Electronic Supplementary Material (ESI) for Chemical Communications

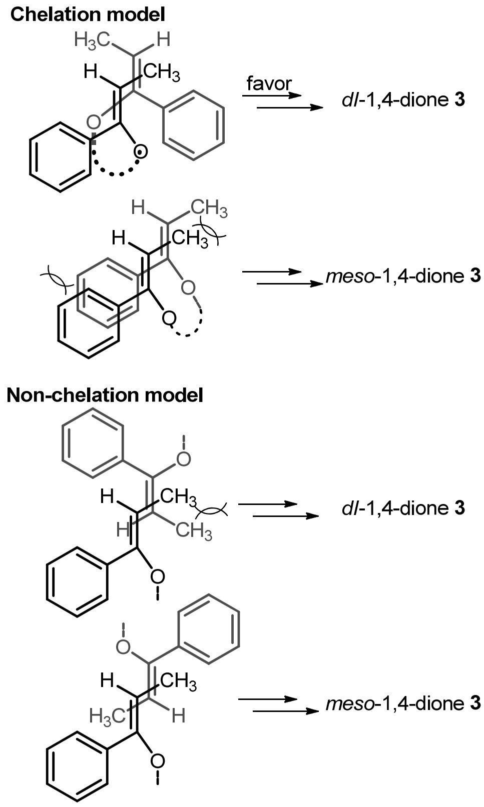
Supplementary Information

Oxovanadium(V)-Induced Diastereoselective Oxidative Homocoupling of Boron Enolates

Toru Amaya,[a] Takaya Masuda,[a] Yusuke Maegawa[a] and Toshikazu Hirao*[a,b]
[a]*Department of Applied Chemistry, Graduate School of Engineering, Osaka University*
Yamada-oka, Suita, Osaka 565-0871, Japan
[b]JST, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Table of Contents

Scheme S1. Representative Configurations of Two Enolates for the Coupling Reaction in Chelation and Non-chelation Models



General. NMR spectra were recorded on a JEOL JNM-ECP 400 spectrometer. Chemical shifts in $CDCl_3$ were reported in ppm on the δ scale relative to a residual solvent (δ 7.26 for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) as an internal standard. $VOCl_3$ (0.00 ppm) was used as an external standard for ^{51}V NMR. Infrared spectra were obtained with a JASCO FT/IR-6200 spectrometer. Mass spectra were measured on a JEOL JMS-DX-303 spectrometer using fast atom bombardment (FAB) mode. Measurement for X-ray crystallography was made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Cu-Kα radiation.

VO(OPr-*i*)$_2$Cl was prepared according to the literature procedure.[i] VO(OPr-*i*)$_3$ and VO(OEt)Cl_2 were donated from Nichia corporation, and they were used after distillation. The dried $CDCl_3$ with MS4A was used for the reaction. The employed enones **1a**,[ii] **1b**,[ii] **1c**,[iii] **1d**,[ii] **1e**,[ii] **1f**,[iv,v] and **1g**[vi,vii] are known compounds. Chalcone (**1h**) was purchased from WAKO Pure Chemical Industries, Ltd. 9-Borabicyclo[3,3,1]nonane (9-BBN) was purchased from Aldrich as a 0.5 M THF solution. The obtained 1,4-diones **3a**,[viii] **3b**,[ix] **3c**,[x] and **3h**[viii] are known compounds.

References

(i) D. C. Crans, H. Chen and R. A. Felty, *J. Am. Chem. Soc.*, 1992, **114**, 4543.

(ii) X.-L. An, J.-R. Chen, C.-F. Li, F.-G. Zhang, Y.-Q. Zou, Y.-C. Guo and W.-J. Xiao, *Chem. Asian J.*, 2010, **5**, 2258.

(iii) S. Tamura, A. Shiomi, M. Kaneko, Y. Ye, M. Yoshida, M. Yoshikawa, T. Kimura, M. Kobayashi and N. Murakami, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 2555.

(iv) M. Strohmeier, K. Leach and M. A. Zajac, *Angew. Chem. Int. Ed.*, 2011, **50**, 12335.

(v) P. Truong, C. S. Shanahan and M. P. Doyle, *Org. Lett.*, 2012, **14**, 3608.

(vi) E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, **20**, 399.

(vii) A. Bugarin, K. D. Jones and B. T. Connell, *Chem. Commun.*, 2010, **46**, 1715.

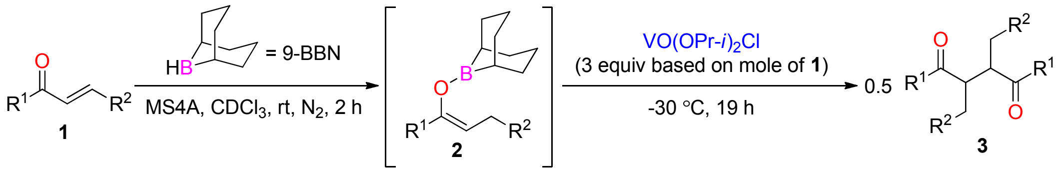
(viii) S. E. Drewes, C. J. Hogan, P. T. Kaye and G. H. P. Roos, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1585.

(ix) H. Ikeda, T. Takasaki, Y. Takahashi, A. Konno, M. Matsumoto, Y. Hoshi, T. Aoki, T. Suzuki, J. L. Goodman and T. Miyashi, *J. Org. Chem.*, 1999, **64**, 1640.

(x) S. G. A. Moinuddin, S. Hishiyama, M.-H. Cho, L. B. Davin and N. G. Lewis, *Org. Biomol. Chem.*, 2003, **1**, 2307.

Oxidative *dl* selective homocoupling of boron enolates

Procedure 1: NMR tube experiment

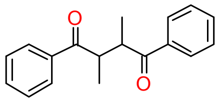


To a $CDCl_3$ (700 µL) solution of α,β-unsaturated carbonyl compound **1** (30 µmol) with a portion of activated MS4A in a J-Young valve-attached NMR tube was added 0.5 M THF solution of 9-borabicyclo[3, 3, 1]nonane (9-BBN) (15 µL, 7.5 µmol) in N_2-filled glove box. After the mixture was shaken at room temperature for 1 min by hand, the 9-BBN solution (15 µL, 7.5 µmol) was added again. The mixture was shaken for more 1 min by hand, followed by further addition of the 9-BBN solution (30 µL, 15 µmol). After the mixture stood at room temperature for 2 h, ^{1}H NMR of the mixture was measured. After the formation of boron enolate **2** was confirmed, the mixture was put in refrigerator (-30 ˚C) for 1 h. Then, it was taken out from refrigerator. VO(OPr-*i*)$_2$Cl (17.1 µL, 90 µmol) was immediately added to the solution. The mixture was shaken for 5 sec, and then it stood in refrigerator (-30 ˚C) for 19 h. Then the mixture was quenched with saturated aqueous $NaHCO_3$. The product was extracted with CH_2Cl_2. The organic layer was washed with water, brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was filtered through a short pad of silica-gel column (h = 2.5 cm, CH_2Cl_2). The mixture was evaporated *in vacuo*. The yield and *dl*/*meso* ratio were determined by ^{1}H NMR using 1,1,2,2-tetrabromoethane as an internal standard. The crude product was purified by preparative thin layer chromatography (CH_2Cl_2) to give the products. The obtained product **3** was further purified by preparative thin layer chromatography (hexane/ethylacetate = 4:1) to give the pure product.

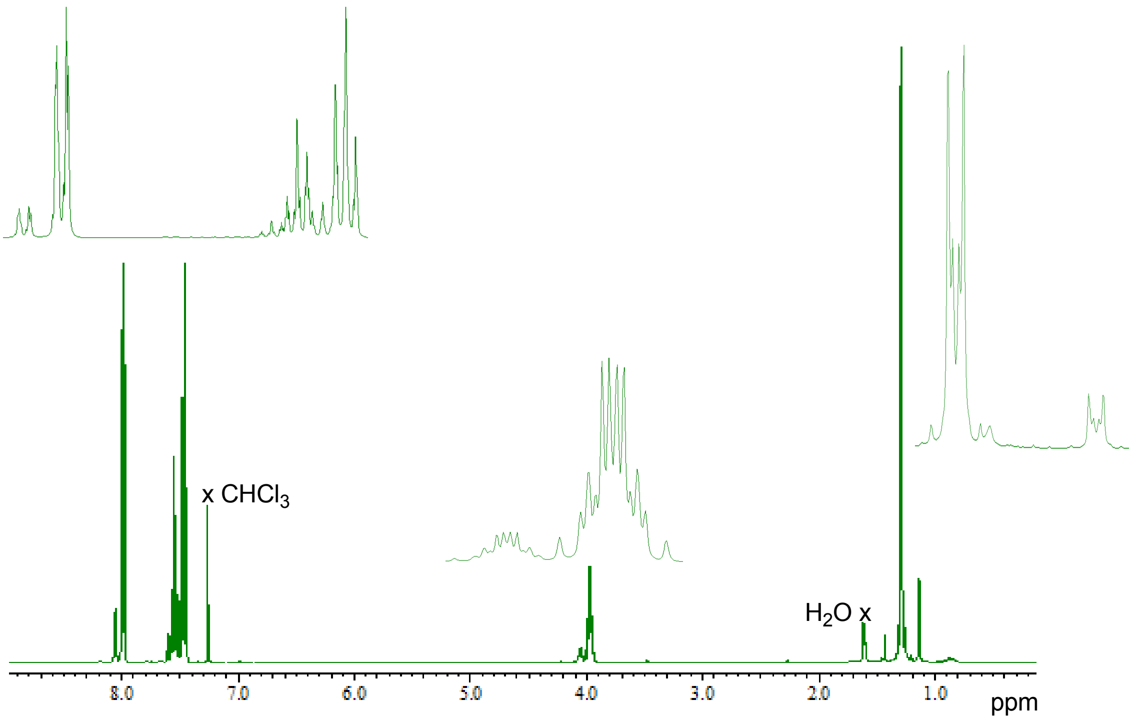
Procedure 2: 100 mg scale reaction

Experiments except work-up were carried out in N_2-filled glove box. Dry CH_2Cl_2 (7 mL), 1.73M CH_2Cl_2 solution of 1-phenylprop-2-en-1-one (**1a**) (437 µL, 0.76 mmol, which corresponds to 100 mg of **1a**), and a portion of activated MS4A were added to a dried 50 mL round-bottomed flask. To the mixture was added 0.5 M THF solution of 9-borabicyclo[3,3,1]nonane (9-BBN) (1.66 mL, 0.83 mmol) at room temperature. After stirring at room temperature for 2 h, the mixture was cooled to -40 ˚C. Then, VO(OPr-*i*)$_2$Cl (431 µL, 2.27 mmol) was immediately added to the solution. The mixture was stirred at -40 ˚C for 24 h. Then, the flask was put out of glove box. The reaction mixture was quenched with saturated aqueous $NaHCO_3$. The product was extracted with Et_2O twice. The combined organic layer was washed with water twice. The aqueous layer was extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by silica-gel column chromatography to give **3a** by eluting with hexane/CH_2Cl_2 = 1:2 to CH_2Cl_2. After evaporation and drying *in vacuo*, 2,3-dimethyl-1,4-diphenylbutane-1,4-dione (**3a**) (a *dl*/*meso* diastereomeric mixture) was obtained as a white solid (93.2 mg, 0.350 mmol, 93% yield, *dl*/*meso* = 86:14).

^{1}H NMR spectrum for **3a** synthesized using procedure 2 (400 MHz, $CDCl_3$)



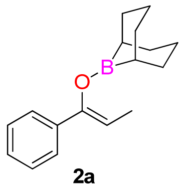
3a



Electronic Supplementary Material (ESI) for Chemical Communications

Boron enolates

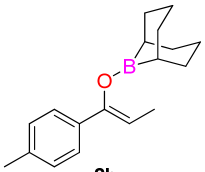
(*Z*)-9-(1-phenylprop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2a)



2a

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13-2.00 (m, 14H), 1.66 (d, 3H, *J* = 6.9 Hz), 5.55 (q, 1H, *J* = 6.9 Hz), 7.12-7.18 (m, 1H), 7.18-7.25 (m, 2H), 7.36-7.41 (m, 2H).

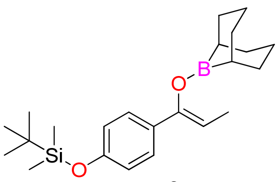
(*Z*)-9-(1-*p*-tolylprop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2b)



2b

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07-1.91 (m, 14H), 1.59 (d, 3H, *J* = 6.9 Hz), 2.19 (s, 3H), 5.44 (q, 1H, *J* = 6.9 Hz), 6.98 (d, 2H, *J* = 8.2 Hz), 7.22 (d, 2H, *J* = 8.2 Hz).

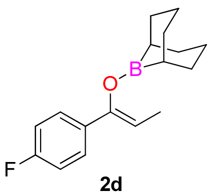
(*Z*)-(4-(1-(9-borabicyclo[3.3.1]nonan-9-yloxy)prop-1-enyl)phenoxy)(*tert*-butyl)dimethylsilane (2c)



2c

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.86 (s, 9H), 1.08-1.94 (m, 14H), 1.59 (d, 3H, *J* = 6.9 Hz), 5.36 (q, 1H, *J* = 6.9 Hz), 6.63-6.68 (m, 2H), 7.18-7.23 (m, 2H).

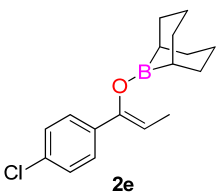
(*Z*)-9-(1-(4-fluorophenyl)prop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2d)



2d

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08-1.93 (m, 14H), 1.61 (d, 3H, *J* = 6.8 Hz), 5.43 (q, 1H, *J* = 6.9 Hz), 6.85-6.91 (m, 2H), 7.32 (m, 2H).

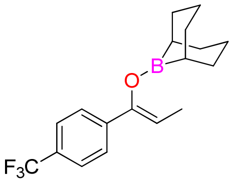
(*Z*)-9-(1-(4-chlorophenyl)prop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2e)



2e

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06-1.70 (m, 14H), 1.58 (d, 3H, *J* = 6.9 Hz), 5.48 (q, 1H, *J* = 6.9 Hz), 7.10-7.15 (m, 2H), 7.23-7.28 (m, 2H).

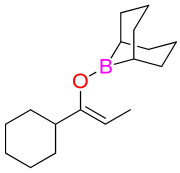
(*Z*)-9-(1-(4-(trifluoromethyl)phenyl)prop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2f)



2f

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07-1.94 (m, 14H), 1.64 (d, 3H, *J* = 6.8 Hz), 5.65 (q, 1H, *J* = 6.9 Hz), 7.42-7.50 (m, 4H).

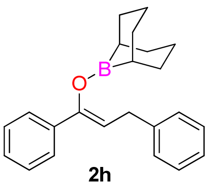
(*Z*)-9-(1-cyclohexylprop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2g)



2g

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99-1.92 (m, 25H), 1.35 (d, 3H, *J* = 6.9 Hz), 4.56 (q, 1H, *J* = 6.9 Hz).

(*Z*)-9-(1,3-diphenylprop-1-enyloxy)-9-borabicyclo[3.3.1]nonane (2h)

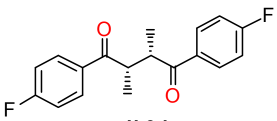


2h

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09-1.90 (m, 16H), 3.39 (d. 2H, *J* = 7.3 Hz), 5.58 (t, 1H, *J* = 7.3 Hz), 7.01-7.19 (m, 8H), 7.36 (m, 2H).

1,4-Diones

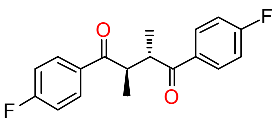
***dl*-1,4-bis(4-fluorophenyl)-2,3-dimethylbutane-1,4-dione (*dl*-3d)**



dl-3d

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.29 (m, 6H), 3.90 (m, 2H), 7.13 (m, 2H), 8.01 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) 15.66, 43.68, 115.71 (d, $J_{C\text{-}F}$ = 22.0 Hz), 131.11 (d, $J_{C\text{-}F}$ =9.6 Hz), 132.39 (d, $J_{C\text{-}F}$ = 2.9 Hz), 164.46, 202.81 ppm; IR(ATR) ν 2980, 2929, 1667, 1598, 1228, 1209, 1156, 971, 849 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{16}F_2O_2$: 302.1118, found [(M+H)$^{+}$]: 303.1199.

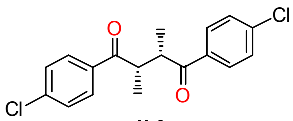
***meso*-1,4-bis(4-fluorophenyl)-2,3-dimethylbutane-1,4-dione (*meso*-3d)**



meso-3d

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.12 (m, 6H), 3.98 (m, 2H), 7.18 (m, 2H), 8.08 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.42, 43.24, 115.91 (d, $J_{C\text{-}F}$ = 21.1 Hz), 131.14 (d, $J_{C\text{-}F}$ =9.6 Hz), 133.14 (d, $J_{C\text{-}F}$ = 2.9 Hz), 164.71, 202.01; IR(ATR) ν 2977, 2937, 1668, 1595, 1225, 1191, 1159, 978, 844 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{16}F_2O_2$: 302.1118, found [(M+H)$^{+}$]: 303.1203.

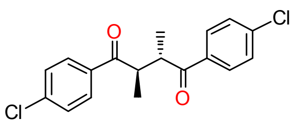
_dl_-1,4-bis(4-chlorophenyl)-2,3-dimethylbutane-1,4-dione (_dl_-3e)



***dl*-3e**

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.28 (m, 6H), 3.89 (m, 2H), 7.44 (m, 2H), 7.92 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.58, 43.72, 128.94, 129.90, 134.32, 139.47, 203.12; IR(ATR) ν 2960, 2928, 1672, 1587, 1092, 970, 842 cm^{-1}, HRMS (FAB) calcd for $C_{18}H_{16}Cl_2O_2$: 334.0527, found [(M+H)$^{+}$]: 335.0604.

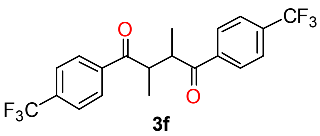
meso-1,4-bis(4-chlorophenyl)-2,3-dimethylbutane-1,4-dione (_meso_-3e)



***meso*-3e**

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.11 (m, 6H), 3.96 (m 2H), 7.48 (m, 2H), 7.99 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.35, 43.28, 129.14, 129.87, 135.01, 139.96, 202.30; IR(ATR) ν 2955, 2928, 1670, 1588, 1091, 977, 841 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{16}Cl_2O_2$: 334.0527, found [(M+H)$^{+}$]: 335.0605.

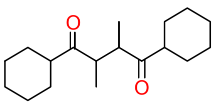
2,3-dimethyl-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (3f)



3f

Major isomer: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.31 (m, 6H), 3.95 (m 2H), 7.75 (d, 2H, J = 8.2 Hz), 8.08 (d, 2H, J = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.43, 44.16, 123.60 (q, $J_{C\text{-}F}$ = 272.7 Hz), 125.75, 128.77, 134.39 (q, $J_{C\text{-}F}$ = 32.6 Hz), 138.75, 203.42; IR(ATR) ν 2971, 2935, 1679, 1319, 1136, 1114, 973, 858 cm^{-1}; HRMS (FAB) calcd for $C_{20}H_{16}F_6O_2$: 402.1054, found [(M+H)$^{+}$]: 403.1127. Minor isomer: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.17 (m, 6H), 4.04 (m 2H), 7.78 (d, 2H, J = 8.2 Hz), 8.14 (d, 2H, J = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.18, 43.61, 123.53 (q, $J_{C\text{-}F}$ = 272.2 Hz), 125.91, 128.78, 134.73 (q, $J_{C\text{-}F}$ = 32.6 Hz), 139.27, 202.41; IR(ATR) ν 2984, 2951, 1680, 1309, 1136, 1108, 974, 849 cm^{-1}; HRMS (FAB) calcd for $C_{20}H_{16}F_6O_2$: 402.1054, found [(M+H)$^{+}$]: 403.1128.

1,4-dicyclohexyl-2,3-dimethylbutane-1,4-dione (3g)

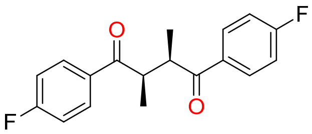


3g

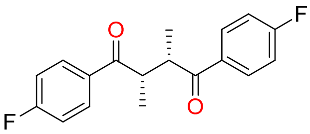
Diastereomeric mixtures. Selectivity was calculated from the integral ratio for the methyl protons. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.92-0.94 (m, $-CH_3$ for minor isomer), 1.04-1.06 (m, $-CH_3$ for minor isomer), 1.0-1.43 (m), 1.60-1.96 (m), 2.38-2.56 (m), 2.92-3.06 (m).

X-ray structures

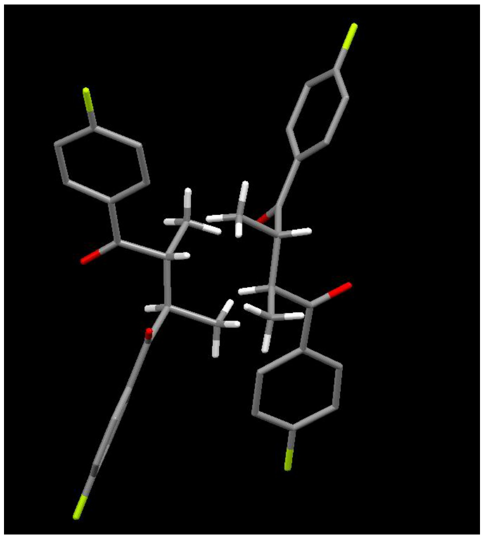
dl-3d



(*R*, *R*)



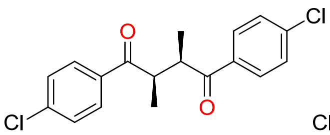
(*S*, *S*)



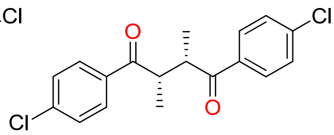
a = 11.1477(5) Å β = 98.775(2) °
b = 13.3381(6) Å V = 1552.5(2) Å^3
c = 10.5647(5) Å Z = 4
$R1$ = 0.1517 $wR2$ = 0.4909
$P2_1/c$ (#14) monoclinic

The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-969201.

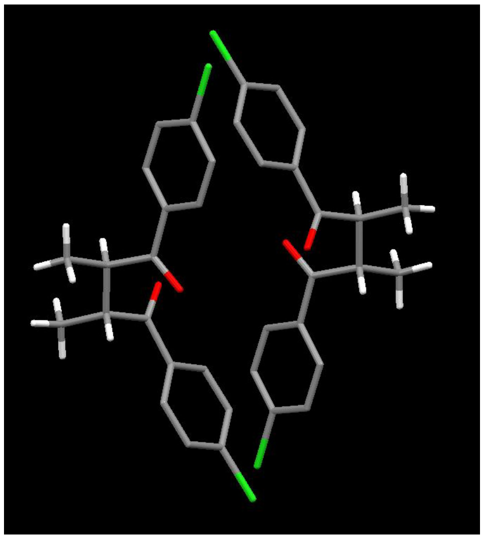
dl-3e



(*R*, *R*)



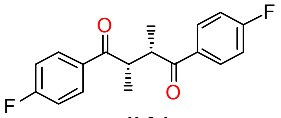
(*S*, *S*)



a = 15.7021(2) Å β = 93.597(1) °
b = 9.6923(1) Å V = 1669.34(4) Å^3
c = 10.9905(2) Å Z = 4
$R1$ = 0.0561 $wR2$ = 0.1675
$P2_1/c$ (#14) monoclinic

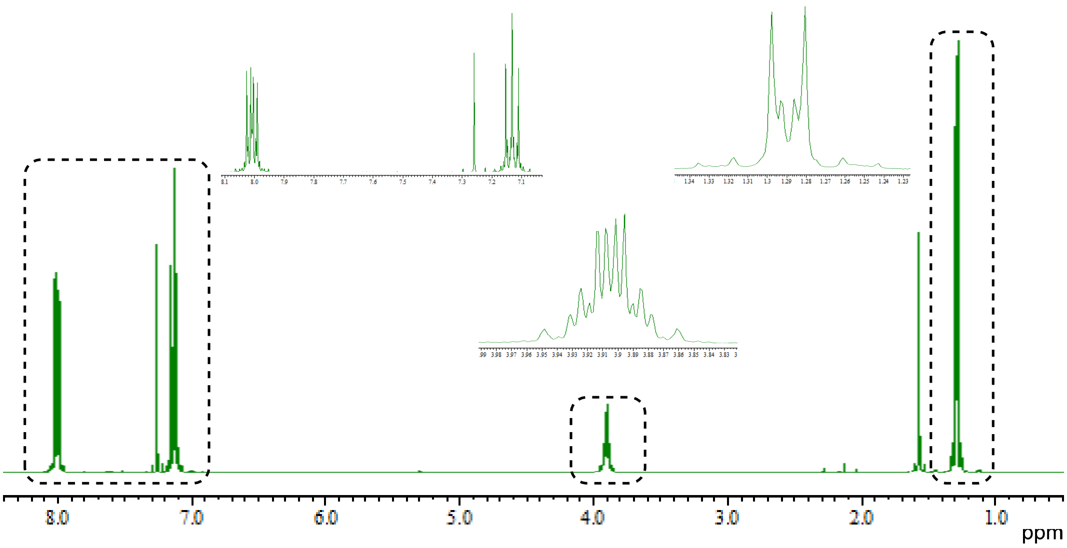
The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-969200.

_dl_-1,4-bis(4-fluorophenyl)-2,3-dimethylbutane-1,4-dione (_dl_-3d)

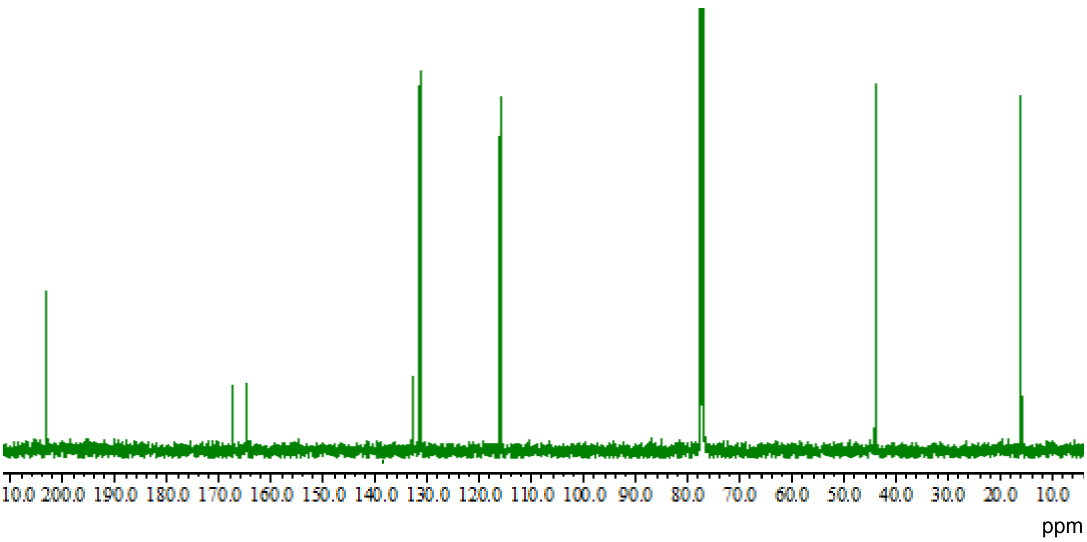


***dl*-3d**

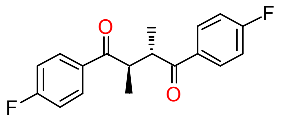
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)

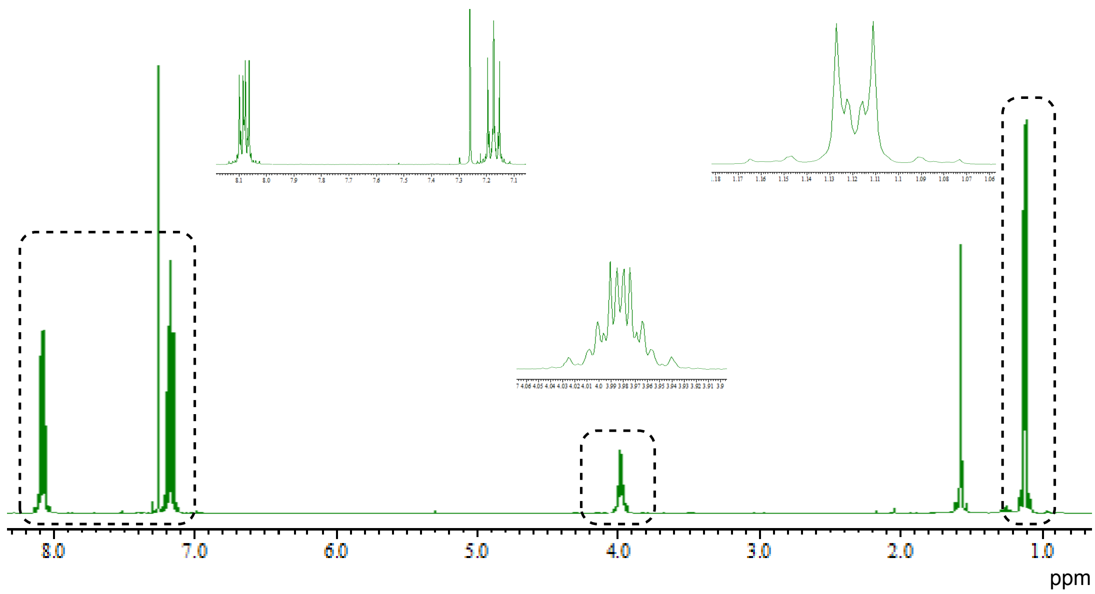


meso-1,4-bis(4-fluorophenyl)-2,3-dimethylbutane-1,4-dione (_meso_-3d)

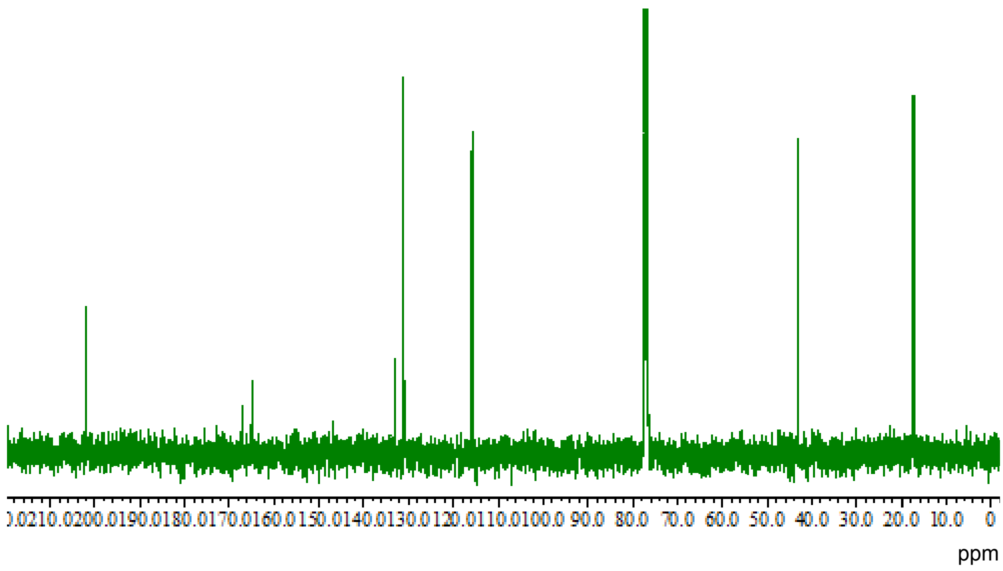


***meso*-3d**

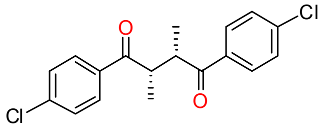
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)

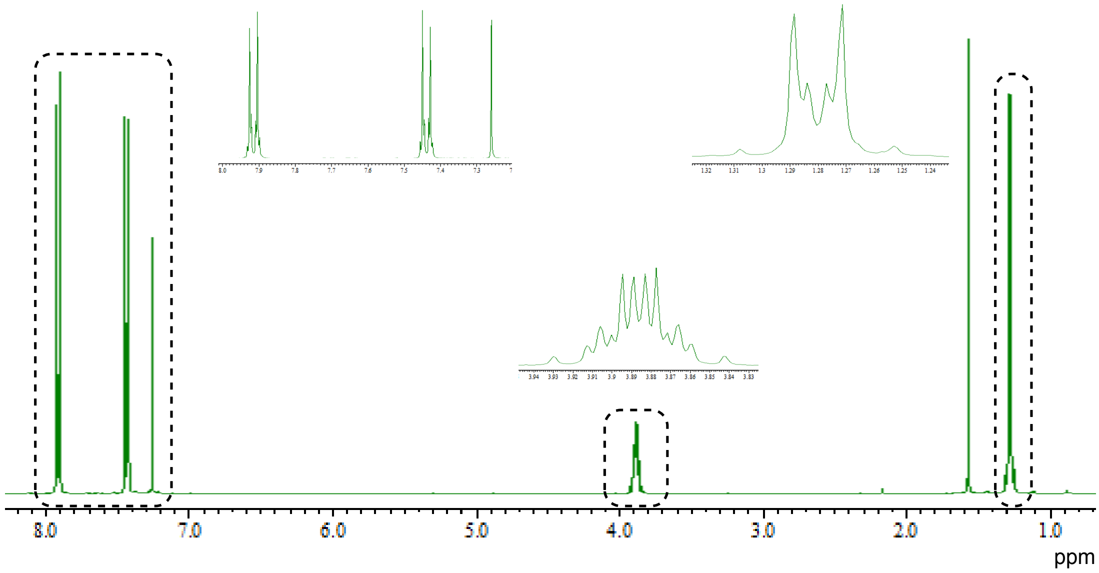


dl-1,4-bis(4-chlorophenyl)-2,3-dimethylbutane-1,4-dione (dl-3e)

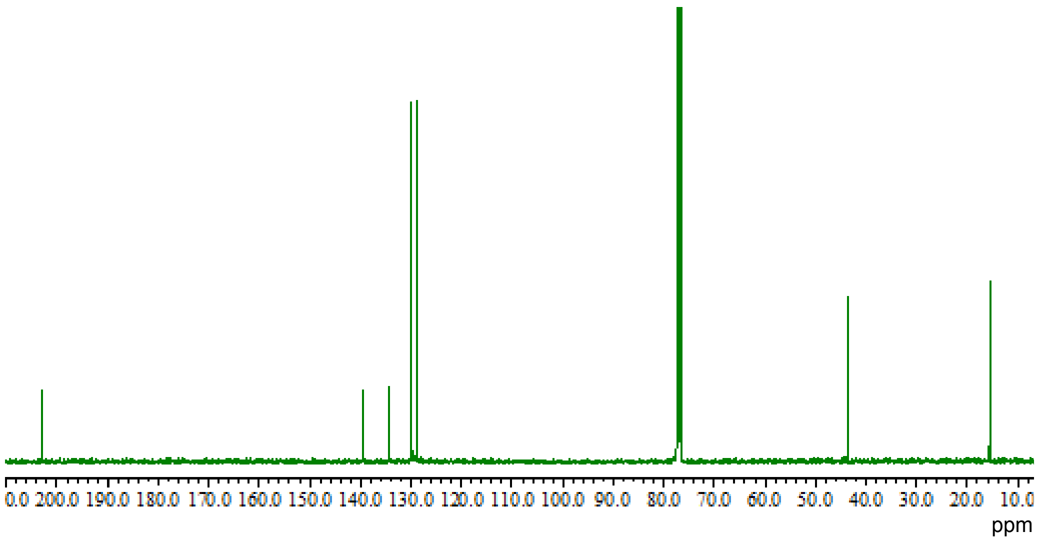


***dl*-3e**

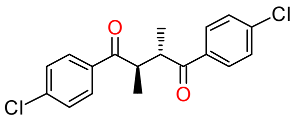
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)

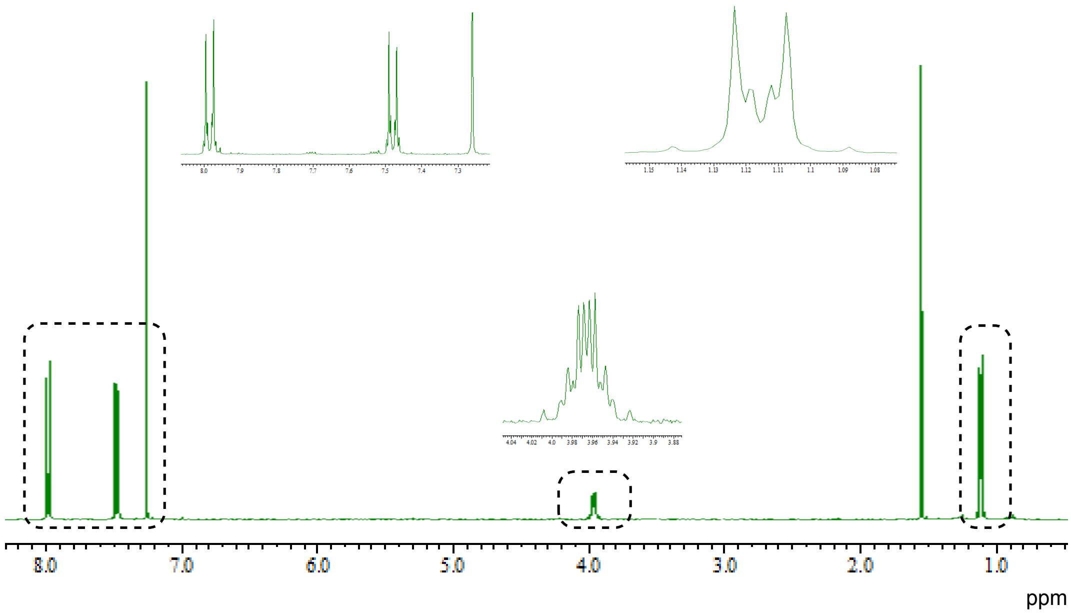


meso-1,4-bis(4-chlorophenyl)-2,3-dimethylbutane-1,4-dione (_meso_-3e)

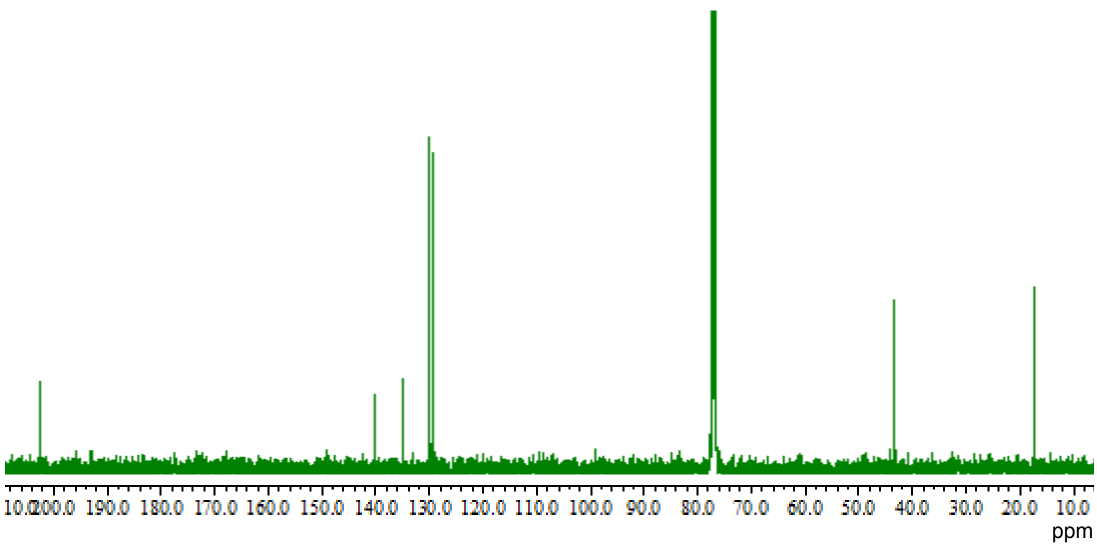


***meso*-3e**

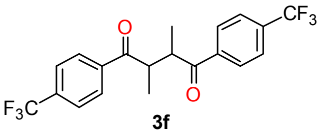
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)



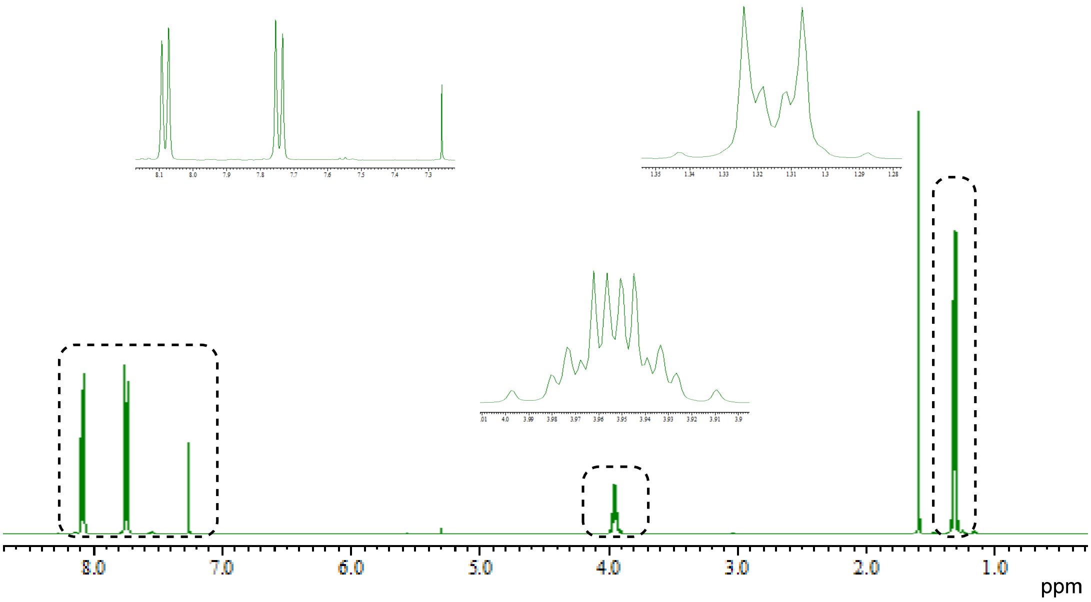
2,3-dimethyl-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (3f)



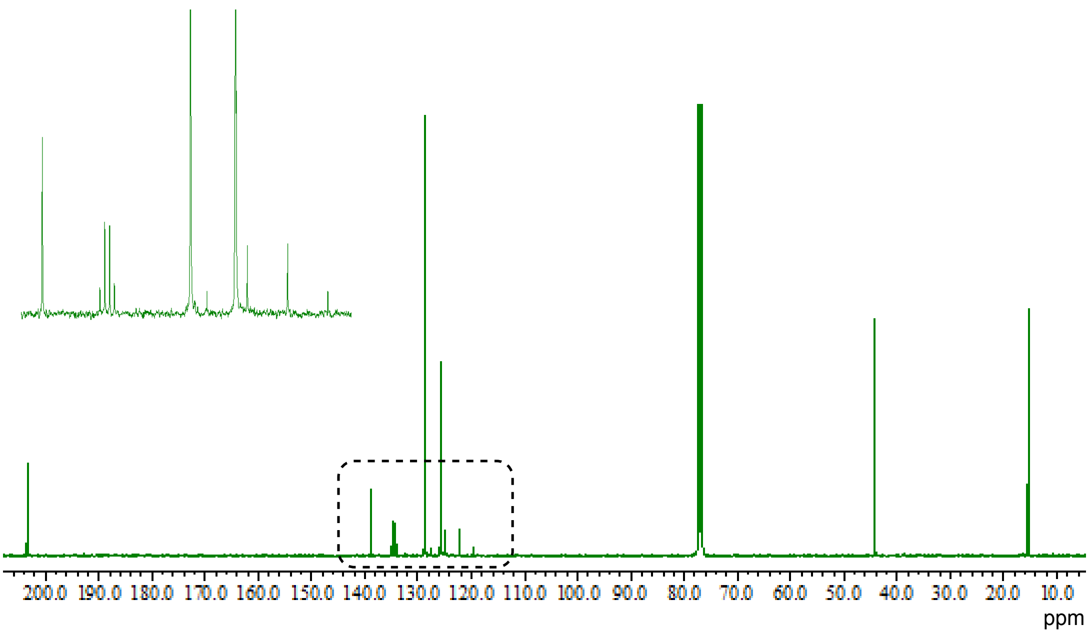
3f

(major isomer)

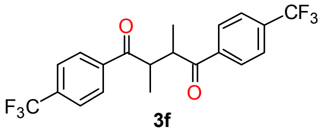
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)



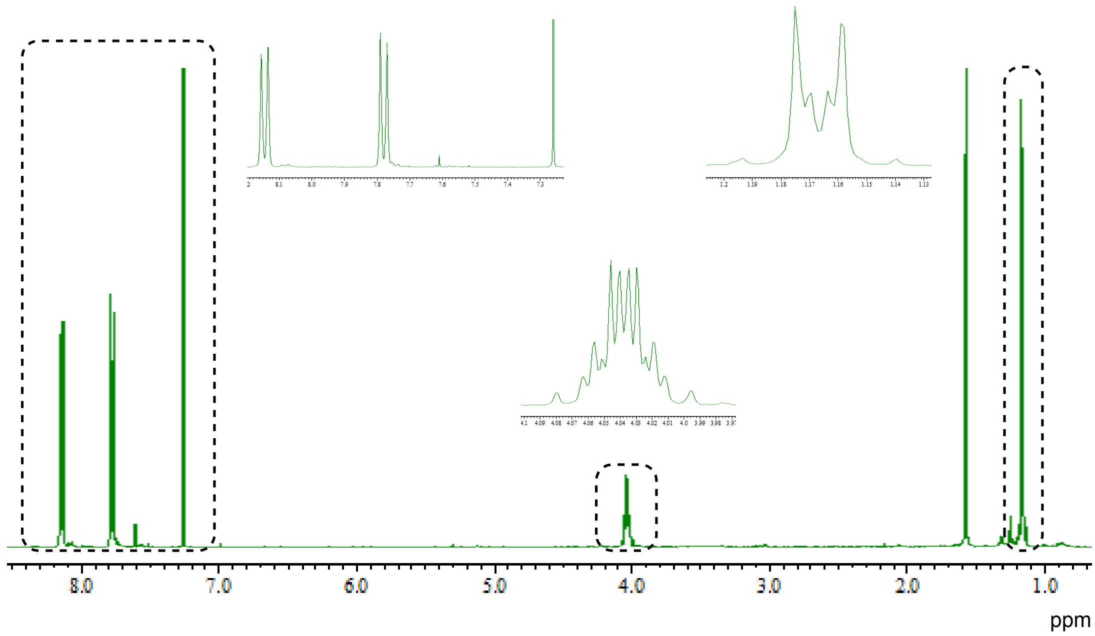
2,3-dimethyl-1,4-bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (3f)



3f

(minor isomer)

[1]H-NMR (400 MHz, $CDCl_3$)



[13]C-NMR (100 MHz, $CDCl_3$)