A Solvent-Reagent Selection Guide for Steglich-type Esterification of Carboxylic Acids - Supporting Information

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Supporting Information

Chemicals

All chemicals used were purchased from Sigma-Aldrich, TCI Europe, Acros Organics or Fluorochem. All reagents were used without further purification. Solvents were dried over 3Å molecular sieves for 24 hours before use, or used as a Sureseal/Acroseal preparation. Aluminium-backed Silicagel 60 F_{254} plates from E. Merck were used for thin layer chromatography. Puriflash 30 µm silica gel prepacked flash chromatography cartridges were used for all chromatographic separations.

NMR

NMR analysis was performed on a Bruker AC 400 MHz spectrometer operating at 400 MHz for ^{1}H-NMR and 101 MHz for ^{13}C-NMR. Samples were run in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO) where appropriate. A 500 MHz Bruker spectrometer, operating at 500 MHz for ^{1}H-NMR and 126 MHz for ^{13}C-NMR was also used for analysis. All chemical shifts are reported in parts per million (ppm), are relative to the internal standard TMS and coupling constants (*J*) are measured in Hertz (Hz). Multiplicity is stated as follows: s-singlet, d-doublet, t-triplet, q-quartet, dd-doublet of doublets, dt-doublet of triplets, dq-doublet of quartets, tt-triplet of triplets, tq-triplet of quartets, ddd-doublet of doublet of doublets, m-multiplet, bs-broad singlet.

IR analysis

All IR analysis was carried out on a Bruker Alpha Platinum FT-IR spectrometer with ATR.

Melting point

Melting points were determined using a Stuart SMP20 melting point apparatus and the values are expressed in degrees Celsius (°C). The parameters for the melting point analysis were set at 5 °C per minute ramp and melting point was determined manually. Melting points are uncorrected.

ESI-MS

High resolution mass spectrometry (HRMS) with accurate mass measurement to four decimal places was obtained for all new compounds described. Mass spectra were recorded in both positive and negative electrospray ionisation mode on a Bruker ESI MicroTOF mass spectrometer.

HPLC Analysis

HPLC for high throughput reaction monitoring used an Agilent 1200 system, with a standard gradient elution method: Waters XBridge 2.1x30 mm column, stationary phase C_{18} 3.5 µm, 0.8 mL/min flow rate, detection at 254 nm; elution with 5-95% MeCN in 0.1% aqueous TFA over 4 minutes. Needle draw height was adjusted appropriately to avoid impact with stirring bars during high-throughput analysis.

General Procedures

General Procedure A – High Throughput Reaction Screening

A 2 mL HPLC vial was charged with 0.2 mmol phenylacetic or benzoic acid as appropriate, benzyl alcohol (0.6 mmol) or phenol (0.6 mmol), triethylamine (0.6 mmol), coupling reagent of choice (0.2 mmol) and solvent of choice (1 mL). The reactions were stirred for 24 h at room temperature using a 7 mm PTFE stirring bar. Analysis was conducted by HPLC-UV according to the general HPLC method above. Samples that contained precipitate were transferred into a Whatman UniPrep syringeless filter vial (0.45 µm).

General Procedure B – Substrate Scope Synthesis

A 10 mL round bottomed flask was charged with Mukaiyama's reagent (2.1 mmol), carboxylic acid of choice (2.0 mmol), alcohol of choice (2.0 mmol), and dimethyl carbonate (4 mL). The suspension was stirred at room temperature and 2,6-lutidine was added (556 µL, 4.8 mmol). The reaction was then heated to 60 °C and stirred under an N_2 atmosphere for 16 hours. Alternatively, the reaction mixtures can be conducted at room temperature for 24 hours. Reaction mixtures were isolated by general procedures C or D.

General Procedure C – Silica Gel Chromatography

Reaction mixtures were absorbed directly onto silica gel *in vacuo* and purified by silica gel chromatography using a gradient elution 0-10% cyclohexane-EtOAc using a prepacked silica gel cartridge (12 g) and eluting over 10 column volumes at a flow rate of 15 mL per minute using a Biotage SP4. UV detector wavelength was set at 254 nm. For compounds containing basic amines, 1% conc. NH_3 was added to the ethyl acetate mobile phase.

General Procedure D – Aqueous Workup Procedure

Reaction mixtures were first diluted with EtOAc to a final volume of 15 mL followed by gravity filtration to remove any precipitated pyridone. The organic filtrate was then washed with water (1 x 10 mL) followed by 2 mL brine to break the resulting emulsion. The organic layer was then washed with 1 M aqueous HCl (1 x 10 mL) to remove the 2,6-lutidine, followed by saturated aqueous $NaHCO_3$ (1 x 10 mL) to attempt remove any unreacted carboxylic acid. The reaction mixture was then concentrated *in vacuo* and adsorbed directly onto a 3 cm plug of silica gel in a 4 cm diameter sinter funnel. The product was then eluted using a single portion of 50 mL 10% EtOAc:cyclohexane under vacuum filter conditions. This simple silica plug filtration allowed for elution of the desired product in one portion directly into a round bottom flask. Solvent was removed *in vacuo* to furnish the desired products.

Further Solvent Screening: Aqueous, Micellar, and Aqueous-Organic Biphasic Mixtures

Entry	Solvent	Reaction	Coupling Reagent	Yield
1	50:50 Water:iPrOAc + 0.05 equiv. Aliquot 336	1	Mukaiyama	41
2	50:50 Water:iPrOAc + 0.05 equiv. Aliquot 336	2	Mukaiyama	38
3	TPGS-750-M	2	Mukaiyama	1
4	TPGS-750-M	3	COMU	64
5	TPGS-750-M	4	COMU	40
6	TPGS-750-M	4	Mukaiyama	17
7	Water	3	Mukaiyama	5
8	10% Aq. SDS	3	Mukaiyama	2
9	50:50 biphasic water:iPrOAc	3	Mukaiyama	0
10	50:50 water:iPrOAc + 0.05 equiv. TBABr	3	Mukaiyama	10
11	50:50 water:iPrOAc + 0.05 equiv. TBABr	4	Mukaiyama	7

Table S1: Aqueous, micellar, and aqueous-organic conditions investigated. Results depicted using a traffic light system. Key: Red = <50% yield, amber = 50–70% yield, green = >70% yield. Conversion at t=24h. Yields determined by HPLC. TPGS-750-M was used as a 2 wt% aqueous solution. Total solvent volume of 1 mL.

Further Concentration Screening

	EDC.HCl DMAP	DIC DMAP	Mukaiyama's Reagent	T_3P	COMU
Solvent					
DMC	2%	0%	0%	5%	66%
Cyclopentanone	0%	0%	0%	5%	36%
iPrOAc	3%	0%	0%	5%	68%
Anisole	1%	0%	0%	5%	70%
DCM	10%	0%	0%	5%	75%
2Me-THF	3%	0%	0%	5%	64%

CPME	4%	0%	0%	5%	70%
DMI	0%	0%	0%	5%	49%

*Table S2: Test reaction results for the coupling of benzoic acid and benzyl alcohol at t=24h. Reaction concentrations of 0.05 M. Reaction **4**.*

Reaction Concentration Optimisation

Attempt to further optimise the percentage yields of EDC-HCl reactions by varying the concentrations were conducted. Optimisation of reaction concentration was conducted across all four reactions **1**-**4** at concentrations of 0.075 M, 0.15 M, and 0.1 M using iPrOAc as solvent. Reactions were conducted in 1 mL of solvent and the stoichiometric ratio of reagents to each other were not altered. Unfortunately, increasing concentration did not improve the yield of the EDC-HCl reactions. One major issue observed was the incomplete solubility of EDC-HCl in the majority of the alternative solvents screened. Addition of an amine base such as TEA did not improve the yield of the reactions either. At this point further optimisation of EDC-HCl reactions was discontinued. Note: as stated in the main manuscript, Lutjen *et al*. successfully optimised the use of EDC-HCl in CH_3CN though an excess of DMAP was required.[1] No further work utilising EDC-HCl was conducted.

Focus was then shifted to the optimisation of reactions conducted using Mukaiyama's reagent and solvents iPrOAc and DMC. Concentrations were varied from 0.05 M, 0.2 M, 0.5 M and 1.0 M and reaction **3** was used as model reaction. 0.2 M concentrations were the conditions used in the initial solvent-reagent screening and are taken from main manuscript Table 4. iPrOAc performed poorly at this concentration when the reaction scale was increased to 5 mmol (28% isolated yield), entry 3 Table S3, as difficulties stirring reaction mixtures due to precipitate and insoluble starting materials was observed. At more dilute concentrations of 0.05 M, no conversion to product was observed in either solvent. Increasing the concentration to 0.5 M gave an excellent isolated yield of 83% on a 5 mmol scale when using DMC. At 1.0 M concentrations, reactions utilising Mukaiyama's reagent gave similar results to the initial screening conditions (75% isolated vs 82%) when using DMC and a moderate isolated yield of 56% when using iPrOAc. Therefore, a concentration of 0.5 M was determined to be most effective. 0.5 M concentrations are also specified in patent literature that utilises Mukaiyama's reagent.[2] All work utilising iPrOAc was halted due to the poorer yields observed on scale up and due to large quantities of benzoic anhydride also observed at 5.0 mmol scale when screening was conducted using benzoic acid starting material.

Reaction concentration was later validated using substrate **11**. The synthesis of 1-(4-bromophenyl)ethyl 2-phenylacetate was conducted at 1.0 M conc. (2.0 mmol substrate in 2 mL solvent), at 60°C overnight. It was observed that the reaction stopped stirring overnight and an isolated yield 68% was achieved after silica gel chromatography. The reaction was repeated at 0.5 M conc. (2.0 mmol starting material acid in 4 mL solvent) and the stirring problems were overcome; an improved isolated yield of 80% was achieved.

Entry	Concentration M	Scale mmol	Solvent	Temperature °C	Yield*
1	0.05	0.05	iPrOAc	19	0
2	0.05	0.05	DMC	19	0
3	0.2	5.0	iPrOAc	60	28
4	0.2	0.2	DMC	19	82
5	0.2	0.2	DMC	60	84
6	0.5	5.0	DMC	60	83
7	1.0	5.0	iPrOAc	60	56
8	1.0	5.0	DMC	60	75

*Table S1: Further optimisation reactions conducted using model reaction **3**. * Yields determined by HPLC-UV. All reactions carried out for 24 hours.*

Workup and Isolation

Workup for esterification reactions utilising Mukaiyama's reagent have traditionally involved filtration of precipitated 1-methylpyridin-2(1H)-one, compound **6**, followed by purification by silica gel chromatography.[3] Calculating the LogP of the pyridone waste product using MarvinSketch predicts a value of 0.24 suggesting that the molecule is water soluble. Similarly protonated 2,6-lutidine should also be water soluble, thus the potential for purifying reaction mixtures using an aqueous organic extraction should be possible. To test this theory the 2 mmol scale synthesis of isopropyl ester **9** was conducted in DMC. The reaction mixture was first diluted with EtOAc to a final volume of 15 mL followed by gravity filtration to remove any precipitated pyridone **6**. The organic filtrate was then washed with water (1 x 10 mL) followed by 2 mL brine to break the resulting emulsion. The organic layer was then washed with 1 M aqueous HCl (1 x 10 mL) to remove the 2,6-lutidine, followed by saturated aqueous $NaHCO_3$ (1 x 10 mL) to attempt remove any unreacted carboxylic acid. TLC analysis of the organic layer showed complete removal of 2,6-lutidine and a faint spot remained for unreacted phenylacetic acid, however a strong baseline impurity still remained and the organic layer had a yellow colour (desired product was a colourless oil). The reaction mixture was then concentrated *in vacuo* and adsorbed directly onto a 3 cm plug of silica gel in a 4 cm diameter sinter funnel. The product was then eluted using a single portion of 50 mL 10% EtOAc:cyclohexane under vacuum filter conditions. This simple silica plug filtration allowed for elution of the desired product in one portion directly into a round bottomed flask. Removal of solvent *in vacuo* gave an excellent purity profile as seen in Fig. S1.

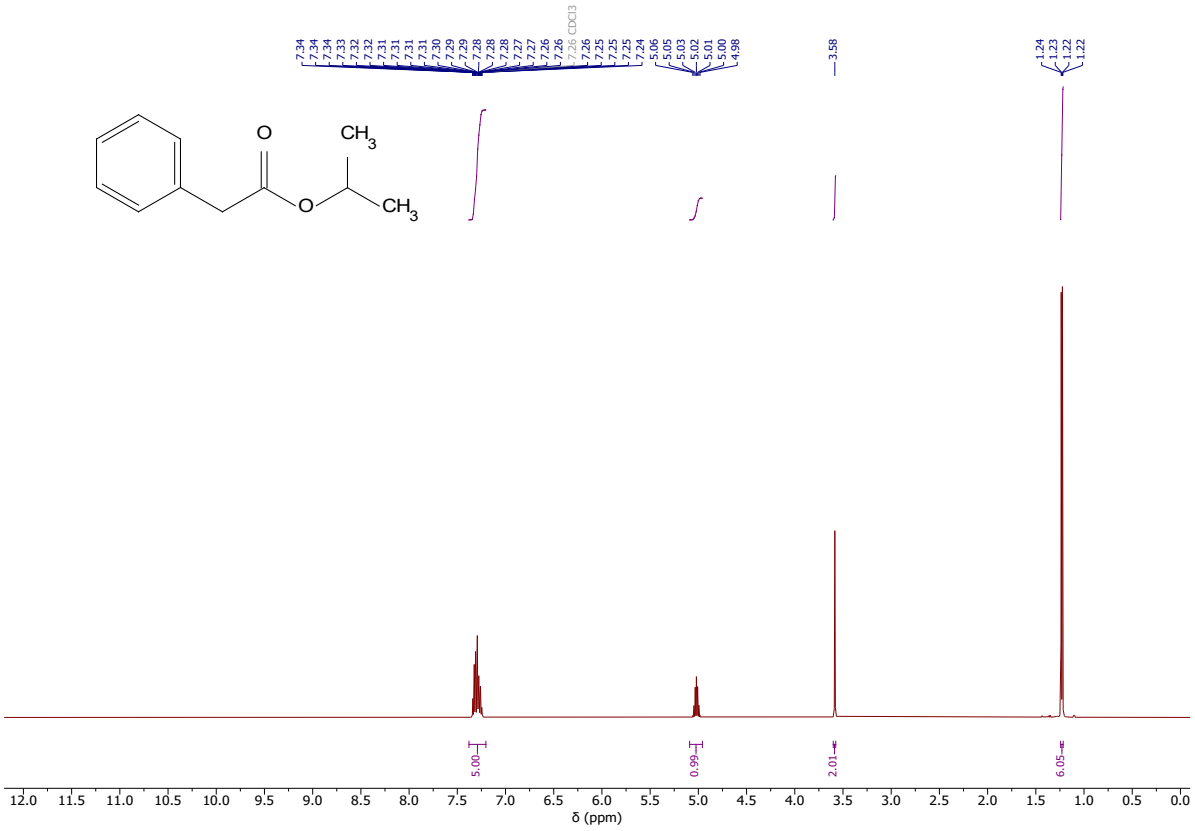


Fig. S1: ^{1}H-NMR of isopropyl ester 9 after workup and filtration. Total isolation time 30 minutes. 92% isolated yield.

Reaction Time

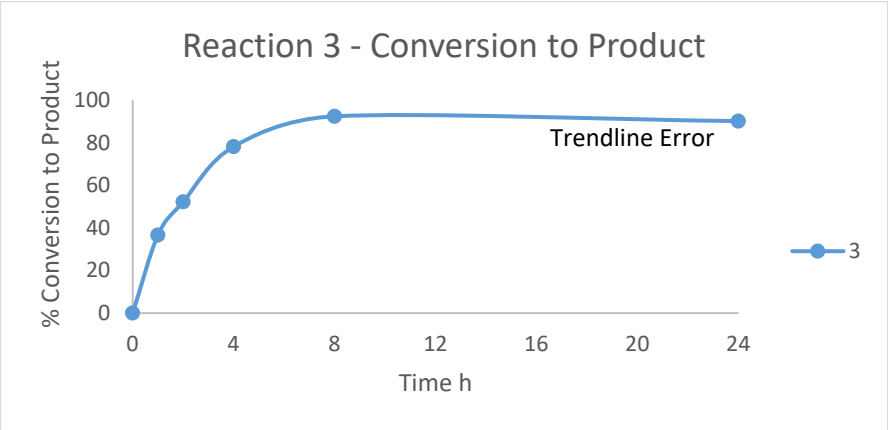
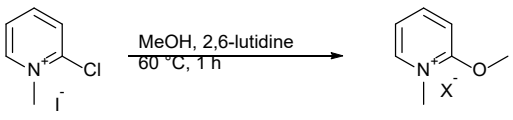


*Fig. S2: Reaction time course plot for the synthesis of **3** conducted at 60 °C using 2,6-lutidine as base and a reaction concentration of 0.5 M.*

Finally, reaction progress was monitored for a 2.0 mmol scale synthesis of ester **3**, 0.5 M concentration. A plateau of 90% conversion to product was observed at t = 8h, Fig. S2.

Mukaiyama's Reagent Deactivation

A control reaction was conducted in which carboxylic acid was omitted from the reaction mixture and quantitative conversion of Mukaiyama's reagent **3** to **23** Fig. S3, was observed within one hour as judged by HRMS analysis, Fig. S4.



3 **23**

Exact Mass calcd.: [M]+ 124.0757
Found: 124.0728

*Fig. S3: Deactivation of Mukaiyama's reagent to methoxy ether **23***

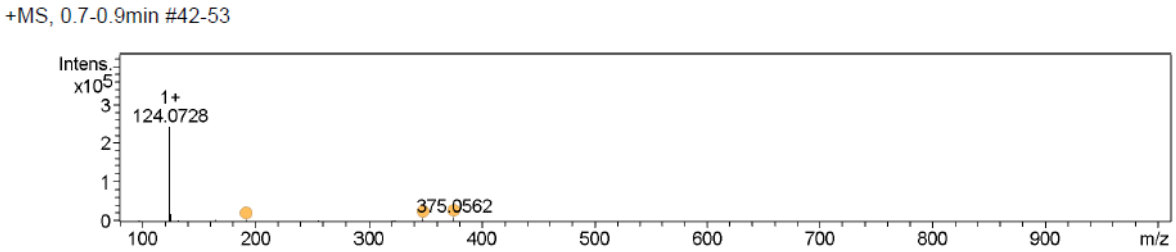
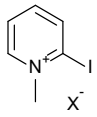


*Fig. S4: HRMS of crude reaction mixture for the generation of methoxy ether **23.***

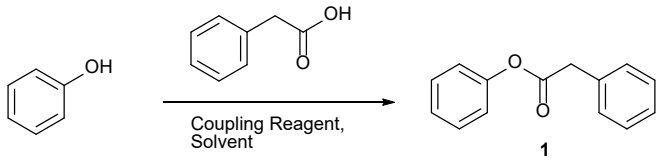
Further to this method of reagent deactivation is the potential for competitive reactivity of Mukaiyama's reagent with nucleophilic counterions, i.e. halogen exchange,[4] in solution to give unreactive 2-iodo species **24** depicted in Fig. S5. **24** was observed in reaction solutions by HRMS. This method of deactivation has previously been described by Zhao *et al*.[5] The use of modified Mukaiyama's reagent in which the chloro counter-ion is replaced with a non-nucleophilic one such as BF_4 has been demonstrated as an effective strategy in overcoming this deactivation process.[6, 7]



24

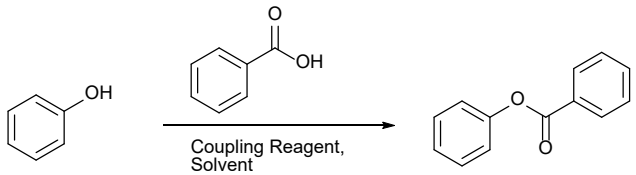
*Fig. S5: Unreactive 2-iodo species **24**.*

Reaction 1: Aryl Alcohol - Alkyl Acid



1

Reaction 2: Aryl Alcohol - Aryl Acid



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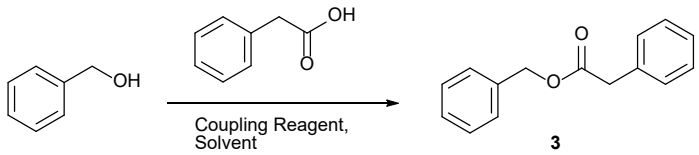
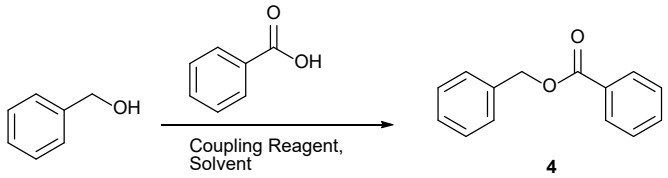
Reaction 3: Alkyl Alcohol - Alkyl Acid



3

Reaction 4: Alkyl Alcohol - Aryl Acid

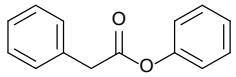


4

Scheme S1: Test reactions chosen for solvent-reagent condition screening. Reaction conditions: 0.2 mmol acid, 0.6 mmol alcohol, 1 mL solvent, 1.0 equivalent of coupling reagent, 3.0 equivalents of TEA if required, 5 mol% DMAP if required. Stir at room temperature for 24 hours.

Compound Characterisation

*Phenyl 2-phenylacetate (**1**)*



Chemical Formula: $C_{14}H_{12}O_2$

Molecular Weight: 212.25 $gmol^{-1}$

Appearance: White solid

1 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) and phenol (188 mg, 2.0 mmol). The product was isolated by general procedure C.

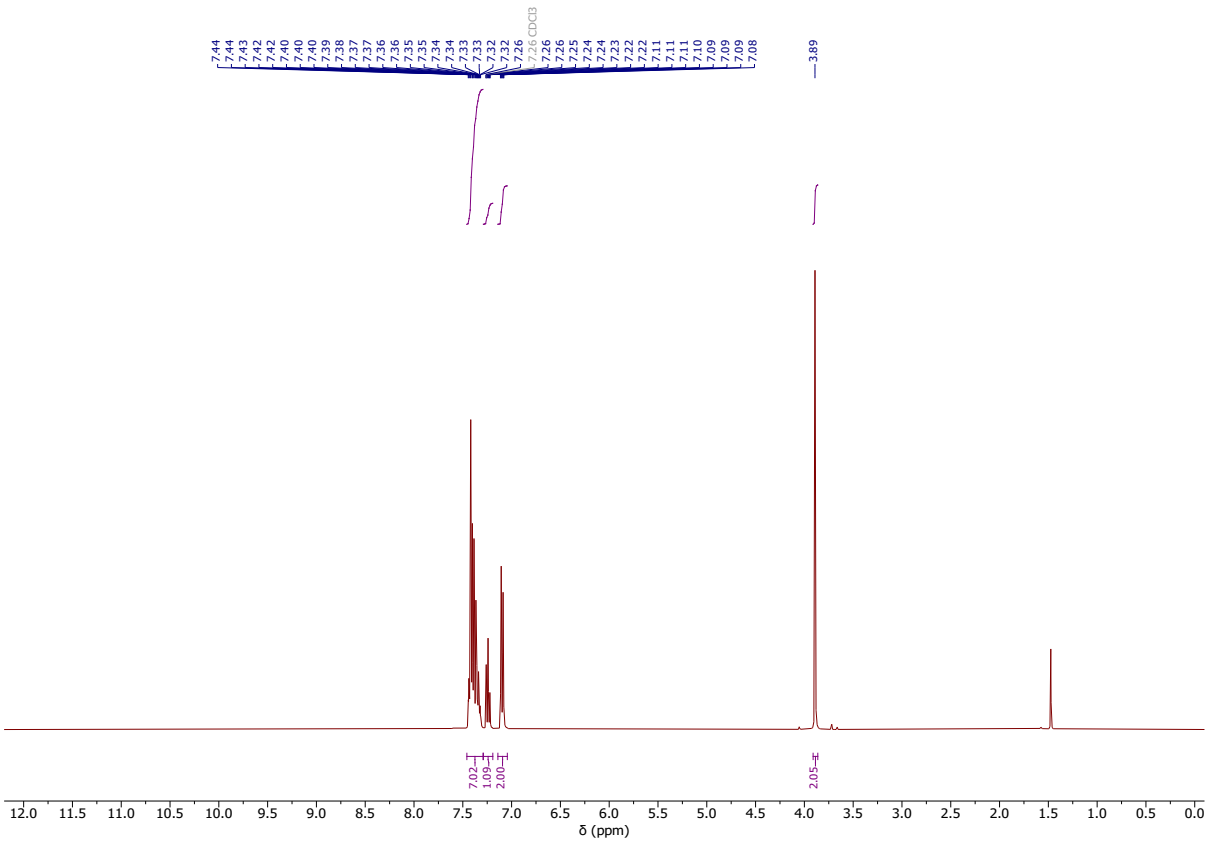
Yield: 92% (390 mg, 1.84 mmol)

δ_H (400 MHz, Chloroform-*d*) 7.46 – 7.29 (7 H, m), 7.29 – 7.19 (1 H, m), 7.14 – 7.04 (2 H, m), 3.89 (2 H, s).

δ_C (126 MHz, Chloroform-*d*) 170.2, 150.9, 133.6, 129.5, 129.4, 128.9, 127.5, 126.0, 121.6, 41.6.

^{1}H- and ^{13}C-NMR were in agreement with the literature.[8]

ESI-MS (+ve) m/z: Found $[M+H]^+$ 213.0908, $C_{14}H_{13}O_2^+$ requires 213.0910.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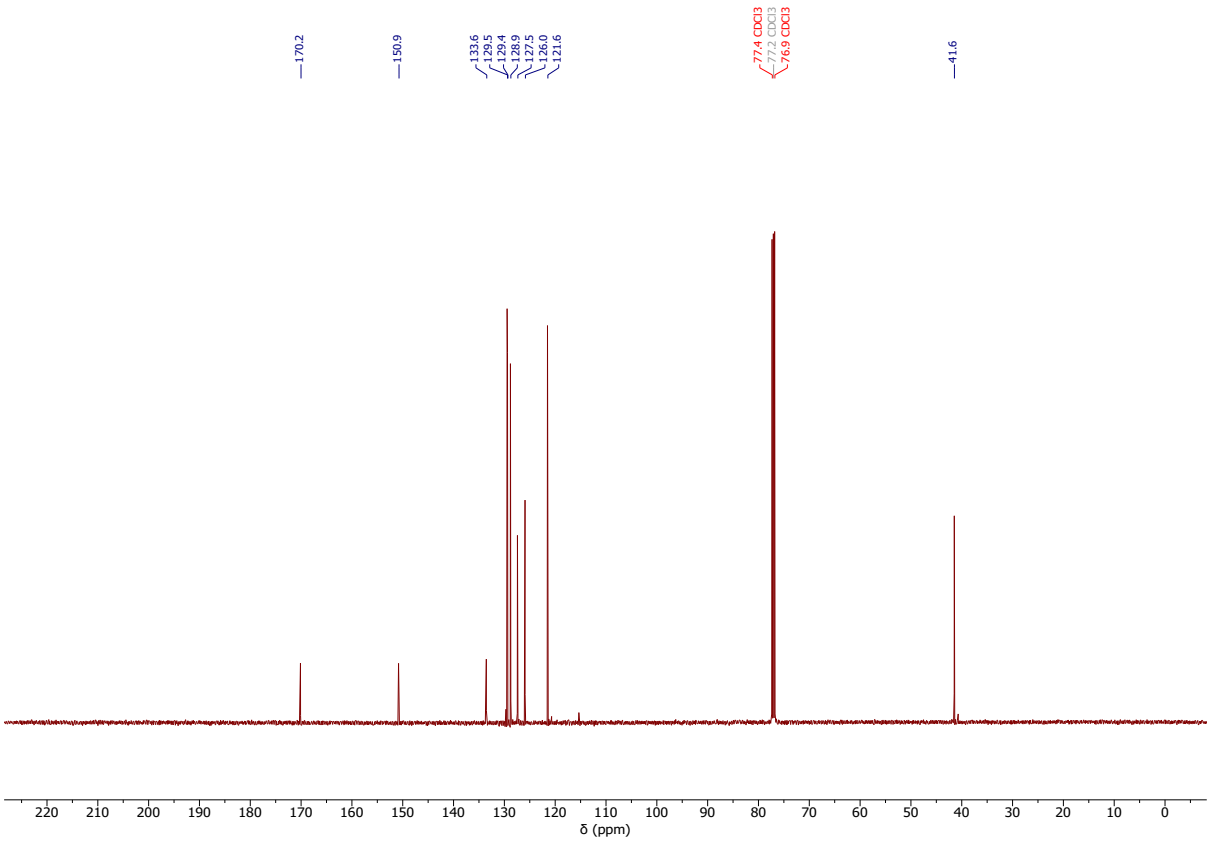
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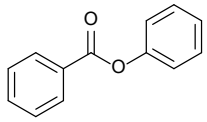
δ (ppm)

*Phenyl benzoate (**2**)*



Chemical Formula: $C_{13}H_{10}O_2$

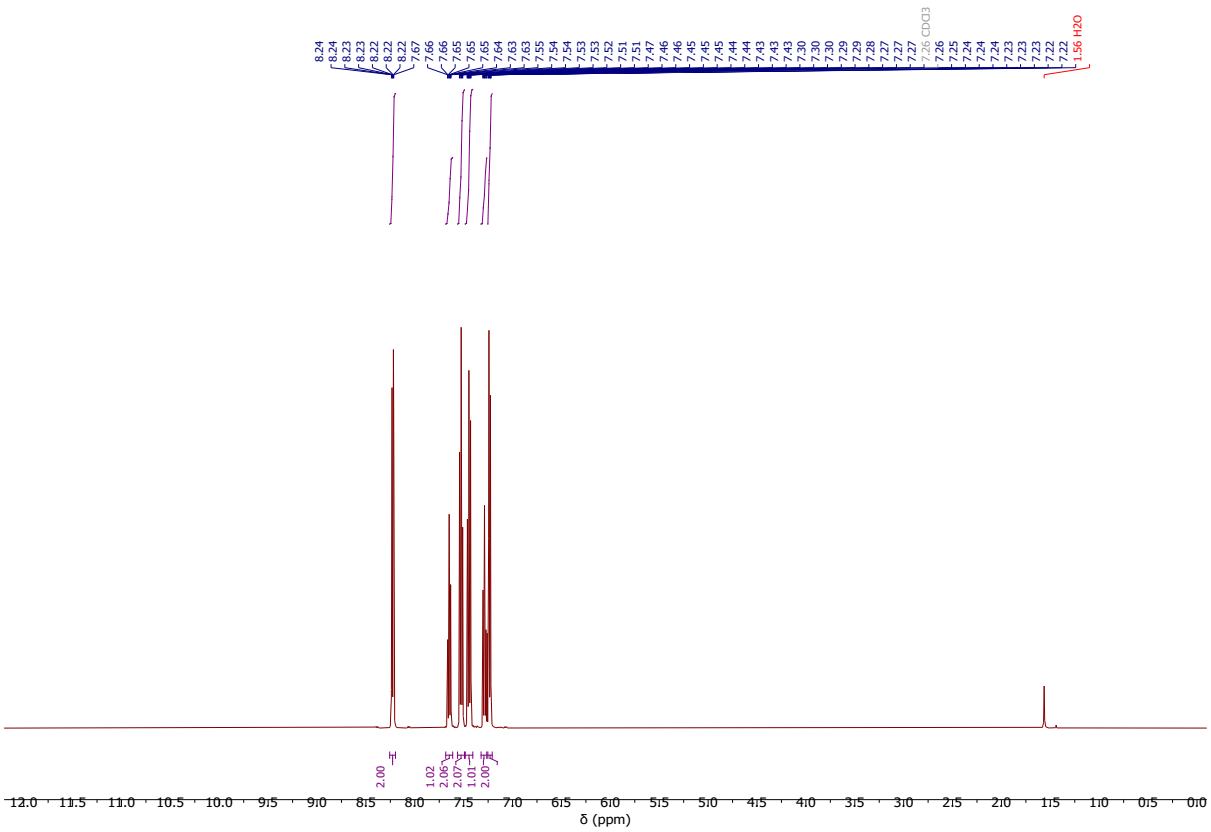
Molecular Weight: 198.22 $gmol^{-1}$

Appearance: White solid

δ_H (500 MHz, Chloroform-*d*) 8.26 – 8.20 (2 H, m), 7.68 – 7.61 (1 H, m), 7.56 – 7.49 (2 H, m), 7.48 – 7.41 (2 H, m), 7.32 – 7.26 (1 H, m), 7.25 – 7.21 (2 H, m).

δ_C (126 MHz, Chloroform-*d*) 165.2, 151.0, 133.6, 130.2, 129.6, 129.5, 128.6, 125.9, 121.7.

ESI-MS (+ve) m/z: Found $[M+H]^+$ 199.0751, $C_{13}H_{11}O_2^+$ requires 199.0754.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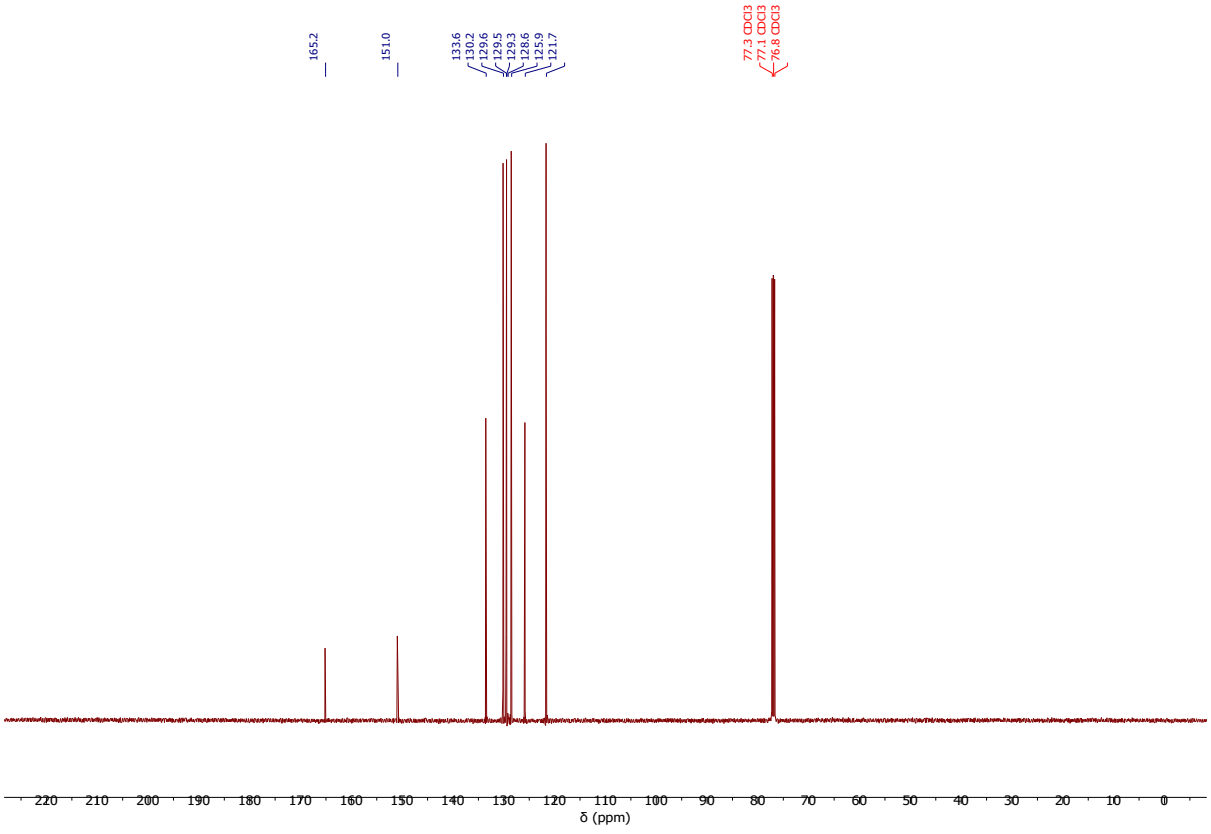
δ (ppm)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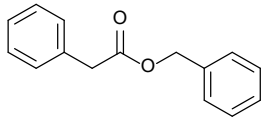
77.1 CDCl3
76.8 CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

*Benzyl phenylacetate (**3**)*



Chemical Formula: $C_{15}H_{14}O_2$

Molecular Weight: 226.28 $gmol^{-1}$

Appearance: Colourless oil

3 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) and benzyl alcohol (208 µL, 2.0 mmol). The product was isolated by general procedure C.

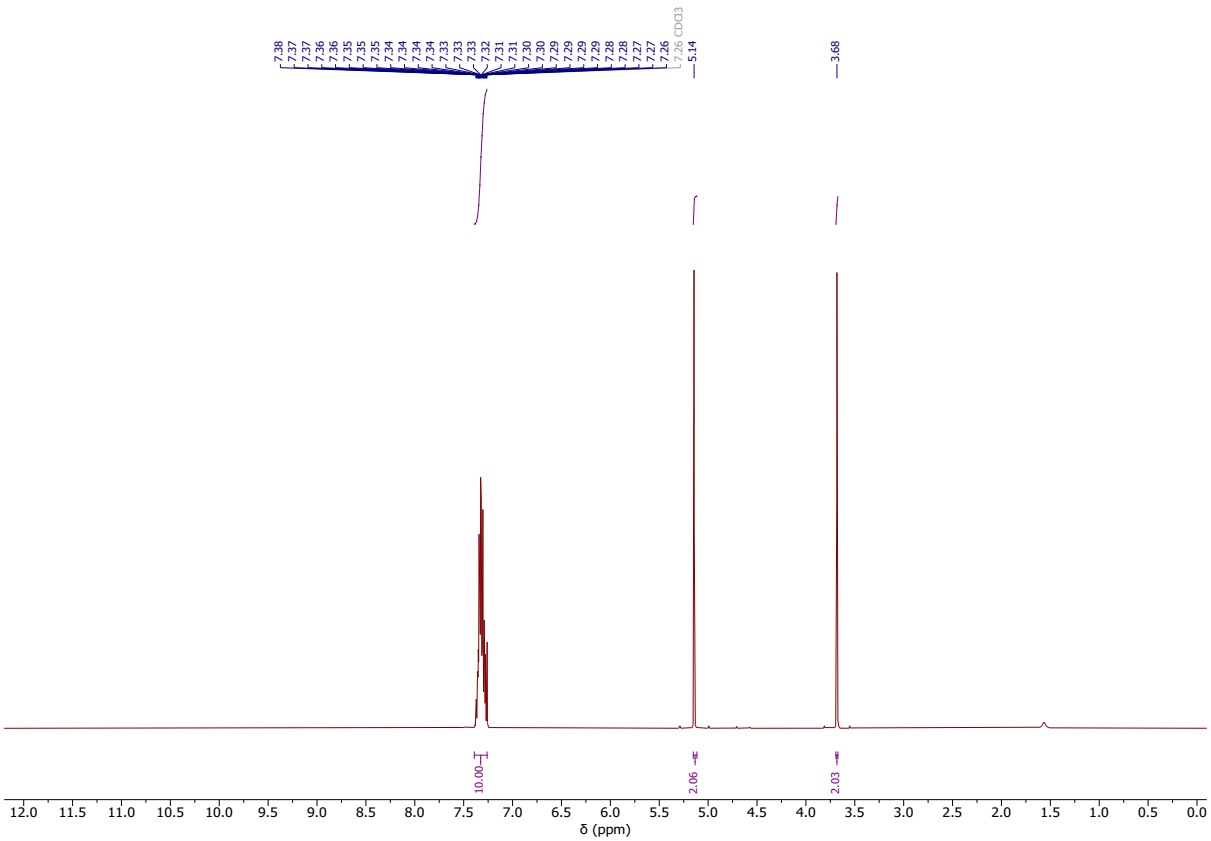
Yield: 75% (339 mg, 1.50 mmol)

δ_H (500 MHz, Chloroform-*d*) 7.39 – 7.26 (10 H, m), 5.14 (2 H, s), 3.68 (2 H, s).

δ_C (126 MHz, Chloroform-*d*) 171.4, 135.9, 133.9, 129.3, 128.6, 128.6, 128.2, 128.1, 127.2, 66.6, 41.4.

^{1}H- and ^{13}C-NMR were in agreement with the literature.[8]

ESI-MS (+ve) m/z: Found $[M+H]^+$ 227.1066, $C_{15}H_{15}O_2^+$ requires 227.1067.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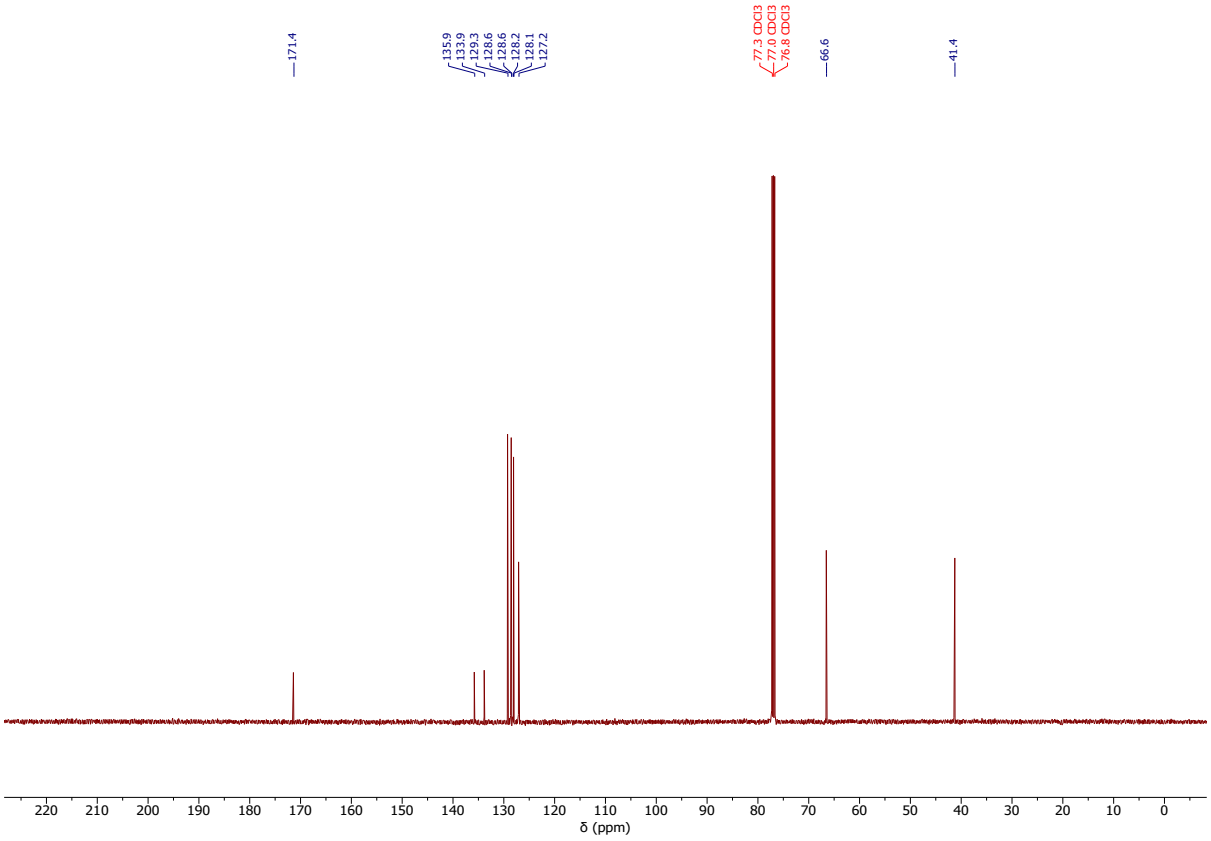
δ (ppm)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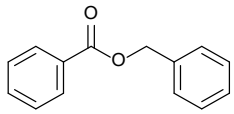
135.9
133.9
129.3
128.6
128.6
128.2
128.1
127.2
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
66.6
41.4
δ (ppm)

*Benzyl benzoate (**4**)*



Chemical Formula: $C_{14}H_{12}O_2$

Molecular Weight: 212.25 $gmol^{-1}$

Appearance: Colourless oil

4 Was synthesised according to general procedure B using benzoic acid (244 mg, 2.0 mmol) and benzyl alcohol (208 µL, 2.0 mmol). The product was isolated by general procedure C.

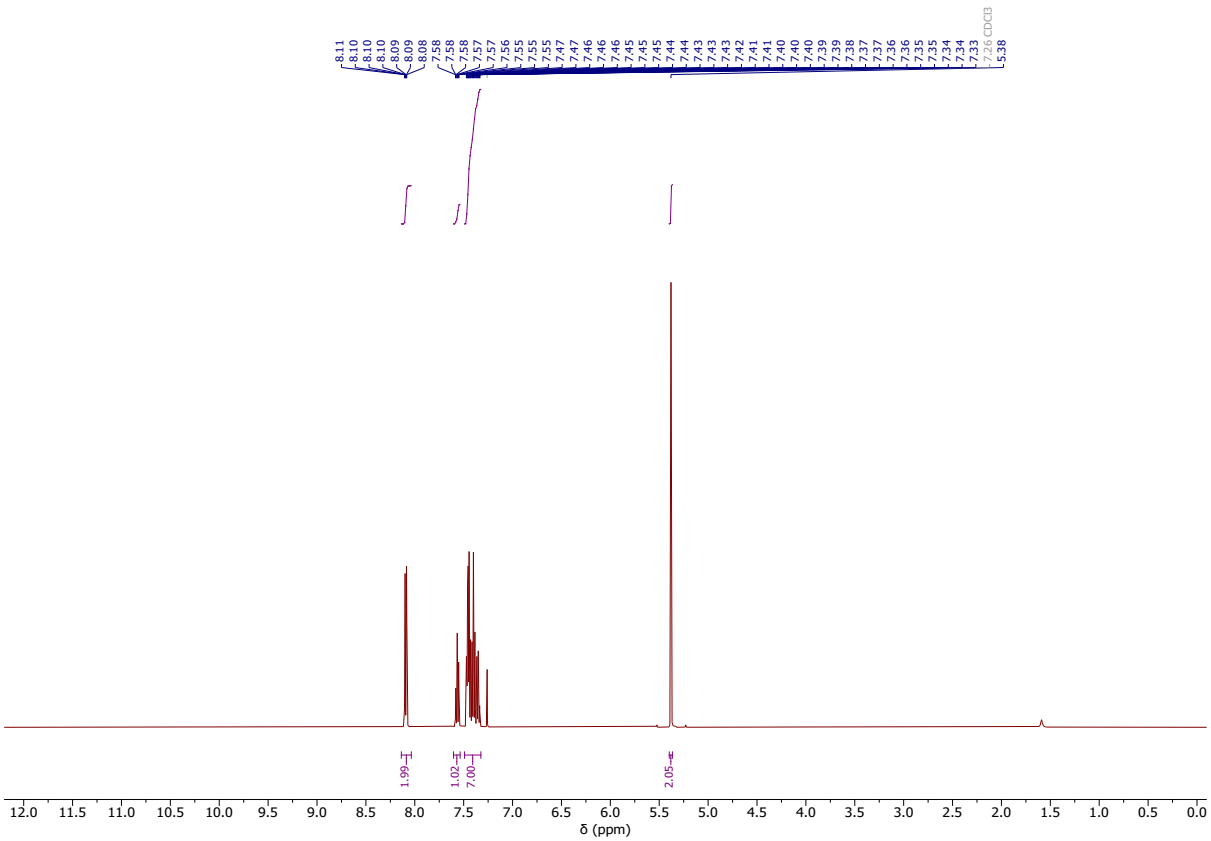
Yield: 75% (318 mg, 1.50 mmol)

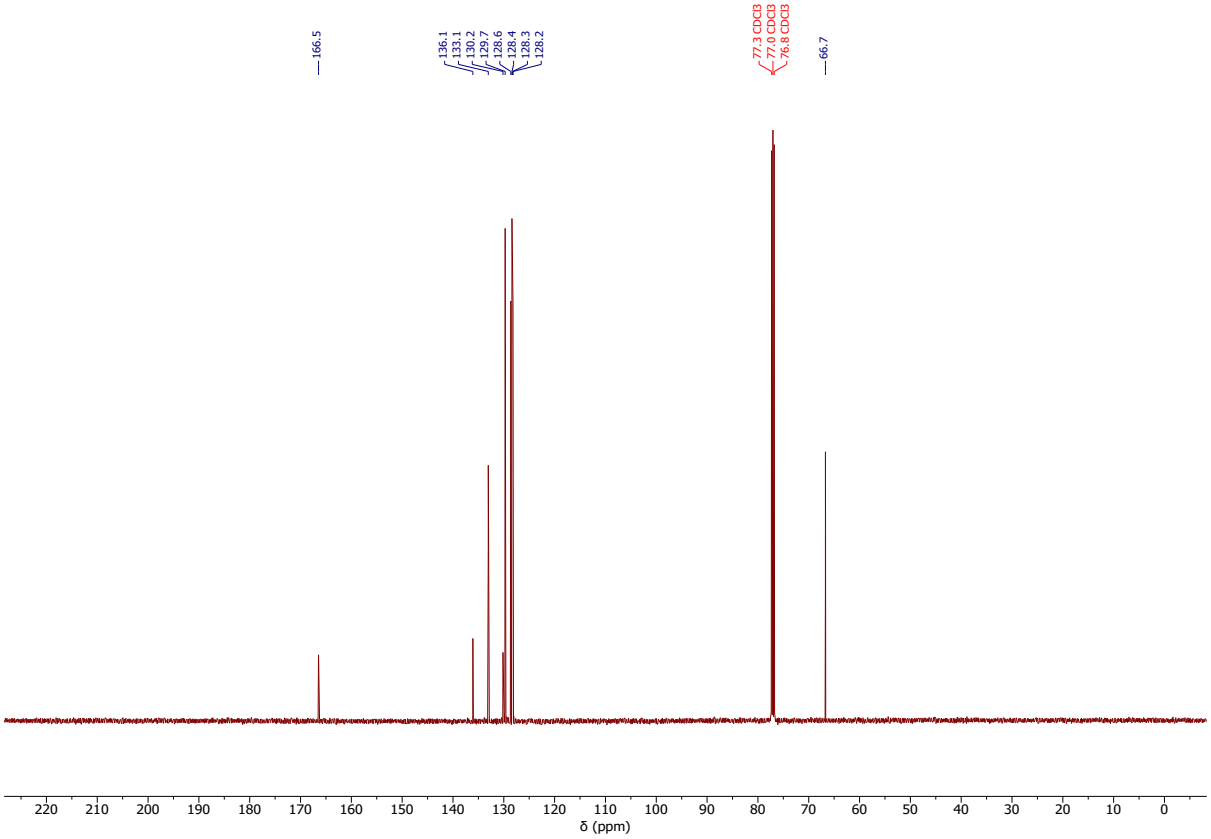
δ_H (500 MHz, Chloroform-*d*) 8.14 – 8.04 (2 H, m), 7.60 – 7.54 (1 H, m), 7.49 – 7.32 (7 H, m), 5.38 (2 H, s).

δ_C (126 MHz, Chloroform-*d*) 166.5, 136.1, 133.1, 130.2, 129.7, 128.6, 128.4, 128.3, 128.2, 66.7.

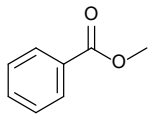
^{1}H- and ^{13}C-NMR were in agreement with the literature.[8]

ESI-MS (+ve) m/z: Found $[M+H]^+$ 213.0907, $C_{14}H_{13}O_2^+$ requires 213.0910.


δ (ppm)


δ (ppm)

*Methyl benzoate (**7**)*



Chemical Formula: $C_8H_8O_2$

Molecular Weight: 136.15 $gmol^{-1}$

Appearance: Colourless Oil

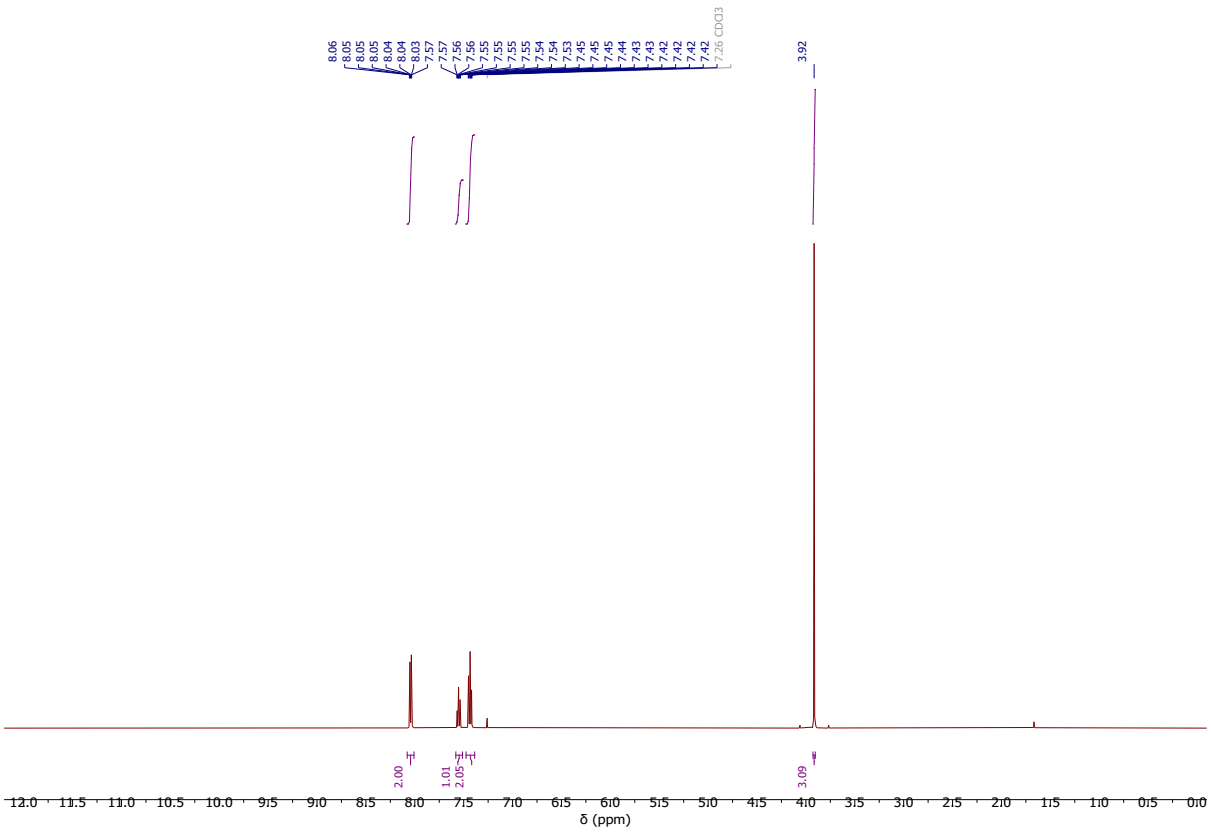
7 Was synthesised according to general procedure B using benzoic acid (244 mg, 2.0 mmol), DMAP (5 mol%, 12 mg, 0.1 mmol) and methanol (242 µL, 6.0 mmol). The product was isolated by general procedure C.

Yield: 86% (234, 1.72 mmol)

δ_H (500 MHz, Chloroform-*d*) 8.08 – 8.01 (2 H, m), 7.55 (1 H, ddt, *J* 7.9, 6.9, 1.3), 7.48 – 7.39 (2 H, m), 3.92 (3 H, s).

δ_C (126 MHz, Chloroform-*d*) 167.2, 133.0, 130.3, 130.1, 129.7, 128.5, 52.2.

^{1}H- and ^{13}C-NMR were in agreement with the literature.[9]


8.06
8.05
8.05
8.05
8.04
8.04
8.03
7.57
7.57
7.56
7.56
7.55
7.55
7.55
7.54
7.54
7.53
7.45
7.45
7.45
7.44
7.43
7.43
7.42
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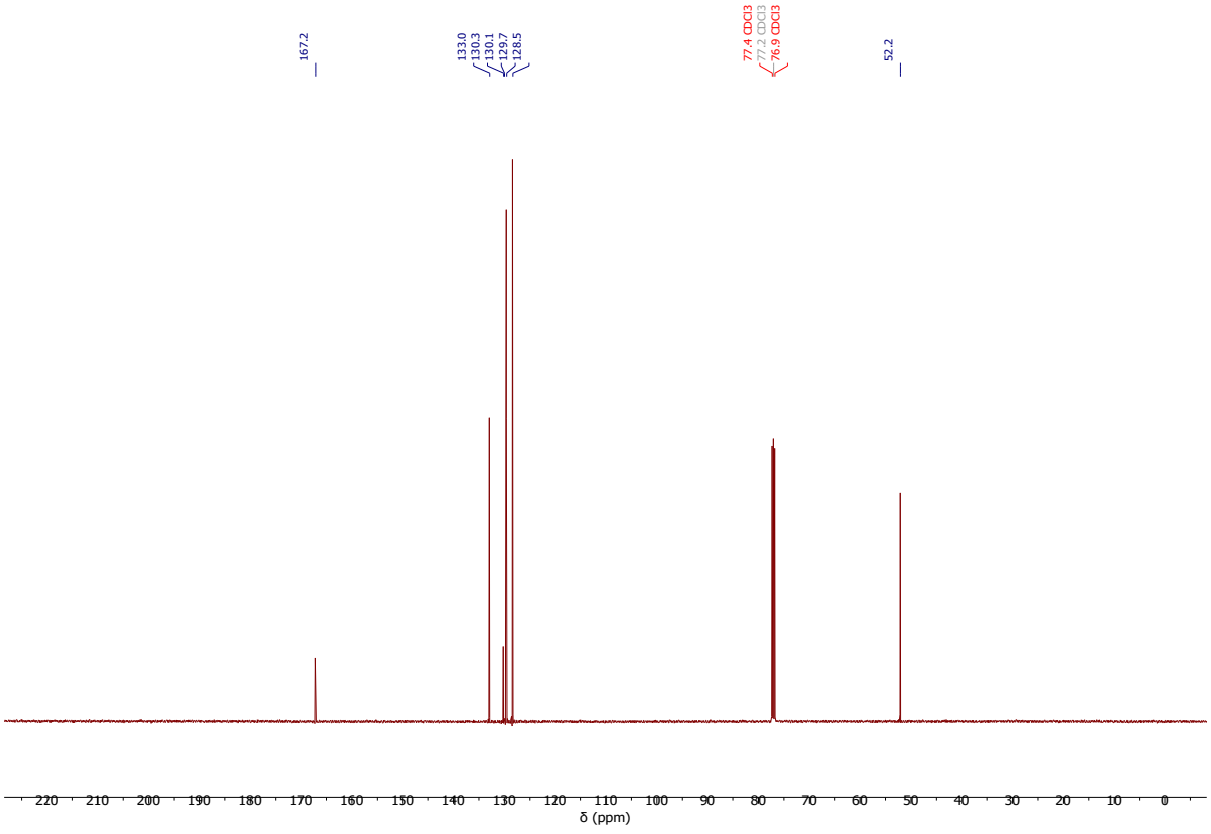
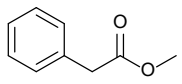
7.42
7.42
7.26 CDCl3
3.92
2.00
1.01
2.05
3.09
δ (ppm)


167.2
133.0
130.3
130.1
129.7
128.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
52.2
δ (ppm)

*Methyl phenylacetate (**8**)*



Chemical Formula: $C_9H_{10}O_2$

Molecular Weight: 150.18 $gmol^{-1}$

Appearance: Colourless Oil

8 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) and methanol (1 mL). 2,6-lutidine was replaced with 1-methylimidazole (383 µL, 4.8 mmol) as the organic base. The product was isolated by general procedure C.

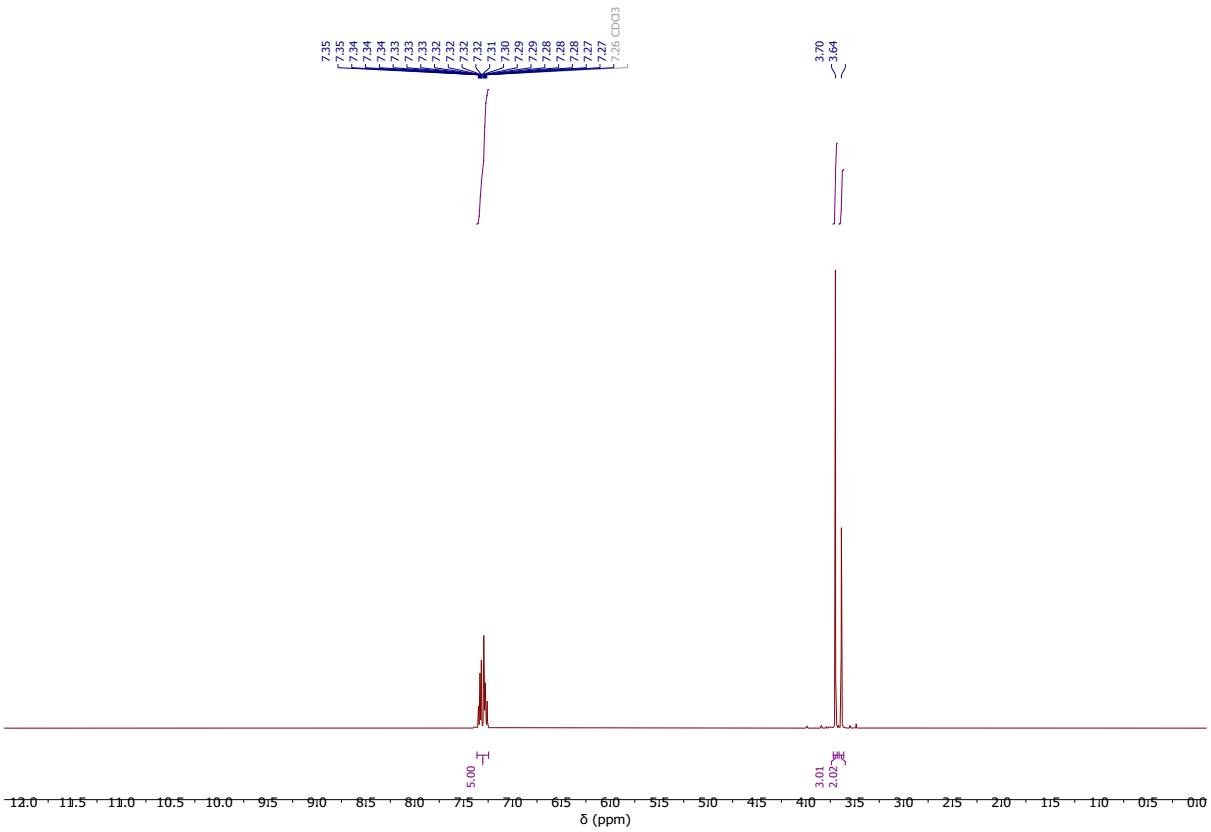
Yield: 80% (240 mg, 1.6 mmol).

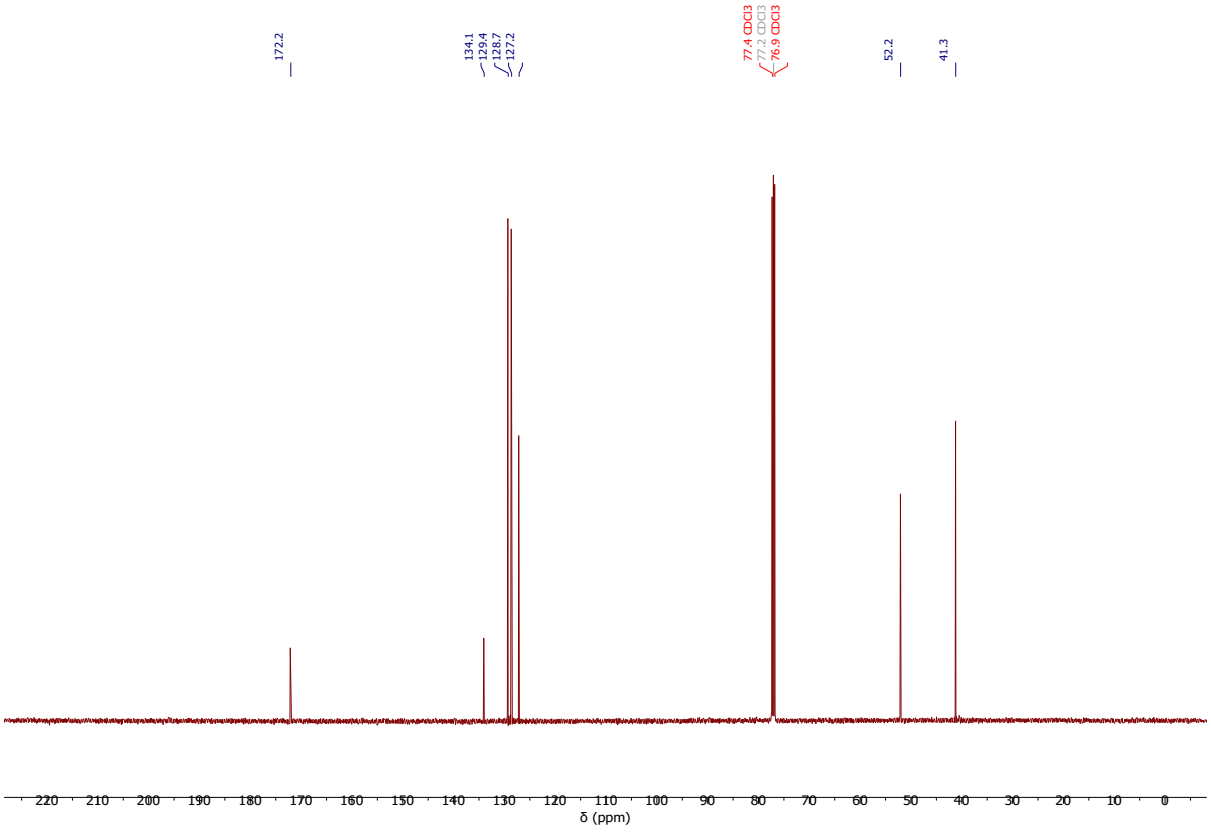
δ_H (500 MHz, Chloroform-*d*) 7.36 – 7.25 (5 H, m), 3.70 (3 H, s), 3.64 (2 H, s).

δ_C (126 MHz, Chloroform-*d*) 172.2, 134.1, 129.4, 128.7, 127.2, 52.2, 41.3.

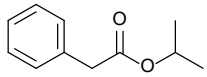
^{1}H- and ^{13}C-NMR were in agreement with the literature.[10]

ESI-MS (+ve) m/z: Found $[M+H]^+$ 151.0754, $C_9H_{11}O_2^+$ requires 151.0754.


7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26 CDCl3
3.70
3.64
5.00
3.01
2.02
δ (ppm)


172.2
134.1
129.4
128.7
127.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
52.2
41.3
δ (ppm)

*Isopropyl 2-phenylacetate (**9**)*



Chemical Formula: $C_{11}H_{14}O_2$

Molecular Weight: 178.23 $gmol^{-1}$

Appearance: Colourless oil

9 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) and isopropyl alcohol (306 µL, 4.0 mmol). The product was isolated by general procedure D.

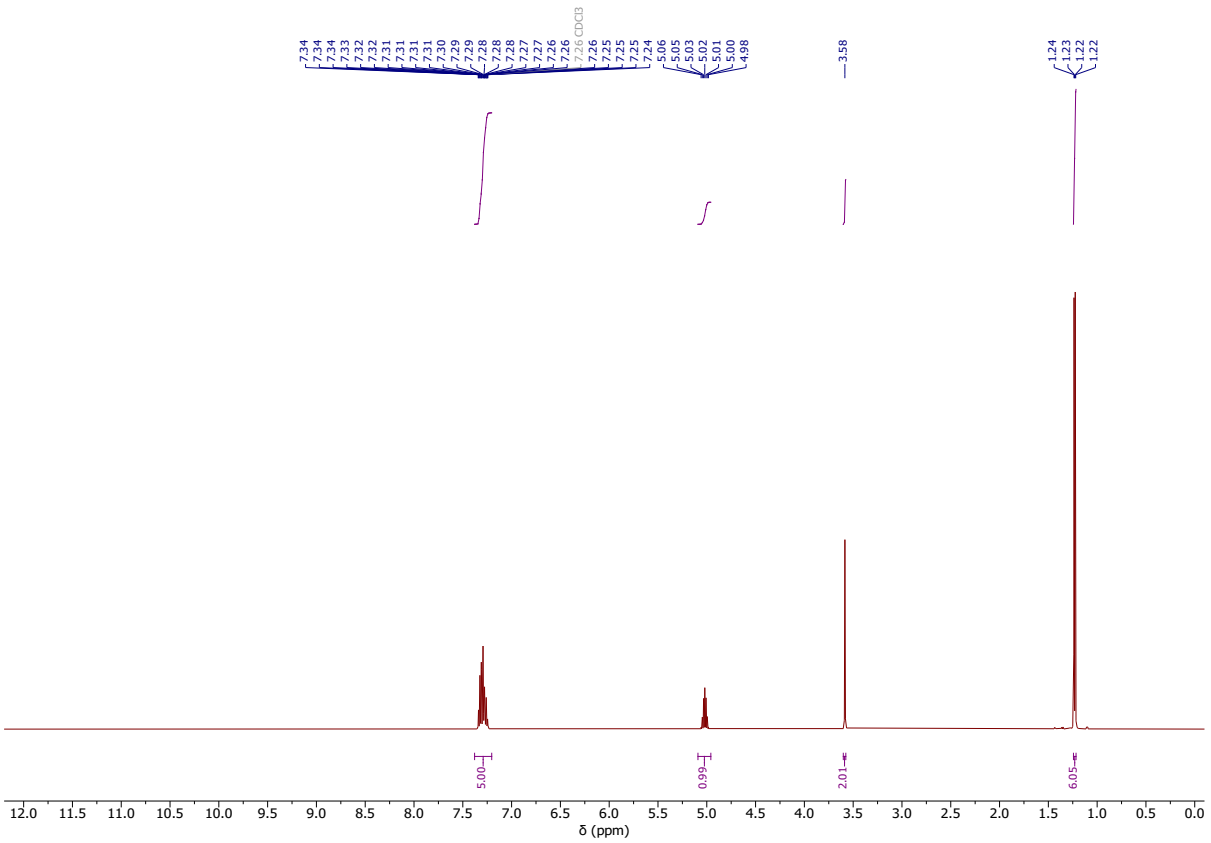
Yield: 92% (326 mg, 1.84 mmol)

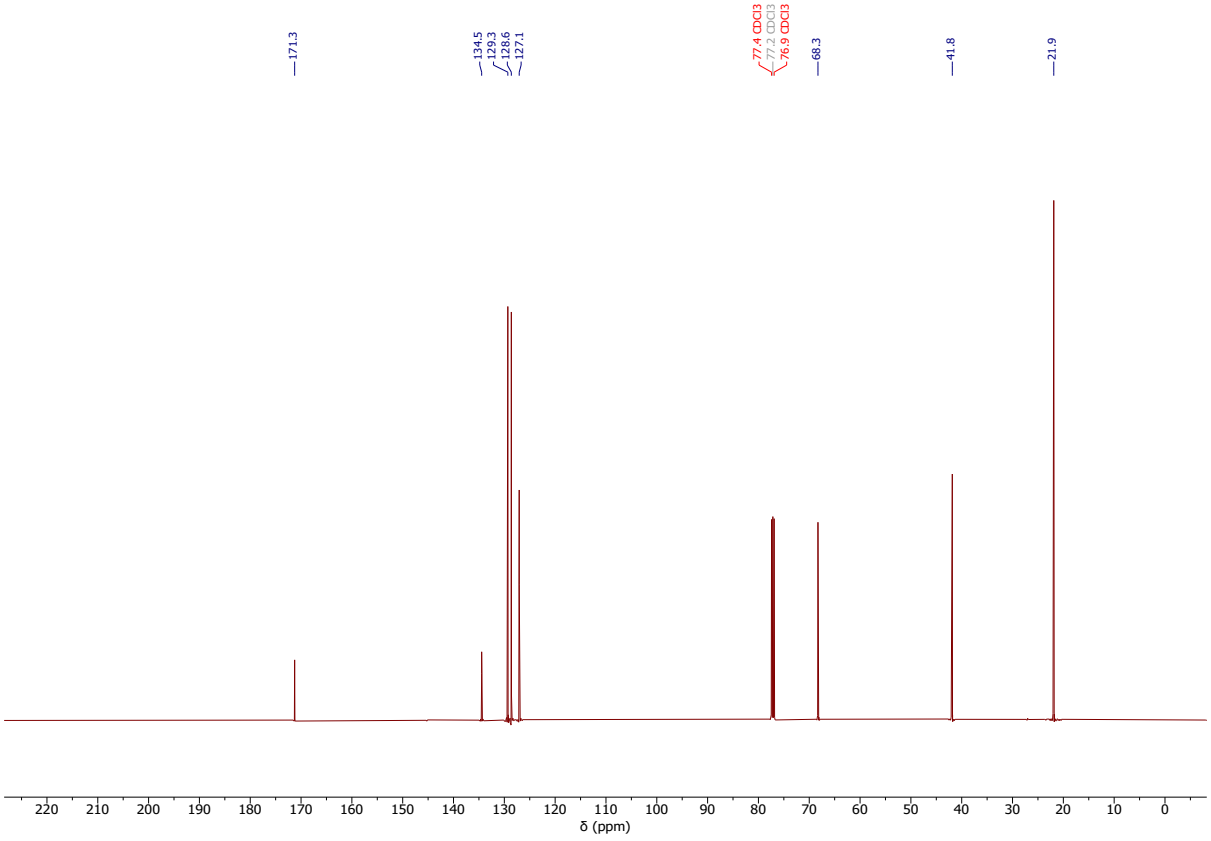
δ_H (500 MHz, Chloroform-*d*) 7.38 – 7.20 (5 H, m), 5.02 (1 H, hept, *J* 6.3), 3.58 (2 H, s), 1.23 (6 H, d, *J* 6.3).

δ_C (126 MHz, Chloroform-*d*) 171.3, 134.5, 129.3, 128.6, 127.1, 68.3, 41.8, 21.9.

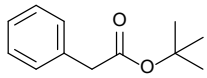
^{1}H- and ^{13}C-NMR were in agreement with the literature.[11]

ESI-MS (+ve) m/z: Found $[M+H]^+$ 179.1068, $C_{11}H_{15}O_2^+$ requires 179.1067.


7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26
7.26 CDCl3
7.26
7.25
7.25
7.25
7.24
5.06
5.05
5.03
5.02
5.01
5.00
4.98
3.58
1.24
1.23
1.22
1.22
5.00
0.99
2.01
6.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


171.3
134.5
129.3
128.6
127.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.3
41.8
21.9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

*tert-Butyl 2-phenylacetate (**10**)*



Chemical Formula: $C_{12}H_{16}O_2$

Molecular Weight: 192.26 $gmol^{-1}$

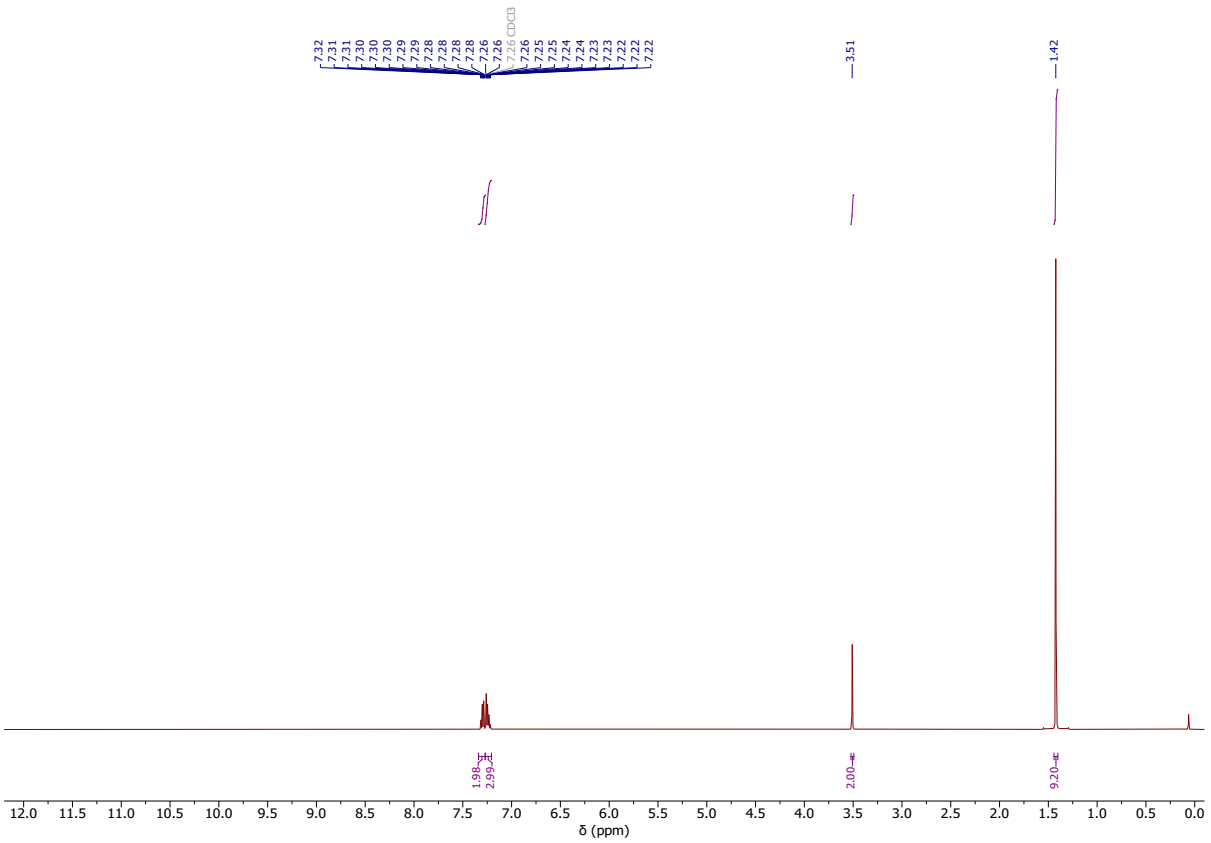
Appearance: Colourless oil

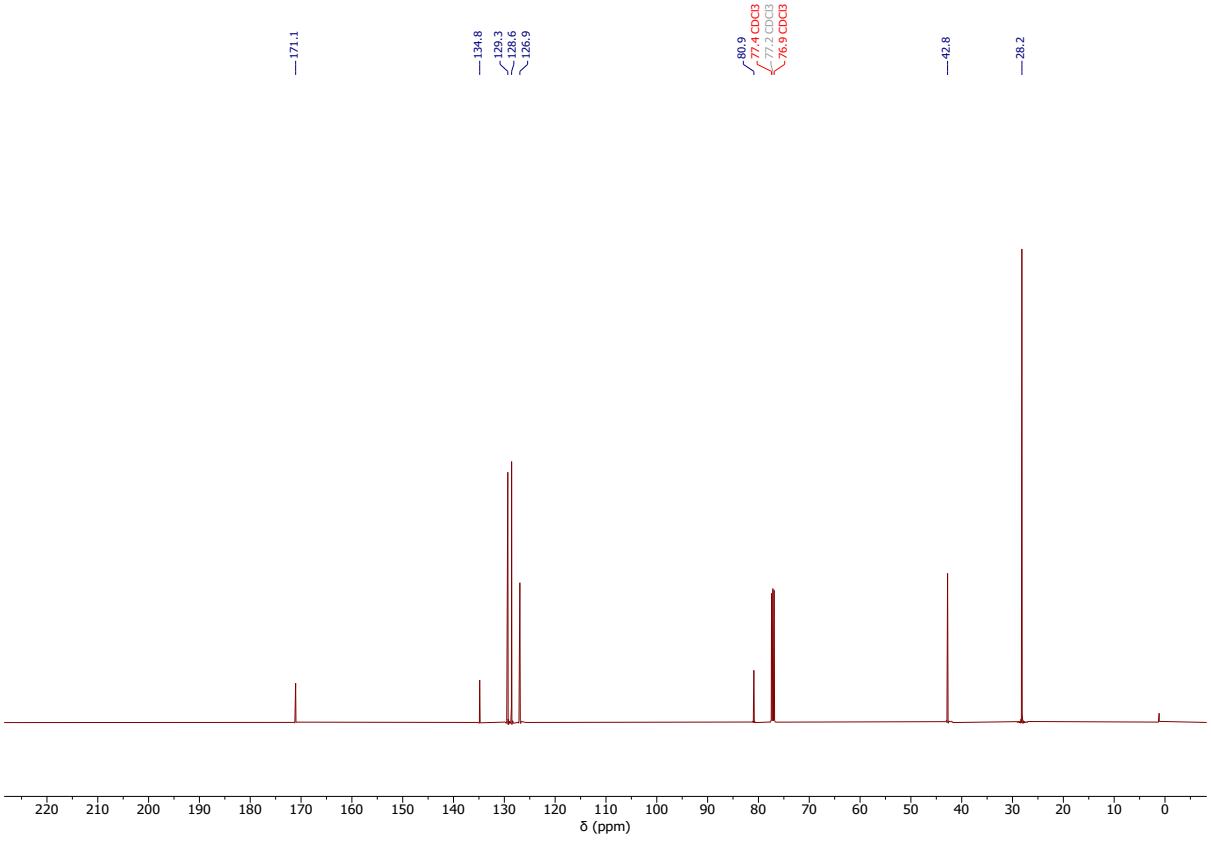
10 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) and *t*-butyl alcohol (190 µL, 2.0 mmol). The product was isolated by general procedure D.

δ_H (500 MHz, Chloroform-*d*) 7.34 – 7.27 (2 H, m), 7.27 – 7.21 (3 H, m), 3.51 (2 H, s), 1.42 (9 H, s).

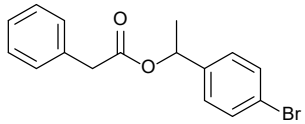
δ_C (126 MHz, Chloroform-*d*) 171.1, 134.8, 129.3, 128.6, 126.9, 80.9, 42.8, 28.2.

^{1}H- and ^{13}C-NMR were in agreement with the literature.[12]


7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.28
7.26
7.26 CDCl3
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.22
3.51
1.42
1.98
2.99
2.00
9.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


171.1
134.8
129.3
128.6
126.9
80.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
42.8
28.2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

*1-(4-bromophenyl)ethyl 2-phenylacetate (**11**)*



Chemical Formula: $C_{16}H_{15}BrO_2$

Molecular Weight: 319.20 $gmol^{-1}$

Appearance: Colourless oil

11 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) and 1-(4-bromophenyl)ethan-1-ol (276 µL, 2.0 mmol). The product was isolated by general procedure D.

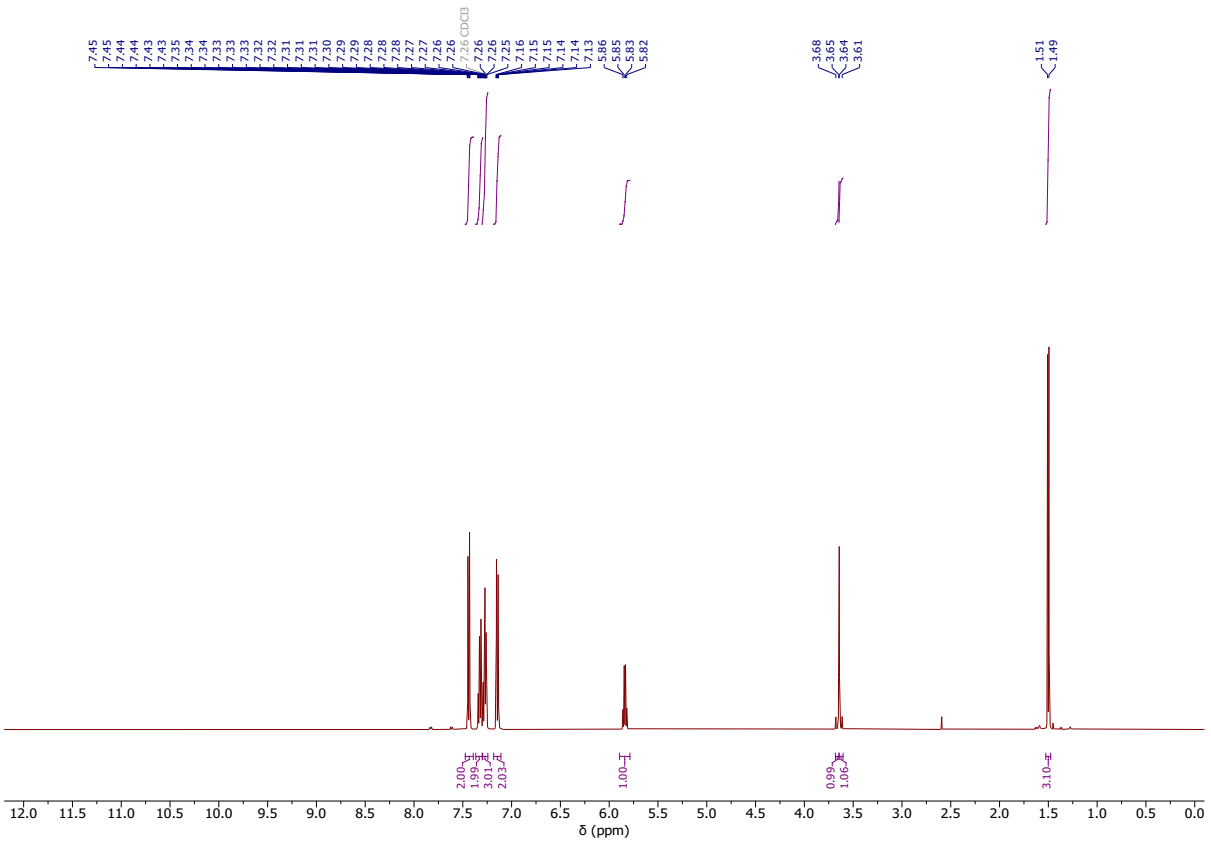
Yield: 80% (520 mg, 1.6 mmol)

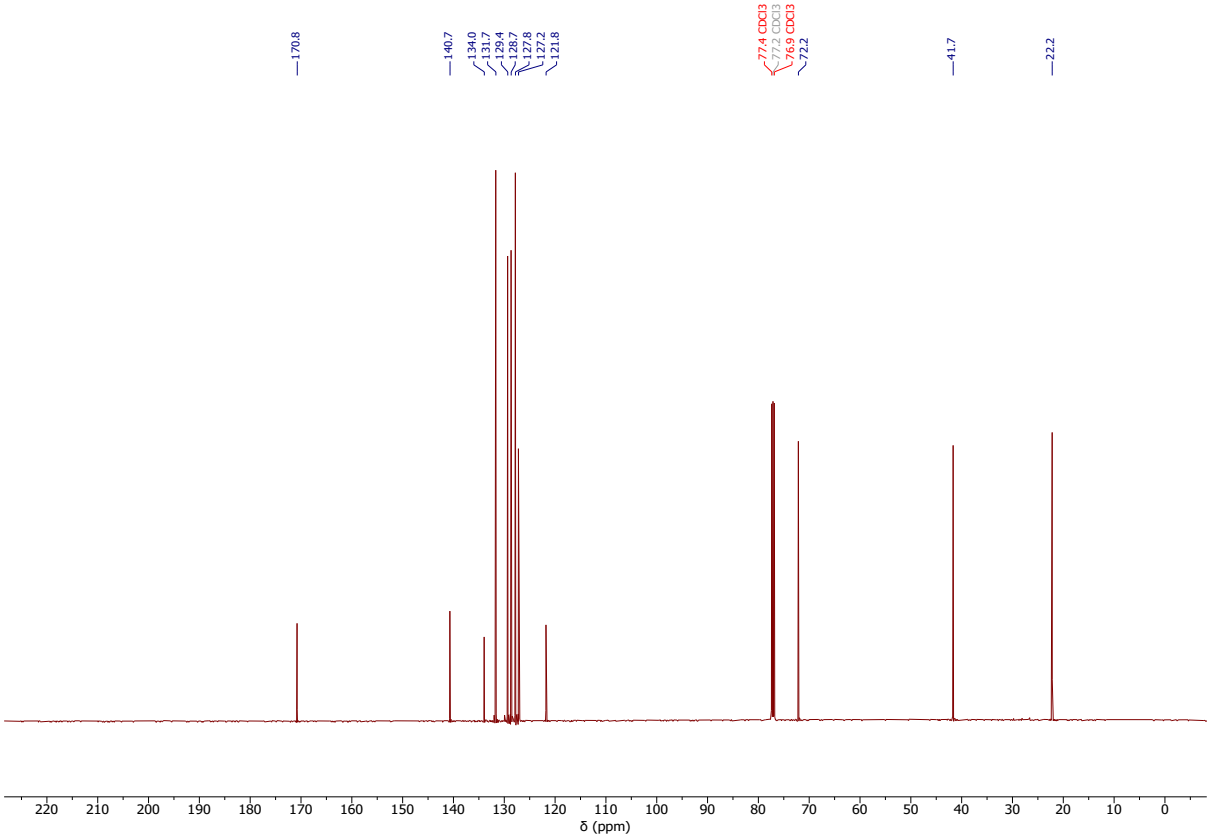
δ_H (500 MHz, Chloroform-*d*) 7.47 – 7.39 (2 H, m), 7.37 – 7.30 (2 H, m), 7.30 – 7.24 (3 H, m), 7.18 – 7.11 (2 H, m), 5.84 (1 H, q, *J* 6.6), 3.66 (1 H, d, *J* 15.1), 3.63 (1 H, d, *J* 15.0), 1.50 (3 H, d, *J* 6.6).

δ_C (126 MHz, Chloroform-*d*) 170.8, 140.7, 134.0, 131.7, 129.4, 128.7, 127.8, 127.2, 121.8, 72.2, 41.7, 22.2.

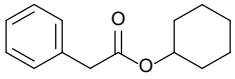
ν_{max}/cm^{-1}:2981, 1730, 2596, 1491, 1454, 1409, 1249, 1150, 1061, 1009, 952, 820, 759, 695, 534.

ESI-MS (+ve) m/z: Found $[M+H]^+$ 319.0327, $C_{16}H_{16}BrO_2^+$ requires 319.0328.


7.45
7.45
7.44
7.44
7.43
7.33
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26
7.26
7.26 CDCl3
7.26
7.25
7.16
7.15
7.15
7.14
7.14
7.13
5.86
5.85
5.83
5.82
3.68
3.65
3.64
3.61
1.51
1.49
2.00
1.99
3.01
2.03
1.00
0.99
1.06
3.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


170.8
140.7
134.0
131.7
129.4
128.7
127.8
127.2
121.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.2
41.7
22.2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

*Cyclohexyl 2-phenylacetate (**12**)*



Chemical Formula: $C_{14}H_{18}O_2$

Molecular Weight: 218.30 $gmol^{-1}$

Appearance: Colourless oil

12 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) and cyclohexanol (208 µL, 2.0 mmol). The product was isolated by general procedure D.

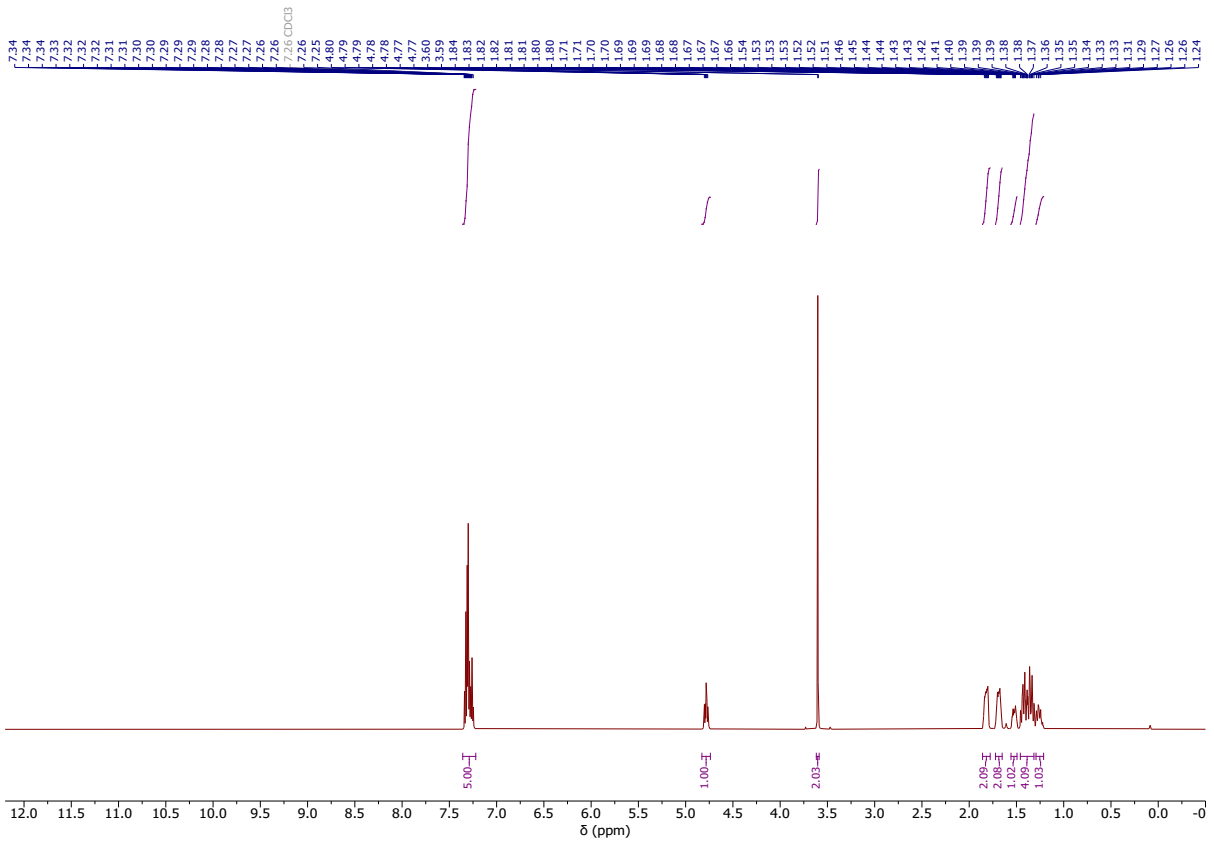
Yield: 83% (361 mg, 1.66 mmol)

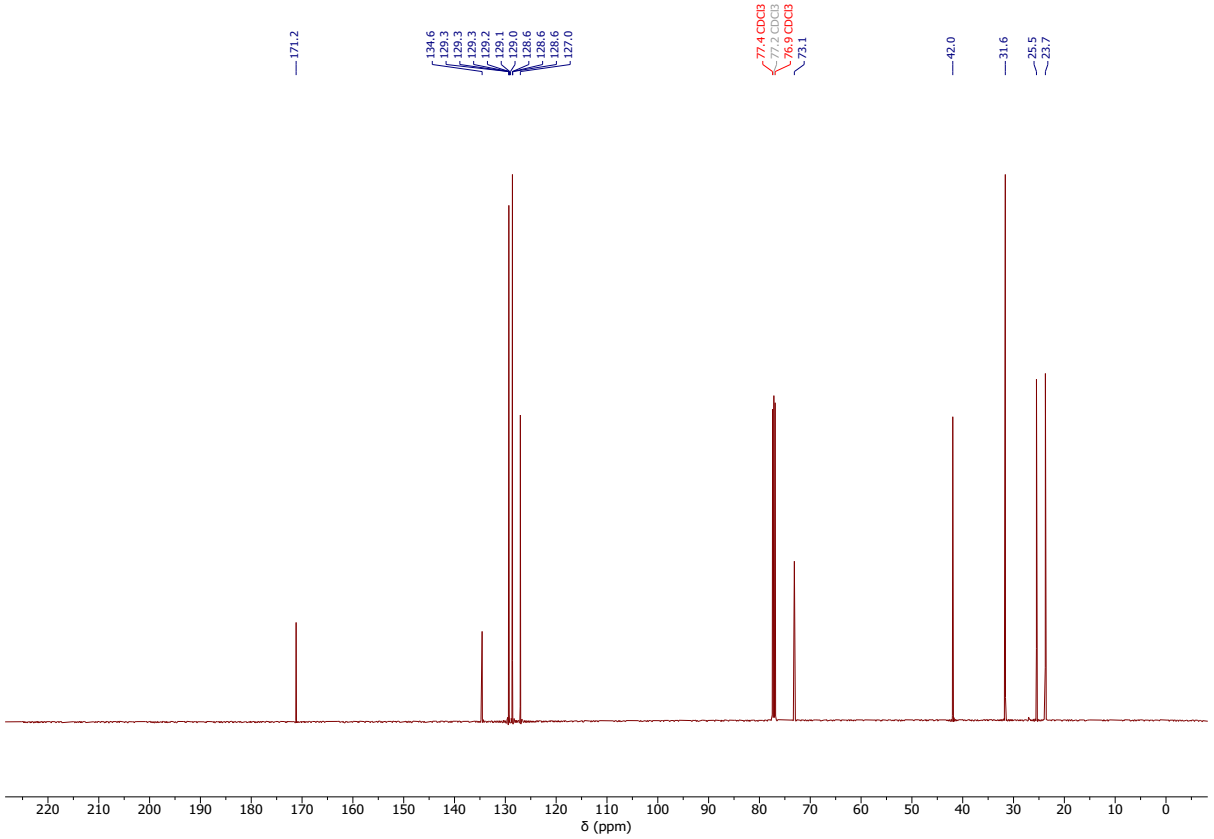
δ_H (500 MHz, Chloroform-*d*) 7.36 – 7.22 (5 H, m), 4.78 (1 H, tt, *J* 9.0, 3.8), 3.60 (2 H, s), 1.86 – 1.78 (2 H, m), 1.72 – 1.65 (2 H, m), 1.56 – 1.49 (1 H, m), 1.46 – 1.31 (4 H, m), 1.29 – 1.21 (1 H, m).

δ_C (126 MHz, Chloroform-*d*) 171.2, 134.6, 129.3, 128.6, 127.0, 73.1, 42.0, 31.6, 25.5, 23.7.

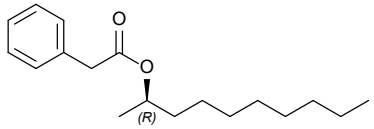
^{1}H- and ^{13}C-NMR were in agreement with the literature.[13]

ESI-MS (+ve) m/z: Found $[M+H]^+$ 219.1378, $C_{14}H_{19}O_2^+$ requires 219.1380.


δ (ppm)


δ (ppm)

*(R)-Decan-2-yl 2-phenylacetate (**13**)*



Chemical Formula: $C_{18}H_{28}O_2$

Molecular Weight: 276.42 $gmol^{-1}$

Appearance: Colourless oil

13 Was synthesised according to general procedure B using phenylacetic acid (190 mg, 1.4 mmol) and (*R*)-decan-2-ol (112 mg, 0.71 mmol). The product was isolated by general procedure D.

Yield: 99% (194 mg, 0.70 mmol)

δ_H (500 MHz, Chloroform-*d*) 7.36 – 7.21 (5 H, m), 4.95 – 4.86 (1 H, m), 3.59 (2 H, s), 1.62 – 1.51 (1 H, m), 1.50 – 1.38 (1 H, m), 1.31 – 1.17 (15 H, m), 0.89 (3 H, t, *J* 7.0).

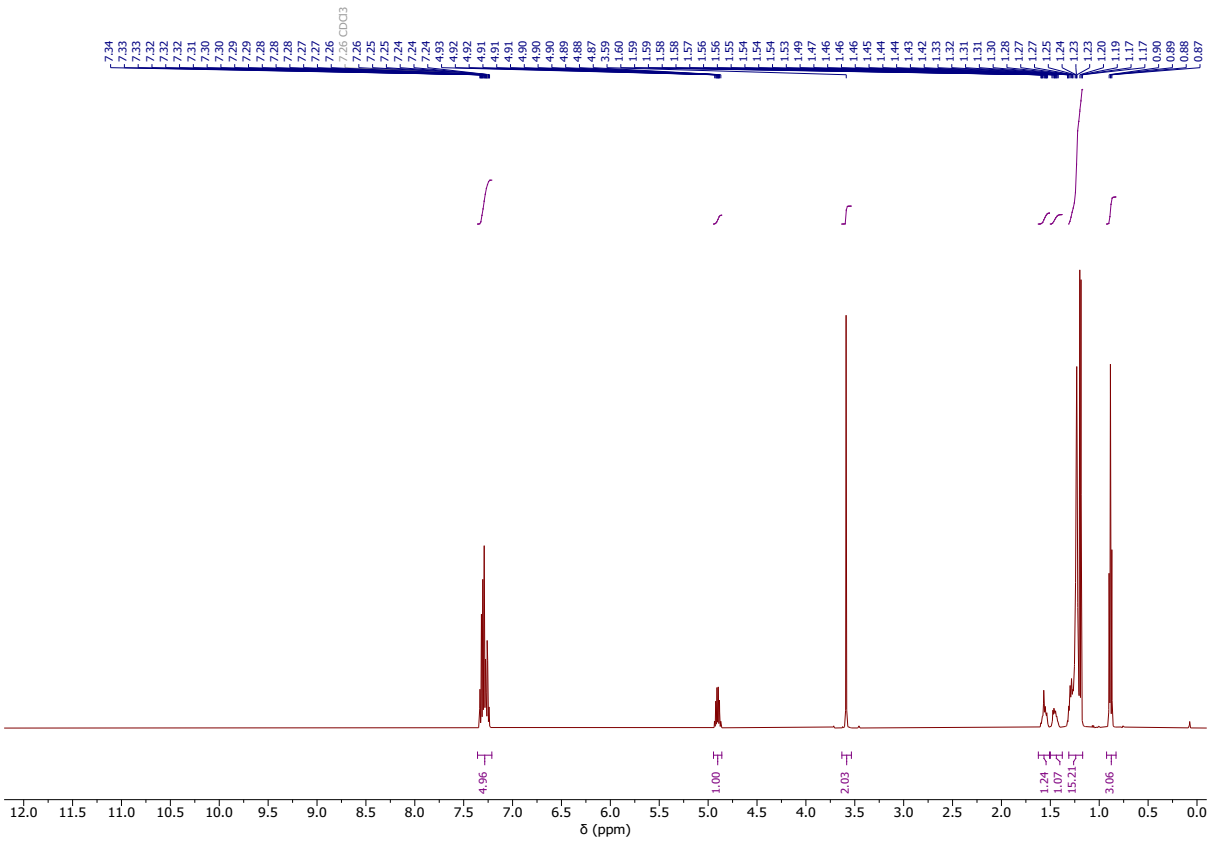
δ_C (126 MHz, Chloroform-*d*) 171.4, 134.5, 129.3, 128.6, 127.1, 71.7, 42.0, 36.0, 32.0, 29.6, 29.5, 29.3, 25.4, 22.8, 20.1, 14.3.

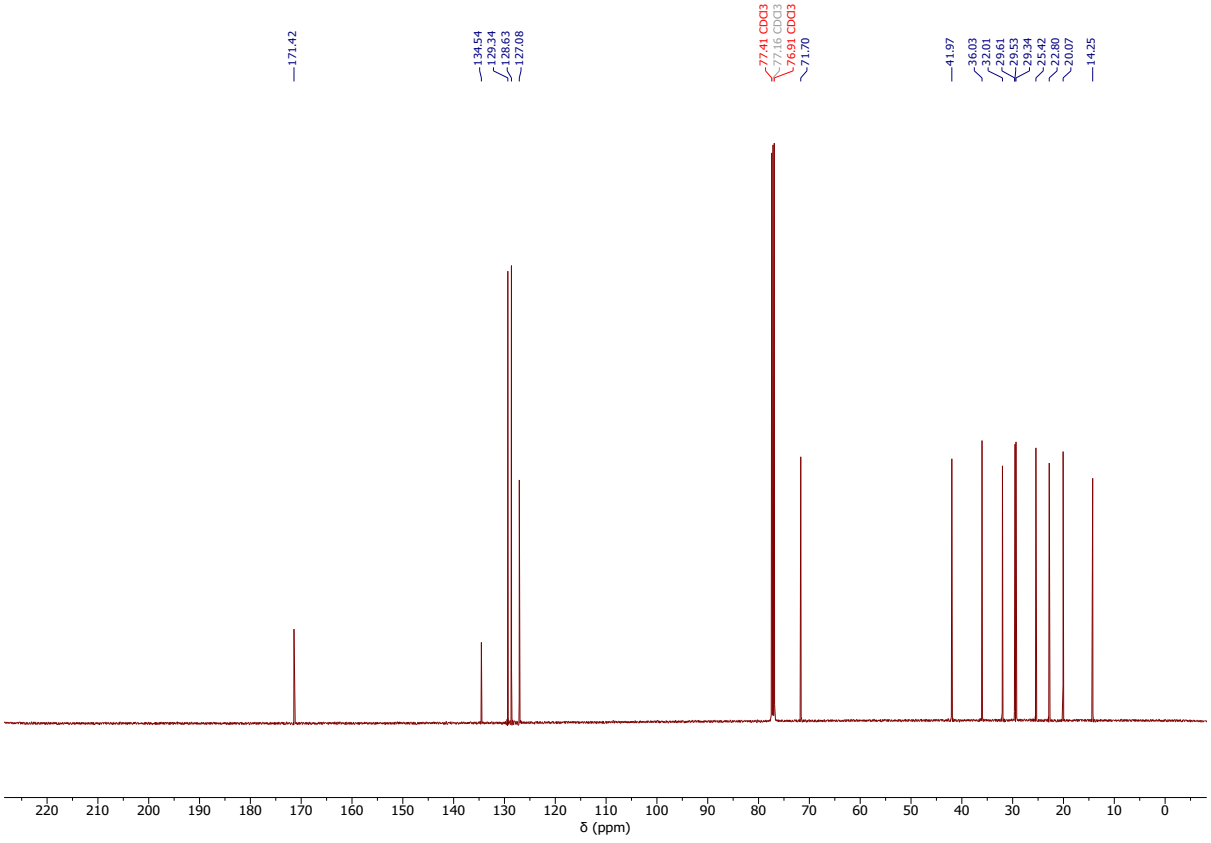
ν_{max}/cm^{-1}: 2925, 2855, 1731, 1497, 1455, 1257, 1121, 1074, 960, 720, 695, 534, 472

ESI-MS (+ve) m/z: Found $[M+H]^+$ 277.2159, $C_{18}H_{29}O_2^+$ requires 277.2162

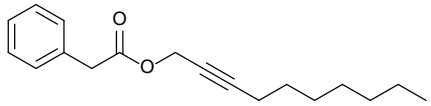
$[\alpha]_D^{25}$ = -7.6 (2.1 c, EtOH)

(*R*)-decan-2-ol: $[\alpha]_D^{20}$ = -8.0 (1.0 c, $CHCl_3$).[14]


7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 CDCl3 7.25 7.25 7.24 7.24 7.24 4.93 4.92 4.92 4.91 4.91 4.91 4.90 4.90 4.90 4.89 4.88 4.87 3.59 1.60 1.59 1.59 1.58 1.58 1.57 1.56 1.56 1.55 1.54 1.54 1.54 1.53 1.49 1.47 1.46 1.46 1.45 1.44 1.44 1.43 1.42 1.33 1.32 1.31 1.31 1.30 1.28 1.27 1.27 1.25 1.24 1.23 1.23 1.20 1.19 1.17 1.17 0.90 0.89 0.88 0.87
4.96
1.00
2.03
1.24
1.07
15.21
3.06
δ (ppm)


171.42
134.54
129.34
128.63
127.08
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
71.70
41.97
36.03
32.01
29.61
29.53
29.34
25.42
22.80
20.07
14.25
δ (ppm)

*Dec-2-yn-1-yl 2-phenylacetate (**14**)*



Chemical Formula: $C_{18}H_{24}O_2$

Molecular Weight: 272.39 $gmol^{-1}$

Appearance: Colourless oil

14 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) dec-2-yn-1-ol (309 mg, 2.0 mmol). The product was isolated by general procedure D.

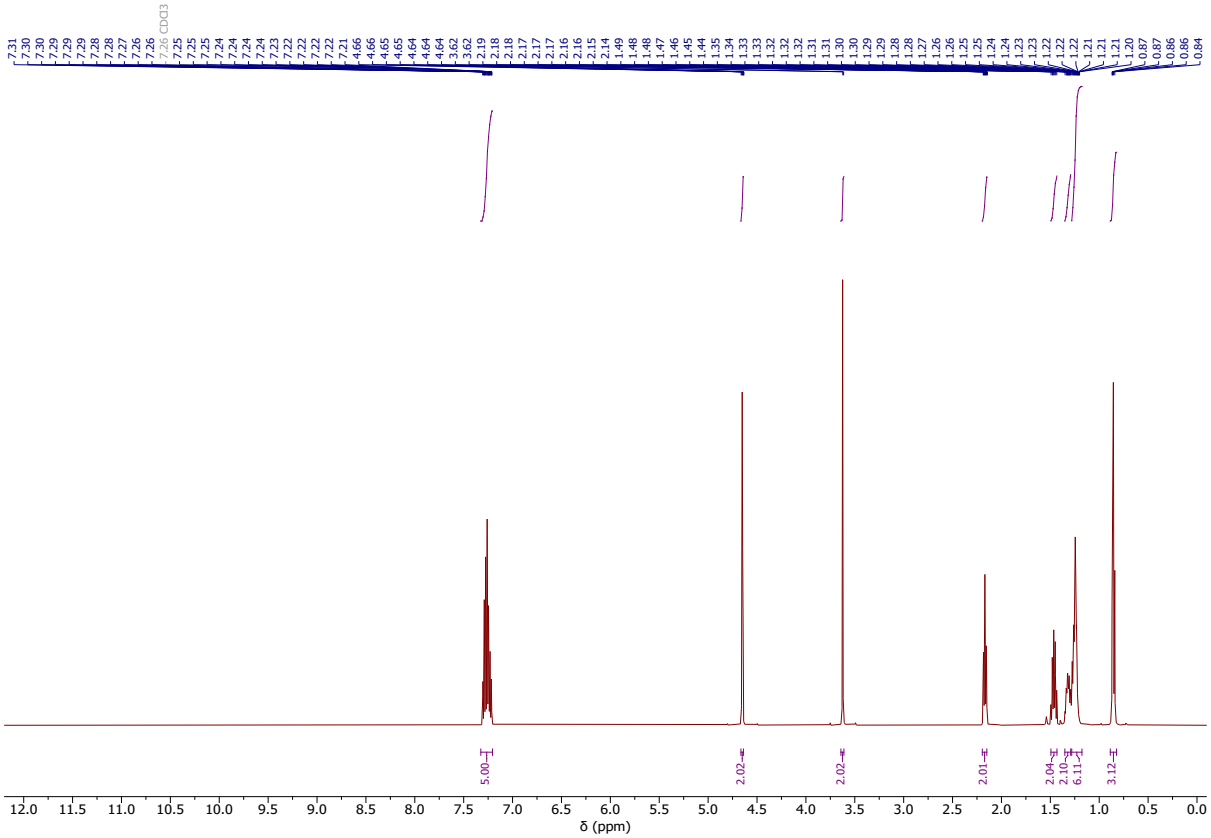
Yield: 81% (443 mg, 1.6 mmol)

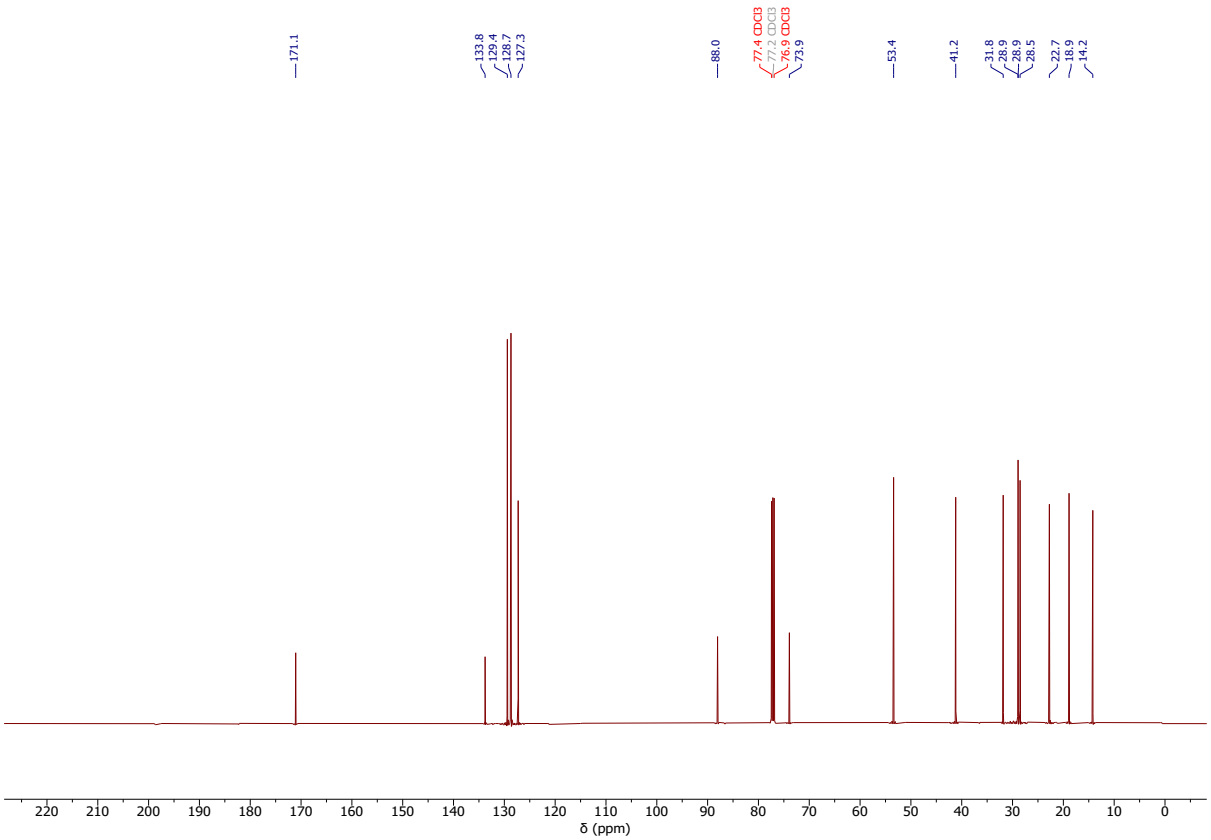
δ_H (500 MHz, Chloroform-*d*) 7.33 – 7.21 (5 H, m), 4.65 (2 H, t, *J* 2.2), 3.62 (2 H, s), 2.17 (2 H, tt, *J* 7.1, 2.2), 1.49 – 1.43 (2 H, m), 1.35 – 1.29 (2 H, m), 1.25 (6 H, ttd, *J* 7.1, 5.8, 4.6, 1.4), 0.87 – 0.82 (3 H, m).

δ_C (126 MHz, Chloroform-*d*) 171.1, 133.8, 129.4, 128.7, 127.3, 88.0, 73.9, 53.4, 41.2, 31.8, 28.91, 28.90, 28.5, 22.7, 18.9, 14.2.

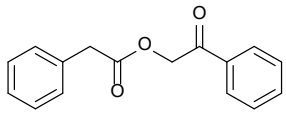
ν_{max}/cm^{-1}: 2928, 2856, 1741, 1497, 1455, 1372, 1239, 1138, 980, 721, 696, 471.

ESI-MS (+ve) m/z: Found $[M+H]^+$ 273.1853, $C_{18}H_{25}O_2^+$ requires 273.1849


δ (ppm)


δ (ppm)

*2-oxo-2-phenylethyl 2-phenylacetate (**15**)*



Chemical Formula: $C_{16}H_{14}O_3$

Molecular Weight: 254.29 $gmol^{-1}$

Appearance: Colourless oil

15 Was synthesised according to general procedure B using phenylacetic acid (272 mg, 2.0 mmol) 2-hydroxy-1-phenylethan-1-one (272 mg, 2.0 mmol). The product was isolated by general procedure C.

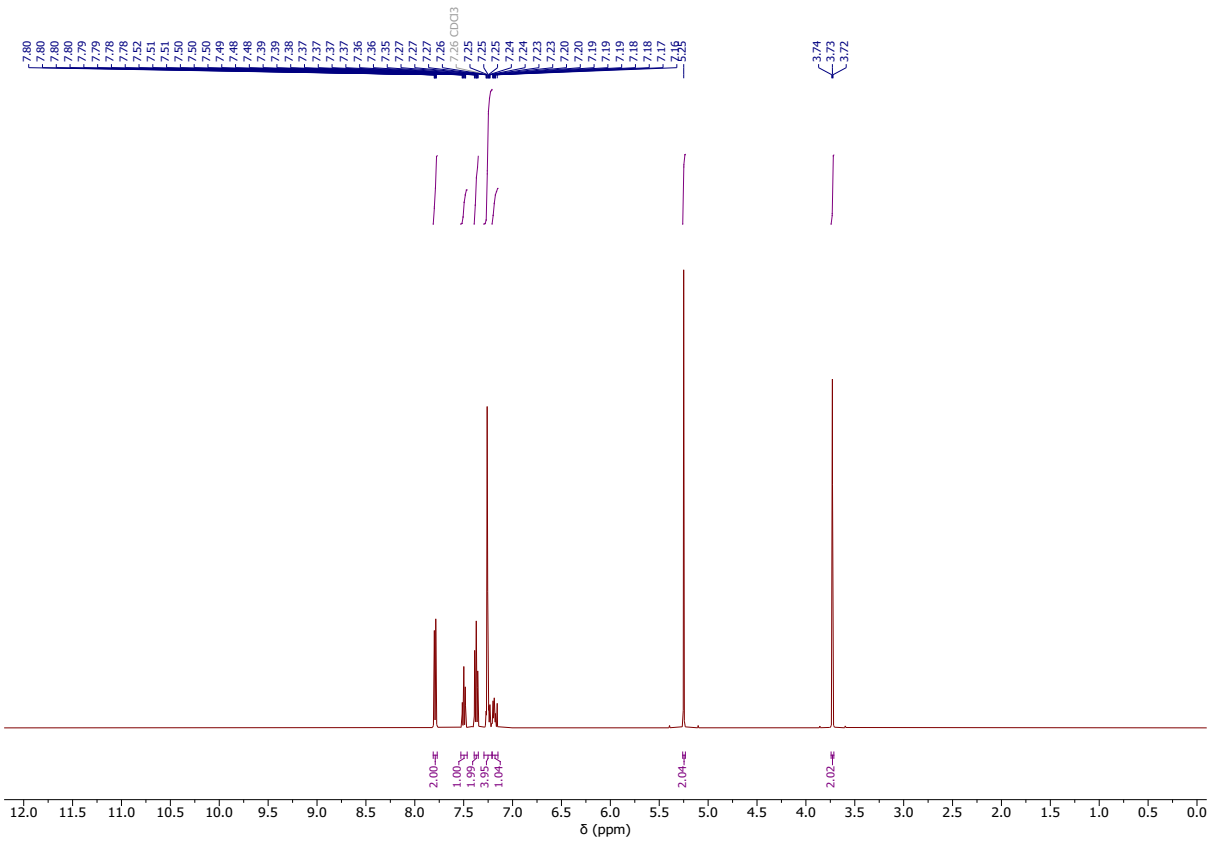
Yield: 87% (441 mg, 1.74 mmol)

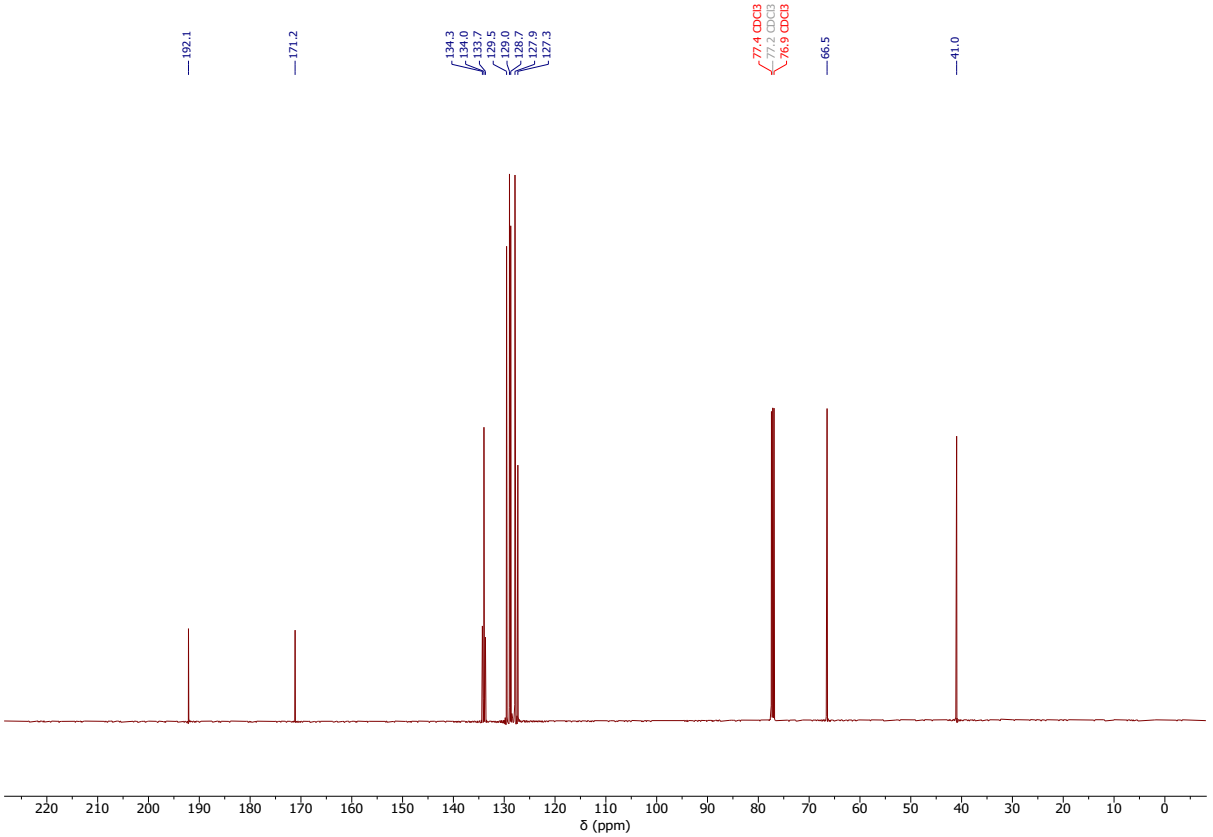
δ_H (500 MHz, Chloroform-*d*) 7.81 – 7.77 (2 H, m), 7.53 – 7.46 (1 H, m), 7.39 – 7.35 (2 H, m), 7.29 – 7.21 (4 H, m), 7.21 – 7.15 (1 H, m), 5.25 (2 H, s), 3.73 (2 H, s).

δ_C (126 MHz, Chloroform-*d*) 192.1, 171.2, 134.3, 134.0, 133.7, 129.5, 129.0, 128.7, 127.9, 127.3, 66.5, 41.0.

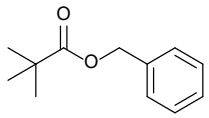
^{1}H- and ^{13}C-NMR were in agreement with the literature.[13]

ESI-MS (+ve) m/z: Found $[M+H]^+$ 255.1015, $C_{16}H_{15}O_3^+$ requires 255.1016.


7.80
7.80
7.80
7.80
7.79
7.79
7.78
7.78
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.48
7.48
7.39
7.39
7.38
7.37
7.37
7.37
7.37
7.36
7.36
7.35
7.27
7.27
7.27
7.26 CDCl3
7.25
7.25
7.25
7.24
7.24
7.23
7.23
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.17
7.16
5.25
3.74
3.73
3.72
2.00
1.00
1.99
3.95
1.04
2.04
2.02
δ (ppm)


192.1
171.2
134.3
134.0
133.7
129.5
129.0
128.7
127.9
127.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
66.5
41.0
δ (ppm)

*Benzyl pivalate (**16**)*



Chemical Formula: $C_{12}H_{16}O_2$

Molecular Weight: 192.26 $gmol^{-1}$

Appearance: Colourless oil

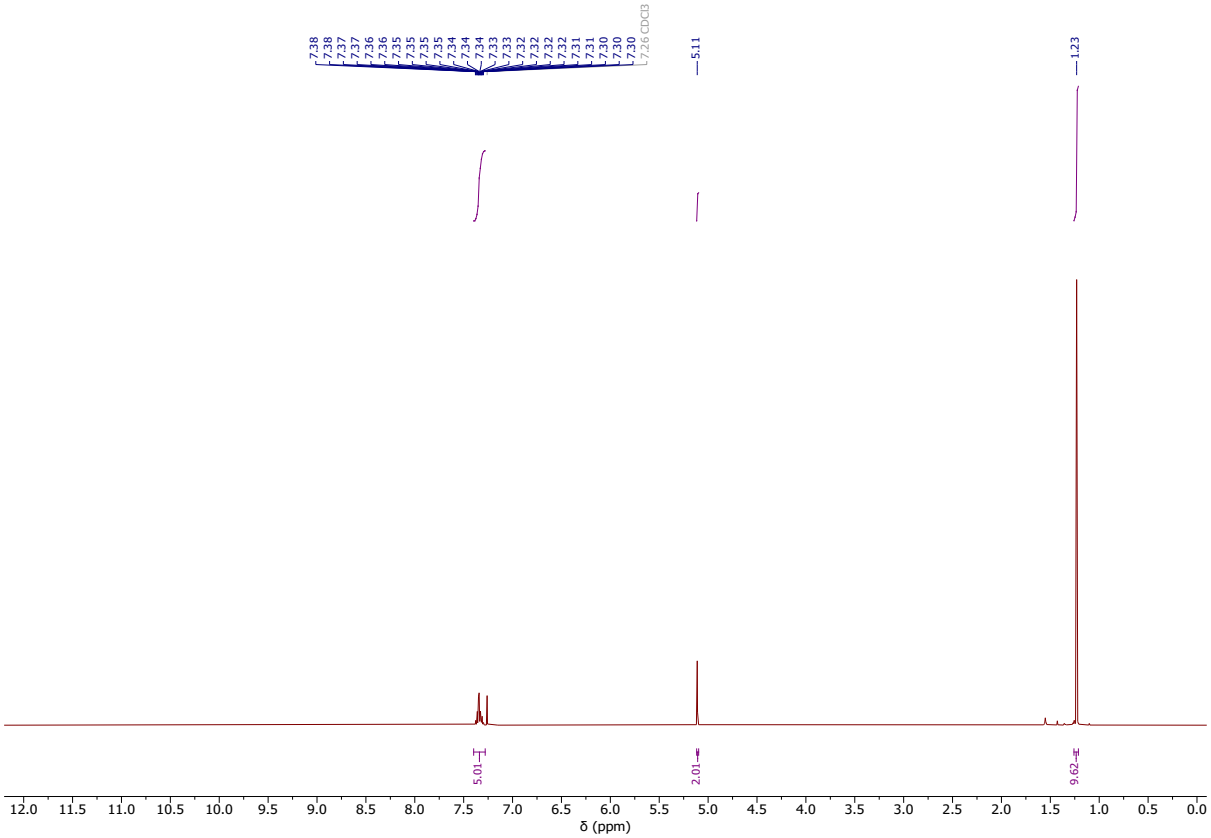
16 Was synthesised according to general procedure B using pivalic acid (204 mg, 2.0 mmol) and benzyl alcohol (208 µL, 2.0 mmol). The product was isolated by general procedure C.

Yield: 50% (193 mg, 1.0 mmol)

δ_H (500 MHz, Chloroform-*d*) 7.39 – 7.28 (5 H, m), 5.11 (2 H, s), 1.23 (9 H, s).

δ C (126 MHz, Chloroform-d) 178.5, 136.6, 128.6, 128.1, 127.8, 66.2, 39.0, 27.3.

^{1}H- and ^{13}C-NMR were in agreement with the literature.[15]


7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.32
7.31
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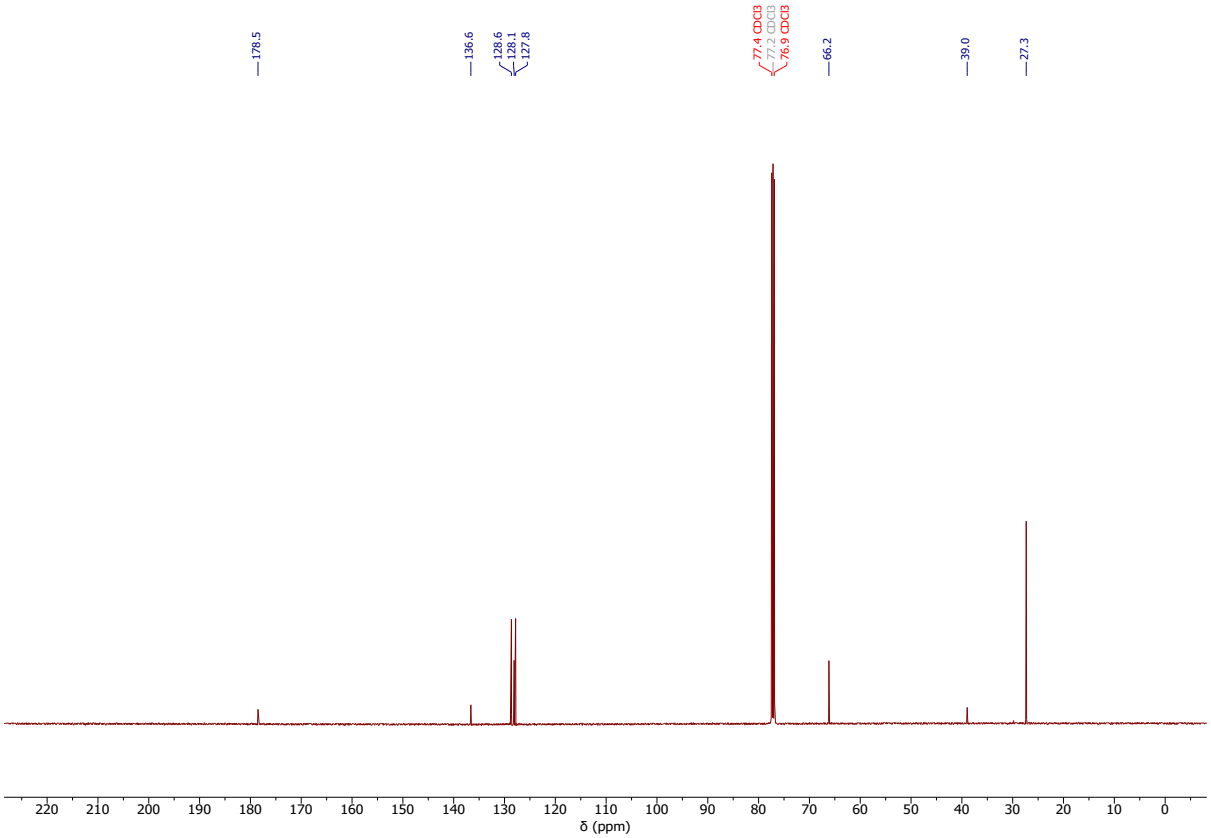
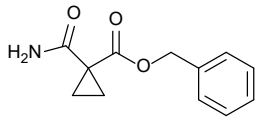
7.26 CDCl3
5.11
1.23
5.01
2.01
9.62
δ (ppm)


178.5
136.6
128.6
128.1
127.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
66.2
39.0
27.3
δ (ppm)

*Benzyl 1-carbamoylcyclopropane-1-carboxylate (**17**)*



Chemical Formula: $C_{12}H_{13}NO_3$

Molecular Weight: 219.24 $gmol^{-1}$

Appearance: White solid

17 Was synthesised according to general procedure B using 1-carbamoylcyclopropane-1-carboxylic acid (244 mg, 1.5 mmol) and benzyl alcohol (156 µL, 1.5 mmol). The product was isolated by general procedure C using a 0-40% EtOAc-cyclohexane gradient.

Yield: 53% (174 mg, 0.80 mmol)

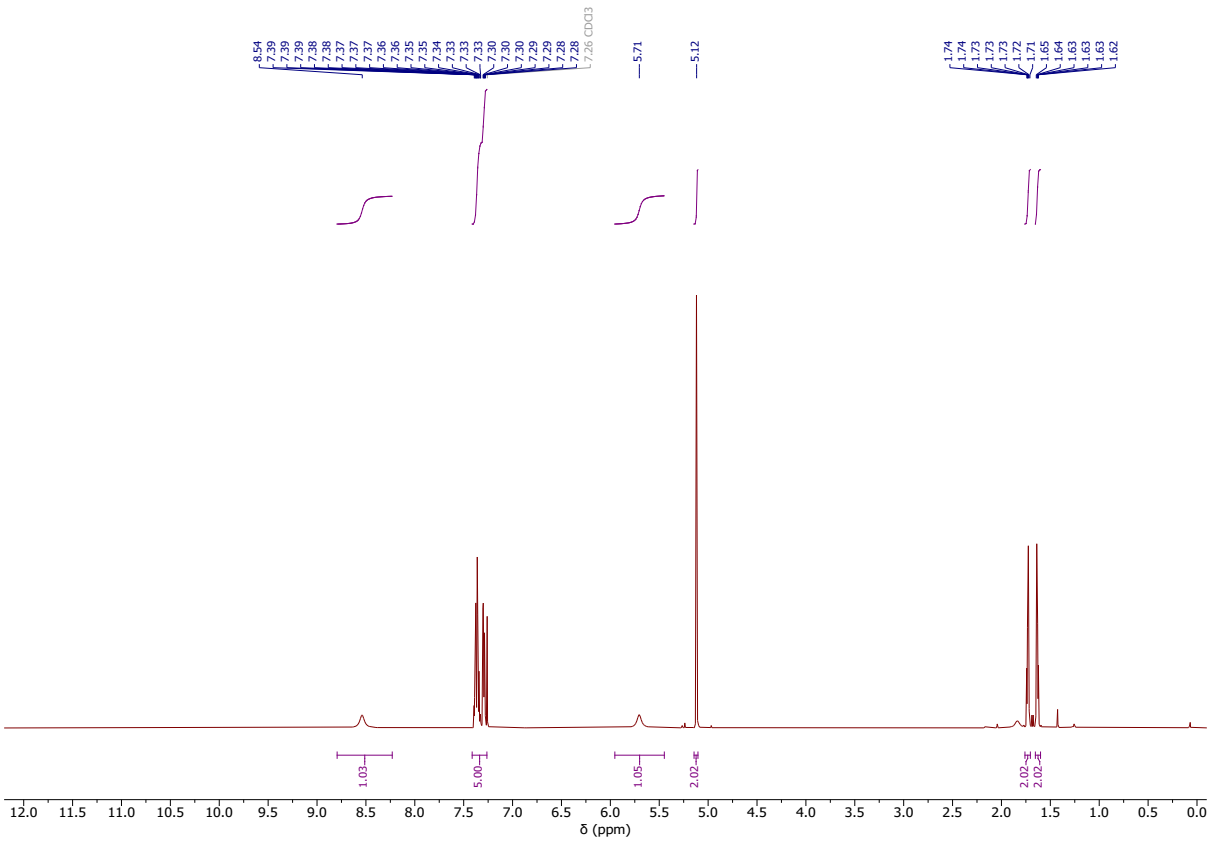
M. P: 130-132 °C

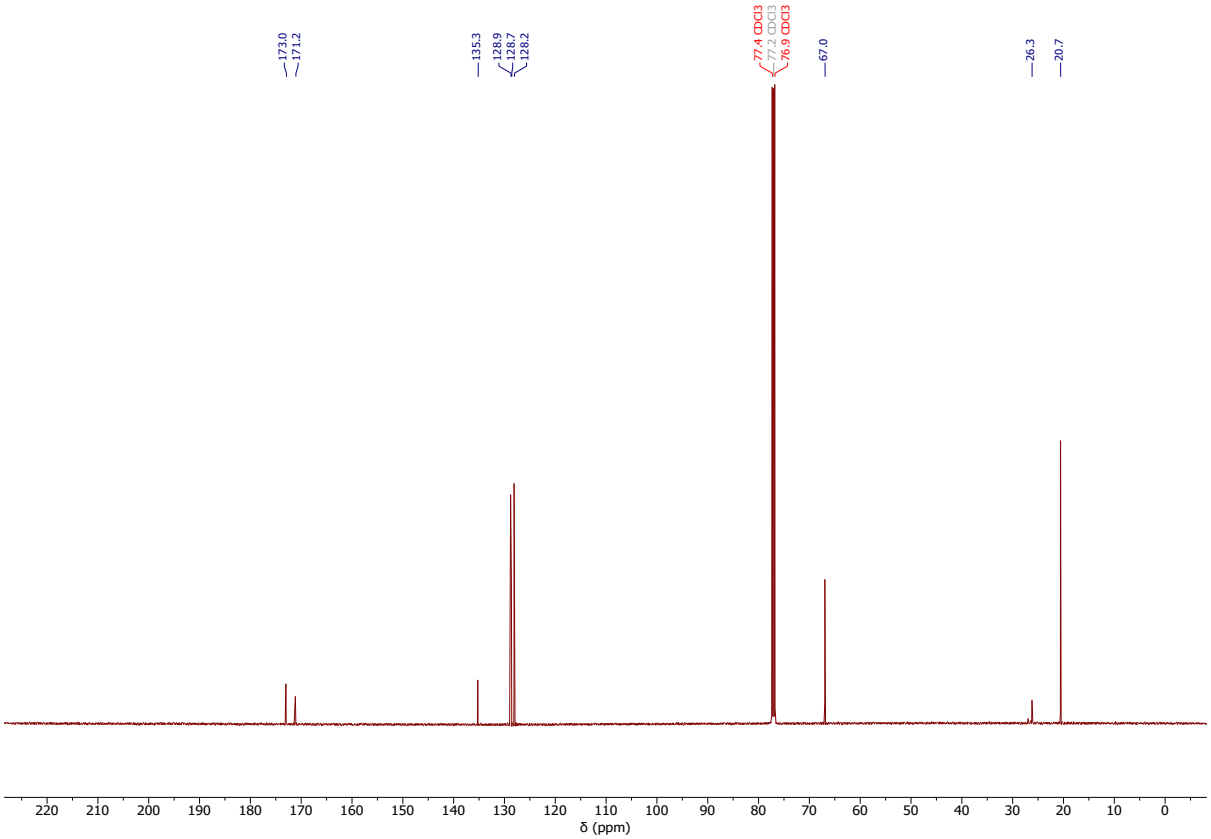
δ_H (500 MHz, Chloroform-*d*) 8.54 (1 H, bs), 7.41 – 7.26 (5 H, m), 5.71 (1 H, bs), 5.12 (2 H, s), 1.76 – 1.71 (2 H, m), 1.65 – 1.60 (2 H, m).

δ_C (126 MHz, Chloroform-*d*) 173.0, 171.2, 135.3, 128.9, 128.7, 128.2, 67.0, 26.3, 20.7.

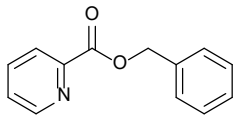
ν_{max}/cm^{-1}: 3403, 3223, 1714, 1667, 1641, 1604, 1459, 1406, 1306, 1140, 976, 840, 750, 699, 623, 585, 528.

ESI-MS (+ve) m/z: Found $[M+H]^+$ 220.0970, $C_{12}H_{14}NO_3^+$ requires 220.0968


8.54
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.26 CDCl3
5.71
5.12
1.74
1.74
1.73
1.73
1.73
1.72
1.71
1.65
1.64
1.63
1.63
1.63
1.62
1.03
5.00
1.05
2.02
2.02
2.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


173.0
171.2
135.3
128.9
128.7
128.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
67.0
26.3
20.7
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

*Benzyl picolinate (**18**)*



Chemical Formula: $C_{13}H_{11}NO_2$

Molecular Weight: 213.24 $gmol^{-1}$

Appearance: Colourless oil

18 Was synthesised according to general procedure B using picolinic acid (246 mg, 2.0 mmol) and benzyl alcohol (208 µL, 1.5 mmol). 2,6-Lutidine was replaced with TEA (609 µL, 4.8 mmol) The product was isolated by general procedure C using a 0-40% EtOAc-cyclohexane gradient with 1% conc. NH_3 added to the EtOAc phase.

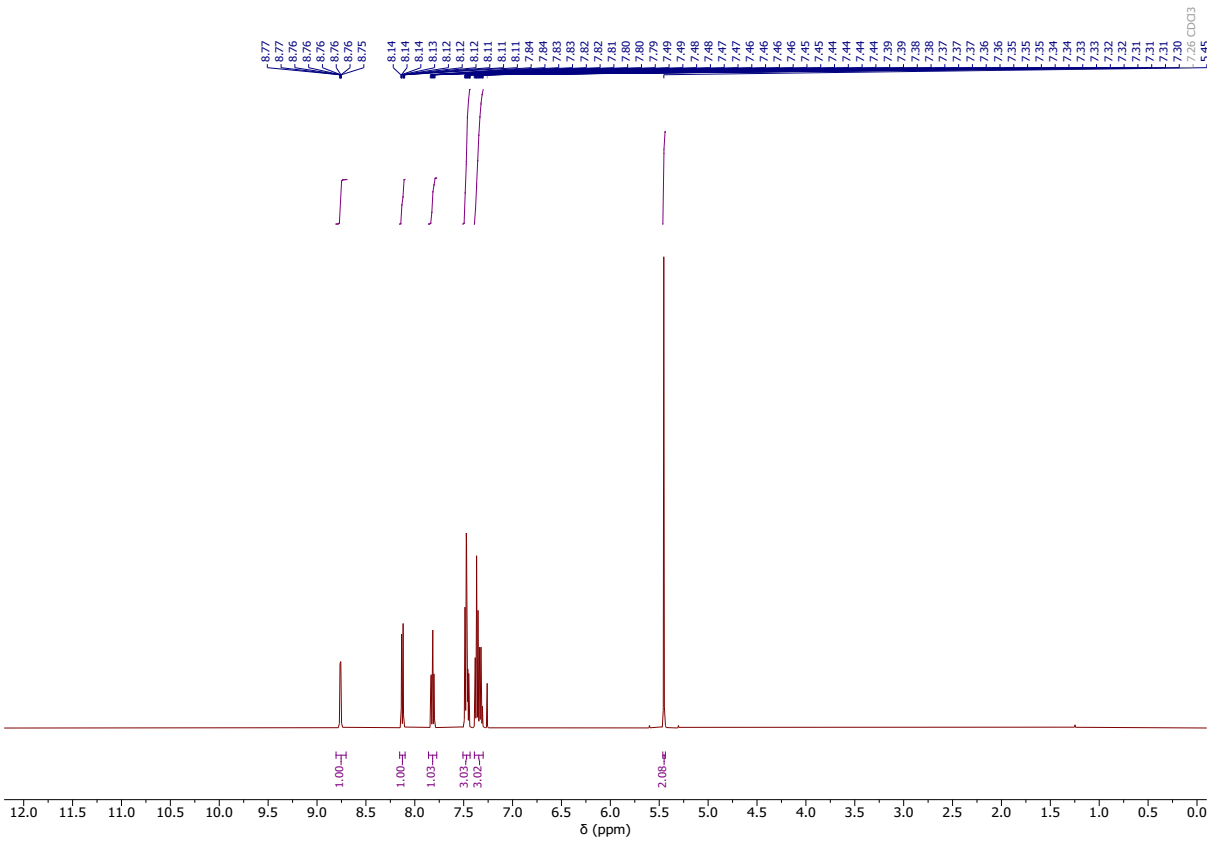
Yield: 88% (374 mg, 1.75 mmol)

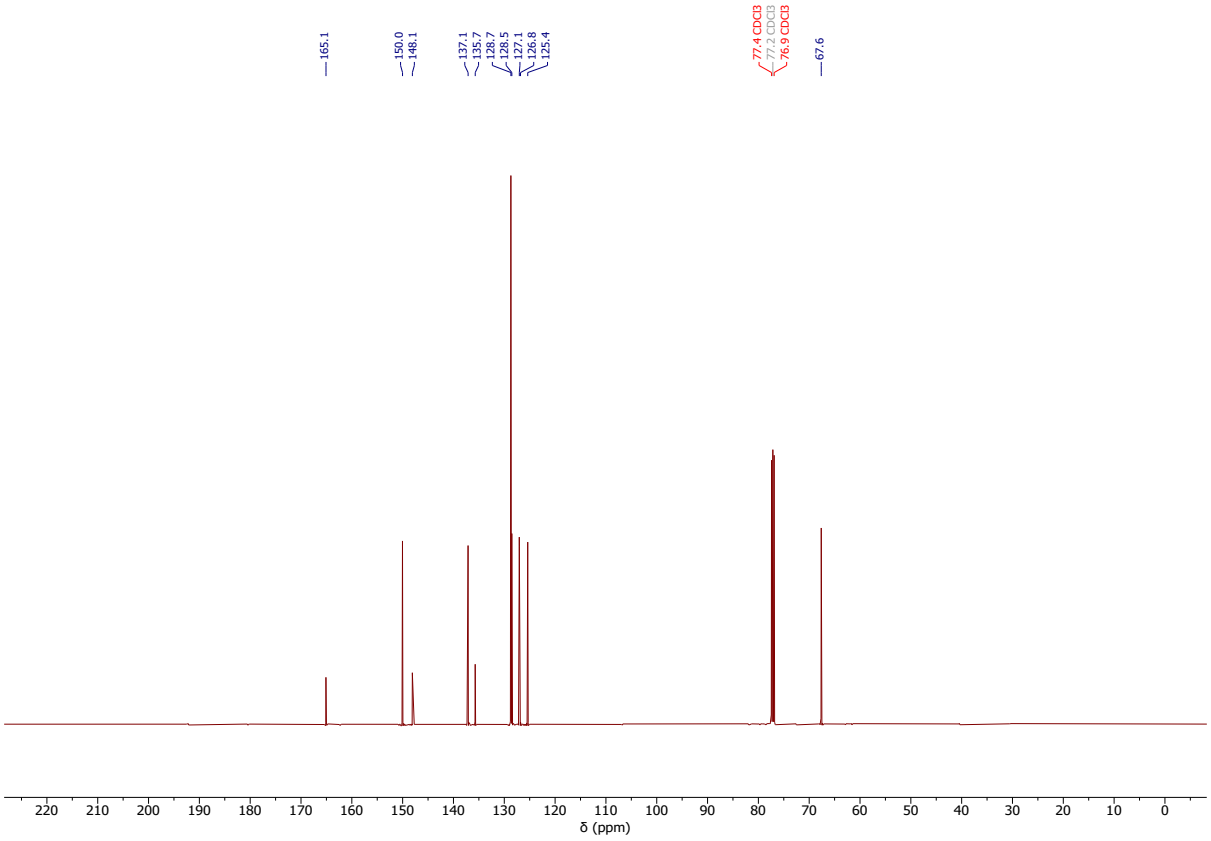
δ_H (500 MHz, Chloroform-*d*) 8.76 (1 H, ddd, *J* 4.7, 1.8, 0.9), 8.13 (1 H, dt, *J* 8.0, 1.1), 7.82 (1 H, td, *J* 7.7, 1.8), 7.47 (3 H, tdd, *J* 7.6, 4.3, 1.5), 7.39 – 7.30 (3 H, m), 5.45 (2 H, s).

δ_C (126 MHz, Chloroform-*d*) 165.1, 150.0, 148.1, 137.1, 135.7, 128.7, 128.5, 127.1, 126.8, 125.4, 67.6.

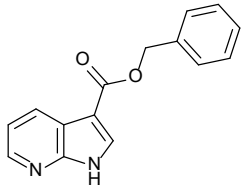
^{1}H- and ^{13}C-NMR were in agreement with the literature.[16]

ESI-MS (+ve) m/z: Found $[M+H]^+$ 214.0854, $C_{13}H_{12}NO_2^+$ requires 214.0863.


8.77
8.76
8.75
8.14
8.13
8.12
8.11
7.84
7.83
7.82
7.81
7.80
7.79
7.49
7.48
7.47
7.46
7.45
7.44
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.26 CDCl3
1.00
1.00
1.03
3.03
3.02
2.08
δ (ppm)


165.1
150.0
148.1
137.1
135.7
128.7
128.5
127.1
126.8
125.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
67.6
δ (ppm)

*Benzyl 1H-pyrrolo[2,3-b]pyridine-3-carboxylate (**19**)*



Chemical Formula: $C_{15}H_{12}N_2O_2$

Molecular Weight: 252.27 $gmol^{-1}$

Appearance: White solid

19 Was synthesised according to general procedure B using 1H-pyrrolo[2,3-b]pyridine-3-carboxylic acid (233 mg, 1.44 mmol) and benzyl alcohol (150 µL, 1.44 mmol). 2,6-Lutidine was replaced with TEA (411 µL, 4.8 mmol) The product was isolated by general procedure C using a 0-40% EtOAc-cyclohexane gradient with 1% conc. NH_3 added to the EtOAc phase.

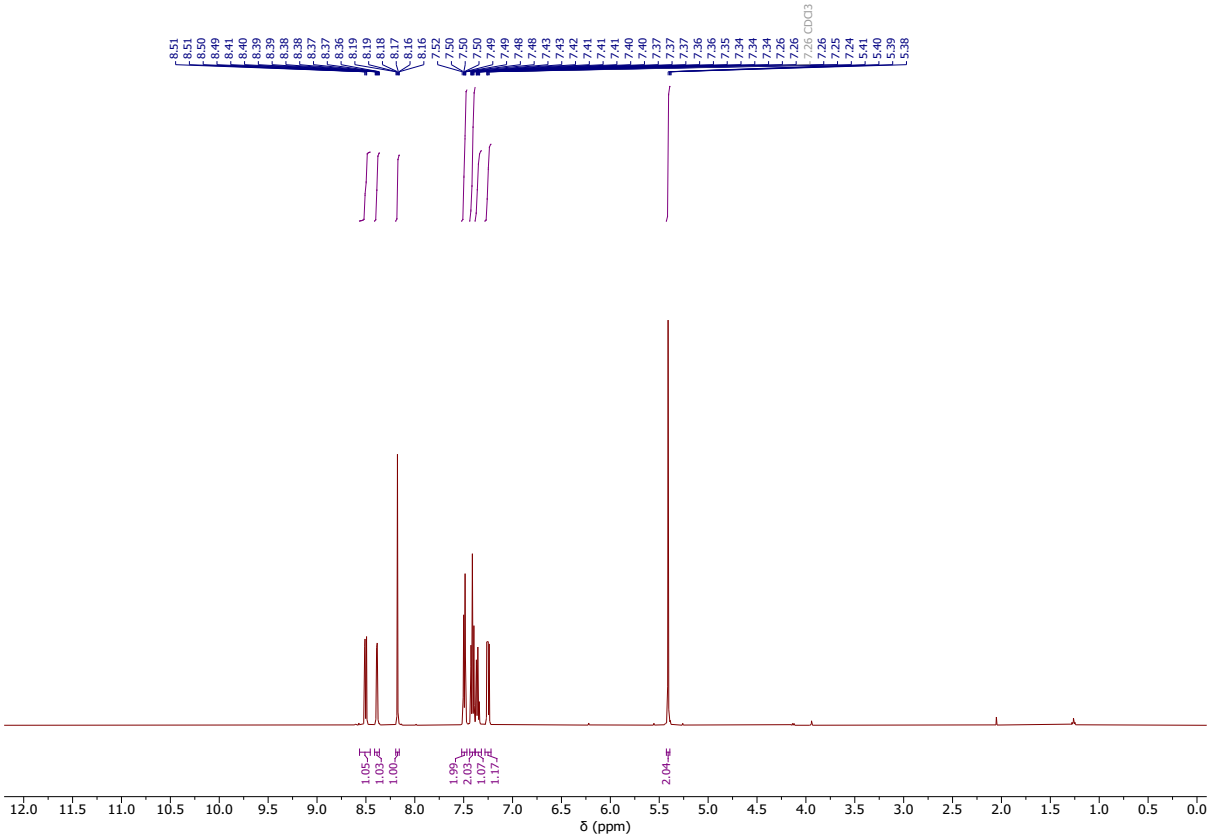
M. P.: 177-179 °C

δ_H (500 MHz, Chloroform-*d*) 8.50 (1 H, dd, *J* 7.9, 1.6), 8.39 (1 H, dd, *J* 4.8, 1.6), 8.18 (1 H, s), 7.52 – 7.47 (2 H, m), 7.44 – 7.38 (2 H, m), 7.38 – 7.32 (1 H, m), 7.25 (1 H, dd, *J* 7.9, 4.8), 5.41 (2 H, s).

δ_C (126 MHz, Chloroform-*d*) 164.5, 149.0, 143.2, 136.6, 132.5, 130.9, 128.7, 128.6, 128.3, 119.5, 118.0, 107.0, 65.9.

ν_{max}/cm^{-1}: 3109, 2865, 1695, 1523, 1492, 1416, 1302, 1282, 1203, 1153, 1119, 1051, 896, 798, 774, 724, 451

ESI-MS (+ve) m/z: Found $[M+H]^+$ 253.0975, $C_{15}H_{13}N_2O_2^+$ requires 253.0972.


8.51
8.51
8.50
8.49
8.41
8.40
8.39
8.39
8.38
8.38
8.37
8.37
8.36
8.19
8.19
8.18
8.17
8.16
8.16
7.52
7.50
7.50
7.50
7.49
7.49
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7.48
7.43
7.43
7.42
7.41
7.41
7.41
7.40
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7.37
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7.36
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7.35
7.34
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7.34
7.26
7.26
7.26 CDCl3
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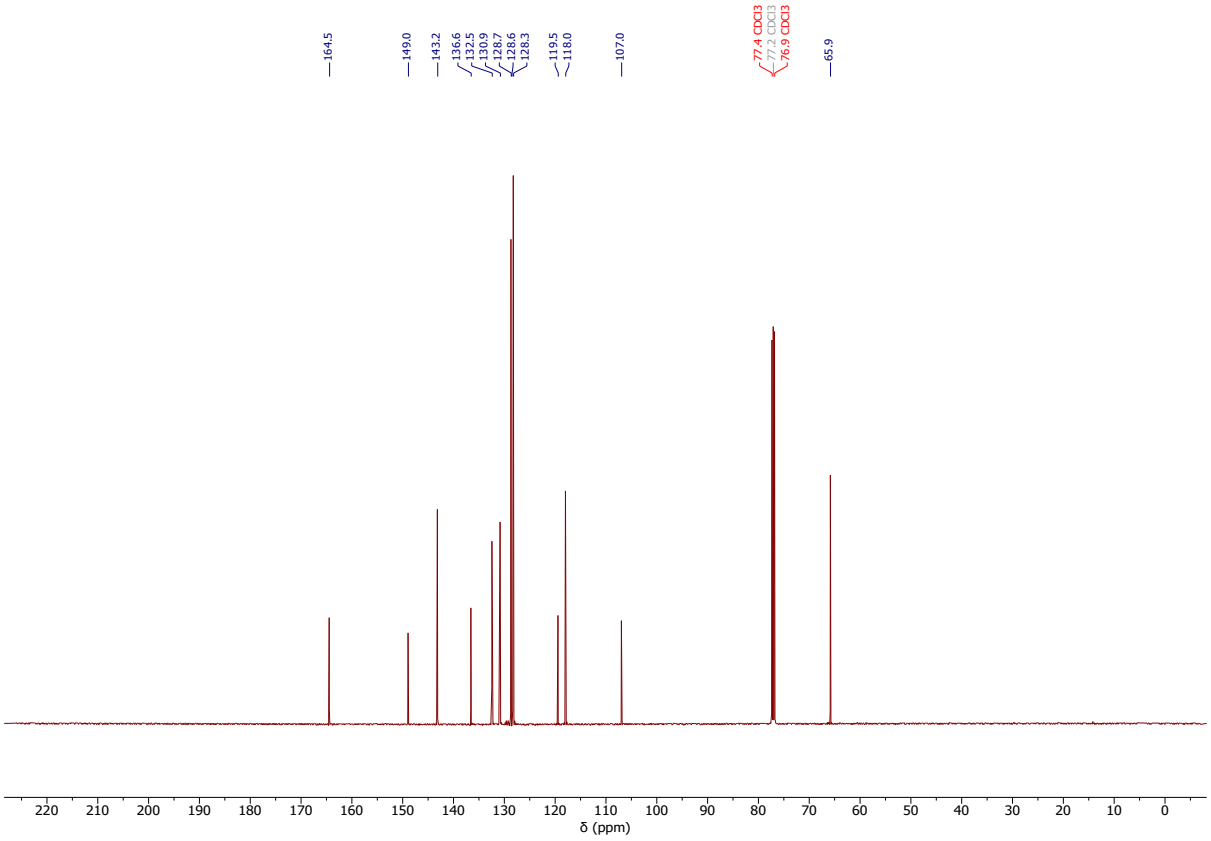
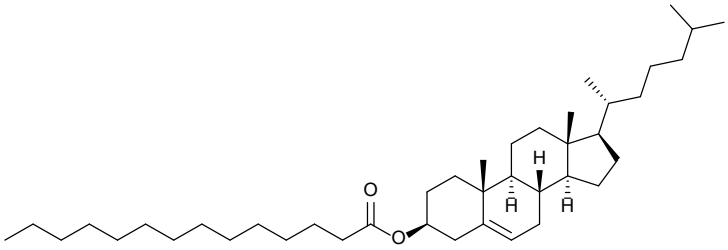
7.24
5.41
5.40
5.39
5.38
1.05
1.03
1.00
1.99
2.03
1.07
1.17
2.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


164.5
149.0
143.2
136.6
132.5
130.9
128.7
128.6
128.3
119.5
118.0
107.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
65.9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

Cholesteryl tetradecanoate (**21**)



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

Chemical Formula: $C_{41}H_{72}O_2$

Molecular Weight: 597.03 $gmol^{-1}$

Appearance: White solid

21 Was synthesised according to general procedure B using tetradecanoic acid (457 mg, 2.00 mmol) and cholesterol (773 mg, 2.00 mmol). The reaction solvent was altered to a 2:3 composition of CPME:DMC (5 mL) to aid solubility of the cholesterol. The product was isolated by general procedure C.

Yield: 34% (408 mg, 0.68 mmol)

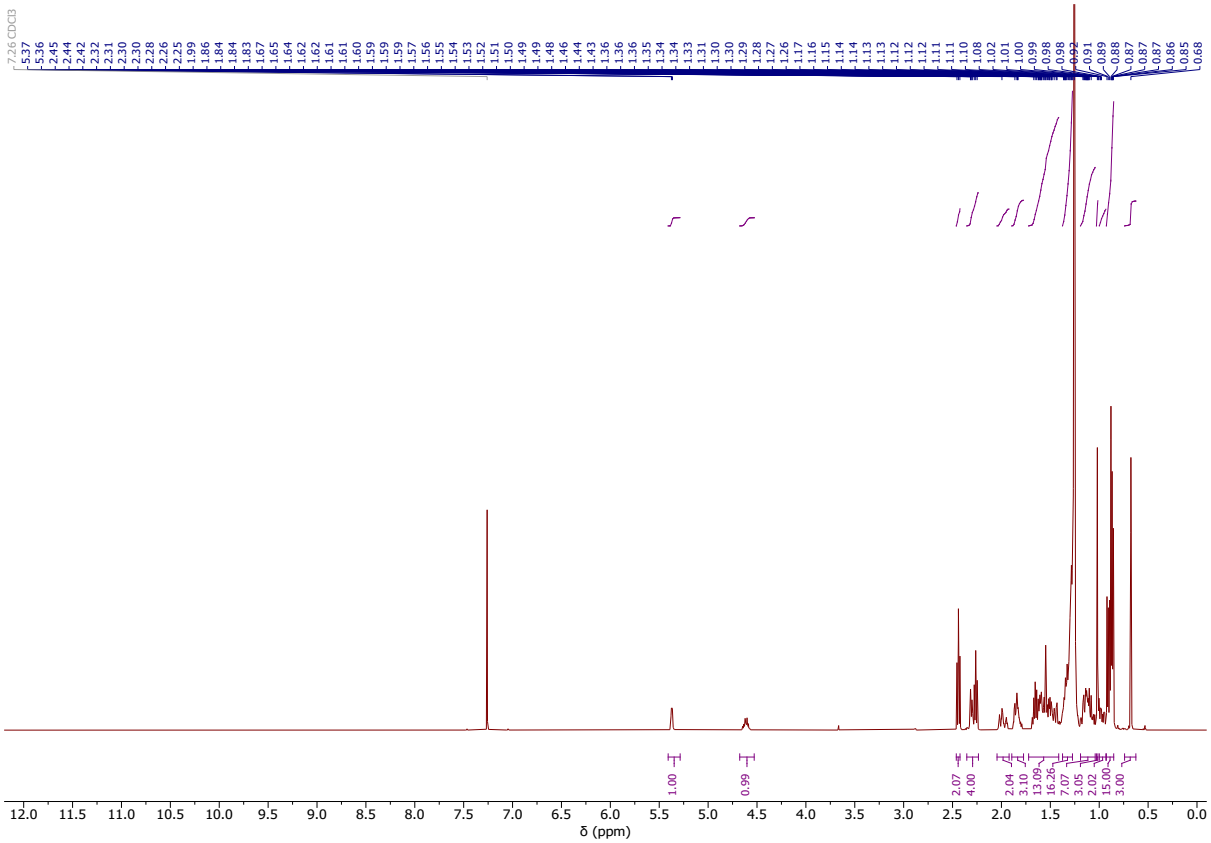
δ_H (500 MHz, Chloroform-*d*) 5.4 (1 H, dt, *J* 3.5, 1.7), 4.7 – 4.5 (1 H, m), 2.4 (2 H, t, *J* 7.5), 2.4 – 2.2 (4 H, m), 2.0 – 1.9 (2 H, m), 1.9 – 1.8 (3 H, m), 1.7 – 1.4 (13 H, m), 1.4 – 1.3 (16 H, m), 1.2 – 1.0 (7 H, m), 1.0 (3 H, s), 1.0 – 0.9 (2 H, m), 0.9 – 0.9 (15 H, m), 0.7 (3 H, s).

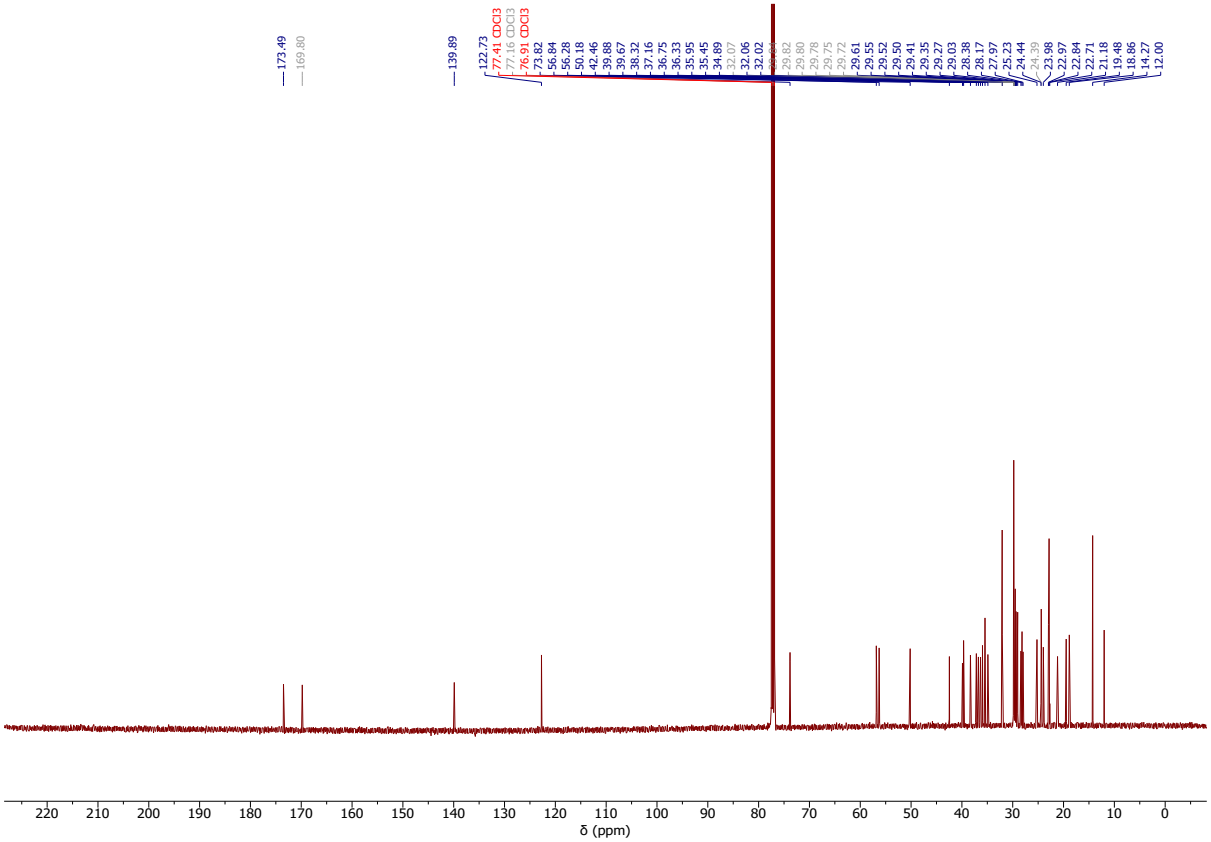
δ_C (126 MHz, Chloroform-*d*) 173.5, 139.9, 122.7, 73.8, 56.8, 56.3, 50.2, 42.5, 39.9, 37.2, 39.7, 38.3, 36.8, 36.3, 35.9, 35.5, 34.9, 32.1, 32.0, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.0, 28.4, 28.2, 28.0, 25.2, 24.4, 24.0, 23.0, 22.8, 22.7, 21.2, 19.5, 18.9, 14.3, 12.0.

^{1}H-NMR was in agreement with the literature. [17]

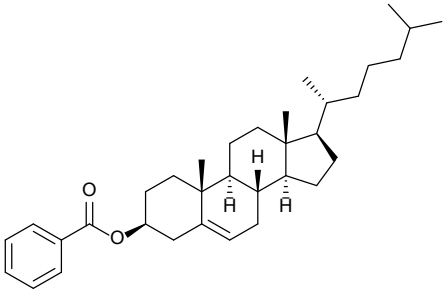
^{13}C-NMR was in agreement with the literature. [18]

ESI-MS (+ve) m/z: Found $[M+Na]^+$ 619.5409, $C_{41}H_{73}NaO_2^+$ requires 619.5425.


δ (ppm)


δ (ppm)

*Cholesteryl benzoate (**22**)*



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

Chemical Formula: $C_{34}H_{50}O_2$

Molecular Weight: 490.77 $gmol^{-1}$

Appearance: White solid

22 Was synthesised according to general procedure B using benzoic acid (244 mg, 2.00 mmol), cholesterol (773 mg, 2.00 mmol) and DMAP (5 mol%, 12 mg, 0.1 mmol). The reaction solvent was altered to a 2:3 composition of CPME:DMC (5 mL) to aid solubility of the cholesterol. The product was isolated by general procedure C.

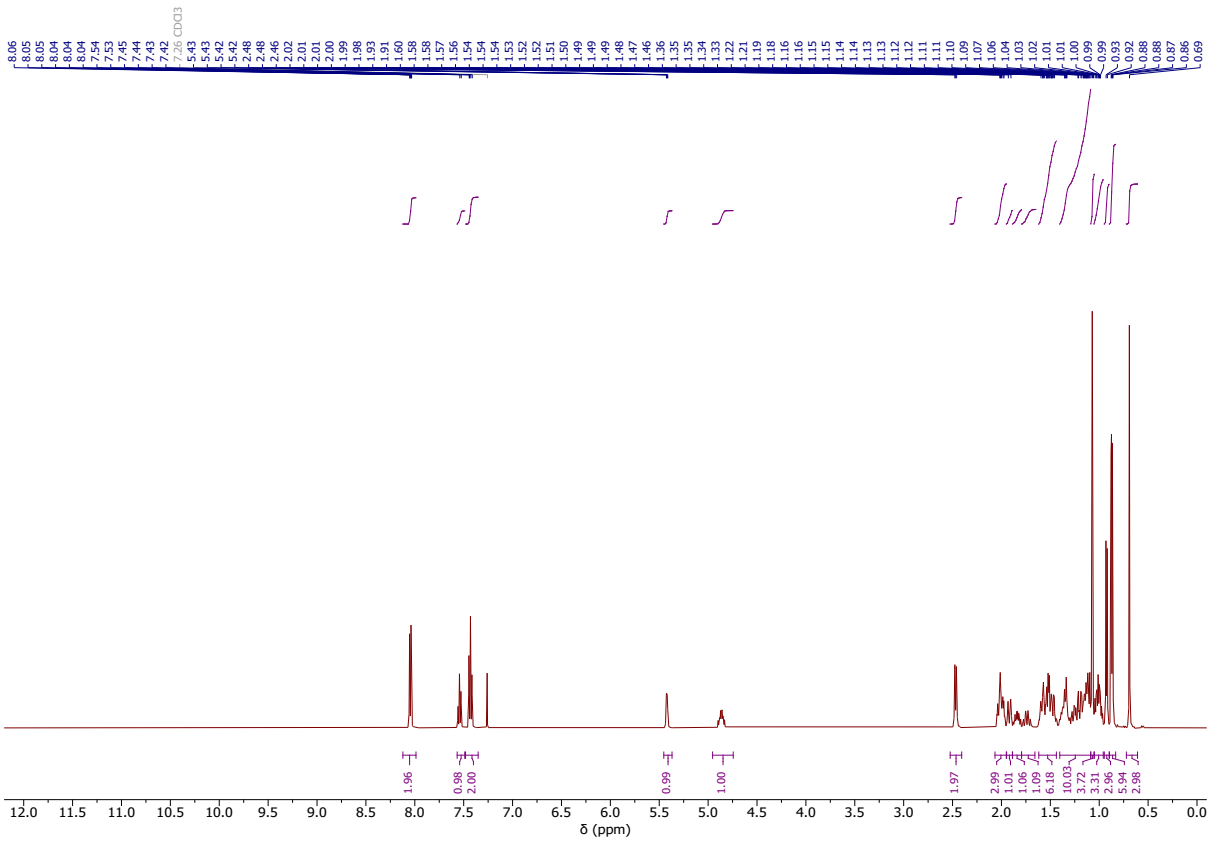
Yield: 34% (330 mg, 0.67 mmol)

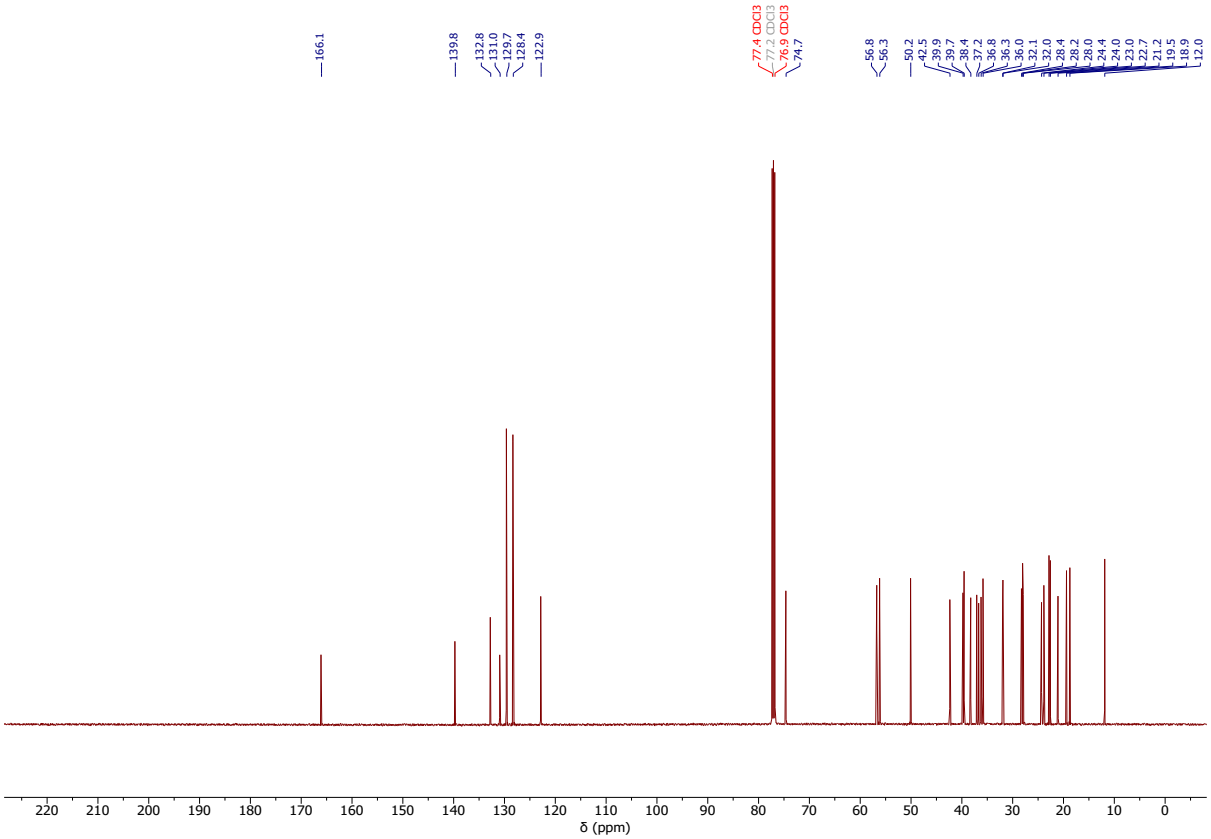
δ_H (500 MHz, Chloroform-*d*) 8.12 – 7.99 (2 H, m), 7.57 – 7.49 (1 H, m), 7.43 (2 H, t, *J* 7.8), 5.42 (1 H, d, *J* 3.1), 4.87 (1 H, ddt, *J* 16.3, 8.3, 4.5), 2.47 (2 H, d, *J* 7.1), 2.07 – 1.95 (3 H, m), 1.92 (1 H, dt, *J* 13.4, 3.6), 1.89 – 1.80 (1 H, m), 1.80 – 1.66 (1 H, m), 1.62 – 1.44 (6 H, m), 1.41 – 1.09 (10 H, m), 1.07 (4 H, s), 1.06 – 0.96 (3 H, m), 0.93 (3 H, d, *J* 6.5), 0.87 (6 H, dd, *J* 6.6, 2.3), 0.69 (3 H, s).

δ_C (126 MHz, Chloroform-*d*) 166.1, 139.8, 132.8, 131.0, 129.7, 128.4, 122.9, 74.7, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.4, 37.2, 36.8, 36.3, 36.0, 32.1, 32.0, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0.

^{1}H- and ^{13}C-NMR were in agreement with the literature.[19]

ESI-MS (+ve) m/z: Found $[M+Na]^+$ 513.3694, $C_{34}H_{50}NaO_2^+$ requires 513.3703.


δ (ppm)


δ (ppm)

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