nature chemistry

SUPPLEMENTARY INFORMATION

DOI: 10.1038/NCHEM.2798

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CO- and HCl-free synthesis of acid chlorides from unsaturated hydrocarbons via shuttle catalysis

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1. General information

The palladium-catalysed reactions were set up in an argon atmosphere glovebox (LABmaster Pro SP, MBraun). The substrates and reagents for catalytic reactions were degassed and stored in the glovebox. $Pd_2(dba)_3$ and butyryl chloride were purchased from Sigma-Aldrich.

^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 500 MHz, at 125 MHz and 470 MHz, respectively on a Bruker spectrometer in $CDCl_3$ at room temperature. ^1H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet and br = broad signal), coupling constant (*J* values) in Hz and integration. Chemical shifts (δ) were reported with respect to the corresponding solvent residual peak at 7.26 ppm for $CDCl_3$ for ^1H NMR. ^{13}C NMR spectra (^1H-broadband decoupled) were reported in ppm using the central peak of $CDCl_3$ (77.16 ppm).

High-resolution mass spectrometric measurements were provided by the Mass Spectrometry Department of the Max-Planck-Institut für Kohlenforschung. The molecular ion $[M]^+$, $[M+H]^+$ and $[M+Na]^+$ are given in m/z units.

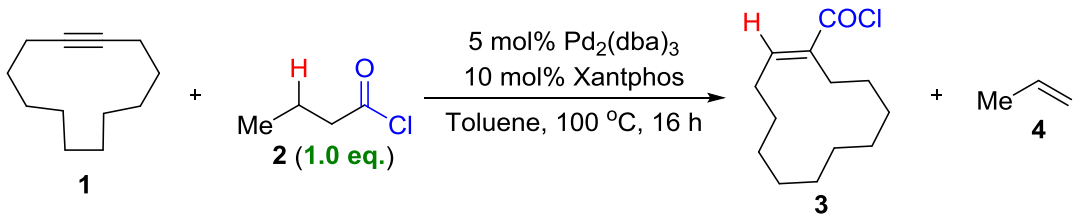
IR spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer. The spectra were measured in the neat state on a UATR Two crystal plate. Selected absorption bands are reported in wavenumbers (cm^{-1}).

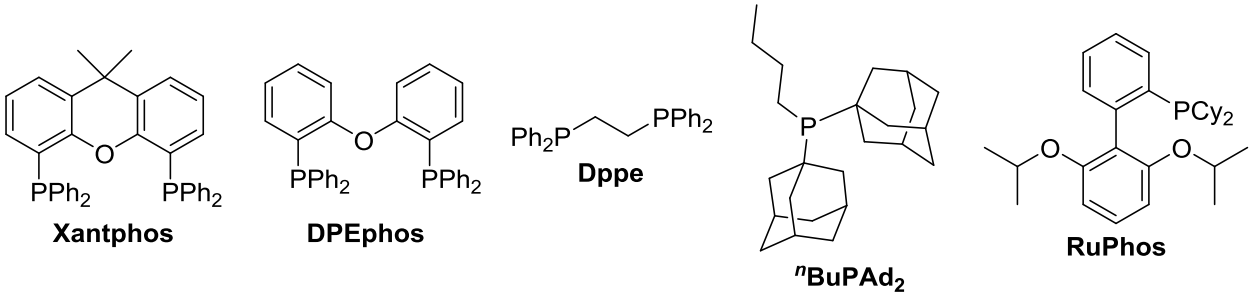
Thin Layer Chromatography analyses were performed on silica gel coated glass plates (0.25 mm) with fluorescence indicator UV_{254} (Macherey-Nagel, TLC plates SIL G-25 UV_{254}). For detection of spots, irradiation of UV light at 254 nm or oxidative staining using potassium permanganate solution ($KMnO_4$) was used. Flash column chromatography was conducted with Silica gel 60 (particle size 40–63 μM, Merck) at room temperature and under elevated pressure.

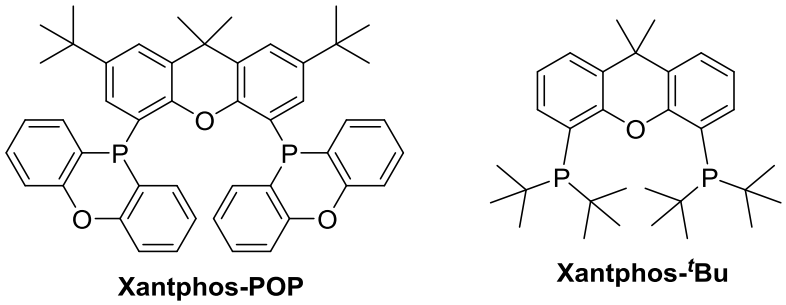
GC analysis information:

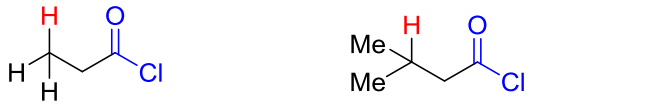
GC:	Shimadzu GC-2025
Column:	OPTIMA 5 - MACHEREY-NAGEL, 30.0 m × 0.25 mm × 0.25 μm
Carrier gas:	He (1.31 mL/min)
Temperature program:	50°C (2 min); 15°C/min to 320°C; 320°C (10 min)
Injector temperature:	250°C
Detector temperature:	340°C
Split ratio:	50
Injection volume:	1 μL

2. Investigating hydrochlorocarbonylation of alkyne (Table 1)









Entry	Variation of the reaction conditions given above[a]	**3** yield/%[b]
1	none	84
2	no $Pd_2(dba)_3$	0
3	no Xantphos	0
4	DPEphos instead of Xantphos	2
5	Dppe instead of Xantphos	0
6	20 mol% P^tBu_3 instead of Xantphos	1
7	20 mol% ^{n}BuPAd$_2$ instead of Xantphos	12
8	20 mol% RuPhos instead of Xantphos	<1
9	20 mol% PPh_3 instead of Xantphos	7
10	Xantphos-POP instead of Xantphos	55
11	Xantphos-^{t}Bu instead of Xantphos	<1

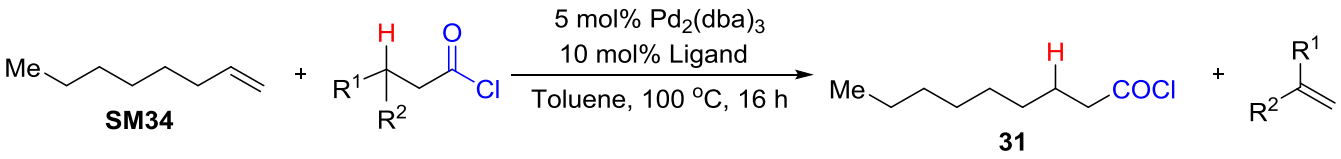
12	**SM1** instead of **2**	82
13	**SM2** instead of **2**	78
14	**SM3** instead of **2**	87
15[c]	open system	84

[a]Reactions carried out on 0.25 mmol scale in toluene (0.5 mL). [b]GC yield based on the corresponding methyl ester using *n*-dodecane as an internal standard.

(Table S1, entry 1): A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol, 1.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). ^{n}Dodecane (50 μL) was added to the solution as an internal standard. The mixture was stirred 10 mins at room temperature. The yield of **3** based on the corresponding methyl ester was measured by GC analysis.

[c](Table S1, entry 15): A 10 mL Schlenk tube equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed Schlenk tube was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol) and **2** (26 uL, 0.25 mmol, 1.0 eq.). The Schlenk tube connected with a reflux condenser was taken out of the glovebox, and was subsequently connected to a continuous flow of argon (positive pressure: 0.4 bar) and heated at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). ^{n}Dodecane (50 μL) was added to the solution as an internal standard. The mixture was stirred 10 mins at room temperature. The yield of **3** based on the corresponding methyl ester was measured by GC analysis.

3. Investigating hydrochlorocarbonylation of alkene[a] (Table 2)

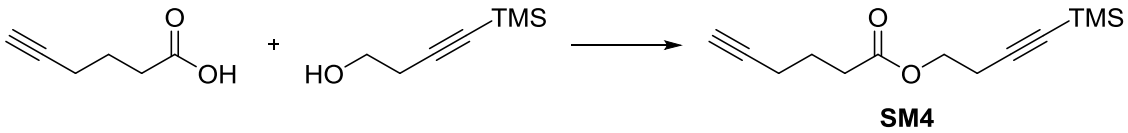


Entry	Ligand	Acid Chloride	**31** yield/%[b]	*l*/*b*[c]
1	Xantphos	1.0 eq. **2**	19	88/12
2	Xantphos	4.0 eq. **2**	28	90/10
3	Xantphos-POP	4.0 eq. **2**	7	92/8
4	Xantphos	8.0 eq. **2**	25	89/11
5	Xantphos	4.0 eq. **SM1**	9	90/10
6	Xantphos	4.0 eq. **SM2**	29	89/11
7	Xantphos	4.0 eq. **SM3**	33	90/10

[a]Reactions carried out on 0.25 mmol scale in toluene (0.5 mL). [b]GC yield of **31** based on the corresponding methyl ester using *n*-dodecane as an internal standard. [c]The *l*/*b* ratio of **31** based on the corresponding methyl ester was determined by GC analysis.

General procedure: A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and ligand (10 mol%, 0.025 mmol). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM34** (28.1 mg, 0.25 mmol), acid chloride and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). [n]Dodecane (50 μL) was added to the solution as an internal standard. The mixture was stirred 10 mins at room temperature. The *l*/*b* ratio of **31** based on the corresponding methyl ester was determined by GC analysis. The yield of **31** based on the corresponding methyl ester was measured by GC analysis.

4. Preparation of substrates



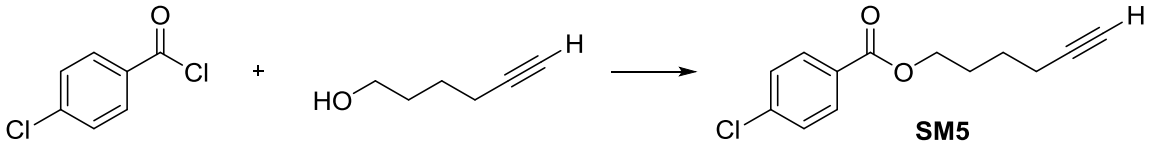
SM4

An argon flushed one-necked flask equipped with a stirring bar was charged with hex-5-ynoic acid (449 mg, 4 mmol, 1 equiv.), 4-(trimethylsilyl)but-3-yn-1-ol (683 mg, 4.8 mmol, 1.2 equiv.) and anhydrous CH_2Cl_2 (40 mL). The mixture was stirred until dissolution, then cooled to 0 °C with an ice-bath. DCC (908 mg, 4.4 mmol, 1.10 equiv.) and DMAP (48.9 mg, 0.4 mmol, 0.10 equiv.) were added portion-wise as solids. The ice-bath was removed and the reaction mixture was stirred overnight at room temperature. The heterogeneous solution was filtered over celite and concentrated under reduced pressure. The crude residue was purified by SiO_2 gel column chromatography (MTBE/Pentane: 1/20) which afforded **SM4** (671 mg, 71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (t, *J* = 7.0 Hz, 2H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 2.27 (td, *J* = 6.9, 2.7 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.86 (p, *J* = 7.1 Hz, 2H), 0.15 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.91, 102.34, 86.66, 83.37, 69.30, 62.33, 32.96, 23.76, 20.47, 18.00, 0.14.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{13}H_{20}O_2SiNa$, 259.112477; found 259.112230.



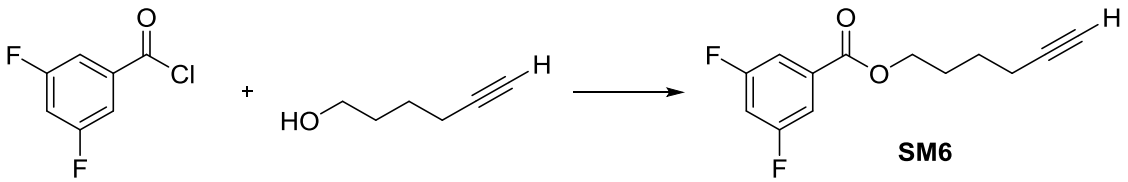
SM5

To a solution of 5-hexyn-1-ol (0.55 mL, 5.00 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (0.5 M, 10 mL) at 0 °C was added successively DMAP (61 mg, 0.5 mmol, 0.1 equiv.), pyridine (1.2 mL, 15 mmol, 3.0 equiv.) and 4-chlorobenzoyl chloride (1.3 mL, 10 mmol, 2.0 eq). The solution was allowed to warm to room temperature and stirred for 1 hour. The volatiles were removed in vacuo, after which the crude reaction mixture was purified by SiO_2 gel column chromatography (EtOAc/Hexanes: 5/95) which afforded **SM5** as a transparent colorless oil (1.09 g, 92 % yield).[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.44 – 7.39 (m, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.28 (td, *J* = 7.0, 2.6 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.94 – 1.87 (m, 2H), 1.73 – 1.65 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.86, 139.49, 131.09, 128.92, 128.84, 83.92, 68.98, 64.85, 27.87, 25.17, 18.27.

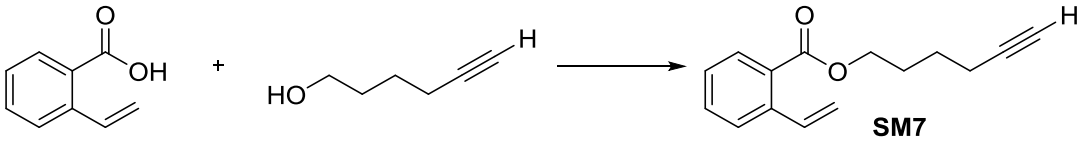
HRMS-ESI (m/z): $[M]^+$ calcd for $C_{13}H_{13}O_2Cl$, 236.060408; found 236.060303.



SM6

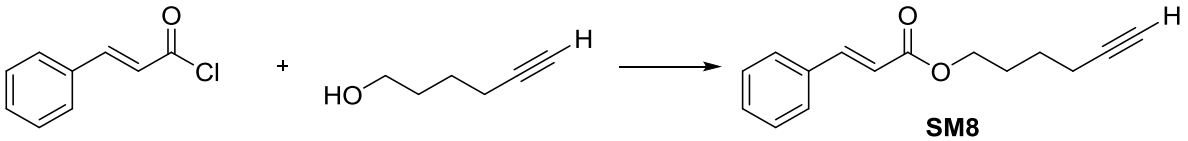
To a solution of 5-hexyn-1-ol (0.55 mL, 5.00 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (0.5 M, 10 mL) at 0 °C was added successively DMAP (61 mg, 0.5 mmol, 0.1 equiv.), pyridine (1.2 mL, 15 mmol, 3.0 equiv.) and 3,5-difluorobenzoyl chloride (1.2 mL, 10 mmol, 2.0 eq). The solution was allowed to warm to room temperature and stirred for 1 hour. The volatiles were removed in vacuo, after which the crude reaction mixture was purified by SiO_2 gel column chromatography (EtOAc/Hexanes: 10/90) which afforded **SM6** as a transparent colorless oil (1.16 g, 97 % yield).[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.01 (tt, *J* = 8.5, 2.4 Hz, 1H), 4.36 (t, *J* = 6.5 Hz, 2H), 2.28 (td, *J* = 7.0, 2.6 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.95 – 1.87 (m, 2H), 1.72 – 1.65 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 164.51 (t, *J* = 3.4 Hz), 163.89 (d, *J* = 12.0 Hz), 161.91 (d, *J* = 11.9 Hz), 133.69 (t, *J* = 9.0 Hz), 112.82 (d, *J* = 6.5 Hz), 112.66 (d, *J* = 6.5 Hz), 108.48 (t, *J* = 25.3 Hz), 83.80, 69.08, 65.39, 27.77, 25.09, 18.24.
^{19}F NMR (470 MHz, $CDCl_3$) δ -108.60.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{13}H_{13}O_2F_2$, 239.087812; found 239.087600.



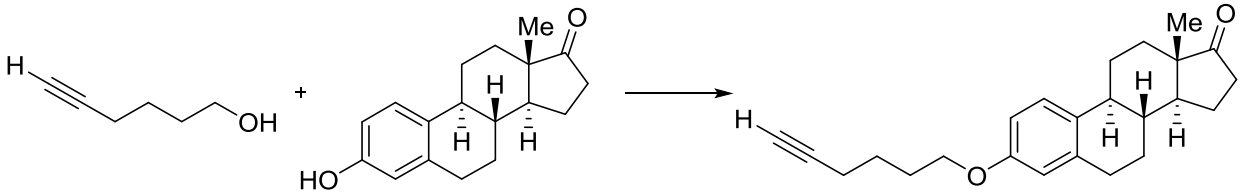
SM7

An argon flushed one-necked flask equipped with a stirring bar was charged with 2-vinylbenzoic acid (310 mg, 2.01 mmol, 1 equiv.), 5-hexyn-1-ol (0.27 mL, 2.41 mmol, 1.2 equiv.) and anhydrous CH_2Cl_2 (20 mL). The mixture was stirred until dissolution, then cooled to 0 °C with an ice-bath. DCC (456 mg, 2.21 mmol, 1.10 equiv.) and DMAP (24.5 mg, 0.20 mmol, 0.10 equiv.) were added portion-wise as solids. The ice-bath was removed and the reaction mixture was stirred 12 hours at room temperature. The heterogeneous solution was filtered over celite and concentrated under reduced pressure. The crude residue was purified by SiO_2 gel column chromatography (MTBE/Pentane: 1/20) which afforded **SM7** as a white solid (329 mg, 72% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.52 – 7.42 (m, 2H), 7.32 (td, *J* = 7.7, 1.2 Hz, 1H), 5.64 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.35 (dd, *J* = 11.0, 1.3 Hz, 1H), 4.34 (t, *J* = 6.4 Hz, 2H), 2.28 (td, *J* = 7.0, 2.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.74 – 1.66 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.53, 139.74, 136.08, 132.20, 130.38, 128.94, 127.52, 127.40, 116.55, 83.98, 68.93, 64.67, 27.91, 25.24, 18.27.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{15}H_{17}O_2$, 229.122305; found 229.122050.



SM8

To a solution of 5-hexyn-1-ol (0.55 mL, 5.00 mmol, 1.00 equiv.) in anhydrous CH_2Cl_2 (0.5 M, 10 mL) at 0 °C was added successively DMAP (61 mg, 0.5 mmol, 0.1 equiv.), pyridine (1.2 mL, 15 mmol, 3.0 equiv.) and cinnamoyl chloride (1.2 mL, 10 mmol, 2.0 eq). The solution was allowed to warm to room temperature and stirred for 1 hour. The volatiles were removed in vacuo, after which the crude reaction mixture was purified by SiO_2 gel column chromatography (EtOAc/Hexanes: 5/95) which afforded **SM8** as a transparent colorless oil (1.05 g, 92% yield).[1]
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.39 (dt, *J* = 4.5, 2.7 Hz, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.24 (t, *J* = 6.5 Hz, 2H), 2.27 (td, *J* = 7.1, 2.7 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.89 – 1.80 (m, 2H), 1.71 – 1.62 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.13, 144.88, 134.56, 130.40, 129.02, 128.20, 118.25, 84.03, 68.88, 64.15, 27.92, 25.14, 18.26.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{15}H_{17}O_2$, 229.122305; found 229.121860.



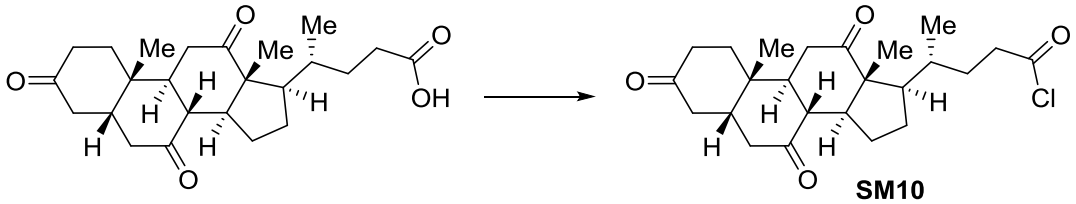
SM9

To a 100mL flask equipped with a stirring bar were dissolved Estrone (0.54 g, 2.0 mmol, 1.0 equiv.), PPh_3 (1.1 g, 4.0 mmol, 2.0 equiv.) and 5-Hexyn-1-ol (330 uL, 3.0 mmol, 1.5 equiv.) in THF (30 mL). The solution was cooled down to 0 °C with an ice-bath. DEAD (0.56 mL, 3.0 mmol, 1.5 equiv.) was added dropwise to the solution, the ice-bath was removed and the resulting solution was stirred 12 hours at room temperature. The volume was reduced in vacuo and the residue was diluted with EtOAc, washed successively 3 times with NaOH (1 M), brine, dried over $MgSO_4$, filtered and concentrated. The crude reaction mixture was purified by SiO_2 gel column chromatography (EtOAc/Hexanes: from 10/90 to 20/80) which afforded **SM9** as a white solid (250 mg, 37 % yield).[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.8 Hz, 1H), 3.96 (t, *J* = 6.3 Hz, 2H), 2.96 – 2.83 (m, 2H), 2.50 (dd, *J* = 19.0, 8.5 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.30 – 2.22 (m, 3H), 2.19 – 2.10 (m, 1H), 2.09 – 1.98 (m, 2H), 1.98 – 1.86 (m, 4H), 1.75 – 1.68 (m, 2H), 1.67 – 1.38 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 221.06, 157.16, 137.87, 132.12, 126.45, 114.68, 112.24, 84.29, 68.73, 67.34, 50.58, 48.17, 44.14, 38.54, 36.03, 31.75, 29.81, 28.48, 26.72, 26.08, 25.22, 21.75, 18.30, 14.02.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{24}H_{30}O_2Na$, 373.213799; found 373.213450.



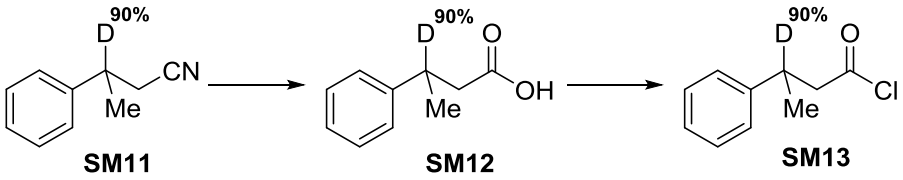
SM10

To a 250mL flask equipped with a reflux condenser and a stirring bar was added dehydrocholic acid (1.0 g, 2.5 mmol, 1.0 equiv.). The solid was dissolved in anhydrous CH_2Cl_2 (100 mL) under an argon atmosphere at room temperature over 10 min. To the solution was added oxalyl chloride (1.7 mL, 20 mmol, 8 equiv.), and the resulting mixture was refluxed for 4 hours under argon. The solvent was evaporated along with excess oxalyl chloride to give **SM10** as a beige solid (0.99 g, 95 %).[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.00 – 2.81 (m, 5H), 2.37 – 2.20 (m, 6H), 2.17 – 2.11 (m, 2H), 2.07 – 1.91 (m, 5H), 1.85 (td, *J* = 11.3, 7.1 Hz, 1H), 1.62 (td, *J* = 14.3, 5.0 Hz, 1H), 1.53 – 1.43 (m, 1H), 1.40 (s, 3H), 1.37 – 1.25 (m, 3H), 1.07 (s, 3H), 0.86 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 211.79, 208.96, 208.57, 174.12, 56.88, 51.75, 48.96, 46.82, 45.56, 45.48, 44.97, 44.55, 42.78, 38.62, 36.48, 36.02, 35.27, 35.10, 30.57, 27.64, 25.09, 21.91, 18.53, 11.82.

HRMS-ESI (m/z): $[M]^+$ calcd for $C_{24}H_{33}O_4Cl$, 420.206738; found 420.206670.

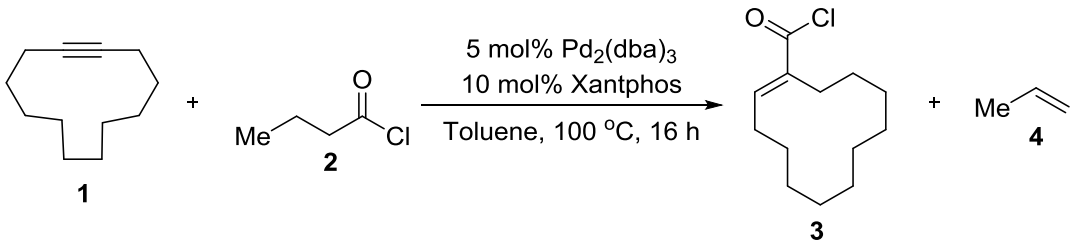


SM11 was prepared according to known procedure. Analytical data are consistent with the literature.[4]

To an aqueous solution of NaOH (32 mL, 1.0 M) in a flask was added **SM11** (1.0 g, 6.8 mmol). The flask was placed into a preheated oil bath and stirred 60 hrs at 100 °C. The reaction was cooled down to room temperature. The aqueous mixture was extracted with MTBE, and the aqueous phase was acidified with conc. HCl. The aqueous phase was extracted three times with MTBE and the combined organic layers were washed with brine solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure by rotary evaporation which afforded **SM12** as a transparent colorless oil (1.10 g, 98% yield, deuteration level: 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.68 (br, 1H), 7.34 – 7.28 (m, 2H), 7.25 – 7.20 (m, 3H), 3.32 – 3.25 (m, 0.1H), 2.68 (d, *J* = 15.5 Hz, 1H), 2.59 (d, *J* = 15.5 Hz, 1H), 1.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.87, 145.51, 128.71, 126.82, 126.65, 42.63, 36.28 (s, C-H), 35.88 (t, *J* = 20.1 Hz, C-D), 21.88. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{10}H_{12}DO_2$, 166.097282; found 166.097480.

Oxalyl chloride (0.52 uL, 6.0 mmol, 2.0 equiv.) was added slowly to a stirred solution of **SM12** (0.5 g, 3.0 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (6 mL) and catalytic DMF (5 uL) at 0 °C. The mixture was stirred for 1 hour at 0 °C and another 16 hours at room temperature. The volatiles were removed in vacuo which afforded **SM13** (0.55 g, quant. yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.26 – 7.20 (m, 3H), 3.40 – 3.33 (m, 0.1H), 3.20 (d, *J* = 16.5 Hz, 1H), 3.11 (d, *J* = 16.5 Hz, 1H), 1.35 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.45, 144.01, 128.88, 127.06, 126.77, 55.09, 36.78 (s, C-H), 36.39 (t, *J* = 20.1 Hz, C-D), 21.32. **HRMS-ESI** (m/z): $[M]^+$ calcd for $C_{10}H_{10}DOCl$, 183.056120; found 183.056038.

5. Scope of the transfer hydrochlorocarbonylation

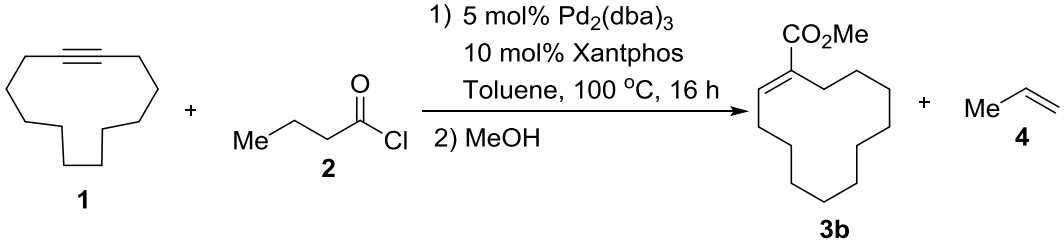


A 50 mL pressure tube equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.25 mmol, 228 mg) and Xantphos (10 mol%, 0.5 mmol, 288 mg). The unsealed pressure tube was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (10 mL) was added, followed by **1** (821 mg, 5 mmol), **2** (520 uL, 5 mmol) and the pressure tube was sealed. The pressure tube was taken out of the glovebox and heated at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. The volatiles were distilled off under vacuum. The residue was directly purified by bulb-to-bulb distillation (Büchi Glass oven B-585) to give **3** in 78% yield (892 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.2 Hz, 1H), 2.41 (t, *J* = 6.7 Hz, 2H), 2.33 (q, *J* = 7.6 Hz, 2H), 1.65 – 1.57 (m, 4H), 1.43 – 1.33 (m, 10H), 1.26 – 1.20 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.18, 153.75, 137.27, 26.97, 26.00, 25.82, 25.17, 25.12, 24.98, 24.79, 23.59, 23.02, 22.17.

HRMS-EI (m/z): $[M]^+$ calcd for $C_{13}H_{21}OCl$, 228.128093; found 228.127885.



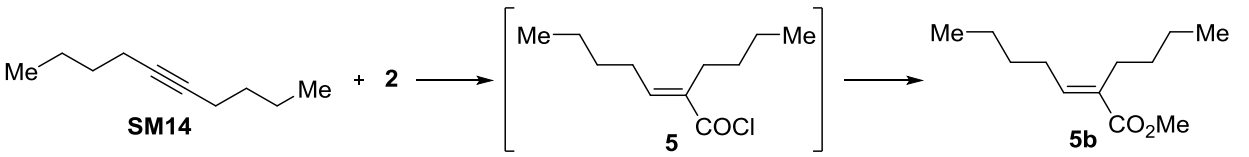
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **3b** (45.4 mg, yield: 81%).

IR (film) 2926, 2858, 1712, 1640 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (t, *J* = 8.2 Hz, 1H), 3.73 (s, 3H), 2.36 (t, *J* = 6.7 Hz, 2H), 2.21 (q, *J* = 7.4 Hz, 2H), 1.59 – 1.51 (m, 4H), 1.44 – 1.29 (m, 10H), 1.26 – 1.19 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.83, 143.27, 132.23, 51.67, 26.55, 26.12, 25.90, 25.26, 25.01, 24.93, 23.71, 23.70, 23.05, 22.25.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{14}H_{24}O_2Na$, 247.166849; found 247.166770.



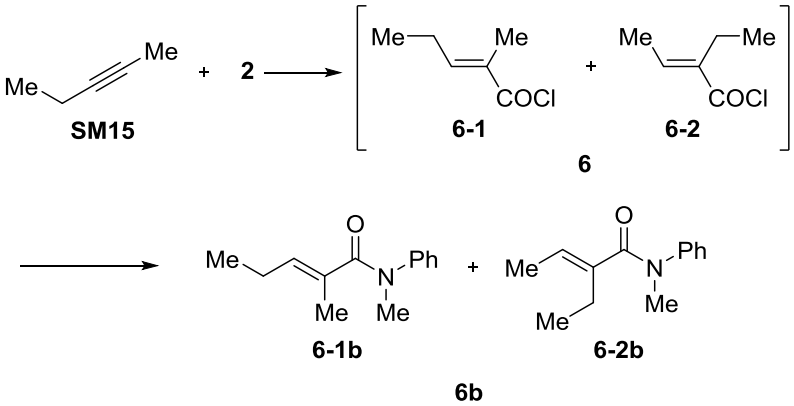
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM14** (34.6 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **5b** (38.2 mg, yield: 77%).

IR (film) 2956, 2929, 2861, 1714, 1645 cm^{-1}.

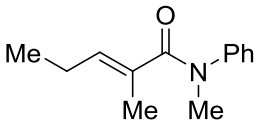
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (t, *J* = 7.5 Hz, 1H), 3.72 (s, 3H), 2.31 – 2.26 (m, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.45 – 1.30 (m, 8H), 0.94 – 0.88 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.75, 142.92, 132.47, 51.70, 31.71, 31.15, 28.38, 26.67, 22.83, 22.62, 14.10, 14.05.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{22}O_2Na$, 221.151199; found 221.151050.

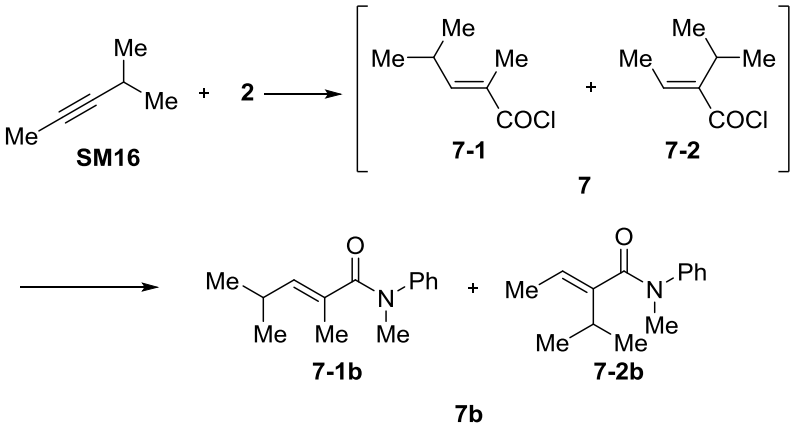


A 25 mL pressure tube equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed pressure tube was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM15** (24 uL, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the pressure tube was sealed. The pressure tube was taken out of the glovebox and heated at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **6b** was determined by ^{1}H NMR analysis (**6-1b**/**6-2b**: 85/15). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 2/1) to give **6b** (20.3 mg, yield: 40%).



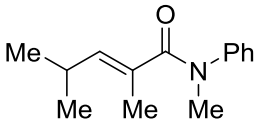
6-1b

IR (film) 2963, 2931, 2873, 1634, 1594, 1494, 1363, 698 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.23 – 7.18 (m, 1H), 7.12 – 7.07 (m, 2H), 5.53 (tq, *J* = 7.4, 1.6 Hz, 1H), 3.34 (s, 3H), 1.91 – 1.81 (m, 2H), 1.60 – 1.60 (m, 3H), 0.70 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 173.58, 145.39, 137.55, 130.93, 129.17, 126.62, 126.56, 37.80, 21.05, 14.25, 12.91.
HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{13}H_{17}NONa$, 226.120233; found 226.120370.



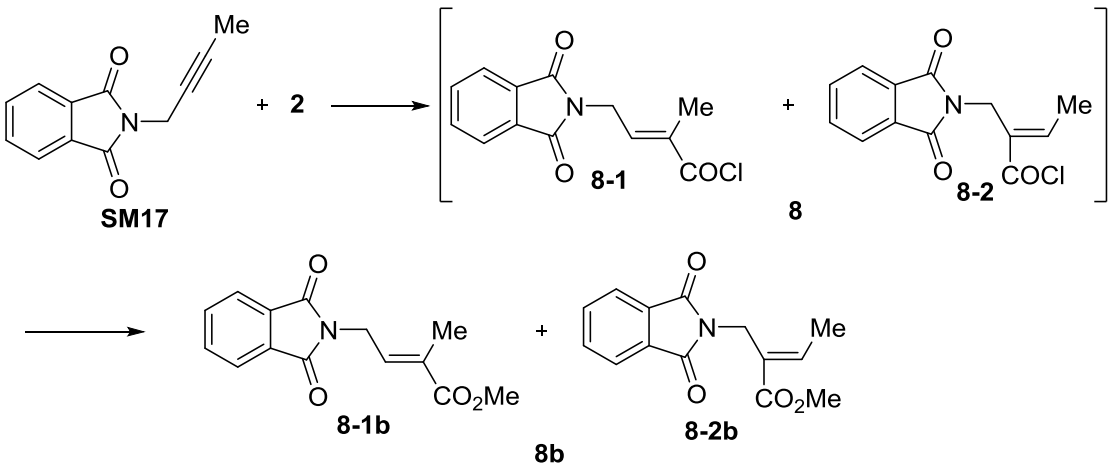
SM16 **7-1** **7-2** **7** **7-1b** **7-2b** **7b**

A 25 mL pressure tube equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed pressure tube was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM16** (29 uL, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the pressure tube was sealed. The pressure tube was taken out of the glovebox and heated at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **7b** was determined by ^{1}H NMR analysis (**7-1b**/**7-2b**: 98/2). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 2/1) to give **7b** (29.3 mg, yield: 54%).

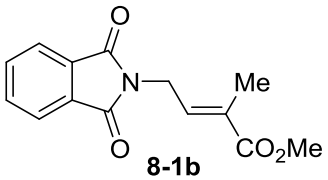


7-1b

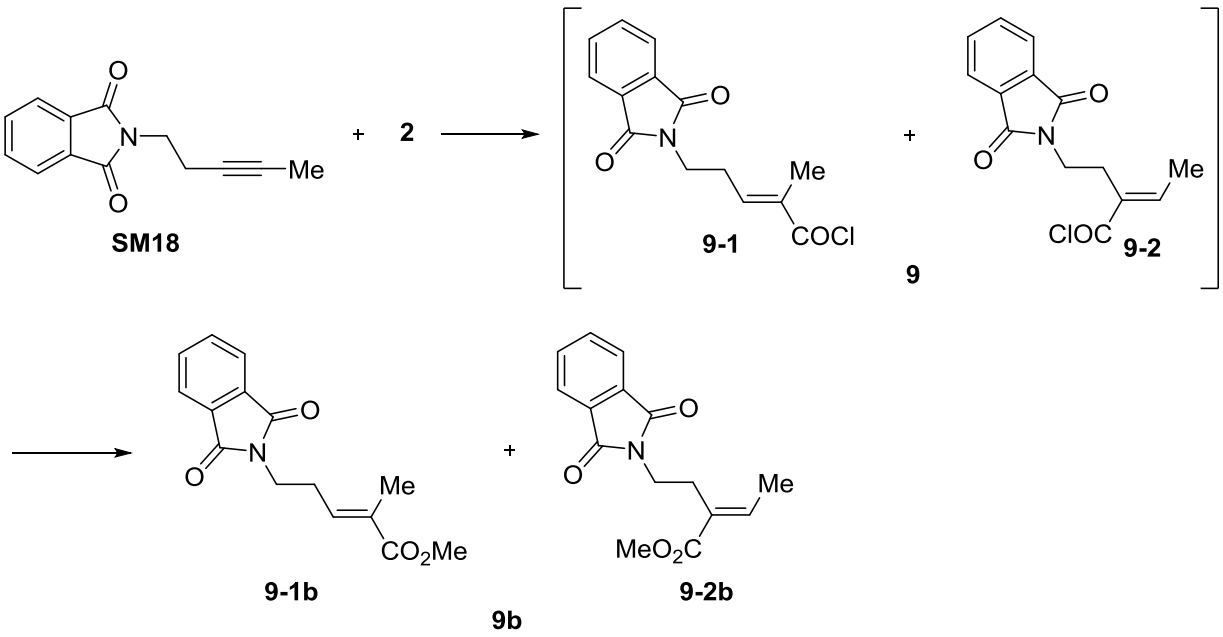
IR (film) 2957, 2925, 2868, 1636, 1595, 1494, 1362, 698 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.06 (m, 2H), 5.23 (dq, *J* = 9.4, 1.5 Hz, 1H), 3.34 (s, 3H), 2.30 (ddt, *J* = 13.3, 9.5, 6.6 Hz, 1H), 1.65 (d, *J* = 1.6 Hz, 3H), 0.67 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 173.67, 145.59, 142.79, 129.13, 128.84, 126.63, 126.53, 37.65, 27.00, 21.75, 14.36.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{14}H_{20}NO$, 218.153939; found 218.154040.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM17** (49.8 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **8b** was determined by GC analysis (**8-1b**/**8-2b**: 85/15). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 4/1) to give **8-1b** (44.1 mg, yield: 68%). GC yield of **8-2b**: 12%.



IR (film) 2951, 2919, 1769, 1705, 1650, 1611, 713 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 6.66 (tq, *J* = 6.8, 1.5 Hz, 1H), 4.44 (dq, *J* = 6.8, 1.0 Hz, 2H), 3.72 (s, 3H), 2.03 (q, *J* = 1.5, 1.0 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.90, 167.88, 134.59, 134.25, 132.20, 131.13, 123.54, 52.12, 35.87, 12.84.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{14}H_{14}O_4N$, 260.091734; found 260.091330.



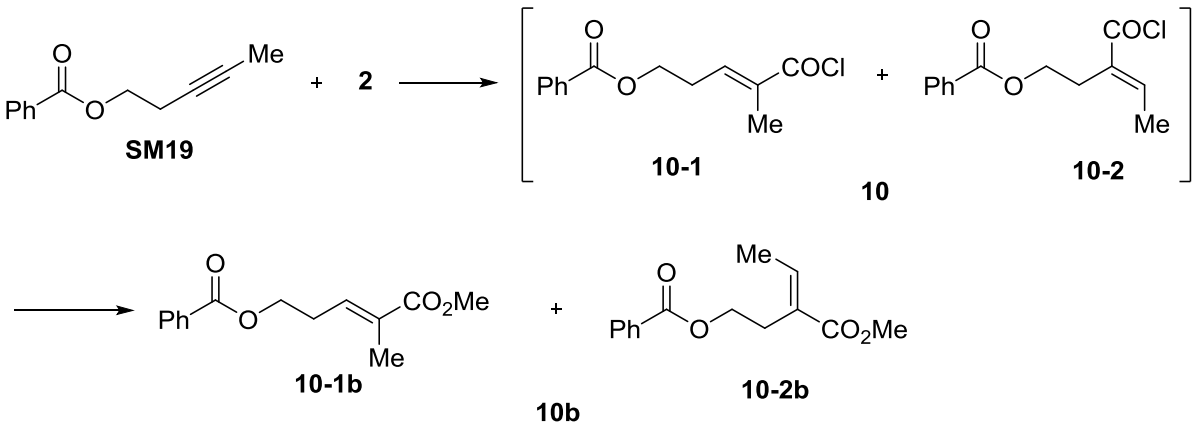
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM18**[5] (53.3 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **9b** was determined by ^1H NMR analysis (**9-1b**/**9-2b**: 64/36). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 4/1) to give **9b** (40.3 mg, yield: 59%).

IR (film) 2953, 1771, 1701, 1645, 1614, 717 cm^{-1}.

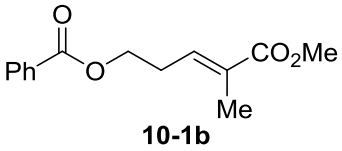
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 3.12H), 7.73 – 7.69 (m, 3.12H), 6.92 (q, *J* = 7.2 Hz, 0.56H), 6.74 (tq, *J* = 7.5, 1.5 Hz, 1H), 3.83 (t, *J* = 6.8 Hz, 1.12H), 3.80 (t, *J* = 6.8 Hz, 2H), 3.74 (s, 1.68H), 3.72 (s, 3H), 2.72 (t, *J* = 6.8 Hz, 1.12H), 2.59 (qd, *J* = 7.4, 1.0 Hz, 2H), 1.82 (q, *J* = 1.1 Hz, 3H), 1.72 (d, *J* = 7.2 Hz, 1.68H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.40, 168.31, 168.27, 167.73, 140.41, 137.20, 134.17, 134.02, 132.19, 132.14, 130.46, 129.58, 123.46, 123.33, 51.98, 51.96, 36.88, 36.69, 28.05, 25.70, 14.37, 12.65.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{15}NO_4Na$, 296.089328; found 296.089290.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM19**[6] (47.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **10b** was determined by ^1H NMR analysis (**10-1b**/**10-2b**: 56/44). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 2/1) to give **10b** (40.3 mg, yield: 65%).



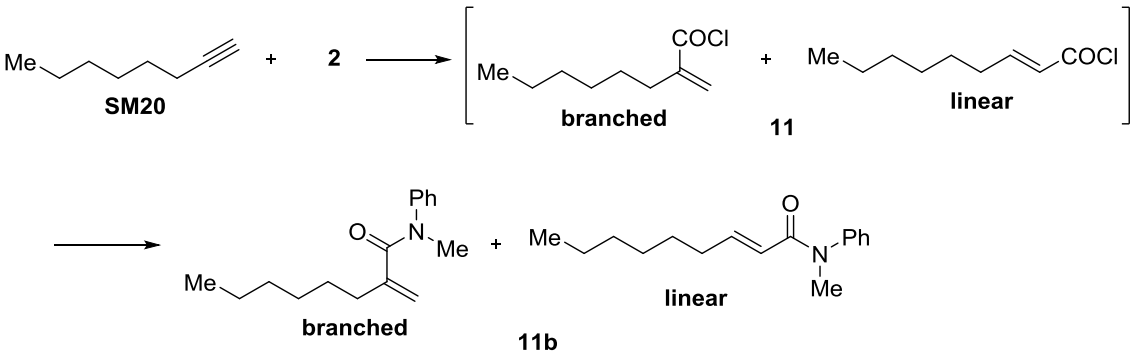
10-1b

IR (film) 2953, 1713, 1653, 1602, 1584, 1267, 710 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dt, *J* = 8.4, 1.5 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.47 – 7.41 (m, 2H), 6.83 (tq, *J* = 7.3, 1.5 Hz, 1H), 4.41 (t, *J* = 6.6 Hz, 2H), 3.75 (s, 3H), 2.70 – 2.63 (m, 2H), 1.90 (q, *J* = 1.1 Hz, 3H).

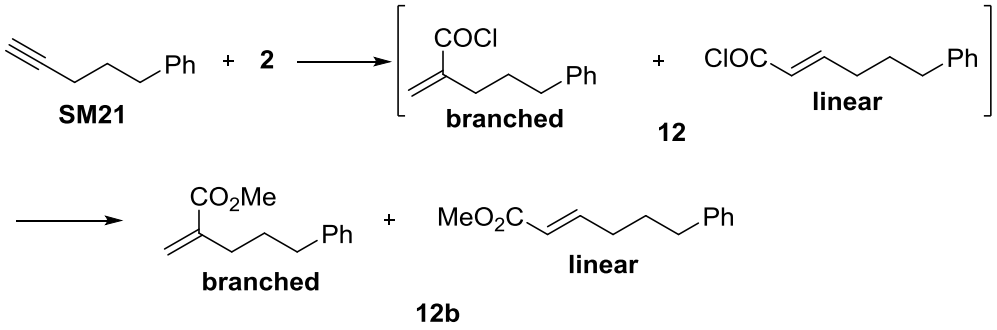
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.38, 166.64, 137.18, 133.17, 130.32, 130.21, 129.73, 128.53, 63.38, 51.99, 28.47, 12.78.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{14}H_{16}O_4Na$, 271.094079; found 271.094110.

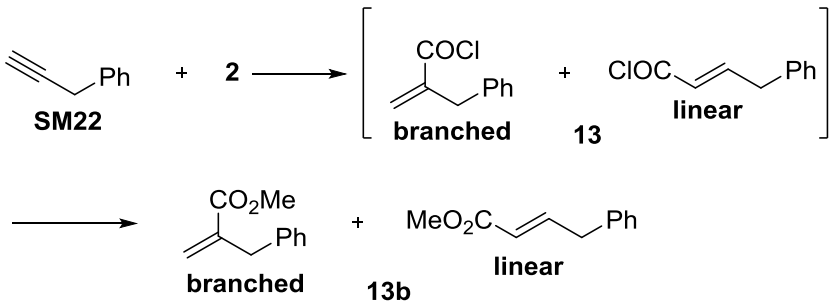


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the

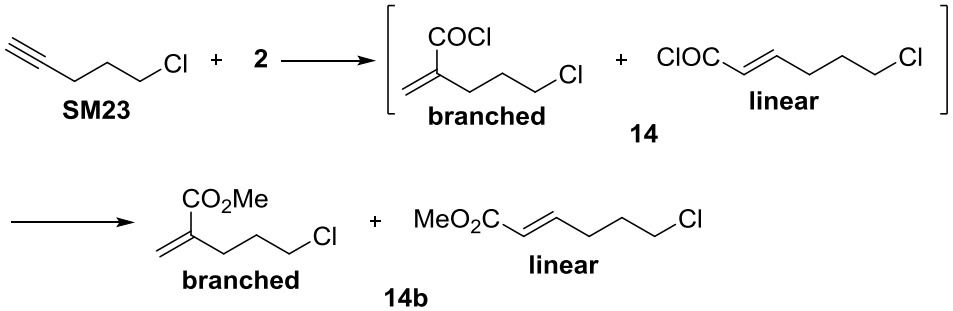
glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM20** (27.6 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **11b** was determined by GC analysis (**b/l**: 83/17). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 4/1) to give **11b** (branched product: 38.7 mg, isolated yield: 63%; linear product yield: 13% based on GC). Branched product: **IR** (film) 2927, 2856, 1739, 1650, 1624, 1595, 1366, 698 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.17 – 7.05 (m, 2H), 5.03 (d, *J* = 4.6 Hz, 2H), 3.35 (s, 3H), 2.05 (t, *J* = 7.0 Hz, 2H)., 1.36 (p, *J* = 7.2 Hz, 2H), 1.29 – 1.19 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.01, 145.54, 144.69, 129.28, 127.00, 126.92, 118.12, 37.96, 33.84, 31.77, 29.04, 27.60, 22.72, 14.22. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{16}H_{23}NONa$, 268.167183; found 268.166930.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM21** (36.1 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **12b** was determined by GC analysis (**b/l**: 83/17). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **12b** (branched product: 30.1 mg, isolated yield: 59%; linear product yield: 12% based on GC). Branched product: **IR** (film) 3027, 2949, 2860, 1719, 1630, 1603, 1169, 699 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 6.16 (dt, *J* = 1.3, 0.7 Hz, 1H), 5.54 (q, *J* = 1.4 Hz, 1H), 3.75 (s, 3H), 2.67 – 2.62 (m, 2H), 2.38 – 2.33 (m, 2H), 1.85 – 1.77 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.86, 142.22, 140.54, 128.55, 128.45, 125.92, 124.96, 51.93, 35.54, 31.68, 30.17. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{13}H_{16}O_2Na$, 227.104249; found 227.104160.

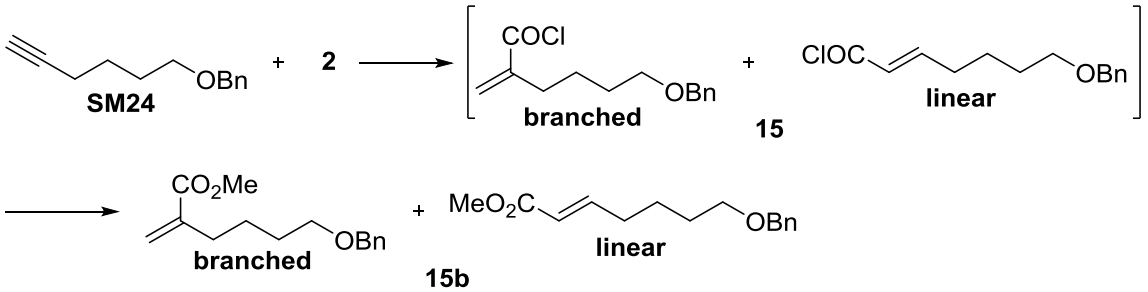


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM22** (29.0 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **13b** was determined by GC analysis (**b**/**l**: 86/14). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **13b** (branched product: 23.1 mg, isolated yield: 52%; linear product yield: 9% based on GC). Branched product: **IR** (film) 3029, 2951, 1717, 1632, 1603, 1134, 700 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 6.24 (dt, *J* = 1.7, 0.9 Hz, 1H), 5.46 (q, *J* = 1.4 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.53, 140.25, 138.83, 129.18, 128.57, 126.49, 126.41, 52.05, 38.21. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}O_2Na$, 199.072949; found 199.072990.

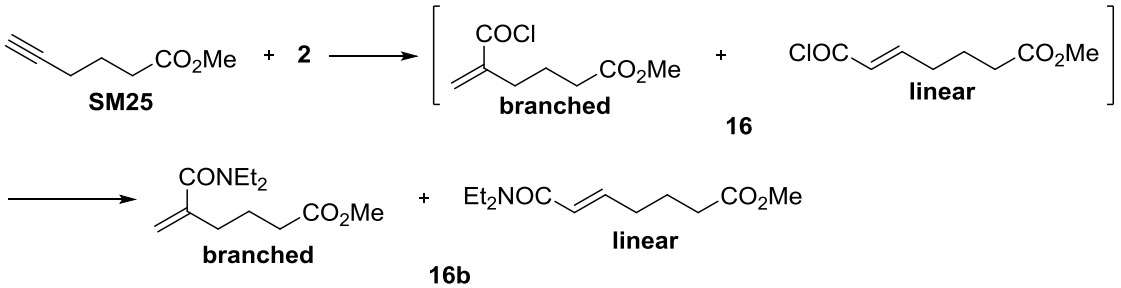


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM23** (25.6 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **14b** was determined by GC analysis (**b**/**l**: 86/14). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **14b** (branched product: 19.6 mg, isolated yield: 48%; linear product yield: 8% based on GC). Branched product: **IR** (film) 2953,

1719, 1631 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.20 (d, *J* = 1.2 Hz, 1H), 5.61 (q, *J* = 1.3 Hz, 1H), 3.76 (s, 3H), 3.55 (t, *J* = 6.5 Hz, 2H), 2.51 – 2.44 (m, 2H), 2.00 – 1.92 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.48, 139.09, 126.13, 52.04, 44.33, 31.26, 29.40. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_7H_{11}O_2ClNa$, 185.033977; found 185.034120.

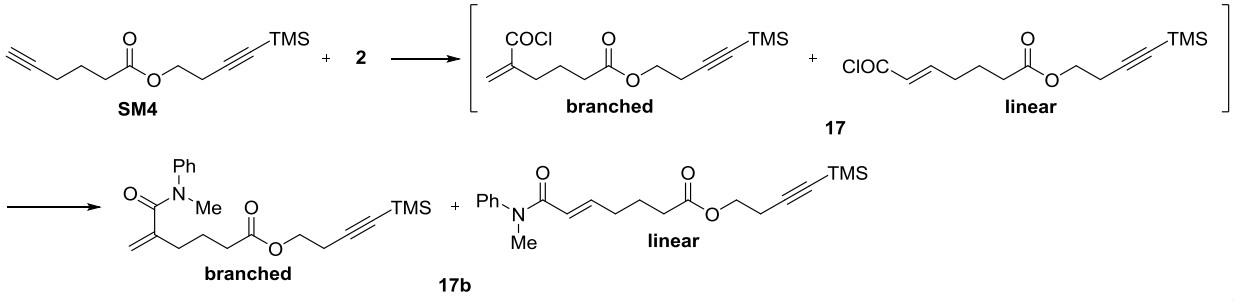


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM24**[7] (47.1 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **15b** was determined by GC analysis (**b/l**: 84/16). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **15b** (branched product: 36.0 mg, isolated yield: 58%; linear product yield: 11% based on GC). Branched product: **IR** (film) 2948, 2863, 1718, 1630, 1147, 736, 697 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.31 – 7.26 (m, 1H), 6.17 – 6.12 (m, 1H), 5.53 (q, *J* = 1.4 Hz, 1H), 4.50 (s, 2H), 3.75 (s, 3H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.37 – 2.28 (m, 2H), 1.69 – 1.62 (m, 2H), 1.61 – 1.53 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.86, 140.57, 138.72, 128.46, 127.73, 127.61, 124.90, 73.03, 70.23, 51.89, 31.76, 29.43, 25.14. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{15}H_{20}O_3Na$, 271.130464; found 271.130280.

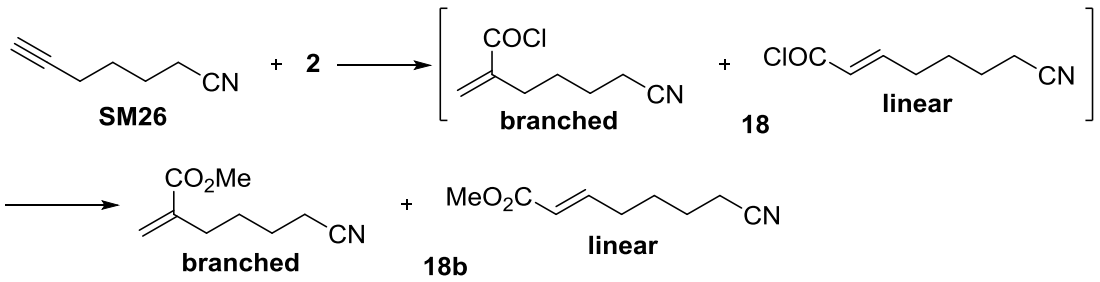


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM25**[8] (31.5 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature.

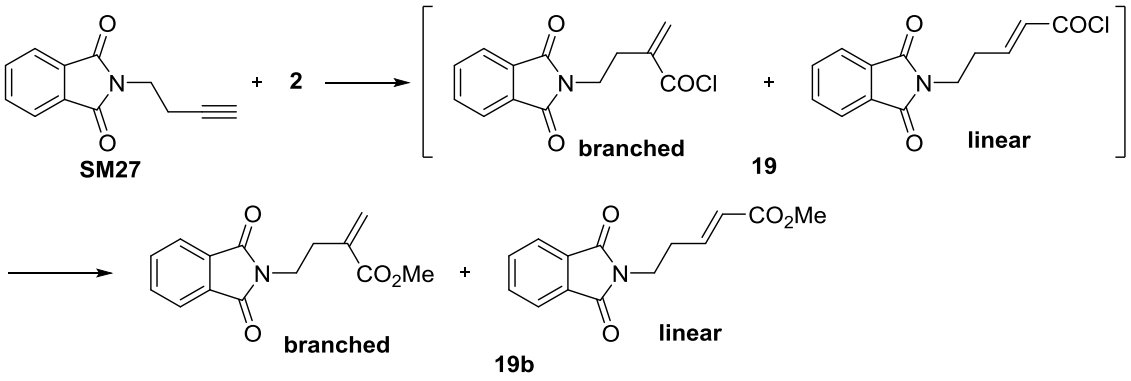
The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution diethylamine (26 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **16b** was determined by GC analysis (**b/l**: 85/15). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 2/1) to give **16b** (branched product: 30.9 mg, isolated yield: 54%; linear product yield: 10% based on GC). Branched product: **IR** (film) 3214, 2972, 1735, 1615, 1433 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.11 (td, *J* = 1.6, 0.9 Hz, 1H), 5.05 (q, *J* = 1.0 Hz, 1H), 3.66 (s, 3H), 3.44 – 3.32 (m, 4H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.34 – 2.28 (m, 2H), 1.81 (p, *J* = 7.6 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.90, 171.66, 144.83, 113.51, 51.68, 42.78, 38.76, 33.70, 33.51, 22.79, 14.49, 12.91. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{12}H_{21}NO_3Na$, 250.141363; found 250.141270.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM4** (59.1 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **17b** was determined by GC analysis (**b/l**: 85/15). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 4/1) to give **17b** (branched product: 53.7 mg, isolated yield: 58%; linear product yield: 10% based on GC). Branched product: **IR** (film) 2958, 2179, 1735, 1650, 1624, 1595, 1495, 840, 761, 699 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.27 – 7.23 (m, 1H), 7.15 – 7.11 (m, 2H), 5.10 – 5.01 (m, 2H), 4.14 (t, *J* = 7.0 Hz, 2H), 3.34 (s, 3H), 2.54 (t, *J* = 7.1 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 2.11 (t, *J* = 7.6 Hz, 2H), 1.73 (p, *J* = 7.6 Hz, 2H), 0.13 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.14, 171.48, 144.57, 144.10, 129.40, 127.15, 126.92, 119.16, 102.36, 86.62, 62.26, 37.98, 33.45, 33.05, 22.87, 20.47, 0.14. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{21}H_{30}NO_3Si$, 372.198947; found 372.198790.

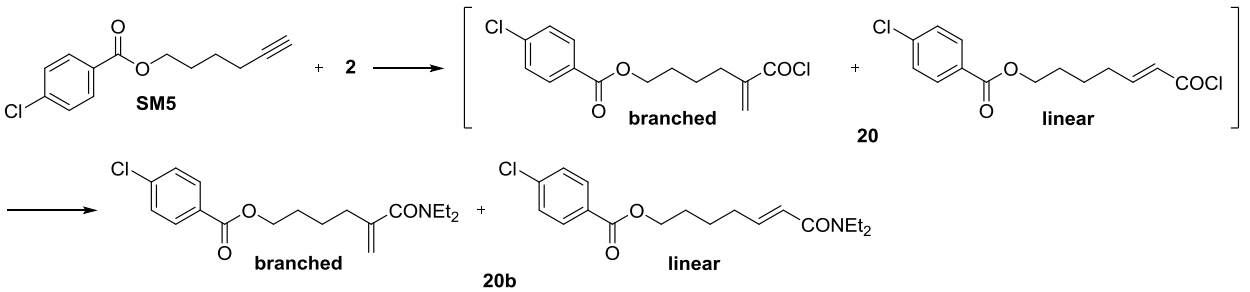


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM26**[9] (26.8 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **18b** was determined by GC analysis (**b/l**: 89/11). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 10/1) to give **18b** (branched product: 27.2 mg, isolated yield: 65%; linear product yield: 8% based on GC). Branched product: **IR** (film) 2952, 2869, 2247, 1716, 1631, 1137 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.18 (dt, *J* = 1.3, 0.6 Hz, 1H), 5.57 (q, *J* = 1.3 Hz, 1H), 3.76 (s, 3H), 2.39 – 2.32 (m, 4H), 1.73 – 1.59 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.55, 139.71, 125.57, 119.67, 52.04, 31.20, 27.63, 25.03, 17.13. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_9H_{13}NO_2Na$, 190.083848; found 190.083710.

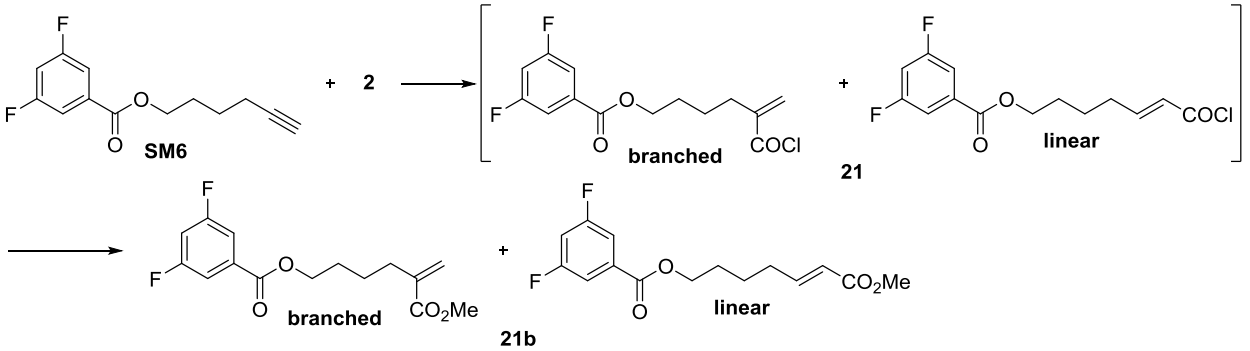


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM27** (49.8 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **19b** was determined by GC analysis (**b/l**: 85/15). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 4/1) to give **19b** (branched product: 39.7 mg, isolated yield: 61%; linear product yield: 11% based on GC). Branched product: **IR** (film) 2948,

1773, 1713, 1703, 1629, 713 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.14 (d, *J* = 1.1 Hz, 1H), 5.53 (q, *J* = 1.1 Hz, 1H), 3.89 (t, *J* = 6.7 Hz, 2H), 3.78 (d, *J* = 1.1 Hz, 3H), 2.70 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.36, 166.96, 137.25, 134.04, 132.16, 127.49, 123.38, 52.15, 36.98, 31.59. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{14}H_{13}NO_4Na$, 282.073678; found 282.073510.

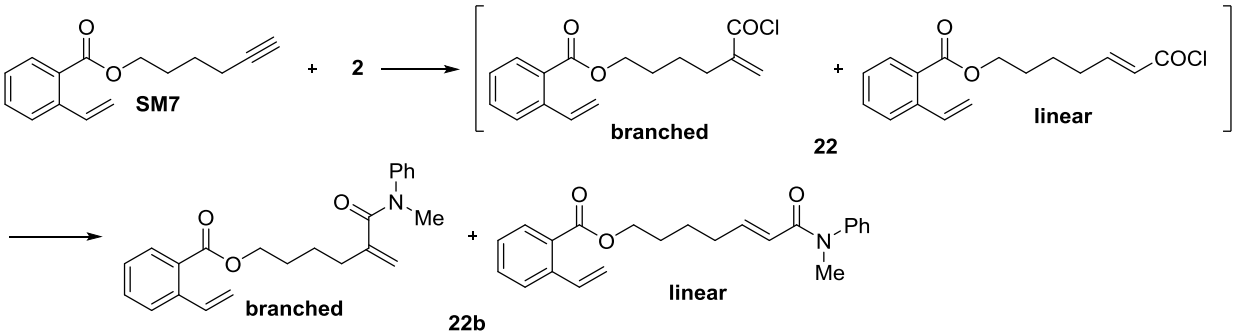


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM5** (59.2 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature. The 2 and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution diethylamine (26 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **20b** was determined by GC analysis (**b/l**: 86/14). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 2/1) to give **20b** (branched product: 54.5 mg, isolated yield: 65%; linear product yield: 10% based on GC). Branched product: **IR** (film) 2935, 1717, 1616, 1595, 1270, 1090, 760 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.42 – 7.37 (m, 2H), 5.12 (q, *J* = 1.4 Hz, 1H), 5.05 (q, *J* = 1.0 Hz, 1H), 4.32 (t, *J* = 6.5 Hz, 2H), 3.50 – 3.28 (m, 4H), 2.40 – 2.28 (m, 2H), 1.88 – 1.76 (m, 2H), 1.66 – 1.57 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.77, 165.89, 145.28, 139.44, 131.08, 128.95, 128.82, 113.28, 65.11, 42.74, 38.73, 34.16, 28.49, 24.13, 14.51, 12.90. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{18}H_{24}NO_3ClNa$, 360.133691; found 360.133570.

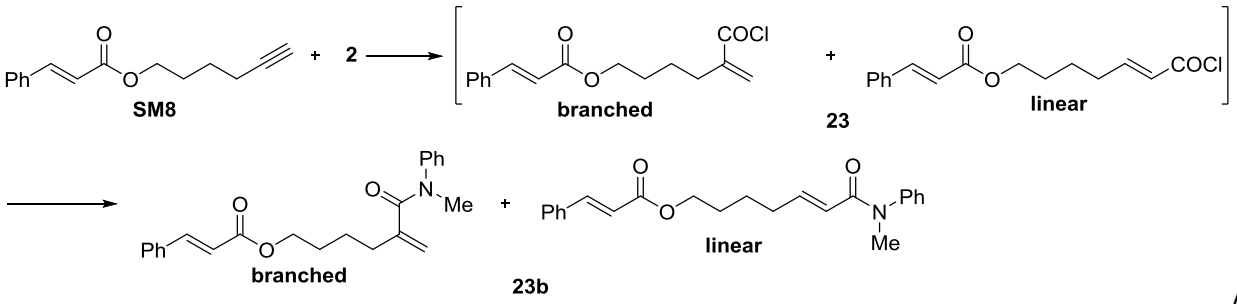


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM6** (59.6 mg, 0.25 mmol), **2**

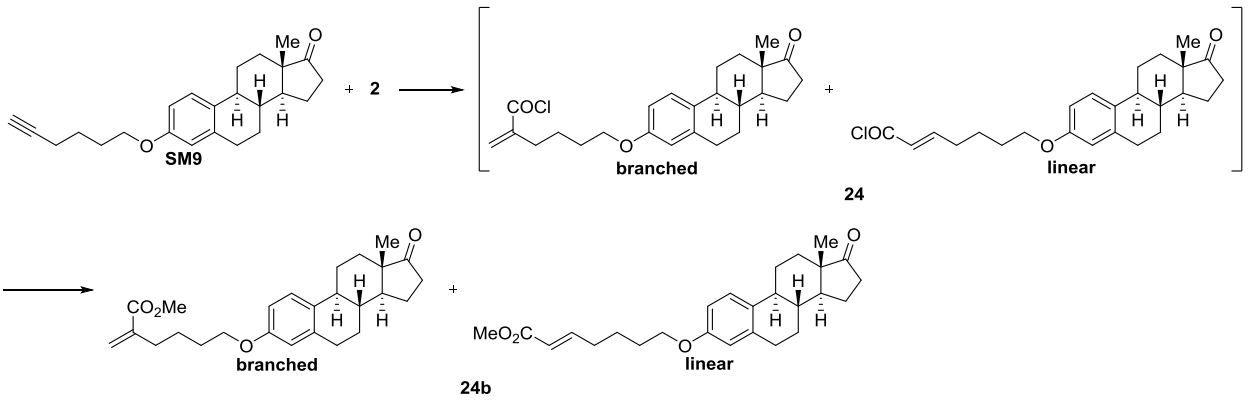
(104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **21b** was determined by GC analysis (**b/l**: 86/14). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 15/1) to give **21b** (branched product: 45.5 mg, isolated yield: 61%; linear product yield: 10% based on GC). Branched product: **IR** (film) 2953, 1720, 1622, 1597, 1324, 988, 767 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H), 7.01 (tt, *J* = 8.5, 2.4 Hz, 1H), 6.20 – 6.14 (m, 1H), 5.57 (q, *J* = 1.4 Hz, 1H), 4.34 (t, *J* = 6.6 Hz, 2H), 3.75 (s, 3H), 2.43 – 2.33 (m, 2H), 1.85 – 1.75 (m, 2H), 1.67 – 1.59 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167,70, 164.54 (t, *J* = 3.4 Hz), 163.88 (d, *J* = 11.9 Hz), 161.90 (d, *J* = 11.8 Hz), 140,18, 133.75 (t, *J* = 9.1 Hz), 125.33, 112.82 (d, *J* = 6.5 Hz), 112.65 (d, *J* = 6.5 Hz), 108.45 (t, *J* = 25.3 Hz), 65.65, 51.99, 31.66, 28.28, 24.97. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -108.63. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{15}H_{17}O_4F_2$, 299.108942; found 299.108600.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM7** (57.1 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **22b** was determined by GC analysis (**b/l**: 85/15). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 2/1) to give **22b** (branched product: 57.2 mg, isolated yield: 63%; linear product yield: 11% based on GC). Branched product: **IR** (film) 2939, 1713, 1648, 1623, 1594, 1250, 768, 699 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.48 (ddd, *J* = 7.7, 6.4, 1.2 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.34 – 7.29 (m, 3H), 7.25 – 7.20 (m, 1H), 7.13 (dd, *J* = 8.3, 1.1 Hz, 2H), 5.64 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.33 (dd, *J* = 11.0, 1.3 Hz, 1H), 5.07 (s, 2H), 4.26 (t, *J* = 6.5 Hz, 2H), 3.34 (s, 3H), 2.12 (t, *J* = 7.7 Hz, 2H), 1.70 (dt, *J* = 14.6, 6.7 Hz, 2H), 1.58 – 1.51 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.67, 167.54, 144.80, 144.54, 139.67, 136.06, 132.16, 130.37, 129.36, 128.98, 127.51, 127.35, 127.13, 126.89, 118.71, 116.52, 64.90, 37.96, 33.36, 28.32, 24.20. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{23}H_{26}NO_3$, 364.190719; found 364.190370.

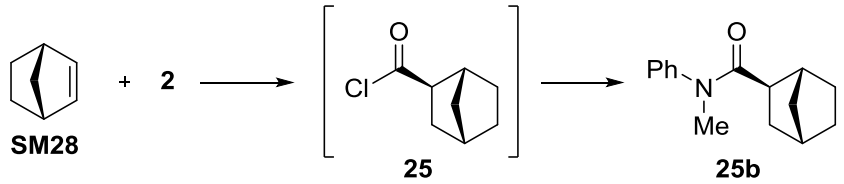


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM8** (57.1 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **23b** was determined by GC analysis (**b/l**: 88/12). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 2/1) to give **23b** (branched product: 52.0 mg, isolated yield: 57%; linear product yield: 8% based on GC). Branched product: **IR** (film) 2943, 1708, 1637, 1594, 1166, 767 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.53 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.07 (s, 2H), 4.16 (s, 2H), 3.35 (s, 3H), 2.12 (t, *J* = 7.7 Hz, 2H), 1.65 (dt, *J* = 14.6, 6.7 Hz, 2H), 1.51 (p, *J* = 7.6, 7.2 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.70, 167.15, 144.84, 144.82, 144.60, 134.58, 130.39, 129.38, 129.03, 128.21, 127.13, 126.92, 118.71, 118.32, 64.42, 37.99, 33.42, 28.38, 24.16. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{23}H_{26}NO_3$, 364.190719; found 364.190340.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM9** (87.6 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature

and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **24b** was determined by GC analysis (**b/l**: 86/14). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 5/1) to give **24b** (branched product: 74.1 mg, isolated yield: 72%; linear product yield: 12% based on GC). Branched product: **IR** (film) 2945, 2878, 1735, 1718, 1634, 1610, 1573 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 6.19 – 6.13 (m, 1H), 5.56 (q, *J* = 1.4 Hz, 1H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.76 (s, 3H), 2.98 – 2.78 (m, 2H), 2.50 (dd, *J* = 18.9, 8.5 Hz, 1H), 2.37 (t, *J* = 7.3 Hz, 3H), 2.29 – 2.19 (m, 1H), 2.18 – 2.09 (m, 1H), 2.09 – 2.03 (m, 1H), 2.03 – 1.97 (m, 1H), 1.95 (d, *J* = 11.8 Hz, 1H), 1.86 – 1.75 (m, 2H), 1.69 – 1.61 (m, 2H), 1.61 – 1.38 (m, 6H), 0.91 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 221.05, 167.84, 157.20, 140.46, 137.84, 132.06, 126.43, 125.03, 114.68, 112.26, 67.71, 51.95, 50.57, 48.16, 44.13, 38.54, 36.02, 31.74, 31.70, 29.80, 29.01, 26.71, 26.07, 25.04, 21.74, 14.01. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{26}H_{34}O_4Na$, 433.234929; found 433.234770.



SM28 **25** **25b**

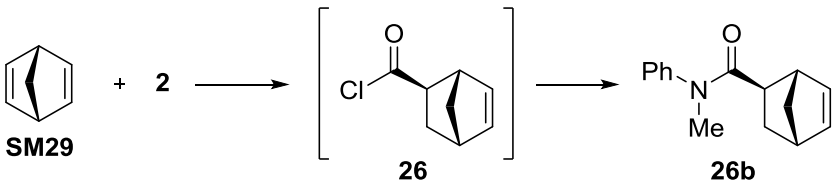
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM28** (23.5 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 5/1) to give **25b** (55.0 mg, yield: 96%).

IR (film) 2951, 2869, 1738, 1654, 1596, 1495, 701 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.21 – 7.15 (m, 2H), 3.24 (s, 3H), 2.30 (s, 1H), 2.21 (s, 1H), 2.15 (dd, *J* = 9.4, 5.6 Hz, 1H), 1.78 (d, *J* = 9.0 Hz, 2H), 1.46 – 1.27 (m, 2H), 1.12 (d, *J* = 6.8 Hz, 2H), 0.94 (t, *J* = 10.0 Hz, 1H), 0.74 (t, *J* = 10.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.34, 144.54, 129.70, 127.85, 127.63, 44.35, 41.84, 37.73, 36.80, 36.06, 35.96, 29.70, 28.50.

HRMS-EI (m/z): $[M+H]^+$ calcd for $C_{15}H_{20}NO$, 230.153939; found 230.153750.



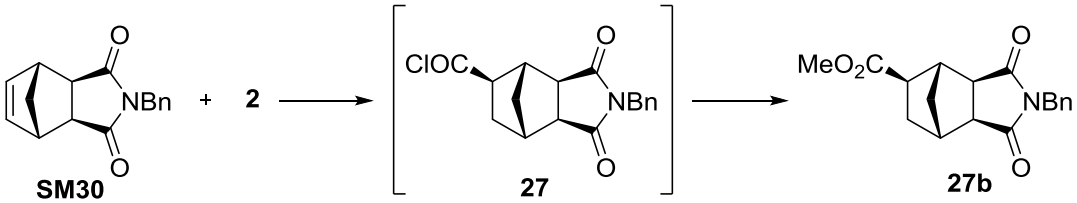
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM29** (23.0 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 5/1) to give **26b** (37.5 mg, yield: 66%).

IR (film) 3059, 2971, 2941, 2871, 1651, 1595, 1495 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.21 – 7.16 (m, 2H), 5.96 (dd, *J* = 5.7, 2.9 Hz, 1H), 5.84 (dd, *J* = 5.8, 3.1 Hz, 1H), 3.27 (s, 3H), 2.85 (d, *J* = 11.6 Hz, 2H), 2.04 (dd, *J* = 9.1, 4.7 Hz, 1H), 1.88 (d, *J* = 8.3 Hz, 1H), 1.82 (dt, *J* = 11.3, 4.2 Hz, 1H), 1.33 (d, *J* = 8.1 Hz, 1H), 0.99 (t, *J* = 9.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.28, 144.41, 138.01, 136.30, 129.74, 127.81, 127.72, 47.01, 46.80, 41.75, 41.29, 37.88, 32.05.

HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{15}H_{18}NO$, 228.138289; found 228.138060.

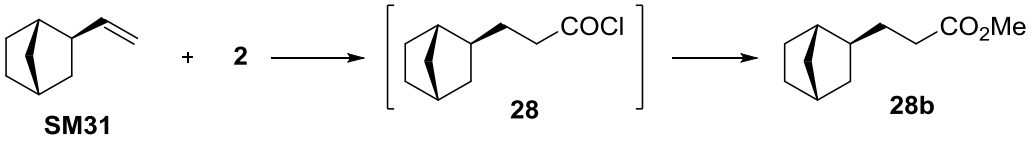


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM30**[10] (63.3 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 1/1) to give **27b** (75.2 mg, yield: 96%).

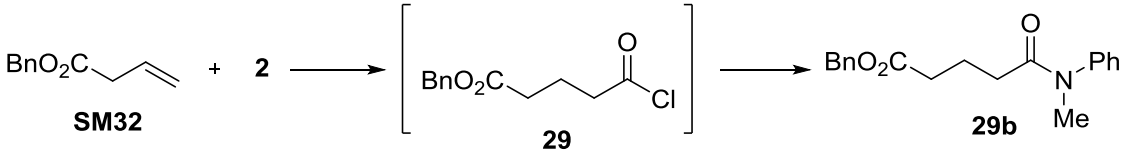
IR (film) 2952, 1770, 1731, 1693, 1171, 701 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dt, *J* = 8.2, 2.1 Hz, 2H), 7.32 – 7.26 (m, 3H), 4.61 (s, 2H), 3.67 (s, 3H), 2.98 (s, 1H), 2.75 (d, *J* = 4.1 Hz, 1H), 2.66 (q, *J* = 7.1 Hz, 2H), 2.47 – 2.41 (m, 1H), 2.02 (dt, *J* = 13.1, 4.8 Hz, 1H), 1.63 (ddd, *J* = 13.1, 9.1, 2.5 Hz, 1H), 1.40 (dt, *J* = 11.5, 1.5 Hz, 1H), 0.93 (ddt, *J* = 11.5, 2.6, 1.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.00, 177.57, 174.77, 135.96, 128.95, 128.81, 128.14, 52.22, 48.46, 48.28, 45.01, 43.70, 42.65, 39.72, 32.78, 31.51.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{18}H_{20}NO_4$, 314.138684; found 314.138280.

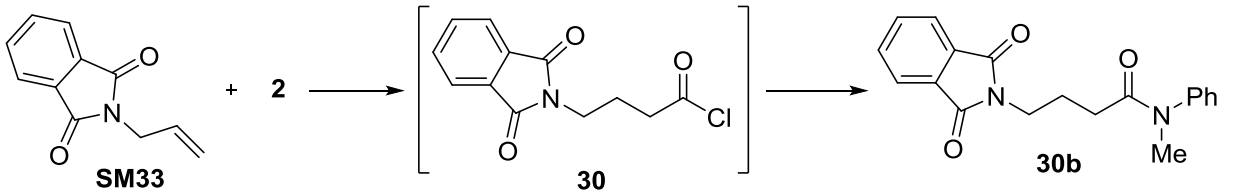


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM31** (30.6 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The regioselectivity of **28b** was determined by GC analysis (**l/b**: 85/15). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **28b** (linear product: 15.3 mg, isolated yield: 34%; branched product: 6% based on GC). Linear product: **IR** (film) 2947, 2869, 1738 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.27 (t, *J* = 7.7 Hz, 2H), 2.19 (s, 1H), 1.95 (d, *J* = 3.0 Hz, 1H), 1.65 – 1.58 (m, 1H), 1.52 – 1.39 (m, 4H), 1.38 – 1.32 (m, 1H), 1.31 – 1.27 (m, 1H), 1.17 – 1.09 (m, 2H), 1.09 – 1.05 (m, 1H), 1.02 – 0.97 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.60, 51.61, 41.95, 41.05, 38.02, 36.68, 35.38, 32.79, 31.97, 30.17, 28.86. **HRMS-ESI** (m/z): $[M+Na]^+$ calcd for $C_{11}H_{18}O_2Na$, 205.119899; found 205.119940.

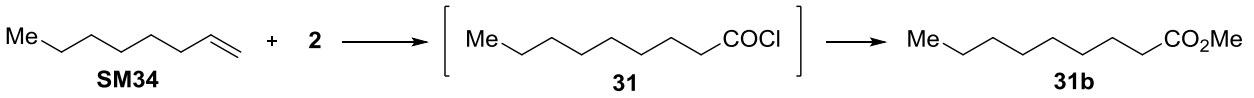


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM32**[11] (44.1 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **29b** was determined by GC analysis (**l/b**: 85/15). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 2/1) to give **29b** (linear product: 25.8 mg, isolated yield: 33%; branched product yield: 6% based on GC). Linear product: **IR** (film) 3034, 2920, 1732, 1652, 1595, 1496, 698 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 8H), 7.14 (d, *J* = 7.4 Hz, 2H), 5.05 (s, 2H), 3.25 (s, 3H), 2.34 (t, *J* = 7.3 Hz, 2H), 2.12 (t, *J* = 7.3 Hz, 2H), 1.92 (p, *J* = 7.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.13, 172.28,

144.12, 136.14, 129.95, 128.66, 128.29, 128.26, 127.95, 127.44, 66.23, 37.46, 33.67, 33.19, 20.82. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{19}H_{22}NO_3$, 312.159419; found 312.158990.

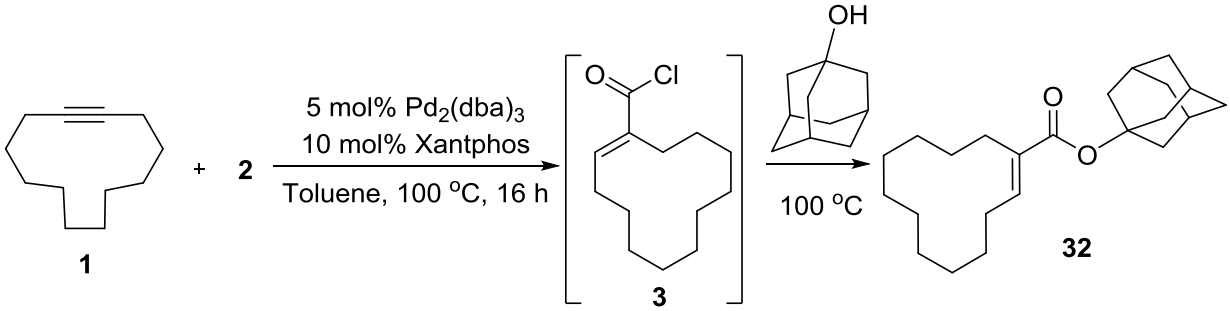


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM33** (46.8 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution *N*-methylaniline (27 uL, 0.25 mmol) was added. The mixture was stirred 10 mins at room temperature. The regioselectivity of **30b** was determined by GC analysis (**l/b**: 83/17). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 1/1) to give **30b** (linear product: 30.1 mg, isolated yield: 37%; branched product yield: 8% based on GC). Linear product: **IR** (film) 2937, 1770, 1705, 1651, 1595, 1393, 717, 700 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.34 – 7.29 (m, 2H), 7.23 – 7.18 (m, 1H), 7.18 – 7.14 (m, 2H), 3.63 (t, *J* = 6.7 Hz, 2H), 3.21 (s, 3H), 2.09 (t, *J* = 7.3 Hz, 2H), 1.95 (p, *J* = 7.0 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.81, 168.38, 144.06, 133.93, 132.23, 129.79, 127.81, 127.44, 123.21, 37.53, 37.37, 31.61, 24.46. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_{19}H_{19}N_2O_3$, 323.139018; found 323.138740.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM34** (28.1 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). ^{n}Dodecane (50 μL) was added to the solution as an internal standard. The mixture was stirred 10 mins at room temperature. The regioselectivity of **31b** was determined by GC analysis (**l/b**: 90/10). The yield of **31b** was measured by GC analysis (GC yield: 28%).

6. One-pot synthesis of carbonyl-containing products



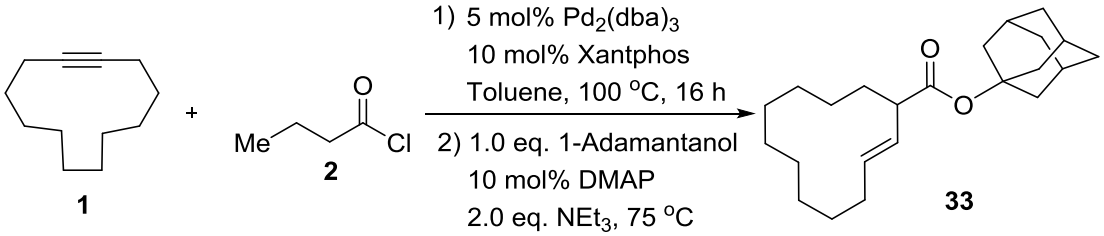
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature and 1-Adamantanol (38.1 mg, 0.25 mmol) was added. The mixture was stirred overnight at 100 °C. The reaction was cooled down to room temperature. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **32** (68.9 mg, yield: 80%).

IR (film) 2910, 2852, 1725, 1457, 1159, 1056 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.64 (t, *J* = 8.2 Hz, 1H), 2.30 (t, *J* = 6.8 Hz, 2H), 2.20 – 2.14 (m, 11H), 1.71 – 1.63 (m, 6H), 1.59 – 1.50 (m, 4H), 1.42 – 1.27 (m, 10H), 1.26 – 1.21 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.51, 141.77, 133.94, 80.05, 41.58, 36.46, 30.99, 26.62, 26.22, 25.86, 25.17, 25.09, 24.95, 23.85, 23.76, 23.01, 22.32.

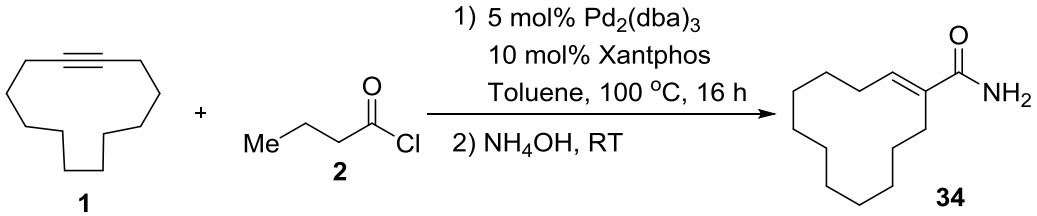
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{23}H_{37}O_2$, 345.278805; found 345.278440.



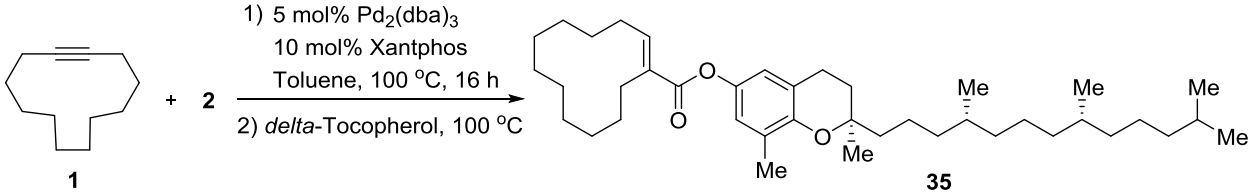
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. To the solution 1-Adamantanol (38.1 mg, 0.25 mmol), DMAP (3.1 mg, 0.025 mmol) and NEt_3 (70 uL, 0.5 mmol) were added sequentially. The mixture was stirred overnight at 75 °C. The reaction was cooled down to room temperature. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **33** (60.3 mg, yield: 70%).

IR (film) 2909, 2851, 1702, 1639, 1467, 1058 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52 – 5.38 (m, 2H), 2.83 (ddd, *J* = 10.6, 8.9, 3.6 Hz, 1H), 2.24 – 2.18 (m, 1H), 2.17 – 2.13 (m, 3H), 2.09 (d, *J* = 3.0 Hz, 5H), 2.02 – 1.93 (m, 1H), 1.80 – 1.72 (m, 1H), 1.69 – 1.61 (m, 6H), 1.61 – 1.40 (m, 4H), 1.37 – 1.14 (m, 12H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 174.35, 133.85, 128.93, 80.28, 50.53, 41.46, 36.39, 32.29, 30.98, 30.68, 26.31, 25.80, 24.94, 24.86, 24.82, 24.69, 24.08.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{23}H_{37}O_2$, 345.278805; found 345.278410.

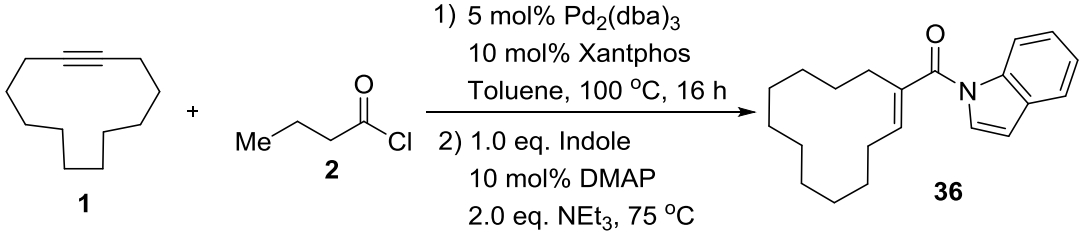


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature and 24% aqueous ammonium hydroxide solution (73 uL, 0.5 mmol) was added. The mixture was stirred 2 hours at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (2.5 mL) and the mixture was extracted with methyl *tert*-butyl ether (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 1/5) to give **34** (34.5 mg, yield: 66%).
IR (film) 3422, 3367, 3169, 2925, 2854, 1634, 1656, 1607, 1407, 613 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.30 (t, *J* = 8.0 Hz, 1H), 5.47 (br, 2H), 2.39 (t, *J* = 6.8 Hz, 2H), 2.21 (q, *J* = 7.4 Hz, 2H), 1.59 – 1.51 (m, 4H), 1.44 – 1.24 (m, 12H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.61, 137.34, 135.77, 26.42, 26.17, 25.53, 25.07, 25.00, 24.87, 23.92, 23.92, 22.79, 22.29.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{13}H_{24}NO$, 210.185239; found 210.185120.

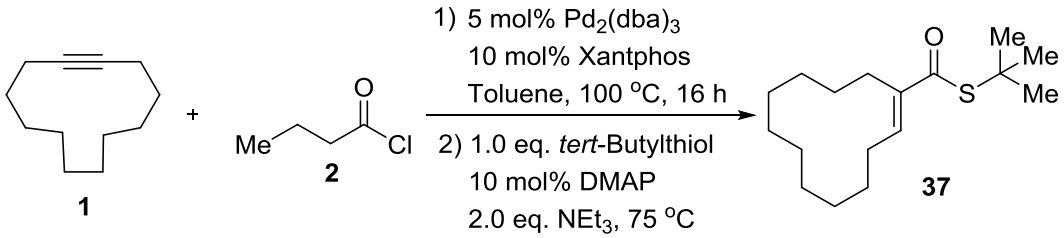


A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature and *delta*-Tocopherol (100.7 mg, 0.25 mmol) was added. The mixture was stirred overnight at 100 °C. The reaction was cooled down to room temperature. The mixture was concentrated under reduced

pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **35** (119.0 mg, yield: 80%).
IR (film) 2925, 2859, 1727, 1639, 1468, 1151, 732 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (t, *J* = 8.2 Hz, 1H), 6.67 (dd, *J* = 25.3, 2.8 Hz, 2H), 2.76 – 2.68 (m, 2H), 2.45 (t, *J* = 6.7 Hz, 2H), 2.28 (q, *J* = 7.4 Hz, 2H), 2.14 (s, 3H), 1.84 – 1.70 (m, 2H), 1.69 – 1.63 (m, 2H), 1.62 – 1.49 (m, 5H), 1.47 – 1.02 (m, 33H), 0.88 – 0.83 (m, 12H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 167.47, 149.69, 144.68, 142.99, 132.13, 127.37, 121.43, 121.06, 119.31, 76.20, 40.23, 39.53, 37.60, 37.59, 37.44, 32.96, 32.85, 31.23, 28.14, 26.56, 26.13, 25.23, 25.03, 25.02, 24.96, 24.61, 24.38, 23.87, 23.79, 23.05, 22.88, 22.79, 22.62, 22.32, 21.13, 19.91, 19.81, 16.26.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{40}H_{67}O_3$, 595.508470; found 595.508160.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. To the solution Indole (29.3 mg, 0.25 mmol), DMAP (3.1 mg, 0.025 mmol) and NEt_3 (70 uL, 0.5 mmol) were added sequentially. The mixture was stirred overnight at 75 °C. The reaction was cooled down to room temperature. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 5/1) to give **36** (51.8 mg, yield: 67%).
IR (film) 2926, 2854, 1681, 1605, 1584, 1532, 1327, 749, 724 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.3 Hz, 1H), 7.58 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.46 (d, *J* = 3.7 Hz, 1H), 7.35 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.60 (dd, *J* = 3.7, 0.7 Hz, 1H), 5.96 (t, *J* = 8.0 Hz, 1H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.33 (q, *J* = 7.2 Hz, 2H), 1.63 (dt, *J* = 11.4, 5.6 Hz, 2H), 1.58 – 1.52 (m, 2H), 1.50 – 1.39 (m, 10H), 1.37 – 1.30 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 170.69, 139.40, 136.64, 135.97, 130.97, 127.28, 124.85, 123.74, 120.86, 116.60, 108.02, 26.45, 25.51, 25.48, 25.02, 24.92, 24.69, 24.30, 22.46, 22.34.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{21}H_{28}NO$, 310.216538; found 310.216260.



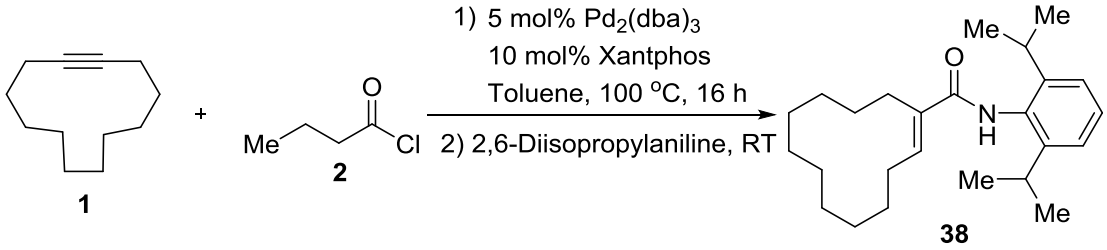
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature. To the solution *tert*-Butylthiol (22.5 mg, 0.25 mmol), DMAP (3.1 mg, 0.025 mmol) and NEt_3 (70 uL, 0.5 mmol) were added sequentially. The mixture was stirred overnight at 75 ^oC. The reaction was cooled down to room temperature. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **37** (45.9 mg, yield: 65%).

IR (film) 2924, 2859, 1739, 1651 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (t, *J* = 8.0 Hz, 1H), 2.38 (t, *J* = 6.8 Hz, 2H), 2.21 (q, *J* = 7.3 Hz, 2H), 1.59 – 1.52 (m, 4H), 1.48 (s, 9H), 1.42 – 1.31 (m, 10H), 1.27 – 1.20 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 195.82, 142.16, 140.01, 47.51, 30.08, 26.29, 26.19, 25.82, 25.25, 25.05, 25.03, 23.98, 23.88, 22.94, 22.28.

HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{17}H_{31}OS$, 283.209013; found 283.208870.



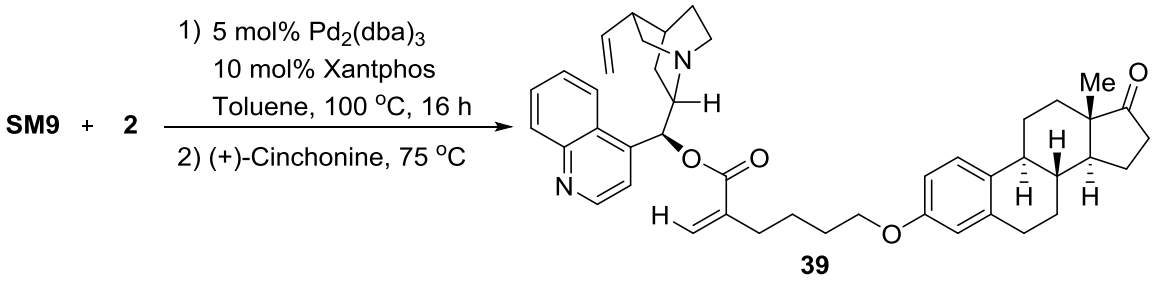
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and 2,6-Diisopropylaniline (44.3 mg, 0.25 mmol) was added. The mixture was stirred overnight at room temperature. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 5/1) to give **38** (53.6 mg, yield: 58%).

IR (film) 3288, 2963, 2925, 2866, 1738, 1654, 1617, 1496, 1468, 737 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.18 (d, *J* = 7.7 Hz, 2H), 6.89 (br, 1H), 6.30 (t, *J* = 7.9 Hz, 1H), 3.08 (hept, *J* = 6.9 Hz, 2H), 2.53 (t, *J* = 6.7 Hz, 2H), 2.29 (q, *J* = 7.2 Hz, 2H), 1.66 – 1.56 (m, 4H), 1.50 – 1.38 (m, 8H), 1.38 – 1.31 (m, 4H), 1.22 (s, 6H), 1.21 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.51, 146.44, 138.12, 135.23, 131.44, 128.37, 123.51, 28.97, 26.68, 25.97, 25.44, 25.14, 25.00, 24.84, 24.22, 23.77, 22.69, 22.36.

HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{25}H_{40}NO$, 370.310439; found 370.310230.



39

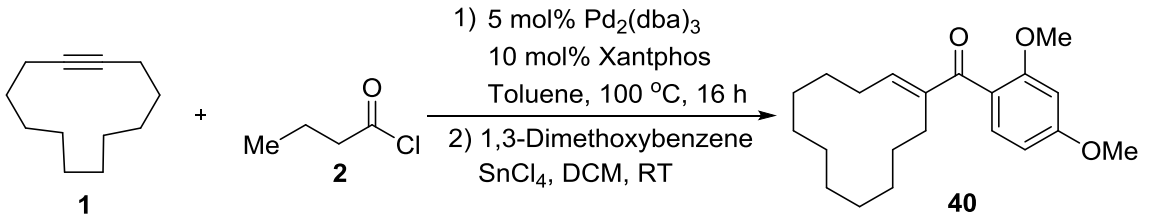
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM9** (87.6 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** was distilled off under vacuum, then anhydrous toluene (1 mL) was added. To the solution (+)-Cinchonine (73.6 mg, 0.25 mmol) was added. The mixture was stirred overnight at 75 °C. The reaction was cooled down to room temperature and was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (ethyl acetate/ methanol: 5/1) to give **39** (92.5 mg, yield: 55%).

IR (film) 2936, 2871, 1735, 1609, 1593, 1571, 1264, 733, 702 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.5 Hz, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 4.5 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.83 – 6.53 (m, 3H), 6.28 (s, 1H), 6.00 (ddd, *J* = 17.3, 10.4, 7.1 Hz, 1H), 5.65 (s, 1H), 5.11 (dd, *J* = 19.5, 8.4 Hz, 2H), 3.93 – 3.89 (m, 1H), 3.36 (q, *J* = 8.5 Hz, 1H), 3.03 – 2.67 (m, 6H), 2.50 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.42 – 2.21 (m, 5H), 2.14 (dt, *J* = 18.8, 8.9 Hz, 1H), 2.08 – 1.89 (m, 4H), 1.88 – 1.83 (m, 1H), 1.77 (dt, *J* = 14.4, 6.4 Hz, 2H), 1.67 – 1.46 (m, 10H), 1.46 – 1.38 (m, 2H), 0.90 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 221.03, 157.13, 150.03, 148.71, 140.36, 137.85, 132.10, 130.59, 130.55, 129.39, 127.14, 126.44, 126.08, 125.83, 123.53, 118.47, 115.42, 114.64, 114.60, 112.20, 112.18, 67.53, 59.88, 59.66, 50.55, 49.85, 49.15, 48.14, 45.92, 44.11, 39.56, 38.52, 36.01, 32.13, 31.72, 29.83, 29.79, 29.01, 27.80, 26.69, 26.06, 25.06, 21.72, 13.99.

HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{44}H_{53}N_2O_4$, 673.399982; found 673.400600.



1 **2** **40**

A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and

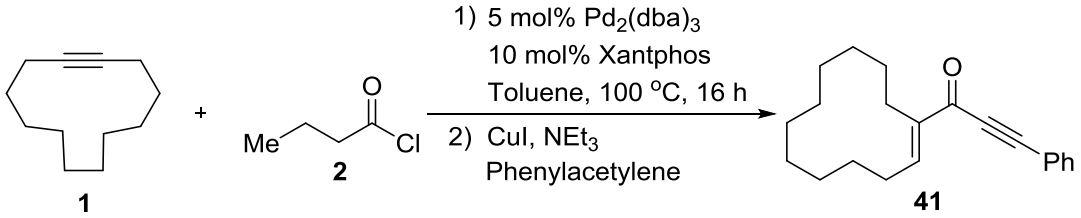
toluene were distilled off under vacuum, then anhydrous CH_2Cl_2 (1 mL) was added. To the solution 1,3-Dimethoxybenzene (34.5 mg, 0.25 mmol) and $SnCl_4$ (29 uL, 0.25 mmol) were added. The mixture was stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 5/1) to give **40** (58.7 mg, yield: 71%).[12]

IR (film) 2925, 2851, 1635, 1602, 1577, 1501 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 6.16 (t, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 2.50 (t, *J* = 6.8 Hz, 2H), 2.25 (q, *J* = 7.4 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.52 – 1.37 (m, 10H), 1.36 – 1.29 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.54, 162.50, 158.89, 146.18, 142.92, 131.18, 123.16, 104.32, 98.72, 55.58, 55.53, 26.30, 26.20, 25.86, 25.13, 25.08, 25.02, 24.11, 22.95, 22.93, 22.37.

HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{21}H_{31}O_3$, 331.226770; found 331.226470.



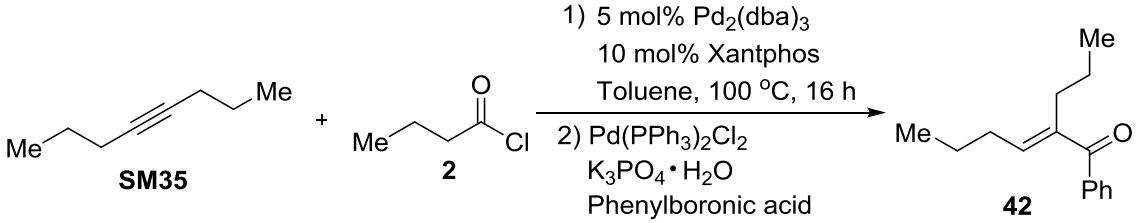
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. To the solution CuI (4 mol%, 0.01 mmol, 1.9 mg), NEt_3 (70 uL, 0.5 mmol) and Phenylacetylene (27.5 uL, 0.25 mmol) were added sequentially. The mixture was stirred 3 hours at room temperature. After that time, the mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **41** (52.3 mg, yield: 71%).[13]

IR (film) 2926, 2858, 2201, 1717, 1624, 1285, 756, 689 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.40 – 7.35 (m, 2H), 7.25 (t, *J* = 8.1 Hz, 1H), 2.43 (t, *J* = 6.8 Hz, 2H), 2.38 (q, *J* = 7.7 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.62 – 1.56 (m, 2H), 1.47 – 1.35 (m, 10H), 1.27 – 1.21 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.76, 151.21, 142.77, 132.82, 130.33, 128.69, 120.79, 90.85, 86.68, 26.80, 26.26, 26.10, 25.36, 25.08, 23.65, 23.13, 22.54, 22.24.

HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{21}H_{27}O$, 295.205640; found 295.205520.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was

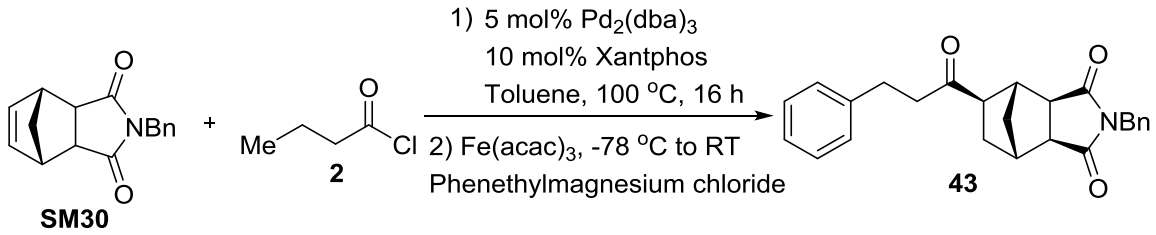
sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM35** (27.6 mg, 0.25 mmol), **2** (26 uL, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^{o}C) stir plate and the reaction mixture was stirred at 100 ^{o}C for 16 hours. After that time, the reaction was cooled down to room temperature. To the solution $Pd(PPh_3)_2Cl_2$ (2 mol%, 0.005 mmol, 3.5 mg), K_3PO_4 monohydrate (69.1 mg, 0.3 mmol, 1.2 eq.) and Phenylboronic acid (36.6 mg, 0.3 mmol, 1.2 eq.) were added sequentially. The mixture was stirred 4 hours at 80 ^{o}C. The reaction was cooled down to room temperature and was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **42** (24.9 mg, yield: 46%).[14]

IR (film) 2960, 2932, 2872, 1725, 1648, 1598, 1578, 702 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.52 – 7.48 (m, 1H), 7.43 – 7.38 (m, 2H), 6.20 (t, *J* = 7.4 Hz, 1H), 2.49 – 2.44 (m, 2H), 2.27 (q, *J* = 7.4 Hz, 2H), 1.52 – 1.41 (m, 4H), 0.95 (td, *J* = 7.4, 5.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.19, 145.86, 141.39, 139.25, 131.54, 129.51, 128.15, 31.03, 28.85, 22.38, 22.36, 14.32, 14.13.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{20}ONa$, 239.140634; found 239.140420.



A 15 mL Schlenk tube equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed Schlenk tube was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM30**[10] (63.3 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the Schlenk tube was sealed. The Schlenk tube was taken out of the glovebox and heated at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum, then anhydrous THF (1 mL) was added. To the solution $Fe(acac)_3$ (2.6 mg, 0.0075 mmol, 3 mol%) and Phenethylmagnesium chloride (1 M in THF, 250 uL, 0.25 mmol) were added at -78 °C under argon. After being stirred for 15 mins at that temperature, the reaction was quenched with saturated aqueous NH_4Cl (2.5 mL) and the mixture was extracted with methyl *tert*-butyl ether (3 × 5 mL) after reaching ambient temperature. The combined organic layers were dried over anhydrous Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography on silica (*n*-pentane/methyl *tert*-butyl ether: 2/1) providing **43** (67.8 mg, 70%).[15]

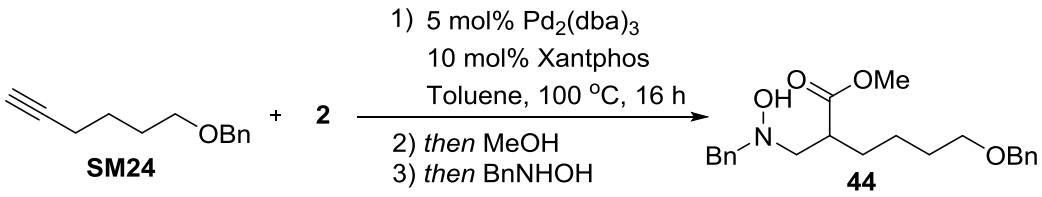
IR (film) 3029, 2947, 1769, 1693, 1603, 1585 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 7H), 7.18 (dd, *J* = 18.1, 7.3 Hz, 3H), 4.60 (s, 2H), 2.92 – 2.80 (m, 4H), 2.80 – 2.72 (m, 1H), 2.71 (d, *J* = 4.1 Hz, 1H), 2.67 – 2.61 (m, 2H), 2.47 (dd, *J* = 8.6, 5.3 Hz, 1H), 1.98 (dt, *J* = 12.8, 4.8 Hz, 1H), 1.44 (ddd, *J* = 12.2, 8.8, 2.5 Hz, 1H), 1.19 (t, *J* = 5.7 Hz, 1H), 0.82 (d, *J* = 11.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 209.02, 177.94, 177.65, 140.97, 135.93, 128.95, 128.81, 128.68, 128.45, 128.15, 126.37, 52.47, 48.77, 48.53, 43.62, 42.79, 42.63, 39.73, 31.03, 31.01, 30.04.

HRMS-EI (m/z): $[M+H]^+$ calcd for $C_{25}H_{26}NO_3$, 388.190719; found 388.190160.

7. Synthetic applications and labelling experiments



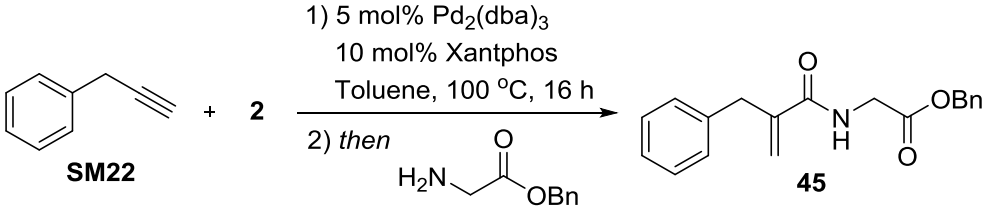
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM24** (47.1 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. To the solution were directly added triethylamine (0.31 mL, 2.2 mmol, 9.0 eq.) and *N*-Benzylhydroxylamine hydrochloride (0.20 g, 1.2 mmol, 5.0 eq.). The solution was stirred 24 hours at room temperature. Distilled water and MTBE were added and the organic layer was taken out, dried, filtered and concentrated to recover an orange crude oil, which was further purified by SiO_2 gel column chromatography (*n*-pentane/methyl *tert*-butyl ether: 5/1) which afforded **44** as a clear yellow oil (31 mg, yield: 33%).

IR (film) 3030, 2928, 2859, 1776, 1733, 1622, 1096, 735, 697 cm^{-1}.

^{1}H NMR δ 7.36 – 7.26 (m, 10H), 5.01 (s, 1H), 4.49 (s, 2H), 3.87 – 3.75 (m, 2H), 3.68 (s, 3H), 3.45 (t, *J* = 6.5 Hz, 2H), 2.98 (dd, *J* = 11.9, 8.9 Hz, 1H), 2.88 – 2.74 (m, 2H), 1.67 – 1.57 (m, 3H), 1.56 – 1.46 (m, 1H), 1.43 – 1.32 (m, 2H).

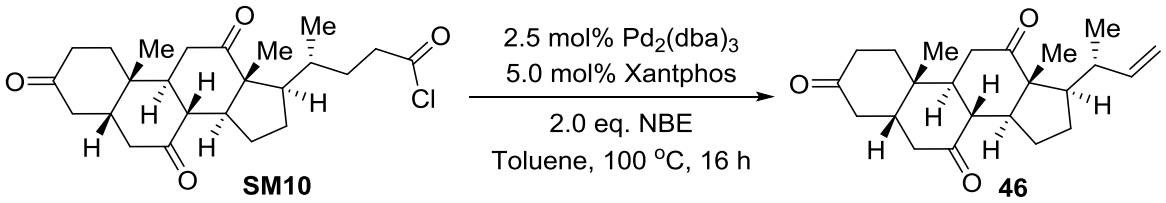
^{13}C NMR (125 MHz, $CDCl_3$) δ 176.18, 138.70, 137.52, 129.39, 128.48, 128.42, 127.76, 127.64, 127.49, 73.02, 70.17, 65.15, 61.91, 51.68, 44.60, 30.22, 29.70, 24.21.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{22}H_{29}O_4N_1Na$, 394.198878; found 394.198520.



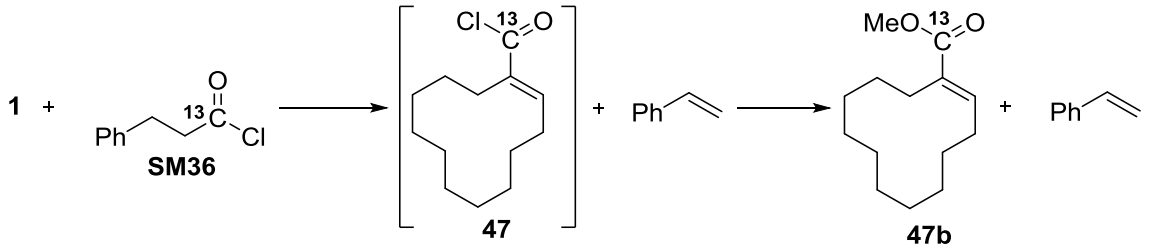
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM22** (29.0 mg, 0.25 mmol), **2** (104 uL, 1.0 mmol, 4.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature. The **2** and toluene were distilled off under vacuum. Anhydrous CH_2Cl_2 (1 mL) was added, followed by dropwise addition of trimethylamine (0.14 mL, 1.0 mmol, 4.0 equiv.) and glycine benzyl ester hydrochloride (202 mg, 1.0 mmol, 4.0 equiv.). The reaction was stirred 14 hours at room temperature. The reaction was diluted with MTBE and washed with saturated $NaHCO_3$ solution. The organic layer was dried, filtered and concentrated under reduced pressure to recover

an orange crude oil, which was further purified by SiO_2 gel column chromatography (*n*-pentane/methyl *tert*-butyl ether: 2/1) which afforded **45** as a transparent colorless oil (30 mg, yield: 39%).
IR (film) 3331, 3030, 2922, 2851, 1746, 1657, 1619, 1174, 730, 697 cm^{-1}.
^{1}H NMR δ 7.40 – 7.32 (m, 5H), 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 6.26 (s, 1H), 5.84 (s, 1H), 5.29 (s, 1H), 5.18 (s, 2H), 4.10 (d, *J* = 5.1 Hz, 2H), 3.67 (s, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.89, 168.16, 143.76, 138.24, 135.23, 129.09, 128.80, 128.77, 128.72, 128.52, 126.74, 120.83, 67.41, 41.76, 38.57.
HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{19}O_3N_1Na$, 332.125713; found 332.125340.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (2.5 mol%, 0.00625 mmol, 5.7 mg) and Xantphos (5 mol%, 0.0125 mmol, 7.2 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **SM10** (105.2 mg, 0.25 mmol), **SM28** Norbornene (47.1 mg, 0.5 mmol, 2.0 eq.) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 °C) stir plate and the reaction mixture was stirred at 100 °C for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). The mixture was stirred 10 mins at room temperature. The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 5/1) to give **46** (78.4 mg, yield: 88%).
IR (film) 2969, 2873, 1702, 1639, 908 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (ddd, *J* = 17.1, 10.2, 8.3 Hz, 1H), 4.95 (ddd, *J* = 17.1, 1.9, 0.8 Hz, 1H), 4.88 (dd, *J* = 10.2, 2.0 Hz, 1H), 2.95 – 2.87 (m, 2H), 2.84 (t, *J* = 12.8 Hz, 1H), 2.38 – 2.31 (m, 2H), 2.30 – 2.23 (m, 3H), 2.22 – 2.19 (m, 1H), 2.17 – 2.12 (m, 2H), 2.09 (q, *J* = 9.3 Hz, 1H), 2.03 (dd, *J* = 13.2, 2.3 Hz, 2H), 2.00 – 1.94 (m, 1H), 1.90 – 1.80 (m, 2H), 1.62 (td, *J* = 14.3, 4.9 Hz, 1H), 1.40 (s, 3H), 1.36 – 1.27 (m, 2H), 1.08 (s, 3H), 0.98 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 211.98, 209.14, 208.87, 144.22, 112.90, 56.83, 51.65, 49.07, 47.02, 45.51, 45.36, 45.14, 42.95, 41.52, 38.74, 36.66, 36.16, 35.44, 27.49, 25.18, 22.07, 20.93, 12.31.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{23}H_{33}O_3$, 357.242420; found 357.242170.

8. Labelling studies



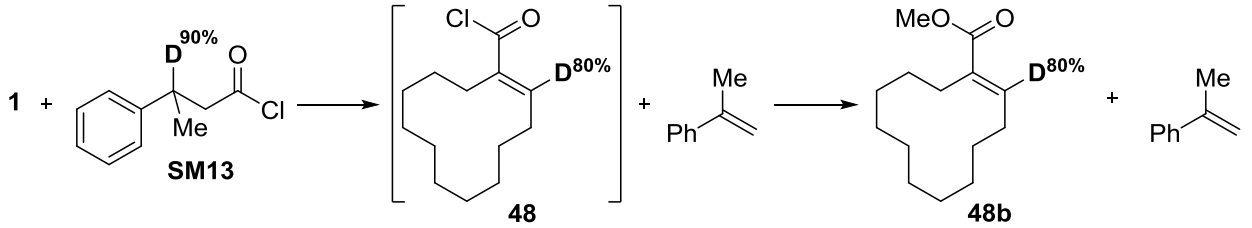
A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **SM36**[16] (42.4, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). ^{n}Dodecane (50 μL) was added to the solution as an internal standard. The mixture was stirred 10 mins at room temperature. The yield of styrene was determined by GC analysis (GC yield: 88%). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **47b** (42.3 mg, yield: 75%).

IR (film) 2928, 2859, 1738, 1674 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (q, *J* = 8.0 Hz, 1H), 3.73 (d, *J* = 3.7 Hz, 3H), 2.36 (q, *J* = 6.4 Hz, 2H), 2.21 (q, *J* = 7.6 Hz, 2H), 1.59 – 1.52 (m, 4H), 1.43 – 1.30 (m, 10H), 1.26 – 1.20 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.82, 143.26 (d, *J* = 2.1 Hz), 132.22 (d, *J* = 69.3 Hz), 51.67 (d, *J* = 2.6 Hz), 26.55, 26.12, 25.90 (d, *J* = 5.6 Hz), 25.26, 25.01, 24.93, 23.72, 23.69, 23.05, 22.25.

HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{13}{}^{13}CH_{25}O_2$, 226.18826; found 226.18834.



A 15 mL screw-cap vial equipped with a stirring bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.0125 mmol, 11.4 mg) and Xantphos (10 mol%, 0.025 mmol, 14.4 mg). The unsealed vial was sequentially evacuated and flushed 3 times with argon in the antechamber of the glovebox. In the glovebox, anhydrous toluene (0.5 mL) was added, followed by **1** (41.1 mg, 0.25 mmol), **SM13** (45.9, 0.25 mmol) and the vial was sealed. The vial was taken out of the glovebox, transfer to a prestirred (500 rpm) and preheated (100 ^oC) stir plate and the reaction mixture was stirred at 100 ^oC for 16 hours. After that time, the reaction was cooled down to room temperature and quenched with MeOH (2 mL). ^{n}Dodecane (50 μL) was added to the solution as an internal standard. The mixture was stirred 10 mins at room temperature. The yield of alpha-methylstyrene was determined by GC analysis (GC yield: 82%). The reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (*n*-pentane/methyl *tert*-butyl ether: 20/1) to give **48b** (42.8 mg, yield: 76%, deuteration level: 80%).

IR (film) 2927, 2858, 1714, 1628 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (t, *J* = 7.5 Hz, 0.2H), 3.73 (s, 3H), 2.36 (t, *J* = 6.8 Hz, 2H), 2.21 (t, *J* = 7.0 Hz, 2H), 1.59 – 1.53 (m, 4H), 1.43 – 1.30 (m, 10H), 1.26 – 1.20 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.83, 143.27, 132.14, 51.67, 26.55, 26.11, 25.80, 25.26, 25.02, 24.93, 23.70, 23.67, 23.05, 22.25.
HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{14}H_{24}DO_2$, 226.191182; found 226.191190.

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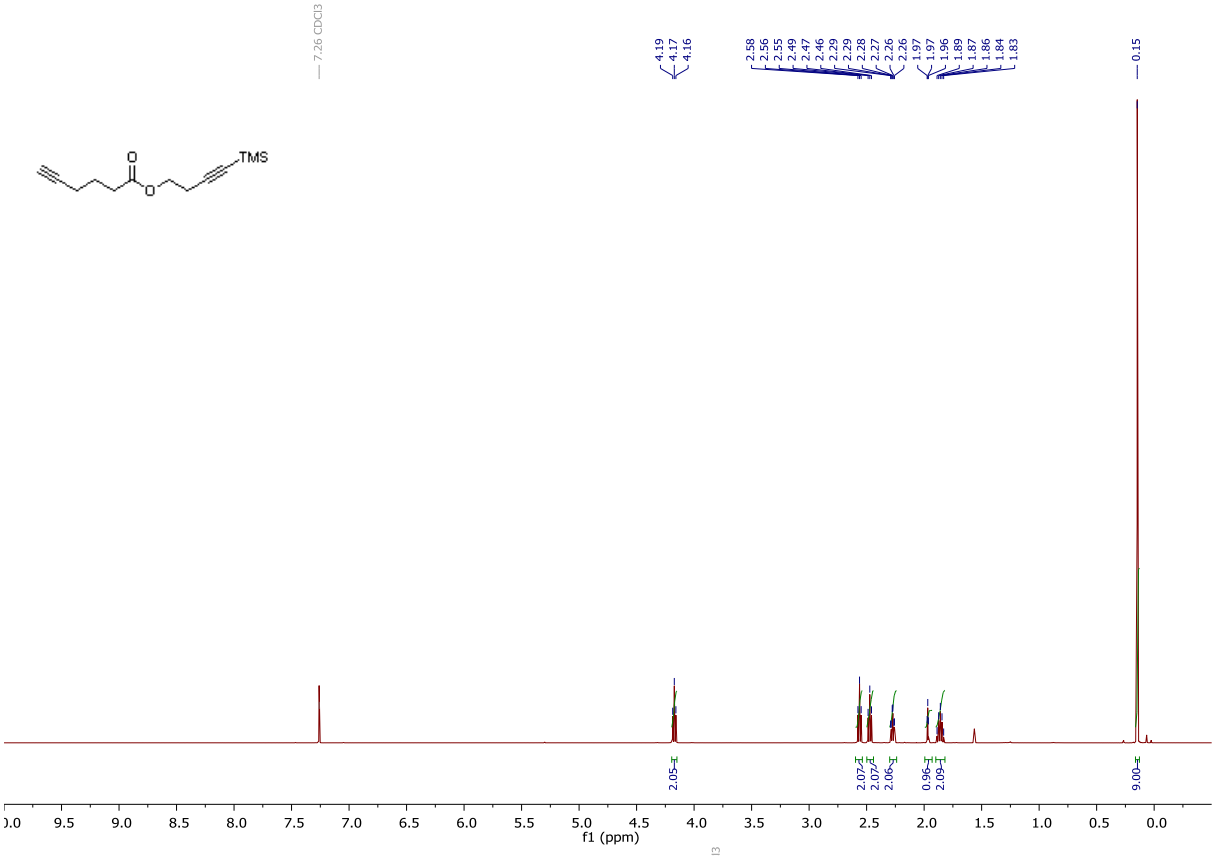
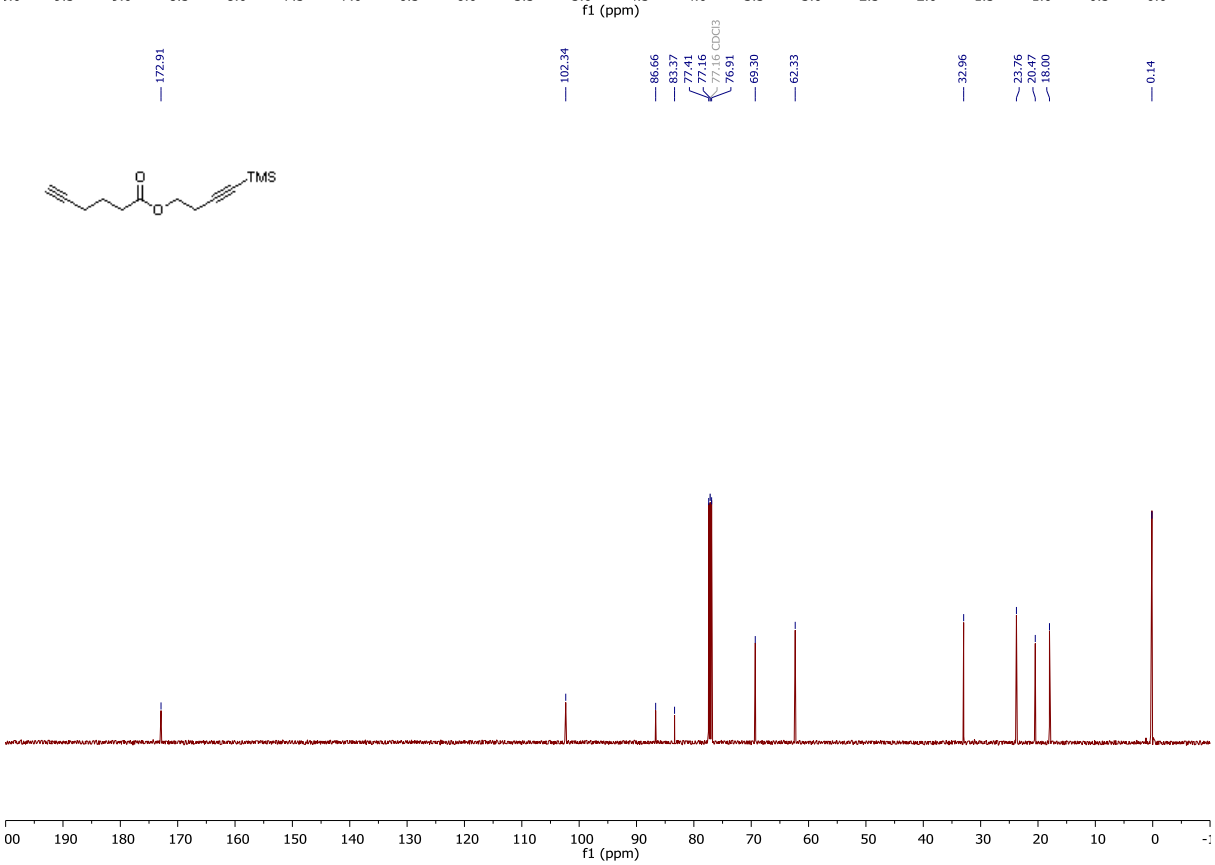
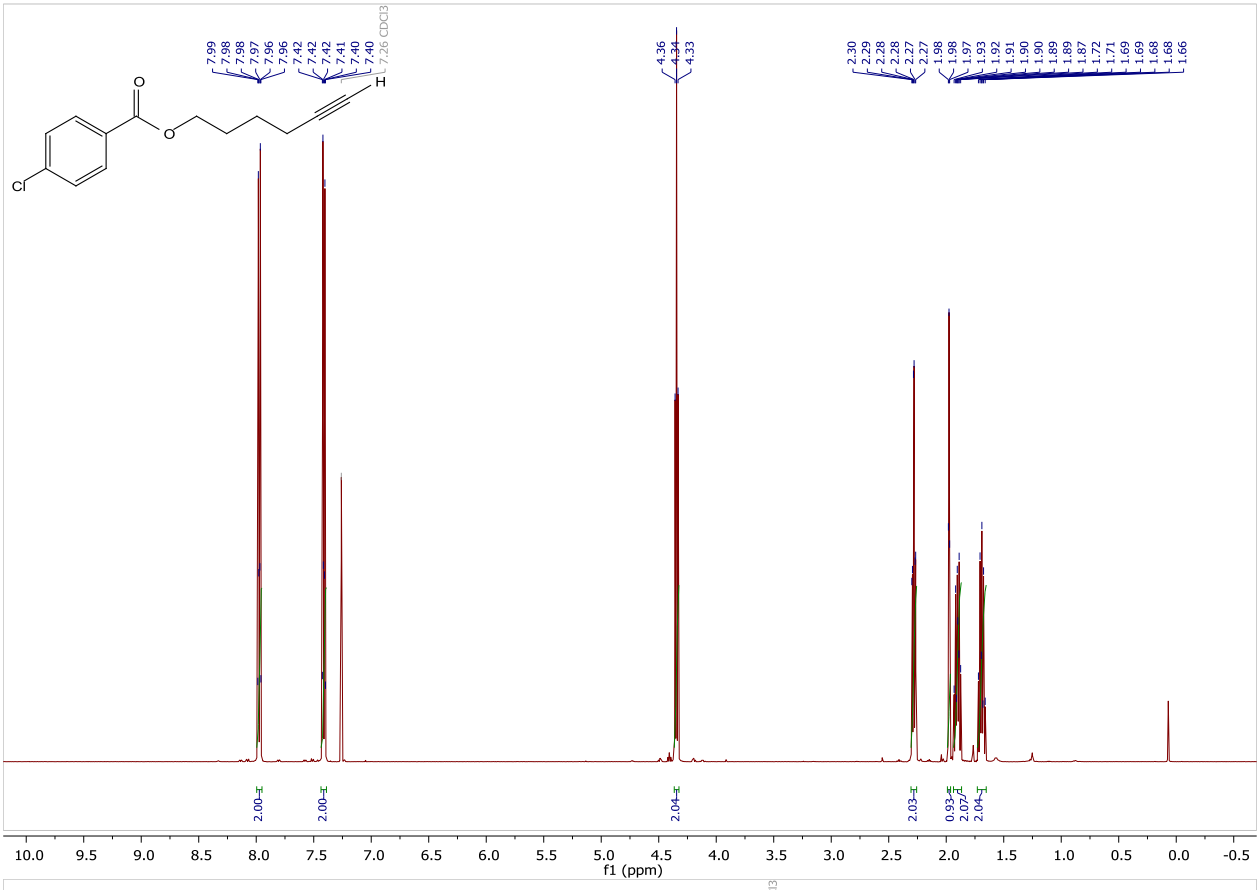
10. NMR Spectra



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7.98
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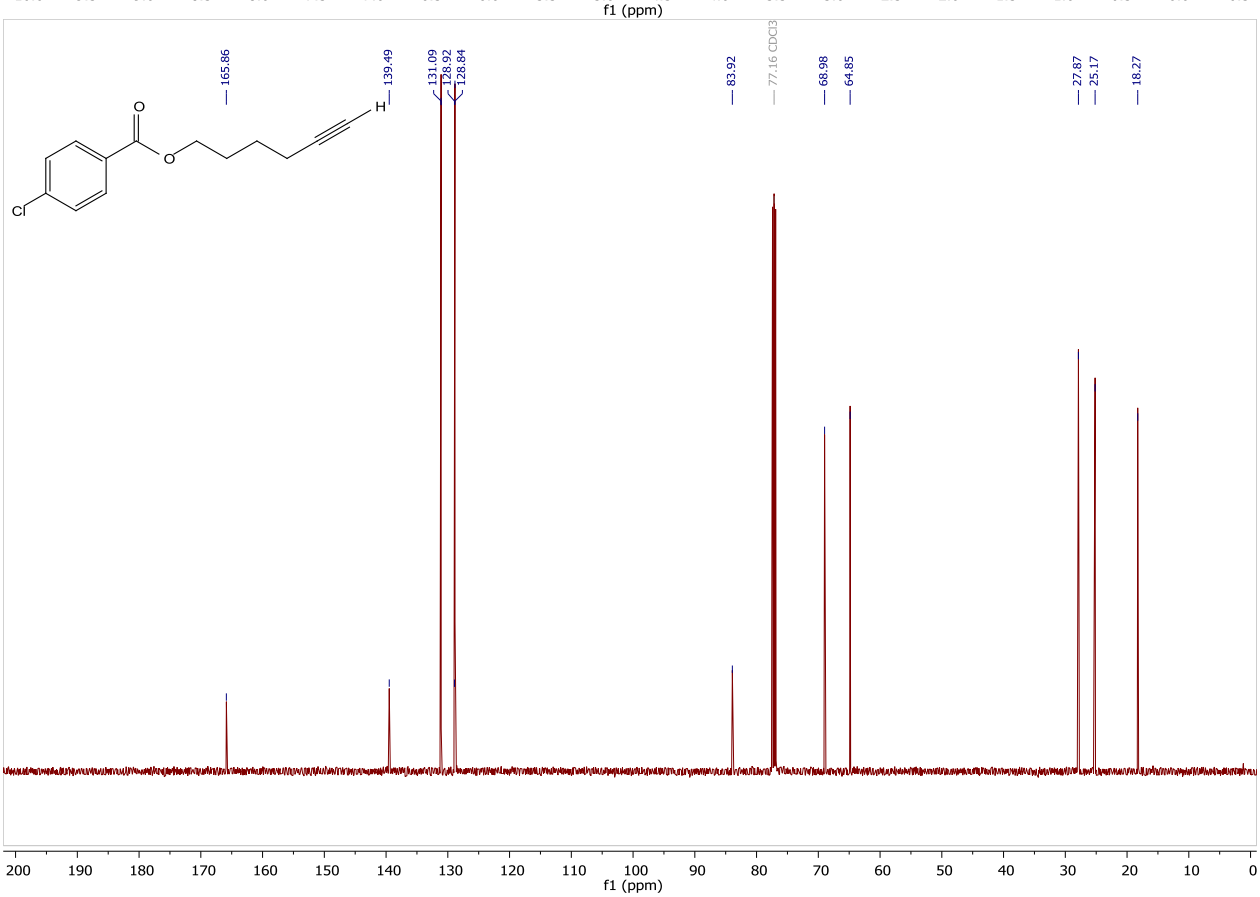
7.97
7.96
7.96
7.42
7.42
7.42
7.41
7.40
7.40
7.26 CDCl3
4.36
4.34
4.33
2.30
2.29
2.28
2.28
2.27
2.27
1.98
1.98
1.97
1.93
1.92
1.91
1.90
1.90
1.89
1.89
1.87
1.72
1.71
1.69
1.69
1.68
1.68
1.66
O
O
Cl
H
2.00
2.00
2.04
2.03
0.93
2.07
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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139.49
131.09
128.92
128.84
83.92
77.16 CDCl3
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18.27
O
O
Cl
H
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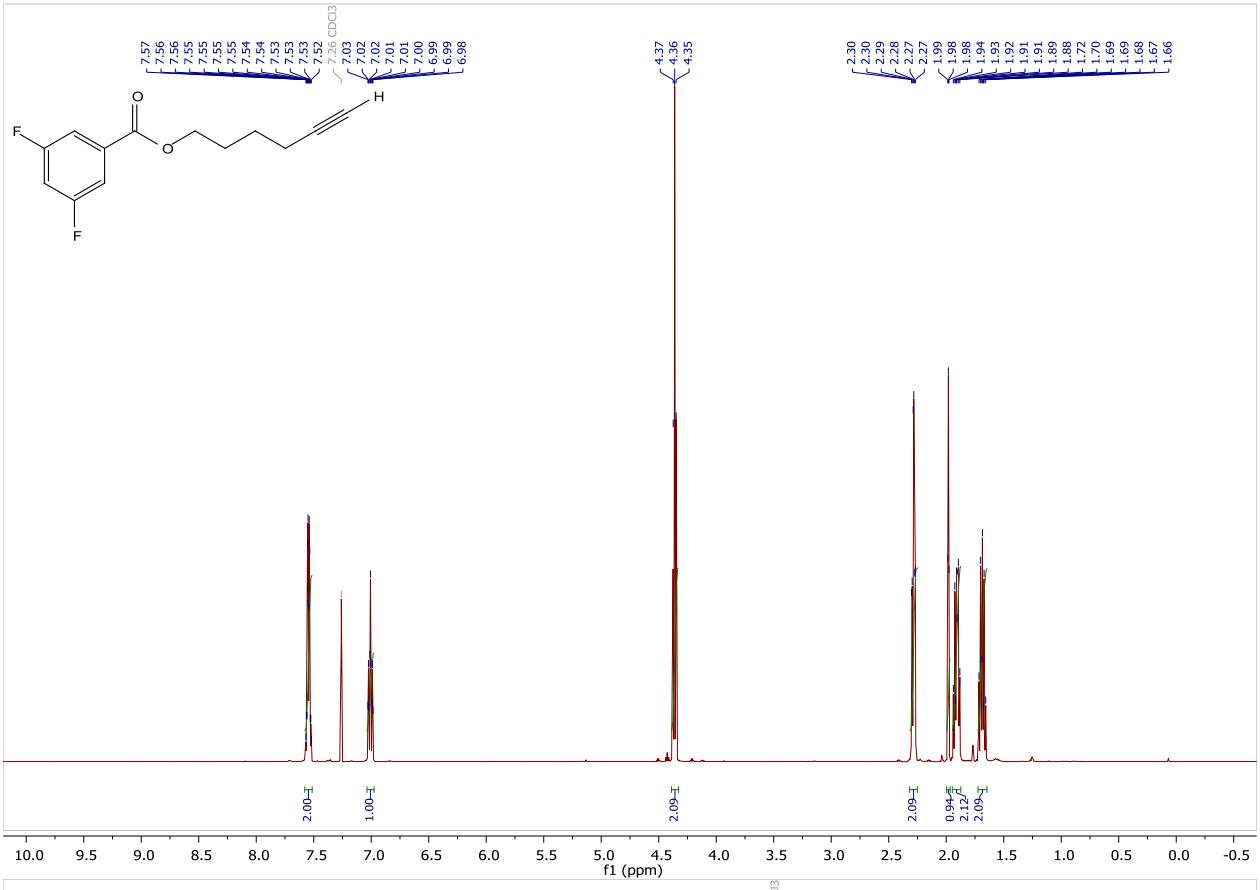
f1 (ppm)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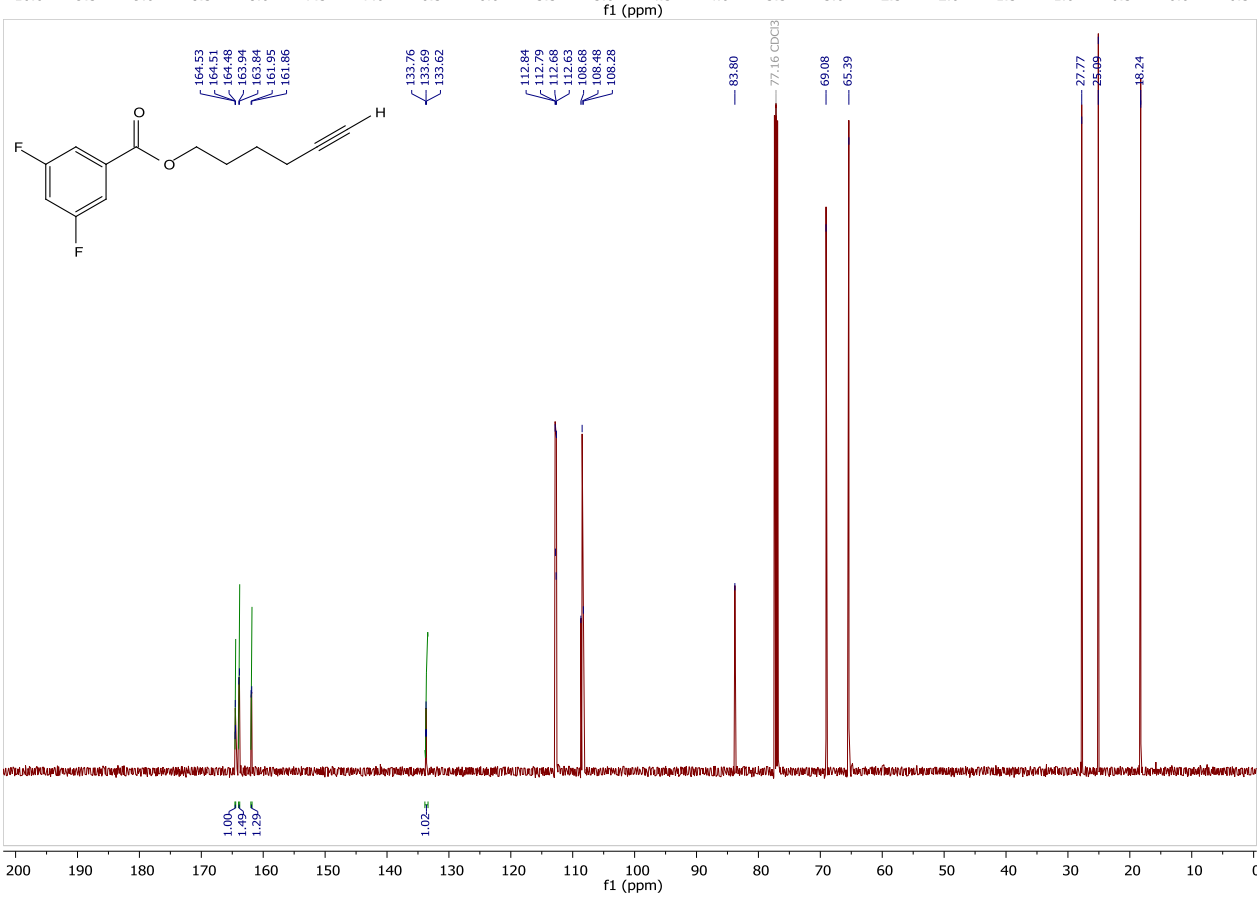
7.26 CDCl3
7.03 7.02 7.02 7.01 7.01 7.00 6.99 6.99 6.98
4.37 4.36 4.35
2.30 2.30 2.29 2.28 2.27 2.27 1.99 1.98 1.98 1.94 1.93 1.92 1.91 1.91 1.89 1.88 1.72 1.70 1.69 1.69 1.68 1.67 1.66
O
H
F
O
F
2.00 1.00 2.09 2.09 0.94 2.12 2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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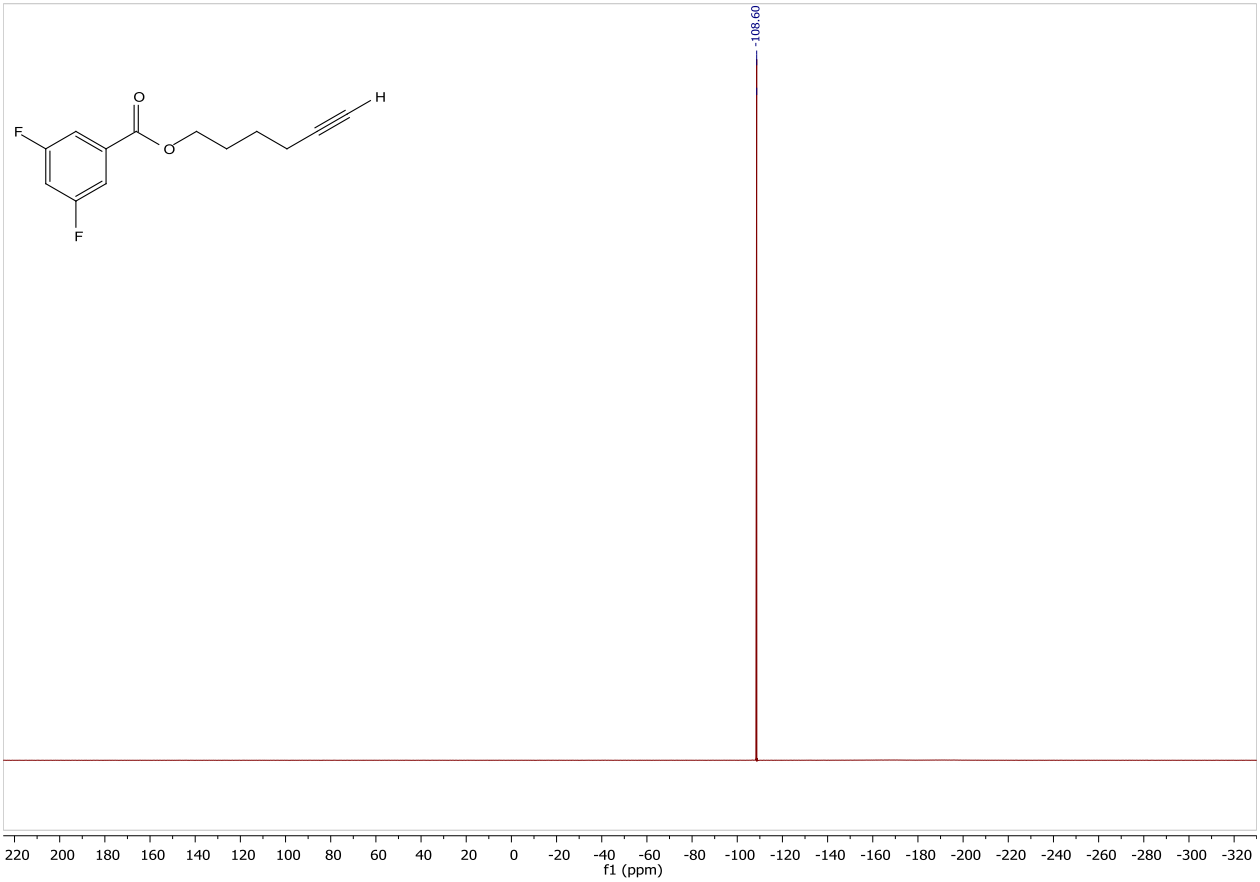
133.76 133.69 133.62
112.84 112.79 112.68 112.63 108.68 108.48 108.28
83.80
77.16 CDCl3
69.08
65.39
27.77
25.09
18.24
O
H
F
O
F
1.00 1.49 1.29 1.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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H
F
O
F
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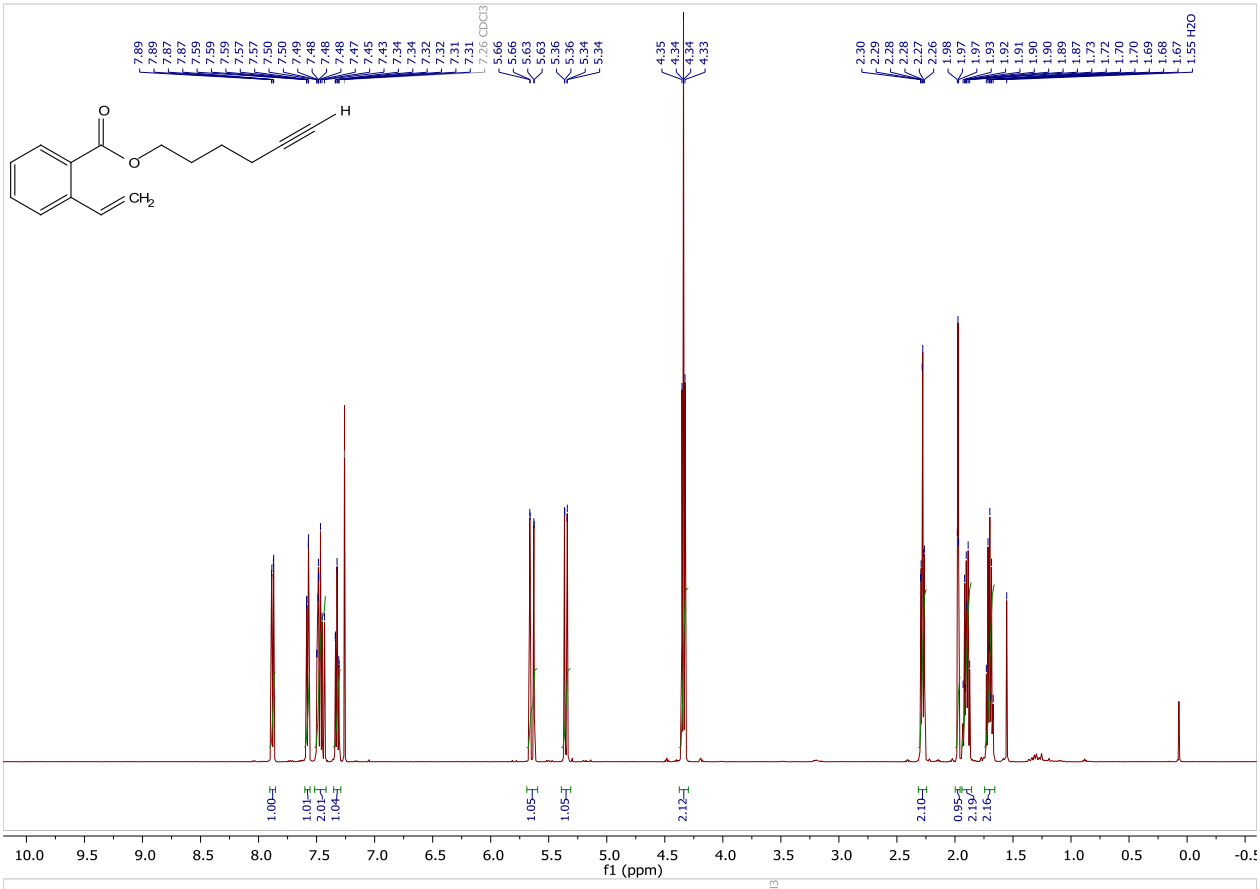
f1 (ppm)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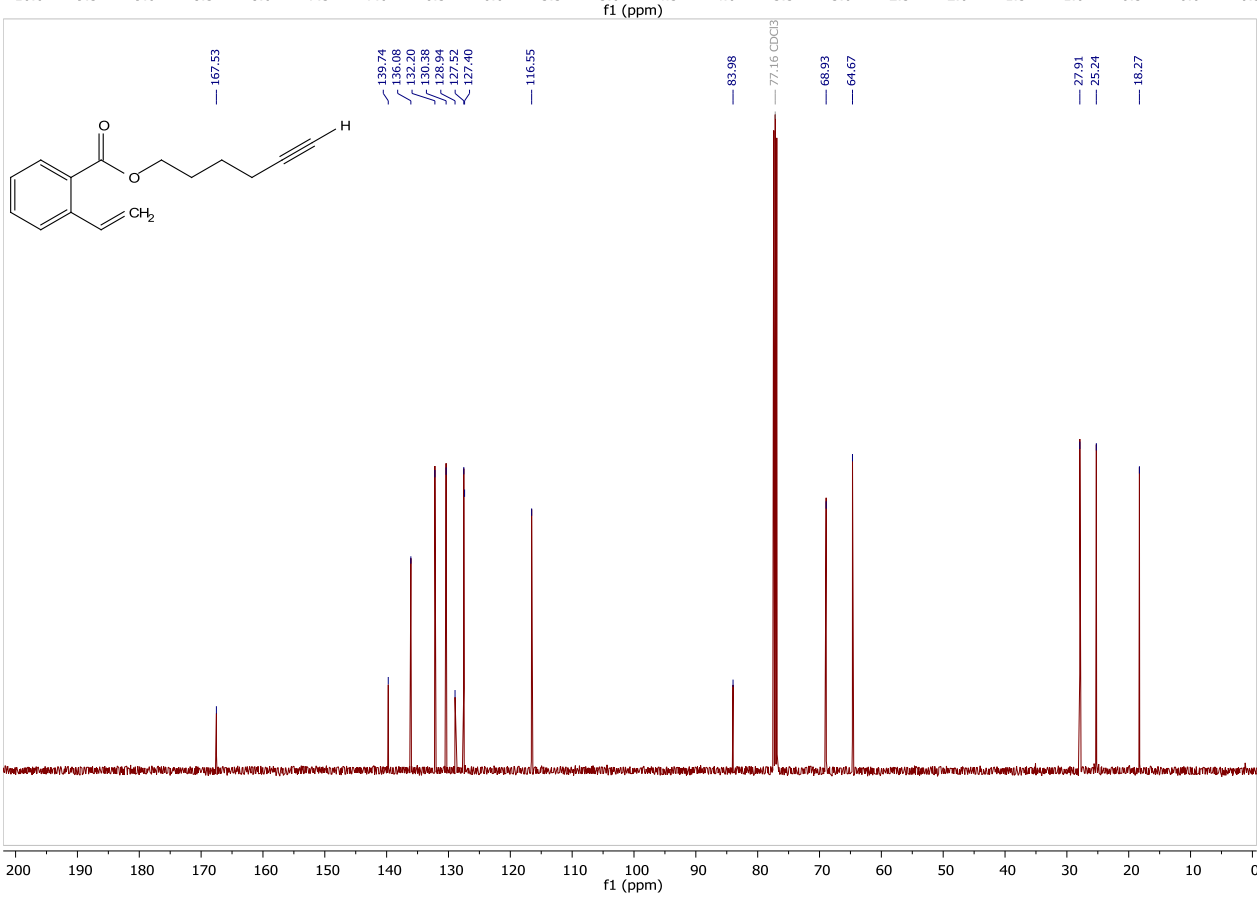
7.48
7.47
7.45
7.43
7.34
7.34
7.32
7.31
7.31
7.26 CDCl3
5.66
5.66
5.63
5.63
5.36
5.36
5.34
5.34
4.35
4.34
4.34
4.33
2.30
2.29
2.28
2.28
2.27
2.26
1.98
1.97
1.97
1.93
1.92
1.91
1.90
1.90
1.89
1.87
1.73
1.72
1.70
1.70
1.69
1.68
1.67
1.55 H2O
O
O
H
CH2
1.00
1.01
2.01
1.04
1.05
1.05
2.12
2.10
0.95
2.19
2.16
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 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.16 CDCl3
68.93
64.67
27.91
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18.27
O
O
H
CH2
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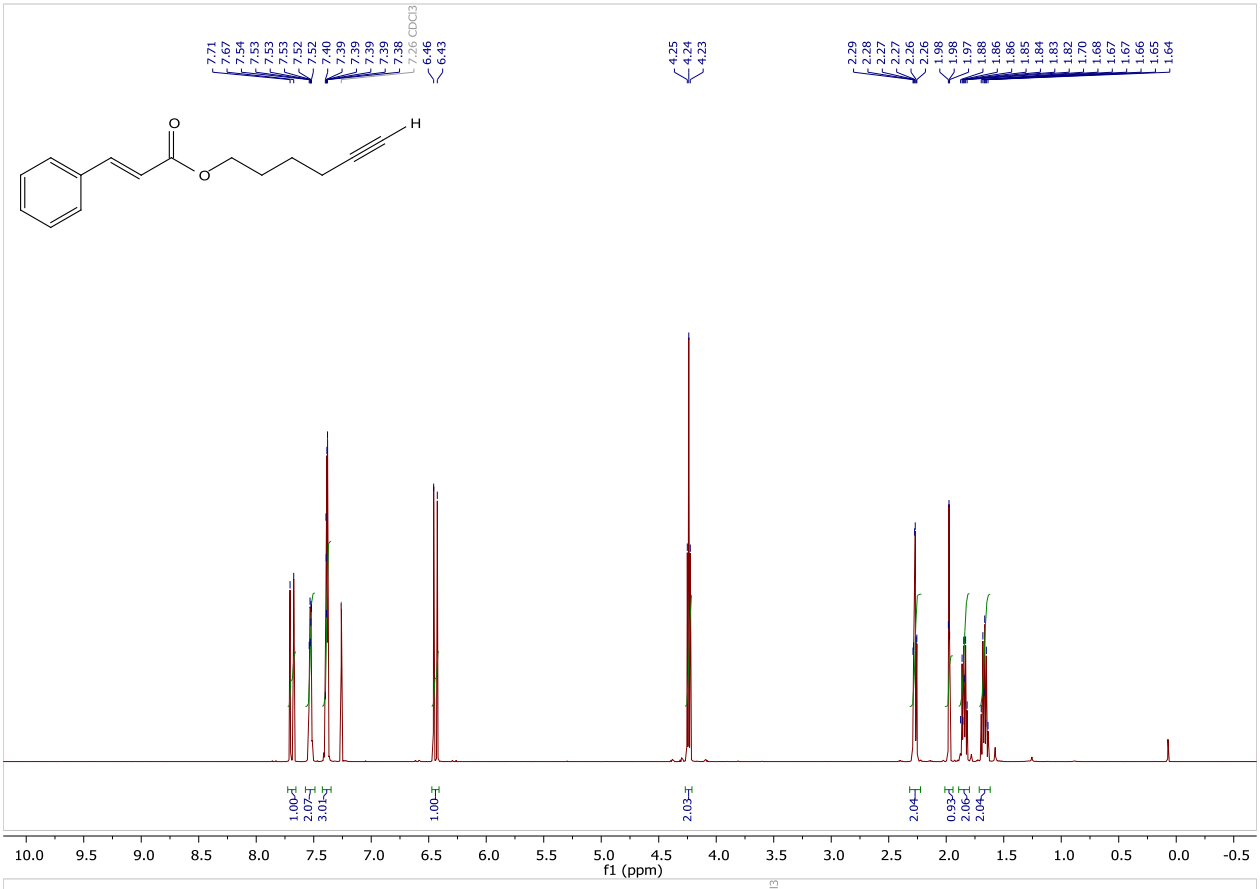
f1 (ppm)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7.53
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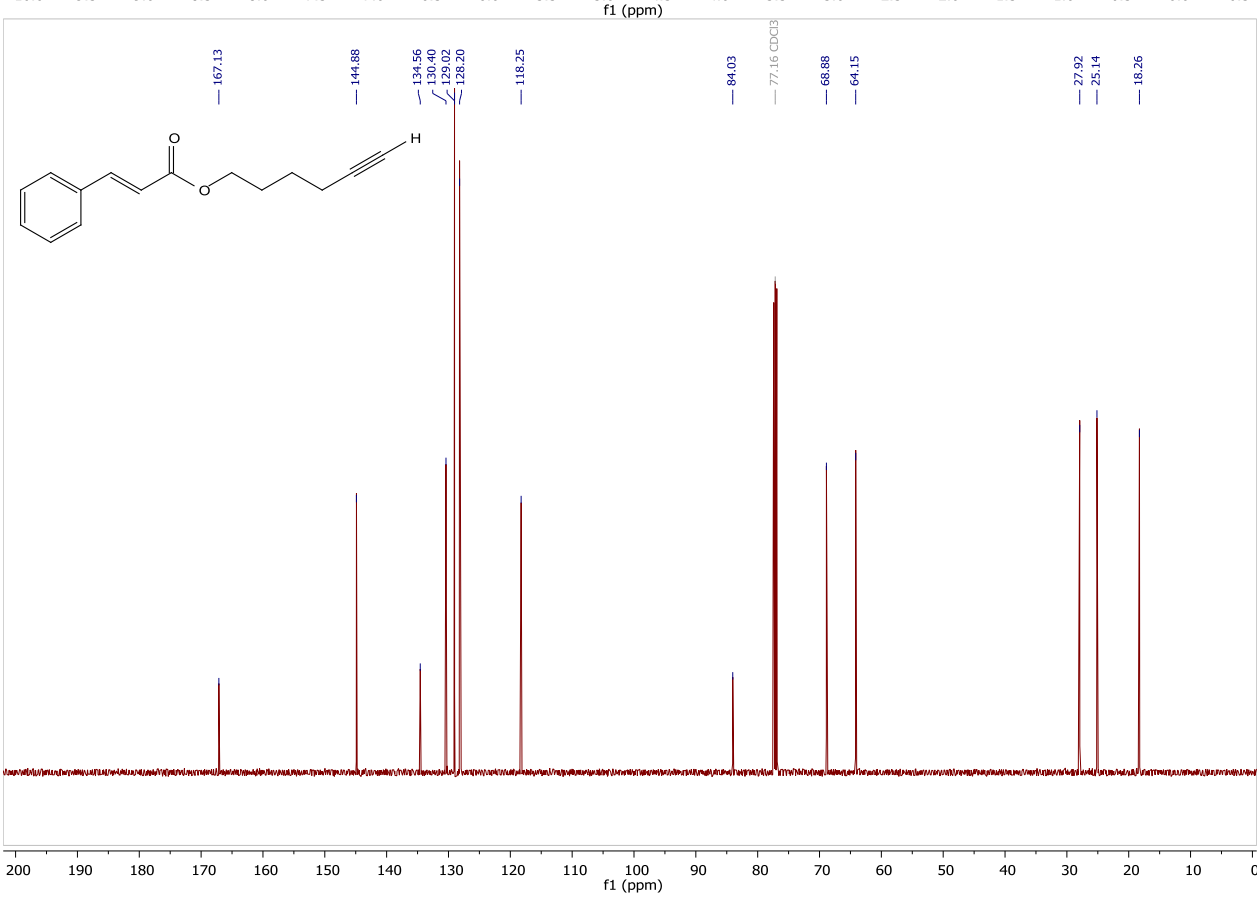
7.52
7.40
7.39
7.39
7.39
7.39
7.38
7.26 CDCl3
6.46
6.43
4.25
4.24
4.23
2.29
2.28
2.27
2.27
2.26
2.26
1.98
1.98
1.97
1.88
1.86
1.86
1.85
1.84
1.83
1.82
1.70
1.68
1.67
1.67
1.66
1.65
1.64
O
O
H
1.00
2.07
3.01
1.00
2.03
2.04
0.93
2.06
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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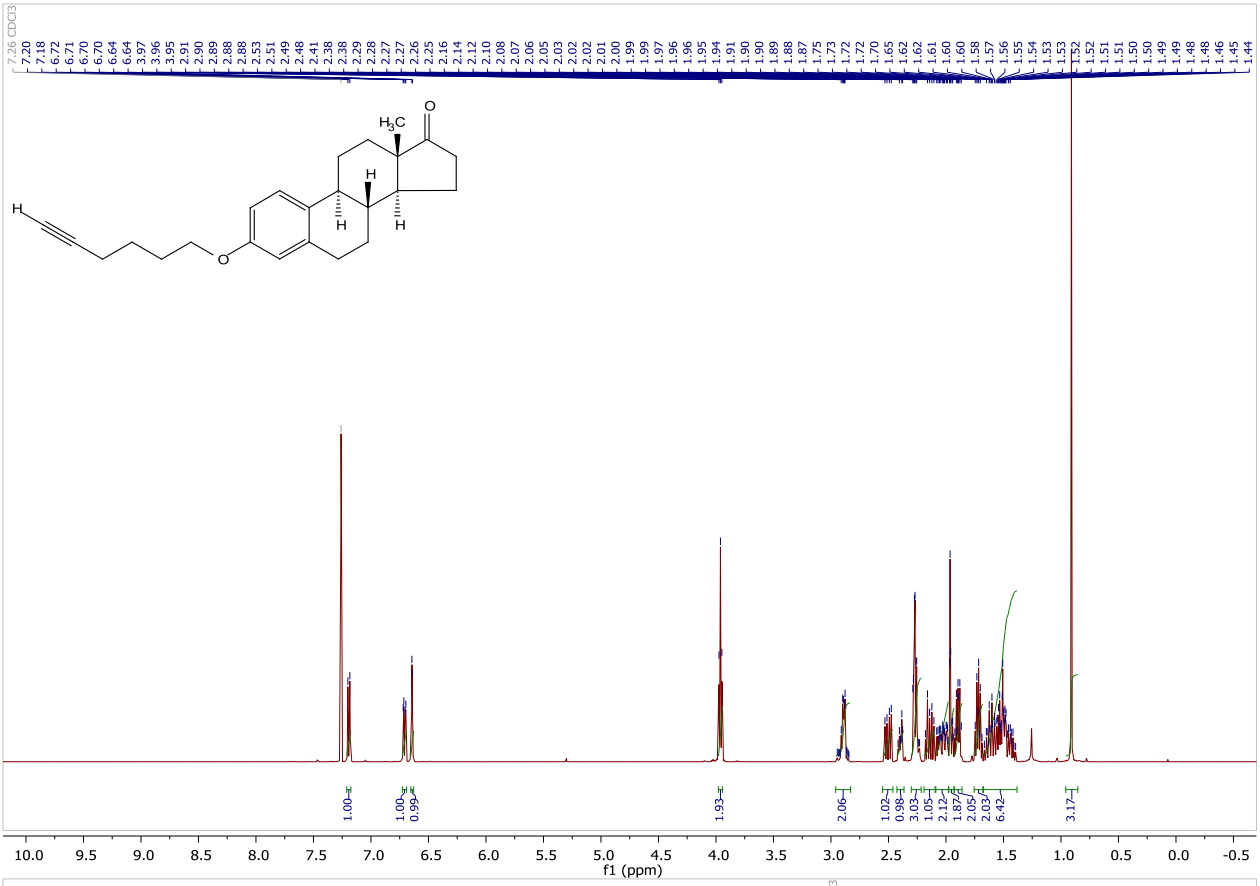
134.56
130.40
129.02
128.20
118.25
84.03
77.16 CDCl3
68.88
64.15
27.92
25.14
18.26
O
O
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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H3C
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H
H
H
H
O
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1.00
0.99
1.93
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3.03
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2.12
1.87
2.05
2.03
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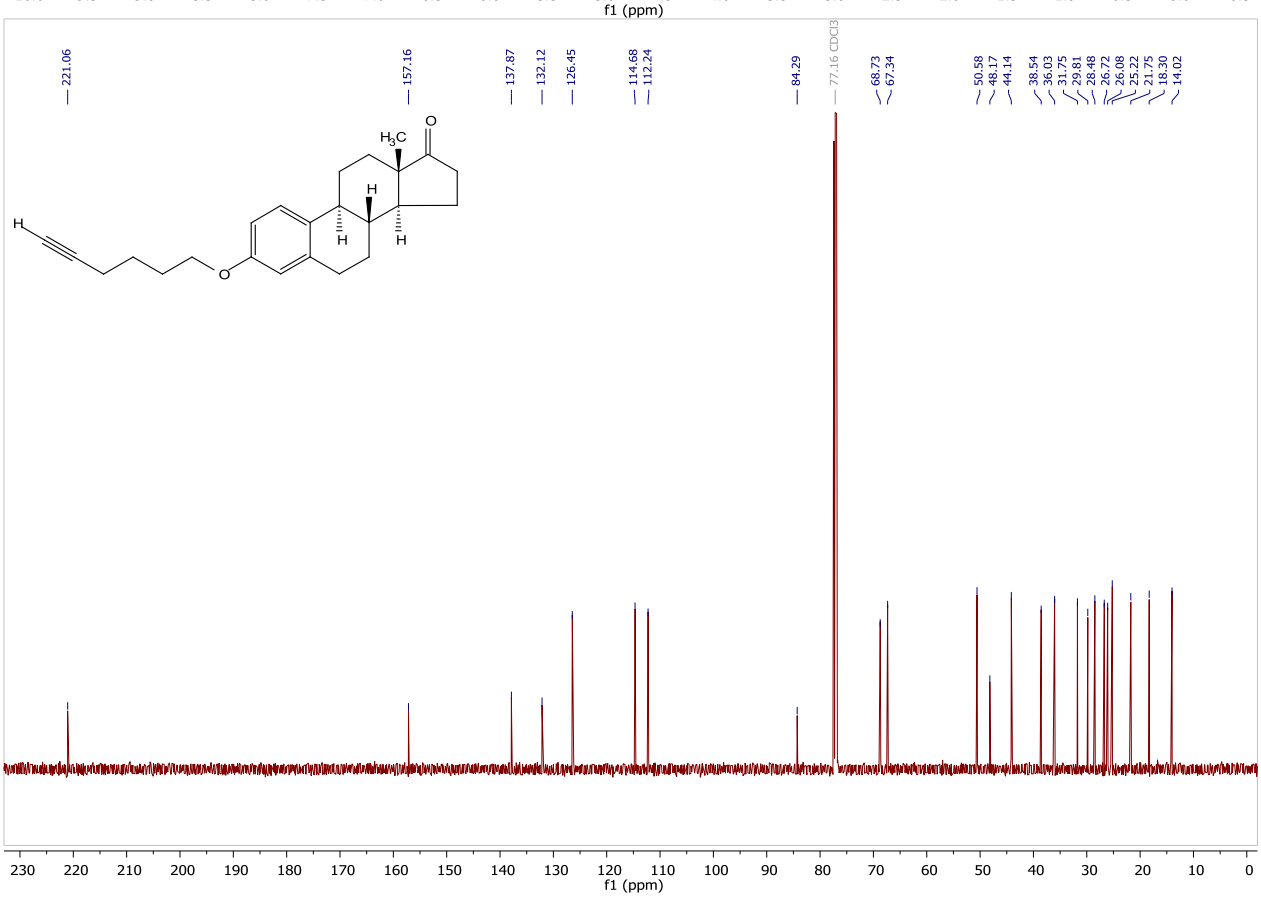
3.17
f1 (ppm)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114.68
112.24
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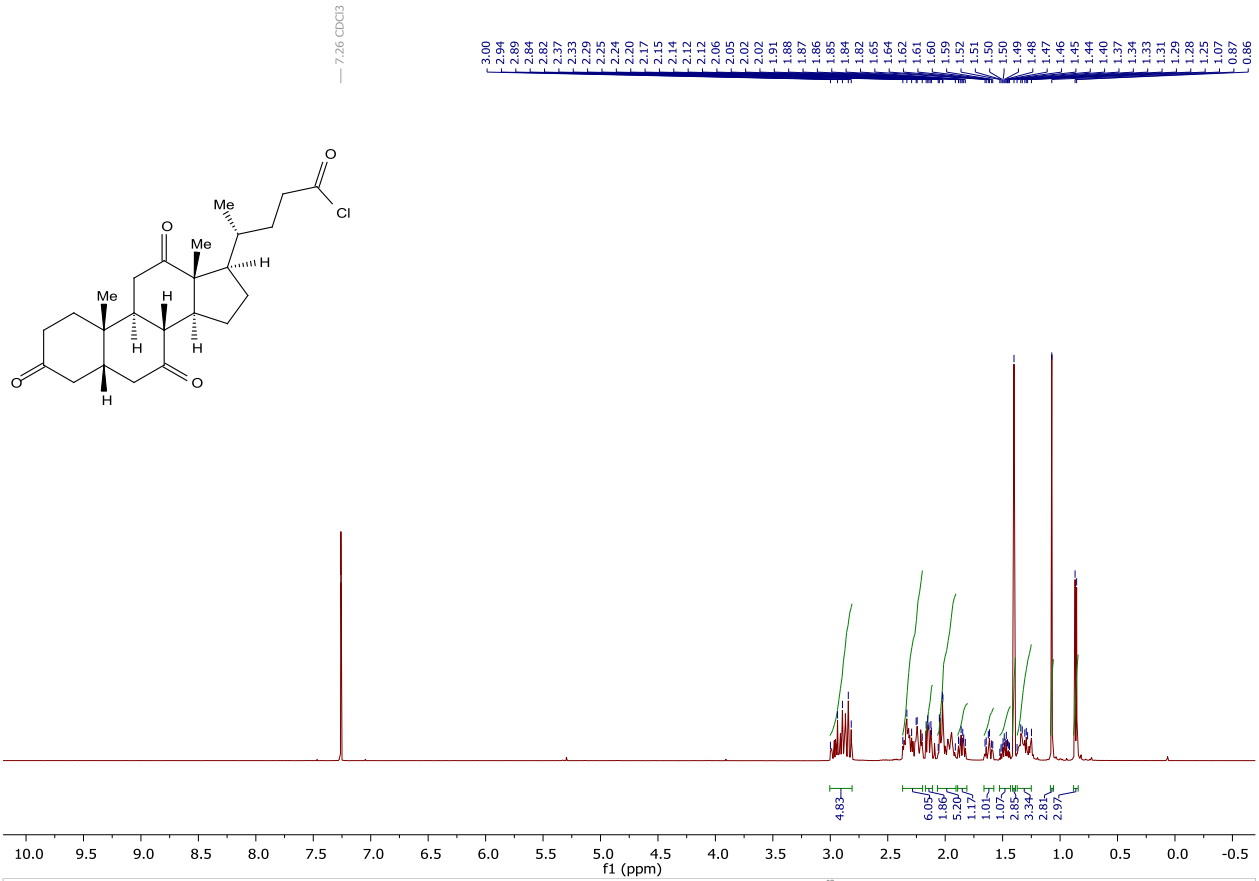
68.73
67.34
50.58
48.17
44.14
38.54
36.03
31.75
29.81
28.48
26.72
26.08
25.22
21.75
18.30
14.02
H3C
O
H
H
H
H
O
f1 (ppm)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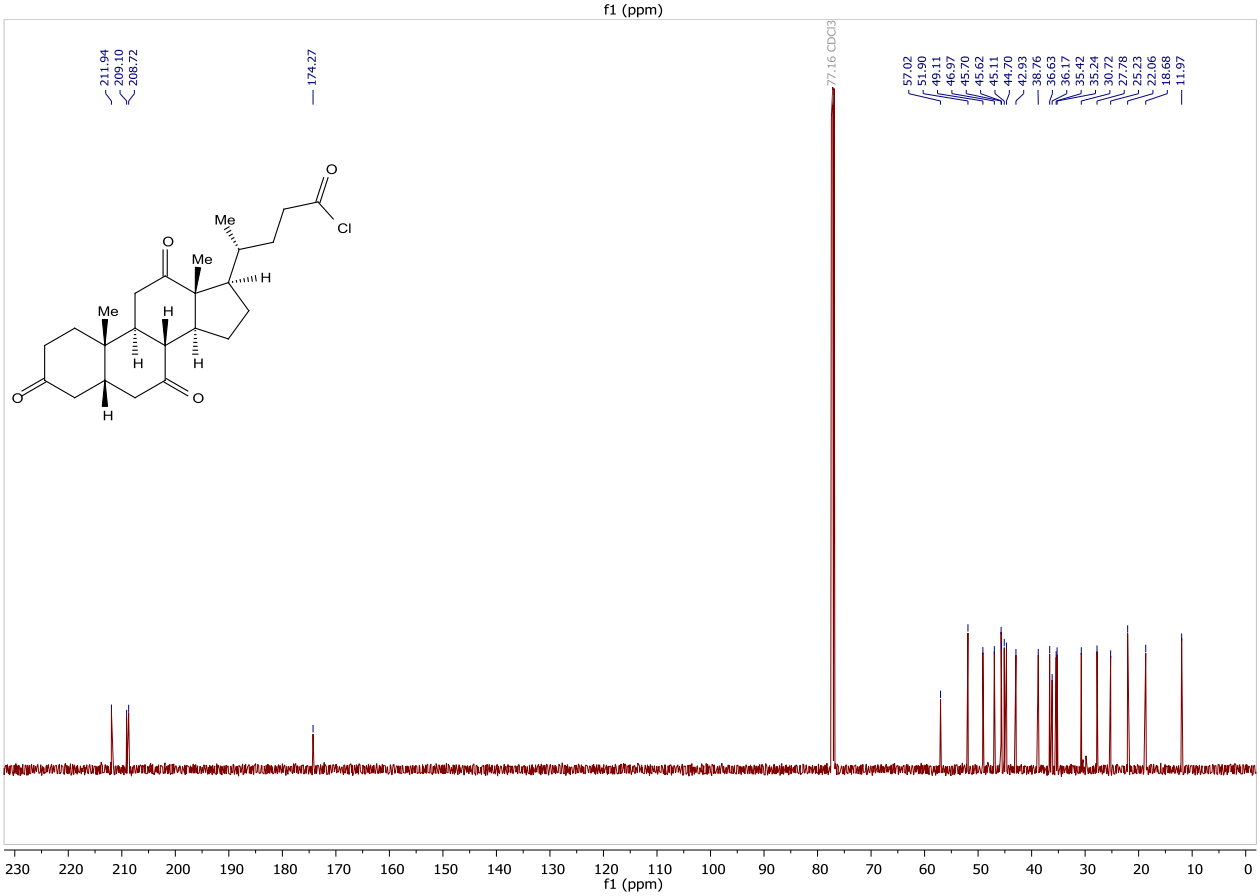
Me
O
Cl
Me
H
H
H
H
O
O
H
4.83
6.05
1.86
5.20
1.17
1.01
1.07
2.85
3.34
2.81
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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209.10
208.72
174.27
77.16 CDCl3
57.02
51.90
49.11
46.97
45.70
45.62
45.11
44.70
42.93
38.76
36.63
36.17
35.42
35.24
30.72
27.78
25.23
22.06
18.68
11.97
Me
O
Cl
Me
H
H
H
H
O
O
H
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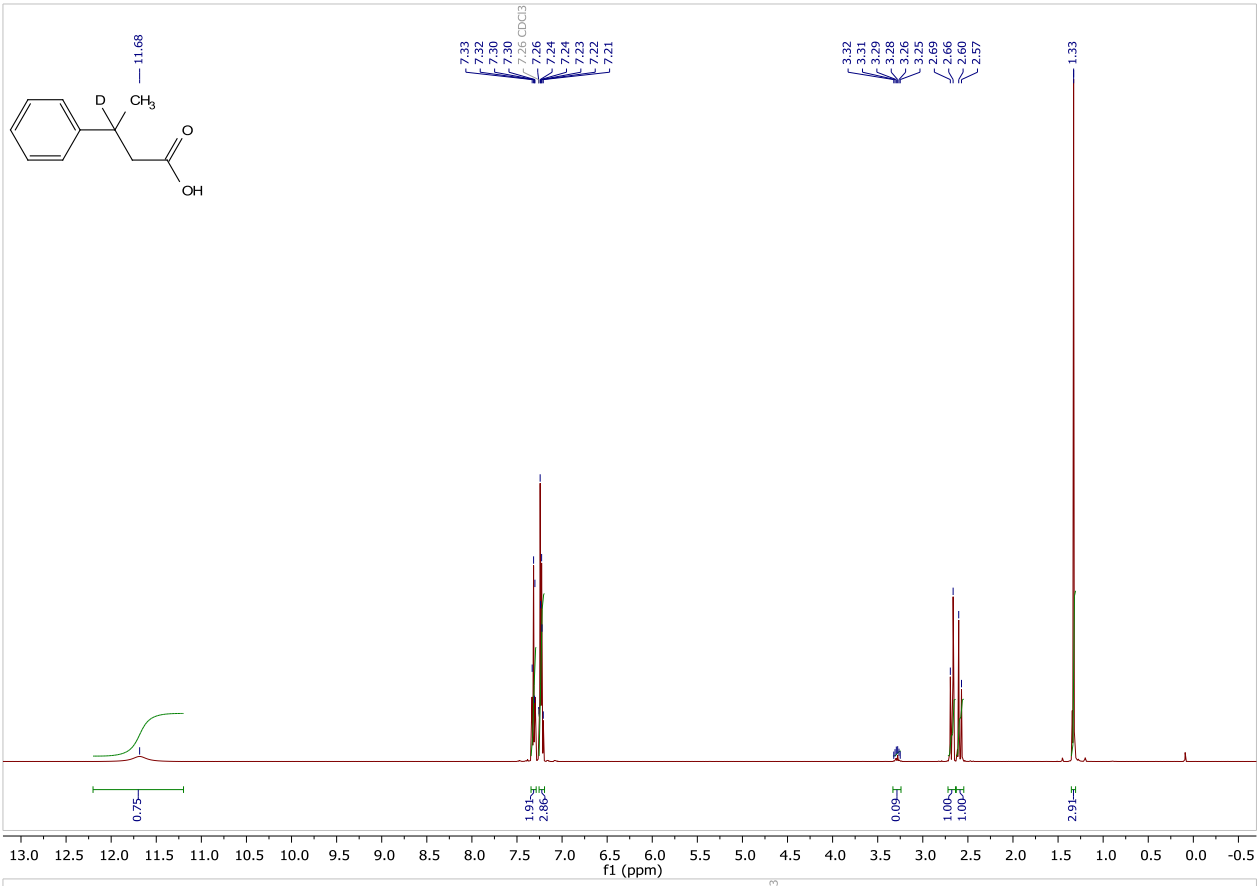
f1 (ppm)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D
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O
OH
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7.32
7.30
7.30
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7.23
7.22
7.21
3.32
3.31
3.29
3.28
3.26
3.25
2.69
2.66
2.60
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1.33
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1.91
2.86
0.09
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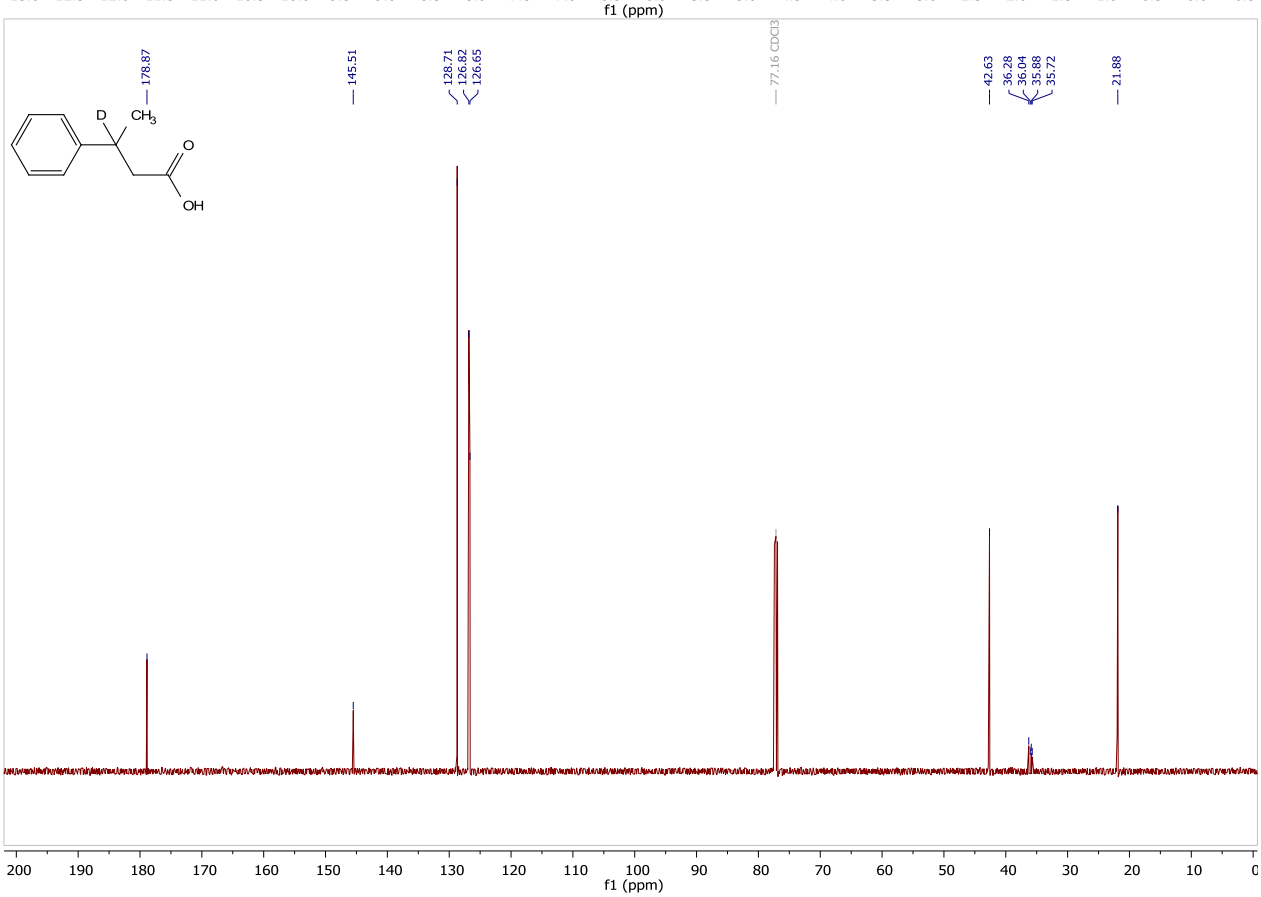
1.00
2.91
f1 (ppm)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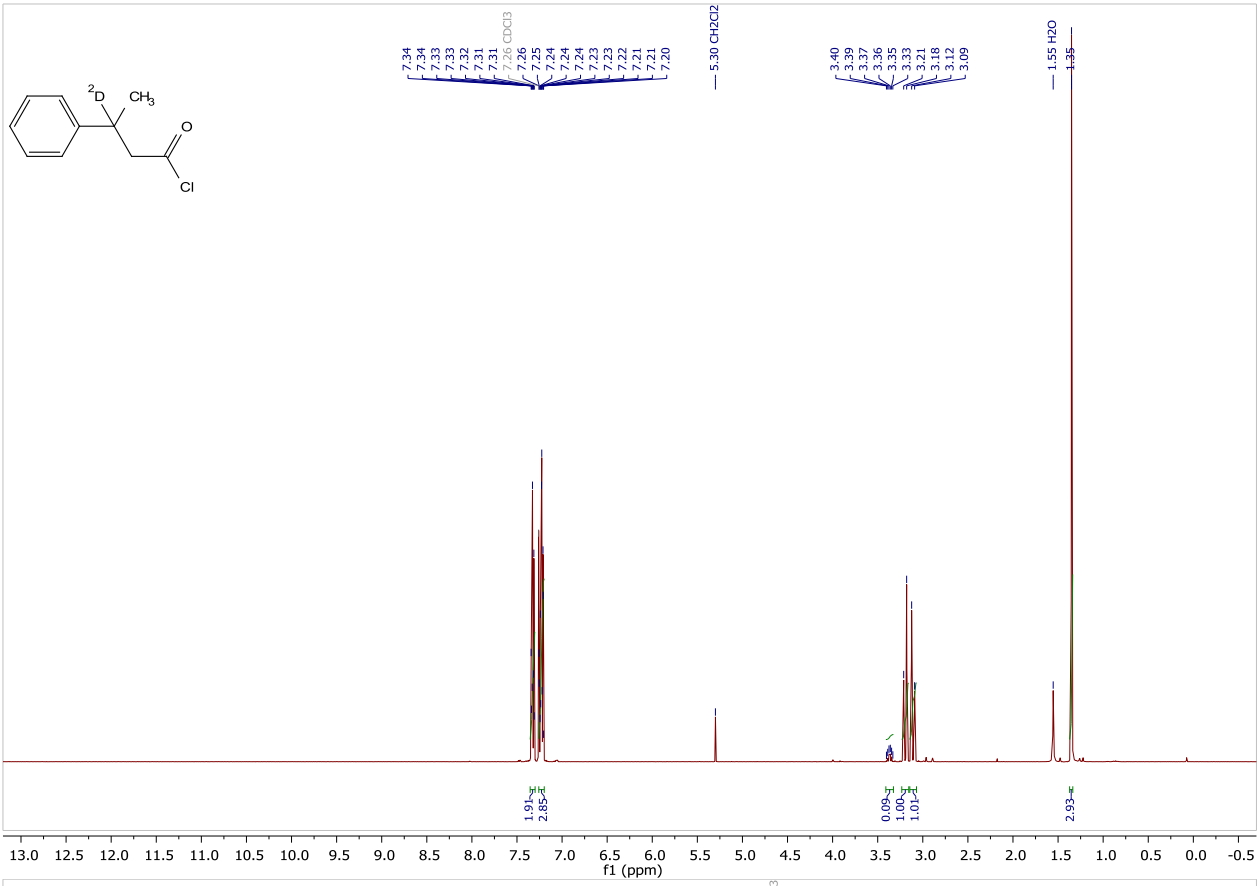
21.88
f1 (ppm)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7.33
7.33
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7.31
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7.25
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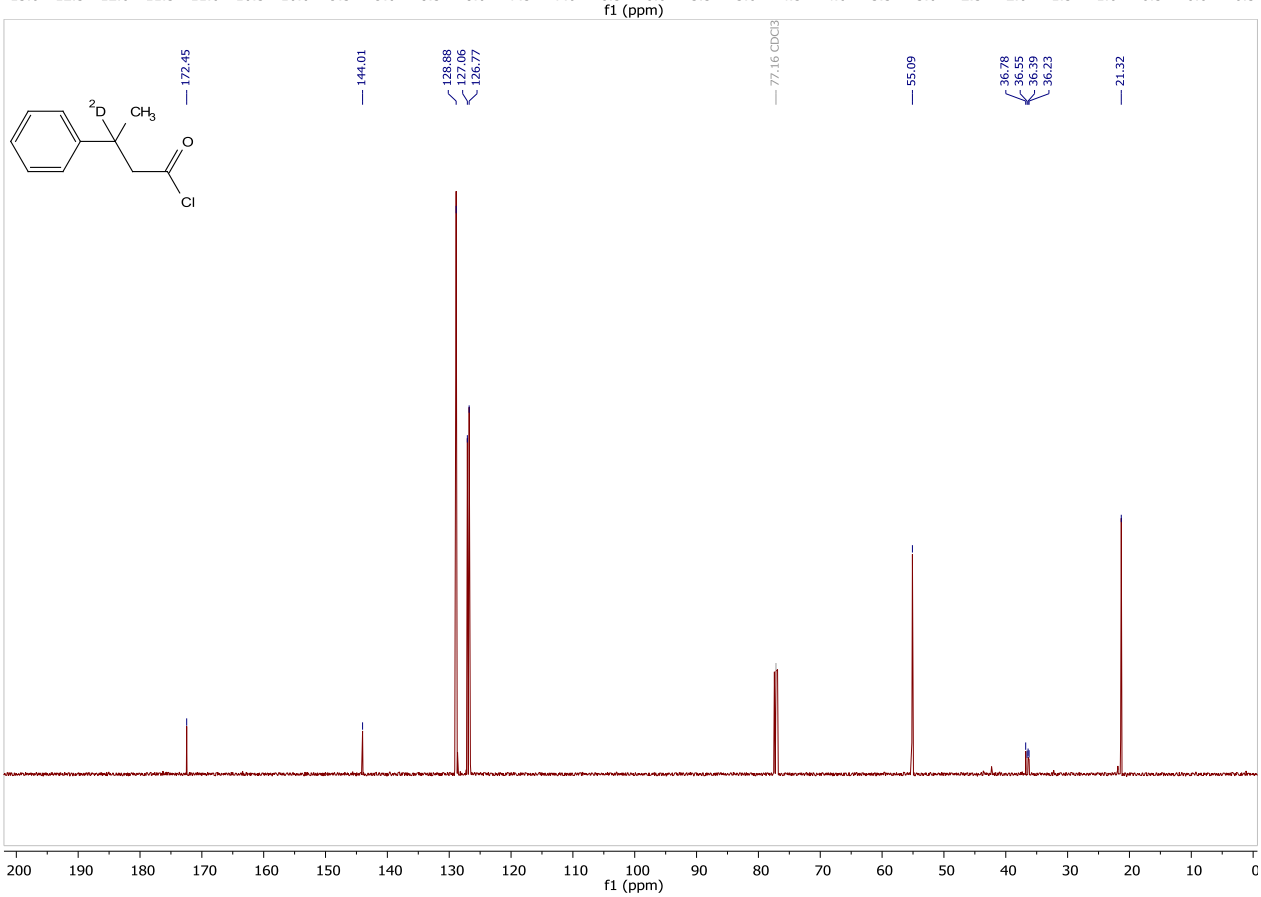
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.20
5.30 CH2Cl2
3.40
3.39
3.37
3.36
3.35
3.33
3.21
3.18
3.12
3.09
1.55 H2O
1.35
1.91
2.85
0.09
1.00
1.01
2.93
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
2D
CH3
O
Cl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36.55
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21.32
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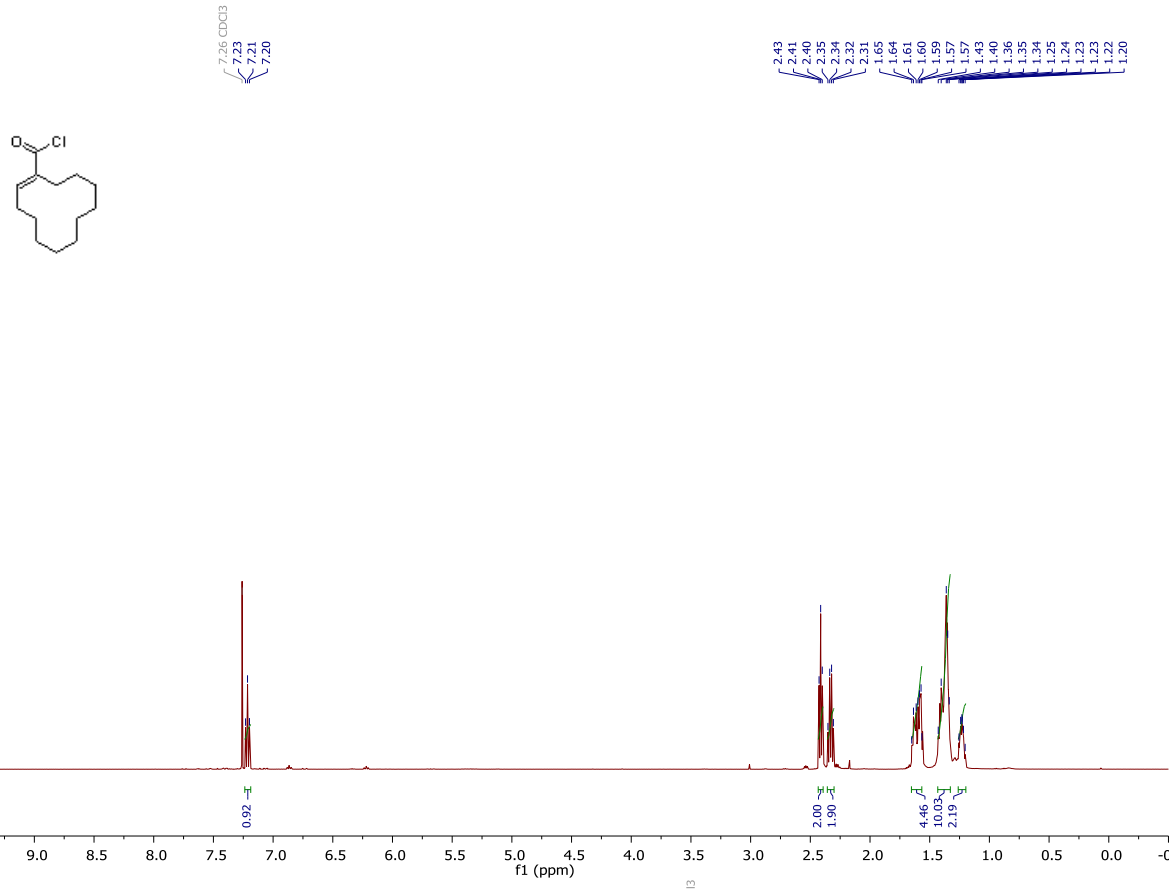
f1 (ppm)
2D
CH3
O
Cl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2.34
2.32
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1.64
1.61
1.60
1.59
1.57
1.57
1.43
1.40
1.36
1.35
1.34
1.25
1.24
1.23
1.23
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1.20
O
Cl
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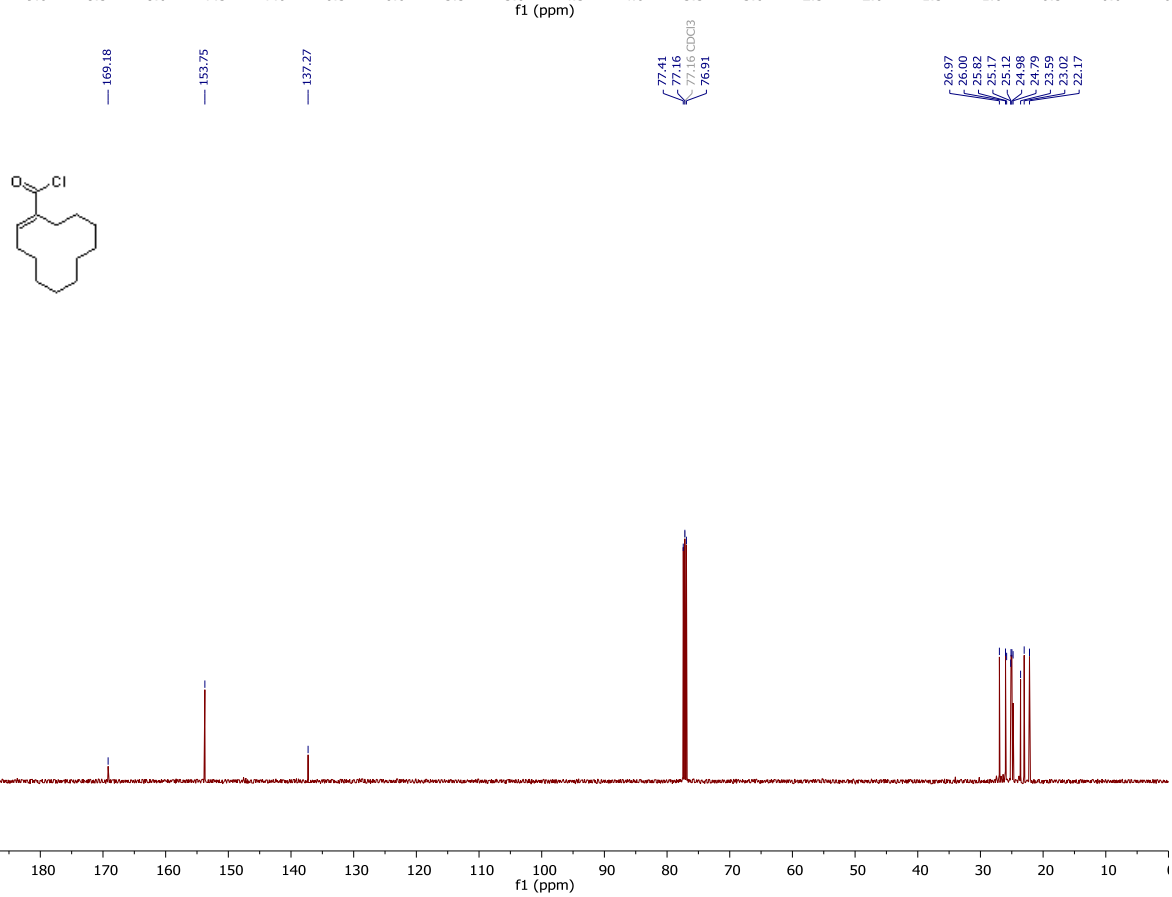
2.00
1.90
4.46
10.03
2.19
f1 (ppm)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77.16
77.16 CDCl3
76.91
26.97
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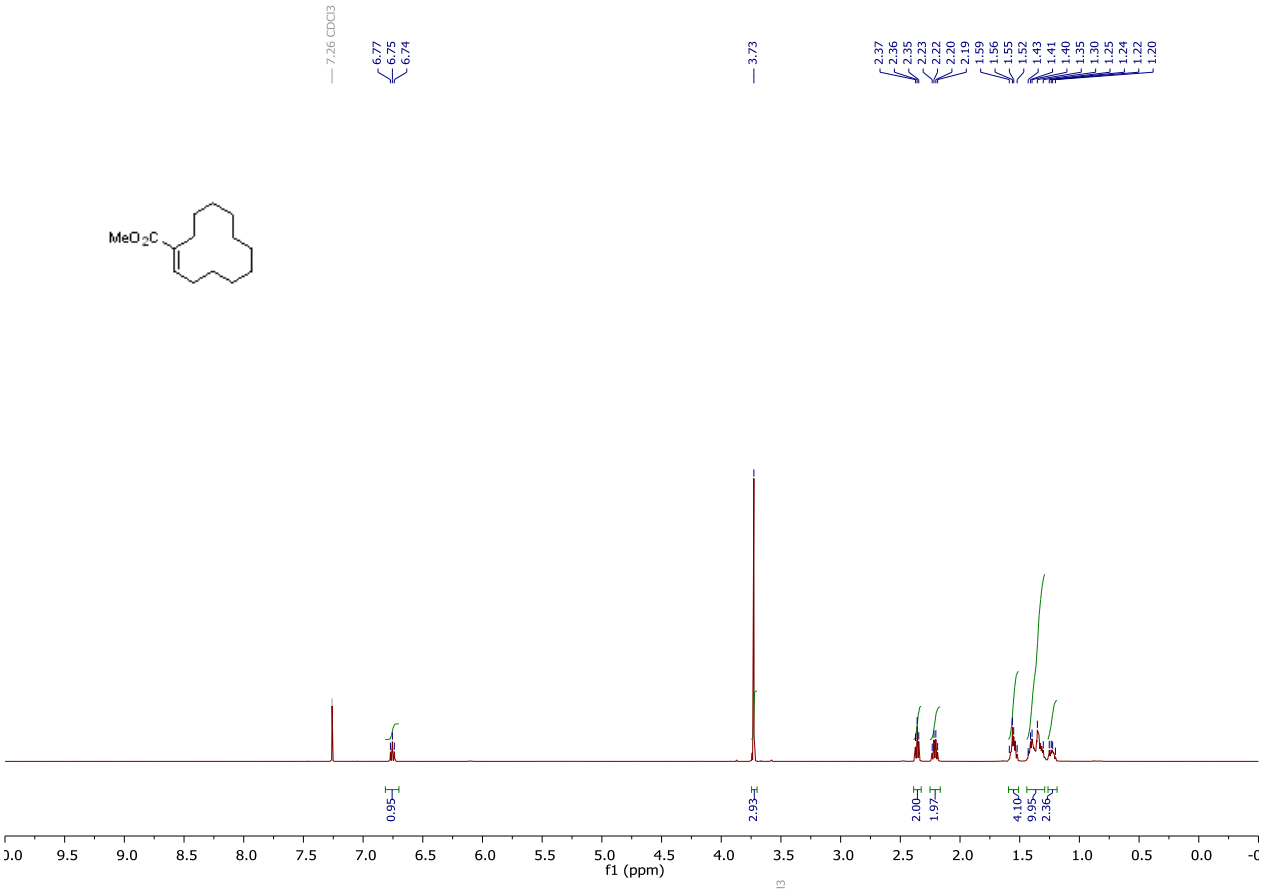
25.17
25.12
24.98
24.79
23.59
23.02
22.17
O
Cl
f1 (ppm)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6.74
3.73
2.37
2.36
2.35
2.23
2.22
2.20
2.19
1.59
1.56
1.55
1.52
1.43
1.41
1.40
1.35
1.30
1.25
1.24
1.22
1.20
MeO2C
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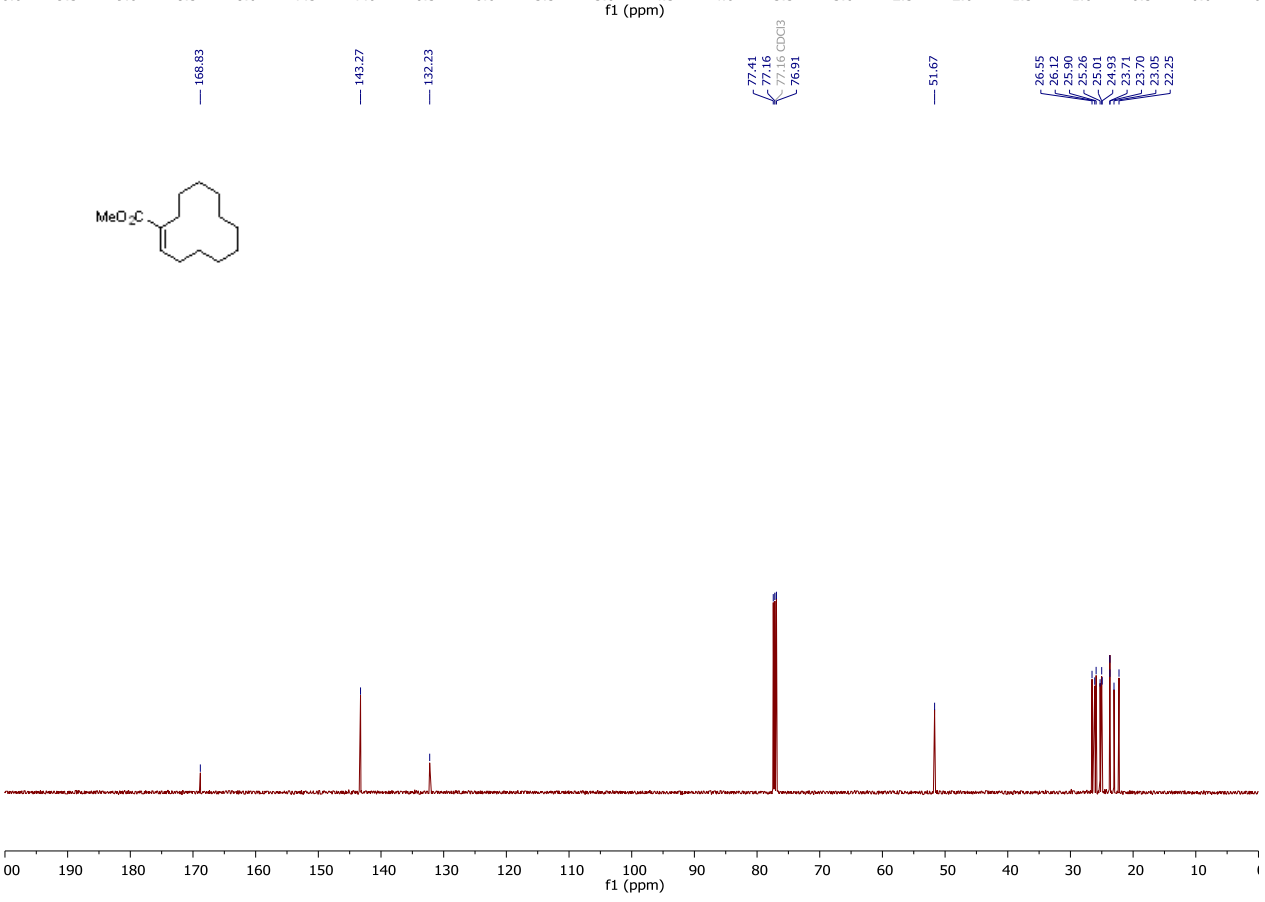
2.93
2.00
1.97
4.10
9.95
2.36
f1 (ppm)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77.16
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51.67
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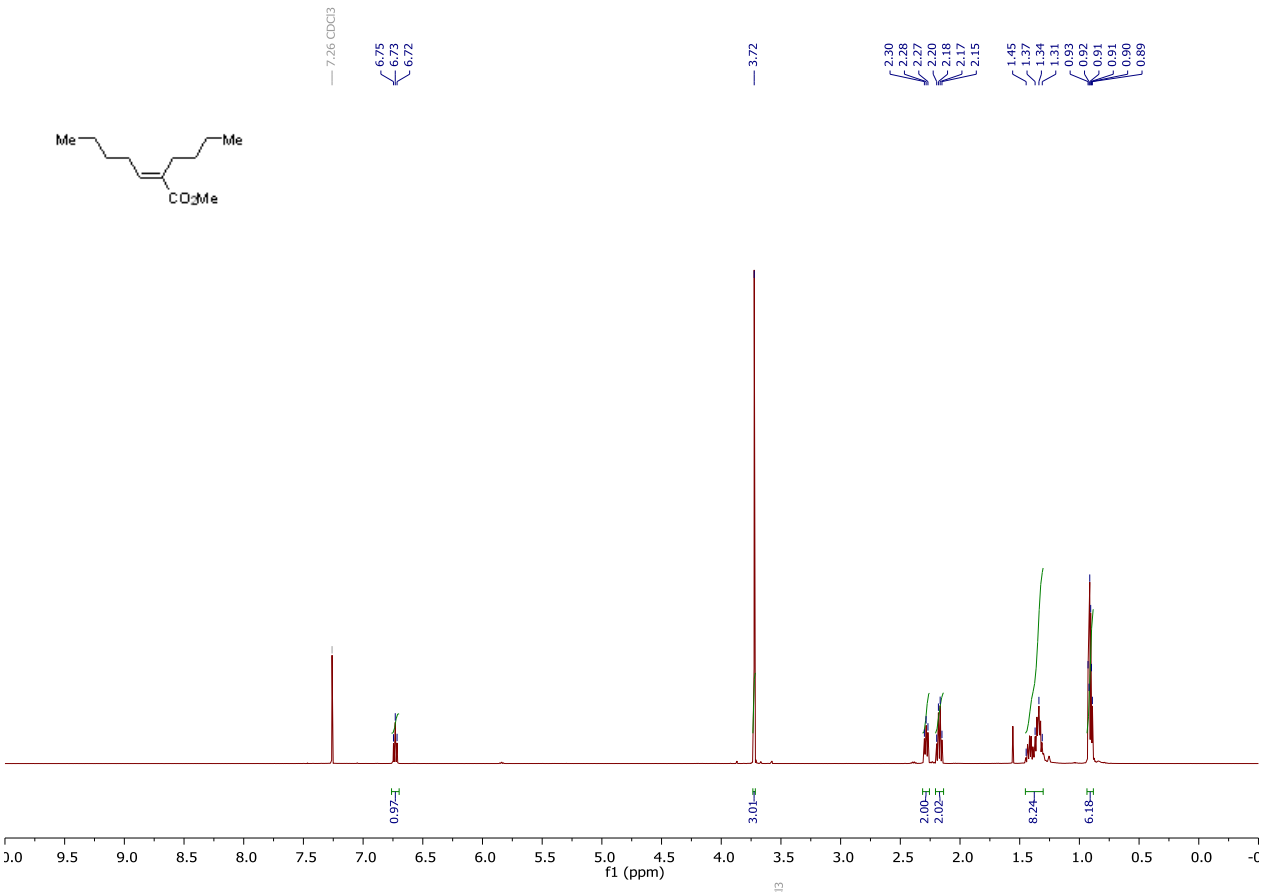
25.26
25.01
24.93
23.71
23.70
23.05
22.25
MeO2C
f1 (ppm)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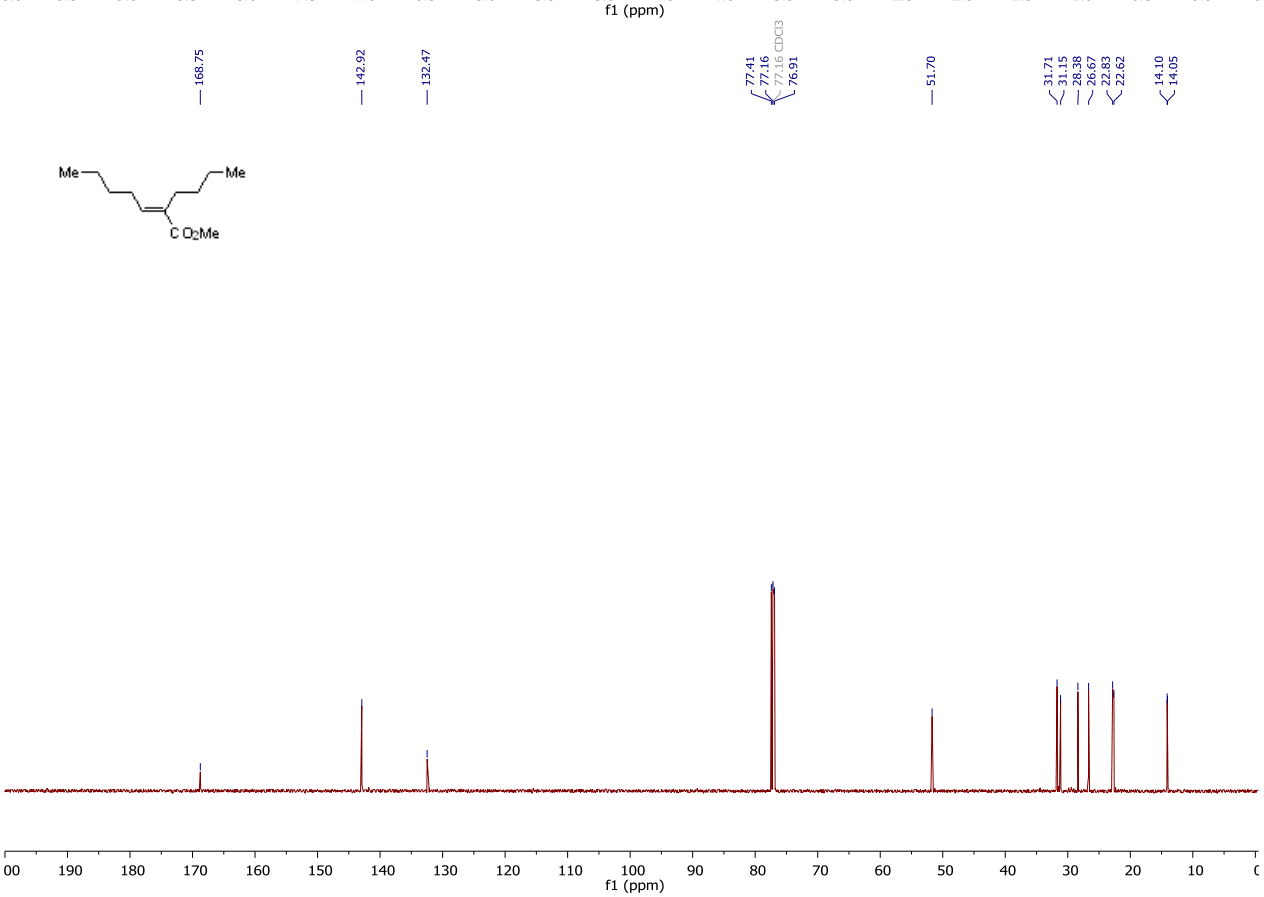
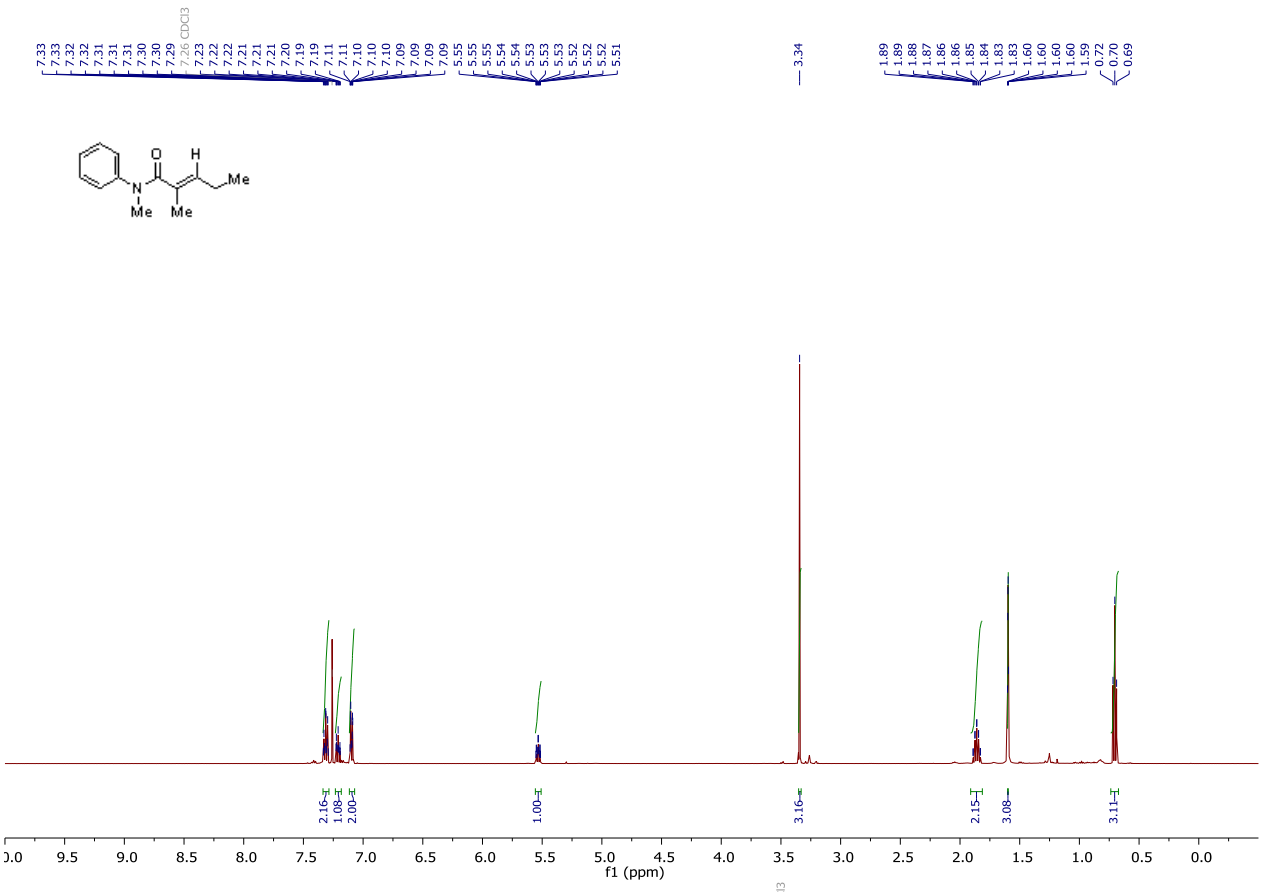
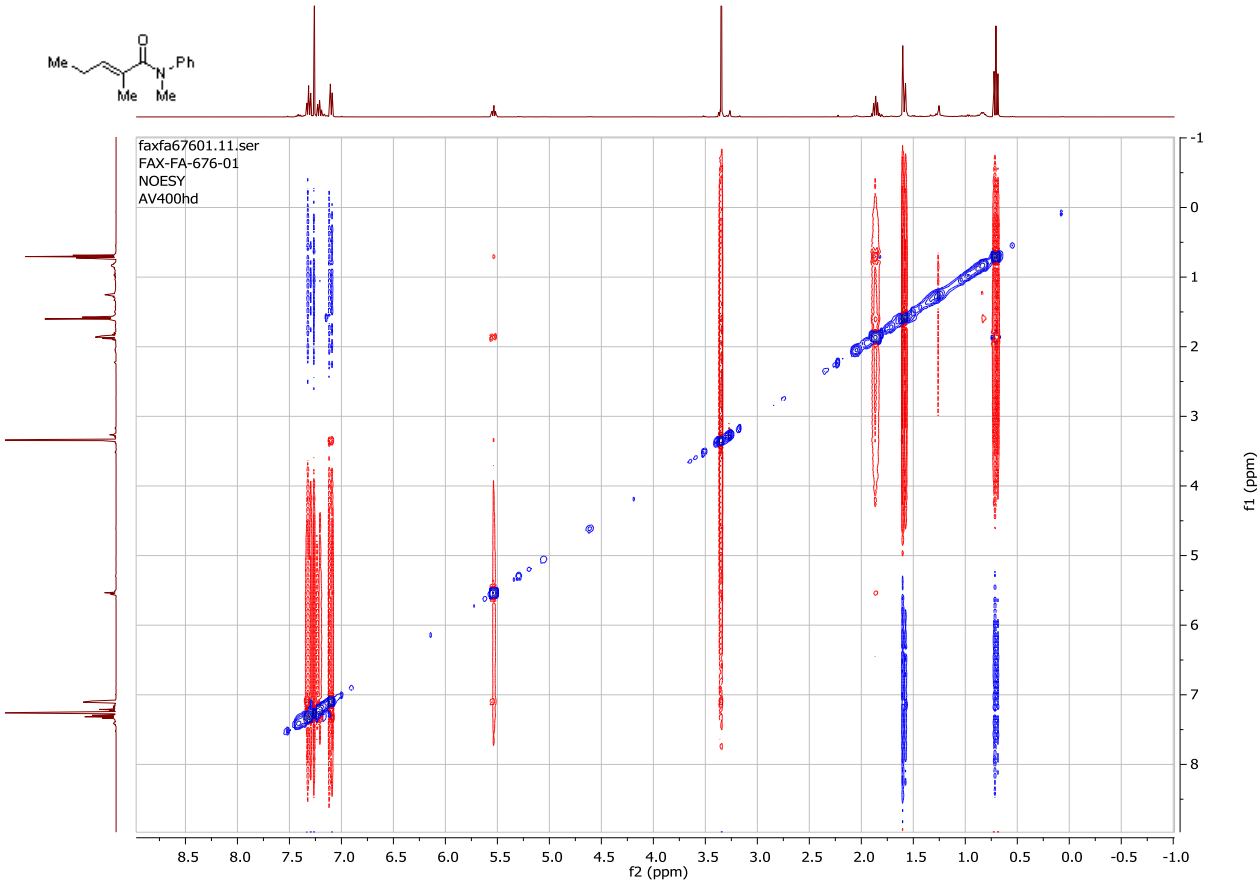
6.73
6.72
3.72
2.30
2.28
2.27
2.20
2.18
2.17
2.15
1.45
1.37
1.34
1.31
0.93
0.92
0.91
0.91
0.90
0.89
Me
Me
CO2Me
0.97
3.01
2.00
2.02
8.24
6.18
f1 (ppm)


168.75
142.92
132.47
77.41
77.16
77.16 CDCl3
76.91
51.70
31.71
31.15
28.38
26.67
22.83
22.62
14.10
14.05
Me
Me
CO2Me
f1 (ppm)


7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.26 CDCl3 7.23 7.22 7.22 7.21 7.21 7.21 7.20 7.19 7.19 7.11 7.11 7.10 7.10 7.09 7.09 7.09 7.09 5.55 5.55 5.55 5.54 5.54 5.53 5.53 5.53 5.52 5.52 5.52 5.51
3.34
1.89 1.89 1.88 1.87 1.86 1.86 1.85 1.84 1.83 1.83 1.60 1.60 1.60 1.60 1.59 0.72 0.70 0.69
O H N Me Me Me
2.16 1.08 2.00 1.00 3.16 2.15 3.08 3.11
f1 (ppm)
173.58 145.39 137.55 130.93 129.17 126.62 126.56 77.41 77.16 77.16 CDCl3 76.91 37.80 21.05 14.25 12.91
O H N Me Me Me
f1 (ppm)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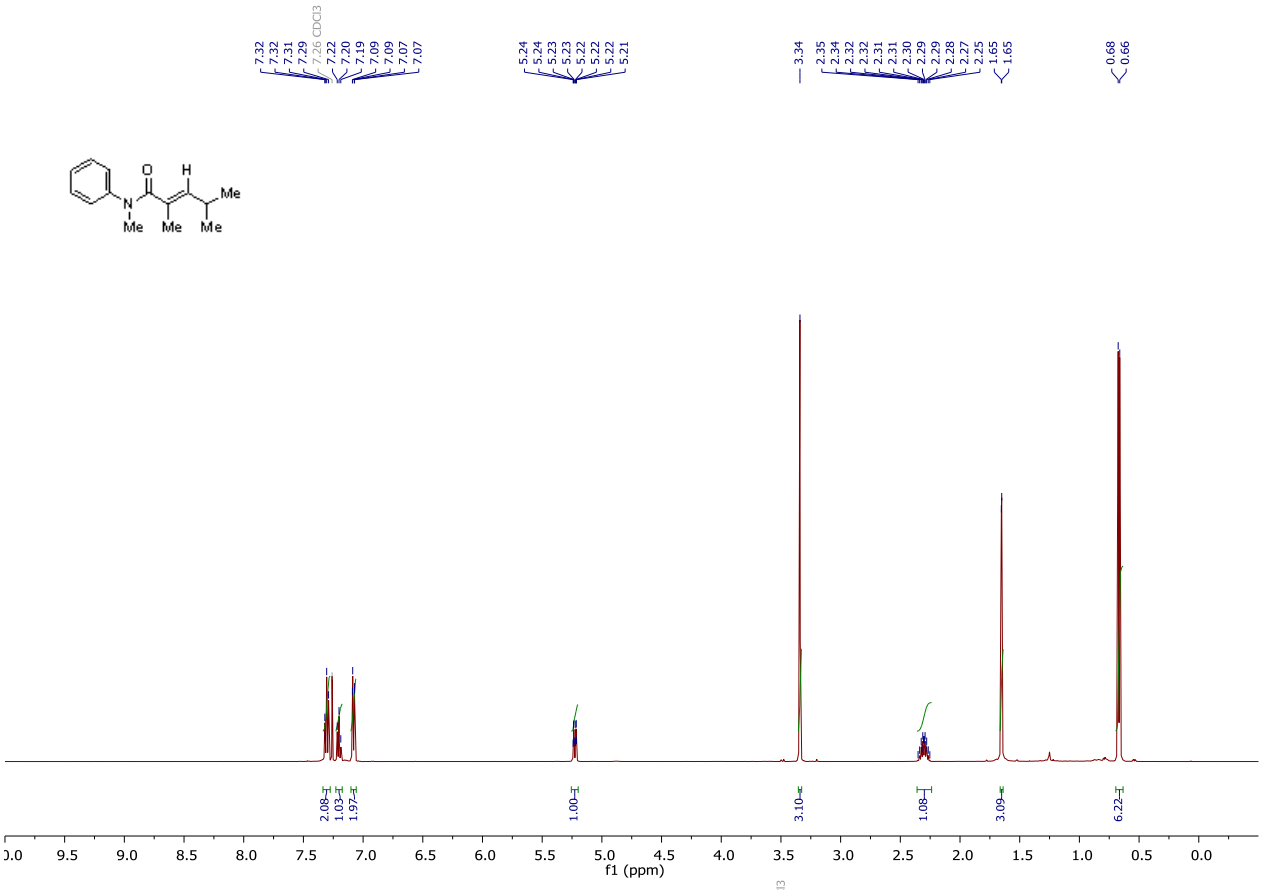
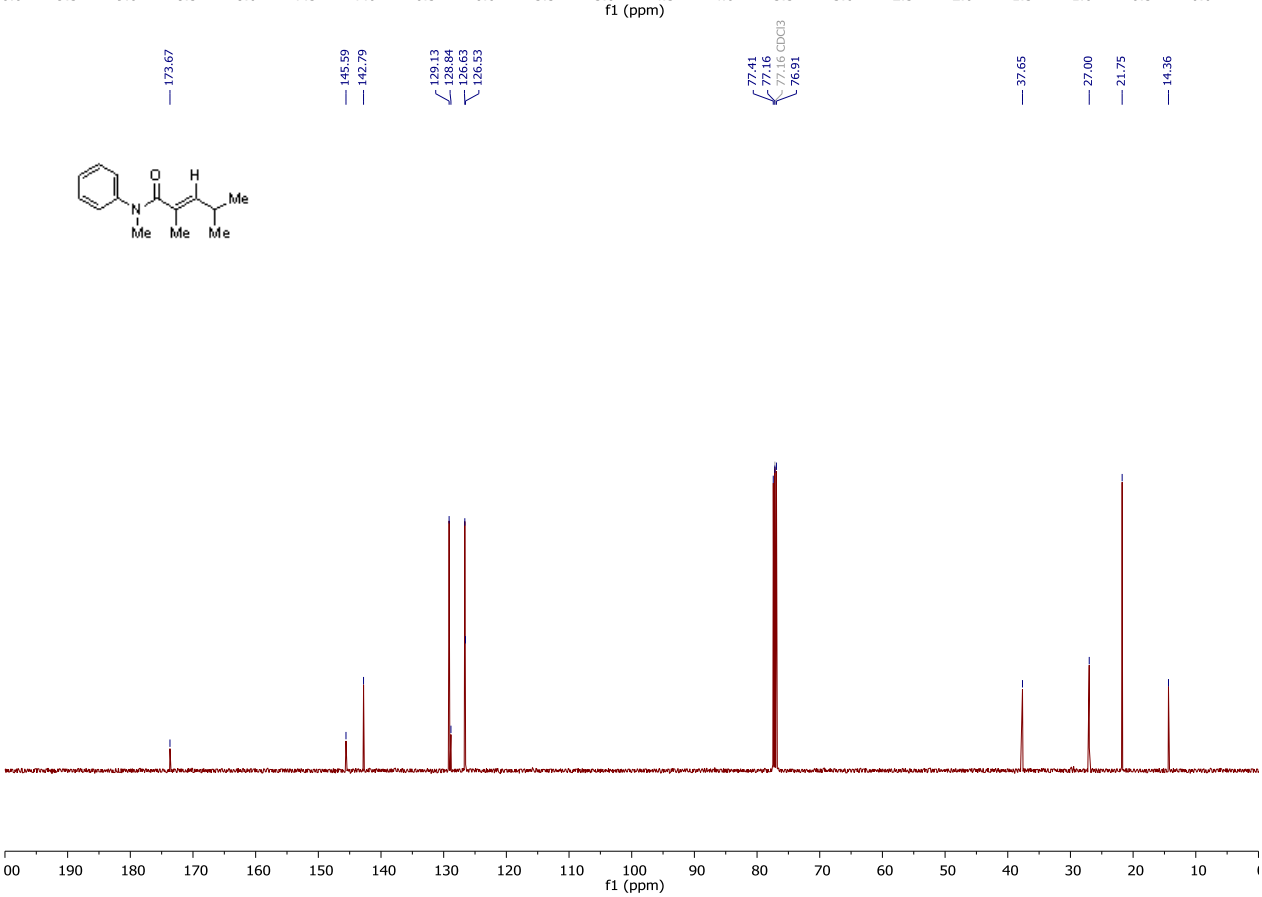
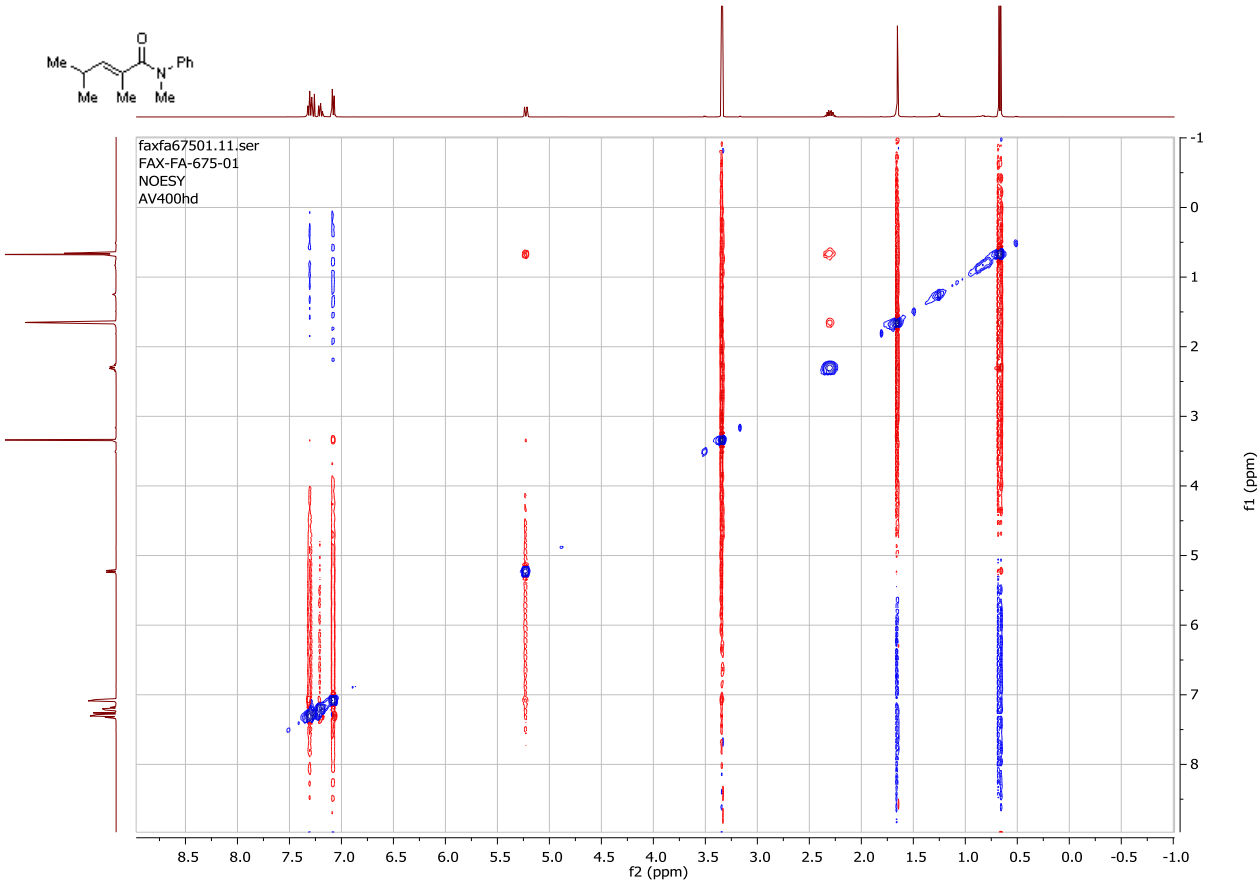
FAX-FA-676-01
NOESY
AV400hd
f2 (ppm)
f1 (ppm)


7.32
7.32
7.31
7.29
7.26 CDCl3
7.22
7.20
7.19
7.09
7.09
7.07
7.07
5.24
5.24
5.23
5.23
5.22
5.22
5.22
5.21
3.34
2.35
2.34
2.32
2.32
2.31
2.30
2.29
2.29
2.28
2.27
2.25
1.65
1.65
0.68
0.66
O
H
N
Me
Me
Me
Me
2.08
1.03
1.97
1.00
3.10
1.08
3.09
6.22
f1 (ppm)


173.67
145.59
142.79
129.13
128.84
126.63
126.53
77.41
77.16
77.16 CDCl3
76.91
37.65
27.00
21.75
14.36
O
H
N
Me
Me
Me
Me
f1 (ppm)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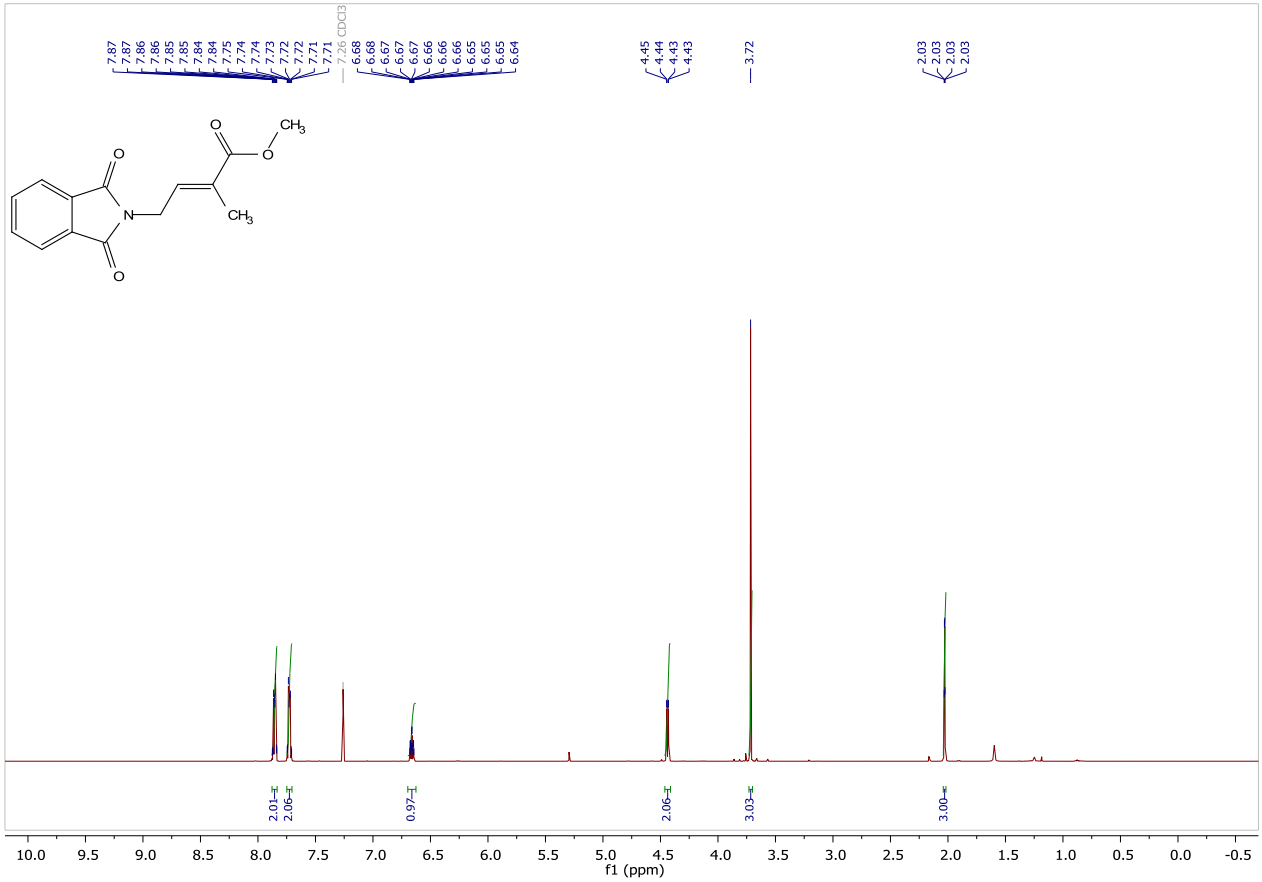
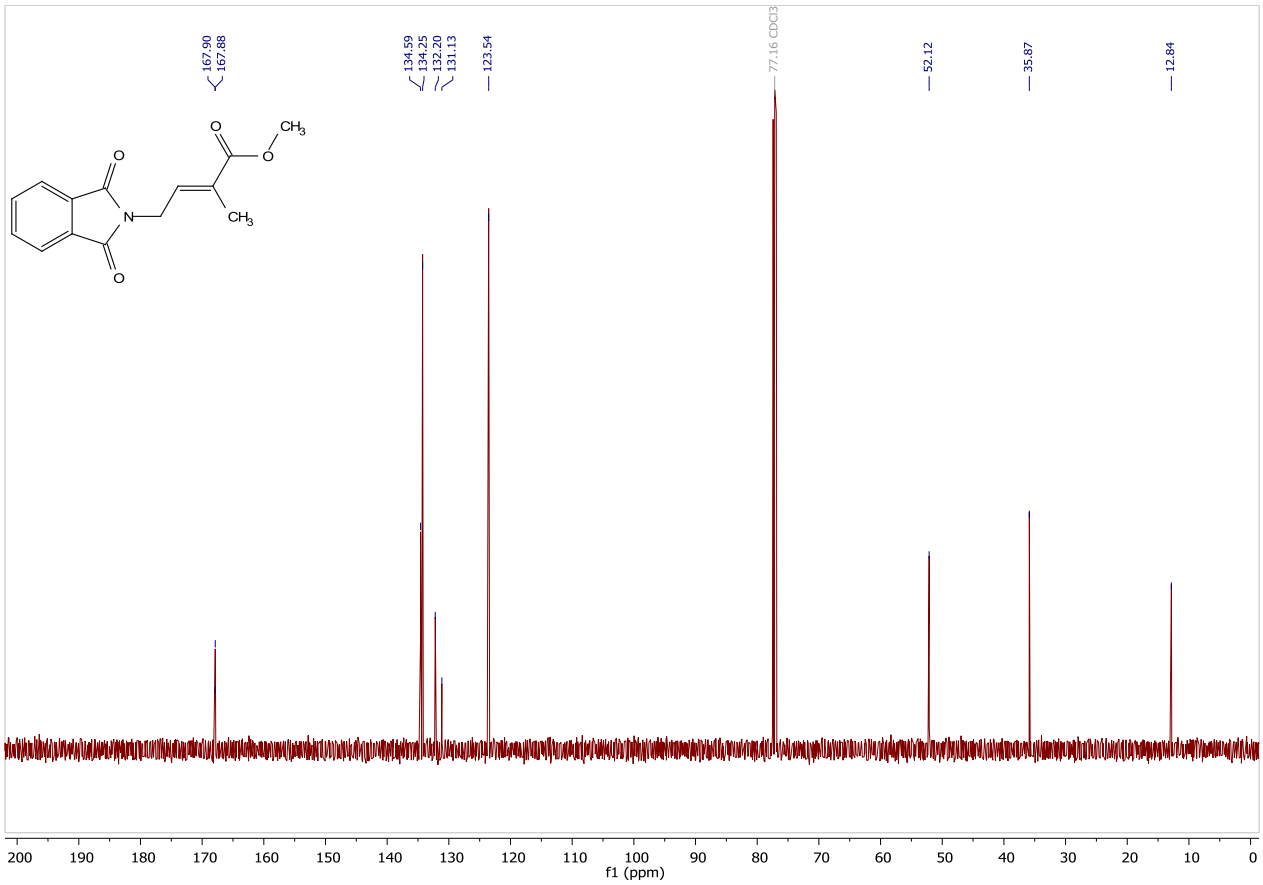
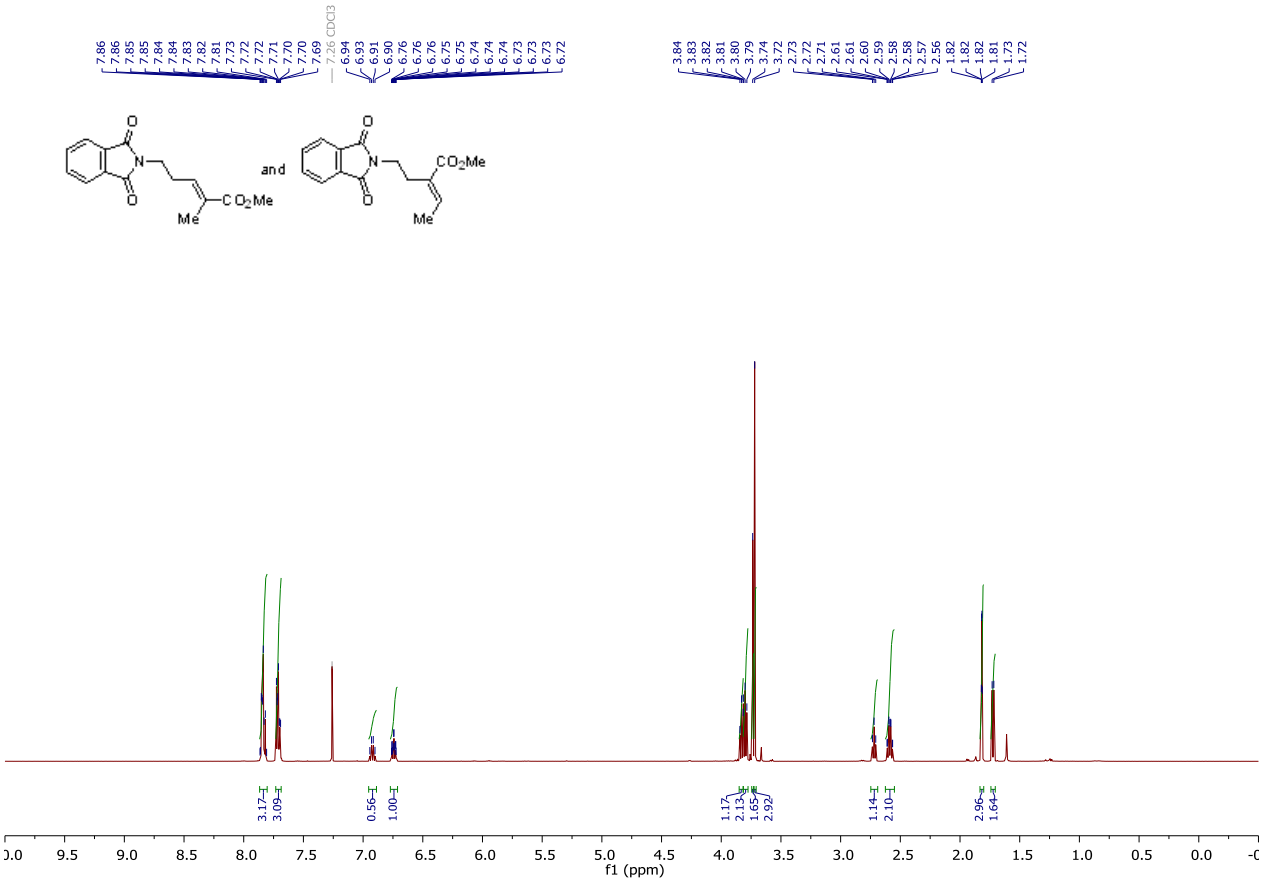
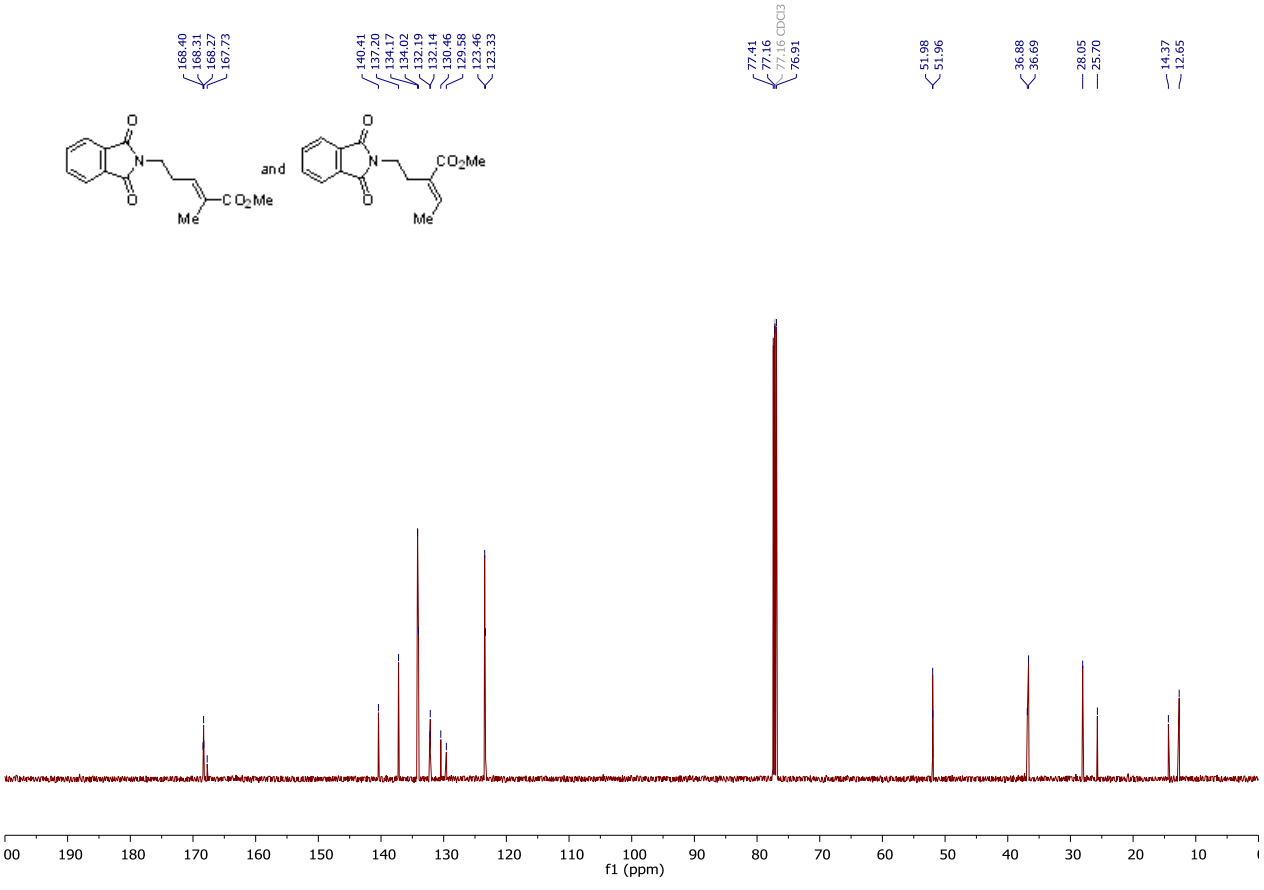
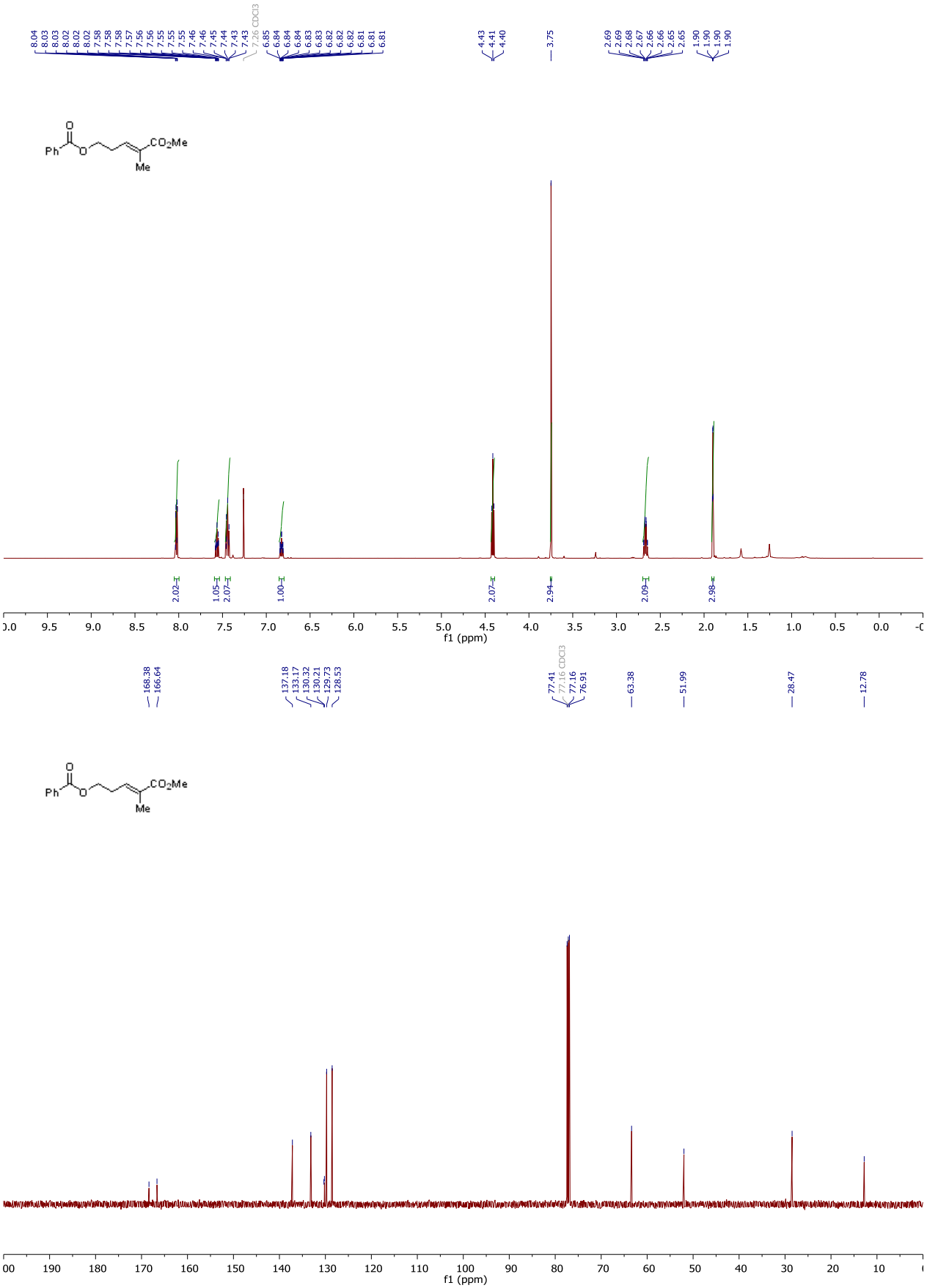
NOESY
AV400hd
f2 (ppm)
f1 (ppm)

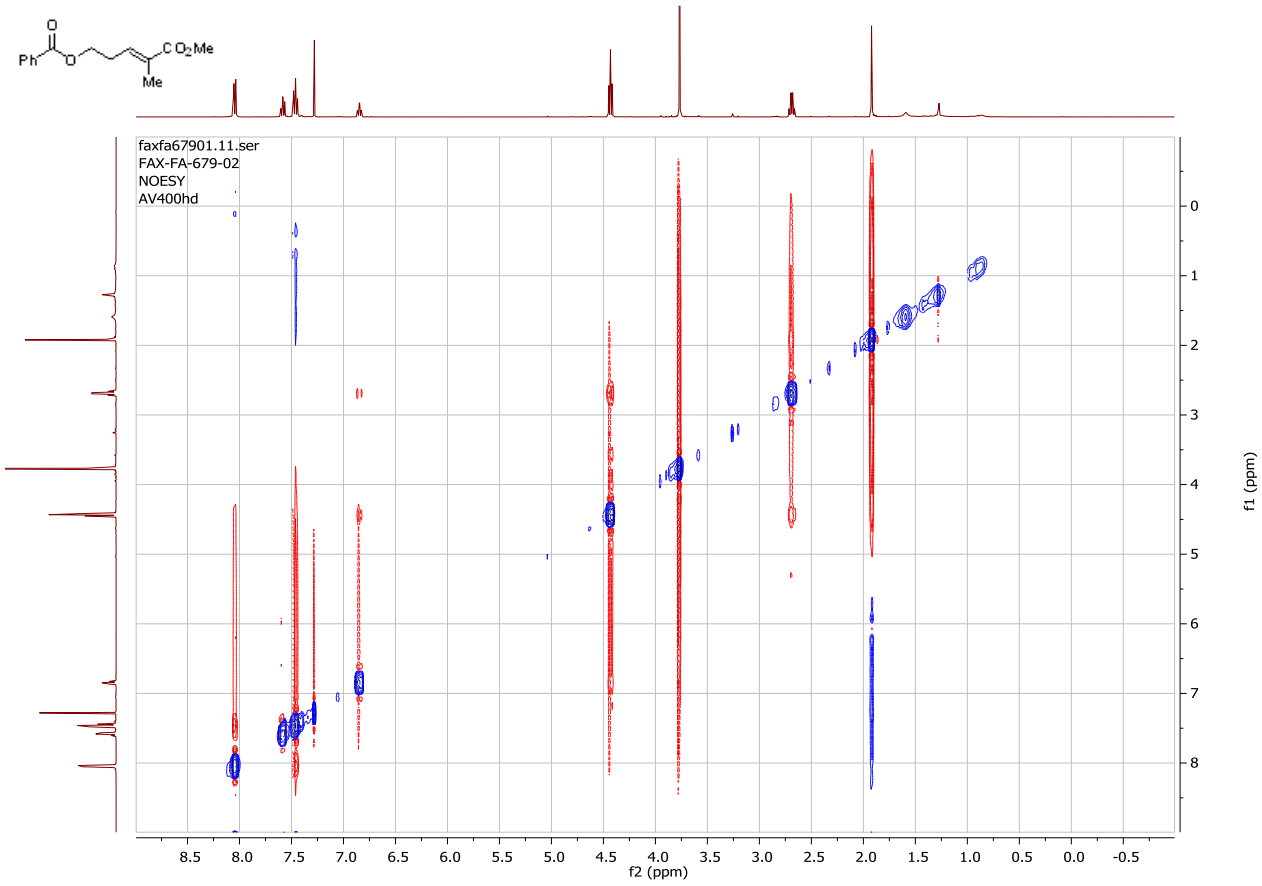

7.87
7.87
7.86
7.86
7.85
7.85
7.84
7.84
7.75
7.74
7.74
7.73
7.72
7.72
7.71
7.71
7.26 CDCl3
6.68
6.68
6.67
6.67
6.67
6.66
6.66
6.66
6.65
6.65
6.65
6.64
4.45
4.44
4.43
4.43
3.72
2.03
2.03
2.03
2.03
O
O
CH3
O
O
N
CH3
O
2.01
2.06
0.97
2.06
3.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.90
167.88
134.59
134.25
132.20
131.13
123.54
77.16 CDCl3
52.12
35.87
12.84
O
O
CH3
O
O
N
CH3
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.86
7.86
7.85
7.85
7.84
7.84
7.83
7.82
7.81
7.73
7.72
7.72
7.71
7.70
7.70
7.69
7.26 CDCl3
6.94
6.93
6.91
6.90
6.76
6.76
6.76
6.75
6.75
6.74
6.74
6.74
6.73
6.73
6.72
3.84
3.83
3.82
3.81
3.80
3.79
3.74
3.72
2.73
2.72
2.71
2.61
2.61
2.60
2.59
2.58
2.58
2.57
2.56
1.82
1.82
1.82
1.81
1.73
1.72
and
CO2Me
Me
CO2Me
Me
3.17
3.09
0.56
1.00
1.17
2.13
1.65
2.92
1.14
2.10
2.96
1.64
f1 (ppm)


168.40
168.31
168.27
167.73
140.41
137.20
134.17
134.02
132.19
132.14
130.46
129.58
123.46
123.33
77.41
77.16
77.16 CDCl3
76.91
51.98
51.96
36.88
36.69
28.05
25.70
14.37
12.65
and
CO2Me
Me
CO2Me
Me
f1 (ppm)


8.04 8.03 8.03 8.02 8.02 8.02 8.02 7.58 7.58 7.58 7.57 7.56 7.56 7.55 7.55 7.55 7.46 7.46 7.45 7.44 7.43 7.43 7.26 CDCl3
6.85 6.84 6.84 6.84 6.84 6.83 6.83 6.82 6.82 6.82 6.81 6.81 6.81
4.43 4.41 4.40
3.75
2.69 2.69 2.68 2.67 2.66 2.66 2.65 2.65
1.90 1.90 1.90 1.90
Ph
O
O
CO2Me
Me
2.02 1.05 2.07 1.00 2.07 2.94 2.09 2.98
f1 (ppm)
168.38 166.64
137.18 133.17 130.32 130.21 129.73 128.53
77.41 77.16 CDCl3 77.16 76.91
63.38
51.99
28.47
12.78
f1 (ppm)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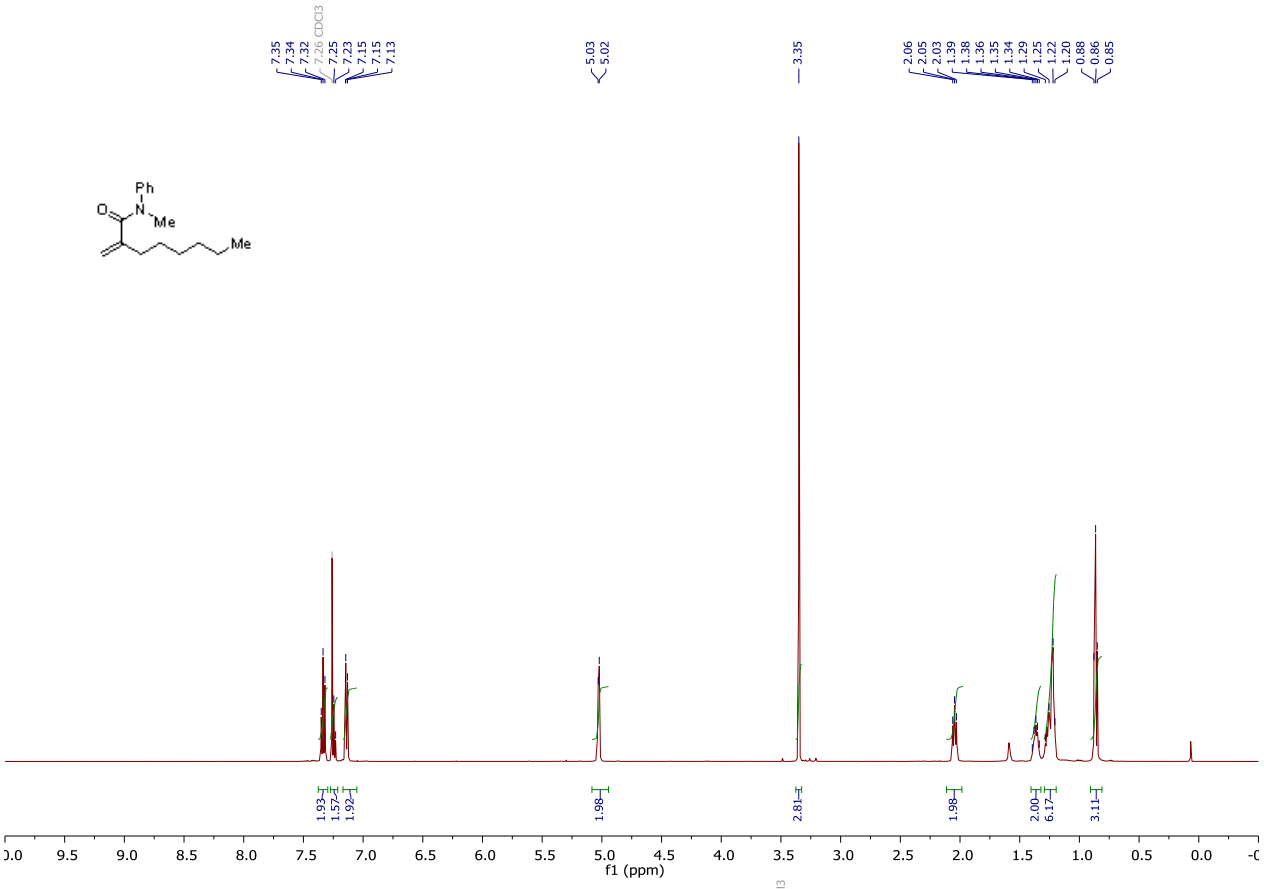
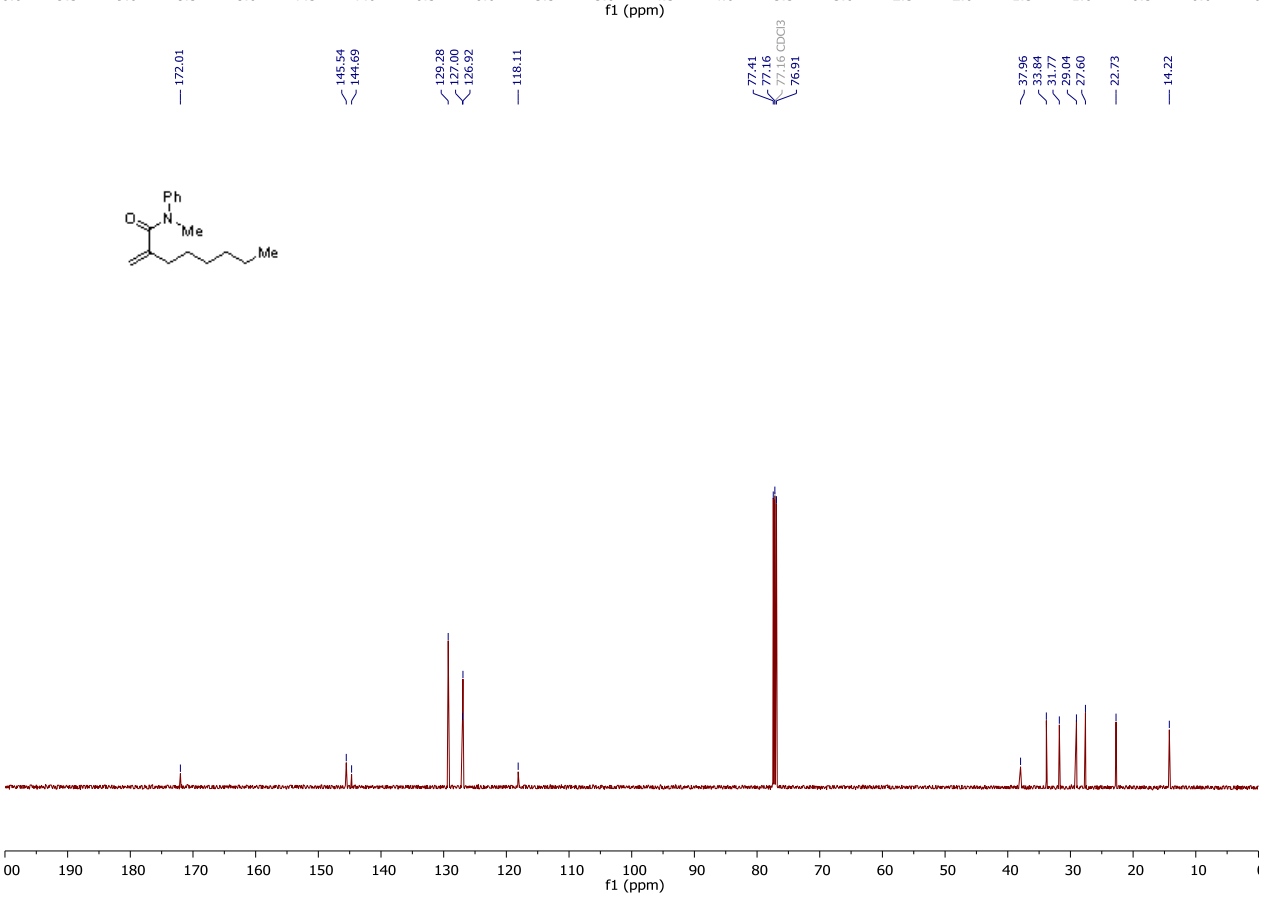
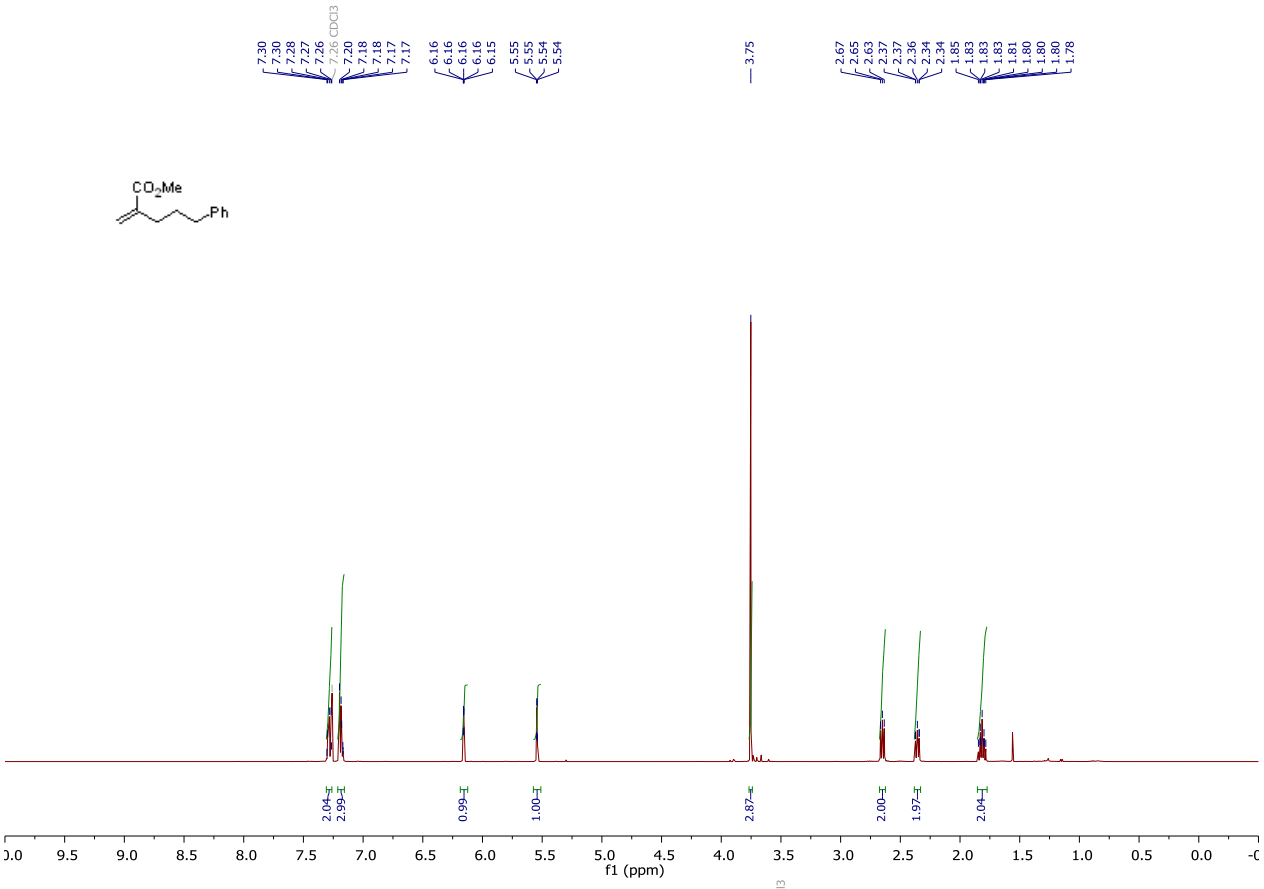
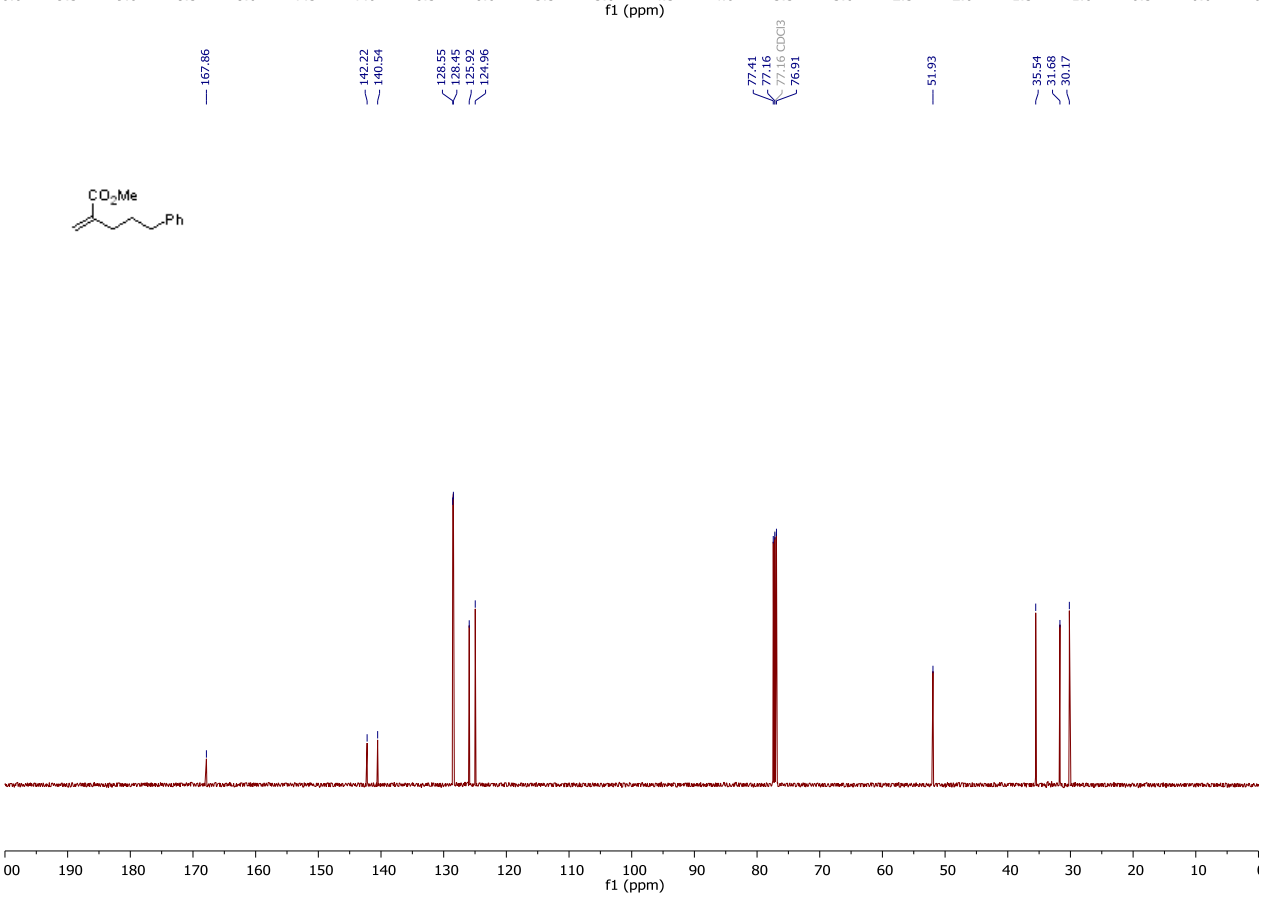
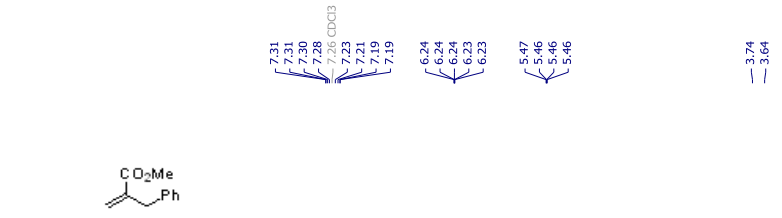
FAX-FA-679-02
NOESY
AV400hd
f2 (ppm)
f1 (ppm)


7.35
7.34
7.32
7.26 CDCl3
7.25
7.23
7.15
7.15
7.13
5.03
5.02
3.35
2.06
2.05
2.03
1.39
1.38
1.36
1.35
1.34
1.29
1.25
1.22
1.20
0.88
0.86
0.85
Ph
N
Me
O
Me
1.93
1.57
1.92
1.98
2.81
1.98
2.00
6.17
3.11
f1 (ppm)

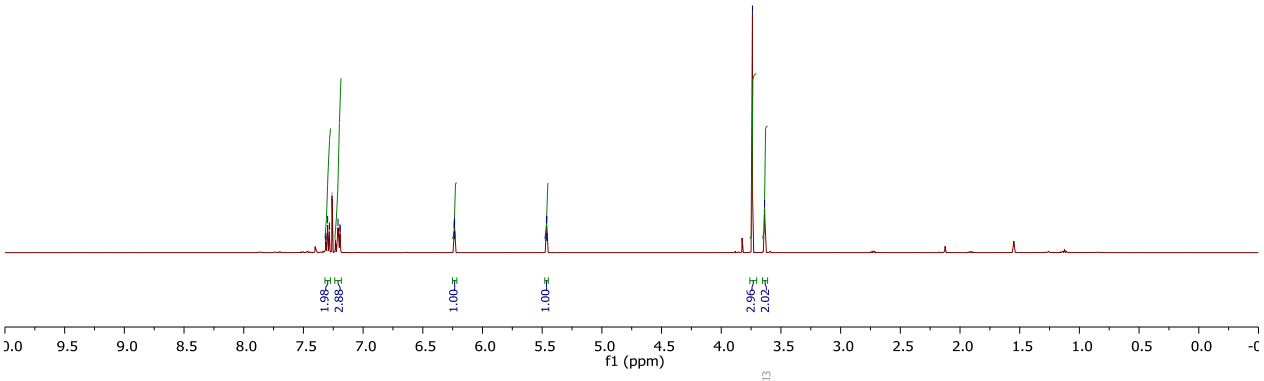

172.01
145.54
144.69
129.28
127.00
126.92
118.11
77.41
77.16
77.16 CDCl3
76.91
37.96
33.84
31.77
29.04
27.60
22.73
14.22
Ph
N
Me
O
Me
f1 (ppm)

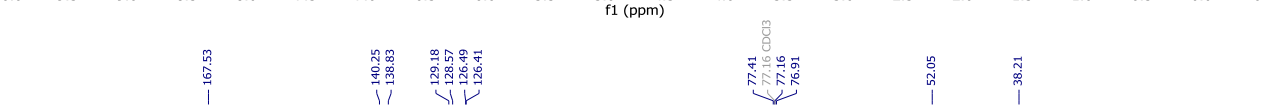

7.30
7.30
7.28
7.27
7.26
7.26 CDCl3
7.20
7.18
7.18
7.17
7.17
6.16
6.16
6.16
6.16
6.15
5.55
5.55
5.54
5.54
3.75
2.67
2.65
2.63
2.37
2.37
2.36
2.34
2.34
1.85
1.83
1.83
1.83
1.81
1.80
1.80
1.80
1.78
CO2Me
Ph
2.04
2.99
0.99
1.00
2.87
2.00
1.97
2.04
f1 (ppm)


167.86
142.22
140.54
128.55
128.45
125.92
124.96
77.41
77.16
77.16 CDCl3
76.91
51.93
35.54
31.68
30.17
CO2Me
Ph
f1 (ppm)

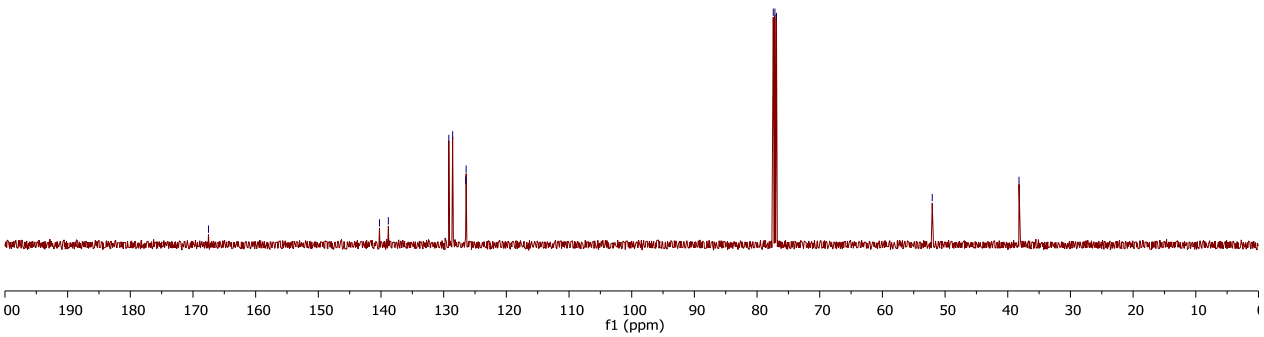

7.31
7.31
7.30
7.28
7.26 CDCl3
7.23
7.21
7.19
7.19
6.24
6.24
6.24
6.23
6.23
5.47
5.46
5.46
5.46
3.74
3.64

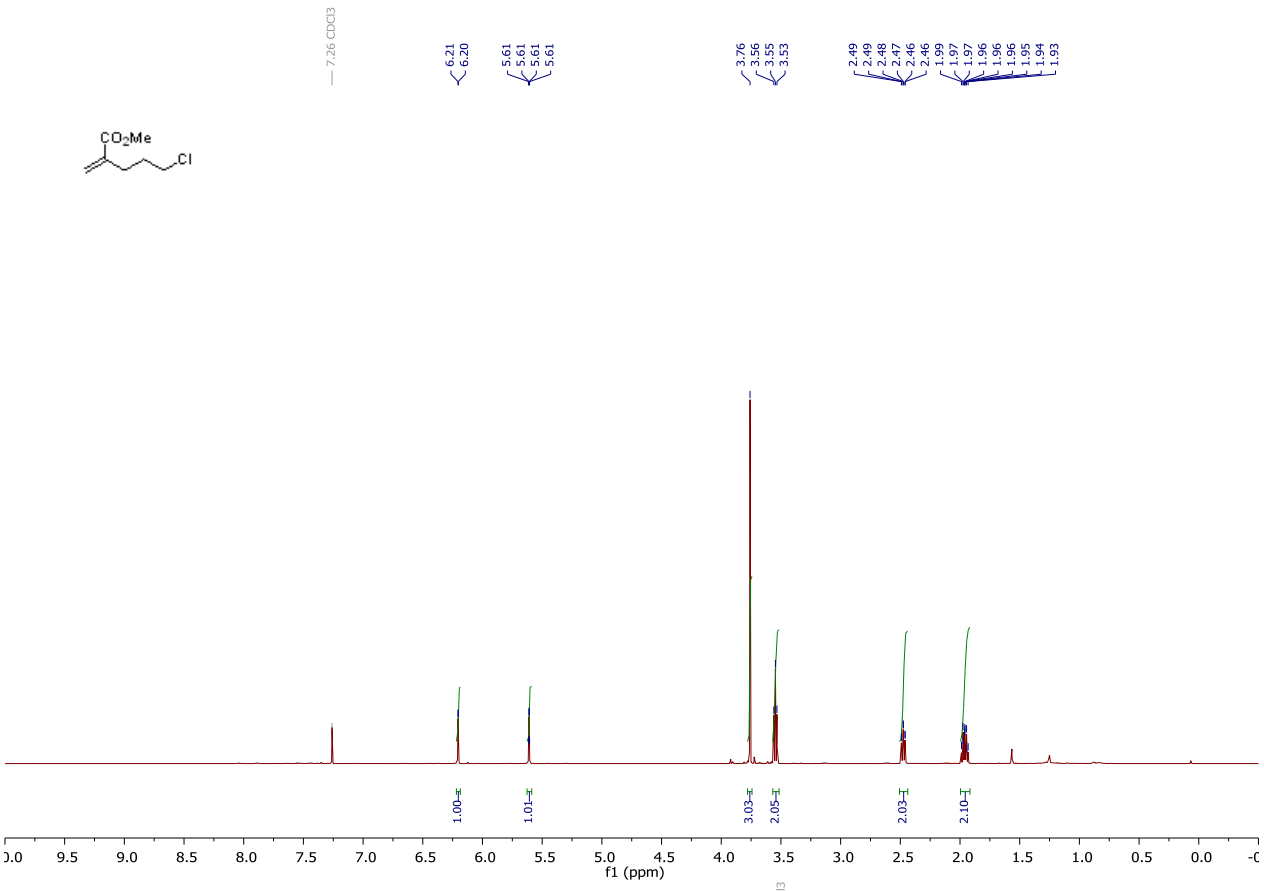
CO2Me
Ph

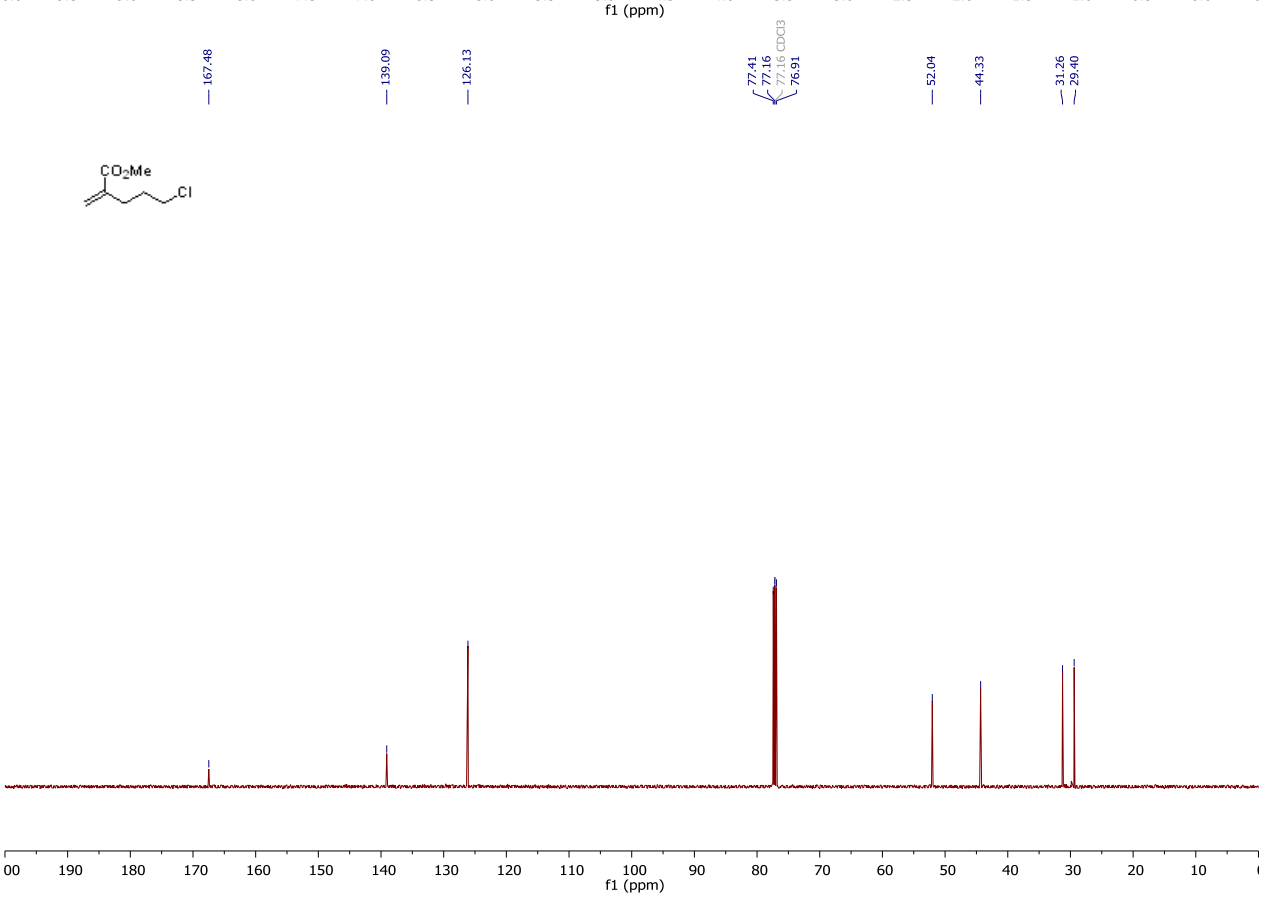

1.98
2.88
1.00
1.00
2.96
2.02
f1 (ppm)

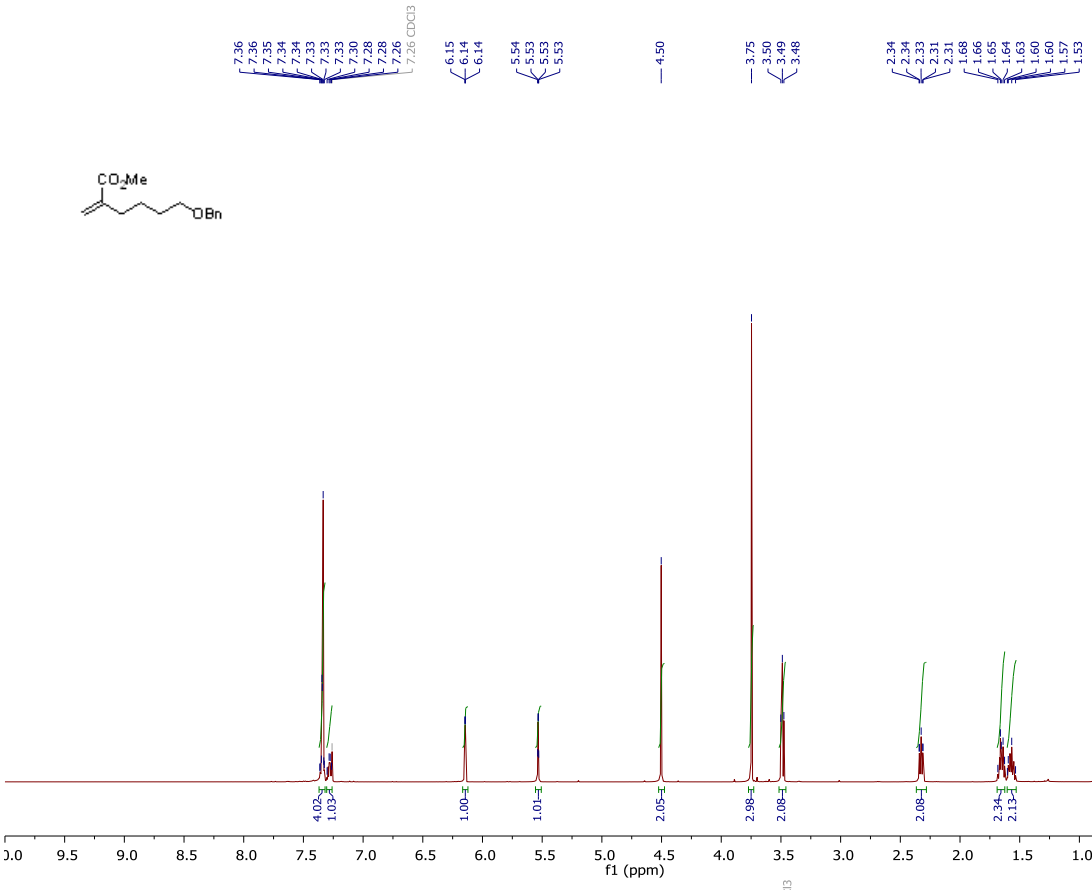

167.53
140.25
138.83
129.18
128.57
126.49
126.41
77.41
77.16 CDCl3
77.16
76.91
52.05
38.21


CO2Me
Ph


f1 (ppm)


7.26 CDCl3
6.21
6.20
5.61
5.61
5.61
5.61
3.76
3.56
3.55
3.53
2.49
2.49
2.48
2.47
2.46
2.46
1.99
1.97
1.97
1.96
1.96
1.96
1.95
1.94
1.93
CO2Me
Cl
1.00
1.01
3.03
2.05
2.03
2.10
f1 (ppm)


167.48
139.09
126.13
77.41
77.16
77.16 CDCl3
76.91
52.04
44.33
31.26
29.40
CO2Me
Cl
f1 (ppm)


7.36
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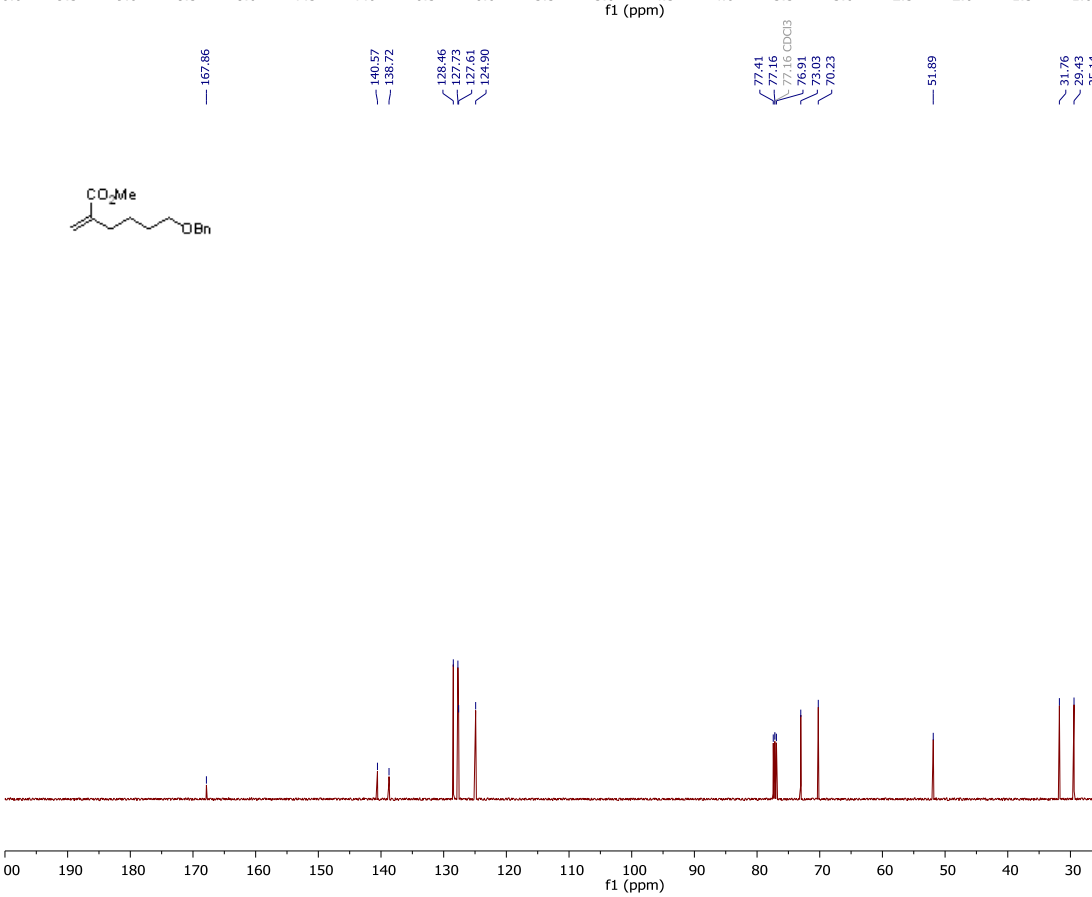
7.34
7.33
7.33
7.33
7.30
7.28
7.28
7.26
7.26 CDCl3
6.15
6.14
6.14
5.54
5.53
5.53
5.53
4.50
3.75
3.50
3.49
3.48
2.34
2.34
2.33
2.31
2.31
1.68
1.66
1.65
1.64
1.63
1.60
1.60
1.57
1.53
CO2Me
OBn
4.02
1.03
1.00
1.01
2.05
2.98
2.08
2.08
2.34
2.13
f1 (ppm)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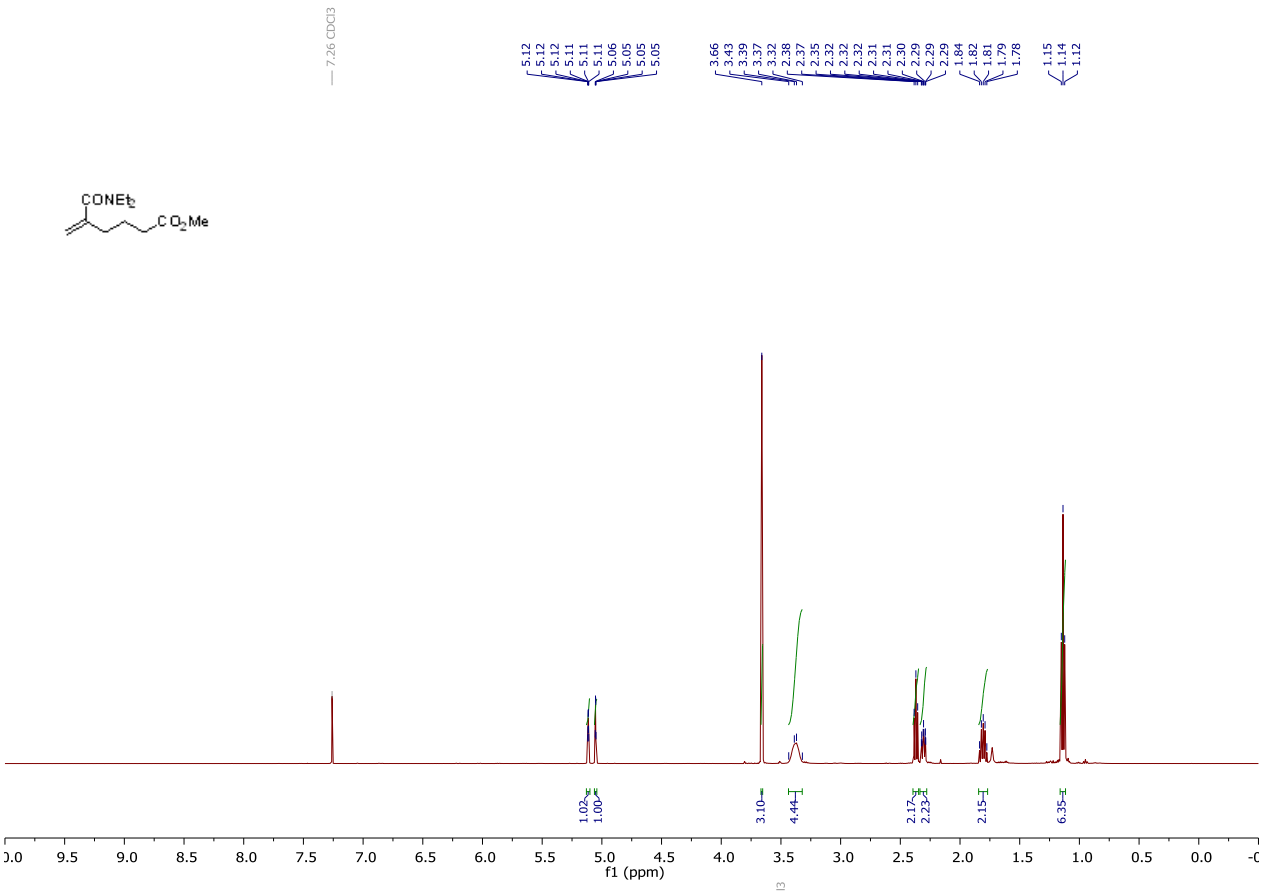
140.57
138.72
128.46
127.73
127.61
124.90
77.41
77.16
77.16 CDCl3
76.91
73.03
70.23
51.89
31.76
29.43
25.14
CO2Me
OBn
f1 (ppm)


7.26 CDCl3
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5.12
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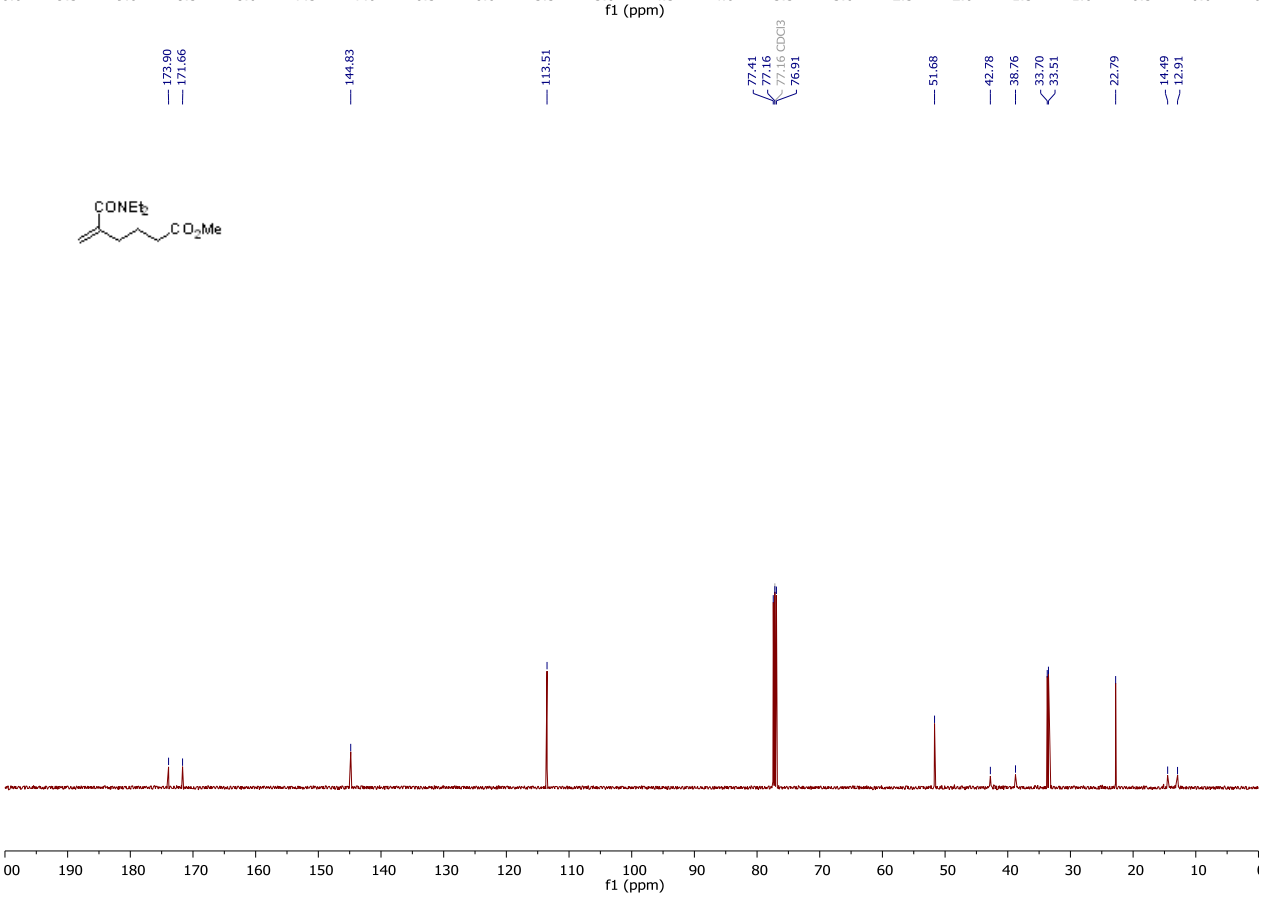
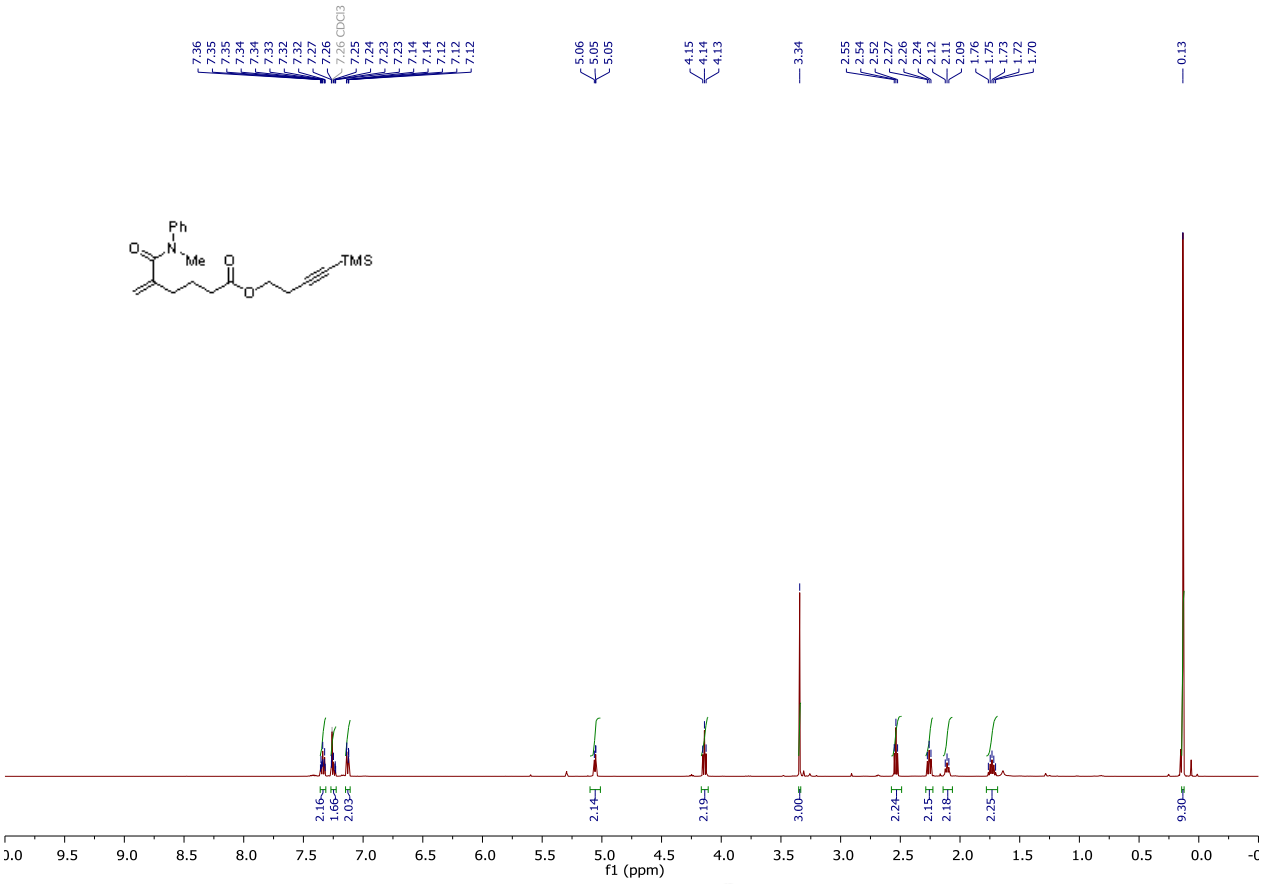
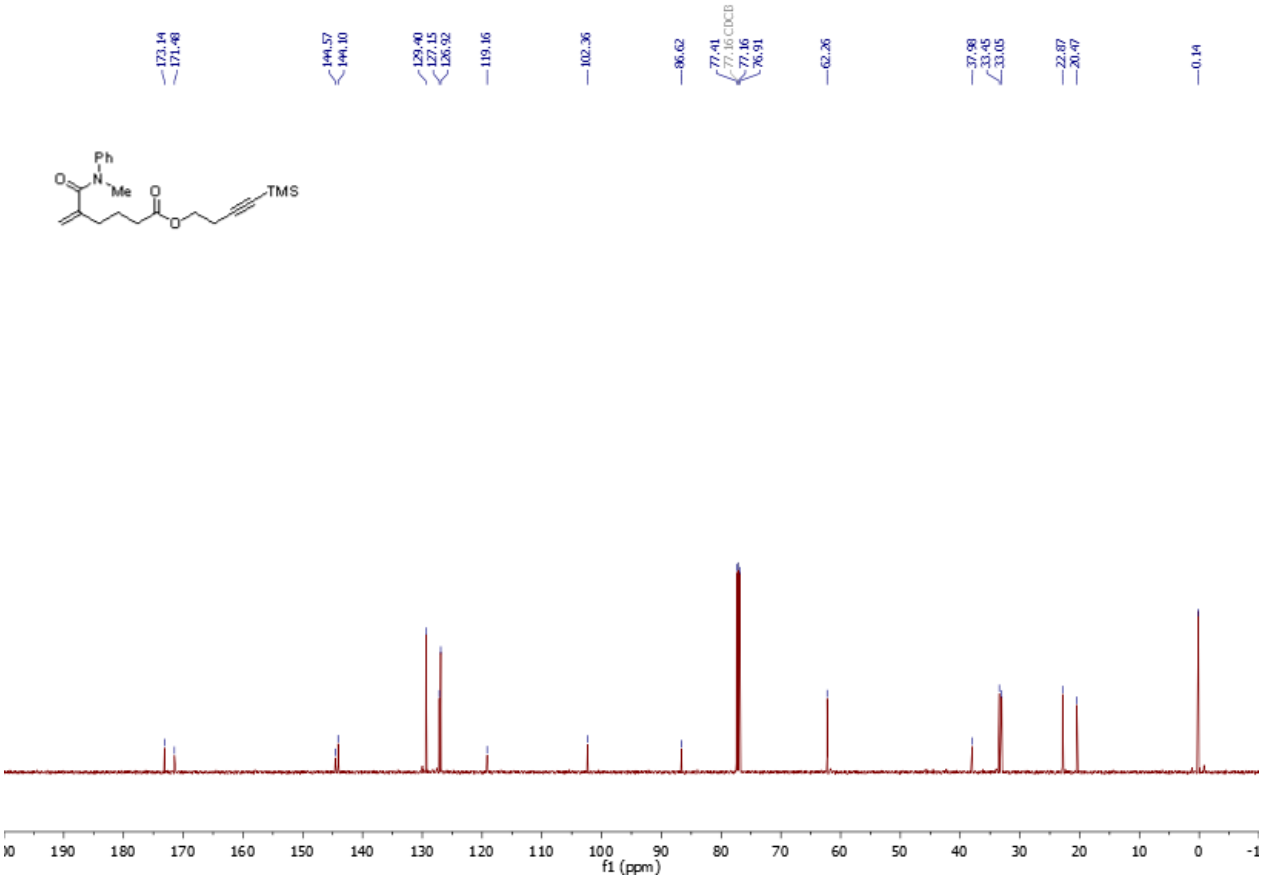
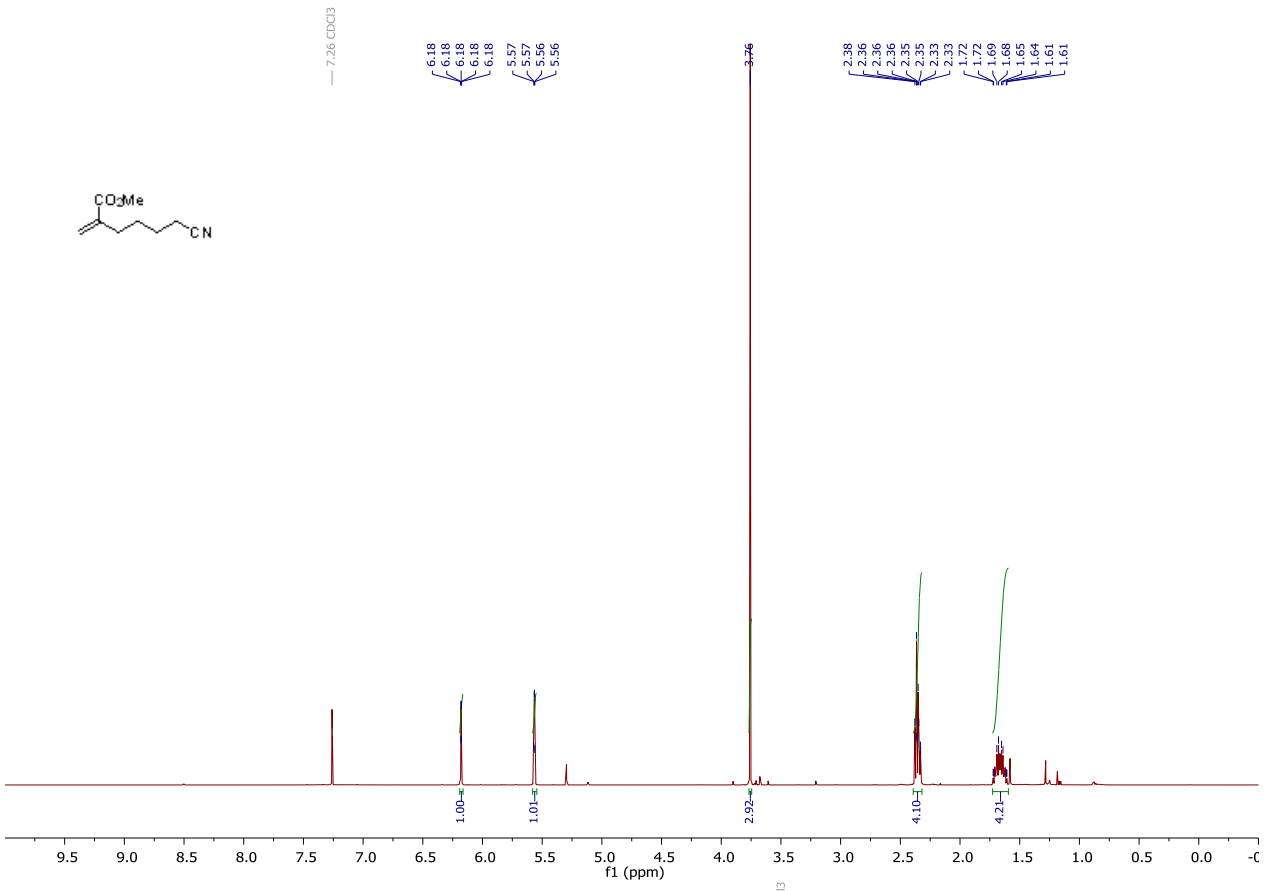
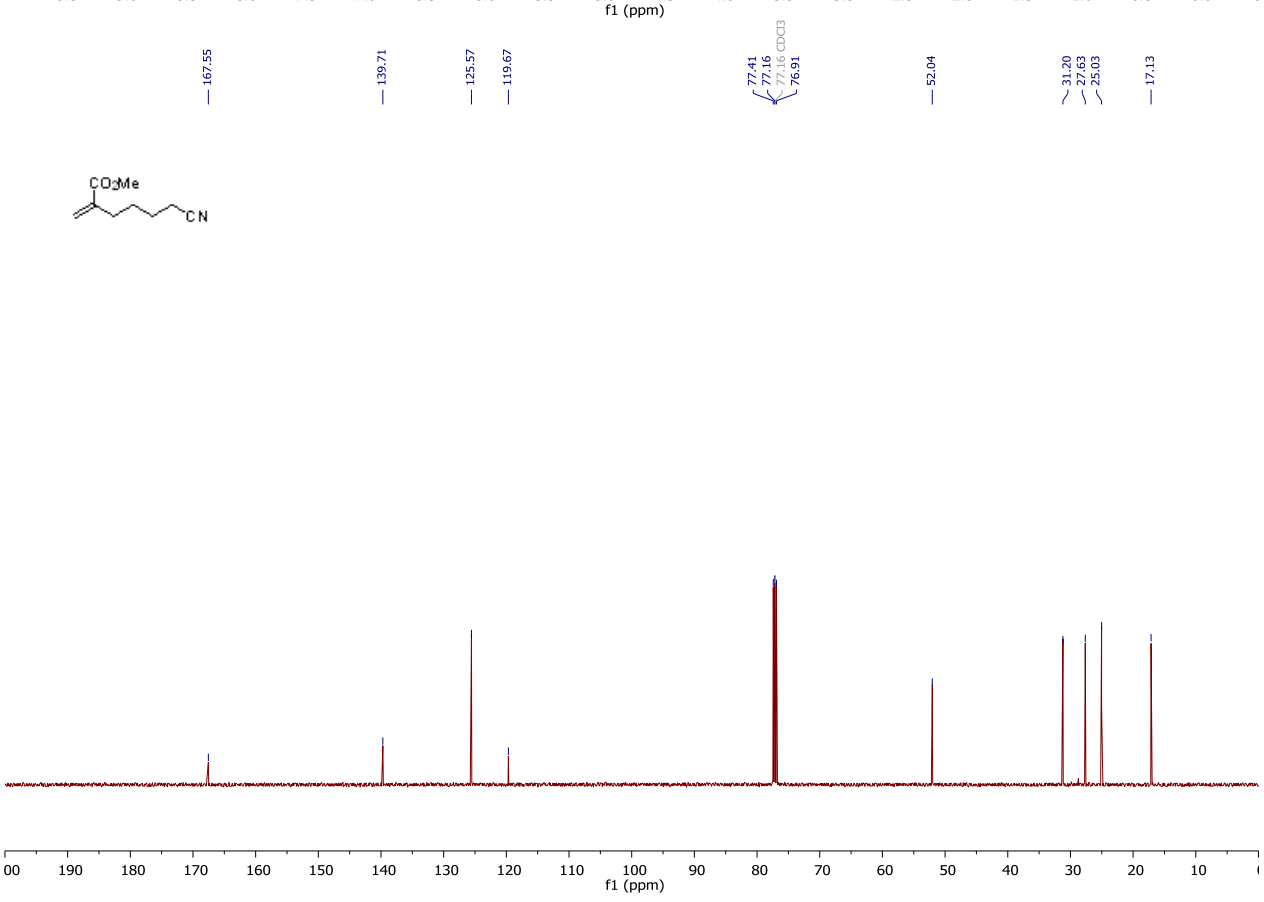
5.11
5.11
5.11
5.06
5.05
5.05
5.05
3.66
3.43
3.39
3.37
3.32
2.38
2.37
2.35
2.32
2.32
2.32
2.31
2.31
2.30
2.29
2.29
2.29
1.84
1.82
1.81
1.79
1.78
1.15
1.14
1.12
CONEt2
CO2Me
1.02
1.00
3.10
4.44
2.17
2.23
2.15
6.35
f1 (ppm)

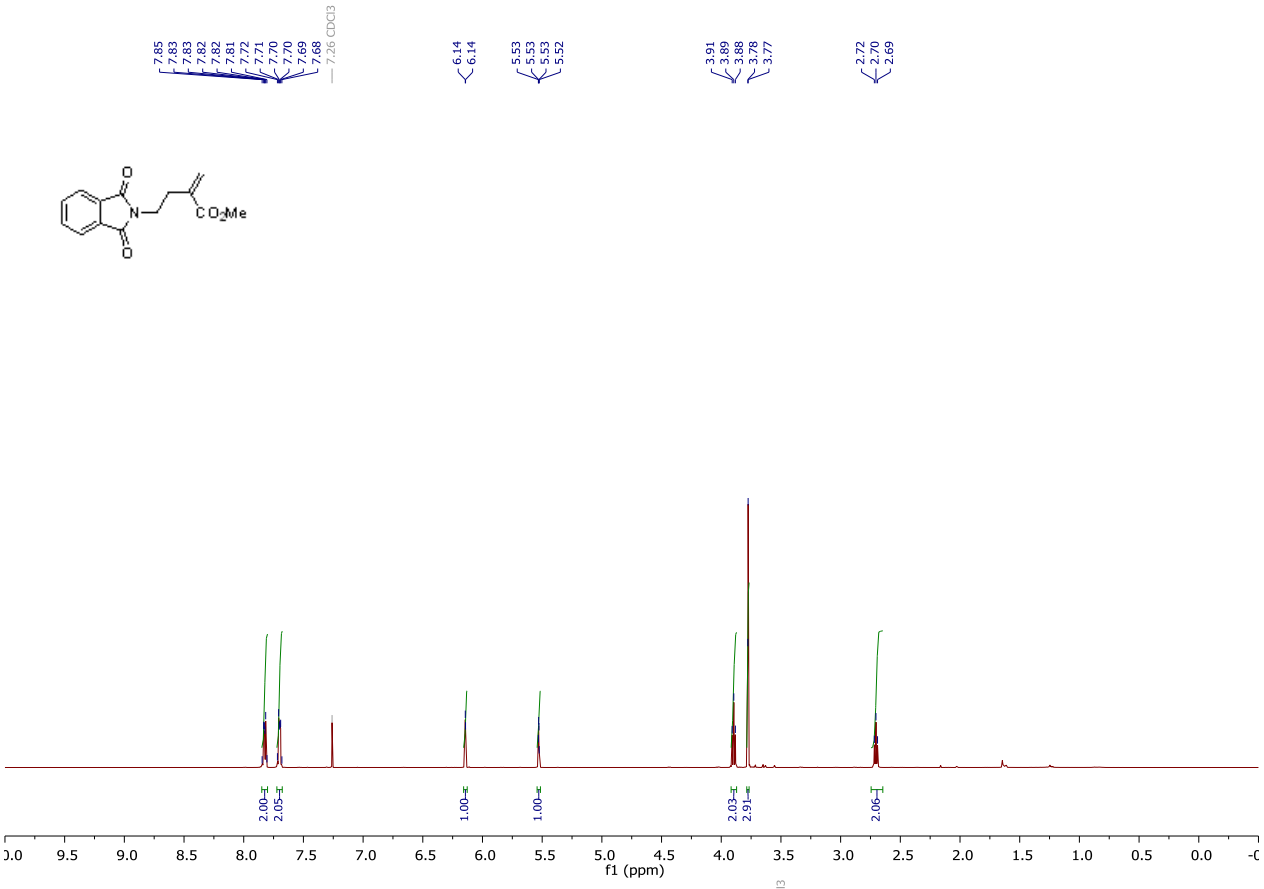

173.90
171.66
144.83
113.51
77.41
77.16
77.16 CDCl3
76.91
51.68
42.78
38.76
33.70
33.51
22.79
14.49
12.91
CONEt2
CO2Me
f1 (ppm)

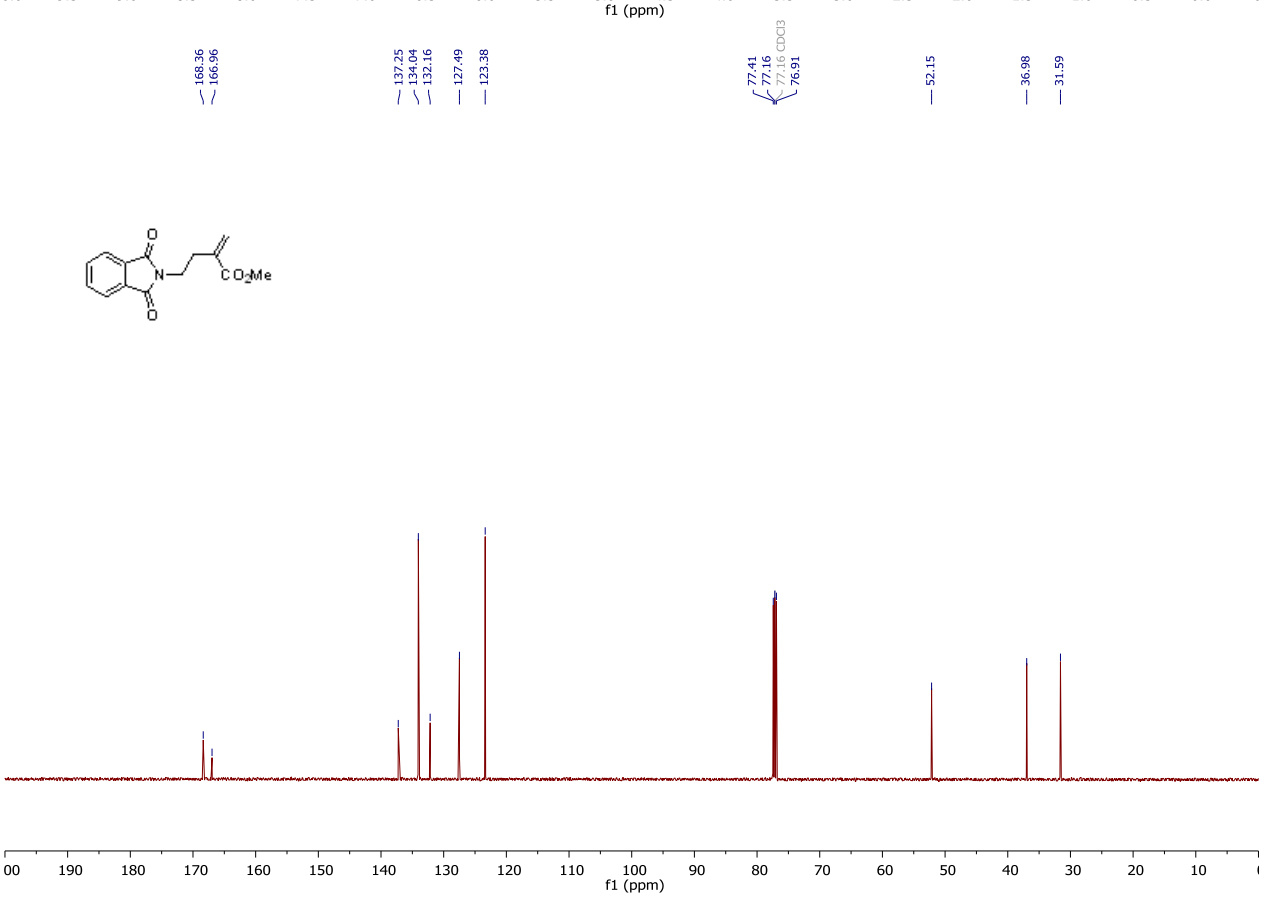

Ph
N
Me
O
O
O
TMS
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.27
7.26
7.26 CDCl3
7.25
7.24
7.23
7.23
7.14
7.14
7.12
7.12
7.12
5.06
5.05
5.05
4.15
4.14
4.13
3.34
2.55
2.54
2.52
2.27
2.26
2.24
2.12
2.11
2.09
1.76
1.75
1.73
1.72
1.70
0.13
2.16
1.66
2.03
2.14
2.19
3.00
2.24
2.15
2.18
2.25
9.30
f1 (ppm)

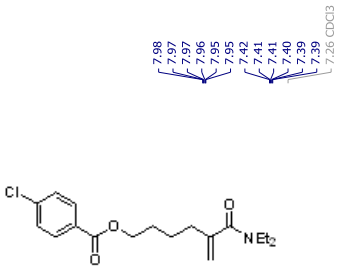

Ph
N
Me
O
O
O
TMS
173.14
171.48
144.57
144.10
129.40
127.15
126.92
119.16
102.36
86.62
77.41
77.16 CDCl3
77.16
76.91
62.26
37.98
33.45
33.05
22.87
20.47
0.14
f1 (ppm)

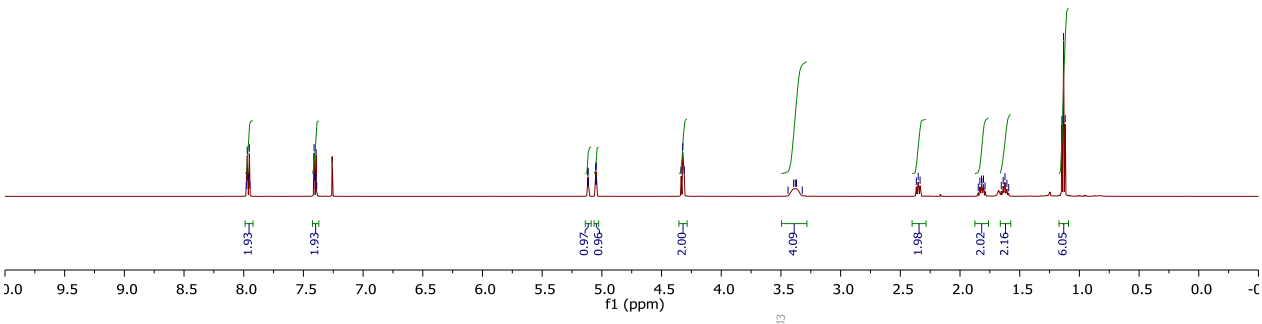

7.26 CDCl3
6.18
6.18
6.18
6.18
6.18
5.57
5.57
5.56
5.56
5.56
3.76
2.38
2.36
2.36
2.36
2.35
2.35
2.33
2.33
1.72
1.72
1.69
1.68
1.65
1.64
1.61
1.61
CO2Me
CN
1.00
1.01
2.92
4.10
4.21
f1 (ppm)

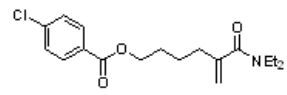

167.55
139.71
125.57
119.67
77.41
77.16
77.16 CDCl3
76.91
52.04
31.20
27.63
25.03
17.13
CO2Me
CN
f1 (ppm)

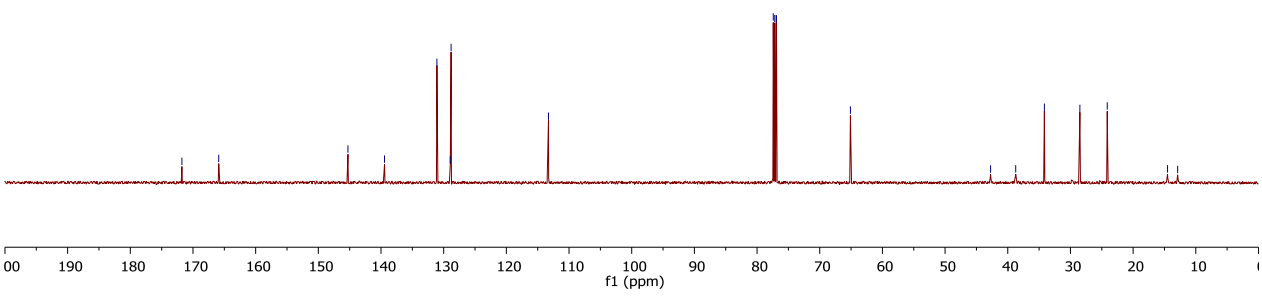

7.85
7.83
7.83
7.82
7.82
7.81
7.72
7.71
7.70
7.70
7.69
7.68
7.26 CDCl3
6.14
6.14
5.53
5.53
5.53
5.52
3.91
3.89
3.88
3.78
3.77
2.72
2.70
2.69
O
N
CO2Me
O
2.00
2.05
1.00
1.00
2.03
2.91
2.06
f1 (ppm)

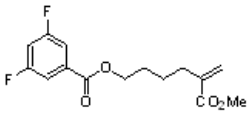

168.36
166.96
137.25
134.04
132.16
127.49
123.38
77.41
77.16
77.16 CDCl3
76.91
52.15
36.98
31.59
O
N
CO2Me
O
f1 (ppm)

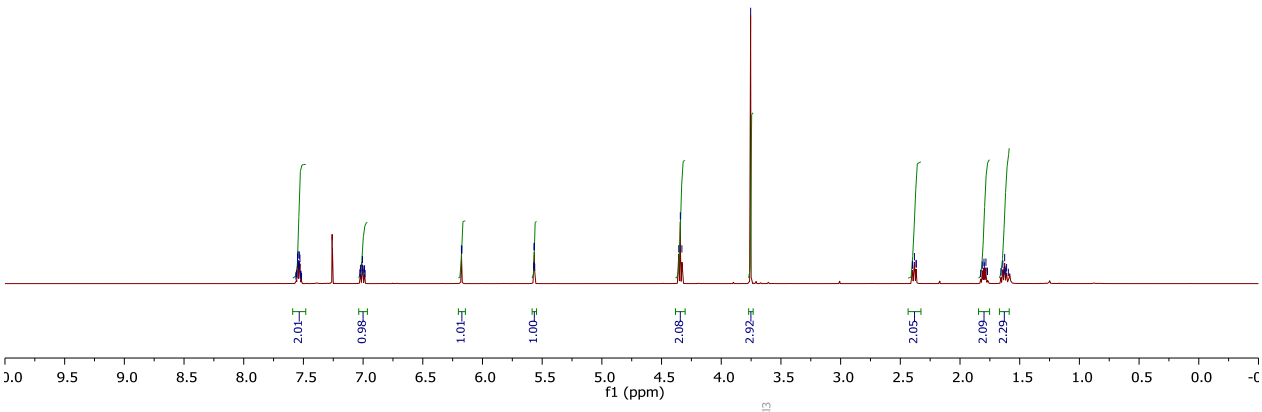


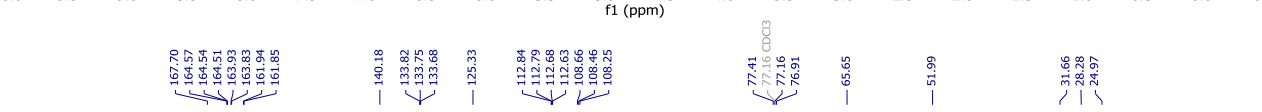


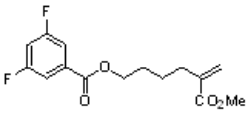


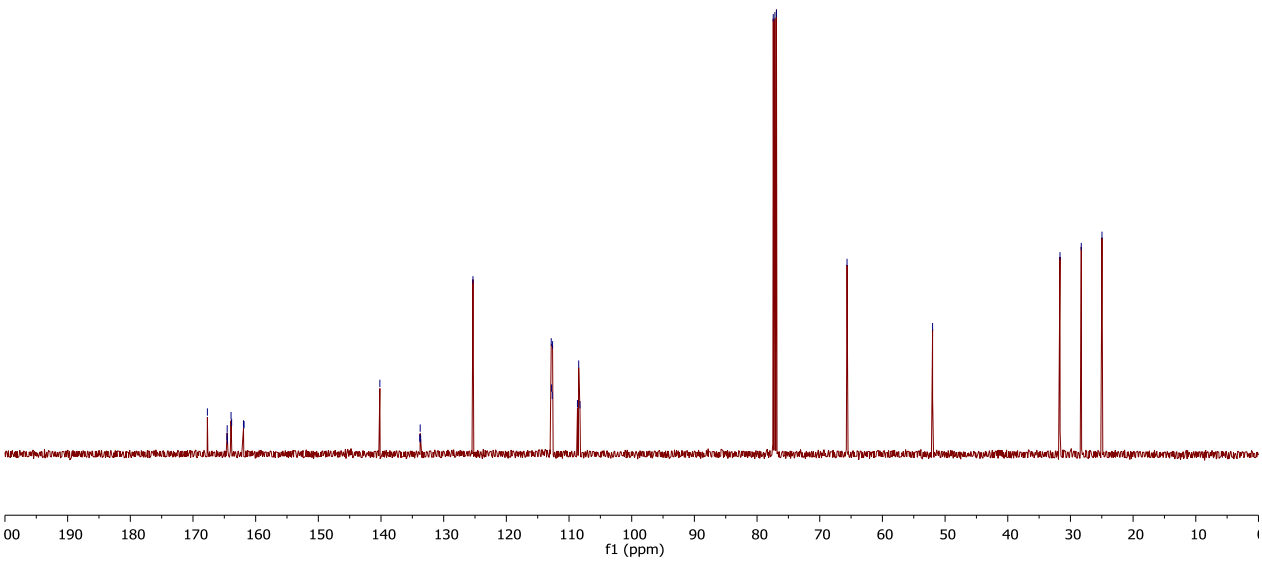


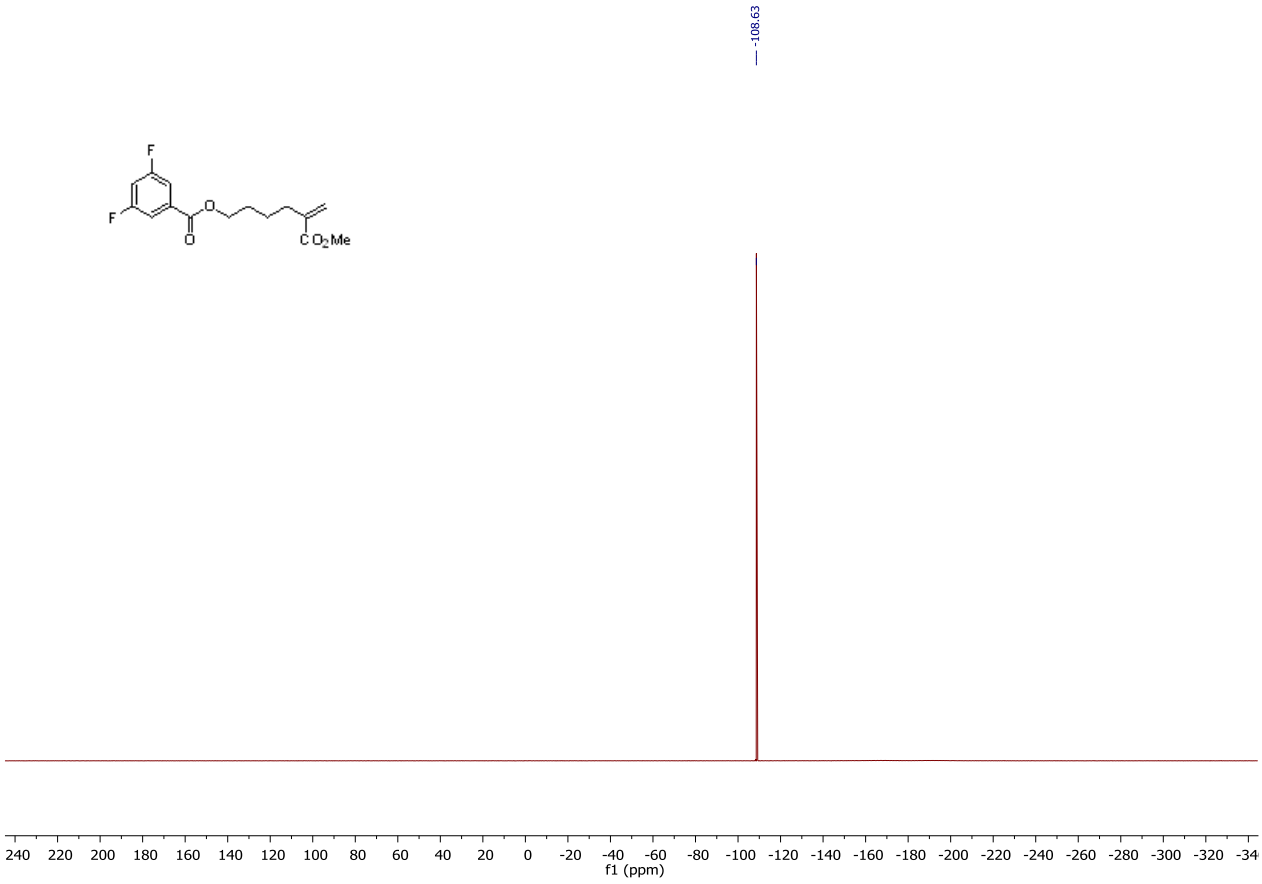


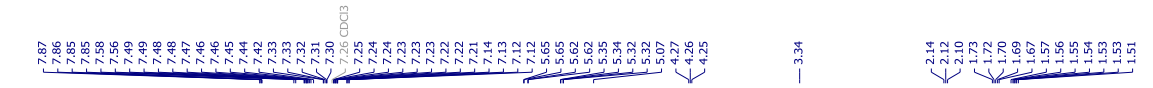


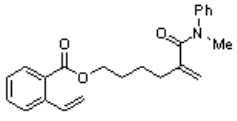


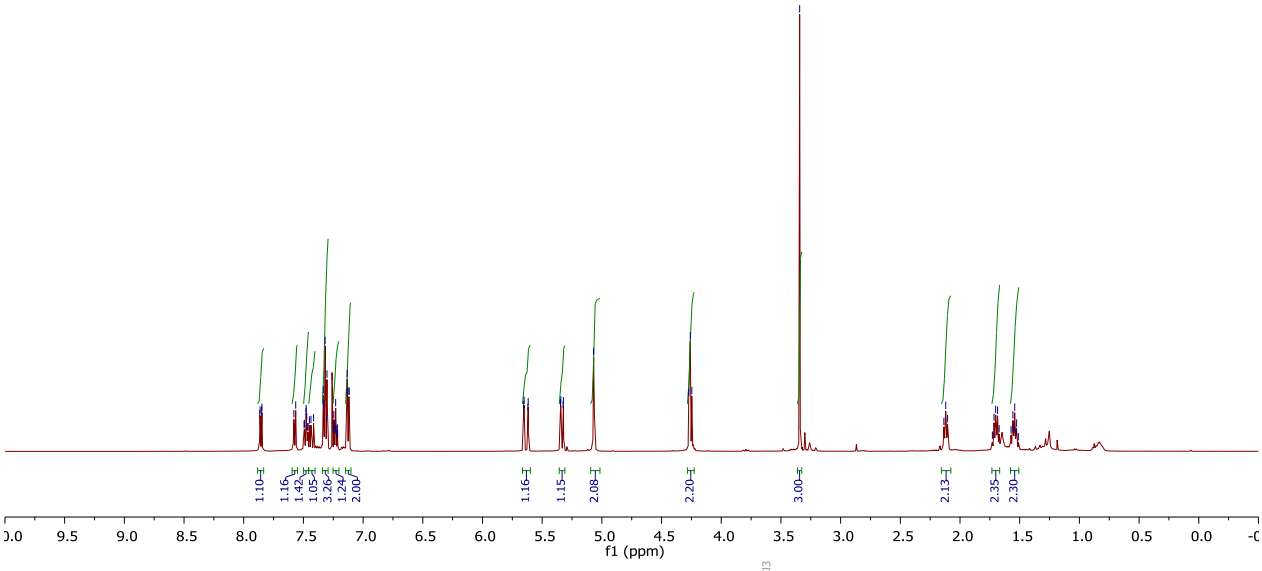


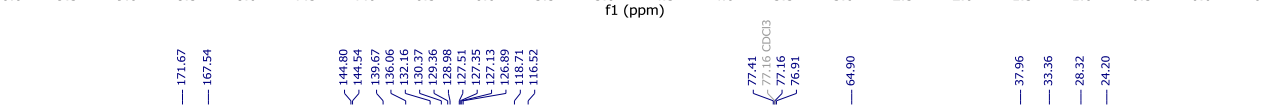


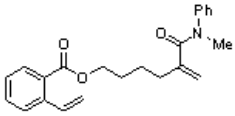

-108.63
F
F
O
O
CO2Me
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300 -320 -34
f1 (ppm)

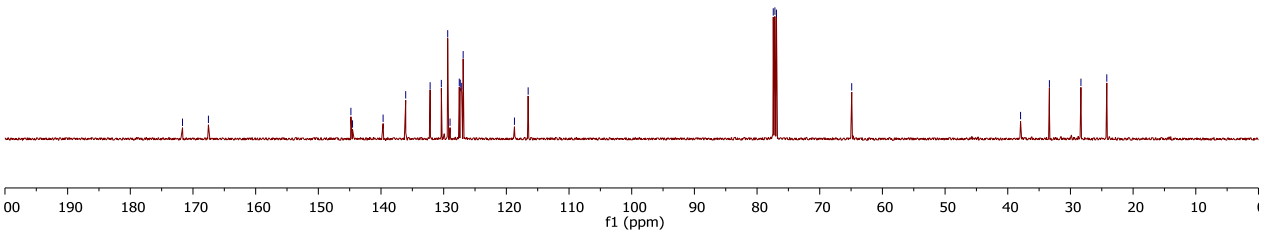

7.87
7.86
7.85
7.85
7.58
7.56
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.42
7.33
7.32
7.31
7.30
7.26 CDCl3
7.25
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
7.14
7.13
7.12
7.12
5.65
5.62
5.62
5.35
5.34
5.32
5.32
5.07
4.27
4.26
4.25
3.34
2.14
2.12
2.10
1.73
1.72
1.70
1.69
1.67
1.57
1.56
1.55
1.54
1.53
1.53
1.51

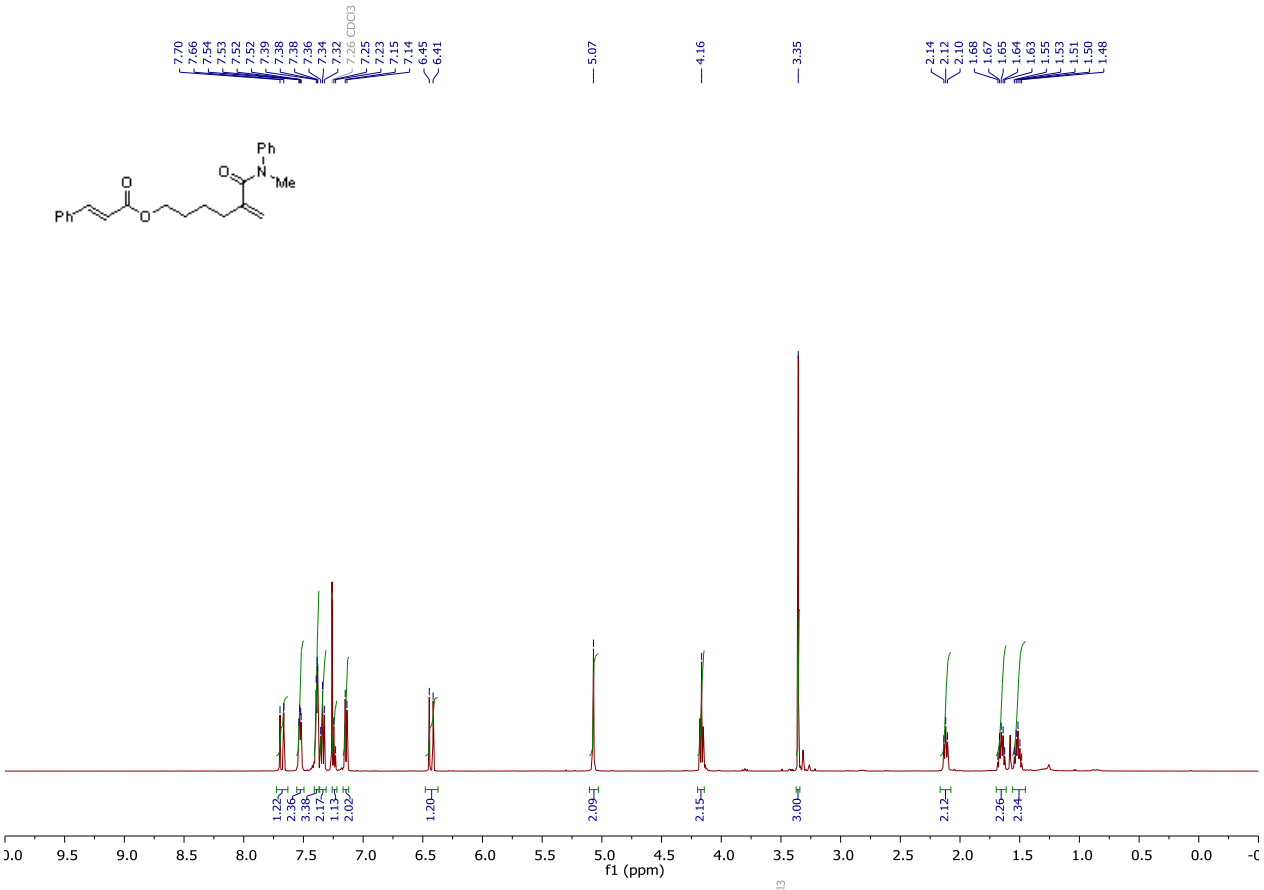

Ph
N
Me
O
O

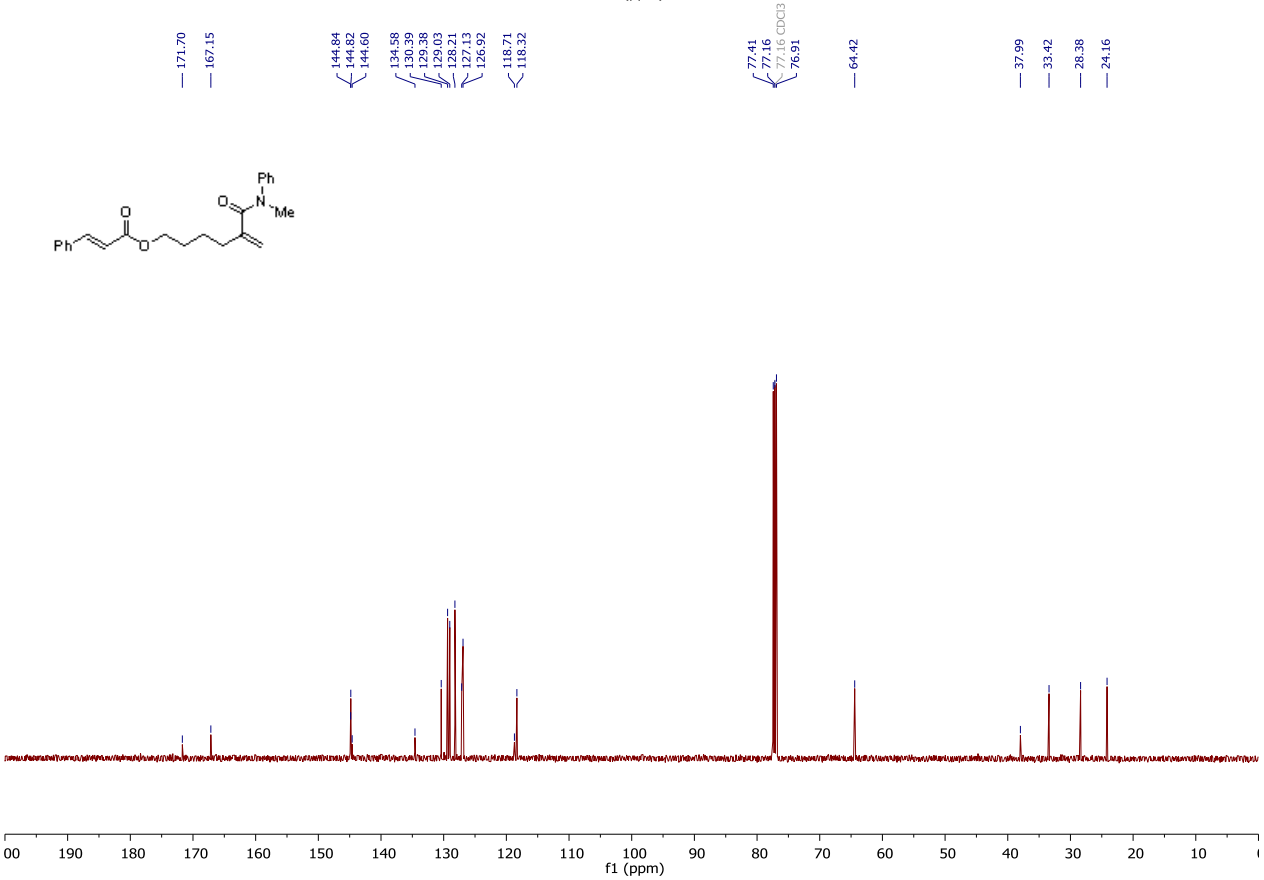

1.10
1.16
1.42
1.05
3.26
1.24
2.00
1.16
1.15
2.08
2.20
3.00
2.13
2.35
2.30
f1 (ppm)


171.67
167.54
144.80
144.54
139.67
136.06
132.16
130.37
129.36
128.98
127.51
127.35
127.13
126.89
118.71
116.52
77.41
77.16 CDCl3
76.91
64.90
37.96
33.36
28.32
24.20


Ph
N
Me
O
O


f1 (ppm)


7.70
7.66
7.54
7.53
7.52
7.52
7.39
7.38
7.38
7.36
7.34
7.32
7.26 CDCl3
7.25
7.23
7.15
7.14
6.45
6.41
5.07
4.16
3.35
2.14
2.12
2.10
1.68
1.67
1.65
1.64
1.63
1.55
1.53
1.51
1.50
1.48
Ph
N
Me
O
O
Ph
1.22
2.36
3.38
2.17
1.13
2.02
1.20
2.09
2.15
3.00
2.12
2.26
2.34
f1 (ppm)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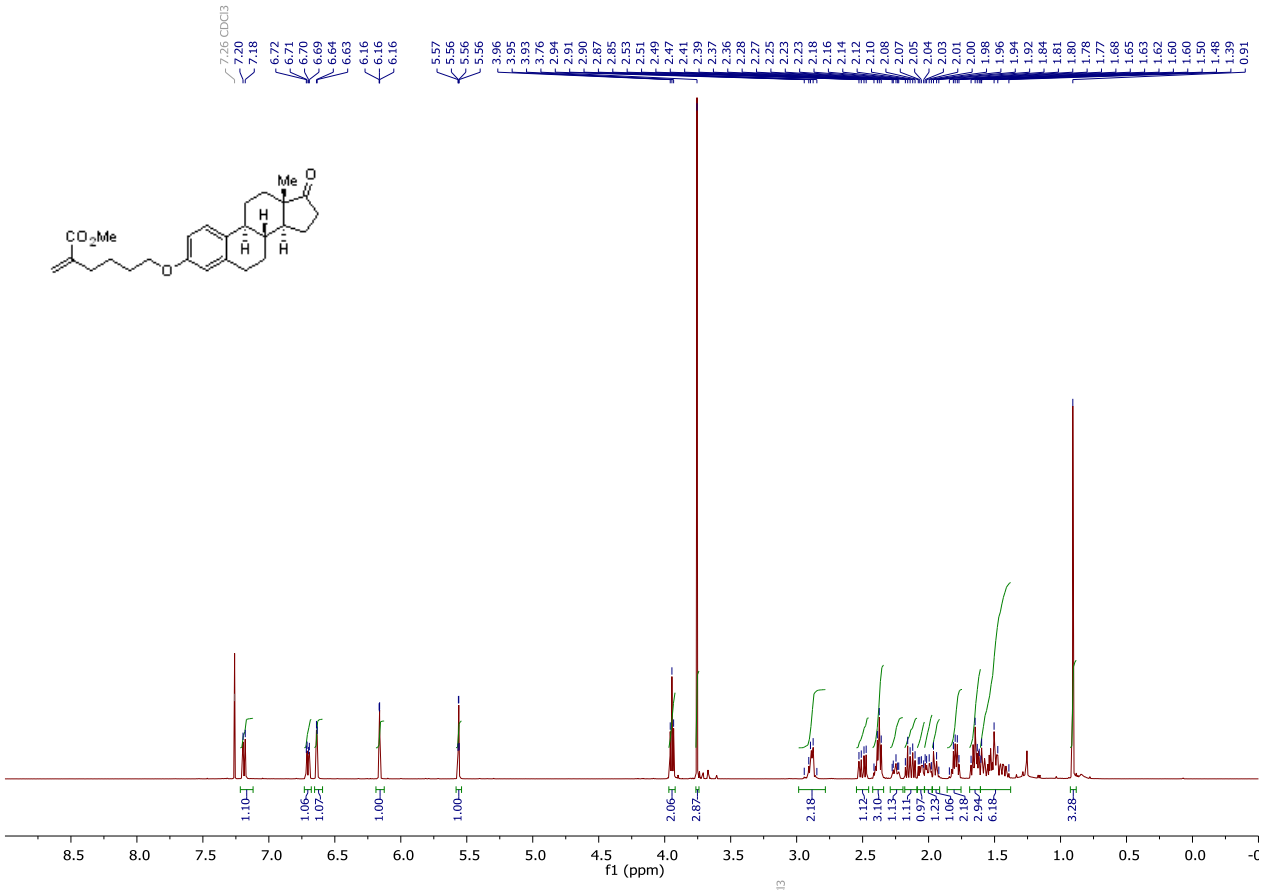
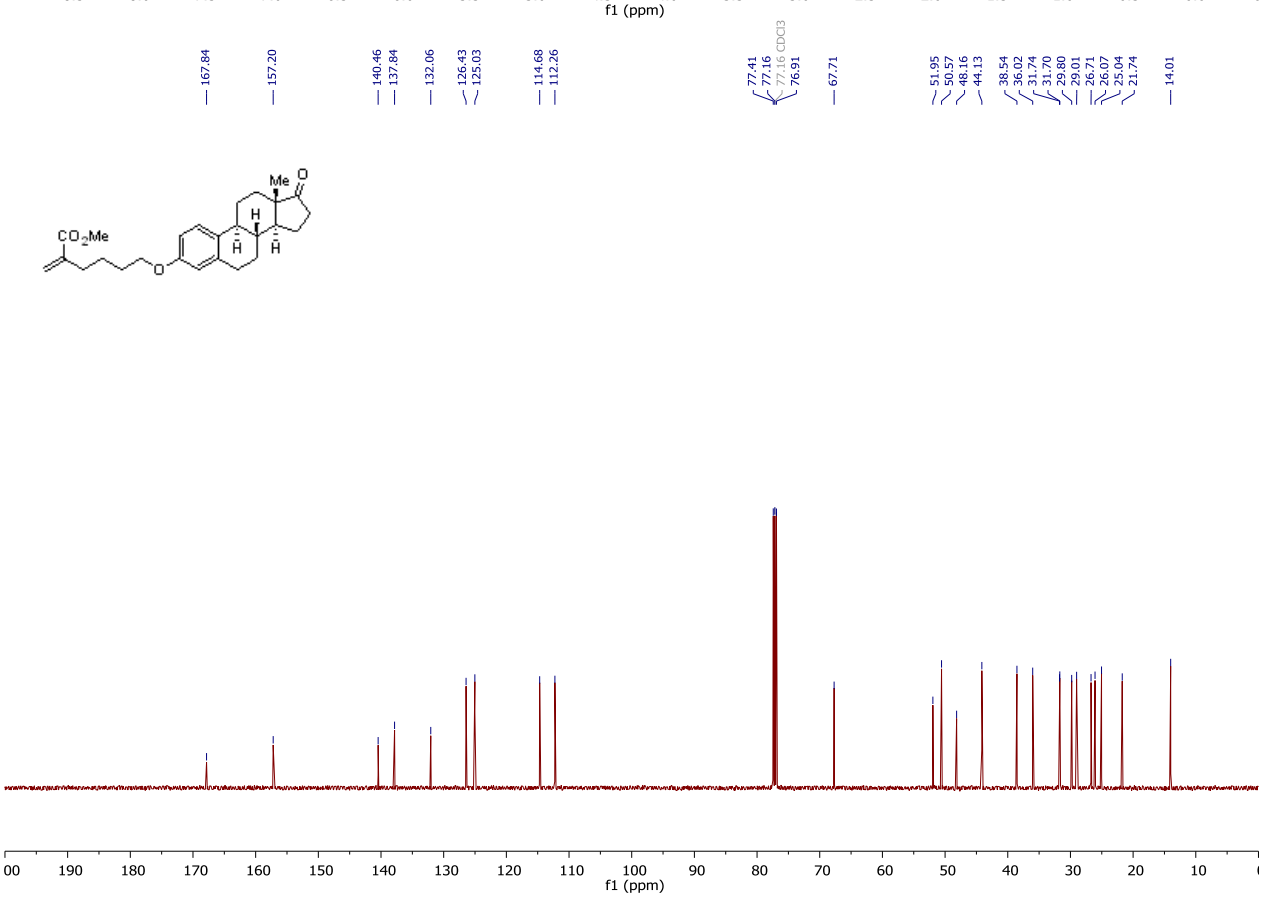
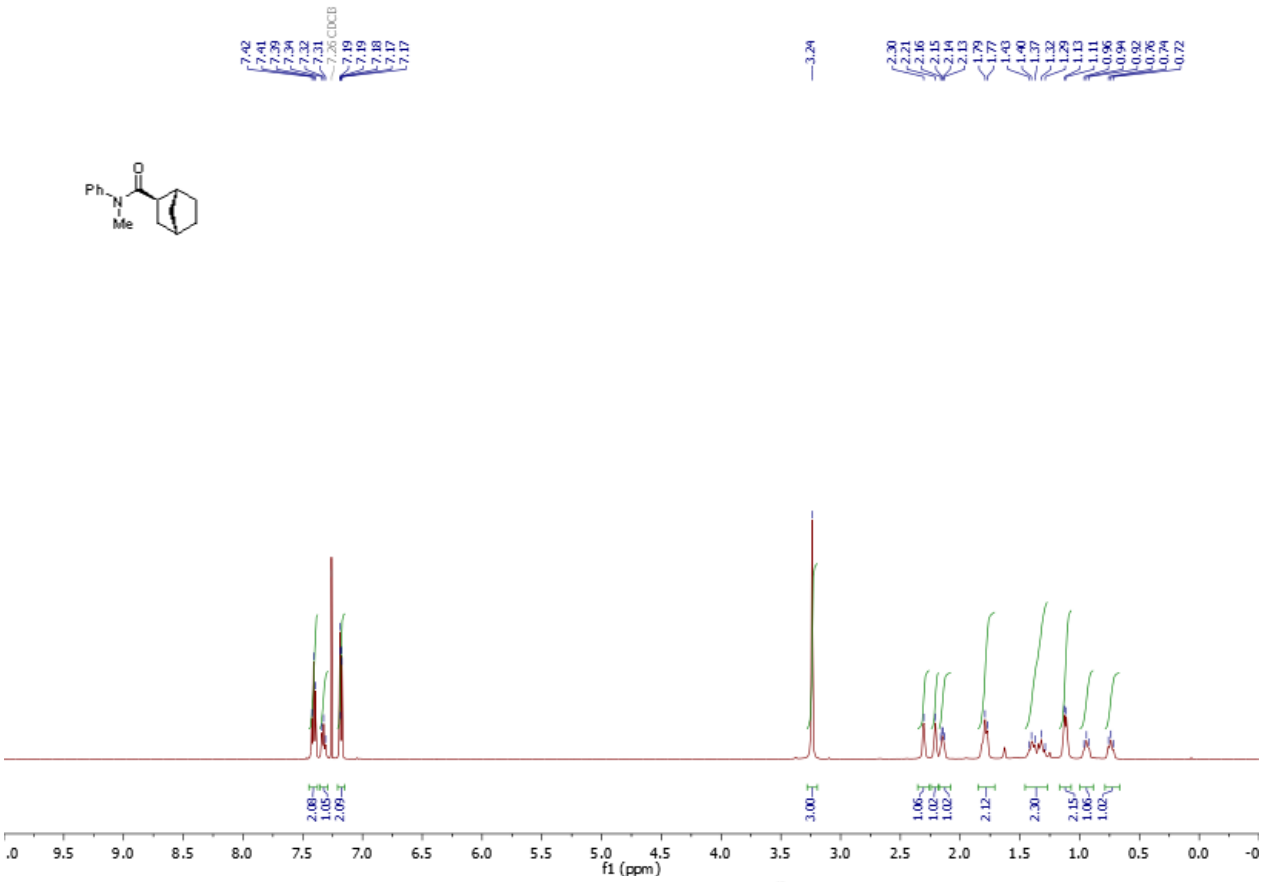
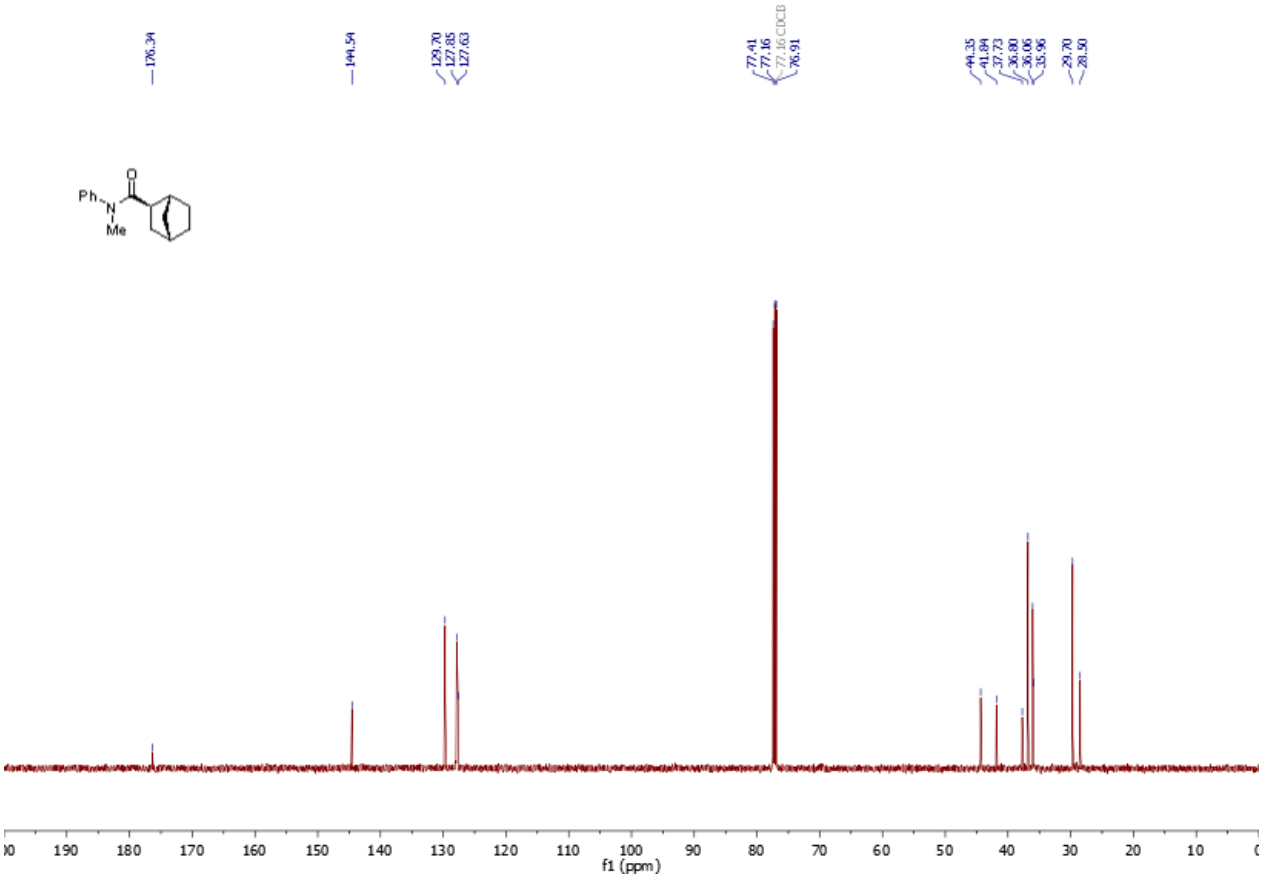
167.15
144.84
144.82
144.60
134.58
130.39
129.38
129.03
128.21
127.13
126.92
118.71
118.32
77.41
77.16
77.16 CDCl3
76.91
64.42
37.99
33.42
28.38
24.16
Ph
N
Me
O
O
Ph
f1 (ppm)


Me
O
H
H
H
CO2Me
O
f1 (ppm)


Me
O
H
H
H
CO2Me
O
f1 (ppm)


7.42
7.41
7.39
7.34
7.32
7.31
7.26 CDCB
7.19
7.19
7.18
7.17
7.17
3.24
2.30
2.21
2.16
2.15
2.14
2.13
1.79
1.77
1.63
1.40
1.37
1.32
1.29
1.13
1.11
0.96
0.94
0.92
0.76
0.74
0.72
Ph
N
Me
O
2.08
1.05
2.09
3.00
1.06
1.02
1.02
2.12
2.30
2.15
1.06
1.02
f1 (ppm)


176.34
144.54
129.70
127.85
127.63
77.41
77.16
77.16 CDCB
76.91
44.35
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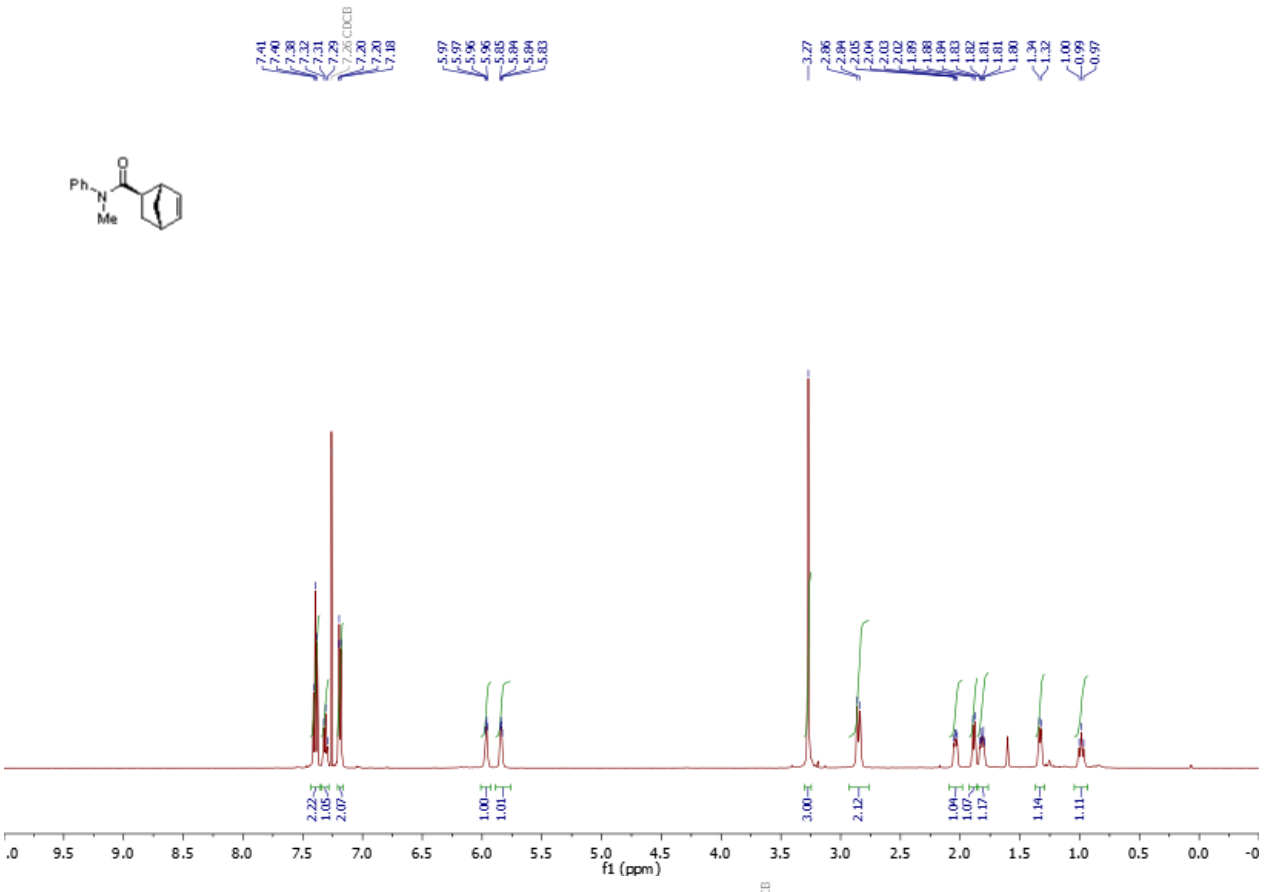
37.73
36.80
36.06
35.96
29.70
28.50
Ph
N
Me
O
f1 (ppm)


7.41
7.40
7.38
7.32
7.31
7.29
7.26 CDCB
7.20
7.20
7.18
5.97
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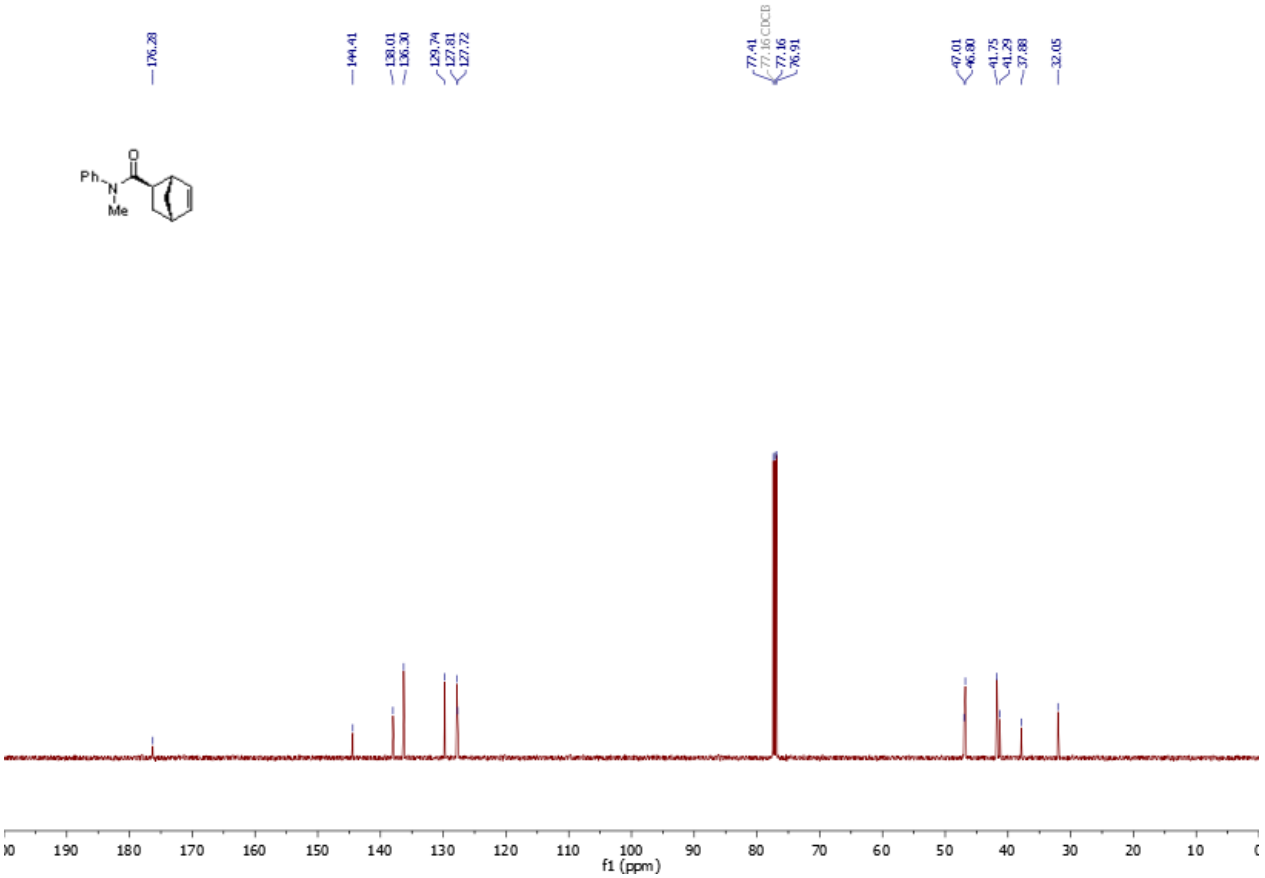
5.96
5.96
5.85
5.84
5.84
5.83
3.27
2.86
2.84
2.05
2.04
2.03
2.02
1.89
1.88
1.84
1.83
1.82
1.81
1.81
1.80
1.34
1.32
1.00
0.99
0.97
Ph
N
Me
O
2.22
1.05
2.07
1.00
1.01
3.00
2.12
1.04
1.07
1.17
1.14
1.11
f1 (ppm)


176.28
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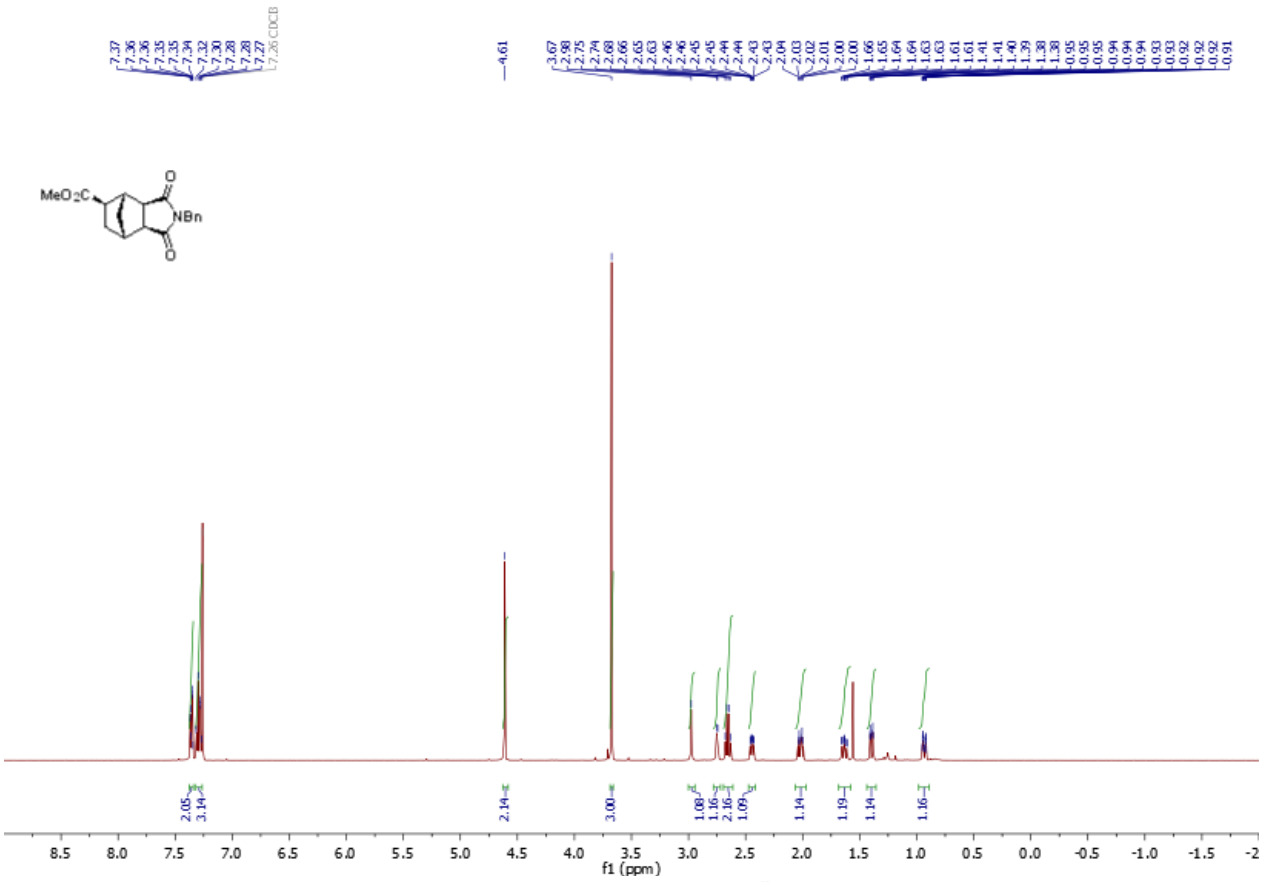
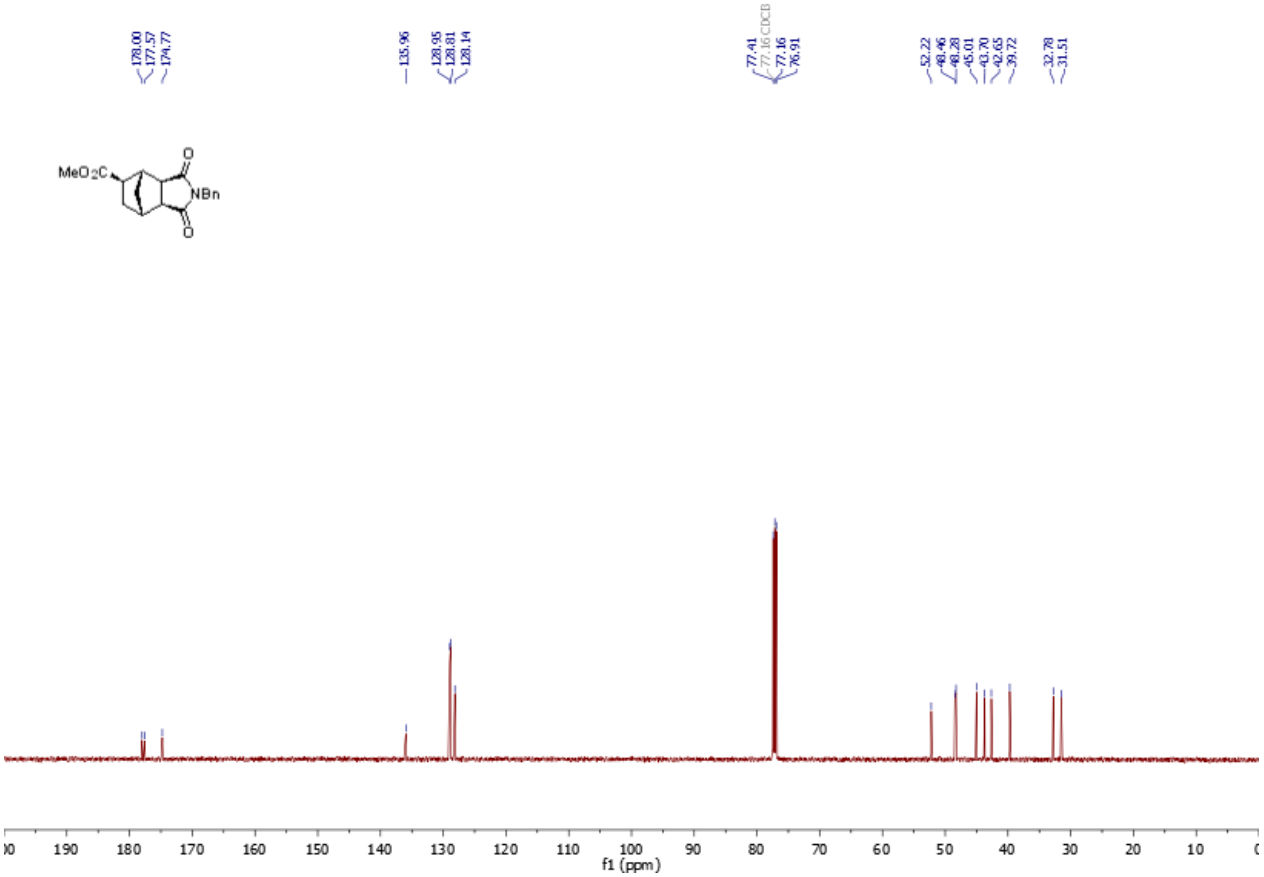
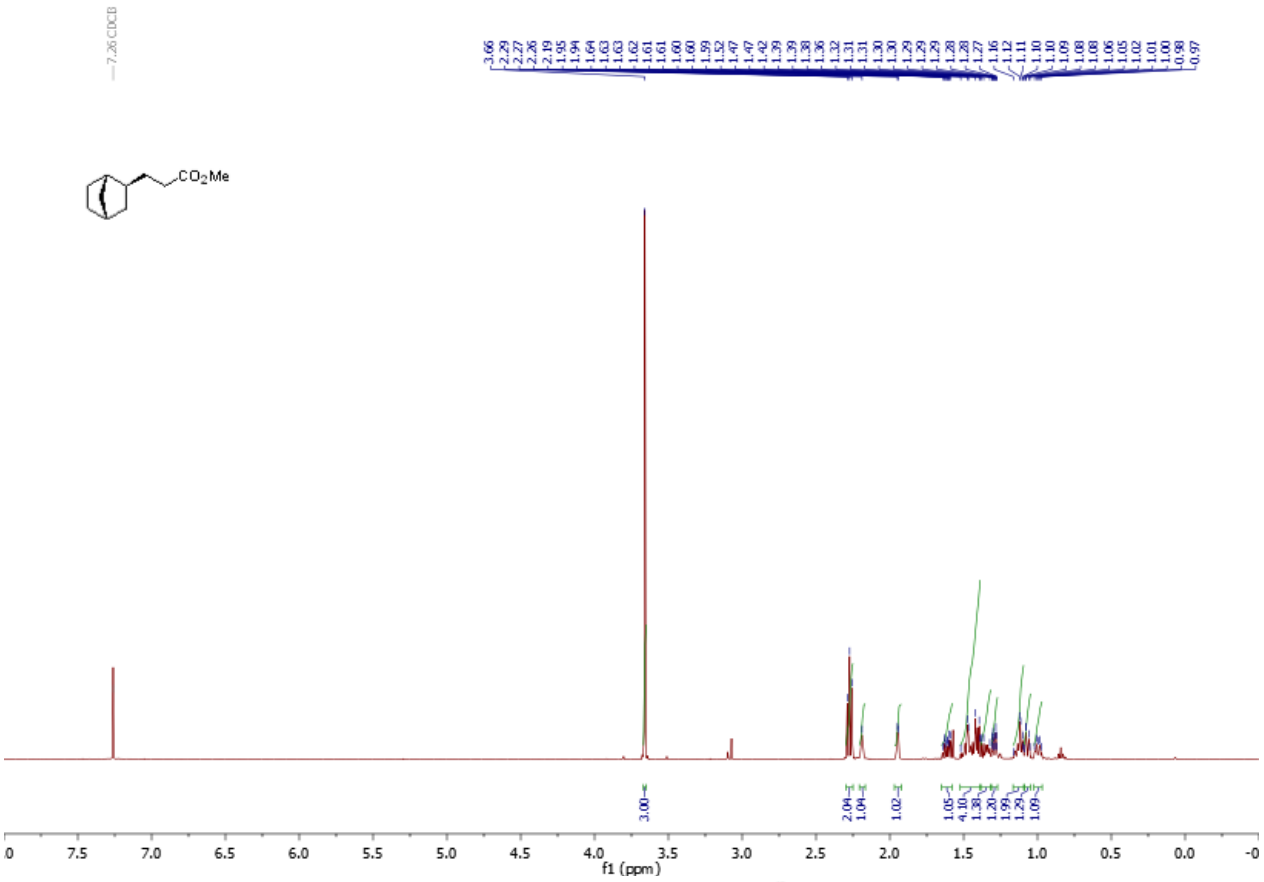
138.01
136.30
129.74
127.81
127.72
77.41
77.16 CDCB
77.16
76.91
47.01
46.80
41.75
41.29
37.88
32.05
Ph
N
Me
O
f1 (ppm)


MeO2C
NBn
f1 (ppm)


MeO2C
NBn
f1 (ppm)


7.26 CDCB
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2.29
2.27
2.26
2.19
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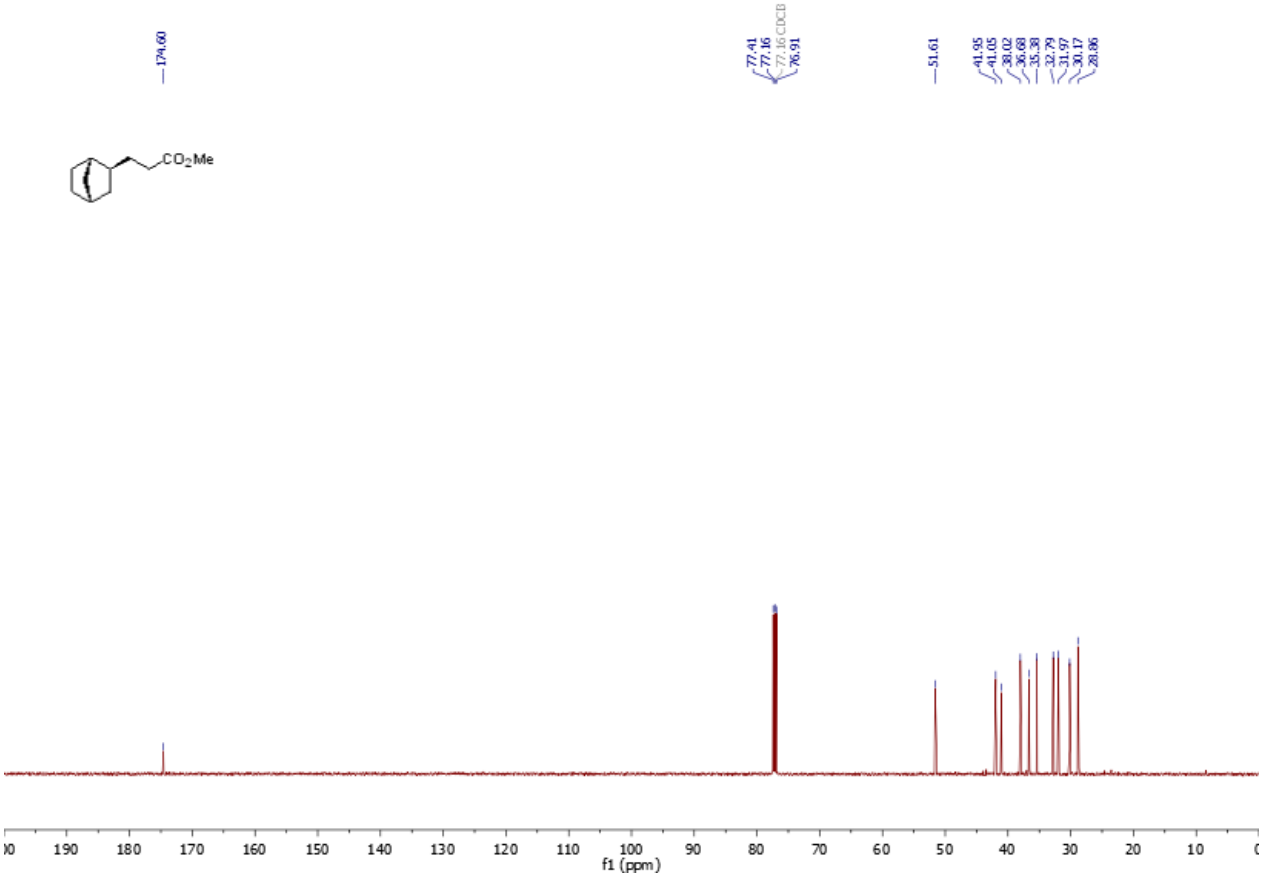
1.94
1.64
1.63
1.63
1.62
1.61
1.61
1.60
1.60
1.59
1.52
1.47
1.47
1.42
1.39
1.39
1.38
1.36
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.29
1.28
1.28
1.27
1.16
1.12
1.11
1.10
1.10
1.09
1.08
1.08
1.06
1.05
1.02
1.01
1.00
0.98
0.97
CO2Me
3.00
2.04
1.04
1.02
1.05
4.10
1.38
1.20
1.95
1.29
1.09
f1 (ppm)


179.60
77.41
77.16
77.16 CDCB
76.91
51.61
41.95
41.05
38.02
36.68
35.38
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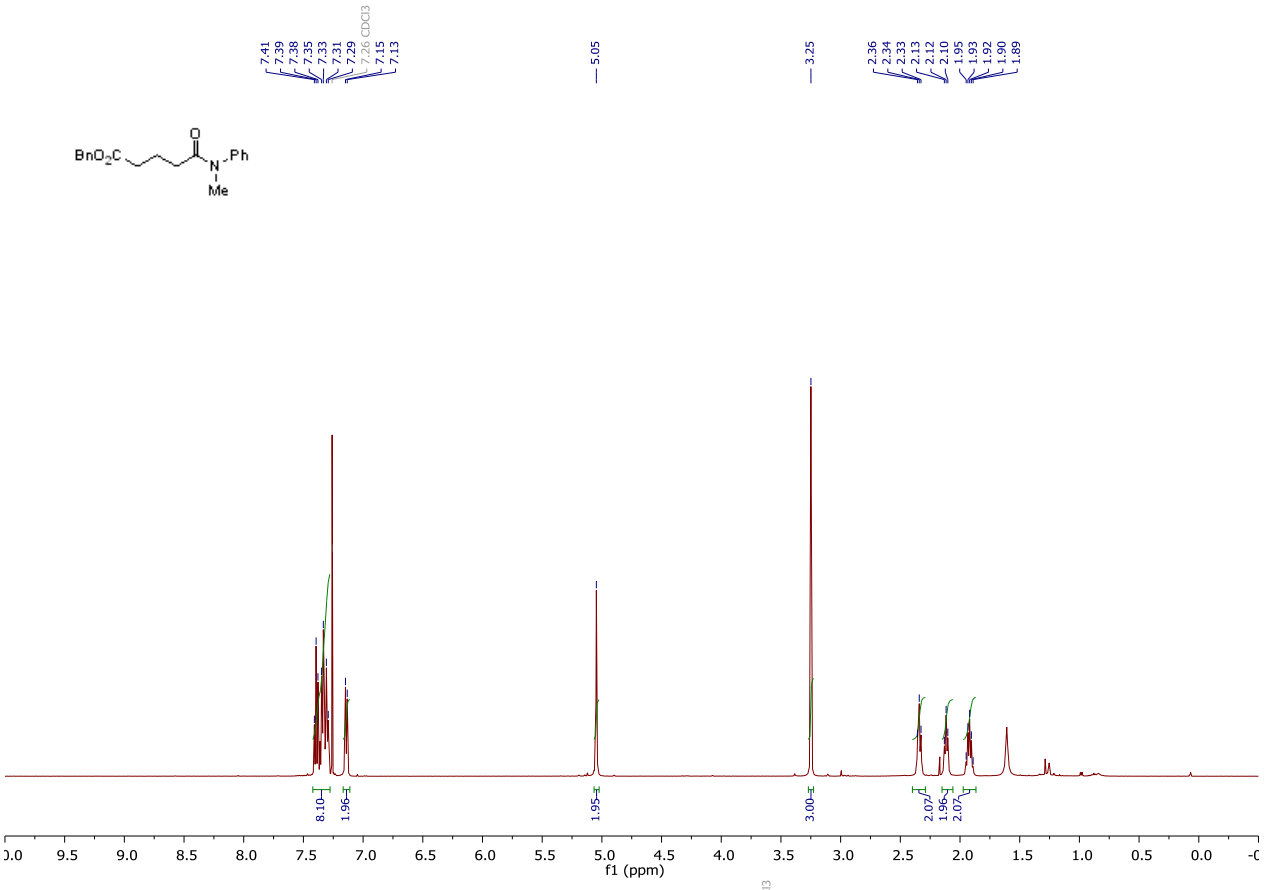
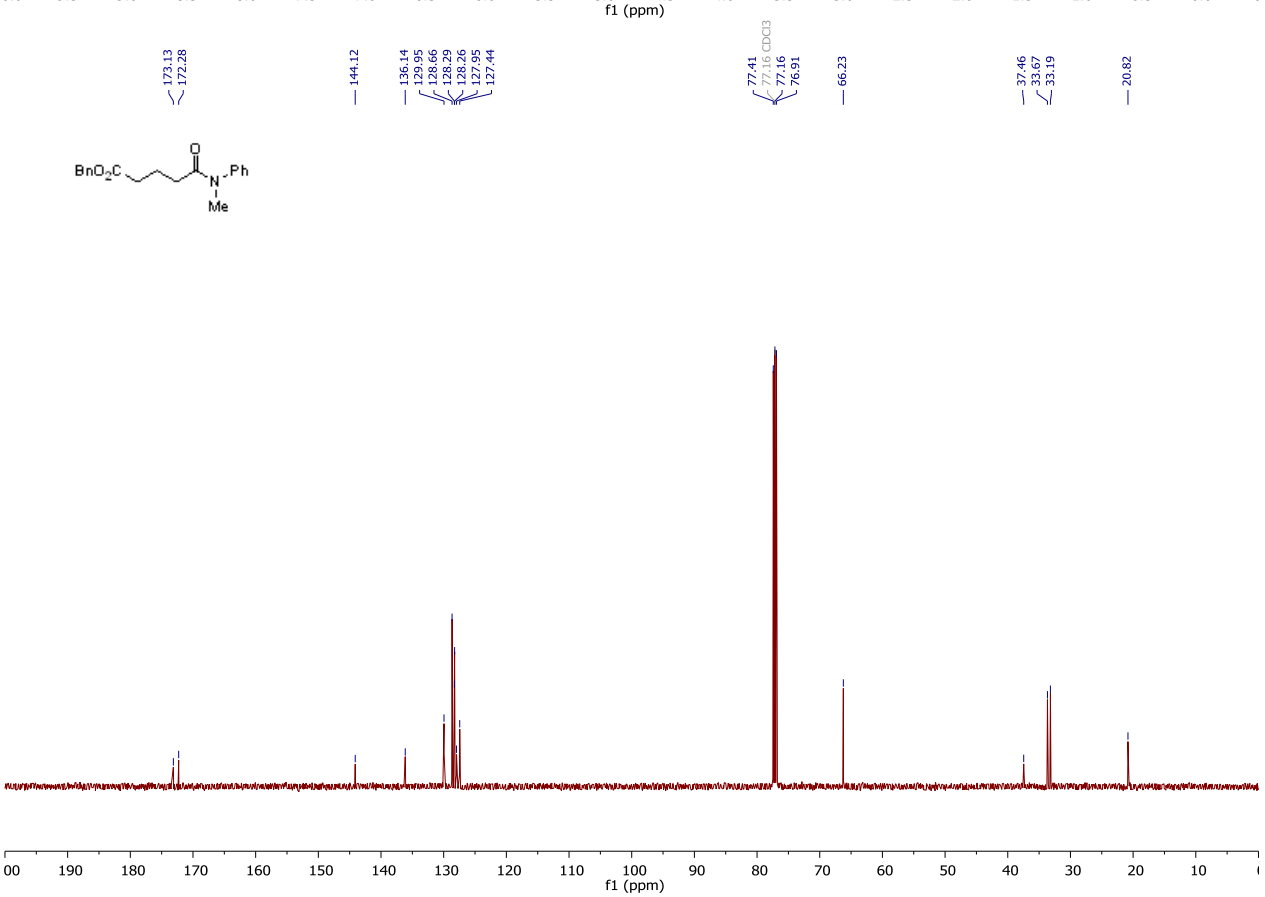
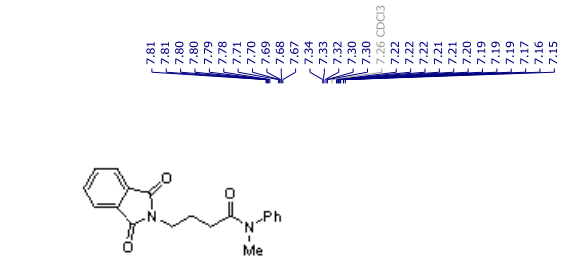
31.97
30.17
28.06
CO2Me
f1 (ppm)


7.41
7.39
7.38
7.35
7.33
7.31
7.29
7.26 CDCl3
7.15
7.13
5.05
3.25
2.36
2.34
2.33
2.13
2.12
2.10
1.95
1.93
1.92
1.90
1.89
BnO2C
O
N
Ph
Me
8.10
1.96
1.95
3.00
2.07
1.96
2.07
f1 (ppm)


173.13
172.28
144.12
136.14
129.95
128.66
128.29
128.26
127.95
127.44
77.41
77.16 CDCl3
77.16
76.91
66.23
37.46
33.67
33.19
20.82
BnO2C
O
N
Ph
Me
f1 (ppm)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7.81
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7.79
7.78
7.71
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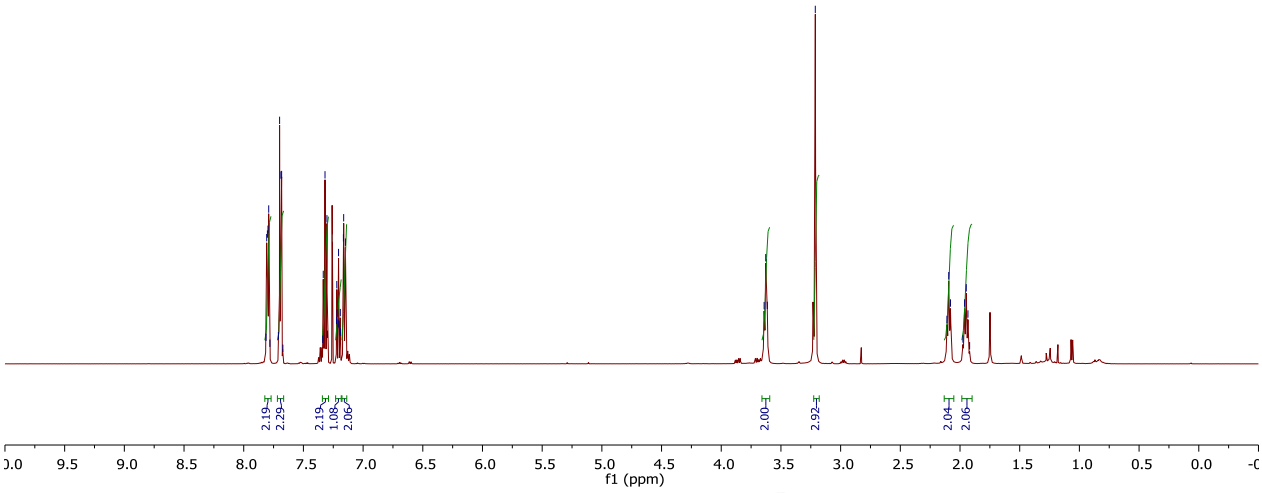
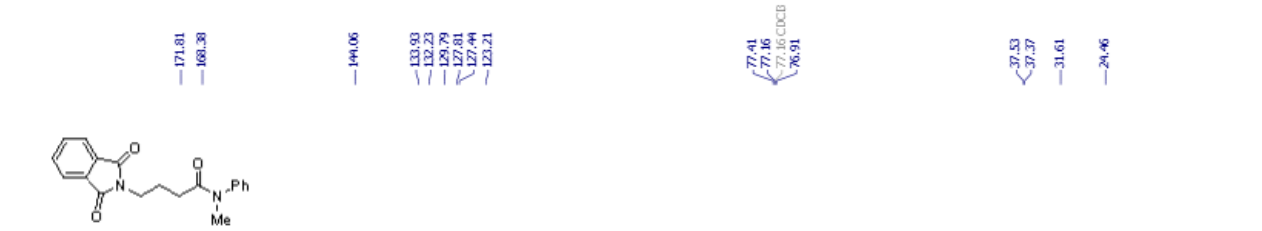
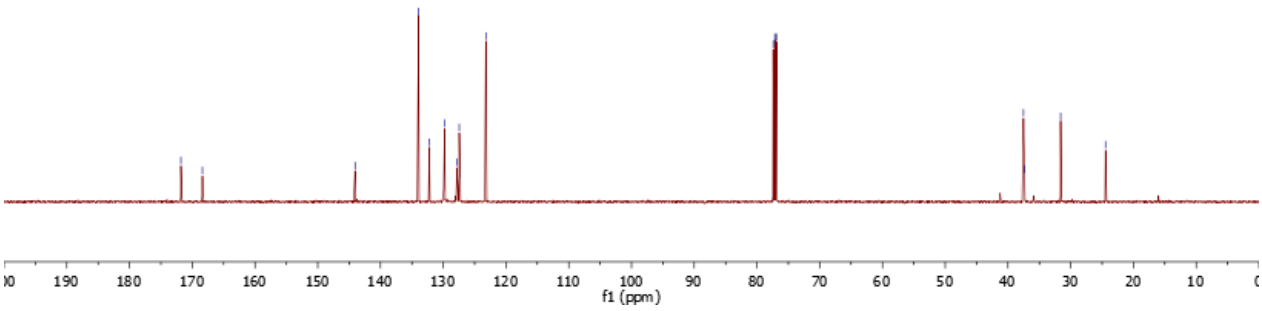
7.68
7.67
7.34
7.33
7.32
7.30
7.30
7.26 CDCl3
7.22
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.19
7.17
7.16
7.15
3.64
3.63
3.61
3.21
2.11
2.09
2.08
1.98
1.96
1.95
1.93
1.92

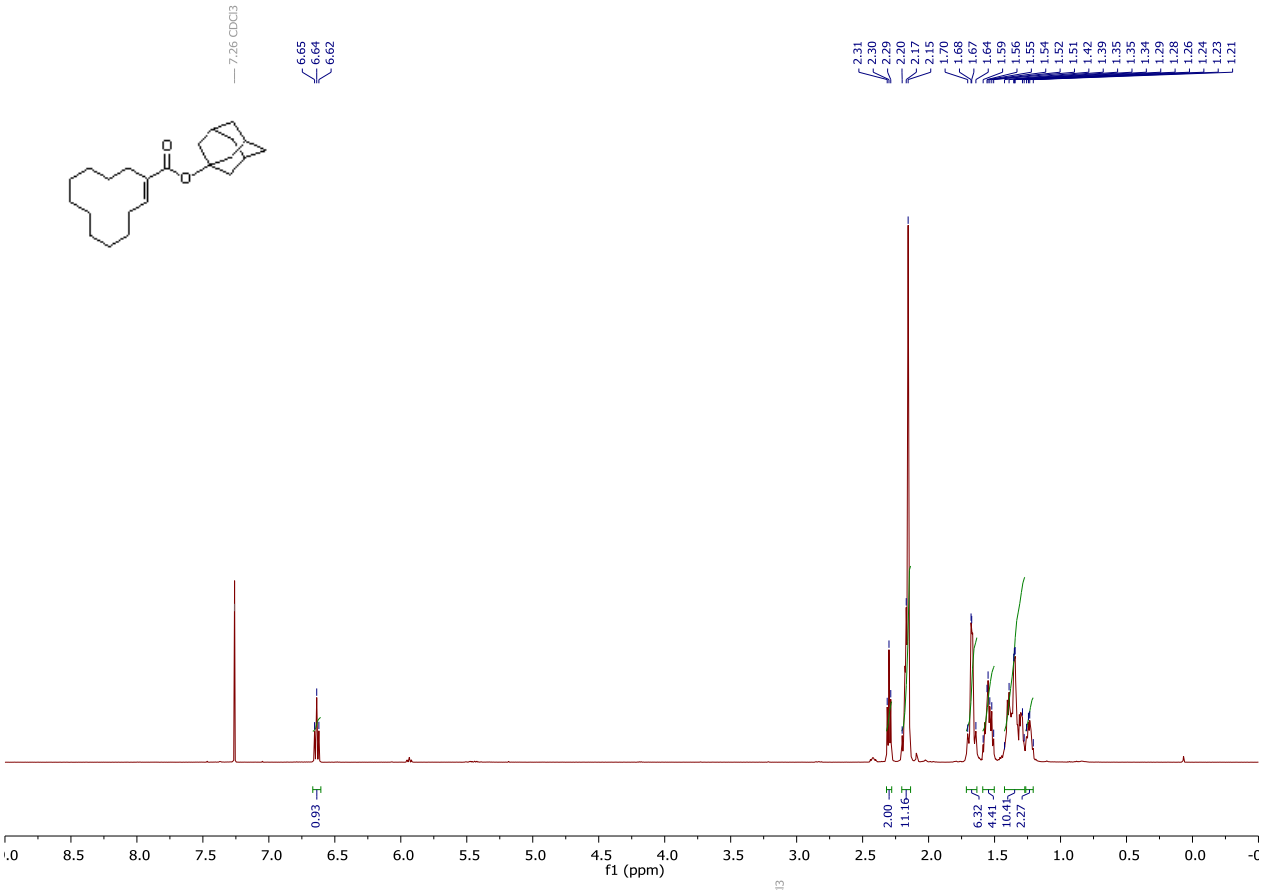
O
O
N
O
N
Ph
Me

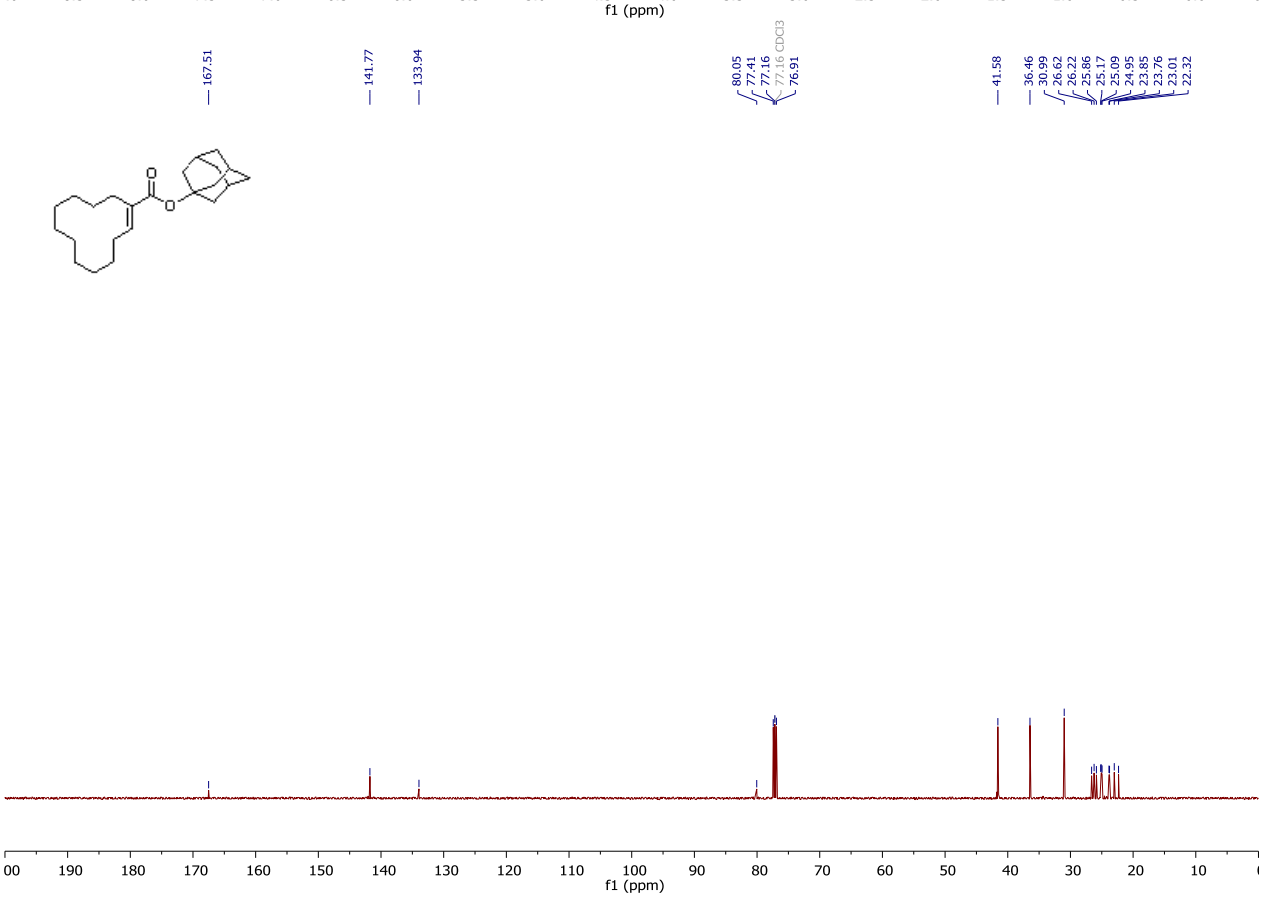

2.19
2.29
2.19
1.08
2.06
2.00
2.92
2.04
2.06
f1 (ppm)

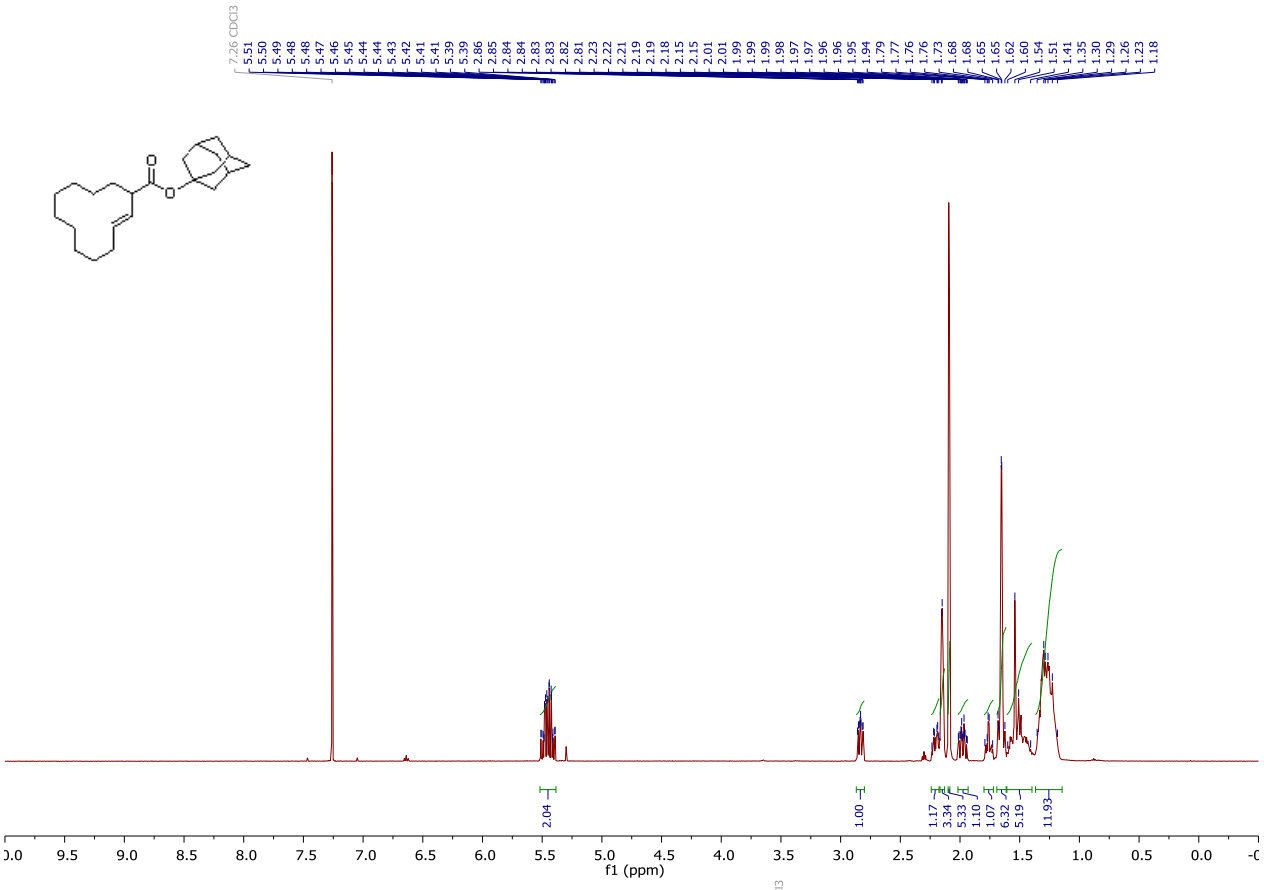

171.81
168.38
140.06
133.93
132.23
129.79
127.81
127.44
123.21
77.41
77.16
77.16 CDCl3
76.91
37.53
37.37
31.61
24.46

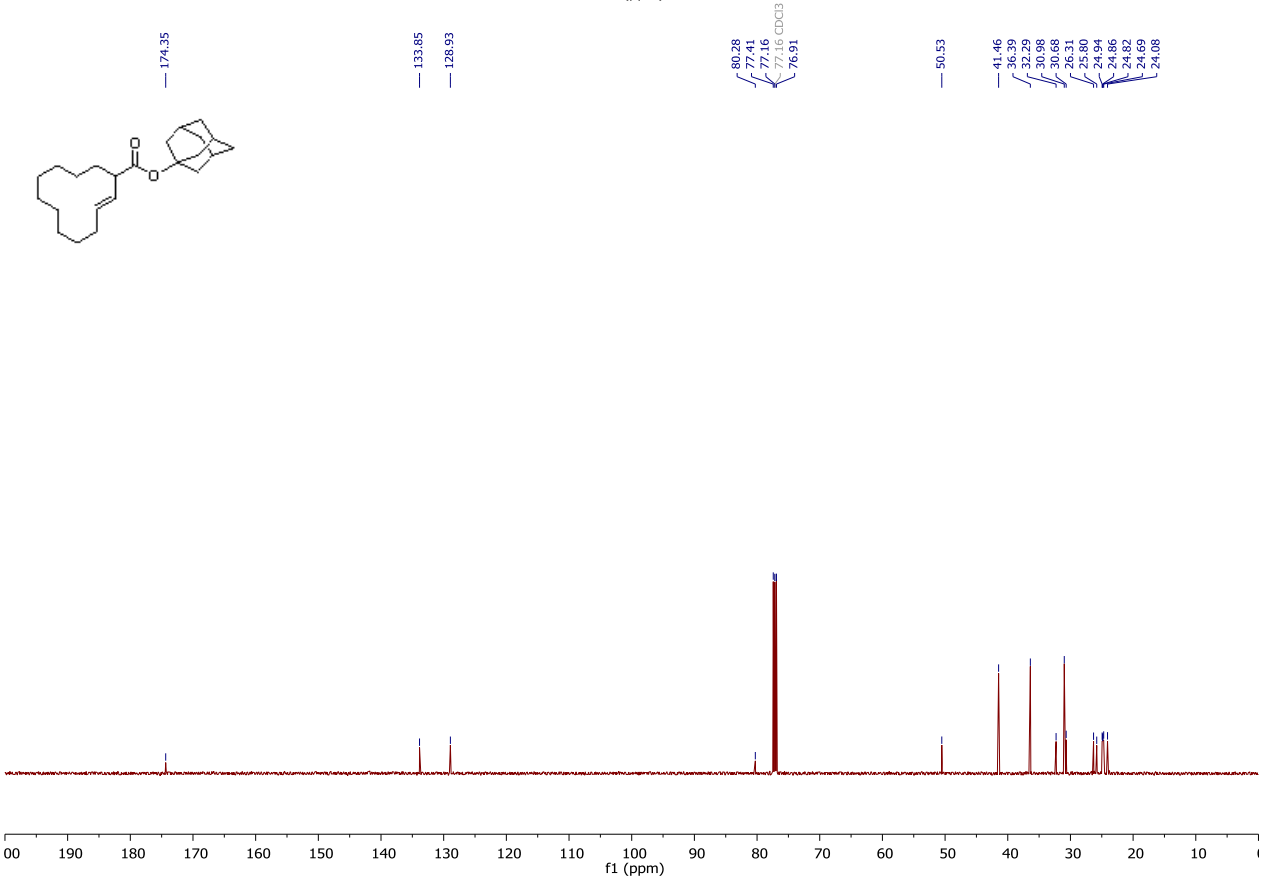
O
O
N
O
N
Ph
Me


f1 (ppm)


7.26 CDCl3
6.65
6.64
6.62
2.31
2.30
2.29
2.20
2.17
2.15
1.70
1.68
1.67
1.64
1.59
1.56
1.55
1.54
1.52
1.51
1.42
1.39
1.35
1.34
1.29
1.28
1.26
1.24
1.23
1.21
0.93
2.00
11.16
6.32
4.41
10.41
2.27
f1 (ppm)


167.51
141.77
133.94
80.05
77.41
77.16
77.16 CDCl3
76.91
41.58
36.46
30.99
26.62
26.22
25.86
25.17
25.09
24.95
23.85
23.76
23.01
22.32
f1 (ppm)


7.26 CDCl3
5.51 5.50 5.49 5.48 5.48 5.47 5.46 5.45 5.44 5.44 5.43 5.42 5.41 5.41 5.39 5.39 2.86 2.85 2.84 2.84 2.83 2.83 2.82 2.81 2.23 2.22 2.21 2.19 2.19 2.18 2.15 2.15 2.01 2.01 1.99 1.99 1.99 1.98 1.97 1.97 1.96 1.96 1.95 1.94 1.79 1.77 1.76 1.76 1.73 1.68 1.68 1.65 1.65 1.62 1.60 1.54 1.51 1.41 1.35 1.30 1.29 1.26 1.23 1.18
2.04
1.00
1.17
3.34
5.33
1.10
1.07
6.32
5.19
11.93
f1 (ppm)


174.35
133.85
128.93
80.28
77.41
77.16
77.16 CDCl3
76.91
50.53
41.46
36.39
32.29
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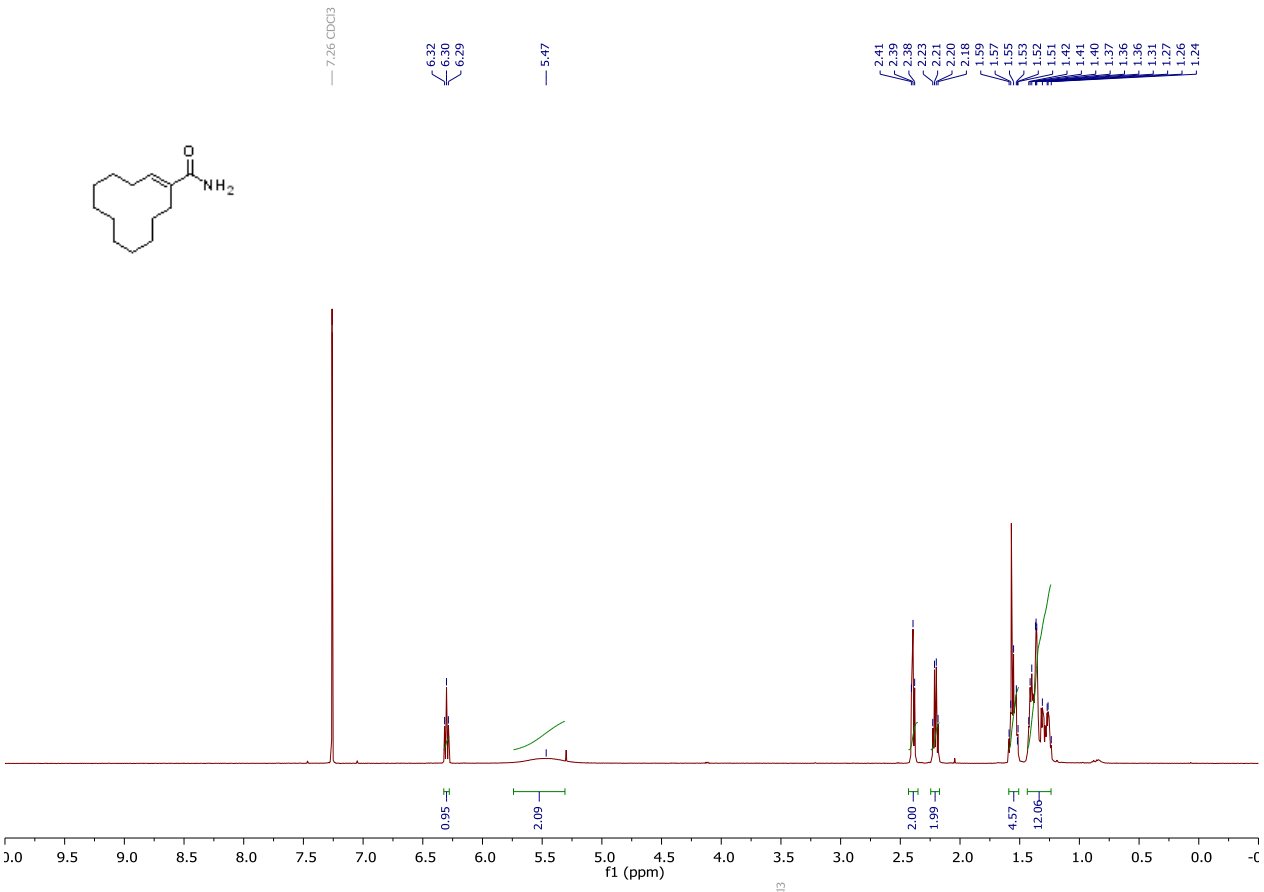
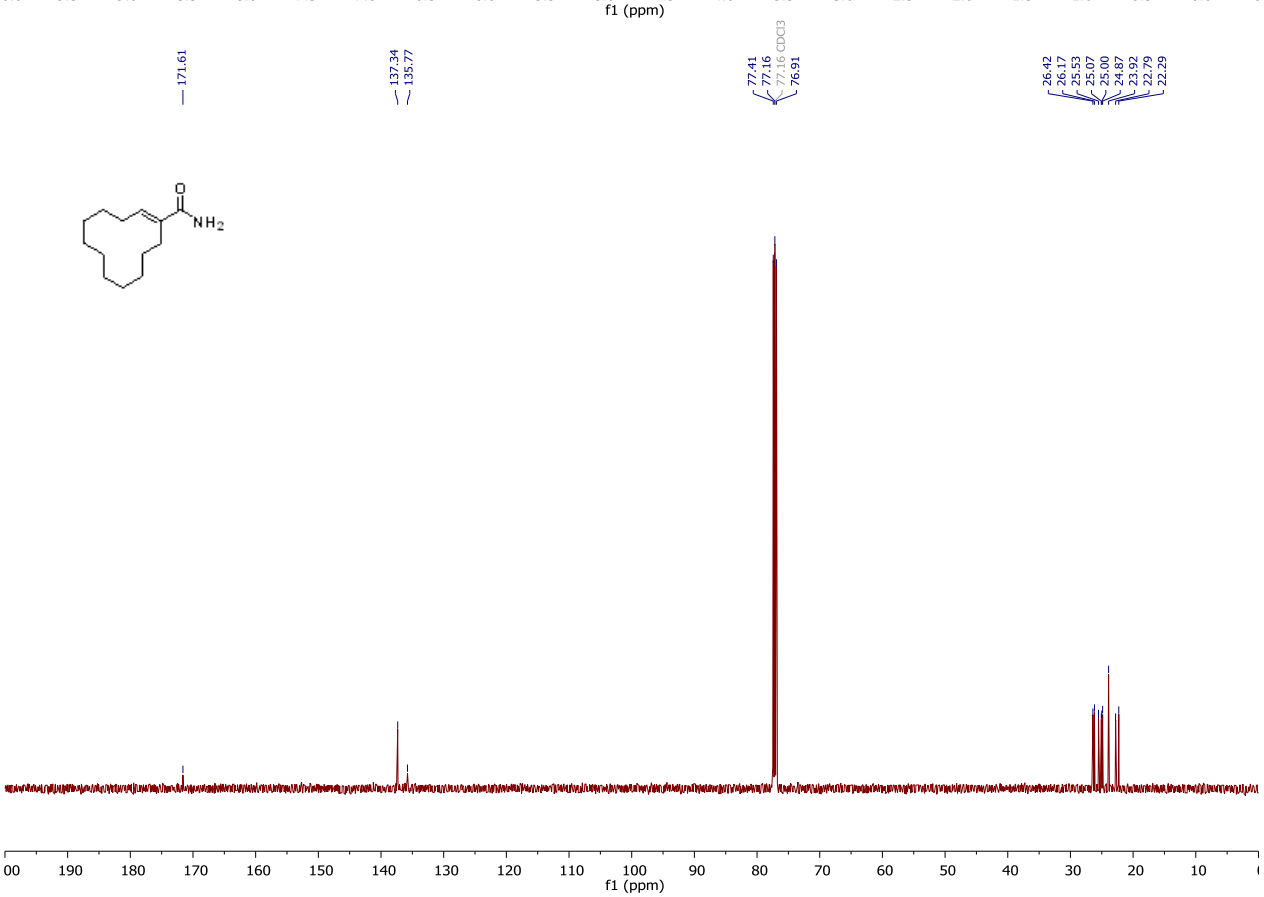
30.68
26.31
25.80
24.94
24.86
24.82
24.69
24.08
f1 (ppm)


7.26 CDCl3
6.32
6.30
6.29
5.47
2.41
2.39
2.38
2.23
2.21
2.20
2.18
1.59
1.57
1.55
1.53
1.52
1.51
1.42
1.41
1.40
1.37
1.36
1.31
1.27
1.26
1.24
NH2
O
0.95
2.09
2.00
1.99
4.57
12.06
f1 (ppm)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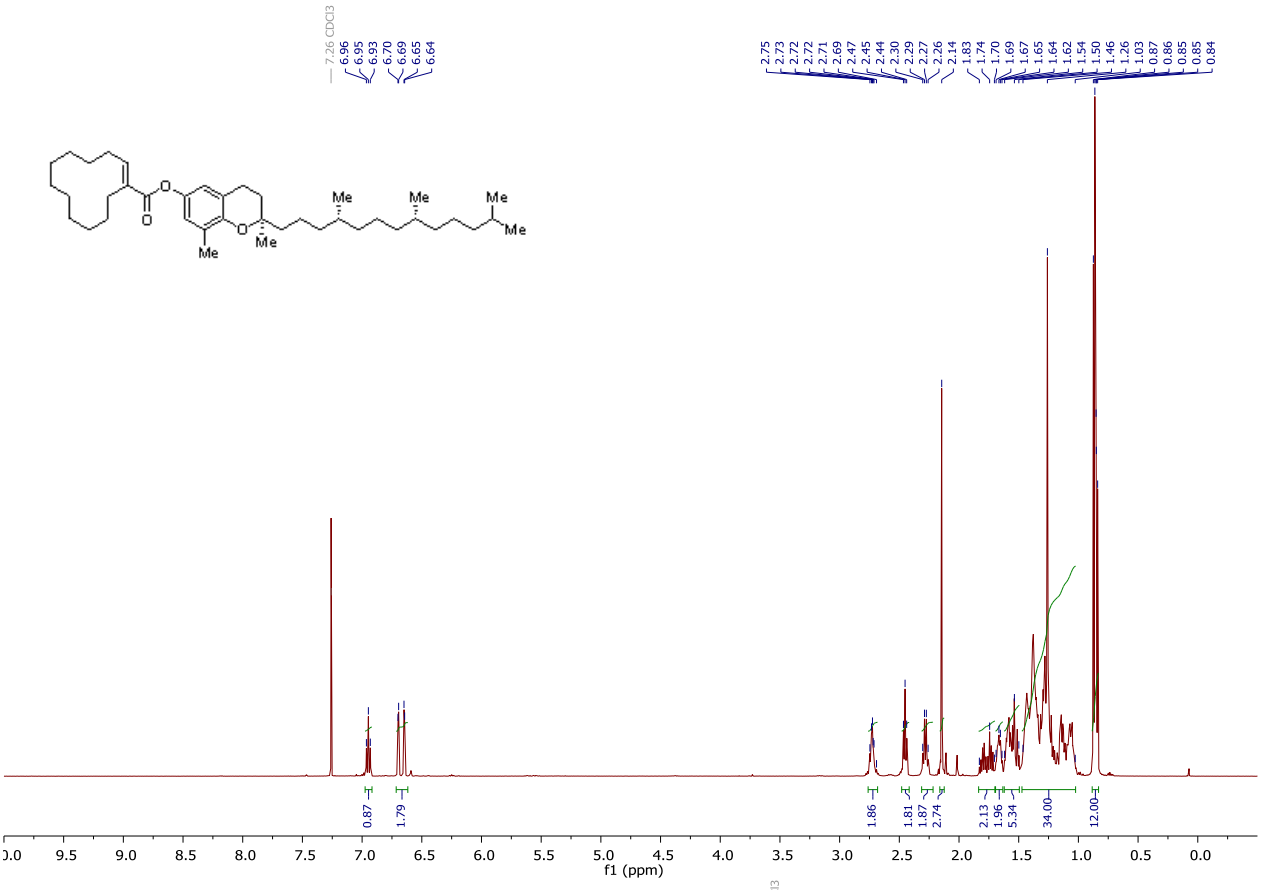
137.34
135.77
77.41
77.16
77.16 CDCl3
76.91
26.42
26.17
25.53
25.07
25.00
24.87
23.92
22.79
22.29
NH2
O
f1 (ppm)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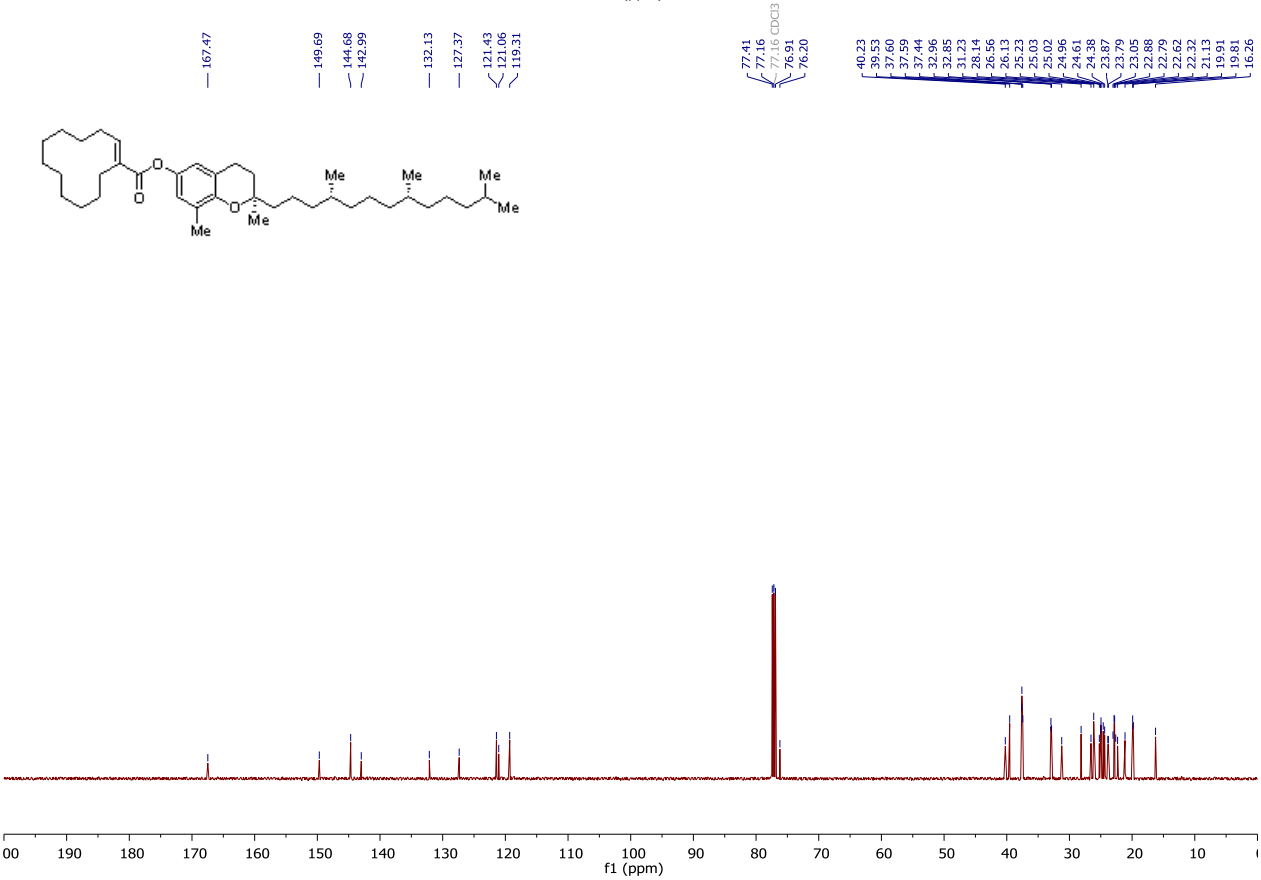
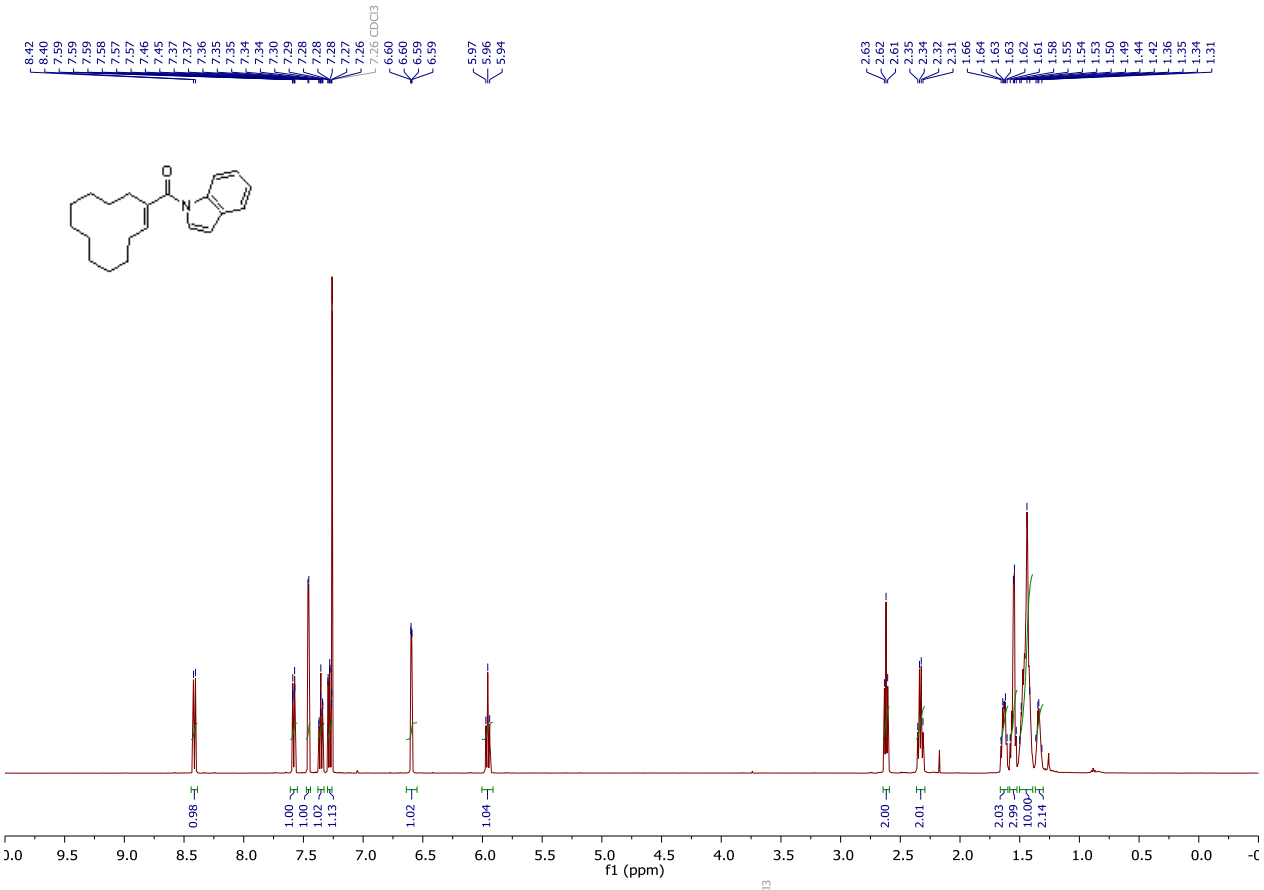
6.96
6.95
6.93
6.70
6.69
6.65
6.64
2.75
2.73
2.72
2.72
2.71
2.69
2.47
2.45
2.44
2.30
2.29
2.27
2.26
2.14
1.83
1.74
1.70
1.69
1.67
1.65
1.64
1.62
1.54
1.50
1.46
1.26
1.03
0.87
0.86
0.85
0.85
0.84
Me
Me
Me
Me
Me
Me
O
O
O
0.87
1.79
1.86
1.81
1.87
2.74
2.13
1.96
5.34
34.00
12.00
f1 (ppm)


167.47
149.69
144.68
142.99
132.13
127.37
121.43
121.06
119.31
77.41
77.16
77.16 CDCl3
76.91
76.20
40.23
39.53
37.60
37.59
37.44
32.96
32.85
31.23
28.14
26.56
26.13
25.23
25.03
25.02
24.96
24.61
24.38
23.87
23.79
23.05
22.88
22.79
22.62
22.32
21.13
19.91
19.81
16.26
Me
Me
Me
Me
Me
Me
O
O
O
f1 (ppm)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8.40
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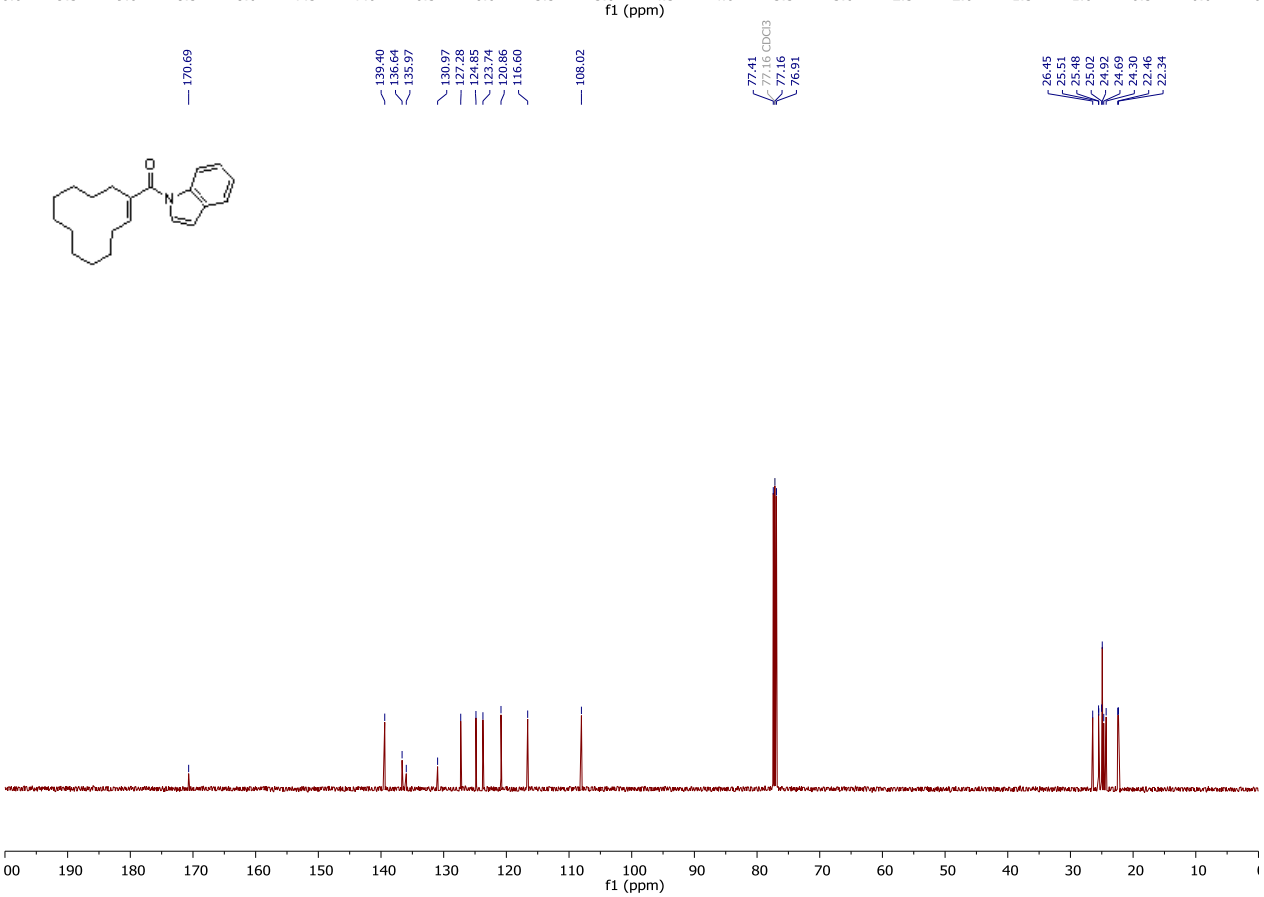
7.59
7.58
7.57
7.57
7.46
7.45
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.30
7.29
7.28
7.28
7.28
7.27
7.26
7.26 CDCl3
6.60
6.60
6.59
6.59
5.97
5.96
5.94
2.63
2.62
2.61
2.35
2.34
2.32
2.31
1.66
1.64
1.63
1.63
1.62
1.61
1.58
1.55
1.54
1.53
1.50
1.49
1.44
1.42
1.36
1.35
1.34
1.31
O
N
0.98
1.00
1.00
1.02
1.13
1.02
1.04
2.00
2.01
2.03
2.99
10.00
2.14
f1 (ppm)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139.40
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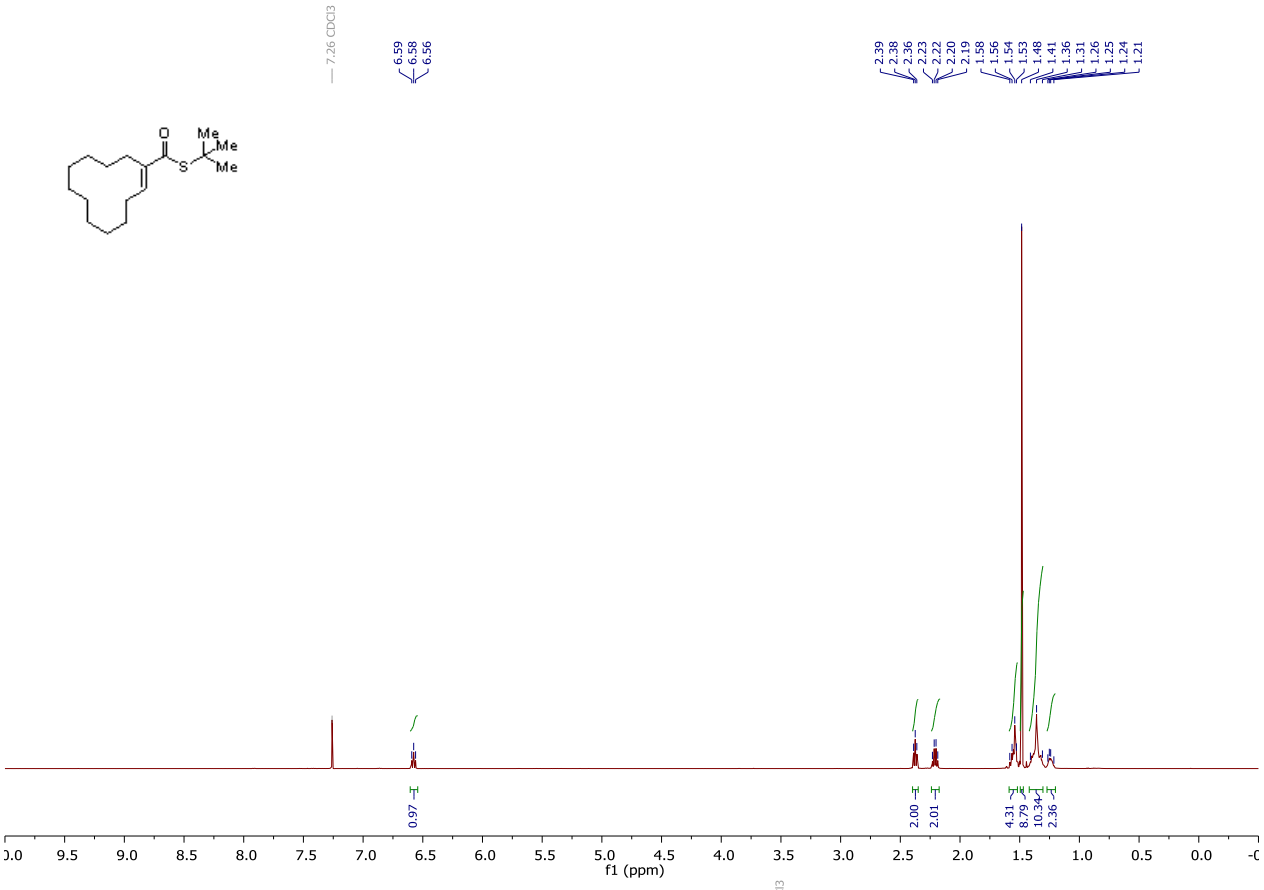
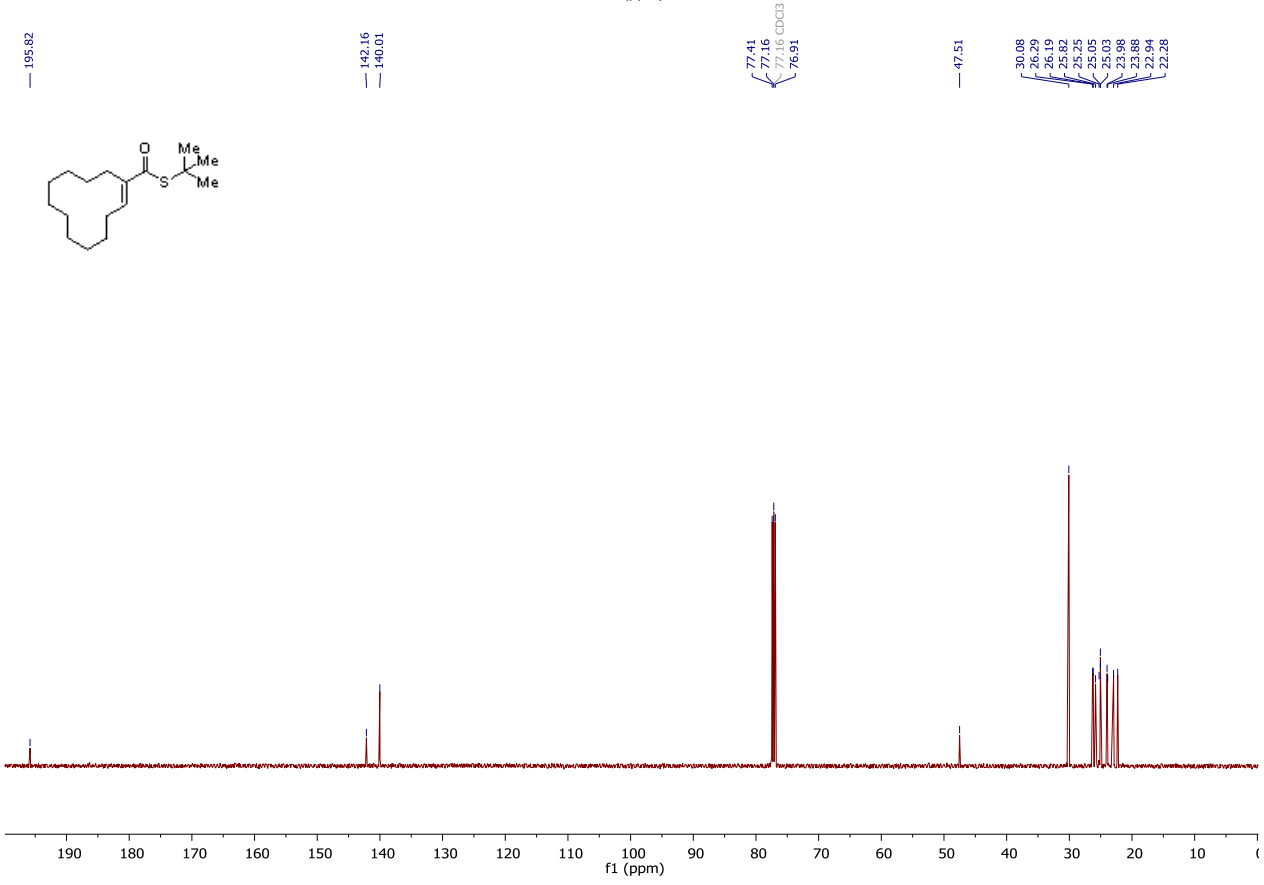
135.97
130.97
127.28
124.65
123.74
120.86
116.60
108.02
77.41
77.16 CDCl3
76.91
26.45
25.51
25.48
25.02
24.92
24.69
24.30
22.46
22.34
O
N
f1 (ppm)


7.26 CDCl3
6.59
6.58
6.56
2.39
2.38
2.36
2.23
2.22
2.20
2.19
1.58
1.56
1.54
1.53
1.48
1.41
1.36
1.31
1.26
1.25
1.24
1.21
O
S
Me
Me
Me
0.97
2.00
2.01
4.31
8.79
10.34
2.36
f1 (ppm)


195.82
142.16
140.01
77.41
77.16
77.16 CDCl3
76.91
47.51
30.08
26.29
26.19
25.82
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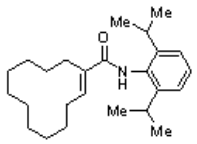
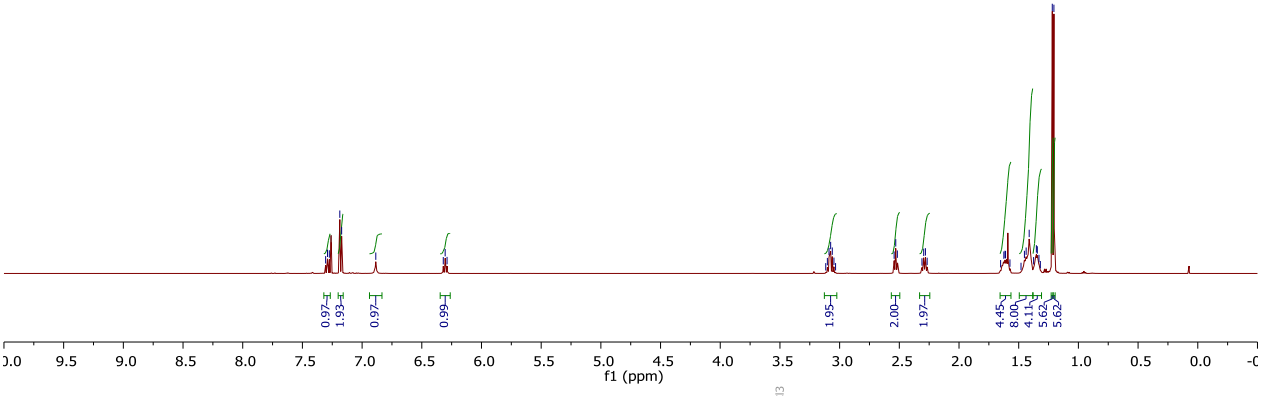
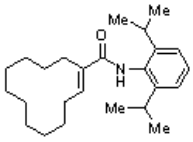
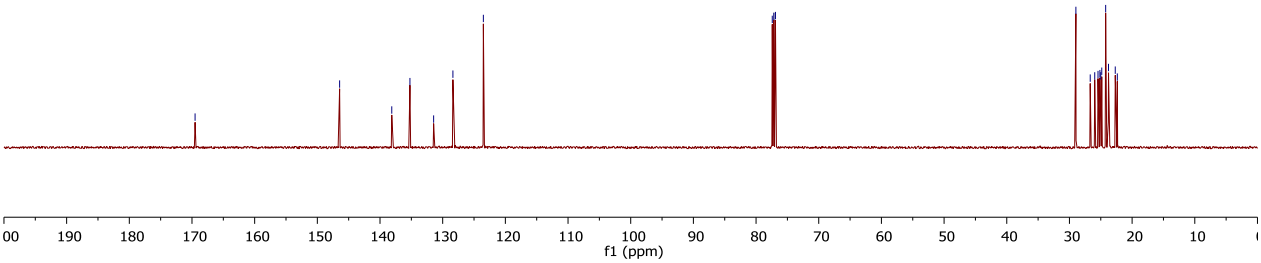
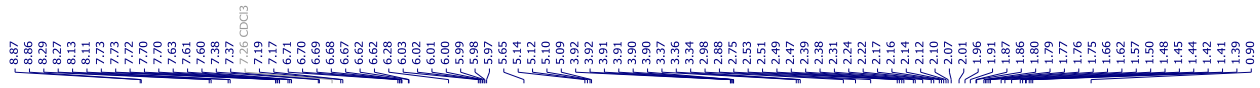
25.05
25.03
23.98
23.88
22.94
22.28
O
S
Me
Me
Me
f1 (ppm)

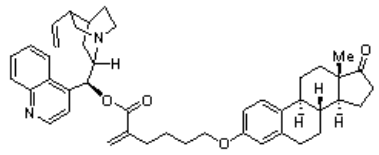

Me
Me
O
N
H
Me
Me

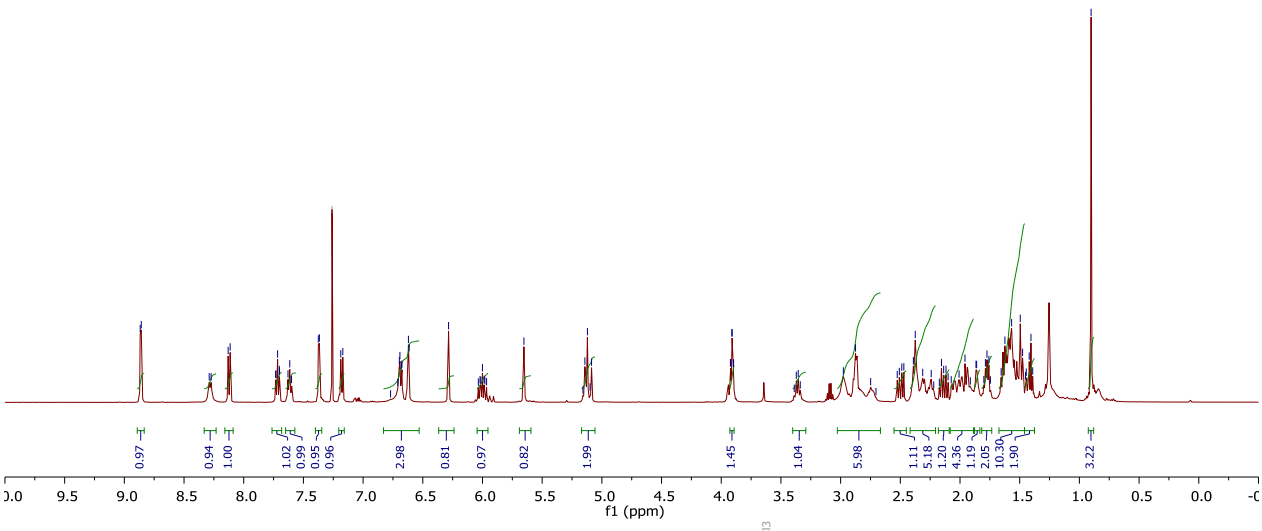

f1 (ppm)

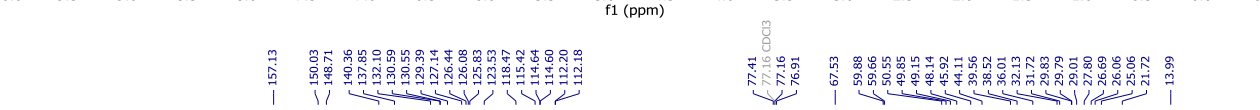

Me
Me
O
N
H
Me
Me

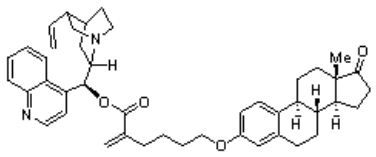

f1 (ppm)

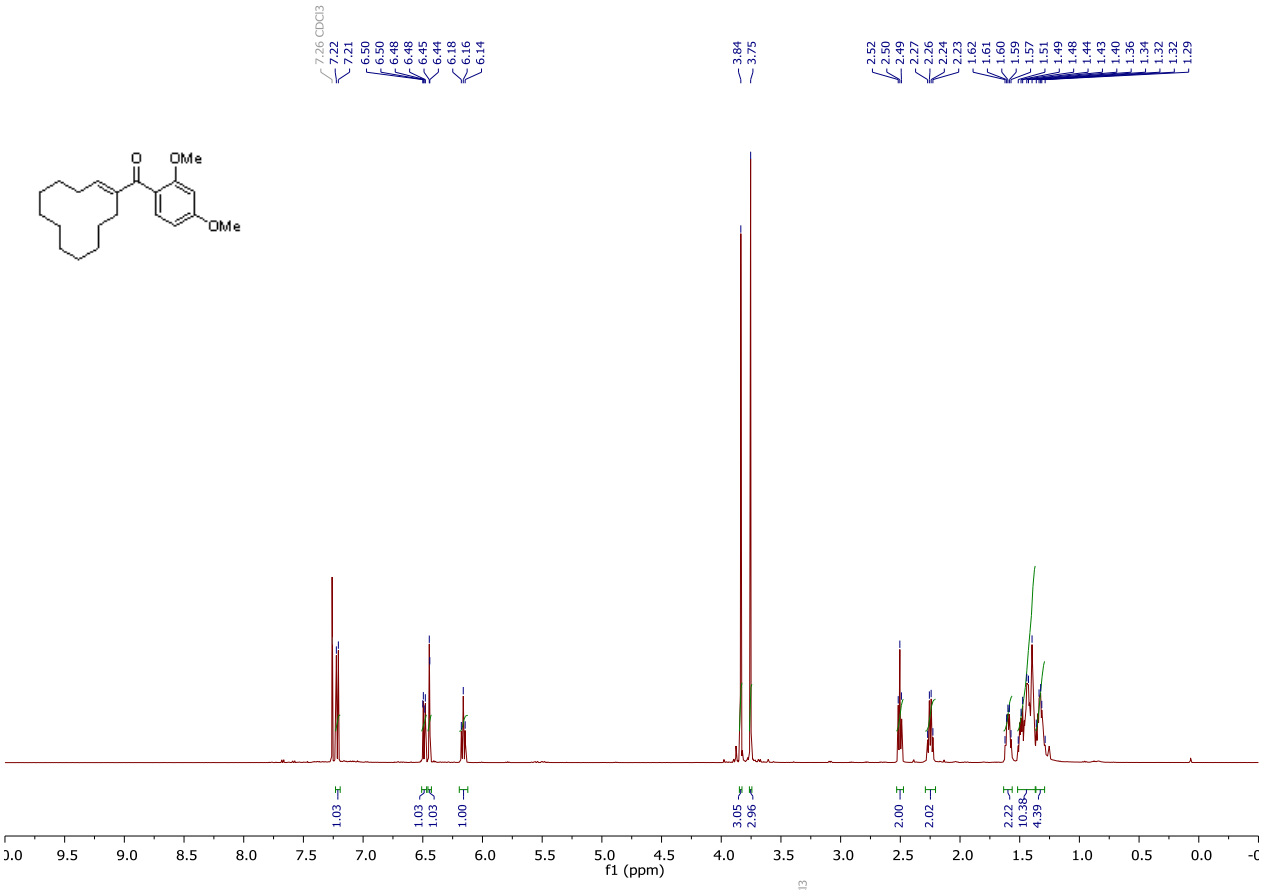








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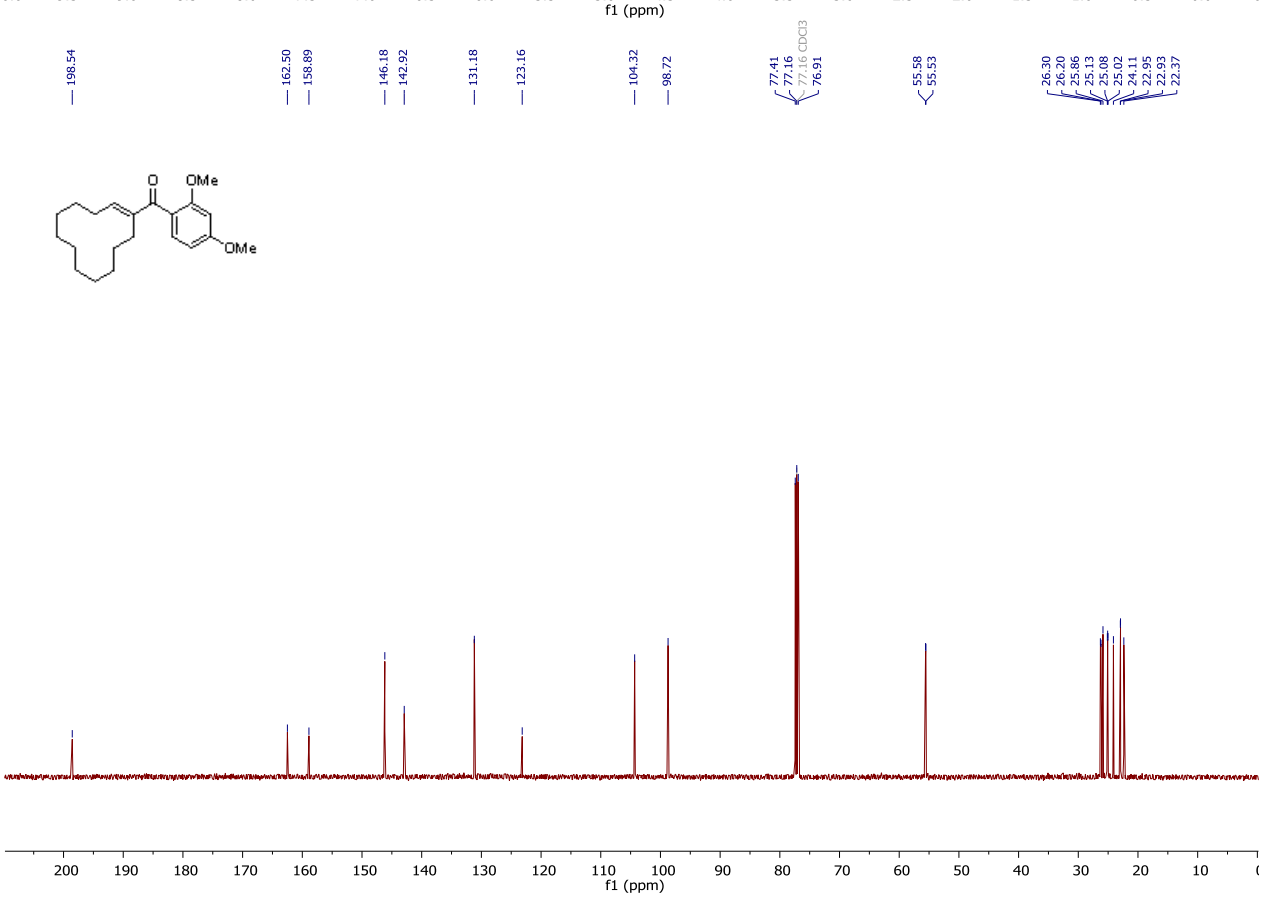
6.48
6.45
6.44
6.18
6.16
6.14
3.84
3.75
2.52
2.50
2.49
2.27
2.26
2.24
2.23
1.62
1.61
1.60
1.59
1.57
1.51
1.49
1.48
1.44
1.43
1.40
1.36
1.34
1.32
1.29
O
OMe
OMe
1.03
1.03
1.03
1.00
3.05
2.96
2.00
2.02
2.22
10.38
4.39
f1 (ppm)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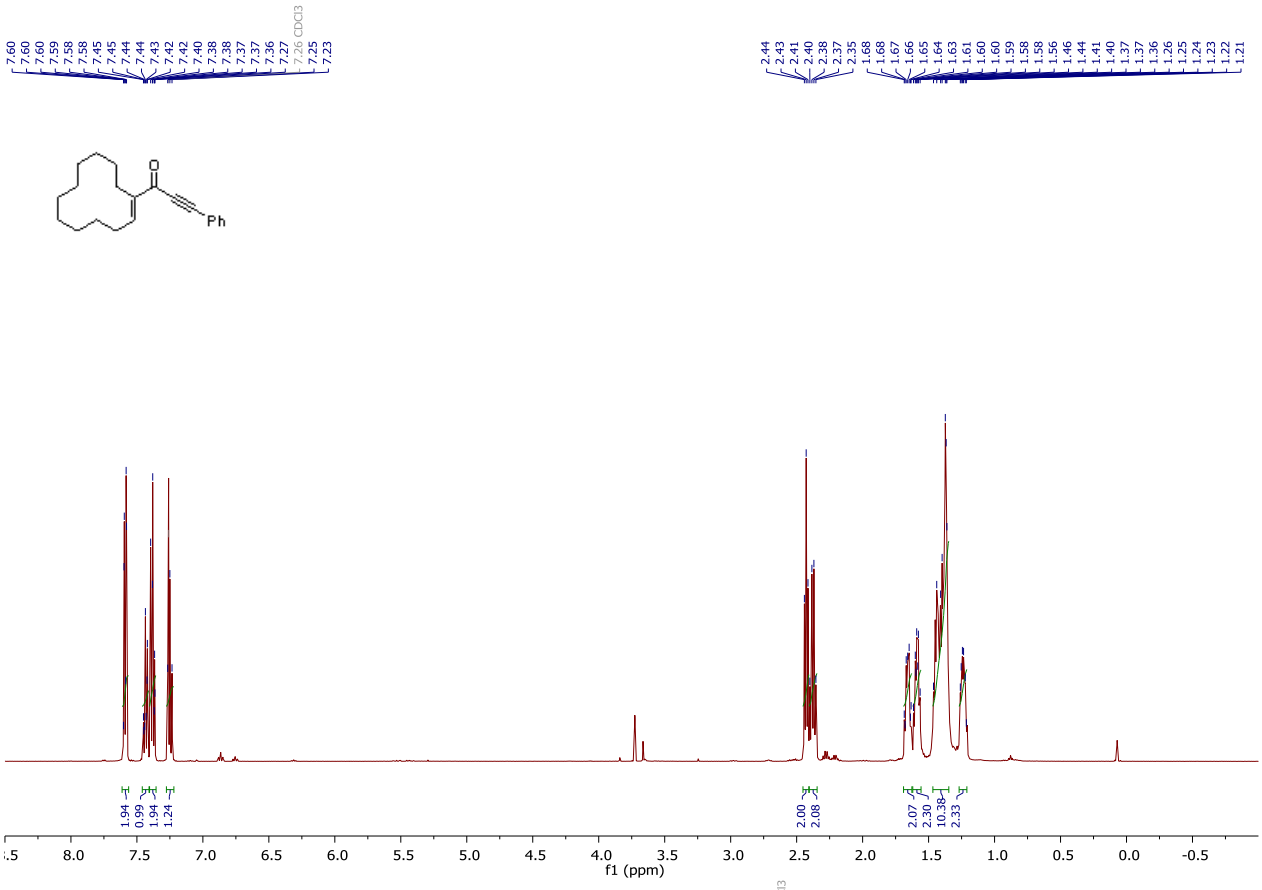
131.18
123.16
104.32
98.72
77.41
77.16
77.16 CDCl3
76.91
55.58
55.53
26.30
26.20
25.86
25.13
25.08
25.02
24.11
22.95
22.93
22.37
O
OMe
OMe
f1 (ppm)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7.60
7.60
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7.58
7.45
7.45
7.44
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7.43
7.42
7.42
7.40
7.38
7.38
7.37
7.37
7.36
7.27
7.26 CDCl3
7.25
7.23
2.44
2.43
2.41
2.40
2.38
2.37
2.35
1.68
1.68
1.67
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1.41
1.40
1.37
1.37
1.36
1.26
1.25
1.24
1.23
1.22
1.21
O
Ph
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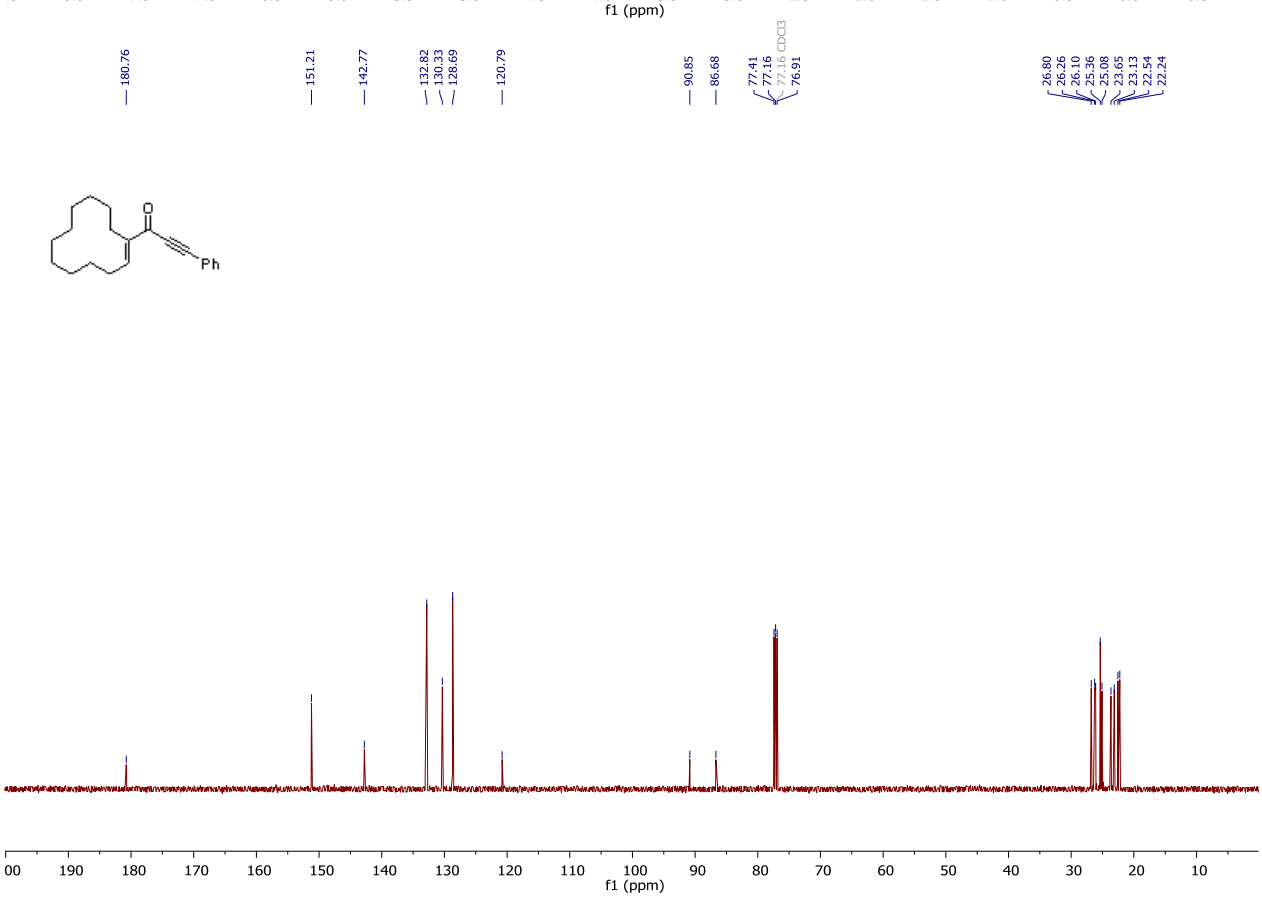
1.94
1.24
2.00
2.08
2.07
2.30
10.38
2.33
f1 (ppm)


180.76
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142.77
132.82
130.33
128.69
120.79
90.85
86.68
77.41
77.16
77.16 CDCl3
76.91
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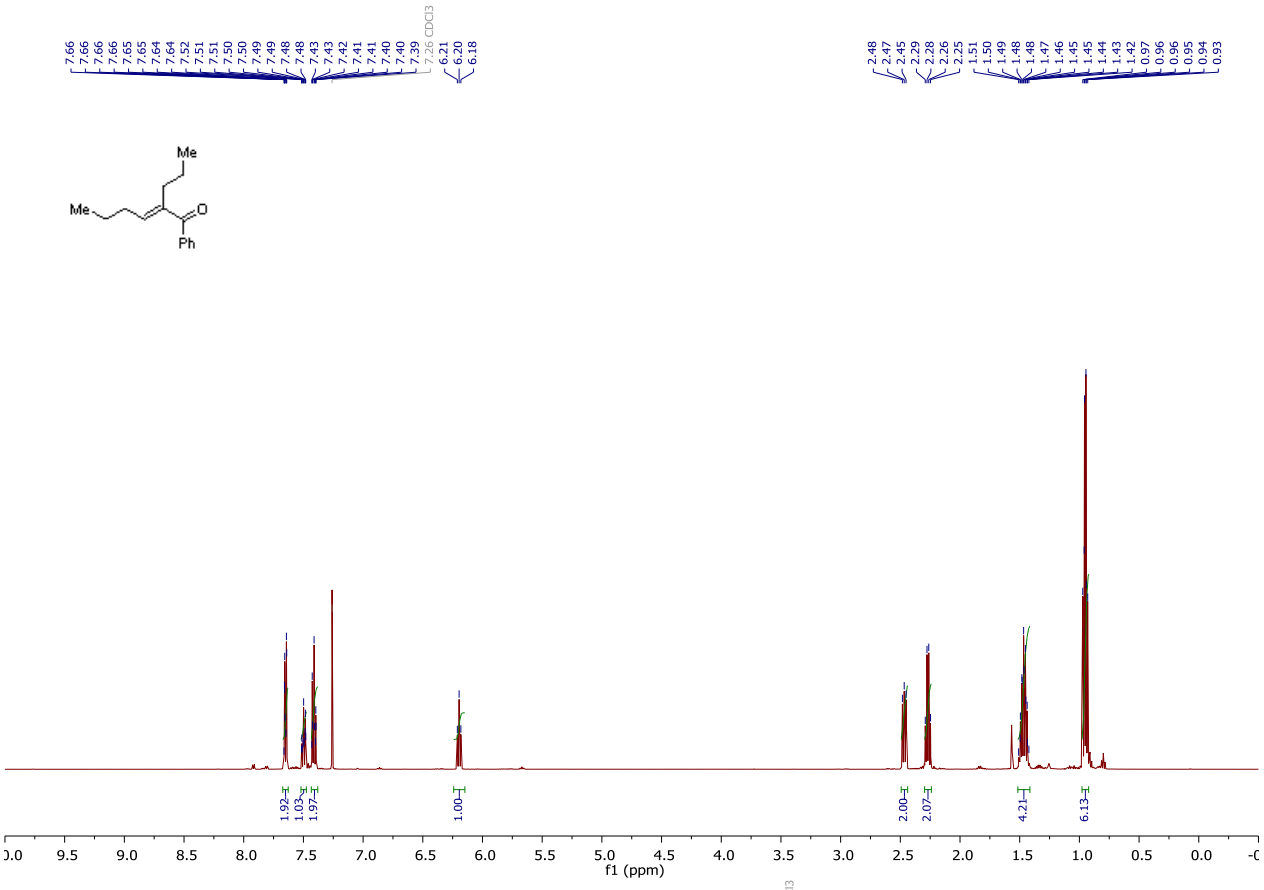
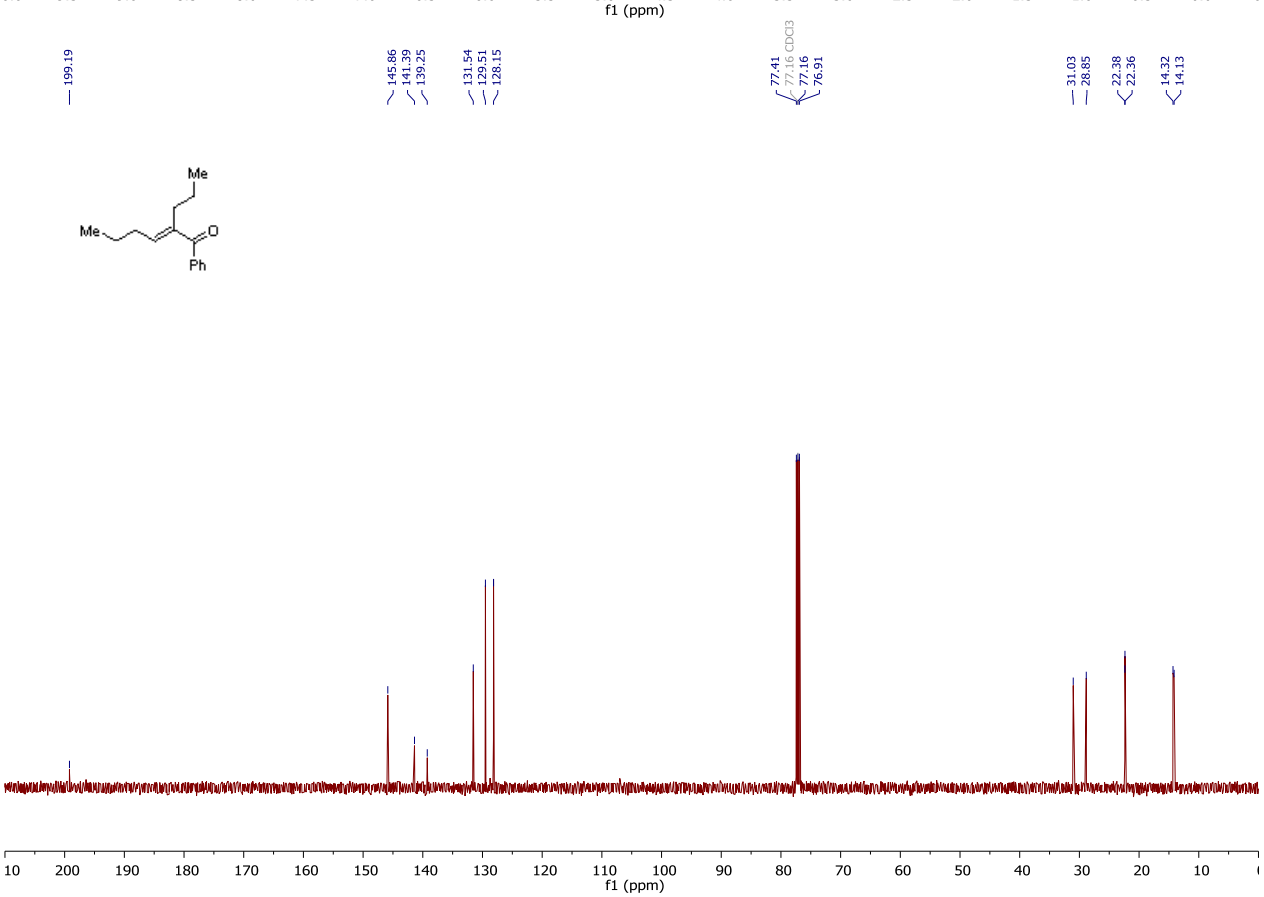
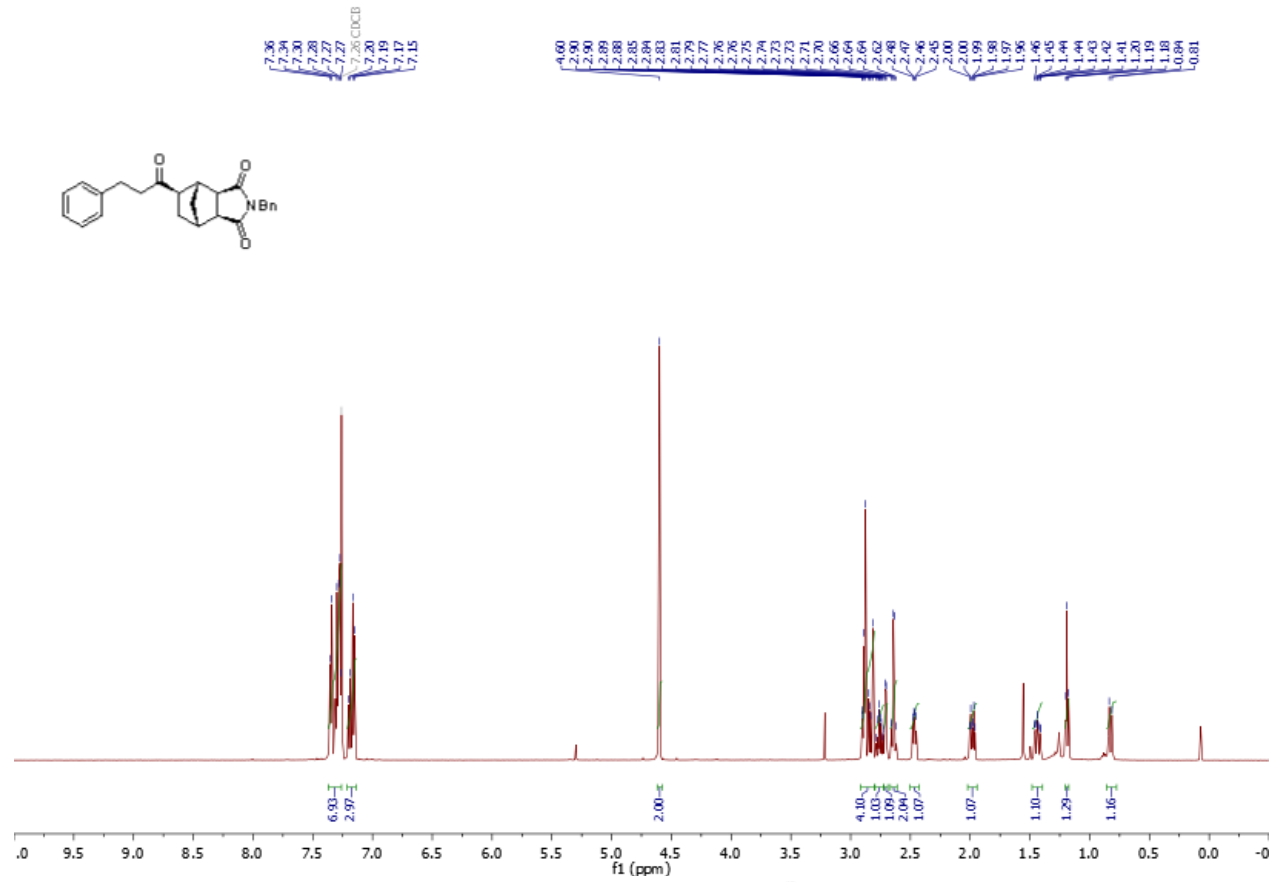
26.26
26.10
25.36
25.08
23.65
23.13
22.54
22.24
O
Ph
f1 (ppm)


7.66 7.66 7.66 7.66 7.65 7.65 7.64 7.64 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.43 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.26 CDCl3 6.21 6.20 6.18
2.48 2.47 2.45 2.29 2.28 2.26 2.25 1.51 1.50 1.49 1.48 1.48 1.47 1.46 1.45 1.45 1.44 1.43 1.42 0.97 0.96 0.96 0.95 0.94 0.93
Me
Me
O
Ph
1.92 1.03 1.97 1.00 2.00 2.07 4.21 6.13
f1 (ppm)


199.19
145.86 141.39 139.25 131.54 129.51 128.15
77.41 77.16 CDCl3 77.16 76.91
31.03 28.85 22.38 22.36 14.32 14.13
Me
Me
O
Ph
f1 (ppm)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7.34
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7.28
7.27
7.26 CDCB
7.20
7.19
7.17
7.15
4.60
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2.90
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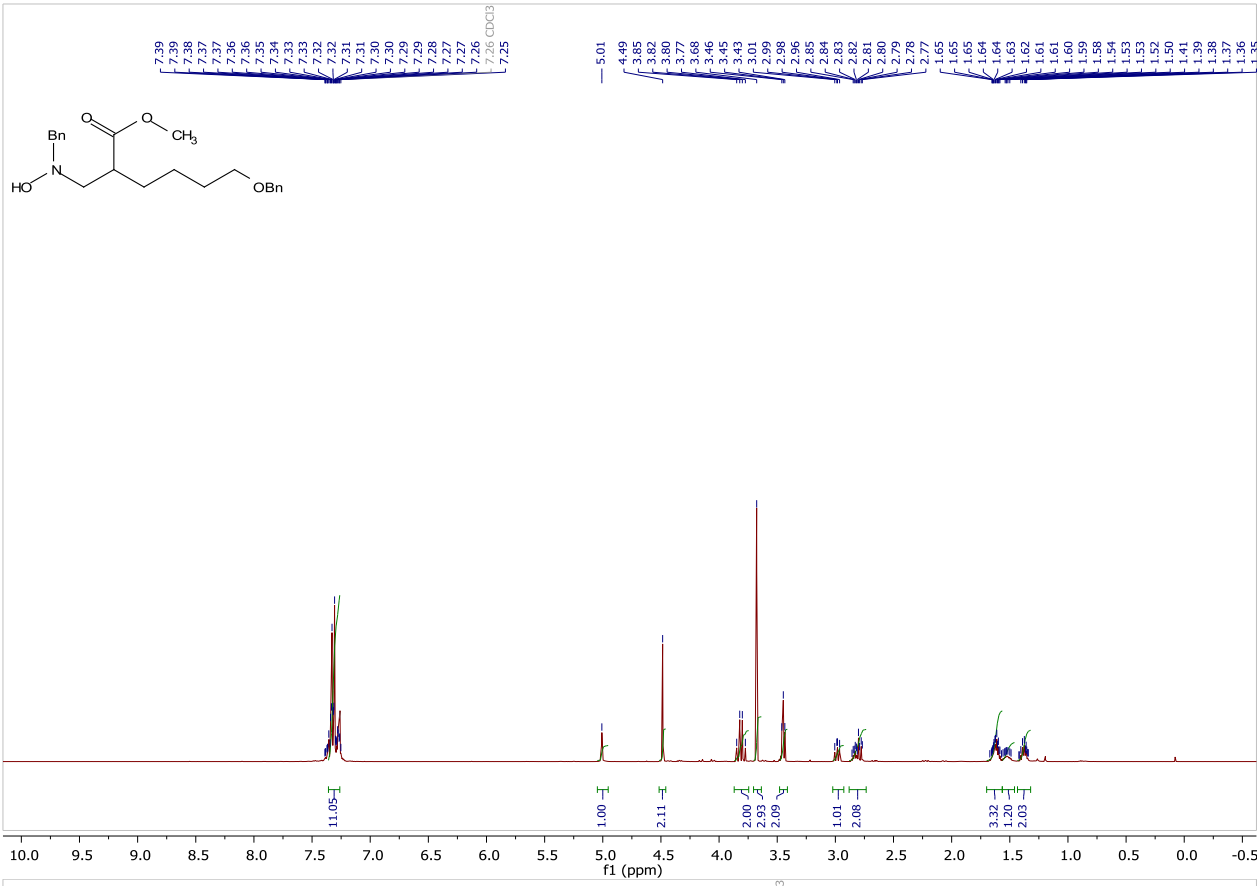
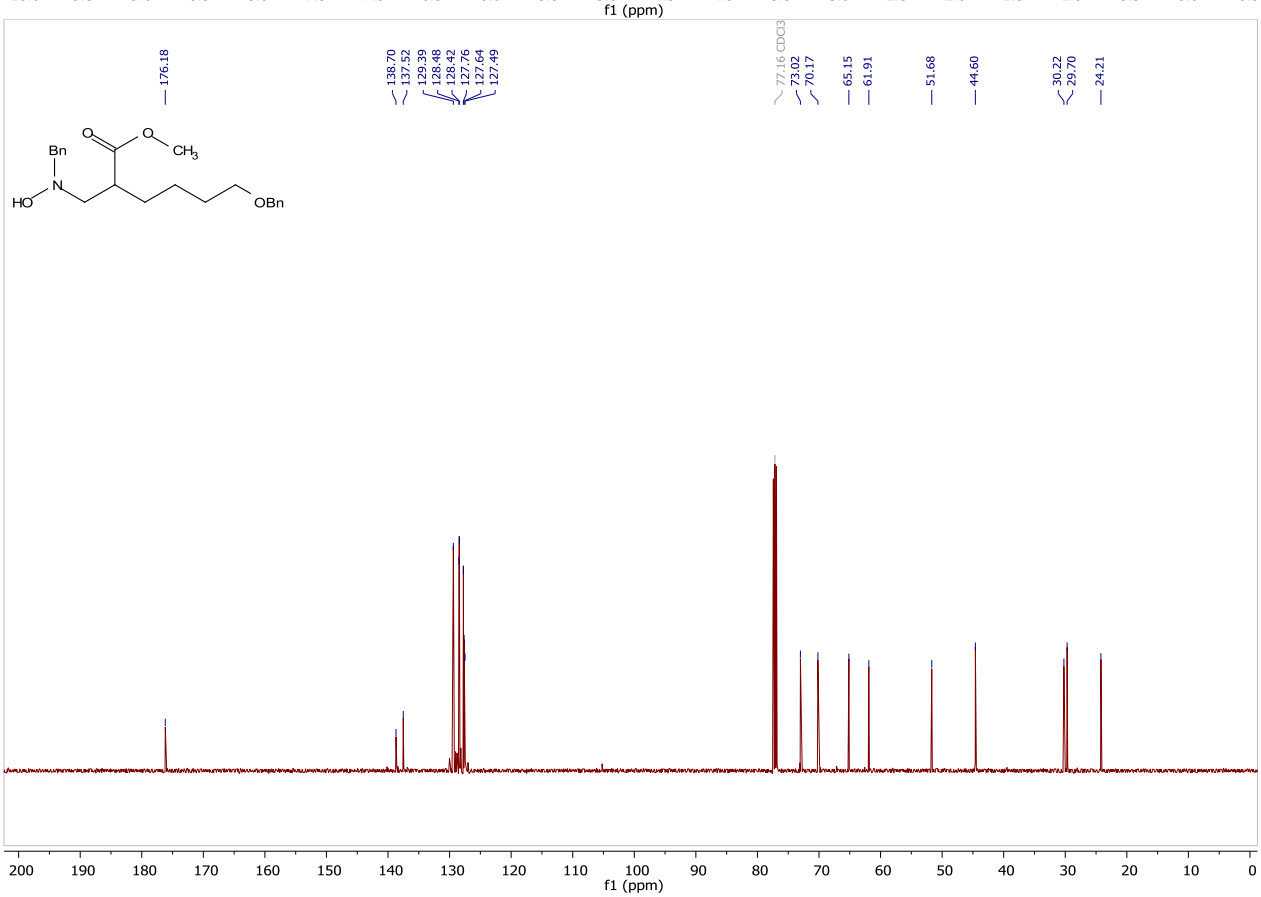
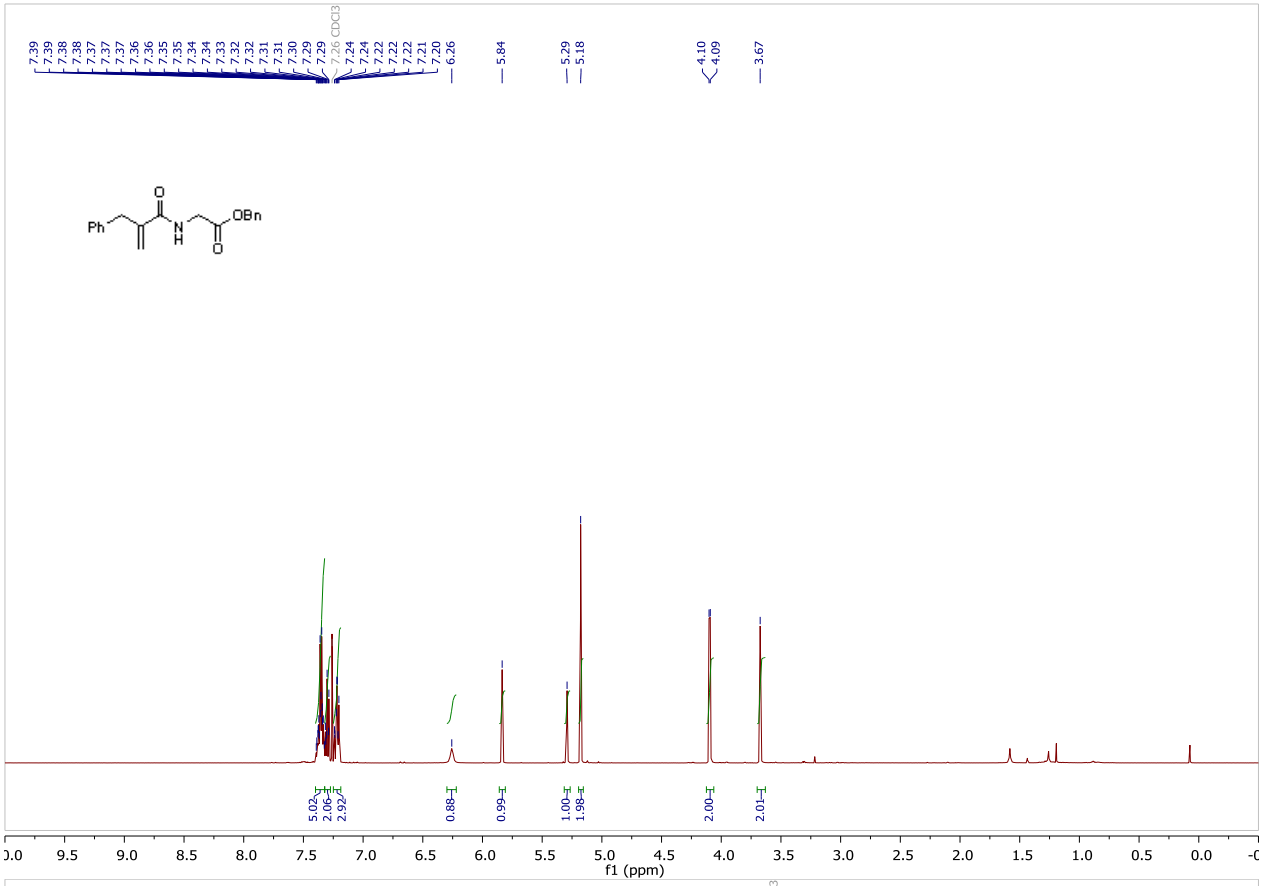
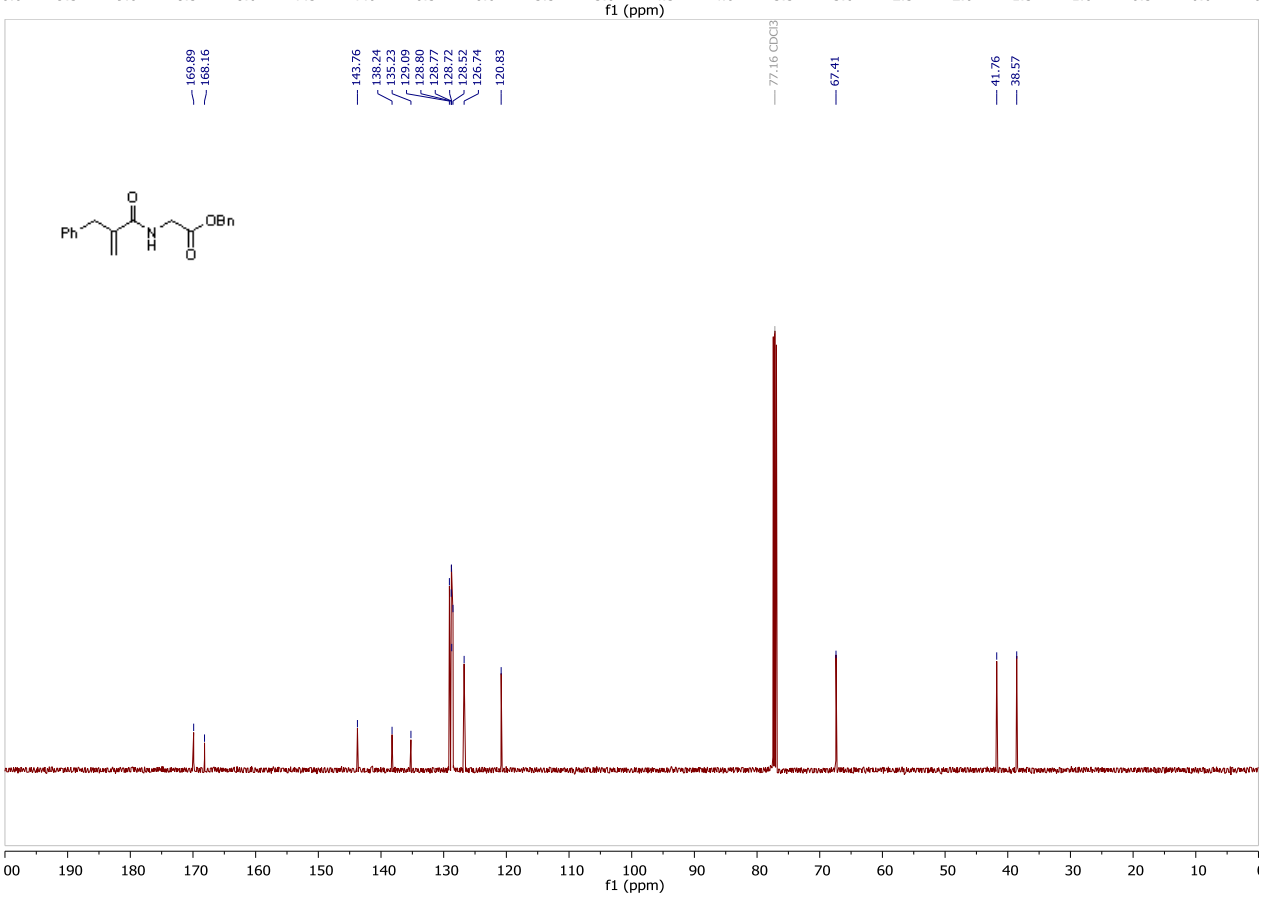
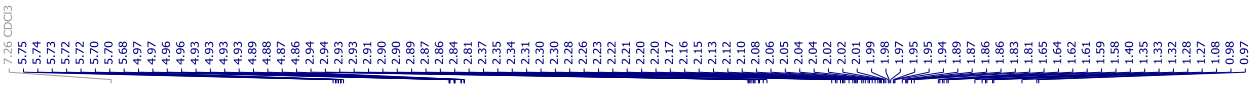
2.88
2.85
2.84
2.83
2.81
2.79
2.77
2.76
2.76
2.75
2.74
2.73
2.73
2.71
2.70
2.66
2.64
2.64
2.62
2.48
2.47
2.46
2.45
2.00
2.00
1.99
1.98
1.97
1.96
1.46
1.45
1.44
1.44
1.43
1.42
1.41
1.20
1.19
1.18
0.84
0.81
O
O
NBn
O
6.93
2.97
2.00
4.10
1.03
1.09
2.04
1.07
1.07
1.10
1.29
1.16
f1 (ppm)
177.94
177.65
140.97
135.93
128.95
128.81
128.68
128.45
128.15
126.37
77.41
77.16
77.16 CDCB
76.91
52.47
48.77
48.53
43.62
42.79
42.63
39.73
31.03
31.01
30.04
O
O
NBn
O
f1 (ppm)

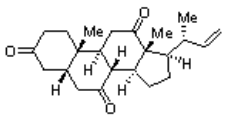

Bn
N
HO
O
O
CH3
OBn
f1 (ppm)

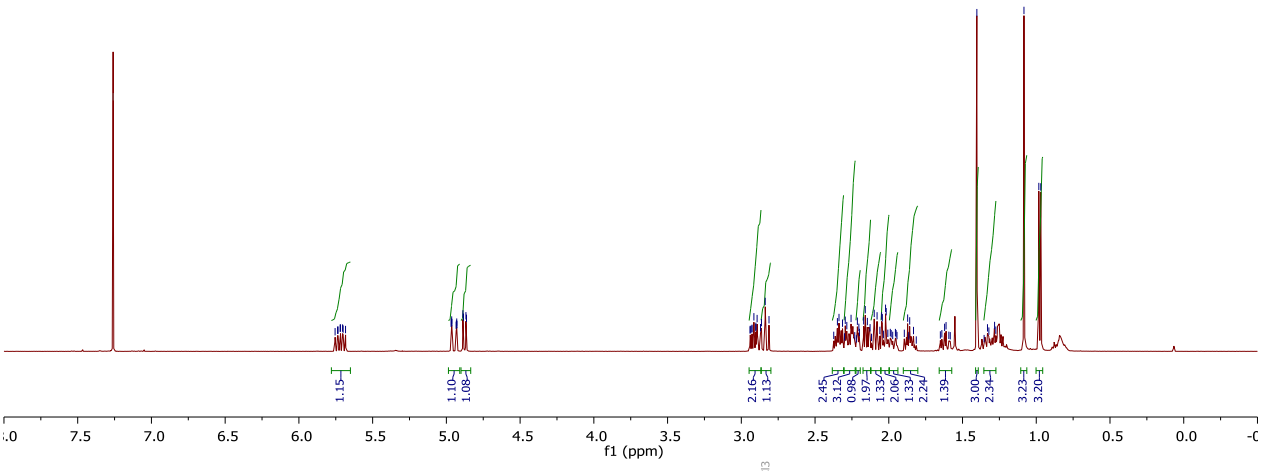

Bn
N
HO
O
O
CH3
OBn
f1 (ppm)

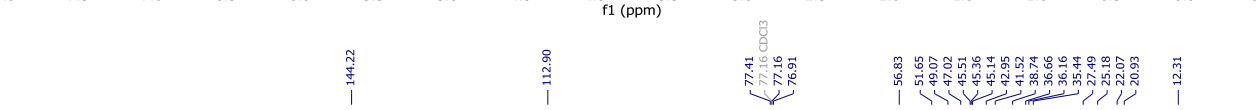

7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.26 CDCl3
7.24
7.24
7.22
7.22
7.22
7.21
7.20
6.26
5.84
5.29
5.18
4.10
4.09
3.67
Ph
O
N
H
OBn
O
5.02
2.06
2.92
0.88
0.99
1.00
1.98
2.00
2.01
f1 (ppm)

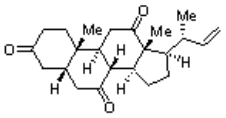

169.89
168.16
143.76
138.24
135.23
129.09
128.80
128.77
128.72
128.52
126.74
120.83
77.16 CDCl3
67.41
41.76
38.57
Ph
O
N
H
OBn
O
f1 (ppm)

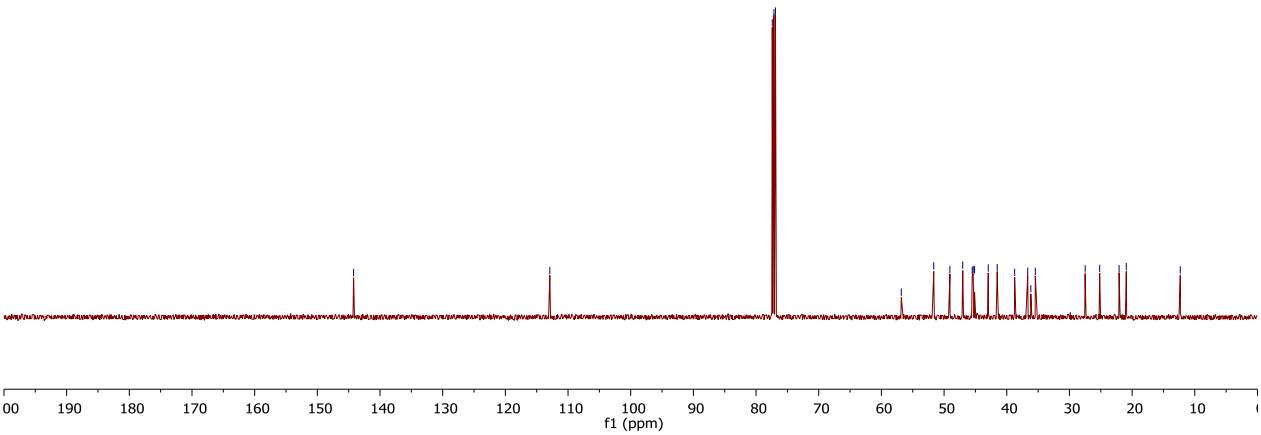


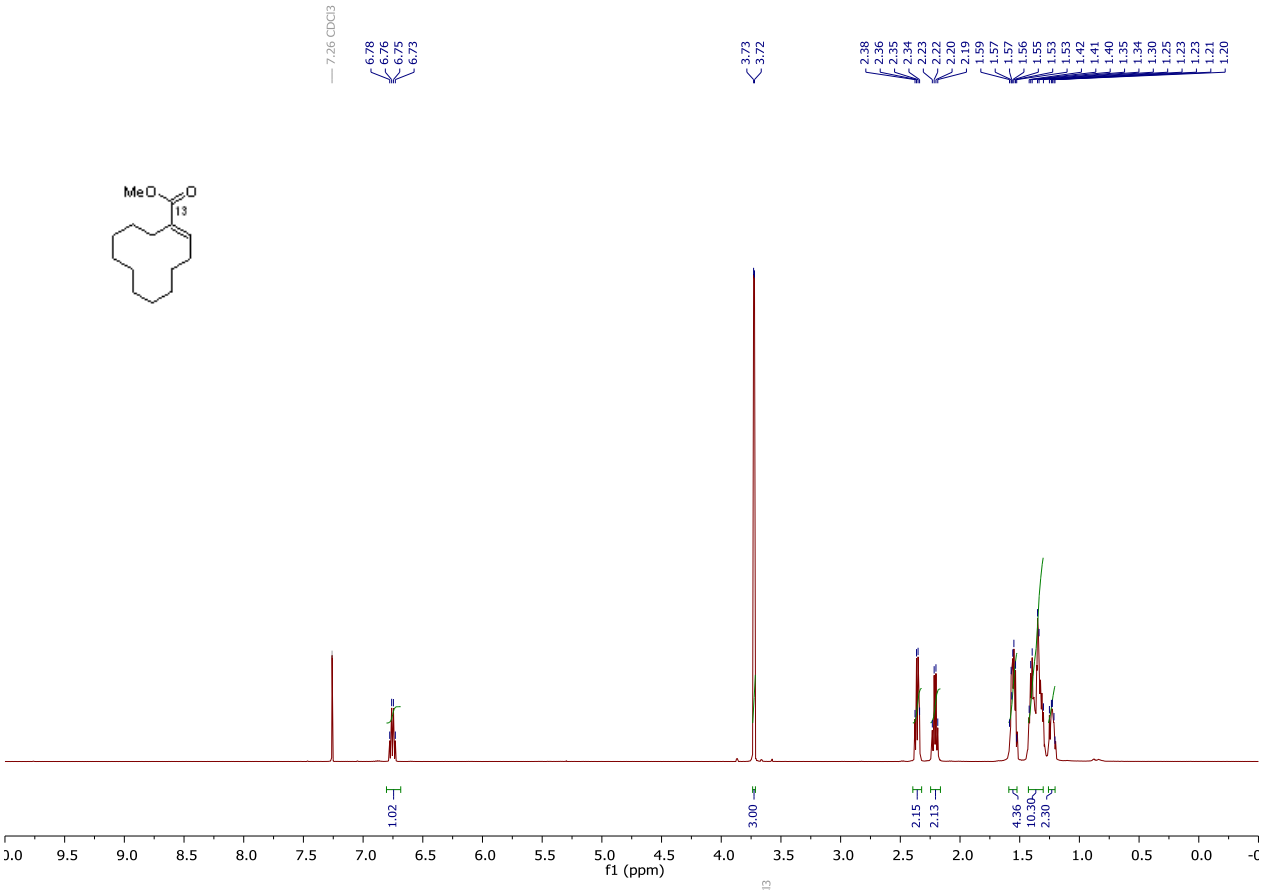


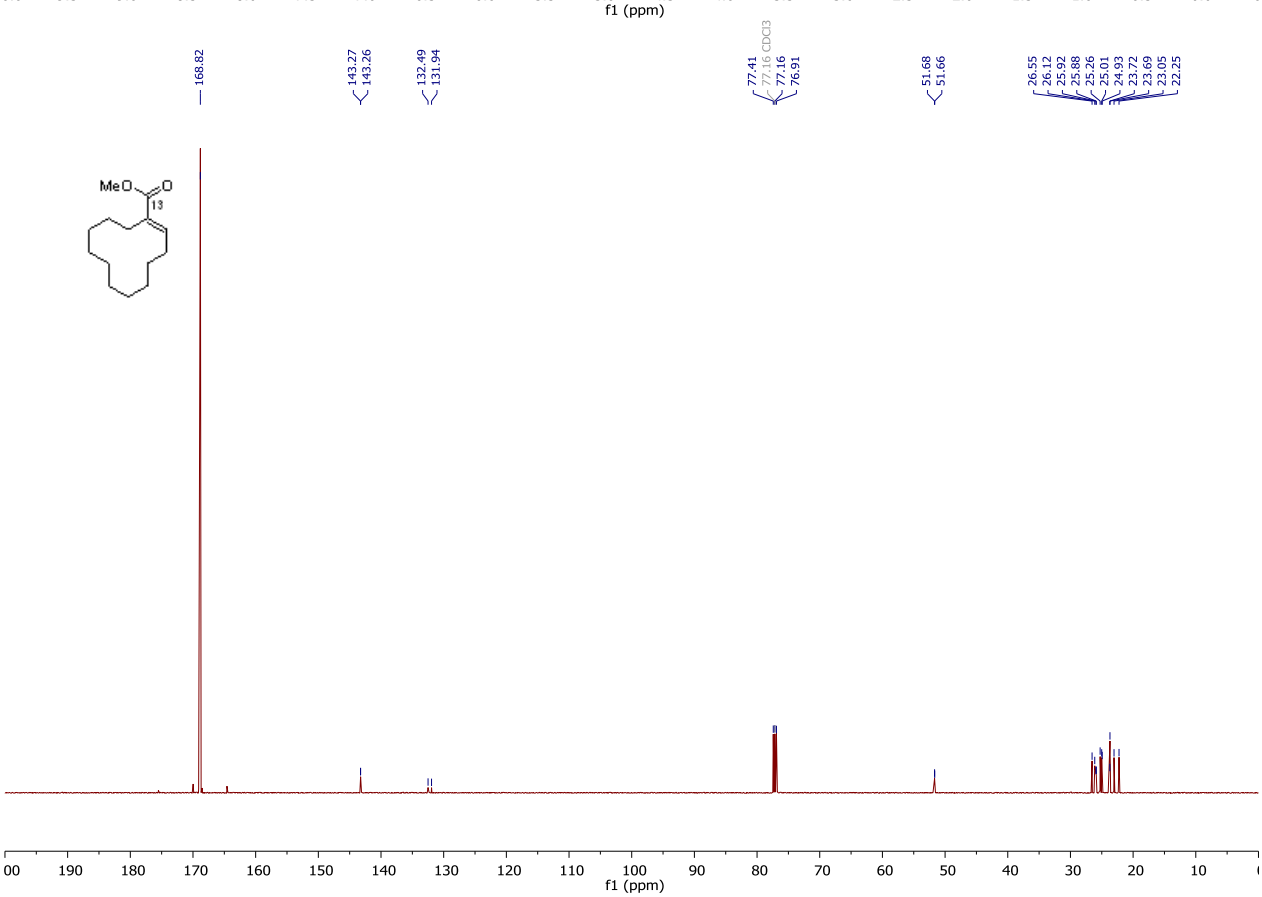


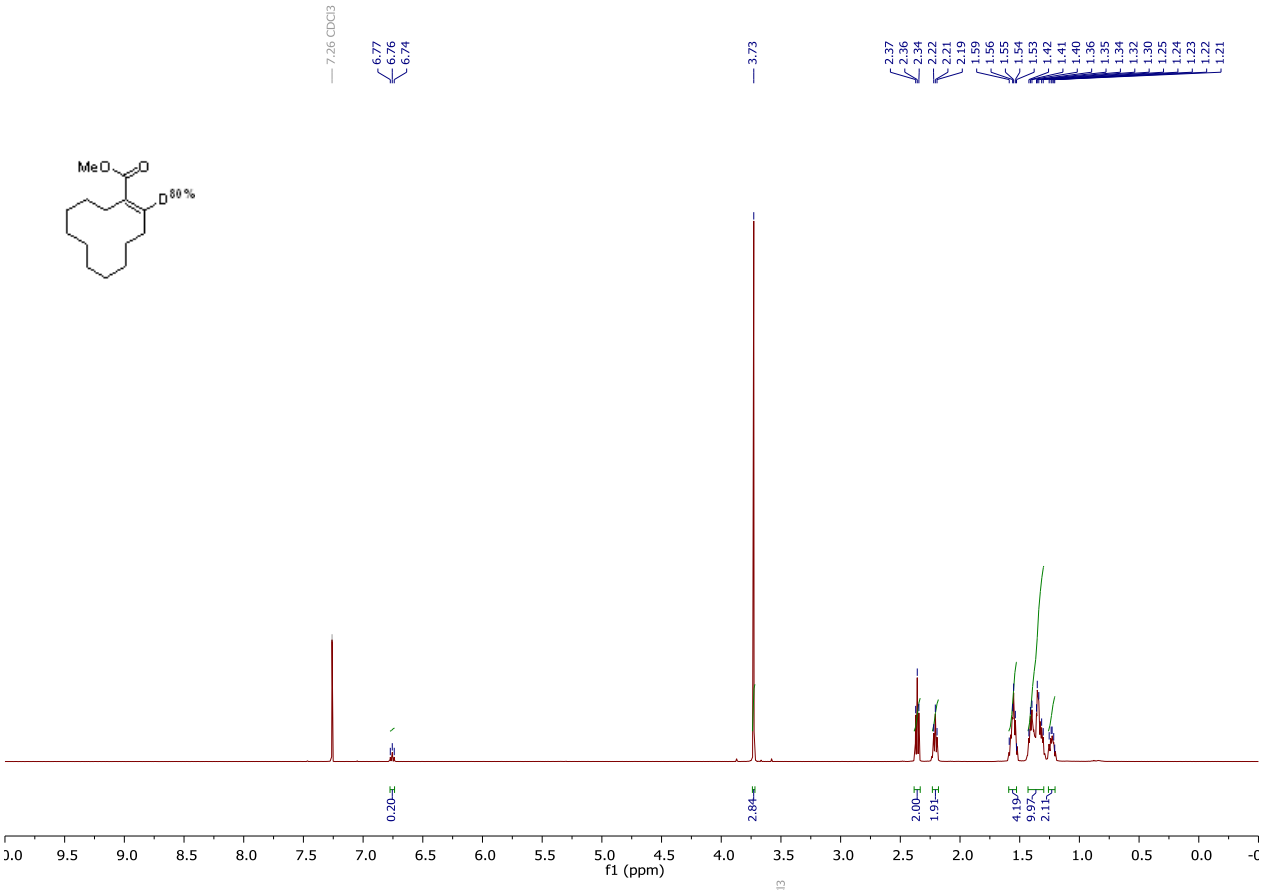


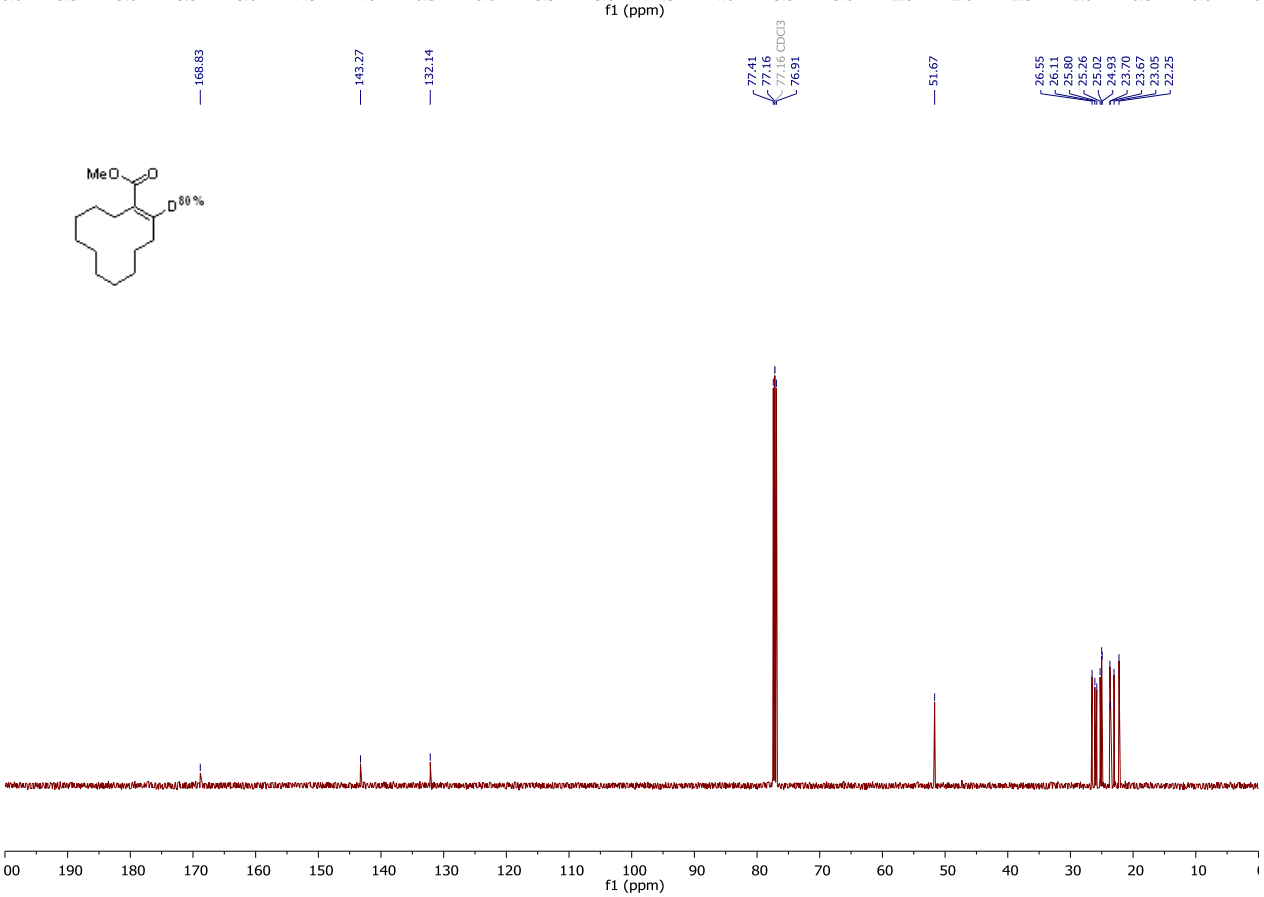





7.26 CDCl3
6.78
6.76
6.75
6.73
3.73
3.72
2.38
2.36
2.35
2.34
2.23
2.22
2.20
2.19
1.59
1.57
1.57
1.56
1.55
1.53
1.53
1.42
1.41
1.40
1.35
1.34
1.30
1.25
1.23
1.23
1.21
1.20
MeO
O
13
1.02
3.00
2.15
2.13
4.36
10.30
2.30
f1 (ppm)


168.82
143.27
143.26
132.49
131.94
77.41
77.16 CDCl3
77.16
76.91
51.68
51.66
26.55
26.12
25.92
25.88
25.26
25.01
24.93
23.72
23.69
23.05
22.25
MeO
O
13
f1 (ppm)


7.26 CDCl3
6.77
6.76
6.74
3.73
2.37
2.36
2.34
2.22
2.21
2.19
1.59
1.56
1.55
1.54
1.53
1.42
1.41
1.40
1.36
1.35
1.34
1.32
1.30
1.25
1.24
1.23
1.22
1.21
MeO
O
D 80 %
0.20
2.84
2.00
1.91
4.19
9.97
2.11
f1 (ppm)


168.83
143.27
132.14
77.41
77.16
77.16 CDCl3
76.91
51.67
26.55
26.11
25.80
25.26
25.02
24.93
23.70
23.67
23.05
22.25
MeO
O
D 80 %
f1 (ppm)