Supporting Information

For

Reductive Alkylation of Active Methylene Compounds with Carbonyl Derivatives, Calcium Hydride and a Heterogeneous Catalyst

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1. General information

All reagents were obtained from commercial sources and used as received. CaH_2 90-95% 2 mm & down (ref: 19106) was purchased from Alfa Aesar®. Cs_2CO_3 99.9% (metal basis, ref 202126-100g) and Ni 65 wt. % silica/alumina (190 m²/g, ref: 208779-100g) were purchased from Sigma Aldrich®. 5% Pt/SiO_2 (Escat 2351), 5% Pt/C (ref: 78-1600), 5% Pd/C (Escat 1431), 5% Pd/SiO_2 (Escat 1351), 5% Pd/alumina (ref: 46-1950), 5% Ru/C (ref: 44-4050), 5% Ru/alumina (ref: 44-3910) and Nickel, 64% powder on silica, reduced and stabilised (Ni-5249P, ref: 28-1900) were purchased from Strem Chemicals, Inc.. 5% Pt/alumina and 5% Rh/C (ref: 19.544.47, lot 7002311) were purchased from Janssen Chimica. Solvents were used as AcroSeal®.

The complete references of the used sealed tubes are: ACE pressure tubes, #15 Ace-Thred, order code (8648-03), length (10.2 cm), body O.D. (25.4 mm), capacity (15 mL), pressure rating (150 PSI or 10.3 bar). The pressure tube was closed by a back seal PTFE plug 5845 with a 210 O-ring for #15 Ace-Thred in FETFE™ or silicone.

All reactions were performed under the inert atmosphere of argon. Silica gel (40–63 micron) was used for column chromatography. Thin layer chromatography was performed on pre-

coated silica gel 60–F 254 plates. UV light and mainly $KMnO_4$ were used for analysis of the TLC plates.

All compounds were characterised by spectroscopic data. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ALS 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), a DRX 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) or a Bruker DRX 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer, in $CDCl_3$, CD_3OD or DMSO-d_6 at 293K. Chemical shifts are reported in parts per million (ppm) and are calibrated on residual solvent peaks: $CDCl_3$ 7.26 ppm in ^{1}H and 77.16 ppm in ^{13}C, CD_3OD 3.31 ppm in ^{1}H and 49.00 ppm in ^{13}C or DMSO-d_6 2.50 ppm in ^{1}H and 39.52 ppm in ^{13}C.[1] Spin-spin coupling constants (*J)* are given in Hz. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad).

IR spectra were recorded on a Spectro Nicolet IS10 Smart ITR with an ATR diamond. Melting points were recorded on a Heizbank system Kofler Type WME (Wagner & Munz).

High-Resolution Mass Spectra (HRMS) were recorded on a MicroTOFQ II - Bruker Daltonics spectrometer with an Electrospray Ionization (ESI) ion source.
GC-MS analyses were performed on a DSQ-Thermofinnigan spectrometer equipped with a quadrupole analyzer and a DB-5MS capillary column (30.0 m × 0.25mm × 0.25μm). The carrier gas was helium, at a flow rate of 1 mL/min. Column temperature was initially 70 °C for 2 min, then was gradually increased to 310 °C at 15 °C/min and finally kept at 310 °C for 10 min. The injector temperature was 220 °C and the transfer line temperature was 280 °C.

GC analyses were performed on a Shimadzu Gas Chromatograph GC-2025 equipped with a ZB-5-MS column (30.0 m × 0.25mm × 0.25μm). The carrier gas was N_2 at a flow rate of 1.27 mL/min. Column temperature was initially 70 °C for 2 min, then was gradually increased to 280 °C at 15 °C/min and finally kept at 280 °C for 15 min. The injector temperature was 250 °C and for detection a FID was used at 280 °C.

[1] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997,** *62,* 7512-7515.

2. General procedure

General procedure A: reductive alkylation of methylcyanoacetate with Pt/SiO_2

In a sealed tube was introduced dodecane (68 mg, 0.40 mmol, 10 mol%), an aldehyde or a ketone (4.00 mmol, 1 equiv.), methylcyanoacetate (0.428 mL, 4.8 mmol, 1.2 equiv.) and toluene (2 mL, [S] = 2 M). The reaction vessel was flashed with argon, followed by the addition of Pt/SiO_2 5% (155 mg, 0.04 mmol, 1 mol%) and CaH_2 90% (110 mg, 2.35 mmol, 59 mol%). After the addition of CaH_2, the tube was sealed and introduced in a preheated oil bath at 60 °C. The reaction was stirred at 700 rpm for 15 hours. The reaction was cooled to room temperature, suspended in dichloromethane and filtered on Millipore. The filtrate was added to a 250 mL volumetric flask and diluted to 250 mL. A sample of the solution was injected in GC. From the relative area of the product and dodecane, the conversion to the monoalkylated methylcyanoacetate was calculated. Purification was carried out by flash column chromatography using a gradient of cyclohexane/ethyl acetate.

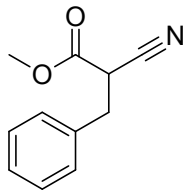
General procedure B: reductive alkylation of methylcyanoacetate with Pd/C

In a sealed tube was introduced dodecane (68 mg, 0.40 mmol, 10 mol%), an aldehyde or a ketone (4.00 mmol, 1 equiv.), methylcyanoacetate (0.396 mg, 4.0 mmol, 1.0 equiv.) and toluene (3 mL, [S] = 1.3 M). The reaction vessel was flashed with argon, followed by the addition of Pd/C 5% (85 mg, 0.04 mmol, 1 mol%) and CaH_2 90% (110 mg, 2.35 mmol, 59 mol%). After the addition of CaH_2, the tube was rapidly sealed and introduced in a preheated oil bath at 60 °C. The reaction was stirred at 700 rpm for 15 hours. The reaction was cooled to room temperature, suspended in dichloromethane and filtered through Millipore. The analysis and purification were carried out in a similar manner than General procedure A.

General procedure C:

In a sealed tube was introduced dodecane (70.0 mg, 0.40 mmol, 10 mol%), an aldehyde or a ketone (4.00 mmol, 1 equiv.), dimethylmalonate (528 mg, 4.00 mmol, 1 equiv.) or dimedone (561 mg, 4 mmol, 1 equiv.) or 1,3-dimethylbarbituric acid (624 mg, 4.00 mmol, 1 equiv.) and CPME (3 mL, [S] = 1.3 M). The reaction was flashed with argon, followed by the addition of Pd/C 5% (85 mg, 0.04 mmol, 1 mol%), CaH_2 90% (110 mg, 2.35 mmol, 59 mol%) and Cs_2CO_3 (130 mg, 0.4 mmol, 10 mol%). After the addition of Cs_2CO_3, the tube was sealed and introduced in a preheated oil bath at 100 °C. The reaction was stirred at 1200 rpm for 15 hours. The reaction was cooled to room temperature, suspended in dichloromethane or ethyl acetate or a mixture of thereof and filtered on a pad of celite. The analysis and purification were carried out in a similar manner than General procedure A.

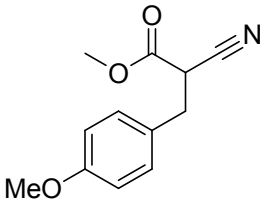
3. Characterisation



Chemical Formula: $C_{11}H_{11}NO_2$
Molecular Weight: 189,21

Methyl 2-cyano-3-phenylpropionate [57519-78-5] (4b)[2]

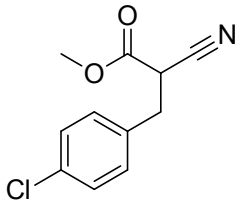
Colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.39–7.25 (m, 5 H, CH_{ar}), 3.80 (s, 3 H, CO_2CH_3), 3.74 (dd, *J* = 8.4, 5.8 Hz, 1 H, C*H*-CO_2CH_3), 3.29 (dd, *J* = 13.9, 5.8 Hz, 1 H, Ph-C*H*), 3.19 (dd, *J* = 13.9, 8.4 Hz, 1 H, Ph-C*H*) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 166.1 (C_q, O-C=O), 135.3 (C_q, C_{Ar}), 129.1 (2 CH, C_{Ar}), 128.9 (2 CH, C_{Ar}), 127.9 (CH, C_{Ar}), 116.1 (C_q, CN), 53.6 (CH_3), 39.6 (CH), 35.8 (CH_2) ppm. **GC:** retention time: 10.3 min. **IR (neat):** υ max = 3031, 2955, 2251, 1744, 1604, 1497, 1455, 1436, 1342, 1264, 1210, 1081, 1028, 748, 699 cm^{-1}. **HRMS (ESI +):** calcd for $C_{11}H_{11}NNaO_2$ $[M+Na]^+$ 212.0682, found 212.0681.



Chemical Formula: $C_{12}H_{13}NO_3$
Molecular Weight: 219,24

Methyl 2-cyano-3-(4-methoxyphenyl)propanoate [75140-48-6] (6b)[2]

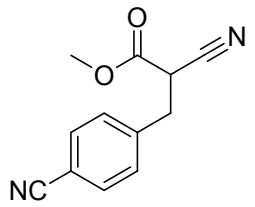
6b was obtained following the general procedure B starting from 4-methoxybenzaldehyde (545 mg, 4.0 mmol) and methylcyanoacetate (396 mg, 4.0 mmol, 1.0 equiv.) in toluene (3 mL, [S] = 1.3 M) with Pd/C 5% (170 mg, 2 mol%) and Cs_2CO_3 (10 mol%). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (476 mg, 54%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.19 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 6.87 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 3.80 (s, 3 H, CH_3), 3.79 (s, 3 H, CH_3), 3.70 (dd, *J* = 8.3, 5.8 Hz, 1 H, C*H*), 3.26–3.11 (m, 2 H, CH_2) ppm. **IR (neat):** υ max = 3020, 2956, 1744, 1612, 1584, 1513, 1437, 1299, 1246, 1178, 1112, 1029, 834, 810, 785, 707 cm^{-1}. **GC:** retention time: 12.23 min.



Chemical Formula: $C_{11}H_{10}ClNO_2$
Molecular Weight: 223,66

Methyl 2-cyano-3-(4-chlorophenyl)propionate [189697-36-7] (8b)[2]

8b was obtained following the general procedure A starting from 4-chlorobenzaldehyde (560 mg, 4.0 mmol), methylcyanoacetate (0.428 mL, 4.8 mmol, 1.2 equiv.) and toluene (2 mL, [S] = 2 M). Purification by flash column chromatography using cyclohexane/ethyl acetate afforded the title compound (550 mg, 61%). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.32 (d, *J* = 8.6 Hz, 2 H, CH_{Ar}), 7.21 (d, *J* = 8.6 Hz, 2 H, CH_{Ar}), 3.80 (s, 3 H, CH_3), 3.72 (dd, *J* = 8.2, 5.8 Hz, 1 H, CH), 3.29-3.14 (m, 2 H, CH_2) ppm. **HRMS (ESI +):** calcd for $C_{11}H_{10}NClNNaO_2$ $[M+Na]^+$ 246.0292 found 246.0288. **GC:** retention time: 12.02 min.



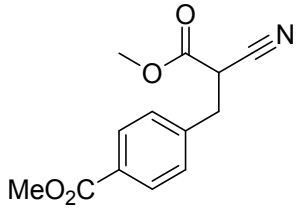
Chemical Formula: $C_{12}H_{10}N_2O_2$
Molecular Weight: 214,22

Methyl 2-cyano-3-(4-cyanophenyl)propanoate [676272-25-6] (10b)[3]

10b was obtained following the general procedure B starting from 4-cyanobenzaldehyde (524 mg, 4.0 mmol) and methylcyanoacetate (396 mg, 4.0 mmol, 1.0 equiv.) in toluene (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (617 mg, GC purity 91%, 65% yield corrected) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.67 (d, *J* =

[2] S. Nakamura, H. Sugimoto, T. Ohwada, *J. Org. Chem.* **2008**, *73*, 4219-4224.

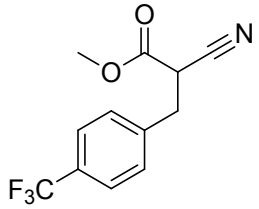
8.5 Hz, 2 H, CH_{Ar}), 7.40 (d, *J* = 8.5 Hz, 2 H, CH_{Ar}), 3.81 (s, 3 H, CO_2CH_3), 3.80–3.76 (m, 1 H, C*H*), 3.37–3.22 (m, 2 H, CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 165.4 (C, *C*O_2Me), 140.6 (C), 132.6 (CH), 129.9 (CH), 118.4 (C), 115.6 (C, CN), 111.7 (C), 53.7 (CH_3), 38.7 (CH), 35.2 (CH_2) ppm. **IR (neat):** υ max = 3030, 2957, 2228 (CN), 1744 (CO_2Me), 1610, 1506, 1436, 1415, 1345, 1265, 1214, 1179, 1114, 1020, 855, 815, 783 cm^{-1}. **HRMS (ESI +):** calcd for $C_{12}H_{11}N_2O_2$ $[M+H]^+$ 215.0815 found 215.0812. **GC:** retention time: 12.96 min.



Chemical Formula: $C_{13}H_{13}NO_4$
Molecular Weight: 247,25

Methyl 2-cyano-3-(4-methylbenzoate)propanoate (12b)

12b was obtained following the general procedure B starting from methyl 4-formylbenzoate (656 mg, 4.0 mmol) and methylcyanoacetate (396 mg, 4.0 mmol, 1.0 equiv.) in toluene (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (690 mg, 70%) as a white solid. **MP:** 71 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.2 Hz, 2 H, CH_{Ar}), 7.33 (d, *J* = 8.2 Hz, 2 H, CH_{Ar}), 3.89 (s, 3 H, CO_2CH_3), 3.80–3.76 (m, 4 H, CO_2CH_3+ C*H*), 3.35–3.19 (m, 2 H, CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 168.7 (C, *C*O_2Me), 165.8 (C, *C*O_2Me), 140.4 (C), 130.2 (CH), 129.8 (C), 129.2 (CH), 115.8 (C, CN), 53.7 (CH_3), 52.2 (CH_3), 39.0 (CH), 35.5 (CH_2) ppm. **IR (neat):** υ max = 3030, 2963, 2901, 2251 (CN), 1733(CO_2Me), 1717 (CO_2Me), 1610, 1511, 1439, 1416, 1324, 1297, 1270, 1175, 1099, 1020, 968, 953, 893, 883, 810, 765, 705, 638 cm^{-1}. **HRMS (ESI +):** calcd for $C_{13}H_{13}NNaO_4$ $[M+Na]^+$ 270.0737 found 270.0731. **GC:** retention time: 13.51 min.



Chemical Formula:
$C_{12}H_{10}F_3NO_2$
Molecular Weight: 257,21

Methyl 2-cyano-3-(4-trifluoromethylphenyl)propionate [676272-24-5] (14b)[4]

14b was obtained following the general procedure B starting from 4-trifluoromethylbenzaldehyde (706 mg, 4.06 mmol) and methylcyanoacetate (477 mg, 4.82 mmol, 1.2 equiv.) in toluene (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (810 mg, 78%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 8.1 Hz, 2 H, CH_{Ar}), 7.41 (d, *J* = 8.1 Hz, 2 H, CH_{Ar}), 3.81 (s, 3 H, CO_2CH_3), 3.80–3.75 (m, 1 H, C*H*), 3.38–3.23 (m, 2 H, CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 165.7 (C, *C*O_2Me), 139.3 (C), 130.2 (q, *J* = 32.5 Hz, C), 129.6 (CH), 125.9 (q, *J* = 3.7 Hz, CH), 124.1 (q, *J* = 271.8 Hz, C), 115.8 (C, CN), 53.8 (CH_3), 39.1 (CH), 35.3 (CH_2) ppm. **HRMS (ESI +):** calcd for $C_{12}H_{10}F_3NNaO_2$ $[M+Na]^+$ 280.0556 found 280.0565. **GC:** retention time: 10.27 min.

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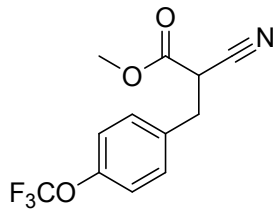
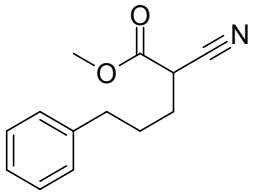
[3] X. Yang, T. Fox, H. Berke, *Org. Biomol. Chem.* **2012**, *10*, 852-860.
[4] S. Nakamura, H. Sugimoto, T. Ohwada, *J. Org. Chem.* **2008**, *73*, 4219-4224.



Chemical Formula: $C_{12}H_{10}F_3NO_3$
Molecular Weight: 273,21

Methyl 2-cyano-3-(4-trifluoromethoxyphenyl)propionate (16b)

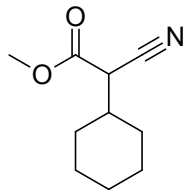
16b was obtained following the general procedure B starting from 4-trifluoromethoxybenzaldehyde (760 mg, 4.00 mmol) and methylcyanoacetate (396 mg, 4.00 mmol, 1.0 equiv.) in toluene (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (519 mg, 47%) of the desired product as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.31 (d, *J* = 8.4 Hz, 2 H, CH_{Ar}), 7.20 (d, *J* = 8.4 Hz, 2 H, CH_{Ar}), 3.81 (s, 3 H, CO_2CH_3), 3.76–3.71 (m, 1 H, C*H*), 3.32–3.17 (m, 2 H, CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 165.8 (C, *C*O_2Me), 148.9 (q, *J* = 1.8 Hz, C), 134.0 (C), 130.7 (CH), 121.4 (CH), 120.5 (q, *J* = 257.2 Hz, C), 115.9 (C, CN), 53.7 (CH_3), 39.3 (CH), 34.9 (CH_2) ppm. **IR (neat):** υ max = 3030, 2959, 2225 (CN), 1748 (CO_2Me), 1717 (CO_2Me), 1510, 1438, 1252, 1198, 1156, 1108, 1020, 921, 857, 815, 673 cm^{-1}. **HRMS (ESI +):** calcd for $C_{12}H_{10}F_3NNaO_3$ $[M+Na]^+$ 296.0505 found 296.0507. **GC:** retention time: 10.25 min.



Chemical Formula: $C_{13}H_{15}NO_2$
Molecular Weight: 217,26

Methyl 2-cyano-5-phenylpentanoate [1025483-41-3] (18b)[2]

18b was obtained following the general procedure B starting from 3-phenylpropionaldehyde (536 mg, 4.00 mmol) and methylcyanoacetate (396 mg, 4.00 mmol, 1.0 equiv.) in toluene (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (720 mg, 83%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.32-7.27 (m, 2 H, CH_{Ar}), 7.23-7.16 (m, 3 H, CH_{Ar}), 3.81 (s, 3 H, CO_2CH_3), 3.51 (t, *J* = 6.9 Hz, 1 H, C*H*), 2.69 (t, *J* = 7.3 Hz, 2 H, CH_2), 2.02-1.92 (m, 2 H), 1.90-1.78 (m, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 166.5 (C, *C*O_2Me), 140.8 (C), 128.5 (CH), 128.3 (CH), 126.2 (CH), 116.4 (C, CN), 53.4 (CH_3), 37.2 (CH), 34.9 (CH_2), 29.2 (CH_2), 28.3 (CH_2) ppm. **IR (neat):** υ max = 3027, 2935, 2864, 2250 (CN), 1745 (CO_2Me), 1603, 1496, 1453, 1436, 1256, 1208, 1177, 1087, 1001, 916, 749, 699 cm^{-1}. **HRMS (ESI +):** calcd for $C_{13}H_{15}NNaO_2$ $[M+Na]^+$ 240.0995 found 240.0994. **GC:** retention time: 12.03 min.

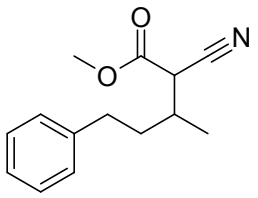


Chemical Formula: $C_{10}H_{15}NO_2$
Molecular Weight: 181,23

Cyano(cyclohexyl)acetic acid methyl ester [80627-89-0] (20b)[5]

20b was obtained following the general procedure B starting from cyclohexanone (393 mg, 4.01 mmol) and methylcyanoacetate (412 mg, 4.16 mmol, 1.04 equiv.) in toluene (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (465 mg, 64%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 3.81 (s, 3 H, CO_2CH_3), 3.39 (d, *J* = 5.6 Hz, 1 H, CN-C*H*), 2.11-1.99 (m, 1 H, C*H*), 1.84-1.67 (m, 5 H), 1.36-1.14 (m, 5 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 166.2 (C, *C*O_2Me), 115.5 (C, CN), 53.1 (CH or CH_3), 44.2 (CH or CH_3), 38.6 (CH or CH_3), 30.8 (CH_2), 29.2 (CH_2), 25.6 (CH_2), 25.4 (CH_2), 25.3 (CH_2) ppm. **IR (neat):** υ max = 2929, 2855, 2250 (CN), 1744 (CO_2Me), 1449, 1436, 1253, 1204, 1166, 1013, 899 cm^{-1}. **HRMS (ESI +):** calcd for $C_{10}H_{15}NNaO_2$ $[M+Na]^+$ 204.0995 found 204.0995. **GC:** retention time: 9.46 min.

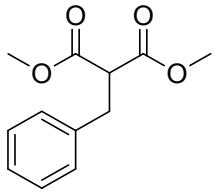
[5] D. B. Ramachary, M. Kishor, Y. Vijayendar Reddy, *Eur. J. Org. Chem.* **2008**, 975-993.



Chemical Formula: $C_{14}H_{17}NO_2$
Molecular Weight: 231,29

Methyl 2-cyano-3-methyl-5-phenylpentanoate [1629235-94-4] and [1629235-95-5] (22b)[6]

22b was obtained following the general procedure B starting from 4-phenyl-butan-2-one (593 mg, 4.00 mmol) and methylcyanoacetate (396 mg, 4.00 mmol, 1.00 equiv.) in toluene (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded a mixture of diastereoisomers (dia1 and dai2) of the title product (44 mg, 5%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.32-7.27 (m, 4.63 H, CH_{Ar}, 2 H dia1 + 2 H dia2), 7.23-7.16 (m, 7.25 H, CH_{Ar}, 3 H dia1 + 3 H dia2), 3.81 (s, 4.26 H, CO_2CH_3, 3 H dia1), 3.79 (s, 3 H, CO_2CH_3, 3 H dia2), 3.57 (d, *J* = 4.5 Hz, 1.46 H, CN-C*H*, 1 H dia1), 3.57 (d, *J* = 5.0 Hz, 1.00 H, CN-C*H*, 1 H dia2), 2.81–2.52 (m, 5 H, CH_2, 2 H dia1 + 2 H dia2), 2.36–2.22 (m, 2.52 H, C*H*, 1 H dia1 + 1 H dia2), 1.90-1.63 (m, 5.26 H, CH_2, 2 H dia1 + 2 H dia2), 1.18 (d, *J* = 6.9 Hz, 3 H, CH_3, 3 H dia2), 1.13 (d, *J* = 6.7 Hz, 4.46 H, CH_3, 3 H dia1) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 166.6 (C, *C*O_2Me, dia1), 166.3 (C, *C*O_2Me, dia2), 141.1 (C, dia2), 140.9 (C, dia1), 128.7 (CH, dia1), 128.6 (CH, dia2), 128.4 (CH, dia1 + dia2), 126.35 (CH, dia1), 126.28 (CH, dia2), 115.7 (C, CN, dia2), 115.2 (C, CN, dia1), 53.5 (CH_3, CO_2Me, dia1), 53.4 (CH_3, CO_2Me, dia2), 44.4 (CH, dia2), 43.7 (CH, dia1), 36.5 (CH_2, dia1), 34.9 (CH_2, dia2), 34.21 (CH, dia2), 34.17 (CH, dia1), 33.2 (CH_2, dia1), 33.1 (CH_2, dia2), 17.7 (CH_3, CH-CH_3, dia2), 16.5 (CH_3, CH-CH_3, dia1) ppm. **IR (neat):** υ max = 3027, 2928, 2225 (CN), 1744 (CO_2Me), 1602 (CO_2Me), 1496, 1454, 1436, 1387, 1254, 1203, 1176, 1009, 912, 747, 699 cm^{-1}. **HRMS (ESI +):** calcd for $C_{14}H_{18}NO_2$ $[M+H]^+$ 232.1332 found 232.1331. **GC:** retention time: 12.27 min. **GC/MS:** retention time: 11.68 min.



Chemical Formula: $C_{12}H_{14}O_4$
Molecular Weight: 222,24

Dimethyl benzylmalonate [49769-78-0] (28b)[7]

28b was obtained following the general procedure C starting from dodecane (70.4 mg, 0.41 mmol, 10 mol%), benzaldehyde (426 mg, 4.02 mmol, 1 equiv.), dimethylmalonate (533 mg, 4.04 mmol, 1 equiv.) and CPME (2 mL, [S] = 2 M). From the relative area of the product and dodecane, the conversion to dimethyl benzylmalonate was calculated to be 79%. Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate: 100/0 to 95/5 afforded the title compound (634 mg, 71%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.28–7.18 (m, 5 H, 5 CH_{ar}), 3.70 (s, 6 H, 2 CO_2CH_3), 3.68 (t, *J* = 7.9 Hz, 1 H, C*H*), 3.22 (d, *J* = 7.9 Hz, 2 H, Ph-CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 169.3 (C_q, 2 O-C=O), 138.7 (C_q, C_{Ar}), 128.8 (2 CH), 128.6 (2 CH), 126.8 (C_q), 53.6 (CH_3), 52.5 (CH), 34.8 (CH_2) ppm. **GC:** retention time: 10.7 min. **IR (neat):** υ max = 3064, 3030, 2954, 2924, 2849, 1732, 1604, 1496, 1455, 1435, 1343, 1275, 1220, 1147, 1024, 751, 699 cm^{-1}. **HRMS (ESI +):** calcd for $C_{11}H_{11}NNaO_2$ $[M+Na]^+$ 245.0784, found 245.0784.

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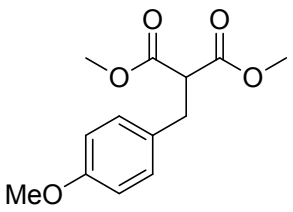
[6] C. Hayashi, T. Hayashi, S. Kikuchi, T. Yamada, *Chem. Lett.* **2014**, *43*, 565-567.
A. Wetzel, S. Wockel, M. Schelwies, M. K. Brinks, F. Rominger, P. Hofmann, M. Limbach, *Org. Lett.* **2013**, *15*, 266-269.

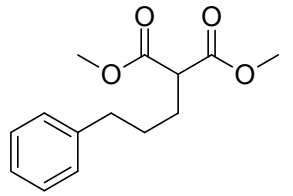
[7] Q. Xu, B. Cheng, X. Ye, H. Zhai, *Org. Lett.* **2009**, *11*, 4136-4138.



Chemical Formula: $C_{13}H_{16}O_5$
Molecular Weight: 252,26

Dimethyl 2-(4'-methoxybenzyl)malonate [15378-09-3] (29b)[8]

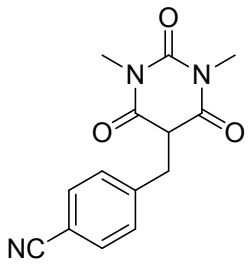
29b was obtained following the general procedure C starting from 4-methoxybenzaldehyde (544 mg, 4.00 mmol), dimethylmalonate (528 mg, 4.00 mmol, 1 equiv.) and CPME (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (531 mg, 53%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.09 (d, *J* = 8.7 Hz, 2 H, C*H*$_{Ar}$), 6.79 (d, *J* = 8.7 Hz, 2 H, C*H*$_{Ar}$), 3.75 (s, 3 H, OC*H*$_3$), 3.68 (s, 6 H, 2 CO_2CH_3), 3.62 (t, *J* = 7.8 Hz, C*H*), 3.14 (d, *J* = 7.8 Hz, 2 H, C*H*$_2$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 169.3 (C, *C*O_2Me), 158.5 (C), 129.8 (CH), 129.7 (C), 113.9 (CH), 55.2 (CH_3 or CH), 53.9 (CH_3 or CH), 52.6 (CH_3 or CH), 34.0 (CH_2) ppm. **IR (neat):** υ max = 3030, 2954, 1731 (CO_2Me), 1612, 1512, 1435, 1343, 1244, 1176, 1110, 1029, 822, 754 cm^{-1}. **GC:** retention time: 12.54 min. **GC/MS:** retention time: 11.83 min.



Chemical Formula: $C_{14}H_{18}O_4$
Molecular Weight: 250,29

2-(3-phenylpropyl)-malonic acid dimethyl ester [3708-34-7] (31b)[9]

31b was obtained following the general procedure C starting from 3-phenylpropionaldehyde (543 mg, 4.05 mmol), dimethylmalonate (528 mg, 4.00 mmol) and CPME (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (461 mg, 46%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.31-7.15 (m, 5 H, C*H*$_{Ar}$), 3.73 (s, 6 H, 2 CO_2CH_3), 3.38 (t, *J* = 7.6 Hz, C*H*), 2.64 (t, *J* = 7.7 Hz, 2 H, C*H*$_2$), 1.99-1.91 (m, 2 H, CH_2), 1.69-1.59 (m, 2 H, CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 169.8 (C, *C*O_2Me), 141.6 (C), 128.4 (CH), 126.0 (CH), 52.5 (CH_3 or CH), 51.6 (CH_3 or CH), 35.5 (CH_2), 29.1 (CH_2), 28.5 (CH_2) ppm. **IR (neat):** υ max = 3026, 2953, 2861, 1732 (CO_2Me), 1603, 1496, 1453, 1435, 1343, 1197, 1144, 1056, 1003, 914, 806, 748, 699 cm^{-1}. **HRMS (ESI +):** calcd for $C_{14}H_{18}NaO_4$ $[M+Na]^+$ 273.1097 found 273.1104. **GC:** retention time: 12.42 min.



Chemical Formula: $C_{14}H_{13}N_3O_3$
Molecular Weight: 271,27

5-(4-Cyanobenzyl)-1,3-dimethyl-hexahydropyrimidin-2,4,6-trion [81762-45-0] (32b)[10]

32b was obtained following the general procedure C starting from 4-cyanobenzaldehyde (524 mg, 4.00 mmol), 1,3-dimethylbarbituric acid (624 mg, 4.00 mmol, 1 equiv.) and CPME (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (609 mg, 56%) as a white solid. **MP:** 132 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 8.4 Hz, 2 H, C*H*$_{Ar}$), 7.25 (d, *J* = 8.4 Hz, 2 H, C*H*$_{Ar}$), 3.81 (t, *J* = 4.9 Hz, 1 H, C*H*), 3.54 (d, *J* = 4.9 Hz, C*H*$_2$), 3.19 (s, 6 H, 2 C*H*$_3$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 167.4 (C), 150.9 (C), 141.8 (C), 132.3 (CH), 130.1 (CH), 118.5 (C), 111.4 (C), 50.1 (CH_3 or CH), 35.2 (CH_2), 28.5 (CH_3 or CH) ppm. **IR (neat):** υ max = 3408, 2952, 2226, 1744, 1667, 1609, 1502, 1442, 1416, 1378, 1303, 1283, 1193, 1116, 1097, 10005, 878, 819, 755 cm^{-1}. **HRMS (ESI +):** calcd for $C_{14}H_{14}N_3O_3$ $[M+H]^+$ 272.1030 found 272.1022. **GC:** retention time: 15.52 min.

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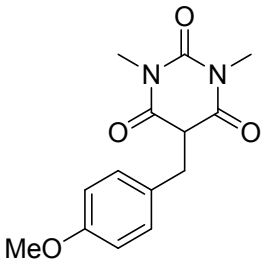
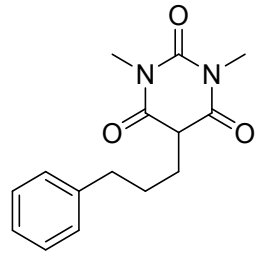
[8] A. R. Mohite R. G. Bhat, *Org. Lett.* **2013**, *15*, 4564-4567.
[9] D. B. Ramachary, C. Venkaiah, Y. Vijayendar Reddy, M. Kishor, *Org. Biomol. Chem.* **2009**, *7*, 2053-2062.
[10] K. Rehse, W.-D. Kapp, *Arch. Pharm. (Weinheim, Ger.)* **1982**, *315*, 346-353.



Chemical Formula: $C_{14}H_{16}N_2O_4$
Molecular Weight: 276,29

5-(4-Methoxybenzyl)-1,3-dimethylpyrimidine-2,4,6-trione [114656-99-4] (33b)[11]

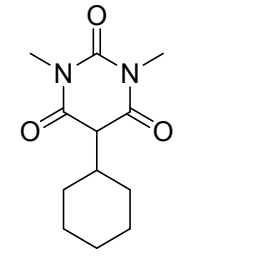
33b was obtained following the general procedure C from 4-methoxybenzaldehyde (545 mg, 4.00 mmol), 1,3-dimethylbarbituric acid (624 mg, 4.00 mmol, 1 equiv.) and CPME (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (279 mg, 25%) as a white solid. **MP:** 116 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.92 (d, *J* = 8.5 Hz, 2 H, C*H*$_{Ar}$), 6.73 (d, *J* = 8.5 Hz, 2 H, C*H*$_{Ar}$), 3.74-3.70 (m, 4 H, OC*H*$_3$ + C*H*), 3.39 (d, *J* = 4.6 Hz, C*H*$_2$), 3.11 (s, 6 H, 2 C*H*$_3$) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 168.5 (C), 159.1 (C), 151.1 (C), 130.1 (CH), 127.1 (C), 114.0 (CH), 55.2 (CH_3 or CH), 50.9 (CH_3 or CH), 37.2 (CH_2), 28.3 (CH_3 or CH) ppm. **IR (neat):** υ max = 2956, 2937, 2843, 1742, 1656, 1612, 1514, 1460, 1437, 1420, 1282, 1246, 1179, 1150, 1030, 1004, 936, 863, 814, 762, 724, 611 cm^{-1}. **HRMS (ESI +):** calcd for $C_{14}H_{16}N_2NaO_4$ $[M+Na]^+$ 299.1002 found 299.1003. **GC:** retention time: 14.81 min.



Chemical Formula: $C_{15}H_{18}N_2O_3$
Molecular Weight: 274,32

1,3-dimethyl-5-(3-phenylpropyl)pyrimidine-2,4,6-trione [82657-34-9] (34b)[12]

34b was obtained following the general procedure C starting from 3-phenylpropionaldehyde (536 mg, 4.00 mmol), 1,3-dimethylbarbituric acid (624 mg, 4.00 mmol, 1 equiv.) and CPME (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (722 mg, 66%) as a colorless oil. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.29-7.24 (m, 2 H, C*H*$_{Ar}$), 7.20-7.13 (m, 3 H, C*H*$_{Ar}$), 3.48 (t, *J* = 5.4 Hz, 1 H, C*H*), 3.28 (s, 6 H, 2 C*H*$_3$), 2.62 (t, *J* = 7.8 Hz, 2 H, C*H*$_2$), 2.2-2.13 (m, 2 H, CH_2), 1.68-1.57 (m, 2 H, CH_2) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 168.6 (C), 151.6 (C), 141.2 (C), 128.5 (CH), 128.4 (CH), 126.1 (CH), 48.9 (CH_3 or CH), 35.6 (CH_2), 30.8 (CH_2), 28.6 (CH_3 or CH), 28.0 (CH_2) ppm. **IR (neat):** υ max = 3030, 2934, 1670, 1603, 1450, 1419, 1374, 1320, 1282, 1113, 1078, 1047, 997, 752, 699 cm^{-1}. **HRMS (ESI +):** calcd for $C_{15}H_{19}N_2O_3$ $[M+H]^+$ 275.1390 found 275.1394. **GC:** retention time: 15.26 min.



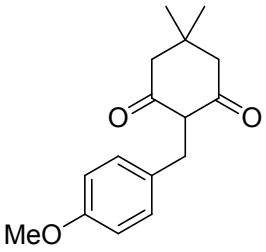
Chemical Formula:
$C_{12}H_{18}N_2O_3$
Molecular Weight: 238,28

5-cyclohexyl-1,3-dimethylpyrimidine-2,4,6-trione [7391-65-3] (35b)[5]

35b was obtained following the general procedure C starting from cyclohexanone (393 mg, 4.00 mmol), 1,3-dimethylbarbituric acid (624 mg, 4.00 mmol, 1 equiv.) and CPME (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (739 mg, 78%) as a white solid. **MP:** 147 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 3.33 (d, *J* = 3.8 Hz, 1 H, C*H*-C(=O)-N), 3.30 (s, 6 H, 2 CH_3), 2.26-2.15 (m, 1 H, C*H*), 1.77-1.74 (m, 2 H), 1.67-1.61 (m, 3 H), 1.33-1.18 (m, 4 H), 1.12-1.09 (m, 1 H, CH) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 168.6 (C), 152.0 (C), 55.6 (CH_3 or CH), 44.1 (CH_3 or CH), 30.0 (CH_2), 28.3 (CH_3 or CH), 26.3 (CH_2), 25.6 (CH_2) ppm. **IR (neat):** υ max = 2945, 2908, 2852, 1656, 1460, 1439, 1413, 1362, 1320, 1284, 1261, 1219, 1145, 1113, 1020, 989, 921, 807, 762, 665, 628 cm^{-1}. **HRMS (ESI +):** calcd for $C_{12}H_{19}N_2O_3$ $[M+H]^+$ 239.1390 found

[11] K. Tanaka, X. Chen, F. Yoneda, *Tetrahedron* **1988**, *44*, 3241-3249.
[12] B. S. Jursic, E. D. Stevens, *Tetrahedron Lett.* **2003**, *44*, 2203-2210.

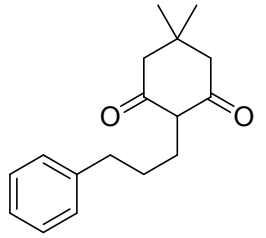
239.1395. **GC:** retention time: 12.90 min.



Chemical Formula: $C_{16}H_{20}O_3$
Molecular Weight: 260,33

2-[(4-Methoxyphenyl)methyl]-5,5-dimethyl-1,3-cyclohexanedione [33802-37-8] (37b)

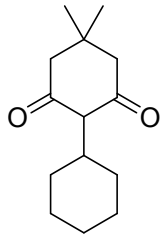
37b was obtained following the general procedure C starting from 4-methoxybenzaldehyde (545 mg, 4.00 mmol), dimedone (560 mg, 4.00 mmol, 1 equiv.), CPME (3 mL, [S] = 1.3 M) and Pd/C (2 mol%). Extraction under acidic conditions (HCl (1 M) until pH = 2) afforded the title compound (624 mg, 60%) as a white solid. **MP:** 190 °C.[13] **^{1}H NMR (300 MHz, CD_3OD):** δ 7.10 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 6.72 (d, *J* = 8.8 Hz, 2 H, CH_{Ar}), 3.72 (s, 3 H, OCH_3), 3.50 (s, 2 H, CH_2), 3.30 (s, 4 H, 2 CH_2), 1.04 (s, 6 H, 2 CH_3) ppm. **^{13}C NMR (75 MHz, CD_3OD):** δ 159.0 (C), 135.1 (C), 130.3 (CH), 115.8 (C), 114.3 (CH), 55.6 (CH_3 or CH), 33.0 (C), 28.5 (CH_3), 27.3 (CH_2) ppm. **IR (neat):** υ max = 3030, 2959, 1581, 1549, 1509, 1468, 1370, 1344, 1301, 1243, 1213, 1194, 1174, 1149, 1105, 1032, 922, 885, 871, 771, 631, 599 cm^{-1}. **HRMS (ESI +):** calcd for $C_{16}H_{20}NaO_3$ $[M+Na]^+$ 283.1305 found 283.1302. **GC:** retention time: 14.90 min.



Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

2-[(3'-phenylpropyl]-5,5-dimethyl-1,3-cyclohexanedione (38b)

38b was obtained following the general procedure C starting from 3-phenylpropionaldehyde (536 mg, 4.00 mmol), dimedone (560 mg, 4.00 mmol, 1 equiv.) and CPME (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (552 mg, 54%) as a white solid. **MP:** 149 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.29-7.10 (m, 5 H, CH_{Ar}), 3.81 (br. s, 1 H, O*H*), 2.73 (d, *J* = 13.1 Hz, 2 H, CH_2), 2.59 (t, *J* = 7.3 Hz, 2 H, CH_2), 2.39 (d, *J* = 13.1 Hz, 2 H, CH_2), 1.92-1.86 (m, 2 H, CH_2), 1.65-1.60 (m, 2 H, CH_2), 1.15 (s, 3 H, CH_3), 0.76 (s, 3 H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 206.0 (C), 141.0 (C), 128.5 (2 CH), 128.4 (2 CH), 128.2 (1 CH), 89.3 (C), 50.9 (CH_2), 38.8 (CH_2), 35.2 (CH_2), 31.5 (C), 30.6 (CH_3 or CH), 26.3 (CH_3 or CH), 24.5 (CH_2) ppm. **IR (neat):** υ max = 3408 (OH, H-bonded), 3060, 3030, 2958, 2871, 1729 (C=O, ketone), 1696 (C=O, insaturated ketone), 1602, 1496, 1460, 1422, 1371, 1324, 1246, 1232, 1202, 1158, 1133, 1083, 1069, 1039, 1030, 982, 957, 907, 745, 699, 637, 613, 567 cm^{-1}. **GC:** retention time: 14.69 min.



Chemical Formula:
$C_{14}H_{22}O_2$
Molecular Weight: 222,32

2-[(cyclohexyl]-5,5-dimethyl-1,3-cyclohexanedione (39b)

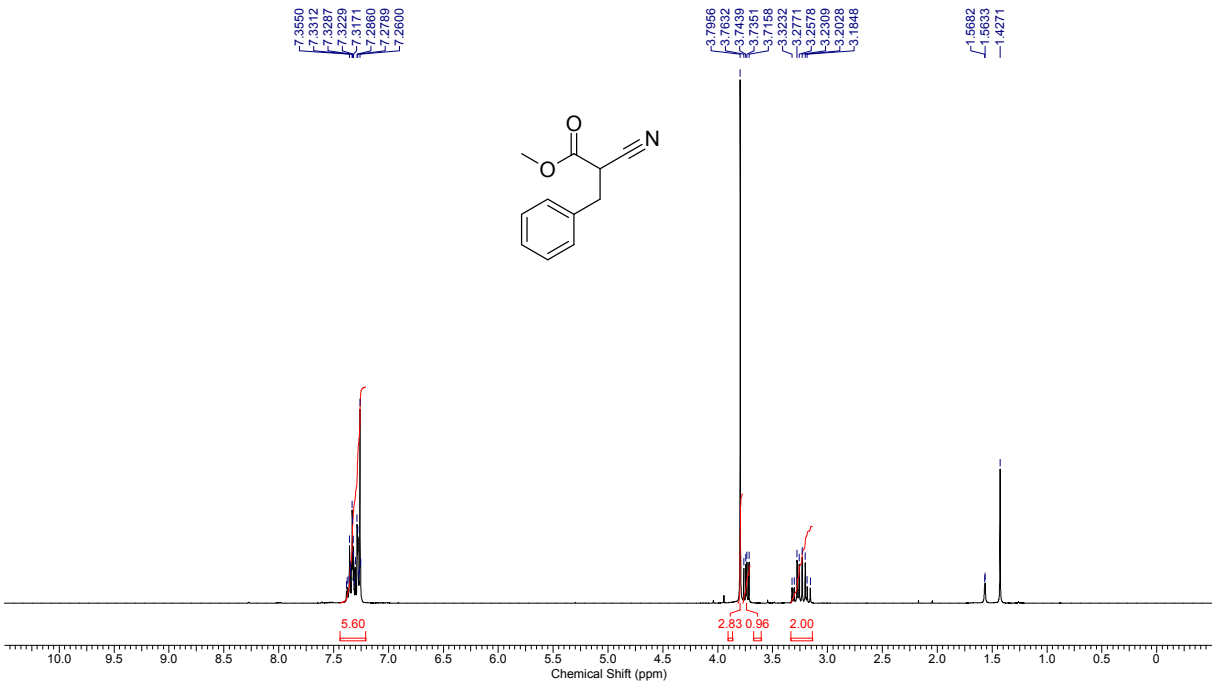
39b was obtained following the general procedure C starting from cyclohexanone (393 mg, 4.00 mmol), dimedone (561 mg, 4.00 mmol, 1 equiv.) and CPME (3 mL, [S] = 1.3 M). Purification by flash column chromatography using a gradient of cyclohexane/ethyl acetate afforded the title compound (550 mg, 62%) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 9.27 (s, 1 H), 2.76 (d, *J* = 13.7 Hz, 2 H), 2.50 (d, *J* = 13.7 Hz, 2 H), 2.02 (tt, *J* = 11.9, 3.4 Hz, 1 H, C*H*), 1.79–1.76 (m, 2 H, CH_2), 1.63–1.60 (m, 1 H, C*H*), 1.48–1.44 (m, 2 H, CH_2), 1.34–1.25 (m, 2 H, CH_2), 1.20 (s, 3 H, CH_3), 1.16-1.09 (m, 2 H, CH_2), 0.88 (s, 3 H, CH_3) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 200.1 (C), 101.7 (C), 52.7 (2 CH_2), 44.7 (CH), 30.7 (C), 30.6 (CH_3), 26.7 (CH_2), 26.3 (CH_2), 26.1 (CH_3), 25.6 (CH_2)

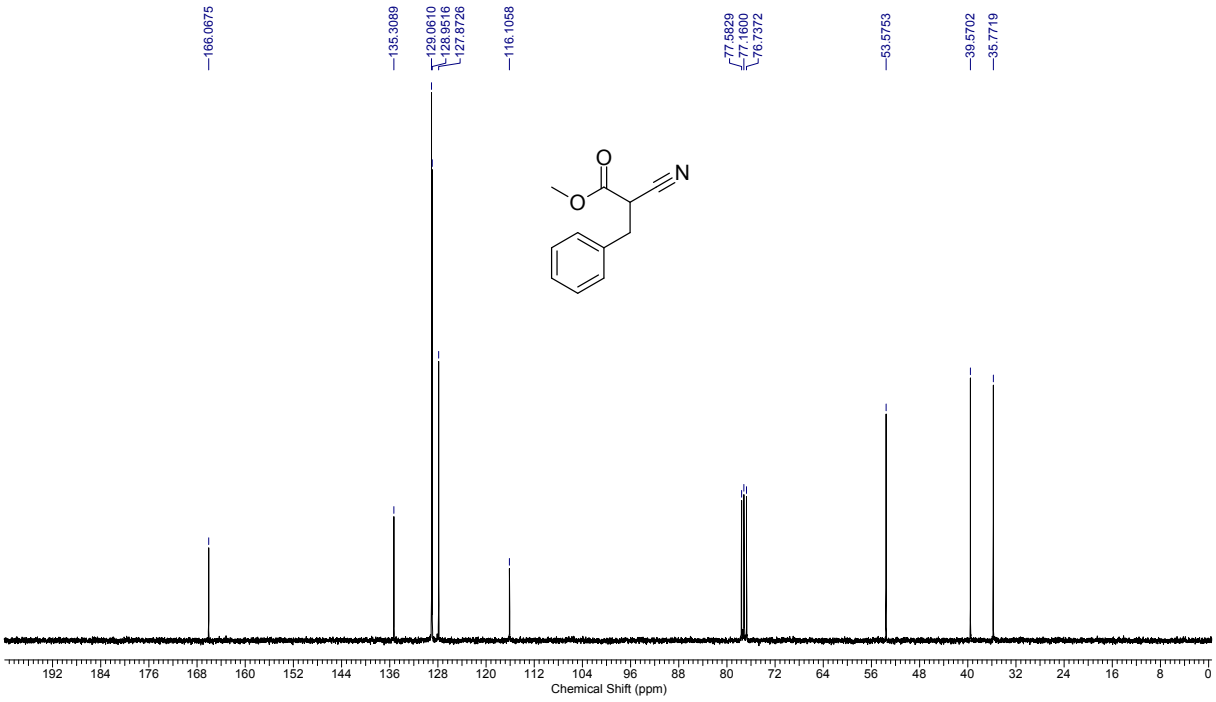
[13] M. Sekiya, K. Suzuki, *Chem. Pharm. Bull.* **1971,** *19*, 1540-1545.

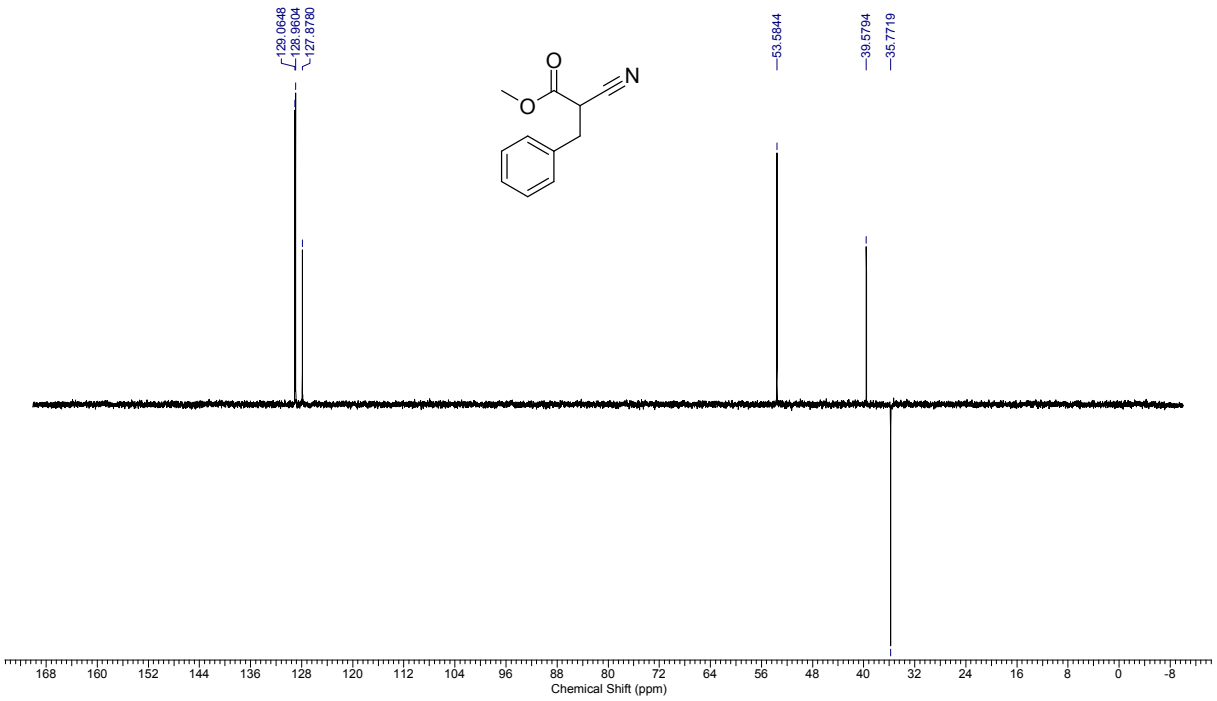
ppm. **EI-MS** m/z (%): 222 (20, $M^{+\cdot}$), 141 (100), 95 (60), 83 (21), 67 (80), 55 (14). **GC:** retention time: 11.89 min. **GC/MS:** retention time: 11.28 min.

4. Spectra

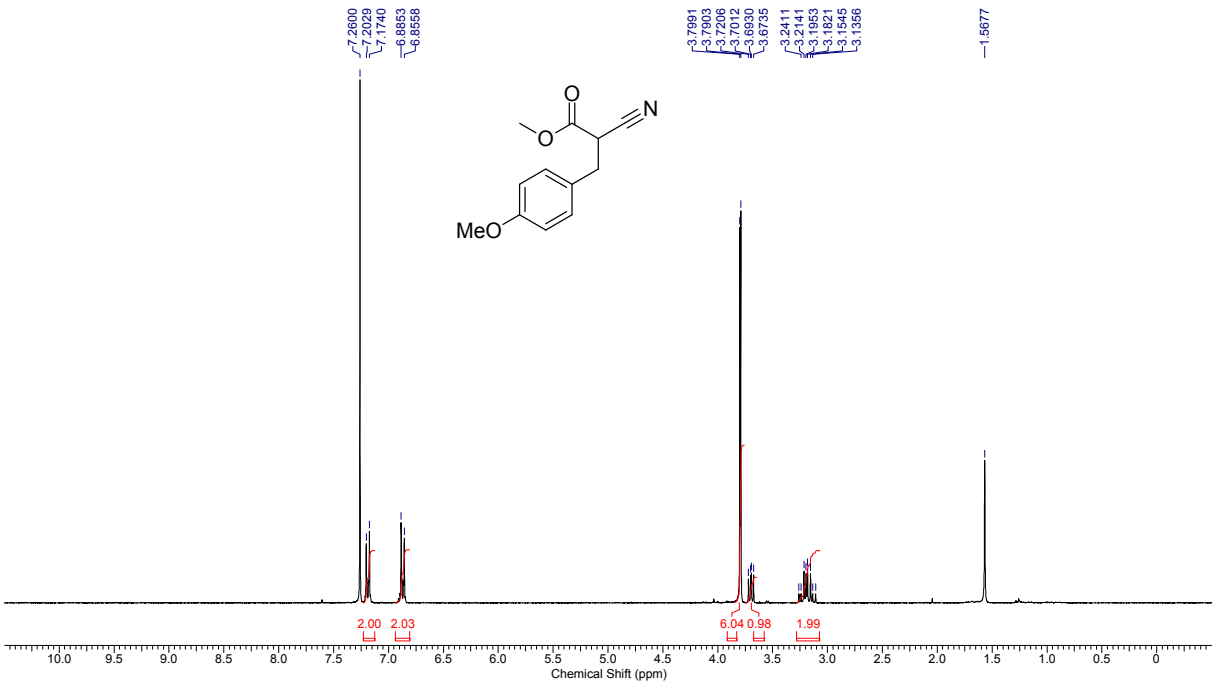
Methyl 2-cyano-3-phenylpropionate [57519-78-5] (4b)



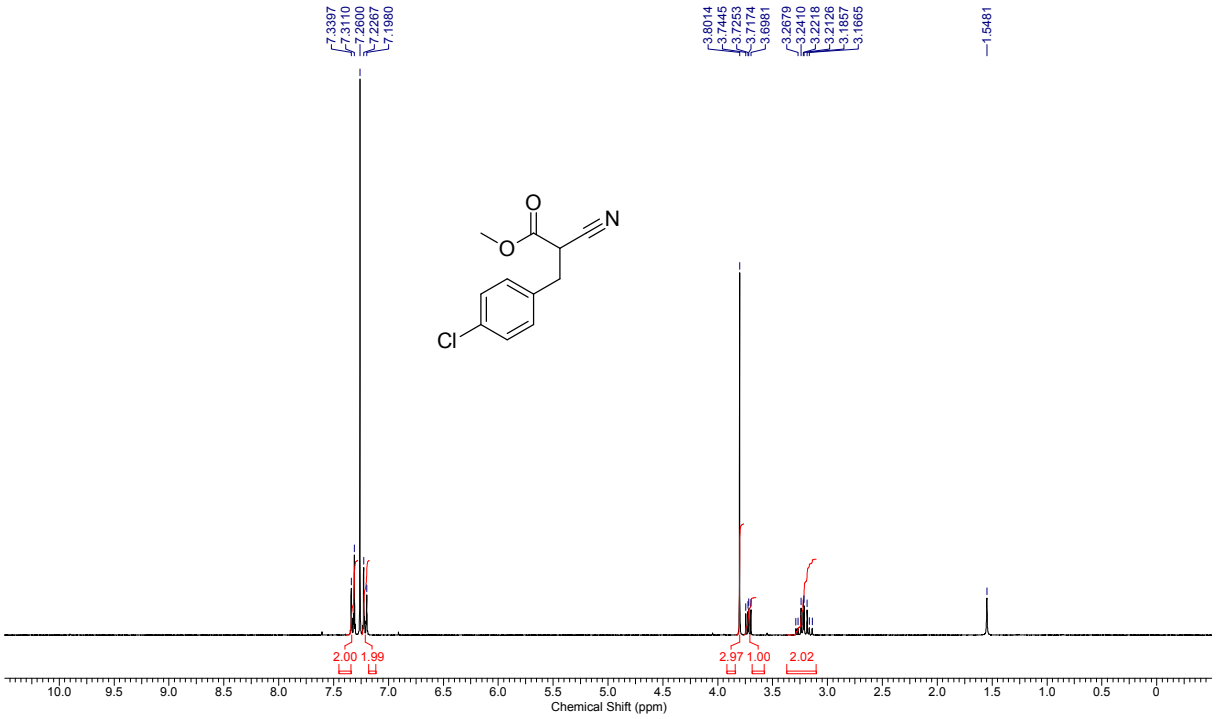




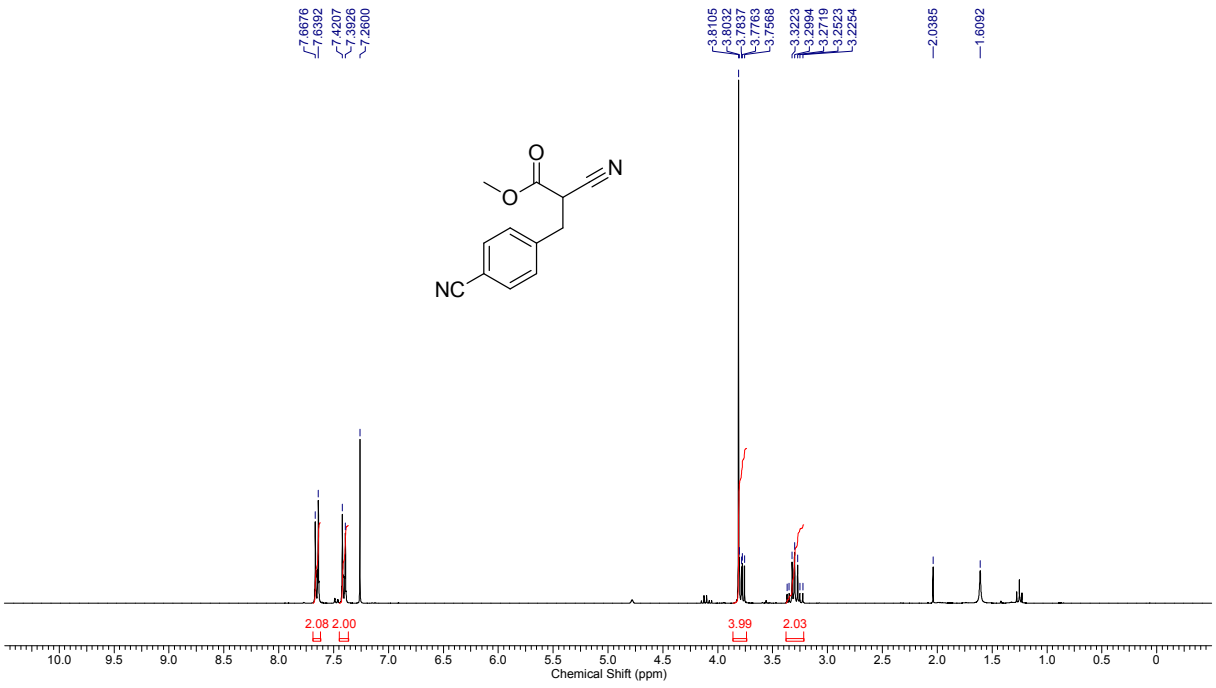
Methyl 2-cyano-3-(4-methoxyphenyl)propanoate [75140-48-6] (6b)

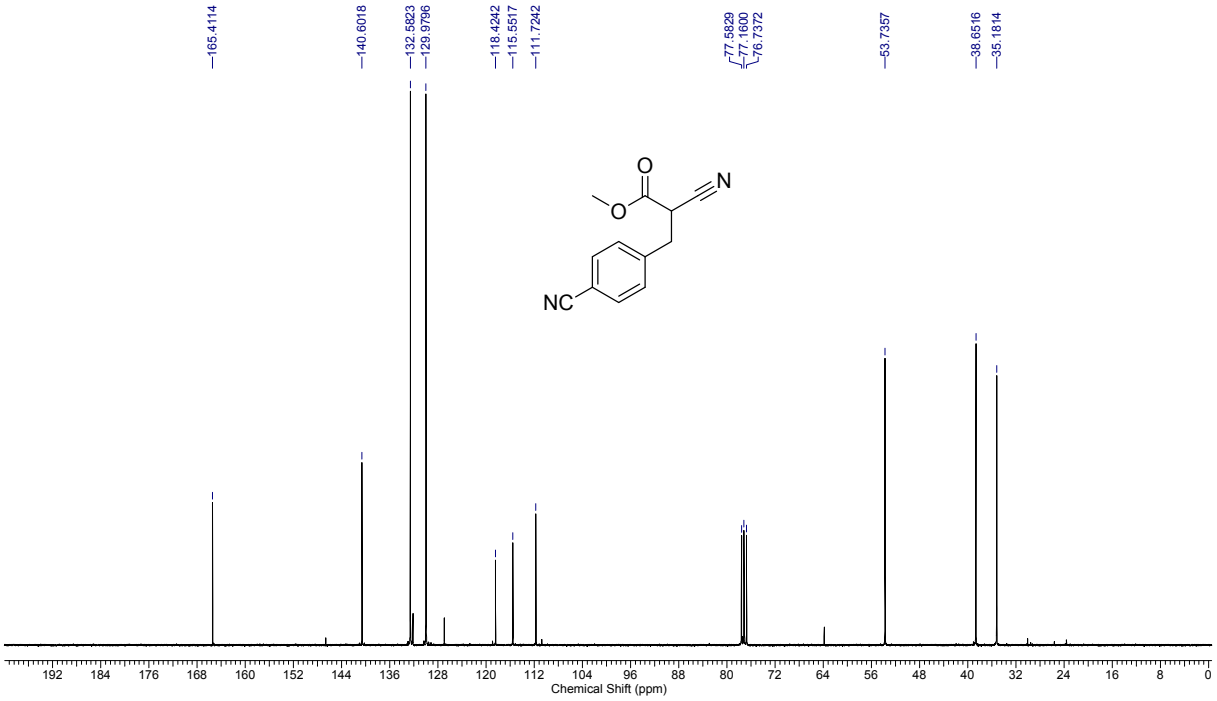


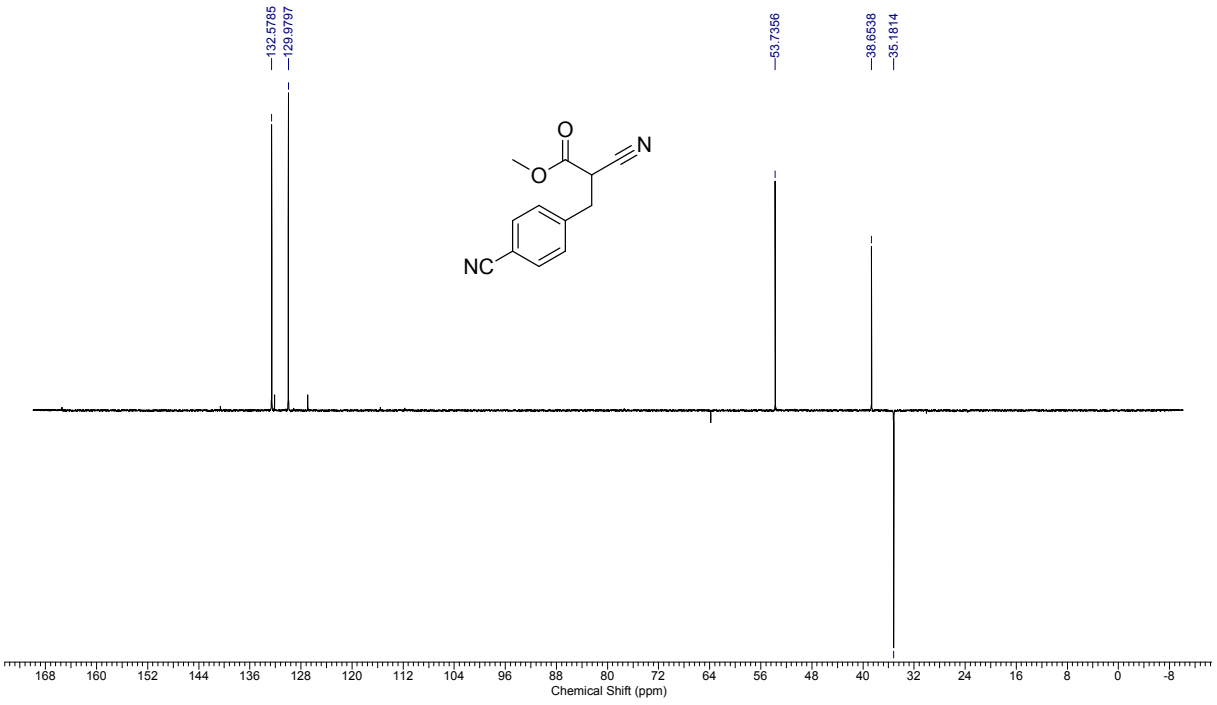
Methyl 2-cyano-3-(4-chlorophenyl)propionate [189697-36-7] (8b)



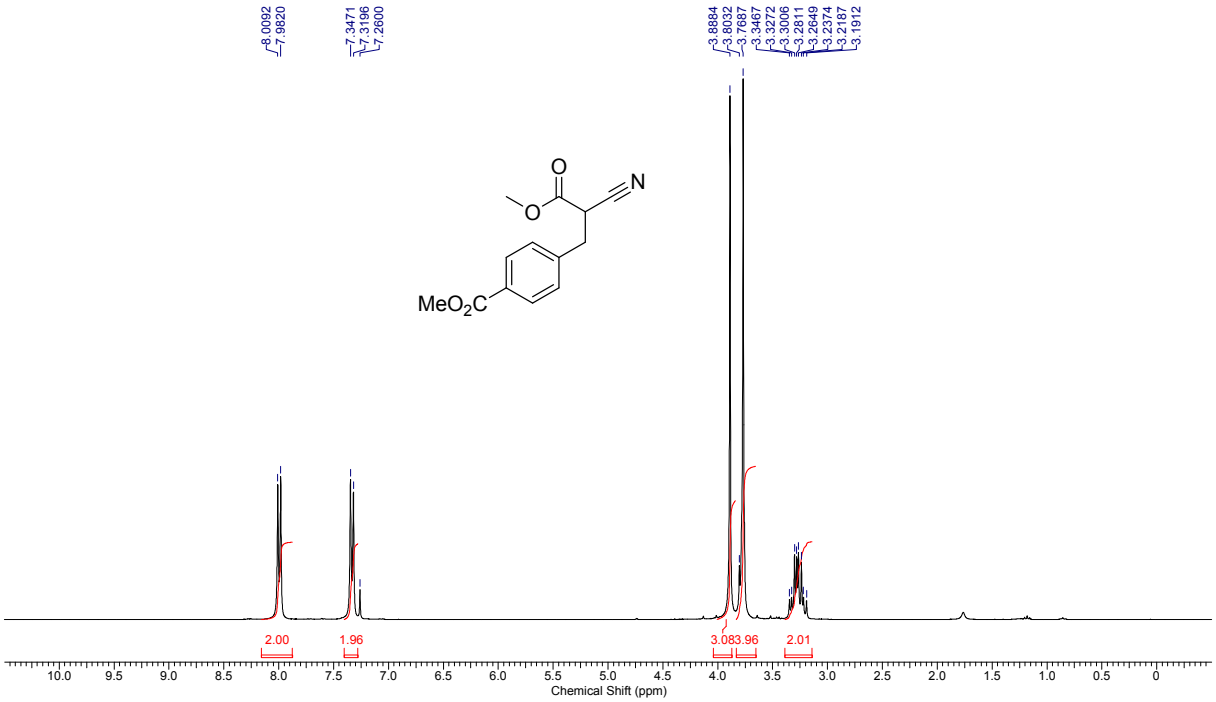
Methyl 2-cyano-3-(4-cyanophenyl)propanoate [676272-25-6] (10b)

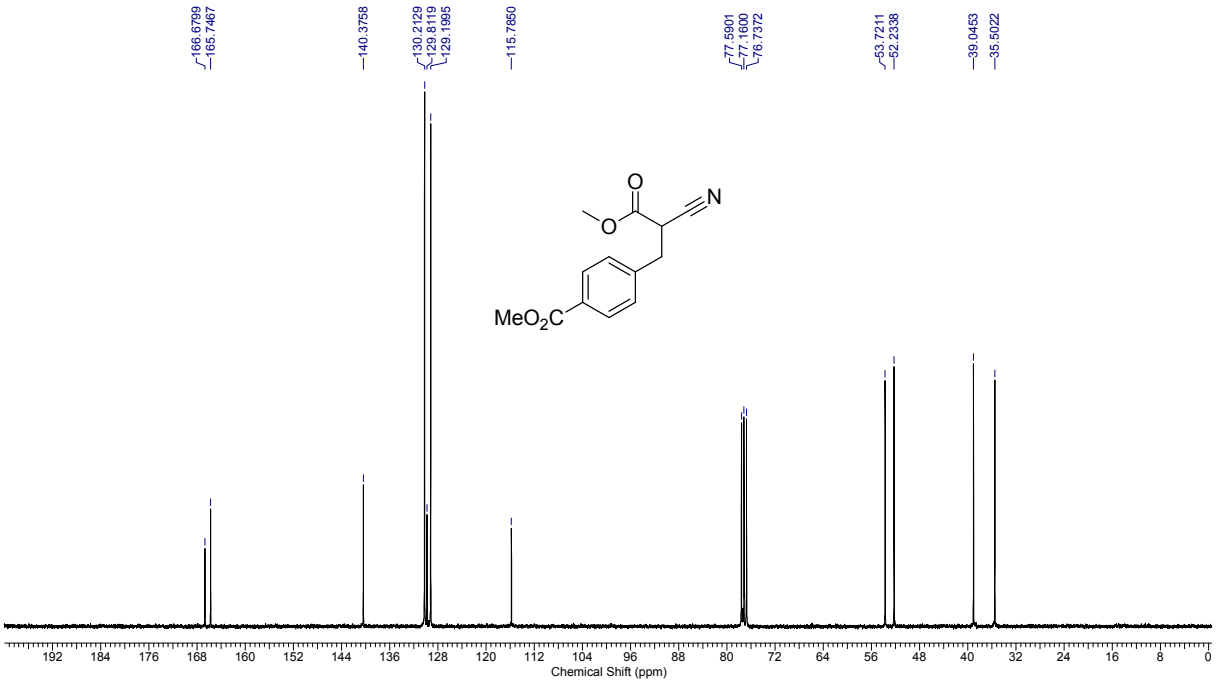


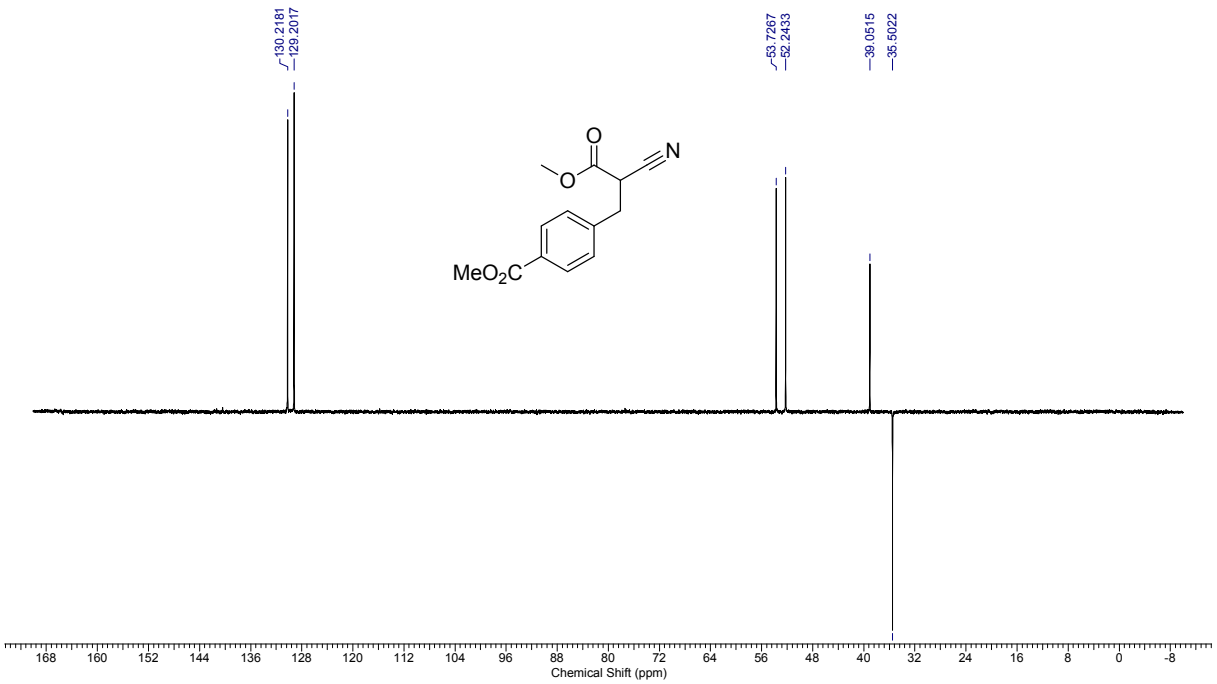

165.4114
140.6018
132.5823
129.9796
118.4242
115.5517
111.7242
77.5829
77.1600
76.7372
53.7357
38.6516
35.1814
O
O
N
NC
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


132.5785
129.9797
53.7356
38.6538
35.1814
O
O
N
NC
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

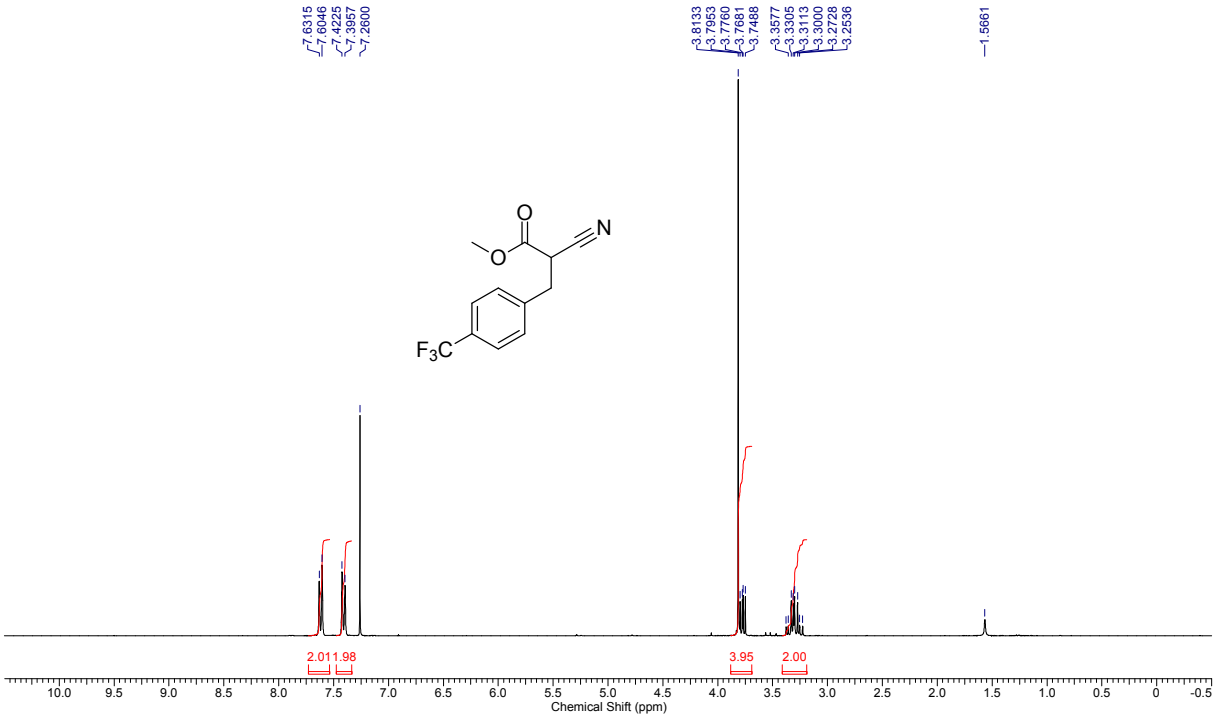
Methyl 2-cyano-3-(4-methylbenzoate)propanoate (12b)

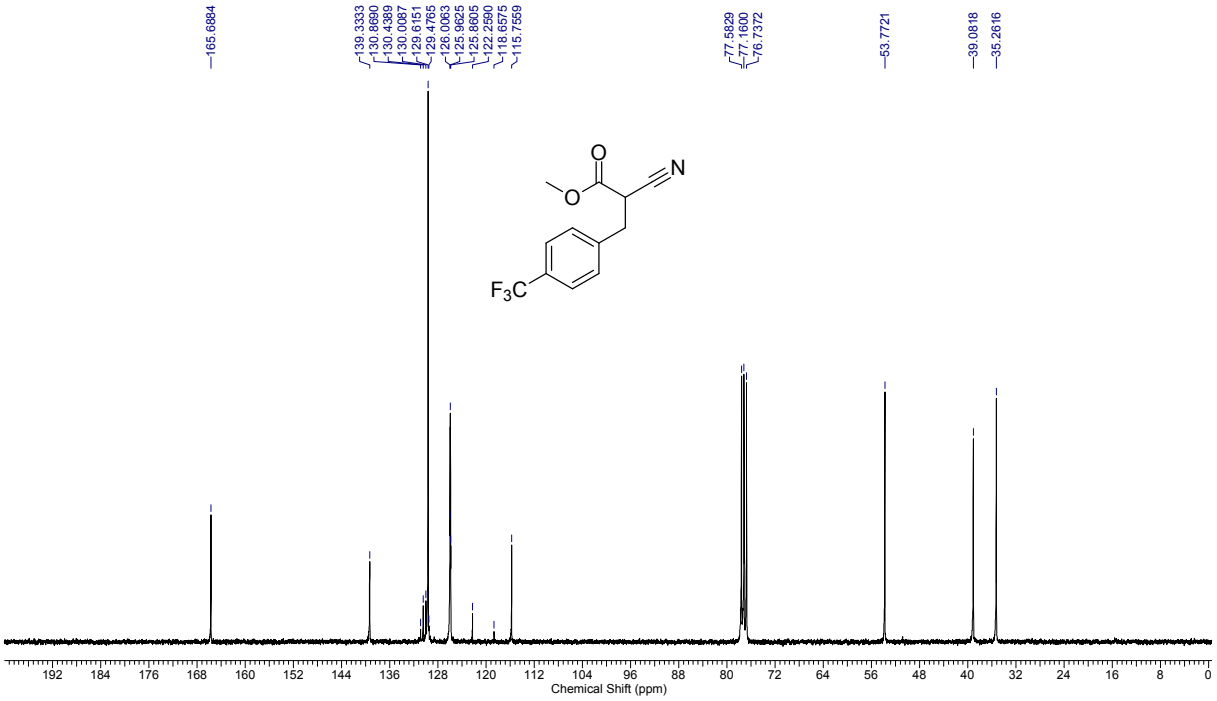


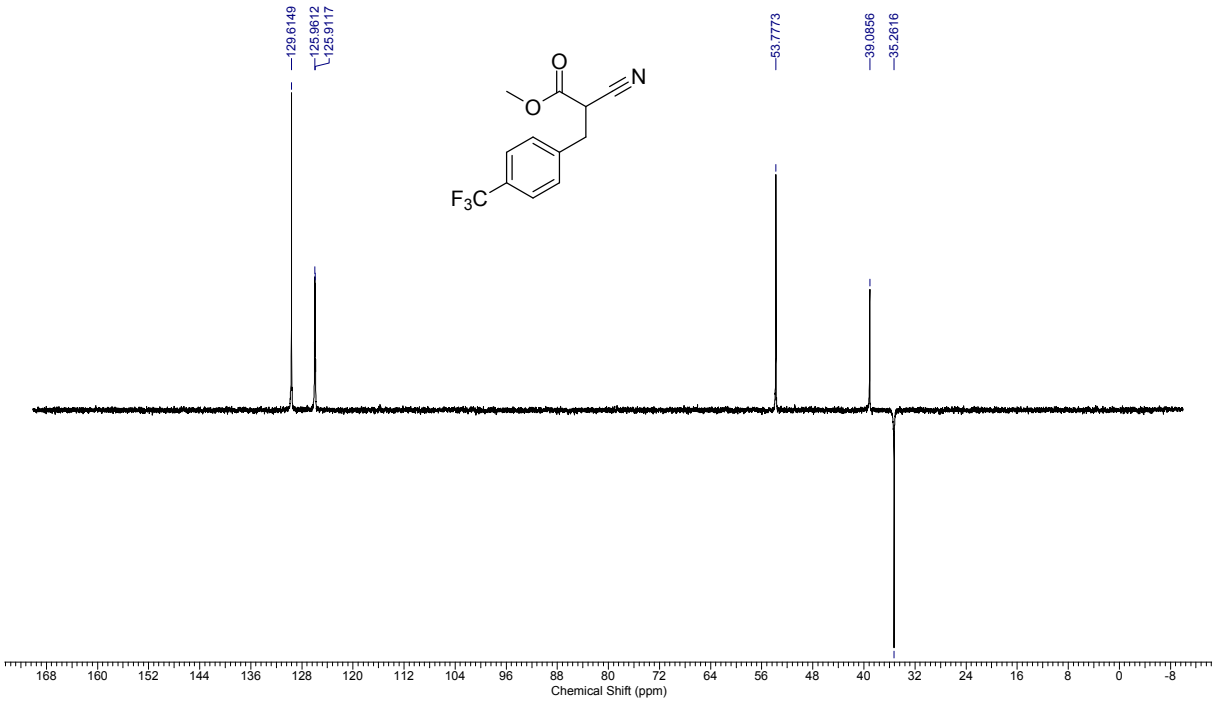




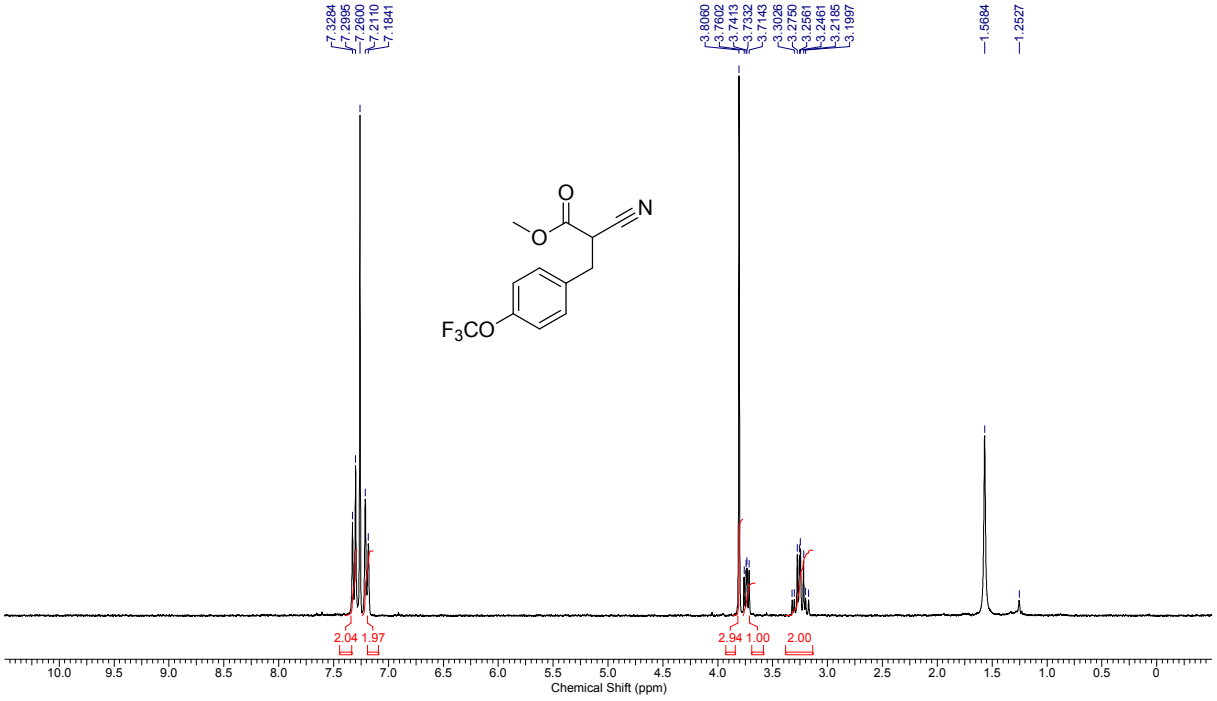
Methyl 2-cyano-3-(4-trifluoromethylphenyl)propionate [676272-24-5] (14b)

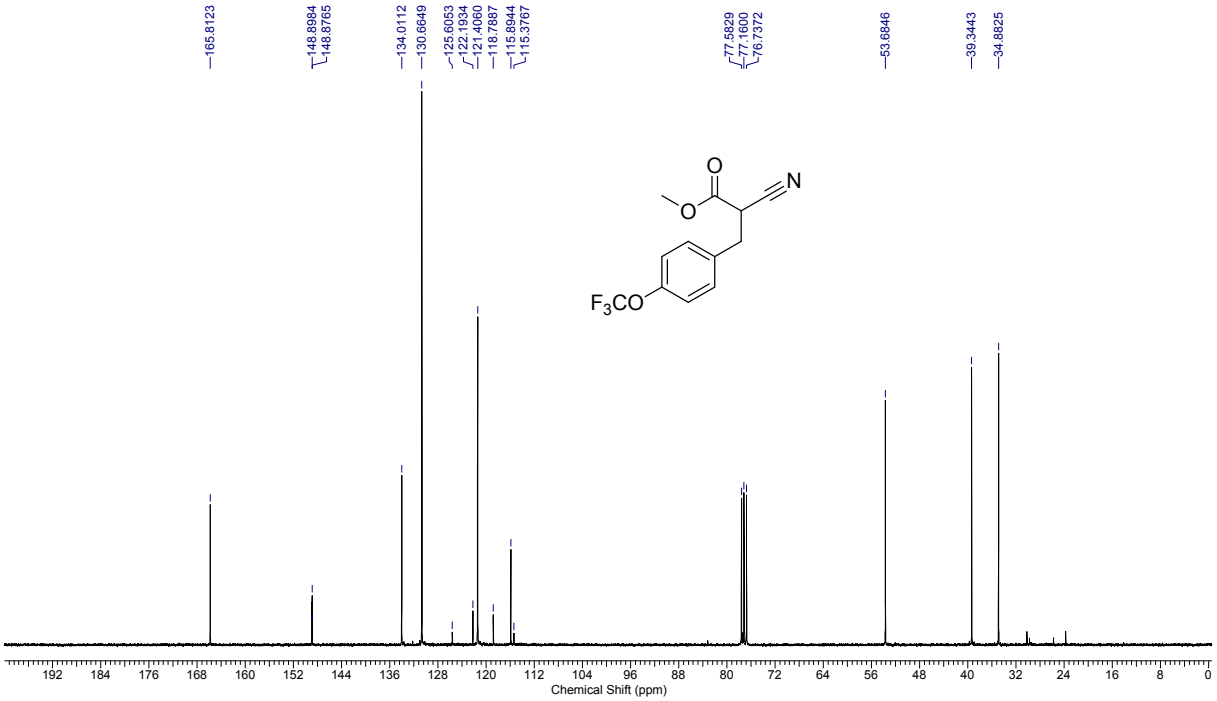


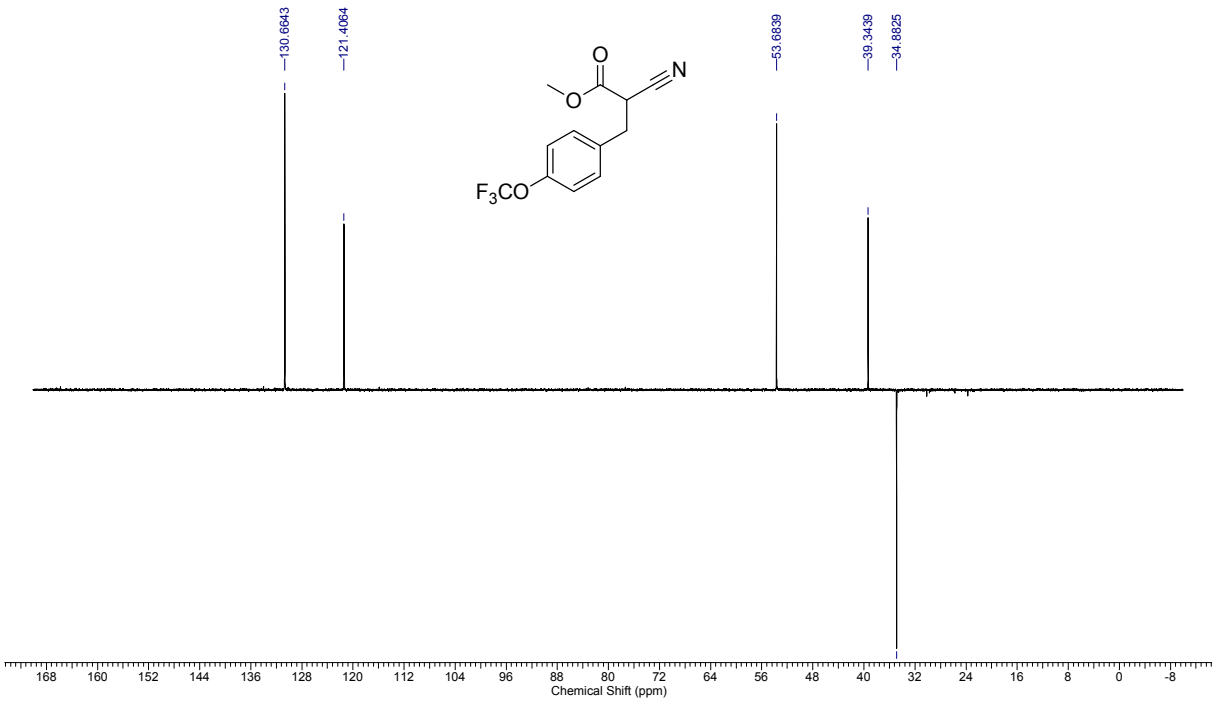

165.6884
139.3333
130.8690
130.4389
130.0087
129.6151
128.4765
126.0063
125.9625
125.8605
122.2390
118.6575
115.7559
77.5829
77.1600
76.7372
53.7721
39.0818
35.2616
O
O
N
F3C
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


129.6149
125.9612
125.9117
53.7773
39.0856
35.2616
O
O
N
F3C
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

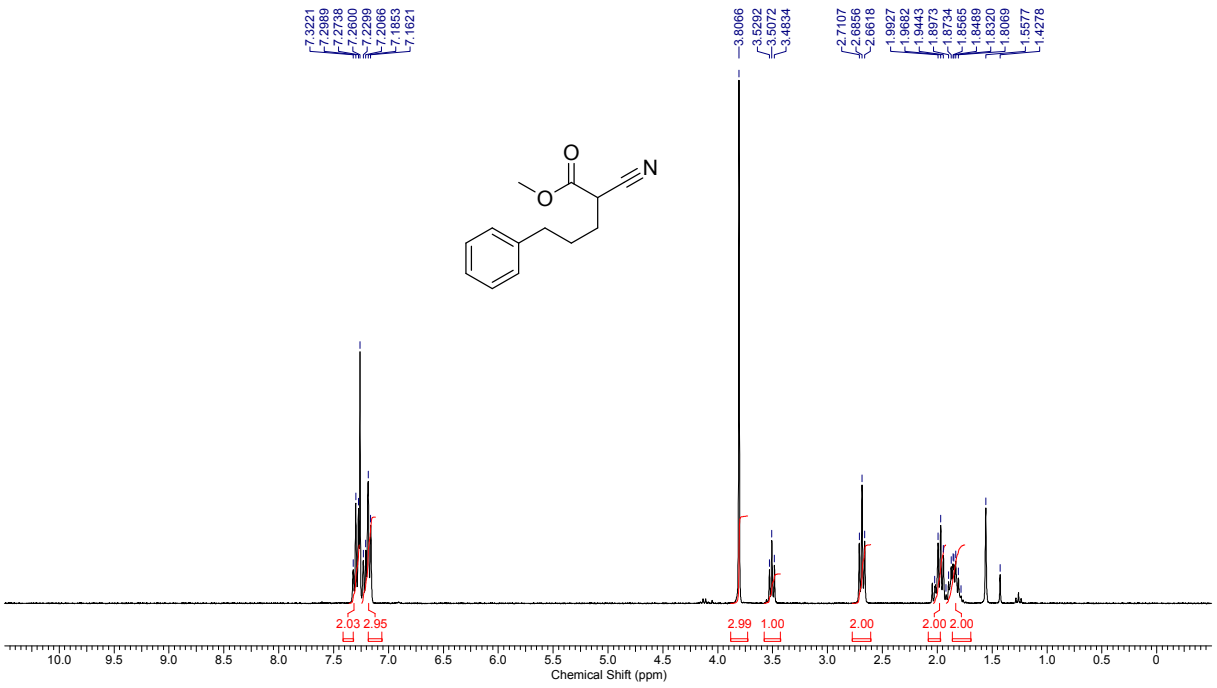
Methyl 2-cyano-3-(4-trifluoromethoxyphenyl)propionate (16b)

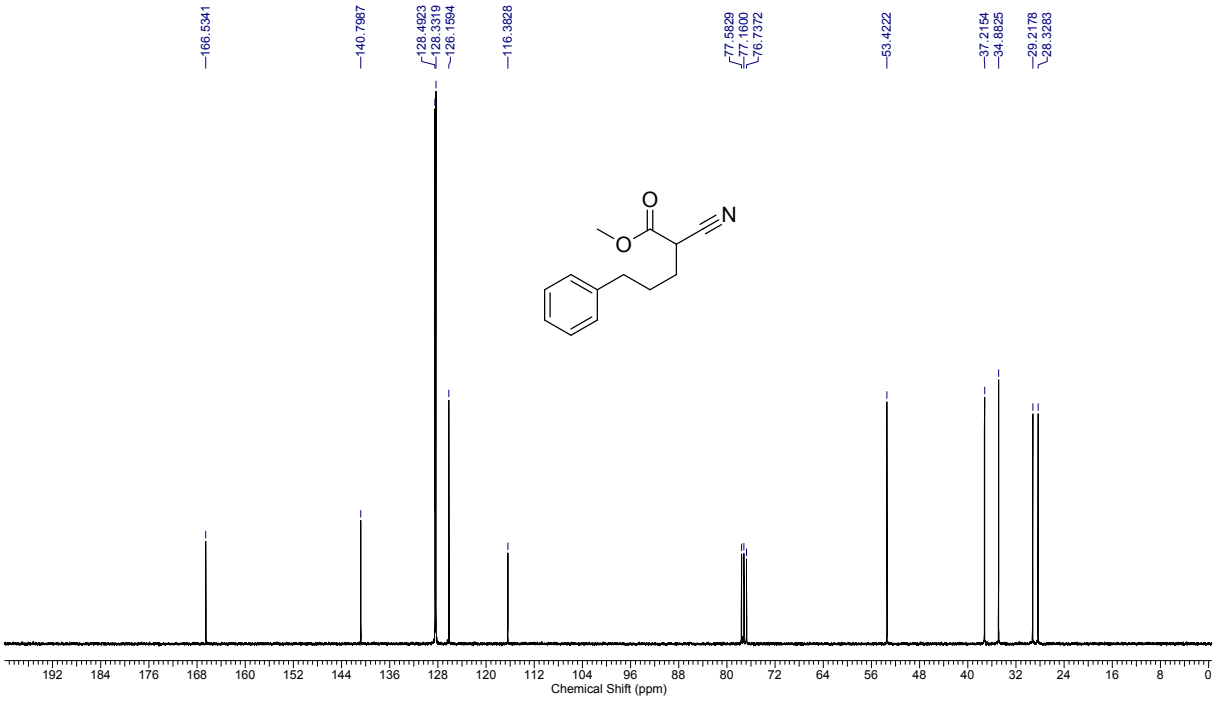


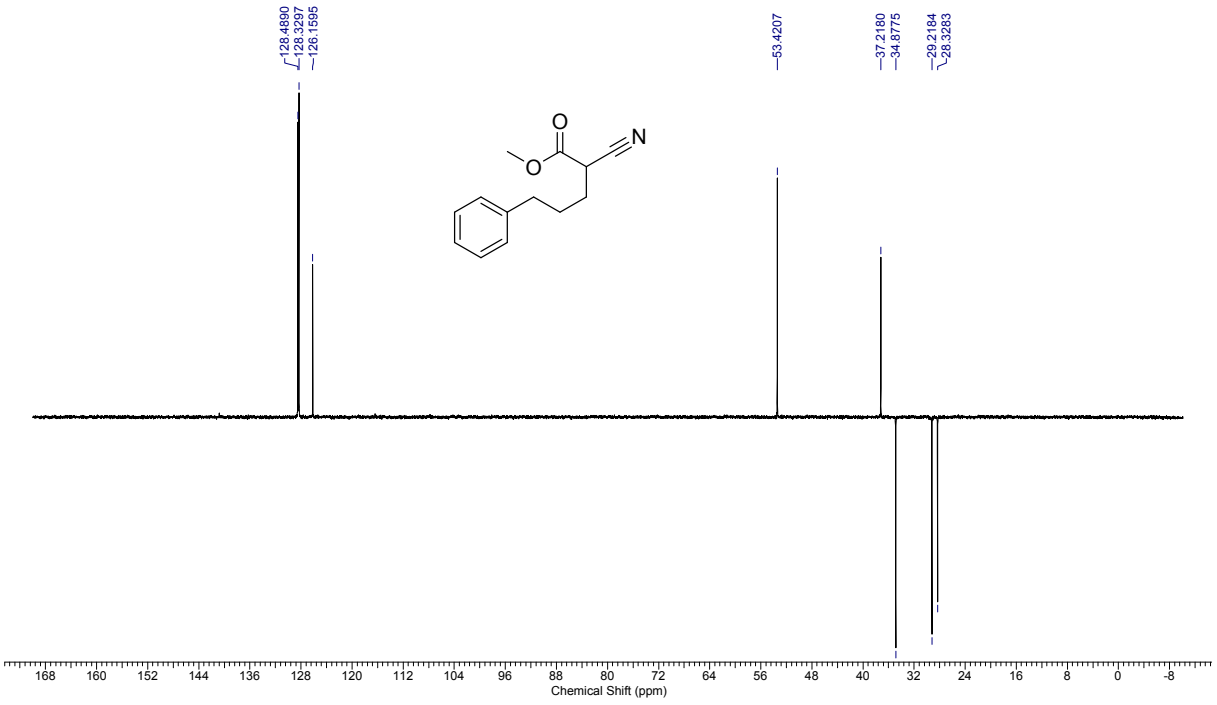




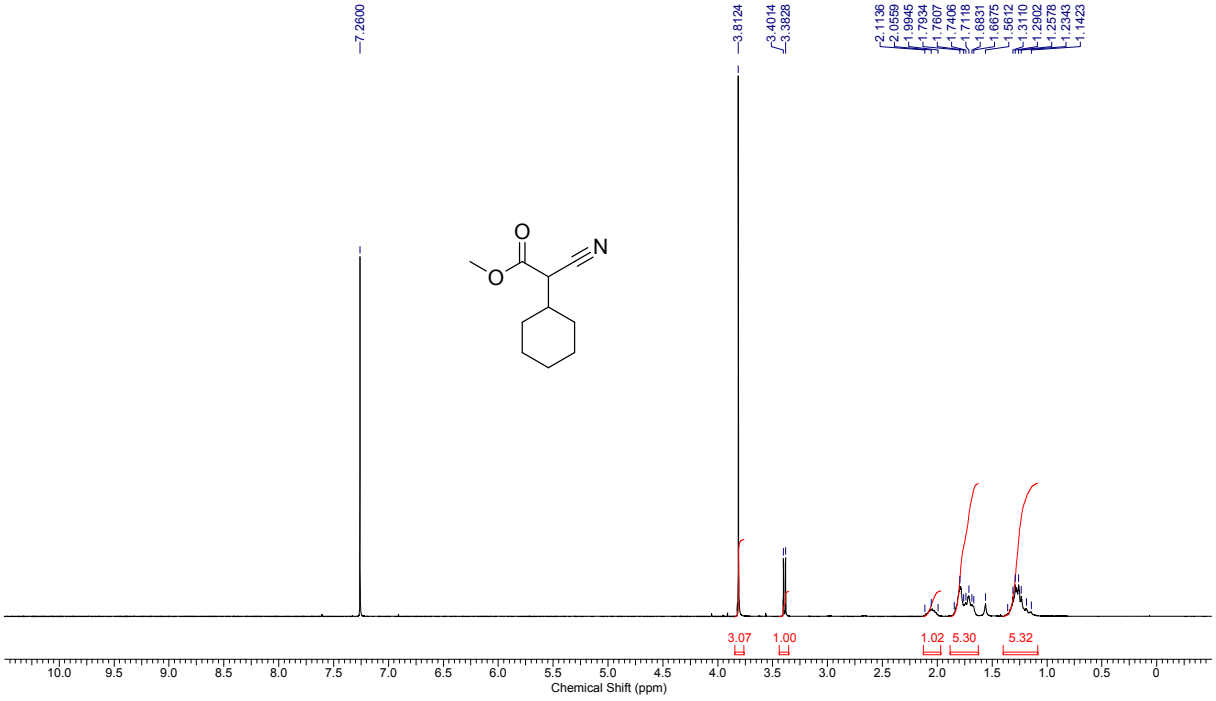
Methyl 2-cyano-5-phenylpentanoate [1025483-41-3] (18b)

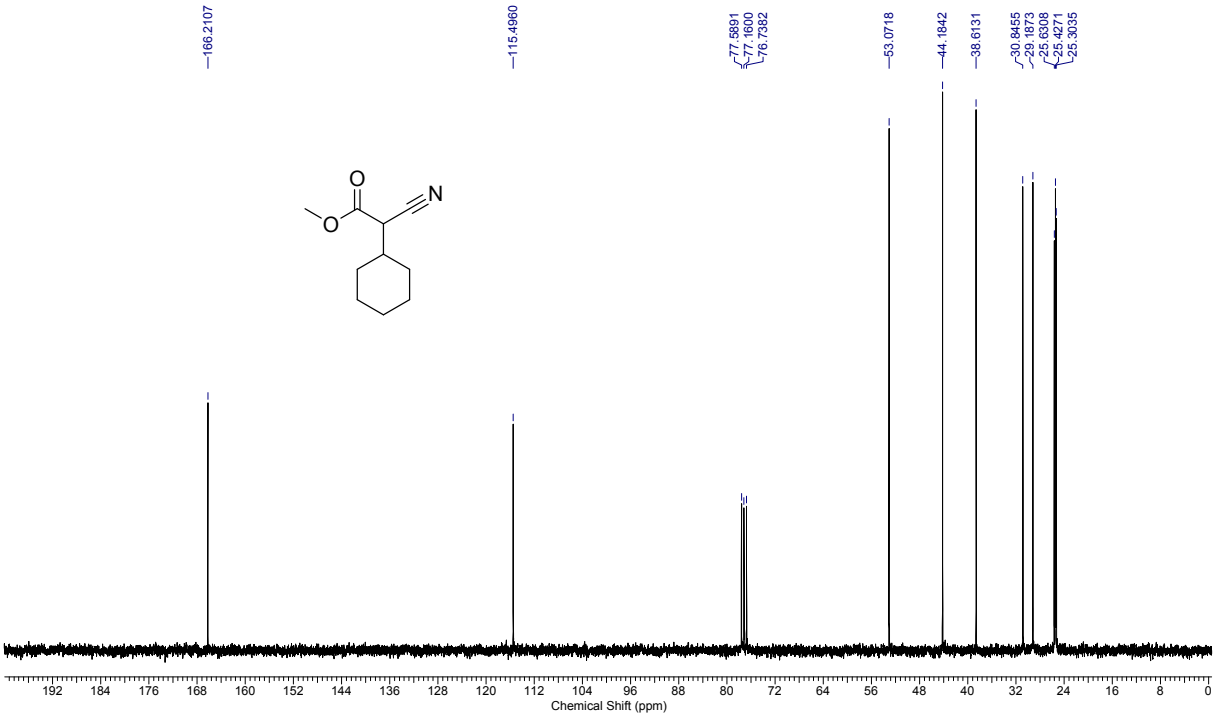


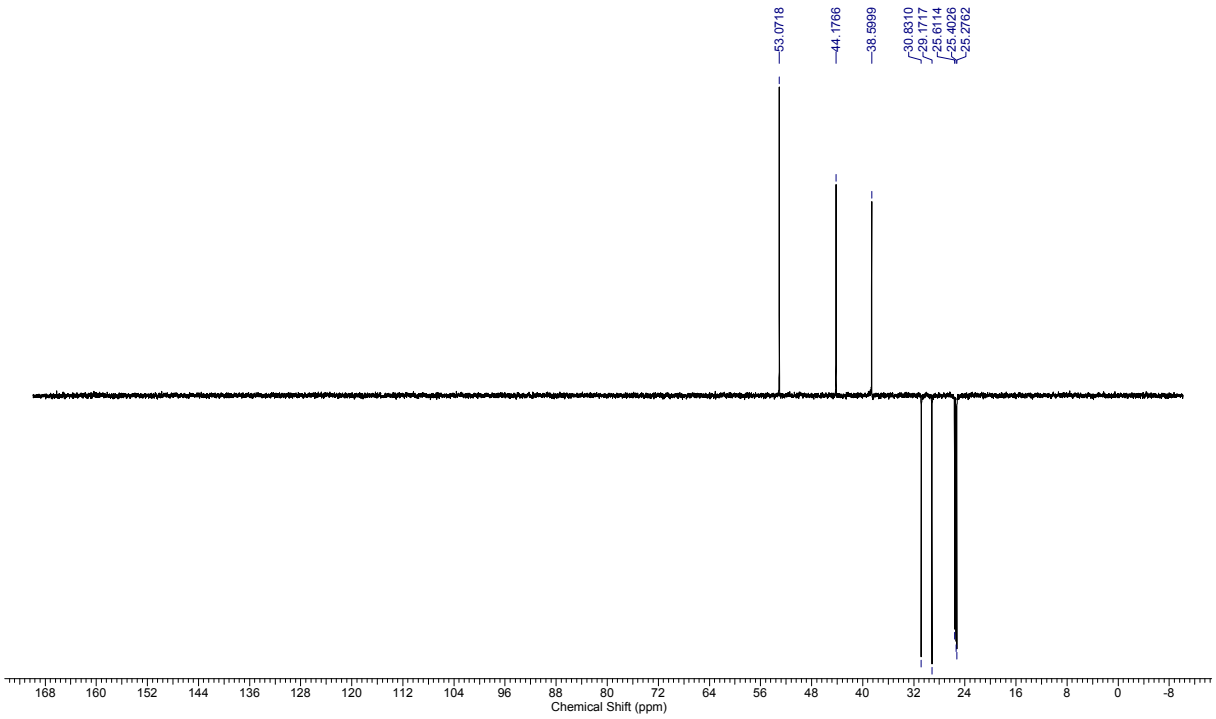

166.5341
140.7987
128.4923
128.3319
126.1594
116.3828
77.5829
77.1600
76.7372
53.4222
37.2154
34.8825
29.2178
28.3283
O
O
N
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


128.4890
128.3297
126.1595
53.4207
37.2180
34.8775
29.2184
28.3283
O
O
N
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

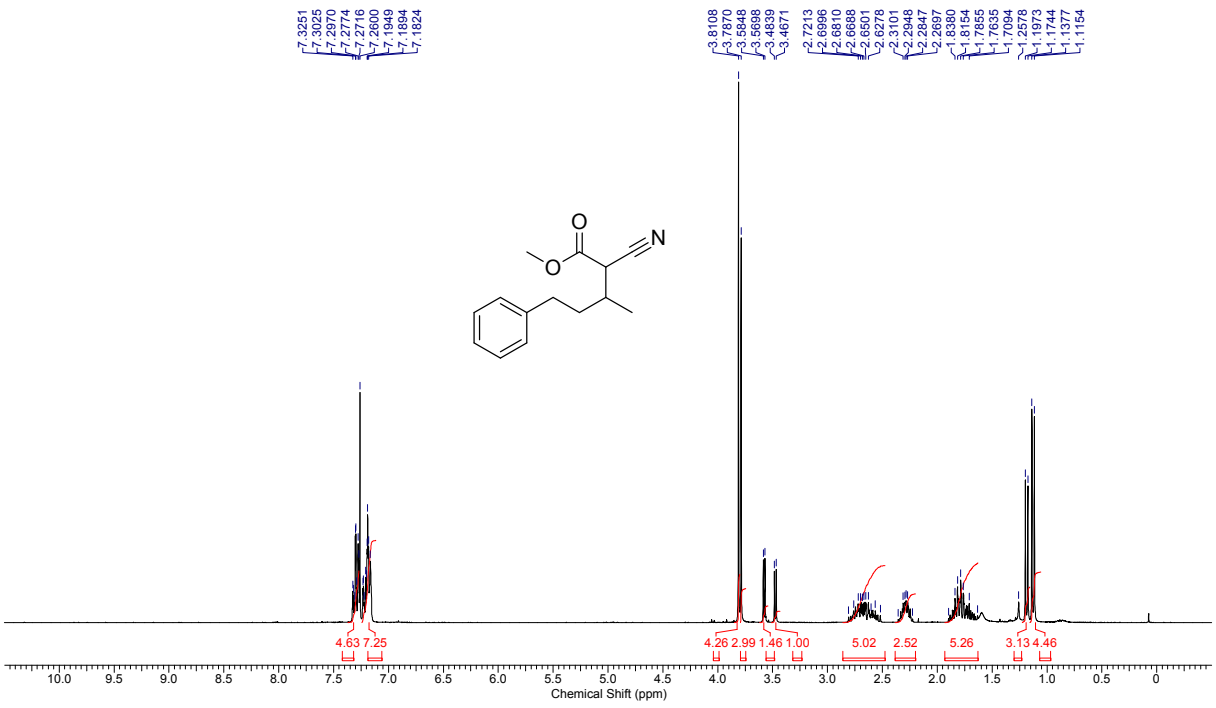
Cyano(cyclohexyl)acetic acid methyl ester [80627-89-0] (20b)

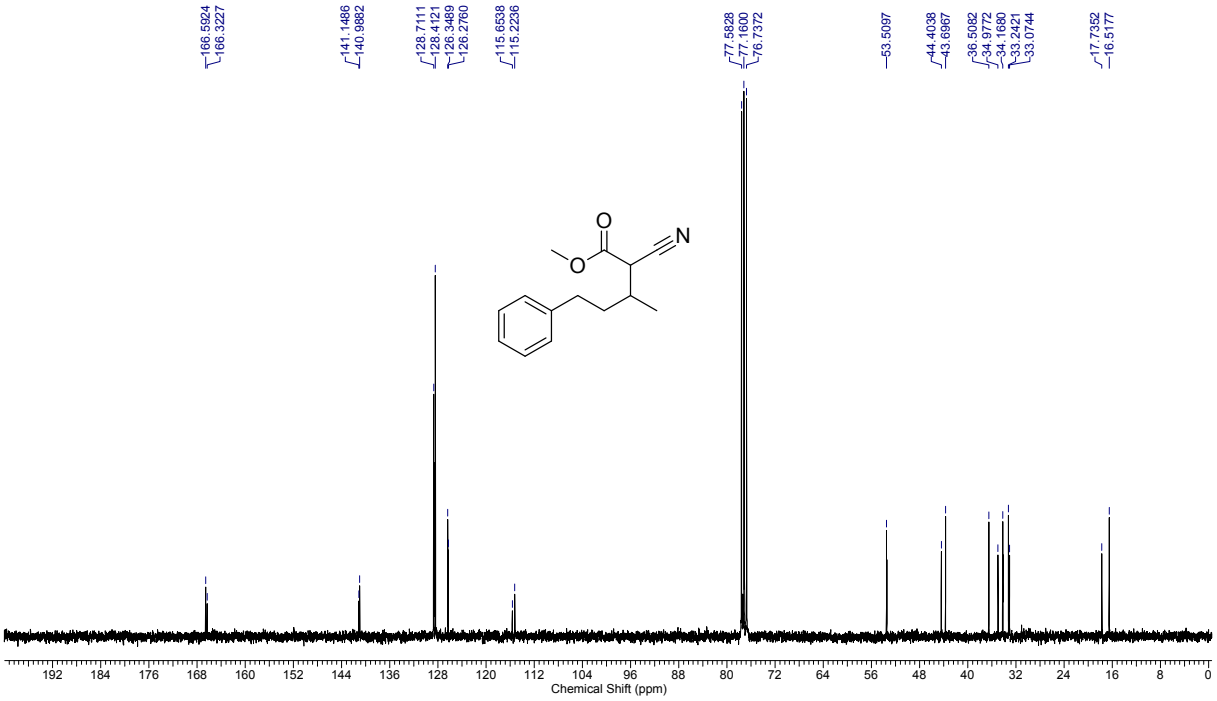


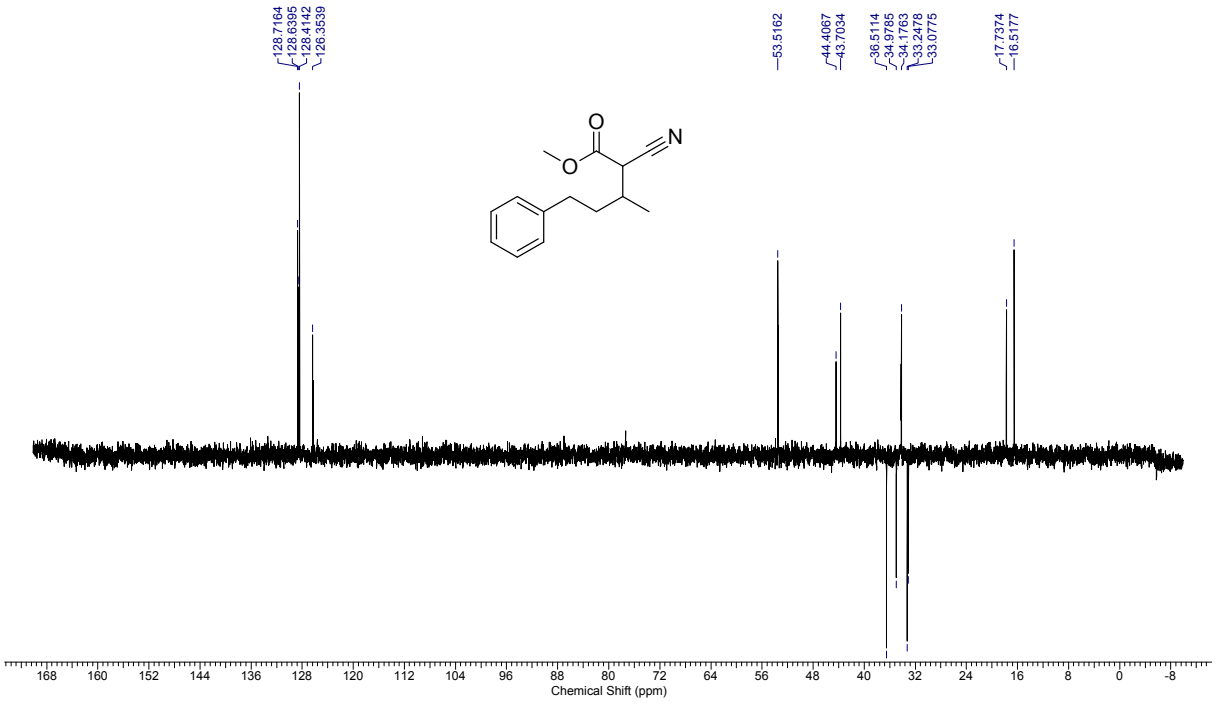




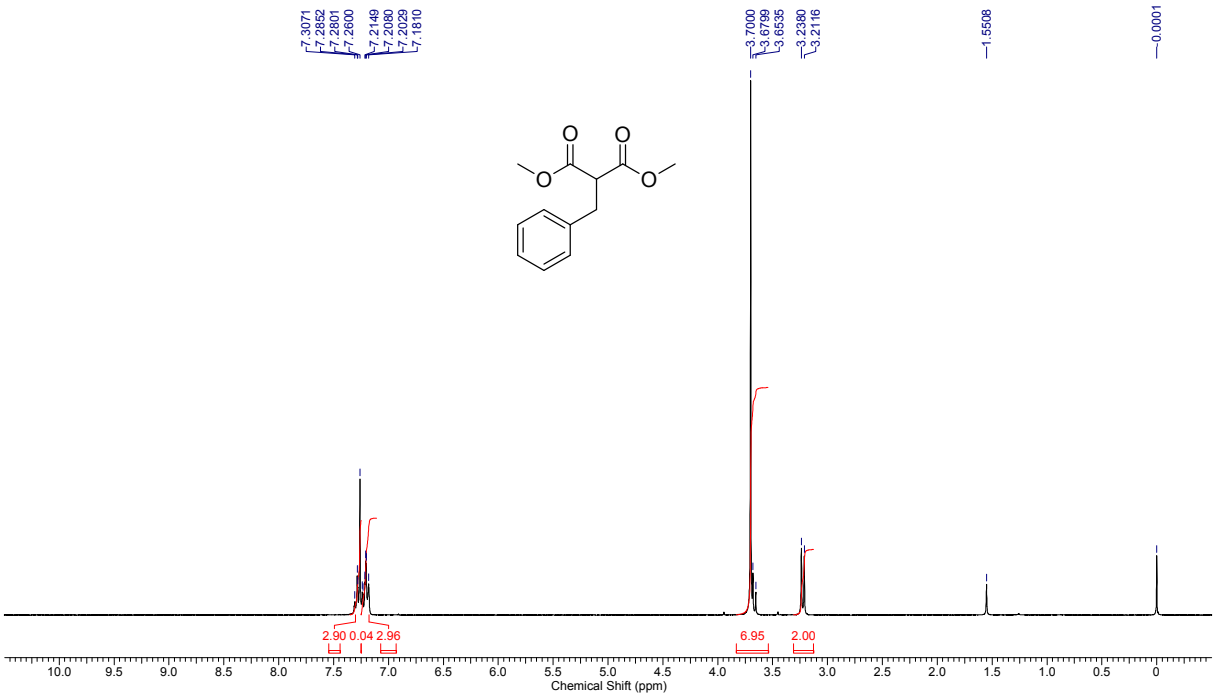
Methyl 2-cyano-3-methyl-5-phenylpentanoate [1629235-94-4] and [1629235-95-5] (22b)

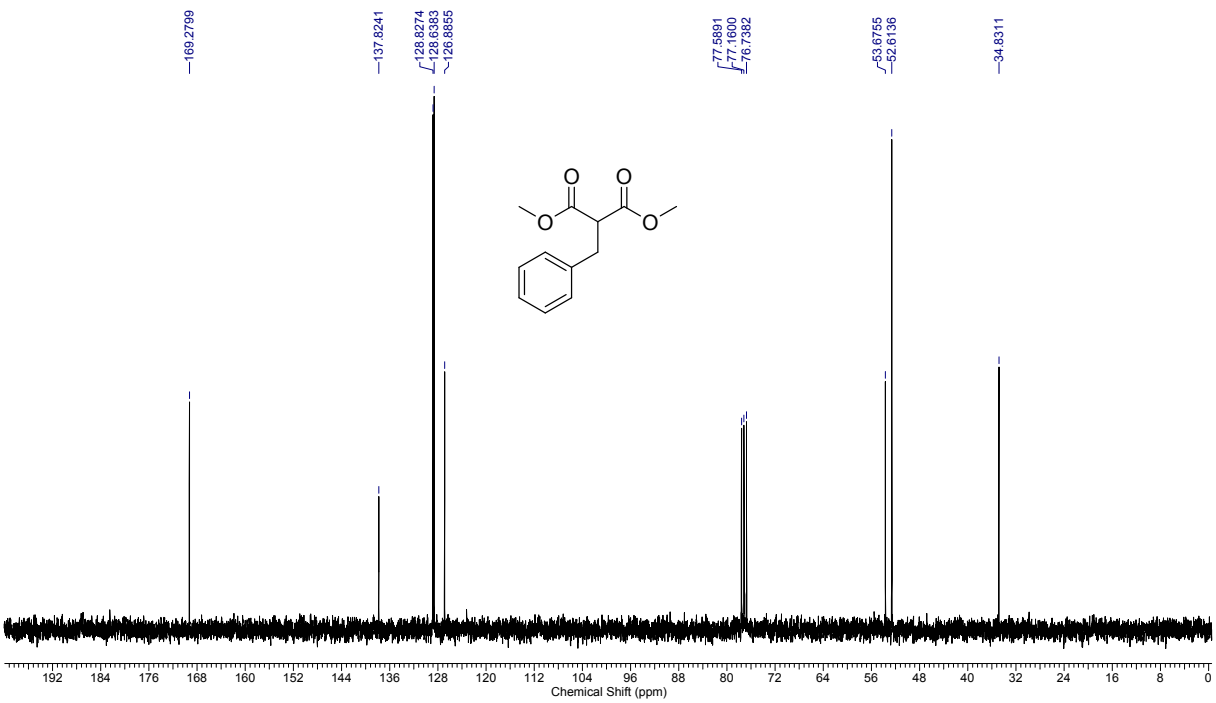



166.5924
166.3227
141.1486
140.9882
128.7111
128.4121
126.3489
126.2760
115.6538
115.2236
77.5828
77.1600
76.7372
53.5097
44.4038
43.6967
36.5082
34.9772
34.1680
33.2421
33.0744
17.7352
16.5177
O
O
N
Chemical Shift (ppm)

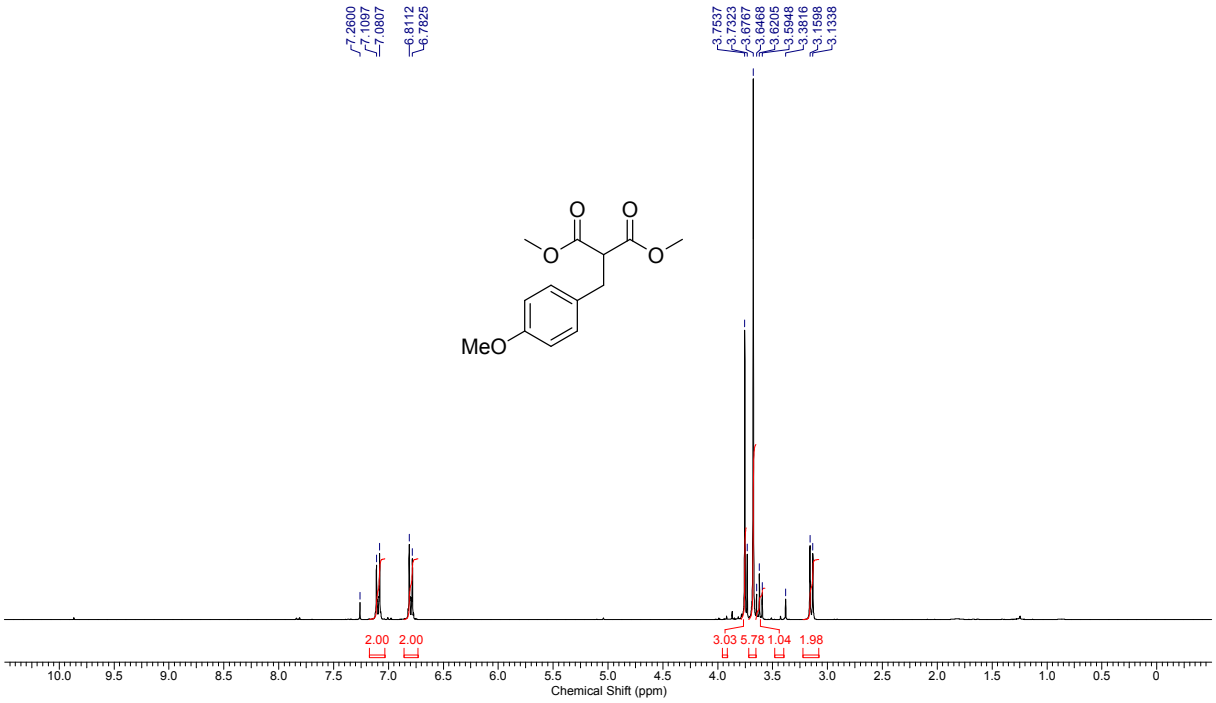

128.7164
128.6395
128.4142
126.3539
53.5162
44.4067
43.7034
36.5114
34.9785
34.1763
33.2478
33.0775
17.7374
16.5177
O
O
N
Chemical Shift (ppm)

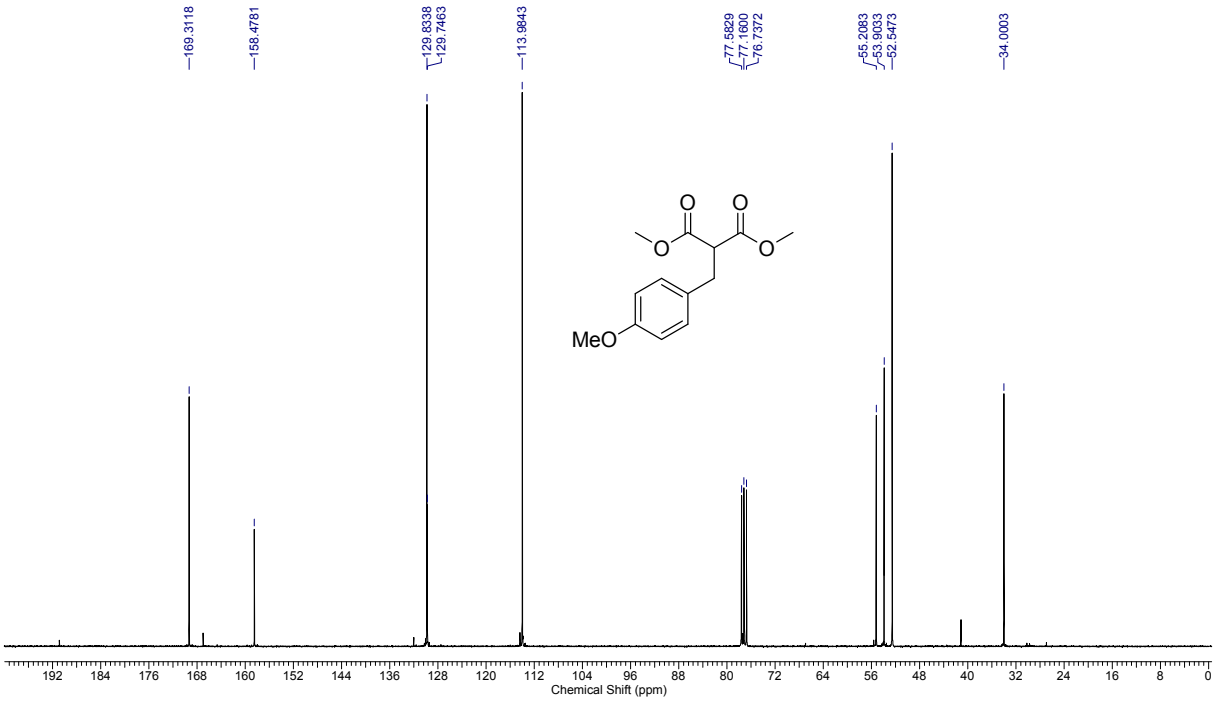
Dimethyl benzylmalonate [49769-78-0] (28b)

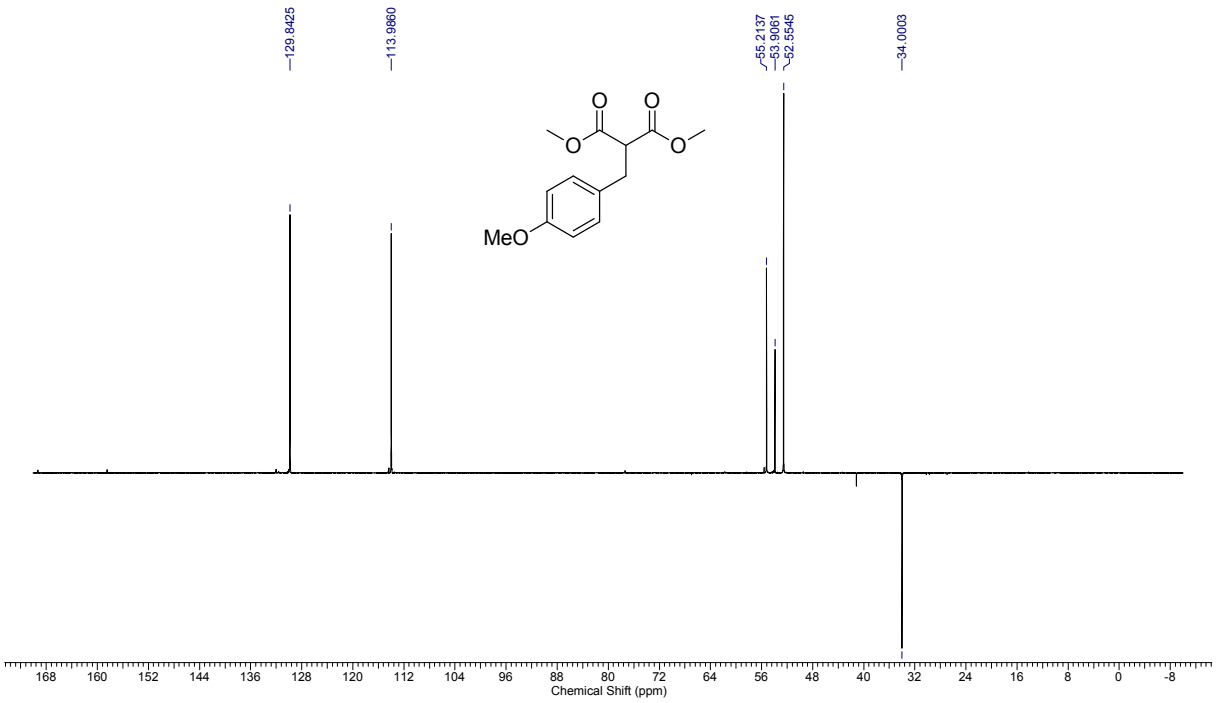




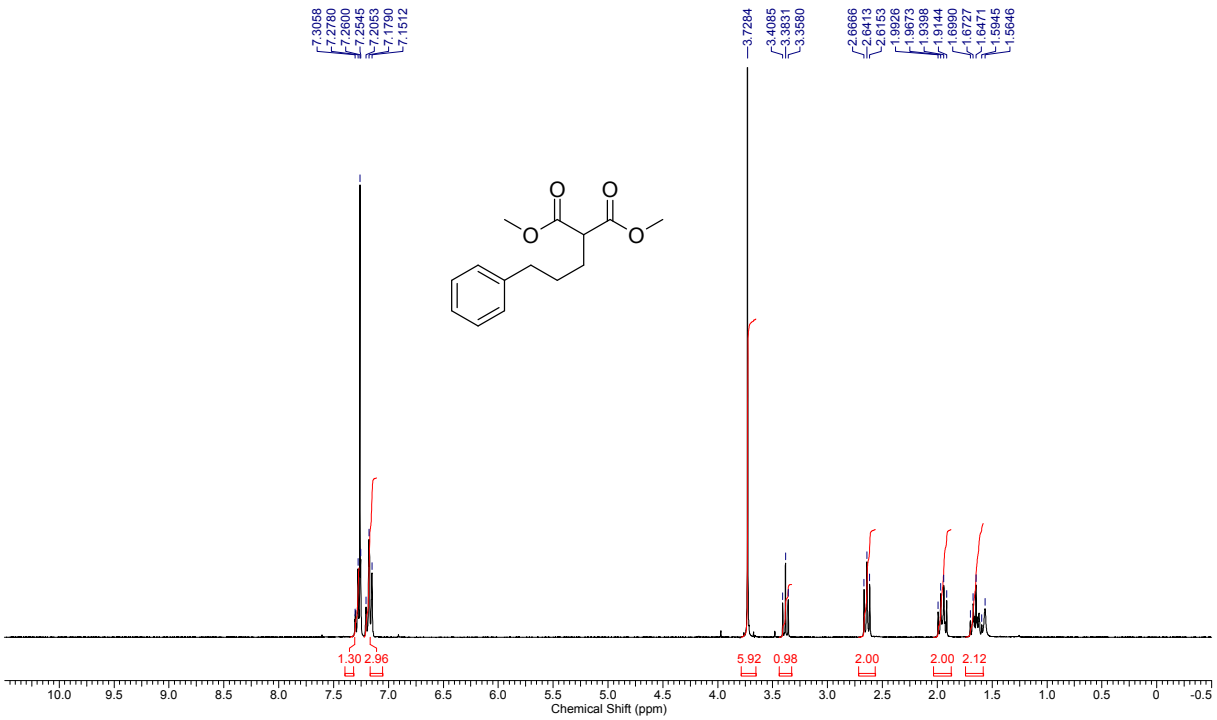
Dimethyl 2-(4'-methoxybenzyl)malonate [15378-09-3] (29b)

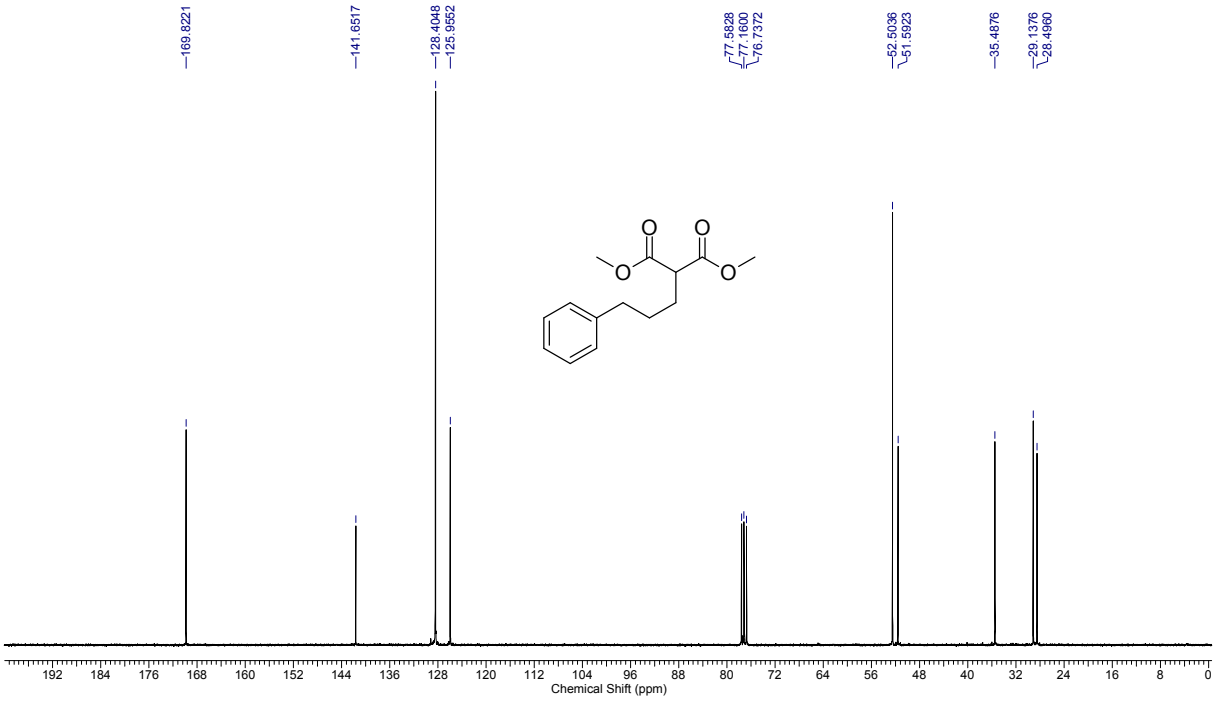






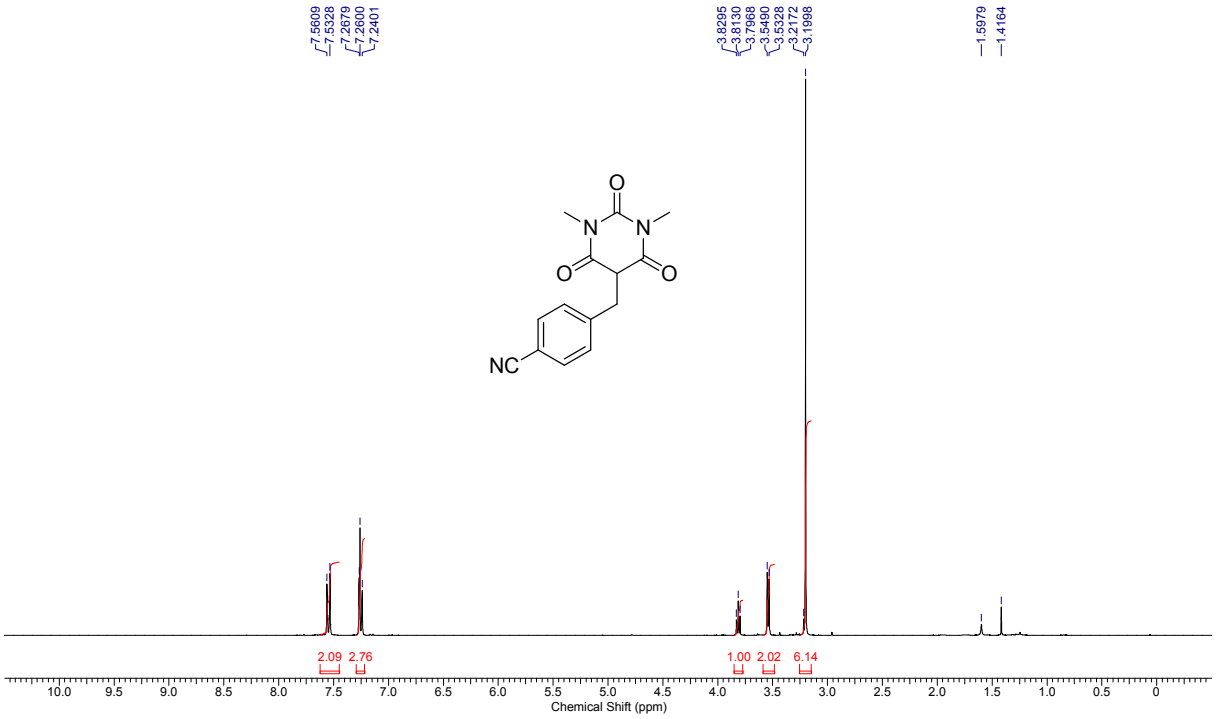
2-(3-phenylpropyl)-malonic acid dimethyl ester [3708-34-7] (31b)

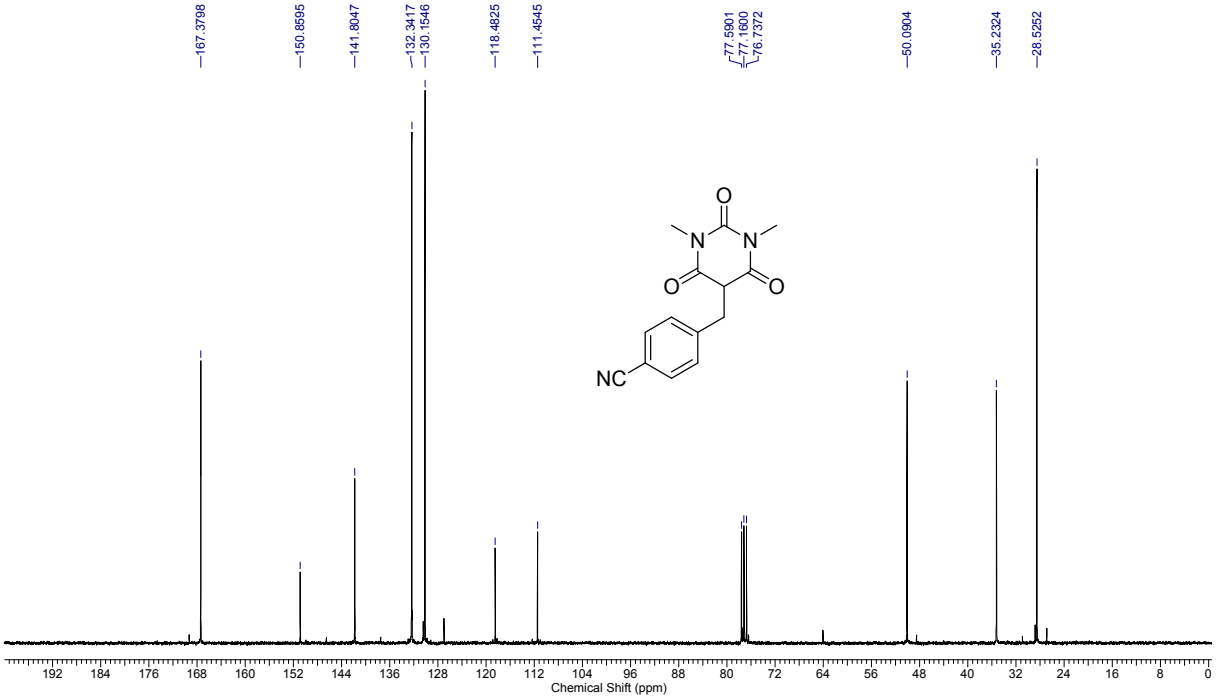


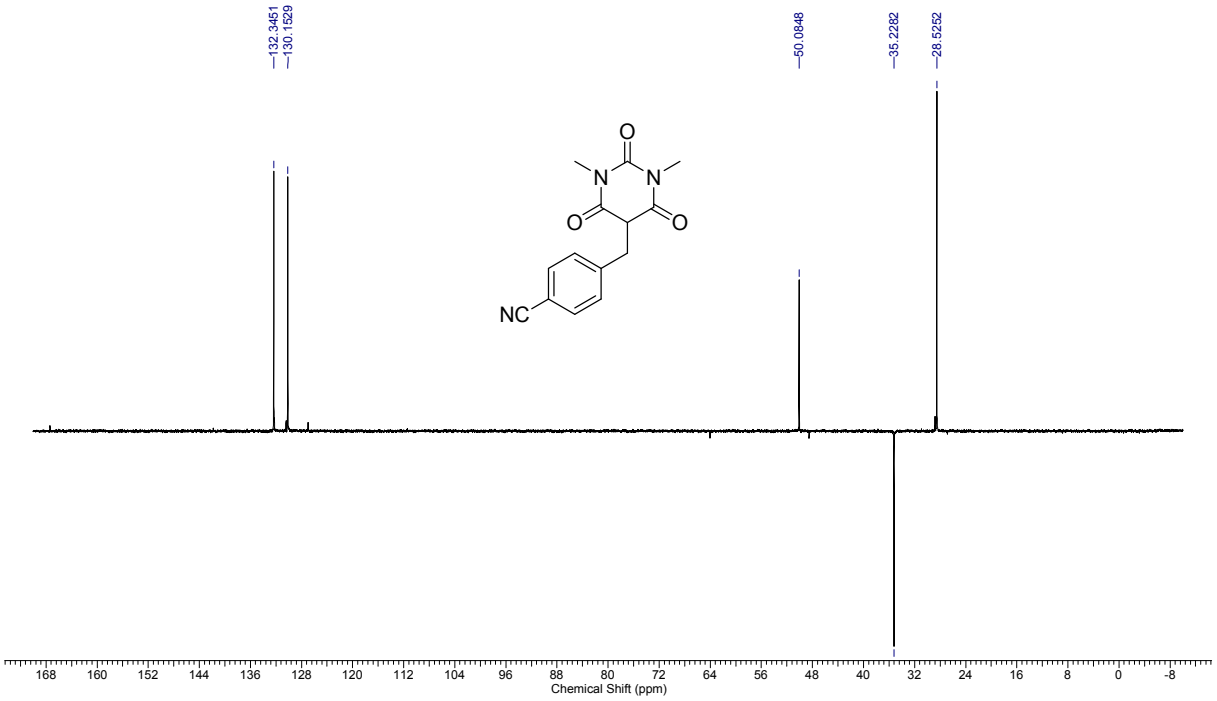

169.8221
141.6517
128.4048
125.9552
77.5828
77.1600
76.7372
52.5036
51.5923
35.4876
29.1376
28.4960
O
O
O
O
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


128.3985
125.9535
52.5005
51.5885
35.4847
29.1333
28.4960
O
O
O
O
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

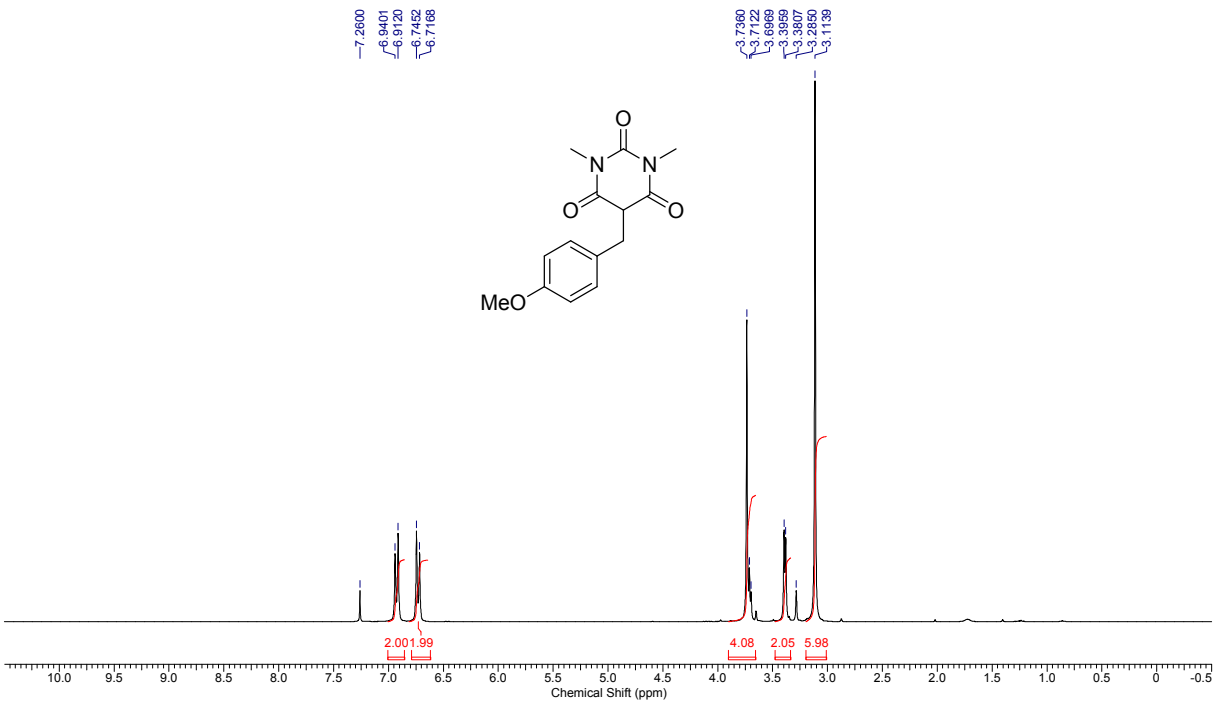
5-(4-Cyanobenzyl)-1,3-dimethyl-hexahydropyrimidin-2,4,6-trion [81762-45-0] (32b)

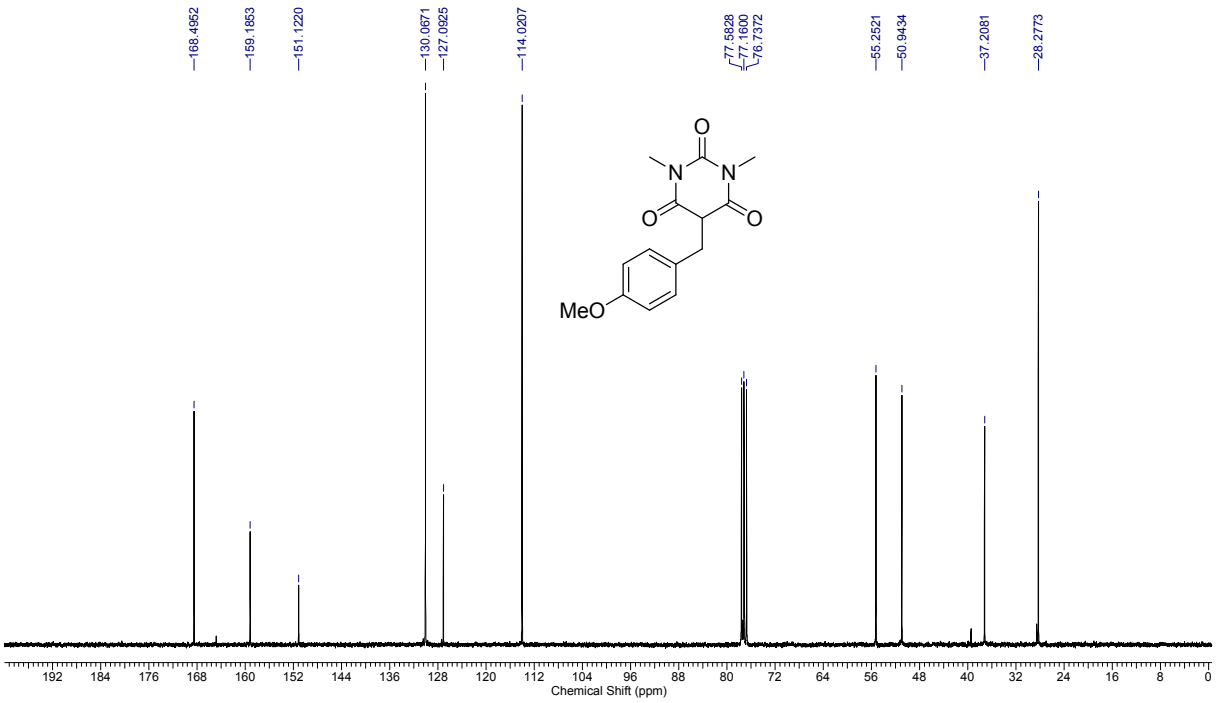


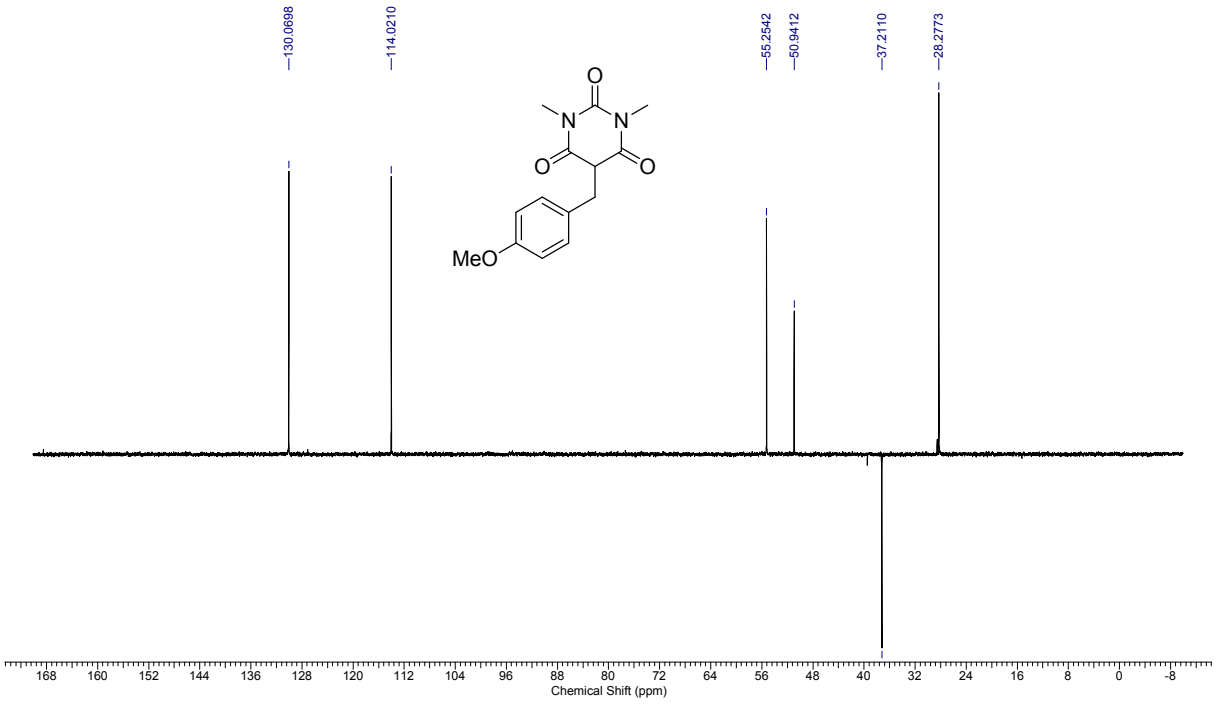




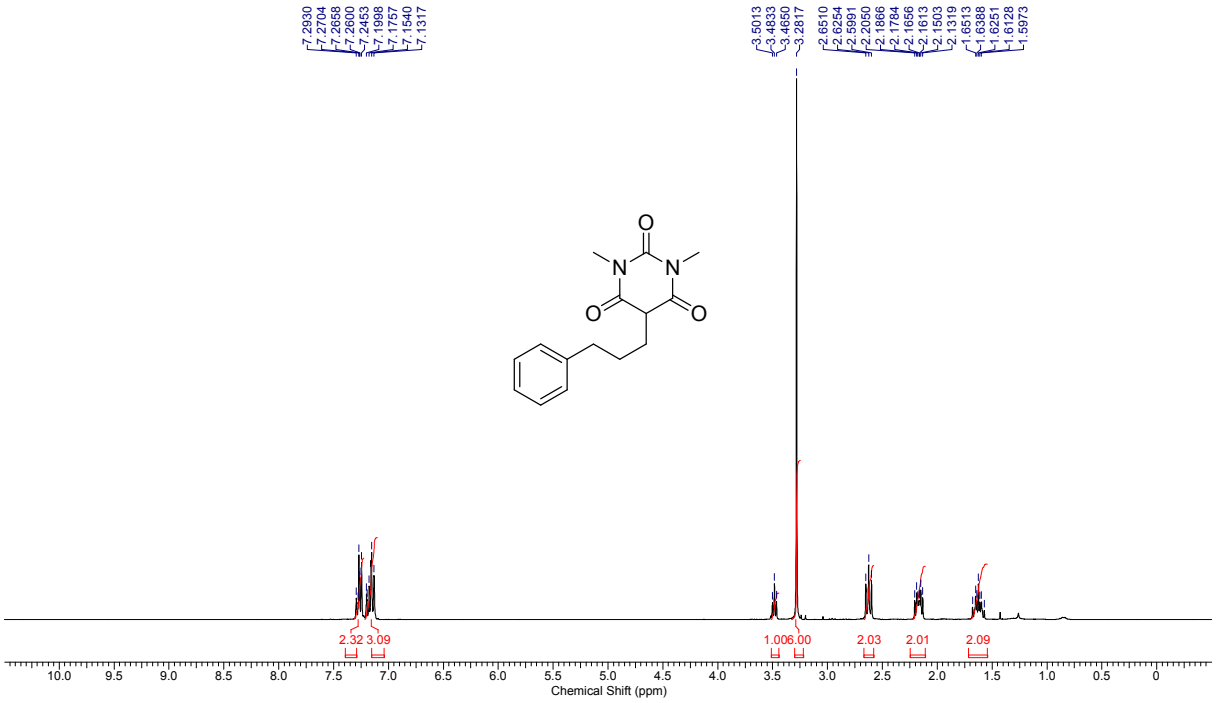
5-(4-Methoxybenzyl)-1,3-dimethylpyrimidine-2,4,6-trione [114656-99-4] (33b)

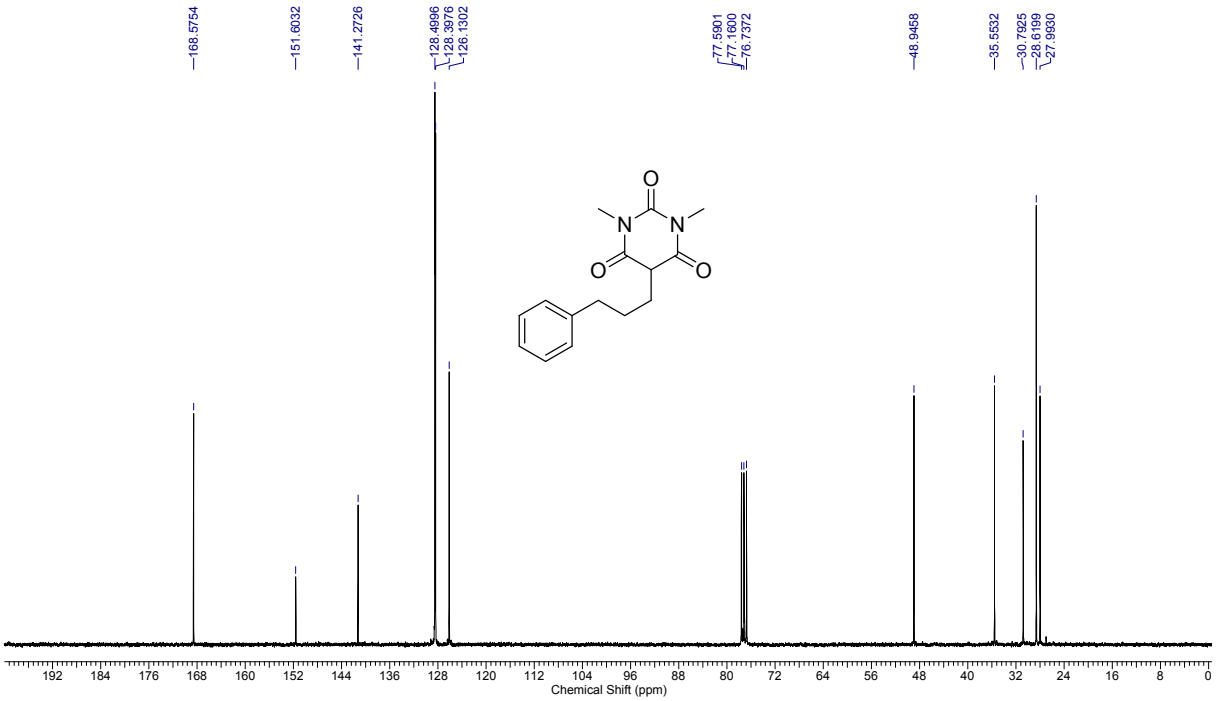


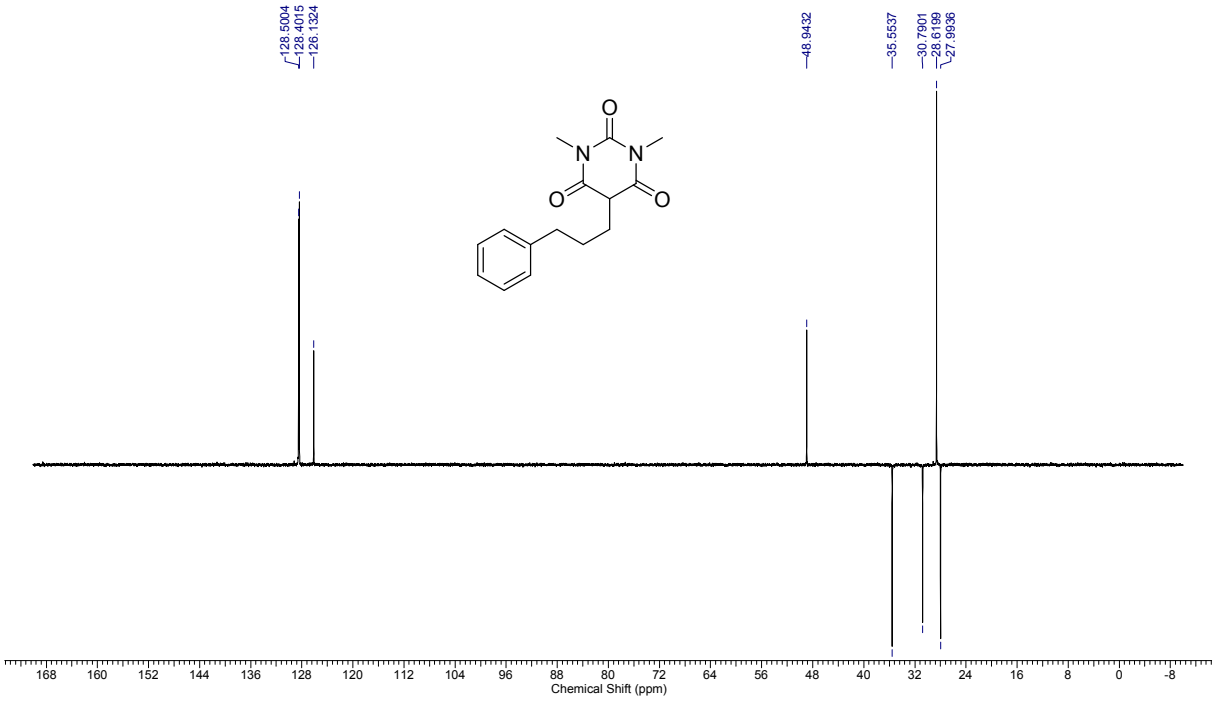

168.4952
159.1853
151.1220
130.0671
127.0925
114.0207
77.5828
77.1600
76.7372
55.2521
50.9434
37.2081
28.2773
O
N
N
O
O
MeO
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


130.0698
114.0210
55.2542
50.9412
37.2110
28.2773
O
N
N
O
O
MeO
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

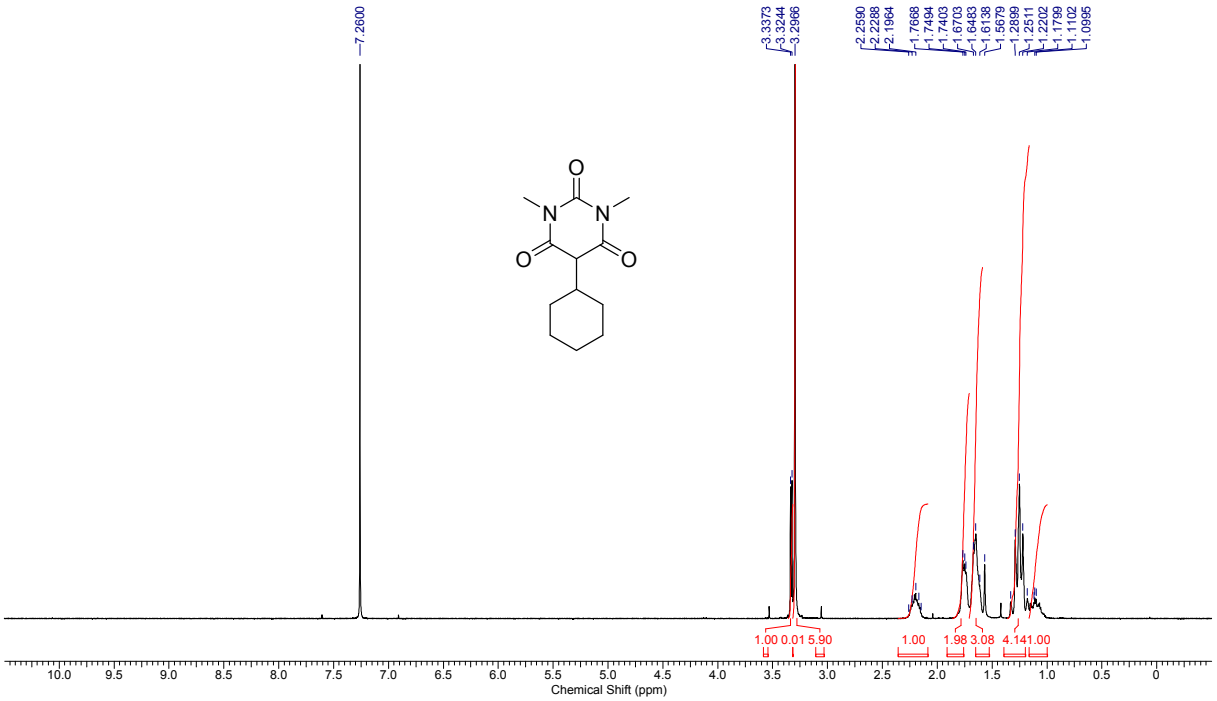
1,3-dimethyl-5-(3-phenylpropyl)pyrimidine-2,4,6-trione [82657-34-9] (34b)

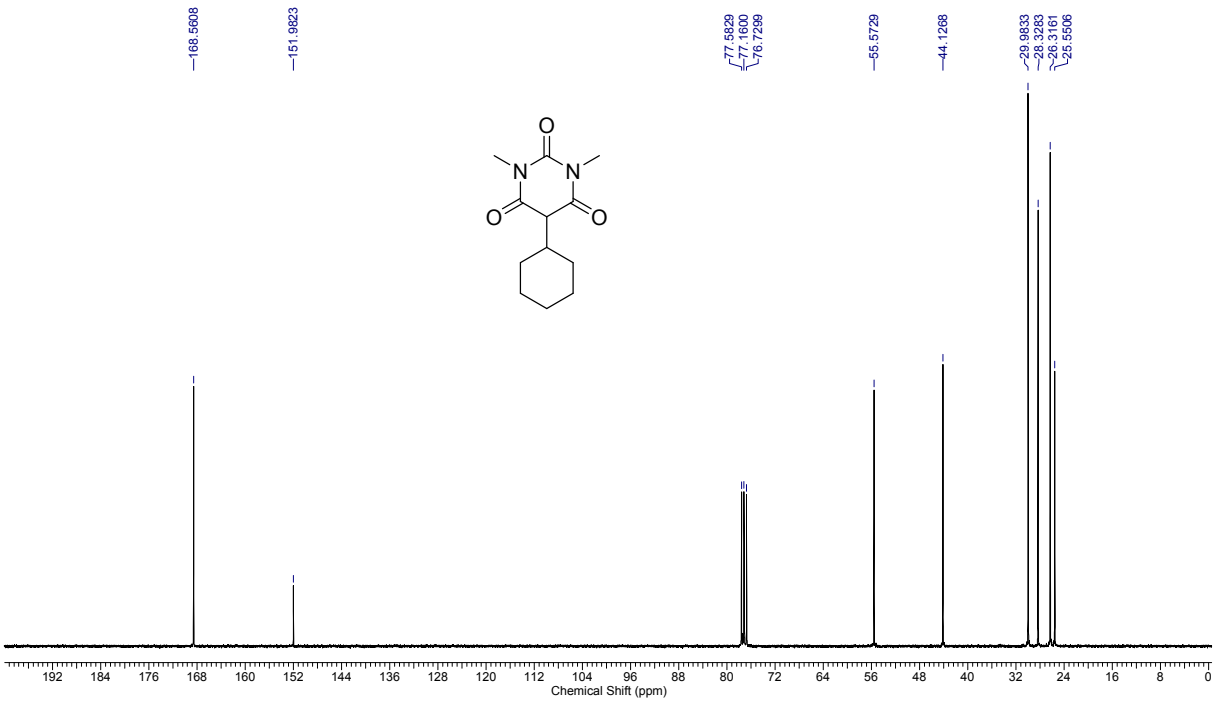






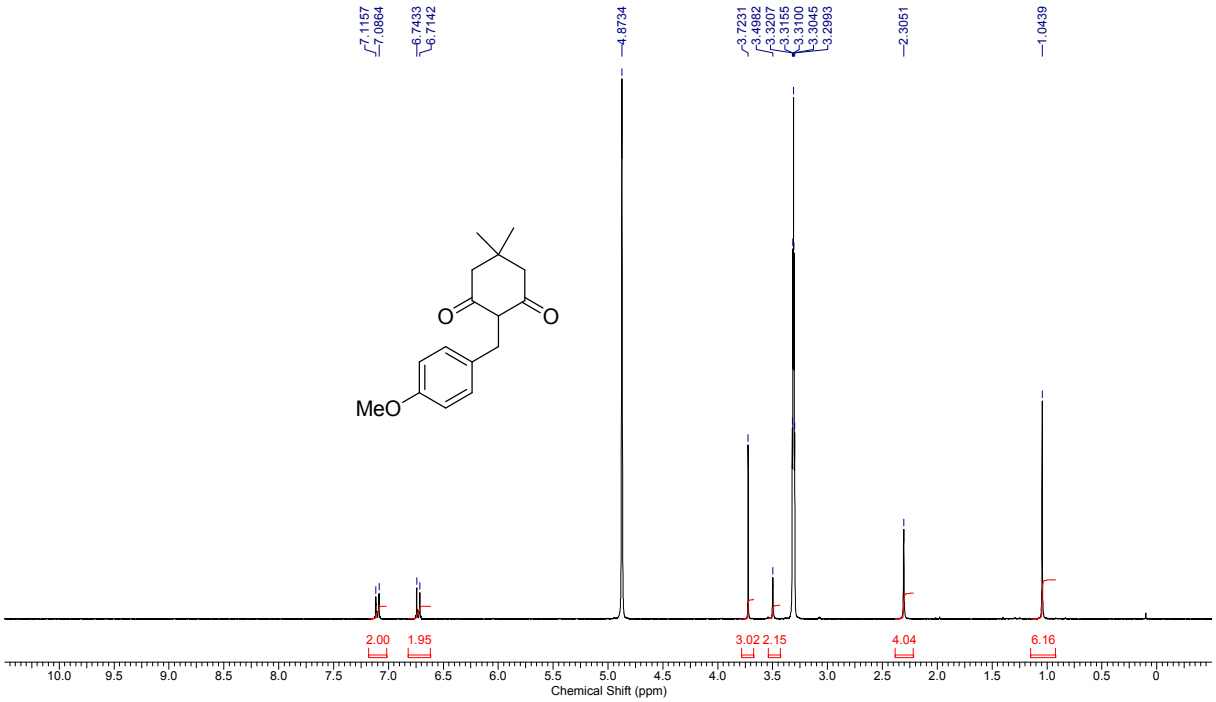
5-cyclohexyl-1,3-dimethylpyrimidine-2,4,6-trione [7391-65-3] (35b)

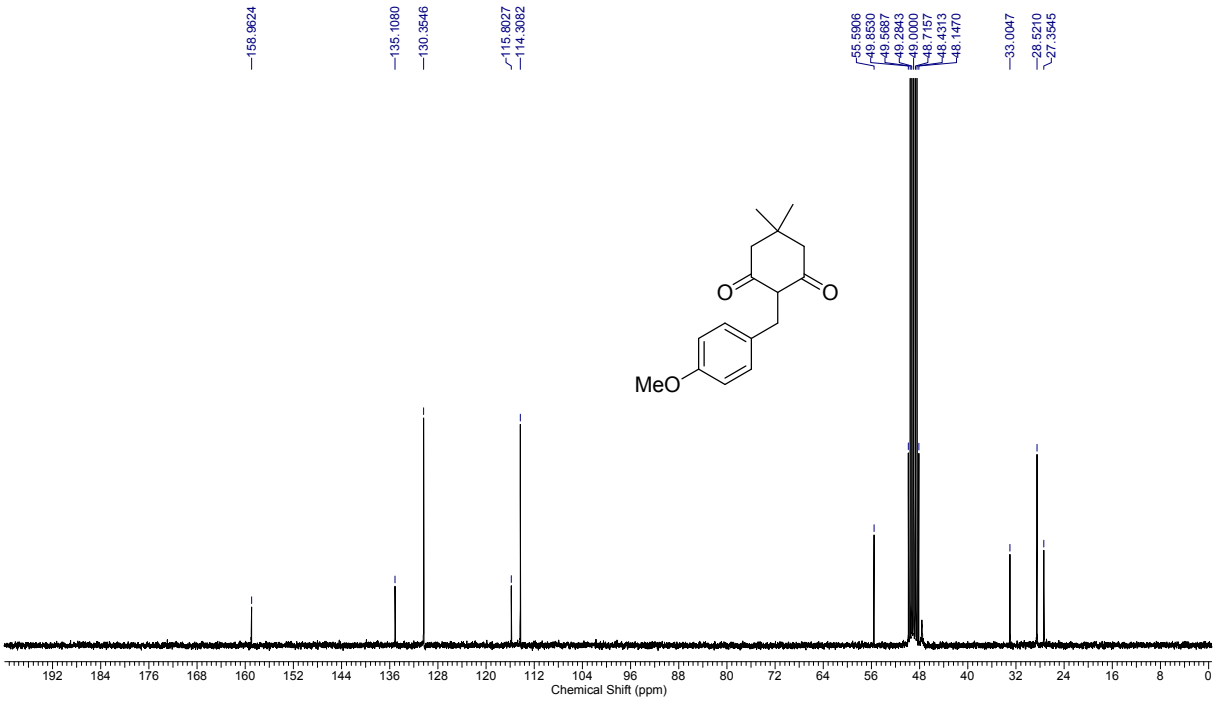


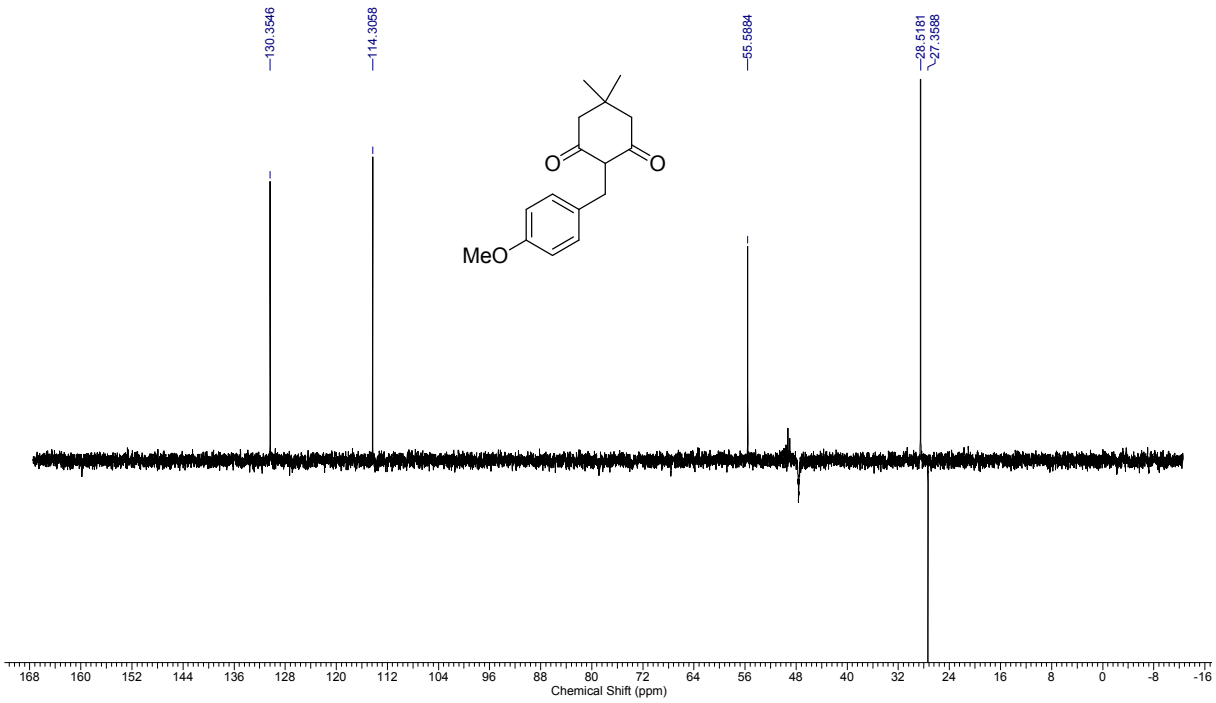

168.5608
151.9823
77.5829
77.1600
76.7299
55.5729
44.1268
29.9833
28.3283
26.3161
25.5506
O
N
N
O
O
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


55.5729
44.1283
29.9805
28.3323
26.3159
25.5522
O
N
N
O
O
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

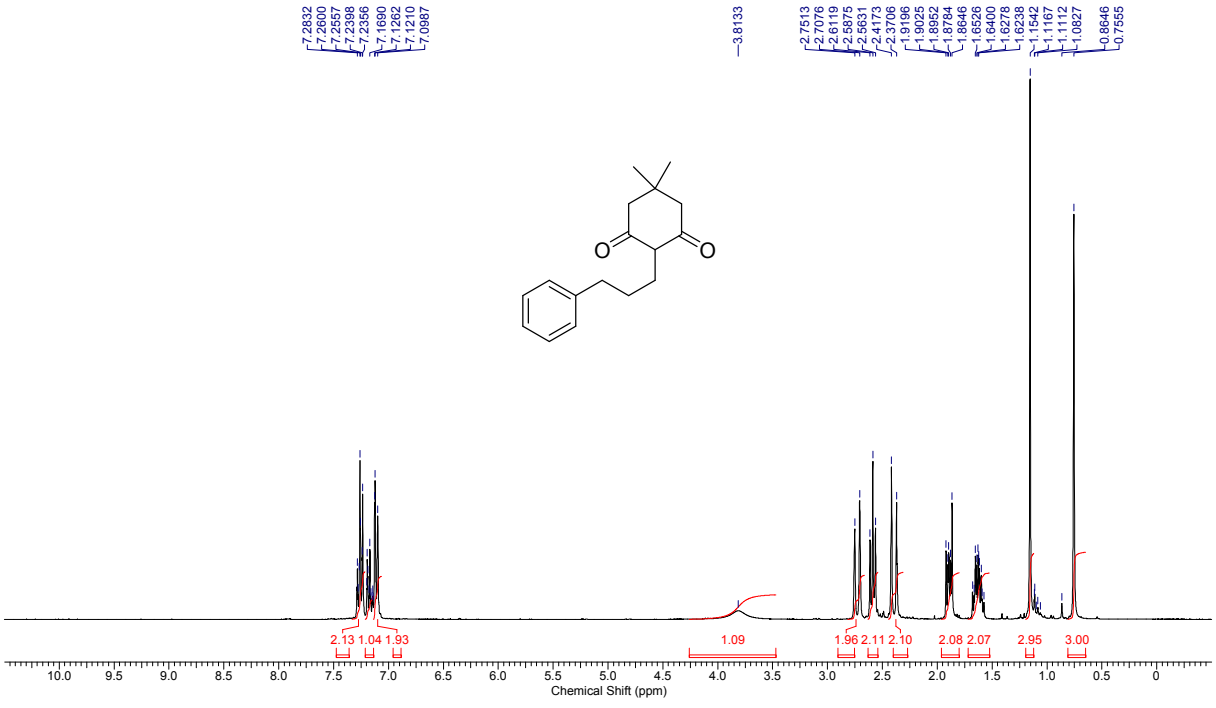
2-[(4-Methoxyphenyl)methyl]-5,5-dimethyl-1,3-cyclohexanedione [33802-37-8] (37b)

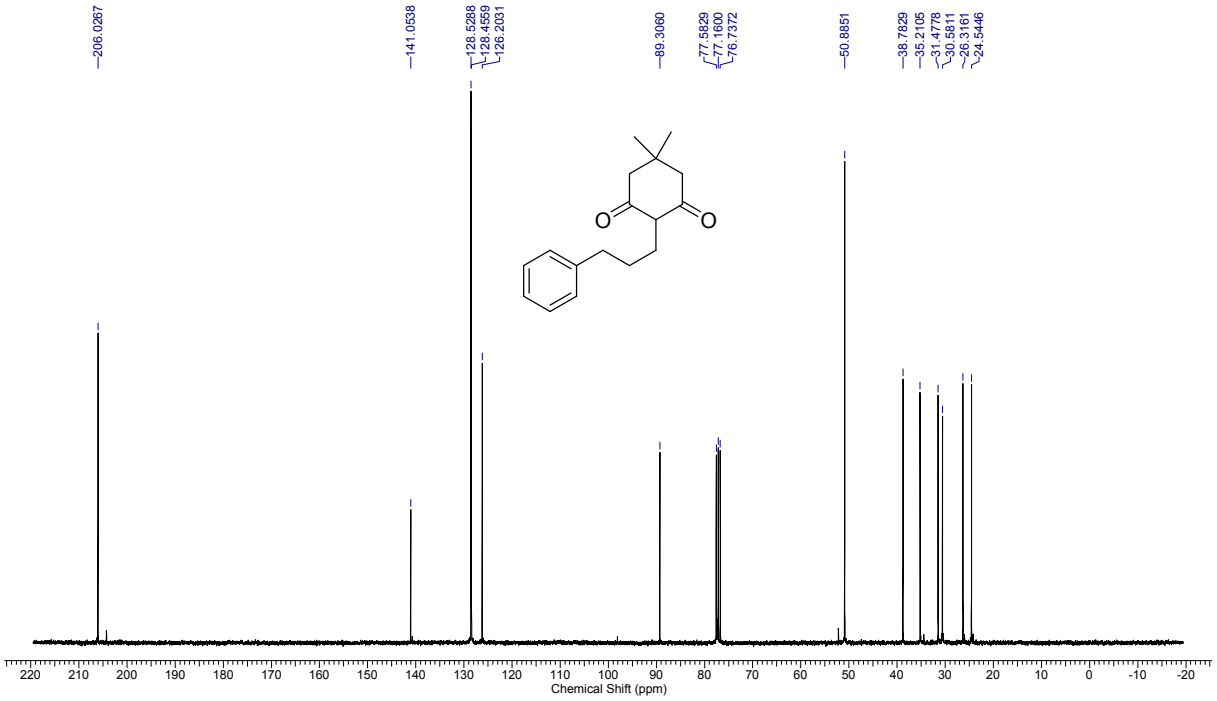


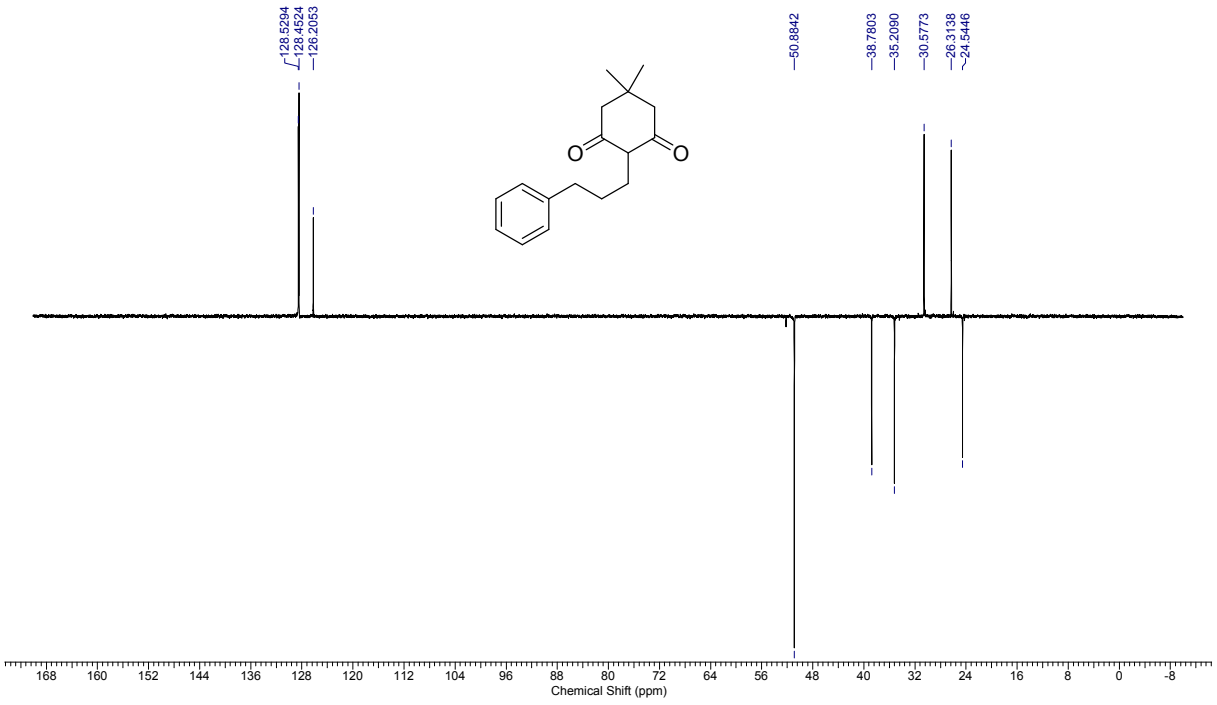




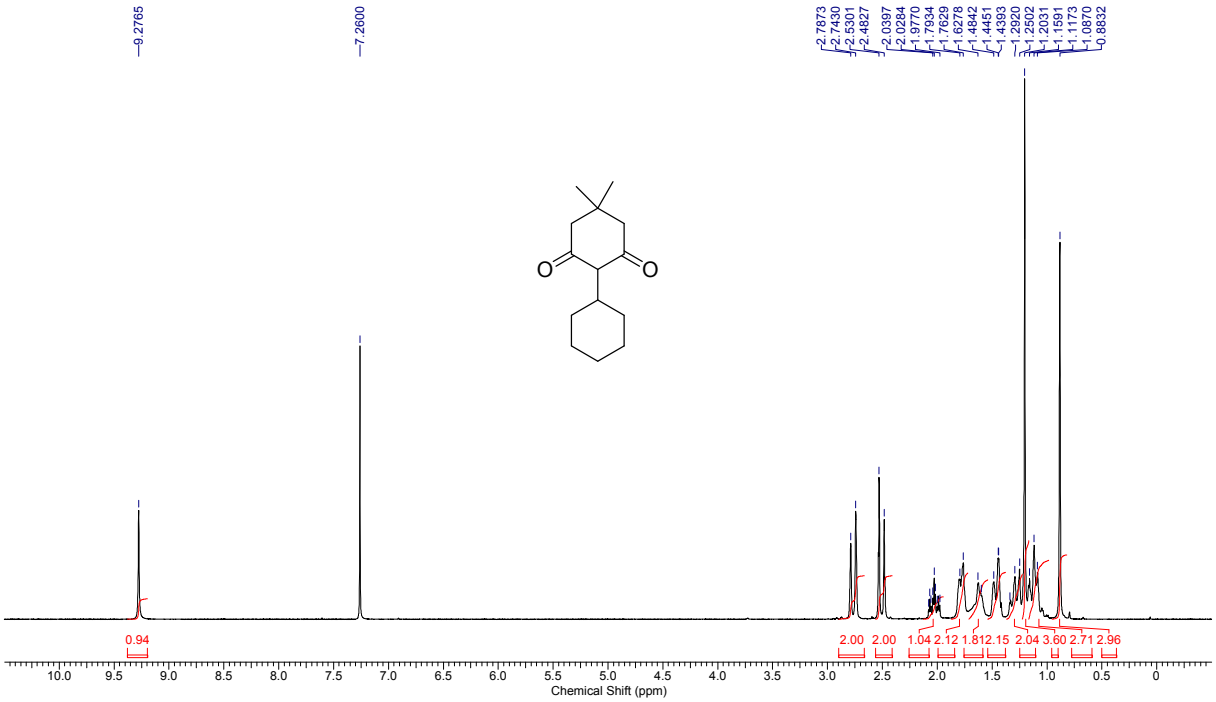
2-[(3'-phenylpropyl]-5,5-dimethyl-1,3-cyclohexanedione (38)

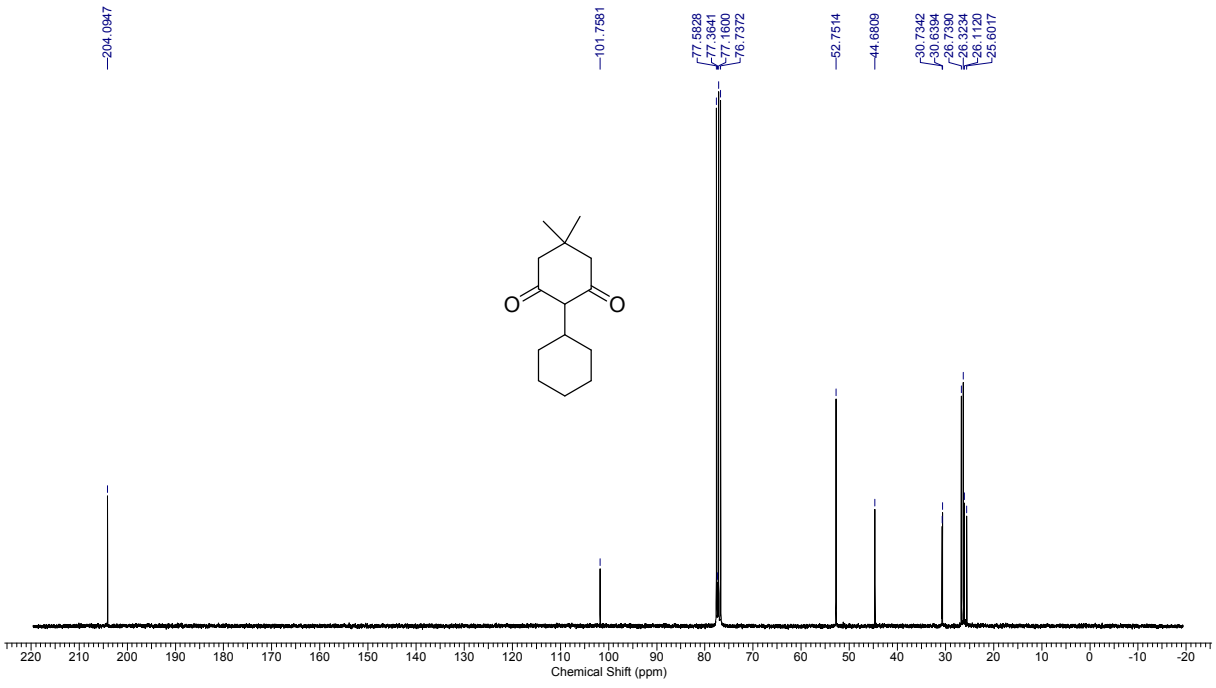


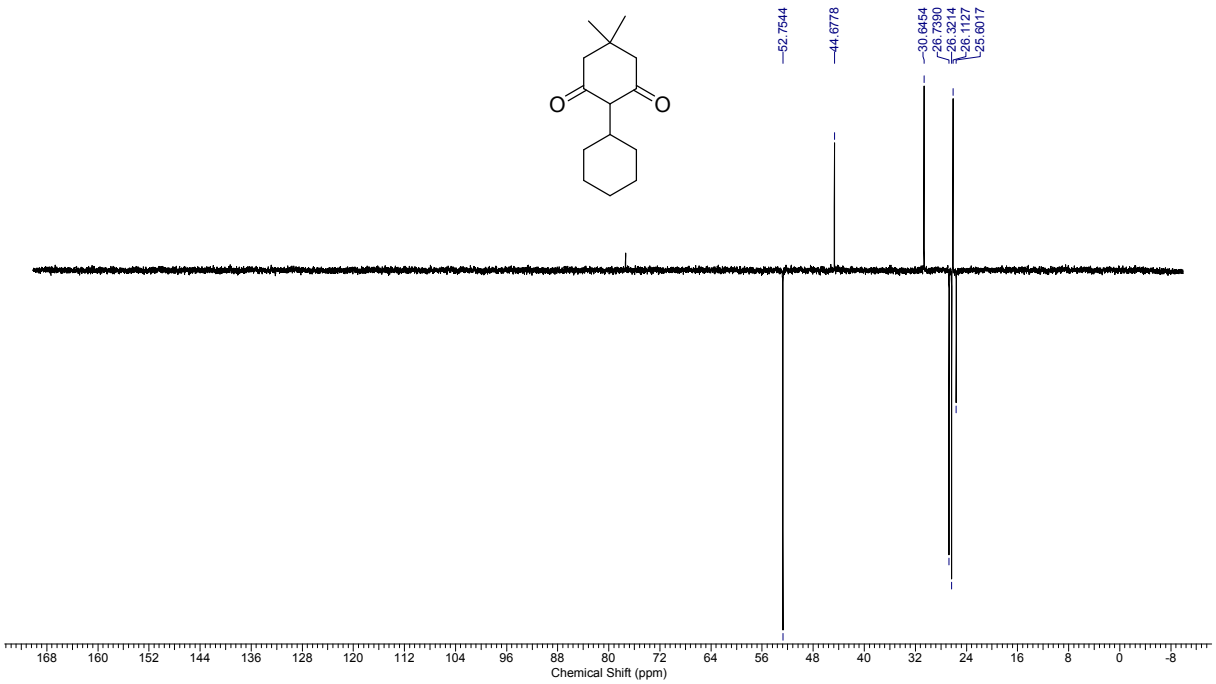

206.0267
141.0538
128.5288
128.4559
126.2031
89.3060
77.5829
77.1600
76.7372
50.8851
38.7829
35.2105
31.4778
30.5811
26.3161
24.5446
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift (ppm)

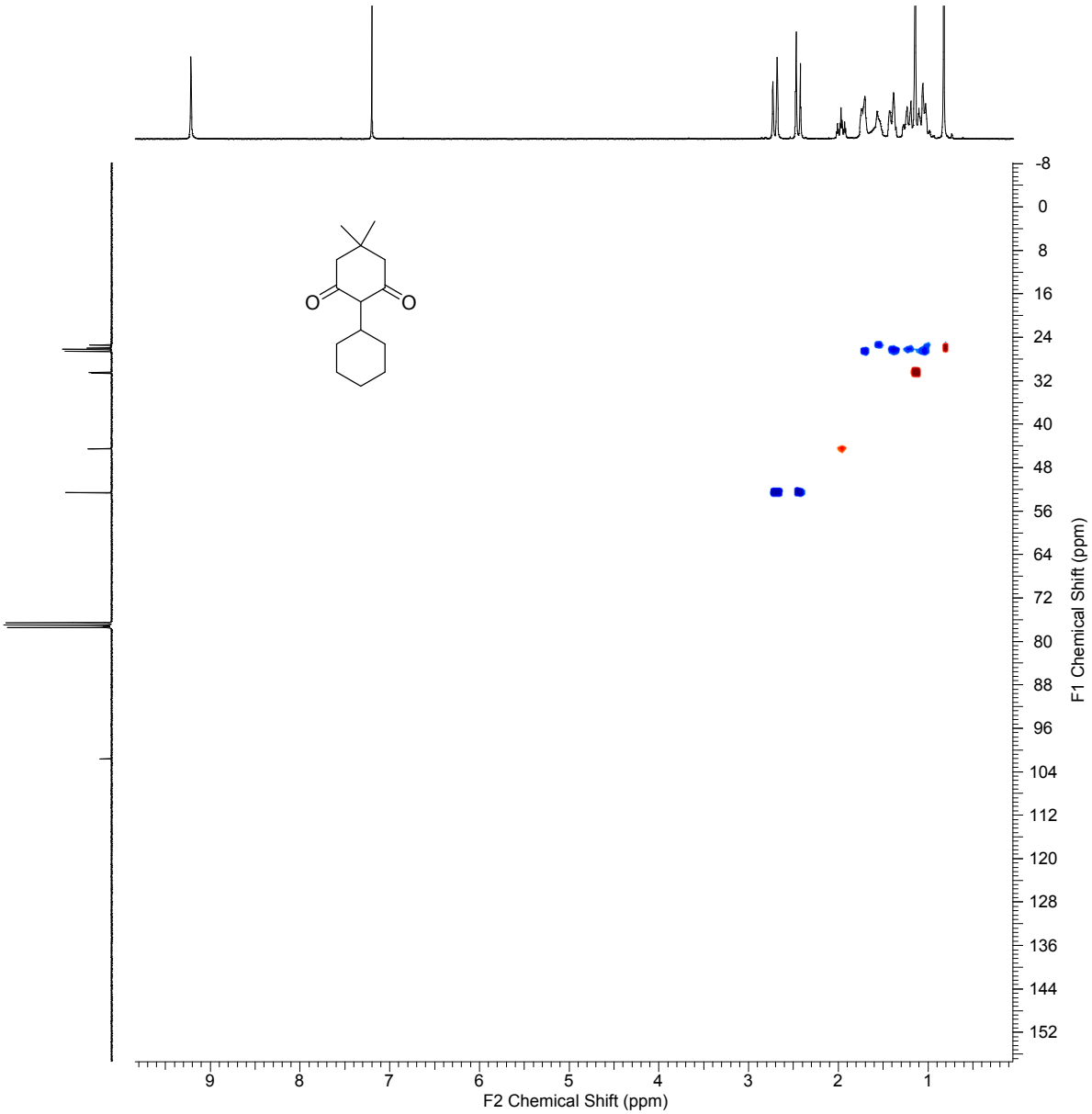

128.5294
128.4524
126.2053
50.8842
38.7803
35.2090
30.5773
26.3138
24.5446
O
O
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)

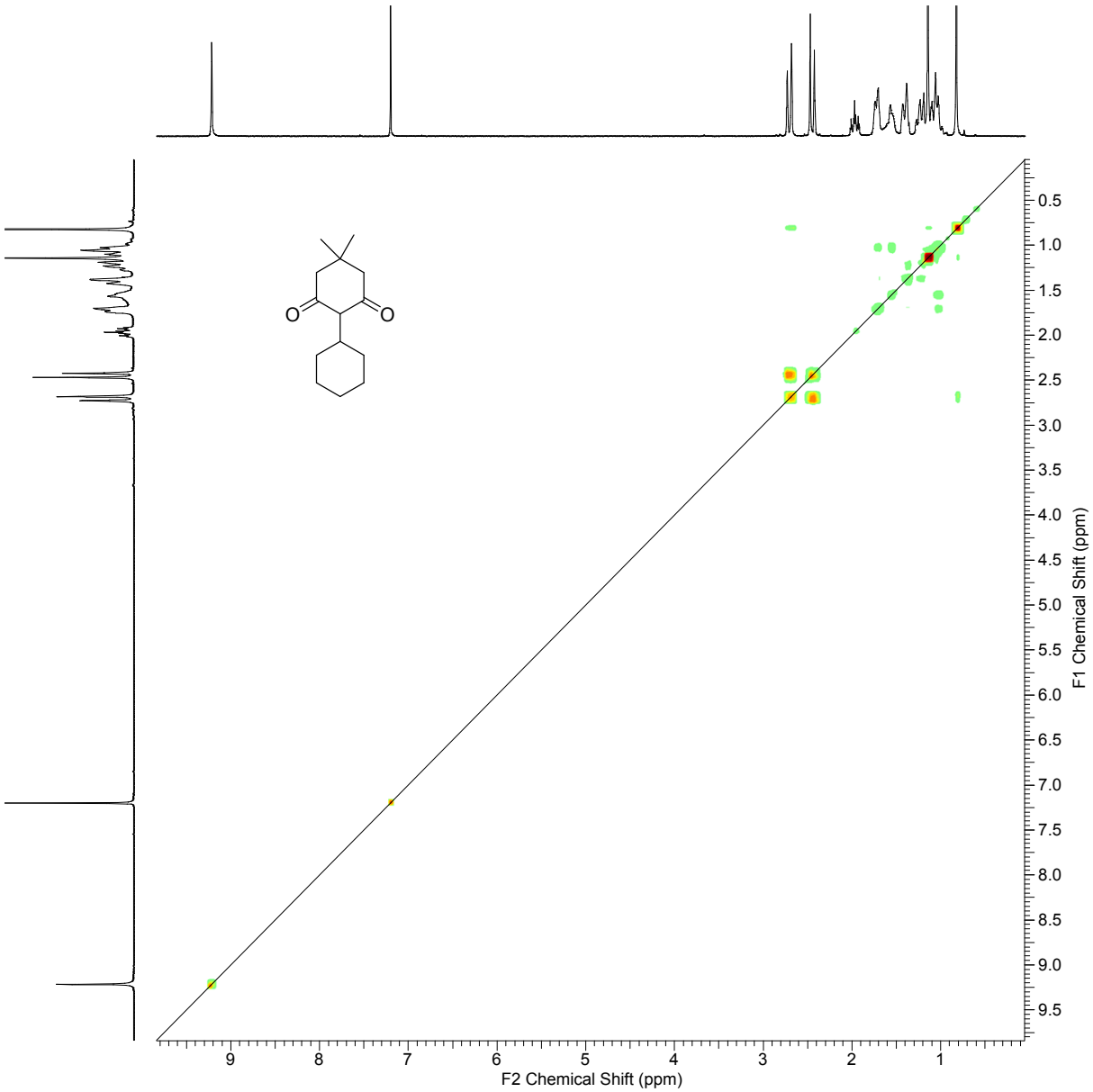
2-[(cyclohexyl]-5,5-dimethyl-1,3-cyclohexanedione (39b)

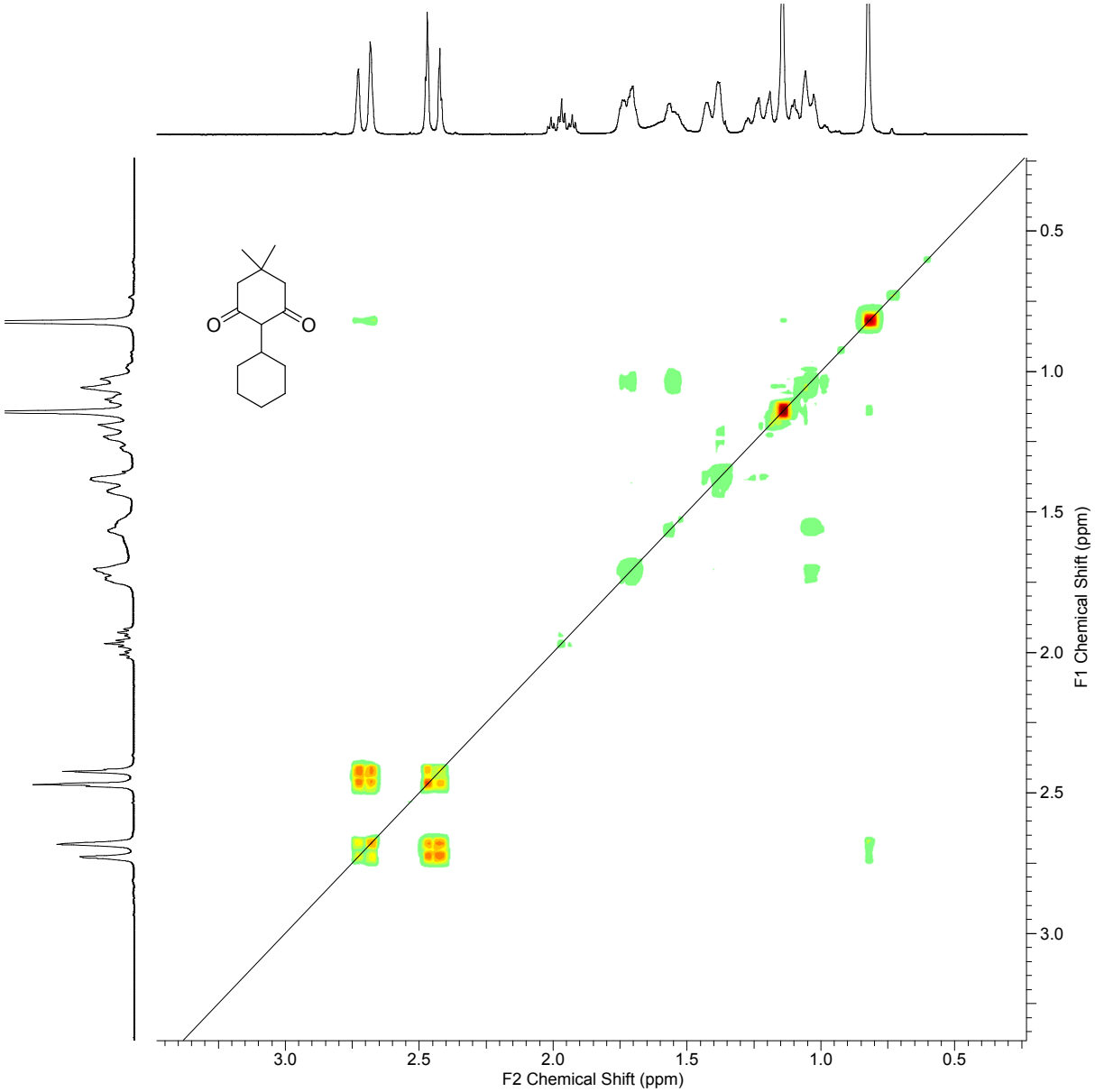


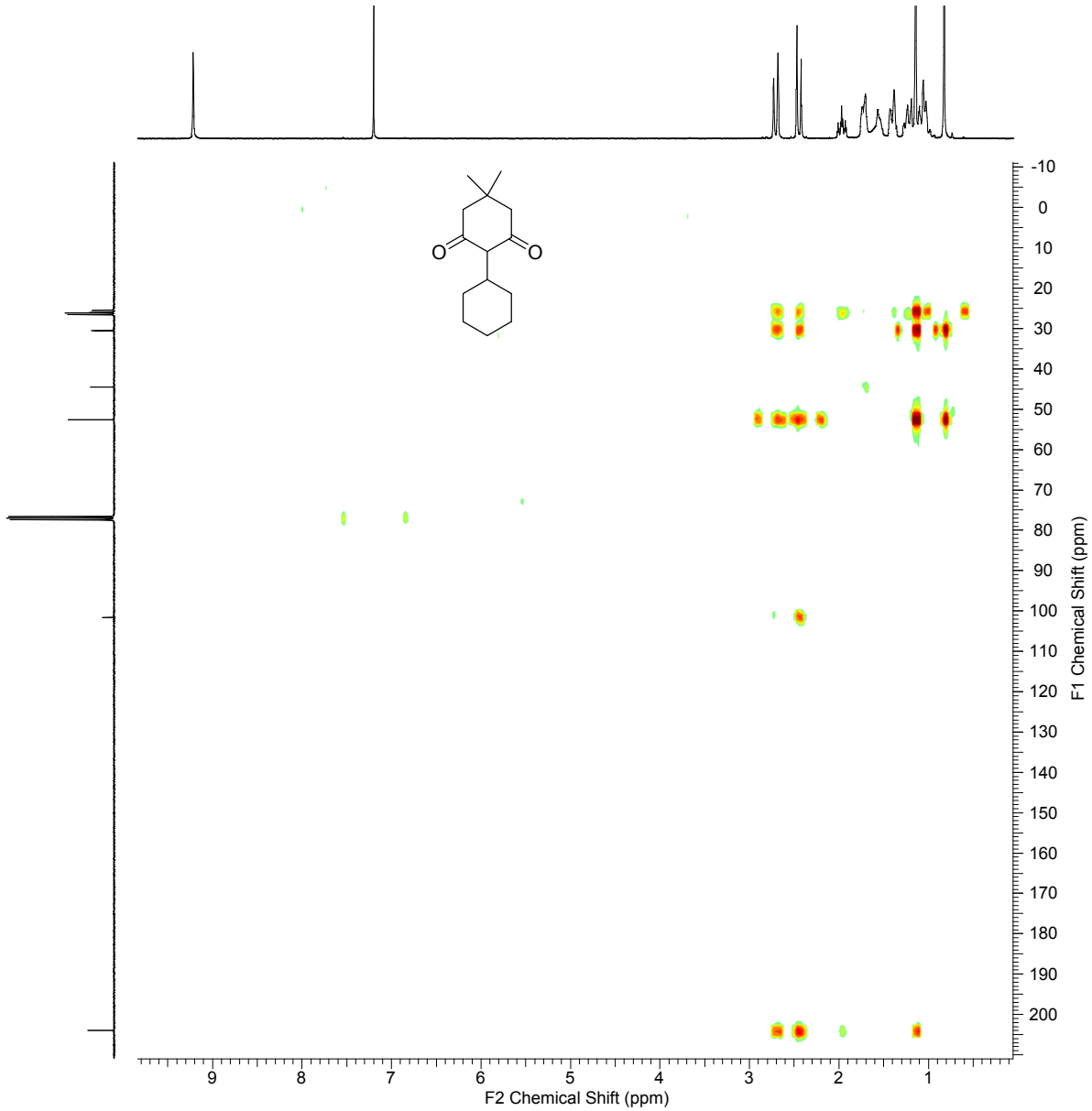



52.7544
44.6778
30.6454
26.7390
26.3214
26.1127
25.6017
O
O
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)


O
O
-8
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
152
F1 Chemical Shift (ppm)
9
8
7
6
5
4
3
2
1
F2 Chemical Shift (ppm)


O
O
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)


O
O
3.0
2.5
2.0
1.5
1.0
0.5
F2 Chemical Shift (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
F1 Chemical Shift (ppm)


O
O
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
F1 Chemical Shift (ppm)
9
8
7
6
5
4
3
2
1
F2 Chemical Shift (ppm)