Supplementary Material

Attempted Reactions of Methoxyallene with Dimethyl 2-Arylcyclopropane Dicarboxylates (D–A Cyclopropanes); Dual Catalytic Activity of Scandium Triflate $Sc(OTf)_3$ and Unexpected Formation of the MeOH Adducts

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Collection of the ^{1}H, ^{13}C, and ^{19}F NMR spectra registered for products **3a**-**l** and **4** S2

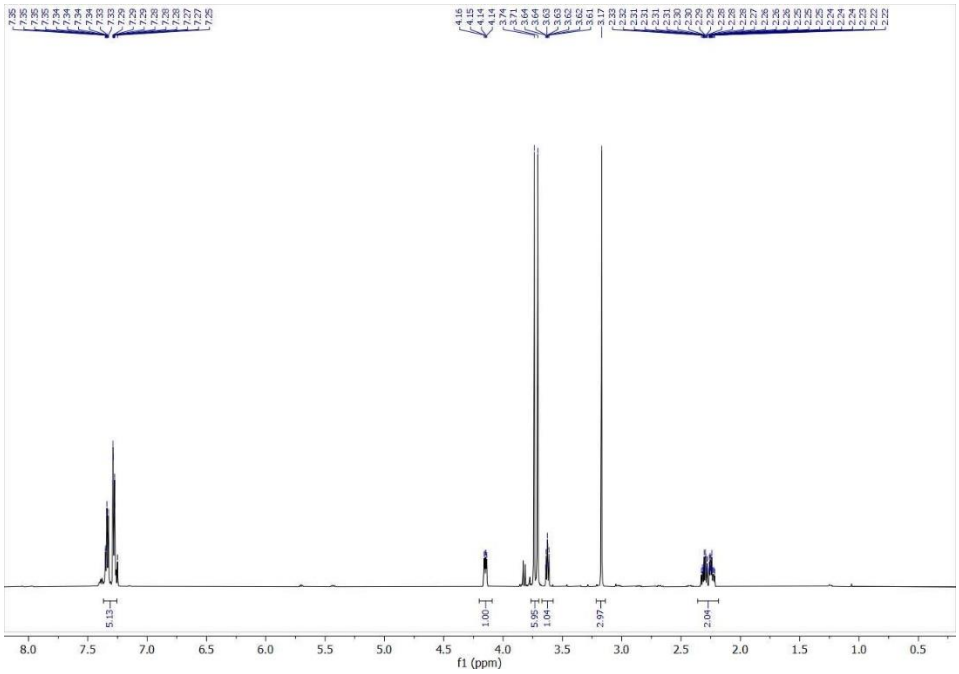

Figure SM1. ^{1}H NMR spectrum of dimethyl 2-(2-methoxy-2-phenylethyl)malonate (**3a**).

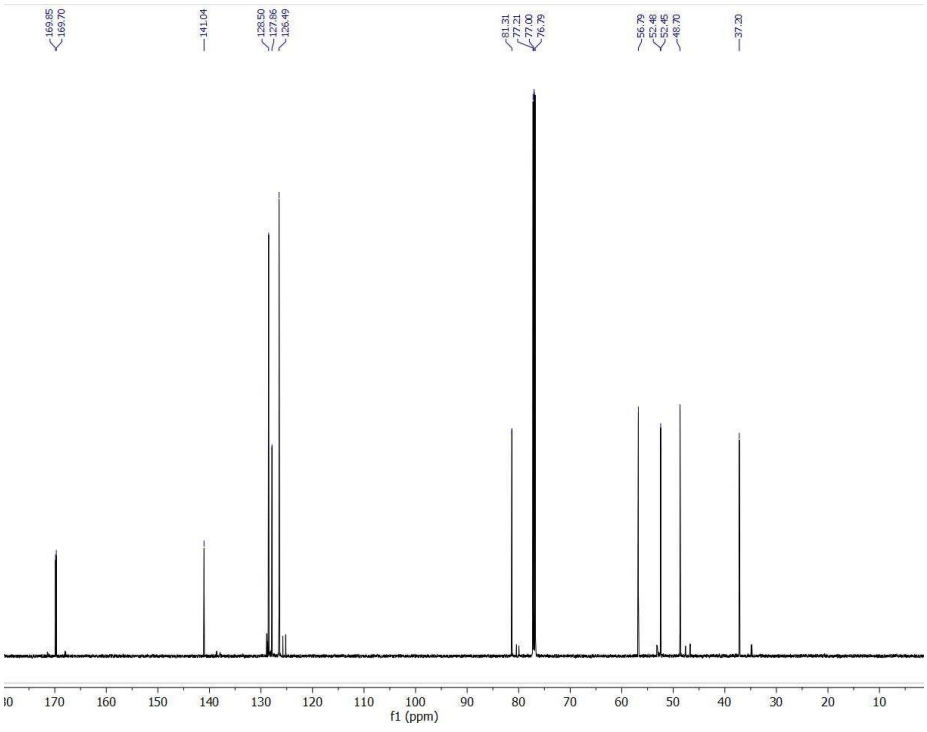

Figure SM2. ^{13}C NMR spectrum of dimethyl 2-(2-methoxy-2-phenylethyl)malonate (**3a**).

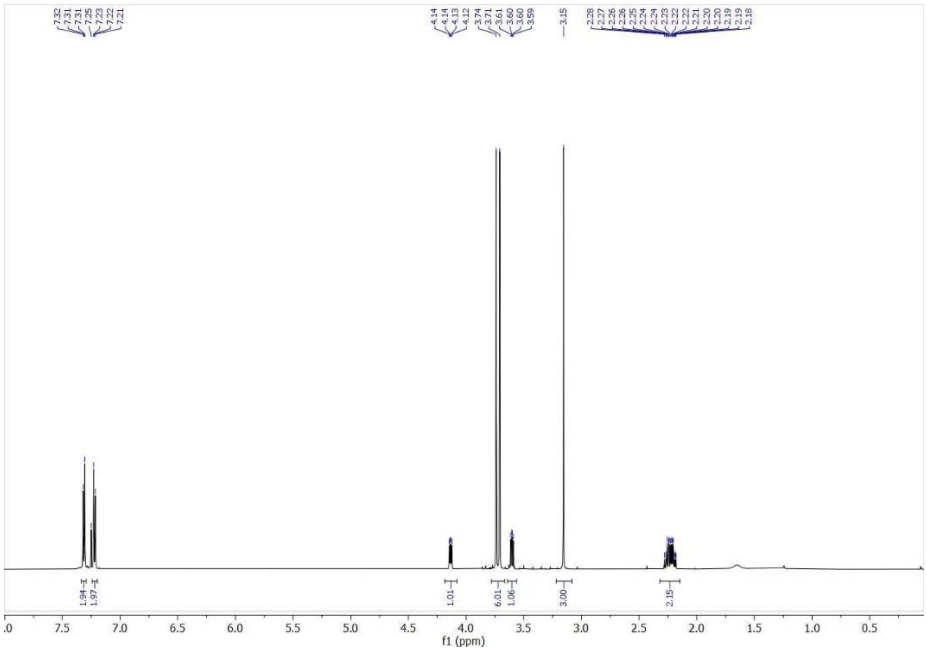

Figure SM3. ^{1}H spectrum of dimethyl 2-(2-(4-chlorophenyl)-2-methoxyethyl)malonate (**3b**).

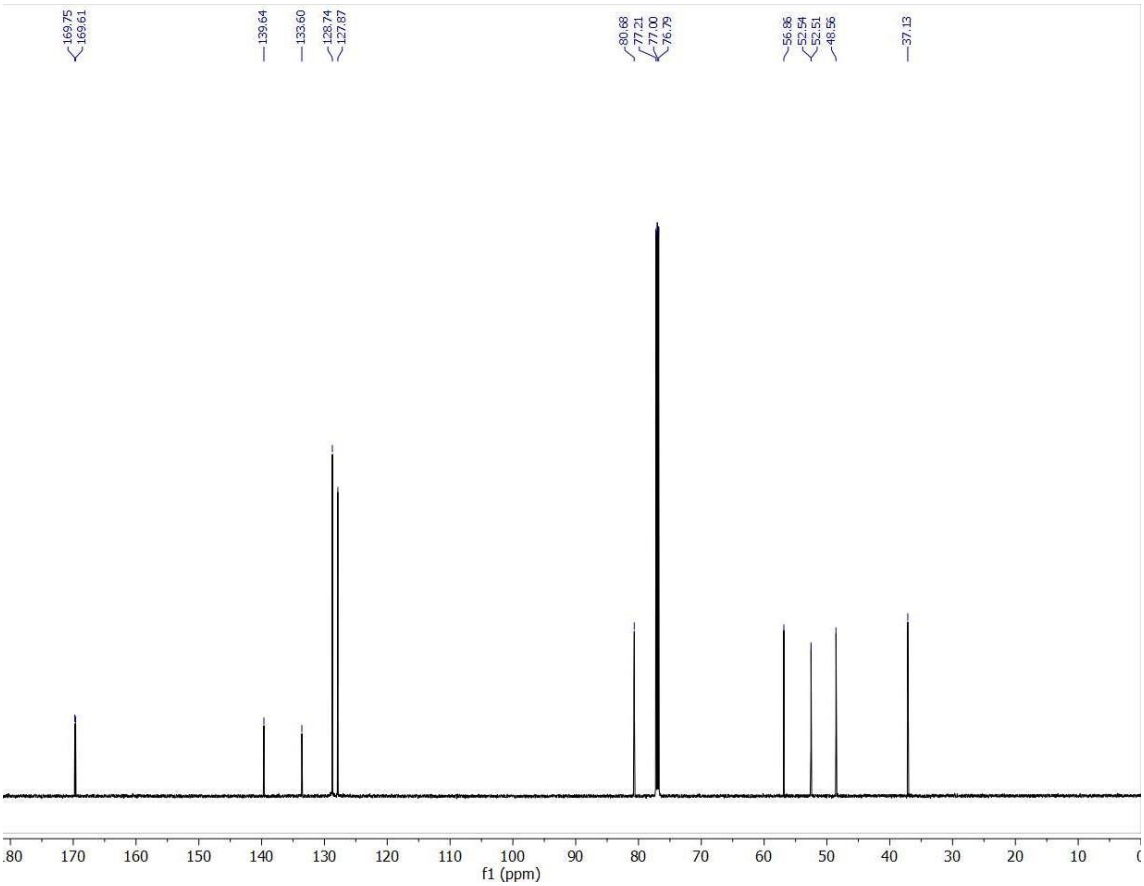

Figure SM4. ^{13}C NMR spectrum of dimethyl 2-(2-(4-chlorophenyl)-2-methoxyethyl)malonate (**3b**).

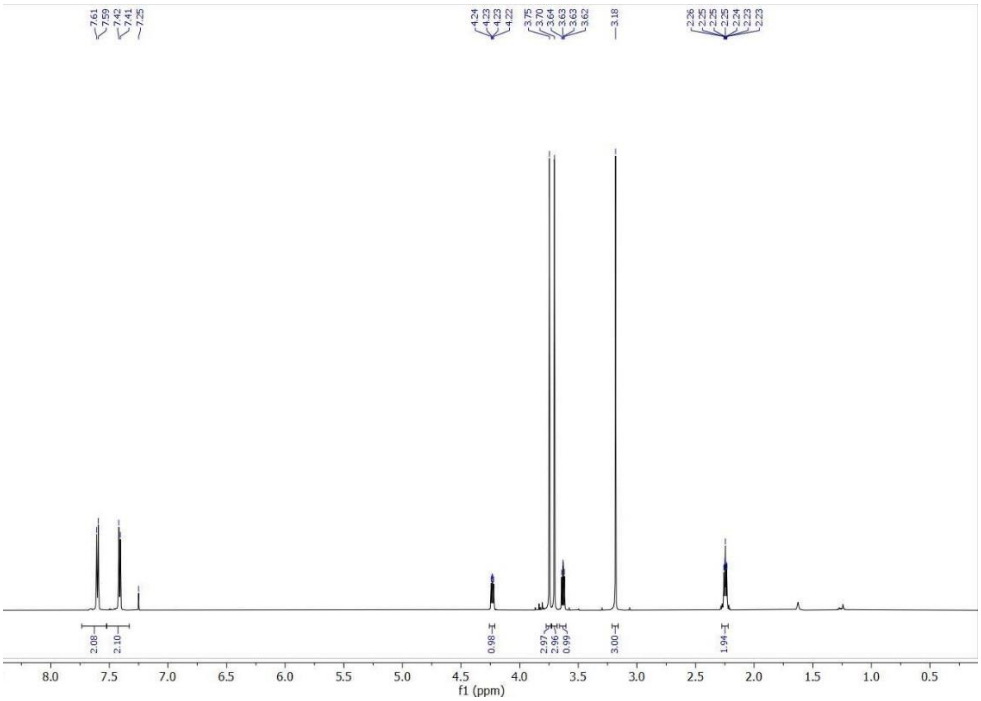

Figure SM5. ^{1}H spectrum of dimethyl 2-(2-methoxy-2-(4-trifluoromethyl)phenylethyl)malonate (**3c**).

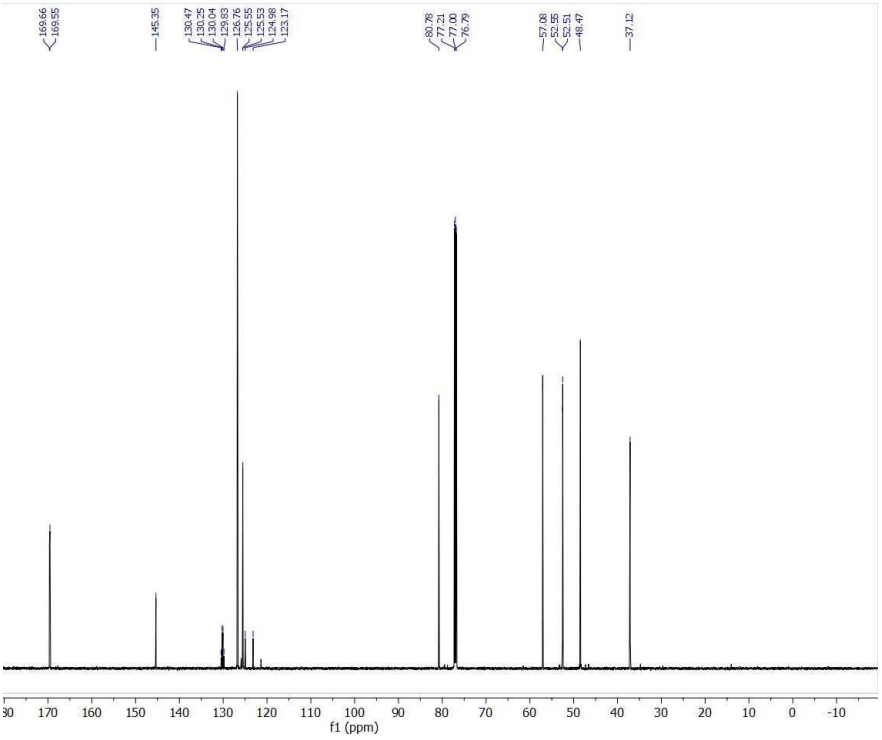

Figure SM6. ^{13}C NMR spectrum of dimethyl 2-(2-methoxy-2-(4-trifluoromethyl)phenylethyl)malonate (**3c**).

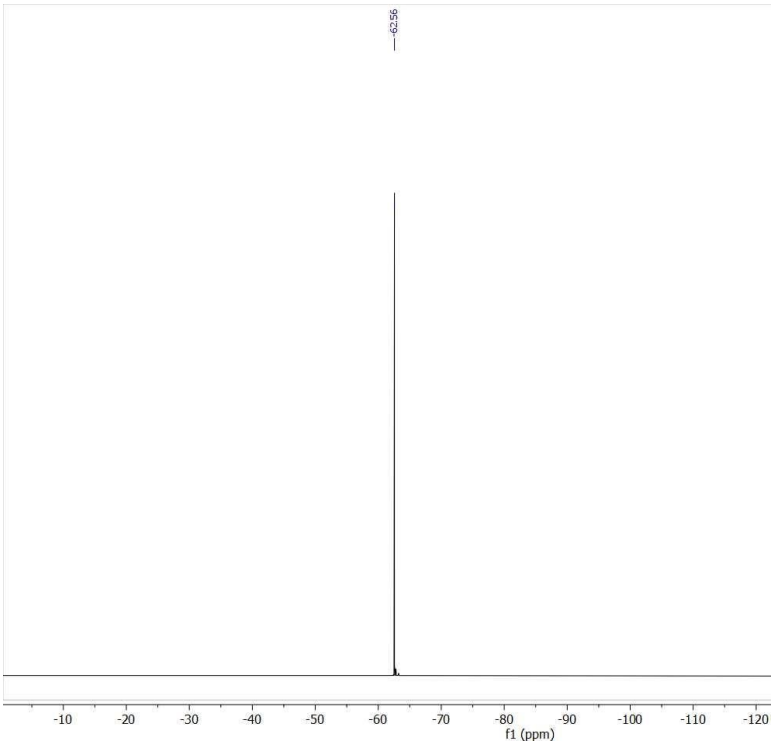

Figure SM7. ^{19}F NMR spectrum of dimethyl 2-(2-methoxy-2-(4-trifluoromethyl)phenylethyl)malonate (**3c**).

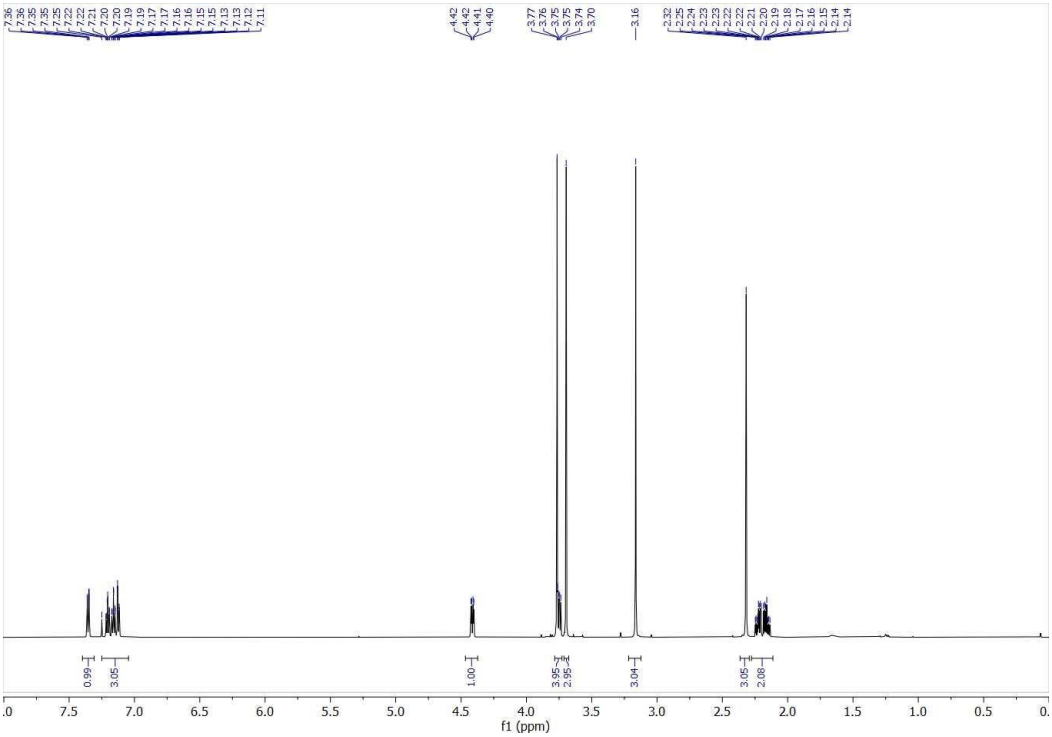

Figure SM8. ^{1}H NMR spectrum of dimethyl 2-(2-methoxy-2-(*o*-tolyl))ethyl)malonate (**3d**).

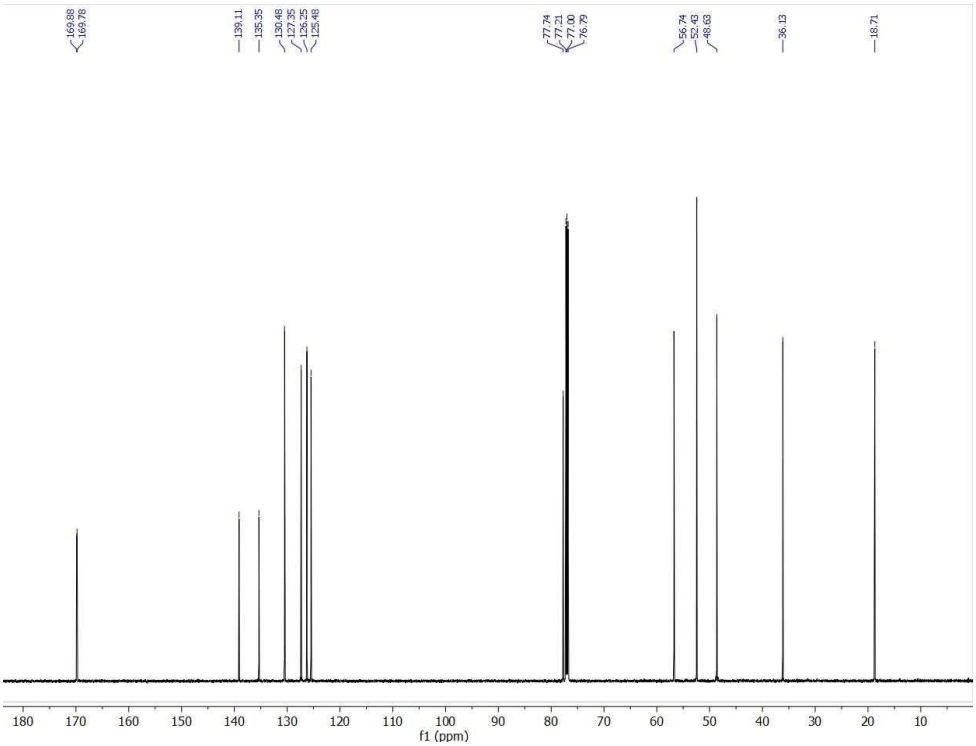

Figure SM9. ^{13}C NMR spectrum of dimethyl 2-(2-methoxy-2-(*o*-tolyl))ethyl)malonate (**3d**).

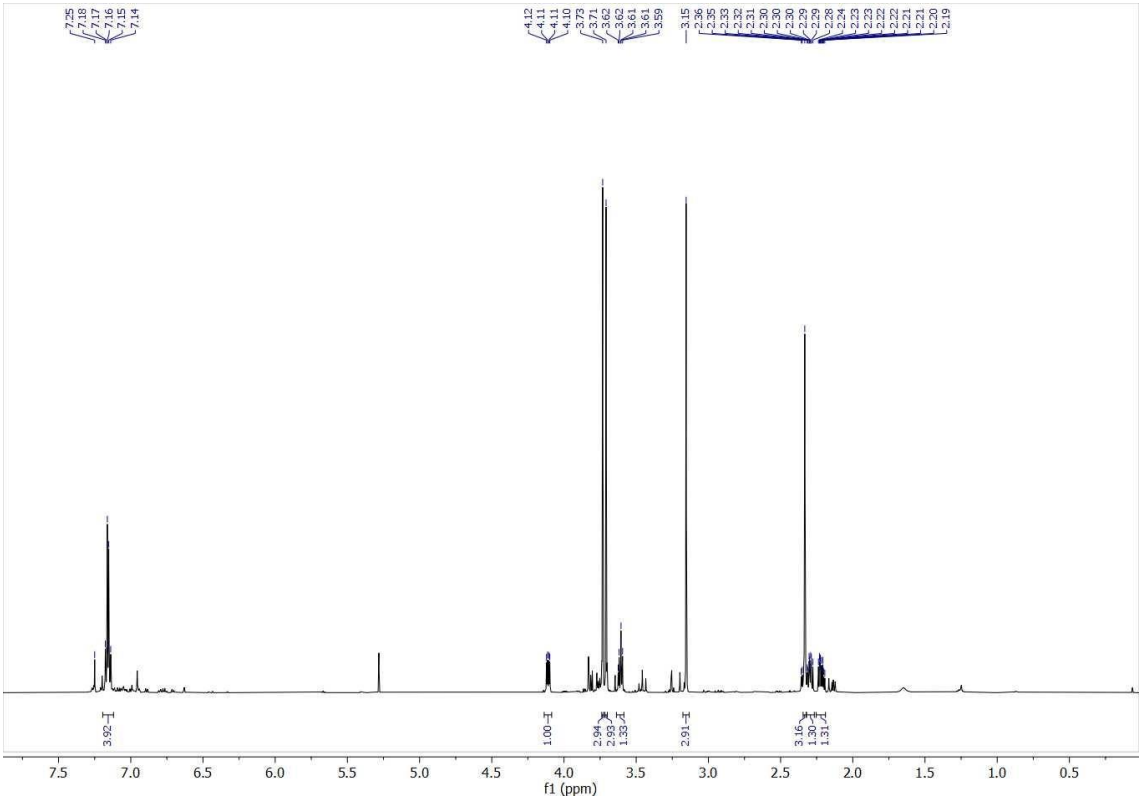

Figure SM10. ^{1}H NMR spectrum of dimethyl 2-(2-methoxy-2-(*p*-tolyl))ethyl)malonate (**3e**).

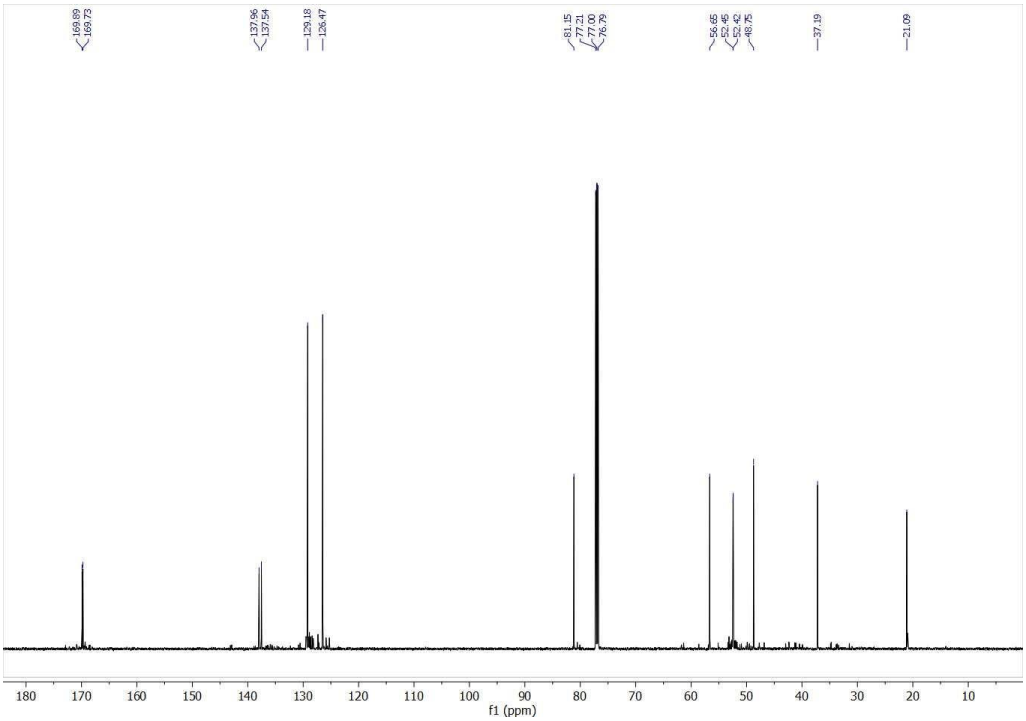

Figure SM11. ^{13}C NMR spectrum of dimethyl 2-(2-methoxy-2-(*p*-tolyl))ethyl)malonate (**3e**).

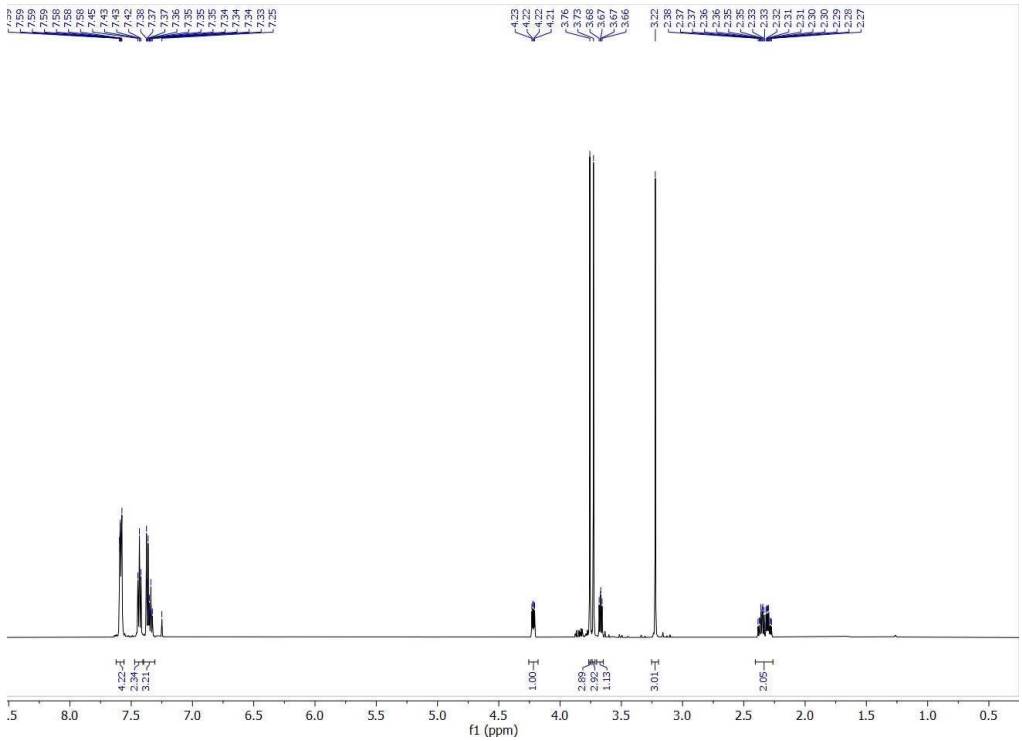

Figure SM12. ^{1}H NMR spectrum of dimethyl 2-(2-([1,1'-biphenyl]-4-yl)-2-methoxyethyl)malonate (**3f**).

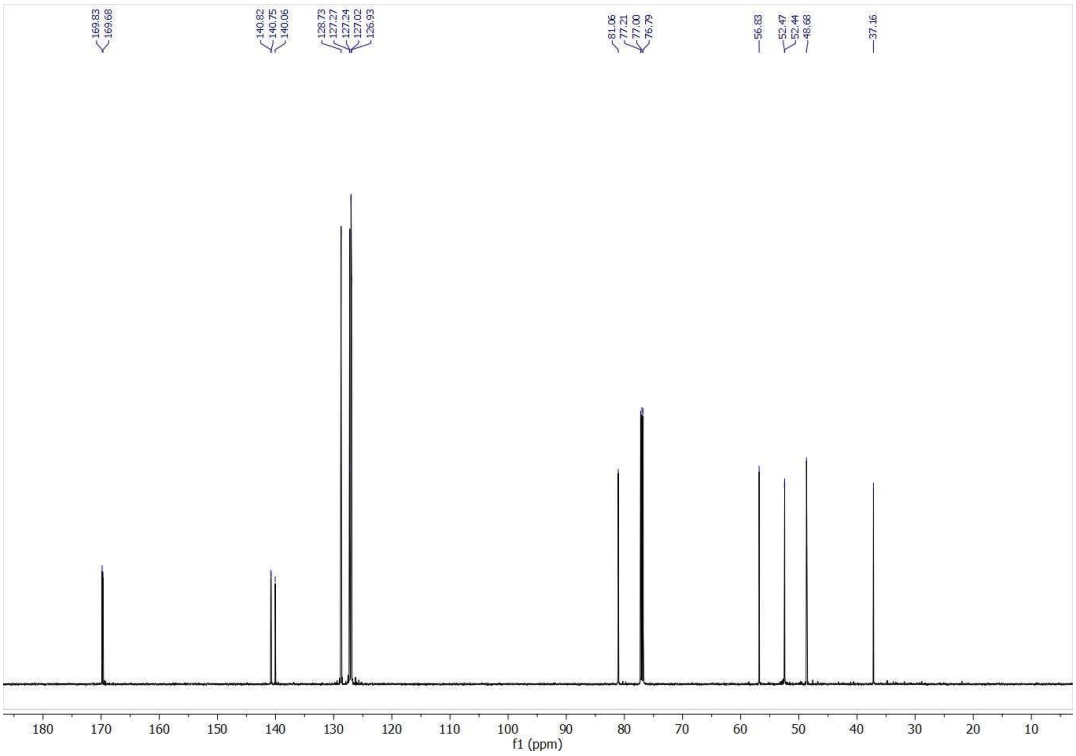

Figure SM13. ^{13}C NMR spectrum of dimethyl 2-(2-([1,1'-biphenyl]-4-yl)-2-methoxyethyl)malonate (**3f**).

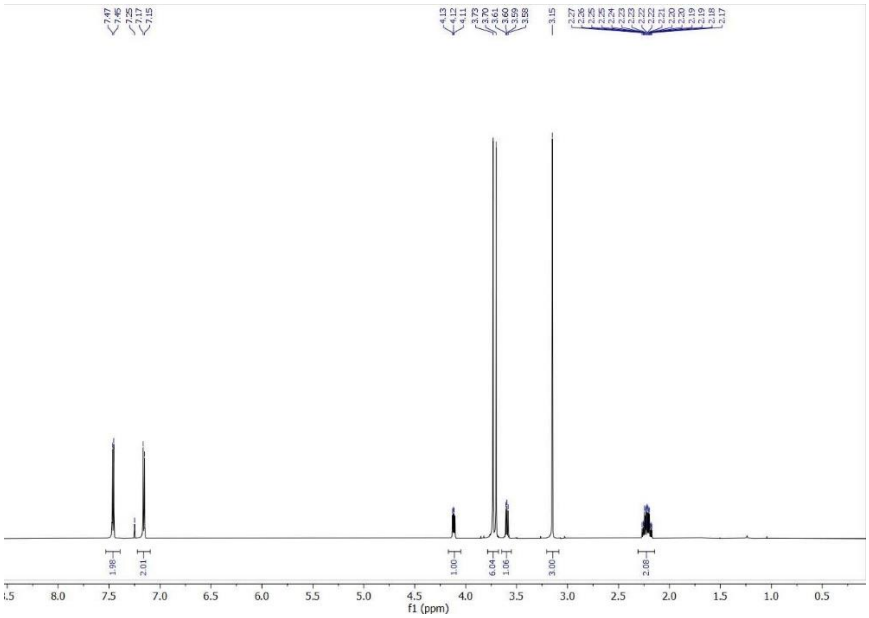

Figure SM14. ^{1}H NMR spectrum of dimethyl 2-(2-(4-bromophenyl)-2-methoxyethyl)malonate (**3g**).

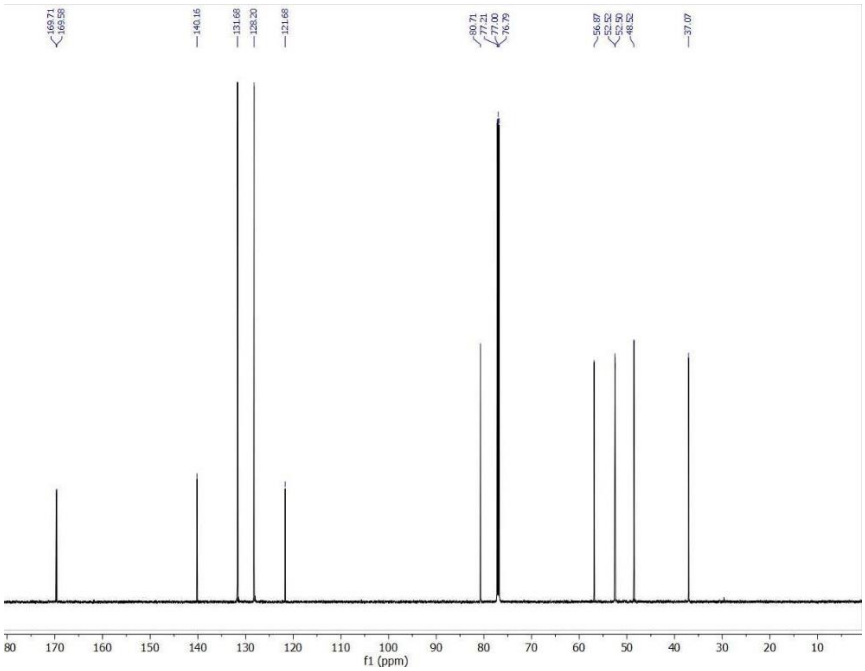

Figure SM15. ^{13}C NMR spectrum of dimethyl 2-(2-(4-bromophenyl)-2-methoxyethyl)malonate (**3g**).

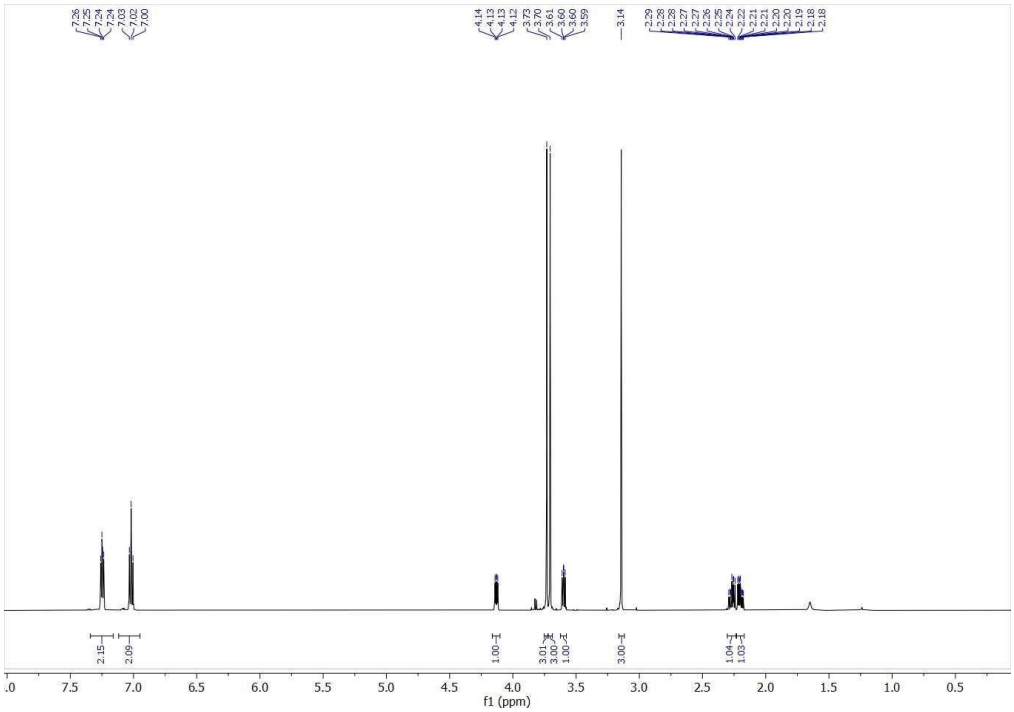

Figure SM16. ^{1}H NMR spectrum of dimethyl 2-(2-(4-fluorophenyl)-2-methoxyethyl)malonate (**3h**).

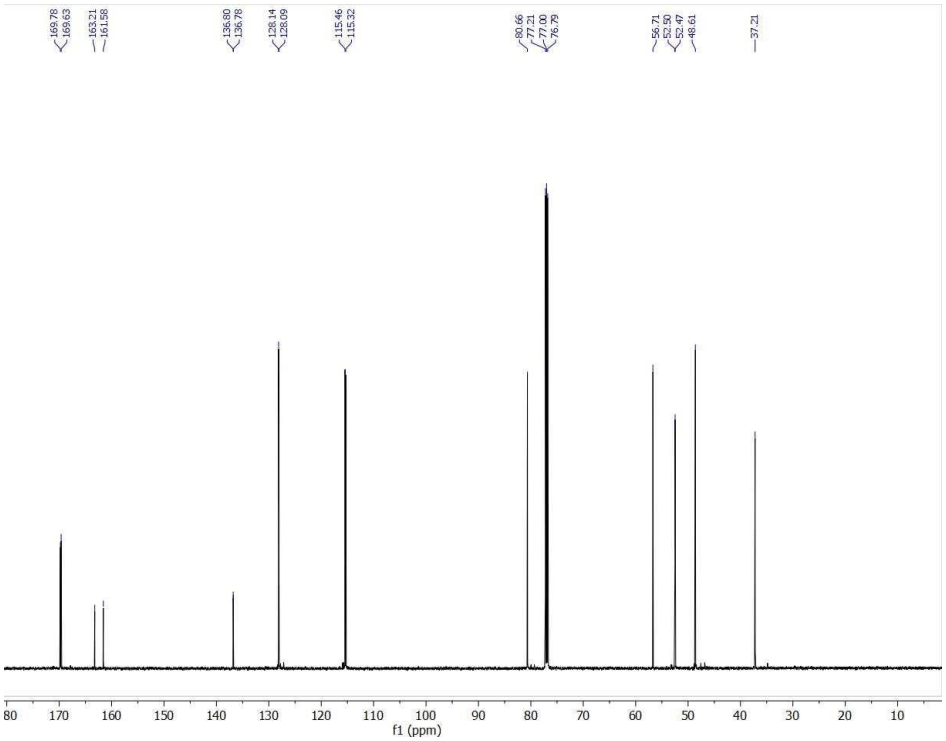

Figure SM17. ^{13}C NMR spectrum of dimethyl 2-(2-(4-fluorophenyl)-2-methoxyethyl)malonate (**3h**).

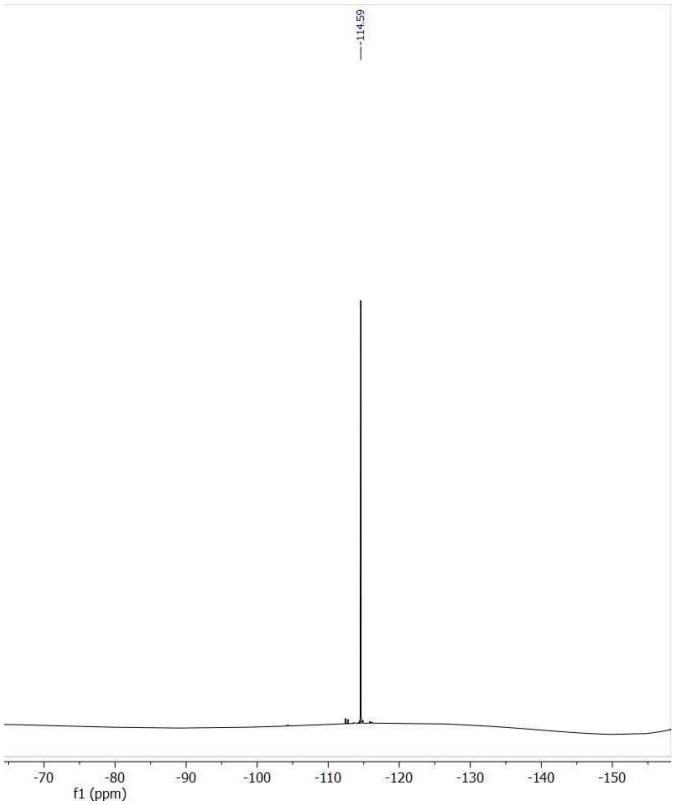

Figure SM18. ^{19}F NMR spectrum dimethyl 2-(2-(4-fluorophenyl)-2-methoxyethyl)malonate (**3h**).

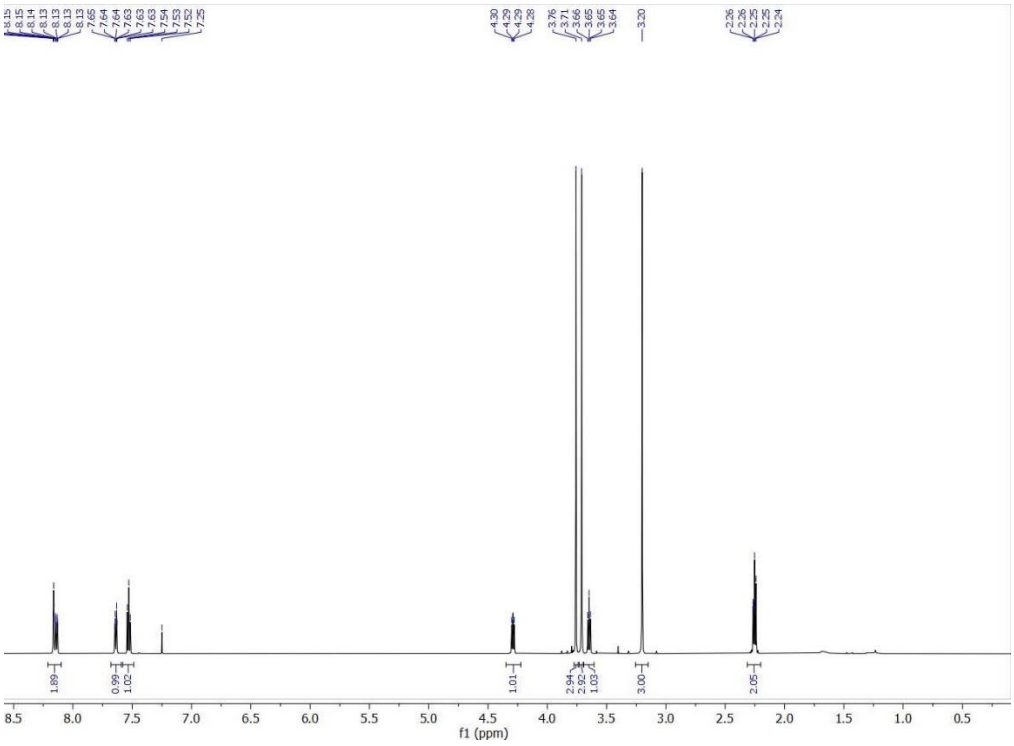

Figure SM19. ^{1}H NMR spectrum of dimethyl 2-(2-methoxy-3-nitrophenyl)ethyl)malonate (**3i**).

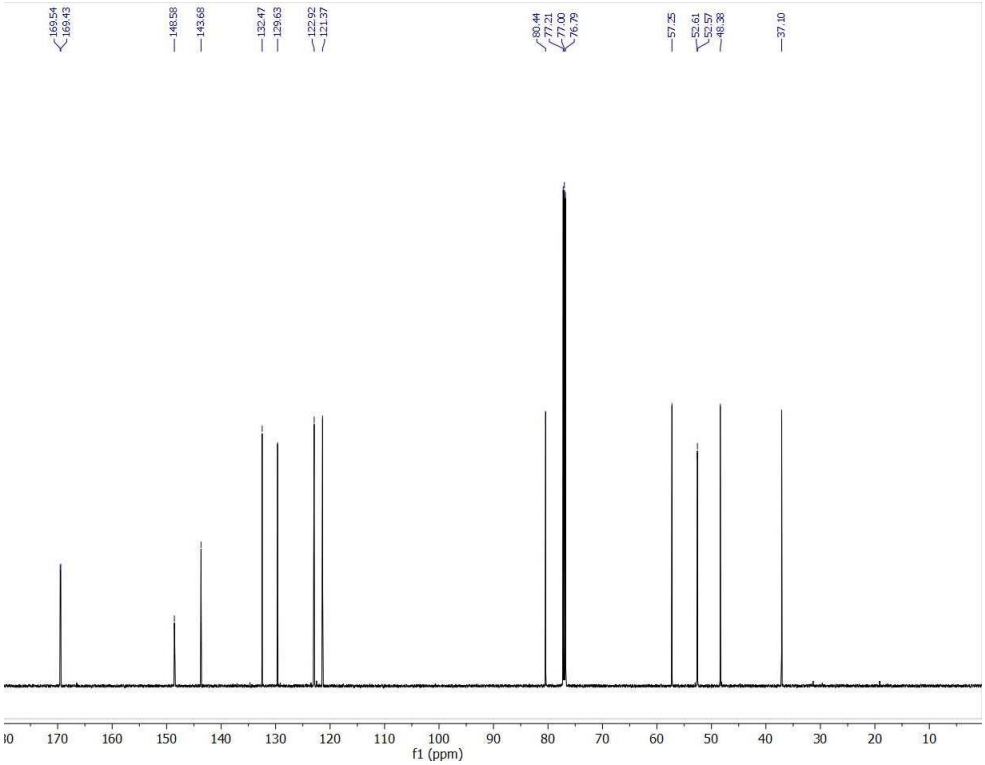

Figure SM20. ^{13}C NMR spectrum of dimethyl 2-(2-methoxy-3-nitrophenyl)ethyl)malonate (**3i**).

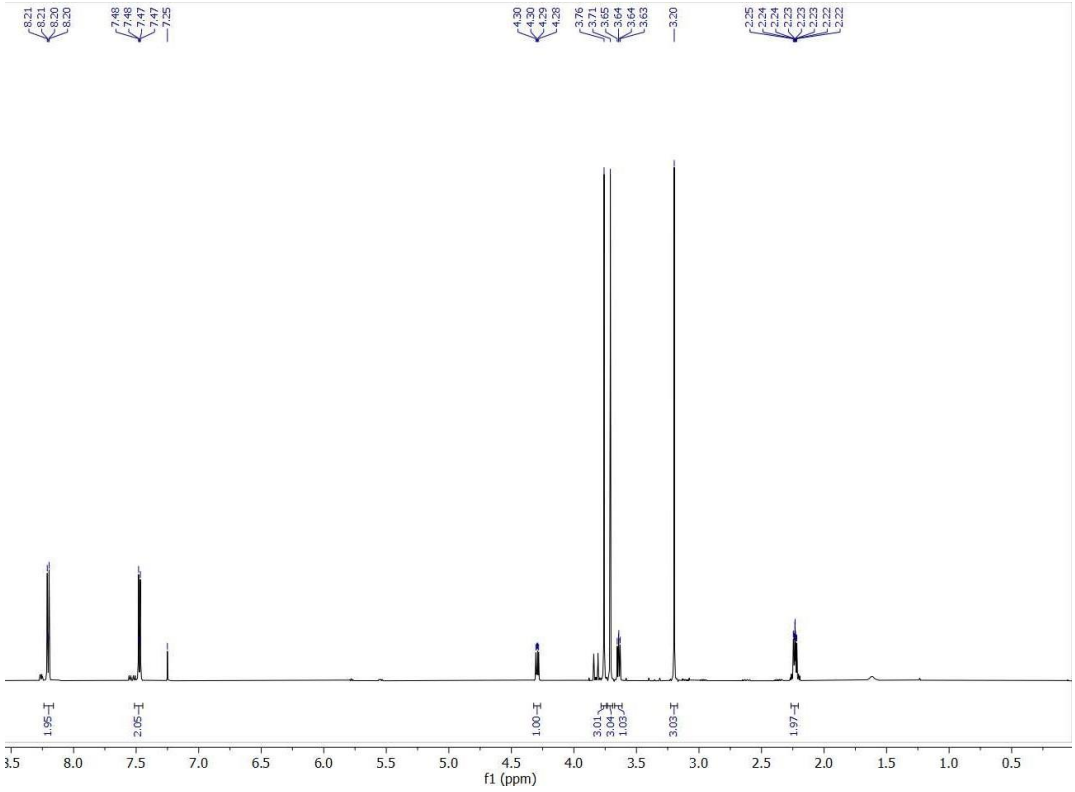

Figure SM21. ^{1}H NMR spectrum of dimethyl 2-(2-methoxy-4-nitrophenyl)ethyl)malonate (**3j**).

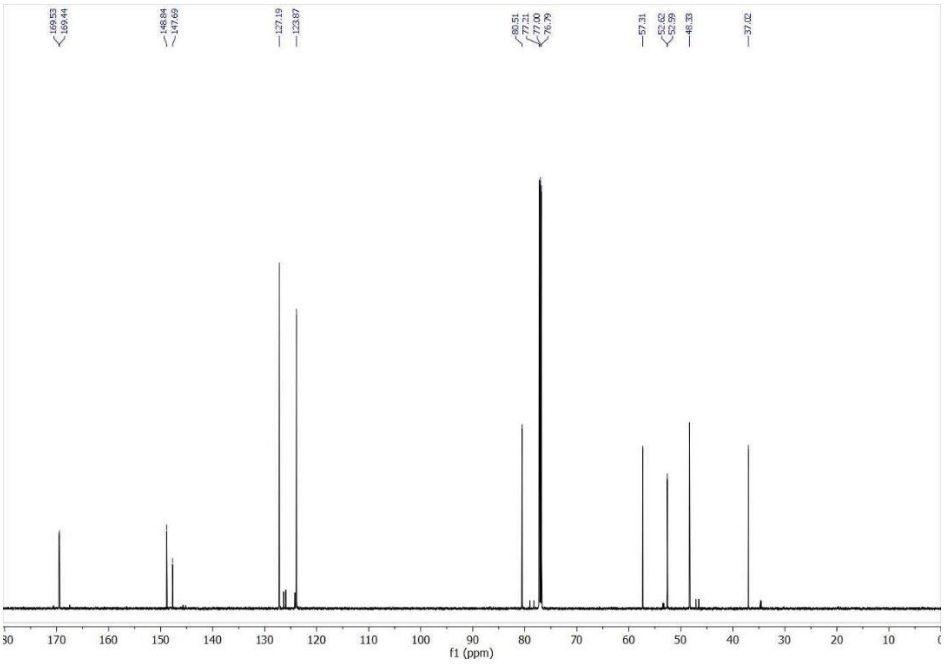

Figure SM22. ^{13}C NMR spectrum of dimethyl 2-(2-methoxy-4-nitrophenyl)ethyl)malonate (**3j**).

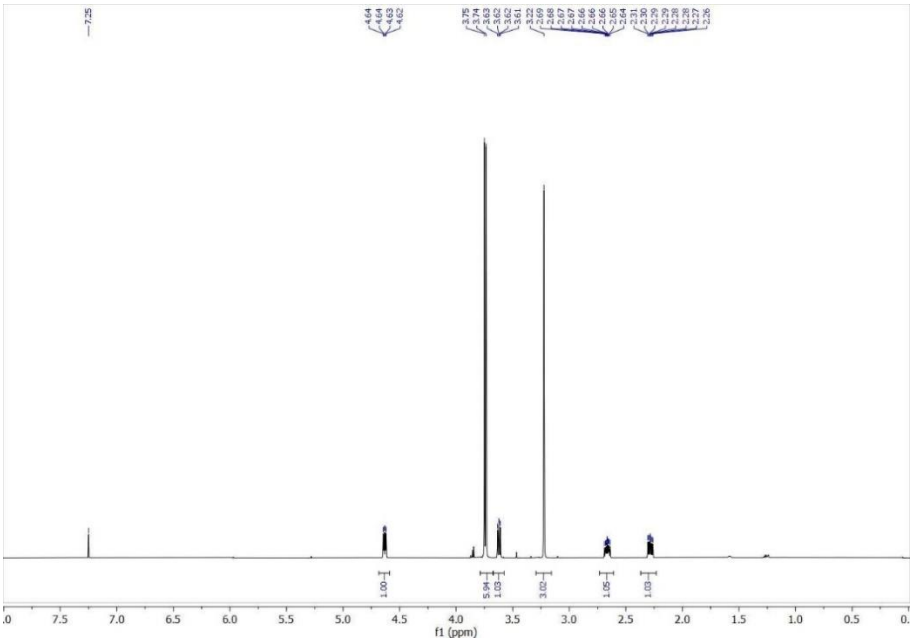

Figure SM23. ^{1}H NMR spectrum of dimethyl 2-(2-methoxy-2-(perfluorophenyl)ethyl)malonate (**3k**).

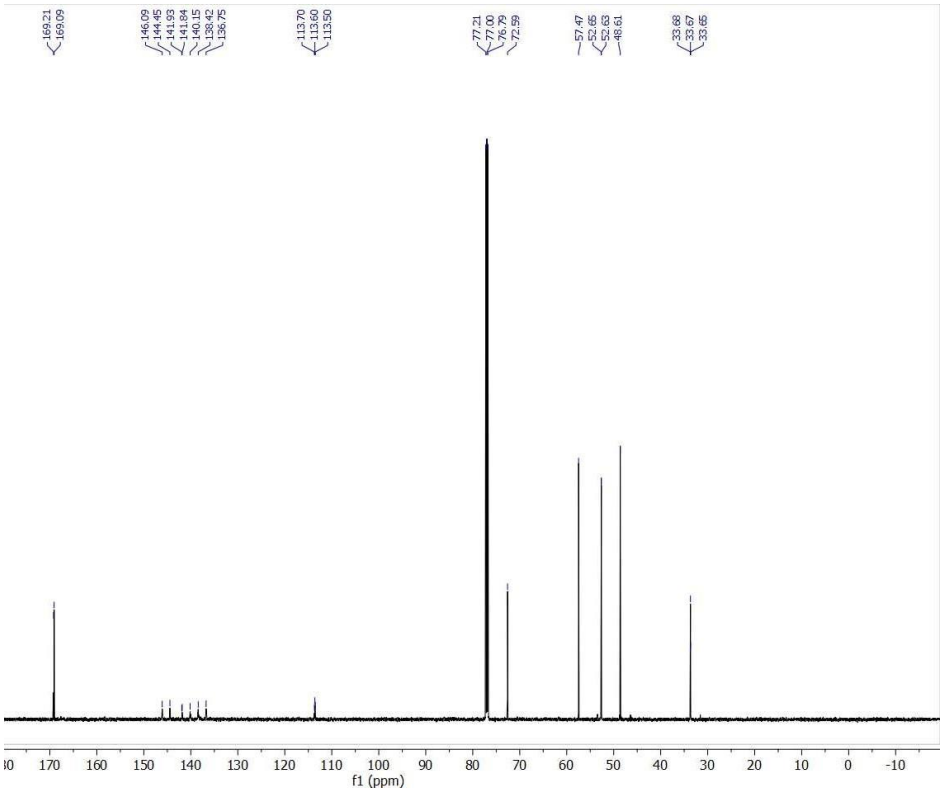

Figure SM24. ^{13}C NMR spectrum of dimethyl 2-(2-methoxy-2-(perfluorophenyl)ethyl)malonate (**3k**).

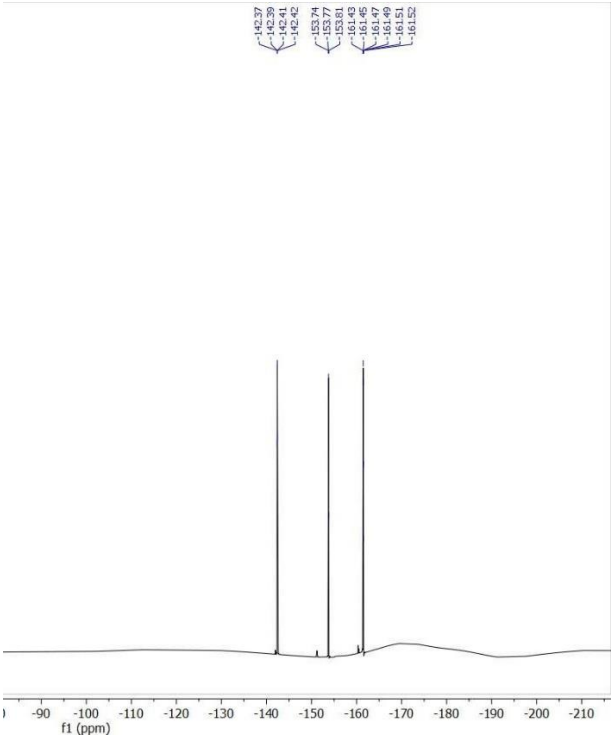

Figure SM25. ^{19}F NMR spectrum of dimethyl 2-(2-methoxy-2-(perfluorophenyl)ethyl)malonate (**3k**).

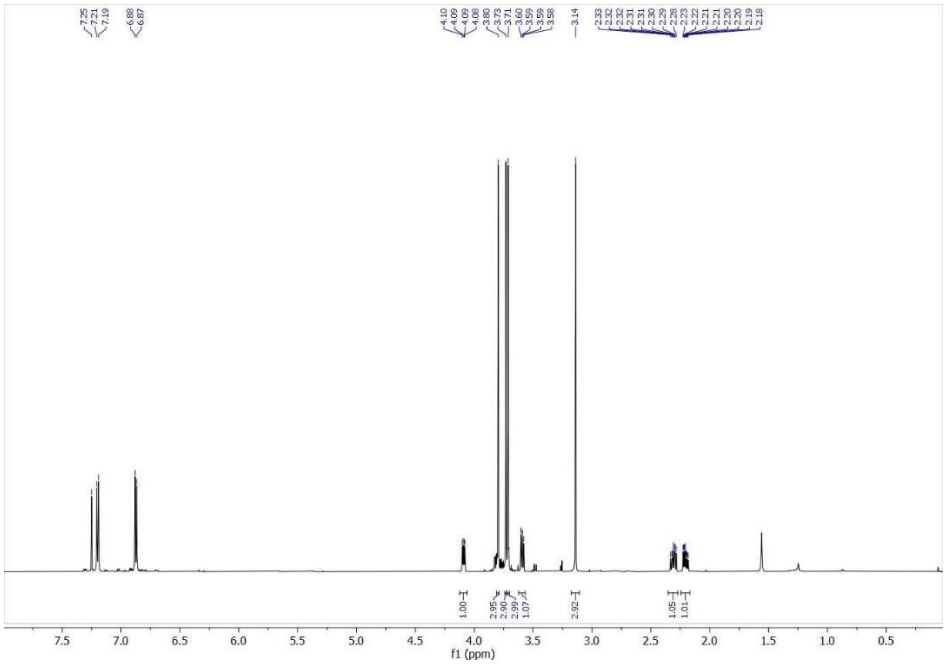

Figure SM26. ^{1}H NMR spectrum of dimethyl 2-(2-methoxy-2-(4-methoxyphenyl)ethyl)malonate (**3l**).

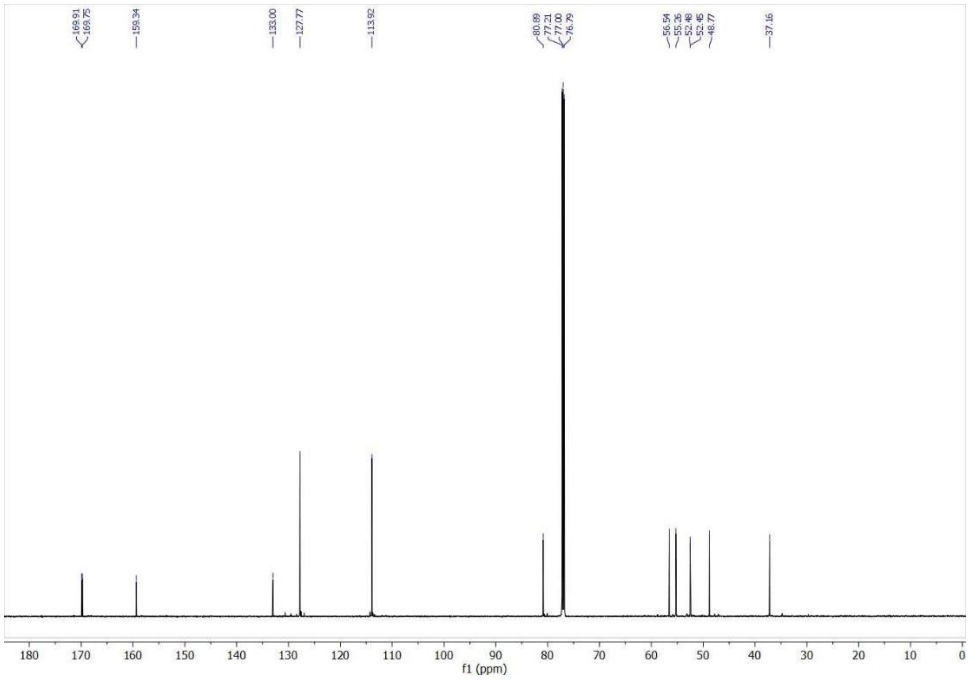

Figure SM27. ^{13}C NMR spectrum of dimethyl 2-(2-methoxy-2-(4-methoxyphenyl)ethyl)malonate (**3l**).

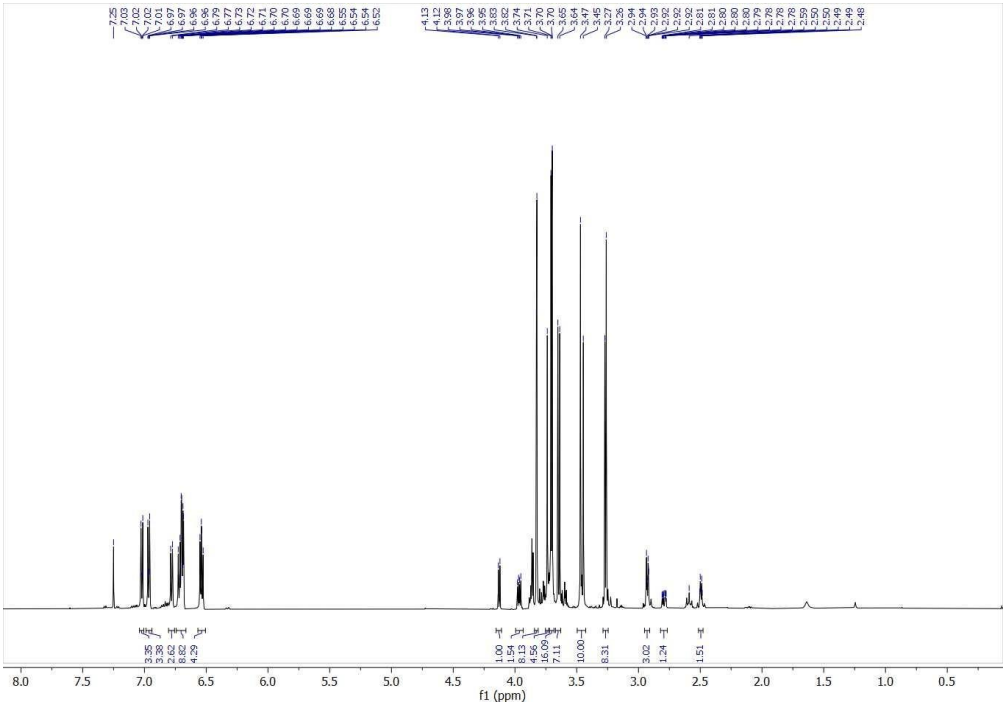

Figure SM28. ^{1}H NMR spectrum of mixture of *cis*- and *trans*-dimethyl 6-methoxy-(3-methoxy-2-(methoxycarbonyl)-3-oxopropyl-4-(4-methoxyphenyl)3,4-dihydronaphtalene-2,2-(1*H*)-dicarboxylate) (*cis*- and *trans*-**4**).

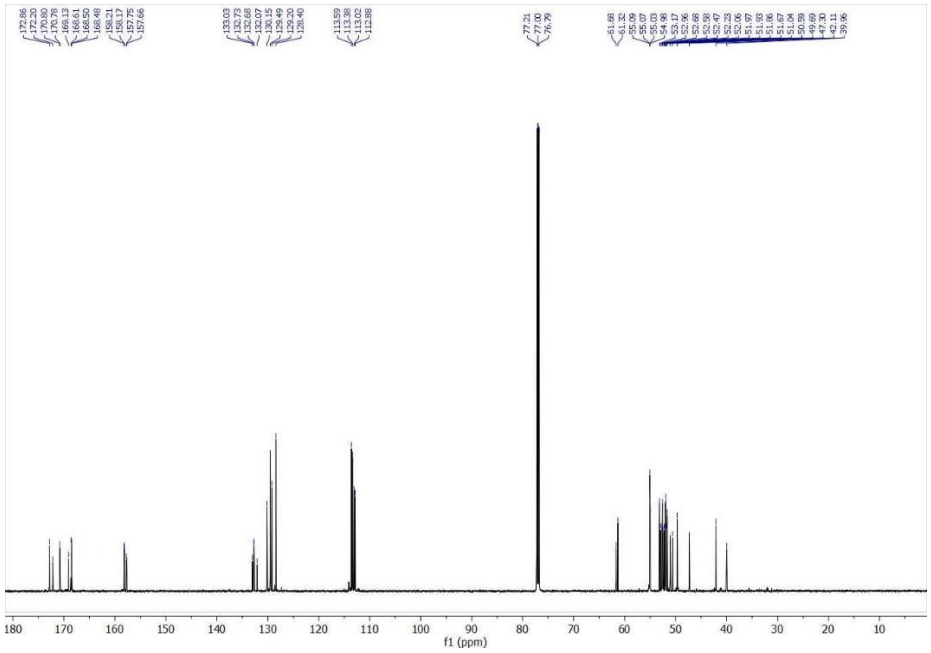

Figure SM29. ^{13}C NMR spectrum of mixture of *cis*- and *trans*-dimethyl 6-methoxy-(3-methoxy-2-(methoxycarbonyl)-3-oxopropyl-4-(4-methoxyphenyl)3,4-dihydronaphtalene-2,2-(1*H*)-dicarboxylate) (*cis*- and *trans*-**4**).