Supporting Information

Iron-Catalyzed Photoinduced LMCT: a 1° C-H Abstraction Enables Skeletal Rearrangements and C(sp3)-H Alkylation

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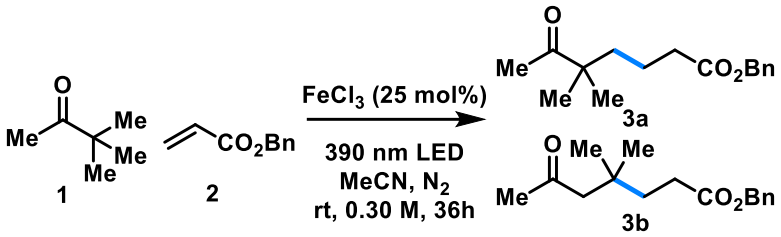
Materials and Methods

Unless otherwise noted, all reactions were performed in oven-dried glassware and carried out under an atmosphere of nitrogen with magnetic stirring. All photochemical reactions were run in 1.5 dram vials fitted with Teflon caps under irradiation from a PR-160 Kessil 40W LED lamp with Teflon stir-bars under vigorous magnetic stirring. All photochemical reactions were set up in a nitrogen glovebox, although optimization experiments showed that the reactions could also be set up on the benchtop without significant loss of yield. Thin layer chromatography was performed on SiliCycle® 250 μm 60 Å plates. Visualization was accomplished with 254 nm ultraviolet light, 2,4-dinitrophenylhydrazine, iodine or potassium permanganate stains.

^{1}H NMR spectra were recorded on Bruker 400 or 500 MHz spectrometers at ambient temperature. Chemical shift is reported in parts per million (ppm) from $CDCl_3$ (7.26 ppm) with multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constants (Hz). ^{13}C NMR was recorded on Bruker 500 or 400 MHz spectrometers (126 MHz) at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ (77.15 ppm). Mass spectra were recorded on an Agilent 7890B GC System 5977B MSD GCMS with an EI ionization method. High resolution mass spectra (HRMS) were obtained from the Columbia University Chemistry Department Mass Spectrometry Facility on a Waters XEVO G2XS QToF mass spectrometer equipped with a UPC2 SFC inlet and a LockSpray source with one of the following three probes: electrospray ionization (ESI) probe, atmospheric pressure chemical ionization (APCI) probe, or atmospheric pressure solids analysis probe (ASAP). Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR Spectrometer. UV-vis spectra were recorded on a Beckman-Coulter DU720 General Purpose UV/Vis Spectrophotometer.

Unless otherwise mentioned, all starting materials were obtained from commercial sources including Millipore-Sigma, TCI, and Alfa-Aesar. Anhydrous $FeCl_3$ and anhydrous acetonitrile were obtained from Millipore-Sigma.

Optimization Studies



Entry	Deviation from Standard Conditions	Yield (%)	*ir* (3a:3b)
1	**none**	**64**	**1:1.4**
2	60 °C, 0.10 M	67	1:10
3	60 °C	65	1:4
4	added LiCl (62.5 mol%)	52	1:1
5	0% $FeCl_3$	0	-
6	in the dark	0	-
7	irradiate at 390nm 1 h, then dark	2	n.d.
8	427 nm LEDs	3	n.d.
9	under air	47	1:1
10	10 µL H_2O as an additive	12	1.5:1

To an oven-dried 1.5 dram vial was added $FeCl_3$ (25 mol%). A magnetic stir bar was added and the vial was transferred to a glovebox. Anhydrous acetonitrile (1 mL, 0.30 M) was then added, followed by pinacolone (5 equiv., 1.5 mmol) and benzyl acrylate (1 equiv., 0.3 mmol). The vial was sealed and then placed on a stir plate 2-3 inches away from a 390 nm Kessil lamp. Ambient temperature (28 °C) was maintained with the use of a fan above the set-up. After 36 hours, the reaction mixture was concentrated in vacuo and flushed through a silica plug using dichloromethane as the eluent. The solvent was removed again in vacuo and the reaction yield and isomeric ratio determined by NMR using 1,3,5-trimethoxybenzene as the internal standard.

Experiments at 60 °C were carried out with the fan turned off.

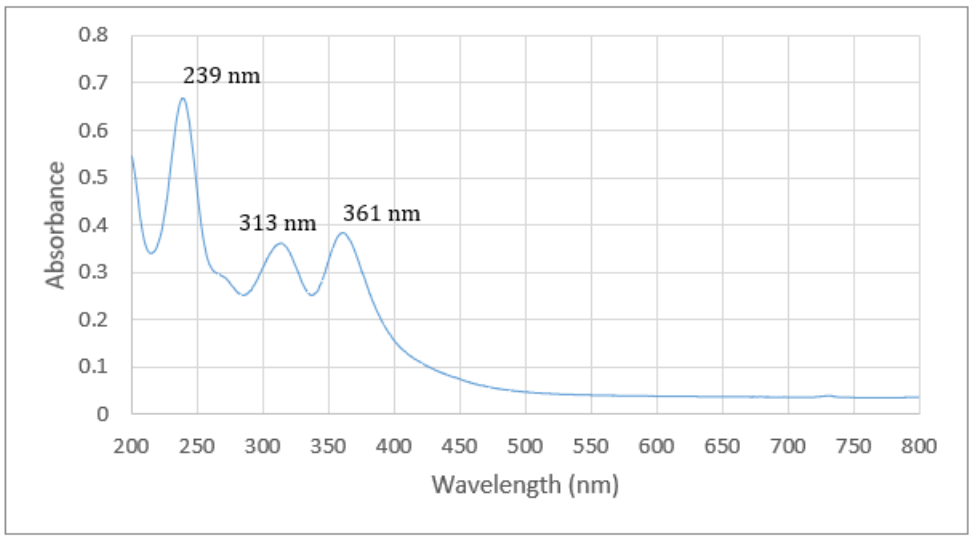
Mass balance

Control experiments in the absence of $FeCl_3$ (Table 1, Entry 5) resulted in complete polymerization of benzyl acrylate, likely promoted by the intense 390 nm LED irradiation. Thus, oligomerization pathways may unproductively consume some of the acceptor (the limiting reagent), leading to lowered yields. However, the fact that we are able to observe effective reaction (with yields of up to 70-80% with some substrates) suggests that the iron catalyst must play a role in suppressing runaway chain processes like polymerization. Even in sluggish reactions that do not reach completion, there is often unreacted benzyl acrylate remaining in the crude mixture. There is precedent for $FeCl_3$ acting as a polymerization inhibitor through chlorination of alkyl radical species.[1–3] Given the proposed mechanism of our reaction, with an Fe(II) species trapping the radical formed after Giese addition to form an Fe(III) enolate, it is possible that the structurally similar radical from a growing polymer chain could also be similarly trapped, which would also further chain growth.

UV-vis studies

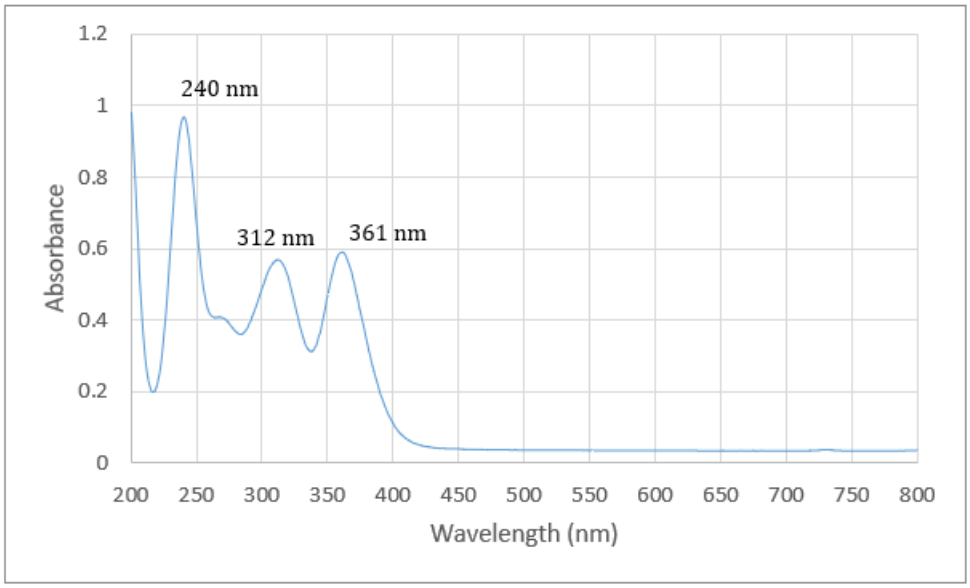
Sample preparation (75 μM $FeCl_3$ in MeCN)

$FeCl_3$ (12.1 mg, 0.075 mmol) was dissolved in 1.0 mL of acetonitrile. The resultant solution was stirred for 15 minutes, and a 3.0 μL aliquot was drawn and added to 3.0 mL of acetonitrile in a quartz cuvette.



Sample preparation (75 μM $FeCl_3$, 187.5 μM LiCl in MeCN)

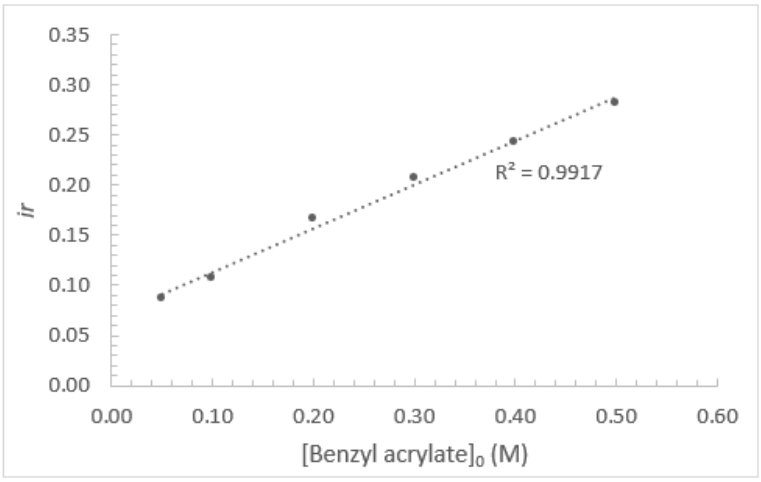
$FeCl_3$ (12.1 mg, 0.075 mmol) and LiCl (7.9 mg, 0.1875 mmol, 2.5 equiv.) were dissolved in 1.0 mL of acetonitrile. The resultant solution was stirred for 15 minutes, and a 3.0 μL aliquot was drawn and added to 3.0 mL of acetonitrile in a quartz cuvette.



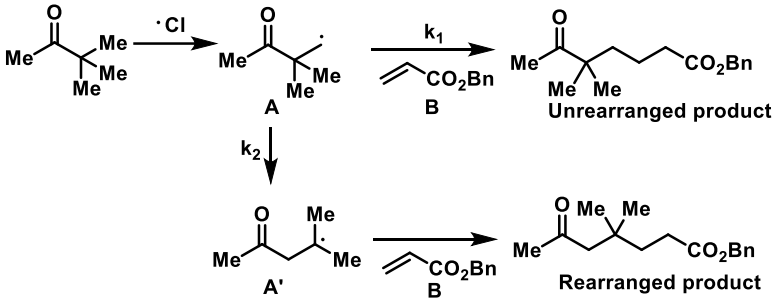
Mechanistic and Kinetic Studies

Relationship between acrylate concentration and R_M

To oven-dried 1.5 dram vials were added $FeCl_3$ (25 mol%). Magnetic stir bars were added and the vials were transferred to a glovebox. Anhydrous acetonitrile (0.4 – 4.0 mL) was then added, followed by pinacolone (5 equiv., 1.0 mmol) and benzyl acrylate (1 equiv., 0.2 mmol). The initial concentration of benzyl acrylate was therefore varied from 0.05M to 0.50 M. The vials were sealed and then placed on a stir plate 2-3 inches away from a 390 nm Kessil lamp. No fan was used, allowing the temperature to reach 60 °C. After 36 hours, the reaction mixture was concentrated in vacuo and flushed through a silica plug using dichloromethane as the eluent. The solvent was removed again in vacuo and the ratio of unrearranged over rearranged product, the isomeric ratio (*ir)*, was determined by NMR using 1,3,5-trimethoxybenzene as the internal standard.



On the basis of the observed linear dependence of *ir* on [benzyl acrylate]$_0$, we propose the following model of the 1,2-rearrangement kinetics.

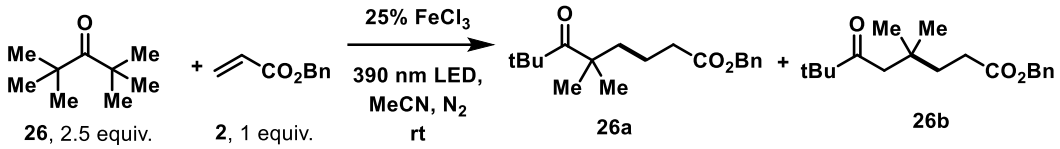


$$ir = \frac{[Unrearranged\ pdt.]}{[Rearranged\ pdt.]} = \frac{k_1[A][B]}{k_2[A]} = \frac{k_1}{k_2}[B] \approx \frac{k_1}{k_2}[B]_0$$

Abstraction of a C-H bond from pinacolone yields a primary radical A, which can be consumed by two possible reaction pathways. Direct addition to benzyl acrylate (**k**$_1$) yields the unrearranged product. Rearrangement via a cyclopropyl intermediate to the more stable tertiary radical A' (**k**$_2$) may also occur. A' may then be trapped by benzyl acrylate to yield the rearranged product.

The strong dependence of *ir* on the concentration of acrylate suggests against a Curtin-Hammett kinetics regime wherein A and A' are in rapid equilibrium and the ratio of products depends mainly on the barrier to radical addition to the acrylate. We would expect concentration to have little to no effect on *ir* in a Curtin-Hammett scenario, since both radical additions (of either the primary or tertiary radical) to benzyl acrylate would be bimolecular.

Determining k_1 via initial rate experiments



To an oven-dried 1.5 dram vial was added $FeCl_3$ (25 mol%). A magnetic stir bar was added and the vial was transferred to a glovebox. Anhydrous acetonitrile (3 mL) was then added, followed by di-tert-butyl ketone (2.5 equiv.) and benzyl acrylate (**1 equiv., 0.20 M**). The vial was sealed and then placed on a stir plate 2-3 inches away from a 390 nm Kessil lamp. Ambient temperature (28 °C) was maintained with the use of a fan above the set-up. After **3 hours**, the reaction mixture was concentrated in vacuo and flushed through a silica plug using dichloromethane as the eluent. The solvent was removed again in vacuo and the reaction yield and R_M determined by NMR using 1,3,5-trimethoxybenzene as the internal standard.

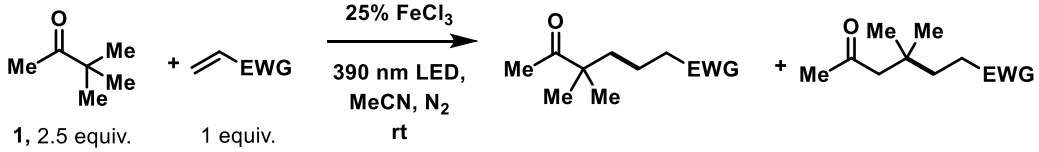
From the earlier equation, we can find $\mathbf{k_1}$, the rate constant for addition of the primary radical to benzyl acrylate. The value of $\mathbf{k_2}$ for di-tert-butylketone is known to be 1.7×10^5 s^{-1} at 25 °C in CCl_4.[4]

$$ir = \frac{k_1}{k_2}[B]_0$$

We found a *ir* value of 0.272. This gave $\mathbf{k_1}$ = 2.3×10^5 M^{-1} s^{-1} under our reaction conditions (28°C in MeCN). Given the similar structure of the primary radical formed from initial HAT, we assumed an equivalent $\mathbf{k_1}$ value for the addition of the pinacolone primary radical to benzyl acrylate.

The experiment was then repeated with pinacolone as the substrate in place of di-tert-butyl ketone. We found an *ir* value of 1.6. Using the same equation above, we obtained a value for the rate constant of 1,2-migration for pinacolone, $\mathbf{k_2}$ = 2.9×10^4 s^{-1}. This value was then used to calculate the values of $\mathbf{k_1}$ for acceptors other than benzyl acrylate.

Initial rate experiments with other acceptors



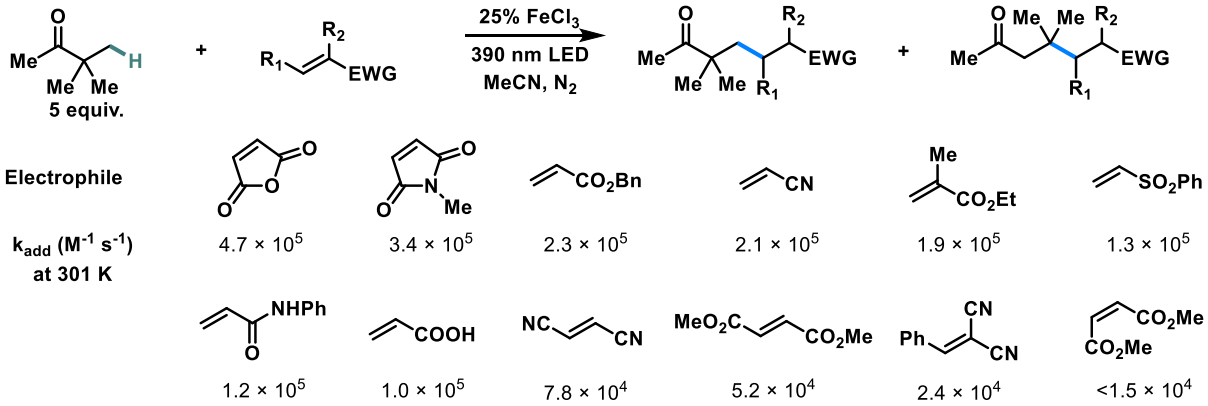
To an oven-dried 1.5 dram vial was added $FeCl_3$ (25 mol%) and the appropriate acceptor (if solid) (**2 equiv., 0.20 M**). A magnetic stir bar was added and the vial was transferred to a glovebox. Anhydrous acetonitrile (3 mL) was then added, followed by pinacolone (2.5 equiv.) and the appropriate acceptor (if liquid) (**1 equiv., 0.20 M**). (In the reaction with acrylic acid, 1 equiv. of trifluoroacetic acid was also added at this point). The vial was sealed and then placed on a stir plate 2-3 inches away from a 390 nm Kessil lamp. Ambient temperature (28 °C) was maintained with the use of a fan above the set-up. After **1-12 hours**, the reaction mixture was concentrated in vacuo and flushed through a silica plug using dichloromethane as the eluent. The solvent was removed again in vacuo and the reaction yield and *ir* determined by NMR using 1,3,5-trimethoxybenzene as the internal standard.

Reaction time used:

- Maleic anhydride, N-methylmaleimide: 1 hour
- All other acceptors: 3 hours
- Dimethyl maleate: 12 hours

The reaction yields were generally below 20% within the time frame with accompanying low conversion of starting material, and the effective concentration of the acceptor was assumed to be equal to the initial concentration of acceptor (i.e. 0.20 M). For dimethyl maleate, no clear peak for the minor isomer could be observed even after 12 hours, so the *ir* is taken to be <1:10.

Comparison of rate constants to literature values



Alkene	k_{add}(Me•)	k_{add}(tBu•)	k_{add}(pinacolyl•)
Methyl acrylate	3.4×10^5[Ref. 5,6] 3.8×10^5[Ref. 7]	1.1×10^6[Ref. 5,6]	
Benzyl acrylate			2.3×10^5
Methyl methacrylate	4.9×10^5[Ref. 5,6]	6.6×10^5[Ref. 5,6]	
Ethyl methacrylate			1.9×10^5
Acrylonitrile	6.1×10^5[Ref. 5,6]	5.2×10^6[Ref. 5,6]	2.1×10^5
Acrylic acid	3.0×10^6[Ref. 8]#		1.0×10^5
Fumaronitrile	1.7×10^6[Ref. 9] (338 K)		7.8×10^4
Diethyl fumarate	1.7×10^6[Ref. 9] (338 K) 7.5×10^5[Ref. 6]		
Dimethyl fumarate		2.0×10^5[Ref. 6]	5.2×10^4
Diethyl maleate	2.9×10^5[Ref. 9] (338 K) 7.5×10^4[Ref. 6]		
Dimethyl maleate		7.7×10^4[Ref. 6]	$< 1.5 \times 10^4$

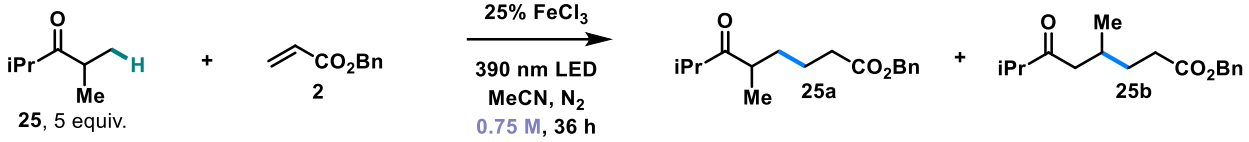
All rate constants given in units of M^{-1} s^{-1} at temperatures near 300K unless otherwise noted. #At pH 2.

We compared our measured rate constants with literature values for the addition of methyl and tert-butyl radicals.[5–9] Our rate constants were generally in reasonable agreement with the literature values. Broadly speaking, our values were almost always smaller than the corresponding values for methyl radical or tert-butyl radical, which can be rationalized in terms of the pinacolyl radical being (1) significantly more sterically hindered than a methyl radical, though less so than a tert-butyl radical, (2) less nucleophilic than a tert-butyl radical (pentyl radical adds to methyl acrylate at a sixth of the rate of the 1,1-dimethylpropyl radical[7]) and (3) close to an electron-withdrawing carbonyl group. Comparing the rate constants for methyl/ethyl methacrylate and acrylonitrile, the pinacolyl radical has a rate constant of approximately one-third that of methyl radical. For disubstituted alkenes, the rate constant is roughly an order of magnitude smaller than that of methyl radical, which is likely due to the increased importance of steric effects in the addition to these acceptors. Tert-butyl radical adds to terminal alkenes (methyl acrylate and acrylonitrile) faster than methyl radical, but only adds at comparable or lower rates to the disubstituted alkenes (fumarate and maleate). Similar steric effects are likely at play for the neopentyl-like pinacolyl radical in our reactions.

Besides 8 alkenes for which absolute rate constant data was available (rate constants for the addition of hydroxyalkyl radicals to maleic anhydride are known[10]), we were also able to measure the rate constants for the 4 other alkenes for which the rate constants of alkyl radical addition were not known, to the best of our knowledge. As noted in the discussion, the rate constants for addition to maleic anhydride, N-methylmaleimide and benzylidenemalononitrile are significantly lower than expected on the basis of ionic electrophilicity. All three are much stronger electrophiles than the acrylates and acrylonitriles, but the rate constants of the former two are only slightly higher and that of the latter is significantly lower. Part of this discrepancy is likely attributable to the strong steric effects of the neopentyl radical, leading to a high sensitivity towards β-substitution on the alkene. With a large phenyl substituent,

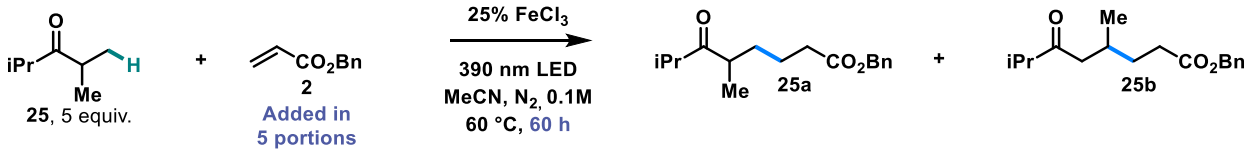
benzylidenemalononitrile likely causes significant steric hindrance for the approach of the bulky neopentyl radical to the alkene. The other factor that causes general 'compression' of the rate constant data to a fairly small range (only slightly more than an order of magnitude in our case) is the generally high exothermicity of Giese additions, given the formation of a C-C sigma bond at the expense of a pi bond. Giese addition transition states are therefore generally early,[6] and hence broadly less sensitive to the electrophilicity or structural features of the acceptor compared to analogous ionic reactions that may be less thermodynamically downhill.

Increased concentration



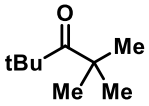
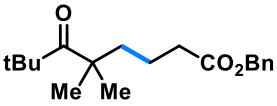
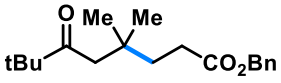
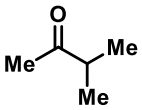
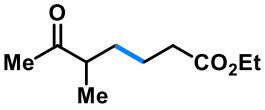
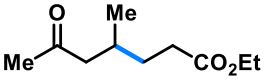
To an oven-dried 1.5 dram vial was added $FeCl_3$ (25 mol%). A magnetic stir bar was added and the vial was transferred to a glovebox. Anhydrous acetonitrile (0.4 mL, **0.75 M**) was then added, followed by 2,4-dimethyl-3-pentanone (5 equiv.) and benzyl acrylate (1 equiv., 0.3 mmol). The vial was sealed and then placed on a stir plate 2-3 inches away from a 390 nm Kessil lamp. Ambient temperature (28 °C) was maintained with the use of a fan above the set-up. After 36 hours, the reaction mixture was concentrated in vacuo and flushed through a silica plug using dichloromethane as the eluent. The solvent was removed again in vacuo and the reaction yield and *ir* determined by NMR using 1,3,5-trimethoxybenzene as the internal standard.

Portionwise addition of electrophile



To an oven-dried 1.5 dram vial was added $FeCl_3$ (25 mol%). A magnetic stir bar was added and the vial was transferred to a glovebox. Anhydrous acetonitrile (1 mL, **0.10 M**) was then added, followed by pinacolone (5 equiv.) and benzyl acrylate (**0.20 equiv.**). The vial was sealed and then placed on a stir plate 2-3 inches away from a 390 nm Kessil lamp. A fan was not used, allowing the temperature to reach 60 °C. Every 12 hours, the vial was transferred into a glovebox and another portion of benzyl acrylate (**0.20 equiv.**) was added, for a total of five portions. After 60 hours, the reaction mixture was concentrated in vacuo and flushed through a silica plug using dichloromethane as the eluent. The solvent was removed again in vacuo and the reaction yield and *ir* determined by NMR using 1,3,5-trimethoxybenzene as the internal standard.

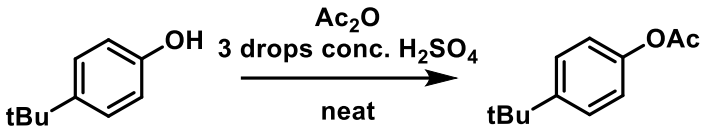
Additional Products

Substrate	Unrearranged	Rearranged	Conditions A rt, 0.33 M	Conditions B 60 °C, 0.1 M
 26	 26a	 26b	69%, 1:7	60%, 1:20
 27	 27a	 27b	54%, 11:1	44%, 1.3:1

Starting Material Preparation

4-(tert-butyl)phenyl acetate

Prepared in accordance to reported methods.[11]

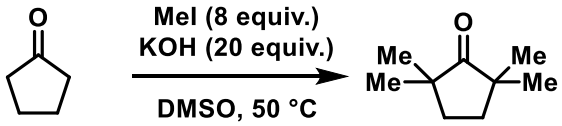


To a mixture of 4-tertbutylphenol (3.00 g, 20 mmol) and acetic anhydride (1.89 mL, 20 mmol) was added three drops of concentrated H_2SO_4 at room temperature. The reaction mixture was stirred for 30 min and poured into water (10 mL), then extracted with ethyl acetate (3 x 20 mL), dried with $MgSO_4$ and concentrated under reduced pressure to yield the product as a pale yellow oil (3.71g, 96% yield). The NMR spectrum of the product was in agreement with literature precedent.[12,13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.03 – 6.98 (m, 2H), 2.29 (s, 3H), 1.32 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.84, 148.74, 148.45, 126.45, 120.98, 34.60, 31.54, 21.29.

2,2,5,5-tetramethylcyclopentanone

Prepared in accordance to reported methods.[14]

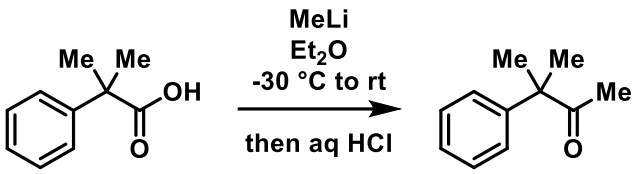


In a round-bottomed flask equipped with a reflux condenser, dimethyl sulfoxide (20 mL) was heated to 50 °C. Cyclopentanone (0.846 g, 10 mmol), methyl iodide (5.0 mL, 80 mmol) and potassium hydroxide (11.2 g, 200 mmol) were then added and the resultant mixture stirred for 1 h. The mixture was extracted with pentane (3×10mL). The combined organic phases were washed with deionized water (3×10 mL), dried with $MgSO_4$ and concentrated under reduced pressure. The resultant crude product was then passed through a short plug of silica (5% ethyl acetate/hexanes) to obtain the product as a colorless oil (726 mg, 52% yield). The NMR spectrum of the product was in agreement with literature precedent.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.76 (s, 3H), 1.04 (s, 12H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 227.22, 45.44, 35.01, 25.06.

3-methyl-3-phenylbutan-2-one

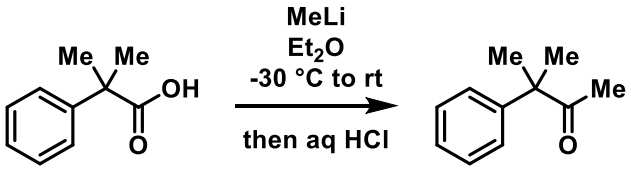
Prepared in accordance to reported methods.[15,16]



To a stirring solution of 2-phenylisobutyric acid (1.23 g, 7.5 mmol) in diethyl ether (50 mL, 0.15M) at −30 °C was added a solution of methyllithium (1.6 M in diethyl ether, 14.0 mL, 3.0 equiv.) dropwise. The resulting solution was allowed to warm to room temperature and kept stirring for 1.5 h. The reaction was then cooled to 0 °C and poured into iced hydrogen chloride solution, extracted with hexanes (3×20 mL). The organic phase was combined, dried with $MgSO_4$, concentrated under reduced pressure and purified with column chromatography on silica gel (5% ethyl acetate/hexanes) to afford the product as a colorless oil (702 mg, 58% yield). The NMR spectrum of the product was in agreement with literature precedent.[17]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.26 (m, 3H), 1.92 (s, 3H), 1.48 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.31, 144.22, 128.89, 126.99, 126.07, 52.61, 25.66, 25.26.

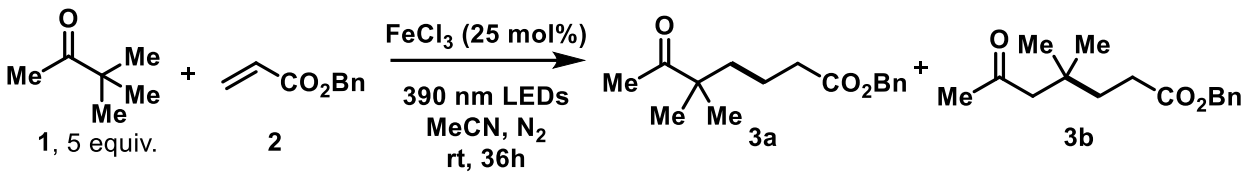
2-*tert*-butylbenzothiazole



Pivaloyl chloride (1.20 g) was added at room temperature to a stirred solution of 2-aminobenzenethiol (1.25 g, 10 mmol) in THF (10 mL) and stirred at room temperature for 2 h when TLC monitoring revealed complete consumption of 2-aminobenzenethiol. Then 5 equivalents H_2SO_4 (980 mg) were added and the reaction was allowed to stir at room temperature for 1 h until complete consumption of the intermediate amide was noted by TLC. The reaction mixture was diluted with water and then brought to pH 10 by the slow addition of 1M NaOH. The solution was extracted with ethyl acetate (3 x 20 mL), washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to a yellow oil. This oil was further purified via silica gel flash column chromatography (20% ethyl acetate/hexanes) to furnish a colorless oil (1.03 g, 54% yield). The NMR spectrum of the product was in agreement with literature precedent.[18]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 1.53 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 182.03, 153.42, 135.14, 125.90, 124.68, 122.83, 121.62.

Standard Reaction Conditions



A) To an oven-dried 1.5 dram vial was added $FeCl_3$ (25 mol%). Any solid reactants were also added at this stage. A magnetic stir bar was added and the vial was transferred to a glovebox. Anhydrous acetonitrile (1 mL, 0.30 M) was then added, followed by the C-H substrate (5 equiv., 1.5 mmol) and the electron-deficient alkene (1 equiv., 0.3 mmol). The vial was sealed and then placed on a stir plate 2-3 inches away from a 390 nm Kessil lamp. Ambient temperature (28 °C) was maintained with the use of a fan above the set-up. After 36 hours, the reaction mixture was concentrated in vacuo and purified using silica gel flash column chromatography, using ethyl acetate/hexanes as the eluent.

B) Identical to standard reaction conditions A, but using 3 mL of anhydrous acetonitrile instead (0.10 M) and without a fan (allowing the reaction to reach a temperature of 60 °C due to the heat dissipated by the LED lamps).

C) [For acyl chlorides] Identical to standard reaction conditions A, but upon completion of the reaction, K_3PO_4 (1 equiv.) and ethanol (1 mL) were added. The solution was then stirred overnight to ensure complete solvolysis, then concentrated in vacuo and purified via silica gel flash column chromatography.

Characterization of Products

Nucleophile Scope

ir = the ratio of unrearranged to rearranged product.

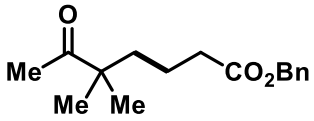
3a/3b

Conditions A: Yield = 59%, ***ir*** = 1:1.4

Conditions B: Yield = 64%, ***ir*** = 1:10

From pinacolone

3a Benzyl 5,5-dimethyl-6-oxoheptanoate (unrearranged product) – minor



^{1}H NMR (400 MHz, $CDCl_3$) Characteristic peaks: δ 2.09 (s, 3H, C**H**$_3$CO-), 1.10 (s, 6H, dimethyl).

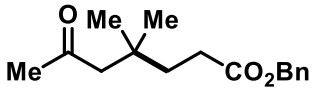
^{13}C NMR (126 MHz, $CDCl_3$) δ 213.77, 176.45, 60.33, 47.66, 39.98, 37.35, 28.85, 25.08, 24.39, 24.31, 17.29, 14.37.

Using Conditions B: We were able to separate 40.1 mg of product from mixed fractions containing both isomers as well as 10.4 mg containing only the rearranged product.

ir for the mixed fractions determined by comparing the integral of the peaks at 2.12 ppm (s, 3H, C**H**$_3$CO-) and 0.99 ppm (s, 6H, dimethyl) to those of the characteristic peaks. ***ir*** = 1:7.4

Taking into account the 10.4 mg of rearranged product isolated separately gives an overall ***ir*** = 1:10.

3b Benzyl 4,4-dimethyl-6-oxoheptanoate (rearranged product) – major



Colorless oil. R_f = 0.40 (5:1 hexanes : ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 5.11 (s, 2H), 2.40 – 2.26 (m, 4H), 2.12 (s, 3H), 1.77 – 1.63 (m, 2H), 0.99 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.37, 173.77, 135.97, 128.59, 128.30, 128.26, 66.32, 53.55, 36.69, 33.08, 32.52, 29.62, 26.80.

IR, film (cm^{-1}): 2956, 1732, 1715, 1497, 1454, 1361, 1298, 1211, 971, 747, 698.

LRMS m/z (EI): calculated for $C_{16}H_{22}O_3$ [M^+] 262.16, found 262.1.

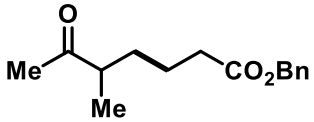
4a/4b

Conditions A: Yield = 54%, ***ir*** = 11:1

Conditions B: Yield = 45%, ***ir*** = 1.6:1 (NMR yield)

From 3-methyl-2-butanone and benzyl acrylate

4a Benzyl 5-methyl-6-oxoheptanoate (unrearranged product) – major

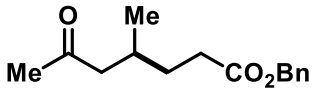


Yellow oil. R_f = 0.45 (5:1 hexanes : ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 5.11 (s, 2H), 2.49 (h, *J* = 6.8 Hz, 1H), 2.36 (td, *J* = 7.1, 1.2 Hz, 2H), 2.11 (s, 3H), 1.76 – 1.53 (m, 3H), 1.42 – 1.30 (m, 1H), 1.08 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.21, 173.18, 136.12, 128.66, 128.33, 66.29, 46.95, 34.25, 32.13, 28.07, 22.67, 16.27.
IR, film (cm^{-1}): 2935, 1732, 1709, 1497, 1455, 1355, 1212, 1151, 1111, 747, 697.
LRMS m/z (EI): calculated for $C_{15}H_{20}O_3$ [M^+] 248.14, found 248.1.

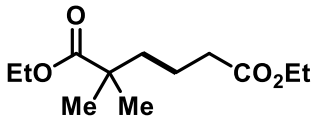
4b Benzyl 4-methyl-6-oxoheptanoate (rearranged product) – minor



^{1}H NMR (500 MHz, $CDCl_3$) Characteristic peaks: δ 0.90 (d, 3H, MeC(O)-CH_2-CH**Me**-).
ir determined by comparing the integral of the peak at 1.08 ppm (MeC(O)-CH**Me**-CH_2-) to the characteristic peak at 0.90 ppm.

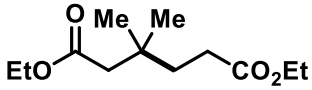
5a/5b
Conditions C: Yield = 30%, ***ir*** = 4:1
(Identical to Conditions A, but with additional workup in alkaline ethanol after completion)
From pivaloyl chloride

5a Diethyl 2,2-dimethylhexanedioate (unrearranged product) – major



Colorless oil. R_f = 0.50 (5:1 hexanes : ethyl acetate).
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (d, *J* = 7.1, 4H), 2.27 (m, 2H), 1.61 – 1.48 (m, 4H), 1.25 (t, *J* = 7.1, 6H), 1.17 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 177.87, 173.55, 60.45, 60.39, 42.17, 40.08, 34.78, 27.12, 25.19, 20.65, 14.38, 14.36.
IR, film (cm^{-1}): 2977, 1729, 1472, 1370, 1248, 1175, 1030.
HRMS m/z (ASAP): calculated for $C_{12}H_{22}O_4$ $[M+H]^+$ 231.1596, found 231.1588.

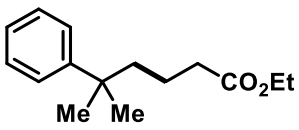
5b Diethyl 2,2-dimethylhexanedioate (rearranged product) – minor



^{1}H NMR (500 MHz, $CDCl_3$) Characteristic peaks 2.33 – 2.29 (m, 2H), 2.18 (s, 2H, EtO_2C-**CH_2**-Me_2-), 1.73 – 1.64 (m, 2H), 1.01 (s, 6H, EtO_2C-CH_2-**Me_2**-).
ir determined by comparing the integral of the peak at 1.17 ppm (s, 6H, EtO_2C-C**Me_2**-) to the characteristic peak at 1.01 ppm.

6a/6b
Conditions A: Yield = 42%, ***ir*** = 16:1
Conditions B: Yield = 25%, ***ir*** = 2.4:1 (NMR yield)
From tert-butylbenzene

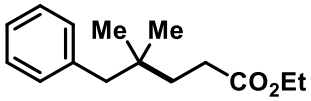
6a Ethyl 5-methyl-5-phenylhexanoate (unrearranged product) – major



Yellow oil. Rf = 0.3 (9:1 hexanes : ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.20 – 7.15 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.20 (t, *J* = 7.4 Hz, 2H), 1.75 – 1.55 (m, 2H), 1.44 – 1.36 (m, 2H), 1.32 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.65, 149.10, 128.10, 125.78, 125.50, 60.17, 43.94, 37.61, 34.82, 28.88, 20.41, 14.26.
IR, film (cm^{-1}): 2962, 1732, 1496, 1446, 1369, 1263, 1184, 1159, 1029, 932, 859, 764, 699, 566, 547
LRMS m/z (EI): calculated for $C_{15}H_{22}O_2$ [M^+] 234.16, found 234.1.

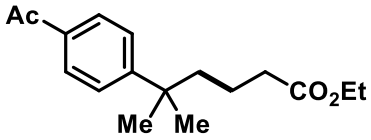
6b Ethyl 4,4-dimethyl-5-phenylpentanoate (rearranged product) – minor



^{1}H NMR (500 MHz, $CDCl_3$) 2.52 (s, 2H), 2.38 – 2.31 (m, 2H), 0.87 (s, 6H).
ir determined by comparing the integral of the peak at 1.32 ppm (s, 6H, Ar-C**Me$_2$**-CH_2-) to the characteristic peak at 0.87 ppm (s, 6H, Ar-CH_2-C**Me$_2$**-).

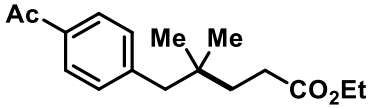
7a/7b
Conditions A: Yield = 28%, ***ir*** = 1:13
Conditions B: Yield = 58%, ***ir*** = <1:20 (NMR yield)
From 4'-tert-butylacetophenone

7a Ethyl 5-(4-acetylphenyl)-5-methylhexanoate (unrearranged product) – minor



^{1}H NMR (400 MHz, $CDCl_3$) Characteristic peaks δ 2.19 (t, J = 7.4 Hz, 2H, -**CH_2**-CO_2Et), 1.33 (s, 6H, Ar-C**Me$_2$**-)
ir determined by comparing the integrals of the peak at 0.85 ppm (s, 6H, Ar-CH_2-C**Me$_2$**-) to the characteristic peak at 1.33 ppm.

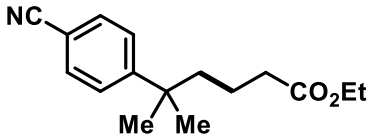
7b Ethyl 5-(4-acetylphenyl)-4,4-dimethylpentanoate (rearranged product) – major



Yellow oil. R_f = 0.3 (9:1 hexanes : ethyl acetate).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.23 – 7.17 (m, 2H), 4.11 (q, J = 7.1 Hz, 2H), 2.56 (overlapping singlets, 5H, **CH_3**C(O) + benzylic **CH_2**), 2.35 – 2.28 (m, 2H), 1.62 – 1.55 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H), 0.85 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.96, 174.14, 144.76, 135.24, 130.81, 127.96, 60.45, 48.32, 36.81, 34.19, 29.80, 26.63, 26.38, 14.31.
IR, film (cm^{-1}): 2961, 1730, 1681, 1506, 1414, 1358, 1266, 1182, 1125, 1021, 956, 826, 780, 689, 601, 585
LRMS m/z (EI): calculated for $C_{17}H_{24}O_3$ [M^+] 276.17, found 276.1.

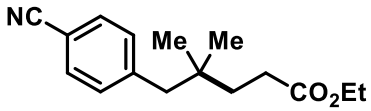
8a/8b
Conditions A: Yield = 30%, ***ir*** = 1:8
Conditions B: Yield = 54%, ***ir*** = <1:20
From 4-tert-butylbenzonitrile

8a Ethyl 5-(4-cyanophenyl)-5-methylhexanoate (unrearranged product) – minor



^{1}H NMR (400 MHz, $CDCl_3$) Characteristic peaks δ 2.20 (t, J = 7.3 Hz, 2H, -**CH_2**-CO_2Et), 1.31 (s, 6H, Ar-C**Me$_2$**-)
ir determined by comparing the integrals of the peak at 0.86 ppm (s, 6H, Ar-CH_2-C**Me$_2$**-) to the characteristic peak at 1.31 ppm.

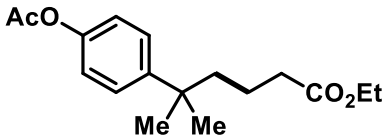
8b Ethyl 5-(4-cyanophenyl)-4,4-dimethylpentanoate (rearranged product) – major



Yellow oil. R_f = 0.2 (9:1 hexanes : ethyl acetate).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 2H), 7.25 – 7.18 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 2.56 (s, 2H), 2.36 – 2.27 (m, 2H), 1.62 – 1.53 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H), 0.85 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.97, 144.62, 131.65, 131.32, 119.10, 110.11, 60.50, 48.50, 36.78, 34.25, 29.75, 26.30, 14.30.
IR, film (cm^{-1}): 2961, 2871, 2227, 1729, 1607, 1505, 1469, 1416, 1370, 1297, 1263, 1177, 1127, 1024, 853, 826, 781, 566, 533
LRMS m/z (EI): calculated for $C_{16}H_{21}NO_2$ [M^+] 259.16, found 259.1.

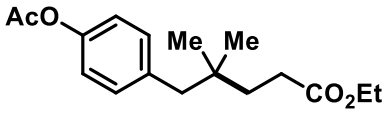
9a/9b
Conditions A: Yield = 46%, ***ir*** = >20:1
Conditions B: Yield = 35%, ***ir*** = 1:1
From 4-(tert-butyl)phenyl acetate

9a Ethyl 5-(4-acetoxyphenyl)-5-methylhexanoate (unrearranged product) – major



Yellow oil. Rf = 0.3 (9:1 hexanes : ethyl acetate).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.04 – 6.90 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.20 (t, *J* = 7.3 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.41 (m, 2H), 1.30 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.71, 169.72, 148.55, 146.78, 126.93, 121.04, 60.32, 44.06, 37.55, 34.89, 29.04, 21.30, 20.47, 14.37.
IR, film (cm^{-1}): 2961, 1761, 1731, 1605, 1506, 1467, 1368, 1299, 1193, 1168, 1099, 1016, 911, 847, 662, 594, 564
LRMS m/z (EI): calculated for $C_{17}H_{24}O_4$ [M^+] 292.17, found 292.1.

9b Ethyl 5-(4-acetoxyphenyl)-4,4-dimethylpentanoate (rearranged product) – minor

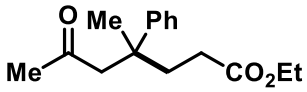


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 2H), 6.99 – 6.96 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.50 (s, 2H), 2.37 – 2.30 (m, 2H), 1.61 – 1.55 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 6H).
ir determined by comparing the integral of the peak at 1.30 ppm (s, 6H, Ar-C**Me$_2$**-CH_2-) to the characteristic peak at 0.86 ppm (s, 6H, Ar-CH_2-C**Me$_2$**-).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.36, 169.75, 149.10, 136.46, 131.53, 120.88, 60.47, 47.77, 36.78, 34.00, 29.90, 26.33, 21.30, 14.36.
LRMS m/z (EI): calculated for $C_{17}H_{24}O_4$ [M^+] 292.17, found 292.1.
[Peaks assigned from the 1:1 mixture with the unrearranged product]

10b
Conditions A: Yield = 8%, ***ir*** = <1:20
Conditions B: Yield = 19%, ***ir*** = <1:20
From 3-methyl-3-phenylbutan-2-one

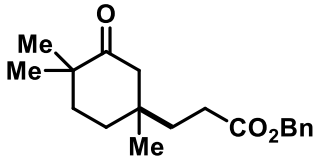
10b Ethyl 4-methyl-6-oxo-4-phenylheptanoate (rearranged product) – exclusive



Pale yellow oil. R_f = 0.3 (5:1 hexanes : ethyl acetate).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.20 (m, 1H), 4.05 (qd, J = 7.1, 2.1 Hz, 2H), 2.92 (d, J = 14.5 Hz, 1H), 2.61 (d, J = 14.5 Hz, 1H), 2.25 – 2.10 (m, 2H), 2.03 – 1.87 (m, 2H), 1.79 (s, 3H, **CH_3**C(O)-, confirmed by HMBC), 1.45 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 207.65, 173.77, 145.24, 128.64, 126.45, 126.19, 60.49, 56.24, 40.14, 37.72, 32.09, 29.59, 23.33, 14.29.
IR, film (cm^{-1}): 2978, 1731, 1446, 1376, 1299, 1180, 1031, 765, 702, 547
LRMS m/z (EI): calculated for $C_{15}H_{22}O_2$ [M^+] 262.16, found 262.1.

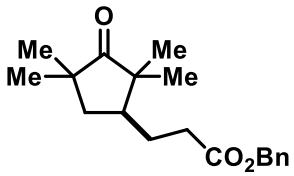
11b
Conditions A: Yield = 37%, ***ir*** = <1:20
Conditions B: Yield = 41%, ***ir*** = <1:20
From 2,2,5,5-tetramethylcyclopentanone

11b Benzyl 3-(1,4,4-trimethyl-3-oxocyclohexyl)propanoate (rearranged product) – exclusive product



Colorless oil. R_f = 0.35 (9:1 hexanes : ethyl acetate).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.11 (s, 2H), 2.38 – 2.27 (m, 3H), 2.11 (dd, J = 13.8, 1.7 Hz, 1H), 1.72 – 1.61 (m, 5H), 1.54 – 1.46 (m, 1H), 1.10 (s, 3H), 1.08 (s, 3H), 0.87 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 215.63, 173.62, 135.97, 128.70, 128.43, 128.41, 66.51, 49.66, 44.33, 38.80, 36.67, 36.42, 32.46, 29.05, 25.28, 25.17, 24.36.
IR, film (cm^{-1}): 2960, 2929, 2867, 1733, 1703, 1497, 1455, 1422, 1384, 1365, 1303, 1214, 1161, 1079, 1028, 967, 910, 747, 698, 507
LRMS m/z (EI): calculated for $C_{19}H_{26}O_3$ [M^+] 302.19, found 302.2.

11c Benzyl 3-(2,2,4,4-tetramethyl-3-oxocyclopentyl)propanoate – side product (alkylation at methylene positions)
Conditions A: Yield = 15%
Conditions B: Yield = 20%



Colorless oil. R_f = 0.4 (9:1 hexanes : ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.14 (d, J = 1.7 Hz, 2H), 2.48 (ddd, J = 15.2, 9.2, 5.8 Hz, 1H), 2.39 (ddd, J = 15.8, 8.9, 6.9 Hz, 1H), 1.87 (dd, J = 12.5, 6.1 Hz, 1H), 1.79 (dddd, J = 12.2, 10.2, 6.1, 4.1 Hz, 1H), 1.54 (dddd, J = 13.3, 10.2, 8.9, 5.8 Hz, 1H), 1.42 – 1.31 (m, 1H), 1.09 (s, 3H), 1.04 (s, 3H), 0.95 (s, 3H), 0.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 226.94, 173.42, 136.05, 128.71, 128.49, 128.45, 66.44, 48.46, 44.88, 43.25, 41.26, 32.80, 25.85, 25.35, 25.06, 23.99, 18.79.

IR, film (cm^{-1}): 2961, 2868, 1733, 1497, 1457, 1362, 1215, 1166, 1133, 1063, 1028, 903, 750, 698, 580, 487

LRMS m/z (EI): calculated for $C_{19}H_{26}O_3$ [M^+] 302.19, found 302.2.

12a/12b

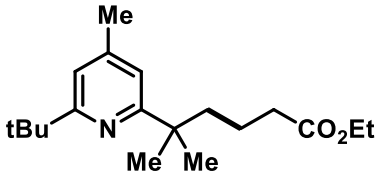
Modified Conditions A: Yield = 20%, ***ir*** = 1.4:1

Modified Conditions B: Yield = 44%, ***ir*** = 1:1.6

(5 equiv. of CF_3COOH was used as an additive under both conditions. 50 mol% of $FeCl_3$ was used.)

From 2,6-di-*tert*-butyl-4-methylpyridine

12a Ethyl 5-(6-(tert-butyl)-4-methylpyridin-2-yl)-5-methylhexanoate (unrearranged product)



Colorless oil. R_f = 0.6 (9:1 hexanes : ethyl acetate)

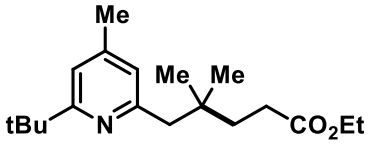
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.85 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.44 – 1.37 (m, 2H), 1.32 (s, 9H), 1.31 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.06, 167.60, 166.08, 146.57, 117.29, 116.34, 60.20, 42.78, 40.42, 37.51, 35.23, 30.26, 28.03, 21.63, 20.72, 14.37.

IR, film (cm^{-1}): 2958, 1736, 1600, 1567, 1265, 1185, 853

LRMS m/z (EI): calculated for $C_{19}H_{31}NO_2$ [M^+] 305.24, found 305.1

12b Ethyl 5-(6-(tert-butyl)-4-methylpyridin-2-yl)-4,4-dimethylpentanoate (rearranged product)



Colorless oil. R_f = 0.5 (9:1 hexanes : ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.68 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 2H), 2.55 – 2.45 (m, 2H), 2.28 (s, 3H), 1.63 – 1.47 (m, 3H), 1.31 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.79, 168.18, 158.07, 146.26, 122.49, 116.97, 60.25, 49.13, 37.26, 36.22, 34.19, 30.27, 30.03, 27.61, 21.33, 14.39.

IR, film (cm^{-1}): 2955, 2868, 1735, 1602, 1566, 1253, 1185, 855

LRMS m/z (EI): calculated for $C_{19}H_{31}NO_2$ [M^+] 305.24, found 305.1

13b

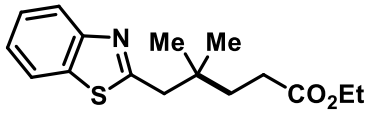
Modified Conditions A: Yield = Trace

Modified Conditions B: Yield = 34%, ***ir*** = <1:20

(5 equiv. of CF_3COOH was used as an additive under both conditions)

From 2-*tert*-butylbenzothiazole

13b Ethyl 5-(benzo[d]thiazol-2-yl)-4,4-dimethylpentanoate (rearranged product) – exclusive product



Colorless oil. R_f = 0.4 (5:1 hexanes : ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1H), 7.84 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 1H), 7.45 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.36 (ddd, *J* = 7.9, 7.2, 1.2 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.02 (s, 2H), 2.52 – 2.22 (m, 2H), 1.97 – 1.69 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.93, 168.12, 153.30, 135.48, 125.85, 124.75, 122.73, 121.29, 60.41, 45.91, 36.77, 34.27, 29.70, 26.79, 14.23.

IR, film (cm^{-1}): 2959, 1733, 1512, 1436, 1242, 1169, 760

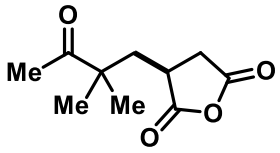
LRMS m/z (EI): calculated for $C_{16}H_{21}NO_2S$ [M^+] 291.13, found 291.1

Acceptor Scope

ir = the ratio of unrearranged to rearranged product.

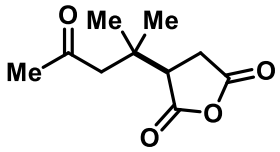
14a/14b
Conditions A: Yield = 38%, ***ir*** = 1:1
Conditions B: Yield = 57%, ***ir*** = 1:8 (NMR yield)
From maleic anhydride

14a 3-(2,2-dimethyl-3-oxobutyl)dihydrofuran-2,5-dione (unrearranged product) – minor



^{1}H NMR (500 MHz, $CDCl_3$) δ 3.15 – 3.05 (m, 1H), 3.05 – 2.94 (m, 1H), 2.70 (dd, J = 18.3, 7.0 Hz, 1H), 2.30 (dd, J = 14.4, 3.7 Hz, 1H), 2.15 (s, 3H), 1.82 (dd, J = 14.4, 8.9 Hz, 1H), 1.23 (s, 3H), 1.21 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 212.85, 174.26, 169.78, 47.27, 40.54, 38.19, 36.31, 25.40, 25.22, 24.71.
LRMS m/z (EI): calculated for $C_{10}H_{14}O_4$ [M^+] 198.09, found 198.1.

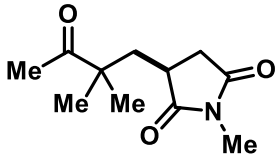
14b 3-(2-methyl-4-oxopentan-2-yl)dihydrofuran-2,5-dione (rearranged product) – major



Colorless oil. R_f = 0.30 (4:1 hexanes : ethyl acetate, 1% acetic acid).
^{1}H NMR (500 MHz, $CDCl_3$)) 1H NMR δ 3.88 (dd, *J* = 10.2, 6.5 Hz, 1H), 3.11 – 2.87 (m, 2H), 2.78 (dd, *J* = 18.9, 6.7 Hz, 1H), 2.45 (d, *J* = 17.9 Hz, 1H), 2.15 (s, 3H), 1.11 (s, 3H), 1.04 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 207.92, 172.53, 170.10, 51.49, 46.73, 34.84, 31.76, 31.06, 25.50, 24.24.
IR, film (cm^{-1}): 2967, 1859, 1775, 1707, 1471, 1413, 1366, 1294, 1219, 1159, 1074, 1054, 915, 722.
LRMS m/z (EI): calculated for $C_{10}H_{14}O_4$ [M^+] 198.09, found 198.1.

15a/15b
Conditions A: Yield = 86%, ***ir*** = 1:1.2
Conditions B: Yield = 51%, ***ir*** = 1:8 (NMR yield)
From N-methylmaleimide

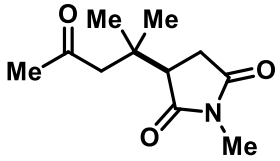
15a 3-(2,2-dimethyl-3-oxobutyl)-1-methylpyrrolidine-2,5-dione (unrearranged product)



Colorless oil. R_f = 0.3 (1:1 hexanes : ethyl acetate).
^{1}H NMR (500 MHz, $CDCl_3$)) δ 2.95 (s, 3H), 2.84 (dd, *J* = 18.2, 8.9 Hz, 1H), 2.65 (tdd, *J* = 9.1, 5.2, 3.5 Hz, 1H), 2.42 – 2.28 (m, 2H), 2.18 (s, 3H), 1.62 (dd, *J* = 14.3, 9.7 Hz, 1H), 1.19 (overlapping singlets, *J* = 4.3Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 213.02, 180.07, 176.43, 47.44, 41.30, 37.32, 36.75, 25.43, 25.11, 25.07, 24.79.
IR, film (cm^{-1}): 2969, 1775, 1690, 1435, 1383, 1358, 1280, 1124, 877.

LRMS m/z (EI): calculated for $C_{11}H_{17}NO_3$ [M^+] 211.11, found 211.1.

15b 1-methyl-3-(2-methyl-4-oxopentan-2-yl)pyrrolidine-2,5-dione (rearranged product)



Colorless oil. R_f = 0.35 (1:1 hexanes : ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (dd, *J* = 9.3, 5.0 Hz, 1H), 3.04 (d, *J* = 17.5 Hz, 1H), 2.93 (s, 3H), 2.70 (dd, *J* = 18.5, 9.3 Hz, 1H), 2.54 – 2.40 (m, 2H), 2.15 (s, 3H), 1.08 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.20, 179.02, 176.63, 52.05, 45.79, 34.85, 31.89, 31.23, 25.63, 24.68, 23.82.

IR, film (cm^{-1}): 2961, 1770, 1688, 1434, 1382, 1366, 1280, 1157, 1122, 952, 697.

LRMS m/z (EI): calculated for $C_{11}H_{17}NO_3$ [M^+] 211.11, found 211.1.

The two isomers could be isolated separately. ***ir*** for Conditions A was determined from the isolated yields of the two products.

For Conditions B, ***ir*** was determined by comparing the combined integrals of the methyl peaks at 1.19 (overlapping singlets, 6H) to that of the methyl peaks at 1.08 (s, 3H) and 0.93 (s, 3H).

Ratio found = 1:7.7

NMR yield = 6%:45% (combined = 51%) using 1,3,5-trimethoxybenzene as internal standard.

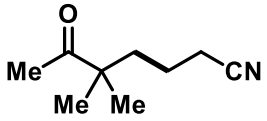
16a/16b

Conditions A: Yield = 54%, ***ir*** = 1:1.4

Conditions B: Yield = 66%, ***ir*** = 1:10

From acrylonitrile

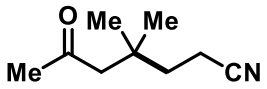
16a 5,5-dimethyl-6-oxoheptanenitrile (unrearranged product) – minor



^{1}H NMR Characteristic peaks: 1.13 (s, 6H, -C**Me$_2$**-)

ir was determined by the relative integral of the characteristic peak at 1.13 ppm against the integral of the peak at 1.01 ppm (s, 6H).

16b 4,4-dimethyl-6-oxoheptanenitrile (rearranged product) – major



Colorless oil. R_f = 0.40 (3:1 hexanes : ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 2H), 2.28 (m, 2H), 2.11 (s, 3H), 1.78 (m, 2H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.74, 120.29, 77.47, 77.15, 76.83, 52.86, 36.59, 33.18, 32.35, 26.90, 12.53.

IR, film (cm^{-1}): 2961, 2875, 2246, 1705, 1472, 1424, 1363, 1214, 1158, 1133, 975, 922, 756, 605, 536.

LRMS m/z (EI): calculated for $C_9H_{15}NO$ [M^+] 153.12, found 153.1.

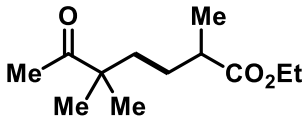
17a/17b

Conditions A: Yield = 35%, ***ir*** = 1.2:1

Conditions B: Yield = 47%, ***ir*** = 1:9

From ethyl methacrylate

17a Ethyl 2,5,5-trimethyl-6-oxoheptanoate (unrearranged product) – minor

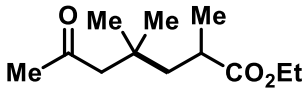


^{1}H NMR (500 MHz, $CDCl_3$) Characteristic peaks: δ 1.08 (overlapping singlets, *J* = 5.3 Hz, 6H, MeC(O)-C**Me$_2$**-CH_2-)

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.77, 176.45, 60.33, 47.66, 39.98, 37.35, 28.85, 25.08, 24.39, 24.31, 17.29, 14.37.

ir was determined by the relative integral of the characteristic peak at 1.08 ppm against the peak at 0.95 ppm (MeC(O)-CH_2-C**Me$_2$**-).

17b Ethyl 2,4,4-trimethyl-6-oxoheptanoate (rearranged product) – major



Colorless oil. R_f = 0.45 (5:1 hexanes : ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.09 (q, *J* = 7.1, 2H), 2.45 (dqd, *J* = 9.8, 7.0, 2.8 Hz, 1H), 2.37 – 2.26 (m, 2H), 2.09 (s, 3H), 1.92 (dd, *J* = 14.2, 9.4 Hz, 1H), 1.35 (dd, *J* = 14.2, 2.8 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 0.95 (overlapping singlets, *J* = 2.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.56, 177.74, 60.39, 53.92, 45.88, 36.04, 33.83, 32.56, 27.31, 27.08, 20.43, 14.23.

IR, film (cm^{-1}): 2972, 1729, 1705, 1463, 1363, 1249, 1155, 1096, 1054, 1025.

LRMS m/z (EI): calculated for $C_{12}H_{22}O_3$ [M^+] 214.16, found 214.2.

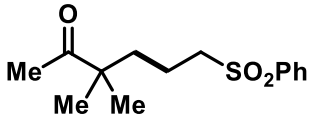
18a/18b

Conditions A: Yield = 25%, ***ir*** = 1:1

Conditions B: Yield = 41%, ***ir*** = 1:7

From phenyl vinyl sulfone

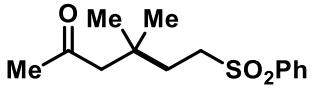
18a 3,3-dimethyl-6-(phenylsulfonyl)hexan-2-one (unrearranged product) – minor



^{1}H NMR Characteristic peaks: 2.08 (s, 3H, -CO**Me**), 1.09 (s, 6H, -C**Me$_2$**-)

ir was determined by the relative integral of the characteristic peak at 1.09 ppm against the integral of the peak at 0.95 ppm (s, 6H).

18b 4,4-dimethyl-6-(phenylsulfonyl)hexan-2-one (rearranged product) – major



Yellow oil. R_f = 0.50 (1:1 hexanes : ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.70 – 7.61 (m, 1H), 7.62 – 7.48 (m, 2H), 3.19 – 2.98 (m, 2H), 2.27 (s, 2H), 2.07 (s, 3H), 1.79 – 1.69 (m, 2H), 0.95 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.66, 139.13, 133.82, 129.40, 128.16, 53.21, 52.50, 33.94, 32.94, 32.45, 26.98.

IR, film (cm^{-1}): 2959, 2874, 1709, 1473, 1447, 1408, 1363, 1218, 1145, 1087, 1025, 999, 745, 690, 587, 562, 538.

LRMS m/z (EI): calculated for $C_{14}H_{20}O_3S$ [M^+] 268.11, found 268.1.

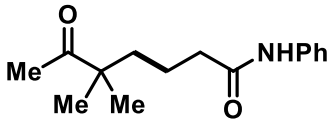
19a/19b

Conditions A: Yield = 46%, ***ir*** = 1:1.7

Conditions B: Yield = 61%, ***ir*** = 1:10

From N-phenylacrylamide

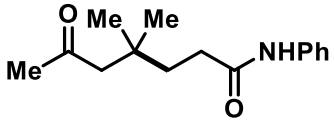
19a 5,5-dimethyl-6-oxo-N-phenylheptanamide (unrearranged product) – minor



^{1}H NMR Characteristic peaks: 2.12 (s, 3H, -CO**Me**), 1.57 (m, 4H, -C**H$_2$**C**H$_2$**CH$_2$**CONHPh**), 1.12 (s, 6H, -C**Me$_2$**-)

ir was determined by the relative integral of the characteristic peak at 1.12 ppm against the integral of the peak at 1.00 ppm.

19b 4,4-dimethyl-6-oxo-N-phenylheptanamide (rearranged product) – major



Yellow oil. R_f = 0.30 (1:1 hexanes : ethyl acetate).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (broad s, 1H), 7.54 (m, 2H), 7.35 – 7.19 (m, 2H, overlaps with $CHCl_3$ peak), 7.06 (t, *J* = 7.4 Hz, 1H), 2.43 – 2.24 (m, 4H), 2.14 (s, 3H), 1.84 – 1.65 (m, 2H), 1.00 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 209.68, 172.02, 138.36, 128.98, 124.08, 119.86, 53.07, 37.32, 33.66, 33.23, 32.91, 27.48.

IR, film (cm^{-1}): 3306 (broad), 3137, 3061, 2959, 1697, 1662, 1600, 1542, 1499, 1442, 1362, 1313, 1251, 1156, 966, 903, 756, 694, 549, 508.

LRMS m/z (EI): calculated for $C_{15}H_{21}NO_2$ [M^+] 247.16, found 247.1.

20a/20b

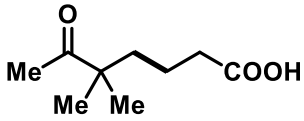
Conditions A: Yield = 43%, ***ir*** = 1:3

Conditions B: Yield = 62%, ***ir*** = 1:15

1 equiv. of trifluoroacetic acid was used as an additive under both conditions, but the procedure was otherwise identical.

From acrylic acid

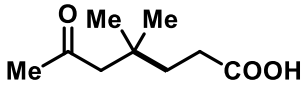
20a 5,5-dimethyl-6-oxoheptanoic acid (unrearranged product) – minor



^{1}H NMR Characteristic peaks: 2.08 (s, 3H, -CO**Me**), 1.11 (s, 6H, -C**Me$_2$**-)

ir was determined by the relative integral of the characteristic peak at 1.11 ppm against the integral of the peak at 0.99 ppm.

20b 4,4-dimethyl-6-oxoheptanoic acid (rearranged product) – major



Colorless oil. R_f = 0.40 (4:1 hexanes : ethyl acetate, 1% acetic acid).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 2.37 – 2.24 (m, 2H), 2.12 (s, 3H), 1.77 – 1.59 (m, 2H), 0.99 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 208.75, 180.25, 53.58, 36.42, 33.14, 32.57, 29.49, 26.90.
IR, film (cm^{-1}): 3500-2500 (broad), 2959, 2875, 1702, 1471, 1415, 1363, 1300, 1214, 1158, 1046, 926, 608, 532.
LRMS m/z (EI): calculated for $C_9H_{16}O_3$ [M^+] 172.11, found 172.1.

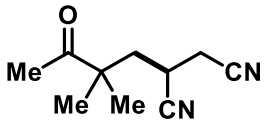
21a/21b

Conditions A: Yield = 63%, ***ir*** = 1:2.3

Conditions B: Yield = 73%, ***ir*** = 1:14

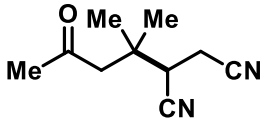
From fumaronitrile

21a 2-(2,2-dimethyl-3-oxobutyl)succinonitrile (unrearranged product) – minor



^{1}H NMR Characteristic peaks: δ 2.91 (dtd, *J* = 8.1, 6.3, 5.0 Hz, 1H, methine C**H**), 1.32 (s, 3H), 1.23 (s, 3H) (MeC(O)-C**Me$_2$**-CH_2-)
^{13}C NMR (126 MHz, $CDCl_3$) δ 212.47, 119.84, 115.77, 47.35, 40.38, 25.76, 25.18, 24.80, 23.91, 22.65.
R_M was determined by the relative integral of the characteristic peak at 1.32 ppm (s, 3H) against half the integral of the peak at 1.14 ppm (overlapping singlets, 6H, MeC(O)-CH_2-C**Me$_2$**-).

21b 2-(2-methyl-4-oxopentan-2-yl)succinonitrile (rearranged product) – major



Colorless oil. R_f = 0.40 (3:1 hexanes : ethyl acetate).
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.68 (dd, *J* = 8.7, 5.9 Hz, 1H), 2.71 – 2.57 (m, 3H), 2.49 (d, *J* = 18.0 Hz, 1H), 2.14 (s, 3H), 1.14 (overlapping singlets, *J* = 7.2 Hz, 6H)
^{13}C NMR (126 MHz, $CDCl_3$) δ 207.01, 118.32, 116.63, 51.29, 36.67, 35.46, 31.70, 25.18, 24.09, 16.69.
IR, film (cm^{-1}): 2971, 2243, 1708, 1470, 1421, 1364, 1181, 1157, 1055, 1033, 1005, 626, 554.
LRMS m/z (EI): calculated for $C_{10}H_{14}N_2O$ [M^+] 178.11, found 178.1.

22a/22b

Conditions A: Yield = 32%, ***ir*** = 1:5

Conditions B: Yield = 50%, ***ir*** = 1:18. Ratio of **22b:22c** = 6:1

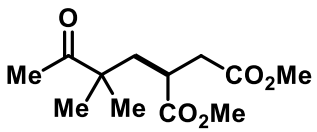
From dimethyl fumarate

Conditions A: Yield = 32%, ***ir*** = 1:15

Conditions B: Yield = 50%, ***ir*** < 1:20. Ratio of **22b:22c** = 5:1

From dimethyl maleate

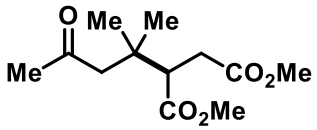
22a Dimethyl 2-(2,2-dimethyl-3-oxobutyl)succinate (unrearranged product) – minor



^{1}H NMR Characteristic peaks: 3.65 (s, 3H, -CO_2**Me**), 3.63 (s, 3H, -CO_2**Me**), 1.18 (s, 3H, -C**Me$_2$**-), 1.12 (s, 3H, -C**Me$_2$**-)

ir was determined by the relative integral of the characteristic peak at 1.18 ppm and 1.12 ppm against the integral of the peaks at 1.10 ppm and 1.02 ppm.

22b Dimethyl 2-(2-methyl-4-oxopentan-2-yl)succinate (rearranged product) – major



Yellow oil. R_f = 0.25 (1:1 hexanes : ethyl acetate).

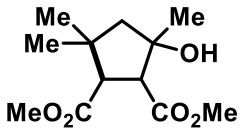
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.64 (s, 3H), 3.04 (dd, *J* = 12.0, 3.2 Hz, 1H), 2.76 (dd, *J* = 16.7, 12.0 Hz, 1H), 2.54 (d, *J* = 16.6 Hz, 1H), 2.46 (dd, *J* = 16.7, 3.2 Hz, 1H), 2.32 (d, *J* = 16.5 Hz, 1H), 2.11 (s, 3H), 1.10 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 207.37, 174.44, 172.86, 52.08, 51.95, 51.64, 49.14, 35.10, 32.27, 32.14, 25.59, 25.18.

IR, film (cm^{-1}): 2955, 1728, 1436, 1364, 1261, 1191, 1159, 1092, 999, 925, 887, 845, 736, 667, 609, 500.

LRMS m/z (EI): calculated for $C_{12}H_{20}O_5$ [M^+] 244.13, found 244.1.

22c Dimethyl-3-hydroxy-3,5,5-trimethylcyclopentane-1,2-dicarboxylate (rearranged and cyclized product)



^{1}H NMR (500 MHz, $CDCl_3$) Characteristic peaks: δ 3.68 (s, 3H), 3.66 (s, 3H), 3.22 (d, *J* = 12.2 Hz, 1H), 3.15 (d, *J* = 12.2 Hz, 1H), 1.85 (d, *J* = 14.0 Hz, 1H), 1.69 (d, *J* = 14.0 Hz, 1H), 1.41 (s, 3H), 1.27 (s, 3H), 0.87 (s, 3H).
The ratio of acyclic:cyclic product was determined by the relative integral of the characteristic peaks at 1.41 ppm and 1.27 ppm against the integral of the peaks at 1.10 ppm and 1.02 ppm.

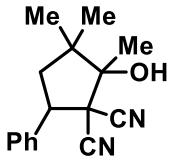
24a/24b

Conditions A: Yield = 57%, ***ir*** = 1:8.6

Conditions B: Yield = 70%, ***ir*** = <1:20

From benzylidenemalononitrile

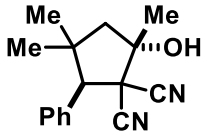
24a 2-hydroxy-2,3,3-trimethyl-5-phenylcyclopentane-1,1-dicarbonitrile (unrearranged product) – minor



^{1}H NMR Characteristic peaks: δ 2.55 (broad s, 1H, -C(O**H**)Me-) 1.62 (s, 3H, -C(OH)**Me**-), 1.35 (s, 3H, -C**Me$_2$**-), 1.18 (s, 3H, -C**Me$_2$**-)

ir was determined by the relative integral of the characteristic peak at 1.35 ppm against the integral of the peak at 1.06 ppm (s, 3H).

24b 2-hydroxy-2,4,4-trimethyl-5-phenylcyclopentane-1,1-dicarbonitrile (rearranged product) – major



White solid. R_f = 0.40 (3:1 hexanes : ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.46 – 7.35 (m, 3H), 3.90 (s, 1H), 2.73 (broad d, *J* = 2.0 Hz, 1H), 2.21 – 2.08 (m, 2H), 1.74 (s, 3H), 1.21 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.28, 130.00, 128.74, 128.63, 115.82, 114.30, 83.69, 61.15, 52.57, 52.06, 40.88, 31.64, 27.87, 24.39.

IR, film (cm^{-1}): 3482 (broad), 2968, 2932, 2252, 1498, 1453, 1389, 1367, 1220, 1194, 1172, 1121, 1070, 1052, 951, 935, 853, 732, 700, 528.

LRMS m/z (EI): calculated for $C_{16}H_{18}N_2O$ [M^+] 254.14, found 254.1.

The relative stereochemistry of **24b** was assigned by X-ray crystallography. Please refer to the cif file for further information.

Additional Products

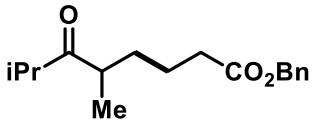
25a/25b

Conditions A: Yield = 60%, ***ir*** = 3:1

Conditions B: Yield = 56%, ***ir*** = 1:3

From 2,4-dimethyl-3-pentanone

25a Benzyl 5,7-dimethyl-6-oxooctanoate (unrearranged product) – major



Yield = 65%, yellow oil. R_f = 0.40 (5:1 hexanes : ethyl acetate).

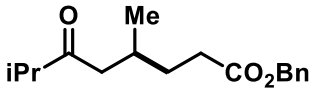
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5H), 5.11 (s, 2H), 2.69 (m, 2H), 2.45 – 2.22 (m, 2H), 1.74 – 1.46 (m, 3H), 1.38 – 1.18 (m, 1H), 1.15 – 0.97 (m, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 217.90, 173.15, 136.08, 128.57, 128.23, 66.19, 44.11, 39.62, 34.28, 32.39, 22.86, 18.34, 16.81.

IR, film (cm^{-1}): 2966, 2933, 2873, 1734, 1708, 1497, 1456, 1381, 1242, 1212, 1159, 1027, 1001, 738, 697.

LRMS m/z (EI): calculated for $C_{17}H_{24}O_3$ [M^+] 276.17, found 276.2.

25b Benzyl 4,7-dimethyl-6-oxooctanoate (rearranged product)



^{1}H NMR (400 MHz, $CDCl_3$) Characteristic peaks: δ 2.54 (sept, *J* = 6.9 Hz, 1H, $(CH_3)_2$C**H**C(O)-CH_2-CHMe-), 2.05 (tdt, *J* = 8.0, 6.9, 5.6 Hz, 1H, Me_2CHC(O)-CH_2-C**H**Me-), 0.89 (d, *J* = 6.7 Hz, 3H, Me_2CHC(O)-CH_2-CH**Me**-).

ir determined by comparing the integral of the peak at 2.69 ppm (overlapping sept., 2H, Me_2C**H**C(O)-C**H**Me-CH_2-). to the sum of the characteristic peaks at 2.54 ppm (sept.,) and 2.05 ppm (m,).

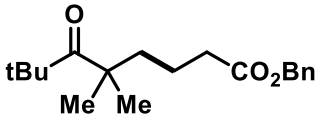
26a/26b

Conditions A: Yield = 69%, ***ir*** = 1:7

Conditions B: Yield = 60%, ***ir*** = 1:20

From di-tert-butyl ketone

26a Benzyl 5,5,7,7-tetramethyl-6-oxooctanoate (unrearranged product) – minor

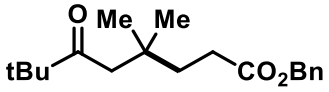


^{1}H NMR (400 MHz, $CDCl_3$) Characteristic peaks δ 1.23 (s, 6H, Me_3CC(O)-C**Me$_2$**-), 1.21 (s, 9H, **Me$_3$**CC(O)-CMe_2-)

ir determined by comparing the integrals of the peak at 0.99 ppm (s, 6H, Me_3CC(O)-CH_2-C**Me$_2$**-) and 1.10 ppm (s, 9H, **Me$_3$**CC(O)-CH_2-CMe_2-) to the characteristic peaks at 1.23 ppm and 1.21 ppm respectively.

LRMS m/z (EI): calculated for $C_{19}H_{28}O_3$ [M^+] 304.20, found 304.2.

26b Benzyl 4,4,7,7-tetramethyl-6-oxooctanoate (rearranged product) – major



Yellow oil. Rf = 0.3 (9:1 hexanes : ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 5H), 5.10 (s, 2H), 2.37 (s, 2H), 2.34 – 2.28 (m, 2H), 1.81 – 1.73 (m, 2H), 1.10 (s, 9H), 0.99 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.94, 173.95, 136.17, 128.64, 128.33, 128.27, 66.31, 45.90, 44.86, 36.71, 32.78, 29.83, 26.94, 26.47.

IR, film (cm^{-1}): 2957, 1734, 1705, 1456, 1385, 1365, 1297, 1153, 1067, 1004, 975, 915, 844, 746, 697, 579, 501

LRMS m/z (EI): calculated for $C_{19}H_{28}O_3$ [M^+] 304.20, found 304.2.

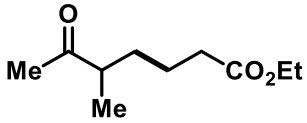
27a/27b

Conditions A: Yield = 54%, ***ir*** = 11:1

Conditions B: Yield = 44%, ***ir*** = 1.3:1 (NMR yield)

From 3-methyl-2-butanone and ethyl acrylate

27a Ethyl 5-methyl-6-oxoheptanoate (unrearranged product) – major



Colorless oil. R_f = 0.40 (5:1 hexanes : ethyl acetate).

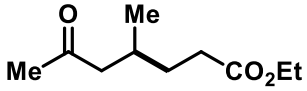
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.10 (q, *J* = 7.1 Hz, 2H), 2.50 (h, *J* = 6.9 Hz, 1H), 2.28 (td, *J* = 7.3, 2.0 Hz, 2H), 2.12 (s, 3H), 1.72 – 1.47 (m, 3H), 1.41 – 1.31 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.41, 173.43, 60.40, 46.99, 34.29, 32.17, 28.14, 22.68, 16.30, 14.34.

IR, film (cm^{-1}): 2972, 2939, 1731, 1711, 1459, 1370, 1246, 1178, 1156, 1097, 1031.

LRMS m/z (EI): calculated for C10H18O_3 [M^+] 186.13, found 186.2.

27b Ethyl 4-methyl-6-oxoheptanoate (rearranged product) – minor



^{1}H NMR (500 MHz, $CDCl_3$) Characteristic peaks: δ 2.11 (s, 3H, **Me**C(O)-CH_2-CHMe-) 0.89 (d, 3H, MeC(O)-CH_2-CH**Me**-).

ir determined by comparing the integral of the peak at 1.08 ppm (MeC(O)-CH**Me**-CH_2-) to the characteristic peak at 0.89 ppm.

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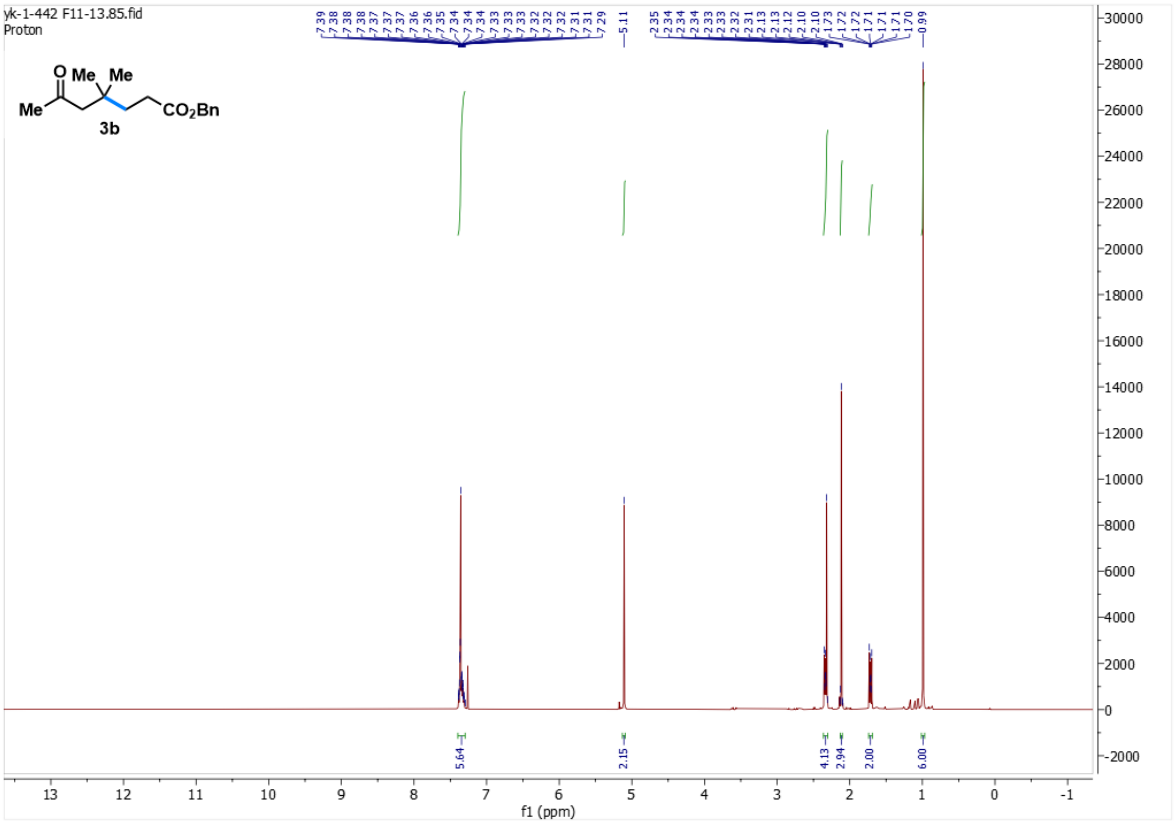
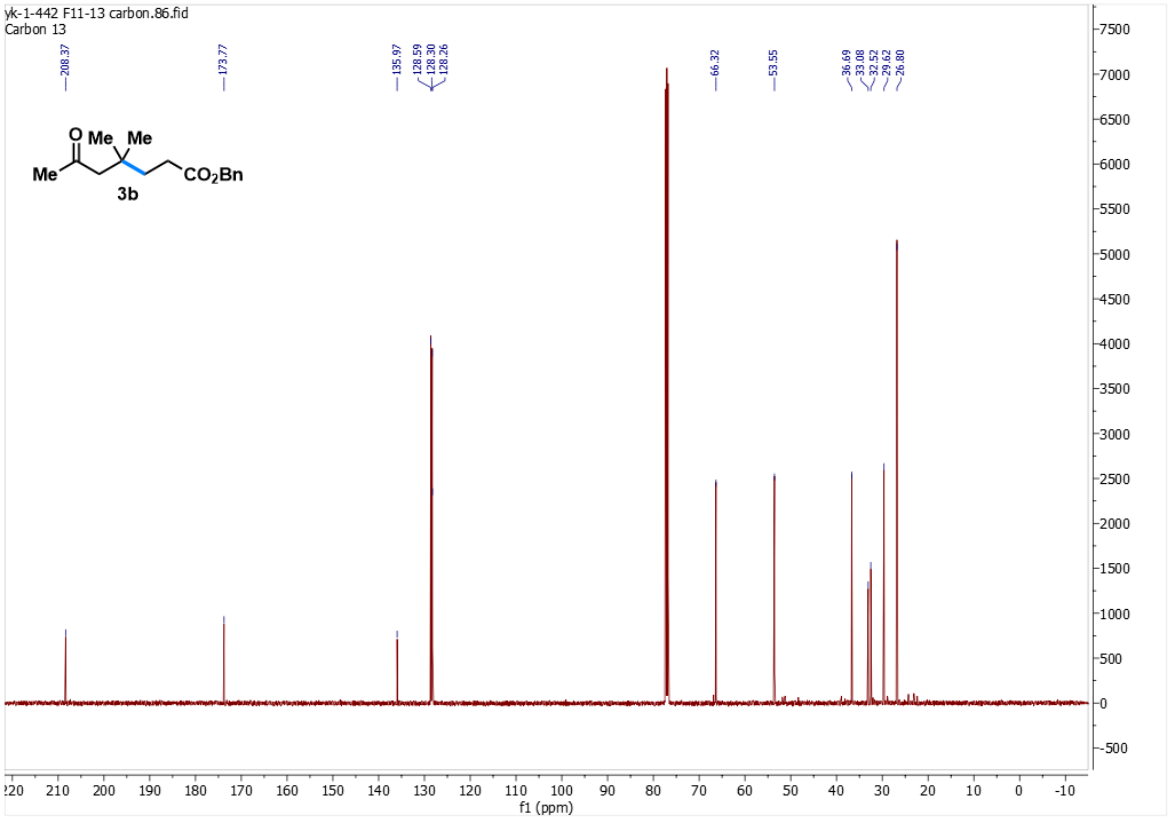
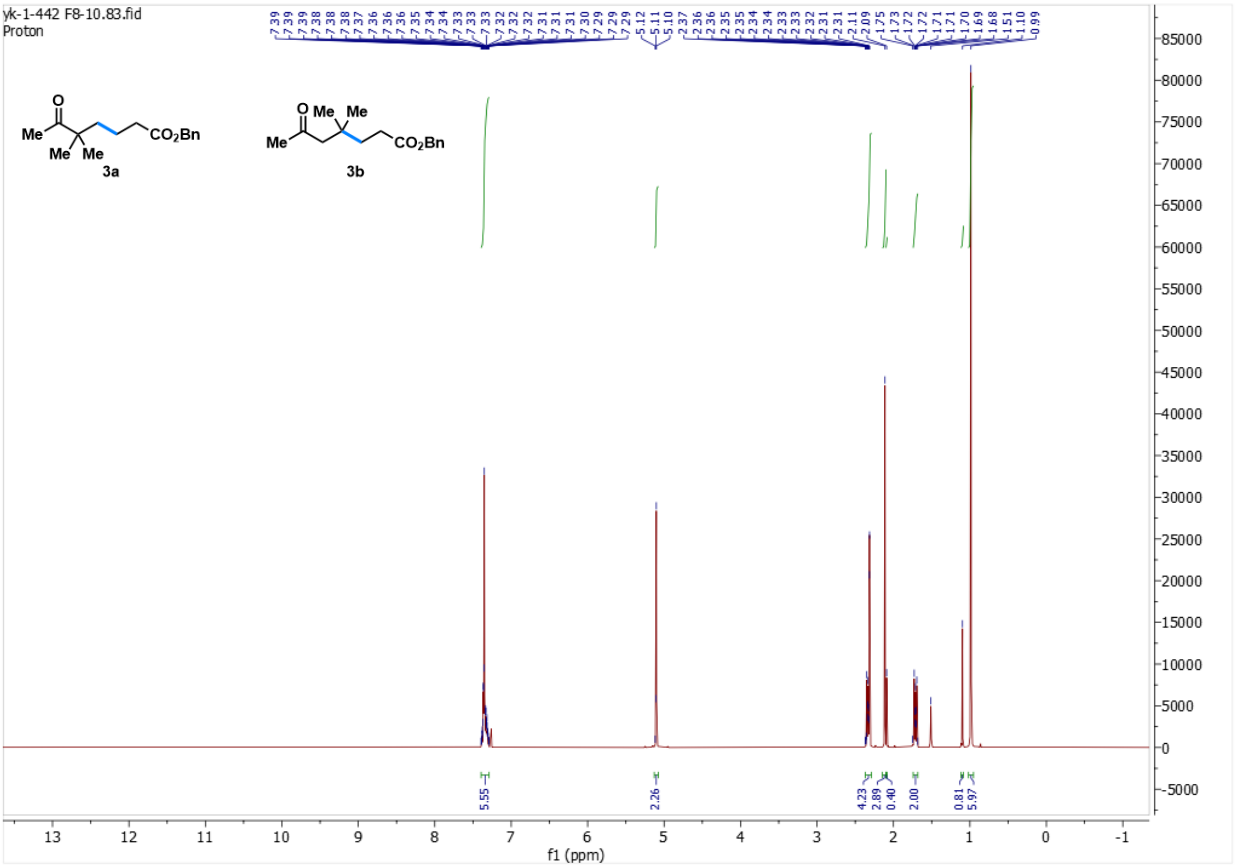
NMR Spectra


yk-1-442 F11-13.85.fid
Proton
O Me Me
Me
CO2Bn
3b
f1 (ppm)


yk-1-442 F11-13 carbon.86.fid
Carbon 13
208.37
173.77
135.97
128.59
128.30
128.26
66.32
53.55
36.69
33.08
32.52
29.62
26.80
O Me Me
Me
CO2Bn
3b
f1 (ppm)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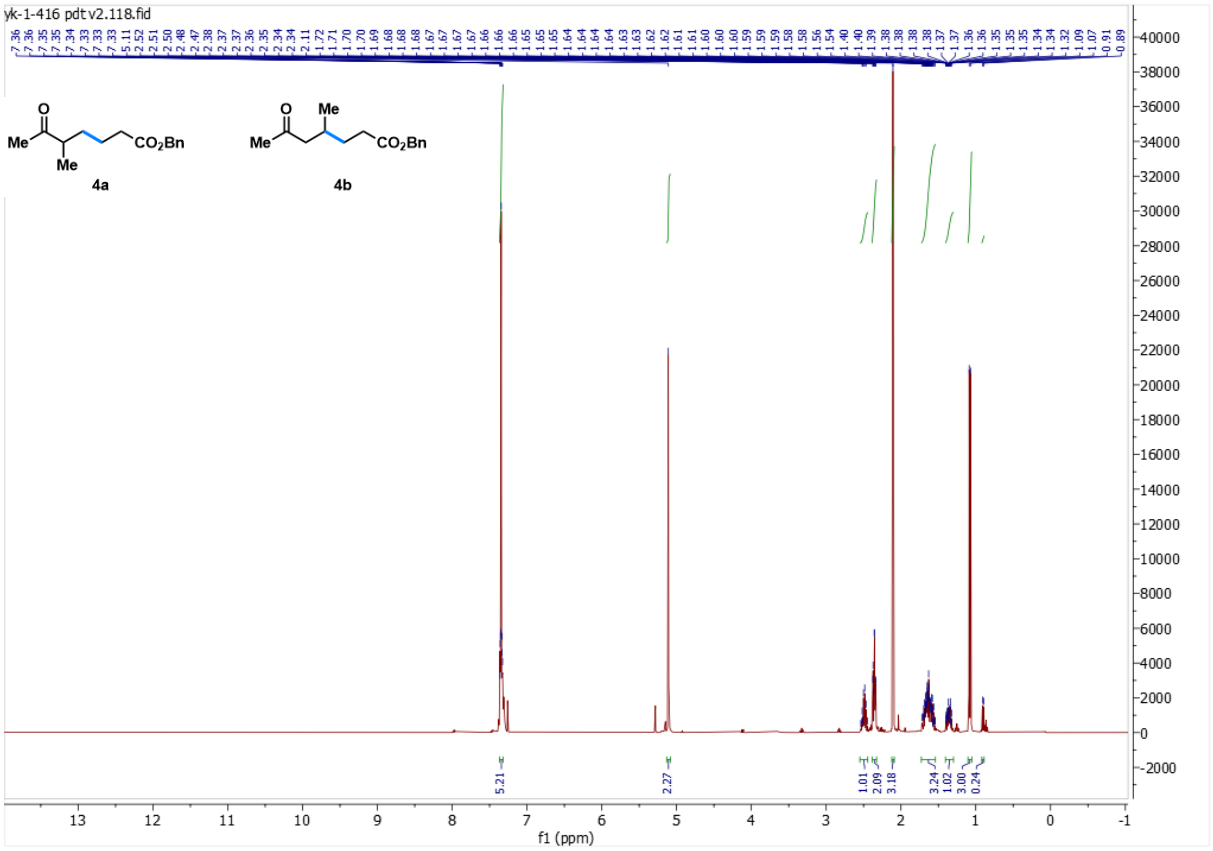
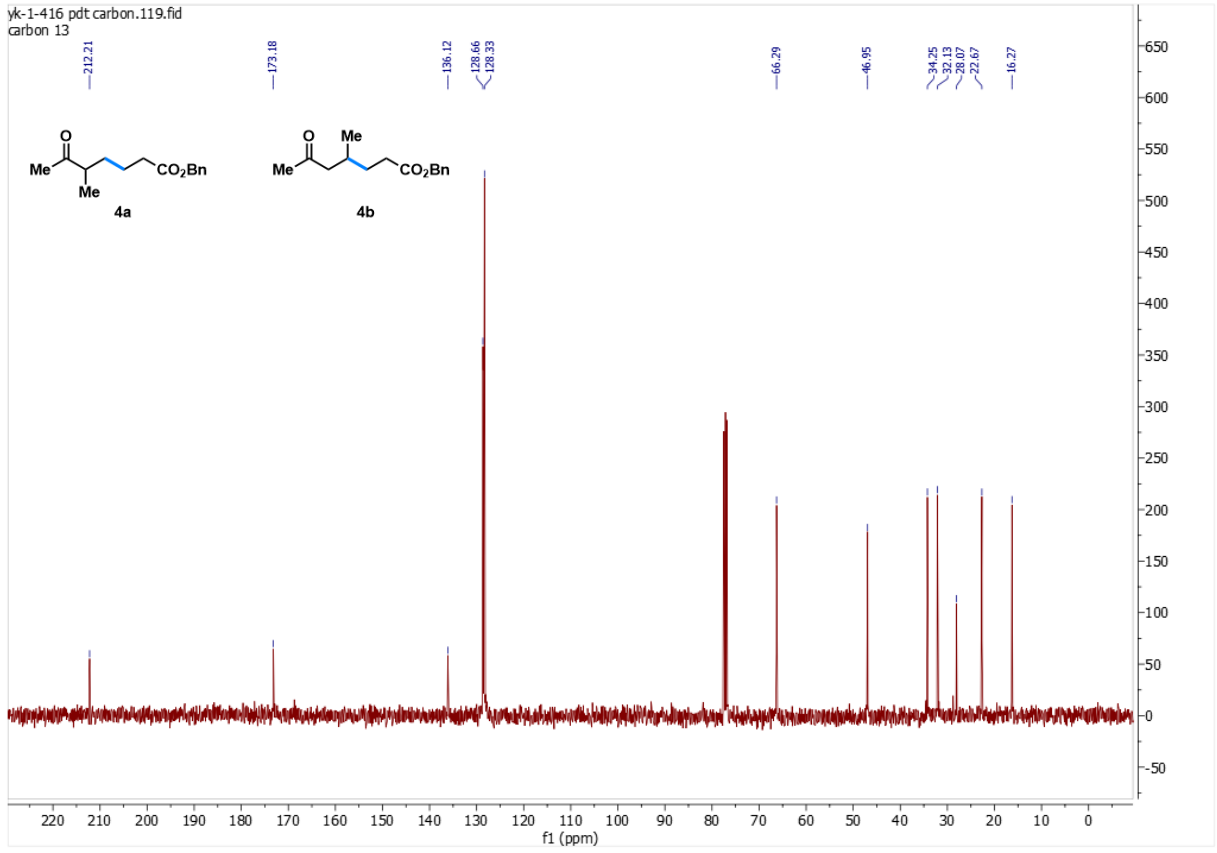
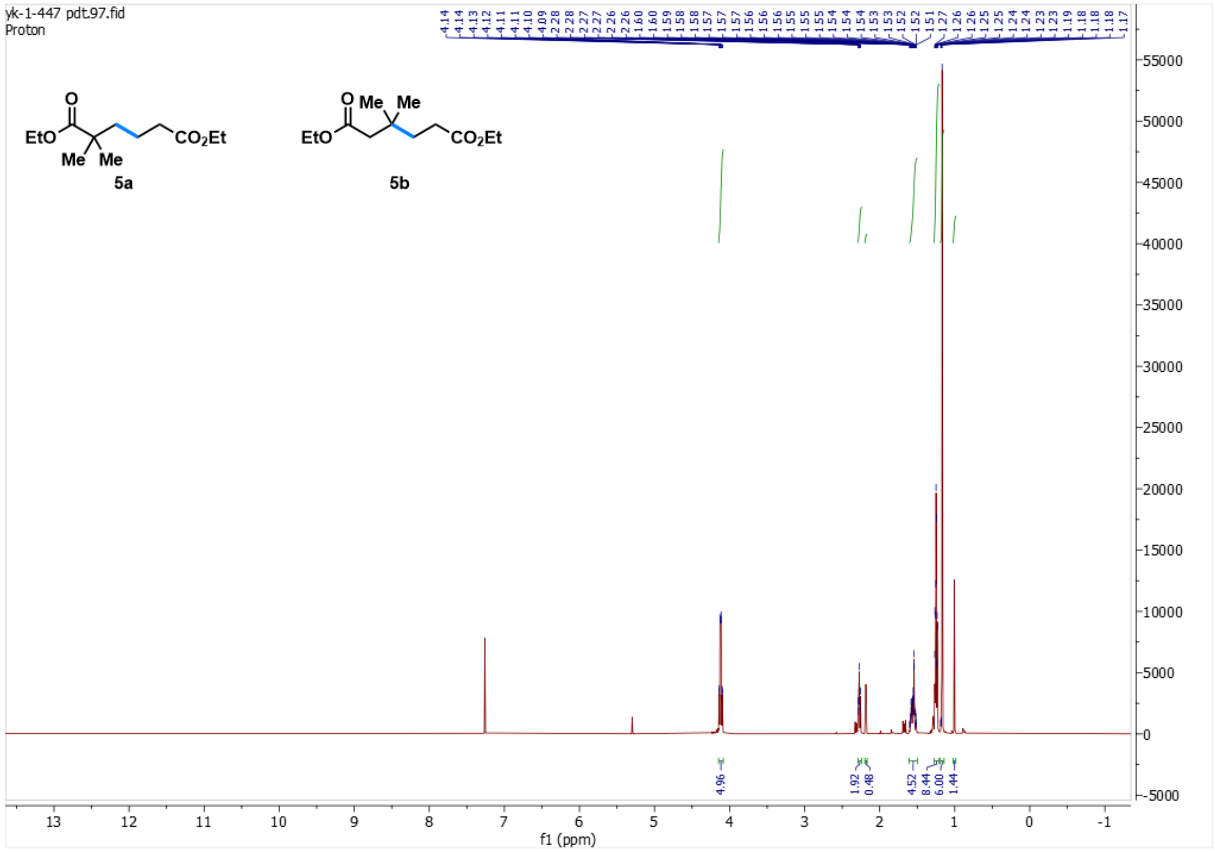
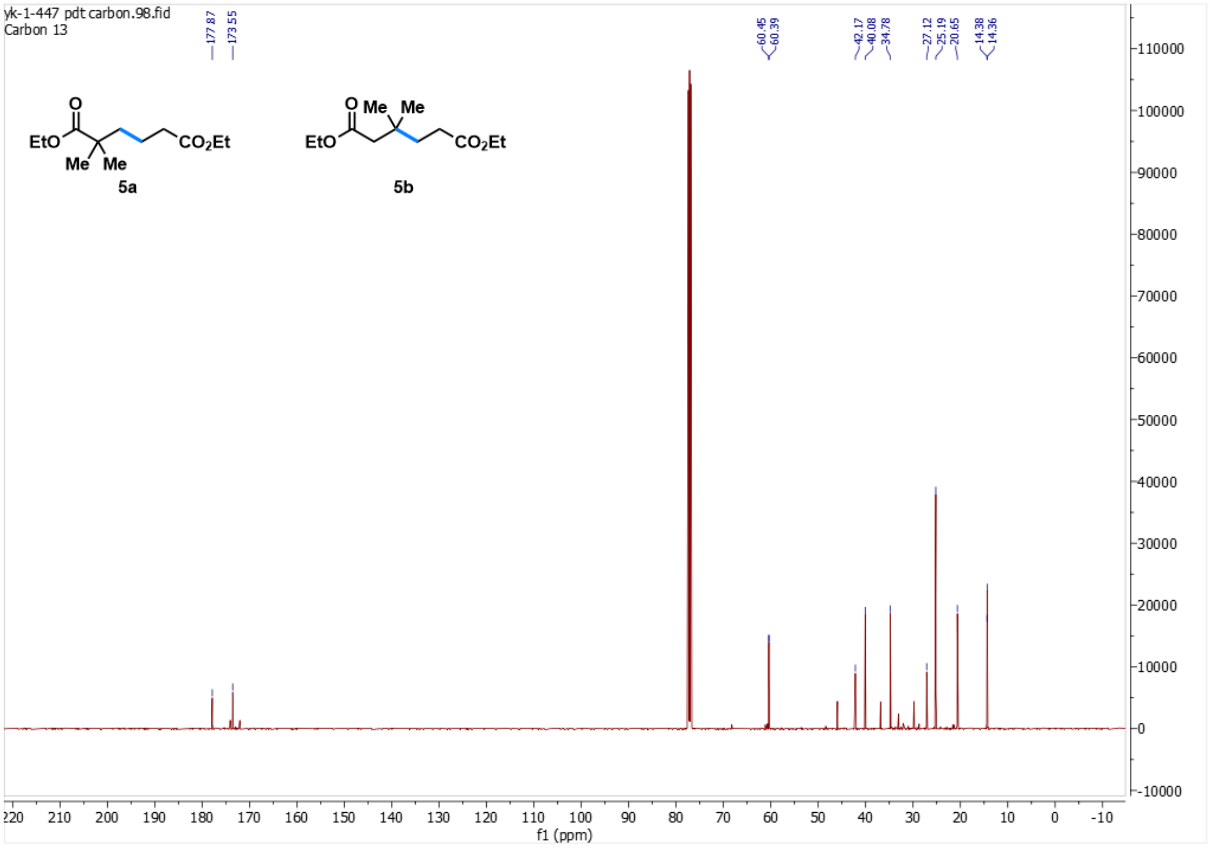
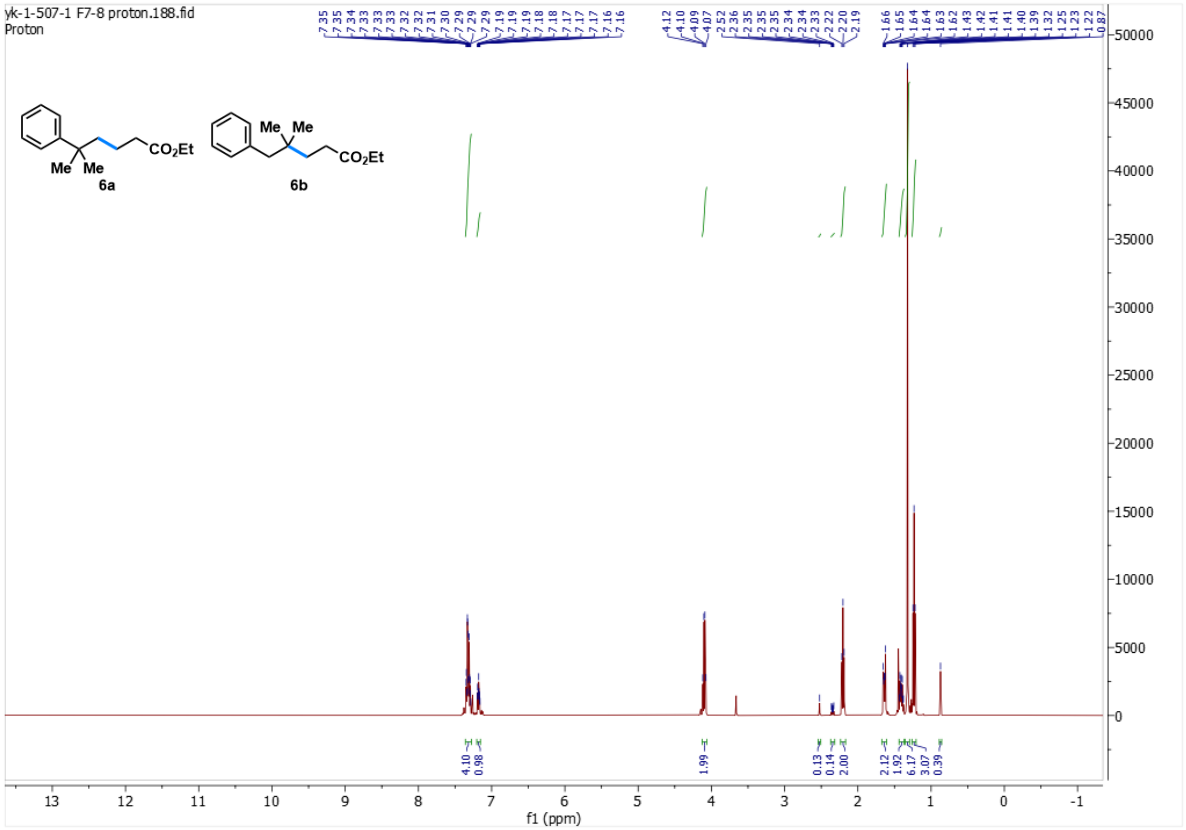
Proton
3a
3b
f1 (ppm)

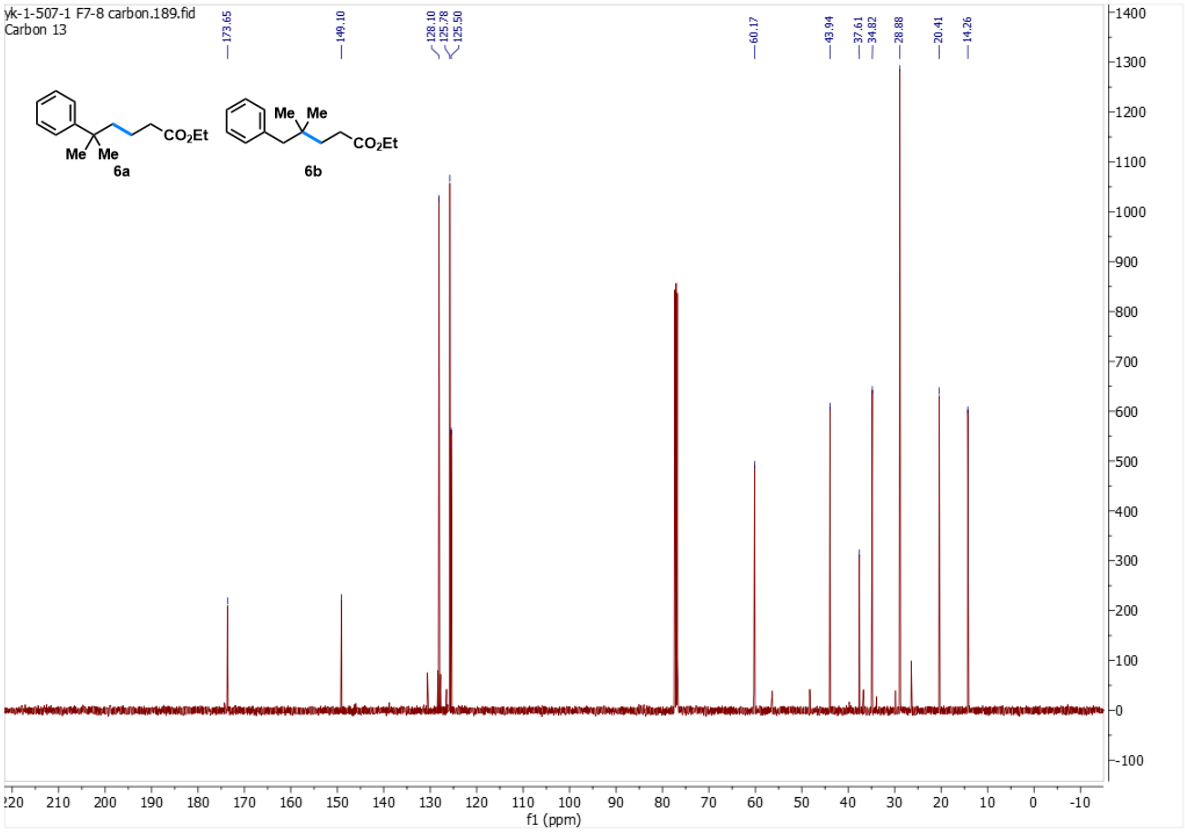

yk-1-416 pdt v2.118.fid
4a
4b
f1 (ppm)

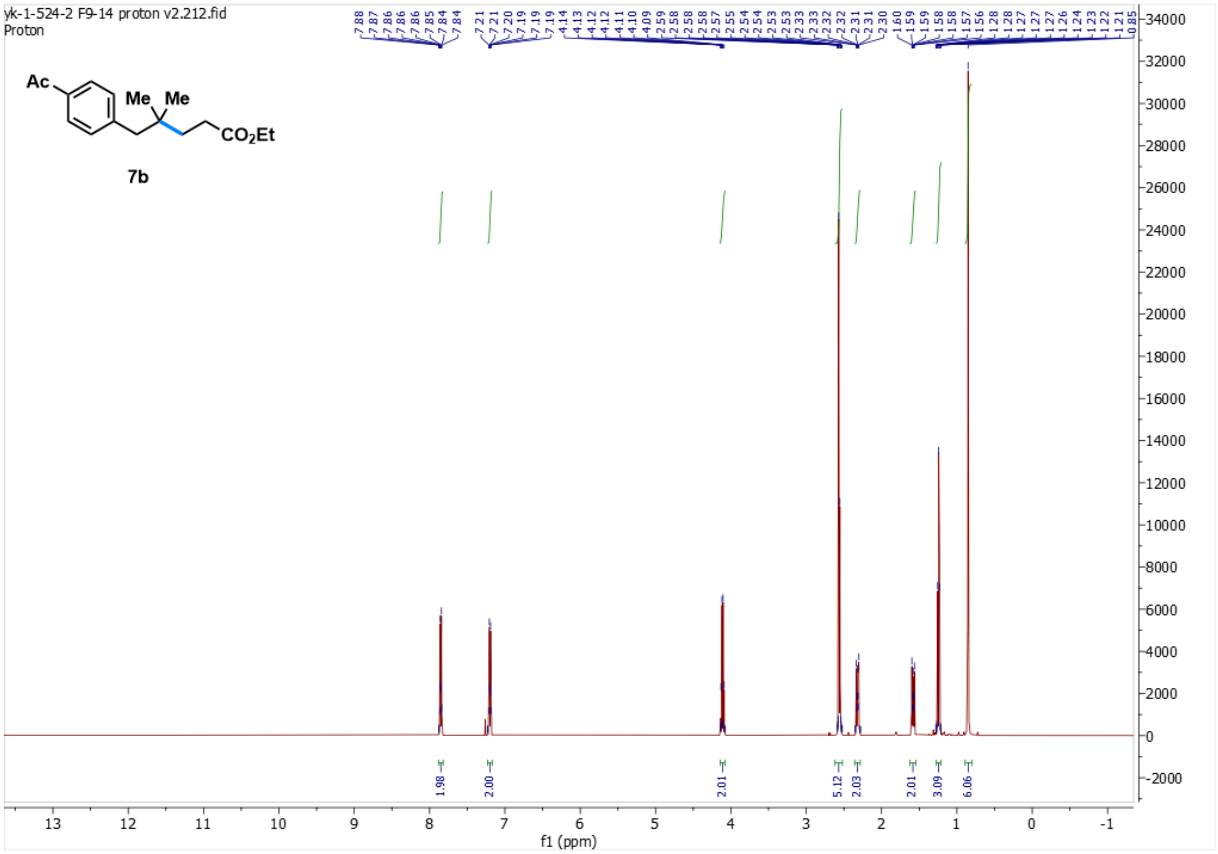

yk-1-416 pdt carbon.119.fid
carbon 13
212.21
173.18
136.12
128.66
128.33
66.29
46.95
34.25
32.13
28.07
22.67
16.27
4a
4b
f1 (ppm)

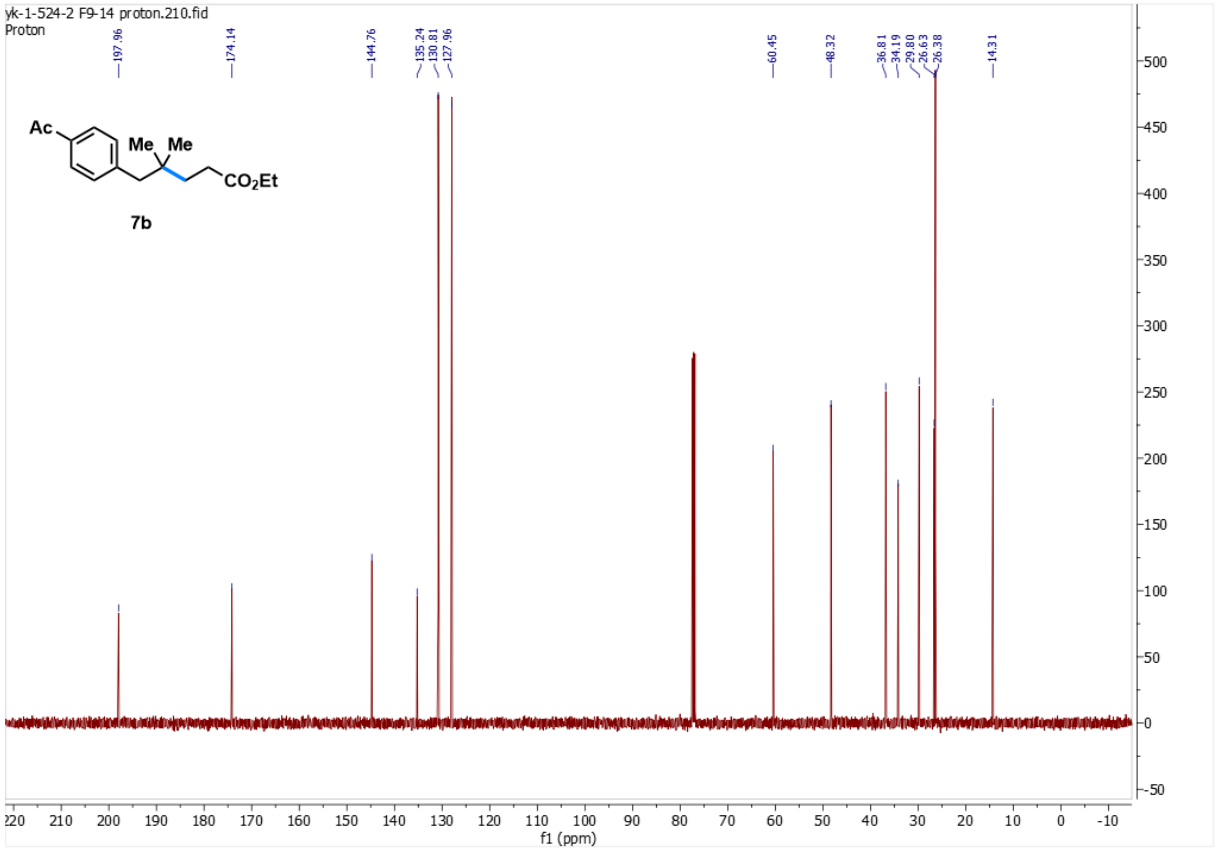

yk-1-447 pdt.97.fid
Proton
5a
5b
f1 (ppm)

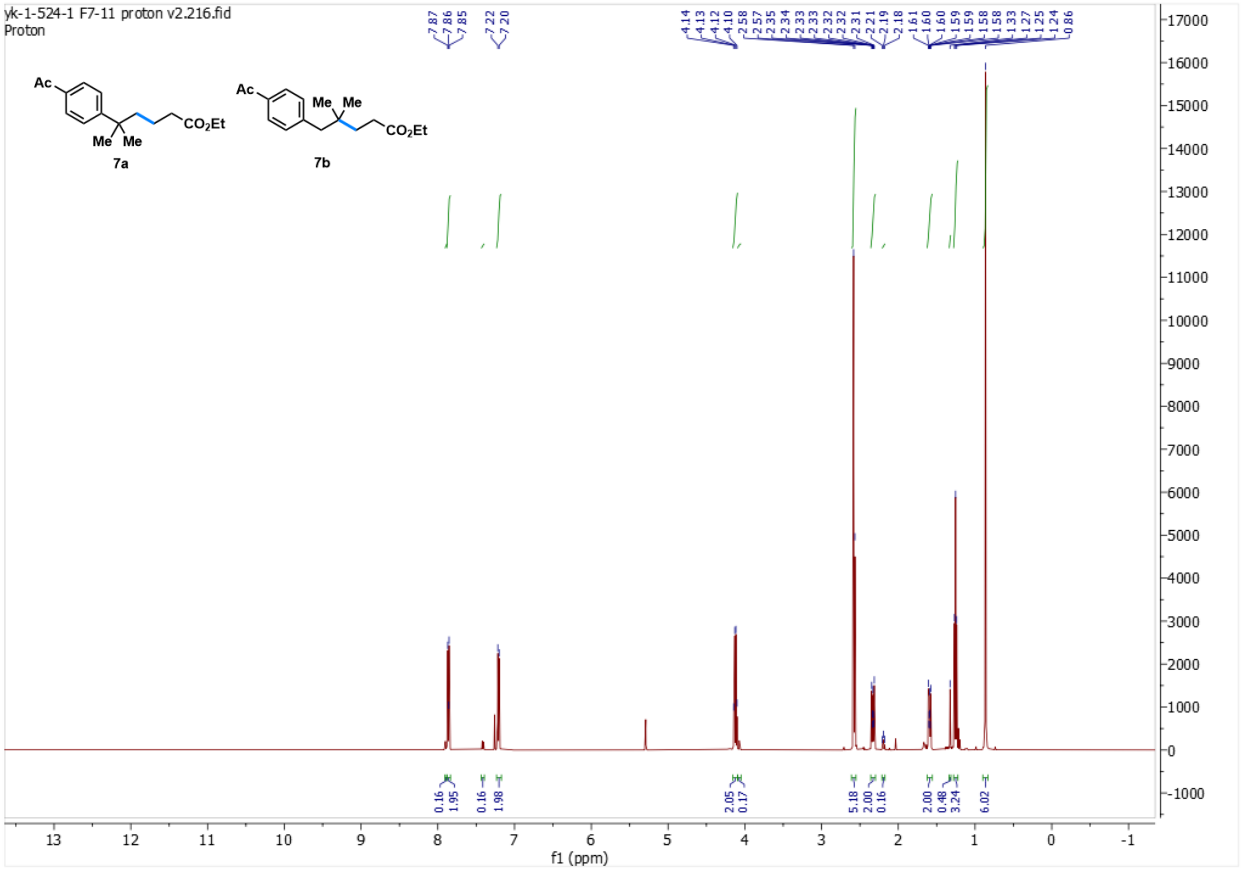

yk-1-447 pdt carbon.98.fid
Carbon 13
5a
5b
f1 (ppm)

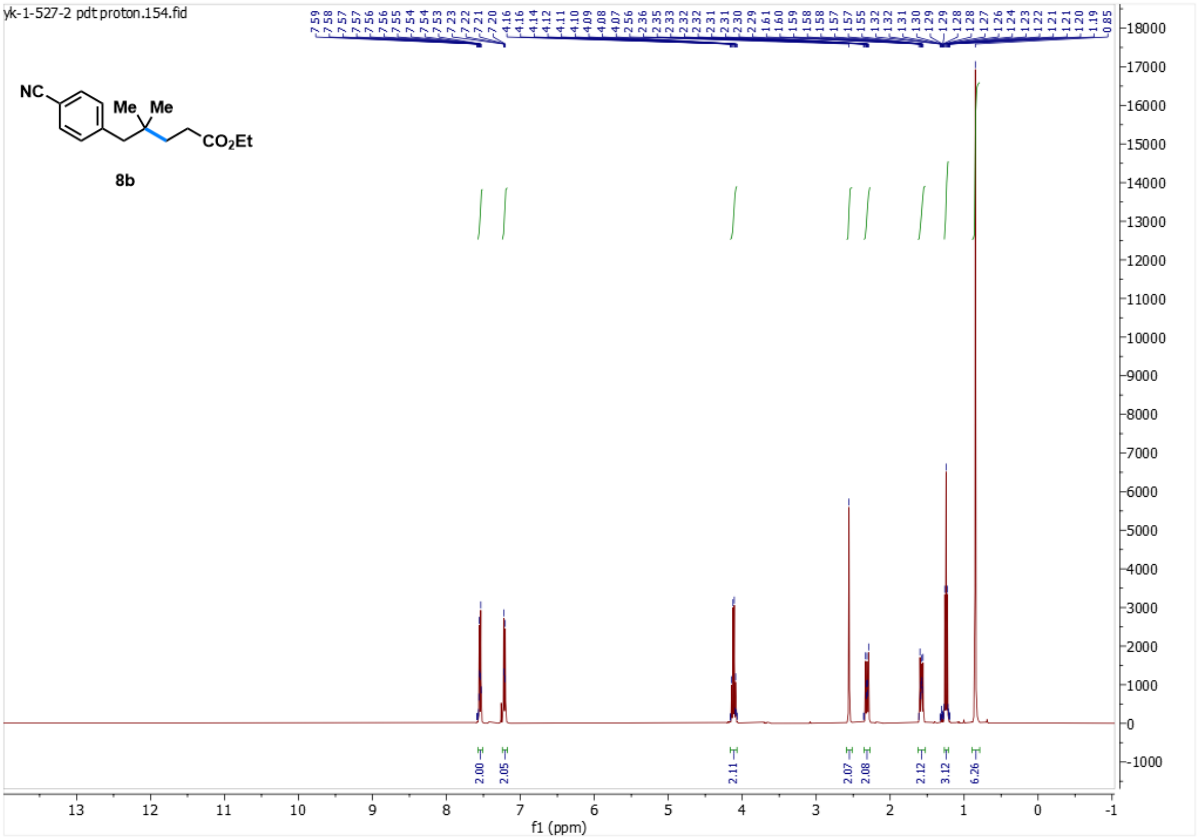

yk-1-507-1 F7-8 proton.188.fid
Proton
CO2Et
Me Me
6a
Me Me
CO2Et
6b
f1 (ppm)

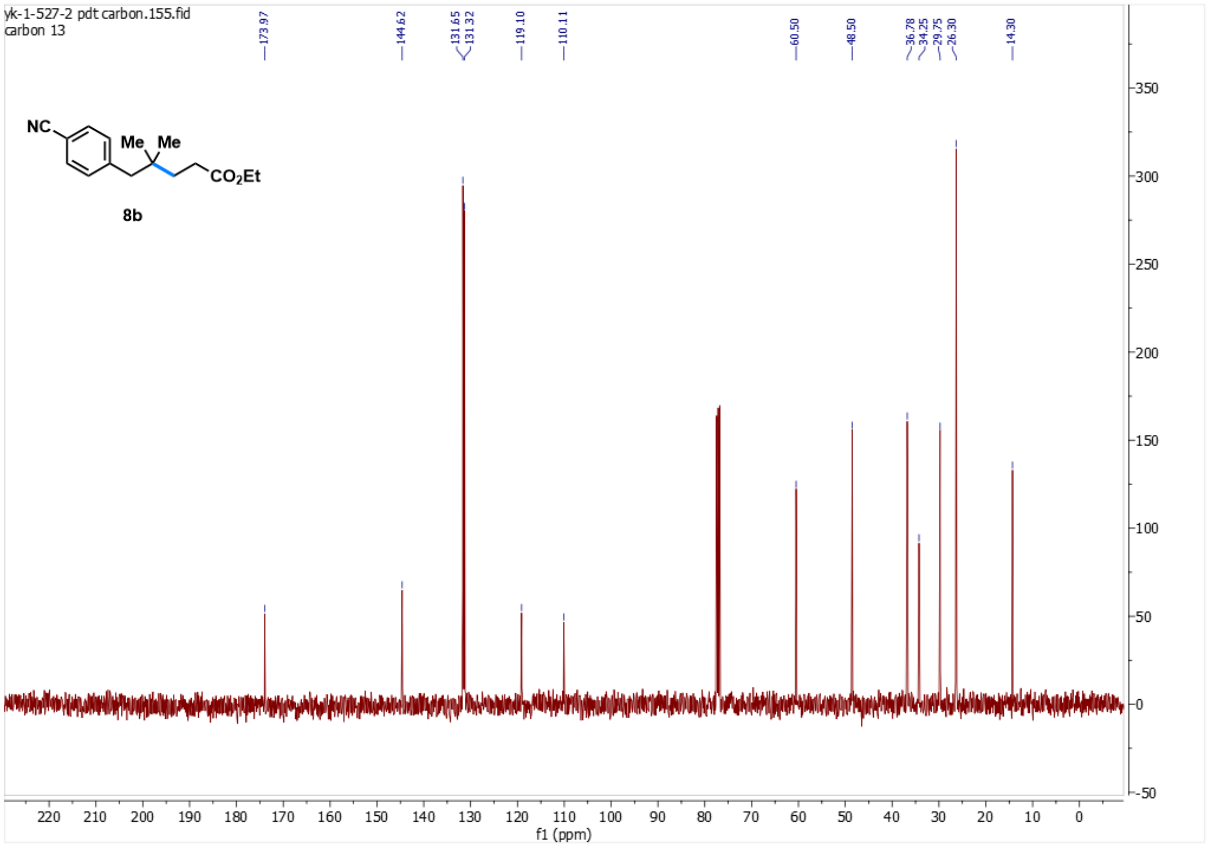

yk-1-507-1 F7-8 carbon.189.fid
Carbon 13
173.65
149.10
128.10
125.78
125.50
60.17
43.94
37.61
34.82
28.88
20.41
14.26
CO2Et
Me Me
6a
Me Me
CO2Et
6b
f1 (ppm)

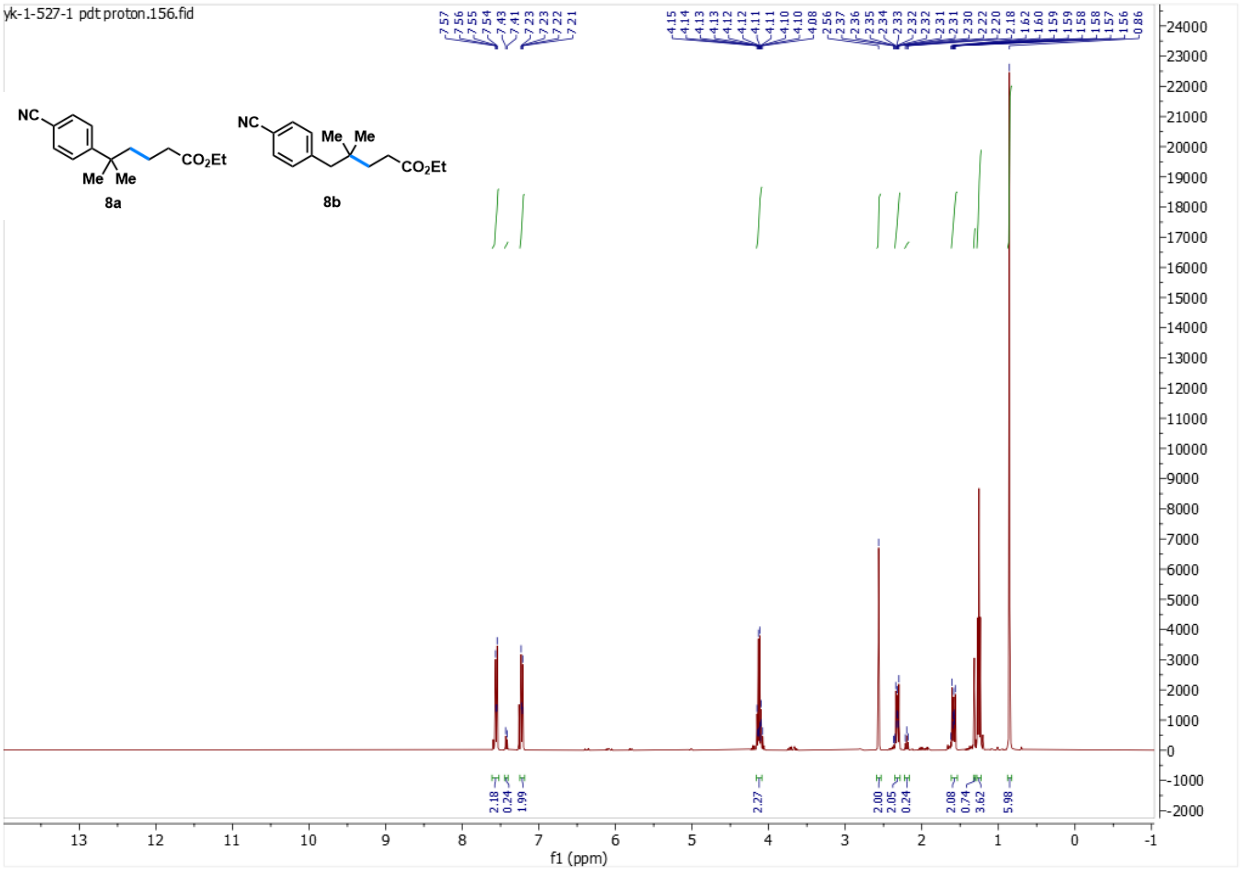

yk-1-524-2 F9-14 proton v2.212.fid
Proton
Ac
Me
Me
CO2Et
7b
1.98
2.00
2.01
5.12
2.03
2.01
3.09
6.06
f1 (ppm)

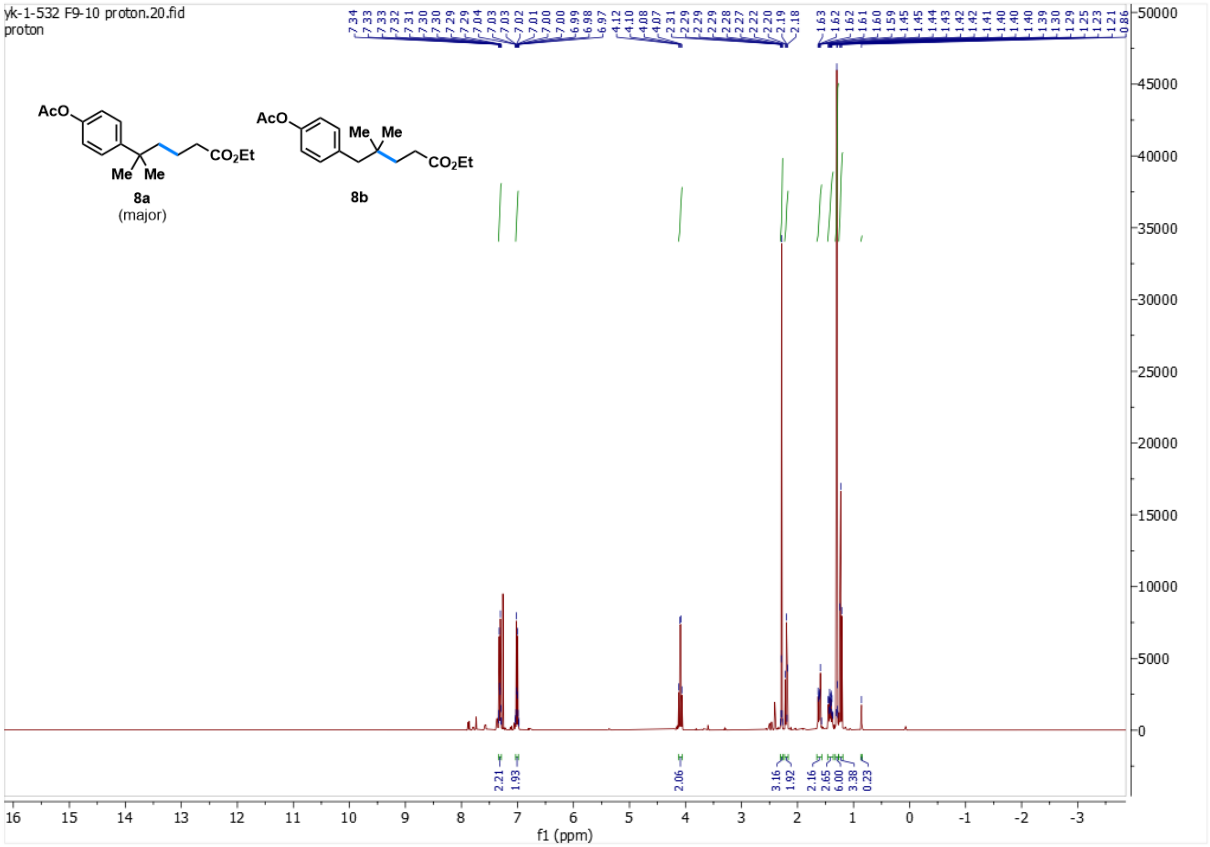

yk-1-524-2 F9-14 proton.210.fid
Proton
197.96
174.14
144.76
135.24
130.81
127.96
60.45
48.32
36.81
34.19
29.80
26.63
26.38
14.31
Ac
Me
Me
CO2Et
7b
f1 (ppm)

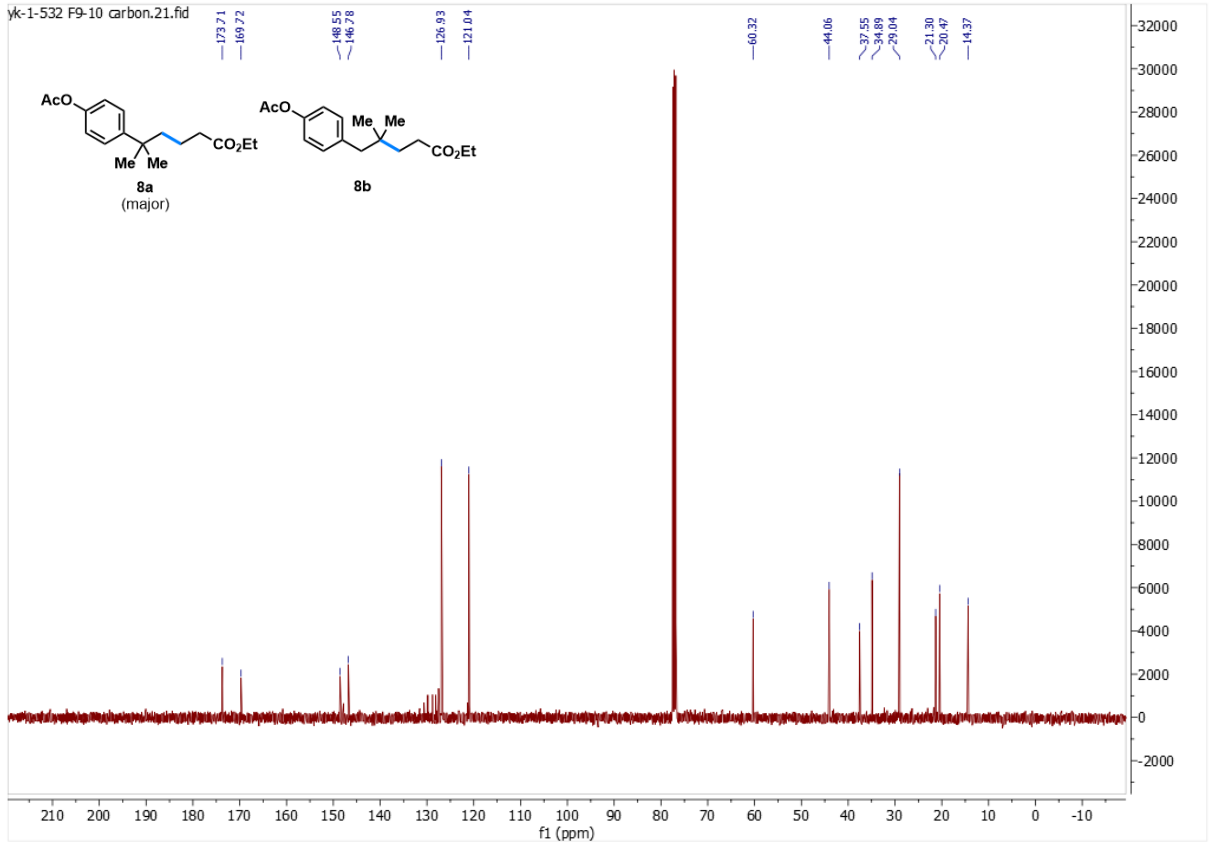

yk-1-524-1 F7-11 proton v2.216.fid
Proton
Ac
CO2Et
Me Me
7a
Ac
Me Me
CO2Et
7b
f1 (ppm)


yk-1-527-2 pdt proton.154.fid
NC
Me Me
CO2Et
8b
f1 (ppm)


yk-1-527-2 pdt carbon.155.fid
carbon 13
173.97
144.62
131.65
131.32
119.10
110.11
60.50
48.50
36.78
34.25
29.75
26.30
14.30
NC
Me Me
CO2Et
8b
f1 (ppm)


yk-1-527-1 pdt proton.156.fid
NC
CO2Et
Me Me
8a
NC
Me Me
CO2Et
8b
f1 (ppm)


yk-1-532 F9-10 proton.20.fid
proton
AcO
CO2Et
Me Me
8a
(major)
AcO
Me Me
CO2Et
8b
f1 (ppm)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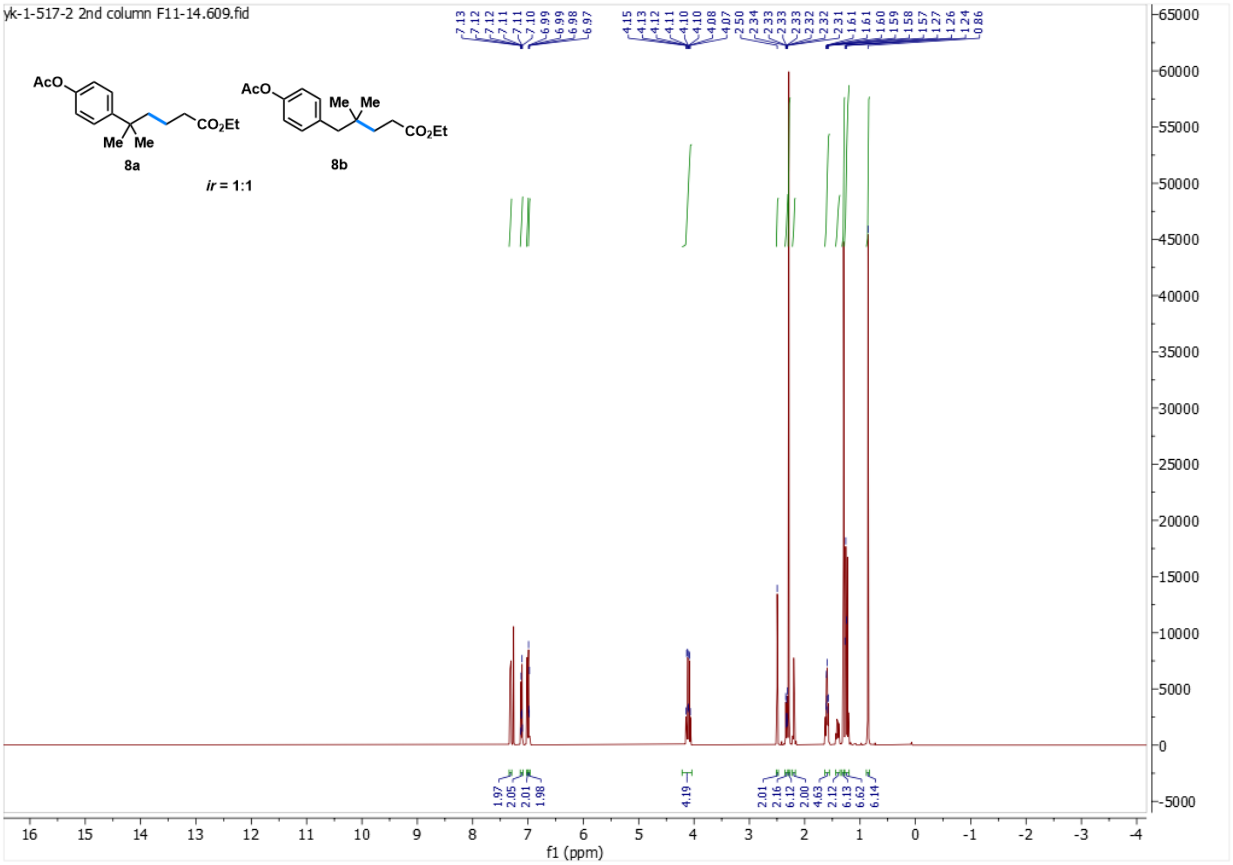
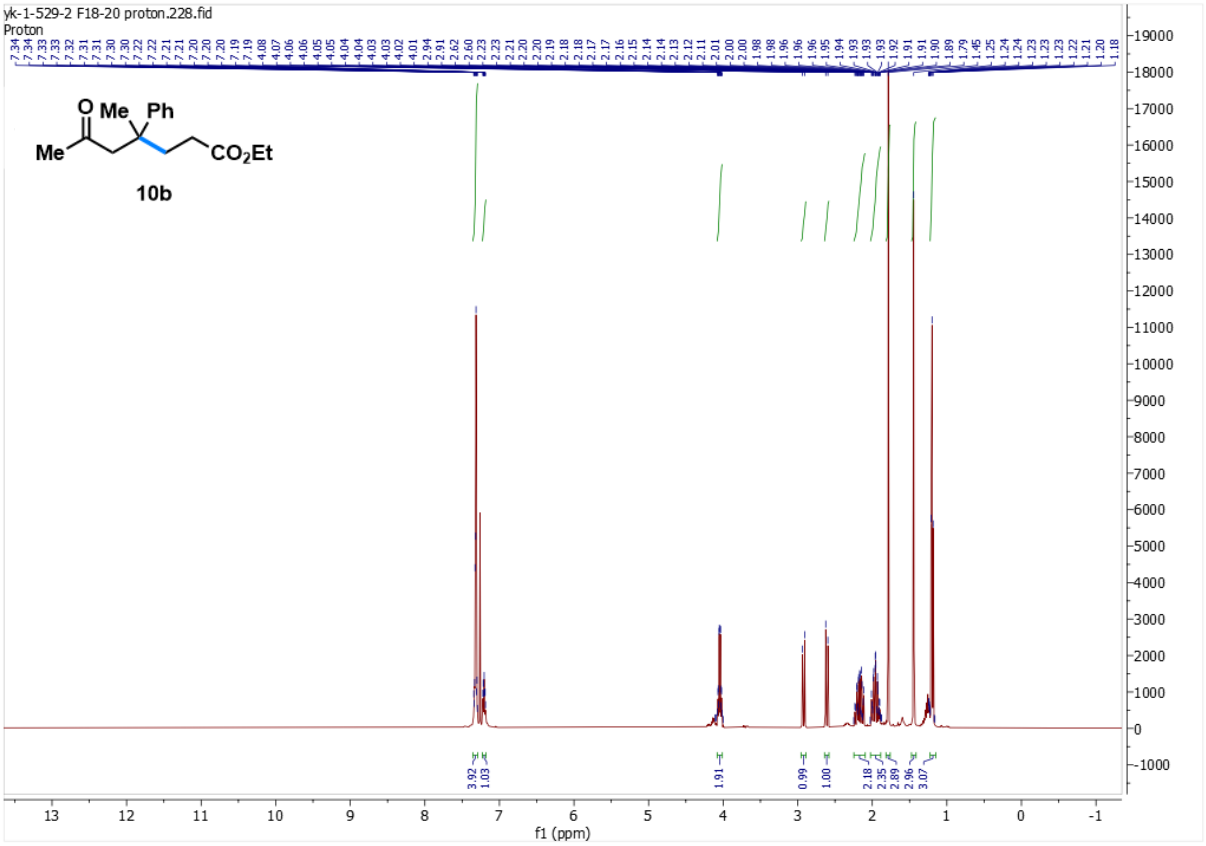
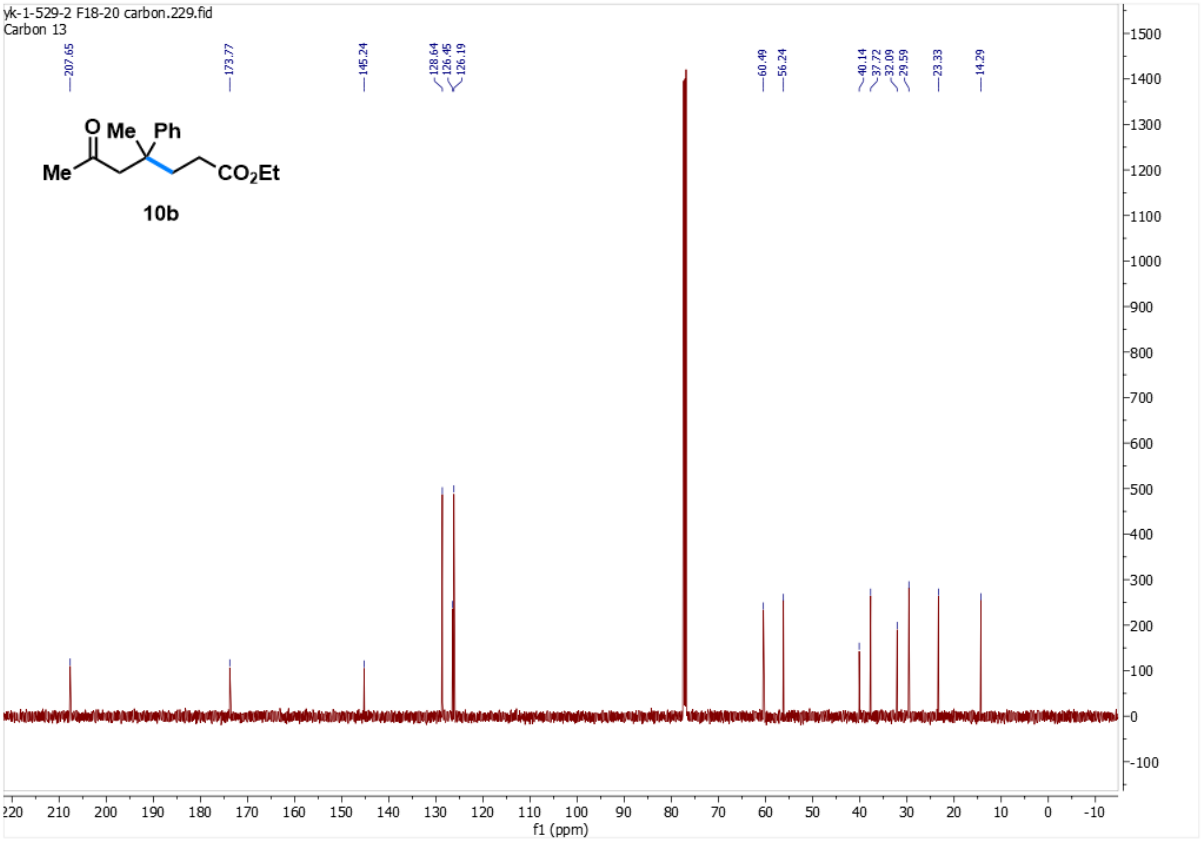
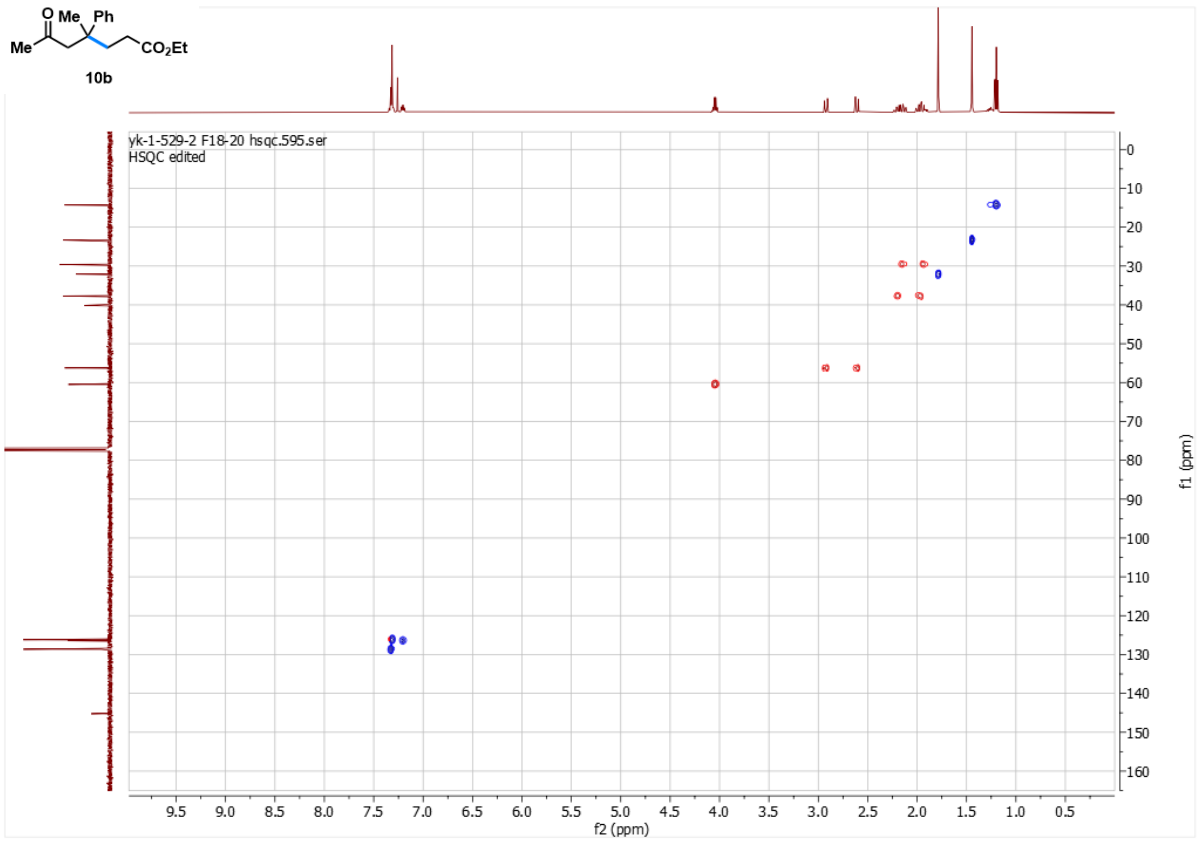
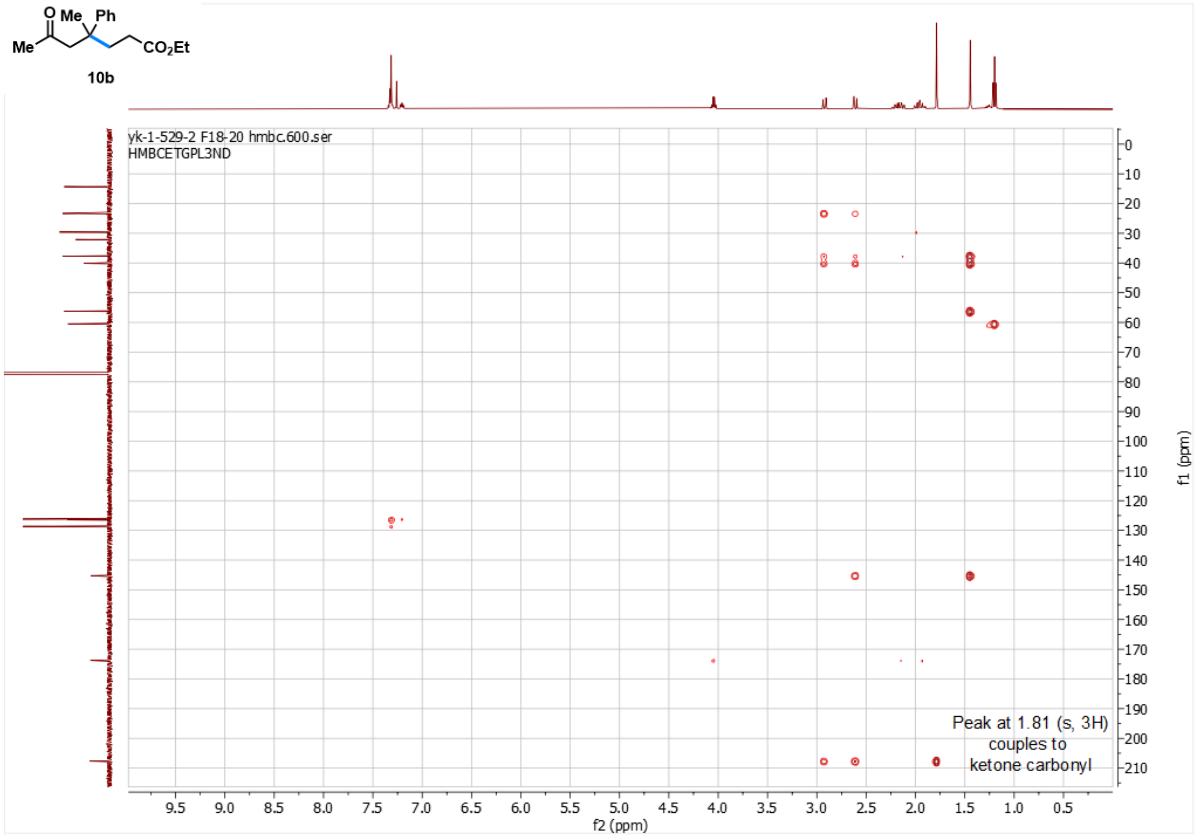
AcO
CO2Et
Me Me
8a
(major)
AcO
Me Me
CO2Et
8b
f1 (ppm)

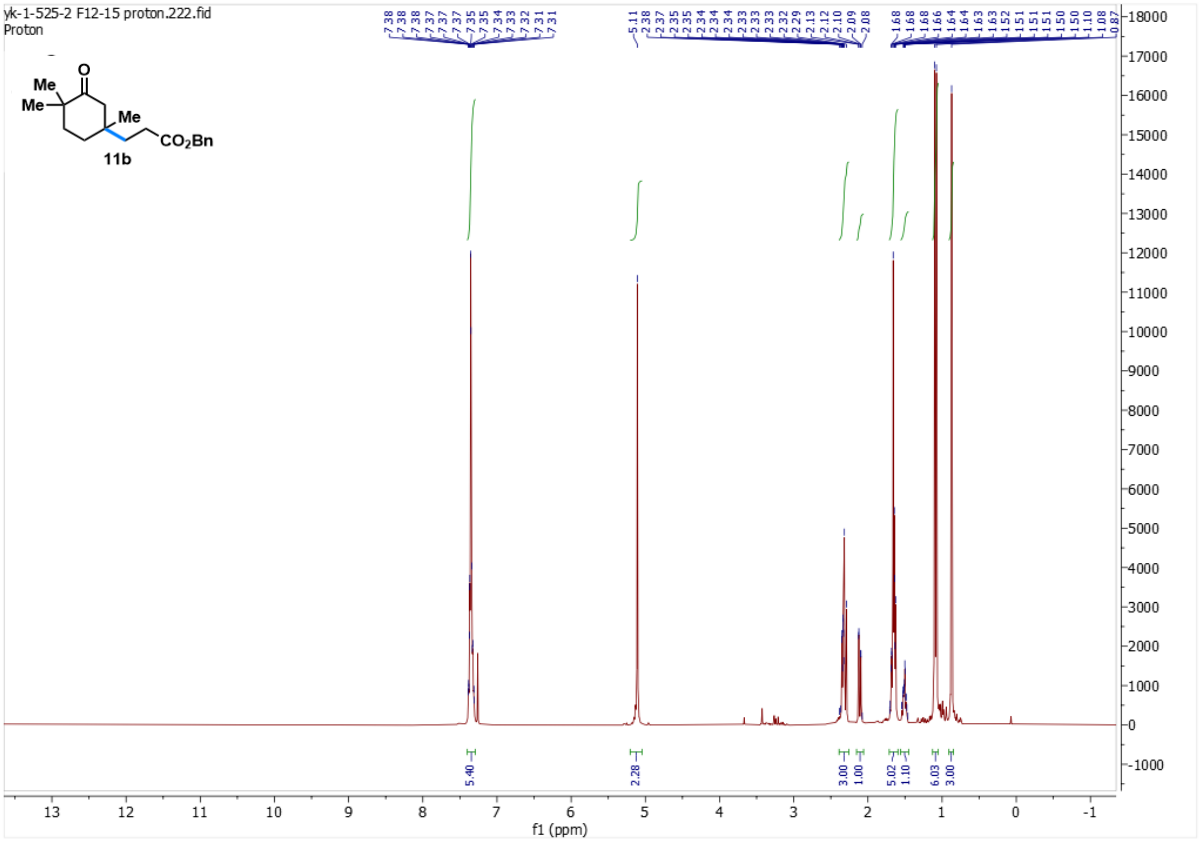

yk-1-517-2 2nd column F11-14.609.fid
AcO
CO2Et
Me Me
8a
AcO
Me Me
CO2Et
8b
ir = 1:1
f1 (ppm)

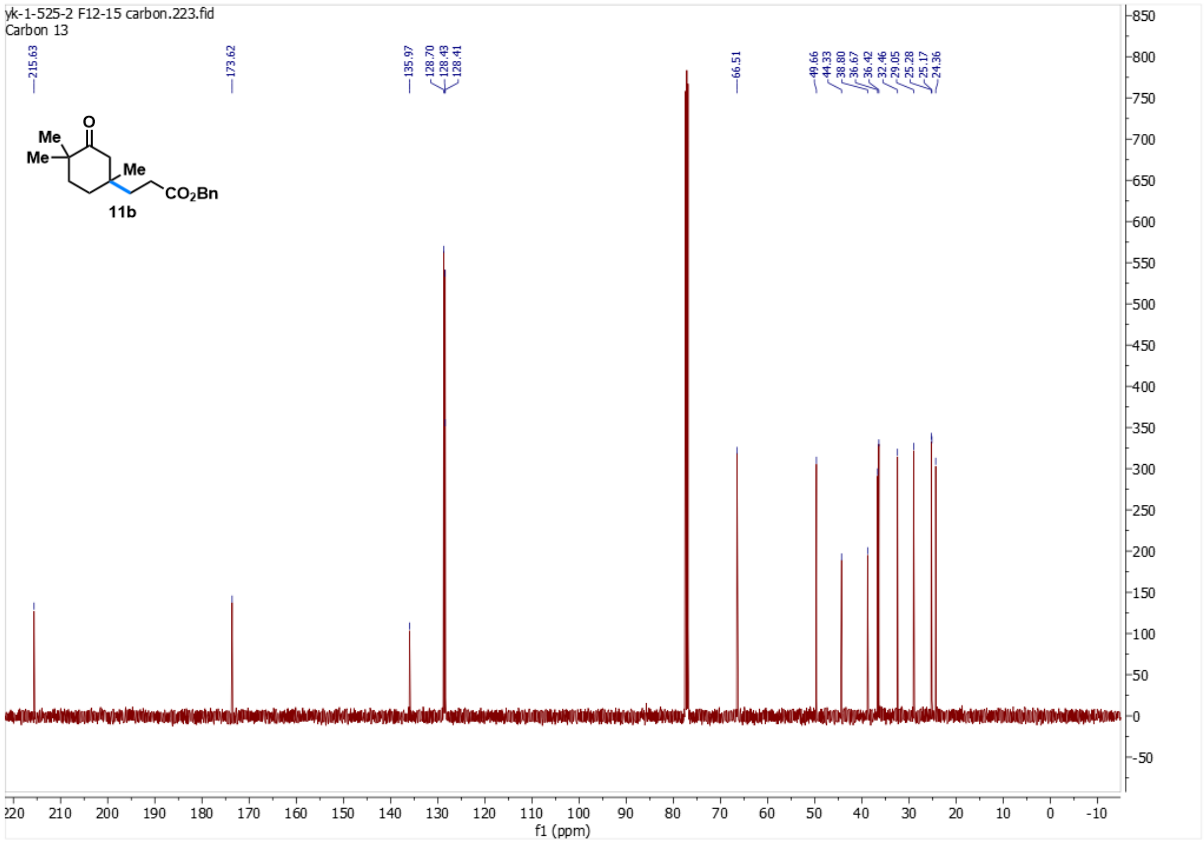

yk-1-529-2 F18-20 proton.228.fid
Proton
O Me Ph
Me
CO2Et
10b
f1 (ppm)

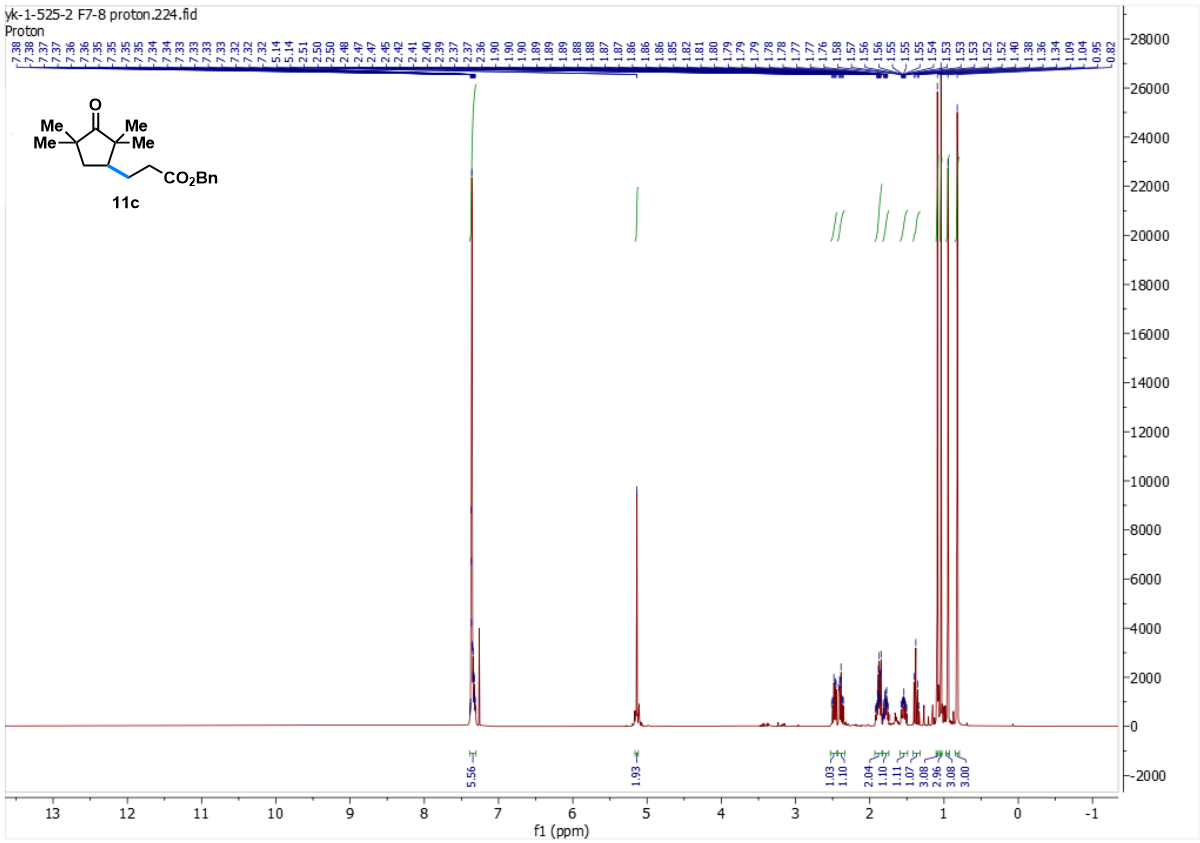

yk-1-529-2 F18-20 carbon.229.fid
Carbon 13
207.65
173.77
145.24
128.64
126.45
126.19
60.49
56.24
40.14
37.72
32.09
29.59
23.33
14.29
O Me Ph
Me
CO2Et
10b
f1 (ppm)

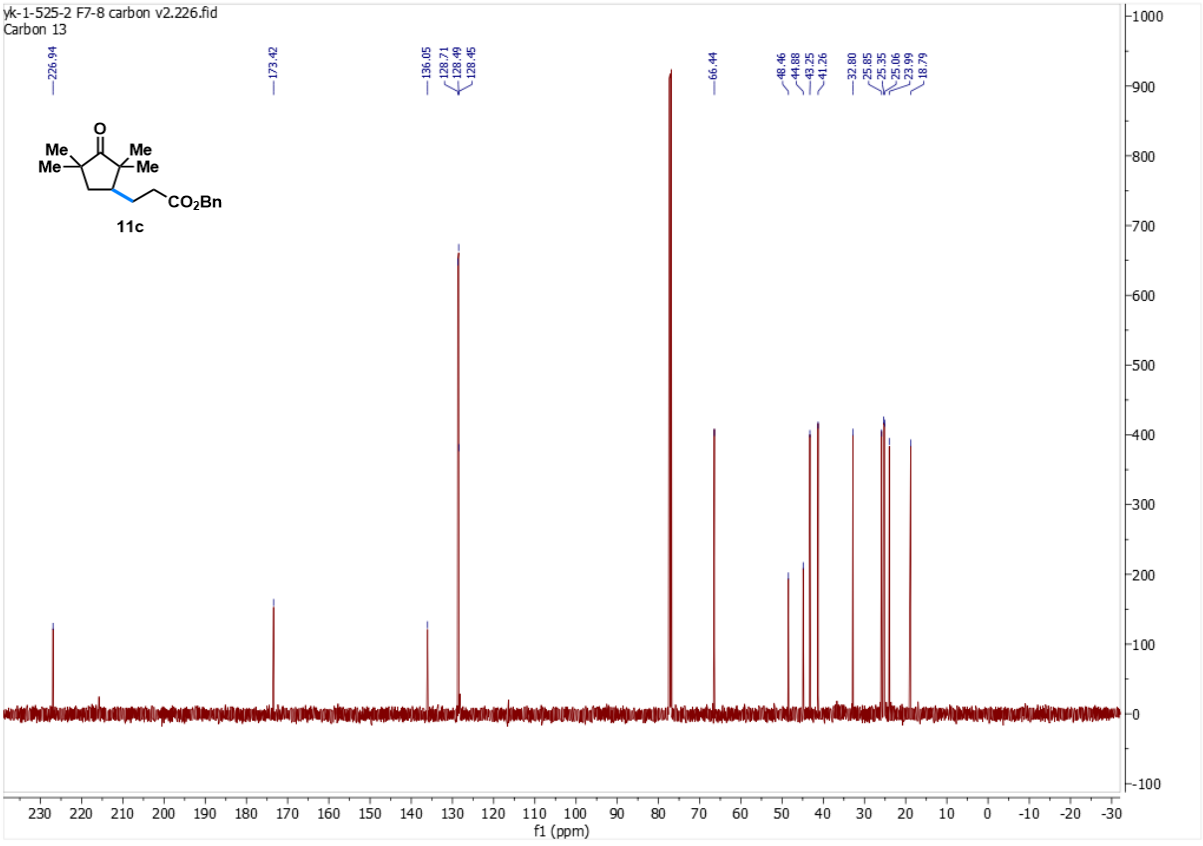

10b
yk-1-529-2 F18-20 hsqc.595.ser
HSQC edited
f2 (ppm)
f1 (ppm)

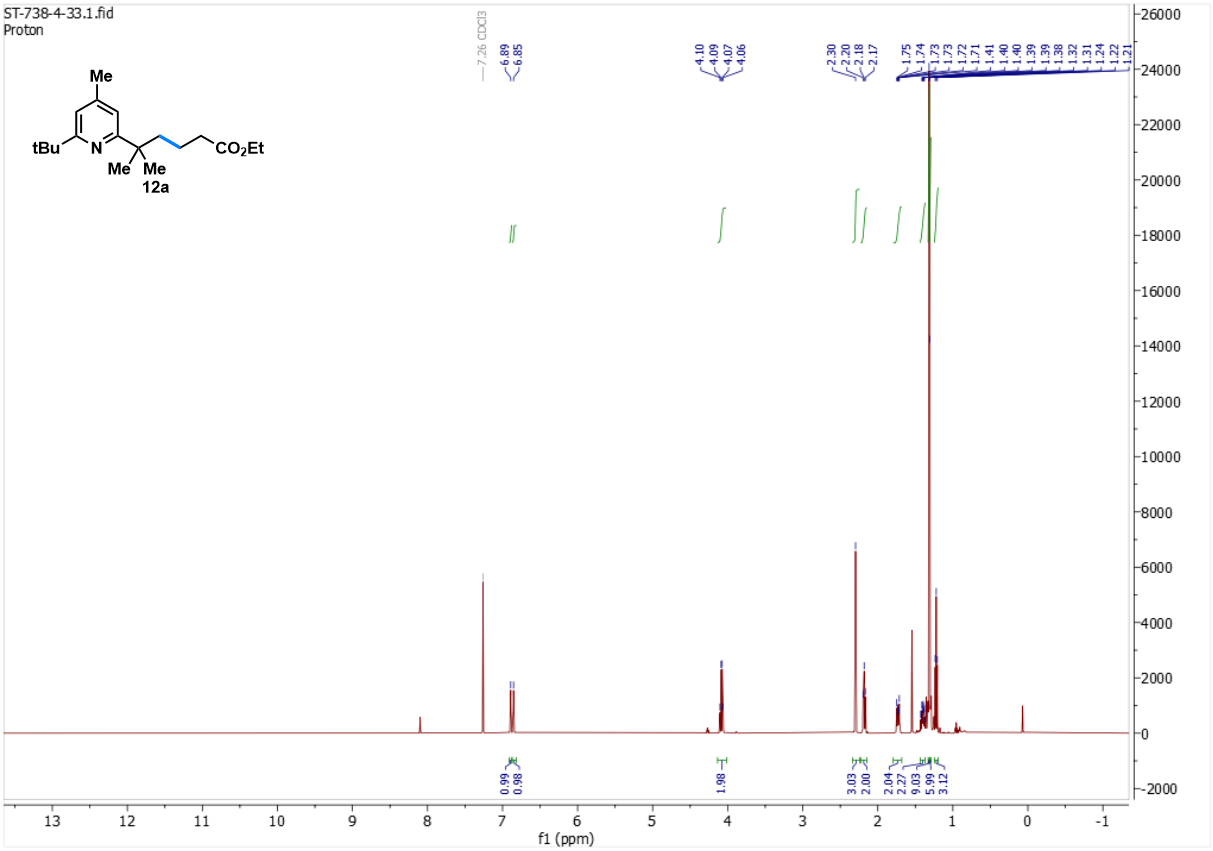

10b
yk-1-529-2 F18-20 hmbc.600.ser
HMBCETGPL3ND
Peak at 1.81 (s, 3H)
couples to
ketone carbonyl
f2 (ppm)
f1 (ppm)

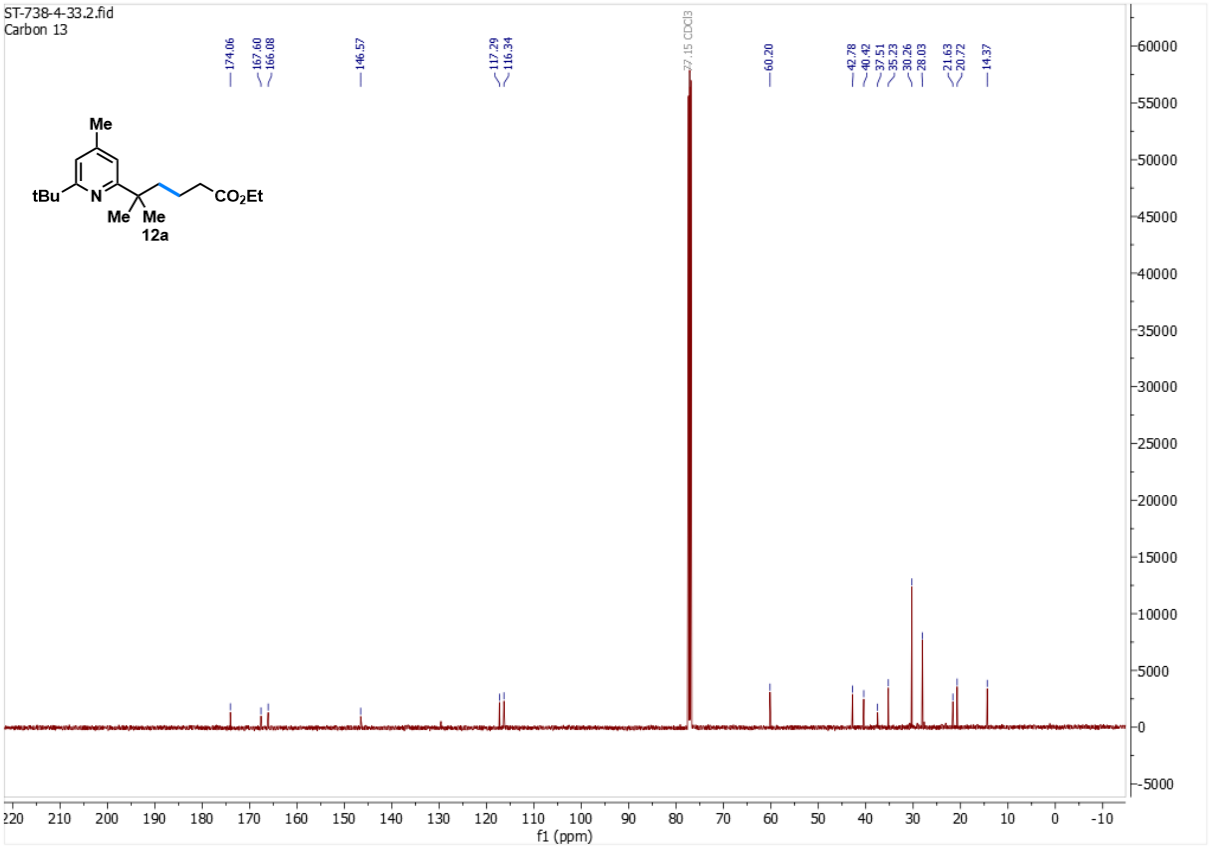

yk-1-525-2 F12-15 proton.222.fid
Proton
Me
Me
Me
CO2Bn
11b
f1 (ppm)

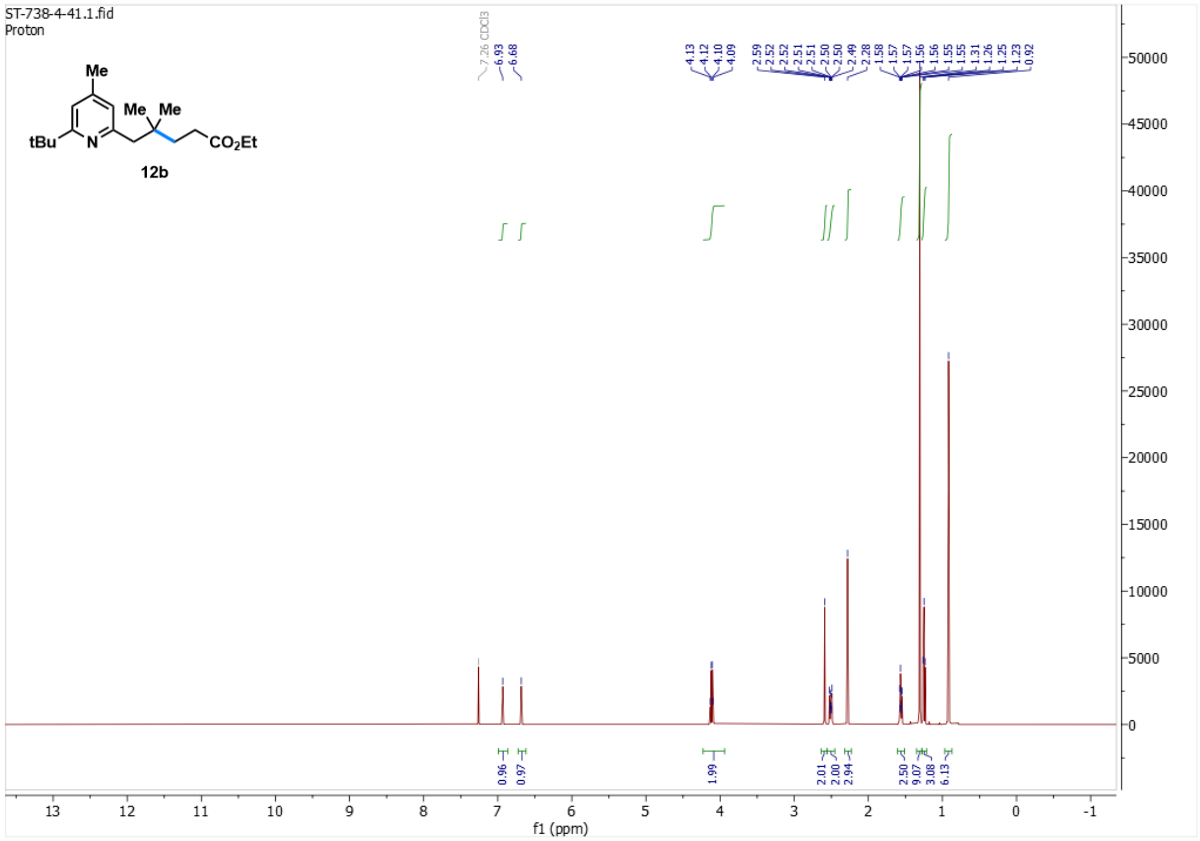

yk-1-525-2 F12-15 carbon.223.fid
Carbon 13
215.63
173.62
135.97
128.70
128.43
128.41
66.51
49.66
44.33
38.80
36.67
36.42
32.46
29.05
25.28
25.17
24.36
Me
Me
Me
CO2Bn
11b
f1 (ppm)

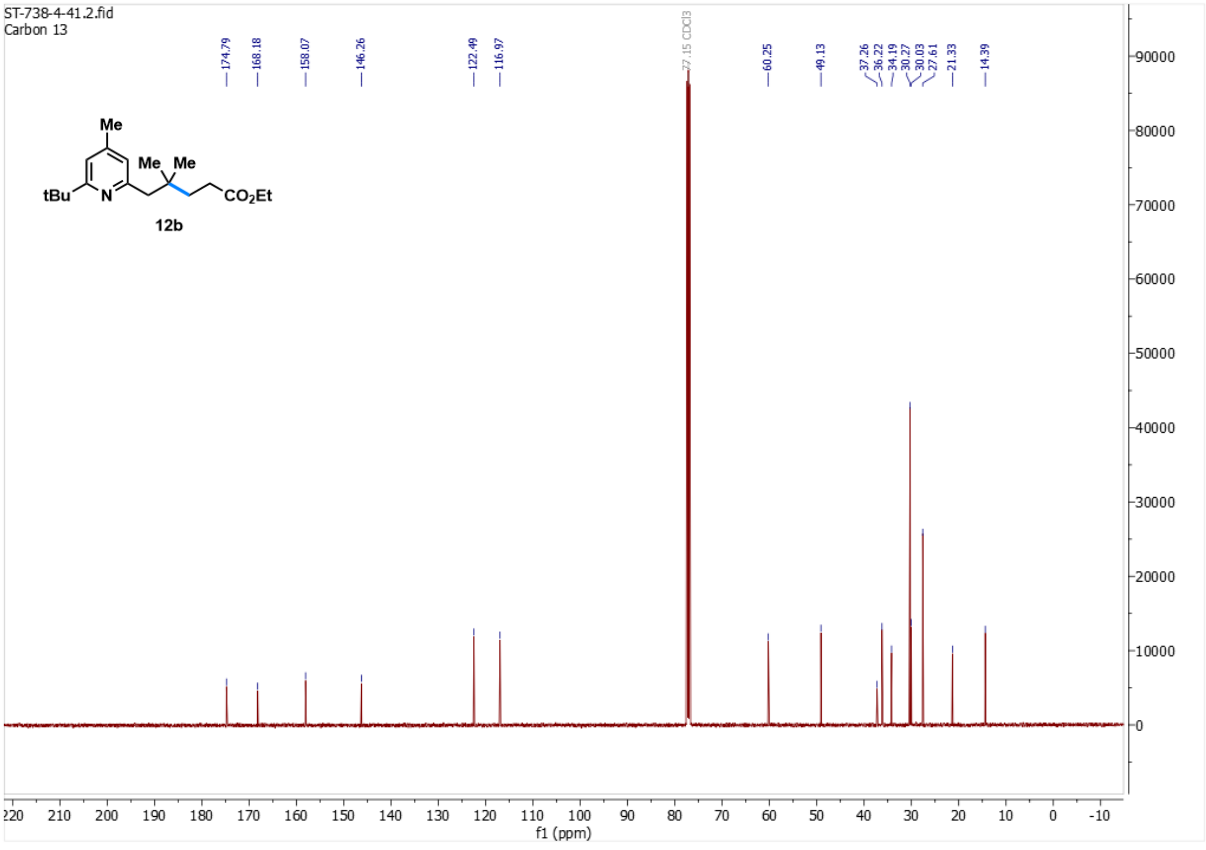

yk-1-525-2 F7-8 proton.224.fid
Proton
Me
Me
Me
Me
O
CO2Bn
11c
f1 (ppm)

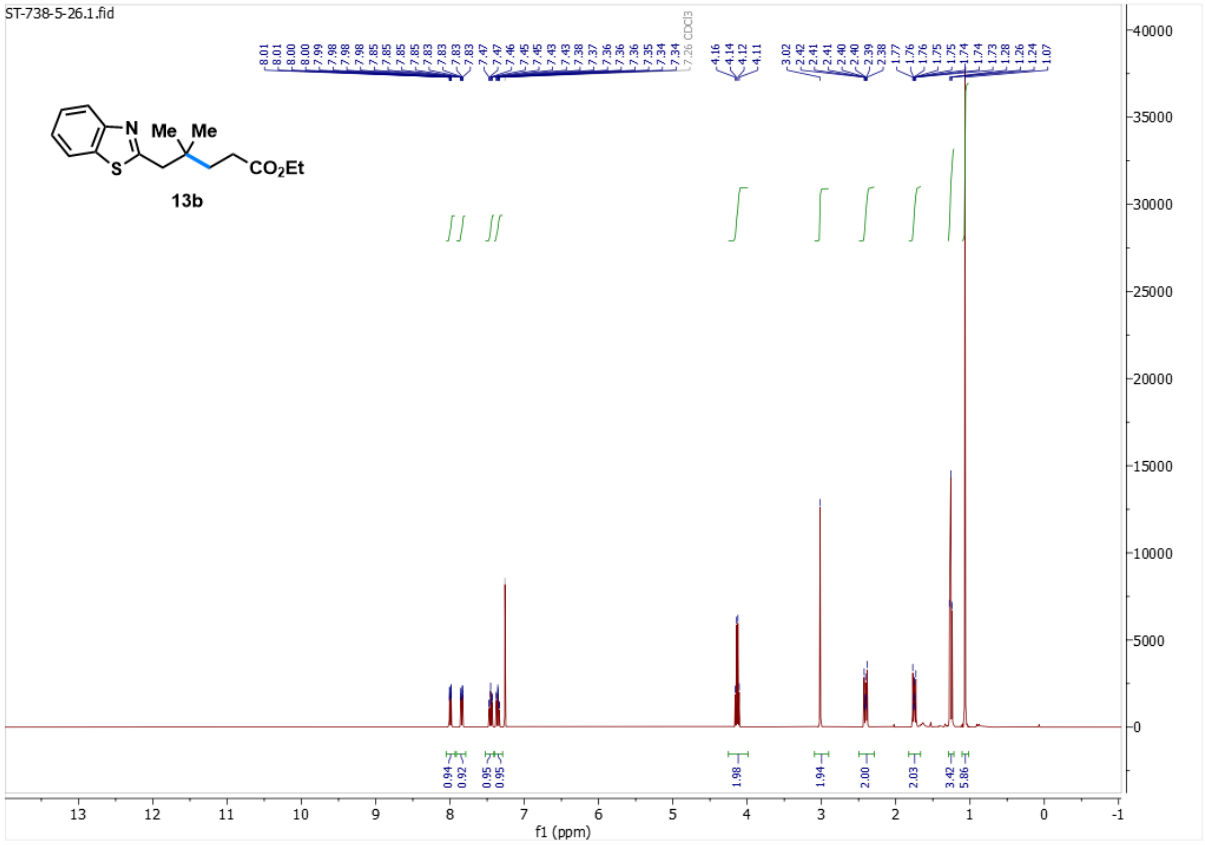

yk-1-525-2 F7-8 carbon v2.226.fid
Carbon 13
226.94
173.42
136.05
128.71
128.49
128.45
66.44
48.46
44.88
43.25
41.26
32.80
25.85
25.35
25.06
23.99
18.79
Me
Me
Me
Me
O
CO2Bn
11c
f1 (ppm)

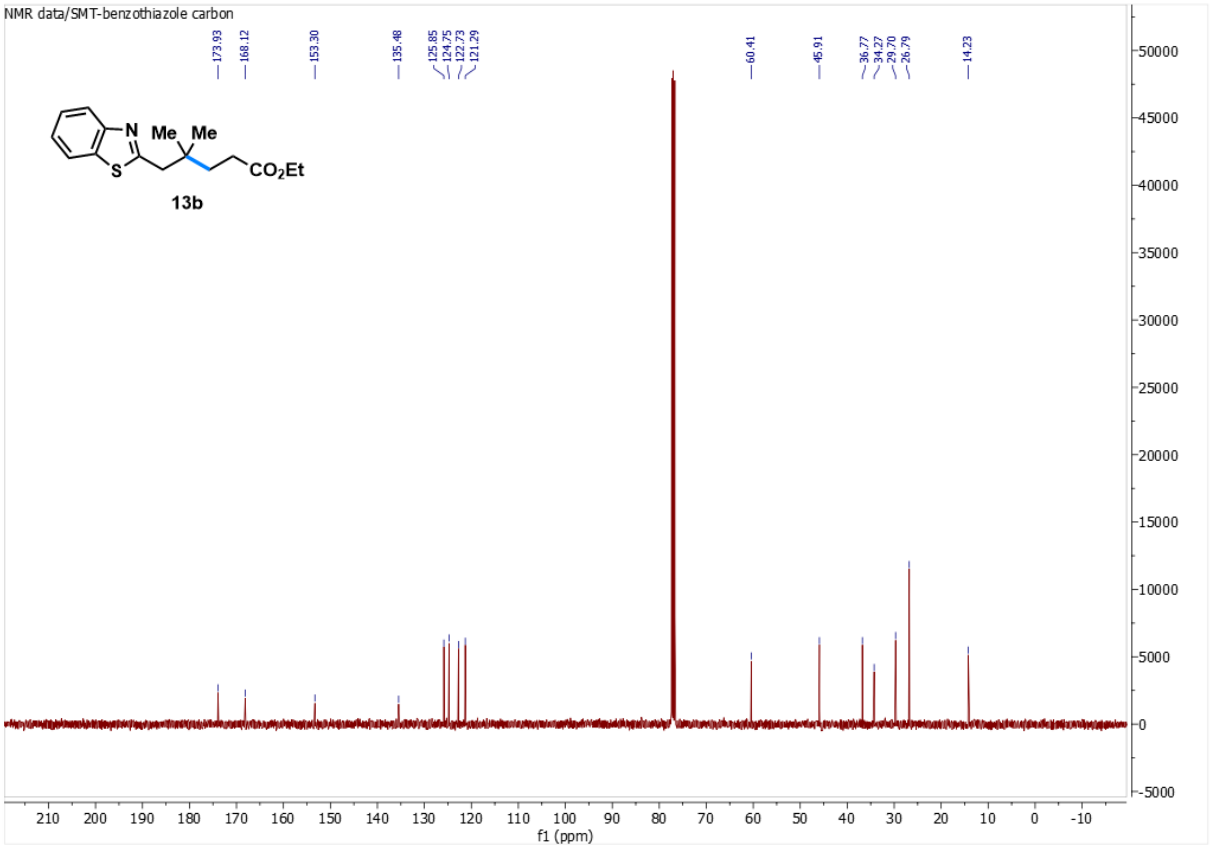

ST-738-4-33.1.fid
Proton
Me
tBu
N
Me
Me
CO2Et
12a
f1 (ppm)

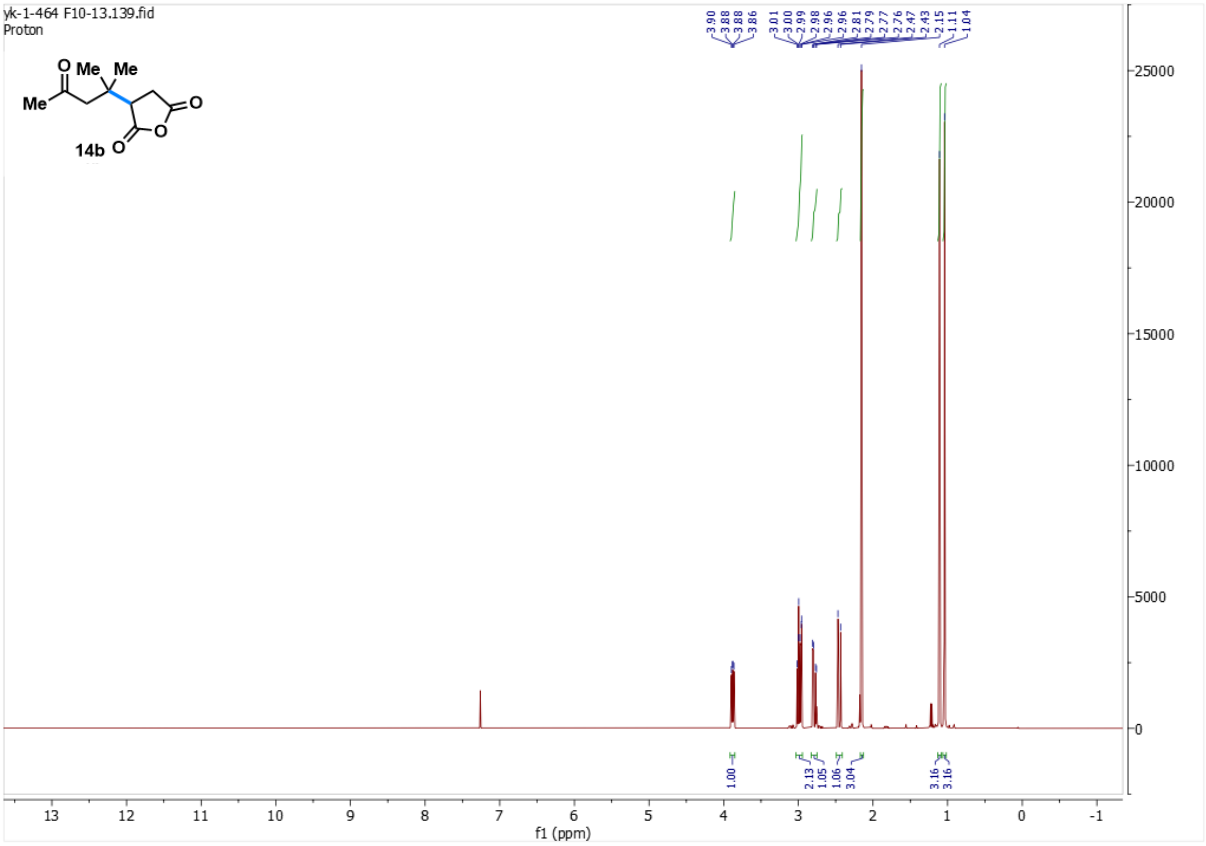

ST-738-4-33.2.fid
Carbon 13
Me
tBu
N
Me
Me
CO2Et
12a
f1 (ppm)

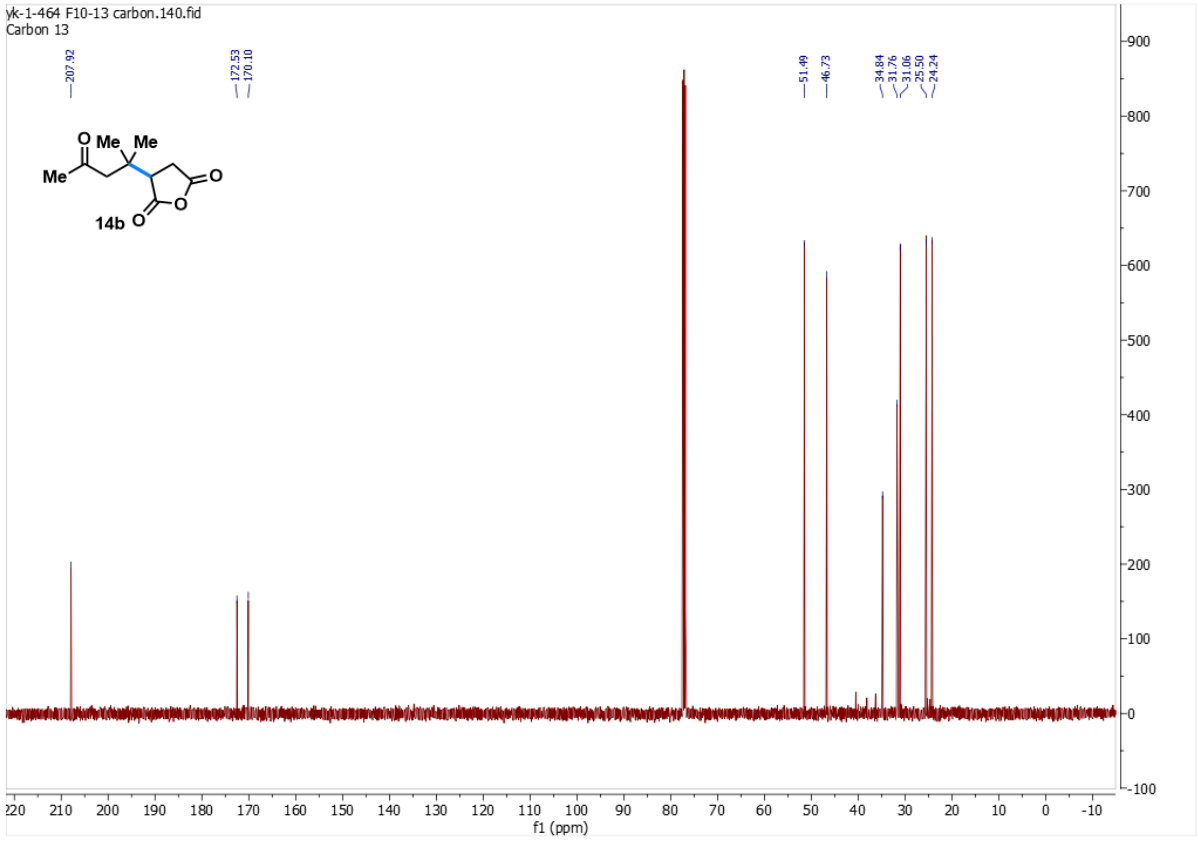

ST-738-4-41.1.fid
Proton
Me
Me Me
tBu
N
CO2Et
12b
7.26 CDCl3
6.93
6.68
4.13
4.12
4.10
4.09
2.59
2.52
2.52
2.51
2.51
2.50
2.50
2.49
2.28
1.58
1.57
1.57
1.56
1.56
1.55
1.55
1.31
1.26
1.25
1.23
0.92
0.96
0.97
1.99
2.01
2.00
2.94
2.50
9.07
3.08
6.13
f1 (ppm)

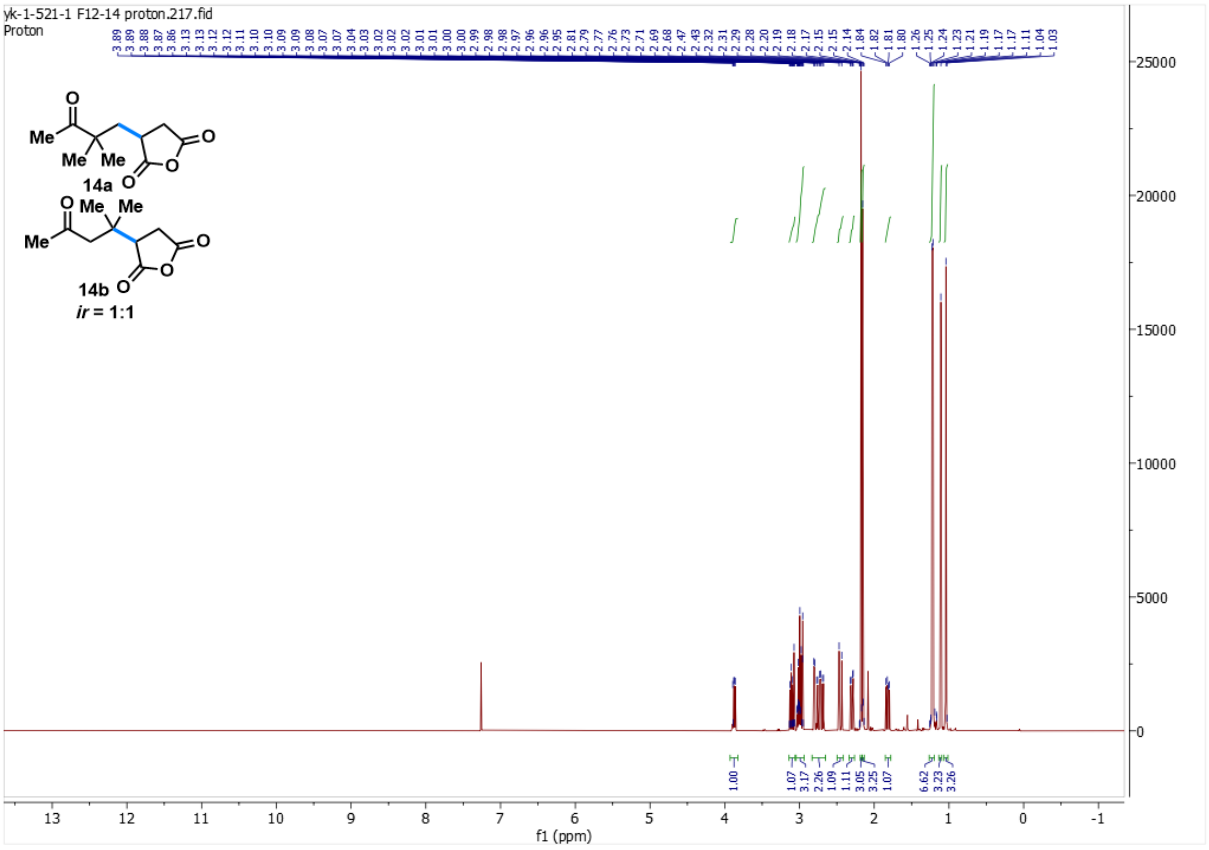

ST-738-4-41.2.fid
Carbon 13
Me
Me Me
tBu
N
CO2Et
12b
174.79
168.18
158.07
146.26
122.49
116.97
77.15 CDCl3
60.25
49.13
37.26
36.22
34.19
30.27
30.03
27.61
21.33
14.39
f1 (ppm)

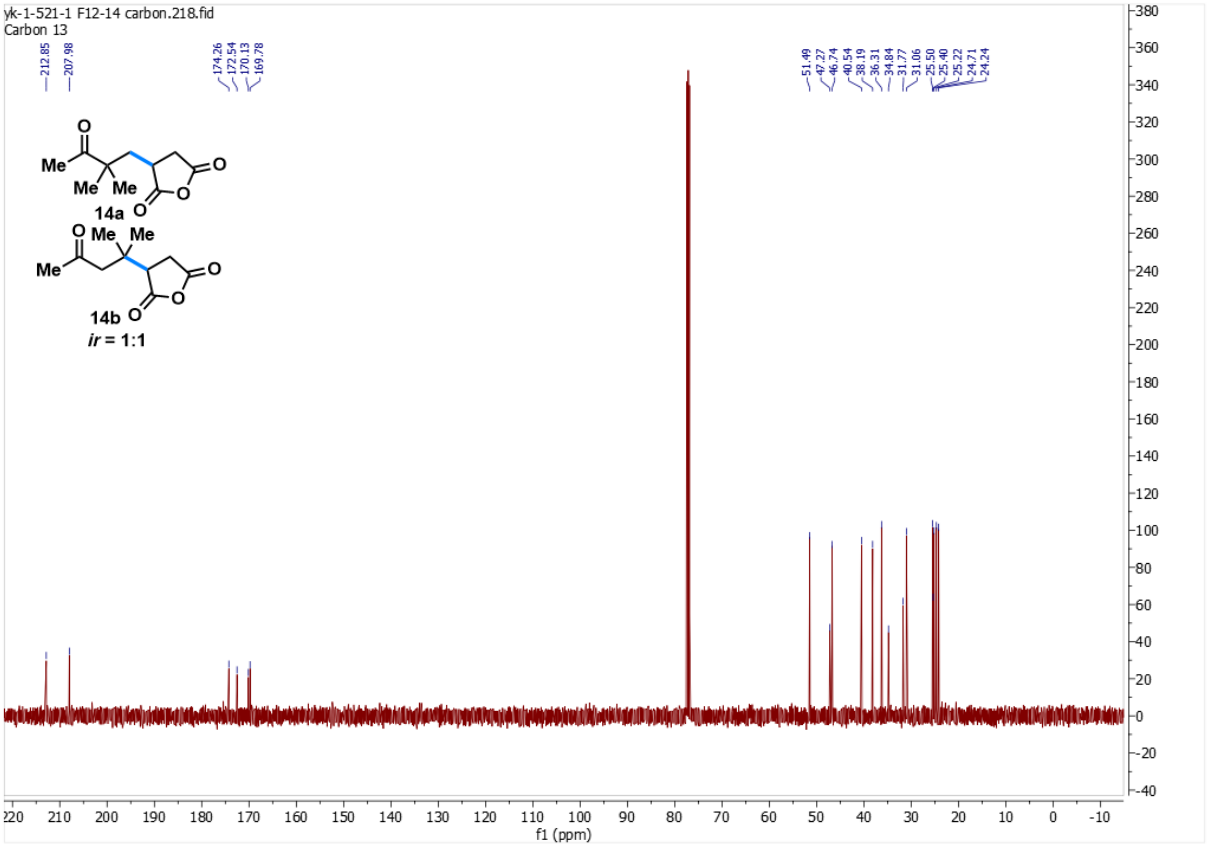

ST-738-5-26.1.fid
Me Me
CO2Et
13b
f1 (ppm)

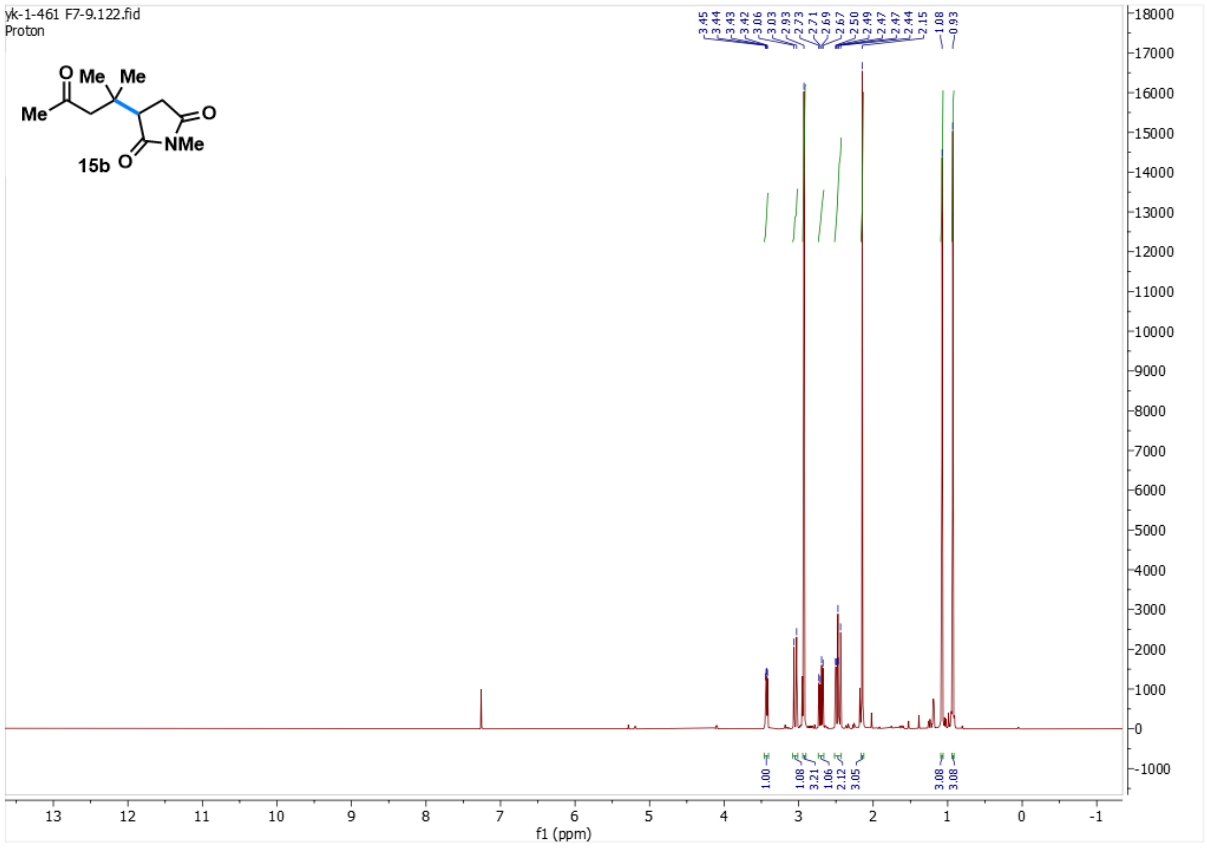

NMR data/SMT-benzothiazole carbon
Me Me
CO2Et
13b
f1 (ppm)

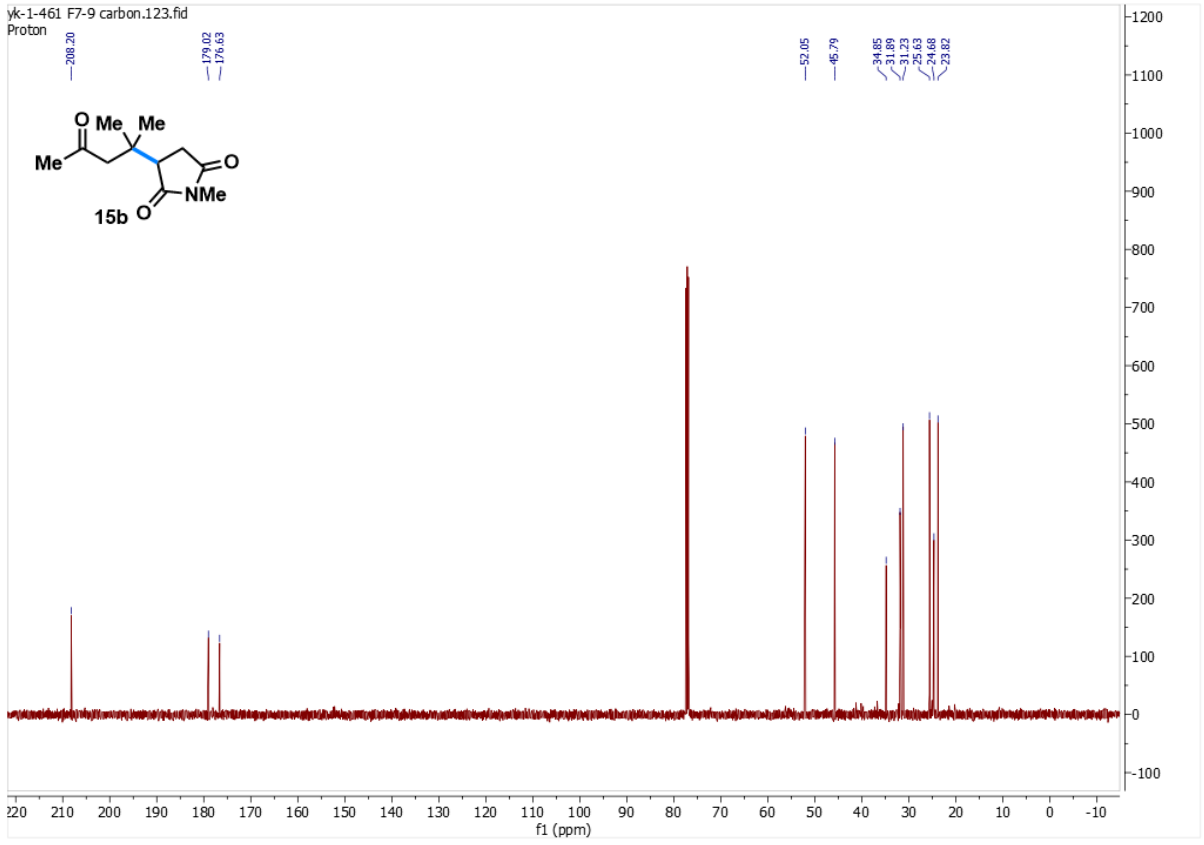

yk-1-464 F10-13.139.fid
Proton
Me
Me
Me
O
O
O
O
14b
3.90
3.88
3.88
3.86
3.01
3.00
2.99
2.98
2.96
2.96
2.81
2.79
2.77
2.76
2.47
2.43
2.15
1.11
1.04
1.00
2.13
1.05
1.06
3.04
3.16
3.16
25000
20000
15000
10000
5000
0
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

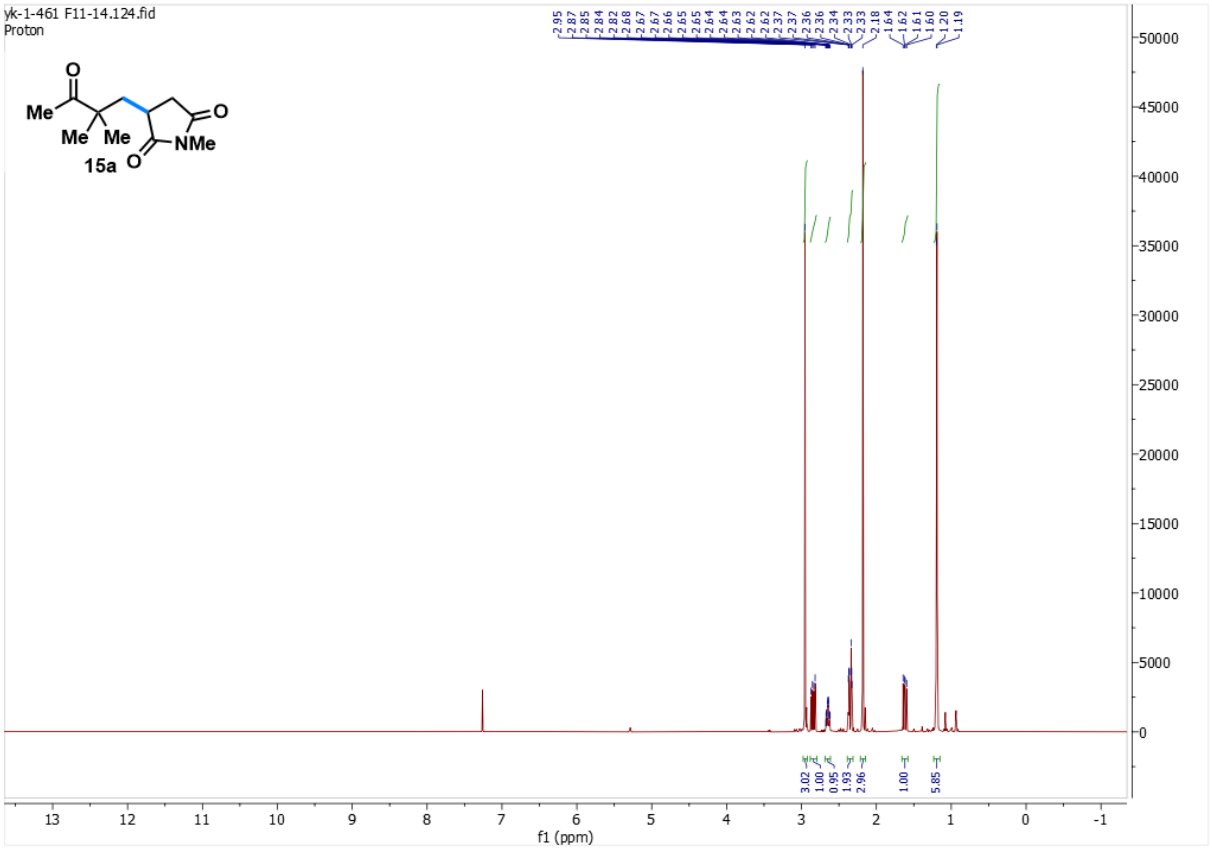

yk-1-464 F10-13 carbon.140.fid
Carbon 13
207.92
172.53
170.10
51.49
46.73
34.84
31.76
31.06
25.50
24.24
Me
Me
Me
O
O
O
O
14b
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

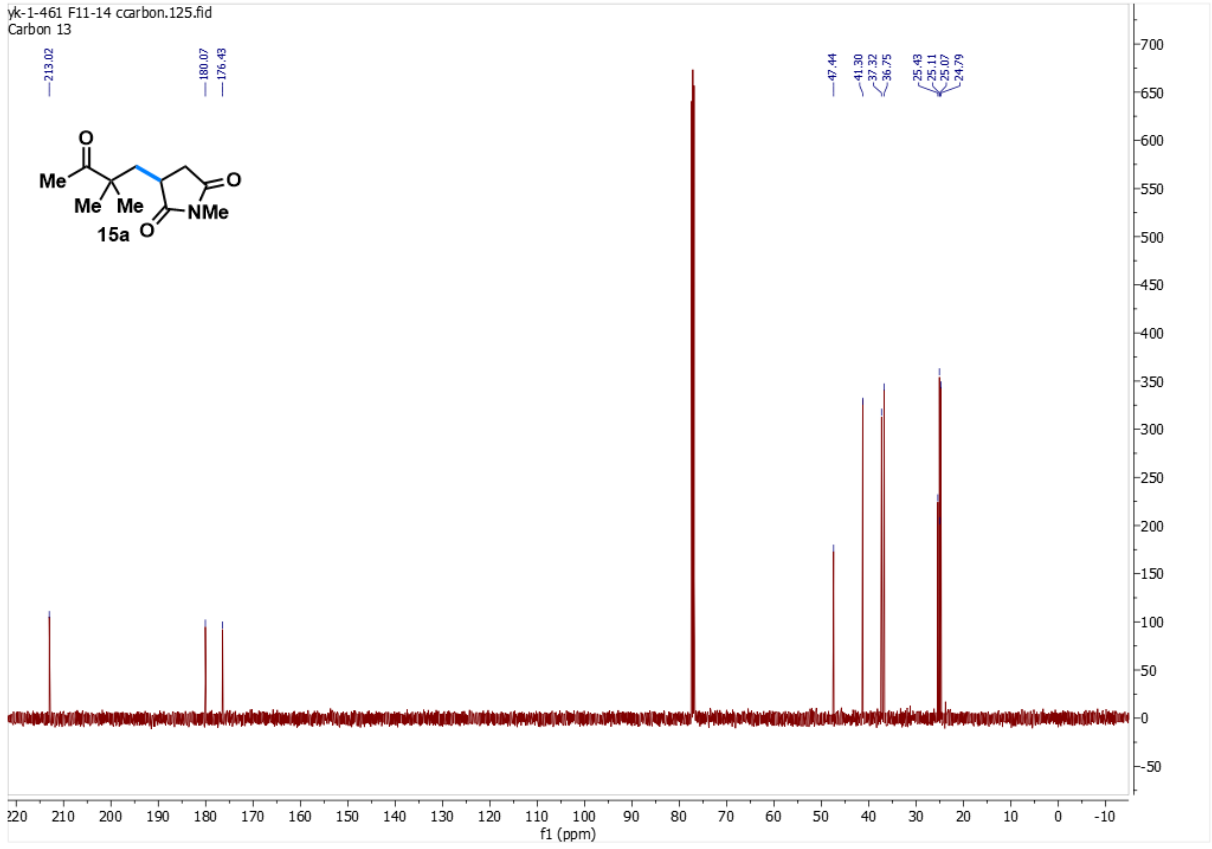

yk-1-521-1 F12-14 proton.217.fid
Proton
14a
14b
ir = 1:1
f1 (ppm)

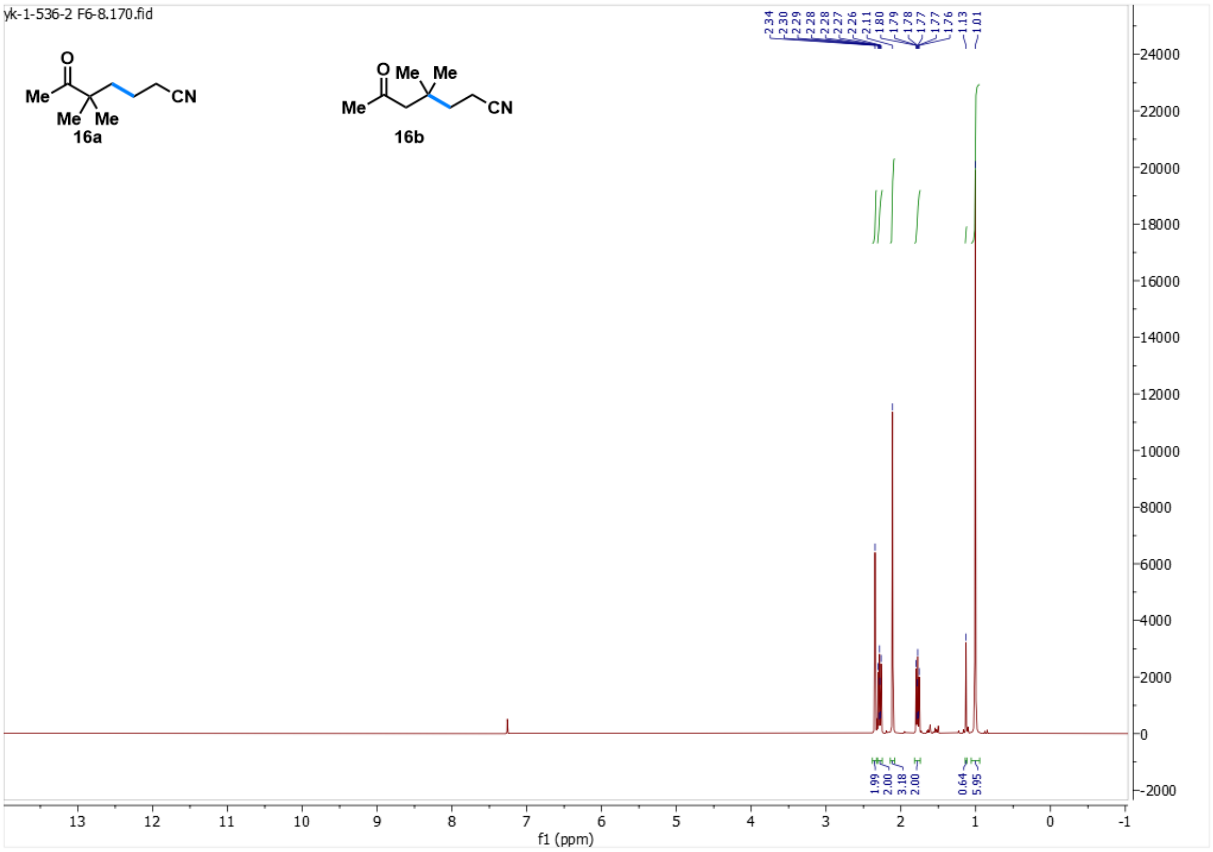

yk-1-521-1 F12-14 carbon.218.fid
Carbon 13
14a
14b
ir = 1:1
f1 (ppm)

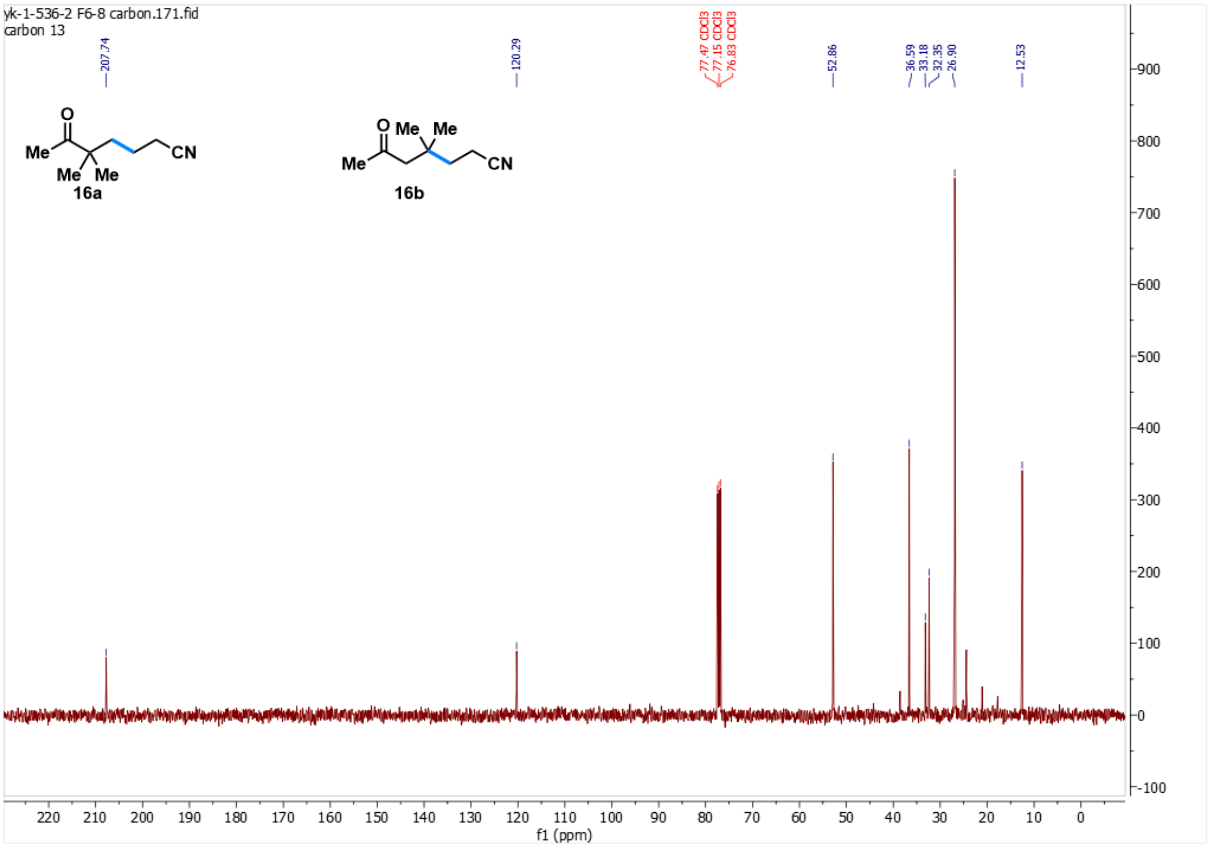

yk-1-461 F7-9.122.fid
Proton
Me
Me
Me
O
O
NMe
O
15b
f1 (ppm)

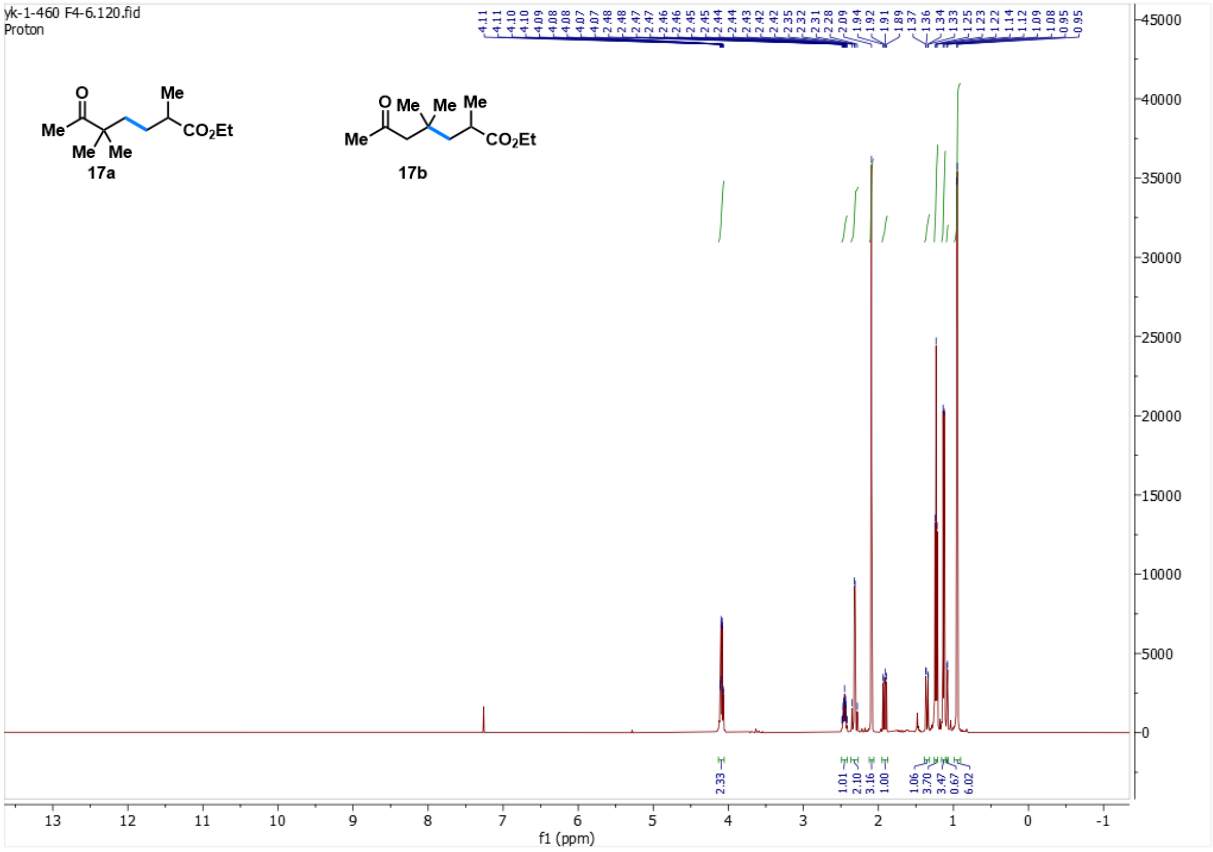

yk-1-461 F7-9 carbon.123.fid
Proton
Me
Me
Me
O
O
NMe
O
15b
f1 (ppm)

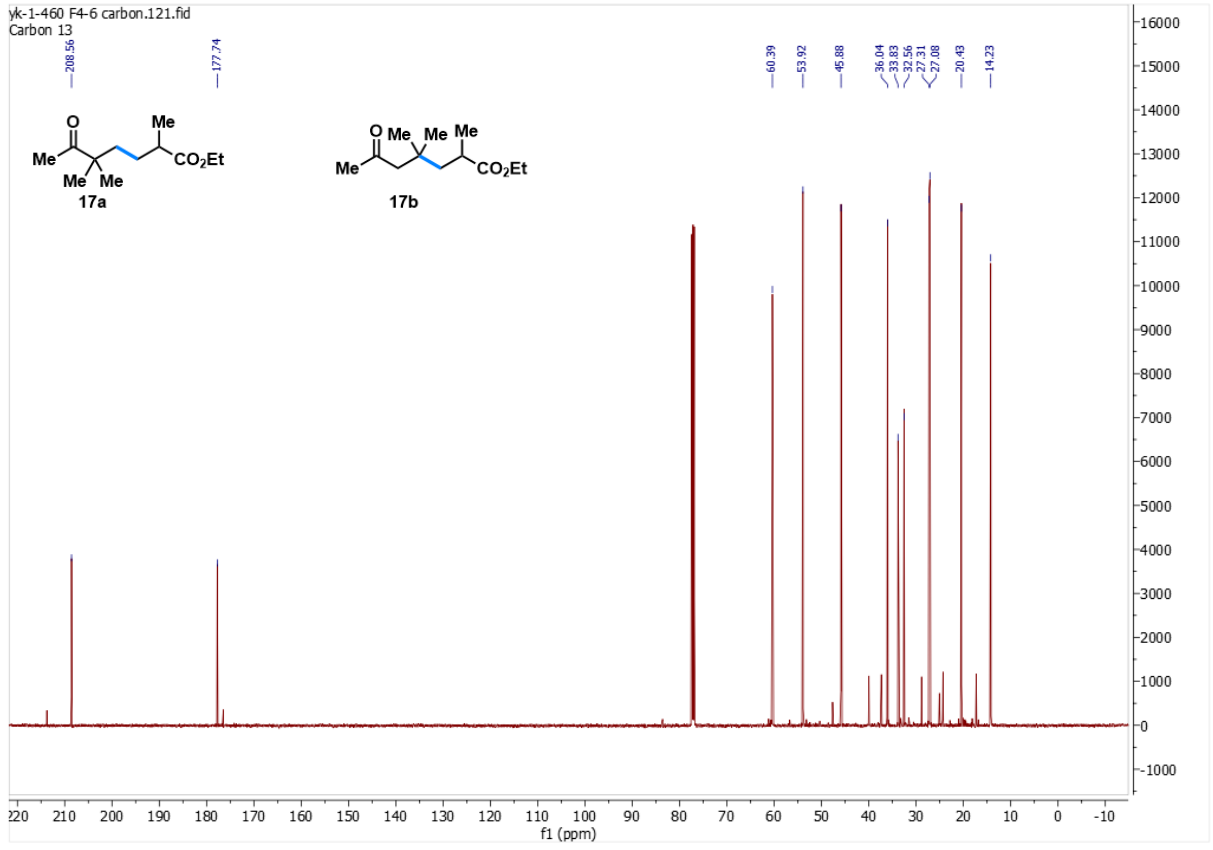

yk-1-461 F11-14.124.fid
Proton
Me
Me
Me
O
NMe
O
O
15a
f1 (ppm)

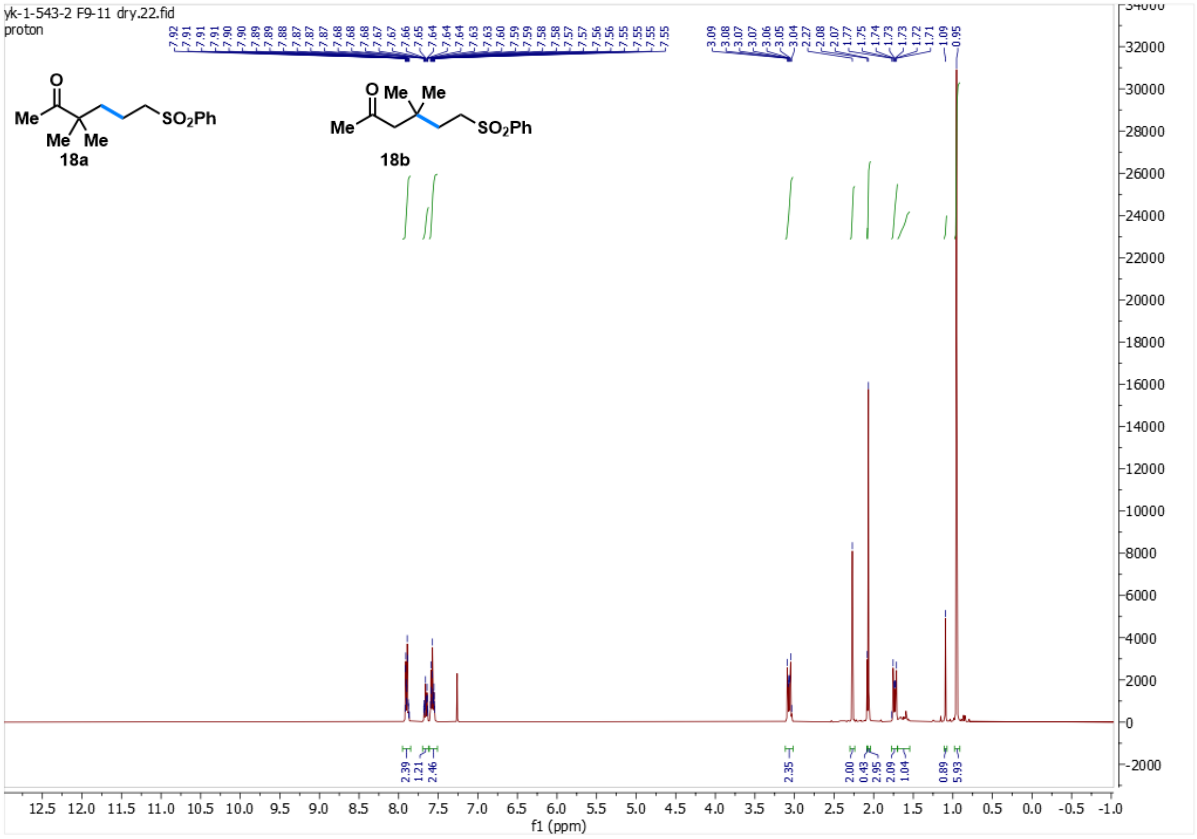

yk-1-461 F11-14 ccarbon.125.fid
Carbon 13
213.02
180.07
176.43
47.44
41.30
37.32
36.75
25.43
25.11
25.07
24.79
Me
Me
Me
O
NMe
O
O
15a
f1 (ppm)

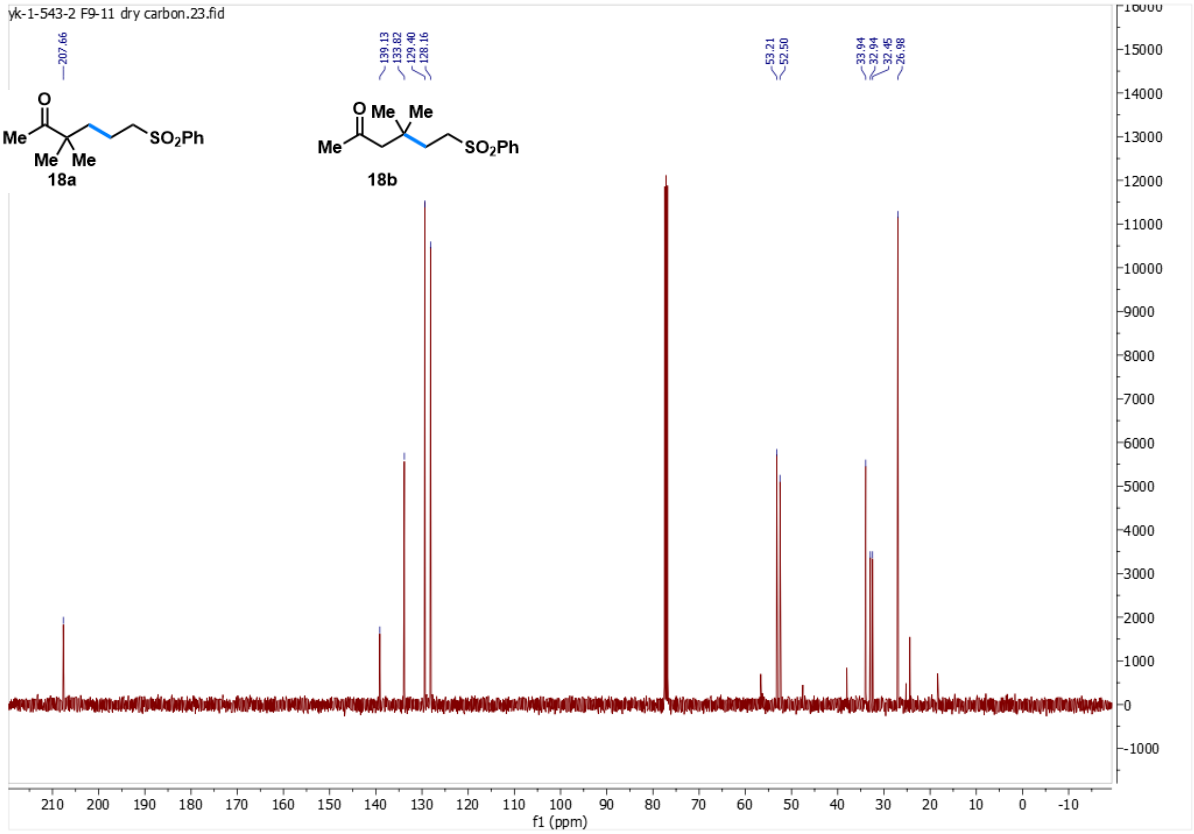

yk-1-536-2 F6-8.170.fid
16a
16b
f1 (ppm)

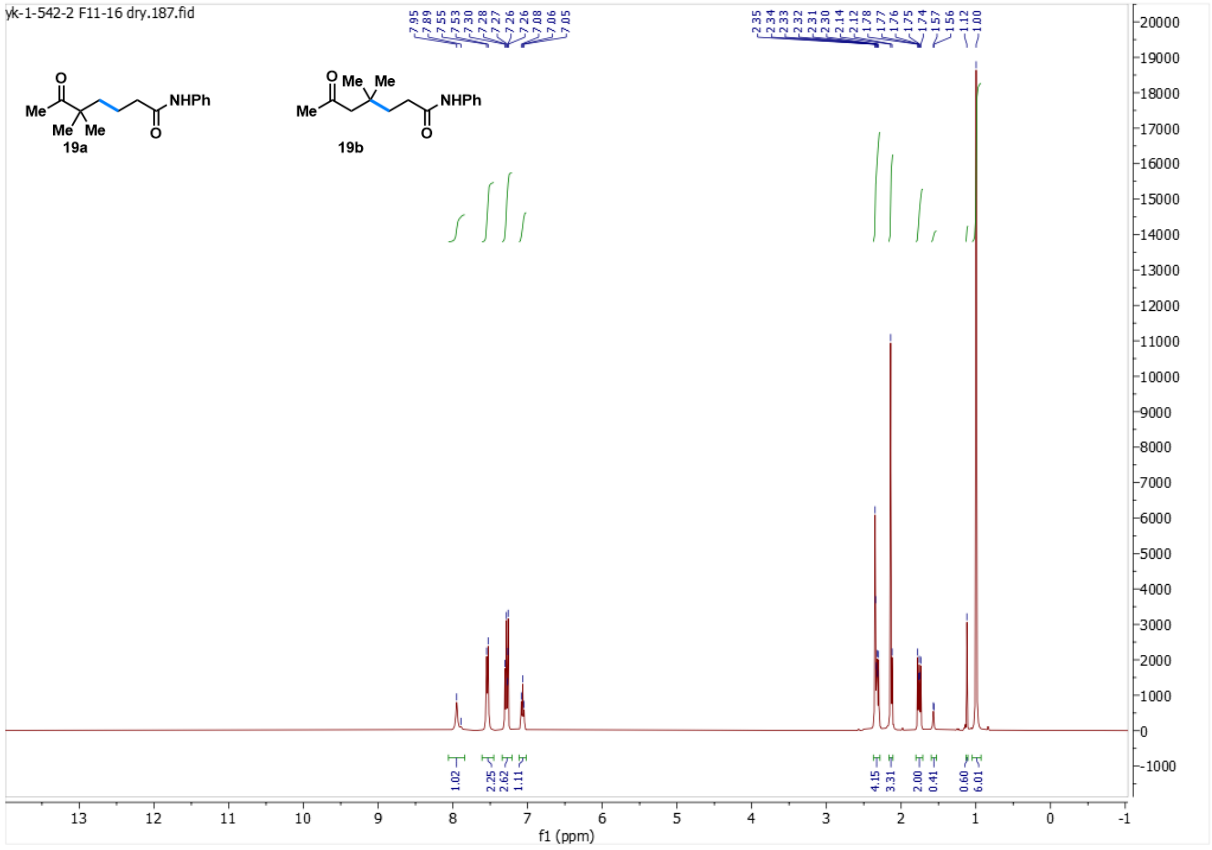

yk-1-536-2 F6-8 carbon.171.fid
carbon 13
207.74
120.29
77.47 CDCl3
77.15 CDCl3
76.83 CDCl3
52.86
36.59
33.18
32.35
26.90
12.53
16a
16b
f1 (ppm)

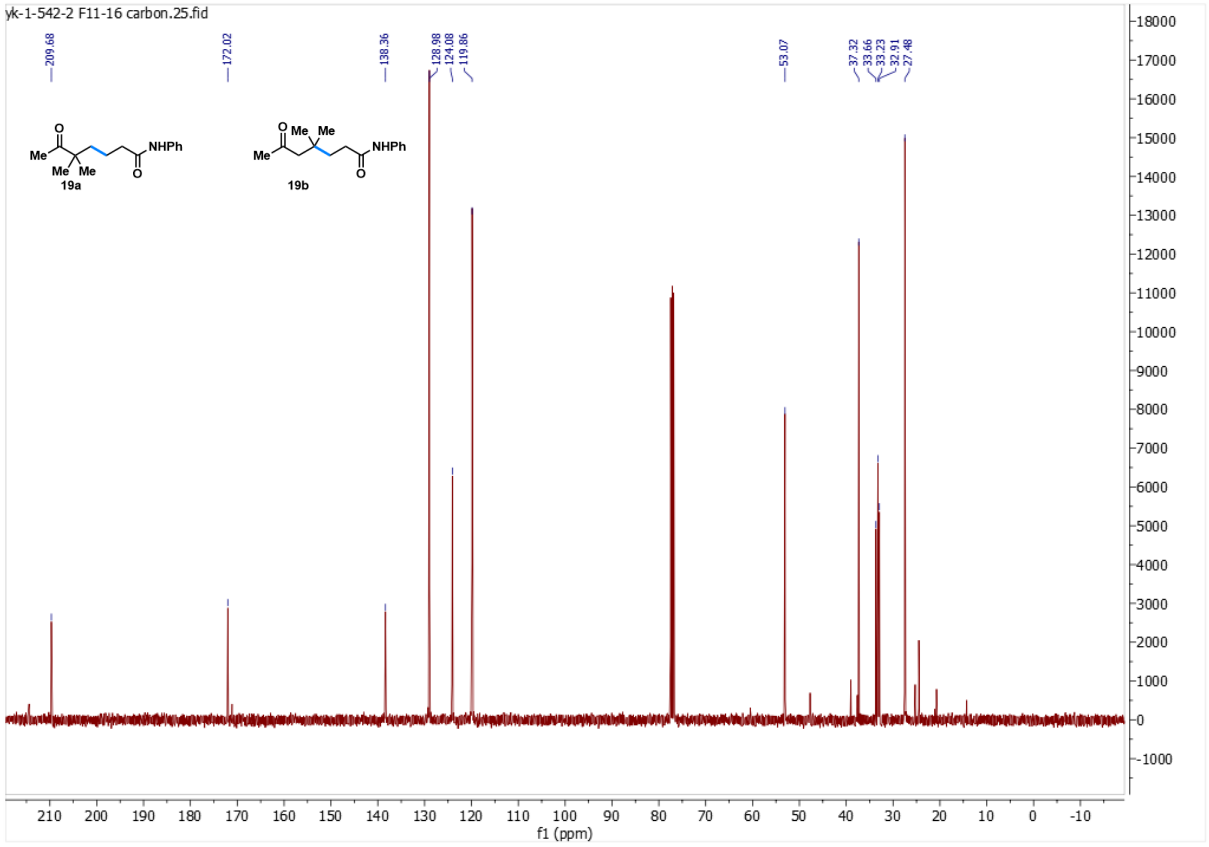

yk-1-460 F4-6.120.fid
Proton
17a
17b
f1 (ppm)

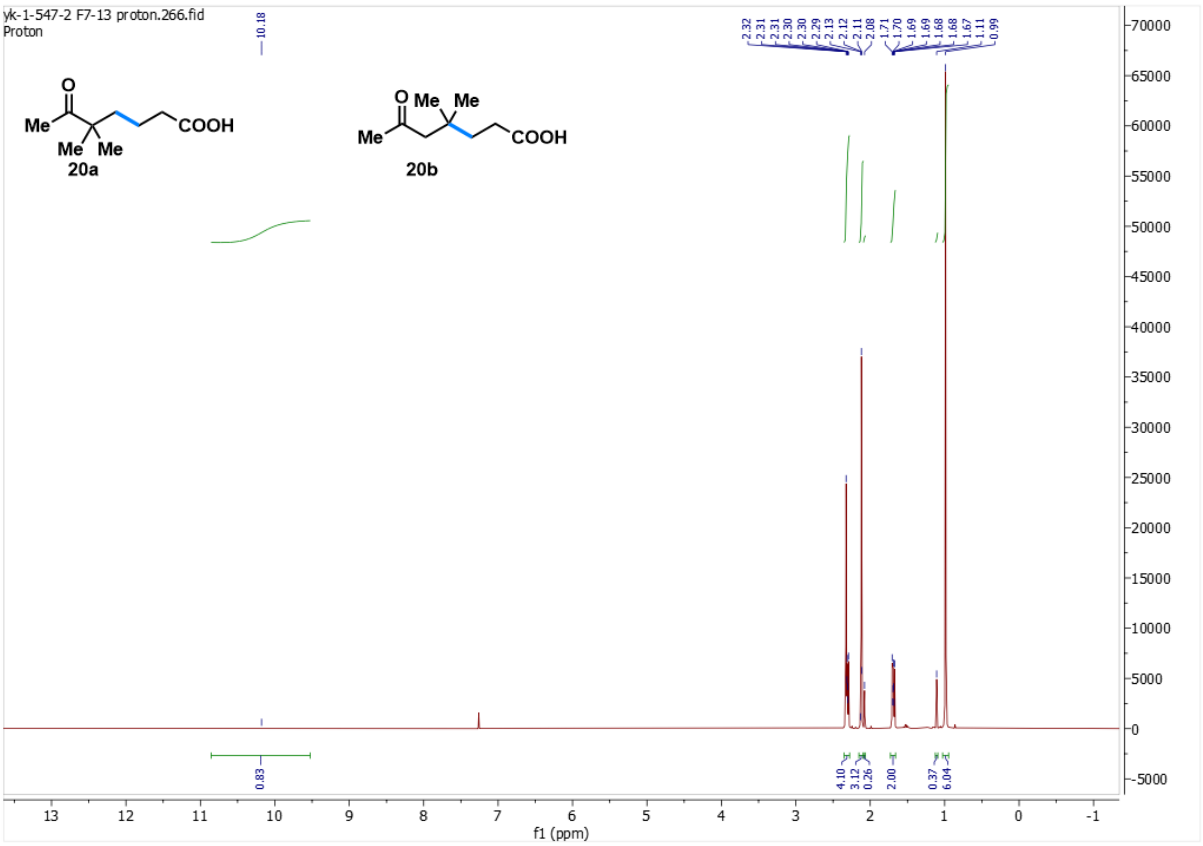

yk-1-460 F4-6 carbon.121.fid
Carbon 13
208.56
177.74
60.39
53.92
45.88
36.04
33.83
32.56
27.31
27.08
20.43
14.23
17a
17b
f1 (ppm)

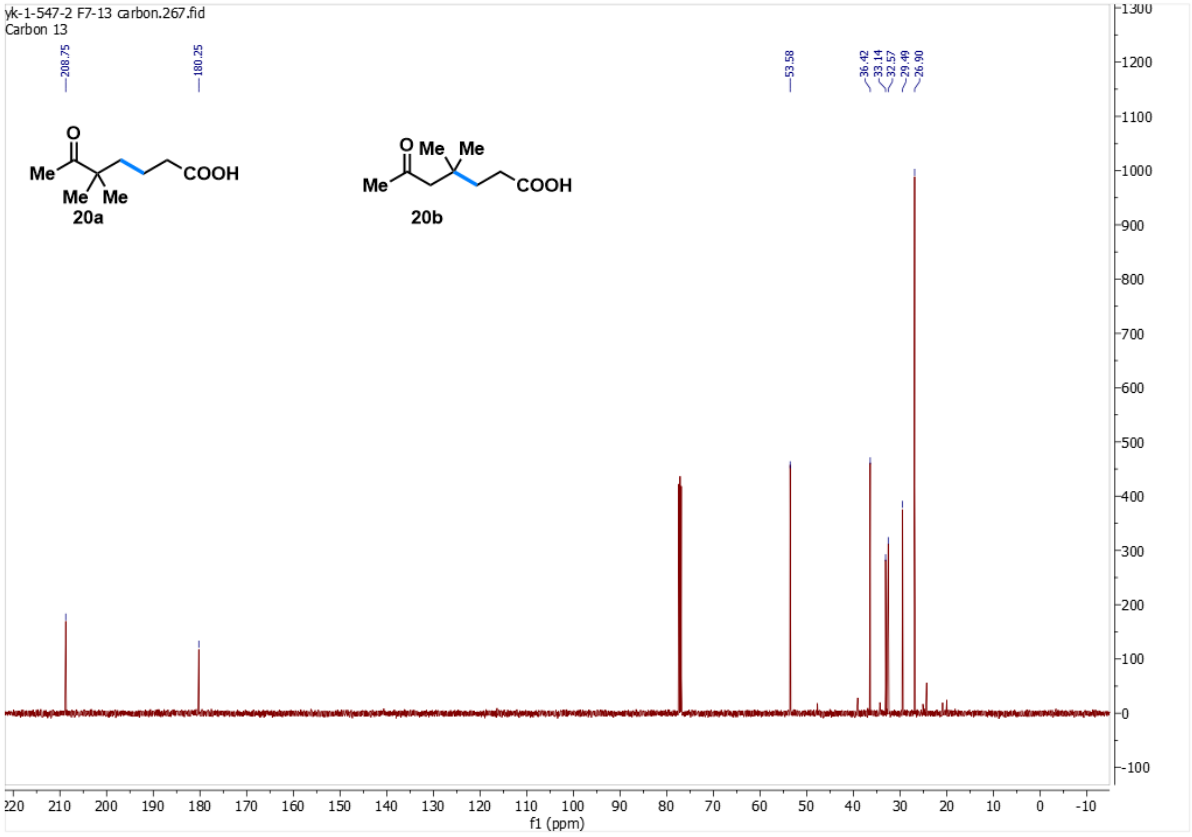

yk-1-543-2 F9-11 dry.22.fid
proton
18a
18b
f1 (ppm)

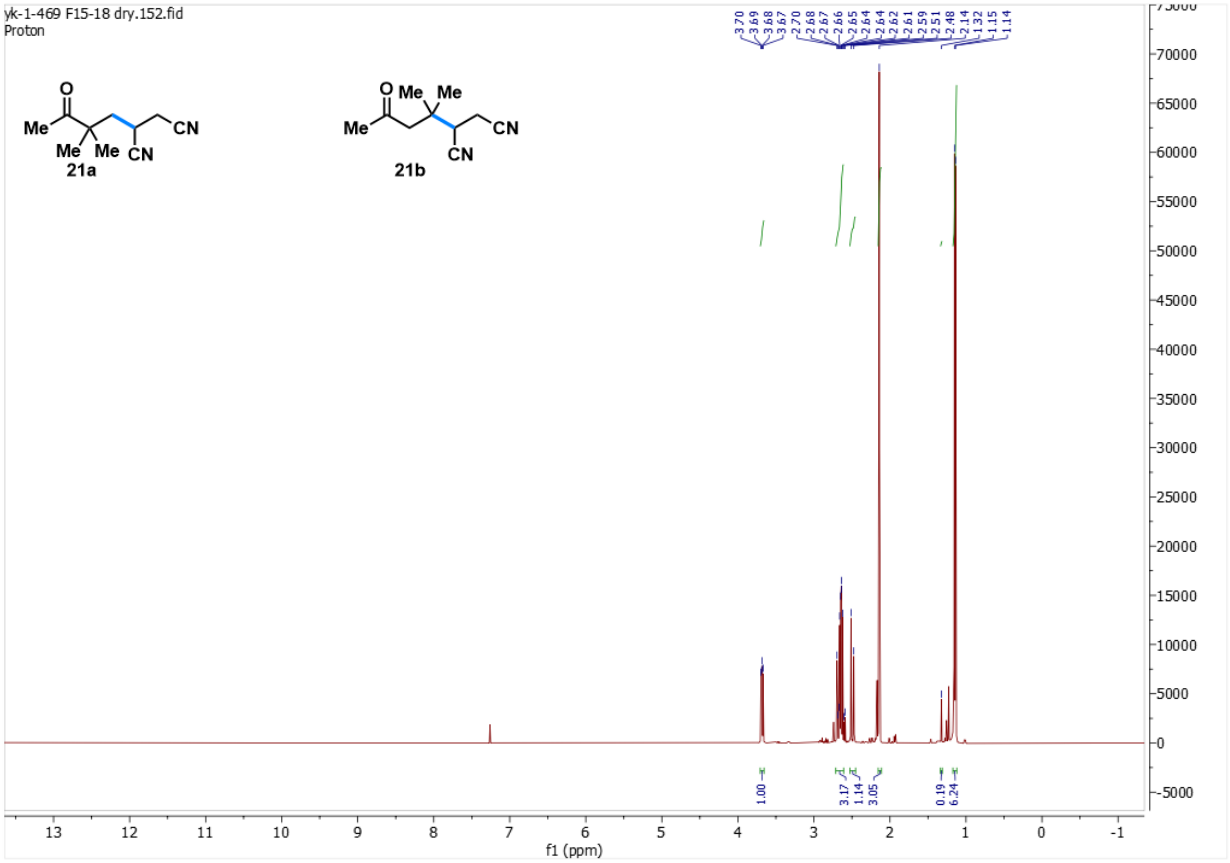

yk-1-543-2 F9-11 dry carbon.23.fid
18a
18b
f1 (ppm)

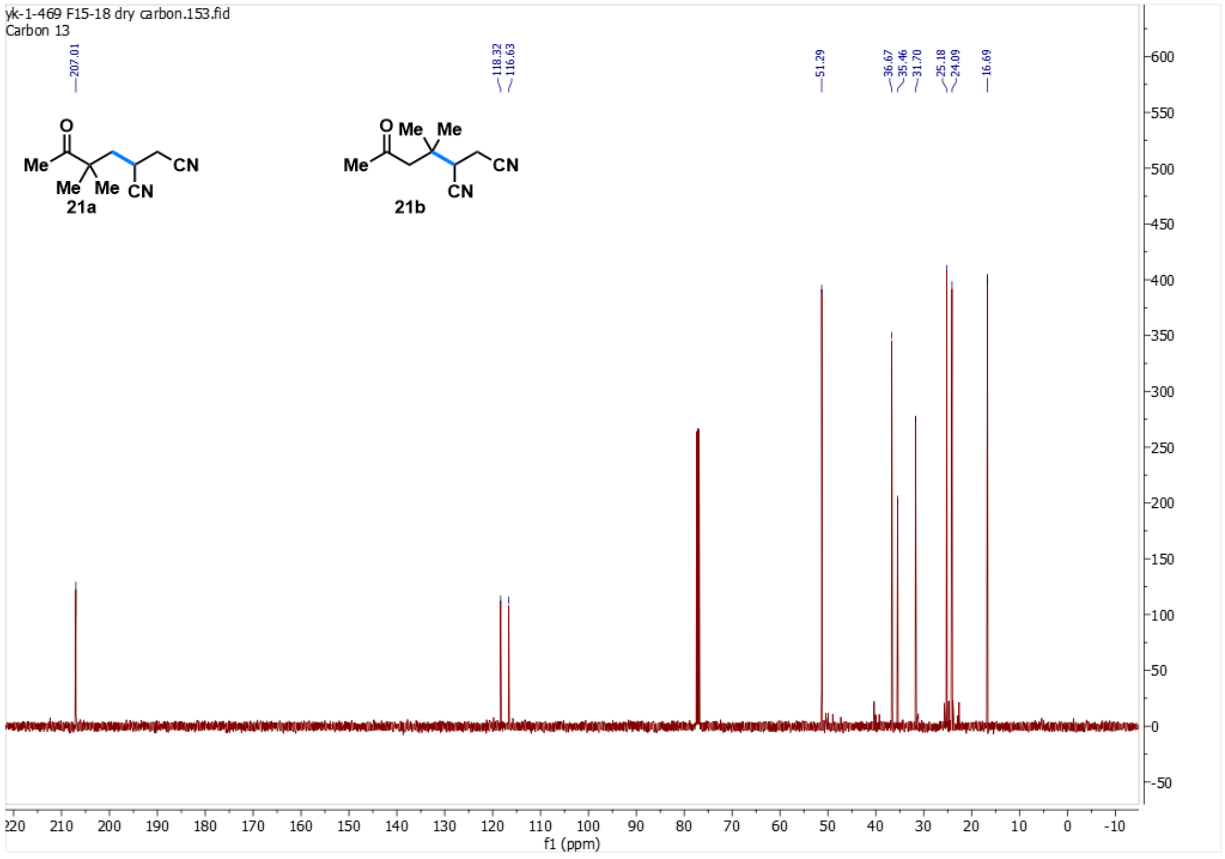

yk-1-542-2 F11-16 dry.187.fid
19a
19b
f1 (ppm)

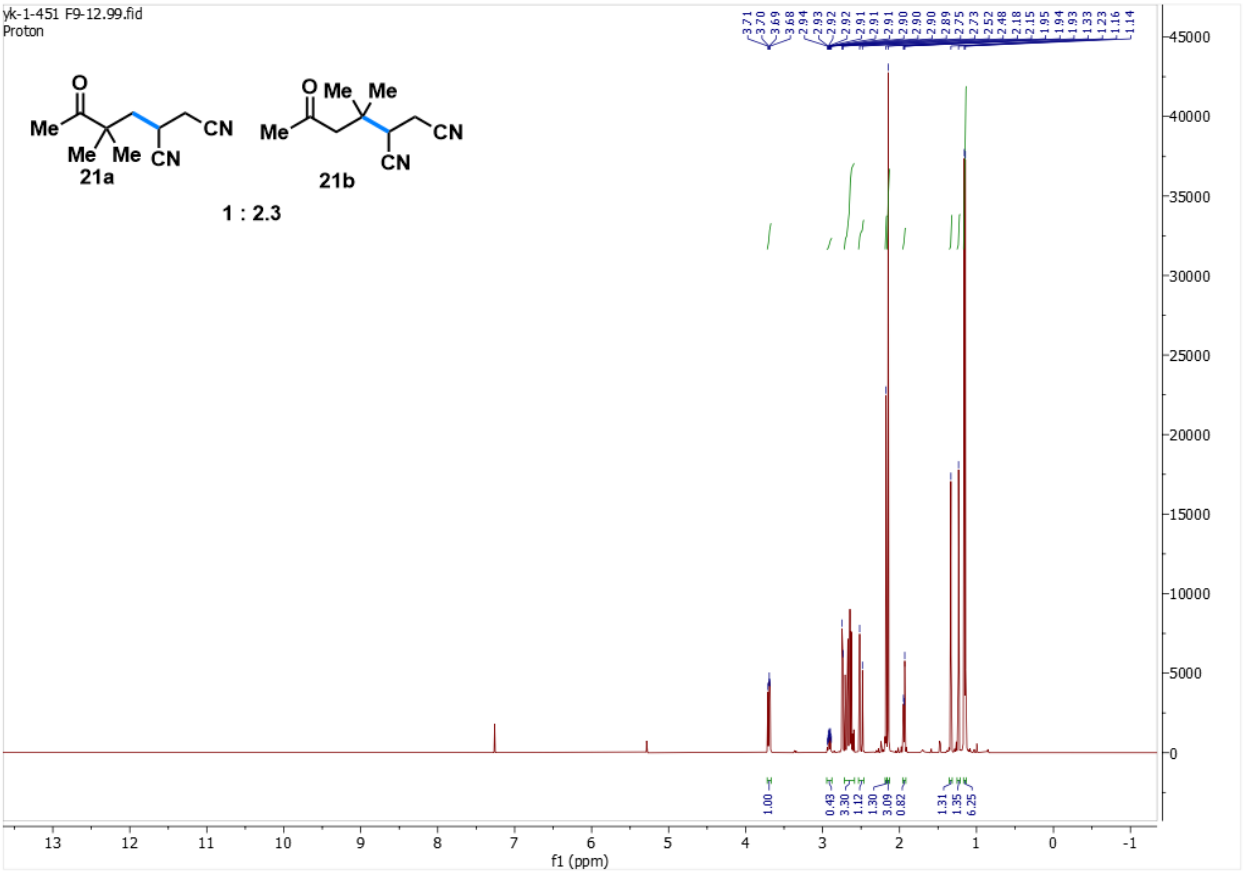

yk-1-542-2 F11-16 carbon.25.fid
19a
19b
f1 (ppm)

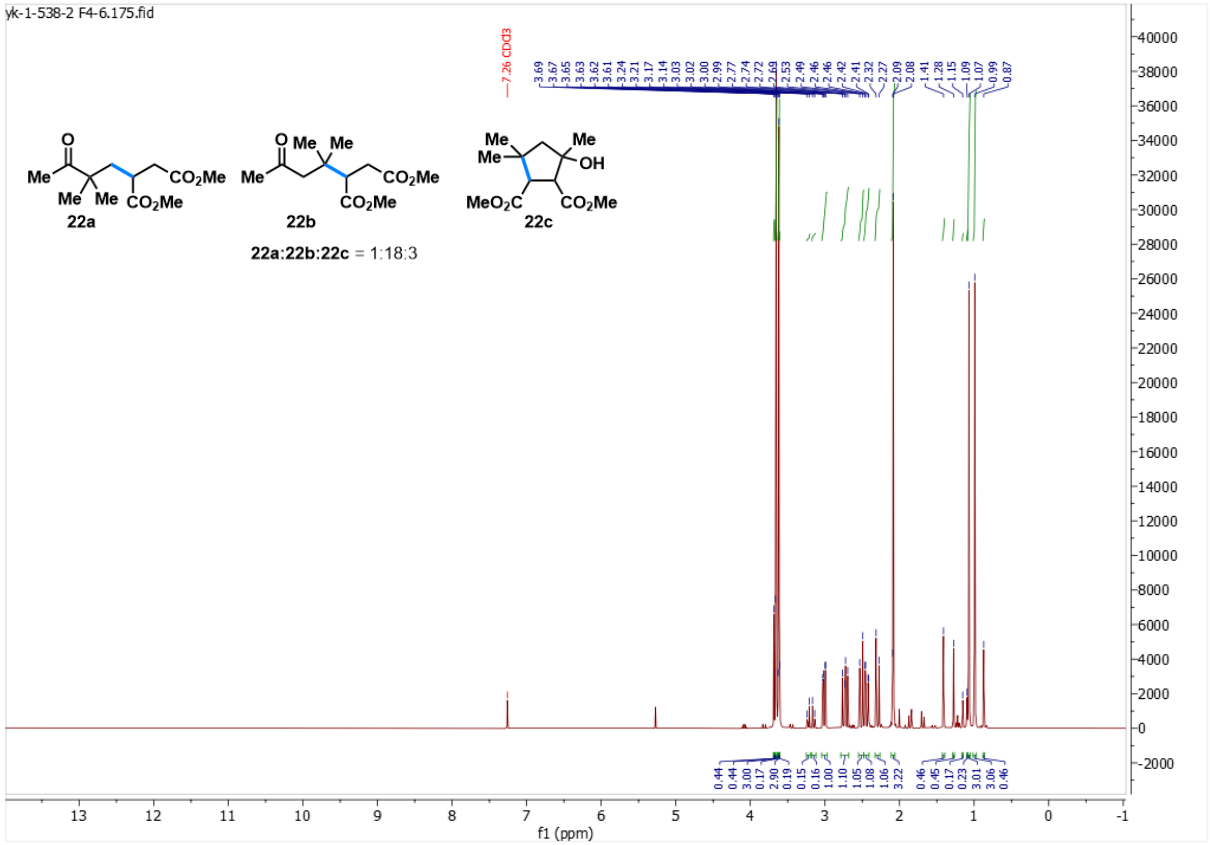

yk-1-547-2 F7-13 proton.266.fid
Proton
10.18
2.32
2.31
2.31
2.30
2.30
2.29
2.13
2.12
2.11
2.08
1.71
1.70
1.69
1.69
1.68
1.68
1.67
1.11
0.99
Me
Me Me
COOH
20a
O Me Me
Me
COOH
20b
0.83
4.10
3.12
0.26
2.00
0.37
6.04
f1 (ppm)

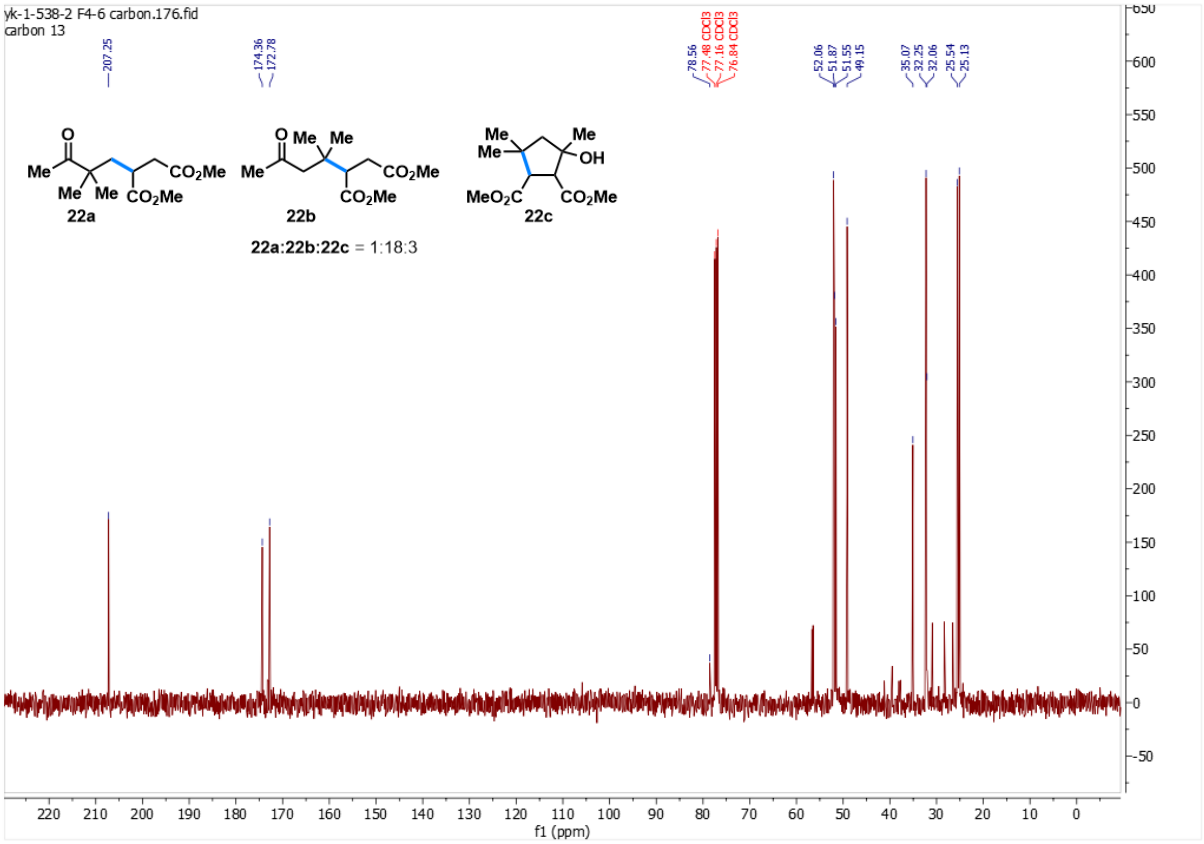

yk-1-547-2 F7-13 carbon.267.fid
Carbon 13
208.75
180.25
53.58
36.42
33.14
32.57
29.49
26.90
Me
Me Me
COOH
20a
O Me Me
Me
COOH
20b
f1 (ppm)

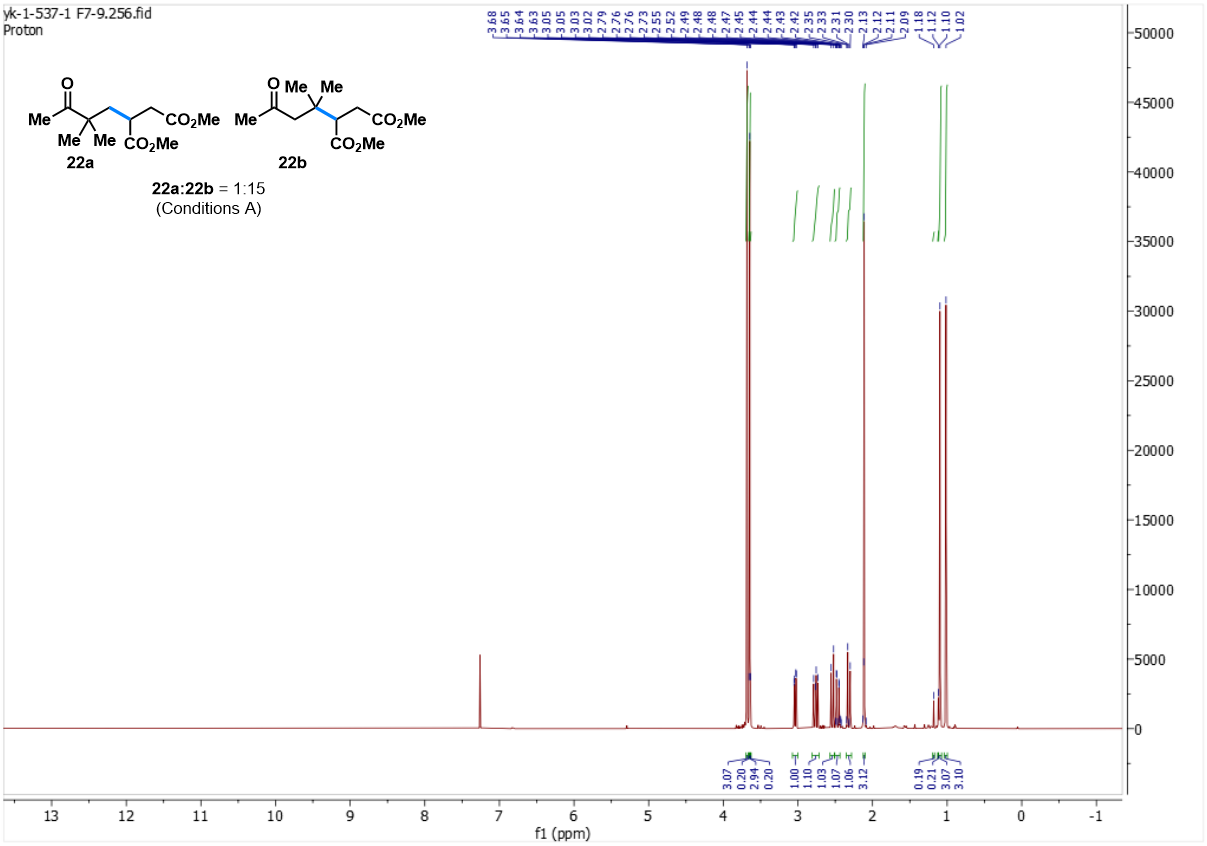

yk-1-469 F15-18 dry.152.fid
Proton
21a
21b
f1 (ppm)

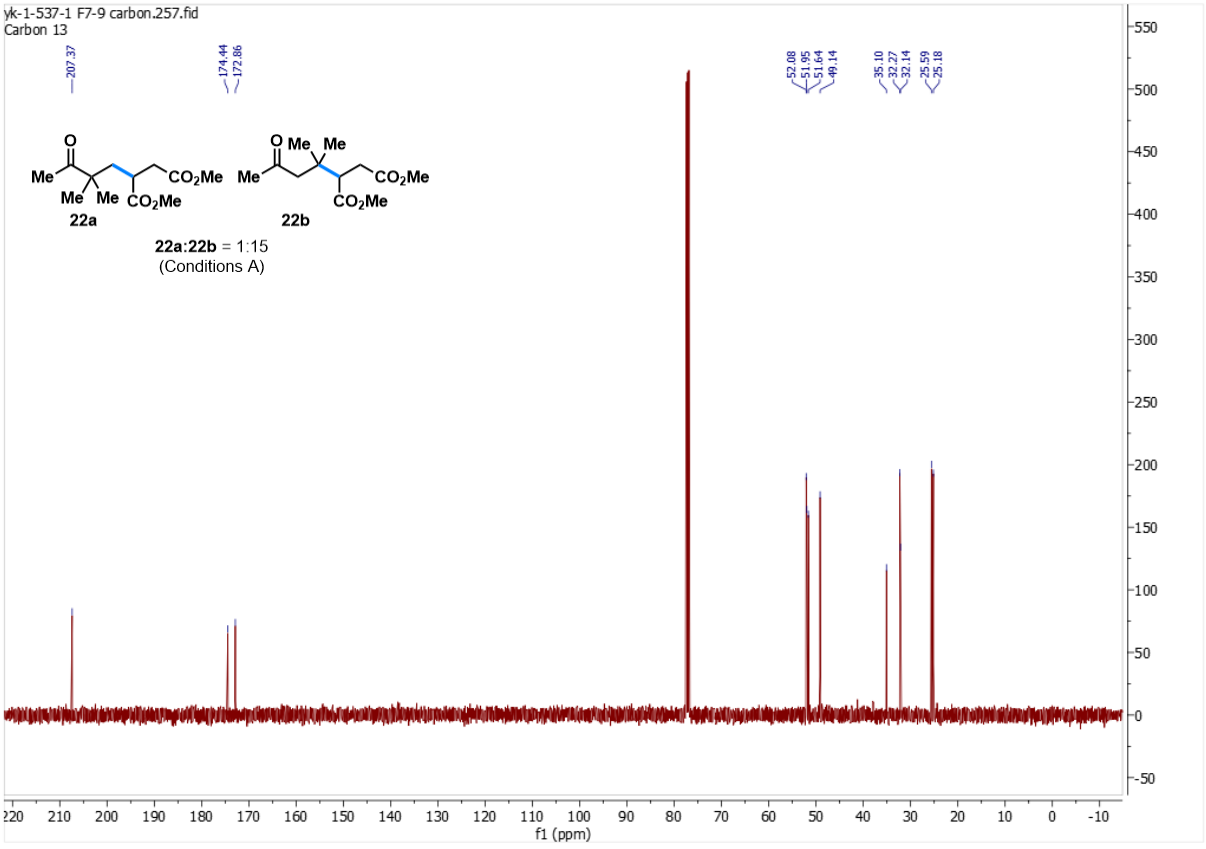

yk-1-469 F15-18 dry carbon.153.fid
Carbon 13
21a
21b
f1 (ppm)

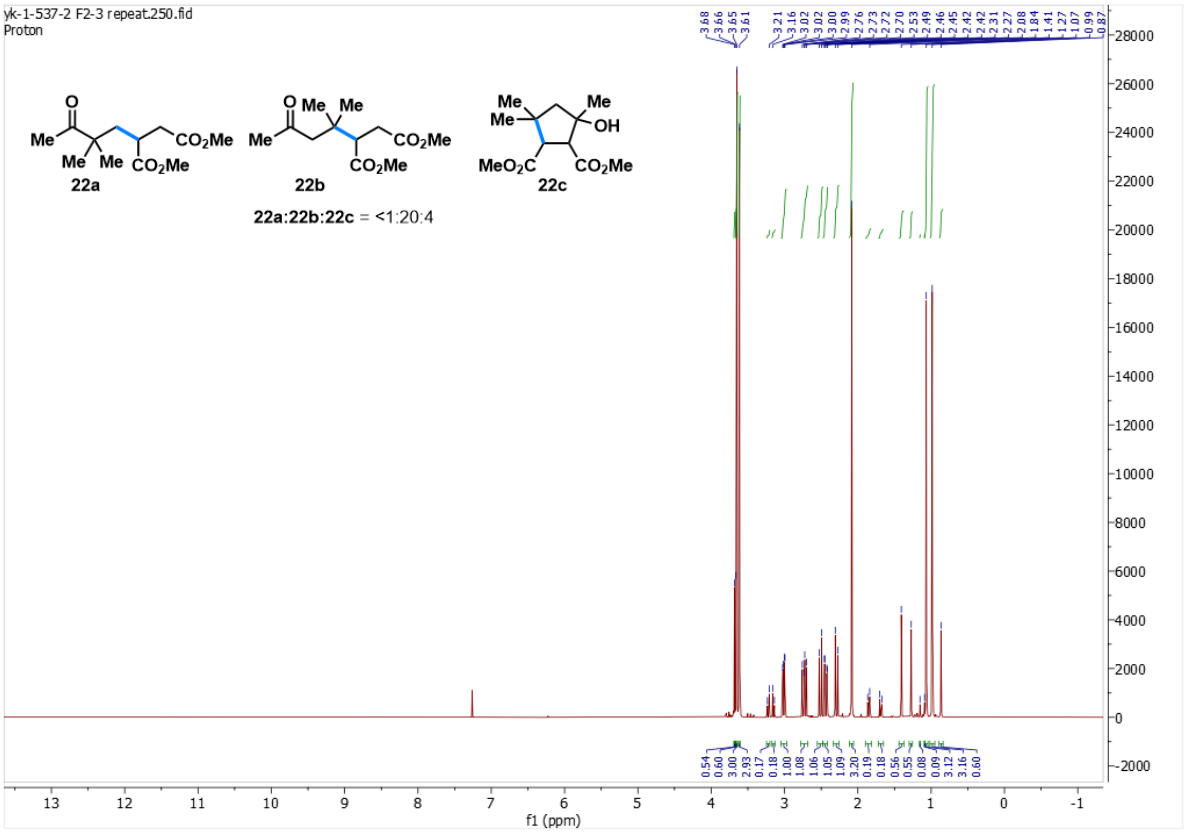

yk-1-451 F9-12.99.fid
Proton
21a
21b
1 : 2.3
f1 (ppm)

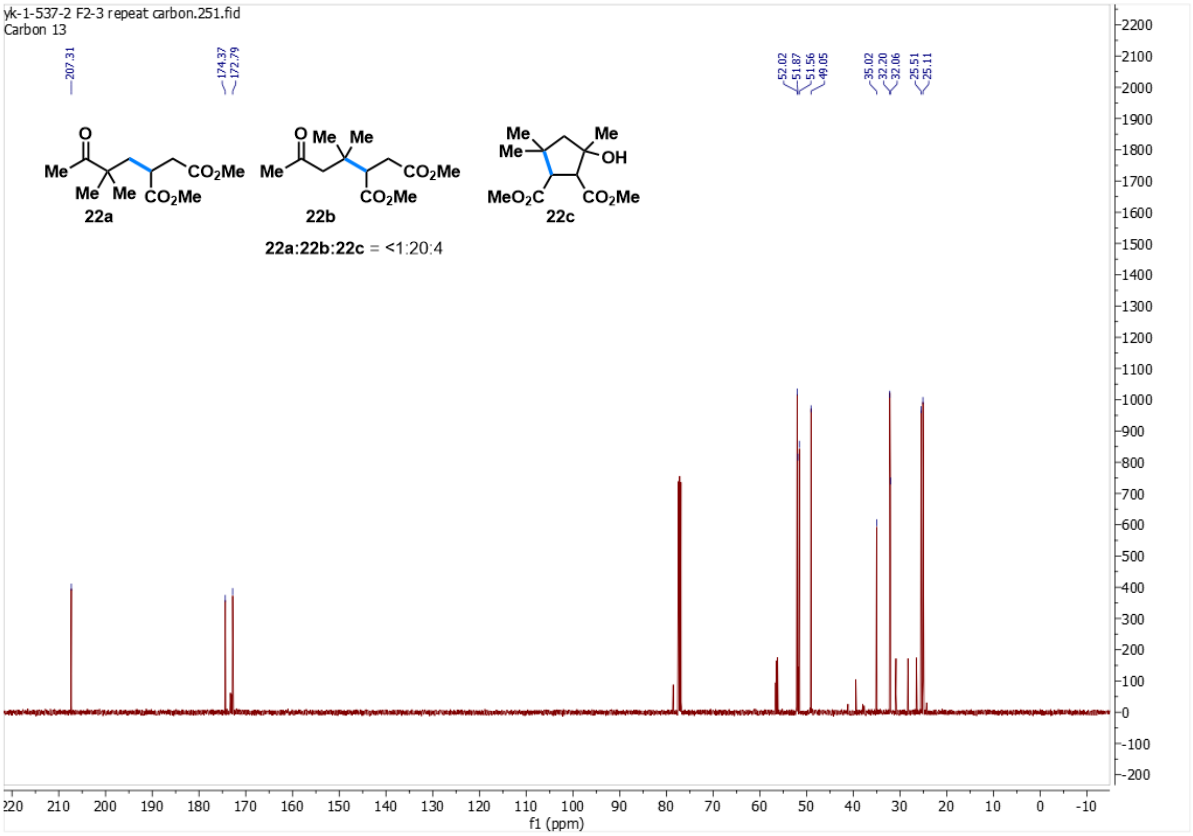

yk-1-538-2 F4-6.175.fid
22a
22b
22c
22a:22b:22c = 1:18:3
f1 (ppm)

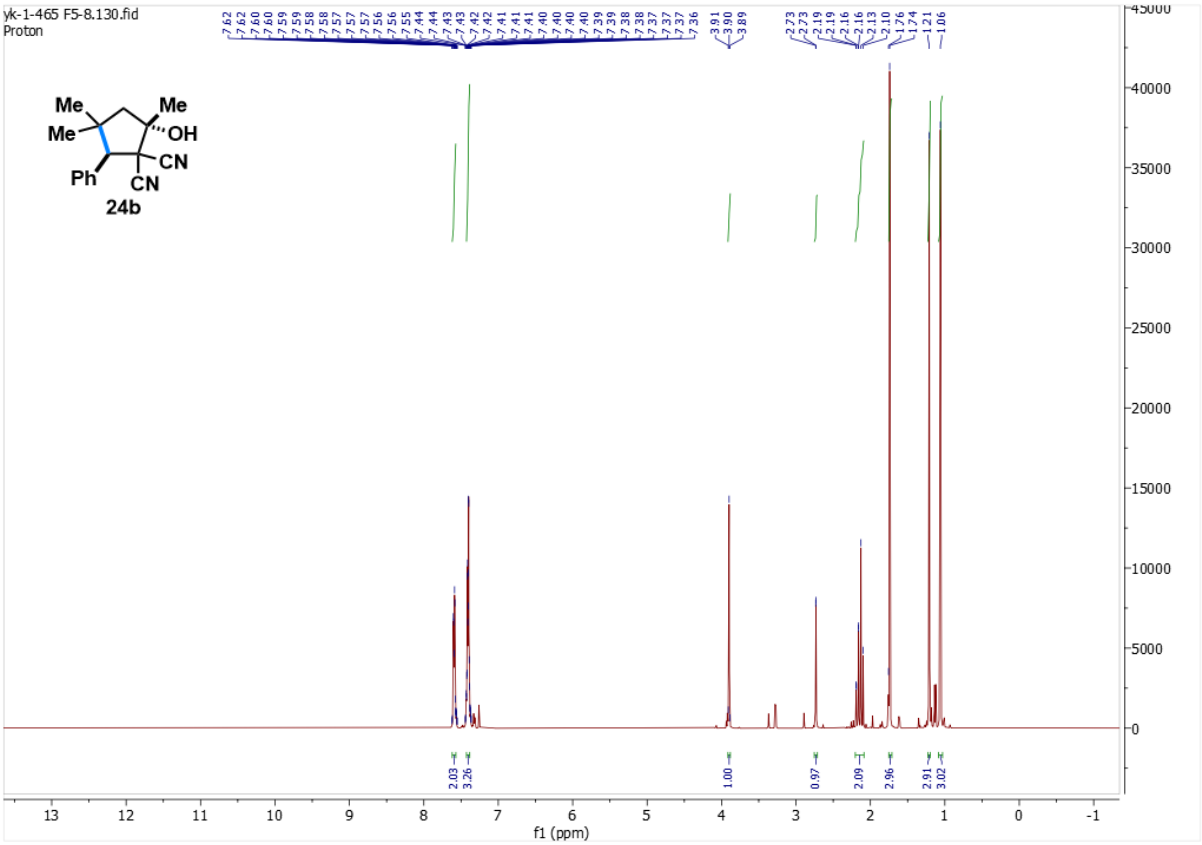

yk-1-538-2 F4-6 carbon.176.fid
carbon 13
22a
22b
22c
22a:22b:22c = 1:18:3
f1 (ppm)

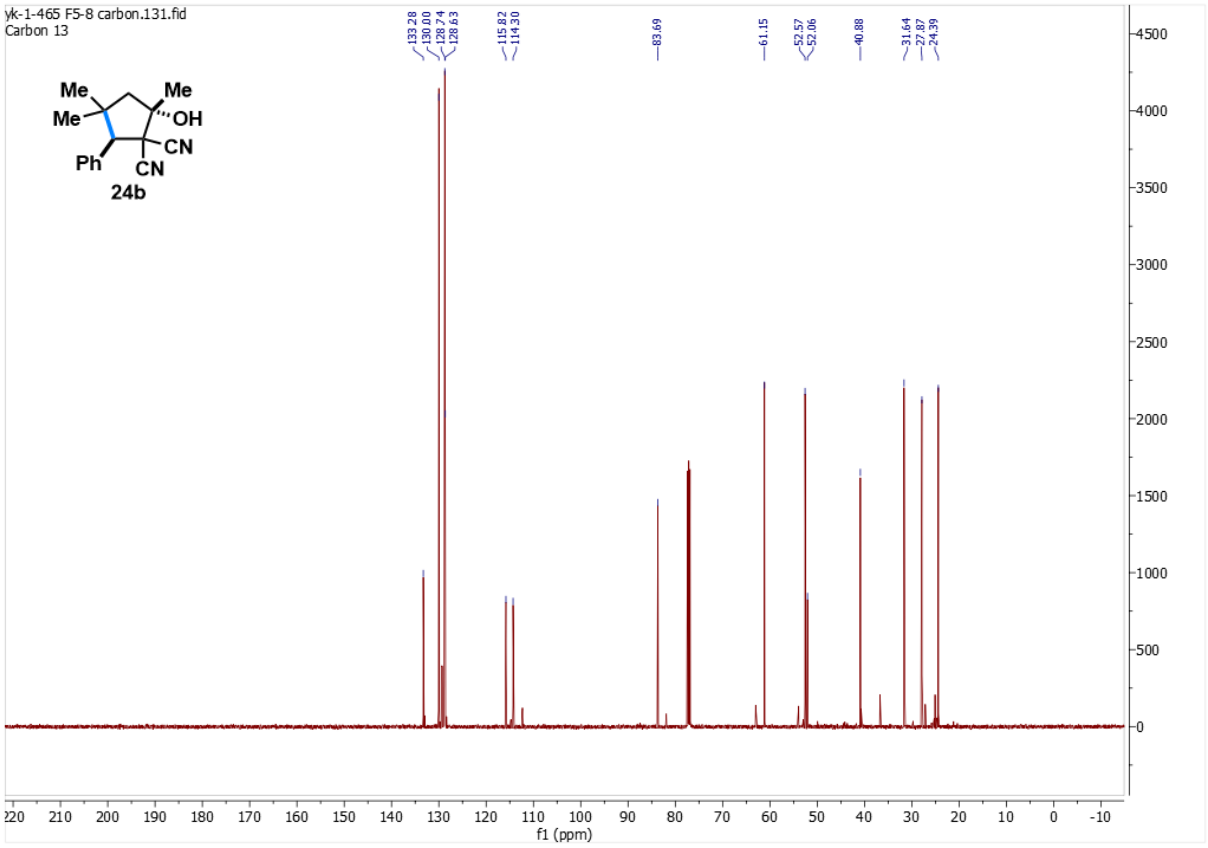

yk-1-537-1 F7-9.256.fid
Proton
22a
22b
22a:22b = 1:15
(Conditions A)
f1 (ppm)

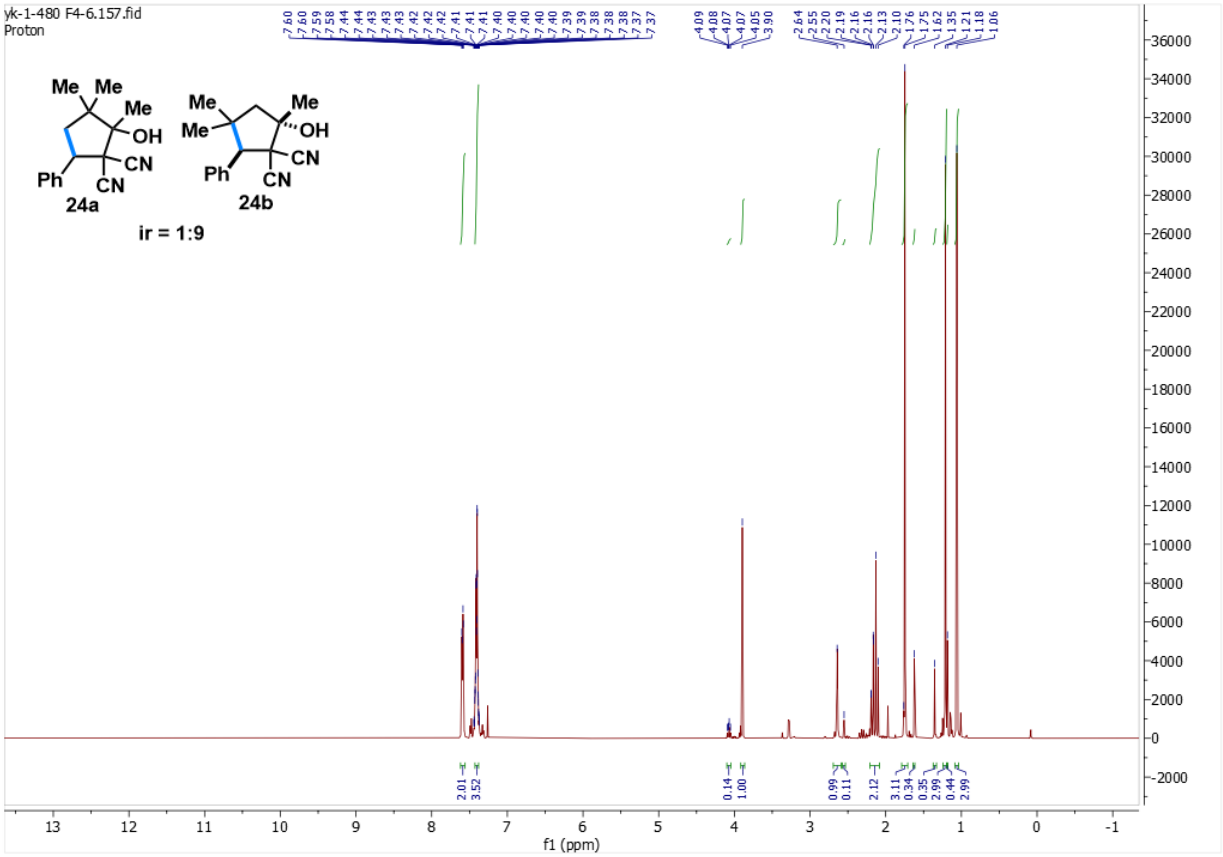

yk-1-537-1 F7-9 carbon.257.fid
Carbon 13
22a
22b
22a:22b = 1:15
(Conditions A)
f1 (ppm)

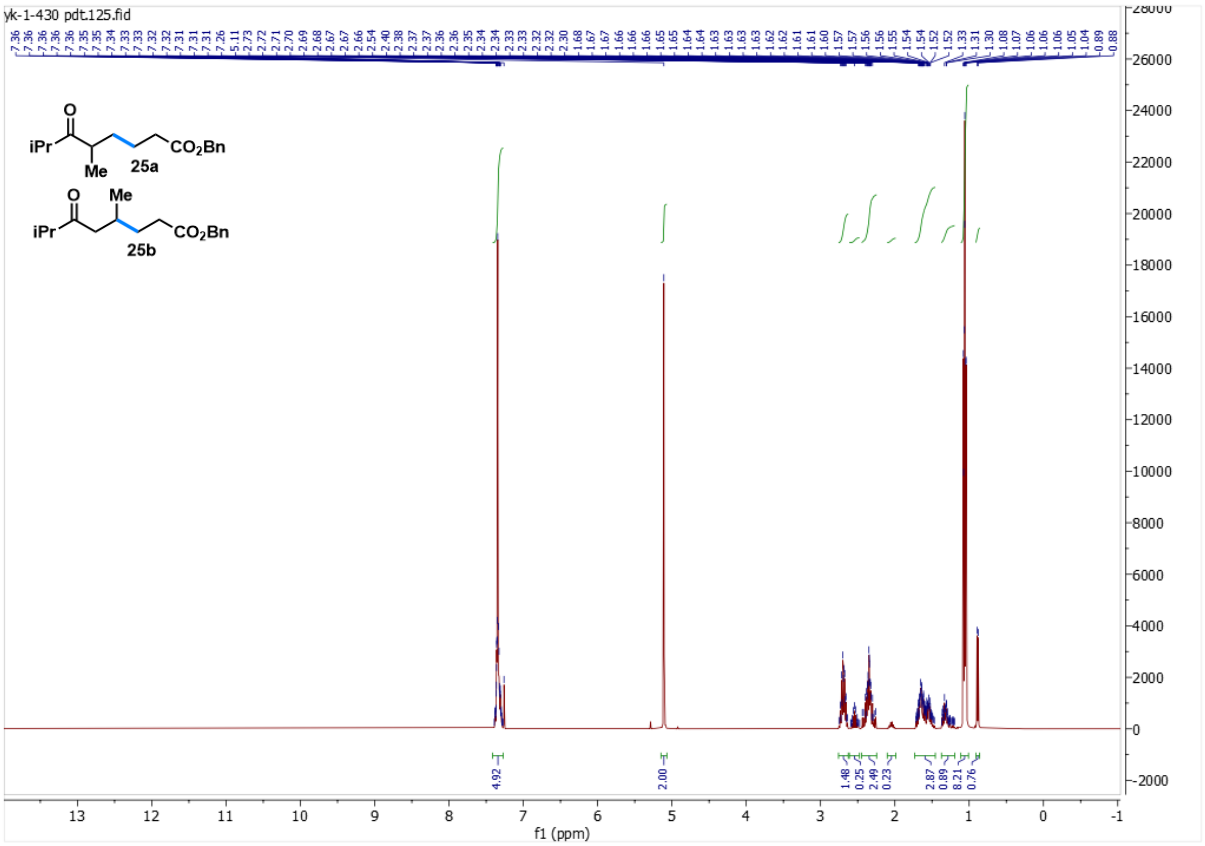

yk-1-537-2 F2-3 repeat.250.fid
Proton
22a
22b
22c
22a:22b:22c = <1:20:4
f1 (ppm)

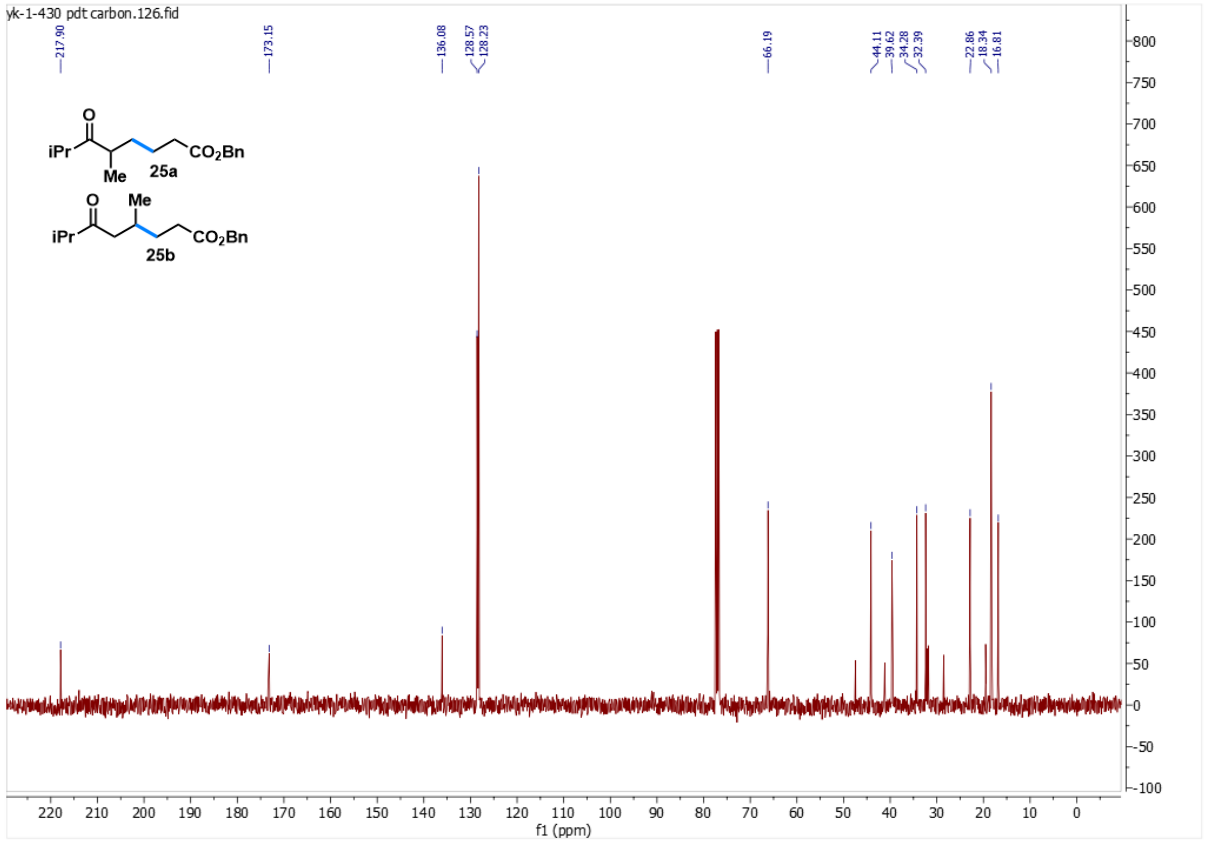

yk-1-537-2 F2-3 repeat carbon.251.fid
Carbon 13
22a
22b
22c
22a:22b:22c = <1:20:4
f1 (ppm)

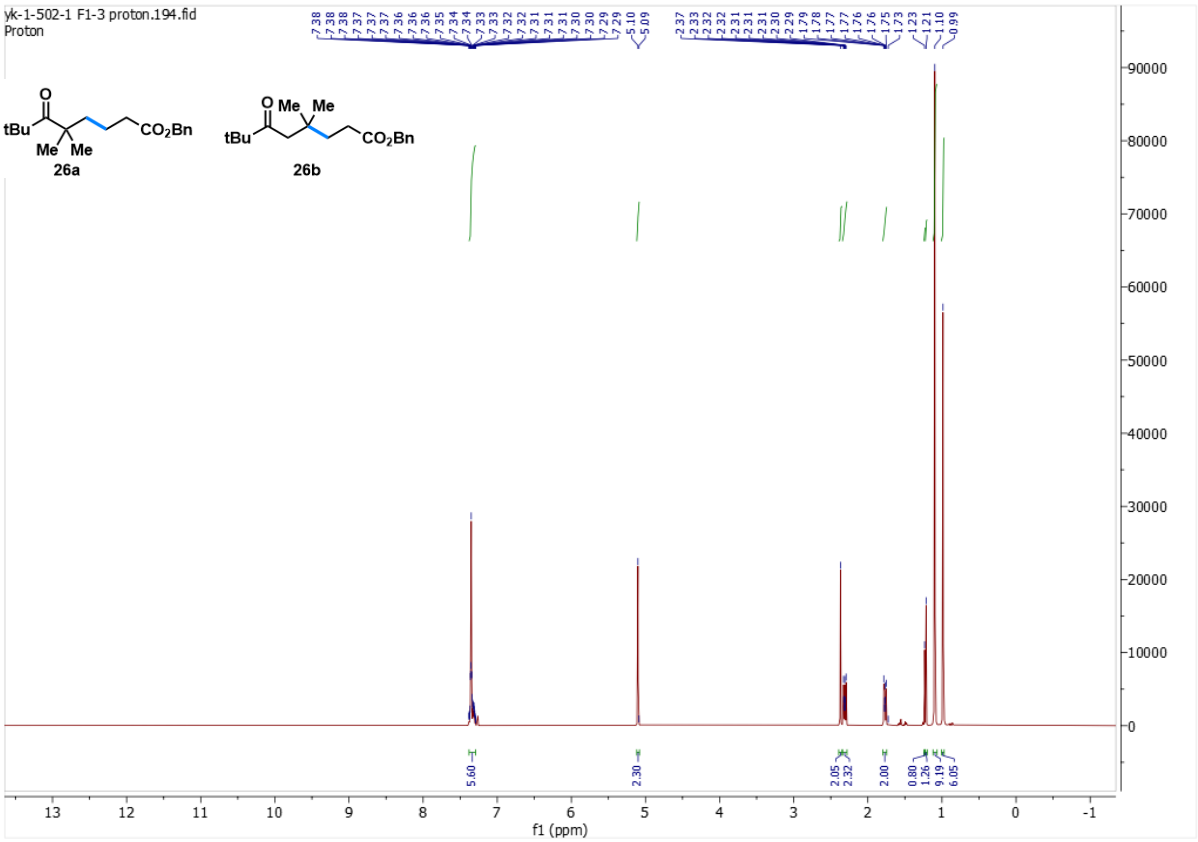

yk-1-465 F5-8.130.fid
Proton
Me
Me
Me
OH
CN
Ph
CN
24b
f1 (ppm)

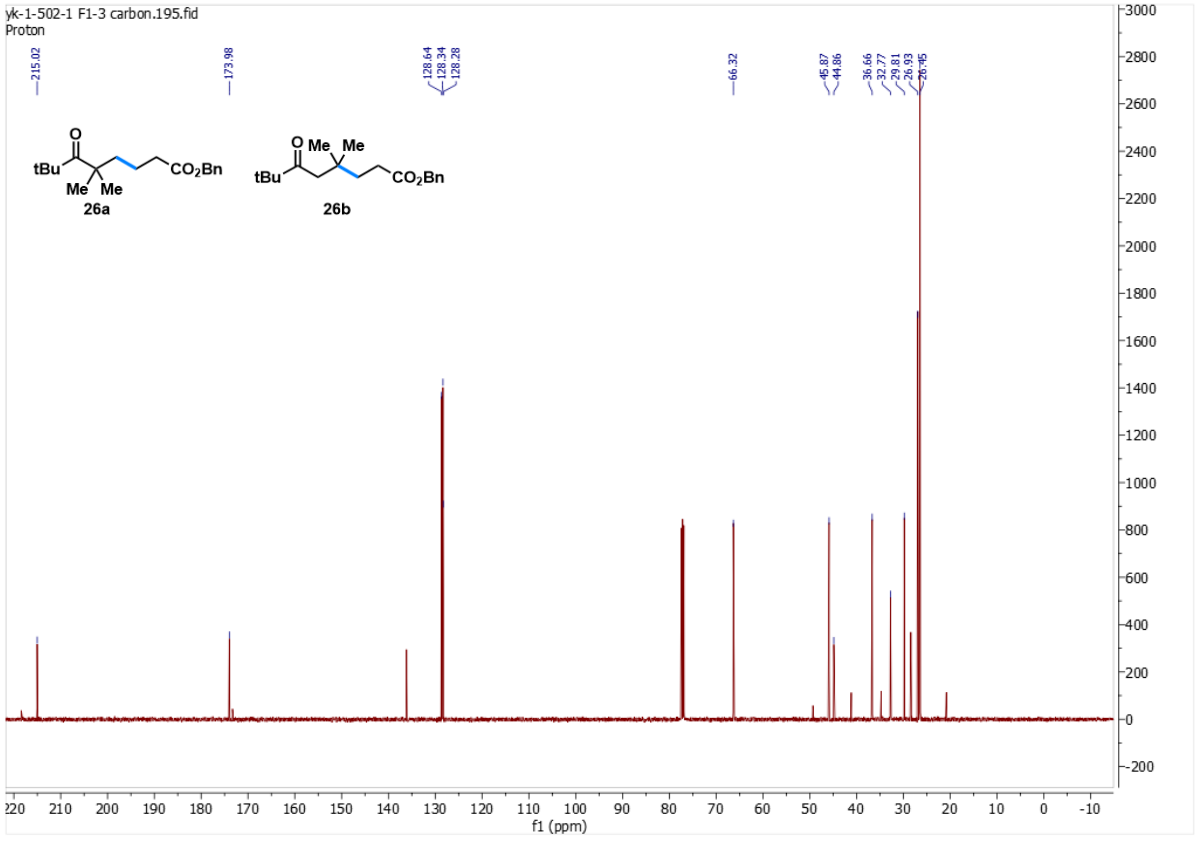

yk-1-465 F5-8 carbon.131.fid
Carbon 13
Me
Me
Me
OH
CN
Ph
CN
24b
f1 (ppm)

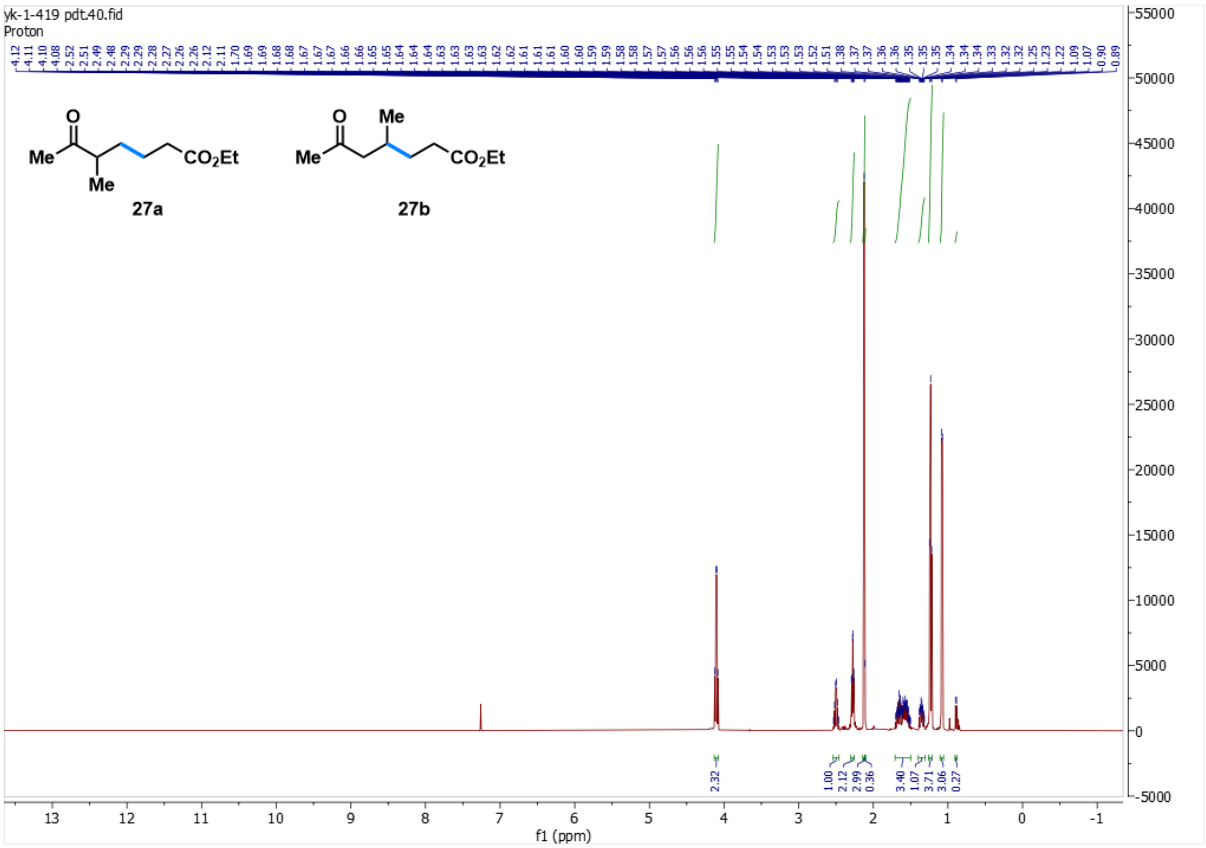

yk-1-480 F4-6.157.fid
Proton
Me Me
Me
OH
CN
Ph
CN
24a
Me
Me
Me
OH
CN
Ph
CN
24b
ir = 1:9
f1 (ppm)

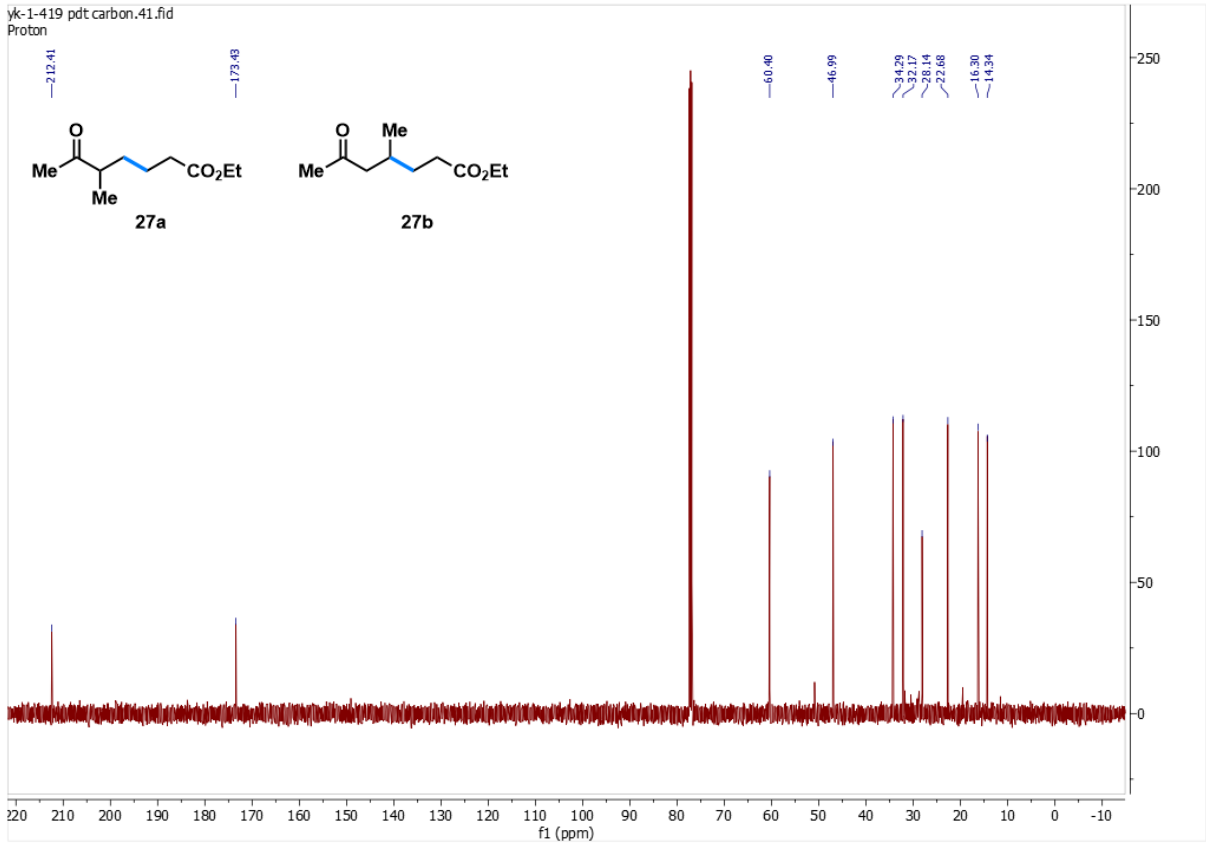

yk-1-430 pdt.125.fid
iPr
Me
CO2Bn
25a
25b
4.92
2.00
1.48
0.25
2.49
0.23
2.87
0.89
8.21
0.76
f1 (ppm)


yk-1-430 pdt carbon.126.fid
217.90
173.15
136.08
128.57
128.23
66.19
44.11
39.62
34.28
32.39
22.86
18.34
16.81
iPr
Me
CO2Bn
25a
25b
f1 (ppm)


yk-1-502-1 F1-3 proton.194.fid
Proton
tBu
Me Me
CO2Bn
26a
O Me Me
tBu
CO2Bn
26b
f1 (ppm)


yk-1-502-1 F1-3 carbon.195.fid
Proton
215.02
173.98
128.64
128.34
128.28
66.32
45.87
44.86
36.66
32.77
29.81
29.03
26.45
tBu
Me Me
CO2Bn
26a
O Me Me
tBu
CO2Bn
26b
f1 (ppm)


yk-1-419 pdt.40.fid
Proton
27a
27b
f1 (ppm)


yk-1-419 pdt carbon.41.fid
Proton
27a
27b
f1 (ppm)