Supplementary Information for:

Palladium-Catalyzed Remote Internal C(sp^3)-H Bond Chlorination of Alkenes

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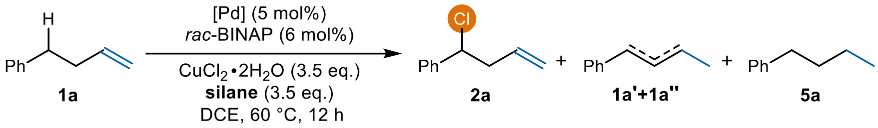
1. General Information

Commercial reagents were purchased from Tansoole (adamas), Bide Pharm, alfa, TCI, and Acros Organics and without further purification. Liquid olefin substrates were distilled before use. Dry solvents were purchased from Tansoole and used directly without further purification. All experiments were performed in oven-dried or flame-dried glassware in N_2-filled glovebox. Reactions were monitored using either thin-layer chromatography (TLC) or gas chromatography (SHIMADZU Nexis GC-2030) with an FID detector. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Heidolph rotary evaporator. Purification and isolation of products were performed via silica gel chromatography (either column or preparative thin-layer chromatography). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Ascend 400M spectrometer. ^{1}H NMR spectra were internally referenced to the residual solvent signal or TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm). Infrared (IR) spectra were obtained on a Thermo IS5 spectrometer and are reported in terms of absorption frequency (cm^{-1}). Melting points of all the final compounds were recorded on a melting point instrument in capillary tubes. GC-MS analyses were performed with SHIMADZU Nexis GC-2030 and GC-MS-QP2020 NX with an EI detection system. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Enantiomeric ratio for enantioselective reactions were determined by a Shimadzu system HPLC equipped with SPD-20A detector and LC-20AT pump. The mass analysis mode of the HRMS was orbitrap. Alkenes **1b**[1], **1c**[1], **1d**[1], **1h**[1], **1j**[2], **1k**[1], **ll**[3], **lm**[4], **1n**[5], **1o**[6], **1p**,[7] **1q**[8], **1r**[8], **1s**[9], **1u**[10], **1w**[11] **1ab**[12], **1ac**[13], **1ad**[14], **1ag**[15], **3g**[16], **3h**[17], **3l**[18] are known compounds and synthesized according to reported methods. Racemic 1.1'-binaphthyl-2.2'-diphemyl phosphine (*rac*-BINAP) was used in this study.

2. Reaction optimization

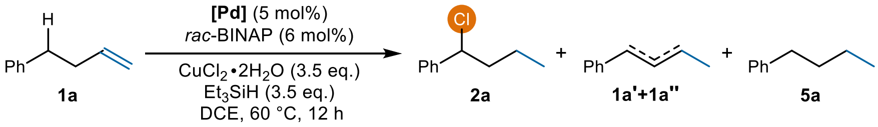
Table S1. Screening of silanes.



entry	silane	**2a** (%)	**1a +1a'+ 1a''** (%)	**5a** (%)
1	^{t}BuSi(Me)$_2$H	/	3	90
2	(^{i}Pr)$_3$SiH	/	5	95
3	Ph$_2$SiH$_2$	60	25	7
4	(EtO)$_3$SiH	<5	82	10
5	Ph$_3$SiH	/	88	10
6	Et$_3$SiH	65	12	10

Determined by GC using 1,3,5-trimethoxybenzene as an internal standard.

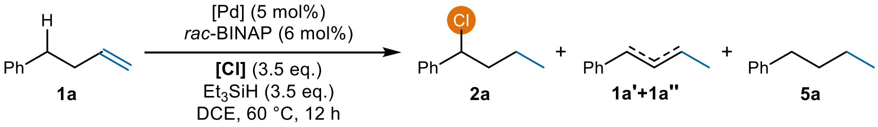
Table S2. Screening of palladium precatalysts.



entry	[Pd]	**2a** (%)	**1a +1a'+ 1a''** (%)	**5a** (%)
1	Pd(PhCN)$_2$Cl$_2$	65	12	10
2	Pd(CH$_3$CN)$_2$Cl$_2$	/	78	3
3	PdBr$_2$	15	50	34
4	Pd(OAc)$_2$	2	trace	94
5	Pd(PPh$_3$)$_2$Cl$_2$	18	trace	80
6	PdCl$_2$	6	32	60
7	Pd(TFA)$_2$	13	16	69

Determined by GC using 1,3,5-trimethoxybenzene as an internal standard.

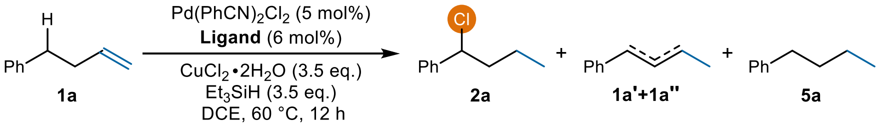
Table S3. Screening of chlorinating reagents.



entry	[Cl]	**2a** (%)	**1a +1a'+ 1a''** (%)	**5a** (%)
1	CuCl$_2$ •2H$_2$O	65	12	10
2	NCS	/	74	25
3	NCP	/	41	55
4	Oxone+LiCl	/	92	7
5	^{t}BuOCl	/	/	/
6	PhICl$_2$	multiple isomers[a]	/	/

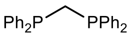
Determined by GC using 1,3,5-trimethoxybenzene as an internal standard.
[a] using DPEphos (Bis[(2-diphenylphosphino)phenyl]ether).

Table S4. Screening of ligands.

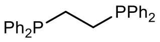


entry	**ligand**	**2a** (%)	**1a +1a'+ 1a''** (%)	**5a** (%)
1	dppm	/	97	/
2	dppe	7	82	5
3	dppp	18	78	2
4	dppb	/	95	/
5	dppf	19	75	2
6	*rac*-BINAP	66	18	8
7	DPEPhos	/	94	5
8	XantPhos	/	99	/
9	2,2'-Bipyridine	/	/	93
10	1,10-Phenanthroline	/	/	95
11	**L1**	/	/	97
12	**L2**	/	/	94
13	**L3**	/	/	92
14	**L4**	/	/	95
15	**L5**	/	/	94
16	**L6**	/	/	96
17	**L7**	/	/	92
18	**L8**	/	/	97
19	without ligand	/	96	/

Determined by GC using 1,3,5-trimethoxybenzene as an internal standard.

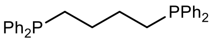


dppm

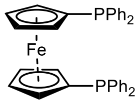


dppe

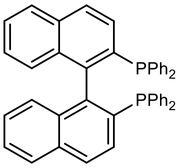
dppp



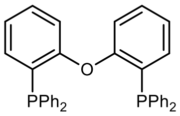
dppb



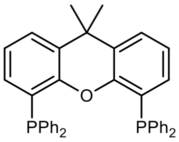
dppf



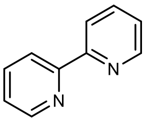
rac-BINAP



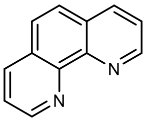
DPEphos



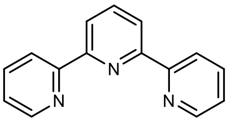
Xantphos



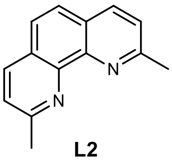
2,2'-Bipyridine



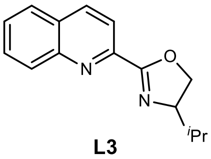
1,10-Phenanthroline



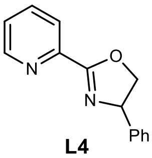
L1



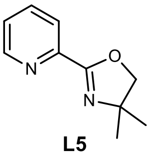
L2



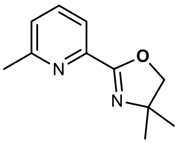
L3



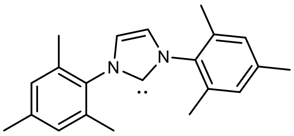
L4



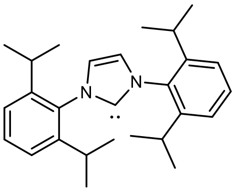
L5



L6

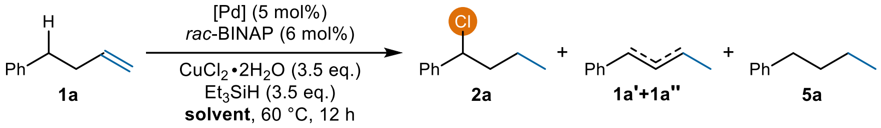


L7



L8

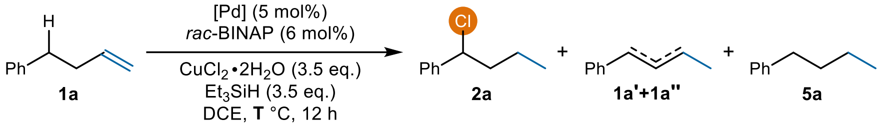
Table S5. Screening of solvents.



entry	**solvent**	**2a** (%)	**1a +1a'+ 1a''** (%)	**5a** (%)
1	DCE	65	12	10
2	DCM[a]	36	48	10
3	THF	2	90	7
4	Tol	/	86	13
5	MeOH	/	97	2
6	TFA	/	93	5
7	EA	/	97	2
8	MeCN	/	73	25
9	Et_2O[b]	/	95	3
10	Cyclohexane	/	68	30
11	DMA	/	94	5

Determined by GC using 1,3,5-trimethoxybenzene as an internal standard. [a] 40 °C. [b] 35 °C. DCE, 1,2-Dichloroethane. DCM, Dichloromethane; THF, Tetrahydrofuran; Tol, Toluene; TFA, Trifluoroacetic acid; EA, Ethyl acetate; DMA, N,N-Dimethylformamide.

Table S6. Screening of reaction temperature.

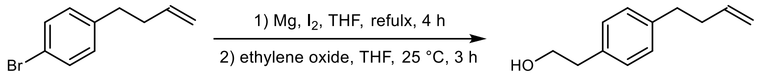


entry	**T**	**2a** (%)	**1a +1a'+ 1a''** (%)	**5a** (%)
1	0	28	57	12
2	40	45	40	10
3	60	65	18	12
4	80	16	63	17

Determined by GC using 1,3,5-trimethoxybenzene as an internal standard.

3. Synthesis of substrates

1e was synthesized based on the following method:

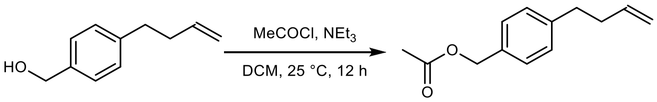


1e

To a mixture of Mg (0.576 g, 24.0 mmol, 1.2 eq.) and a grain of iodine, a solution of 1-bromo-4-(but-3-en-1-yl)benzene (4.2 g, 20.0 mmol, 1.0 eq.) in THF (50 mL) was added slowly under N_2. The mixture was refluxed for 4 h. Then the ethylene oxide (13.3 mL, 3.0 M in THF, 40 mmol, 2 eq.) was added dropwise over 20 min under 0 °C. After stirring for an additional 30 min, the reaction mixture was warmed to 25 °C and stirred for 3 h. The mixture was quenched with H_2O (30 mL) and extracted with EA (3 × 20 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 10:1) to obtain the desired alkene **1e** as a colorless oil (2.7 g, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 4H), 5.89 – 5.81 (m, 1H), 5.06 (dd, *J* = 17.2, 1.8 Hz, 1H), 4.99 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.84 (t, *J* = 6.6 Hz, 2H), 2.84 (t, *J* = 6.6 Hz, 2H), 2.72 – 2.68 (m, 2H), 2.40 – 2.35 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.0, 138.1, 135.8, 128.9, 128.6, 114.9, 63.7, 38.7, 35.5, 34.9. **IR** (neat): 3469, 2822, 2089, 1634, 1491, 1451, 1384, 1351, 913, 749, 699 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{12}H_{16}NaO$: 199.1099, found: 199.1089.

1f was synthesized based on the following method:

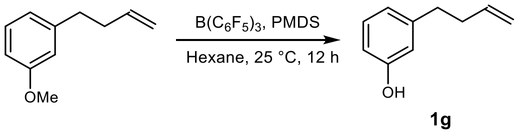


1f

To a solution of (4-(but-3-en-1-yl)phenyl)methanol (0.81 g, 5.0 mmol, 1.0 eq.) and Et_3N (1.26 g, 12.5 mmol, 2.5 eq.) in DCM (25 mL), MeCOCl (0.78 g, 10 mmol, 2 eq.) was added dropwise over 10 min at 0 °C. After stirring for an additional 20 min, the mixture was warmed to 25 °C and stirred for 12 h. The reaction was quenched with H_2O (10 mL), and extracted with DCM (3 × 20 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 30:1) to obtain the pure **1f** as a colorless oil (0.85 g, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 5.96 – 5.74 (m, 1H), 5.08 (s, 2H), 5.05 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.99 (dd, *J* = 10.2, 1.8 Hz, 1H), 2.78 – 2.68 (m, 2H), 2.46 – 2.32 (m, 2H), 2.10 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.9, 142.0, 137.9, 133.4, 128.6, 128.4, 115.0, 66.2, 35.3, 35.0, 21.0. **IR** (neat): 3444, 2931, 2085, 1738, 1633, 1598, 1516, 1491, 1384, 1352, 1228, 1020, 911 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{16}NaO_2$: 227.1048, found: 227.1043.

1g was synthesized based on the following method:

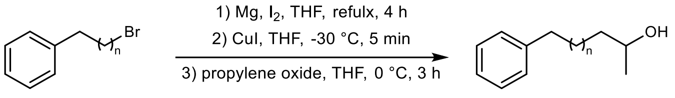


1g

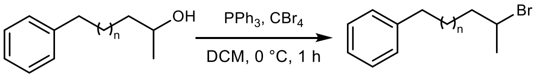
According to the reported literature,[19] pentamethyldisiloxane (1.85 g, 12.5 mmol, 2.5 eq.) was added to a solution of 1-(but-3-en-1-yl)-3-methoxybenzene (0.81 g, 5.0 mmol, 1.0 eq.) in hexanes (25 mL), and the mixture was stirred for 2 min. A solution of $B(C_6F_5)_3$ (21 mg, 0.04 mmol) in hexane (10 mL) was then added to the reaction mixture, and the reaction mixture was stirred at 25 °C for 12 h. The reaction was quenched with 1% HCl in EtOH (50 mL) and extracted with DCM (3 × 20 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 5:1) to provide the alkene **1g** as a colorless oil (0.45 g, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.13 (m, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.71 – 6.62 (m, 2H), 5.98 – 5.78 (m, 1H), 5.05 (dd, *J* = 17.2, 1.7 Hz, 1H), 4.99 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.83 (s, 1H), 2.74 – 2.62 (m, 2H), 2.44 – 2.26 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4, 143.8, 138.0, 129.5, 121.0, 115.3, 115.0, 112.8, 35.3, 35.2. **IR** (neat): 3524, 3016, 2921, 2089, 1634, 1489, 1383, 1351, 1157, 698 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{10}H_{12}NaO$:171.0786, found:171.0783.

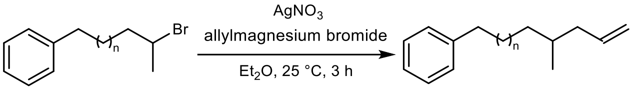
1v, **1x** and **1y** were synthesized based on the following method:



To a mixture of Mg (24.0 mmol, 1.2 eq.) and a grain of iodine, a solution of RBr (20.0 mmol, 1.0 eq.) in THF (50 mL) were added slowly under N_2. The mixture was refluxed for 4 h and then cooled to -30 °C. The solution was then added slowly to a mixture of CuI (20 mmol, 1.0 eq.) in THF (30 mL) and stirred for 5 min at -30 °C. Propylene oxide (20.0 mmol, 1.0 eq.) was added, and the reaction mixture was warmed to 0 °C and stirred for 3 h. The mixture was quenched with H_2O (30 mL) and extracted with EA (3 × 20 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 10:1) to obtain the desired alcohol.

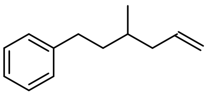


CBr_4 (8 mmol, 1.33 eq.) and alcohol (6.0 mmol, 1.0 eq.) were dissolved in dry DCM (10 mL). Then, PPh_3 (8 mmol, 1.33 eq.) was added portion-wise at 0 °C and the reaction mixture was stirred for additional 1 h. The mixture was quenched with H_2O (10 mL) and extracted with DCM (3 × 10 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE) to obtain the secondary alkyl bromide.



According to the reported literature,[20] anhydrous diethyl ether (15 mL) and alkyl bromide (5.0 mmol, 1.0 eq.) were added to silver nitrate (0.05 mmol, 0.01 eq.) under N_2. Allylmagnesium bromide (6.5 mmol, 2 M in THF, 3.25 mL, 1.3 eq.) was then added to the reaction mixture at 25 °C. The solution was stirred for 3 h. After the reaction was completed, the mixture was quenched with H_2O (10 mL) and extracted with EA (3 × 10 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE) to obtain the desired alkene.

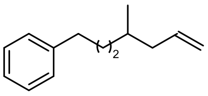
(3-methylhex-5-en-1-yl)benzene (1v)[21]



1v

Colorless oil, 0.42 g, 49% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.34 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 5.86 – 5.76 (m, 1H), 5.06 – 5.00 (m, 2H), 2.73 – 2.57 (m, 2H), 2.18 – 2.11 (m, 1H), 2.02 – 1.94 (m, 1H), 1.71 – 1.66 (m, 1H), 1.63 – 1.57 (m, 1H), 1.52 – 1.45 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 137.4, 128.33, 128.26, 125.6, 115.7, 41.3, 38.4, 33.4, 32.4, 19.4. **IR** (neat): 2925, 2362, 1630, 1496, 1455, 1379, 1350, 993, 911, 745, 697 cm^{-1}.

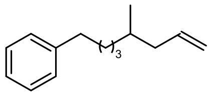
(4-methylhept-6-en-1-yl)benzene (1x)



1x

Colorless oil, 0.56 g, 60% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.21 – 7.11 (m, 3H), 5.88 – 5.69 (m, 1H), 5.12 – 4.80 (m, 2H), 2.60 – 2.56 (m, 2H), 2.09 – 2.03 (m, 1H), 1.91 – 1.85 (m, 1H), 1.64 – 1.48 (m, 3H), 1.41 – 1.34 (m, 1H), 1.22 – 1.15 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.8, 137.6, 128.4, 128.2, 125.6, 115.5, 41.3, 36.2, 32.7, 29.1, 19.4. **IR** (neat): 2963, 1630, 1458, 1384, 1350, 910, 762, 735 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{20}Na$: 211.1457, found: 211.1456.

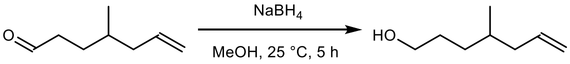
(5-methyloct-7-en-1-yl)benzene (1y)



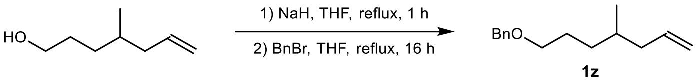
1y

Colorless oil, 0.56 g, 55% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.18 – 7.16 (m, 3H), 5.79 –5.75 (m, 1H), 5.04 – 4.89 (m, 2H), 2.60 (t, J = 7.8 Hz, 2H), 2.08 – 2.02 (m, 1H), 1.91 – 1.84 (m, 1H), 1.61 – 1.58 (m, 2H), 1.50 – 1.48 (m, 1H), 1.37 – 1.30 (m, 3H), 1.16 – 1.13 (m, 1H), 0.86 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.9, 137.7, 128.4, 128.2, 125.6, 115.4, 41.4, 36.3, 36.0, 32.7, 31.7, 26.8, 19.4. **IR** (neat): 2928, 2856, 1630, 1496, 1453, 1378, 1350, 911, 744, 697, 618 cm^{-1}. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{23}$: 203.1794, found: 203.1792.

1z and **1aa** was synthesized based on the following method:



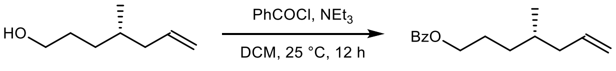
4-methylhept-6-enal was prepared according to the reported literature.[22] 4-Methylhept-6-enal (6.3 g, 50 mmol, 1.0 eq.) was dissolved in MeOH (100 mL). Then, $NaBH_4$ (2.2 g, 60 mmol, 1.2 eq.) was added portion-wise at 0 °C. The reaction was warmed to 25 °C and stirred for 5 h. After the reaction was completed, the mixture was quenched with H_2O (20 mL) and extracted with DCM (3 × 20 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA= 10:1) to obtain the desired alcohol (5.1 g, 79% yield).



A solution of 4-methylhept-6-en-1-ol (0.51 g, 4.0 mmol, 1.0 eq.) in THF (10 mL) was added dropwise to a suspension of NaH (0.24 g, a 60% dispersion in mineral oil, 6.0 mmol, 1.5 eq.) in THF (10 mL). The reaction mixture was heated to reflux for 1 h, and then benzyl bromide (0.86 g, 5 mmol, 1.2 eq.) was added. The resulting solution was refluxed for 16 h. After the reaction was completed, the mixture was quenched with H_2O (10 mL). The residue was extracted with EA (3 × 20 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 100:1) to obtain the desired product **1z** as a colorless oil (0.6 g, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 4H), 7.30 – 7.27 (m, 1H), 5.85– 5.73 (m, 1H), 5.02 – 4.97 (m, 2H), 4.51 (s, 2H), 3.46 (t, *J* = 6.7 Hz, 2H), 2.10 – 2.05 (m, 1H), 1.94 – 1.89 (m, 1H), 1.73 – 1.64 (m, 2H), 1.53 – 1.38 (m, 2H), 1.23 – 1.15 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 137.5, 128.3, 127.6, 127.5, 115.6, 72.9, 70.7, 41.3, 32.9, 32.7, 27.3, 19.4. **IR** (neat): 2367, 1630, 1512, 1463, 1394, 1350, 736, 695 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{22}ONa$: 241.1563, found: 241.1562.

(*S*)-**1aa** was synthesized based on the following method:



(*S*)-**1aa**

To a solution of (*S*)-4-methylhept-6-en-1-ol (0.64 g, 5.0 mmol, 1.0 eq.) and Et_3N (1.26 g, 12.5 mmol, 2.5 eq.) in DCM (25 mL), benzoyl chloride (1.4 g, 10 mmol, 2 eq.) was added dropwise for 20 min at 0 °C. After additional stirring for 20 min, the mixture was warmed to 25 °C and stirring was continued for 12 h. After the reaction was completed, the reaction was quenched with H_2O (10 mL), and extracted with DCM (3 × 20 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 30:1) to obtain the pure (*S*)-**1aa** as a colorless oil (0.56 g, 48% yield).

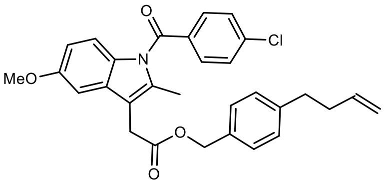
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H), 7.57 – 7.47 (m, 1H), 7.45 – 7.42 (m, 2H), 5.82 – 5.74 (m, 1H), 5.06 – 5.00 (m, 1H), 4.99 – 4.97 (m, 1H), 4.30 (t, *J* = 6.7 Hz, 2H), 2.11 – 2.05 (m, 1H), 1.97 – 1.90 (m, 1H), 1.86 – 1.70 (m, 2H), 1.66 – 1.54 (m, 1H), 1.52 – 1.45 (m, 1H), 1.33 – 1.21 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.6, 137.2, 132.8, 130.5, 129.5, 128.3, 115.8, 65.3, 41.2, 32.6, 32.5, 26.3, 19.3. **IR** (neat): 2925, 1630, 1382, 1350, 1273, 1111, 761, 709, 617 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{20}O_2Na$: 255.1356, found: 255.1353.

1ae, **1af**, **1ah**, and **1ai** were synthesized based on the following method:

$$R^1COOH + R^2OH \xrightarrow[\text{DCM, 25 °C, 12 h}]{\text{DMAP, DCC}} R^1COOR^2$$

Carboxylic acid (5 mmol) and corresponding alcohol (6 mmol, 1.2 eq.) were added sequentially to a solution of DCC (6 mmol, 1.2 eq.) and DMAP (0.025 mmol, 0.05 eq.) in anhydrous DCM (10 mL) under N_2. The reaction mixture was stirred for 12 h at 25 °C. After the reaction was completed, the mixture was quenched with H_2O (20 mL), and extracted with DCM (3 × 20 mL). The combined organic layer was dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 15:1) to obtain the pure product.

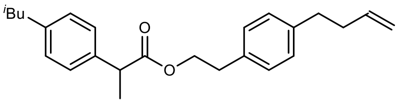
Indomethacin derivatives (1ae)



1ae

White solid, 2 g, 80% yield, mp: 94–95 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.98 – 5.84 (m, 1H), 5.15 (s, 2H), 5.08 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.02 (dd, *J* = 10.2, 1.7 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 2H), 2.76 – 2.45 (m, 2H), 2.44 – 2.36 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 168.3, 156.0, 142.1, 139.2, 137.8, 135.9, 133.9, 133.2, 131.2, 130.8, 130.6, 129.1, 128.6, 128.3, 115.1, 114.9, 112.5, 111.8, 101.1, 66.7, 55.6, 35.4, 35.0, 30.4, 13.4. **IR** (neat): 2954, 2931, 2868, 2365, 1734, 1631, 1604, 1514, 1383, 1349, 1242, 1118, 1071, 995, 912, 946, 801, 735, 630 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{28}ClNO_4Na$: 524.1599, found: 524.1597.

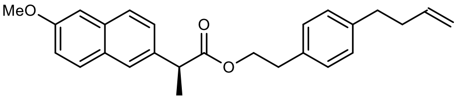
Ibuprofen derivatives (1af)



1af

Colorless oil, 1.09 g, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.1 Hz, 2H), 7.11 – 7.03 (m, 4H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.84 (m, 1H), 5.03 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.00 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.32 – 4.17 (m, 2H), 3.66 (q, *J* = 7.2 Hz, 1H), 2.86 – 2.82 (m, 2H), 2.68 – 2.64 (m, 2H), 2.45 (d, *J* = 7.1 Hz, 2H), 2.37 – 2.31 (m, 2H), 1.90 – 1.78 (m, 1H), 1.45 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 140.4, 139.9, 138.0, 137.7, 135.2, 129.2, 128.8, 128.4, 127.2, 114.8, 65.2, 45.1, 45.0, 35.4, 34.9, 34.6, 30.1, 22.4, 18.4. **IR** (neat): 2924, 2868, 2362, 1727, 1631, 1615, 1509, 1473, 1456, 1444, 1389, 1350, 1321, 1264, 1190, 1144, 1130, 1048, 997, 910, 843, 803, 763, 586 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{32}O_2Na$: 387.2295, found: 387.2291.

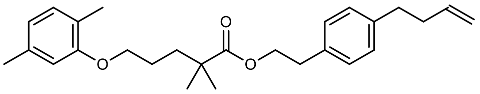
Naproxen derivatives (1ah)



1ah

White solid, 0.77 g, 40% yield, mp: 82–83 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.7, 2.6 Hz, 2H), 7.63 (d, *J* = 1.8 Hz, 1H), 7.36 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.19 – 7.09 (m, 2H), 6.96 (s, 4H), 5.84 – 5.82 (m, 1H), 5.04 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.00 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.34 – 4.20 (m, 2H), 3.91 (s, 3H), 3.82 (q, *J* = 7.2 Hz, 1H), 2.65 – 2.57 (m, 2H), 2.73 – 2.58 (m, 2H), 2.34 – 2.28 (m, 2H), 1.55 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 157.6, 139.9, 138.1, 135.6, 135.1, 133.7, 129.3, 128.9, 128.8, 128.4, 127.1, 126.3, 126.0, 118.9, 114.8, 105.6, 65.3, 55.3, 45.5, 35.4, 34.9, 34.6, 18.4. **IR** (neat): 2361, 2343, 1731, 1631, 1606, 1506, 1485, 1457, 1418, 1388, 1350, 1264, 1231, 1175, 1091, 1032, 912, 851, 810, 743, 668 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{28}O_3Na$: 411.1931, found: 411.1927.

Gemfibrozil derivatives (1ai)

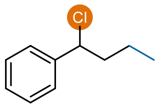


1ai

Colorless oil, 1.35 g, 66% yield. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.18 – 7.06 (m, 4H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.68 – 6.60 (m, 1H), 6.58 (d, *J* = 1.6 Hz, 1H), 5.90 – 5.78 (m, 1H), 5.04 (dd, *J* = 17.2, 1.8 Hz, 1H), 4.98 (dd, *J* = 9.9, 1.8 Hz, 1H)., 4.26 (t, *J* = 7.0 Hz, 2H), 3.84 (q, *J* = 3.2 Hz, 2H), 2.90 (t, *J* = 6.9 Hz, 2H), 2.70 – 2.66 (m, 2H), 2.37 – 2.31 (m, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.69 – 1.67 (m, 4H), 1.17 (s, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 177.7, 156.9, 140.0, 138.0, 136.4, 135.3, 130.3, 128.8, 128.5, 123.5, 120.6, 114.9, 111.9, 67.9, 65.0, 42.0, 37.1, 35.5, 34.9, 34.7, 25.14, 25.10, 21.4, 15.8. **IR (neat)**: 1734, 1630, 1477, 1457, 1352, 1323, 1261, 1223, 1142, 1088, 1067, 1036, 912, 755, 617 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{27}H_{36}O_3Na$: 431.2557, found: 431.2554.

4. Procedure for remote hydrochlorination of alkenes

(1–chlorobutyl)benzene (2a)[23]

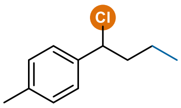


2a

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 65% yield (10.9 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 4H), 7.25 – 7.17 (m, 1H), 4.79 (dd, *J* = 8.2, 6.4 Hz, 1H), 2.17 – 2.10 (m, 1H), 2.03 – 1.96 (m, 1H), 1.54 – 1.29 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 128.6, 128.2, 126.8, 63.6, 42.1, 20.4, 13.5.

1–(1–chlorobutyl)–4–methylbenzene (2b)



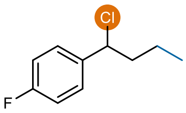
2b

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 60% yield (11.0 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.85 (dd,

J = 8.1, 6.5 Hz, 1H), 2.34 (s, 3H), 2.17 – 2.09 (m, 1H), 2.04 – 1.95 (m, 1H), 1.56 – 1.40 (m, 1H), 1.43 – 1.23 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.1, 138.0, 129.2, 126.8, 63.6, 42.0, 21.1, 20.4, 13.4. **IR** (neat): 2960, 2359, 1631, 1515, 1457, 1351 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{11}H_{15}ClNa$: 205.0755, found: 205.0751.

1–(1–chlorobutyl)–4–fluorobenzene (2c)

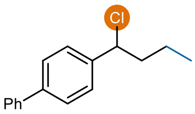


2c

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 62% yield (11.5 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.06 – 7.01 (m, 2H), 4.85 (dd, J = 8.2, 6.5 Hz, 1H), 2.13 – 2.06 (m, 1H), 2.02 – 1.93 (m, 1H), 1.54 – 1.45 (m, 1H), 1.39 – 1.29 (m, 1H), 0.94 (t, J = 7.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ – 113.8. **^{13}C NMR** (101 MHz, $CDCl_3$) δ162.4 (d, J = 247.1 Hz), 137.9 (d, J = 3.3 Hz), 128.7 (d, J = 8.3 Hz), 115.5 (d, J = 21.6 Hz), 62.7, 42.1, 20.3, 13.4. **IR** (neat): 2362, 1630, 1603, 1384, 1351,762, 668 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{10}H_{12}ClFNa$: 209.0509, found: 209.0501.

4–(1–chlorobutyl)–1,1'–biphenyl (2d)



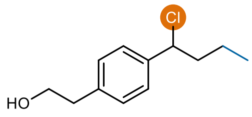
2d

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred

to a second 1-dram vial. To this vial, Et$_3$SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and CuCl$_2$·2H$_2$O (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 63% yield (15.4 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et$_3$N in PE.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62 – 7.58 (m, 4H), 7.48 – 7.41 (m, 4H), 7.38 – 7.35 (m, 1H), 4.92 (dd, *J* = 8.2, 6.4 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.11 – 2.02 (m, 1H), 1.59 – 1.52 (m, 1H), 1.46 – 1.39 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 141.13, 140.96, 140.6, 128.8, 127.43, 127.38, 127.33, 127.1, 63.3, 42.0, 20.3, 13.5. **IR** (neat): 2924, 2362, 1630, 1384, 1350, 762, 668 cm^{-1}. **HRMS** (ESI): m/z [M]$^+$ calcd for C$_{16}$H$_{17}$Cl: 244.1013, found: 244.1009.

(4–(1–chlorobutyl)phenyl)methanol (2e)

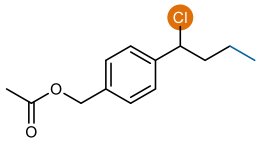


2e

In a N$_2$-filled glovebox, Pd(PhCN)$_2$Cl$_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et$_3$SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and CuCl$_2$·2H$_2$O (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 10:1) to obtain the title compound as colorless oil in 61% yield (13.0 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et$_3$N in PE.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.26 (m, 2H), 7.25 – 7.16 (m, 2H), 4.86 (dd, J = 8.2, 6.5 Hz, 1H), 3.87 (t, *J* = 6.5 Hz, 2H), 2.87 (t, *J* = 6.5 Hz, 2H), 2.13 – 2.07 (m, 1H), 2.04 – 1.96 (m, 1H), 1.53 – 1.46 (m, 1H), 1.37 – 1.32 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 140.2, 138.6, 129.2, 127.2, 63.5, 63.4, 42.0, 38.8, 20.3, 13.4. **IR** (neat): 2360, 1630, 1457, 1386, 1350, 1117, 762, 619 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for C$_{12}$H$_{17}$ClONa: 235.0860, found: 235.0862.

4–(1–chlorobutyl)benzyl acetate (2f)

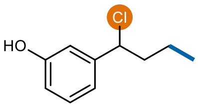


2f

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2\cdot2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 30:1) to obtain the title compound as colorless oil in 62% yield (15.0 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 5.10 (s, 2H), 4.86 (dd, *J* = 8.2, 6.4 Hz, 1H), 2.18 – 2.07 (m, 4H), 2.04 – 1.97 (m, 1H), 1.49 – 1.46 (m, 1H), 1.40 – 1.34 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 142.0, 135.9, 128.5, 127.2, 65.8, 63.1, 42.0, 21.0, 20.3, 13.4. **IR** (neat): 2927, 2259, 2342, 1631, 1457, 1385, 1351 cm^{-1}. **HRMS** (ESI): m/z $[M]^+$ calcd for $C_{13}H_{17}ClO_2$: 240.0912, found: 240.0913.

3–(1–chlorobutyl)phenol (2g)

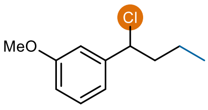


2g

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2\cdot2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 5:1) to obtain the title compound as brown oil in 57% yield (11.0 mg, 95% purity, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 1H), 6.96 – 6.92 (m, 1H), 6.90 – 6.84 (m, 1H), 6.80 – 6.75 (m, 1H), 4.84 – 4.76 (m, 2H), 2.10 – 2.04 (m, 1H), 2.02 – 1.97 (m, 1H), 1.52 – 1.45 (m, 1H), 1.40 – 1.32 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.6, 143.8, 129.8, 119.5, 115.2, 113.9, 63.1, 42.0, 20.2, 13.4. **IR** (neat): 2932, 1631, 1456, 1380, 1531 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{10}H_{13}ClONa$: 207.0547, found: 207.0540.

1–(1–chlorobutyl)–3–methoxybenzene (2h)

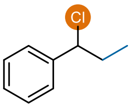


2h

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 30:1) to obtain the title compound as colorless oil in 61% yield (12.1 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 6.97 – 6.92 (m, 2H), 6.82 (m, 1H), 4.76 (dd, J = 8.1, 6.4 Hz, 1H), 3.82 (s, 3H), 2.17 – 2.06 (m, 1H), 2.04 – 1.95 (m, 1H), 1.53 – 1.45 (m, 1H), 1.42 – 1.30 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 143.5, 129.6, 119.3, 113.6, 112.6, 63.4, 55.3, 42.0, 20.3, 13.4. **IR** (neat): 2924, 2853, 2361, 1631, 1457, 1382, 1350, 761 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{11}H_{15}ClONa$: 221.0704, found: 221.0706.

(1–chloropropyl)benzene (2i)[23]

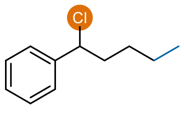


2i

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 62% yield (9.6 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 4.83 (dd, *J* =7.1 Hz, 1H), 2.17 – 2.01 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 128.5, 128.1, 126.8, 65.4, 33.2, 11.7.

(1–chloropentyl)benzene (2j, 2r, 2s)[24]

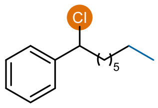


2j

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 62% yield (11.3 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 7.25 – 7.16 (m, 1H), 4.77 (dd, *J* = 8.1, 6.5 Hz, 1H), 2.15 – 1.90 (m, 2H), 1.48 – 1.16 (m, 4H), 0.82 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 128.6, 128.2, 127.0, 63.9, 39.8, 29.2, 22.1, 13.9.

(1–chlorooctyl)benzene (2k)[25]



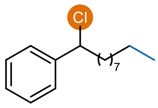
2k

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred

to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 47% yield (10.5 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 4H), 7.26 – 7.16 (m, 1H), 4.77 (dd, *J* = 8.0, 6.5 Hz, 1H), 2.11 – 1.88 (m, 2H), 1.26 – 1.17 (m, 10H), 0.80 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 128.6, 128.2, 127.0, 63.9, 40.0, 31.8, 29.1, 29.0, 27.1, 22.6, 14.1.

(1-chlorodecyl)benzene (2l)

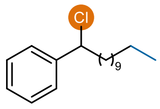


2l

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 44% yield (11.1 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 4H), 7.26 – 7.16 (m, 1H), 4.77 (dd, *J* = 8.0, 6.5 Hz, 1H), 2.18 – 2.08 (m, 1H), 2.06 – 1.97 (m, 1H), 1.49 – 1.45 (m, 1H), 1.26 – 1.17 (m ,13H), 0.80 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.0, 128.6, 128.2, 126.9, 63.9, 40.0, 31.9, 29.5, 29.4, 29.3, 29.0, 27.1, 22.7, 14.1. **IR** (neat): 3445, 1593, 1385, 1352, 517 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{16}H_{25}ClNa$: 275.1542, found: 275.1538.

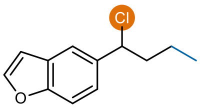
(1-chlorododecyl)benzene (2m)


2m

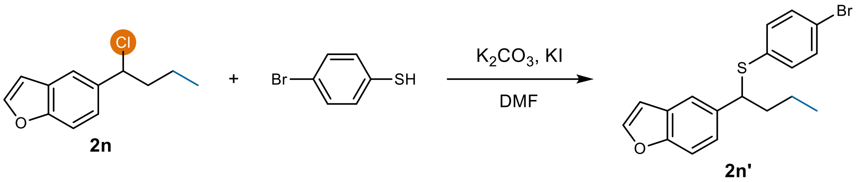
In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 42% yield (11.8 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 4H), 7.26 – 7.16 (m, 1H), 4.77 (dd, *J* = 8.0, 6.5 Hz, 1H), 2.18 – 2.08 (m, 1H), 2.07 – 1.97 (m, 1H), 1.49 – 1.45 (m, 1H), 1.26 – 1.17 (m ,17H), 0.80 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.0, 128.6, 128.2, 126.9, 63.9, 40.0, 31.9, 29.6, 29.5, 29.4, 29.3, 29.0, 27.1, 22.7, 14.1. **IR** (neat): 3483, 2822, 2099, 1593, 1385, 1532 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{29}ClNa$: 303.1855, found: 303.1852.

5-(1-chlorobutyl)benzofuran (2n)


2n

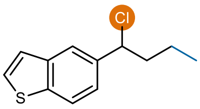
In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated. The product is prone to decomposition on silica gel, and the yield (52%) is determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.



To confirm the structure of the product, we transformed it into the corresponding thioether. The crude product was dissolved in anhydrous DMF (1 mL), and then 4-bromothiophenol (38 mg, 0.2 mmol, 2 eq.), potassium iodide (KI, 41.5 mg, 0.25 mmol, 2.5 eq.), and potassium carbonate (K_2CO_3, 34.5 mg, 0.25 mmol, 2.5 eq.) were added. The reaction mixture was heated at 80 °C for 24 h. The reaction was monitored by TLC. After the reaction was completed, the mixture was quenched with H_2O (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phase was dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (PE) to obtain the pure product **2n′** as colorless oil in 40% yield (14.4 mg, in two steps).

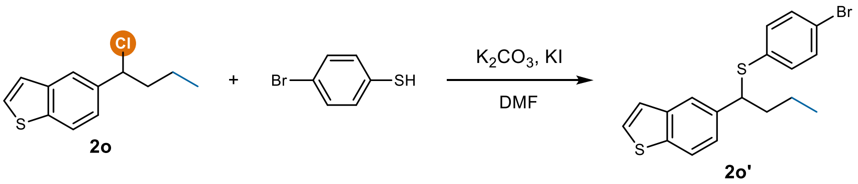
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.31 – 7.26 (m, 2H), 7.20 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.70 (dd, *J* = 2.2, 1.0 Hz, 1H), 4.21 (dd, *J* = 8.8, 6.2 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.38 – 1.28 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ154.1, 145.4, 136.4, 134.5, 133.7, 131.7, 127.4, 124.2, 121.0, 120.2, 111.3, 106.6, 53.6, 38.8, 20.8, 13.7. **IR** (neat): 3451, 2823, 2909, 1594, 1384, 1352, 519 cm^{-1}. **HRMS** (ESI): m/z $[M]^+$ calcd for $C_{18}H_{17}BrOS$: 360.0183, found: 360.0180.

5-(1-chlorobutyl)benzo[b]thiophene (2o)



2o

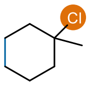
In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 ℃ for 12 h. After this time, the reaction was concentrated. The product is prone to decomposition on silica gel, and the yield (54%) is determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.



To confirm the structure of the product, we transformed it into the corresponding thioether. The crude product was dissolved in anhydrous DMF (1 mL), and then 4-bromothiophenol (38 mg, 0.2 mmol, 2 eq.), potassium iodide (KI, 41.5 mg, 0.25 mmol, 2.5 eq.), and potassium carbonate (K_2CO_3, 34.5 mg, 0.25 mmol, 2.5 eq.) were added. The reaction mixture was heated at 80 °C for 24 h. The reaction was monitored by TLC. After the reaction was completed, the mixture was quenched with H_2O (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phase was dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (PE) to obtain the pure product **2o′** as colorless oil in 44% yield (16.5 mg, in two steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 1.7 Hz, 1H), 7.42 (d, J = 5.4 Hz, 1H), 7.28 – 7.25 (m, 4H), 7.12 – 7.05 (m, 2H), 4.22 (dd, J = 8.8, 6.3 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.39 – 1.26 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.6, 138.5, 138.1, 134.4, 133.7, 131.7, 126.8, 124.2, 123.8, 122.7, 122.5, 121.1, 53.6, 38.6, 20.8, 13.7. **IR** (neat): 3448, 2106, 1593, 1471, 1384, 1350, 1090 cm^{-1}. **HRMS** (ESI): m/z $[M]^+$ calcd for $C_{18}H_{17}BrS_2$: 375.9955, found: 375.9949.

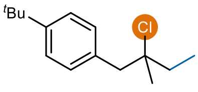
1-chloro-1-methylcyclohexane (2t)



2t

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (1.9 mg, 0.005 mmol), *rac*-BINAP (3.7 mg, 0.006 mmol) and *d*$_4$-DCE (0.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After the reaction was completed and detected by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard (56% yield). **^{1}H NMR** (500 MHz, *d*$_4$-DCE) δ 1.96 – 1.86 (m, 2H), 1.80 – 1.61 (m, 3H), 1.60 (s, 3H), 1.58 – 1.51 (m, 4H), 1.24 – 1.16 (m, 1H), **^{13}C NMR** (126 MHz, *d*$_4$-DCE) δ 74.2, 43.2, 35.3, 26.8, 23.4. The data was accordance with literature reports.[26]

1–(tert–butyl)–4–(2–chloro–2–methylbutyl)benzene (2u)

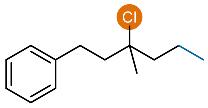


2u

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 58% yield (13.8 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 2H), 7.20 – 7.18 (m, 2H), 3.09 – 3.00 (m, 2H), 1.84 – 1.70 (m, 2H), 1.48 (s, 3H), 1.32 (s, 9H), 1.09 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.5, 133.8, 130.5, 124.8, 74.8, 49.4, 36.3, 34.4, 31.4, 29.0, 9.3. **IR** (neat): 2966, 1631, 1382, 1384, 1350, 1110, 911, 763 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{23}ClNa$: 261.1381, found: 261.1377.

(3–chloro–3–methylhexyl)benzene (2v)

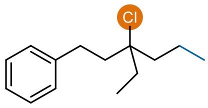


2v

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 61% yield (12.9 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 2.81 – 2.76 (m, 2H), 2.03 – 1.99 (m, 2H), 1.86 – 1.70 (m, 2H), 1.59 (s, 3H), 1.57 – 1.40 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 128.44, 128.39, 125.9, 74.3, 46.5, 46.0, 31.2, 29.8, 18.0, 14.3. **IR** (neat): 2361, 1630, 1384, 1350, 913, 744, 697, 618 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{19}ClNa$: 233.1068, found: 233.1064.

(4-chloro-4-ethylheptyl)benzene (2w)

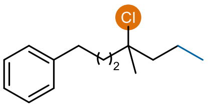


2w

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 56% yield (12.6 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), δ 7.20 – 7.19 (m, 3H), 2.77 – 2.69 (m, 2H), 2.06 – 2.00 (m, 2H), 1.86 (q, $J = 7.4$ Hz, 2H), 1.83 – 1.75 (m, 2H), 1.50 – 1.41 (m, 2H), 1.01 (t, $J = 7.4$ Hz, 3H), 0.95 (t, $J = 7.3$ Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.9, 128.5, 128.4, 125.9, 78.5, 43.0, 42.9, 33.9, 30.8, 17.6, 14.3, 8.8. **IR (neat)**: 3452, 2823, 2089, 1593, 1384, 1352, 518, 1593 cm^{-1}. **HRMS** (ESI): m/z $[M]^+$ calcd for $C_{14}H_{21}Cl$: 224.1332, found: 224.1330.

(4–chloro–4–methylheptyl)benzene (2x)

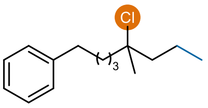


2x

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 59% yield (13.3 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 2.65 – 2.61 (m, 2H), 1.79 – 1.73 (m, 3H), 1.72 – 1.67 (m, 3H), 1.50 (s, 3H), 1.48 – 1.37 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.1, 128.4, 128.3, 125.8, 74.8, 46.3, 43.6, 36.0, 29.8, 26.5, 18.0, 14.2. **IR** (neat): 2361, 1630, 1382, 1350, 736, 698 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{21}ClNa$: 247.1229, found: 247.1221.

(5–chloro–5–methyloctyl)benzene (2y)



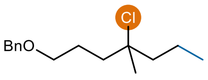
2y

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred

to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 58% yield (13.9 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 2.66 – 2.62 (m, 2H), 1.80 – 1.76 (m, 2H),1.71 – 1.58 (m, 4H), 1.55 – 1.41 (m, 7H). 0.94 (d, *J* = 7.3 Hz, 3H.) **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 128.4, 128.3, 125.7, 75.0, 46.4, 44.0, 35.9, 31.7, 29.8, 24.4, 18.0, 14.3. **IR** (neat): 2958, 1630, 1458, 1381, 1350, 762, 735 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{23}ClNa$: 261.1386, found: 261.1379.

(((4–chloro–4–methylheptyl)oxy)methyl)benzene (2z)

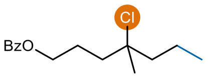


2z

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 50:1) to obtain the title compound as colorless oil in 60% yield (15.3 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.29 – 7.26 (m, 1H), 4.51 (s, 2H), 3.51 – 3.48 (m, 2H), 1.86 – 1.66 (m, 6H), 1.50 (s, 3H), 1.52 – 1.44 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5, 128.4, 127.6, 127.5, 74.7, 72.9, 70.3, 46.4, 40.7, 29.8, 25.2, 18.0, 14.2. **IR** (neat): 2369, 1630, 1506, 1456, 1386, 1351, 1102, 761, 734, 695 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{23}ClONa$: 277.1330, found: 277.1327.

5–chloro–5–methyloctyl benzoate (2aa)

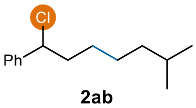


2aa

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 30:1) to obtain the title compound as colorless oil in 58% yield (15.6 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.58 – 7.55 (m, 1H), 7.47 – 7.43 (m, 2H), 4.35 (t, *J* = 6.2 Hz, 2H), 2.00 – 1.94 (m, 2H), 1.92 – 1.85 (m, 2H), 1.79 – 1.73 (m, 2H), 1.55 (s, 3H), 1.52 – 1.42 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 132.9, 130.3, 129.5, 128.4, 70.0, 64.9, 46.4, 40.5, 29.7, 24.3, 18.0, 14.2. **IR** (neat): 2925, 1630, 1486, 1385, 1350, 1116, 911, 836, 763, 733, 696, 617 cm^{-1}. **HRMS** (ESI): m/z $[M]^+$ calcd for $C_{15}H_{21}ClO_2$: 268.1432, found: 268.1428.

chloro-6-methylheptyl)benzene (2ab)

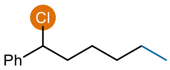


2ab

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 ℃ for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil as a 4 :1 mixture of **2ab** and **2ab'** in 51% yield (11.5 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (500 MHz, $CDCl_3$) 7.38 – 7.28 (m, 5.4H), 7.19 – 7.15 (m, 0.9H), 4.84 (dd, *J* = 8.1, 6.5 Hz, 1H), 2.66 – 2.62 (m, 0.56H), 2.16 – 2.09 (m, 1H), 2.06 – 1.99 (m, 1H), 1.74 – 1.71 (m, 0.58H), 1.68 – 1.62 (m, 0.6H), 1.55 (s, 1.8H), 1.56 – 1.45 (m, 2H), 1.36 – 1.24 (m, 4.6H), 1.17 – 1.13 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.7, 142.0, 128.6, 128.4, 128.3, 128.2, 127.0, 125.7, 76.8, 71.3, 63.9, 46.0, 40.1, 38.7, 35.9, 31.4, 29.7, 27.9, 27.3, 26.8, 25.0, 22.6. **IR** (neat): 3470, 3015, 2090, 1635, 1506, 1489, 1455, 1384, 1351, 695 cm^{-1}. **HRMS** (ESI): m/z $[M]^+$ calcd for $C_{14}H_{21}ClNa$: 247.1229, found: 247.1227.

(1-chlorohexyl)benzene (2ac)[27]

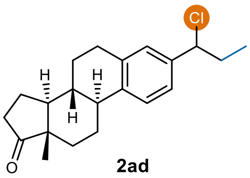


2ac

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2 \cdot 2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 52% yield (10.2 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 4.85 (dd, *J* = 8.1, 6.6 Hz, 1H), 2.17 –2.08, (m, 1H), 2.06 – 1.96 (m, 1H), 1.56 – 1.41 (m, 1H), 1.38 – 1.24 (m, 5H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.1, 128.6, 128.3, 127.0, 64.1, 40.1, 31.4, 27.0, 22.6, 14.1.

Estrone derivatives (2ad)

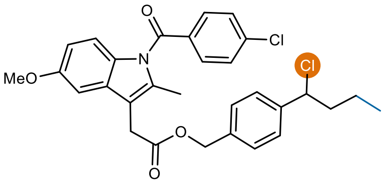


2ad

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2 \cdot 2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 10:1) to obtain the title compound as viscous liquid in 63% yield (20.8 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.7 Hz, 1H),7.18 – 7.14 (m, 1H), 7.03 (t, *J* = 2.8 Hz, 1H), 4.67 (dd, *J* = 8.0, 6.3 Hz, 1H), 2.85 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.43 – 2.40 (m, 1H), 2.39 – 2.28 (m, 1H), 2.23 (td, *J* = 10.7, 4.2 Hz, 1H), 2.14 – 1.96 (m, 5H), 1.68 – 1.31 (m, 7H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.8, 139.9, 139.3, 136.8, 127.6, 125.7, 124.4, 65.5, 50.5, 48.0, 44.4, 38.1, 35.9, 33.0, 31.6, 29.7, 26.5, 25.7, 21.6, 13.8, 11.9. **IR** (neat): 2931. 2853, 1631, 1457, 1385, 1351, 1115, 761 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{27}ClONa$: 353.1643, found: 353.1640.

Indomethacin derivatives (2ae)



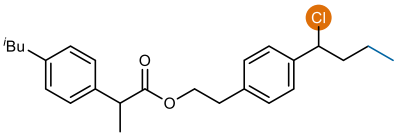
2ae

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2 \cdot 2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 5:1) to obtain the title compound as viscous liquid in 50% yield (26.9 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 2H), 7.48 – 7.45 (m, 2H), 7.35 – 7.33 (m, 2H), 7.29 – 7.26 (m, 2H), 6.93 – 6.88 (m, 2H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.13

(s, 2H), 4.85 (dd, $J = 8.2, 6.4$ Hz, 1H), 3.76 (s, 3H), 3.71 (s, 2H), 2.37 (s, 3H), 2.15 – 2.06 (m, 1H), 2.02 – 1.93 (m, 1H), 1.51 – 1.46 (m, 1H), 1.42 – 1.28 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.6, 168.3, 156.1, 142.2, 139.3, 136.0, 135.7, 133.9, 131.2, 130.8, 130.6, 129.1, 128.4, 127.2, 115.0, 112.4, 111.9, 101.2, 66.3, 63.0, 55.7, 42.0, 30.4, 20.3, 13.45, 13.40. **IR** (neat): 2361, 1676, 1654, 1617, 1571, 1541, 1458, 1395, 1382, 1350, 736, 698 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{30}H_{29}Cl_2NO_4Na$: 560.1366, found: 560.1362.

Ibuprofen derivatives (2af)

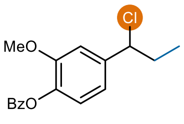


2af

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel gel (PE/EA = 20:1) to obtain the title compound as colorless oil in 42% yield (16.9 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 7.16 – 7.14 (m, 2H), 7.09 – 7.06 (m, 4H), 4.83 (dd, $J = 8.3, 6.3$ Hz, 1H), 4.35 – 4.18 (m, 2H), 3.66 (q, $J = 7.2$ Hz, 1H), 2.90 – 2.84 (m, 2H), 2.45 (d, $J = 7.2$ Hz, 2H), 2.17 – 1.78 (m, 3H), 1.42 – 1.27 (m, 5H), 0.98 – 0.86 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 140.5, 140.2, 137.9, 137.6, 129.3, 129.1, 127.2, 127.0, 64.9, 63.4, 45.1, 45.0, 42.0, 34.7, 30.2, 22.4, 20.3, 18.4, 13.4. **IR** (neat): 1773, 1631, 1457, 1384, 1351, 1161, 617 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{33}ClO_2Na$: 423.2061, found: 423.2061.

Eugenol derivatives (2ag)

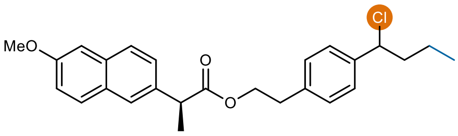


2ag

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 20:1) to obtain the title compound as green solid in 43% yield (13.0 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

mp: 68–69 °C, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 – 8.18 (m, 2H), 7.68 – 7.59 (m, 1H), 7.53 – 7.50 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 7.00 – 6.98 (m, 1H), 4.79 (dd, *J* = 8.0, 6.3 Hz, 1H), 3.84 (s, 3H), 2.23 – 2.01 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.6, 151.4, 140.7, 139.7, 135.5, 130.3, 129.3, 128.5, 122.8, 119.3, 111.2, 65.2, 56.0, 33.4, 11.7. **IR** (neat): 2362, 1630, 1385, 1384, 1350, 762, 668 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{17}ClO_3Na$: 327.0758, found: 327.0755.

Naproxen derivatives (2ah)

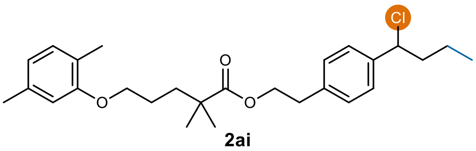


2ah

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 20:1) to obtain the title compound as white solid in 48% yield (20.4 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

mp: 80–81°C, ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.06 (m, 2H), 7.63 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.35 (m, 1H), 7.19 – 7.06 (m, 4H) 7.01 – 6.93 (m, 2H), 4.77 (dd, *J* = 6.3, 1.7 Hz, 1H), 4.35 – 4.18 (m, 2H), 3.92 (s, 3H), 3.90 – 3.77 (m, 1H), 2.85 – 2.82 (m, 2H), 2.12 – 1.99 (m, 1H), 1.98 – 1.85 (m, 1H), 1.55 (d, *J* = 7.1 Hz, 3H), 1.50 – 1.47 (m, 1H), 1.35 – 1.28 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 174.5, 157.6, 140.1, 137.8, 133.7, 129.3, 129.1, 128.9, 127.2, 126.9, 126.2, 126.0, 119.0, 105.6, 65.0, 63.4, 55.3, 45.5, 41.9, 34.6, 20.3, 18.2, 13.4. **IR** (neat): 1631, 1385, 1350, 913, 762 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{26}H_{29}ClO_3Na$: 447.1697, found: 447.1695.

Gemfibrozil derivatives (2ai)

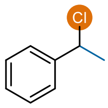


2ai

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 20:1) to obtain the title compound as colorless oil in 43% yield (19.1 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.2 (m, 2H), 7.23 – 7.16 (m, 2H), 7.10 – 6.90 (m, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 1.6 Hz, 1H), 4.82 (dd, *J* = 8.2, 6.4 Hz, 1H), 4.27 (t, *J* = 6.9 Hz, 2H), 3.91 – 3.82 (m, 2H), 2.93 (t, *J* = 6.9 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 2.09 –2.01 (m, 1H), 1.99 – 1.93 (m, 1H), 1.68 – 1.65 (m, 4H), 1.57 – 1.40 (m, 1H), 1.40 – 1.23 (m, 1H), 1.17 (s, 6H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 177.7, 156.9, 140.3, 138.0, 136.5, 130.3, 129.1, 127.0, 123.5, 120.7, 111.9, 67.8, 64.6, 63.3, 42.0, 41.9, 37.1, 34.8, 25.14, 25.12, 25.09, 21.4, 20.3, 15.8, 13.4. **IR** (neat): 2925, 1727, 1631, 1614, 1508, 1473, 1414, 1389, 1350, 1321, 1264, 1191, 1144, 1130, 1048, 997, 909, 803, 762, 735 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{25}H_{37}ClO_2Na$: 423.2061, found: 423.2059.

(1–chloroethyl)benzene (4a)[23]

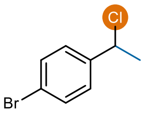


4a

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 78% yield (11.0 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 –7.30 (m, 2H),7.24 –7.19 (m, 1H), 5.09 (q, *J* = 6.8 Hz, 1H) 1.85 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 128.6, 128.3 126.5, 58.8, 26.4.

1–bromo–4–(1–chloroethyl)benzene (4b)[28]

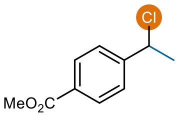


4b

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 80% yield (17.4 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.33 – 7.25 (m, 2H), 5.04 (q, *J* = 6.8 Hz, 1H), 1.82 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 131.8, 128.3, 122.1, 57.8, 26.4.

Methyl 4–(1–chloroethyl)benzoate (4c)[28]

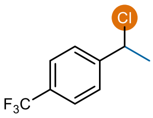


4c

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 50:1) to obtain the title compound as colorless oil in 80% yield (15.9 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.52 – 7.45 (m, 2H), 5.10 (q, *J* = 6.8 Hz, 1H), 3.92 (s, 3H), 1.85 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 147.6, 132.2, 130.0, 126.6, 57.8, 52.3, 26.4.

1–(1–chloroethyl)–4–(trifluoromethyl)benzene (4d)[23]

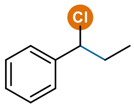


4d

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 68% yield (14.2 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 5.11 (q, *J* = 6.8 Hz, 1H), 1.85 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3, 130.4 (q, *J* = 32 Hz), 127.5, 126.0, 124.5, 57.4, 26.4.

(1–chloropropyl)benzene (4e)[23]

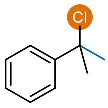


4e

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 63% yield (9.7 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (m, 5H), 4.83 (dd, *J* =7.1 Hz, 1H), 2.17 – 2.01 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 128.5, 128.1, 126.8, 65.4, 33.2, 11.7.

(2–chloropropan–2–yl)benzene (4f)[29]

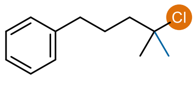


4f

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 60% yield (9.2 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.27 – 7.10 (m, 3H), 1.99 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 127.2, 125.6, 123.2, 71.5, 30.6.

(4–chloro–4–methylpentyl)benzene (4g)[30]

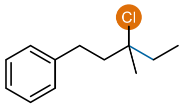


4g

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 62% yield (12.2 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 2.65 (t, *J* = 7.1 Hz, 2H), 1.91 – 1.74 (m, 4H), 1.57 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 128.3, 128.2, 125.8, 70.8, 45.5, 35.8, 32.4, 26.9.

(3–chloro–3–methylpentyl)benzene (4h)[31]

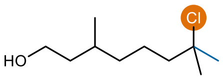


4h

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE) to obtain the title compound as colorless oil in 63% yield (12.4 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.28 – 7.25 (m, 3H), 2.96 – 2.74 (m, 2H), 2.17 – 1.98 (m, 2H), 1.96 – 1.80 (m, 2H), 1.65 (s, 3H), 1.10 (t, *J* = 7.4 Hz, 3H) **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 128.6, 128.3, 126.1, 74.6, 45.7, 37.0, 31.3, 29.3, 9.3.

7–chloro–3,7–dimethyloctan–1–ol (4i)[32]

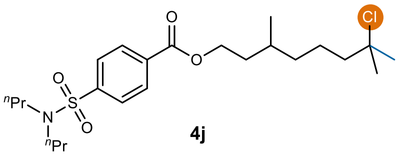


4i

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 10:1) to obtain the title compound as colorless oil in 70% yield (13.4 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 – 3.69 (m, 2H), 1.82 – 1.67 (m, 2H), 1.64 – 1.57 (m, 2H), 1.57 (s, 6H), 1.50 – 1.36 (m, 5H), 1.36 – 1.30 (m, 1H), 0.91 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 71.3, 61.2, 46.2, 40.1, 37.2, 32.5, 29.4, 22.7, 19.6.

Probenecid derivatives (4j)



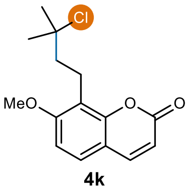
4j

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2·2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 15:1) to obtain the title compound as colorless oil in 72% yield

(33.0 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.09 (m, 2H), 7.91 – 7.81 (m, 2H), 4.46 – 4.33 (m, 2H), 3.14 – 3.05 (m, 4H), 1.90 – 1.79 (m, 1H), 1.77 – 1.60 (m, 4H), 1.59 – 1.50 (m, 12H), 1.42 –1.34 (m, 1H), 1.28 – 1.19 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** δ 165.3, 144.2, 133.7, 130.2, 127.0, 71.1, 64.1, 49.9, 46.2, 36.9, 35.4, 32.5, 29.9, 22.4, 21.9, 19.5, 11.1. **IR** (neat): 2967, 1718, 1631, 1457, 1385, 1350, 1273, 1159, 1106, 764, 742 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{23}H_{38}ClNO_4SNa$: 482.2102, found: 482.2101.

Osthole derivatives (4k)

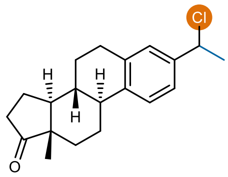


4k

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 5:1) to obtain the title compound as white solid in 63% yield (17.7 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 9.5 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.17 (d, *J* = 9.5 Hz, 1H), 3.86 (s, 3H), 3.00 – 2.91 (m, 2H), 1.99 – 1.87 (m, 2H), 1.62 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2, 160.3, 152.9, 143.8, 126.5, 117.7, 112.9, 112.8, 107.2, 70.73, 70.71, 56.1, 44.5, 32.2, 18.7. **IR** (neat): 2971, 1650, 1496, 1350, 1271, 1248, 1114, 1080 cm^{-1}. mp: 89–90 °C. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{15}H_{17}ClNaO_3$: 303.0764, found: 303.0760.

Estrone derivatives (4l)[33]



4l

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The reaction mixture was stirred at 60 °C for 12 h. After this time, the reaction was concentrated and purified by preparative thin-layer chromatography on silica gel (PE/EA = 10:1) to obtain the title compound as white solid in 80% yield (25.5 mg, average of two runs). Notes: silica gel need be prewetted with 1% Et_3N in PE.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.1 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 7.15 (s, 1H), 5.06 (q, J = 6.8 Hz, 1H), 2.93 – 2.91 (m, 2H), 2.54 – 2.39 (m, 2H), 2.30 (t, J = 6.8 Hz, 1H), 2.21 – 1.91 (m, 4H), 1.83 (d, J = 6.8 Hz, 3H), 1.71 – 1.38 (m, 6H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.7, 140.1, 139.8, 136.7, 127.0, 125.6, 123.8, 58.6, 58.5, 50.3, 47.8, 44.2, 37.9, 35.7, 31.4, 29.3, 26.2, 25.5, 21.5, 13.7.

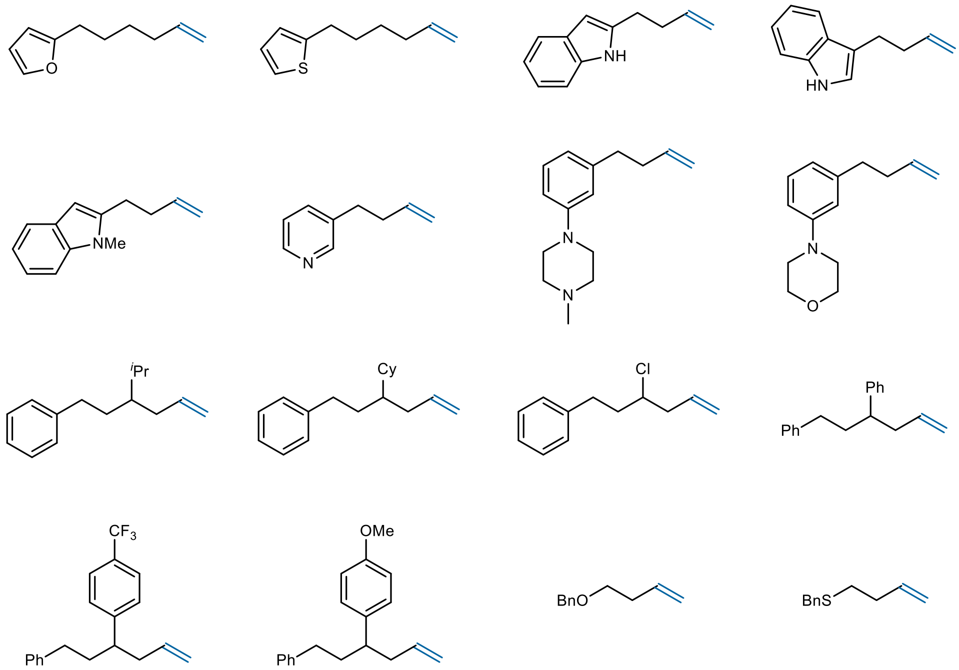
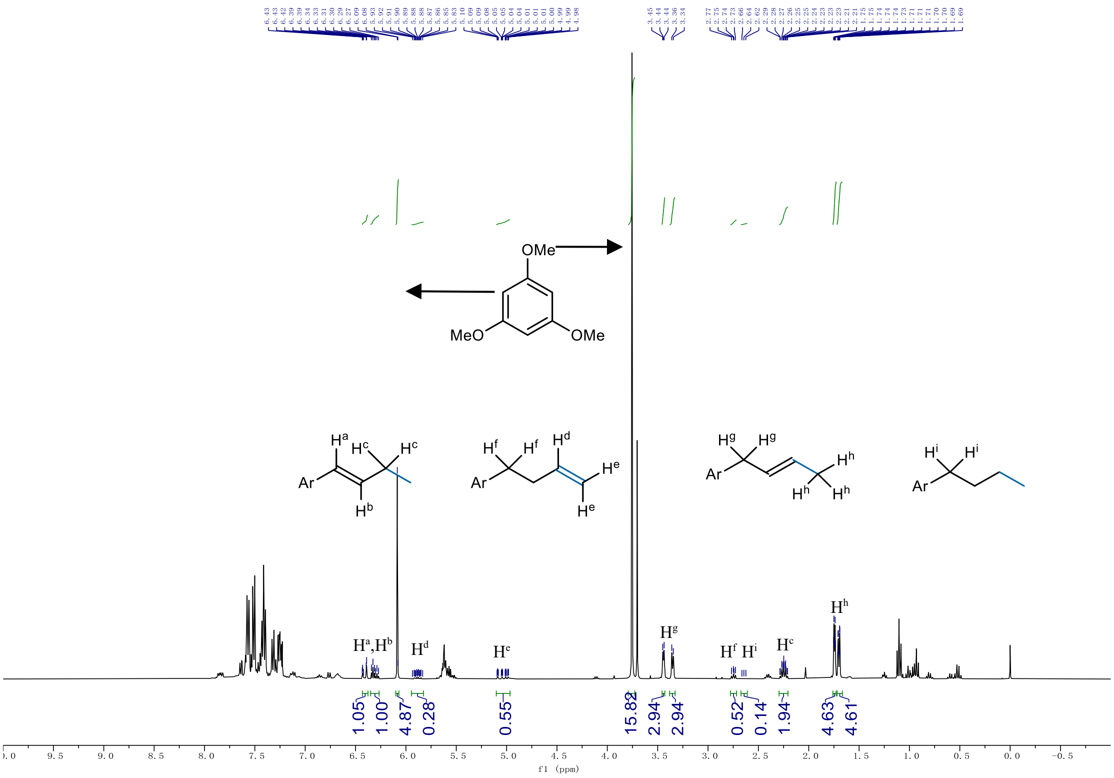


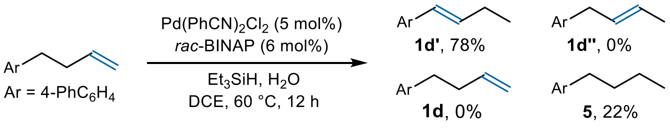
Fig. S1 Unsuccessful alkenes for remote hydrochlorination.

5.Mechanistic Studies

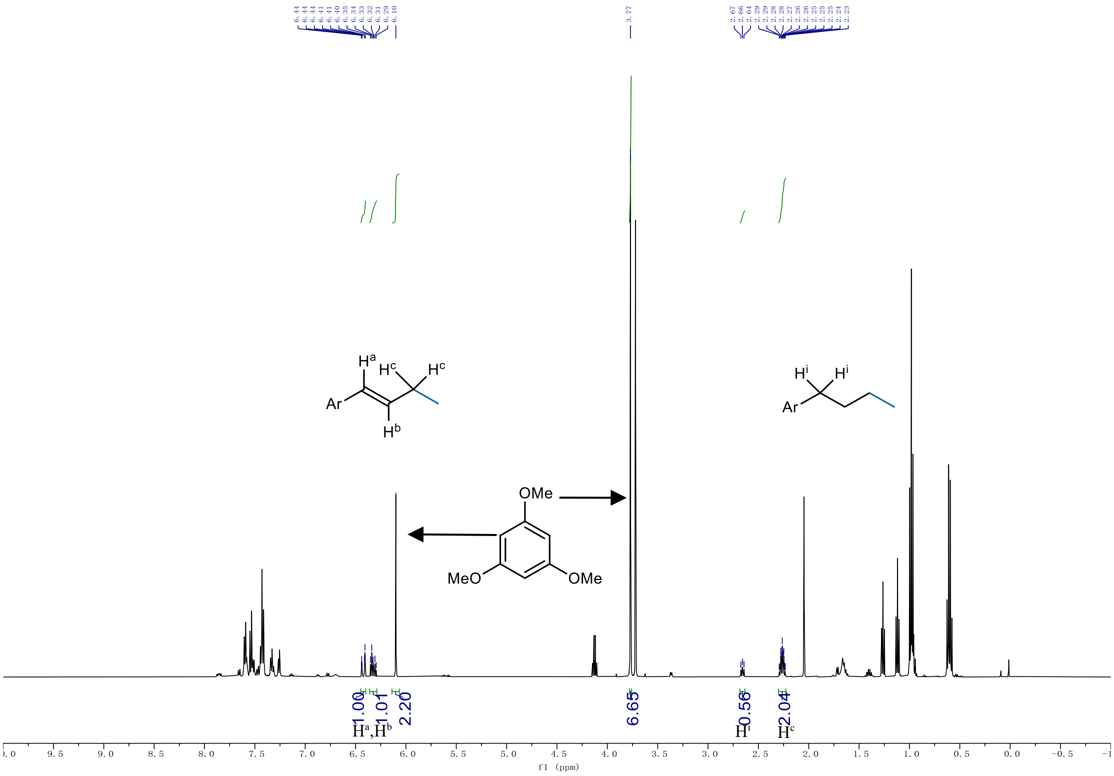
5.1. Alkene isomerization in the absence of $CuCl_2$ $2H_2O$

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), and olefin (0.10 mmol) were added sequentially. The mixture was stirred at 60 °C for 12 h. The yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard.



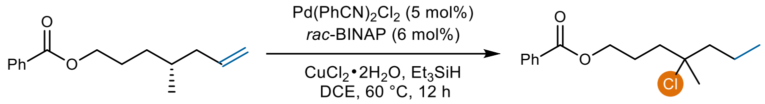


In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), and H_2O (12.6 mg, 0.7 mmol) were added sequentially. The mixture was stirred at 60 °C for 12 h. The yield was determined by **^{1}H** NMR using 1,3,5-trimethoxybenzene as the internal standard.



5.2. Hydrochlorination of stereocenter-containing alkene

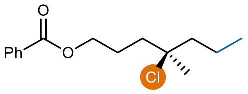
In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), (*S*)-**1aa** (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (59.7 mg, 0.35 mmol) were added sequentially. The mixture was stirred at 60 °C for 12 h. The crude material was purified by preparative thin-layer chromatography to afford the title compound as a colorless liquid in 60% yield.



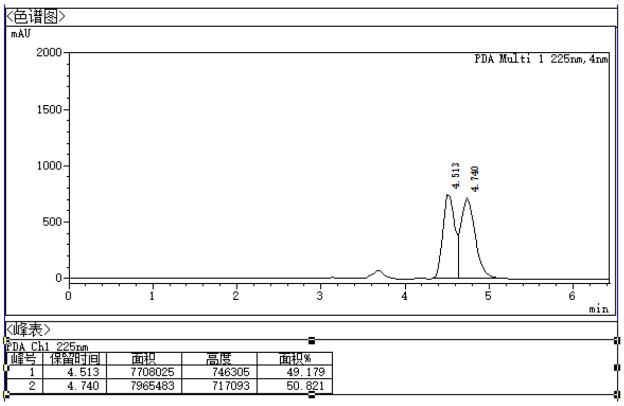
(*S*)-**1aa**, 99% ee

2aa, 60%, **0% ee**

HPLC analysis CHIRALCEL OD–H column (0.5% ^{i}PrOH in hexane, 1 mL/min).



rac-2aa



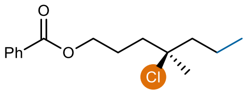
<峰表>

PDA Ch1 225nm

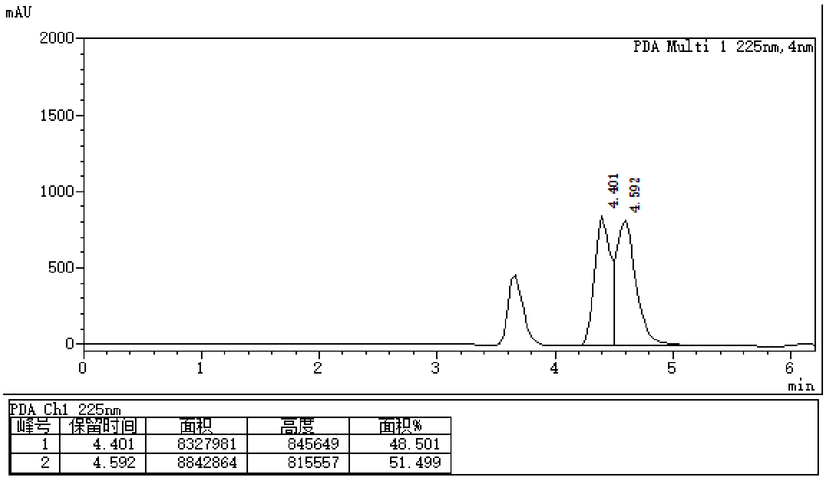
峰号	保留时间	面积	高度	面积%
1	4.513	7708025	746305	49.179
2	4.740	7965483	717093	50.821

Translation of Chinese characters to English:

Peak	Retention time	Area	Height	Area %
1	4.513	7708025	746305	49.179
2	4.740	7965483	717093	50.821



2aa



PDA Ch1 225nm

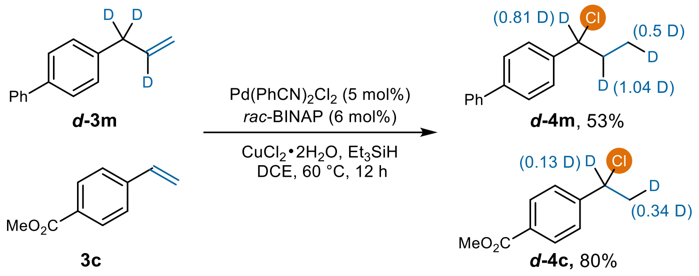
峰号	保留时间	面积	高度	面积%
1	4.401	8327981	845649	48.501
2	4.592	8842864	815557	51.499

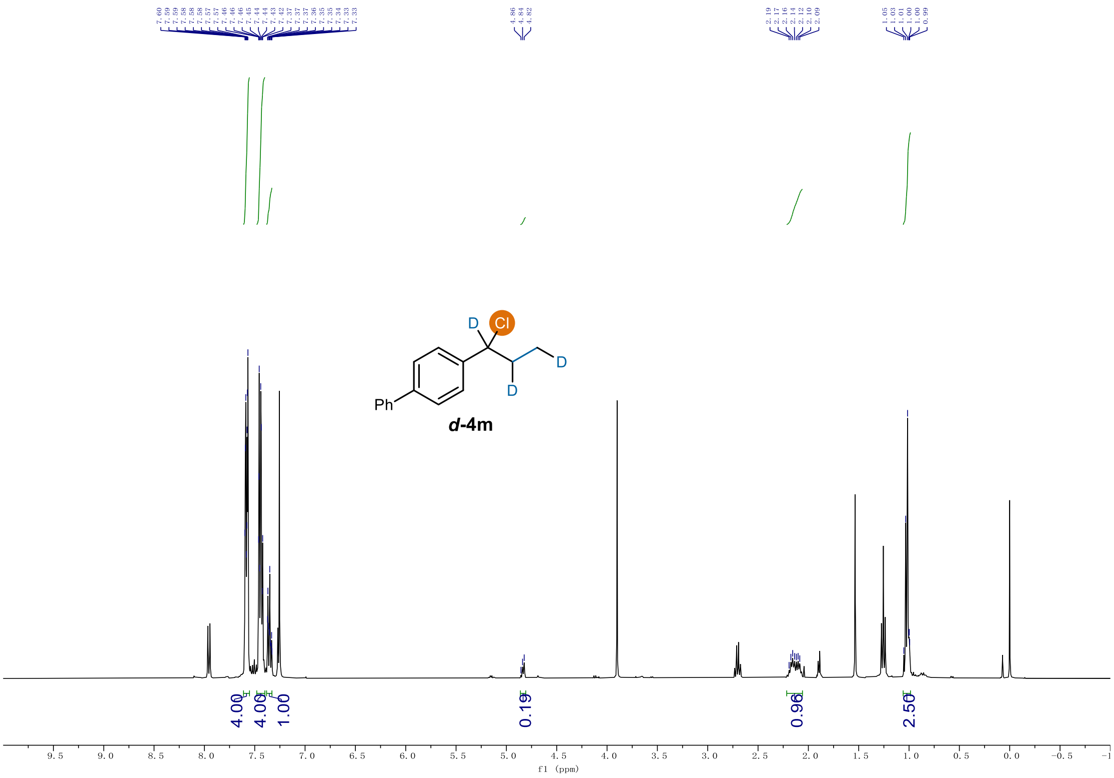
Translation of Chinese characters to English:

Peak	Retention time	Area	Height	Area %
1	4.401	8327981	845649	48.501
2	4.592	8842864	815557	51.499

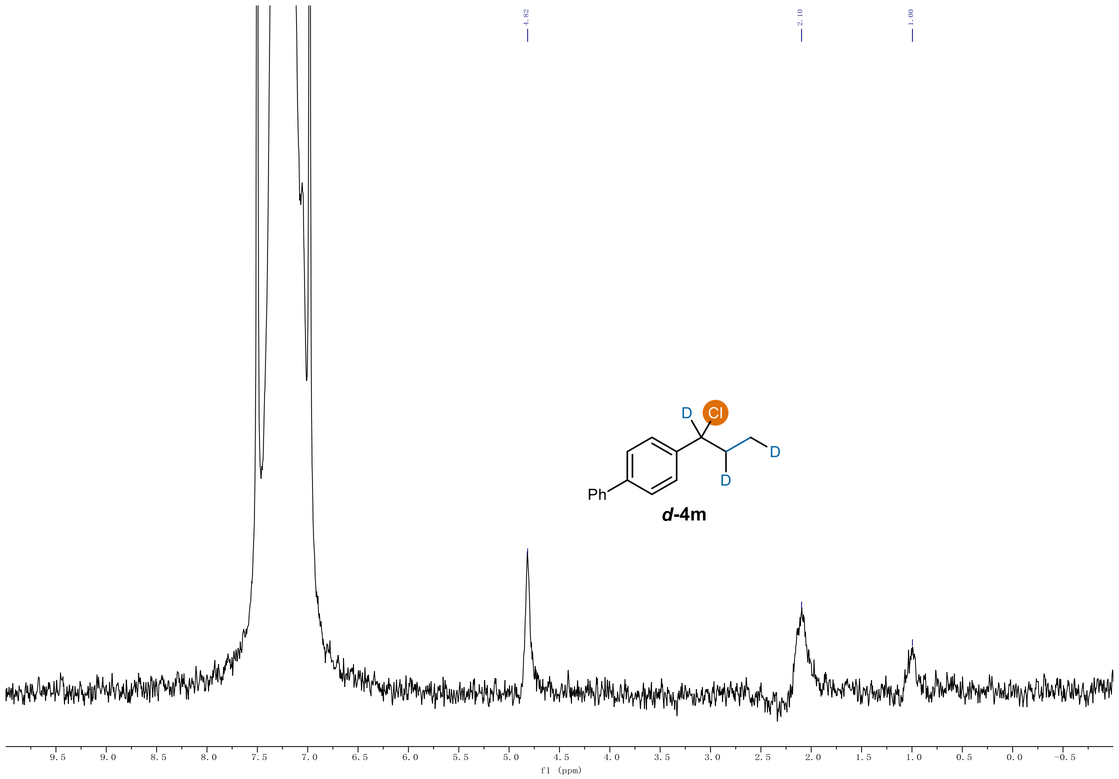
5.3. Crossover experiments

In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 1.0 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (81.4 mg, 0.7 mmol), ***d*-3m** (0.10 mmol), **3c** (0.10 mmol), and $CuCl_2{\cdot}2H_2O$ (119.4 mg, 0.7 mmol) were added sequentially. The mixture was stirred at 60 °C for 12 h. The crude material was purified by preparative thin-layer chromatography to provide ***d*-4m** with 53% yield and ***d*-4c** with 80% yield.

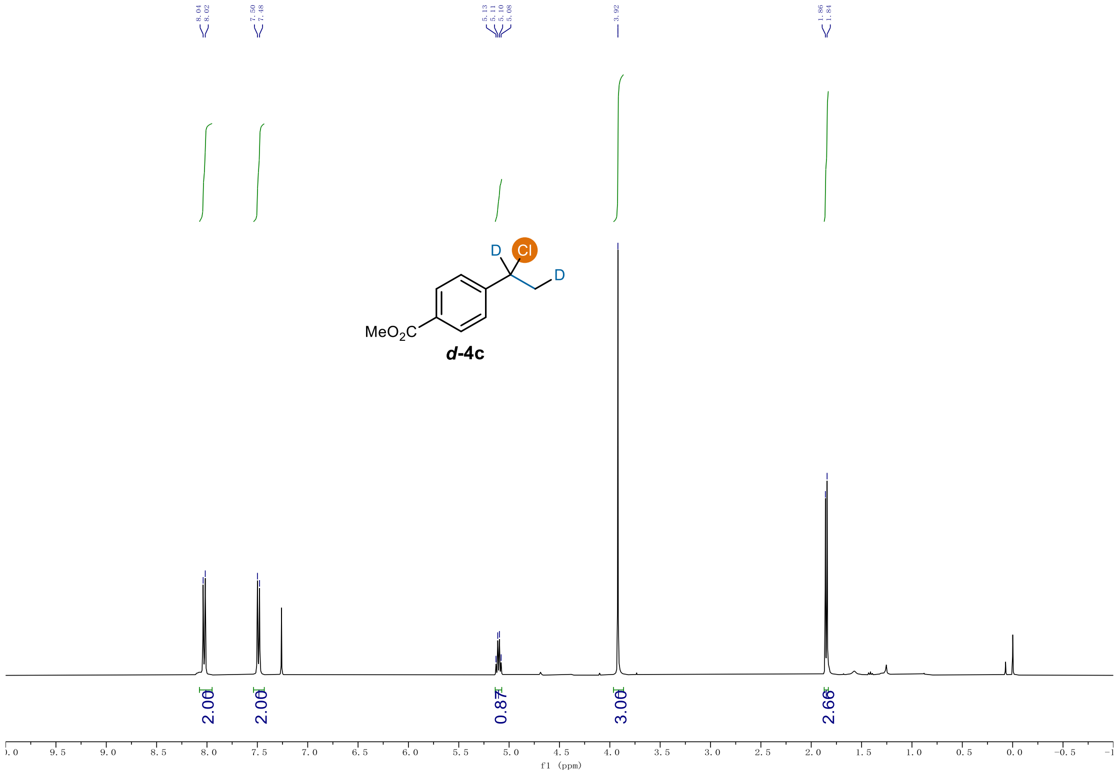




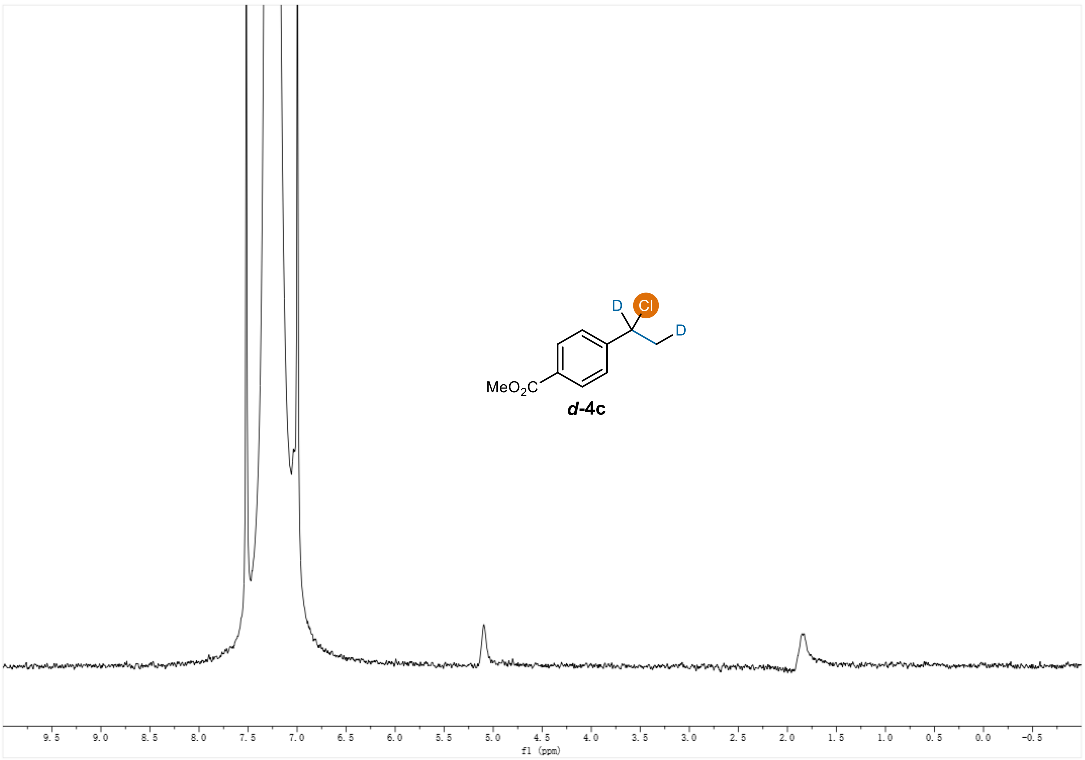
^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)] for ***d*-4m**



^{2}H NMR [61 MHz, $CDCl_3$ (δ 7.26 ppm)] for ***d*-4m**



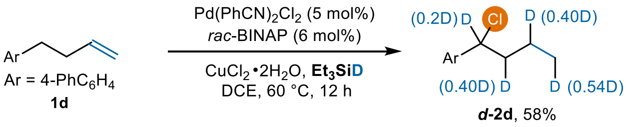
^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)] for ***d*-4c**

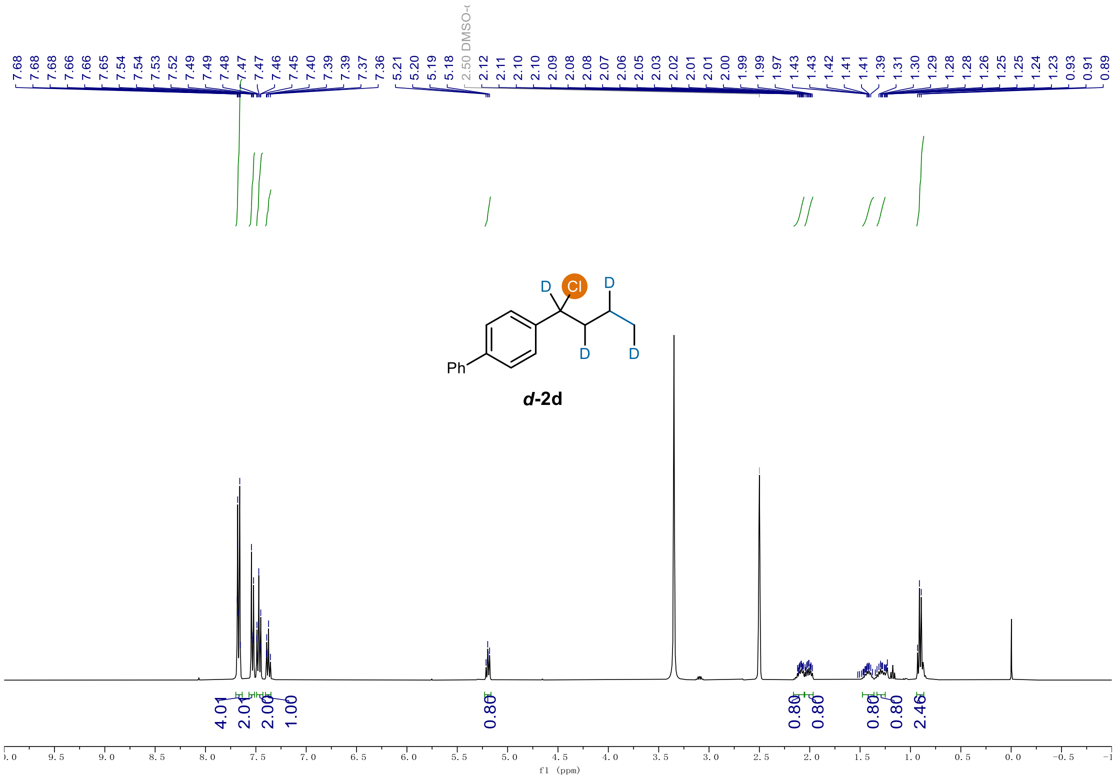


^{2}H NMR [61 MHz, CDCl$_3$ (δ 7.26 ppm)] for ***d*-4c**

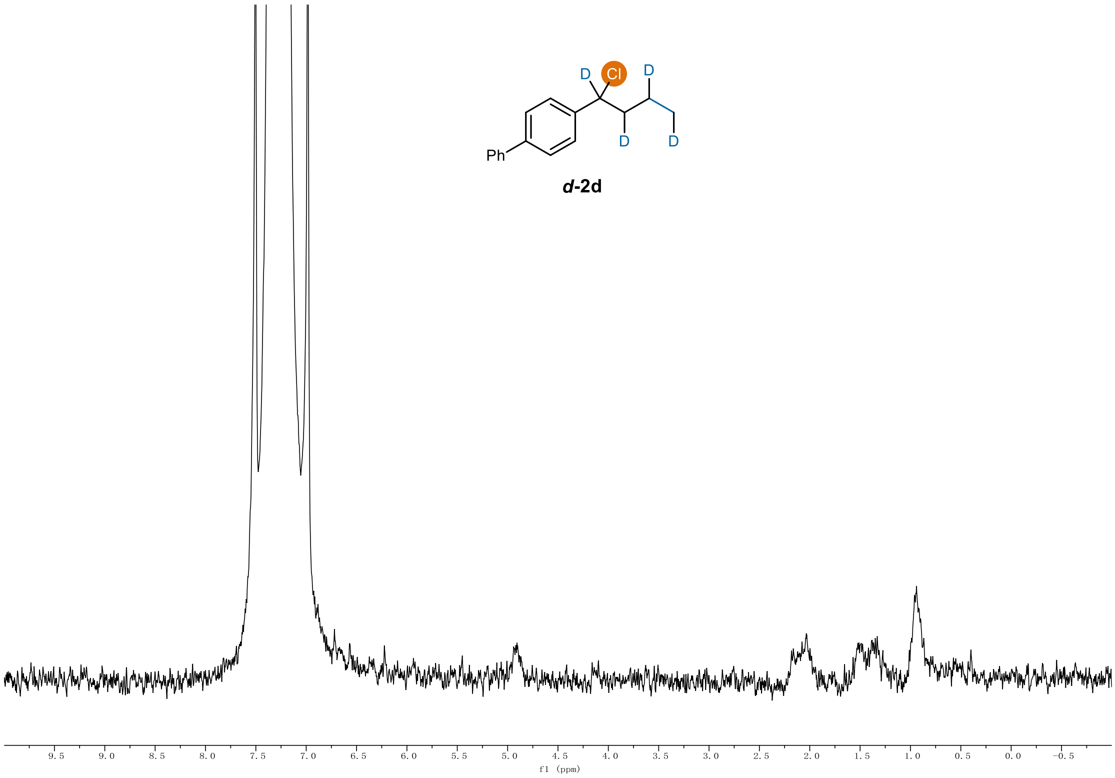
5.4. Deuterium-labelling experiments

In a N$_2$-filled glovebox, Pd(PhCN)$_2$Cl$_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et$_3$SiD (41.3 mg, 0.35 mmol), alkene (0.10 mmol), and CuCl$_2$·2H$_2$O (59.7 mg, 0.35 mmol) were added sequentially. The mixture was stirred at 60 °C for 12 h. The crude material was purified by preparative thin-layer chromatography to provide the title compound ***d*-2d** as a colorless liquid in 58% yield.



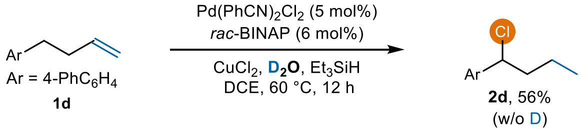


^{1}H NMR [400 MHz, DMSO-d_6 (δ 2.50 ppm)] for ***d*-2d**



^{2}H NMR [61 MHz, $CDCl_3$ (δ 7.26 ppm)] for ***d*-2d**

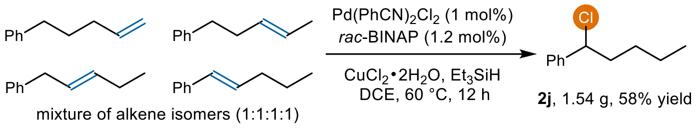
In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (5.7 mg, 0.015 mmol), *rac*-BINAP (11.2 mg, 0.018 mmol) and DCE (1.5 mL) were added sequentially to a 1-dram vial. The resulting mixture was stirred at ambient temperature for 15 min. A 0.5 mL aliquot of this mixture was then transferred to a second 1-dram vial. To this vial, Et_3SiH (40.7 mg, 0.35 mmol), olefin (0.10 mmol), $CuCl_2$ (47.0 mg, 0.35 mmol), and D_2O (14.0 mg, 0.7 mmol) were added sequentially. The mixture was stirred at 60 ℃ for 12 h. The crude material was purified by preparative thin-layer chromatography to provide the title compound as a colorless liquid in 56% yield.



1d

2d, 56%
(w/o D)

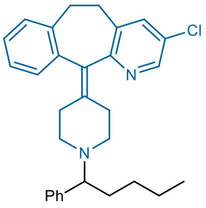
6. Regioconvergent hydrochlorination of a mixture of alkene isomers



In a N_2-filled glovebox, $Pd(PhCN)_2Cl_2$ (55 mg, 0.146 mmol), *rac*-BINAP (110 mg, 0.175 mmol) and DCE (73 mL) were added to a 1-dram vial containing. The resulting mixture was stirred at ambient temperature for 15 min. Then Et_3SiH (5.9 g, 51.1 mmol), alkene (2.13 g, 14.6 mmol), and $CuCl_2·2H_2O$ (8.7 g, 51.1 mmol) were added sequentially to the reaction. The mixture was stirred at 60 °C for 12 h. The crude product was purified by chromatography on silica gel using 0.5% Et_3N in hexanes. The product was isolated as a clear oil (1.54 g, 58% yield).

7. Synthetic applications

Desloratadine derivatives (6)

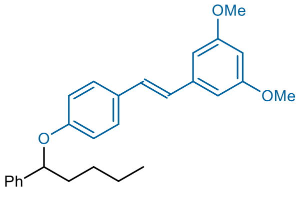


6

To a solution of **2j** (36.4 mg, 0.2 mmol) in anhydrous MeCN (2 mL) were added Desloratadine (124.3 mg, 0.4 mmol, 2 eq.), potassium iodide (KI, 83 mg, 0.5 mmol, 2.5 eq.) and potassium carbonate (K_2CO_3, 69.1 mg, 0.5 mmol, 2.5 eq.). The reaction mixture was heated at 80 °C for 24 h. The reaction was monitored by TLC. After the reaction was completed, the mixture was quenched with H_2O (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA= 10:1) to obtain the desired product **6**.

White solid, mp: 96–97 °C. 67.5 mg, 74% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 – 8.35 (m, 1H), 7.38 (dd, J = 7.5, 1.6 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.19 – 7. 16 (m, 2H), 7.12 – 7.00 (m, 4H), 3.32 – 3.21 (m, 3H), 2.82 – 2.67 (m, 4H), 2.58 – 2.22 (m, 4H), 2.15 – 1.95 (m, 2H), 1.90 – 1.70 (m, 2H), 1.35 – 1.12 (m, 2H), 1.10 – 1.00 (m, 1H), 1.08 – 1.03 (m, 1H), 0.81 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.8, 146.5, 140.4, 139.6, 139.5, 137.8, 137.1, 133.4, 132.5, 132.1, 131.0, 128.9, 128.6, 127.9, 126.9, 125.88, 125.87, 121.9, 69.9, 52.3, 51.0, 32.5, 31.8, 31.4, 28.8, 22.8, 14.0. **IR** (neat): 2361, 1630, 1601, 1436, 1384, 1350, 1115, 764, 701, 617 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{27}H_{33}N_2Na$: 425.2087, found: 425.2084.

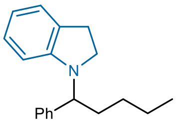
Pterostilbene derivatives (7)


7

To a solution of **2j** (36.4 mg, 0.2 mmol) in anhydrous DMF (2 mL) were added Pterostilbene (102.4 mg, 0.4 mmol, 2 eq.), potassium iodide (KI, 83 mg, 0.5 mmol, 2.5 eq.) and potassium carbonate (K_2CO_3, 69 mg, 0.5 mmol, 2.5 eq.). The reaction mixture was heated at 80 °C for 24 h. The reaction was monitored by TLC. After the reaction was completed, the mixture was quenched with H_2O (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phase was dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 25:1) to obtain the pure product **7**.

Colorless oil, 44.2 mg, 55% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 6H), 7.26 – 7.22 (m, 1H), 6.96 (d, *J* = 16.2 Hz, 1H), 6.87 – 6.79 (m, 3H), 6.61 (d, *J* = 2.3 Hz, 2H), 6.35 (t, *J* = 2.2 Hz, 1H), 5.09 (dd, *J* = 7.8, 5.2 Hz, 1H), 3.80 (s, 6H), 2.06 – 1.94 (m, 1H), 1.88 – 1.78 (m, 1H), 1.56 – 1.43 (m, 1H), 1.42 – 1.29 (m, 3H), 0.90 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 158.2, 142.1, 139.7, 129.7, 128.8, 128.5, 127.6, 127.4, 126.4, 125.9, 116.1, 104.3, 99.5, 80.3, 55.3, 38.4, 27.9, 22.5, 14.0. **IR** (neat)**:** 2955, 1630, 1598, 1507, 1457, 1384, 1350, 1274, 1245, 1203, 1151, 1066, 959, 913, 761, 700 cm^{-1}. **HRMS** (ESI): m/z [M+Na]$^+$ calcd for $C_{27}H_{30}O_3Na$: 425.2087, found: 425.2084.

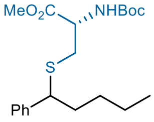
Indoline derivatives (8)


8

To a solution of **2j** (36.4 mg, 0.2 mmol) in anhydrous MeCN (2 mL) were added Indoline (47.6 mg, 0.4 mmol, 2 eq.), potassium iodide (KI, 83 mg, 0.5 mmol, 2.5 eq.) and potassium carbonate (K_2CO_3, 69 mg, 0.5 mmol, 2.5 eq.). The reaction mixture was heated at 80 °C for 24 h. The reaction was monitored by TLC. After the reaction was completed, the mixture was quenched with H_2O (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phase was dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 20:1) to obtain the pure product **8**.

Colorless oil, 42.9 mg, 81% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 4H), 7.20 – 7.09 (m, 1H), 6.92 (m, 2H), 6.51 – 6.42 (m, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 4.48 (t, *J* = 7.5 Hz, 1H), 3.43 – 3.32 (m, 1H), 3.24 – 3.13 (m, 1H), 2.93 – 2.74 (m, 2H), 2.02 – 1.82 (m, 2H), 1.38 – 1.13 (m, 4H), 0.82 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 140.9, 129.5, 128.3, 127.8, 127.2, 127.0, 124.4, 116.3, 106.3, 58.9, 47.0, 31.0, 29.0, 28.1, 22.7, 14.1. **IR** (neat)**:** 2930, 2858, 2360, 1631, 1606, 1488, 1472, 1350, 1155, 1024, 910, 739, 699 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{23}NNa$: 288.1723, found: 288.1718.

Cysteine derivatives (9)

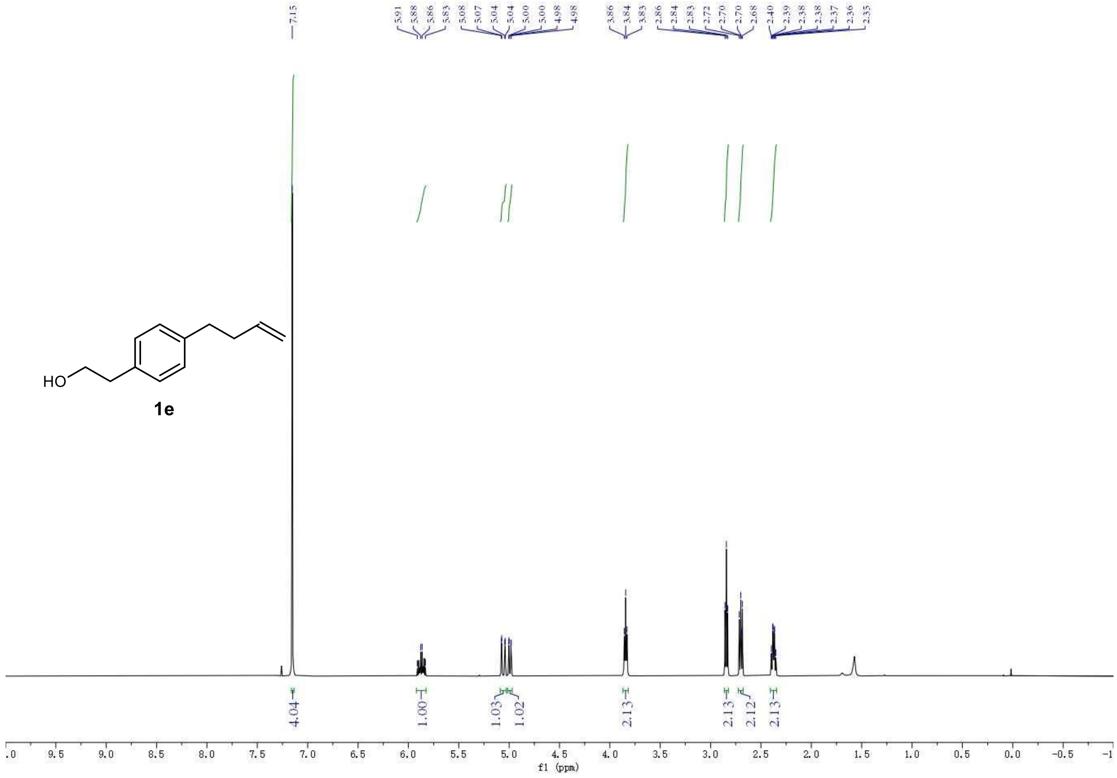


9

To a solution of **2j** (36.4 mg, 0.2 mmol) in anhydrous DMF (2 mL) were added Cysteine (94 mg, 0.4 mmol, 2 eq.), potassium iodide (KI, 83 mg, 0.5 mmol, 2.5 eq.) and potassium carbonate (K_2CO_3, 69 mg, 0.5 mmol, 2.5 eq.). The reaction mixture was heated at 80 °C for 24 h. The reaction was monitored by TLC. After the reaction was completed, the mixture was quenched with H_2O (5 mL) and extracted with DCM (3 × 5 mL). The combined organic phase was dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 15:1) to obtain the pure product **9**.

white solid, mp: 44–45 °C, 61.7 mg, 81% yield, 1:1 dr, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 4H), 7.20 – 7.09 (m, 1H), 5.20 – 5.23 (m, 1H), 4.50 – 4.36 (m, 1H), 3.83 – 3.65 (m, 4H), 2.78 – 2.54 (m, 2H), 1.91 – 1.73 (m, 2H), 1.47 (s, 4.5H), 1.43 (s, 4.5H), 1.30 – 1.13 (m, 4H), 0.86 – 0.81 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 171.6, 155.2, 155.0, 142.32, 142.3, 128.55, 128.51, 128.4, 127.9, 127.8, 127.3, 127.2, 80.04, 53.1, 52.44, 52.40, 50.3, 50.0, 36.3, 36.2, 33.3, 33.2, 29.8, 29.7, 28.32, 28.28, 22.4, 22.3, 13.9. **IR** (neat)**:** 2957, 2858, 2362, 1748, 1716, 1603, 1492, 1453, 1457, 1385, 1261, 1157, 910, 913, 739, 699 cm^{-1}. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{31}NO_4SNa$: 404.1866, found: 404.1864.

9. Spectra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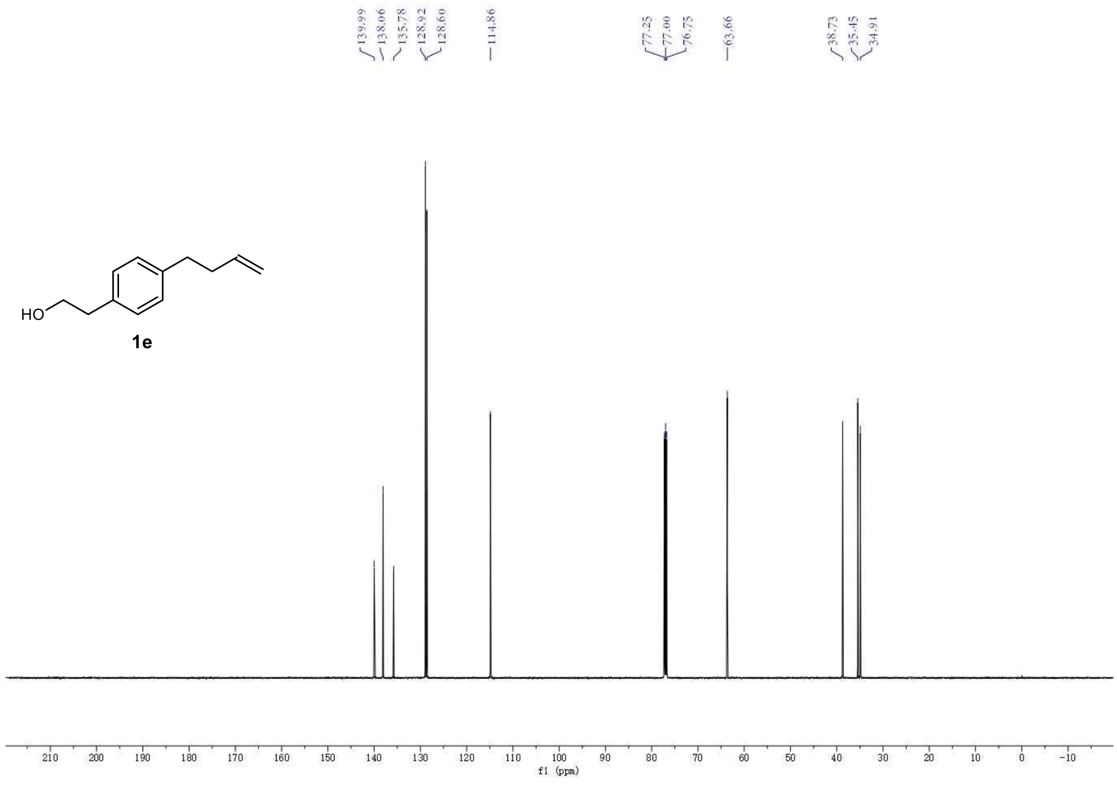
f1 (ppm)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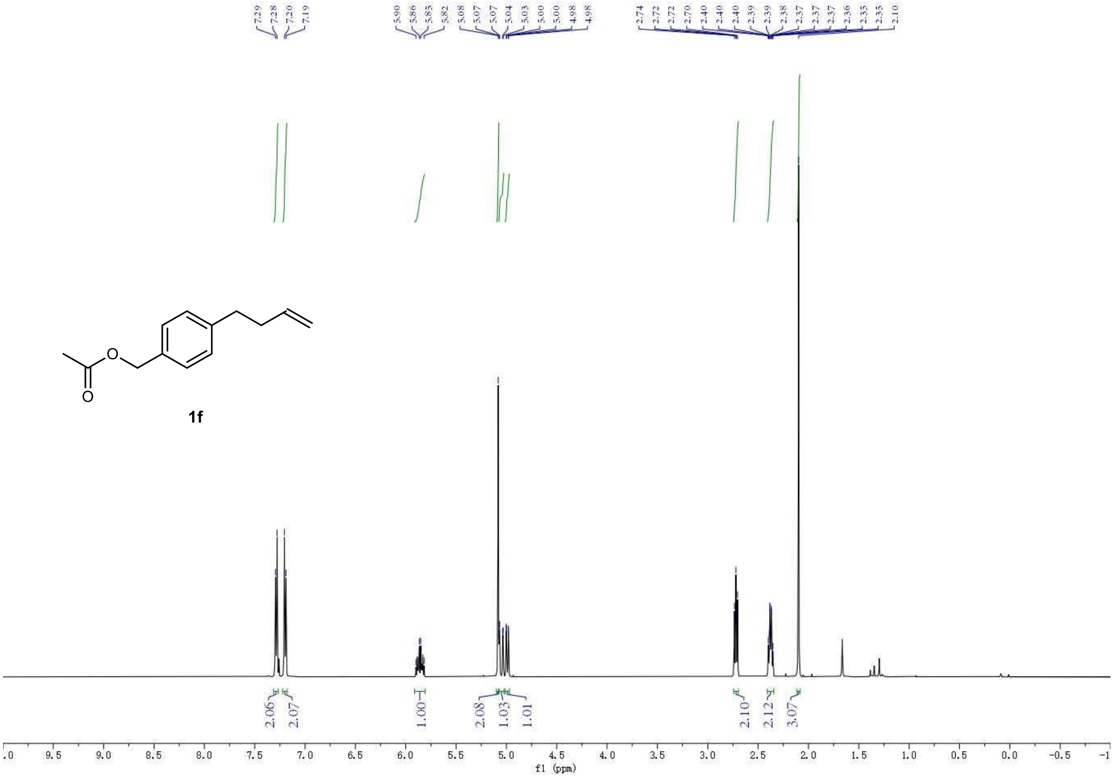
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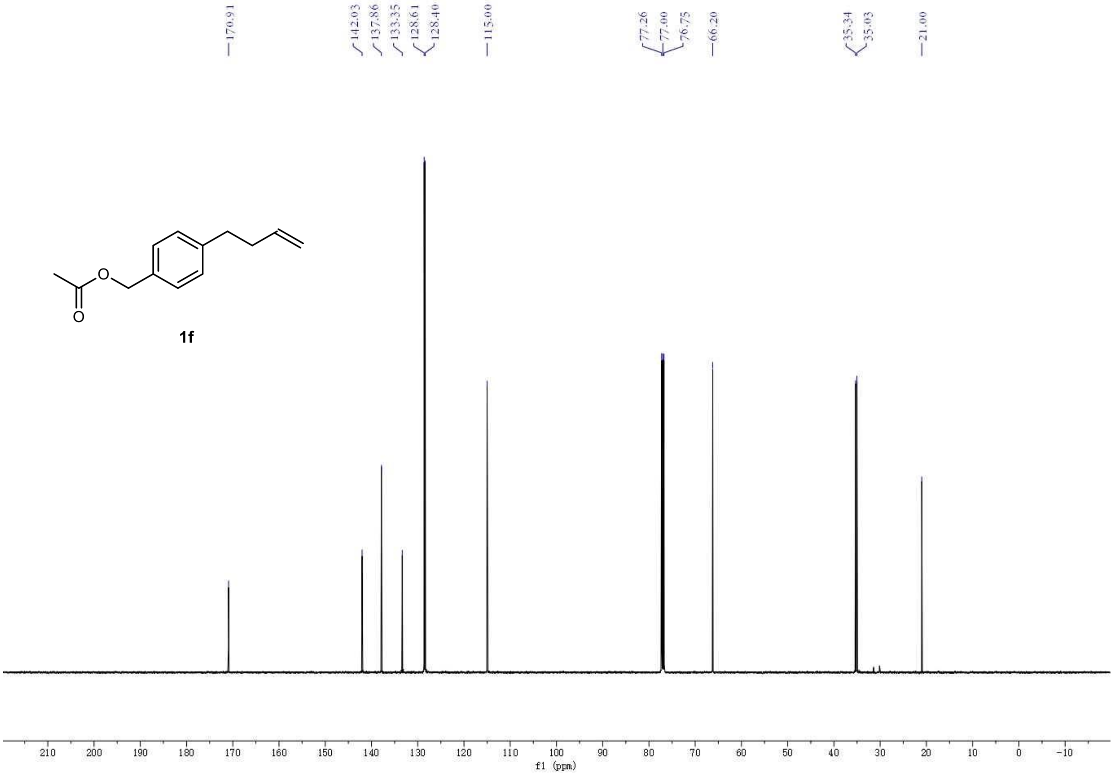
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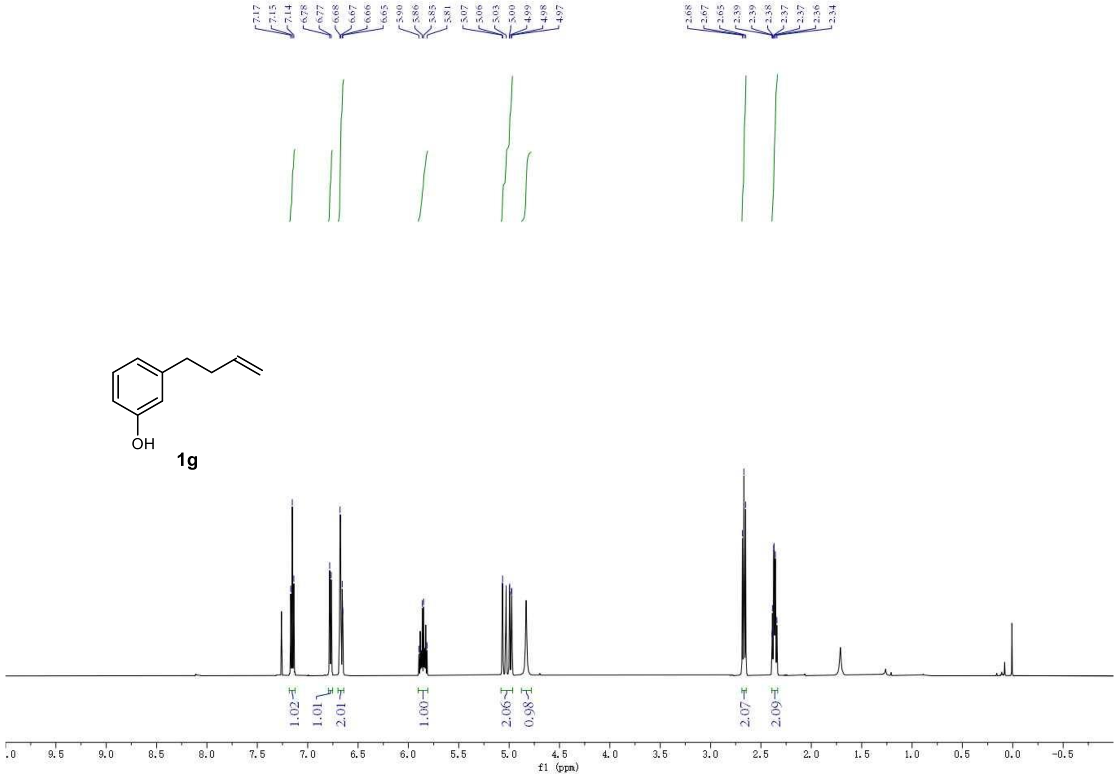
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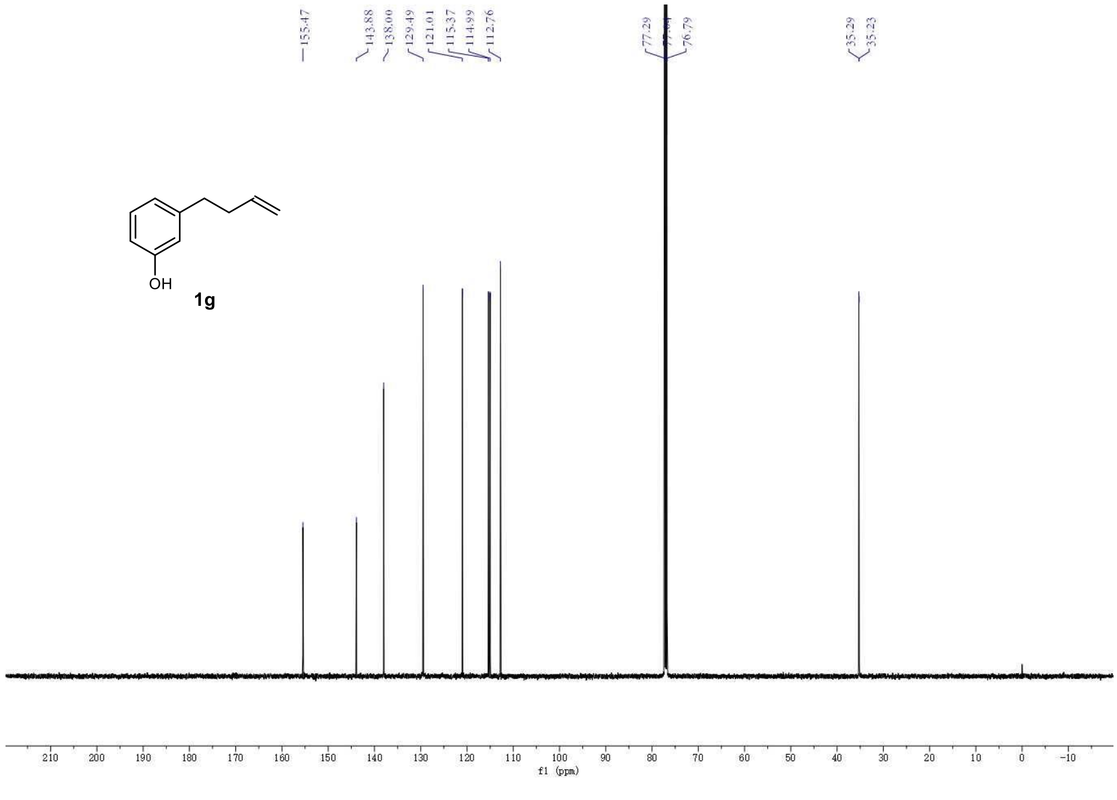
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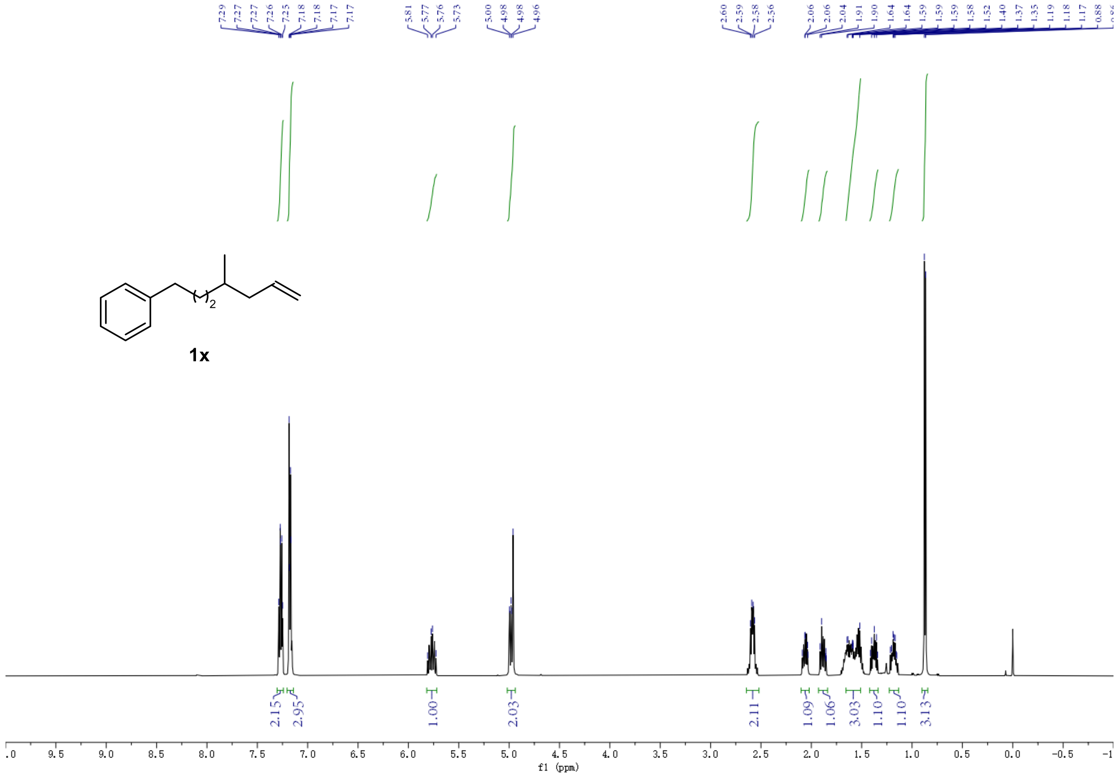
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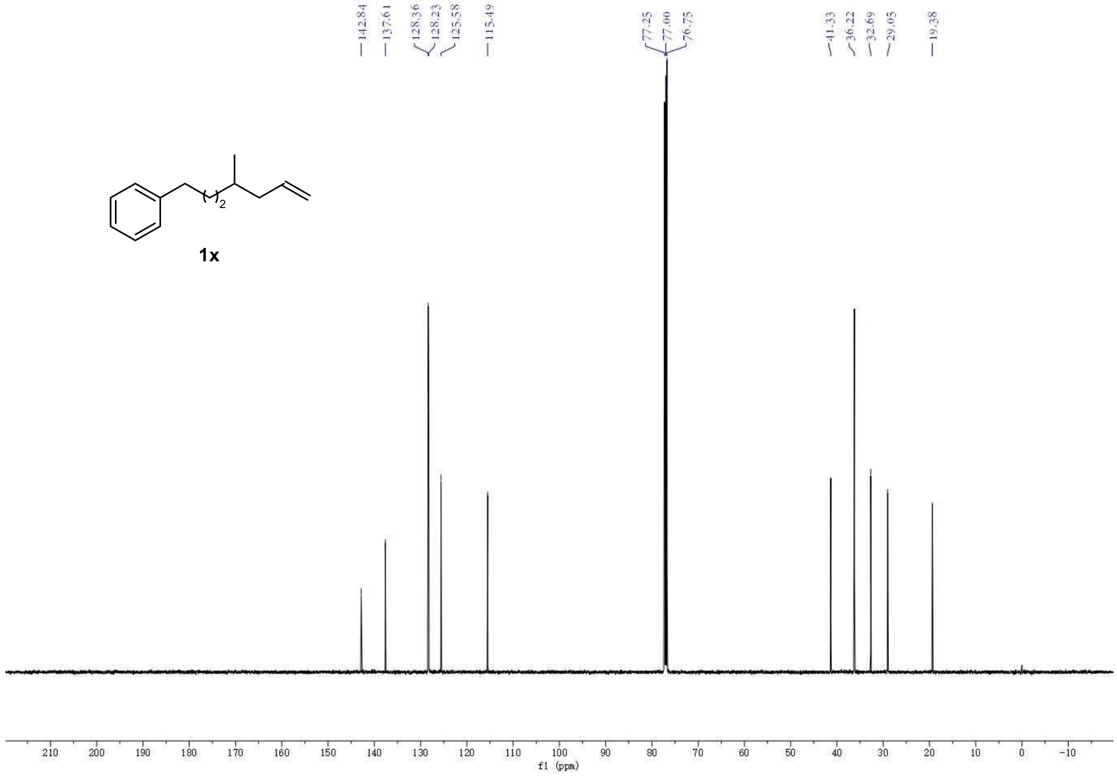
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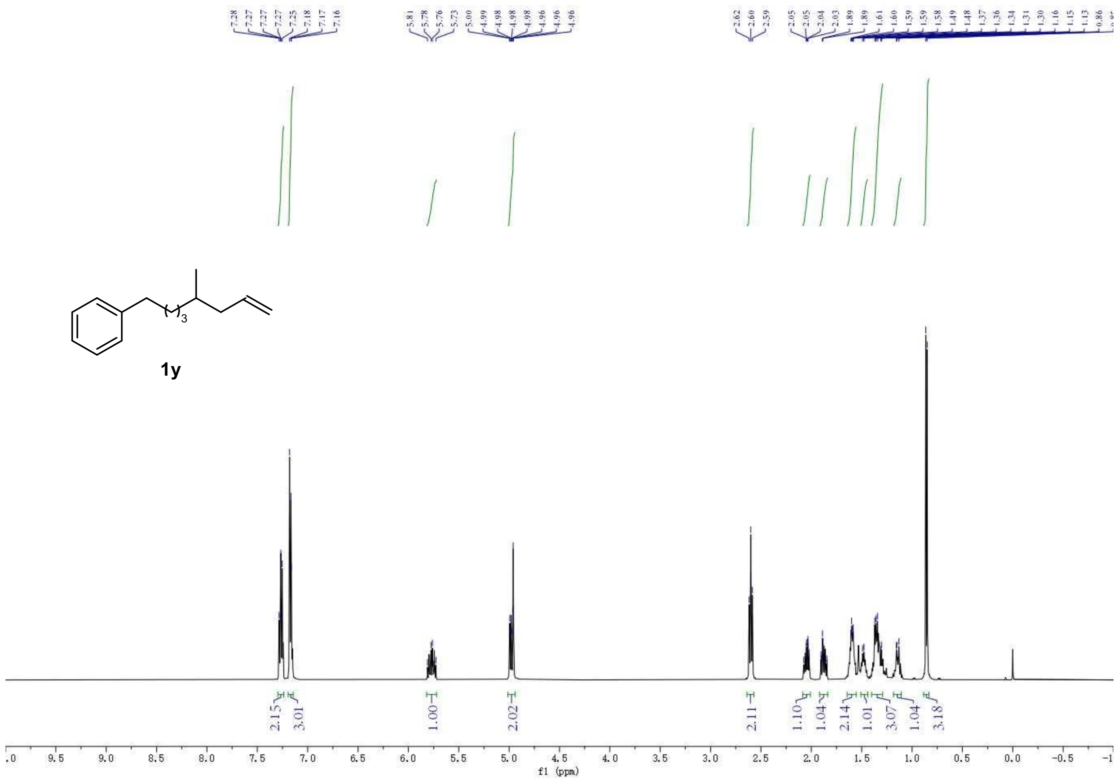
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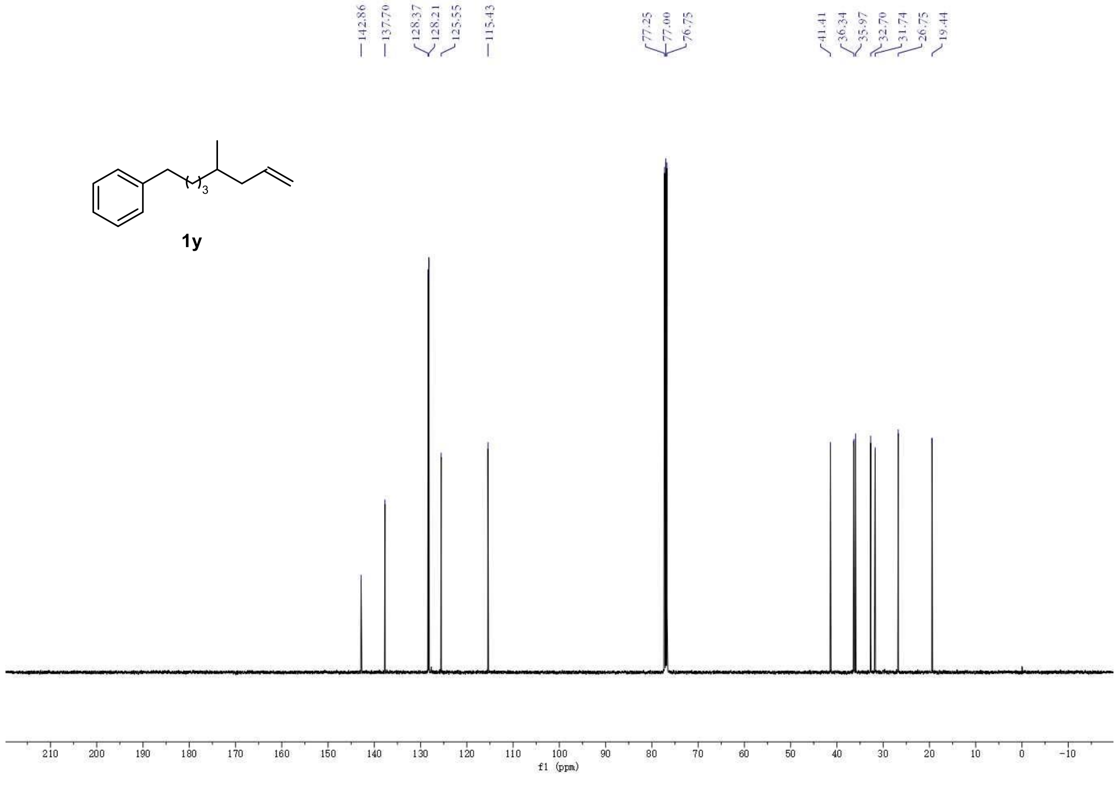
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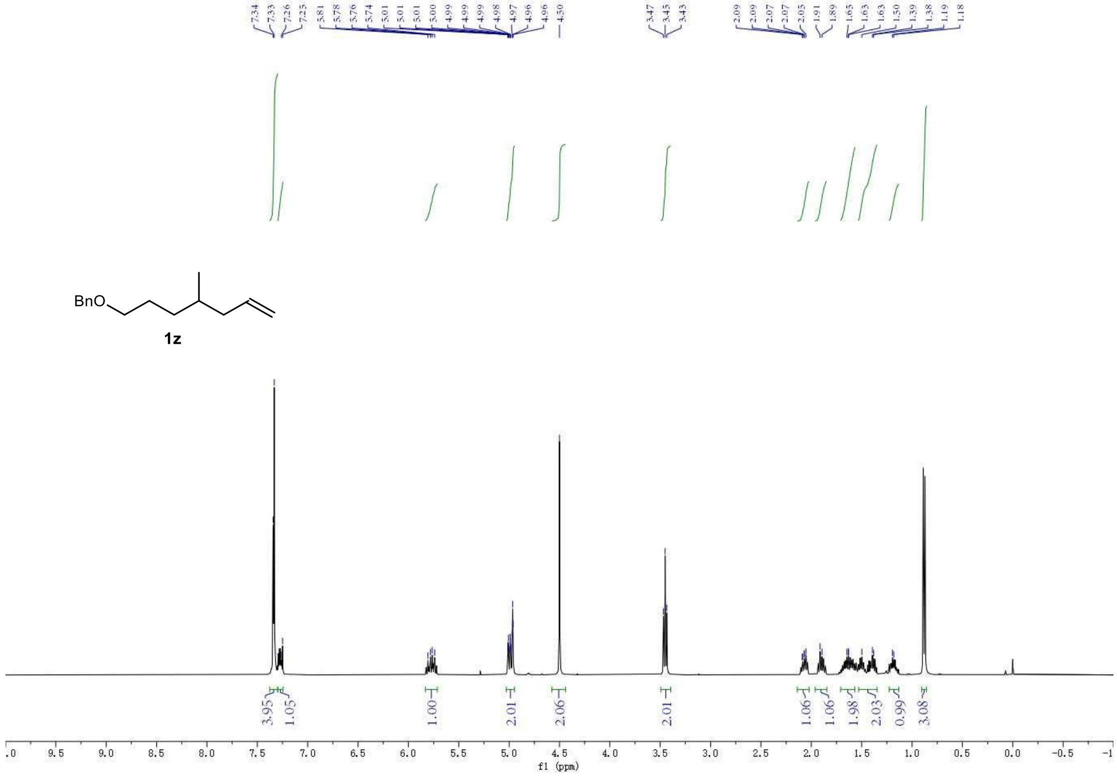
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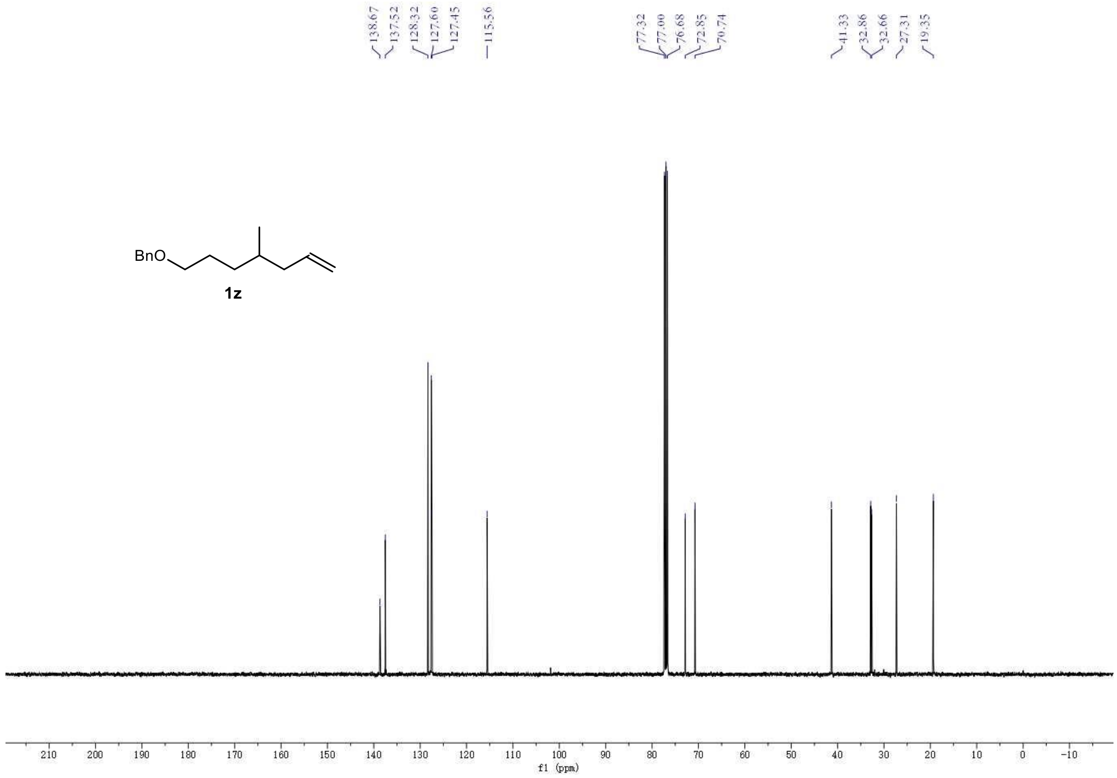
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27.31
19.35
BnO
1z
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200
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180
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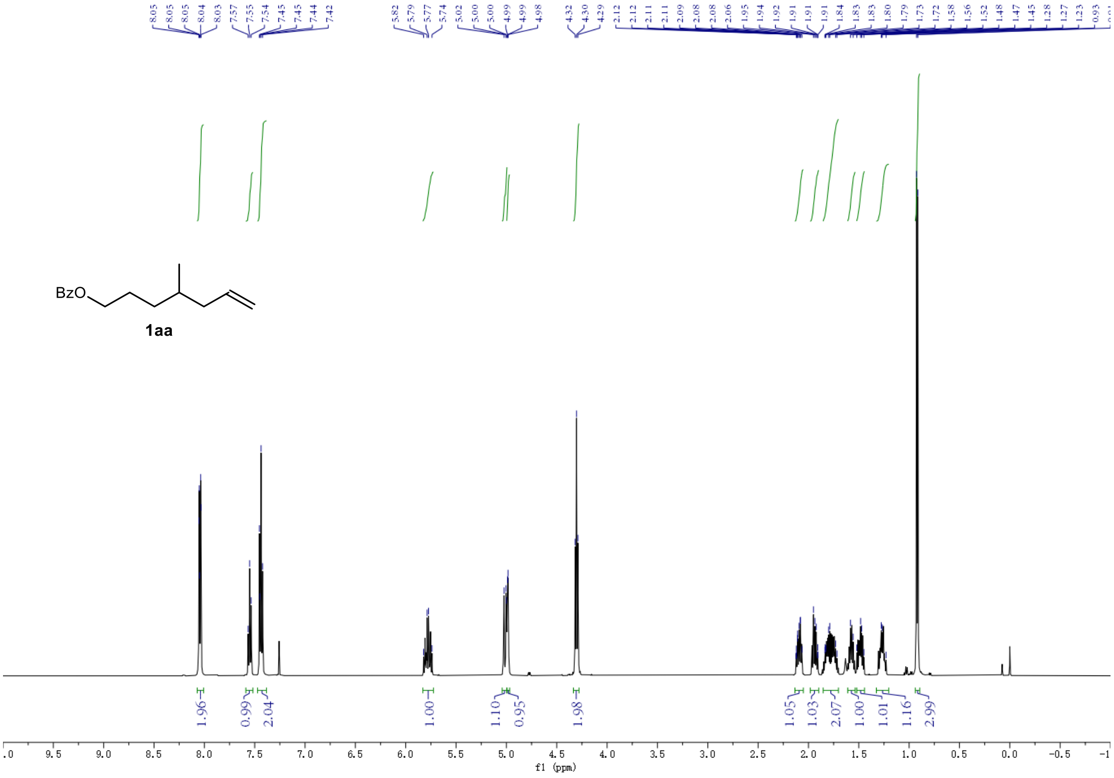
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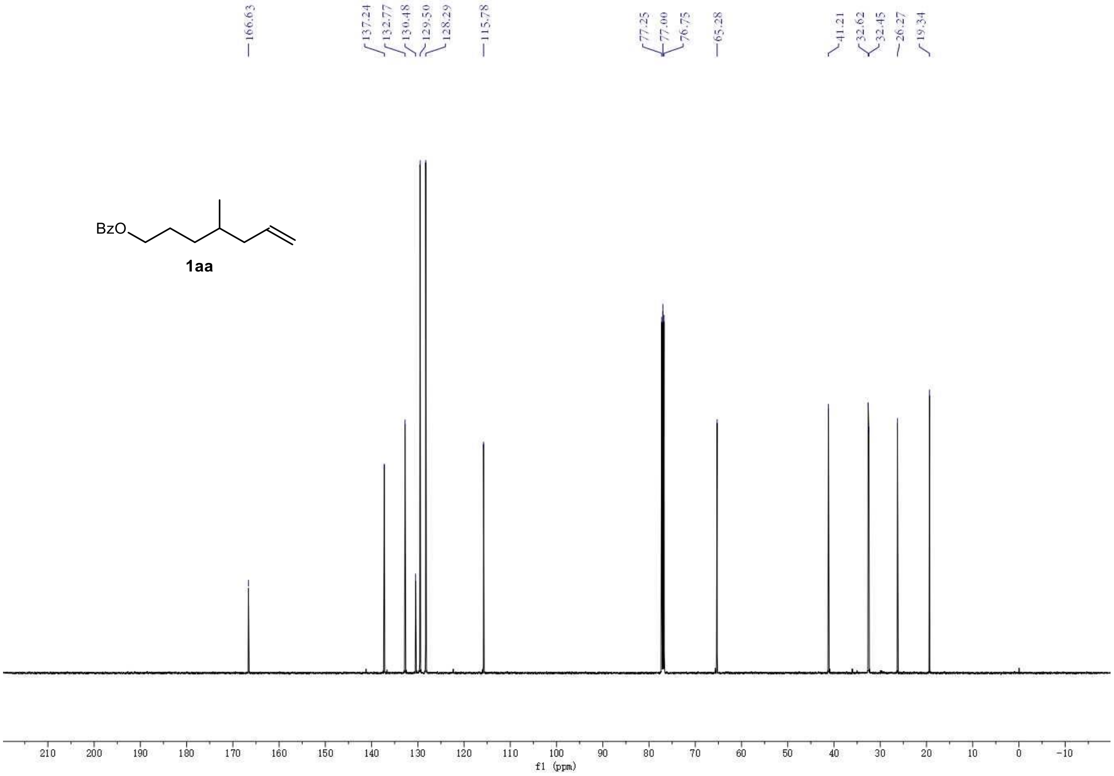
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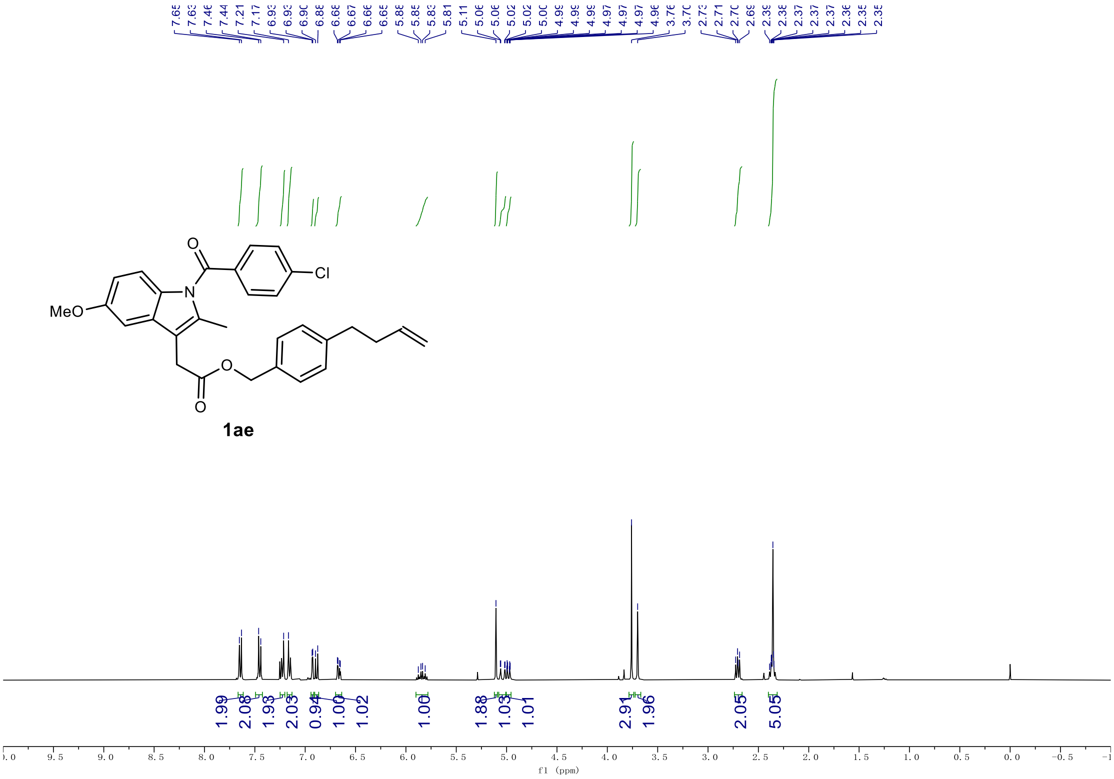
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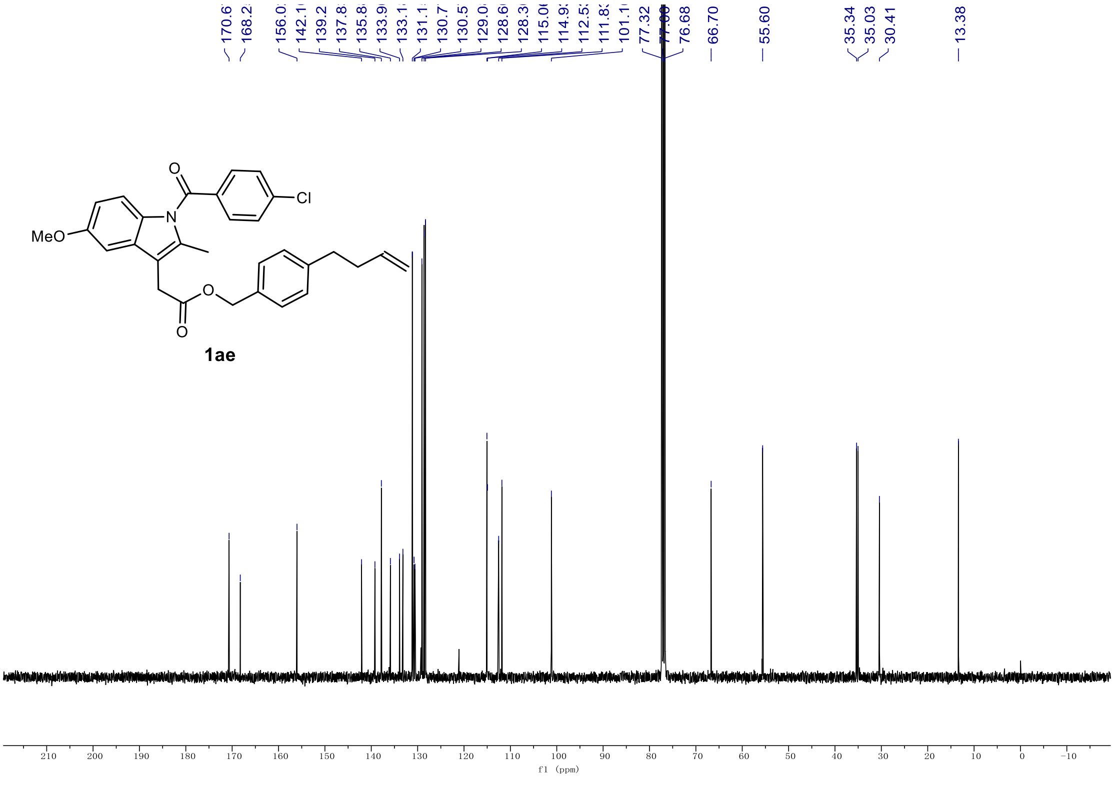
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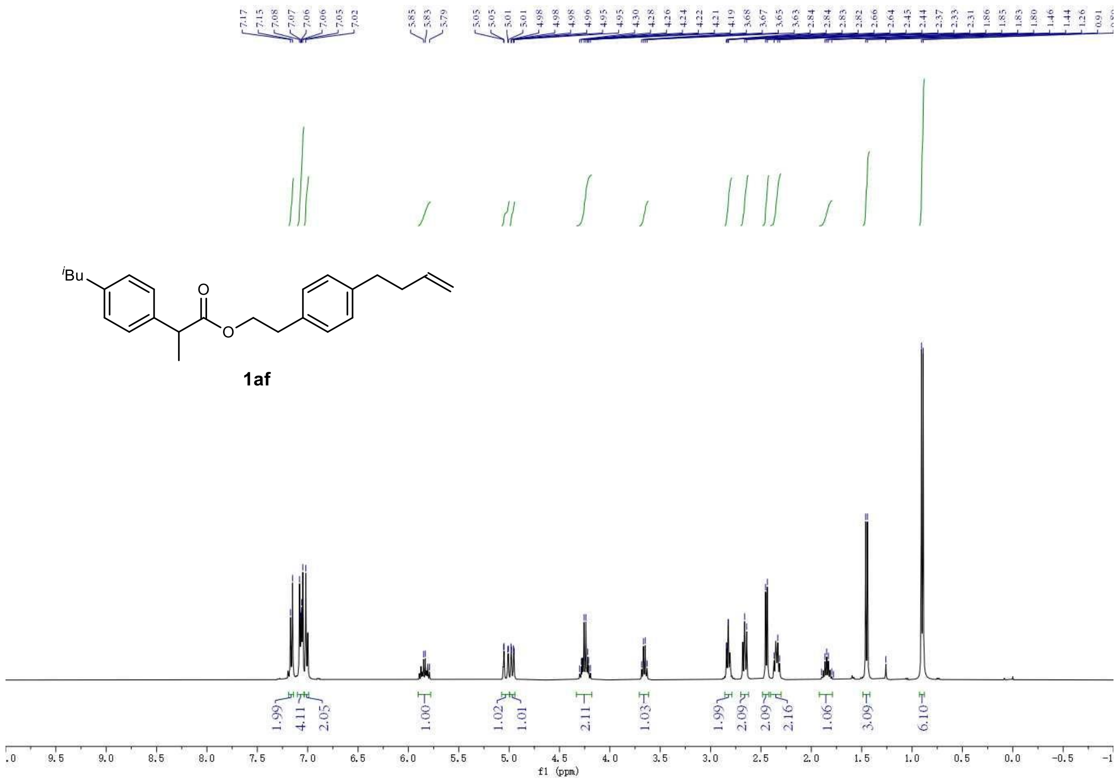
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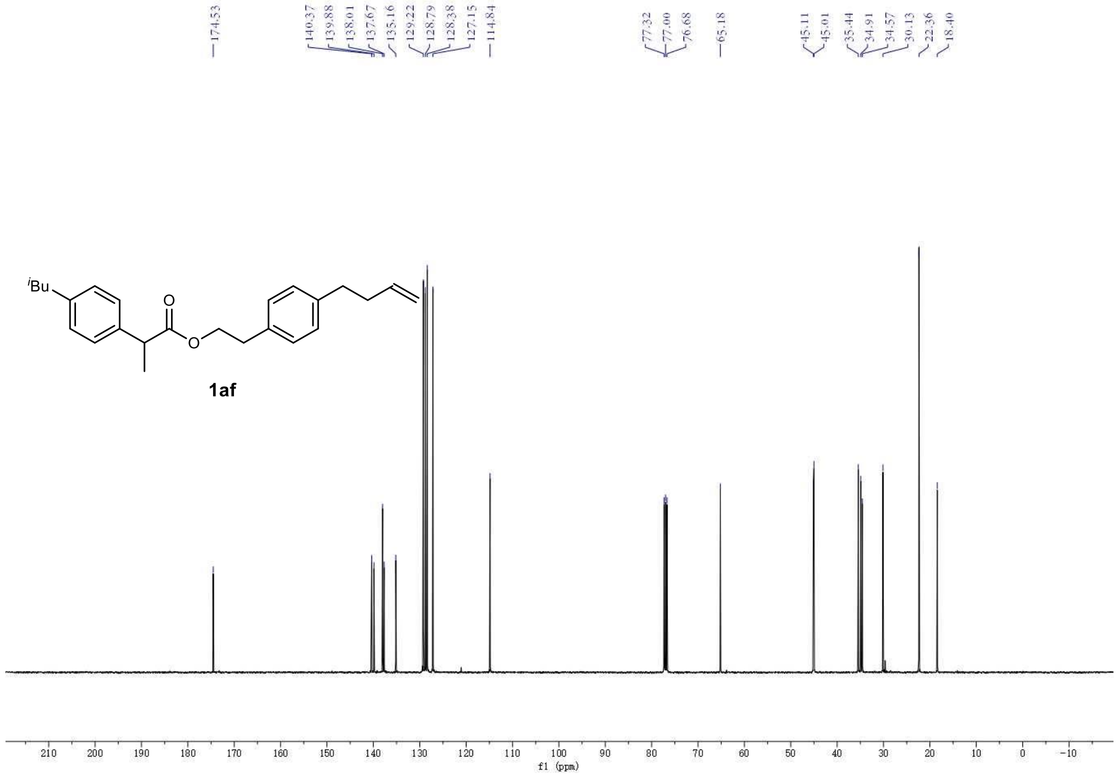
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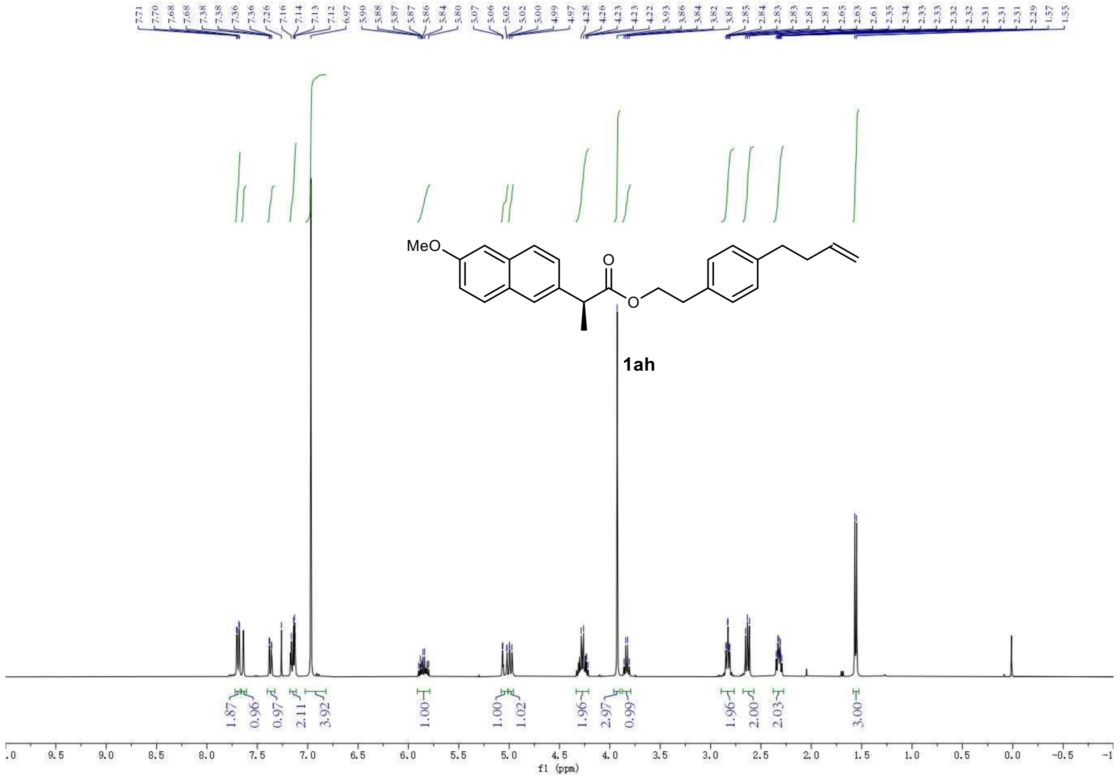
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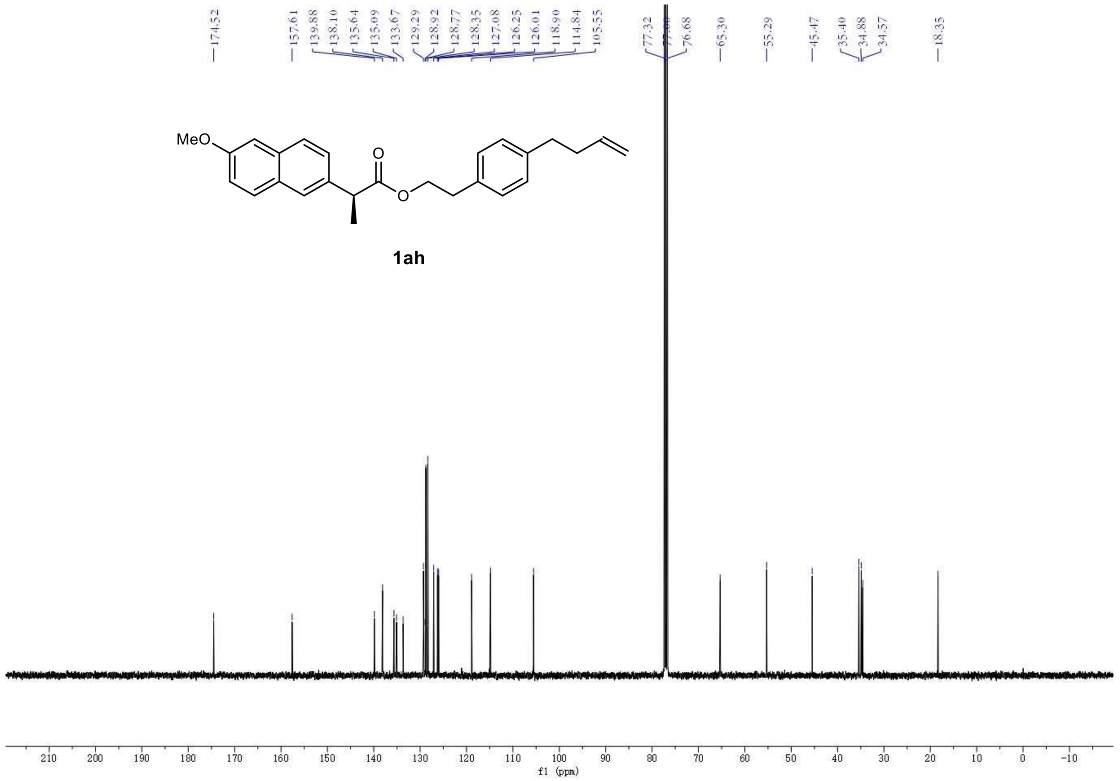
f1 (ppm)

1ah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55.29
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35.40
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34.57
18.35
210
200
190
180
170
160
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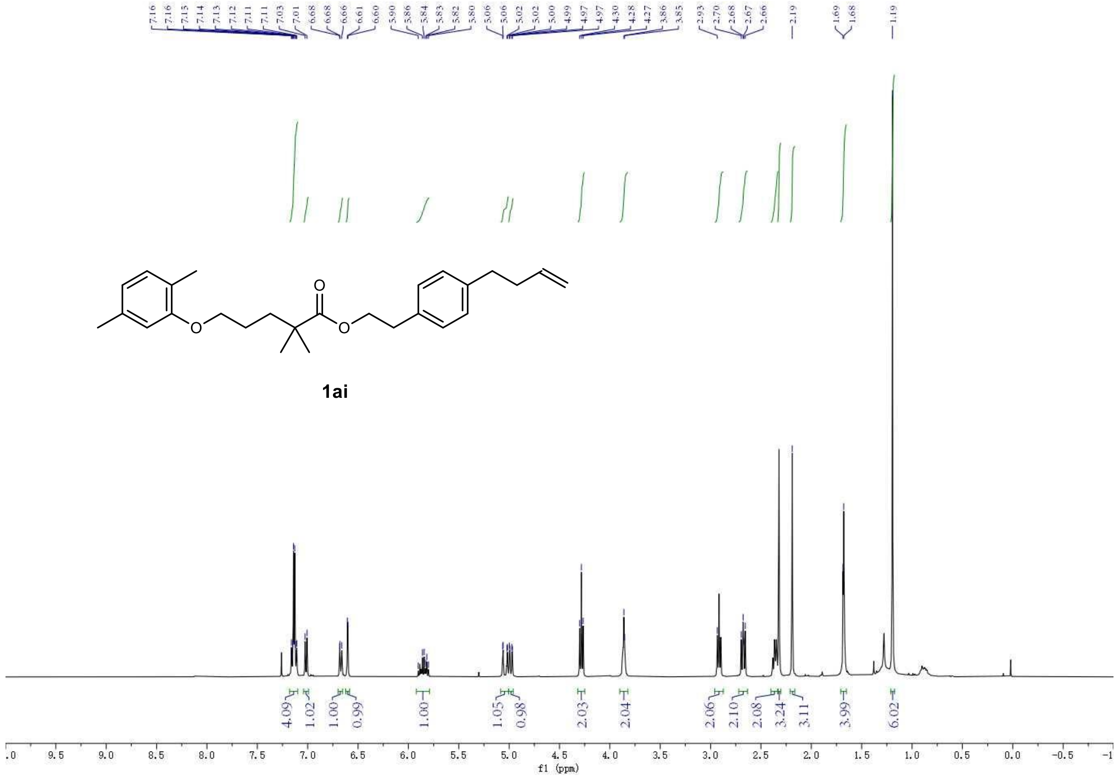
f1 (ppm)

1ah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6.60
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5.84
5.83
5.82
5.80
5.06
5.06
5.02
5.02
5.00
4.99
4.97
4.97
4.30
4.28
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3.86
3.85
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2.68
2.67
2.66
2.19
1.69
1.68
1.19
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O
O
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1.00
1.05
0.98
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2.04
2.06
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3.99
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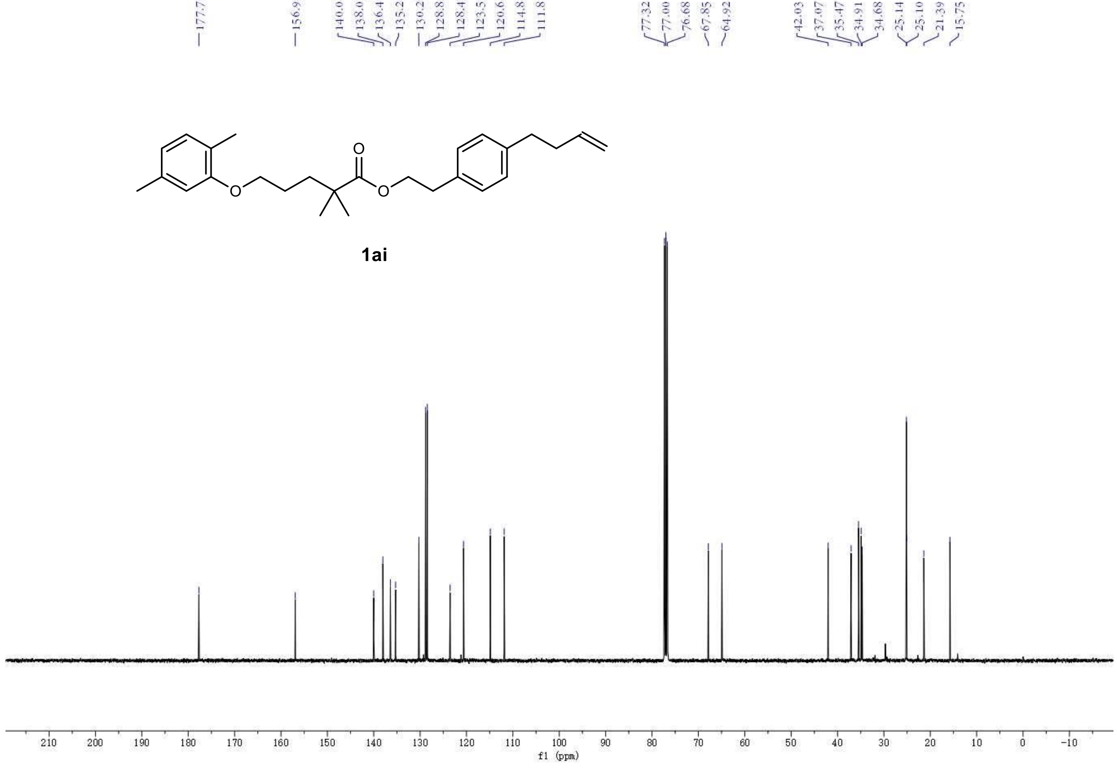
f1 (ppm)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76.68
67.85
64.92
42.03
37.07
35.47
34.91
34.68
25.14
25.10
21.39
15.75
O
O
O
1ai
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200
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180
170
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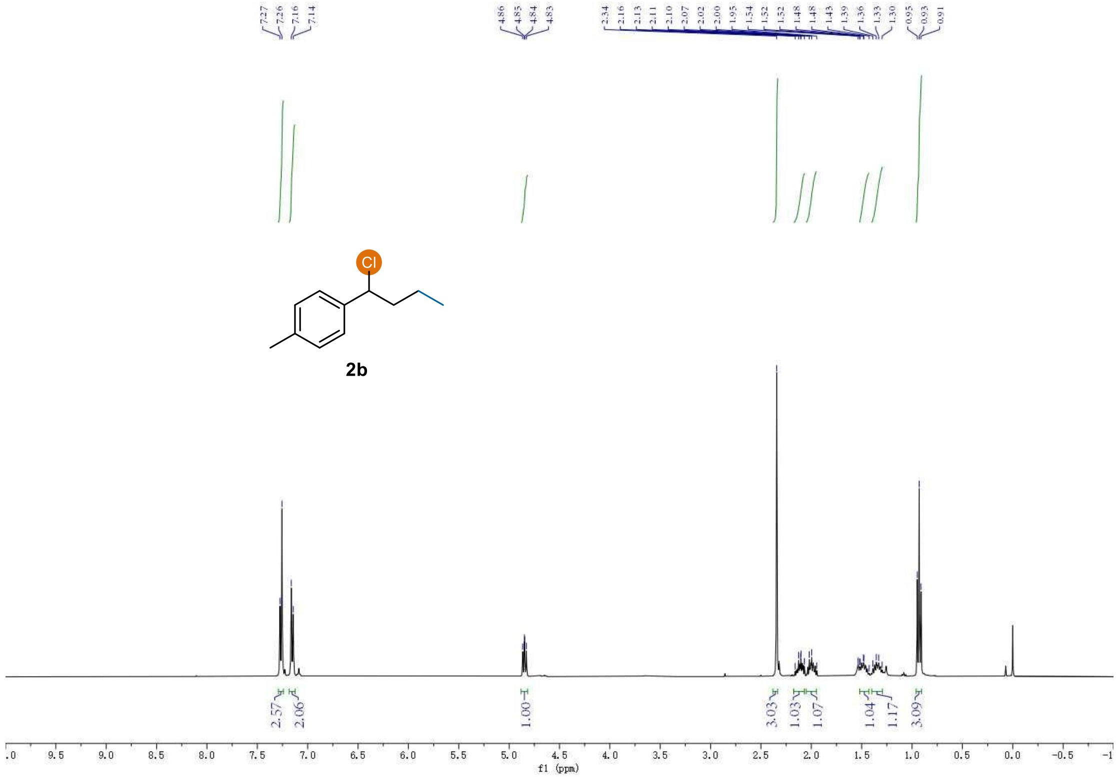
f1 (ppm)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1.48
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1.39
1.36
1.33
1.30
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0.93
0.91
Cl
2b
2.57
2.06
1.00
3.03
1.03
1.07
1.04
1.17
3.09
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9.0
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4.5
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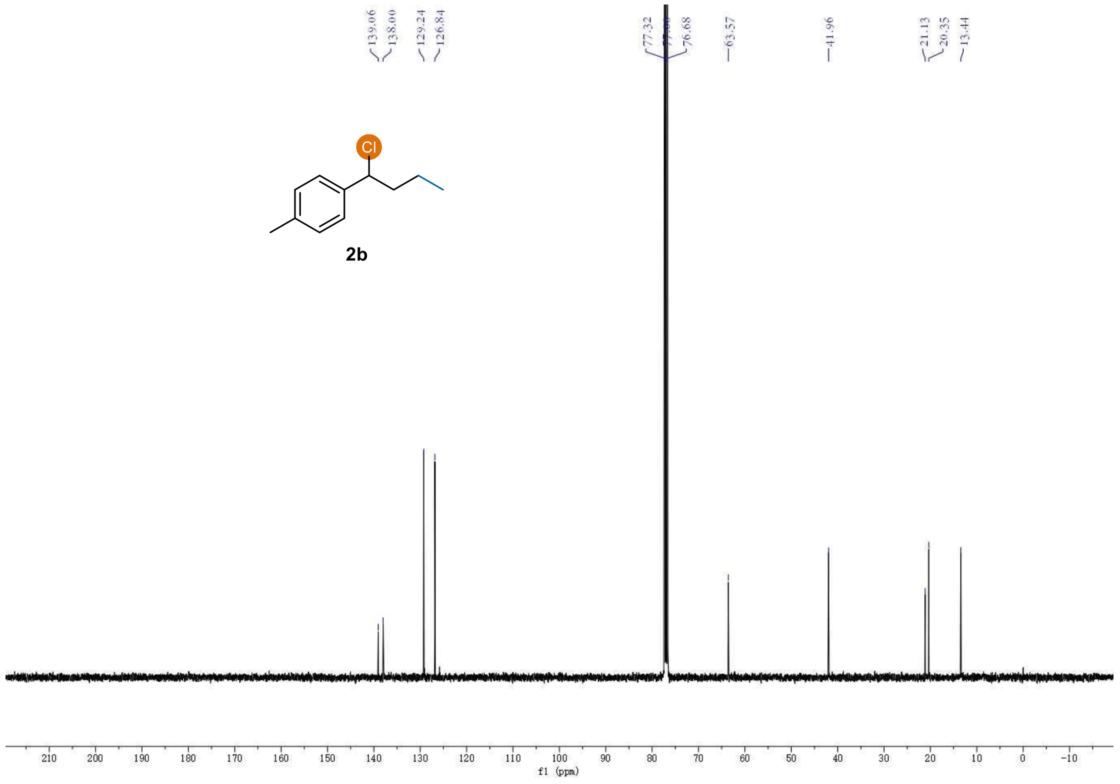
f1 (ppm)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Cl
2b
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200
190
180
170
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100
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80
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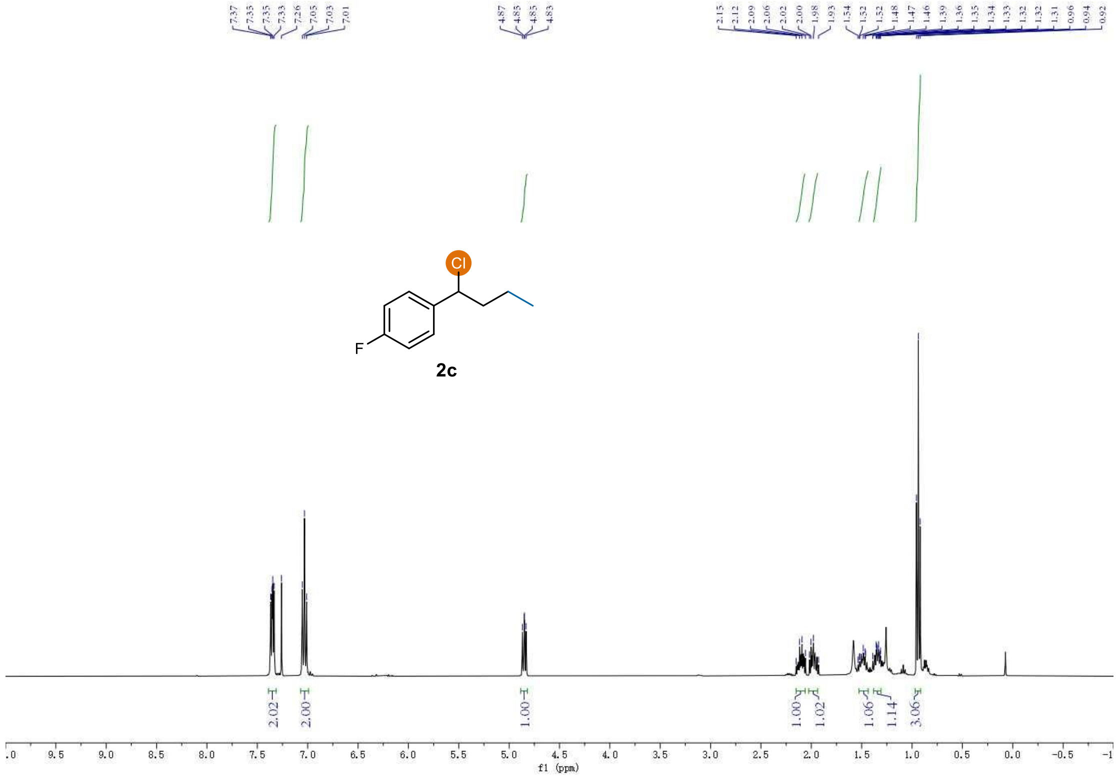
f1 (ppm)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2.09
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1.52
1.52
1.48
1.47
1.46
1.39
1.36
1.35
1.34
1.33
1.32
1.32
1.31
0.96
0.94
0.92
Cl
F
2c
2.02
2.00
1.00
1.00
1.02
1.06
1.14
3.06
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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5.0
4.5
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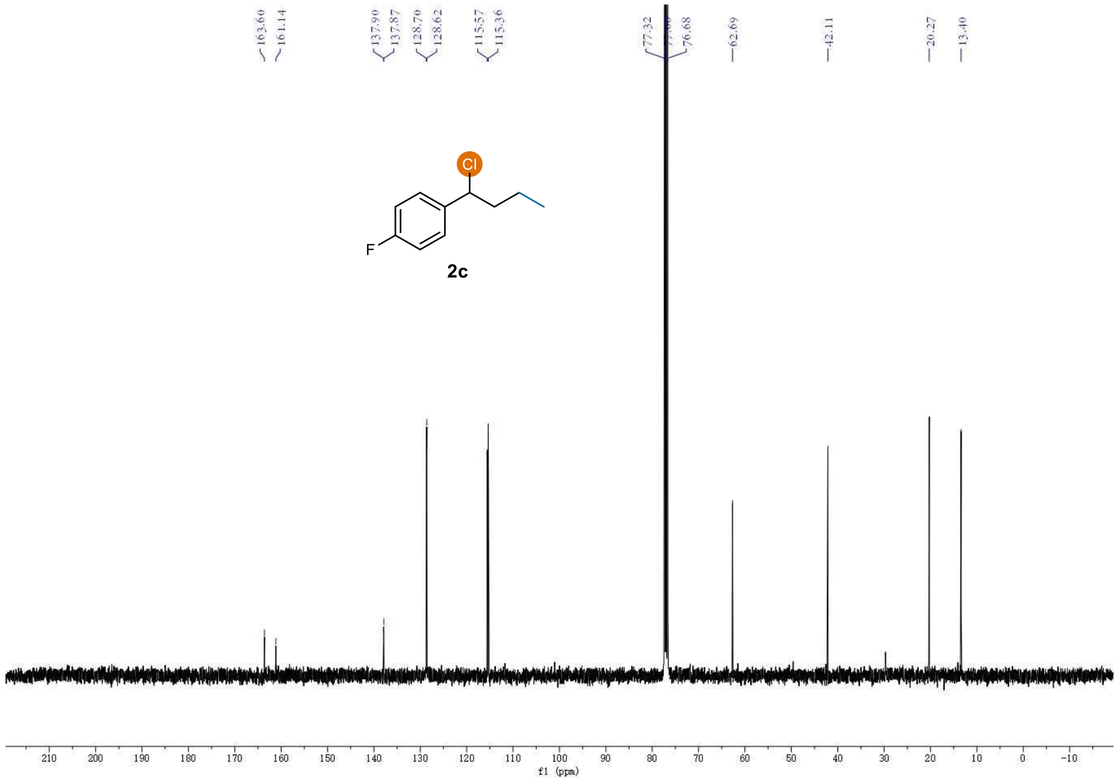
-1
f1 (ppm)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115.57
115.36
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77.00
76.68
62.69
42.11
20.27
13.40
Cl
F
2c
210
200
190
180
170
160
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140
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120
110
100
90
80
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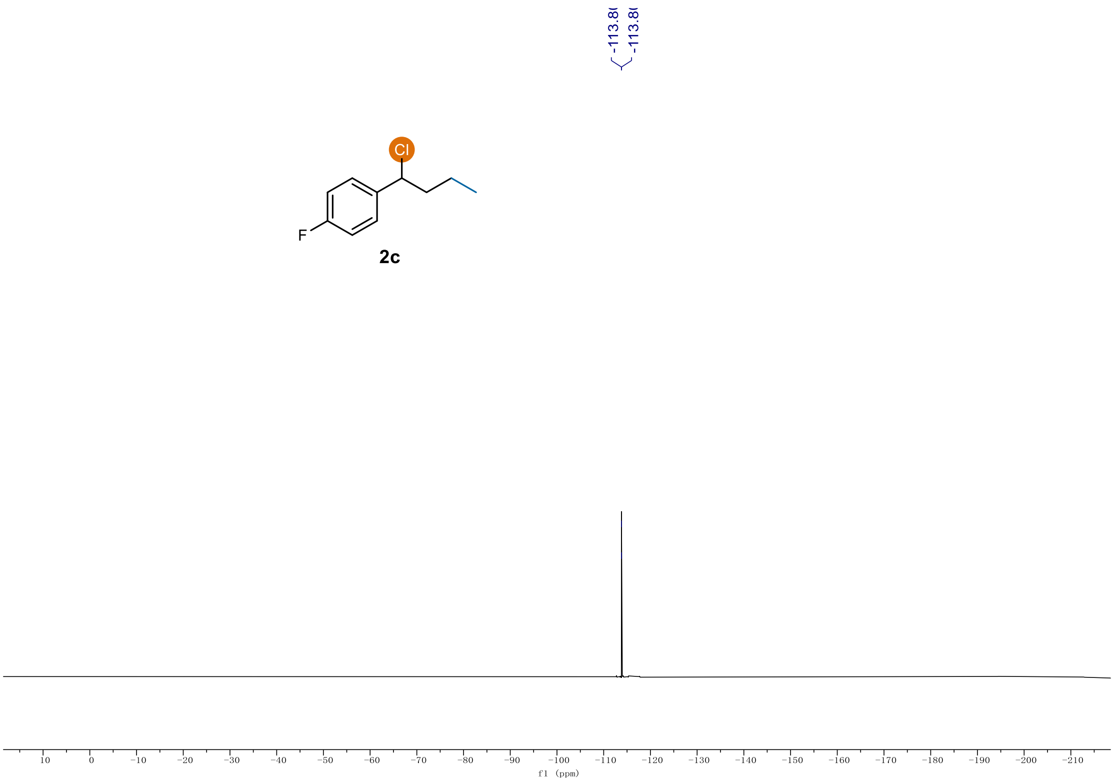
60
50
40
30
20
10
0
-10
f1 (ppm)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-113.8
Cl
F
2c
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0
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-20
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-60
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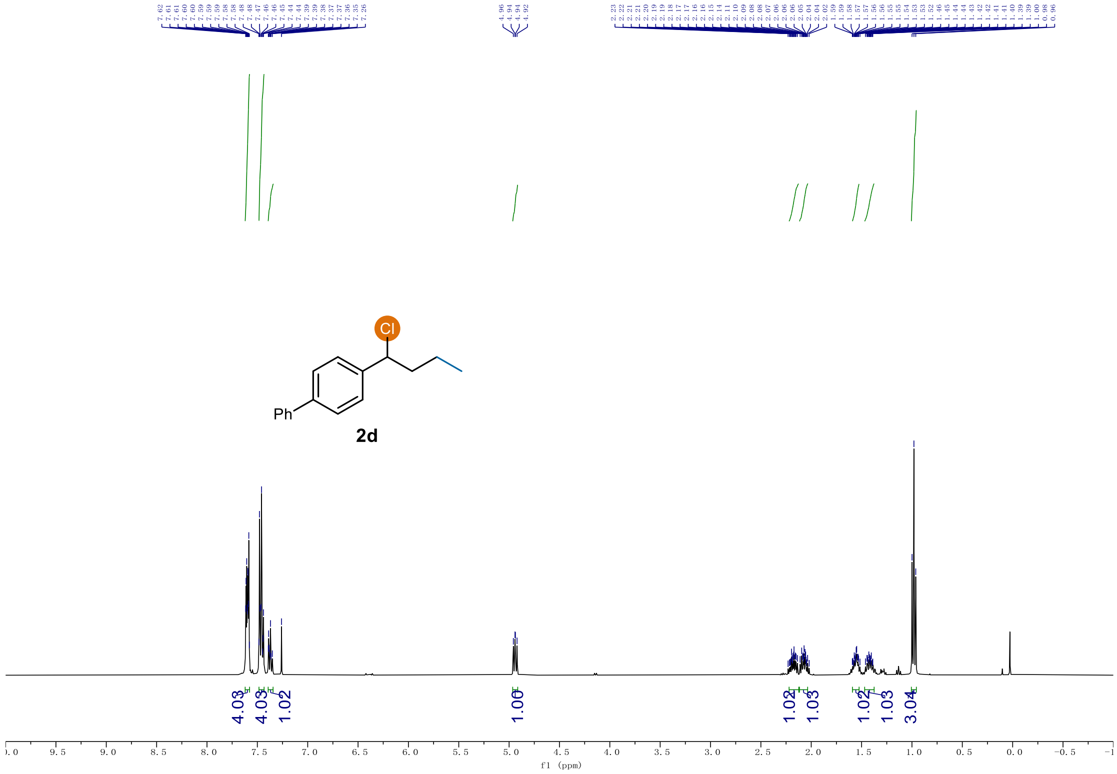
-190
-200
-210
f1 (ppm)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7.47
7.46
7.46
7.45
7.44
7.44
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7.39
7.38
7.37
7.37
7.36
7.35
7.26
4.96
4.94
4.94
4.92
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2.22
2.21
2.21
2.20
2.19
2.19
2.18
2.17
2.17
2.16
2.16
2.15
2.14
2.11
2.10
2.09
2.08
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2.07
2.06
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2.05
2.04
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2.02
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1.55
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1.41
1.40
1.39
1.39
1.00
0.98
0.96
Cl
Ph
2d
4.03
4.03
1.02
1.00
1.02
1.03
1.02
1.03
3.04
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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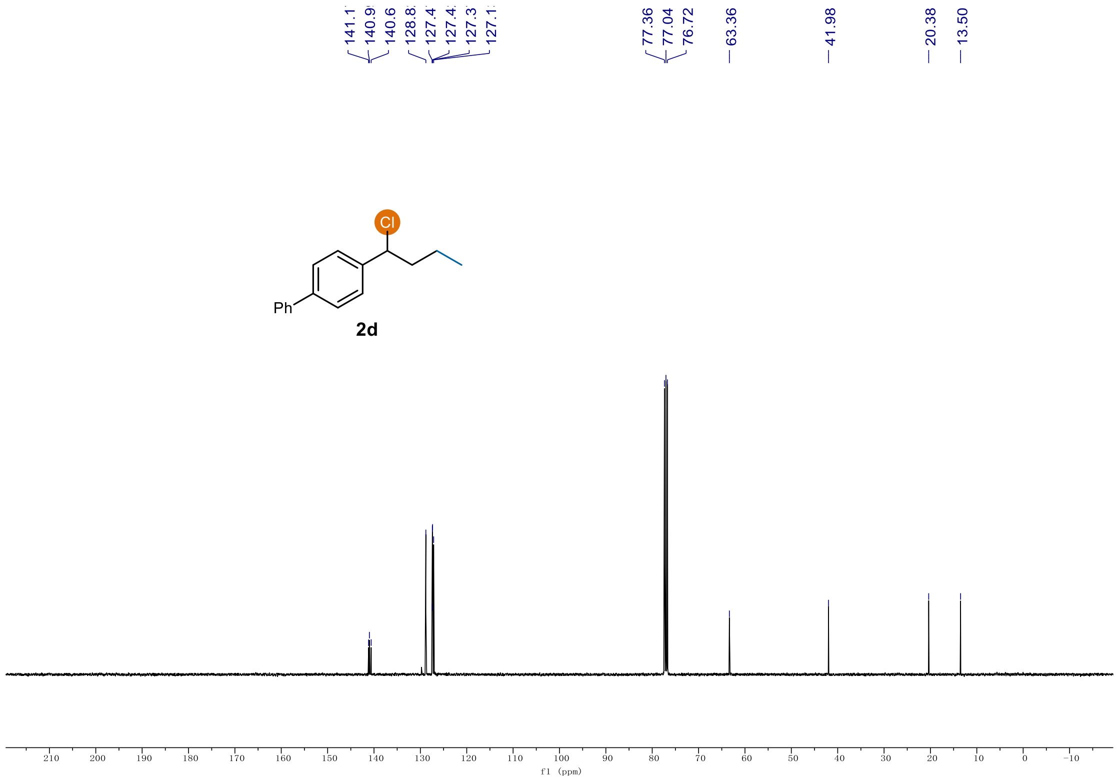
0.0
-0.5
-1
f1 (ppm)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127.4
127.3
127.1
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77.04
76.72
63.36
41.98
20.38
13.50
Cl
Ph
2d
210
200
190
180
170
160
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140
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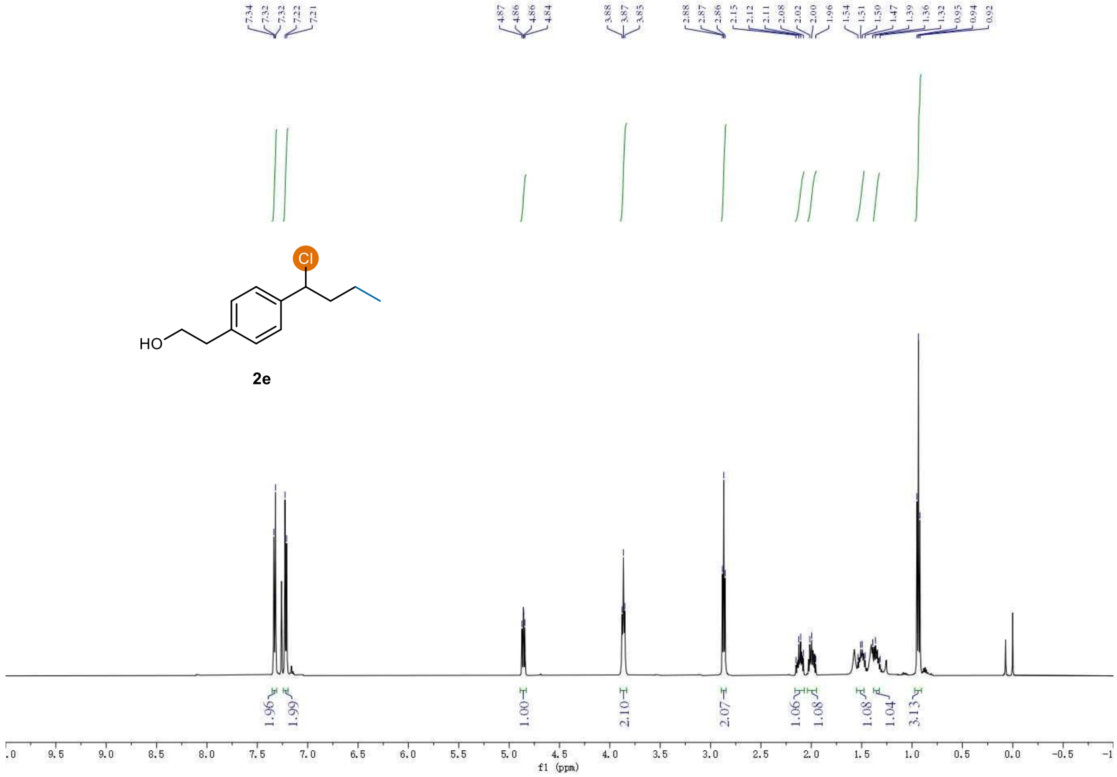
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2.88
2.87
2.86
2.15
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2.11
2.08
2.02
2.00
1.96
1.54
1.51
1.50
1.47
1.39
1.36
1.32
0.95
0.94
0.92
Cl
HO
2e
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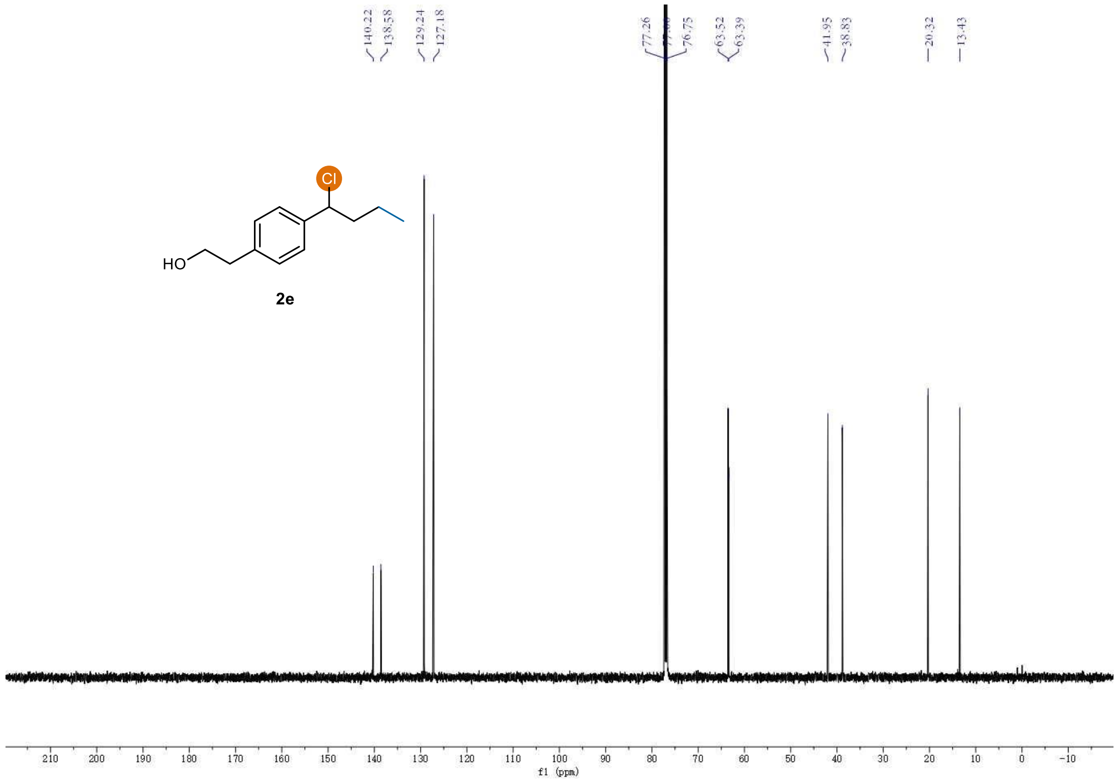
1.00
2.10
2.07
1.06
1.08
1.08
1.04
3.13
f1 (ppm)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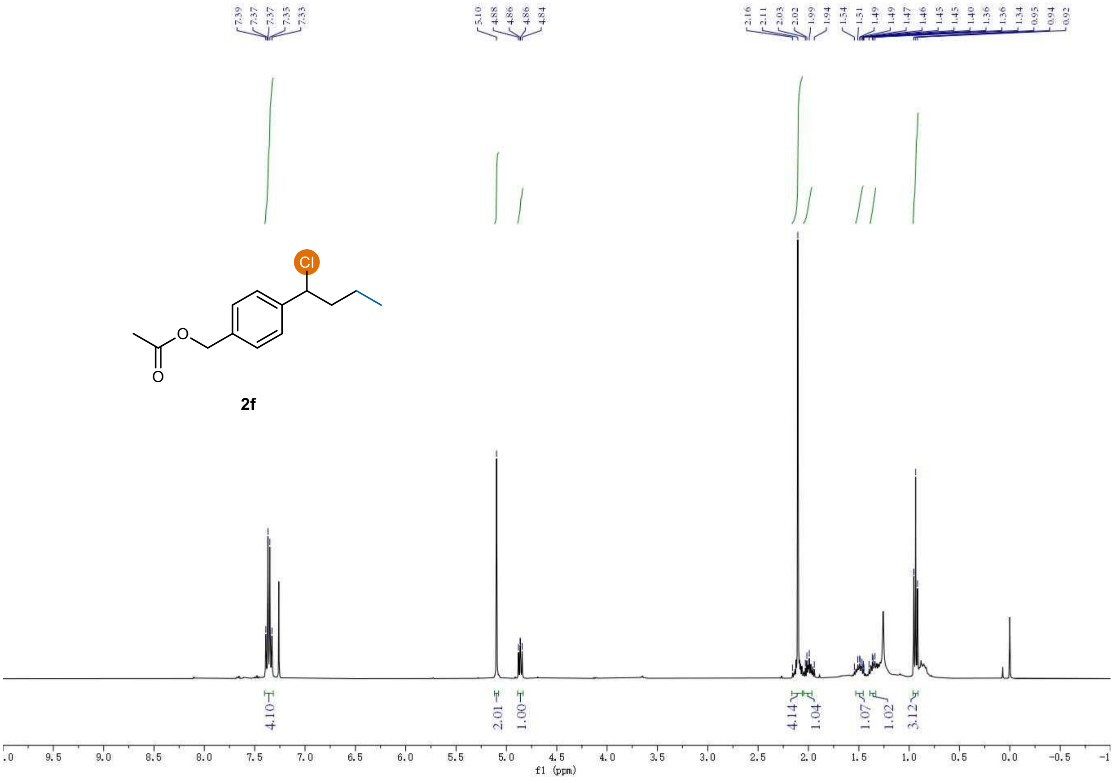
13.43
Cl
HO
2e
f1 (ppm)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7.33
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4.86
4.86
4.84
2.16
2.11
2.03
2.02
1.99
1.94
1.54
1.51
1.49
1.49
1.47
1.46
1.45
1.45
1.40
1.36
1.36
1.34
0.95
0.94
0.92
Cl
O
O
4.10
2.01
1.00
4.14
1.04
1.07
1.02
3.12
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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1.0
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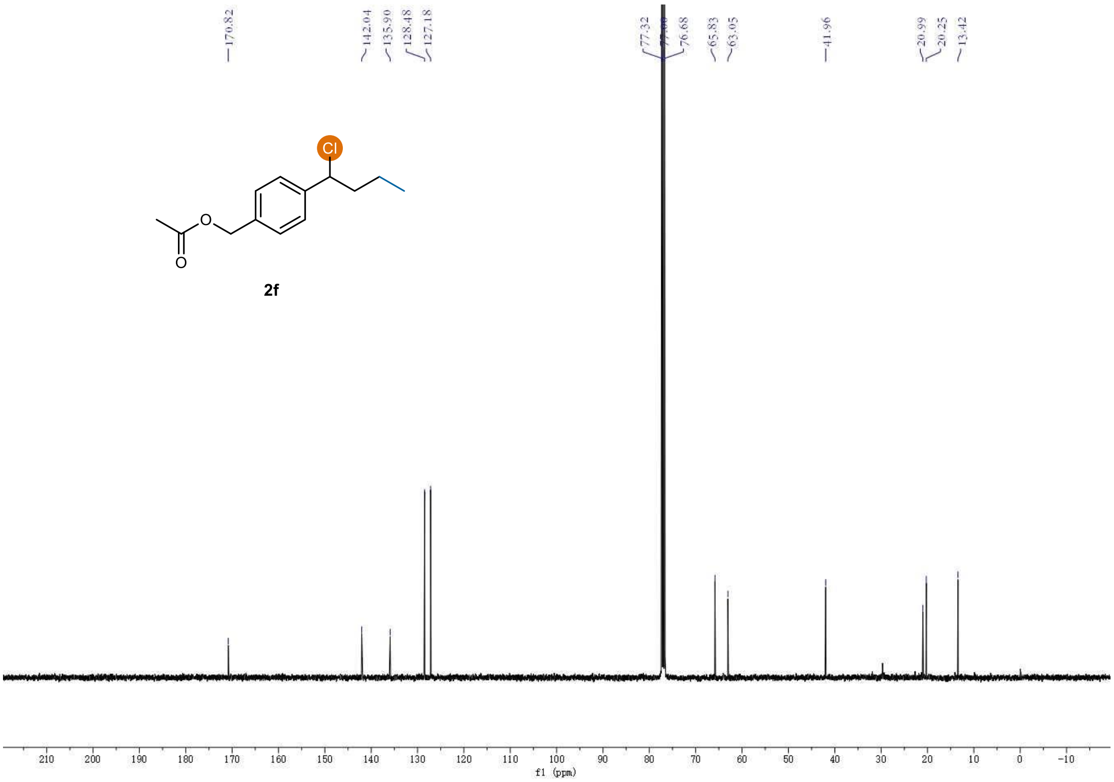
-1
f1 (ppm)

2f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77.32
77.00
76.68
65.83
63.05
41.96
20.99
20.25
13.42
Cl
O
O
210
200
190
180
170
160
150
140
130
120
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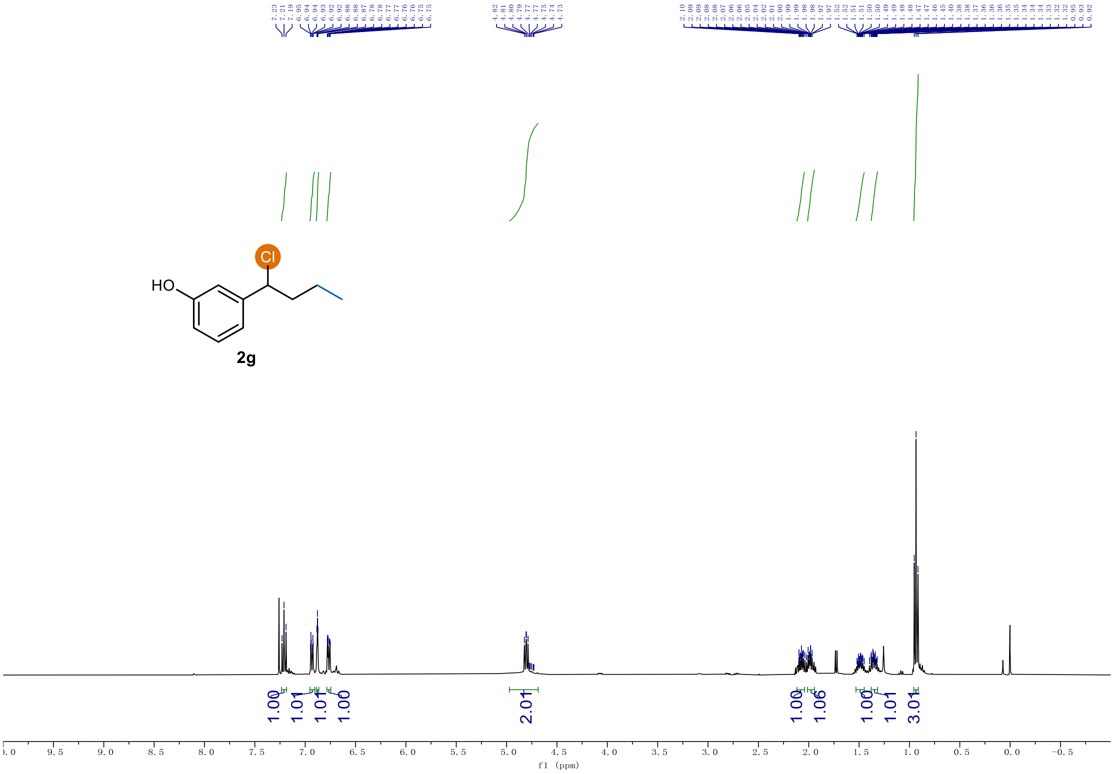
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2f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6.87
6.78
6.78
6.77
6.77
6.76
6.76
6.75
6.75
4.82
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4.80
4.79
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4.77
4.75
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2.09
2.08
2.08
2.07
2.06
2.06
2.05
2.04
2.02
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2.00
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1.99
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1.51
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1.33
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1.32
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0.93
0.92
HO
Cl
2g
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1.01
1.00
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1.00
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1.00
1.01
3.01
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9.0
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7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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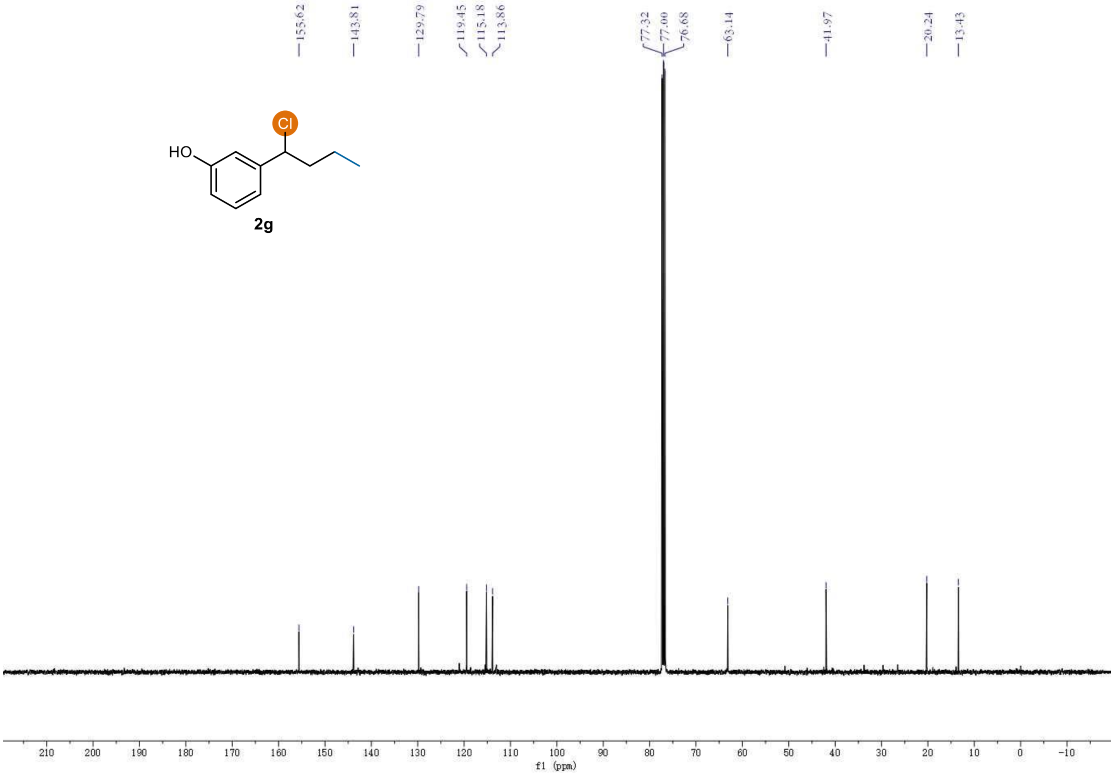
f1 (ppm)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41.97
20.24
13.43
HO
Cl
2g
210
200
190
180
170
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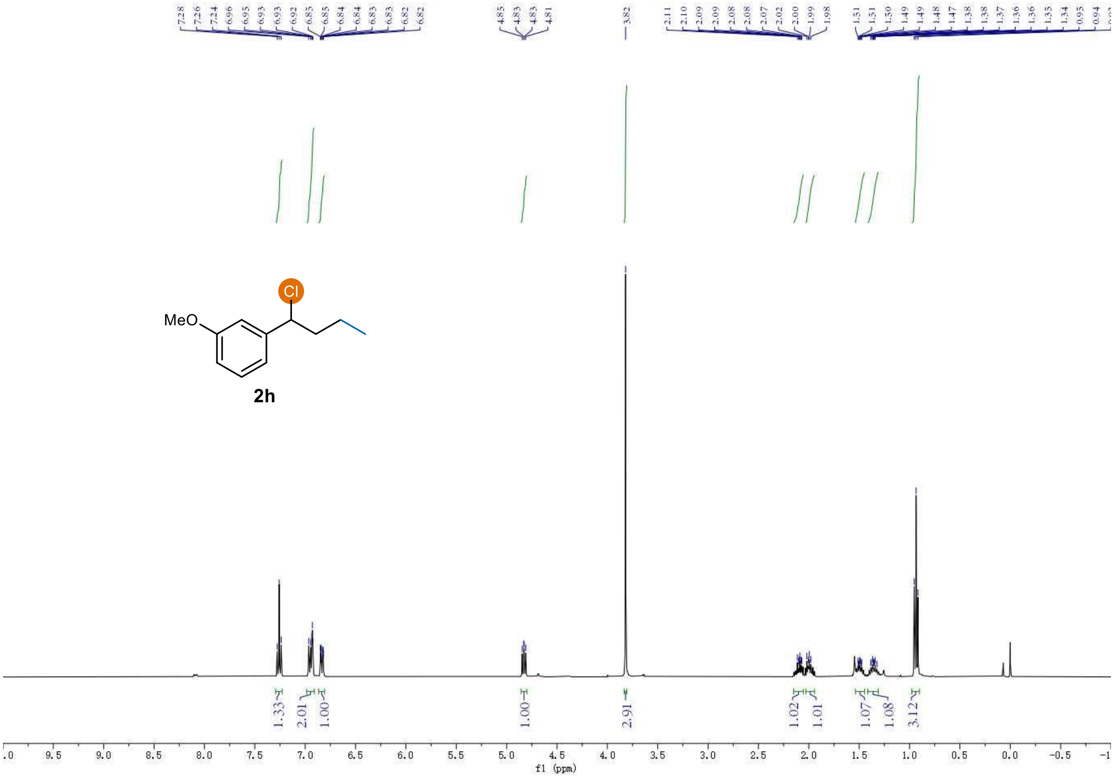
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.82
4.85
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2.09
2.09
2.08
2.08
2.07
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1.49
1.48
1.47
1.38
1.38
1.37
1.36
1.36
1.35
1.34
0.95
0.94
Cl
MeO
2h
1.33
2.01
1.00
1.00
2.91
1.02
1.01
1.07
1.08
3.12
9.5
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8.5
8.0
7.5
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6.5
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5.0
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2.5
2.0
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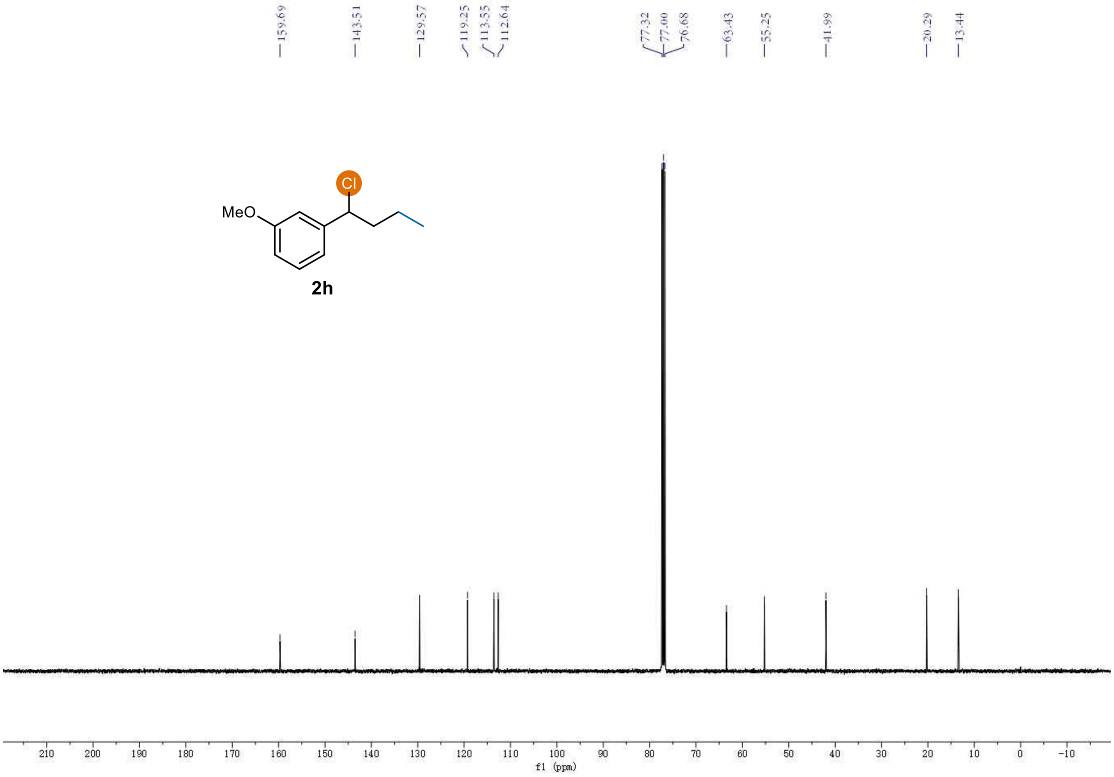
0.5
0.0
-0.5
f1 (ppm)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Cl
MeO
2h
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200
190
180
170
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100
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80
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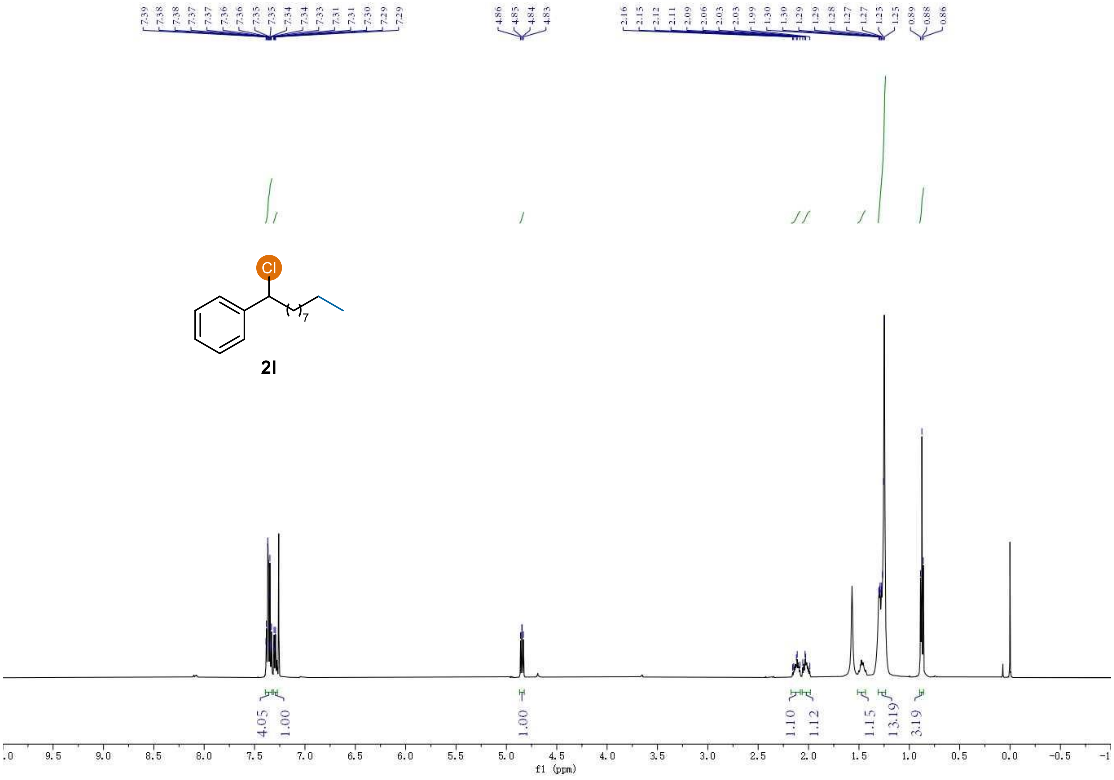
-10
f1 (ppm)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7.31
7.30
7.29
7.29
4.86
4.85
4.84
4.83
2.16
2.15
2.12
2.11
2.09
2.06
2.03
2.03
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Cl
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.0
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6.5
6.0
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4.5
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1.5
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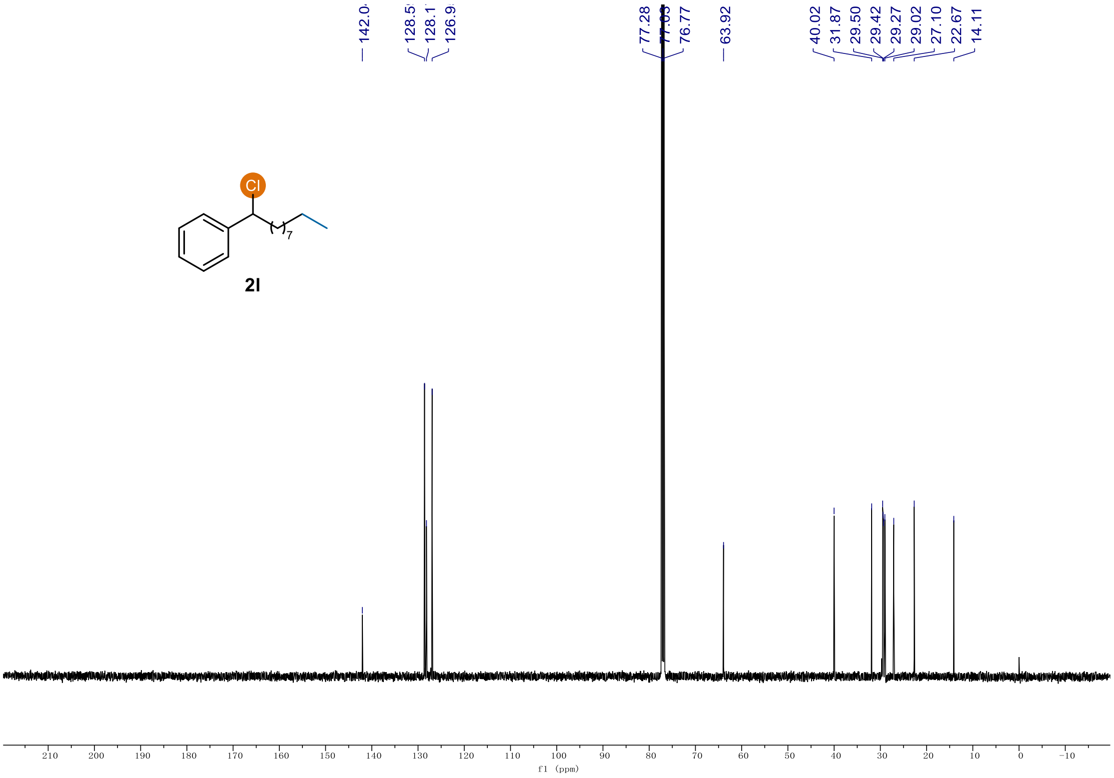
0.0
-0.5
-1
f1 (ppm)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22.67
14.11
Cl
7
2l
210
200
190
180
170
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100
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80
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30
20
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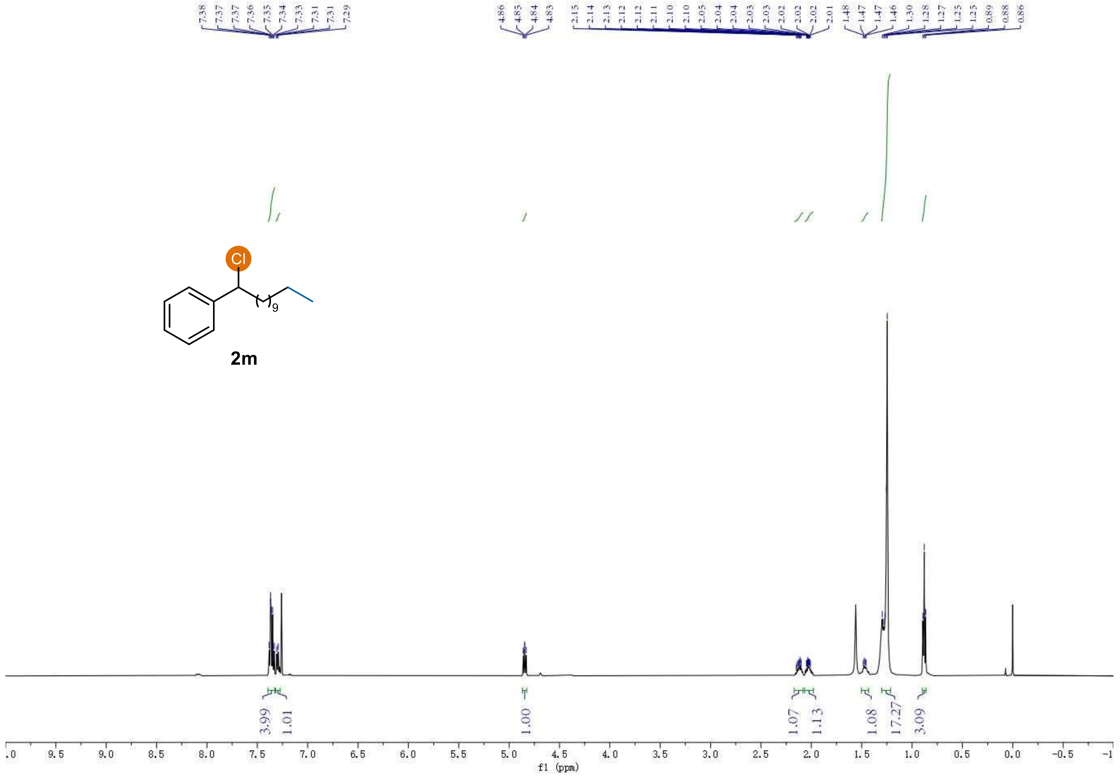
0
-10
f1 (ppm)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4.84
4.83
2.15
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2.13
2.12
2.12
2.11
2.10
2.05
2.04
2.04
2.03
2.03
2.02
2.02
2.02
2.01
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1.27
1.25
1.25
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0.88
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Cl
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1.00
1.07
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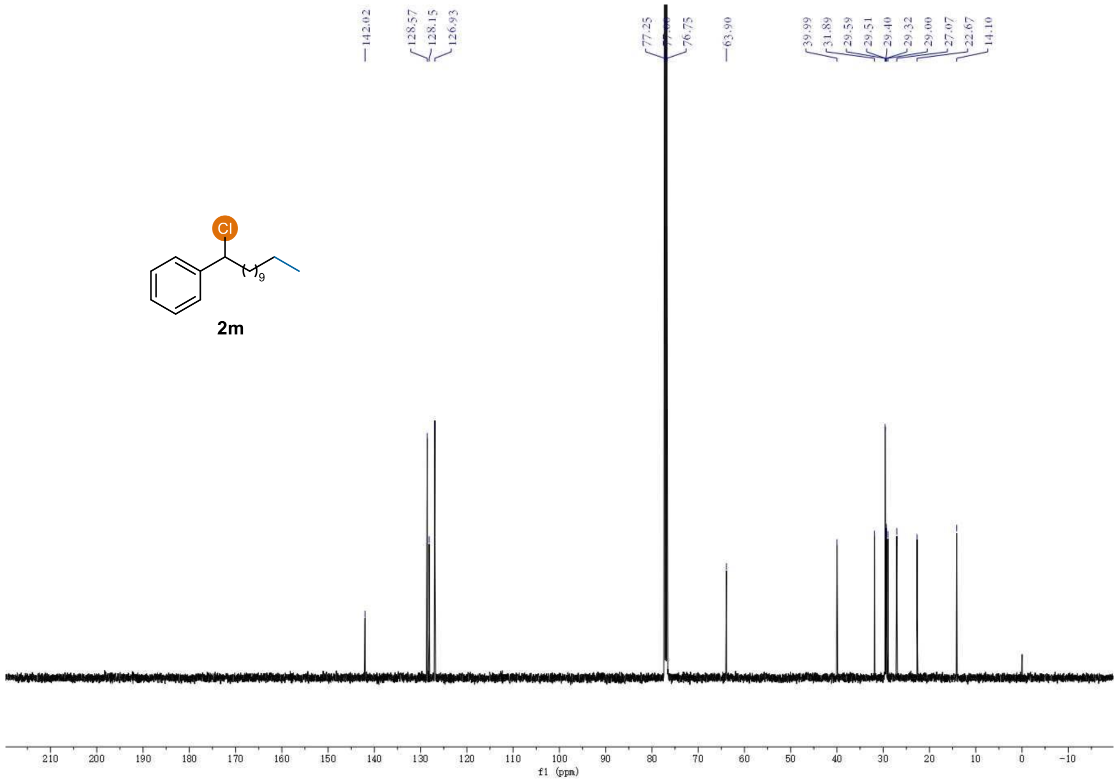
1.08
17.27
3.09
f1 (ppm)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27.07
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14.10
Cl
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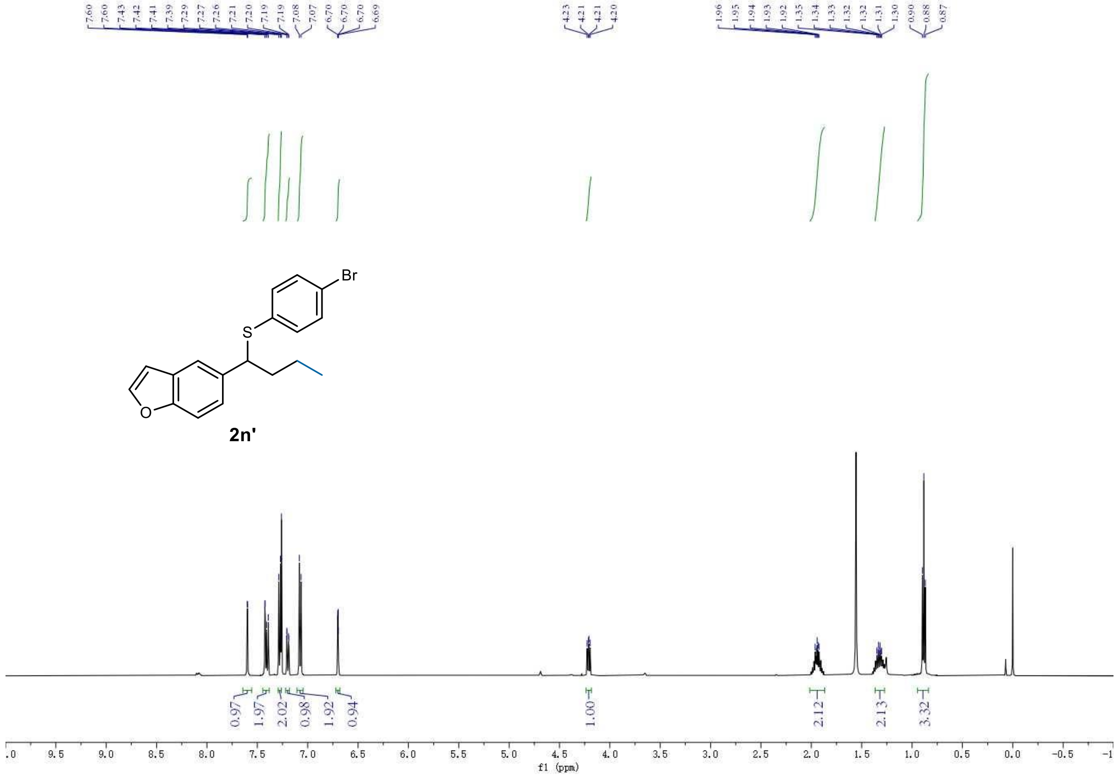
2m
f1 (ppm)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6.70
6.69
4.23
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4.21
4.20
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1.94
1.93
1.92
1.35
1.34
1.33
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1.32
1.31
1.30
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0.87
Br
S
O
0.97
1.97
2.02
0.98
1.92
0.94
1.00
2.12
2.13
3.32
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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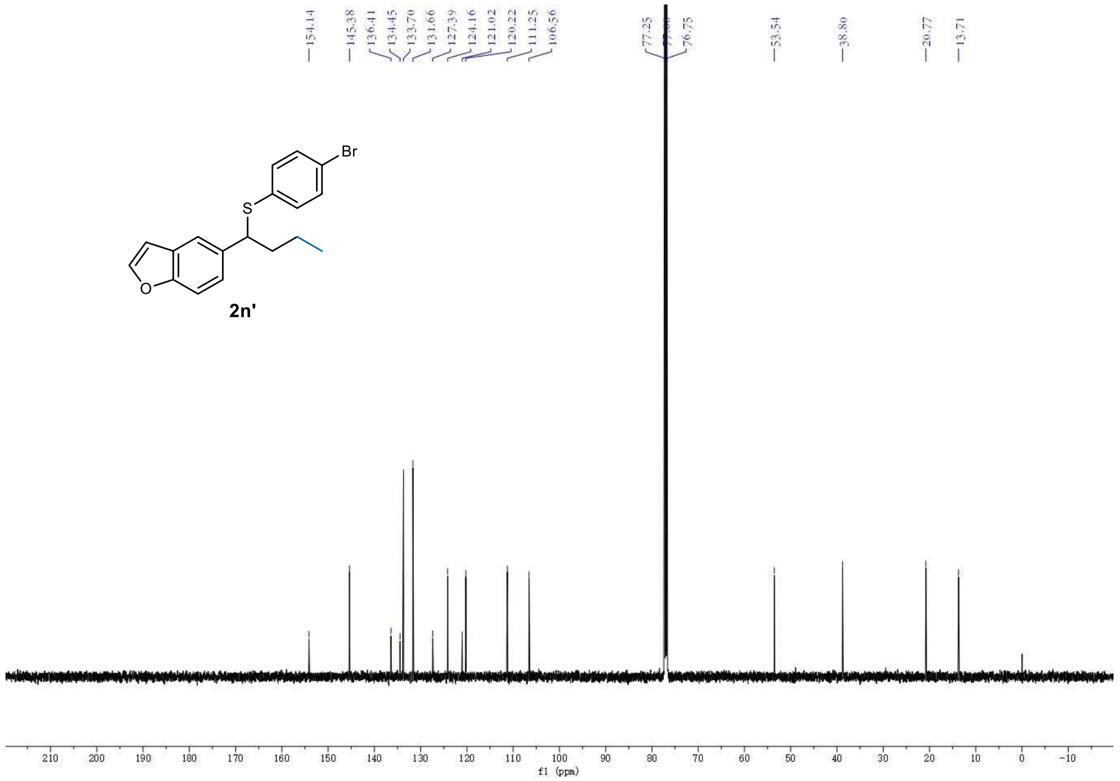
0.0
-0.5
f1 (ppm)

2n'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121.02
120.22
111.25
106.56
77.25
76.75
53.54
38.80
20.77
13.71
Br
S
O
210
200
190
180
170
160
150
140
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120
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100
90
80
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60
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40
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20
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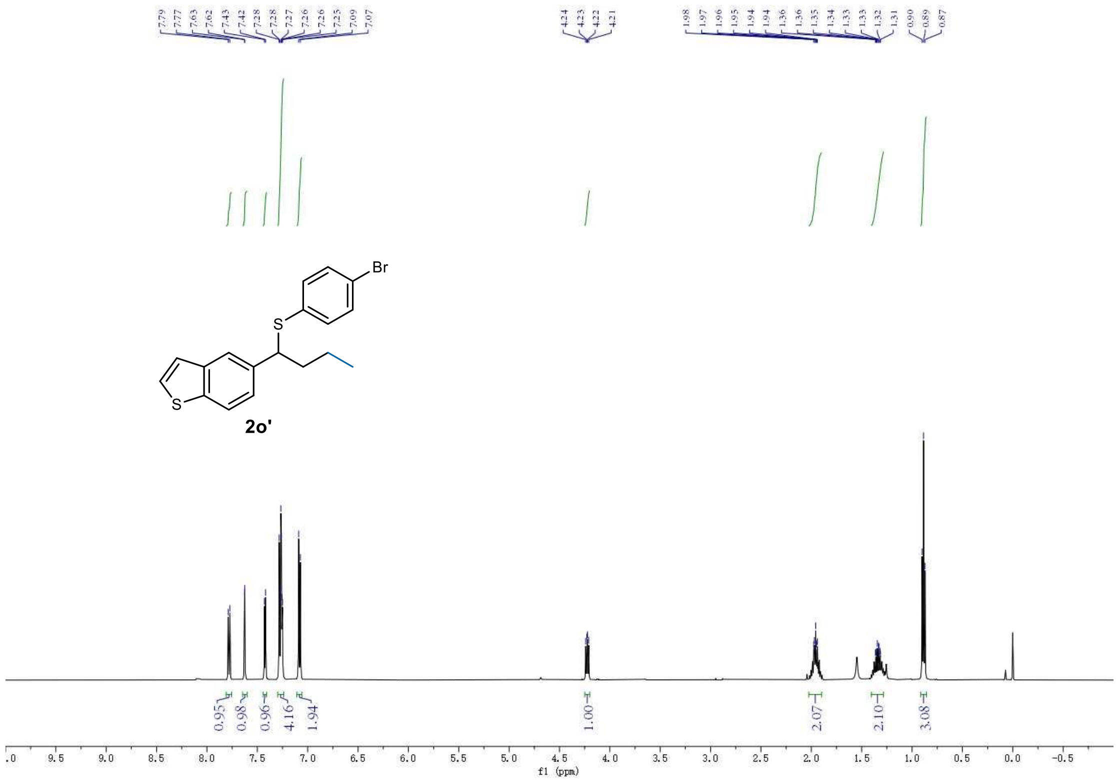
f1 (ppm)

2n'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7.09
7.07
4.24
4.23
4.22
4.21
1.98
1.97
1.96
1.95
1.94
1.94
1.36
1.36
1.35
1.34
1.33
1.33
1.32
1.31
0.90
0.89
0.87
Br
S
S
2o'
0.95
0.98
0.96
4.16
1.94
1.00
2.07
2.10
3.08
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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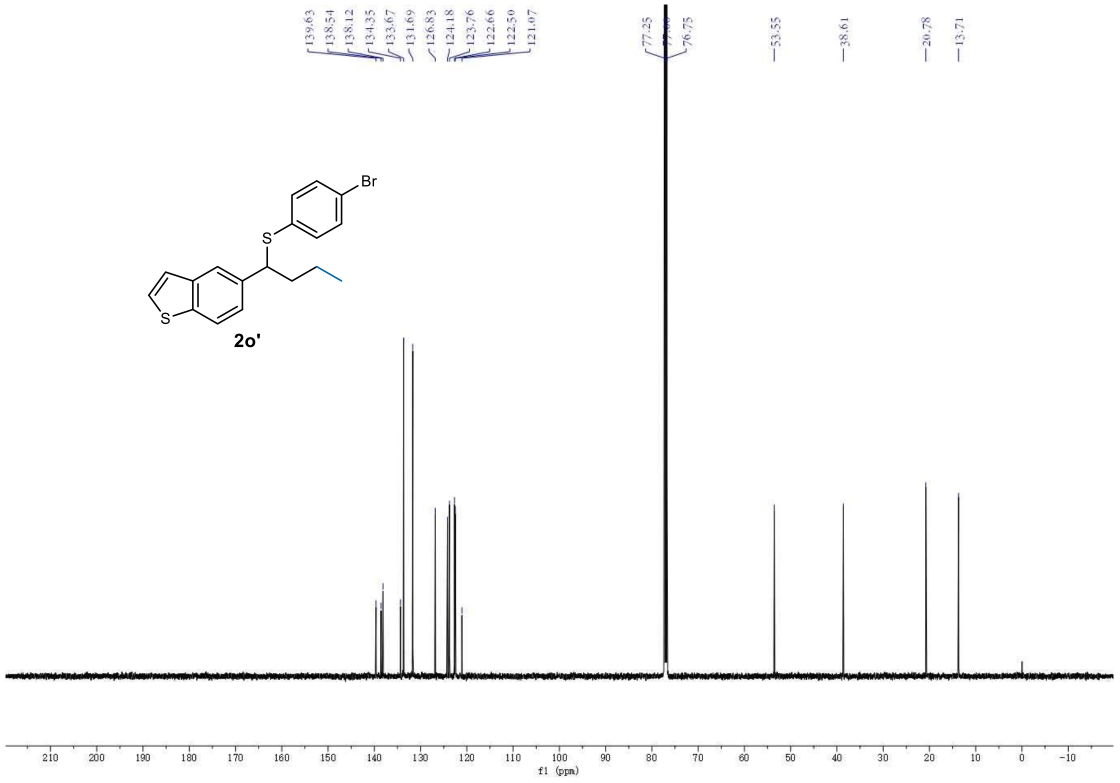
-0.5
f1 (ppm)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122.66
122.50
121.07
77.25
76.75
53.55
38.61
20.78
13.71
Br
S
S
2o'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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30
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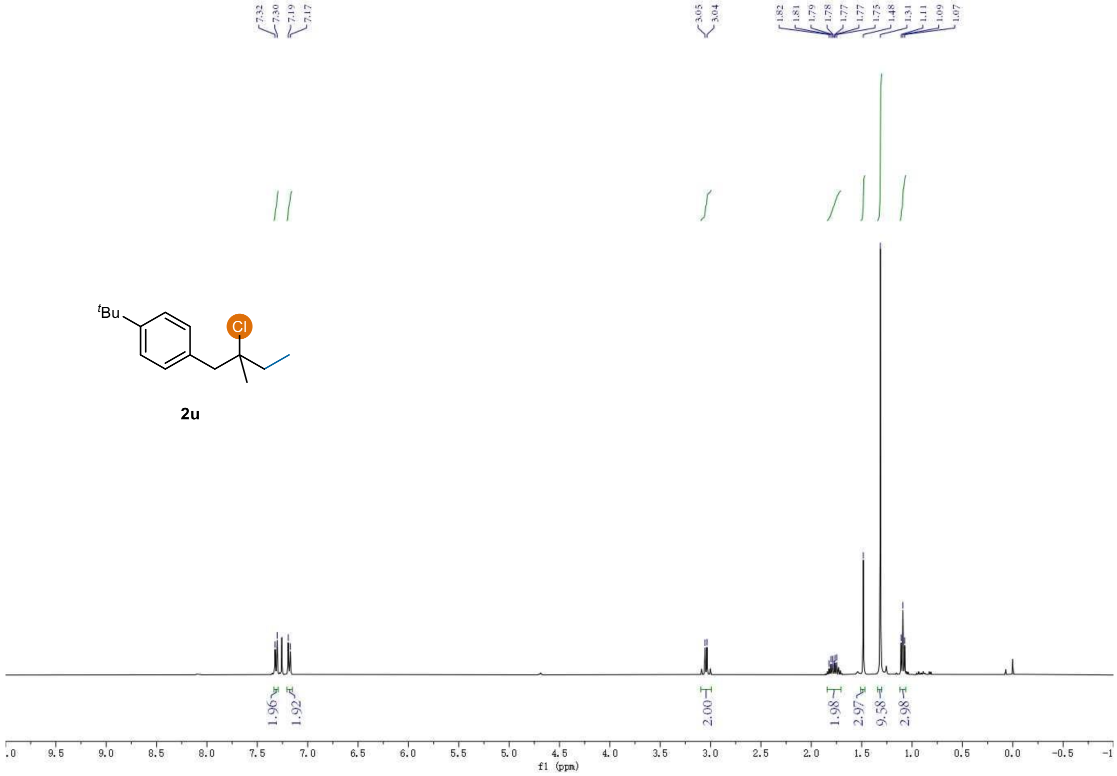
-10
f1 (ppm)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1.78
1.77
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1.75
1.48
1.31
1.11
1.09
1.07
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Cl
2u
1.96
1.92
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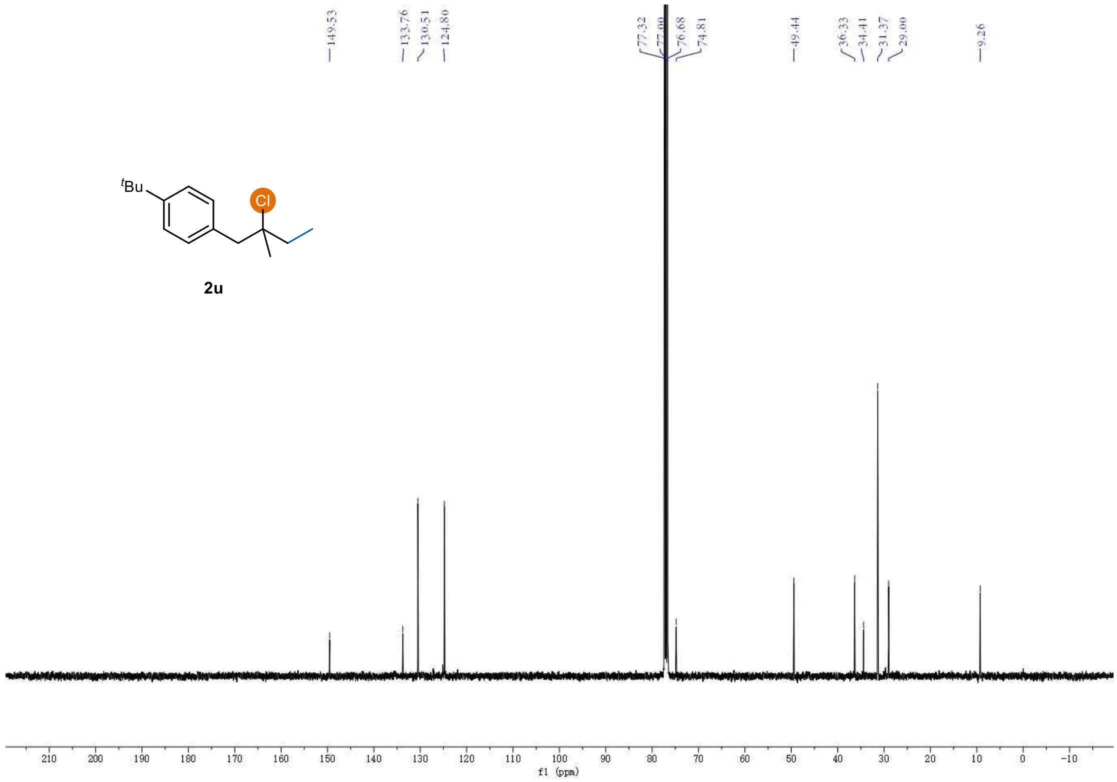
2.97
9.58
2.98
f1 (ppm)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36.33
34.41
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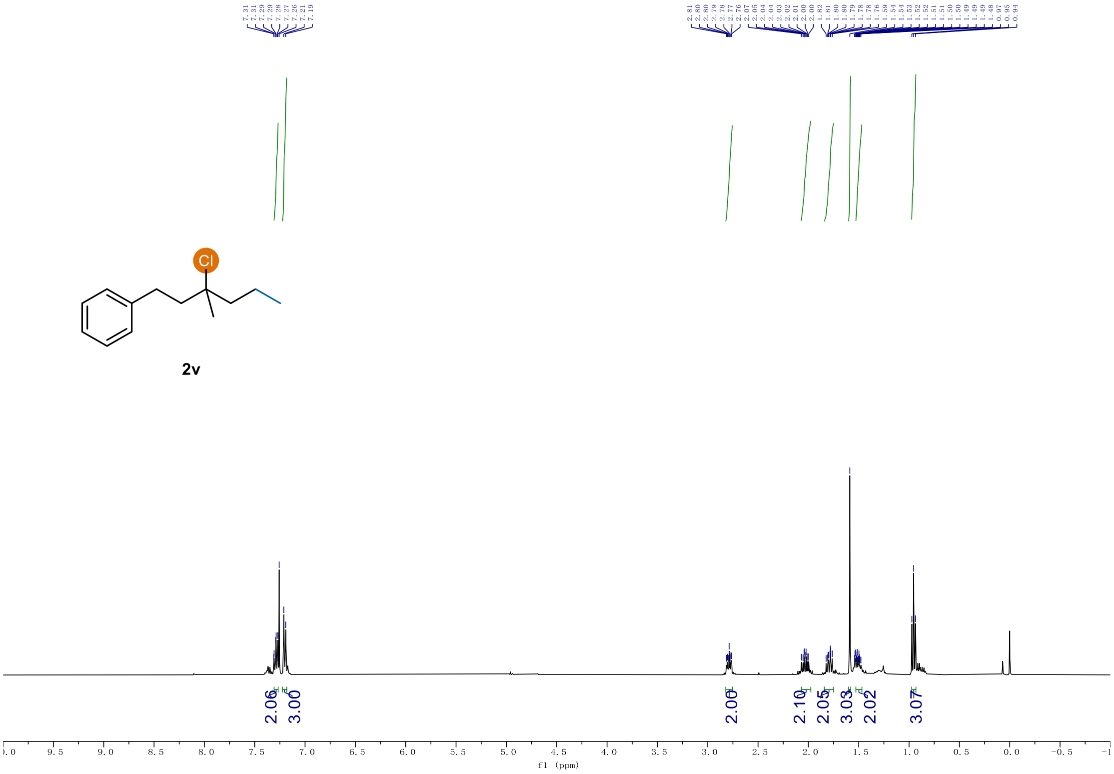
29.00
9.26
tBu
Cl
2u
f1 (ppm)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2.79
2.78
2.77
2.76
2.07
2.05
2.04
2.04
2.03
2.02
2.01
2.00
2.00
1.82
1.81
1.80
1.80
1.79
1.78
1.78
1.76
1.59
1.54
1.54
1.53
1.52
1.52
1.51
1.51
1.50
1.50
1.49
1.49
1.48
0.97
0.95
0.94
Cl
2v
2.06
3.00
2.00
2.10
2.05
3.03
2.02
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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0.0
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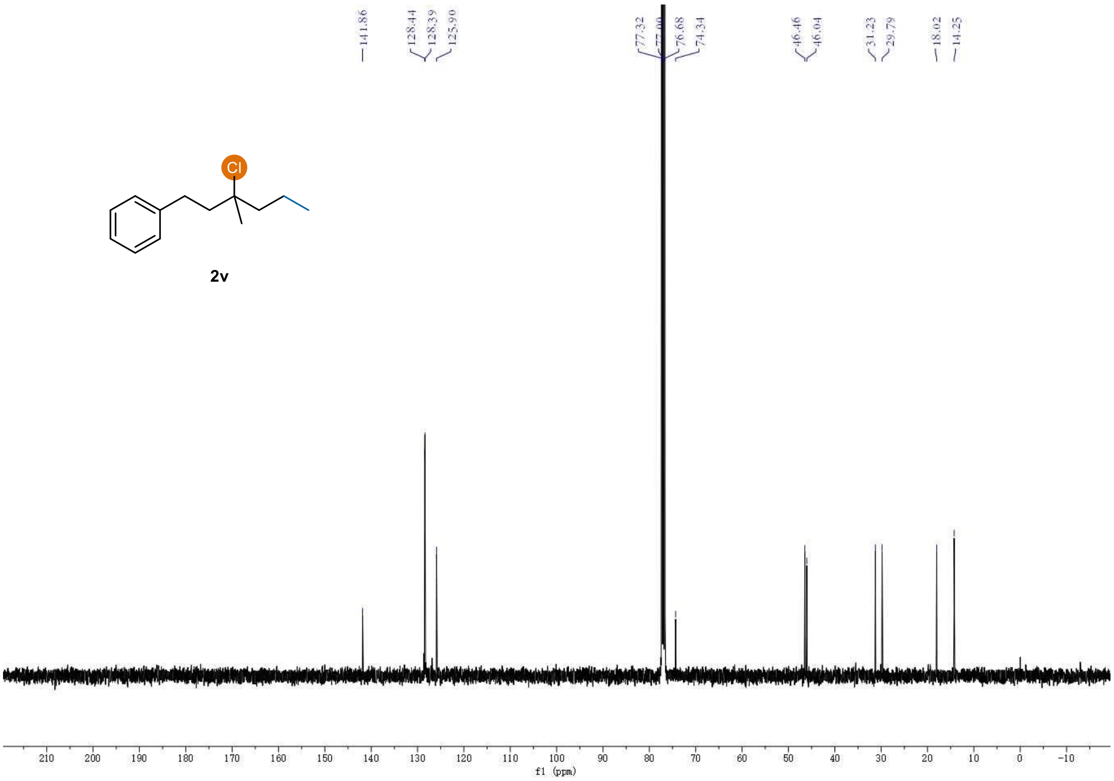
-1
f1 (ppm)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77.00
76.68
74.34
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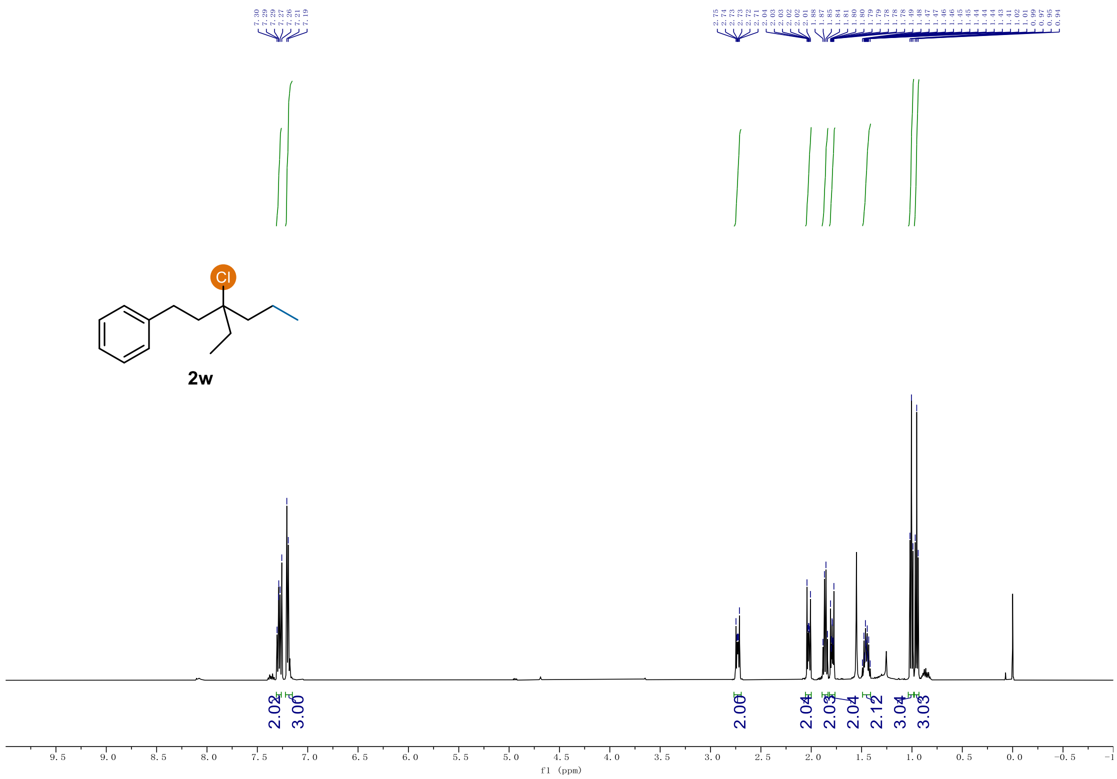
46.04
31.23
29.79
18.02
14.25
Cl
2v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.29
7.29
7.27
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7.21
7.19
2.75
2.74
2.73
2.73
2.72
2.71
2.04
2.03
2.03
2.02
2.02
2.01
1.88
1.87
1.85
1.84
1.81
1.80
1.80
1.79
1.79
1.78
1.78
1.78
1.49
1.48
1.47
1.47
1.46
1.46
1.45
1.45
1.44
1.44
1.44
1.43
1.41
1.02
1.01
0.99
0.97
0.95
0.94
Cl
2w
2.02
3.00
2.00
2.04
2.03
2.04
2.12
3.04
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
1.5
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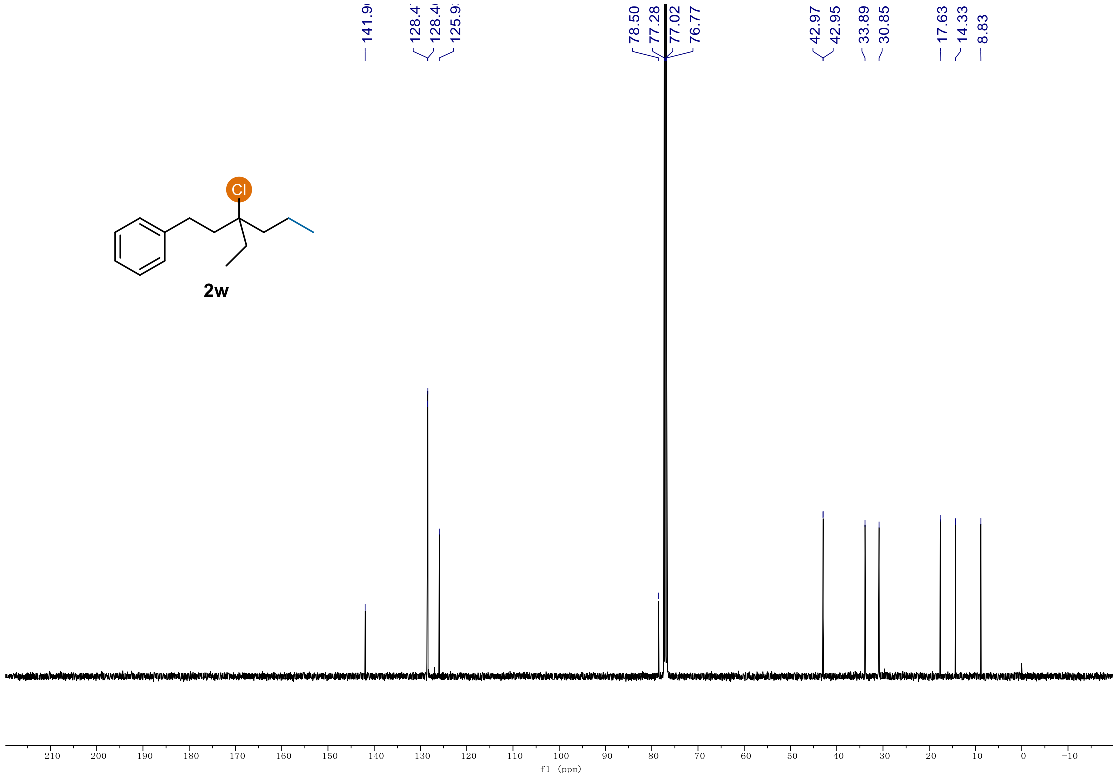
0.0
-0.5
-1
f1 (ppm)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77.28
77.02
76.77
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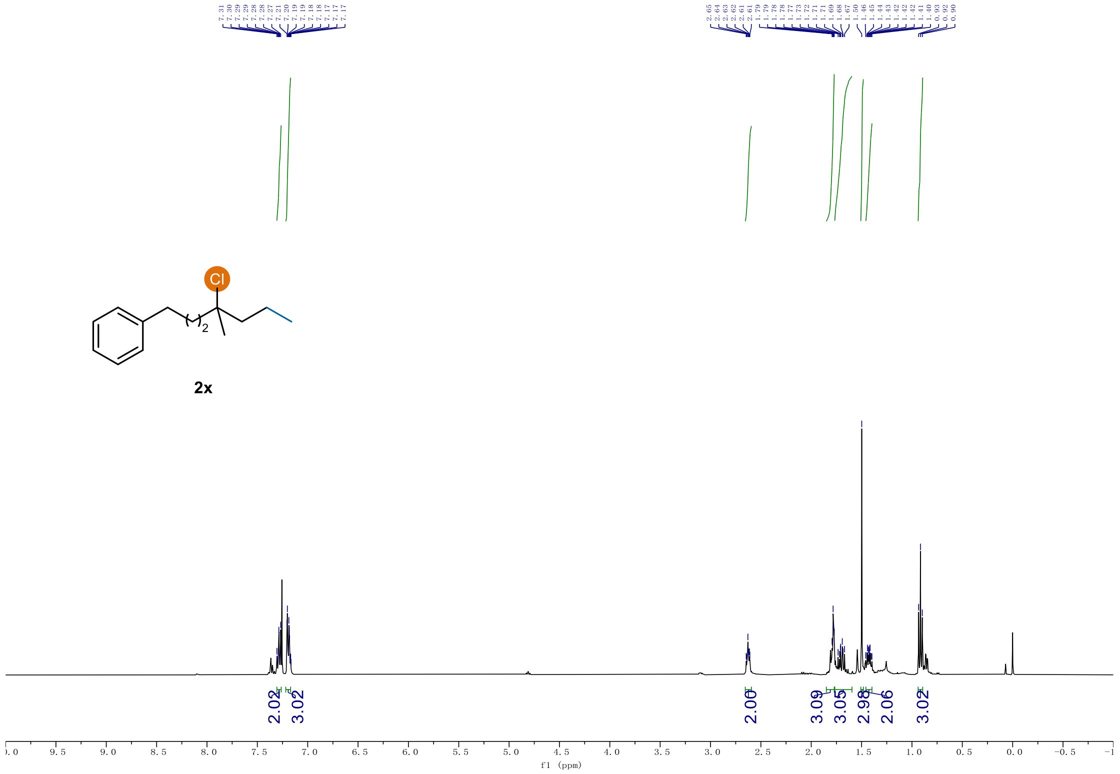
42.95
33.89
30.85
17.63
14.33
8.83
Cl
2w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.27
7.21
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7.17
7.17
7.17
2.65
2.64
2.63
2.62
2.61
2.61
1.79
1.79
1.78
1.78
1.77
1.73
1.72
1.71
1.71
1.69
1.68
1.67
1.50
1.46
1.45
1.44
1.43
1.42
1.42
1.42
1.41
1.40
0.93
0.92
0.90
Cl
2
2x
2.02
3.02
2.00
3.09
3.05
2.98
2.06
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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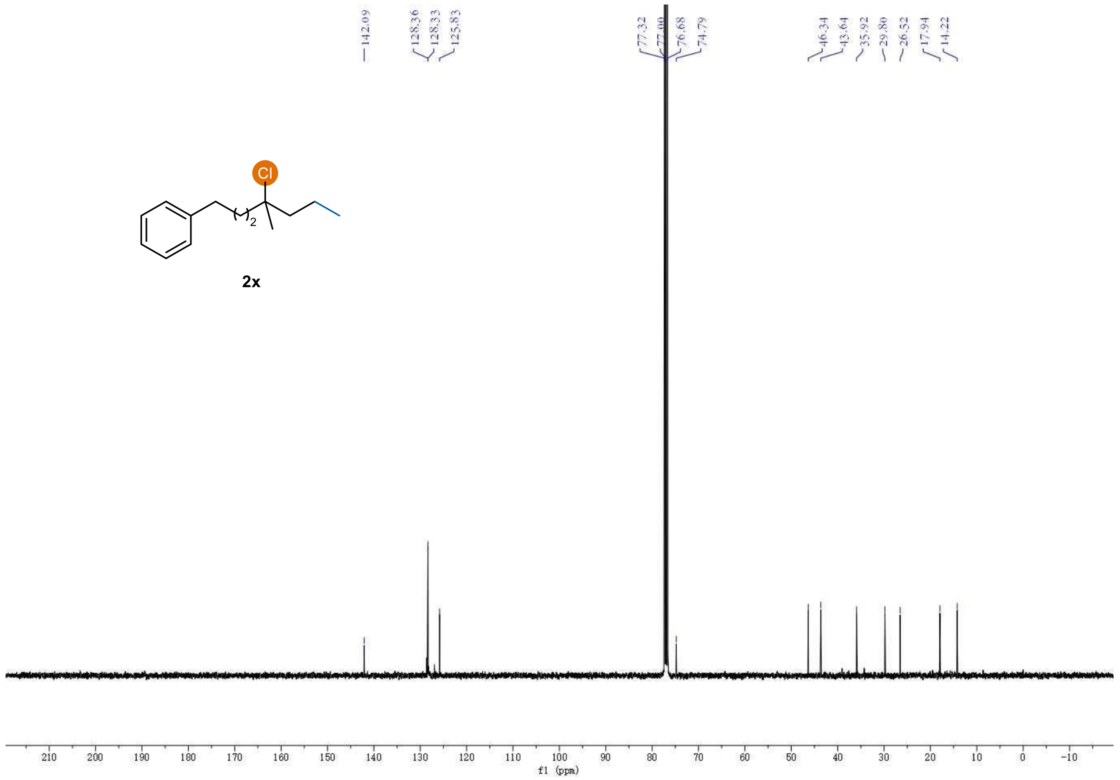
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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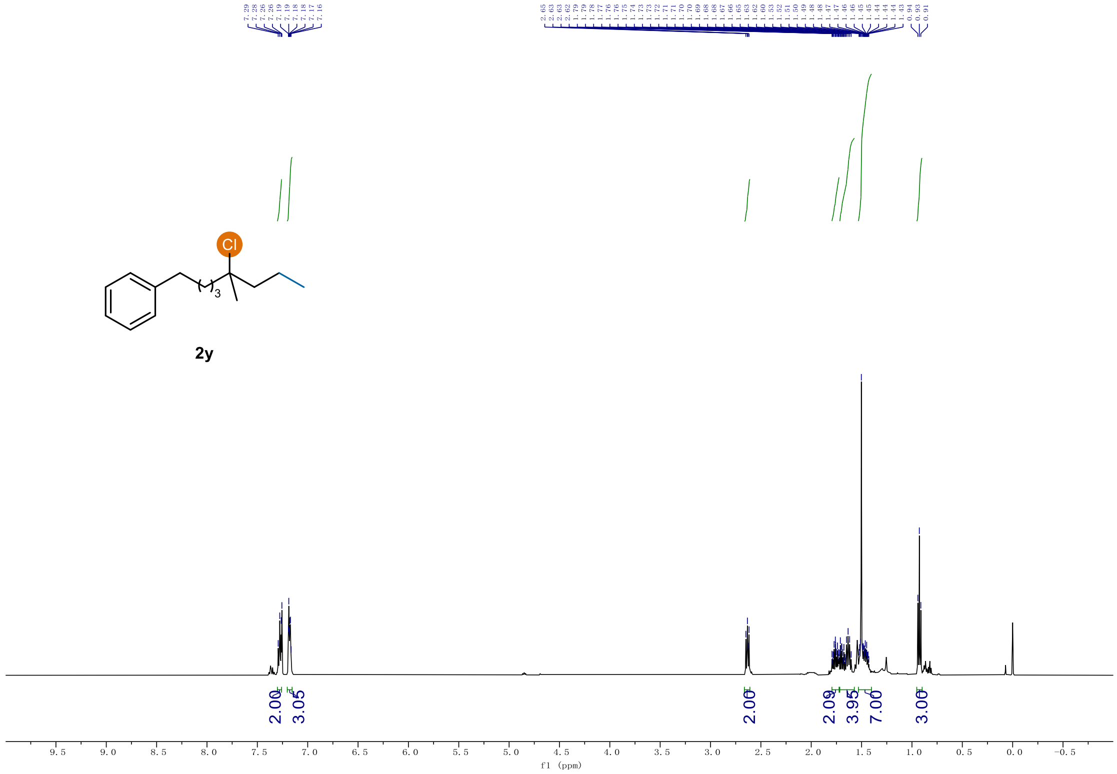
77.00
76.68
74.79
46.34
43.64
35.92
29.80
26.52
17.94
14.22
Cl
2
2x
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.16
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2.63
2.62
1.79
1.79
1.78
1.77
1.76
1.76
1.75
1.74
1.73
1.73
1.72
1.71
1.71
1.70
1.70
1.69
1.68
1.68
1.67
1.66
1.65
1.63
1.62
1.60
1.53
1.52
1.51
1.50
1.49
1.48
1.48
1.47
1.47
1.46
1.46
1.45
1.45
1.44
1.44
1.44
1.43
0.94
0.93
0.91
Cl
3
2y
2.00
3.05
2.00
2.09
3.95
7.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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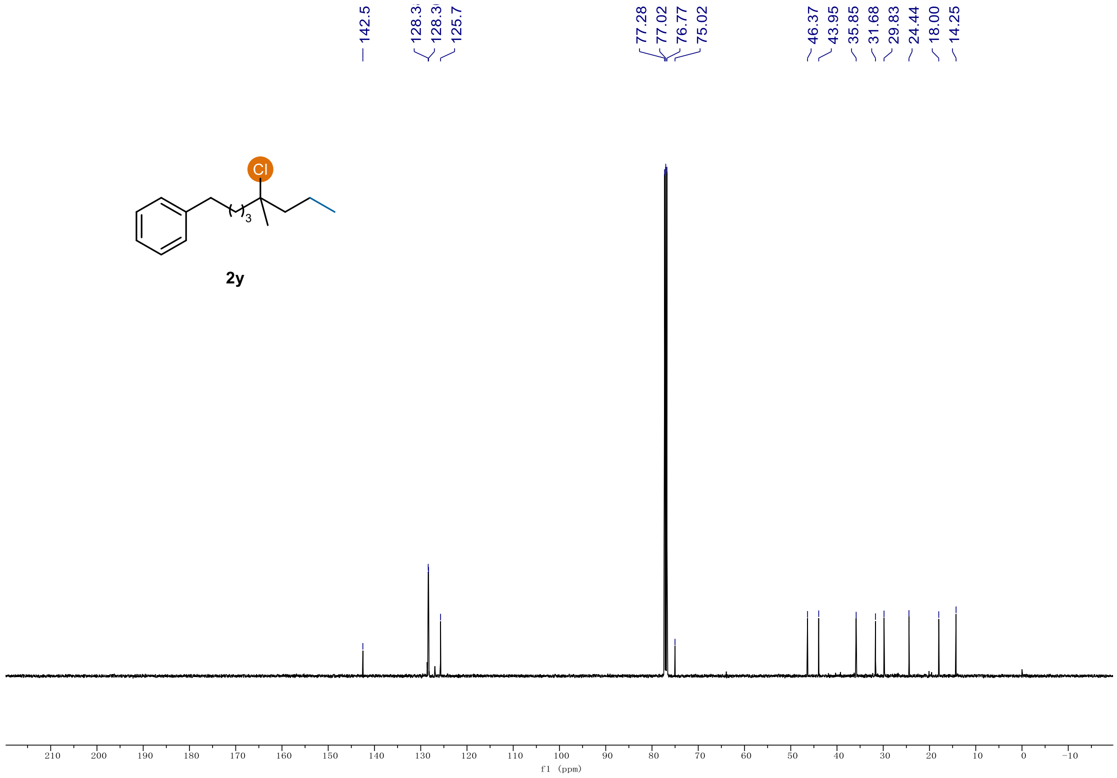
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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77.02
76.77
75.02
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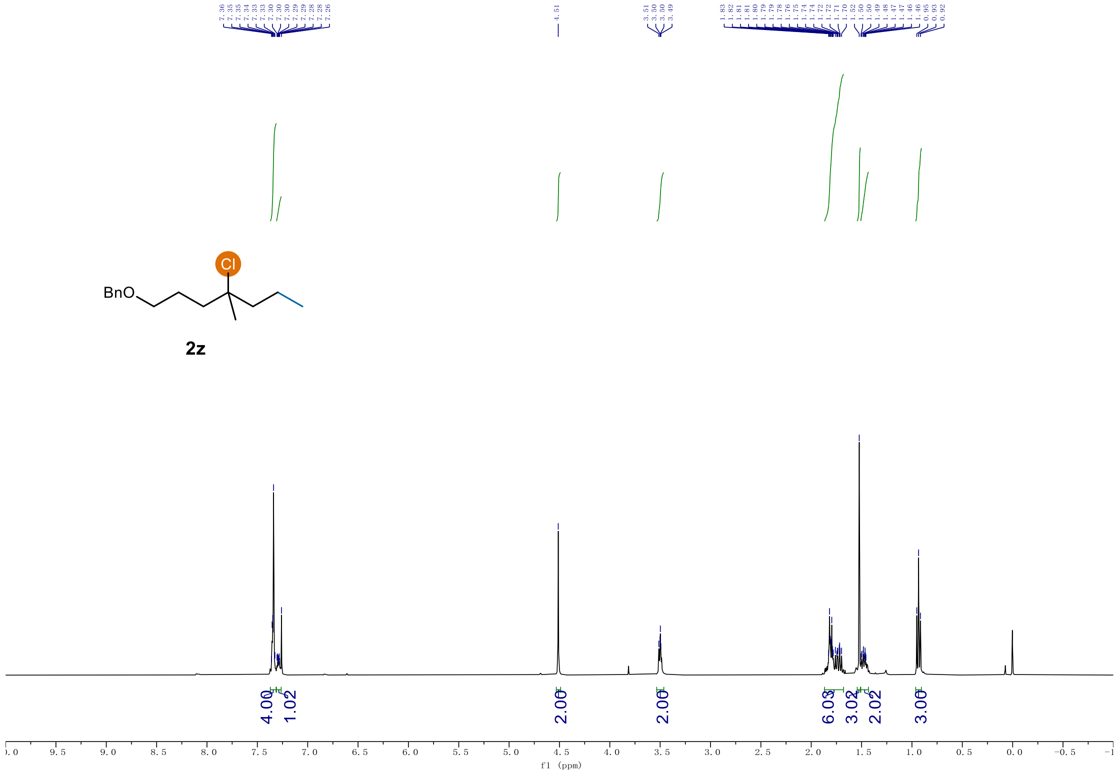
43.95
35.85
31.68
29.83
24.44
18.00
14.25
Cl
3
2y
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.35
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7.30
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7.29
7.29
7.28
7.28
7.26
4.51
3.51
3.50
3.50
3.49
1.83
1.82
1.81
1.81
1.80
1.79
1.79
1.78
1.76
1.75
1.74
1.74
1.72
1.72
1.71
1.70
1.52
1.50
1.50
1.49
1.48
1.47
1.47
1.46
1.46
0.95
0.93
0.92
Cl
BnO
2z
4.00
1.02
2.00
2.00
6.03
3.02
2.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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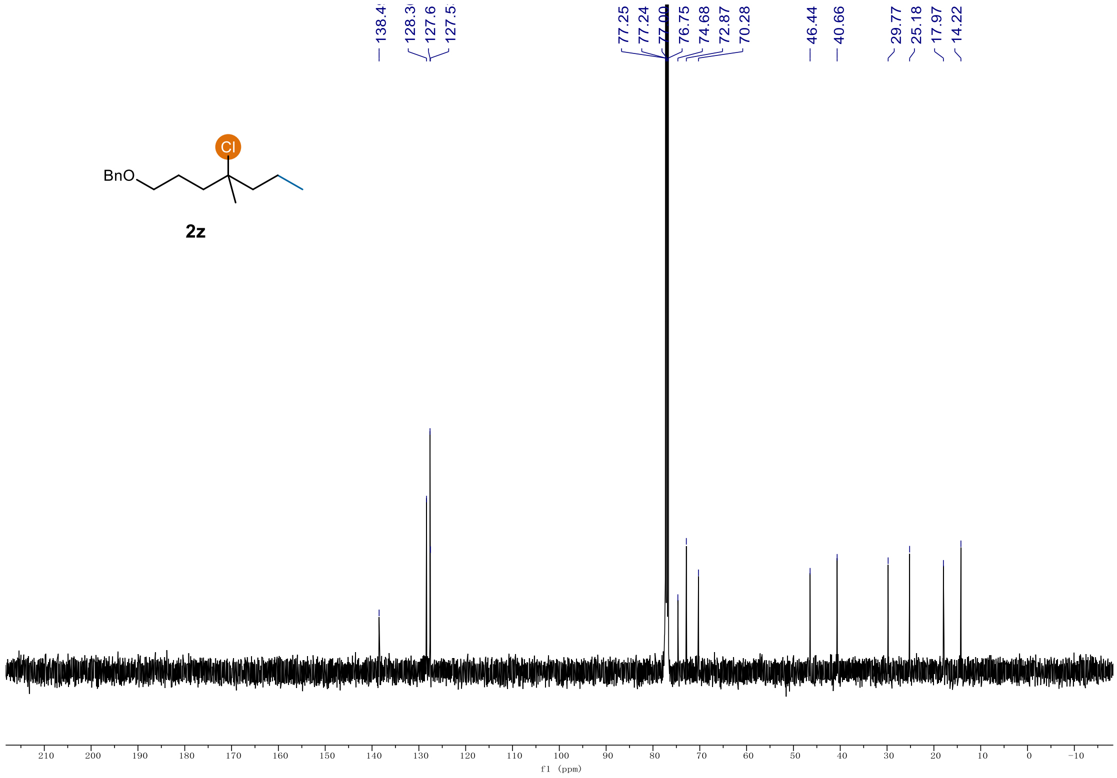
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)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72.87
70.28
46.44
40.66
29.77
25.18
17.97
14.22
Cl
BnO
2z
210
200
190
180
170
160
150
140
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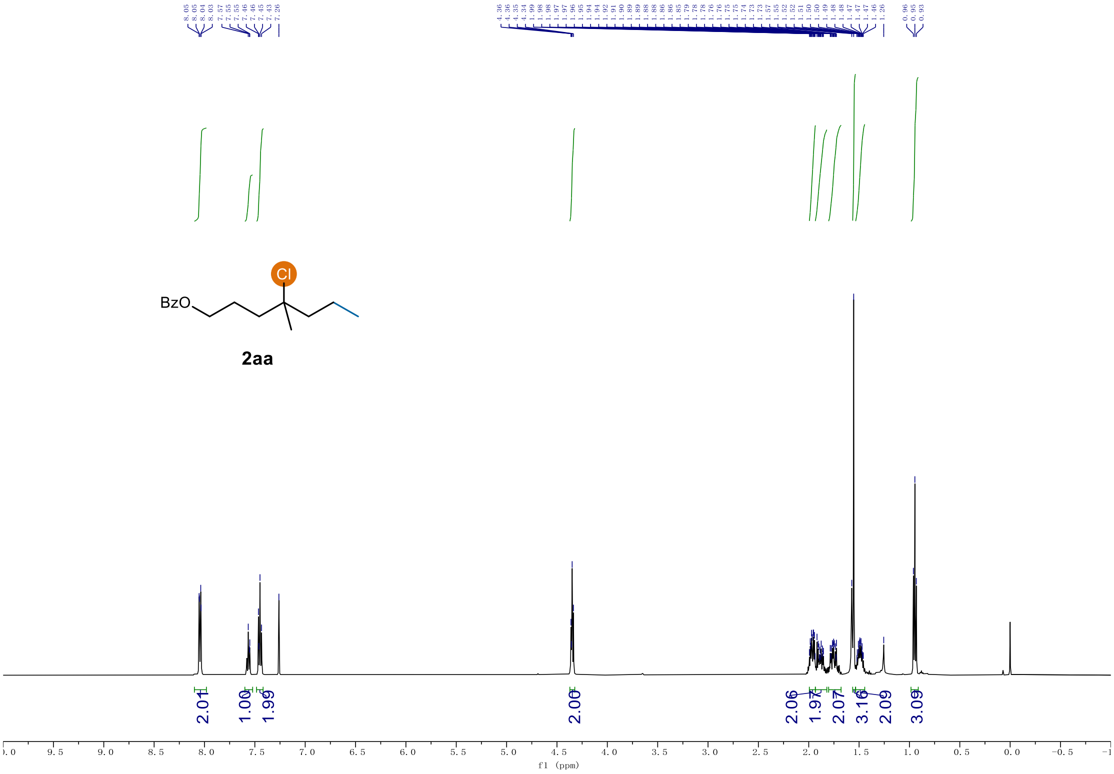
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.45
7.43
7.26
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4.35
4.34
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1.98
1.97
1.97
1.96
1.95
1.94
1.94
1.92
1.91
1.90
1.89
1.89
1.88
1.88
1.86
1.86
1.85
1.79
1.78
1.78
1.76
1.76
1.75
1.75
1.74
1.73
1.73
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1.55
1.52
1.52
1.51
1.50
1.50
1.49
1.48
1.48
1.47
1.47
1.47
1.46
1.26
0.96
0.95
0.93
Cl
BzO
2.01
1.00
1.99
2.00
2.06
1.97
2.07
3.16
2.09
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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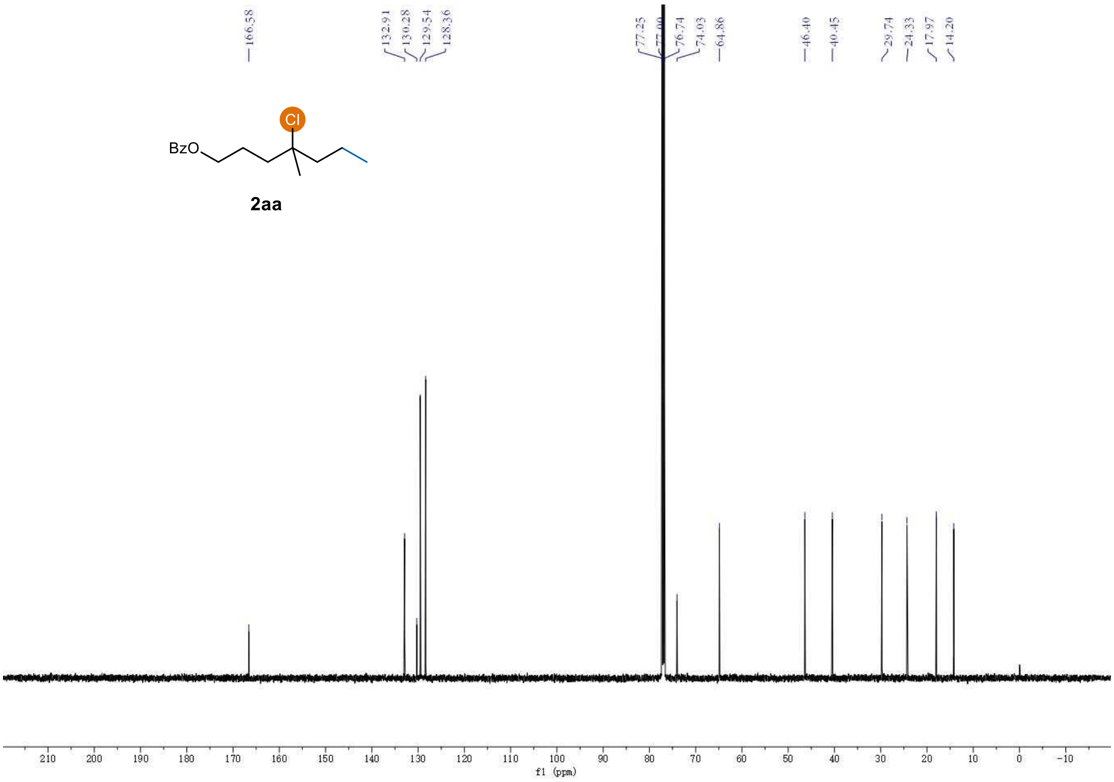
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

2aa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76.74
74.03
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46.40
40.45
29.74
24.33
17.97
14.20
Cl
BzO
210
200
190
180
170
160
150
140
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120
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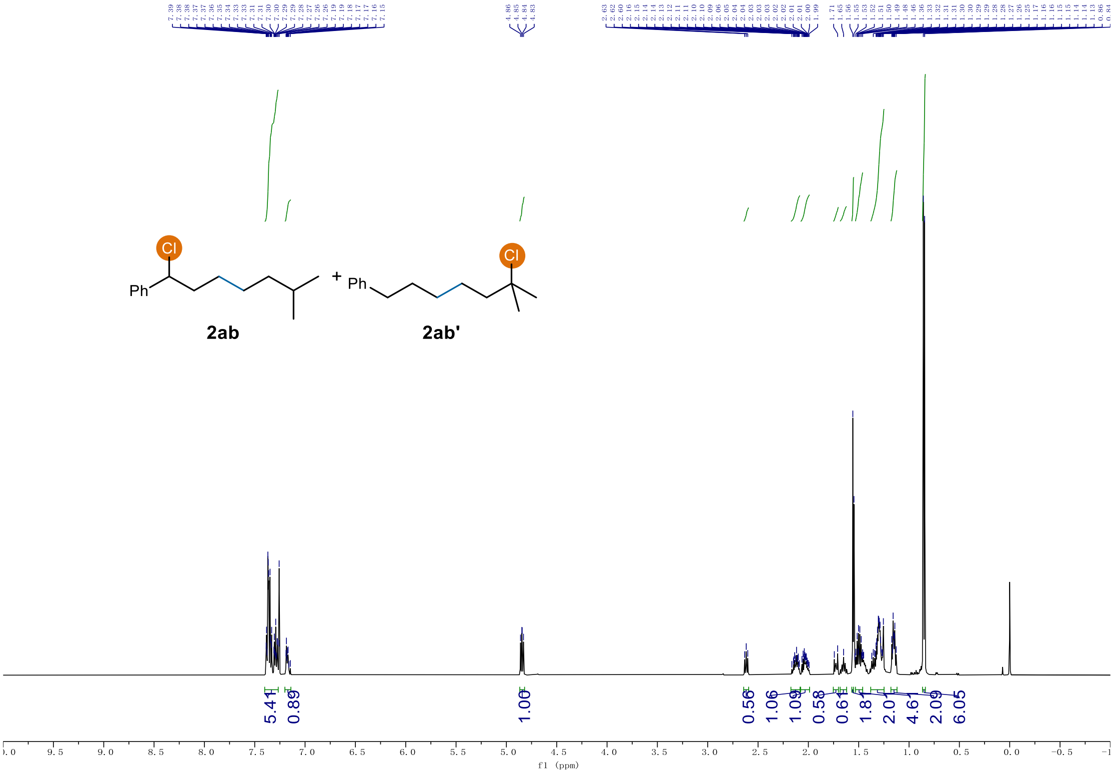
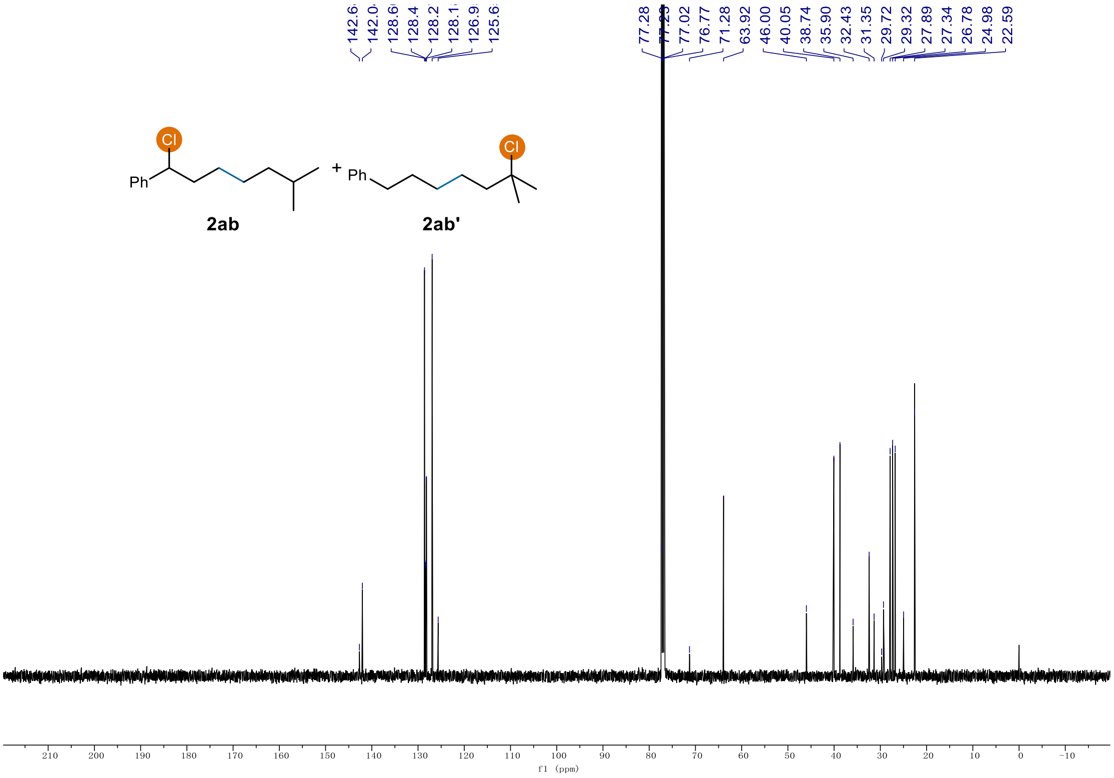
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2aa



Cl
Ph
2ab
+
Ph
Cl
2ab'
5.41
0.89
1.00
0.56
1.06
1.09
0.58
0.61
1.87
2.07
4.61
2.09
6.05
f1 (ppm)



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128.1
126.9
125.6
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77.23
77.02
76.77
71.28
63.92
46.00
40.05
38.74
35.90
32.43
31.35
29.72
29.32
27.89
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26.78
24.98
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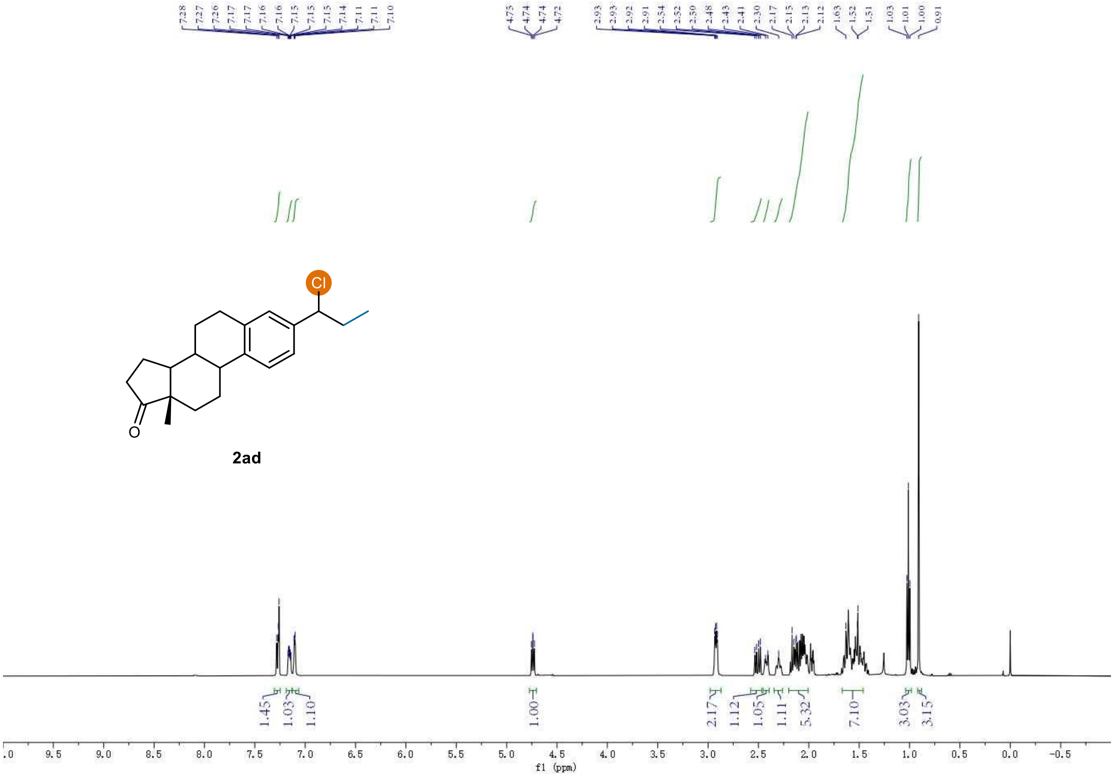
Ph
2ab
+
Ph
Cl
2ab'
f1 (ppm)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7.14
7.11
7.11
7.10
4.75
4.74
4.74
4.72
2.93
2.93
2.92
2.91
2.54
2.52
2.50
2.48
2.43
2.41
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2.17
2.15
2.13
2.12
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1.51
1.03
1.01
1.00
0.91
Cl
O
2ad
1.45
1.03
1.10
1.00
2.17
1.12
1.05
1.11
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7.10
3.03
3.15
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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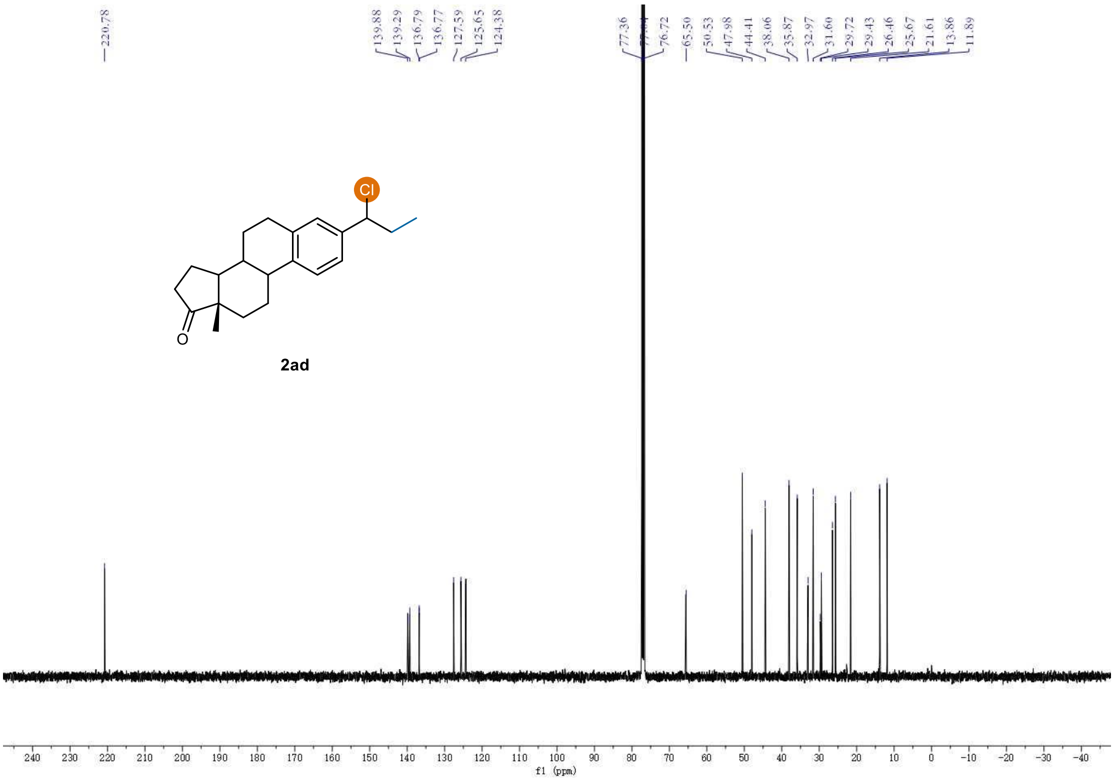
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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76.72
65.50
50.53
47.98
44.41
38.06
35.87
32.97
31.60
29.72
29.43
26.46
25.67
21.61
13.86
11.89
Cl
O
2ad
240
230
220
210
200
190
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170
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150
140
130
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80
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60
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40
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20
10
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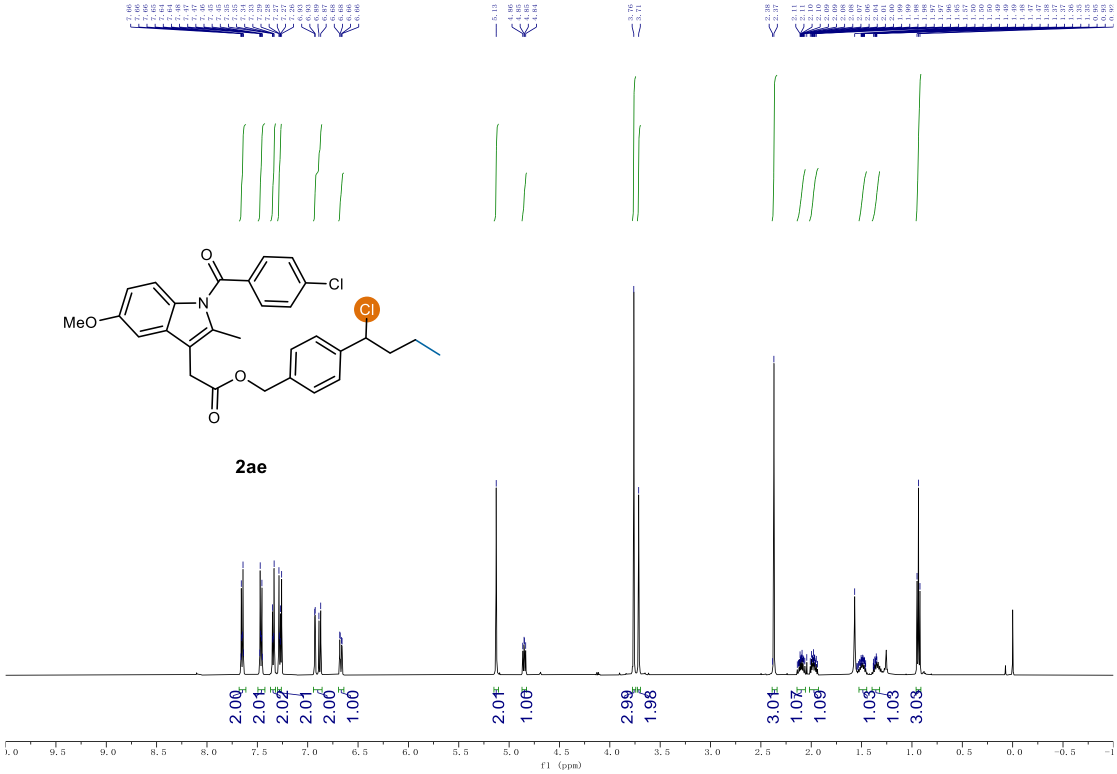
-10
-20
-30
-40
f1 (ppm)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7.33
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7.27
7.27
7.26
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6.93
6.89
6.87
6.68
6.68
6.66
6.66
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2.09
2.08
2.08
2.07
2.06
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1.99
1.98
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1.50
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Cl
Cl
O
O
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1.00
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1.03
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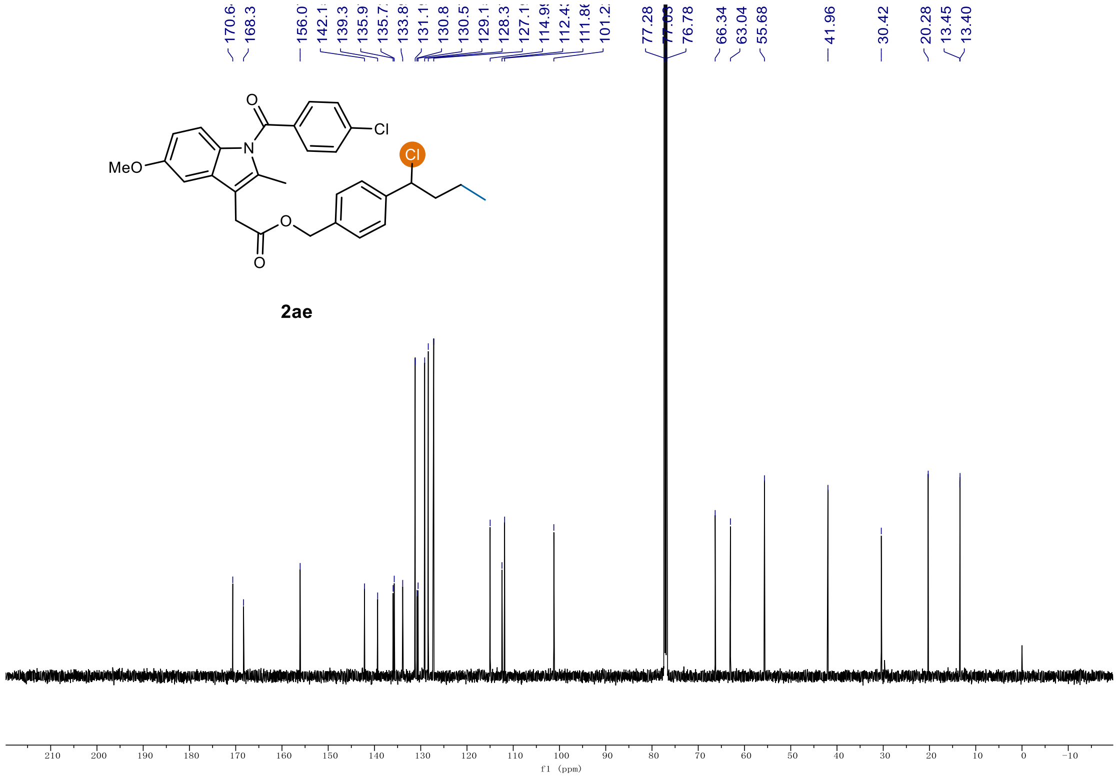
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111.8
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76.78
66.34
63.04
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41.96
30.42
20.28
13.45
13.40
MeO
N
O
Cl
Cl
O
O
2ae
210
200
190
180
170
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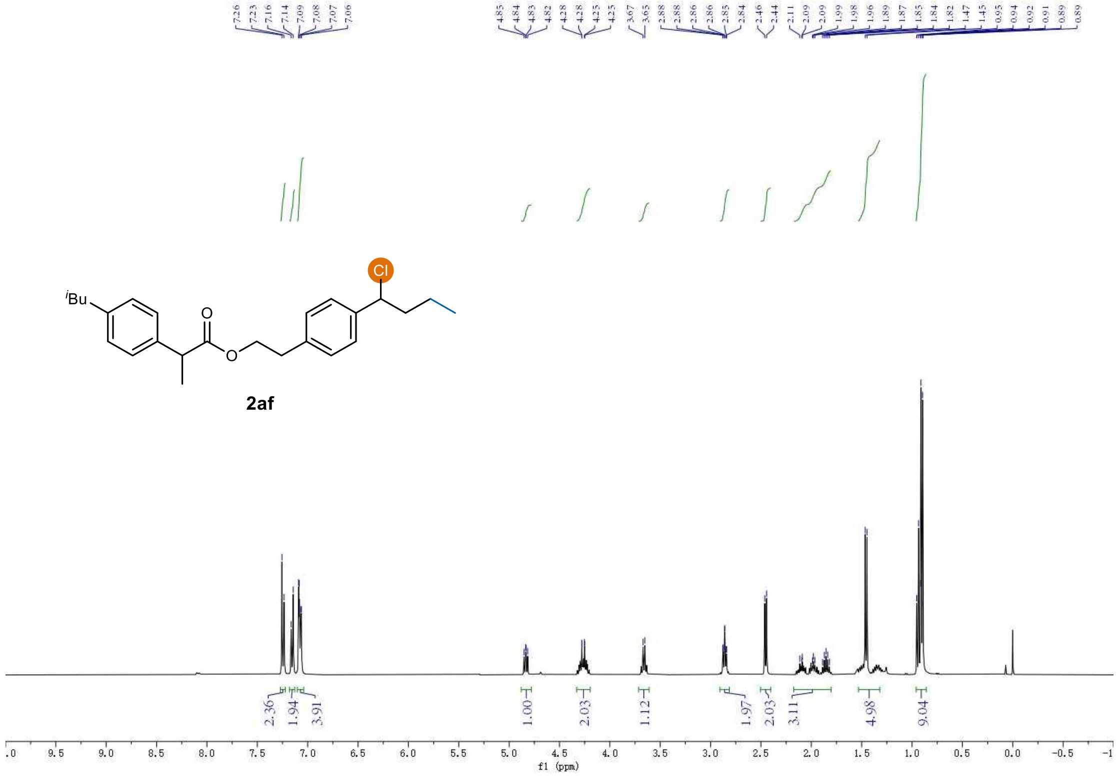
f1 (ppm)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Cl
^{i}Bu
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O
2af
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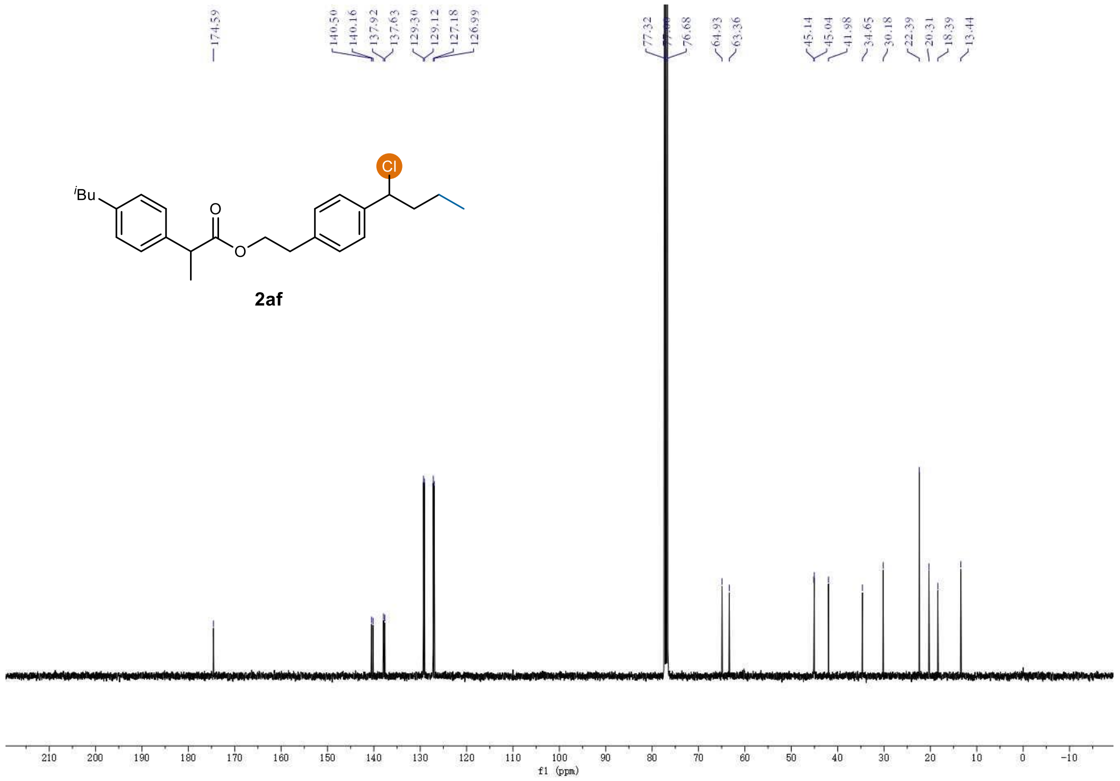
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45.04
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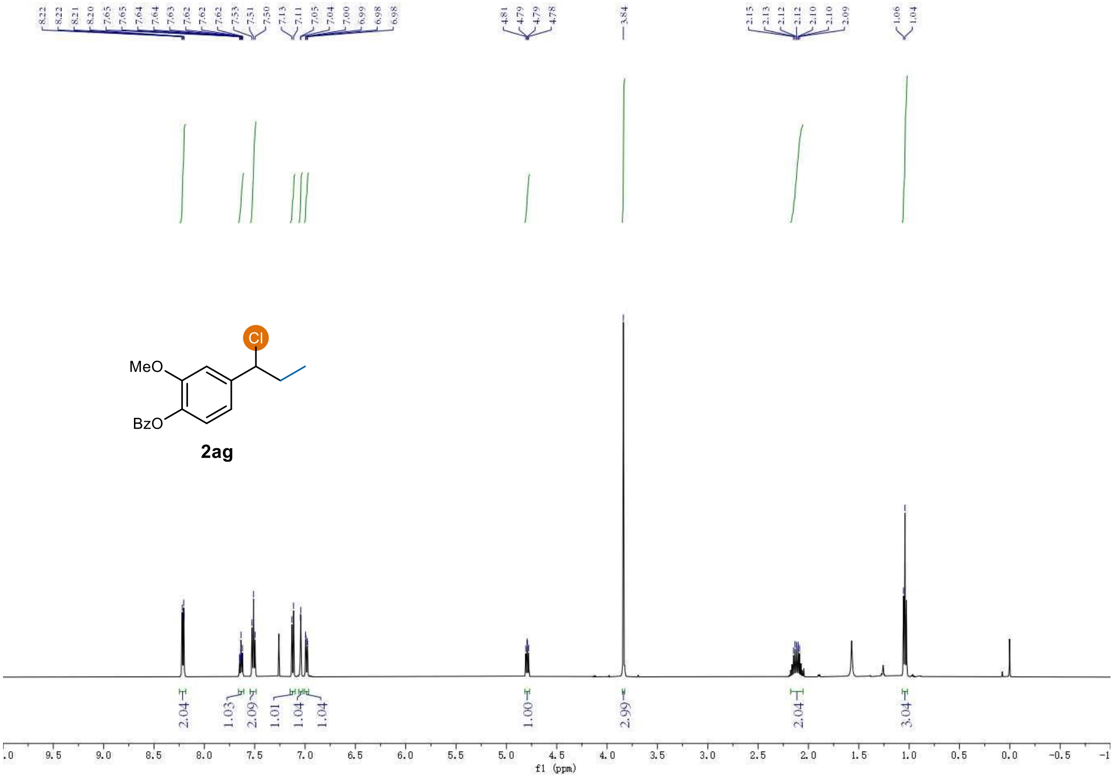
^{i}Bu
O
O
2af
f1 (ppm)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7.13
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6.98
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4.79
4.78
3.84
2.15
2.13
2.12
2.12
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2.10
2.09
1.06
1.04
Cl
MeO
BzO
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1.04
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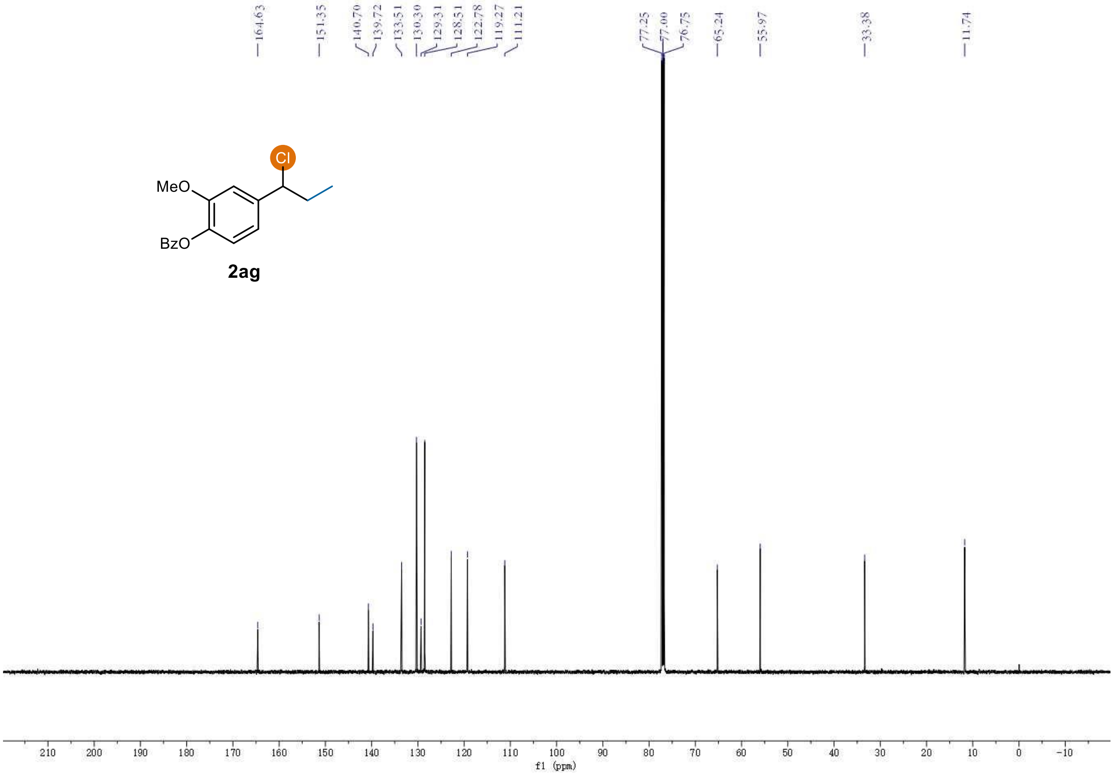
3.04
f1 (ppm)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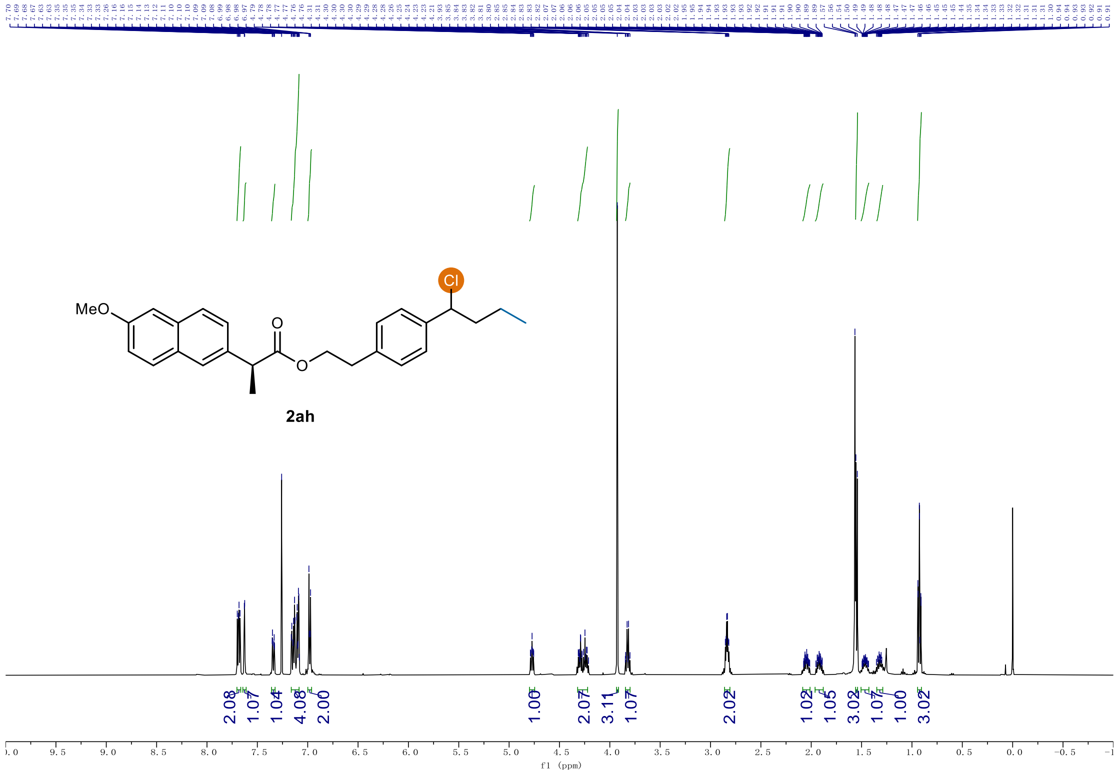
BzO
2ag
f1 (ppm)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0.91
MeO
O
O
Cl
2ah
2.08
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1.04
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1.00
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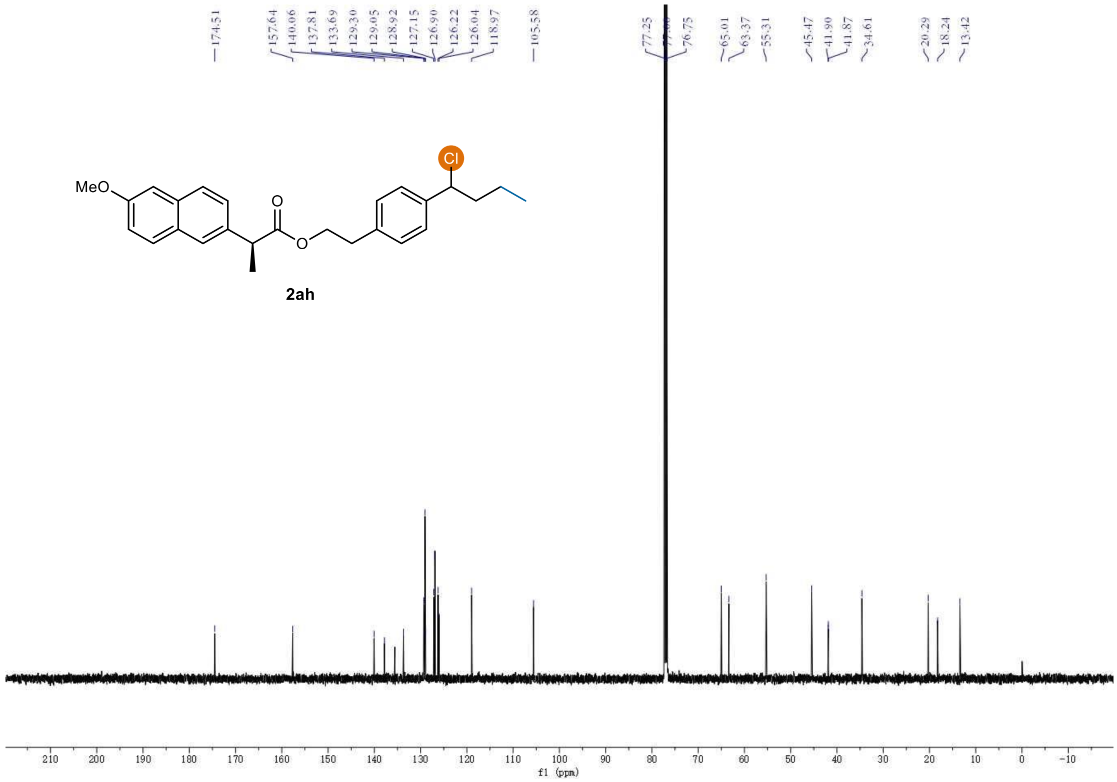
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13.42
MeO
O
O
Cl
2ah
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200
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180
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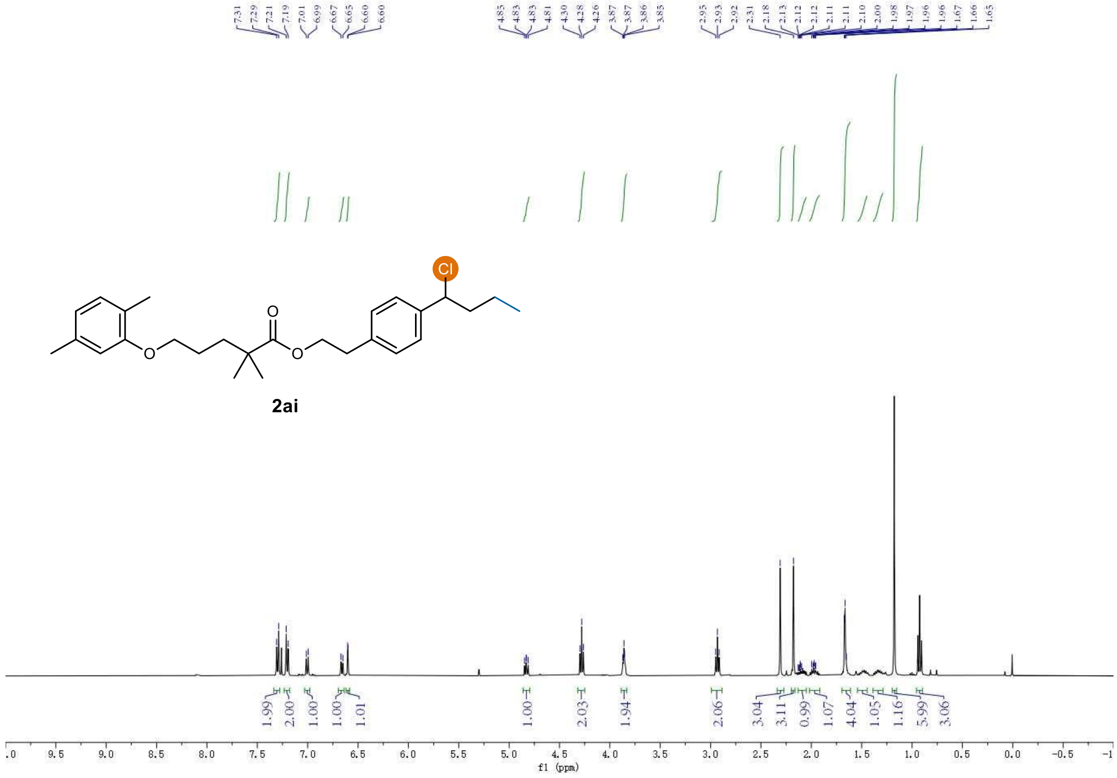
f1 (ppm)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4.83
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4.28
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3.87
3.86
3.85
2.95
2.93
2.92
2.31
2.18
2.13
2.12
2.12
2.11
2.11
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1.96
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1.66
1.65
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O
O
2ai
1.99
2.00
1.00
1.00
1.01
1.00
2.03
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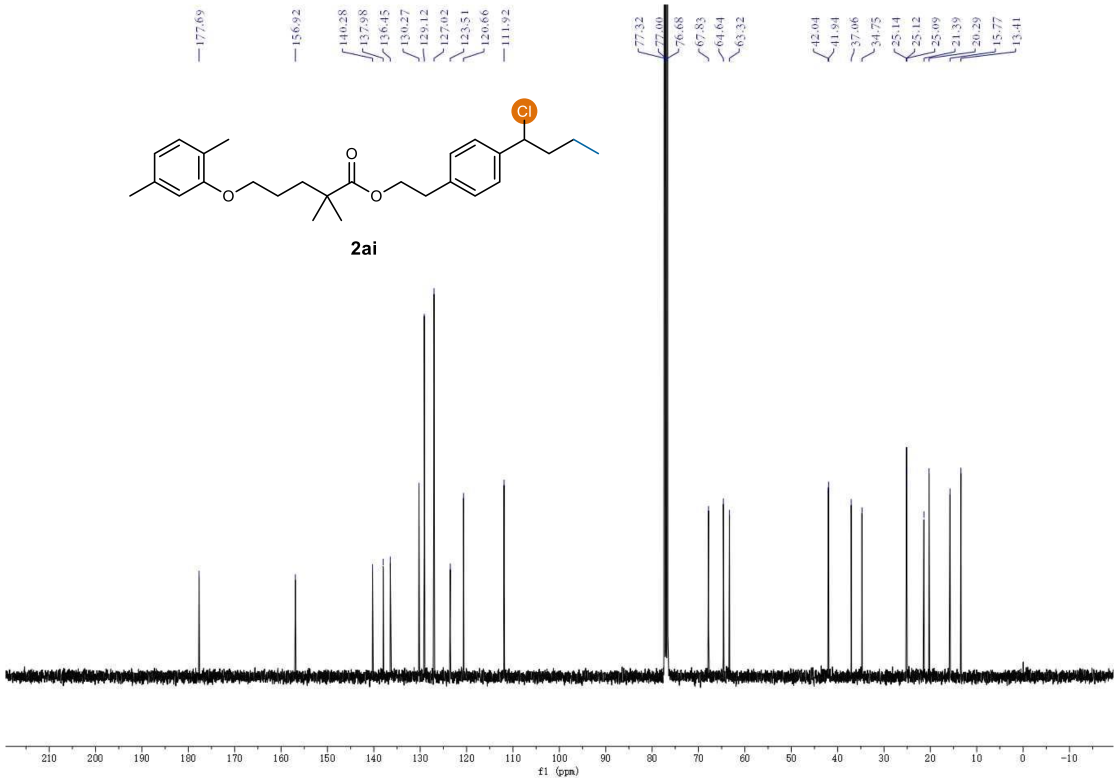
f1 (ppm)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64.64
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42.04
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37.06
34.75
25.14
25.12
25.09
21.39
20.29
15.77
13.41
Cl
O
O
O
2ai
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200
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180
170
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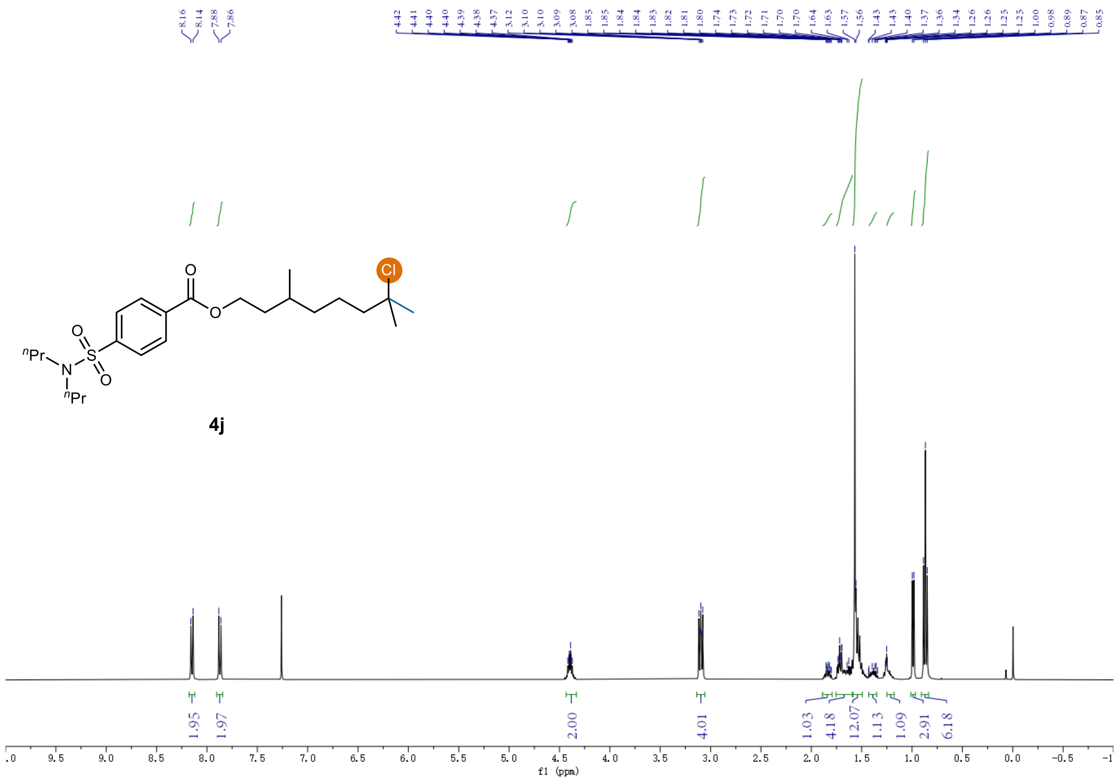
f1 (ppm)



4j

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3.08
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1.83
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O
O
S
O
N
^{n}Pr
^{n}Pr
O
Cl
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1.09
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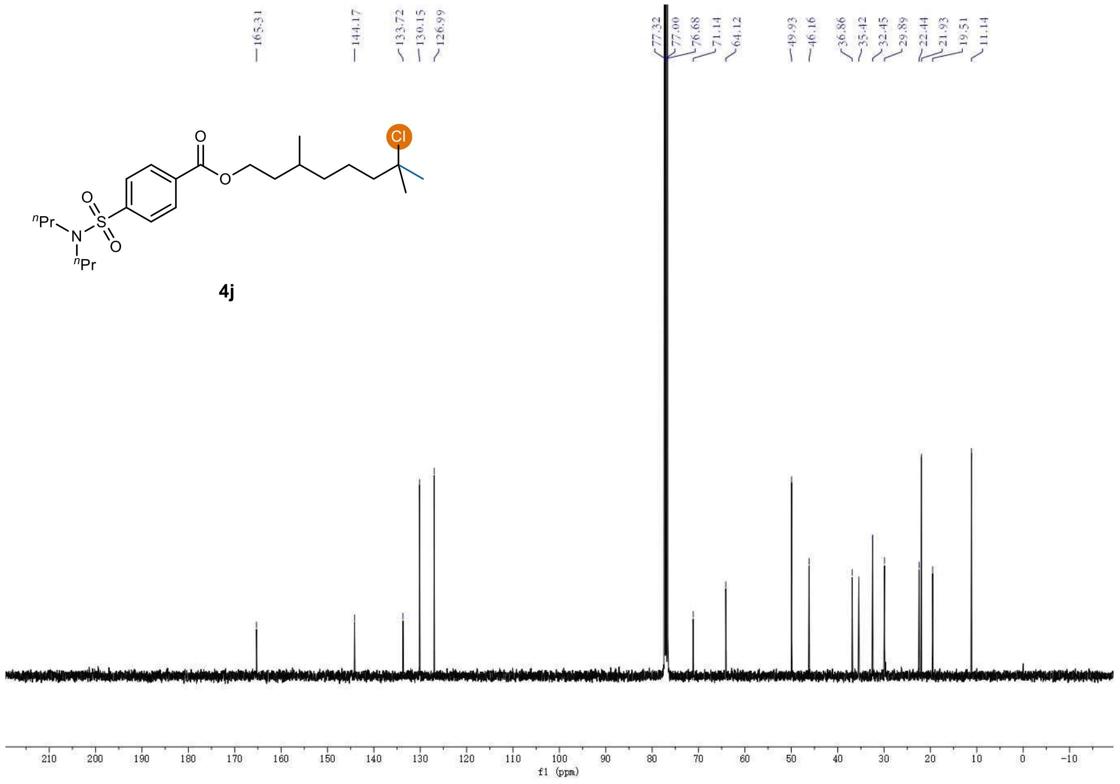
f1 (ppm)



4j

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77.00
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71.14
64.12
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46.16
36.86
35.42
32.45
29.89
22.44
21.93
19.51
11.14
O
O
S
O
N
^{n}Pr
^{n}Pr
O
Cl
210
200
190
180
170
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100
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80
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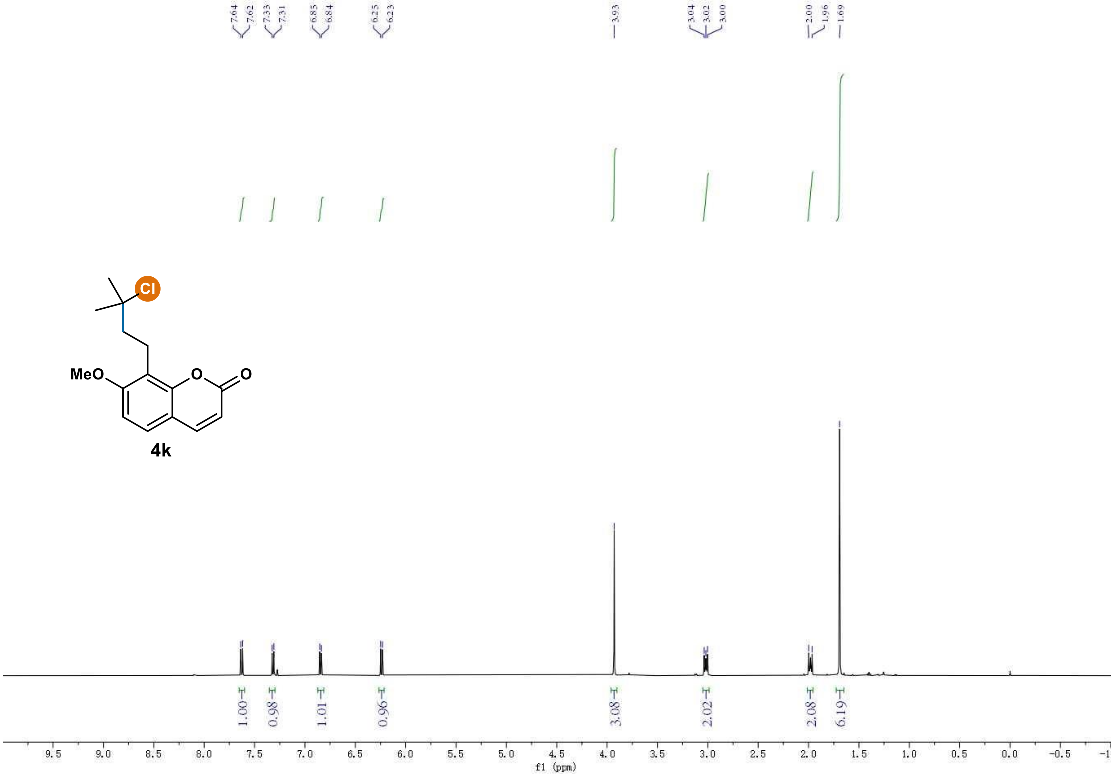
f1 (ppm)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2.00
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1.69
Cl
MeO
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O
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0.98
1.01
0.96
3.08
2.02
2.08
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4.5
4.0
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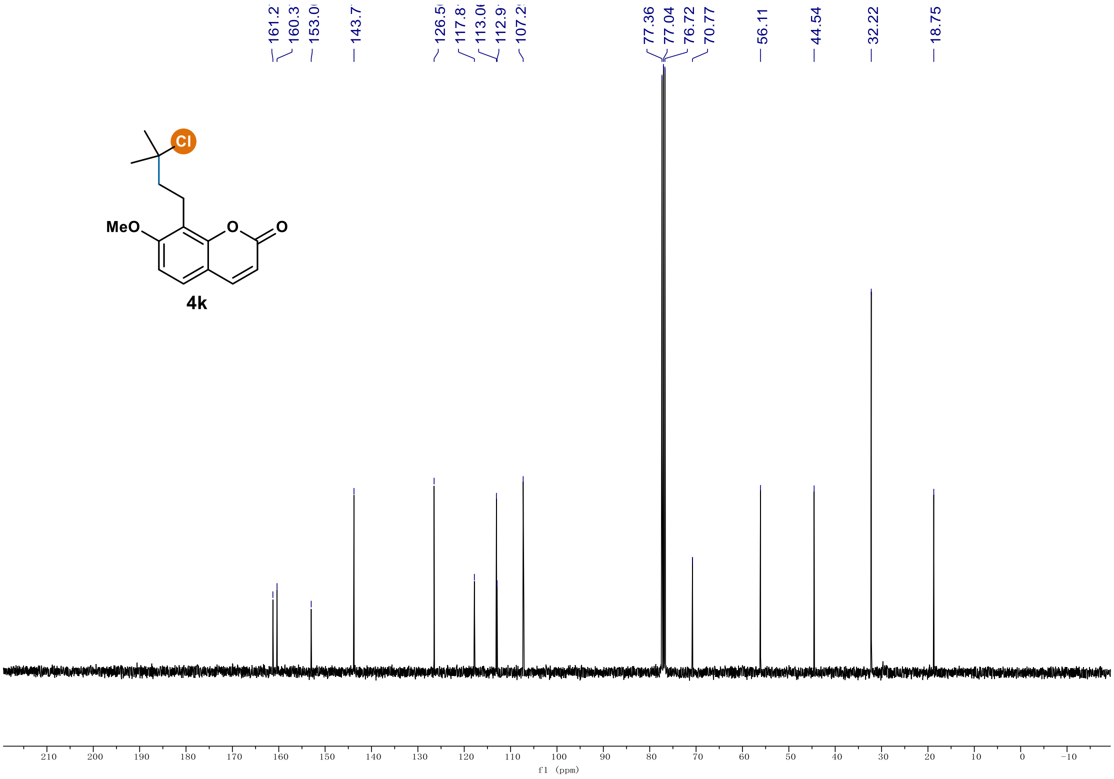
f1 (ppm)

4k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18.75
Cl
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O
O
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200
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180
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160
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100
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20
10
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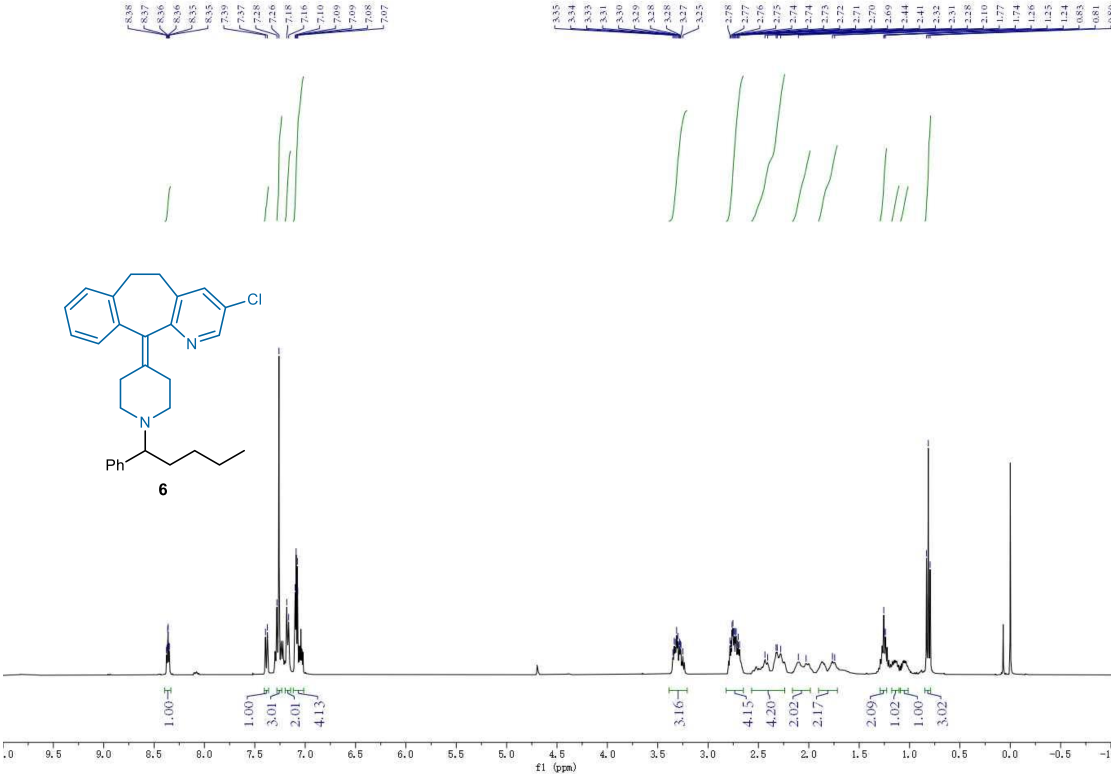
f1 (ppm)

4k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0.81
Cl
N
N
Ph
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1.00
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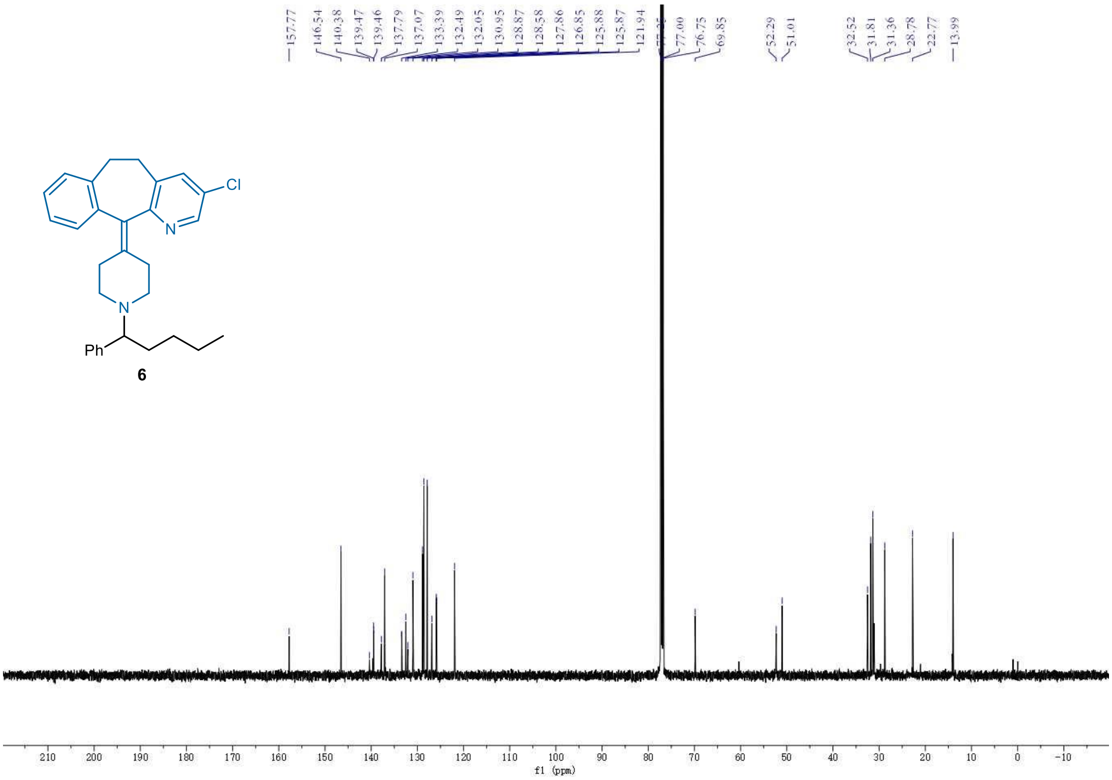
3.02
f1 (ppm)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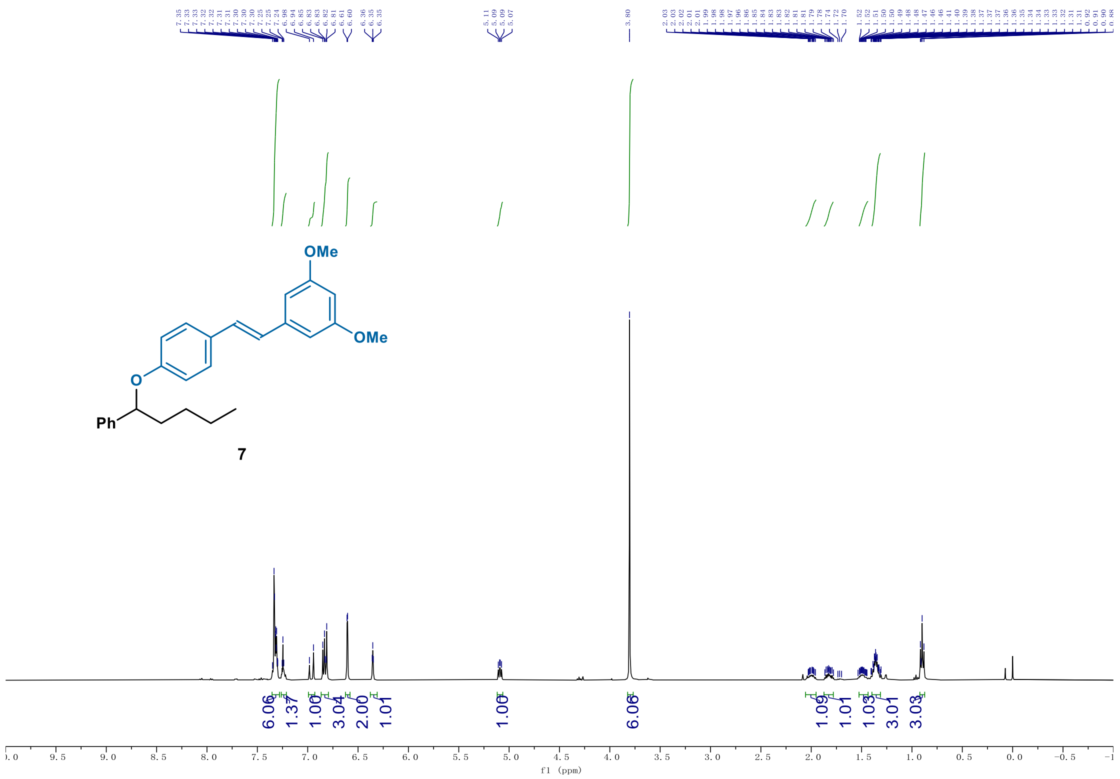
Ph
6
f1 (ppm)


OMe
OMe
O
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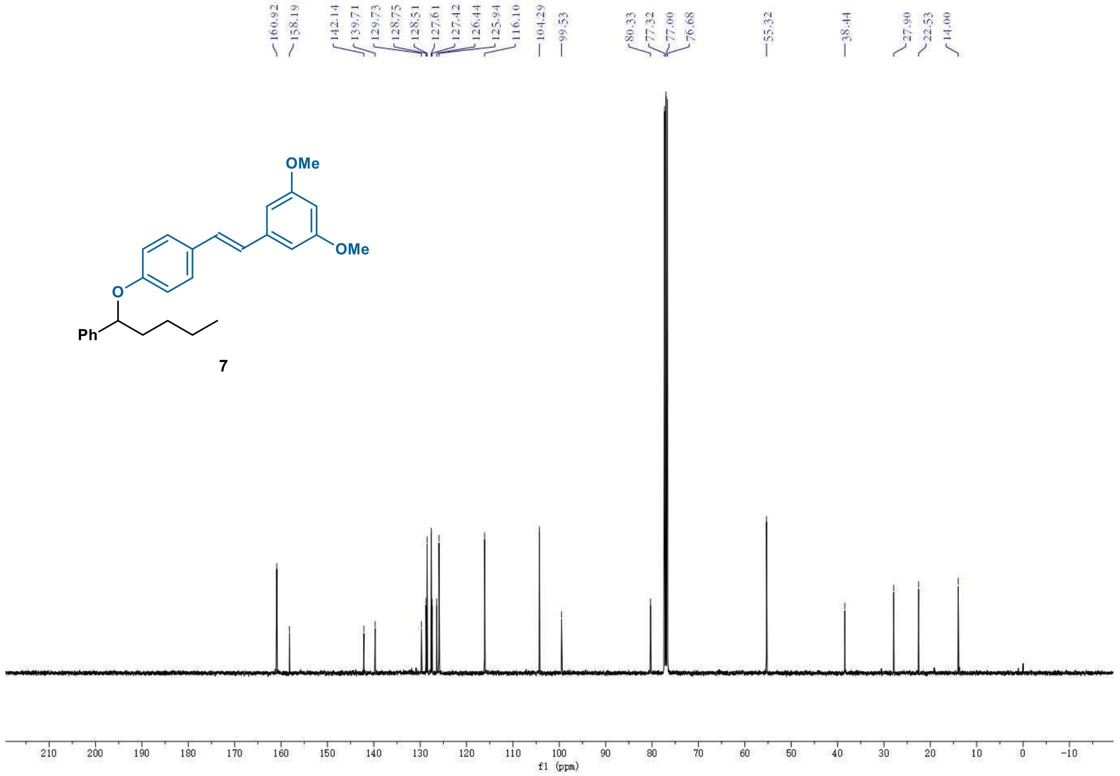
3.01
3.03
f1 (ppm)

7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22.53
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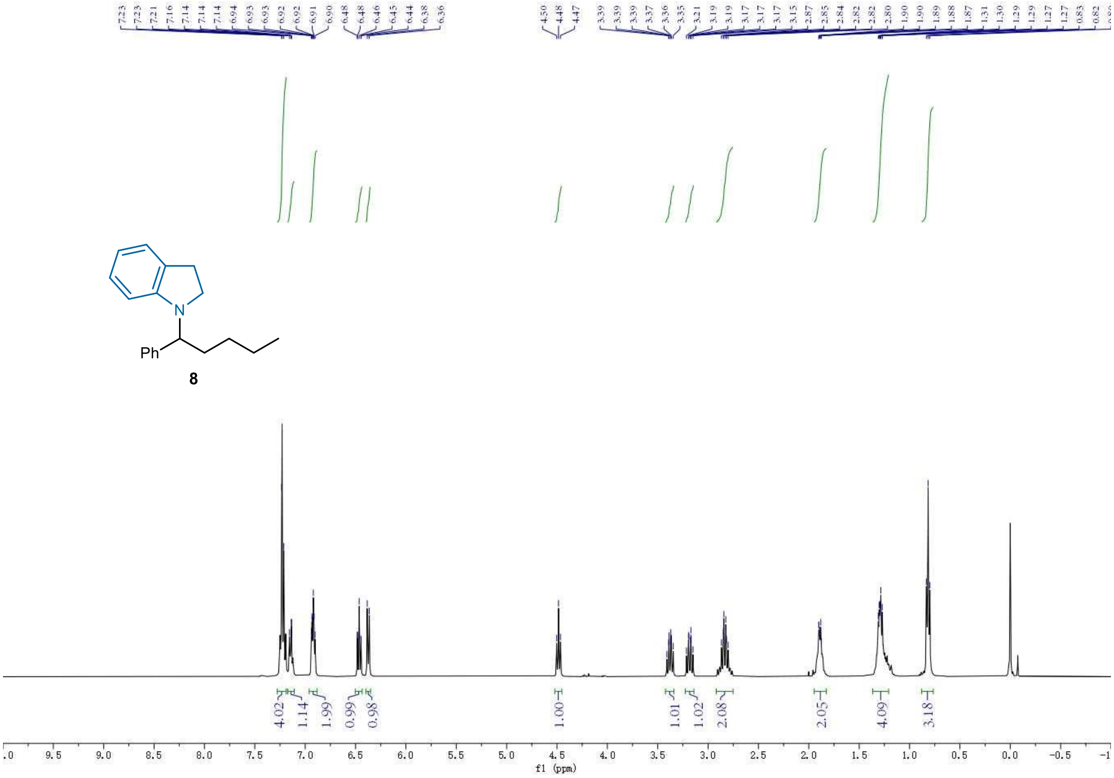
OMe
OMe
O
Ph
f1 (ppm)

7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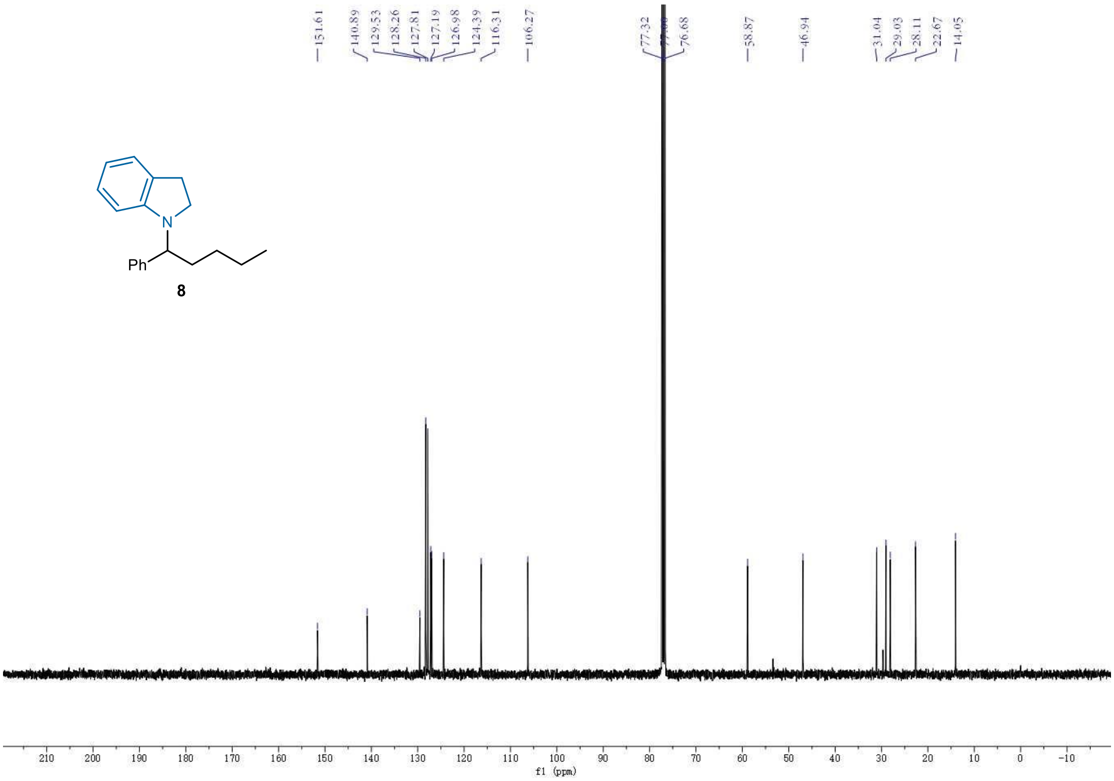
f1 (ppm)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29.03
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22.67
14.05
N
Ph
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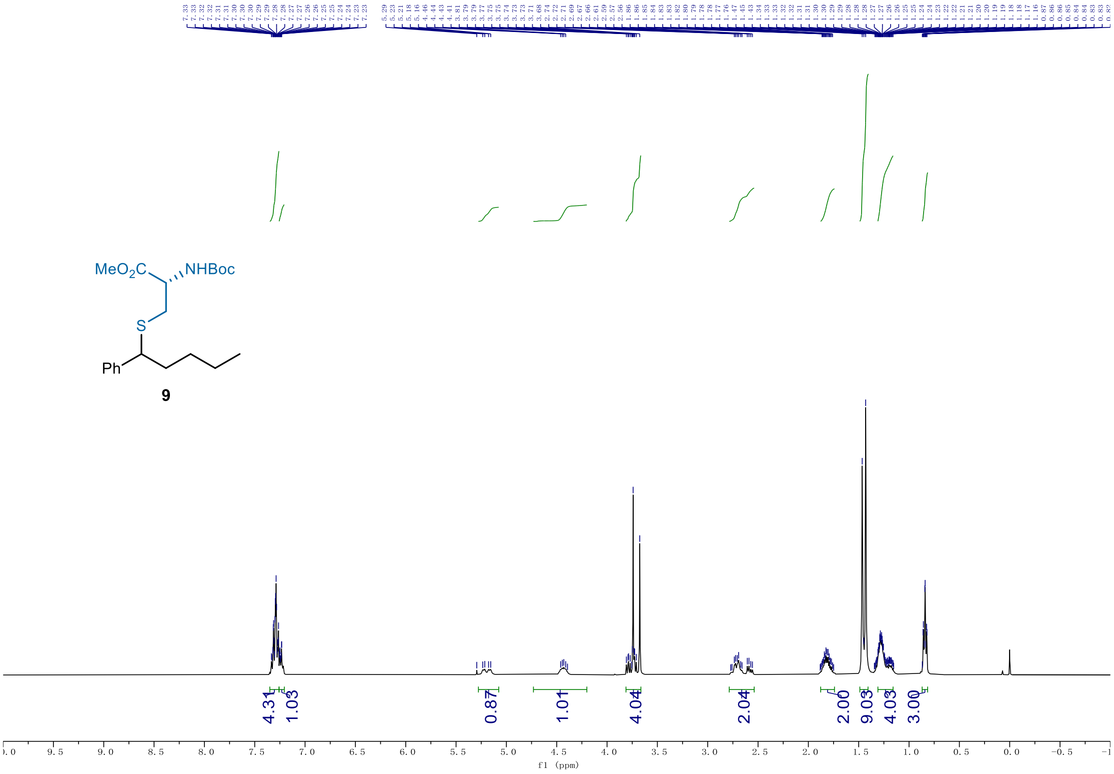
f1 (ppm)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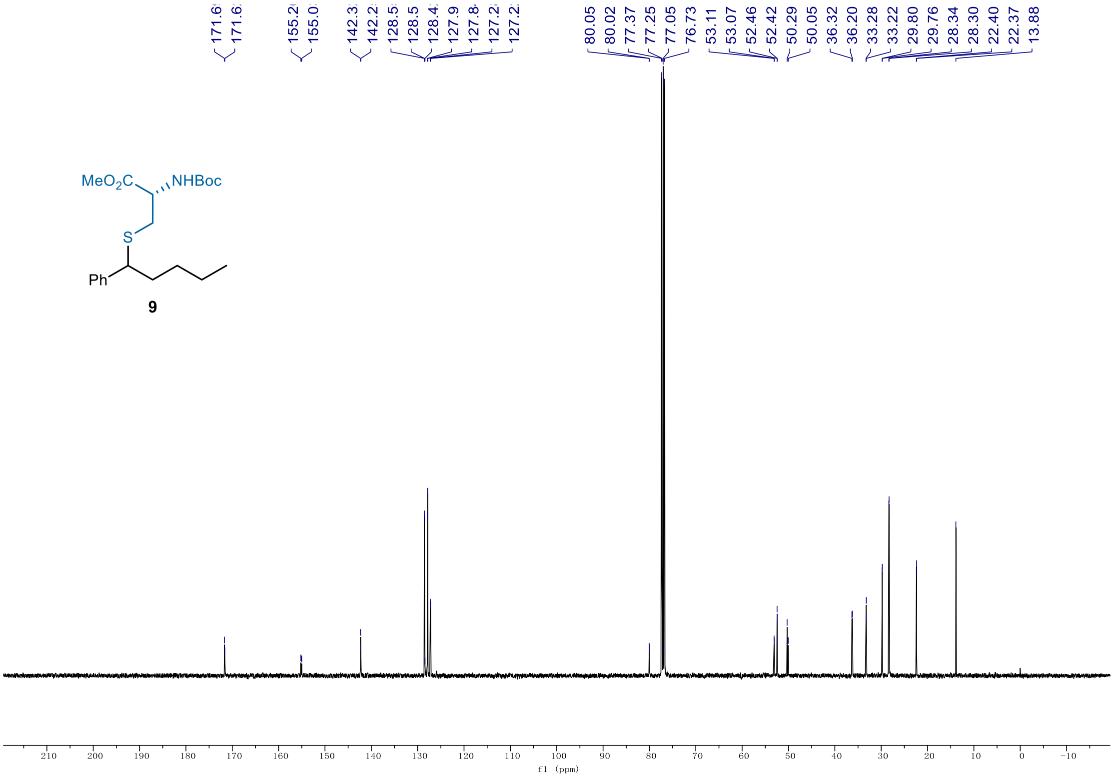
1.24
1.24
1.23
1.22
1.22
1.21
1.21
1.20
1.20
1.19
1.19
1.18
1.18
1.17
1.16
0.87
0.86
0.86
0.85
0.84
0.84
0.83
0.83
0.82
MeO$_2$C
NHBoc
S
Ph
9
4.31
1.03
0.87
1.01
4.04
2.04
2.00
9.03
4.03
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


171.6
171.6
155.2
155.0
142.3
142.2
128.5
128.5
128.4
127.9
127.8
127.2
127.2
80.05
80.02
77.37
77.25
77.05
76.73
53.11
53.07
52.46
52.42
50.29
50.05
36.32
36.20
33.28
33.22
29.80
29.76
28.34
28.30
22.40
22.37
13.88
MeO$_2$C
NHBoc
S
Ph
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

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