Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Reversal of regioselectivity in the reactions of donor-acceptor cyclopropanes with electrophilic alkenes

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Abstract: Cyclopropanes bearing donor and acceptor groups at the opposite ends of the C-C bond should react with both nucleophiles and electrophiles. Their reactivity towards nucleophilic reagents is well explored while only few specific electrophiles give desired products. The methods are limited by the specific philicity of the carbon atoms resulting from the strong polarization of the central C-C bond. Herein, we report a strategy that reverses the standard regioselectivity of these methods and thus complements the classical approach. The use of vitamin B_{12} catalysis enables the transformation of initially electrophilic center into a radical that as such reacts with electrophilic SOMOphiles.

a - these authors contributed equally

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1. General Information

All solvents and commercially available reagents were purchased as reagent grade and were used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC), using 0.20 mm Merck silica plates (60F-254) and visualized using UV-light, anisaldehyde or cerium molybdate stain, with heat as a developing agent. Colum chromatography was performed on Merck silica gel 60 (230-400 mesh). Yields refer to spectroscopically (^{1}H NMR) homogeneous materials. NMR spectra were recorded on Bruker 400 MHz or Varian 500 MHz and calibrated using residual undeuterated solvent ($CHCl_3$ – 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR) or TMS as an internal reference. Low-resolution mass spectra (LRMS) were recorded on an Applied Biosystems API 365 mass spectrometer using electrospray ionization (ESI) technique. High-resolution mass spectra (HRMS) were recorded on a Waters AutoSpec Premier instrument using electron ionization (EI) or a Waters SYNAPT G2-S HDMS instrument using electrospray ionization (ESI) with time of flight detector (TOF). Elemental analysis (C, H, N) were performed using a PERKIN-ELMER 240 Elemental Analyzer. Cyclic voltammograms were recorded using Bio-Logic SP-50 potentiostat. GC-MS analyses were performed using Shimadzu GCMS-QP2010 SE gas chromatograph with FID detector and Zebron ZB 5MSi column. Melting points were recorded on a Marienfeld MPM-H2 melting point apparatus and are uncorrected.

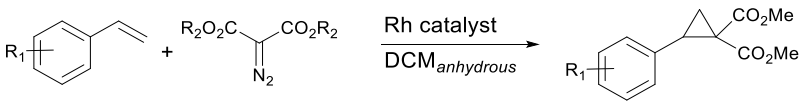
2. General synthetic procedures

2.1 Starting materials

Dimethyl diazomalonate,[1] dibutyl diazomalonate,[1] 2-diazo-3-oxo-butyric acid methyl ester,[2] 2-phenyl-acrylic acid methyl ester,[3] 1,2-diphenylprop-2-en-1-one,[4] $(CN)(H_2O)Cby(OMe)_7$ (**HME**, **2**),[5] $Co(dmgH)_2py^iPr$ (x)[6] were synthesized according to the literature procedures.

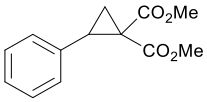
2.2 Preparation of donor-acceptor cyclopropanes 3, S1-S.

Donor-acceptor cyclopropanes **1a-k** were prepared according to slightly modified literature procedure:[7]



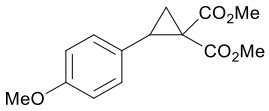
A solution of the corresponding styrene (1.0 equiv.), Rh catalyst (0.5 mol%) in anhydrous dichloromethane was stirred under argon atmosphere at 0 °C. Diazomalonate (1.3 equiv.) in dichloromethane was added dropwise over 30 min via syringe. Cooling bath was removed and the mixture was stirred overnight at ambient temperature. The solvent was removed *in vacuo* and crude product was purified by column chromatography.

Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (3)



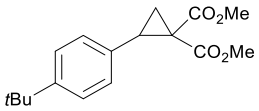
Synthesized according to general procedure from 520 mg (5.0 mmol) of styrene and 1 g (6.5 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 11 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 702 mg of **3** (3.0 mmol, 60%) as a white solid. All analytical data were consistent with that previously reported.

Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (S1)



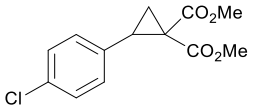
Synthesized according to general procedure from 268 mg (2.0 mmol) of 4-methoxystyrene and 411 mg (2.6 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 4.4 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 343 mg of **S1** (1.3 mmol, 67%) as a white solid. All analytical data were consistent with that previously reported.

Dimethyl 2-(4-(tert-butyl)phenyl)cyclopropane-1,1-dicarboxylate (S2)



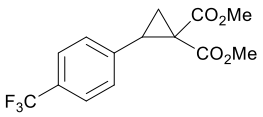
Synthesized according to general procedure from 400 mg (2.5 mmol) of 4-*tert*-butylstyrene and 514 mg (3.25 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 5.5 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 645 mg of **S2** (2.2 mmol, 89%) as a white solid. All analytical data were consistent with that previously reported.[8]

Dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (S3)



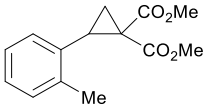
Synthesized according to general procedure from 276 mg (2.0 mmol) of 4-chlorostyrene and 411 mg (2.6 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 4.4 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 440 mg of **S3** (1.6 mmol, 82%) as a white solid. All analytical data were consistent with that previously reported.[9]

Dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate (S4)



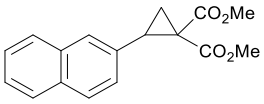
Synthesized according to general procedure from 344 mg (2.0 mmol) of 4-trifluoromethyl styrene and 411 mg (2.6 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 4.4 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 441 mg of **S4** (1.5 mmol, 73%) as colorless oil. All analytical data were consistent with that previously reported.[9]

Dimethyl 2-(o-tolyl)cyclopropane-1,1-dicarboxylate (S5)



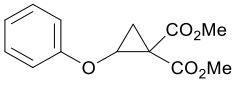
Synthesized according to general procedure from 295 mg (2.5 mmol) of 2-methylstyrene and 514 mg (3.25 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 5.5 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 533 mg of **S5** (2.2 mmol, 86%) as a white solid. All analytical data were consistent with that previously reported.[10]

Dimethyl 2-(naphthalene-2-yl)cyclopropane-1,1-dicarboxylate (S6)



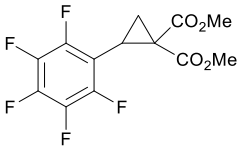
Synthesized according to general procedure from 770 mg (5 mmol) of 2-vinylnaphthalene and 1 g (6.5 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 11 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 284 mg of **S6** (1 mmol, 20%) as a white solid. All analytical data were consistent with that previously reported.[11]

2-Phenoxycyclopropane-1,1-dimethylester (S7)



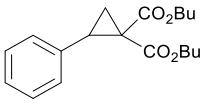
Synthesized according to general procedure from 300 mg (2.5 mmol) of vinyloxybenzene and 514 mg (3.25 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 5.5 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 363 mg of **S7** (1.5 mmol, 58%) as colorless oil. All analytical data were consistent with that previously reported.[12]

Dimethyl 2-(perfluorophenyl)cyclopropane-1,1-dicarboxylate (S8)



Synthesized according to general procedure from 295 mg (2 mmol) of perfluorostyrene and 411 mg (2.6 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 4.4 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 395 mg of **S8** (1.2 mmol, 61%) as colorless oil. All analytical data were consistent with that previously reported.[9]

Dibutyl 2-phenylcyclopropane-1,1-dicarboxylate (S9)



Synthesized according to general procedure from 416 mg (4 mmol) of styrene and 1.3 g (5.2 mmol, 1.3 equiv.) of dibutyl 2-diazomalonate using 8.8 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 712 mg of **S9** (2.2 mmol, 56%) as colorless oil.

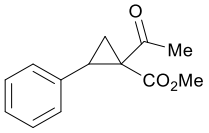
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.25 (m, 1H), 7.25 – 7.17 (m, 4H), 4.22 (dt, J = 10.8, 6.6 Hz, 1H), 4.14 (dt, J = 10.8, 6.5 Hz, 1H), 3.77 (t, J = 6.6 Hz, 2H), 3.20 (t, J = 8.6 Hz, 1H), 2.15 (dd, J = 8.0, 5.1 Hz, 1H), 1.69 (dd, J = 9.2, 5.1 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.45 – 1.35 (m, 2H), 1.28 – 1.20 (m, 2H), 1.15 – 1.04 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H), 0.77 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 166.8, 134.8, 128.5, 128.1, 127.3, 65.5, 65.1, 37.6, 32.1, 30.6, 30.3, 19.1, 18.81, 18.77, 13.6, 13.5.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{19}H_{26}O_4Na$: 341.1729, found: 341.1731.

Elemental analysis (%) calculated for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23, found: C, 71.66; H, 8.40.

Methyl 1-acetyl-2-phenylcyclopropanecarboxylate (S10)

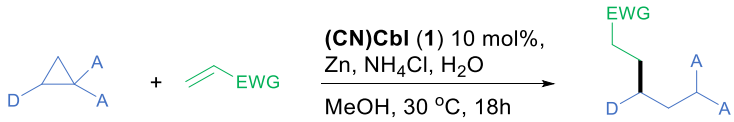


218 Synthesized according to general procedure from 208 mg (2 mmol) of styrene and 369 mg (2.6 mmol, 1.3 equiv.) of dimethyl 2-diazomalonate using 4.4 mg (0.5 mol%) of $Rh_2(OAc)_4$ as a catalyst (*c* = 1M). Column chromatography (10:90 AcOEt/Hexanes) afforded 288 mg of **S10** (1.3 mmol, 66%, mixture of diastereomers 20:80) as colorless oil. All analytical data were consistent with that previously reported.[13]

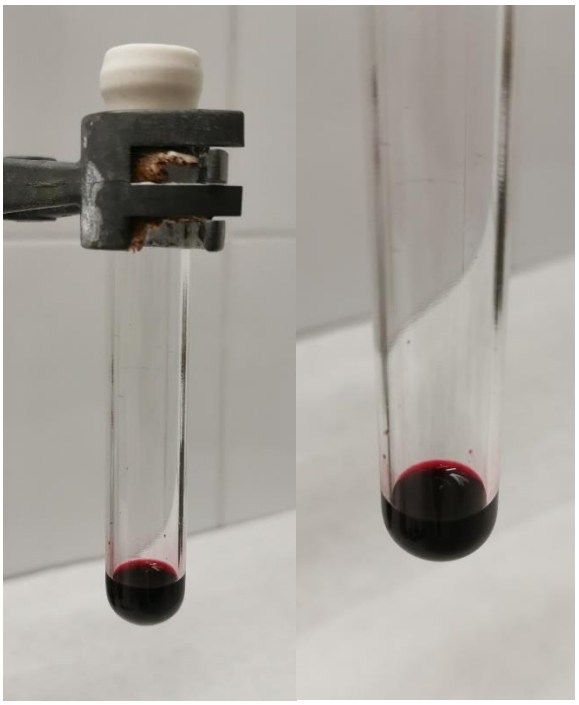
2.3 Procedure for zinc activation[5]

Zinc powder (5.0 g) was suspended in 10% aq. HCl (50 ml) and grinded in mortar for 2 – 3 min. Subsequently, the solution was filtered and the zinc precipitate was washed successively with water (50 ml), acetone (50 ml), MeOH (50 ml), and Et_2O (50 ml). The resulting precipitate was transferred to the mortar, grinded and dried *in vacuo* to afford light grey powder which was then stored under argon atmosphere and used for maximum 1 month.

2.4 General procedure A for the opening and alkylation of D-A cyclopropanes



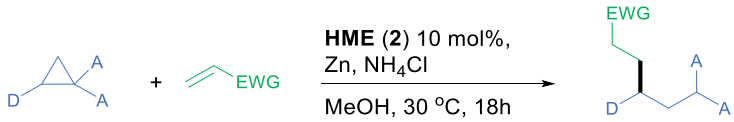
A glass reaction tube (inner diameter = 18 mm) equipped with a magnetic bar and sealed with a septum was charged with a donor-acceptor cyclopropane (0.2 mmol, 1.0 equiv.), vitamin B_{12} (27 mg, 0.02 mmol, 10 mol%), NH_4Cl (16 mg, 0.3 mmol, 1.5 equiv.), and activated zinc 39 mg, 0.6 mmol, 3.0 equiv.). Subsequently, MeOH (1.0 ml) was added and the resulting mixture was degassed 3x by a simplified freeze-thaw method using dry ice as a cooling agent. Then, an electrophilic alkene (1 mmol, 5 equiv.) and H_2O (20 µl) were added under argon. The reaction tube was placed in ultrasonic bath for 30 s in order to break up zinc lumps. Subsequently, it was transferred into oil bath set on 30 °C for 18 h. After that time, the mixture was diluted with AcOEt, filtered through a cotton pad, and concentrated *in vacuo*. A crude product was purified using column chromatography.



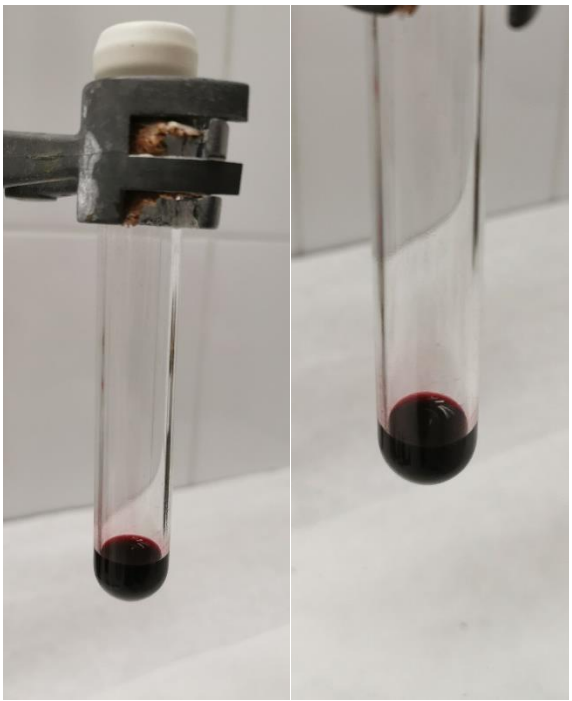
Reaction mixture before reduction of (CN)Cbl (**1**) – Co(III) form

Reaction mixture after reduction of (CN)Cbl (**1**) to the Co(I) form

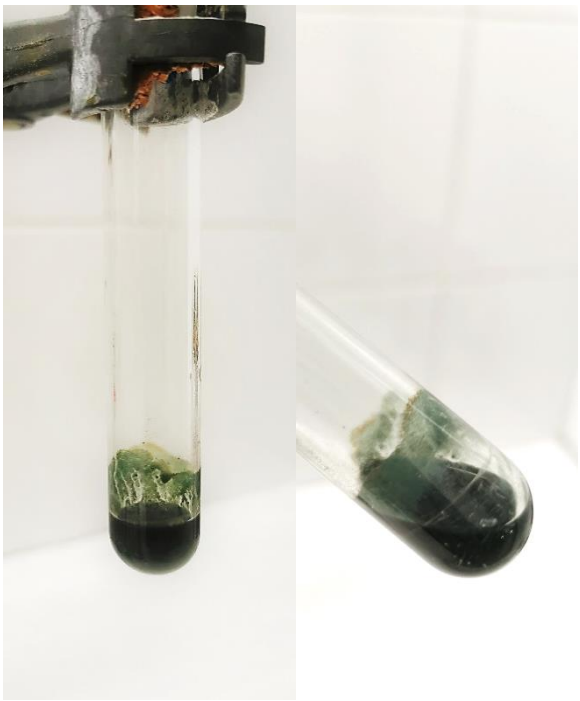
2.5 General procedure B for the opening and alkylation of D-A cyclopropanes



A glass reaction tube (inner diameter = 18 mm) equipped with a magnetic bar and sealed with a septum was charged with a donor-acceptor cyclopropane (0.2 mmol, 1.0 equiv.), HME (x) (24 mg, 0.02 mmol, 10 mol%), NH_4Cl (16 mg, 0.3 mmol, 1.5 equiv.), and activated zinc 39 mg, 0.6 mmol, 3.0 equiv.). Subsequently, MeOH (1.0 ml) was added and the resulting mixture was degassed 3x by simplified freeze-thaw method using dry ice as a cooling agent. Then, an electrophilic alkene (1 mmol, 5 equiv.) was added under argon. The reaction tube was placed in ultrasonic bath for 30 s in order to break up zinc lumps. Subsequently, it was transferred into oil bath set on 30 °C for 18 h. After that time, the mixture was diluted with AcOEt, filtered through a cotton pad, and concentrated *in vacuo*. A crude product was purified using column chromatography.



Reaction mixture before reduction of HME (**2**) – Co(III) form



Reaction mixture after reduction of HME (**2**) to the Co(I) form

3. Optimization details

3.1 Optimization of substrates ratio[a]

Entry	DAC **3** [mmol]	Michael acceptor **4a** [mmol]	Ratio **3**:**4a**	Yield of 5**a** [%][b]
1	0.1	0.15	1:1.5	14
2	0.1	0.3	1:3	24
3	0.1	0.5	1:5	50
4	0.1	1	1:10	71

[a] (CN)Cbl **1** (6 mol%), Zn (6 equiv), NH_4Cl (3 equiv), MeOH (*c* = 0.1 M), 18 h under Argon atmosphere, rt, blue LEDs (455 nm, 9 W). [b] GC yield.

3.2 Optimization of solvent

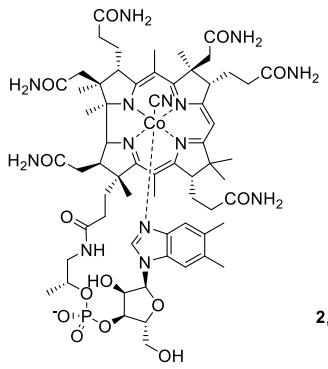
Entry	solvent	*c* of substrate **3** [M]	Yield of **5a** [%][b]
1	MeOH	0.03	37
2	MeOH	0.1	50
3	**MeOH**	**0.2**	**65**
4	MeOH	0.4	58
5	$MeOH_{anhydrous}$	0.2	61
6	**MeOH + H_2O (5 equiv.)**	**0.2**	**70**
7	MeOH + H_2O (10 equiv.)	0.2	64
8	MeOH + H_2O (25 equiv.)	0.2	54
9	*i*PrOH	0.2	0
10	DMF	0.2	11
11	EtOH	0.2	8
12	CF_3CH_2OH	0.2	7

[a] DAC **3** (0.10 mmol, 1 equiv.), alkene **4a** (0.5 mmol, 5 equiv.), (CN)Cbl **1** (6 mol%), Zn (3 equiv.), NH_4Cl (1.5 equiv.), 18 h under Argon atmosphere, rt, blue LEDs (455 nm, 9 W). [b] GC yield.

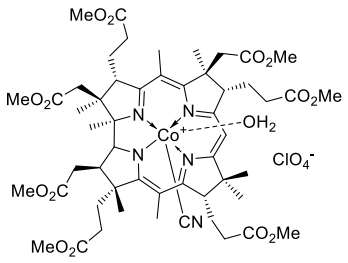
3.2 Cobalt catalysts screening[a]

Entry	Catalyst	Catalyst loading [mol%]	Yield of **5a** [%][b]
1	(CN)Cbl (**1**)	3	46
2	(CN)Cbl (**1**)	6	65
3	(CN)Cbl (**1**)	**10**	**73**
4	HME (**2**)	10	66
5	$Cbl(OH_2)^+Cl^-$ (**9**)	10	74
6	$Co(dmgH)_2py^iPr$ (**S11**)	10	0
7	HME Co(II) (**S12**)[c]	10	0

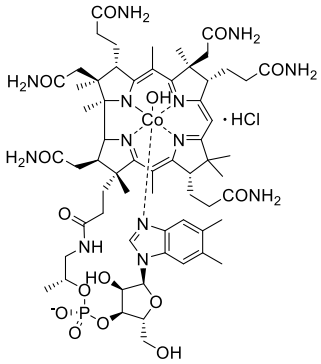
[a] DAC **3** (0.10 mmol, 1 equiv.), alkene **4a** (0.5 mmol, 5 equiv.), Zn (3 equiv.), NH_4Cl (1.5 equiv), MeOH (*c* = 0.1 M), 18 h under Argon atmosphere, rt, blue LEDs (455 nm, 9 W). [b] GC yield. [c] No zinc added.



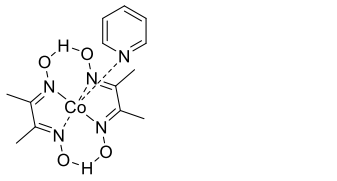
1, **(CN)Cbl**, Cyanocobalamin, **Vitamin B_{12}**



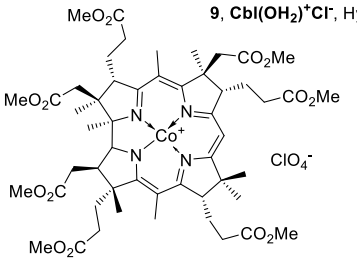
2, Aqua(cyano)heptamethyl cobyrinate (**HME**)



9, **$Cbl(OH_2)^+Cl^-$**, Hydroxocobalamin hydrochloride



S11, Chloro(pyridine)bis (dimethylglyoximato)cobalt(III)



S12, Heptamethyl cobyrinate(II)

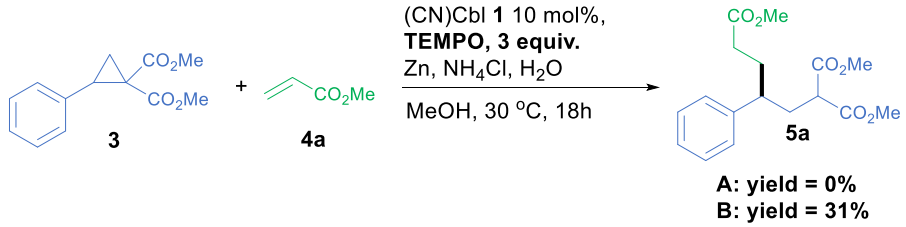
3.4 Activation mode for the cleavage of Co-C bond[a]

Entry	Activation mode for the cleavage of Co-C bond	Yield of **5a** [%][b]
1	Blue LEDs	73
2	No light, room temperature	62
3	**Heating: 30 °C**	**77**
4	Heating: 40 °C	59

[a] DAC **3** (0.10 mmol, 1 equiv.), alkene **4a** (0.5 mmol, 5 equiv.), (CN)Cbl **1** (10 mol%), Zn (3 equiv), NH_4Cl (1.5 equiv), MeOH (*c* = 0.1 M), 18 h under Argon atmosphere, rt, blue LEDs (455 nm, 9 W). [b] GC yield.

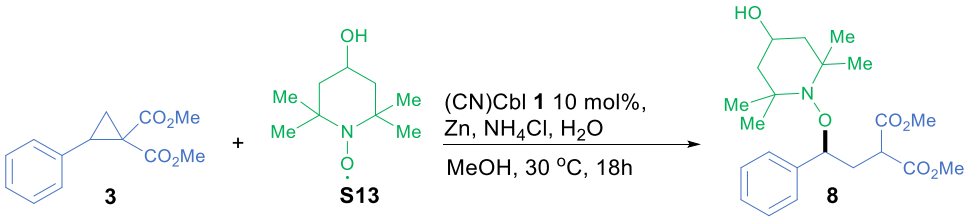
4. Mechanistic experiments

4.1 Experiment with radical trap



Experiment A: The reaction was set up according to general procedure A. Subsequently, 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO, 3 equiv.) was added and the reaction was stirred at 30 °C for 18 h. The reaction was then worked up as usual and analyzed with GC/FID with dodecane as a standard. In this case **we did not observe formation of a product**.

Experiment B: The reaction was set up according to general procedure A and it was stirred at 30 °C for 3 h. Subsequently, TEMPO (3 equiv.) was added and the reaction was stirred at 30 °C for another 15 h. The reaction was then worked up as usual and analyzed with GC/FID with dodecane as a standard. In this case **we observed formation of a product 5a in diminished yield (31%)**.



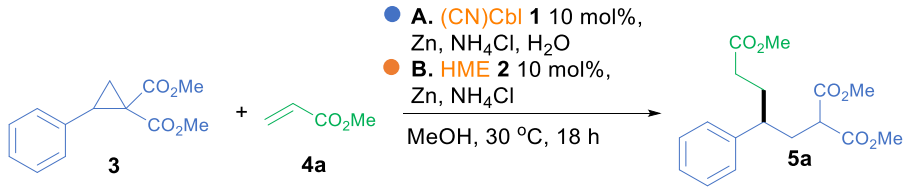
Experiment C: The reaction was set up according to general procedure A. Subsequently, TEMPOL (3 equiv.) was added and the reaction was stirred at 30 °C for 18 h. The reaction was then worked up as usual and analyzed with GC/FID with dodecane as a standard. In this case **we did not observe formation of a product**. The reaction was further investigated with ESI MS. HRMS ESI(+) analysis indicates formation of TEMPO adduct **8**.

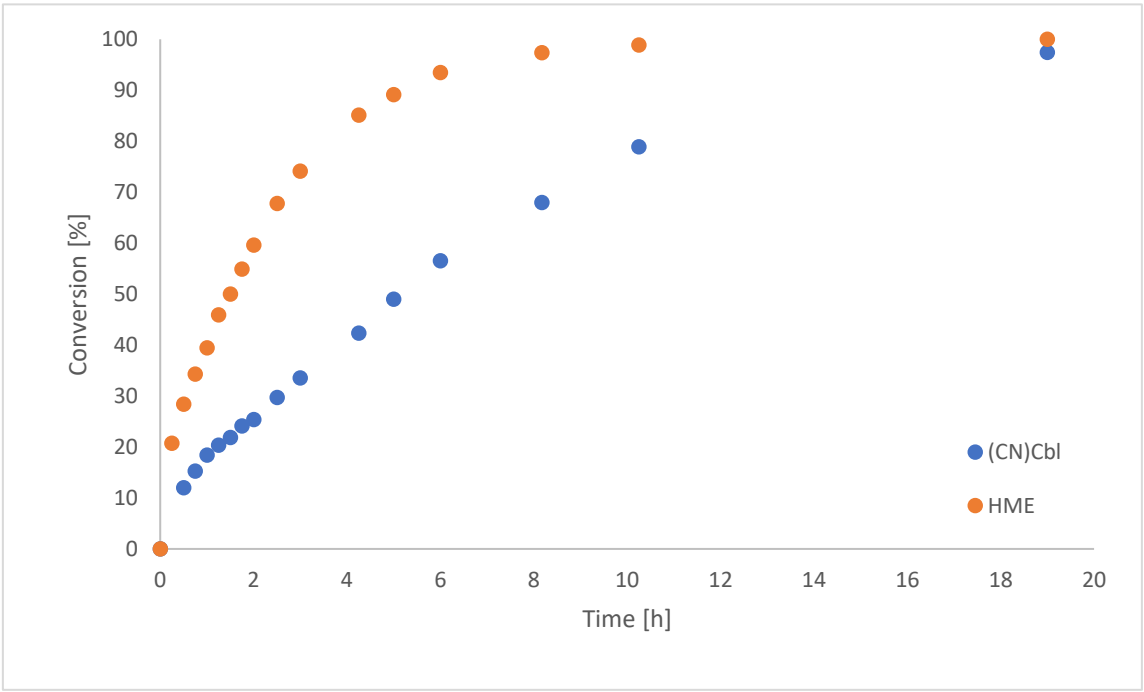
HRMS (ESI) $[M+Na]^+$ calculated for $C_{22}H_{34}NO_6$: 408.2378, found: 408.2386.

4.2 Kinetic studies

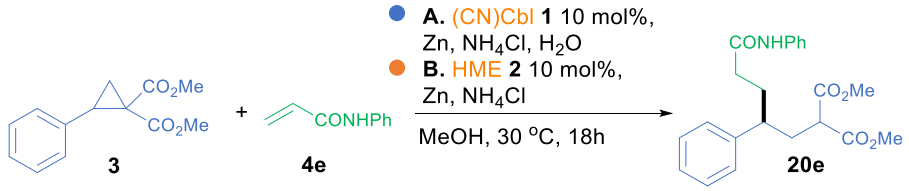
The reactions for individual compounds were set up following general procedures A or B on a 0.3 mmol scale with the addition of 1,3,5-trimetoxybenzene as an internal standard. The reactions were conducted for 18 – 20 hours and monitored by GC/FID.

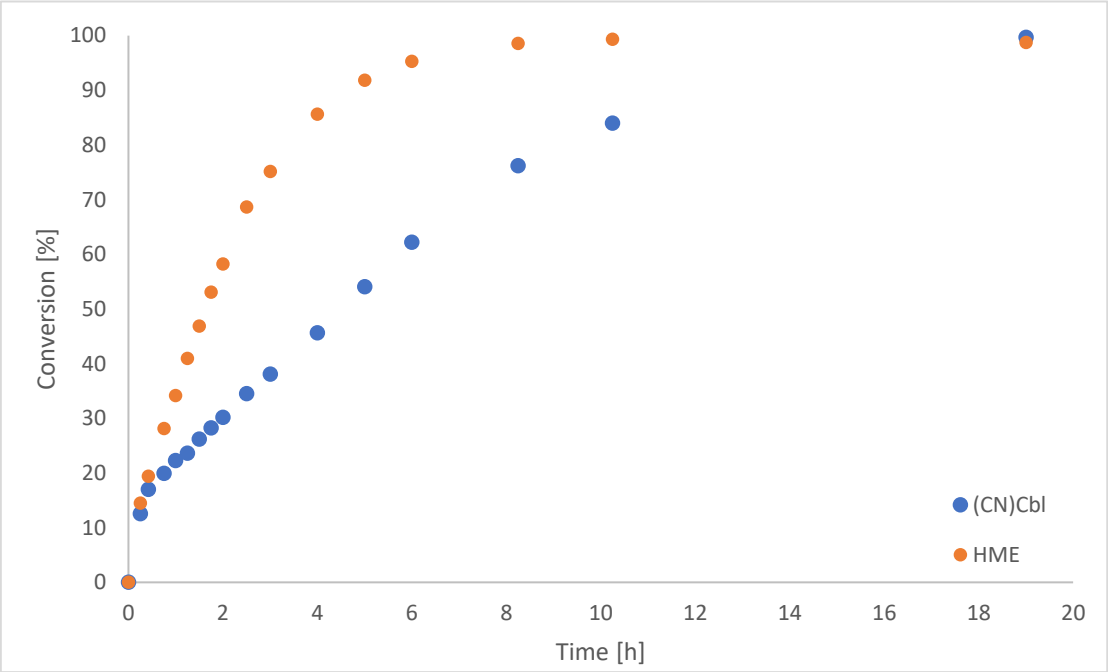
A. Kinetic studies of model reaction



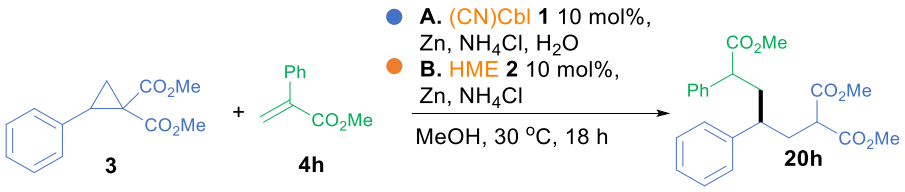


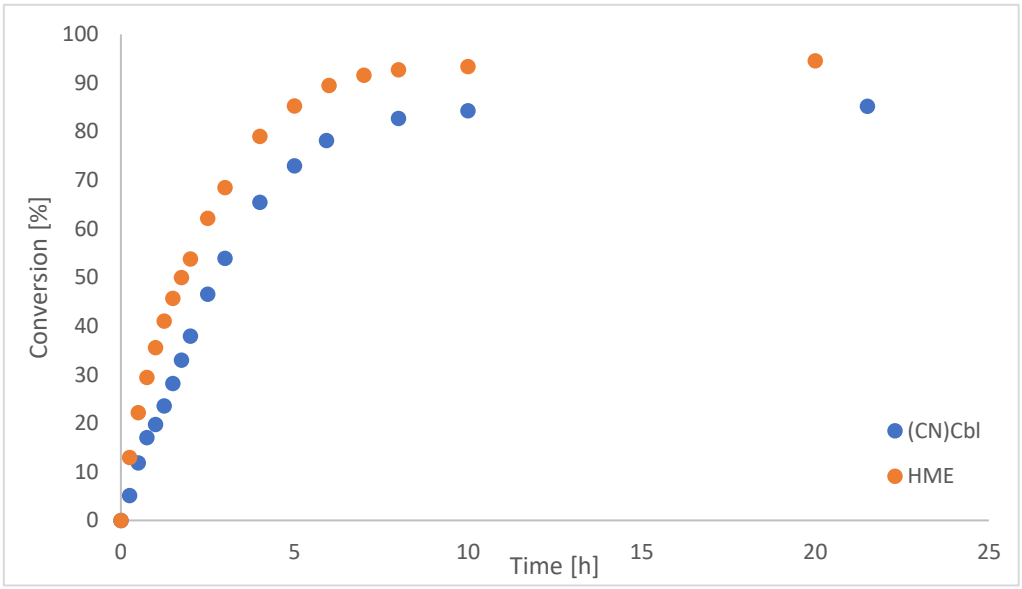
B. Kinetic studies of reaction of D-A cyclopropane 3 and olefin 4e.





C. Kinetic studies of reaction of D-A cyclopropane 3 and olefin 4h.

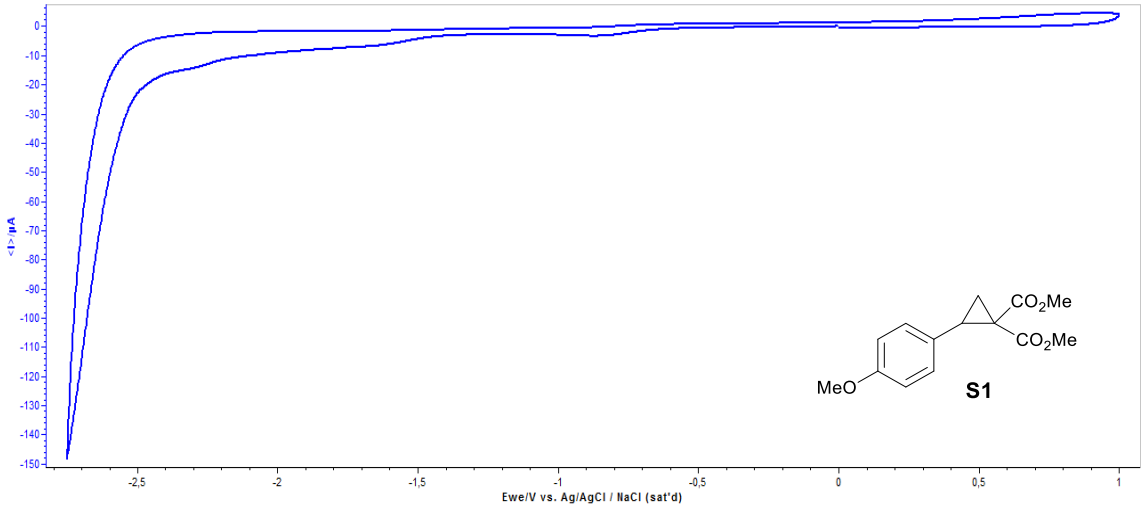


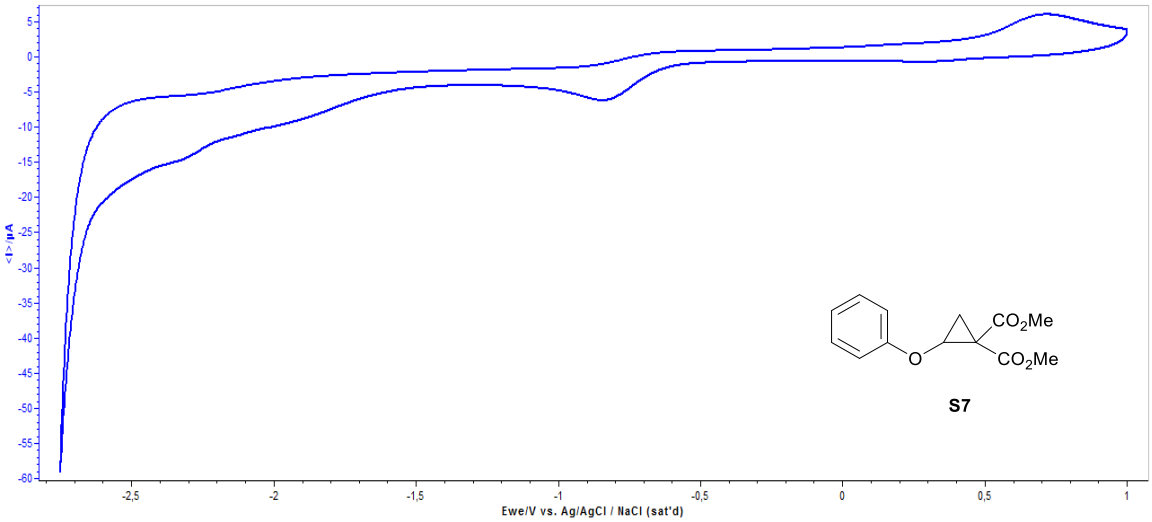


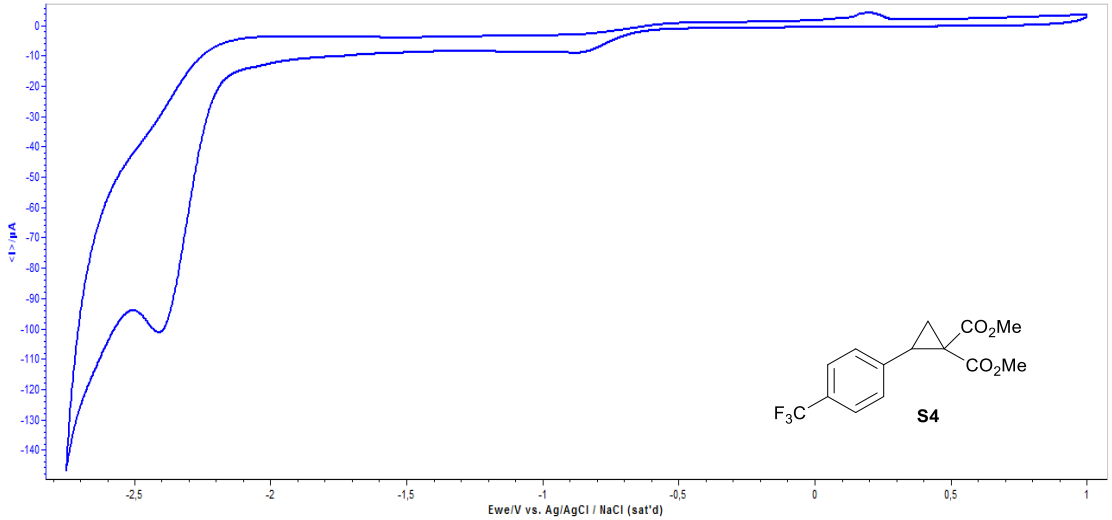
In all studied reactions the conversion rate of the substrate was higher for the ones catalyzed by HME (**2**). This observation is in accordance with our previous studies.

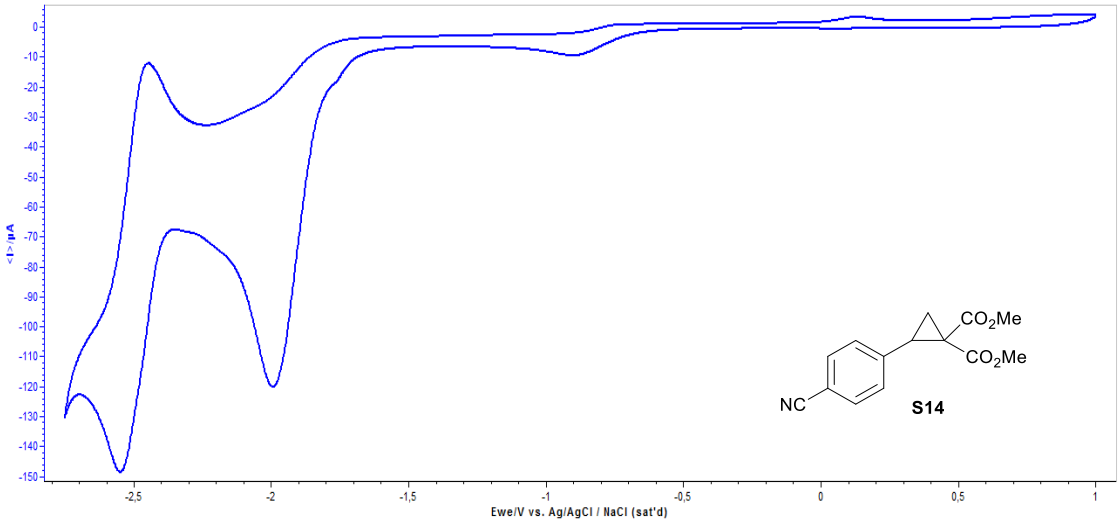
4.3 CV studies

A cylindrical three-electrode cell was equipped with a glassy carbon working electrode, a 25 mm platinum wire as the counter electrode and Ag/AgCl (3.0 M NaCl) electrode as the reference electrode. The scan rate for a typical experiment was 100 $mV \cdot s^{-1}$. The solution of donor-acceptor cyclopropane ($1.0 \cdot 10^{-2}$ M) and *n*-Bu_4NClO_4 (0.1 M) in dry MeCN was deaerated by Ar gas bubbling before the measurement, and the cyclic voltammetry was carried out under an Ar gas atmosphere at room temperature.



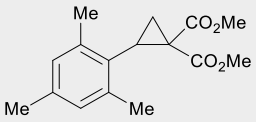
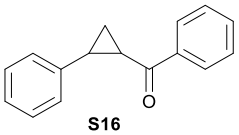
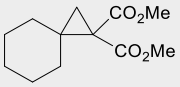
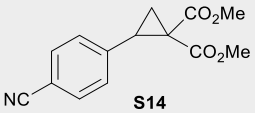
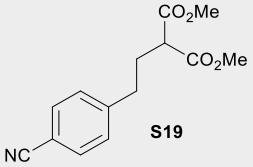
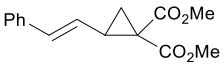
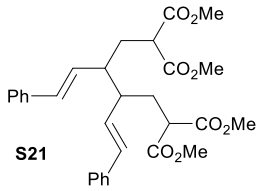
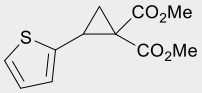
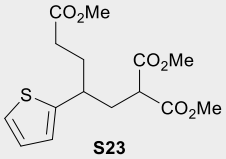






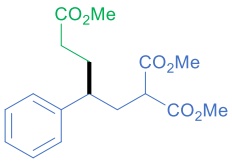
CV studies show correlation between the reaction performance and reduction potentials of selected D-A cyclopropanes. In the reaction of cyclopropane **S4** we observed significant amount of side-product being the result of opening and reduction of cyclopropane. In case of cyclopropane **S14**, the easiest to reduce, the product of opening and reduction reaction exclusively formed.

4.4 Unsuccessful examples

Entry	Substrate	Outcome	Product
1	 **S15**	No conversion	-
2	 **S16**	No conversion	-
3	 **S17**	No conversion	-
4	 **S18**	No conversion	-
5	 **S14**	DAC opened and reduced	 **S19**
6	 **S20**	Radical dimer **S21** as the only product	 **S21**
7	 **S22**	<10% of product **S23**	 **S23**

5. Scope and characterization of new compounds

Trimethyl 3-phenylpentane-1,1,5-tricarboxylate (5a)



Following General Procedure A, compound **5a** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 20:80 AcOEt/Hexanes) to afford 51 mg of compound **5a** as colorless oil. (**Yield = 79%**)

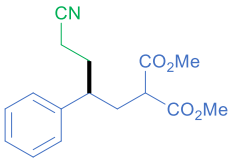
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 7.12 – 7.09 (m, 2H), 3.73 (s, 3H), 3.60 (s, 3H), 3.60 (s, 3H), 3.14 (dd, *J* = 9.8, 5.2 Hz, 1H), 2.58 – 2.52 (m, 1H), 2.36 – 2.29 (m, 1H), 2.22 – 2.08 (m, 3H), 2.09 – 1.95 (m, 1H), 1.96 – 1.82 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 169.67, 169.65, 142.2, 128.7, 127.8, 127.0, 52.43, 52.43, 51.4, 49.8, 43.3, 35.4, 32.0, 31.8.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{22}O_6Na$: 345.1314, found: 345.1318.

Elemental analysis (%) calculated for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88, found: C, 63.54; H, 6.98.

Dimethyl 2-(4-cyano-2-phenylbutyl)malonate (5b)



Following General Procedure A, compound **5b** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and acrylonitrile (**4b**) (53 mg, 1.0 mmol). The crude product was purified by column chromatography (20:80 AcOEt/Hexanes) to afford 42 mg of compound **5b** as colorless oil. (**Yield = 72%**)

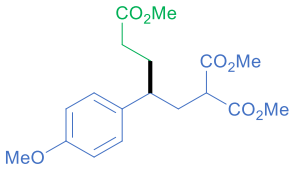
^{1}H NMR (400 MHz, $CDCl_3$) 1H NMR δ 7.38 – 7.29 (m, 2H), 7.29 – 7.22 (m, 1H), 7.17 – 7.08 (m, 2H), 3.75 (s, 3H), 3.60 (s, 3H), 3.14 (dd, *J* = 9.8, 5.1 Hz, 1H), 2.68 (tt, *J* = 10.8, 4.3), 2.33 (ddd, *J* = 14.2, 9.8, 4.4 Hz, 1H), 2.24 – 2.11 (m, 2H), 2.11 – 1.98 (m, 2H), 1.95 – 1.81 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.44, 169.40, 140.5, 129.1, 127.7, 127.5, 119.1, 52.6, 52.5, 49.6, 42.8, 35.1, 32.3, 15.3.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{16}H_{19}NO_4$: 312.1213, found: 312.1212.

Elemental analysis (%) calculated for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84, found: C, 66.39; H, 6.69; N, 4.84.

Trimethyl 3-(4-methoxyphenyl)pentane-1,1,5-tricarboxylate (10a)



Following General Procedure A, compound **10a** was obtained from D-A cyclopropane **S1** (47 mg, 0.20 mmol) (and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 20:80 AcOEt/Hexanes) to afford 51 mg of compound **10a** as colorless oil. (**Yield = 73%**)

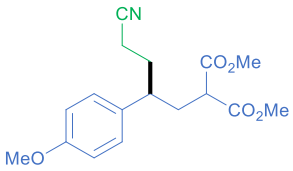
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 – 6.99 (m, 2H), 6.86 – 6.81 (m, 2H), 3.78 (s, 3H), 3.73 (s, 3H), 3.60 (s, 3H), 3.59 (s, 3H), 3.14 (dd, *J* = 9.9, 5.0 Hz, 1H), 2.50 (tt, *J* = 9.9, 4.6 Hz, 1H), 2.29 (ddd, *J* = 14.2, 9.9, 4.4 Hz, 1H), 2.21 – 2.03 (m, 3H), 2.05 – 1.92 (m, 1H), 1.89 – 1.79 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 169.8, 169.7, 158.5, 134.0, 128.7, 114.1, 55.2, 52.4, 51.4, 49.8, 42.4, 35.6, 32.1, 31.9.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{18}H_{24}O_7Na$: 375.1418, found: 375.1420.

Elemental analysis (%) calculated for $C_{18}H_{24}O_7$: C, 61.35; H, 6.87, found: C, 61.13; H, 7.06.

Dimethyl 2-(4-cyano-2-(4-methoxyphenyl)butyl)malonate (10b)



Following General Procedure A, compound **10b** was obtained from D-A cyclopropane **S1** (53 mg, 0.20 mmol) and acrylonitrile (**4b**) (53 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 20:80 AcOEt/Hexanes) to afford 45 mg of compound **10b** as colorless oil. (**Yield = 70%**)

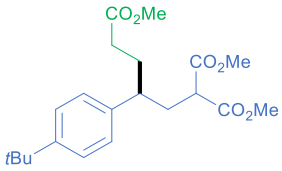
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 – 7.01 (m, 2H), 6.90 – 6.84 (m, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 3.61 (s, 3H), 3.14 (dd, *J* = 9.9, 4.9 Hz, 1H), 2.69 – 2.56 (m, 1H), 2.30 (m, 1H), 2.24 – 2.09 (m, 2H), 2.09 – 1.97 (m, 2H), 1.93 – 1.76 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.52, 169.45, 158.9, 132.3, 128.6, 119.2, 114.5, 55.2, 52.6, 52.5, 49.6, 42.0, 35.3, 32.4, 15.3.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{21}NO_5Na$: 342.1321, found: 342.1317.

Elemental analysis (%) calculated for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39, found: C, 64.00; H, 6.66; N, 4.55.

Trimethyl 3-(4-(*tert*-butyl)phenyl)pentane-1,1,5-tricarboxylate (11a)



Following General Procedure A, compound **11a** was obtained from D-A cyclopropane **S2** (58 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (20:80 AcOEt/Hexanes) to afford 57 mg of compound **11a** as colorless oil. (**Yield = 75%**)

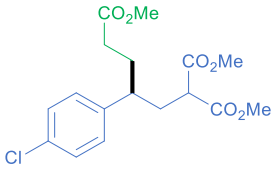
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.3 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 3.73 (s, 3H), 3.59 (s, 6H), 3.17 (dd, *J* = 9.7, 5.3 Hz, 1H), 2.51 (tt, *J* = 9.9, 4.7 Hz, 1H), 2.30 (ddd, *J* = 14.0, 9.7, 4.5 Hz, 1H), 2.22 – 2.06 (m, 3H), 2.06 – 1.94 (m, 1H), 1.94 – 1.81 (m, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 169.75, 169.73, 149.6, 138.9, 127.4, 125.5, 52.41, 52.39, 51.4, 49.8, 42.8, 35.5, 34.4, 32.1, 31.8, 31.3.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{21}H_{30}O_6Na$: 401.1941, found: 401.1940.

Elemental analysis (%) calculated for $C_{21}H_{30}O_6$: C, 66.65; H, 7.99, found: C, 66.42; H, 8.00.

Trimethyl 3-(4-chlorophenyl)pentane-1,1,5-tricarboxylate (12a)



Following General Procedure A, compound **12a** was obtained from D-A cyclopropane **S3** (54 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 20:80 AcOEt/Hexanes) to afford 43 mg of compound **12a** as colorless oil. (**Yield = 60%**)

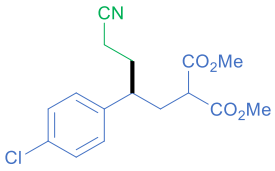
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.07 – 7.03 (m, 2H), 3.73 (s, 3H), 3.61 (s, 3H), 3.60 (s, 3H), 3.11 (dd, *J* = 9.8, 5.2 Hz, 1H), 2.55 (tt, *J* = 10.0, 4.7 Hz, 1H), 2.31 (ddd, *J* = 14.2, 9.8, 4.5 Hz, 1H), 2.19 – 2.06 (m, 3H), 2.05 – 1.97 (m, 1H), 1.89 – 1.81 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 169.52, 169.50, 140.7, 132.7, 129.1, 128.9, 52.53, 52.51, 51.5, 49.6, 42.7, 35.3, 31.9, 31.7.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{21}ClO_6Na$: 379.0923, found: 379.0924.

Elemental analysis (%) calculated for $C_{17}H_{21}ClO_6$: C, 57.23; H, 5.93, found: C, 57.12; H, 6.05.

Dimethyl 2-(4-cyano-2-(4-chlorophenyl)butyl)malonate (12b)



Following General Procedure A, compound **12b** was obtained from D-A cyclopropane **S3** (54 mg, 0.20 mmol) (and acrylonitrile (**4b**) (53 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 20:80 AcOEt/Hexanes) to afford 46 mg of compound **12b** as colorless oil. (**Yield = 71%**)

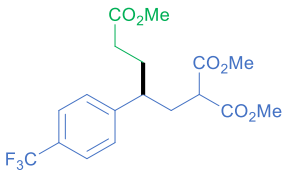
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H), 3.60 (s, 3H), 3.09 (dd, *J* = 9.8, 5.1 Hz, 1H), 2.68 (tt, *J* = 10.6, 4.1 Hz, 1H), 2.31 (ddd, *J* = 14.1, 9.9, 4.3 Hz, 1H), 2.24 – 2.08 (m, 2H), 2.09 – 1.98 (m, 2H), 1.88 – 1.81 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.23, 169.19, 139.0, 133.3, 129.2, 129.0, 118.8, 52.6, 52.5, 49.4, 42.1, 35.0, 32.0, 15.2.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{16}H_{18}NO_4NaCl$: 346.0826, found: 346.0822.

Elemental analysis (%) calculated for $C_{16}H_{18}ClNO_4$: C, 59.35; H, 5.60; N, 4.33, found: C, 59.18; H, 5.57; N, 4.40.

Trimethyl 3-(4-(trifluoromethyl)phenyl)pentane-1,1,5-tricarboxylate (13a)



Following General Procedure A, compound **13a** was obtained from D-A cyclopropane **S4** (60 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 20:80 AcOEt/Hexanes) to afford 43 mg of compound **13a** as colorless oil. (**Yield = 55%**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 3.60 (s, 6H), 3.10 (dd, *J* = 9.6, 5.3 Hz, 1H), 2.66 (tt, *J* = 9.7, 4.6 Hz, 1H), 2.34 (ddd, *J* = 14.1, 9.6, 4.6 Hz, 1H), 2.21 – 2.00 (m, 4H), 1.96 – 1.85 (m, 1H).

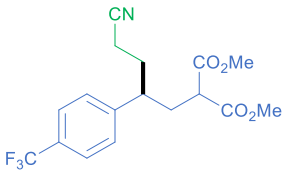
^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 169.40, 169.39 146.5, 129.3 (q, *J* = 32.6 Hz), 128.2, 125.7 (q, *J* = 3.8 Hz), 124.1 (q, *J* =271.9 Hz), 52.56, 52.51, 51.54, 49.61, 43.08, 35.16, 31.79, 31.53.

^{19}F NMR (470 MHz, $CDCl_3$) δ -62.6.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{18}H_{21}F_3O_6Na$: 413.1184, found: 413.1188.

Elemental analysis (%) calculated for $C_{18}H_{21}F_3O_6$: C, 55.38; H, 5.42, found: C, 55.36; H, 5.32.

Dimethyl 2-(4-cyano-2-(4-(trifluoromethyl)phenyl)butyl)malonate (13b)



Following General Procedure A, compound **13b** was obtained from D-A cyclopropane **S4** (60 mg, 0.20 mmol) and acrylonitrile (**4b**) (53 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 20:80 AcOEt/Hexanes) to afford 44 mg of compound **13b** as colorless oil. (**Yield = 61%**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H)., 3.75 (s, 3H), 3.60 (s, 3H), 3.09 (dd, *J* = 9.7, 5.2 Hz, 1H), 2.80 (tt, *J* = 10.6, 4.6 Hz, 1H), 2.36 (ddd, *J* = 14.1, 9.7, 4.4 Hz, 1H), 2.27 – 2.15 (m, 2H), 2.14 – 2.00 (m, 2H), 1.96 – 1.85 (m, 1H).

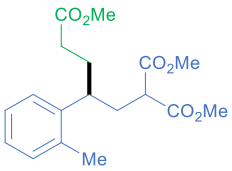
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.16, 169.15, 144.9, 129.95 (q, *J* = 32.7 Hz), 128.1, 126.06 (q, *J* = 3.8 Hz), 123.90 (q, *J* = 272.1 Hz), 118.7, 52.7, 52.6, 49.4, 42.6, 34.8, 31.9, 15.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.65.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{18}NO_4Na\ F_3$: 380.1090, found: 380.1086.

Elemental analysis (%) calculated for $C_{17}H_{18}F_3NO_4$: C, 57.14; H, 5.08; N, 3.92, found: C, 57.09; H, 5.08; N, 3.73.

Trimethyl 3-(2-methylphenyl)pentane-1,1,5-tricarboxylate (14a)



A: Following General Procedure A, compound **14a** was obtained from D-A cyclopropane **S5** (50 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (15:85 AcOEt/Hexanes) to afford 31 mg of compound **14a** as colorless oil. (**Yield = 46%)** After the reaction, substrate could be seen on TLC and GC chromatogram. Therefore, additional reaction was conducted:

B: Following General Procedure A compound **14a** was obtained from D-A cyclopropane **S5** (50 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The reaction time was prolonged from 18 to 48 h. The crude product was purified by column chromatography (gradually from 5:95 to 15:85 Acetone/Hexanes) to afford 41 mg of compound **14a** as colorless oil. (**Yield = 61%**)

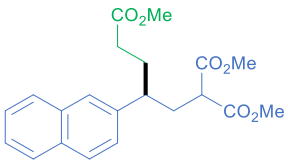
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.04 (m, 4H), 3.71 (s, 3H), 3.61 (s, 3H), 3.59 (s, 3H), 3.17 (dd, *J* = 9.2, 5.7 Hz, 1H), 2.97 (tt, *J* = 10.0, 5.2 Hz, 1H), 2.31 (ddd, *J* = 14.3, 9.2, 5.2 Hz, 1H), 2.22 (s, 3H), 2.21 – 2.08 (m, 3H), 2.08 – 1.95 (m, 1H), 1.94 – 1.80 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 169.73, 169.67, 140.5, 136.6, 130.5, 126.6, 126.4, 125.7, 52.44, 52.42, 51.4, 49.7, 35.2, 31.8, 31.6, 19.5.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{18}H_{24}O_6Na$: 359.1469, found: 359.1471.

Elemental analysis (%) calculated for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19, found: C, 64.31; H, 7.29.

Trimethyl 3-naphthylpentane-1,1,5-tricarboxylate (15a)



Following General Procedure A, compound **15a** was obtained from D-A cyclopropane **S6** (57 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 10:90 to 20:80 AcOEt/Hexanes) to afford 38 mg of compound **15a** as colorless oil. (**Yield = 51%**)

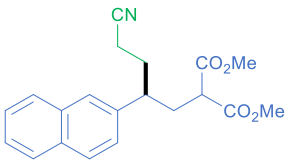
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.73 (m, 3H), 7.54 (s, 1H), 7.52 – 7.40 (m, 2H), 7.28 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.74 (s, 3H), 3.57 (s, 3H), 3.54 (s, 3H), 3.18 (dd, *J* = 9.7, 5.2 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.41 (ddd, *J* = 14.2, 9.7, 4.5 Hz, 1H), 2.33 – 2.22 (m, 1H), 2.21 – 2.07 (m, 3H), 2.07 – 1.94 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 169.65, 169.64, 139.5, 133.5, 132.6, 128.7, 127.6, 127.1, 126.1, 125.7, 125.2, 52.44, 52.38, 51.4, 49.8, 43.4, 35.4, 32.0, 31.6.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{21}H_{24}O_6Na$: 395.1469, found: 395.1471.

Elemental analysis (%) calculated for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50, found: C, 67.46; H, 6.47.

Dimethyl 2-(4-cyano-2-naphthylbutyl)malonate (15b)



Following General Procedure A, compound **15b** was obtained from D-A cyclopropane **S6** (57 mg, 0.20 mmol) and acrylonitrile (**4b**) (53 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 10:90 to 20:80 AcOEt/Hexanes) to afford 53 mg of compound **15b** as colorless oil. (**Yield = 78%**)

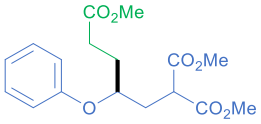
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.75 (m, 3H), 7.59 (s, 1H), 7.53 – 7.43 (m, 2H), 7.29 – 7.24 (m, 1H), 3.76 (s, 3H), 3.54 (s, 3H), 3.16 (dd, *J* = 9.8, 5.1 Hz, 1H), 2.92 – 2.85 (m, 1H), 2.41 (ddd, *J* = 14.1, 9.8, 4.4 Hz, 1H), 2.33 – 2.25 (m, 1H), 2.24 – 1.96 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 137.8, 133.4, 132.8, 129.1, 127.6, 127.3, 126.4, 126.0, 124.5, 119.1, 52.6, 52.4, 49.6, 42.9, 35.0, 32.1, 15.3.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{20}H_{21}NO_4Na$: 362.1360, found: 362.1368.

Elemental analysis (%) calculated for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13, found: C, 70.52; H, 6.21; N, 4.16.

Trimethyl 3-phenoxypentane-1,1,5-tricarboxylate (16a)



A: Following General Procedure A, compound **16a** was obtained from D-A cyclopropane **S7** (50 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 10:90 to 20:80 AcOEt/Hexanes) to afford 14 mg of compound **16a** as colorless oil. (**Yield = 21%**)

B: Following General Procedure B, compound **16a** was obtained from D-A cyclopropane **S7** (57 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 10:90 to 20:80 AcOEt/Hexanes) to afford 24 mg of compound **16a** as colorless oil. (**Yield = 35%**)

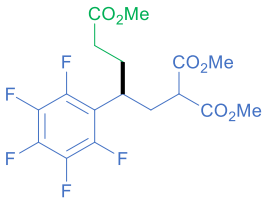
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 2H), 4.43 (p, *J* = 5.9 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 3H), 3.66 – 3.61 (m, 3H + 1 H), 2.47 – 2.40 (m, 2H), 2.31 – 2.24 (m, 2H), 2.07 – 1.92 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 169.7, 169.5, 157.8, 129.6, 121.2, 115.7, 73.9, 52.6, 52.6, 51.6, 48.1, 33.1, 29.3, 28.8.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{22}O_7Na$: 361.1262, found: 361.1263.

Elemental analysis (%) calculated for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55, found: C, 60.11; H, 6.51.

Trimethyl 3-(perfluorophenyl)pentane-1,1,5-tricarboxylate (17a)



Following General Procedure A, compound **17a** was obtained from D-A cyclopropane **S8** (65 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 10:90 Acetone/Hexanes) to afford 19 mg of compound **17a** as colorless oil. (**Yield = 23%**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.67 (s, 3H), 3.63 (s, 3H), 3.16 – 3.12 (m, 2H), 2.41 – 2.33 (m, 2H), 2.25 – 2.16 (m, 2H), 2.13 – 2.04 (m, 2H).

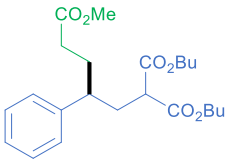
^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 168.95, 168.93, 146.6 – 146.4 (m), 144.6 – 144.4 (m) (from: 145.5, d, *J* = 246.1 Hz, C-F), 141.2 – 141.0 (m), 139.2 – 139.0 (m) (from: 140.1, d, *J* = 253.7 Hz, C-F), 138.7 – 138.5 (m), 136.7 – 136.5 (m) (from: 137.6, d, *J* = 252.0 Hz, C-F), 115.0 (t, *J* = 15.4 Hz, C), 52.71, 52.68, 51.7, 49.9, 33.3, 32.3, 32.0, 28.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ -141.59, -155.27 (t, *J* = 20.8 Hz), -161.42 (td, *J* = 21.8, 7.8 Hz).

HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{17}F_5O_6Na$: 435.0846, found: 435.0843.

Elemental analysis (%) calculated for $C_{17}H_{17}F_5O_6$: C, 49.52; H, 4.16, found: C, 49.53; H, 4.14.

1,1-di-*n*-Butyl 5-methyl 3-phenylpentane-1,1,5-tricarboxylate (18a)



Following General Procedure A, compound **18a** was obtained from D-A cyclopropane **S9** (64 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (10:90 AcOEt/Hexanes) to afford 24 mg of compound **18a** as colorless oil. (**Yield = 30%**)

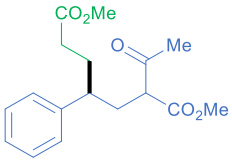
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.18 (m, 1H), 7.12 – 7.08 (m, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 4.06 – 3.94 (m, 2H), 3.59 (s, 3H), 3.10 (dd, *J* = 9.9, 5.0 Hz, 1H), 2.56 (tt, *J* = 9.9, 4.7 Hz, 1H), 2.30 (ddd, *J* = 14.3, 9.9, 4.6 Hz, 1H), 2.21 – 2.09 (m, 3H), 2.07 – 1.96 (m, 1H), 1.95 – 1.83 (m, 1H), 1.65 – 1.56 (m, 2H), 1.56 – 1.49 (m, 2H), 1.40 – 1.27 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 169.39, 169.36, 142.3, 128.7, 127.8, 126.9, 65.2, 65.1, 51.4, 50.1, 43.2, 35.4, 32.1, 31.8, 30.5, 30.4, 19.00, 18.94, 13.6.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{23}H_{34}O_6Na$: 429.2255, found: 429.2253.

Elemental analysis (%) calculated for $C_{23}H_{34}O_6$: C, 67.96; H, 8.43, found: C, 68.23; H, 8.67.

Dimethyl 2-acetyl-4-phenylheptanedioate (19a)



Following General Procedure A, compound **19a** was obtained from D-A cyclopropane **S10** (44 mg, 0.20 mmol) and methyl acrylate (**4a**) (86 mg, 1.0 mmol). The crude product was purified by column chromatography (20:80 AcOEt/Hexanes) to afford 21 mg of compound **19a** as colorless oil (mixture of diastereomers, ratio = 48:52). (**Yield = 35%**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.75 (s, 1H from enolate) 7.31 – 7.28 (m, 2H + 2H +2H), 7.25 – 7.19 (m, 1H + 1H + 1H), 7.09 – 7.07 (m, 2H + 2H +2H), 3.73 (s, 3H), 3.69 (s, 3H from enolate) 3.60 (s, 3H from enolate) 3.59 (s, 3H), 3.58 (s, 3H), 3.26 (dd, *J* = 9.3, 5.3 Hz, 1H), 3.18 (dd, *J* = 10.0, 4.4 Hz, 1H), 2.55 – 2.45 (m, 1H + 1H), 2.35 – 2.22 (m, 1H = 1H), 2.20 – 1.94 (m, 4H + 4H), 2.13 (s, 3H), 2.03 (s, 3H), 1.93 – 1.81 (m, 1H + 1H).

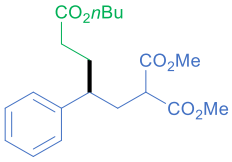
*Most of the enolate protons could not be clearly specified, therefore they are not listed above.

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 202.7, 173.66, 173.66, 170.1, 169.9, 142.35, 142.32, 128.78, 128.76, 127.73, 127.71, 126.98, 126.95, 57.6, 57.0, 52.37, 52.34, 51.5, 43.4, 43.1, 34.6, 34.5, 32.02, 31.97, 31.9, 31.8, 29.7, 28.7.

HRMS (ESI) $[M-H]^-$ calculated for $C_{17}H_{21}O_5$: 305.1383, found: 305.1389.

Elemental analysis (%) calculated for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24, found: C, 66.39; H, 7.31.

5-*n*-Butyl 1,1-dimethyl 3-phenylpentane-1,1,5-tricarboxylate (5c)



Following General Procedure A, compound **5c** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and *n*-butyl acrylate (**4c**) (128 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 10:90 AcOEt/Hexanes) to afford 52 mg of compound **5c** as colorless oil. (**Yield = 72%**)

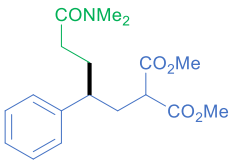
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 7.13 – 7.09 (m, 2H), 4.09 – 3.94 (m, 2H), 3.73 (s, 3H), 3.60 (s, 3H), 3.15 (dd, *J* = 9.8, 5.2 Hz, 1H), 2.56 (tt, *J* = 9.8, 4.6 Hz, 1H), 2.32 (ddd, *J* = 14.2, 9.8, 4.4 Hz, 1H), 2.23 – 1.96 (m, 4H), 1.95 – 1.82 (m, 1H), 1.64 – 1.45 (m, 2H), 1.42 – 1.28 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 169.67, 169.64, 142.2, 128.7, 127.8, 126.9, 64.2, 52.4, 49.8, 43.3, 35.5, 32.3, 31.8, 30.6, 19.1, 13.6.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{20}H_{28}O_6Na$: 387.1784, found: 387.1782.

Elemental analysis (%) calculated for $C_{20}H_{28}O_6$: C, 65.92; H, 7.74, found: C, 66.01; H, 7.84.

Dimethyl 2-(5-(dimethylamino)-5-oxo-2-phenylpentyl)malonate (5d)



Following General Procedure A, compound **xa** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and *N*,*N*-dimethylacrylamide (**4d**) (99 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 40:60 to 80:20 AcOEt/Hexanes) to afford 45 mg of compound **5d** as yellowish oil. (**Yield = 66%**)

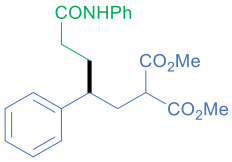
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 7.16 – 7.10 (m, 2H), 3.73 (s, 3H), 3.59 (s, 3H), 3.17 (dd, *J* = 9.5, 5.4 Hz, 1H), 2.88 (s, 3H), 2.81 (s, 3H), 2.65 – 2.52 (m, 1H), 2.33 (ddd, *J* = 14.2, 9.6, 4.6 Hz, 1H), 2.22 – 2.00 (m, 4H), 1.95 – 1.85 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 169.75, 169.74, 142.7, 128.7, 127.8, 126.8, 52.42, 52.39, 49.8, 43.4, 37.0, 35.6, 35.3, 31.9, 31.1.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{18}H_{25}NO_5Na$: 358.1630, found: 358.1632.

Elemental analysis (%) calculated for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18, found: C, 64.43; H, 7.66; N, 4.23.

Dimethyl 2-(5-oxo-2-phenyl-5-(phenylamino)pentyl)malonate (5e)



Following General Procedure B, compound **5e** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and *N*-phenylacrylamide (**4e**) (147 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 20:80 to 25:75 AcOEt/Hexanes) to afford 53 mg of compound **5e** as yellowish oil. (**Yield = 69%**)

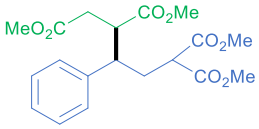
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 7.14 (d, *J* = 7.0 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 3.18 (dd, *J* = 9.8, 5.1 Hz, 1H), 2.67 – 2.55 (m, 1H), 2.37 (ddd, *J* = 14.0, 9.8, 4.3 Hz, 1H), 2.23 – 2.11 (m, 4H), 2.07 – 1.92 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.75, 169.68, 142.4, 137.9, 128.9, 128.8, 127.8, 127.0, 124.1, 119.7, 52.5, 52.4, 49.7, 43.2, 35.4, 32.1.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{22}H_{25}NO_5Na$: 406.1630, found: 406.1633.

Elemental analysis (%) calculated for $C_{22}H_{25}NO_5$: C, 68.91; H, 6.57; N, 3.65, found: C, 68.91; H, 6.64; N, 3.65.

Tetramethyl 3-phenylpentane-1,1,4,5-tetracarboxylate (5f)



A: Following General Procedure B, compound **5f** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and dimethyl fumarate (**4f**) (144 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 15:85 to 25:75 AcOEt/Hexanes) to afford 48 mg of compound **xa** in dimethyl fumarate reaction as colorless oil (mixture of diastereomers, ratio = 40:60). (**Yield = 63%**)

B: Following General Procedure B, compound **5f** was obtained 0 D-A cyclopropane **3** (47 mg, 0.20 mmol) and dimethyl maleate (**4f'**) (144 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 15:85 to 25:75 AcOEt/Hexanes) to afford 36 mg of compound **5f** as colorless oil (mixture of diastereomers, ratio = 40:60). (**Yield = 47%**)

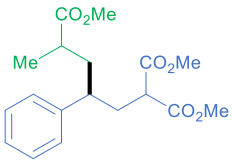
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.18 (m, 3H + 3H), 7.14 – 7.06 (m, 2H + 2H), 3.75 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.62 (s, 3H), 3.61 (s, 3H), 3.56 (s, 3H), 3.54 (s, 3H), 3.49 (s, 3H), 3.18 – 3.06 (m, 2H), 3.06 – 2.99 (m, 2H), 2.96 – 2.86 (m, 1H), 2.84 – 2.68 (m, 1H + 1H), 2.62 – 2.47 (m, 1H + 1H), 2.44 – 2.18 (m, 2H + 2H), 2.13 (dd, *J* = 16.8, 3.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 173.5, 172.2, 172.0, 169.44, 169.37, 169.2, 169.1, 139.3, 139.0, 129.0, 128.6, 128.3, 128.2, 127.6, 127.5, 52.5, 52.5, 52.4, 52.0, 51.8, 51.7, 49.7, 49.6, 47.5, 47.4, 45.8, 45.3, 35.1, 33.5, 32.8, 30.9.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{19}H_{24}O_8Na$: 403.1369, found: 403.1366.

Elemental analysis (%) calculated for $C_{19}H_{24}O_8$: C, 59.99; H, 6.36, found: C, 60.08; H, 6.40.

Trimethyl 3-phenylhexane-1,1,5-tricarboxylate (5g)



Following General Procedure A, compound **5g** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and methyl methacrylate (**4g**) (100 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually 5:95 to 10:90 Acetone/Hexanes) to afford 52 mg of compound **5g** as colorless oil (mixture of diastereomers, ratio = 32:68). (**Yield = 78%**)

Following General Procedure B, compound **5g** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and methyl methacrylate (**4g**) (100 mg, 1.0 mmol). The crude product was purified by column chromatography (15:85 AcOEt/Hexanes) to afford 52 mg of compound **5g** as colorless oil (mixture of diastereomers, ratio = 33:67). (**Yield = 78%**)

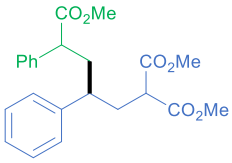
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H + 2H), 7.24 – 7.18 (m, 1H + 1H), 7.14 – 7.06 (m, 2H + 2H), 3.73 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 3.59 (s, 3H), 3.58 (s, 3H), 3.52 (s, 3H), 3.18 – 3.08 (m, 1H + 1H), 2.67 – 2.52 (m, 1H + 1H), 2.36 – 2.17 (m, 2H + 2H), 2.16 – 1.98 (m, 2H + 2H), 1.78 – 1.59 (m, 1H + 1H), 1.10 (d, *J* = 7.0 Hz, 3H), 1.06 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 176.7, 169.7, 169.6, 142.6, 142.0, 128.7, 128.6, 127.81, 127.79, 126.9, 126.8, 52.42, 52.39, 51.5, 49.8, 49.7, 41.7, 41.4, 41.0, 40.1, 37.3, 37.2, 35.8, 35.5, 17.8, 16.6.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{18}H_{24}O_6Na$: 359.1471, found: 359.1475.

Elemental analysis (%) calculated for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19, found: C, 64.08; H, 7.22.

Trimethyl 3,5-diphenylpentane-1,1,5-tricarboxylate (5h)



Following General Procedure A, compound **5h** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and methyl 2-phenylacrylate (**4h**) (162 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 10:90 to 15:85 AcOEt/Hexanes) to afford 54 mg of compound **5h** as yellowish oil (mixture of diastereomers, ratio = 45:55). (**Yield = 67%**)

Following General Procedure B, compound **5h** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and methyl 2-phenylacrylate (**4h**) (162 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 10:90 to 15:85 AcOEt/Hexanes) to afford 64 mg of compound **5h** as yellowish oil (mixture of diastereomers, ratio = 45:55). (**Yield = 80%**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 6H + 6H), 7.19 – 7.14 (m, 2H + 2H), 7.09 – 7.01 (m, 2H + 2H), 3.69 (s, 3H), 3.64 (s, 3H), 3.61 (s, 3H), 3.59 (s, 3H), 3.53 (s, 3H), 3.51 (s,

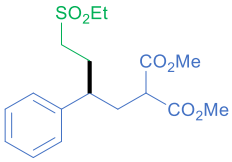
3H), 3.38 (dd, *J* = 9.5, 5.4 Hz, 1H), 3.30 (dd, *J* = 9.7, 5.2 Hz, 1H), 3.15 (dd, *J* = 9.4, 5.5 Hz, 1H), 3.09 (dd, *J* = 9.0, 5.8 Hz, 1H), 2.61 – 2.44 (m, 2H), 2.42 – 2.07 (m, 7H), 2.02 – 1.90 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 173.9, 169.6, 169.5, 169.52, 169.46, 142.4, 141.9, 139.1, 138.2, 128.74, 128.67, 128.6, 128.2, 128.0, 127.73, 127.69, 127.4, 127.2, 126.99, 126.96, 52.39, 52.38, 52.32, 52.30, 51.9, 51.9, 49.81, 49.77, 49.1, 49.0, 41.8, 41.1, 40.7, 39.4, 35.9, 35.3.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{23}H_{26}O_6Na$: 421.1627, found: 421.1631.

Elemental analysis (%) calculated for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58, found: C, 69.00; H, 6.71.

Dimethyl 2-(4-(ethylsulfonyl)-2-phenylbutyl)malonate (5i)



Following General Procedure B, compound **5i** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and ethyl vinyl sulfone (**4i**) (120 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 20:80 to 40:60 AcOEt/Hexanes) to afford 21 mg of compound **5i** as colorless oil. (**Yield = 30%**)

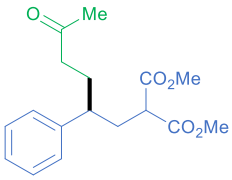
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.15 – 7.10 (m, 2H), 3.74 (s, 3H), 3.61 (s, 3H), 3.14 (dd, *J* = 9.9, 5.0 Hz, 1H), 2.89 (q, *J* = 7.5 Hz, 2H), 2.80 (ddd, *J* = 13.8, 11.3, 5.3 Hz, 1H), 2.72 – 2.61 (m, 2H), 2.35 (ddd, *J* = 14.2, 9.9, 4.4 Hz, 1H), 2.29 – 2.14 (m, 2H), 2.14 – 2.02 (m, 1H), 1.30 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.46, 169.42, 140.9, 129.1, 127.6, 127.5, 52.56, 52.53, 50.0, 49.5, 47.1, 42.7, 35.4, 28.60, 6.5.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{24}O_6S$: 379.1191, found: 379.1194.

Elemental analysis (%) calculated for $C_{17}H_{24}O_6S$: 57.29; H, 6.79, found: C, 57.45; H, 7.04.

Dimethyl 2-(5-oxo-2-phenylhexyl)malonate (5j)



Following General Procedure B, compound **5j** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and methyl vinyl ketone (**4j**) (70 mg, 1.0 mmol). The crude product was purified by column chromatography (20:80 AcOEt/Hexanes) to afford 26 mg of compound **5j** as colorless oil. (**Yield = 43%**)

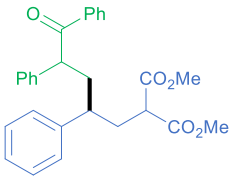
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.26 – 7.17 (m, 1H), 7.13 – 7.06 (m, 2H), 3.73 (s, 3H), 3.60 (s, 3H), 3.14 (dd, *J* = 9.8, 5.2 Hz, 1H), 2.52 (tt, *J* = 10.0, 4.8 Hz, 1H), 2.36 – 2.07 (m, 4H), 2.01 (s, 3H), 2.01 – 1.91 (m, 1H), 1.88 – 1.76 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 169.7, 142.5, 128.7, 127.7, 126.9, 52.42, 52.40, 49.8, 43.1, 41.4, 35.6, 30.4, 29.9.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{22}O_5Na$: 329.1365, found: 329.1375.

Elemental analysis (%) calculated for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24, found: C, 66.49; H, 7.30.

Dimethyl 2-(5-oxo-2,4,5-triphenylpentyl)malonate (5k)



Following General Procedure B, compound **5k** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and 1,2-diphenyl-2-propen-1-one (**4k**) (208 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 5:95 to 10:90 AcOEt/Hexanes) to afford 67 mg of compound **5k** as yellowish oil (mixture of diastereomers, ratio = 40:60). (**Yield = 77%**)

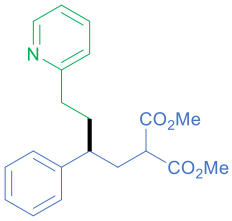
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H + 2H), 7.46 – 7.38 (m, 1H + 1H), 7.37 – 7.10 (m, 12H + 10H), 7.05 – 7.00 (m, 2H), 4.37 – 4.27 (m, 1H + 1H), 3.71 (s, 3H), 3.58 (s, 3H), 3.56 (s, 3H), 3.52 (s, 3H), 3.19 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.12 (dd, *J* = 8.9, 6.1 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.58 (tt, *J* = 10.1, 4.8 Hz, 1H), 2.45 – 2.11 (m, 5H + 2H), 1.96 (ddd, *J* = 13.9, 9.7, 4.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 169.7, 169.6, 169.54, 169.46, 142.8, 142.5, 139.6, 138.5, 136.9, 136.4, 132.8, 132.7, 128.9, 128.8, 128.73, 128.65, 128.54, 128.50, 128.4, 128.3, 128.11, 128.0, 127.9, 127.1, 126.98, 126.89, 52.43, 52.36, 52.30, 52.26, 50.92, 50.90, 49.90, 49.84, 41.84, 41.2, 41.0, 39.8, 36.1, 35.6.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{28}H_{28}O_5Na$: 467.1834, found: 467.1833.

Elemental analysis (%) calculated for $C_{28}H_{28}O_5$: C, 75.66; H, 6.35, found: C, 75.70; H, 6.40.

Dimethyl 2-(2-phenyl-4-(pyridin-2-yl)butyl)malonate (5l)



Following General Procedure B, compound **5l** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and 2-vinylpyridine (**4l**) (105 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 30:70 to 40:60 AcOEt/Hexanes) to afford 57 mg of compound **5l** as colorless oil. (**Yield = 83%**)

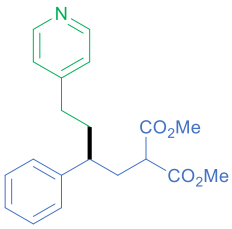
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.0 Hz, 1H), 7.52 (td, *J* = 7.7, 1.9 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 7.17 – 7.11 (m, 2H), 7.05 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 3.70 (s, 3H), 3.58 (s, 3H), 3.15 (dd, *J* = 9.8, 5.2 Hz, 1H), 2.71 – 2.52 (m, 3H), 2.36 (ddd, *J* = 14.2, 9.8, 4.5 Hz, 1H), 2.21 – 2.08 (m, 2H), 2.07 – 1.96 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.72, 169.69, 161.6, 149.1, 142.9, 136.3, 128.6, 127.8, 126.7, 122.8, 121.0, 52.3, 49.8, 43.6, 36.7, 36.1, 35.6.

HRMS (ESI) $[M+H]^+$ calculated for $C_{20}H_{24}NO_4$: 342.1705, found: 342.1704.

Elemental analysis (%) calculated for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10, found: C, 70.14; H, 6.70; N 4.16.

Dimethyl 2-(2-phenyl-4-(pyridin-4-yl)butyl)malonate (5m)



Following General Procedure B, compound **5m** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and 4-vinylpyridine (**4m**) (105 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 30:70 to 40:60 AcOEt/Hexanes) to afford 49 mg of compound **5m** as yellowish oil. (**Yield = 72%**)

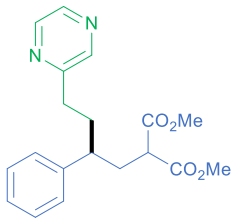
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.9 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 5.1 Hz, 2H), 3.70 (s, 3H), 3.58 (s, 3H), 3.12 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.57 – 2.48 (m, 1H), 2.48 – 2.39 (m, 2H), 2.34 (ddd, *J* = 14.2, 9.9, 4.3 Hz, 1H), 2.14 (ddd, *J* = 13.9, 10.9, 5.0 Hz, 1H), 2.04 – 1.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 150.9, 149.6, 142.5, 128.7, 127.7, 126.9, 123.8, 52.4, 49.7, 43.2, 37.2, 35.5, 32.9.

HRMS (ESI) $[M+H]^+$ calculated for $C_{20}H_{24}NO_4$: 342.1705, found: 342.1708.

Elemental analysis (%) calculated for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10, found: C, 69.96; H, 6.91; N, 3.96.

Dimethyl 2-(2-phenyl-4-(pyrazin-2-yl)butyl)malonate (5n)



Following General Procedure B, compound **5n** was obtained from D-A cyclopropane **3** (47 mg, 0.20 mmol) and 2-vinylpyrazine (**4n**) (106 mg, 1.0 mmol). The crude product was purified by column chromatography (gradually from 25:75 to 40:60 AcOEt/Hexanes) to afford 52 mg of compound **5n** as an off-white solid. (**Yield = 75%**)

m.p. 77.0 – 77.9 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.34 (d, *J* = 2.5 Hz, 1H), 8.30 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.17 (m, 1H), 7.17 – 7.11 (m, 2H), 3.71 (s, 3H), 3.60 (s, 3H), 3.17 (dd, *J* = 9.5, 5.3 Hz, 1H), 2.74 – 2.58 (m, 3H), 2.37 (ddd, *J* = 14.1, 9.6, 4.6 Hz, 1H), 2.23 – 2.01 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.66, 169.64, 157.3, 144.6, 144.0, 142.8, 142.1, 128.8, 127.9, 126.9, 52.3, 49.9, 43.7, 36.0, 35.7, 33.3.

HRMS (ESI) $[M+Na]^+$ calculated for $C_{19}H_{22}N_2O_4Na$: 365.1477, found: 365.1482.

Elemental analysis (%) calculated for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18, found: C, 66.85; H, 6.49; N; 8.05.

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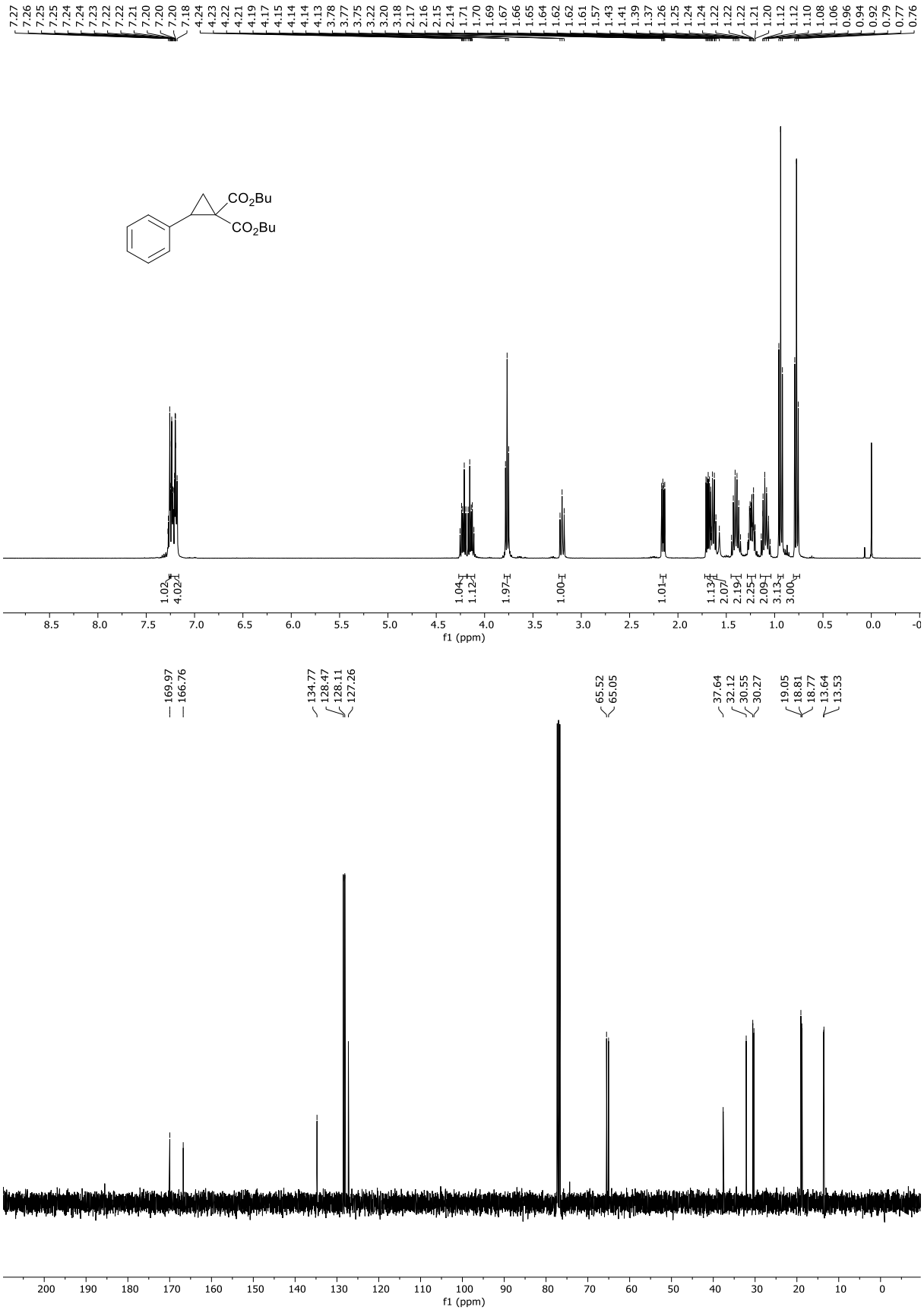
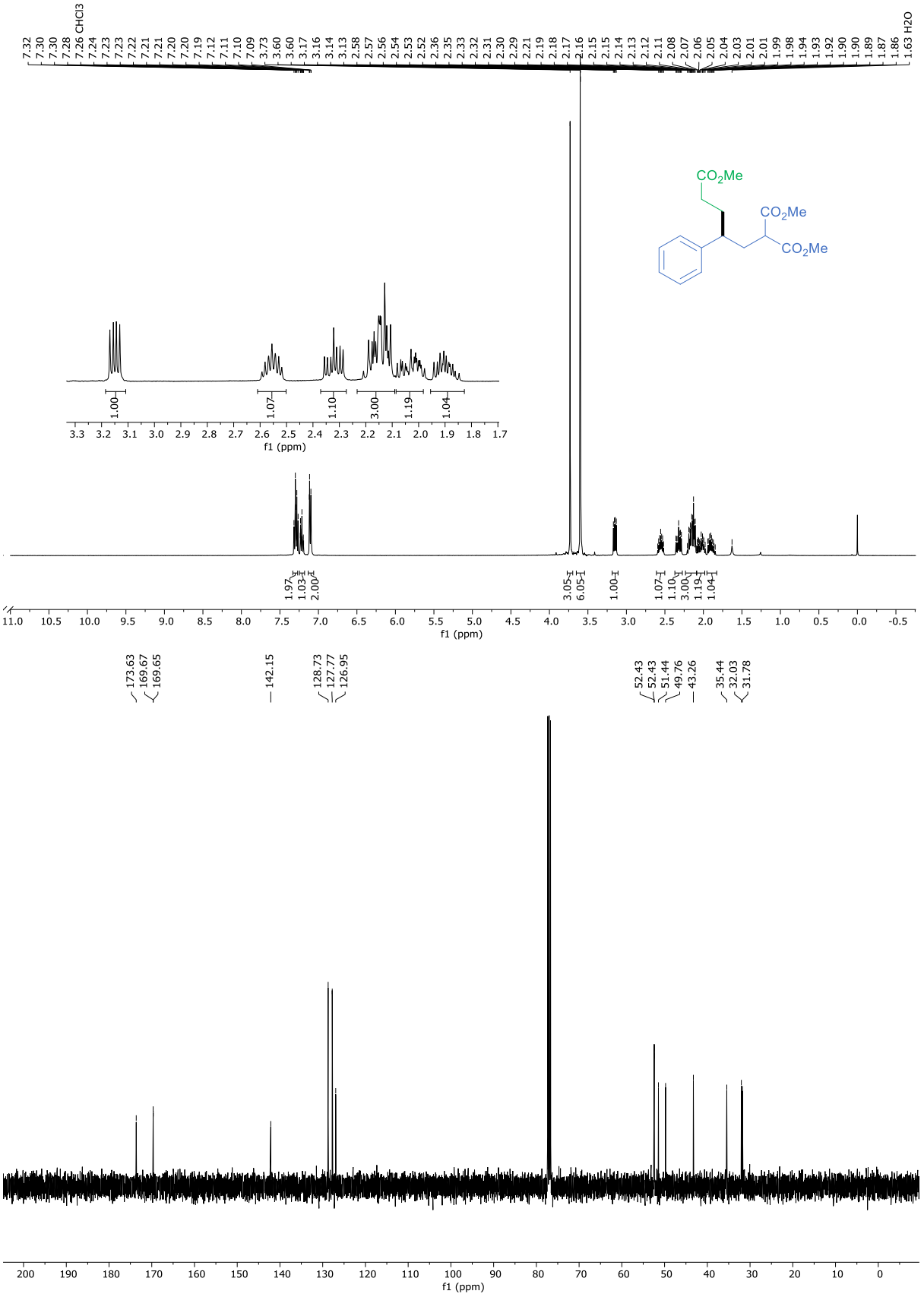
7. NMR spectra

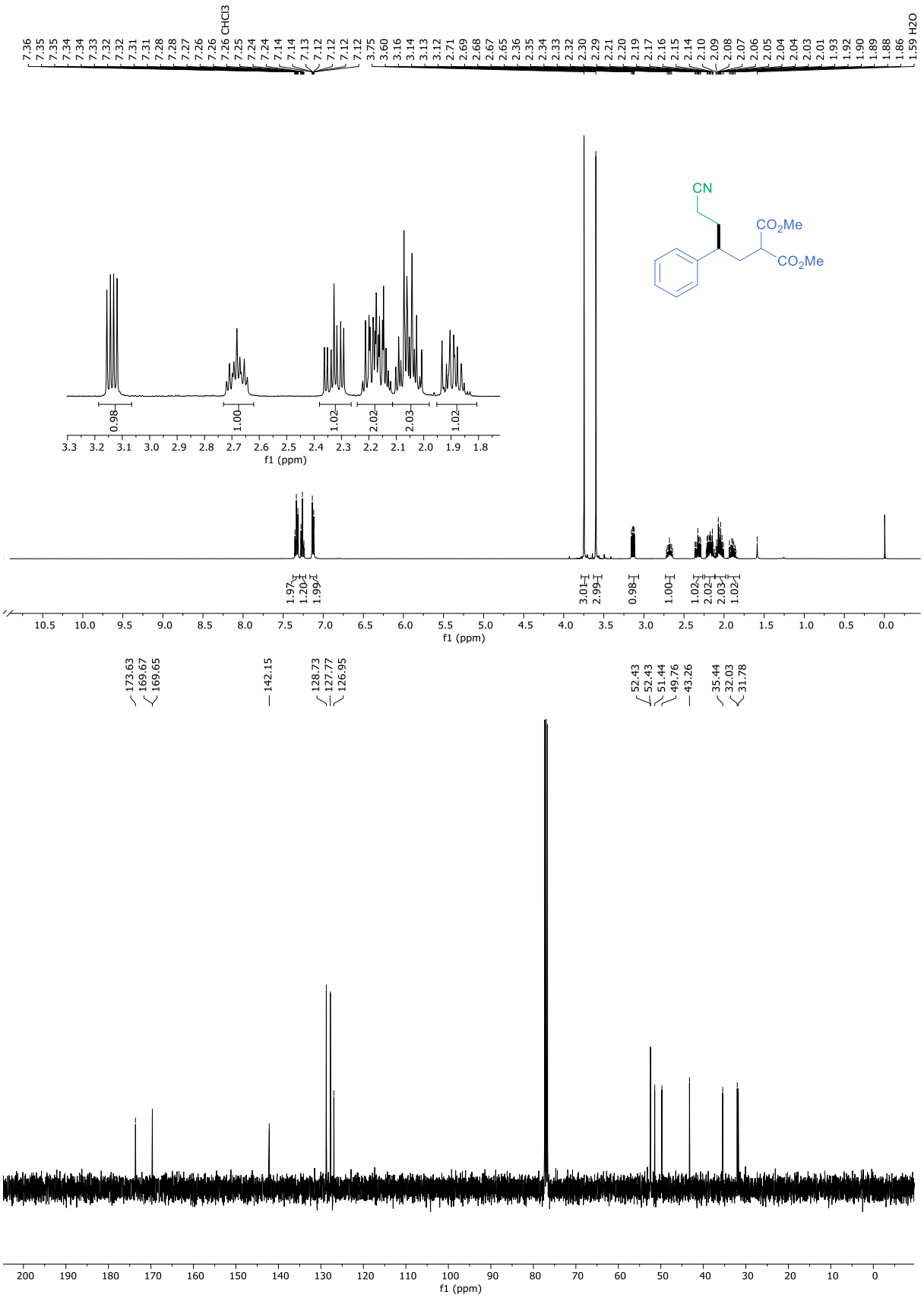
Dibutyl 2-phenylcyclopropane-1,1-dicarboxylate (S9)



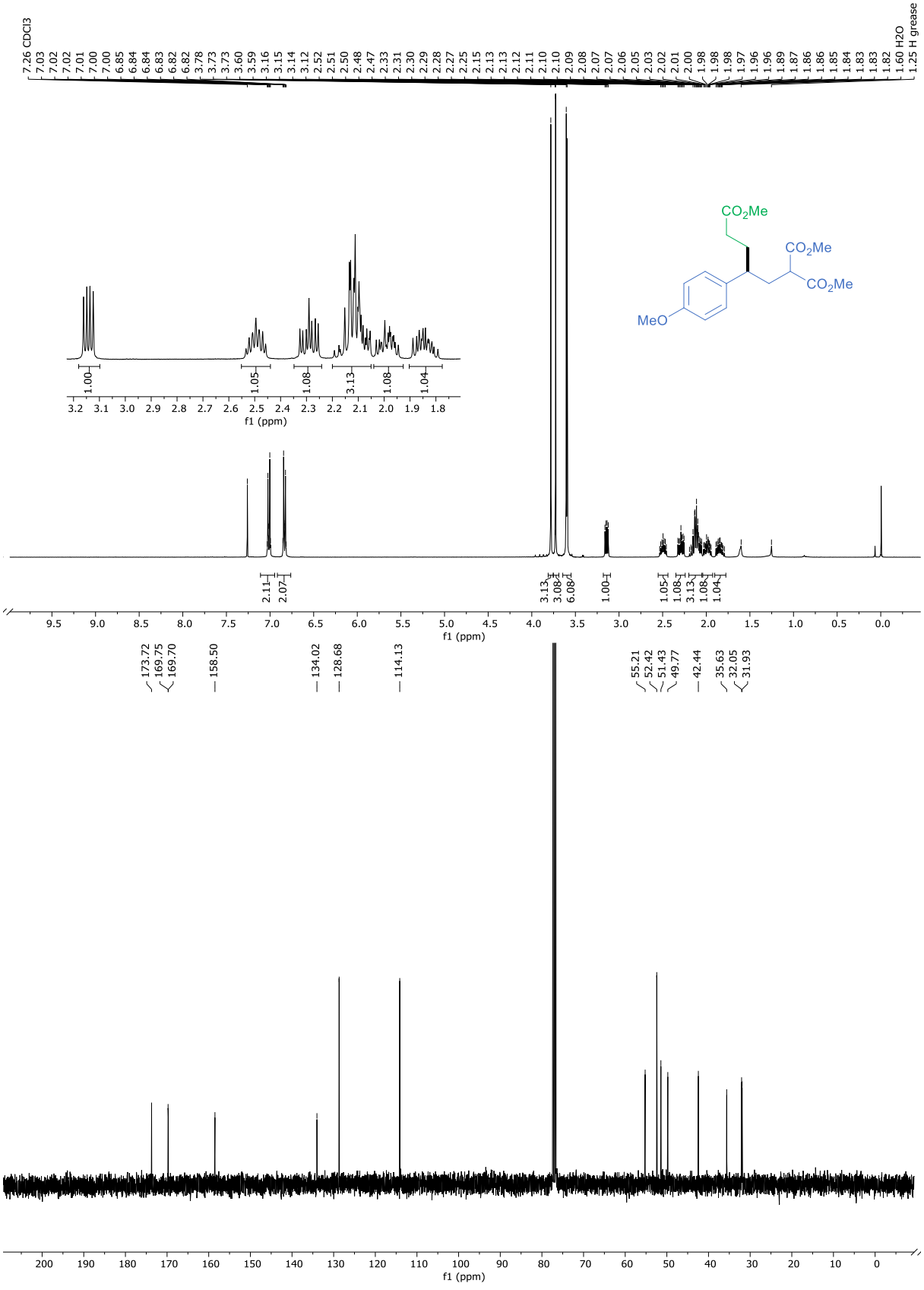
Trimethyl 3-phenylpentane-1,1,5-tricarboxylate (5a)



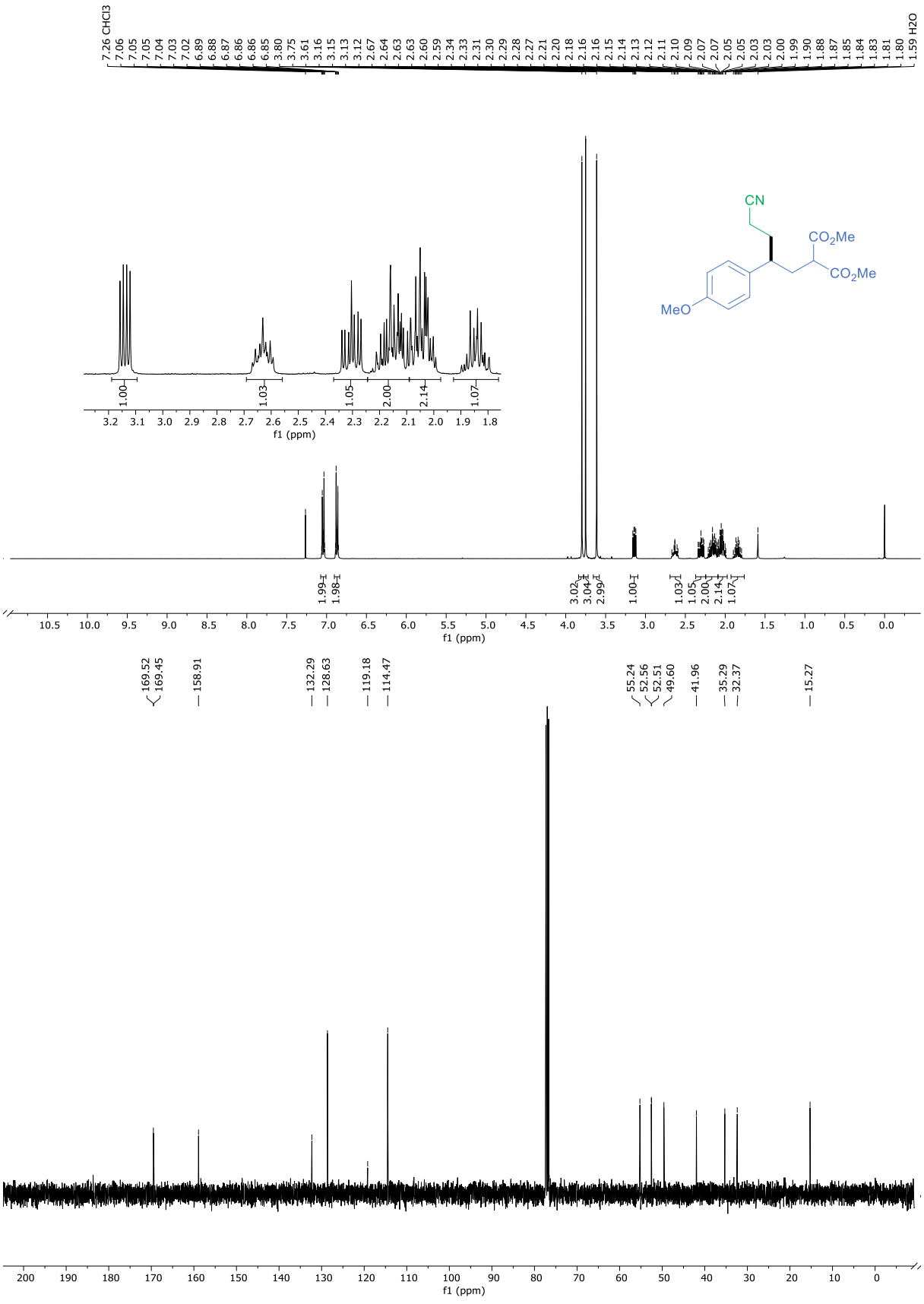
Dimethyl 2-(4-cyano-2-phenylbutyl)malonate (5b)



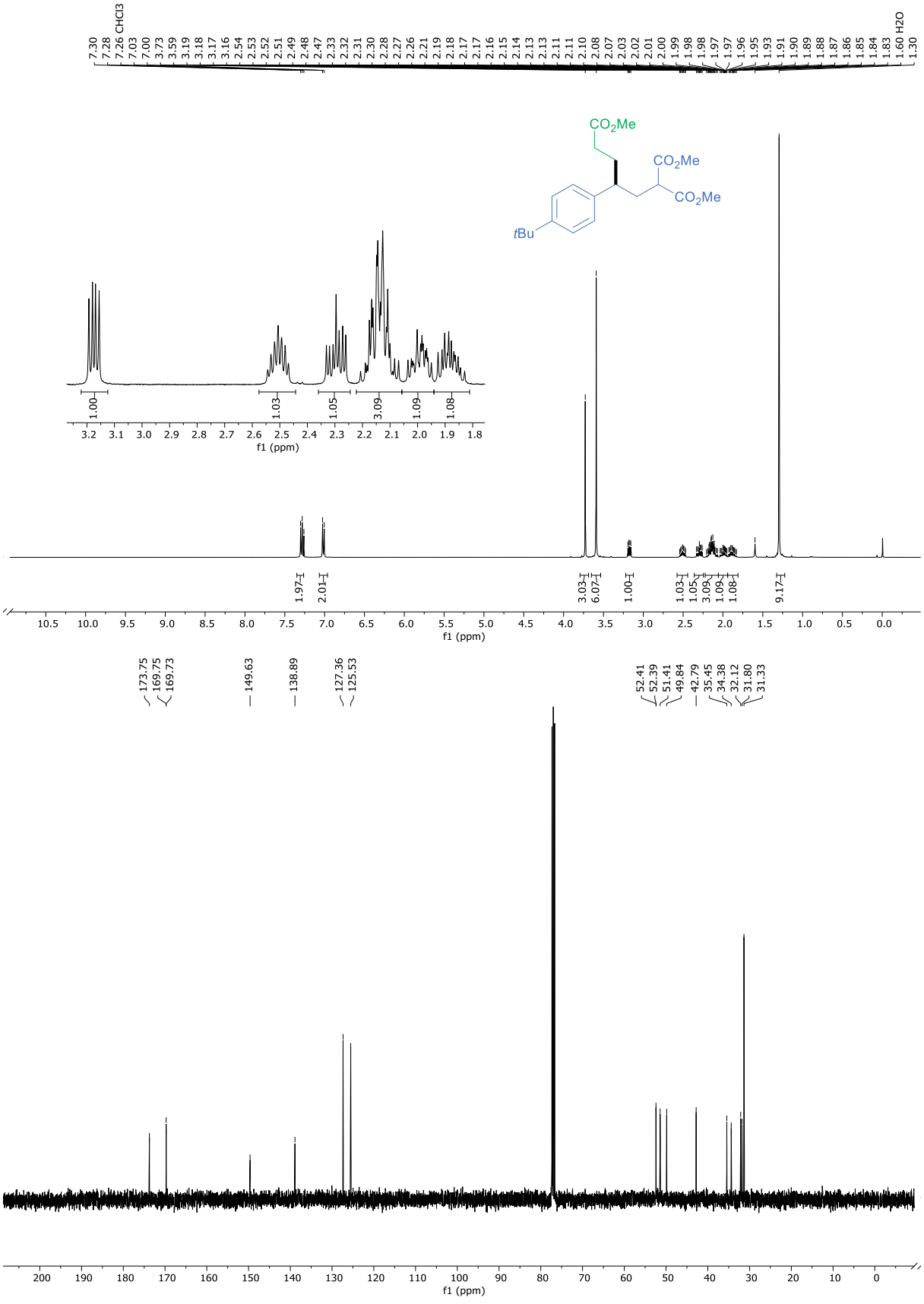
Trimethyl 3-(4-methoxyphenyl)pentane-1,1,5-tricarboxylate (10a)



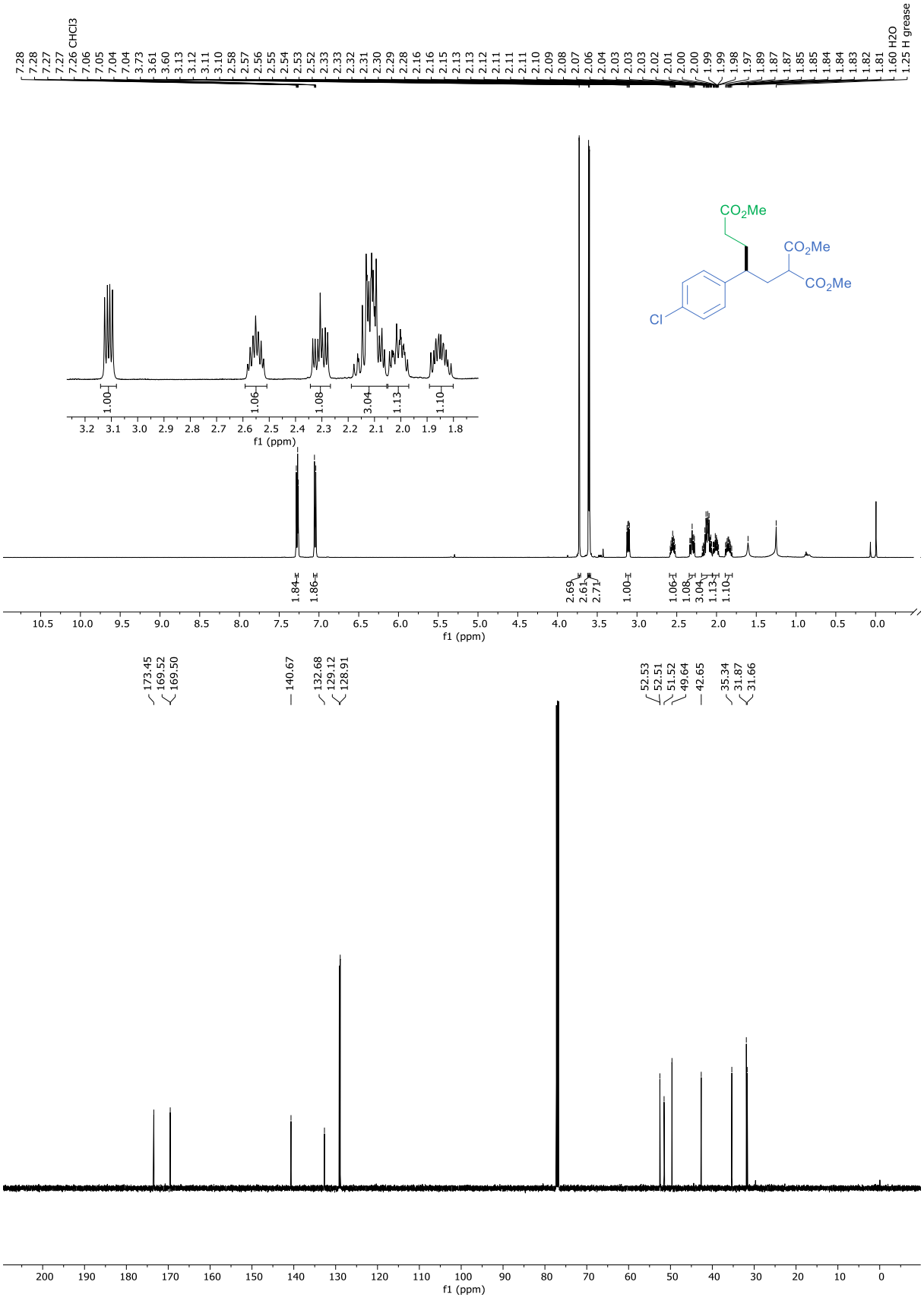
Dimethyl 2-(4-cyano-2-(4-methoxyphenyl)butyl)malonate (10b)



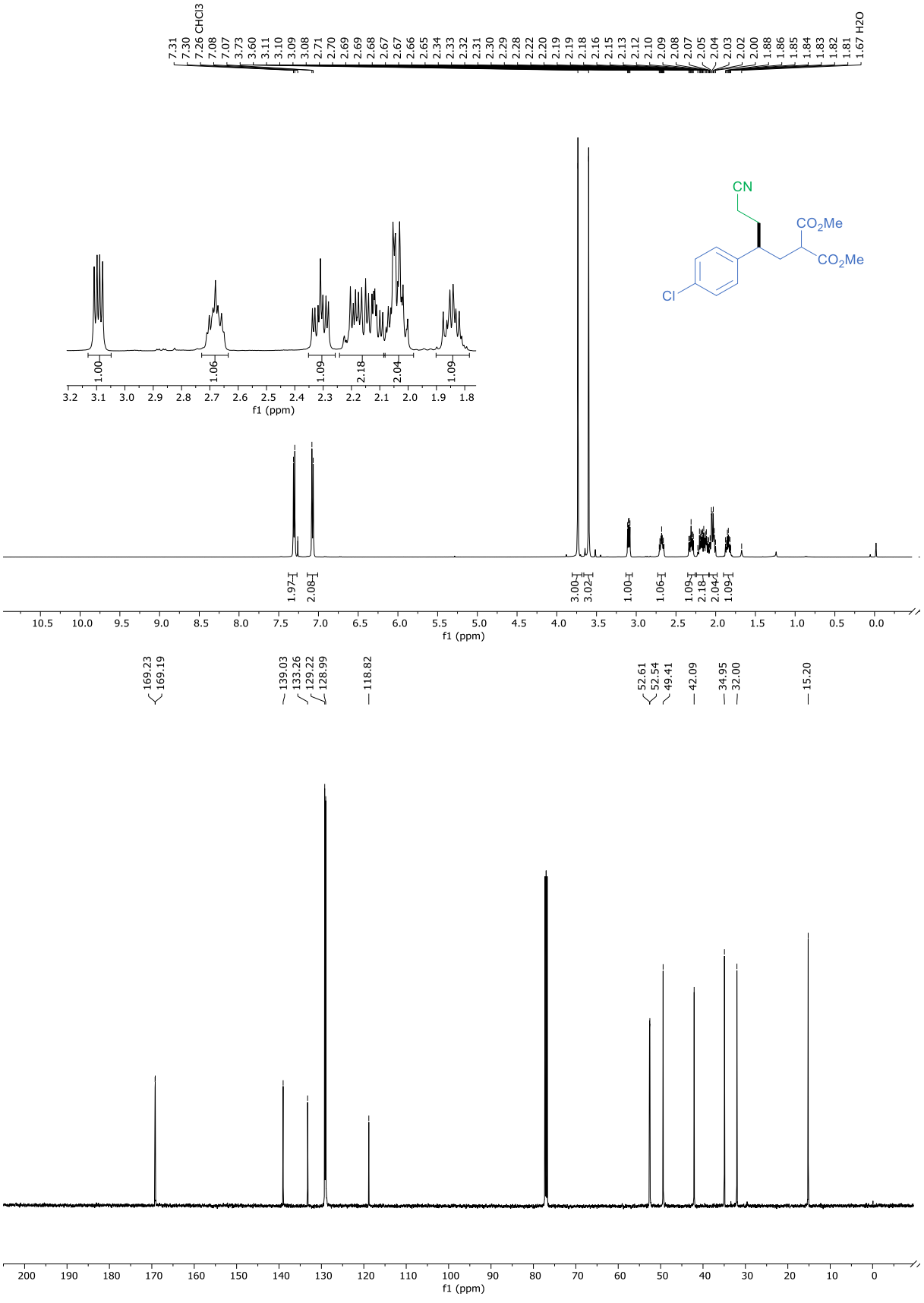
Trimethyl 3-(4-(*tert*-butyl)phenyl)pentane-1,1,5-tricarboxylate (11a)



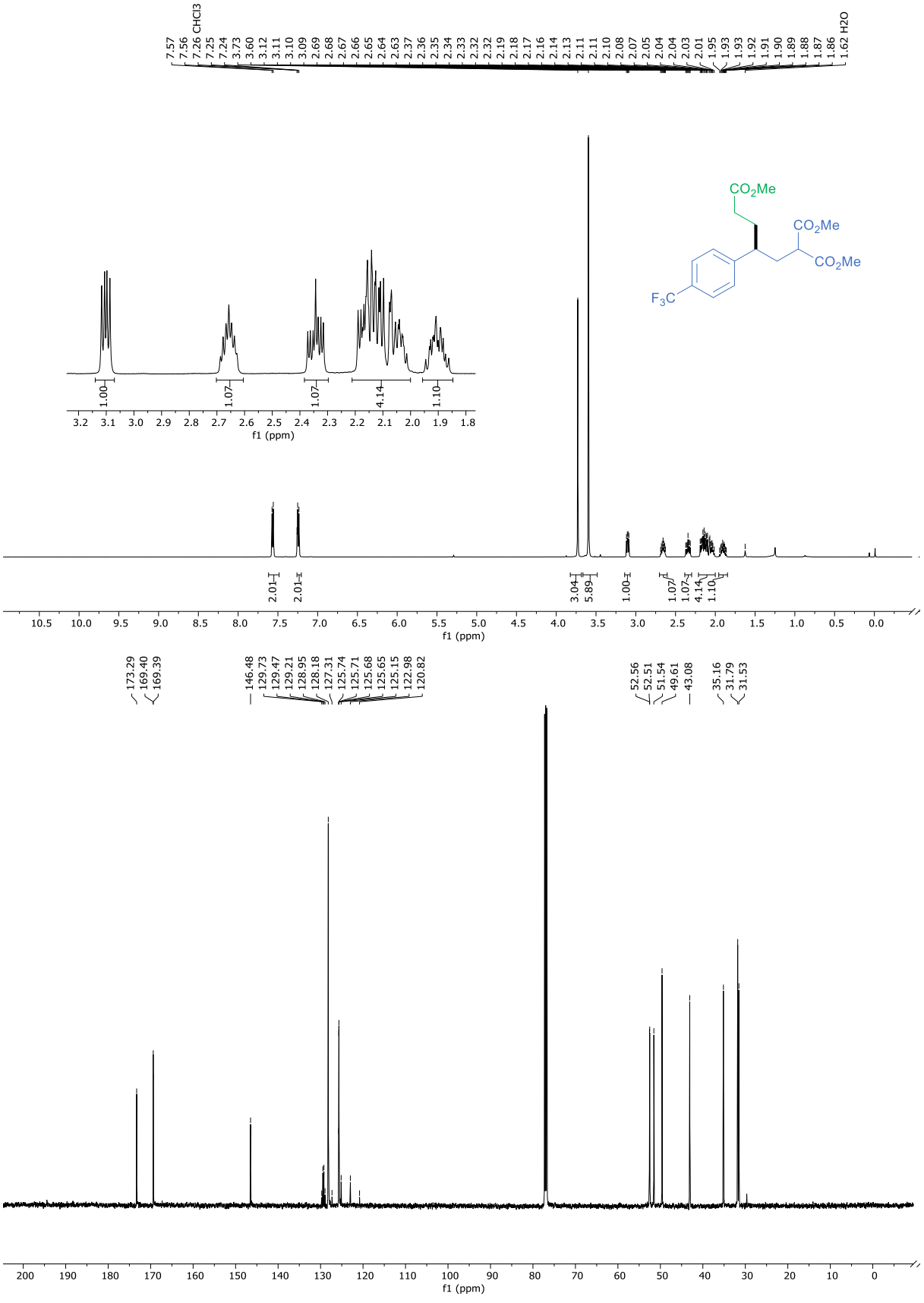
Trimethyl 3-(4-chlorophenyl)pentane-1,1,5-tricarboxylate (12a)

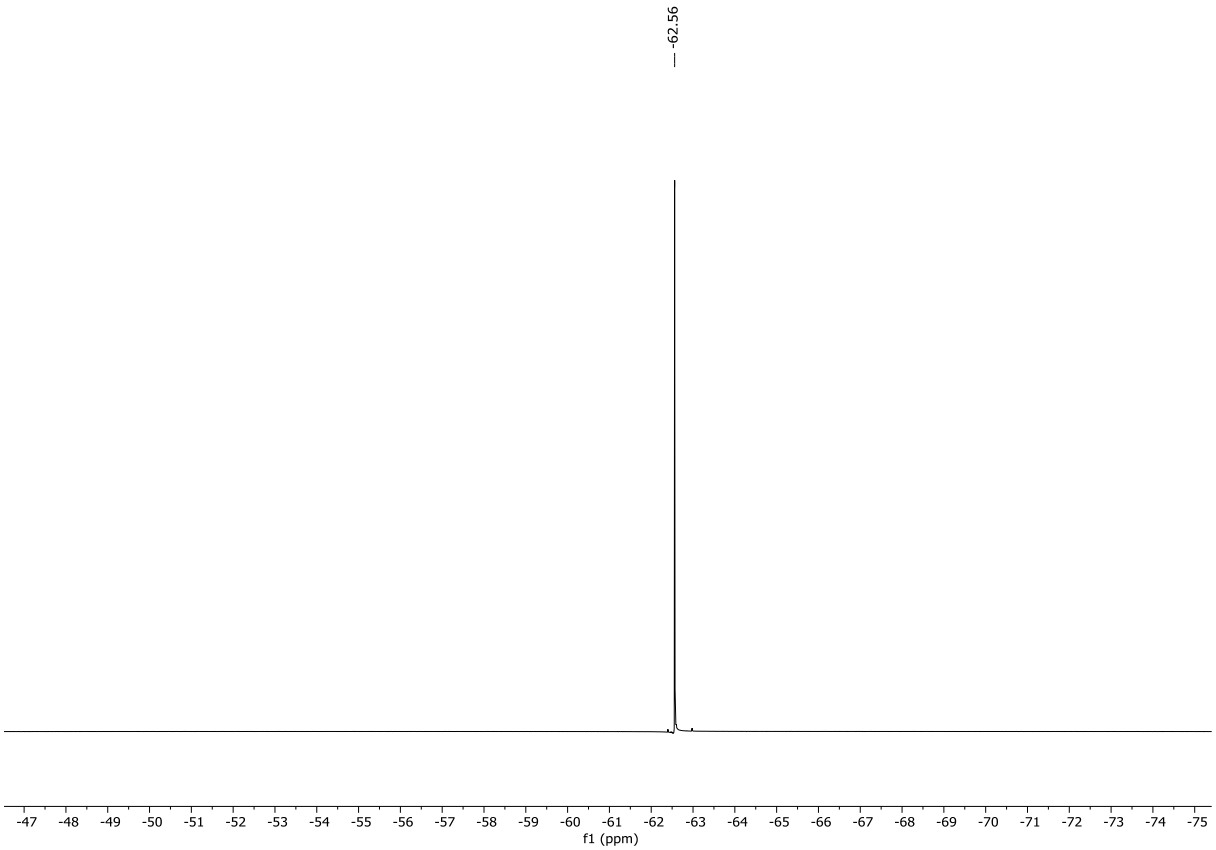


Dimethyl 2-(4-cyano-2-(4-chlorophenyl)butyl)malonate (12b)

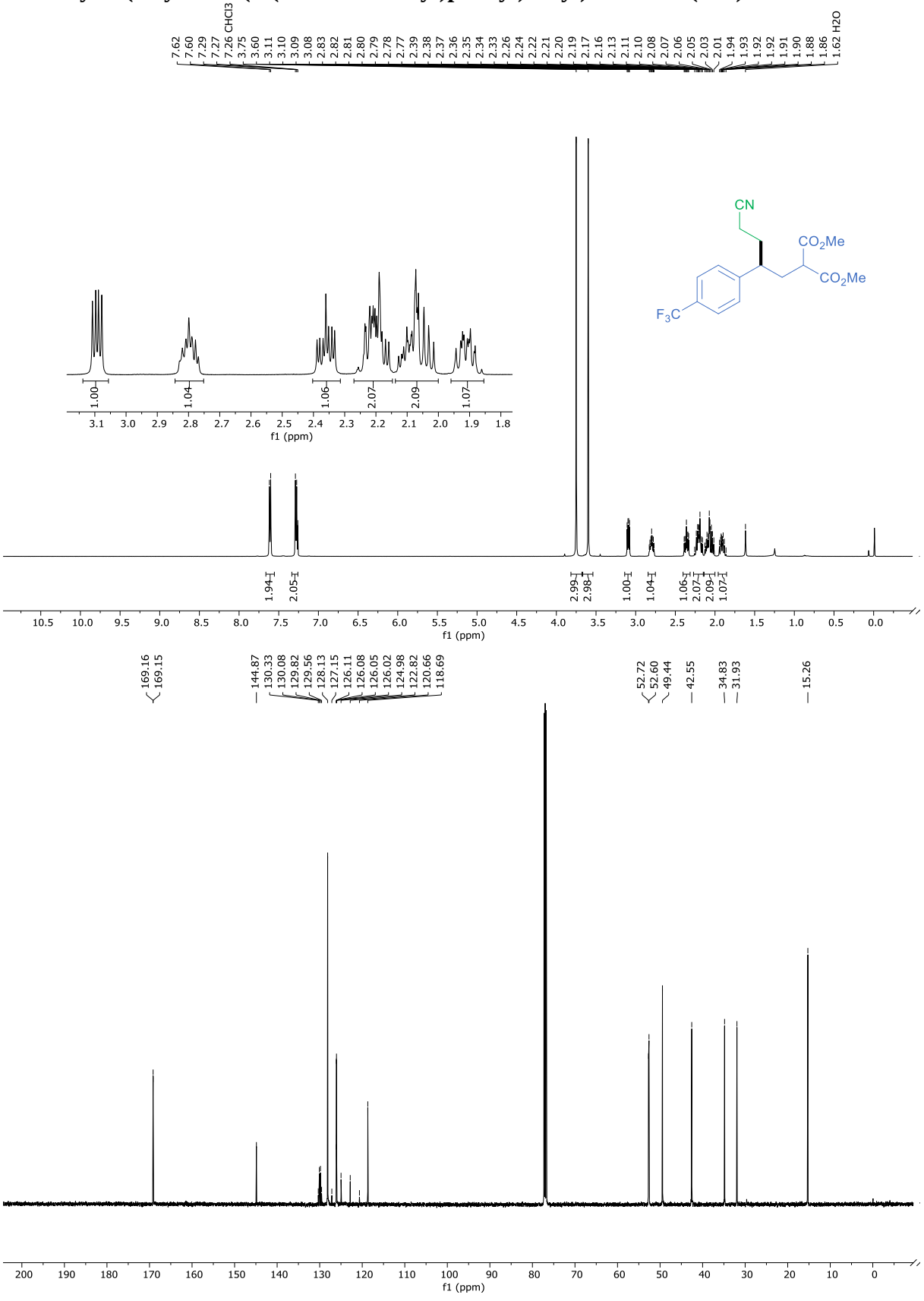


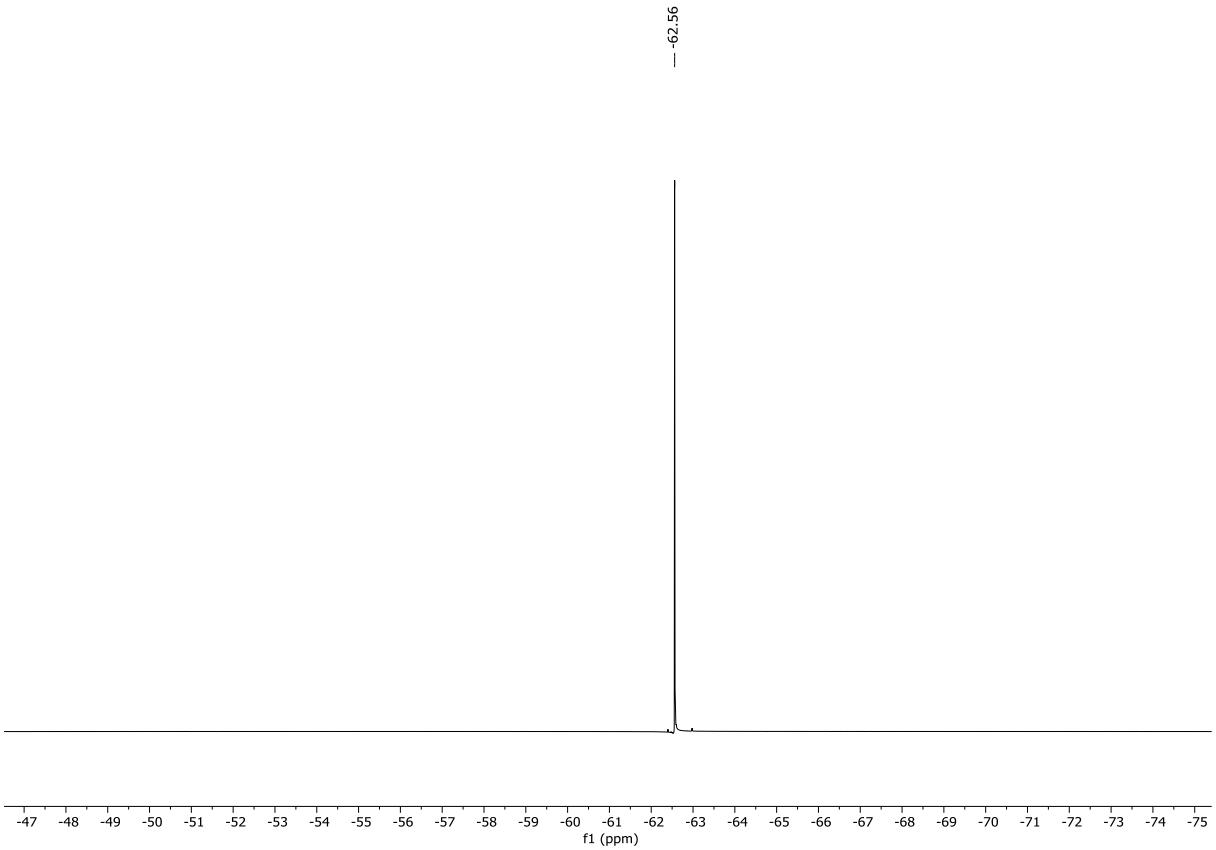
Trimethyl 3-(4-(trifluoromethyl)phenyl)pentane-1,1,5-tricarboxylate (13a)



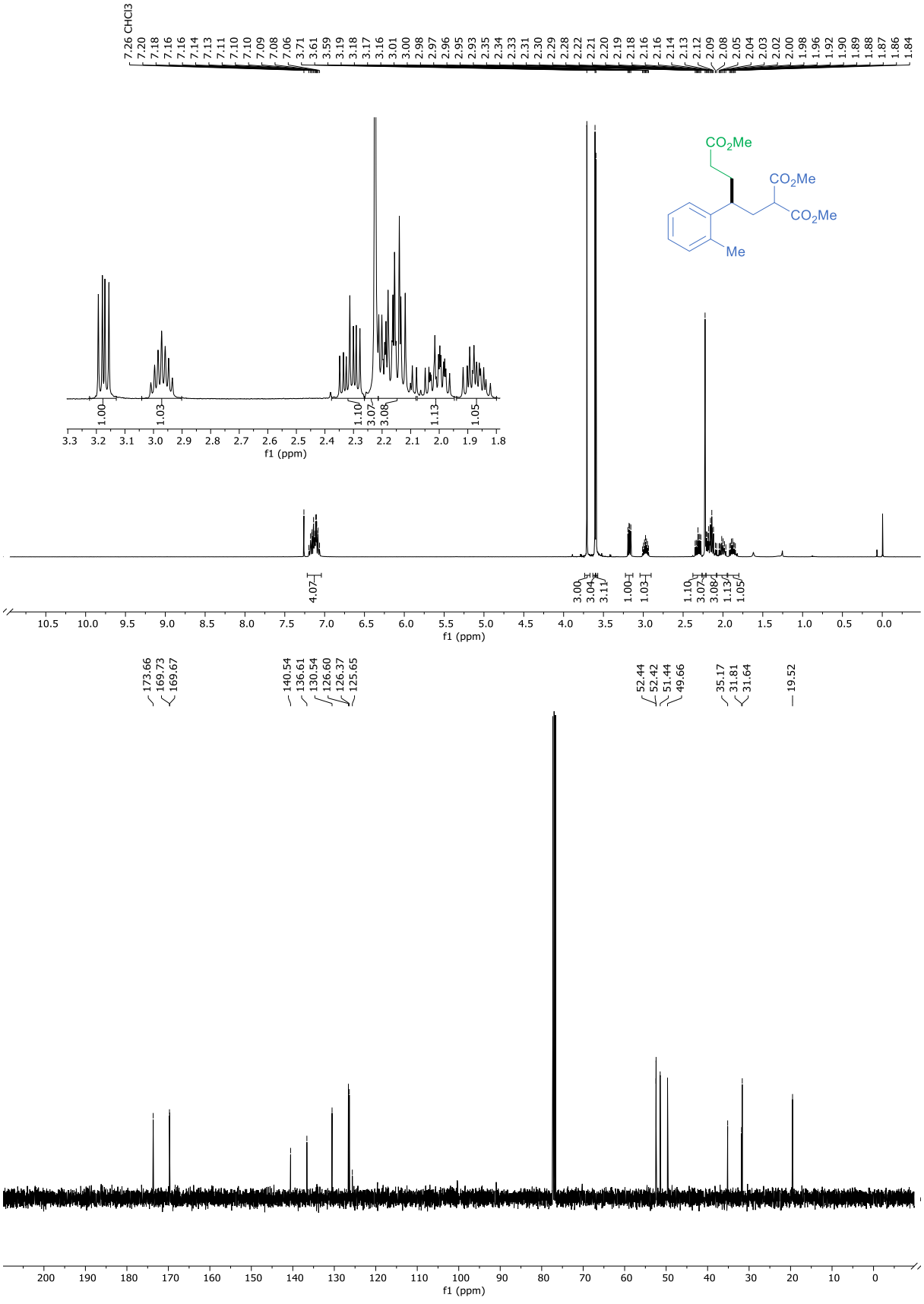

-62.56
-47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75
f1 (ppm)

Dimethyl 2-(4-cyano-2-(4-(trifluoromethyl)phenyl)butyl)malonate (13b)

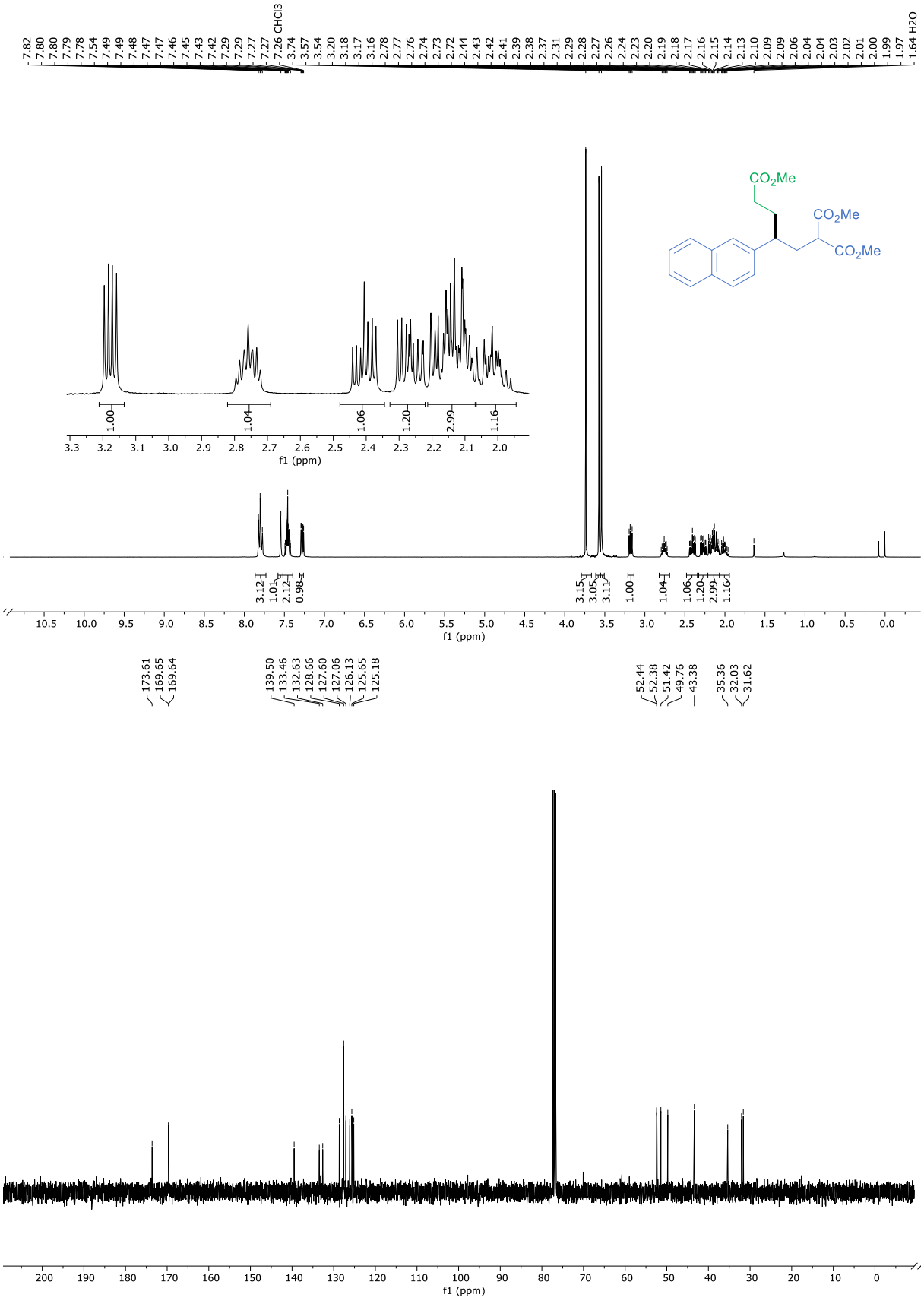



-62.56
-47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75
f1 (ppm)

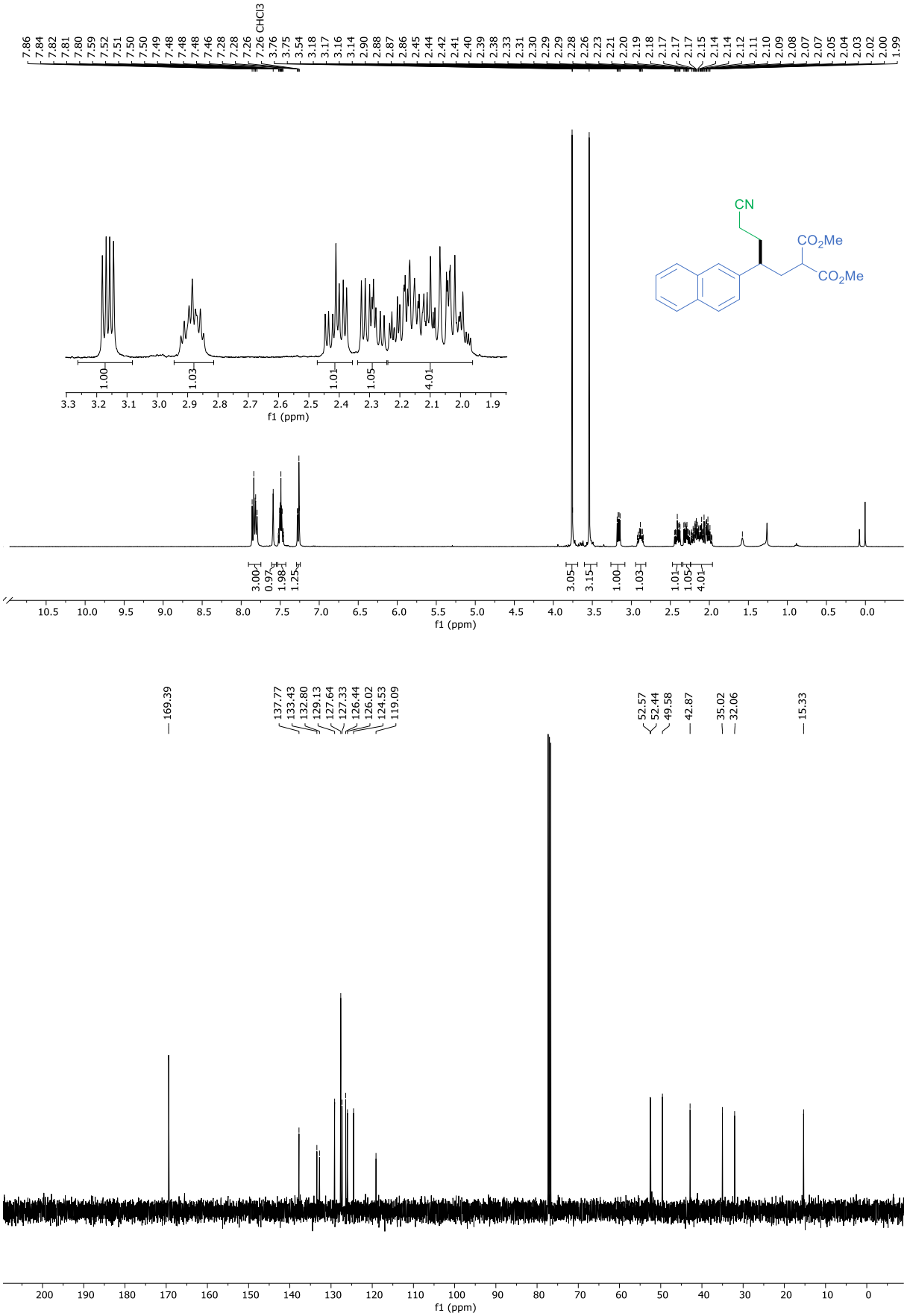
Trimethyl 3-(2-methylphenyl)pentane-1,1,5-tricarboxylate (14a)



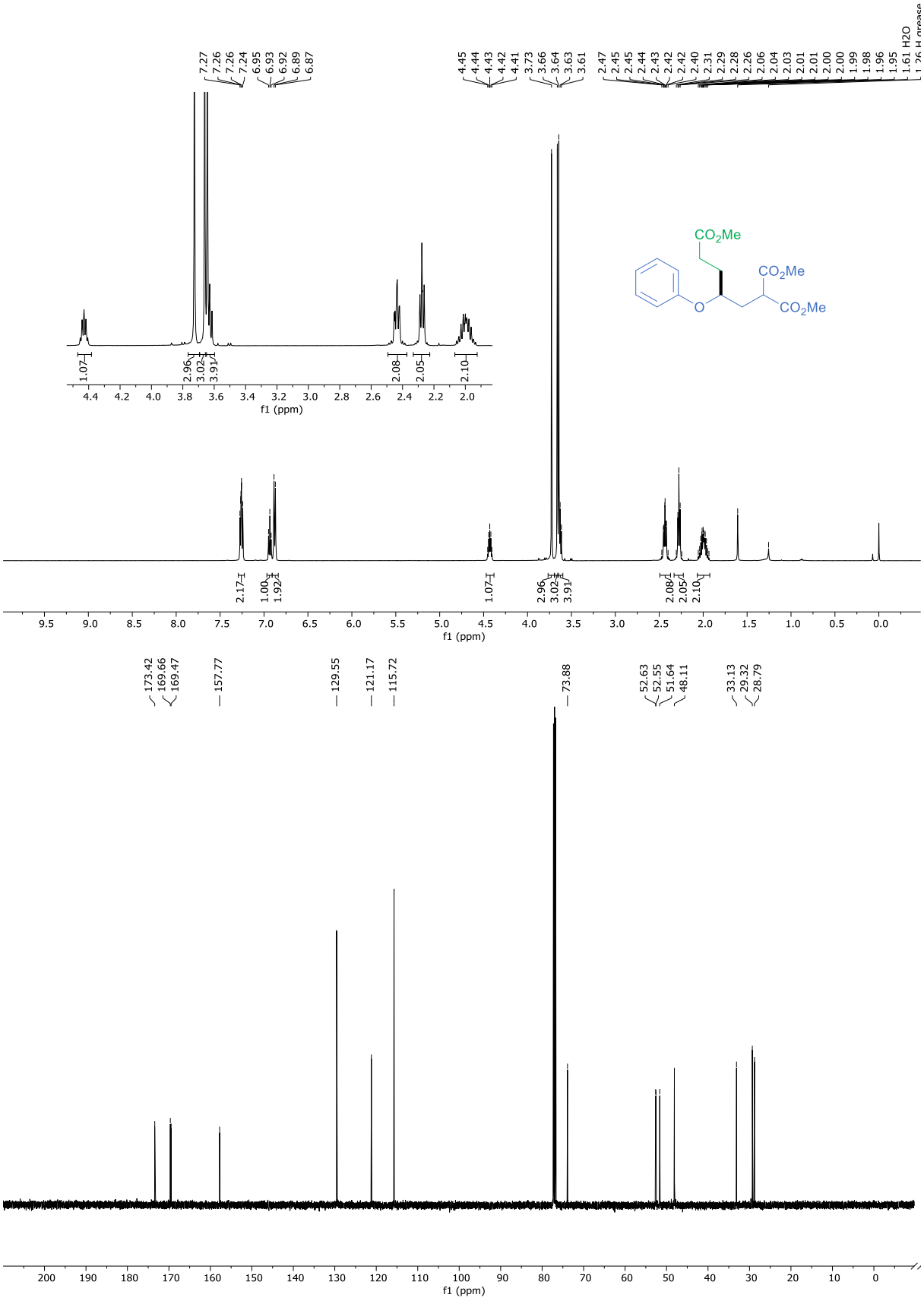
Trimethyl 3-naphthylpentane-1,1,5-tricarboxylate (15a)



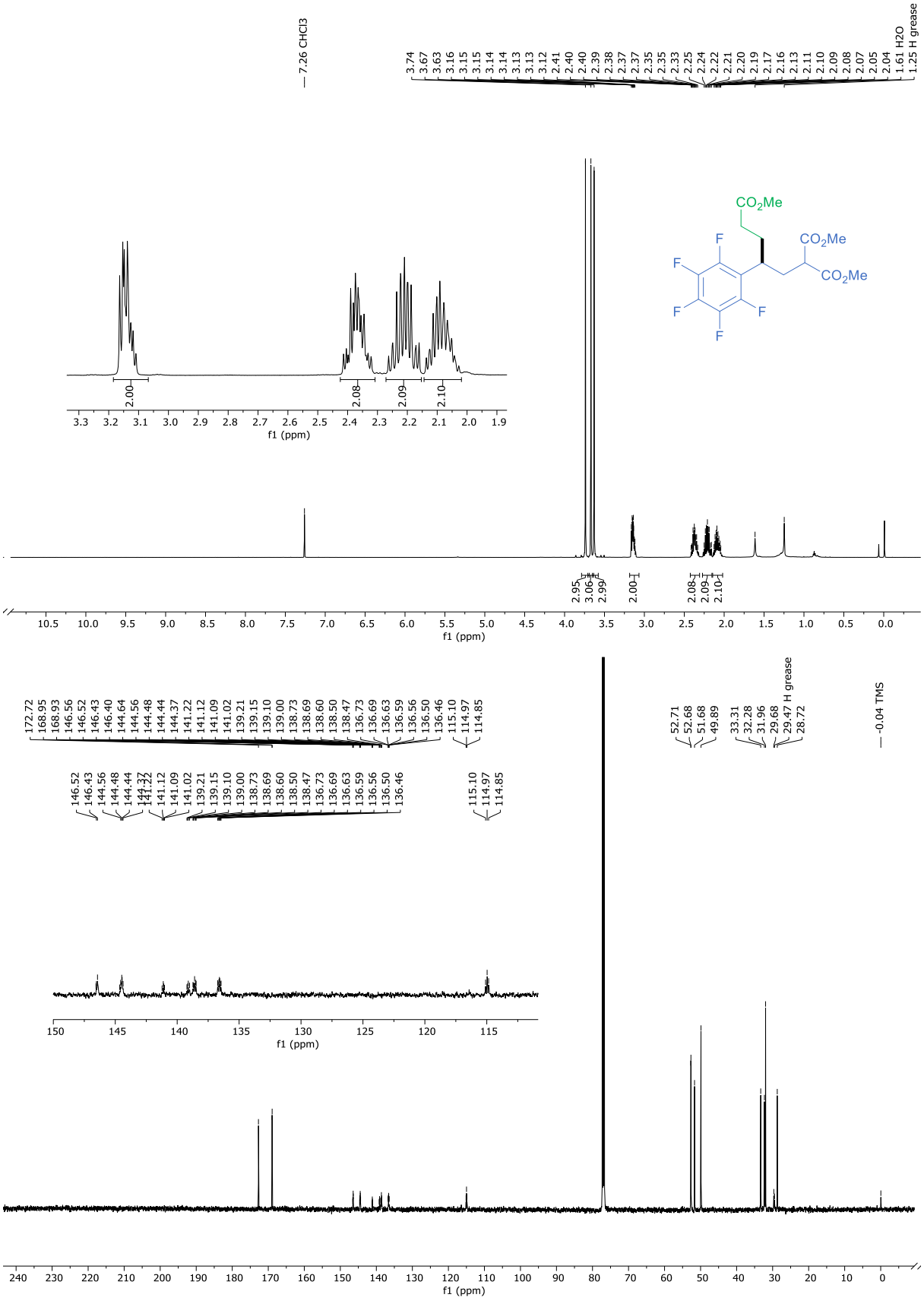
Dimethyl 2-(4-cyano-2-naphthylbutyl)malonate (15b)

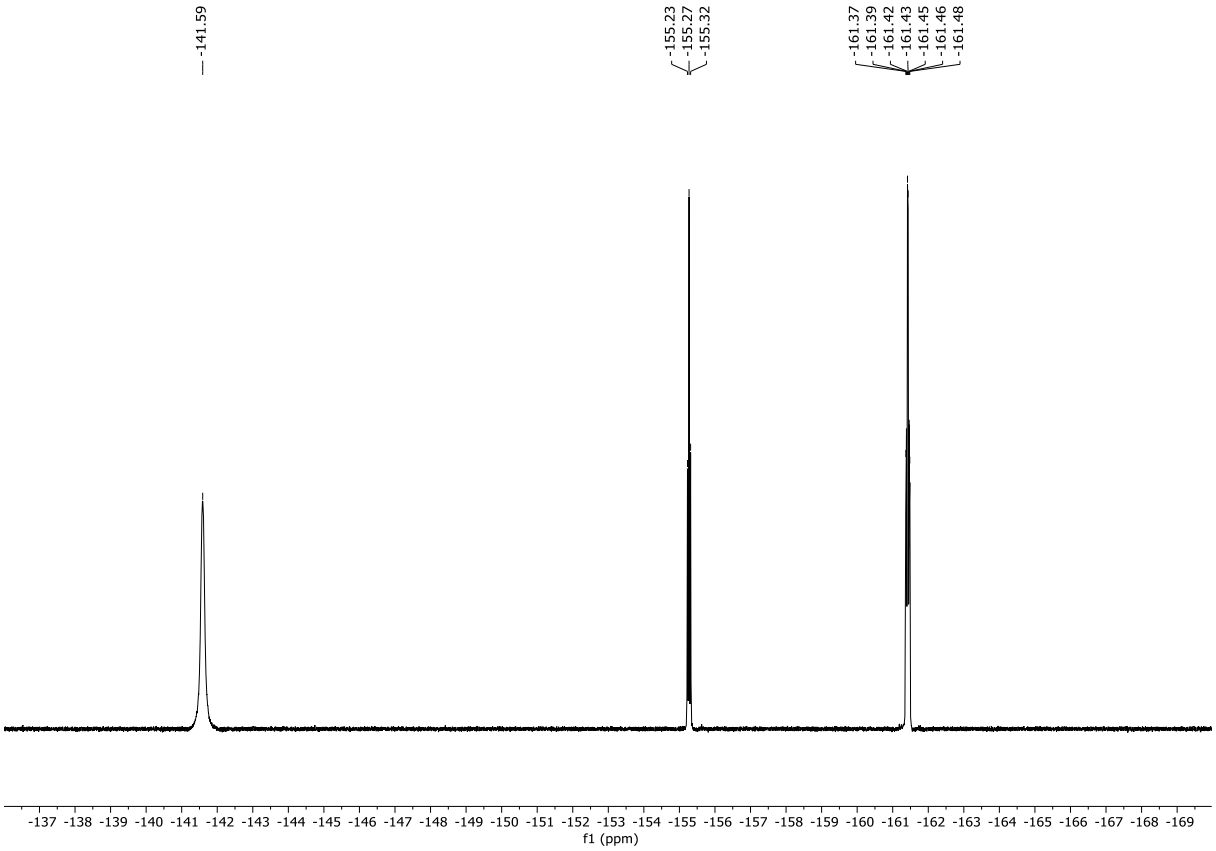


Trimethyl 3-phenoxypentane-1,1,5-tricarboxylate (16a)

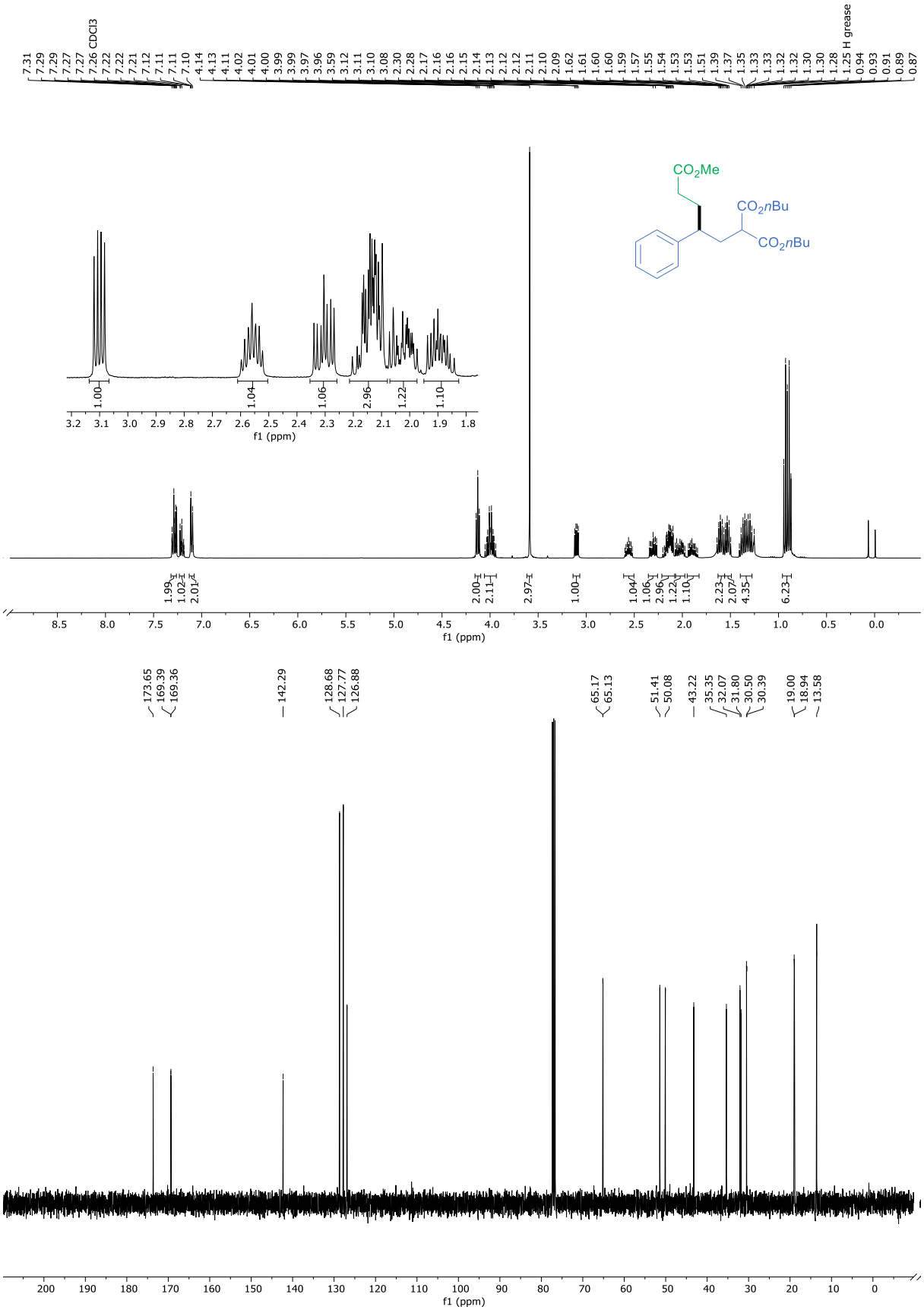


Trimethyl 3-(perfluorophenyl)pentane-1,1,5-tricarboxylate (17a)



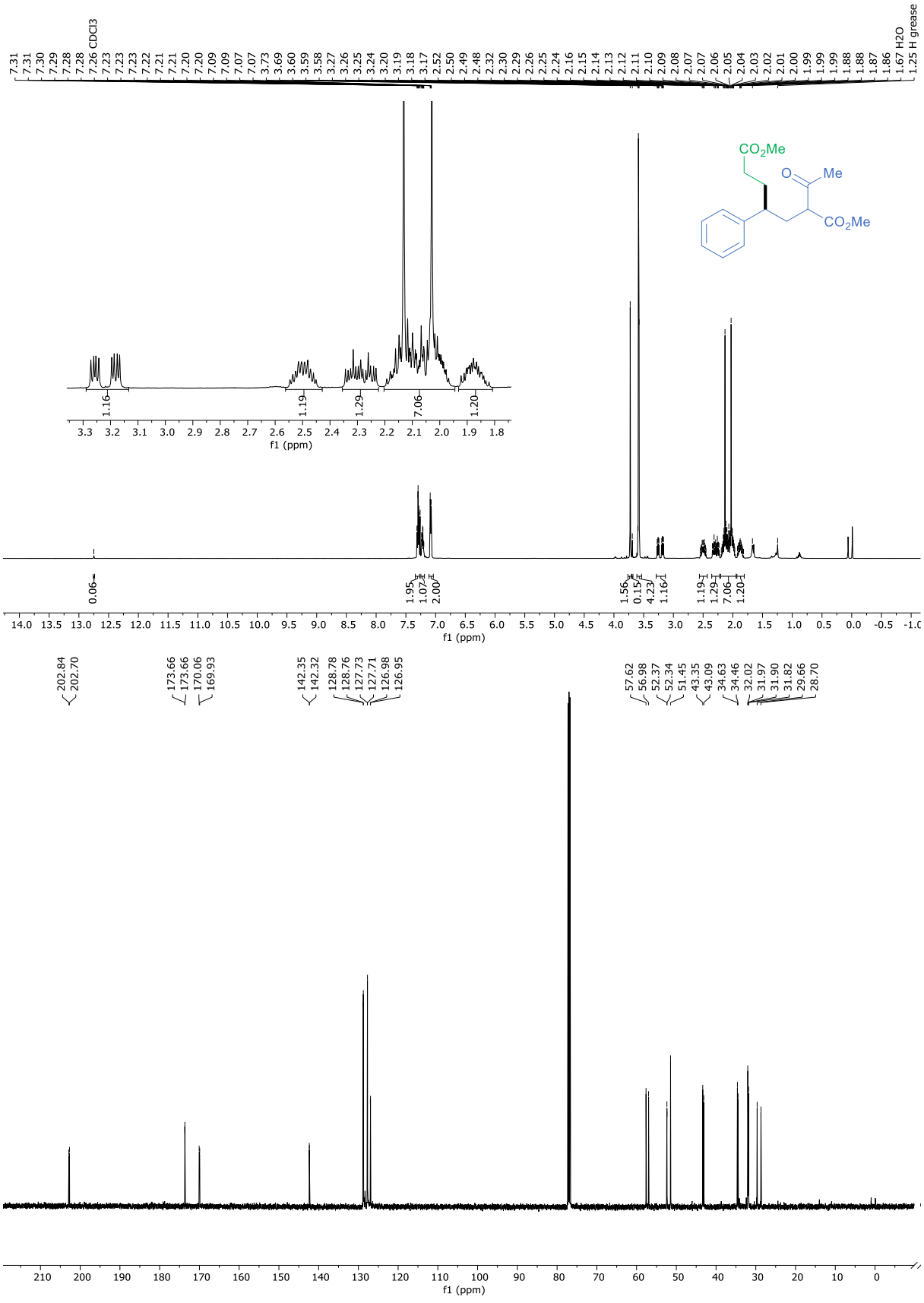

-141.59
-155.23
-155.27
-155.32
-161.37
-161.39
-161.42
-161.43
-161.45
-161.46
-161.48
-137 -138 -139 -140 -141 -142 -143 -144 -145 -146 -147 -148 -149 -150 -151 -152 -153 -154 -155 -156 -157 -158 -159 -160 -161 -162 -163 -164 -165 -166 -167 -168 -169
f1 (ppm)

1,1-di-*n*-Butyl 5-methyl 3-phenylpentane-1,1,5-tricarboxylate (18a)

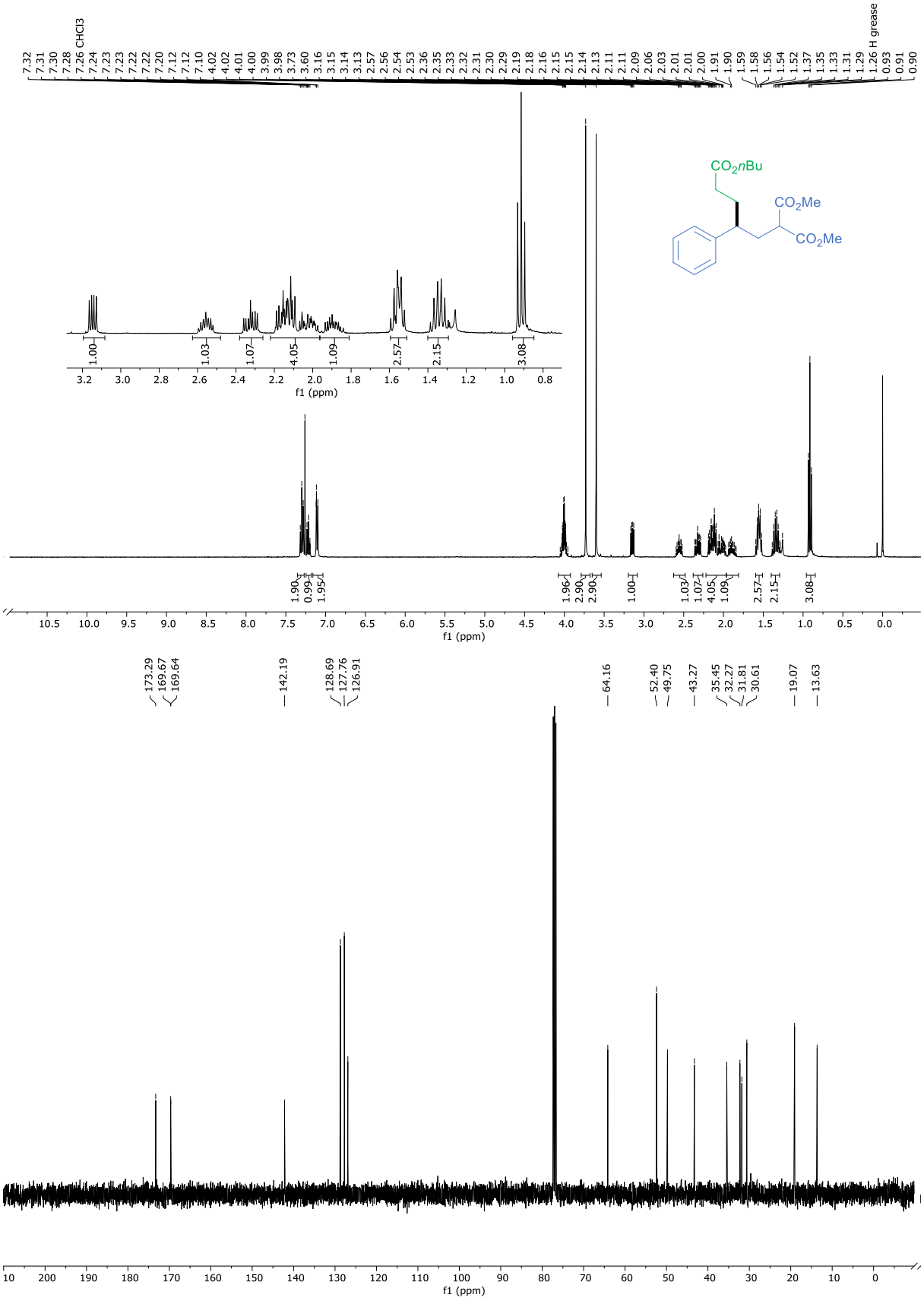


Dimethyl 2-acetyl-4-phenylheptanedioate (19a)

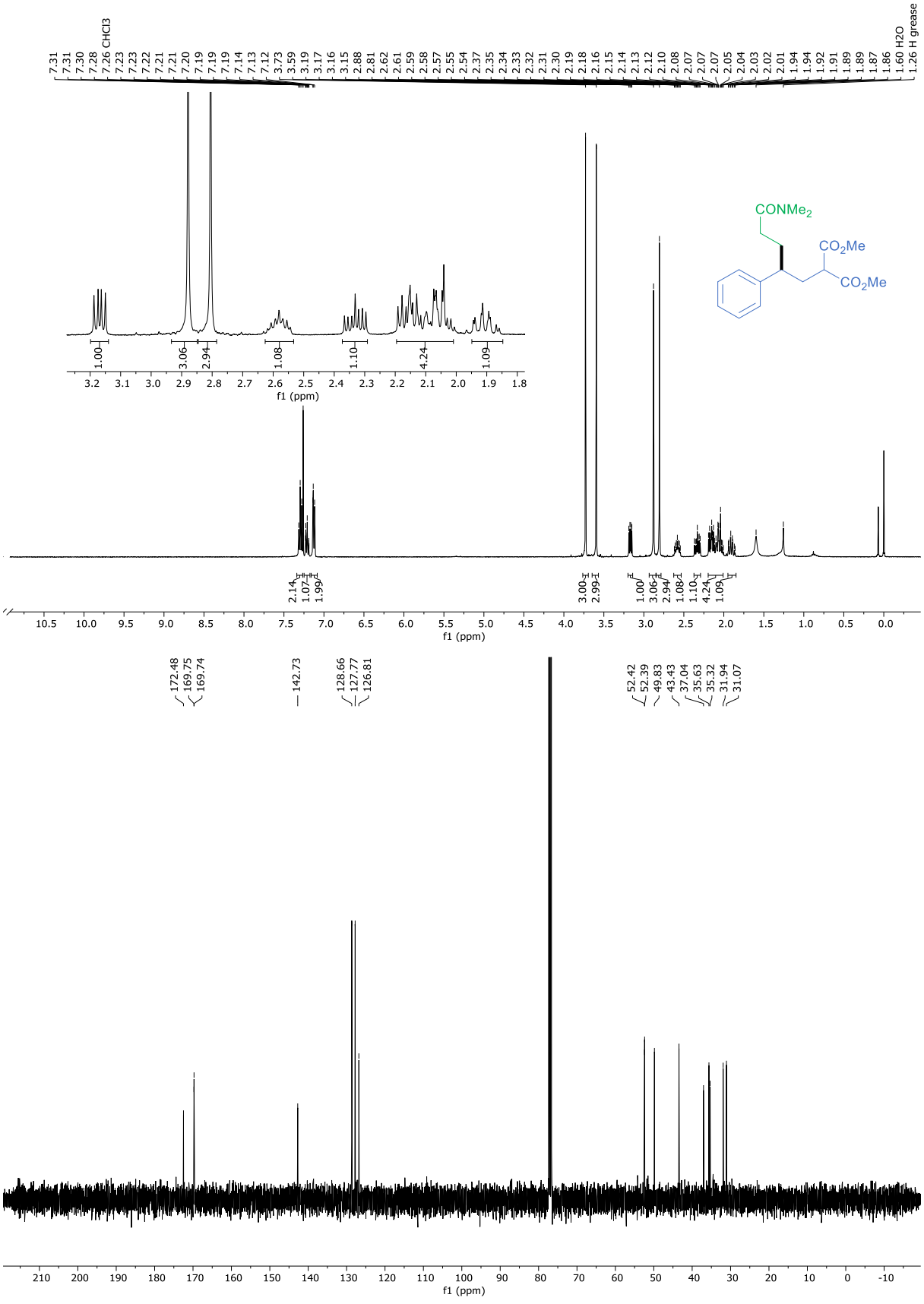
*as mixture of diastereomers and enolate



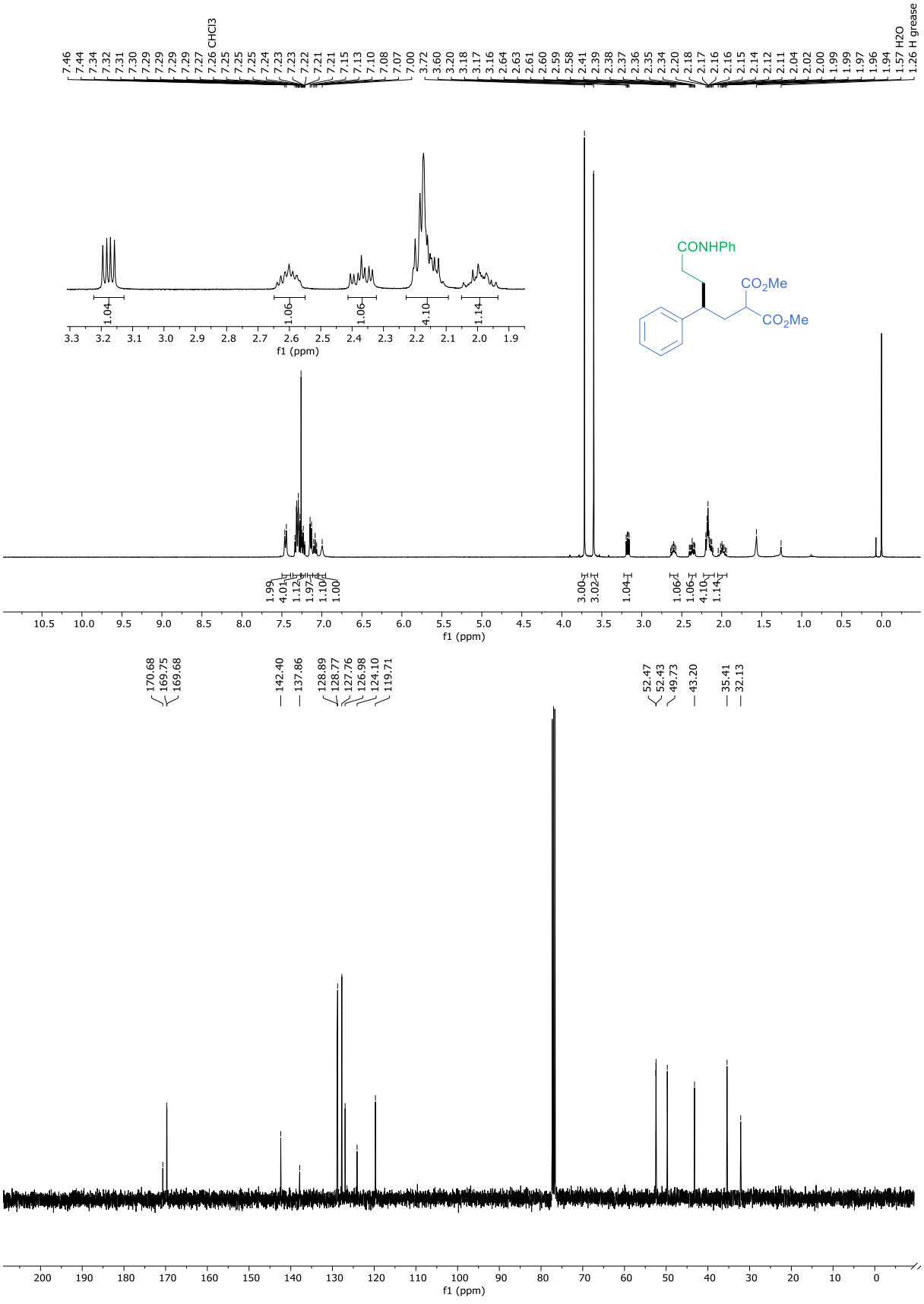
5-*n*-Butyl 1,1-dimethyl 3-phenylpentane-1,1,5-tricarboxylate (5c)



Dimethyl 2-(5-(dimethylamino)-5-oxo-2-phenylpentyl)malonate (5d)

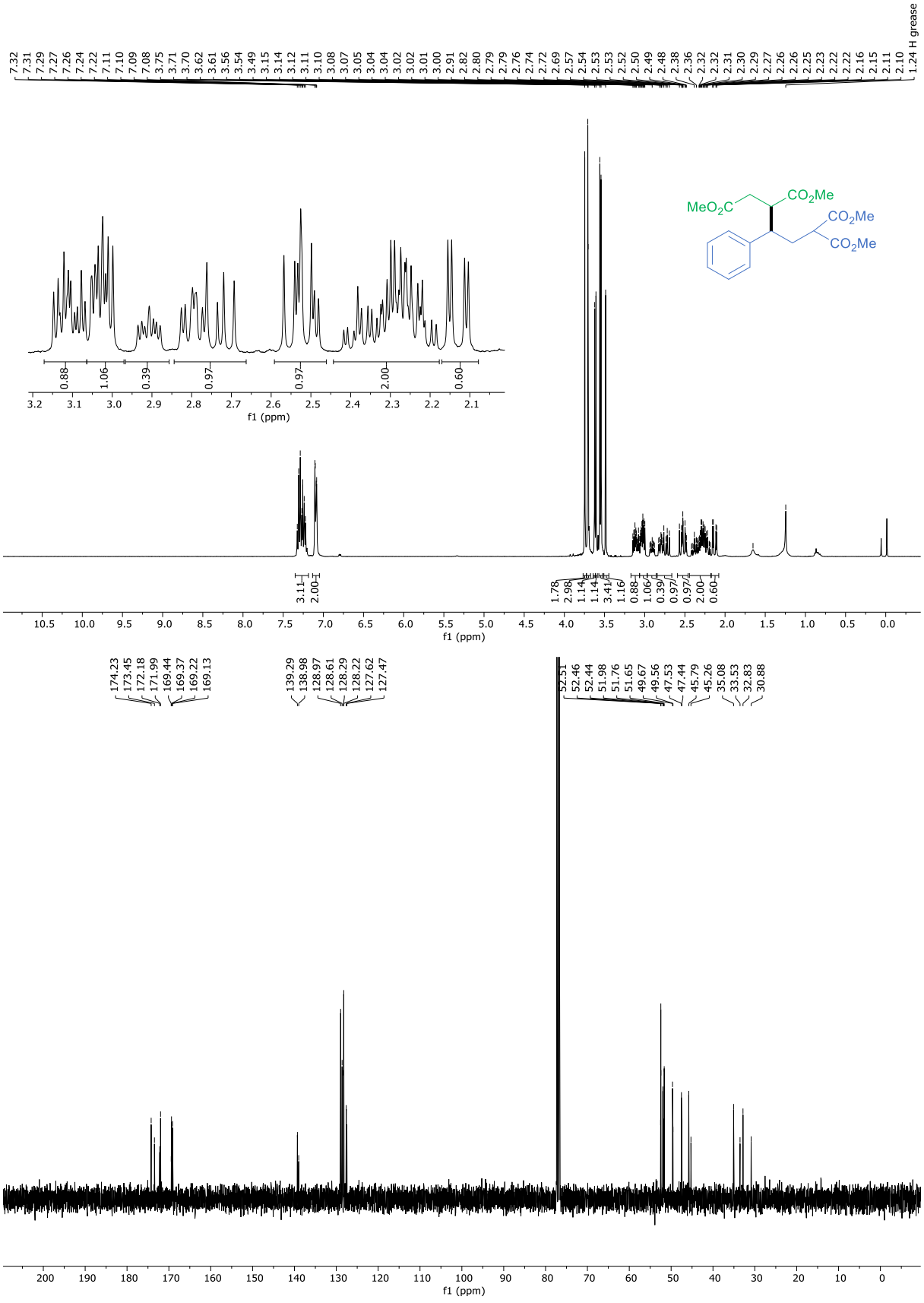


Dimethyl 2-(5-oxo-2-phenyl-5-(phenylamino)pentyl)malonate (5e)



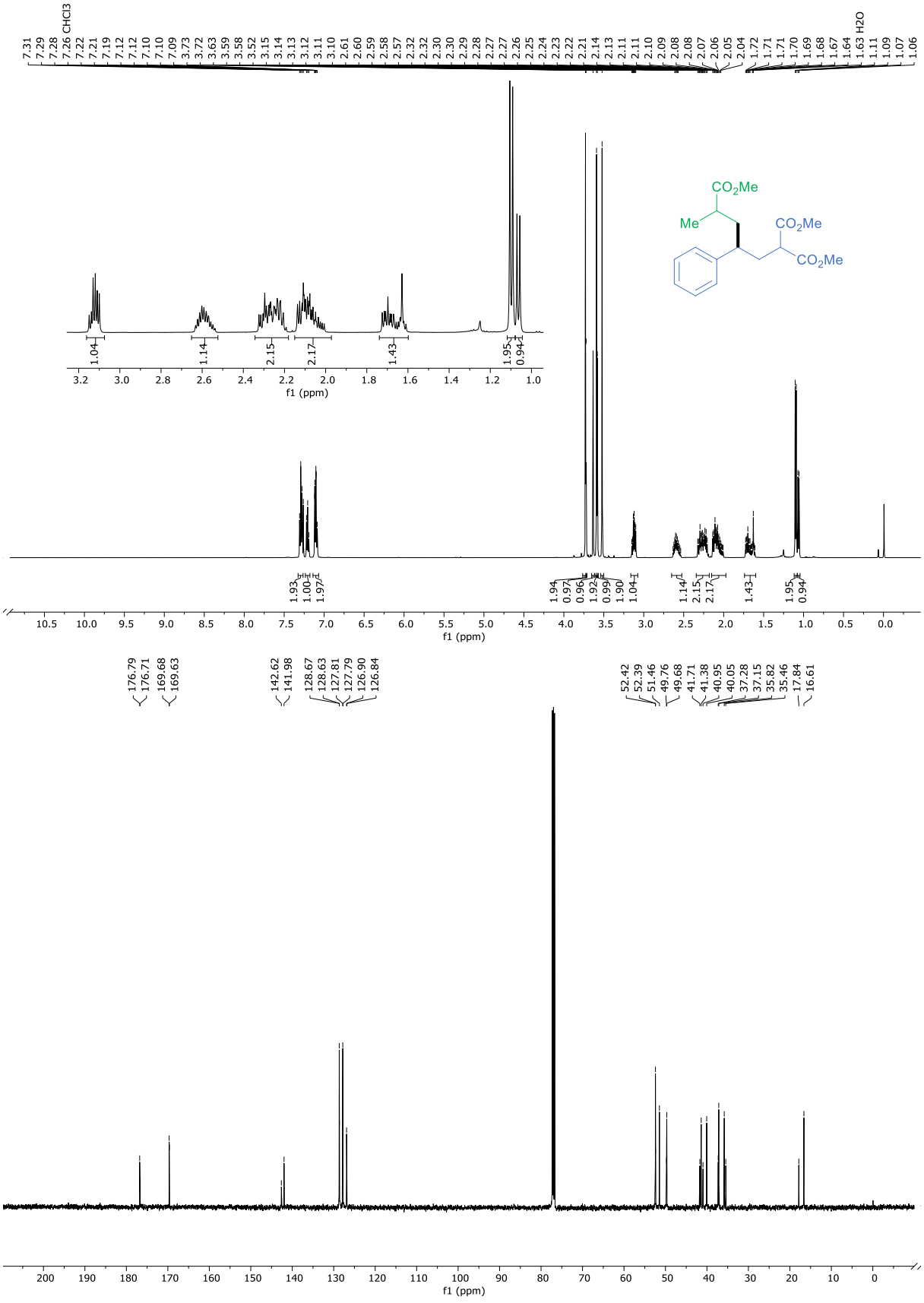
Tetramethyl 3-phenylpentane-1,1,4,5-tetracarboxylate (5f)

*as mixture of diastereomers



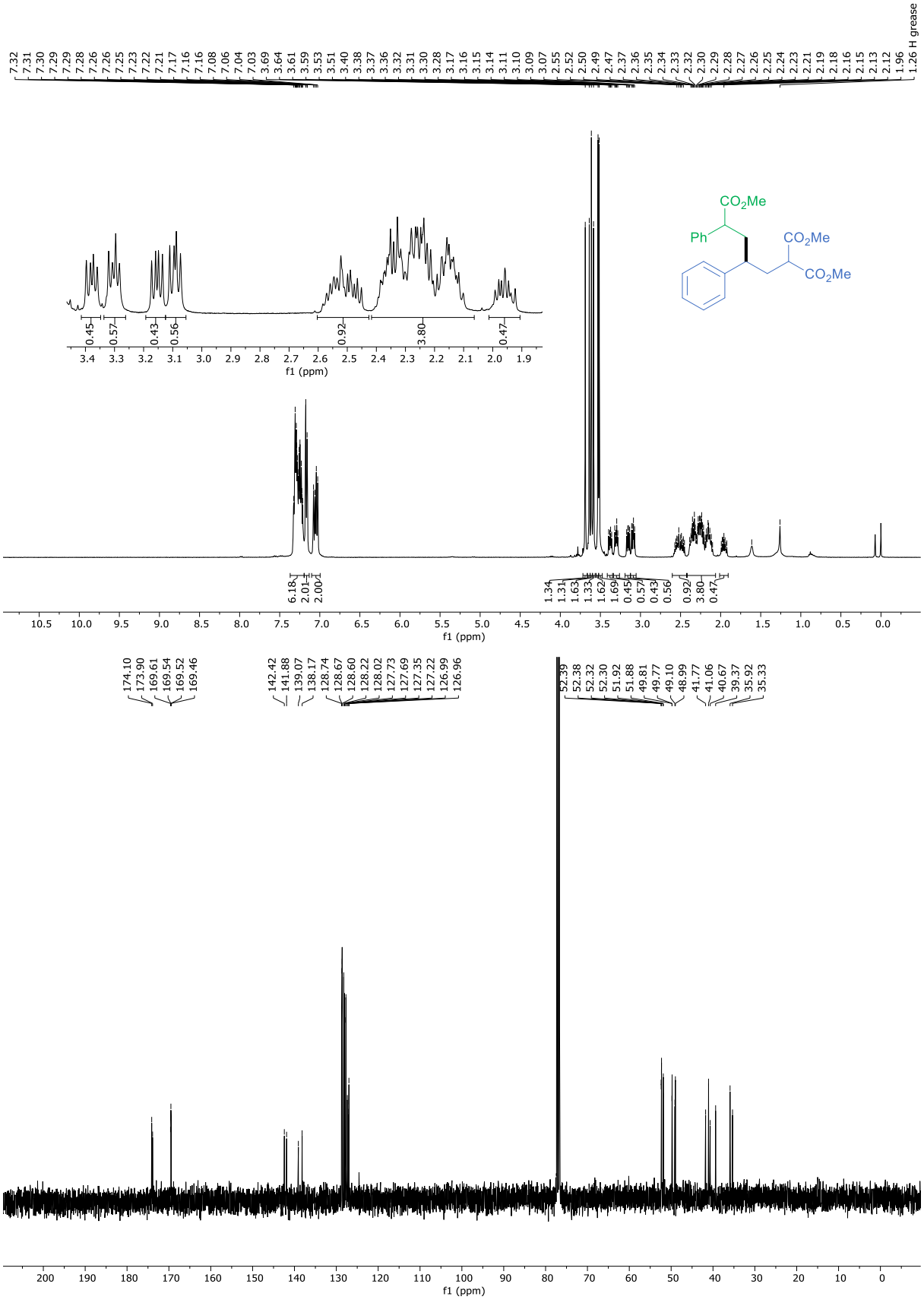
Trimethyl 3-phenylhexane-1,1,5-tricarboxylate (5g)

*as mixture of diastereomers

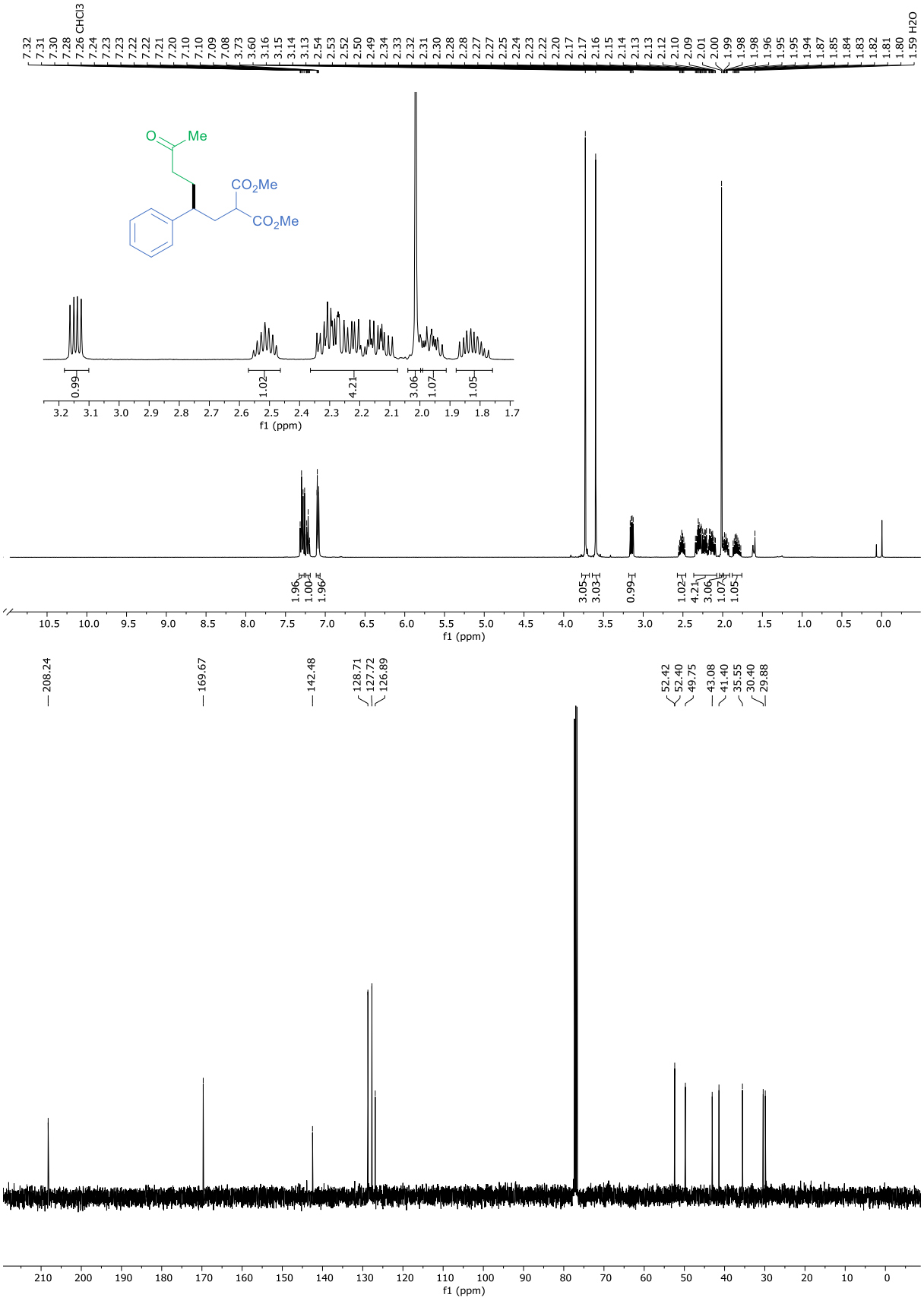


Trimethyl 3,5-diphenylpentane-1,1,5-tricarboxylate (5h)

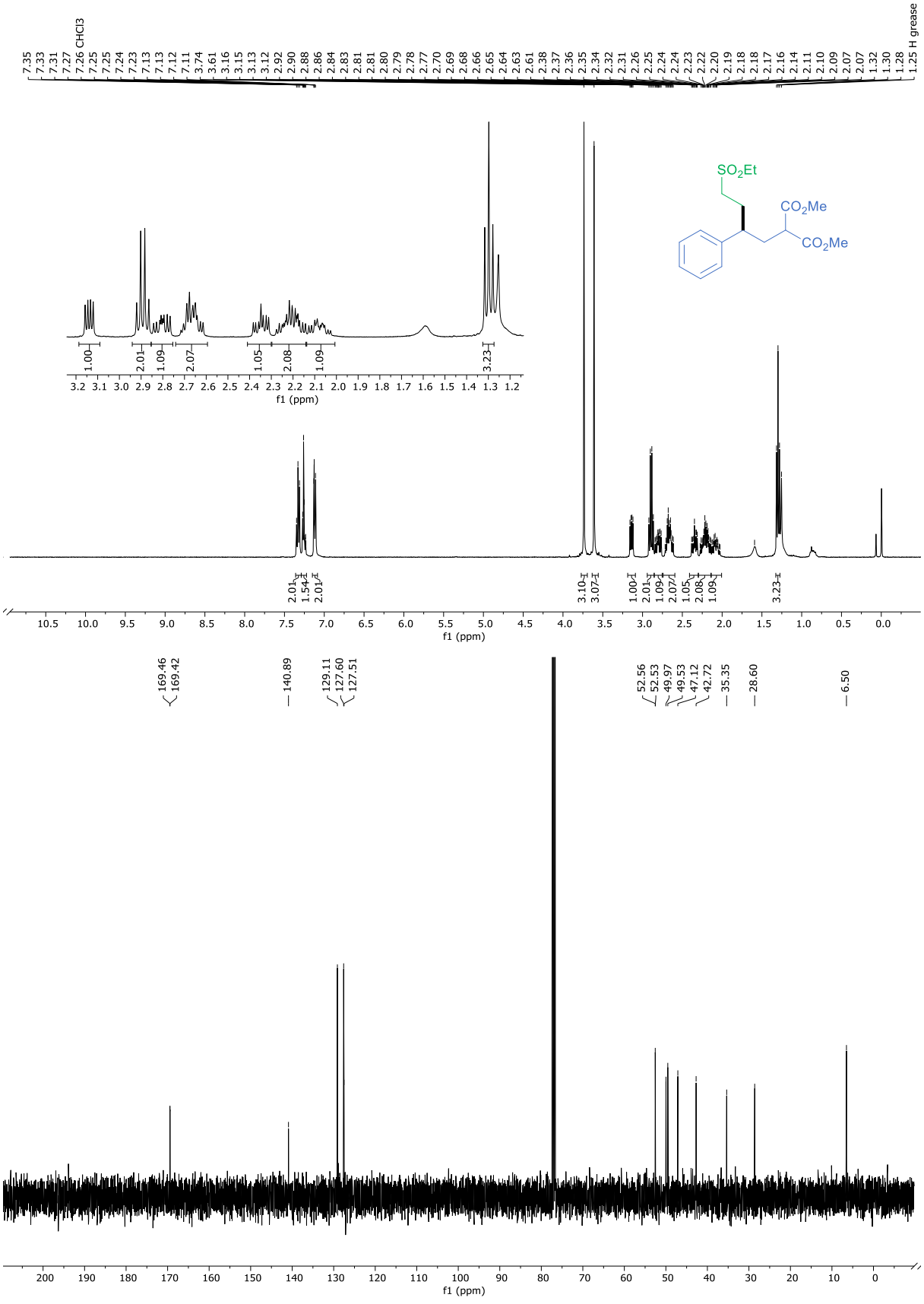
*as mixture of diastereomers



Dimethyl 2-(5-oxo-2-phenylhexyl)malonate (5i)

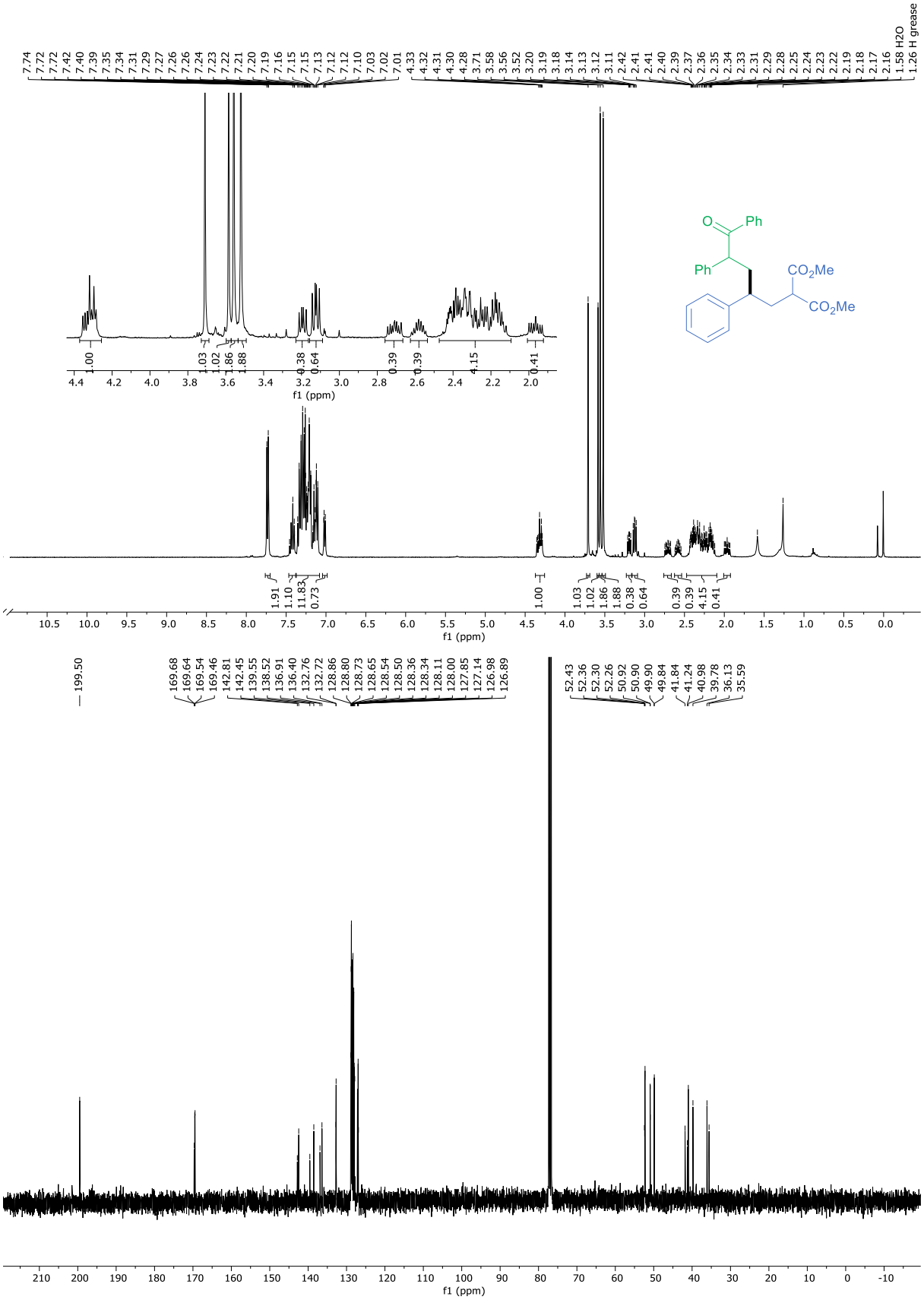


Dimethyl 2-(4-(ethylsulfonyl)-2-phenylbutyl)malonate (5j)

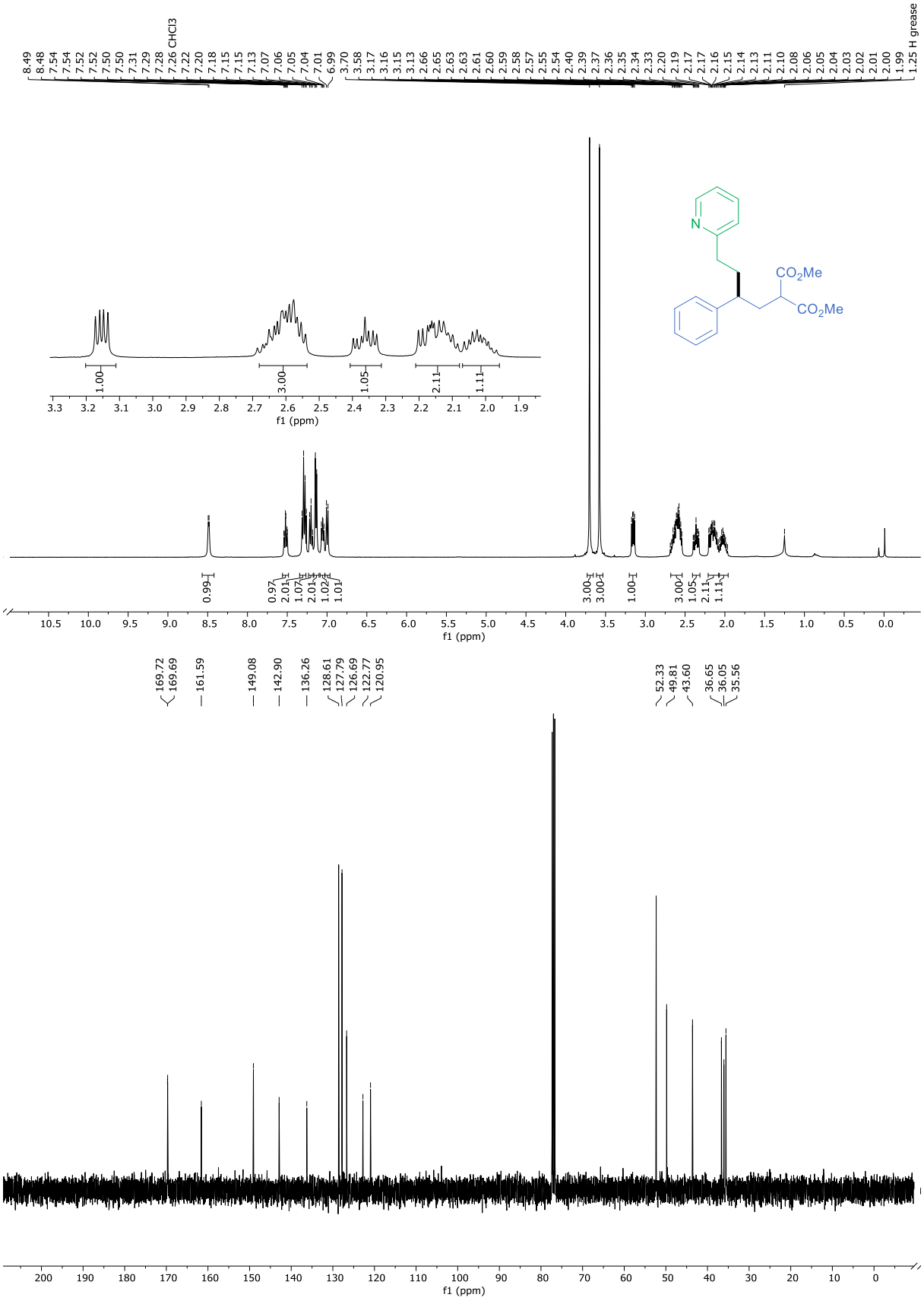


Dimethyl 2-(5-oxo-2,4,5-triphenylpentyl)malonate (5k)

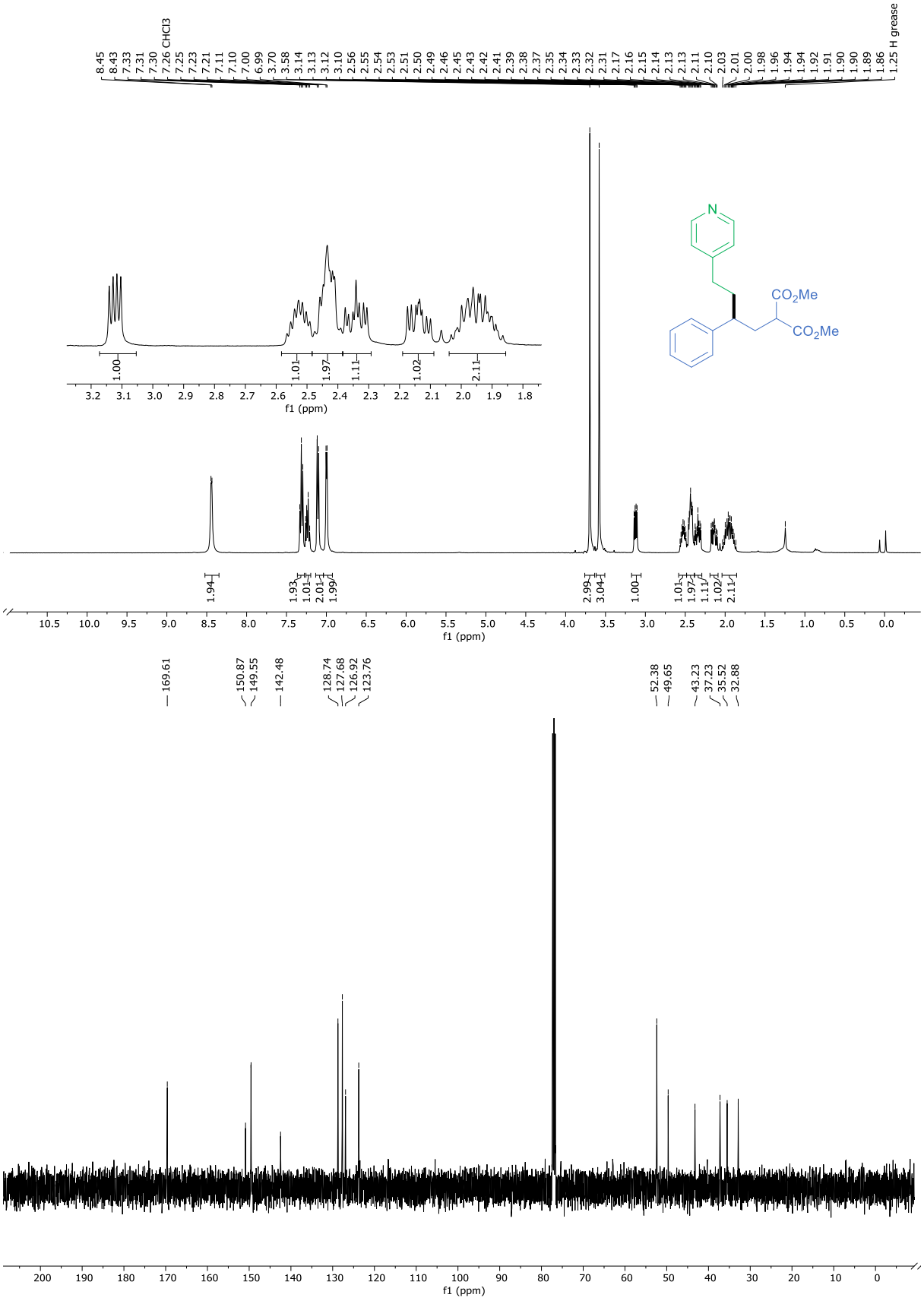
*as mixture of diastereomers



Dimethyl 2-(2-phenyl-4-(pyridin-2-yl)butyl)malonate (5l)



Dimethyl 2-(2-phenyl-4-(pyridin-4-yl)butyl)malonate (5m)



Dimethyl 2-(2-phenyl-4-(pyrazin-2-yl)butyl)malonate (5n)