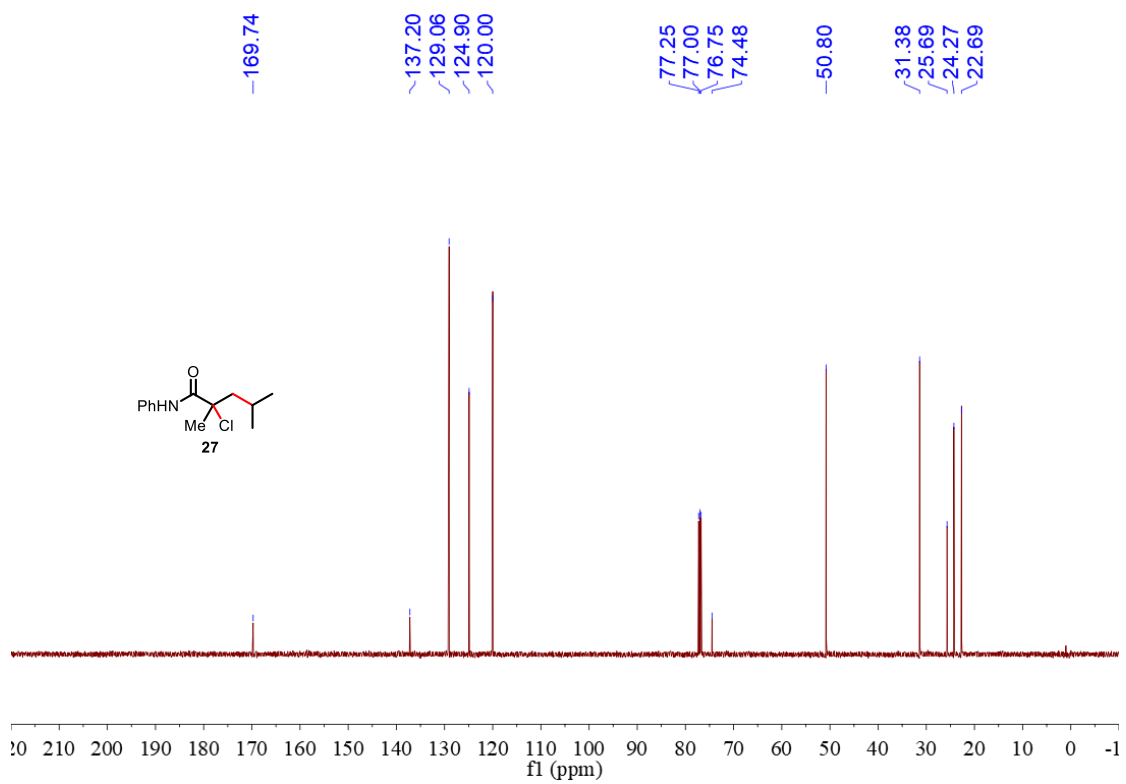
Supplementary Figure 81. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **26**



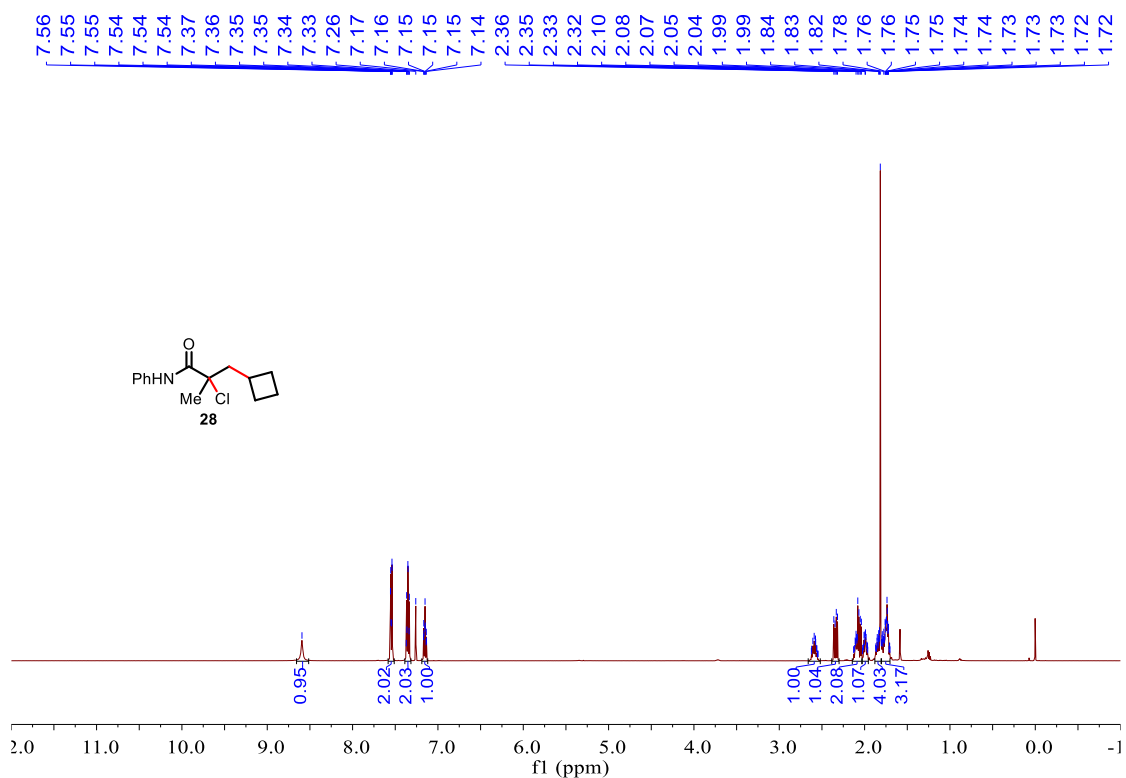
Supplementary Figure 82. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **26**



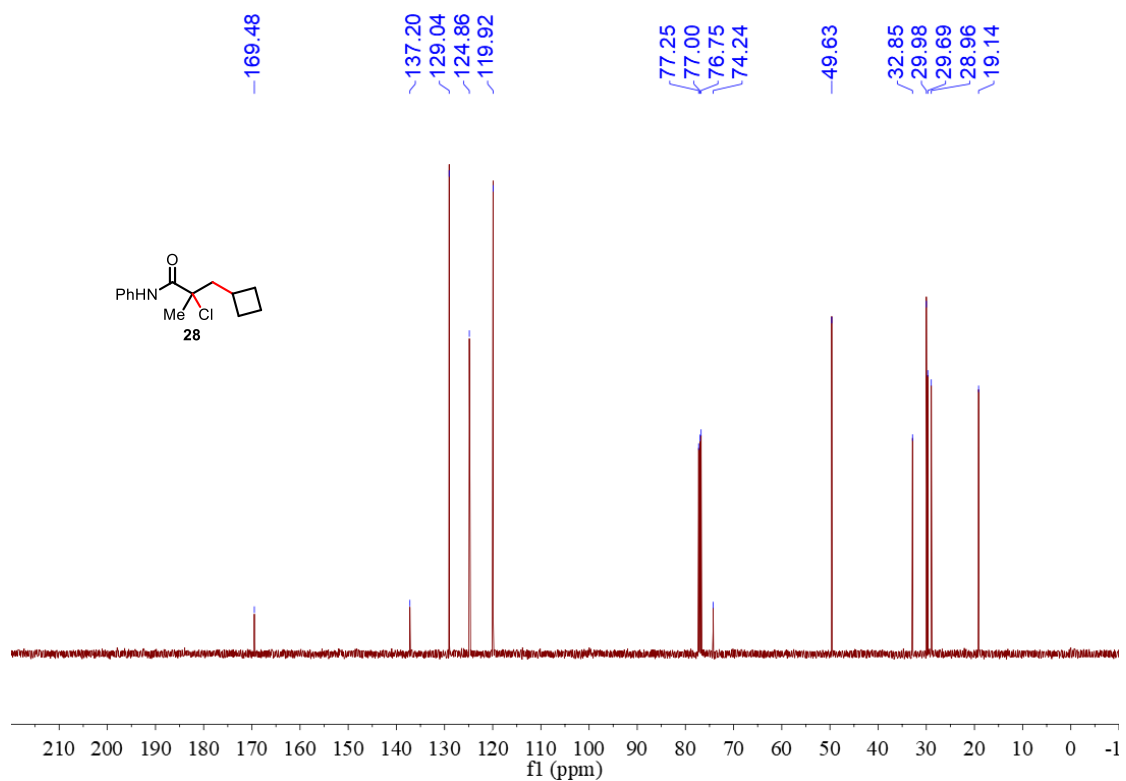
Supplementary Figure 83. ^1H NMR (500 MHz, CDCl_3) spectrum for compound **27**



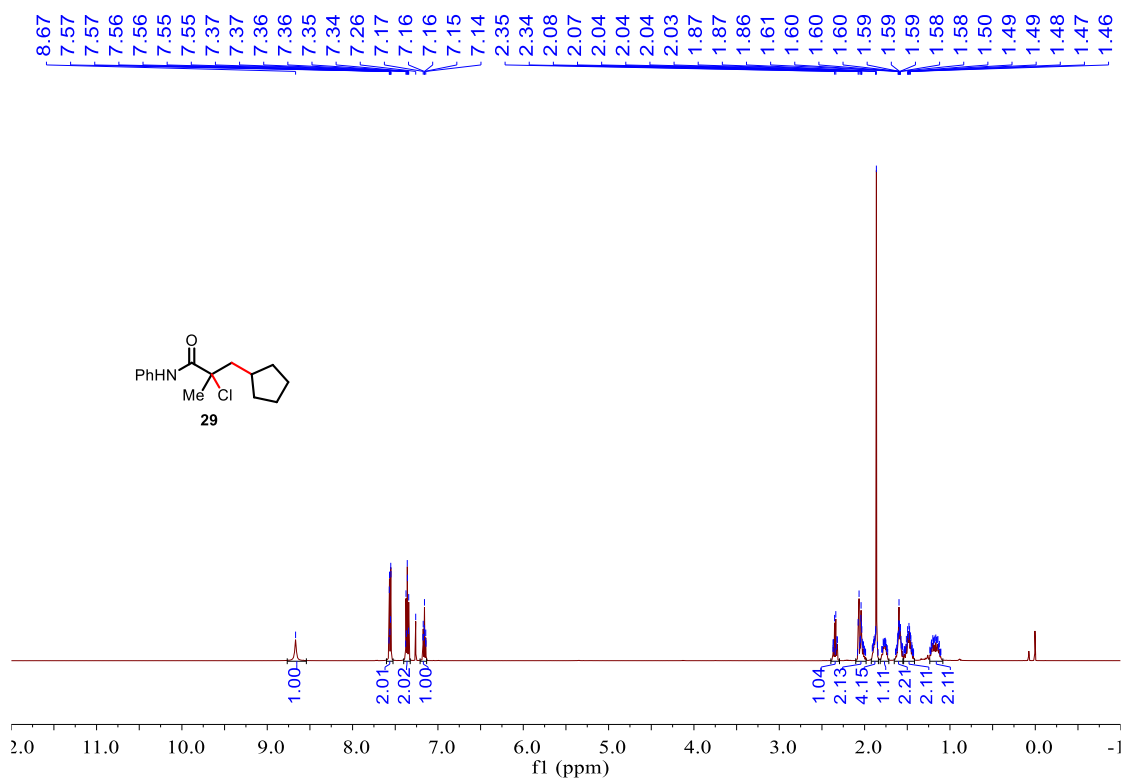
Supplementary Figure 84. ^{13}C NMR (126 MHz, CDCl_3) spectrum for compound **27**



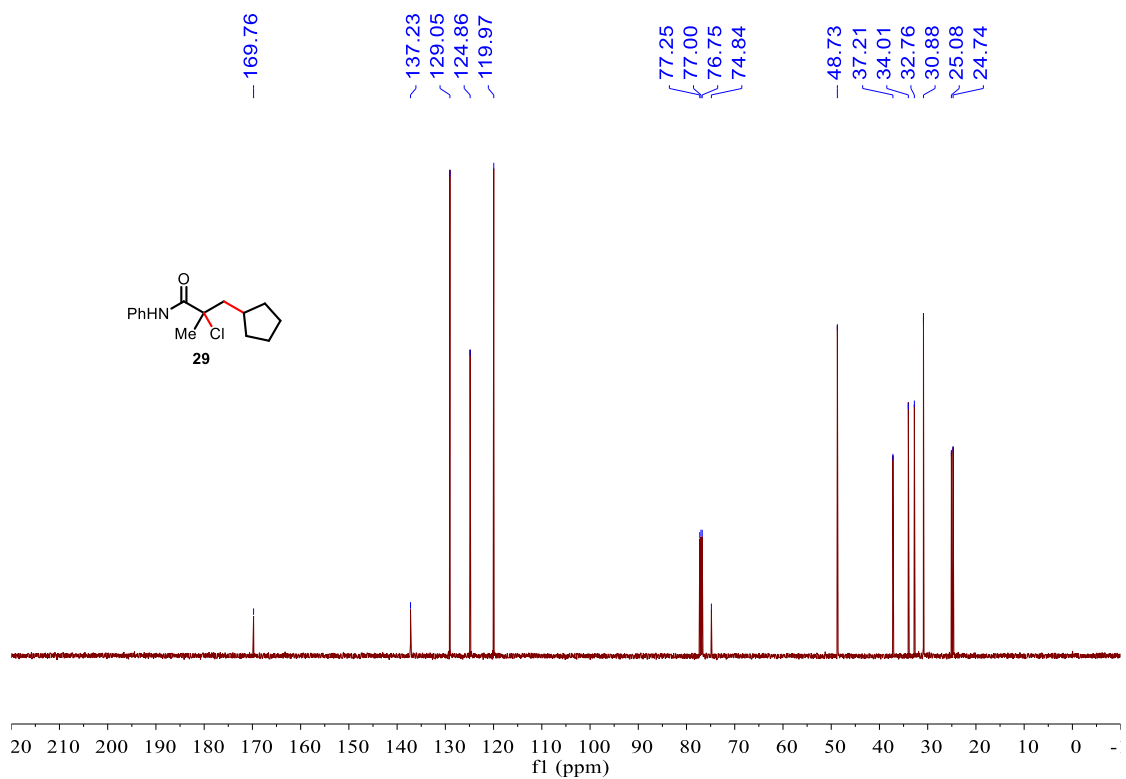
Supplementary Figure 85. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **28**



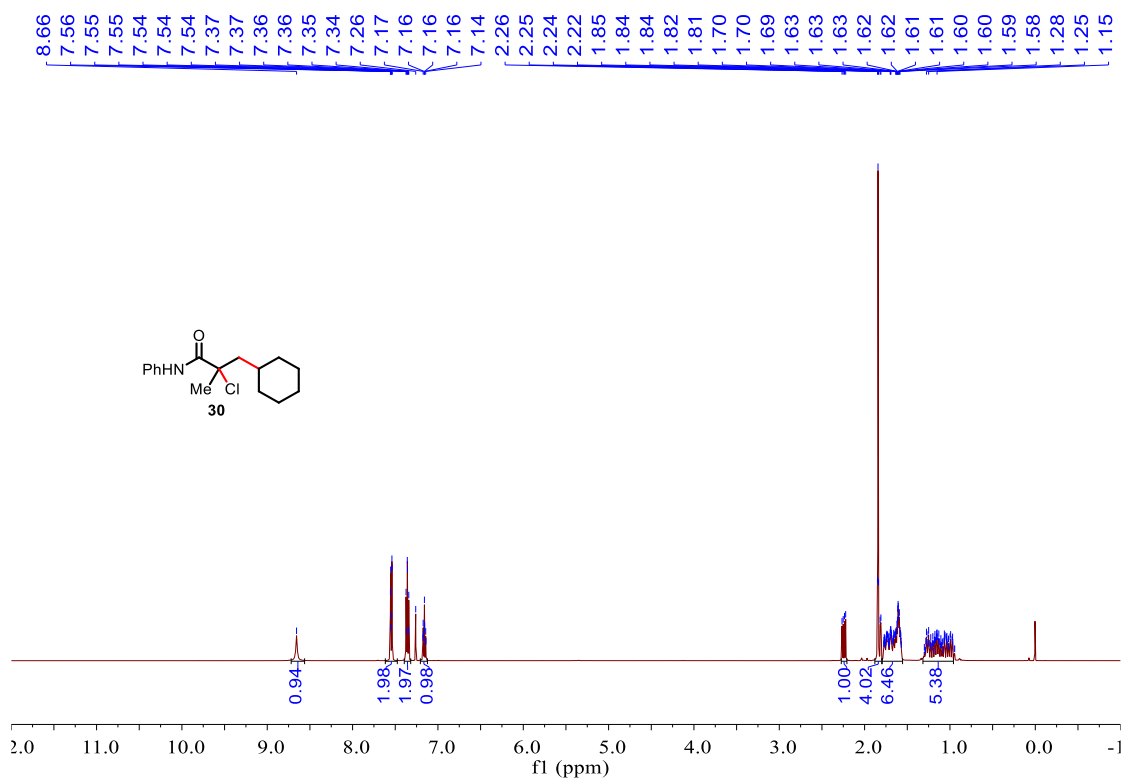
Supplementary Figure 86. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **28**



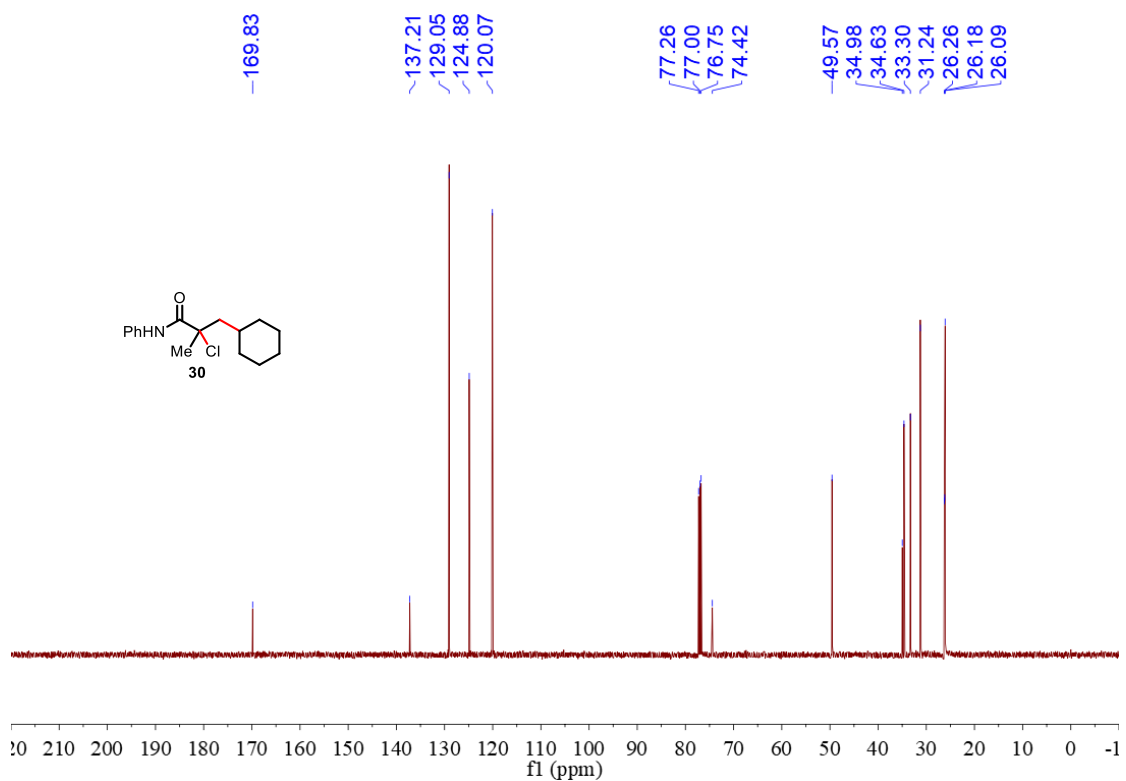
Supplementary Figure 87. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **29**



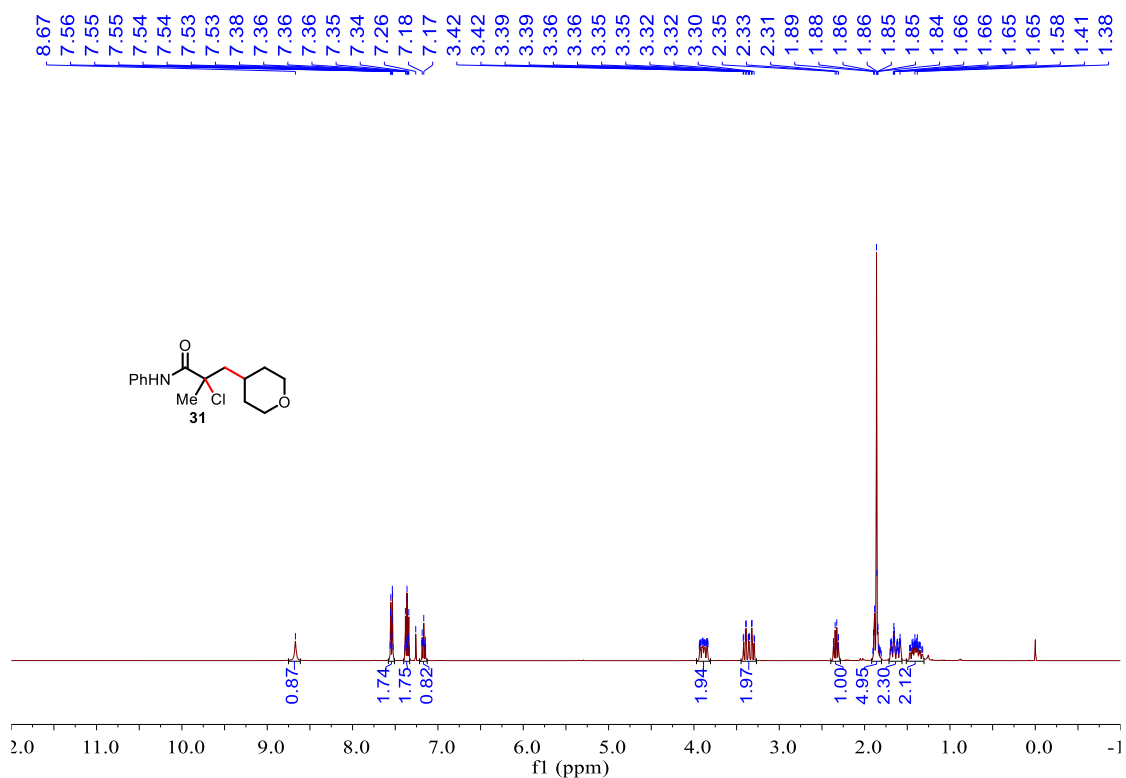
Supplementary Figure 88. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **29**



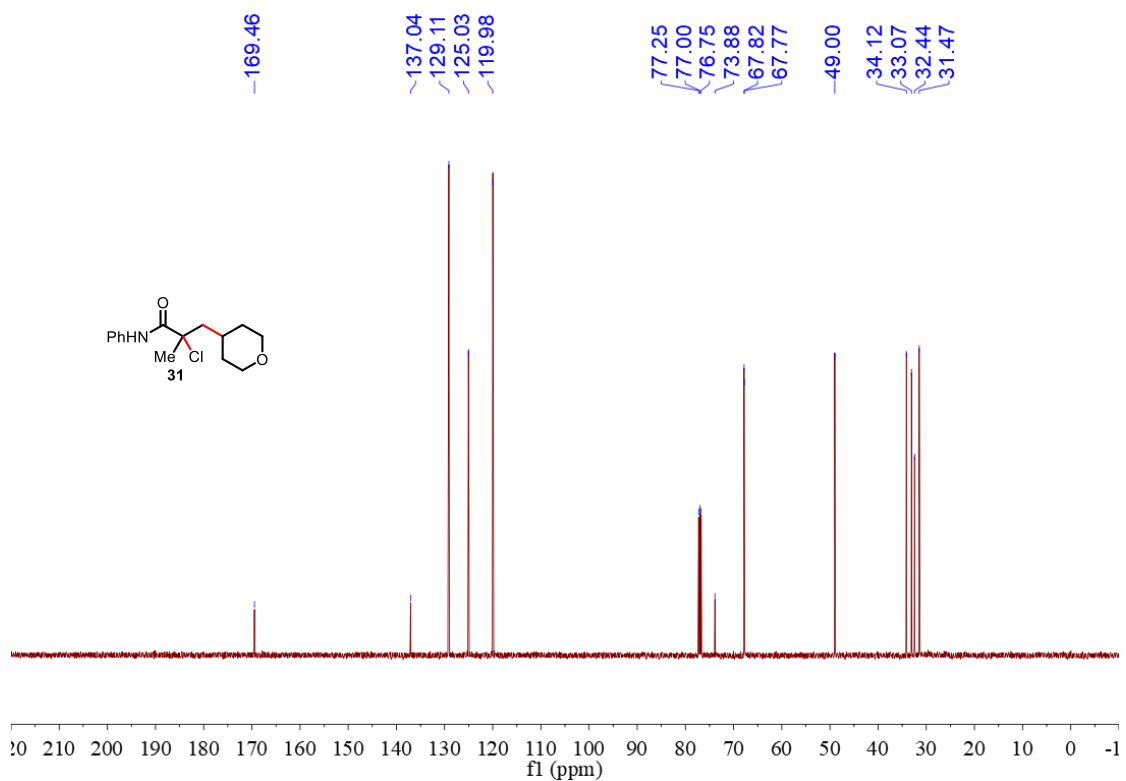
Supplementary Figure 89. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **30**



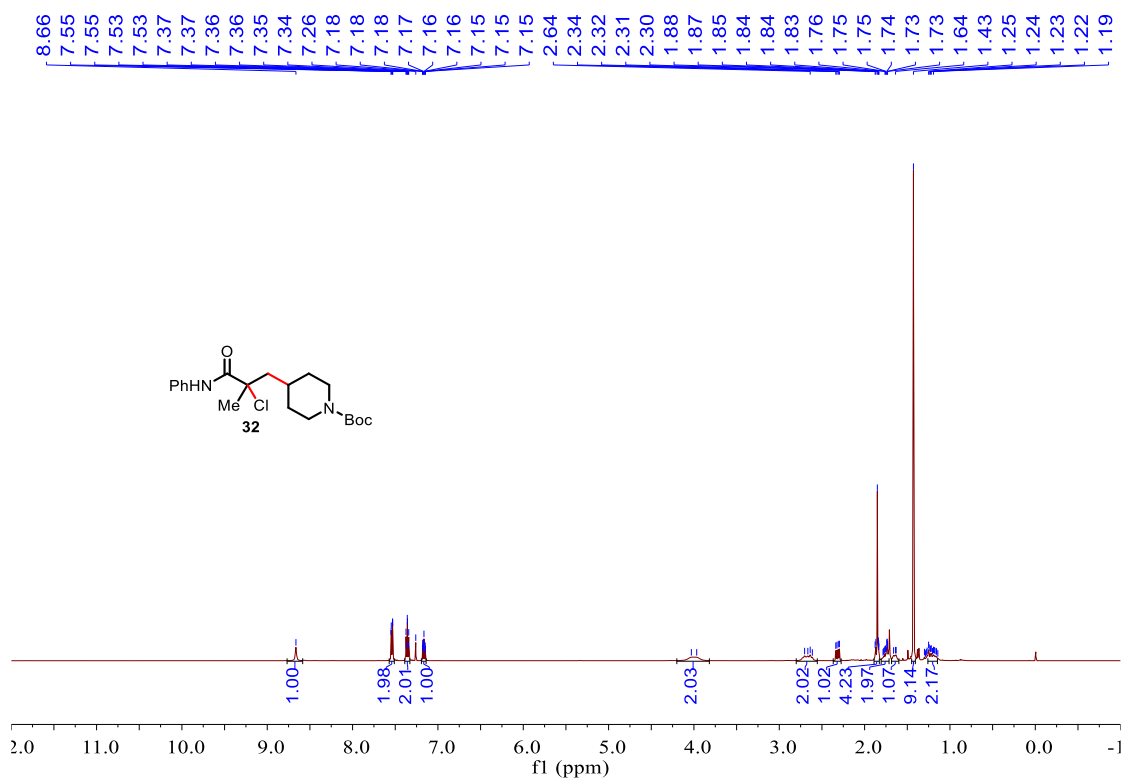
Supplementary Figure 90. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **30**



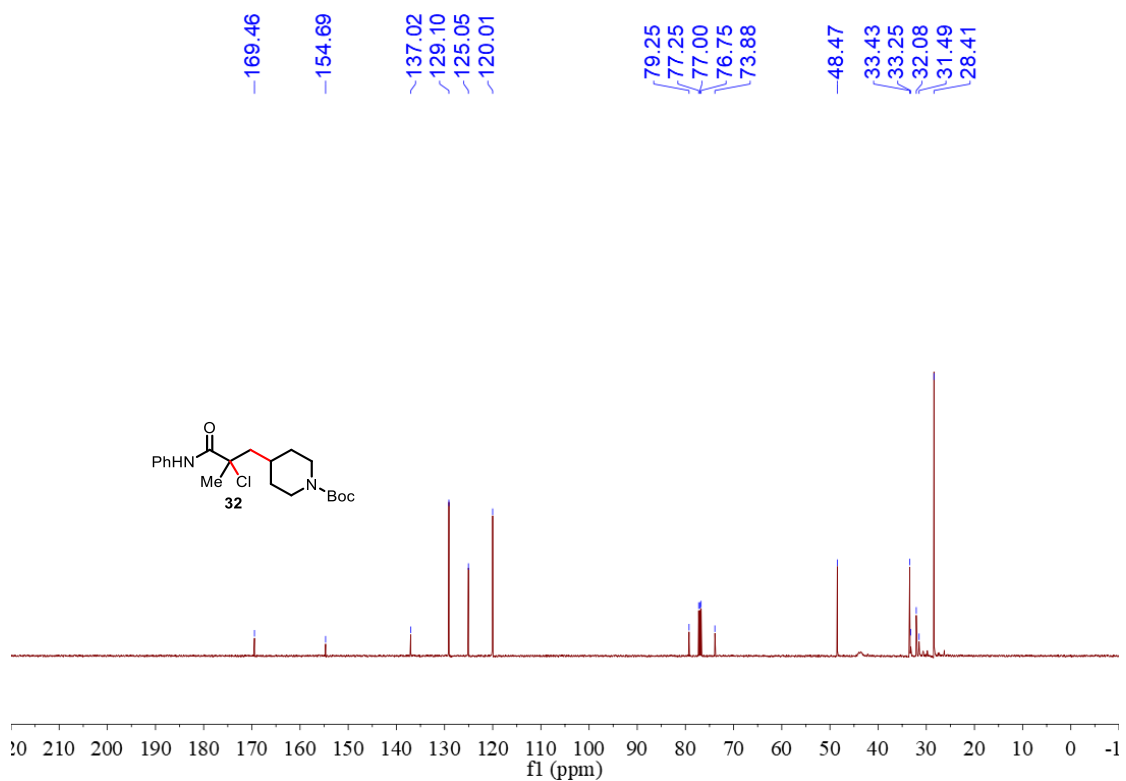
Supplementary Figure 91. ¹H NMR (400 MHz, CDCl₃) spectrum for compound **31**



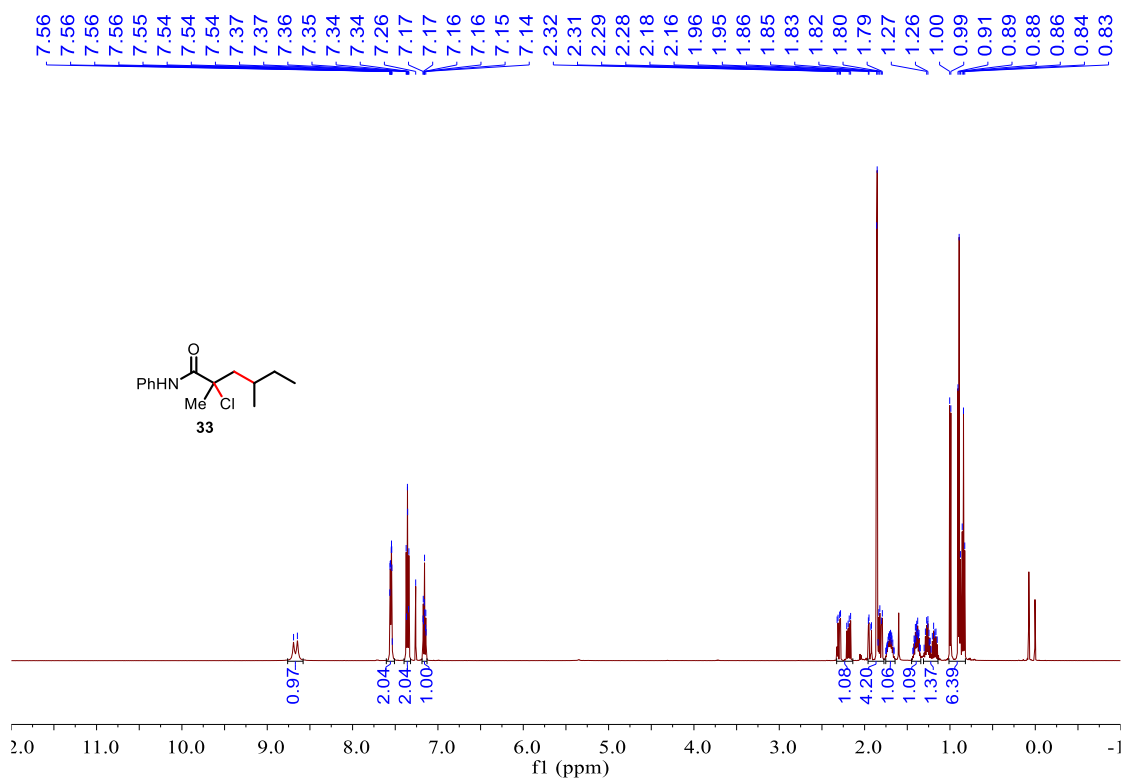
Supplementary Figure 92. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **31**



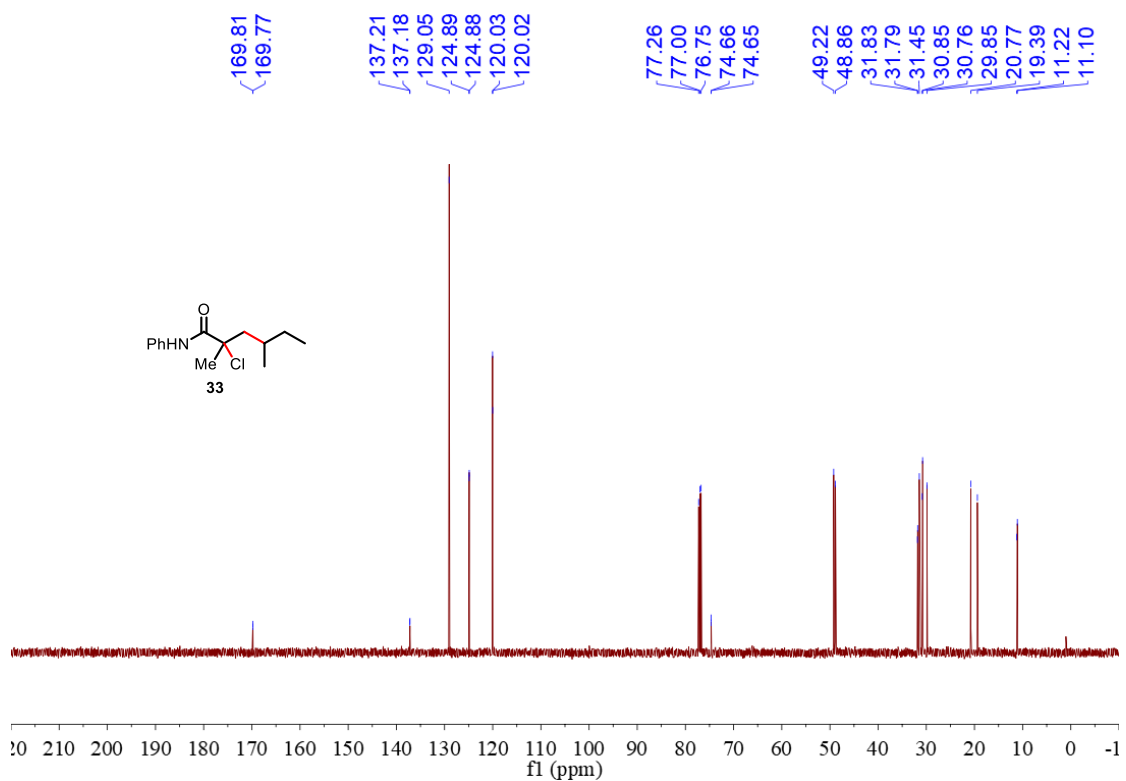
Supplementary Figure 93. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **32**



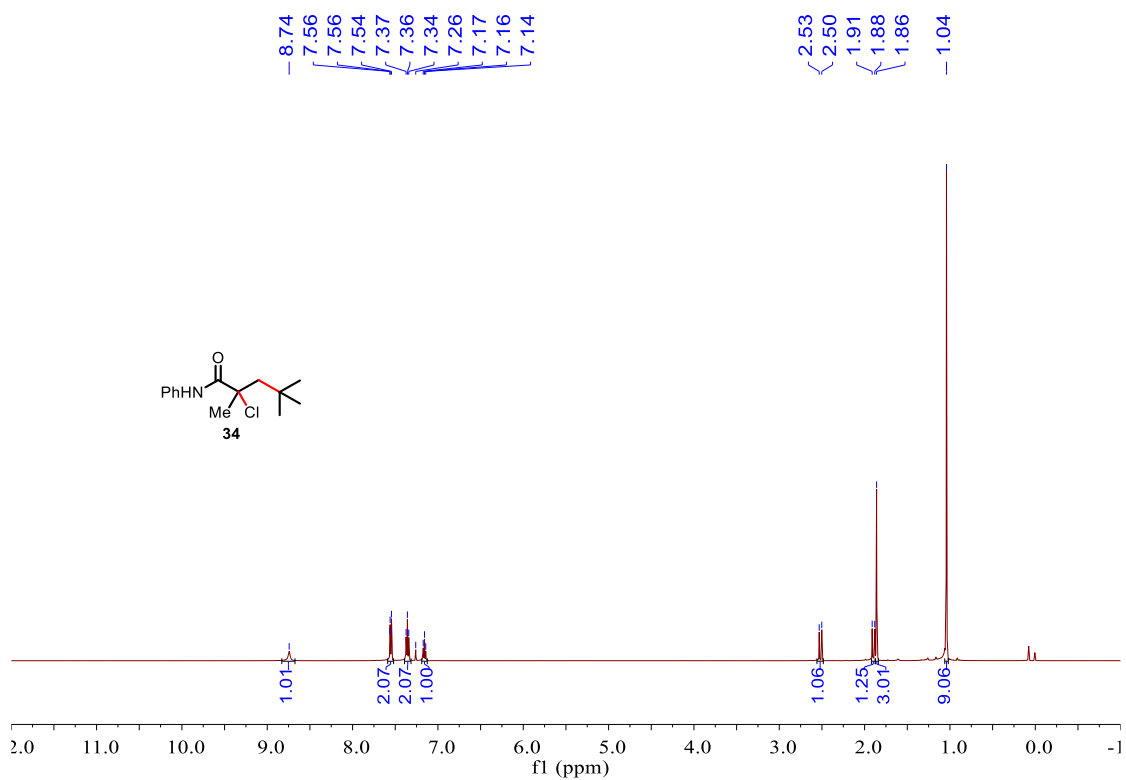
Supplementary Figure 94. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **32**



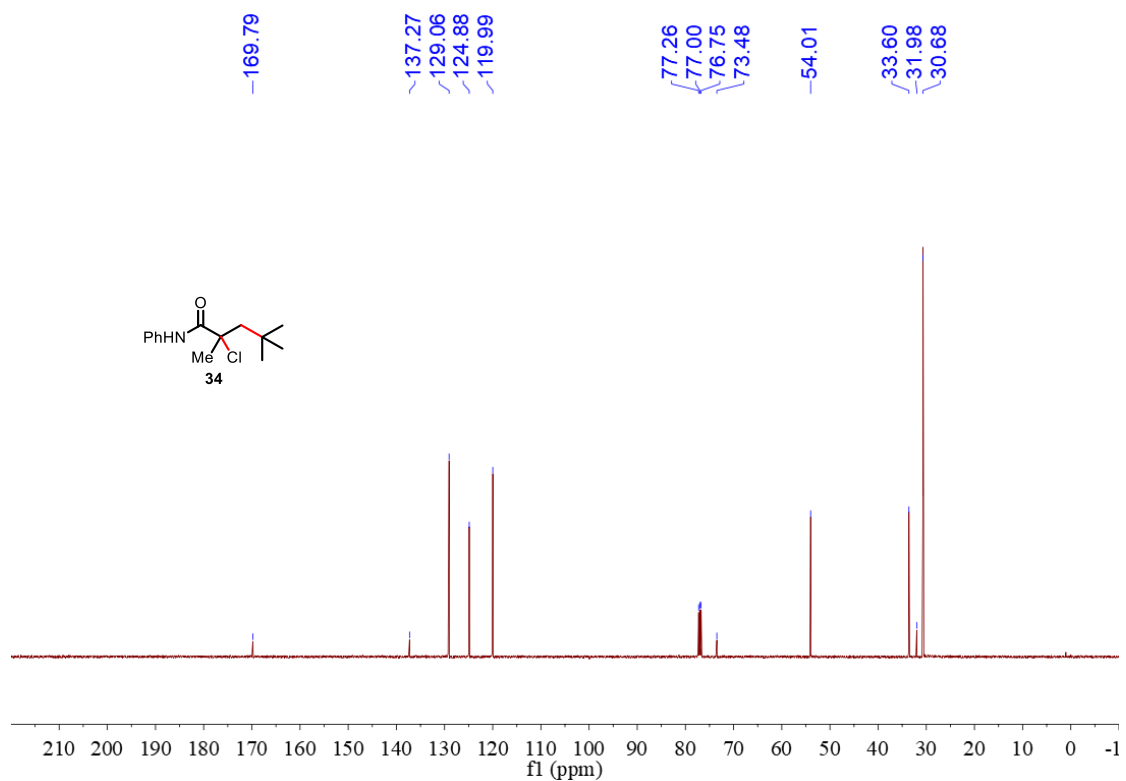
Supplementary Figure 95. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **33**



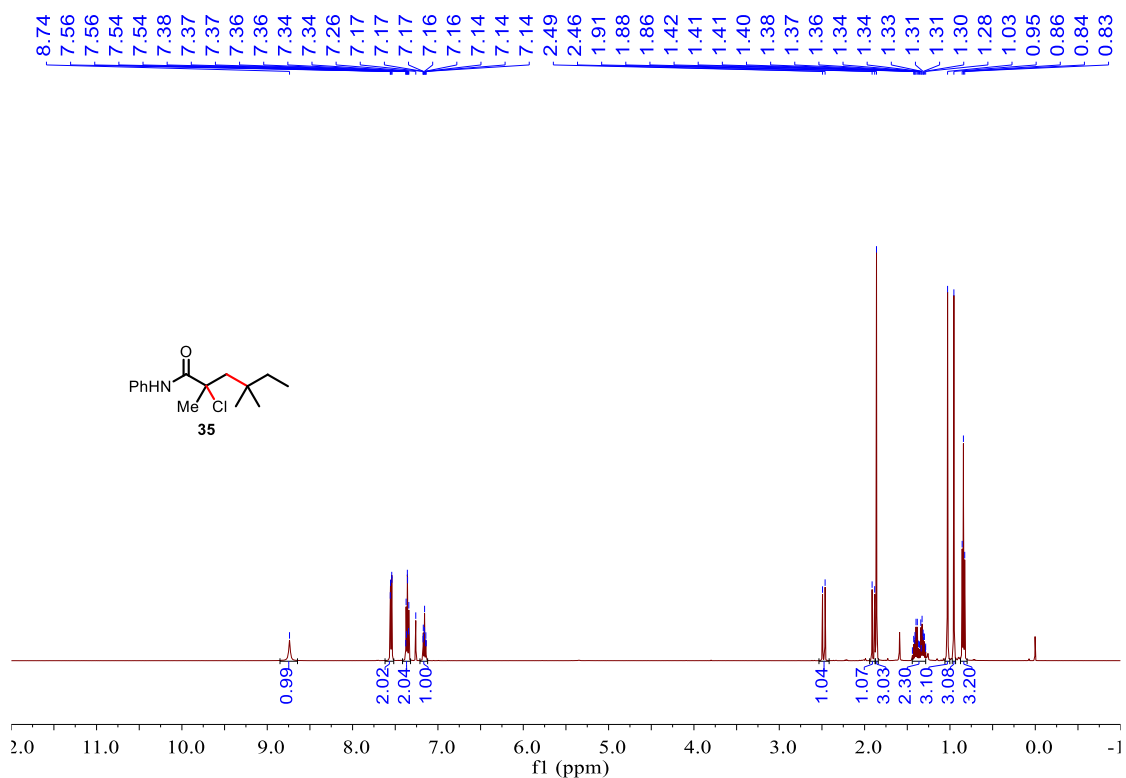
Supplementary Figure 96. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **33**



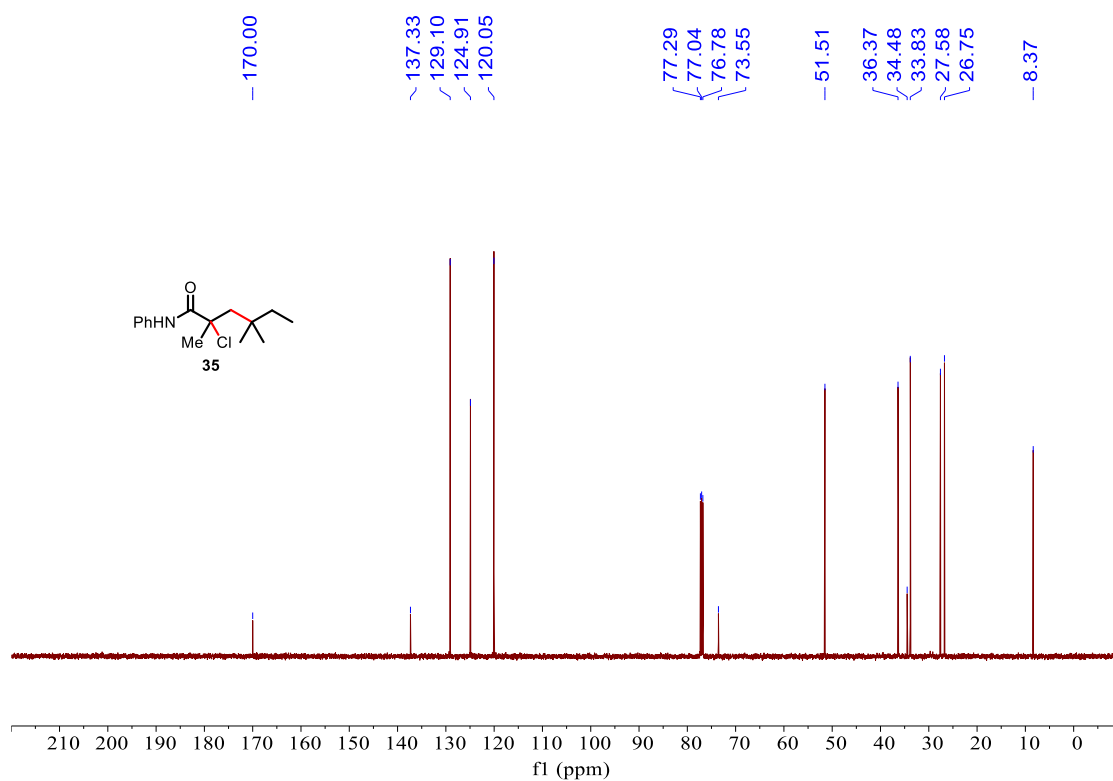
Supplementary Figure 97. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **34**



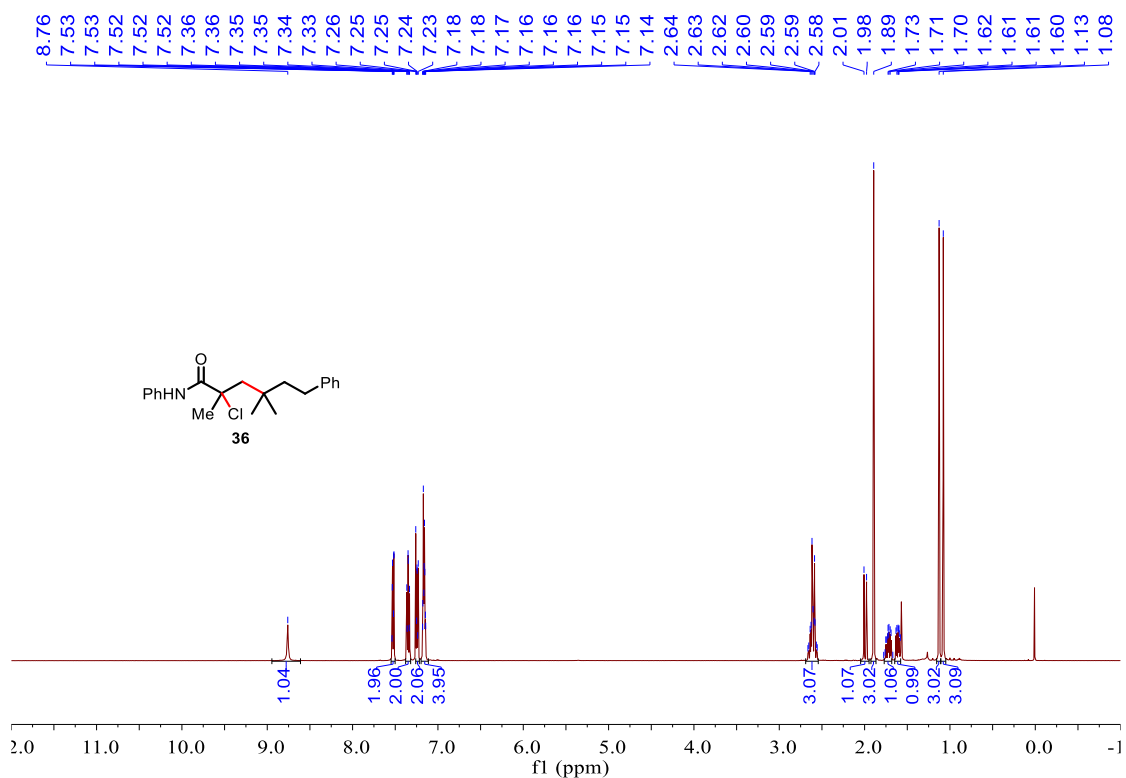
Supplementary Figure 98. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **34**



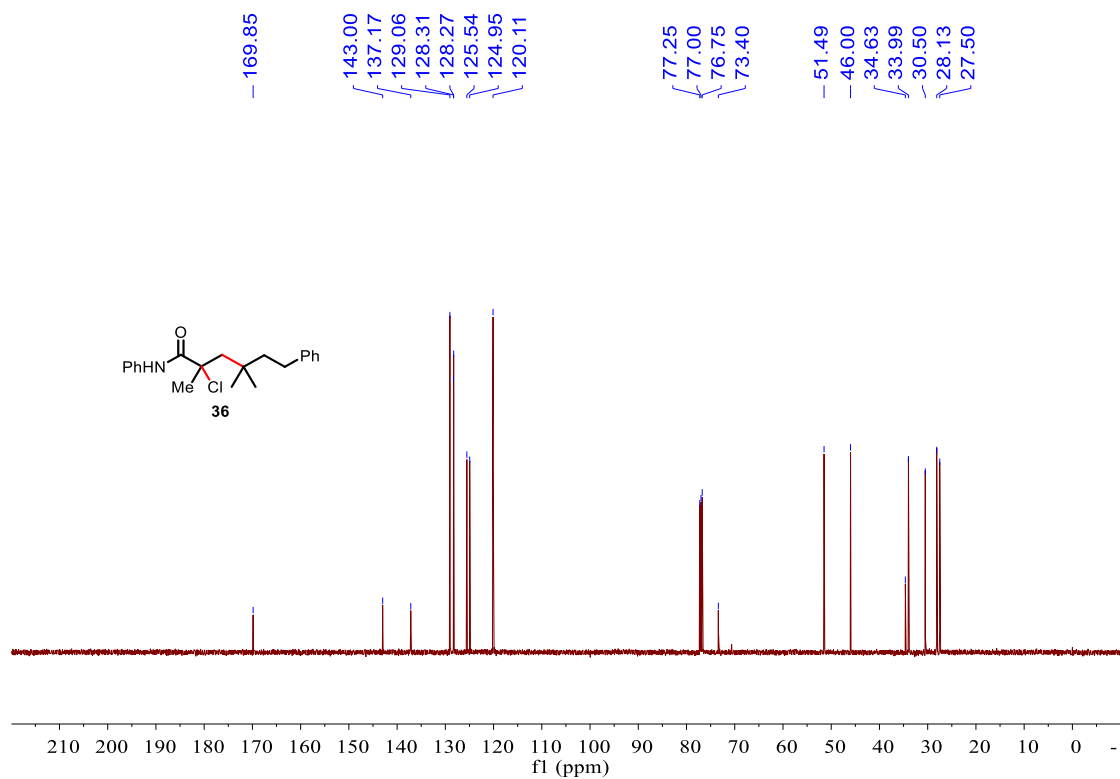
Supplementary Figure 99. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **35**



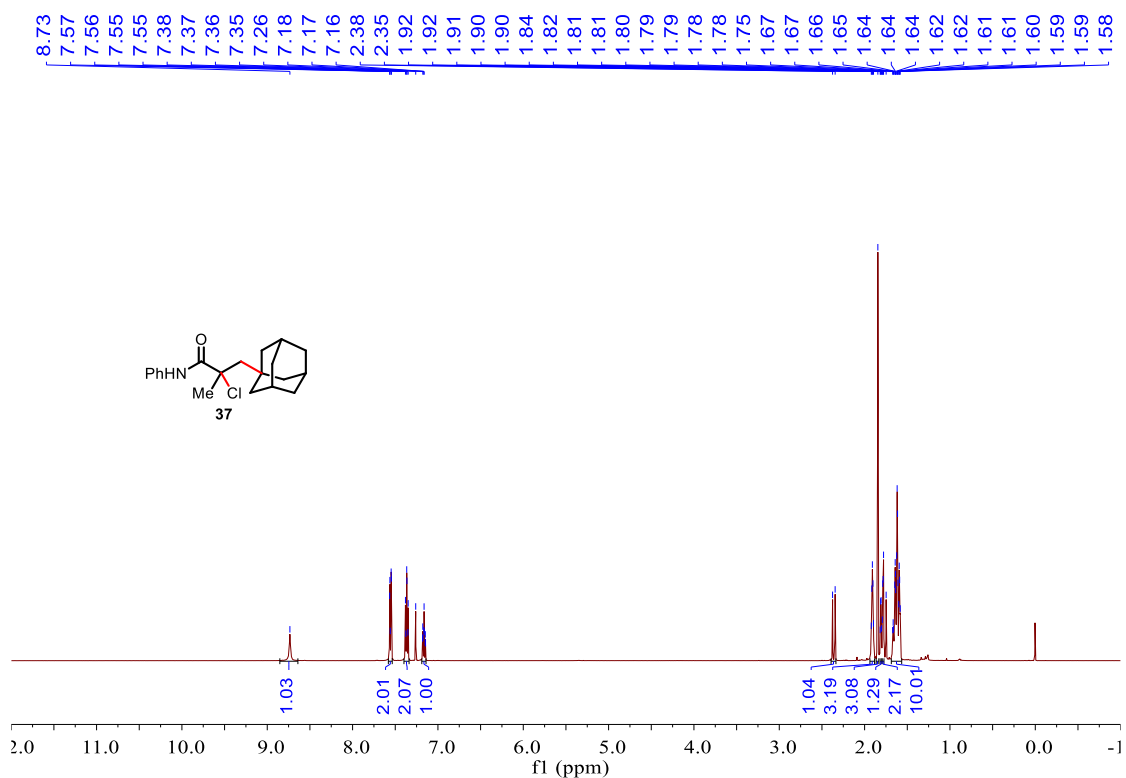
Supplementary Figure 100. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **35**



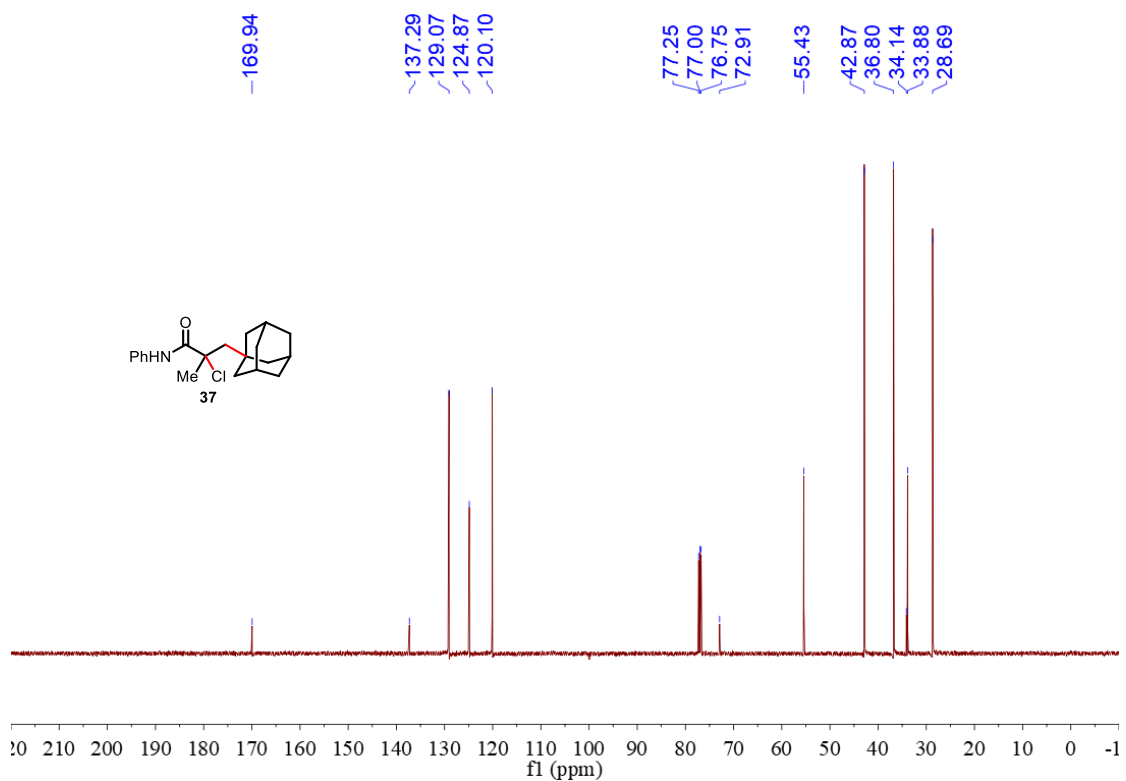
Supplementary Figure 101. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **36**



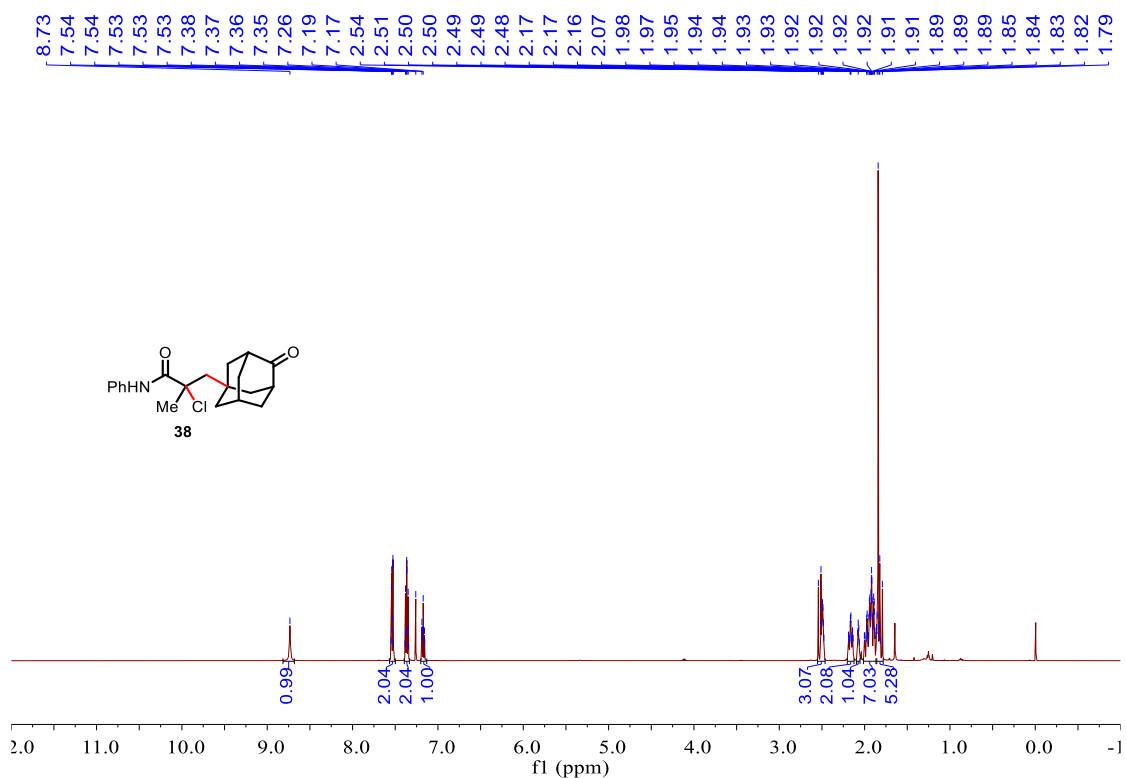
Supplementary Figure 102. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **36**



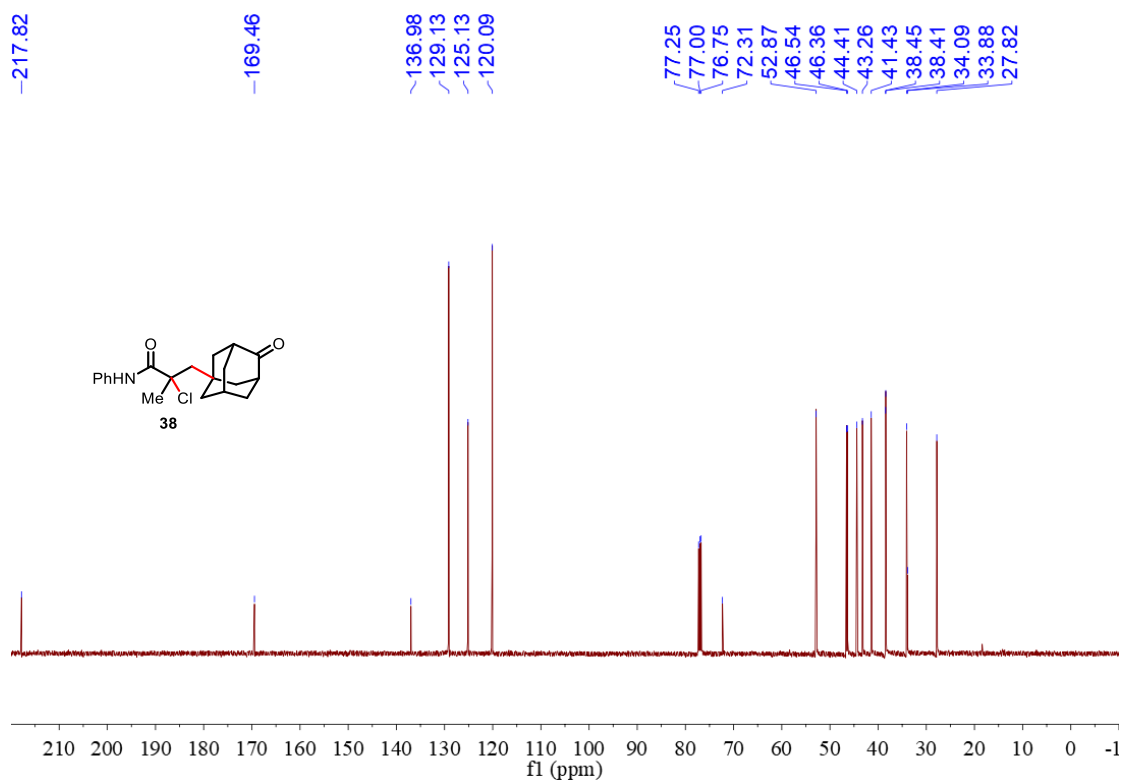
Supplementary Figure 103. ¹H NMR (500 MHz, CDCl₃) spectrum for compound 37



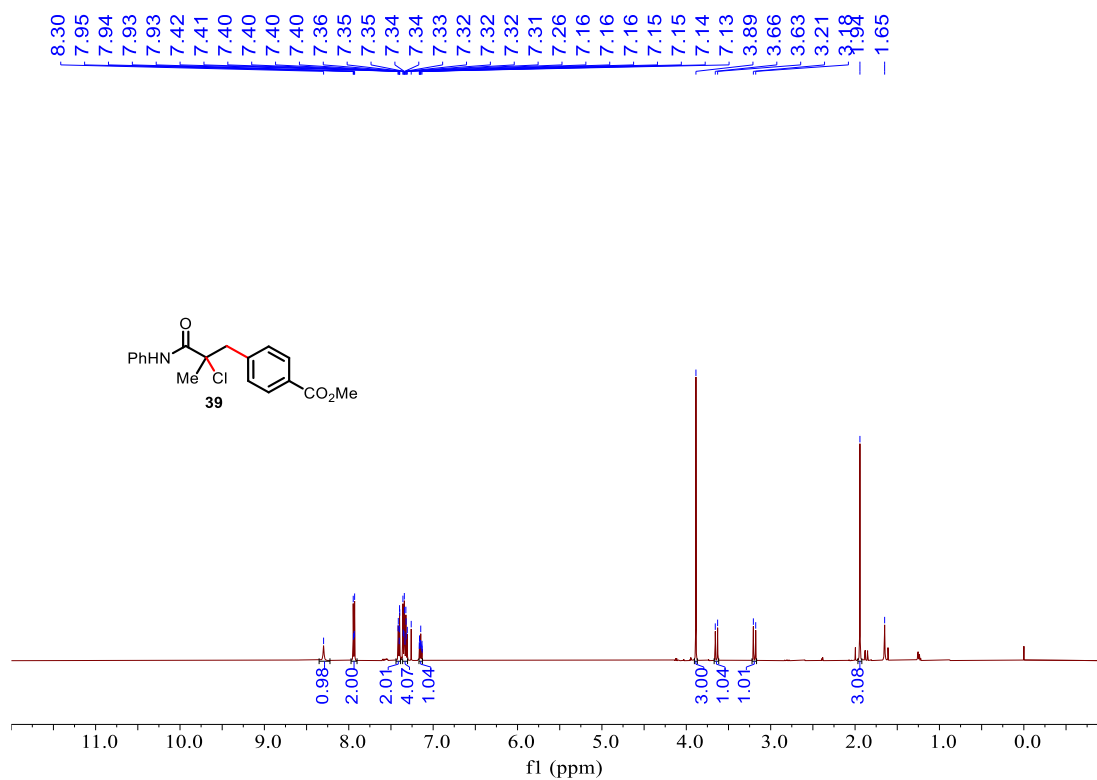
Supplementary Figure 104. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound 37



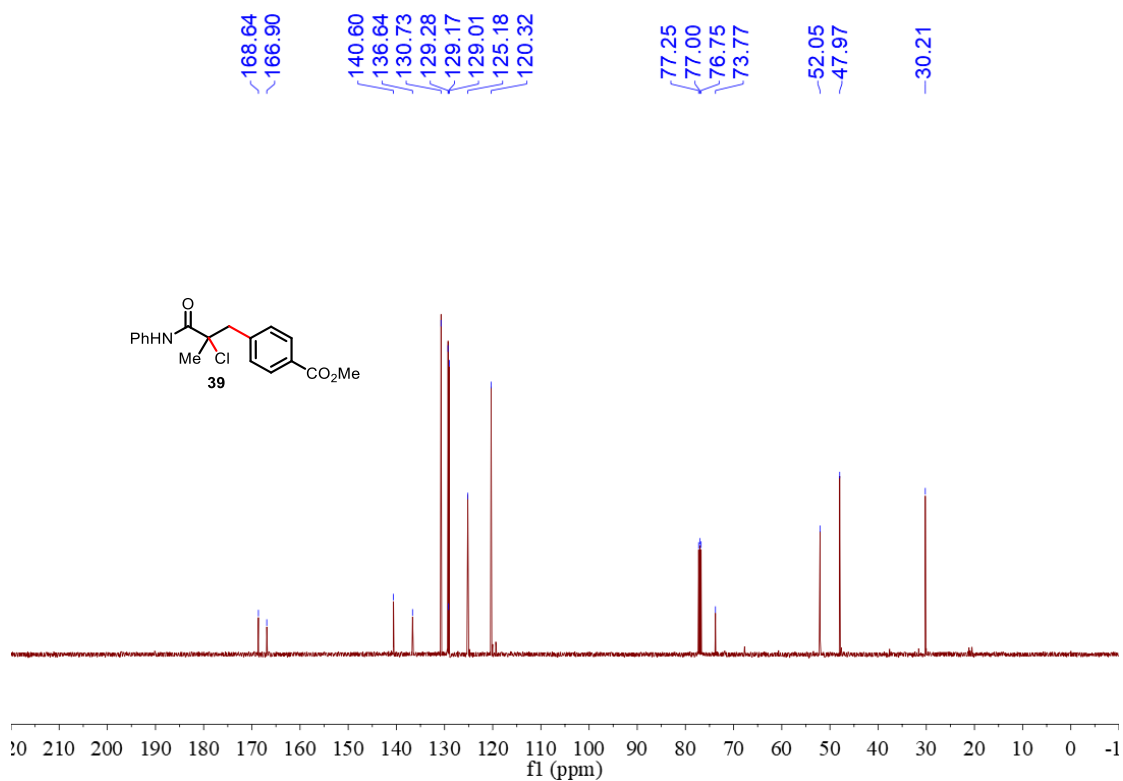
Supplementary Figure 105. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **38**



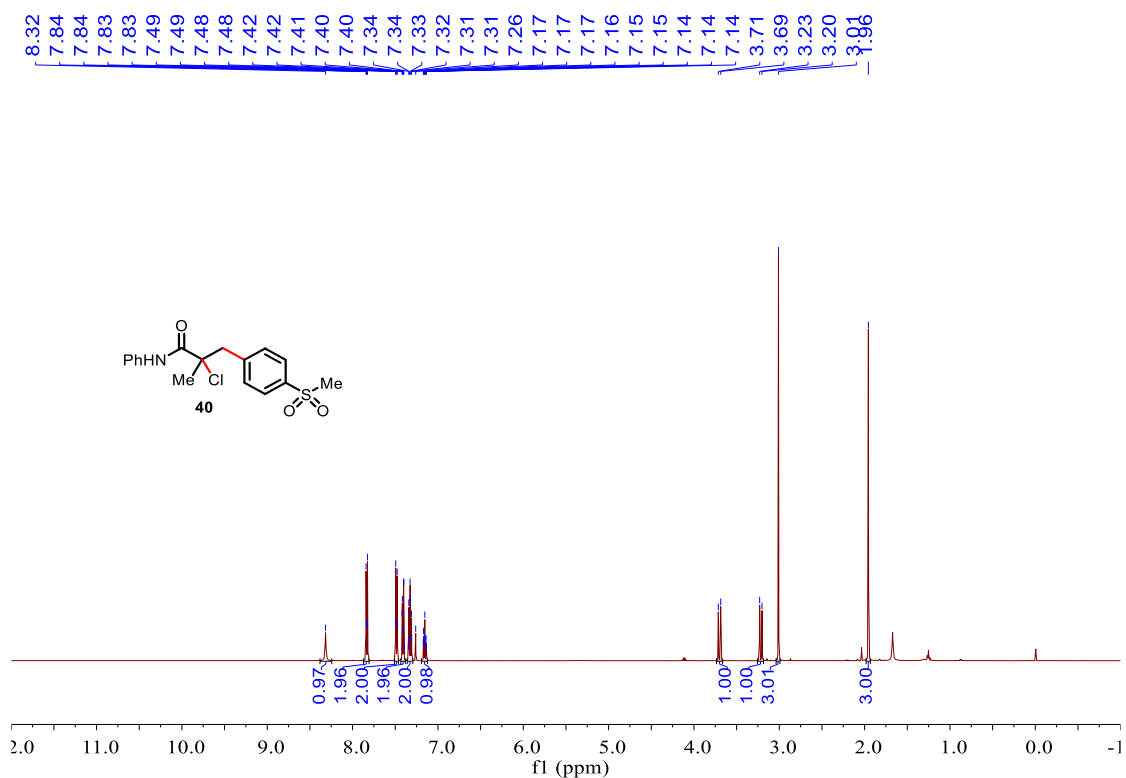
Supplementary Figure 106. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **38**



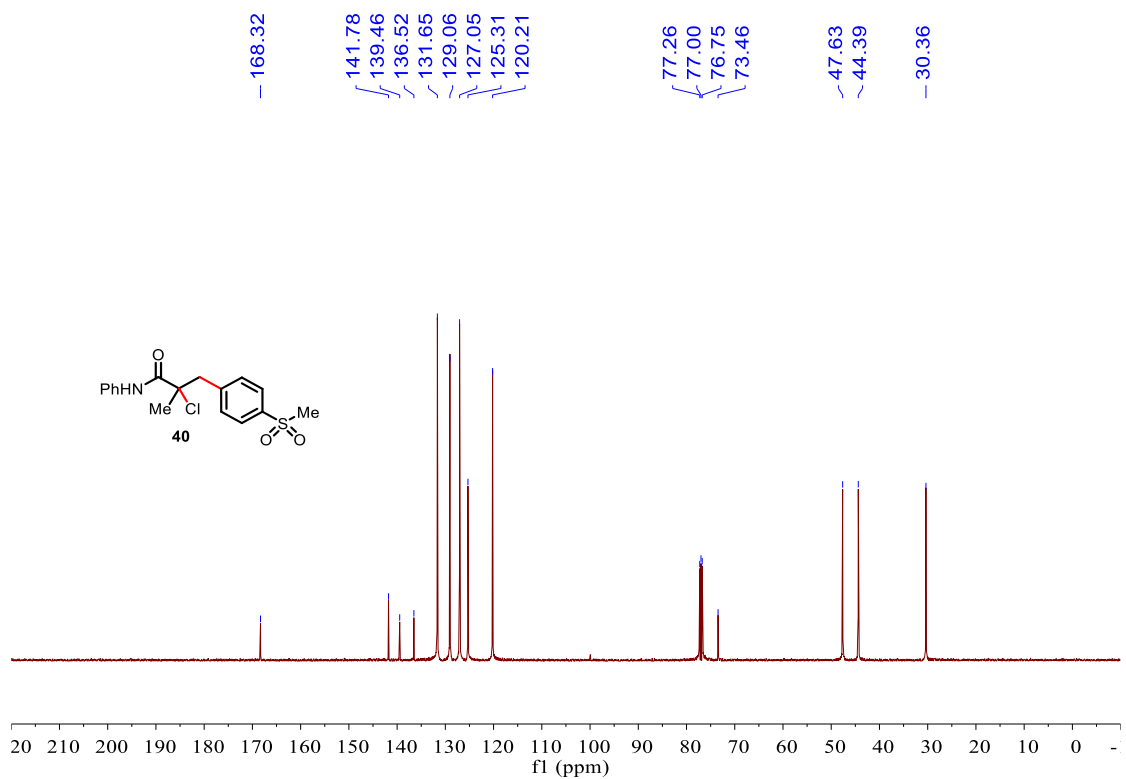
Supplementary Figure 107. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **39**



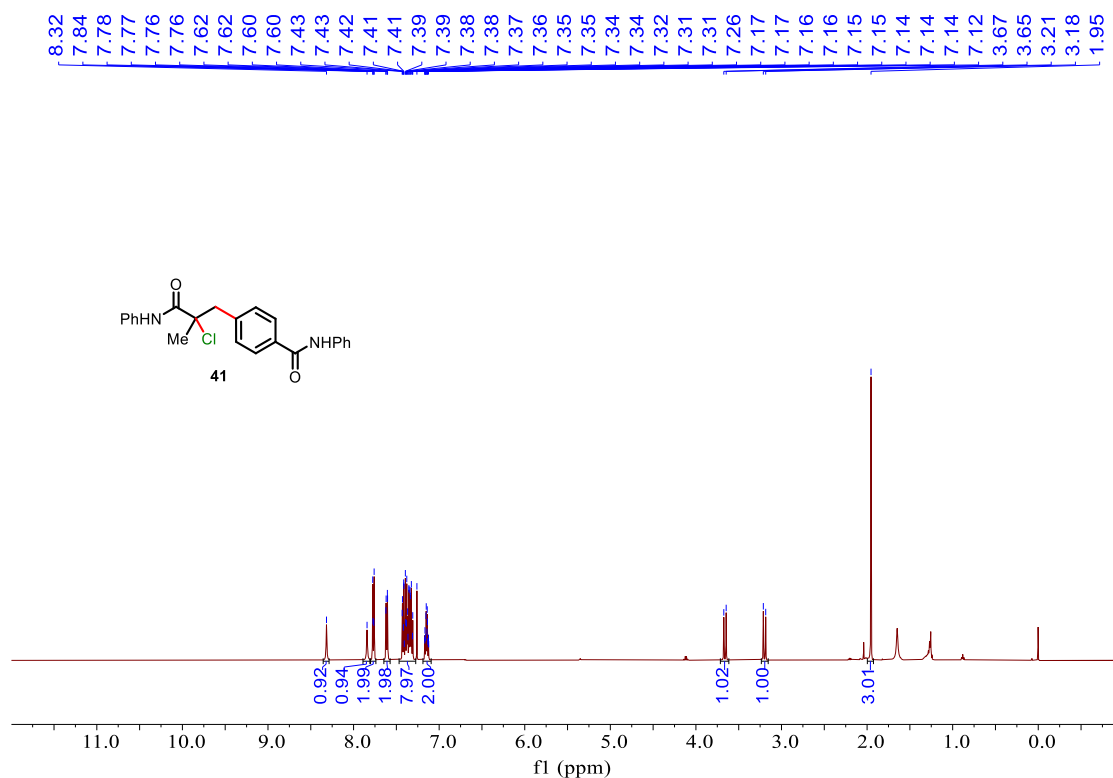
Supplementary Figure 108. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **39**



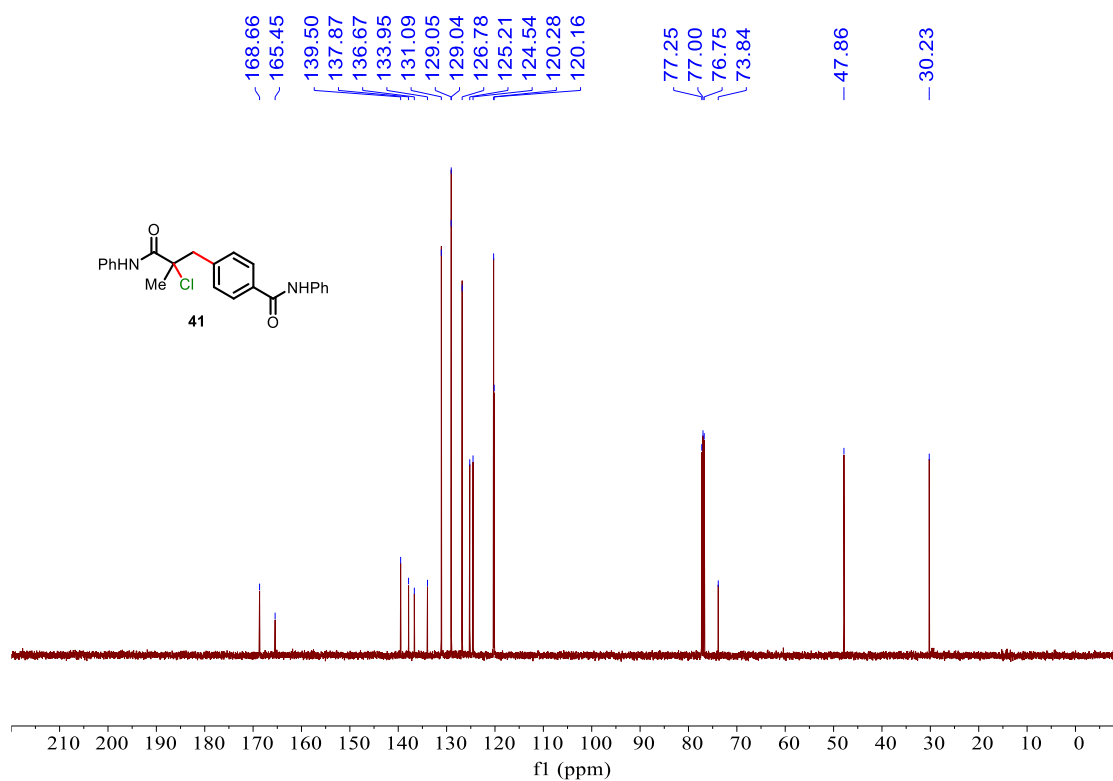
Supplementary Figure 109. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **40**



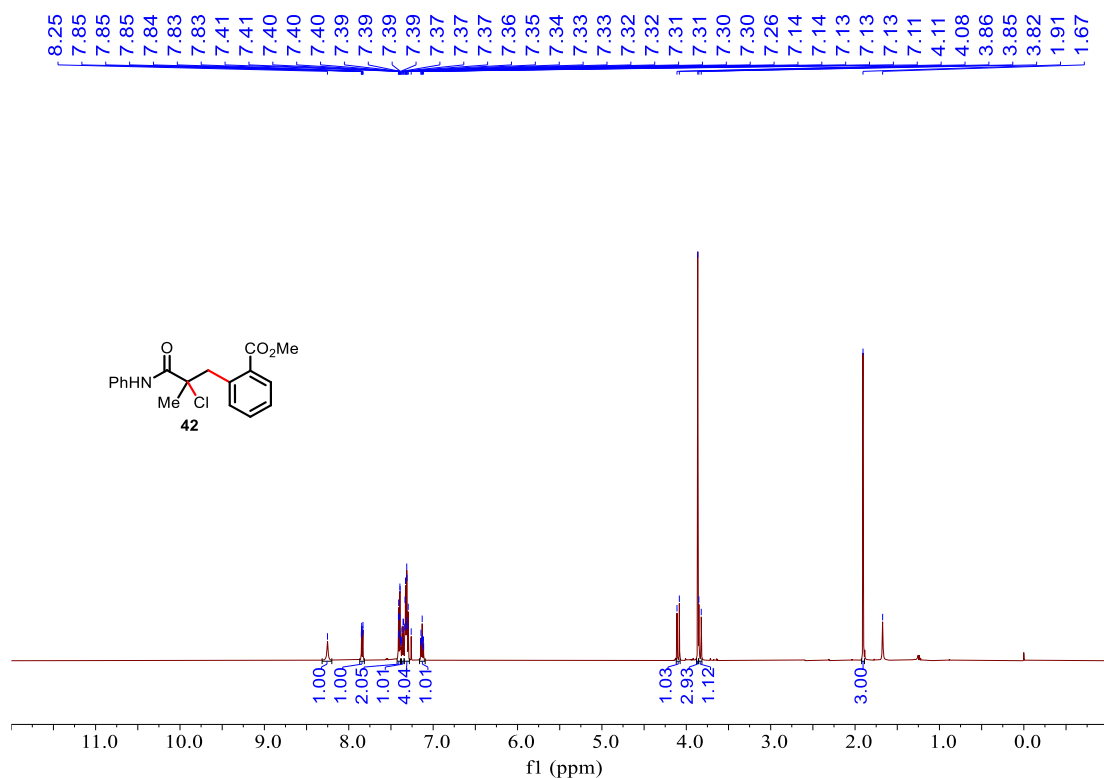
Supplementary Figure 110. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **40**



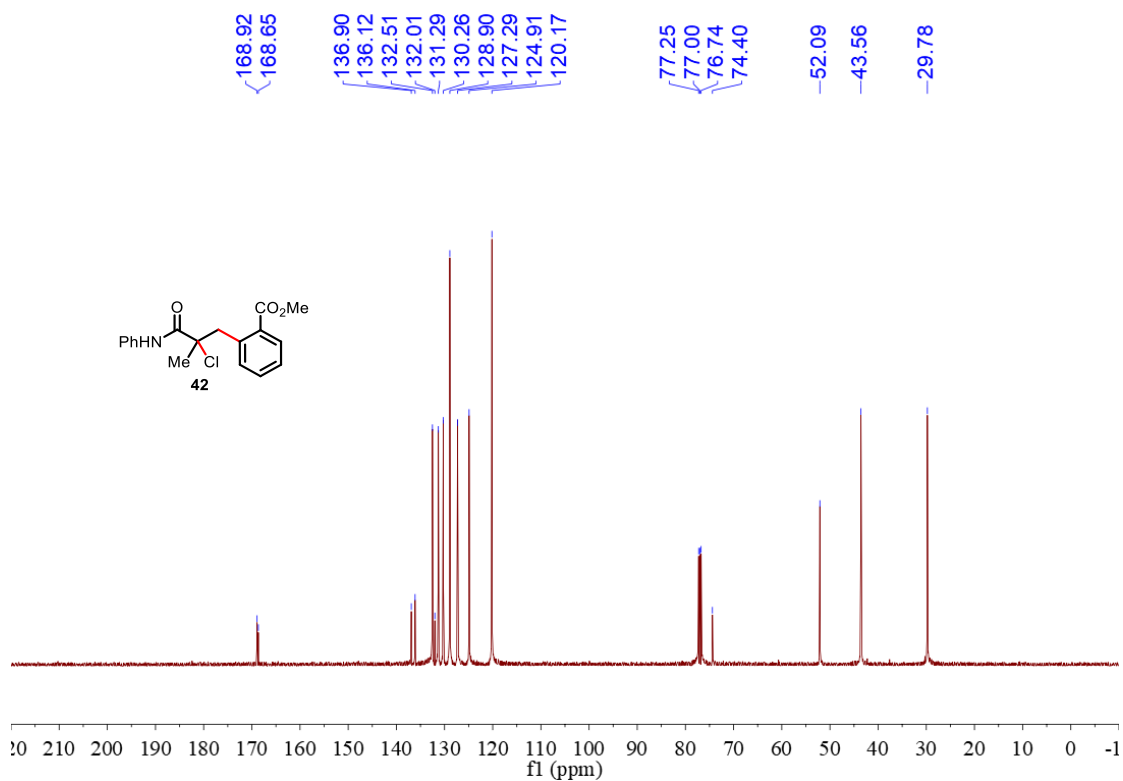
Supplementary Figure 111. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **41**



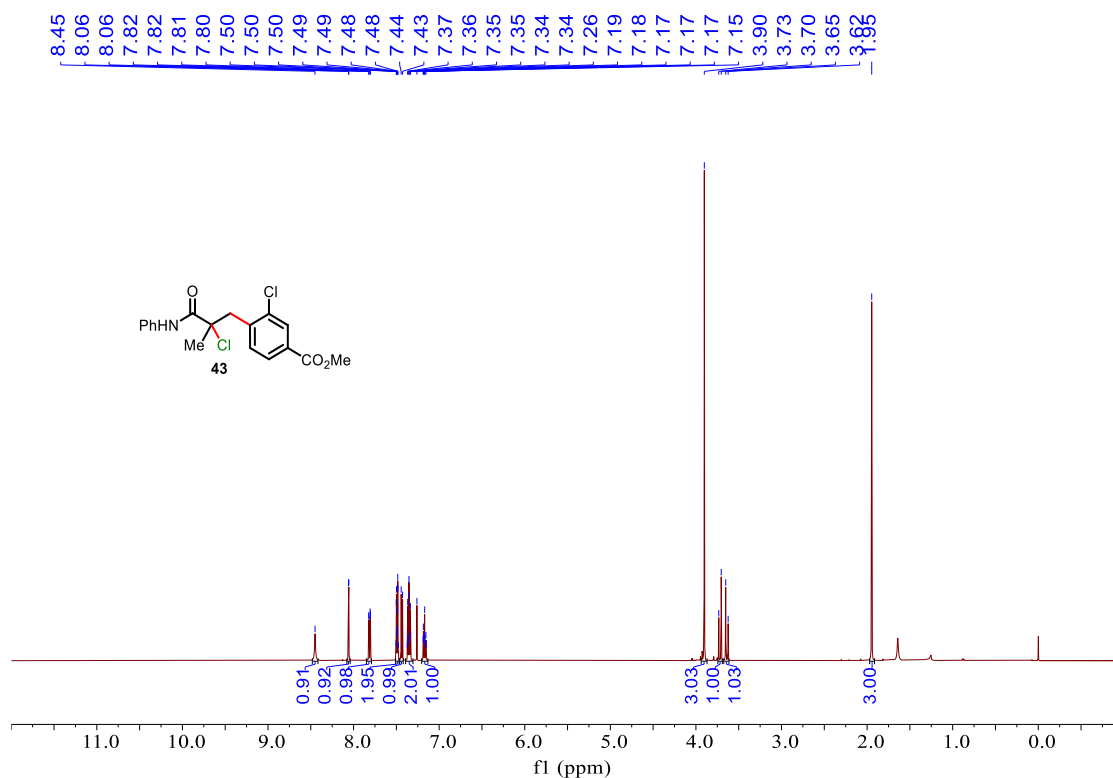
Supplementary Figure 112. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **41**



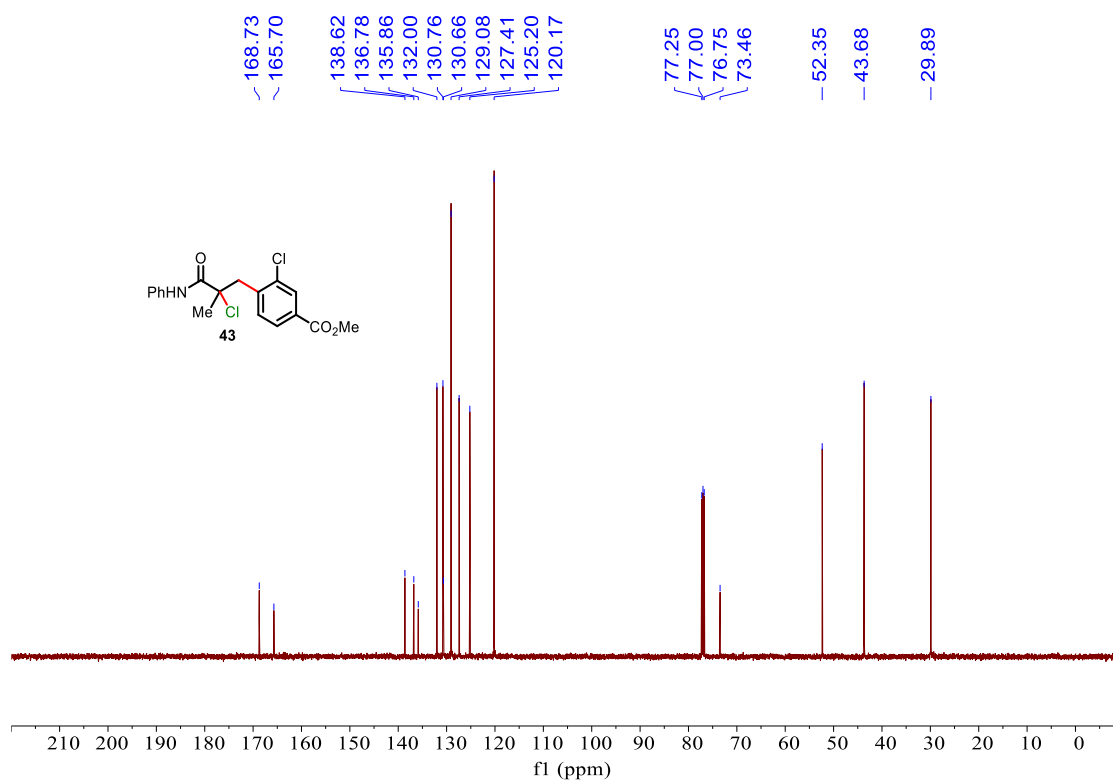
Supplementary Figure 113. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **42**



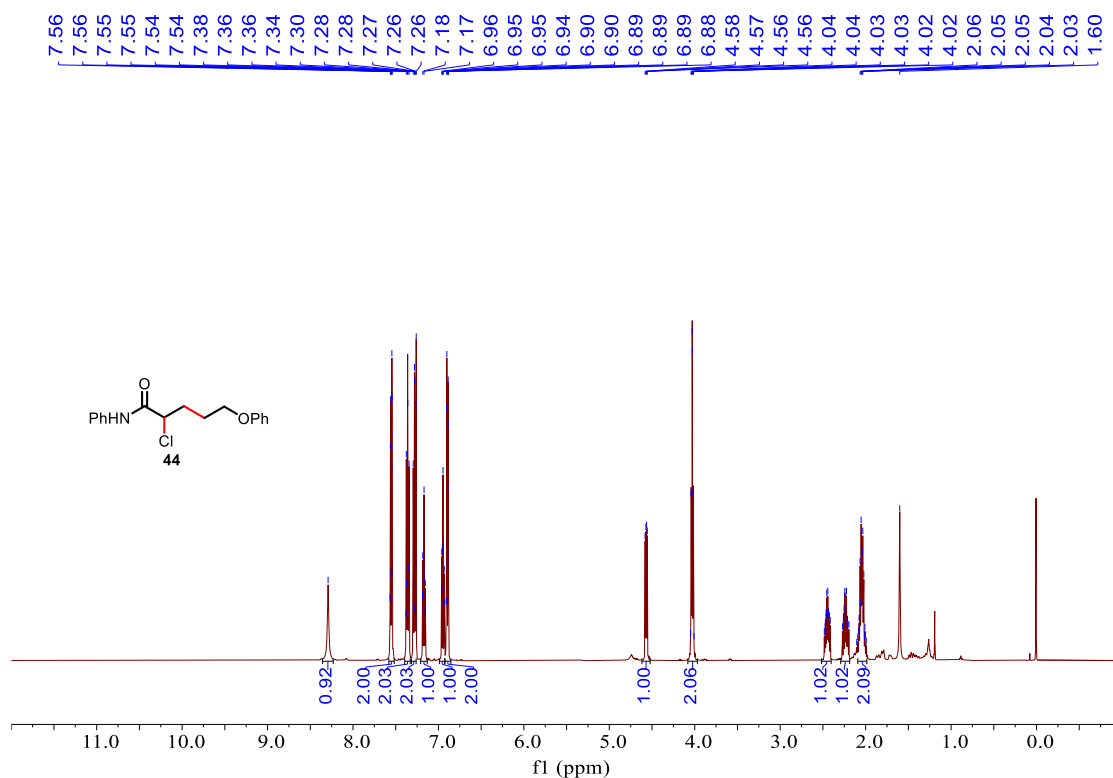
Supplementary Figure 114. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **42**



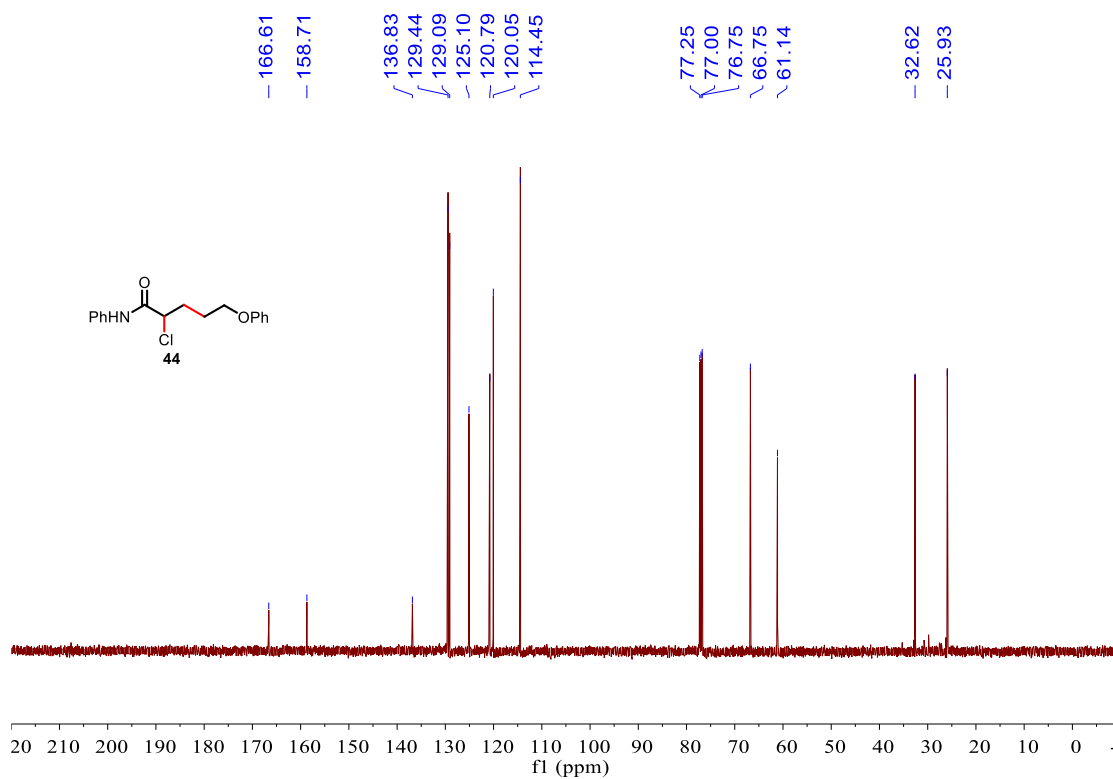
Supplementary Figure 115. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **43**



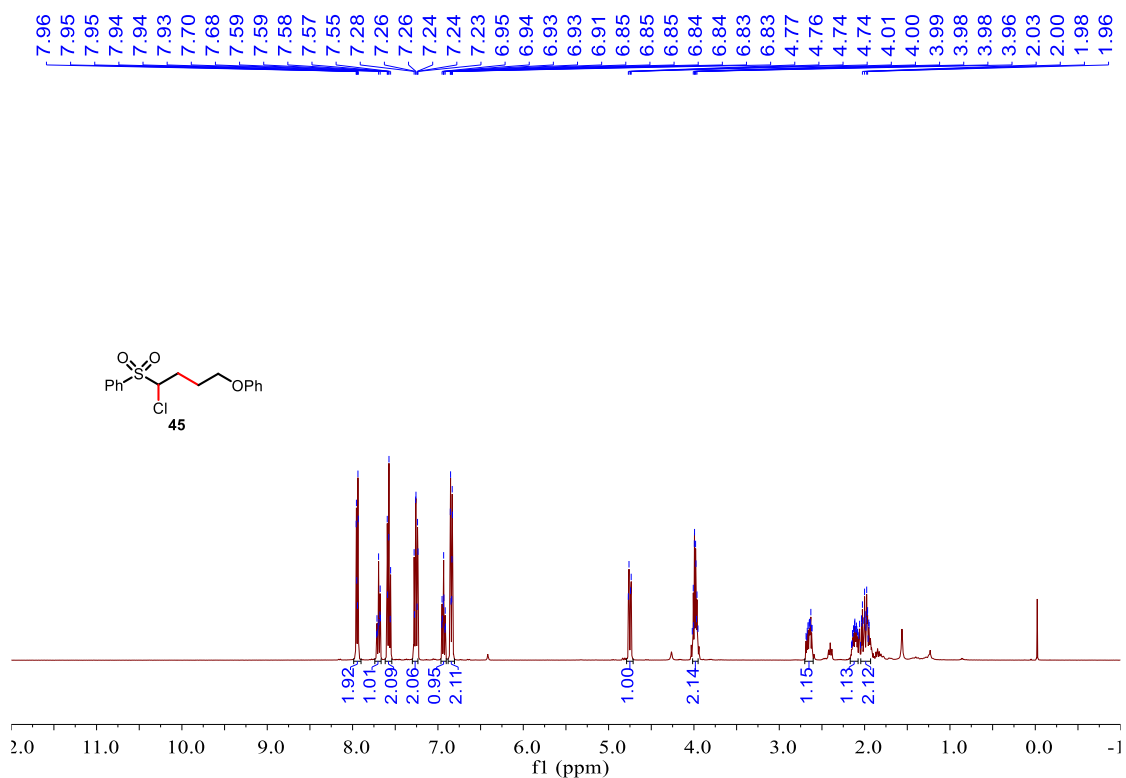
Supplementary Figure 116. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **43**



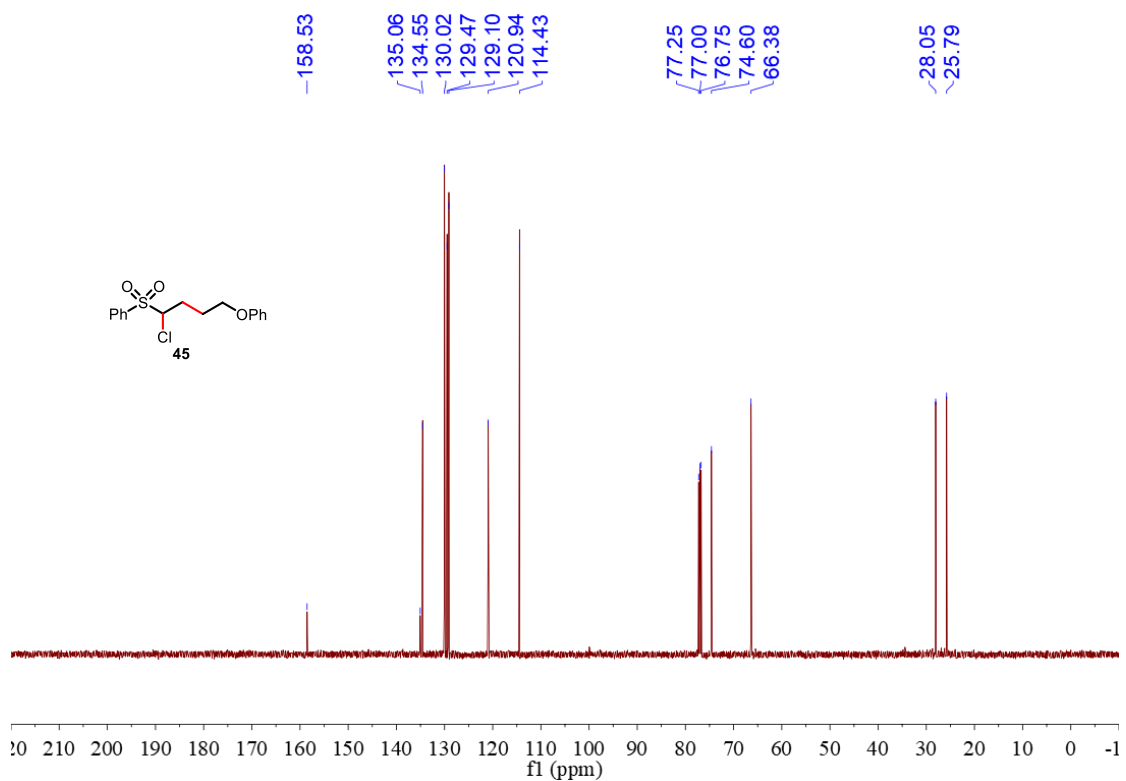
Supplementary Figure 117. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **44**



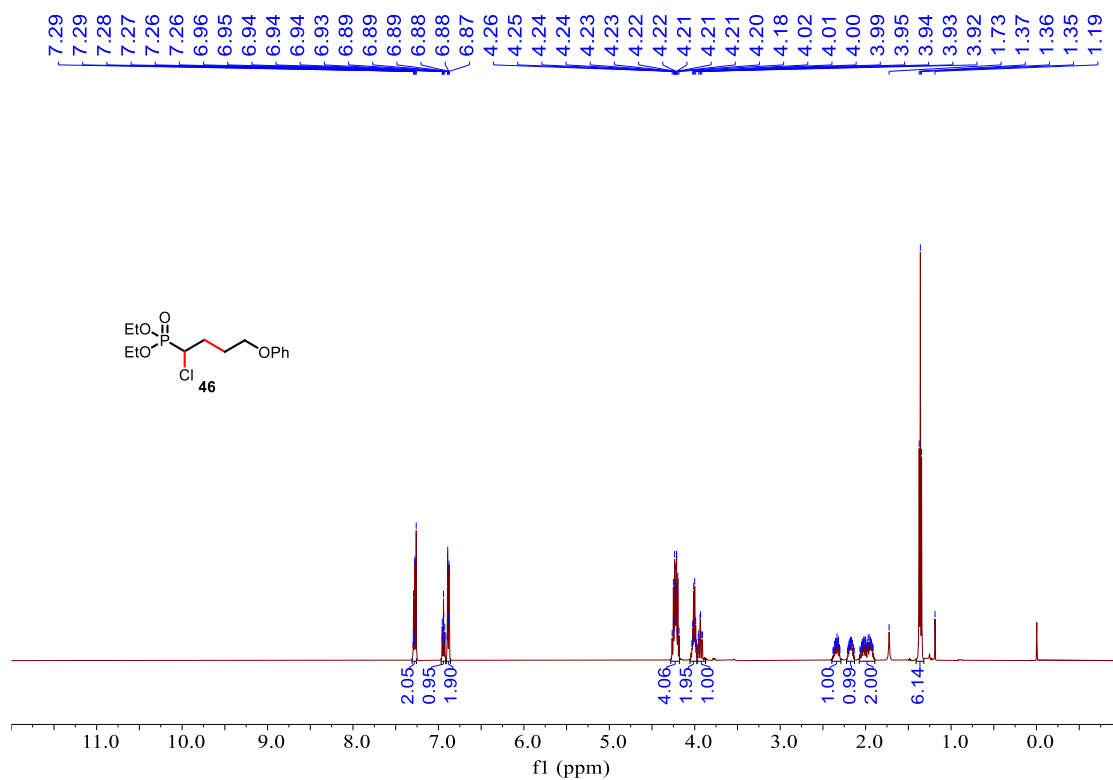
Supplementary Figure 118. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **44**



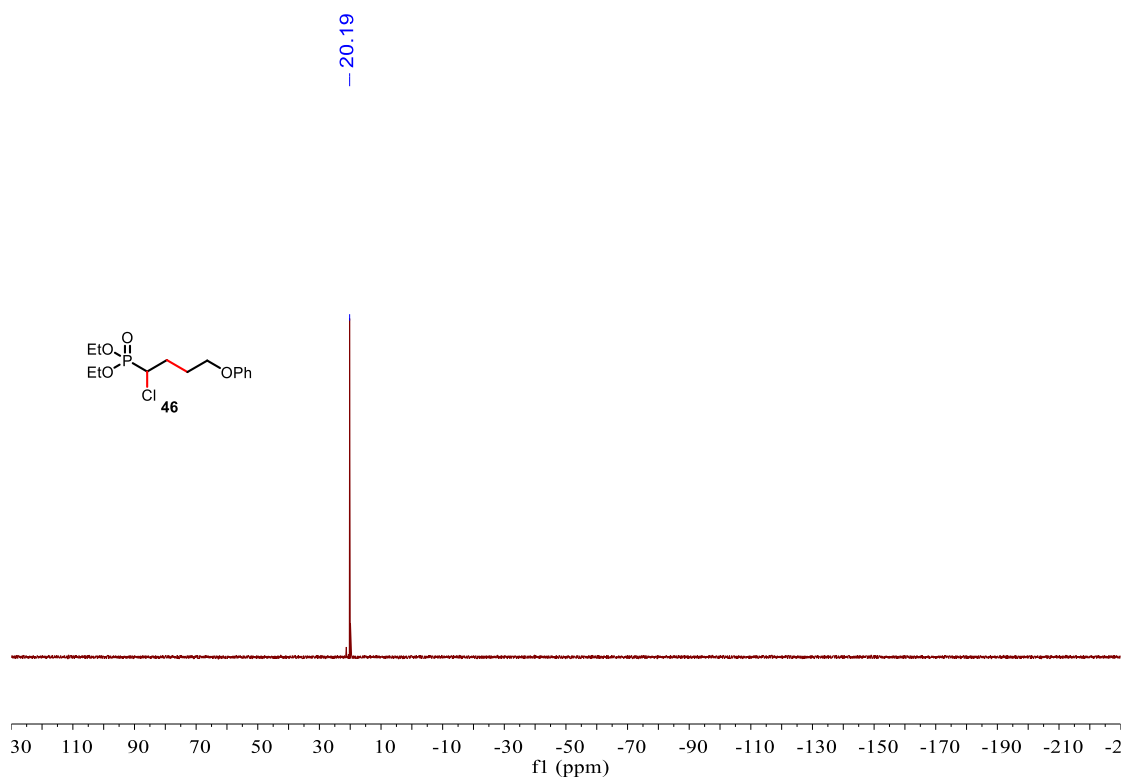
Supplementary Figure 119. ¹H NMR (400 MHz, CDCl₃) spectrum for compound **45**



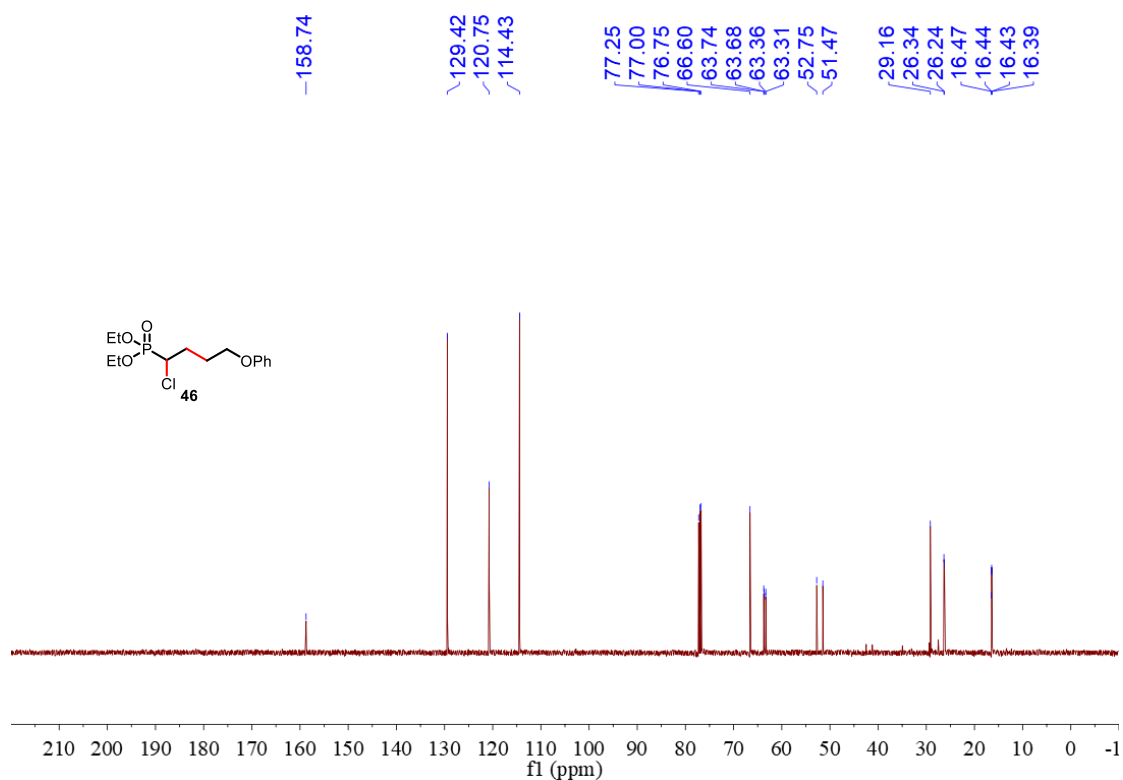
Supplementary Figure 120. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **45**



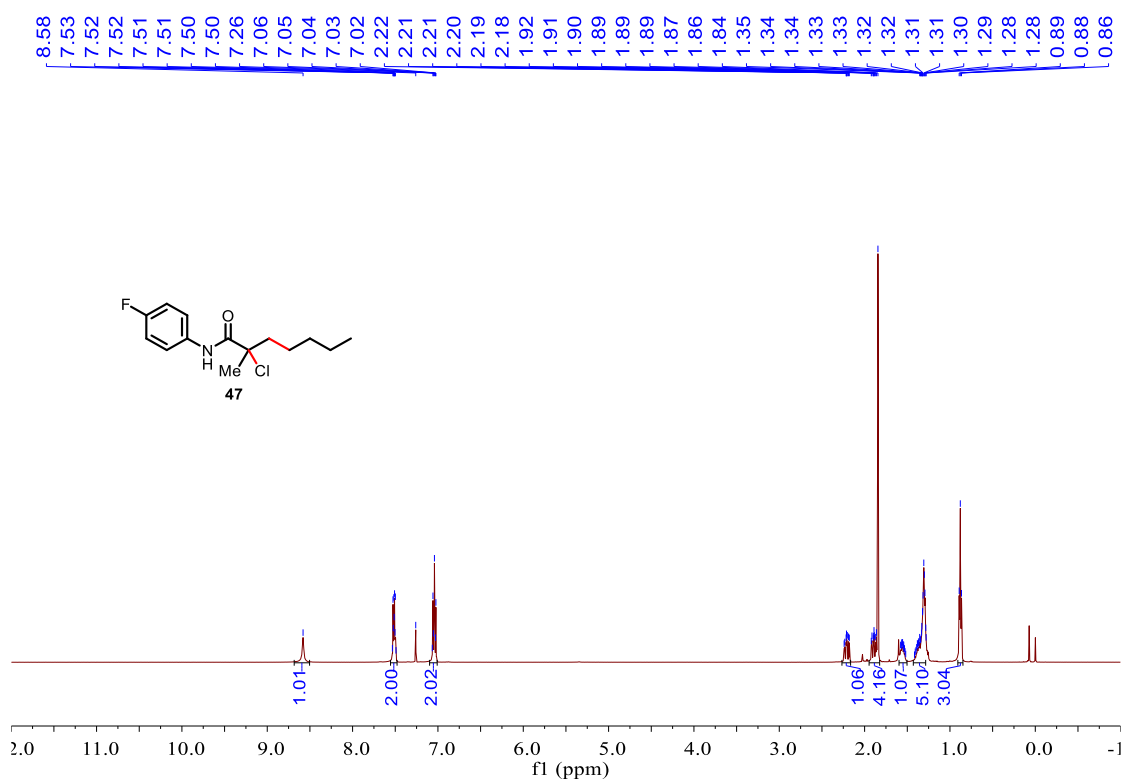
Supplementary Figure 121. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **46**



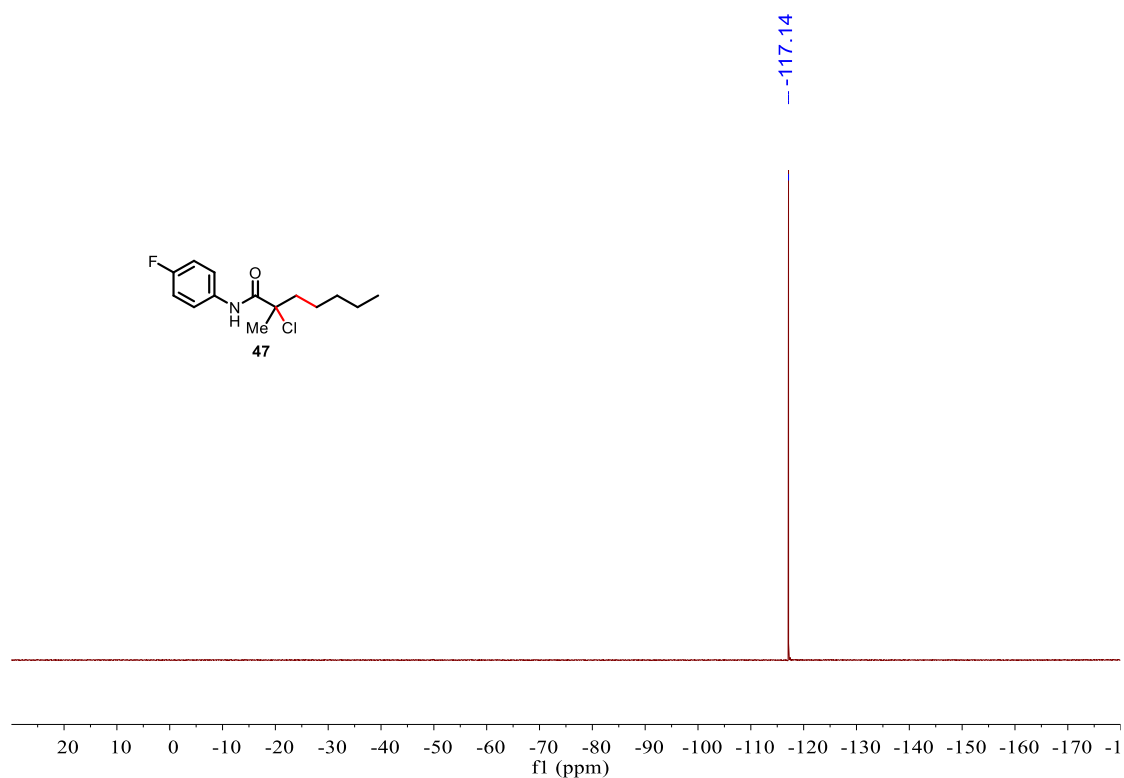
Supplementary Figure 122. ³¹P NMR (202 MHz, CDCl₃) spectrum for compound **46**



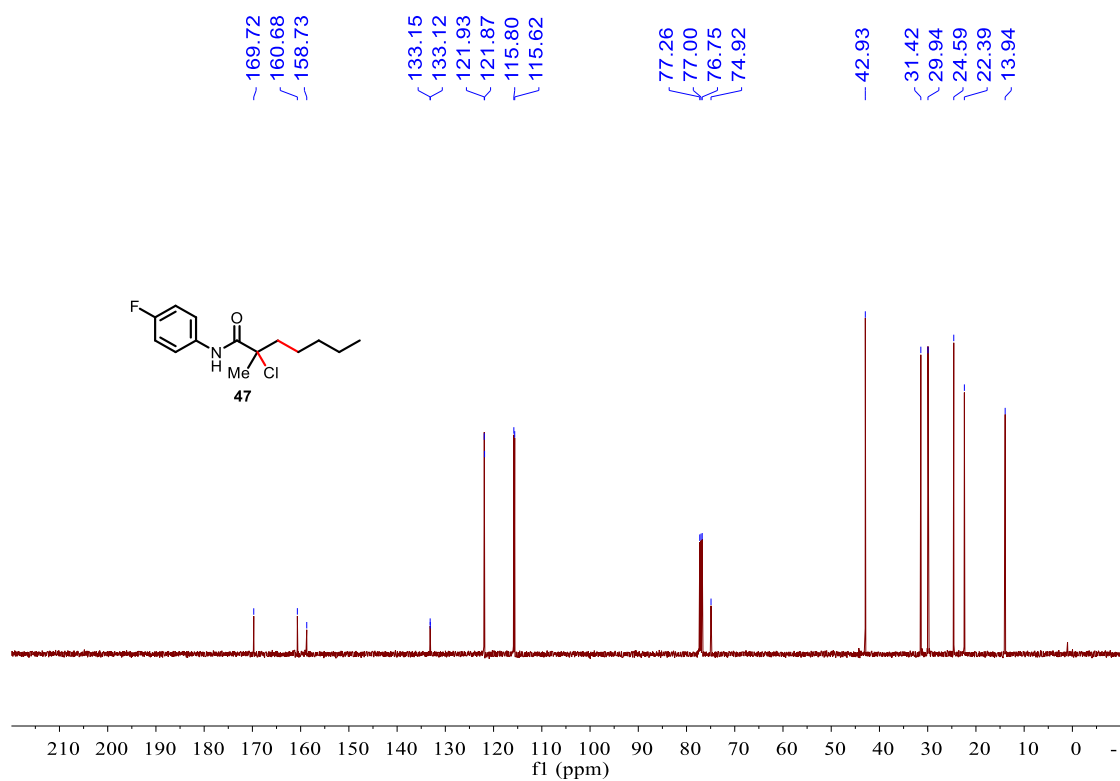
Supplementary Figure 123. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound 46



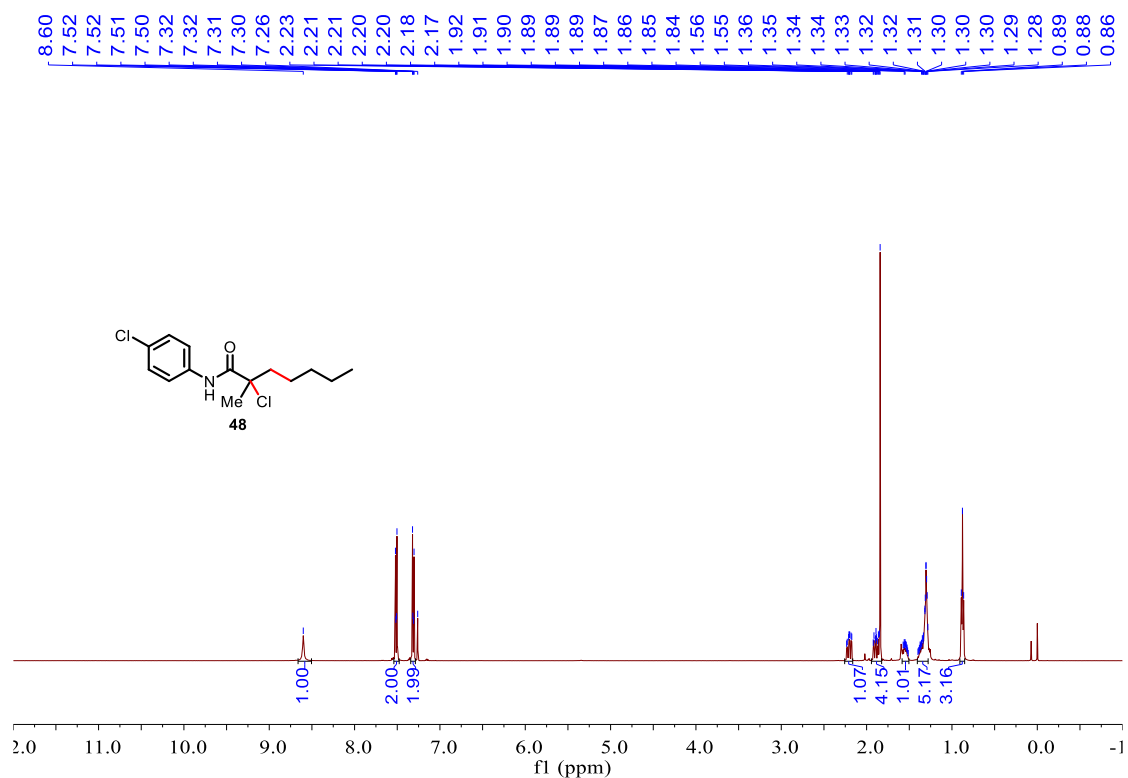
Supplementary Figure 124. ¹H NMR (500 MHz, CDCl₃) spectrum for compound 47



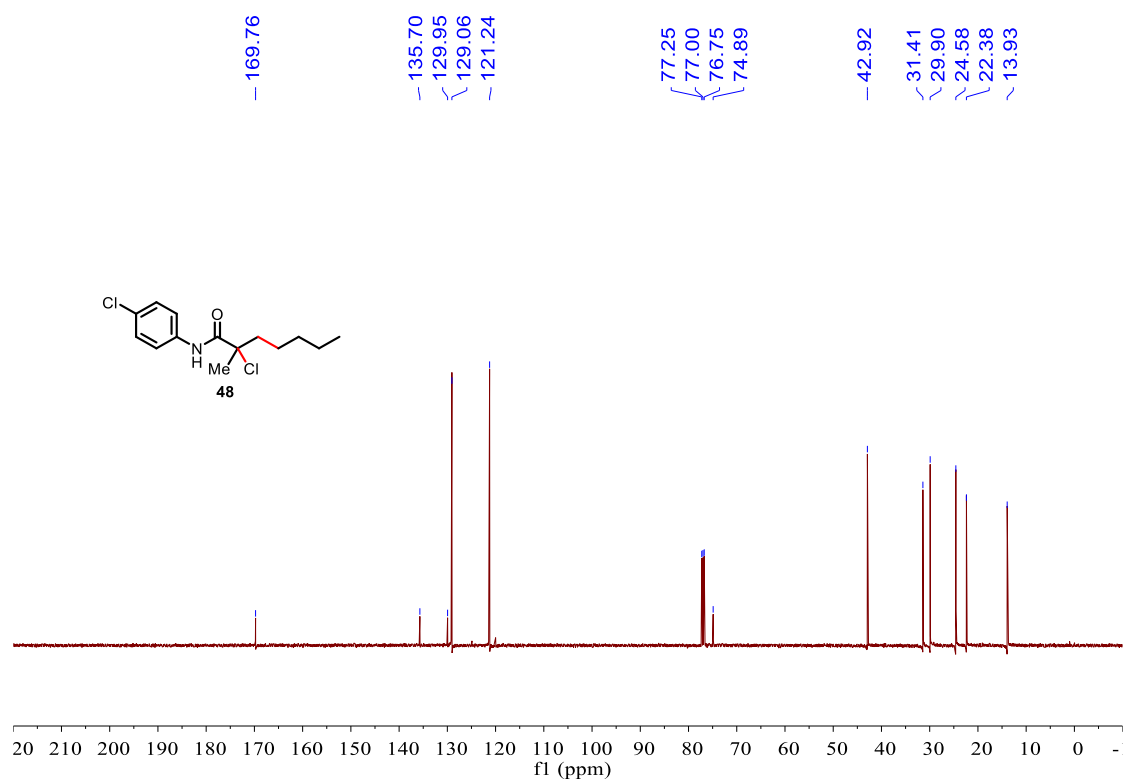
Supplementary Figure 125. ¹⁹F NMR (471 MHz, CDCl₃) spectrum for compound **47**



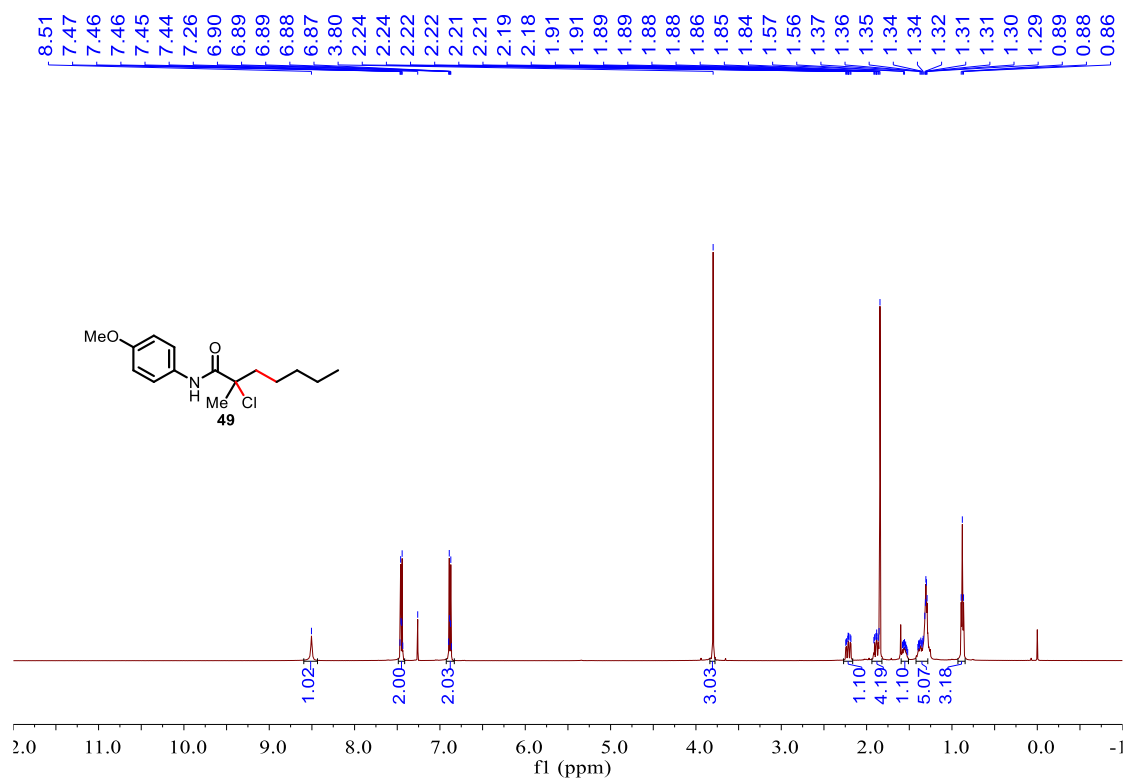
Supplementary Figure 126. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **47**



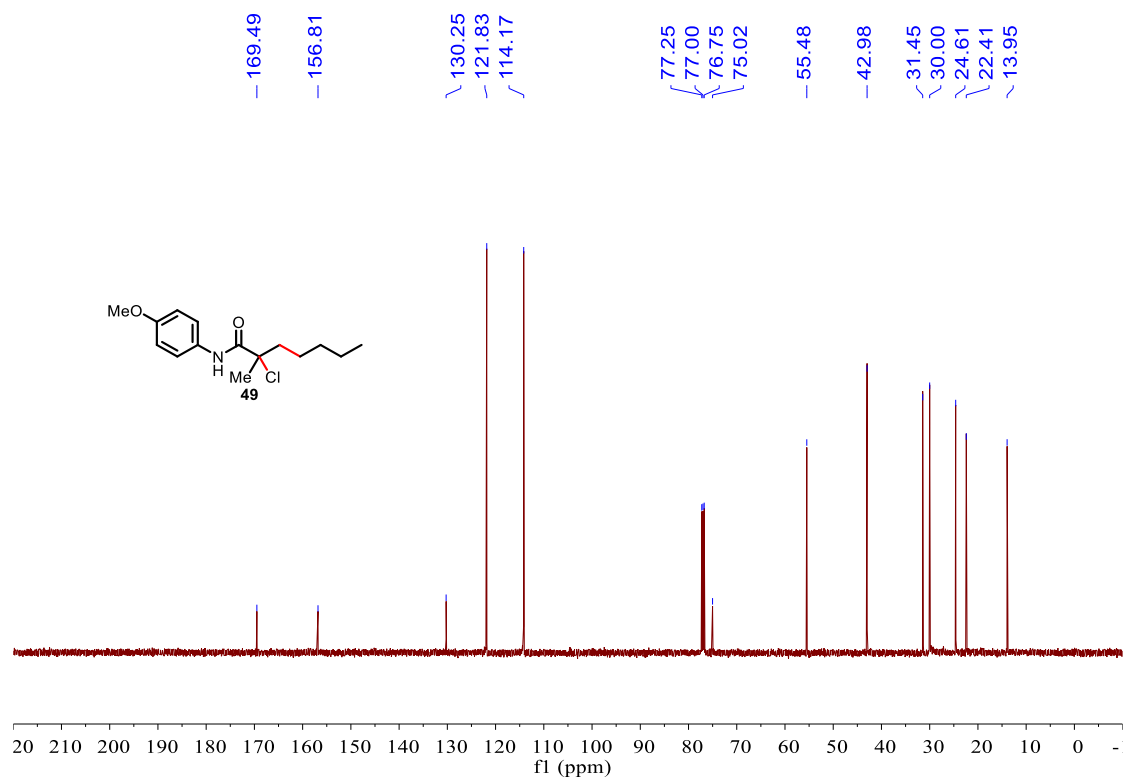
Supplementary Figure 127. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **48**



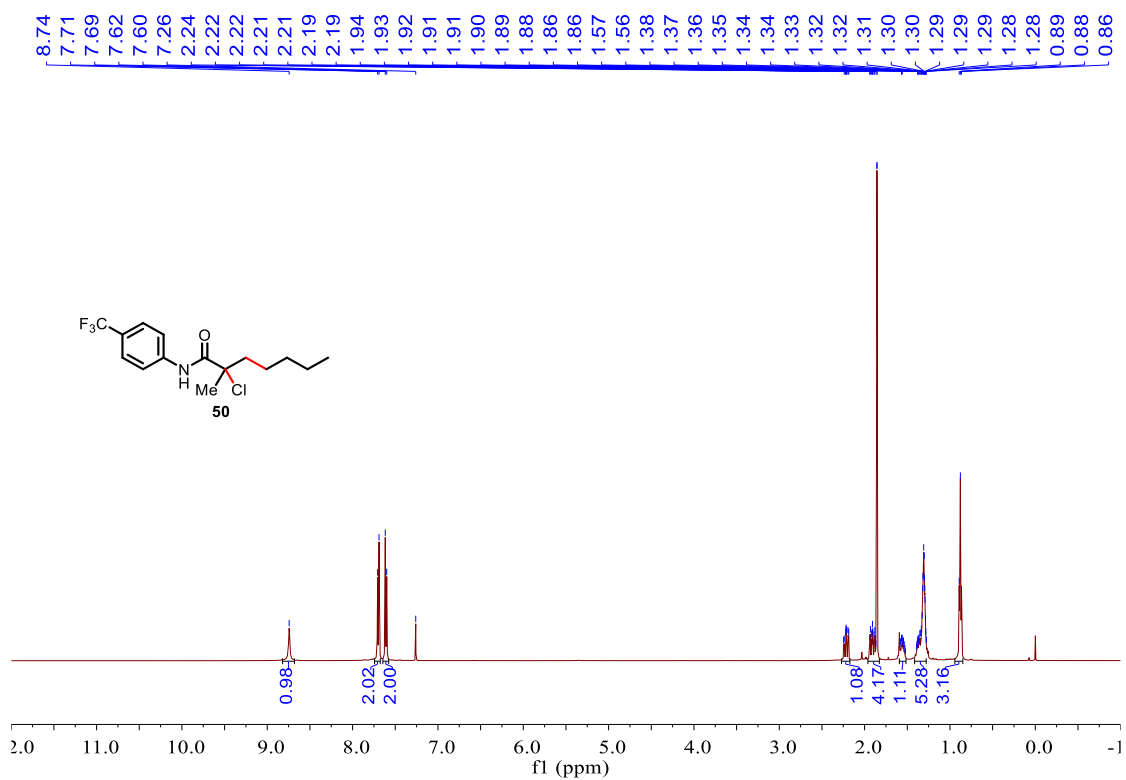
Supplementary Figure 128. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **48**



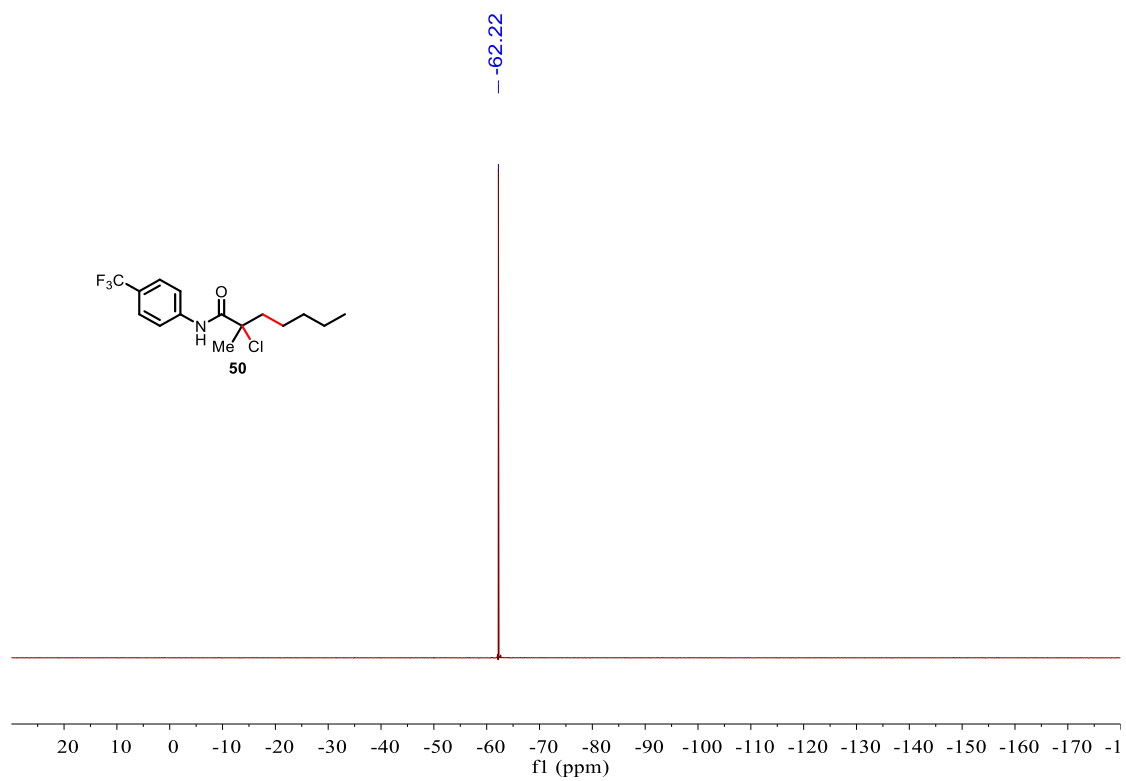
Supplementary Figure 129. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **49**



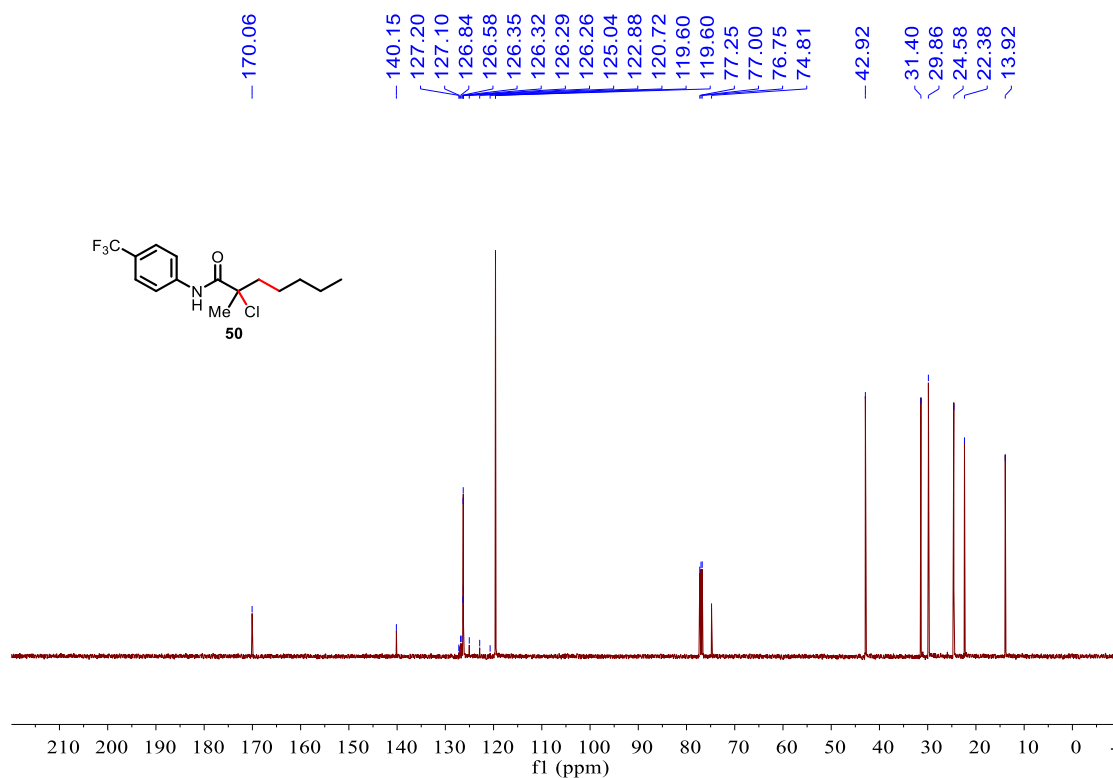
Supplementary Figure 130. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **49**



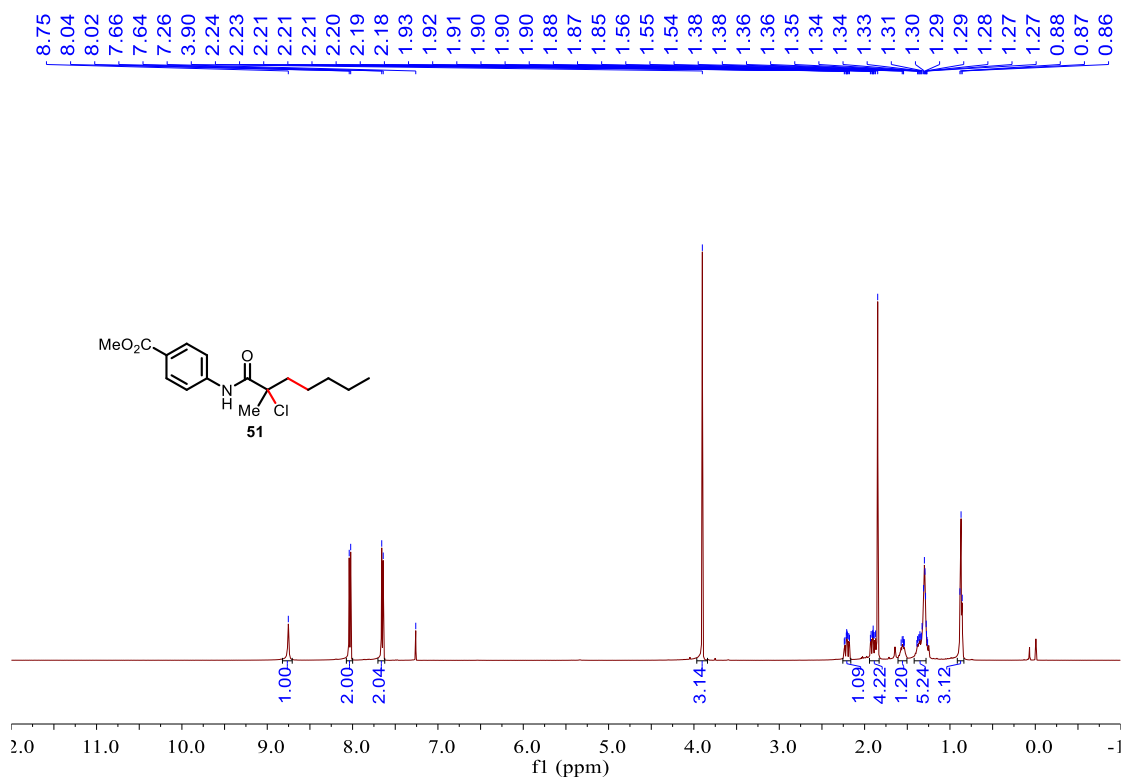
Supplementary Figure 131. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **50**



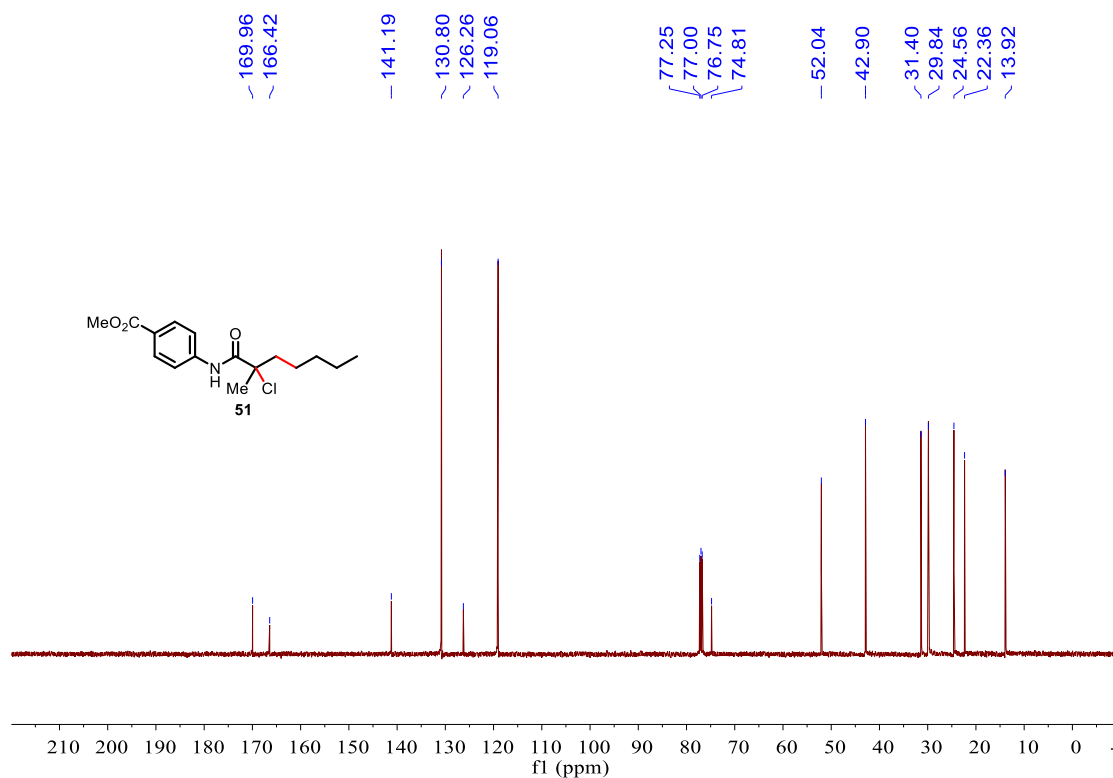
Supplementary Figure 132. ¹⁹F NMR (471 MHz, CDCl₃) spectrum for compound **50**



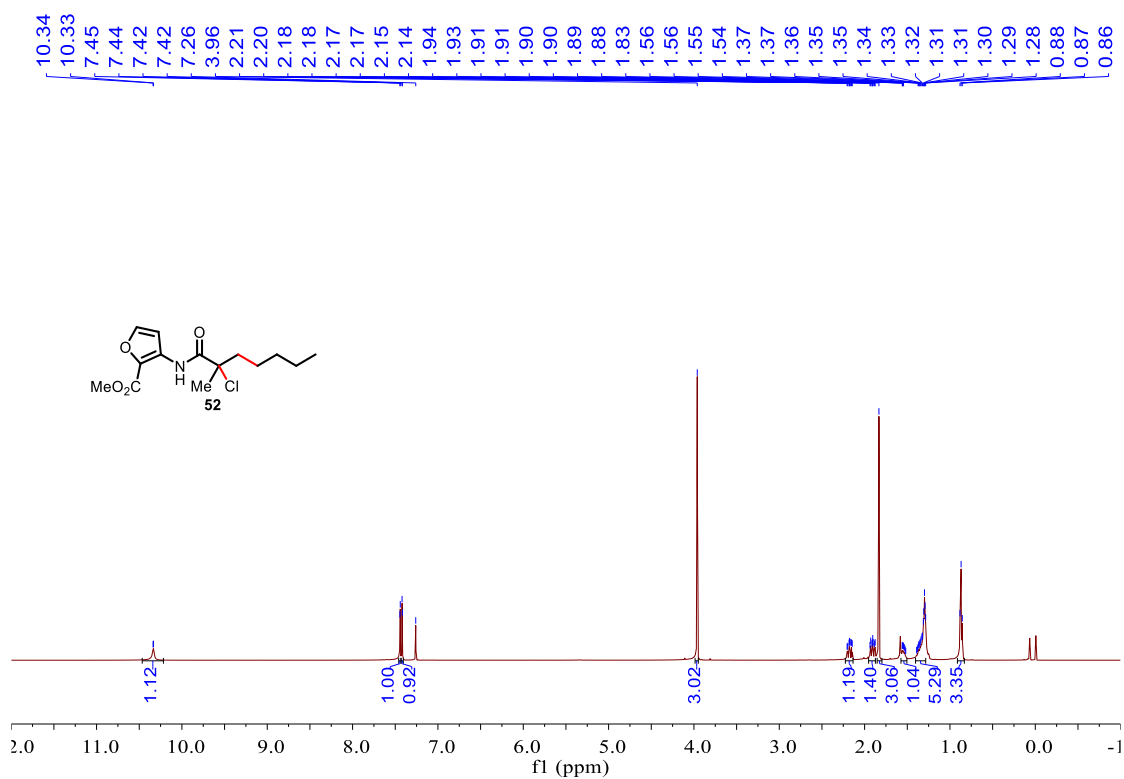
Supplementary Figure 133. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **50**



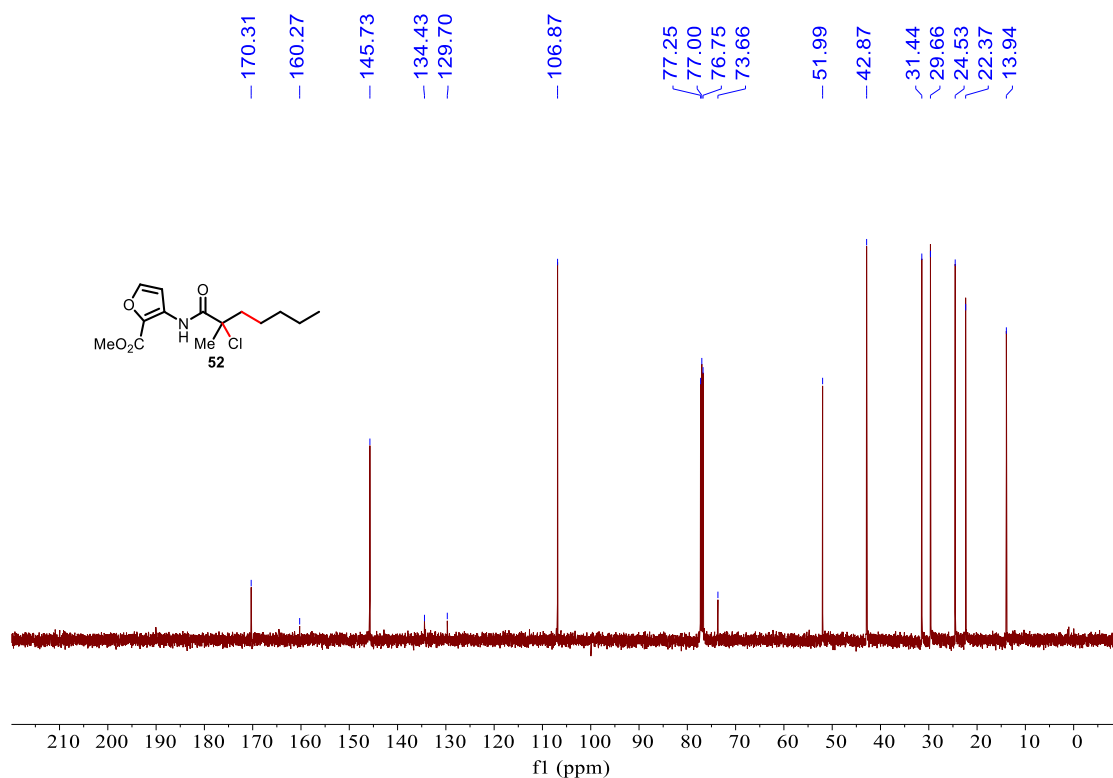
Supplementary Figure 134. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **51**



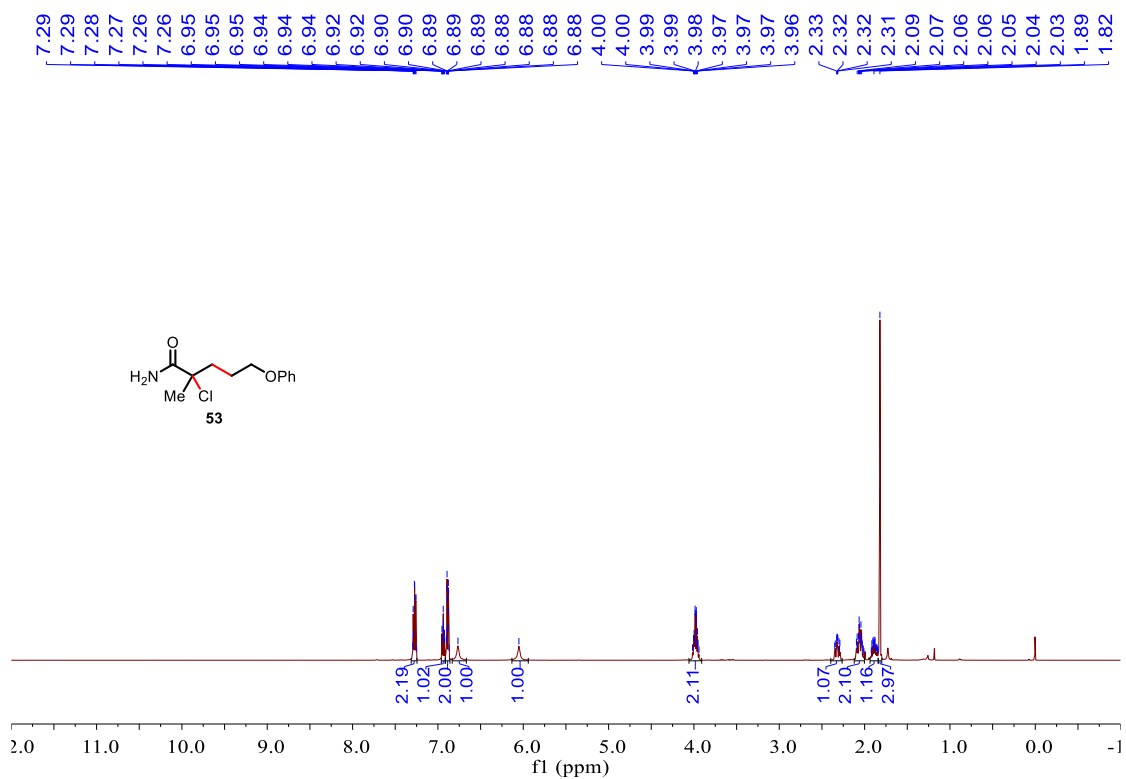
Supplementary Figure 135. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **51**



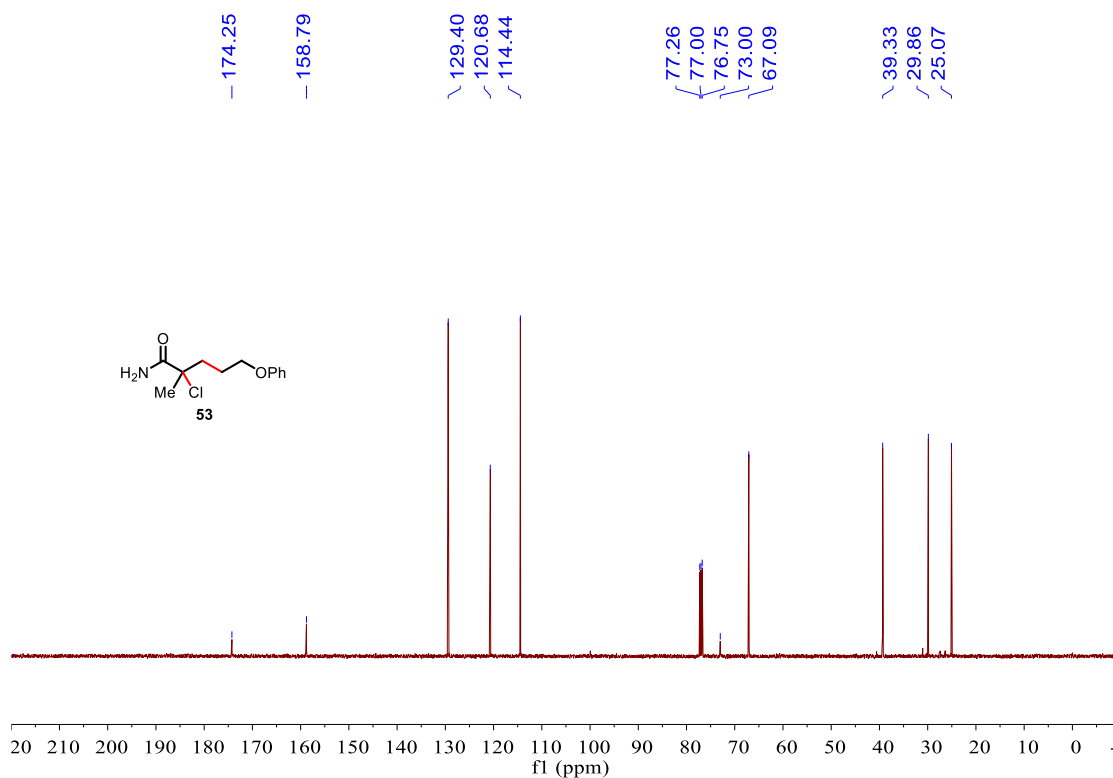
Supplementary Figure 136. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **52**



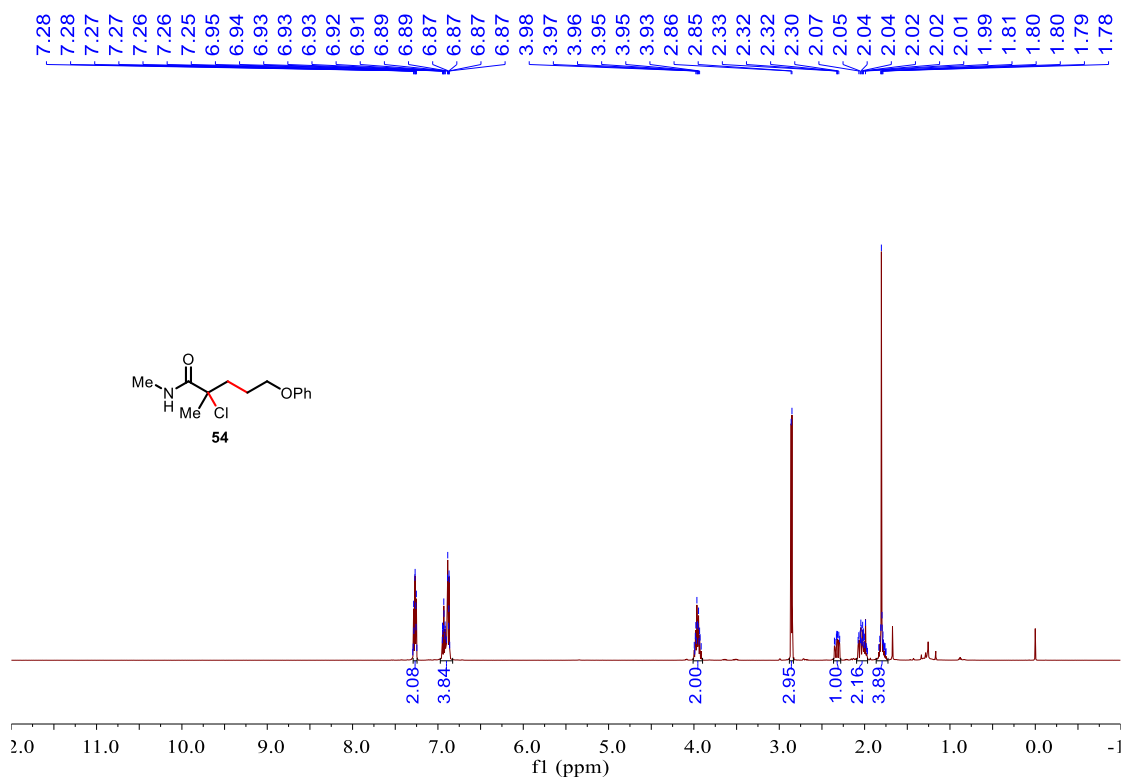
Supplementary Figure 137. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **52**



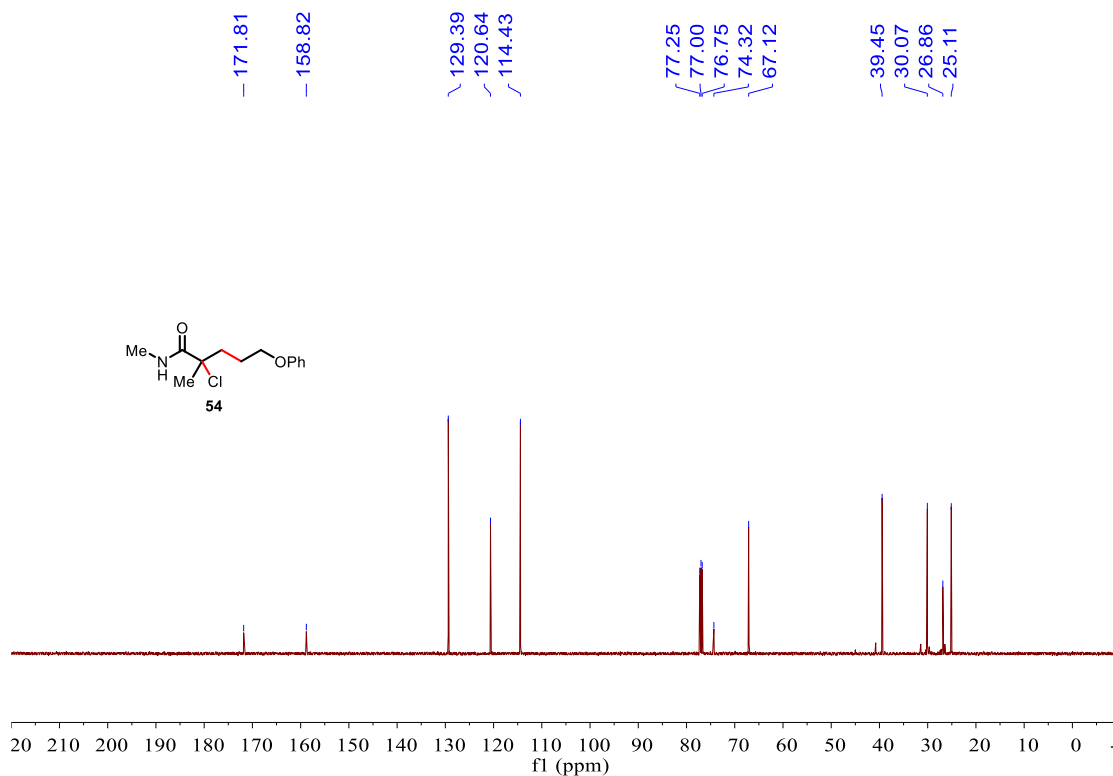
Supplementary Figure 138. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **53**



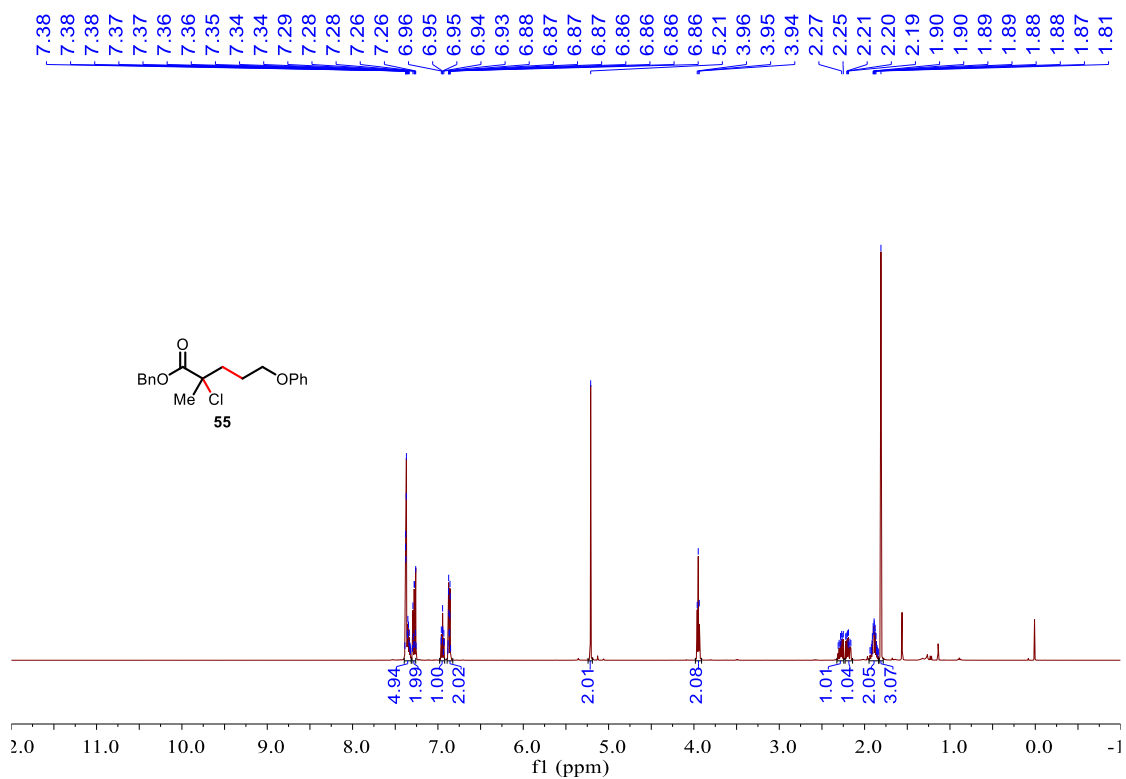
Supplementary Figure 139. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **53**



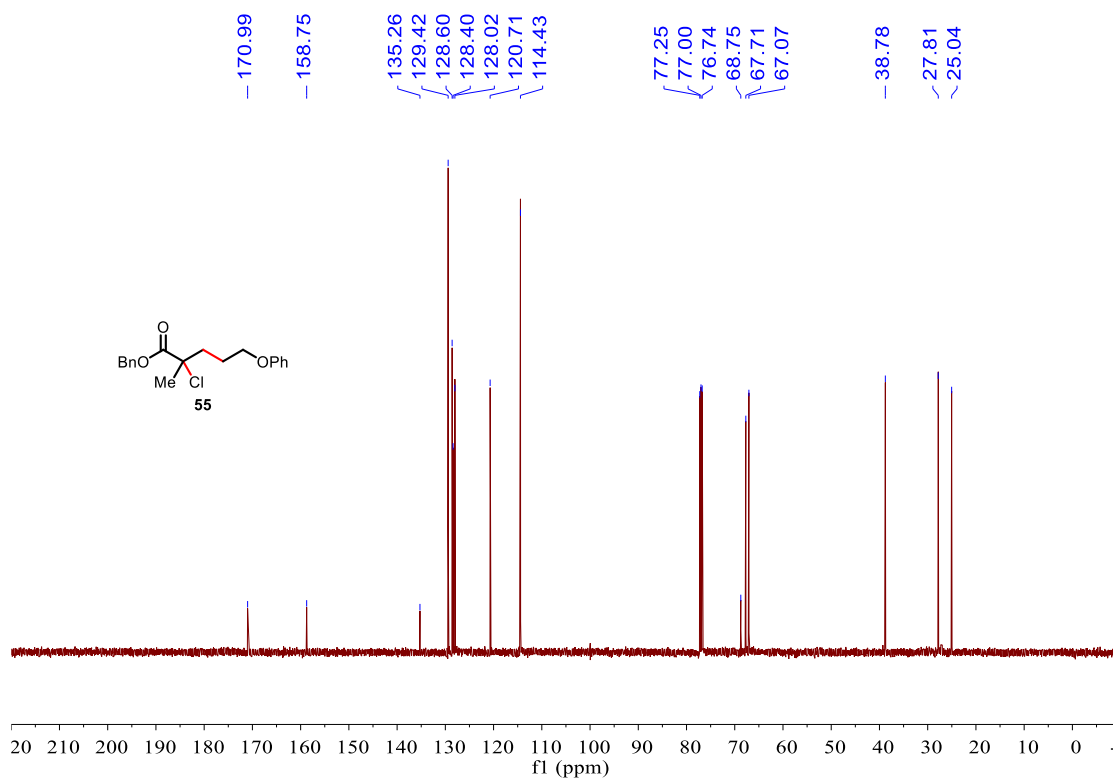
Supplementary Figure 140. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **54**



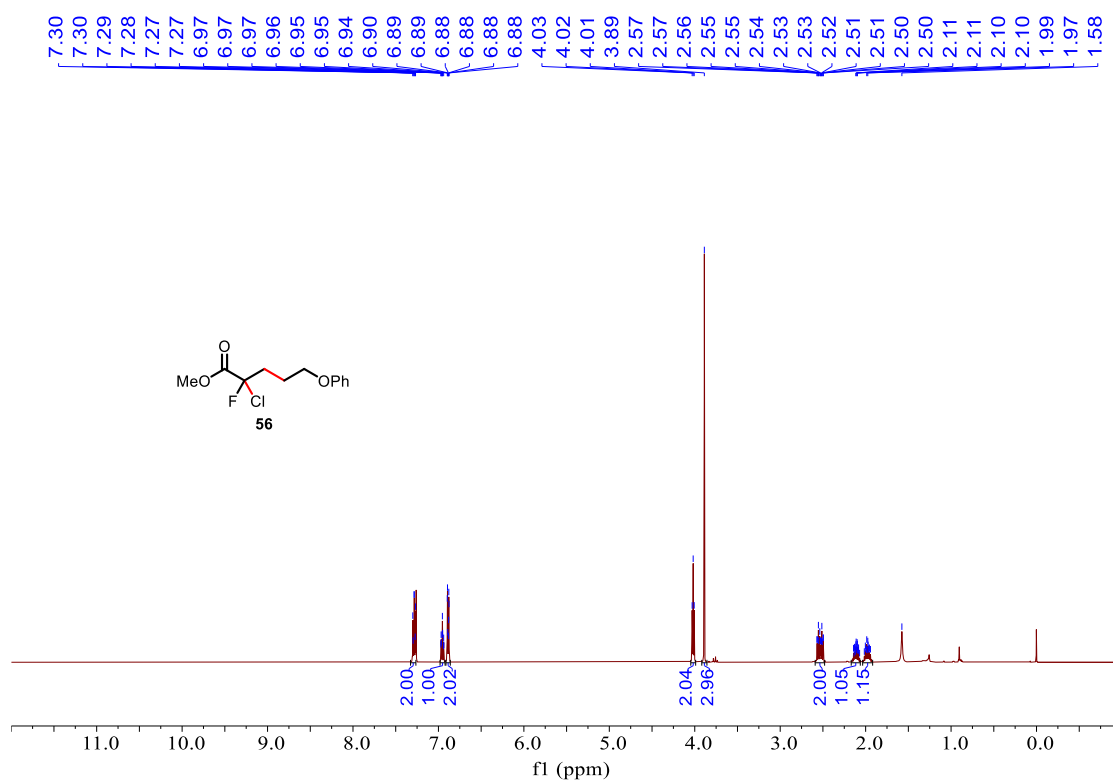
Supplementary Figure 141. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **54**



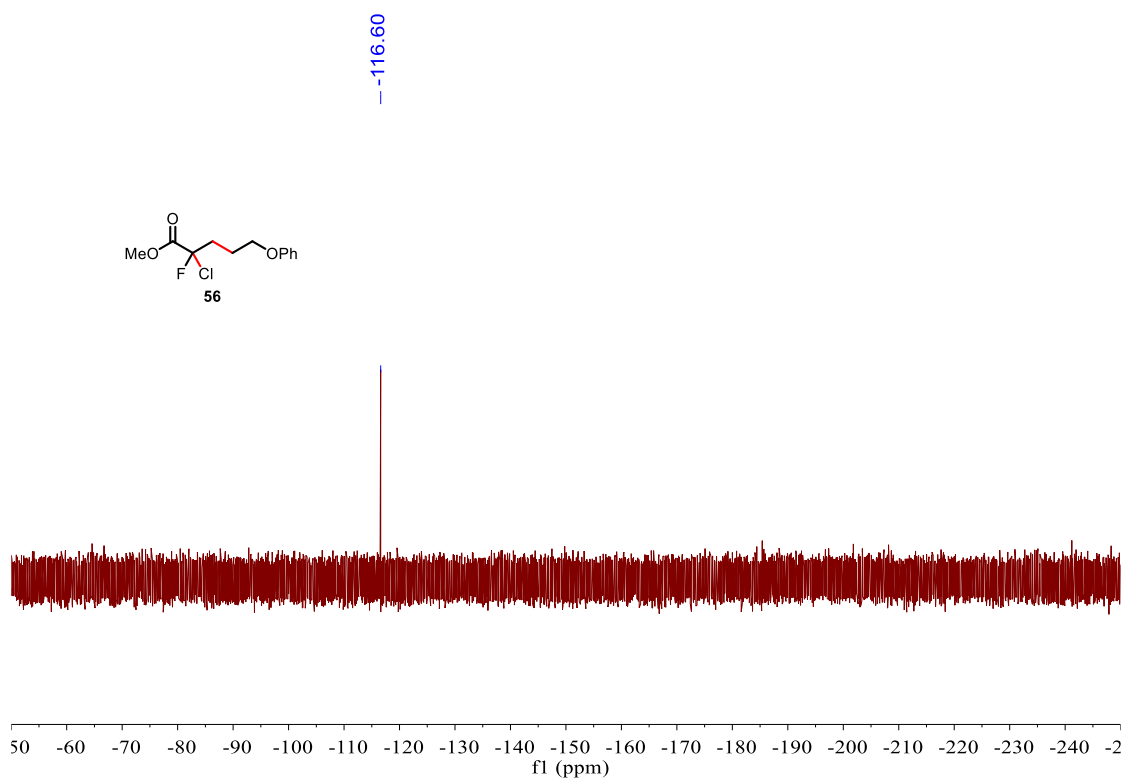
Supplementary Figure 142. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **55**



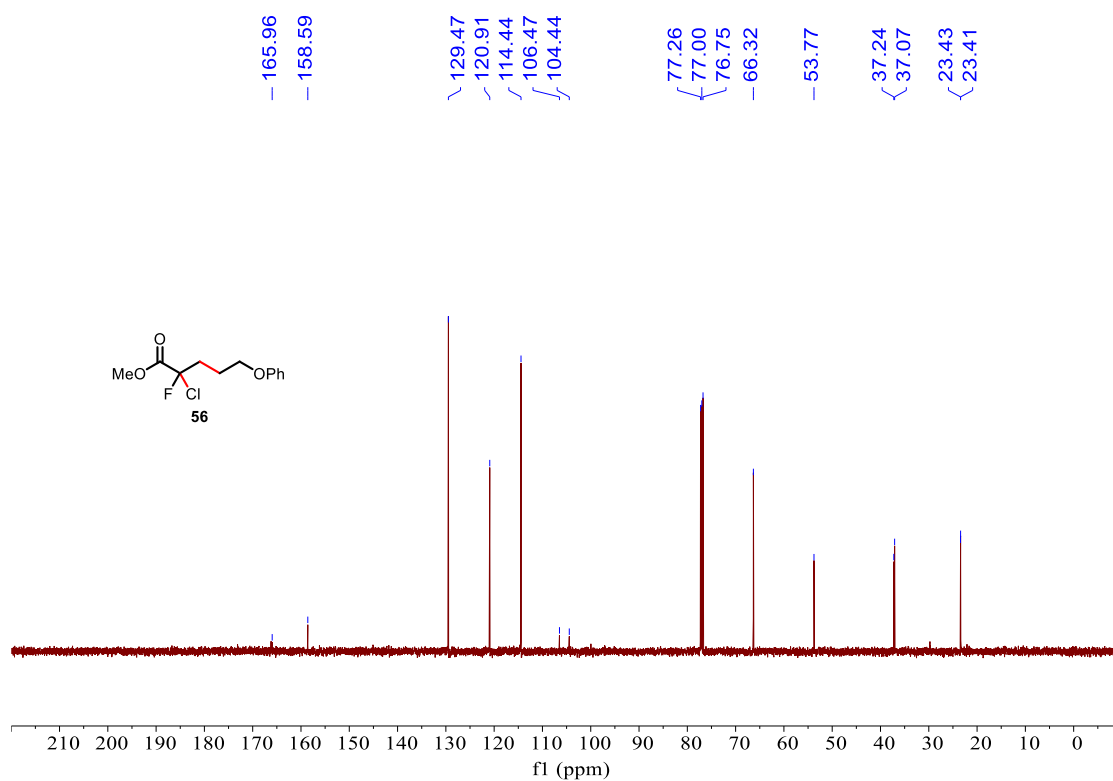
Supplementary Figure 143. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **55**



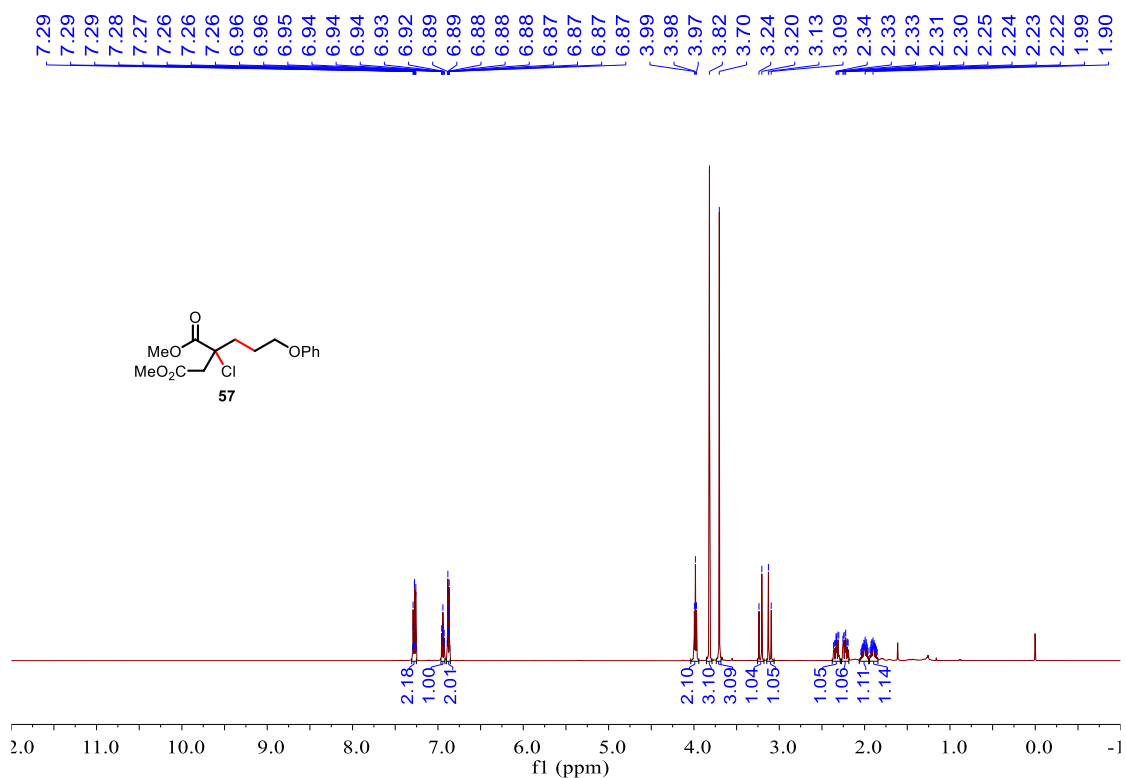
Supplementary Figure 144. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **56**



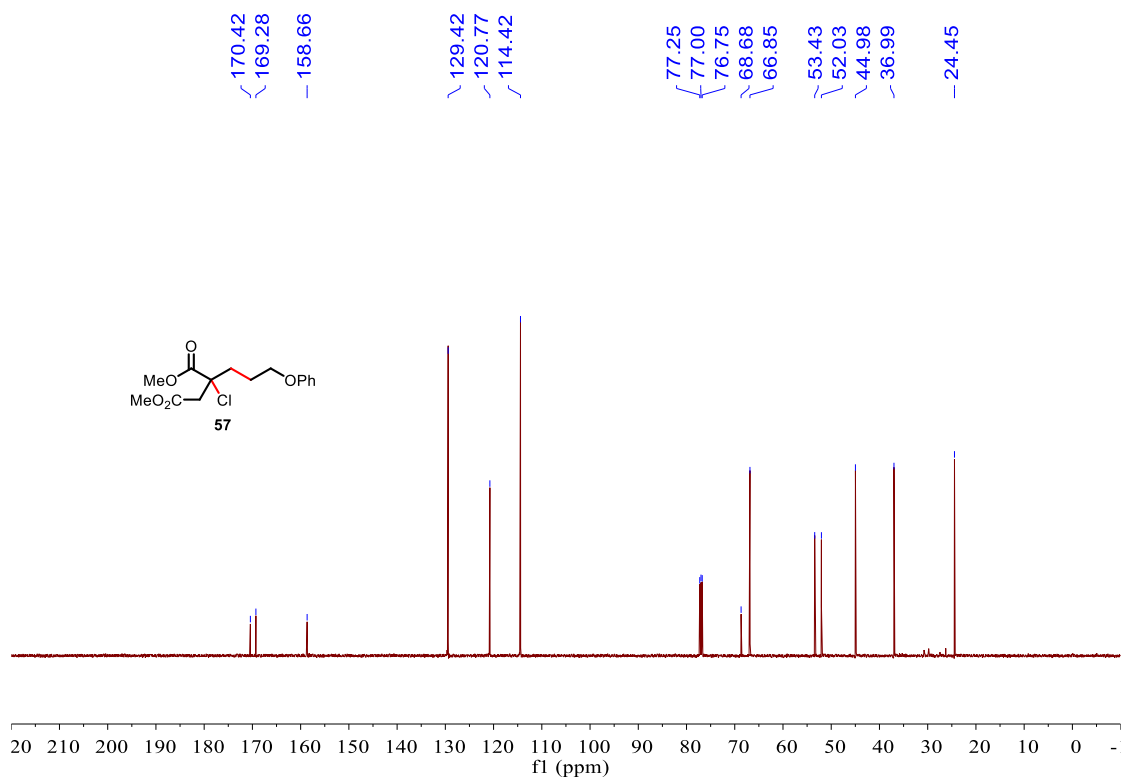
Supplementary Figure 145. ^{19}F NMR (471 MHz, CDCl_3) spectrum for compound **56**



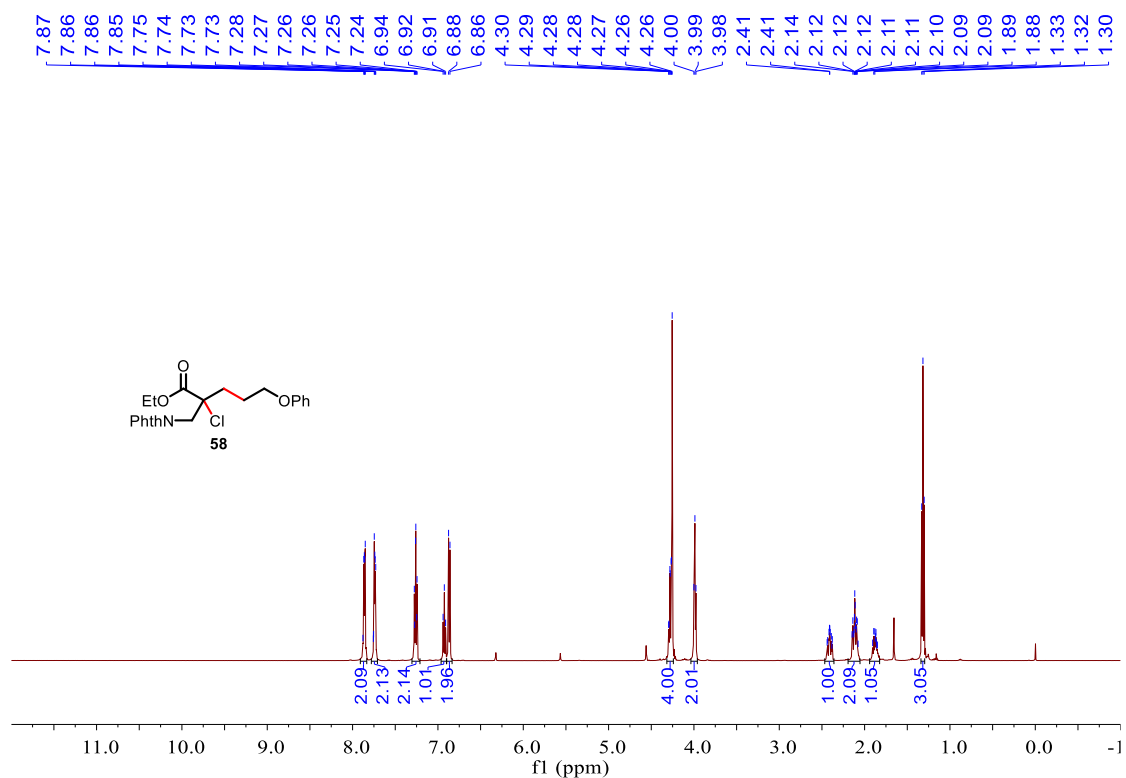
Supplementary Figure 146. ^{13}C NMR (126 MHz, CDCl_3) spectrum for compound **56**



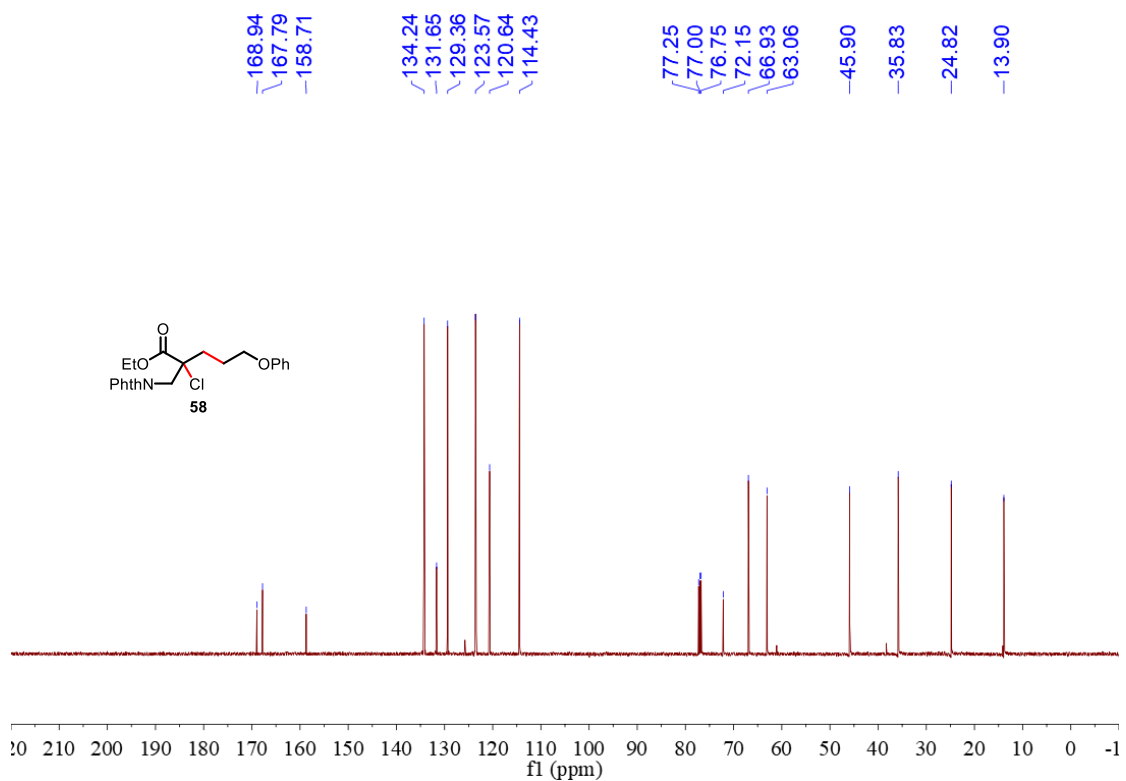
Supplementary Figure 147. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **57**



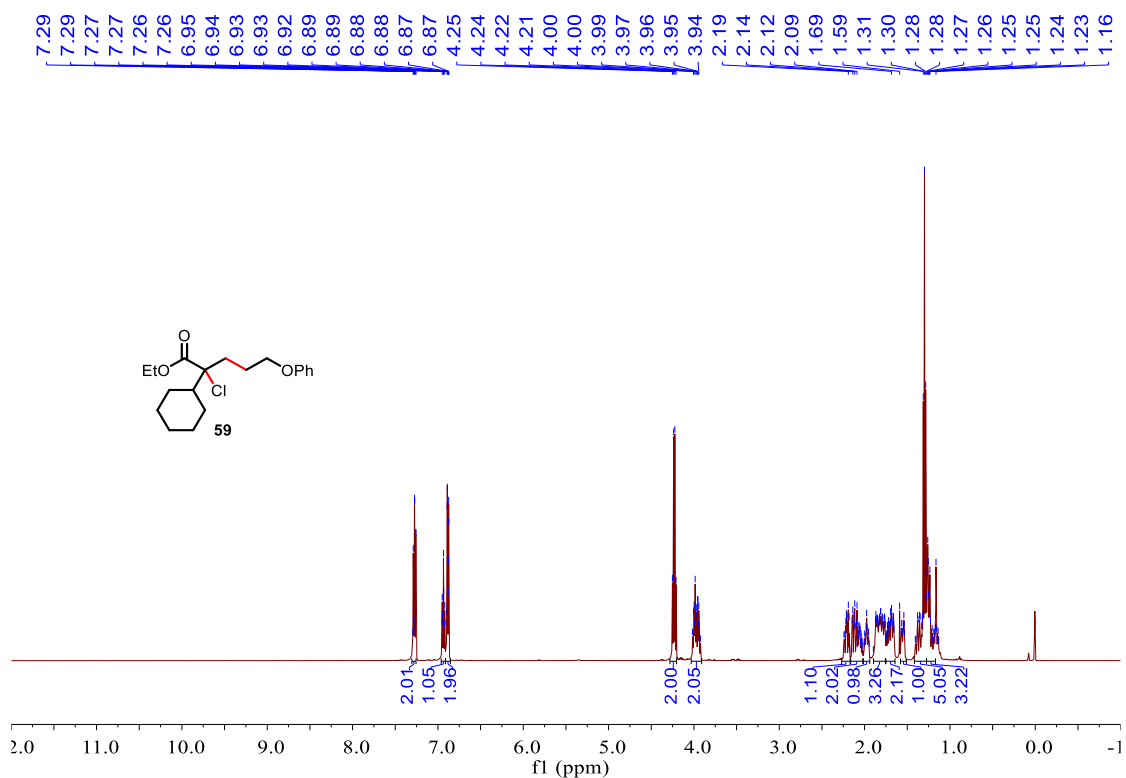
Supplementary Figure 148. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **57**



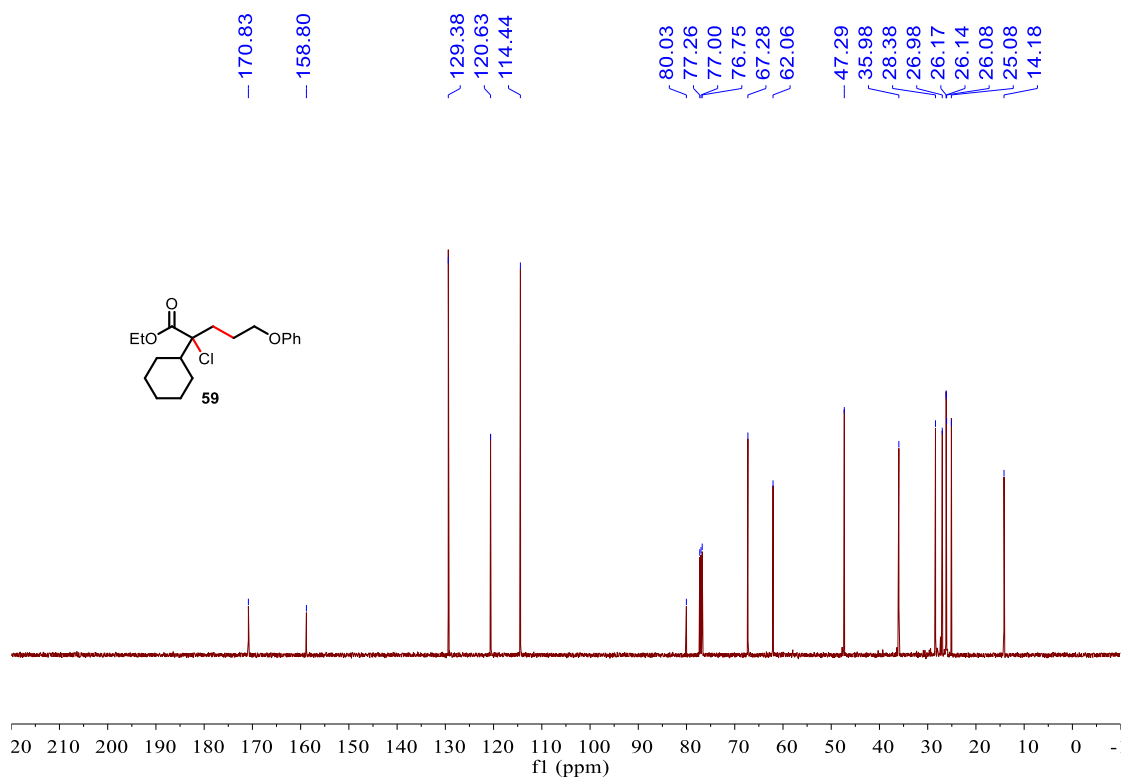
Supplementary Figure 149. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **58**



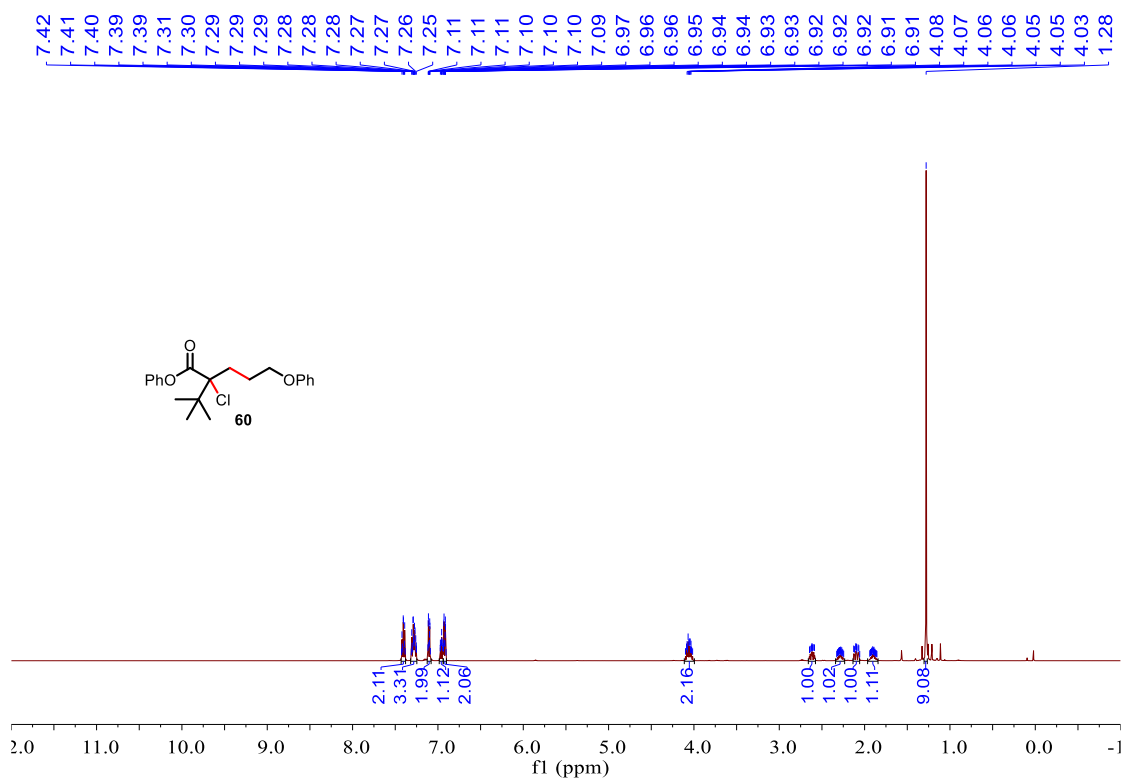
Supplementary Figure 150. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **58**



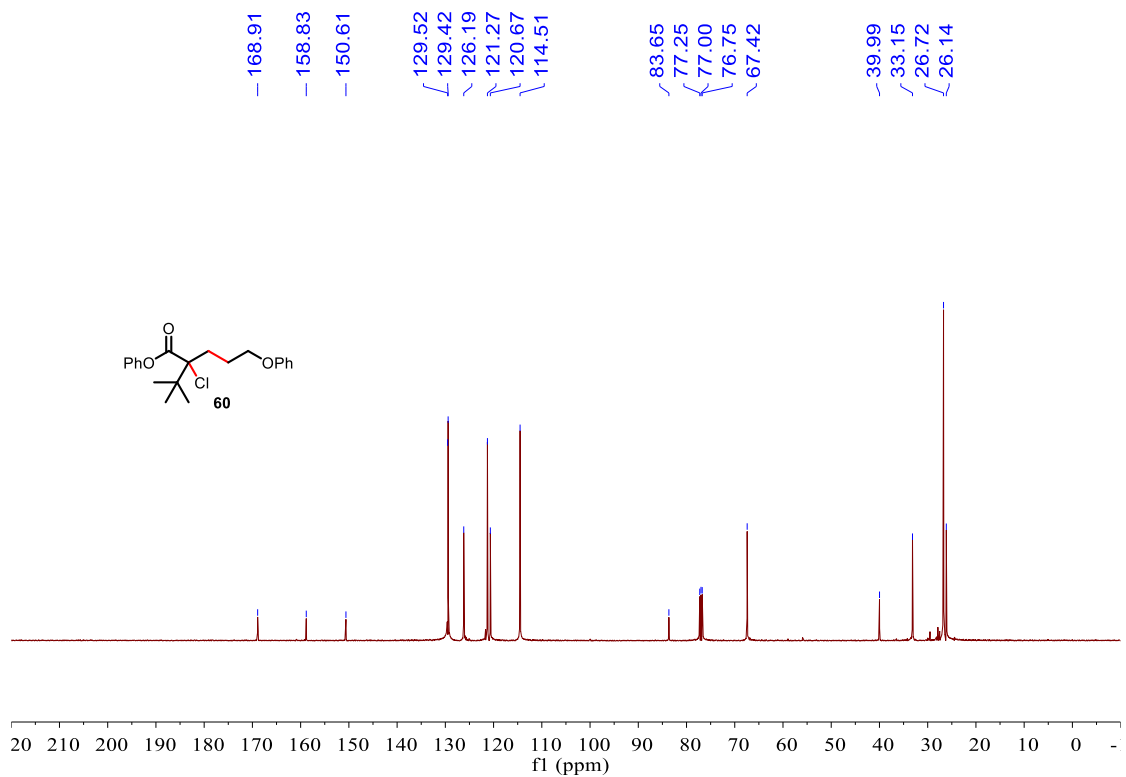
Supplementary Figure 151. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **59**



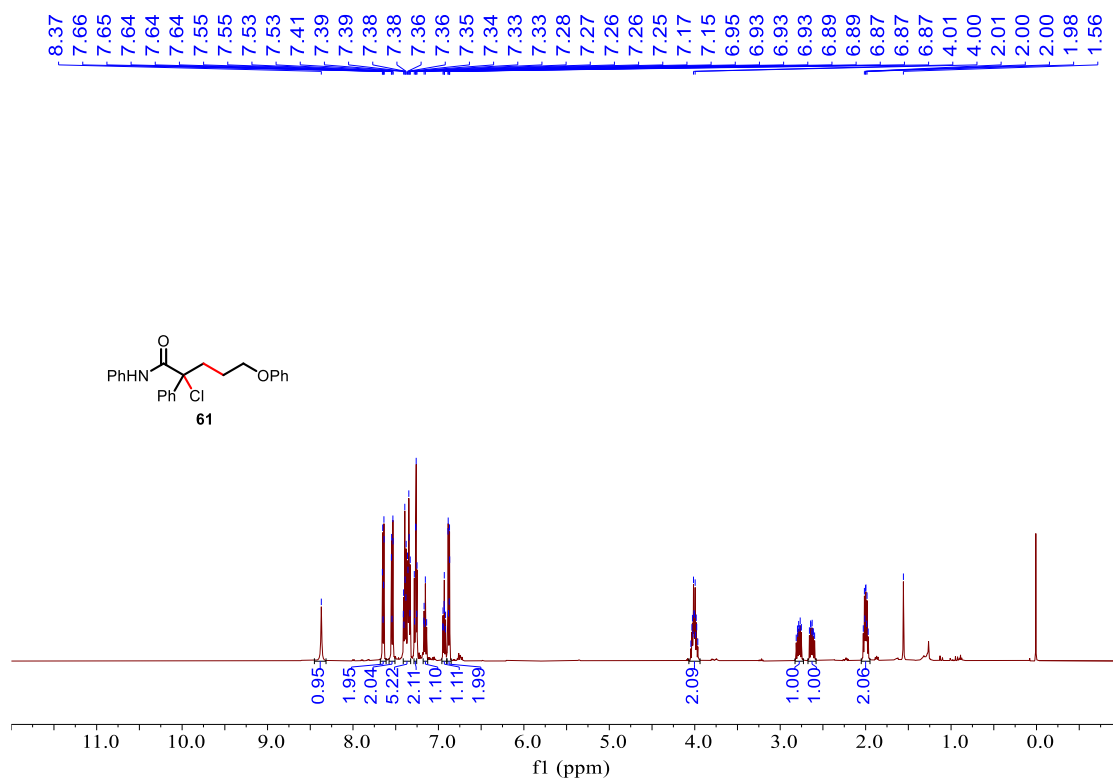
Supplementary Figure 152. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **59**



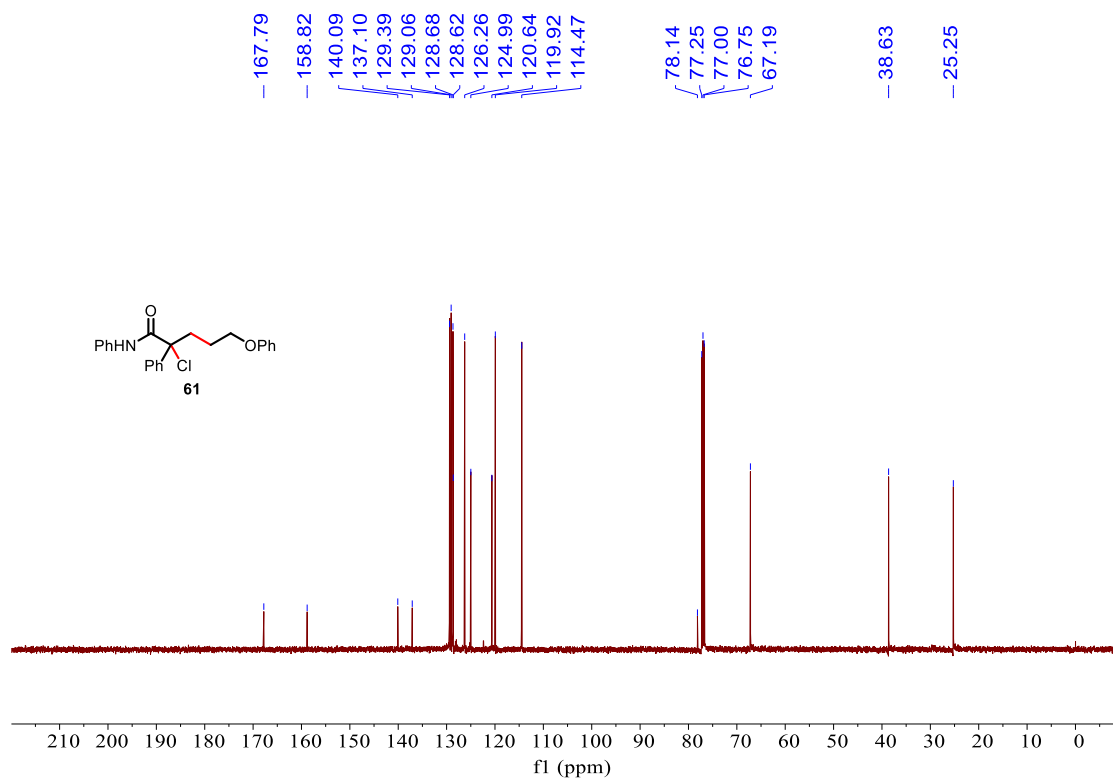
Supplementary Figure 153. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **60**



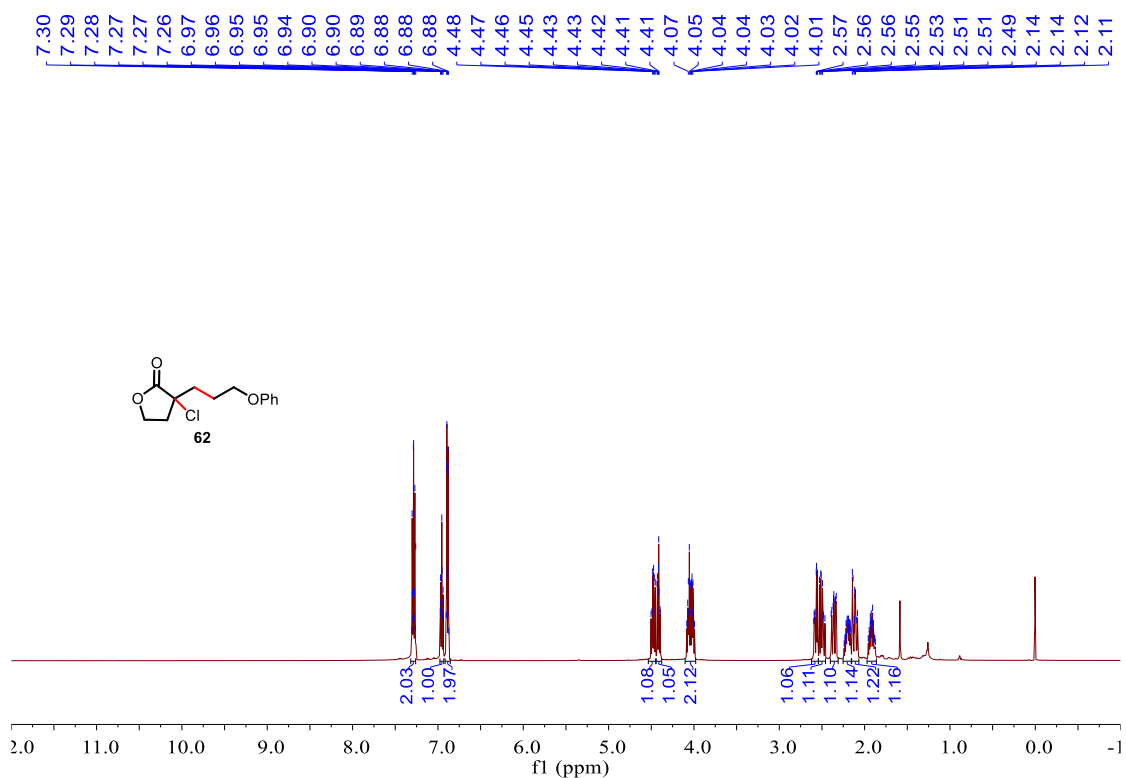
Supplementary Figure 154. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **60**



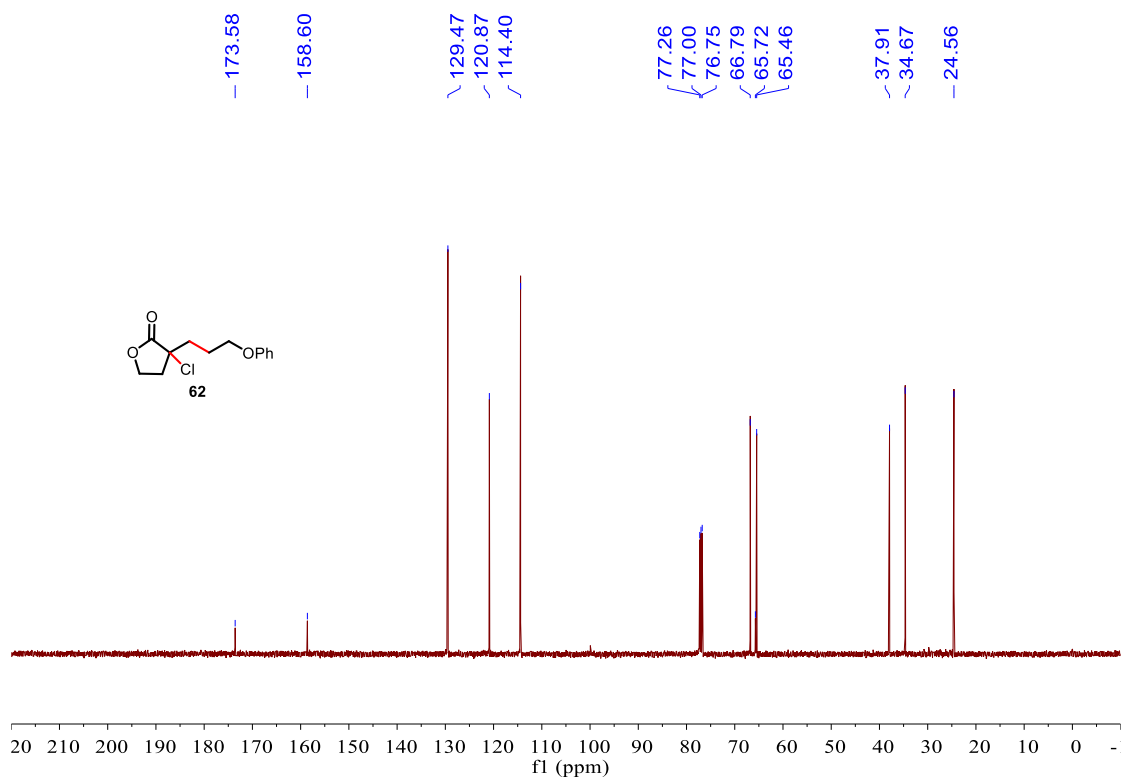
Supplementary Figure 155. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **61**



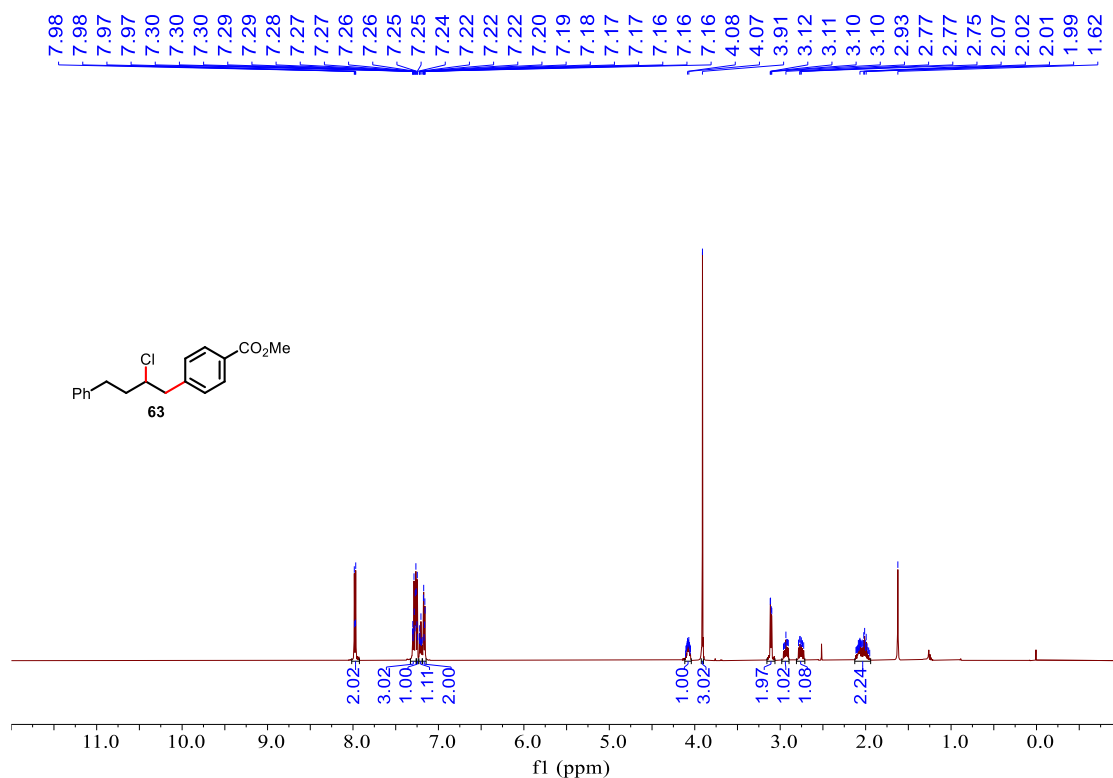
Supplementary Figure 156. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **61**



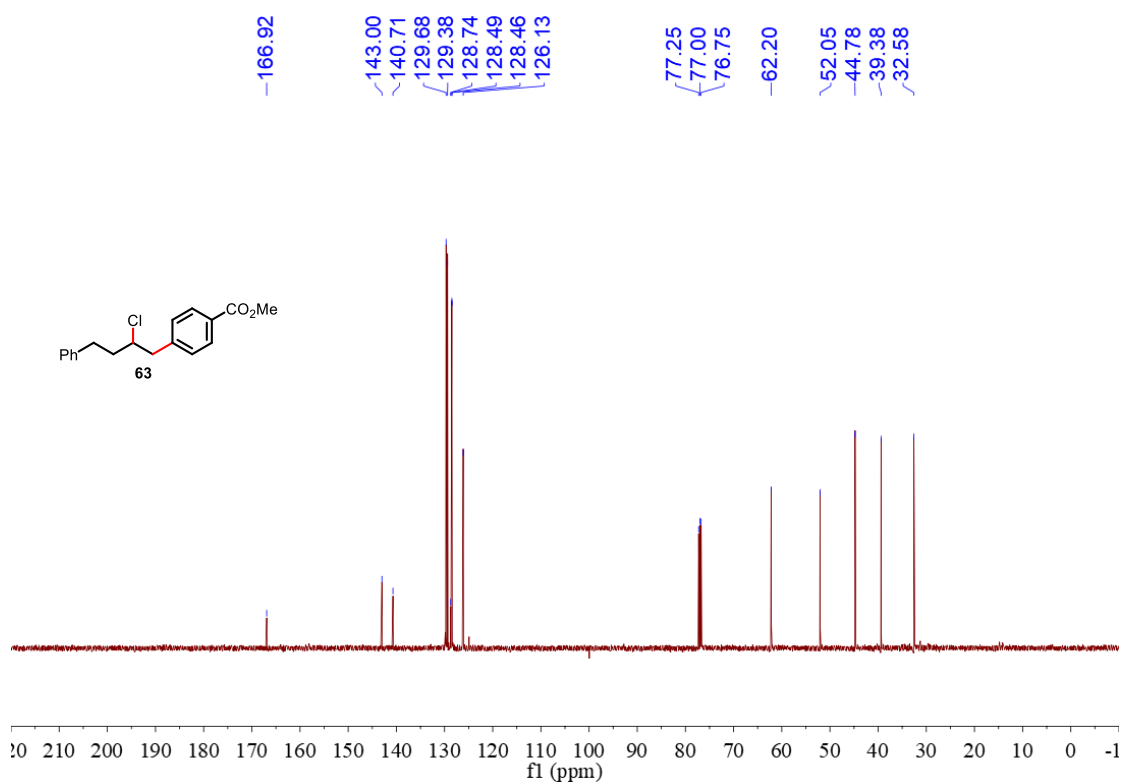
Supplementary Figure 157. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **62**



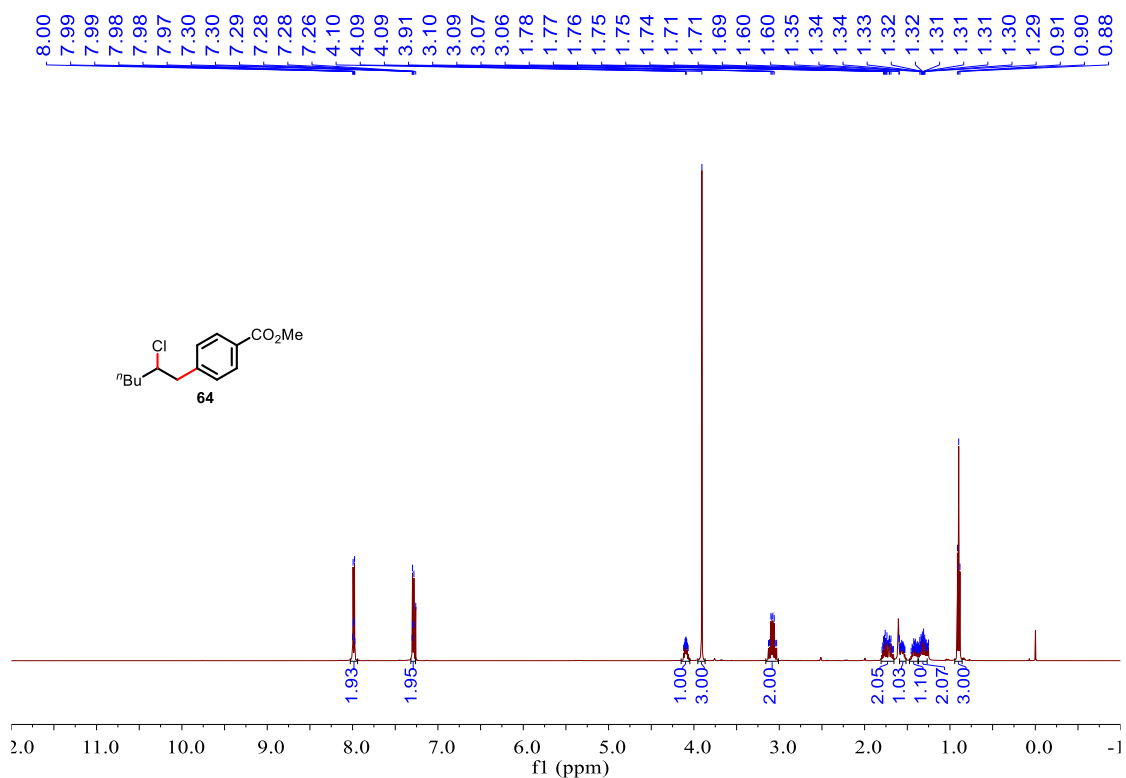
Supplementary Figure 158. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **62**



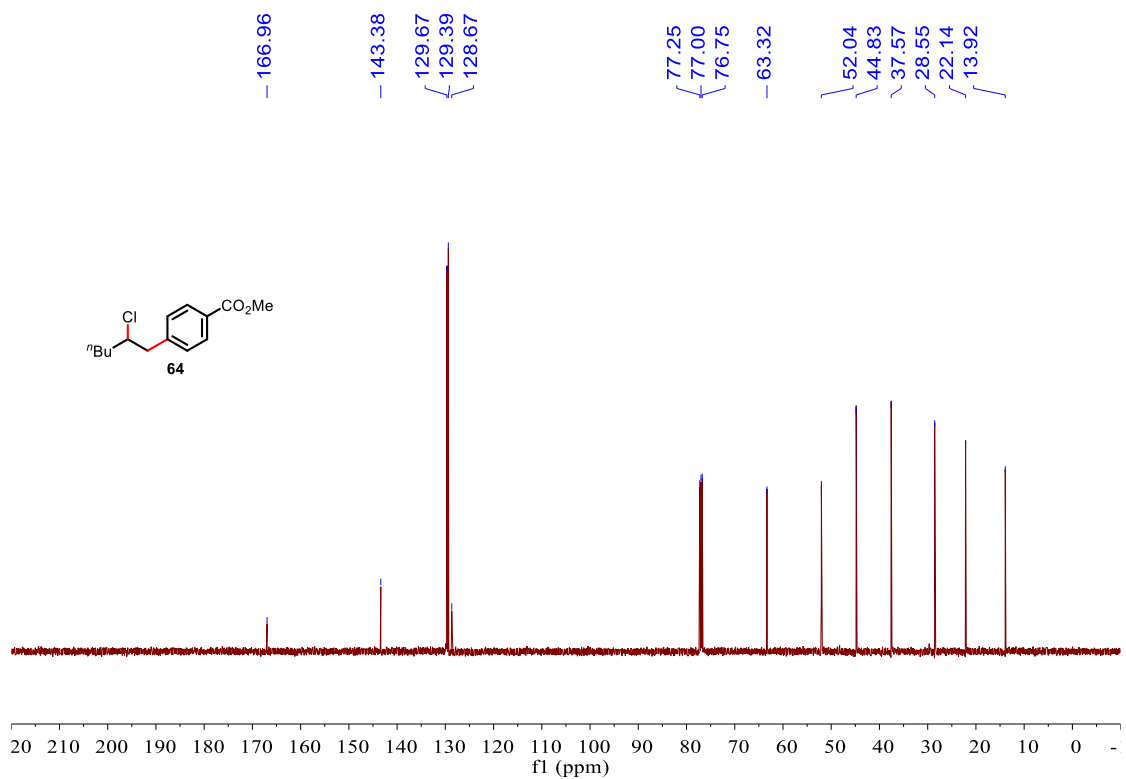
Supplementary Figure 159. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **63**



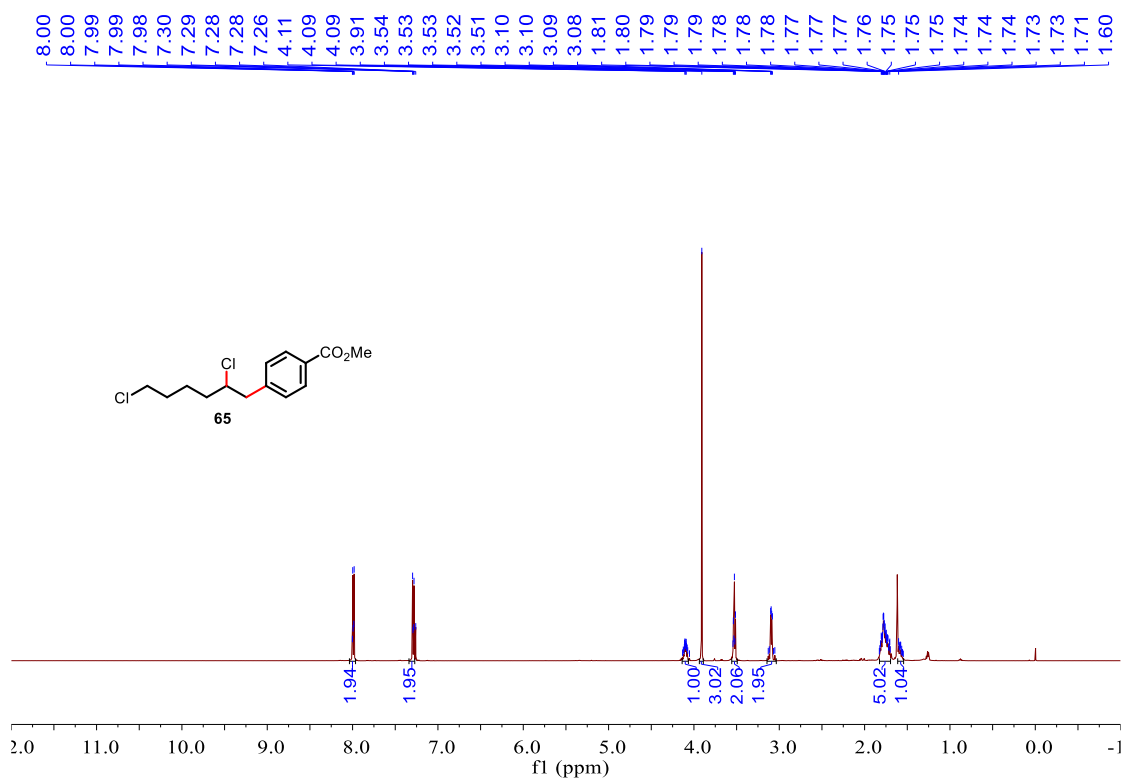
Supplementary Figure 160. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **63**



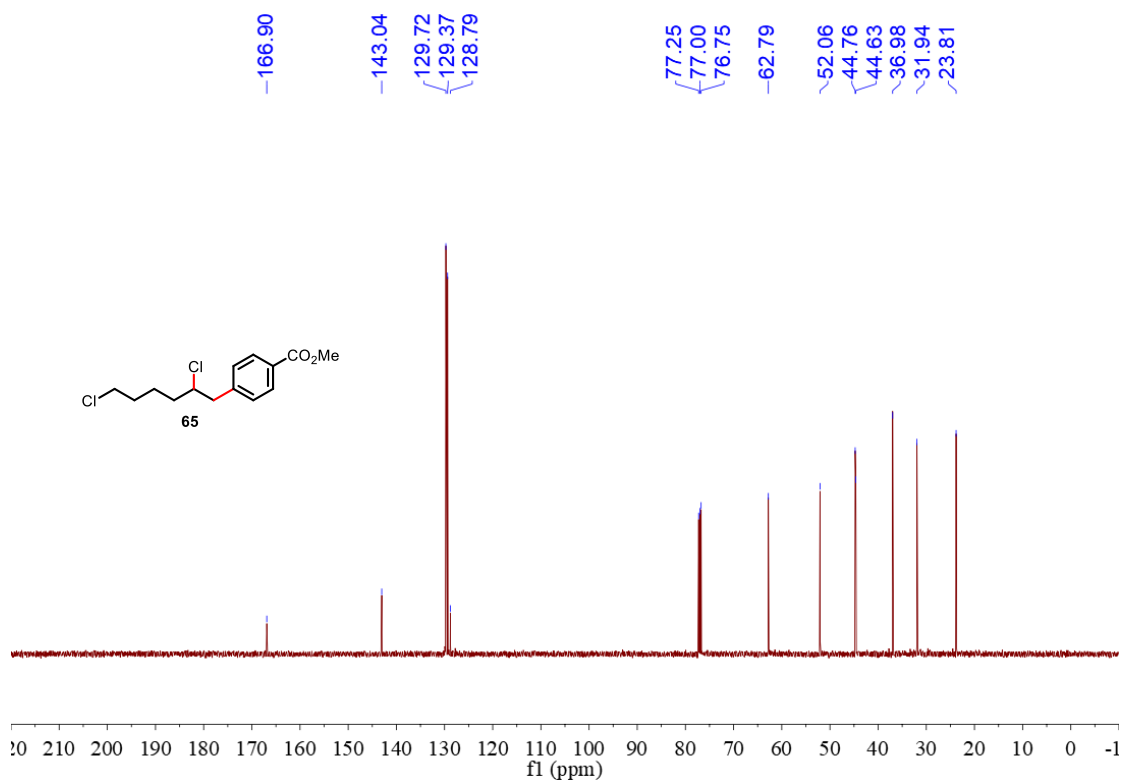
Supplementary Figure 161. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **64**



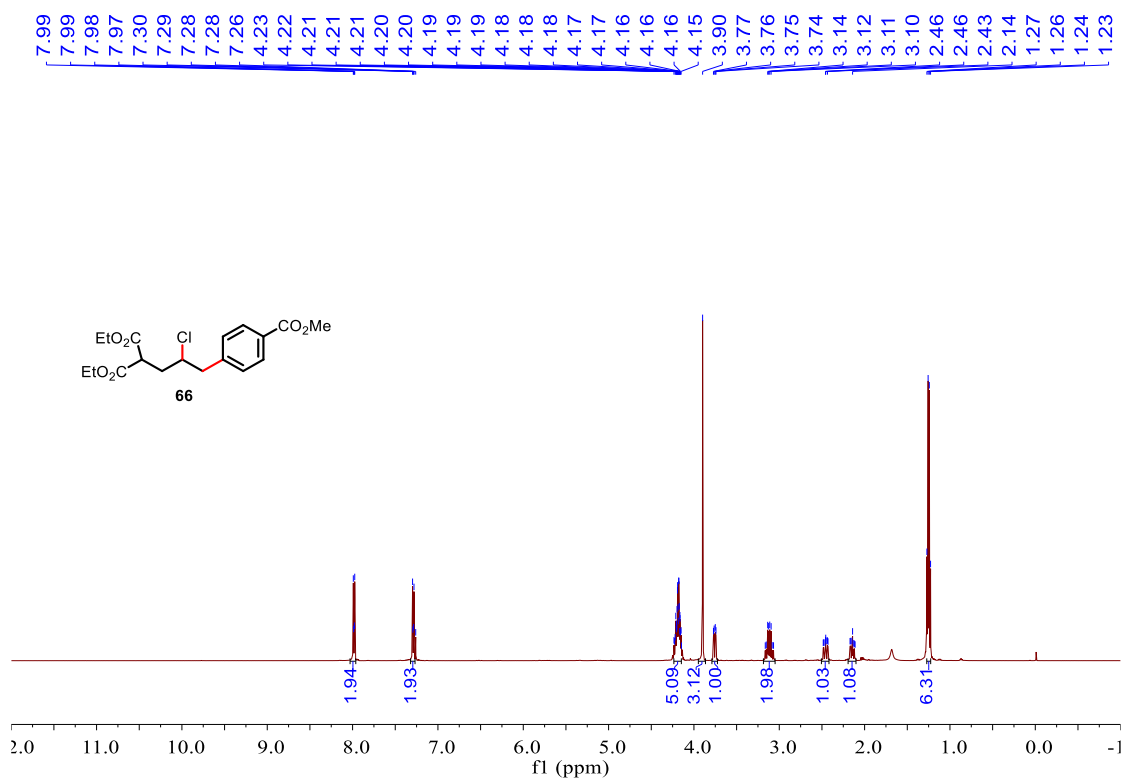
Supplementary Figure 162. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **64**



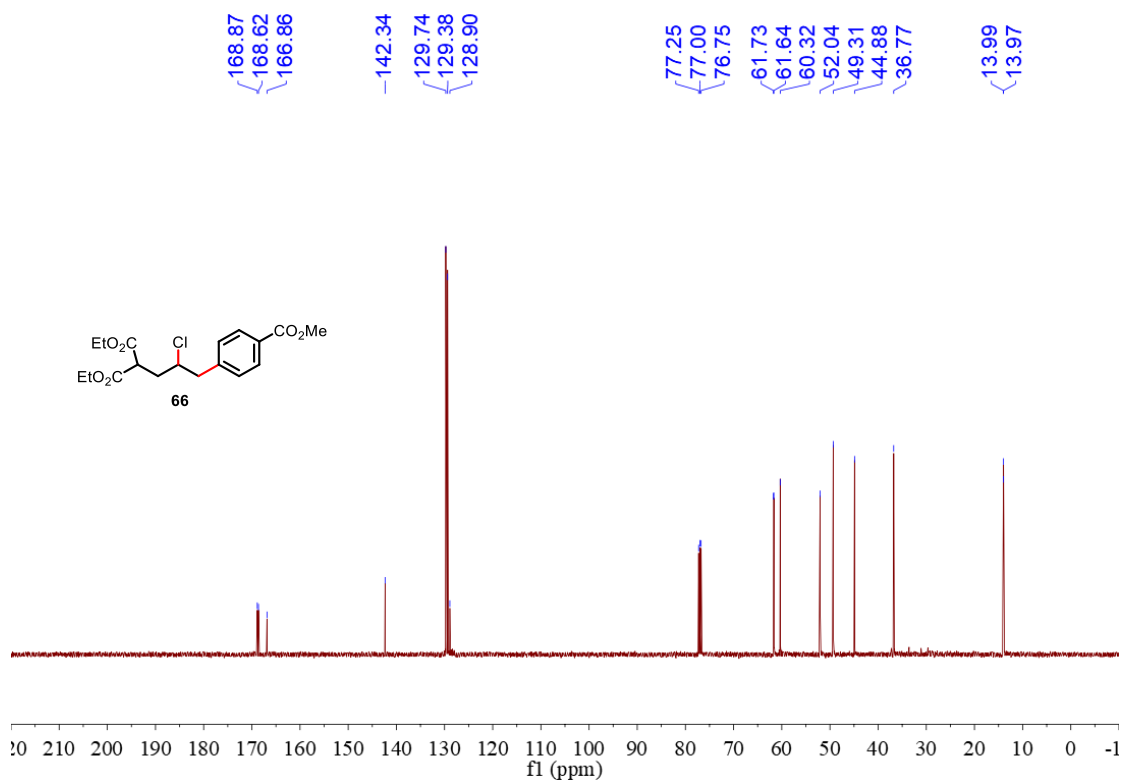
Supplementary Figure 163. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **65**



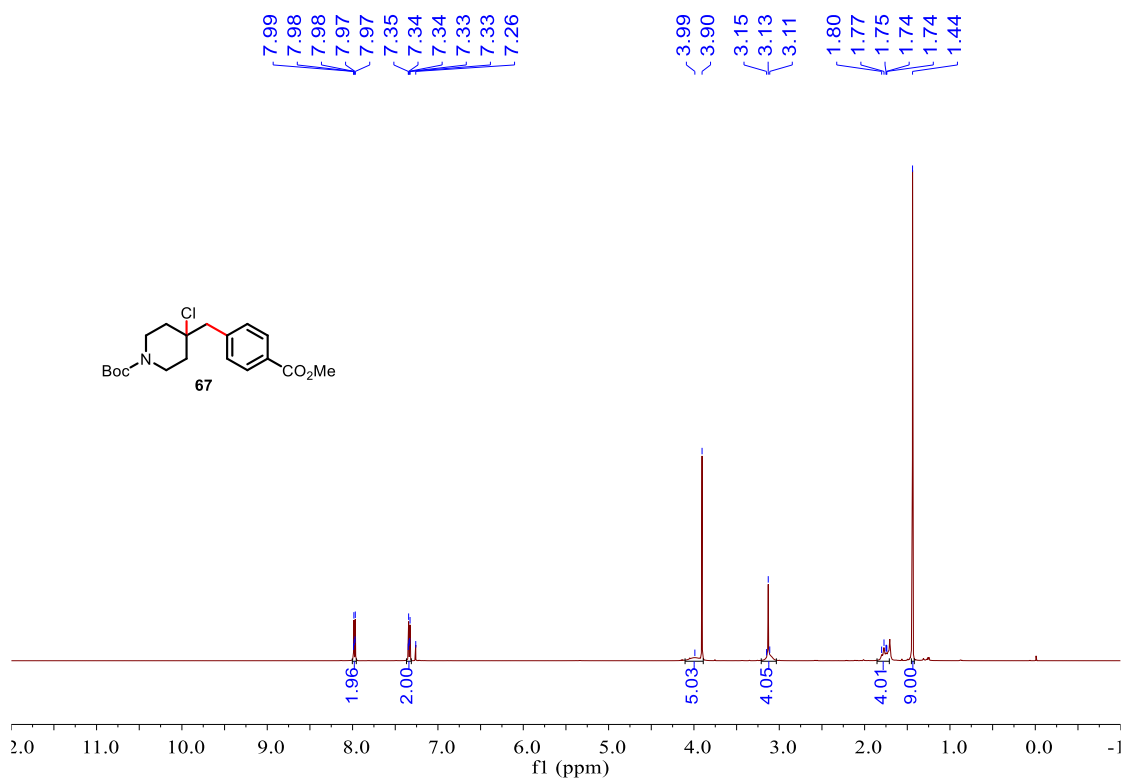
Supplementary Figure 164. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **65**



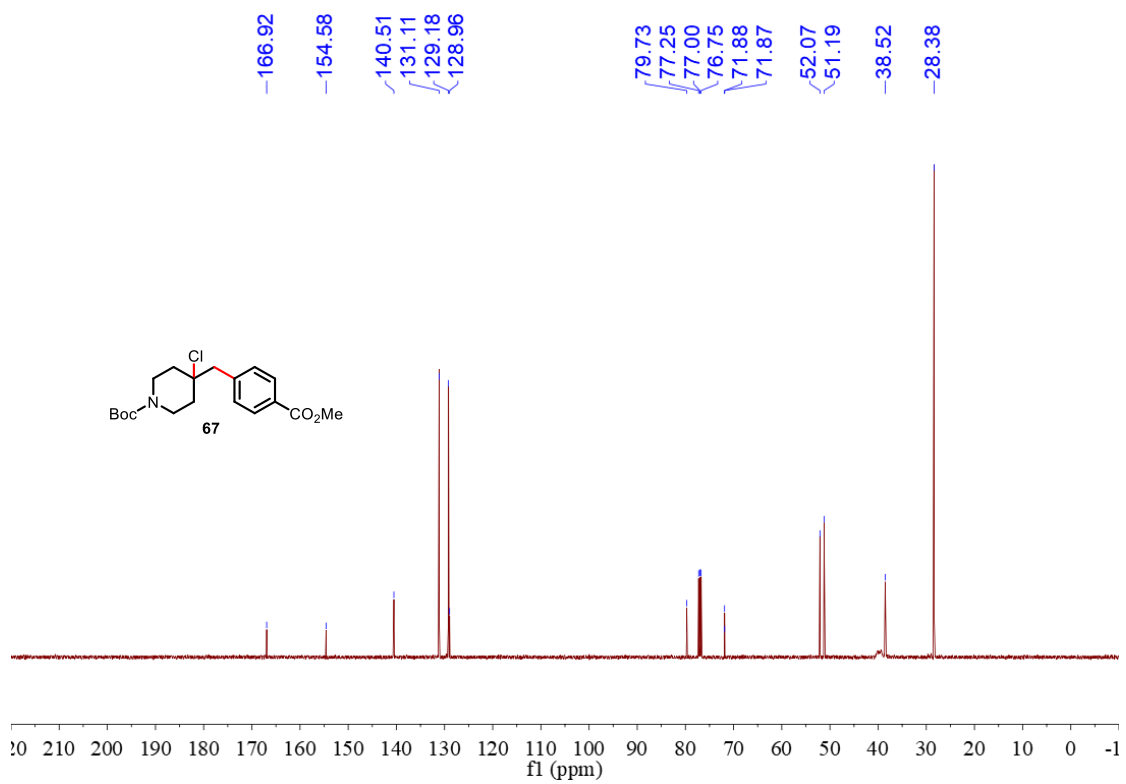
Supplementary Figure 165. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **66**



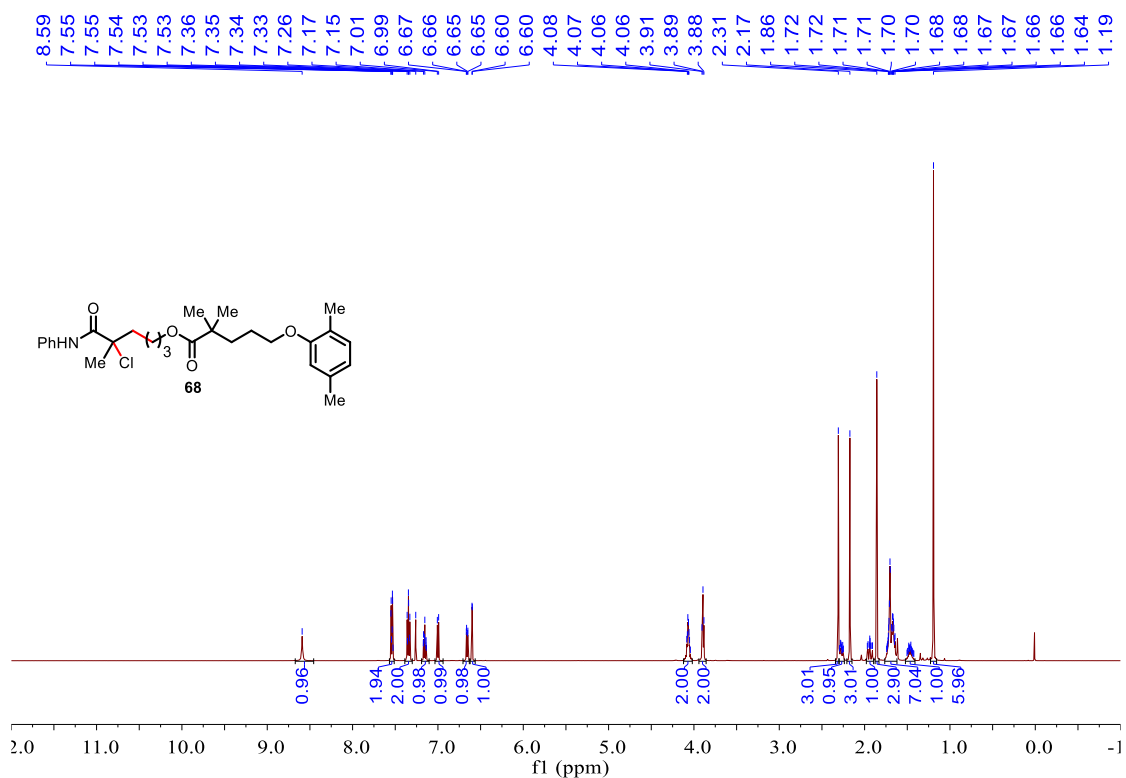
Supplementary Figure 166. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **66**



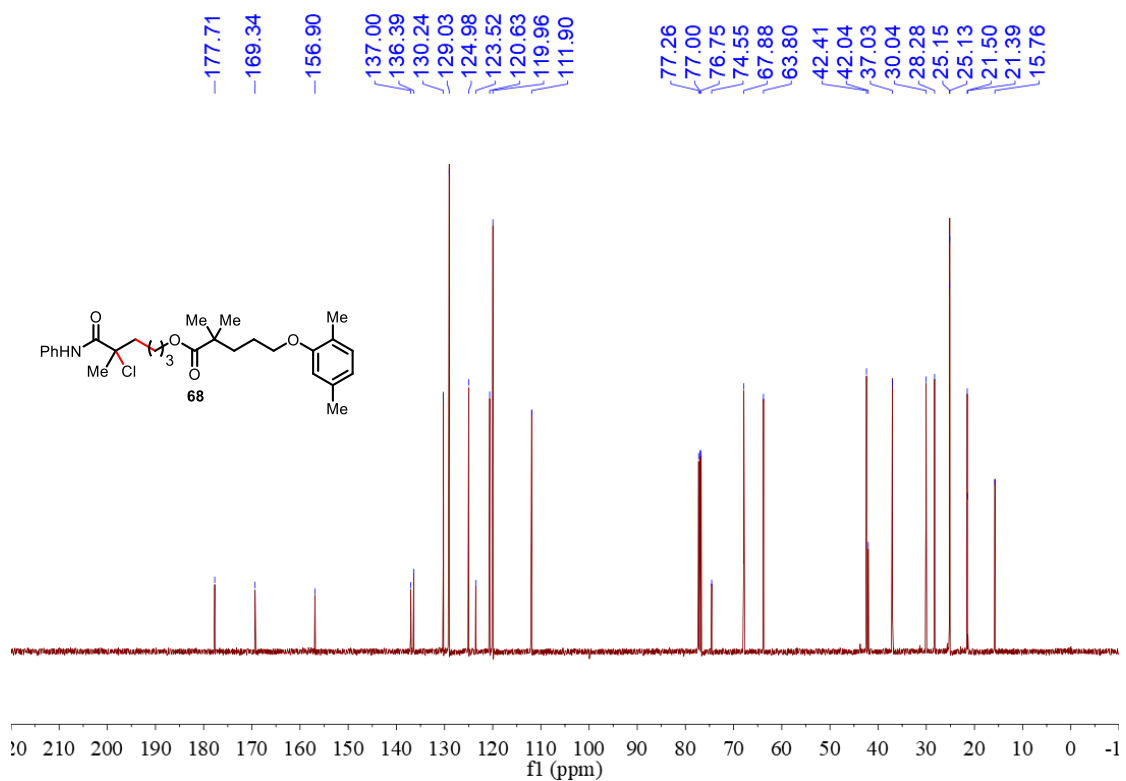
Supplementary Figure 167. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **67**



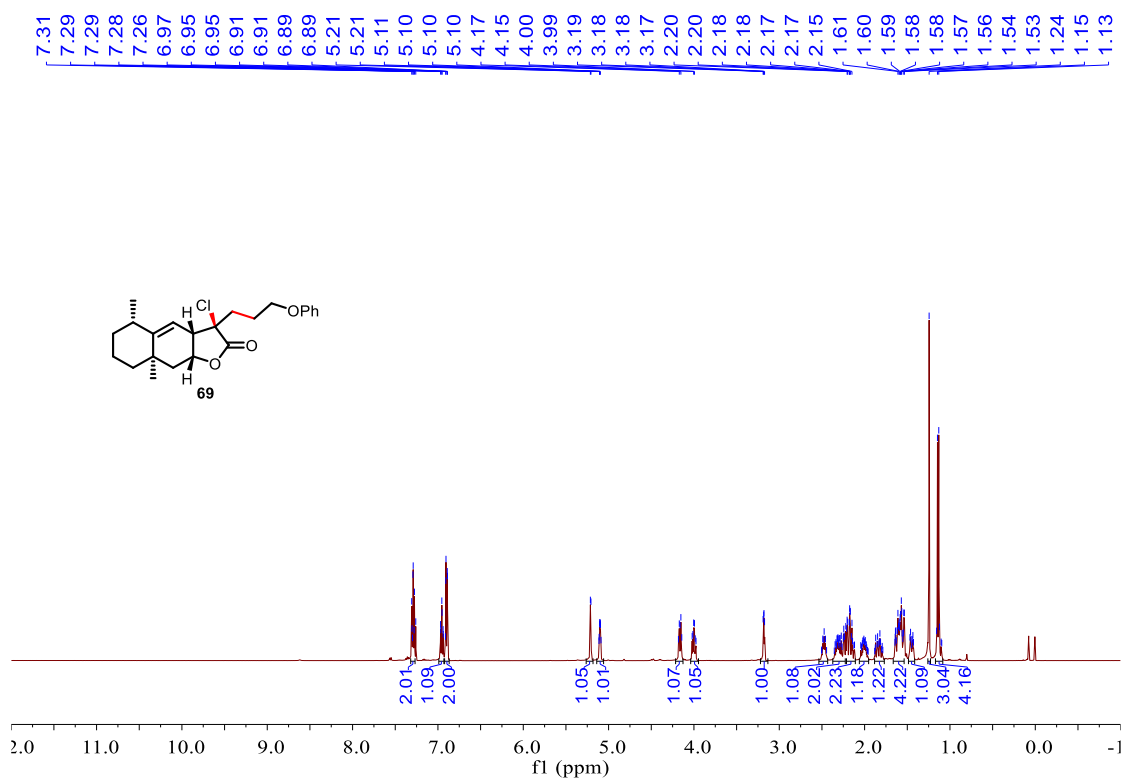
Supplementary Figure 168. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **67**



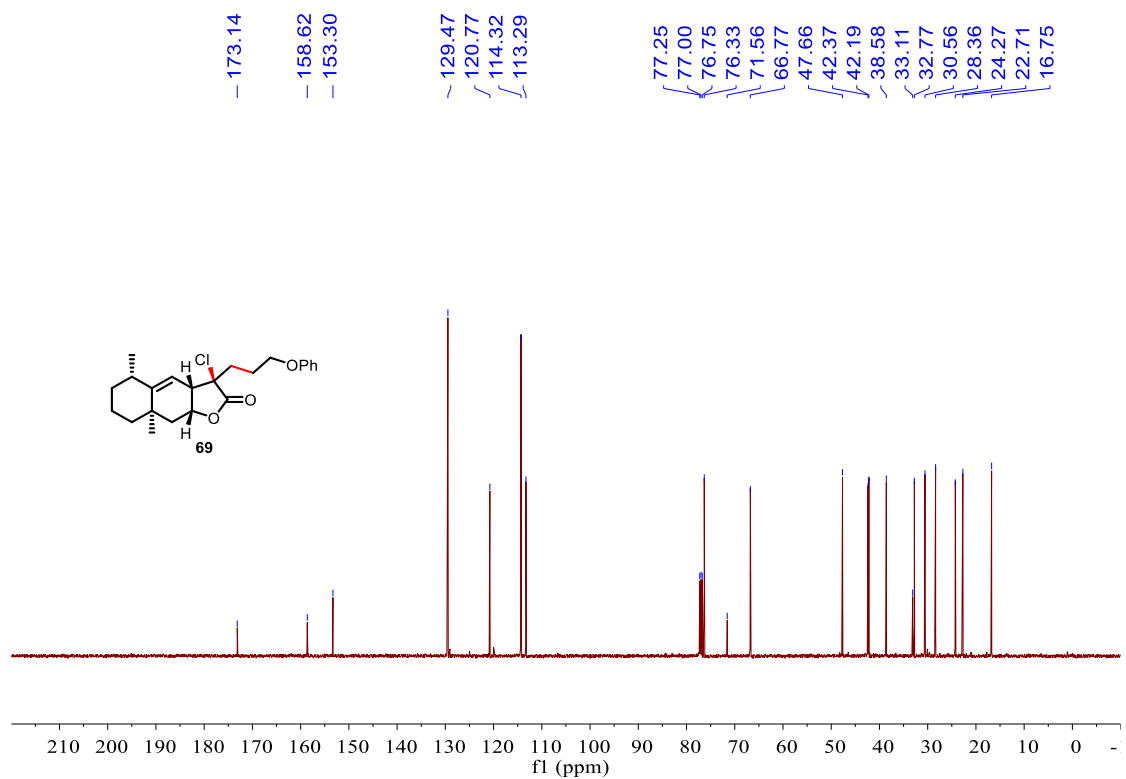
Supplementary Figure 169. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **68**



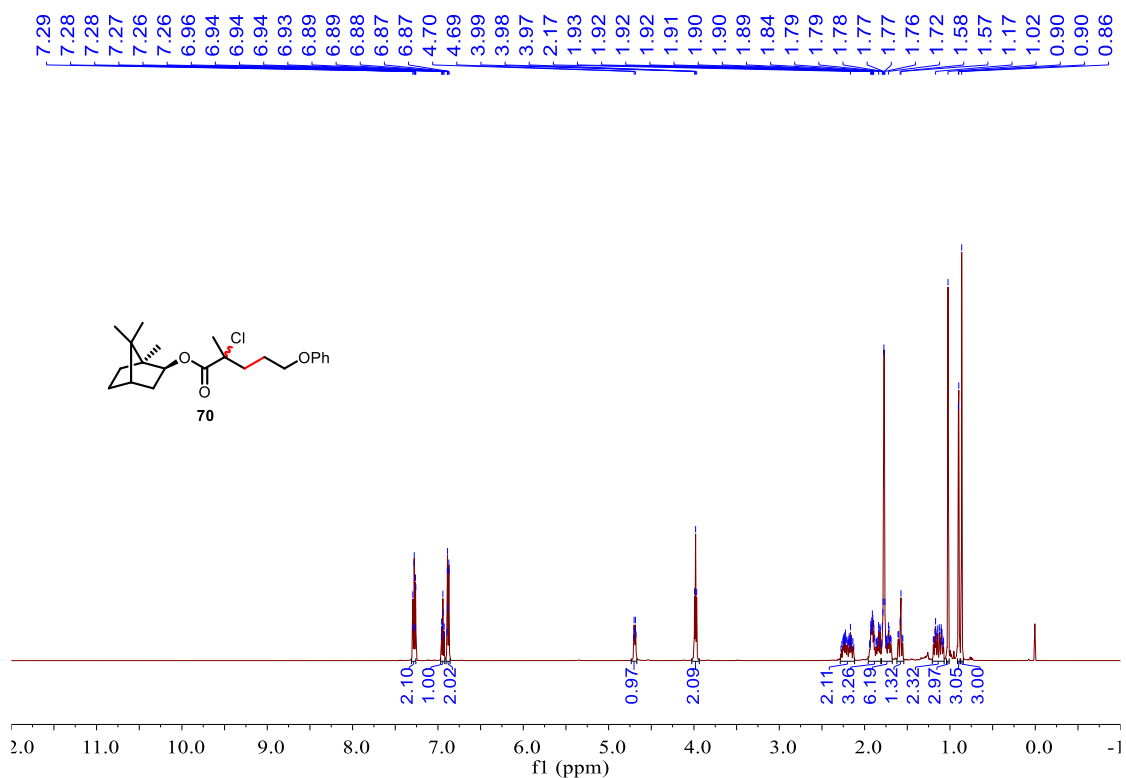
Supplementary Figure 170. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **68**



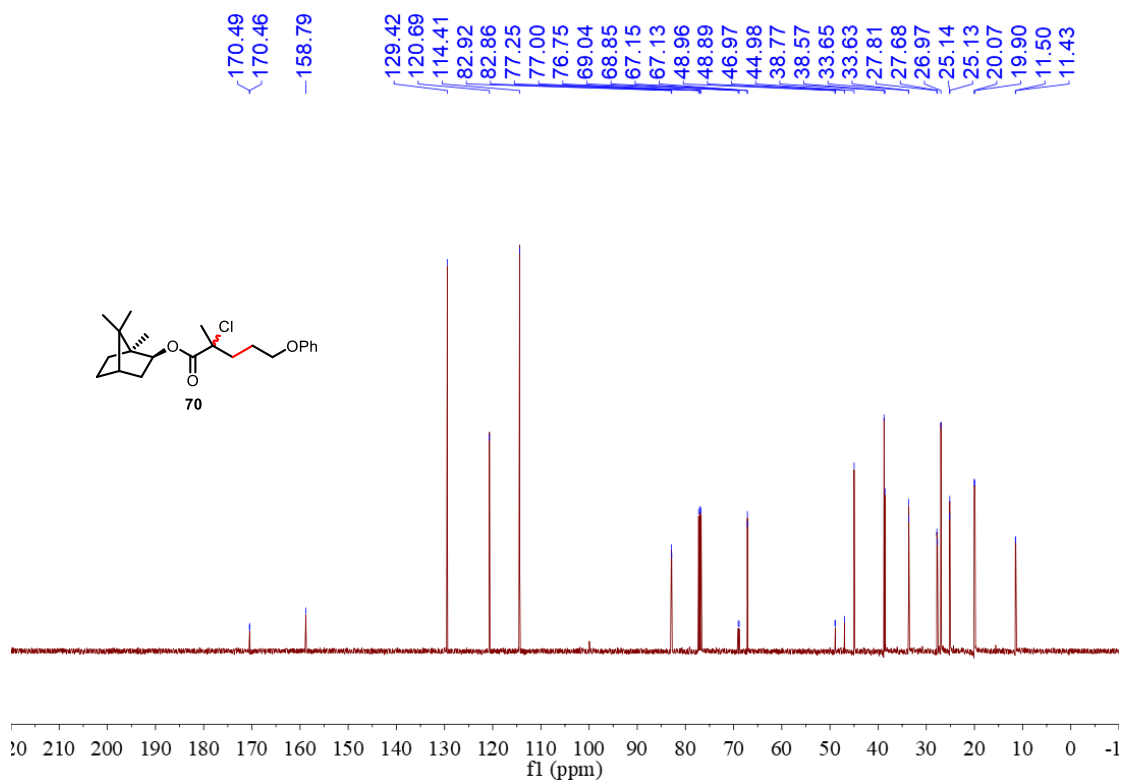
Supplementary Figure 171. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **69**



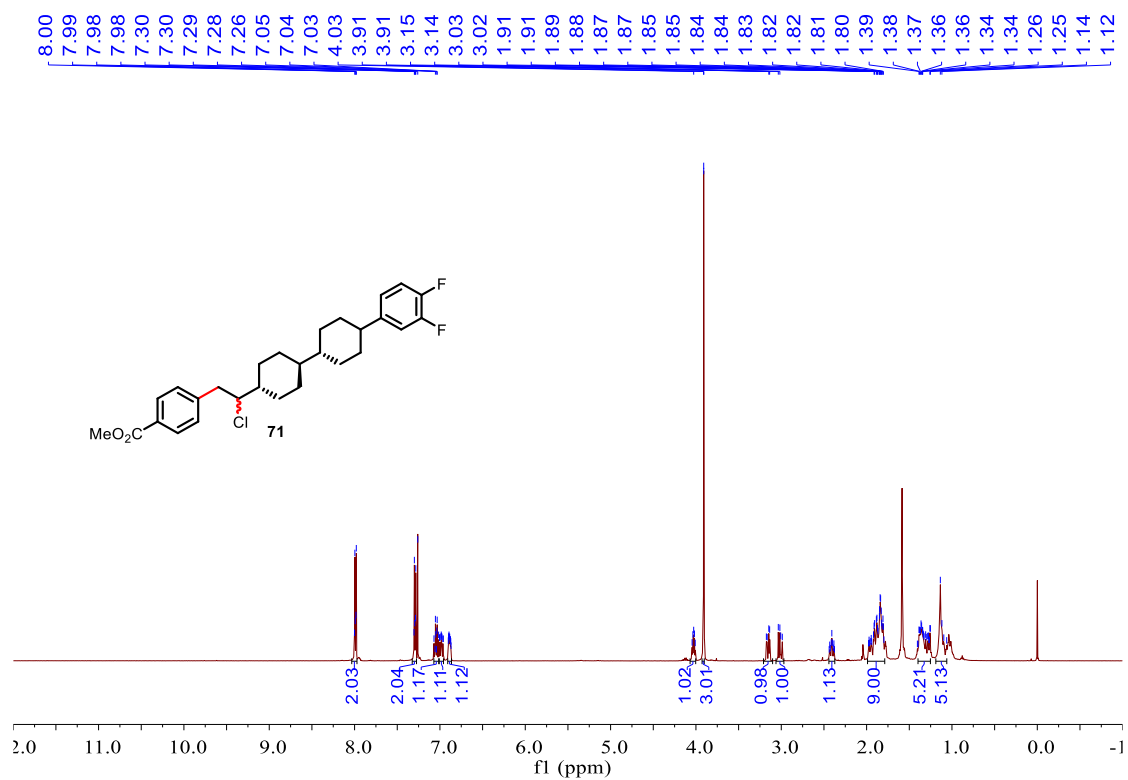
Supplementary Figure 172. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **69**



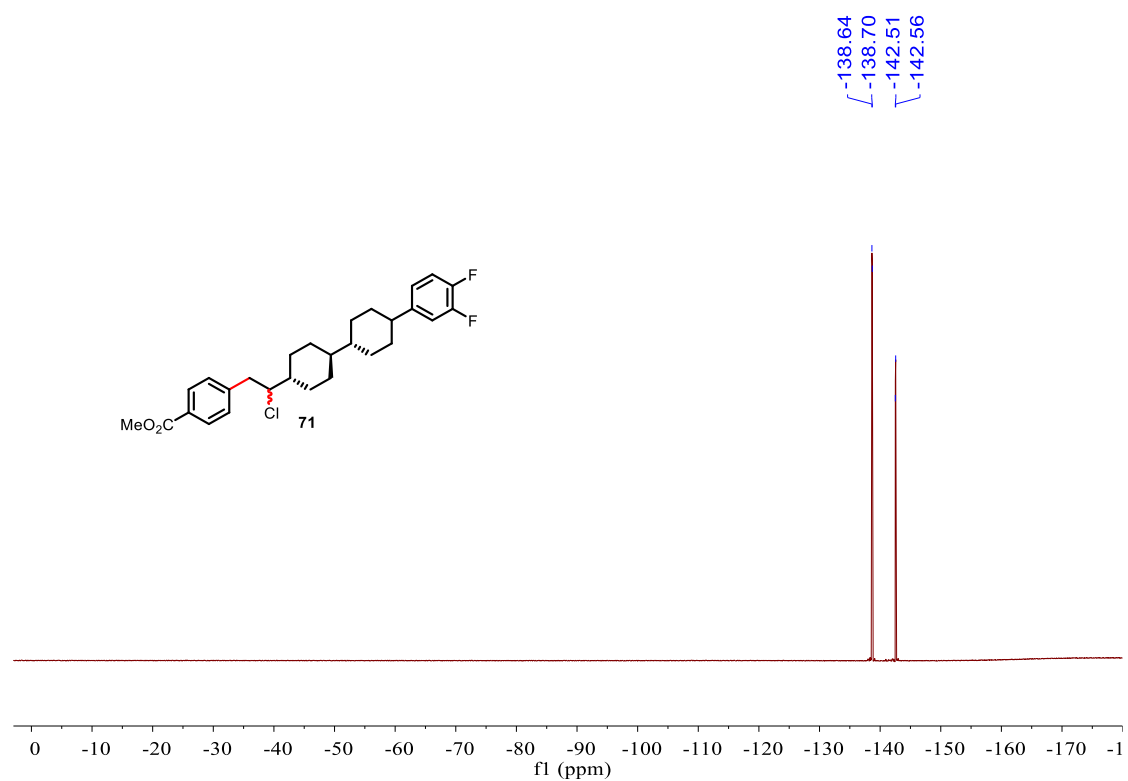
Supplementary Figure 173. ¹H NMR (500 MHz, CDCl₃) spectrum for compound 70



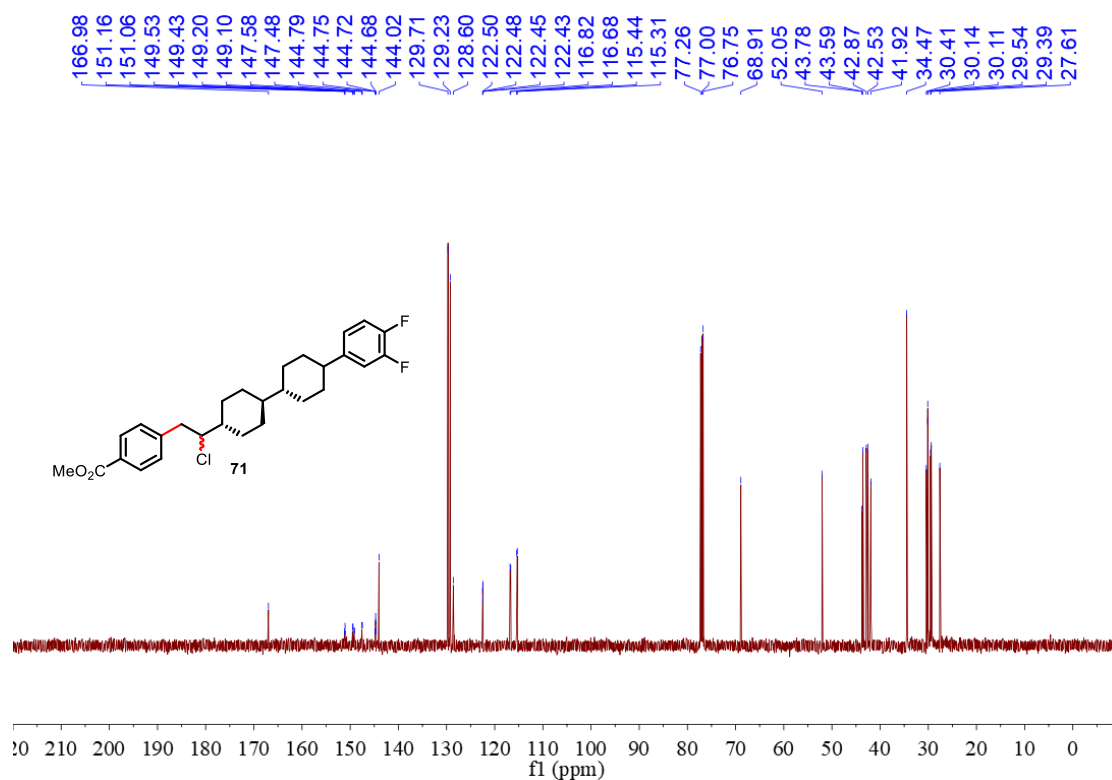
Supplementary Figure 174. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound 70



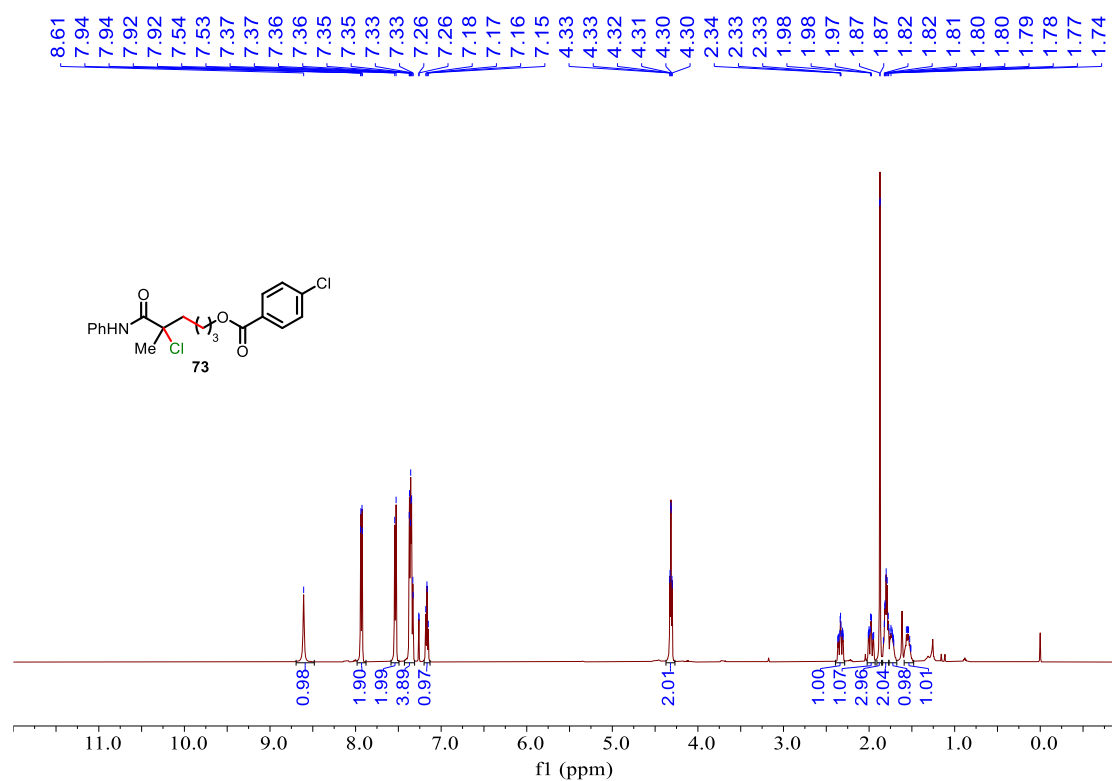
Supplementary Figure 175. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **71**



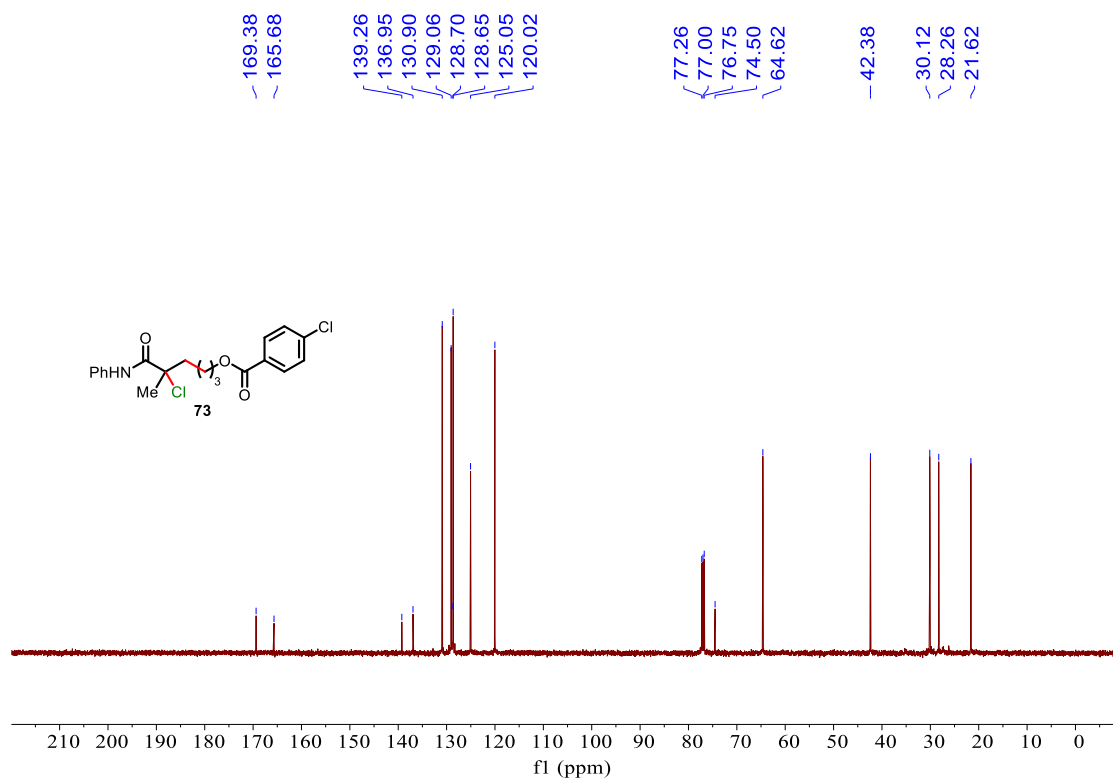
Supplementary Figure 176. ¹⁹F NMR (376 MHz, CDCl₃) spectrum for compound **71**



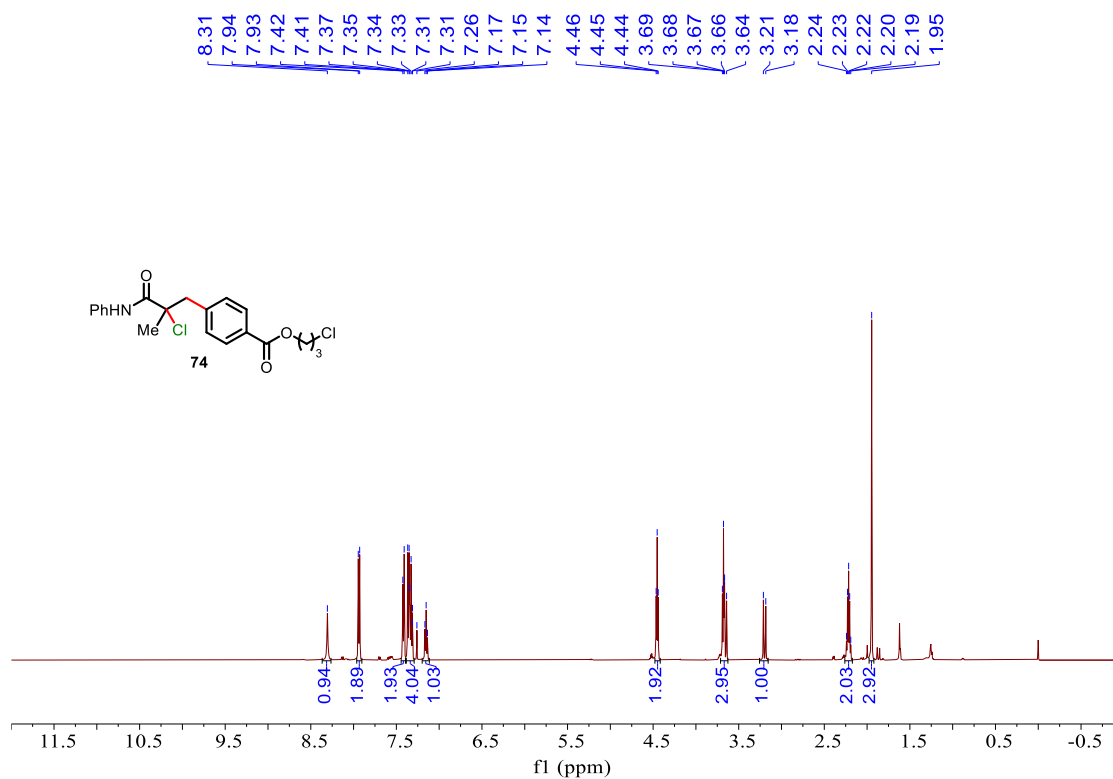
Supplementary Figure 177. ^{13}C NMR (126 MHz, CDCl_3) spectrum for compound **71**



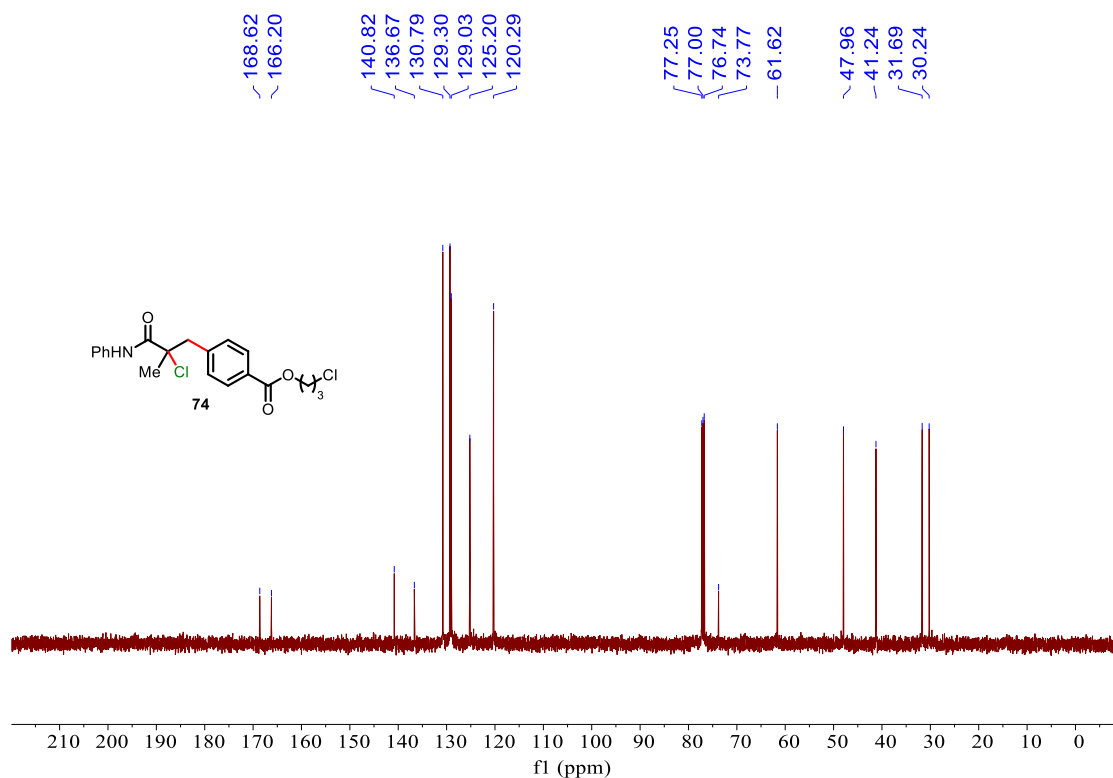
Supplementary Figure 178. ^1H NMR (500 MHz, CDCl_3) spectrum for compound **73**



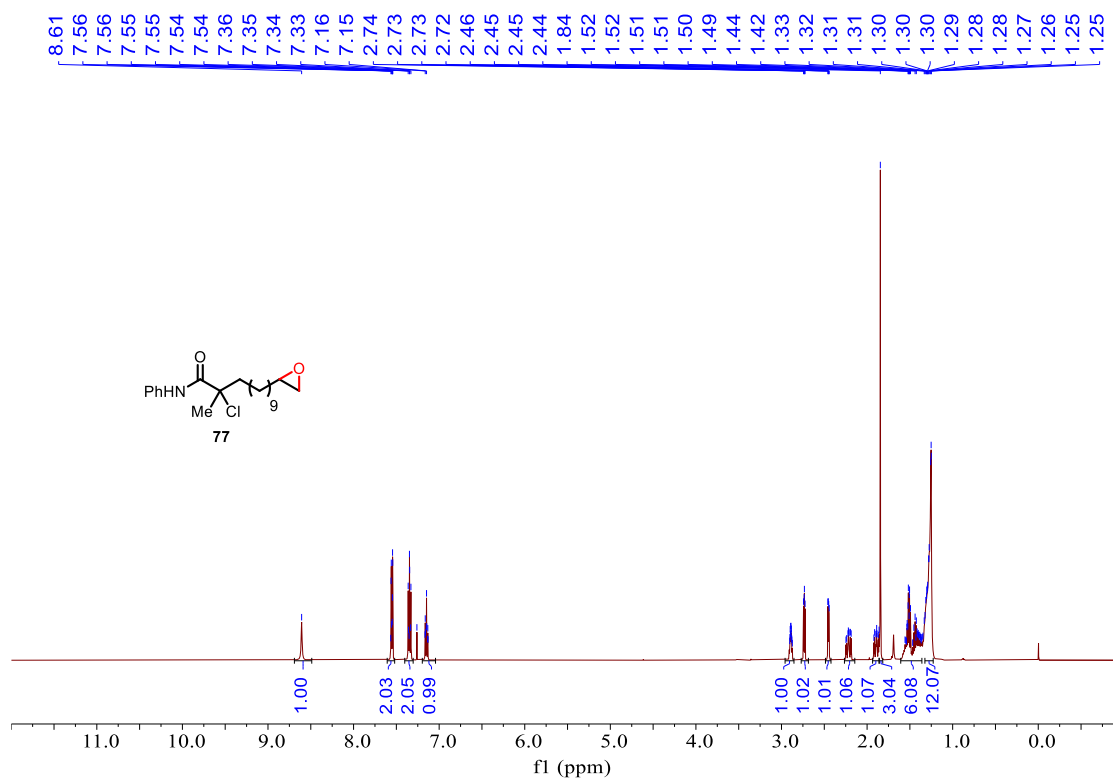
Supplementary Figure 179. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound 73



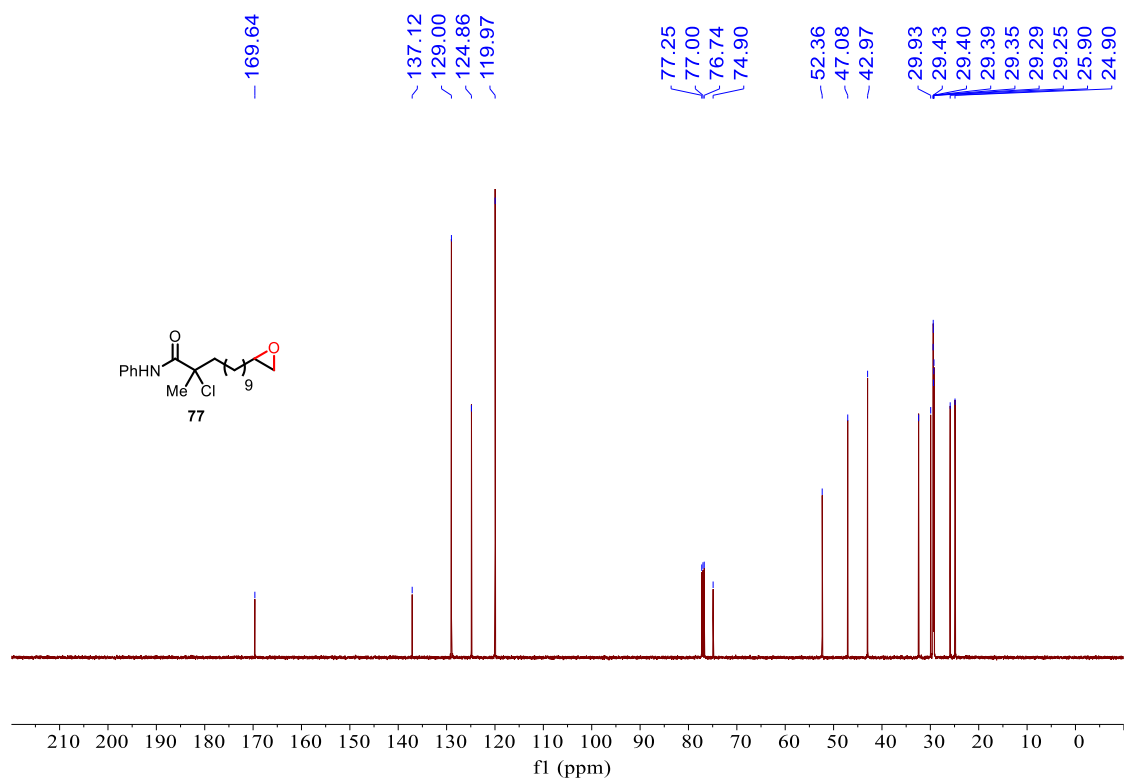
Supplementary Figure 180. ¹H NMR (500 MHz, CDCl₃) spectrum for compound 74



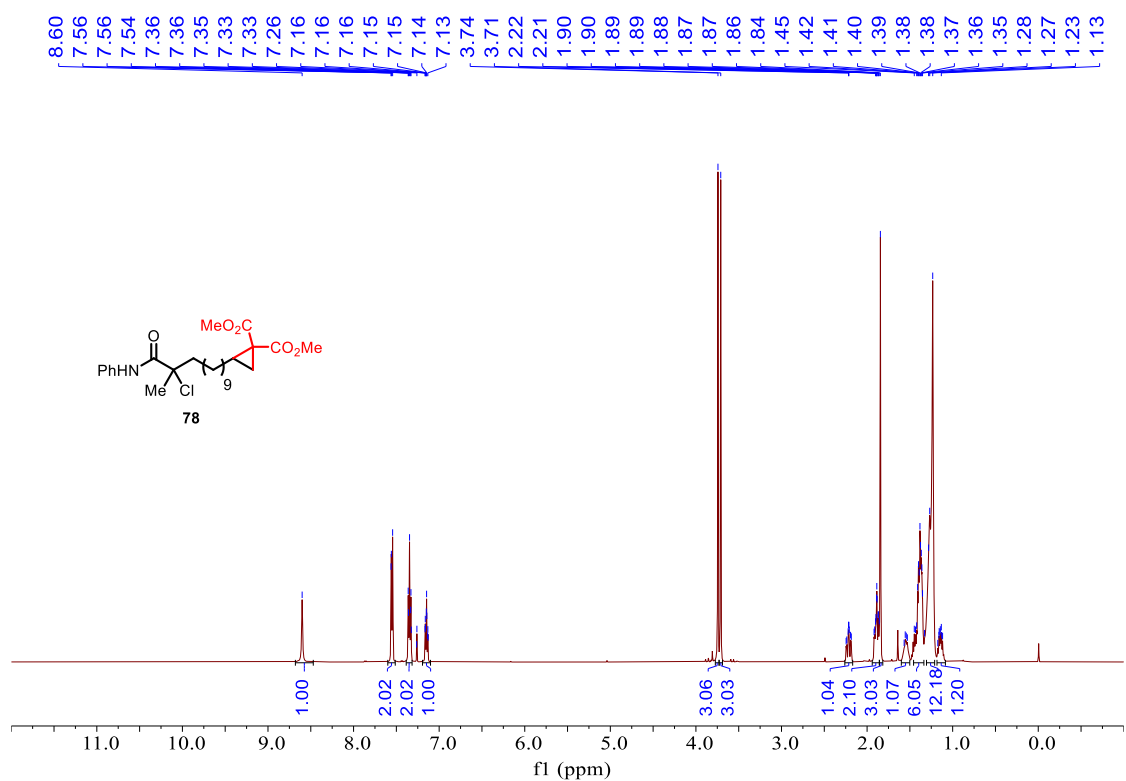
Supplementary Figure 181. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound 74



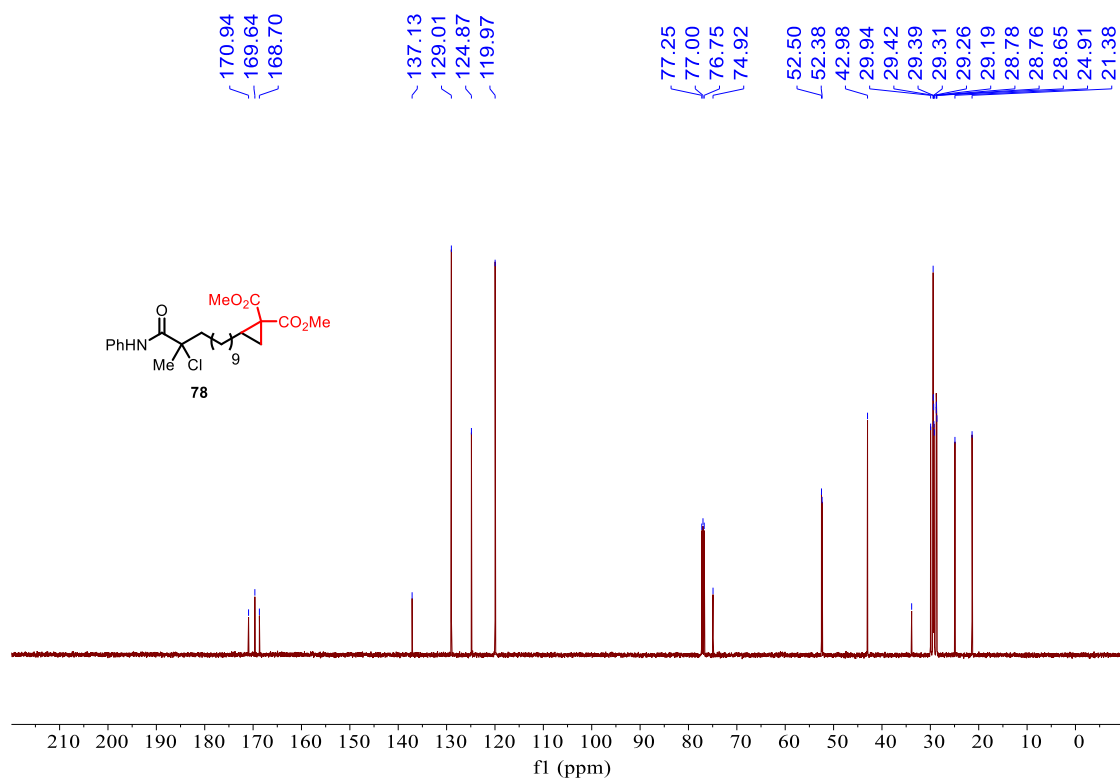
Supplementary Figure 182. ¹H NMR (500 MHz, CDCl₃) spectrum for compound 77



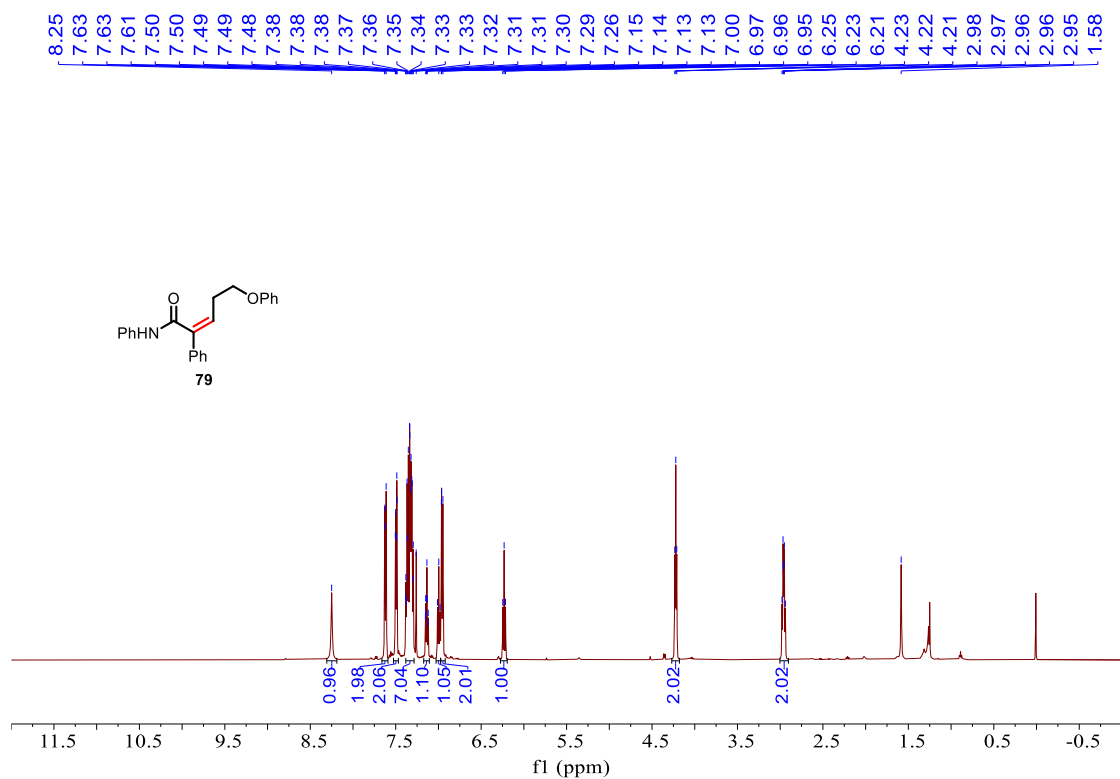
Supplementary Figure 183. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **77**



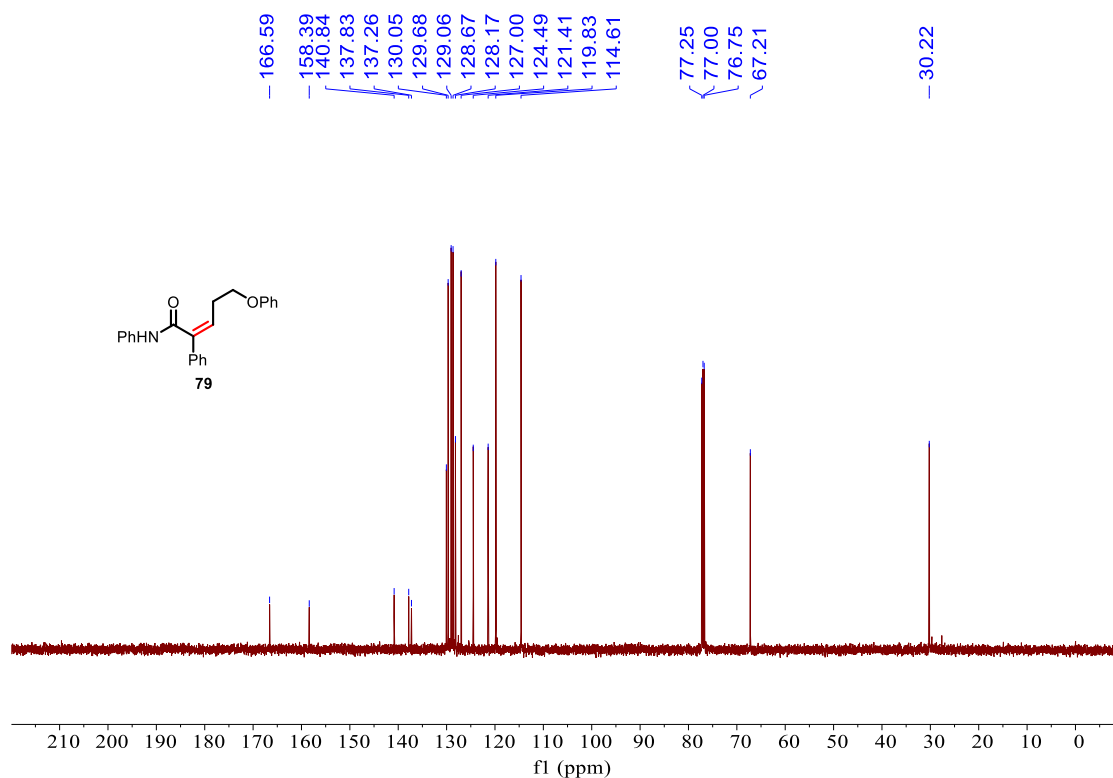
Supplementary Figure 184. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **78**



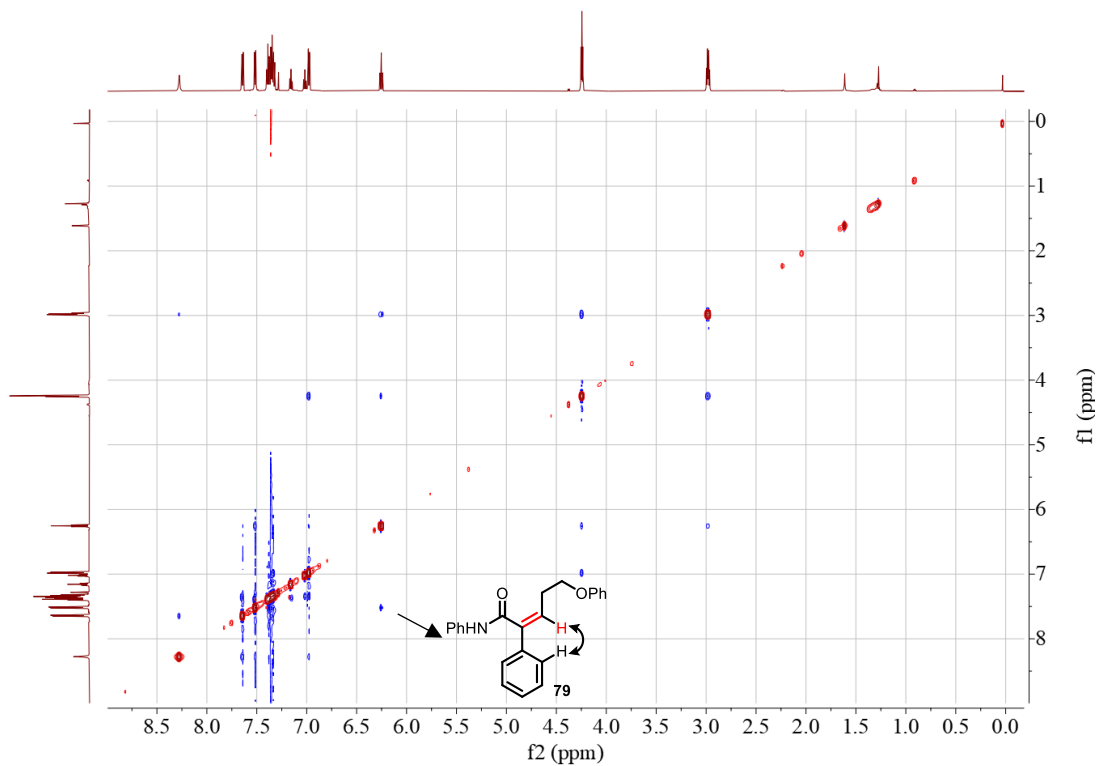
Supplementary Figure 185. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **78**



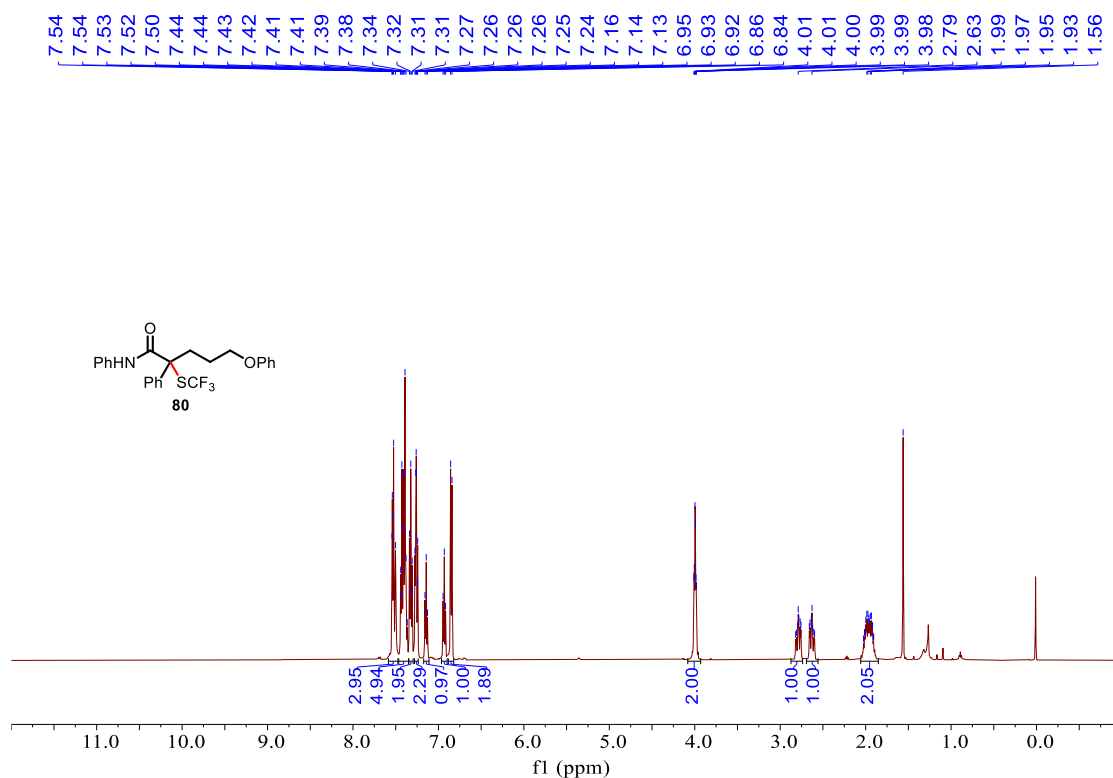
Supplementary Figure 186. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **79**



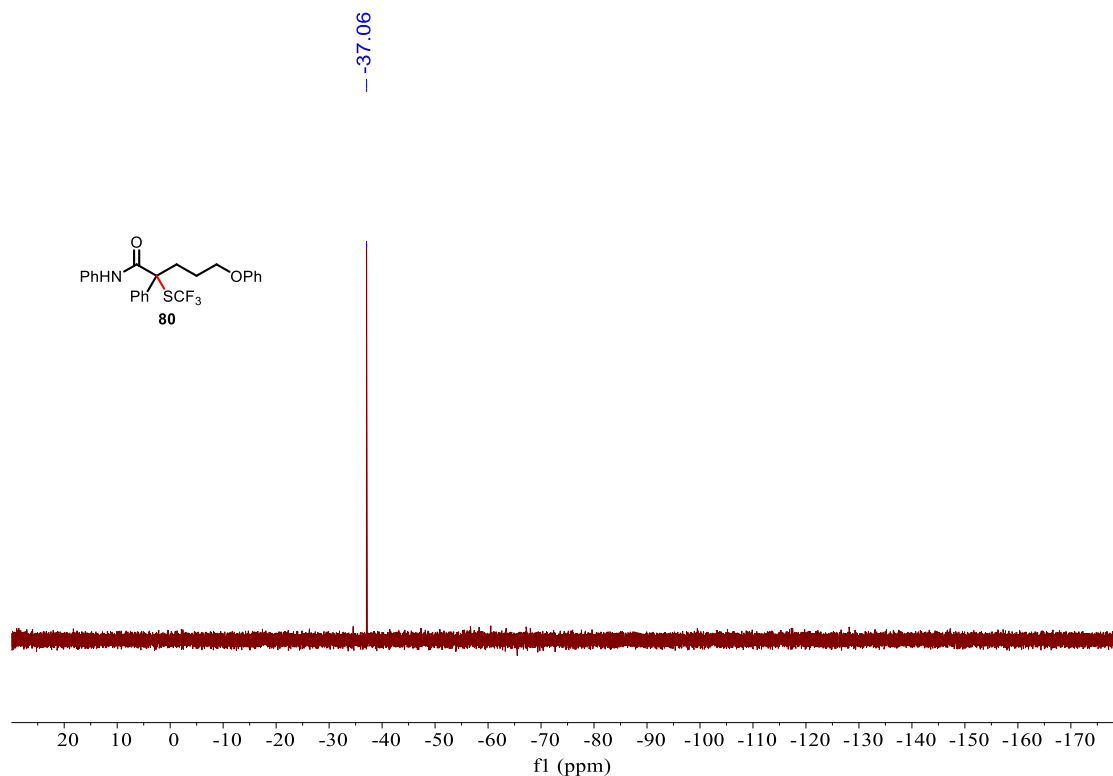
Supplementary Figure 187. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **79**



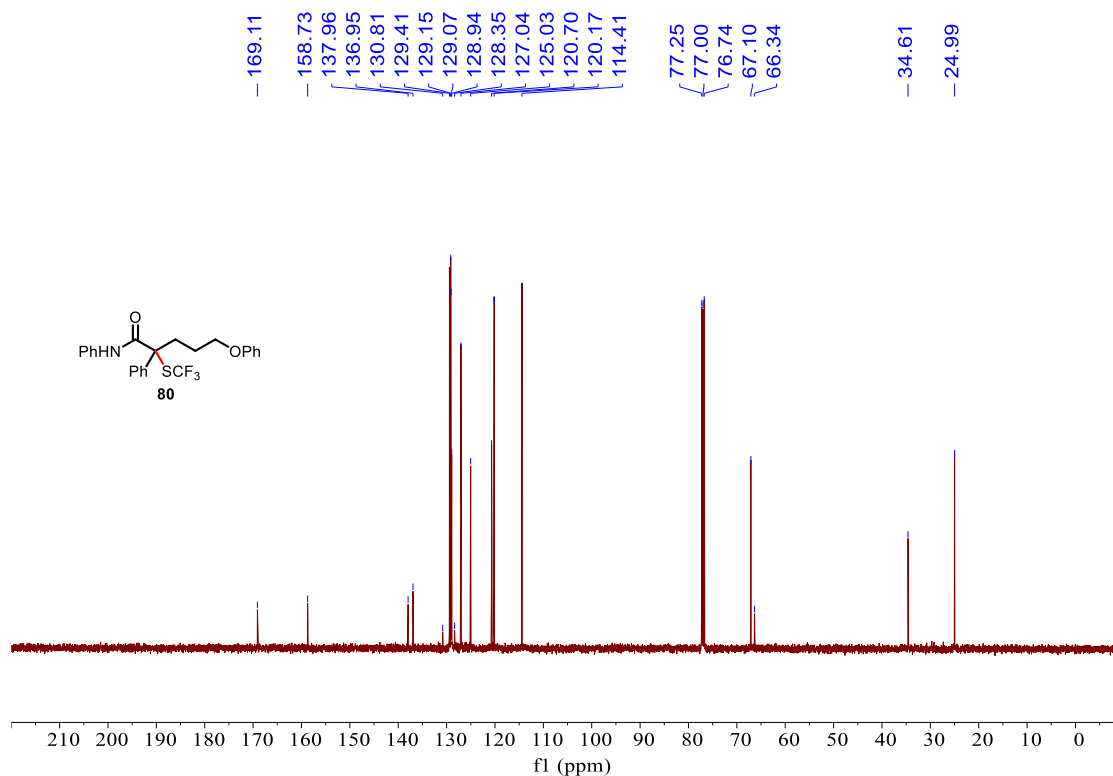
Supplementary Figure 188. NOE spectrum for compound **79**



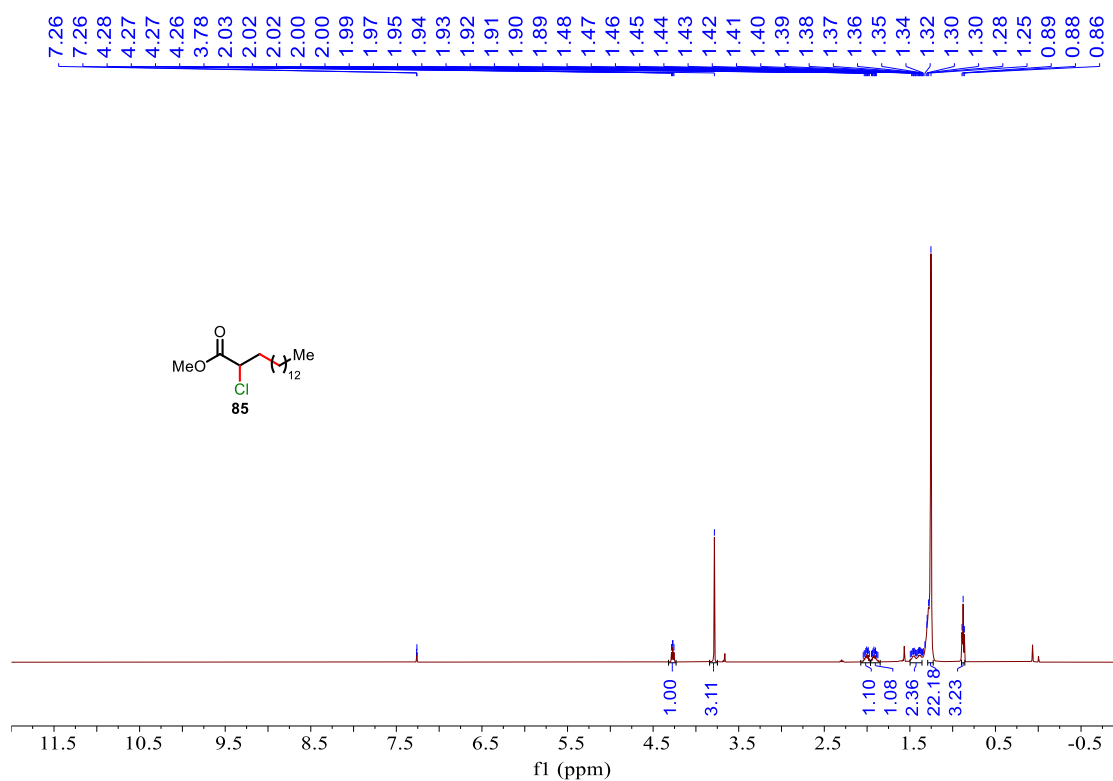
Supplementary Figure 189. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **80**



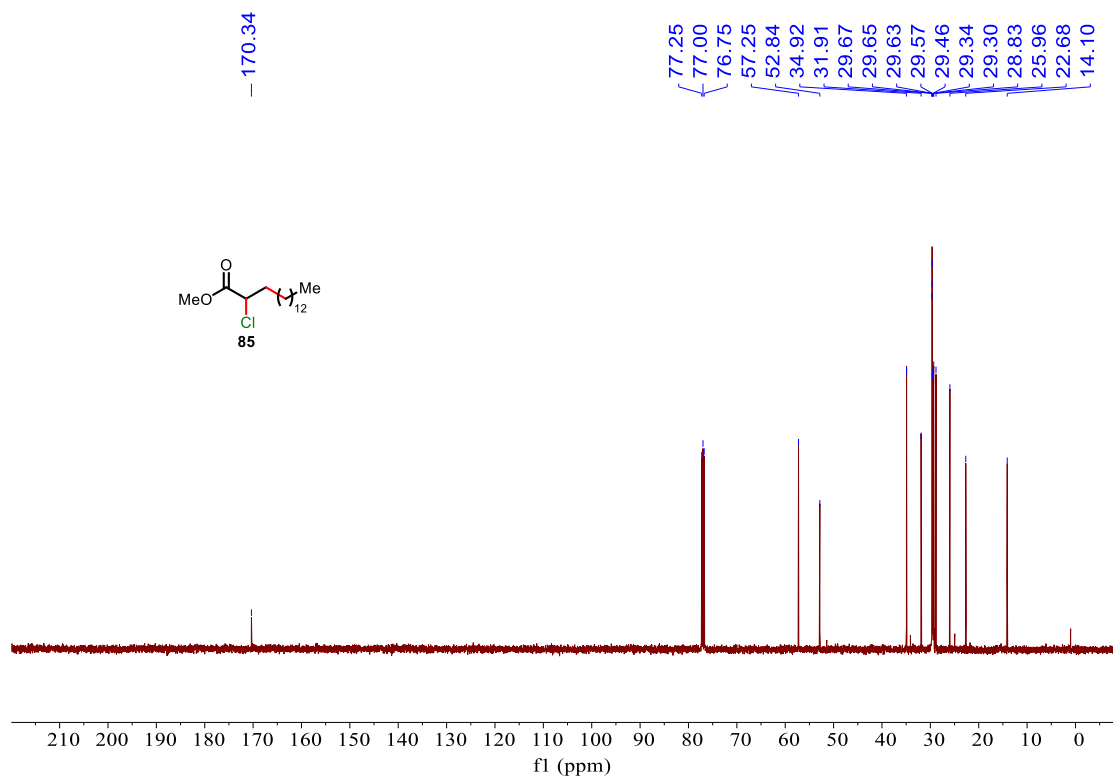
Supplementary Figure 190. ¹⁹F NMR (376 MHz, CDCl₃) spectrum for compound **80**



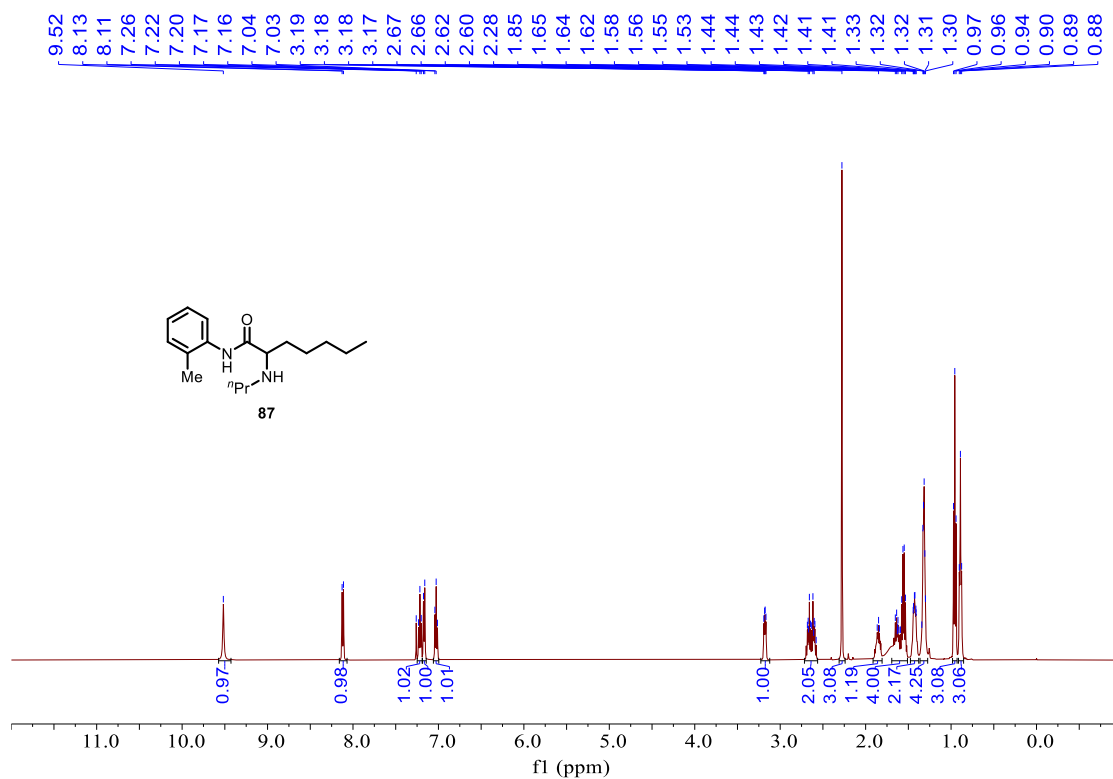
Supplementary Figure 191. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **80**



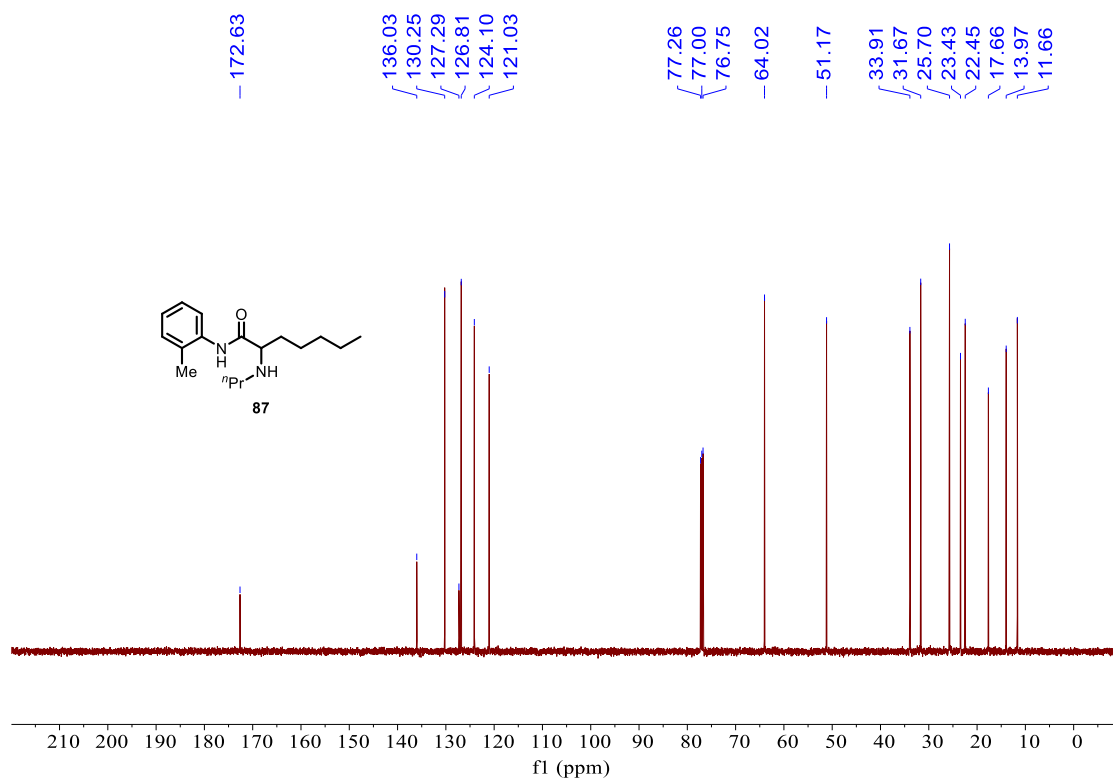
Supplementary Figure 192. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **85**



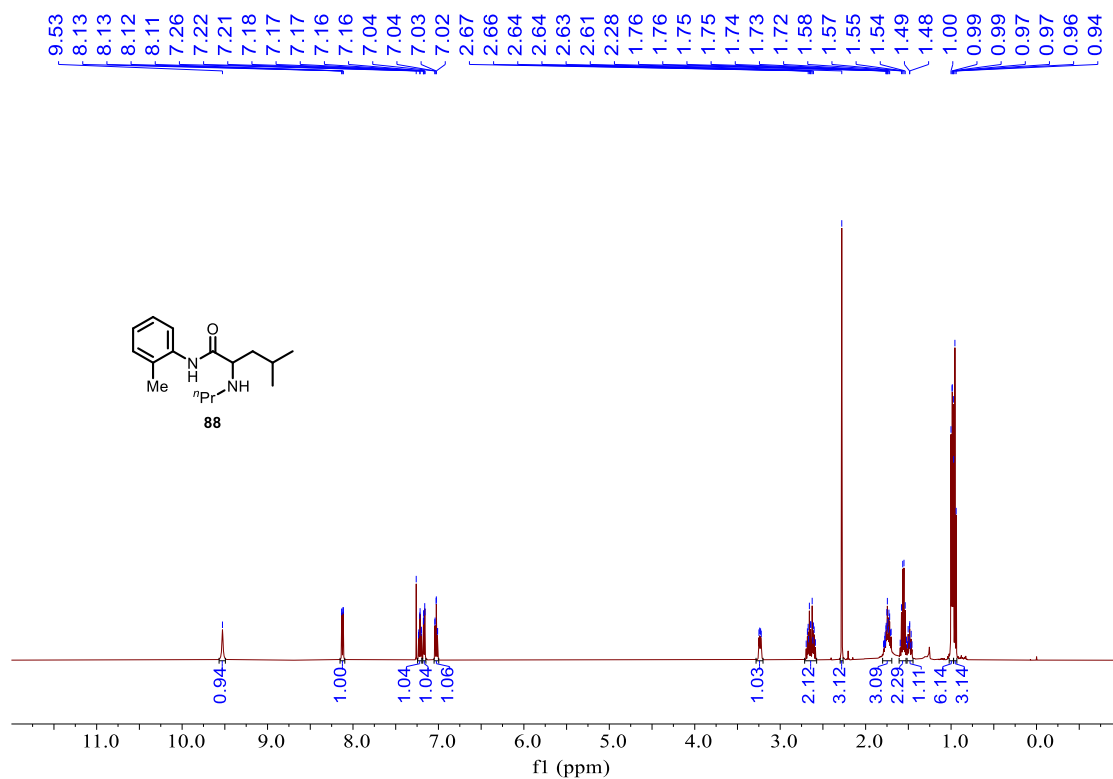
Supplementary Figure 193. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **85**



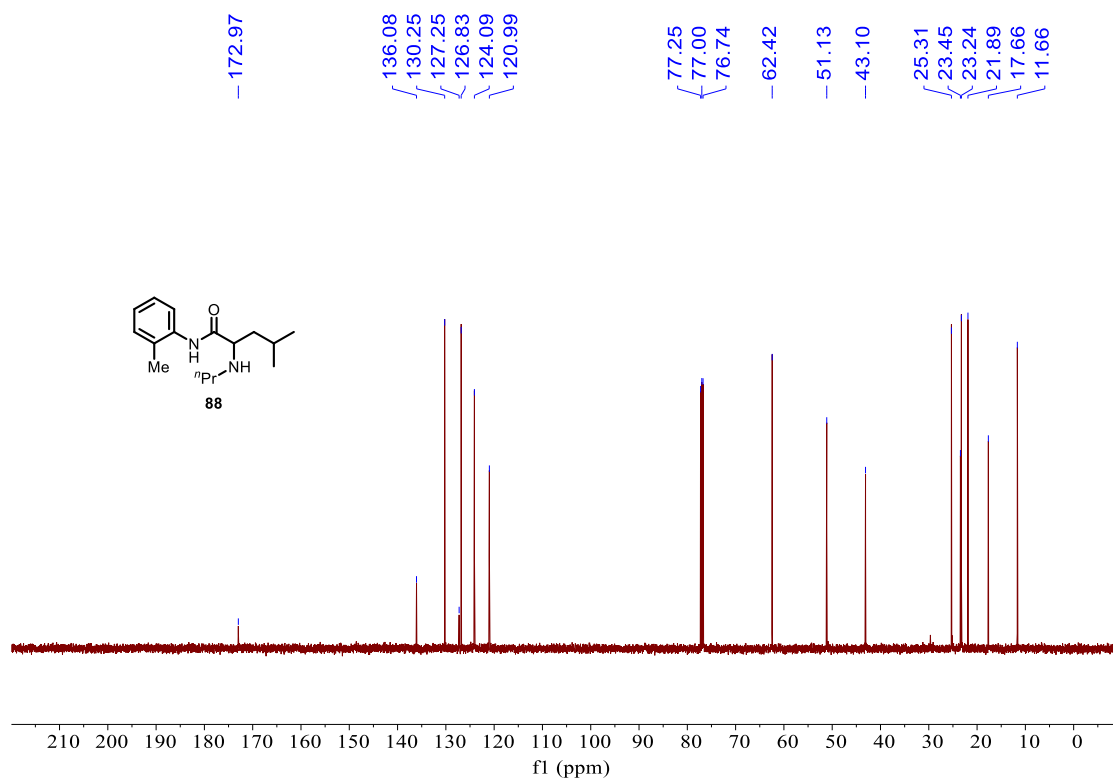
Supplementary Figure 194. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **87**



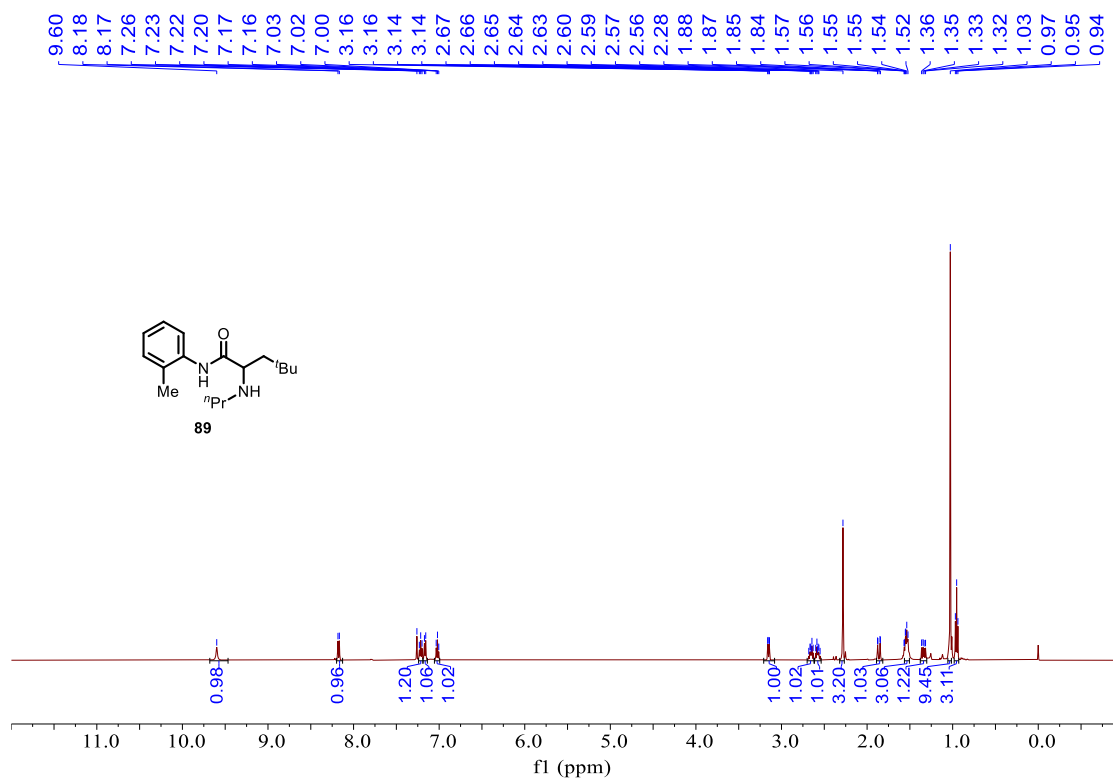
Supplementary Figure 195. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **87**



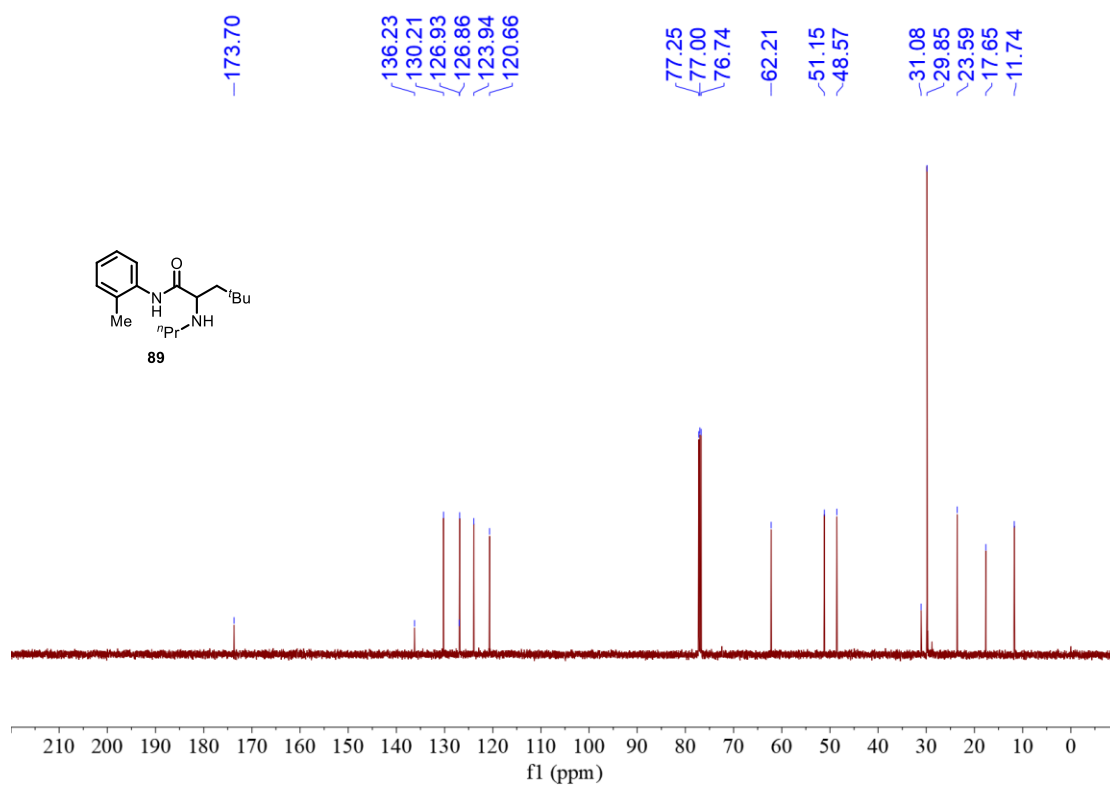
Supplementary Figure 196. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **88**



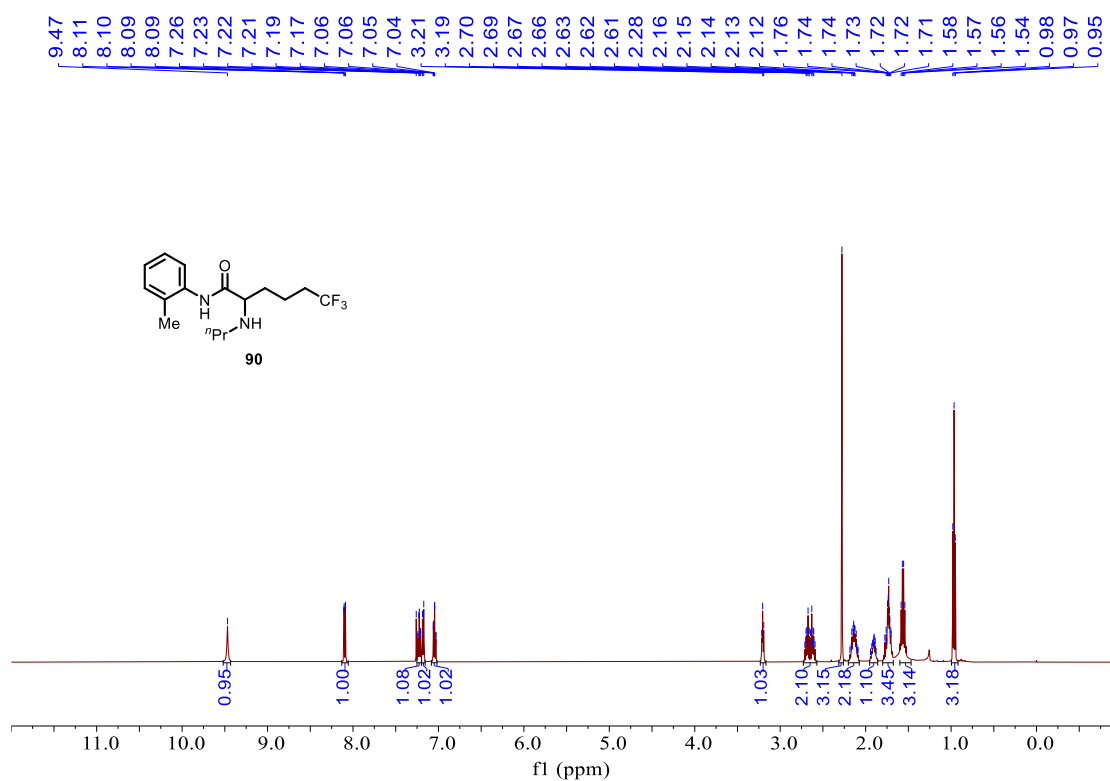
Supplementary Figure 197. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **88**



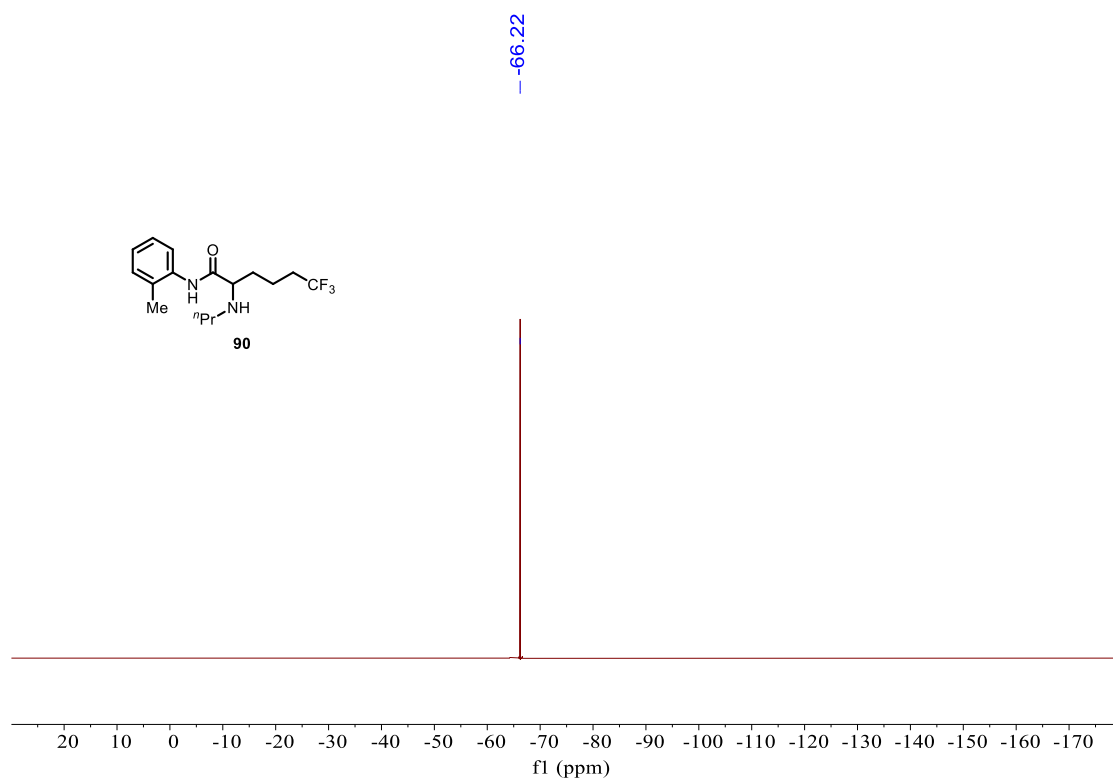
Supplementary Figure 198. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **89**



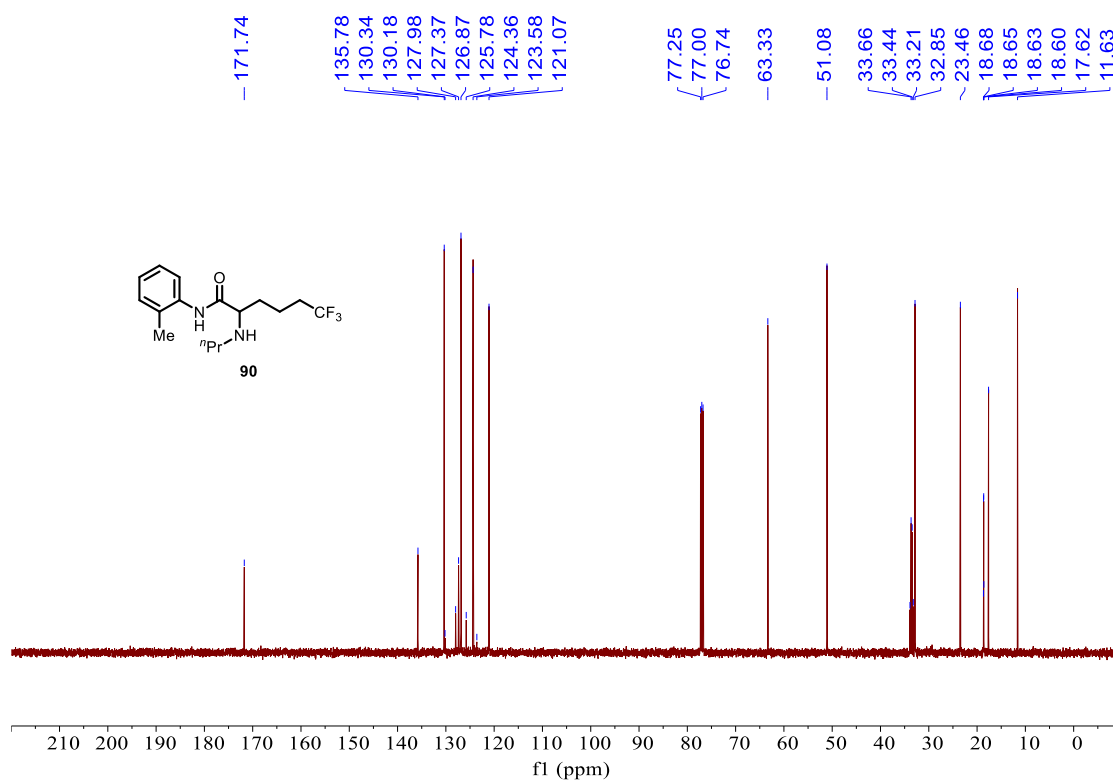
Supplementary Figure 199. ^{13}C NMR (126 MHz, CDCl_3) spectrum for compound **89**



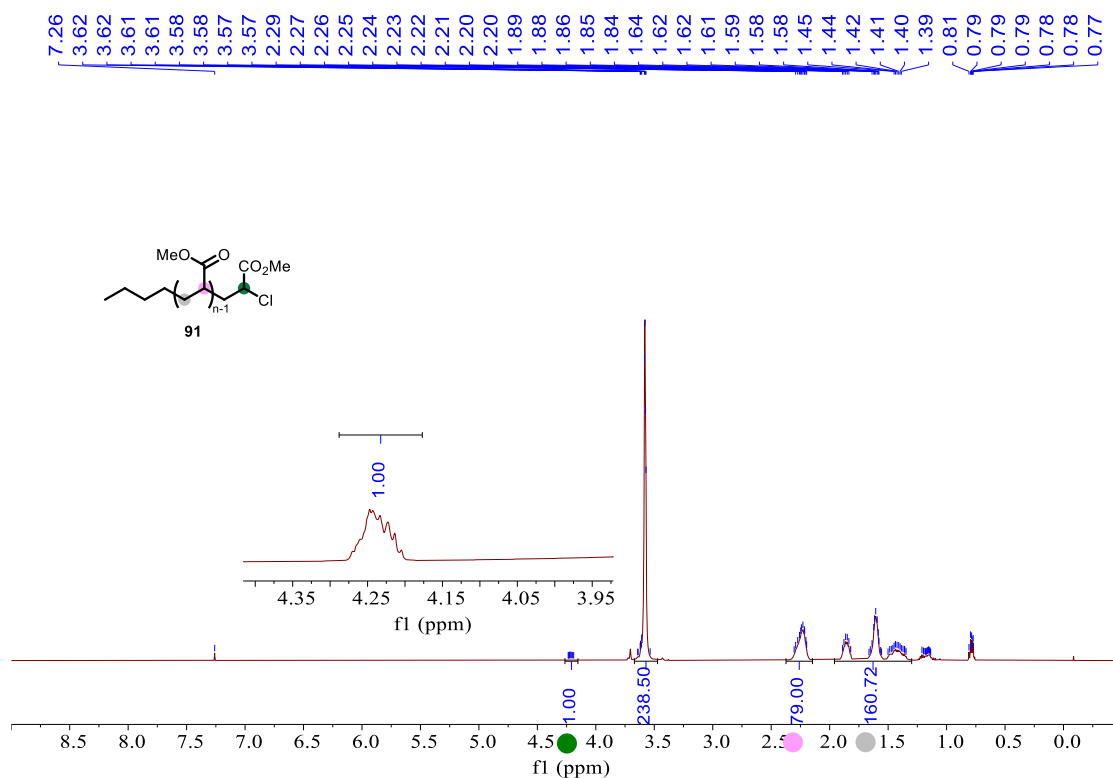
Supplementary Figure 200. ^1H NMR (500 MHz, CDCl_3) spectrum for compound **90**



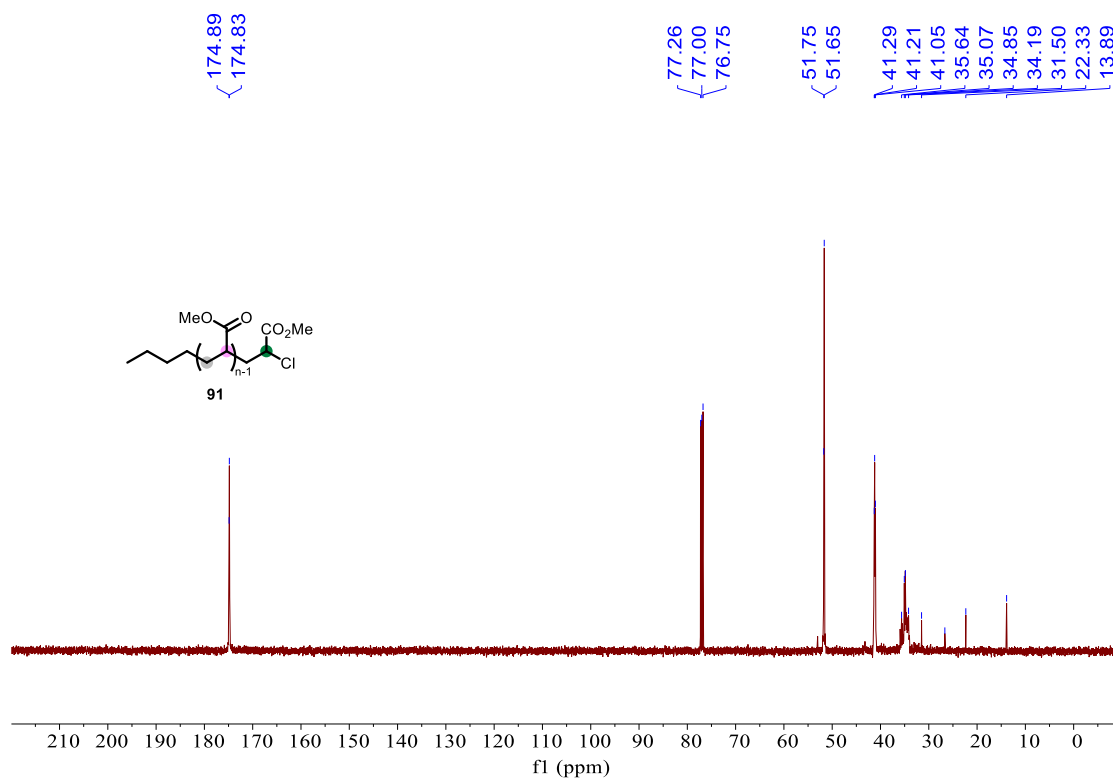
Supplementary Figure 201. ¹⁹F NMR (471 MHz, CDCl₃) spectrum for compound **90**



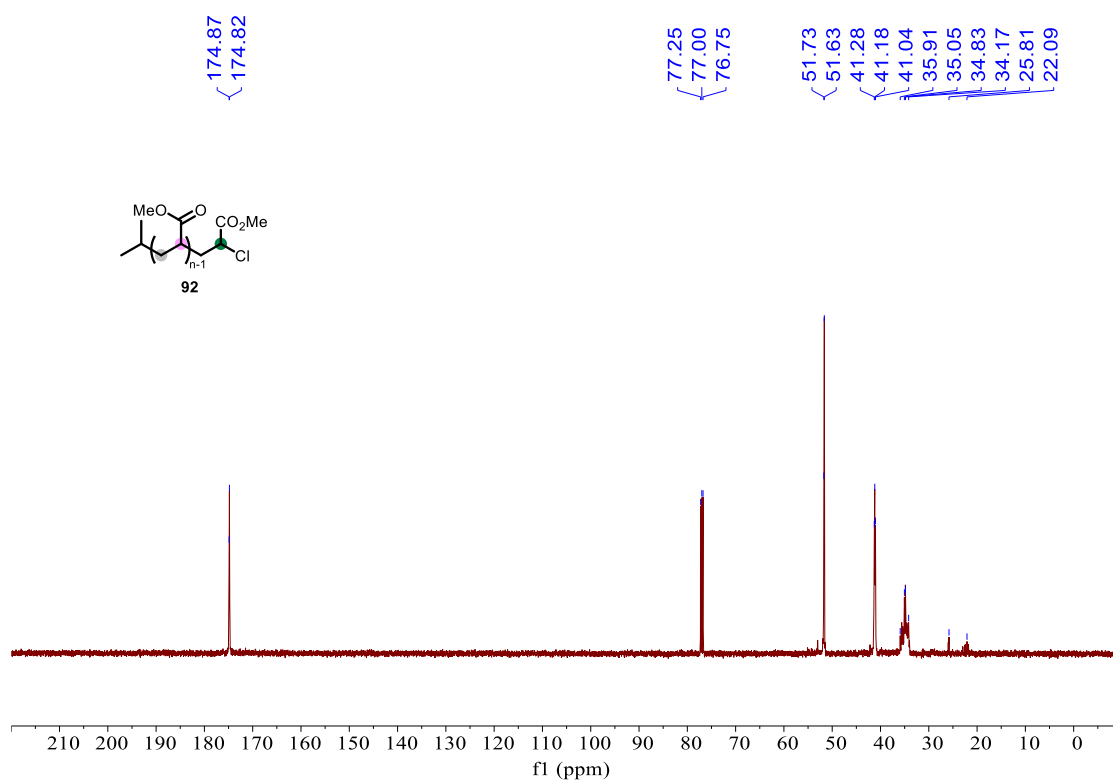
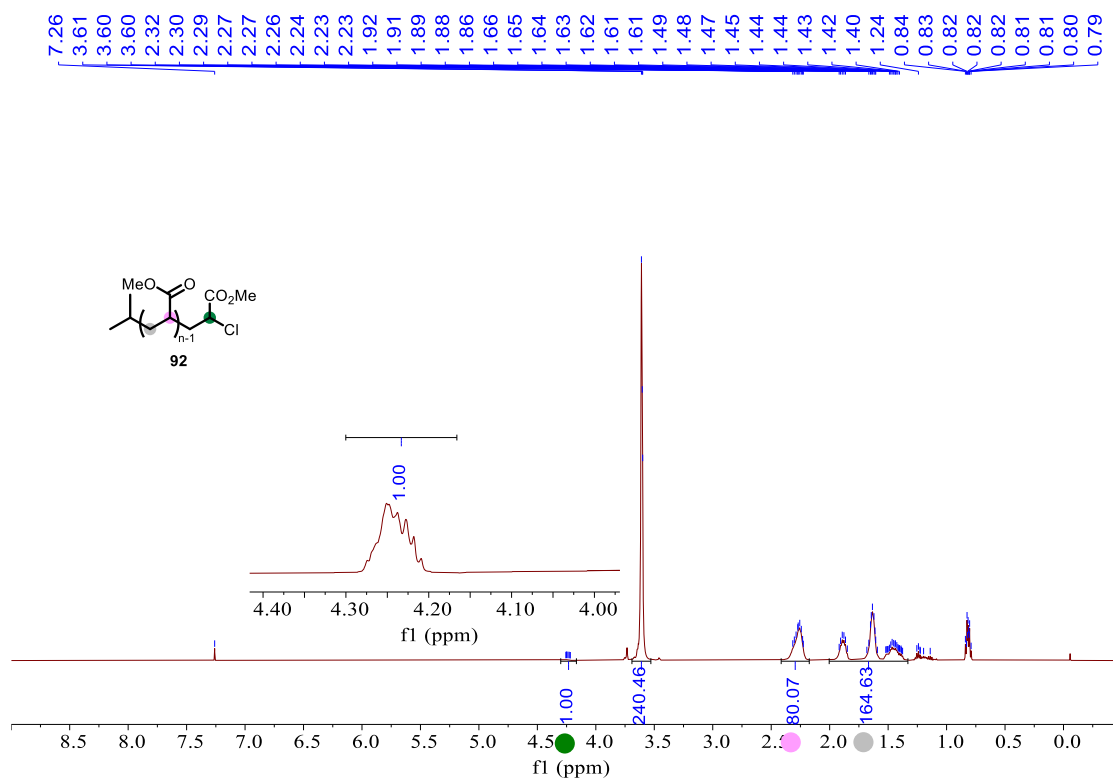
Supplementary Figure 202. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **90**

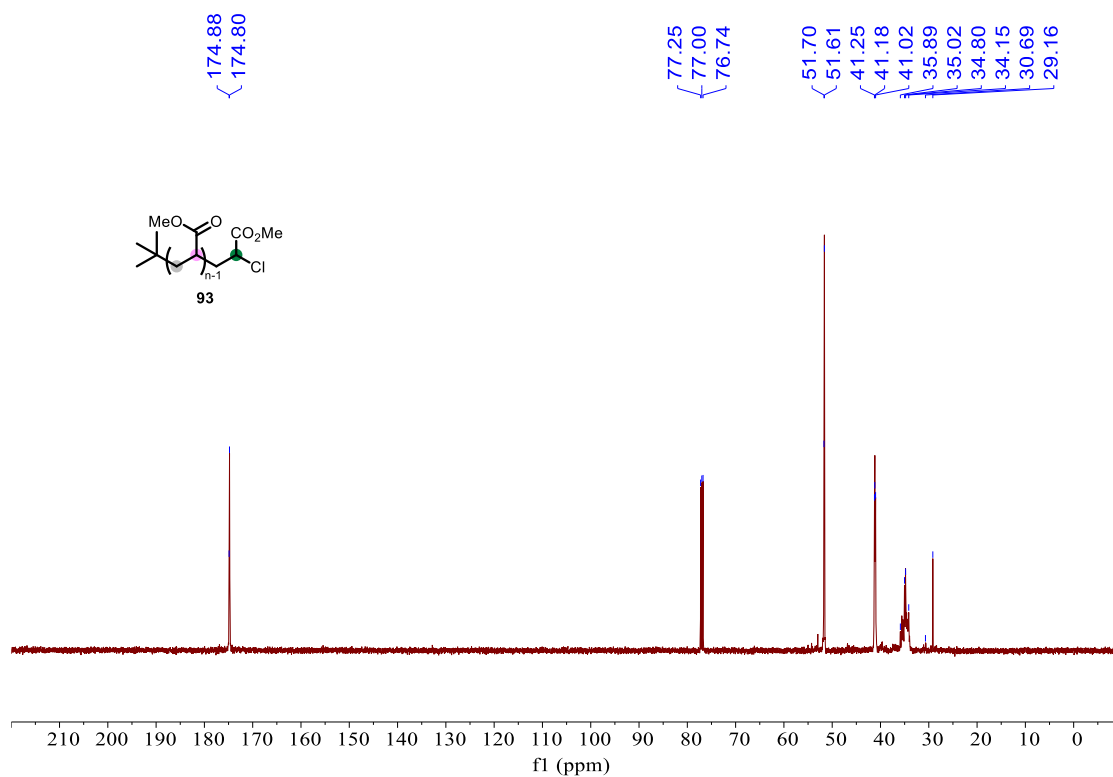
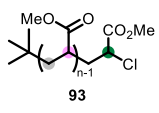


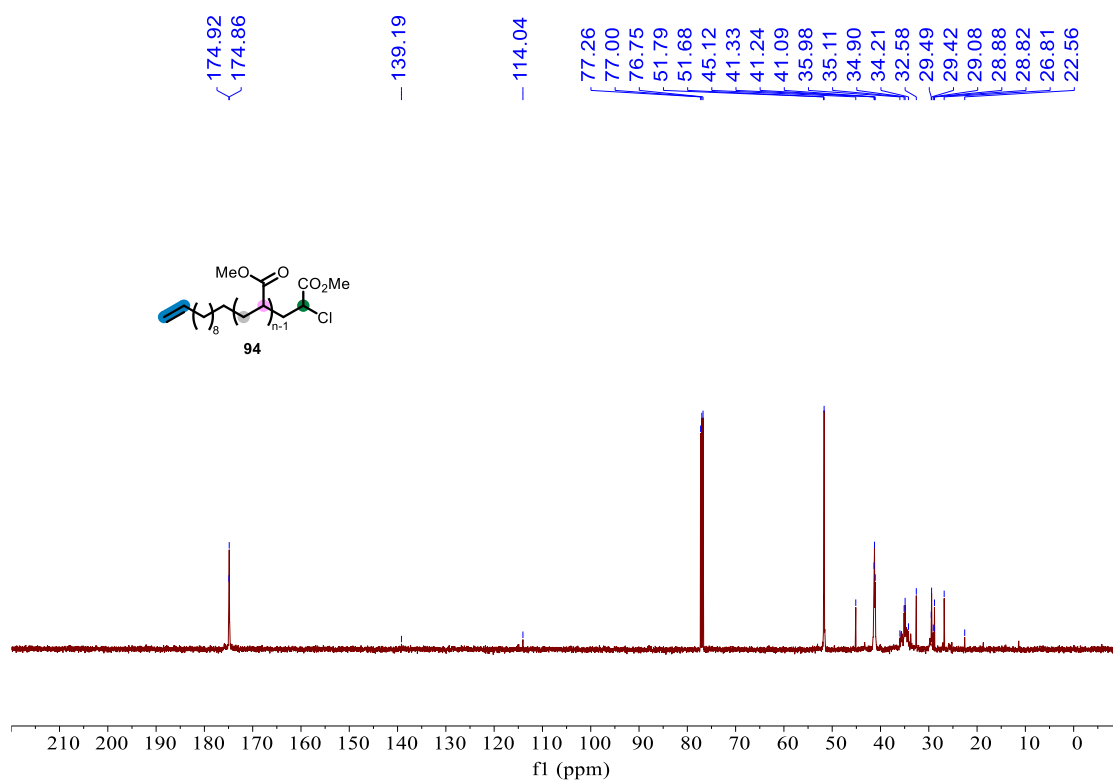
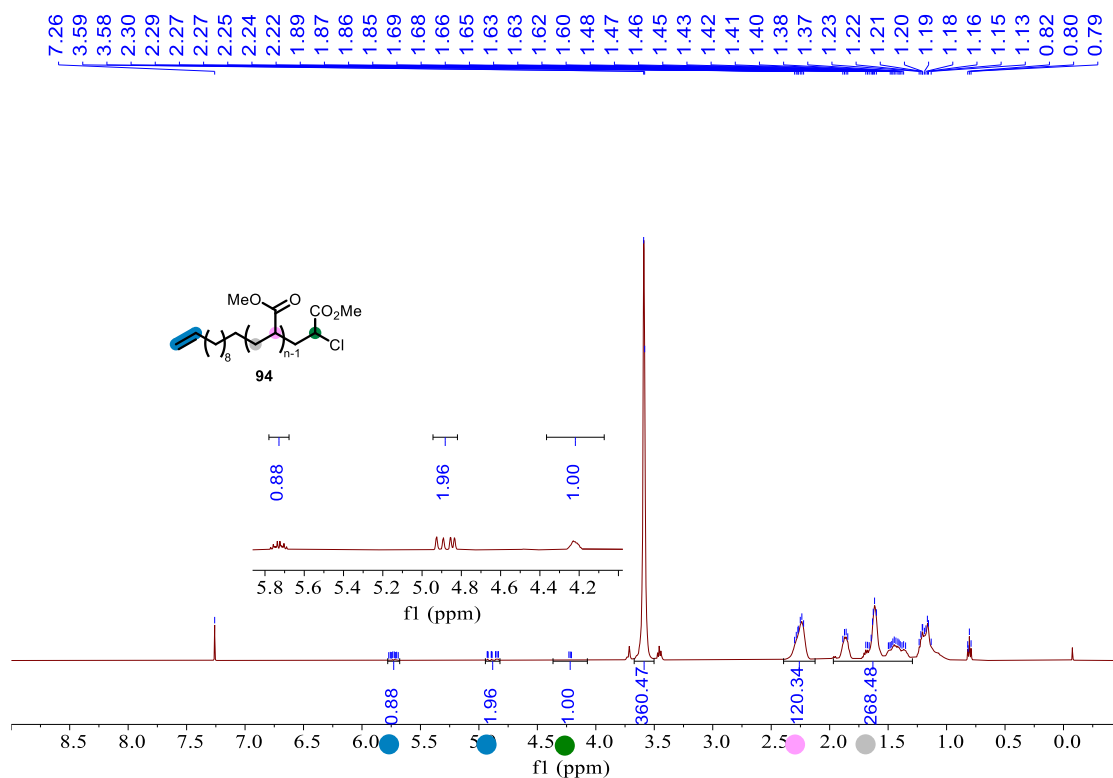
Supplementary Figure 203. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **91**

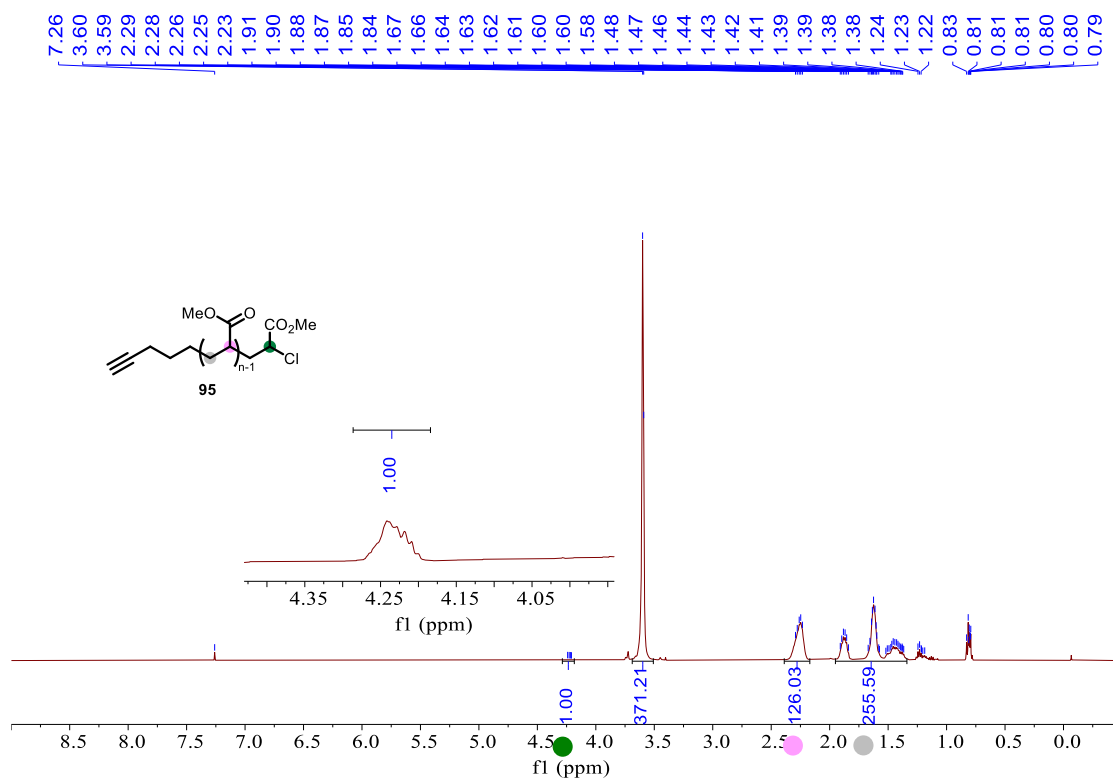


Supplementary Figure 204. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **91**

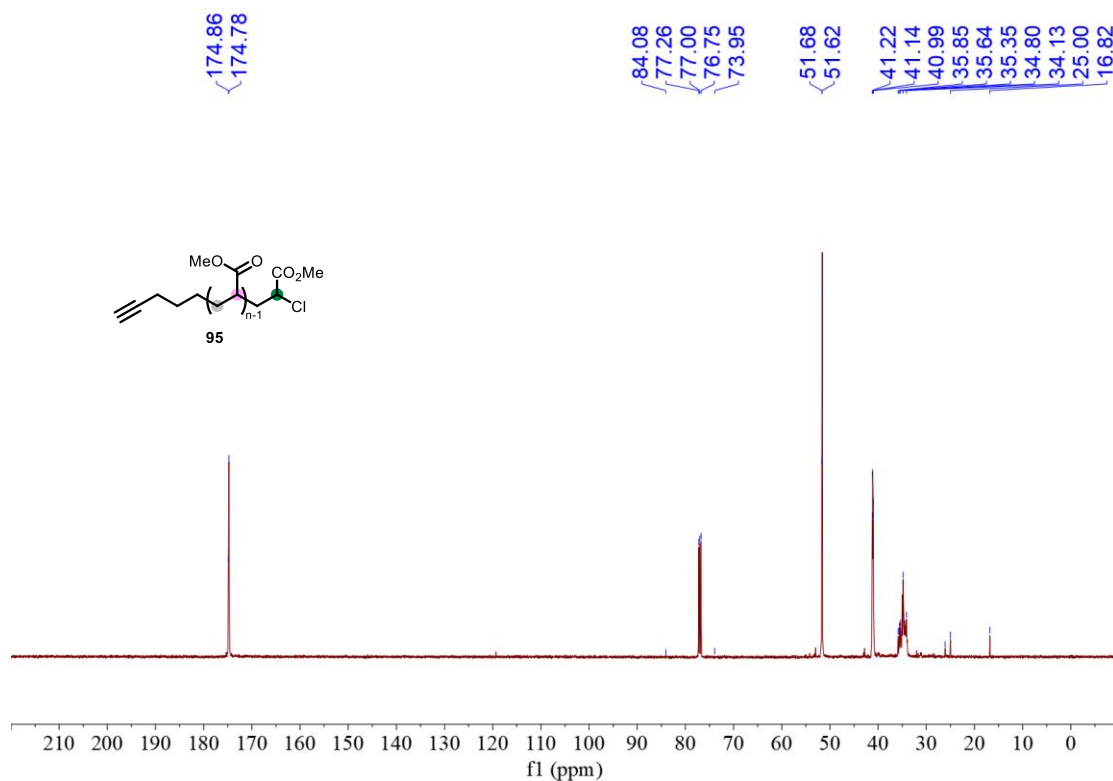




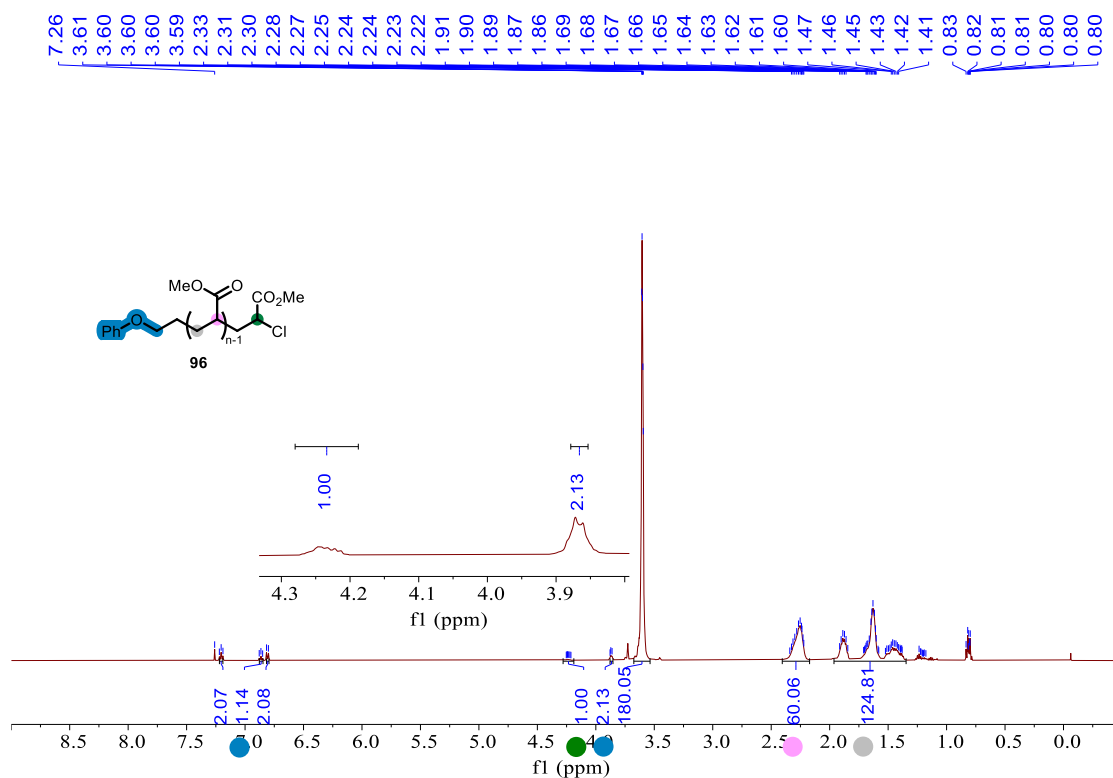




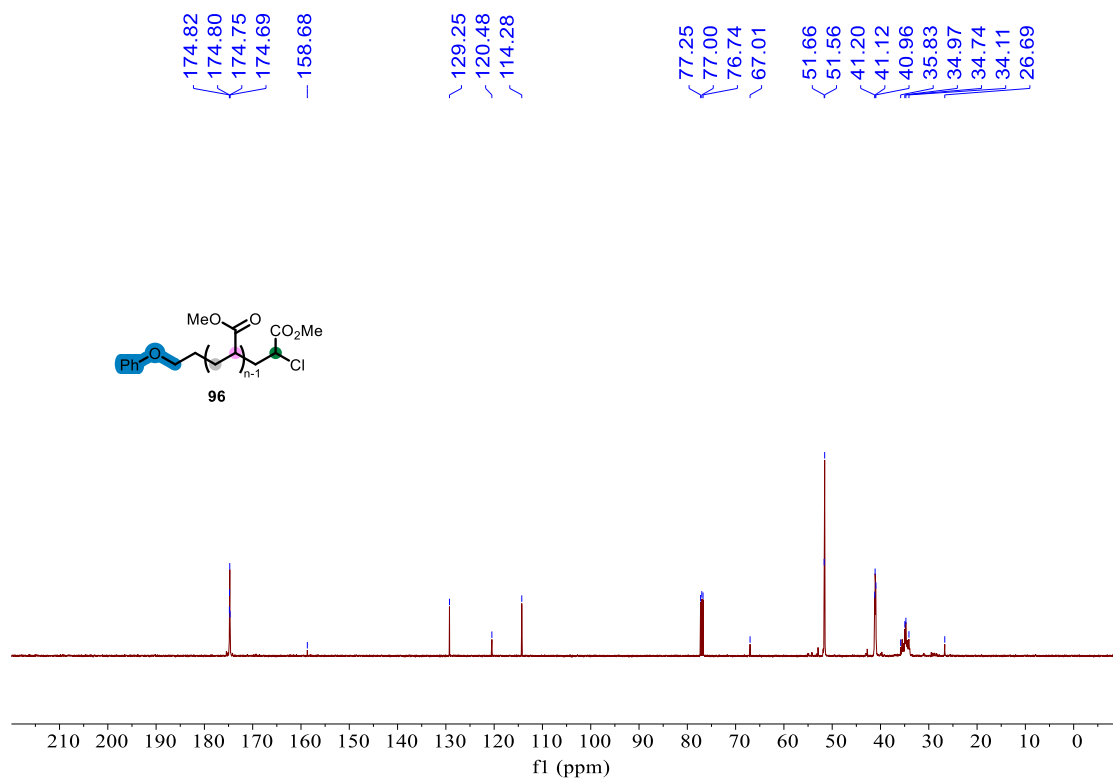
Supplementary Figure 211. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **95**



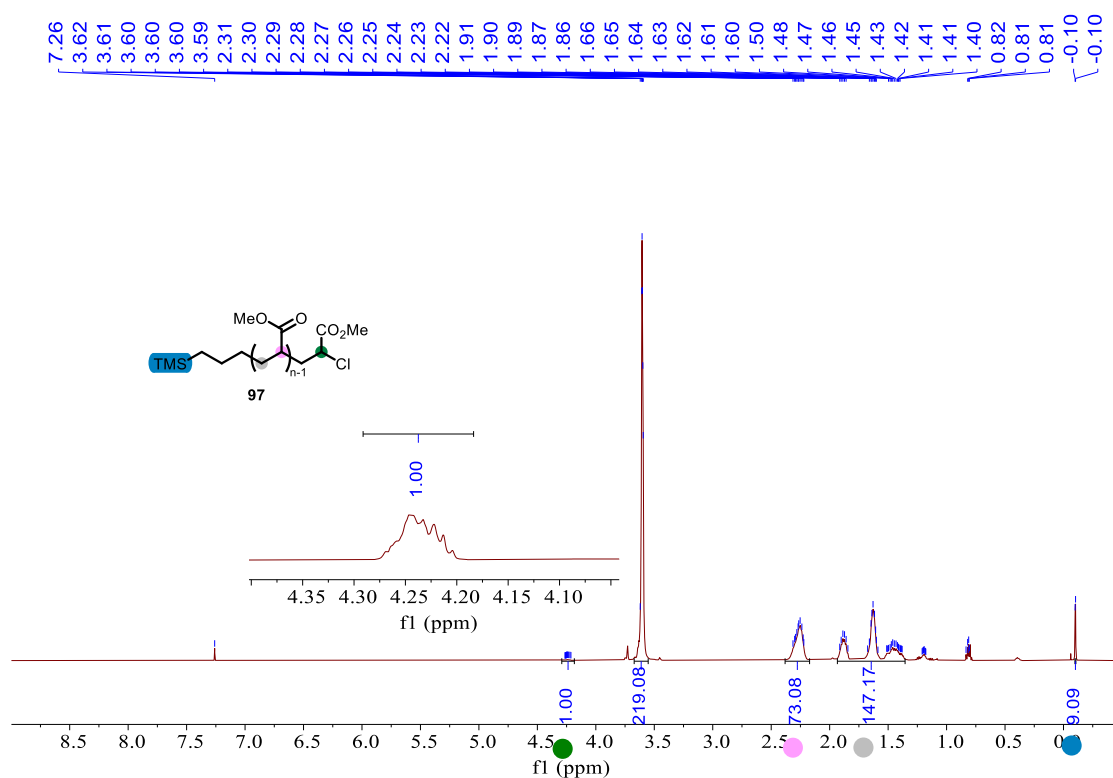
Supplementary Figure 212. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **95**



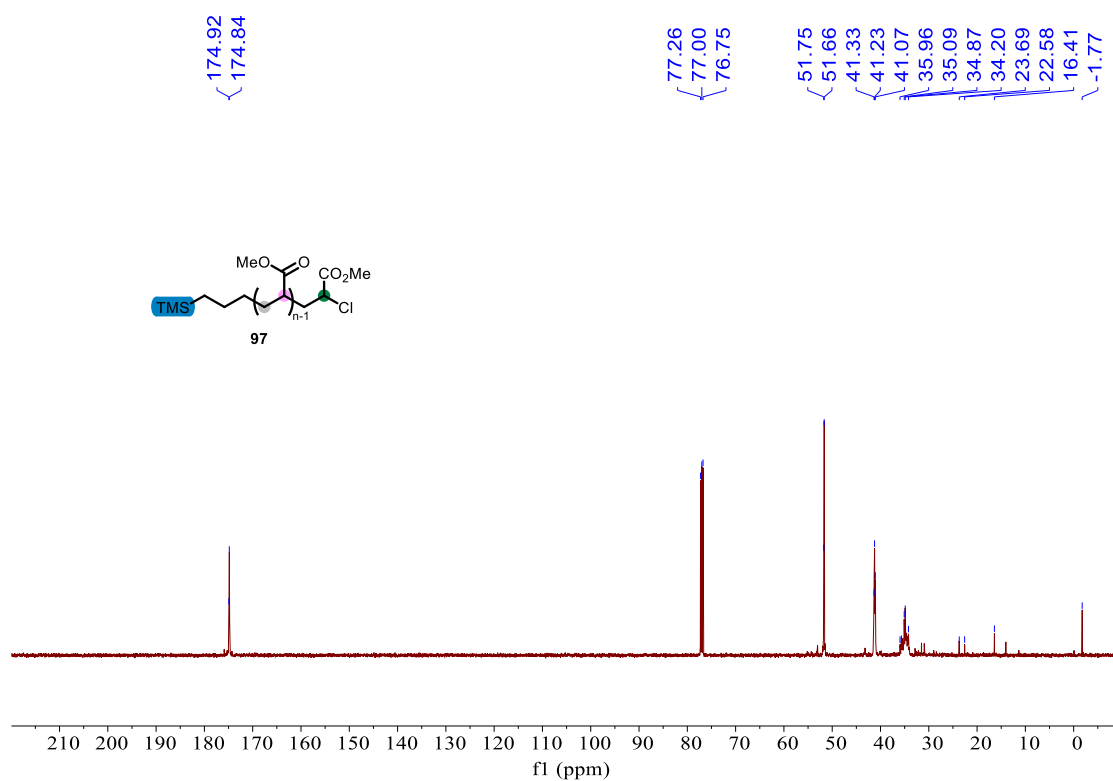
Supplementary Figure 213. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **96**



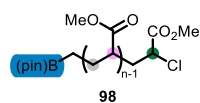
Supplementary Figure 214. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **96**



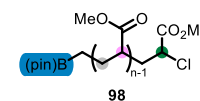
Supplementary Figure 215. ^1H NMR (500 MHz, CDCl_3) spectrum for compound **97**



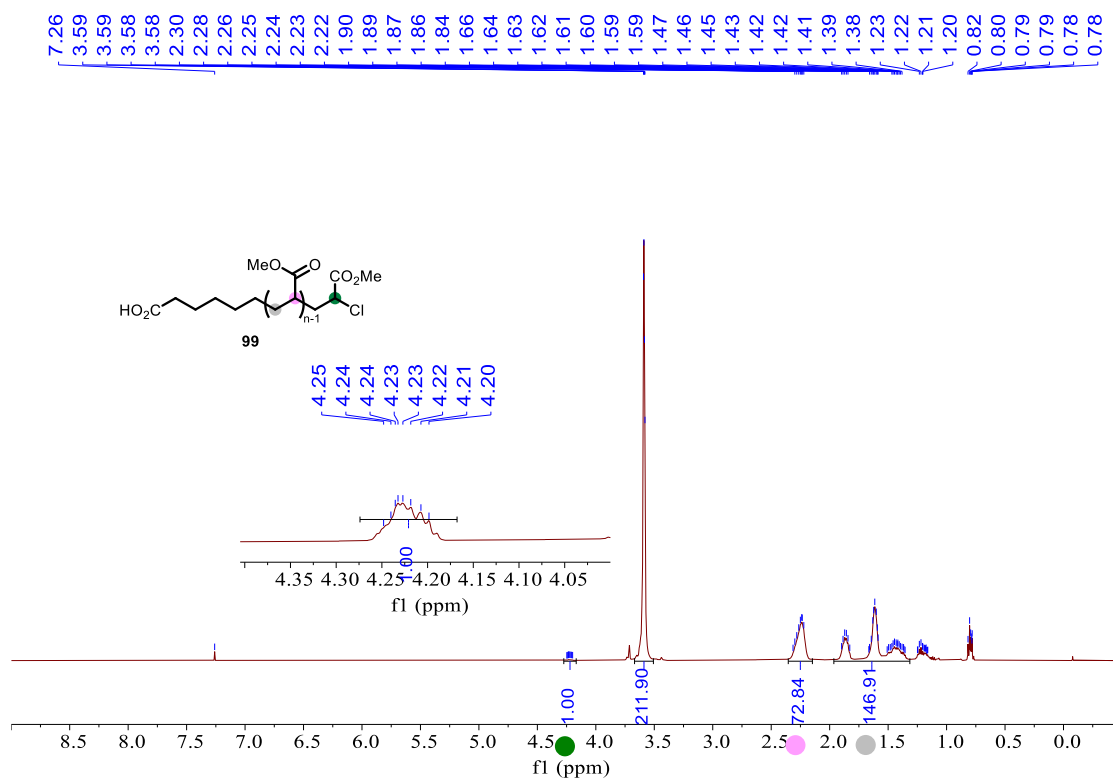
Supplementary Figure 216. ^{13}C NMR (126 MHz, CDCl_3) spectrum for compound **97**



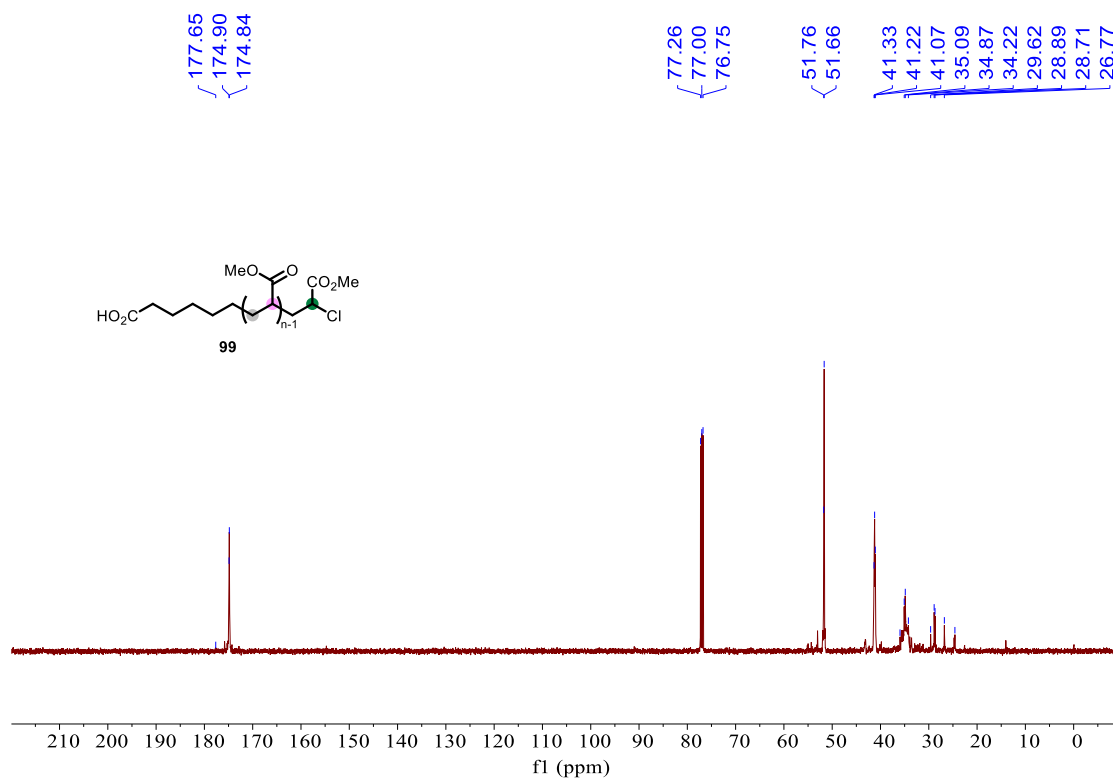




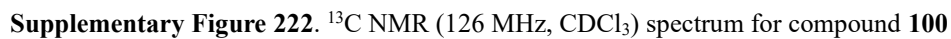
166

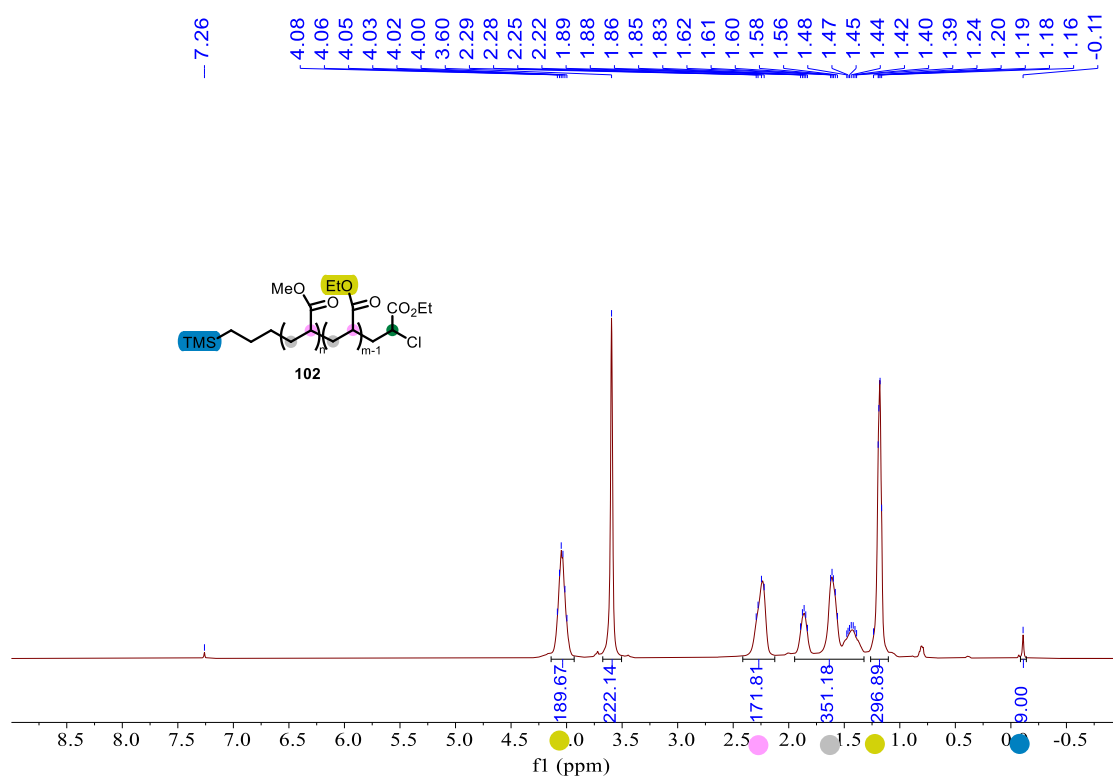


Supplementary Figure 219. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **99**

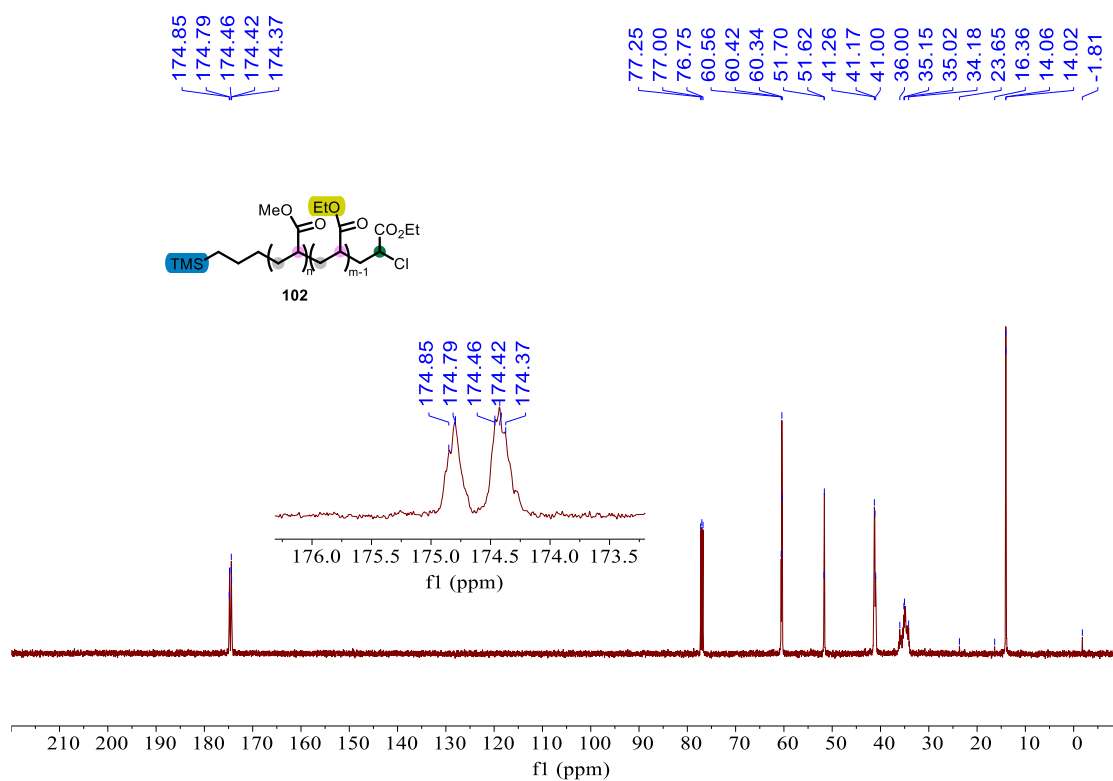


Supplementary Figure 220. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **99**

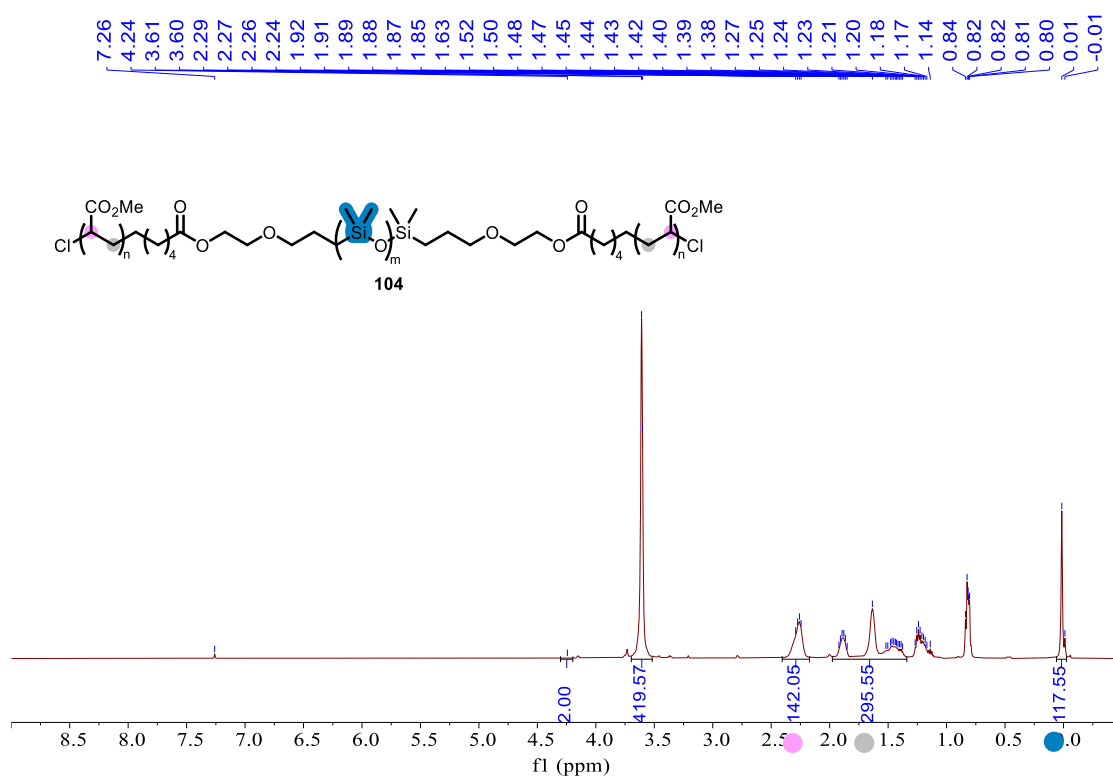




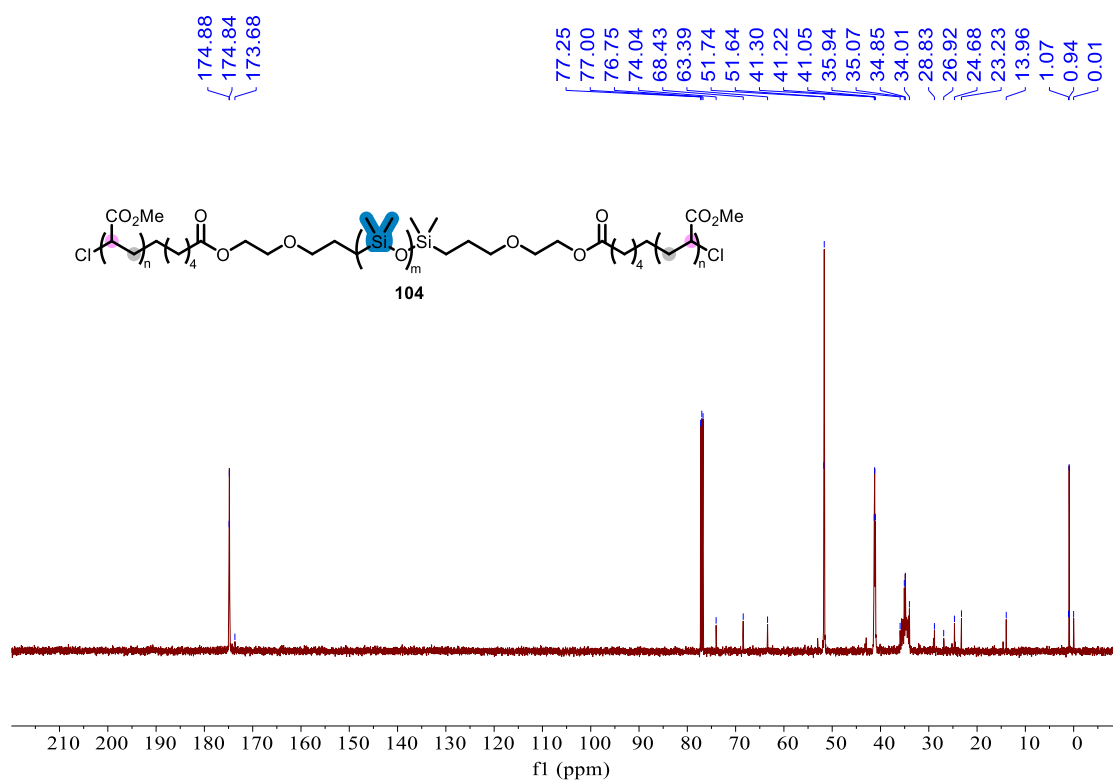
Supplementary Figure 223. ¹H NMR (500 MHz, CDCl₃) spectrum for compound **102**



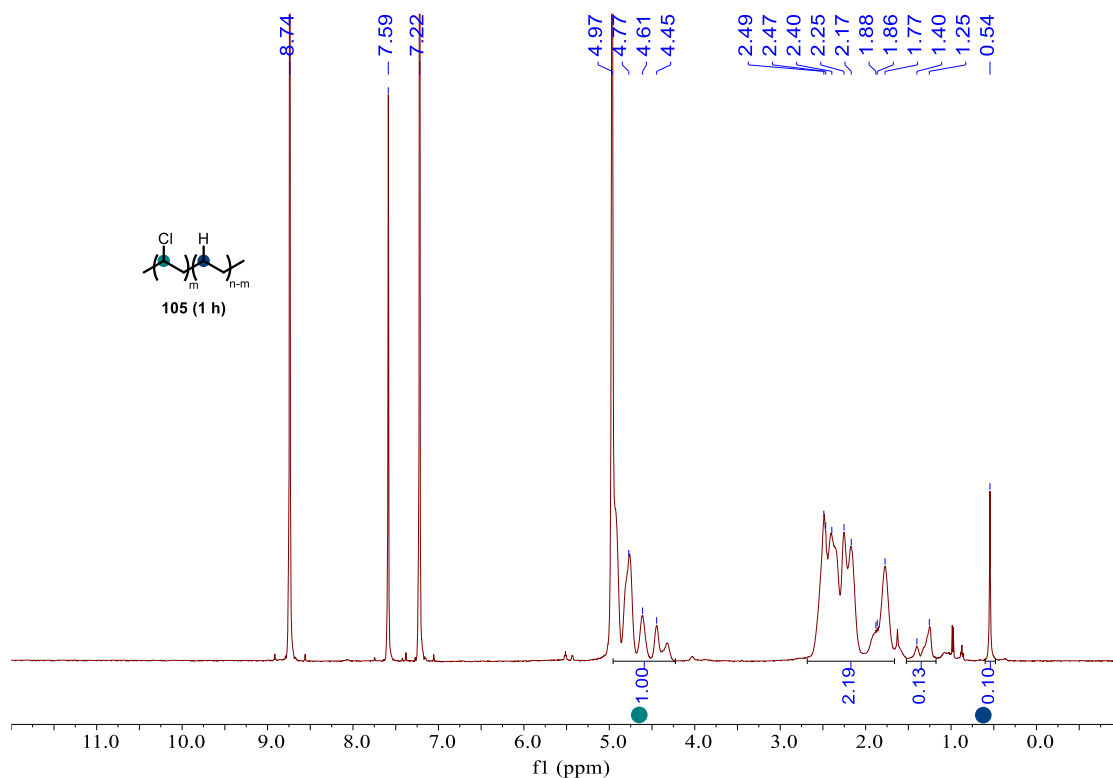
Supplementary Figure 224. ¹³C NMR (126 MHz, CDCl₃) spectrum for compound **102**



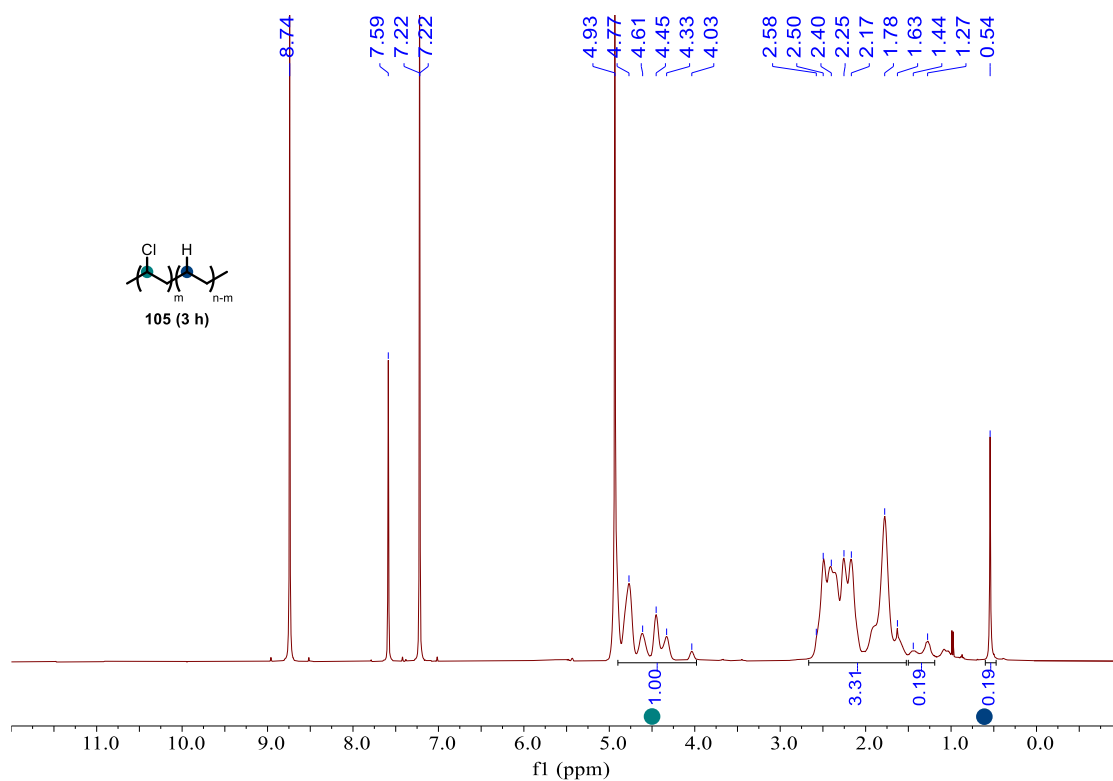
Supplementary Figure 225. ^1H NMR (500 MHz, CDCl_3) spectrum for compound **104**



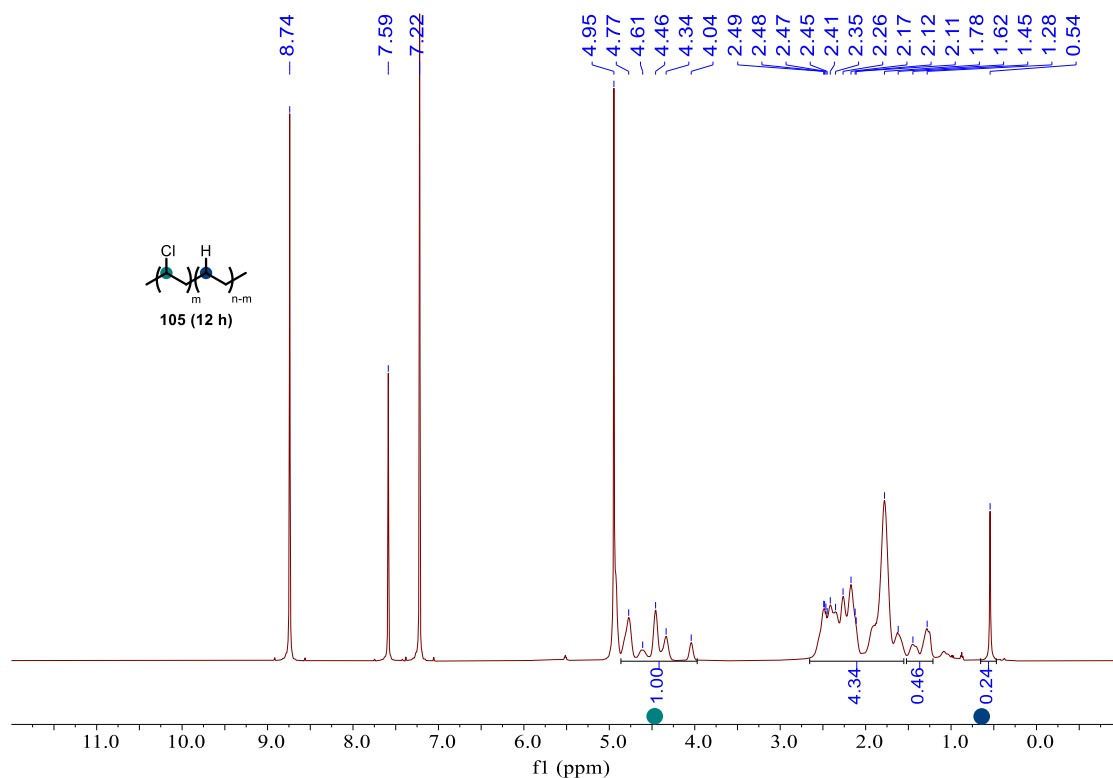
Supplementary Figure 226. ^{13}C NMR (126 MHz, CDCl_3) spectrum for compound **104**



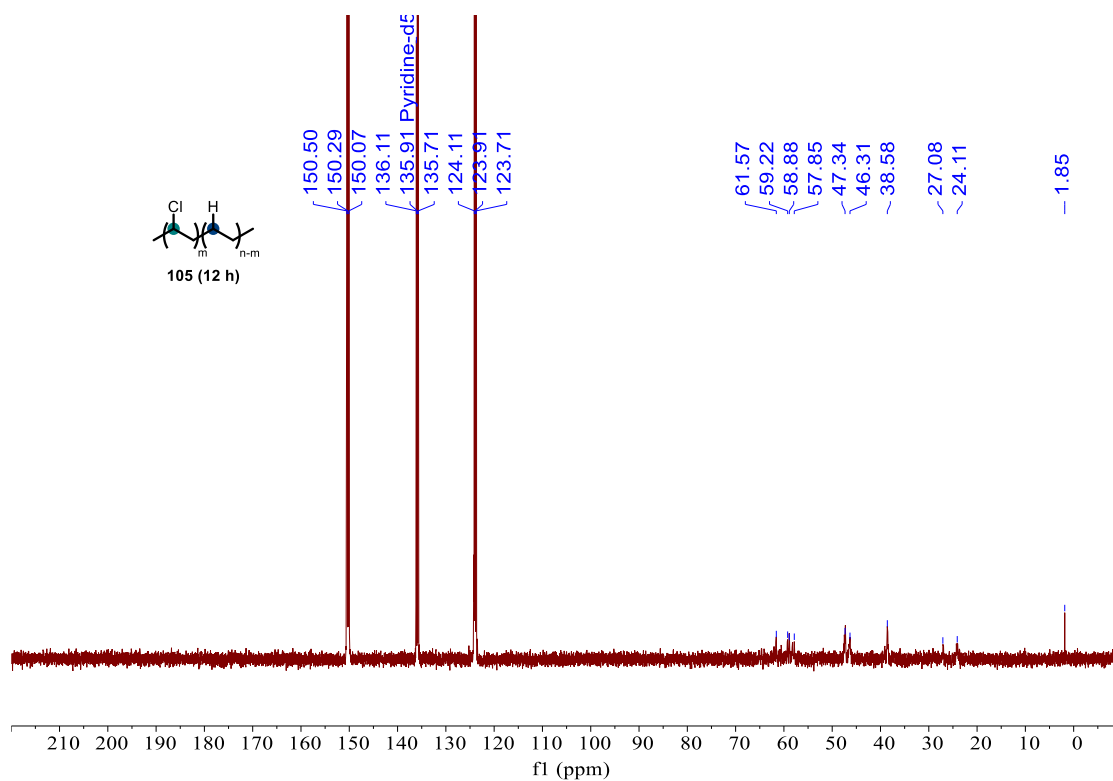
Supplementary Figure 227. ^1H NMR (500 MHz, Pyridine- d_5) spectrum for compound **105 (1 h)**



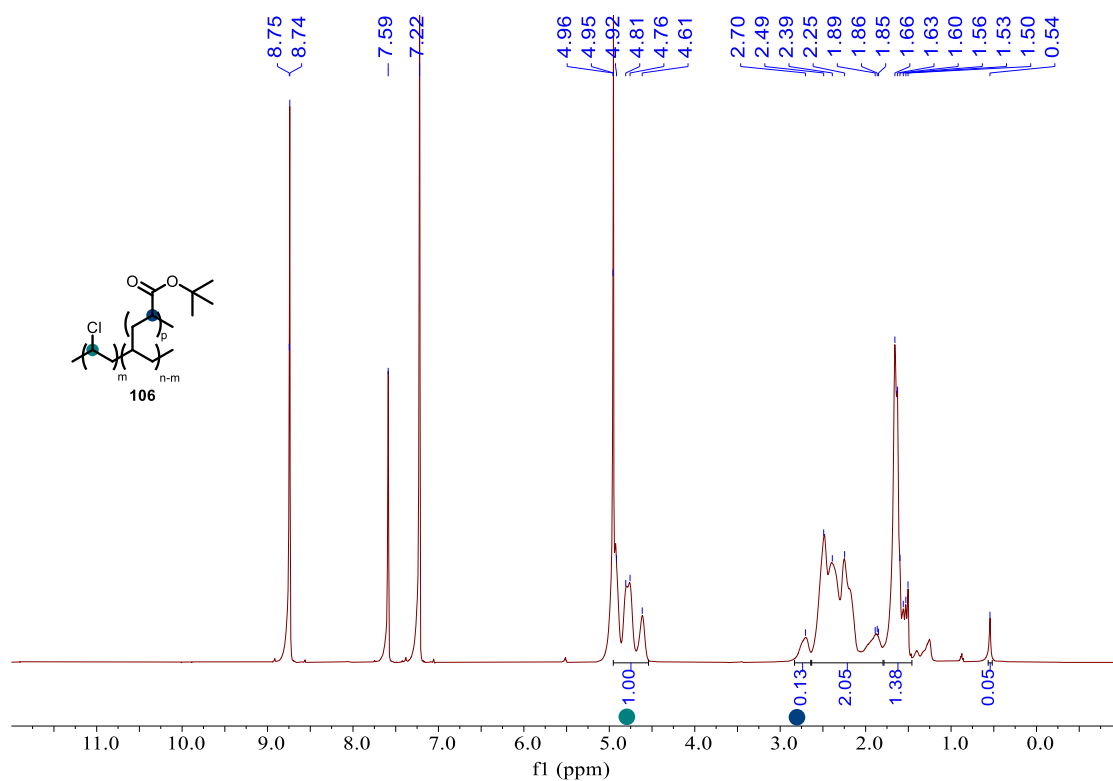
Supplementary Figure 228. ^1H NMR (500 MHz, Pyridine- d_5) spectrum for compound **105 (3 h)**



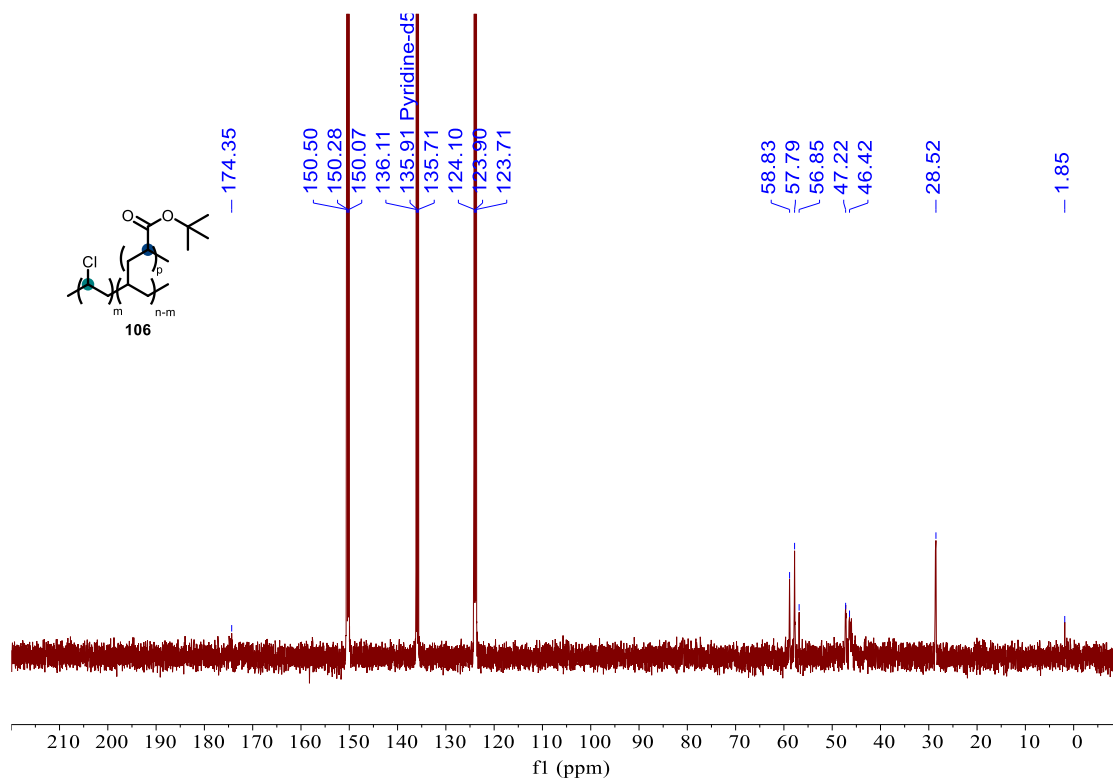
Supplementary Figure 229. ¹H NMR (500 MHz, Pyridine-d₅) spectrum for compound **105 (12 h)**



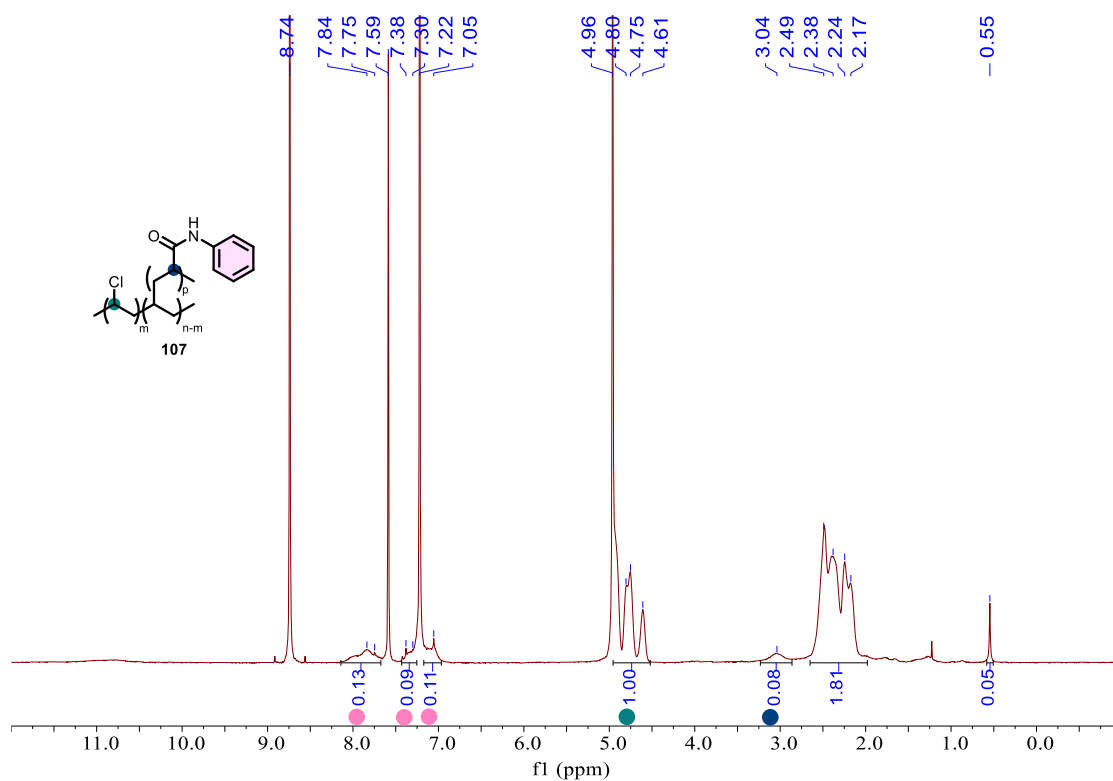
Supplementary Figure 230. ¹³C NMR (126 MHz, Pyridine-d₅) spectrum for compound **105 (12 h)**



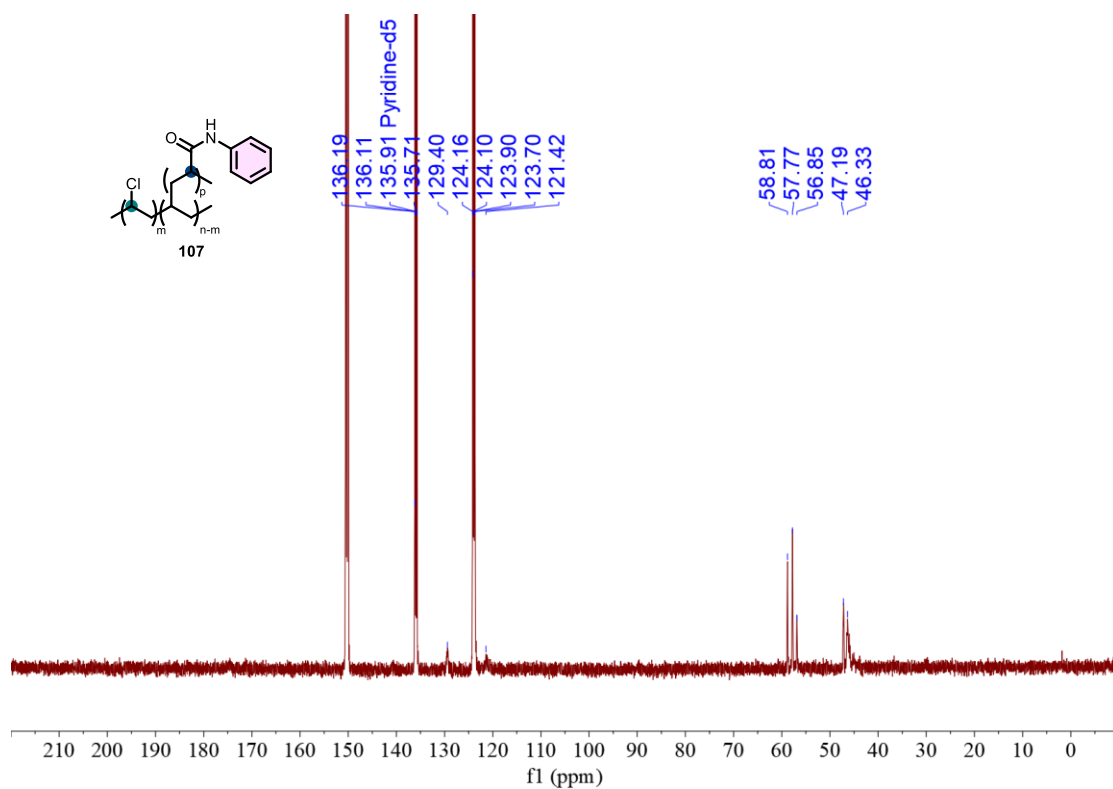
Supplementary Figure 231. ¹H NMR (500 MHz, Pyridine-d₅) spectrum for compound **106**



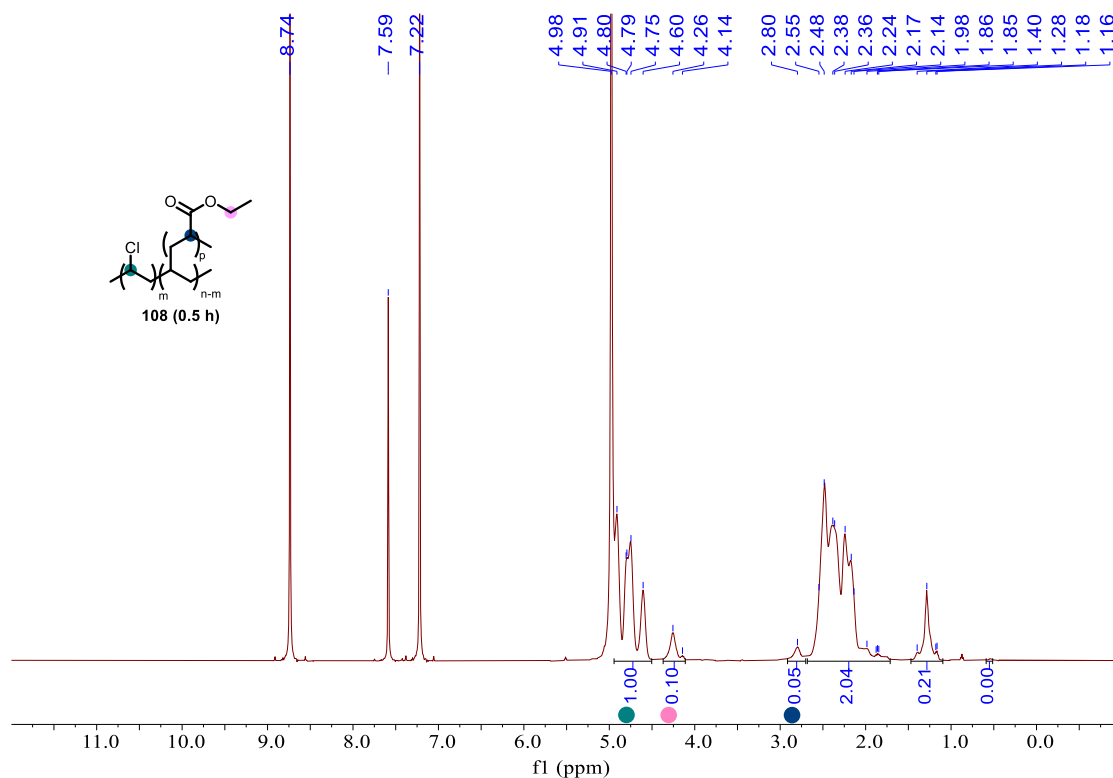
Supplementary Figure 232. ¹³C NMR (126 MHz, Pyridine-d₅) spectrum for compound **106**



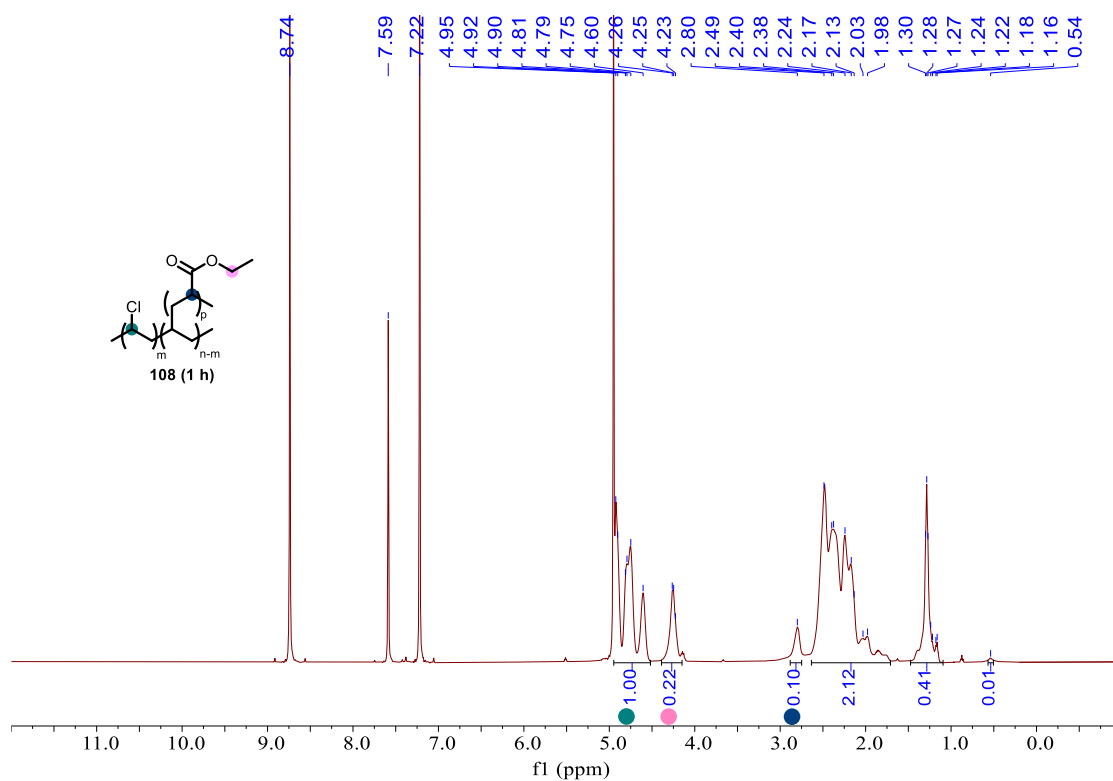
Supplementary Figure 233. ¹H NMR (500 MHz, Pyridine-d₅) spectrum for compound **107**



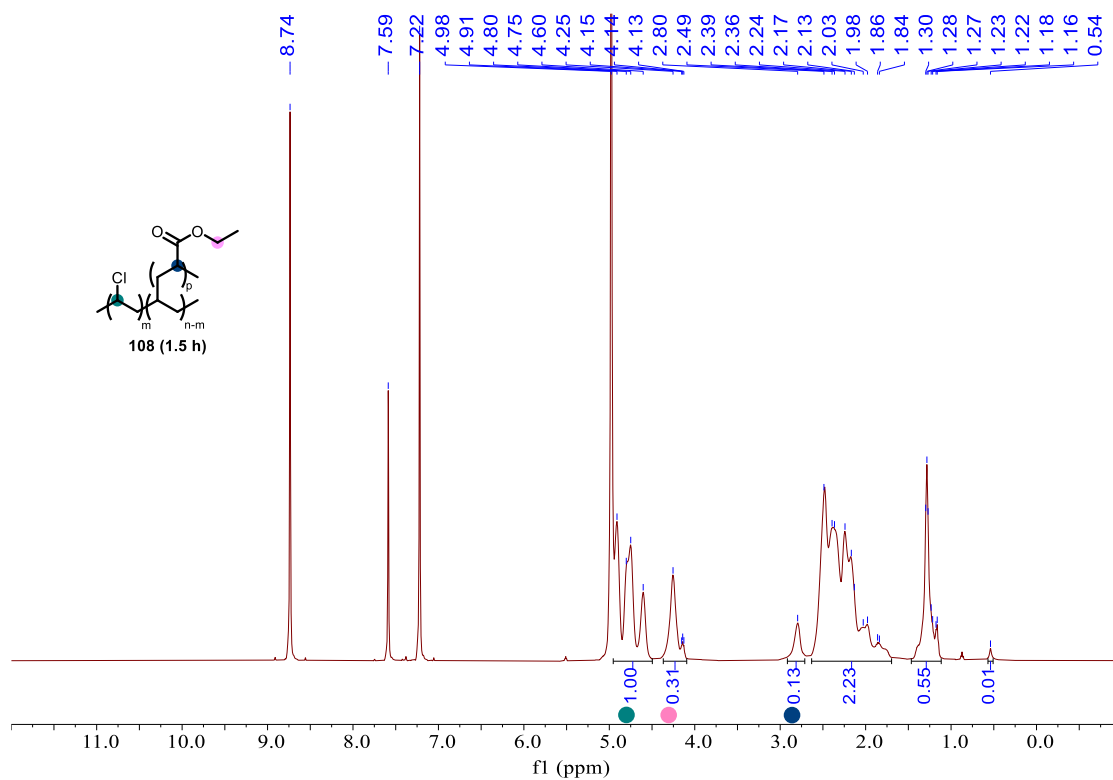
Supplementary Figure 234. ¹³C NMR (126 MHz, Pyridine-d₅) spectrum for compound **107**



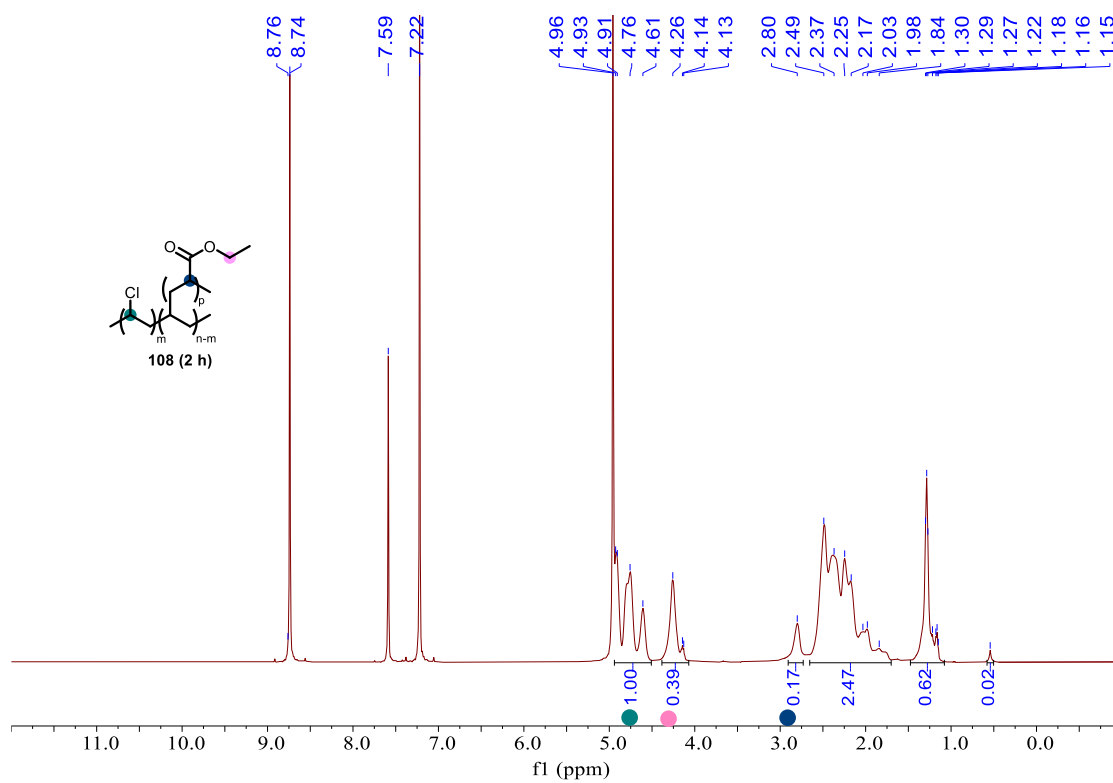
Supplementary Figure 235. ^1H NMR (500 MHz, Pyridine- d_5) spectrum for compound **108 (0.5 h)**



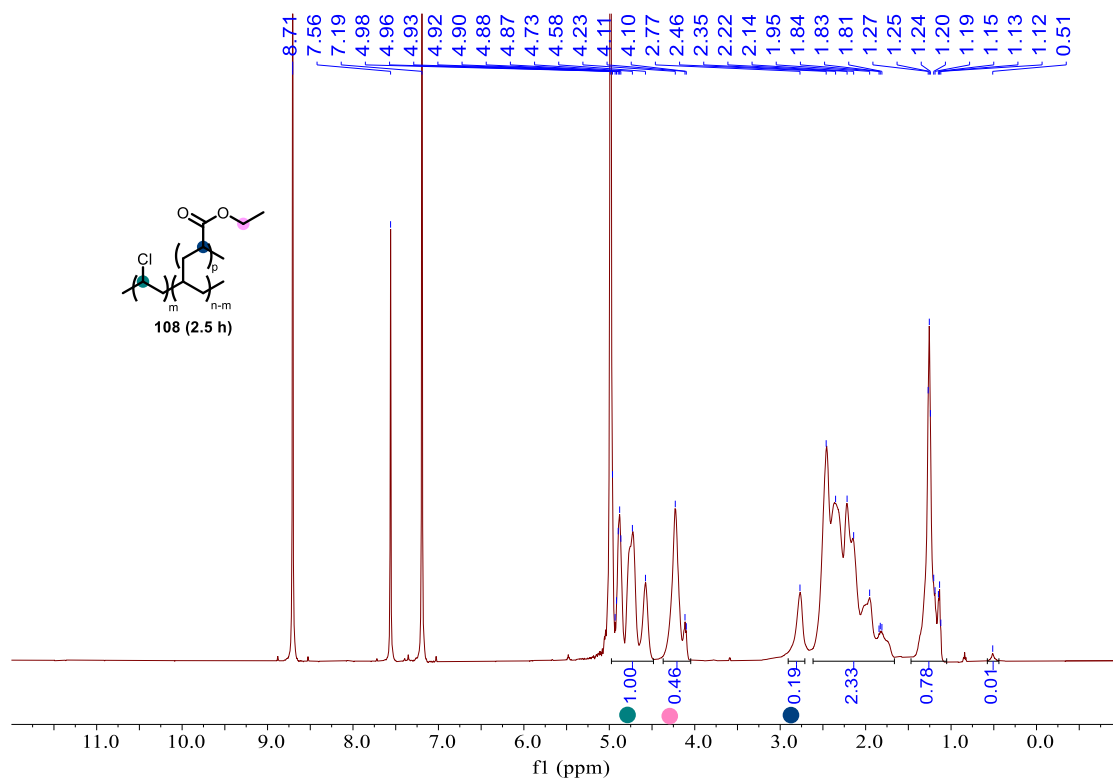
Supplementary Figure 236. ^1H NMR (500 MHz, Pyridine- d_5) spectrum for compound **108 (1 h)**



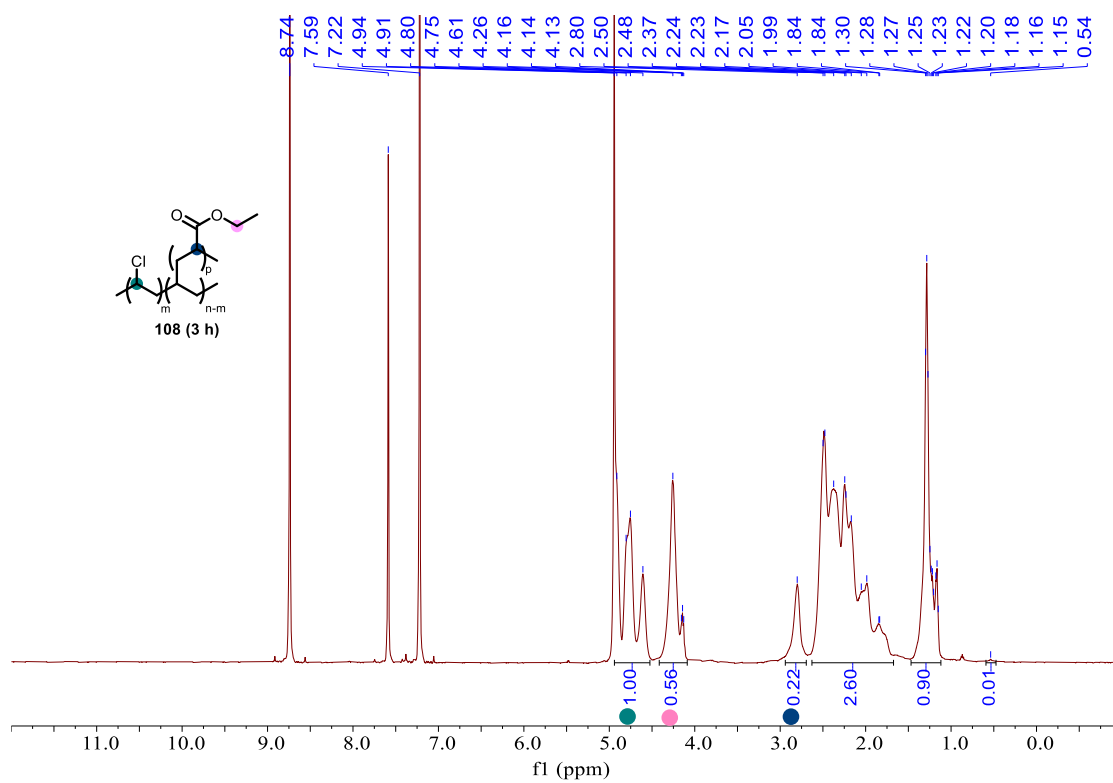
Supplementary Figure 237. ^1H NMR (500 MHz, Pyridine- d_5) spectrum for compound **108** (1.5 h)



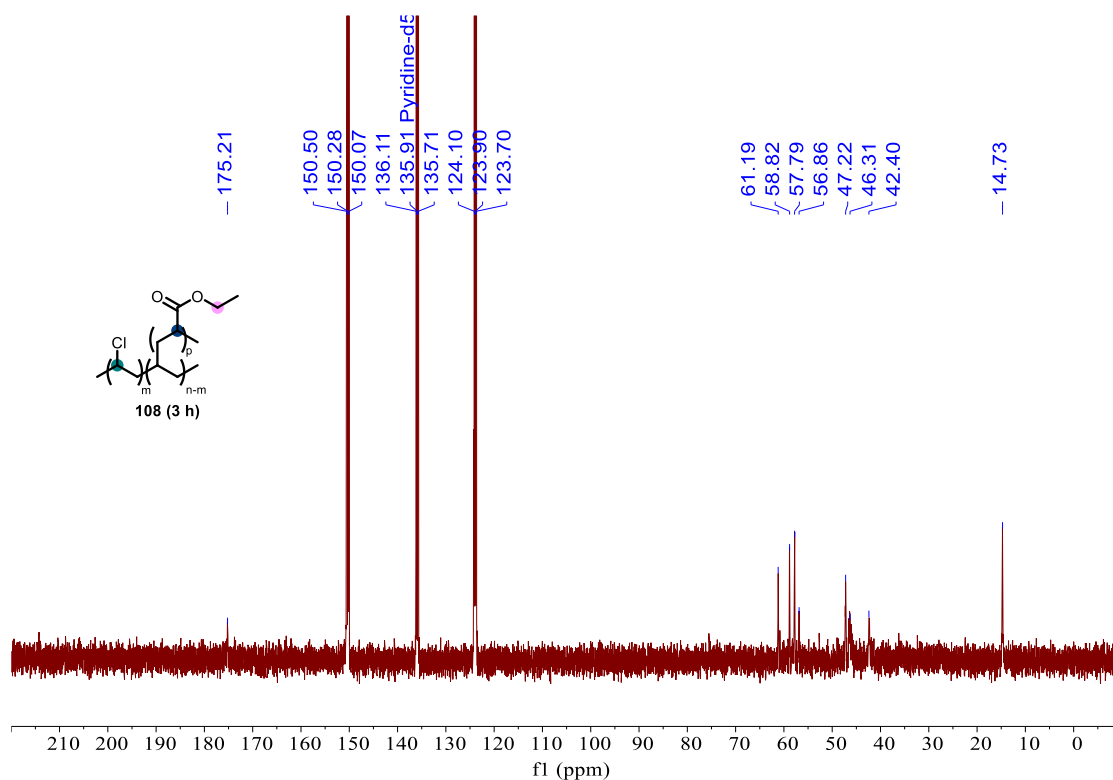
Supplementary Figure 238. ^1H NMR (500 MHz, Pyridine- d_5) spectrum for compound **108** (2 h)



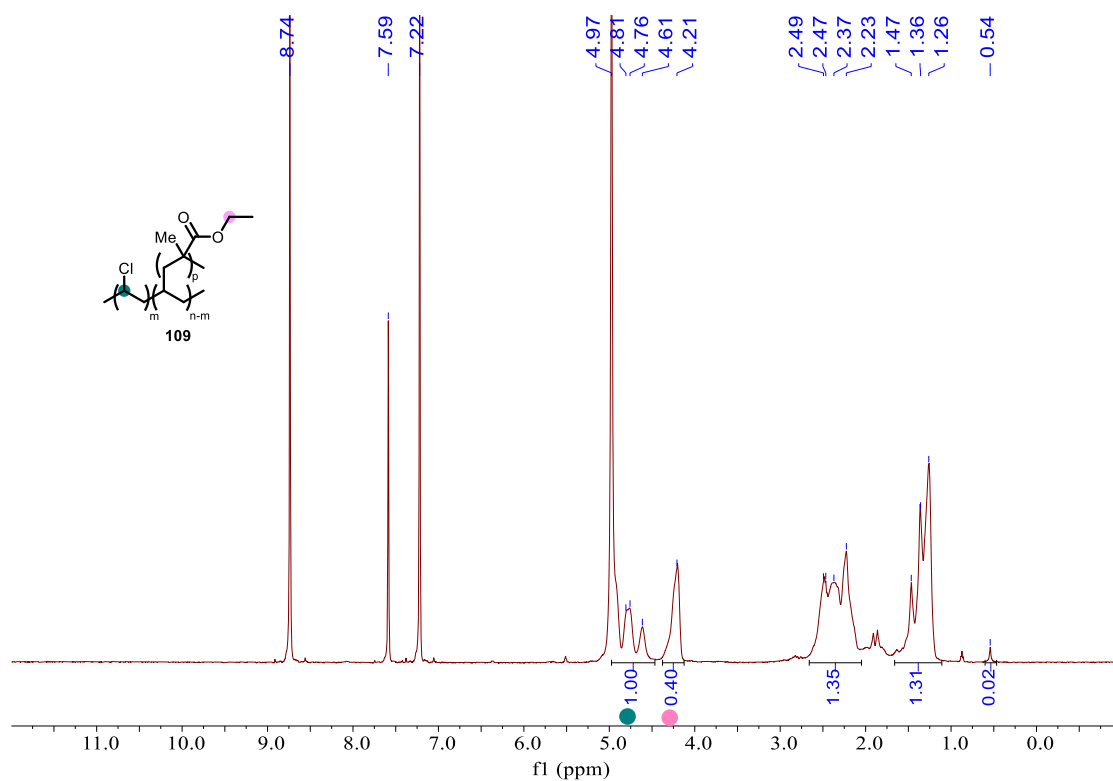
Supplementary Figure 239. ¹H NMR (500 MHz, Pyridine-d₅) spectrum for compound **108** (2.5 h)



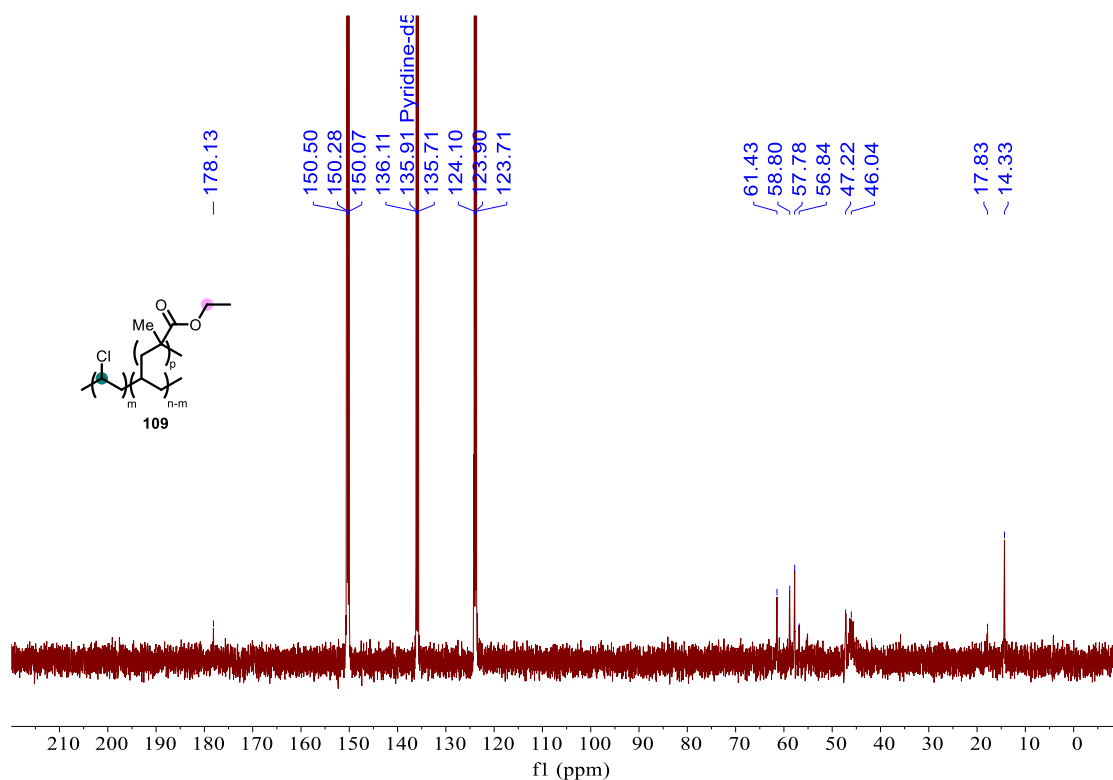
Supplementary Figure 240. ¹H NMR (500 MHz, Pyridine-d₅) spectrum for compound **108** (3 h)



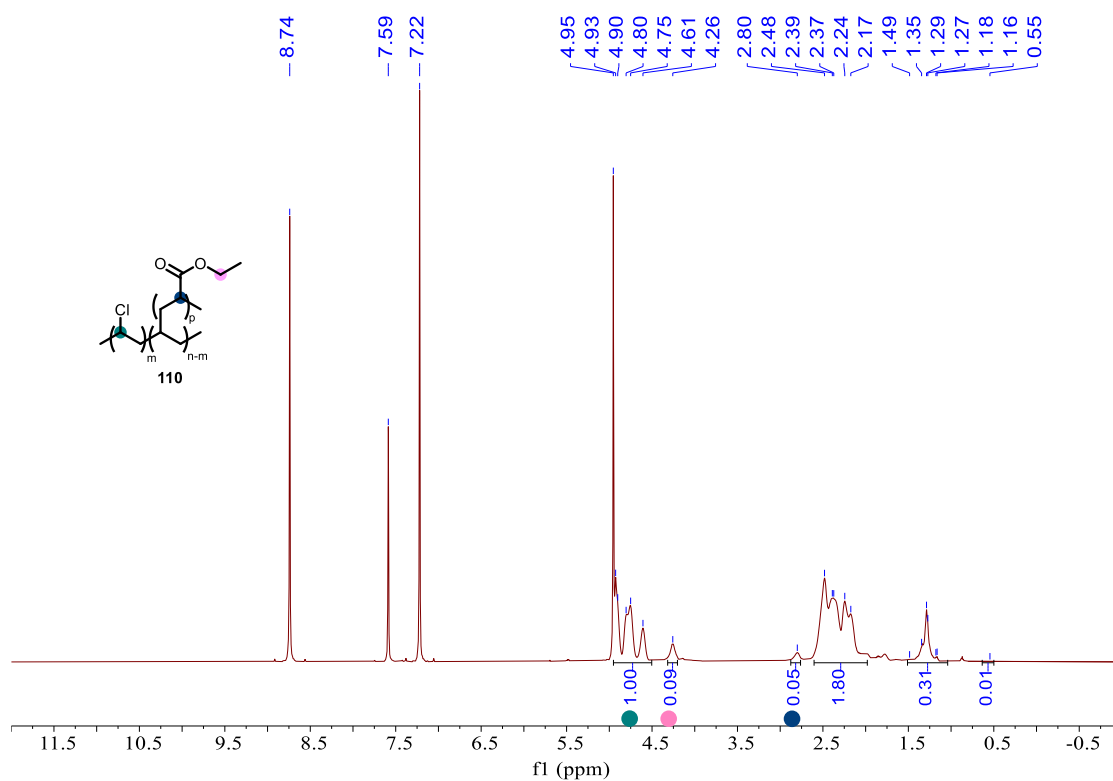
Supplementary Figure 241. ¹³C NMR (126 MHz, Pyridine-d₅) spectrum for compound **108 (3 h)**



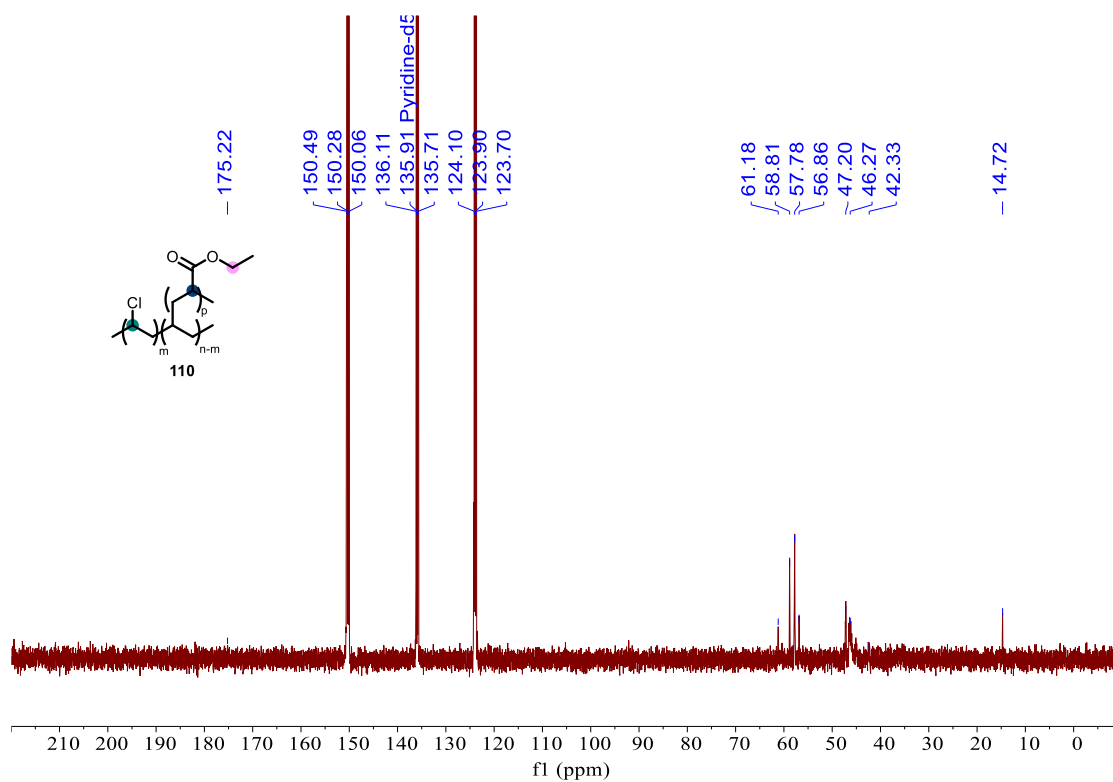
Supplementary Figure 242. ¹H NMR (500 MHz, Pyridine-d₅) spectrum for compound **109**



Supplementary Figure 243. ^{13}C NMR (126 MHz, Pyridine-d₅) spectrum for compound **109**



Supplementary Figure 244. ^1H NMR (500 MHz, Pyridine-d₅) spectrum for compound **110**



Supplementary Figure 245. ¹³C NMR (126 MHz, Pyridine-d₅) spectrum for compound **110**

12. Cartesian Coordinates of All the Optimized Geometries

cat.A1

Cu	22.861071000000	16.102349000000	17.718414000000
Cu	24.307499000000	15.941817000000	19.817420000000
P	24.372481000000	16.561860000000	16.133879000000
P	26.021257000000	16.848433000000	18.705446000000
P	22.793756000000	16.214322000000	21.445140000000
P	21.170918000000	16.907343000000	18.934112000000
C	24.286789000000	15.390349000000	14.667586000000
C	25.215540000000	14.171032000000	14.794040000000
H	26.274657000000	14.495404000000	14.847361000000
H	24.991599000000	13.638840000000	15.746256000000
C	25.029636000000	13.206746000000	13.612659000000
H	25.693154000000	12.326359000000	13.743233000000
H	25.358241000000	13.715006000000	12.678418000000
C	23.569619000000	12.764651000000	13.457902000000
H	23.459693000000	12.094057000000	12.580054000000
H	23.272123000000	12.169494000000	14.350579000000
C	22.638541000000	13.975616000000	13.329479000000
H	21.577993000000	13.651877000000	13.269881000000
H	22.858569000000	14.513227000000	12.379784000000
C	22.817047000000	14.941001000000	14.507457000000
H	22.504643000000	14.437749000000	15.451395000000
H	22.150492000000	15.819942000000	14.393925000000
C	24.341621000000	18.278307000000	15.398431000000
C	23.019798000000	18.524317000000	14.649227000000
H	22.973729000000	17.866610000000	13.753541000000
H	22.160907000000	18.246246000000	15.295686000000
C	22.912256000000	19.988623000000	14.202420000000
H	22.853366000000	20.639438000000	15.104331000000
H	21.967290000000	20.142808000000	13.640632000000
C	24.119264000000	20.400993000000	13.350069000000
H	24.106057000000	19.820669000000	12.400052000000
H	24.045973000000	21.471626000000	13.065876000000
C	25.440606000000	20.132643000000	14.081145000000
H	25.508180000000	20.793326000000	14.975277000000
H	26.304393000000	20.391468000000	13.433659000000
C	25.553939000000	18.670299000000	14.541244000000
H	26.497426000000	18.529977000000	15.107600000000
H	25.610969000000	18.002483000000	13.653068000000
C	26.111180000000	18.712540000000	18.645738000000
C	27.480626000000	19.280901000000	18.241515000000
H	28.227608000000	19.036005000000	19.028120000000

H	27.840030000000	18.808302000000	17.303224000000
C	27.405796000000	20.806426000000	18.074362000000
H	26.734925000000	21.041912000000	17.217253000000
H	28.407124000000	21.207585000000	17.812312000000
C	26.867130000000	21.483953000000	19.341059000000
H	27.590391000000	21.327650000000	20.173053000000
H	26.793150000000	22.581346000000	19.190478000000
C	25.503921000000	20.906741000000	19.743550000000
H	24.758772000000	21.149587000000	18.953839000000
H	25.136789000000	21.378708000000	20.679534000000
C	25.564119000000	19.383774000000	19.917387000000
H	26.214735000000	19.140941000000	20.784643000000
H	24.560403000000	18.970627000000	20.149928000000
C	27.632928000000	16.202823000000	19.397353000000
C	27.728688000000	16.590729000000	20.887225000000
H	27.751211000000	17.693525000000	21.000553000000
H	26.801080000000	16.240911000000	21.397089000000
C	28.951708000000	15.965686000000	21.571173000000
H	28.956516000000	16.242622000000	22.646281000000
H	29.877861000000	16.397703000000	21.130040000000
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H	29.877472000000	14.010705000000	21.879346000000
H	28.095432000000	14.003416000000	21.929164000000
C	28.913521000000	14.060650000000	19.919223000000
H	28.898667000000	12.957463000000	19.797092000000
H	29.835194000000	14.423574000000	19.411642000000
C	27.686924000000	14.670839000000	19.228072000000
H	26.759042000000	14.231774000000	19.662815000000
H	27.687861000000	14.396318000000	18.153391000000
C	22.855416000000	17.803567000000	22.422646000000
C	24.189303000000	17.947418000000	23.176644000000
H	25.039972000000	17.736552000000	22.495036000000
H	24.235043000000	17.193278000000	23.992876000000
C	24.313817000000	19.350821000000	23.786198000000
H	25.269772000000	19.438037000000	24.343701000000
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C	23.124538000000	19.667672000000	24.702272000000
H	23.155325000000	18.986788000000	25.582705000000
H	23.207099000000	20.700384000000	25.101303000000
C	21.787345000000	19.483720000000	23.973405000000
H	21.703336000000	20.242824000000	23.162934000000
H	20.937832000000	19.665926000000	24.664348000000
C	21.662373000000	18.084629000000	23.348152000000
H	21.629526000000	17.317464000000	24.153532000000

H	20.704661000000	18.007623000000	22.793574000000
C	22.849379000000	14.822894000000	22.704670000000
C	21.963310000000	13.625560000000	22.316549000000
H	22.232798000000	13.296718000000	21.287232000000
H	20.896591000000	13.927731000000	22.290211000000
C	22.139089000000	12.453521000000	23.293387000000
H	21.760668000000	12.757158000000	24.295371000000
H	21.509921000000	11.599926000000	22.964741000000
C	23.606223000000	12.027042000000	23.417276000000
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H	23.708097000000	11.197363000000	24.147774000000
C	24.487443000000	13.213373000000	23.823043000000
H	25.555599000000	12.913247000000	23.869196000000
H	24.208141000000	13.547790000000	24.847448000000
C	24.325080000000	14.385299000000	22.847430000000
H	24.957535000000	15.239611000000	23.162511000000
H	24.696112000000	14.083699000000	21.840241000000
C	19.544902000000	16.403321000000	18.163190000000
C	19.506586000000	14.868883000000	18.011488000000
H	20.409534000000	14.546936000000	17.442454000000
H	19.569155000000	14.373422000000	19.002020000000
C	18.248319000000	14.398679000000	17.269574000000
H	17.350955000000	14.635044000000	17.884265000000
H	18.272940000000	13.294366000000	17.159368000000
C	18.118329000000	15.077492000000	15.901572000000
H	18.969874000000	14.762910000000	15.256093000000
H	17.191836000000	14.745280000000	15.388370000000
C	18.135250000000	16.602733000000	16.047362000000
H	17.232110000000	16.928527000000	16.610591000000
H	18.080719000000	17.093902000000	15.053254000000
C	19.389082000000	17.085163000000	16.789239000000
H	19.358991000000	18.187338000000	16.902837000000
H	20.292887000000	16.856282000000	16.178029000000
C	21.125474000000	18.748248000000	19.248303000000
C	19.772116000000	19.287139000000	19.742198000000
H	19.011511000000	19.169208000000	18.939622000000
H	19.412161000000	18.700008000000	20.612775000000
C	19.880904000000	20.774450000000	20.110933000000
H	20.565070000000	20.881521000000	20.983200000000
H	18.890679000000	21.155777000000	20.436951000000
C	20.420652000000	21.602253000000	18.937504000000
H	19.688212000000	21.565908000000	18.099736000000
H	20.514849000000	22.669652000000	19.227708000000
C	21.770595000000	21.059349000000	18.452199000000

H	22.521956000000	21.181874000000	19.263644000000
H	22.143772000000	21.644971000000	17.585560000000
C	21.684942000000	19.574001000000	18.076904000000
H	21.036129000000	19.453791000000	17.183444000000
H	22.684532000000	19.181846000000	17.794767000000
C	26.051934000000	16.360477000000	16.910368000000
H	26.868819000000	16.855781000000	16.347384000000
H	26.245998000000	15.270496000000	16.909552000000
C	21.111933000000	16.183676000000	20.648320000000
H	20.317405000000	16.644383000000	21.269169000000
H	20.862287000000	15.114238000000	20.508989000000
Cl	23.552913000000	13.954445000000	18.629123000000
H	24.589664000000	15.971184000000	13.767737000000
H	24.326704000000	18.936659000000	16.296280000000
H	25.392219000000	18.950843000000	17.830958000000
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H	22.856050000000	18.578710000000	21.623212000000
H	22.494082000000	15.234098000000	23.675808000000
H	18.721016000000	16.728121000000	18.836662000000
H	21.856507000000	18.857704000000	20.079890000000

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Cu	22.862693000000	16.455968000000	17.751658000000
Cu	24.276985000000	16.330818000000	19.782795000000
P	24.415497000000	16.610066000000	16.159845000000
P	26.126845000000	16.855823000000	18.680969000000
P	22.746993000000	16.264394000000	21.396620000000
P	21.035714000000	16.885323000000	18.940275000000
C	24.255167000000	15.427283000000	14.698307000000
C	25.130325000000	14.168884000000	14.816241000000
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H	24.886984000000	13.644140000000	15.767875000000
C	24.897855000000	13.216424000000	13.632938000000
H	25.522638000000	12.307462000000	13.759343000000
H	25.245347000000	13.712236000000	12.698907000000
C	23.419342000000	12.840184000000	13.482393000000
H	23.276299000000	12.177996000000	12.602927000000
H	23.098539000000	12.256260000000	14.374383000000
C	22.543543000000	14.092195000000	13.360842000000
H	21.469263000000	13.816097000000	13.305286000000
H	22.783163000000	14.621262000000	12.411089000000
C	22.767937000000	15.046112000000	14.540765000000
H	22.434720000000	14.560469000000	15.485789000000
H	22.141560000000	15.954781000000	14.429942000000

C	24.455220000000	18.327206000000	15.423430000000
C	23.157597000000	18.619596000000	14.647751000000
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H	23.073438000000	20.744456000000	15.077849000000
H	22.193976000000	20.268697000000	13.602903000000
C	24.359704000000	20.434650000000	13.350043000000
H	24.341405000000	19.844000000000	12.406542000000
H	24.335951000000	21.503913000000	13.052697000000
C	25.653651000000	20.122130000000	14.111178000000
H	25.729081000000	20.789120000000	14.999718000000
H	26.541082000000	20.337651000000	13.480046000000
C	25.700537000000	18.661304000000	14.588264000000
H	26.625181000000	18.494698000000	15.178097000000
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C	26.312652000000	18.710769000000	18.604368000000
C	27.706300000000	19.235519000000	18.230812000000
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H	28.071369000000	18.753078000000	17.299524000000
C	27.668021000000	20.763067000000	18.060758000000
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H	28.684470000000	21.141942000000	17.824893000000
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H	27.811048000000	21.288816000000	20.160985000000
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C	25.726478000000	20.916715000000	19.689589000000
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C	25.752215000000	19.393528000000	19.865035000000
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C	27.727516000000	16.120113000000	19.340889000000
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C	29.117499000000	15.896729000000	21.472062000000
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C	28.831120000000	13.900512000000	19.960866000000
H	28.701814000000	12.798652000000	19.916864000000

H	29.764852000000	14.130870000000	19.400254000000
C	27.643346000000	14.582984000000	19.269571000000
H	26.696886000000	14.263901000000	19.764121000000
H	27.577491000000	14.244662000000	18.215216000000
C	22.701984000000	17.843217000000	22.394856000000
C	24.025299000000	18.067956000000	23.148606000000
H	24.885179000000	17.941826000000	22.457730000000
H	24.134386000000	17.298877000000	23.944534000000
C	24.042795000000	19.459516000000	23.796276000000
H	24.993825000000	19.606446000000	24.349515000000
H	24.018492000000	20.232326000000	22.994757000000
C	22.840452000000	19.651198000000	24.729797000000
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C	21.516472000000	19.389847000000	24.000810000000
H	21.366503000000	20.168385000000	23.218803000000
H	20.660386000000	19.479829000000	24.701762000000
C	21.492814000000	18.007025000000	23.328744000000
H	21.517873000000	17.212248000000	24.106778000000
H	20.542483000000	17.880800000000	22.770497000000
C	22.918731000000	14.860513000000	22.644402000000
C	22.110406000000	13.606387000000	22.271543000000
H	22.394303000000	13.286659000000	21.243403000000
H	21.026113000000	13.837369000000	22.250307000000
C	22.371136000000	12.456119000000	23.255899000000
H	21.981444000000	12.742816000000	24.258505000000
H	21.796827000000	11.560190000000	22.939459000000
C	23.864188000000	12.128482000000	23.370696000000
H	24.230760000000	11.748397000000	22.390528000000
H	24.025915000000	11.313471000000	24.106913000000
C	24.668996000000	13.373364000000	23.759431000000
H	25.755424000000	13.144793000000	23.794030000000
H	24.380167000000	13.694582000000	24.785400000000
C	24.419943000000	14.525850000000	22.779049000000
H	24.991772000000	15.424660000000	23.086350000000
H	24.806308000000	14.253283000000	21.770193000000
C	19.386395000000	16.344800000000	18.216483000000
C	19.345344000000	14.808898000000	18.105413000000
H	20.258559000000	14.469662000000	17.563372000000
H	19.385239000000	14.343316000000	19.111487000000
C	18.098623000000	14.315168000000	17.358108000000
H	17.192724000000	14.554800000000	17.958967000000
H	18.133637000000	13.208966000000	17.269881000000
C	17.973624000000	14.965648000000	15.976319000000

H	18.834904000000	14.650245000000	15.344256000000
H	17.055869000000	14.612306000000	15.461459000000
C	17.970751000000	16.493033000000	16.095269000000
H	17.061094000000	16.817115000000	16.648995000000
H	17.914365000000	16.966541000000	15.092565000000
C	19.217050000000	17.000360000000	16.832453000000
H	19.176948000000	18.104344000000	16.927774000000
H	20.125883000000	16.770342000000	16.227079000000
C	20.948287000000	18.720787000000	19.262807000000
C	19.596387000000	19.263790000000	19.747551000000
H	18.837420000000	19.156363000000	18.941900000000
H	19.229437000000	18.677855000000	20.616367000000
C	19.729303000000	20.749359000000	20.120562000000
H	20.408247000000	20.839680000000	20.998744000000
H	18.744047000000	21.148283000000	20.440506000000
C	20.292234000000	21.575980000000	18.955787000000
H	19.562623000000	21.560118000000	18.114950000000
H	20.402942000000	22.639053000000	19.256043000000
C	21.634030000000	21.016393000000	18.463025000000
H	22.396701000000	21.125303000000	19.267242000000
H	22.006951000000	21.598752000000	17.593979000000
C	21.518016000000	19.534194000000	18.087418000000
H	20.867726000000	19.421382000000	17.193986000000
H	22.514117000000	19.114122000000	17.817270000000
C	26.088617000000	16.305327000000	16.908690000000
H	26.917590000000	16.749037000000	16.321896000000
H	26.229843000000	15.207818000000	16.924764000000
C	21.068702000000	16.087944000000	20.617583000000
H	20.242698000000	16.445588000000	21.264920000000
H	20.919508000000	15.005181000000	20.442627000000
Cl	23.568165000000	14.257004000000	18.604306000000
H	24.580968000000	16.001336000000	13.801319000000
H	24.451143000000	18.986709000000	16.320345000000
H	25.619857000000	18.970832000000	17.775090000000
H	28.565232000000	16.482587000000	18.704157000000
H	22.645002000000	18.631737000000	21.612265000000
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2			
C	-1.952043000000	-0.408621000000	-0.000107000000
C	-0.682921000000	0.445106000000	0.000105000000
C	0.599397000000	-0.397412000000	-0.000095000000

C	1.847837000000	0.469231000000	0.000123000000
Cl	3.365213000000	-0.533860000000	-0.000128000000
H	-2.865027000000	0.220282000000	0.000052000000
H	-1.994158000000	-1.064504000000	-0.894707000000
H	-1.994152000000	-1.064952000000	0.894165000000
H	-0.680298000000	1.115364000000	0.887972000000
H	-0.680290000000	1.115797000000	-0.887435000000
H	0.615677000000	-1.061595000000	-0.891207000000
H	0.615668000000	-1.062032000000	0.890691000000
H	1.902548000000	1.113373000000	0.899273000000
H	1.902548000000	1.113823000000	-0.898704000000

TS1

Cu	22.716597000000	17.606093000000	18.024276000000
Cu	23.981178000000	18.577741000000	19.935914000000
P	24.488287000000	17.258046000000	16.735950000000
P	25.660016000000	19.497774000000	18.549908000000
P	22.298425000000	17.740556000000	21.400724000000
P	20.721565000000	18.216785000000	18.762408000000
C	25.094991000000	15.526966000000	16.346365000000
C	25.483719000000	14.782101000000	17.637024000000
H	26.287543000000	15.316166000000	18.183106000000
H	24.604667000000	14.772145000000	18.315557000000
C	25.914811000000	13.336237000000	17.357346000000
H	26.156090000000	12.831597000000	18.316674000000
H	26.852282000000	13.340534000000	16.757142000000
C	24.828763000000	12.565856000000	16.598835000000
H	25.164513000000	11.530623000000	16.380513000000
H	23.926721000000	12.477247000000	17.245785000000
C	24.449880000000	13.292132000000	15.304281000000
H	23.633409000000	12.755786000000	14.776730000000
H	25.323357000000	13.291328000000	14.614220000000
C	24.022097000000	14.743256000000	15.567644000000
H	23.075842000000	14.757162000000	16.156496000000
H	23.798338000000	15.245450000000	14.605225000000
C	24.218928000000	18.166444000000	15.119300000000
C	22.788609000000	18.001722000000	14.574262000000
H	22.623680000000	16.951092000000	14.252187000000
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C	22.561101000000	18.944120000000	13.385172000000
H	22.625666000000	19.996835000000	13.744286000000
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C	23.606108000000	18.717613000000	12.284024000000
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H	23.557715000000	23.172561000000	16.940240000000
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C	28.459600000000	21.136007000000	21.233621000000
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P	20.599049000000	17.923367000000	19.553598000000
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11

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P	20.779386000000	16.904690000000	18.921806000000
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H	24.439623000000	14.042550000000	15.424607000000
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H	24.999031000000	14.454123000000	12.411925000000
C	23.010721000000	13.807768000000	12.994546000000
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C	22.358664000000	15.195319000000	13.015254000000
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H	22.742191000000	15.797687000000	12.161310000000
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H	22.211252000000	15.364716000000	15.175416000000

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H	23.514611000000	18.840788000000	13.916946000000
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C	25.330019000000	20.984967000000	13.729714000000
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C	26.508290000000	20.307395000000	14.440279000000
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cat.B

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C	25.827227000000	16.682386000000	17.004024000000
H	26.809269000000	16.726456000000	16.488562000000
H	25.548743000000	15.616234000000	17.111705000000
C	20.626802000000	15.931781000000	18.857943000000
H	19.699837000000	15.679319000000	19.412055000000
H	20.826255000000	15.103769000000	18.149044000000
Cl	23.121439000000	19.712244000000	18.864998000000
Cl	21.475831000000	19.501138000000	15.262132000000
H	25.196885000000	15.904667000000	14.238907000000
H	26.182696000000	19.170830000000	15.952449000000
H	25.891769000000	19.576458000000	17.923131000000
H	28.114654000000	16.796518000000	19.489640000000
H	20.808313000000	17.491862000000	21.283194000000
H	21.563273000000	13.676050000000	20.360744000000
H	19.154924000000	17.973438000000	15.918243000000
H	20.661975000000	19.011506000000	19.565820000000
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C	17.608632000000	19.653234000000	13.681400000000
C	16.392947000000	19.848439000000	14.349734000000
C	16.283837000000	20.801594000000	15.384319000000
C	17.434335000000	21.565032000000	15.661060000000
C	18.624876000000	21.309600000000	14.972157000000
N	18.715828000000	20.368892000000	14.018155000000
N	19.078129000000	18.581441000000	12.125319000000
C	19.374498000000	17.694859000000	11.159440000000
C	18.418066000000	16.820536000000	10.638640000000
C	17.089773000000	16.855879000000	11.120562000000
C	16.800583000000	17.812521000000	12.111280000000
Cu	20.416229000000	19.702788000000	13.180805000000
Cl	22.154571000000	19.767763000000	11.760188000000
C	16.038212000000	15.883710000000	10.576758000000
C	16.542550000000	14.436682000000	10.786654000000
C	15.850934000000	16.157366000000	9.066100000000
C	14.684392000000	16.041933000000	11.288846000000
C	14.986540000000	20.925595000000	16.188701000000
C	15.020287000000	22.123008000000	17.153312000000
C	14.828361000000	19.621424000000	17.009876000000
C	13.785584000000	21.088433000000	15.230472000000
H	15.525700000000	19.235056000000	14.072716000000

H	17.435732000000	22.341744000000	16.435702000000
H	19.548942000000	21.856699000000	15.210193000000
H	20.419751000000	17.701770000000	10.810004000000
H	18.722058000000	16.108130000000	9.858886000000
H	15.788038000000	17.895004000000	12.522669000000
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H	15.792324000000	13.720394000000	10.394982000000
H	17.498113000000	14.247992000000	10.258642000000
H	15.494596000000	17.192734000000	8.891696000000
H	15.098648000000	15.457207000000	8.649540000000
H	16.795278000000	16.017018000000	8.503589000000
H	13.962256000000	15.310674000000	10.875232000000
H	14.770852000000	15.850971000000	12.377881000000
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H	15.168561000000	23.079734000000	16.612870000000
H	14.056134000000	22.186179000000	17.695432000000
H	15.822191000000	22.023807000000	17.912402000000
H	14.759002000000	18.731056000000	16.353298000000
H	13.904460000000	19.672080000000	17.621051000000
H	15.690066000000	19.477070000000	17.693445000000
H	12.850383000000	21.177962000000	15.818859000000
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H	13.671060000000	20.219390000000	14.553029000000

TS2

Cu	22.680701000000	18.102074000000	17.073119000000
Cu	23.790260000000	17.418583000000	19.348719000000
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P	25.940402000000	17.262667000000	18.720312000000
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C	24.229040000000	16.158647000000	14.621389000000
C	23.624772000000	14.872709000000	15.212954000000
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H	22.679041000000	15.127914000000	15.739627000000
C	23.346082000000	13.835342000000	14.115707000000
H	22.887689000000	12.929566000000	14.565984000000
H	24.313913000000	13.512350000000	13.670819000000
C	22.446488000000	14.403783000000	13.010950000000
H	22.299733000000	13.652972000000	12.206344000000
H	21.439973000000	14.611114000000	13.434389000000
C	23.023123000000	15.701962000000	12.433957000000
H	22.329538000000	16.139405000000	11.684924000000
H	23.969905000000	15.477571000000	11.893097000000

C	23.312753000000	16.737578000000	13.529221000000
H	22.358271000000	17.065817000000	13.998984000000
H	23.749512000000	17.649190000000	13.076989000000
C	25.576980000000	18.787505000000	15.130550000000
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C	25.629316000000	21.126056000000	14.166132000000
H	26.249189000000	21.522015000000	15.003014000000
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C	26.757456000000	18.930888000000	18.554423000000
C	28.115884000000	18.954437000000	17.837700000000
H	28.868277000000	18.420619000000	18.459329000000
H	28.073214000000	18.415712000000	16.868409000000
C	28.576201000000	20.403107000000	17.611490000000
H	27.866846000000	20.896269000000	16.908498000000
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C	28.623711000000	21.193512000000	18.925710000000
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C	27.285488000000	21.127703000000	19.674448000000
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C	26.884665000000	16.279708000000	21.146272000000
H	26.958813000000	17.331805000000	21.486907000000
H	25.829821000000	15.971820000000	21.322739000000
C	27.820764000000	15.384444000000	21.967789000000
H	27.562966000000	15.463159000000	23.044797000000
H	28.866003000000	15.753465000000	21.865237000000
C	27.747684000000	13.927496000000	21.497711000000
H	28.445813000000	13.292420000000	22.082130000000

H	26.724251000000	13.534083000000	21.690817000000
C	28.055392000000	13.820530000000	19.999731000000
H	27.962573000000	12.768542000000	19.656027000000
H	29.113143000000	14.118320000000	19.822724000000
C	27.135824000000	14.717143000000	19.158175000000
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H	27.426080000000	14.650534000000	18.090310000000
C	21.379006000000	16.714192000000	21.568939000000
C	22.465987000000	17.216420000000	22.538579000000
H	23.151261000000	17.908876000000	22.001884000000
H	23.088684000000	16.364575000000	22.886826000000
C	21.824947000000	17.912793000000	23.747032000000
H	22.611942000000	18.243138000000	24.456713000000
H	21.305609000000	18.833385000000	23.396515000000
C	20.812405000000	16.998784000000	24.450798000000
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H	20.338006000000	17.531209000000	25.301618000000
C	19.741489000000	16.490729000000	23.476198000000
H	19.133649000000	17.351448000000	23.116087000000
H	19.039833000000	15.801821000000	23.991383000000
C	20.371852000000	15.786364000000	22.264558000000
H	20.891531000000	14.864420000000	22.603972000000
H	19.581675000000	15.459591000000	21.555657000000
C	22.449153000000	14.260485000000	20.141189000000
C	23.025854000000	13.719981000000	18.818178000000
H	23.954732000000	14.287545000000	18.584219000000
H	22.333741000000	13.905919000000	17.971482000000
C	23.343341000000	12.221369000000	18.904160000000
H	22.393617000000	11.656243000000	19.036720000000
H	23.782974000000	11.879326000000	17.943447000000
C	24.286792000000	11.911021000000	20.071825000000
H	25.277338000000	12.376689000000	19.873624000000
H	24.464347000000	10.817918000000	20.147896000000
C	23.730479000000	12.455507000000	21.392286000000
H	24.449393000000	12.278855000000	22.220039000000
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C	23.404194000000	13.953995000000	21.306902000000
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H	17.949450000000	15.955701000000	17.744561000000
H	17.426408000000	17.636513000000	17.473605000000
C	16.909615000000	16.276170000000	15.866603000000

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H	15.933282000000	15.996392000000	16.315295000000
C	17.495404000000	15.114175000000	15.060083000000
H	17.623704000000	14.229422000000	15.723710000000
H	16.793328000000	14.806057000000	14.256450000000
C	18.853661000000	15.504207000000	14.469153000000
H	18.712974000000	16.333459000000	13.745372000000
H	19.292231000000	14.660622000000	13.896217000000
C	19.831909000000	15.953563000000	15.559927000000
H	20.791736000000	16.279987000000	15.113285000000
H	20.068937000000	15.077347000000	16.203407000000
C	19.802943000000	18.874021000000	18.833785000000
C	18.697833000000	18.486767000000	19.832394000000
H	17.766156000000	18.224308000000	19.290940000000
H	18.969250000000	17.592797000000	20.426980000000
C	18.409059000000	19.665617000000	20.775267000000
H	19.320594000000	19.876040000000	21.379920000000
H	17.612537000000	19.383656000000	21.495879000000
C	18.010167000000	20.924575000000	19.993771000000
H	17.039653000000	20.735998000000	19.480136000000
H	17.839600000000	21.775313000000	20.686499000000
C	19.065332000000	21.288002000000	18.941588000000
H	20.007598000000	21.593807000000	19.449166000000
H	18.732755000000	22.161486000000	18.341682000000
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C	25.855281000000	16.601494000000	16.987814000000
H	26.832877000000	16.628246000000	16.462875000000
H	25.556107000000	15.540518000000	17.091026000000
C	20.652253000000	16.060776000000	18.799742000000
H	19.709078000000	15.860497000000	19.347443000000
H	20.823055000000	15.204724000000	18.118085000000
Cl	23.244985000000	19.699159000000	18.853436000000
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C	19.467014000000	17.874024000000	11.413276000000
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Cu	20.259639000000	20.049668000000	13.349128000000
Cl	22.009399000000	19.877965000000	11.917262000000
C	16.305377000000	15.813268000000	10.701243000000
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C	14.585713000000	21.944003000000	17.246139000000
C	14.645215000000	19.436548000000	17.136005000000
C	13.477758000000	20.767330000000	15.325036000000
H	15.420945000000	19.061508000000	14.229530000000
H	16.954107000000	22.423619000000	16.516424000000
H	19.140253000000	22.107181000000	15.346799000000
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H	18.993729000000	16.246717000000	10.092062000000
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H	14.270187000000	15.081841000000	10.914817000000
H	14.972512000000	15.676808000000	12.449880000000
H	14.415784000000	16.841013000000	11.197239000000
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H	13.618324000000	21.914141000000	17.784993000000
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H	13.460485000000	19.886121000000	14.653711000000
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C	1.261545000000	-1.041998000000	0.214156000000
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C	-0.244100000000	-2.718436000000	1.160052000000
C	0.838693000000	-3.617111000000	1.100666000000
C	2.074323000000	-3.193246000000	0.596973000000
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C	3.301031000000	1.664122000000	-1.125550000000
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C	0.690603000000	1.372968000000	-0.347219000000
Cu	4.053388000000	-1.206362000000	-0.531910000000
Cl	4.946612000000	-3.251315000000	-0.905147000000
C	0.079616000000	3.784813000000	-0.906911000000
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C	-1.971544000000	-2.189518000000	2.891486000000
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Cl	6.006997000000	-0.080529000000	-0.723759000000

TS3

C	-0.634350000000	-2.398299000000	1.606923000000
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C	2.404244000000	-1.356736000000	-0.718066000000
C	3.254626000000	-0.085084000000	-0.783300000000
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C	5.290748000000	1.082947000000	-1.798547000000
N	-0.441808000000	-1.496309000000	2.632144000000
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C	0.250448000000	-3.464108000000	-0.496767000000
H	1.635425000000	-0.780416000000	1.216516000000
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H	2.026762000000	-1.608318000000	-1.732635000000
H	3.039620000000	-2.209947000000	-0.396001000000
H	3.634116000000	0.145934000000	0.237930000000
H	2.611464000000	0.778761000000	-1.068015000000
H	4.048288000000	-0.411466000000	-2.773910000000
H	5.065128000000	-1.054518000000	-1.471230000000
H	6.137147000000	0.983143000000	-2.508124000000
H	5.715610000000	1.313880000000	-0.798937000000
H	4.691380000000	1.963479000000	-2.112595000000
H	0.463001000000	-0.994573000000	2.651792000000
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H	-3.209113000000	-0.665910000000	7.114719000000
H	-1.016717000000	0.501823000000	6.700373000000
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H	1.215446000000	-3.782298000000	-0.933151000000
H	-0.318803000000	-4.333367000000	-0.123948000000
H	-0.340915000000	-3.002304000000	-1.322772000000

C	0.052535000000	-3.842375000000	5.882801000000
C	0.888253000000	-2.864299000000	6.619675000000
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C	1.368754000000	-1.441268000000	8.544834000000
C	2.527483000000	-1.028656000000	7.846902000000
C	2.790521000000	-1.529128000000	6.571390000000
N	1.993136000000	-2.429744000000	5.962656000000
N	0.371420000000	-4.000218000000	4.572497000000
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C	-1.385630000000	-5.631671000000	4.361515000000
C	-1.753747000000	-5.479334000000	5.712168000000
C	-0.991401000000	-4.569125000000	6.473012000000
Cu	1.912894000000	-2.747636000000	3.926648000000
Cl	2.618047000000	-0.557308000000	3.424425000000
C	-2.914087000000	-6.242741000000	6.361385000000
C	-3.599291000000	-7.198032000000	5.370029000000
C	-3.957975000000	-5.218794000000	6.865507000000
C	-2.372262000000	-7.064381000000	7.553791000000
C	1.022560000000	-0.841815000000	9.911767000000
C	0.824437000000	0.682862000000	9.737577000000
C	2.188583000000	-1.107097000000	10.891229000000
C	-0.266341000000	-1.443931000000	10.495919000000
H	-0.371352000000	-2.734151000000	8.370770000000
H	3.225050000000	-0.298865000000	8.282155000000
H	3.656474000000	-1.180886000000	5.988363000000
H	-0.000746000000	-4.992434000000	2.793165000000
H	-1.917694000000	-6.320882000000	3.693750000000
H	-1.206306000000	-4.431544000000	7.541163000000
H	-2.898223000000	-7.965816000000	4.984854000000
H	-4.430234000000	-7.725900000000	5.878846000000
H	-4.026978000000	-6.652813000000	4.504695000000
H	-3.523352000000	-4.511655000000	7.599882000000
H	-4.797990000000	-5.749492000000	7.358148000000
H	-4.368710000000	-4.627177000000	6.022729000000
H	-3.202167000000	-7.623214000000	8.032149000000
H	-1.610677000000	-7.796671000000	7.217243000000
H	-1.911219000000	-6.417820000000	8.326776000000
H	0.004010000000	0.894696000000	9.021763000000
H	0.561301000000	1.142363000000	10.712102000000
H	1.743503000000	1.176547000000	9.364418000000
H	2.351320000000	-2.195310000000	11.028807000000
H	1.955025000000	-0.664389000000	11.880883000000
H	3.136949000000	-0.658123000000	10.535167000000
H	-0.472814000000	-0.986616000000	11.483784000000

H	-1.143329000000	-1.248425000000	9.846082000000
H	-0.179555000000	-2.539479000000	10.642509000000
Cl	2.197036000000	-3.764445000000	1.853653000000

TS3'

Cu	22.489661000000	17.939934000000	17.867751000000
Cu	24.221868000000	16.614571000000	19.557168000000
P	24.297758000000	18.020337000000	16.073168000000
P	26.028870000000	16.417970000000	18.247212000000
P	22.793399000000	16.195173000000	21.236424000000
P	20.560052000000	17.177657000000	19.261301000000
C	23.667184000000	17.484591000000	14.378875000000
C	24.687082000000	16.731112000000	13.506467000000
H	25.642065000000	17.291219000000	13.431242000000
H	24.929584000000	15.759727000000	13.988466000000
C	24.116185000000	16.452879000000	12.107696000000
H	24.862638000000	15.897302000000	11.501785000000
H	23.940081000000	17.419685000000	11.584295000000
C	22.799151000000	15.671389000000	12.191370000000
H	22.385471000000	15.495370000000	11.176149000000
H	23.000939000000	14.668032000000	12.629940000000
C	21.779154000000	16.407798000000	13.067787000000
H	20.843067000000	15.817379000000	13.164018000000
H	21.501560000000	17.364870000000	12.571900000000
C	22.342551000000	16.712019000000	14.462438000000
H	22.492111000000	15.768213000000	15.028279000000
H	21.612963000000	17.307016000000	15.046788000000
C	25.538689000000	19.411808000000	15.636069000000
C	25.646581000000	20.461993000000	16.751592000000
H	24.674366000000	20.985385000000	16.813554000000
H	25.784736000000	19.989586000000	17.742073000000
C	26.746772000000	21.492174000000	16.476872000000
H	27.737962000000	20.984145000000	16.478555000000
H	26.773902000000	22.235250000000	17.302685000000
C	26.522863000000	22.187002000000	15.130242000000
H	25.587096000000	22.787350000000	15.185724000000
H	27.344778000000	22.900694000000	14.911307000000
C	26.392713000000	21.157819000000	14.002569000000
H	27.366984000000	20.634239000000	13.875109000000
H	26.178060000000	21.661325000000	13.036205000000
C	25.301311000000	20.111513000000	14.284331000000
H	25.289986000000	19.380581000000	13.453823000000
H	24.307700000000	20.606248000000	14.289586000000
C	27.388923000000	17.674848000000	18.478133000000

C	28.706727000000	17.369606000000	17.749333000000
H	29.178898000000	16.468636000000	18.198868000000
H	28.519431000000	17.132249000000	16.680728000000
C	29.676056000000	18.556223000000	17.865767000000
H	29.248123000000	19.426138000000	17.317926000000
H	30.636514000000	18.310399000000	17.365976000000
C	29.915010000000	18.947647000000	19.329804000000
H	30.441918000000	18.113867000000	19.846613000000
H	30.587838000000	19.828937000000	19.388786000000
C	28.594302000000	19.231271000000	20.058000000000
H	28.111469000000	20.128452000000	19.608036000000
H	28.782247000000	19.475865000000	21.124574000000
C	27.626007000000	18.044593000000	19.953390000000
H	28.048687000000	17.173973000000	20.500258000000
H	26.655269000000	18.285214000000	20.434133000000
C	26.849862000000	14.733485000000	18.226036000000
C	27.383471000000	14.405691000000	19.635229000000
H	28.122310000000	15.167373000000	19.956400000000
H	26.537394000000	14.466275000000	20.356971000000
C	28.016704000000	13.008924000000	19.703635000000
H	28.340394000000	12.799610000000	20.745123000000
H	28.937627000000	12.996099000000	19.078423000000
C	27.055975000000	11.923317000000	19.207037000000
H	27.549125000000	10.928919000000	19.228981000000
H	26.185047000000	11.859067000000	19.897255000000
C	26.553050000000	12.244466000000	17.795786000000
H	25.829815000000	11.474840000000	17.453284000000
H	27.409149000000	12.211851000000	17.084726000000
C	25.896421000000	13.630165000000	17.731726000000
H	24.977023000000	13.638629000000	18.356880000000
H	25.565006000000	13.836877000000	16.694017000000
C	22.499774000000	17.567242000000	22.463534000000
C	23.797887000000	18.218265000000	22.977448000000
H	24.447046000000	18.476575000000	22.116753000000
H	24.358511000000	17.496527000000	23.607806000000
C	23.477314000000	19.469102000000	23.807858000000
H	24.415982000000	19.913151000000	24.200676000000
H	23.021605000000	20.235574000000	23.141253000000
C	22.507426000000	19.158043000000	24.955537000000
H	23.008509000000	18.477298000000	25.680233000000
H	22.259203000000	20.084662000000	25.514602000000
C	21.228037000000	18.484437000000	24.442252000000
H	20.666855000000	19.198765000000	23.797933000000
H	20.555584000000	18.225862000000	25.286934000000

C	21.546782000000	17.226349000000	23.620141000000
H	22.025538000000	16.468966000000	24.278614000000
H	20.609047000000	16.770724000000	23.241886000000
C	23.096441000000	14.598832000000	22.163604000000
C	23.312437000000	13.463106000000	21.142707000000
H	24.138937000000	13.765925000000	20.461025000000
H	22.415601000000	13.334966000000	20.502753000000
C	23.672094000000	12.132673000000	21.816096000000
H	22.802827000000	11.772717000000	22.410773000000
H	23.861009000000	11.364672000000	21.036360000000
C	24.889821000000	12.280090000000	22.735252000000
H	25.782414000000	12.535017000000	22.120211000000
H	25.117051000000	11.316858000000	23.238139000000
C	24.659872000000	13.386724000000	23.768734000000
H	25.555186000000	13.515164000000	24.412443000000
H	23.825196000000	13.091017000000	24.443267000000
C	24.311756000000	14.724476000000	23.100808000000
H	24.120674000000	15.488339000000	23.880039000000
H	25.185048000000	15.083059000000	22.508922000000
C	19.272547000000	16.310179000000	18.176908000000
C	19.323258000000	14.774319000000	18.170199000000
H	20.335658000000	14.444121000000	17.852736000000
H	19.158086000000	14.380529000000	19.193915000000
C	18.270829000000	14.189723000000	17.215272000000
H	17.253818000000	14.433766000000	17.597319000000
H	18.347627000000	13.081992000000	17.210531000000
C	18.417379000000	14.747848000000	15.794440000000
H	19.401470000000	14.435119000000	15.376884000000
H	17.640261000000	14.319330000000	15.127173000000
C	18.339267000000	16.278561000000	15.798999000000
H	17.319041000000	16.595142000000	16.112940000000
H	18.493946000000	16.682173000000	14.775699000000
C	19.377103000000	16.882760000000	16.751886000000
H	19.288510000000	17.988859000000	16.772321000000
H	20.396593000000	16.657992000000	16.377056000000
C	19.453885000000	18.307765000000	20.291787000000
C	18.417926000000	17.601333000000	21.186139000000
H	17.699618000000	17.037226000000	20.551157000000
H	18.901164000000	16.859989000000	21.853022000000
C	17.646979000000	18.623685000000	22.037231000000
H	18.358553000000	19.113329000000	22.739814000000
H	16.897530000000	18.097431000000	22.665123000000
C	16.970963000000	19.692601000000	21.170365000000
H	16.180218000000	19.211478000000	20.551597000000

H	16.458219000000	20.441937000000	21.809484000000
C	17.983662000000	20.376696000000	20.244555000000
H	18.707037000000	20.961341000000	20.856117000000
H	17.474342000000	21.105268000000	19.579183000000
C	18.757149000000	19.354214000000	19.399674000000
H	18.041137000000	18.830809000000	18.728084000000
H	19.496135000000	19.855601000000	18.744640000000
C	25.508169000000	16.645302000000	16.478629000000
H	26.399485000000	16.732559000000	15.824964000000
H	24.976310000000	15.710408000000	16.221924000000
C	21.116751000000	15.893734000000	20.493582000000
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Cl	22.779843000000	15.529754000000	17.731600000000
H	23.436211000000	18.457967000000	13.893781000000
H	26.511193000000	18.874807000000	15.564699000000
H	26.938782000000	18.570710000000	18.000961000000
H	27.706762000000	14.803727000000	17.519072000000
H	22.005458000000	18.325603000000	21.814629000000
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H	18.290784000000	16.609621000000	18.605674000000
H	20.162430000000	18.838680000000	20.965402000000
C	22.153190000000	20.975621000000	17.784918000000
C	22.642618000000	21.416611000000	19.094816000000
O	21.480935000000	19.916069000000	17.641185000000
C	23.724331000000	22.440342000000	19.241726000000
C	23.192654000000	23.882735000000	19.436032000000
C	24.324029000000	24.900942000000	19.588788000000
C	23.826686000000	26.336876000000	19.781683000000
C	24.959563000000	27.352285000000	19.938492000000
N	22.467848000000	21.779907000000	16.708440000000
C	22.135425000000	21.632473000000	15.354578000000
C	21.436104000000	20.519516000000	14.829662000000
C	21.196667000000	20.443787000000	13.449901000000
C	21.634594000000	21.453533000000	12.577221000000
C	22.311721000000	22.568502000000	13.103348000000
C	22.556202000000	22.662513000000	14.477185000000
C	21.799094000000	21.118949000000	20.281359000000
H	24.424946000000	22.418367000000	18.382037000000
H	24.325945000000	22.170075000000	20.135811000000
H	22.534139000000	23.912614000000	20.330066000000
H	22.548960000000	24.165530000000	18.573565000000
H	24.984502000000	24.854831000000	18.693210000000

H	24.964221000000	24.609375000000	20.451640000000
H	23.162388000000	26.374406000000	20.673633000000
H	23.185556000000	26.618419000000	18.916790000000
H	25.594673000000	27.112385000000	20.817023000000
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H	25.620105000000	27.359117000000	19.046017000000
H	22.974839000000	22.642372000000	16.922393000000
H	21.101968000000	19.725497000000	15.504991000000
H	20.657437000000	19.569833000000	13.053543000000
H	21.446372000000	21.376294000000	11.496104000000
H	22.657073000000	23.373727000000	12.437351000000
H	23.094100000000	23.531700000000	14.887615000000
H	20.992004000000	21.885498000000	20.362580000000
H	21.305149000000	20.139639000000	20.182552000000
H	22.385404000000	21.154203000000	21.218878000000

3

C	-1.486647000000	-0.110917000000	-0.065635000000
C	-0.302699000000	-1.080815000000	0.208278000000
O	-1.818232000000	0.054810000000	-1.243974000000
C	0.960208000000	-0.481678000000	-0.435630000000
Cl	0.025133000000	-1.261604000000	2.031546000000
C	2.224367000000	-1.339062000000	-0.378537000000
C	3.436615000000	-0.637995000000	-0.998130000000
C	4.713479000000	-1.483488000000	-0.966386000000
C	5.923056000000	-0.782379000000	-1.586070000000
N	-2.067727000000	0.489370000000	1.010301000000
C	-3.143433000000	1.396031000000	1.046882000000
C	-3.812827000000	1.855674000000	-0.109967000000
C	-4.877320000000	2.760529000000	0.022189000000
C	-5.289689000000	3.217555000000	1.284387000000
C	-4.621778000000	2.757779000000	2.432833000000
C	-3.557773000000	1.854945000000	2.318664000000
C	-0.680269000000	-2.467097000000	-0.314603000000
H	1.149930000000	0.505221000000	0.038708000000
H	0.689042000000	-0.274619000000	-1.492976000000
H	2.053208000000	-2.301941000000	-0.905967000000
H	2.445554000000	-1.598346000000	0.679577000000
H	3.618994000000	0.324116000000	-0.467539000000
H	3.203793000000	-0.360563000000	-2.051314000000
H	4.524847000000	-2.444668000000	-1.494791000000
H	4.938439000000	-1.760232000000	0.087896000000
H	6.830557000000	-1.418667000000	-1.549266000000
H	6.155435000000	0.164340000000	-1.054132000000

H	5.736585000000	-0.524754000000	-2.649988000000
H	-1.661738000000	0.234548000000	1.918782000000
H	-3.489171000000	1.496265000000	-1.093283000000
H	-5.392274000000	3.112567000000	-0.885178000000
H	-6.125870000000	3.927141000000	1.374134000000
H	-4.930975000000	3.104583000000	3.430778000000
H	-3.034633000000	1.494462000000	3.218561000000
H	0.136033000000	-3.192368000000	-0.142863000000
H	-1.596623000000	-2.836030000000	0.185063000000
H	-0.875599000000	-2.392710000000	-1.402347000000

TS-ATRP

C	-1.008404000000	-0.412680000000	0.309472000000
C	-0.085001000000	-1.260193000000	-0.492187000000
O	-2.231719000000	-0.365501000000	0.084469000000
C	1.401831000000	-0.986174000000	-0.450103000000
C	2.289950000000	-1.903522000000	-1.296818000000
C	3.780894000000	-1.606688000000	-1.116643000000
C	4.692765000000	-2.511442000000	-1.950506000000
C	6.181085000000	-2.212337000000	-1.765111000000
N	-0.409628000000	0.278760000000	1.349427000000
C	-0.999066000000	1.004600000000	2.394298000000
C	-2.385033000000	1.280846000000	2.474123000000
C	-2.888373000000	1.985355000000	3.579144000000
C	-2.042300000000	2.426937000000	4.609864000000
C	-0.664541000000	2.159012000000	4.524442000000
C	-0.146369000000	1.459670000000	3.429464000000
C	-0.678387000000	-1.844843000000	-1.736350000000
H	1.763169000000	-1.035678000000	0.601477000000
H	1.567594000000	0.069954000000	-0.778725000000
H	2.022197000000	-1.807232000000	-2.370928000000
H	2.094251000000	-2.965396000000	-1.028989000000
H	4.046970000000	-1.707281000000	-0.039761000000
H	3.978728000000	-0.541878000000	-1.376666000000
H	4.420402000000	-2.411079000000	-3.025013000000
H	4.487604000000	-3.573271000000	-1.687506000000
H	6.815326000000	-2.885298000000	-2.377166000000
H	6.486476000000	-2.335849000000	-0.704635000000
H	6.420450000000	-1.168049000000	-2.057033000000
H	0.598176000000	0.137078000000	1.450297000000
H	-3.041384000000	0.930469000000	1.669776000000
H	-3.969134000000	2.190825000000	3.630400000000
H	-2.451337000000	2.973992000000	5.472510000000
H	0.017557000000	2.484289000000	5.325013000000

H	0.930161000000	1.233544000000	3.378876000000
H	-0.193254000000	-2.799608000000	-2.017806000000
H	-1.766135000000	-1.998904000000	-1.614009000000
H	-0.532008000000	-1.147389000000	-2.594527000000
C	0.356330000000	-2.175760000000	3.127298000000
C	-0.656761000000	-2.719642000000	2.178610000000
O	1.549353000000	-1.999763000000	2.809244000000
C	-0.208511000000	-3.108426000000	0.931576000000
N	-0.139698000000	-1.856746000000	4.377243000000
C	0.493925000000	-1.220980000000	5.453745000000
C	1.863464000000	-0.865681000000	5.456283000000
C	2.404806000000	-0.200516000000	6.566782000000
C	1.613454000000	0.115730000000	7.683362000000
C	0.254733000000	-0.247410000000	7.683513000000
C	-0.301178000000	-0.908672000000	6.583002000000
C	-2.119710000000	-2.714439000000	2.528190000000
H	-0.900375000000	-3.609006000000	0.240020000000
H	0.869818000000	-3.244100000000	0.772690000000
H	-1.134440000000	-2.043621000000	4.522434000000
H	2.475632000000	-1.111753000000	4.581924000000
H	3.471139000000	0.074137000000	6.554094000000
H	2.050416000000	0.638135000000	8.547566000000
H	-0.382881000000	-0.010119000000	8.548971000000
H	-1.369121000000	-1.179386000000	6.581026000000
H	-2.340196000000	-3.362050000000	3.405918000000
H	-2.479092000000	-1.692000000000	2.778390000000
H	-2.727793000000	-3.082736000000	1.681471000000

Radical-ATRP

C	-1.240554000000	-0.476256000000	0.280887000000
C	-0.261084000000	-1.539485000000	-0.279319000000
O	-2.412810000000	-0.402163000000	-0.098466000000
C	1.213158000000	-1.068541000000	-0.198128000000
C	2.244089000000	-1.964694000000	-0.890502000000
C	3.682684000000	-1.516901000000	-0.616116000000
C	4.739759000000	-2.371132000000	-1.321877000000
C	6.173473000000	-1.917080000000	-1.043809000000
N	-0.728452000000	0.293125000000	1.304072000000
C	-1.408096000000	1.078204000000	2.251729000000
C	-2.774921000000	1.423696000000	2.141661000000
C	-3.381480000000	2.177341000000	3.158986000000
C	-2.654054000000	2.598431000000	4.284004000000
C	-1.293576000000	2.257873000000	4.388144000000
C	-0.673756000000	1.505786000000	3.383680000000

C	-0.657225000000	-1.853889000000	-1.728489000000
H	1.525303000000	-0.991345000000	0.864523000000
H	1.277963000000	-0.046999000000	-0.634201000000
H	2.067115000000	-1.977437000000	-1.987177000000
H	2.125068000000	-3.015525000000	-0.546292000000
H	3.866088000000	-1.536577000000	0.482195000000
H	3.803630000000	-0.452971000000	-0.923479000000
H	4.547044000000	-2.355853000000	-2.418005000000
H	4.615094000000	-3.432498000000	-1.010673000000
H	6.916125000000	-2.554613000000	-1.565252000000
H	6.403231000000	-1.953933000000	0.042029000000
H	6.335518000000	-0.870773000000	-1.378837000000
H	0.267830000000	0.163856000000	1.497742000000
H	-3.339206000000	1.088056000000	1.264414000000
H	-4.446818000000	2.439043000000	3.063962000000
H	-3.142089000000	3.187823000000	5.074642000000
H	-0.706371000000	2.572783000000	5.264426000000
H	0.387833000000	1.226846000000	3.476098000000
H	-0.142374000000	-2.766389000000	-2.085021000000
H	-1.749728000000	-2.012162000000	-1.796169000000
H	-0.386209000000	-1.015517000000	-2.402401000000
C	0.401590000000	-2.393185000000	2.926382000000
C	-0.760533000000	-2.596669000000	2.056514000000
O	1.569711000000	-2.654029000000	2.563685000000
C	-0.507107000000	-2.840822000000	0.602556000000
N	0.107681000000	-1.848585000000	4.173342000000
C	0.979898000000	-1.385323000000	5.164252000000
C	2.382942000000	-1.574396000000	5.125977000000
C	3.180523000000	-1.058852000000	6.158813000000
C	2.614681000000	-0.358392000000	7.236773000000
C	1.220624000000	-0.173888000000	7.276121000000
C	0.410168000000	-0.678927000000	6.253799000000
C	-2.162615000000	-2.479182000000	2.568644000000
H	-1.379834000000	-3.367481000000	0.169329000000
H	0.387223000000	-3.485167000000	0.481273000000
H	-0.876378000000	-1.631000000000	4.345759000000
H	2.820446000000	-2.119232000000	4.282353000000
H	4.270154000000	-1.212447000000	6.115415000000
H	3.252173000000	0.040508000000	8.039998000000
H	0.756738000000	0.372751000000	8.111641000000
H	-0.680226000000	-0.524580000000	6.282400000000
H	-2.320202000000	-3.077792000000	3.492414000000
H	-2.433617000000	-1.427287000000	2.827251000000
H	-2.893938000000	-2.814693000000	1.810294000000

1			
C	1.516162000000	0.154784000000	0.113850000000
C	2.605341000000	-0.484014000000	-0.721670000000
O	1.755974000000	1.018297000000	0.967357000000
C	3.869439000000	-0.065578000000	-0.492503000000
N	0.245911000000	-0.308072000000	-0.161144000000
C	-0.981017000000	0.065326000000	0.411772000000
C	-1.104114000000	1.039908000000	1.429871000000
C	-2.373349000000	1.349927000000	1.941927000000
C	-3.528004000000	0.710182000000	1.462930000000
C	-3.403940000000	-0.258235000000	0.451097000000
C	-2.145557000000	-0.579258000000	-0.070874000000
C	2.264779000000	-1.531641000000	-1.750798000000
H	4.719691000000	-0.477935000000	-1.056963000000
H	4.061924000000	0.702772000000	0.271661000000
H	0.172647000000	-1.024893000000	-0.886720000000
H	-0.201341000000	1.537450000000	1.800627000000
H	-2.455171000000	2.110508000000	2.734054000000
H	-4.517121000000	0.962610000000	1.873650000000
H	-4.296558000000	-0.771629000000	0.061776000000
H	-2.051905000000	-1.338322000000	-0.864180000000
H	1.773882000000	-2.415783000000	-1.289590000000
H	1.569795000000	-1.137778000000	-2.523629000000
H	3.175757000000	-1.886111000000	-2.268485000000

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