Supporting Information

Highly regio- and enantioselective hydrogenation of conjugated *α*-substituted dienoic acids

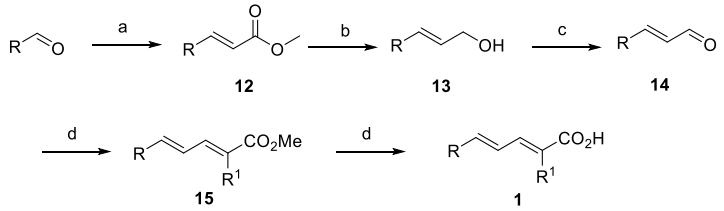
Xian Liu [a], Song Liu [b], Quanjun Wang [a], Gang Zhou[a], Lin Yao [a], Qin Ouyang [d], Ru Jiang[*a], Yu Lan[*b,c], Weiping Chen[*a]
[a]School of Pharmacy, Fourth Military Medical University, 169 Changle West Road, Xi'an, 710032, China.
[b]School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China. E-mail: lanyu@cqu.edu.cn
[c]Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou Henan, 450001, China.
[d]College of Pharmacy, Third Military Medical University, Chongqing 400038, China
Email: jiangru@fmmu.edu.cn, 1539247436@qq.com

Contents

1. General information

Unless otherwise noted, all commercially available chemicals including solvents were used without further purification. (S_C,S_C,R_{Fc},R_{Fc},R_P,R_P)-**TriFer** was prepared according to published procedures[1]. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 spectrophotometer. High-Resolution Mass Spectroscopy (HRMS) was carried out on a VARIA FT-ICR MS. High performance liquid chromatography (HPLC) was performed on an Agilent 1260 series using Daicel Chiralcel chiral column. ^{1}H NMR and ^{13}C NMR spectra were provided for reported compounds.

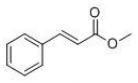
2. Preperation of substrates 1



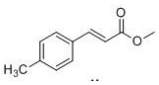
Reagents and conditions: a) *n*-BuLi (1.2 equiv.), methyl diethyl phosphonoacetate (1.2 equiv.) / THF, 0 °C→ r.t.; b) DIBAL-H (2.2 equiv.) / DCM, 0 °C; c) DMP (2.0 equiv.) / DCM； d) *n*-BuLi (1.2 equiv.), methyl 2-(diethoxyphosphoryl)- propanoate (1.2 equiv.) / THF, 0 °C→ r.t.; e) NaOH (3.0 equiv.), MeOH

2.1 General procedure for the preparation of methyl cinnamate derivatives 12:

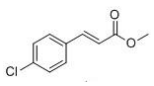
n-BuLi (24 mL, 60 mmol, 2.5 M solution in hexane) was added dropwise to a solution of methyl diethyl phosphonoacetate (12.6g, 60 mmol) in dry THF (150 mL) at 0 °C under nitrogen and was stirred for 30 minutes. A solution of benzaldehyde (50 mmol) in THF (50 mL) was added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After the completion of reaction monitored by TLC analysis, the reaction was quenched by addition of saturated ammonium chloride and the resulting aqueous phase was extracted 3 times with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The desired methyl cinnamate derivative **12** was obtained by silica-gel flash column chromatography (EtOAc/PE). The NMR spectra of compounds **12** accord with reported literatures [2-8].



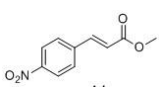
12a obtained from benzaldehyde (5.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 8.0g, 99% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.53- 7.40 (m, 2H), 7.39- 7.26 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7.



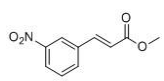
12b obtained from 4-methylbenzaldehyde (6.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 8.6 g, 98% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.48- 7.32 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 3.80 (d, *J* = 1.4 Hz, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 144.9, 140.7, 131.7, 129.8, 128.1, 116.7, 51.7, 21.5.



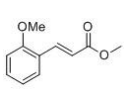
12c obtained from 4-chlorobenzaldehyde (7.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 9.6 g, 98% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.55- 7.31 (m, 4H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 143.4, 136.2, 132.9, 129.2, 129.2, 118.4, 51.8.



12d obtained from 4-nitrobenzaldehdye (7.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, light yellow solid, 10.0 g, 97% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.2 Hz, 2H), 7.97- 7.44 (m, 3H), 6.57 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 148.5, 141.9, 140.5, 128.7, 124.2, 122.1, 52.1.

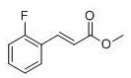


12e obtained from 3-nitrobenzaldehyde (7.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 10.0 g, 97% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (t, *J* = 2.0 Hz, 1H), 8.24 (m, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 16.1 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 16.1 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 148.7, 142.0, 136.1, 133.6, 130.0, 124.6, 122.5, 121.0, 52.0.

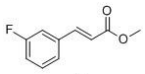


12f obtained from 2-methoxybenzaldehyde (6.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, light yellow solid, 9.3 g, 97% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 16.2 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.40- 7.26 (m, 1H), 7.05- 6.72 (m, 2H), 6.53 (d, *J* = 16.2 Hz,

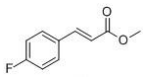
1H), 3.86 (d, *J* = 2.2 Hz, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 158.3, 140.3, 131.5, 128.9, 123.3, 120.7, 118.3, 111.1, 55.4, 51.6.



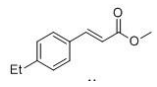
12g obtained from 2-fluorobenzaldehyde (6.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 8.9 g, 99% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 16.2 Hz, 1H), 7.55- 7.51 (m, 1H), 7.38- 7.33 (m, 1H), 7.18- 7.05 (m, 2H), 6.55 (d, *J* = 16.3 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 162.6, 160.1, 137.5, 131.7, 129.1, 124.4, 120.4, 116.2, 51.8.



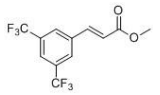
12h obtained from 3-fluorobenzaldehyde (6.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 8.8 g, 98% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 16.1 Hz, 1H), 7.44- 7.18 (m, 3H), 7.15- 6.99 (m, 1H), 6.43 (dd, *J* = 16.0, 2.1 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 164.2, 143.4, 136.6, 130.4, 124.1, 119.2, 117.1, 114.3, 51.8.



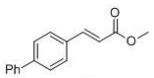
12i obtained from 4-fluorobenzaldehyde (6.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 8.9 g, 99% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.52- 7.49 (m, 2H), 7.19- 7.05 (m, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 165.1, 143.6, 130.6, 123.0, 117.5, 116.1, 51.7.



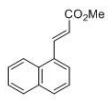
12j obtained from 4-ethylbenzylaldehyde (6.7 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 9.2 g, 97% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 147.0, 144.9, 131.9, 128.5, 128.2, 116.7, 51.6, 28.8, 15.4.



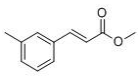
12k obtained from 3,5-bis(trifluoromethyl)benzaldehyde (12.1 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 14.5 g, 97% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94- 7.70 (m, 4H), 6.58 (d, *J* = 16.1 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 141.2, 136.5, 132.5, 127.7, 124.3, 123.4, 121.7, 52.1.



12l obtained from 4-phenylbenzaldehyde (9.1 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 11.7 g, 98% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.66- 7.55 (m, 6H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.41- 7.32 (m, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 144.4, 143.1, 140.2, 133.3, 128.9, 128.6, 127.9, 127.6, 127.1, 117.6, 51.8.



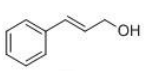
12m obtained from 1-naphthaldehyde (7.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow oil, 10.6 g, 96% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 15.8 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.86- 7.70 (m, 3H), 7.54- 7.41 (m, 3H), 6.51 (d, *J* = 15.7 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 141.9, 133.7, 131.7, 131.4, 130.6, 128.8, 126.9, 126.3, 125.5, 125.0, 123.4, 120.4, 51.8.



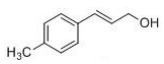
12s obtained from 3-methylbenzaldehyde (6.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 8.5 g, 97% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, J = 16.0 Hz, 1H), 7.33 (d, *J* = 6.6 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H),6.43 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 144.8, 138.5, 134.4, 131.1, 128.8, 128.7, 125.3, 118.0, 51.6, 21.4.

2.2 General procedure for the preparation of cinnamyl alcohol derivatives 13:

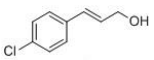
DIBAL-H (100 mL, 0.1 mol, 1 M solution in toluene) was added dropwise to a solution of methyl cinnamate derivative **12** (40 mmol) in DCM (200 mL) through 30 minutes at -78 °C under nitrogen. After completion of reaction monitored by TLC analysis, the reaction mixture was quenched by MeOH and allowed to warm to ambient temperature gradually. Then, the saturated aqueous solution of Rochelles salt was added and the resulting emulsion was stirred at ambient temperature until emulsion was clear-up. The organic phase was extracted 3 times with ethyl acetate, and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The desired cinnamyl alcohol derivative **13** was obtained by silica-gel flash column chromatography (EtOAc/PE). The NMR spectra of compounds **13** accord with reported literatures [9-15].



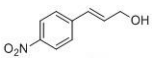
13a obtained from **12a** (6.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 5.1 g, 95% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29- 7.16 (m, 5H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.24- 6.16 (m, 1H), 4.12 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.0, 134.2, 128.7, 128.3, 126.8, 125.0, 45.5.



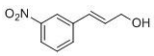
13b obtained from **12b** (7.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 5.9 g, 98% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.0, 5.8 Hz, 1H), 4.30 (dd, J = 5.8, 1.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.6, 133.9, 131.2, 129.3, 127.5, 126.4, 63.8, 21.2.



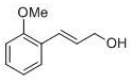
13c obtained from **12c** (7.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 6.5 g, 96% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31- 7.26 (m, 4H), 6.67- 6.46 (m, 1H), 6.32 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.31 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.2, 133.3, 129.7, 129.2, 128.8, 127.7, 63.5.



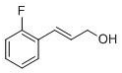
13d obtained from **12d** (8.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 6.7 g, 94% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.79- 6.66 (m, 1H), 6.55 (dt, *J* = 16.0, 5.1 Hz, 1H), 4.50- 4.30 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.0, 143.3, 133.6, 128.3, 126.9, 124.1, 63.1.



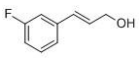
13e obtained from **12e** (8.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 6.8 g, 95% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25- 8.19 (m, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.71- 7.64 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 6.69 (dd, *J* = 15.9, 1.8 Hz, 1H), 6.54- 6.47 (m, 1H), 4.43- 4.36 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6, 138.6, 132.3, 132.0, 129.5, 128.2, 122.2, 121.0, 63.1.



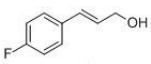
13f obtained from **12f** (7.7 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 6.3 g, 96% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.30- 7.22 (m, 1H), 6.94- 6.84 (m, 3H), 6.40- 6.32 (m, 1H), 4.30 (d, *J* = 5.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.7, 129.4, 128.8, 127.0, 126.1, 125.7, 120.7, 110.8, 64.2, 55.4.



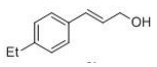
13g obtained from **12g** (7.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 5.8 g, 96% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46- 7.41 (m, 1H), 7.28- 7.26 (m, 1H), 7.21- 7.02 (m, 2H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.47- 6.42 (m, 1H), 4.33 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.3, 131.2, 128.9, 127.5, 124.5, 124.3, 123.4, 115.7, 63.8.



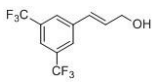
13h obtained from **12h** (7.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 5.7 g, 95% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30- 7.21 (m, 1H), 7.11- 7.03 (m, 2H), 6.97- 6.89 (m, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.35- 6.28 (m, 1H), 4.28 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1, 139.1, 130.0, 129.5, 122.3, 114.5, 113.6, 112.8, 63.2.



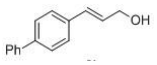
13i obtained from **12i** (7.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 5.9 g, 97% yiled.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.31 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4, 132.8, 130.0, 128.2, 127.9, 115.5, 63.6.



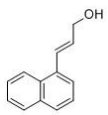
13j obtained from **12j** (7.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 6.3 g, 98% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32- 7.30 (m, 2H), 7.26- 7.10 (m, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.36- 6.26 (m, 1H), 4.31 (d, *J* = 5.7 Hz, 2H), 2.64 (q, *J* = 8.0 Hz, 2H), 1.23 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.0, 134.1, 131.3, 128.1, 127.5, 126.5, 63.9, 28.6, 15.5.



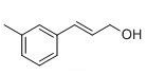
13k obtained from **12k** (11.9 g)after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 10.2 g, 95% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 22.9 Hz, 3H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.56- 6.50 (m, 1H), 4.41 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 132.9, 131.9, 127.6, 126.2, 124.6, 121.4, 62.9.



13l obtained from **12l** (9.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 8.2 g, 98% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68- 7.52 (m, 4H), 7.48- 7.42 (m, 4H), 7.39- 7.30 (m, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.45- 6.38 (m, 1H), 4.35 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.7, 140.5, 135.7, 130.7, 128.8, 128.6, 127.4, 127.3, 127.0, 126.9, 63.8.



13m obtained from **12m** (8.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, light yellow solid, 7.0 g, 95% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14- 8.11 (m, 1H), 7.87- 7.78 (m, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.54- 7.36 (m, 4H), 6.43- 6.36 (m, 1H), 4.43 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.5, 133.6, 131.8, 131.2, 128.6, 128.1, 128.0, 126.1, 125.8, 125.7, 123.9, 123.8, 63.9.

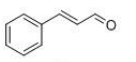


13s obtained from **12s** (7.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 5.7 g, 96% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33- 7.10 (m, 3H), 7.08- 6.93 (m, 1H), 6.54 (dd,

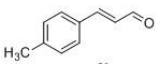
J = 15.9, 1.6 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.27 (d, *J* = 5.7 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.2, 136.7, 131.1, 128.5, 128.5, 128.4, 127.3, 123.6, 63.6, 21.4.

2.3 General procedure for the preparation of cinnamaldehyde derivatives 14:

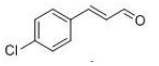
DMP (Dess-Martin periodiane, 25.4 g, 60 mmol) was added to a solution of cinnamyl alcohol derivative **13** (30 mmol) in DCM (150 mL). The reaction mixture was stirred at ambient temperature until the completion of reaction monitored by TLC analysis. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ and the aqueous phase was extracted 3 times with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* filtration. The desired cinnamaldehyde derivative **14** was obtained by silica-gel flash column chromaography (EtOAc/PE). The NMR spectra of compounds **14** accord with reported literatures [16-21].



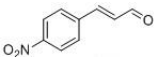
14a was obtained from **13a** (4.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 3.6 g, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.59- 7.35 (m, 6H), 6.73 (dd, *J* = 15.9, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.8, 152.9, 134.0, 131.3, 129.1, 128.6, 128.5.



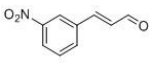
14b was obtained from **13b** (4.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow oil, 4.1 g, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.66 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 5.7 Hz, 3H), 7.22 (d, *J* = 7.7 Hz, 2H), 6.69- 6.63 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.8, 153.0, 142.0, 131.4, 129.9, 128.6, 127.7, 21.6.



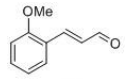
14c was obtained from **13c** (5.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 4.6 g, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.71 (d, *J* = 7.5 Hz, 1H), 7.52- 7.40 (m, 5H), 6.69 (dd, *J* = 15.9, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.3, 151.0, 137.3, 132.5, 129.6, 129.5, 129.0.



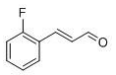
14d was obtained from **13d** (5.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 4.7 g, 90% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.79 (d, *J* = 7.4 Hz, 1H), 8.43- 8.29 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 16.0 Hz, 1H), 6.82 (dd, *J* = 16.1, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.8, 149.0, 148.8, 139.9, 131.8, 129.0, 124.3.



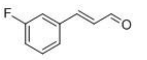
14e was obtained from **13e** (5.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, light yellow solid, 4.8 g, 91% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.78 (d, *J* = 7.4 Hz, 1H), 8.43 (t, *J* = 2.0 Hz, 1H), 8.30 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 16.1 Hz, 1H), 6.83 (dd, *J* = 16.1, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.8, 149.0, 135.7, 133.6, 130.9, 130.3, 125.4, 123.1, 77.2.



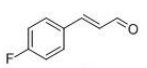
14f was obtained from **13f** (4.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 4.4 g, 89% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.69 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 16.1 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.44- 7.40 (m, 1H), 7.05- 6.88 (m, 2H), 6.79 (dd, *J* = 16.1, 7.9 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.6, 158.3, 148.3, 132.7, 129.1, 128.9, 123.0, 120.9, 111.3, 55.6.



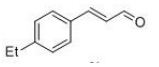
14g was obtained from **13g** (4.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 4.1 g, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.72 (d, *J* = 7.5 Hz, 1H), 7.75- 7.53 (m, 2H), 7.43- 7.41 (m, 1H), 7.30- 7.01 (m, 2H), 6.79 (dd, *J* = 16.4, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.9, 161.2, 144.8, 132.9, 130.5, 128.9, 124.8, 122.2, 116.5.



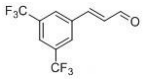
14h was obtained from **13h** (4.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 4.0 g, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.72 (d, *J* = 7.6 Hz, 1H), 7.47- 7.13 (m, 5H), 6.70 (dd, *J* = 16.0, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.4, 164.3, 151.0, 136.2, 130.7, 129.7, 124.4, 118.3, 114.8.



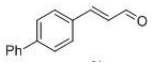
14i was obtained from **13i** (4.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, light yellow oil, 4.2 g, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.69 (d, *J* = 7.7 Hz, 1H), 7.60- 7.55 (m, 2H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.16- 7.10 (m, 2H), 6.66 (dd, *J* = 16.0, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.6, 163.2, 151.5, 130.6, 130.5, 128.3, 116.4.



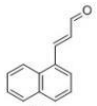
14j was obtained from **13j** (4.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 4.4 g, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.71 (dd, *J* = 7.7, 2.2 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.3 Hz, 3H), 7.29 (d, *J* = 6.5 Hz, 2H), 6.75- 6.68 (m, 1H), 2.72 (q, *J* = 8.0 Hz, 2H), 1.28 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.8, 153.0, 148.3, 131.6, 128.7, 128.7, 127.8, 28.9, 15.3.



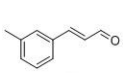
14k was obtained from **13k** (8.1 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 7.1 g, 89% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.79 (d, *J* = 7.3 Hz, 1H), 7.97 (d, *J* = 22.1 Hz, 3H), 7.54 (d, *J* = 16.1 Hz, 1H), 6.84 (dd, *J* = 16.1, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.4, 147.9, 136.1, 132.6, 131.4, 127.9, 124.2, 121.5.



14l was obtained from **13l** (6.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 5.7 g, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.73 (d, *J* = 7.7 Hz, 1H), 7.74- 7.58 (m, 6H), 7.57- 7.34 (m, 4H), 6.77 (dd, *J* = 15.9, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.7, 152.3, 144.1, 139.9, 133.0, 129.0, 129.0, 128.5, 128.1, 127.8, 127.1.



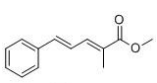
14m was obtained from **13m** (5.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 4.9 g, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 (d, *J* = 7.7 Hz, 1H), 8.36-8.17 (m, 2H), 7.97- 7.82 (m, 3H), 7.64- 7.51 (m, 3H), 6.88- 6.81 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.7, 149.4, 133.8, 131.7, 131.2, 130.9, 130.2, 129.0, 127.3, 126.5, 125.8, 125.5, 122.8.



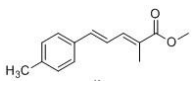
14s was obtained from **13s** (4.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow oil, 4.1 g, 93% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.69 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.44 (dd, *J* = 15.9, 1.6 Hz, 1H), 7.40- 7.28 (m, 3H), 7.25 (d, *J* = 7.0 Hz, 1H), 6.70 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.9, 153.2, 138.9, 134.0, 132.2, 129.2, 129.0, 128.4, 125.8, 21.3.

2.4 General procedure for the preparation of (2*E*,4*E*)-methyl 2-methyl-5-phenylpenta-2,4- dienoate derivatives 15a- 15n and 15s- 15t:

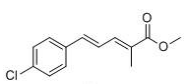
n-BuLi (14.5 mL, 36 mmol, 2.5 M solution in hexane) was added dropwise to a solution of methyl 2-(diethoxyphosphoryl)acetate derivatives (36 mmol) in dry THF (60 mL) at 0 °C under nitrogen and was stirred for 30 minutes. Cinnamaldehyde derivative **14** (30 mmol) in THF (60 mL) was added to the reaction mixture. The resulting mixture was stirred at ambient temperature until the completion of reaction monitored by TLC analysis. The reaction was quenched by addition of saturated ammonium chloride and the resulting aqueous phase was extracted 3 times with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The desired 2-methyl-5-phenylpenta-2,4-dienoate derivative **15** was obtained by silica-gel flash column chromatography (EtOAc/PE). The NMR spectra of compounds **15a-c** accord with reported literatures [22].



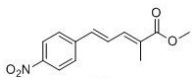
14a (4.0 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15a** (5.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 95% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56- 7.42 (m, 2H), 7.39- 7.24 (m, 4H), 7.07 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.87 (d, *J* = 15.4 Hz, 1H), 3.79 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 139.1, 138.5, 136.6, 128.8, 128.7, 127.1, 127.1, 123.9, 51.9, 12.9.



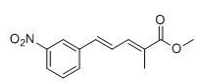
14b (4.4 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15b** (6.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 93% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 (t, *J* = 9.2 Hz, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.02 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.84 (d, *J* = 15.4 Hz, 1H), 3.78 (s, 3H), 2.36 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.9, 139.2, 138.9, 138.8, 133.9, 129.5, 127.0, 126.5, 122.9, 51.8, 21.4, 12.9.



14c (5.0 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15c** (6.7 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 94% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49- 7.28 (m, 5H), 7.03 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.81 (d, *J* = 15.5 Hz, 1H), 3.79 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 138.1, 137.6, 135.1, 134.4, 129.0, 128.2, 127.7, 124.4, 51.9, 12.9.

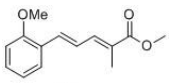


14d (5.3 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15d** (6.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 93% yield, m.p. 123- 125 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 9.0, 2.2 Hz, 2H), 7.64- 7.62 (m, 2H), 7.39 (d, *J* = 11.4 Hz, 1H), 7.23 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.92 (d, *J* = 15.4 Hz, 1H), 3.83 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 147.4, 142.9, 137.1, 136.0, 130.3, 128.0, 127.5, 124.2, 52.1, 13.2. HRMS (ESI) m/z: Calcd for $C_{13}H_{14}NO_4$ $[M+H]^+$: 248.0923; found 248.0916.

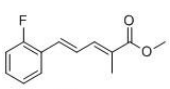


14e (5.3 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15e** (7.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, light yellow solid, 94% yield, m.p. 120-121 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 2.0 Hz, 1H), 8.14 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 11.3 Hz, 1H), 7.18 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.89 (d, *J* = 15.4 Hz,

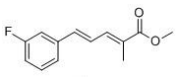
1H), 3.81 (s, 3H), 2.10 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 148.7, 138.3, 137.2, 135.9, 132.7, 129.7, 129.6, 126.7, 122.9, 121.3, 52.1, 13.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_4$ 248.0923; found 248.0912.



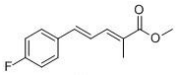
14f (4.9 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15f** (6.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 95% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.48- 7.38 (m, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 15.5 Hz, 1H), 7.10 (dd, *J* = 15.5, 11.2 Hz, 1H), 6.97- 6.88 (m, 2H), 3.83 (d, *J* = 39.5 Hz, 6H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 157.4, 139.5, 134.3, 129.8, 127.2, 126.3, 125.6, 124.5, 120.7, 111.1, 55.5, 51.8, 12.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}O_3$ 233.1178; found 233.1177.



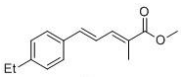
14g (4.5 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15g** (6.1 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 93% yield, m.p. 88- 89 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56- 7.52 (m, 1H), 7.37 (d, *J* = 11.2 Hz, 1H), 7.27- 6.98 (m, 5H), 3.79 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 161.9, 159.4, 138.6, 131.3, 130.0, 127.9, 127.8, 126.2, 124.4, 116.0, 52.0, 13.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}FO_2$ 221.0978; found 221.0975.



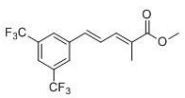
14h (4.5 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15h** (6.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 94% yield, m.p. 92- 93 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35- 7.16 (m, 4H), 7.08- 6.95 (m, 2H), 6.80 (d, *J* = 15.4 Hz, 1H), 3.78 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 161.9, 138.9, 137.9, 137.6, 130.2, 128.2, 125.1, 123.0, 115.5, 113.3, 51.9, 13.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_4FO_2$ 221.0978; found 221.0972.



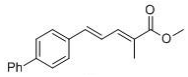
14i (4.5 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15i** (6.1 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 93% yield, m.p. 98- 101 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52- 7.39 (m, 2H), 7.34 (dd, *J* = 11.2, 1.7 Hz, 1H), 7.12- 6.90 (m, 3H), 6.81 (d, *J* = 15.4 Hz, 1H), 3.78 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 161.7, 138.3, 137.8, 132.8, 128.7, 127.2, 123.6, 115.8, 51.9, 12.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}FO_2$ 221.0978; found 221.0968.



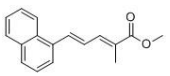
14j (4.8 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15j** (6.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 95% yield, m.p. 78- 79 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 19.0, 9.5 Hz, 3H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.02 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.85 (d, *J* = 15.4 Hz, 1H), 3.79 (d, *J* = 9.1 Hz, 3H), 2.66 (q, *J* = 7.5 Hz, 2H), 2.05 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 145.3, 139.2, 138.8, 134.1, 128.3, 127.1, 126.5, 123.0, 51.9, 28.7, 15.5, 12.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}O_2$ 231.1385; found 231.1381.



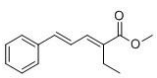
14k (8.0 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15k** (9.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 93% yield, m.p. 95- 96 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 2H), 7.77 (s, 1H), 7.35 (d, *J* = 11.3 Hz, 1H), 7.30- 7.08 (m, 1H), 6.89 (d, *J* = 15.4 Hz, 1H), 3.81 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 138.6, 136.9, 135.2, 132.2, 130.3, 127.3, 126.6, 124.5, 121.7, 52.1, 13.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}F_7O_2$ 339.0820; found 339.0806.



14l (6.2 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15l** (7.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 95% yield, m.p. 165- 167 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73- 7.52 (m, 6H), 7.51- 7.29 (m, 4H), 7.10 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.90 (d, *J* = 15.4 Hz, 1H), 3.79 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 141.5, 140.4, 138.7, 138.5, 135.6, 128.9, 127.6, 127.5, 127.4, 127.1, 127.0, 123.9, 51.9, 13.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}O_2$ 278.1385, found 279.1378.

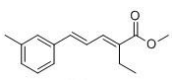


14m (5.5 g) reacted with methyl 2-(diethoxyphosphoryl)propanoate (8.1 g) to yield **15m** (7.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 93% yield, m.p. 78- 80 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.95- 7.33 (m, 8H), 7.14 (dd, *J* = 15.2, 11.5 Hz, 1H), 3.82 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 138.7, 135.9, 133.9, 133.7, 131.2, 129.1, 128.7, 127.4, 126.6, 126.5, 126.0, 125.6, 124.0, 123.3, 52.0, 13.0. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}O_2Na$ 275.1048; found 275.1050.

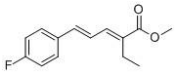


14a (4.0 g) reacted with methyl 2-(diethoxyphosphoryl)butanoate (8.6 g) to yield **15n** (6.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluentafter silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 96% yield, m.p. 86- 87 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55- 7.42 (m, 2H), 7.39 - 7.19 (m, 4H), 7.06 (dd, *J* = 15.4, 11.4 Hz, 1H), 6.87 (d, *J* = 15.4 Hz, 1H), 3.78 (s, 3H), 2.53 (q, *J* =

7.5 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 139.4, 138.1, 136.6, 133.6, 128.8, 128.8, 127.1, 123.6, 51.8, 20.6, 14.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1229; found 217.1200.



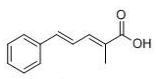
14s (4.4 g) reacted with methyl 2-(diethoxyphosphoryl)butanoate (8.6 g) to yield **15s** (6.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 95% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36- 7.19 (m, 5H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.04 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.85 (d, *J* = 15.4 Hz, 1H), 3.79 (s, 3H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 139.6, 138.4, 138.3, 136.5, 133.4, 129.6, 128.7, 127.7, 124.3, 123.4, 51.8, 21.4, 20.6, 14.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}O_2$ 231.1385; found 231.1378.



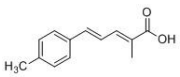
14i (4.5 g) reacted with methyl 2-(diethoxyphosphoryl)butanoate (8.6 g) to yield **15t** (6.7 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 96% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53- 7.37 (m, 2H), 7.30 (d, *J* = 11.3 Hz, 1H), 7.13- 6.91 (m, 3H), 6.83 (d, *J* = 15.4 Hz, 1H), 3.79 (s, 3H), 2.52 (q, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 164.2, 161.7, 138.0, 133.6, 132.8, 128.7, 123.3, 115.8, 51.8, 20.6, 14.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{16}FO_2$ 235.1134; found 235.1129.

2.5 General procedure for the preparation of (2*E*,4*E*)-2-methyl-5-phenylpenta-2,4-dienoic acid derivatives 1a- 1n, 1s- 1t and 1u- 1v:

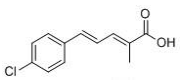
NaOH (1.2 g, 30 mmol) was added to the solution of 2-methyl-5-phenylpenta-2,4-dienoate derivative **15** (10 mmol) in MeOH (20 mL). The resulting mixture was stirred overnight under nitrogen at room temperature. The resulting solution was acidified with 2N HCl. The aqueous phase was extracted three times with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The cinnamate acid derivative **1** was purified by recrystallisation from EtOAc and petroleum ether. The NMR spectra of compounds **1a and 1c** accords with reported literatures [23].



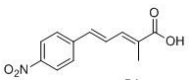
1a obtained from **15a** (2.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 1.7 g, 92% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53- 7.29 (m, 6H), 7.08 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.92 (d, *J* = 15.4 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 140.7, 140.3, 136.4, 129.0, 128.8, 127.2, 126.4, 123.8, 12.6.



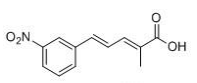
1b obtained from **15b** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 1.9 g, 93% yield, m.p. 204- 205 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 30.0, 9.5 Hz, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.04 (dd, *J* = 15.5, 11.2 Hz, 1H), 6.89 (d, *J* = 15.4 Hz, 1H), 2.37 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 140.8, 140.3, 139.2, 133.7, 129.6, 127.2, 125.7, 122.9, 21.4, 12.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}O_2$ 203.1072; found 203.1069.



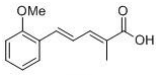
1c obtained from **15c** (2.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 2.0 g, 92% yield.^{1}H NMR (400 MHz, DMSO-d_6) δ 12.33 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 11.0 Hz, 2H), 7.09- 6.68 (m, 1H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.5, 137.9, 137.6, 135.9, 133.4, 129.3, 129.2, 128.9, 125.6, 13.3.



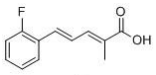
1d obtained from **15d** (2.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 2.1 g, 91% yield, m.p. 218- 219 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (dd, *J* = 8.6, 2.6 Hz, 2H), 7.91 (dd, *J* = 8.7, 2.6 Hz, 2H), 7.54- 7.46 (m, 1H), 7.29 (d, *J* = 11.4 Hz, 1H), 7.13 (d, *J* = 15.3 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.4, 147.3, 143.6, 137.2, 136.5, 131.3, 129.3, 128.6, 124.4, 13.5. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_{10}NO_4$ 232.0610; found 232.0609.



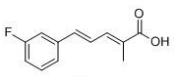
1e obtained from **15e** (2.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 2.0 g, 90% yield, m.p. 208- 209 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ 12.37 (s, 1H), 8.45 (s, 1H), 8.29- 7.99 (m, 2H), 7.80- 7.57 (m, 1H), 7.47 (t, *J* = 13.6 Hz, 1H), 7.19 (dd, *J* = 52.9, 13.5 Hz, 2H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.4, 148.9, 138.8, 137.4, 136.6, 133.6, 130.6, 130.3, 127.6, 123.3, 122.0, 13.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}NO_4$ 234.0766; found 234.0763.



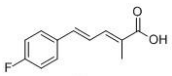
1f obtained from **15f** (2.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, light yellow solid, 2.2 g, 92% yield, m.p. 206- 208 °C. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.59 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40- 7.31 (m, 1H), 7.34- 7.22 (m, 1H), 7.25- 7.13 (m, 2H), 7.03- 6.90 (m, 2H), 3.89 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 170.6, 157.5, 139.6, 134.2, 129.7, 127.0, 126.2, 125.2, 124.0, 120.4, 110.9, 54.7, 11.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{18}O_3$ 247.1334; found 247.1331.



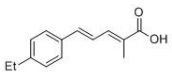
1g obtained from **15g** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 1.9 g, 94% yield, m.p. 142- 143°C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73- 7.44 (m, 2H), 7.36- 7.27 (m, 1H), 7.23- 7.12 (m, 2H), 7.11- 6.99 (m, 2H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.6, 162.0, 159.5, 140.6, 132.4, 130.1, 127.9, 127.2, 126.1, 124.4, 116.0, 12.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}FO_2$ 207.0821; found 207.0819.



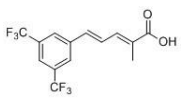
1h obtained from **15h** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 1.9 g, 94% yield, m.p. 176- 178 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 11.3 Hz, 1H), 7.28- 7.15 (m, 3H), 7.12- 6.93 (m, 2H), 6.87 (d, *J* = 15.4 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.5, 164.3, 161.9, 139.9, 138.7, 130.3, 127.4, 125.0, 123.2, 115.7, 113.4, 12.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}FO_2$ 207.0821; found 207.0809.



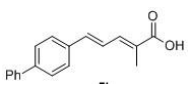
1i obtained from **15i** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 1.9 g, 94% yield, m.p. 189- 190 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53- 7.41 (m, 3H), 7.11- 7.02 (m, 2H), 7.01- 6.93 (m, 1H), 6.87 (d, *J* = 15.4 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 164.3, 140.4, 138.8, 132.7, 128.9, 126.4, 123.5, 115.9, 12.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}FO_2$ 207.0821; found 207.0810.



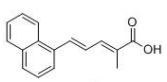
1j obtained from **15j** (2.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 2.0 g, 94% yield, m.p. 174- 176 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 21.2, 9.5 Hz, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.04 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.90 (d, *J* = 15.4 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.06 (s, 3H), 1.25 (t, *J* = 7.5, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 145.6, 140.9, 140.3, 133.9, 128.4, 127.3, 125.7, 122.9, 28.8, 15.4, 12.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1229; found 217.1219.



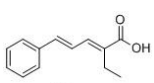
1k obtained from **15k** (3.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 3.0 g, 92% yield, m.p. 200- 201 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 2H), 7.80 (s, 1H), 7.46 (d, *J* = 11.2 Hz, 1H), 7.18 (d, *J* = 11.8 Hz, 1H), 6.94 (d, *J* = 15.4 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 138.8, 138.4, 136.2, 132.1, 129.3, 127.2, 126.7, 124.5, 121.9, 12.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{11}F_6O_4$ 325.0663; found 325.0657.



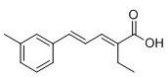
1l obtained from **15l** (2.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 2.5 g, 94% yield, m.p. 207- 209 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76- 7.29 (m, 10H), 7.13 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.96 (d, *J* = 15.4 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 141.7, 140.6, 140.4, 139.8, 135.4, 128.9, 127.7, 127.7, 127.5, 127.0, 126.3, 123.8,12.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}O_2$ 265.1229; found 265.1221.



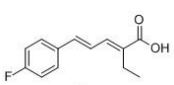
1m obtained from **15m** (2.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 2.2 g, 91% yield, m.p. 205- 206 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.93- 7.45 (m, 8H), 7.18 (dd, *J* = 15.2, 11.5 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 140.7, 136.9, 133.8, 133.7, 131.2, 129.4, 128.8, 126.6, 126.6, 126.5, 126.1, 125.6, 124.2, 123.3, 12.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}O_2$ 239.1072; found 239.1067.



1n obtained from **15n** (2.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 1.9 g, 92% yield, m.p. 125- 126 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 18.7, 9.4 Hz, 3H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 14.5 Hz, 1H), 7.08 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.93 (d, *J* = 15.4 Hz, 1H), 2.54 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 140.5, 140.3, 136.4, 132.8, 129.0, 128.8, 127.2, 123.4, 20.3, 14.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}O_2$ 203.1072; found 203.1060.

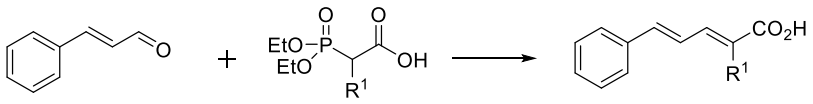


1s obtained from **15s** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 2.0 g, 91% yield, m.p. 148- 149 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 11.4 Hz, 1H), 7.34- 7.21 (m, 3H), 7.16- 6.97 (m, 2H), 6.90 (d, *J* = 15.4 Hz, 1H), 2.54 (q, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 1.14 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 140.7, 140.4, 138.4, 136.4, 132.6, 129.9, 128.7, 127.9, 124.5, 123.2, 21.4, 20.3, 14.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1228; found 217.1223.



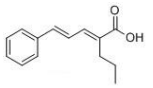
1t obtained from **15t** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 2.0 g, 92% yield, m.p. 162- 163 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51- 7.42 (m, 3H), 7.08 - 6.96 (m, 3H), 6.89 (d, *J* = 15.4 Hz, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 164.3, 140.0, 139.1, 132.9, 132.6, 128.9, 123.2, 115.9, 20.3, 14.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}FO_2$ 221.0978; found 221.0973.

2.7 General procedure for the preparation of (2*E*,4*E*)-2-substituted-5-phenylpenta-2,4-dienoic acid derivatives 1o- 1r:

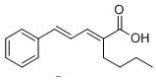


Reagents and conditions: LDA (2.5 equiv.), diethoxyphosphoryl acids (1.2 equiv.) / THF, 0 °C→ r.t.

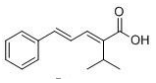
LDA (12.5 mL, 2.0 M solution in hexane) was added dropwise to a solution of diethoxyphosphoryl acids (12 mmol) in dry THF (40 mL) at 0 °C under nitrogen and was stirred for 30 minutes. A solution of cinnamaldehyde **14a** (10 mmol) in THF (10 mL) was added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After the completion of reaction monitored by TLC analysis, the reaction was quenched by addition of saturated ammonium chloride and the resulting aqueous phase was extracted 3 times with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The desired cinnamate acid derivatives **1o- 1r** were obtained by silica-gel flash column chromatography (EtOAc/PE).



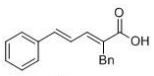
Cinnamaldehyde **1a** (1.1 g) was reacted with 2-(diethoxyphosphoryl)pentanoic acid (2.9 g) to yield **1o** (1.9 g) as white solid in 88% yield after silica-gel flash column chromatography using PE and EtOAc as eluent, m.p. 143- 144 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64- 7.46 (m, 3H), 7.45- 7.29 (m, 3H), 7.08 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.93 (d, *J* = 15.4 Hz, 1H), 2.50 (dd, *J* = 8.5, 6.7 Hz, 2H), 1.56 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1, 140.9, 140.4, 136.4, 131.2, 129.0, 128.8, 127.2, 123.7, 28.9, 23.0, 14.0. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{15}O_2$ 215.1072; found 215.1071.



Cinnamaldehyde **1a** (1.1 g) was reacted with 2-(diethoxyphosphoryl)hexanoic acid (3.0 g)to yield **1p** (2.0 g) as white solid in 89% yield after silica-gel flash column chromatography using PE and EtOAc as eluent, m.p. 172- 173°C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51- 7.36 (m, 3H), 7.33- 7.29 (m, 3H), 7.07 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.92 (d, *J* = 15.4 Hz, 1H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.68- 1.07 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 140.6, 140.3, 136.5, 131.5, 128.9, 128.8, 127.2, 123.7, 32.0, 26.7, 22.7, 14.0. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{17}O_2$ 229.1229; found 229.1230.

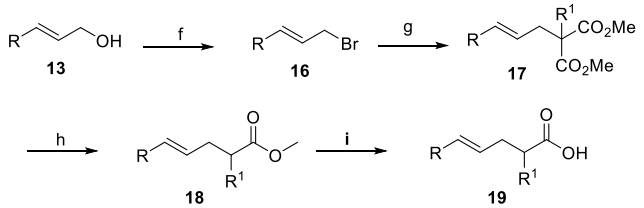


Cinnamaldehyde **1a** (1.1 g) was reacted with 2-(diethoxyphosphoryl)-3-methylbutanoic acid (2.9 g) to yield **1q** (1.8 g) as white solid in 87% yield after silica-gel flash column chromatography using PE and EtOAc as eluent, m.p. 101- 102 °C . ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59- 7.43 (m, 2H), 7.43- 7.28 (m, 4H), 7.19 (dd, *J* = 15.3, 11.5 Hz, 1H), 6.91 (d, *J* = 15.2 Hz, 1H), 3.24- 3.15 (m, 1H), 1.30 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 140.4, 139.9, 136.5, 136.2, 128.9, 128.8, 127.2, 123.2, 27.8, 21.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2$ 215.1072; found 215.1071.



Cinnamaldehyde **1a** (1.1 g) was reacted with 2-(diethoxyphosphoryl)-3-phenylpropanoic acid (3.5 g) to yield **1r** (2.3 g) as white solid in 87% yield after silica-gel flash column chromatography using PE and EtOAc as eluent, m.p. 109- 110 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 11.3 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.41- 7.04 (m, 9H), 7.00 (d, *J* = 15.4 Hz, 1H), 3.88 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 142.0, 141.5, 139.4, 136.2, 129.2, 129.1, 128.9, 128.5, 128.3, 127.4, 126.2, 123.5, 32.4. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{15}O_2$ 263.1072; found 263.1075.

3. Preperation of racemic (*E*)-2-methyl-5-phenylpent-4-enoic acids 19



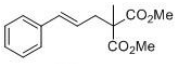
Reagents and conditions: f) PBr_3 (2.0 equiv.)/ Et_2O, 0 °C→ r.t.; g) NaH (1.2 equiv.), methylmalonic acid dimethylester (1.1 equiv.)/ THF, 0 °C→ r.t.; h) LiCl (2.0 equiv.), H_2O (2.0 equiv.)/ DMSO; i) NaOH (3.0 equiv.)/ MeOH

3.1 General procedure for the preparation of (*E*)-dimethyl 2-cinnamyl-2-methylmalonate derivatives 17:

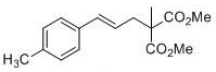
PBr_3 (2.8 mL, 30 mol) was added dropwise to a solution of cinnamyl alcohol derivative **13** (15 mmol) in Et_2O (45 mL) at 0 °C. The resulting mixture was stirred at ambient temperature until the completion of reaction monitored by TLC analysis. The

reaction was quenched by slow addition of 10% Na_2CO_3 aqueous solution. The aqueous phase was extracted three times with Et_2O and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The desired cinnamyl bromide derivative **16** was obtained and used directly without further purification.

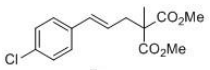
Dimethyl 2-ethylmalonate derivatives (16.5 mmol) was added dropwise to a solution of NaH (0.72 g, 18 mmol, 60% suspended in mineral oil) in dry THF (45 mL) under nitrogen at 0 °C. After stirring for 30 minutes at the same temperature, cinnamyl bromide derivative **16** in dry THF (7.5 mL) was added dropwise. The resulting mixture was stirred at room temperature until the completion of reaction monitored by TLC analysis. The reaction was quenched by addition of saturated ammonium chloride and the resulting aqueous phase was extracted tree times with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The desired (*E*)-dimethyl 2-cinnamyl-2-methylmalonate derivative **17** was obtained by silica-gel flash column chromatography (EtOAc/PE). The NMR spectra of compounds **17a, 17c and 17d** accord with reported literatures [24-25].



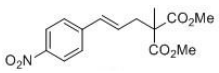
Cinnamyl alcohol **13a** (2.0 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17a** (3.3 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 85% yield . ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34- 7.20 (m, 5H), 6.47- 6.42 (m, 1H), 6.12- 6.04 (m, 1H), 3.74 (s, 6H), 2.77 (dd, *J* = 7.5, 1.3 Hz, 2H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 137.1, 134.1, 128.5, 127.4, 126.2, 124.1, 54.0, 52.6, 39.5, 20.1.



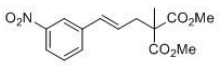
Cinnamyl alcohol **13b** (2.2 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17b** (3.7 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 89% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26- 7.21 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.04- 6.00 (m, 1H), 3.73 (s, 6H), 2.75 (d, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 137.2, 134.3, 134.0, 129.2, 126.1, 123.0, 54.0, 52.5, 39.5, 21.2, 20.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O_4$ 277.1438; found 277.1440.



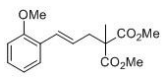
Cinnamyl alcohol **13c** (2.5 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17c** (3.7 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (s, 4H), 6.42- 6.37 (m, 1H), 6.11- 6.03 (m, 1H), 3.74 (s, 6H), 2.76 (d, *J* = 7.5 Hz, 2H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 135.5, 133.0, 132.9, 128.7, 127.4, 125.0, 53.9, 52.6, 39.5, 20.1.



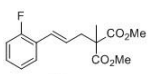
Cinnamyl alcohol **13d** (2.7 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17d** (3.9 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J* = 8.8, 2.5 Hz, 2H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.39- 6.28 (m, 1H), 3.75 (s, 6H), 2.81 (d, *J* = 7.5 Hz, 2H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 146.9, 143.4, 132.1, 129.7, 126.7, 124.0, 53.8, 52.7, 39.6, 20.3.



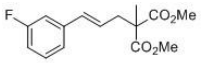
Cinnamyl alcohol **13e** (2.7 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17e** (4.0 g) as white solid after silica-gel flash column chromatography using PE and EtOAc as eluent, 87% yield, m.p. 88- 89 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16- 8.05 (m, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.49- 7.44 (m, 1H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.31- 6.23 (m, 1H), 3.75 (s, 6H), 2.81 (d, *J* = 7.5 Hz, 2H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 148.6, 138.8, 132.0, 131.8, 129.4, 127.9, 122.0, 120.8, 53.8, 52.6, 39.4, 20.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{17}NO_6Na$ 330.0954; found 330.0948.



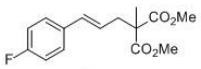
Cinnamyl alcohol **13f** (2.5 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17f** (3.7 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.90- 6.75 (m, 3H), 6.09- 6.01 (m, 1H), 3.80 (s, 3H), 3.73 (s, 6H), 2.79 (d, *J* = 7.4 Hz, 2H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 156.4, 129.0, 128.5, 126.7, 126.2, 124.6, 120.6, 110.7, 55.4, 54.1, 52.5, 39.8, 20.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for$C_{16}H_{21}O_5$ 293.1389; found 293.1386.



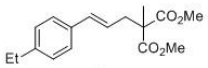
Cinnamyl alcohol **13g** (2.3 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17g** (3.7 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (t, *J* = 7.7 Hz, 1H), 7.19- 7.00 (m, 3H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.20- 6.12 (m, 1H), 3.74 (s, 6H), 2.79 (d, *J* = 7.6 Hz, 2H), 1.45 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 128.7, 127.3, 126.9, 126.5, 124.9, 124.0, 115.7, 115.5, 54.0, 52.6, 39.8, 20.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}FO_4$ 281.1184; found 281.1187.



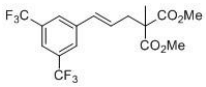
Cinnamyl alcohol **13h** (2.3 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17h** (3.5 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 12.7, 6.2 Hz, 1H), 7.05 (dd, *J* = 22.2, 9.0 Hz, 2H), 6.93-6.89 (m, 1H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.15- 6.07 (m, 1H), 3.74 (s, *J* = 1.4 Hz, 6H), 2.77 (d, *J* = 7.5 Hz, 2H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 164.3, 139.4, 133.0, 129.9, 125.7, 122.1, 114.2, 112.7, 53.9, 52.6, 39.4, 20.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}FO_4$ 281.1184; found 281.1183.



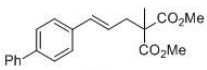
Cinnamyl alcohol **13i** (2.3 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17i** (3.6 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33-7.27 (m, 2H), 7.04-6.95 (m, 2H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.04- .96 (m, 1H), 3.73 (s, 6H), 2.75 (d, *J* = 7.6 Hz, 2H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 132.9, 127.8, 127.7, 123.9, 115.5, 115.3, 53.9, 52.6, 39.4, 20.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}FO_4$ 281.1184; found 281.1180.



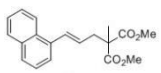
Cinnamyl alcohol **13j** (2.3 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17j** (3.7 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.07- 5.99 (m, 1H), 3.73 (d, *J* = 1.7 Hz, 6H), 2.76 (d, *J* = 7.5 Hz, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.47(s, 3H), 1.22 (t, *J* = 7.6, 3H). ^{13}C NMR (101 MHz, Chloroform -*d*) δ 172.4, 143.7, 134.6, 134.0, 128.0, 126.2, 123.1, 54.0, 52.6, 39.5, 28.6, 20.0, 15.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}O_4$ 291.1596; found 291.1592.



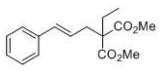
Cinnamyl alcohol **13k** (4.0 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17k** (5.1 g) as white solid after silica-gel flash column chromatography using PE and EtOAc as eluent, 85% yield, m. p. 90- 91 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 4.1 Hz, 3H), 6.53 (dd, *J* = 15.9, 8.8 Hz, 1H), 6.34- 6.27 (m, 1H), 3.76 (s, 6H), 2.81 (d, *J* = 7.4 Hz, 2H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 139.0, 131.6, 128.8, 126.0, 124.6, 121.9, 120.8, 53.8, 52.7, 39.5, 20.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}F_6O_4$ 399.1031; found 399.1022.



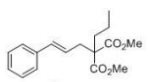
Cinnamyl alcohol **13l** (3.2 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17l** (4.4 g) as white solid after silica-gel flash column chromatography using PE and EtOAc as eluent, 87% yield, m.p. 88- 89 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60- 7.31 (m, 9H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.17- 6.10 (m, 1H), 3.75 (s, 6H), 2.81- 2.70 (m, 2H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 140.7, 140.2, 136.1, 133.7, 128.8, 127.3, 127.2, 126.9, 126.7, 124.3, 54.0, 52.6, 39.6, 20.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_4$ 339.1596; found 339.1591.



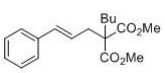
Cinnamyl alcohol **13m** (2.8 g) was reacted with dimethyl 2-methylmalonate (2.4 g) to yield **17m** (4.1 g) as white solid after silica-gel flash column chromatography using PE and EtOAc as eluent, 88% yield, m.p. 76- 78 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.86- 7.76 (m, 2H), 7.55- 7.40 (m, 4H), 7.26- 7.19 (m, 1H), 6.17- 6.09 (m, 1H), 3.76 (s, 6H), 2.92 (dd, *J* = 7.6, 1.4 Hz, 2H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 135.0, 133.5, 131.7, 131.1, 128.5, 127.9, 127.6, 126.0, 125.8, 125.7, 124.0, 123.8, 54.1, 52.6, 39.9, 20.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}O_4Na$ 335.1259; found 335.1252.



Cinnamyl alcohol **13a** (2.0 g) was reacted with dimethyl 2-ethylmalonate (2.6 g) to yield **17n** (3.5 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48- 7.19 (m, 5H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.06- 5.98 (m, 1H), 3.73 (s, 6H), 2.80 (d, *J* = 7.6 Hz, 2H), 2.01- 1.92 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 137.1, 133.7, 128.5, 127.4, 126.2, 124.1, 58.5, 52.4, 35.9, 25.7, 8.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O_4$ 277.1440; found 277.1430.

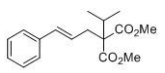


Cinnamyl alcohol **13a** (2.0 g) was reacted with dimethyl 2-propylmalonate (2.6 g) to yield **17o** (3.8 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34- 7.21 (m, 5H), 6.43 (d, *J* = 15.5 Hz, 1H), 6.06- 5.99 (m, 1H), 3.72 (s, 6H), 2.80 (dd, *J* = 7.6, 1.4 Hz, 2H), 1.92- 1.87 (m, 2H), 1.26 (q, *J* = 5.7, 4.5 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 137.1, 133.7, 128.4, 127.4, 126.2, 124.2, 58.1, 52.4, 36.6, 35.0, 17.5, 14.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}O_4$ 291.1596; found 291.1592.

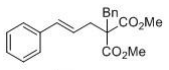


Cinnamyl alcohol **13a** (2.0 g) was reacted with dimethyl 2-butylmalonate (2.8 g) to yield **17p** (3.9 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 86% yield. ^{1}H

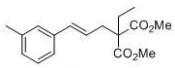
NMR (400 MHz, Chloroform-*d*) δ 7.33- 7.21 (m, 5H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.06- 5.98 (m, 1H), 3.73 (s, 6H), 2.80 (dd, *J* = 7.6, 1.3 Hz, 2H), 1.94- 1.90 (m, 2H), 1.35- 1.19 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.9, 137.2, 133.7, 128.5, 127.4, 126.2, 124.2, 58.0, 52.4, 36.4, 32.4, 26.2, 22.9, 13.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}O_4$ 305.1753; found 305.1749.



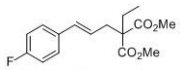
Cinnamyl alcohol **13a** (2.0 g) was reacted with dimethyl 2-isopropylmalonate (2.6 g) to yield **17q** (3.6 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33- 7.13 (m, 5H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.18- 6.10 (m, 1H), 3.72 (s, 6H), 2.80 (d, *J* = 7.5 Hz, 2H), 2.42- 2.35 (m, 1H), 1.01 (dd, *J* = 6.9, 1.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 137.3, 133.2, 128.5, 127.3, 126.2, 125.2, 62.7, 52.0, 37.6, 32.4, 18.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}O_4$ 291.1596; found 291.1589.



Cinnamyl alcohol **13a** (2.0 g) was reacted with dimethyl 2-benzylmalonate (3.3 g) to yield **17r** (4.2 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51- 7.04 (m, 10H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.30- 5.95 (m, 1H), 3.95- 3.55 (m, 6H), 3.26 (d, *J* = 27.9 Hz, 2H), 2.78 (dd, *J* = 54.1, 7.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 137.1, 135.9, 134.2, 130.0, 128.6, 128.4, 127.5, 127.1, 126.3, 124.2, 59.4, 52.4, 38.7, 36.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_4$ 339.1596; found 339.1593.



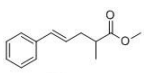
Cinnamyl alcohol **13s** (2.2 g) was reacted with dimethyl 2-ethylmalonate (2.6 g) to yield **1s** (3.8 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28- 7.10 (m, 3H), 7.04- 6.97 (m, 1H), 6.43- 6.37 (m, 1H), 6.04- 5.96 (m, 1H), 3.73 (s, 6H), 2.79 (dd, *J* = 7.5, 1.3 Hz, 2H), 2.33 (s, 3H), 2.01- 1.94 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 138.1, 137.0, 133.8, 128.4, 128.2, 126.9, 123.8, 123.4, 58.8, 52.4, 35.9, 25.7, 21.4, 8.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}O_4$ 291.1596; found 291.1590.



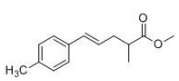
Cinnamyl alcohol **13i** (2.3 g) was reacted with dimethyl 2-ethylmalonate (2.6 g) to yield **17t** (3.8 g) as colorless oil after silica-gel flash column chromatography using PE and EtOAc as eluent, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30- 7.25 (m, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 6.40 (d, *J* = 15.7 Hz, 1H), 5.97- 5.90 (m, 1H), 3.73 (s, 6H), 2.78 (dd, *J* = 7.5, 1.4 Hz, 2H), 1.97 (q, *J* = 7.5 Hz, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 163.4, 161.0, 132.5, 127.7, 123.9, 115.4, 58.5, 52.4, 35.9, 25.8, 8.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}FO_4$ 295.1345; found 295.1340.

3.2 General procedure for the preparation of (*E*)-methyl 2-methyl-5-phenylpent-4-enoate derivatives 18:

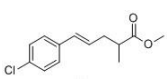
The solution of dimethyl 2-cinnamyl-2-methylmalonate derivative **17** (10 mmol), LiCl (848 mg, 20 mmol), water (360 mg, 20 mmol) in DMSO (50 mL) was stirred at 130 °C under nitrogen for about 16 h. The reaction was quenched by addition of water and the aqueous phase was extracted 3 times with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The desired (*E*)-methyl 2-methyl-5-phenylpent-4-enoate derivative **18** was obtained by silica-gel flash column chromatography (EtOAc/PE). The NMR spectra of compounds **18a and 18i** accord with reported literatures [26].



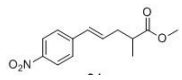
18a (1.7 g) was obtained from **17a** (2.6 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34- 7.18 (m, 5H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.18- 6.10 (m, 1H), 3.67 (s, 3H), 2.63- 2.53 (m, 2H), 2.37- 2.30 (m, 1H), 1.20 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 137.4, 132.1, 128.5, 127.2, 127.2, 126.1, 51.7, 39.6, 37.1, 16.7.



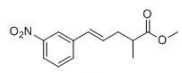
18b (1.9 g) was obtained from **17b** (2.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.04- 6.12 (m, 1H), 3.67 (s, 3H), 2.64- 2.53 (m, 2H), 2.29- 2.36 (m, 4H), 1.20 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.6, 136.9, 134.6, 131.9, 129.2, 126.1, 126.0, 51.6, 39.7, 37.1, 21.2, 16.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1385; found 219.1384.



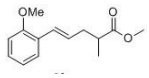
18c (2.0 g) was obtained from **17c** (3.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (s, 4H), 6.36 (dd, *J* = 15.7, 1.5 Hz, 1H), 6.06- 6.15 (m, 1H), 3.67 (s, 3H), 2.51-2.63 (m, 2H), 2.36- 2.29 (m, 1H), 1.20 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.4, 135.8, 132.7, 130.9, 128.6, 127.9, 127.3, 51.7, 39.5, 37.0, 16.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}ClO_2$ 239.0839; found 239.0834.



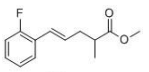
18d (2.0 g) was obtained from **17d** (3.1 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18- 8.14 (m, 2H), 7.48- 7.44 (m, 2H), 6.52- 6.48 (m, 1H), 6.41- 6.33 (m, 1H), 3.70 (s, 3H), 2.69- 2.59 (m, 2H), 2.45- 2.38 (m, 1H), 1.24 (d, *J* = 5.2 Hz, 3H).. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 146.7, 143.8, 132.6, 130.3, 126.6, 124.0, 51.7, 39.3, 37.0, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NO_4$ 250.1079; found 250.1101.



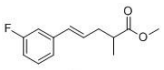
18e (2.1 g) was obtained from **17e** (3.1 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 82% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.70 (s, 3H), 2.68- 2.57 (m, 2H), 2.40 (dt, *J* = 13.5, 6.9 Hz, 1H), 1.23 (d, *J* = 4.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 148.6, 139.1, 131.9, 130.8, 130.0, 129.4, 121.8, 120.6, 51.7, 39.3, 36.9, 16.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NO_4$ 250.1079; found 250.1074.



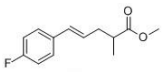
18f (2.0 g) was obtained from **17f** (2.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 87% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41- 6.83 (m, 4H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.16- 6.09 (m, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 2.64- 2.54 (m, 2H), 2.40- 2.32 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.6, 156.4, 128.2, 127.8, 126.8, 126.6, 126.5, 120.6, 110.8, 55.4, 51.6, 39.7, 37.5, 16.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}O_3$ 235.1334; found 235.1331.



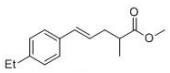
18g (1.9 g) was obtained from **17g** (2.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43- 7.39 (m, 1H), 7.16 (t, *J* = 6.5 Hz, 1H), 7.08- 6.98 (m, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.26- 6.18 (m, 1H), 3.69 (s, 3H), 2.65- 2.55 (m, 2H), 2.39- 2.35 (m, 1H), 1.21 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.4, 161.2, 129.9, 128.4, 127.2, 125.1, 124.5, 124.0, 115.6, 51.7, 39.5, 37.4, 16.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}FO_2$ 223.1134; found 223.1127.



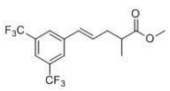
18h (1.9 g) was obtained from **17h** (2.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26- 7.22 (m, 1H), 7.06 (dd, *J* = 20.9, 8.8 Hz, 2H), 6.98- 6.87 (m, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.19- 6.12 (m, 1H), 3.68 (s, 3H), 2.64- 2.53 (m, 2H), 2.38- 2.31 (m, 1H), 1.21 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.4, 164.3, 139.7, 131.1, 129.9, 128.7, 122.0, 113.9, 112.5, 51.7, 39.5, 36.9, 16.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}FO_2$ 223.1134; found 223.1126.



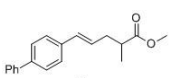
18i (2.0 g) was obtained from **17i** (2.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 87% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (dd, *J* = 10.7, 4.2 Hz, 2H), 7.02- 6.95 (m, 2H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.09- 6.01 (m, 1H), 3.67 (s, 3H), 2.63- 2.51 (m, 2H), 2.36- 2.29 (m, 1H), 1.20 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.4, 163.3, 133.6, 130.9, 127.5, 127.0, 115.3, 51.6, 39.6, 36.9, 16.7.



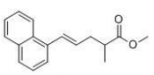
18j (2.0 g) was obtained from **17j** (2.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.09- 6.05 (m, 1H), 3.67 (s, 3H), 2.65- 2.52 (m, 4H), 2.36- 2.29 (m, 1H), 1.29- 1.19 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.6, 143.4, 134.9, 132.0, 128.0, 126.2, 126.1, 51.6, 39.7, 37.1, 28.6, 16.7, 15.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}O_2$ 233.1542; found 233.1535.



18k (2.9 g) was obtained from **17k** (4.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 13.6 Hz, 3H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.37- 6.30 (m, 1H), 3.70 (s, 3H), 2.68- 2.58 (m, 2H), 2.39 (dd, *J* = 13.9, 6.5 Hz, 1H), 1.23 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 139.3, 131.7, 129.6, 125.9, 124.7, 122.0, 120.6, 51.8, 39.2, 36.9, 16.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}F_6O_2$ 341.0976; found 341.0972.

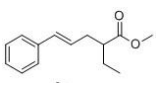


18l (2.5 g) was obtained from **17l** (3.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 88% yield, m.p. 107- 108 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60- 7.25 (m, 9H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.23- 6.15 (m, 1H), 3.69 (s, 3H), 2.65- 2.55 (m, 2H), 2.38- 2.35 (m, 1H), 1.22 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 148.5, 140.8, 139.9, 136.4, 131.7, 128.8, 127.4, 127.2, 126.9, 126.5, 51.7, 39.6, 37.1, 16.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}O_2$ 281.1541; found 281.1536.

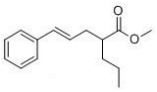


18m (2.2 g) was obtained from **17m** (3.1 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.77 (dd, *J* = 33.4, 8.0 Hz, 2H), 7.52- 7.38 (m, 4H), 7.21- 7.13 (m, 1H), 6.18- 6.10 (m, 1H), 3.68 (s, 3H), 2.71- 2.63 (m, 2H), 2.50- 2.44 (m, 1H), 1.26 (dd, *J* = 6.4, 2.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 135.3, 133.5, 131.2,

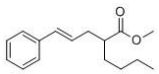
130.6, 129.6, 128.5, 127.6, 125.9, 125.7, 125.7, 123.9, 123.8, 51.6, 39.7, 37.5, 16.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}O_2$ 255.1385; found 255.1379.



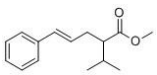
18n (2.0 g) was obtained from **17n** (2.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34- 7.17 (m, 5H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.7, 6.9 Hz, 1H), 3.67 (s, 3H), 2.55- 2.35 (m, 3H), 1.72- 1.56 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 137.4, 131.9, 128.5, 127.3, 127.2, 126.1, 51.5, 47.2, 35.3, 25.0, 11.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1358; found 219.1374.



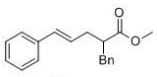
18o (2.1 g) was obtained from **17o** (2.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34- 7.18 (m, 5H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.17- 6.11 (m, 1H), 3.67 (s, 3H), 2.55- 2.38 (m, 3H), 1.66- 1.25 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2, 137.4, 131.9, 128.5, 127.3, 127.1, 126.1, 51.5, 45.5, 35.7, 34.1, 20.6, 14.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}O_2$ 233.1541; found 233.1537.



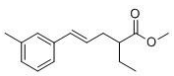
18p (2.2 g) was obtained from **17p** (3.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34- 7.18 (m, 5H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.16- 6.11 (m, 1H), 3.67 (s, 3H), 2.53- 2.38 (m, 3H), 1.67 - 1.52 (m, 2H), 1.34- 1.23 (m, 4H), 0.88 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2, 137.4, 131.9, 128.5, 127.3, 127.1, 126.1, 51.5, 45.7, 35.7, 31.7, 29.5, 22.6, 14.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}O_2$ 247.1698; found 247.1694.



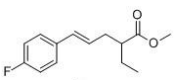
18q (2.1 g) was obtained from **17q** (2.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33- 7.17 (m, 5H), 6.41 (dd, *J* = 15.8, 1.5 Hz, 1H), 6.16- 6.09 (m, 1H), 3.65 (s, 3H), 2.49- 2.32 (m, 3H), 1.96- 1.91 (m, 1H), 0.97 (dd, *J* = 16.1, 6.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.5, 137.5, 131.6, 128.5, 127.7, 127.1, 126.1, 52.7, 51.2, 33.2, 30.3, 20.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}O_2$ 233.1541; found 233.1535.



18r (2.5 g) was obtained from **17r** (3.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 89% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48- 7.07 (m, 10H), 6.40 (dd, *J* = 15.8, 11.1 Hz, 1H), 6.17- 6.07 (m, 1H), 3.74- 3.37 (m, 3H), 3.08- 2.71 (m, 3H), 2.55- 2.37 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.4, 132.4, 129.0, 128.9, 128.6, 128.6, 128.5, 127.3, 126.9, 126.5, 126.2, 51.6, 47.7, 38.2, 35.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}O_2$ 281.1541; found 281.1537.



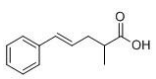
18s (2.1 g) was obtained from **17s** (2.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20- 6.99 (m, 4H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.15- 6.08 (m, 1H), 3.67 (s, 3H), 2.53 – 2.36 (m, 3H), 2.33 (s, 3H), 1.73- 1.61 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 138.0, 137.4, 132.0, 128.4, 127.9, 127.1, 126.8, 123.3, 51.4, 47.2, 35.3, 24.9, 21.4, 11.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{21}O_2$ 233.1541; found 233.1535.



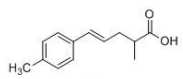
18t (2.2 g) was obtained from **17t** (2.9 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30- 7.26 (m, 2H), 7.00- 6.95 (m, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.00- 6.08 (m, 1H), 3.67 (s, 3H), 2.52- 2.34 (m, 3H), 1.70- 1.56 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 133.5, 130.7, 127.5, 127.0, 115.4, 115.2, 51.5, 47.2, 35.2, 25.0, 11.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}FO_2$ 237.1291; found 237.1284.

3.3 General procedure for the preparation of (*E*)-2-methyl-5-phenylpent-4-enoic acid derivatives 19:

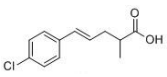
NaOH (1.2 g, 30 mmol) was added to the solution of methyl 2-methyl-5-phenylpent-4-enoate derivative **18** (10 mmol) in MeOH (30 mL). The resulting mixture was stirred overnight at room temperature. The resulting solution was acidified with concentrated HCl. The aqueous phase was extracted three times with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. (*E*)-2-methyl-5-phenylpent-4-enoic acid derivative **19** was purified by silica-gel flash column chromatography (EtOAc/PE). The NMR spectra of compounds **19a** and **19n** accord with reported literatures [27-29].



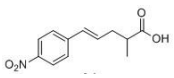
19a (1.7 g) was obtained from **18a** (2.0 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35- 7.19 (m, 5H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.20- 6.13 (m, 1H), 2.66- 2.57 (m, 2H), 2.39- 2.34 (m, 1H), 1.23 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.3, 137.3, 132.4, 128.5, 127.2, 126.8, 126.2, 39.5, 36.7, 16.4.



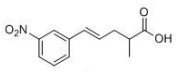
19b (1.9 g) was obtained from **18b** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 91% yield, m.p. 49- 51 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.17- 6.07 (m, 1H), 2.68- 2.52 (m, 2H), 2.32 (s, 4H), 1.22 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.3, 137.0, 134.5, 132.3, 129.2, 126.1, 125.7, 39.5, 36.7, 21.1, 16.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}O_2$ 205.1229; found 205.1224.



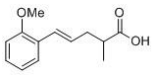
19c (1.9 g) was obtained from **18c** (2.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 85% yield, m.p. 69- 70 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 1.6 Hz, 4H), 6.42- 6.38 (m, 1H), 6.18- 6.10 (m, 1H), 2.66- 2.55 (m, 2H), 2.36 (dt, *J* = 13.7, 6.6 Hz, 1H), 1.24- 1.22 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.0, 135.8, 132.8, 131.2, 128.6, 127.5, 127.3, 39.4, 36.6, 16.5. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{12}H_{12}ClO_2$ 223.0526; found 223.0529.



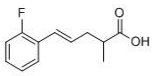
19d (2.0 g) was obtained from **18d** (2.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 87% yield, m.p. 97- 98 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.66 (s, 1H), 8.19- 8.14 (m, 2H), 7.47- 7.41 (m, 2H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.42- 6.35 (m, 1H), 2.72- 2.62 (m, 2H), 2.48- 2.40 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.2, 146.7, 143.7, 132.1, 130.6, 126.6, 124.0, 39.2, 36.7, 16.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}NO_4$ 236.0923; found 236.0940.



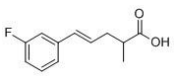
19e (2.1 g) was obtained from **18e** (2.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 86% yield, m.p. 85- 86 °C . ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 8.05 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.34 (dd, *J* = 15.2, 7.7 Hz, 1H), 2.69- 2.61 (m, 2H), 2.44- 2.40 (m, 1H), 1.26 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.0, 148.6, 139.0, 132.0, 130.3, 130.3, 129.4, 121.8, 120.7, 39.2, 36.5, 16.6. HRMS (ESI) m/z: $[M+NH_4]^+$ Calcd for $C_{12}H_{17}N_2O_4$ 253.1188; found 253.1182.



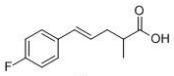
19f (1.9 g) was obtained from **18f** (2.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, yellow solid, 86% yield, m.p. 76- 77 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.25- 7.18 (m, 1H), 6.92- 6.75 (m, 3H), 6.20- 6.12 (m, 1H), 3.83 (s, 3H), 2.66- 2.59 (m, 2H), 2.42- 2.34 (m, 1H), 1.23 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.2, 156.4, 128.2, 127.5, 127.1, 126.6, 126.4, 120.6, 110.9, 55.5, 39.5, 37.1, 16.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{16}O_3Na$ 243.0997; found 243.0996.



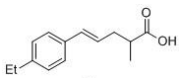
19g (1.8 g) was obtained from **18g** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 85% yield, m.p. 70- 71 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (t, *J* = 7.7 Hz, 1H), 7.20- 7.15 (m, 1H), 7.09- 6.98 (m, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.28- 6.21 (m, 1H), 2.67- 2.56 (m, 2H), 2.43- 2.36 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.4, 161.3, 158.8, 129.6, 128.4, 127.2, 124.8, 124.0, 115.6, 39.4, 37.0, 16.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}FO_2$ 209.0978; found 209.0970.



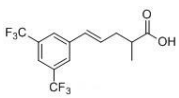
19h (1.7 g) was obtained from **18h** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 84% yield, m.p. 103- 104 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.1 Hz, 1H), 7.10- 7.03 (m, 2H), 6.95- 6.88 (m, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.14- 6.22 (m, 1H), 2.67- 2.55 (m, 2H), 2.41- 2.33 (m, 1H), 1.24 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.2, 161.9, 139.6, 131.4, 129.9, 128.3, 122.0, 114.0, 112.6, 39.3, 36.5, 16.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}FO_2$ 209.0978; found 209.0968.



19i (1.8 g) was obtained from **18i** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 85% yield, m.p. 86- 87 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31- 7.25 (m, 2H), 6.98 (t, *J* = 8.5 Hz, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.3, 7.8 Hz, 1H), 2.65- 2.55 (m, 2H), 2.37- 2.33 (m, 1H), 1.23 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.5, 163.3, 133.4, 131.2, 127.6, 126.5, 115.4, 39.5, 36.6, 16.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}FO_2$ 209.0978; found 209.0963.

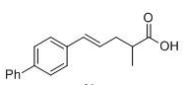


19j (1.9 g) was obtained from **18j** (2.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 86% yield, m.p. 77- 76 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (s, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.15- 6.08 (m, 1H), 2.65- 2.53 (m, 4H), 2.39- 2.31 (m, 1H), 1.26- 1.20 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.9, 143.4, 134.8, 132.3, 128.0, 126.1, 125.8, 39.5, 36.7, 28.6, 16.4, 15.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1385; found 219.1375.

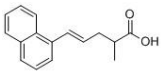


19k (2.7 g) was obtained from **18k** (3.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 84% yield, m.p. 96- 97 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 13.9 Hz, 3H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.39- 6.31 (m, 1H), 2.72- 2.61 (m, 2H), 2.47- 2.39 (m, 1H), 1.27

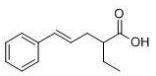
(d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 139.2, 132.0, 131.5, 129.9, 125.9, 122.0 120.7, 39.0, 36.5, 16.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}F_6O_2$ 327.0820; found 327.0807.



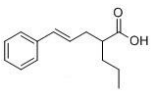
19l (2.4 g) was obtained from **18l** (2.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 89% yield, m.p. 127- 128 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60- 7.31 (m, 9H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.25- 6.18 (m, 1H), 2.69- 2.38 (m, 3H), 1.25 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.6, 140.8, 140.0, 136.4, 132.0, 128.8, 127.2, 127.0, 126.9, 126.6, 39.4, 36.8, 16.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}O_2$ 267.1385; found 267.1378.



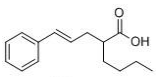
19m (2.3 g) was obtained from **18m** (2.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 87% yield, m.p. 86- 88 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09- 8.07 (m, 1H), 7.83 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.54- 7.43 (m, 4H), 7.24- 7.16 (m, 1H), 6.20- 6.13 (m, 1H), 2.76- 2.53 (m, 2H), 2.51- 2.45 (m, 1H), 1.29 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.3, 135.2, 133.6, 131.1, 130.1, 129.9, 128.5, 127.6, 125.9, 125.7, 125.6, 123.9, 123.8, 39.6, 37.1, 16.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{16}O_2Na$ 263.1048; found 263.1044.



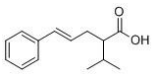
19n (1.8 g) was obtained from **18n** (2.2 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40- 7.23 (m, 5H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.24- 6.17 (m, 1H), 2.63- 2.42 (m, 3H), 1.79- 1.63 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.1, 137.4, 132.2, 128.5, 127.2, 126.9, 126.2, 47.0, 34.9, 24.6, 11.6.



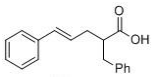
19o (1.9 g) was obtained from **18o** (2.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 87% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35- 7.26 (m, 4H), 7.23- 7.19 (m, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.20- 6.12 (m, 1H), 2.56- 2.38 (m, 3H), 1.68- 1.52 (m, 2H), 1.42- 1.25 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.1, 137.3, 132.2, 128.5, 127.2, 126.9, 126.1, 45.2, 35.4, 33.7, 20.5, 14.0. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{17}O_2$ 217.1229; found 217.1228.



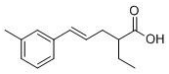
19p (2.0 g) was obtained from **18p** (2.5 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 85% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35- 7.17 (m, 5H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.20- 6.12 (m, 1H), 2.57- 2.39 (m, 3H), 1.70- 1.52 (m, 2H), 1.33 (q, *J* = 4.0 Hz, 4H), 0.89- 0.88 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.4, 137.3, 132.2, 128.5, 127.2, 126.9, 126.1, 45.4, 35.3, 31.3, 29.4, 22.6, 13.9. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{19}O_2$ 231.1385; found 231.1386.



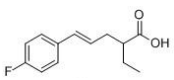
19q (1.9 g) was obtained from **18q** (2.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, light yellow oil, 87% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35- 7.26 (m, 3H), 7.24- 7.14 (m, 2H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.21- 6.13 (m, 1H), 2.54- 2.32 (m, 3H), 2.01- 1.94 (m, 1H), 1.03- 0.99 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.8, 141.9, 137.4, 133.4, 131.9, 128.5, 127.2, 126.1, 52.2, 32.8, 30.1, 20.1. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{17}O_2$ 217.1229; found 217.1228.



19r (2.3 g) was obtained from **18r** (2.8 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, white solid, 87% yield, m.p. 65- 66 °C.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49- 7.15 (m, 10H), 6.44 (dd, *J* = 15.8, 13.0 Hz, 1H), 6.19- 6.11 (m, 1H), 3.10- 2.74 (m, 3H), 2.61- 2.42 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.8, 137.2, 132.7, 129.0, 128.9, 128.7, 128.5, 127.3, 126.6, 126.4, 126.2, 47.2, 37.6, 34.8. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{17}O_2$ 265.1229; found 265.1231.

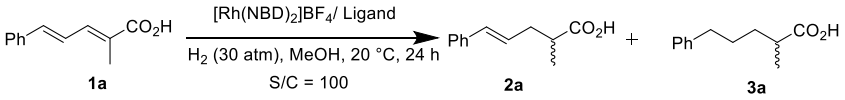


19s (2.0 g) was obtained from **18s** (2.3 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 88% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18- 7.12 (m, 3H), 7.04- 7.01 (m, 1H), 6.43- 6.38 (m, 1H), 6.16- 6.12 (m, 1H), 2.54- 2.38 (m, 3H), 2.32 (s, 3H), 1.69- 1.63 (m, 2H), 0.99- 0.94 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.1, 138.0, 137.3, 132.3, 128.4, 128.0, 126.9, 126.7, 123.3, 47.0, 34.9, 24.6, 21.4, 11.6. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{17}O_2$ 217.1229; found 217.1228.



19t (2.0 g) was obtained from **18t** (2.4 g) after silica-gel flash column chromatography using PE and EtOAc as eluent, colorless oil, 87% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31- 7.26 (m, 2H), 6.99- 6.74 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.09- 6.03 (m, 1H), 2.55- 2.37 (m, 3H), 1.74- 1.60 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.6, 163.3, 133.5, 131.0, 127.6, 126.6, 115.3, 46.9, 34.8, 24.6, 11.6. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{13}H_{14}FO_2$ 221.0978; found 221.0977.

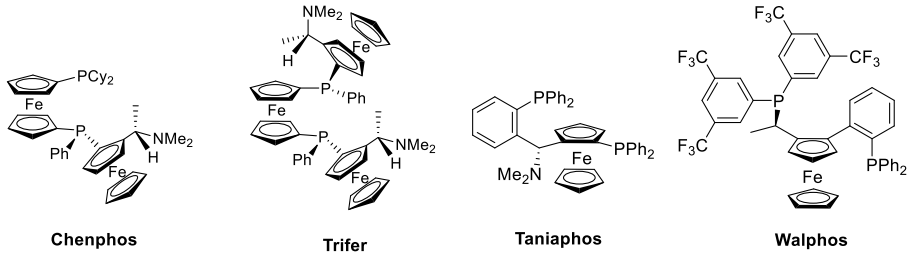
4.Screening ligands for the asymmetric hydrogenation of conjugated *α*-substituted dienoic acids 1



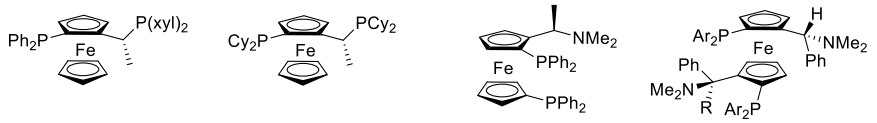
1a 2a 3a

Entry	Ligand	Conv. (%)[b]	Ratio of 2a (%)[b]	*ee* of 2a (%)[c]
1	Trifer	16	100	>99.9
2	Chenphos	17	100	89
3	Taniaphos	100	0	N.A.
4	Walphos	52	45	N.A.
5	Josiphos 1	47	22	N.A.
6	Josiphos 2	100	0	N.A.
7	BPPFA	trace	N.D.	N.D.
8	MandyPhos	trace	N.D.	N.D.

[a] Reaction conditions: 0.2 mmol scale, [substrate] = 0.2 mol·L^{-1}, solvent = 1 mL, 1.0 mol% of catalyst ([Rh(NBD)$_2$]BF$_4$: Ligand= 1:1.1). [b] Determined by ^{1}H NMR analysis. [c] Determined by chiral HPLC analysis using a chiral column.



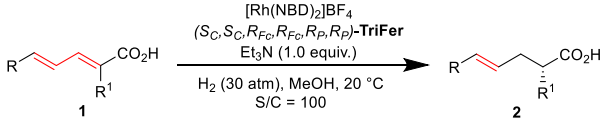
Chenphos Trifer Taniaphos Walphos



SL-J005-1 SL-J003-1 bppfa Mandyphos
Ar = 3,5-Me$_2$-4MeOPh

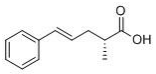
5.Asymmetric hydrogentaion of conjugated *α*-substituted dienoic acids 1

5.1 General procedure for the asymmetric hydrogenation

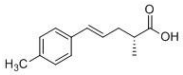


The experiment was operated in glove box filled with argon. A solution of (S_C,S_C,R_{Fc},R_{Fc},R_P,R_P)-TriFer (2.00 mg, 0.0022 mmol) and [Rh(NBD)$_2$]BF$_4$ (0.75 mg, 0.002 mmol) in MeOH (1.0 mL) was stirred for 30 min. The resulting clear orange solution was transferred into a hydrogenation tube equipped with a stir bar and substrate **1** (0.2 mmol) and triethylamine (27.6 μL, 0.2 mmol) was added successively. The hydrogenation tube was put into an autoclave. The air in the autoclave was replaced with hydrogen three times. The autoclave was charged with hydrogen to 30 atm, and the reaction mixture was stirred at room temperature for a certain time. After releasing the hydrogen, the reaction mixture was concentrated to move MeOH and most Et$_3$N. The crude product was the purified by flash chromatography on a short silica gel column and concentrated *in vacuo* to give the pure product. The *ee* values of most products were obtained by chiral HPLC .The *ee* values of products **2d**, **2g**, **2i**, **2l**, **2p** were

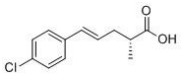
obtained from determination of the corresponding amide by chiral HPLC, and the derivatization operation is as follows. The product was reacted with aniline (1.1 equiv.) in the presence of EDCI (1.1 equiv.) in DCM for 0.5 hour to afford the corresponding amide.



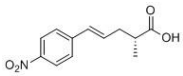
2a：37 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77- 7.09 (m, 5H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, J = 15.5, 7.0 Hz, 1H), 2.93- 2.50 (m, 2H), 2.47- 2.19 (m, 1H), 1.23 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 137.3, 132.4, 128.5, 127.2, 126.8, 126.1, 77.3, 77.0, 76.7, 39.5, 36.7, 16.4. $[\alpha]_D^{20}$ = -37.2 (*c* 1.36, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OJ-3 column, hexane: isopropanol = 97:3; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 6.64 min (major).



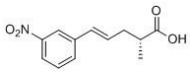
2b：39 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 11.6 Hz, 2H), 6.57-6.28 (m, 1H), 6.23-5.96 (m, 1H), 2.71-2.49 (m, 2H), 2.43-2.21 (m, 4H), 1.22 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 137.0, 134.5, 132.3, 129.2, 126.0, 125.8, 39.5, 36.7, 21.2, 16.4. $[\alpha]_D^{20}$ = -35.1 (*c* 1.44, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OJ-3 column, hexane: isopropanol = 95:5; flow rate = 0.5 mL/min; UV detection at 254 nm; t_R = 4.59 min (major).



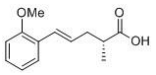
2c：43 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 96% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 10.3 Hz, 4H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.6, 7.1 Hz, 1H), 2.74- 2.48 (m, 2H), 2.36 (dt, *J* = 13.0, 6.3 Hz, 1H), 1.23 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 135.8, 132.8, 131.2, 128.6, 127.5, 127.3, 39.4, 36.6, 16.5. $[\alpha]_D^{20}$ = -33.4 (*c* 1.51, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IA-U column, hexane: isopropanol = 98:2; flow rate = 0.5 mL/min; UV detection at 254 nm; t_R = 5.01 min (major).



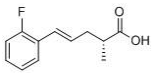
2d：46 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 97% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.60- 6.23 (m, 2H), 2.67-2.50 (m, 2H), 2.45- 2.24 (m, 1H), 1.20 (d, *J* = 5.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 182.0, 146.7, 143.6, 132.4, 130.4, 126.5, 123.9, 39.7, 36.9, 16.7. $[\alpha]_D^{20}$ = -28.3 (*c* 1.23, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OD-3 column, hexane: isopropanol = 95:5; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 3.89 min (major).



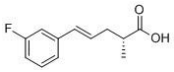
2e：46 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 97% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.41- 6.19 (m, 1H), 2.71- 2.61 (m, 2H), 2.52- 2.27 (m, 1H), 1.26 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.0, 148.6, 139.0, 132.0, 130.3, 129.4, 121.8, 120.7, 39.2, 36.5, 16.6. $[\alpha]_D^{20}$ = -30.6 (*c* 1.10, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OD-3 column, hexane: isopropanol = 90:10; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 2.39 min (major), 6.50 min(minor).



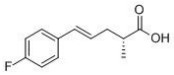
2f：43 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 97% yield, 98% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46- 7.33 (m, 1H), 7.23- 7.14 (m, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.6, 7.0 Hz, 1H), 3.83 (s, 3H), 2.66- 2.59 (m, 2H), 2.45- 2.23 (m, 1H), 1.23 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.5, 156.4, 128.3, 127.5, 127.1, 126.3, 127.5, 127.1, 126.6, 120.6, 110.9, 55.5, 39.6, 37.1, 16.4. $[\alpha]_D^{20}$ = -34.2 (*c* 1.20, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IA-U column, hexane: isopropanol = 98:2; flow rate = 0.5 mL/min; UV detection at 230 nm; t_R = 4.81 min (major), 5.30 min(minor).



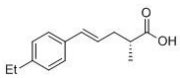
2g: 41 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49- 7.34 (m, 1H), 7.20- 7.15 (m, 1H), 7.11- 6.93 (m, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.7, 7.1 Hz, 1H), 2.91- 2.50 (m, 2H), 2.40 (dd, *J* = 15.6, 8.9 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.5, 161.2, 158.8, 129.5, 128.4, 127.2, 124.9, 124.0, 115.7, 39.4, 37.0, 16.4. $[\alpha]_D^{20}$ = -39.2 (*c* 2.0, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OD-3 column, hexane: isopropanol = 90:10; flow rate = 0.5 mL/min; UV detection at 254 nm; t_R = 5.44 min (major).



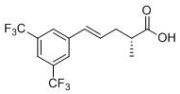
2h: 41 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, 97% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37- 7.18 (m, 2H), 7.07 (dd, *J* = 21.0, 9.0 Hz, 2H), 6.93- 6.88 (m, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.18 (dt, *J* = 15.4, 7.0 Hz, 1H), 2.88- 2.49 (m, 2H), 2.37 (dt, *J* = 13.4, 6.6 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.0, 164.3, 161.9, 139.6, 131.4, 129.9, 128.3, 122.0, 114.0, 112.6, 39.3, 36.5, 16.5.$[\alpha]_D^{20}$ = -41.2 (*c* 1.30, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OJ-3 column, hexane: isopropanol = 95:5; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 3.52 min (major), 3.86 min (minor).



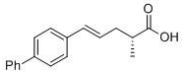
2i: 41 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, 98% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34- 7.19 (m, 2H), 7.07- 6.88 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.21- 5.82 (m, 1H), 2.66- 2.55 (m, 2H), 2.41- 2.20 (m, 1H), 1.23 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.1, 163.3, 160.9, 133.4, 131.2, 127.6, 126.5, 115.4, 39.4, 36.6, 16.5.$[\alpha]_D^{20}$ = -40.6 (*c* 1.30, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OD-3 column, hexane: isopropanol = 90:10; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 5.65 min (major), 7.55 min (minor).



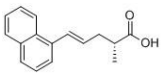
2j: 42 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 97% yield, 99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30- 7.23 (m, 2H), 7.18- 7.08 (m, 2H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.24- 5.85 (m, 1H), 2.74- 2.51 (m, 4H), 2.46- 2.24 (m, 1H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.4, 143.4, 134.8, 132.3, 128.0, 126.1, 125.8, 39.5, 36.7, 28.6, 16.4, 15.6. $[\alpha]_D^{20}$ = -35.9 (*c* 1.44, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OJ-3 column, hexane: isopropanol = 97:3; flow rate = 0.5 mL/min; UV detection at 220 nm; t_R = 5.74 min (major), 6.35 min (minor).



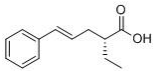
2k: 64 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, 97% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 14.0 Hz, 3H), 6.52 (d, J = 15.9 Hz, 1H), 6.43- 6.25 (m, 1H), 2.72- 2.62 (m, 2H), 2.42 (dd, *J* = 13.9, 6.5 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9, 139.2, 132.0, 131.7, 131.2, 129.9, 125.9, 124.7, 121.9, 120.7, 39.0, 36.5, 16.6.$[\alpha]_D^{20}$ = -39.2 (*c* 2.42, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OJ-3 column, hexane: isopropanol = 97:3; flow rate = 0.5 mL/min; UV detection at 254 nm; t_R = 2.42 min (minor), 2.88 min (major).



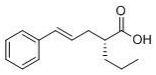
2l: 52 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, 98% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90- 7.30 (m, 10H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.23 (dd, *J* = 15.2, 7.5 Hz, 1H), 2.73- 2.51 (m, 2H), 2.45- 2.19 (m, 1H), 1.25 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.2, 140.8, 140.0, 136.3, 132.0, 128.8, 127.2, 127.0, 126.9, 126.6, 39.5, 36.8, 16.5. $[\alpha]_D^{20}$ = -63.2 (*c* 1.32, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak OJ-3 column, hexane: isopropanol = 98:2; flow rate = 0.3 mL/min; UV detection at 298 nm; t_R = 6.05 min (minor), 7.07 min (major).



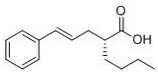
2m：47 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 97% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28- 7.96 (m, 1H), 7.90- 7.64 (m, 2H), 7.63- 7.28 (m, 4H), 7.21- 6.98 (m, 1H), 6.37- 5.95 (m, 1H), 2.74- 2.67 (m, 2H), 2.56- 2.32 (m, 1H), 1.29 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.4, 135.2, 133.6, 131.1, 130.1, 129.9, 128.5, 127.6, 125.9, 125.7, 125.7, 124.0, 123.9, 39.6, 37.1, 16.5. $[\alpha]_D^{20}$ = -32.7 (*c* 1.43, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IB-U column, hexane: isopropanol = 98:2; flow rate = 0.6 mL/min; UV detection at 210 nm; t_R = 3.71 min (major).



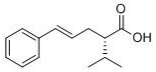
2n：40 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, 98% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56- 7.07 (m, 8H), 6.44 (d, J = 15.9 Hz, 1H), 6.28- 5.95 (m, 1H), 2.75- 2.26 (m, 3H), 1.87- 1.50 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.0, 137.3, 132.2, 128.5, 127.2, 126.9, 126.1, 46.9, 34.9, 24.6, 11.6.$[\alpha]_D^{20}$ = -34.8 (*c* 1.43, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IA-U column, hexane: isopropanol = 95:5; flow rate = 0.5 mL/min; UV detection at 254 nm; t_R = 2.42 min (major), 2.67 min (minor).



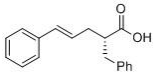
2o：43 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54- 7.02 (m, 5H), 6.44 (d, J = 15.7 Hz, 1H), 6.28- 5.98 (m, 1H), 2.77- 2.24 (m, 3H), 1.78- 1.29 (m, 4H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.9, 137.3, 132.2, 128.5, 127.2, 126.9, 126.1, 45.3, 35.3, 33.7, 20.5, 14.0. $[\alpha]_D^{20}$ = -52.3 (*c* 1.56, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AS-3 column, hexane: isopropanol = 99:1; flow rate = 0.5 mL/min; UV detection at 254 nm; t_R = 8.22 min (major).



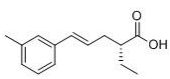
2p：45 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, 99% *ee*, ^{1}H NMR (400 MHz, CDCl*3*) δ 7.49- 7.05 (m, 5H), 6.44 (d, J = 15.8 Hz, 1H), 6.24- 6.02 (m, 1H), 2.56- 2.39 (m, 3H), 1.81- 1.43 (m, 2H), 1.33- 1.26 m, 4H), 0.89 (t, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 137.4, 132.2, 128.5, 127.2, 127.0, 126.2, 45.5, 35.3, 31.3, 29.4, 22.6, 14.0. $[\alpha]_D^{20}$ = -60.2 (*c* 1.72, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IA-U column, hexane: isopropanol = 95:5; flow rate = 0.5 mL/min; UV detection at 254 nm; t_R = 2.79 min (major), 4.21 min (minor).



2q：43 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (tt, J = 23.9, 8.1 Hz, 5H), 6.44 (d, J = 15.8 Hz, 1H), 6.26- 5.98 (m, 1H), 2.57- 2.21 (m, 3H), 2.09- 1.79 (m, 1H), 0.99 (t, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8, 137.4, 131.9, 128.5, 127.3, 127.1, 126.1, 52.3, 32.7, 30.1, 20.1.$[\alpha]_D^{20}$ = -55.4 (*c* 1.33, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AS-3 column, hexane: isopropanol = 99:1; flow rate = 0.5 mL/min; UV detection at 230 nm; t_R = 5.86 min (major).

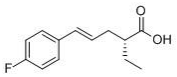


2r (prepared by hydrogenation of substrate 1r by [Rh-$(NBD)_2$]BF_4- ChenPhos complex)：52 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, 97% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29- 7.10 (m, 10H), 6.38 (d, J = 15.5 Hz, 1H), 6.11 (dd, J = 15.7, 8.5 Hz, 1H), 3.11- 2.65 (m, 3H), 2.58- 2.25 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.8, 138.8, 137.2, 132.7, 129.0, 128.9, 128.5, 127.3, 126.5, 126.4, 126.2, 47.2, 37.6, 34.7. $[\alpha]_D^{20}$ = -71.5 (*c* 2.13, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IA-U column, hexane: isopropanol = 95:5; flow rate = 0.5 mL/min; UV detection at 254 nm; t_R = 3.25 min (major), 3.57 min (minor).



2s：43 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, >99.9% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20- 7.12 (m, 3H), 7.01 (d, J = 7.1 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.6, 7.0 Hz, 1H), 2.62-

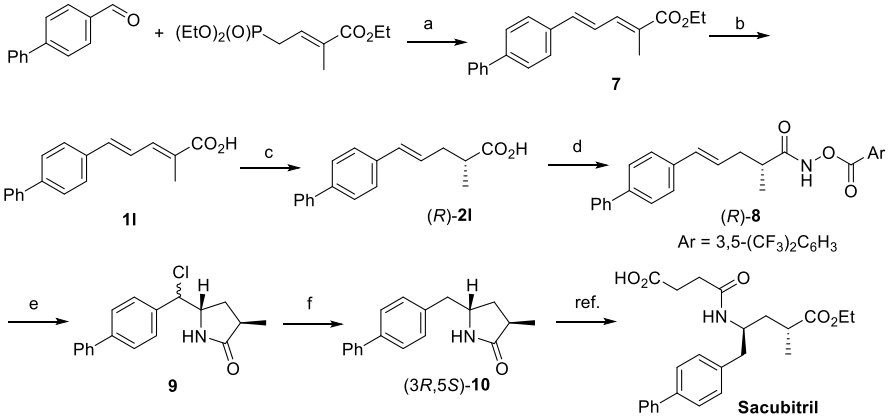
2.34 (m, 3H), 2.32 (s, 3H), 1.71- 1.60 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 182.3, 138.1, 137.3, 132.3, 128.5, 128.0, 126.9, 126.7, 123.3, 47.1, 34.9, 24.6, 21.4, 11.7. $[\alpha]_D^{20}$ = -42.4 (c 1.67, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IA-U column, hexane: isopropanol = 98:2; flow rate = 0.5 mL/min; UV detection at 230 nm; t_R = 3.92 min (major).



2t：43 mg after silica-gel flash column chromatography using PE and EtOAc as eluent, 98% yield, 97% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41- 7.17 (m, 2H), 6.97 (t, J = 8.6 Hz, 2H), 6.40 (d, J = 15.8 Hz, 1H), 6.20- 5.93 (m, 1H), 2.74- 2.23 (m, 3H), 1.79- 1.47 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.5, 163.3, 160.9, 133.5, 131.0, 127.6, 126.6, 115.5, 115.2, 46.9, 34.8, 24.6, 11.6. $[\alpha]_D^{20}$ = -46.8 (c 1.23, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IA-U column, hexane: isopropanol = 95:5; flow rate = 0.5 mL/min; UV detection at 230 nm; t_R = 2.68 min (major), 2.92 min (minor).

6. Asymmetric synthesis of the intermediate of sacubitril

6.1 Synthesis route of the intermediate (3*R*, 5*S*)-10 of sacubitril



Reagents and conditions: a) *n*-BuLi (1.2 equiv.), ethyl 4-(diethoxyphosphoryl)-2-methylbut-2-enoate (1.3 equiv.) / THF, 0 °C→ r.t.; b) NaOH (3.0 equiv.), MeOH; c) 1.0 mol% of catalyst ($[Rh(NBD)_2]BF_4$: (S_C,S_C,R_{Fc},R_{Fc},R_P,R_P)-TriFer = 1:1.1), MeOH, H_2 (30 atm), r.t.; d) step1: CDI (2.0 equiv.), hydroxylammonium chloride (4.0 equiv.), DMF, r.t.; step 2: 3,5-bis(trifluoromethyl) benzoyl chloride (1.1 equiv), Et_3N (1.1 equiv.), EtOAc, 0 °C→ r.t.; e) $FeCl_2$ (0.1 equiv.), 1,10-phenanthroline (0.2 equiv.), TBAC (2.5 equiv.), DCM; f) Pd/C (0.1 equiv.), MeOH.

Ethyl (2*E*,4*E*)-5-([1,1'-biphenyl]-4-yl)-2-methylpenta-2,4-dienoate 7

n-BuLi (7.9 ml, 19.75 mmol, 2.5 M solution in hexane) was added dropwise to a solution of ethyl 4-(diethoxyphosphoryl)-2-methylbut-2-enoate[30] (5.22 g, 19.75 mmol) in dry THF (0.3 M solution) at 0 °C under nitrogen and was stirred for 30 minutes. A solution of 4-Biphenylcarboxaldehyde (3 g, 16.46 mmol) in THF (1.0 M solution) was added to the reaction mixture. The resulting mixture was stirred at ambient temperature. After the completion of reaction monitored by TLC analysis, the reaction was quenched by addition of saturated ammonium chloride and the resulting aqueous phase was extracted 3 times with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The desired ethyl (2*E*,4*E*)-5-([1,1'-biphenyl]- 4-yl)-2-methylpenta-2,4-dienoate **7** (4.66 g, 97%, m.p. 108- 109 °C) as white solid was obtained by silica-gel flash column chromatography using PE and EtOAc as eluent. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63- 7.34 (m, 9H), 7.11 (dd, J = 15.4, 11.3 Hz, 1H), 6.94- 6.89 (m, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.07 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 141.4, 140.4, 138.5, 138.2, 135.7, 127.7, 128.9, 127.6, 127.5, 127.4, 126.9, 124.0, 60.7, 14.4, 12.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}O_2Na$ 315.1361; found 315.1357.

(2*E*,4*E*)-5-([1,1'-biphenyl]-4-yl)-2-methylpenta-2,4-dienoic acid 1l

NaOH (1.64 g, 41.0 mmol) was added to the solution of (2*E*,4*E*)-5-([1,1'-biphenyl]-4-yl)- 2-methylpenta-2,4-dienoate **7** (4.0 g, 13.68 mmol) in MeOH (10 ml) and H_2O (2 ml). The resulting mixture was stirred overnight under nitrogen at room temperature. The resulting solution was acidified with 2N HCl. The aqueous phase was extracted three times with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* after filtration. The cinnamate acid derivative **1l** (3.4 g, 94%) was purified by recrystallisation from EtOAc and petroleum ether.

(*R*)-5-([1,1'-biphenyl]-4-yl)-2-methylpent-4-enoic acid ((*R*)-2l)

The experiment was operated in glove box filled with argon. A solution of (S_C,S_C,R_{Fc},R_{Fc},R_P,R_P)-TriFer (15.5 mg, 0.017 mmol) and $[Rh(NBD)_2]BF_4$ (5.7 mg, 0.015 mmol) in MeOH (15.0 mL) was stirred for 30 min. The resulting clear orange solution was transferred into a hydrogenation tube equipped with a stir bar and substrate **1l** (2.0 g, 7.57 mmol) and triethylamine (1.05 mL, 7.57 mmol) was added successively. The hydrogenation tube was put into an autoclave. The air in the autoclave was replaced with hydrogen three times. The autoclave was charged with hydrogen to 30 atm, and the reaction mixture was stirred at room temperature for 32 h. After releasing the hydrogen, the reaction mixture was concentrated on a rotary evaporator. The product (*R*)-5-([1,1'-biphenyl]-4-yl)-2- methylpent-4-enoic acid (*R*)-**2l** (1.96 g, 98%, 98% *ee*) was purified by flash chromatography on silica gel column using PE and EtOAc as eluent.

(*R*)-5-([1,1'-biphenyl]-4-yl)-N-(3,5-bis(trifluoromethyl)benzoyloxy)-2-methylpent-4-enamide ((*R*)-8)

CDI (1.65 g, 10.18 mmol) was added to a solution of (*R*)-5-([1,1'-biphenyl]-4-yl)-2- methylpent-4-enoic acid (*R*)-**2l** (1.5 g, 5.09 mmol) in DMF (10 ml) at r.t.. The reaction mixture was stirred for 0.5 h and then hydroxylammonium chloride (1.41g, 20.26 mmol) was added. After being stirred for another 2 h, the reaction mixture was quenched by addition of water (5 ml). The aqueous phase was extracted with EtOAc three times and the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4, and concentrated *in vaccuo* after filtration. The crude product hydroxamates was used directly without further purification. The crude hydroxamates was disolloved in EtOAc. Et_3N (0.78 ml, 5.60 mmol) was added dropwise to the aboved solution at -5 °C. After 10 min, 2,5-bis(trifluoromethyl)benzoyl chloride (1.12 g, 5.60 mmol) is added over 10 min at the same temperature. The resulting solution is warmed to r.t. and left to stir for 0.5 h before quenched by addition of water. The aqueous phase was extracted with EtOAc three times and the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4, and concentrated *in vaccuo* after filtration. The product *(R)*-5-([1,1'-biphenyl]-4-yl)-N-(3,5-bis(trifluoromethyl)benzoyloxy)-2- methylpent-4-enamide (*R*)-**8** (2.26g, 88%, m.p. 119- 122 °C, $[\alpha]_D^{20}$ = -132.1 (*c* 0.06, $CHCl_3$)) as white solid was obtained by silica-gel flash column chromatography using PE and EtOAc as eluent. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 2H), 8.13 (s, 1H), 7.60- 7.26 (m, 9H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.32- 6.24 (m, 1H), 2.71 – 2.40 (m, 3H), 1.33 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.5, 162.7, 140.6, 140.2, 136.1, 132.8, 132.6, 130.1, 128.8, 127.6, 127.3, 127.2, 126.9, 126.6, 126.4, 123.9, 38.7, 37.2, 17.3. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{27}H_{20}F_6NO_3$ 520.1348; found 520.1348.

(3*R*,5*S*)-5-([1,1'-biphenyl]-4-ylchloromethyl)-3-methylpyrrolidin-2-one 9

To a flame-dried sealable vial was added $FeCl_2$ (41.1 mg, 0.32 mmol) and 1,10- phenanthroline (117.8 mg, 0.65 mmol). After the vial was evacuated and backfilled with N_2 three times, anhydrous DCM (6.0 ml) was added and the resulting solution was stirred at r.t. for 20 min. (*R*)-5-([1,1'-biphenyl]- 4-yl)-N-(3,5-bis(trifluoromethyl)benzoyloxy)-2-methylpent- 4-enamide (*R*)-**8** (1.6 g, 3.24 mmol) and anhydrous TBAC (2.25 g, 8.1 mmol) were dissolved in anhydrous DCM (16.0 ml) in flame- dried vial B under Ar. Vial B was cooled down to 0 °C and the solution in vial A was transferred to Vial B dropwise. The resulting solution was left to stir at r.t. for 2.5 h before quenched by addition of water. The aqueous phase was extracted with EtOAc three times. The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated *in vaccuo* after filtration. The product (3*R*,5*S*)-5-([1,1'-biphenyl]- 4-ylchloromethyl)-3-methylpyrrolidin-2-one **9** (835 mg, 86 %, m.p. 189-190 °C, $[\alpha]_D^{20}$ = -10.2 (*c* 0.06, $CHCl_3$)) as white solid was obtained by silica-gel flash column chromatography using PE and EtOAc as eluent. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 8.7 Hz, 4H), 7.48- 7.36 (m, 5H), 5.66 (br, 1H), 4.71 (d, *J* = 7.8 Hz, 1H), 4.10-4.05 (m, 1H), 2.47- 2.41 (m, 1H), 2.29 (q, *J* = 7.8 Hz, 1H), 2.08- 2.01 (m, 1H), 1.17 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.1, 142.2, 140.1, 136.4, 128.9, 128.3, 127.8, 127.7, 127.1, 64.6, 58.0, 34.4, 33.5, 16.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{18}ClNONa$ 322.0975; found 322.0968.

(3*R*,5*S*)-5-([1,1'-biphenyl]-4-ylmethyl)-3-methylpyrrolidin-2-one ((3*R*, 5*S*)-10)

To a solution of (3*R*,5*S*)-5-([1,1'-biphenyl]-4-ylchloromethyl)-3-methylpyrrolidin-2-one **9** (1.84 g, 6.16 mmol) in MeOH (20.0 ml) was added Pd/C (184 mg). The resulting mixture was stired 5 h under hydrogen at r.t. before filtration. The concentrated crude product was purified by flash column chromatography on silica gel using PE and EtOAc as eluent to give (3*R*,5*S*)-5-([1,1'-biphenyl]-4-ylmethyl)-3-methylpyrrolidin-2-one (3*R*, 5*S*)-**10** [31] (1.55 g, 95%, m.p. 132- 133 °C, $[\alpha]_D^{20}$ = 72.4 (*c* 0.04, $CHCl_3$)) as white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 12.6, 7.7 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 2H), 6.25 (s, 1H), 3.94- 3.73 (m, 1H), 2.96- 2.69 (m, 2H), 2.47 (q, *J* = 7.8 Hz, 1H), 2.14 (dd, *J* = 12.4, 8.8 Hz, 1H), 1.91 (dd, *J* = 14.1, 6.4 Hz, 1H), 1.19 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.3, 140.7, 139.8, 136.7, 129.5, 128.8, 127.5, 127.3, 127.0, 53.4, 42.4, 35.1, 34.9, 16.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{19}NONa$ 288.1365; found 288.1359.

7. Computational Methods

All DFT calculations were carried out with the GAUSSIAN 09 series of programs[32]. Density functional B3-LYP[33] with a standard 6-31G(d) basis set (LANL08[34] basis set for Rh and Fe) was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies. All minima have zero imaginary frequency and all transition states have only one imaginary frequency. The solvent effects were considered by single point calculations on the gas-phase stationary points with a continuum solvation model SMD.[35] The DFT method M06[36] functional with the 6-311+G(d) (LANL08 basis set for Rh and Fe) basis set was used to calculate the single point energies with methanol as solvent and provide highly accurate energy information. The energies given in this report are the M06 calculated Gibbs free energies in methanol solvent.

8. B3LYP and M06 absolute calculation energies, enthalpies, and free energies

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$H_{(corr\text{-}B3LYP)}$[2]	$G_{(corr\text{-}B3LYP)}$[3]	$E_{(solv\text{-}M06)}$[4]	IF[5]
CP1	-3209.764040	0.977378	0.835631	-3208.774850	-
H_2	-1.175482	0.013450	-0.001342	-1.167988	-
TS1	-3210.939957	0.992562	0.850013	-3209.930247	-845.8
CP2	-3210.949241	0.993930	0.850316	-3209.941784	-
1a	-614.935820	0.225418	0.169921	-614.673727	-
CP3	-3825.907906	1.222943	1.045525	-3824.638459	-
TS2	-3825.867360	1.220210	1.044952	-3824.617711	-554.3
CP4	-3825.903808	1.225496	1.050166	-3824.650406	-
CP5	-3825.875565	1.226844	1.056551	-3824.631972	-
TS3	-3825.862499	1.224371	1.055655	-3824.627348	-753.9
CP6	-3825.923440	1.229583	1.048938	-3824.67502	-
(*R*)-2a	-616.149072	0.249195	0.191282	-615.887552	-
TS4	-3825.851138	1.224537	1.053305	-3824.606262	-890.5
CP7	-3825.907165	1.223031	1.045728	-3824.637994	-
TS5	-3825.872731	1.220863	1.046978	-3824.607291	-515.0
CP8	-3825.874265	1.224416	1.048057	-3824.624412	-
TS6	-3825.835483	1.221650	1.046113	-3824.60576	-801.2
CP9	-3825.924106	1.229519	1.050128	-3824.675077	-
(*S*)-2a	-616.149004	0.249114	0.190928	-615.887339	-

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to enthalpy calculated by B3LYP in gas phase. [3]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M06 in toluene solvent. [5]The B3LYP calculated imaginary frequencies for the transition states.

9. B3LYP geometries for all the optimized compounds and transition states

CP1

Fe	0.48911400	2.59280000	1.79645500	C	-3.10398900	-1.63593800	4.38303300
P	-1.72721400	0.41767500	0.43697100	H	-3.40855000	-2.10985500	5.31177400
P	1.67088300	0.40986600	-0.43016500	C	2.48512500	2.67698700	1.29230700
C	-2.31827400	-0.40480300	1.98280000	H	2.85713700	3.32758500	0.51529800
C	1.96605400	1.34507900	1.10957300	C	-1.60968300	-1.50366700	2.48487400
C	-1.35351000	2.10085800	1.04140300	H	-0.75411400	-1.86915500	1.92432000
C	-3.81847200	-0.53966900	3.88990900	C	-2.00113800	-2.11878200	3.67720700
H	-4.67803400	-0.16046300	4.43574700	H	-1.44433200	-2.97223000	4.05402300
C	1.84220600	1.67239700	-1.77585200	C	1.49625200	0.90334700	2.39809300
				H	0.99364700	-0.03321200	

2.59544400			
C	-0.54461000	4.27615600	
1.09979100			
H	-0.07910200	5.20669200	
0.80247300			
C	-3.43182900	0.06980800	
2.69536200			
H	-3.99951800	0.91444800	
2.31860000			
C	1.73253800	1.93838200	
3.34581400			
H	1.45092200	1.91613600	
4.39043700			
C	2.02788800	3.54229100	-
3.87500200			
H	2.09996800	4.26589700	-
4.68190800			
C	3.08517500	3.38870800	-
2.97447200			
H	3.98359800	3.99030600	-
3.08227800			
C	2.99656400	2.45831400	-
1.93781100			
H	3.83962000	2.32670000	-
1.26967300			
C	0.88428000	2.75468000	-
3.73745000			
H	0.06110900	2.86082600	-
4.43868000			
C	-1.48270600	2.60650300	
2.38711000			
H	-1.84941800	2.05546500	
3.24003000			
C	0.79386600	1.82645400	-
2.69675100			
H	-0.09677100	1.21192000	-
2.58543900			
C	-0.76790000	3.15460000	
0.25439500			
H	-0.50845600	3.09377200	-
0.79234000			
C	2.34006900	3.03246200	
2.66391700			
H	2.59944900	3.98913600	
3.09835500			
C	-0.98446000	3.93965700	
2.41293200			
H	-0.91147800	4.56837400	
3.29081000			
Rh	-0.24729300	-0.81558200	-
0.66944000			
Fe	-5.20176000	0.09154400	-
0.79104000			
C	-3.15946900	0.65225300	-
0.68260800			
C	-6.50974000	0.08066400	
0.83141000			
C	-3.42490900	-0.10042100	-
1.89378900			
C	-4.02268700	1.80128100	-
0.68854700			
H	-4.06774800	2.55156500	
0.08926100			
C	-6.18202900	-1.74163500	-
0.54537200			
H	-5.84732300	-2.69759600	-
0.92416300			
C	-4.78327400	1.79192800	-
1.88734400			
H	-5.53948200	2.51270000	-
2.16877000			
C	-7.22356600	0.31047500	-
0.38180700			
H	-7.78838100	1.19983200	-
0.62823500			
C	-5.86671900	-1.18918400	
0.73068900			
H	-5.24455300	-1.64397900	
1.48841600			
C	-4.42581600	0.62609500	-
2.62238400			
H	-4.86595900	0.32957000	-
3.56418400			
C	-7.01890300	-0.81434400	-
1.23464700			
H	-7.40652700	-0.92928200	-
2.23836700			
H	-6.46017000	0.75760000	
1.67353300			
C	-2.66493300	-1.26792100	-
2.51095800			
H	-1.89770800	-0.81584500	-
3.15372300			
C	-3.56859800	-2.13059500	-
3.41378400			
H	-3.95254400	-1.52426100	-
4.23769400			
H	-4.42577500	-2.53505200	-
2.87049400			
H	-3.01492900	-2.95685700	-
3.86715900			
N	-1.84976200	-2.08294000	-
1.52995900			
C	-0.91182200	-2.98474700	-
2.24628900			
H	-1.42611100	-3.80721300	-
2.76030400			
H	-0.22135800	-3.42441700	-
1.51852500			
H	-0.34316200	-2.41525200	-
2.98931600			
C	-2.67725600	-2.88975500	-
0.60341600			
H	-2.01983200	-3.37435900	
0.12041200			
H	-3.24178300	-3.66235800	-
1.14217900			
H	-3.37030700	-2.23945400	-
0.07351000			
Fe	5.14060300	-0.63922900	-
0.51089900			
C	3.07821200	-0.72573400	-

0.80372700			
C	7.16229200	-0.24667800	-
0.76127000			
C	3.53809200	-1.90662700	-
0.08791900			
C	3.77231700	-0.70661400	-
2.07030700			
H	3.66958700	0.05146500	-
2.83246200			
C	6.05653000	-0.00715800	
1.25143600			
H	5.68345000	-0.18808000	
2.25048500			
C	4.63741500	-1.82945300	-
2.13693500			
H	5.31716500	-2.05931000	-
2.94688800			
C	6.42372100	0.97371300	-
0.80737600			
H	6.37350400	1.65061700	-
1.65020500			
C	6.93589600	-0.85272700	
0.51030900			
H	7.33605000	-1.80267400	
0.83932100			
C	4.49895500	-2.55965300	-
0.92462100			
H	5.05995300	-3.44564400	-
0.66058500			
C	5.74397800	1.12200900	
0.43843300			
H	5.09124600	1.93506300	
0.72403100			
H	7.76095900	-0.65790400	-
1.56327700			
C	3.04691200	-2.45533400	
1.23698200			
H	2.71284100	-1.60885800	
1.84737800			
C	4.16325500	-3.17551100	
2.02337300			
H	5.01536000	-2.50758100	
2.16643300			
H	4.52366500	-4.07087200	
1.50721900			
H	3.80947800	-3.48337300	
3.01157800			
N	1.82153000	-3.28414400	
1.02881900			
C	1.21530400	-3.68706300	
2.29657300			
H	1.78667200	-4.46188300	
2.83620200			
H	0.21487900	-4.09325300	
2.10728400			
H	1.11623600	-2.81951400	
2.95718900			
C	2.00664600	-4.45968300	
0.17669800			
H	1.03139000	-4.93546300	
0.01924300			
H	2.67329900	-5.22531900	
0.61151400			
H	2.40666100	-4.16887800	-
0.79710600			

H_2

H	0.00000000	0.00000000
0.37139400		
H	0.00000000	0.00000000	-
0.37139400			

TS1

Fe	0.18411700	3.18967800	-
0.76046700			
P	-1.92282500	0.60313600	
0.22008300			
P	1.70004600	0.20353600	
0.03730500			
C	-2.63650100	0.54297600	
1.92549400			
C	1.68489600	1.79523200	-
0.84894900			
C	1.14345900	0.42641700	
2.77618300			
H	0.19744700	-0.02975400	
2.51206000			
C	2.62219700	1.35474900	
4.45069000			
H	2.82356500	1.63097500	
5.48176600			
C	-1.55199400	2.39054200	
0.02938300			
C	-4.03000200	1.48116300	
3.68157200			
H	-4.67601300	2.27771400	
4.04009000			
C	-3.74668500	0.38610500	
4.50345800			
H	-4.17485700	0.32850000	
5.50002400			
C	2.10395800	0.64416700	
1.77959800			
C	3.33765500	1.20933400	
2.14138600			
H	4.10144700	1.35111000	
1.38824300			
C	1.10008000	1.98607500	-
2.15106500			
H	0.58584500	1.22693700	-
2.72630000			
C	1.39744500	0.78307200	
4.10307800			
H	0.63837200	0.60919600	
4.86066000			
C	-2.35123600	-0.54692500	
2.76107600			
H	-1.68748300	-1.33210800	
2.41024000			
C	-2.90517800	-0.62730800	
4.04205800			
H	-2.67366800	-1.47729100	

4.67805700
C 2.21968400 3.06377400 -
0.43532500
H 2.68313000 3.27312000
0.51805300
C -1.37632300 4.55991600 -
0.77934300
H -1.42335200 5.41725100 -
1.43802200
C -3.47950700 1.56040200
2.40213900
H -3.69992700 2.42231000
1.78001200
C 1.96677200 4.01219500 -
1.46705800
H 2.20702900 5.06671400 -
1.42791800
C 3.59299600 1.56331900
3.46701600
H 4.55163500 2.00046100
3.73276900
C -0.87404800 3.19476500
1.01279200
H -0.49641000 2.84581800
1.96419500
C -1.84788300 3.24993600 -
1.08558700
H -2.32088400 2.94949200 -
2.00930000
C 1.27907600 3.34855500 -
2.52548100
H 0.91143100 3.80981000 -
3.43276800
C -0.77800000 4.52546400
0.51414000
H -0.29247400 5.35341000
1.01394500
Rh -0.20109200 -1.05913000 -
0.33741400
Fe -5.27669700 -0.40508100 -
0.80674100
C -3.31082400 0.35713000 -
0.94529400
C -6.52471800 -0.01256900
0.81111800
C -3.48409000 -0.73912500 -
1.88170800
C -4.30815700 1.35180500 -
1.24418300
H -4.45056400 2.27610100 -
0.70277300
C -6.08857100 -2.14159500
0.03414700
H -5.68767000 -3.14115400 -
0.06015700
C -5.05531400 0.91984600 -
2.36949300
H -5.88948800 1.43940700 -
2.82203900
C -7.29438100 -0.21748100 -
0.37235600
H -7.93906000 0.51123000 -
0.84596600
C -5.77998800 -1.20243100
1.06333600
H -5.09623400 -1.35314700
1.88746900
C -4.56786700 -0.36116300 -
2.74805500
H -4.98131100 -0.95468200 -
3.54927100
C -7.02267600 -1.53225200 -
0.85457300
H -7.43228400 -1.97764400 -
1.75168200
H -6.49225400 0.89244400
1.40206100
C -2.61146100 -1.96206700 -
2.17281700
H -1.81365800 -1.61788900 -
2.84562600
C -3.42185500 -3.02753500 -
2.94259400
H -3.80086800 -2.59584600 -
3.87064700
H -4.27854500 -3.38919400 -
2.36655100
H -2.80792200 -3.87894500 -
3.23712300
N -1.82841700 -2.53073300 -
0.99356700
C -1.08737200 -3.75149000 -
1.43318600
H -1.76964500 -4.58634600 -
1.62858400
H -0.40376900 -4.04815800 -
0.63885700
H -0.50762200 -3.53467400 -
2.33260000
C -2.69080200 -2.94909600
0.13662800
H -2.04843100 -3.32575700
0.93600800
H -3.37630900 -3.75239800 -
0.16429600
H -3.27170700 -2.10867500
0.50551200
H 0.82670500 -2.05659700 -
1.03652400
H 0.75958300 -2.20799900
0.20409300
Fe 5.18325700 -0.35484100 -
1.03755700
C 3.14292200 -0.66313900 -
0.69348600
C 7.03661200 0.09894200 -
1.85855100
C 3.90073300 -1.78064700 -
0.16763900
C 3.43119100 -0.57261000 -
2.10270800
H 3.03947900 0.17411300 -

2.77887300
C 6.47419700 0.53838100
0.33723900
H 6.39520300 0.45740100
1.41332600
C 4.33989000 -1.61005900 -
2.44550600
H 4.77845500 -1.77399200 -
3.42116300
C 6.21536700 1.26529000 -
1.84069300
H 5.89030200 1.82990100 -
2.70455900
C 7.19617700 -0.35026800 -
0.51430400
H 7.74333800 -1.22924100 -
0.19967700
C 4.63446200 -2.34220200 -
1.25999300
H 5.33906000 -3.15975700 -
1.18897500
C 5.87116200 1.53941400 -
0.48557000
H 5.25243300 2.36281000 -
0.15592700
H 7.43824800 -0.38164400 -
2.74099500
C 3.83167100 -2.34369800
1.23991900
H 3.68902500 -1.50417700
1.92554400
C 5.12765400 -3.06094300
1.66499600
H 5.96939700 -2.36253800
1.64048700
H 5.37427800 -3.90516200
1.01369900
H 5.04037600 -3.44430200
2.68654900
N 2.59554000 -3.16248500
1.38223000
C 2.20240300 -3.35906000
2.77549400
H 2.88792700 -4.01188000
3.34417900
H 1.20881900 -3.82088100
2.80509600
H 2.14386500 -2.39199600
3.28456900
C 2.61699000 -4.42980600
0.65604100
H 1.62036100 -4.88392200
0.70462900
H 3.33251500 -5.16388800
1.06509500
H 2.86119600 -4.25794300 -
0.39595600

CP2

Fe -0.48742100 -2.08945300
2.22556600
P 1.81248400 -0.20196900
0.63894900
P -1.73779400 -0.41804500 -
0.49056500
C 2.47164300 0.84227800
2.00817700
C -1.92967200 -1.02366600
1.22238300
C 1.41020600 -1.75309200
1.51996500
C 4.01246600 1.25742300
3.84072800
H 4.87227700 0.95275300
4.43097900
C -1.87046700 -1.93116100 -
1.53621900
C 3.33748300 2.44327000
4.14805900
H 3.67452900 3.06134900
4.97522900
C -2.46711800 -2.27741400
1.68618200
H -2.82774500 -3.08190100
1.06239800
C 1.80051900 2.02986800
2.32744700
H 0.94053900 2.32592000
1.73584600
C 2.23057700 2.82814700
3.39068400
H 1.70195200 3.74782300
3.62591400
C -1.48911100 -0.30378700
2.38913300
H -0.98607900 0.65273100
2.38241000
C 0.55018700 -3.87577000
1.90276600
H 0.08656100 -4.84046500
1.74322600
C 3.58344300 0.46184800
2.77768600
H 4.11340800 -0.45679400
2.54674500
C -1.76423300 -1.09552300
3.54066100
H -1.51132200 -0.83838700
4.56088700
C -1.95380300 -4.23621800 -
3.14745300
H -1.98735500 -5.12714000 -
3.76778500
C -3.05022000 -3.89492400 -
2.35173200
H -3.93994100 -4.51846000 -
2.35572900
C -3.01184300 -2.74997600 -
1.55403400
H -3.87953800 -2.47922900 -
0.96318200
C -0.81946800 -3.42284800 -

3.15040800			
H	0.03271600	-3.67512600	-
3.77499100			
C	1.44964800	-2.01651100	
2.93425700			
H	1.78067200	-1.32730200	
3.69753900			
C	-0.78262400	-2.27820600	-
2.35165400			
H	0.10302500	-1.64541800	-
2.36776800			
C	0.84648700	-2.91909500	
0.89175300			
H	0.65453800	-3.04075200	-
0.16489300			
C	-2.36609500	-2.31245100	
3.10687100			
H	-2.64825100	-3.14399700	
3.73942300			
C	0.91719300	-3.31822900	
3.16214400			
H	0.77845300	-3.78257300	
4.12975800			
Rh	0.21050700	0.68038800	-
1.00307100			
H	-0.46356500	1.85295900	-
0.25933900			
H	-0.71628600	1.21124600	-
2.17760400			
Fe	5.23962400	-0.32288300	-
0.76048800			
C	3.19076000	-0.72250600	-
0.46264200			
C	6.62511700	-0.06704000	
0.76874900			
C	3.43377000	-0.28852000	-
1.83256200			
C	3.99544100	-1.89319500	-
0.23343200			
H	4.03380600	-2.44627800	
0.69518600			
C	6.27772000	1.48961500	-
0.89890600			
H	5.95203900	2.37483600	-
1.42784200			
C	4.69860800	-2.20748000	-
1.42318900			
H	5.40457900	-3.01680900	-
1.55426900			
C	7.27148300	-0.53525500	-
0.41413000			
H	7.79845600	-1.47413700	-
0.52150100			
C	6.01232700	1.18612600	
0.46849700			
H	5.43734500	1.79007700	
1.15646900			
C	4.36474000	-1.22623300	-
2.39709200			
H	4.77530900	-1.19214200	-
3.39601600			
C	7.05361800	0.42489200	-
1.44620300			
H	7.39455800	0.34566400	-
2.47009200			
H	6.59463800	-0.58262300	
1.71928900			
C	2.75033800	0.76258900	-
2.71571100			
H	1.98997300	0.22248000	-
3.29927800			
C	3.73674700	1.36853500	-
3.73579500			
H	4.22368200	0.57258800	-
4.30145600			
H	4.51993800	1.95313500	-
3.24774900			
H	3.22453600	1.99851100	-
4.46533300			
N	1.93171700	1.80841900	-
1.97988800			
C	1.28942600	2.73789900	-
2.95747300			
H	2.02749600	3.40740700	-
3.41604300			
H	0.55038100	3.33771900	-
2.42710400			
H	0.77748500	2.16705000	-
3.73321100			
C	2.74866600	2.64721200	-
1.06843700			
H	2.08084200	3.31471700	-
0.52119800			
H	3.46508500	3.25939800	-
1.63171800			
H	3.29583300	2.03132100	-
0.35984400			
Fe	-5.26998900	0.45887900	-
0.56601900			
C	-3.22460100	0.56167500	-
0.93438000			
C	-7.27376200	-0.06046200	-
0.72282800			
C	-3.70068800	1.81425700	-
0.37583300			
C	-3.94689800	0.34074800	-
2.16085800			
H	-3.83230100	-0.51184600	-
2.81374200			
C	-6.15410900	0.11936000	
1.28864100			
H	-5.78507200	0.49999700	
2.23182100			
C	-4.84902700	1.41833100	-
2.35915200			
H	-5.55956700	1.50928300	-
3.17012200			
C	-6.48397200	-1.23659900	-
0.55158900			
H	-6.41230700	-2.05686700	-
1.25369900			
C	-7.07187300	0.77634100	

0.41492000
H -7.51436200 1.75156700
0.57000400
C -4.70076900 2.31788900 -
1.26871400
H -5.28345300 3.21571000 -
1.11447800
C -5.79476000 -1.12582700
0.69307800
H -5.11177500 -1.84849700
1.11707600
H -7.88958100 0.17231700 -
1.58148100
C -3.20936700 2.54881500
0.85732300
H -2.95957000 1.80360100
1.62043300
C -4.29665000 3.46581800
1.45738100
H -5.21243500 2.89613400
1.63354400
H -4.54402900 4.30360700
0.79770900
H -3.97385200 3.88135200
2.41605300
N -1.92303000 3.25410900
0.56825900
C -1.36350500 3.89772400
1.75592500
H -1.92659200 4.78753300
2.08223800
H -0.33878100 4.22055400
1.54179900
H -1.33718600 3.18772500
2.58955000
C -1.97307600 4.19524600 -
0.55178600
H -0.96663800 4.59571400 -
0.71547000
H -2.64537600 5.05178600 -
0.37577100
H -2.28862500 3.68159200 -
1.46170000

1a

C 0.85079200 -0.67199000 -
0.00038000
H 0.66280600 -1.74601900 -
0.00073600
C -0.22823900 0.14833800
0.00003300
H -0.08691800 1.22599500
0.00056500
C 2.26296400 -0.29511300 -
0.00024000
C 3.23484700 -1.31462800
0.00005400
C 2.70954200 1.04234900 -
0.00037000
C 4.59577400 -1.01596800
0.00030600
H 2.90991300 -2.35251800
0.00010700
C 4.06808300 1.34060800 -
0.00010900
H 1.98876100 1.85461200 -
0.00077900
C 5.01893200 0.31418700
0.00025300
H 5.32517700 -1.82141800
0.00054000
H 4.38998800 2.37861400 -
0.00021400
H 6.07910300 0.55184000
0.00046400
C -1.57582000 -0.36288900
0.00002700
H -1.68246500 -1.44635100 -
0.00049600
C -2.73243500 0.34892200
0.00012000
C -3.98340100 -0.45191000
0.00005500
C -2.84846400 1.85085900
0.00029000
H -3.40191700 2.20228000
0.87905600
H -1.87056800 2.33778000 -
0.00120600
H -3.40446500 2.20215700 -
0.87692200
O -4.06378600 -1.66757400
0.00012000
O -5.09818100 0.33103500 -
0.00017100
H -5.84912500 -0.29124200 -
0.00020200

CP3

Fe 3.14672600 1.94517800 -
1.68704500
P 0.17290400 2.20164300
0.17699100
P 1.95987800 -1.14337300 -
0.39571300
C 0.05994300 3.22762400
1.72146300
C 2.98984700 -0.11920300 -
1.52143800
C 1.69134500 2.91508900 -
0.58023400
C 0.48235600 5.27990200
2.96174000
H 0.89990600 6.28247800
2.99729300
C 1.40538400 -2.47865400 -
1.56549100
C -0.15162900 4.74265900
4.08455800
H -0.23224800 5.32668000
4.99716000
C 2.55323300 0.33474300 -

2.81746300			
H	1.57145700	0.17805900	-
3.24215500			
C	-0.56048300	2.68949900	
2.86041300			
H	-0.95389000	1.67960200	
2.83684400			
C	-0.66866200	3.44718100	
4.03047900			
H	-1.15163000	3.01639800	
4.90352100			
C	4.35383700	0.29528000	-
1.37603500			
H	4.96979800	0.12254800	-
0.50720600			
C	3.16524500	3.99808900	-
2.01158800			
H	3.58088700	4.47248900	-
2.89107300			
C	0.59027100	4.52798700	
1.79078500			
H	1.10231600	4.95547100	
0.93448900			
C	4.75386500	0.97273500	-
2.56554200			
H	5.71850200	1.43230700	-
2.73781100			
C	0.62666000	-4.63189000	-
3.20590200			
H	0.33003100	-5.46616200	-
3.83560900			
C	1.81227400	-3.94117400	-
3.46897300			
H	2.44097200	-4.23510600	-
4.30507900			
C	2.20061800	-2.87637200	-
2.65418600			
H	3.13088600	-2.36045800	-
2.86445400			
C	-0.16971500	-4.24767600	-
2.12571400			
H	-1.08890300	-4.78485500	-
1.90689500			
C	2.97400400	3.00566600	
0.06151500			
H	3.21274100	2.62053800	
1.04132700			
C	0.21324100	-3.17745400	-
1.31137000			
H	-0.41298300	-2.88649100	-
0.47424100			
C	1.82475700	3.53503500	-
1.86736800			
H	1.04172100	3.62923600	-
2.60708300			
C	3.64303700	0.99250600	-
3.45923100			
H	3.61734500	1.46332700	-
4.43333300			
C	3.87247600	3.67977800	-
0.81539300			
H	4.92085600	3.87003600	-
0.62544900			
Rh	0.18166200	-0.25367800	
0.71153300			
H	1.26008200	0.06985700	
1.76972800			
H	0.25882400	-1.70481800	
1.32780100			
Fe	-3.13829300	3.30506500	-
0.69372400			
C	-1.08866600	3.00934600	-
0.91893000			
C	-3.93221200	3.99780000	
1.09244900			
C	-1.80157300	2.43484800	-
2.04883700			
C	-1.41345000	4.40739500	-
0.89014400			
H	-1.07740700	5.10958800	-
0.14180500			
C	-4.58101600	2.01642400	
0.10455300			
H	-4.69635200	0.95921900	-
0.08841800			
C	-2.29459700	4.70358500	-
1.96519700			
H	-2.74494900	5.66553000	-
2.17253100			
C	-4.80911100	4.31108000	
0.01128900			
H	-5.09154500	5.30421400	-
0.31251500			
C	-3.78978200	2.58097200	
1.14910600			
H	-3.16353900	2.03341200	
1.83737500			
C	-2.54044400	3.49811000	-
2.67517000			
H	-3.18125100	3.40659400	-
3.54279400			
C	-5.21115200	3.08633300	-
0.60051100			
H	-5.87468900	2.99491200	-
1.45117200			
H	-3.42643400	4.71047000	
1.73003900			
C	-1.51903100	1.08485200	-
2.67412500			
H	-0.71303900	0.61340500	-
2.10586800			
C	-1.08845800	1.23332600	-
4.13873900			
H	-0.25559900	1.94029700	-
4.17968000			
H	-1.88715000	1.63811100	-
4.76796100			
H	-0.74253200	0.29086500	-
4.57252900			
N	-2.65933500	0.06114700	-
2.52185400			
C	-2.30361800	-1.27736000	-

3.09306400			
H	-2.33797200	-1.23862700	-
4.18222000			
H	-3.03111800	-2.00155200	-
2.72430700			
H	-1.31363300	-1.56686100	-
2.74418800			
C	-3.99002700	0.50026300	-
3.03253000			
H	-4.72429600	-0.26561500	-
2.77458100			
H	-3.94527900	0.60678100	-
4.11804000			
H	-4.25811400	1.44377900	-
2.56287700			
C	-6.62535800	-3.12440700	
0.28359200			
H	-6.16728400	-3.31992100	-
0.68756600			
C	-5.91030300	-2.39277000	
1.17405600			
H	-6.32619000	-2.18493400	
2.15567400			
C	-7.95446900	-3.70385700	
0.45769300			
C	-8.49896800	-4.47291400	-
0.58938400			
C	-8.72794500	-3.53049500	
1.62406100			
C	-9.76209800	-5.04996000	-
0.47968800			
H	-7.91667200	-4.61856800	-
1.49661700			
C	-9.98923700	-4.10579200	
1.73310800			
H	-8.34222100	-2.94017400	
2.44984100			
C	-10.51288100	-4.86826400	
0.68304900			
H	-10.15999600	-5.64073900	-
1.29993900			
H	-10.56971200	-3.96020400	
2.63980900			
H	-11.49859100	-5.31559500	
0.77293500			
C	-4.60538800	-1.86360900	
0.86459100			
H	-4.23170900	-2.07899300	-
0.13549800			
C	-3.78717900	-1.13739100	
1.67308200			
C	-2.47569800	-0.68814100	
1.12690700			
C	-4.07807600	-0.78734000	
3.10981700			
H	-4.20959800	0.29396400	
3.24077700			
H	-3.23943800	-1.08082300	
3.74927300			
H	-4.97991300	-1.27971600	
3.47936100			
O	-2.15418900	-0.88377500	-
0.10144100			
O	-1.65317800	-0.12511800	
1.91686700			
H	-2.70197000	-0.12129500	-
1.48136300			
Fe	4.98834600	-2.95871000	
0.63401500			
C	3.07451300	-2.10603100	
0.72094000			
C	6.51752600	-4.31574000	
0.29015700			
C	3.84610300	-1.69869900	
1.88067600			
C	3.01503100	-3.54749900	
0.73953300			
H	2.52667700	-4.16718400	
0.00333200			
C	6.72216100	-2.04770800	-
0.08507400			
H	6.99134000	-1.00642100	
0.03422800			
C	3.72320800	-4.02174300	
1.87404400			
H	3.88572600	-5.05988400	
2.13217300			
C	5.85398300	-4.01131100	-
0.93619300			
H	5.31939100	-4.71486300	-
1.56049400			
C	7.05438400	-3.10335700	
0.81607800			
H	7.59062300	-2.99891900	
1.75011600			
C	4.24302400	-2.89330300	
2.56297900			
H	4.86272100	-2.93015100	
3.44820600			
C	5.98237200	-2.61059400	-
1.16926400			
H	5.57516100	-2.06569000	-
2.00883500			
H	6.56847400	-5.28895700	
0.76043100			
C	4.08623400	-0.30434900	
2.42977200			
H	4.14200000	0.39594600	
1.58667400			
C	5.42501300	-0.20651100	
3.19348800			
H	6.24515000	-0.57507900	
2.57073000			
H	5.41560400	-0.79125100	
4.11922700			
H	5.64512600	0.83066500	
3.46257900			
N	2.90496500	0.14708100	
3.21583000			
C	3.06153900	1.49097100	
3.76544500			
H	3.72626700	1.53180800	

4.64583300
H 2.08139300 1.87607900
4.06286500
H 3.47323700 2.16552200
3.00841200
C 2.42115300 -0.77189600
4.24437500
H 1.52044800 -0.33976700
4.69192400
H 3.14858500 -0.94799100
5.05706300
H 2.14585700 -1.73104400
3.80326600

TS2

Fe -1.50826900 -1.95025900
2.72534900
P 1.42317600 -0.57468700
1.24929500
P -1.99405600 -0.52078700 -
0.47343700
C 2.40595200 0.68309900
2.19931100
C -2.51211200 -1.53711200
0.96509900
C 0.42524400 -1.23825200
2.64949300
C 3.49183400 1.47299700
4.22846400
H 3.75372800 1.31692400
5.27137500
C -2.61678400 -1.60878200 -
1.85466100
C 3.87982300 2.64652100
3.57551500
H 4.44686800 3.40454700
4.10857500
C -2.22626200 -2.94542300
1.08638600
H -1.64287700 -3.53344400
0.39176900
C 2.78323600 1.87057800
1.56323600
H 2.47583500 2.04886000
0.54195200
C 3.51967700 2.84590000
2.24280800
H 3.79642100 3.76236400
1.72921300
C -3.31994600 -1.17987100
2.09396200
H -3.69305900 -0.19096600
2.31052000
C -0.38652900 -2.59220700
4.35389800
H -0.61967400 -3.46679100
4.94717600
C 2.75702600 0.50077000
3.54971900
H 2.44966900 -0.39452700
4.08020900
C -3.53871700 -2.34661400
2.88454100
H -4.07976400 -2.38374000
3.82108600
C -3.66363900 -3.10155500 -
4.00994100
H -4.06808100 -3.67567300 -
4.83879500
C -4.23595700 -3.20191000 -
2.73930500
H -5.08938800 -3.85420300 -
2.57514300
C -3.72193100 -2.46063300 -
1.67419500
H -4.19108700 -2.54446600 -
0.70118100
C -2.57219900 -2.25484500 -
4.20590000
H -2.11651300 -2.16032300 -
5.18762100
C -0.38306900 -0.43843000
3.53002200
H -0.58217400 0.61590700
3.41153000
C -2.05417100 -1.51872900 -
3.13667200
H -1.20970100 -0.86845500 -
3.31708600
C 0.41684700 -2.57340400
3.17675700
H 0.92614600 -3.42420900
2.74694800
C -2.87073600 -3.43925400
2.25786200
H -2.82134500 -4.45400100
2.63071800
C -0.87326700 -1.27077300
4.57700700
H -1.53947700 -0.96298100
5.37237800
Rh 0.23516700 0.22312600 -
0.73399900
H -0.30582300 1.40372700
0.11361100
H -0.47711600 0.84613500 -
2.06228000
Fe 4.42594600 -2.14171400
0.00719100
C 2.63935400 -1.98076300
1.07328000
C 6.00649600 -0.80147200
0.05883300
C 2.59778100 -3.17081100
0.22955000
C 3.76834800 -2.14110600
1.95147600
H 4.10394900 -1.41527900
2.67592400
C 4.75282500 -1.21403300 -
1.83803300
H 4.01932300 -1.11608400 -

2.62657500
C 4.41273900 -3.37482300 1.66975400
H 5.31629100 -3.74212400 2.13850700
C 6.44376400 -2.03971100 -0.49583300
H 7.20397400 -2.68952000 -0.08265600
C 4.96374100 -0.29260400 -0.76908300
H 4.41038600 0.61501400 -0.57955200
C 3.70547200 -4.00243400 0.61315600
H 3.96282800 -4.95706300 0.17241900
C 5.67388300 -2.29208600 -1.66889200
H 5.78472900 -3.15015300 -2.31863300
H 6.36951600 -0.34785100 0.97150900
C 1.42819700 -3.66949400 -0.60299800
H 0.60915100 -2.95434600 -0.49705300
C 0.95638000 -5.05009300 -0.12717200
H 0.74594700 -5.00118100 0.94431900
H 1.71866100 -5.82083400 -0.27472600
H 0.03869900 -5.36741000 -0.63084500
N 1.67298300 -3.65749500 -2.11852100
C 0.46763200 -4.06177300 -2.90715900
H 0.36383200 -5.14784500 -2.91202800
H 0.60171600 -3.68949500 -3.92472900
H -0.41693300 -3.59225800 -2.47953400
C 2.87008800 -4.39867200 -2.59768300
H 2.98452900 -4.20160600 -3.66590200
H 2.73087200 -5.47102200 -2.44090100
H 3.74647400 -4.04347800 -2.06174200
C 3.12877500 3.65095000 -1.40190800
H 4.01723600 3.02361300 -1.31775100
C 1.95746000 3.04587700 -1.71362600
H 1.05896900 3.64772400 -1.82269100
C 3.36543000 5.07711600 -1.17386600
C 4.66826700 5.50204400 -0.84614200
C 2.35605600 6.05760800 -1.26836200
C 4.95338400 6.84673900 -0.61528200
H 5.46450200 4.76379200 -0.78017200
C 2.64123600 7.39955600 -1.03899800
H 1.34224600 5.77042400 -1.53181700
C 3.94030800 7.80205000 -0.70977700
H 5.96699900 7.14842600 -0.36666500
H 1.84882000 8.13849000 -1.12051600
H 4.15870400 8.85134600 -0.53383700
C 1.82205100 1.61981000 -1.95606100
H 2.69273500 1.00208800 -1.76562400
C 0.87136900 1.09685300 -2.88024400
C 1.18098500 -0.33695900 -3.31596500
C 0.16854000 1.97689700 -3.89949500
H -0.64482900 1.43862200 -4.39232100
H 0.89611000 2.25832100 -4.66923000
H -0.23325800 2.88893300 -3.45368300
O 1.27046800 -0.66505300 -4.49140100
O 1.31138900 -1.11759000 -2.27555600
H 1.75359900 -2.60480300 -2.32449800
Fe -5.20099200 1.25134300 -0.32150900
C -3.15892300 0.91003700 -0.64342700
C -7.24475000 1.30819800 -0.66292000
C -3.33709300 2.11667500 -0.14718200
C -3.86749000 1.11369000 -1.88546100
H -3.95612500 0.39538000 -2.68550300
C -6.31507300 0.73922800 -1.37109500
H -5.97790400 0.78918500 -2.39799900
C -4.46371900 2.40160700 -

1.87028900
H -5.09432400 2.81735600 -
2.64503800
C -6.77576200 -0.03661100 -
0.75468100
H -6.81534000 -0.66506900 -
1.63452400
C -6.95930200 1.78858300
0.64978700
H -7.16879600 2.78283700
1.02191500
C -4.15372300 3.00678000 -
0.62289900
H -4.50036300 3.97675400 -
0.29355000
C -6.20372500 -0.38822000
0.50311600
H -5.75254600 -1.33695700
0.75620900
H -7.69982600 1.87817600 -
1.46221700
C -2.70469800 2.51084400
1.47116100
H -2.46956700 1.59387600
2.02442900
C -3.66553800 3.34282200
2.34906800
H -4.61444400 2.81619200
2.47827300
H -3.88443500 4.32132600
1.90943000
H -3.23517600 3.51634100
3.33989500
N -1.38323600 3.15545400
1.24393100
C -0.67961700 3.46812700
2.48475700
H -1.08096900 4.35228400
3.01074300
H 0.37619900 3.65579000
2.26553600
H -0.73243800 2.62000300
3.17369600
C -1.36967500 4.31241000
0.35437700
H -0.33052700 4.63521000
0.22976200
H -1.93920600 5.17856200
0.73839400
H -1.76351200 4.04743200 -
0.62882000

CP4

Fe -0.09385000 -2.21031900
2.31539600
P 2.12550400 0.33165800
1.16530800
P -1.80616000 -0.96138400 -
0.64366800
C 2.31367600 1.95105800
2.03577000
C -1.46162100 -2.21074100
0.65631200
C 1.43919100 -0.74785200
2.48252500
C 2.64298100 3.28116900
4.04517900
H 2.78546100 3.33212000
5.12099200
C -2.11507900 -2.03420700 -
2.12234700
C 2.59935200 4.45344100
3.28709000
H 2.70712100 5.41982300
3.77121300
C -0.42475600 -3.20466800
0.50355300
H 0.25917800 -3.25644400 -
0.33209400
C 2.26166300 3.13556400
1.28628200
H 2.09347100 3.09262800
0.21616900
C 2.40861400 4.37813300
1.90600400
H 2.36494200 5.28591000
1.31065900
C -2.12355600 -2.48601200
1.89315800
H -2.93339000 -1.90610300
2.30906200
C 1.09694100 -2.47866500
3.98893500
H 1.19292900 -3.42540300
4.50459100
C 2.50361200 2.03821100
3.42532700
H 2.54193300 1.13621500
4.02798000
C -1.55175700 -3.66343900
2.45911900
H -1.83795900 -4.11623600
3.39966700
C -2.61312400 -3.58010200 -
4.42297900
H -2.80267700 -4.17794500 -
5.30988300
C -2.71931500 -4.15227600 -
3.15428300
H -2.99674800 -5.19761000 -
3.04922700
C -2.47694800 -3.38562700 -
2.01196000
H -2.57287200 -3.84740100 -
1.03579600
C -2.26738900 -2.23261000 -
4.54531200
H -2.19028900 -1.77408700 -
5.52716600
C 0.30261100 -0.42698200
3.30777400
H -0.29626700 0.46682600

3.22999200
C -2.01927400 -1.46944200 -
3.40384900
H -1.77074200 -0.41922300 -
3.51344300
C 1.90731000 -2.03324800
2.90621900
H 2.74300000 -2.57010400
2.48445100
C -0.50736600 -4.11157000
1.59502600
H 0.13927300 -4.96215200
1.76750900
C 0.11437200 -1.47694500
4.24544700
H -0.67343500 -1.53101700
4.98545700
Rh 0.28982600 0.00424400 -
0.30777100
H -0.45902500 1.01099800
0.62360700
H 0.11070500 0.28988200 -
3.55593300
Fe 5.42516000 0.50682600 -
0.13893600
C 3.89285200 -0.24904000
1.04959100
C 5.66684600 2.54267400 -
0.44806600
C 4.53345900 -1.33340700
0.30068700
C 4.92102900 0.36091600
1.85185700
H 4.78681500 1.22001300
2.49065100
C 5.37800700 1.02686000 -
2.17014900
H 4.90691800 0.45649400 -
2.95833300
C 6.15173400 -0.30763800
1.62669600
H 7.10752100 -0.04333000
2.05969300
C 6.90533600 1.86495300 -
0.65151700
H 7.81155800 2.01032600 -
0.07841400
C 4.72546200 2.02173700 -
1.38490200
H 3.69108300 2.31882300 -
1.48143400
C 5.91942500 -1.33929100
0.68293100
H 6.67379700 -2.02040300
0.31134100
C 6.72657400 0.92835600 -
1.71394600
H 7.48644700 0.25849300 -
2.09601400
H 5.46593900 3.28933300
0.30872500
C 3.86037500 -2.49752300 -
0.40865300
H 2.78331700 -2.33546700 -
0.38471500
C 4.21308700 -3.82763700
0.27744300
H 4.04461600 -3.73520100
1.35247900
H 5.26640900 -4.09498100
0.14683300
H 3.59533300 -4.65522400 -
0.08217700
N 4.13114000 -2.59024900 -
1.91807400
C 3.34750300 -3.69083700 -
2.56430200
H 3.77399900 -4.66278900 -
2.31469800
H 3.38753900 -3.53173900 -
3.64311800
H 2.31155800 -3.61334000 -
2.23599000
C 5.56040700 -2.66699500 -
2.33058200
H 5.59608100 -2.63304600 -
3.42158900
H 6.00543700 -3.60188000 -
1.98362000
H 6.09532100 -1.81136900 -
1.92484700
C -0.82999000 3.55980900 -
1.58878400
H 0.01281800 4.02131400 -
1.07261000
C -0.68749800 2.28071600 -
1.99818000
H -1.50769800 1.79415800 -
2.52630700
C -1.99143500 4.43455900 -
1.76235600
C -1.88462100 5.78527600 -
1.37901700
C -3.21827100 3.99864800 -
2.30249900
C -2.95198400 6.66893200 -
1.53197500
H -0.94554200 6.14345700 -
0.96266200
C -4.28329400 4.88085600 -
2.45774700
H -3.34435100 2.95973700 -
2.59210600
C -4.15726700 6.22079200 -
2.07483600
H -2.84108400 7.70718800 -
1.23125100
H -5.21921300 4.52337500 -
2.87908500
H -4.99098600 6.90605100 -
2.19874500
C 0.52696000 1.47083500 -

1.80617300
H 1.34170000 2.09669700 -
1.42881000
C 0.99605700 0.73053400 -
3.07959900
C 1.86787600 -0.46898200 -
2.71145700
C 1.65459300 1.67743500 -
4.09301000
H 1.94957800 1.13259400 -
4.99427500
H 2.55643300 2.14018100 -
3.67812900
H 0.96135900 2.47661300 -
4.37396200
O 2.93891300 -0.69967400 -
3.33133000
O 1.44952800 -1.21400900 -
1.75324300
H 3.70728500 -1.71529100 -
2.38569600
Fe -5.31000300 -0.91975200
0.21331900
C -3.44936000 -0.17197800 -
0.40666000
C -7.17674400 -1.80871900
0.09769900
C -3.97723300 0.69037500
0.63747600
C -4.41668800 -0.17836000 -
1.48284000
H -4.33745900 -0.73934200 -
2.40104300
C -5.72953400 -2.13288800
1.86534100
H -5.27245700 -2.06819500
2.84338200
C -5.51265000 0.64286400 -
1.11400900
H -6.40984800 0.80232400 -
1.69748700
C -6.17352200 -2.73468000 -
0.31949000
H -6.08652000 -3.18054700 -
1.30138700
C -6.90127700 -1.43453300
1.44649500
H -7.46474800 -0.72468500
2.03753800
C -5.25706600 1.14717400
0.19052900
H -5.93696600 1.76069500
0.76473200
C -5.28216600 -2.93692800
0.77439200
H -4.41364700 -3.58027200
0.77575800
H -7.98121200 -1.42456300 -
0.51561800
C -3.29397200 1.20336600
1.89742700
H -2.40444200 0.58611700
2.06334800
C -4.18614700 1.08427700
3.15282500
H -4.37546700 0.03486400
3.39608200
H -5.15779200 1.56924600
3.01778200
H -3.70048700 1.54760800
4.01834900
N -2.76481600 2.56983800
1.65402200
C -1.72489300 2.95477600
2.59816900
H -2.06848700 3.05305600
3.64597200
H -1.31259300 3.92327000
2.29751600
H -0.90361600 2.23469300
2.56483300
C -3.75450200 3.63548200
1.52245500
H -3.23016200 4.56428000
1.27911300
H -4.34861600 3.81391600
2.43814600
H -4.43381700 3.43195400
0.69430400

CP5

Fe -0.44434500 -0.54384000
2.97544000
P 1.76178400 0.97467200
0.75962500
P -1.73052800 -0.84001400 -
0.29273200
C 2.09934700 2.79820300
0.61467500
C -1.50366900 -1.41226900
1.43616200
C 0.92427400 0.87921900
2.38002200
C 2.19164500 5.04137500
1.55586500
H 2.02414500 5.70769400
2.39750100
C -2.11350000 -2.49860300 -
1.08741500
C 2.70229800 5.54060900
0.35768000
H 2.93228400 6.59754400
0.25828100
C -0.36069800 -2.21473500
1.78395100
H 0.42177300 -2.47364100
1.08775500
C 2.60955800 3.31435200 -
0.58701900
H 2.77185500 2.65115300 -
1.42877500
C 2.91605400 4.66993100 -

0.71396900
H 3.31428200 5.04668600 -
1.65248300
C -2.32585300 -1.33576200
2.60952900
H -3.25891100 -0.80022700
2.69161300
C 0.37942400 0.48185300
4.59759600
H 0.41051700 0.10777600
5.61273900
C 1.89877100 3.68117800
1.68745600
H 1.51914400 3.31401700
2.63389000
C -1.69089900 -2.06498000
3.65826200
H -2.04837000 -2.14674000
4.67662600
C -2.69073500 -4.97880700 -
2.32782300
H -2.91302300 -5.93012300 -
2.80261900
C -2.66581300 -4.87118900 -
0.93720400
H -2.87132100 -5.74115800 -
0.31918100
C -2.38365000 -3.64665000 -
0.32592200
H -2.37525400 -3.59675400
0.75560100
C -2.42581100 -3.84862800 -
3.10239600
H -2.44192000 -3.91187300 -
4.18711200
C -0.35649700 1.47384200
2.64216500
H -0.96961000 1.98998100
1.91066000
C -2.13367800 -2.63025100 -
2.48603200
H -1.93614600 -1.77174000 -
3.11673500
C 1.37281900 0.26956600
3.60015200
H 2.30597700 -0.25547200
3.73981800
C -0.48121300 -2.61780400
3.14459900
H 0.23642700 -3.20223100
3.70518000
C -0.68001100 1.23350100
4.01065900
H -1.59523800 1.52226900
4.50982000
Rh 0.70019600 0.10361300 -
1.22977900
H 2.14921500 0.56748300 -
1.53986100
Fe 5.27093700 0.22149200
0.15178200
C 3.47375900 0.36531200
1.22235300
C 5.90785900 1.64995400 -
1.21555600
C 4.06516500 -0.96668700
1.36857200
C 4.44932000 1.29995500
1.71625200
H 4.33765900 2.37323100
1.71449500
C 5.61100700 -0.57904200 -
1.75661900
H 5.17555400 -1.48585200 -
2.15607200
C 5.59572900 0.59664500
2.16666500
H 6.50489100 1.04084900
2.54997500
C 7.02448000 0.92107100 -
0.70984200
H 7.84758000 1.33197900 -
0.14019600
C 5.03957500 0.72247600 -
1.86333900
H 4.09896300 0.95603200 -
2.34016600
C 5.36359500 -0.78637100
1.96165100
H 6.06155000 -1.57517500
2.20854600
C 6.84185300 -0.45435400 -
1.04363100
H 7.52257700 -1.25714700 -
0.79056300
H 5.73169600 2.71026700 -
1.09399800
C 3.35042800 -2.30349100
1.31474200
H 2.33829000 -2.12560100
0.96183800
C 3.32826400 -2.95964400
2.70321600
H 2.90704400 -2.25088900
3.41791600
H 4.33181400 -3.21956200
3.05473900
H 2.70333900 -3.85623300
2.73157000
N 3.87391400 -3.29822500
0.26252800
C 3.07828400 -4.57006900
0.24564400
H 3.34628500 -5.19653000
1.09632000
H 3.30670200 -5.08428200 -
0.68856900
H 2.01846400 -4.31811400
0.26065700
C 5.33028000 -3.61278900
0.30914700
H 5.55828200 -4.27286600 -

0.53033700
H 5.57290000 -4.11904200
1.24563000
H 5.89668600 -2.68986100
0.21317500
C 0.10090900 1.69810700 -
2.79337000
H 1.08795600 2.12966500 -
2.93646600
C -0.05257300 0.35247000 -
3.26175100
H -1.03737000 -0.06979900 -
3.41649300
C -0.96337100 2.71938700 -
2.85357600
C -0.61659300 4.06793000 -
2.63999000
C -2.27585900 2.43738000 -
3.27765800
C -1.53175800 5.09335600 -
2.86544500
H 0.39136100 4.30907500 -
2.31330500
C -3.18850400 3.46433300 -
3.51364600
H -2.58847300 1.41371100 -
3.45434000
C -2.82103600 4.79760400 -
3.31521700
H -1.23292000 6.12603700 -
2.70710700
H -4.18848200 3.22077100 -
3.86169400
H -3.53039200 5.59640000 -
3.51182400
C 1.10467800 -0.43590800 -
3.36646800
H 2.03212100 0.08905000 -
3.59167000
C 1.22813100 -1.93593300 -
3.48496800
C 1.99282800 -2.34811500 -
2.19907900
C 1.92718500 -2.37658400 -
4.77554100
H 2.06388800 -3.46168200 -
4.78352200
H 2.91785400 -1.91984800 -
4.86414100
H 1.33523600 -2.09304900 -
5.65253400
O 3.12195800 -2.88312500 -
2.28266500
O 1.41841300 -2.06345600 -
1.08197900
H 3.65831500 -2.89942700 -
0.70149800
H 0.23881600 -2.39658800 -
3.40834900
Fe -5.34040500 -0.61568400
0.03533300
C -3.39574000 -0.00263100 -
0.43481800
C -7.09248300 -1.70088400 -
0.18956200
C -4.10308600 1.06747400
0.27251900
C -4.17354700 -0.28507800 -
1.62138500
H -3.97165500 -1.06528200 -
2.33716800
C -6.09908700 -1.31326800
1.85664800
H -5.88099600 -0.90310200
2.83398500
C -5.30666900 0.56618100 -
1.66139100
H -6.08990400 0.54651500 -
2.40787600
C -5.98414800 -2.59077300 -
0.06400200
H -5.64427100 -3.29750900 -
0.80916700
C -7.16242200 -0.90839800
0.99522000
H -7.87995900 -0.12269700
1.19252400
C -5.26844600 1.38013900 -
0.50294800
H -6.01787200 2.10749600 -
0.22522900
C -5.37396800 -2.35272900
1.20259500
H -4.50327700 -2.85806800
1.59358300
H -7.74441500 -1.61470100 -
1.04898300
C -3.78057100 1.85611600
1.53943100
H -3.19231100 1.21919000
2.20689500
C -5.06884900 2.25145300
2.30162800
H -5.73262900 1.39239100
2.41642000
H -5.62559300 3.04094300
1.78610800
H -4.82541900 2.62565500
3.30008200
N -2.89531700 3.02103200
1.24643800
C -2.66965400 3.87132100
2.41663400
H -3.53079400 4.51415200
2.66827500
H -1.81239700 4.52527400
2.22052200
H -2.43684800 3.26582500
3.29653500
C -3.30260200 3.85625000
0.11950200
H -2.54880300 4.63588700 -

0.02187300
H -4.27646700 4.35887900
0.27053400
H -3.34923400 3.27164800 -
0.79696200

TS3

Fe 0.43921400 -0.72271700 -
3.01273900
P -1.72260900 0.88373500 -
0.85164200
P 1.63538400 -0.79884000
0.28411400
C -2.07750900 2.71112500 -
0.77710600
C 1.44643300 -1.50168300 -
1.40164300
C -0.91506300 0.73854100 -
2.48823900
C -2.11893500 4.94162900 -
1.75330700
H -1.92617200 5.59163800 -
2.60233900
C 1.83670900 -2.39466100
1.24118300
C -2.64374400 5.46889800 -
0.57338100
H -2.85846600 6.53077600 -
0.49498000
C 0.31302700 -2.32334900 -
1.73679000
H -0.49913900 -2.54390900 -
1.06293200
C -2.60815500 3.25619100
0.40335300
H -2.81222500 2.60686700
1.24713600
C -2.89323800 4.61831900
0.50678200
H -3.30535700 5.01488900
1.43101400
C 2.30508100 -1.50137100 -
2.55263500
H 3.24681800 -0.98361400 -
2.63965000
C -0.38598200 0.21730400 -
4.68552000
H -0.42628400 -0.21069100 -
5.67876700
C -1.84158100 3.57547400 -
1.85762100
H -1.44421300 3.18996500 -
2.78943700
C 1.69898100 -2.28925800 -
3.57441100
H 2.08929200 -2.43543000 -
4.57325600
C 2.15134000 -4.76423900
2.74568200
H 2.27340800 -5.67598200
3.32353700
C 2.31854600 -4.78010300
1.36033700
H 2.57249700 -5.70657000
0.85215100
C 2.16580000 -3.60721800
0.61618100
H 2.30262700 -3.64826300 -
0.45742000
C 1.82277500 -3.56566800
3.38164400
H 1.68773400 -3.53822500
4.45966100
C 0.36918000 1.30916100 -
2.79191600
H 0.99520100 1.85371800 -
2.09338900
C 1.65921200 -2.39943500
2.63290700
H 1.39211700 -1.47979600
3.13800800
C -1.37398000 0.06622900 -
3.67086300
H -2.30800800 -0.46685900 -
3.77273100
C 0.47196400 -2.80563800 -
3.06702500
H -0.23049100 -3.42236900 -
3.61161600
C 0.68184100 0.99324300 -
4.14791600
H 1.59478900 1.24925700 -
4.66841900
Rh -0.46664600 0.22396200
1.17826700
H -1.93561700 0.61053900
1.75026300
Fe -5.27427500 0.24671900 -
0.26560500
C -3.43399600 0.25065500 -
1.27884300
C -5.91038800 1.82280100
0.93024800
C -4.02768600 -1.08649500 -
1.27169700
C -4.38406000 1.11633100 -
1.92292900
H -4.26249900 2.18109400 -
2.05565000
C -5.76057500 -0.35952000
1.68509100
H -5.38675300 -1.24264900
2.18411400
C -5.51661600 0.36174200 -
2.32335800
H -6.40882000 0.75326400 -
2.79427300
C -7.03290200 1.10283200
0.42571800
H -7.80079200 1.49847200 -
0.22592800
C -5.12706800 0.91751800

1.70589500			
H	-4.21067300	1.15363500	
2.22661700			
C	-5.30076100	-0.98489900	-
1.93389100			
H	-5.99761000	-1.79552100	-
2.09962900			
C	-6.94010400	-0.24371300	
0.89044400			
H	-7.64219600	-1.03628000	
0.66483400			
H	-5.67443000	2.85848100	
0.72721900			
C	-3.30639400	-2.39216400	-
1.00204600			
H	-2.33360100	-2.15150300	-
0.57770300			
C	-3.15156700	-3.19204000	-
2.30324400			
H	-2.66759700	-2.55384800	-
3.04518800			
H	-4.11812100	-3.49955500	-
2.71515600			
H	-2.52442300	-4.07892600	-
2.17822900			
N	-3.90441900	-3.27163700	
0.10916700			
C	-3.08446300	-4.50406100	
0.35064000			
H	-3.24719800	-5.23283200	-
0.44360300			
H	-3.39669800	-4.91942300	
1.30985700			
H	-2.03617100	-4.21386000	
0.41703000			
C	-5.34399800	-3.63061300	-
0.02204300			
H	-5.62568900	-4.22043900	
0.85276900			
H	-5.50180400	-4.22418800	-
0.92497200			
H	-5.93695500	-2.71965900	-
0.05148800			
C	0.16181900	2.06331300	
2.43394400			
H	-0.73327600	2.65189200	
2.24789500			
C	-0.03247900	0.85237600	
3.16880500			
H	0.75640500	0.36796300	
3.73213900			
C	1.35844600	2.91318700	
2.54024200			
C	1.22729400	4.28334800	
2.23844900			
C	2.57253900	2.47247500	
3.09852000			
C	2.25502100	5.18275200	
2.51257600			
H	0.29361700	4.64396900	
1.81340800			
C	3.60168800	3.37142300	
3.36984200			
H	2.71151100	1.42334000	
3.33635700			
C	3.44627700	4.73159700	
3.08594300			
H	2.12241200	6.23786500	
2.28943300			
H	4.52542900	3.01042600	
3.81325500			
H	4.24506200	5.43200200	
3.31253400			
C	-1.38911800	0.37397500	
3.22823100			
H	-2.15342500	1.12804000	
3.44321700			
C	-1.74515900	-1.02512700	
3.71524100			
C	-2.25903200	-1.83641500	
2.49888400			
C	-2.72040000	-1.00232800	
4.89533900			
H	-2.96024900	-2.02084400	
5.21110900			
H	-3.66177000	-0.51414400	
4.62244300			
H	-2.28739200	-0.46622900	
5.74733300			
O	-3.38831600	-2.38554400	
2.56525200			
O	-1.49760900	-1.87663600	
1.47449200			
H	-3.77791800	-2.74821800	
1.03516700			
H	-0.81201300	-1.52032300	
4.01218100			
Fe	5.25103900	-0.86046900	
0.07179800			
C	3.34139500	-0.07063800	
0.43257500			
C	6.90675800	-2.04558200	
0.45454400			
C	4.14499300	0.89351900	-
0.32049200			
C	4.06013900	-0.33498300	
1.65895500			
H	3.76432200	-1.04061700	
2.41997800			
C	6.04897200	-1.72064200	-
1.66240200			
H	5.91192800	-1.36160100	-
2.67375400			
C	5.25202000	0.43254300	
1.68084500			
H	6.00918100	0.40977100	
2.45365600			
C	5.74629300	-2.86490700	
0.32069800			
H	5.32158500	-3.50060900	
1.08542300			
C	7.09294000	-1.33517500	-

0.76924300
H 7.87185200 -0.61182100 -
0.97158200
C 5.30759900 1.16928600
0.47130600
H 6.11868400 1.81717000
0.17059500
C 5.21913500 -2.66416100 -
0.98916000
H 4.33391700 -3.12779900 -
1.39813400
H 7.51782900 -1.94970800
1.34242800
C 3.90610900 1.61343700 -
1.64462900
H 3.28327900 0.97737900 -
2.27915300
C 5.23309700 1.85743300 -
2.40429000
H 5.82732400 0.94324600 -
2.45388600
H 5.84501400 2.62920500 -
1.92641200
H 5.03489200 2.18791500 -
3.42797200
N 3.10177800 2.85394500 -
1.45738100
C 2.90303400 3.58437400 -
2.70974900
H 3.79704200 4.13864700 -
3.04421300
H 2.09324600 4.31055700 -
2.57571900
H 2.61479500 2.90072300 -
3.51264200
C 3.59971600 3.77607300 -
0.43969300
H 2.89289400 4.60555600 -
0.35150900
H 4.58934500 4.20791400 -
0.68064700
H 3.65856700 3.28575700
0.53048200

CP6

Fe 3.55611300 -2.13060700 -
0.83537600
P 0.08952000 -1.61680900 -
0.97815400
P 2.22443100 0.56694500
0.73349200
C -0.80130700 -1.19328200 -
2.54783100
C 3.58959800 -0.62592000
0.54963800
C 1.66568800 -2.29658600 -
1.62357900
C -1.25031900 -1.54583000 -
4.91219800
H -1.03878900 -2.07731900 -
5.83603900
C 2.18562100 0.86768800
2.56505300
C -2.21840100 -0.53906100 -
4.88673000
H -2.76526300 -0.28555200 -
5.79055500
C 3.56852900 -1.91498900
1.19770400
H 2.79204800 -2.27083700
1.85947200
C -1.76459900 -0.17265000 -
2.53454300
H -1.95695600 0.37177400 -
1.61574200
C -2.47088000 0.14705200 -
3.69680900
H -3.21467100 0.93884800 -
3.67180800
C 4.78661100 -0.57556300 -
0.24065400
H 5.09539300 0.24685400 -
0.86771100
C 3.41934900 -3.70029300 -
2.19962900
H 4.08836500 -4.55061500 -
2.22868800
C -0.54315400 -1.86957100 -
3.75216500
H 0.21868400 -2.64121400 -
3.79597900
C 5.48064700 -1.81074200 -
0.08600900
H 6.39527000 -2.08805100 -
0.59364700
C 1.91988300 1.29043100
5.33646000
H 1.82420800 1.46053500
6.40502300
C 3.09988300 0.75682300
4.81387300
H 3.92461600 0.50971500
5.47672200
C 3.23233900 0.54390400
3.43846000
H 4.15418800 0.12574800
3.04798000
C 0.86597400 1.61612400
4.47771900
H -0.05108500 2.04448700
4.87258300
C 2.53075100 -1.59396900 -
2.52864700
H 2.37234500 -0.56904900 -
2.83343000
C 1.00069100 1.40708700
3.10383500
H 0.18496500 1.71545200
2.44601100
C 2.22729500 -3.60486000 -
1.42386800
H 1.82440500 -4.37715500 -

0.78384400			
C	4.73453100	-2.63333000	
0.80716400			
H	4.98629500	-3.64357900	
1.10222100			
C	3.60290000	-2.46215100	-
2.88476800			
H	4.43938900	-2.20954900	-
3.52347800			
Rh	0.02371700	0.05884800	
0.50906700			
H	-3.39773100	2.44086800	
1.66393700			
Fe	-2.69463500	-3.80320000	-
0.20444500			
C	-0.71572800	-3.18980200	-
0.43329700			
C	-4.12976800	-3.26281000	-
1.59869700			
C	-0.91891900	-3.70891700	
0.91005800			
C	-1.04974600	-4.24760800	-
1.34801400			
H	-1.03974300	-4.17033600	-
2.42534400			
C	-4.34102300	-2.83640500	
0.66099500			
H	-4.34631300	-2.30896200	
1.60397300			
C	-1.43683100	-5.39539300	-
0.60489200			
H	-1.78290800	-6.33382700	-
1.01772800			
C	-4.50431700	-4.47925500	-
0.95299000			
H	-4.63119500	-5.44156300	-
1.43152400			
C	-4.02592800	-2.25029100	-
0.60062700			
H	-3.72517200	-1.22701700	-
0.76536000			
C	-1.36455100	-5.06855900	
0.77636500			
H	-1.61232400	-5.74088500	
1.58756000			
C	-4.63438500	-4.21591300	
0.44385400			
H	-4.89780800	-4.94369800	
1.20082200			
H	-3.91666000	-3.13869500	-
2.65187700			
C	-0.40566000	-3.06687700	
2.18010400			
H	0.07184600	-2.11846500	
1.89063600			
C	0.61547700	-3.97269000	
2.87997000			
H	1.38462000	-4.24979100	
2.15378700			
H	0.16814800	-4.90391200	
3.24232700			
H	1.11338200	-3.47434400	
3.71711000			
N	-1.49812800	-2.59807900	
3.14275300			
C	-0.94032500	-1.84194600	
4.30846400			
H	-0.46890100	-2.52740300	
5.01392200			
H	-1.76853400	-1.31924400	
4.78825300			
H	-0.21822600	-1.11008600	
3.94508000			
C	-2.44613000	-3.64725400	
3.61620400			
H	-3.22682500	-3.15567500	
4.20006900			
H	-1.91972700	-4.36843400	
4.24488700			
H	-2.89044300	-4.13925000	
2.75358000			
C	-6.94885100	2.70661300	-
0.08927300			
H	-7.43342100	1.72896200	-
0.10465700			
C	-5.62104900	2.73976500	
0.10529400			
H	-5.09759900	3.69637700	
0.13820700			
C	-7.86135000	3.84225700	-
0.29350600			
C	-9.23962000	3.58804200	-
0.40832900			
C	-7.42780400	5.17866200	-
0.38482400			
C	-10.15332400	4.62363400	-
0.60052300			
H	-9.59528800	2.56208600	-
0.34342200			
C	-8.33845500	6.21367100	-
0.57637900			
H	-6.36928500	5.41153200	-
0.31096400			
C	-9.70636900	5.94262000	-
0.68475100			
H	-11.21320400	4.39947900	-
0.68512100			
H	-7.98104500	7.23775800	-
0.64486200			
H	-10.41398500	6.75296500	-
0.83580800			
C	-4.75380200	1.52420000	
0.27388900			
H	-5.36647600	0.61589700	
0.19602900			
C	-3.97159200	1.50327600	
1.61855800			
C	-2.91733100	0.38305300	
1.60057200			
C	-4.89993100	1.42047100	
2.83238900			
H	-4.33572600	1.45469900	

3.76949400
H -5.47249700 0.48694500
2.82427600
H -5.60867800 2.25391300
2.82247500
O -2.97644000 -0.53294300
2.45681000
O -2.03244400 0.48216000
0.67470200
H -2.06512800 -1.85201300
2.62628700
H -4.01579900 1.48984900 -
0.53872500
Fe 4.38894500 3.42928000
0.25809200
C 2.69305200 2.23730900
0.08808500
C 5.78391100 4.70003700
1.12079500
C 3.06002700 2.77203200 -
1.22064800
C 2.45320000 3.38036400
0.94594200
H 2.19931800 3.34225300
1.99326400
C 6.35108300 2.87848900 -
0.17919700
H 6.66501300 2.27223300 -
1.01881500
C 2.65631100 4.57052900
0.20588300
H 2.59134000 5.57824400
0.59458900
C 5.63565300 3.52668200
1.91944100
H 5.29052000 3.49430000
2.94422700
C 6.22493900 4.30063500 -
0.17577500
H 6.40424600 4.95894200 -
1.01570200
C 3.03463000 4.20001400 -
1.10866400
H 3.30006300 4.88890800 -
1.89745600
C 5.98854600 2.40198700
1.11657800
H 5.96470800 1.36681500
1.42678500
H 5.56387500 5.71280300
1.43182400
C 3.33294300 2.08313000 -
2.55004000
H 3.87408900 1.14848800 -
2.35712400
C 4.24341500 2.95015100 -
3.45116200
H 5.12219400 3.28969900 -
2.89669100
H 3.72138000 3.83247400 -
3.83576200
H 4.59302200 2.37575200 -
4.31295300
N 2.06113100 1.66547500 -
3.20661800
C 2.25700500 1.18830700 -
4.57668400
H 2.45650300 1.99394200 -
5.30357900
H 1.35486400 0.65850600 -
4.90113100
H 3.09589800 0.48458800 -
4.62113500
C 0.96985100 2.63802200 -
3.16653000
H 0.08731900 2.18052800 -
3.62434500
H 1.18647400 3.57420100 -
3.71304400
H 0.71762400 2.88781200 -
2.13419400

(*R*)-2a

H 2.49843600 1.10269800
1.01346800
C -0.81996300 -0.34544800 -
0.59470900
H -0.61005800 -1.30060300 -
1.07832800
C 0.21570900 0.47634300 -
0.36311600
H 0.05166200 1.43755900
0.12564200
C -2.23860500 -0.11986900 -
0.27610700
C -3.16499100 -1.13990100 -
0.55708700
C -2.72507100 1.07016100
0.29825100
C -4.52156700 -0.98507700 -
0.27387900
H -2.81046600 -2.06658000 -
1.00294300
C -4.07875600 1.22630500
0.58204700
H -2.04003200 1.88287800
0.52196000
C -4.98542900 0.19985200
0.29845400
H -5.21522000 -1.79035100 -
0.50108200
H -4.43037300 2.15442300
1.02530900
H -6.04160200 0.32564300
0.52048100
C 1.63956400 0.17831700 -
0.73769800
H 1.69891300 -0.78208100 -
1.26567700
C 2.59707100 0.14086500
0.49303400
C 4.03017600 0.05361100 -

0.00438300
C 2.28298200 -1.01079000
1.45034500
H 2.93470000 -0.98215700
2.32942200
H 2.43872200 -1.97456100
0.95552000
H 1.24312300 -0.95404500
1.78503500
O 4.73175300 -0.93413800
0.00342900
O 4.45892100 1.24021000 -
0.51049400
H 5.36568400 1.08128800 -
0.83505700
H 2.00440200 0.95109700 -
1.42814900

TS4

Fe -1.59276900 -1.92317200
2.85420200
P 1.27860300 -0.53127700
1.28916000
P -1.97537500 -0.76323700 -
0.45867300
C 2.30511600 0.68486000
2.25774100
C -2.57057500 -1.58871300
1.07162200
C 0.32595100 -1.22611200
2.70455800
C 3.44906500 1.34767800
4.30527000
H 3.71403400 1.13635900
5.33756100
C -2.77291200 -1.88798300 -
1.73116800
C 3.87653900 2.53132100
3.69829200
H 4.47860600 3.24414200
4.25457000
C -2.39637600 -2.99924200
1.32142300
H -1.86482600 -3.69285200
0.68524900
C 2.72407100 1.88310300
1.67067000
H 2.40930500 2.13304000
0.66954200
C 3.50458000 2.79917700
2.38165500
H 3.79966900 3.73039000
1.90624900
C -3.34316400 -1.06814100
2.16126700
H -3.63565400 -0.03800500
2.28981000
C -0.40467600 -2.63375200
4.40243100
H -0.61564900 -3.52696500
4.97588500
C 2.66558600 0.43679700
3.59682500
H 2.32506000 -0.46075800
4.10095500
C -3.64764000 -2.13707100
3.05529300
H -4.18373800 -2.04464100
3.99082500
C -4.05105400 -3.45167800 -
3.71097600
H -4.54170800 -4.05379700 -
4.47060900
C -4.47754300 -3.50739400 -
2.38342400
H -5.30648100 -4.15132200 -
2.10207500
C -3.85119400 -2.73001600 -
1.40670500
H -4.21688000 -2.78474700 -
0.38989300
C -2.99511100 -2.60589100 -
4.05210000
H -2.66117100 -2.53827800 -
5.08430200
C -0.42471200 -0.44973300
3.65807900
H -0.61990400 0.61086200
3.59772600
C -2.36216100 -1.83173700 -
3.07517100
H -1.54944000 -1.17702800 -
3.35948800
C 0.33443200 -2.58082000
3.18480900
H 0.81180100 -3.42007000
2.69897900
C -3.07162800 -3.33167100
2.53218600
H -3.09650000 -4.30879600
2.99649300
C -0.86582500 -1.31716100
4.69820000
H -1.48572000 -1.03297100
5.53842500
Rh 0.35482500 -0.05965500 -
0.76169900
H 0.55800600 1.47654200 -
0.54054300
H 0.76017000 1.71035000 -
3.57490700
Fe 4.37202500 -2.07856700
0.10466500
C 2.48419000 -1.93584300
1.00172100
C 5.98027000 -0.79833700
0.41094900
C 2.50145200 -3.01682100
0.01458900
C 3.51053600 -2.24341700
1.96290500
H 3.79254800 -1.61884300

2.79568300
C 4.96385800 -1.09259200 -
1.64575700
H 4.34102100 -0.93944300 -
2.51749100
C 4.12883400 -3.47268900
1.61708300
H 4.96051400 -3.93379200
2.13351700
C 6.43685000 -2.03518500 -
0.13157700
H 7.11297500 -2.73016000
0.34890200
C 5.07304800 -0.21851400 -
0.52261500
H 4.54518500 0.71224400 -
0.37743700
C 3.51824500 -3.94631200
0.42857500
H 3.78855800 -4.86088800 -
0.08179700
C 5.81221300 -2.21518200 -
1.40117700
H 5.96541500 -3.05882500 -
2.06170100
H 6.24439400 -0.38943900
1.37716800
C 1.41650800 -3.35733900 -
0.99176900
H 0.68452900 -2.54371100 -
1.00603500
C 0.70562400 -4.65438500 -
0.57514500
H 0.40685100 -4.55865900
0.47185200
H 1.36262700 -5.52728500 -
0.64411100
H -0.19680200 -4.84314000 -
1.16260200
N 1.86301400 -3.42937000 -
2.46534300
C 0.73322400 -3.79686100 -
3.38250600
H 0.53513700 -4.86714200 -
3.31891000
H 1.04056000 -3.53046200 -
4.39482500
H -0.14716300 -3.21627400 -
3.11511300
C 3.04438800 -4.29440200 -
2.75489600
H 3.26965600 -4.20426100 -
3.81932300
H 2.81003600 -5.33417900 -
2.51866700
H 3.89168900 -3.94628300 -
2.17022600
C 2.71202500 3.88927600 -
1.15214700
H 3.67118000 3.42931200 -
0.90864500
C 1.70220900 3.07588900 -
1.52303800
H 0.73554200 3.50060000 -
1.79040200
C 2.69904400 5.35421900 -
1.04267100
C 3.83368100 6.00201500 -
0.51913900
C 1.61273600 6.15443700 -
1.44907000
C 3.87879400 7.38917100 -
0.38624500
H 4.69291300 5.40548200 -
0.21920700
C 1.65745900 7.53952000 -
1.31744700
H 0.73229900 5.69191500 -
1.88509200
C 2.78839500 8.16478600 -
0.78221900
H 4.76707700 7.86362800
0.02155200
H 0.80947000 8.13693000 -
1.64118700
H 2.82019800 9.24602000 -
0.68400200
C 1.82618200 1.59907700 -
1.70279600
H 2.78322500 1.23495000 -
1.32951100
C 1.68219500 1.24354100 -
3.20464600
C 1.46008400 -0.25534900 -
3.28280400
C 2.87349600 1.72878800 -
4.03948500
H 2.74517500 1.44501800 -
5.08930600
H 3.81020100 1.28460900 -
3.68818600
H 2.96690000 2.81651400 -
3.98338800
O 2.33349200 -1.04840200 -
3.69502900
O 0.32344600 -0.65233700 -
2.79851500
H 2.11497400 -2.45036000 -
2.79028200
Fe -4.99521800 1.24097100 -
0.48906500
C -2.96306400 0.77867200 -
0.74122500
C -7.01322700 1.39339800 -
0.92896800
C -3.08117100 2.01781900
0.01118800
C -3.62899500 0.99081200 -
2.00664300
H -3.74952800 0.25676000 -
2.78712000
C -6.21624500 0.83952800

1.16392200
H -5.93257400 0.90110800
2.20555900
C -4.15011200 2.30974400 -
2.03695100
H -4.73633400 2.74115100 -
2.83754800
C -6.61280000 0.02356700 -
0.95914400
H -6.64201700 -0.62993400 -
1.82092400
C -6.76505400 1.89923100
0.38196900
H -6.93732800 2.91414800
0.71515200
C -3.84001900 2.92611200 -
0.79442100
H -4.14680200 3.91850500 -
0.49413900
C -6.12293400 -0.31795000
0.33537100
H -5.73530400 -1.28027700
0.63623100
H -7.39712100 1.96185800 -
1.76575100
C -2.43011700 2.41977900
1.32524300
H -2.05621200 1.50786100
1.80473200
C -3.43270900 3.08359300
2.29566800
H -4.26353300 2.40718400
2.50842000
H -3.85938900 4.00313300
1.88257300
H -2.95089600 3.33804200
3.24470800
N -1.20516900 3.23027300
1.07554000
C -0.42983800 3.45376100
2.29287700
H -0.90119200 4.15516400
3.00459200
H 0.54864700 3.86238300
2.02507000
H -0.25822900 2.50629700
2.81117700
C -1.39897900 4.49958100
0.37825500
H -0.42357200 4.98186400
0.26615300
H -2.05575000 5.21113400
0.91208100
H -1.80597400 4.33408000 -
0.62089100

CP7

Fe 3.29032900 -2.44391500 -
0.53806400
P -0.14518000 -1.80428100 -
0.96944000
P 2.20438000 0.69919100
0.72581100
C -0.91947300 -1.72670300 -
2.65619300
C 3.39999800 -0.68958500
0.56980500
C 1.40956400 -2.70749200 -
1.36189400
C -1.25706400 -2.60156100 -
4.90262000
H -1.03171000 -3.34756700 -
5.65988800
C 2.30104100 1.01468700
2.55583000
C -2.14760400 -1.56246600 -
5.18339900
H -2.62046800 -1.49819600 -
6.15946800
C 3.39692700 -1.84825400
1.42623000
H 2.67012300 -2.06022900
2.19831400
C -1.80353100 -0.67704900 -
2.95235900
H -2.01030200 0.08042200 -
2.20487100
C -2.41595200 -0.60163100 -
4.20693700
H -3.09802700 0.21691200 -
4.42112400
C 4.53862200 -0.81438000 -
0.29156800
H 4.81665900 -0.11447600 -
1.06431400
C 3.09146900 -4.30768300 -
1.43345800
H 3.70092200 -5.16864700 -
1.19140700
C -0.64549600 -2.68192400 -
3.65035400
H 0.05665200 -3.48641100 -
3.45578600
C 5.23344100 -2.01445700
0.04241200
H 6.11349000 -2.39636800 -
0.45852100
C 2.47299300 1.67727800
5.28758600
H 2.54186000 1.93775400
6.34015900
C 3.57207000 1.11936900
4.62954200
H 4.49863200 0.94226100
5.16885300
C 3.48873100 0.79411100
3.27489200
H 4.35514500 0.37349900
2.77676300
C 1.28970000 1.90355800
4.58273600
H 0.43277400 2.34644700

5.08372200			
C	2.36436000	-2.32760100	-2.36692100
H	2.31022800	-1.43956700	-2.97896100
C	1.20097900	1.57353000	3.22655300
H	0.27764300	1.75343400	2.68565300
C	1.87416000	-3.93873700	-0.79008200
H	1.38767900	-4.48989100	0.00268100
C	4.53122400	-2.65091500	1.10787700
H	4.78766900	-3.59870300	1.56305000
C	3.38900300	-3.31705400	-2.41458800
H	4.26433400	-3.29303100	-3.05072100
Rh	0.04175700	0.48340800	0.05196300
H	0.63626600	0.94735800	-1.29695500
H	0.11618900	2.01774700	0.41424900
Fe	-3.12390100	-3.44500000	0.17912400
C	-1.08635600	-3.19674600	-0.18222500
C	-4.49897400	-2.92883200	-1.28559300
C	-1.31041400	-3.45350700	1.23191500
C	-1.60858900	-4.32668400	-0.89750600
H	-1.63710700	-4.42583300	-1.97252800
C	-4.57768200	-2.10111900	0.86346700
H	-4.50225100	-1.42690500	1.70463600
C	-2.14004600	-5.26151000	0.03121000
H	-2.64217500	-6.18815000	-0.21422800
C	-5.03584000	-3.94642600	-0.44086000
H	-5.32174300	-4.94386600	-0.74785600
C	-4.21607000	-1.78855200	-0.47949800
H	-3.77613000	-0.86109000	-0.81364100
C	-1.96554300	-4.72974900	1.33642500
H	-2.27598600	-5.21575200	2.25257800
C	-5.08352700	-3.43597000	0.89078600
H	-5.43749500	-3.97364700	1.76126800
H	-4.29602200	-3.01912300	-2.34417800
C	-0.63974000	-2.72584700	2.37817100
H	-0.00941900	-1.93816000	1.95760400
C	0.22609100	-3.68344500	3.20620500
H	0.92259800	-4.18541500	2.52925500
H	-0.36773300	-4.46257700	3.69365300
H	0.81992500	-3.16531800	3.96456600
N	-1.60313100	-1.92083800	3.27004600
C	-0.88979700	-1.17279300	4.35454300
H	-0.58220900	-1.86099900	5.14246000
H	-1.58139700	-0.43132800	4.75656000
H	-0.02967400	-0.65689100	3.93071000
C	-2.74606800	-2.68861100	3.84304400
H	-3.39820400	-1.98742100	4.36813700
H	-2.36783600	-3.42780600	4.55203800
H	-3.29261700	-3.17247400	3.03644800
C	-6.46422300	3.32542600	-0.41523100
H	-5.98459800	3.28382400	-1.39382200
C	-5.81582500	2.73420200	0.61987400
H	-6.25939300	2.75080200	1.61167200
C	-7.74505700	4.02521100	-0.38971200
C	-8.24663600	4.55760100	-1.59363700
C	-8.51063800	4.19866200	0.78199200
C	-9.46348100	5.23458100	-1.63111500
H	-7.66902200	4.43477400	-2.50683300
C	-9.72517300	4.87458000	0.74447900
H	-8.15302000	3.80425700	1.72849600
C	-10.20803000	5.39548900	-0.46130700
H	-9.82988700	5.63654700	-2.57143700
H	-10.30026400	4.99875900	

1.65787000			
H	-11.15708500	5.92334400	-0.48550900
C	-4.54564000	2.07863100	0.44571600
H	-4.14201000	2.08284700	-0.56490200
C	-3.78641600	1.46203500	1.39210300
C	-2.48922700	0.86717500	0.97776000
C	-4.13092200	1.38417200	2.85847300
H	-3.31374100	1.78335300	3.46967200
H	-4.29469300	0.34799300	3.18845300
H	-5.03674100	1.94427600	3.09906100
O	-2.10022600	0.92910500	-0.23302300
O	-1.73794500	0.31674900	1.86424300
H	-1.95014300	-1.15168500	2.63430100
Fe	4.92253600	3.04385400	-0.06753500
C	2.99418000	2.23678900	0.07168700
C	6.66172700	4.05501700	0.43516700
C	3.24786300	2.67399300	-1.28894300
C	3.14474700	3.39360800	0.92036000
H	3.03699200	3.40520500	1.99409400
C	6.63927500	2.06279300	-0.73025400
H	6.68834500	1.34299900	-1.53683900
C	3.47928400	4.51330200	0.11584400
H	3.69402600	5.51105400	0.47514700
C	6.42665400	3.00189500	1.36914000
H	6.25710600	3.12099000	2.43105000
C	6.79271900	3.47580000	-0.86184200
H	6.95157100	4.01650900	-1.78559200
C	3.55537200	4.07120100	-1.23192100
H	3.83020500	4.68564000	-2.07811700
C	6.41500600	1.77116400	0.64966800
H	6.24445800	0.79047300	1.06968700
H	6.69380500	5.11212000	0.66403300
C	3.08227600	1.90631500	-2.58813300
H	3.33850600	0.85477000	-2.40548700
C	4.03259000	2.42274900	-3.69109300
H	5.06405000	2.44078000	-3.32790200
H	3.77244200	3.43503400	-4.01721700
H	3.99658500	1.77440300	-4.57140100
N	1.64919700	1.87921600	-2.98866900
C	1.41226500	1.12535700	-4.21642200
H	1.71114200	1.66729600	-5.13048000
H	0.34688500	0.88860300	-4.29581300
H	1.96710500	0.18214000	-4.19427600
C	0.96699700	3.17057600	-3.03848600
H	-0.08722600	2.99168500	-3.27290100
H	1.37100200	3.85458500	-3.80630800
H	1.01234300	3.66430700	-2.06663500

TS5

C	2.45459200	4.29367600	1.28874500
H	2.67669500	3.92876700	2.29264300
C	1.34726000	3.81466900	0.68195500
H	1.08818200	4.12775400	-0.32441600
C	3.41664800	5.26392400	0.76490100
C	4.52534100	5.60896800	1.56075700
C	3.29120200	5.87141900	-0.50064400
C	5.47823500	6.52090500	1.11120900
H	4.63496000	5.15406200	2.54249000
C	4.24224300	6.78153300	-0.94940700
H	2.44278700	5.63492000	-1.13610200
C	5.34023300	7.11017500	-0.14655600
H	6.32546100	6.77283700	1.74259100
H	4.12822300	7.24112600	-

1.92719600			
H	6.07937900	7.82335900	-
0.49990100			
C	0.45201400	2.86372700	
1.34605600			
H	0.74765800	2.60405300	
2.36259600			
C	-0.95018200	2.77538700	
1.06732200			
C	-1.73645600	2.00645200	
2.08156700			
C	-1.66240000	3.86606500	
0.30175700			
H	-2.64510600	3.53659400	-
0.03402500			
H	-1.82151800	4.72834500	
0.96392900			
H	-1.09589700	4.22140200	-
0.56245800			
O	-2.89591800	2.35745200	
2.42175100			
O	-1.15118200	0.93553400	
2.50116600			
Fe	-0.28679300	-3.49844100	-
1.13920100			
P	-1.97269700	-0.34713500	-
0.91794800			
P	1.43243500	-1.06334900	
0.73987400			
C	-2.22154300	0.60035900	-
2.50271000			
C	1.12946300	-2.77769900	
0.17042200			
C	-1.64648800	-2.01968000	-
1.63265900			
C	-2.94424400	0.77991300	-
4.82229700			
H	-3.35635500	0.31030200	-
5.71125000			
C	1.75404700	-1.41283400	
2.53794400			
C	-2.59461100	2.13218800	-
4.84169600			
H	-2.74154700	2.72204400	-
5.74200200			
C	0.22038400	-3.67486400	
0.83854800			
H	-0.41265500	-3.42196200	
1.67835000			
C	-1.84375700	1.94803200	-
2.54852400			
H	-1.37448200	2.38969500	-
1.68012800			
C	-2.03608400	2.71269500	-
3.70227700			
H	-1.74026100	3.75846400	-
3.71143300			
C	1.76263500	-3.52482700	-
0.87646800			
H	2.49500400	-3.13949200	-
1.56934700			
C	-1.88367500	-4.25432500	-
2.22696000			
H	-2.19054500	-5.29210600	-
2.21720900			
C	-2.75652800	0.02011300	-
3.66663700			
H	-3.00642300	-1.03481100	-
3.68944000			
C	1.25647300	-4.85766900	-
0.84872200			
H	1.51690300	-5.64707800	-
1.54189200			
C	2.35309400	-1.90196900	
5.24436300			
H	2.58492100	-2.09089300	
6.28890800			
C	2.77033800	-2.80153700	
4.25932400			
H	3.32607700	-3.69377700	
4.53487500			
C	2.47434300	-2.55931700	
2.91836400			
H	2.80924700	-3.26374900	
2.16606800			
C	1.63455900	-0.76448700	
4.87750300			
H	1.30115300	-0.06198100	
5.63696800			
C	-0.76421500	-2.30186400	-
2.73329700			
H	-0.10077600	-1.59036300	-
3.20045300			
C	1.33499400	-0.51911400	
3.53320400			
H	0.74466800	0.34774600	
3.26472500			
C	-2.33111800	-3.24442200	-
1.32616200			
H	-3.05911200	-3.38067300	-
0.53908100			
C	0.31019200	-4.95188400	
0.21408400			
H	-0.27399300	-5.82613200	
0.47034100			
C	-0.92119000	-3.66990200	-
3.10185300			
H	-0.36925100	-4.18508200	-
3.87732100			
Rh	-0.13625200	0.67515200	
0.42638800			
H	0.53424500	0.82105000	-
0.96515700			
H	1.16993400	1.44935800	
0.95598400			
Fe	-5.45086700	0.49387500	-
0.12048500			
C	-3.72789700	-0.67488800	-
0.35461900			
C	-6.25003300	1.81436400	-
1.50606500			
C	-4.28077500	-0.88097000	

0.97946900
C -4.76138100 -1.04153900 -
1.28782600
H -4.69139800 -0.97201300 -
2.36146600
C -5.45593400 2.47633600
0.56142500
H -4.79728700 2.85247200
1.33149100
C -5.91075000 -1.47001600 -
0.57448600
H -6.85655700 -1.76577900 -
1.00916600
C -7.23406200 1.47873000 -
0.52981100
H -8.17157300 0.97195200 -
0.71823800
C -5.15491200 2.42899300 -
0.83217400
H -4.24501300 2.76785300 -
1.30594100
C -5.62402100 -1.36431700
0.81045300
H -6.31246400 -1.61408800
1.60692700
C -6.74486300 1.89112000
0.74522700
H -7.27079400 1.77968400
1.68462600
H -6.30478100 1.60129600 -
2.56539900
C -3.50220000 -0.98367500
2.27811200
H -2.46209600 -0.71466100
2.08941600
C -3.56419100 -2.41671900
2.82630100
H -3.25004200 -3.10156100
2.03345300
H -4.57639900 -2.70903400
3.12386300
H -2.88970500 -2.56530200
3.67407800
N -3.89923400 0.04615800
3.35364700
C -3.09827500 -0.10376800
4.61132300
H -3.44684800 -0.96890800
5.17683000
H -3.24260700 0.80371400
5.20118400
H -2.04748500 -0.19117400
4.34259500
C -5.34929200 0.12639400
3.68318300
H -5.48729200 0.93037800
4.40947700
H -5.68495300 -0.81632900
4.12103300
H -5.90806400 0.35137600
2.77801600
H -3.58893500 0.99529600
2.95888200
Fe 4.99605700 -1.39986900 -
0.08493400
C 3.11036700 -0.52836500
0.17719800
C 6.88131200 -2.12580700
0.37739400
C 3.63664500 -0.17734200 -
1.13177200
C 4.05752900 -0.04466900
1.15425500
H 3.97212800 -0.16727300
2.22347500
C 5.45571400 -3.16270600 -
1.11159100
H 4.99856900 -3.50372700 -
2.03103000
C 5.13597400 0.58365100
0.47903300
H 6.01890700 1.00252400
0.94358000
C 5.89444500 -2.82958900
1.13098300
H 5.80997000 -2.84479600
2.20936900
C 6.60988200 -2.32969400 -
1.00833600
H 7.16445400 -1.90300100 -
1.83364500
C 4.88651300 0.48857000 -
0.91616500
H 5.54981800 0.83678800 -
1.69603600
C 5.01584700 -3.47232800
0.20993000
H 4.15869600 -4.08105000
0.46065500
H 7.67268200 -1.51042900
0.78476200
C 3.00776200 -0.32641800 -
2.50732400
H 2.31316700 -1.17427200 -
2.47704500
C 4.06335800 -0.63530300 -
3.59307800
H 4.67286900 -1.49335800 -
3.30015000
H 4.73695700 0.21075600 -
3.76439200
H 3.58324500 -0.87085900 -
4.54736900
N 2.14868200 0.84702300 -
2.82459100
C 1.47739100 0.72100500 -
4.11544500
H 2.14021500 0.90261400 -
4.98012100
H 0.65192700 1.43787800 -
4.16771100
H 1.05782100 -0.28341800 -

4.22716400
C 2.78181500 2.15789800 -
2.71478800
H 2.02205900 2.92163600 -
2.91495300
H 3.60581000 2.31919100 -
3.43443700
H 3.16444100 2.31991200 -
1.70580900

CP8

C 2.55115300 4.37388300
1.29524400
H 2.56438100 4.26147900
2.38074400
C 1.66243800 3.64031100
0.60357800
H 1.60874100 3.69792200 -
0.48008600
C 3.53231100 5.33375300
0.77225400
C 4.41269200 5.95432600
1.67644800
C 3.63911400 5.66600200 -
0.59189800
C 5.37008200 6.86836400
1.23883700
H 4.34196000 5.71370900
2.73479200
C 4.59415900 6.57837800 -
1.02965700
H 2.96736900 5.21333000 -
1.31576200
C 5.46504400 7.18341900 -
0.11713900
H 6.03899200 7.33504300
1.95646700
H 4.65932400 6.82349500 -
2.08622200
H 6.20780300 7.89685200 -
0.46246300
C 0.70787300 2.69865300
1.26809000
H 0.85754400 2.68352100
2.35568300
C -0.75819600 2.79183800
0.90487700
C -1.64698200 2.26419800
1.99896600
C -1.21174500 4.07954500
0.25411900
H -2.29062400 4.08276800
0.09001100
H -0.99601600 4.92267300
0.92569500
H -0.70148600 4.28312200 -
0.69142600
O -2.58836100 2.87455100
2.50107600
O -1.31799700 1.02250300
2.30785000
Fe -0.37065000 -3.29670800 -
1.50116600
P -2.00164200 -0.13499000 -
1.05425800
P 1.25932900 -1.16875500
0.63677800
C -2.44301500 0.89952100 -
2.53459500
C 0.92680300 -2.85531700
0.01546100
C -1.56844500 -1.68501000 -
1.93589200
C -3.25782200 1.13148300 -
4.81502500
H -3.62829500 0.67163800 -
5.72703300
C 1.48933400 -1.55731500
2.44374400
C -3.10171700 2.51776200 -
4.74182200
H -3.35575700 3.14149000 -
5.59418100
C -0.17721400 -3.64438700
0.50429600
H -0.88370200 -3.33933600
1.26314000
C -2.27009800 2.28614300 -
2.48249300
H -1.85385900 2.72622600 -
1.58943700
C -2.60151700 3.09308000 -
3.57324100
H -2.45974100 4.16858500 -
3.50989100
C 1.59781800 -3.64731300 -
0.97376900
H 2.46036200 -3.34208000 -
1.54603200
C -1.70341500 -3.72038500 -
3.04199400
H -2.01310300 -4.71872200 -
3.32277100
C -2.92699100 0.32610800 -
3.72406600
H -3.03577500 -0.74936000 -
3.81264800
C 0.91161800 -4.89132900 -
1.09819000
H 1.15592400 -5.67940300 -
1.79844800
C 1.96443100 -2.07166900
5.17407100
H 2.15294200 -2.26849300
6.22576100
C 2.25052300 -3.04639200
4.21461100
H 2.65716200 -4.00747900
4.51759900
C 2.01892200 -2.79004000
2.86264400
H 2.24970500 -3.55645900

2.13177600
C 1.42948600 -0.84716300
4.77202100
H 1.19645100 -0.08460200
5.51071700
C -0.47758900 -1.77133000 -
2.86614400
H 0.28227200 -1.01106200 -
2.98088600
C 1.18596800 -0.59313300
3.41791100
H 0.72932000 0.34588200
3.12744100
C -2.32446900 -2.90305000 -
2.05281400
H -3.20144500 -3.16134800 -
1.47619700
C -0.17762300 -4.89325500 -
0.17928500
H -0.90537500 -5.68474400 -
0.05645100
C -0.56846500 -3.01852200 -
3.54834900
H 0.13298200 -3.39500100 -
4.28173800
Rh -0.30425000 0.74076400
0.28680800
H 0.37214200 0.89349300 -
1.10622000
Fe -5.32852500 0.51177800
0.22809200
C -3.66382500 -0.60537400 -
0.36939400
C -6.07653000 2.11468300 -
0.85045600
C -4.08212600 -1.04429100
0.95729500
C -4.79125000 -0.80274800 -
1.24495400
H -4.82327000 -0.54444600 -
2.29216700
C -5.36521600 2.29520700
1.34069900
H -4.73370900 2.51852500
2.18889900
C -5.87393800 -1.34071100 -
0.49993300
H -6.86417600 -1.55313600 -
0.88067800
C -7.09373800 1.57034400 -
0.01086800
H -8.01976400 1.11975100 -
0.34342300
C -5.01170500 2.55867400 -
0.01386000
H -4.08408300 2.99374900 -
0.35136600
C -5.45055900 -1.47051900
0.84785600
H -6.06191600 -1.84110500
1.66054100
C -6.65335700 1.68105700
1.34218900
H -7.20829500 1.35053900
2.21123600
H -6.09308600 2.14764300 -
1.93166900
C -3.18982900 -1.42639600
2.12793600
H -2.15034100 -1.33892300
1.80471800
C -3.46130700 -2.87134600
2.57107700
H -3.44241800 -3.51682900
1.68907100
H -4.44609100 -2.98543600
3.03494200
H -2.70422400 -3.23868500
3.26916400
N -3.22830600 -0.45857900
3.32287800
C -2.35543300 -0.90408700
4.45377100
H -2.81906900 -1.73945400
4.97943200
H -2.23994200 -0.05827700
5.13385200
H -1.37630400 -1.18231900
4.06621900
C -4.57796900 -0.09289900
3.83201300
H -4.45952500 0.72514200
4.54512900
H -5.02588500 -0.95518400
4.33172800
H -5.19570400 0.23246000
2.99943100
H -2.70215500 0.38577800
2.94378400
Fe 4.86983200 -1.50621600
0.16415300
C 2.97251400 -0.64506500
0.16732500
C 6.65217800 -2.23079700
0.93477300
C 3.64167900 -0.37038600 -
1.10144600
C 3.80795200 -0.08425400
1.20655500
H 3.61454600 -0.14317300
2.26703400
C 5.46336200 -3.29728500 -
0.73153200
H 5.14701400 -3.65588800 -
1.70222500
C 4.94782700 0.51604700
0.61474900
H 5.76994600 0.97836600
1.14487000
C 5.55118800 -2.90490200
1.54285200
H 5.29761900 -2.88966200

2.59431900
C 6.59725700 -2.47058400 -0.47085000
H 7.27942800 -2.07161000 -1.21005600
C 4.85199300 0.33123900 -0.78801100
H 5.59357900 0.64171400 -1.51060200
C 4.81944100 -3.56660400 0.51238300
H 3.92520400 -4.15940400 0.64325700
H 7.37799000 -1.61098200 1.44450000
C 3.22163700 -0.64139400 -2.54083600
H 2.61782300 -1.55560500 -2.56006100
C 4.44841500 -0.88410300 -3.45209400
H 5.11810800 -1.62586700 -3.01110300
H 5.02422000 0.03230600 -3.61835500
H 4.13474000 -1.25465300 -4.43193900
N 2.30756700 0.42019400 -3.05086400
C 1.94899100 0.22968700 -4.45688900
H 2.75385400 0.50539600 -5.15996900
H 1.07444500 0.84700200 -4.69125500
H 1.68609900 -0.81626000 -4.64722700
C 2.74989300 1.79617800 -2.83884400
H 1.95173700 2.46880200 -3.17244300
H 3.66380600 2.06258200 -3.40146300
H 2.93142300 1.98204800 -1.77916200
H 1.13099900 1.62262300 1.01955400

TS6

C 2.92712000 4.16534400 1.03022500
H 2.74340800 4.32361300 2.09443700
C 2.09354400 3.34523000 0.36811500
H 2.23812800 3.11109800 -0.68361300
C 4.09062100 4.88981100 0.50038200
C 4.93365500 5.56413100 1.40156000
C 4.40528000 4.94648000 -0.87060100
C 6.05865700 6.25712200 0.95631800
H 4.70194900 5.53975400 2.46400400
C 5.52738500 5.63884100 -1.31637400
H 3.76067300 4.45561800 -1.59329300
C 6.36134800 6.29565600 -0.40536500
H 6.69560100 6.76916400 1.67217700
H 5.75050500 5.67479200 -2.37936000
H 7.23425300 6.83822800 -0.75699300
C 0.93990900 2.67100200 1.04775300
H 0.92455600 2.86796500 2.12528000
C -0.46097300 2.89596300 0.48781100
C -1.58085500 2.74895600 1.53413700
C -0.62386100 4.12595500 -0.39384700
H -1.66762800 4.26099600 -0.67742400
H -0.34236900 5.00756000 0.19726600
H 0.00987300 4.10747700 -1.28420100
O -2.62445800 3.39483800 1.39137300
O -1.32812000 1.90707200 2.48539600
Fe -0.48372600 -3.53071400 -1.23075700
P -2.00824800 -0.28503100 -1.01321400
P 1.16729600 -1.17684200 0.70328700
C -2.56161700 0.59481900 -2.56361800
C 0.92897600 -2.89324600 0.12025700
C -1.75535700 -1.97949800 -1.69756500
C -3.50853100 0.57397100 -4.80899700
H -3.88273700 0.00847300 -5.65785100
C 1.35635400 -1.43623600 2.53200100
C -3.47112700 1.96799200 -4.85582700
H -3.81492600 2.49620200 -5.74047900
C 0.03016700 -3.83994500

0.73087600
H -0.60149400 -3.65291900
1.58839000
C -2.53377400 1.99459700 -
2.62538000
H -2.16318300 2.56307800 -
1.78389300
C -2.98311800 2.67692700 -
3.75686500
H -2.94754200 3.76260200 -
3.77708700
C 1.56118400 -3.55996000 -
0.98002700
H 2.28207700 -3.11980800 -
1.65117400
C -2.14815500 -4.19640600 -
2.27799500
H -2.51613700 -5.21385800 -
2.25507200
C -3.05885500 -0.10768300 -
3.67568900
H -3.09532400 -1.19060100 -
3.67317800
C 1.06792300 -4.89647800 -
1.03905800
H 1.33101000 -5.63483600 -
1.78513700
C 1.87872700 -1.68070800
5.28695400
H 2.08734400 -1.77211700
6.34914100
C 2.19261100 -2.72790200
4.41728500
H 2.64155000 -3.63991400
4.80100400
C 1.94234200 -2.60379100
3.04986600
H 2.21001100 -3.41744800
2.38564000
C 1.29491900 -0.51753600
4.78273100
H 1.04845900 0.30267000
5.45200900
C -0.91901400 -2.31898600 -
2.82114000
H -0.22654600 -1.65715100 -
3.31994500
C 1.02325200 -0.39716700
3.41559100
H 0.54204600 0.50493000
3.04651300
C -2.51064400 -3.15945800 -
1.37115000
H -3.22314400 -3.24727900 -
0.56392000
C 0.12746100 -5.07055700
0.01848600
H -0.44650000 -5.96559500
0.21982000
C -1.17266900 -3.67556500 -
3.17829600
H -0.67167700 -4.22694200 -
3.96332900
Rh -0.26807200 0.71274400
0.14846600
H -0.45321500 1.88825000 -
0.89617500
Fe -5.31092200 0.65149900
0.25398900
C -3.62929700 -0.54914200 -
0.14718500
C -6.05382700 2.02197400 -
1.11721400
C -3.98296200 -0.66518800
1.26070000
C -4.78653100 -0.95449300 -
0.90438500
H -4.85867000 -0.95515400 -
1.98154800
C -5.49916100 2.59387200
1.04890400
H -4.92932400 2.99084300
1.87508800
C -5.82040400 -1.33062400 -
0.00772700
H -6.81846100 -1.64544500 -
0.28253700
C -7.09644600 1.55998600 -
0.25828900
H -7.97516400 1.00654700 -
0.56312600
C -5.07072900 2.65810400 -
0.30620100
H -4.14432800 3.10153300 -
0.63149800
C -5.33931800 -1.13794200
1.31399900
H -5.90689600 -1.32301100
2.21672900
C -6.75181900 1.91243100
1.08231400
H -7.33947700 1.68351300
1.96260800
H -6.00059300 1.87960700 -
2.18830300
C -3.02508400 -0.73040700
2.43766100
H -2.01172500 -0.56197500
2.06213900
C -3.09817900 -2.11961900
3.09152900
H -3.01612600 -2.87587800
2.30584200
H -4.05192300 -2.28778900
3.60256100
H -2.28476000 -2.28841100
3.80176000
N -3.16977100 0.39588000
3.47662600
C -2.34846400 0.15754100
4.70320700
H -2.82614300 -0.58933700

5.33921600
H -2.27297900 1.10644900
5.23749000
H -1.35214500 -0.16889400
4.41458900
C -4.55546000 0.75751100
3.87880100
H -4.50336400 1.65210900
4.50305900
H -4.99622600 -0.06053700
4.45505800
H -5.14724000 0.96055400
2.99168500
H -2.63963600 1.22684100
3.01384900
Fe 4.72486100 -1.60968300
0.08588900
C 2.88125200 -0.63327900
0.27198900
C 6.55313900 -2.41613500
0.63481800
C 3.46474700 -0.29009200 -
1.01218200
C 3.81538700 -0.21170500
1.29153600
H 3.68819600 -0.33497700
2.35632100
C 5.14475700 -3.40993800 -
0.89888100
H 4.71680900 -3.74826100 -
1.83243500
C 4.94966800 0.35861400
0.65805500
H 5.83511500 0.72995000
1.15652700
C 5.50303300 -3.06112300
1.35505400
H 5.37429100 -3.05603900
2.42923300
C 6.33055300 -2.62936600 -
0.75783700
H 6.94137200 -2.24634800 -
1.56476200
C 4.74848600 0.28310700 -
0.74821900
H 5.46844900 0.58687700 -
1.49535200
C 4.63469100 -3.67702700
0.40674000
H 3.73975500 -4.23975000
0.63135500
H 7.35453700 -1.83164900
1.06719700
C 2.80199500 -0.34360600 -
2.37965500
H 1.86972400 -0.90620000 -
2.26187900
C 3.65533500 -1.06521500 -
3.44280900
H 3.79124500 -2.11748900 -
3.17896200
H 4.65176000 -0.62270400 -
3.53726800
H 3.17407300 -1.02226000 -
4.42606500
N 2.36041900 1.02111000 -
2.78316300
C 1.22855200 0.98447600 -
3.70419600
H 1.45100400 0.50202700 -
4.67486900
H 0.90335300 2.00835700 -
3.91595500
H 0.38707400 0.46844400 -
3.23549700
C 3.41115600 1.89206200 -
3.30616700
H 2.98160600 2.88357600 -
3.48692400
H 3.84940800 1.54642000 -
4.25932800
H 4.21417300 2.01071100 -
2.57654800
H 1.20456300 1.54674900
1.05789700

CP9

Fe 3.65445100 -1.98145100 -
0.48655000
P 0.18779400 -1.75545200 -
0.94532600
P 2.02012700 0.70963800
0.72779200
C -0.60603700 -1.47317900 -
2.59448100
C 3.46749000 -0.39031800
0.78467900
C 1.85808100 -2.34349600 -
1.42636100
C -0.83577400 -1.94479700 -
4.96880500
H -0.51092300 -2.48959700 -
5.85104800
C 1.72708100 1.14142500
2.50627200
C -1.87931300 -1.02047700 -
5.05887800
H -2.37070100 -0.84457000 -
6.01169900
C 3.45183200 -1.63336500
1.51718500
H 2.63346100 -1.99273800
2.12356100
C -1.64628600 -0.53590700 -
2.69611600
H -1.95481400 0.02275400 -
1.81808800
C -2.28100400 -0.31705700 -
3.92114000
H -3.08567500 0.41024400 -
3.98605200
C 4.73283600 -0.31845900

0.11157600			
H	5.05631700	0.48064600	-
0.53724000			
C	3.76339000	-3.62012800	-
1.76808800			
H	4.49786100	-4.41116200	-
1.69070600			
C	-0.20004400	-2.16873300	-
3.74560900			
H	0.62016200	-2.87795100	-
3.69688400			
C	5.47525900	-1.49458700	
0.42125700			
H	6.45059900	-1.74691300	
0.02608500			
C	1.01286800	1.65897100	
5.18020000			
H	0.74543600	1.86750600	
6.21216400			
C	2.27613300	1.14677300	
4.87273300			
H	2.99296000	0.95688400	
5.66701000			
C	2.63015400	0.88274900	
3.54676400			
H	3.61130000	0.47623800	
3.32483700			
C	0.09938400	1.91494800	
4.15415100			
H	-0.88097900	2.32417600	
4.38073400			
C	2.74213100	-1.61481800	-
2.28991100			
H	2.52848400	-0.62050900	-
2.66107600			
C	0.45608000	1.66235300	
2.82772800			
H	-0.24997700	1.92809700	
2.03687900			
C	2.50150300	-3.58831400	-
1.10536000			
H	2.10450100	-4.36182000	-
0.46278200			
C	4.68966100	-2.30122400	
1.29478300			
H	4.96710900	-3.27139900	
1.68580400			
C	3.90928400	-2.40494400	-
2.50201100			
H	4.77837500	-2.11391800	-
3.07776100			
Rh	-0.10283700	-0.02259800	
0.44909200			
Fe	-2.48842900	-4.07362400	-
0.20351200			
C	-0.54207600	-3.35718200	-
0.38325500			
C	-3.89496200	-3.62823700	-
1.65913200			
C	-0.76369400	-3.84579100	
0.96847100			
C	-0.78045000	-4.45995800	-
1.27449300			
H	-0.73605300	-4.41425300	-
2.35289100			
C	-4.21646800	-3.19196200	
0.58563500			
H	-4.28429800	-2.65783600	
1.52247700			
C	-1.13027100	-5.60443900	-
0.50828800			
H	-1.40730800	-6.57323100	-
0.90269200			
C	-4.22865400	-4.85655500	-
1.01385000			
H	-4.28436700	-5.82883500	-
1.48559900			
C	-3.88397900	-2.60153900	-
0.67004800			
H	-3.62731100	-1.56598100	-
0.83291300			
C	-1.12794800	-5.23209800	
0.86341400			
H	-1.36668100	-5.89290900	
1.68678700			
C	-4.42640200	-4.58720400	
0.37375700			
H	-4.67778000	-5.32087800	
1.12909300			
H	-3.64657300	-3.50358300	-
2.70455900			
C	-0.32031400	-3.13983600	
2.23177200			
H	0.11280600	-2.17624400	
1.92716100			
C	0.72811100	-3.97090600	
2.98327900			
H	1.53869700	-4.21291200	
2.29044600			
H	0.32232700	-4.92032700	
3.34679000			
H	1.16411500	-3.42992100	
3.82835600			
N	-1.45808300	-2.70100400	
3.15358700			
C	-0.96995900	-1.87319200	
4.30193400			
H	-0.47838100	-2.50561000	
5.04231500			
H	-1.83668000	-1.38085100	
4.74402500			
H	-0.28243400	-1.11442700	
3.92657000			
C	-2.35432200	-3.78629900	
3.64473200			
H	-3.17936300	-3.32095100	
4.18764600			
H	-1.80358600	-4.44946800	
4.31525500			
H	-2.74401400	-4.33719500	
2.79142100			
H	-2.05876900	-2.00517700	

2.60131100			
Fe	4.04970300	3.65315200	-
0.24356000			
C	2.45096500	2.34975100	-
0.01491500			
C	5.26817300	5.07549800	
1.13544800			
C	2.93848500	2.80369600	-
1.31618600			
C	2.05379700	3.53863300	
0.71176000			
H	1.68930500	3.56670200	
1.72579500			
C	6.07482700	3.17373200	
0.10441800			
H	6.52041500	2.51000000	-
0.62500300			
C	2.27733900	4.67845400	-
0.09845900			
H	2.11757400	5.70715200	
0.19607100			
C	5.07106300	3.97612200	
2.02408200			
H	4.59613100	4.01956400	
2.99531300			
C	5.88711600	4.58044600	-
0.05081700			
H	6.14218300	5.16555500	-
0.92469000			
C	2.82401600	4.23169300	-
1.32720500			
H	3.14196300	4.87263200	-
2.13684400			
C	5.57236500	2.80219700	
1.38786500			
H	5.55584100	1.80151700	
1.79634500			
H	4.96477600	6.09891100	
1.31274500			
C	3.41196100	2.03638000	-
2.54323600			
H	3.97110900	1.15291300	-
2.21079800			
C	4.38450500	2.88776600	-
3.39314700			
H	5.15960200	3.32949400	-
2.76168000			
H	3.86936600	3.69877400	-
3.91846400			
H	4.87815600	2.27094100	-
4.14871500			
N	2.25831000	1.49399900	-
3.31623100			
C	2.65791100	0.90912800	-
4.59758000			
H	2.91862700	1.65792400	-
5.36455800			
H	1.83077200	0.30427500	-
4.98512100			
H	3.52430600	0.25182400	-
4.46451100			
C	1.13248500	2.40642200	-
3.51600200			
H	0.33482800	1.85907500	-
4.02844600			
H	1.38034000	3.29172900	-
4.13017300			
H	0.73968600	2.74953000	-
2.55714400			
H	-5.12798200	0.28586100	-
0.27311400			
C	-6.26526300	3.29224100	-
0.52497200			
H	-5.43059300	3.64549400	-
1.13311400			
C	-6.10756600	2.13554600	
0.13807000			
H	-6.91429600	1.75351600	
0.76466700			
C	-7.44453300	4.17198100	-
0.53738300			
C	-7.36413100	5.40004300	-
1.21758500			
C	-8.65761900	3.84981300	
0.10047800			
C	-8.44593400	6.27905200	-
1.25484400			
H	-6.43691900	5.66625500	-
1.72043900			
C	-9.73851200	4.72588500	
0.06418600			
H	-8.76043700	2.90358900	
0.62394900			
C	-9.63880800	5.94603900	-
0.61224500			
H	-8.35683700	7.22260700	-
1.78643700			
H	-10.66568700	4.45568000	
0.56258800			
H	-10.48507100	6.62667500	-
0.63974900			
C	-4.86561100	1.28929500	
0.09465400			
H	-4.14064500	1.70864500	-
0.61283500			
C	-4.19169300	1.13921000	
1.48324200			
C	-3.06791100	0.09679000	
1.47005300			
C	-3.63345100	2.48242300	
1.98923100			
H	-2.84800600	2.84934400	
1.31780200			
H	-3.21454300	2.38290100	
2.99775300			
H	-4.42699800	3.23471400	
2.02398400			
O	-3.05406200	-0.77042300	
2.38038100			
O	-2.20272400	0.20726400	
0.52959400			
H	-4.93589000	0.77648900	

2.20127300

(*S*)-2a

H	1.94941700	0.10052600	-1.81597800
C	-0.84889300	0.63273600	-0.31886000
H	-0.64652300	1.69336100	-0.16250600
C	0.18846600	-0.16002900	-0.63064100
H	0.02728000	-1.22767900	-0.78756500
C	-2.26038300	0.24910000	-0.15734900
C	-3.18607900	1.22849300	0.24472800
C	-2.74083800	-1.05473900	-0.38500500
C	-4.53529700	0.92261500	0.41989200
H	-2.83641700	2.24308700	0.42272600
C	-4.08713900	-1.36207200	-0.21040000
H	-2.05706200	-1.83519700	-0.70622400
C	-4.99282400	-0.37598200	0.19383800
H	-5.22822200	1.69956800	0.73215900
H	-4.43401000	-2.37595900	-0.39291800
H	-6.04332600	-0.61923400	0.32774400
C	1.60539400	0.31309700	-0.79420200
H	1.66377200	1.40091700	-0.67305800
C	2.58341200	-0.36092400	0.19343500
C	4.01932400	-0.02217500	-0.17034000
C	2.31322400	0.03420500	1.66015100
H	2.45504200	1.11215700	1.80238700
H	2.98549600	-0.49506700	2.34135500
H	1.28010400	-0.20726600	1.92715100
O	4.90270500	-0.83701200	0.46303700
O	4.37951300	0.86553500	-0.91263100
H	2.48661500	-1.45260100	0.11534900
H	5.78987700	-0.53074600	0.19466200

10. References

1) Chen, W. et al. *Angew. Chem. Int. Ed.* **46**, 4141- 4144 (2007) ;

2) Ruan, J., Li, X., Saidi, O. & Xiao, J. *J. Am. Chem. Soc.* **8**, 2424–2425 (2008);

3) Elhamifar, D., Karimi, B., Rastegar, J. & Banakar, M.H. *ChemCatChem* **8**, 2418- 2424 (2013).

4) Zeng, Y. et al. *Catalysis Letters* **2**, 200-205 (2013).

5) Liang, B. et al. *Adv. Synth. Catal.* **15**, 1669-1673 (2004).

6) Liu, J. et al. *J. Am. Chem. Soc*. **32**, 10282- 10288 (2018).

7) Gregerson, C. E. et al. *Org. Biomol. Chem.* **28**, 5944- 5948 (2017).

8) Mao, J. et al. *Tetrahedron* **48**, 9067- 9072 (2015).

9) Li, C. et al. *Adv. Synth. Catal.* **8**, 1600- 1604 (2018).

10) Bouziane, A. *Chem. Eur. J.* **18**, 5630- 5637 (2008).

11) Wu, X. et al. *Angew. Chem. Int. Ed.* **40**, 6718- 6722 (2006).

12) BIO-PHARM SOLUTIONS, CO., LTD.- WO2015/88271, A1 (2015).

13) West, T. H. *J. Am. Chem. Soc.* **12**, 4366−4375 (2017).

14) Yang, D., Jiao, G.-S., Yip, Y.-C., Lai, T.-H., Wong, M.-K., *J. Org. Chem.* **13**, 4619- 4624 (2001).

15) Zhang Y. et al. *ACS Med. Chem. Lett.* **7**, 584−587 (2012).

16) Chen, H., Jiang, H., Cai, C., Dong, J. & Fu, W. *Org. Lett.* **5**, 992- 994 (2011).

17) Liu, Y., Cai, L., Xu, S., Pu, W. & Tao, X. *Chem. Commun.* **17**, 2166- 2168 (2018).

18) Chen, X., Zhang, Y., Wan, H., Wang, W. & Zhang, S. *Chem. Commun.* **17**, 3532- 3535 (2016).

19) Liu, J., Zhu, J., Jiang, H., Wang, W. & Li, J. *Chem. Commun.* **3**, 415-417 (2010).

20) Battistuzzi, G., Cacchi, S., & Fabrizi. G. *Org. Lett.* **5**, 777- 780 (2003).

21) Hoffmann-LA Roche Inc. - US6310247, B1 (2001).

22) Myrboh, B., Asokan, C. V., Ila, H. & Junjappa, H. *Synthesis* **1**, 50- 51 (1984).

23) Al-Huniti, M. H., Perez, M. A., Garr, M. K. & M. P. Croatt, *Org. Lett.* **23**, 7375- 7379 (2018).

24) Hayashi, T., Kawatsura, M. & Uozumi, Y. *J. Am. Chem. Soc.* **8**, 1681-1687 (1998).

25) Oliveira, C. C. et al. *Org. Lett.* **19**, 5180- 5183 (2014).

26) Dreier, A. et al. *J. Org. Chem.* **3**, 1638−1648 (2017).

27) Zhou, X. -L., Ren, L., Wang, P.-S. *J. Org. Chem*. **3**, 9794- 9800 (2017).

28) Zhang, Q.-B. et al. *Org. Lett.* **20**, 5256- 5259 (2016).

29) Rudlera, H., Harrisa, P., Bellassoued, M. & Vaissermannc, J. *J. Organom. Chem.* **2**, 186- 202 (2001).

30) Prepared according to reported methods: Solberghe, G. F., & Markó, I. E. *Tetrahedron Lett.* **29**, 5061-5065 (2002).

31) a) NOVARTIS AG - WO2008/83967, A2 (2008); b) Nanjing Ouxin Pharmaceutical Co., Ltd.; Chen Benshun - CN107304179 (2017); c) Wang, Y., Chen, F., Shi, Y. & Tian, W. *Tetrahedron Lett.* **52**, 5928-5930 (2016).

32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.;

Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**.

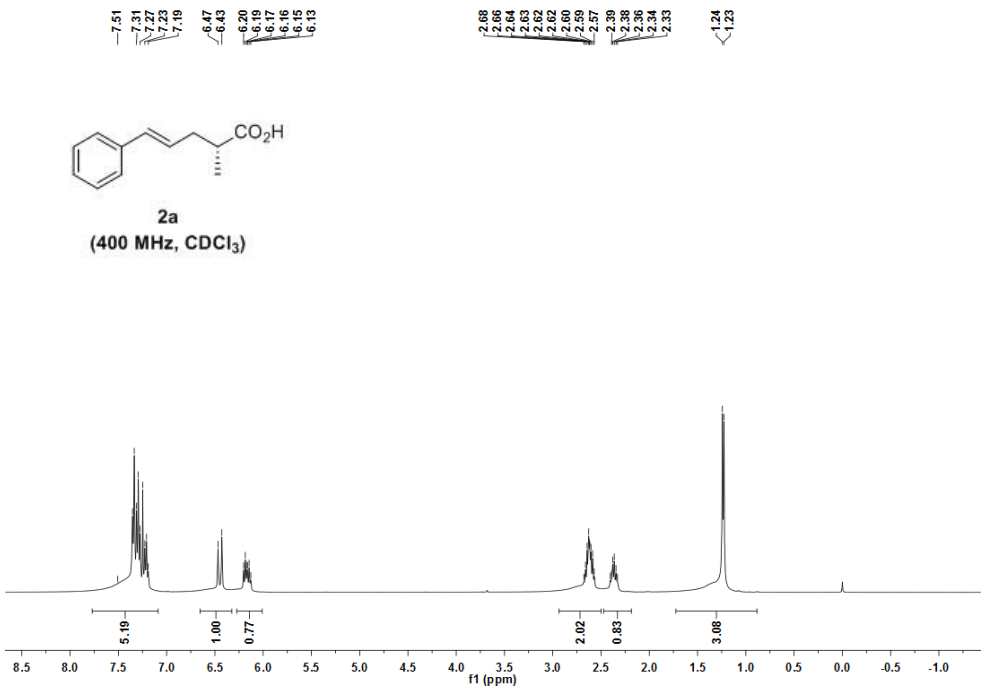
33) (a) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.

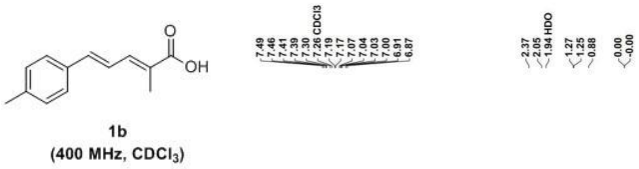
34) (a) Hay, P. J.; Wadt, W. R. *Ab initio* effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82*, 299−310. (b) Hay, P. J.; Wadt, W. R. *Ab initio* effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 284−298. (c) Roy, L. E.; Hay, P. J.; Martin, R. L. Revised basis sets for the LANL effective core potentials. *J. Chem. Theory Comput.*, 2008, **4**, 1029−1031.

35) (a) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Ab initio* study of solvated molecules: a new implementation of the polarizable continuum model. *Chem. Phys. Lett.* **1996**, *255*, 327−335. (b) Cances, E.; Mennucci, B.; Tomasi, J. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. *J. Chem. Phys.* **1997**, *107*, 3032−3041. (c) Barone, V.; Cossi, M.; Tomasi, J. Geometry optimization of molecular structures in solution by the polarizable continuum model. *J. Comput. Chem.* **1998**, *19*, 404−417. (d) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.

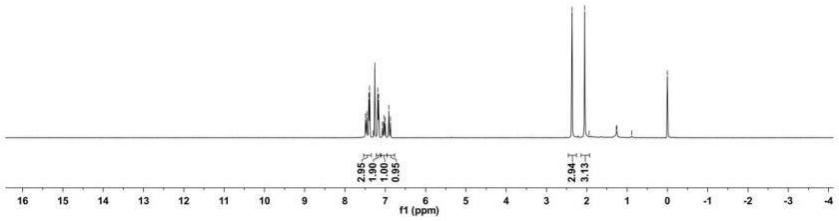
36) (a) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

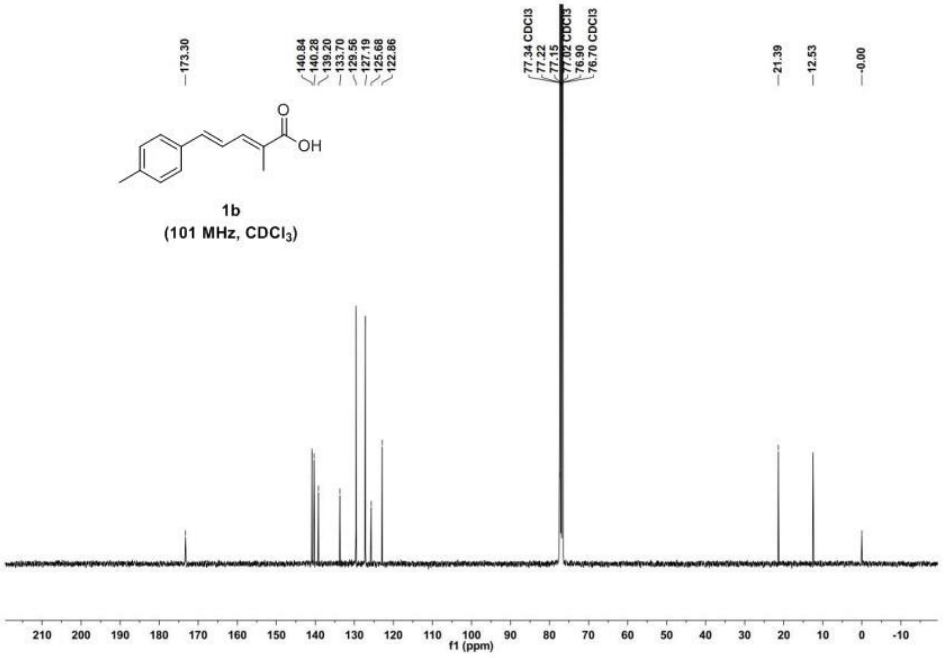
10. **NMR spectra**


7.51
7.31
7.27
7.23
7.19
6.47
6.43
6.20
6.19
6.17
6.16
6.15
6.13
2.68
2.66
2.64
2.63
2.62
2.62
2.60
2.59
2.57
2.39
2.38
2.36
2.34
2.33
1.24
1.23
CO2H
2a
(400 MHz, CDCl3)
5.19
1.00
0.77
2.02
0.83
3.08
f1 (ppm)
182.35
137.32
132.44
128.53
127.24
126.82
126.15
77.35
77.24
77.04
76.72
39.47
36.68
16.44
CO2H
2a
(101 MHz, CDCl3)
f1 (ppm)

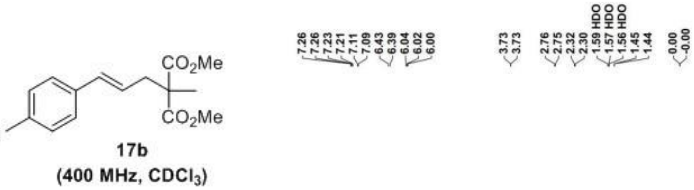


1b
(400 MHz, $CDCl_3$)

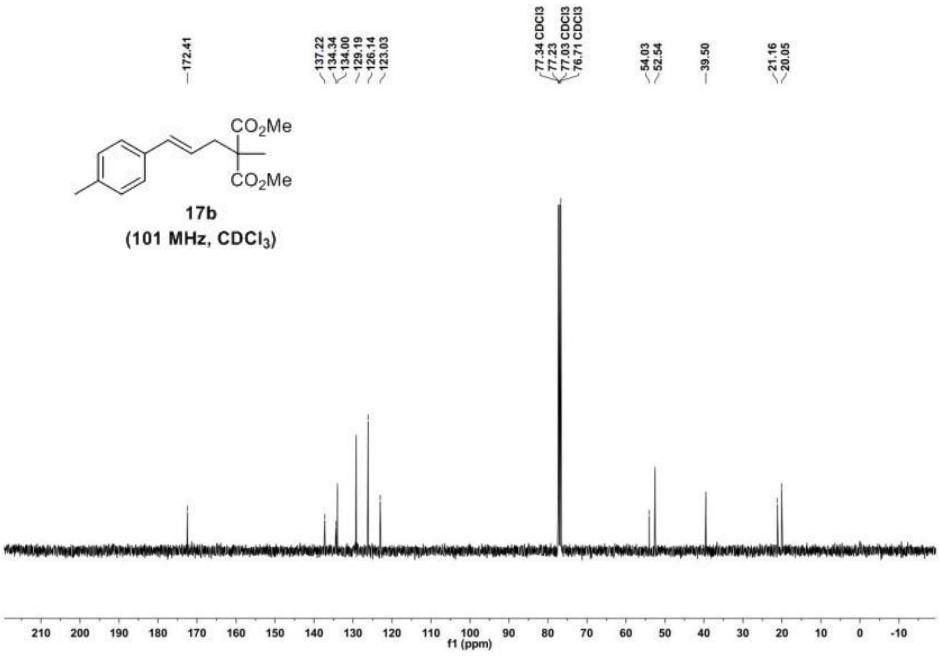




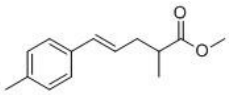
1b
(101 MHz, $CDCl_3$)



17b
(400 MHz, $CDCl_3$)

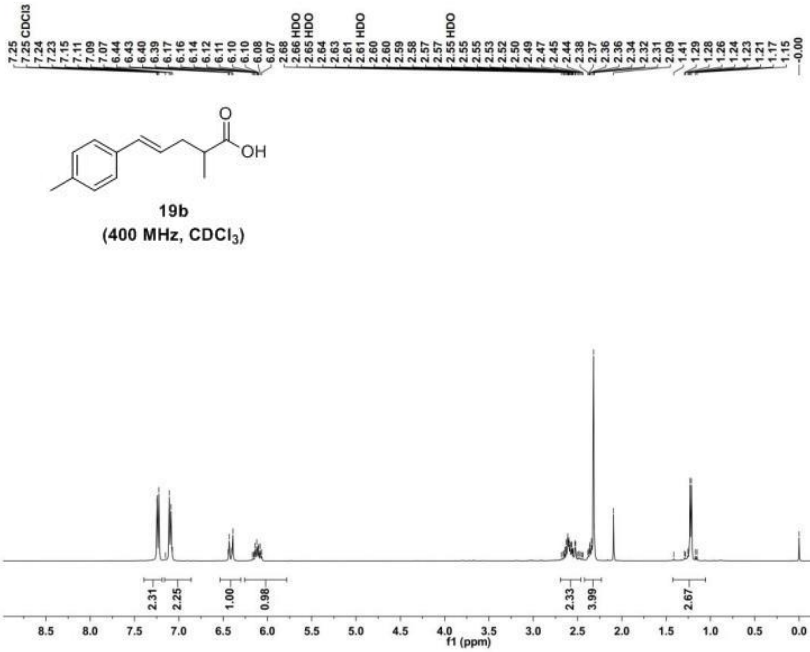


17b
(101 MHz, $CDCl_3$)

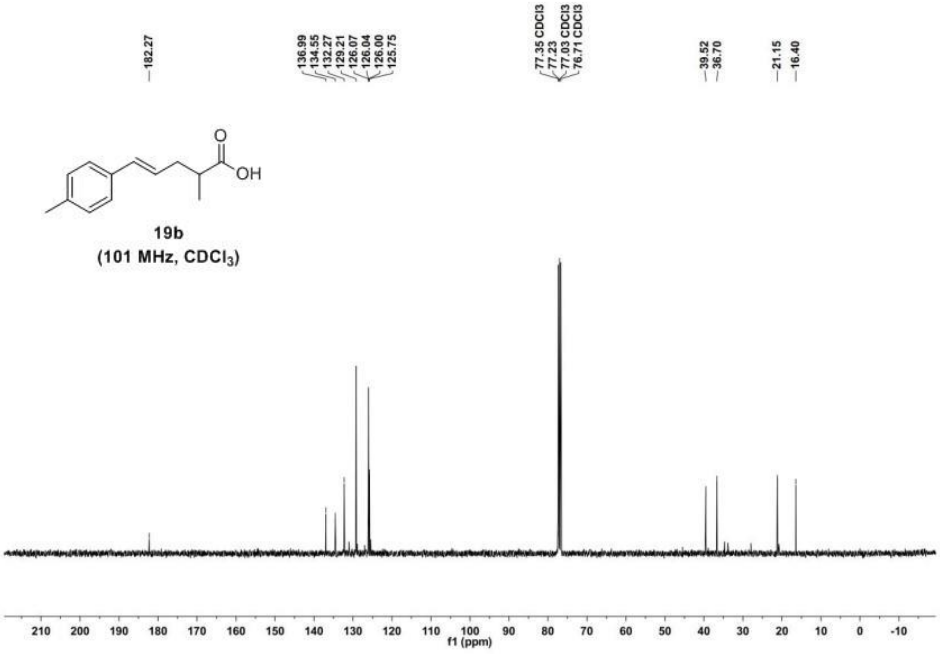


18b
(400 MHz, $CDCl_3$)

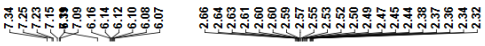
18b
(101 MHz, $CDCl_3$)

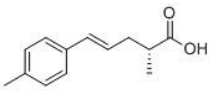


19b
(400 MHz, $CDCl_3$)

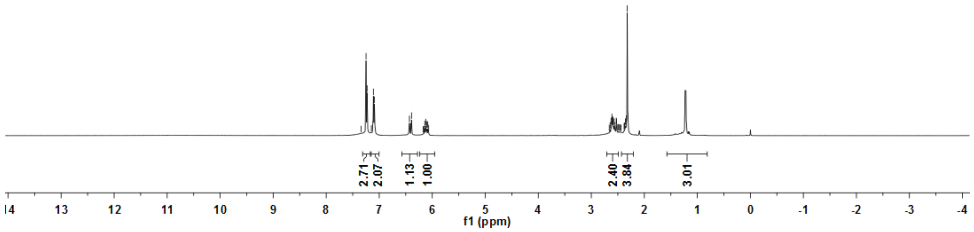


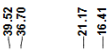
19b
(101 MHz, $CDCl_3$)

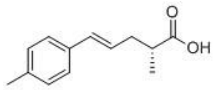




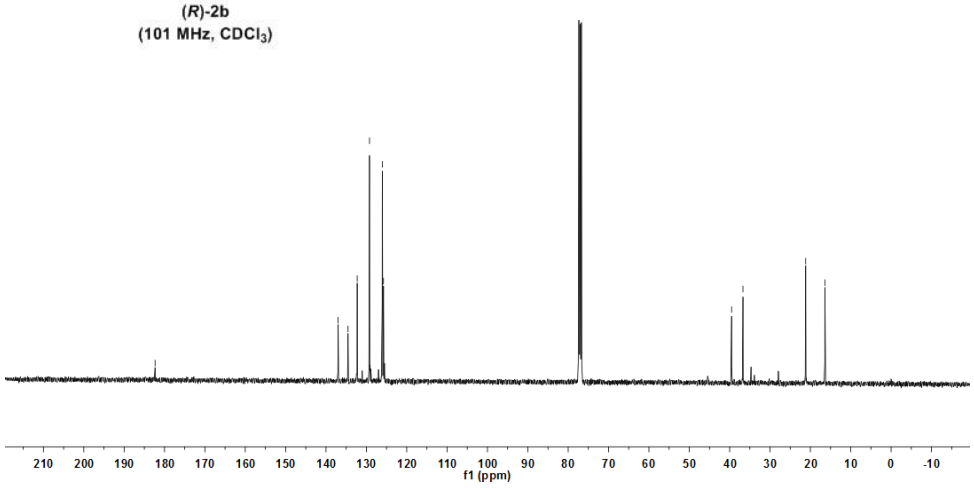
(*R*)-2b
(400 MHz, $CDCl_3$)

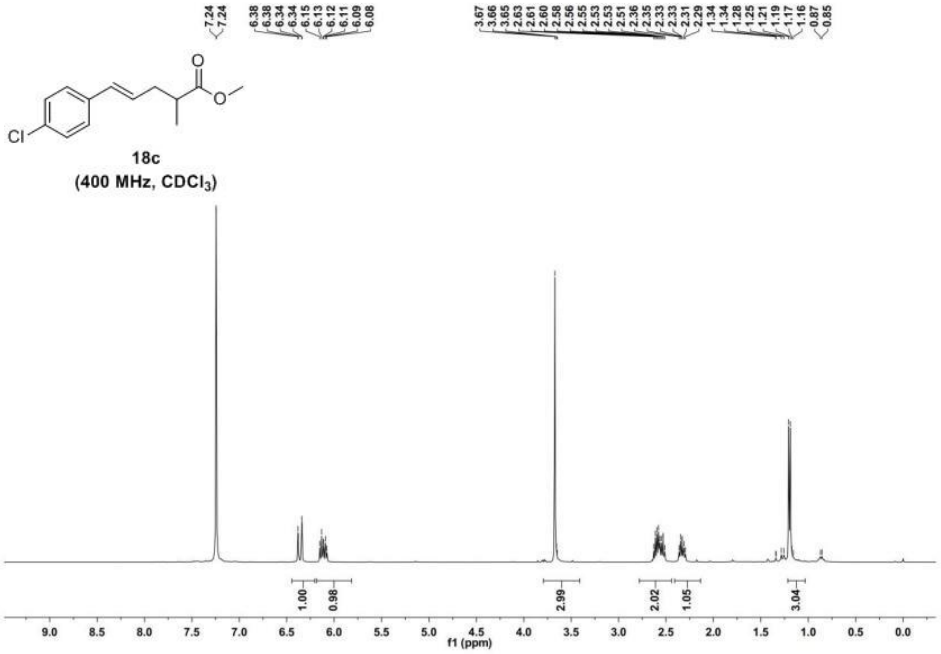


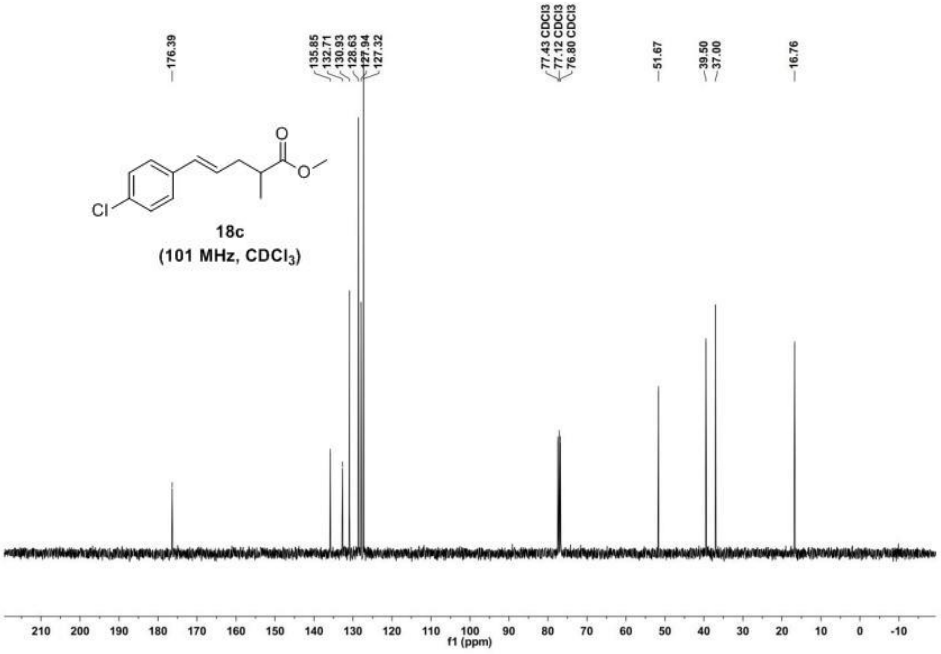


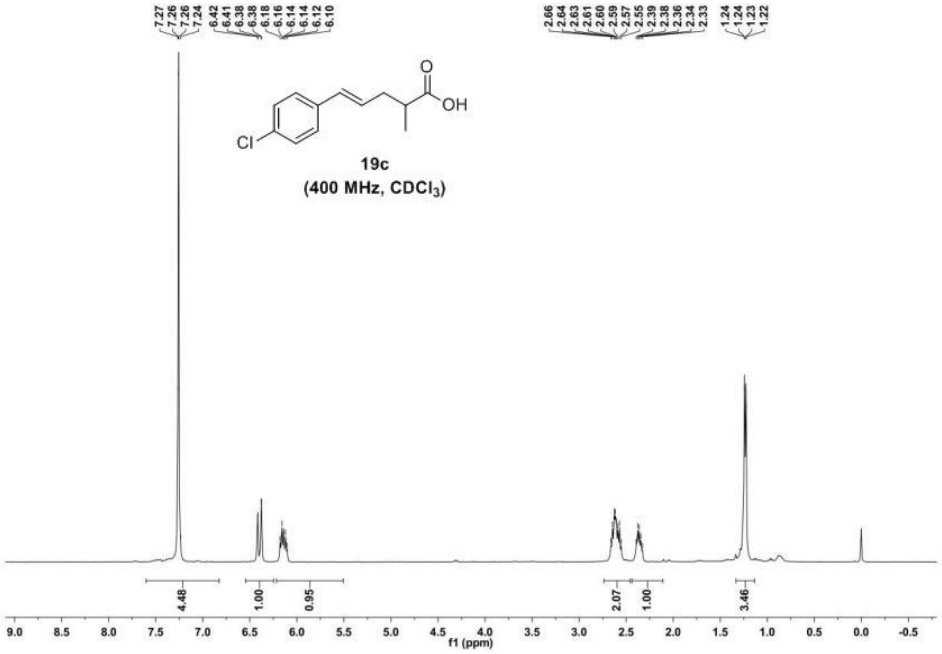


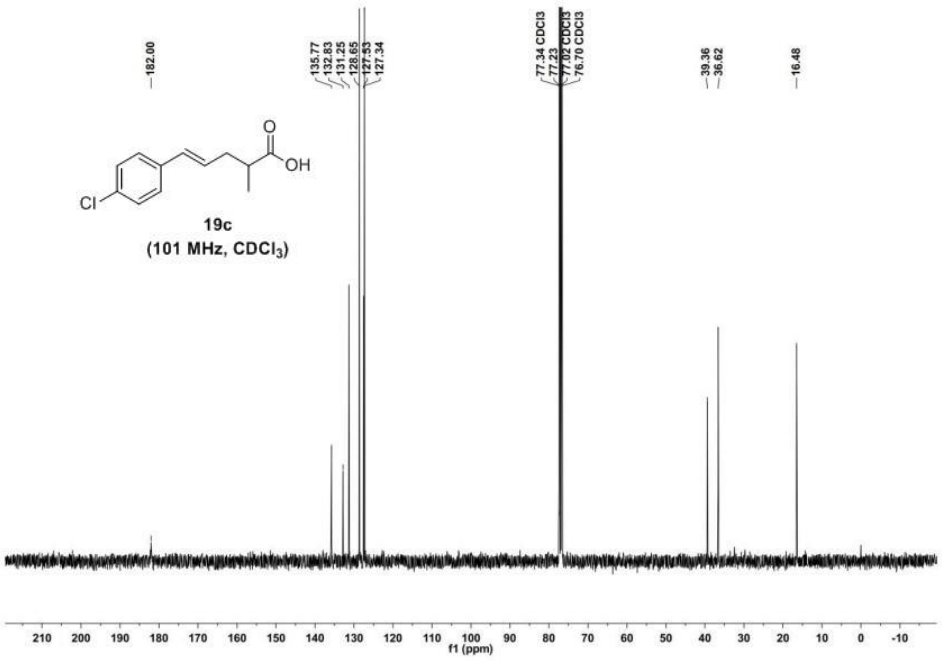
(*R*)-2b
(101 MHz, $CDCl_3$)

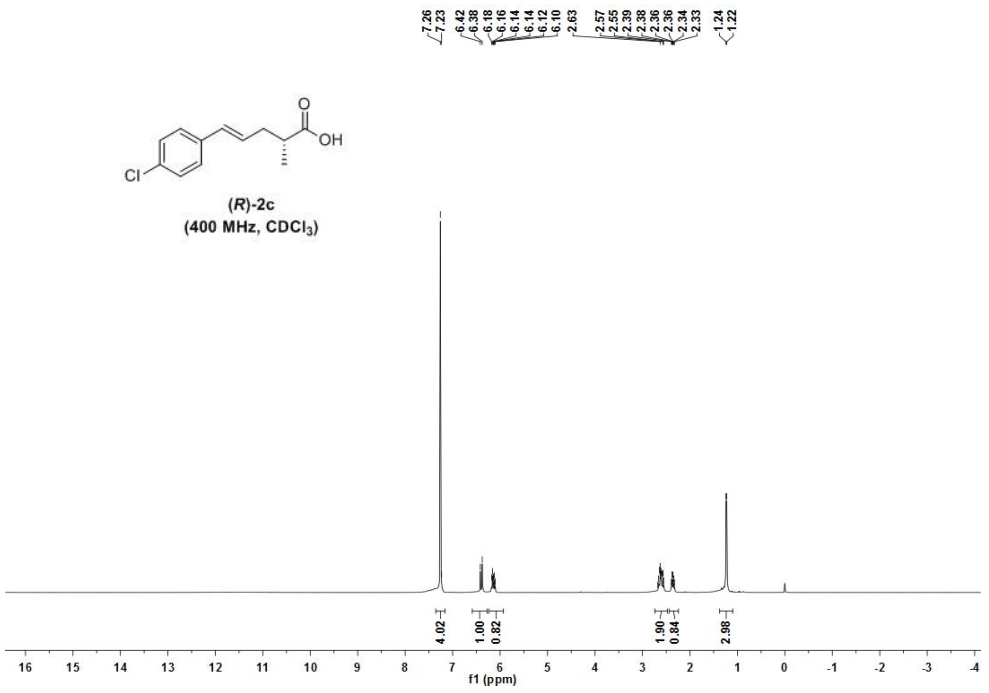


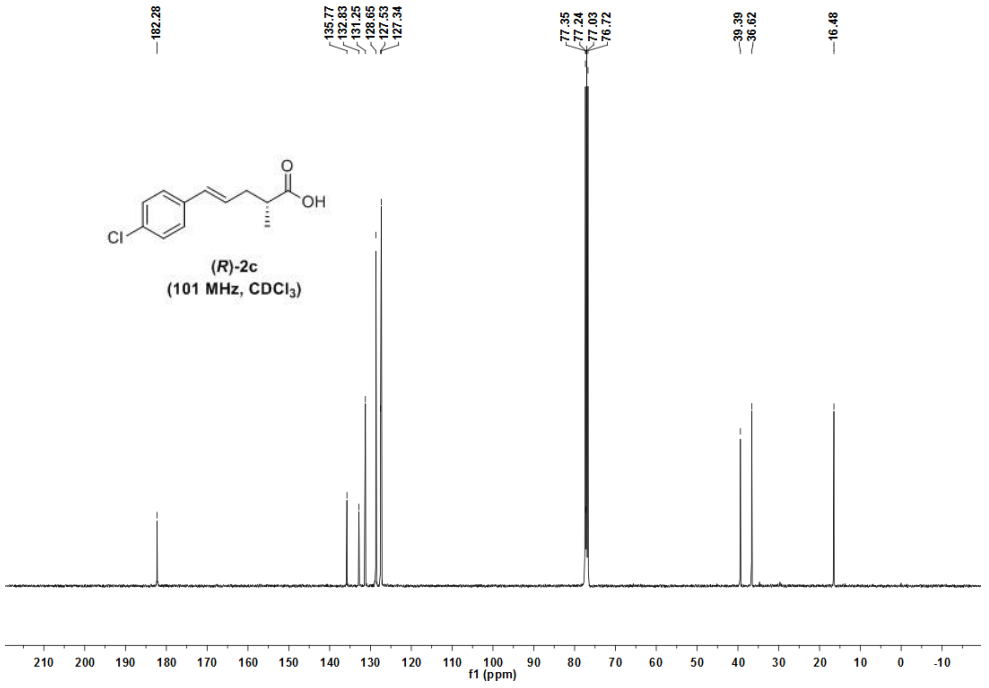

7.24
7.24
6.38
6.38
6.34
6.34
6.15
6.13
6.12
6.11
6.09
6.08
3.67
3.66
3.65
2.63
2.61
2.60
2.58
2.56
2.55
2.53
2.53
2.51
2.36
2.35
2.33
2.33
2.31
2.29
1.34
1.34
1.28
1.25
1.21
1.19
1.17
1.16
0.87
0.85
O
O
Cl
18c
(400 MHz, CDCl3)
1.00
0.98
2.99
2.02
1.05
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

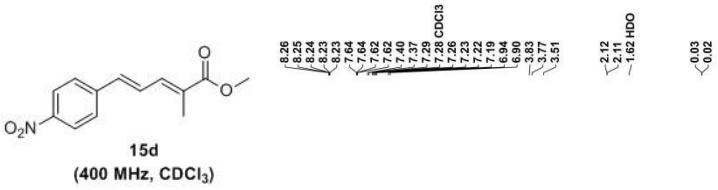

176.39
135.85
132.71
130.93
128.63
127.94
127.32
77.43 CDCl3
77.12 CDCl3
76.80 CDCl3
51.67
39.50
37.00
16.76
O
O
Cl
18c
(101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.27
7.26
7.26
7.24
6.42
6.41
6.38
6.38
6.18
6.16
6.14
6.14
6.12
6.10
2.66
2.64
2.63
2.61
2.60
2.59
2.57
2.55
2.39
2.38
2.36
2.34
2.33
1.24
1.24
1.23
1.22
O
OH
Cl
19c
(400 MHz, CDCl3)
4.48
1.00
0.95
2.07
1.00
3.46
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

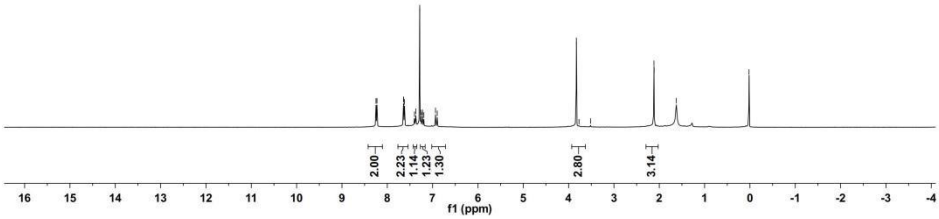

182.00
135.77
132.83
131.25
128.65
127.53
127.34
77.34 CDCl3
77.23
77.02 CDCl3
76.70 CDCl3
39.36
36.62
16.48
O
OH
Cl
19c
(101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

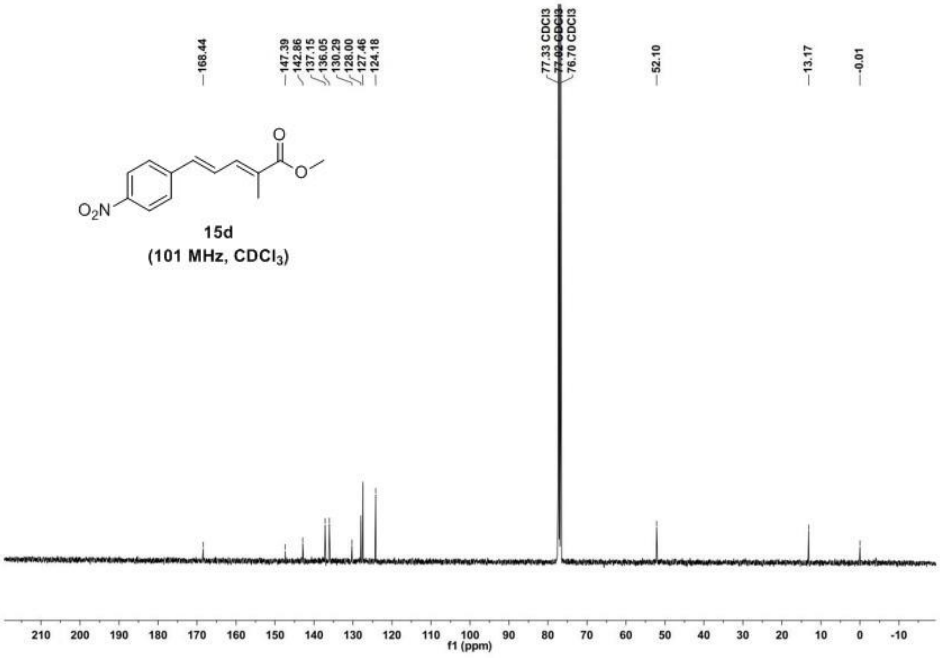

7.26
7.23
6.42
6.38
6.18
6.16
6.14
6.14
6.12
6.10
2.63
2.57
2.55
2.39
2.38
2.36
2.36
2.34
2.33
1.24
1.22
O
OH
Cl
(R)-2c
(400 MHz, CDCl3)
4.02
1.00
0.82
1.90
0.84
2.98
f1 (ppm)


182.28
135.77
132.83
131.25
128.65
127.53
127.34
77.35
77.24
77.03
76.72
39.39
36.62
16.48
O
OH
Cl
(R)-2c
(101 MHz, CDCl3)
f1 (ppm)

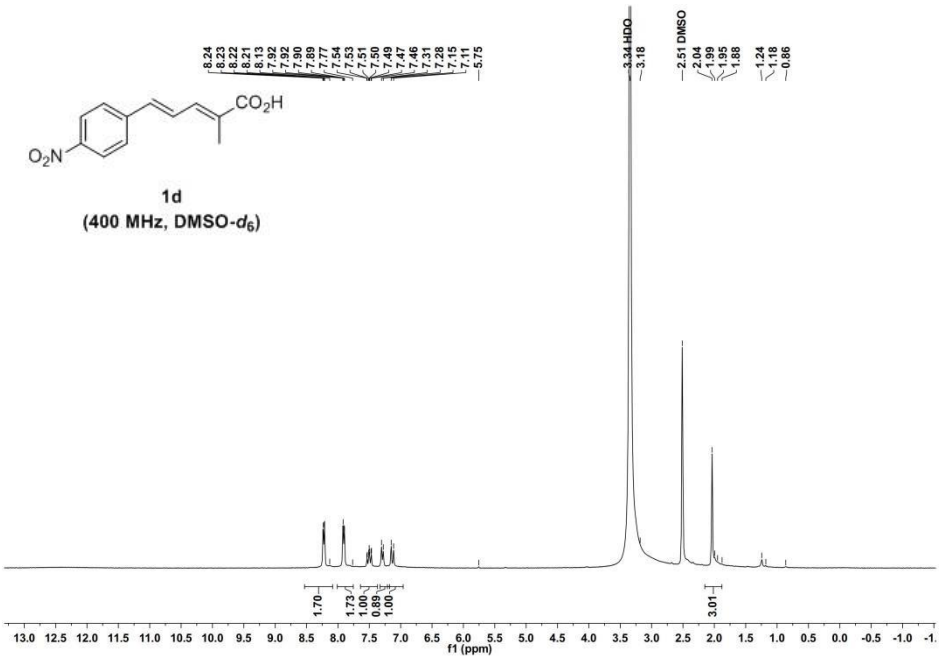


15d
(400 MHz, $CDCl_3$)

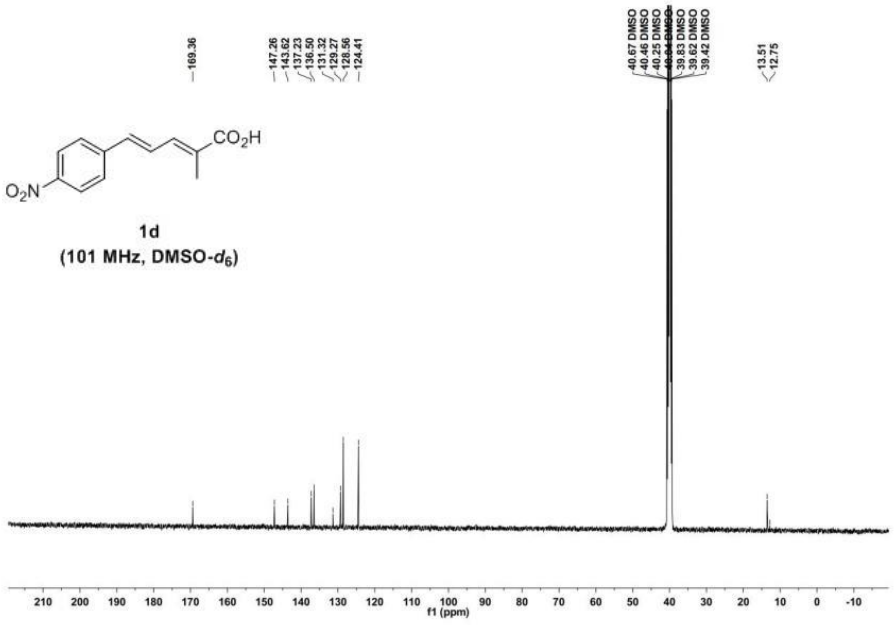




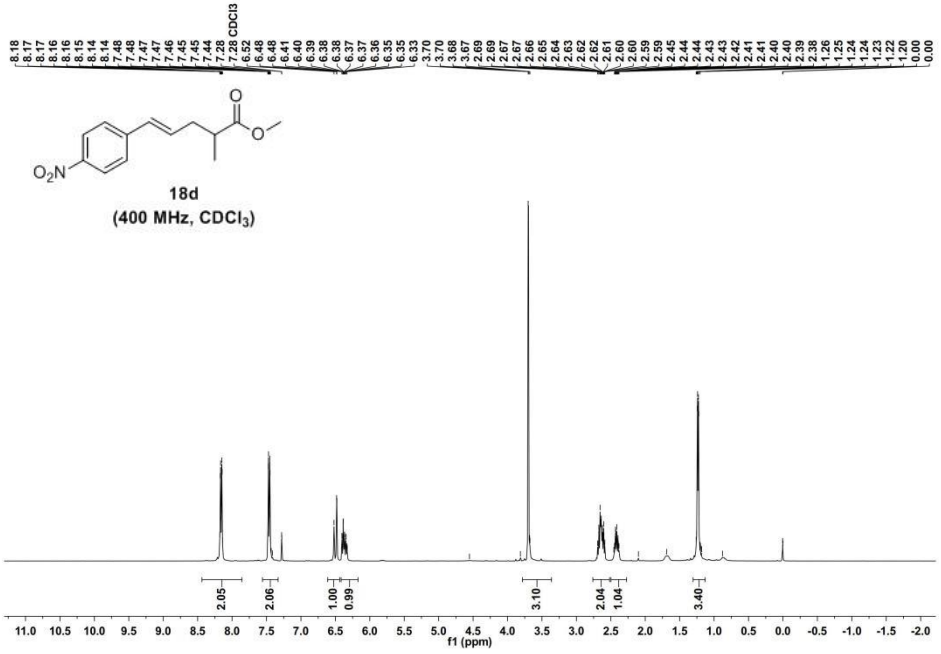
15d
(101 MHz, $CDCl_3$)

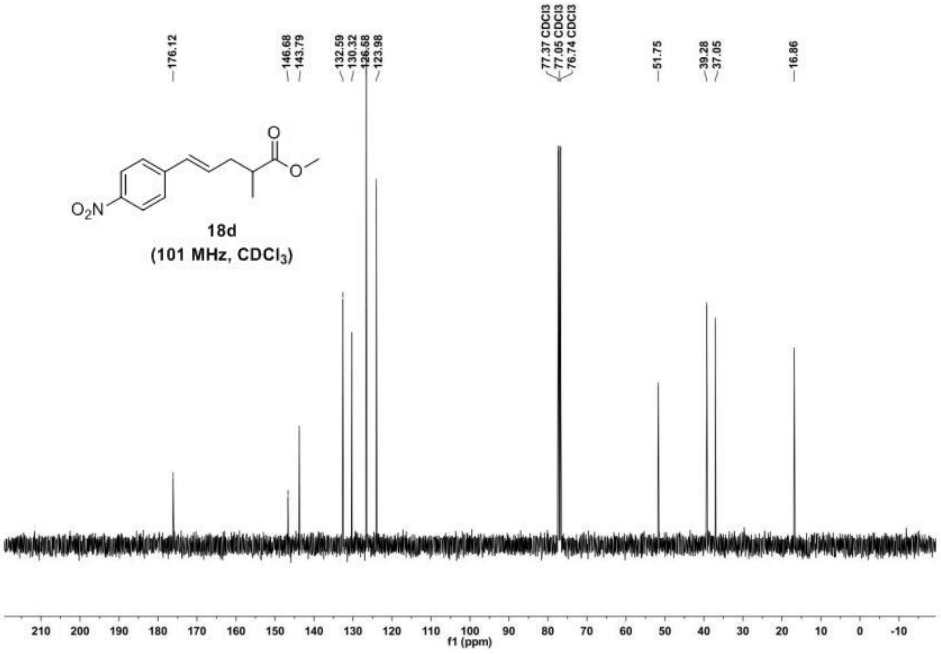


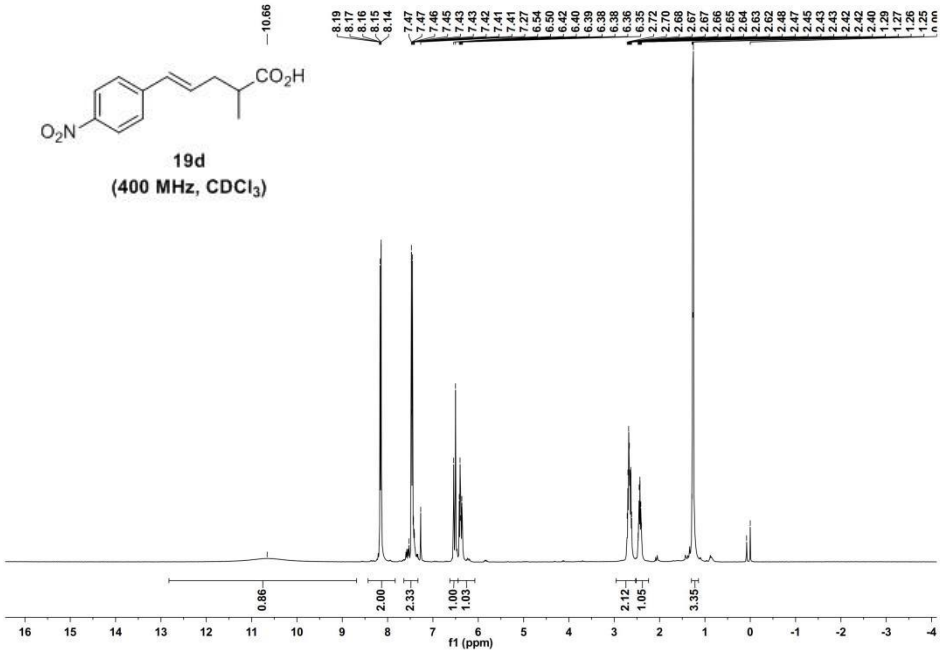
1d
(400 MHz, DMSO-d_6)

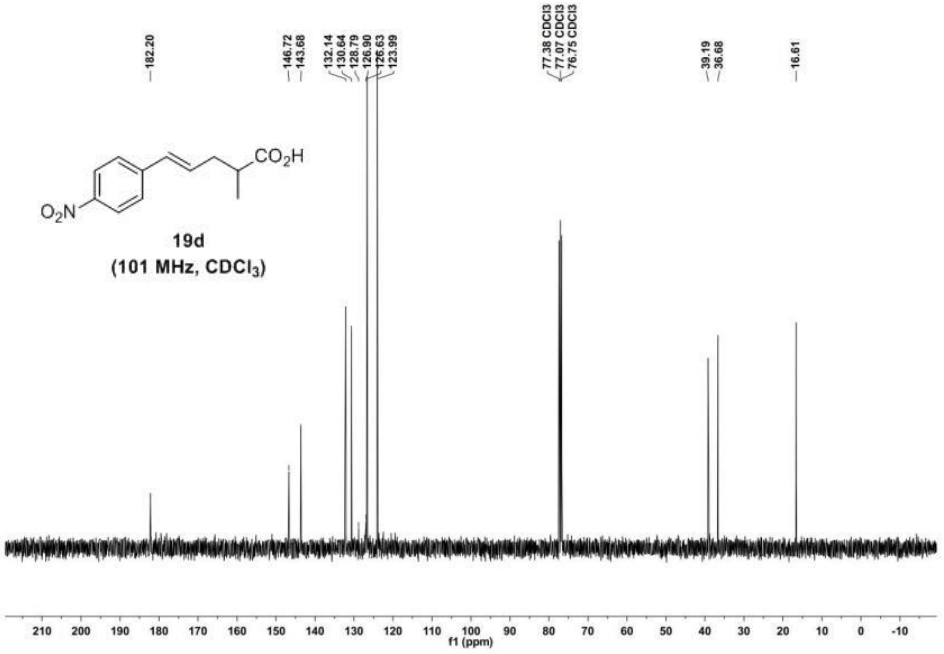


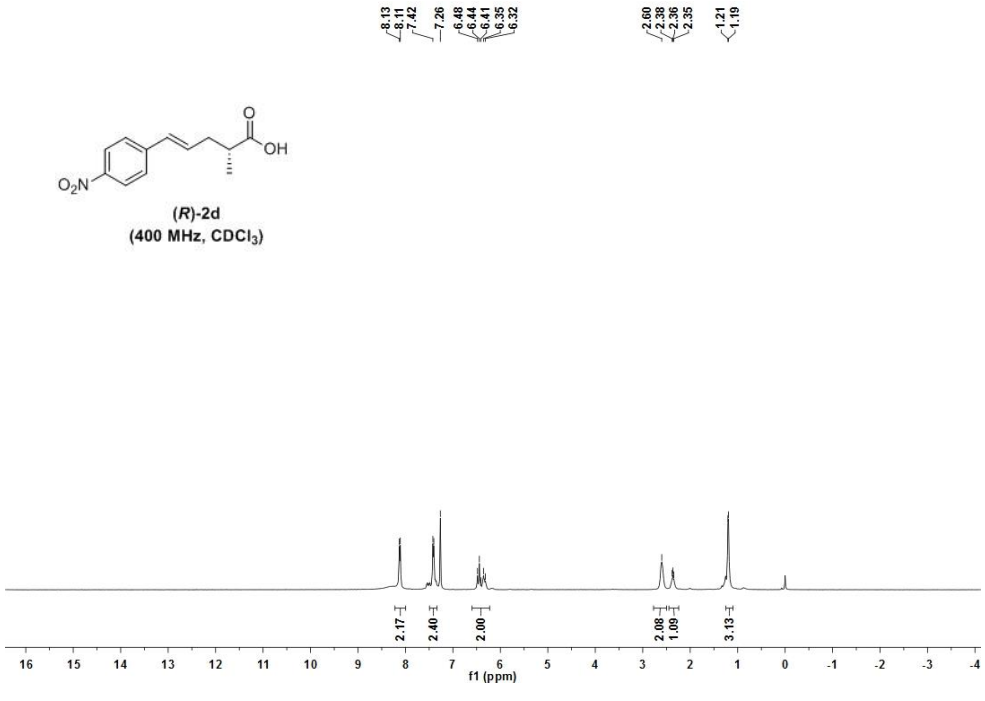
1d
(101 MHz, DMSO-d_6)

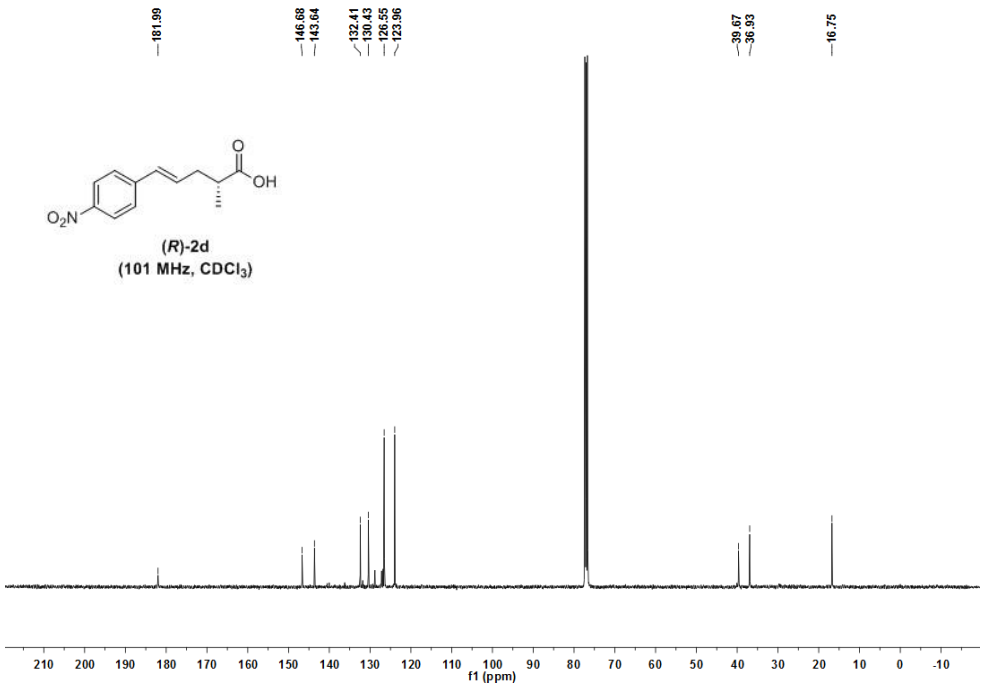

18d
(400 MHz, CDCl3)
f1 (ppm)

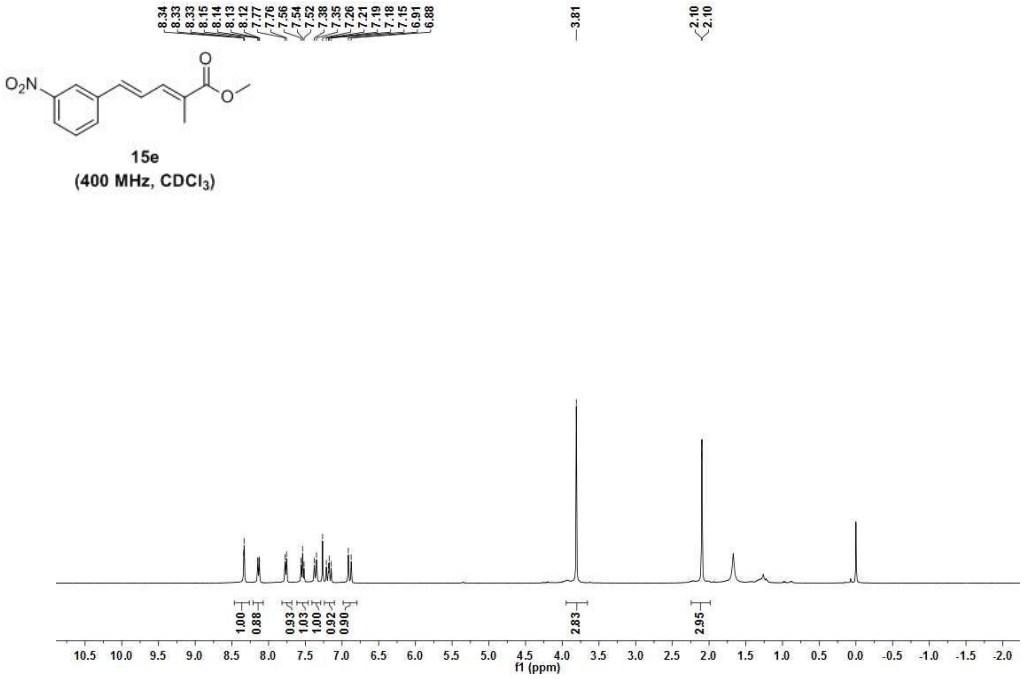

18d
(101 MHz, CDCl3)
f1 (ppm)

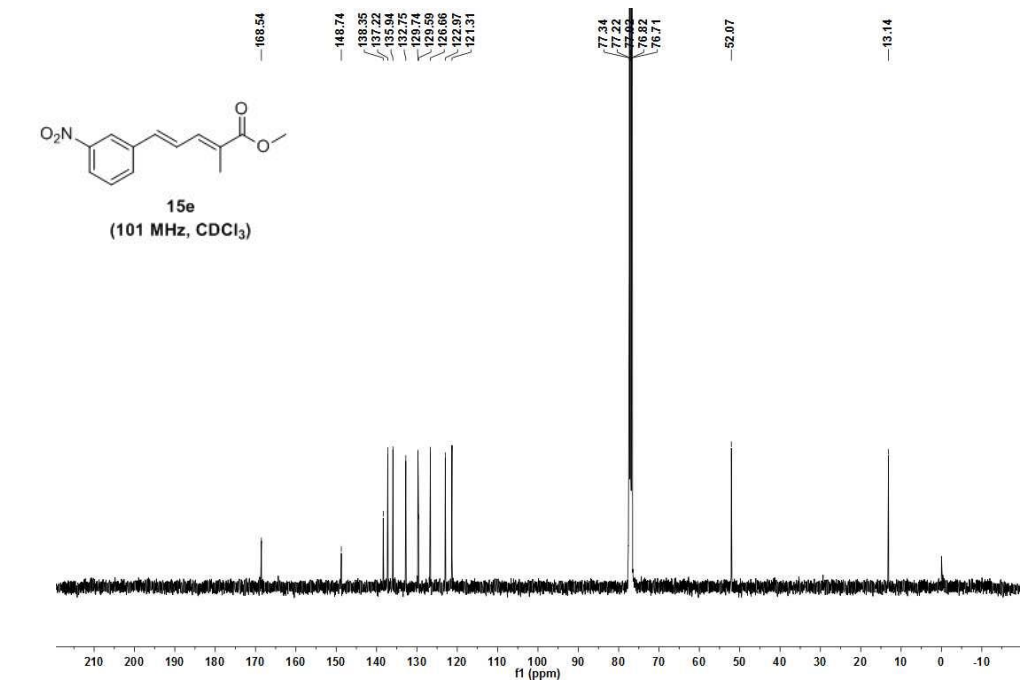

10.66
8.19
8.17
8.16
8.15
8.14
7.47
7.47
7.46
7.45
7.43
7.43
7.42
7.41
7.41
7.27
6.54
6.50
6.42
6.40
6.39
6.38
6.38
6.36
6.35
2.72
2.70
2.68
2.67
2.67
2.66
2.65
2.64
2.63
2.62
2.48
2.47
2.45
2.43
2.43
2.42
2.42
2.40
1.29
1.27
1.26
1.25
CO2H
O2N
19d
(400 MHz, CDCl3)
0.86
2.00
2.33
1.00
1.03
2.12
1.05
3.35
f1 (ppm)

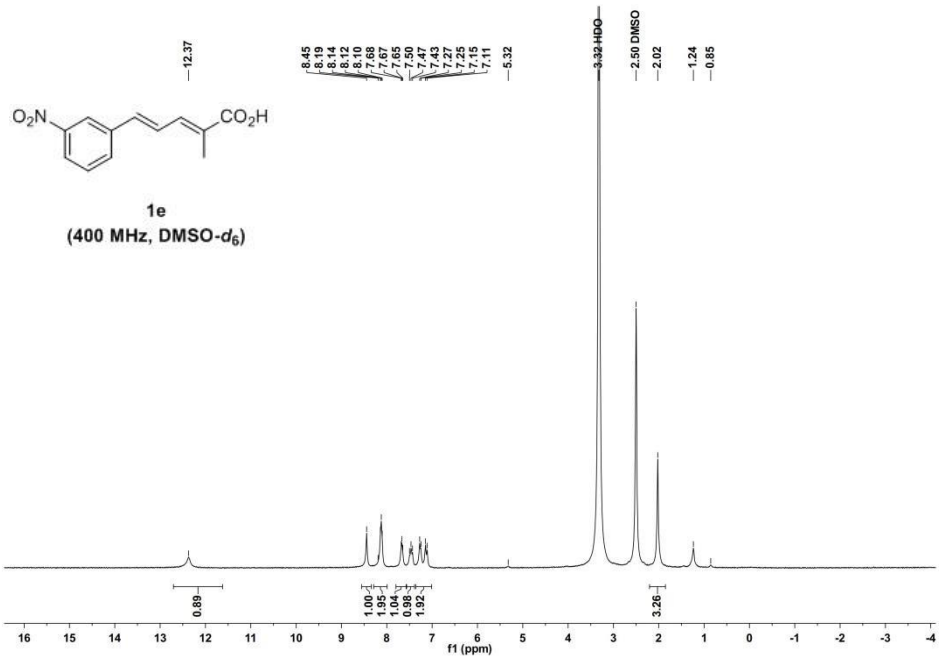

182.20
146.72
143.68
132.14
130.64
128.79
126.90
126.63
123.99
77.38 CDCl3
77.07 CDCl3
76.75 CDCl3
39.19
36.68
16.61
CO2H
O2N
19d
(101 MHz, CDCl3)
f1 (ppm)


8.13
8.11
7.42
7.26
6.48
6.44
6.41
6.35
6.32
2.60
2.38
2.36
2.35
1.21
1.19
O
OH
O2N
(R)-2d
(400 MHz, CDCl3)
2.17
2.40
2.00
2.08
1.09
3.13
f1 (ppm)

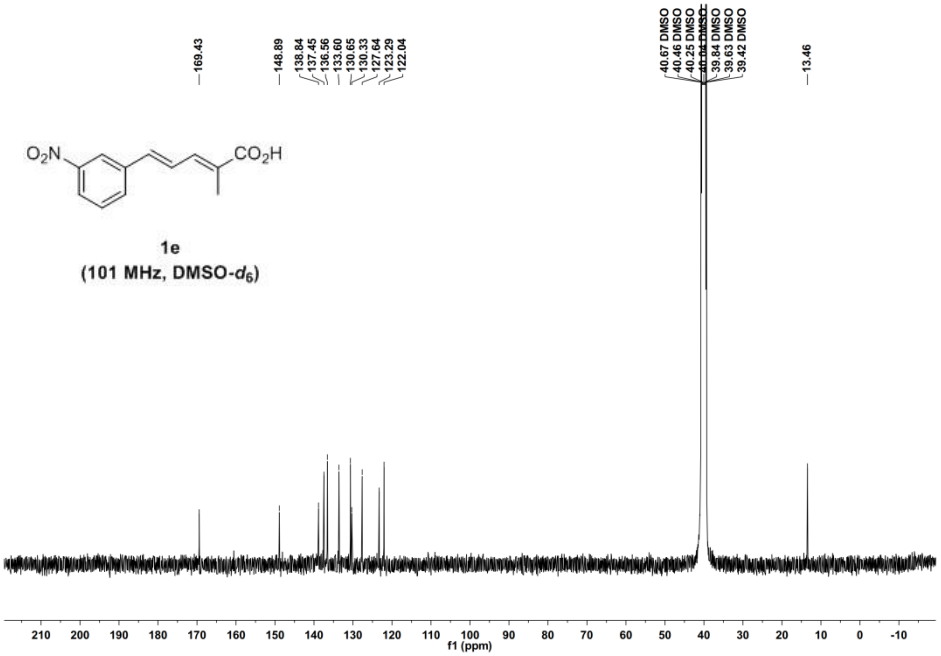

181.99
146.68
143.64
132.41
130.43
126.55
123.96
39.67
36.93
16.75
O
OH
O2N
(R)-2d
(101 MHz, CDCl3)
f1 (ppm)


8.34
8.33
8.33
8.15
8.14
8.13
8.12
7.77
7.76
7.56
7.54
7.52
7.38
7.35
7.26
7.21
7.19
7.18
7.15
6.91
6.88
3.81
2.10
2.10
O2N
O
O
15e
(400 MHz, CDCl3)
1.00
0.88
0.93
1.03
1.00
0.92
0.90
2.83
2.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

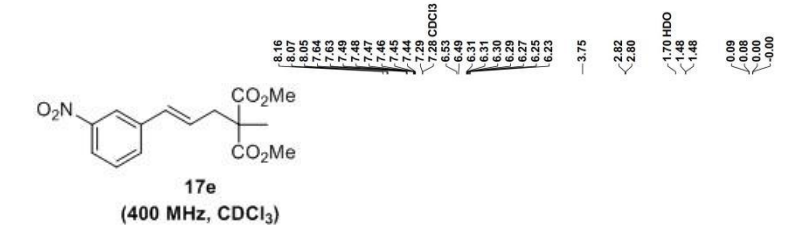

168.54
148.74
138.35
137.22
135.94
133.75
129.74
129.59
126.66
122.97
121.31
77.34
77.22
76.82
76.71
52.07
13.14
O2N
O
O
15e
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



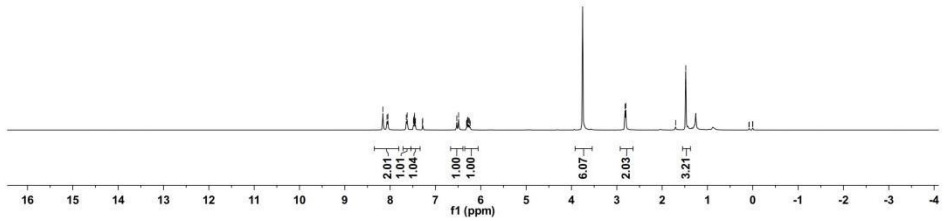
1e
(400 MHz, DMSO-d_6)

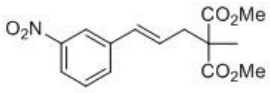


1e
(101 MHz, DMSO-d_6)

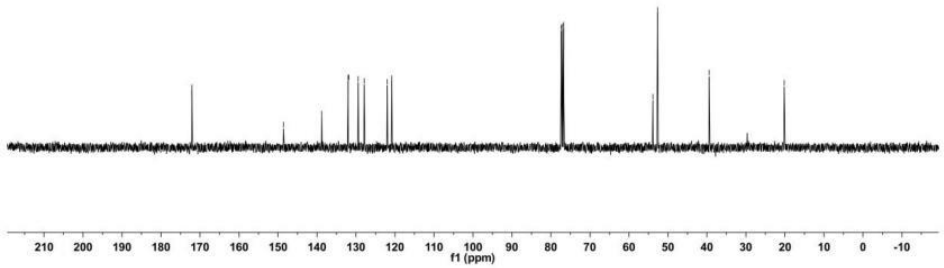


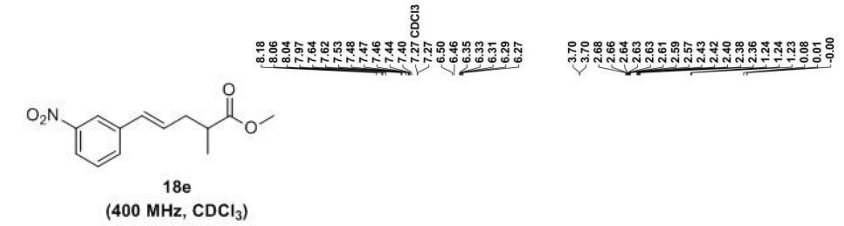
17e
(400 MHz, $CDCl_3$)



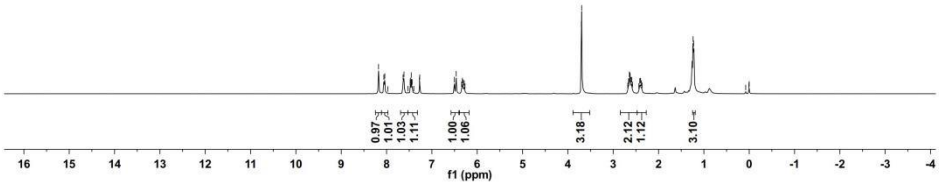


17e
(101 MHz, $CDCl_3$)

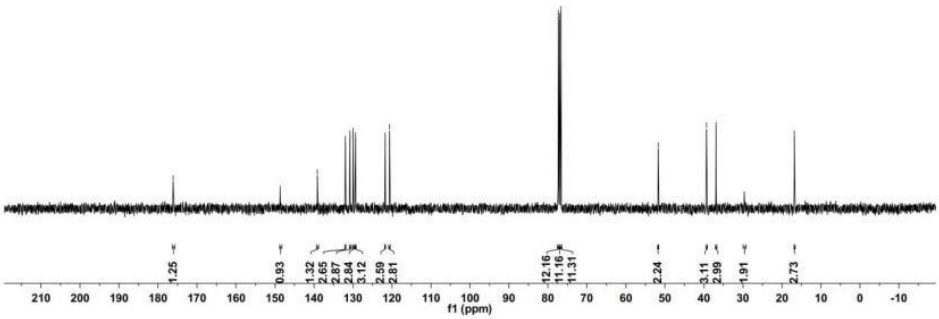


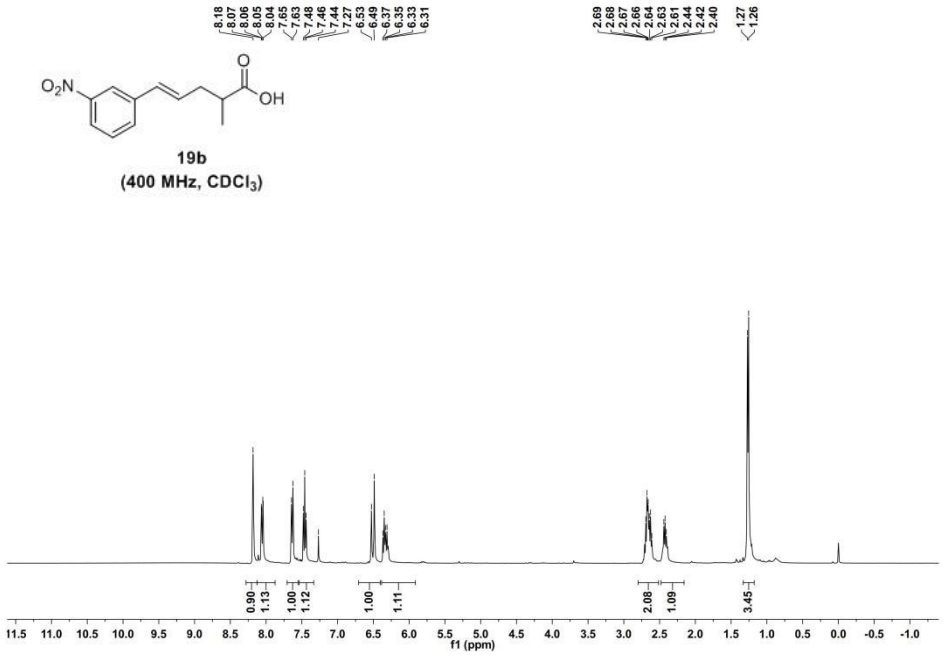


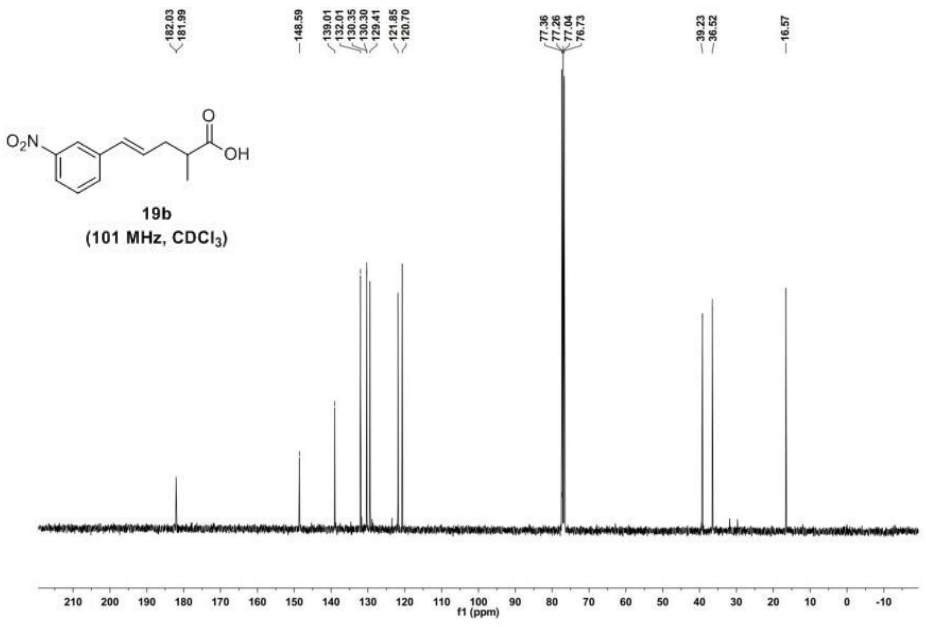
18e
(400 MHz, $CDCl_3$)

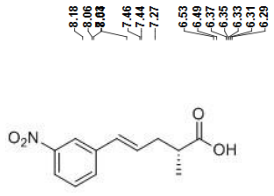


18e
(101 MHz, $CDCl_3$)

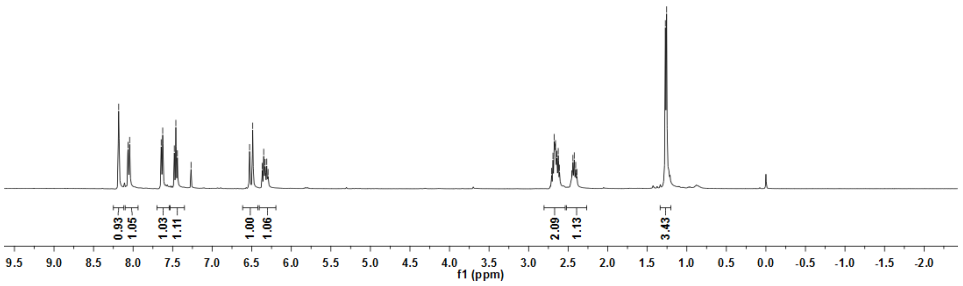


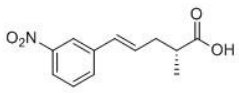

8.18
8.07
8.06
8.05
8.04
7.65
7.63
7.48
7.46
7.44
7.27
6.53
6.49
6.37
6.35
6.33
6.31
2.69
2.68
2.67
2.66
2.64
2.63
2.61
2.44
2.42
2.40
1.27
1.26
O2N
O
OH
19b
(400 MHz, CDCl3)
0.90
1.13
1.00
1.12
1.00
1.11
2.08
1.09
3.45
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


182.03
181.99
148.59
139.01
132.01
130.35
130.30
129.41
121.85
120.70
77.36
77.26
77.04
76.73
39.23
36.52
16.57
O2N
O
OH
19b
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

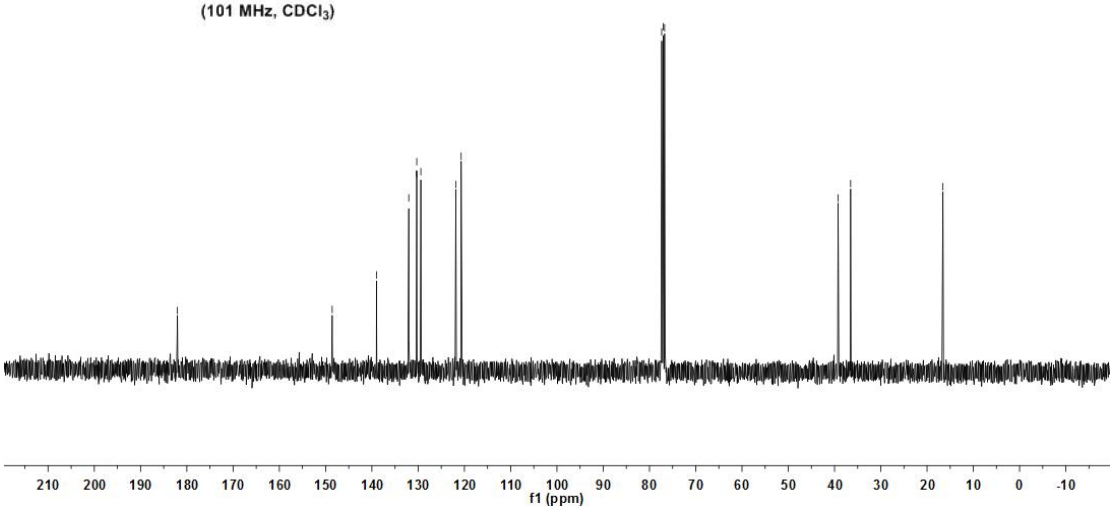


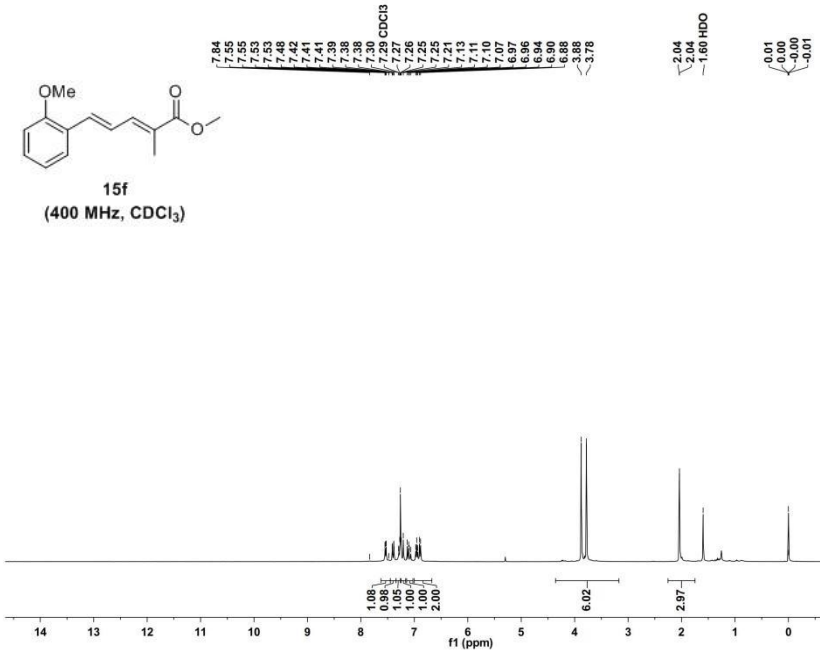
(*R*)-2e
(400 MHz, $CDCl_3$)

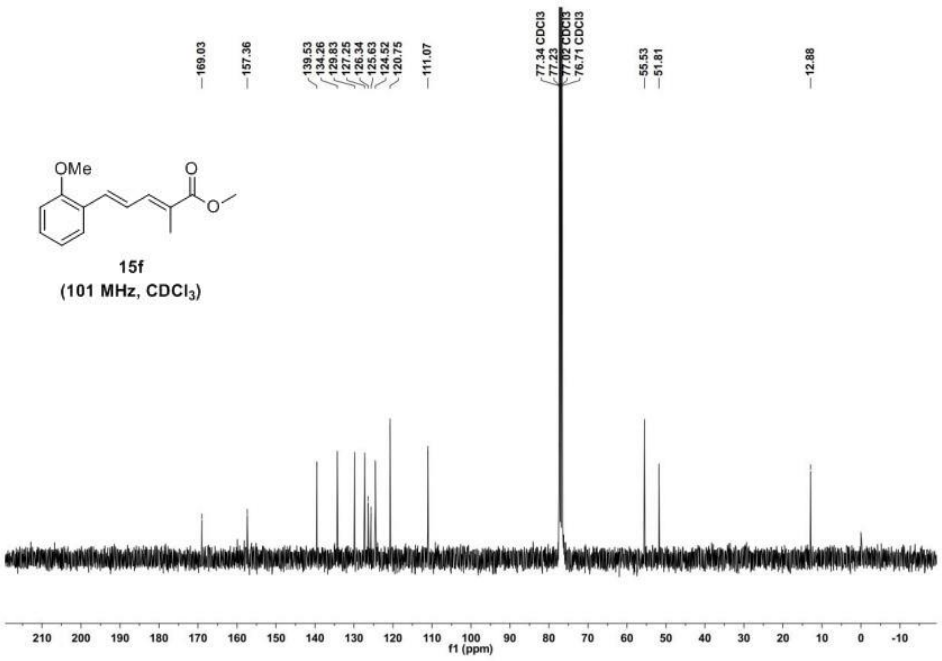


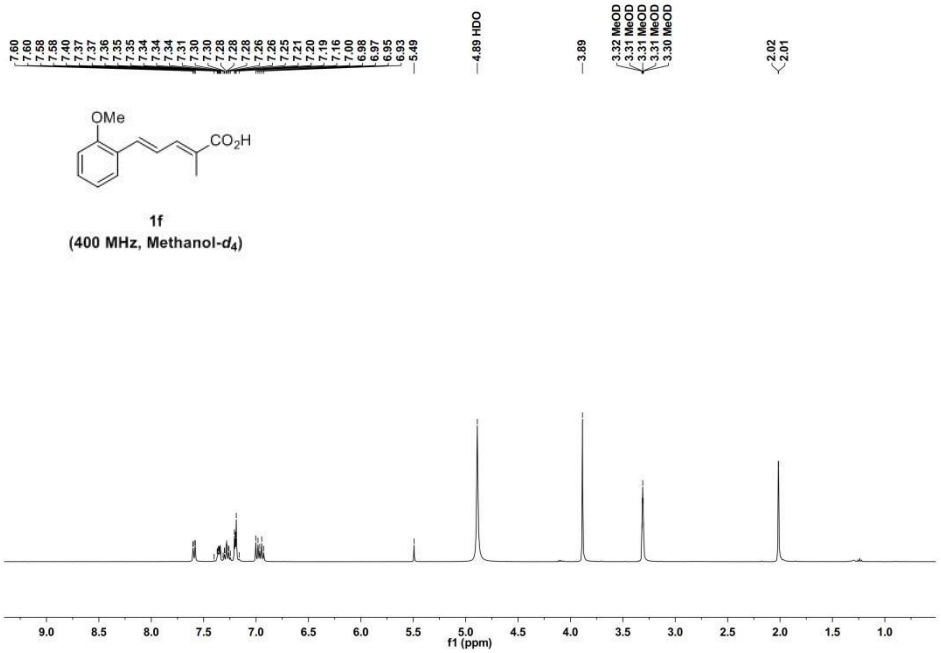


(*R*)-2e
(101 MHz, $CDCl_3$)

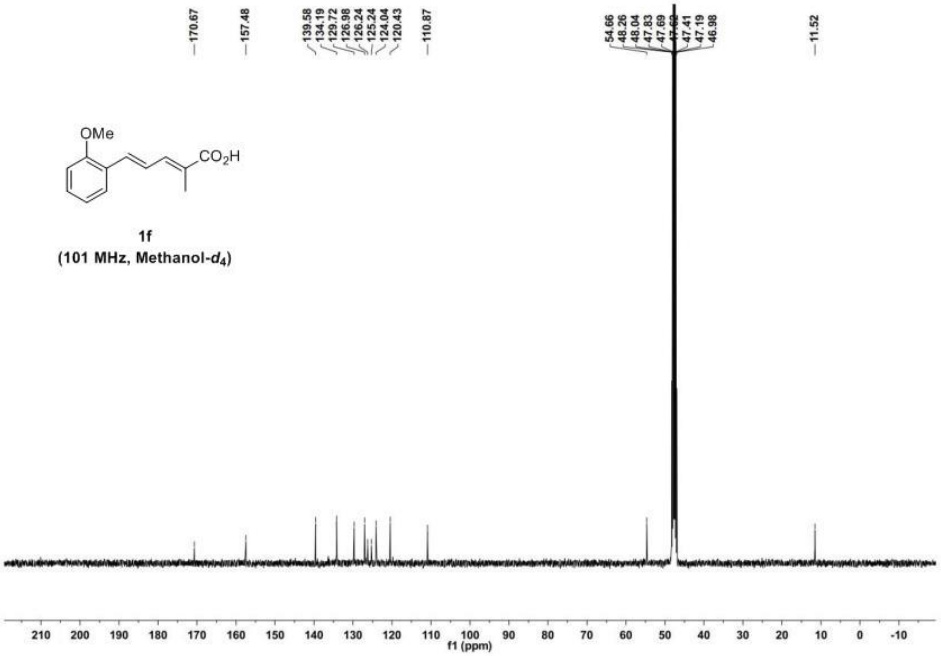



7.84
7.55
7.55
7.53
7.53
7.48
7.42
7.41
7.41
7.39
7.38
7.38
7.30
7.29 CDCl3
7.27
7.26
7.25
7.25
7.21
7.13
7.11
7.10
7.07
6.97
6.96
6.94
6.90
6.88
3.88
3.78
2.04
2.04
1.60 HDO
0.01
0.00
-0.00
-0.01
OMe
O
O
15f
(400 MHz, CDCl3)
1.08
0.98
1.05
1.00
1.00
2.00
6.02
2.97
f1 (ppm)

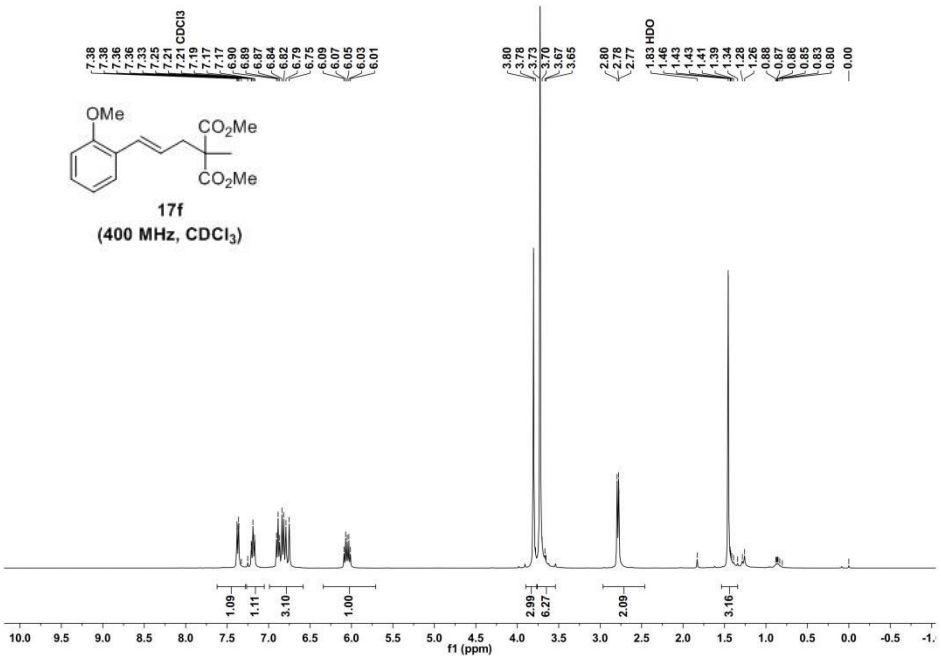

169.03
157.36
139.53
134.26
129.83
127.25
126.34
125.63
124.52
120.75
111.07
77.34 CDCl3
77.23
77.02 CDCl3
76.71 CDCl3
55.53
51.81
12.88
OMe
O
O
15f
(101 MHz, CDCl3)
f1 (ppm)

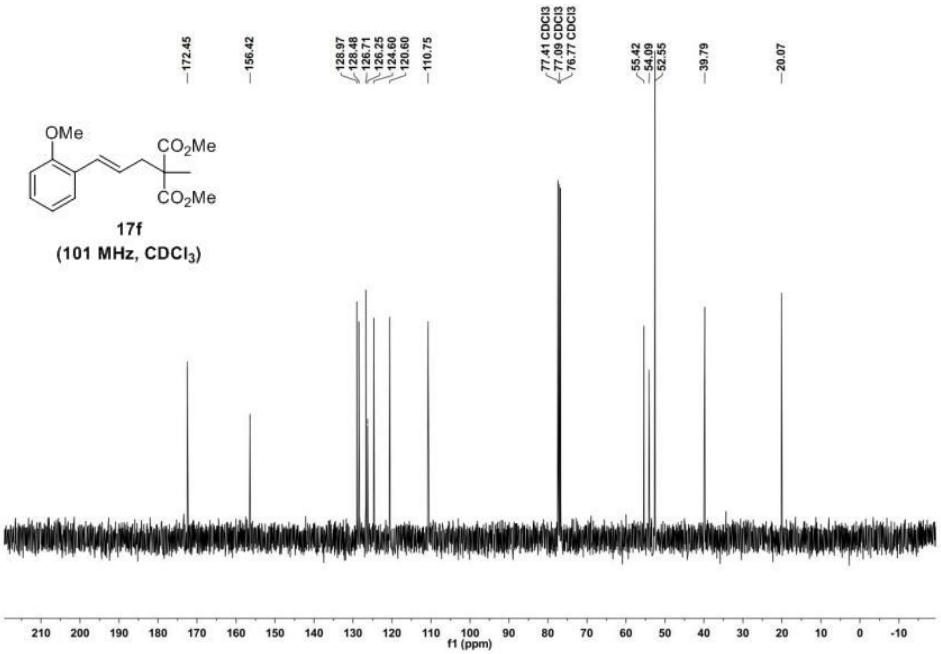


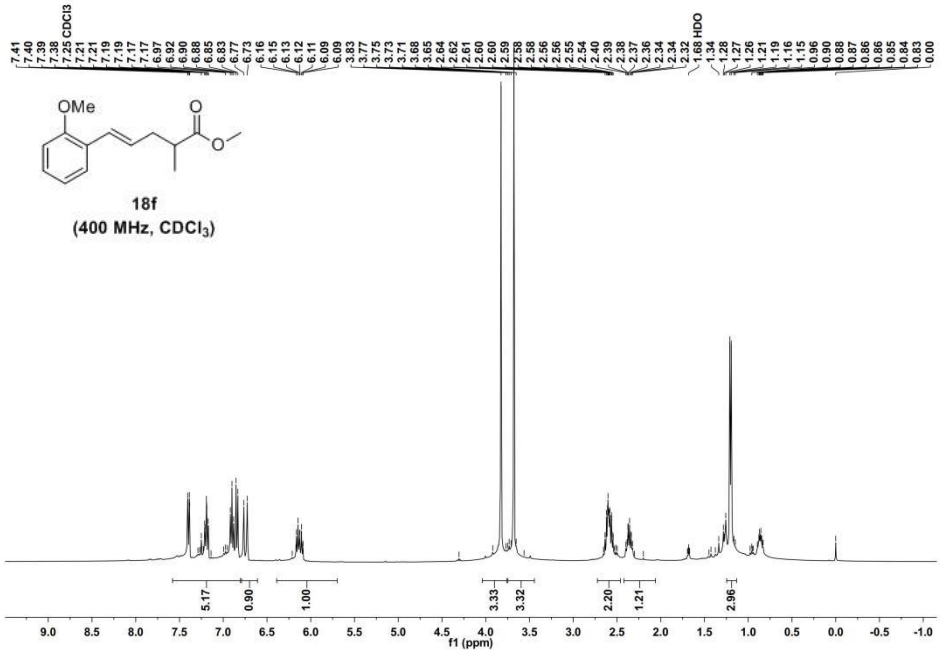
1f
(400 MHz, Methanol-d_4)

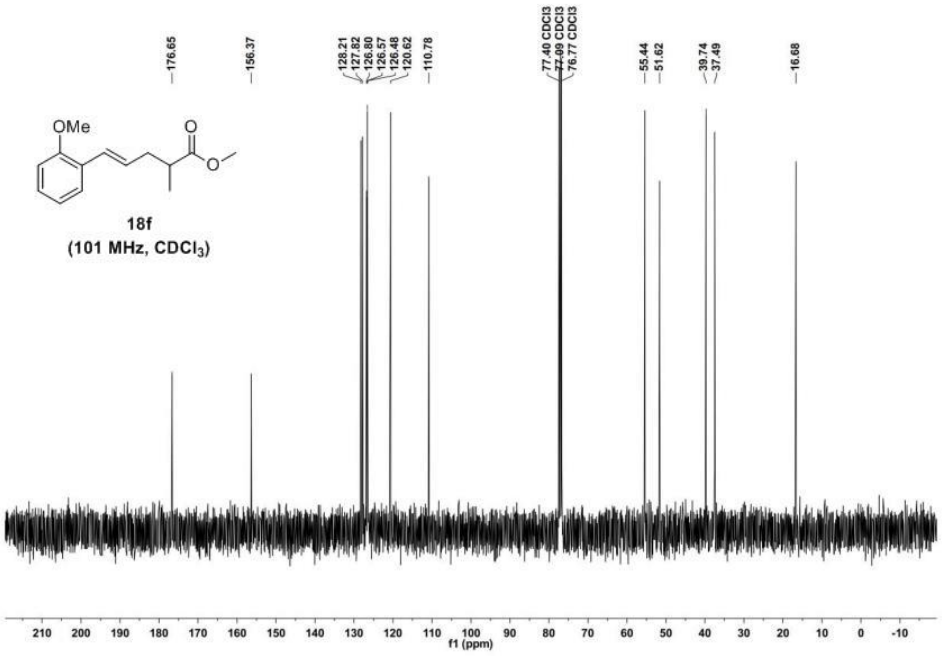


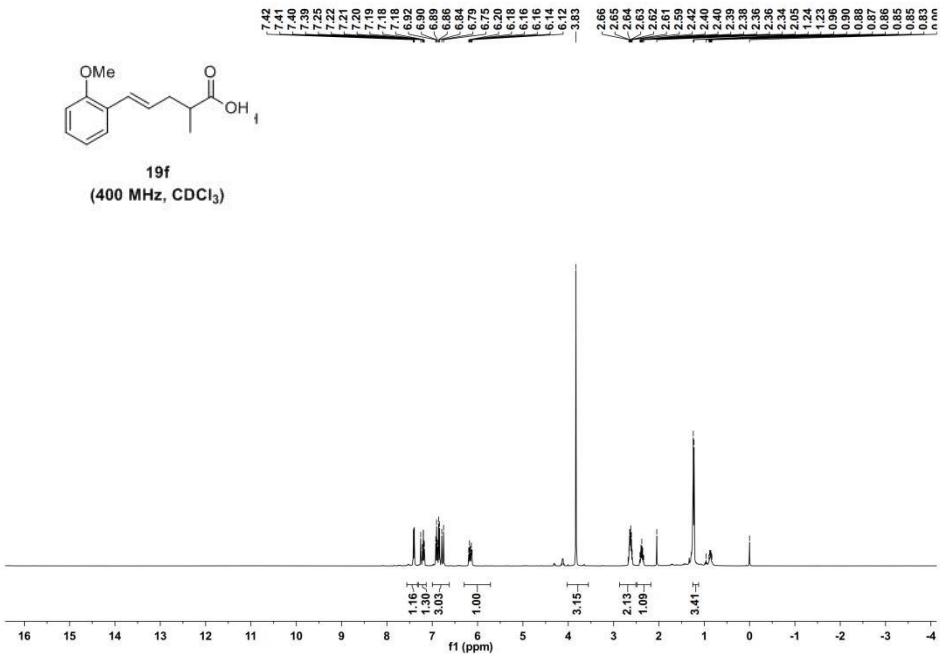
1f
(101 MHz, Methanol-d_4)

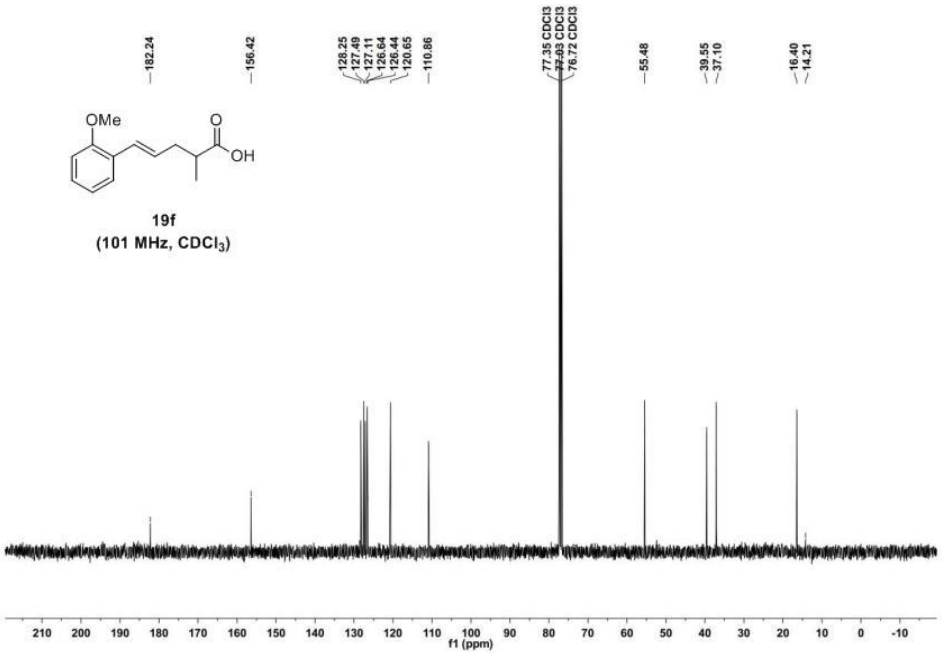

OMe
CO2Me
CO2Me
17f
(400 MHz, CDCl3)
f1 (ppm)

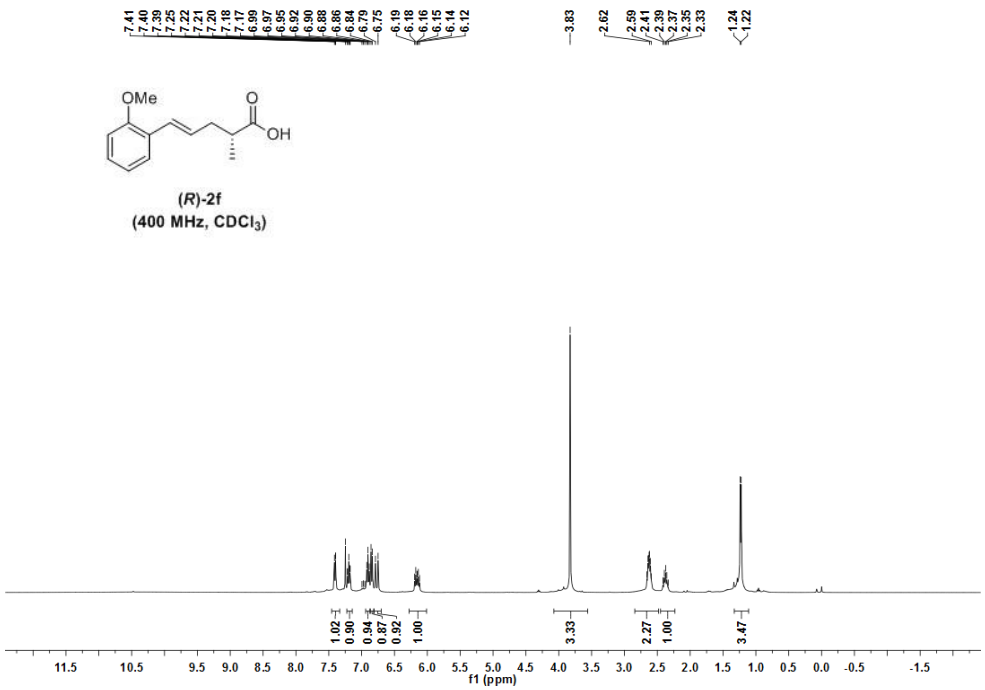

OMe
CO2Me
CO2Me
17f
(101 MHz, CDCl3)
f1 (ppm)

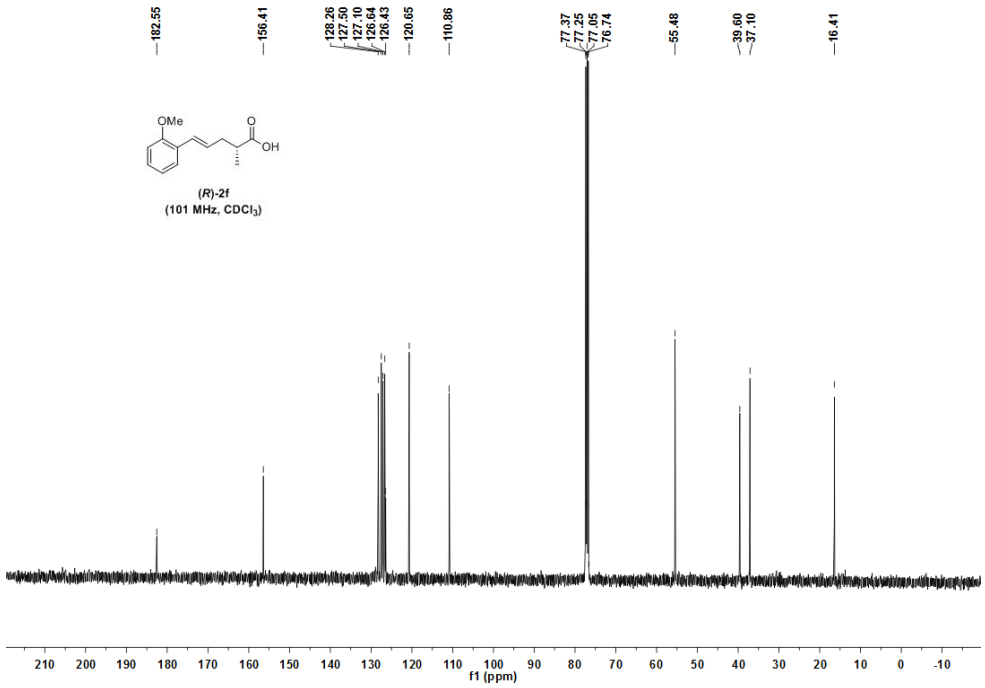

OMe
O
O
18f
(400 MHz, CDCl3)
f1 (ppm)

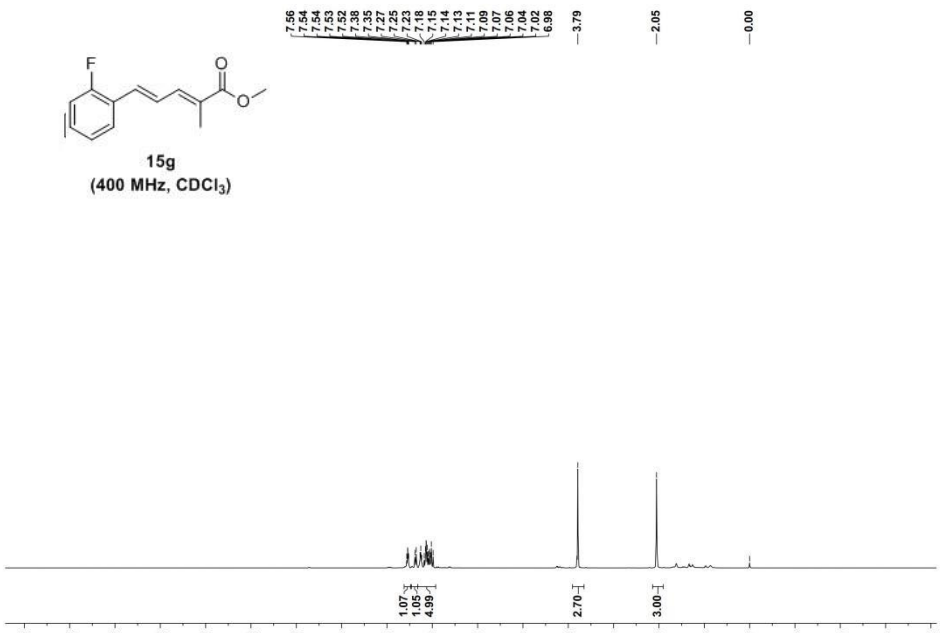

OMe
O
O
18f
(101 MHz, CDCl3)
f1 (ppm)

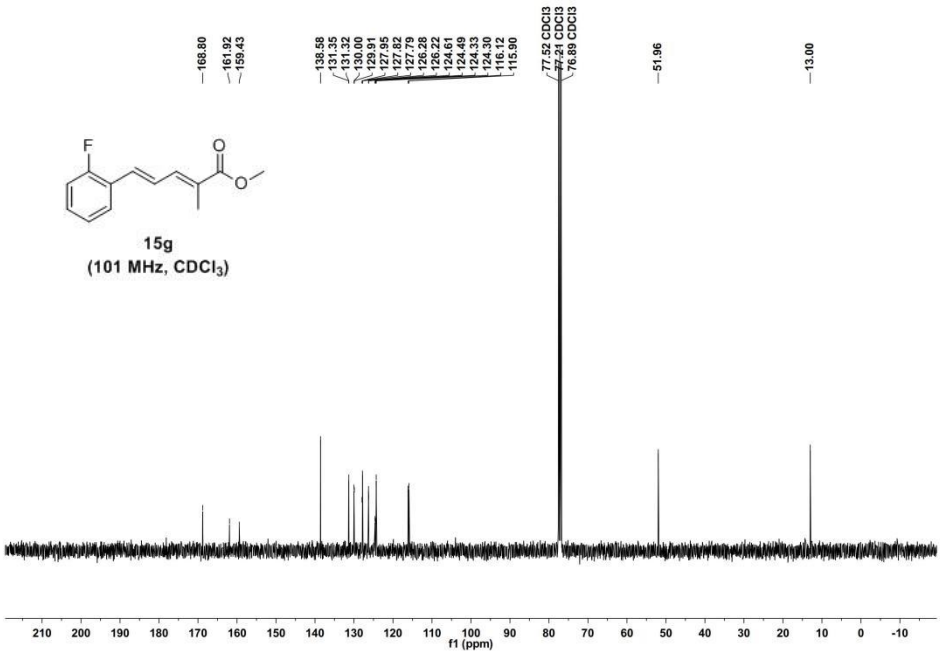

OMe
O
OH
19f
(400 MHz, CDCl3)
f1 (ppm)

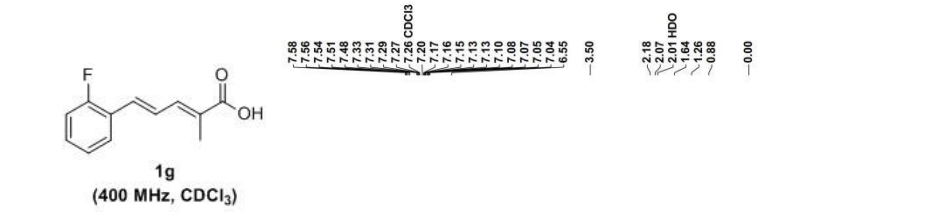

OMe
O
OH
19f
(101 MHz, CDCl3)
f1 (ppm)


7.41
7.40
7.39
7.25
7.22
7.21
7.20
7.18
7.17
6.99
6.97
6.95
6.92
6.90
6.88
6.86
6.84
6.79
6.75
6.19
6.18
6.16
6.15
6.14
6.12
3.83
2.62
2.59
2.41
2.39
2.37
2.35
2.33
1.24
1.22
OMe
O
OH
(R)-2f
(400 MHz, CDCl3)
1.02
0.90
0.94
0.87
0.92
1.00
3.33
2.27
1.00
3.47
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
f1 (ppm)

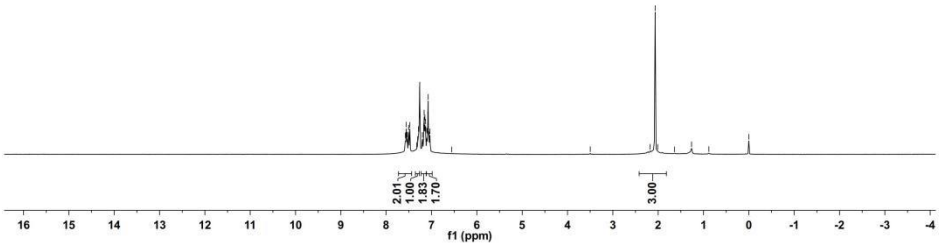

182.55
156.41
128.26
127.50
127.10
126.64
126.43
120.65
110.86
77.37
77.25
77.05
76.74
55.48
39.60
37.10
16.41
OMe
O
OH
(R)-2f
(101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

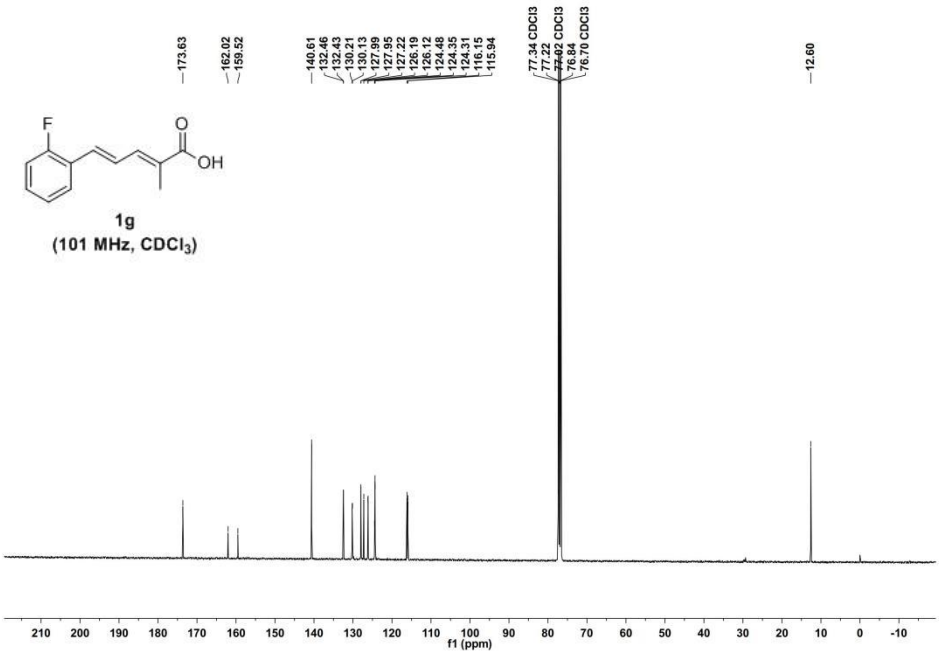

7.56
7.54
7.54
7.53
7.52
7.38
7.35
7.27
7.25
7.23
7.18
7.15
7.14
7.13
7.11
7.09
7.07
7.06
7.04
7.02
6.98
3.79
2.05
0.00
F
O
O
15g
(400 MHz, CDCl3)
1.07
1.05
4.99
2.70
3.00
f1 (ppm)


168.80
161.92
159.43
138.58
131.35
131.32
130.00
129.91
127.95
127.82
127.79
126.28
126.22
124.61
124.49
124.33
124.30
116.12
115.90
77.52 CDCl3
77.24 CDCl3
76.89 CDCl3
51.96
13.00
F
O
O
15g
(101 MHz, CDCl3)
f1 (ppm)

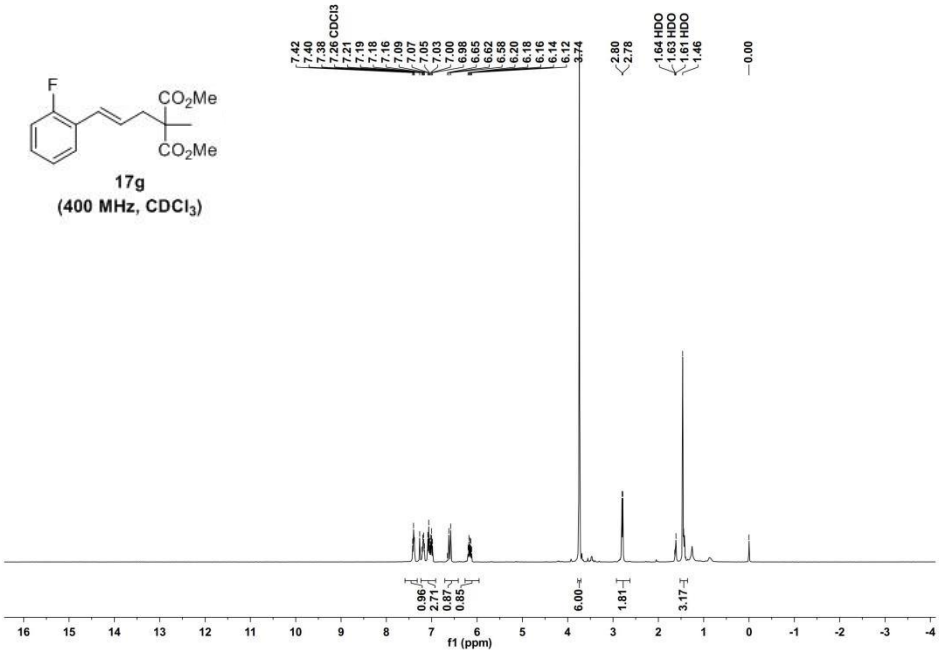


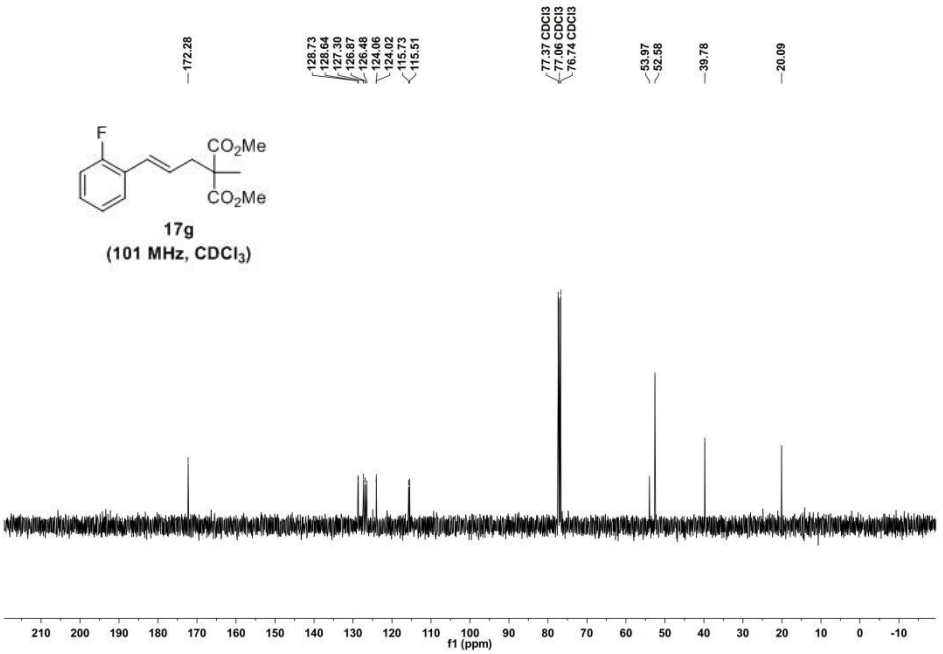
1g
(400 MHz, $CDCl_3$)

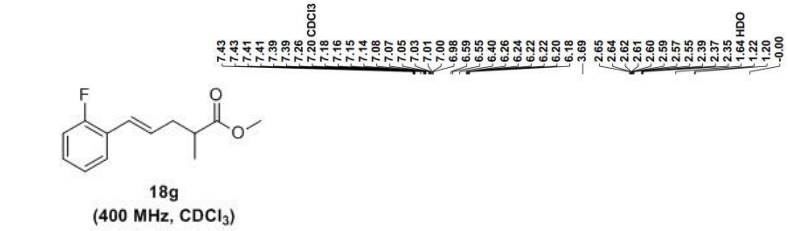




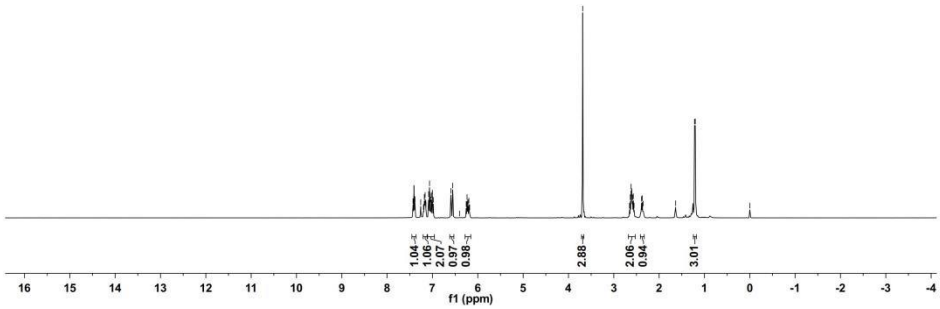
1g
(101 MHz, $CDCl_3$)

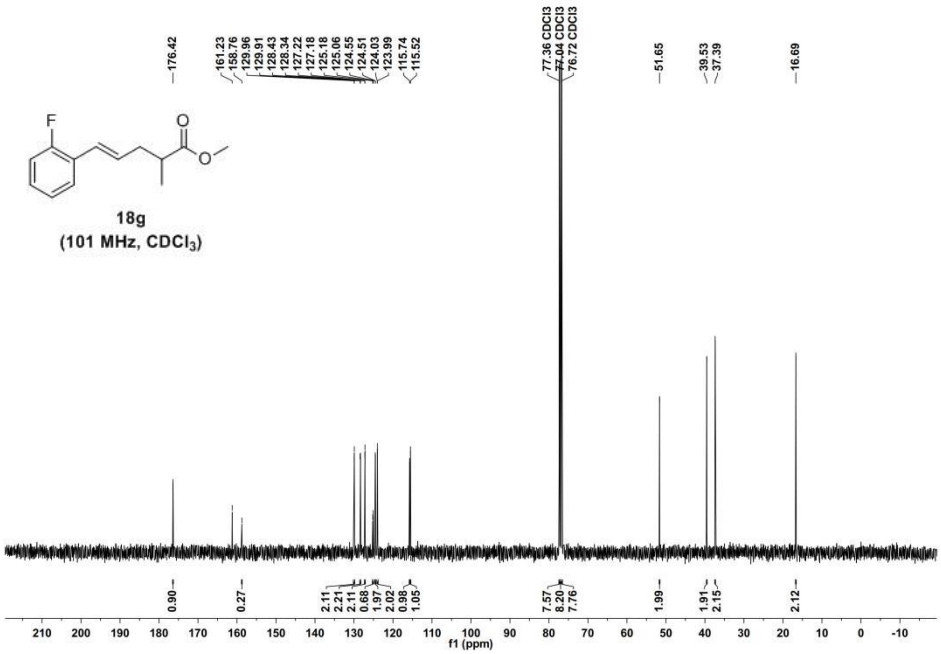

F
CO2Me
CO2Me
17g
(400 MHz, CDCl3)
7.42
7.40
7.38
7.26 CDCl3
7.21
7.19
7.18
7.16
7.09
7.07
7.05
7.03
7.00
6.98
6.65
6.62
6.58
6.20
6.18
6.16
6.14
6.12
3.74
2.80
2.78
1.64 HDO
1.63 HDO
1.61 HDO
1.46
0.00
0.96
2.71
0.87
0.85
6.00
1.81
3.17
f1 (ppm)


172.28
128.73
128.64
127.30
126.87
126.48
124.66
124.02
115.73
115.51
77.37 CDCl3
77.06 CDCl3
76.74 CDCl3
53.97
52.58
39.78
20.09
F
CO2Me
CO2Me
17g
(101 MHz, CDCl3)
f1 (ppm)

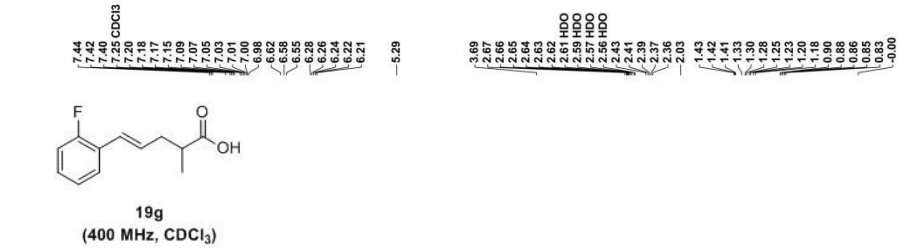


18g
(400 MHz, $CDCl_3$)

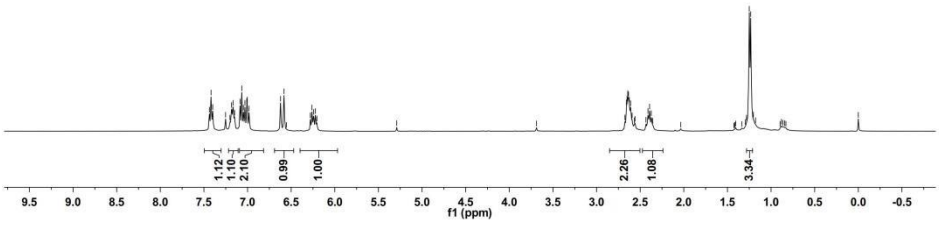


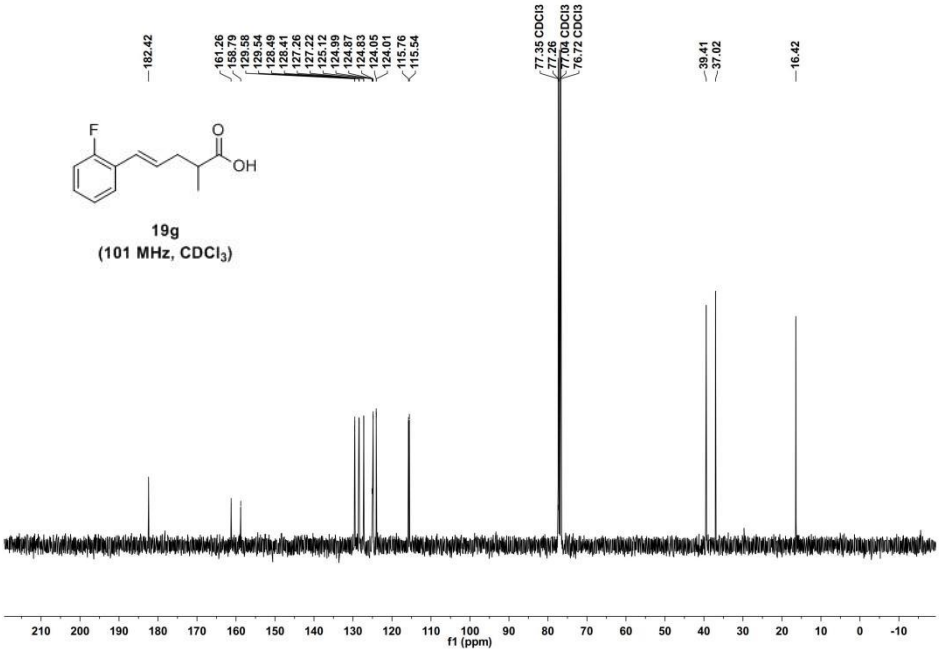


18g
(101 MHz, $CDCl_3$)

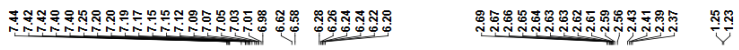


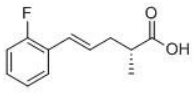
19g
(400 MHz, $CDCl_3$)



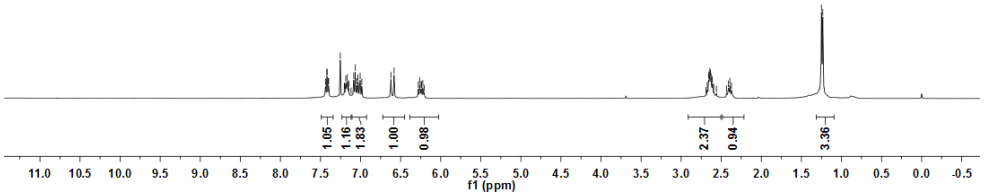


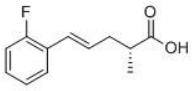
19g
(101 MHz, $CDCl_3$)



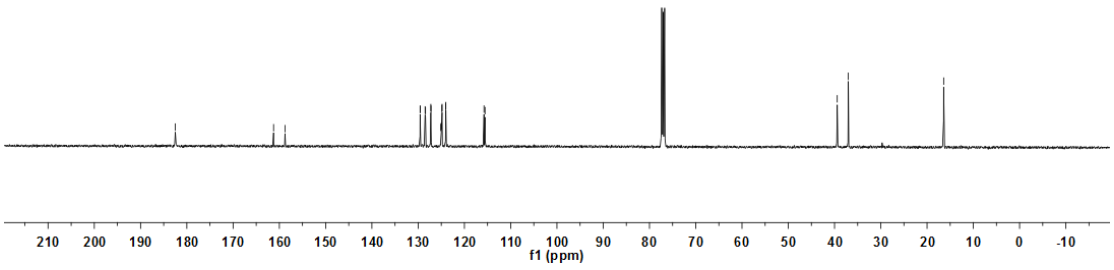


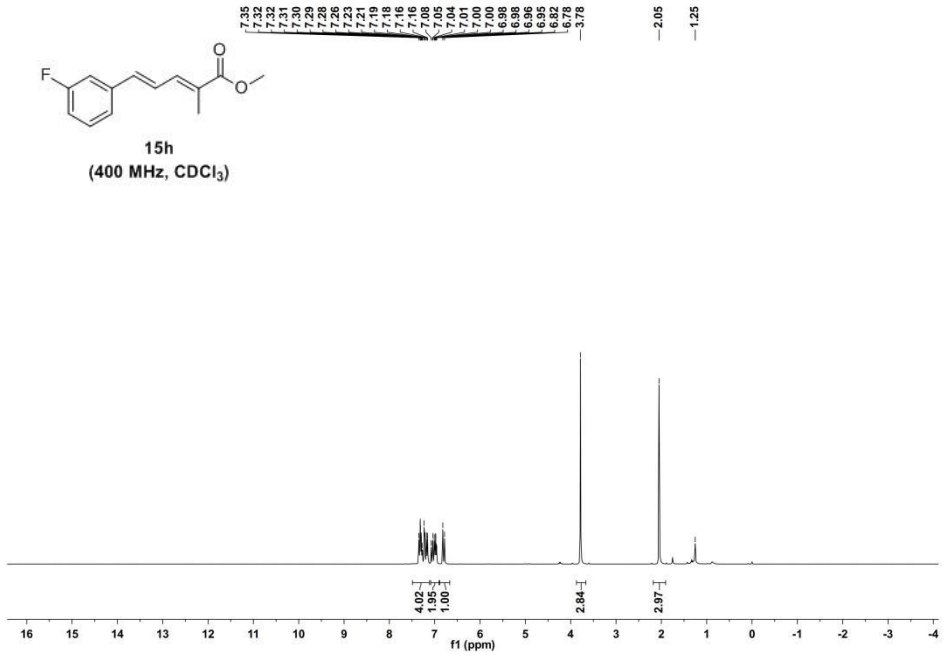
(*R*)-2g
(400 MHz, $CDCl_3$)

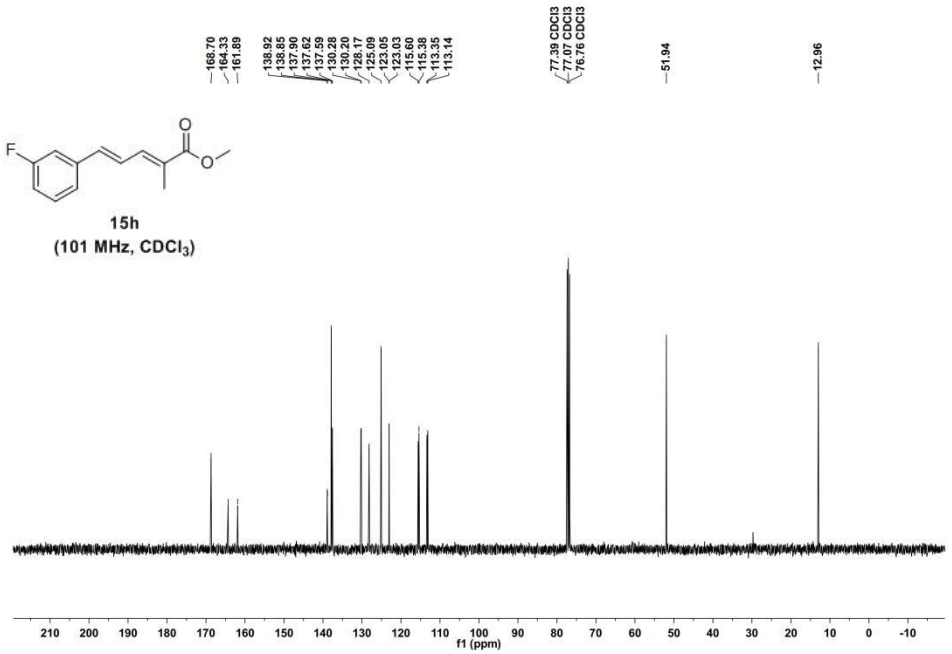


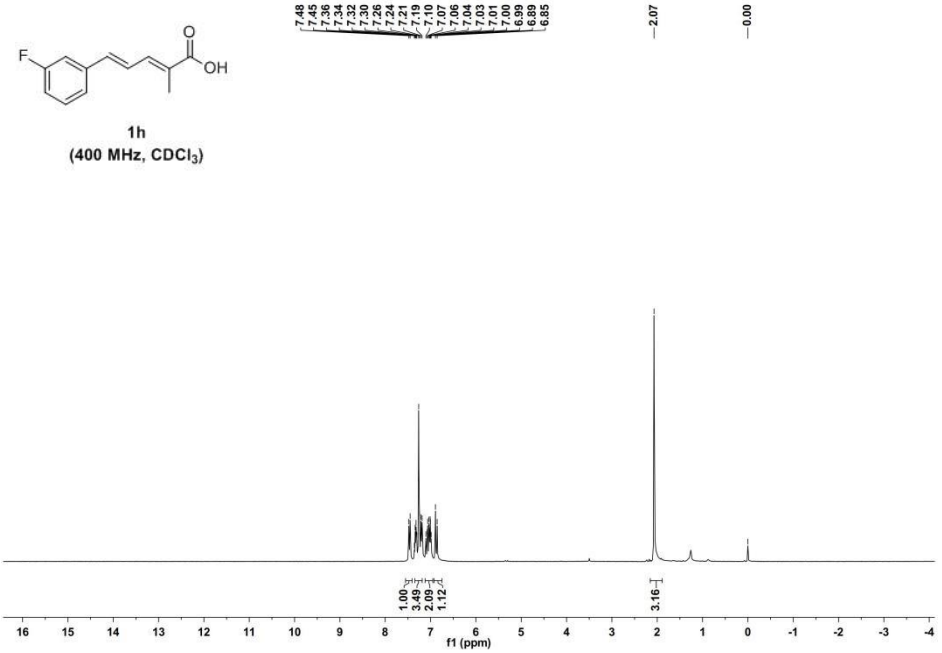


(*R*)-2g
(101 MHz, $CDCl_3$)

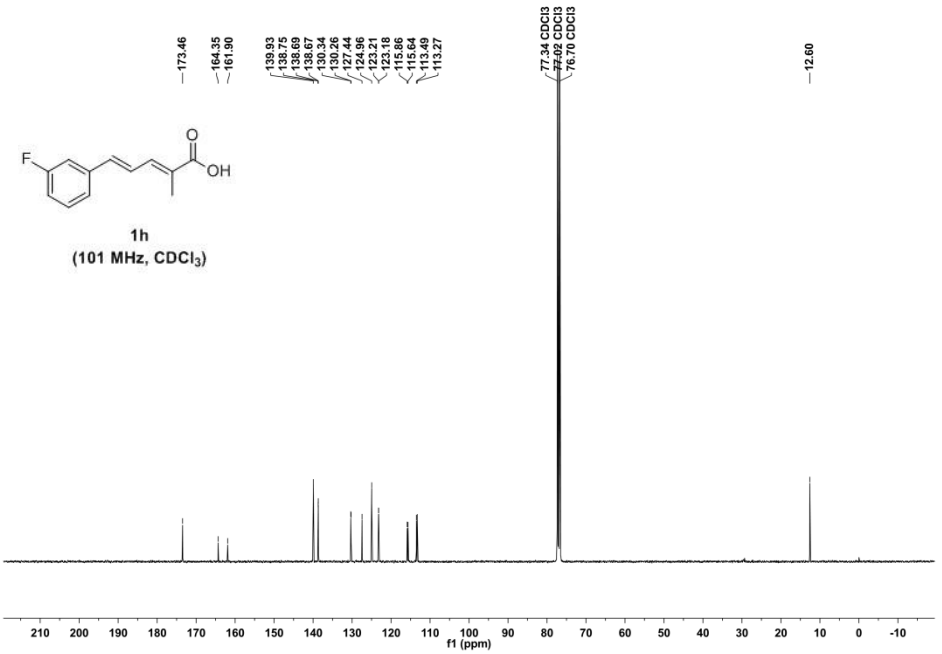



7.35
7.32
7.32
7.31
7.30
7.29
7.28
7.26
7.23
7.21
7.19
7.18
7.16
7.16
7.08
7.05
7.04
7.01
7.00
7.00
6.98
6.98
6.96
6.95
6.82
6.78
3.78
2.05
1.25
F
O
O
15h
(400 MHz, CDCl3)
4.02
1.95
1.00
2.84
2.97
f1 (ppm)

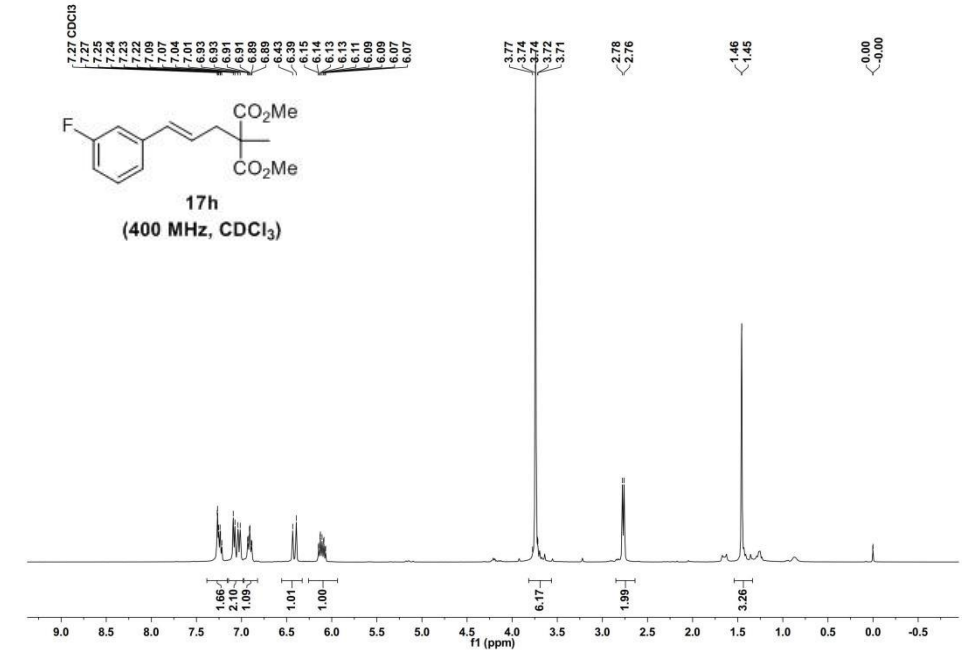

168.70
164.33
161.89
138.92
138.85
137.90
137.62
137.59
130.28
130.20
129.17
125.09
123.05
123.03
115.60
115.38
113.35
113.14
77.39 CDCl3
77.07 CDCl3
76.76 CDCl3
51.94
12.96
F
O
O
15h
(101 MHz, CDCl3)
f1 (ppm)

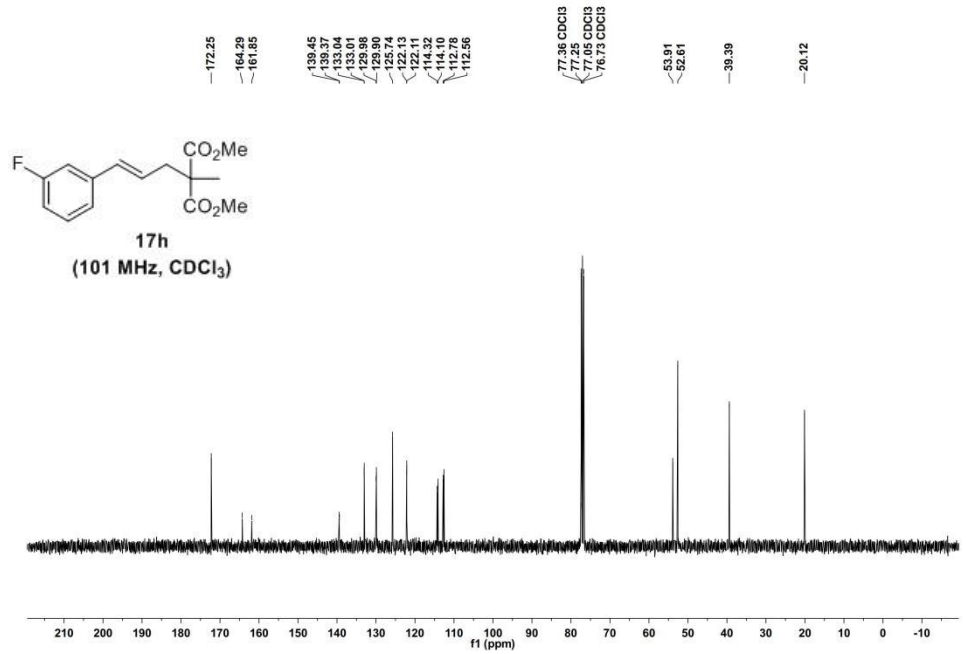


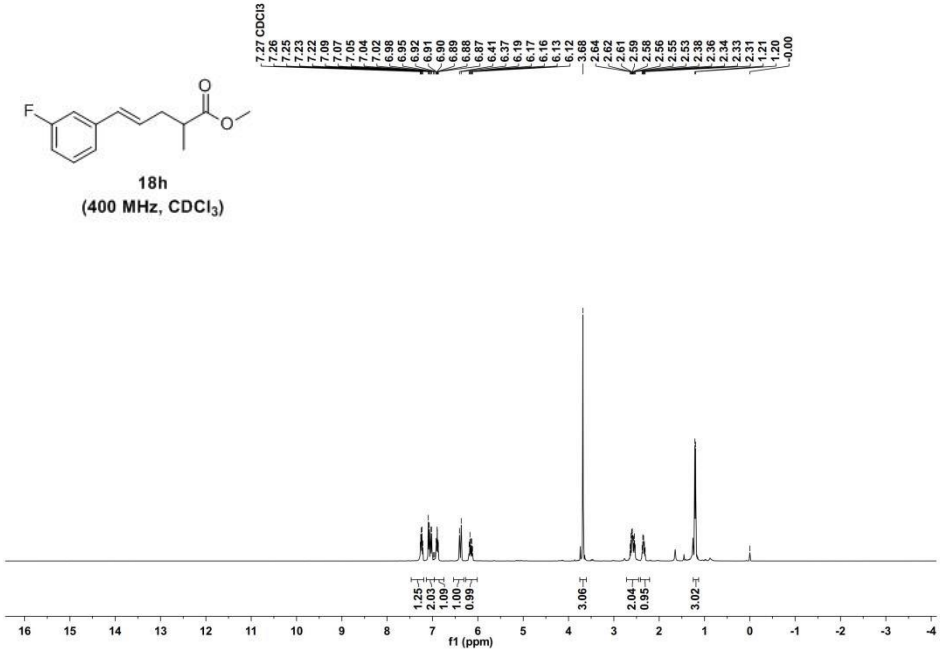
1h
(400 MHz, $CDCl_3$)

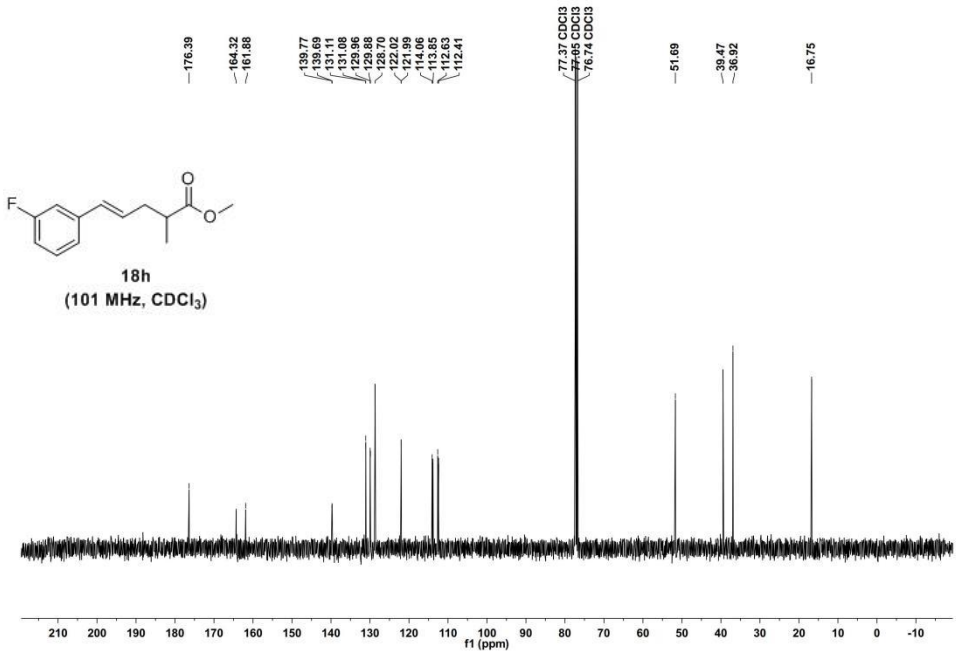


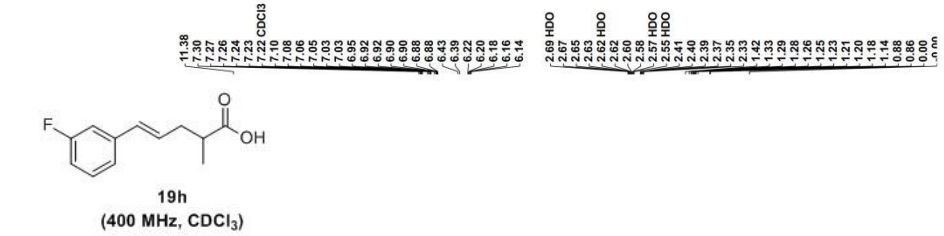
1h
(101 MHz, $CDCl_3$)


7.27 CDCl3
7.27
7.25
7.24
7.23
7.22
7.09
7.07
7.04
7.01
6.93
6.91
6.91
6.89
6.89
6.43
6.39
6.15
6.14
6.13
6.13
6.11
6.09
6.09
6.07
6.07
3.77
3.74
3.74
3.72
3.71
2.78
2.76
1.46
1.45
0.00
-0.00
F
CO2Me
CO2Me
17h
(400 MHz, CDCl3)
1.68
2.10
1.09
1.01
1.00
6.17
1.99
3.26
f1 (ppm)

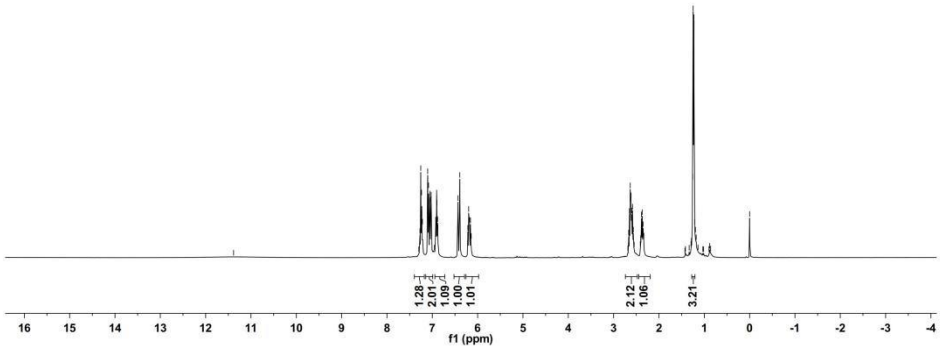

172.25
164.29
161.85
139.45
139.37
133.04
133.01
129.98
129.90
125.74
122.13
122.11
114.32
114.10
112.78
112.56
77.36 CDCl3
77.25
77.05 CDCl3
76.73 CDCl3
53.91
52.61
39.39
20.12
F
CO2Me
CO2Me
17h
(101 MHz, CDCl3)
f1 (ppm)

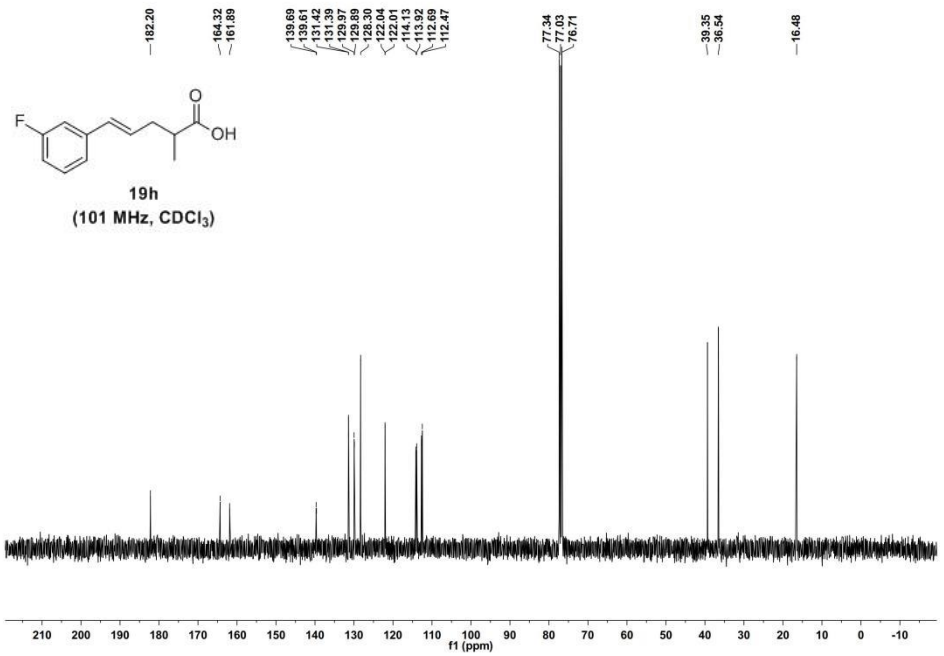

7.27 CDCl3
7.26
7.25
7.23
7.22
7.09
7.07
7.05
7.04
7.02
6.98
6.95
6.92
6.91
6.90
6.89
6.88
6.87
6.41
6.37
6.19
6.17
6.16
6.13
6.12
3.68
2.64
2.62
2.61
2.59
2.58
2.56
2.55
2.53
2.38
2.36
2.34
2.33
2.31
1.21
1.20
0.00
F
O
O
18h
(400 MHz, CDCl3)
1.25
2.03
1.09
1.00
0.99
3.06
2.04
0.95
3.02
f1 (ppm)


176.39
164.32
161.88
139.77
139.69
131.11
131.08
129.96
129.88
128.70
128.62
121.99
114.06
113.85
112.63
112.41
77.37 CDCl3
77.05 CDCl3
76.74 CDCl3
51.69
39.47
36.92
16.75
F
O
O
18h
(101 MHz, CDCl3)
f1 (ppm)

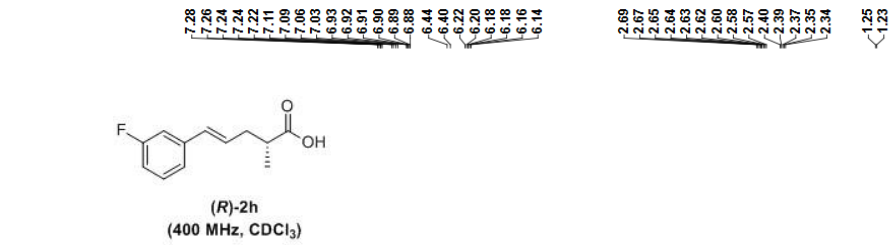


19h
(400 MHz, $CDCl_3$)

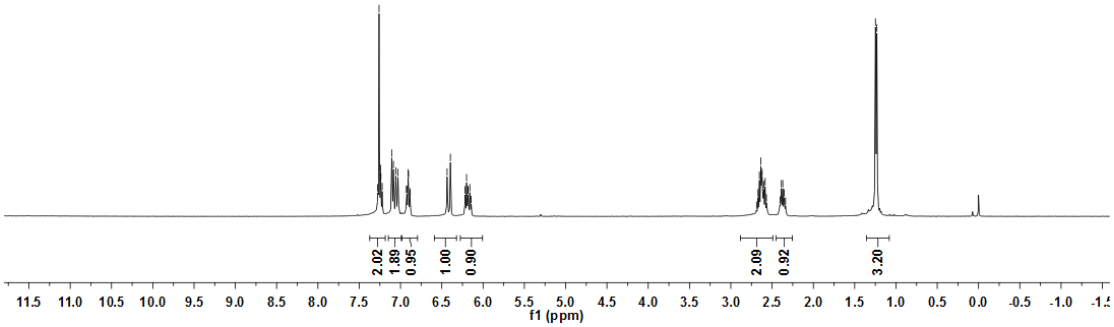


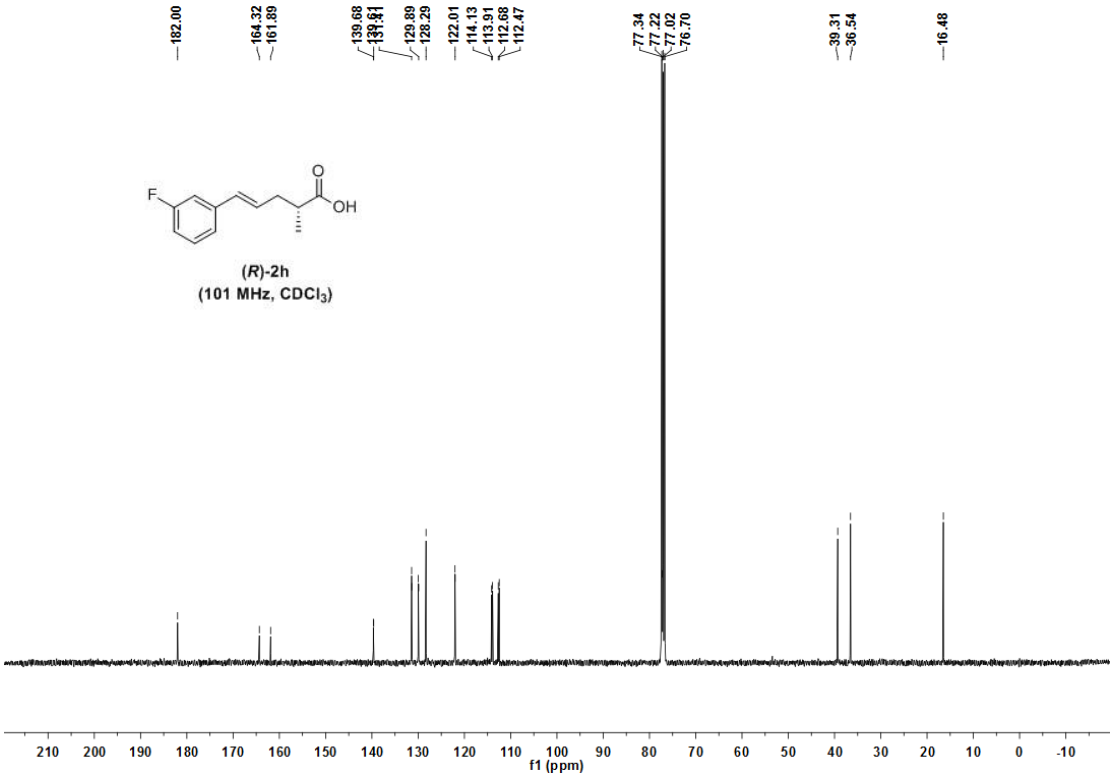


19h
(101 MHz, $CDCl_3$)

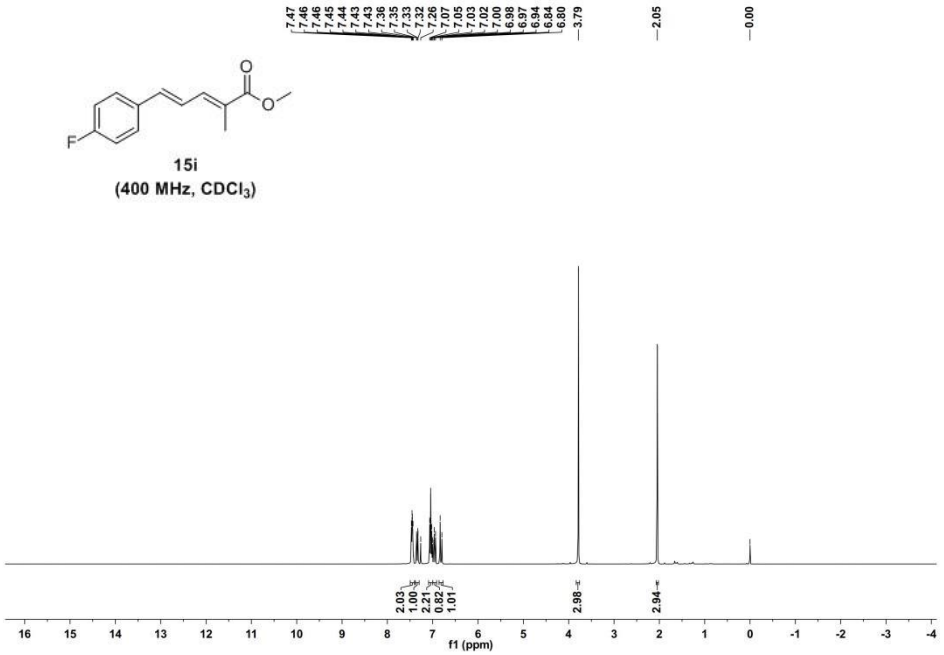


(*R*)-2h
(400 MHz, $CDCl_3$)

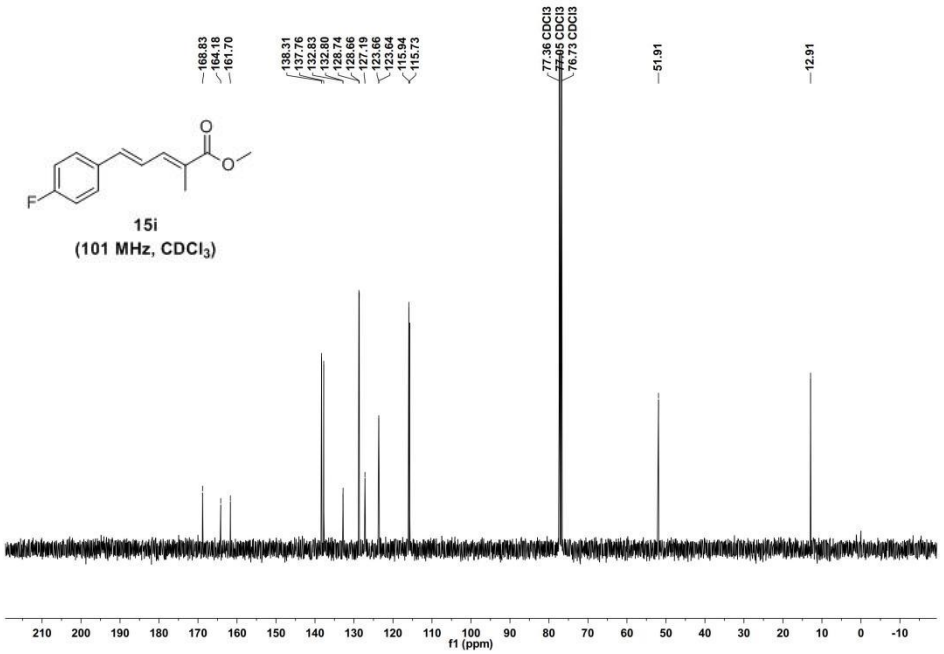




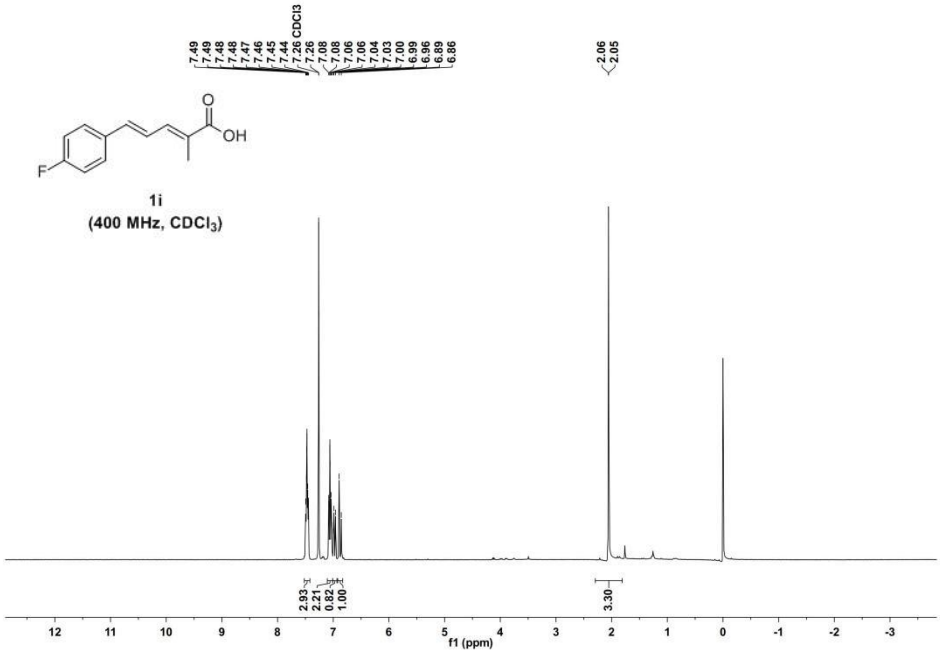
(*R*)-2h
(101 MHz, $CDCl_3$)

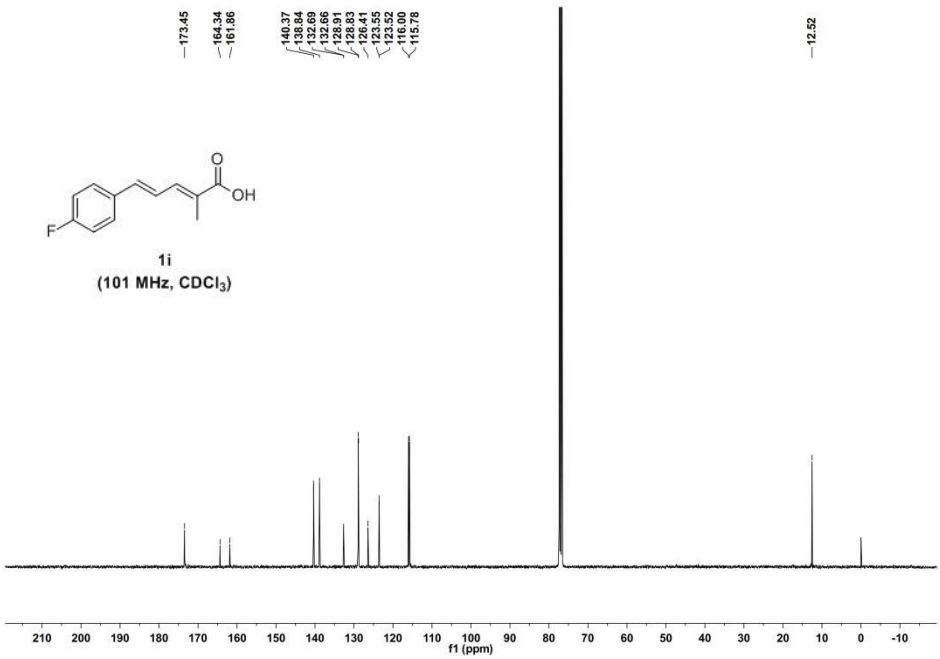


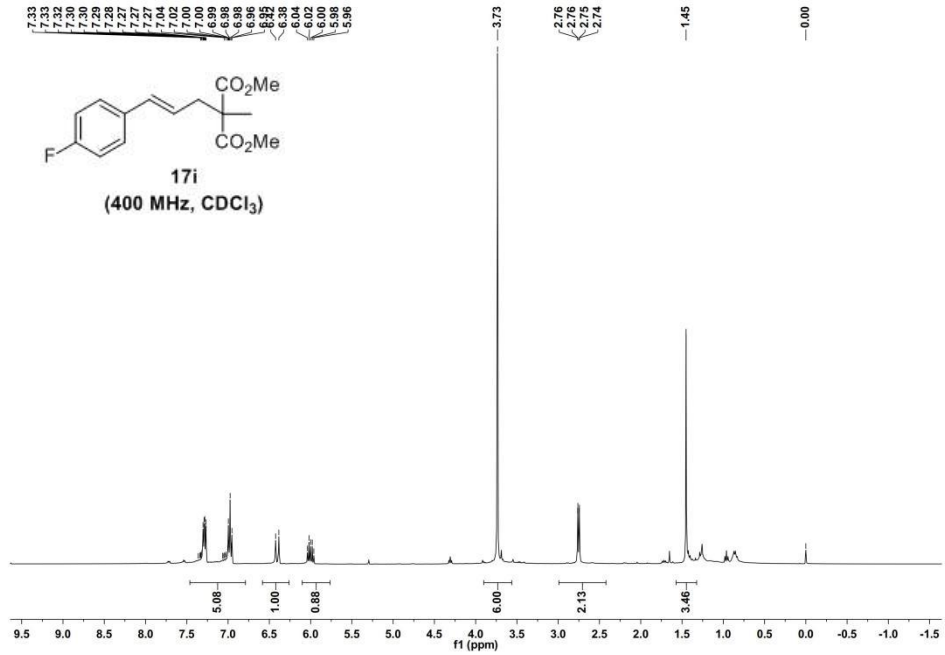
15i
(400 MHz, $CDCl_3$)

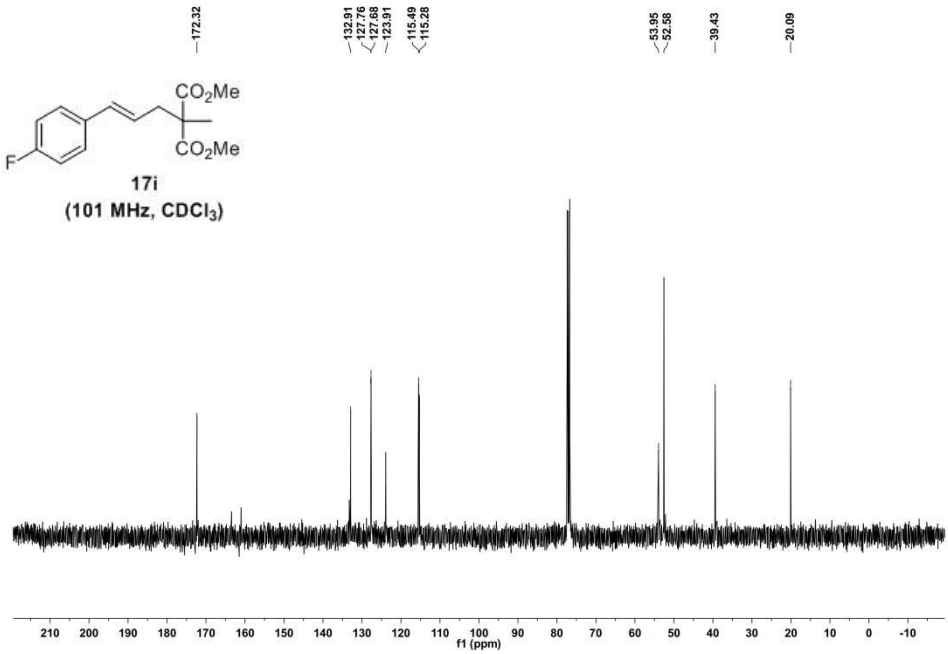


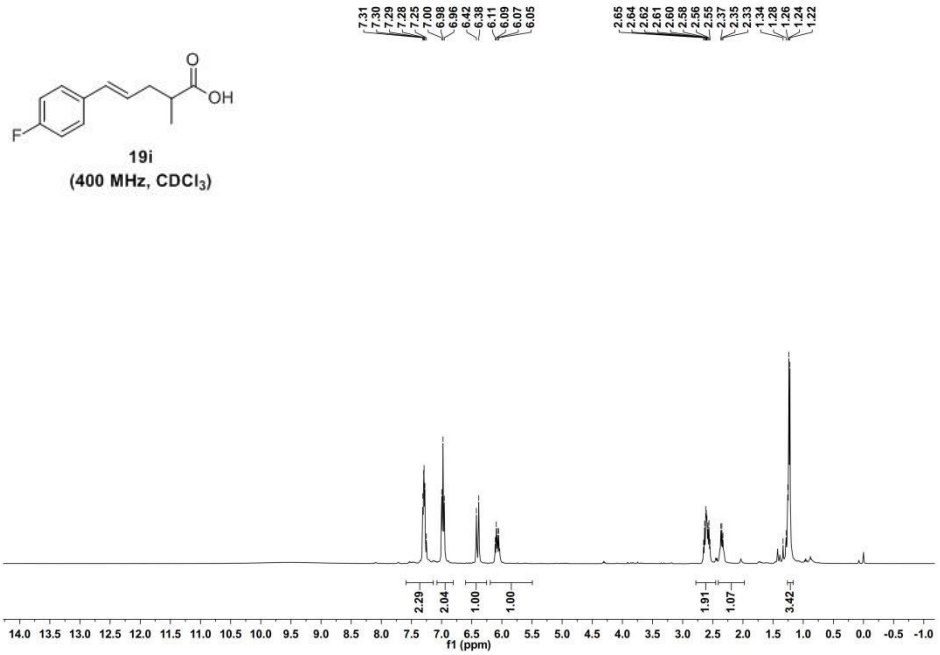
15i
(101 MHz, $CDCl_3$)

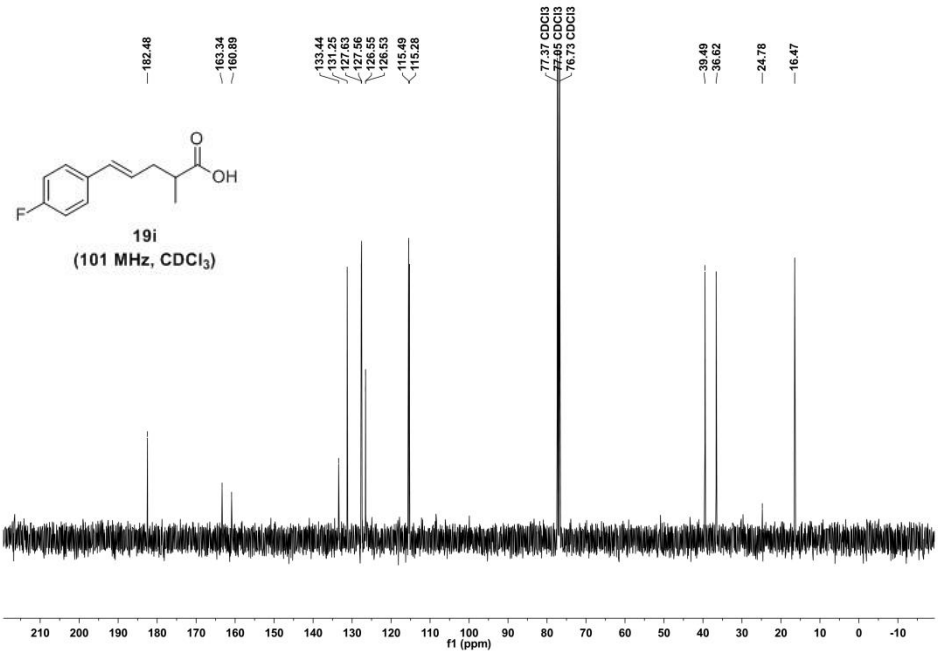

7.49
7.49
7.48
7.48
7.47
7.46
7.45
7.44
7.26 CDCl3
7.08
7.08
7.06
7.06
7.04
7.03
7.00
6.99
6.96
6.89
6.86
2.06
2.05
O
OH
F
1i
(400 MHz, CDCl3)
2.93
2.21
0.82
1.00
3.30
f1 (ppm)

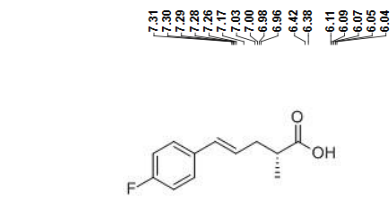

173.45
164.34
161.86
140.37
138.84
132.69
132.66
128.91
128.83
124.41
123.55
123.52
116.00
115.78
12.52
O
OH
F
1i
(101 MHz, CDCl3)
f1 (ppm)


7.33
7.33
7.32
7.30
7.29
7.28
7.27
7.27
7.27
7.04
7.02
7.00
7.00
6.99
6.98
6.98
6.96
6.38
6.04
6.02
6.00
5.98
5.96
3.73
2.76
2.76
2.75
2.74
1.45
0.00
CO2Me
CO2Me
F
17i
(400 MHz, CDCl3)
5.08
1.00
0.88
6.00
2.13
3.46
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

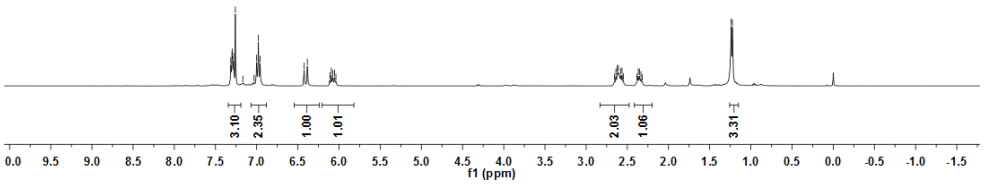

172.32
132.91
127.76
127.68
123.91
115.49
115.28
53.95
52.58
39.43
20.09
CO2Me
CO2Me
F
17i
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

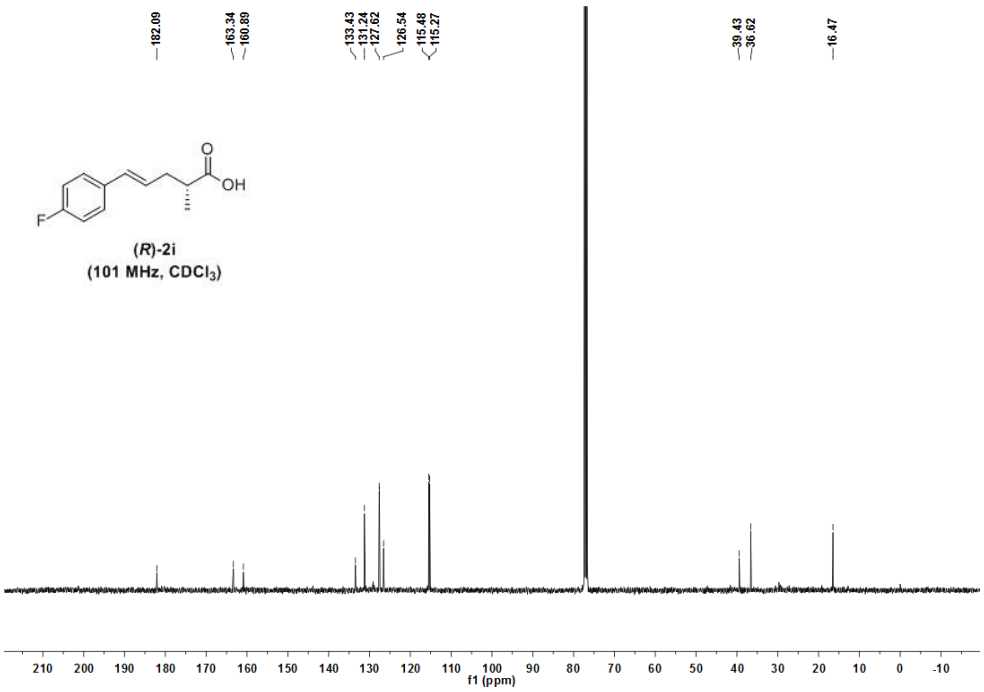

7.31
7.30
7.29
7.28
7.25
7.00
6.98
6.96
6.42
6.38
6.11
6.09
6.07
6.05
2.65
2.64
2.62
2.61
2.60
2.58
2.56
2.55
2.37
2.35
2.33
1.34
1.28
1.26
1.24
1.22
O
OH
F
19i
(400 MHz, CDCl3)
2.29
2.04
1.00
1.00
1.91
1.07
3.42
f1 (ppm)


182.48
163.34
160.89
133.44
131.25
127.63
127.56
126.55
126.53
115.49
115.28
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
39.49
36.62
24.78
16.47
O
OH
F
19i
(101 MHz, CDCl3)
f1 (ppm)

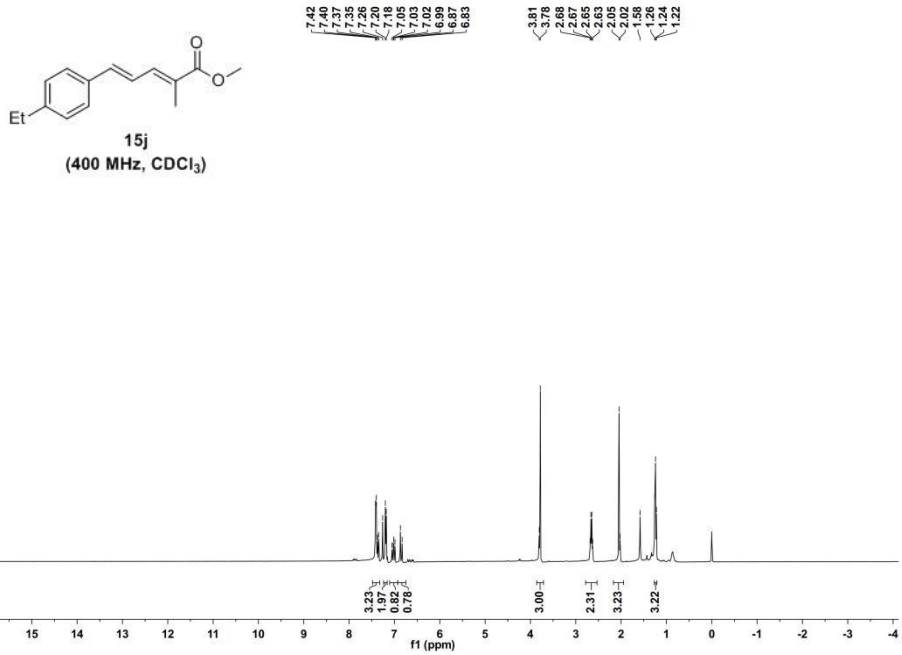


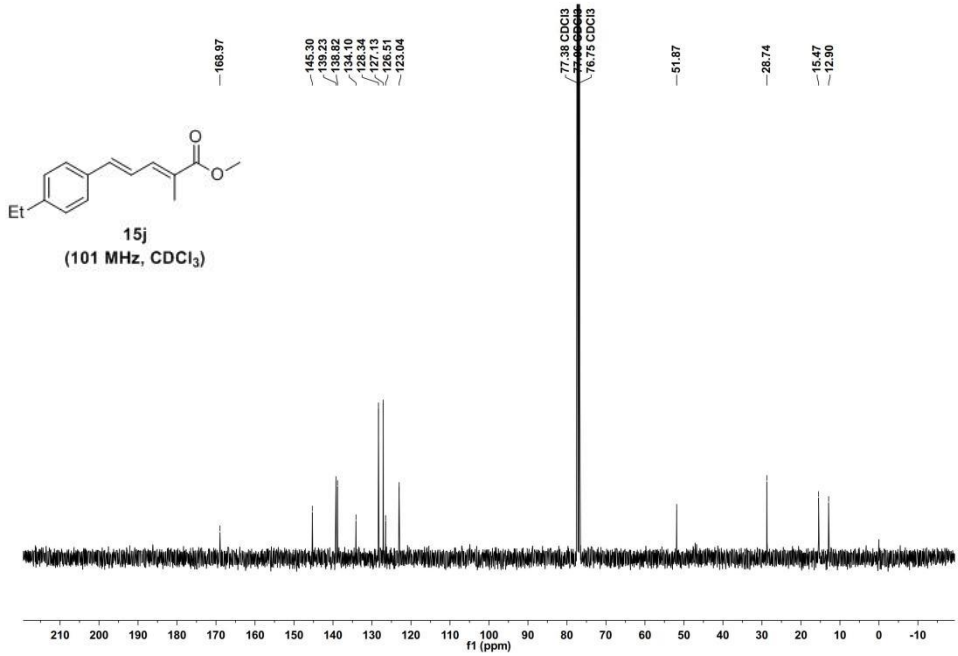
(*R*)-2i
(400 MHz, $CDCl_3$)

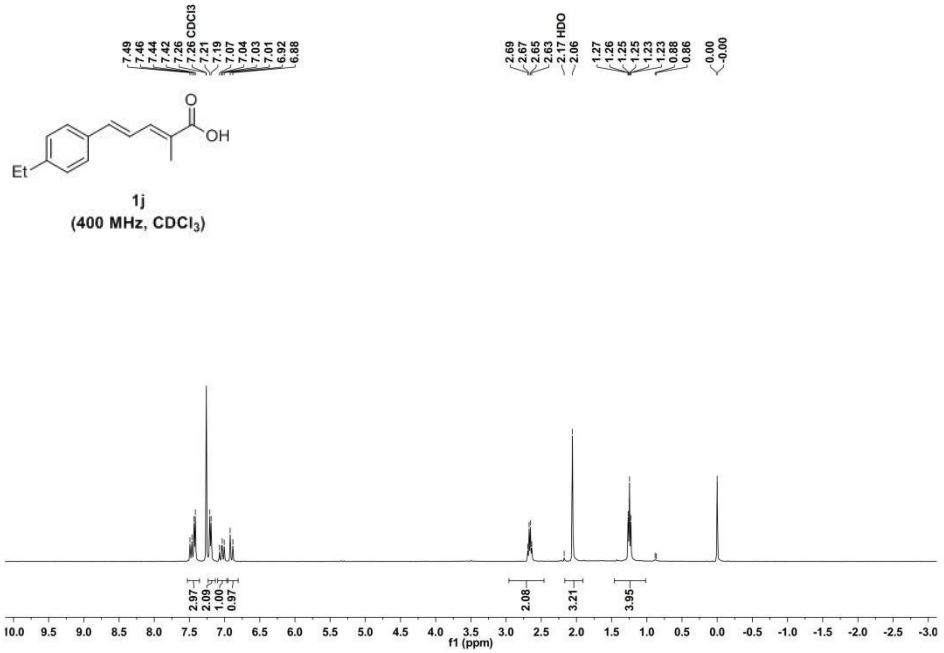




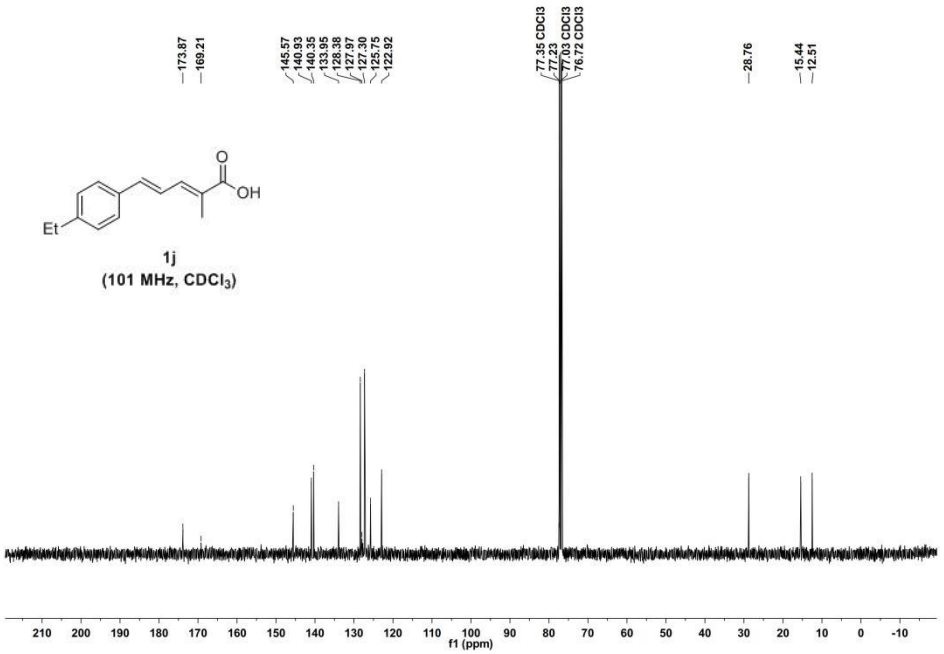
(*R*)-2i
(101 MHz, $CDCl_3$)


7.42
7.40
7.37
7.35
7.26
7.20
7.18
7.05
7.03
7.02
6.99
6.87
6.83
3.81
3.78
2.68
2.67
2.65
2.63
2.05
2.02
1.58
1.26
1.24
1.22
Et
O
O
15j
(400 MHz, CDCl3)
3.23
1.97
0.82
0.78
3.00
2.31
3.23
3.22
f1 (ppm)

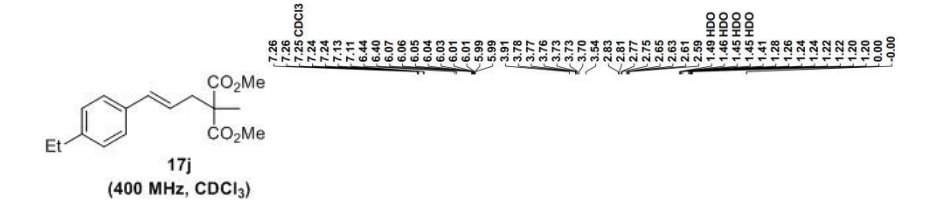

168.97
145.30
139.23
138.82
134.10
128.34
127.13
126.51
123.04
77.38 CDCl3
77.00 CDCl3
76.75 CDCl3
51.87
28.74
15.47
12.90
Et
O
O
15j
(101 MHz, CDCl3)
f1 (ppm)



1j
(400 MHz, $CDCl_3$)

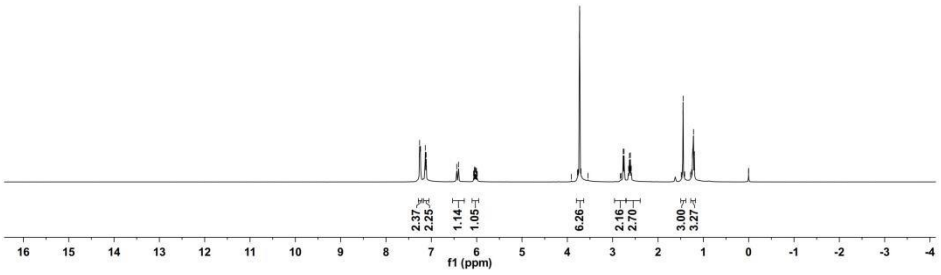


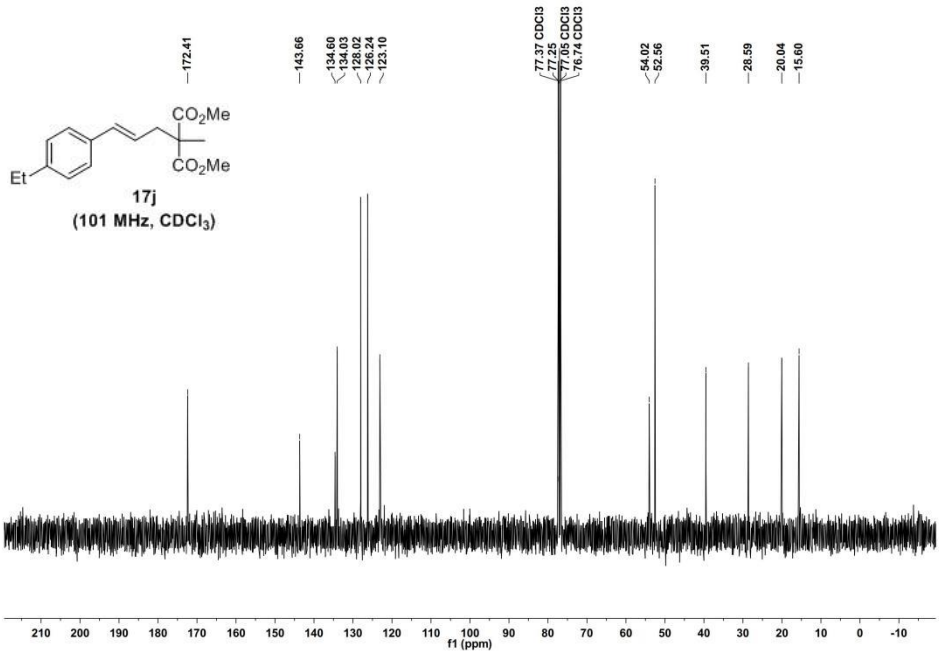
1j
(101 MHz, $CDCl_3$)



17j

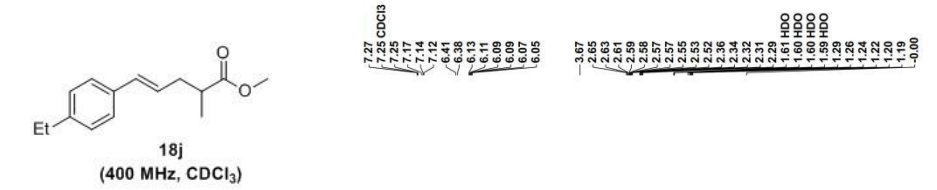
(400 MHz, $CDCl_3$)



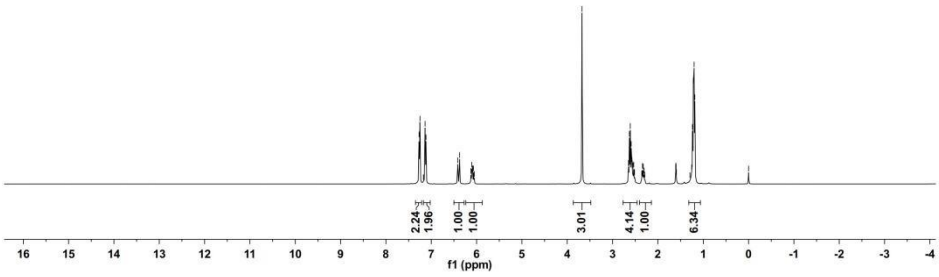


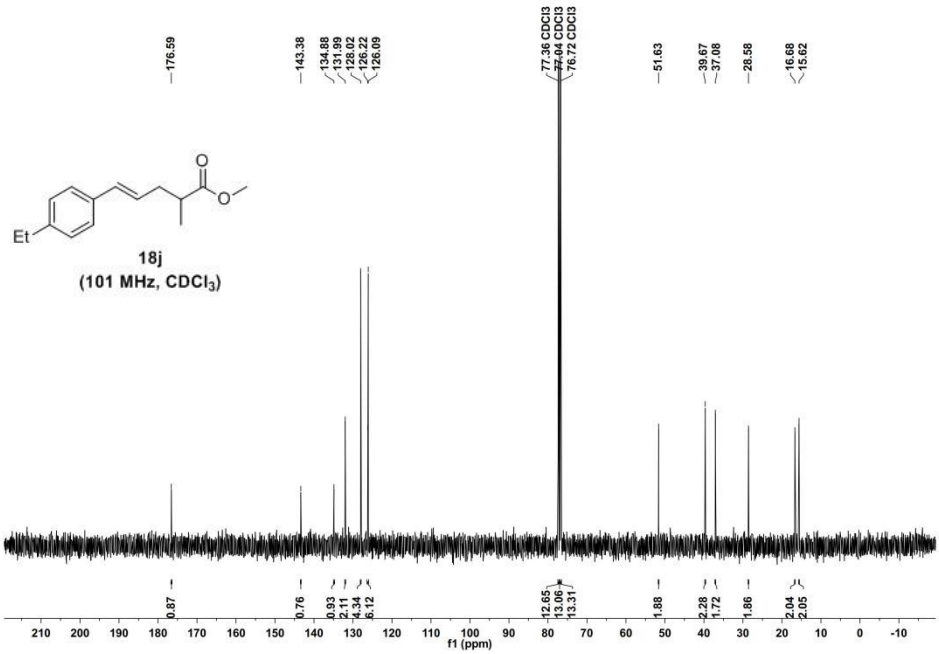
17j

(101 MHz, $CDCl_3$)

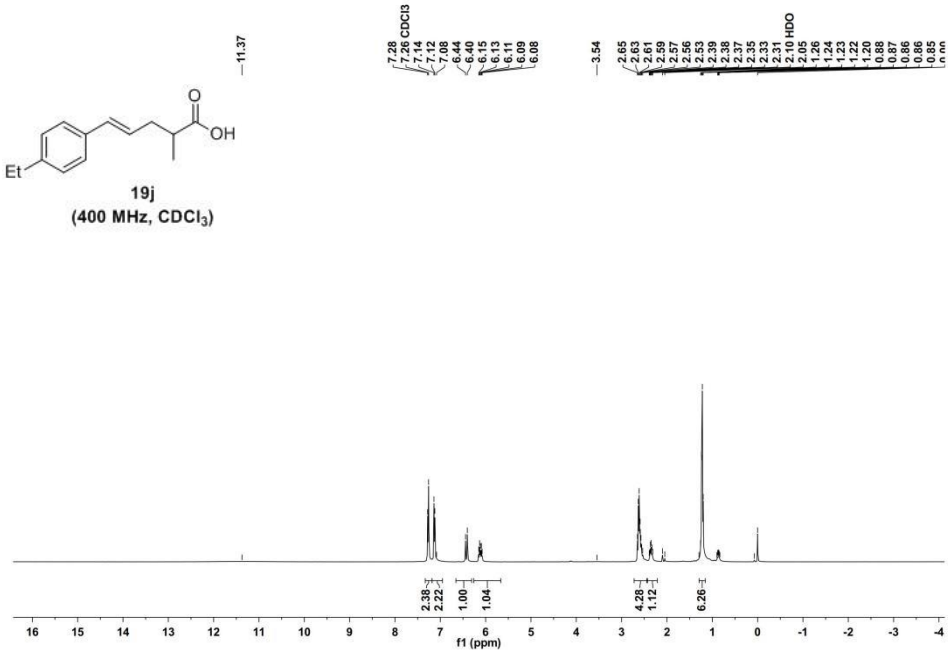


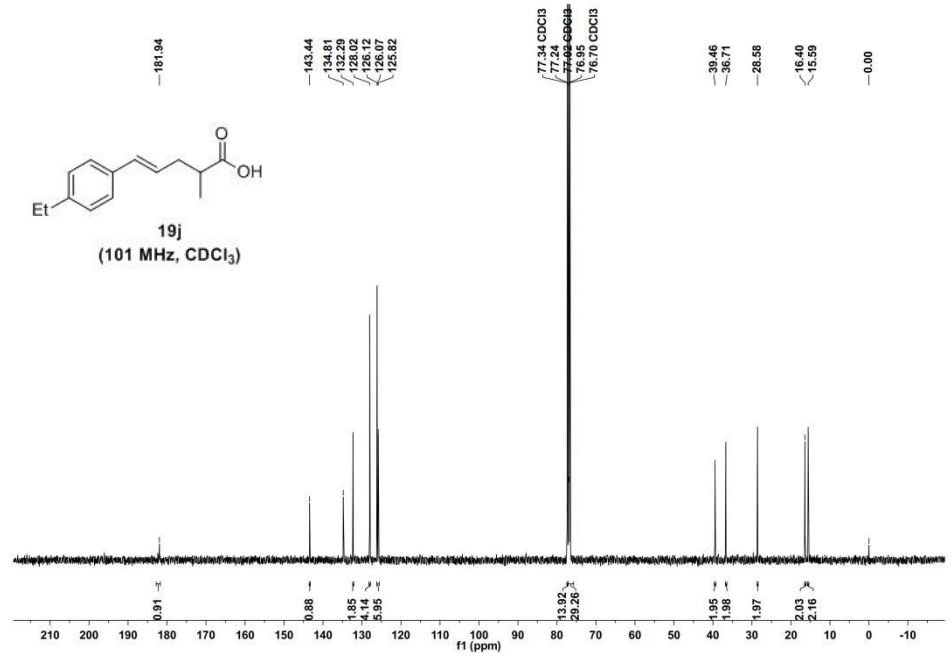
18j
(400 MHz, $CDCl_3$)

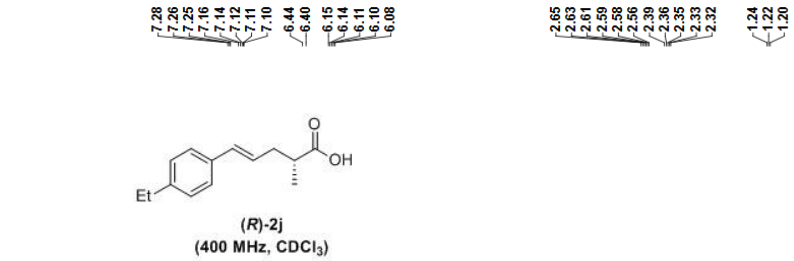




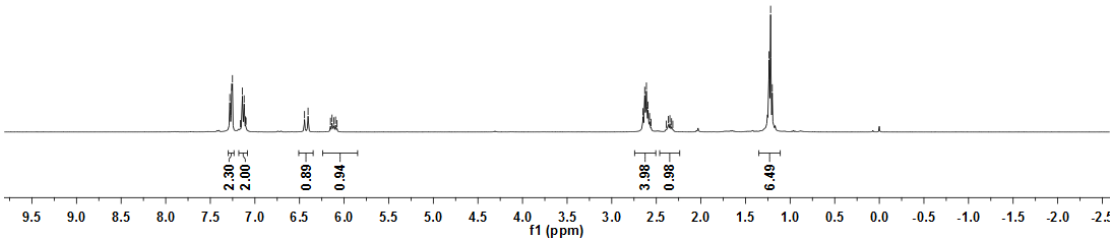
18j
(101 MHz, $CDCl_3$)

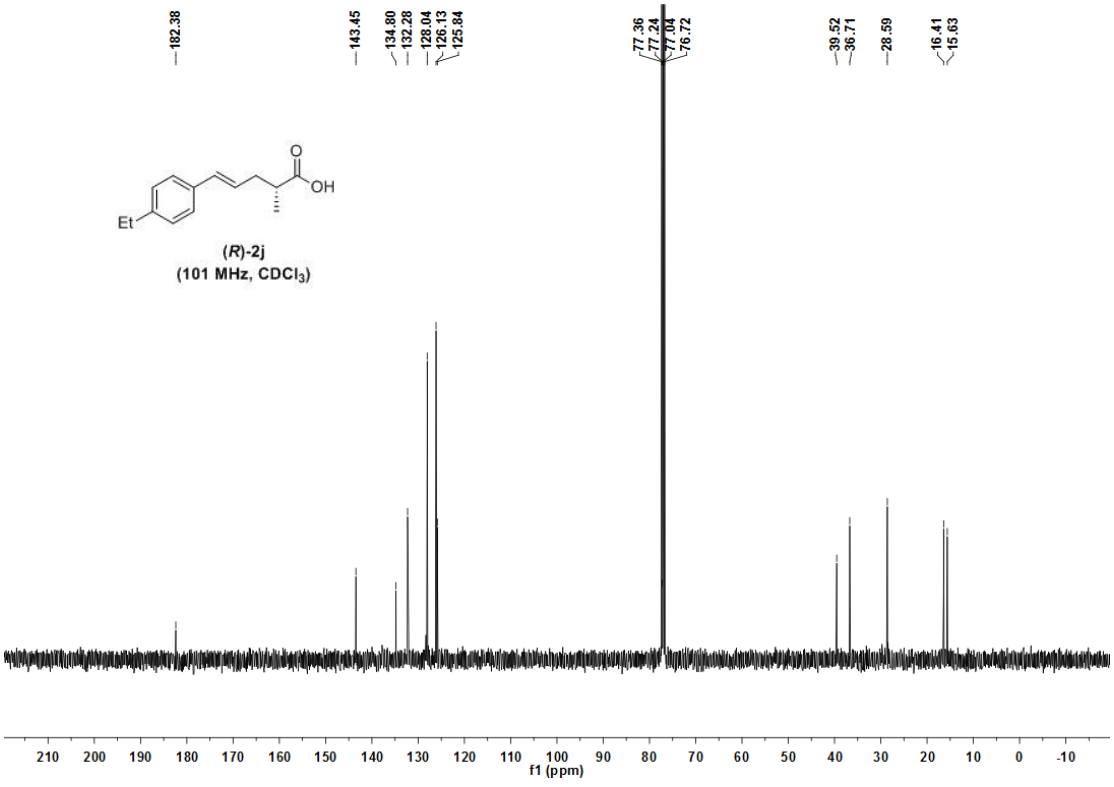

11.37
7.28
7.26 CDCl3
7.14
7.12
7.08
6.44
6.40
6.15
6.13
6.11
6.09
6.08
3.54
2.65
2.63
2.61
2.59
2.57
2.56
2.53
2.39
2.38
2.37
2.35
2.33
2.31
2.10 HDO
2.05
1.26
1.24
1.23
1.22
1.20
0.88
0.87
0.86
0.86
0.85
O
OH
Et
19j
(400 MHz, CDCl3)
2.38
2.22
1.00
1.04
4.28
1.12
6.26
f1 (ppm)


181.94
143.44
134.81
132.29
128.02
126.12
126.07
125.82
77.34 CDCl3
77.24
76.95
76.70 CDCl3
39.46
36.71
28.58
16.40
15.59
0.00
O
OH
Et
19j
(101 MHz, CDCl3)
0.91
0.88
1.85
4.14
5.95
13.92
29.26
1.95
1.98
1.97
2.03
2.16
f1 (ppm)

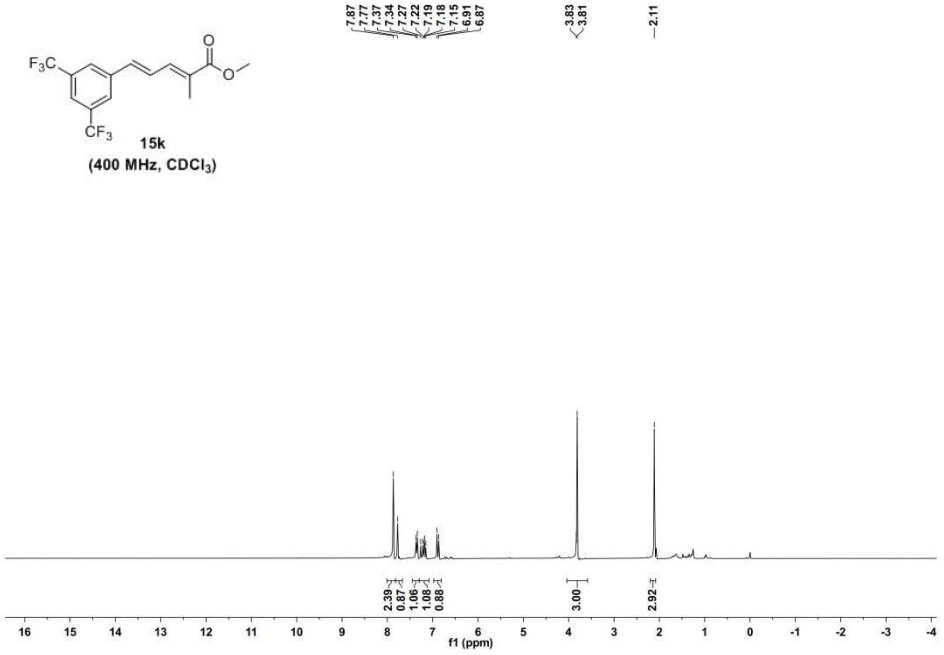


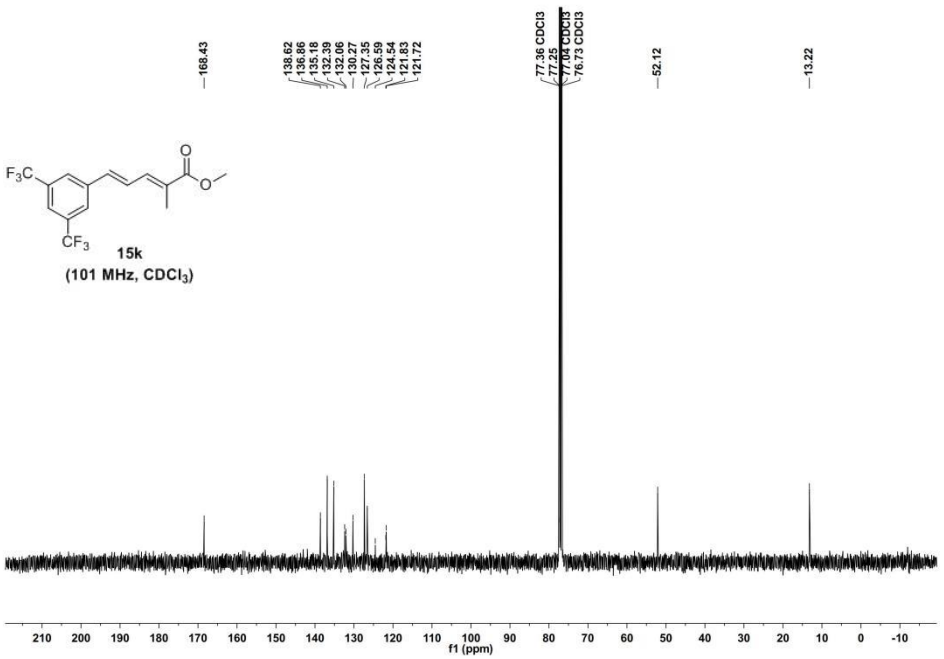
(*R*)-2j
(400 MHz, $CDCl_3$)

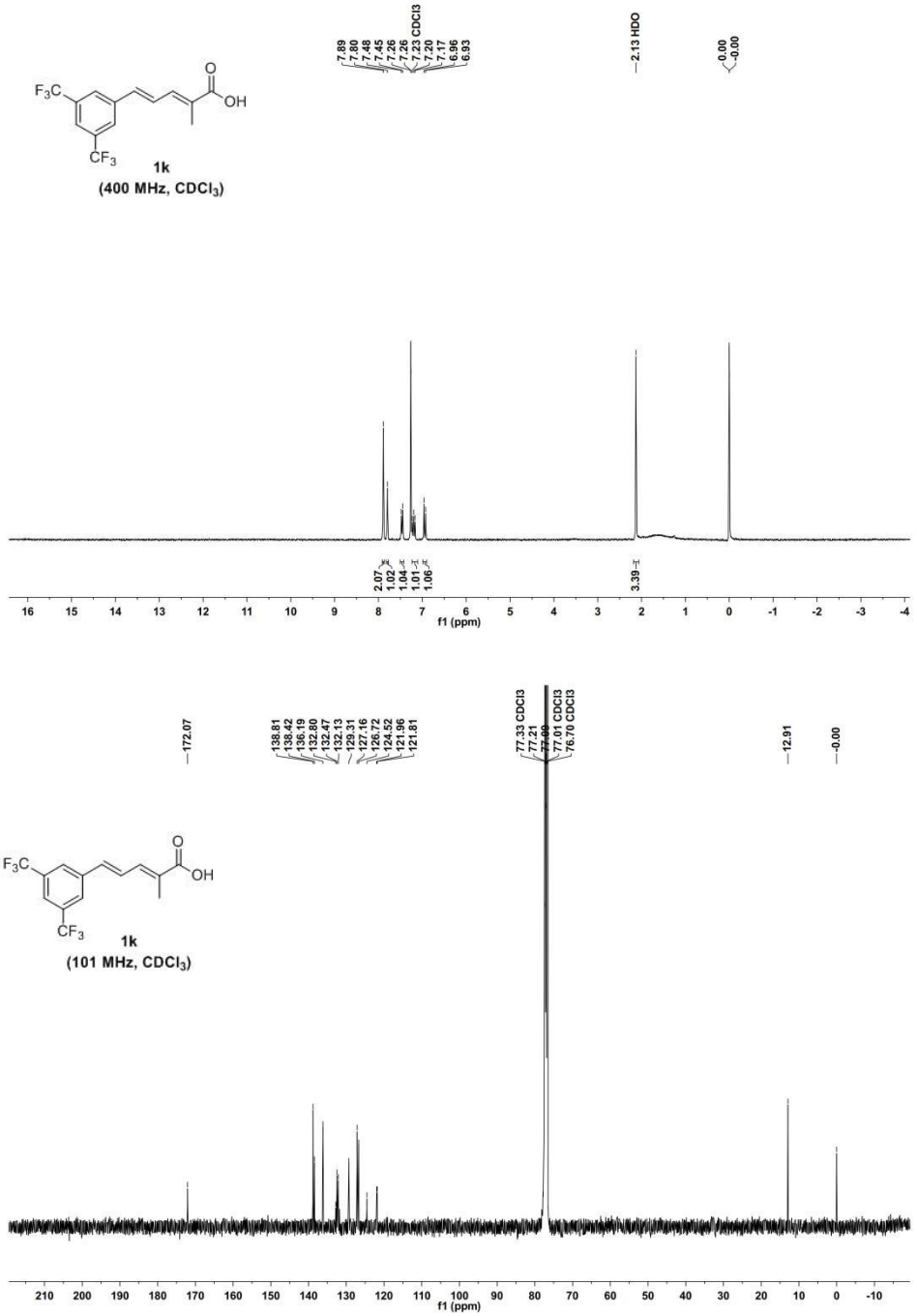


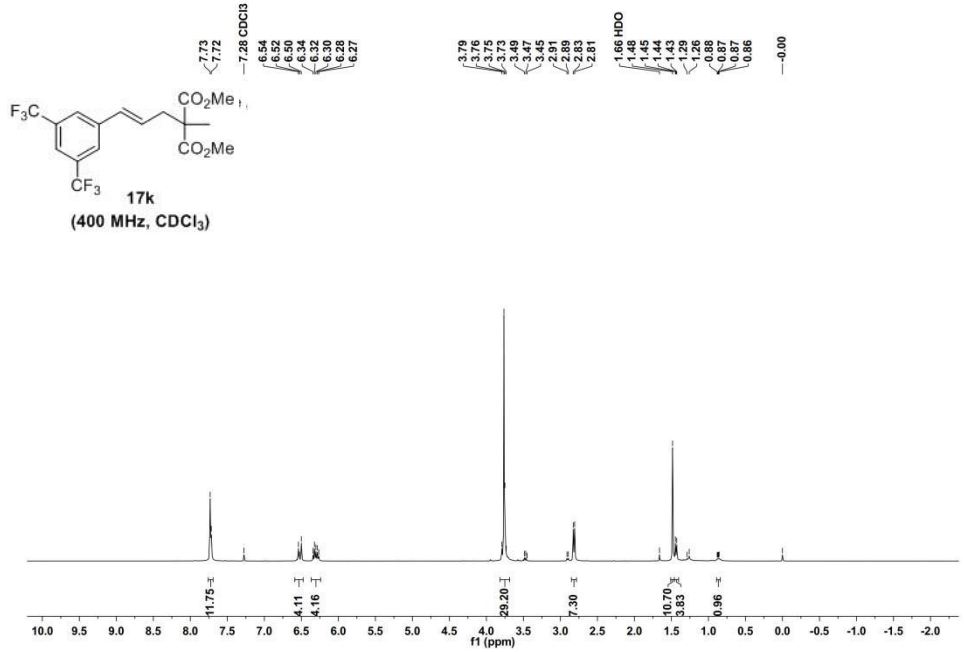


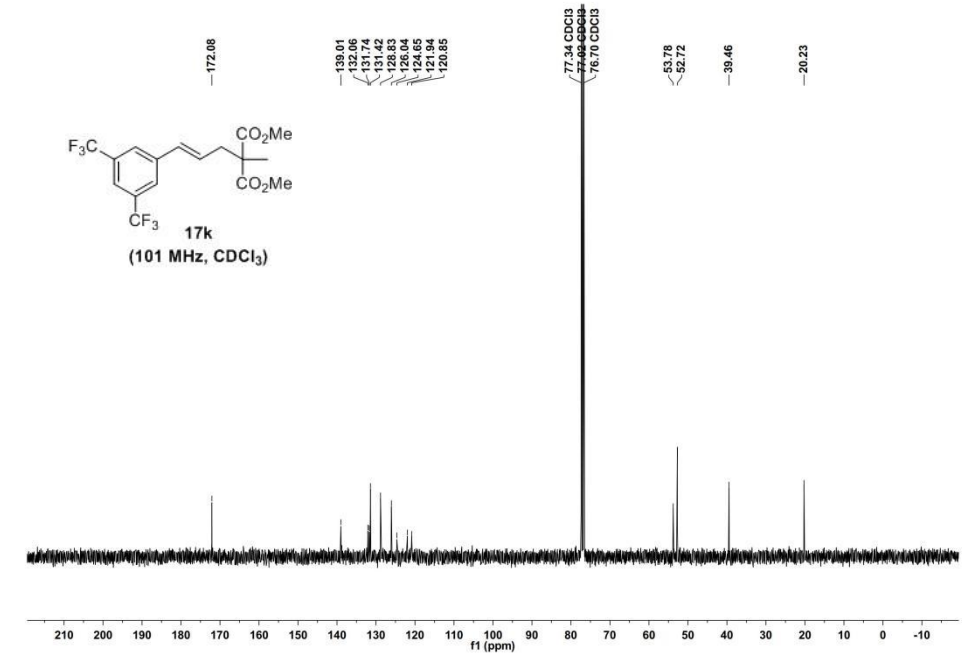
(*R*)-2j
(101 MHz, $CDCl_3$)

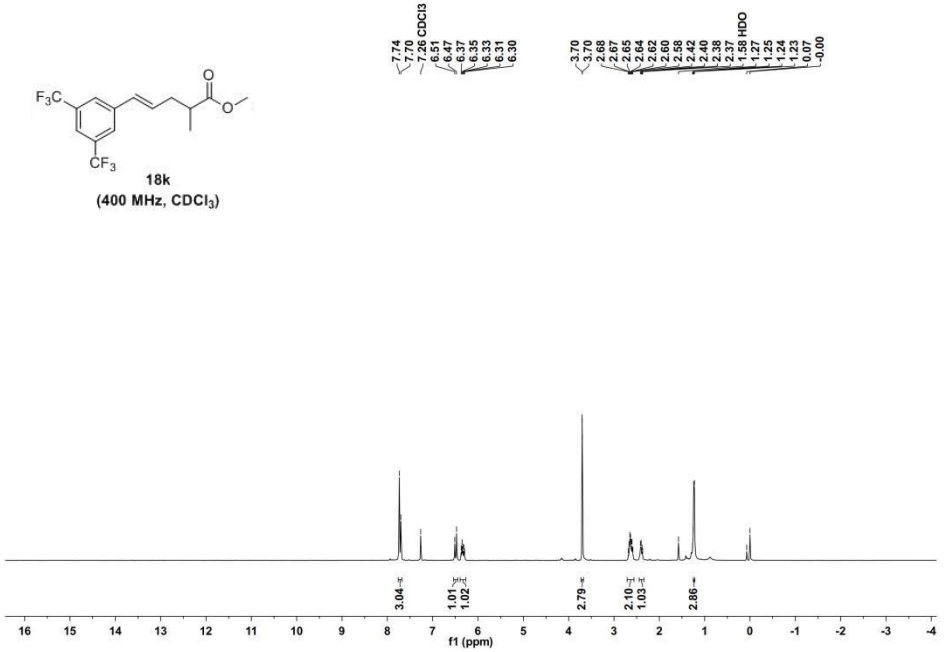

7.87
7.77
7.37
7.34
7.27
7.22
7.19
7.18
7.15
6.91
6.87
3.83
3.81
2.11
F3C
CF3
O
O
15k
(400 MHz, CDCl3)
2.39
0.87
1.06
1.08
0.88
3.00
2.92
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

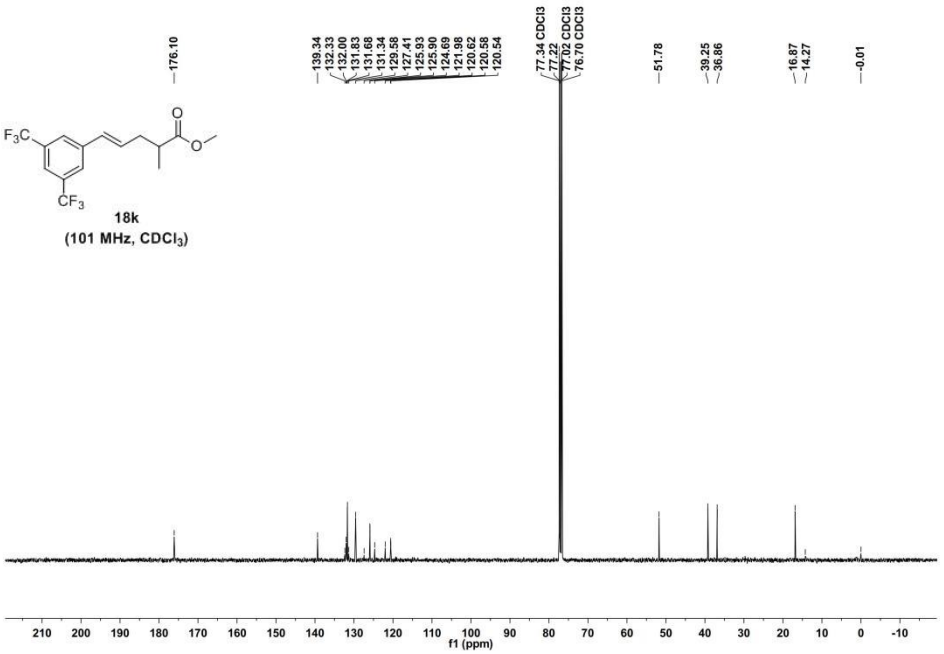

168.43
138.62
136.86
135.18
132.39
132.06
130.27
127.35
126.59
124.54
121.83
121.72
77.36 CDCl3
77.25
77.04 CDCl3
76.73 CDCl3
52.12
13.22
F3C
CF3
O
O
15k
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

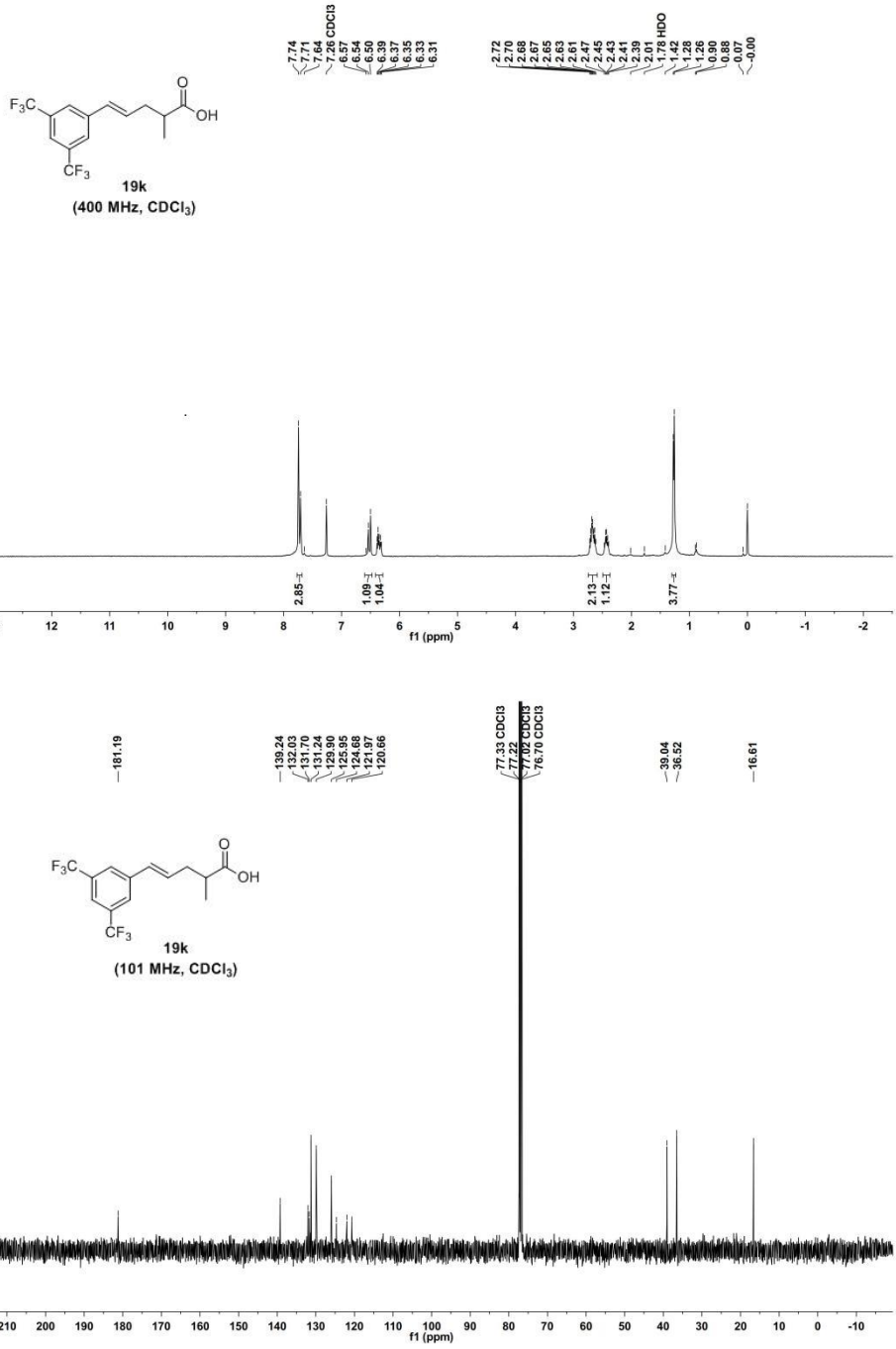

F3C
CF3
O
OH
1k
(400 MHz, CDCl3)
7.89
7.80
7.48
7.45
7.26
7.23 CDCl3
7.20
7.17
6.96
6.93
2.13 HDO
0.00
-0.00
2.07
1.02
1.04
1.01
1.06
3.39
f1 (ppm)
172.07
138.81
138.42
136.19
132.80
132.47
132.13
129.31
127.16
126.72
124.52
121.96
121.81
77.33 CDCl3
77.21
77.00
76.70 CDCl3
12.91
-0.00
1k
(101 MHz, CDCl3)
f1 (ppm)

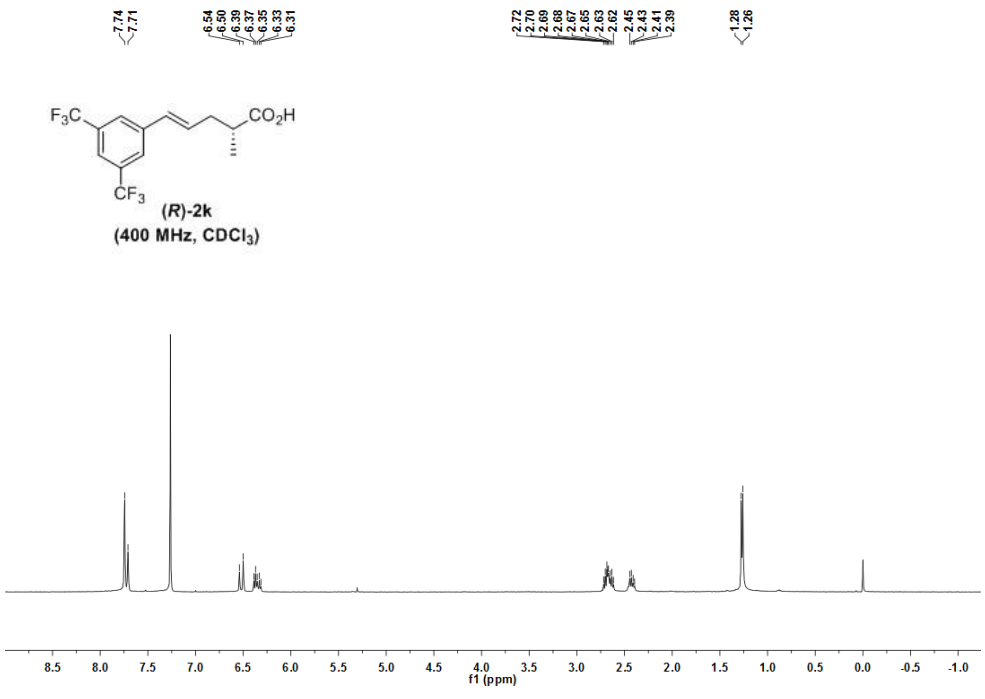

7.73
7.72
7.28 CDCl3
6.54
6.52
6.50
6.34
6.32
6.30
6.28
6.27
3.79
3.76
3.75
3.73
3.49
3.47
3.45
2.91
2.89
2.83
2.81
1.66 HDO
1.48
1.45
1.44
1.43
1.29
1.26
0.88
0.87
0.86
0.00
F3C
CO2Me
CO2Me
CF3
17k
(400 MHz, CDCl3)
11.75
4.11
4.16
29.20
7.30
10.70
3.83
0.96
f1 (ppm)

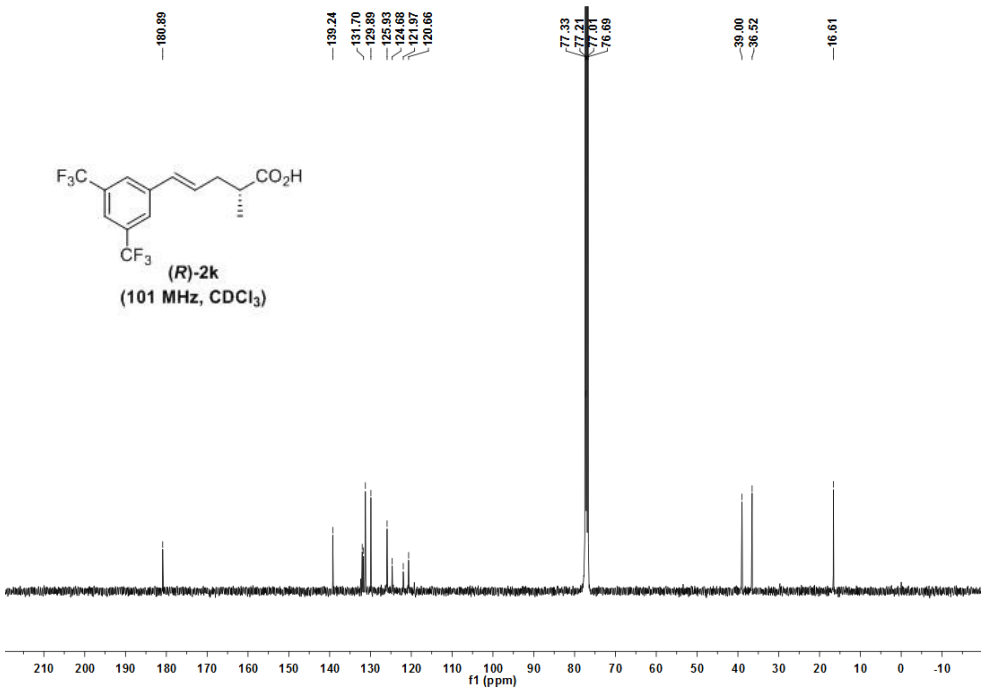

172.08
139.01
132.06
131.74
131.42
128.83
126.04
124.65
121.94
120.85
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
53.78
52.72
39.46
20.23
F3C
CO2Me
CO2Me
CF3
17k
(101 MHz, CDCl3)
f1 (ppm)

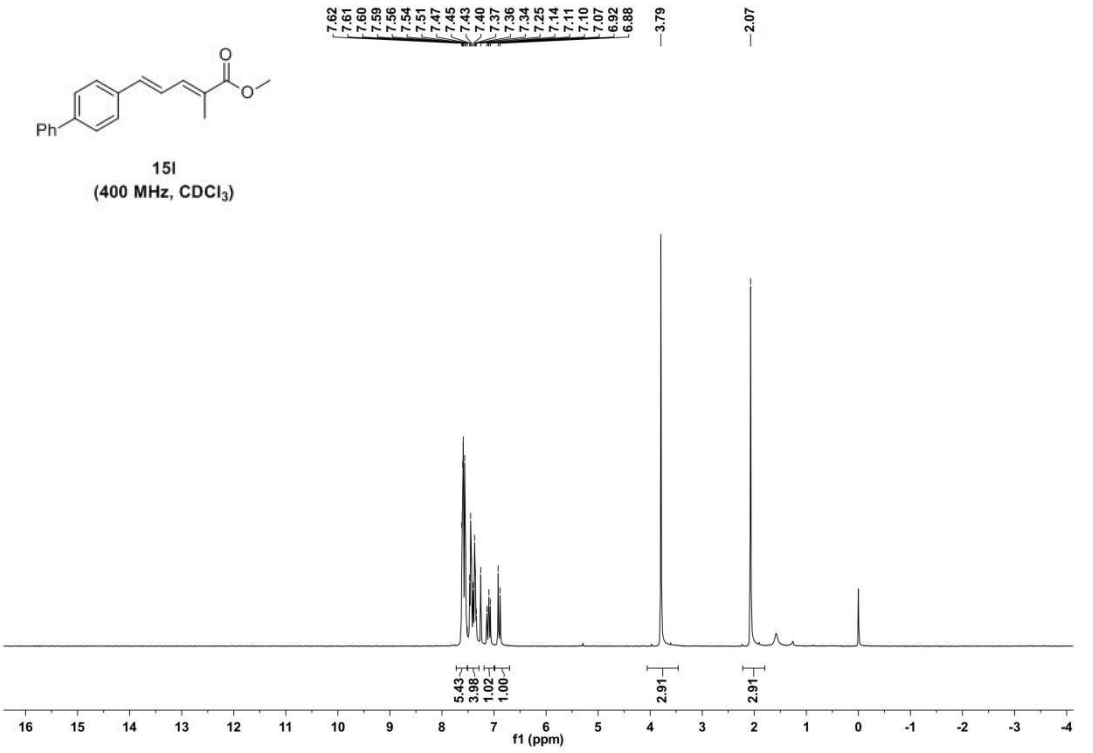

7.74
7.70
7.26 CDCl3
6.51
6.47
6.37
6.35
6.33
6.31
6.30
3.70
3.70
2.68
2.67
2.65
2.64
2.62
2.60
2.58
2.42
2.40
2.38
2.37
1.58 HDO
1.27
1.25
1.24
1.23
0.07
0.00
F3C
CF3
O
O
18k
(400 MHz, CDCl3)
3.04
1.01
1.02
2.79
2.10
1.03
2.86
f1 (ppm)

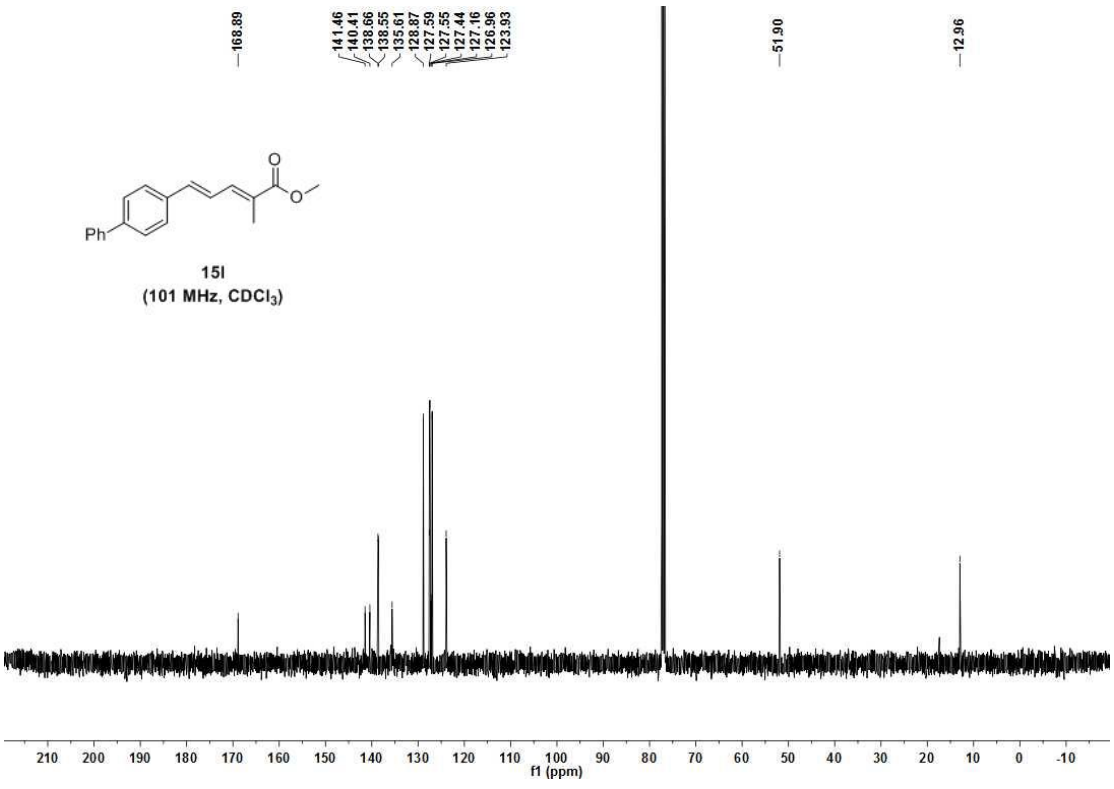

176.10
139.34
132.33
132.00
131.83
131.68
131.34
129.58
127.41
126.93
125.90
124.69
121.98
120.62
120.58
120.54
77.34 CDCl3
77.22
77.02 CDCl3
76.70 CDCl3
51.78
39.25
36.86
16.87
14.27
-0.01
F3C
CF3
O
O
18k
(101 MHz, CDCl3)
f1 (ppm)

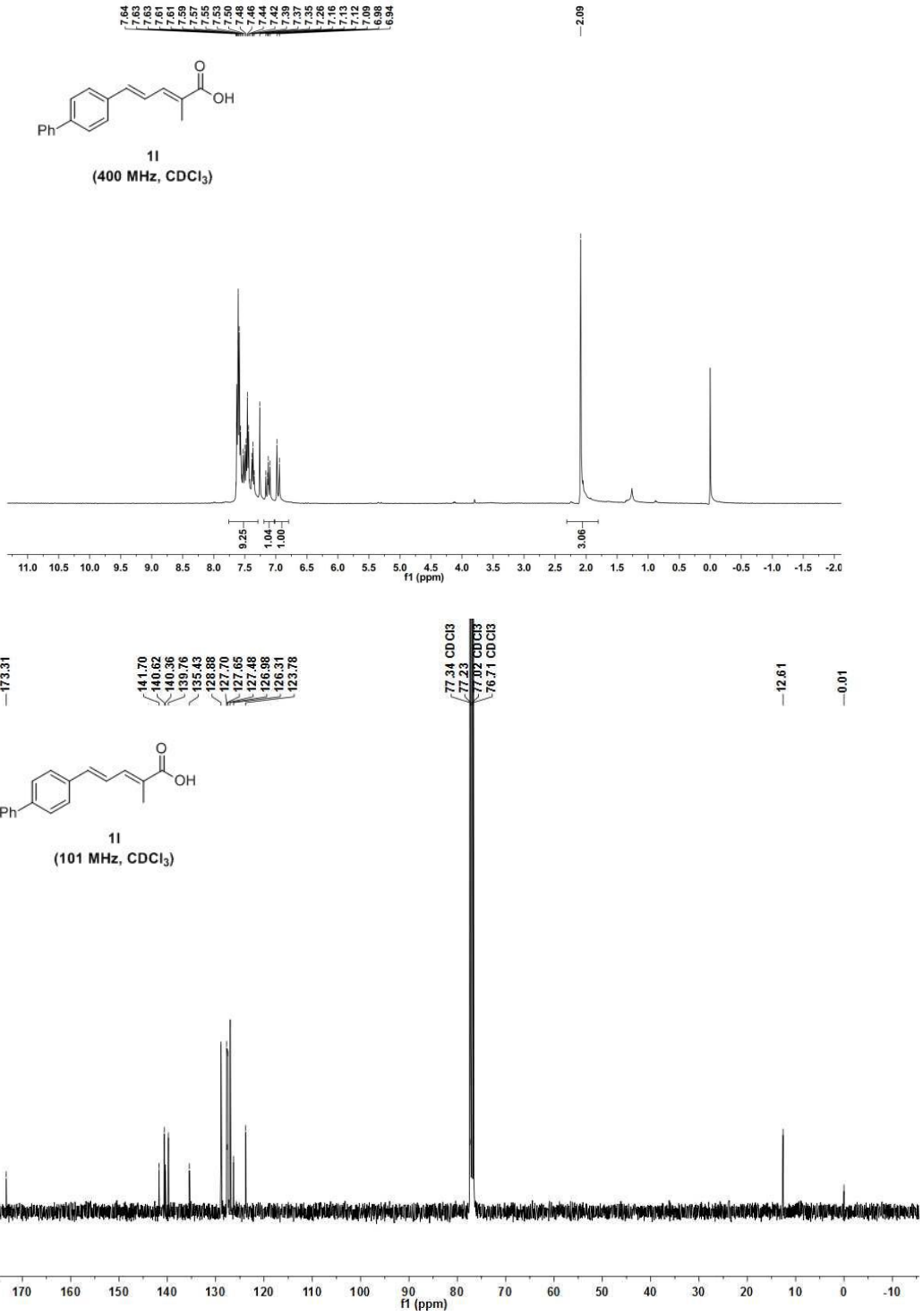

7.74
7.71
7.64
7.26 CDCl3
6.57
6.54
6.50
6.39
6.37
6.35
6.33
6.31
2.72
2.70
2.68
2.67
2.65
2.63
2.61
2.47
2.45
2.43
2.41
2.39
2.01
1.78 HDO
1.42
1.28
1.26
0.90
0.88
0.07
-0.00
F3C
CF3
O
OH
19k
(400 MHz, CDCl3)
2.85
1.09
1.04
2.13
1.12
3.77
f1 (ppm)
181.19
139.24
132.03
131.70
131.24
129.90
125.95
124.68
121.97
120.66
77.33 CDCl3
77.22
77.02 CDCl3
76.70 CDCl3
39.04
36.52
16.61
19k
(101 MHz, CDCl3)
f1 (ppm)

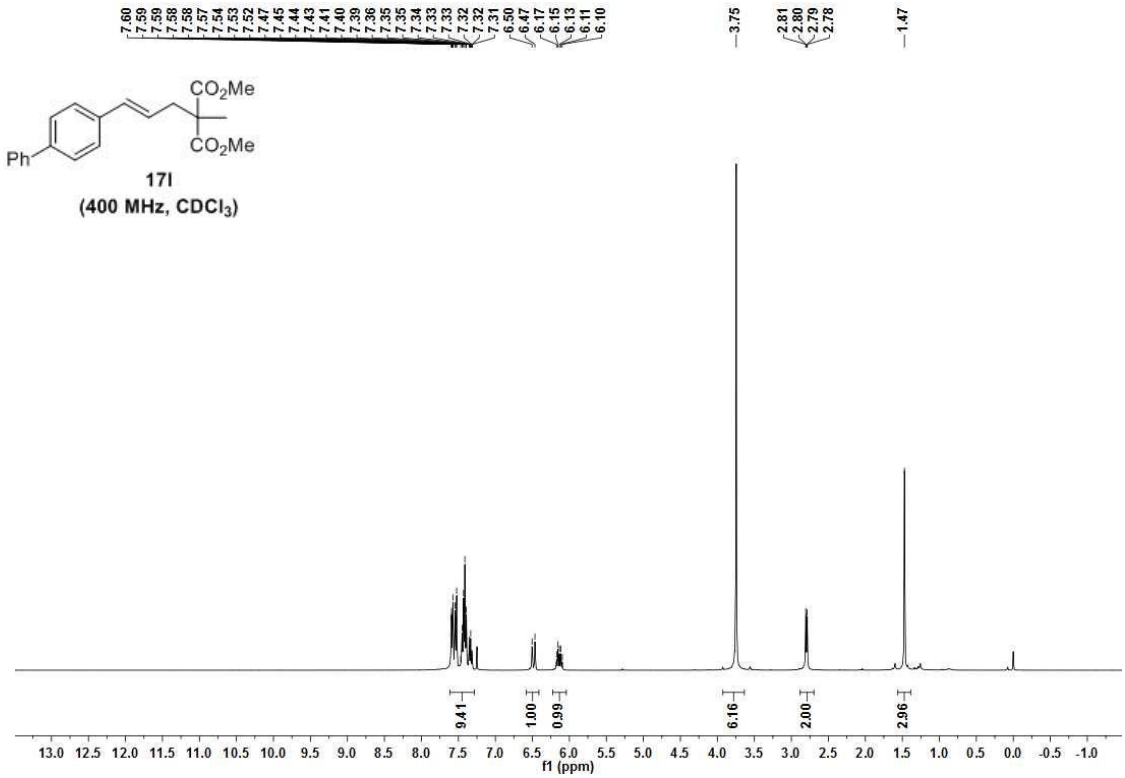

7.74
7.71
6.54
6.50
6.39
6.37
6.35
6.33
6.31
2.72
2.70
2.69
2.68
2.67
2.65
2.63
2.62
2.45
2.43
2.41
2.39
1.28
1.26
F3C
CO2H
CF3
(R)-2k
(400 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

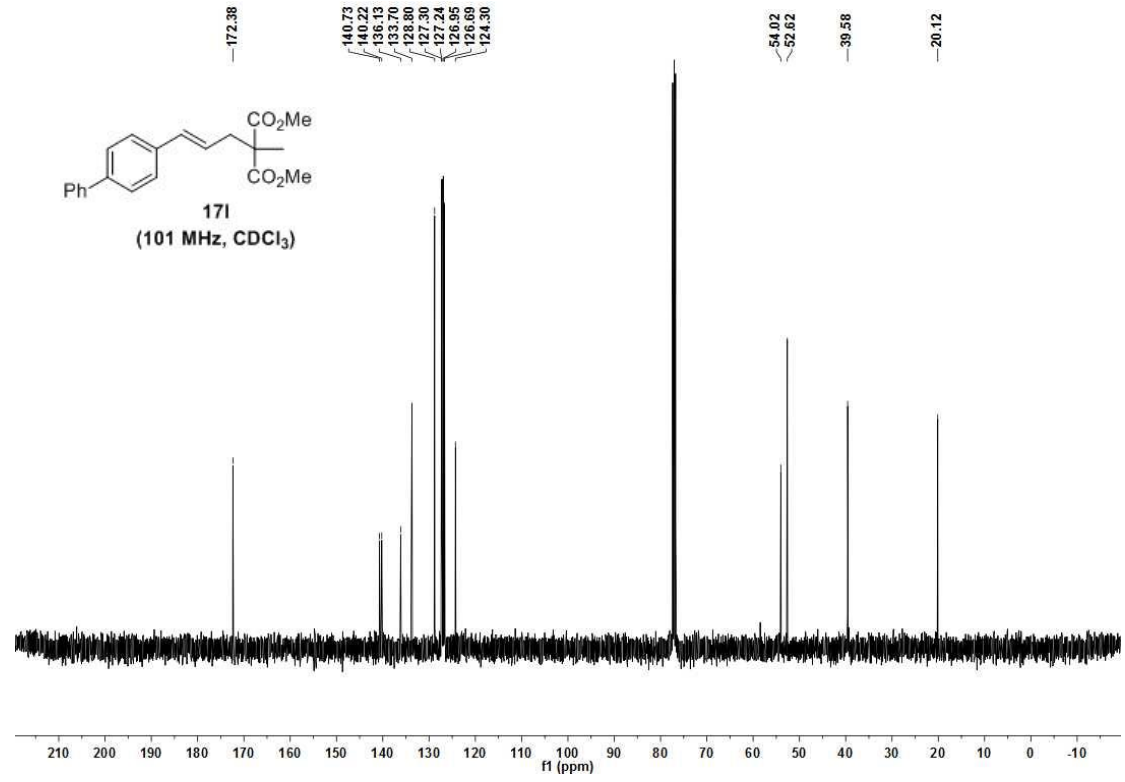

180.89
139.24
131.70
129.89
125.93
124.68
121.97
120.66
77.33
77.21
77.01
76.69
39.00
36.52
16.61
F3C
CO2H
CF3
(R)-2k
(101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

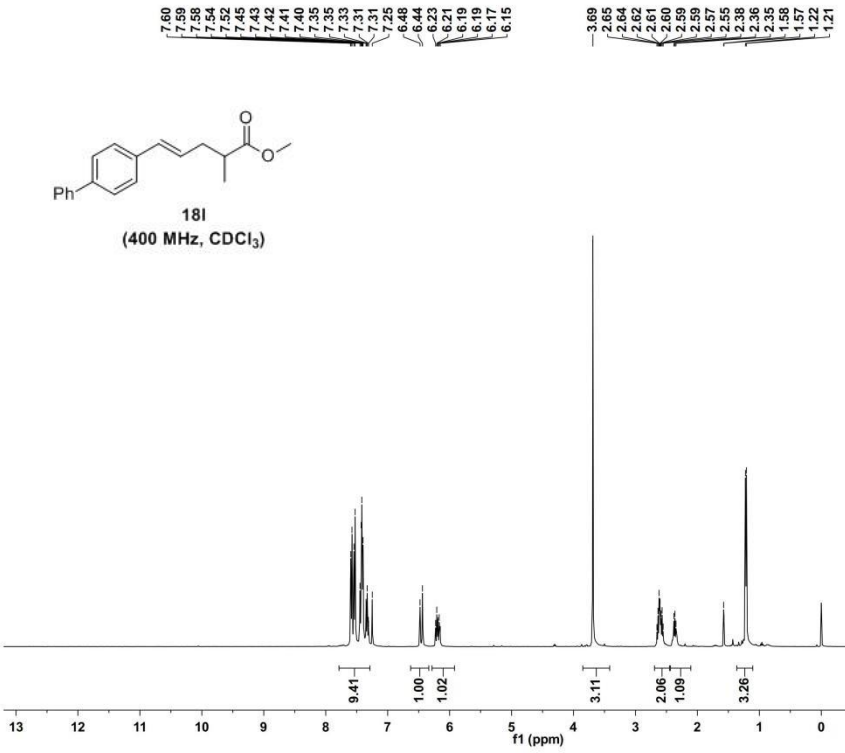

7.62
7.61
7.60
7.59
7.56
7.54
7.51
7.47
7.45
7.43
7.40
7.37
7.36
7.34
7.25
7.14
7.11
7.10
7.07
6.92
6.88
3.79
2.07
O
O
Ph
15l
(400 MHz, CDCl3)
5.43
3.98
1.02
1.00
2.91
2.91
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

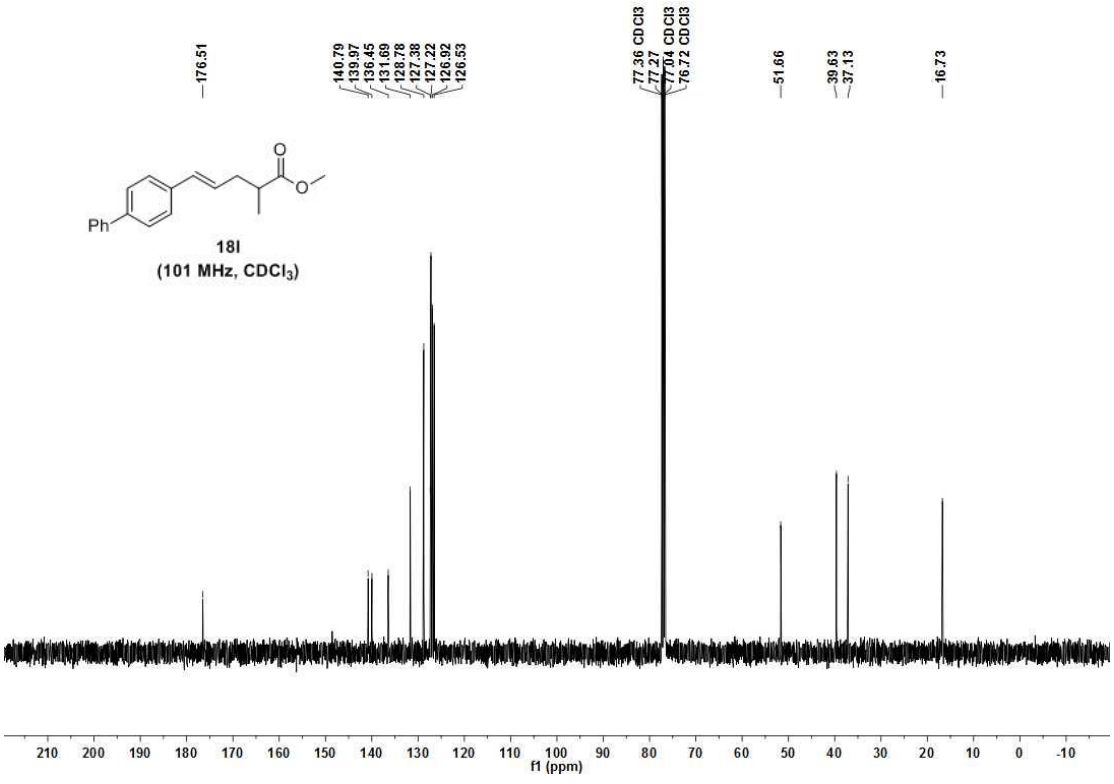

168.89
141.46
140.41
138.66
138.55
135.61
128.87
127.59
127.55
127.44
127.16
126.96
123.93
51.90
12.96
O
O
Ph
15l
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

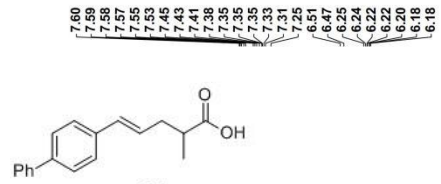

7.64
7.63
7.63
7.61
7.61
7.59
7.57
7.55
7.53
7.50
7.48
7.46
7.44
7.42
7.39
7.37
7.35
7.26
7.16
7.13
7.12
7.09
6.98
6.94
2.09
O
OH
Ph
1l
(400 MHz, CDCl3)
9.25
1.04
1.00
3.06
f1 (ppm)
173.31
141.70
140.62
140.36
139.76
135.43
128.88
127.70
127.65
127.48
126.98
126.31
123.78
77.34 CDCl3
77.23
77.02 CDCl3
76.71 CDCl3
12.61
0.01
O
OH
Ph
1l
(101 MHz, CDCl3)
f1 (ppm)


7.60
7.59
7.59
7.58
7.58
7.57
7.54
7.53
7.52
7.47
7.45
7.44
7.43
7.41
7.40
7.39
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
6.50
6.47
6.17
6.15
6.13
6.11
6.10
3.75
2.81
2.80
2.79
2.78
1.47
CO2Me
CO2Me
Ph
17l
(400 MHz, CDCl3)
9.41
1.00
0.99
6.16
2.00
2.96
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

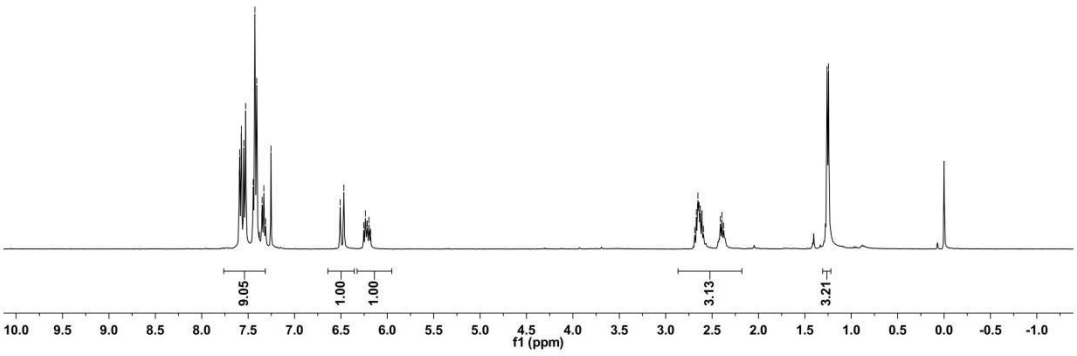

172.38
140.73
140.22
136.13
133.70
128.80
127.30
127.24
126.95
126.69
124.30
54.02
52.62
39.58
20.12
CO2Me
CO2Me
Ph
17l
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

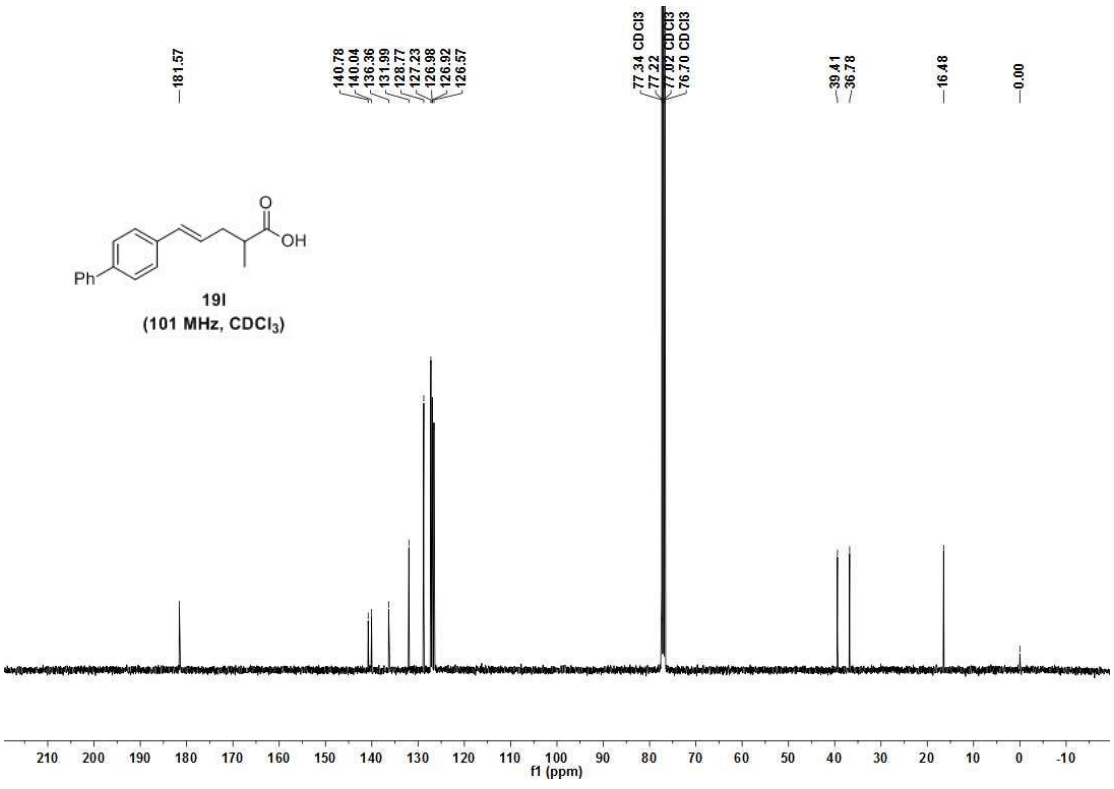

7.60
7.59
7.58
7.54
7.52
7.45
7.43
7.42
7.41
7.40
7.35
7.33
7.31
7.25
6.48
6.44
6.23
6.21
6.19
6.19
6.17
6.15
3.69
2.65
2.64
2.62
2.61
2.60
2.59
2.59
2.57
2.55
2.38
2.36
2.35
1.58
1.57
1.22
1.21
O
O
Ph
18l
(400 MHz, CDCl3)
9.41
1.00
1.02
3.11
2.06
1.09
3.26
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


176.51
140.79
139.97
136.45
131.69
128.78
127.38
127.22
126.92
126.53
77.36 CDCl3
77.27
77.04 CDCl3
76.72 CDCl3
51.66
39.63
37.13
16.73
O
O
Ph
18l
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

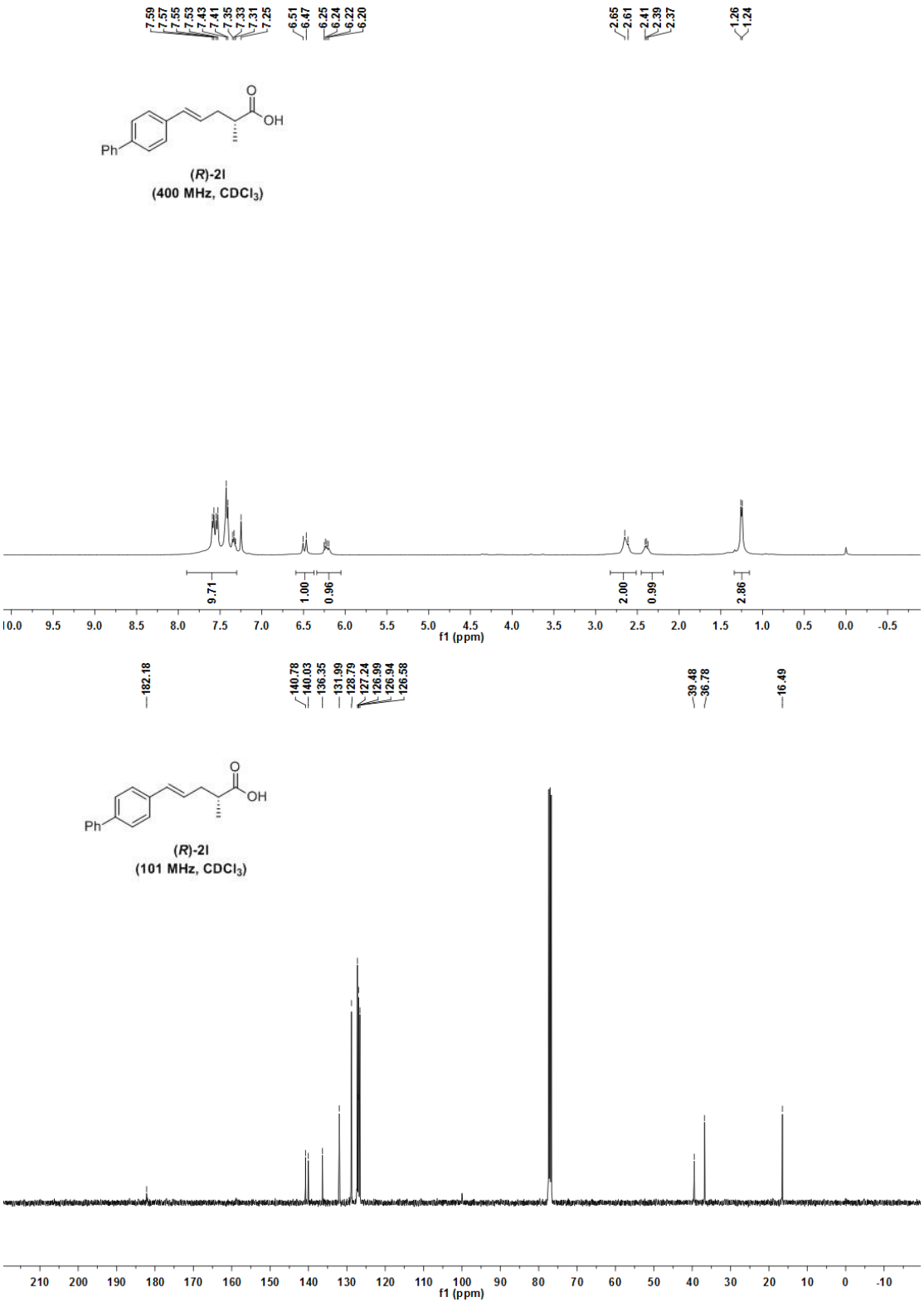


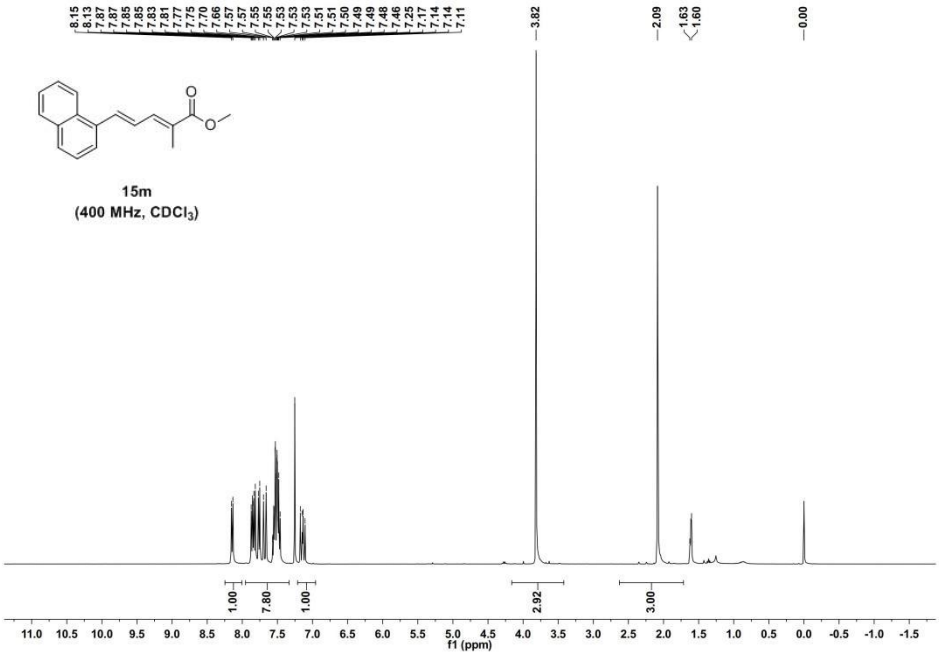
19l
(400 MHz, $CDCl_3$)

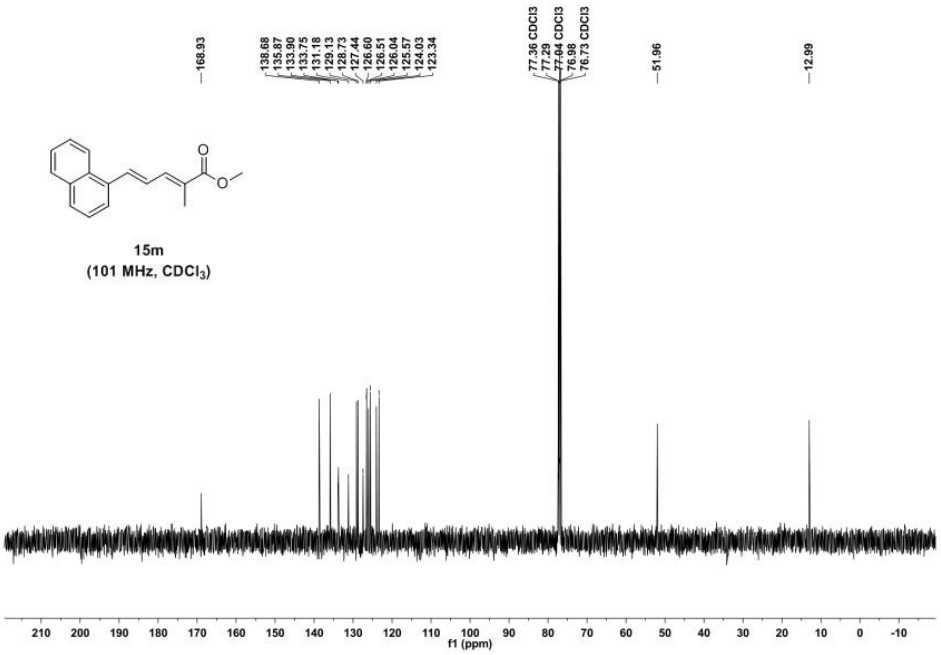


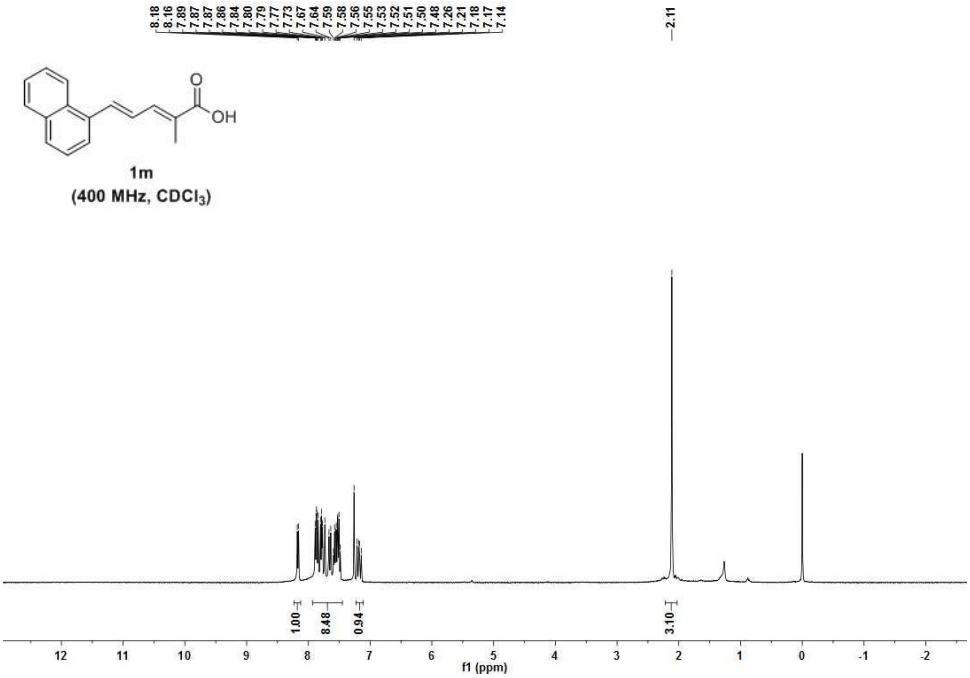


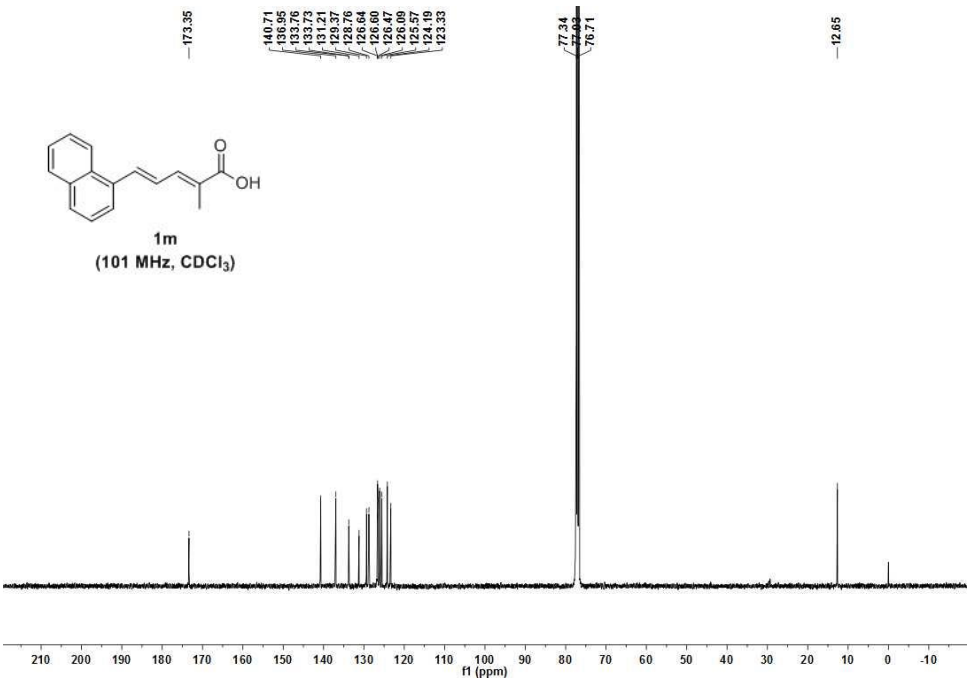
19l
(101 MHz, $CDCl_3$)

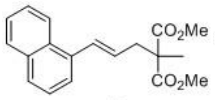

7.59
7.57
7.55
7.53
7.43
7.41
7.35
7.33
7.31
7.25
6.51
6.47
6.25
6.24
6.22
6.20
2.65
2.61
2.41
2.39
2.37
1.26
1.24
O
OH
Ph
(R)-2l
(400 MHz, CDCl3)
9.71
1.00
0.96
2.00
0.99
2.86
f1 (ppm)
182.18
140.78
140.03
136.35
131.99
128.79
127.24
126.99
126.94
126.58
39.48
36.78
16.49
O
OH
Ph
(R)-2l
(101 MHz, CDCl3)
f1 (ppm)


8.15
8.13
7.87
7.87
7.85
7.85
7.83
7.81
7.77
7.75
7.70
7.66
7.57
7.57
7.55
7.55
7.53
7.53
7.53
7.51
7.51
7.50
7.49
7.49
7.48
7.46
7.25
7.17
7.14
7.14
7.11
3.82
2.09
1.63
1.60
0.00
O
O
15m
(400 MHz, CDCl3)
1.00
7.80
1.00
2.92
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

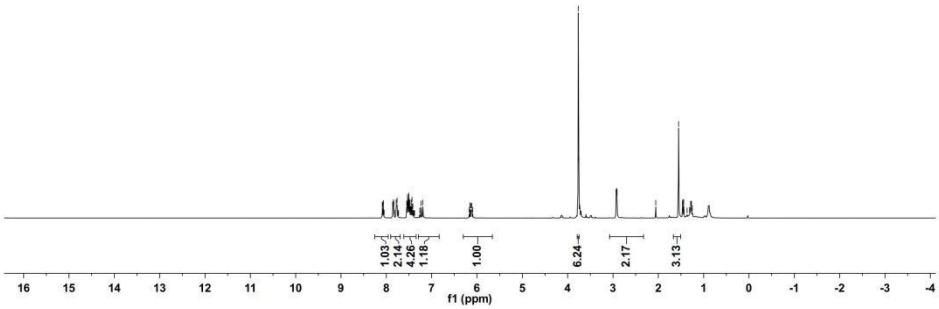

168.93
138.68
135.87
133.90
133.75
131.18
129.13
128.73
127.44
126.60
126.51
126.04
125.57
124.03
123.34
77.36 CDCl3
77.29
77.04 CDCl3
76.98
76.73 CDCl3
51.96
12.99
O
O
15m
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

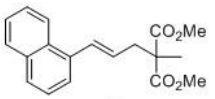

8.18
8.16
7.89
7.87
7.86
7.84
7.80
7.79
7.77
7.73
7.67
7.64
7.59
7.58
7.56
7.55
7.53
7.52
7.51
7.50
7.48
7.26
7.21
7.19
7.17
7.14
2.11
O
OH
1m
(400 MHz, CDCl3)
1.00
8.48
0.94
3.10
f1 (ppm)


173.35
140.71
136.95
133.76
133.73
131.21
129.37
128.76
126.64
126.60
126.47
126.09
125.57
124.19
123.33
77.34
77.03
76.71
12.85
O
OH
1m
(101 MHz, CDCl3)
f1 (ppm)

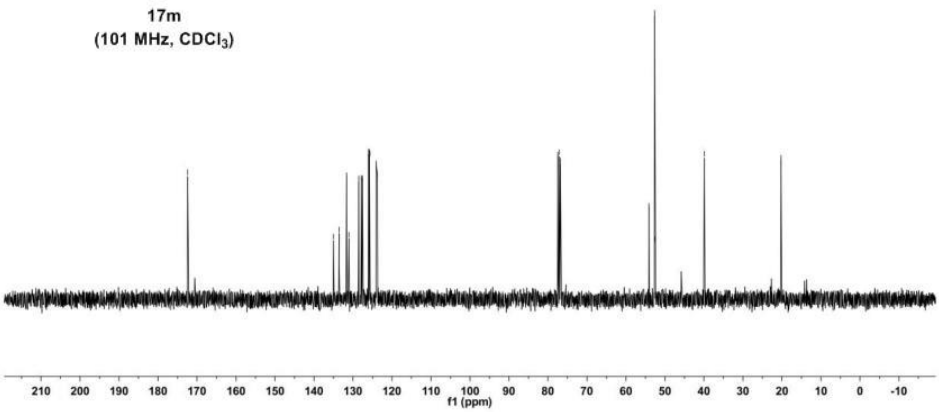


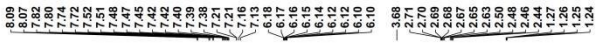
17m
(400 MHz, $CDCl_3$)

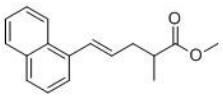




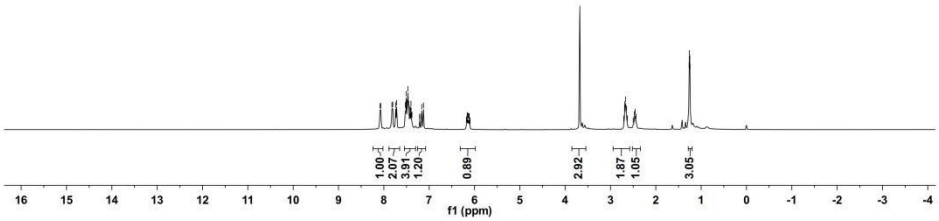
17m
(101 MHz, $CDCl_3$)

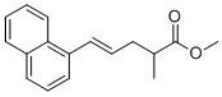




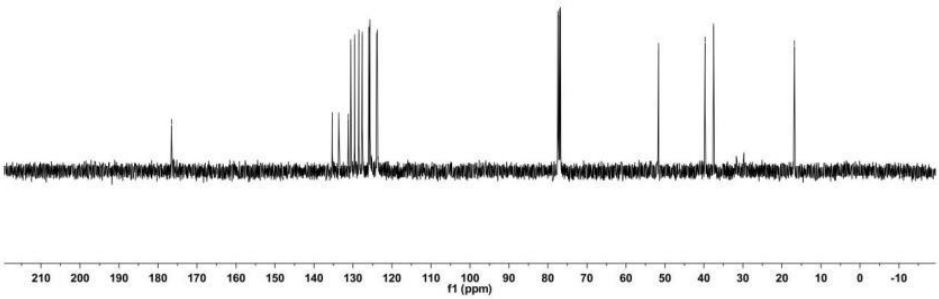


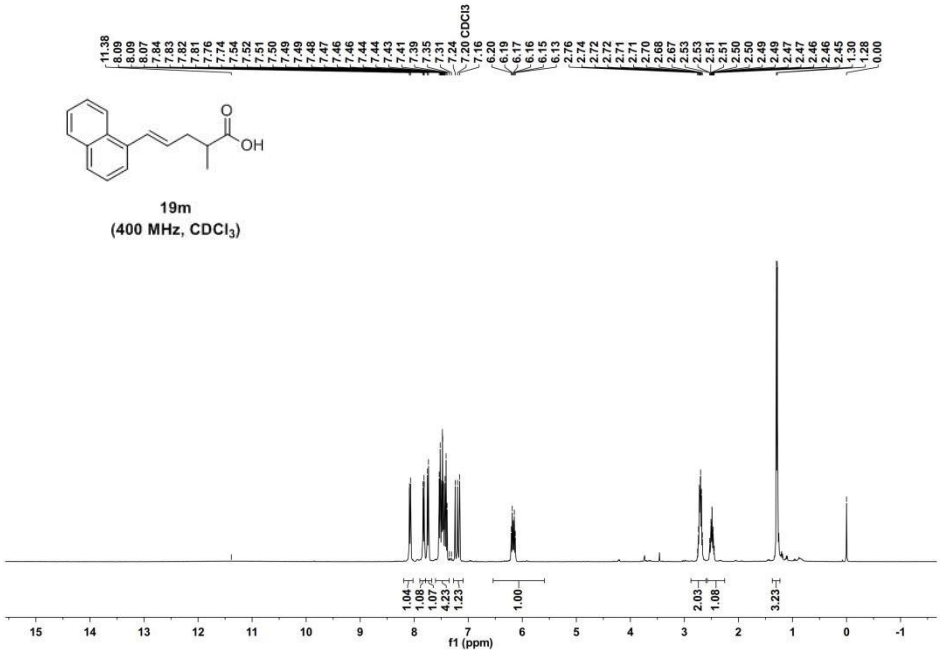
18m
(400 MHz, $CDCl_3$)

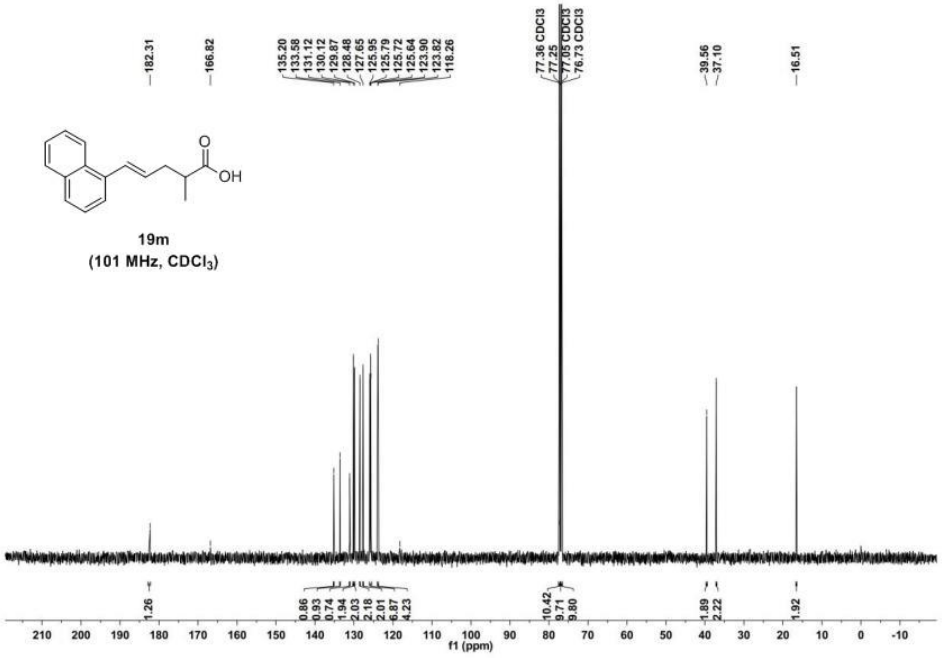


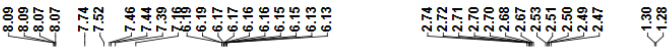


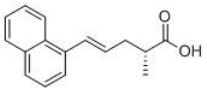
18m
(101 MHz, $CDCl_3$)



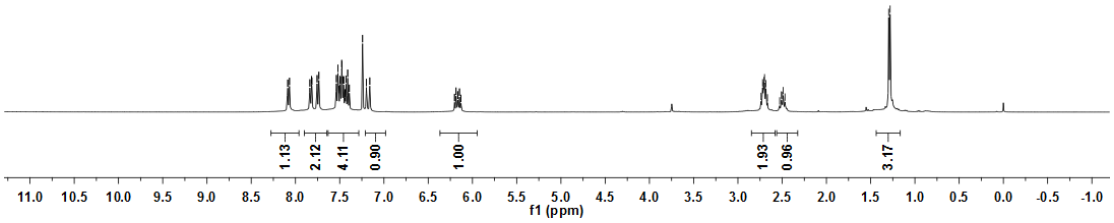

11.38
8.09
8.09
8.07
7.84
7.83
7.82
7.81
7.76
7.74
7.54
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.46
7.46
7.44
7.44
7.43
7.41
7.39
7.35
7.31
7.24
7.20 CDCl3
7.16
6.20
6.19
6.17
6.16
6.15
6.13
2.76
2.74
2.72
2.72
2.71
2.71
2.70
2.68
2.67
2.53
2.53
2.51
2.51
2.50
2.50
2.49
2.49
2.47
2.47
2.46
2.46
2.45
1.30
1.28
0.00
O
OH
19m
(400 MHz, CDCl3)
1.04
1.09
1.07
4.23
1.23
1.00
2.03
1.08
3.23
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

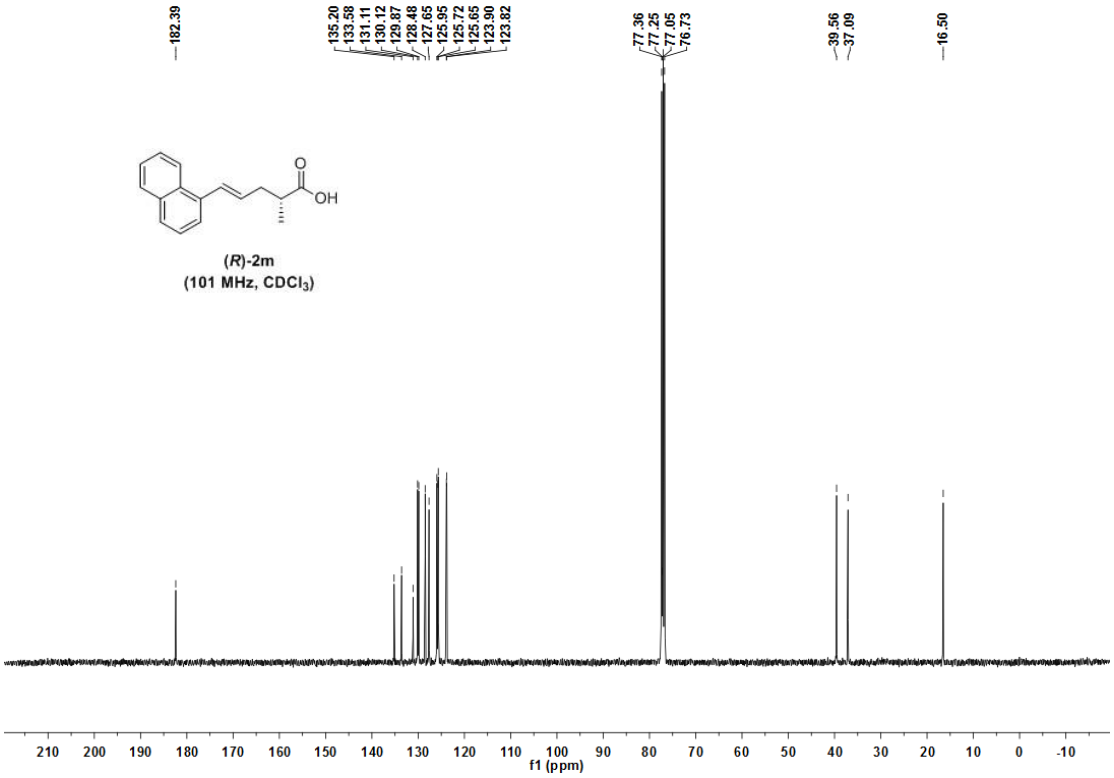

182.31
166.82
135.20
133.58
131.12
130.13
129.87
128.48
127.65
125.95
125.79
125.72
125.64
123.90
123.82
116.26
77.36 CDCl3
77.25
77.05 CDCl3
76.73 CDCl3
39.56
37.10
16.51
O
OH
19m
(101 MHz, CDCl3)
1.26
0.86
0.93
0.74
1.94
2.03
2.18
2.01
6.87
4.23
10.42
9.71
9.80
1.89
2.22
1.92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



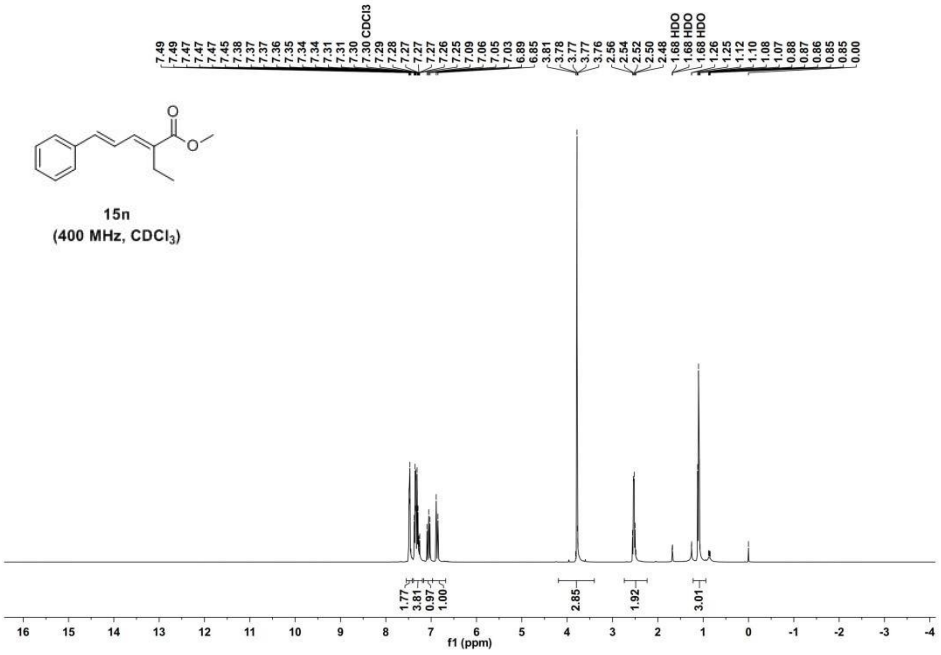


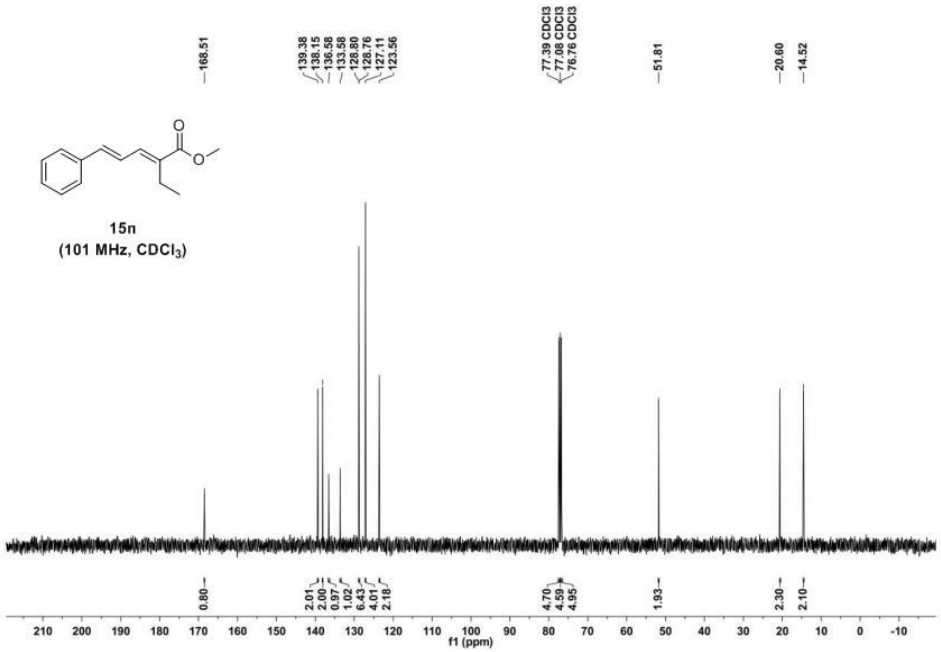
(*R*)-2m
(400 MHz, $CDCl_3$)

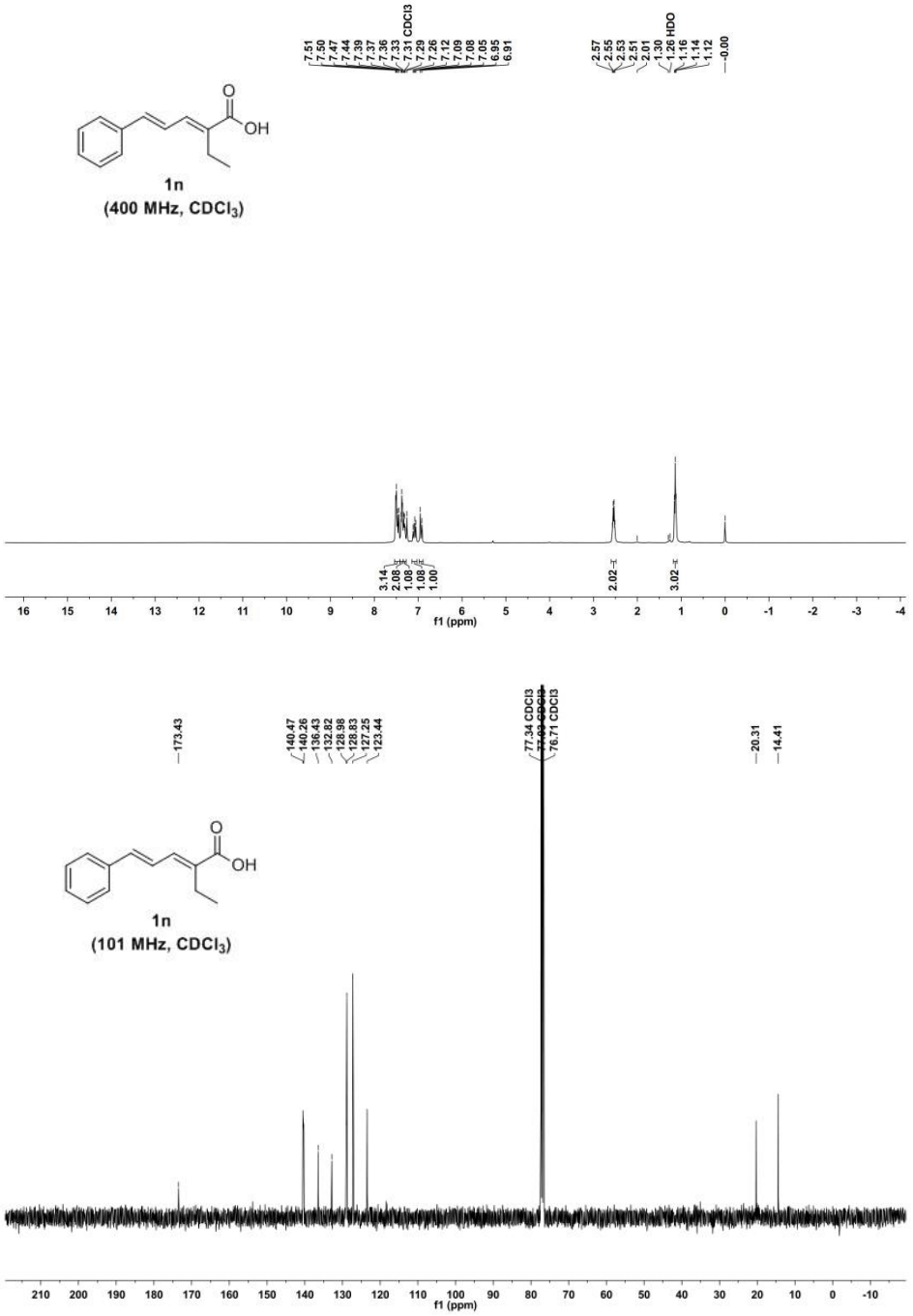


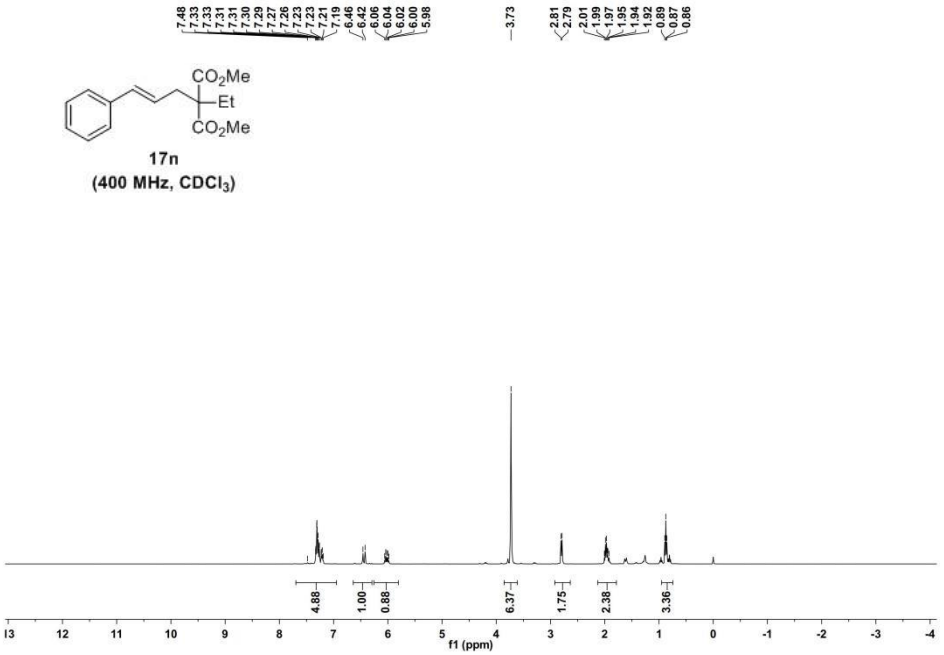


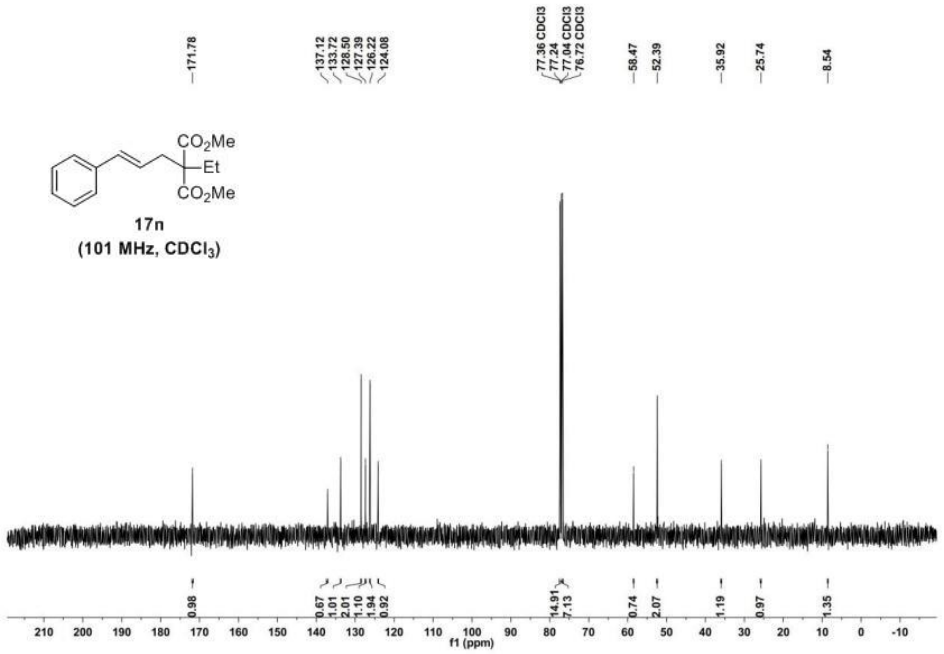
(*R*)-2m
(101 MHz, $CDCl_3$)

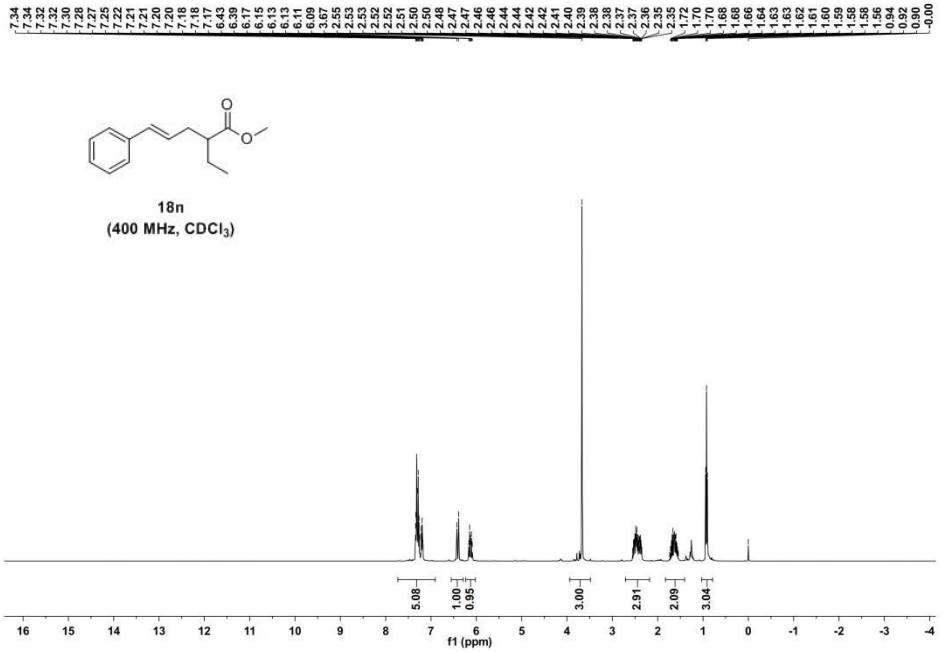

7.49
7.49
7.47
7.47
7.47
7.45
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.31
7.31
7.30
7.30 CDCl3
7.29
7.28
7.27
7.27
7.27
7.26
7.25
7.09
7.06
7.05
7.03
6.89
6.85
3.81
3.78
3.77
3.77
3.76
2.56
2.54
2.52
2.50
2.48
1.68 HDO
1.68 HDO
1.68 HDO
1.26
1.25
1.23
1.10
1.08
1.07
0.88
0.87
0.86
0.85
0.85
0.00
O
O
15n
(400 MHz, CDCl3)
1.77
3.81
0.97
1.00
2.85
1.92
3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

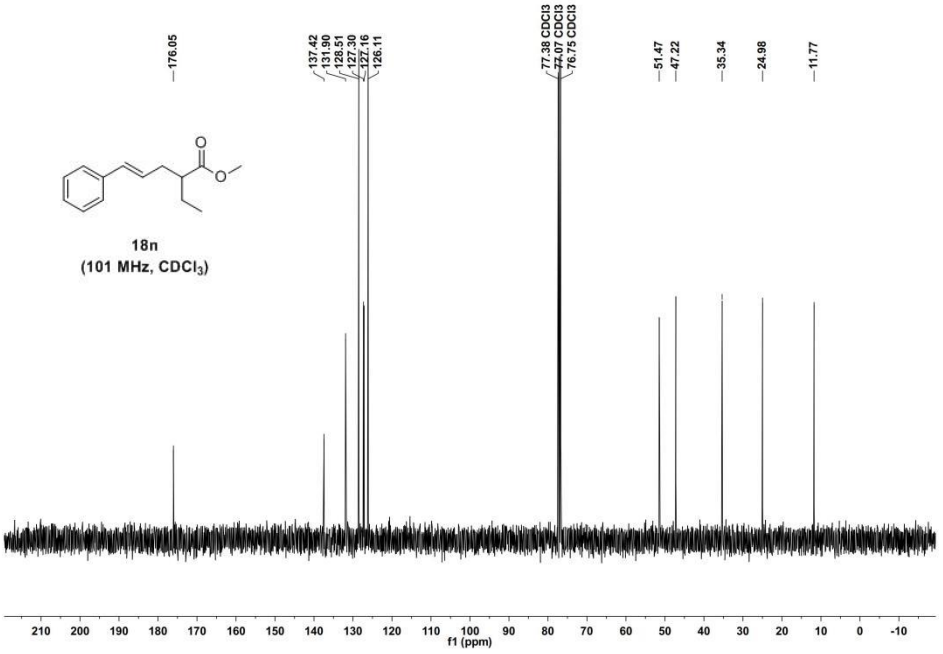

168.51
139.38
138.15
136.58
133.58
128.80
128.76
127.11
123.56
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
51.81
20.60
14.52
O
O
15n
(101 MHz, CDCl3)
0.80
2.01
2.00
0.97
1.02
6.43
4.01
2.18
4.70
4.59
4.55
1.93
2.30
2.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

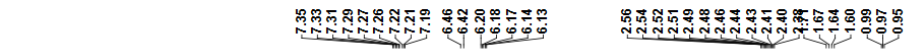

7.51
7.50
7.47
7.44
7.39
7.37
7.36
7.33
7.31 CDCl3
7.29
7.26
7.12
7.09
7.08
7.05
6.95
6.91
2.57
2.55
2.53
2.51
2.01
1.30
1.26 HDO
1.16
1.14
1.12
-0.00
O
OH
1n
(400 MHz, CDCl3)
3.14
2.08
1.08
1.08
1.00
2.02
3.02
f1 (ppm)
173.43
140.47
140.26
136.43
132.82
128.98
128.83
127.25
123.44
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
20.31
14.41
O
OH
1n
(101 MHz, CDCl3)
f1 (ppm)

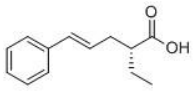

7.48
7.33
7.33
7.31
7.31
7.30
7.29
7.27
7.26
7.23
7.23
7.21
7.19
6.46
6.42
6.06
6.04
6.02
6.00
5.98
3.73
2.81
2.79
2.01
1.99
1.97
1.95
1.94
1.92
0.89
0.87
0.86
CO2Me
Et
CO2Me
17n
(400 MHz, CDCl3)
4.88
1.00
0.88
6.37
1.75
2.38
3.36
f1 (ppm)


171.78
137.12
133.72
128.50
127.39
126.22
124.08
77.36 CDCl3
77.24
77.04 CDCl3
76.72 CDCl3
58.47
52.39
35.92
25.74
8.54
CO2Me
Et
CO2Me
17n
(101 MHz, CDCl3)
0.98
0.67
1.01
2.01
1.10
1.94
0.92
14.91
7.13
0.74
2.07
1.19
0.97
1.35
f1 (ppm)

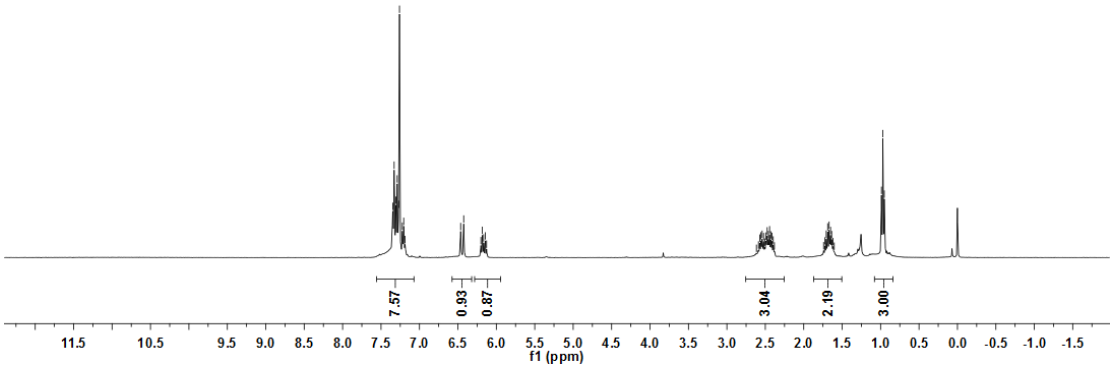

18n
(400 MHz, CDCl3)
5.08
1.00
0.95
3.00
2.91
2.09
3.04
f1 (ppm)

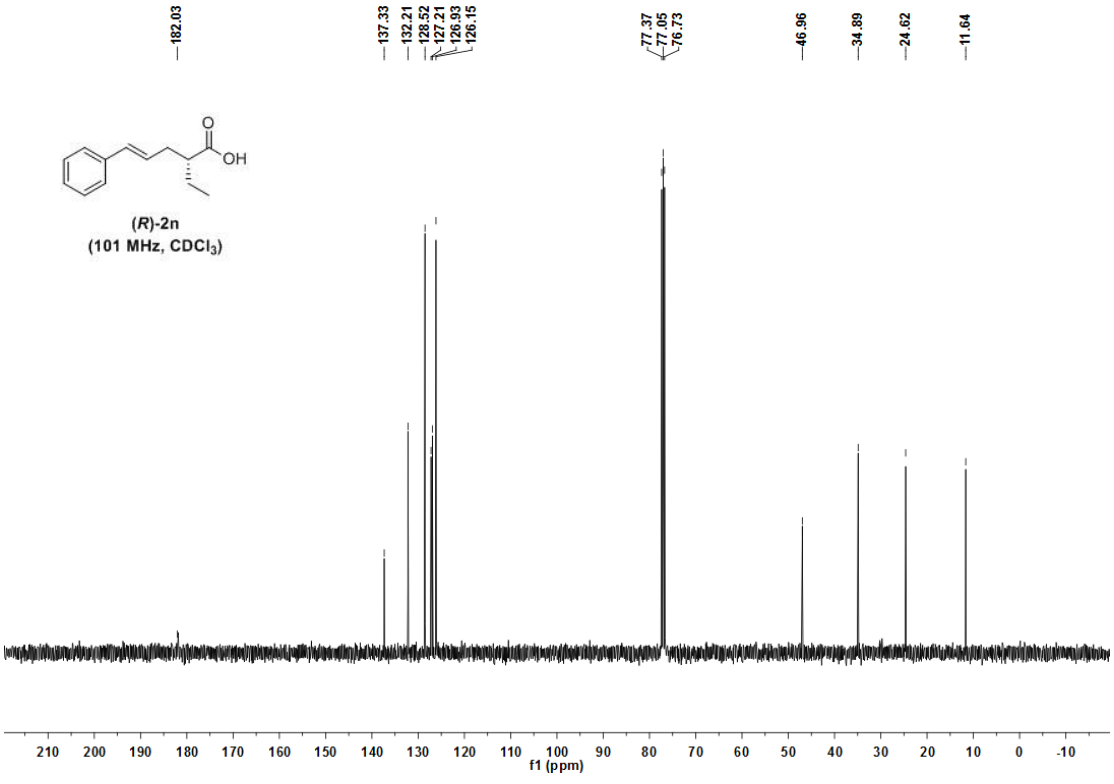

176.05
137.42
131.90
128.51
127.30
127.16
126.11
77.38 CDCl3
77.07 CDCl3
76.75 CDCl3
51.47
47.22
35.34
24.98
11.77
18n
(101 MHz, CDCl3)
f1 (ppm)



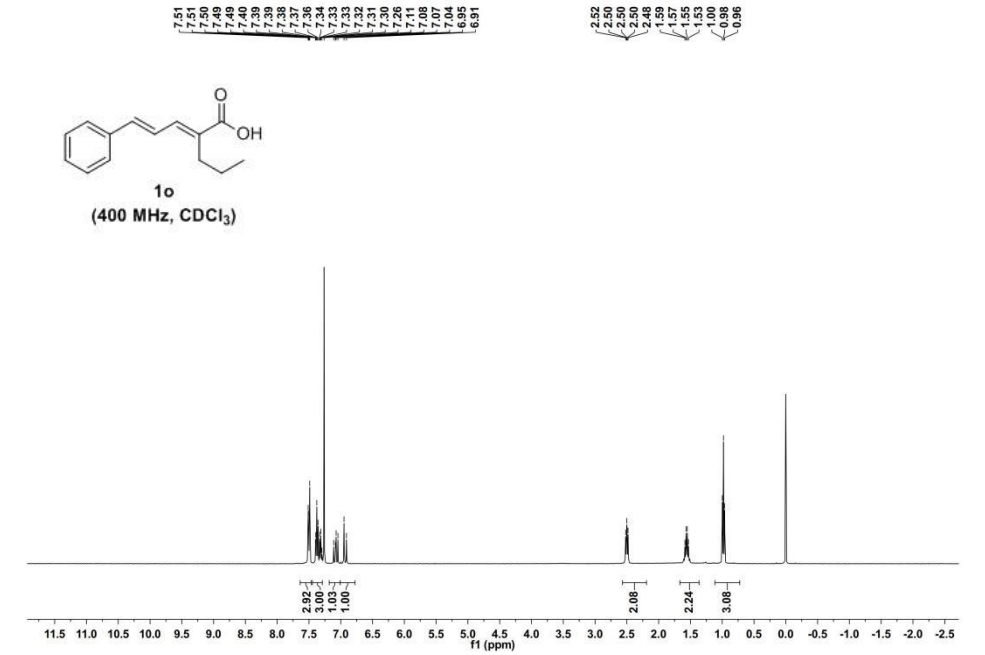


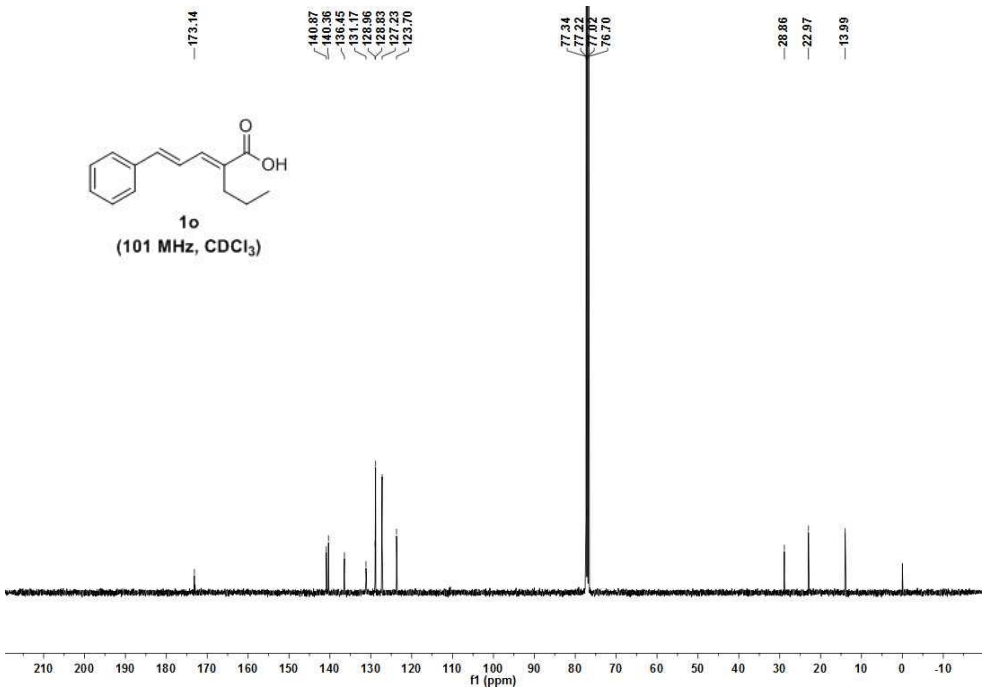
(*R*)-2n
(400 MHz, $CDCl_3$)

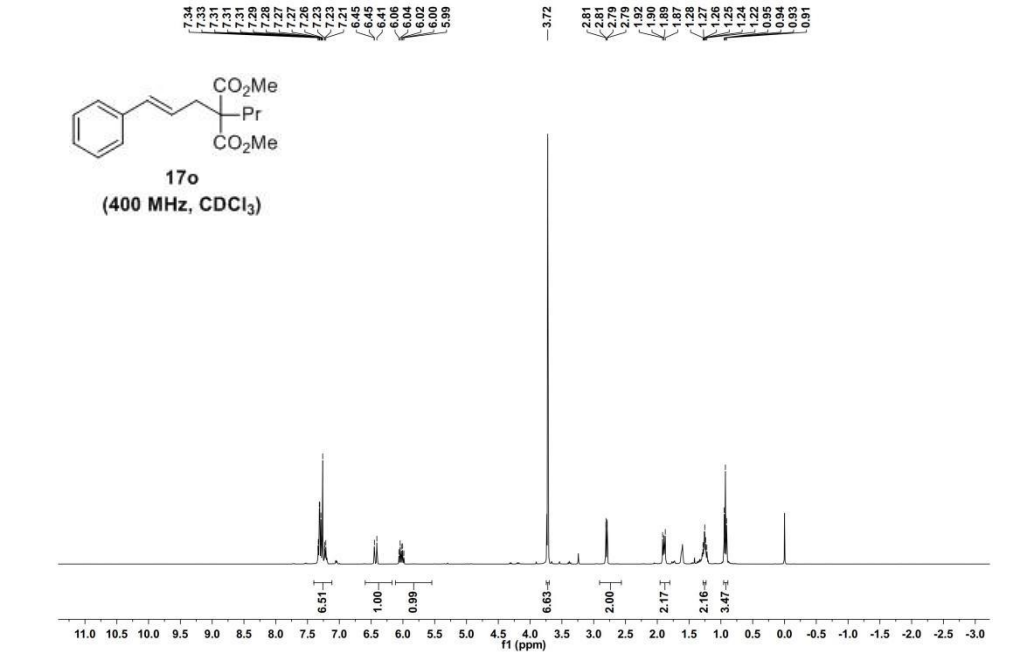


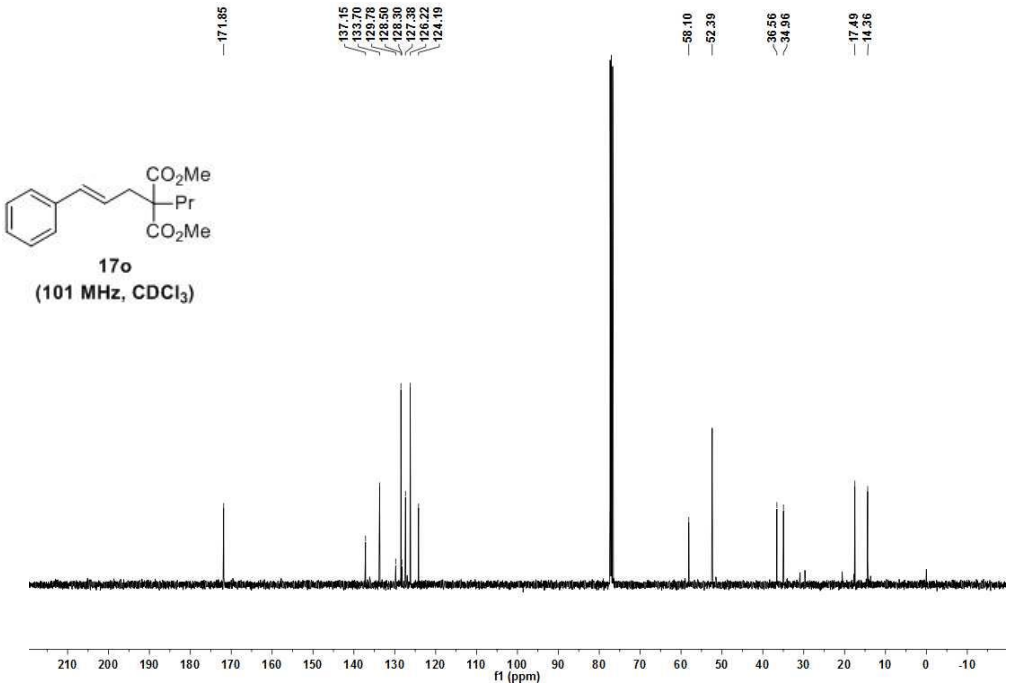


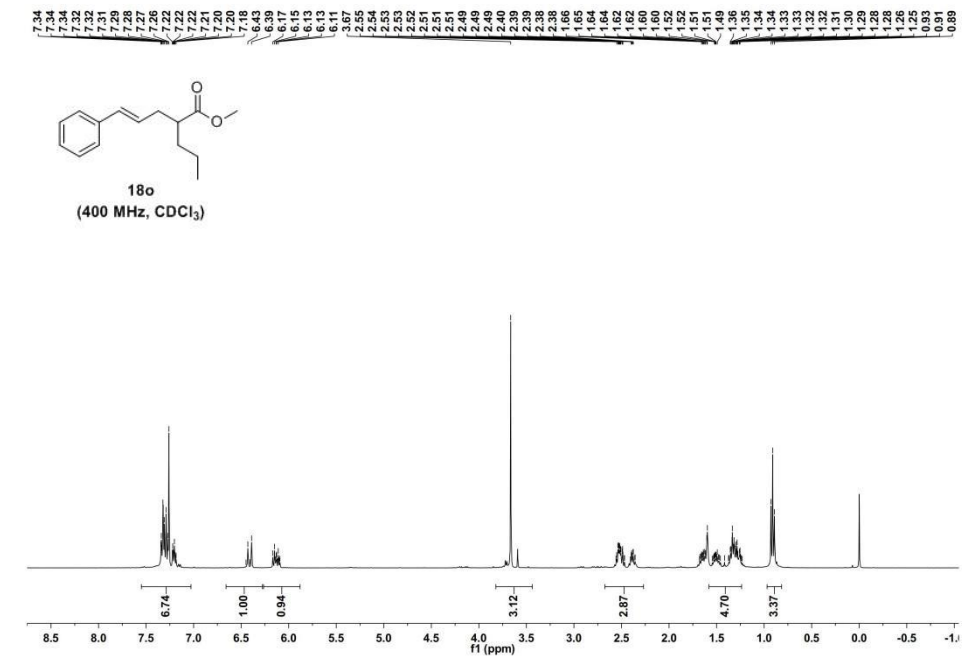
(*R*)-2n
(101 MHz, $CDCl_3$)

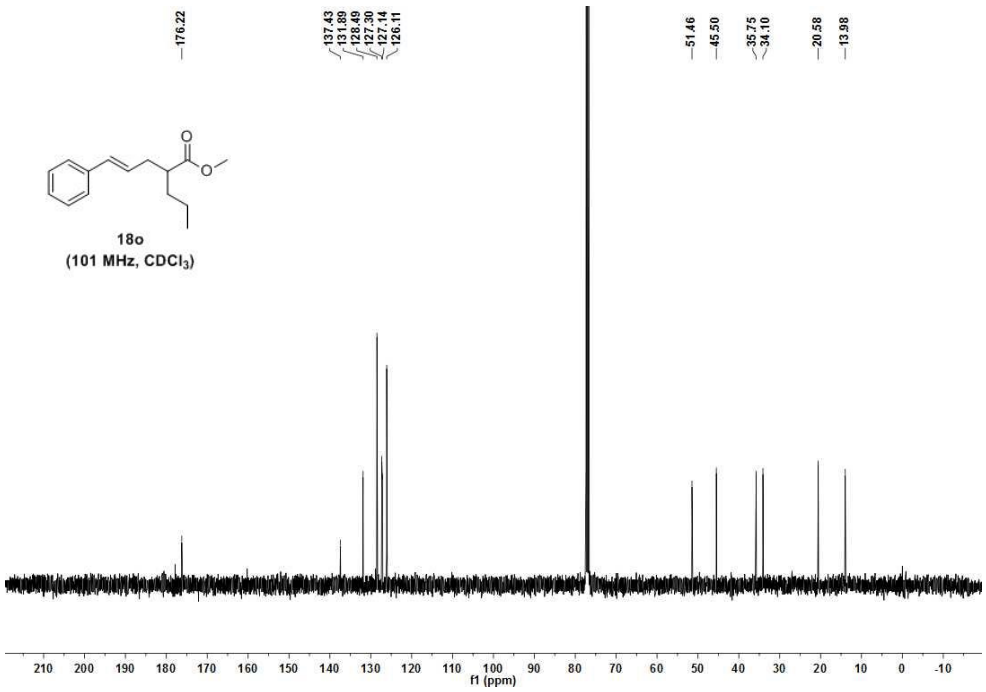

7.51
7.51
7.50
7.49
7.40
7.39
7.39
7.38
7.37
7.36
7.34
7.33
7.33
7.32
7.31
7.30
7.26
7.11
7.08
7.07
7.04
6.95
6.91
2.52
2.50
2.50
2.50
2.48
1.59
1.57
1.55
1.53
1.00
0.98
0.96
O
OH
1o
(400 MHz, CDCl3)
2.92
3.00
1.03
1.00
2.08
2.24
3.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)

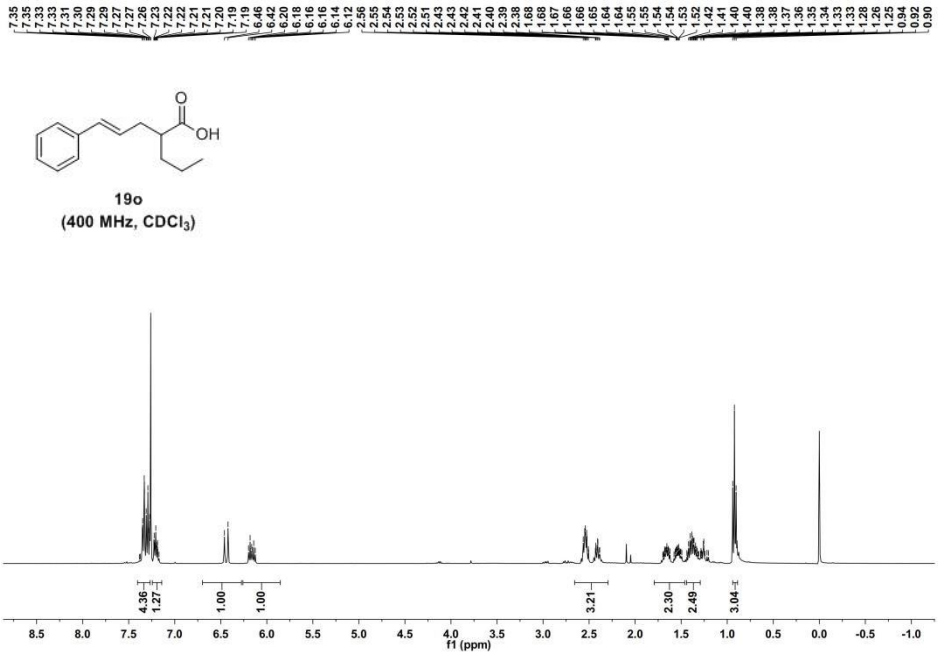

173.14
140.87
140.36
136.45
131.17
128.96
128.83
127.23
123.70
77.34
77.22
77.02
76.70
28.86
22.97
13.99
O
OH
1o
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

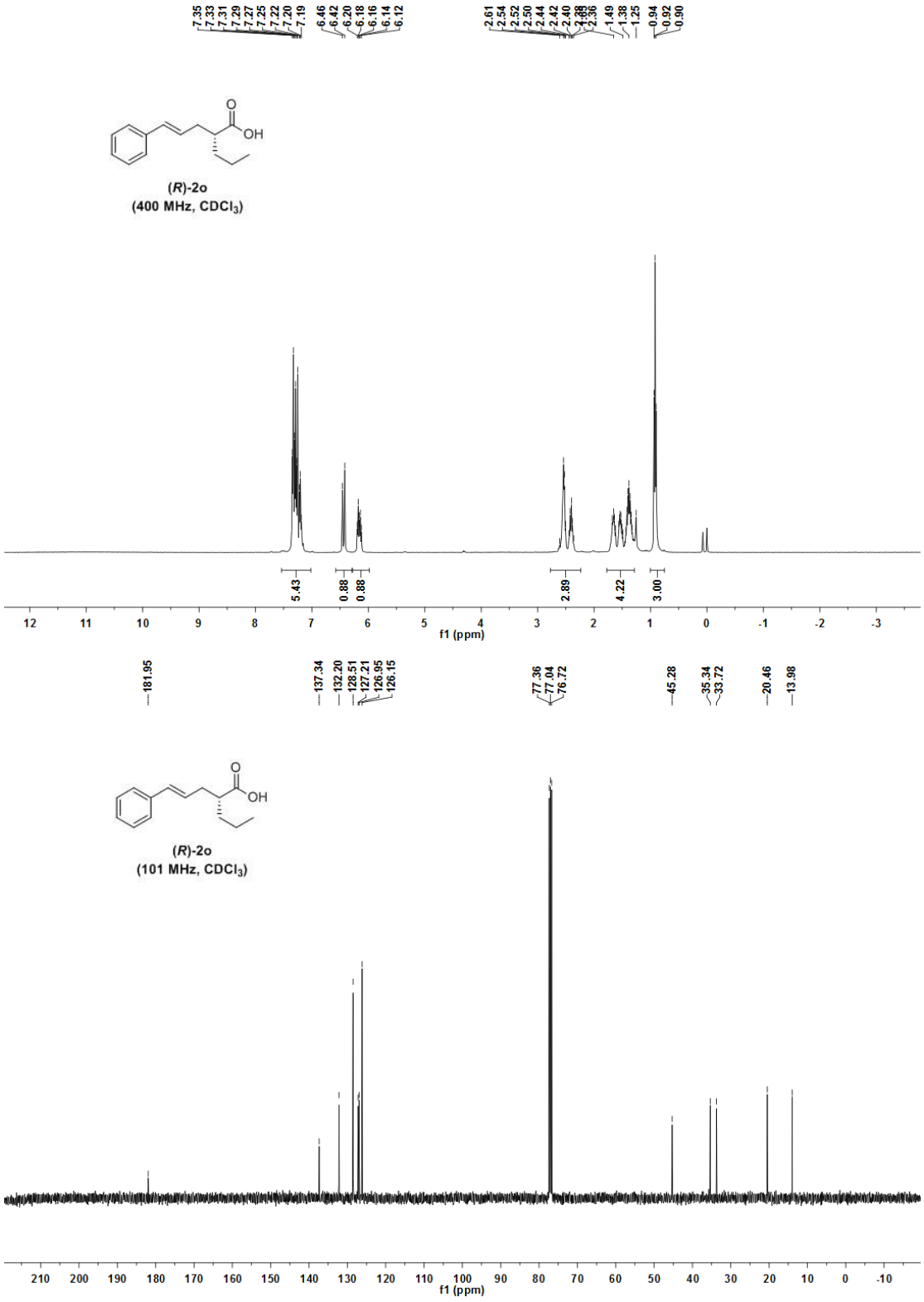

7.34
7.33
7.31
7.31
7.31
7.29
7.28
7.27
7.27
7.26
7.23
7.21
6.45
6.41
6.06
6.04
6.02
6.00
5.99
3.72
2.81
2.81
2.79
2.79
1.92
1.90
1.89
1.87
1.28
1.27
1.26
1.25
1.24
1.22
0.95
0.94
0.93
0.91
CO2Me
Pr
CO2Me
17o
(400 MHz, CDCl3)
6.51
1.00
0.99
6.63
2.00
2.17
2.16
3.47
f1 (ppm)

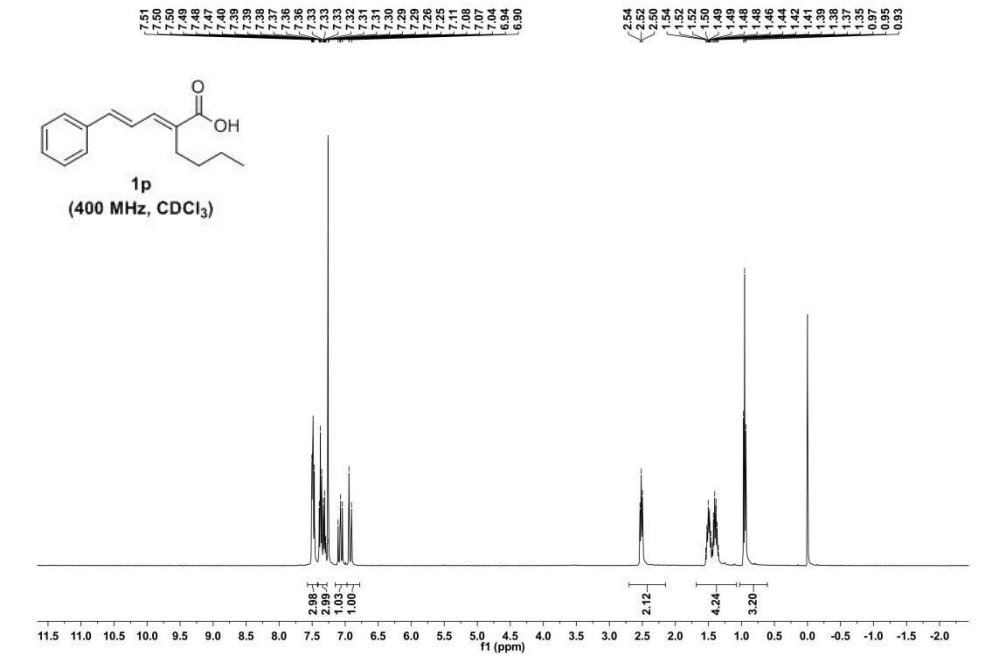

171.85
137.15
133.70
129.78
128.50
128.30
127.38
126.22
124.19
58.10
52.39
36.56
34.96
17.49
14.36
CO2Me
Pr
CO2Me
17o
(101 MHz, CDCl3)
f1 (ppm)

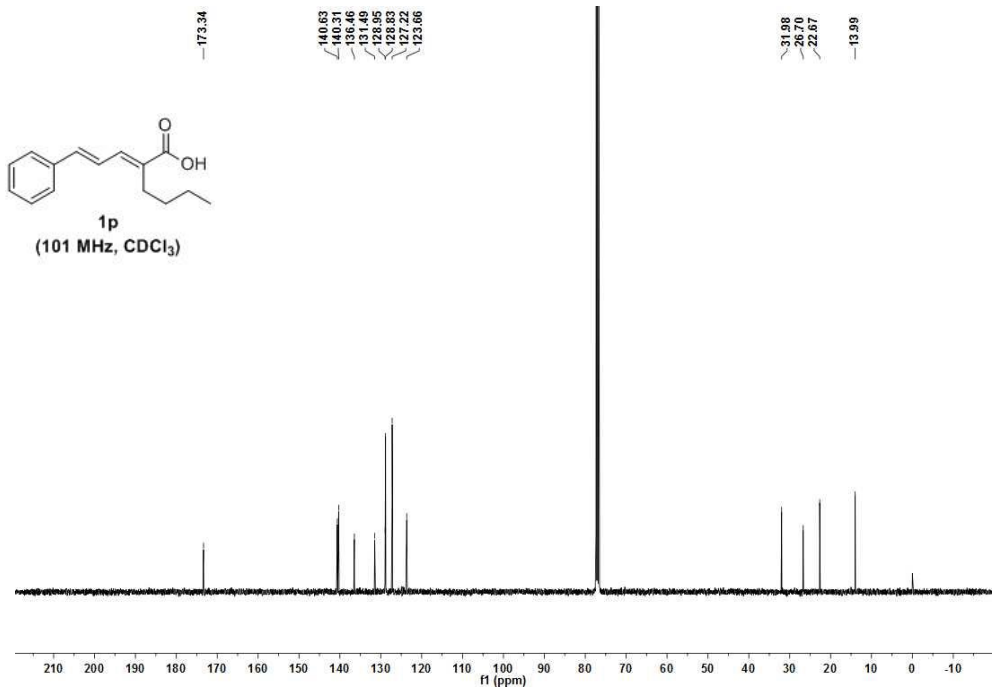

18o
(400 MHz, CDCl3)
6.74
1.00
0.94
3.12
2.87
4.70
3.37
f1 (ppm)

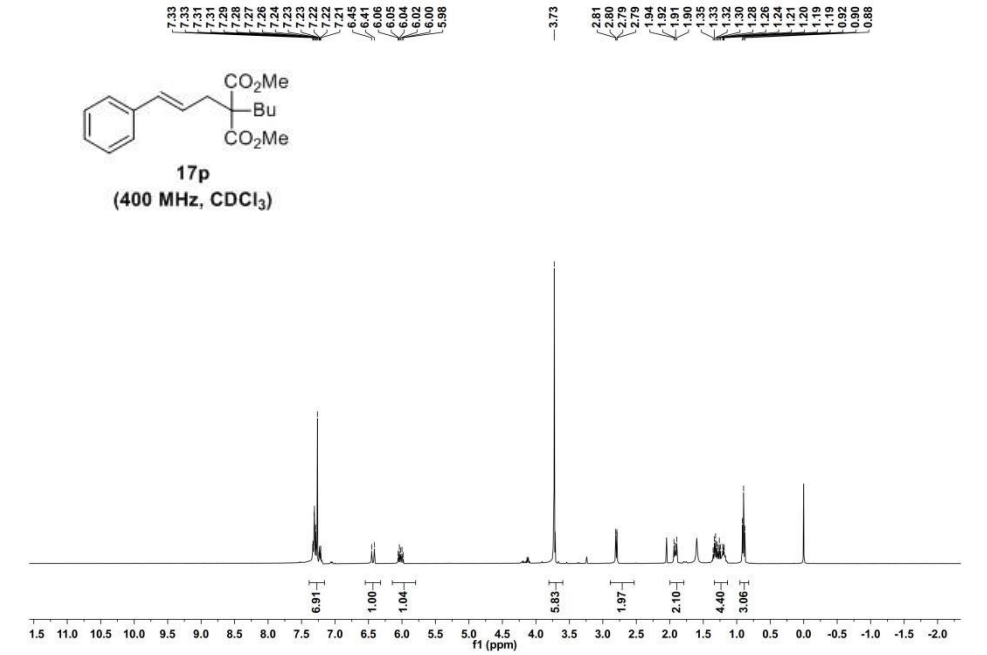

176.22
137.43
131.89
128.49
127.30
127.14
126.11
51.46
45.50
35.75
34.10
20.58
13.98
18o
(101 MHz, CDCl3)
f1 (ppm)

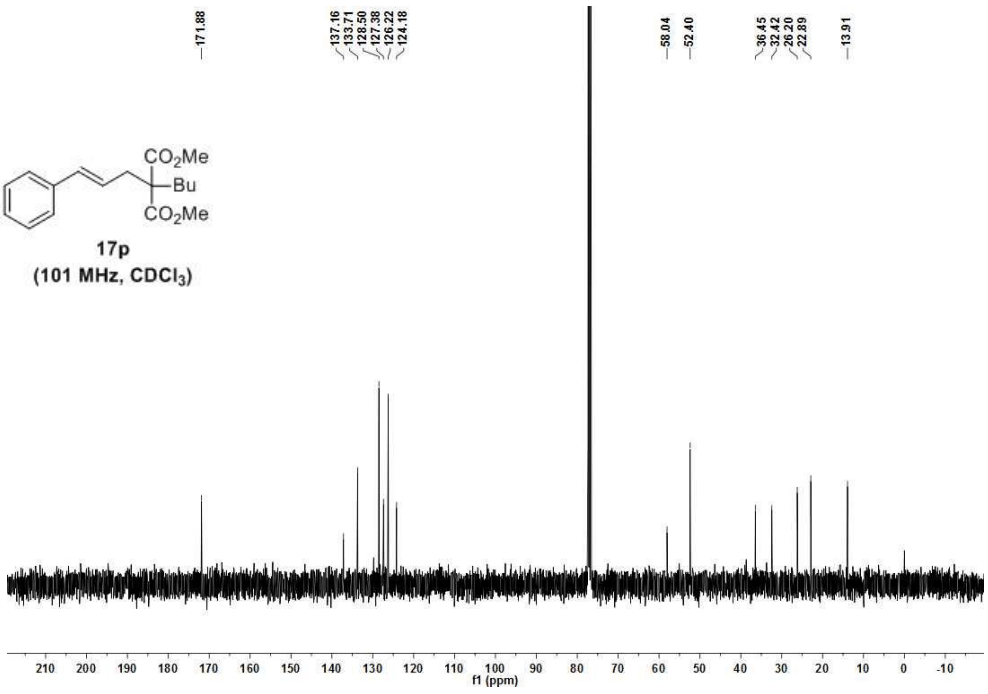

7.35
7.35
7.33
7.33
7.31
7.30
7.29
7.27
7.27
7.26
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
6.46
6.42
6.20
6.18
6.16
6.16
6.14
6.12
2.56
2.55
2.54
2.53
2.52
2.51
2.43
2.43
2.42
2.41
2.40
2.39
2.38
1.68
1.67
1.66
1.66
1.65
1.64
1.64
1.55
1.55
1.54
1.54
1.54
1.53
1.52
1.42
1.41
1.40
1.40
1.38
1.38
1.37
1.36
1.35
1.34
1.33
1.33
1.28
1.26
1.25
0.94
0.92
0.90
O
OH
19o
(400 MHz, CDCl3)
4.36
1.27
1.00
1.00
3.21
2.30
2.49
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
181.11
137.34
132.19
128.89
128.50
128.42
127.20
126.94
126.39
126.14
77.34 CDCl3
77.23
77.02 CDCl3
76.71 CDCl3
45.18
35.37
33.75
20.46
13.96
0.00
O
OH
19o
(101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

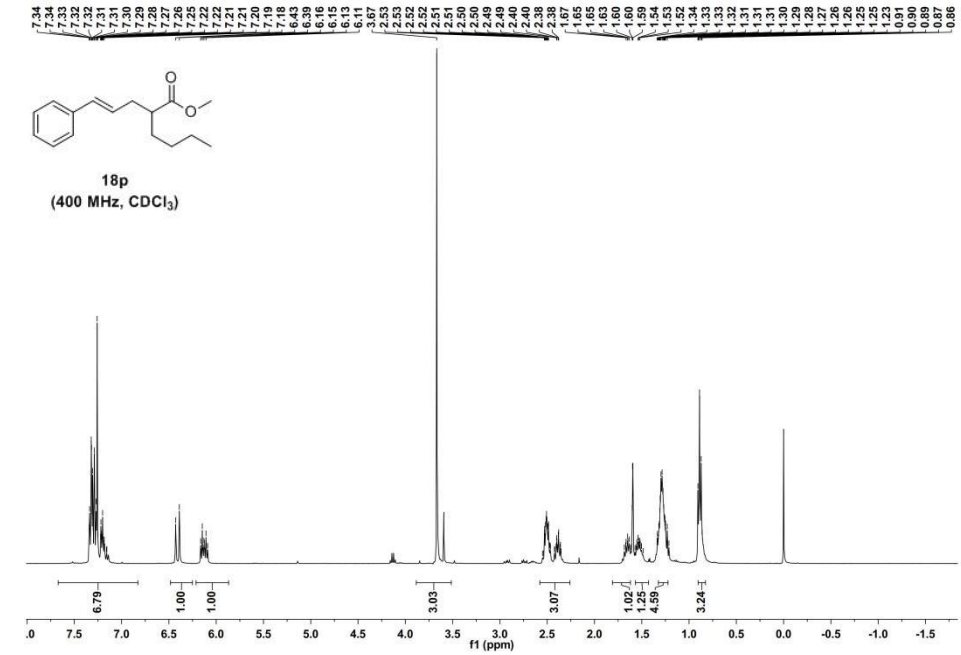

7.35
7.33
7.31
7.29
7.27
7.25
7.22
7.20
7.19
6.46
6.42
6.20
6.18
6.16
6.14
6.12
2.61
2.54
2.52
2.50
2.44
2.42
2.40
2.38
2.36
1.49
1.38
1.25
0.94
0.92
0.90
O
OH
(R)-2o
(400 MHz, CDCl3)
5.43
0.88
0.88
2.89
4.22
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)
181.95
137.34
132.20
128.51
127.21
126.95
126.15
77.36
77.04
76.72
45.28
35.34
33.72
20.46
13.98
O
OH
(R)-2o
(101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

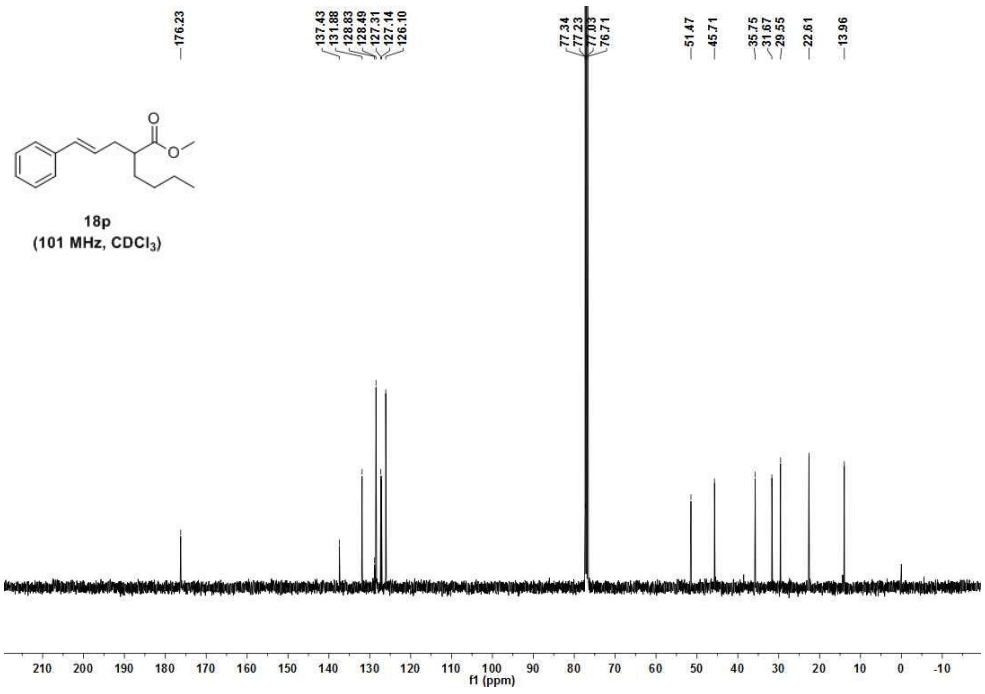

7.51
7.50
7.50
7.49
7.48
7.47
7.40
7.39
7.38
7.37
7.36
7.36
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.26
7.25
7.11
7.08
7.07
7.04
6.94
6.90
2.54
2.52
2.50
1.54
1.52
1.52
1.50
1.49
1.49
1.48
1.48
1.46
1.44
1.42
1.41
1.39
1.38
1.37
1.35
0.97
0.95
0.93
O
OH
1p
(400 MHz, CDCl3)
2.98
2.93
1.03
1.00
2.12
4.24
3.20
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

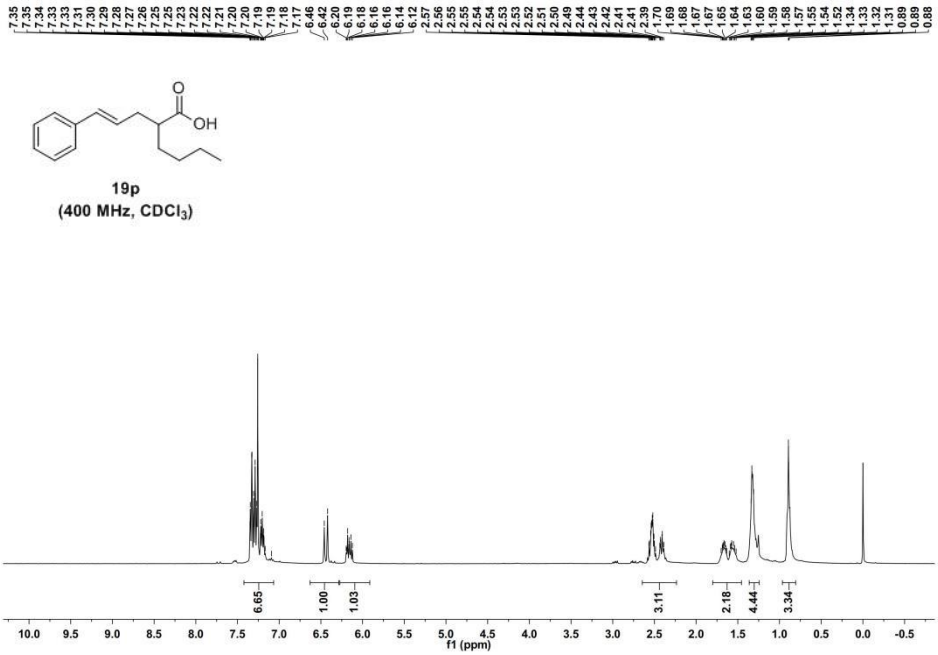

173.34
140.63
140.31
136.46
131.49
128.95
128.83
127.22
123.66
31.98
26.70
22.67
13.99
O
OH
1p
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

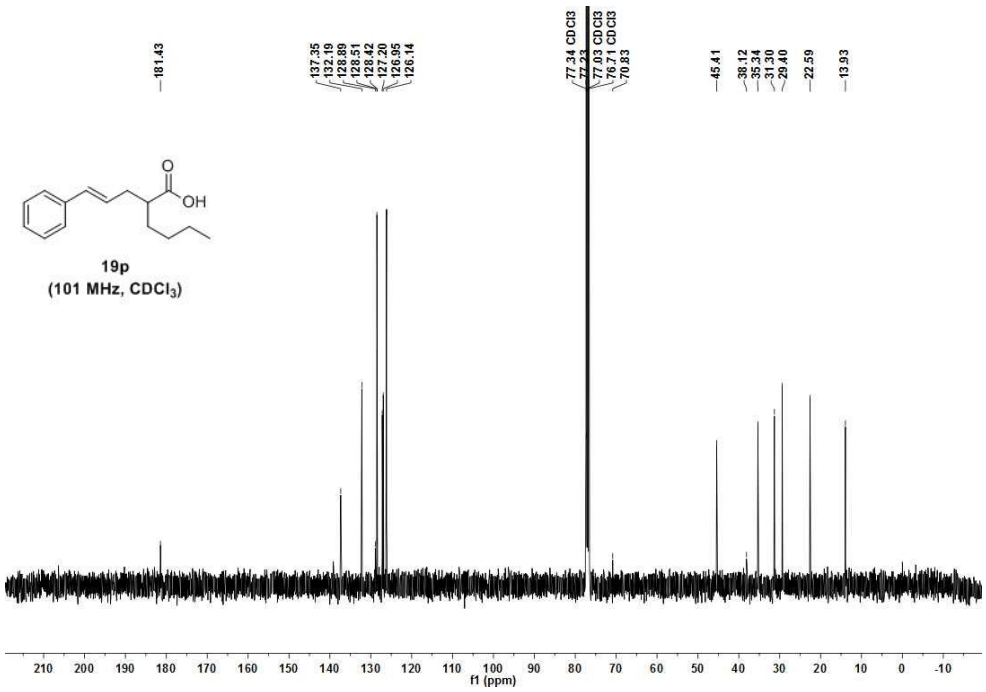

7.33
7.33
7.31
7.31
7.29
7.28
7.27
7.26
7.24
7.23
7.22
7.22
7.21
6.45
6.41
6.06
6.05
6.04
6.02
6.00
5.98
3.73
2.81
2.80
2.79
2.79
1.94
1.92
1.91
1.90
1.35
1.33
1.32
1.30
1.28
1.26
1.24
1.21
1.20
1.19
1.19
0.92
0.90
0.88
CO2Me
Bu
CO2Me
17p
(400 MHz, CDCl3)
6.91
1.00
1.04
5.83
1.97
2.10
4.40
3.06
f1 (ppm)

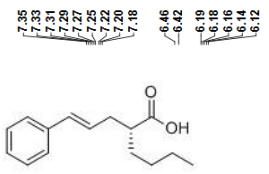

171.88
137.16
133.71
128.50
127.38
126.22
124.18
58.04
52.40
36.45
32.42
26.20
22.89
13.91
CO2Me
Bu
CO2Me
17p
(101 MHz, CDCl3)
f1 (ppm)


18p
(400 MHz, CDCl3)
f1 (ppm)

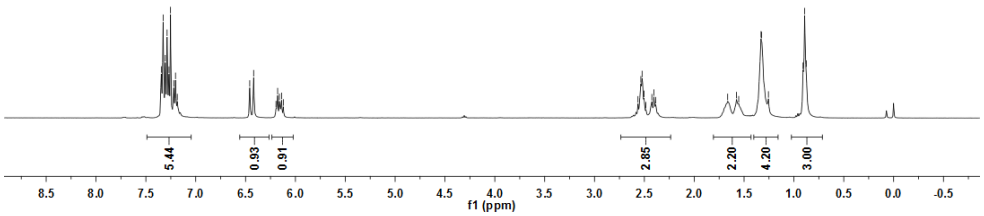

18p
(101 MHz, CDCl3)
f1 (ppm)

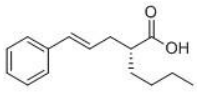

OH
19p
(400 MHz, CDCl3)
6.65
1.00
1.03
3.11
2.18
4.44
3.34
f1 (ppm)


OH
19p
(101 MHz, CDCl3)
181.43
137.35
132.19
128.89
128.51
128.42
127.20
126.95
126.14
77.34 CDCl3
77.23
77.03 CDCl3
76.71 CDCl3
70.83
45.41
38.12
35.34
31.30
29.40
22.59
13.93
f1 (ppm)

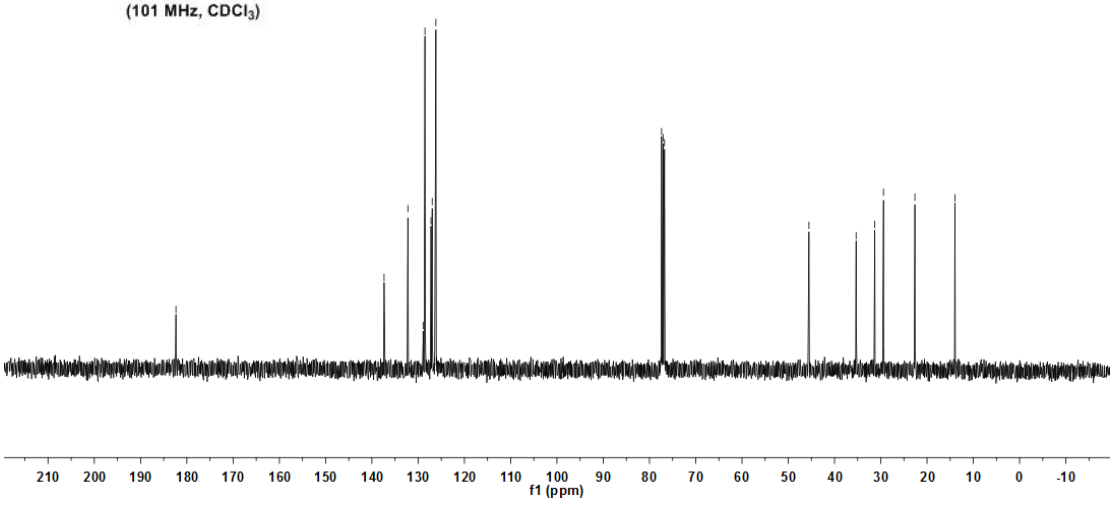


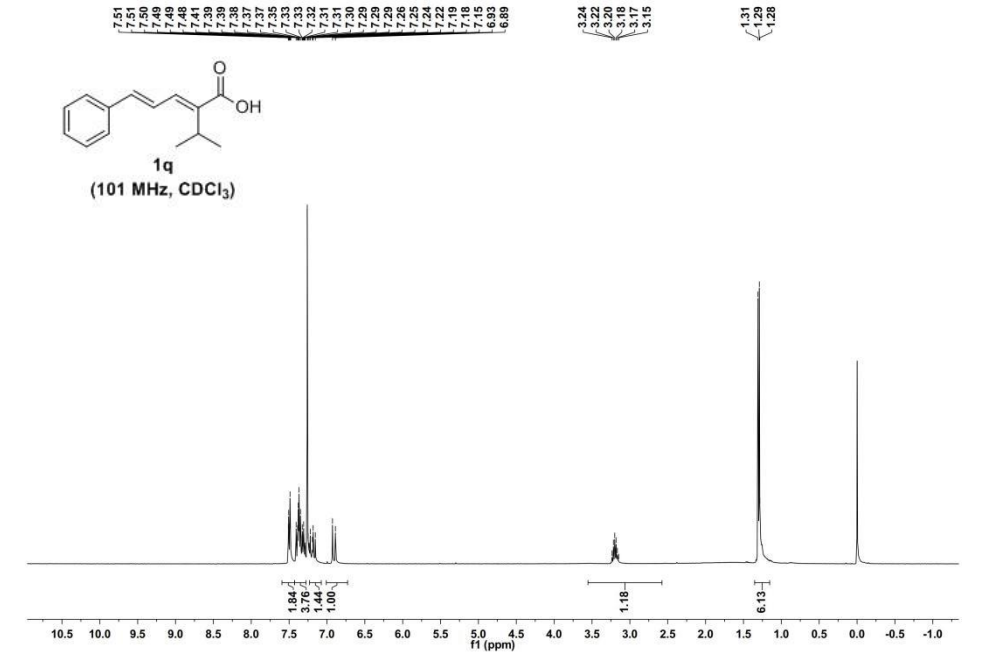
(*R*)-2p
(400 MHz, $CDCl_3$)

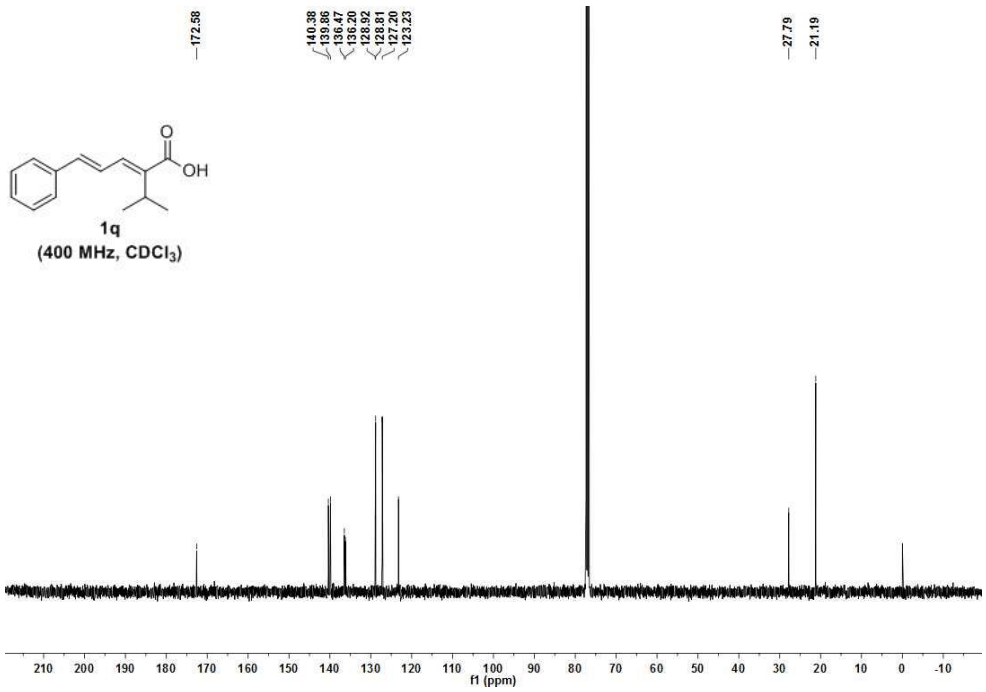


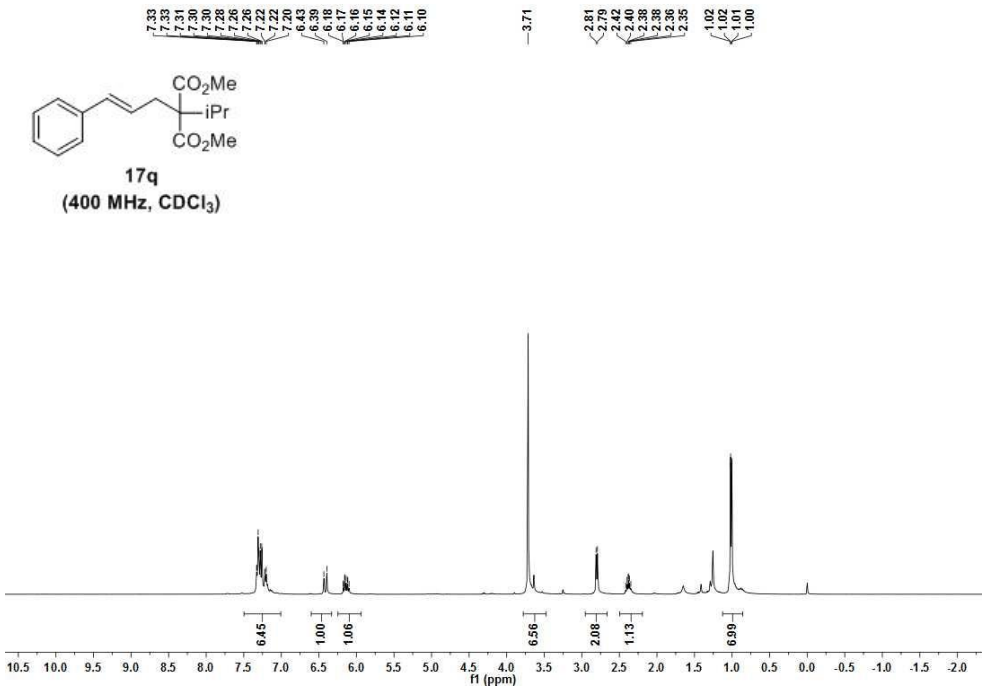


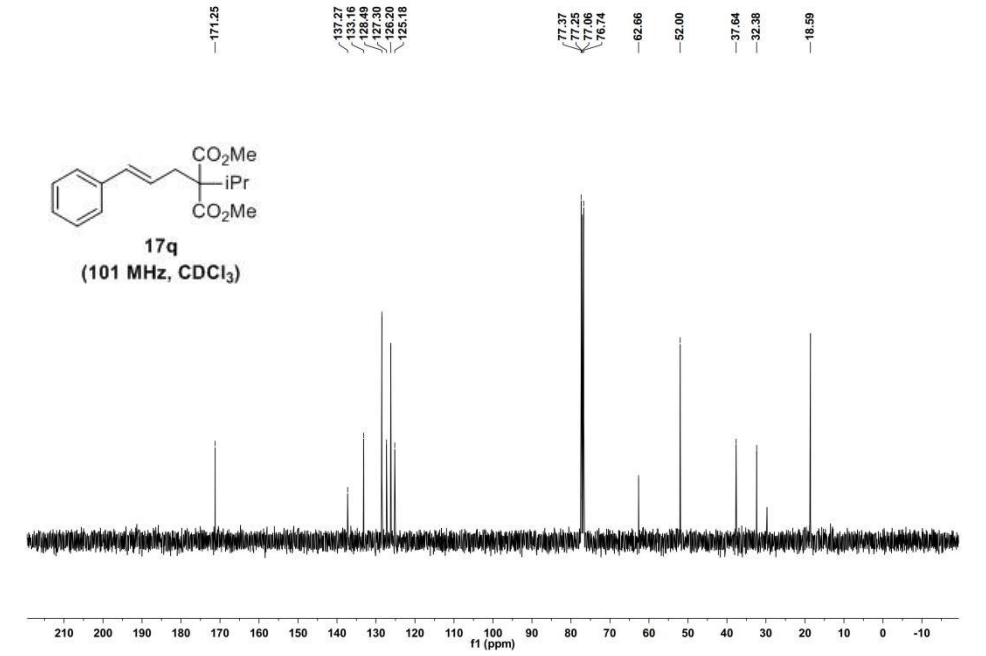
(*R*)-2p
(101 MHz, $CDCl_3$)

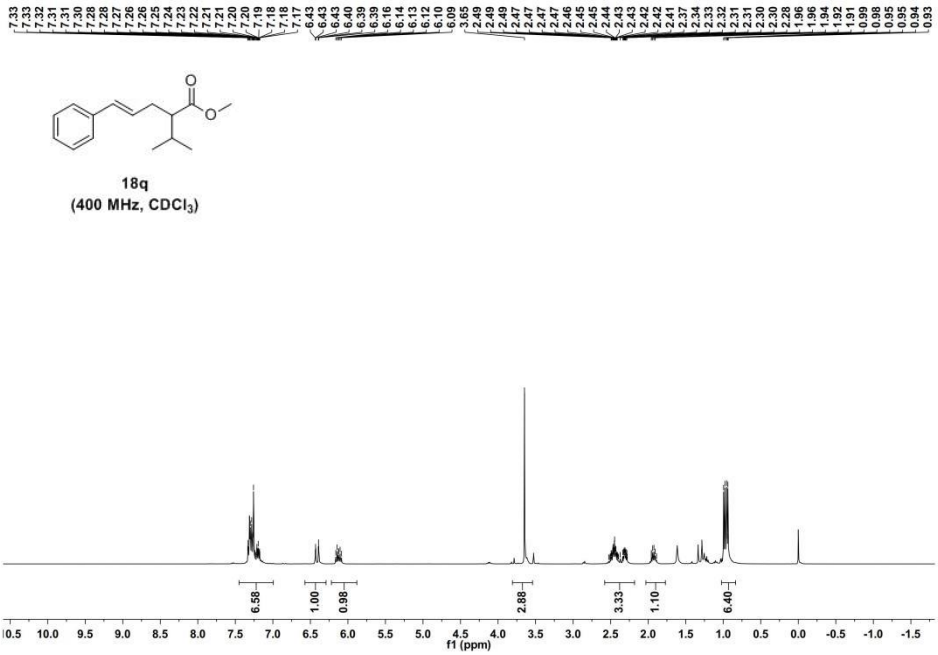


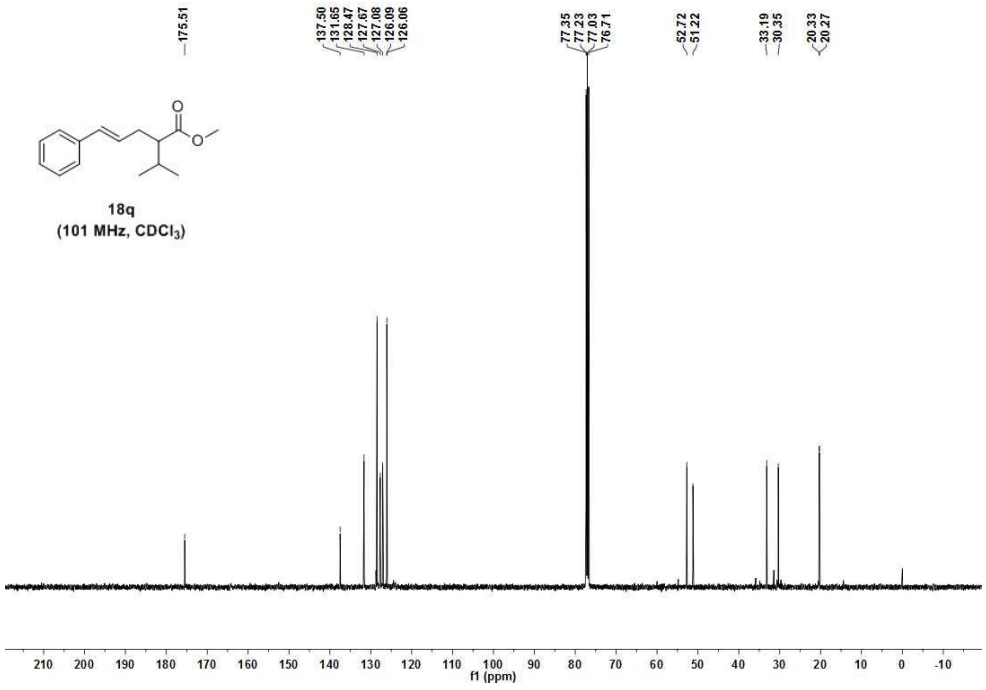

7.51
7.51
7.50
7.49
7.49
7.48
7.41
7.39
7.39
7.38
7.37
7.37
7.35
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.29
7.26
7.25
7.24
7.22
7.19
7.18
7.15
6.93
6.89
3.24
3.22
3.20
3.18
3.17
3.15
1.31
1.29
1.28
O
OH
1q
(101 MHz, CDCl3)
1.84
3.76
1.44
1.00
1.18
6.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

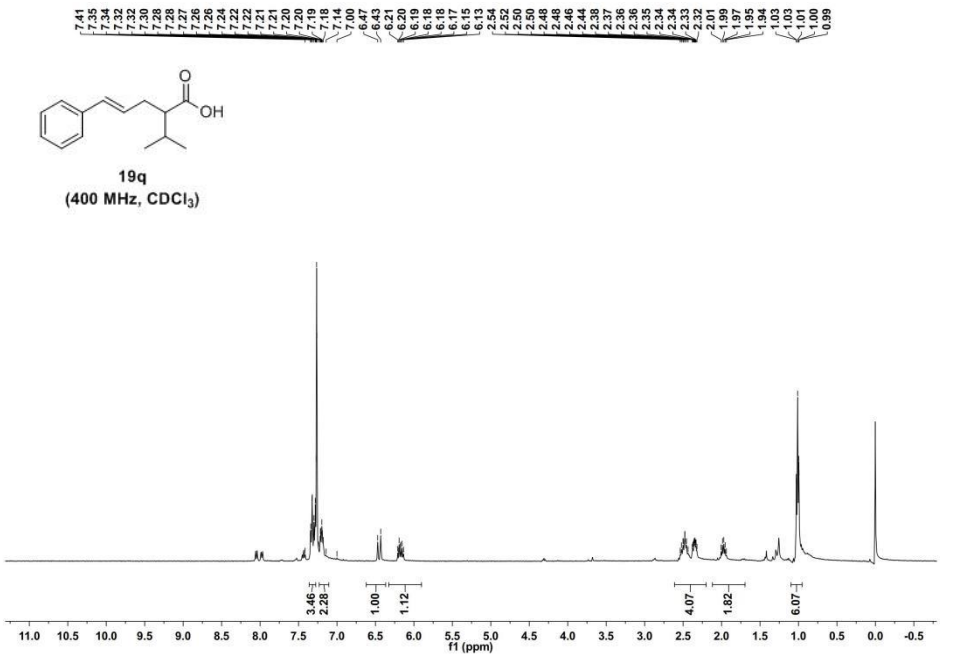

172.58
140.38
139.86
136.47
136.20
128.92
128.81
127.20
123.23
27.79
21.19
O
OH
1q
(400 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

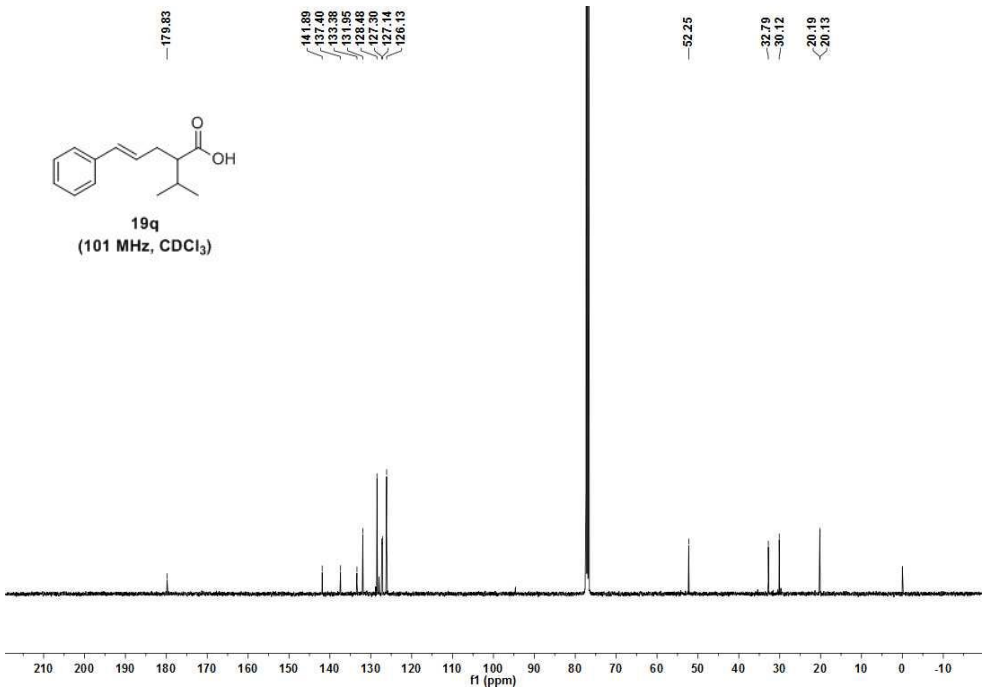

7.33
7.33
7.31
7.30
7.30
7.28
7.26
7.26
7.22
7.20
6.43
6.39
6.18
6.17
6.16
6.15
6.14
6.12
6.11
6.10
3.71
2.81
2.79
2.42
2.40
2.38
2.38
2.36
2.35
1.02
1.02
1.01
1.01
1.00
CO2Me
iPr
CO2Me
17q
(400 MHz, CDCl3)
6.45
1.00
1.06
6.56
2.08
1.13
6.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

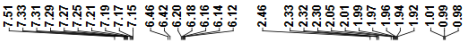

171.25
137.27
133.16
128.49
127.30
126.20
125.18
77.37
77.25
77.06
76.74
62.66
52.00
37.64
32.38
18.59
CO2Me
iPr
CO2Me
17q
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

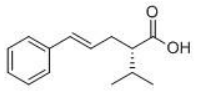

7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.18 7.17 6.43 6.43 6.40 6.40 6.39 6.39 6.16 6.14 6.13 6.12 6.10 6.09 3.65 2.49 2.49 2.49 2.47 2.47 2.47 2.47 2.46 2.45 2.45 2.44 2.43 2.43 2.42 2.42 2.41 2.37 2.34 2.33 2.32 2.31 2.31 2.30 2.30 2.28 1.96 1.96 1.94 1.92 1.91 0.99 0.98 0.95 0.95 0.94 0.93
O
O
18q
(400 MHz, CDCl3)
6.58
1.00
0.98
2.88
3.33
1.10
6.40
f1 (ppm)


175.51
137.50
131.65
128.47
127.67
127.08
126.09
126.06
77.35
77.23
77.03
76.71
52.72
51.22
33.19
30.35
20.33
20.27
O
O
18q
(101 MHz, CDCl3)
f1 (ppm)

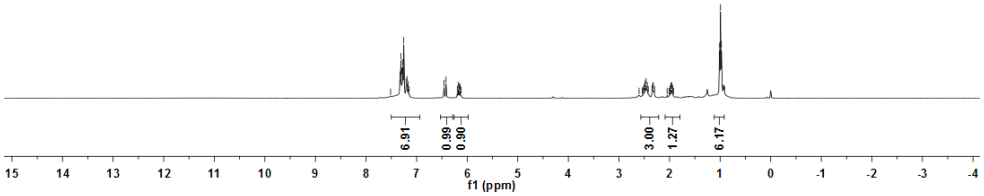

7.41 7.35 7.34 7.32 7.32 7.30 7.28 7.28 7.27 7.26 7.26 7.24 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.14 7.00 6.47 6.43 6.21 6.20 6.19 6.18 6.18 6.17 6.15 6.13 2.54 2.52 2.50 2.50 2.48 2.48 2.46 2.44 2.38 2.37 2.36 2.35 2.34 2.34 2.33 2.32 2.01 1.99 1.97 1.95 1.94 1.03 1.03 1.01 1.00 0.99
O
OH
19q
(400 MHz, CDCl3)
3.46
2.28
1.00
1.12
4.07
1.82
6.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

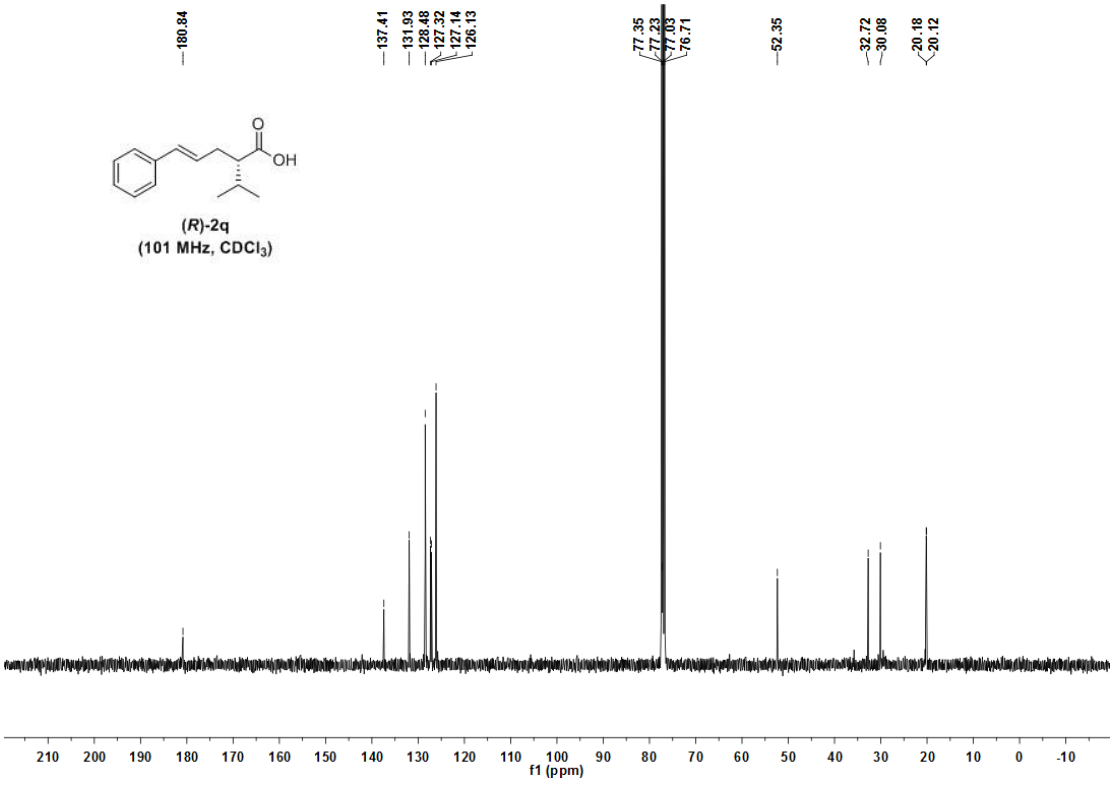

179.83
141.89
137.40
133.38
131.95
128.48
127.30
127.14
126.13
52.25
32.79
30.12
20.19
20.13
O
OH
19q
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



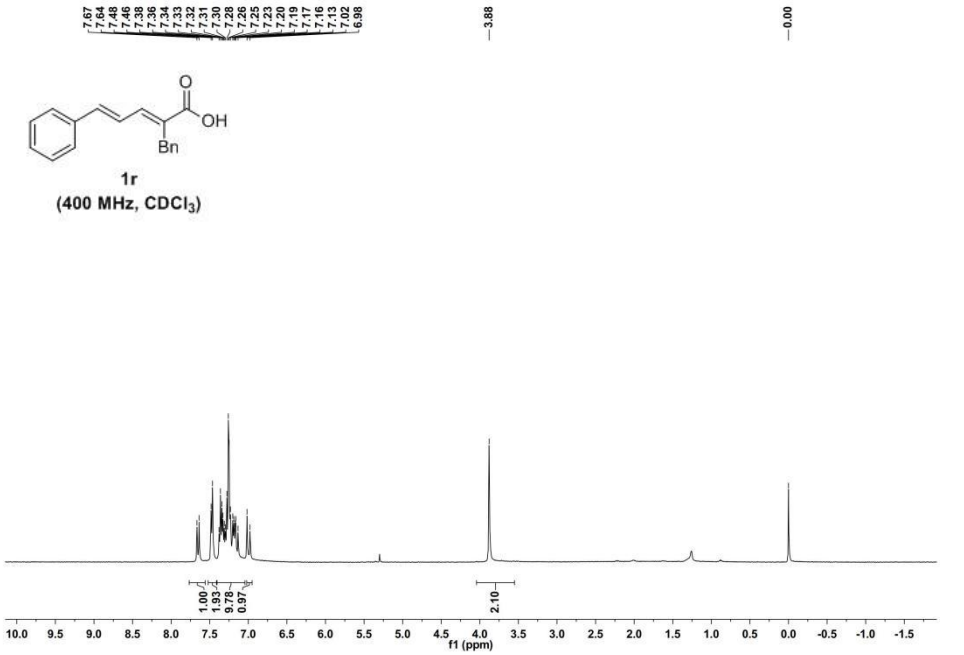


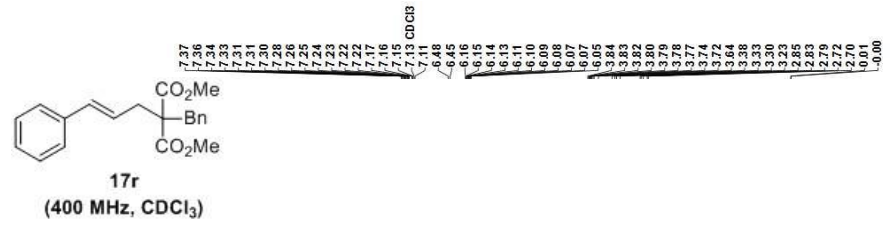
(*R*)-2q
(400 MHz, $CDCl_3$)



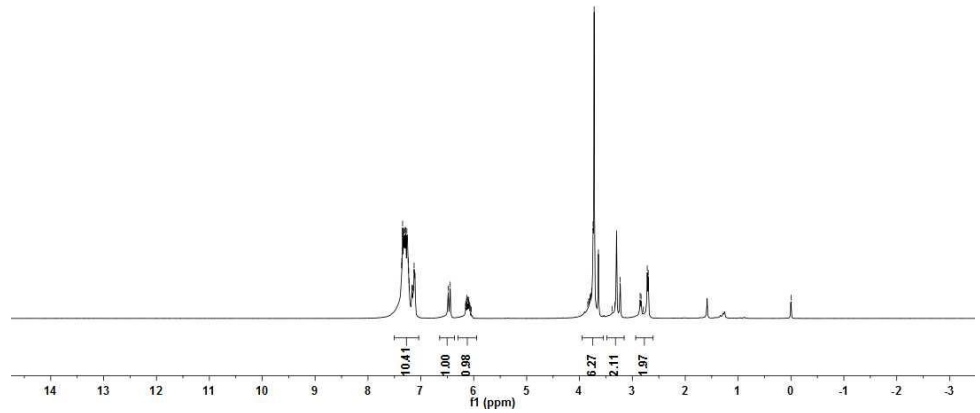


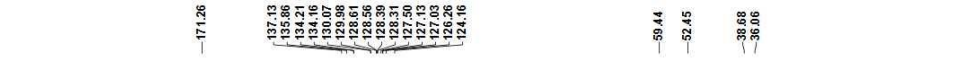
(*R*)-2q
(101 MHz, $CDCl_3$)

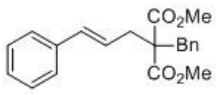

7.67
7.64
7.48
7.46
7.38
7.36
7.34
7.33
7.32
7.31
7.30
7.28
7.26
7.25
7.23
7.20
7.19
7.17
7.16
7.13
7.02
6.98
3.88
0.00
O
OH
Bn
1r
(400 MHz, CDCl3)
1.00
1.93
9.78
0.97
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)
172.75
142.00
141.54
139.42
136.21
129.20
128.86
128.51
128.29
127.37
126.22
123.52
77.34 CDCl3
77.23
77.03 CDCl3
76.71 CDCl3
32.40
O
OH
Bn
1r
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



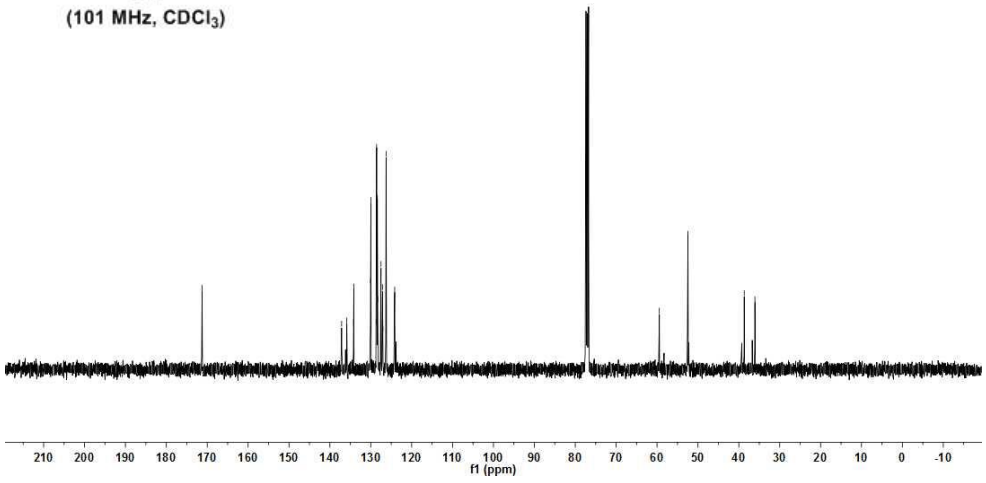
17r
(400 MHz, $CDCl_3$)

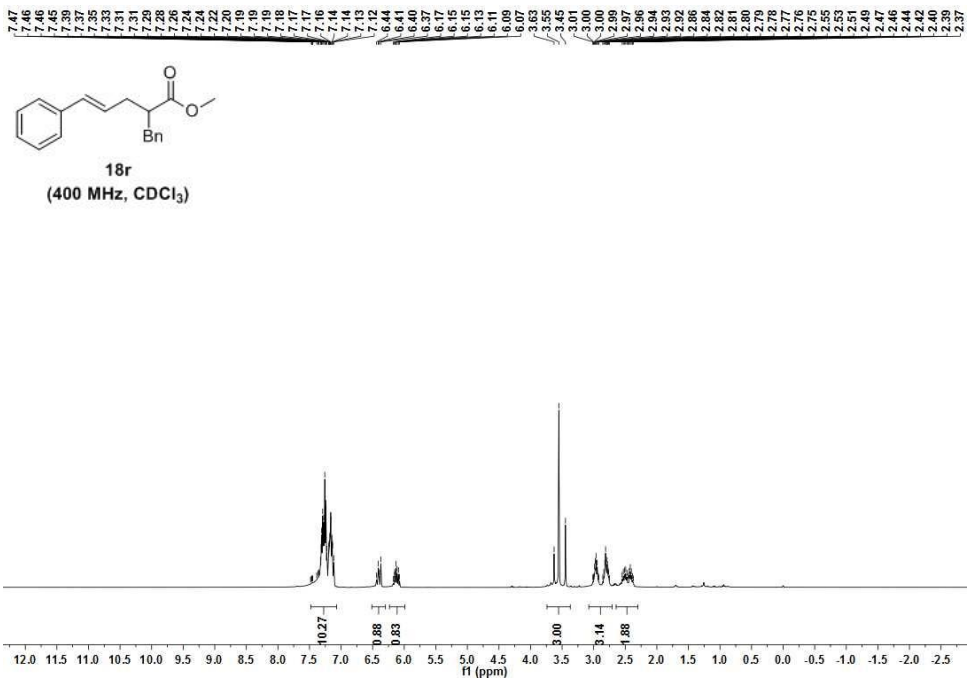


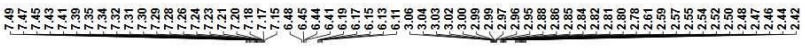


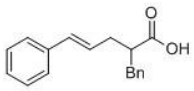


17r
(101 MHz, $CDCl_3$)

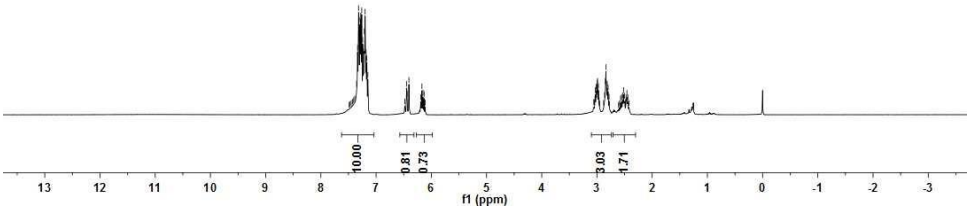


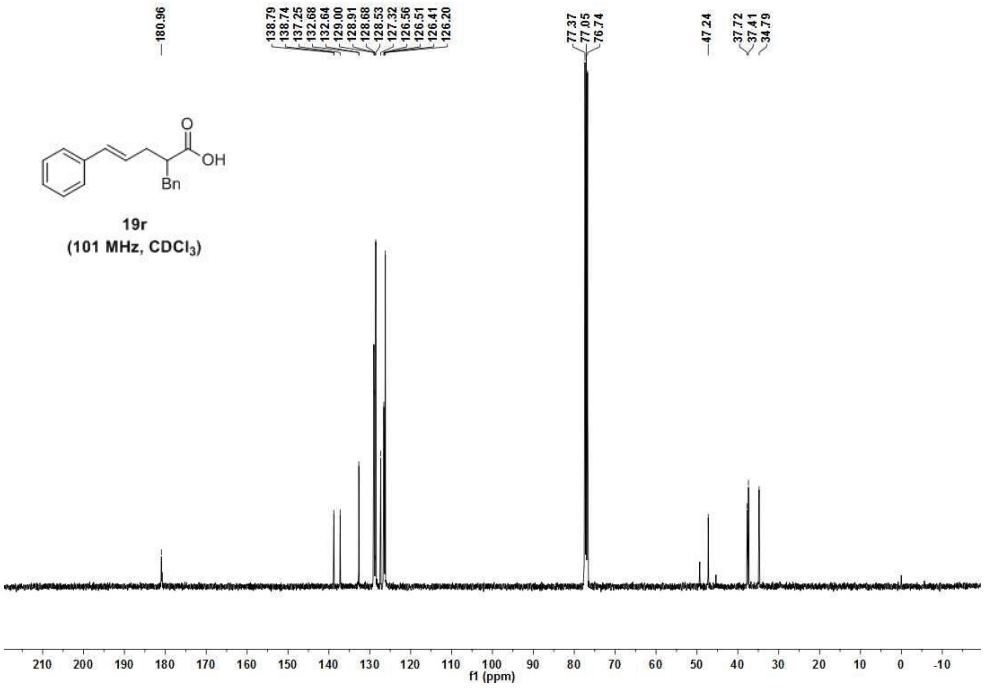

7.47 7.46 7.45 7.39 7.37 7.35 7.33 7.31 7.31 7.29 7.28 7.26 7.24 7.24 7.22 7.20 7.19 7.19 7.18 7.18 7.17 7.16 7.14 7.14 7.13 7.12 6.44 6.41 6.40 6.37 6.17 6.15 6.15 6.13 6.11 6.09 6.07 3.63 3.55 3.45 3.01 3.00 2.99 2.97 2.96 2.94 2.93 2.92 2.86 2.84 2.82 2.81 2.80 2.79 2.78 2.77 2.76 2.75 2.55 2.53 2.51 2.49 2.47 2.46 2.44 2.42 2.40 2.39 2.37
O
O
Bn
18r
(400 MHz, CDCl3)
10.27
0.88
0.83
3.00
3.14
1.88
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)
175.38
139.21
139.17
137.41
132.44
129.04
128.97
128.62
128.55
128.55
127.35
126.87
126.55
126.25
51.62
47.66
38.30
38.01
35.40
O
O
Bn
18r
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



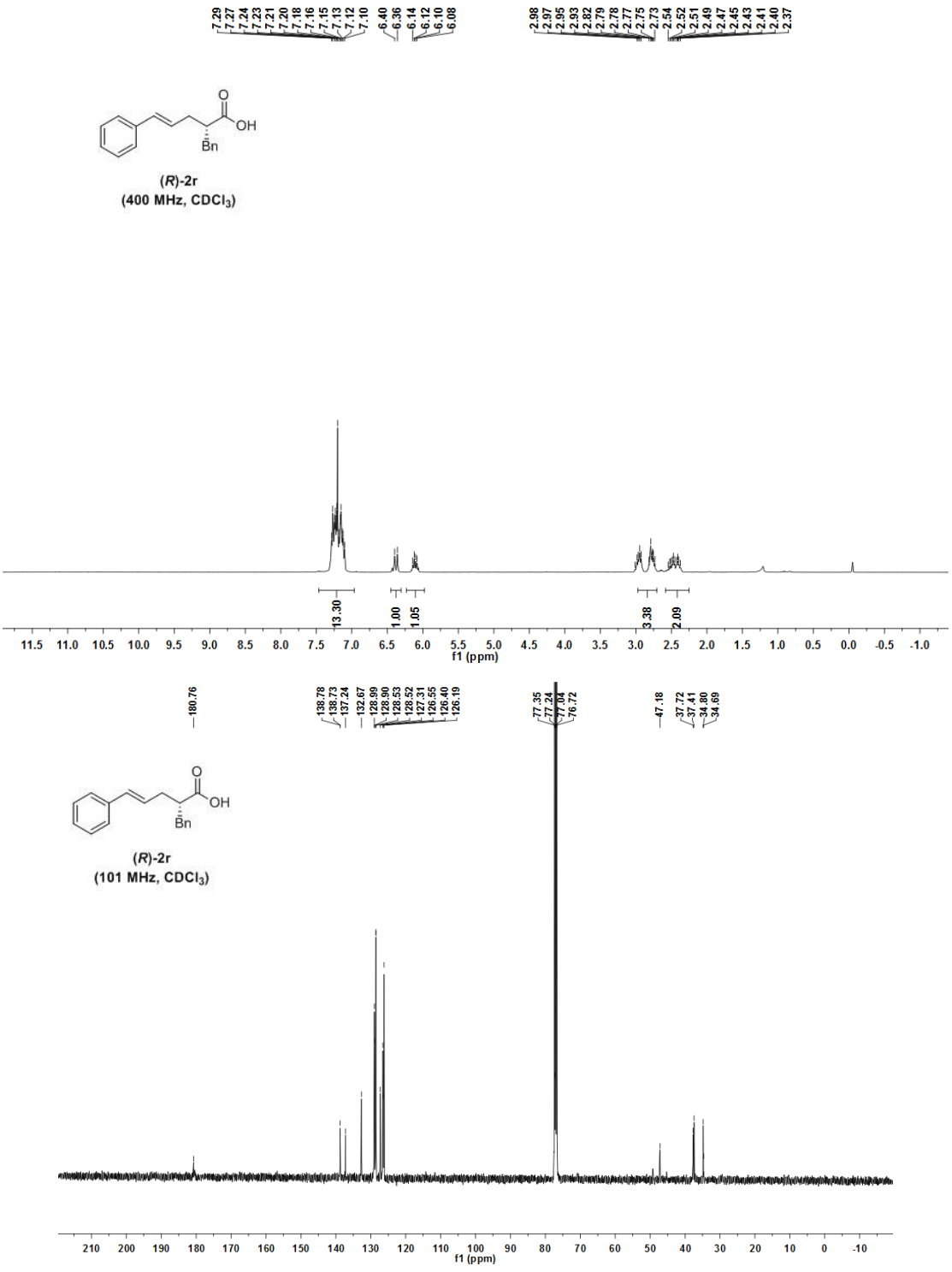


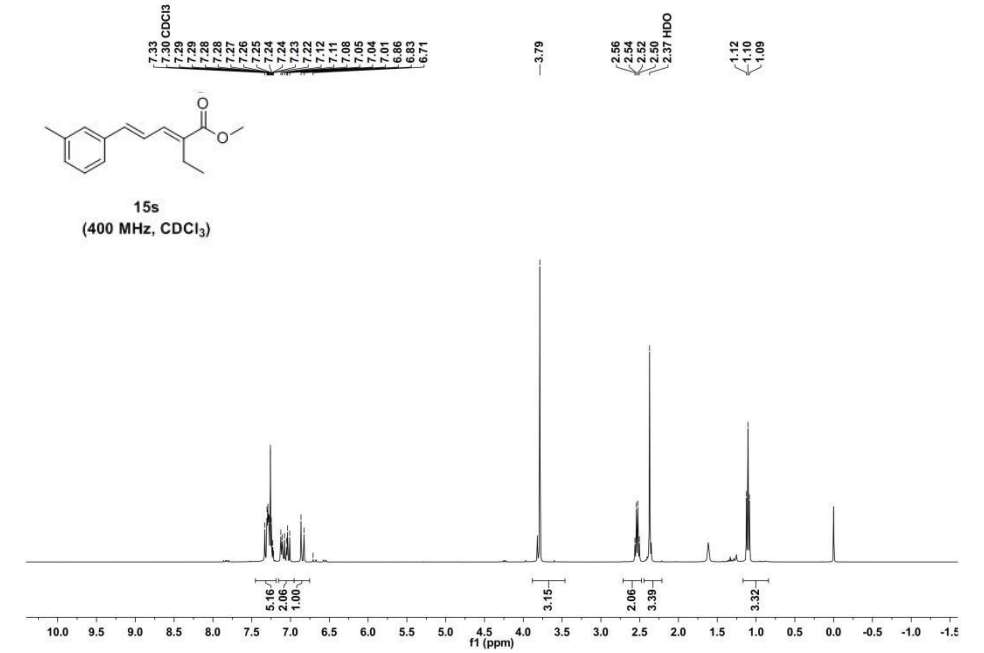
19r
(400 MHz, $CDCl_3$)



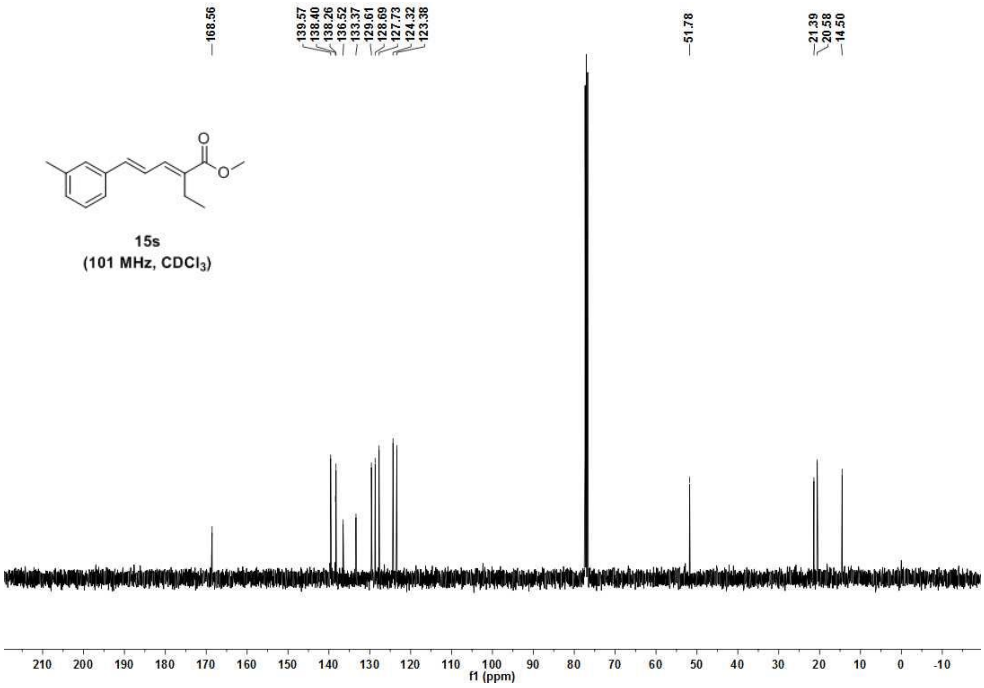


19r
(101 MHz, $CDCl_3$)

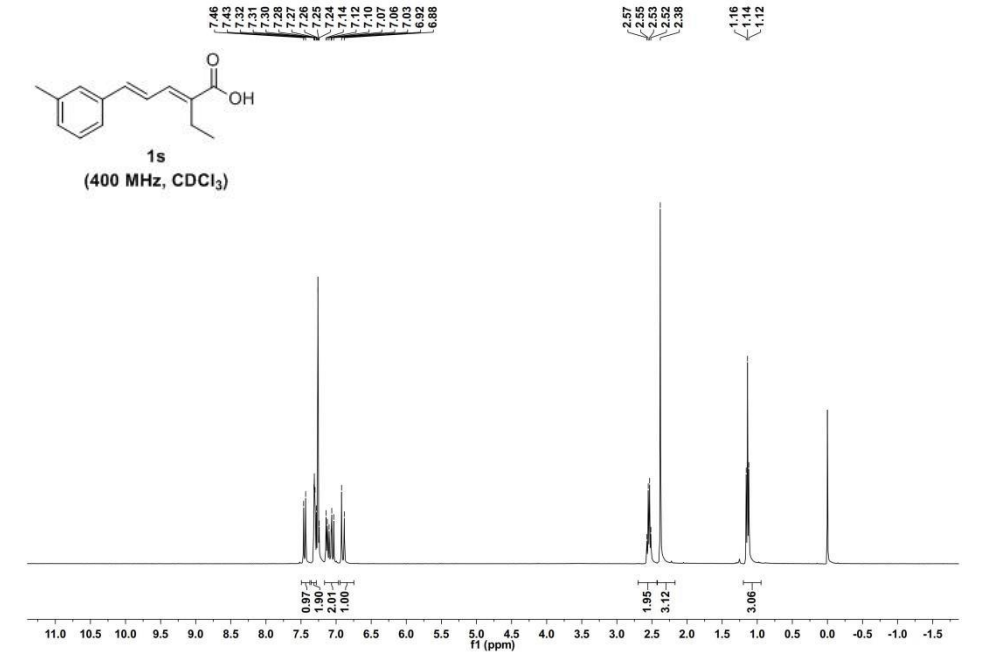

7.29
7.27
7.24
7.23
7.21
7.20
7.18
7.16
7.15
7.13
7.12
7.10
6.40
6.36
6.14
6.12
6.10
6.08
2.98
2.97
2.95
2.93
2.82
2.79
2.78
2.77
2.75
2.73
2.54
2.52
2.51
2.49
2.47
2.45
2.43
2.41
2.40
2.37
O
OH
Bn
(R)-2r
(400 MHz, CDCl3)
13.30
1.00
1.05
3.38
2.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
180.76
138.78
138.73
137.24
132.67
128.99
128.90
128.53
128.52
127.31
126.55
126.40
126.19
77.35
77.24
77.04
76.72
47.18
37.72
37.41
34.80
34.69
O
OH
Bn
(R)-2r
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

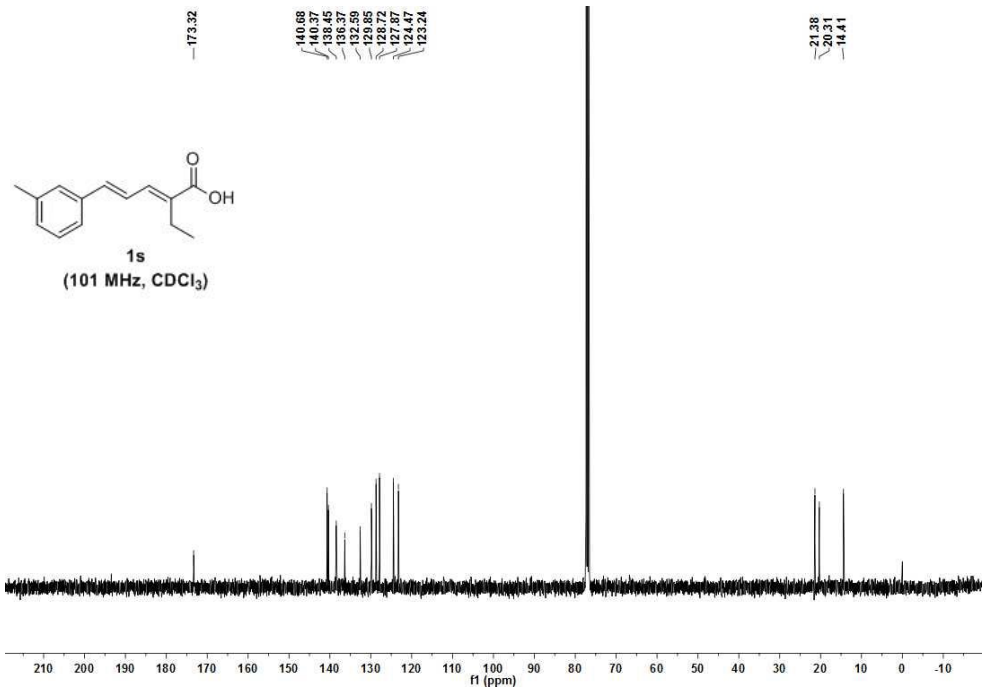


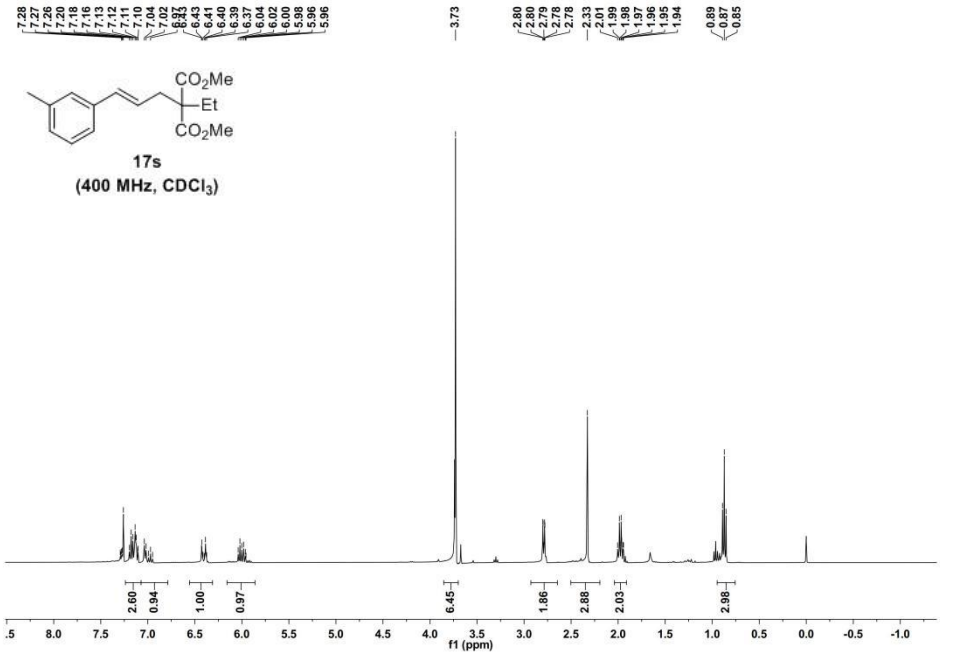
15s
(400 MHz, $CDCl_3$)

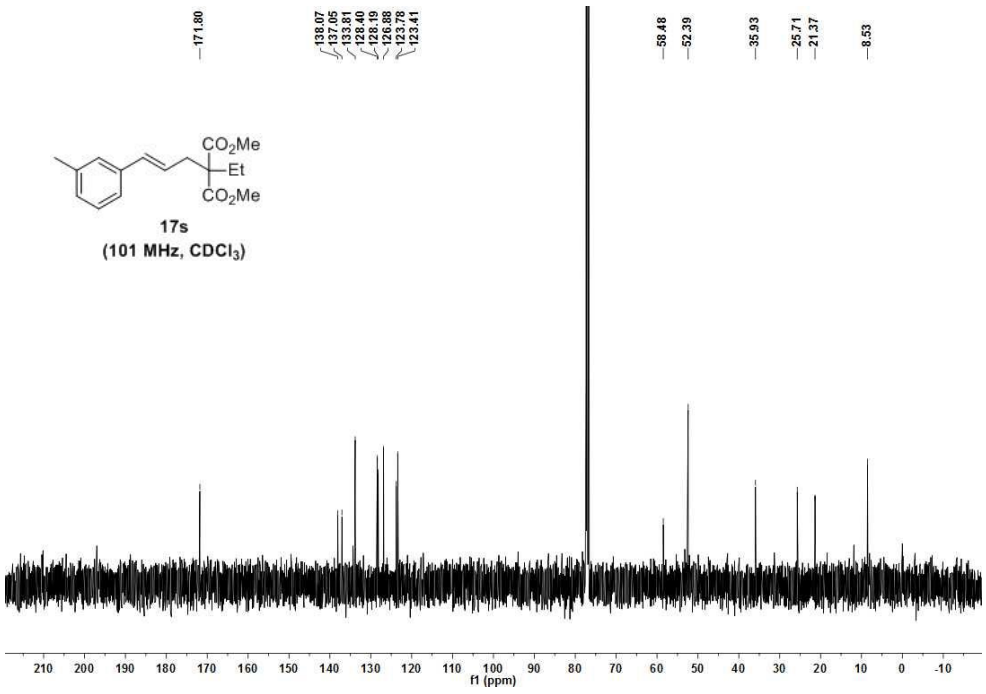


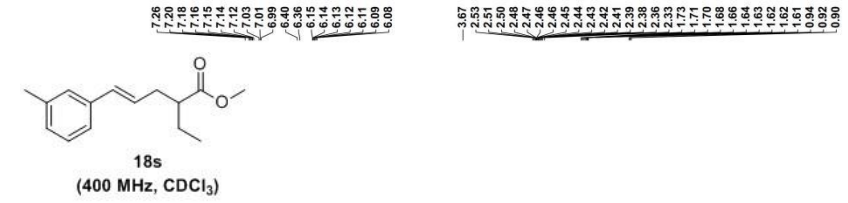
15s
(101 MHz, $CDCl_3$)


7.46
7.43
7.32
7.31
7.30
7.28
7.27
7.26
7.25
7.24
7.14
7.12
7.10
7.07
7.06
7.03
6.92
6.88
2.57
2.55
2.53
2.52
2.38
1.16
1.14
1.12
O
OH
1s
(400 MHz, CDCl3)
0.97
1.90
2.01
1.00
1.95
3.12
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

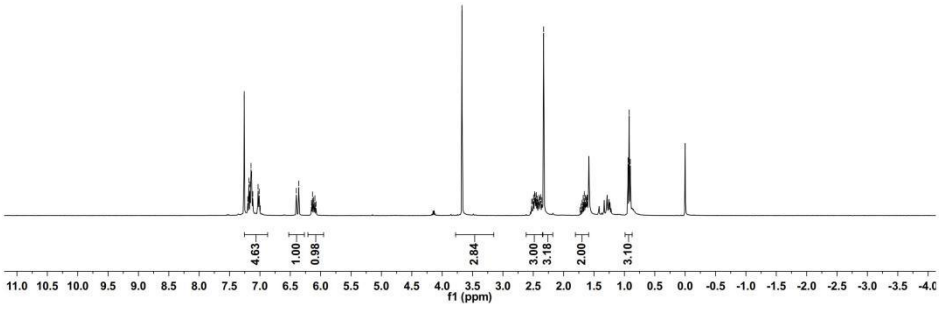

173.32
140.68
140.37
138.45
136.37
132.59
129.85
128.72
127.87
124.47
123.24
21.38
20.31
14.41
O
OH
1s
(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

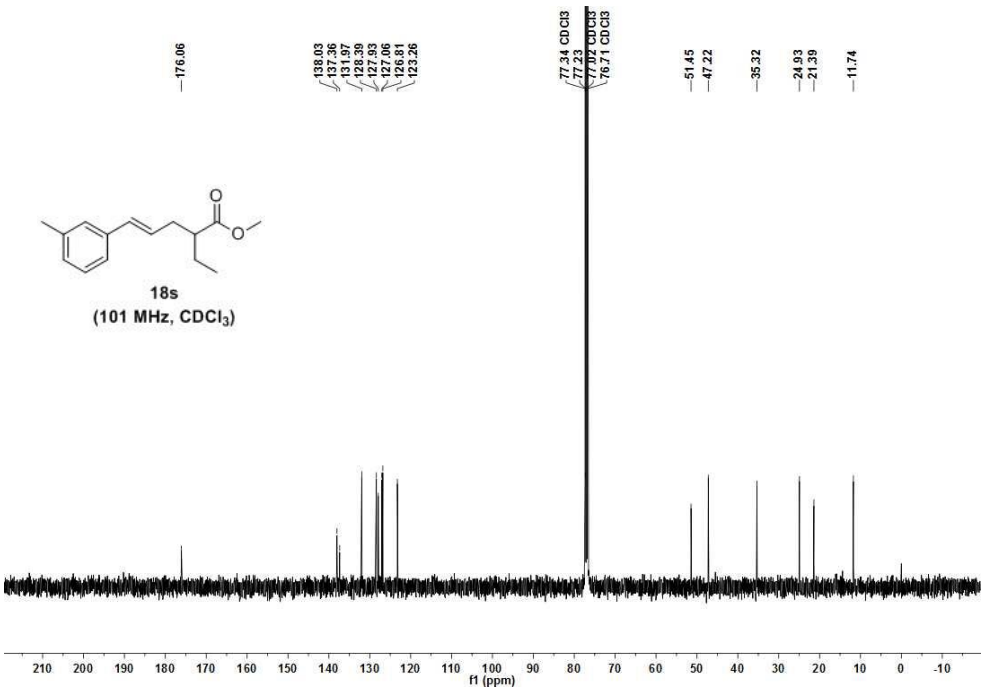

7.28
7.27
7.26
7.20
7.18
7.16
7.13
7.12
7.11
7.10
7.04
7.02
6.43
6.41
6.40
6.39
6.37
6.04
6.02
6.00
5.98
5.96
5.96
3.73
2.80
2.80
2.79
2.78
2.78
2.33
2.01
1.99
1.98
1.97
1.96
1.95
1.94
0.89
0.87
0.85
CO2Me
Et
CO2Me
17s
(400 MHz, CDCl3)
2.60
0.94
1.00
0.97
6.45
1.86
2.88
2.03
2.98
f1 (ppm)


171.80
138.07
137.05
133.81
128.40
128.19
126.88
123.78
123.41
58.48
52.39
35.93
25.71
21.37
8.53
CO2Me
Et
CO2Me
17s
(101 MHz, CDCl3)
f1 (ppm)

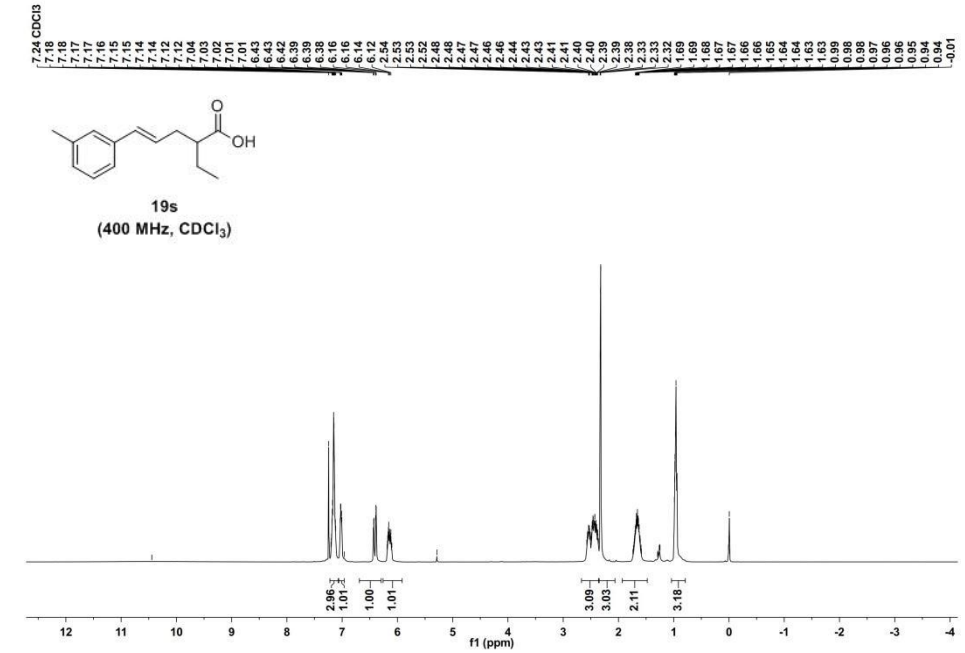


18s
(400 MHz, $CDCl_3$)

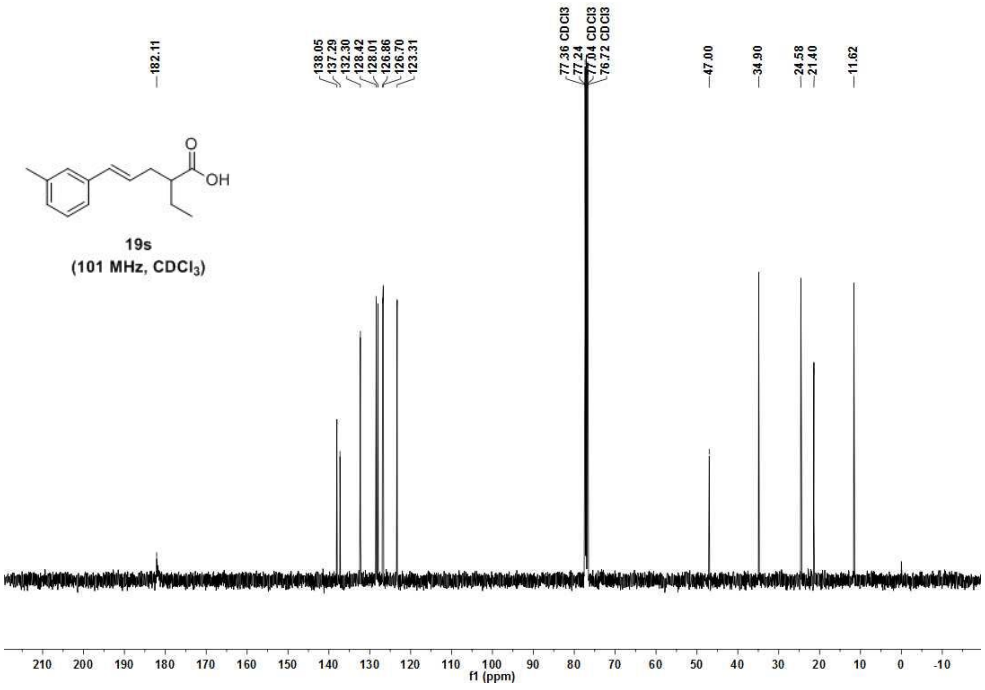




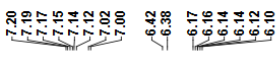
18s
(101 MHz, $CDCl_3$)

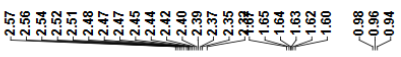


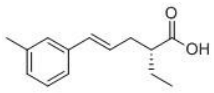
19s
(400 MHz, $CDCl_3$)



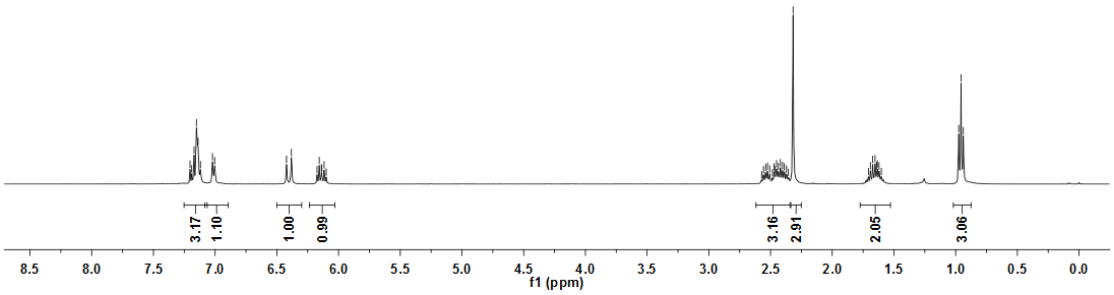
19s
(101 MHz, $CDCl_3$)

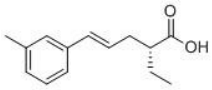




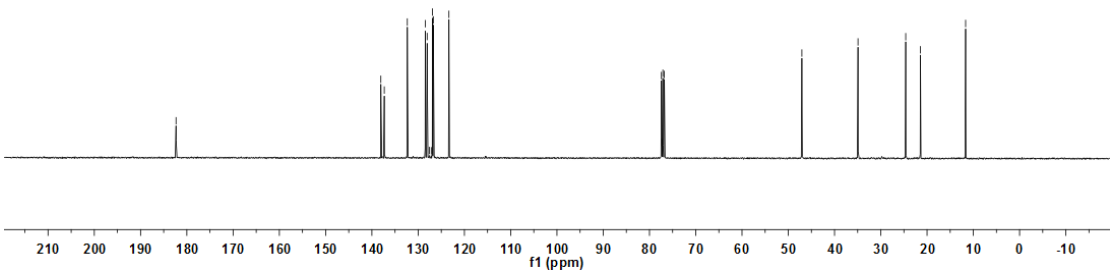


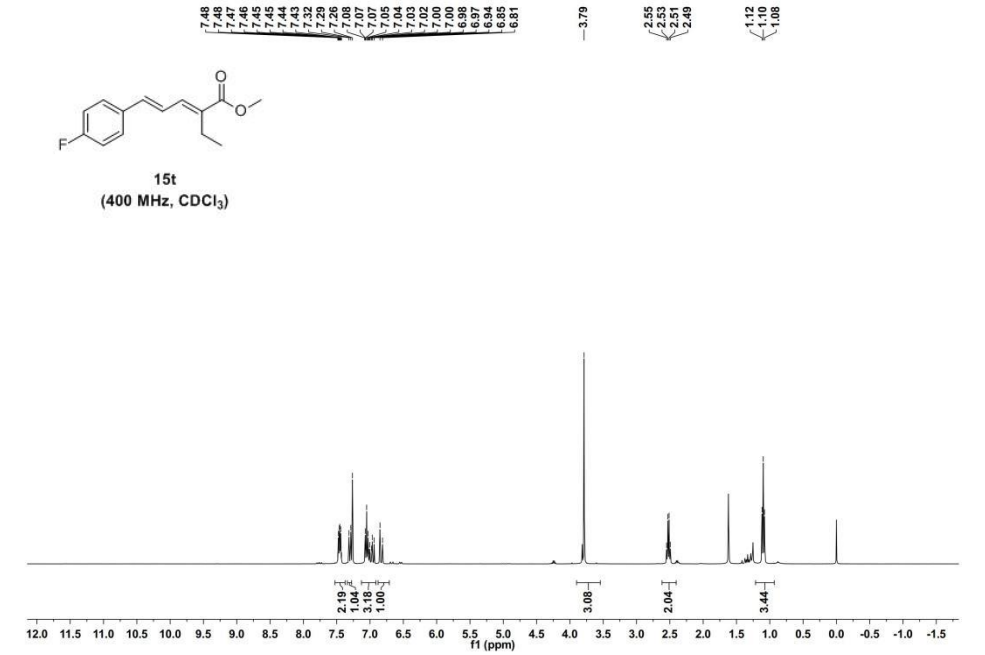
(*R*)-2s
(400 MHz, $CDCl_3$)



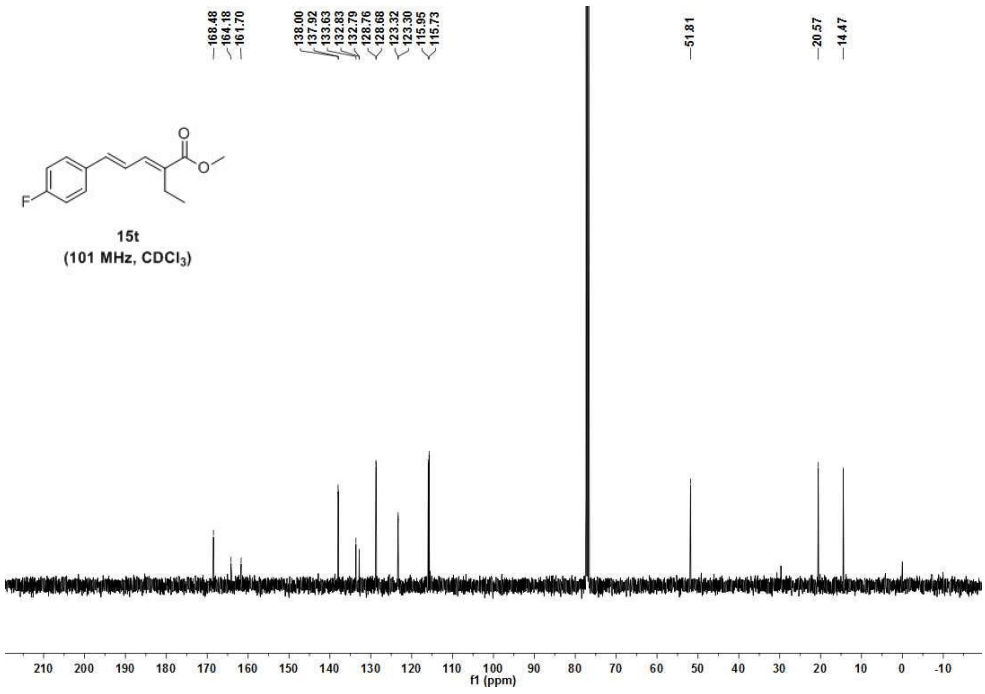


(*R*)-2s
(101 MHz, $CDCl_3$)

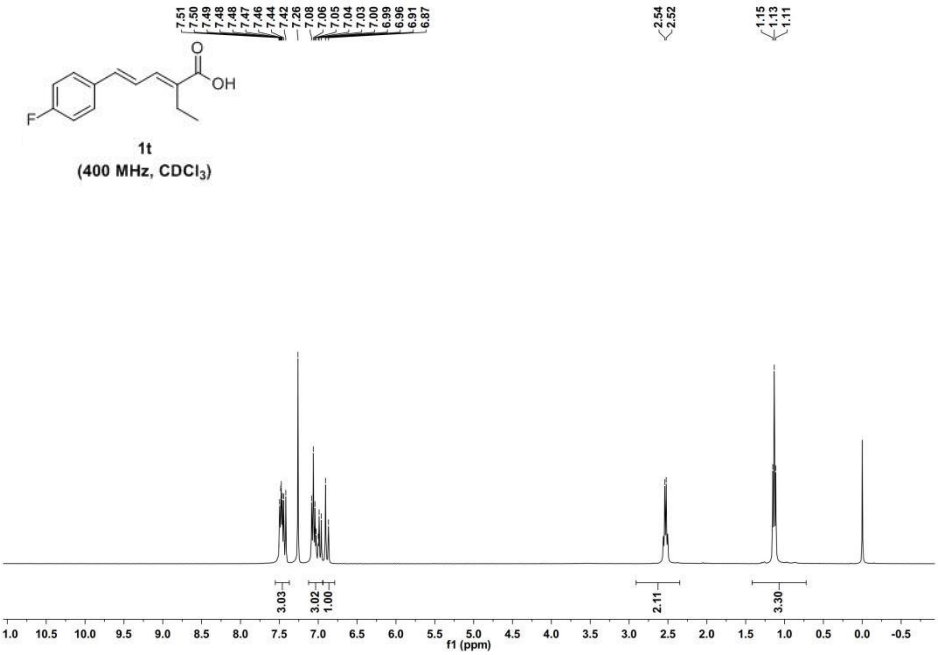




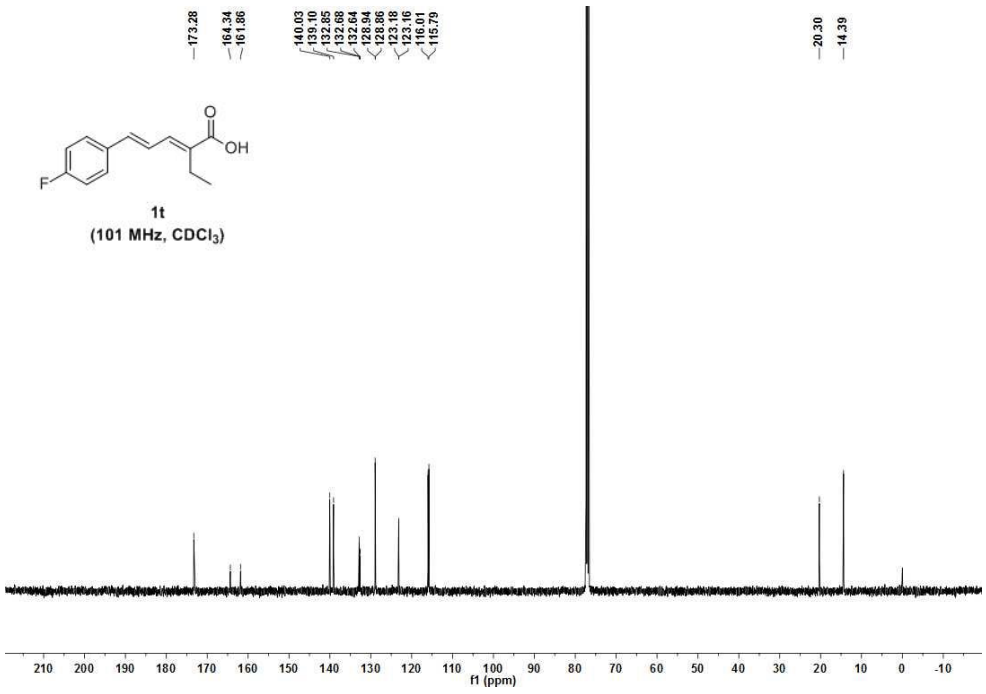
15t
(400 MHz, $CDCl_3$)



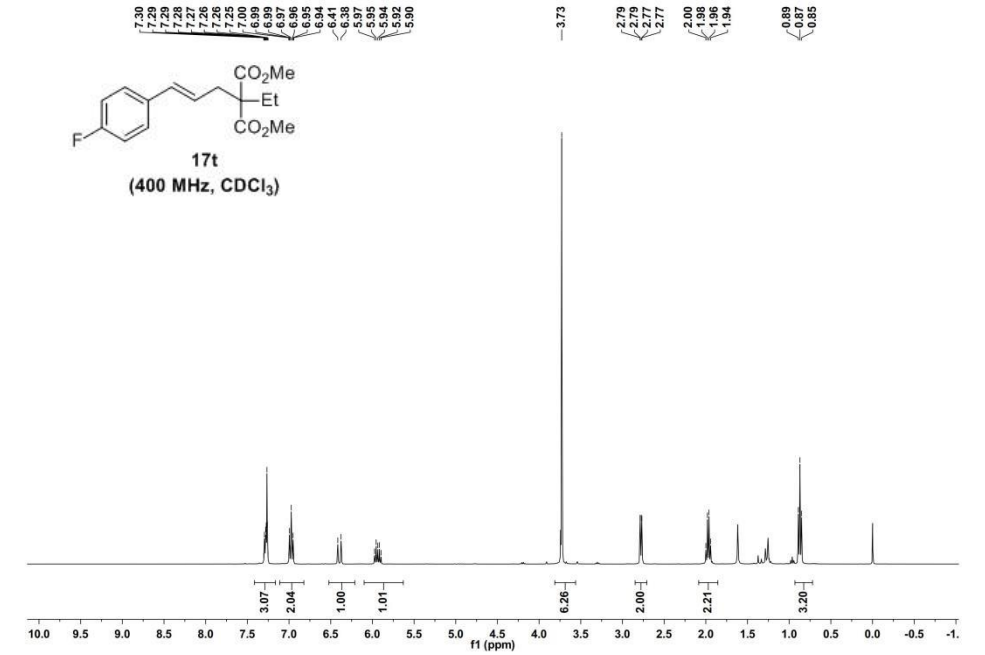
15t
(101 MHz, $CDCl_3$)

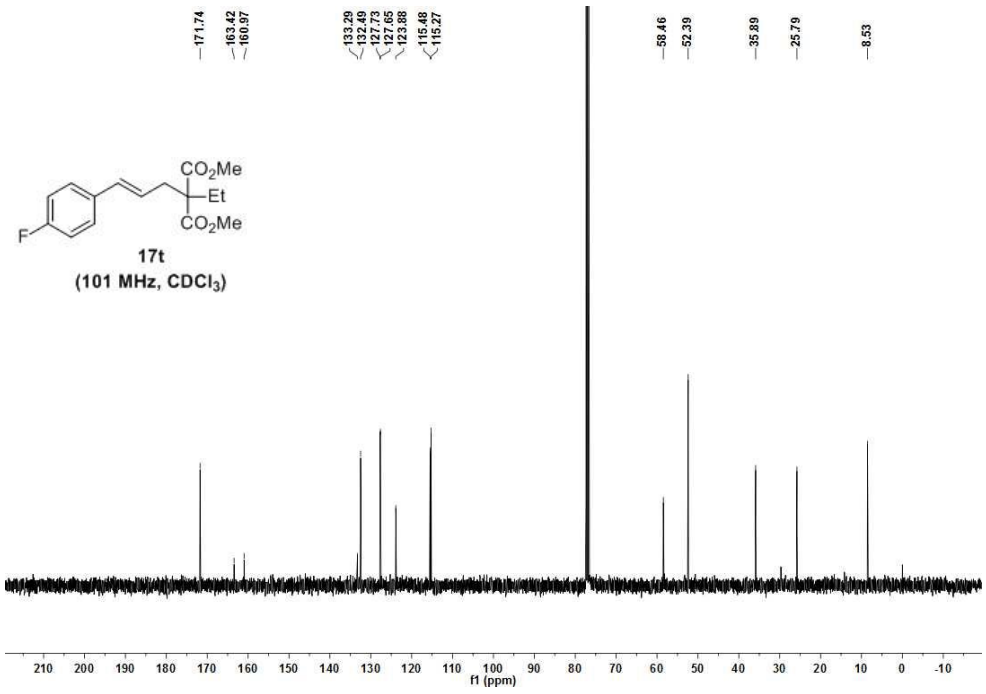


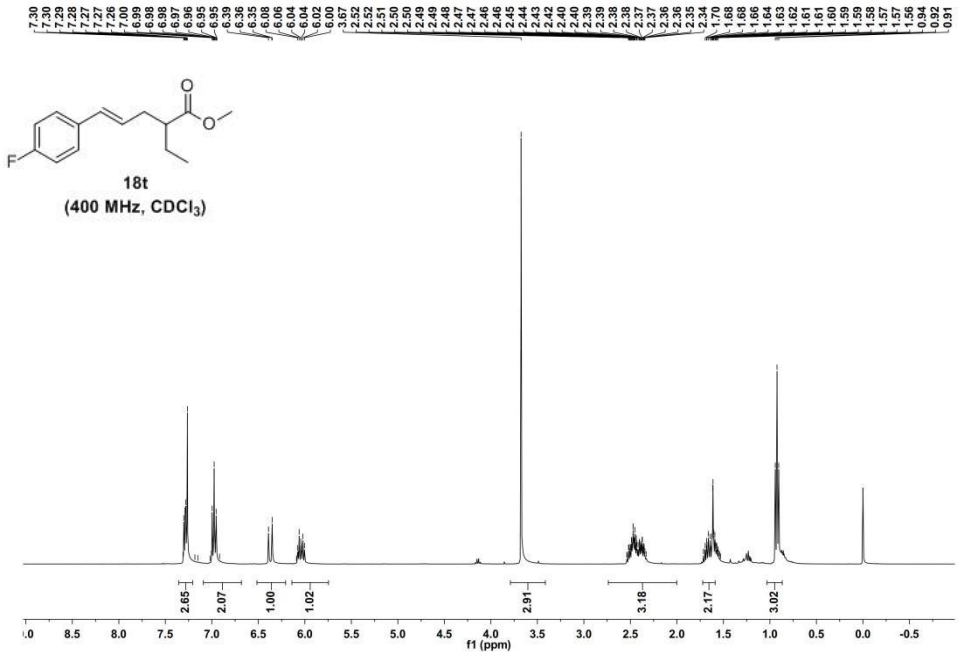
1t
(400 MHz, $CDCl_3$)

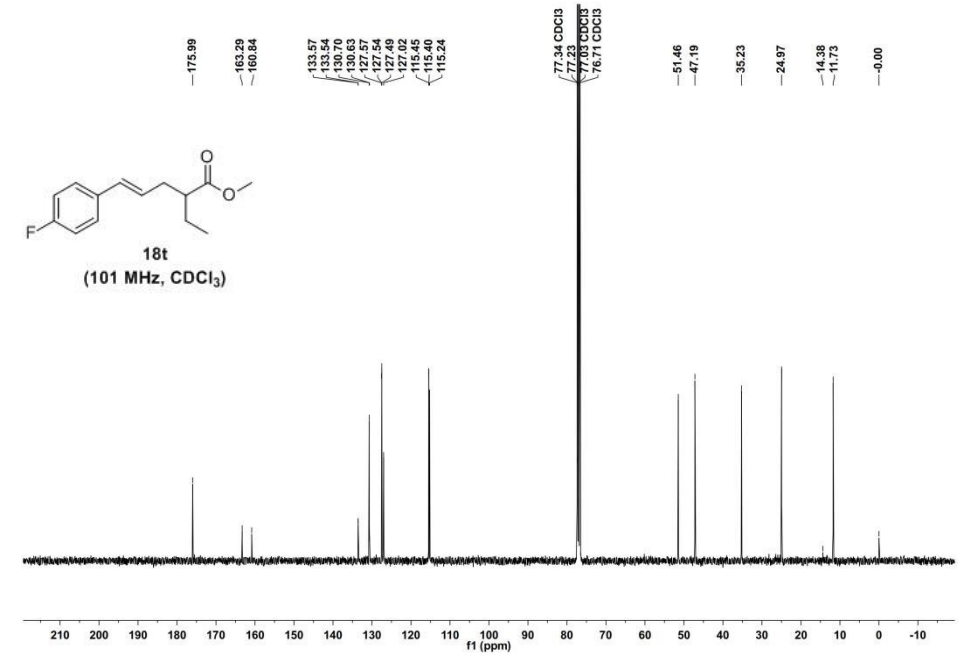


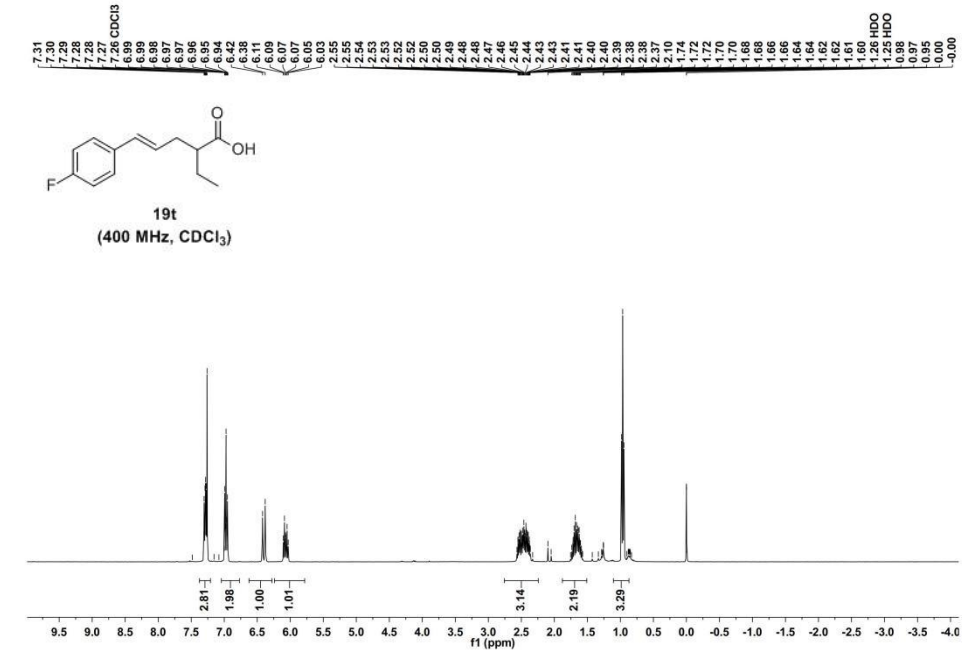
1t
(101 MHz, $CDCl_3$)

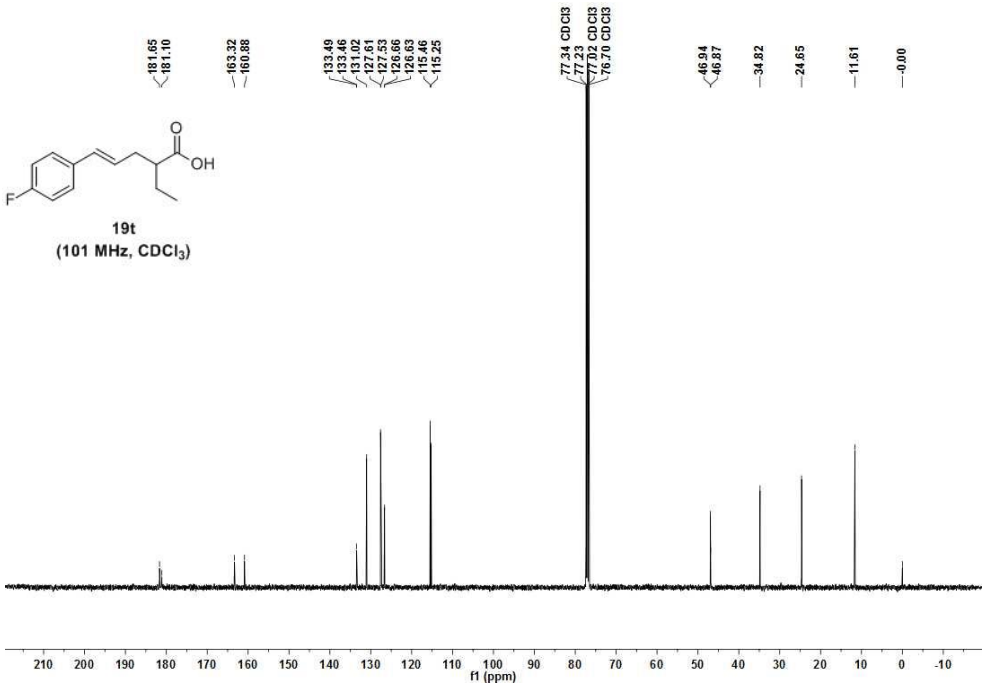

7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.25
7.00
6.99
6.99
6.97
6.96
6.95
6.94
6.41
6.38
5.97
5.95
5.94
5.92
5.90
3.73
2.79
2.79
2.77
2.77
2.00
1.98
1.96
1.94
0.89
0.87
0.85
CO2Me
Et
CO2Me
F
17t
(400 MHz, CDCl3)
3.07
2.04
1.00
1.01
6.26
2.00
2.21
3.20
f1 (ppm)

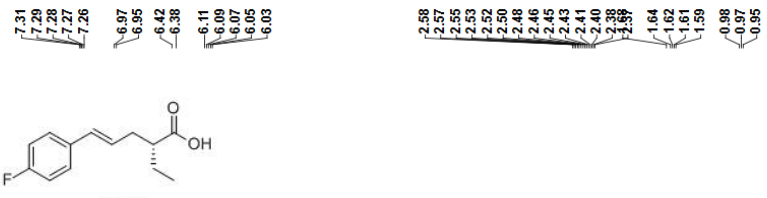

171.74
163.42
160.97
133.29
132.49
127.73
127.65
123.88
115.48
115.27
58.46
52.39
35.89
25.79
8.53
CO2Me
Et
CO2Me
F
17t
(101 MHz, CDCl3)
f1 (ppm)


18t
(400 MHz, CDCl3)
f1 (ppm)

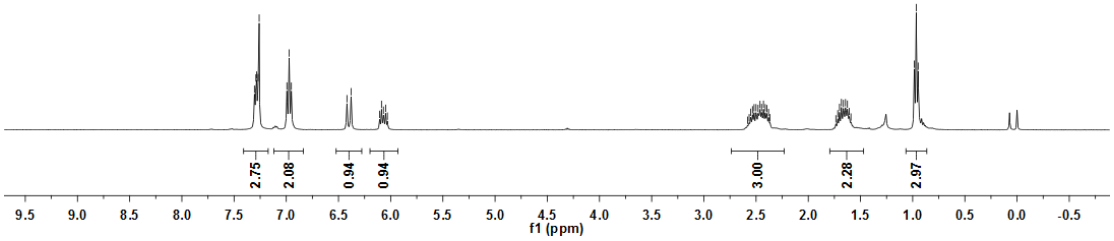

18t
(101 MHz, CDCl3)
f1 (ppm)

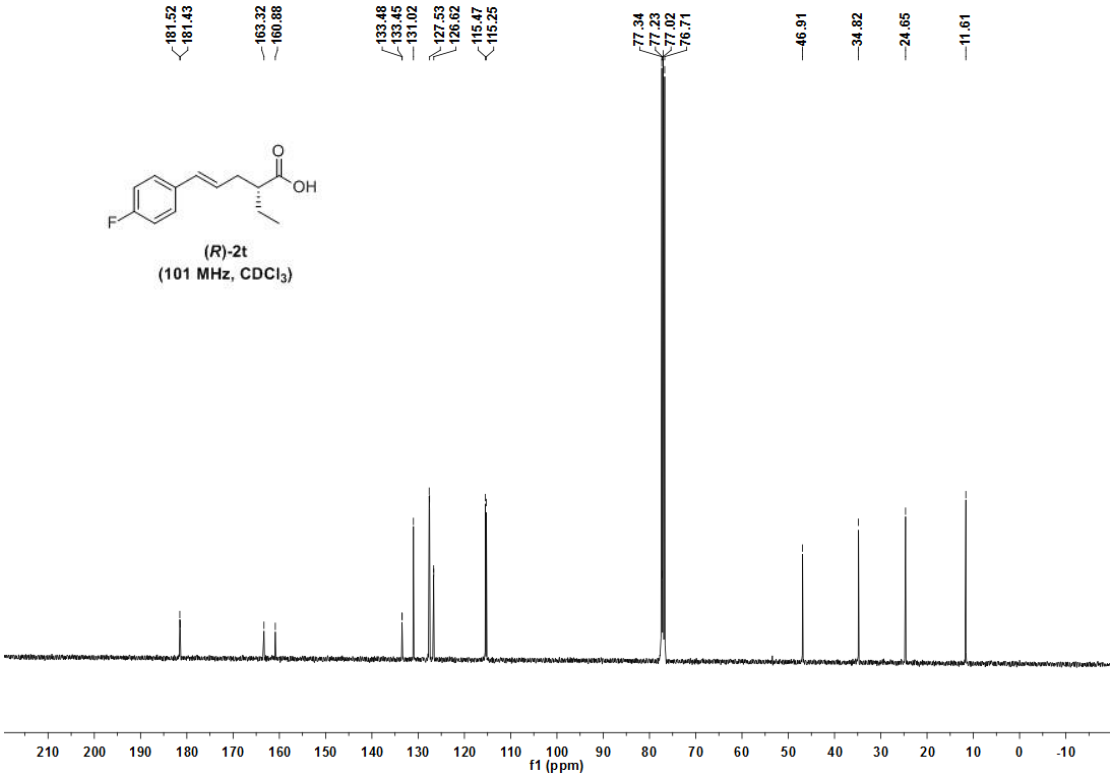

7.31
7.30
7.29
7.28
7.27
7.26 CDCl3
6.99
6.98
6.97
6.96
6.95
6.44
6.42
6.38
6.11
6.09
6.07
6.05
6.03
2.55
2.54
2.53
2.52
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.43
2.41
2.40
2.39
2.38
2.37
2.10
1.74
1.72
1.70
1.68
1.66
1.64
1.62
1.61
1.60
1.26 HDO
1.25 HDO
0.98
0.97
0.95
0.00
-0.00
O
OH
F
19t
(400 MHz, CDCl3)
2.81
1.98
1.00
1.01
3.14
2.19
3.29
f1 (ppm)


181.65
181.10
163.32
160.88
133.49
133.46
131.02
127.61
127.53
126.66
126.63
115.46
115.25
77.34 CDCl3
77.23
77.02 CDCl3
76.70 CDCl3
46.94
46.87
34.82
24.65
11.61
-0.00
O
OH
F
19t
(101 MHz, CDCl3)
f1 (ppm)

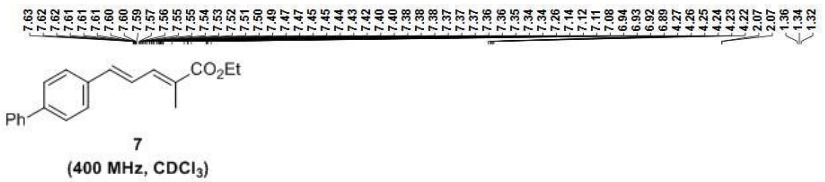


(*R*)-2t
(400 MHz, $CDCl_3$)



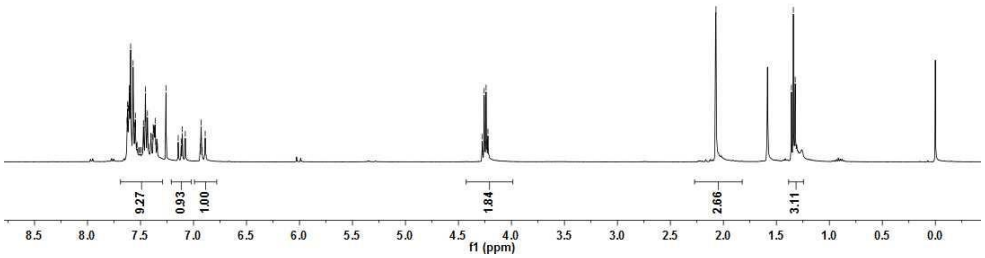


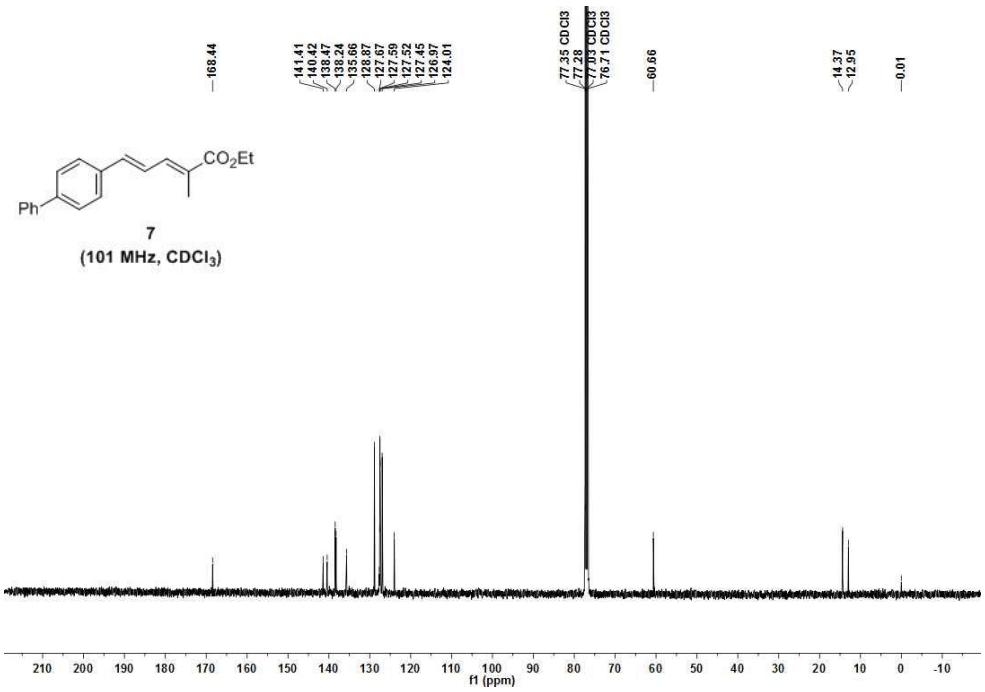
(*R*)-2t
(101 MHz, $CDCl_3$)



7

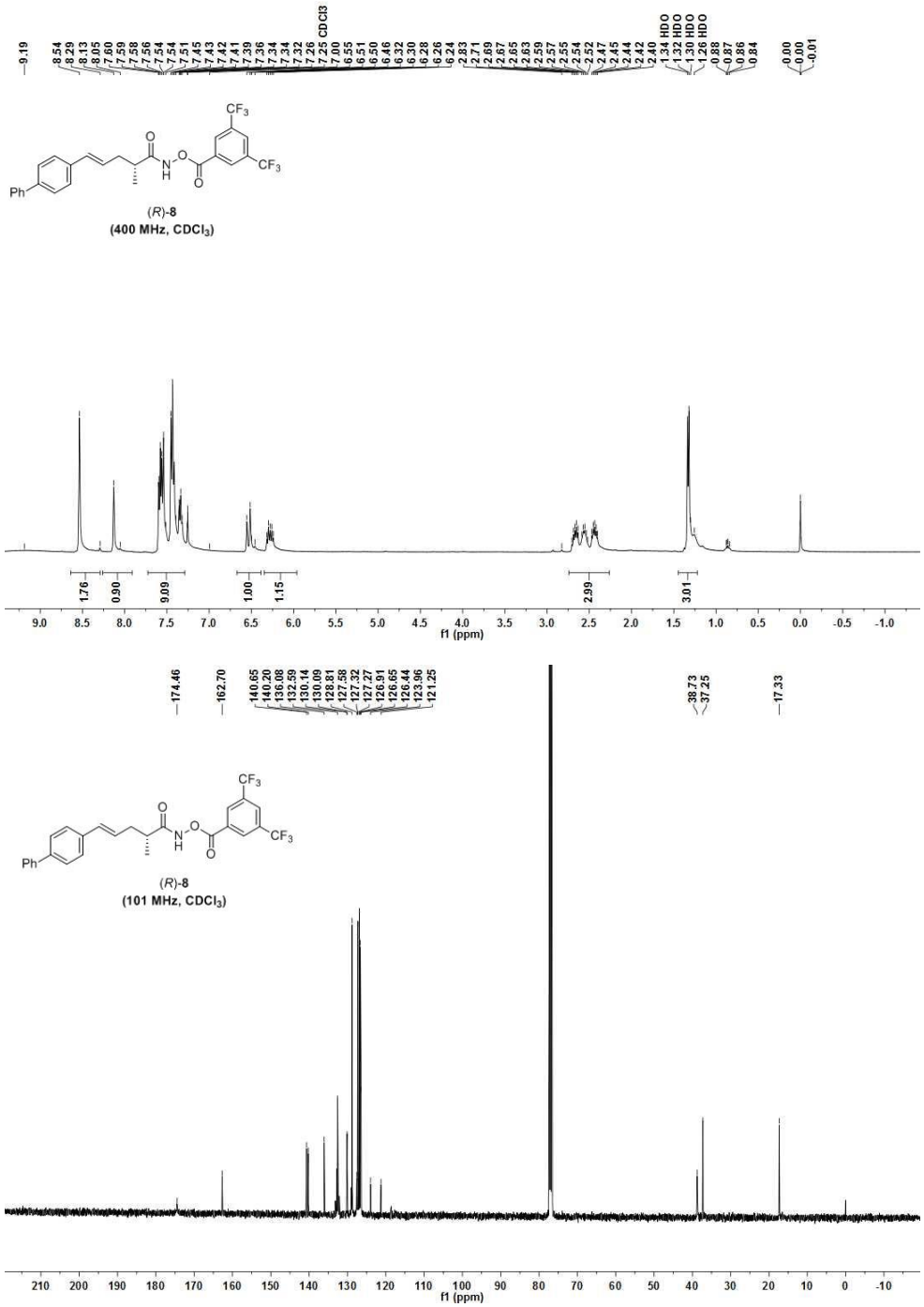
(400 MHz, $CDCl_3$)

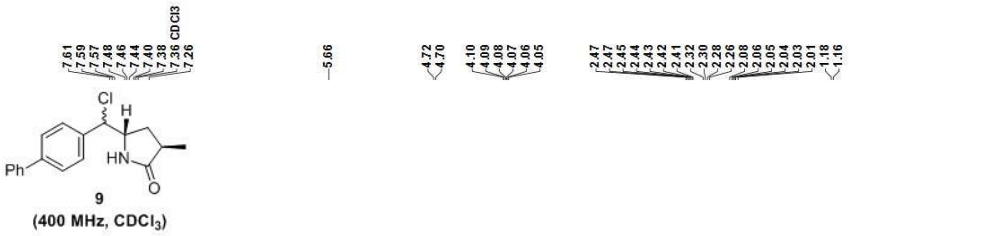




7

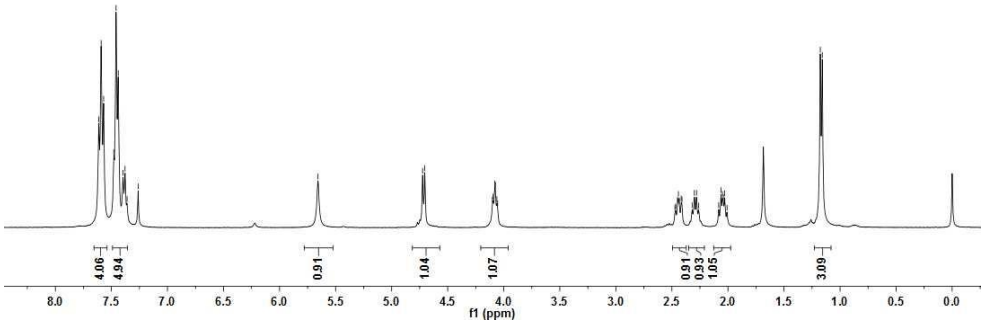
(101 MHz, $CDCl_3$)

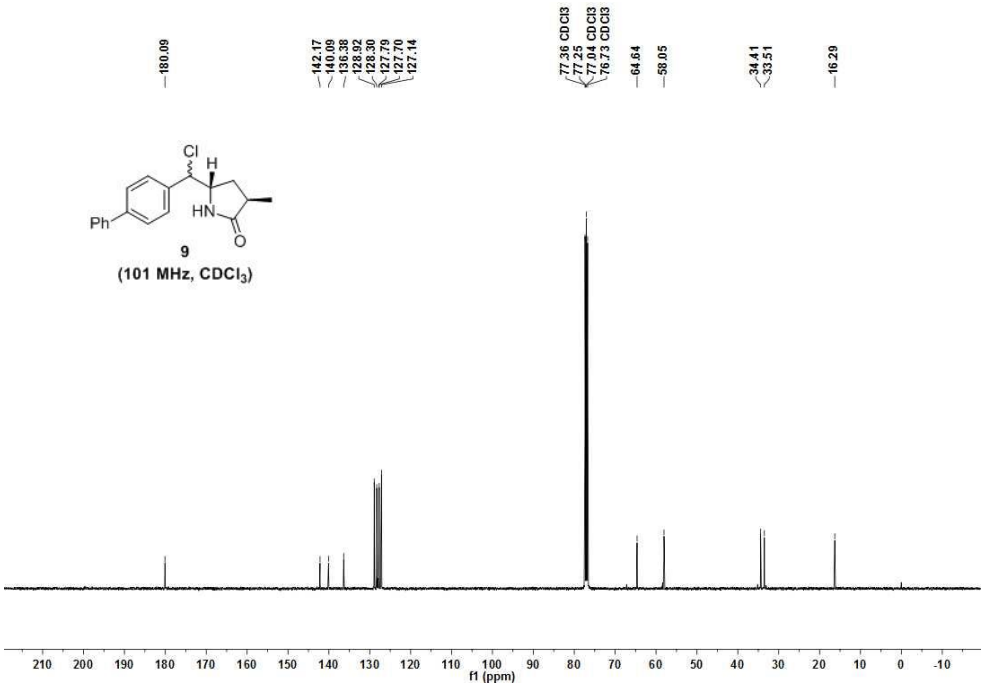

9.19
8.54
8.29
8.13
8.05
7.60
7.59
7.58
7.56
7.54
7.54
7.51
7.45
7.43
7.42
7.41
7.39
7.36
7.34
7.34
7.32
7.32
7.26
CDCl3
7.00
6.55
6.51
6.50
6.46
6.32
6.30
6.28
6.26
6.24
2.83
2.71
2.69
2.67
2.65
2.63
2.59
2.57
2.55
2.54
2.52
2.47
2.45
2.44
2.42
2.40
1.34 HDO
1.32 HDO
1.30 HDO
1.28 HDO
0.89
0.87
0.86
0.84
0.00
0.00
-0.01
CF3
CF3
O
N
O
H
O
Ph
(R)-8
(400 MHz, CDCl3)
1.76
0.90
9.09
1.00
1.15
2.99
3.01
f1 (ppm)
174.46
162.70
140.65
140.20
136.08
132.59
130.14
130.09
128.81
127.58
127.32
127.27
126.91
126.65
126.44
123.96
121.25
38.73
37.25
17.33
CF3
CF3
O
N
O
H
O
Ph
(R)-8
(101 MHz, CDCl3)
f1 (ppm)



9

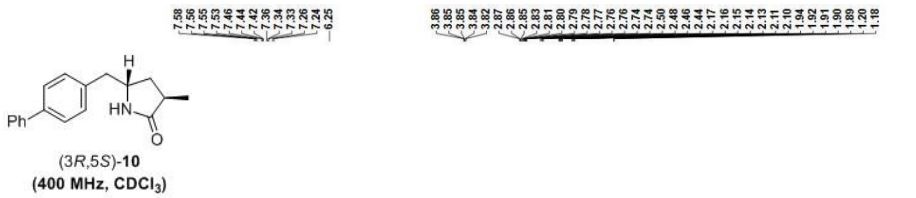
(400 MHz, $CDCl_3$)



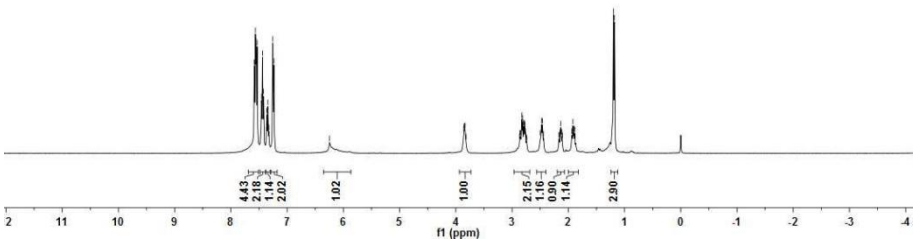


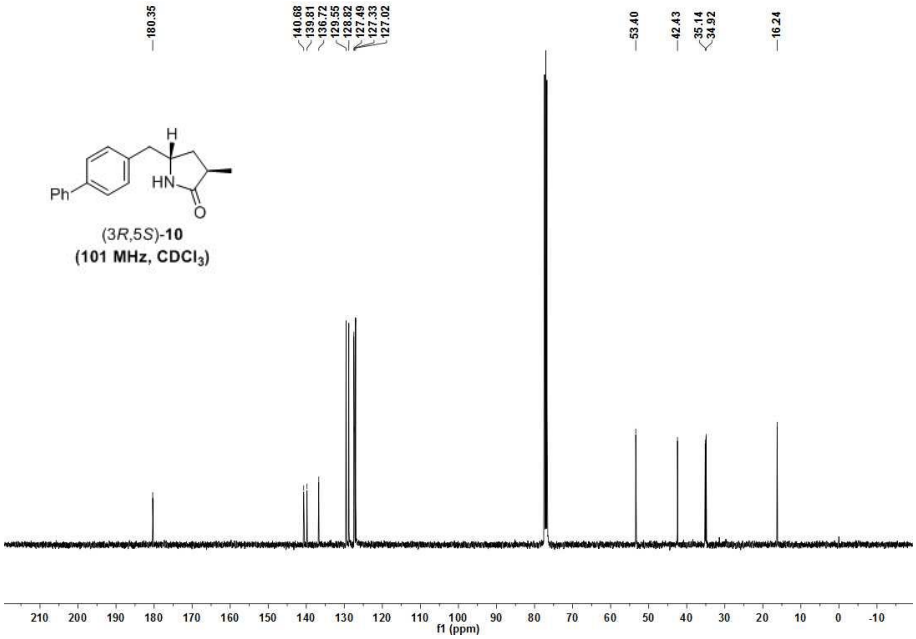
9

(101 MHz, $CDCl_3$)

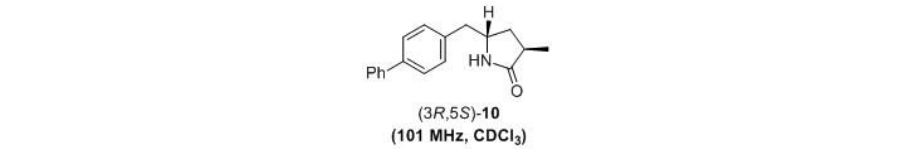


(3*R*,5*S*)-**10**
(400 MHz, $CDCl_3$)



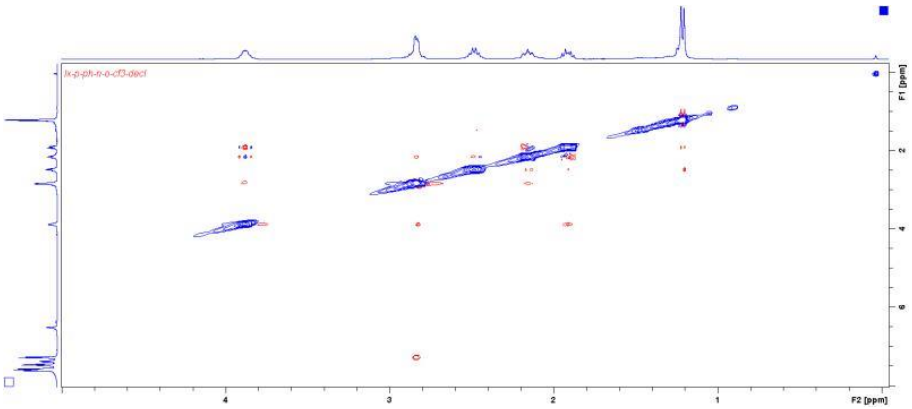


(3*R*,5*S*)-**10**
(101 MHz, $CDCl_3$)

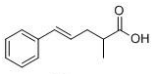


(3*R*,5*S*)-**10**
(101 MHz, $CDCl_3$)

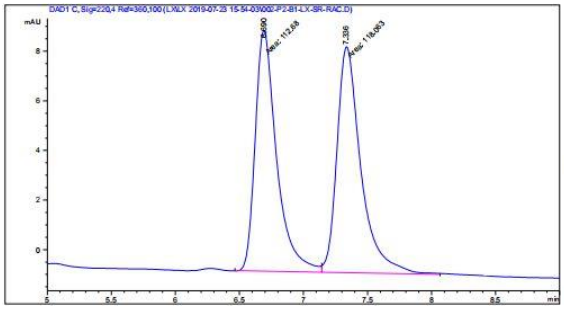
^{1}H-^{1}H NOESY spectrum



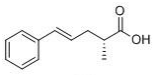
12. HPLC spectra



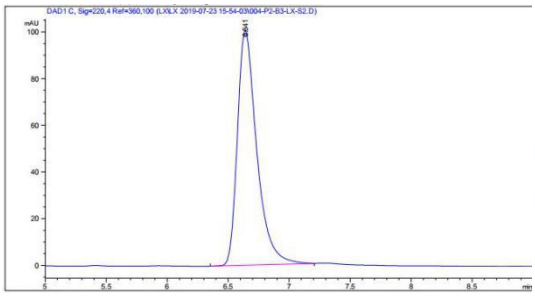
(rac）



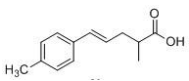
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.690	MF	0.1935	112.67989	9.70590	48.8335
2	7.336	FM	0.2160	118.06313	9.10911	51.1665
Totals :				230.74302	18.81501	



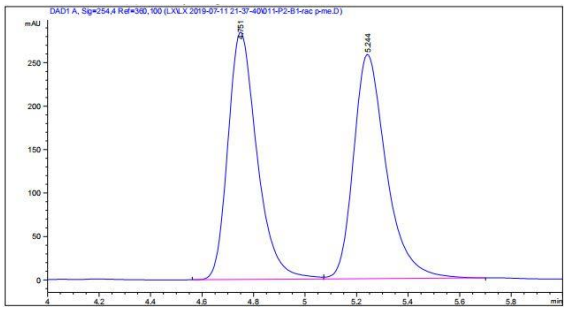
2a



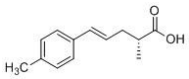
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.641	BB	0.1665	1106.42358	100.43256	100.0000
Totals :				1106.42358	100.43256	



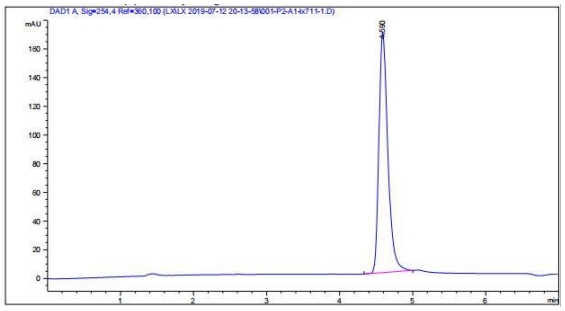
(rac）



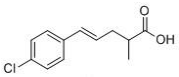
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.751	BV	0.1194	2232.28198	285.05585	49.4854
2	5.244	VB	0.1329	2278.70972	258.23294	50.5146
Totals :				4510.99170	543.28879	



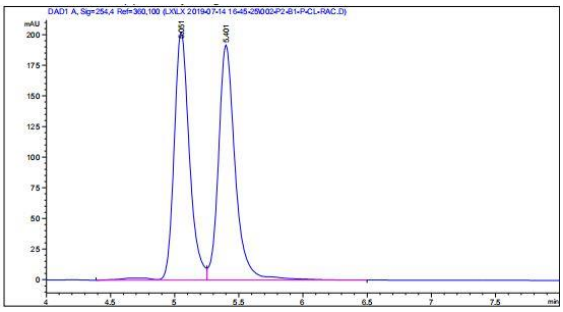
2b



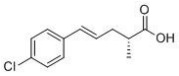
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.590	BB	0.1290	1422.38818	167.63307	100.0000
Totals :				1422.38818	167.63307	



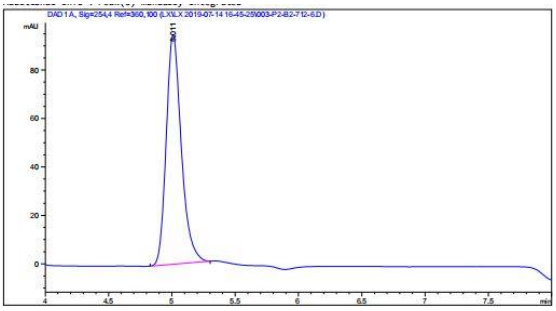
(rac）



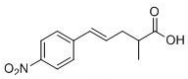
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.051	VV R	0.1232	1681.39539	202.77728	49.2296
2	5.401	VB	0.1354	1734.02344	191.89261	50.7704
Totals :				3415.41882	394.66989	



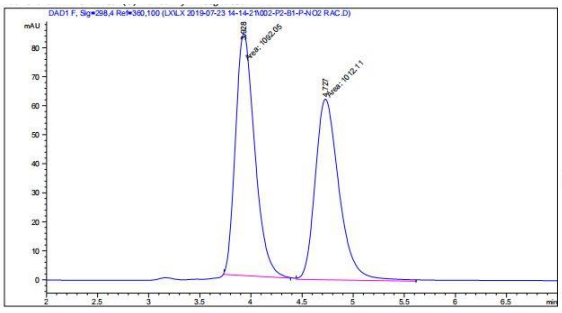
2c



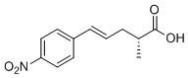
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.011	BB	0.1261	781.37134	94.82230	100.0000
Totals :				781.37134	94.82230	



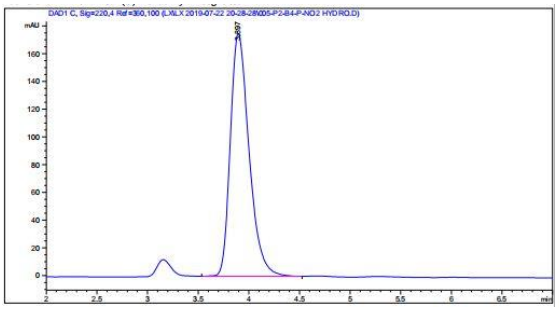
(rac）



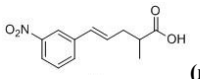
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.928	MM	0.2181	1092.05383	83.44494	51.8997
2	4.727	MM	0.2708	1012.10828	62.28594	48.1003
Totals :				2104.16211	145.73088	



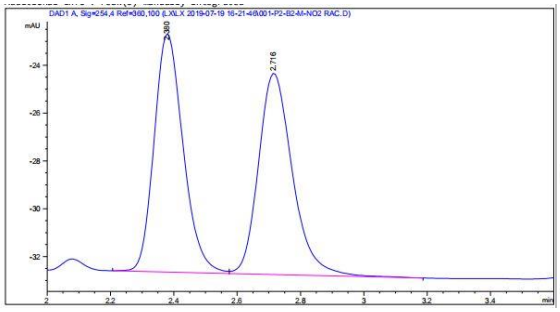
2d



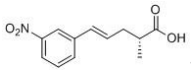
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.897	BB	0.1979	2250.02124	175.08221	100.0000
Totals :				2250.02124	175.08221	



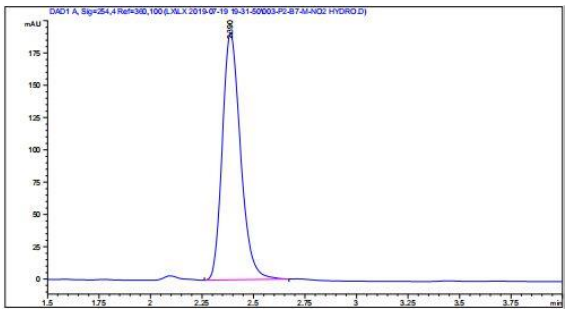
(rac）



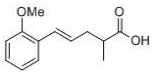
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.380	BV	0.0982	63.38094	9.96290	50.2670
2	2.716	VB	0.1149	62.70757	8.42148	49.7330
Totals :				126.08852	18.38438	



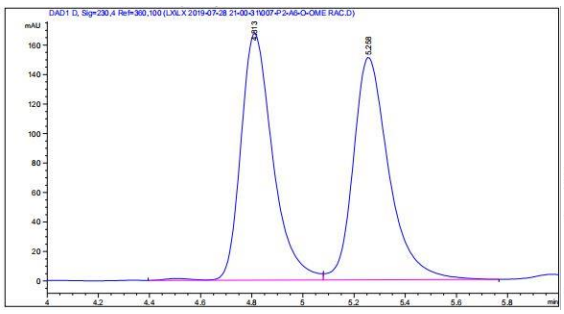
2e



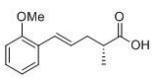
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.390	BB	0.0935	1175.33350	191.66743	99.1298
2	6.502	BB	0.1509	10.31790	1.02940	0.8702
Totals :				1185.65140	192.69684	



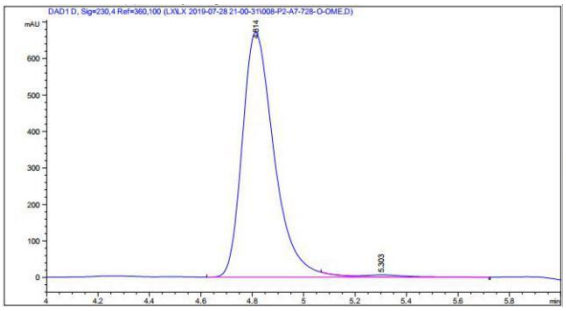
(rac）



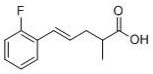
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.813	VV R	0.1325	1449.67419	167.23645	49.9041
2	5.258	VB	0.1446	1455.24451	150.81863	50.0959
Totals :				2904.91870	318.05508	



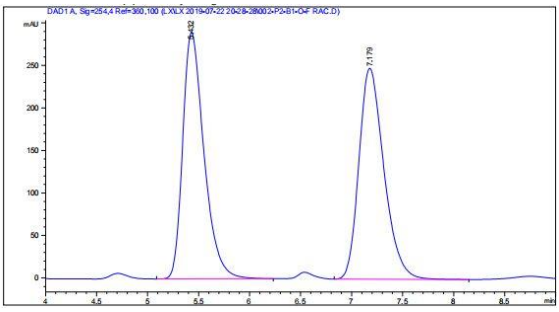
2f



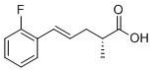
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.814	BV R	0.1305	5788.71045	671.75061	98.7931
2	5.303	VB E	0.1752	70.71915	5.76167	1.2069
Totals :				5859.42960	677.51228	



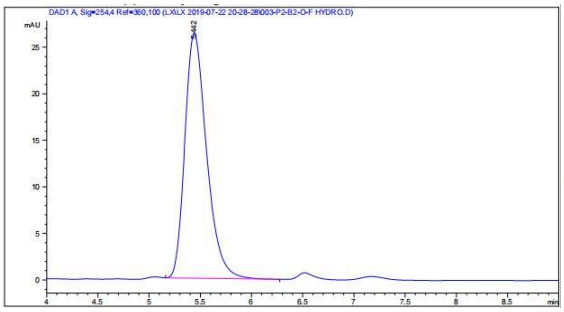
(rac）



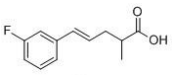
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.432	BB	0.2212	4205.02881	289.96552	49.8572
2	7.179	BB	0.2610	4229.11768	247.96971	50.1428
Totals :				8434.14648	537.93523	



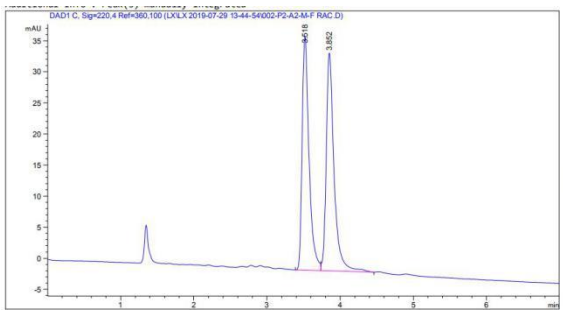
2g



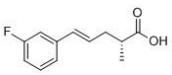
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.442	BB	0.2262	388.68958	26.34040	100.0000
Totals :				388.68958	26.34040	



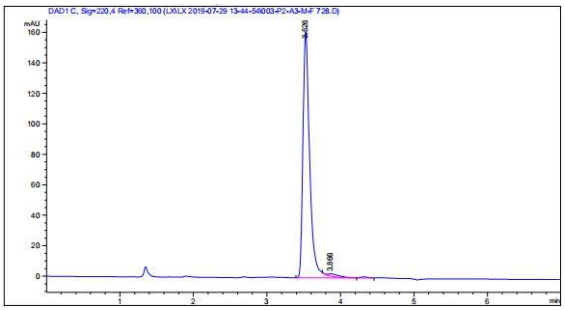
(rac）



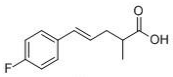
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.518	BV	0.0980	245.68767	37.73634	48.5073
2	3.852	VB	0.1107	260.80899	35.09047	51.4927
Totals :				506.49666	72.82681	



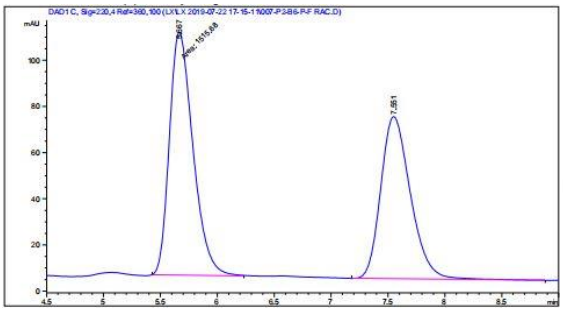
2h



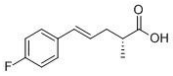
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.526	BV R	0.0952	1041.44580	161.47403	98.2871
2	3.866	VV E	0.1581	18.15015	1.53360	1.7129
Totals :				1059.59595	163.00763	



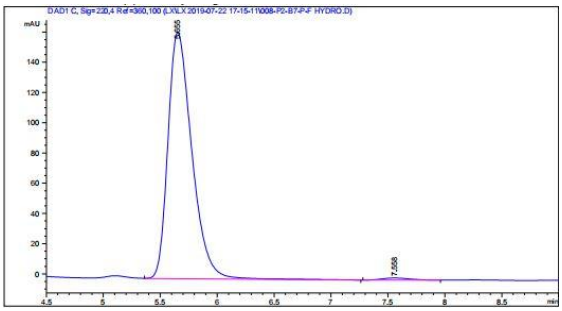
(rac）



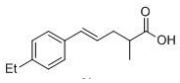
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.667	MM	0.2401	1515.68298	105.20680	54.3120
2	7.551	BB	0.2797	1275.01538	70.25357	45.6880
Totals :				2790.69836	175.46037	



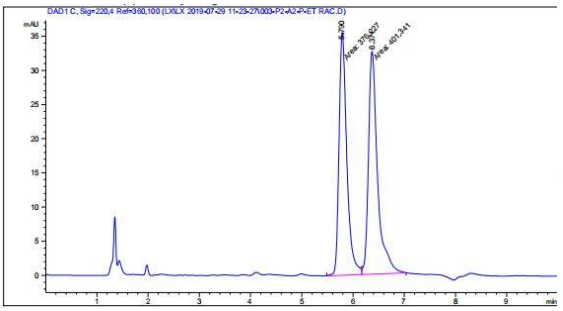
2i



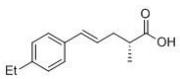
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.655	VB	0.2221	2374.69263	162.85742	99.0228
2	7.558	BB	0.2629	23.43535	1.38832	0.9772
Totals :				2398.12798	164.24574	



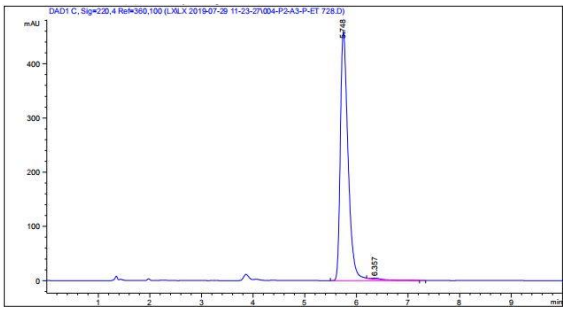
(rac）



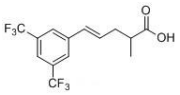
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.790	MF	0.1763	376.22672	35.56728	48.3851
2	6.371	FM	0.2050	401.34079	32.63508	51.6149
Totals :				777.56750	68.20235	



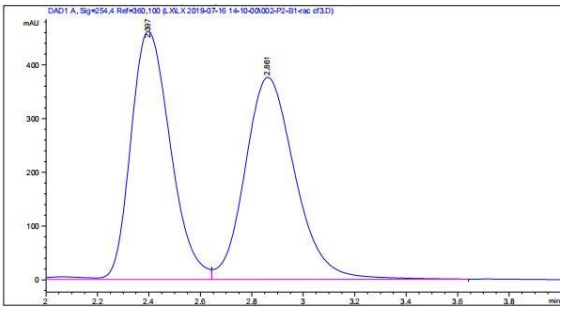
2j



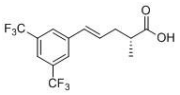
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.748	BV R	0.1584	4811.51465	458.55975	99.3133
2	6.357	VB E	0.2101	33.26685	2.25457	0.6867
Totals :				4844.78150	460.81433	



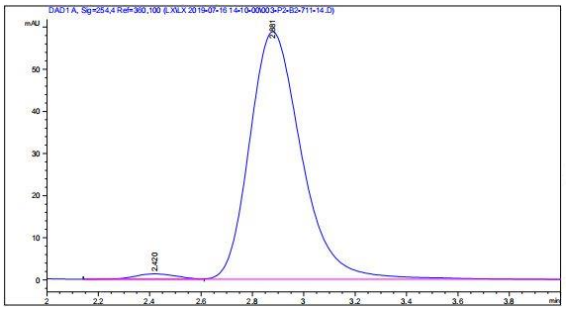
(rac）



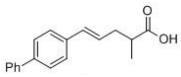
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.397	VV R	0.1657	4954.91260	461.71286	49.5207
2	2.861	VB	0.2088	5050.82129	375.86456	50.4793
Totals :				1.00057e4	837.57742	



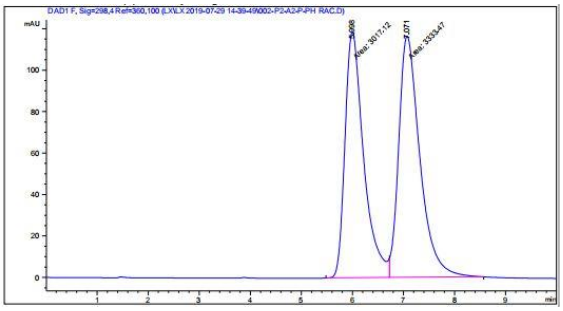
2k



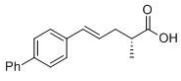
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.420	BV E	0.1787	14.63481	1.28676	1.7384
2	2.881	VB R	0.2160	827.22241	58.83446	98.2616
Totals :				841.85722	60.12121	



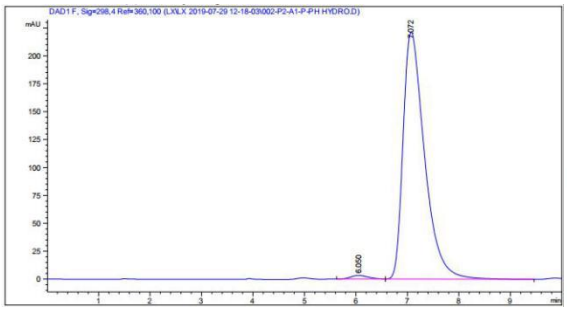
(rac）



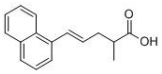
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.998	MF	0.4244	3017.12354	118.49178	47.5093
2	7.071	FM	0.4772	3333.47290	116.41792	52.4907
Totals :				6350.59644	234.90969	



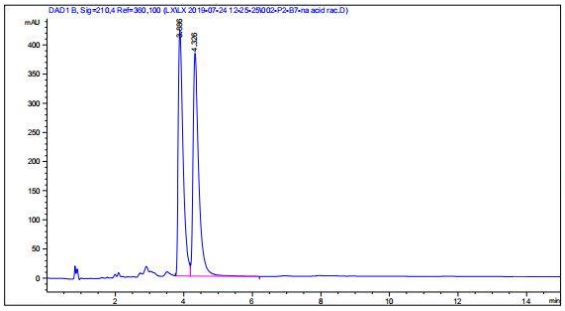
2l



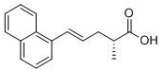
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.050	BV	0.3720	77.55632	3.25480	1.1943
2	7.072	VB	0.4402	6416.18164	221.36650	98.8057
Totals :				6493.73796	224.62130	



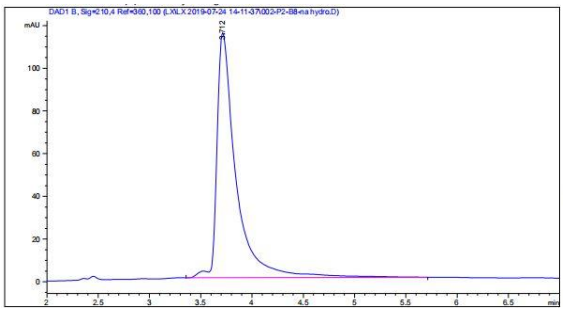
(rac）



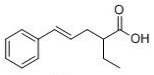
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.886	BV	0.1489	4139.45215	420.33997	48.4037
2	4.326	VB	0.1729	4412.48486	381.58896	51.5963
Totals :				8551.93701	801.92892	



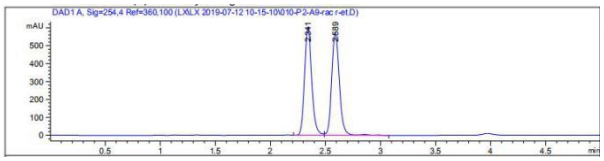
2m



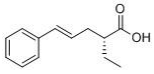
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.712	VB R	0.1852	1489.24451	114.70390	100.0000
Totals :				1489.24451	114.70390	



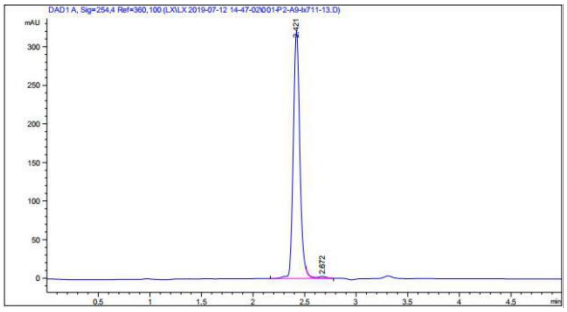
(rac）



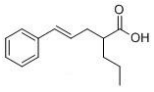
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.341	BV	0.0709	2736.95679	604.16510	49.6410
2	2.589	VV R	0.0736	2776.54688	572.26672	50.3590
Totals :				5513.50366	1176.43182	



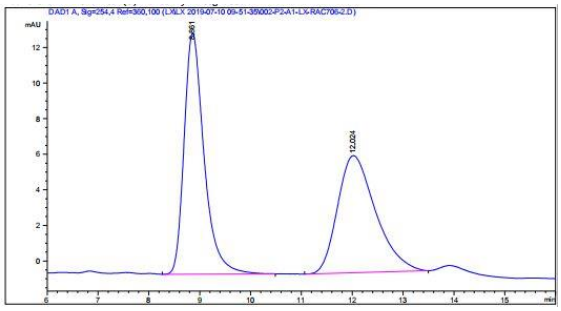
2n



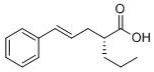
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.421	BV R	0.0694	1414.21851	321.14301	98.8208
2	2.672	VB E	0.0950	16.87515	2.55780	1.1792
Totals :				1431.09366	323.70080	



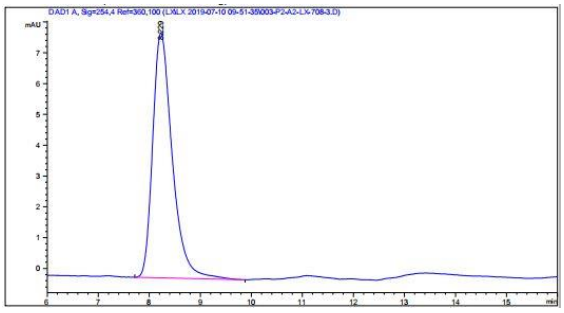
(rac）



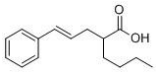
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.861	BB	0.4136	368.61087	13.54217	51.9310
2	12.024	BB	0.7909	341.19855	6.58083	48.0690
Totals :				709.80942	20.12300	



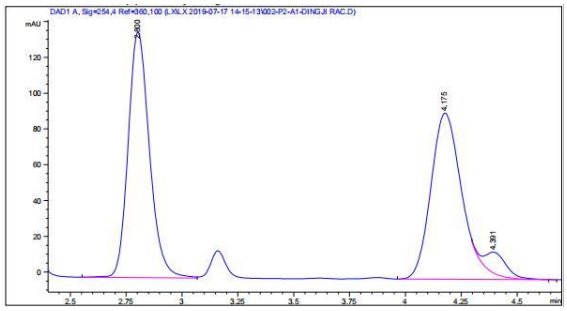
2o



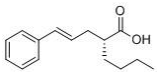
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.229	BB	0.4032	212.05333	7.94895	100.0000
Totals :				212.05333	7.94895	



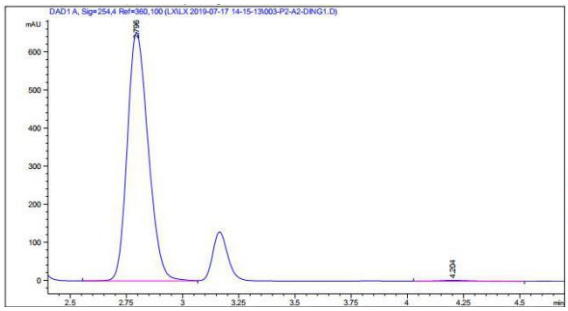
(rac）



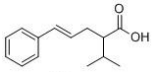
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.800	BV	0.1013	910.16748	137.41219	48.0323
2	4.175	BV R	0.1501	908.42993	92.86027	47.9406
3	4.391	VB E	0.0995	76.30963	11.48726	4.0271
Totals :				1894.90704	241.75971	



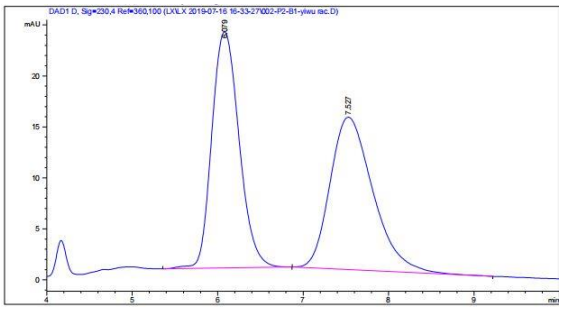
2p



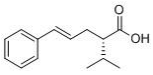
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.796	BV	0.0993	4217.21533	653.40594	99.5179
2	4.204	BB	0.1508	20.42760	2.07525	0.4821
Totals :				4237.64293	655.48119	



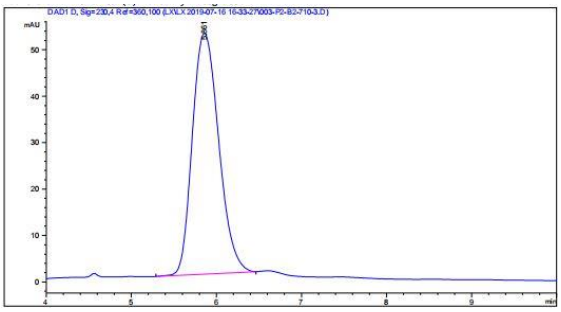
(rac）



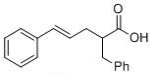
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.079	BB	0.3509	513.66602	23.14322	49.6246
2	7.527	BB	0.5410	521.43793	14.94847	50.3754
Totals :				1035.10394	38.09169	



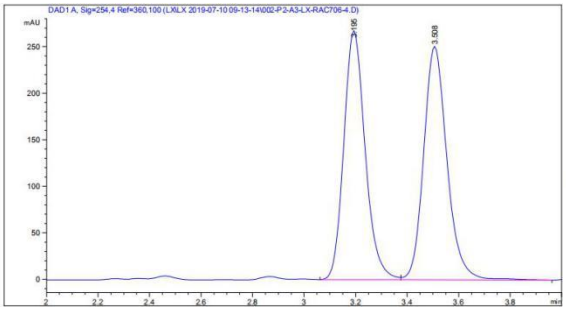
2q



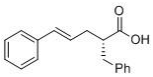
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.861	BB	0.3413	1116.96863	51.84879	100.0000
Totals :				1116.96863	51.84879	



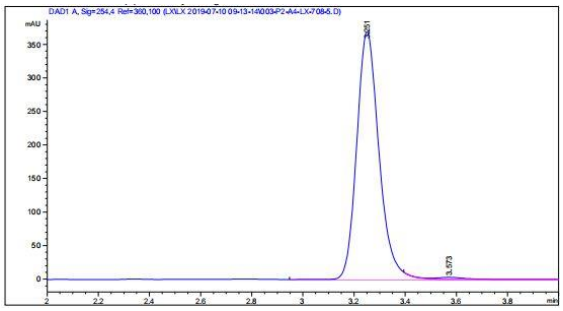
(rac)



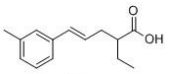
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.195	BV	0.0892	1540.58691	267.46301	49.4389
2	3.508	VB	0.0953	1575.55786	250.81480	50.5611
Totals :				3116.14478	518.27782	



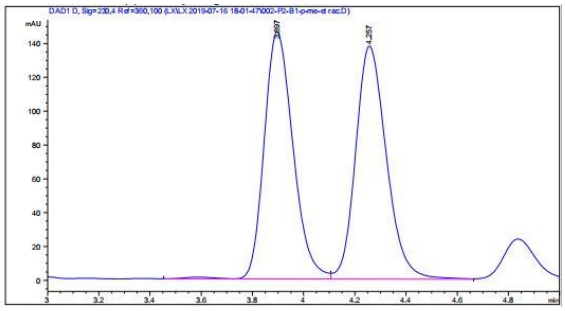
2r



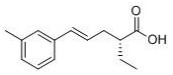
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.251	BV R	0.0945	2234.86182	369.91672	98.6742
2	3.573	VB E	0.1373	30.02761	3.09132	1.3258
Totals :				2264.88942	373.00803	



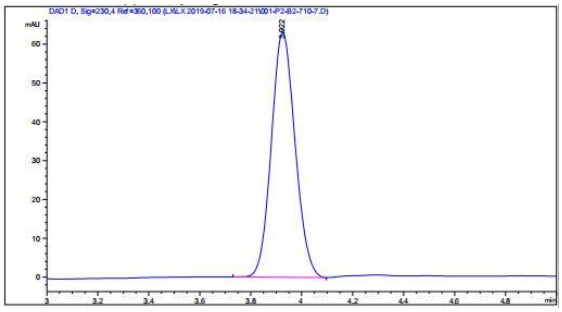
(rac）



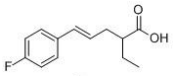
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.897	VV R	0.1209	1147.21936	146.25554	49.9804
2	4.257	VV	0.1292	1148.11951	137.84698	50.0196
Totals :				2295.33887	284.10252	



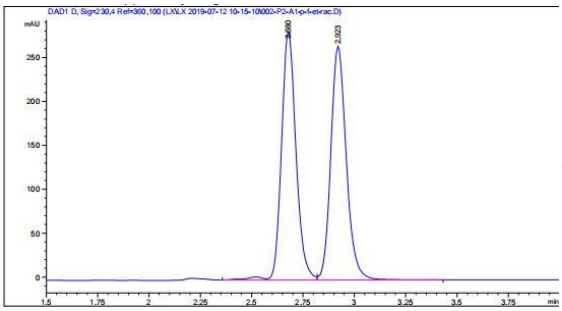
2s



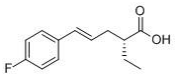
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.922	BB	0.1014	408.09647	63.17123	100.0000
Totals :				408.09647	63.17123	



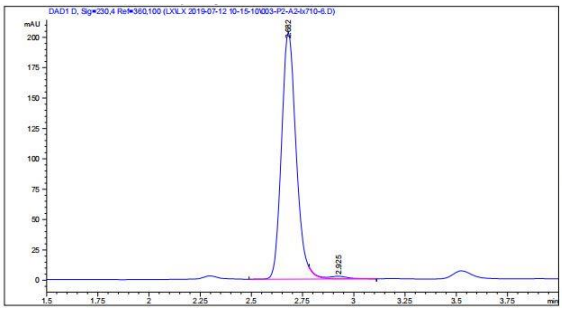
(rac)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.680	VV R	0.0747	1393.73206	282.42035	50.0434
2	2.923	VB	0.0790	1391.31482	265.92856	49.9566
Totals :				2785.04688	548.34891	



2t



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.682	BV R	0.0761	1012.29181	203.34396	98.5194
2	2.925	VB E	0.1012	15.21344	2.13419	1.4806
Totals :				1027.50525	205.47816	