Supporting Information

Enantioselective Epoxidation of β,β-Disubstituted Enamides with a Manganese Catalyst and Aqueous Hydrogen Peroxide

Carlota Clarasó, Laia Vicens, Alfonso Polo and Miquel Costas**

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1) Experimental Section

1.1) Materials

Reagents and solvents used were of commercially available reagent quality unless stated otherwise. Solvents were purchased from SDS and Scharlab. Solvents were purified and dried by passing through an activated alumina purification system (MBraun SPS-800). HPLC quality acetonitrile was employed in epoxidation reactions.

1.2) Instrumentation

IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer using a MKII Golden Gate single reflection ATR system. NMR spectra were taken on a Bruker Ultrashield DPX300 MHz or Bruker Ultrashield AVANCE III400 spectrometer using standard conditions. Elemental analyses of C, H, and N were performed using a CHNS-O EA-2400 elemental analyser from Perkin Helmer. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-QII instrument with an ESI source and a quadrupole analyser at Serveis Tècnics of the University of Girona. Samples were introduced into the mass spectrometer ion source by direct infusion through a syringe pump and were externally calibrated using sodium formate. The X-Ray measurement of **(*S,S*)-^{Me2N}Ohq-Mn** was carried out on a BRUKER SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71 Å). Oxidation products were identified by ^{1}H and ^{13}C-NMR analyses. Chromatographic resolution of enantiomers was performed on HPLC 1200 series Agilent technologies using CHIRALPAK-IA and CHIRALPAK-IC columns using crude reaction mixtures to avoid possible enantiomeric enrichment during purification. Racemic epoxides have been prepared using standard epoxidation conditions using mCPBA,[1] [Mn(OTf)$_2$(^{H,Me}PyTACN)][2] or the racemic version of the catalyst ^{Me2N}Ohq-Mn.

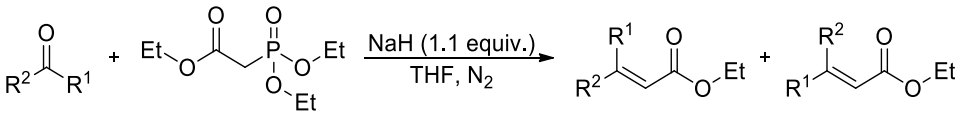
The absolute configuration of the major enantiomer of the epoxide resulting from epoxidation of **S6** with **(*S,S*)-^{Me2N}Ohq-Mn** (Table 2, Entry 4) was determined by single-crystal X-Ray diffraction. The X-Ray measurement was carried out on an AGILENT SUPERNOVA diffractometer equipped with an Atlas CCD detector using graphite-monochromate Cu Kα radiation (λ = 1.54 Å) from an X-Ray tube.

2) Synthesis of substrates

A literature procedure was used to prepare **S1**.[3]

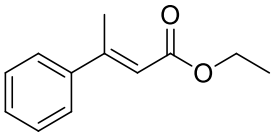
2.1) General procedure A for the synthesis of α,β-unsaturated esters

A literature procedure was used to prepare α,β-unsaturated esters.[4]



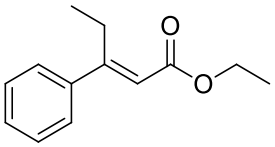
To a suspension of NaH (480 mg, 60% in mineral oil, 12 mmol) in THF (10 mL), a solution of triethyl phosphonoacetate (2.5 mL, 12 mmol) in THF (5 mL) was slowly added. The mixture was stirred at room temperature for 30 min. Then, ketone (10 mmol) in THF (5 mL) was added at 0 °C, and the mixture was stirred at room temperature. After confirmation of consumption of ketone by TLC, a solution of saturated aqueous sodium bicarbonate (15 mL) was added. The mixture was extracted with EtOAc (3 x 25 mL), washed with brine (15 mL) and dried over Mg_2SO_4. After concentration of the organic phase, the residue was purified by silica-gel column chromatography (hexane/EtOAc as eluent) to give (E)-ester and/or (Z)-ester.

(*E*)-ethyl 3-phenylbut-2-enoate (S2)



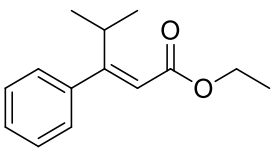
Prepared according to General Procedure A. Hexane/EtOAc 9:1, 80% yield. Spectral data match those previously reported.[5]

Ethyl 3-phenylpent-2-enoate



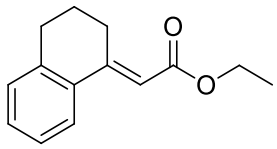
Prepared according to General Procedure A. Hexane/EtOAc 98:2, a 51% yield of **E**, 21% yield of **Z**. Spectral data match those previously reported.[5]

(*E*)-ethyl 4-methyl-3-phenylpent-2-enoate



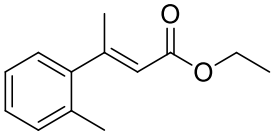
Prepared according to General Procedure A. Hexane/EtOAc 95:5, 28% yield. Spectral data match those previously reported.[6]

(*E*)-ethyl 2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)acetate



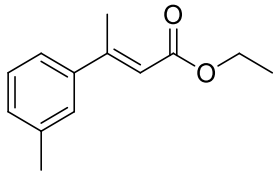
Prepared according to General Procedure A. Hexane/EtOAc 9:1, 7% yield. Spectral data match those previously reported.[7]

***(E)*-Ethyl 3-(o-tolyl)but-2-enoate**



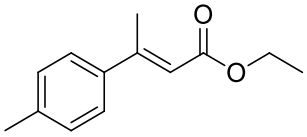
Prepared according to General Procedure A. Hexane/EtOAc 95:5, 51% yield. Spectral data match those previously reported.[8]

(*E*)-ethyl 3-(m-tolyl)but-2-enoate



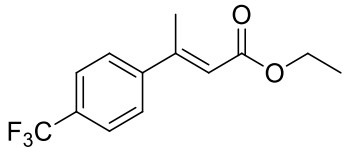
Prepared according to General Procedure A. Hexane/EtOAc 95:5, 84% yield. Spectral data match those previously reported.[8]

(*E*)-ethyl 3-(p-tolyl)but-2-enoate



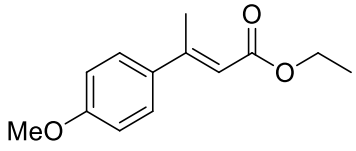
Prepared according to General Procedure A. Hexane/EtOAc 95:5, 73% yield. Spectral data match those previously reported.[5]

(*E*)-ethyl 3-(4-(trifluoromethyl)phenyl)but-2-enoate



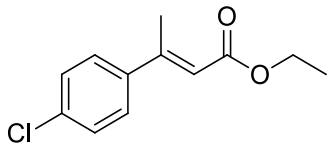
Prepared according to General Procedure A. Hexane/EtOAc 95:5, 73% yield. Spectral data match those previously reported.[5]

(*E*)-ethyl 3-(4-methoxyphenyl)but-2-enoate



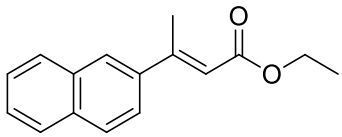
Prepared according to General Procedure A. Hexane/EtOAc 9:1, 77% yield. Spectral data match those previously reported.[9]

(*E*)-ethyl 3-(4-chlorophenyl)but-2-enoate



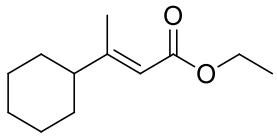
Prepared according to General Procedure A. Hexane/EtOAc 9:1, 77% yield. Spectral data match those previously reported.[5]

(*E*)-ethyl 3-(naphthalen-2-yl)but-2-enoate



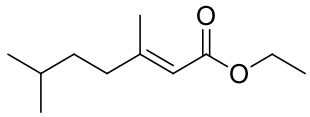
Prepared according to General Procedure A. Hexane/EtOAc 98:02, 73% yield. Spectral data match those previously reported.[5]

(*E*)-ethyl 3-cyclohexylbut-2-enoate



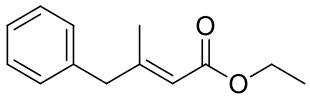
Prepared according to General Procedure A. Hexane/EtOAc 100:0-99:0.1, 67% yield. Spectral data match those previously reported.[10]

Ethyl 3,6-dimethylhept-2-enoate



Prepared according to General Procedure A, an inseparable mixture of E and Z isomers was obtained. Hexane/EtOAc 9:1, 70% yield, **E**:**Z** 81:19. Spectral data match those previously reported.[11]

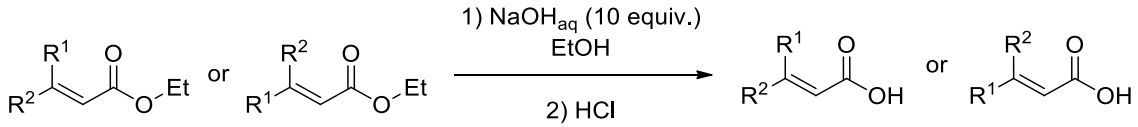
(*E*)-ethyl 3-methyl-4-phenylbut-2-enoate



Prepared according to General Procedure A. Hexane/EtOAc 9:1, 63% yield. Spectral data match those previously reported.[12]

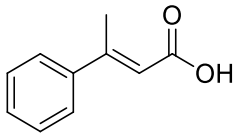
2.2) General procedure B for the synthesis of α,β-unsaturated acids

A slightly modified literature procedure was used to prepare α,β-unsaturated acids.[13]



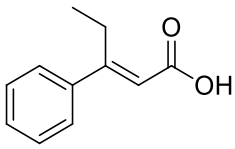
The α,β-unsaturated ester was placed in a 50 mL round-bottom flask, then EtOH (0.5M) was added, the reaction mixture was stirred, and NaOH (10%, 10 equiv.) was added. The reaction mixture was stirred at room temperature or at reflux until no starting material was detected by TLC. Then the pH was adjusted to 1.0 with HCl (1 M). The mixture was extracted with diethyl ether. The combined organic layer was washed with saturated $NaCl_{aq}$ solution, dried over $MgSO_4$, and concentrated in vacuum. If needed, the crude residue was subjected to flash chromatography (hexane/EtOAc) to afford the corresponding α,β-unsaturated acid.

(*E*)-3-phenylbut-2-enoic acid



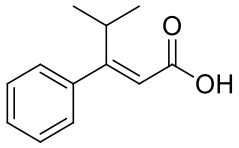
Prepared according to General Procedure B. Hexane/EtOAc 5:1, 90% yield. Spectral data match those previously reported.[13]

3-phenylpent-2-enoic acid



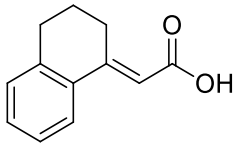
Prepared according to General Procedure B. No further purification is needed for **E**, 72% yield **E**. Hexane/EtOAc 5:2 for **Z**, 90% yield **Z**. Spectral data match those previously reported.[13]

(*E*)-4-methyl-3-phenylpent-2-enoic acid



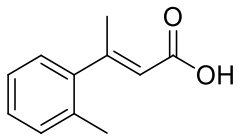
Prepared according to General Procedure B. No further purification is needed, 98% yield. Spectral data match those previously reported.[13]

(*E*)-2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)acetic acid



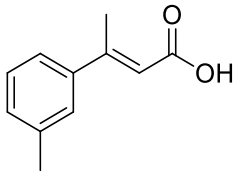
Prepared according to General Procedure B. No further purification is needed, 96% yield. Spectral data match those previously reported.[7]

(*E*)-3-(o-tolyl)but-2-enoic acid



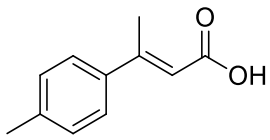
Prepared according to General Procedure B. No further purification is needed, 94% yield. Spectral data match those previously reported.[13]

(*E*)-3-(m-tolyl)but-2-enoic acid



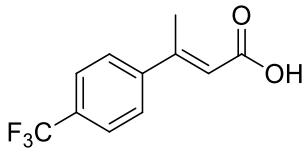
Prepared according to General Procedure B, 95% yield. No further purification is needed, 95% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.35-7.27 (m, 3H), 7.20 (d, J = 6.1 Hz, 1H), 6.17 (s, 1H), 2.60 (s, 3H), 2.39 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm: 172.2, 158.8, 142.1, 138.2, 130.1, 128.5, 127.1, 123.6, 116.2, 21.5, 18.4. HRMS (ESI-MS) m/z calculated for $C_{11}H_{11}O_2$ $[M-H]^-$: 175.0754, found: 175.0747.

(*E*)-3-(p-tolyl)but-2-enoic acid



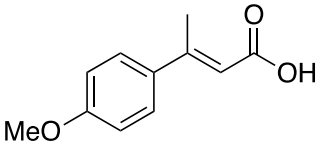
Prepared according to General Procedure B. No further purification is needed, 99% yield. Spectral data match those previously reported.[14]

(*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoic acid



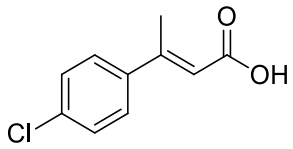
Prepared according to General Procedure B. No further purification is needed, 96% yield. Spectral data match those previously reported.[14]

(*E*)-3-(4-methoxyphenyl)but-2-enoic acid



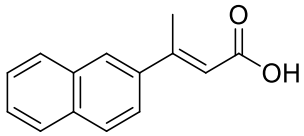
Prepared according to General Procedure B. No further purification is needed, 95% yield. Spectral data match those previously reported.[15]

(*E*)-3-(4-chlorophenyl)but-2-enoic acid



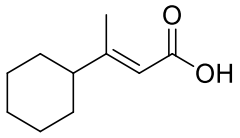
Prepared according to General Procedure B. No further purification is needed, 98% yield. Spectral data match those previously reported.[13]

(*E*)-3-(naphthalen-2-yl)but-2-enoic acid



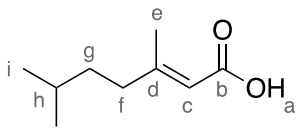
Prepared according to General Procedure B. No further purification is needed, 94% yield. Spectral data match those previously reported.[14]

(*E*)-3-cyclohexylbut-2-enoic acid



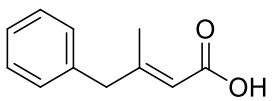
Prepared according to General Procedure B. No further purification is needed, 90% yield. Spectral data match those previously reported.[13]

3,6-Dimethylhept-2-enoic acid



Prepared according to General Procedure B, an inseparable mixture of *E* and *Z* isomers (**E**:**Z** 87:13) was obtained as a white solid. Hexane/EtOAc 9:1-8:2, 86% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 12.19 (s, Ha *E* and *Z* isomers), 5.69 (q, J = 1.1 Hz, H_c *E* isomer), 5.65 (d, J = 1.2 Hz, H_c *Z* isomer), 2.68-2.55 (m, H_f *Z* isomer), 2.23-2.08 (m, H_e and H_f *E* isomer), 1.90 (d, J = 1.4 Hz, H_e Z isomer), 1.62-1.48 (m, H_h *E* and *Z* isomers), 1.41-1.29 (m, H_g *E* and *Z* isomers), 0.90 (m, H_i *E* and *Z* isomers). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm: 172.7 (C_b *E* isomer), 172.2 (C_b *Z* isomer), 164.5 (C_d *Z* isomer), 163.8 (C_d *E* isomer), 115.4 (C_c *Z* isomer), 115.0 (C_c *E* isomer), 39.2 (C_f *E* isomer), 37.3 (C_g *Z* isomer), 36.6 (C_g *E* isomer), 31.7 (C_f *Z* isomer), 28.4 (C_h *Z* isomer), 27.7 (C_h *E* isomer), 25.5 (C_e *E* isomer), 22.4 (H_i *E* and *Z* isomers), 19.1 (H_e *E* isomer). HRMS (ESI-MS) m/z calculated for $C_9H_{15}O_2$ $[M-H]^-$: 155.1067, found: 155.1060.

(*E*)-3-methyl-4-phenylbut-2-enoic acid

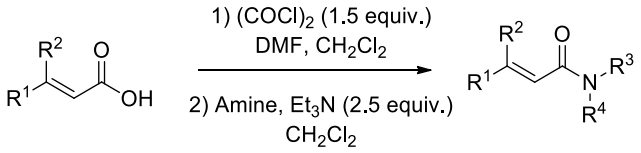


Prepared according to General Procedure B. Hexane/EtOAc 2:1, 31% yield. Spectral data match those previously reported.[16]

2.3) General procedures C and D for the synthesis of α,β-unsaturated amides

Procedure C

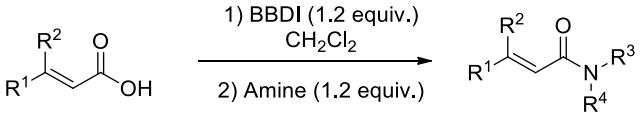
A slightly modified literature procedure was used to prepare **S4**-**S6**, **S8**-**S12** and **S14**-**S27** α,β-unsaturated amides.[17]



To a suspension of the indicated acid (1.0 equiv.) in dichloromethane (0.3 M) was added DMF (0.1 mL/mmol). At ambient temperature, oxalyl chloride (1.5 equiv.) was added dropwise over a period of 0.5 h, forming a homogenous solution. The resulting solution was kept at room temperature for 3 h. Then the solvent was removed under reduced pressure. The residue was dissolved in dry dichloromethane and slowly added dropwise to a solution of the appropriate amine (1.0 equiv.) and Et_3N (2.5 equiv.) in dichloromethane (0.25 M). The reaction mixture was maintained at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phase was washed with NH_4Cl (1 × 80 mL) and brine (1 × 80 mL), dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the crude residue was purified by flash column chromatography on silica gel (hexane/EtOAc/CH_2Cl_2) afforded the desired amides.

Procedure D

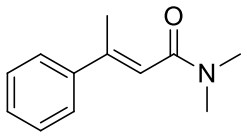
A literature procedure was used to prepare **S3**, **S7** and **S13** α,β-unsaturated amides.[18]



A mixture of the indicated acid (1.0 equiv.) and BBDI (1.2 equiv.) in CH_2Cl_2 (0.4 M) was stirred at room temperature for 30 min. After addition of the corresponding amine (1.2 equiv.) to the mixture, the whole was refluxed 5h. Ethyl acetate (40 mL) was added to the reaction mixture and then the whole was washed with 5% HCl solution (2 x 10 mL)

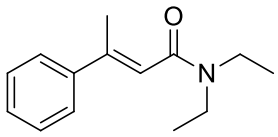
and brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel.

(*E*)-*N,N*-dimethyl-3-phenylbut-2-enamide (S3)



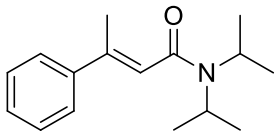
Prepared from **(*E*)-3-phenylbut-2-enoic acid** (200 mg, 1.23 mmol) and dimethylamine 2M in THF (738 μL, 1.48 mmol) using the general procedure D that provided **S3** after purification by flash column chromatography (hexane/EtOAc 1:1) as a white solid (218.4 mg, 94% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.49-7.41 (m, 2H), 7.39-7.27 (m, 3H), 6.27 (d, J = 1.5 Hz, 1H), 3.05 (s, 3H), 3.02 (s, 3H), 2.28 (d, J = 1.2 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm: 168.5, 145.6, 141.9, 128.4, 128.2, 126.0, 119.9, 37.8, 34.8, 17.9. HRMS (ESI-MS) m/z calculated for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1226, found: 190.1226.

(*E*)-*N,N*-diethyl-3-phenylbut-2-enamide (S4)



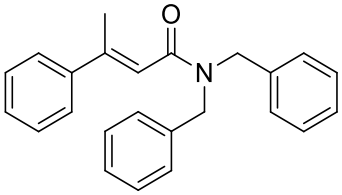
Prepared from **(*E*)-3-phenylbut-2-enoic acid** (200 mg, 1.23 mmol) and diethylamine (128 μL, 1.23 mmol) using the general procedure C that provided **S4** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 10:3:1) as an orange oil (194.9 mg, 73% yield). Spectral data match those previously reported.[19]

(*E*)-*N,N*-diisopropyl-3-phenylbut-2-enamide (S5)



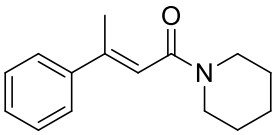
Prepared from **(*E*)-3-phenylbut-2-enoic acid** (200 mg, 1.23 mmol) and diisopropylamine (161 μL, 1.23 mmol) using the general procedure C that provided **S5** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 20:3:1) as a pale yellow oil (162.1 mg, 54% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.45 (dt, J = 8.4, 2.0 Hz, 2H), 7.38-7.27 (m, 3H), 6.26 (d, J = 1.1 Hz, 1H), 4.12 (hept, J = 6.5 Hz, 1H), 3.56 (hept, J = 5.9 Hz, 1H), 2.21 (s, 3H), 1.47 (d, J = 6.9 Hz, 6H), 1.17 (d, J = 6.8 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.0, 141.9, 141.7, 128.4, 127.9, 125.8, 122.6, 49.7, 45.5, 21.1, 20.7, 17.6. HRMS (ESI-MS) m/z calculated for $C_{16}H_{23}NNaO$ $[M+Na]^+$: 268.1672, found: 268.1684.

(*E*)-*N,N*-dibenzyl-3-phenylbut-2-enamide (S6)



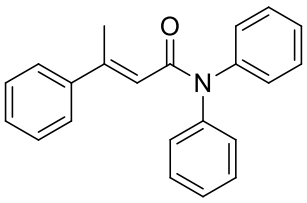
Prepared from **(*E*)-3-phenylbut-2-enoic acid** (940.7 mg, 5.8 mmol) and dibenzylamine (1.2 mL, 5.8 mmol) using the general procedure C that provided **S6** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 4:2:1) as a pale yellow solid (1.71 g, 86% yield). Spectral data match those previously reported.[20]

(*E*)-3-phenyl-1-(piperidin-1-yl)but-2-en-1-one (S7)



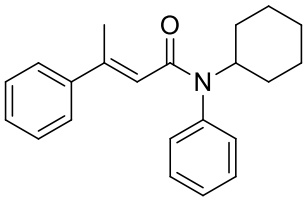
Prepared from **(*E*)-3-phenylbut-2-enoic acid** (474 mg, 2.92 mmol) and piperidine (343 μL, 3.51 mmol) using the general procedure D that provided **S7** after purification by flash column chromatography (hexane/EtOAc 3:2) as an orange oil (596.8 mg, 89% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: δ 7.50-7.39 (m, 2H), 7.39-7.24 (m, 3H), 6.26 (d, J = 1.3 Hz, 1H), 3.69-3.57 (m, 2H), 3.52-3.42 (m, 2H), 2.23 (d, J = 1.3 Hz, 3H), 1.71-1.47 (m, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 167.1, 143.9, 141.6, 128.4, 128.1, 125.9, 120.4, 47.5, 42.3, 26.7, 25.7, 24.6, 17.8. HRMS (ESI-MS) m/z calculated for $C_{15}H_{20}NO$ $[M+H]^+$: 230.1539, found: 230.1544.

(*E*)-*N,N*-diphenyl-3-phenylbut-2-enamide (S8)



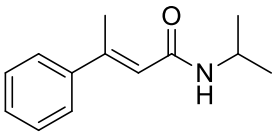
Prepared from **(*E*)-3-phenylbut-2-enoic acid** (200 mg, 1.23 mmol) and diphenylamine (252.3 mg, 1.48 mmol) using the general procedure C that provided **S8** after purification by flash column chromatography (hexane/EtOAc 9:1) as a brown solid (83.3 mg, 22% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.42-7.34 (m, 4H), 7.31-7.20 (m, 11H), 6.08 (s, 1H), 2.56 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 167.2, 150.9, 142.9, 142.7, 129.2, 128.4, 128.4, 126.2, 120.4, 18.1. HRMS (ESI-MS) m/z calculated for $C_{22}H_{20}NO$ $[M+H]^+$: 314.1539, found: 314.1554.

(*E*)-*N*-cyclohexyl-*N*,3-diphenylbut-2-enamide (S9)



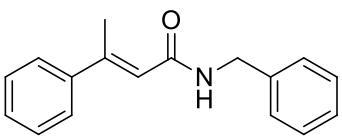
Prepared from **(*E*)-3-phenylbut-2-enoic acid** (400 mg, 2.46 mmol) and *N*-cyclohexylaniline (420.5 mg, 2.46 mmol) using the general procedure C that provided **S9** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 20:3:1) as a waxy orange solid (114.9 mg, 15% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.45-7.35 (m, 3H), 7.22-7.17 (m, 3H), 7.15-7.09 (m, 2H), 7.06-7.03 (m, 2H), 5.71 (d, J = 1.2 Hz, 1H), 4.68 (tt, J = 12.0, 3.4 Hz, 1H), 2.45 (d, J = 1.2 Hz, 3H), 1.94-1.85 (m, 2H), 1.81-1.71 (m, 2H), 1.59 (d, J = 13.0 Hz, 1H), 1.44 (qt, J = 13.2, 3.2 Hz, 2H), 1.12 (qd, J = 12.4, 3.3 Hz, 2H), 0.94 (qt, J = 13.1, 3.8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 166.8, 147.9, 142.9, 139.4, 130.4, 129.0, 128.2, 128.1, 128.0, 126.0, 120.9, 53.9, 31.8, 25.9, 25.5, 18.0. HRMS (ESI-MS) m/z calculated for $C_{22}H_{26}NO$ $[M+H]^+$: 320.2009, found: 320.2018.

(*E*)-*N*-isopropyl-3-phenylbut-2-enamide (S10)



Prepared from **(*E*)-3-phenylbut-2-enoic acid** (200 mg, 1.23 mmol) and isopropylamine (106 μL, 1.23 mmol) using the general procedure C that provided **S10** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 3:1:1) as a bright white solid (136.9 mg, 55% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.46-7.39 (m, 2H), 7.37-7.30 (m, 3H), 5.96 (q, *J* = 1.4 Hz, 1H), 5.45 (d, *J* = 7.7 Hz, 1H), 4.17 (dhept, *J* = 8.0, 6.6 Hz, 1H), 2.54 (d, *J* = 1.4 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 166.1, 150.3, 142. 8, 128.4, 128.4, 126.1, 120.3, 41.2, 22.9, 17.6. HRMS (ESI-MS) m/z calculated for $C_{13}H_{18}NO$ $[M+H]^+$: 204.1383, found: 204.1380.

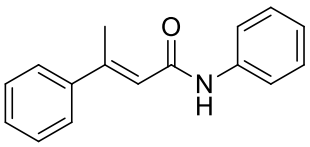
(*E*)-*N*-benzyl-3-phenylbut-2-enamide (S11)



Prepared from **(*E*)-3-phenylbut-2-enoic acid** (200 mg, 1.23 mmol) and benzylamine (136 μL, 1.23 mmol) using the general procedure C that provided **S11** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 3:1:1) as a waxy orange solid (178.1 mg, 58% yield). ^{1}H -NMR (400 MHz, $CDCl_3$) δ ppm: 7.42 (dd, *J* = 7.8, 2.0 Hz, 2H), 7.38-7.24 (m, 8H), 6.15 (s, 1H), 6.05 (q, *J* = 1.3 Hz, 1H), 4.50 (d, *J* = 5.8 Hz, 2H), 2.58 (d, *J*

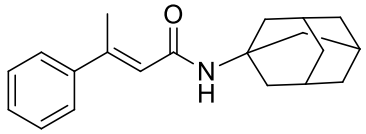
= 1.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 166. 8, 151.3, 142.7, 128.7, 128.6, 128.5, 127.9, 127.5, 126.2, 119.7, 43.5, 17.7. HRMS (ESI-MS) m/z calculated for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1383, found: 252.1374.

(*E*)-*N*-phenyl-3-phenylbut-2-enamide (S12)



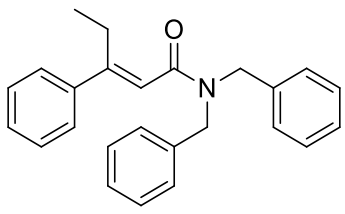
Prepared from **(*E*)-3-phenylbut-2-enoic acid** (200 mg, 1.23 mmol) and phenylamine (113 μL, 1.23 mmol) using the general procedure C that provided **S12** after purification by flash column chromatography (hexane/EtOAc 9:1-9:3) as a waxy white solid (84.9 mg, 29% yield). ^{1}H -NMR (400 MHz, $CDCl_3$) δ ppm: 7.58 (d, J = 7.3 Hz, 2H), 7.51-7.43 (m, 2H), 7.35 (tdd, J = 14.0, 6.4, 1.7 Hz, 6H), 7.11 (t, J = 7.4 Hz, 1H), 6.15 (d, J = 1.3 Hz, 1H), 2.62 (d, J = 1.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 164.9, 153.1, 142.6, 138.1, 129.0, 128.8, 128.5, 126.2, 124.2, 120.0, 119.8, 17.9. HRMS (ESI-MS) m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$: 238.1226, found: 238.1234.

(*E*)-*N*-(adamantan-1-yl)-3-phenylbut-2-enamide (S13)



Prepared from **(*E*)-3-phenylbut-2-enoic acid** (404.5 mg, 2.49 mmol) and 1-adamantylamine (388.9 mg, 2.99 mmol) using the general procedure D that provided **S13** after purification by flash column chromatography (hexane/EtOAc 9:1) as a white solid (383.1 mg, 52% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.45-7.38 (m, 2H), 7.38-7.27 (m, 3H), 5.93 (q, *J* = 1.4 Hz, 1H), 5.28 (s, 1H), 2.52 (d, *J* = 1.4 Hz, 3H), 2.10-2.06 (m, 9H), 1.73-1.664 (m, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 166.3, 149.7, 143.0, 138.4, 128.3, 126.1, 121.4, 52.1, 41.8, 36.4, 29.5, 17.4. HRMS (ESI-MS) m/z calculated for $C_{20}H_{26}NO$ $[M+H]^+$: 296.2009, found: 296.2000.

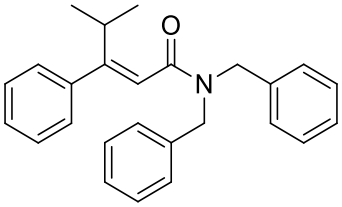
(*E*)-*N,N*-dibenzyl-3-phenylpent-2-enamide (S14)



Prepared from **(*E*)-3-phenylpent-2-enoic acid** (636.9 mg, 3.6 mmol) and dibenzylamine (717 μL, 3.6 mmol) using the general procedure C that provided **S14** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 4:2:1) as a pale yellow oil (954.1 mg, 74% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.43-7.27

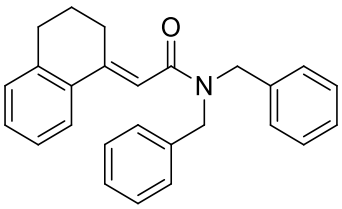
(m, 13H), 7.23-7.16 (m, 2H), 6.29 (s, 1H), 4.67 (s, 2H), 4.52 (s, 2H), 2.91 (q, J = 7.5 Hz, 2H), 1.10 (t, J = 7.5 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm: 168.6, 154.1, 140.8, 137.4, 136.5, 128.9, 128. 7, 128.5, 128.4, 128.2, 127.7, 127.5, 126.9, 126.7, 119.4, 50. 6, 47.3, 25.0, 13.5. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO$ $[M+Na]^+$: 378.1828, found: 378.1828.

(*E*)-*N,N*-dibenzyl-4-methyl-3-phenylpent-2-enamide (S15)



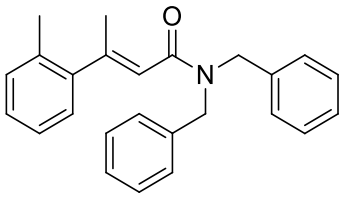
Prepared from **(*E*)-4-methyl-3-phenylpent-2-enoic acid** (400 mg, 2.1 mmol) and dibenzylamine (417 µL, 2.1 mmol) using the general procedure C that provided **S15** after purification by flash column chromatography (hexane/EtOAc 9:1) as a pale yellow oil (707.1 mg, 91% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.38-7.28 (m, 11H), 7.19-7.15 (m, 4H), 5.98 (s, 1H), 4.66 (s, 2H), 4.54 (s, 2H), 3.54 (hept, J = 6.9 Hz, 1H), 1.11 (d, J = 7.0 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.5, 158.1, 140.8, 137.3, 136.6, 128.9, 128.6, 128.4, 128. 1, 127.8, 127.7, 127.5, 127.2, 126.9, 121.0, 50.7, 47.2, 31.3, 21.5. HRMS (ESI-MS) m/z calculated for $C_{26}H_{27}NNaO$ $[M+Na]^+$: 392.1985, found: 392.1992.

(*E*)-*N,N*-dibenzyl-2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)acetamide (S16)



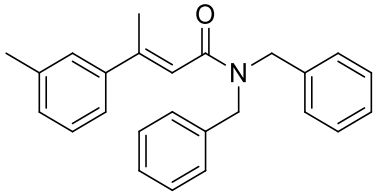
Prepared from **(*E*)-2-(3,4-dihydronaphthalen-1(2*H*)-ylidene) acetic acid** (126.5 mg, 0.7 mmol) and dibenzylamine (133 µL, 0.7 mmol) using the general procedure C that provided **S16** after purification by flash column chromatography (hexane/EtOAc 9:1) as a pale yellow solid (214.6 mg, 87% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.49-7.47 (m, 1H), 7.39-7.29 (m, 8H), 7.21 (td, J = 8.4, 7.6, 1.1 Hz, 3H), 7.12 (dq, J = 6.9, 3.1 Hz, 2H), 6.60 (t, J = 1.7 Hz, 1H), 4.67 (s, 2H), 4.54 (s, 2H), 2.99-2.95 (m, 2H), 2.84 (t, J = 6.2 Hz, 2H), 1.93-1.86 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 169.0, 147.1, 139.1, 137.4, 136.7, 134.3, 129.3, 128.9, 128.7, 128.77, 128.5, 127.7, 127.4, 126.9, 126.2, 124.4, 114.8, 50.6, 47.4, 30.2, 28.6, 23.1. HRMS (ESI-MS) m/z calculated for $C_{26}H_{25}NNaO$ $[M+Na]^+$: 390.1828, found: 390.1822.

(*E*)-*N,N*-dibenzyl-3-(*o*-tolyl)but-2-enamide (S17)



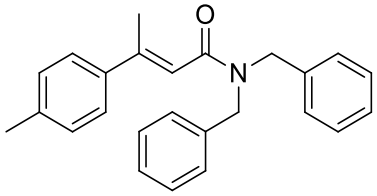
Prepared from **(*E*)-3-(*o*-tolyl)but-2-enoic acid** (400 mg, 2.3 mmol) and dibenzylamine (450 µL, 2.3 mmol) using the general procedure C that provided **S17** after purification by flash column chromatography (hexane/EtOAc 8:2) as a white solid (668.0 mg, 83% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.39-7.29 (m, 8H), 7.20-7.13 (m, 5H), 7.08-7.05 (m, 1H), 6.07 (d, J = 1.4 Hz, 1H), 4.68 (s, 2H), 4.54 (s, 2H), 2.35 (d, J = 1.4 Hz, 3H), 2.24 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.3, 151.0, 143.8, 137.4, 136.6, 134.2, 130.4, 128.9, 128.7, 128.5, 127.7, 127.5, 127.5, 126.7, 125.8, 121.2, 50.3, 47.4, 20.8, 19.8. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO$ $[M+Na]^+$: 378.1828, found: 378.1828.

(*E*)-*N,N*-dibenzyl-3-(*m*-tolyl)but-2-enamide (S18)



Prepared from **(*E*)-3-(*m*-tolyl)but-2-enoic acid** (400 mg, 2.3 mmol) and dibenzylamine (450 µL, 2.3 mmol) using the general procedure C that provided **S18** after purification by flash column chromatography (hexane/EtOAc 8:2) as a white solid (512.6 mg, 64% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.40-7.31 (m, 8H), 7.23-7.20 (m, 5H), 7.13 (d, J = 6.5 Hz, 1H), 6.41 (d, J = 1.2 Hz, 1H), 4.68 (s, 2H), 4.54 (s, 2H), 2.42 (d, J = 1.0 Hz, 3H), 2.35 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.9, 147.8, 142.0, 138.0, 137.4, 136.6, 129.1, 129.0, 128.7, 128.5, 128.4, 127.7, 127.5, 126.9, 126.8, 123.2, 119.3, 50.6, 47.3, 21.5, 18.4. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO$ $[M+Na]^+$: 378.1828, found: 378.1815.

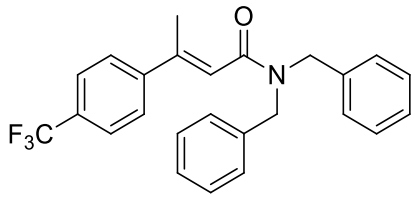
(*E*)-*N,N*-dibenzyl-3-(*p*-tolyl)but-2-enamide (S19)



Prepared from **(*E*)-3-(*m*-tolyl)but-2-enoic acid** (400 mg, 2.3 mmol) and dibenzylamine (450 µL, 2.3 mmol) using the general procedure C that provided **S19** after purification by flash column chromatography (hexane/EtOAc 8:2) as a white solid (595.5 mg, 74% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.39-7.27 (m, 10H), 7.21-7.16 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 1.4 Hz,

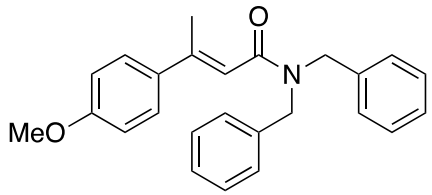
1H), 4.66 (s, 2H), 4.52 (s, 2H), 2.40 (d, J = 1.1 Hz, 3H), 2.34 (s, 3H).^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.9, 147.6, 139.1, 138.3, 137.4, 136.6, 129.1, 128.9, 128.6, 128.4, 127.7, 127.42, 126.9, 125.9, 118.6, 50.5, 47.4, 21.1, 18.2. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO$ $[M+Na]^+$: 378.1828, found: 378.1824.

(*E*)-*N,N*-dibenzyl-3-(4-(trifluoromethyl)phenyl)but-2-enamide (S20)



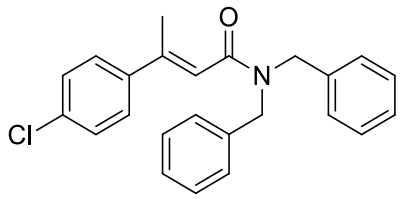
Prepared from **(*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoic acid** (400 mg, 1.7 mmol) and dibenzylamine (345 µL, 1.7 mmol) using the general procedure C that provided **S20** after purification by flash column chromatography (hexane/EtOAc 9:1) as a beige oil (613.3 mg, 86% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.57 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 7.42-7.27 (m, 8H), 7.22-7.15 (m, 2H), 6.43 (d, J = 1.2 Hz, 1H), 4.67 (s, 2H), 4.51 (s, 2H), 2.40 (d, J = 1.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.3, 146.0, 145.4, 137.1, 136.3, 129.0, 128.7, 128. 5, 127.8, 127.6, 126.8, 126.4, 125.5, 125.5, 125.4, 121.4, 50.5, 47.5, 18.2. HRMS (ESI-MS) m/z calculated for $C_{25}H_{22}F_3NNaO$ $[M+Na]^+$: 432.1546, found: 432.1550.

(*E*)-*N,N*-dibenzyl-3-(4-methoxyphenyl)but-2-enamide (S21)



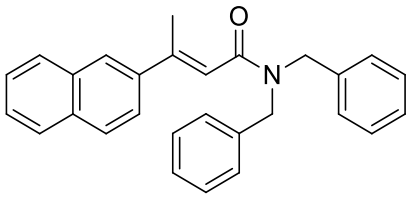
Prepared from **(*E*)-3-(4-methoxyphenyl)but-2-enoic acid** (400 mg, 2.1 mmol) and dibenzylamine (413 µL, 2.1 mmol) using the general procedure C that provided **S21** after purification by flash column chromatography (hexane/EtOAc 8:2) as a white solid (577.4 mg, 75% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.39-7.28 (m, 10H), 7.20 (d, J = 7.1 Hz, 2H), 6.87-6.84 (m, 2H), 6.37 (d, J = 1.3 Hz, 1H), 4.67 (s, 2H), 4.53 (s, 2H), 3.80 (s, 3H), 2.41 (d, J = 1.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 169.0, 159.9, 147.2, 137. 5, 136.7, 134.3, 128.9, 128.6, 128.4, 127.7, 127.4, 127.3, 126.9, 117.7, 113. 8, 55.3, 50. 6, 47.4, 18.2. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO_2$ $[M+Na]^+$: 394.1778, found: 394.1776.

(*E*)-*N,N*-dibenzyl-3-(4-chlorophenyl)but-2-enamide (S22)



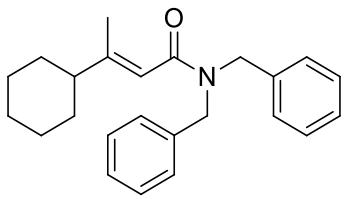
Prepared from **(*E*)-3-(4-chloroyphenyl)but-2-enoic acid** (400 mg, 2.0 mmol) and dibenzylamine (403 µL, 2.0 mmol) using the general procedure C that provided **S22** after purification by flash column chromatography (hexane/EtOAc 9:1) as a white solid (487.0 mg, 64% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.37-7.27 (m, 12H), 7.19-7.17 (m, 2H), 6.38 (q, J = 1.3 Hz, 1H), 4.66 (s, 2H), 4.51 (s, 2H), 2.38 (d, J = 1.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.5, 146.2, 140.3, 137.2, 136.5, 134.3, 129.0, 128.7, 128.6, 128.4, 127.8, 127.5, 127.3, 126.8, 119.9, 50.5, 47.4, 18.2. HRMS (ESI-MS) m/z calculated for $C_{24}H_{22}ClNNaO$ $[M+Na]^+$: 398.1282, found: 398.1281.

(*E*)-*N,N*-dibenzyl-3-(naphthalen-2-yl)but-2-enamide (S23)



Prepared from **(*E*)-3-(naphthalen-2-yl)but-2-enoic acid** (400 mg, 1.9 mmol) and dibenzylamine (374 µL, 1.9 mmol) using the general procedure C that provided **S23** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 9:1:1) as a waxy white solid (587.7 mg, 80% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.87-7.76 (m, 4H), 7.53 (dd, J = 8.6, 1.9 Hz, 1H), 7.51-7.44 (m, 2H), 7.42-7.29 (m, 8H), 7.22 (d, J = 7.0 Hz, 2H), 6.57 (d, J = 1.2 Hz, 1H), 4.71 (s, 2H), 4.57 (s, 2H), 2.57-2.50 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.8, 147.2, 139.1, 137.4, 136.6, 133.2, 133.2, 129.0, 128.7, 128.5, 128.3, 128.1, 127.7, 127.6, 127.5, 126.9, 126.4, 126.4, 125.3, 123.9, 120.0, 50.6, 47.5, 18.2. HRMS (ESI-MS) m/z calculated for $C_{28}H_{25}NNaO$ $[M+Na]^+$: 414.1828, found: 414.1841.

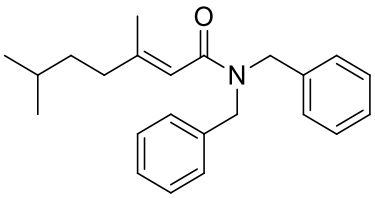
(*E*)-*N,N*-dibenzyl-3-phenylpent-2-enamide (S24)



Prepared from **(*E*)-3-cyclohexylbut-2-enoic acid** (400 mg, 2.4 mmol) and dibenzylamine (471 µL, 2.4 mmol) using the general procedure C that provided **S24** after purification by flash column chromatography (hexane/EtOAc 9:1) as a pale yellow oil (596.1 mg, 72% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.38-7.24 (m, 8H), 7.16 (d, J = 7.0 Hz, 2H), 5.93-5.89 (m, 1H), 4.59 (s, 2H), 4.44 (s, 2H), 1.98 (d, J = 1.2 Hz, 3H), 1.92 (ddd, J = 13.8, 10.0, 2.9 Hz, 1H), 1.80-1.62 (m, 5H), 1.28-1.08 (m, 5H). ^{13}C-NMR

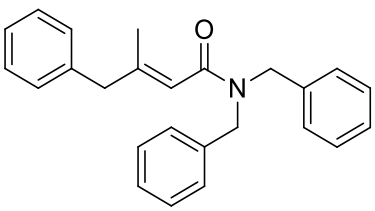
(101 MHz, $CDCl_3$) δ ppm: 169.4, 155.6, 137.6, 136.9, 128.8, 128.6, 128.4, 127.6, 127.3, 126.9, 115.8, 50.4, 47.5, 47.1, 31.5, 26.5, 26.2, 17.2. HRMS (ESI-MS) m/z calculated for $C_{24}H_{29}NNaO$ $[M+Na]^+$: 370.2141, found: 370.2153.

_N,N_-dibenzyl-3,6-dimethylhept-2-enamide (S25)



Prepared from **3,6-dimethylhept-2-enoic acid** (400 mg, 2.6 mmol) and dibenzylamine (508 µL, 2.6 mmol) using the general procedure C that provided **S25** after purification by flash column chromatography (hexane/EtOAc 9:1-8:2) as a pale yellow oil (720.0 mg, 84% yield, ***E:Z*** 78:22). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: δ 7.55-7.22 (m, 8H, *E* and *Z* isomers), 7.17 (d, J = 7.6 Hz, 2H, *E* and *Z* isomers), 5.94 (s, 0.56H, *E* isomer), 5.90 (s, 0.15H, *Z* isomer), 4.61 (s, 2H, *E* and *Z* isomers), 4.46 (s, 2H, *E* and *Z* isomers), 2.48-2.40 (m, 0.32H, *Z* isomer), 2.14-2.05 (m, 1.28H, *E* isomer), 2.03 (s, 1.55H, *E* isomer), 1.81 (s, 0.48H, *Z* isomer), 1.77 (t, J = 6.9 Hz, 0.29H, *Z* isomer), 1.62- 1.44 (m, 1H, *E* and *Z* isomers), 1.40-1.36 (m, 0.38H, *Z* isomer), 1.35-1.26 (m, 1.24H, *E* isomer), 0.93 (d, J = 6.6 Hz, 0.98H, *Z* isomer), 0.85 (d, J = 6.6 Hz, 3.22H, *E* isomer), 0.82 (d, J = 6.6 Hz, 0.80H, *Z* isomer). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 169.0 (*E* isomer), 168.8 (*Z* isomer), 151.9 (*E* isomer), 151.7 (*Z* isomer), 137.6 (*E* isomer), 137.5 (*Z* isomer), 136.9 (*E* isomer), 136.8 (*Z* isomer), 129.0, 128.9, 128.6, 128.56, 128.5, 128.4, 127. 6, 127.3, 126.8, 126.4, 117.9, 117.0, 50.4, 49.7, 47.2, 47.0, 37.9, 37.2, 36.6, 31.9, 28.4, 27.7, 23. 9, 22.5, 18.9. HRMS (ESI-MS) m/z calculated for $C_{23}H_{29}NNaO$ $[M+Na]^+$: 358.2141, found: 358.2144.

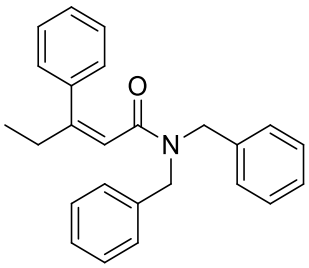
(*E*)-*N,N*-dibenzyl-3-methyl-4-phenylbut-2-enamide (S26)



Prepared from **(*E*)-3-methyl-4-phenylbut-2-enoic acid** (200.0 mg, 1.1 mmol) and dibenzylamine (225 µL, 1.1 mmol) using the general procedure C that provided **S26** after purification by flash column chromatography (hexane/EtOAc 5:1) as a pale yellow oil (329.0 mg, 82% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.38-7.29 (m, 5H), 7.27-7.17 (m, 6H), 7.14-7.11 (m, 2H), 7.09-7.07 (m, 2H), 5.91

(q, J = 1.3 Hz, 1H), 4.62 (s, 2H), 4.42 (s, 2H), 3.38 (d, J = 1.2 Hz, 2H), 2.00 (d, J = 1.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 168.7, 150.1, 138.2, 137.4, 136.7, 129.1, 128.9, 128.6, 128.5, 128.4, 127.6, 127.4, 126.8, 126.5, 119.2, 50.4, 47.4, 46.2, 18.8. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO$ $[M+Na]^+$: 378.1828, found: 378.1836.

(*Z*)-*N,N*-dibenzyl-3-phenylpent-2-enamide (S27)



Prepared from **(*Z*)-3-phenylpent-2-enoic acid** (322.0 mg, 1.8 mmol) and dibenzylamine (362 µL, 1.8 mmol) using the general procedure C that provided **S27** after purification by flash column chromatography (hexane/EtOAc/CH_2Cl_2 4:2:1) as a pale orange oil (974.5 mg, 38% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 7.35-7.29 (m, 8H), 7.23-7.16 (m, 3H), 7.05-7.02 (m, 2H), 6.84 (dd, J = 7.6, 1.7 Hz, 2H), 6.09 (t, J = 1.3 Hz, 1H), 4.46 (s, 2H), 4.30 (s, 2H), 2.48 (qd, J = 7.4, 1.4 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 169.6, 149.7, 139.8, 136.7, 128.8, 128.5, 128.4, 128.3, 127.8, 127.6, 127.2, 119.3, 50.6, 46.3, 31.3, 12.4. HRMS (ESI-MS) m/z calculated for $C_{25}H_{26}NO$ $[M+H]^+$: 356.2009, found: 356.2017.

3) Synthesis of complexes

Bipyrrolidine based **^{NMe2}pdp-Mn**,[21] **^{NMe2}pdp-Fe**,[22] **^{tips}pdp-Mn**[23] and **^{tips}pdp-Fe**[24] complexes were synthesized following previously described procedures.

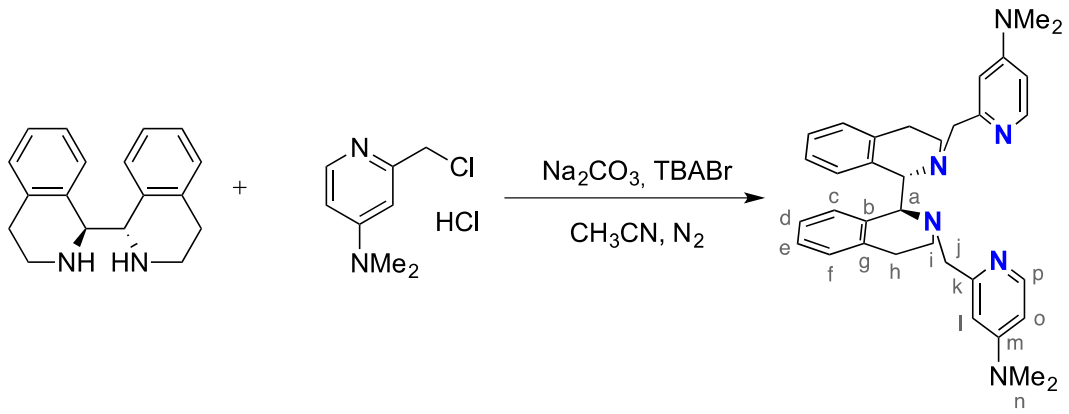
3.1) Synthesis of the Ohq backbone

The (*S*,*S*)-1,1',2,2',3,3',4,4'-octahydro-1,4'-biisoquinoline (**(*S*,*S*)-Ohq**) was synthesized according to a described procedure.[25]

3.2) Synthesis of pyridine synthons

Pyridine synthons 2-chloromethyl-4-dimethylaminopyridine hydrochloride, **^{Me2N}PyCH$_2$Cl·HCl**[26] and 2-chloromethyl-5-triisopropylpyridine hydrochloride, **^{tips}PyCH$_2$Cl·HCl**,[23] were synthesized following previously described procedures.

3.3) Synthesis and characterization of ^{Me2N}Ohq

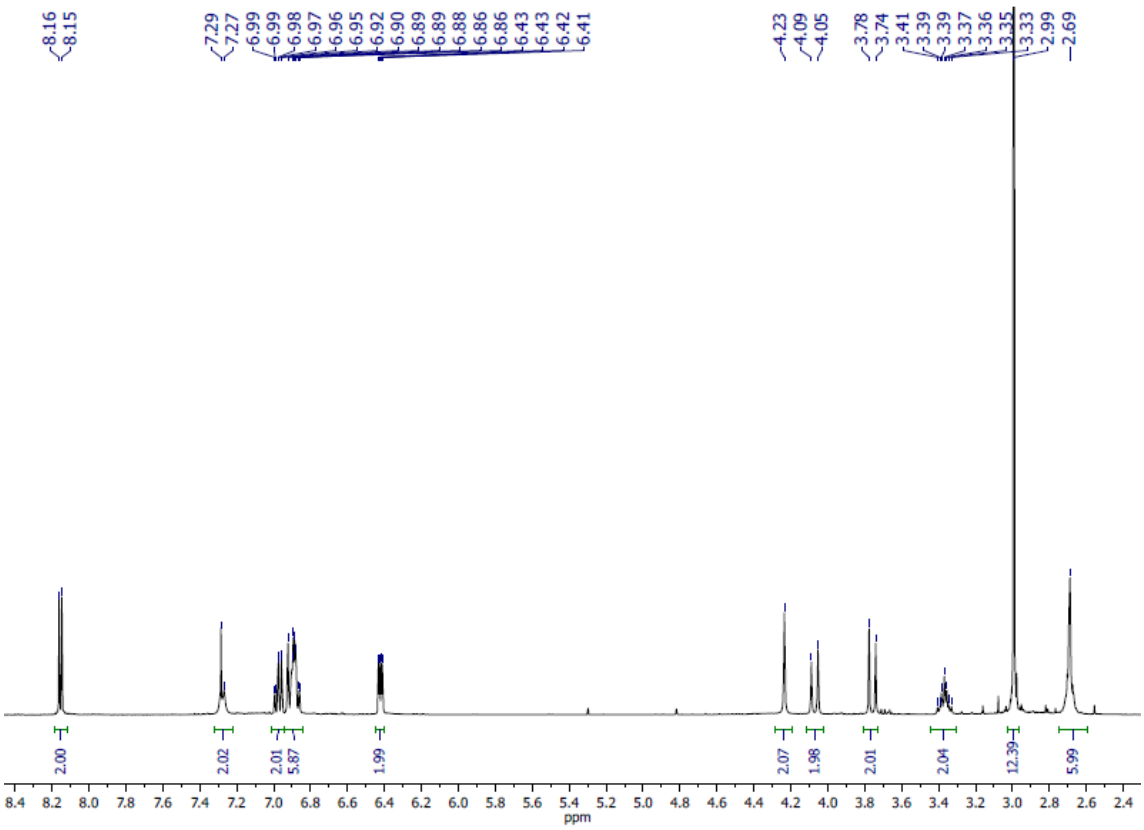


Scheme S1. Synthesis and nomenclature of the new ligands used in this work.

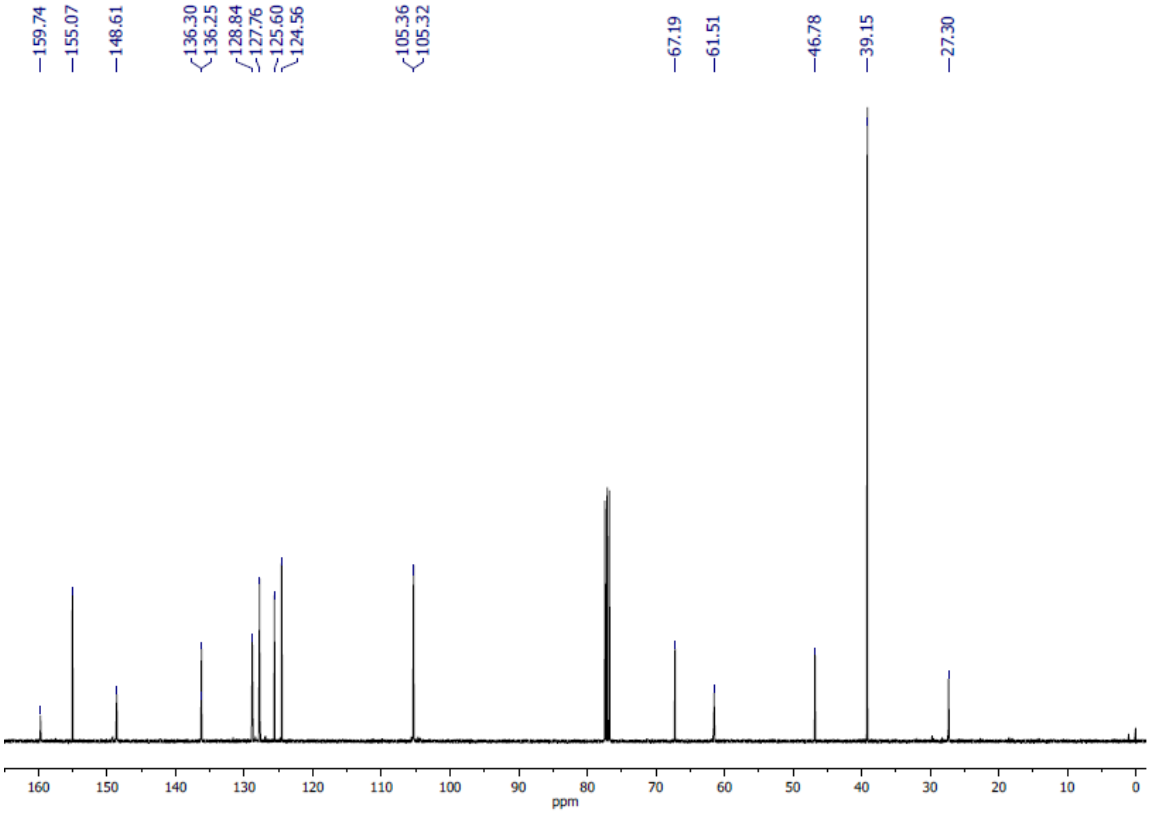
2-chloromethyl-4-dimethylaminopyridine hydrochloride, **^{Me2N}PyCH$_2$Cl·HCl** (400 mg, 1.93 mmol), **(*S*,*S*)-Ohq** (243.1 mg, 0.92 mmol) and anhydrous acetonitrile (45 mL) were mixed in a 100 mL flask. Na_2CO_3 (1.56 g) and tetrabutylammonium bromide, TBABr (20 mg) were added directly as solids and the resulting mixture was heated at reflux under N_2 for 18 hours. After cooling to room temperature, the resulting brown mixture was filtered and the filter cake was washed with CH_2Cl_2. The combined filtrates were evaporated under reduced pressure. To the resulting residue, 1M NaOH (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced

pressure. After, the residue was purified by flash column chromatography (silica CH_2Cl_2:MeOH:NH_3 96:3:1) to provide 334.4 mg (68% yield) of a brown oil. ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 8.15 (2H, d, J 6.0, H_p), 7.28 (2H, d, J 6.7, H_f), 6.99-6.96 (2H, m, H_d), 6.92-6.86 (6H, m, $H_{c,e,l}$), 6.42 (2H, dd, J 2.7, 6.0, H_o), 4.23 (2H, s, H_a), 4.07 (2H, d, J 14.3, H_j), 3.76 (2H, d, J 14.2, $H_{j'}$), 3.41-3.33 (2H, m, H_i), 2.99 (12H, s, H_n), 2.69 (6H, apparent m, $H_{i',h}$). ^{13}C-NMR ($CDCl_3$, 133 MHz, 300K) δ, ppm: 159.7 (C_m), 155.1 (C_k), 148.6 (C_p), 136.30 (C_g or C_b), 136.25 (C_g or C_b), 128.8 (C_f), 127.8 (C_e), 125.6 (C_d), 124.6 (C_c), 105.36 (C_l or C_o), 105.32 (C_l or C_o), 67.2 (C_a), 61.51 (C_j), 46.8 (C_i), 39.15 (C_n), 27.3 (C_h). HRMS (ESI-MS) m/z calculated for $C_{34}H_{41}N_6$ $[M+H]^+$: 533.3387, found: 533.3373. FT-IR (ATR) ν, cm^{-1}: 3057-2808(C-H) sp3, 1595, 1542, 1504, 1431, 1372, 1268, 1220, 1126, 1091, 1061, 999, 939, 805, 726, 579, 453.

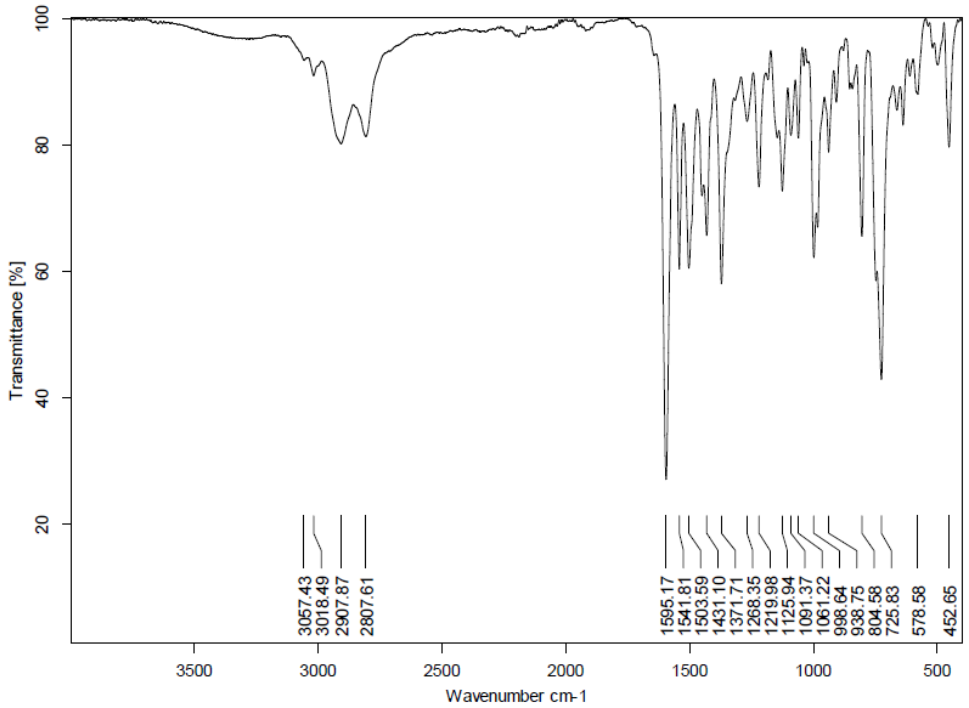
^{1}H-NMR of **^{Me2N}Ohq** in $CDCl_3$



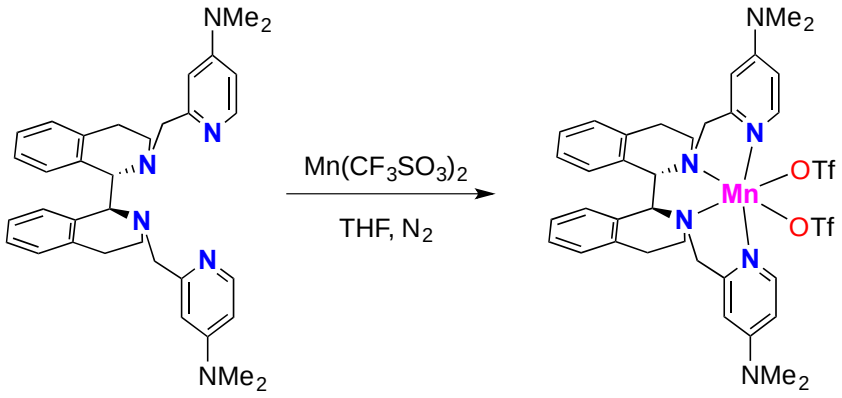
^{13}C-NMR of **^{Me2N}Ohq** in $CDCl_3$



IR of **^{Me2N}Ohq**



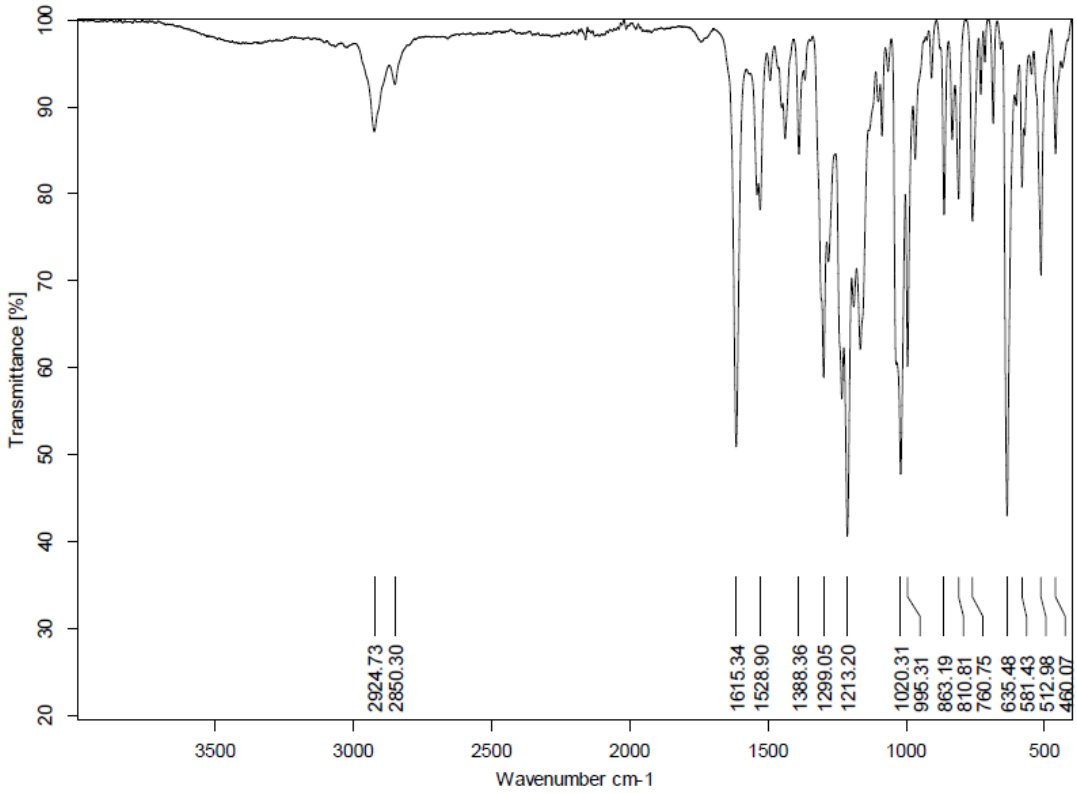
3.4) Synthesis and characterization of ^{Me2N}Ohq-Mn



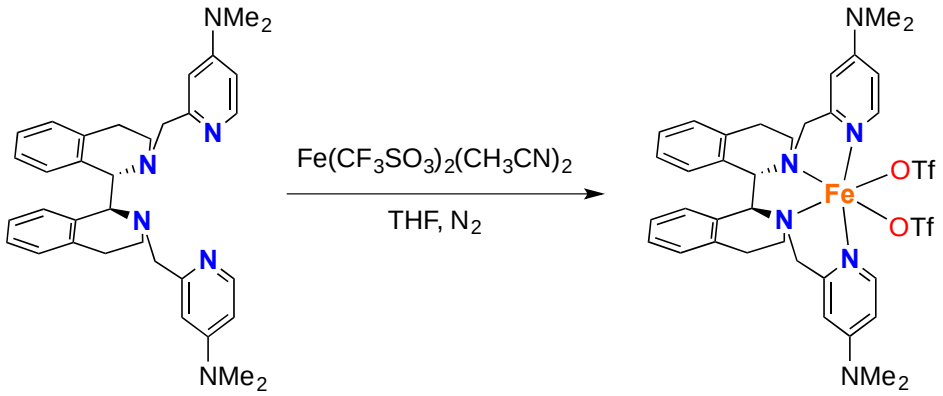
Scheme S2. Synthesis and nomenclature of new manganese triflate complexes used in this work.

^{Me2N}Ohq-Mn was synthesized following a similar procedure described in literature. Under a N_2 atmosphere, a suspension of $Mn(CF_3SO_3)_2$ (68.3 mg, 194 µmol) in anhydrous THF (1 mL) was added drop-wise to a vigorously stirred solution of **^{Me2N}Ohq** (103.1 mg, 194 µmol) in anhydrous THF (1 mL). After stirring overnight, ether was added until complete precipitation. The brown solid was filtered, dried and solved in the minimum quantity of CH_2Cl_2 and the solution filtered off through celite©. Slow hexane diffusion over the resultant solution afforded in a few days white-off crystals (106.0 mg, 62% yield). Anal. calculated for $C_{36}H_{40}F_6MnN_6O_6S_2$: C, 48.81; H, 4.55; N, 9.49. Found: C, 49.27; H, 4.74; N, 9.08. FT-IR (ATR) ν, cm^{-1}: 2925-2850 (C-H)sp3, 1615, 1529, 1388, 1299, 1213, 1020, 995, 863, 810, 761, 635, 581, 513, 460. ESI-HRMS calculated for $C_{35}H_{40}F_3MnN_4O_3S$ $[M\text{-}OTf]^+$: 736.2210, found: 736.2237.

IR of ^{NMe2}**Ohq-Mn**



3.5) Synthesis of ^{Me2N}Ohq-Fe

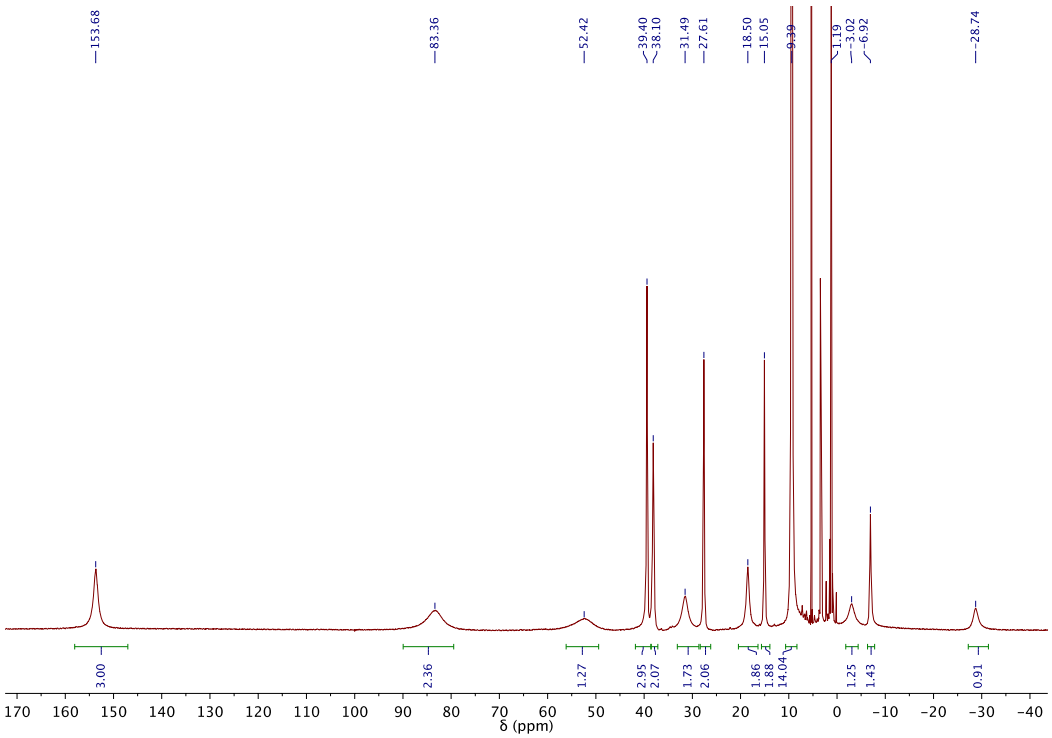


Scheme S3. Synthesis and nomenclature of new iron triflate complexes used in this work.

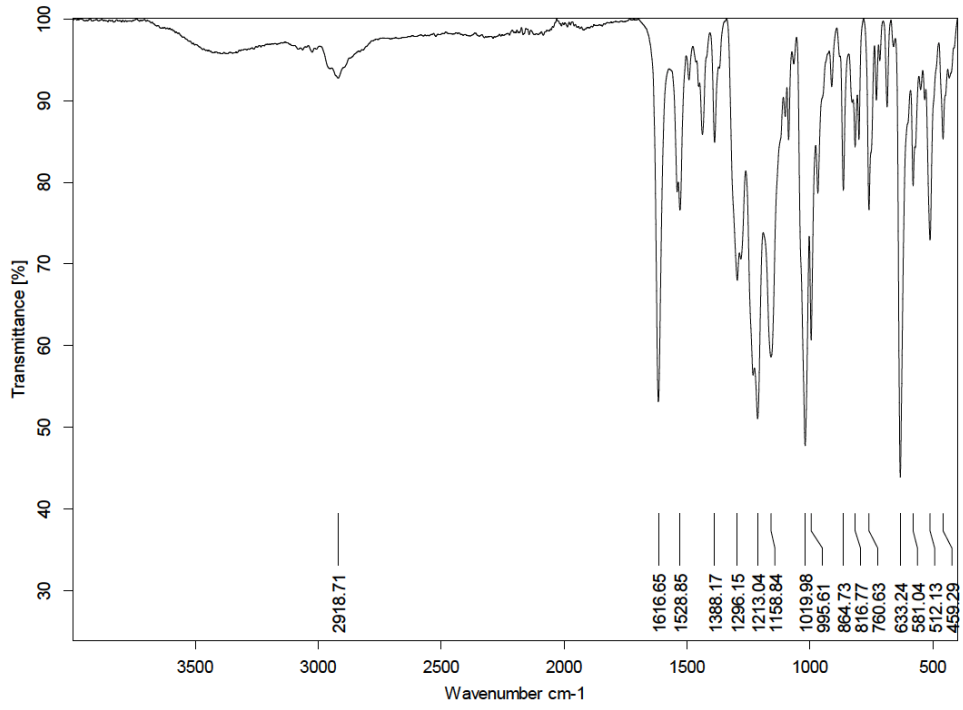
^{Me2N}Ohq-Fe was prepared in a similar manner to **^{Me2N}Ohq-Mn**, starting from **^{Me2N}Ohq** and $Fe(CF_3SO_3)_2(CH_3CN)_2$ in anhydrous THF, and recrystallized by diffusion of diethyl ether to CH_2Cl_2 solution of the complex, to obtain pink crystals, which are unstable under air. Anal. Calcd for $C_{36}H_{40}F_6FeN_6O_6S_2$ 1/2 CH_2Cl_2: C, 47.18 H, 4.45; N, 9.04. Found: C, 47.21; H, 4.28; N, 9.01. FT-IR (ATR) v, cm^{-1}: 2919 (C-H)sp3, 1617, 1529, 1388, 1296, 1213,

1159, 1020, 996, 865, 817, 761, 633, 581, 512, 459. ^{1}H-NMR (CD_2Cl_2, 400 MHz, 300K) δ, ppm: 153.7 (s, 3H), 83.4 (s 2H), 52.4 (s, 1H), 39.4 (s, 3H), 38.1 (s, 2H), 31.5 (s, 2H), 27.6 (s, 2H), 18.5 (s, 2H), 15.1 (s, 2H), 9.39 (s, 14H), -3.02 (s, 1H), -6.9 (s, 1H), 28.7 (s, 1H). ESI-HRMS calculated for $C_{35}H_{40}F_3FeN_4O_3S$ [M-OTf]$^{+}$: 737.2179, found: 737.2179.

^{1}H-NMR of **^{NMe2}Ohq-Fe** in CD_2Cl_2



IR of **^{NMe2}Ohq-Fe**



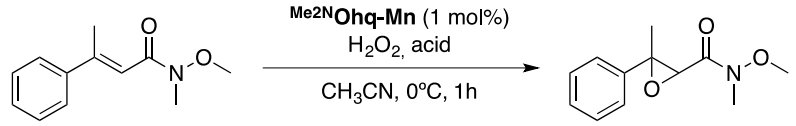
4) Catalytic studies

Hydrogen peroxide solutions employed in the reactions were prepared by diluting commercially available hydrogen peroxide (30% H_2O_2 solution in water, Aldrich) in acetonitrile (1:3 or 1:7 v:v).

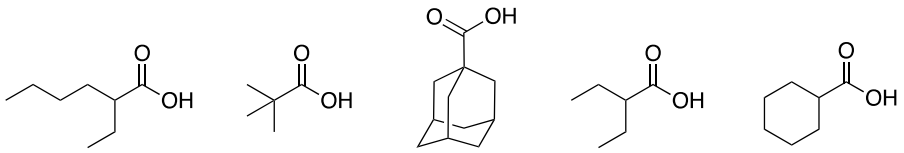
4.1) Reaction conditions (Table 1)

An acetonitrile solution (750 µL) of a given olefin (**S1-S2**) (88 µmols) and the corresponding complex (1 mol% for Mn and 2 mol% for Fe) was prepared in a vial (3 mL) equipped with a stir bar and cooled at 0°C in an ice bath. 14 equiv. (for Mn catalysts) or 1.4 equiv (for Fe catalysts) of carboxylic acid were directly added to the solution. Then, 70 µL of 3:1 (v:v) acetonitrile:hydrogen peroxide solution 30% (2 equiv., 0.18 mmol) were added by syringe pump over a period of 30 min. The solution was further stirred at 0°C for 30 minutes. At this point, 0.5 equiv. of internal standard (1,3,5-trimethoxybenzene) and 5 mL of a saturated aqueous solution of $NaHCO_3$ were added, and the resulting mixture was extracted with 2 mL of CH_2Cl_2 (x3). Then, organic layers were dried over $MgSO_4$ and the solvents were removed under reduced pressure. The resultant product was dissolved in $CDCl_3$ and the yield and conversion were calculated by ^{1}H-NMR. Finally, the solvent was removed under reduced pressure and was dissolved in *n*-hexane/*iso*-propanol and analyzed by HPLC.

4.2) Optimization of epoxidation of S1



Acid:



2-eha pva aca eba chca

Entry	Acid (equiv.)	Equiv. of H_2O_2	Conv (yield,%)[a]	ee (%)[b]
1	2-eha (14)	2	94 (69)	79
4	pva (14)	2	100(79)	69
5	eba (14)	2	95(78)	77
6	aca (5)	2	27(25)	69
7	chca (14)	2	92(73)	65
8	2-eha (5)	2	89(63)	80
9	2-eha (1)	2	89(78)	76
10	eba (5)	2	99(68)	78
11	eba (1)	2	100(73)	74
12	2-eha (1)	3	100(85)	76
13[c]	2-eha (1)	3	77(76)	86
14[c]	2-eha (5)	3	75(64)	88
15[c]	2-eha (14)	3	82(80)	88

[a] Epoxide yields and substrate conversion determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b] ee's determined by HPLC with a chiral stationary phase. [c] Reactions performed at -40°C

4.3) Reaction conditions (Tables 2 and 3)

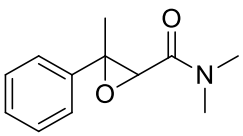
An acetonitrile solution (750 µL) of a given olefin (**S3-S27**) (44 µmols) and **Me2NOhq-Mn** (1 mol%) was prepared in a vial (3 mL) equipped with a stir bar and cooled at -40°C in an acetonitrile frozen bath. 7 µL or 36 µL (neat, 1 or 5 equiv., 44 µmols or 220 µmols) of 2-ethylhexanoic acid were added directly to the solution. Then, 70 µL of 7:1 (v:v) acetonitrile:hydrogen peroxide solution 30% (3 equiv., 0.132 mmol) was added by

syringe pump over a period of 30 min. The solution was further stirred at -40°C for 30 minutes. At this point, 0.5 equiv. of internal standard (1,3,5-trimethoxybenzene) and 5 mL of a saturated aqueous solution of $NaHCO_3$ were added, and the resulting mixture was extracted with 2 mL of CH_2Cl_2 (x3). Then, organic layers were dried over $MgSO_4$, passed through a plug of silica and the solvents were removed under reduced pressure. The resultant product was dissolved in $CDCl_3$ and the yield and conversion were calculated by ^{1}H-NMR. Finally, the solvent was removed under reduced pressure and was dissolved in *n*-hexane/*iso*-propanol and analyzed by HPLC.

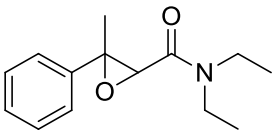
4.4) General procedure for epoxide isolation (Tables 2 and 3)

An acetonitrile solution (0.06M) of a given olefin (**S3-S26**) (0.2 mmol – 1.5 mmol) and **^{Me2N}OhqMn** (1 mol%, 0.6 mM) was prepared in a round-bottom flask equipped with a stir bar and cooled at -40°C in an acetonitrile frozen bath. 1 or 5 equiv. of 2-ethylhexanoic acid (or alternative carboxylic acid) were added directly to the solution. Then, the corresponding equivalents of a 7:1 (v:v) acetonitrile:hydrogen peroxide solution 30% were added by syringe pump over a period of 30 min. The solution was further stirred at -40°C for 30 minutes. At this point, 15 mL of an $NaHCO_3$ saturated aqueous solution was added to the mixture. The resultant solution was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic fractions were dried over $MgSO_4$. The solvent was removed under reduced pressure to afford the epoxide product. This residue was purified by flash column chromatography over silica gel (or neutral alumina) to obtain the pure epoxide.

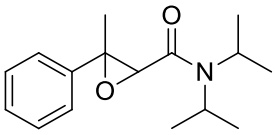
5) Characterization of isolated epoxide products



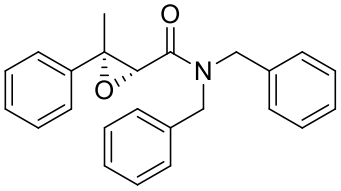
E3, purification by crystallization (CH_2Cl_2:hexane) gave the product as a white solid (94.5 mg, 72% yield, 94% ee). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 7.43 - 7.31 (m, 5H), 3.52 (s, 1H), 3.09 (s, 3H), 2.99 (s, 3H), 1.69 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm: 166.3, 140.4, 128.6, 128.0, 125.1, 63.5, 61.3, 36.2, 35.2, 17.8. HRMS (ESI-MS) m/z calculated for $C_{12}H_{15}NNaO_2$ $[M+Na]^+$: 228.0995, found: 228.1008.



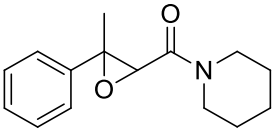
E4, purification by flash chromatography (neutral alumina; hexane:AcOEt 8:2) gave the product as a white solid (108.3 mg, 78% yield, 84:16 ***E:Z***, 96% ee major isomer). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.43-7.31 (m, 5H), 3.58-3.44 (m, 2H), 3.42-3.35 (m, 3H), 1.68 (s, 1H), 1.20 (dt, J = 10.4, 7.1 Hz, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm: 165.5, 140.6, 128.6, 127.9, 125.1, 63.2, 61.3, 41.0, 40.0, 17.7, 14.4, 13.0. HRMS (ESI-MS) m/z calculated for $C_{14}H_{20}NO_2$ $[M+H]^+$: 234.1489, found: 234.1483.



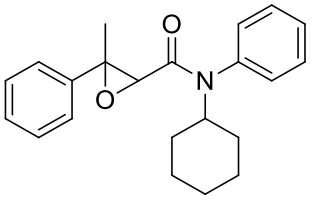
E5, purification by flash chromatography (silica-gel; hexane:AcOEt 9:1) gave the product as a pale yellow solid (110.4 mg, 87% yield, 97% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.39-7.31 (m, 5H), 4.10 (hept, J = 6.7 Hz, 1H), 3.49 (hept, J = 6.8 Hz, 1H), 3.42 (s, 1H), 1.67 (s, 3H), 1.45 (t, J = 6.5 Hz, 6H), 1.27 (dd, J = 6.7, 1.2 Hz, 3H), 1.18 (dd, J = 6.6, 1.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 165.0, 140.7, 128.6, 127.9, 125.0, 64.1, 61.3, 48.0, 46.0, 21.1, 20.9, 20.7, 20.2, 17.9. HRMS (ESI-MS) m/z calculated for $C_{16}H_{23}NNaO_2$ $[M+Na]^+$: 284.1621, found: 284.1616.



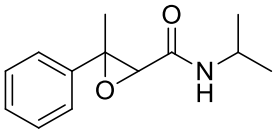
E6, purification by flash chromatography (silica-gel; hexane:AcOEt 8:2) gave the product as a white solid (84.9 mg, 90% yield, 99% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.37-7.24 (m, 13H), 7.15-7.13 (m, 2H), 4.90 (d, J = 14.6 Hz, 1H), 4.56-4.40 (m, 3H), 3.59 (s, 1H), 1.72 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 166.9, 140.1, 136.7, 135.8, 129.0, 128.8, 128.6, 128.5, 128.0, 128.0, 127.7, 126.9, 125.0, 63.1, 61.9, 48.9, 48.0, 17.9. HRMS (ESI-MS) m/z calculated for $C_{24}H_{23}NNaO_2$ $[M+Na]^+$: 380.1621, found: 380.1620.



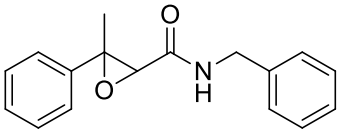
E7, isolated starting with 1 mmol of substrate. Purification by flash chromatography (silica-gel; hexane:AcOEt 1:1) gave the product as a white solid; (58.3 mg, 25% yield, 93% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: δ 7.43-7.31 (m, 5H), 3.67-3.52 (m, 2H), 3.51-3.44 (m, 3H), 1.74-1.67 (m, 6H), 1.65-1.53 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 164.6, 140.5, 128.6, 127.9, 125.0, 63. 6, 61.2, 45. 8, 42.9, 26.6, 25.6, 24.5, 18.0. HRMS (ESI-MS) m/z calculated for $C_{15}H_{19}NNaO_2$ $[M+Na]^+$: 268.1308, found: 268.1317.



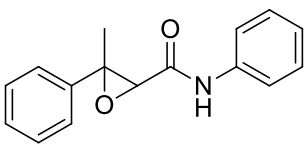
E9, purification by flash chromatography (neutral alumina; hexane:AcOEt 9:1) gave the product as a white solid (96.3 mg, 83% yield, 84% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.39-7.31 (m, 3H), 7.17-7.12 (m, 5H), 6.92-6.89 (m, 2H), 4.65 (tt, J = 12.1, 3.7 Hz, 1H), 3.05 (s, 1H), 1.91-1.85 (m, 2H), 1.77-1.73 (m, 2H), 1.67 (s, 3H), 1.59 (d, J = 13.1 Hz, 1H), 1.45-1.40 (m, 2H), 1.12 (qt, J = 12.6, 3.8 Hz, 2H), 0.93 (qt, J = 13.1, 3.7 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 165.5, 140.4, 137.3, 130.3, 129.5, 128.7, 128.0, 127.6, 125.0, 63.3, 62.0, 54. 6, 31.6, 31.3, 25.7, 25.7, 25.3, 17.73. HRMS (ESI-MS) m/z calculated for $C_{22}H_{26}NO_2$ $[M+H]^+$: 336.1958, found: 336.1949.



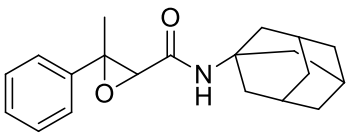
E10, purification by flash chromatography (silica gel; hexane:AcOEt 3:1) gave the product as a white solid (90.0 mg, 78% yield, 89% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.37-7.28 (m, 5H), 6.12 (d, J = 6.5 Hz, 1H), 4.18 (dhept, J = 8.2, 6.5 Hz, 1H), 3.42 (s, 1H), 1.70 (s, 3H), 1.21 (dd, J = 6.6, 3.4 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 165.9, 140.4, 128.5, 128.1, 125.2, 63.7, 63.0, 41.1, 22.8, 22.6, 17.4. HRMS (ESI-MS) m/z calculated for $C_{13}H_{17}NNaO_2$ $[M+Na]^+$: 242.1151, found: 242.1145.



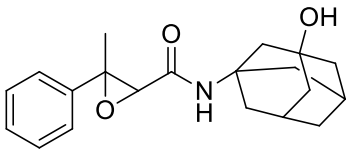
E11, purification by flash chromatography (silica-gel; hexane:AcOEt 3:1) gave the product as a white solid (72.1 mg, 62% yield, 92% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.38-7.28 (m, 10H), 6.60 (s, 1H), 4.52 (qd, J = 14.6, 6.0 Hz, 2H), 3.50 (s, 1H), 1.68 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 166.8, 140.2, 137.6, 128.8, 128.5, 128.1, 128.0, 127.8, 125.2, 63.7, 63.2, 43.1, 17.6. HRMS (ESI-MS) m/z calculated for HRMS (ESI-MS) m/z calculated for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332, found: 268.1353.



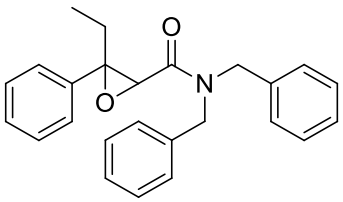
E12, purification by flash chromatography (silica-gel; hexane:AcOEt 7:3) gave the product as a pale pink solid (100.9 mg, 57% yield, 90% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 8.03 (s, 1H), 7.65-7.62 (m, 2H), 7.44-7.34 (m, 7H), 7.22-7.17 (m, 1H), 3.62 (s, 1H), 1.81 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm: 164.9, 140.0, 136.6, 129.2, 128.6, 128.3, 125.3, 124.9, 119.8, 63.9, 63.8, 17.7. HRMS (ESI-MS) m/z calculated for $C_{16}H_{15}NNaO_2$ $[M+Na]^+$: 276.0995, found: 276.100.



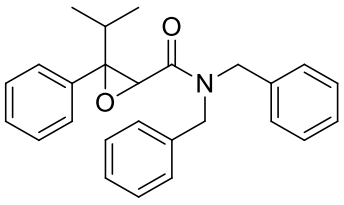
E13, purification by flash chromatography (silica-gel; hexane:AcOEt 8:2) gave the product as a white solid (62.3 mg, 30% yield, 82% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.38-7.30 (m, 5H), 5.98 (s, 1H), 3.36 (s, 1H), 2.14-2.11 (m, 3H), 2.07 (s, 6H), 1.74 (s, 3H), 173-1.72 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 165.8, 140.6, 128.5, 128.0, 125.2, 63.9, 63.0, 52.1, 41.6, 36.3, 29.4 17.4. HRMS (ESI-MS) m/z calculated for $C_{20}H_{25}NNaO_2$ $[M+Na]^+$: 334.1778, found: 334.1787.



EO13, purification by flash chromatography (silica-gel; hexane:AcOEt 8:2) gave the product as a white solid (90.0 mg, 43% yield, 84% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.37-7.30 (m, 5H), 6.07 (s, 1H), 3.36 (s, 1H), 2.33-2.31 (m, 2H), 2.11-2.04 (m, 2H), 2.01-1.94 (m, 4H), 1.77-1.70 (m, 9H), 1.65-1.55 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 165.9, 140.4, 128.5, 128.1, 125.2, 69.1, 63.8, 63.1, 54.5, 49.0, 44.0, 40.3, 40.2, 34.8, 30.6, 17.4. HRMS (ESI-MS) m/z calculated for $C_{20}H_{25}NNaO_3$ $[M+Na]^+$: 350.1727, found: 350.1727.

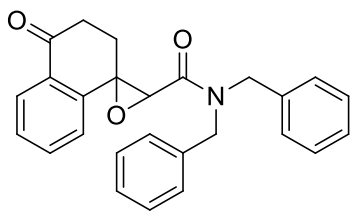


E14, purification by flash chromatography (silica-gel; hexane:AcOEt 8:2) gave the product as a colourless oil (101.47 mg, 84% yield, 99% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.41-7.26 (m, 13H), 7.19-7.17 (m, 2H), 4.91 (d, J = 14.6 Hz, 1H), 4.61 (d, J = 16.6 Hz, 1H), 4.49 (d, J = 16.6 Hz, 1H), 4.41 (d, J = 14.6 Hz, 1H), 3.60 (s, 1H), 2.21 (dq, J = 14.9, 7.5 Hz, 1H), 1.81 (dq, J = 14.6, 7.3 Hz, 1H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 166.9, 138.4, 136.7, 135.8, 129.0, 128.7, 128.6, 128.5, 127.9, 127.8, 127.7, 126.9, 125.7, 66.4, 63.4, 48.9, 47.9, 24.6, 9.4. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO_2$ $[M+Na]^+$: 394.1778, found: 394.1775.

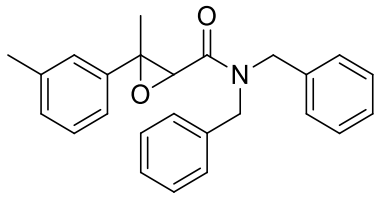


E15, purification by flash chromatography (silica-gel; hexane:AcOEt 8:2) gave the product as a colourless oil (94.4 mg, 33% yield, 85% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.40-7.26 (m, 15H), 5.17 (d, J = 14.5 Hz, 1H), 4.86 (d, J = 16.5 Hz, 1H), 4.55 (d, J = 16.5 Hz, 1H), 4.17 (d, J = 14.5 Hz, 1H), 3.73 (s, 1H), 2.07 (hept, J = 6.8 Hz, 1H), 1.02 (dd, J = 6.9, 5.8 Hz, 6H). ^{13}C-

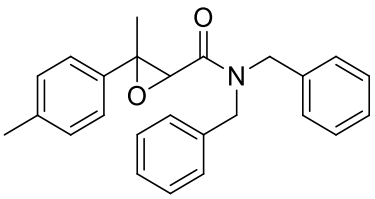
NMR (75 MHz, $CDCl_3$) δ ppm: 167.0, 136.8, 136.7, 135.8, 129.1, 128.7, 128.7, 128.0, 127.9, 127.8, 127.8, 127.7, 127.0, 70.2, 61.9, 49.1, 47.8, 31.7, 19.3, 18.3. HRMS (ESI-MS) m/z calculated for $C_{26}H_{27}NNaO_2$ $[M+Na]^+$: 408.1934, found: 408.1927.



EK16, purification by flash chromatography (silica-gel; hexane:AcOEt 8:2) gave the product as a white solid (65.1 mg, 62% yield, 91% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 8.05 (dd, J = 7.8, 1.3 Hz, 1H), 7.59 (td, J = 7.6, 1.4 Hz, 1H), 7.46 (td, J = 7.6, 1.3 Hz, 1H), 7.37-7.31 (m, 6H), 7.28-7.26 (m, 3H), 7.18-7.15 (m, 2H), 5.03 (d, J = 14.5 Hz, 1H), 4.62 (d, J = 16.4 Hz, 1H), 4.47 (d, J = 16.4 Hz, 1H), 4.33 (d, J = 14.5 Hz, 1H), 3.78 (s, 1H), 2.82-2.81 (m, 1H), 2.66-2.62 (m, 2H), 2.20-2.18 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 196.0, 165.9, 141.0, 136.5, 135.6, 134.4, 133.2, 129.1, 128.9, 128.85, 128.5, 128.2, 128.0, 127.3, 127.0, 123.0, 64.1, 61.1, 49.4, 48.4, 36.8, 26.9. HRMS (ESI-MS) m/z calculated for $C_{26}H_{23}NNaO_3$ $[M+Na]^+$: 420.1570, found: 420.1570.

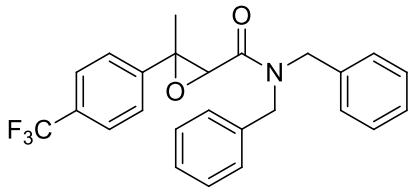


E18, purification by flash chromatography (silica-gel; hexane:AcOEt 8:2) gave the product as a colourless oil (63.8 mg, 64% yield, 98% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.39-7.33 (m, 6H), 7.29 (dd, J = 6.1, 1.9 Hz, 2H), 7.23-7.17 (m, 3H), 7.11-7.08 (m, 3H), 4.92 (d, J = 14.6 Hz, 1H), 4.52 (dt, J = 30.6, 15.5 Hz, 3H), 3.62 (s, 1H), 2.34 (s, 3H), 1.74 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 166.9, 140.1, 138.2, 136.8, 135.9, 129.0, 128.8, 128.6, 128.4, 127.9, 127.7, 126.9, 125.6, 122.1, 63.0, 62.0, 48. 9, 48.0, 21.4, 18.0. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO_2$ $[M+Na]^+$: 394.1778, found: 394.1764.

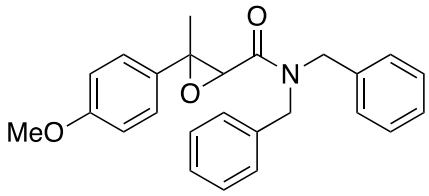


E19, purification by flash chromatography (silica-gel; hexane:AcOEt 8:2) gave the product as a colourless oil (62.3 mg, 74% yield, 99% ee). ^{1}H-NMR (CDCl3, 300 MHz, 300K) δ, ppm: 7.42-7.30 (m, 6H), 7.27 (d, J = 6.3 Hz, 2H), 7.21-7.10 (m, 6H), 4.92 (d, J = 14.6 Hz, 1H), 4.56 (d, J = 16.6 Hz, 1H), 4.47 (d, J = 16.6 Hz, 1H), 4.42 (d, J = 14.6 Hz, 1H), 3.61 (s, 1H), 2.34 (s, 3H), 1.73 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 166.96, 137.78, 137.19, 136.74, 135.82, 129.18, 129.01, 128.72, 128.59,

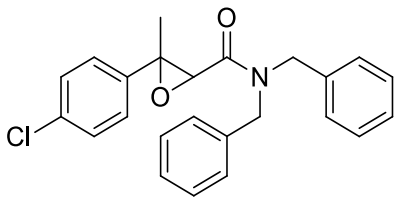
127.93, 127.70, 126.87, 124.97, 63.16, 61.87, 48.87, 47.91, 21.08, 17.94. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO_2$ $[M+Na]^+$: 394.1778, found: 394.1765.



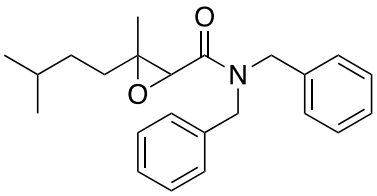
E20, purification by flash chromatography (silica-gel; hexane:AcOEt 9:1) gave the product as a colourless oil (73.3 mg, 65% yield, 98% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.57 (d, J = 8.3 Hz, 2H), 7.40-7.30 (m, 8H), 7.29 (dd, J = 5.3, 2.6 Hz, 2H), 7.17-7.15 (m, 2H), 4.83 (d, J = 14.5 Hz, 1H), 4.57-4.53 (m, 3H), 3.57 (s, 1H), 1.75 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 166.4, 144.1, 136.6, 135.8, 129.1, 128. 8, 128.6, 128.0, 127.8, 126.7, 125.6, 125.5, 125.5, 62.9, 61. 6, 49.1, 48.4, 17.7. HRMS (ESI-MS) m/z calculated for $C_{25}H_{22}F_3NNaO_2$ $[M+Na]^+$: 448.1495, found: 448.1482.



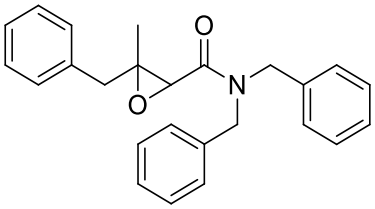
E21, purification by flash chromatography (silica-gel; hexane:AcOEt 7:3) gave the product a a clear oil (51.7 mg, 57% yield, 98% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.44-7.30 (m, 7H), 7.27-7.15 (m, 5H), 6.86-6.82 (m, 2H), 4.92 (d, *J* = 14.6 Hz, 1H), 4.58-4.39 (m, 3H), 3.80 (s, 3H), 3.60 (s, 1H), 1.71 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 167.0, 159.3, 136.7, 135.8, 132.1, 129.0, 128.7, 128.6, 127.0, 127.7, 126.8, 126.3, 113.9, 63.3, 61.7, 55.3, 48.9, 48.0, 17.9. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO_3$ $[M+Na]^+$: 410.1727, found: 410.1736.



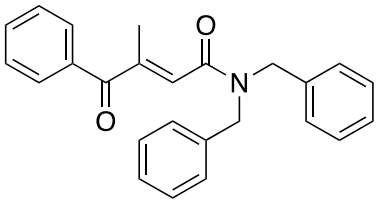
E22, purification by flash chromatography (neutral alumina; hexane:AcOEt 8:3) gave the product as a colourless oil (86.7 mg, 83% yield, 99% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.40-7.33 (m, 6H), 7.29-7.27 (m, 4H), 7.19-7.15 (m, 4H), 4.85 (d, J = 14.6 Hz, 1H), 4.56-4.47 (m, 3H), 3.56 (s, 1H), 1.71 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 166.6, 138.7, 136.6, 135.9, 133.9, 129.1, 128.8, 128.7, 128.6, 128.0, 127.8, 126.7, 126.5, 63.1, 61.5, 49.0, 48.3, 17.8. HRMS (ESI-MS) m/z calculated for $C_{24}H_{22}ClNNaO_2$ $[M+Na]^+$: 414.1231, found: 414.1218.



E25, purification by flash chromatography (silica-gel; hexane:AcOEt 9:1) gave the product as a clear oil (55.0 mg, 51% yield, 95% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.43-7.22 (m, 10H), 4.84 (d, *J* =14.6 Hz, 2H), 4.58-4.41 (m, 3H), 3.48 (s, 1H), 1.59-1.44 (m, 3H), 1.35 (s, 3H), 1.30-1.16 (m, 2H), 0.86 (td, *J* = 6.6, 3.8 Hz, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 167.9, 136.8, 136.1, 129.0, 128.7, 128.5, 127.9, 127.6, 126.9, 126.8, 62.9, 60.0, 49.0, 48.1, 35.3, 33.7, 28.0, 22.5, 17.3. HRMS (ESI-MS) m/z calculated for $C_{23}H_{29}NNaO_2$ $[M+Na]^+$: 374.2091, found: 374.2089.



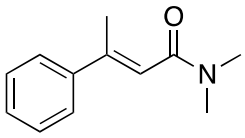
E26, isolated starting with 1.5 mmol of substrate. Purification by flash chromatography (silica-gel; hexane:AcOEt 9:1) gave the product as a white off solid (291.6 mg, 35% yield, 95% ee). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.39-7.10 (m, 15H), 4.81 (d, J = 14.7 Hz, 1H), 4.47-4.30 (m, 3H), 3.40 (s, 1H), 2.93-2.80 (m, 2H), 1.34 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 167.6, 136.8, 135.9, 135.9, 129.6, 129.0, 128.7, 128.5, 128.5, 127.8, 127.6, 126.9, 126.7, 62.6, 59.0, 48.8, 47.9, 43.5, 17.5. HRMS (ESI-MS) m/z calculated for $C_{25}H_{25}NNaO_2$ $[M+Na]^+$: 394.1778, found: 394.1768.



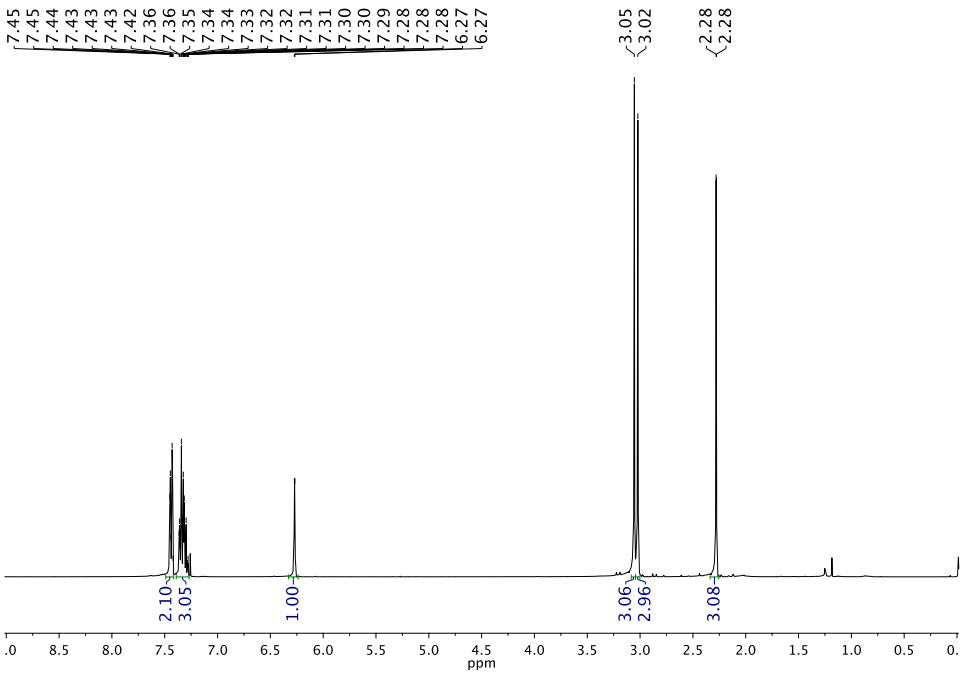
K26, isolated starting with 1.5 mmol of substrate. Purification by flash chromatography (silica-gel; hexane:AcOEt 9:1) gave the product as a white off solid (157.5 mg, 19% yield). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300K) δ, ppm: 7.69-7.67 (m, 2H), 7.54-7.49 (m, 1H), 7.40-7.26 (m, 11H), 7.09-7.07 (m, 2H), 6.59 (d, *J* = 1.4 Hz, 1H), 4.64 (s, 2H), 4.38 (s, 2H), 2.23 (d, *J* = 1.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 197.7, 167.3, 144.1, 136.7, 136.6, 135.8, 132.6, 131.1, 129.5, 129.0, 128.8, 128.5, 128.4, 127.9, 127.7, 126.8, 50.5, 47.4, 15.2. HRMS (ESI-MS) m/z calculated for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802, found: 370.1786.

6) Substrates and products characterization

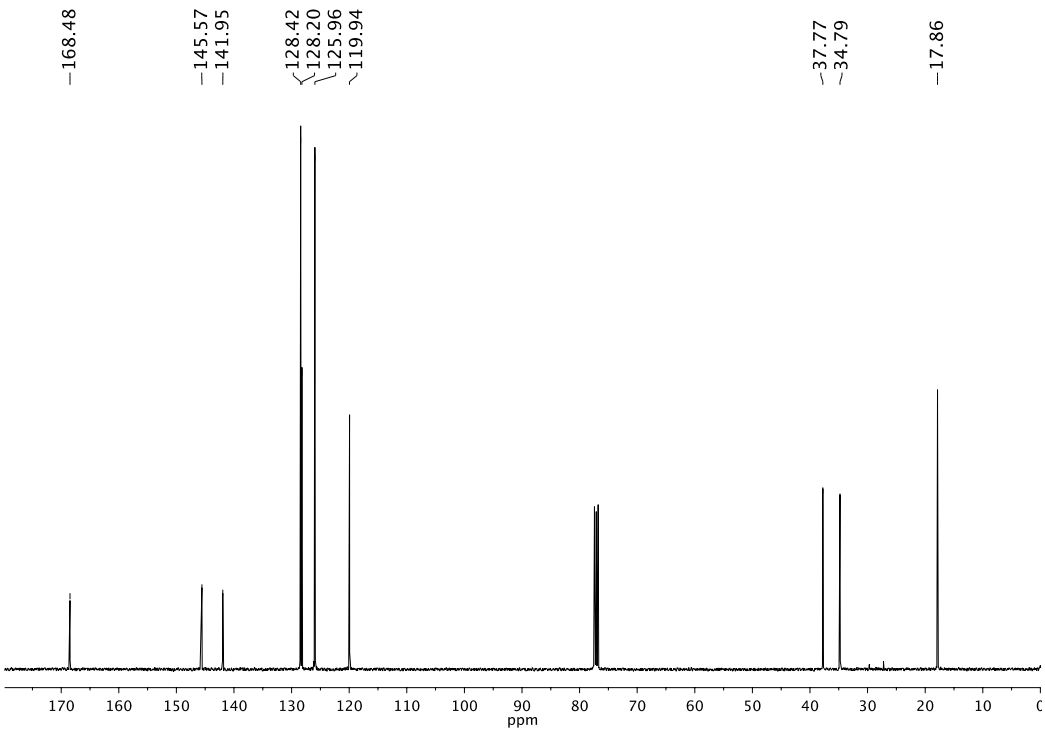
6.1) ^{1}H and ^{13}C-NMR spectra of synthetized substrates

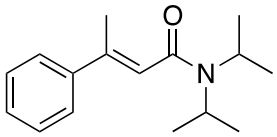


^{1}H-NMR of **S3** in $CDCl_3$

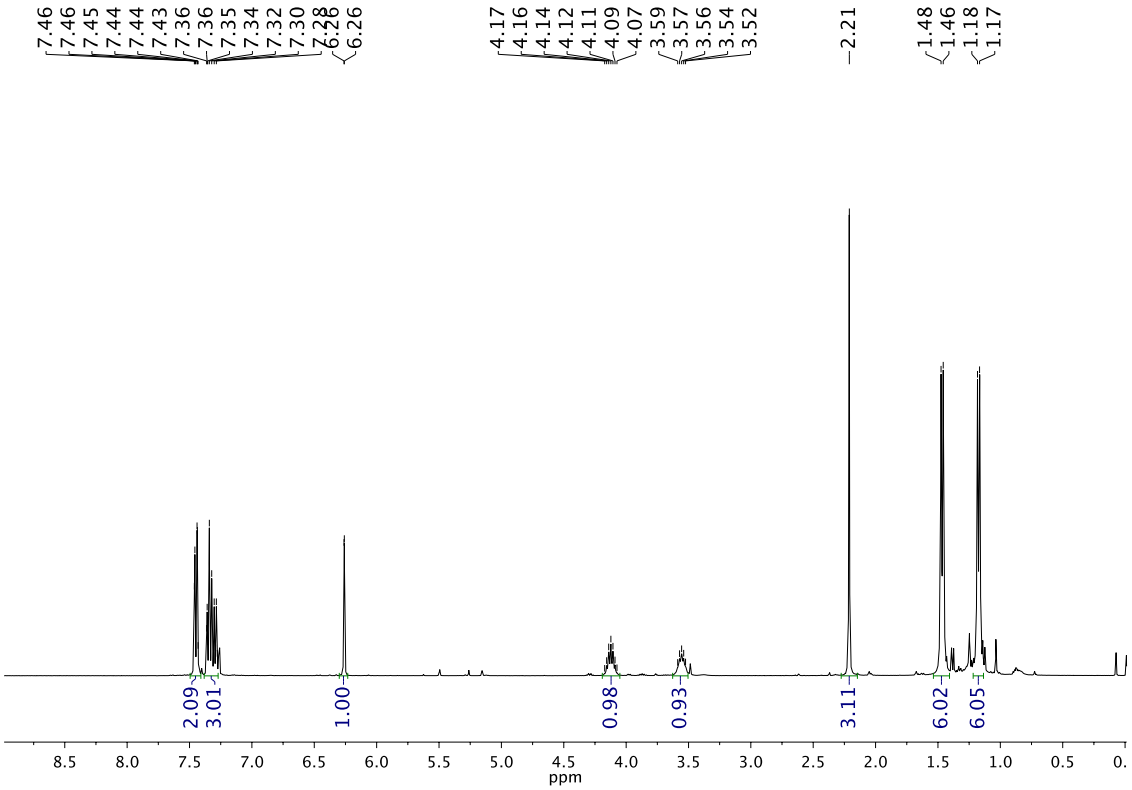


^{13}C-NMR of **S3** in $CDCl_3$

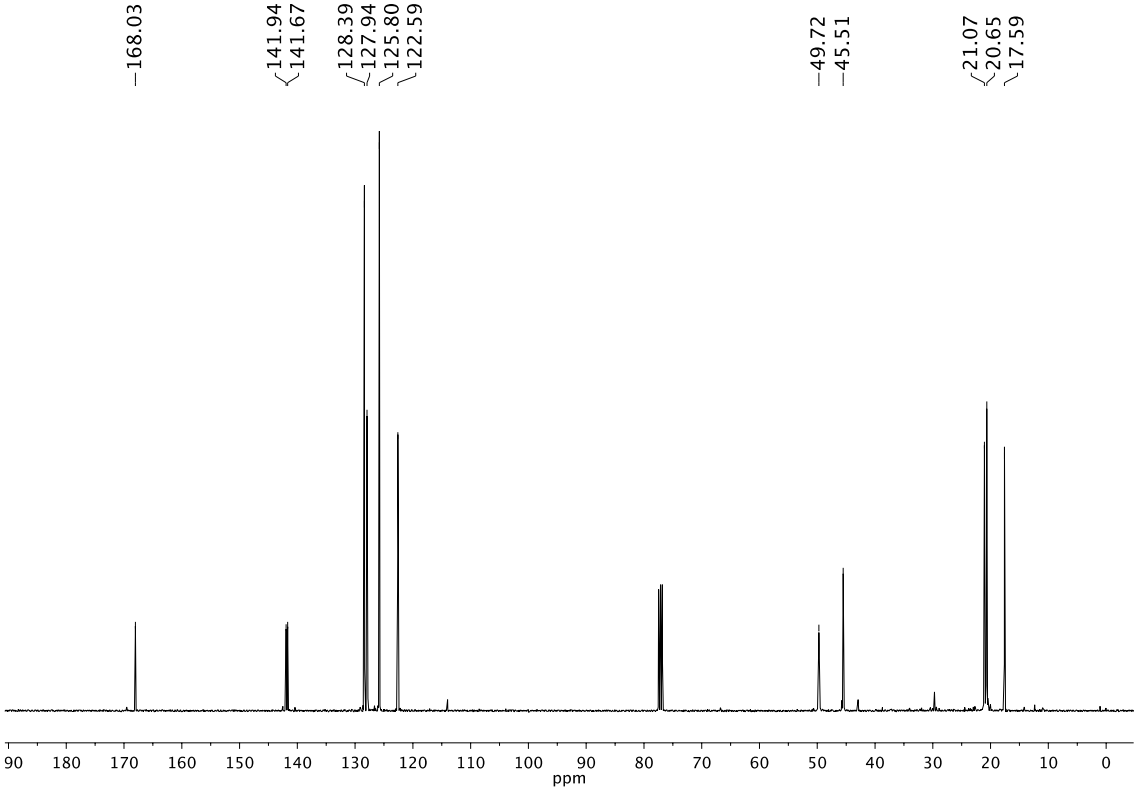


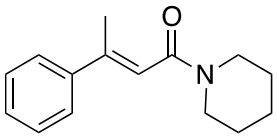


^{1}H-NMR of **S5** in $CDCl_3$

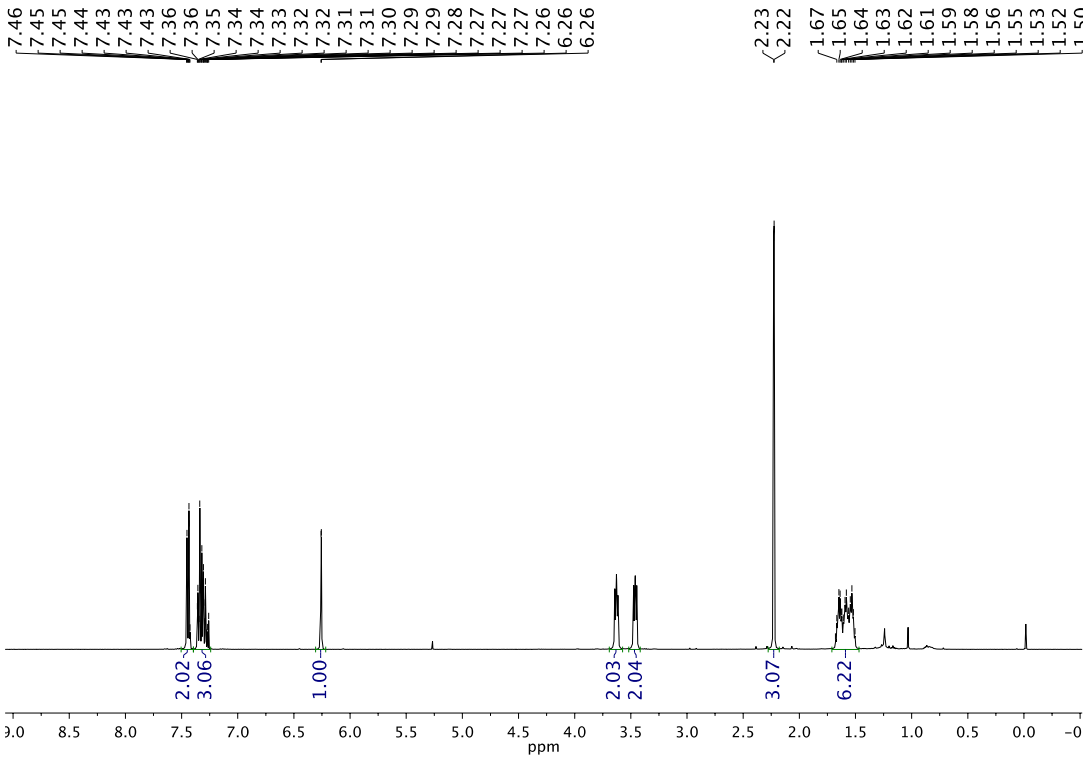


^{13}C-NMR of **S5** in $CDCl_3$

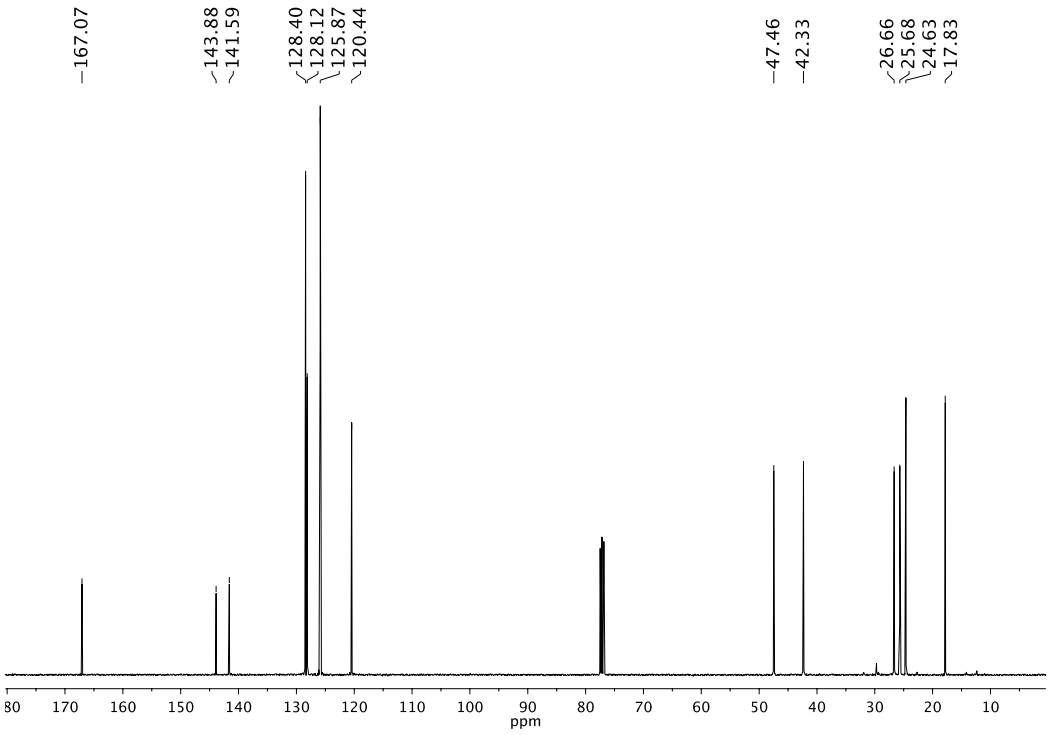


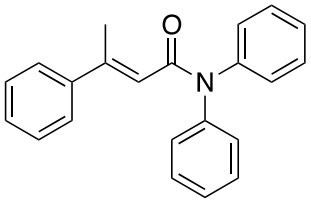


^{1}H-NMR of **S7** in $CDCl_3$

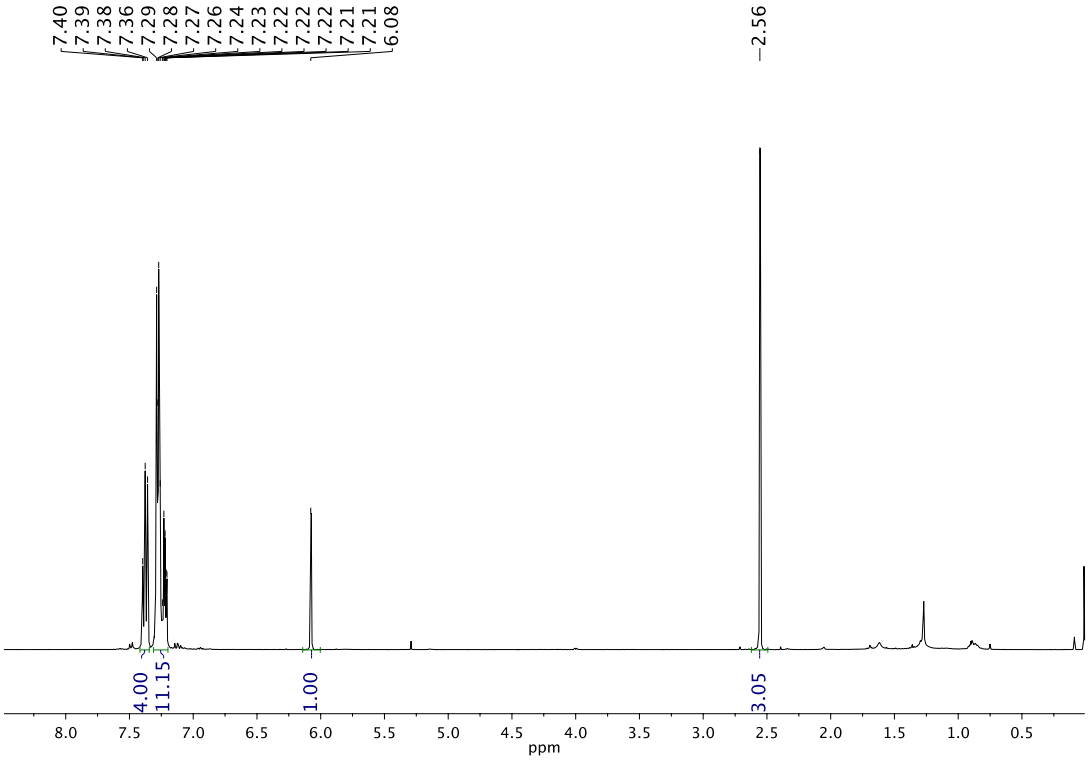


^{13}C-NMR of **S7** in $CDCl_3$

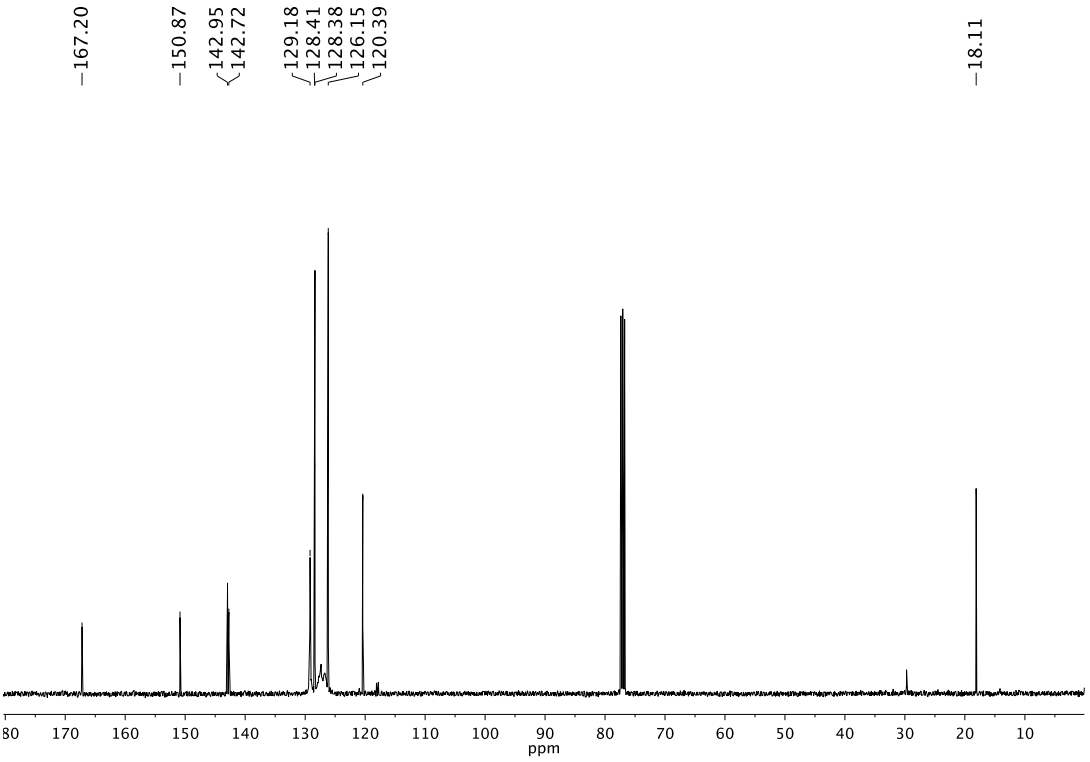


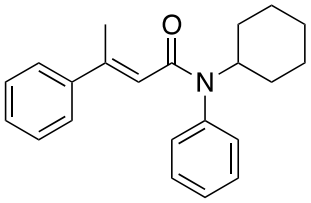


^{1}H-NMR of **S8** in $CDCl_3$

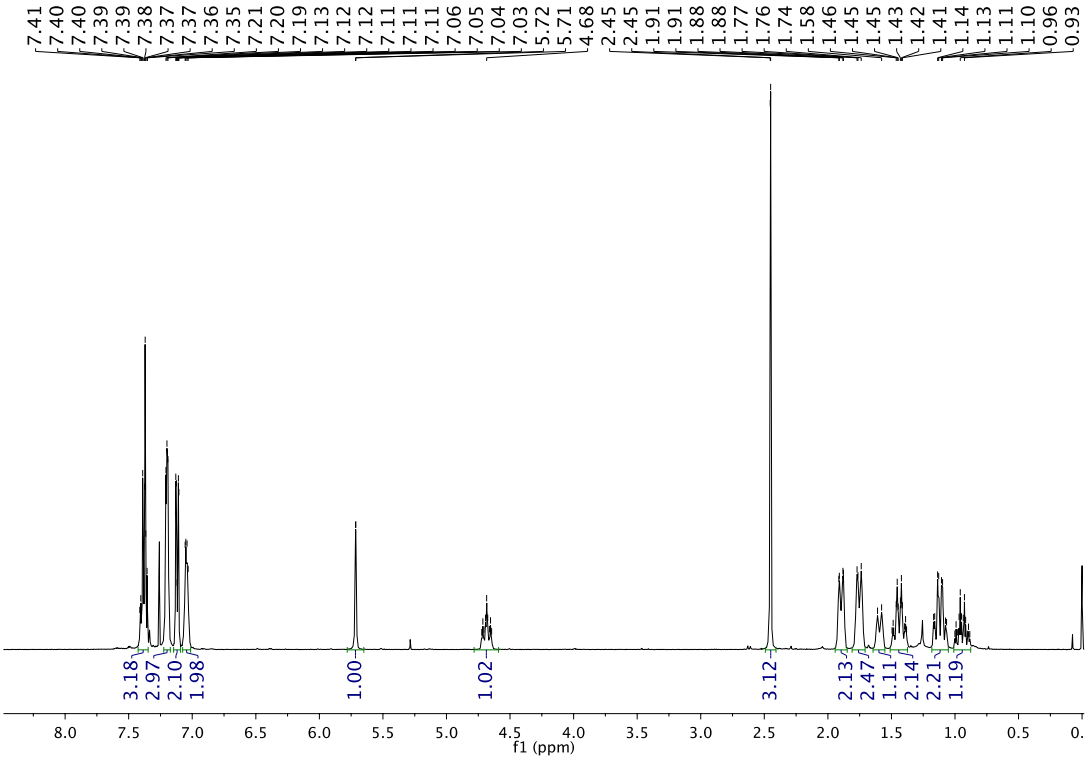


^{13}C-NMR of **S8** in $CDCl_3$

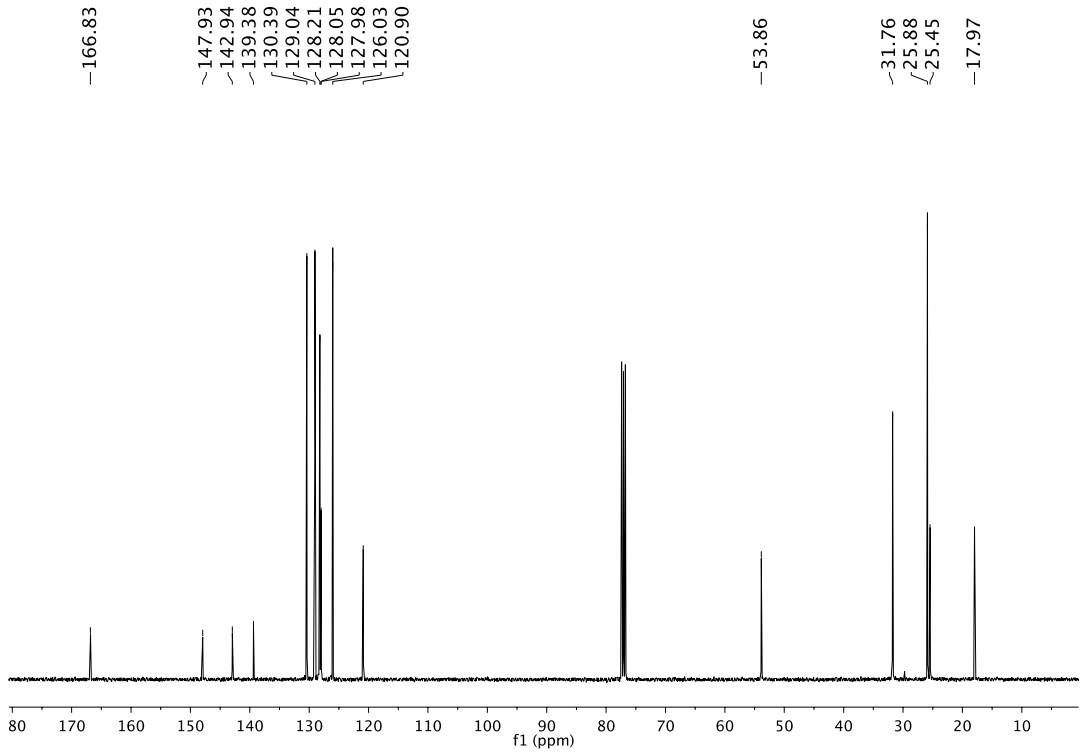


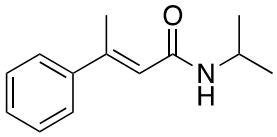


^{1}H-NMR of **S9** in $CDCl_3$

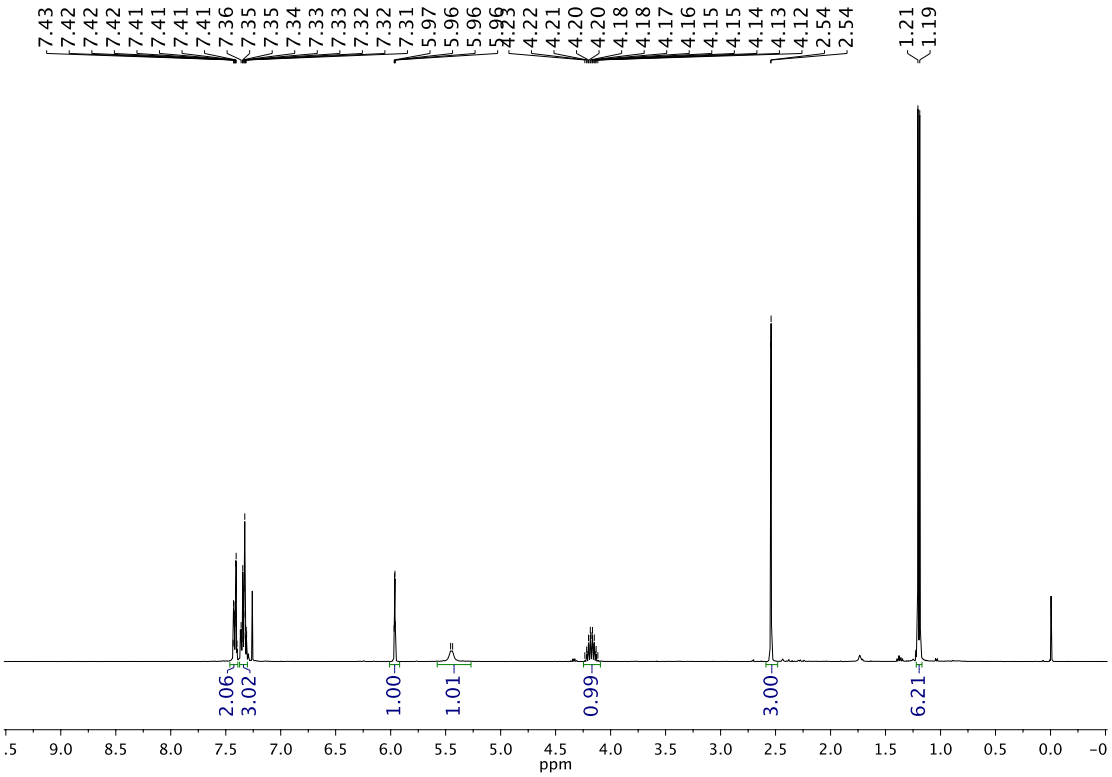


^{13}C-NMR of **S9** in $CDCl_3$

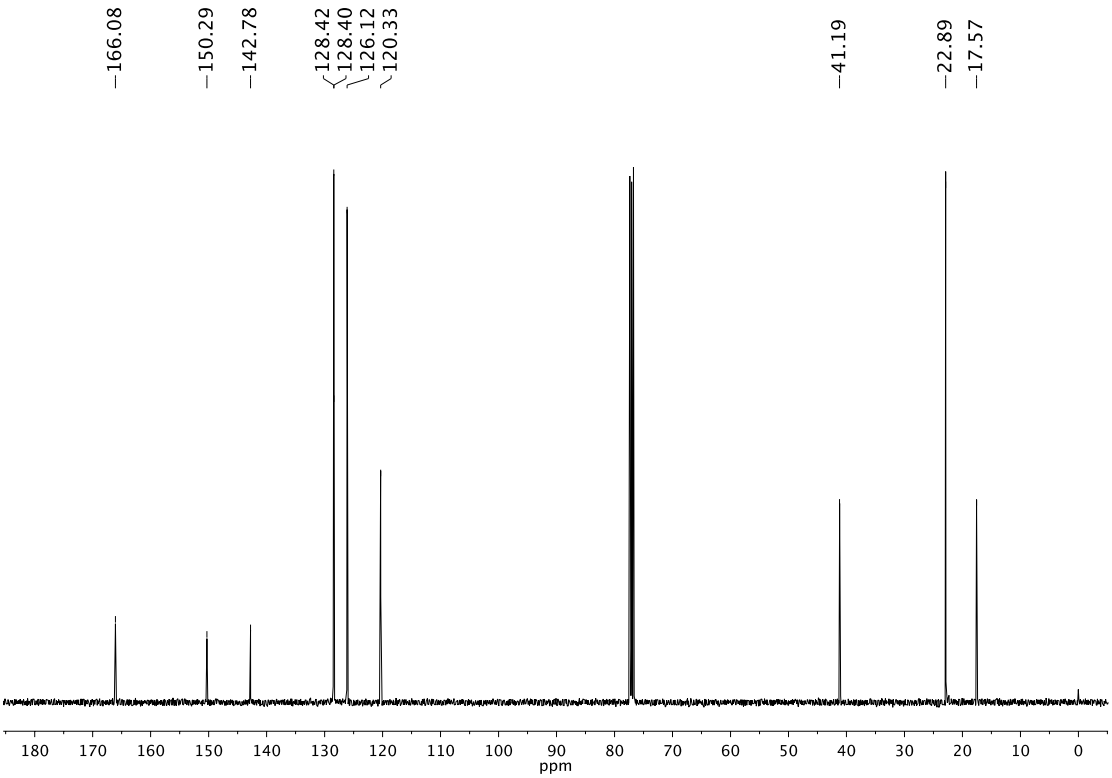


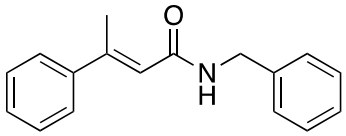


^{1}H-NMR of **S10** in $CDCl_3$

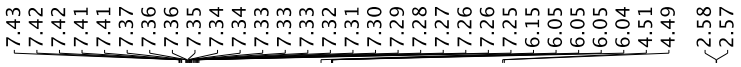


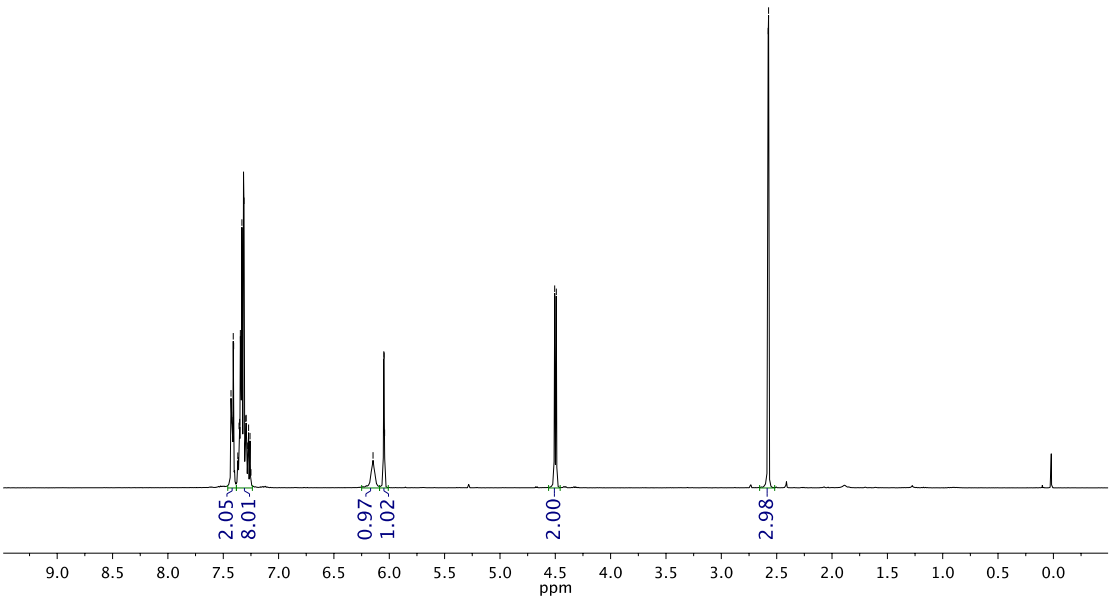
^{13}C-NMR of **S10** in $CDCl_3$



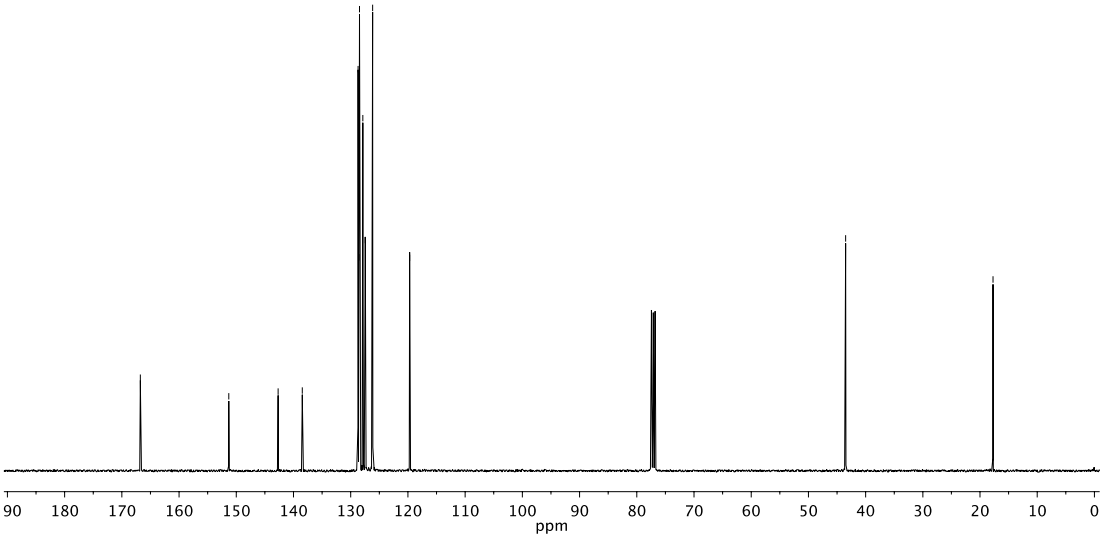


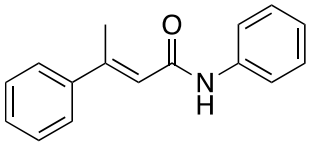
^{1}H-NMR of **S11** in $CDCl_3$



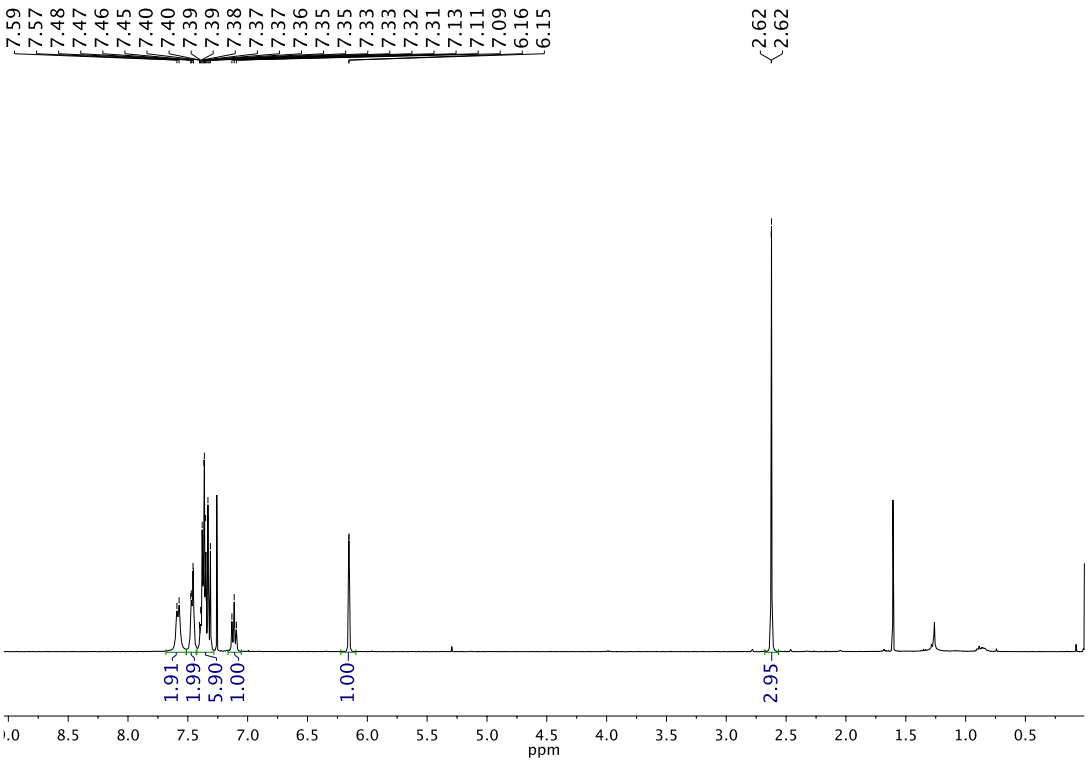


^{13}C-NMR of **S11** in $CDCl_3$

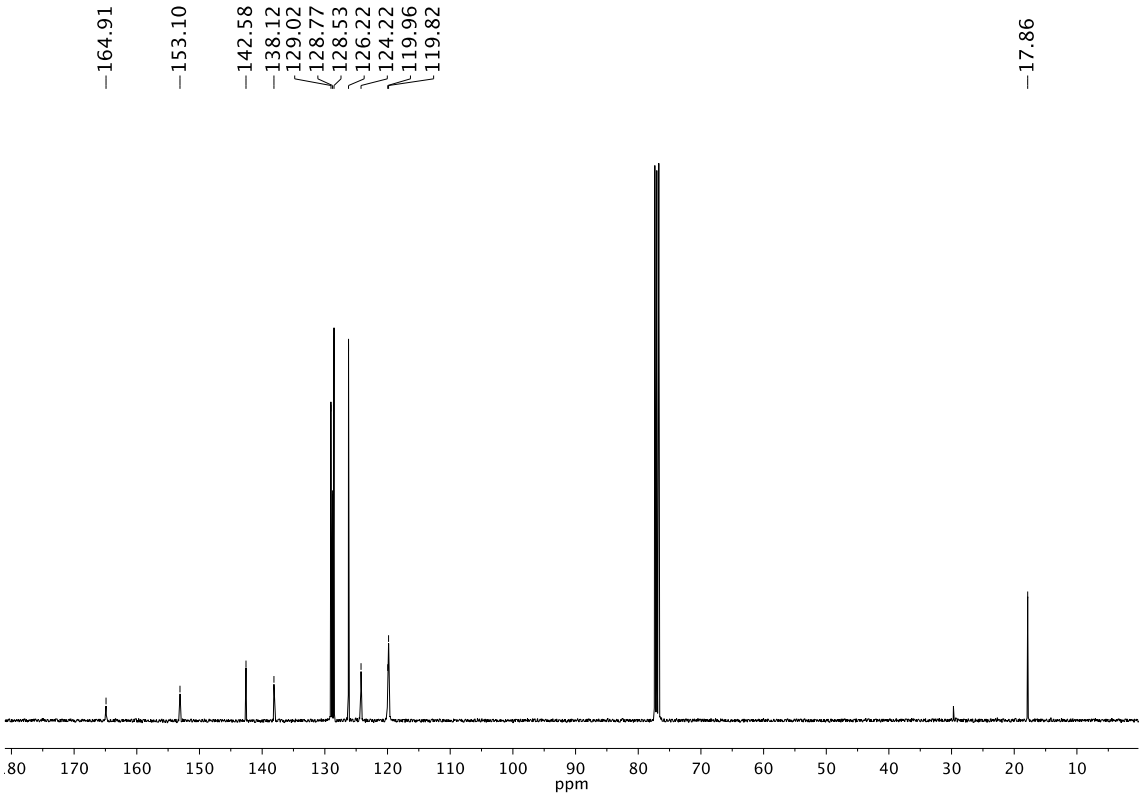


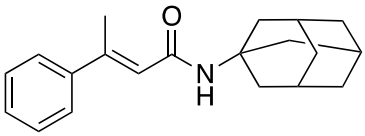


^{1}H-NMR of **S12** in $CDCl_3$

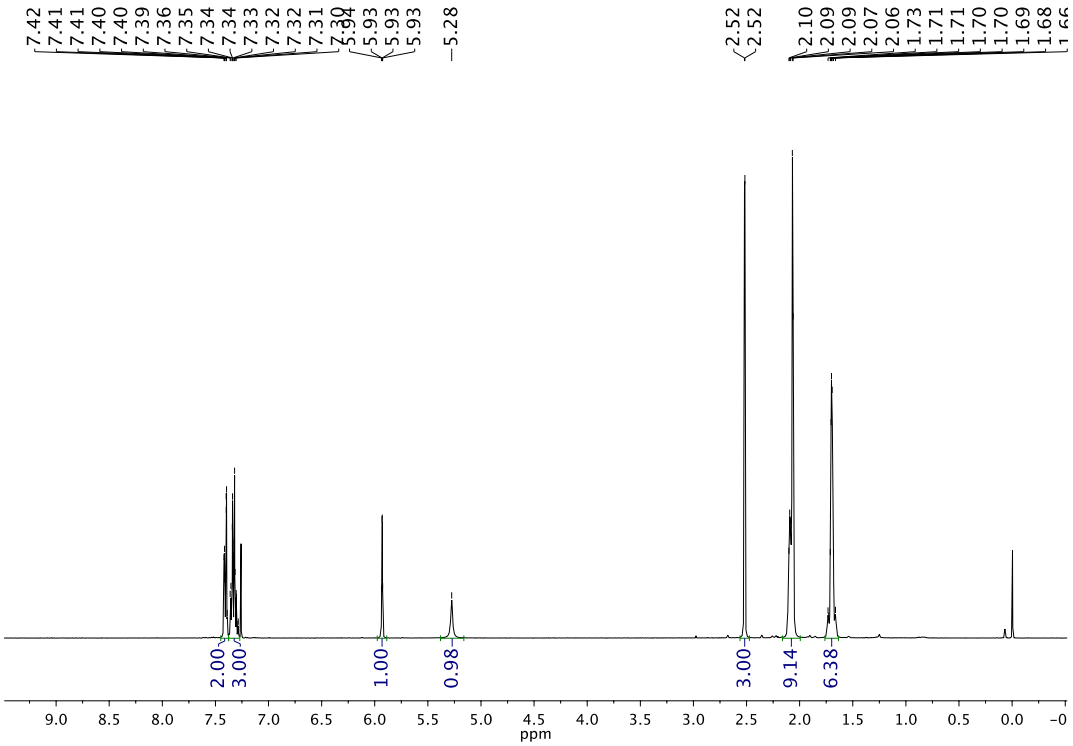


^{13}C-NMR of **S12** in $CDCl_3$

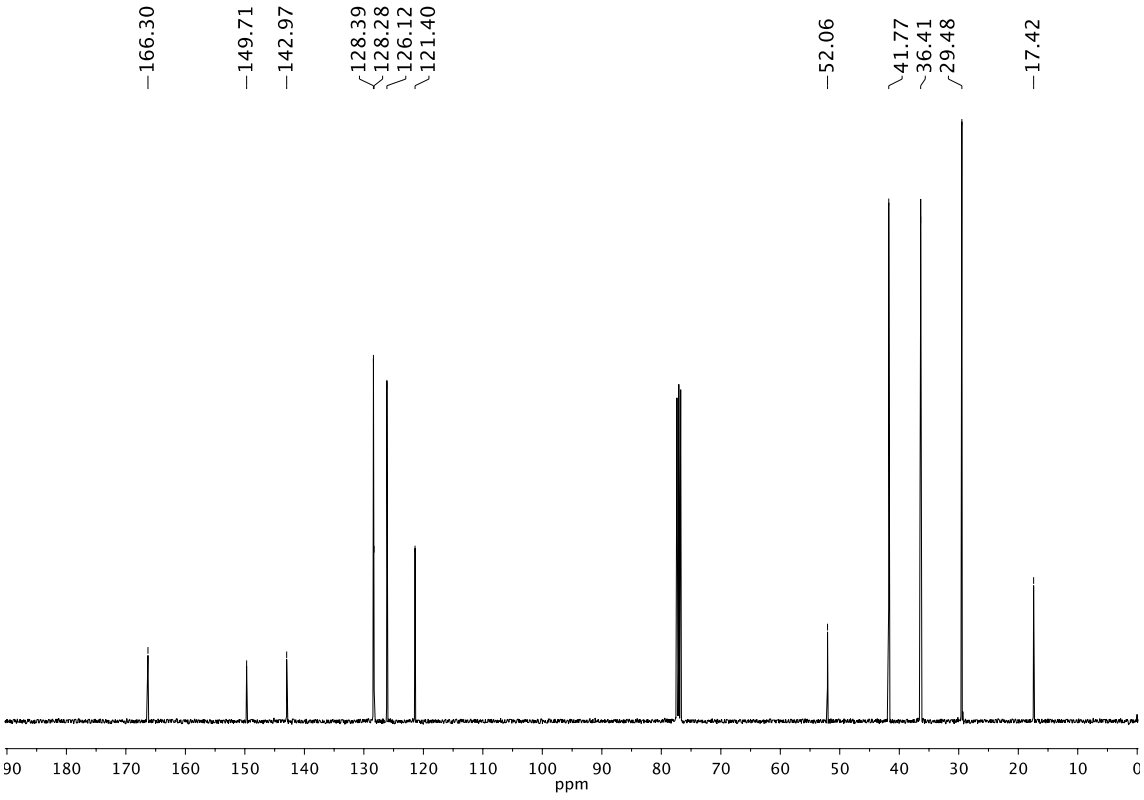


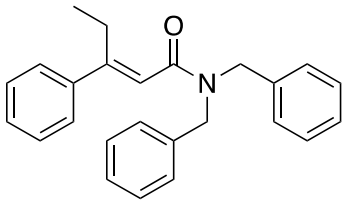


^{1}H-NMR of **S13** in $CDCl_3$

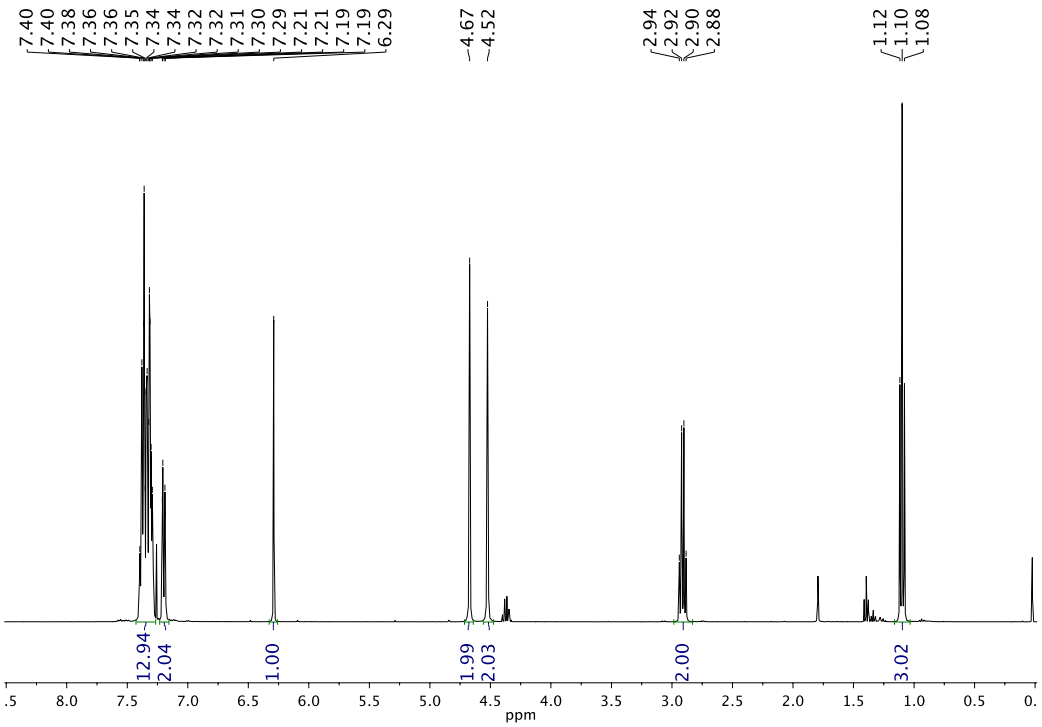


^{13}C-NMR of **S13** in $CDCl_3$

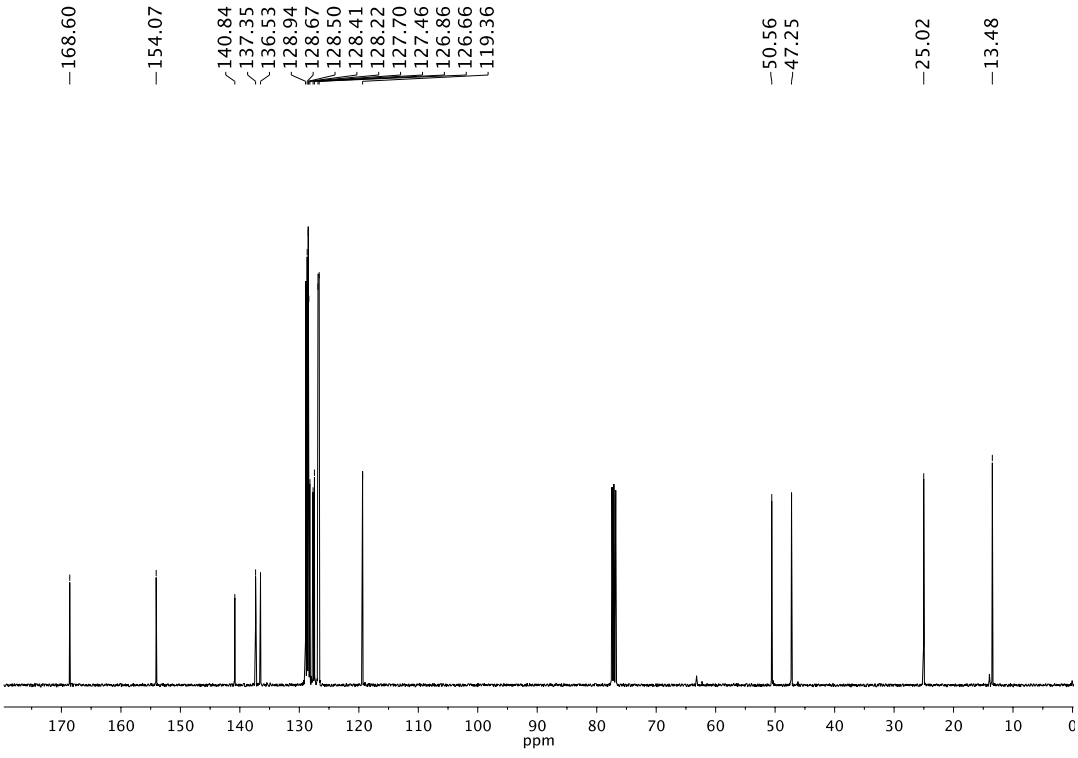


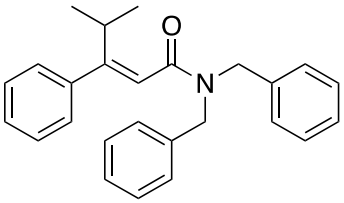


^{1}H-NMR of **S14** in $CDCl_3$

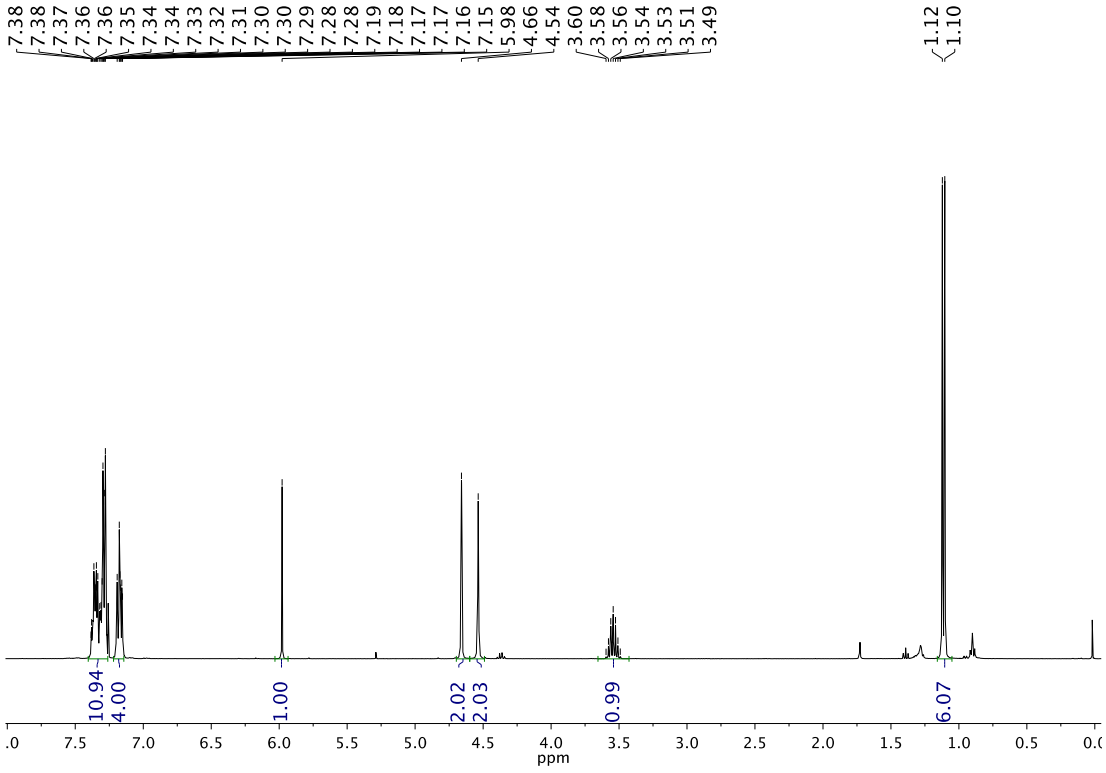


^{13}C-NMR of **S14** in $CDCl_3$

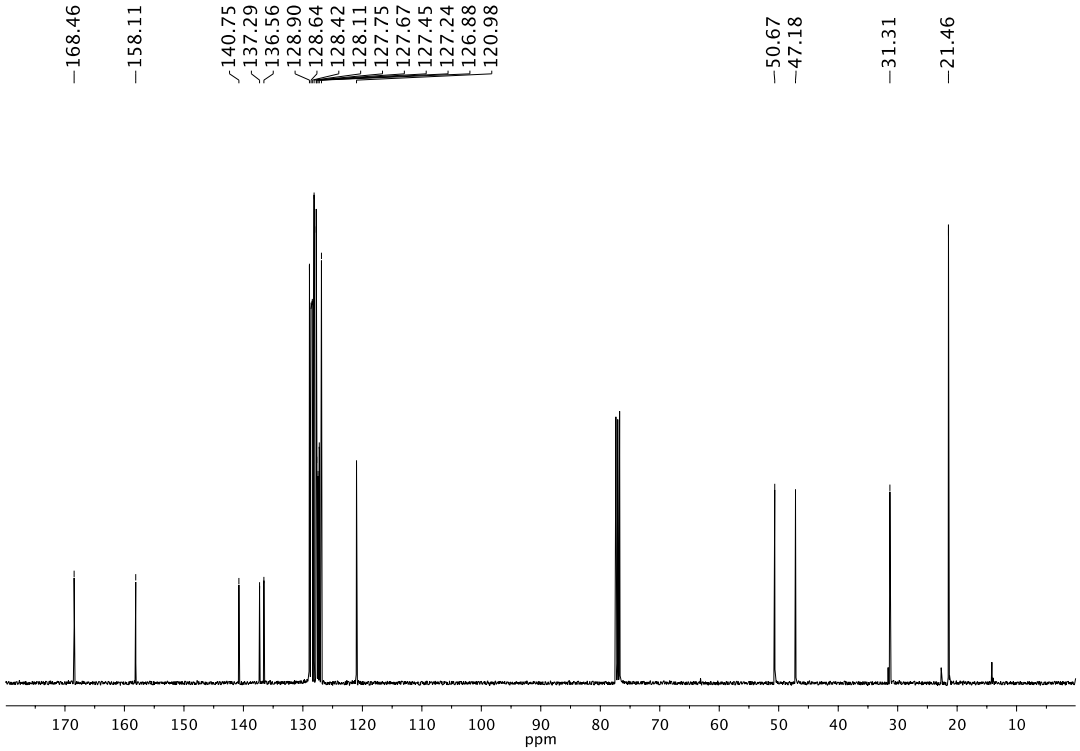


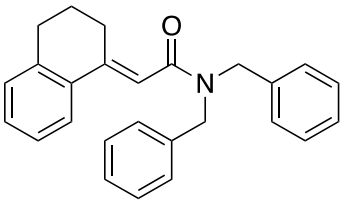


^{1}H-NMR of **S15** in $CDCl_3$

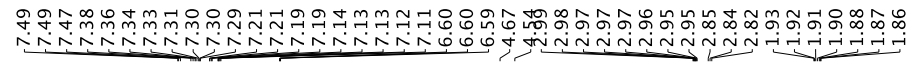


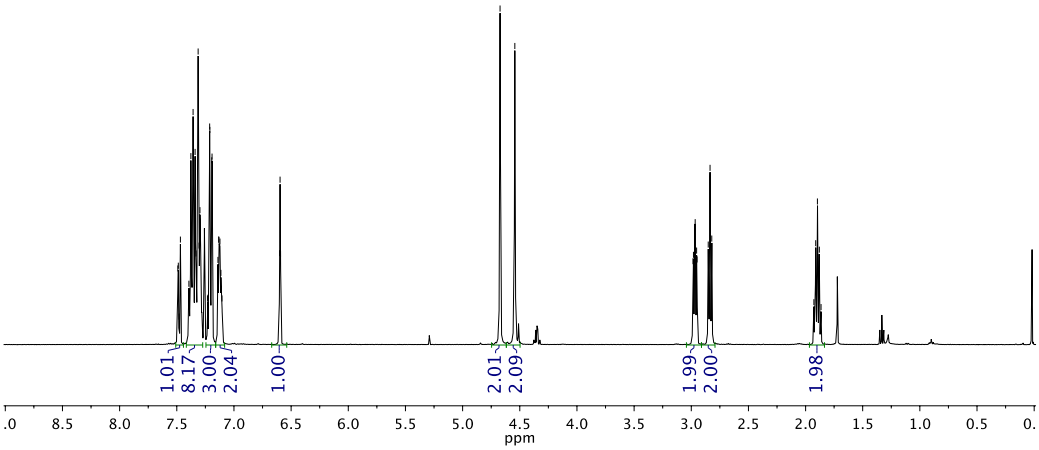
^{13}C-NMR of **S15** in $CDCl_3$



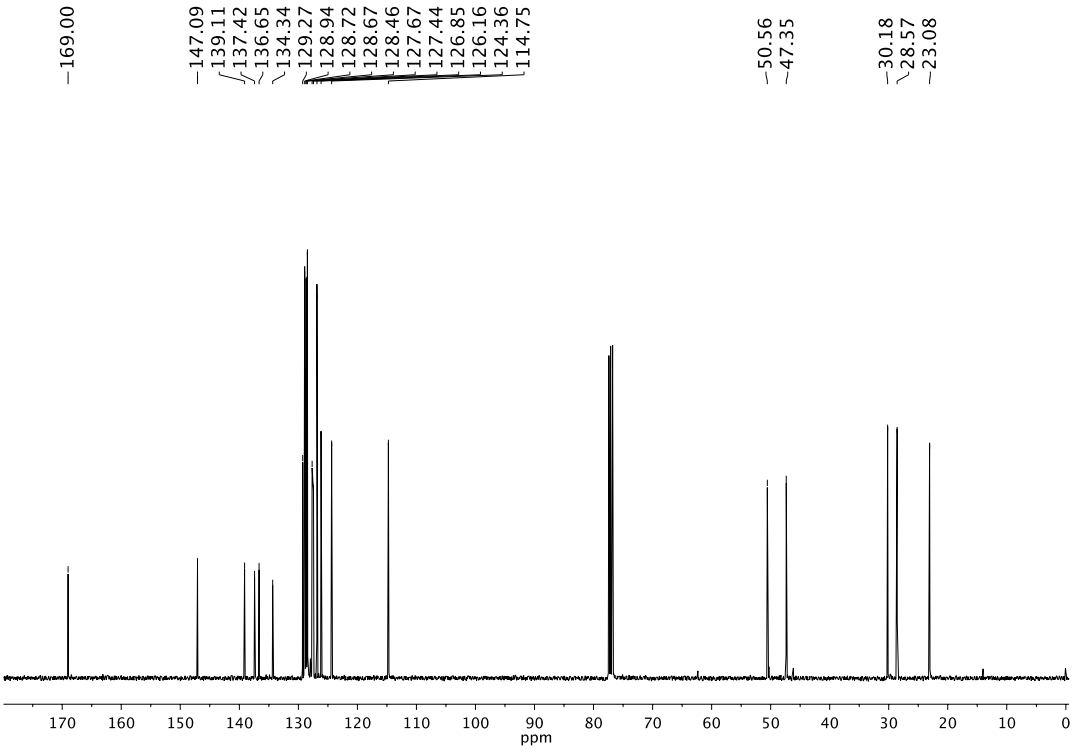


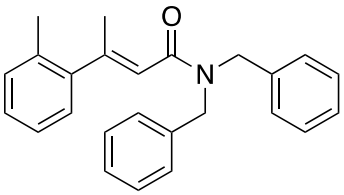
^{1}H-NMR of **S16** in $CDCl_3$



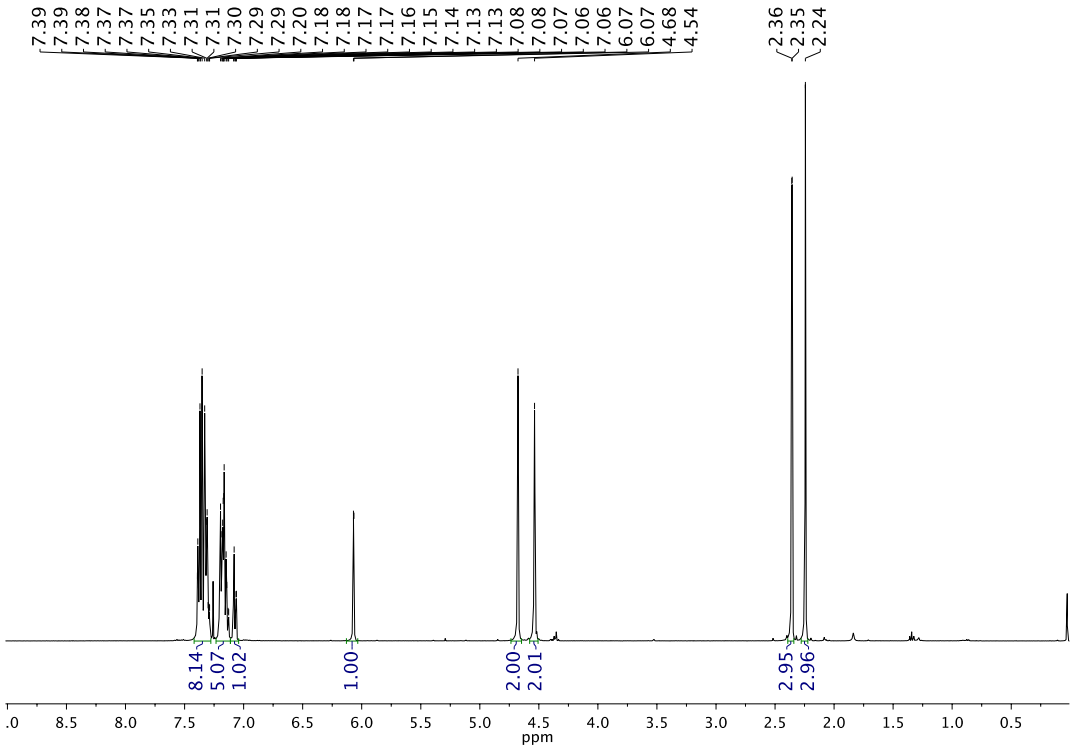


^{13}C-NMR of **S16** in $CDCl_3$

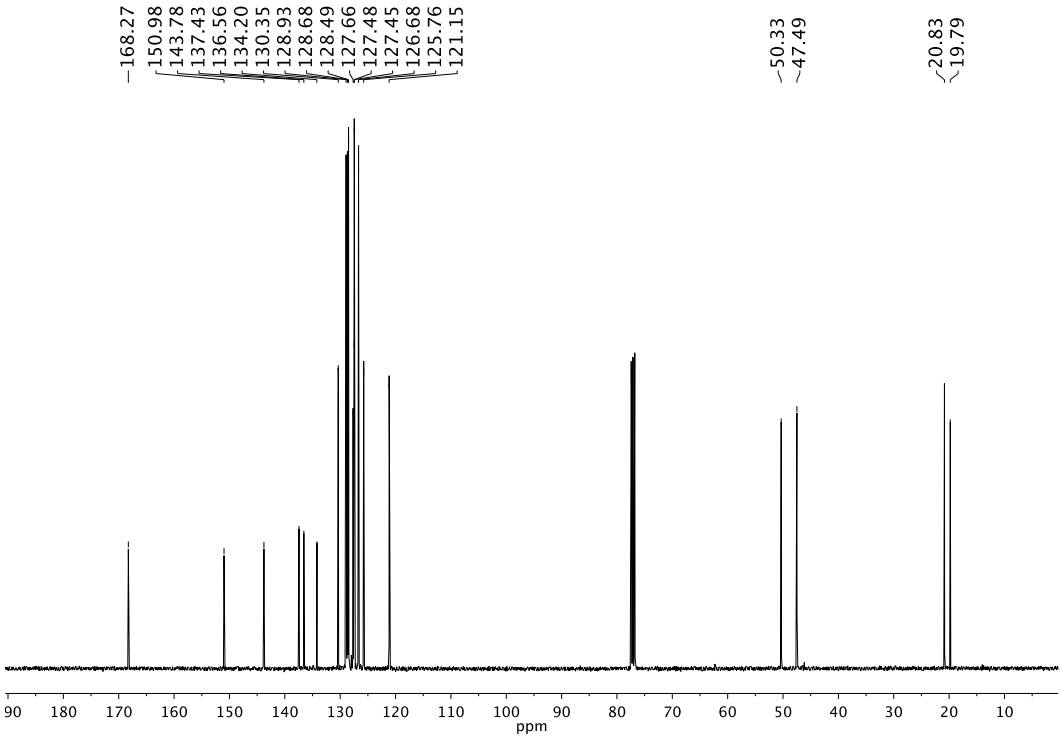


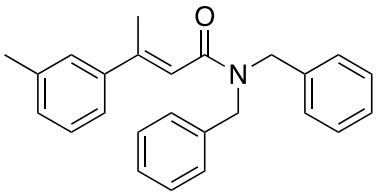


^{1}H-NMR of **S17** in $CDCl_3$

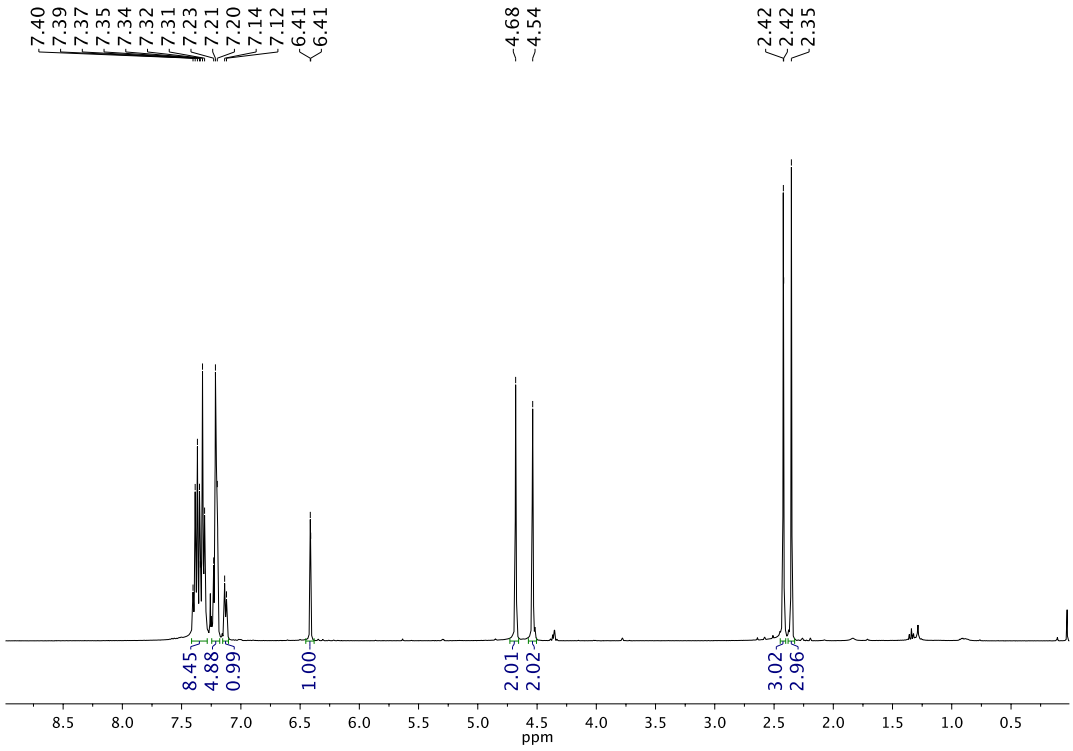


^{13}C-NMR of **S17** in $CDCl_3$

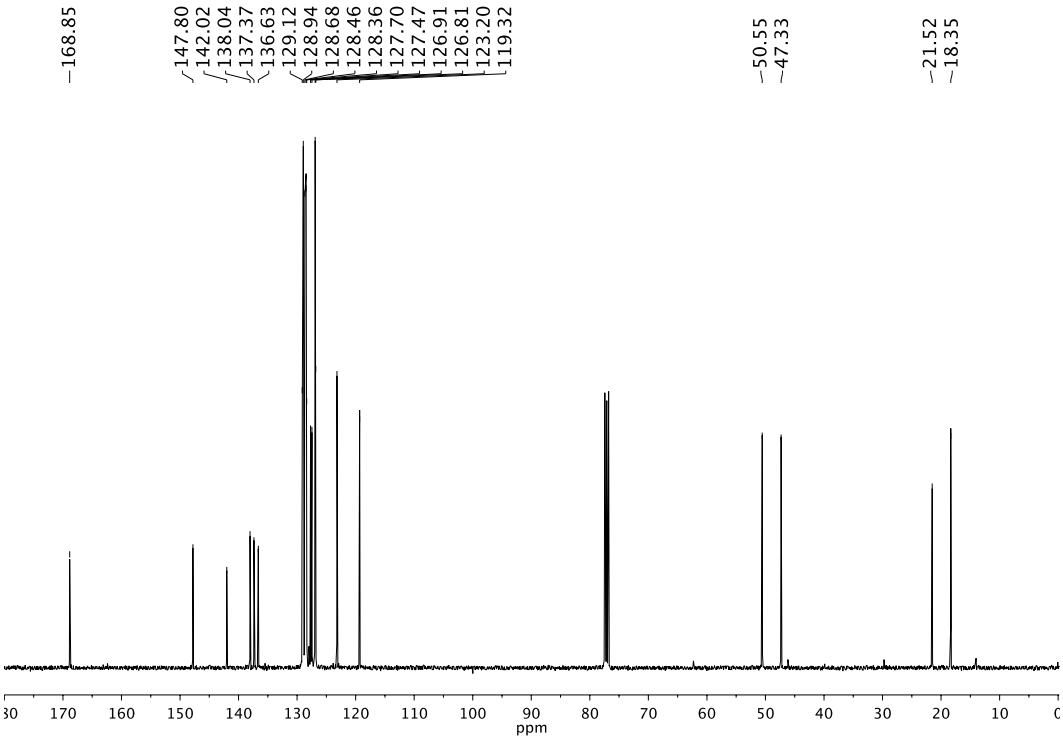


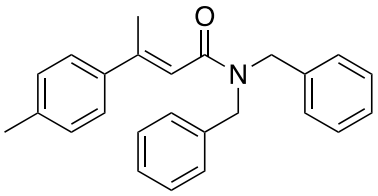


^{1}H-NMR of **S18** in $CDCl_3$

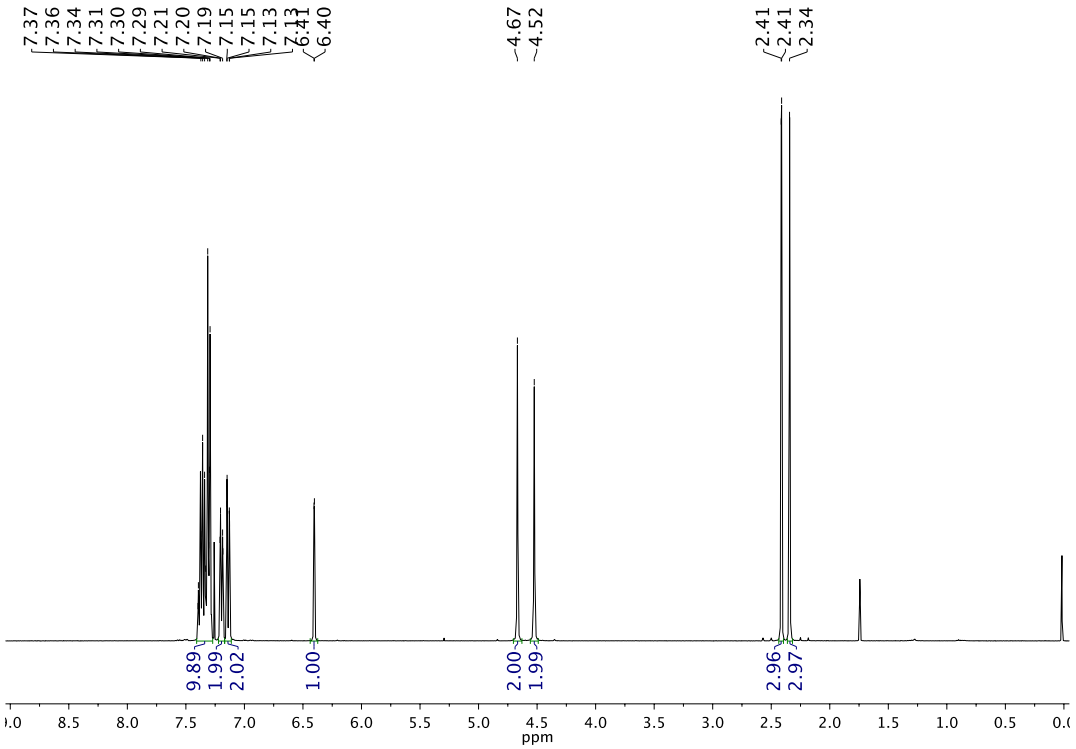


^{13}C-NMR of **S18** in $CDCl_3$

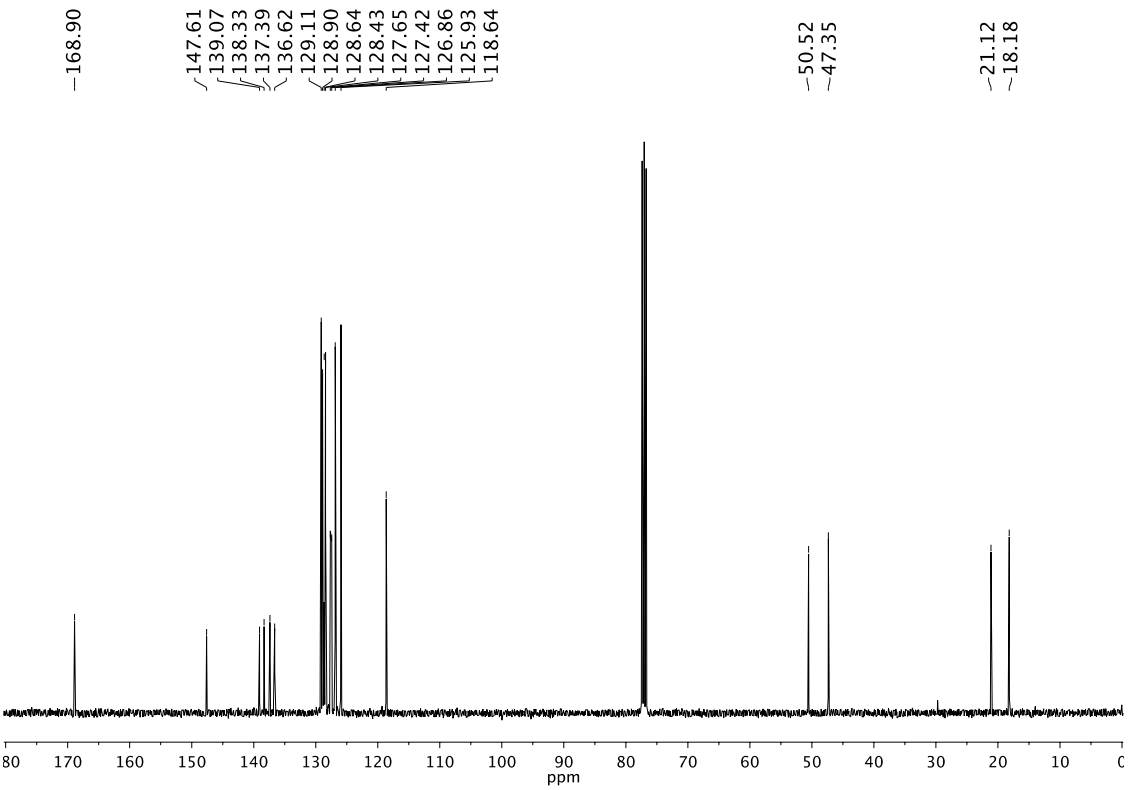


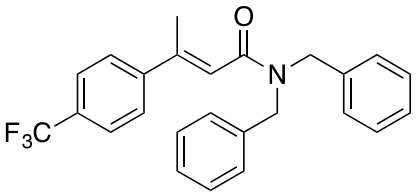


^{1}H-NMR of **S19** in $CDCl_3$

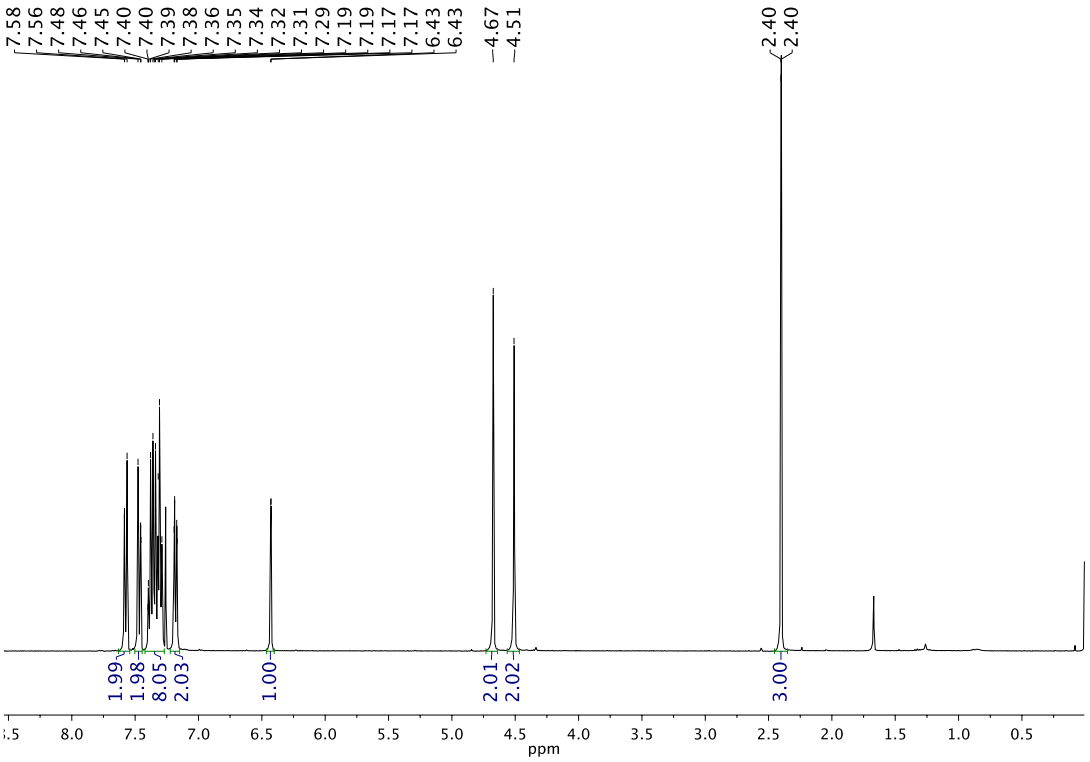


^{13}C-NMR of **S19** in $CDCl_3$

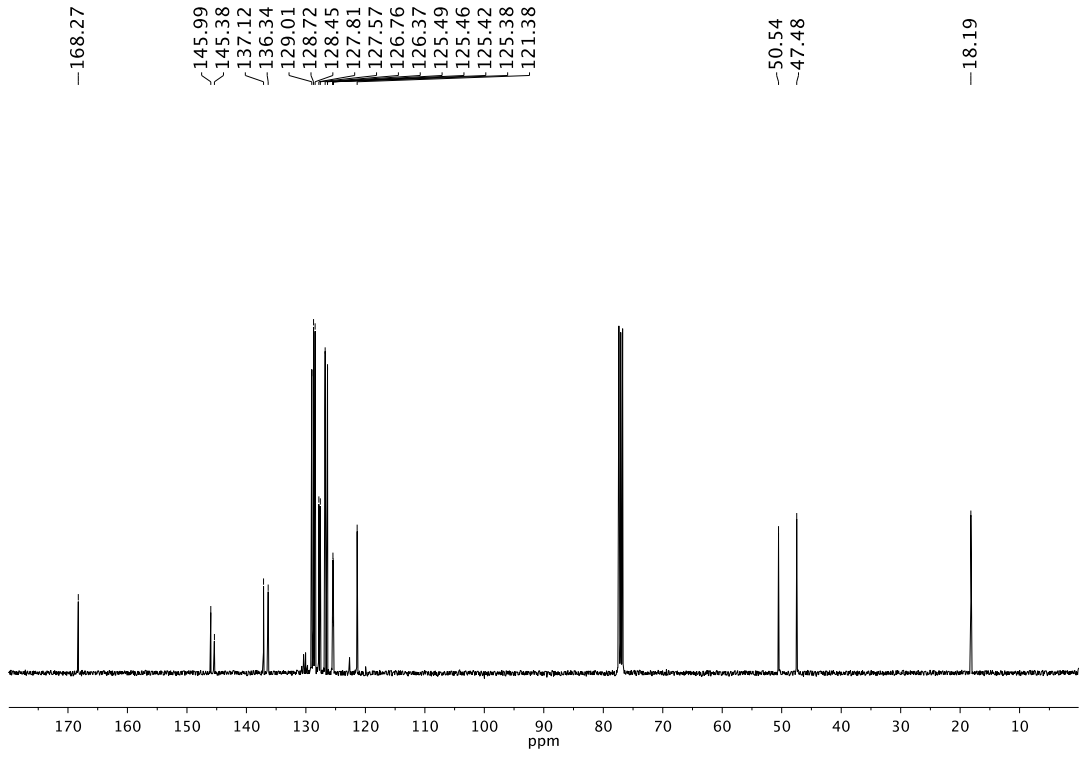


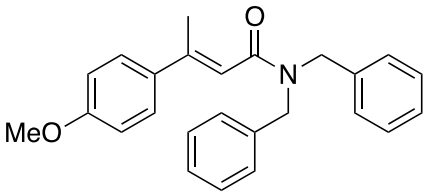


^{1}H-NMR of **S20** in $CDCl_3$

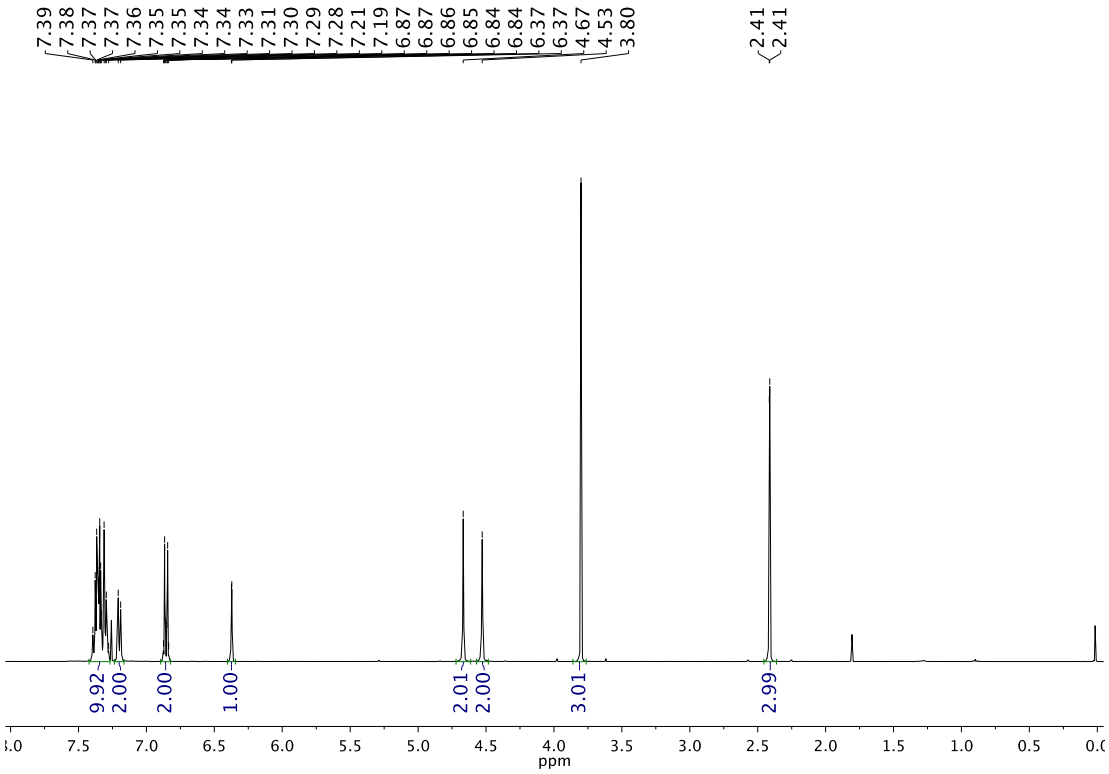


^{13}C-NMR of **S20** in $CDCl_3$

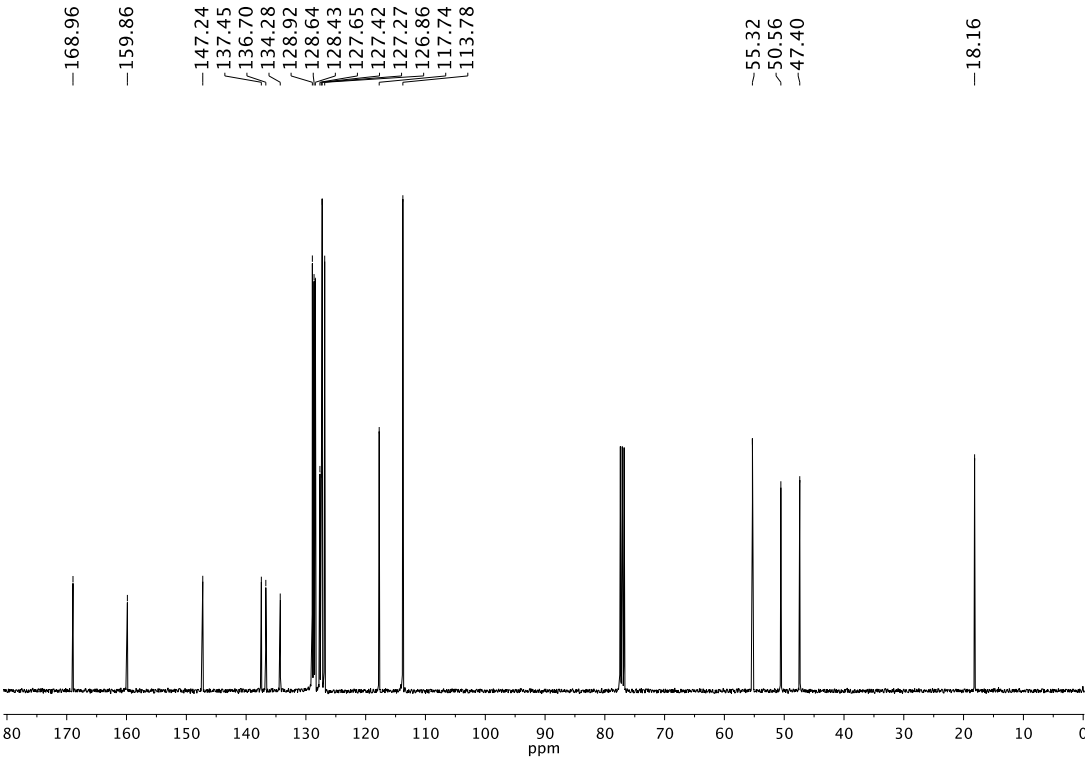


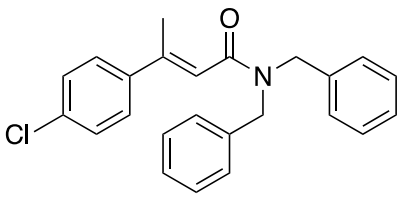


^{1}H-NMR of **S21** in $CDCl_3$

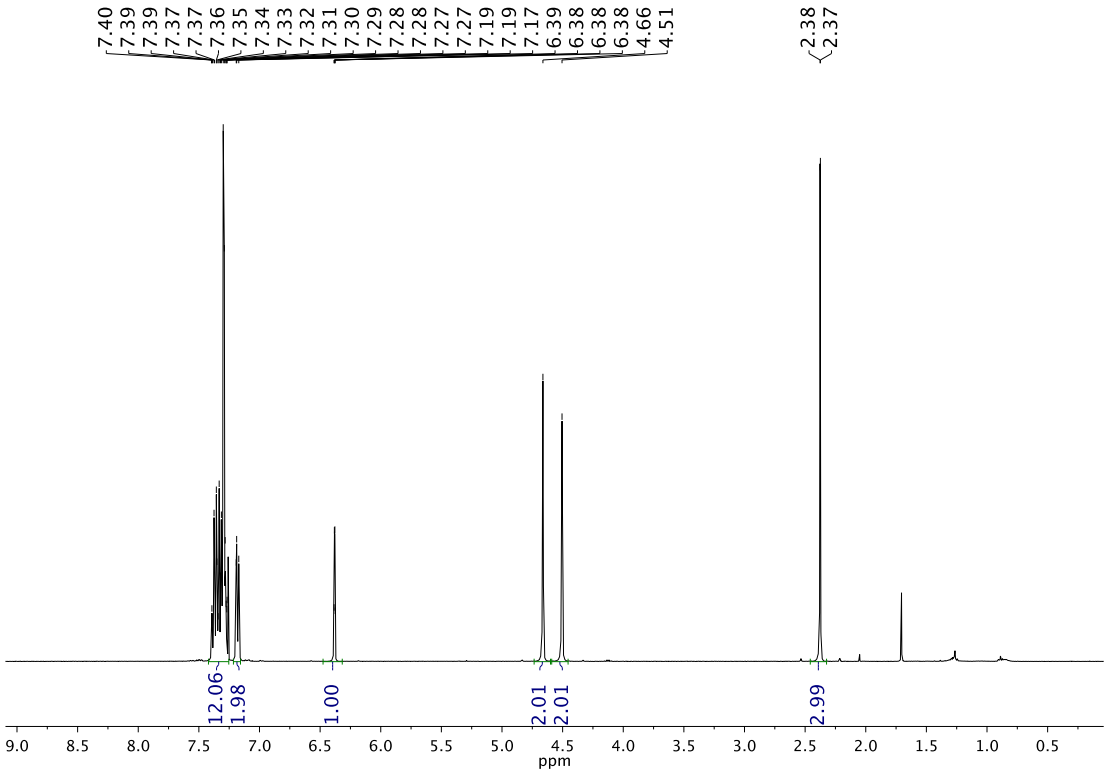


^{13}C-NMR of **S21** in $CDCl_3$

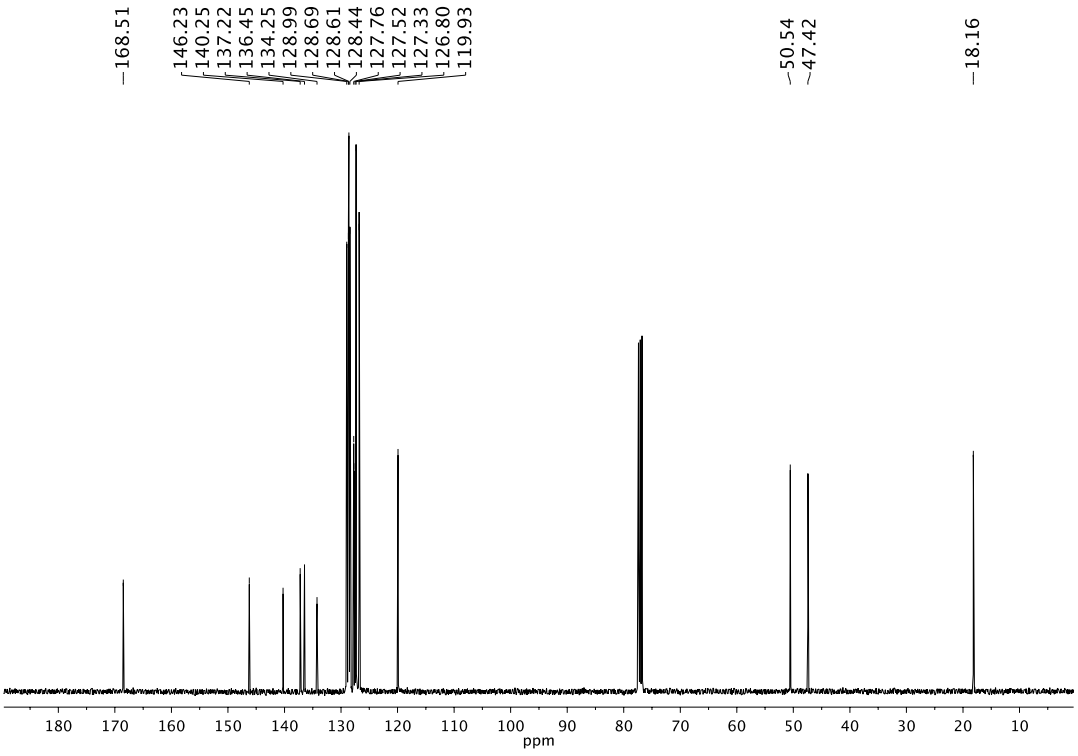


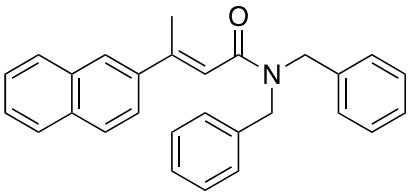


^{1}H-NMR of **S22** in $CDCl_3$



^{13}C-NMR of **S22** in $CDCl_3$





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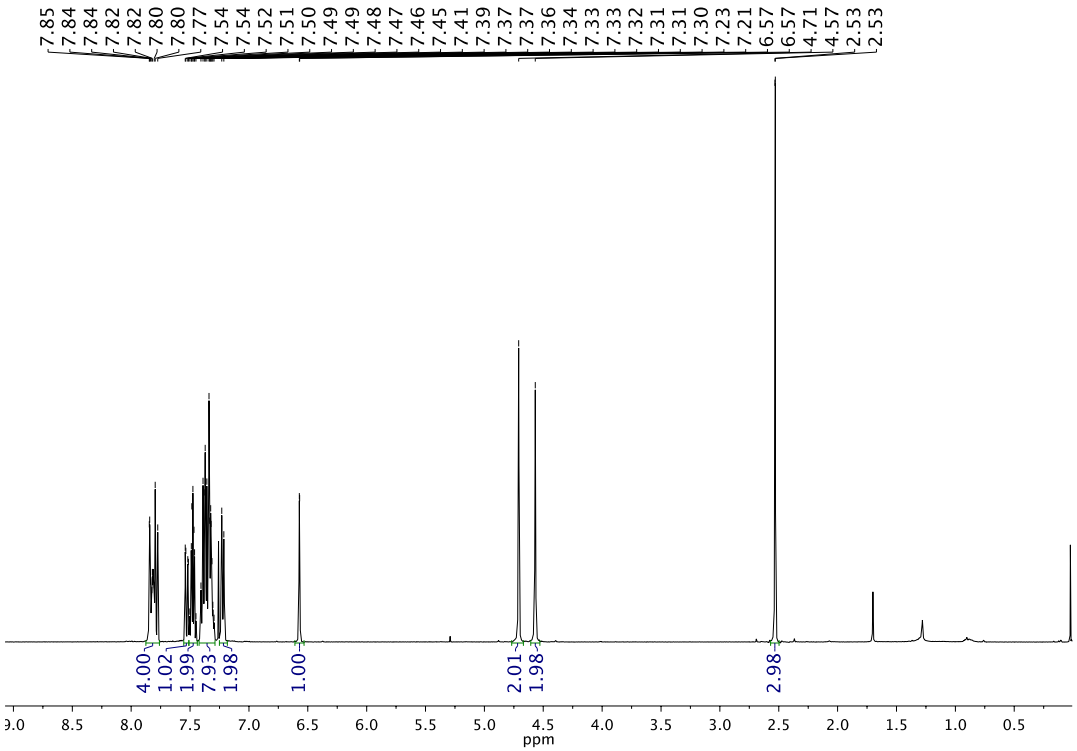

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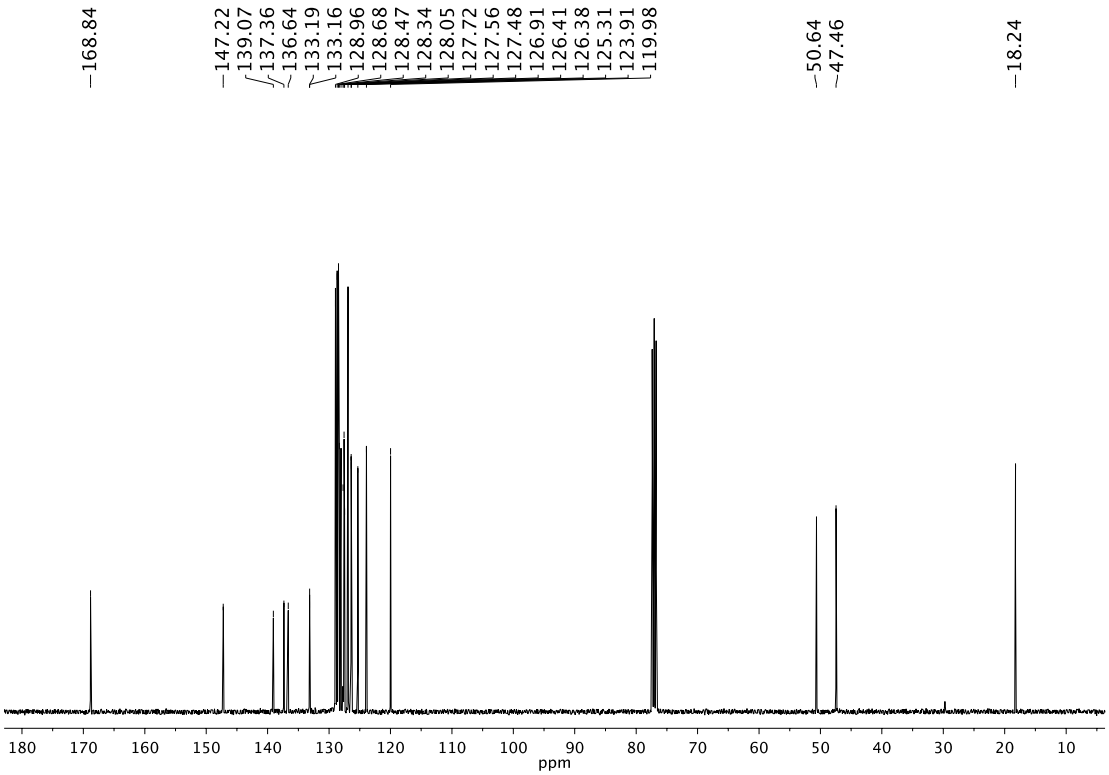
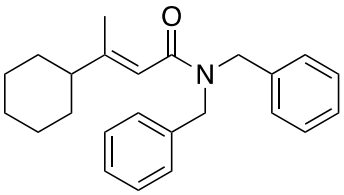
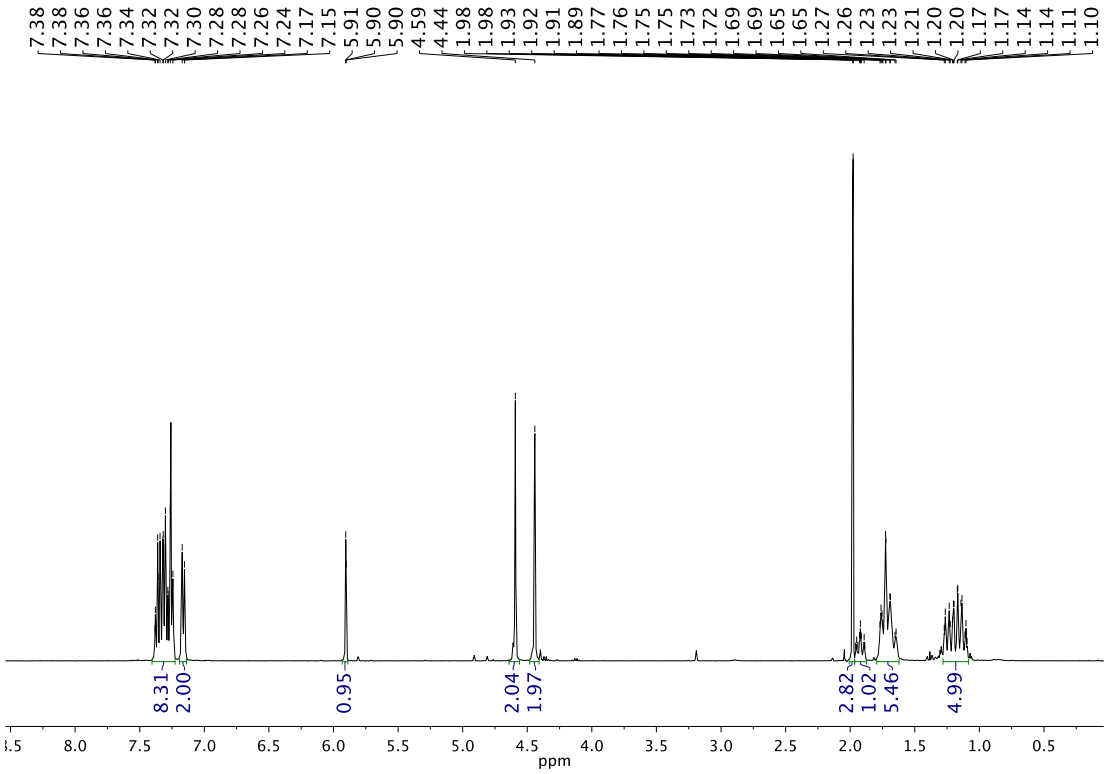
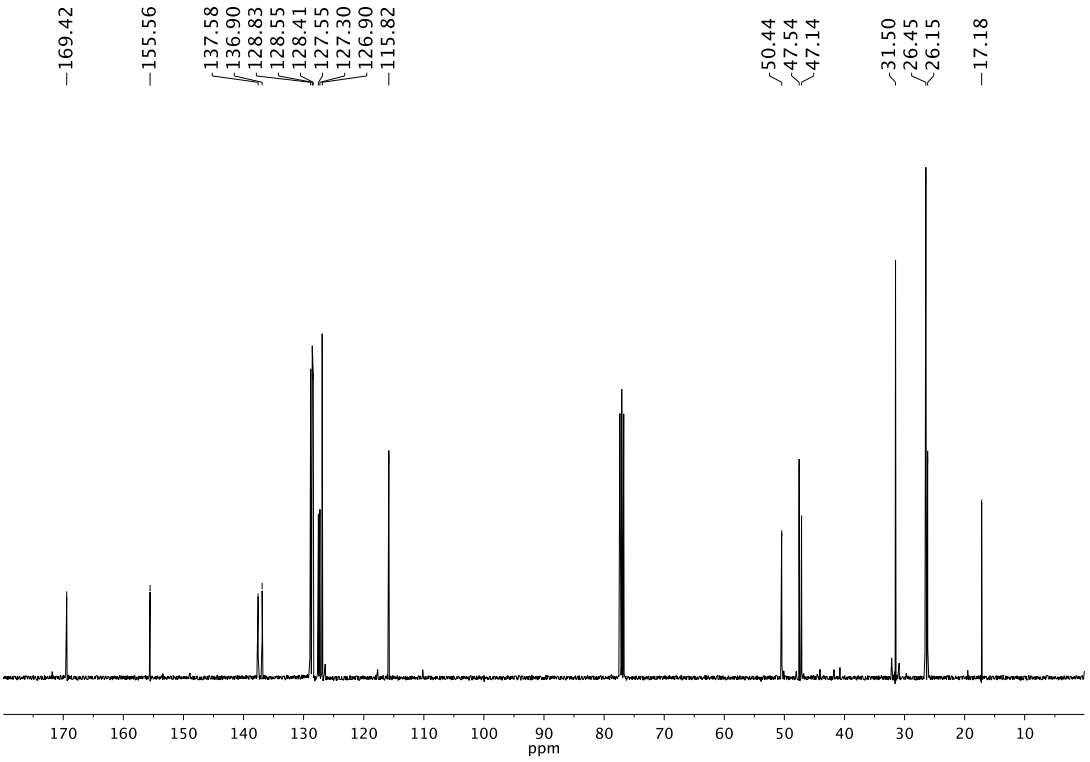


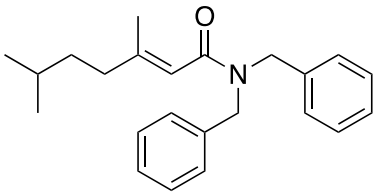


^{1}H-NMR of **S24** in $CDCl_3$

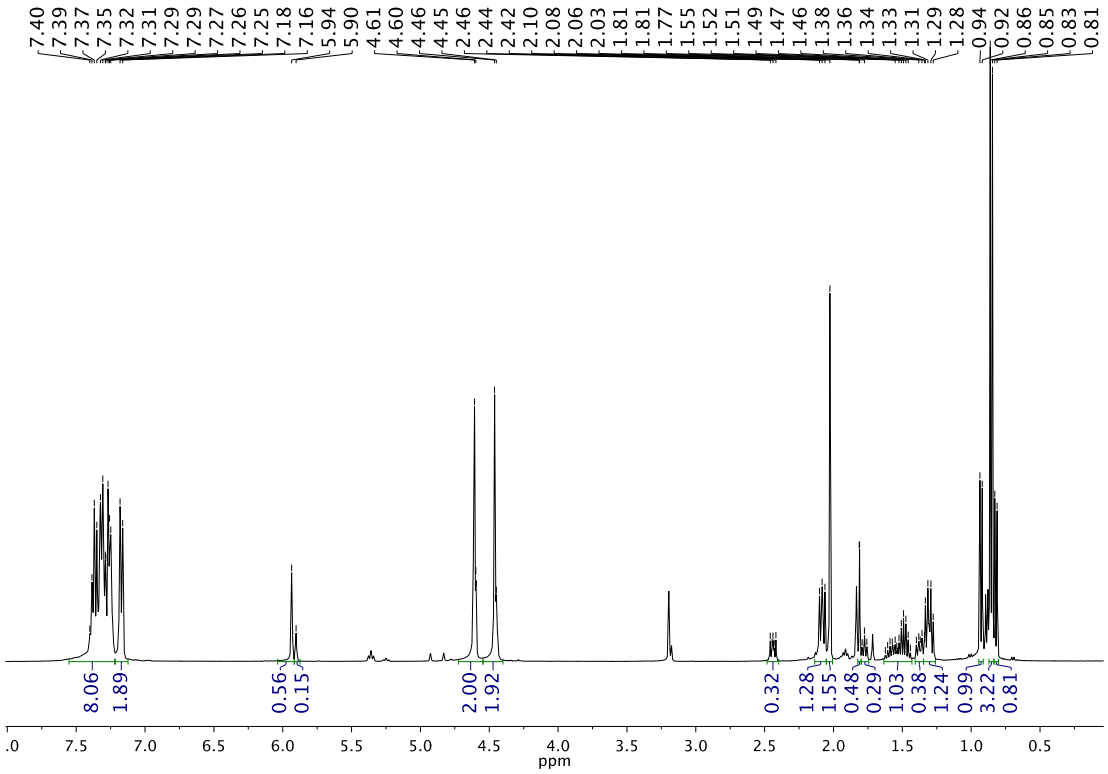


^{13}C-NMR of **S24** in $CDCl_3$

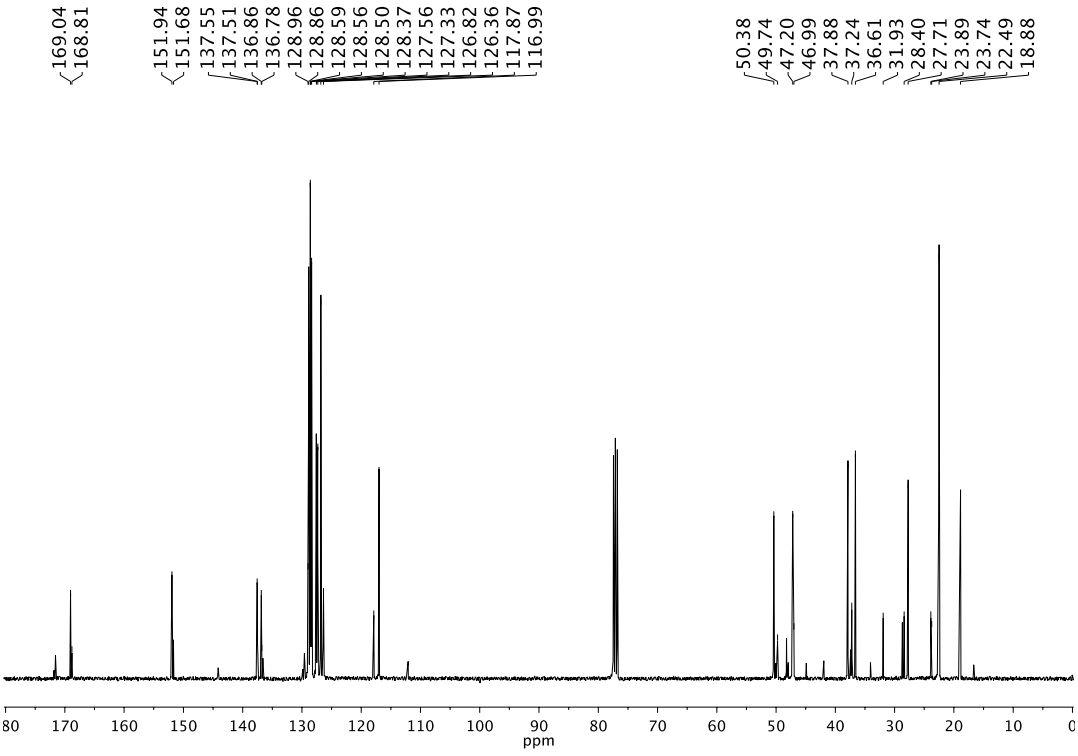


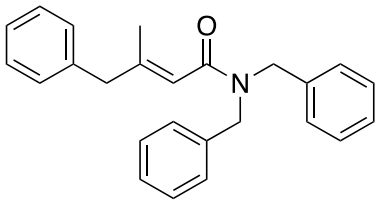


^{1}H-NMR of **S25** in $CDCl_3$

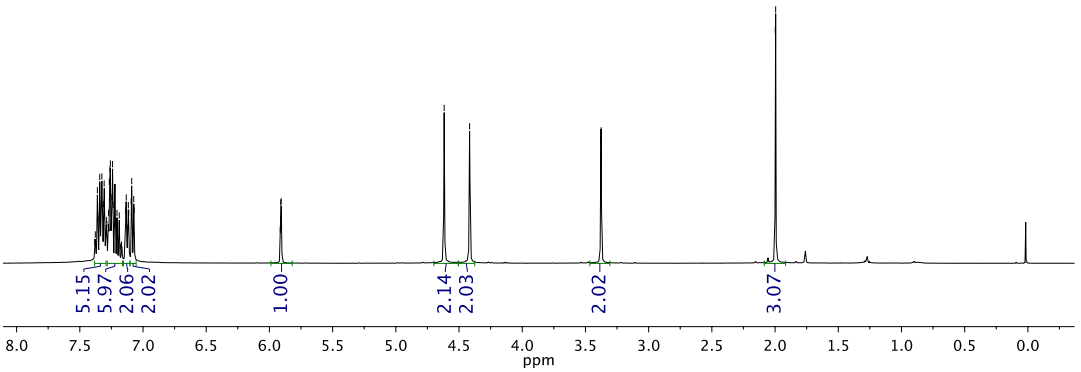


^{13}C-NMR of **S25** in $CDCl_3$

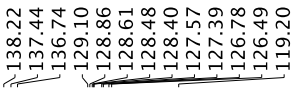


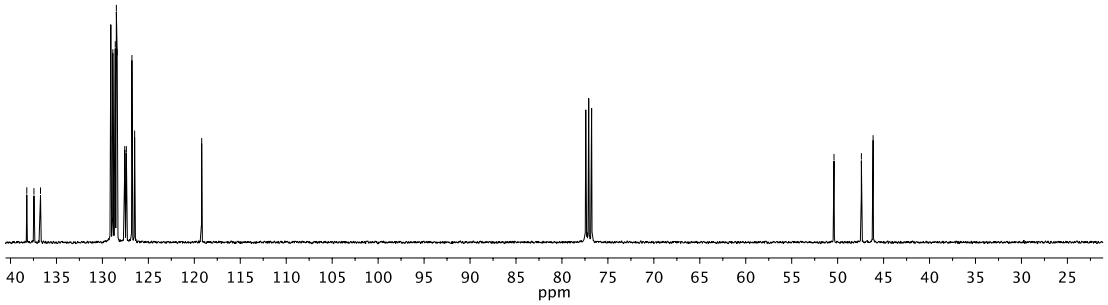


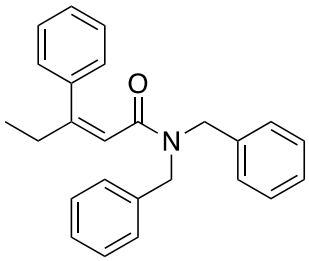
^{1}H-NMR of **S26** in $CDCl_3$



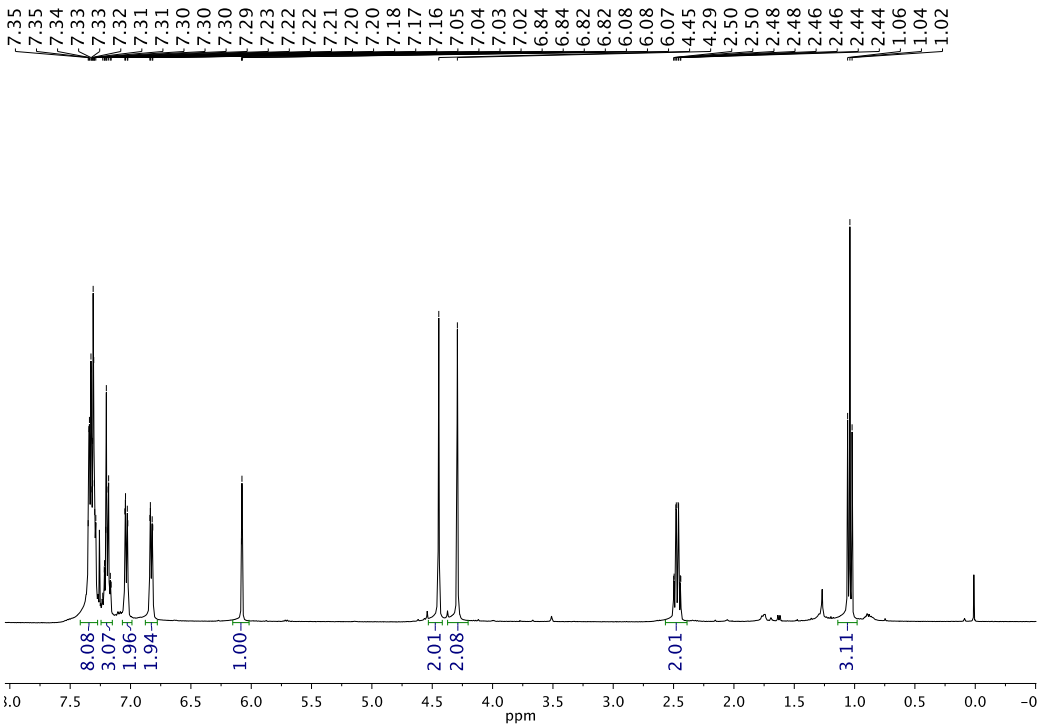
^{13}C-NMR of **S26** in $CDCl_3$



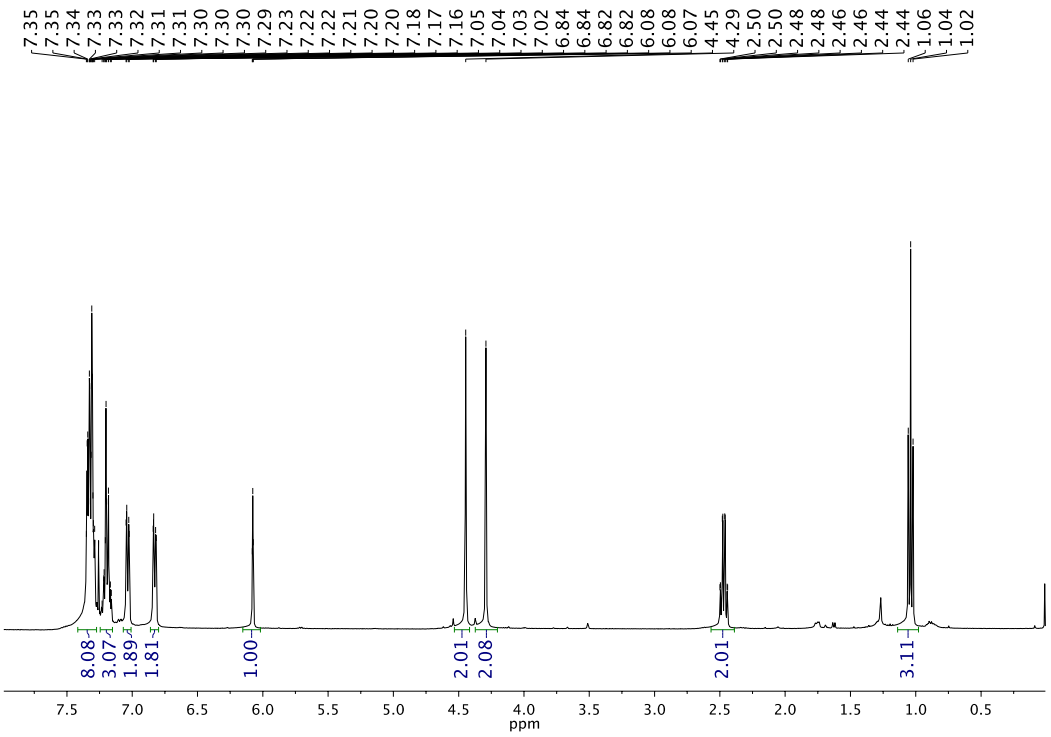




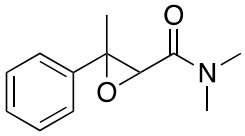
^{1}H-NMR of **S27** in $CDCl_3$



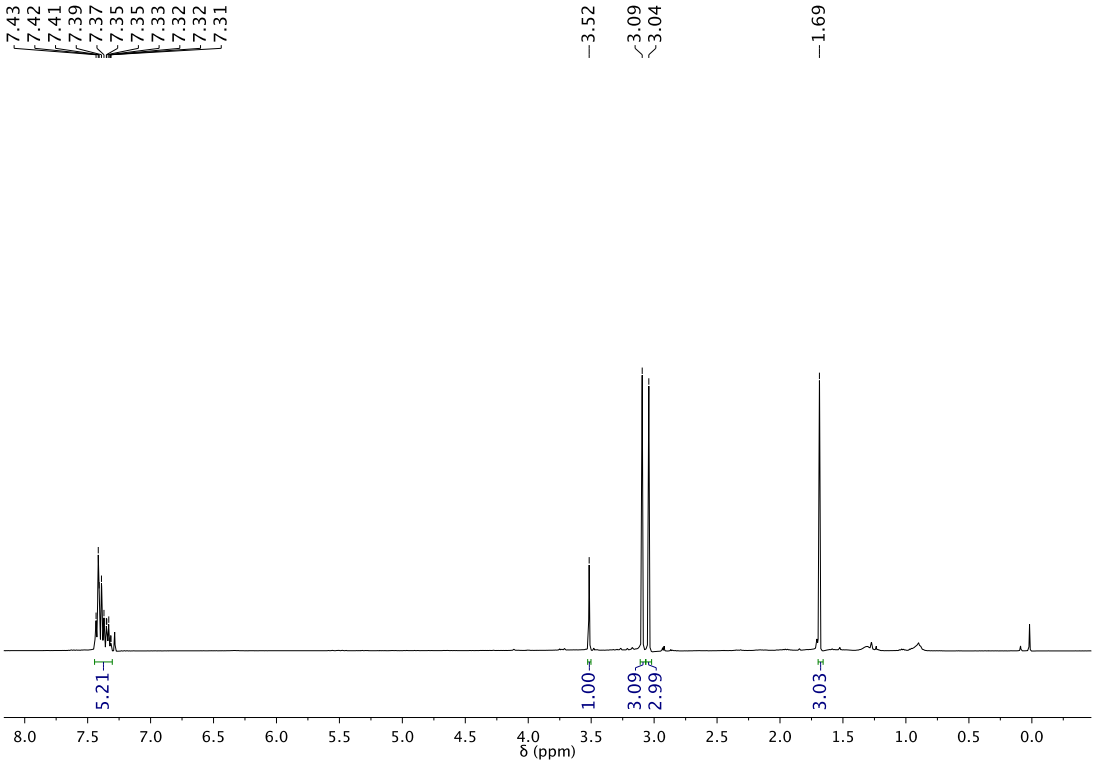
^{13}C-NMR of **S27** in $CDCl_3$



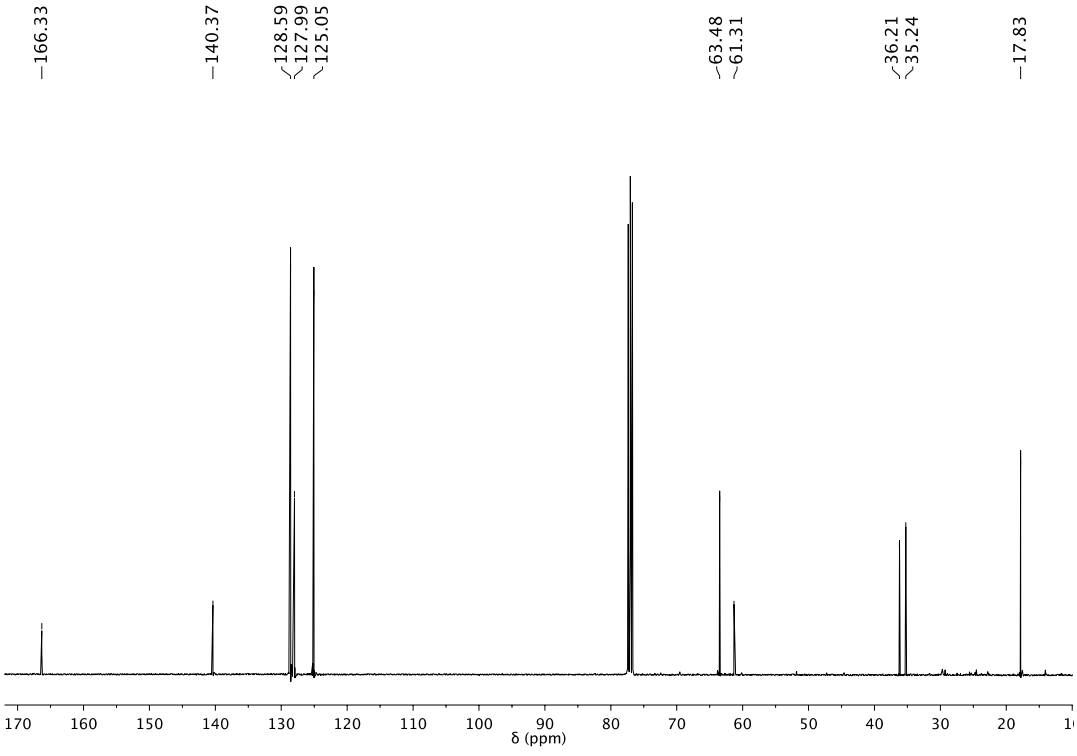
6.2) ^{1}H and ^{13}C-NMR spectra of isolated products

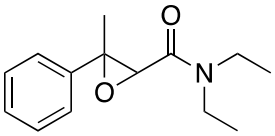


^{1}H-NMR of **E3** in $CDCl_3$

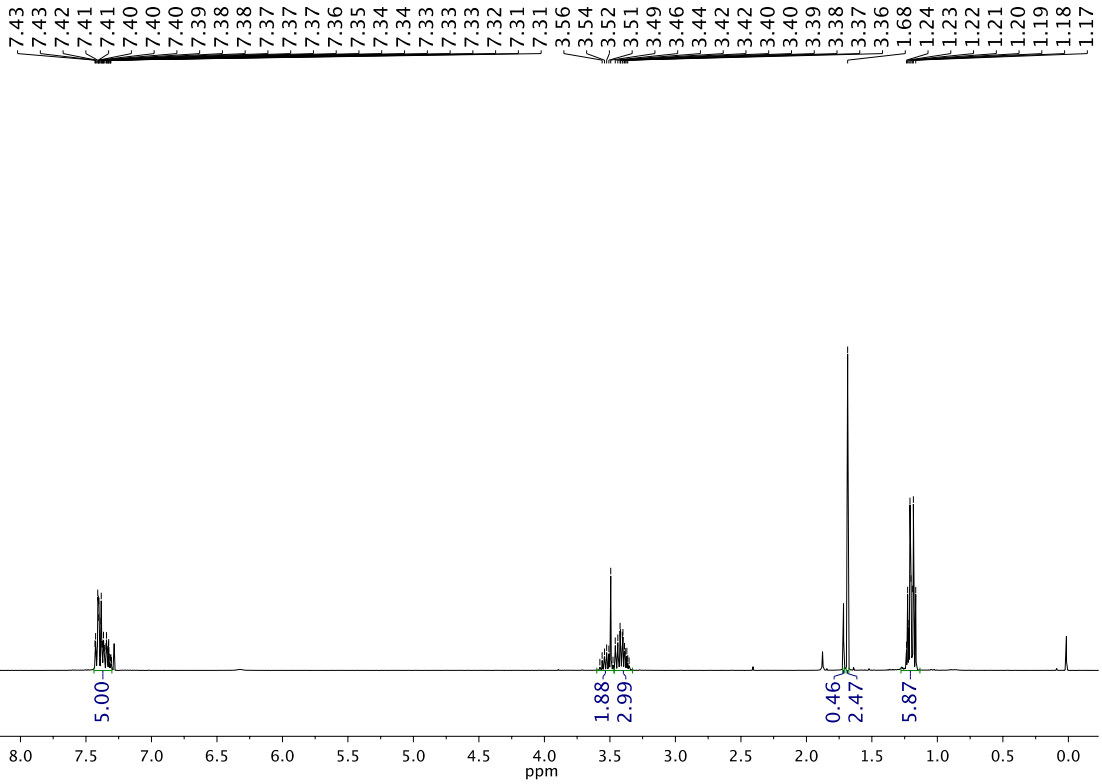


^{13}C-NMR of **E3** in $CDCl_3$

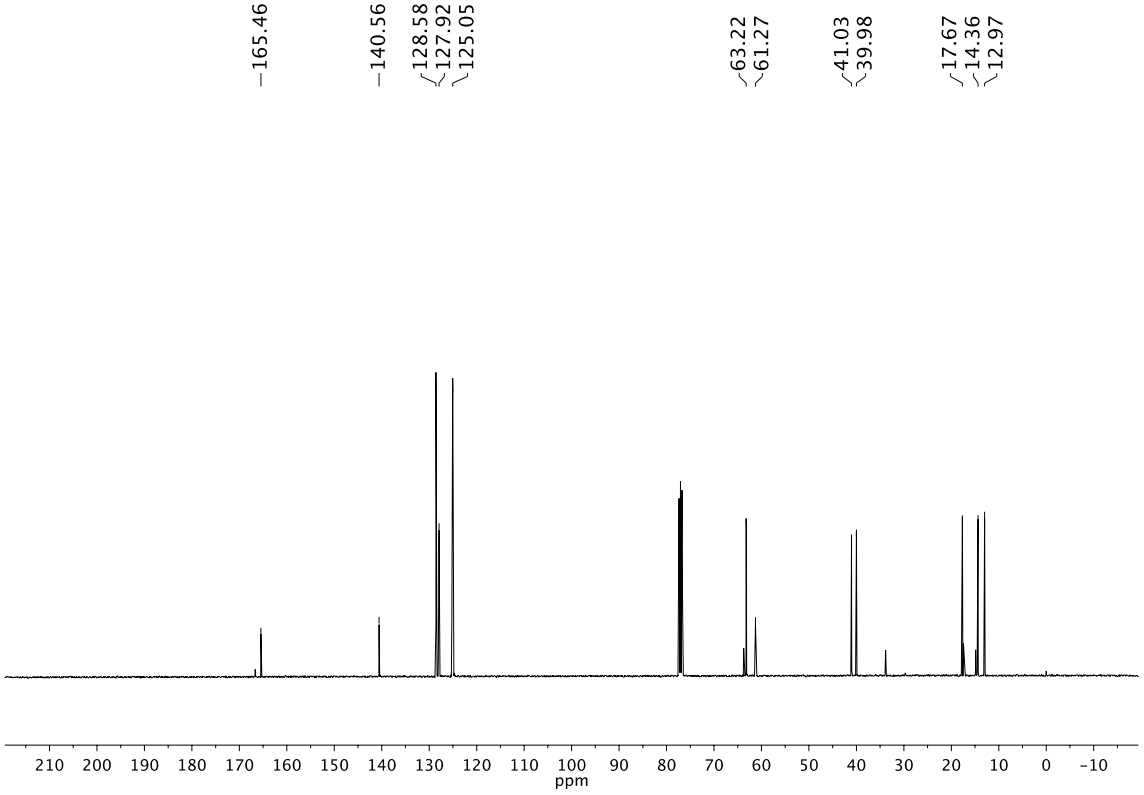


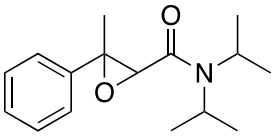


^{1}H-NMR of **E4** in $CDCl_3$

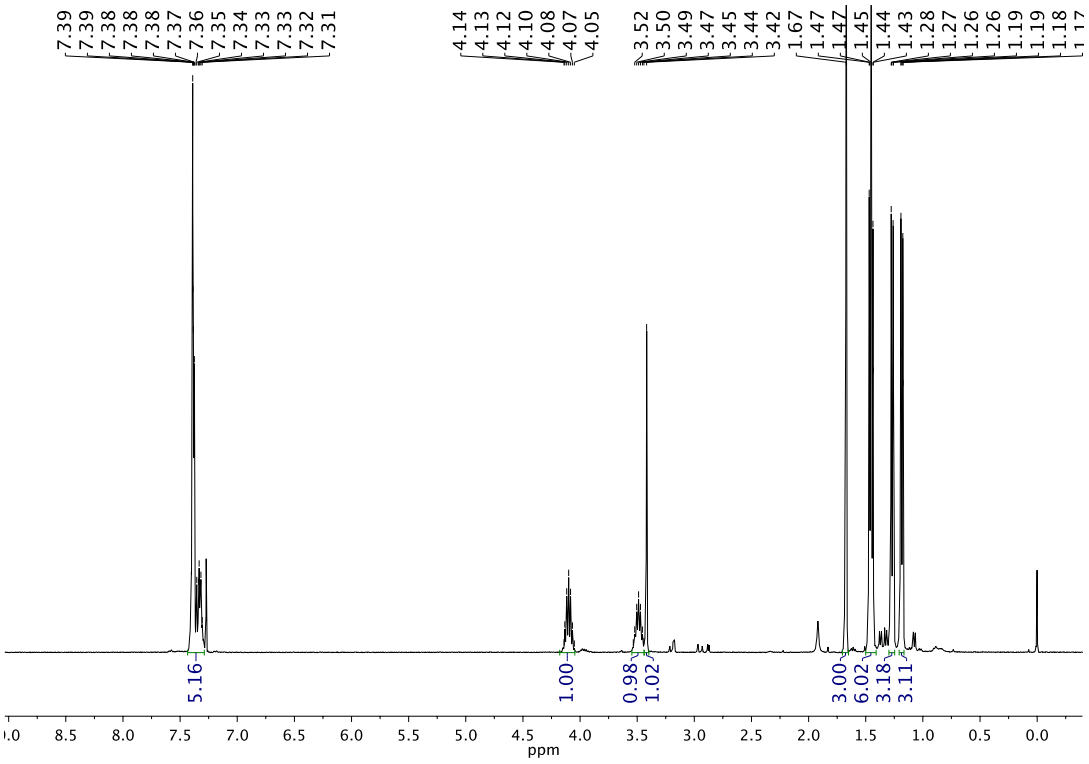


^{13}C-NMR of **E4** in $CDCl_3$

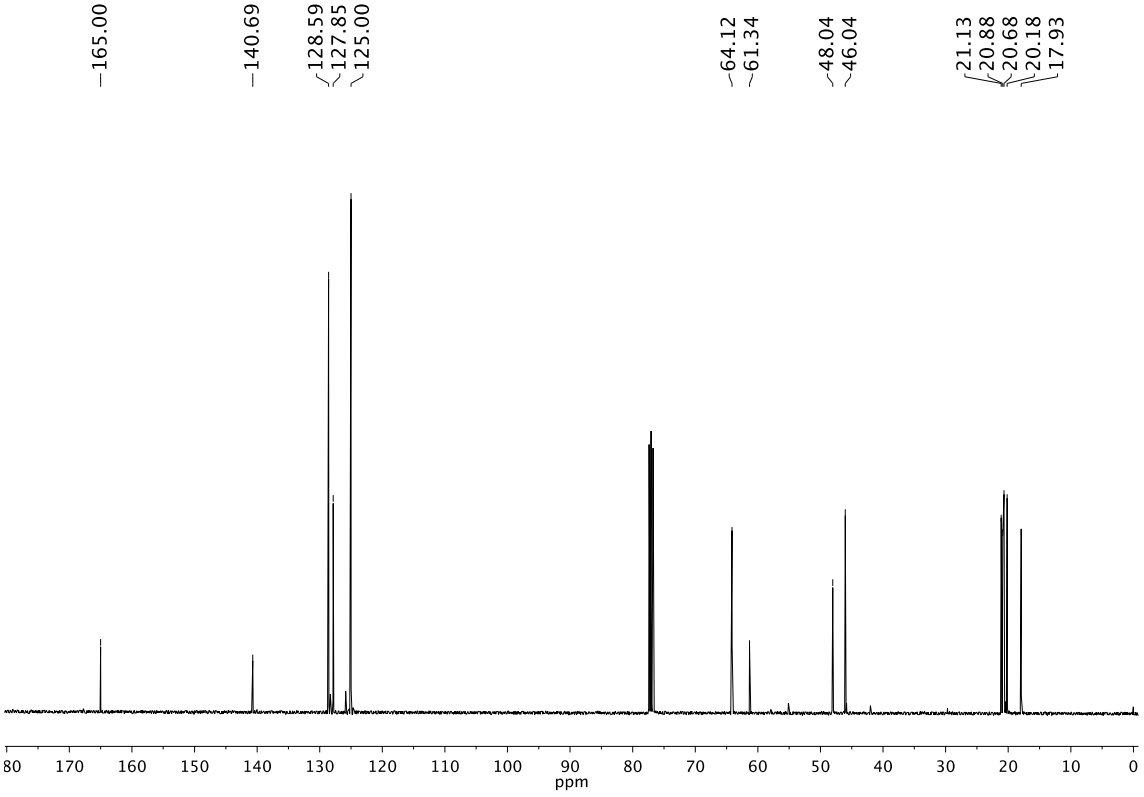


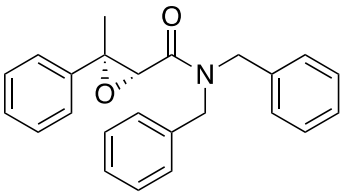


^{1}H-NMR of **E5** in $CDCl_3$

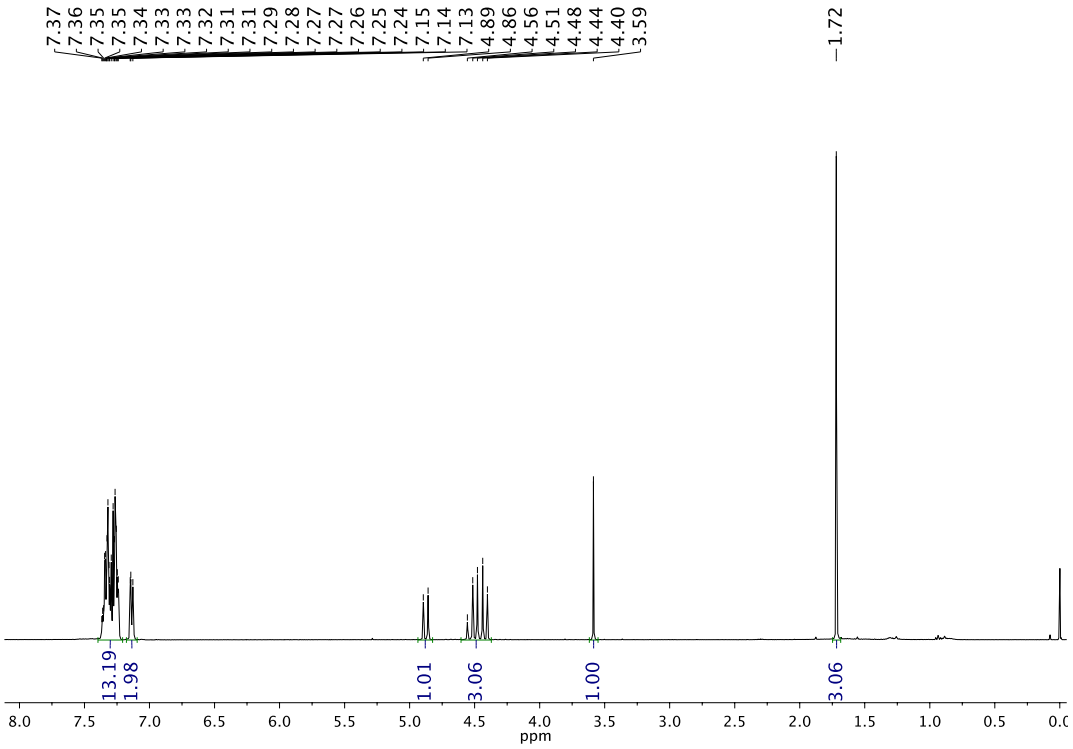


^{13}C-NMR of **E5** in $CDCl_3$

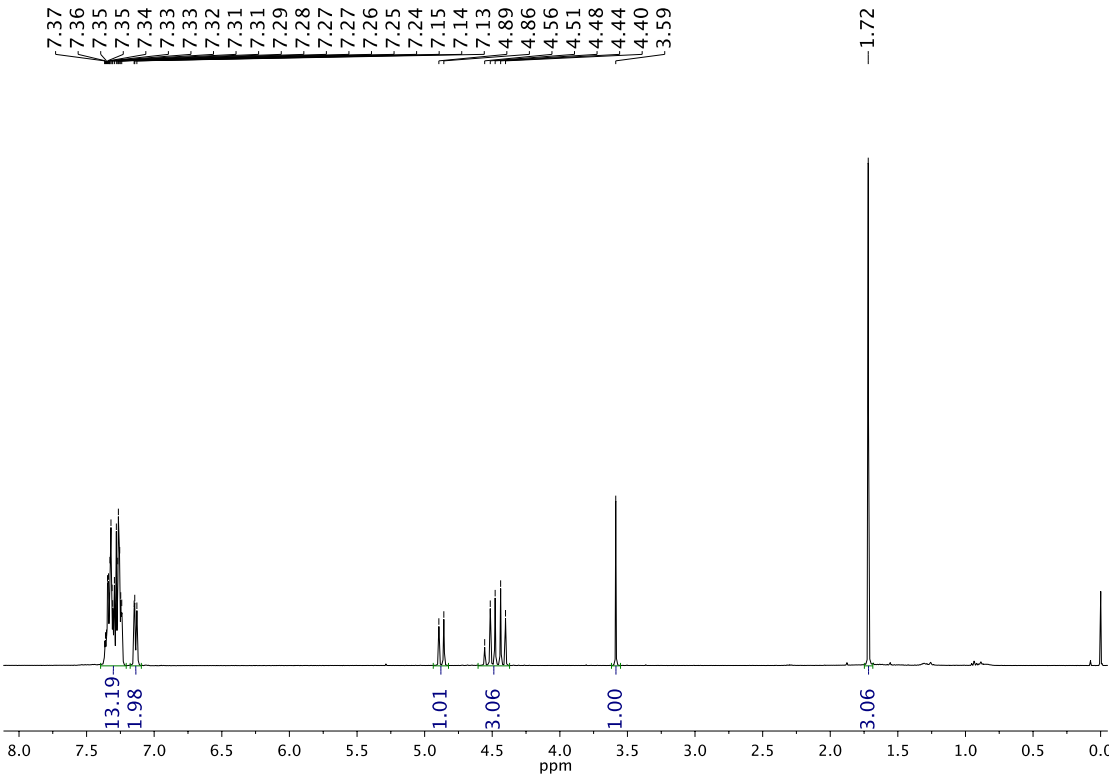


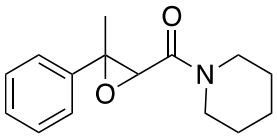


^{1}H-NMR of **E6** in $CDCl_3$

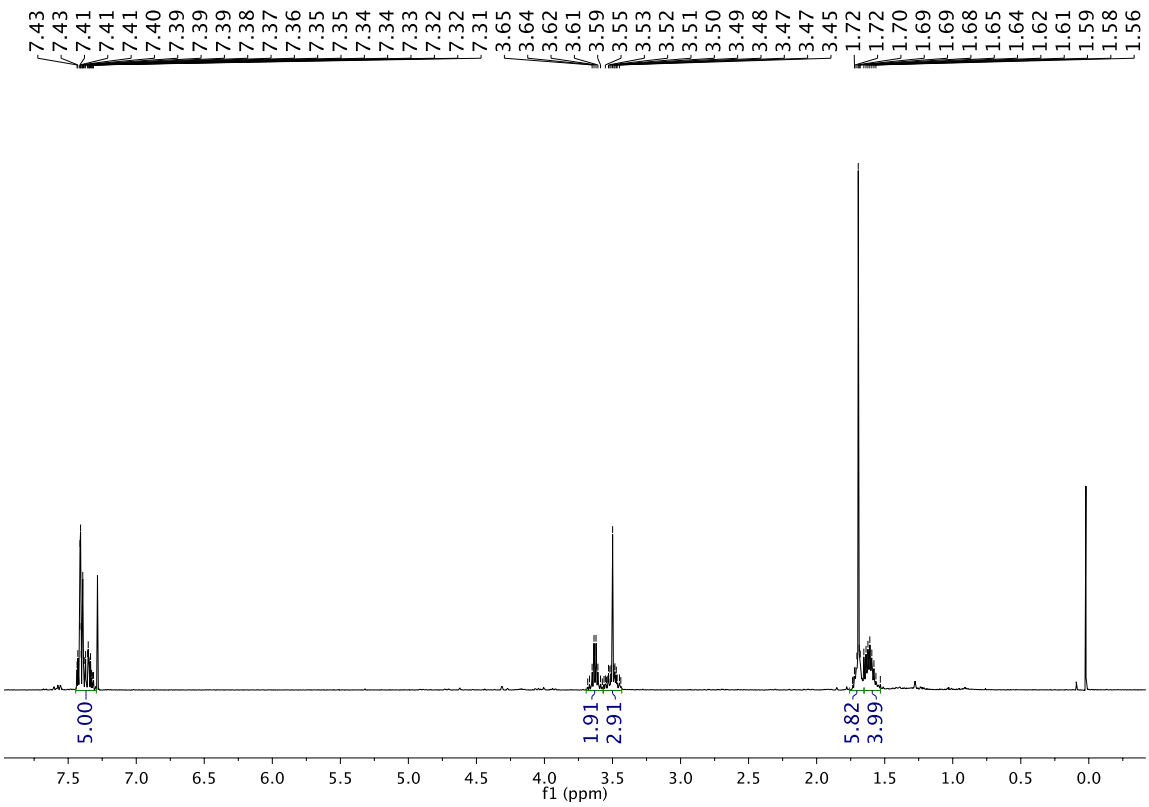


^{13}C-NMR of **E6** in $CDCl_3$

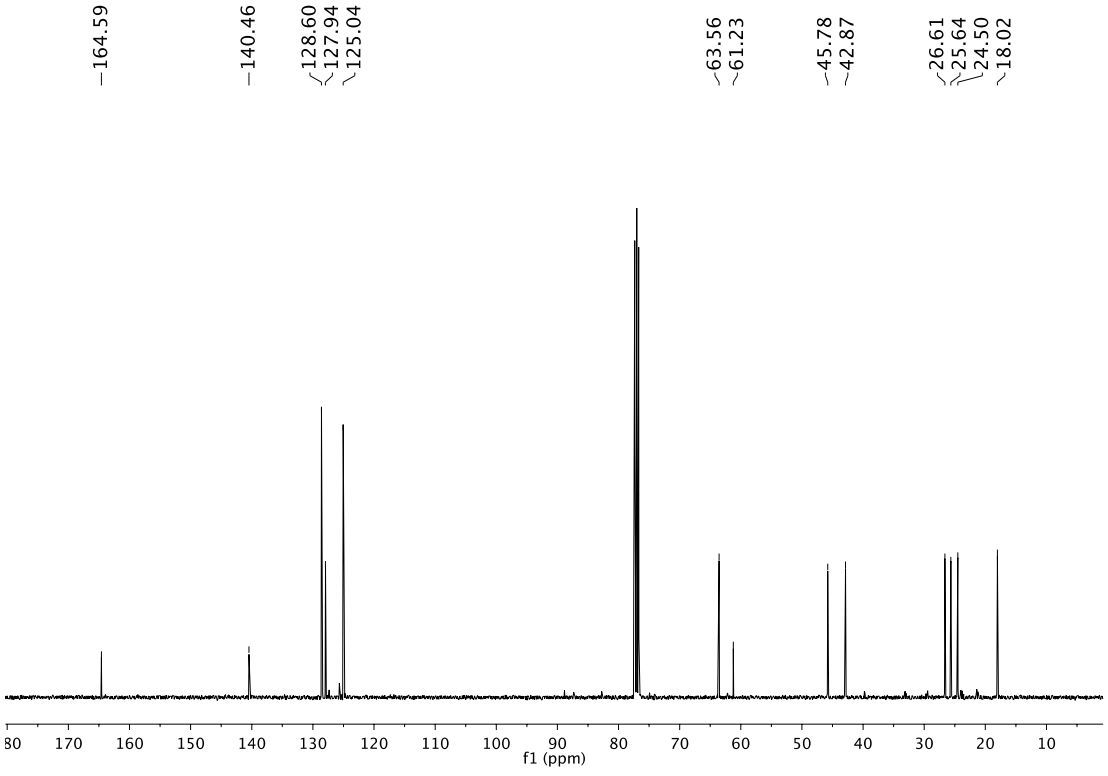


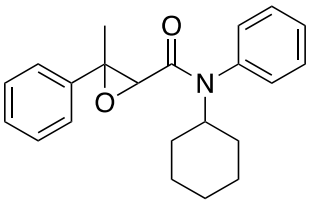


^{1}H-NMR of **E7** in $CDCl_3$

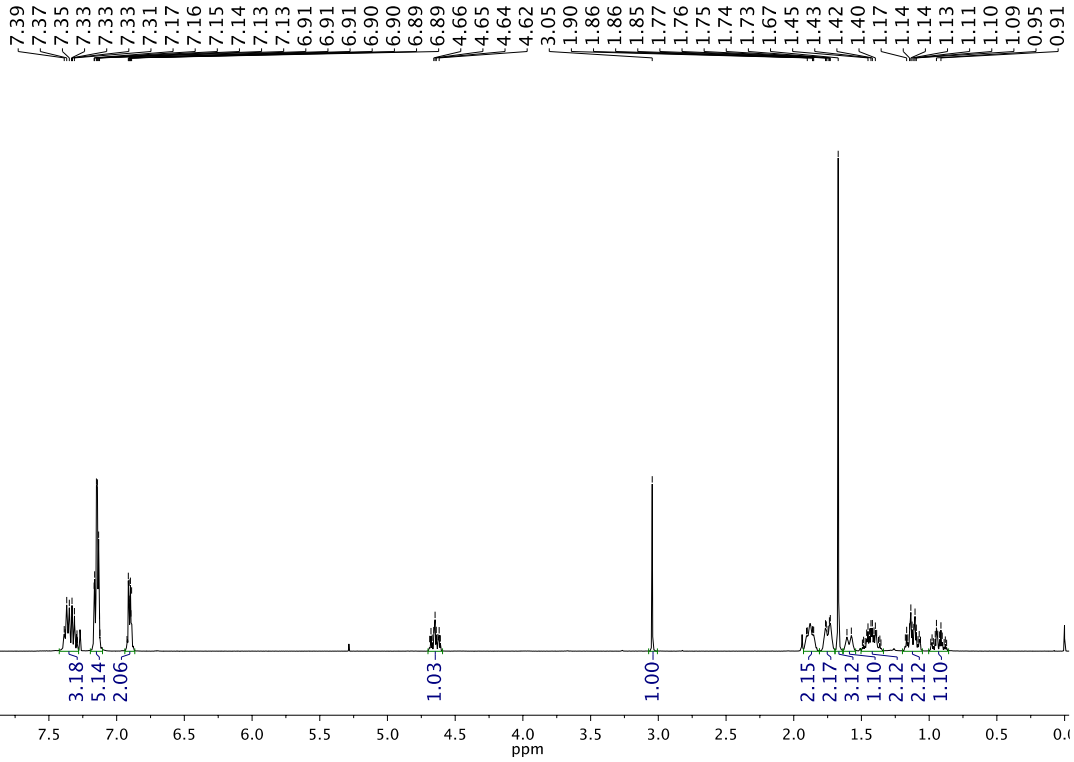


^{13}C-NMR of **E7** in $CDCl_3$

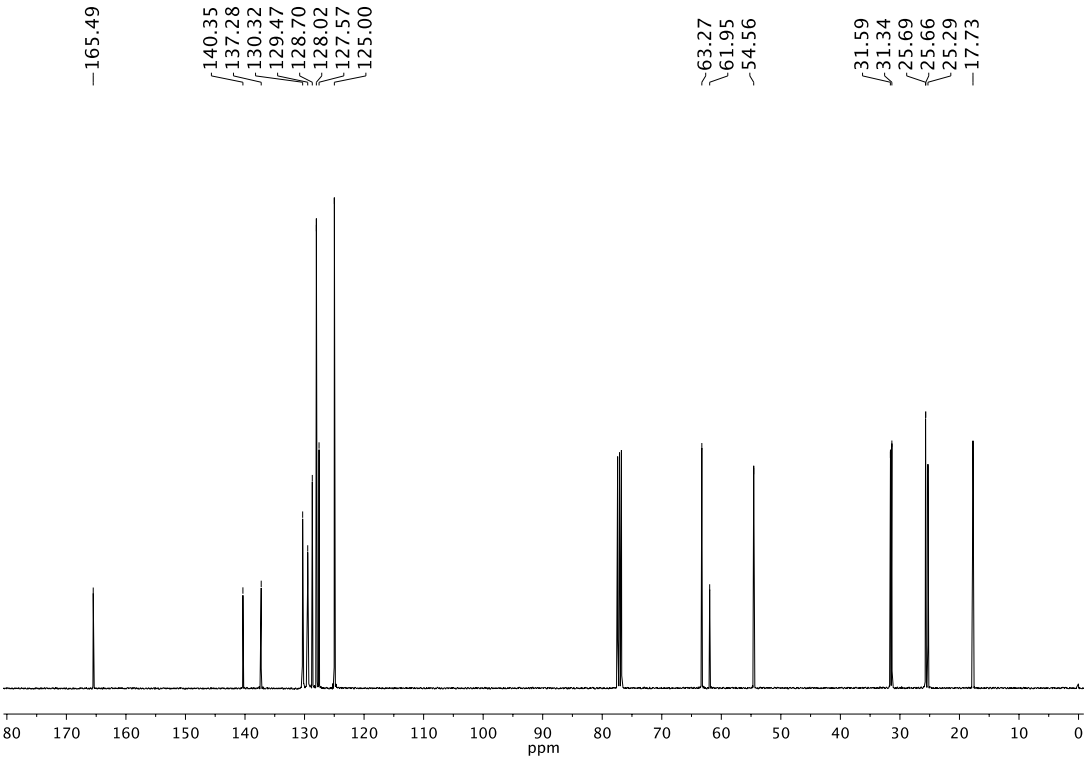


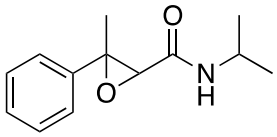


^{1}H-NMR of **E9** in $CDCl_3$

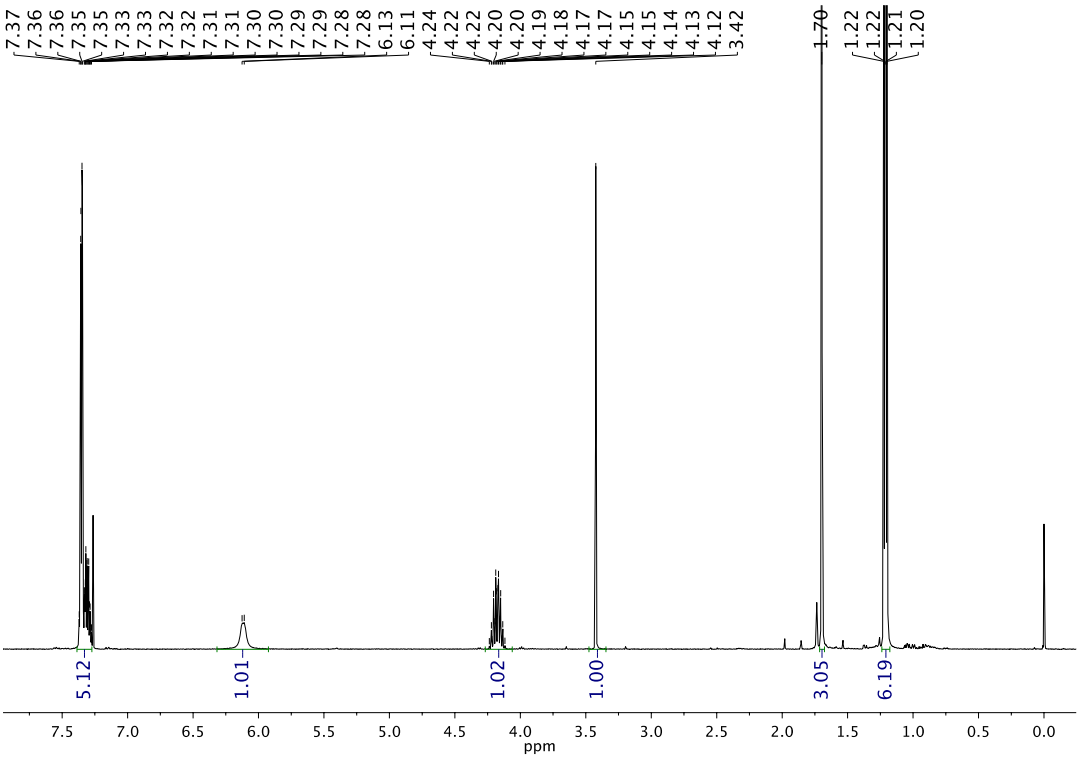


^{13}C-NMR of **E9** in $CDCl_3$

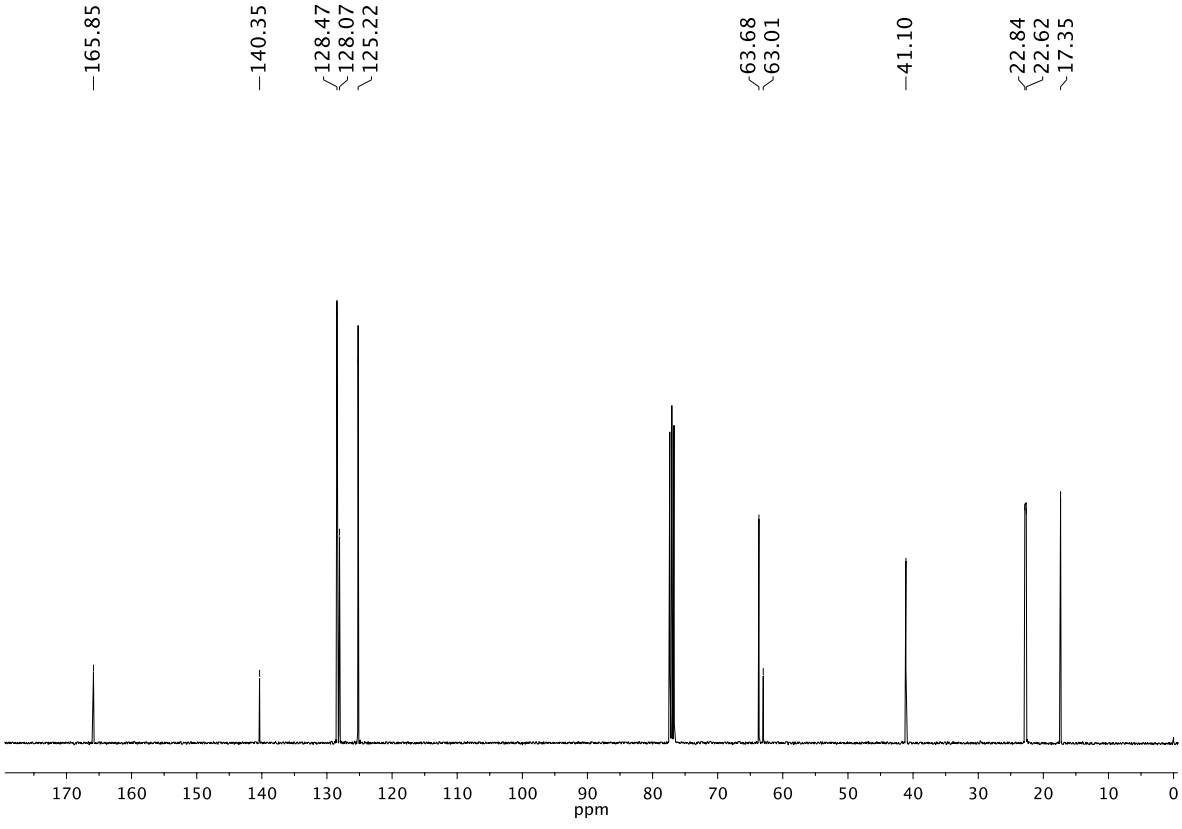


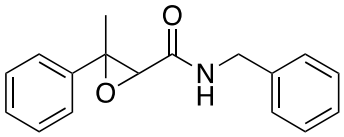


^{1}H-NMR of **E10** in $CDCl_3$

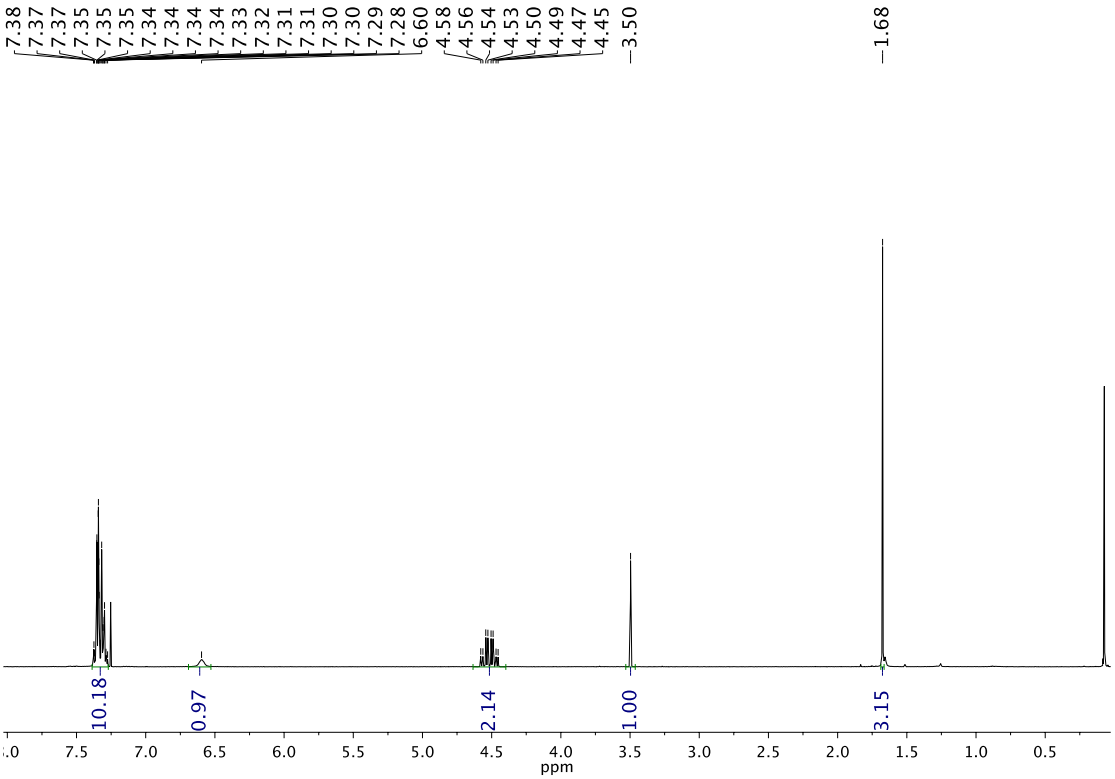


^{13}C-NMR of **E10** in $CDCl_3$

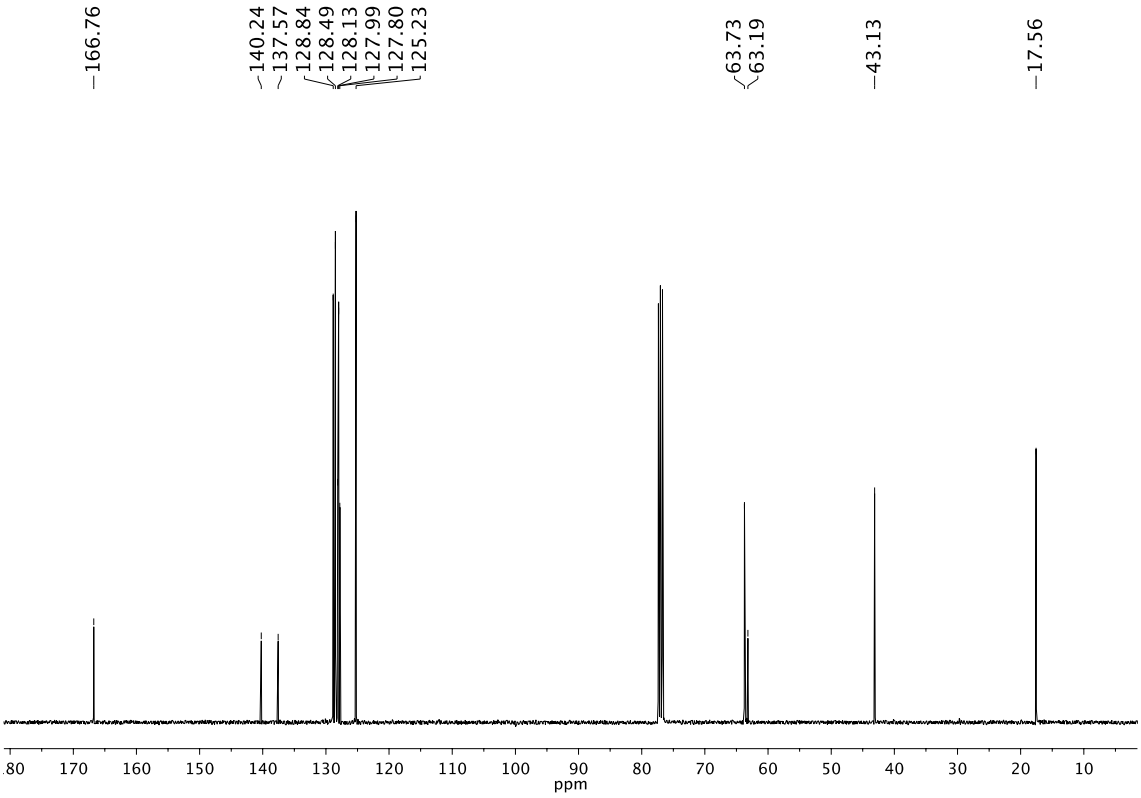


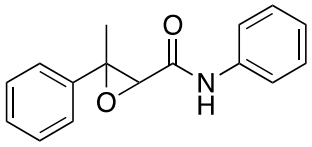


^{1}H-NMR of **E11** in $CDCl_3$

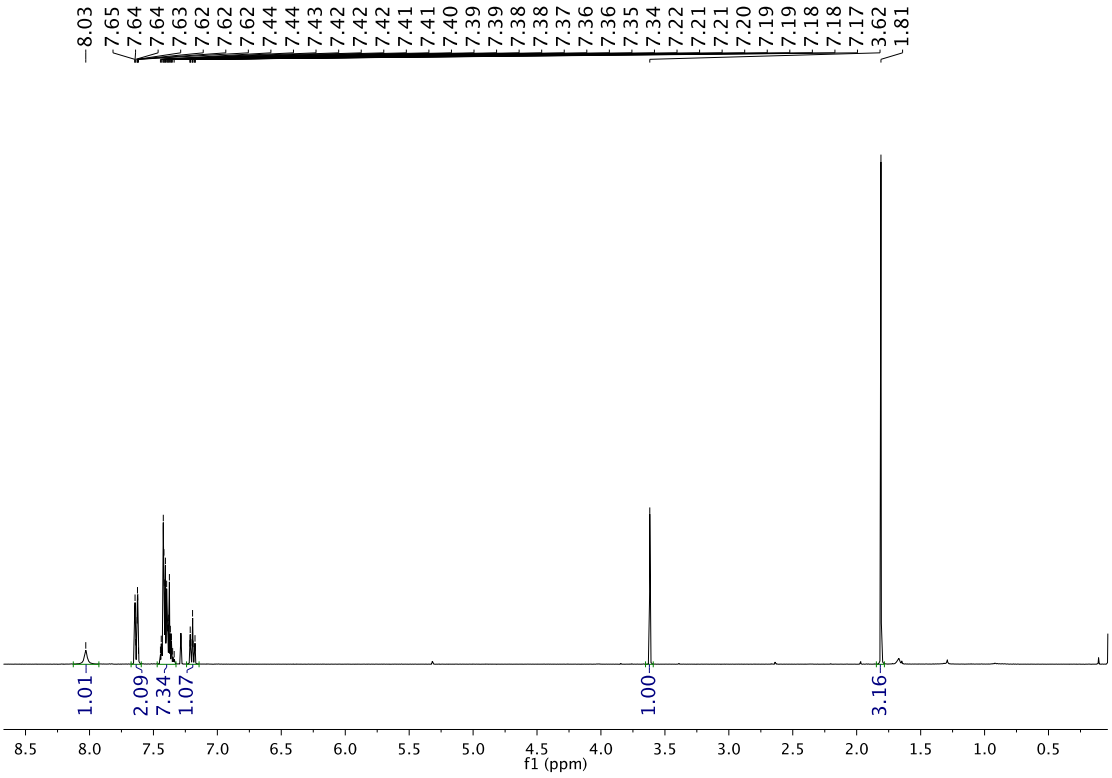


^{13}C-NMR of **E11** in $CDCl_3$

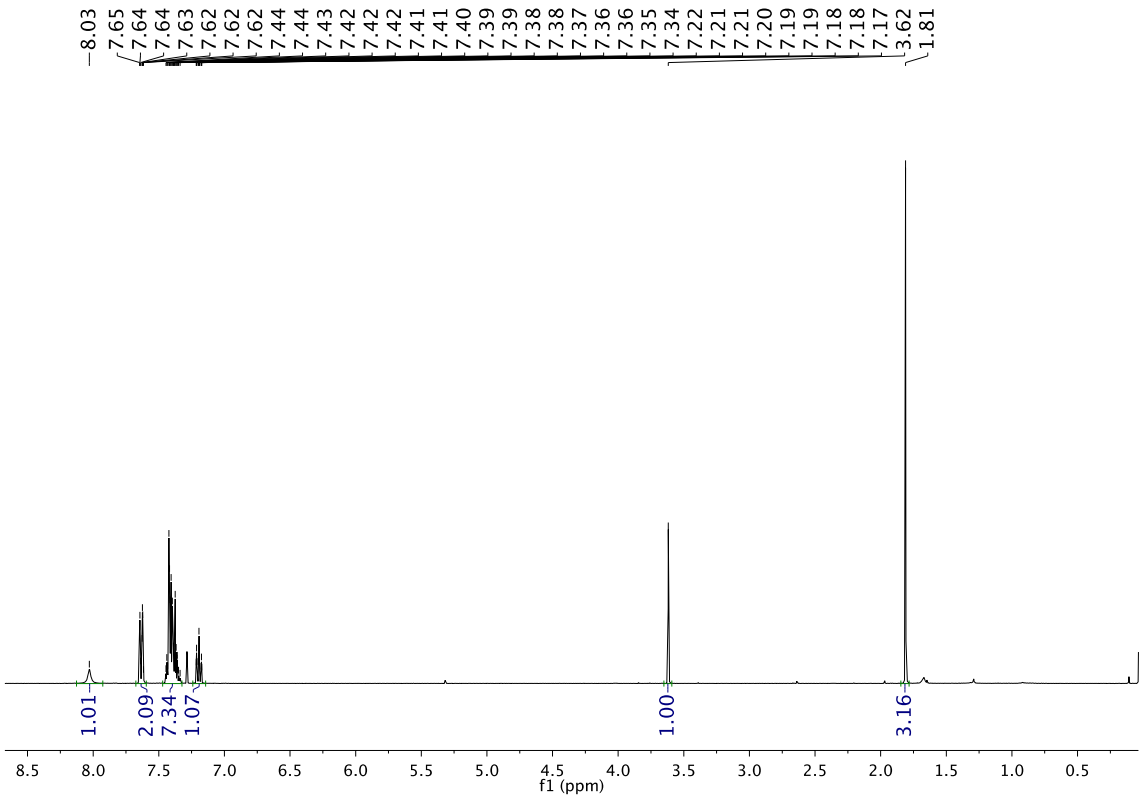


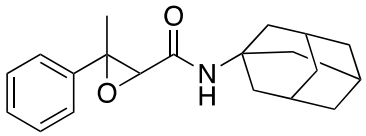


^{1}H-NMR of **E12** in $CDCl_3$

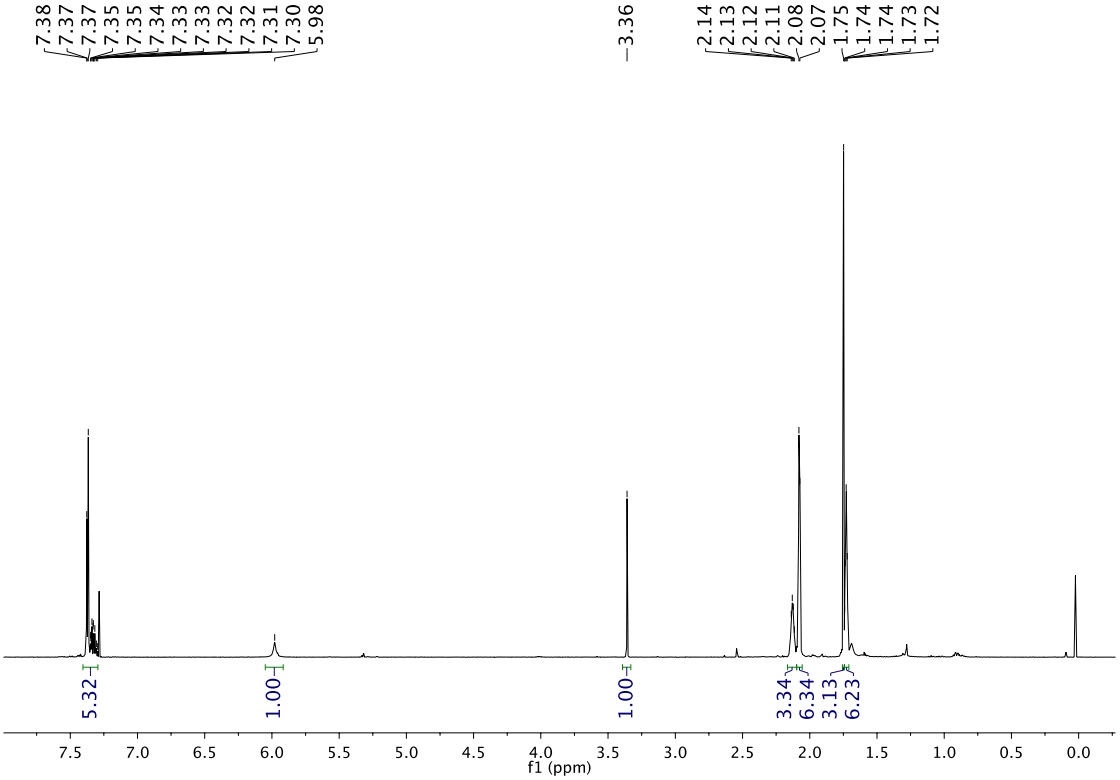


^{13}C-NMR of **E12** in $CDCl_3$

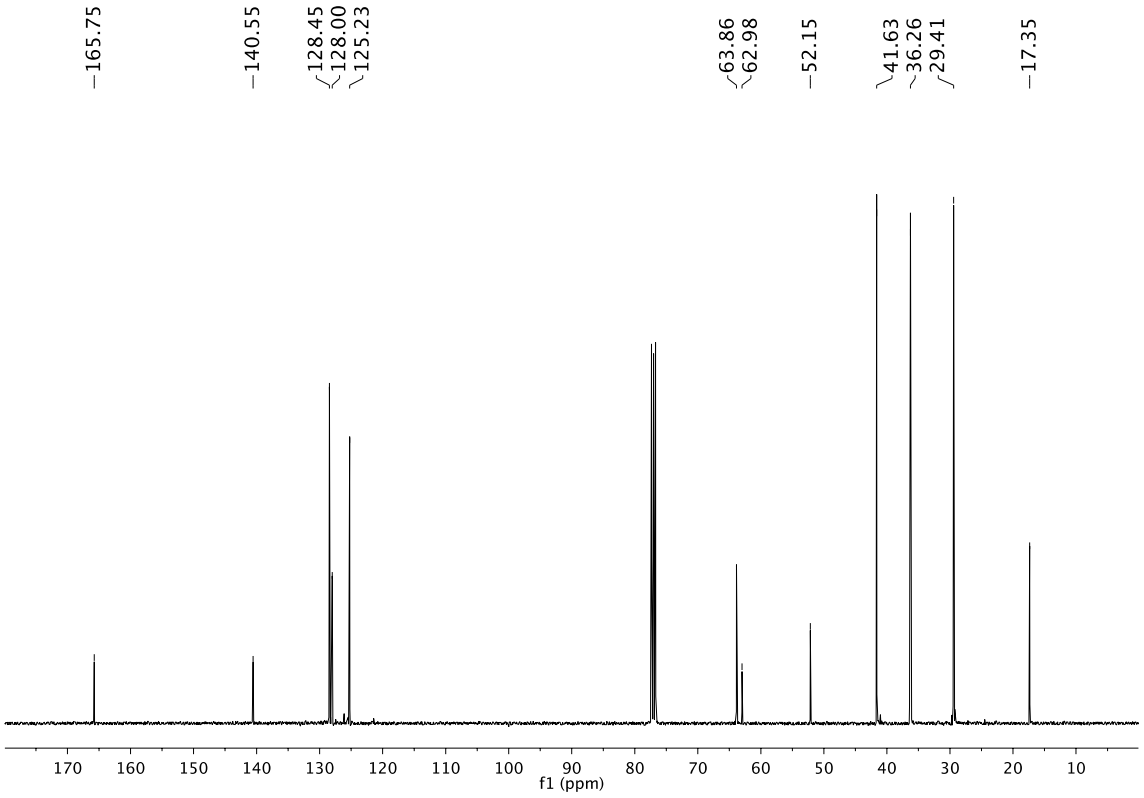


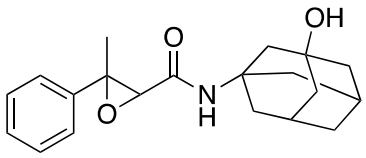


^{1}H-NMR of **E13** in $CDCl_3$

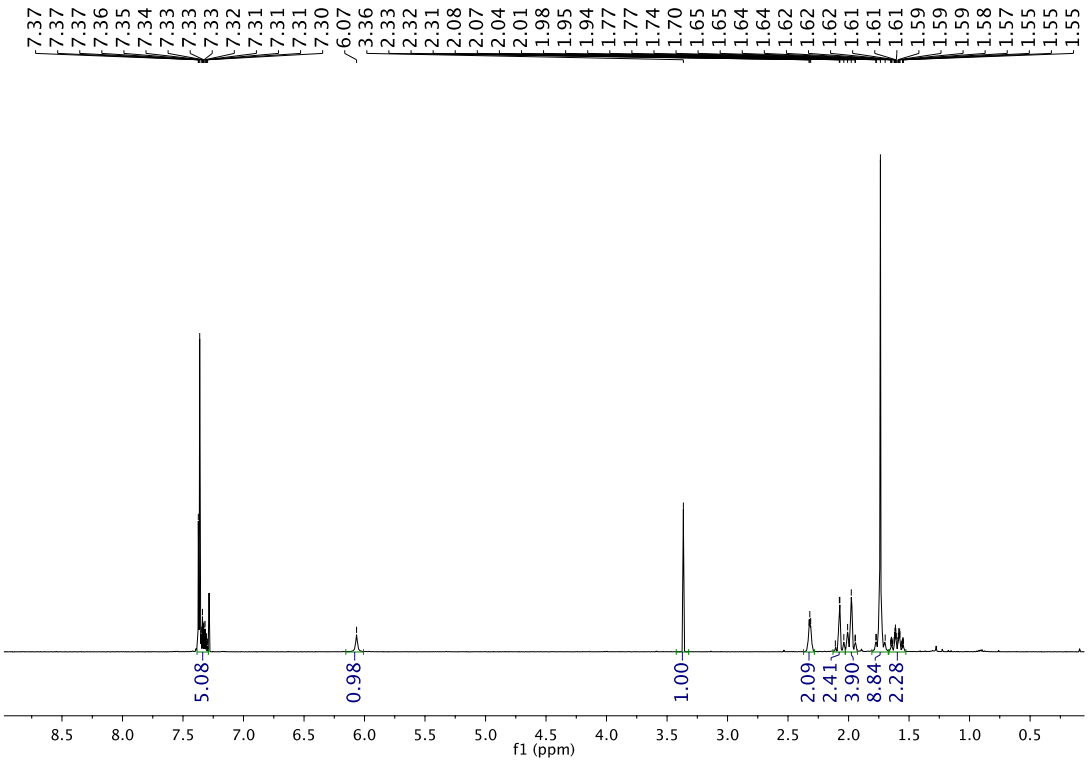


^{13}C-NMR of **E13** in $CDCl_3$

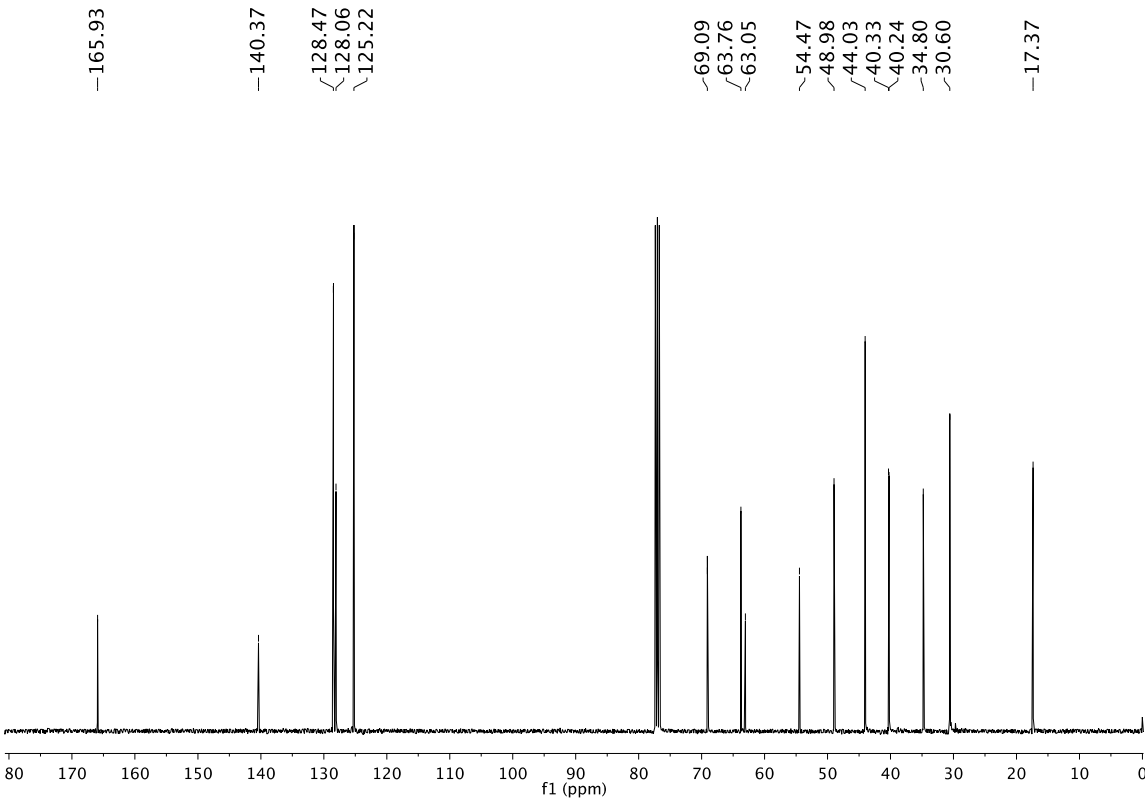


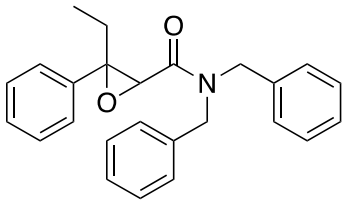


^{1}H-NMR of **EO13** in $CDCl_3$

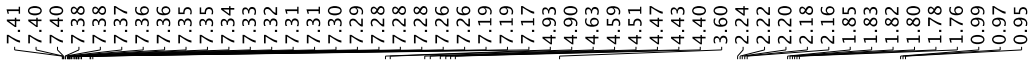


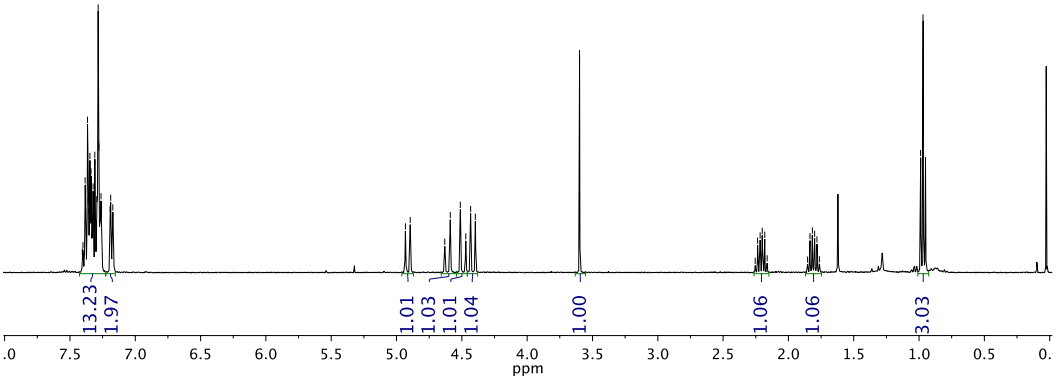
^{13}C-NMR of **EO13** in $CDCl_3$



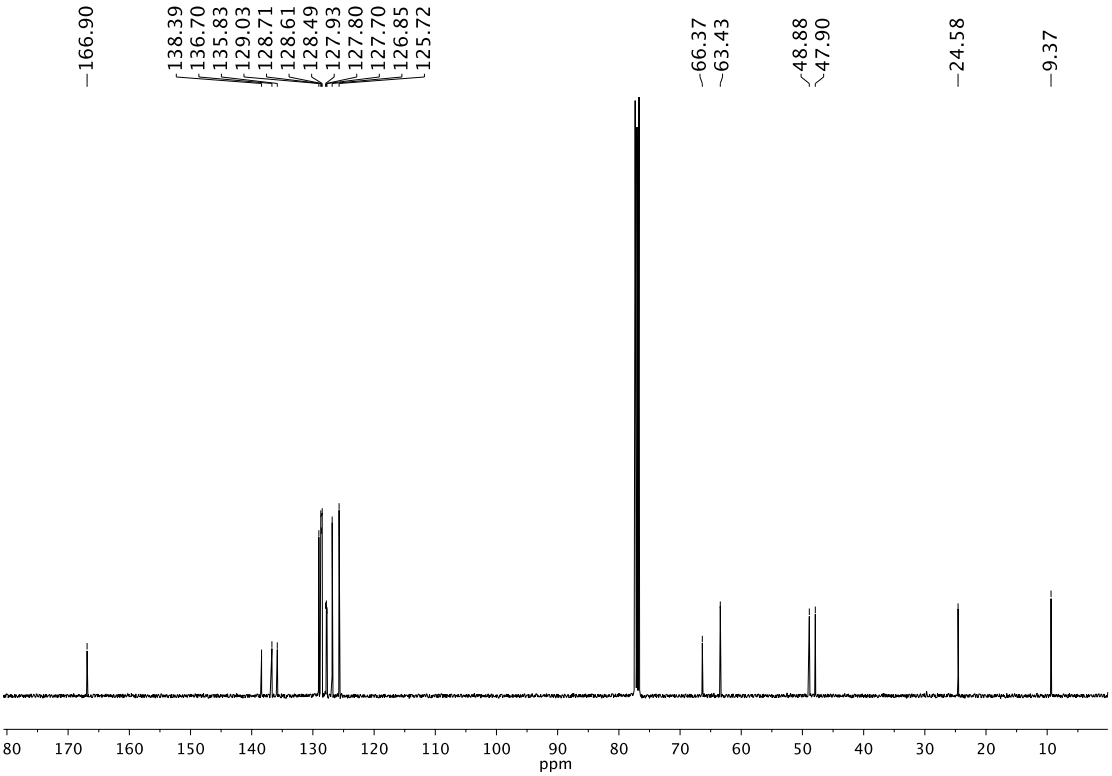


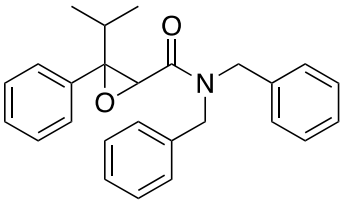
^{1}H-NMR of **E14** in $CDCl_3$



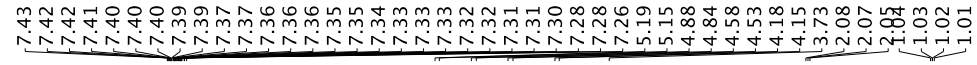


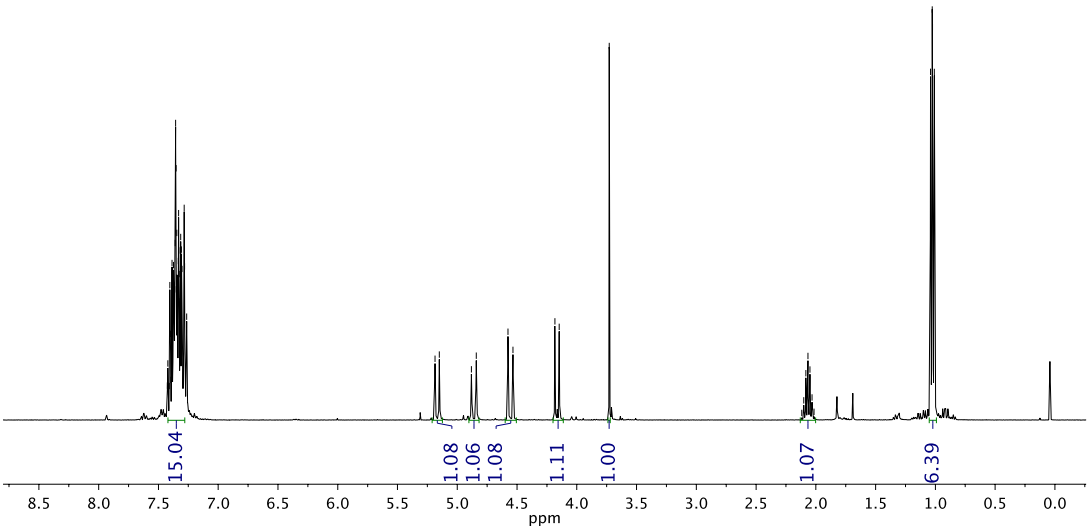
^{13}C-NMR of **E14** in $CDCl_3$



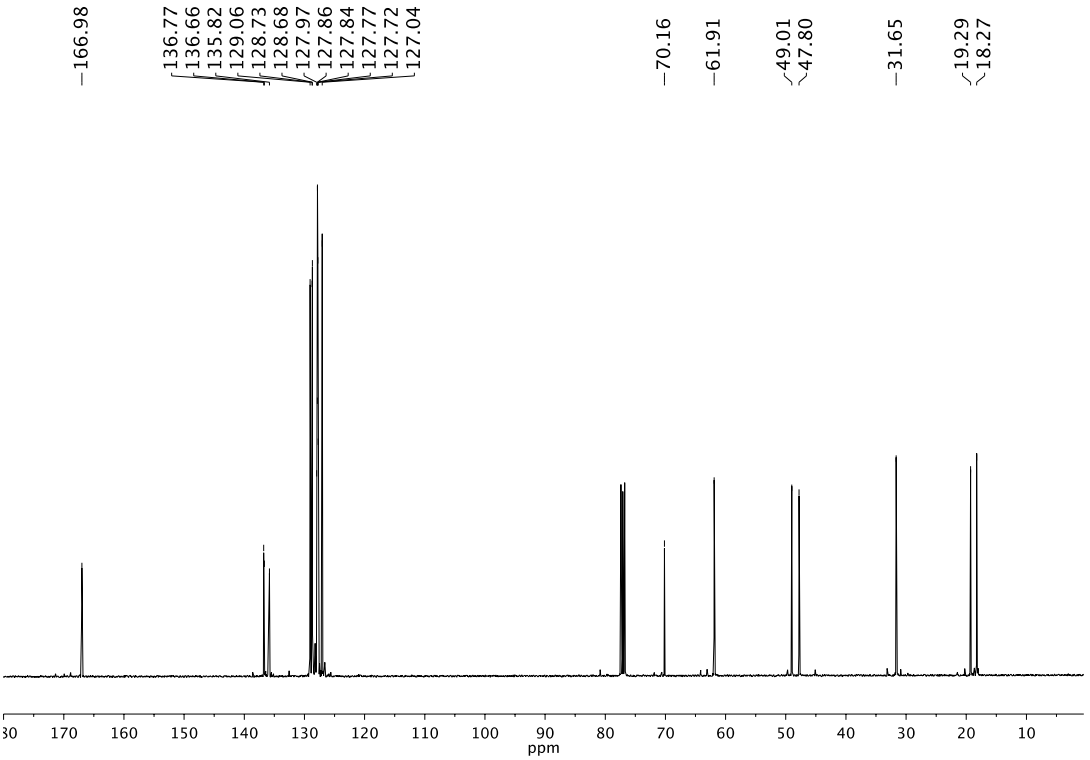


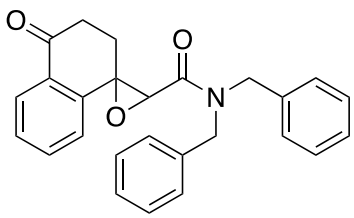
^{1}H-NMR of **E15** in $CDCl_3$



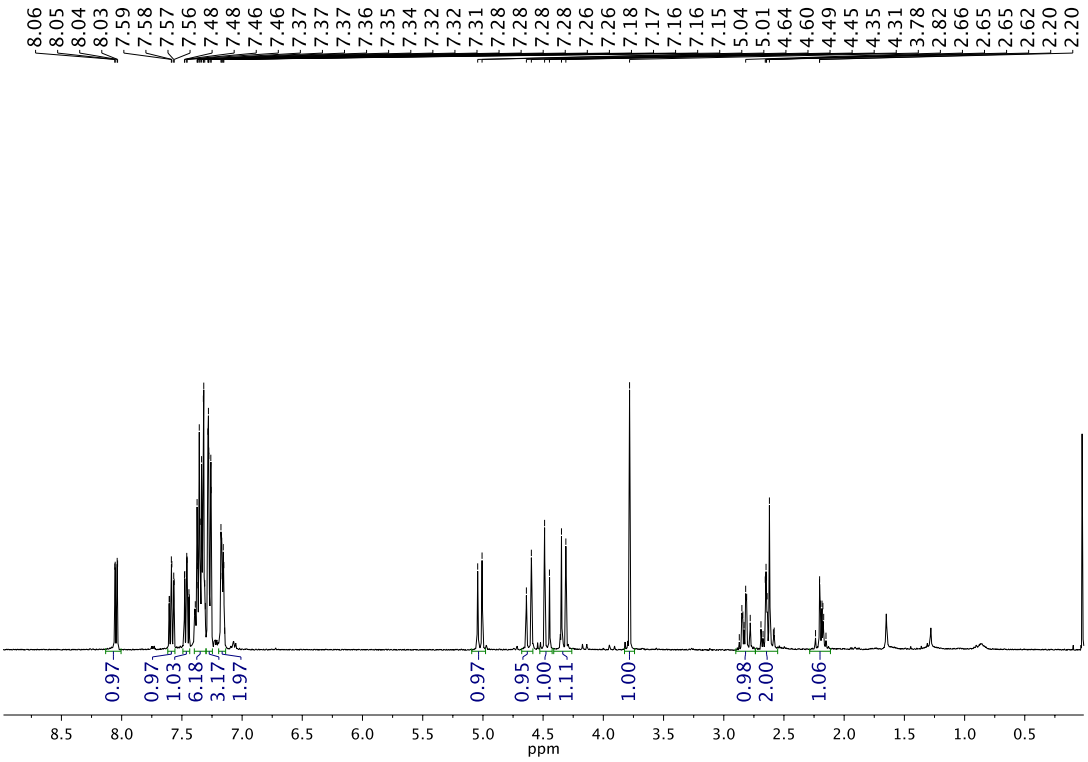


^{13}C-NMR of **E15** in $CDCl_3$

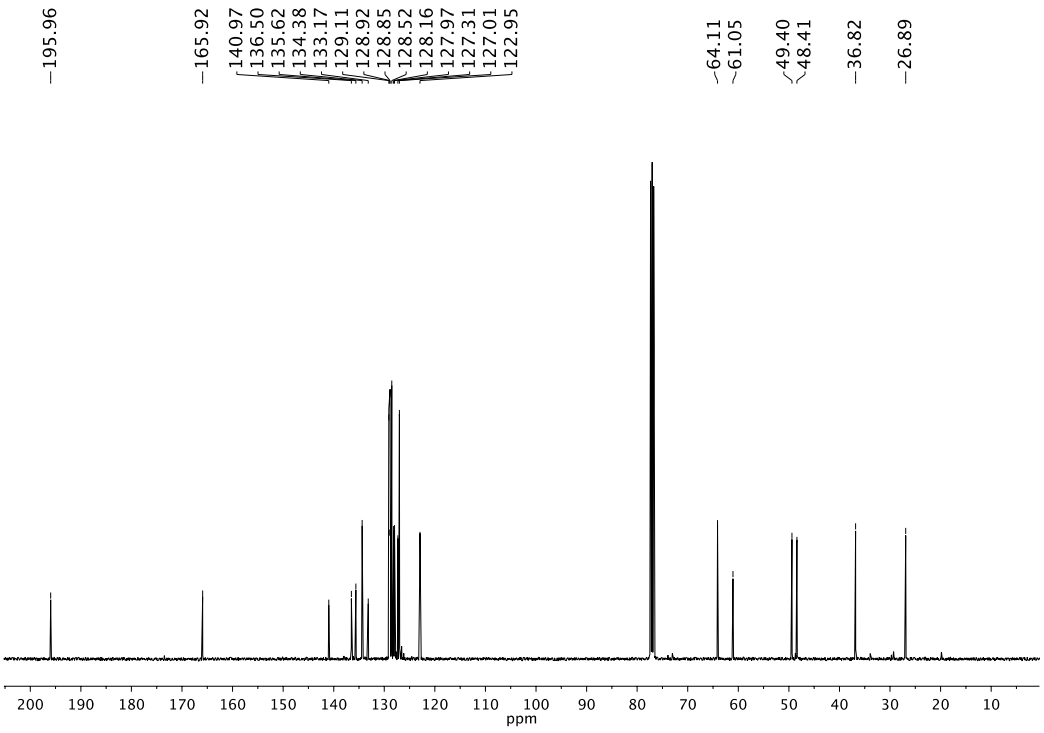


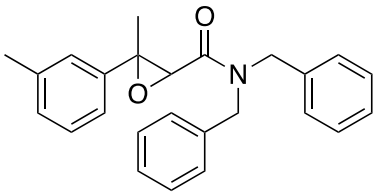


^{1}H-NMR of **EK16** in $CDCl_3$

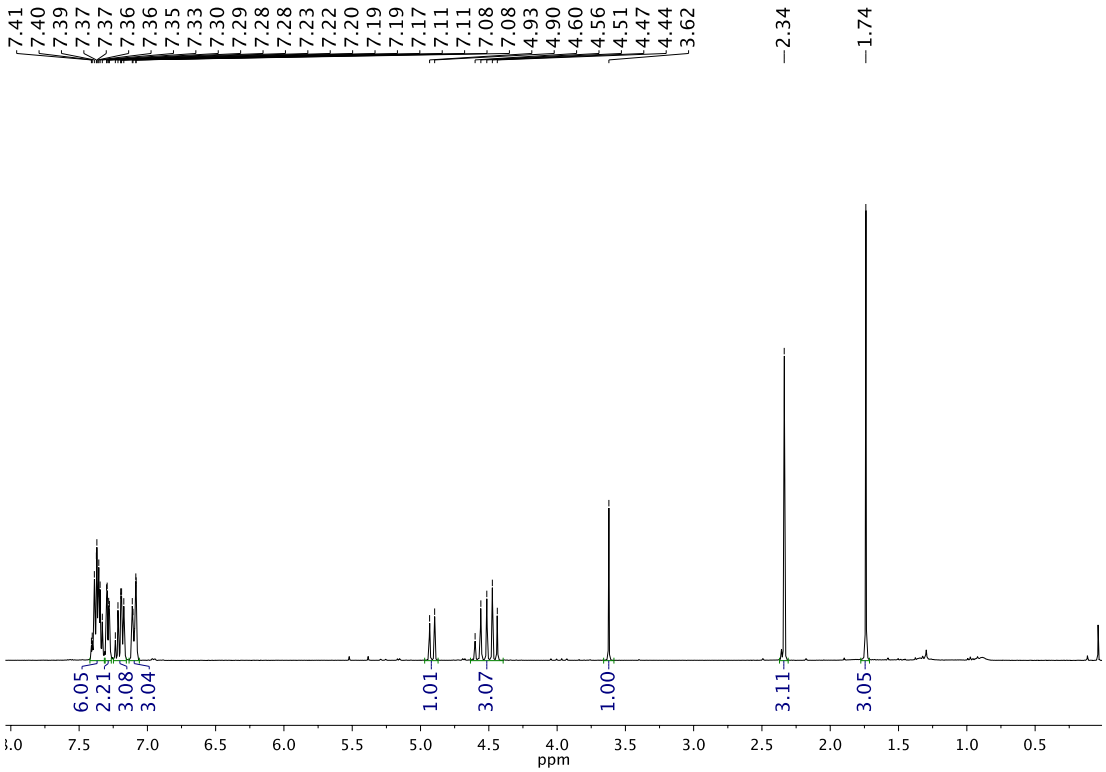


^{13}C-NMR of **EK16** in $CDCl_3$

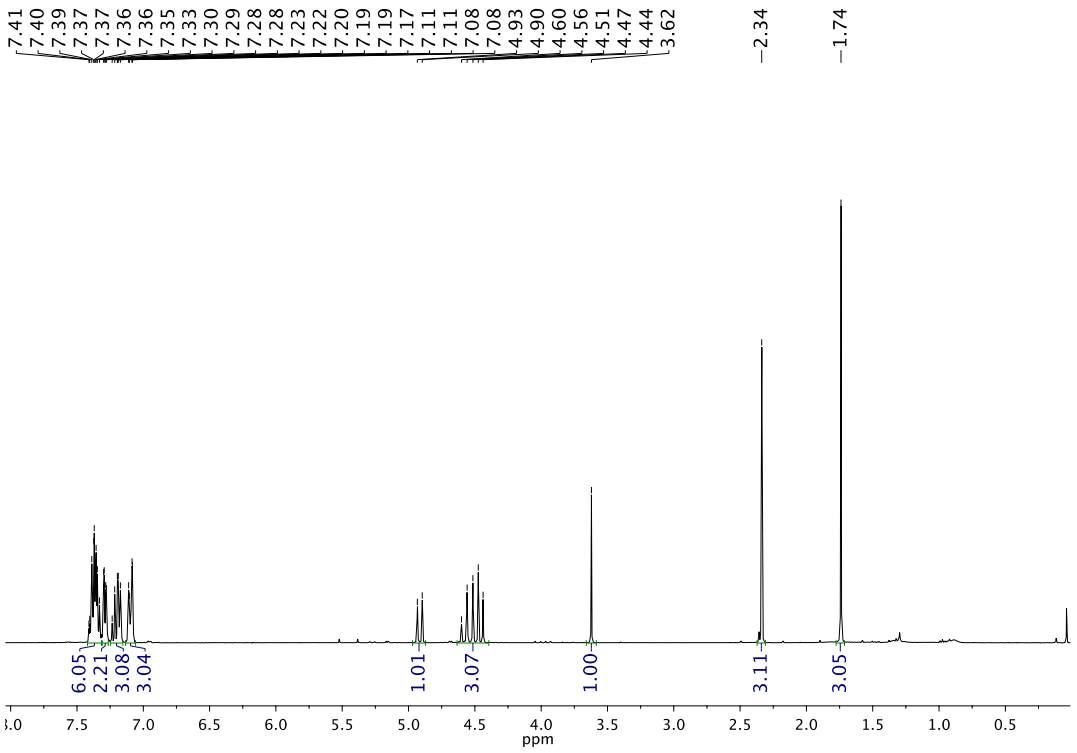


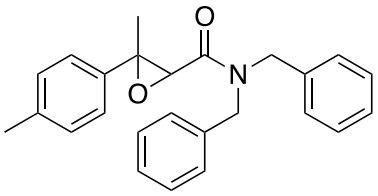


^{1}H-NMR of **E18** in $CDCl_3$

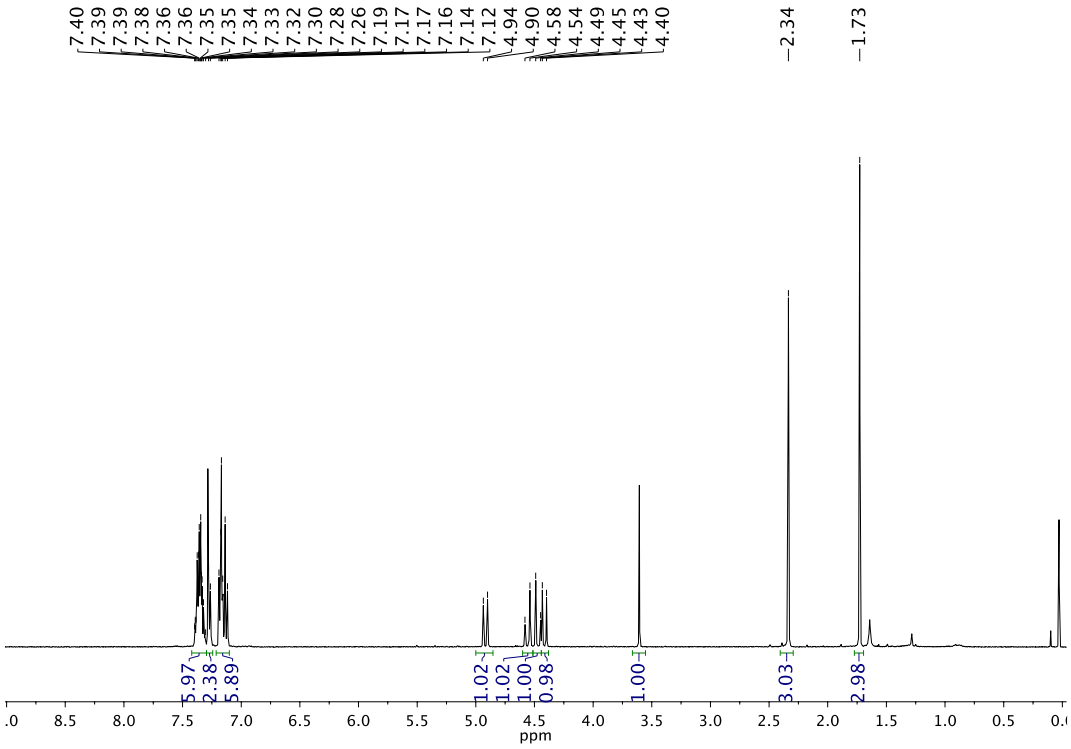


^{13}C-NMR of **E18** in $CDCl_3$

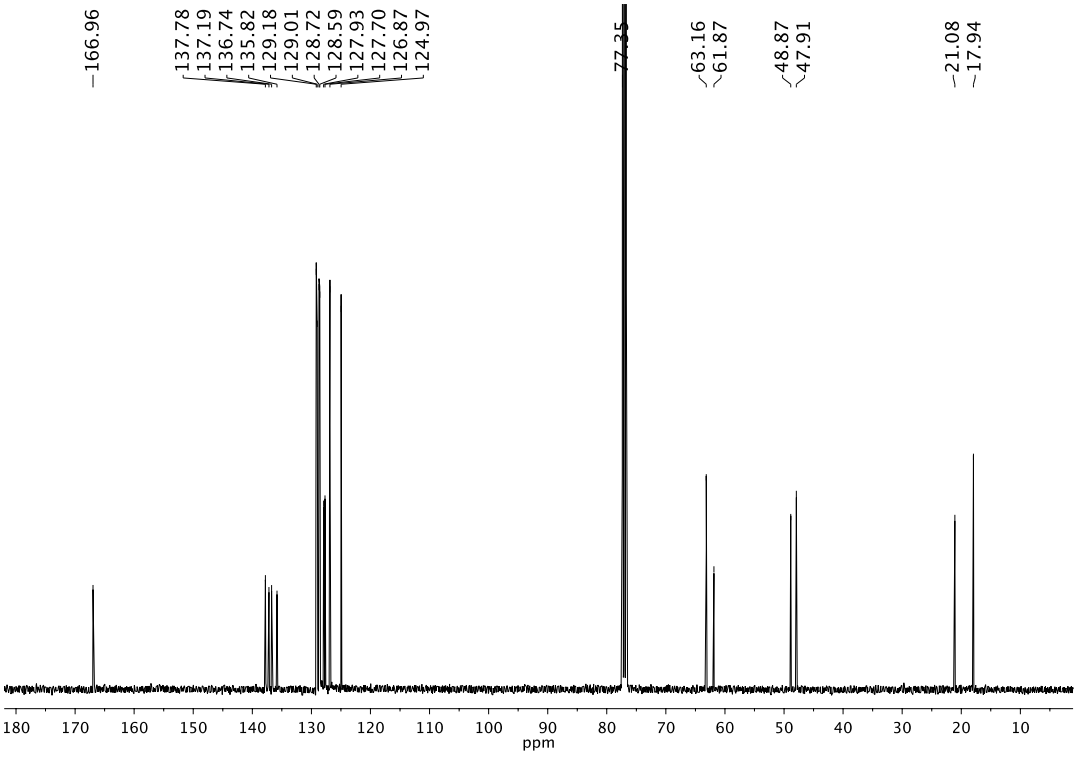


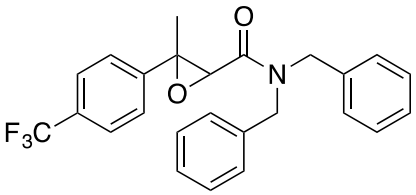


^{1}H-NMR of **E19** in $CDCl_3$

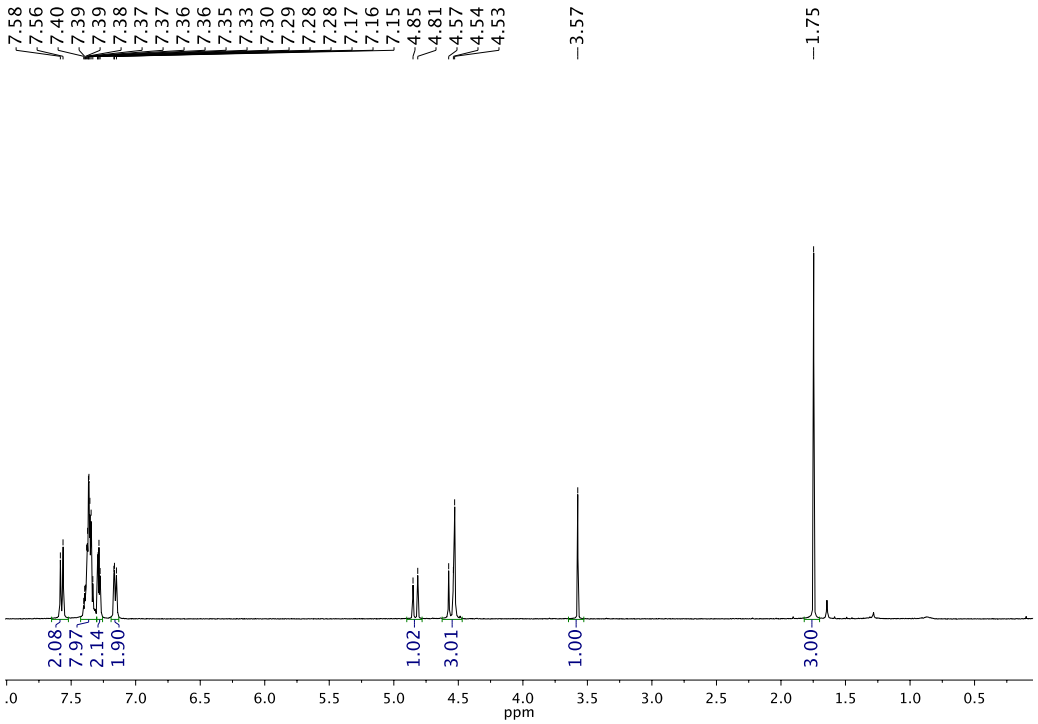


^{13}C-NMR of **E19** in $CDCl_3$

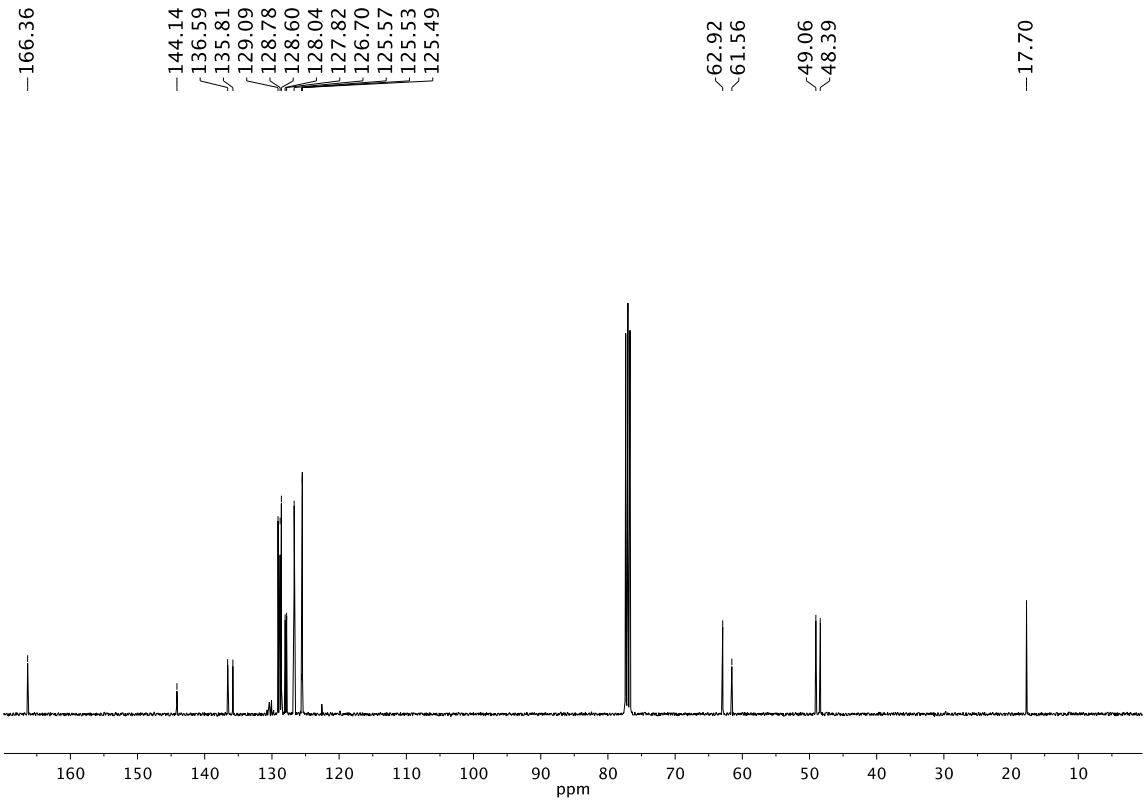


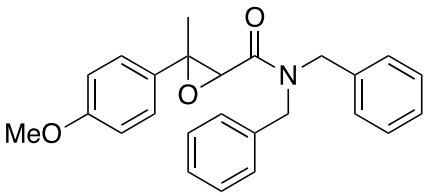


^{1}H-NMR of **E20** in $CDCl_3$

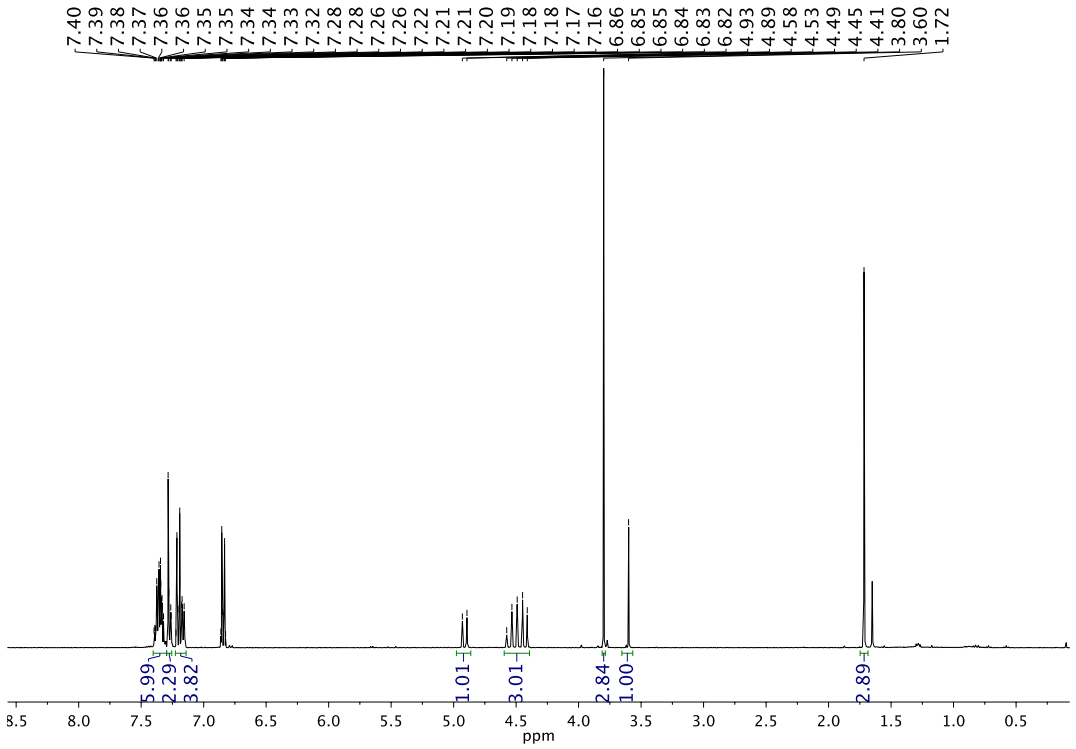


^{13}C-NMR of **E20** in $CDCl_3$

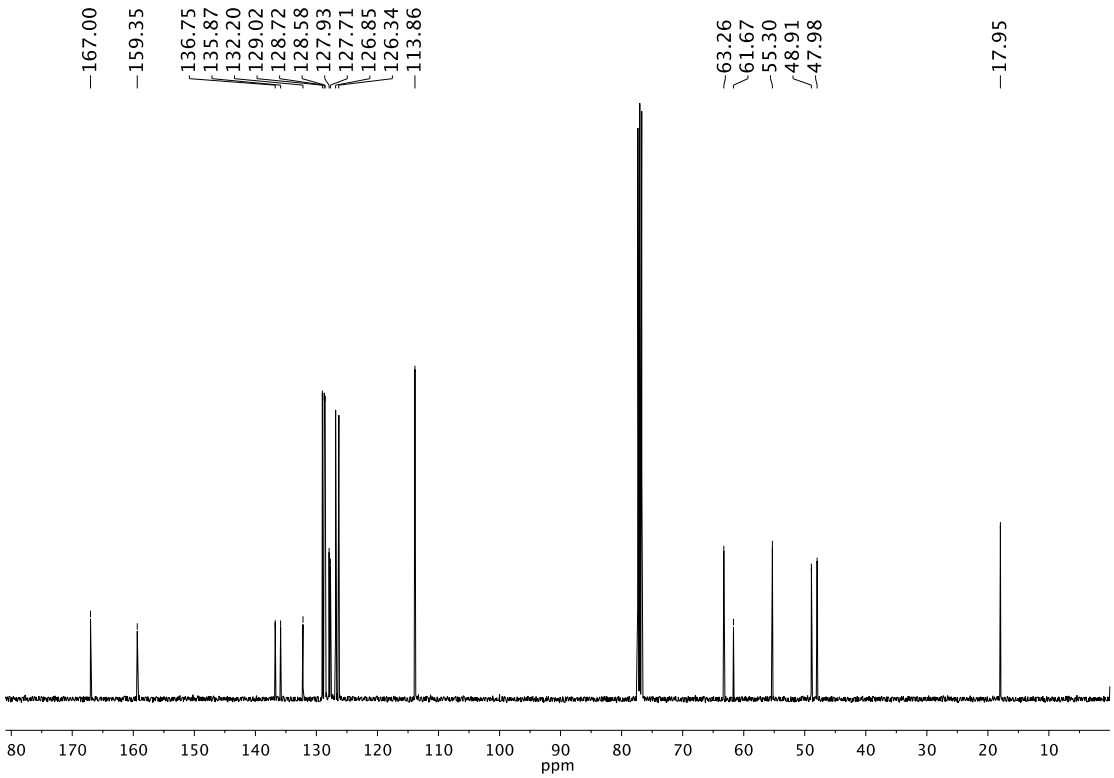


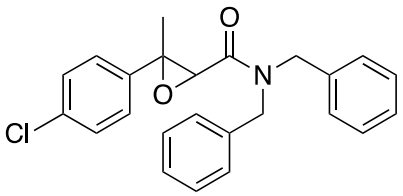


^{1}H-NMR of **E21** in $CDCl_3$

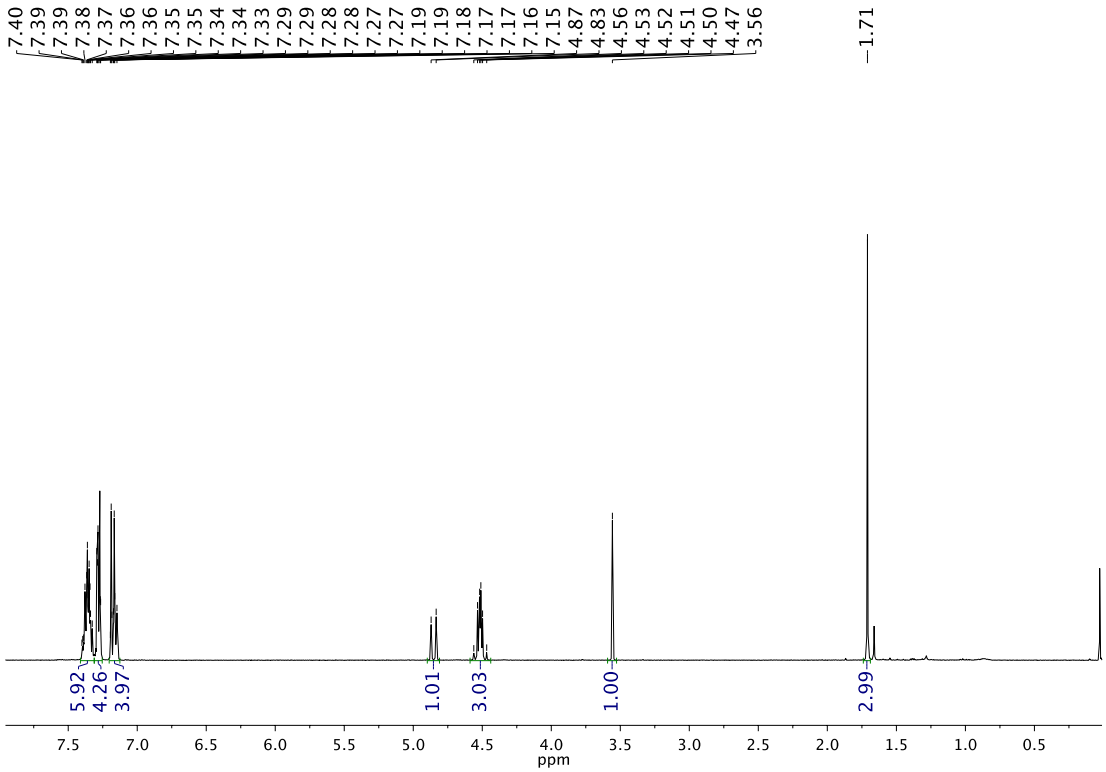


^{13}C-NMR of **E21** in $CDCl_3$

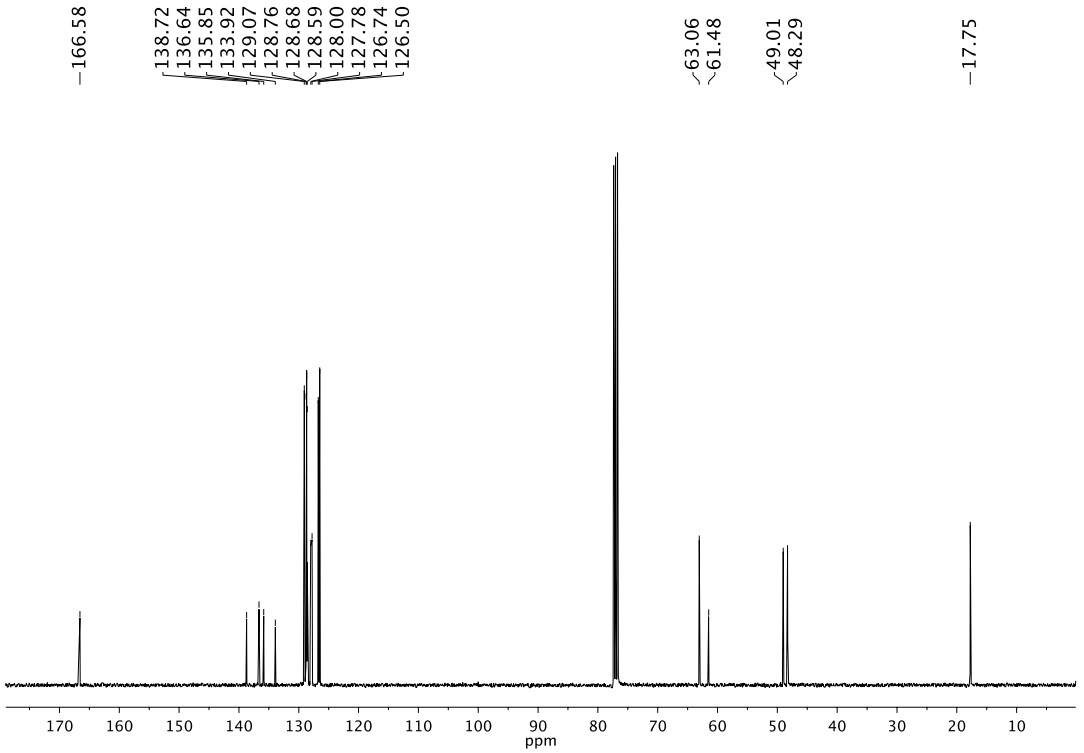


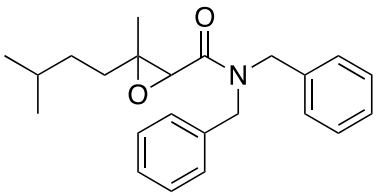


^{1}H-NMR of **E22** in $CDCl_3$



^{13}C-NMR of **E22** in $CDCl_3$





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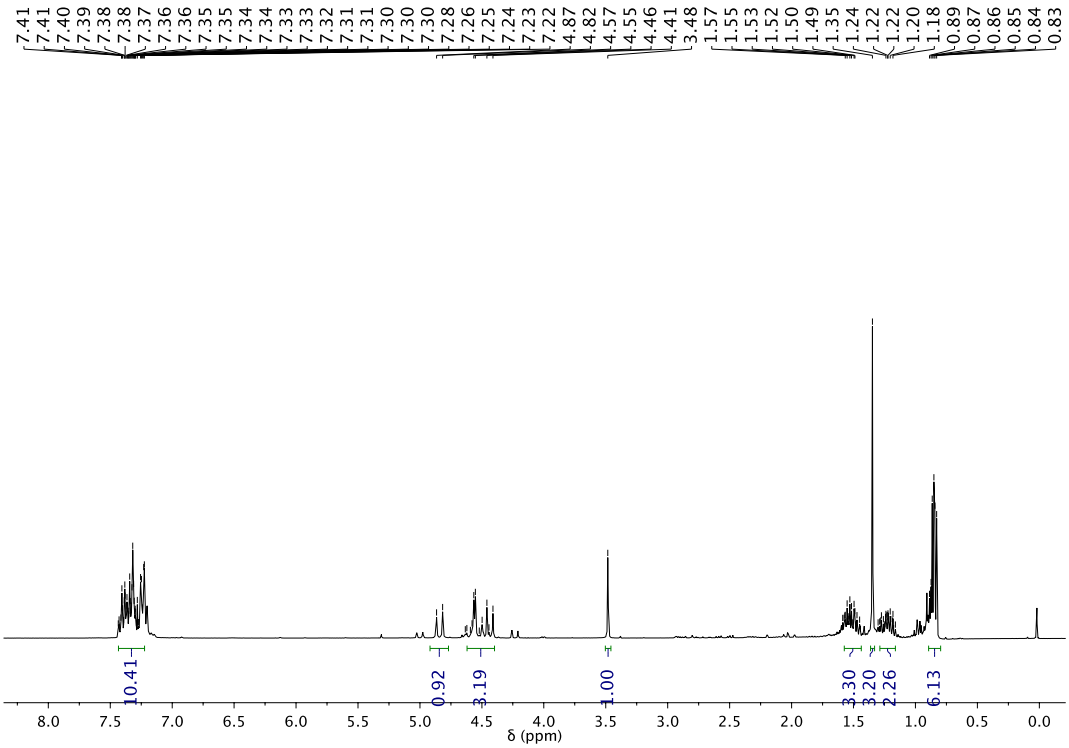
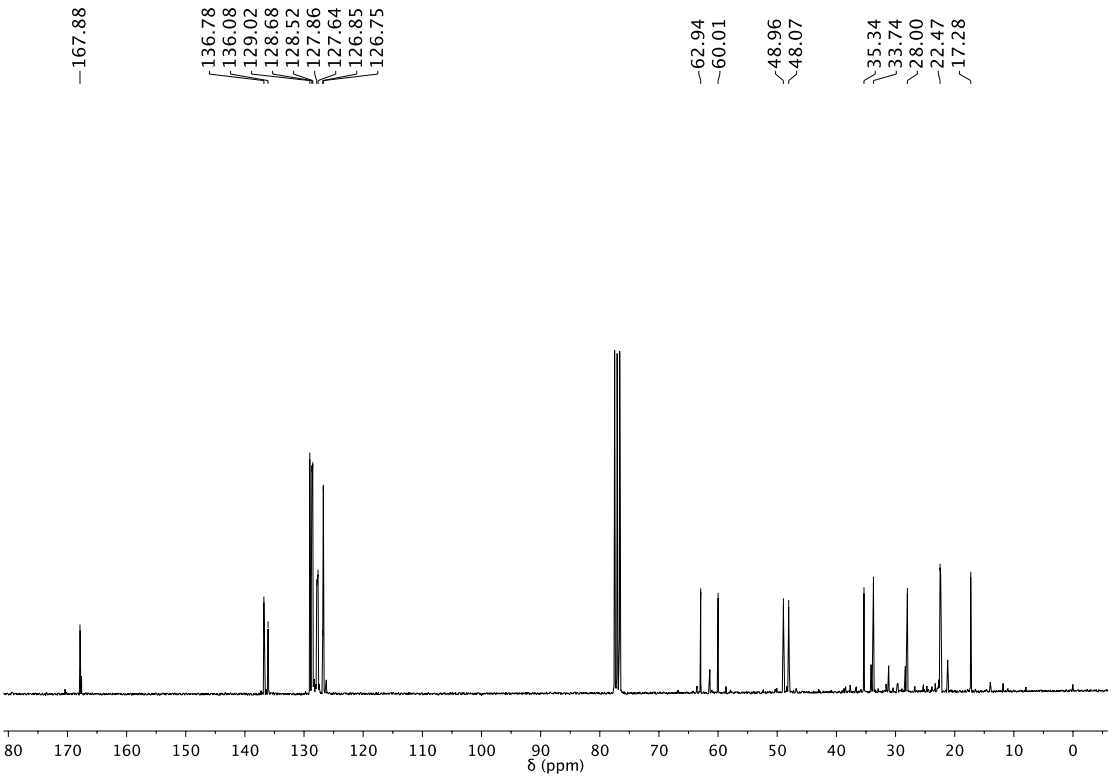
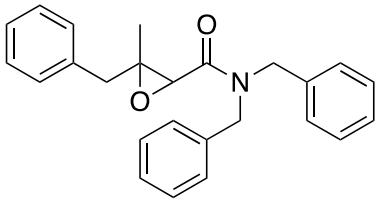
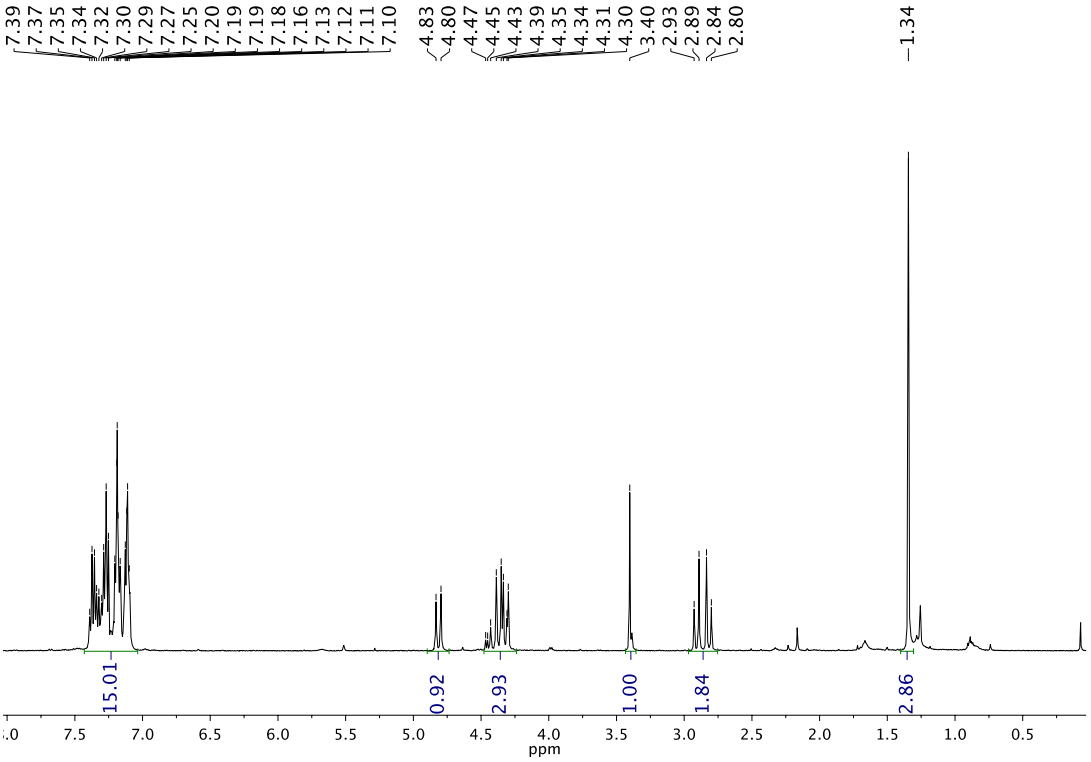


^{13}C-NMR of **E25** in $CDCl_3$

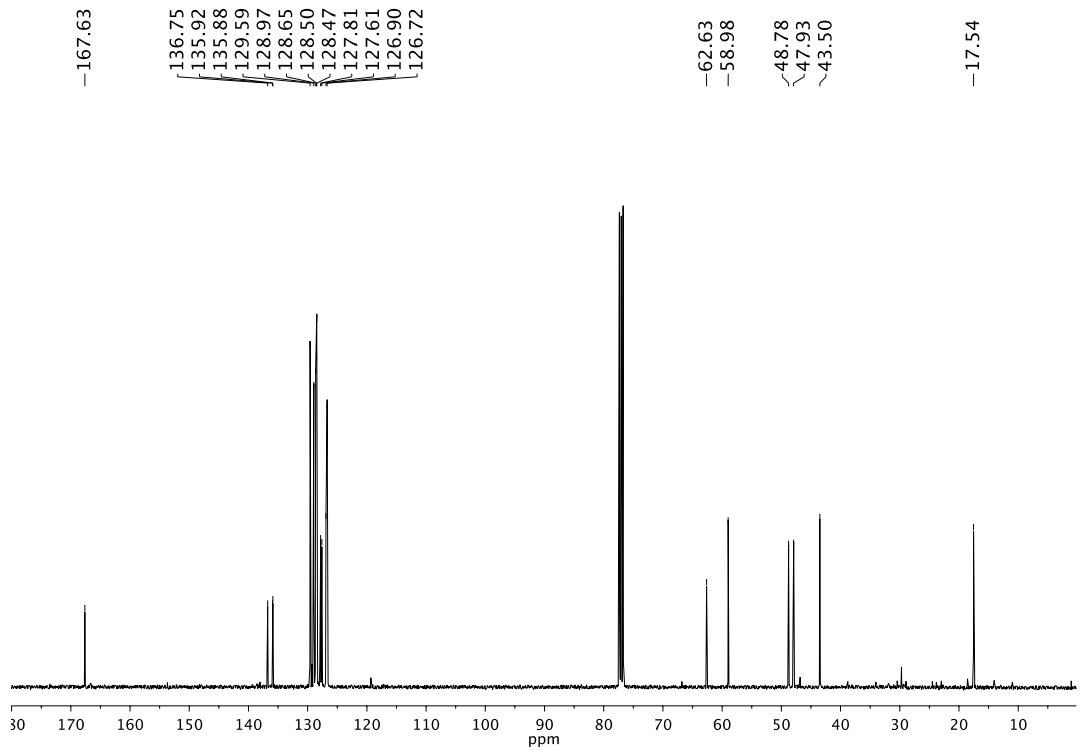


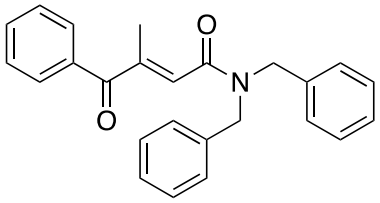


^{1}H-NMR of **E26** in $CDCl_3$

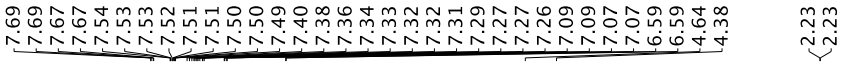


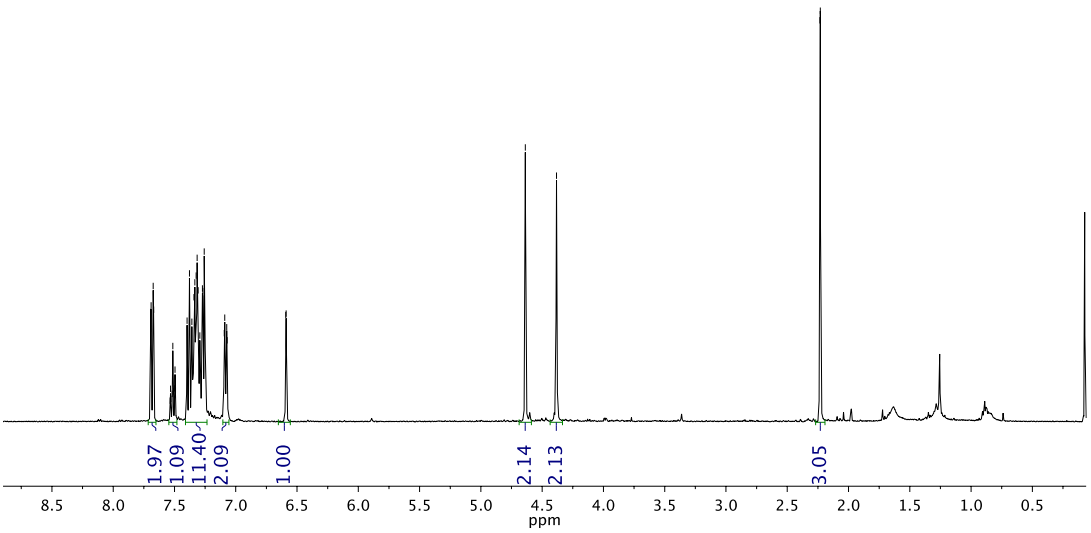
^{13}C-NMR of **E26** in $CDCl_3$



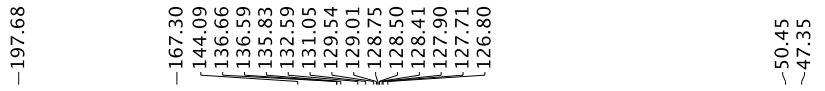


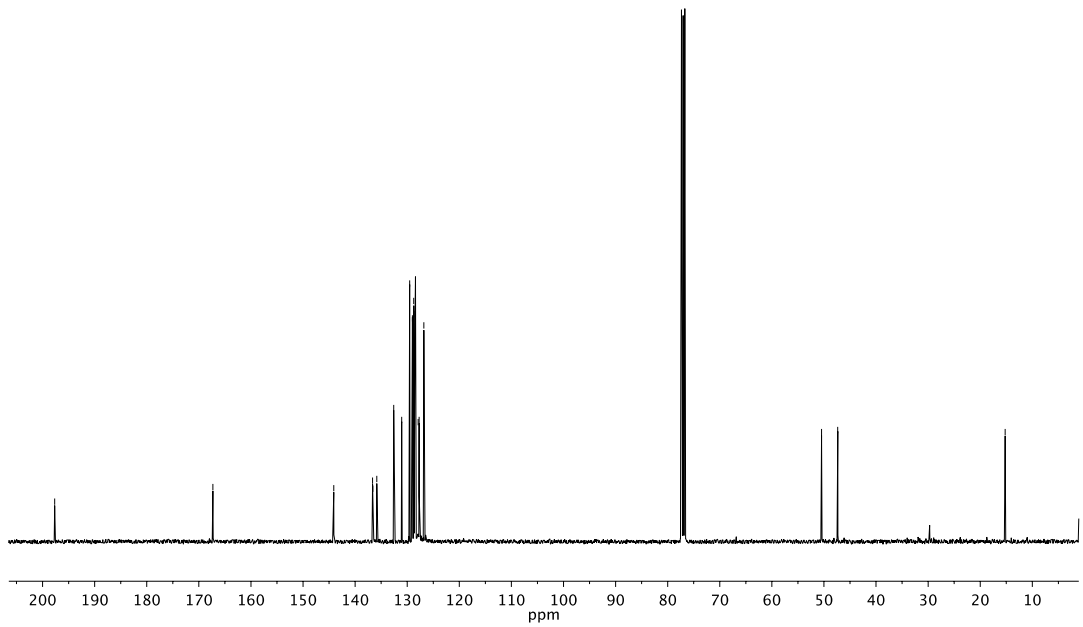
^{1}H-NMR of **K26** in $CDCl_3$





^{13}C-NMR of **K26** in $CDCl_3$

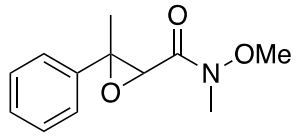




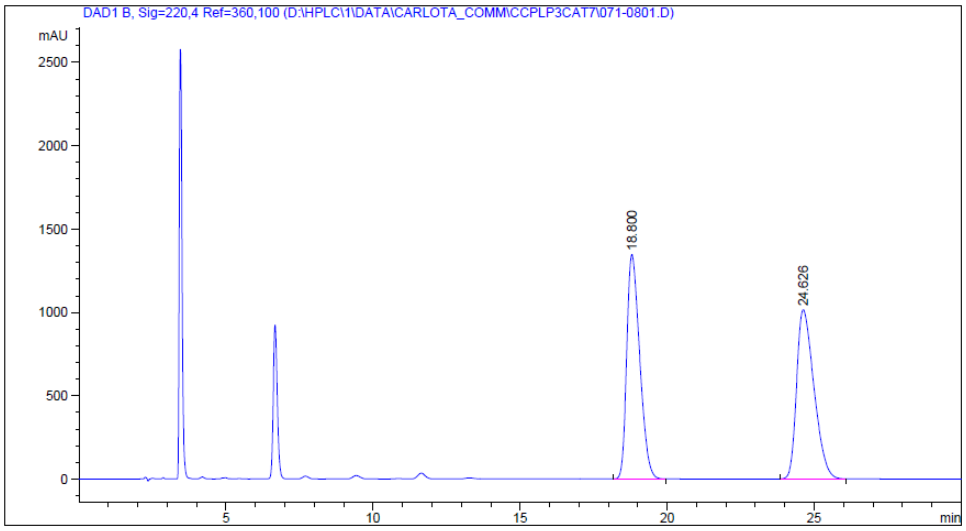
6.3) HPLC of products

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25°C, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 18.8 min, t_R(epoxide 2) = 24.6 min

E1

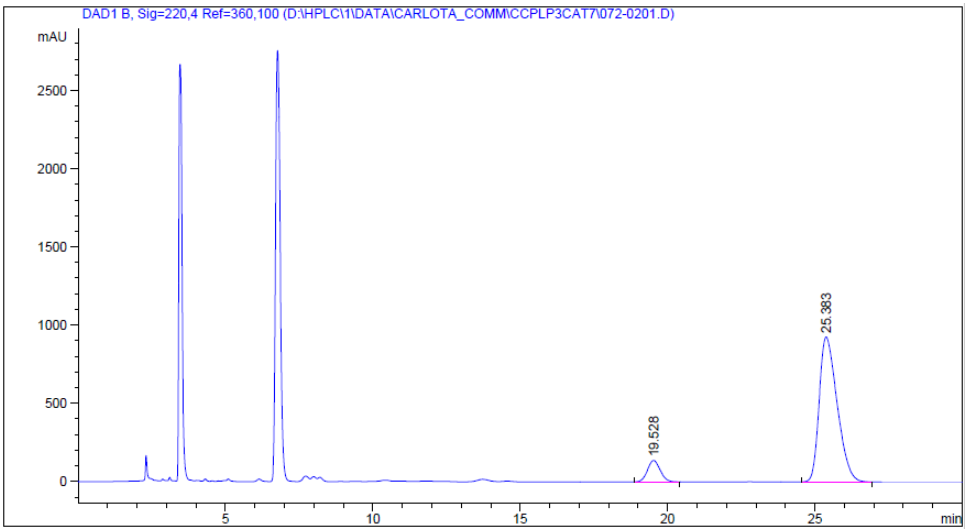


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	18.800	1	BB	4.11784e4	1347.11108	49.7614
2	24.626	1	BB	4.15734e4	1015.33740	50.2386

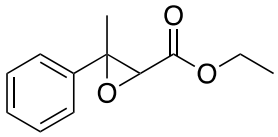
Table 1 entry 6



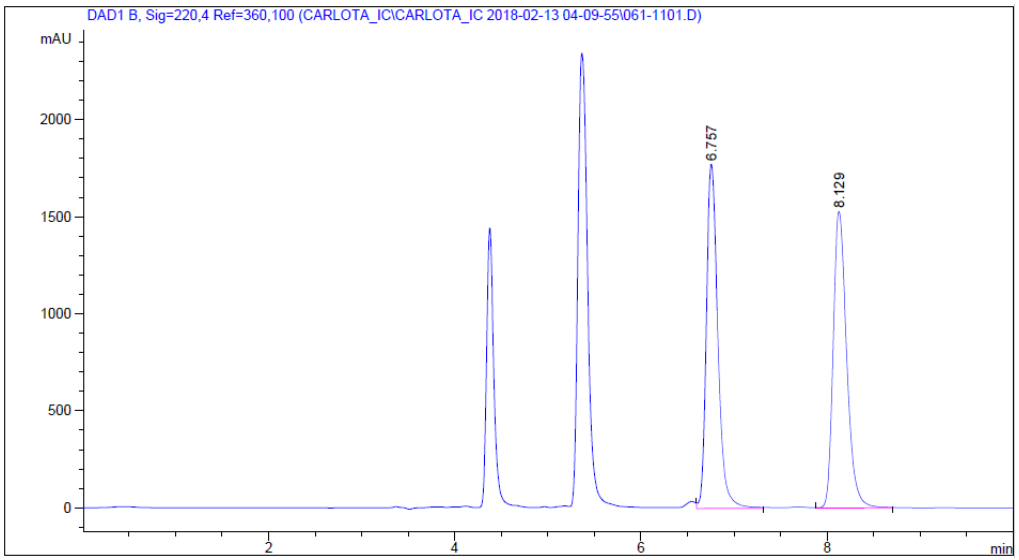
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	19.523	1	BB	3512.89844	117.43418	9.2651
2	25.396	1	BB	3.44026e4	824.78369	90.7349

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 85/15, 25°C, flow rate = 1 mL/min, λ = 220 nm, t_R(epoxide 1) = 6.8 min, t_R(epoxide 2) = 8.1 min

E2

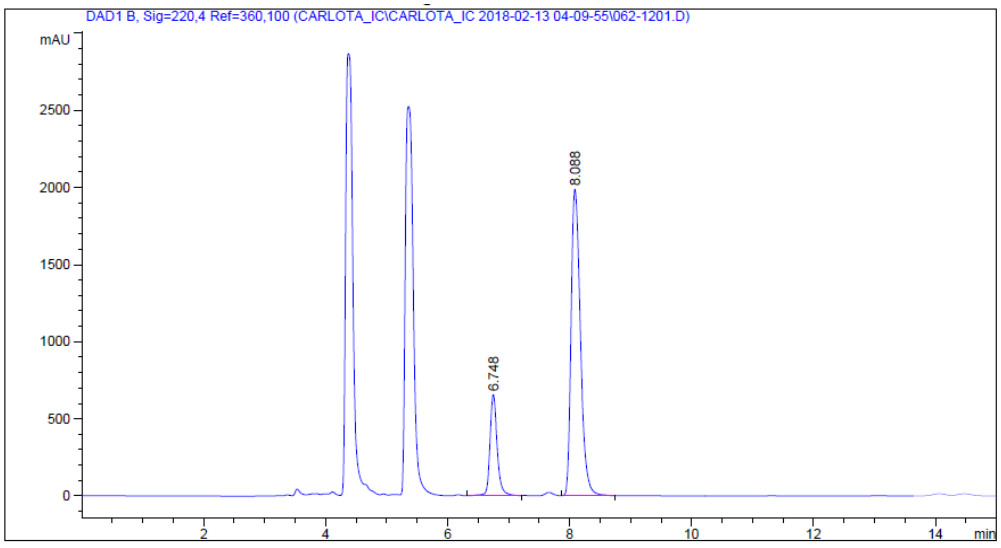


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.757	1	VB	1.51438e4	1772.59021	49.6569
2	8.129	1	VB	1.53531e4	1526.95422	50.3431

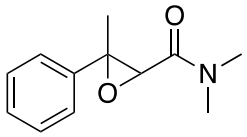
Table 1 entry 12



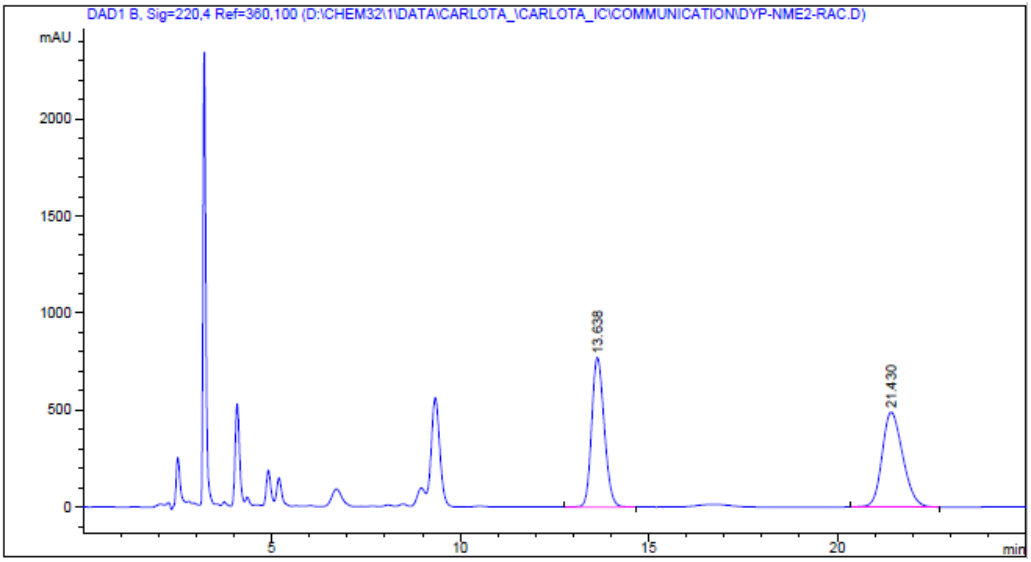
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.748	1	VB	5398.91650	654.49652	20.3683
2	8.088	1	VB	2.11075e4	1986.78088	79.6317

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 70/30, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 13.6 min, t_R(epoxide 2) = 21.4 min

E3

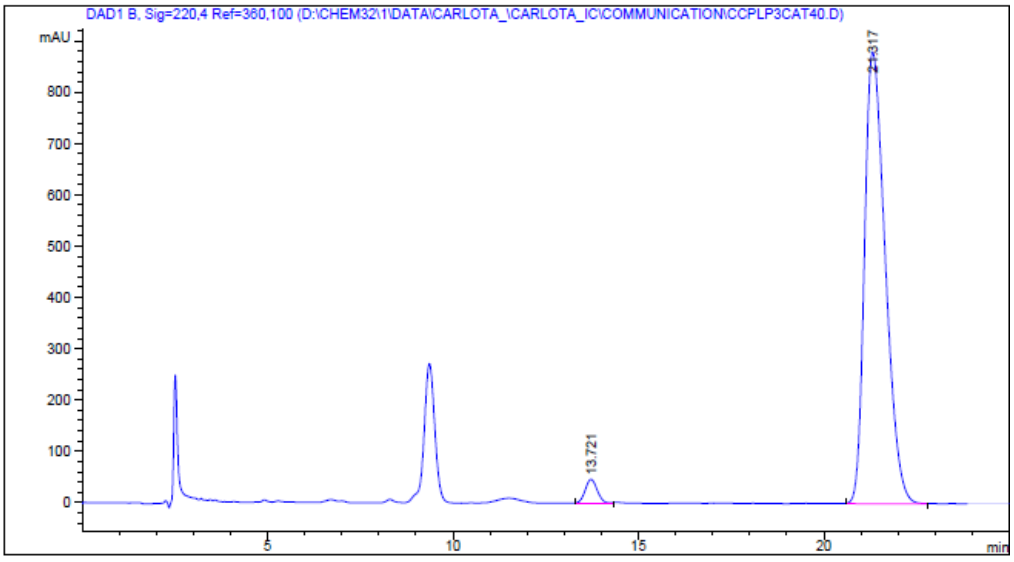


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	13.638	1	VB	1.80679e4	771.54340	49.1032
2	21.430	1	BB	1.87279e4	489.59921	50.8968

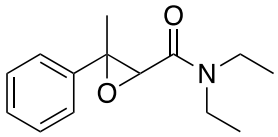
Table 2 entry 1



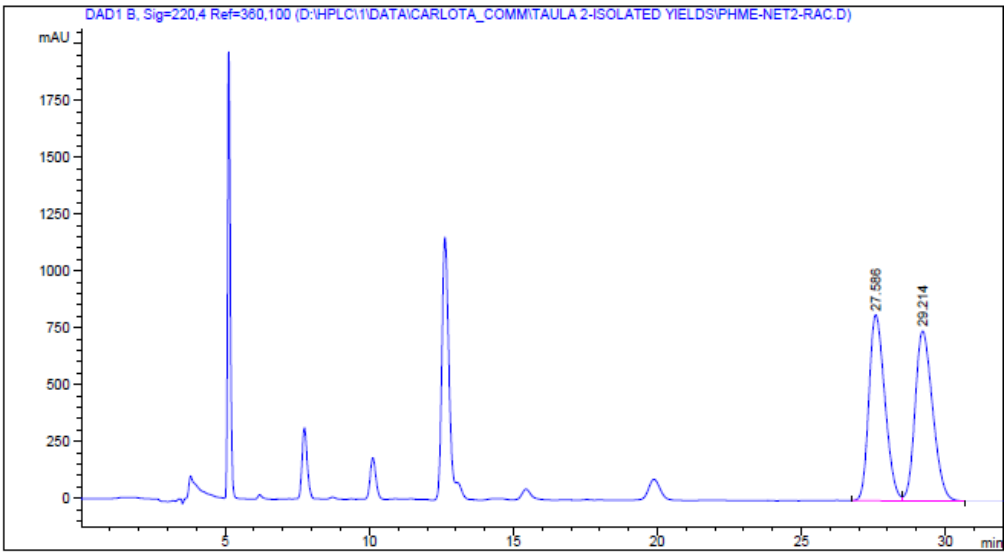
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	13.721	1	BB	1027.15967	46.21970	2.9187
2	21.317	1	BB	3.41651e4	880.51752	97.0813

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25ºC, flow rate = 1 mL/min, λ = 220 nm, t_R(epoxide 1) = 27.6 min, t_R(epoxide 2) = 29.2 min

E4

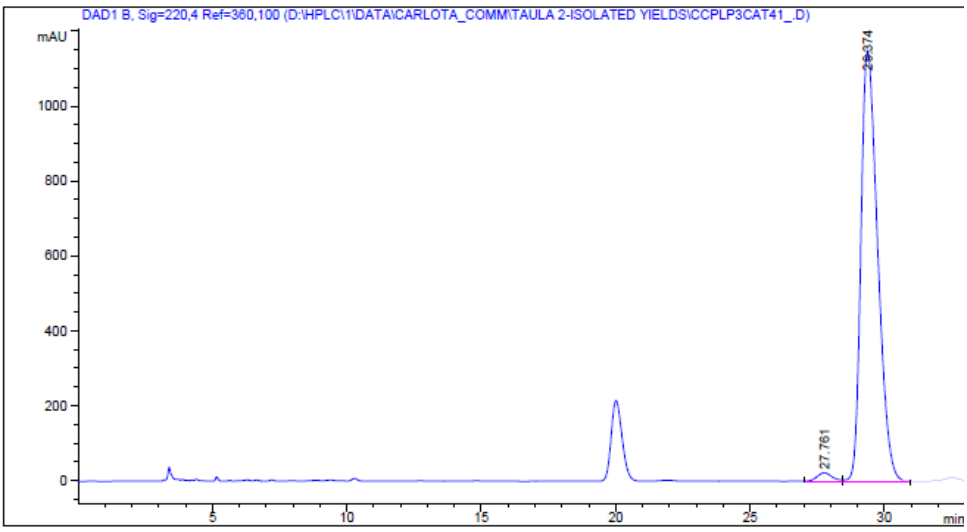


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	27.586	1	BV	3.14809e4	817.74231	49.8199
2	29.214	1	VB	3.17084e4	746.91663	50.1801

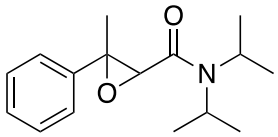
Table 2 entry 2



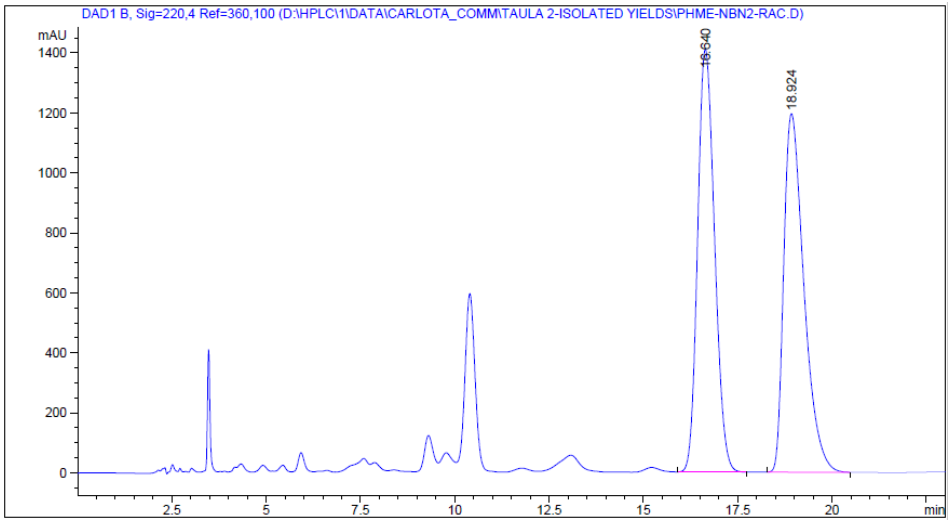
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	27.529	1	BV	1178.49048	31.06512	2.0298
2	28.819	1	VB	5.68811e4	1314.43506	97.9702

HPLC analysis: Chiralpack IC, n-Hex:iPrOH = 80/20, flow rate = 1 mL/min, λ = 220 nm, 25ºC, t.r.e1 = 16.6 min, t.r.e2 = 18.9 min.

E5

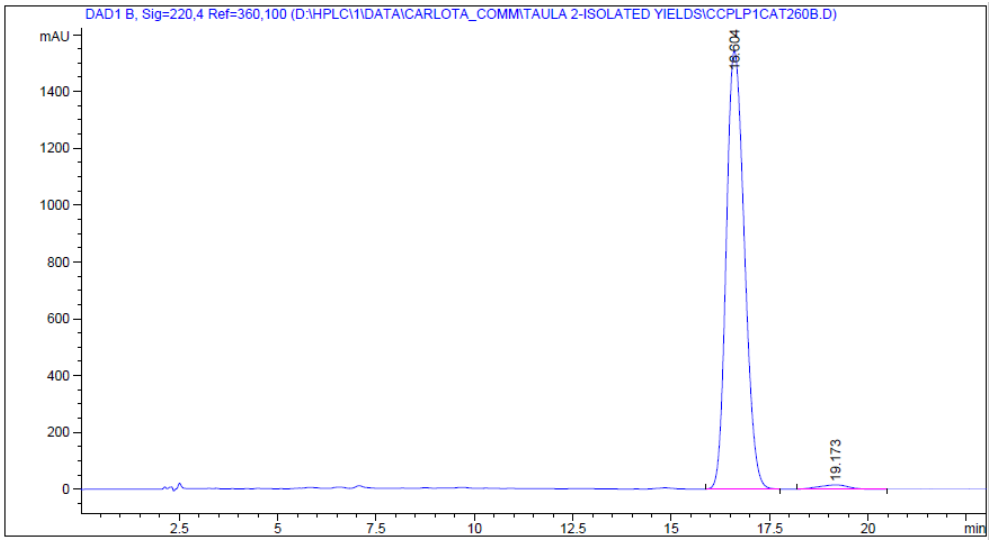


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	16.640	1	VB	4.40184e4	1410.32996	49.7785
2	18.924	1	BB	4.44101e4	1195.04138	50.2215

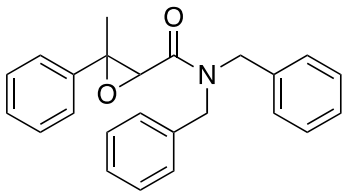
Table 2 entry 3



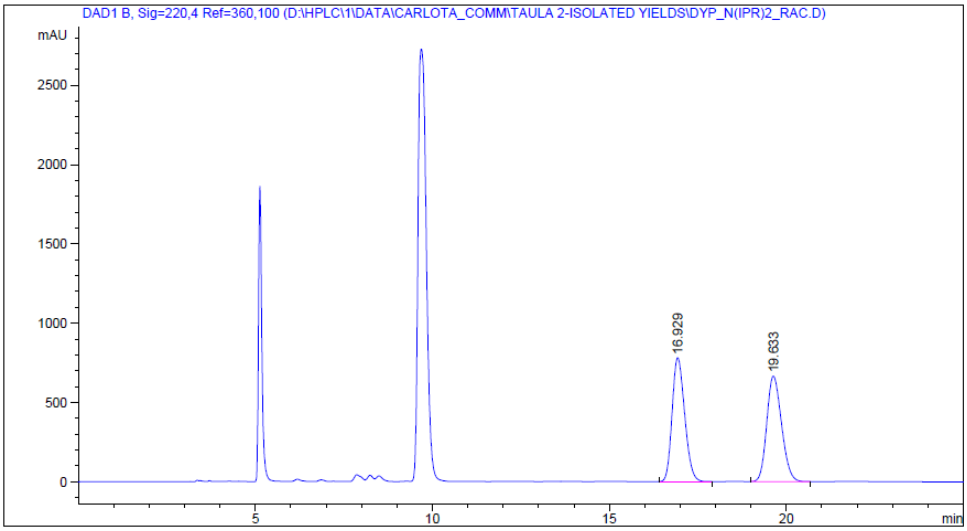
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	16.604	1	BB	4.94818e4	1542.41870	98.5111
2	19.173	1	BB	747.89185	14.96057	1.4889

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25ºC, flow rate = 1 mL/min, λ = 220 nm, t_R(epoxide 1) = 16.9 min, t_R(epoxide 2) = 19.6 min

E6

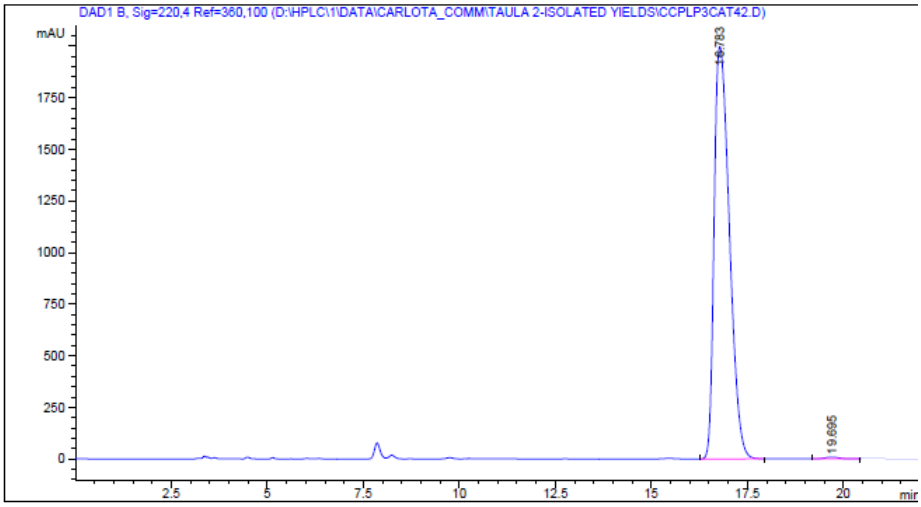


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	16.929	1	BB	1.92740e4	781.71869	49.9245
2	19.633	1	BB	1.93324e4	665.41058	50.0755

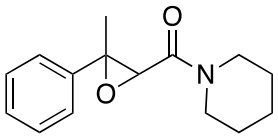
Table 2 entry 4



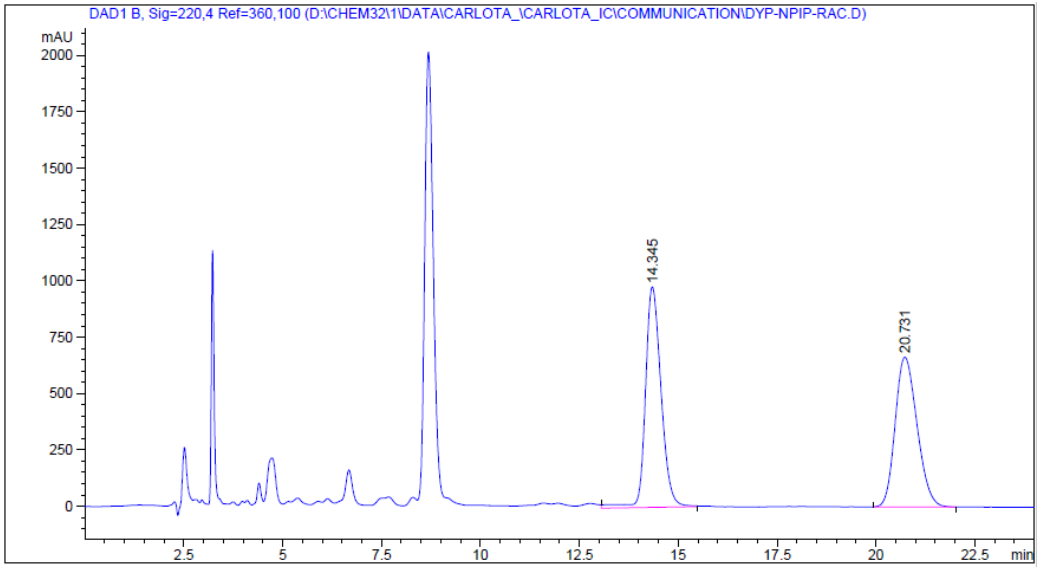
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	16.783	1	BB	5.51819e4	1997.44031	99.6465
2	19.695	1	BB	195.74757	7.57158	0.3535

HPLC analysis: Chiralpack IC, n-Hex:iPrOH = 70/30, flow rate = 1.5 mL/min, λ = 220 nm, 25ºC, t.r.e1 = 14.3 min, t.r.e2 = 20.7 min.

E7

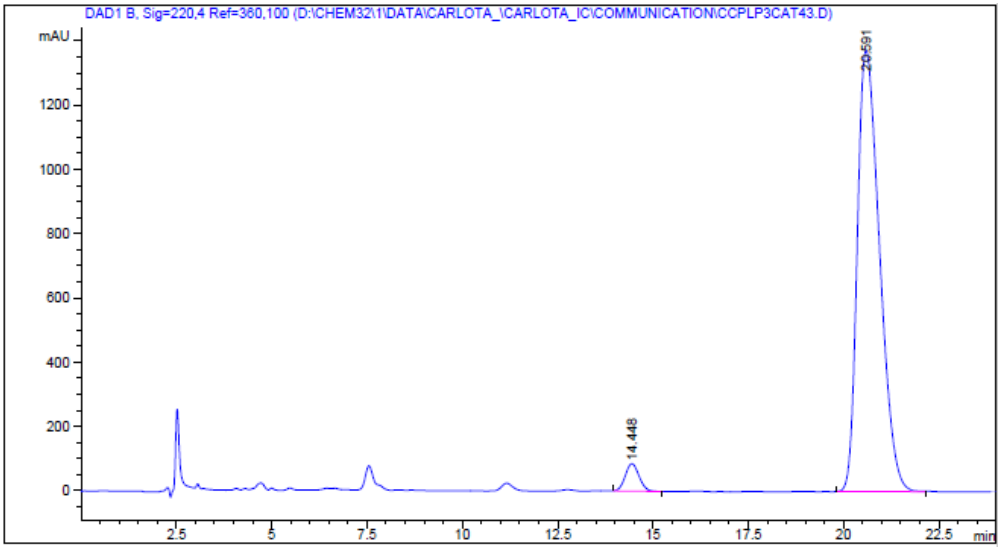


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	14.345	1	VB	2.69810e4	977.88995	51.3664
2	20.731	1	BB	2.55455e4	664.34735	48.6336

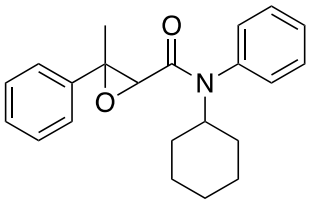
Table 2 entry 5



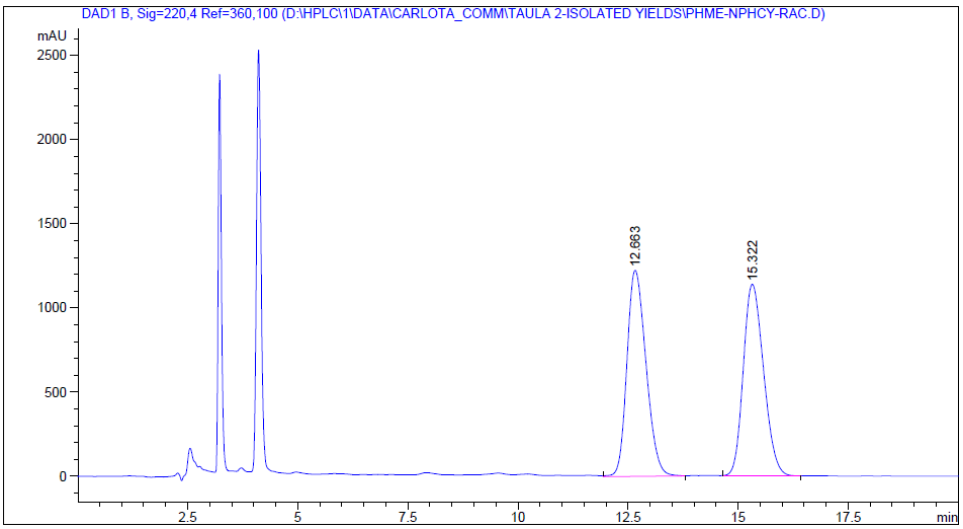
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	14.448	1	BB	2165.39771	85.76028	3.7432
2	20.591	1	BB	5.56833e4	1372.46448	96.2568

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 70/30, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 12.6 min, t_R(epoxide 2) = 15.3 min

E9

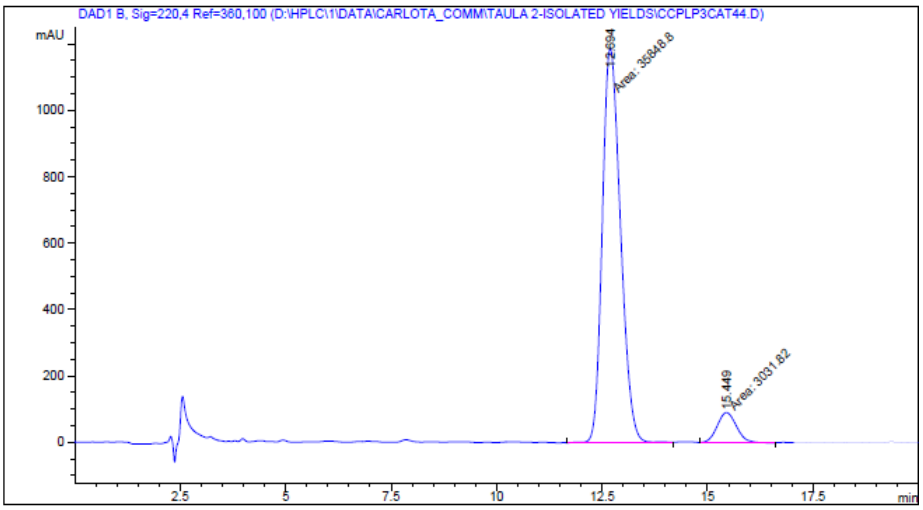


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.663	1	VV	3.68422e4	1223.34424	50.2886
2	15.322	1	BV	3.64194e4	1137.42798	49.7114

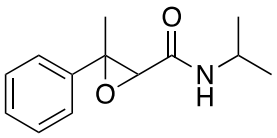
Table 2 entry 7



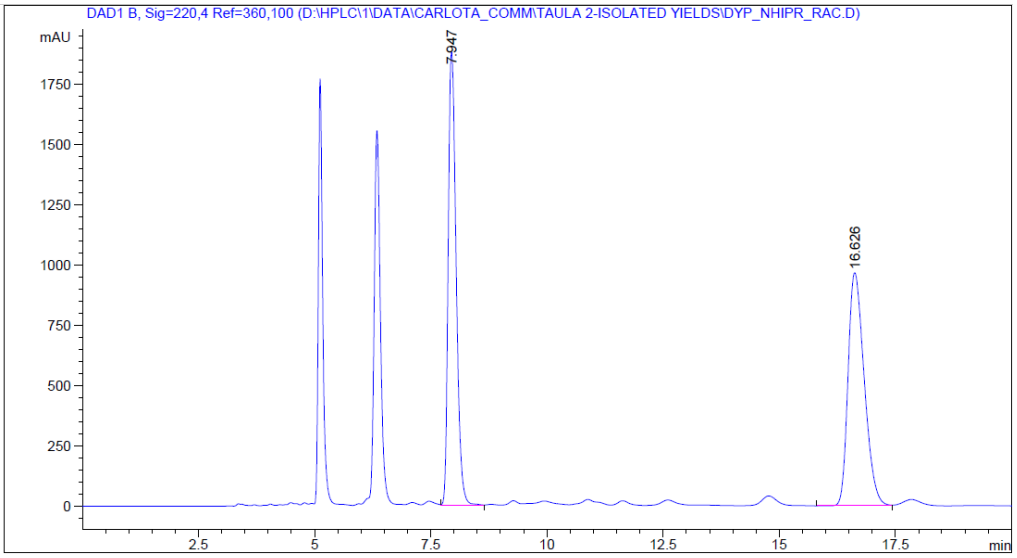
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.694	1	MF	3.58488e4	1189.14258	92.2022
2	15.449	1	FM	3031.81714	92.51637	7.7978

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25°C, flow rate = 1 mL/min, λ = 220 nm, t_R(epoxide 1) = 7.9 min, t_R(epoxide 2) = 16.6 min

E10

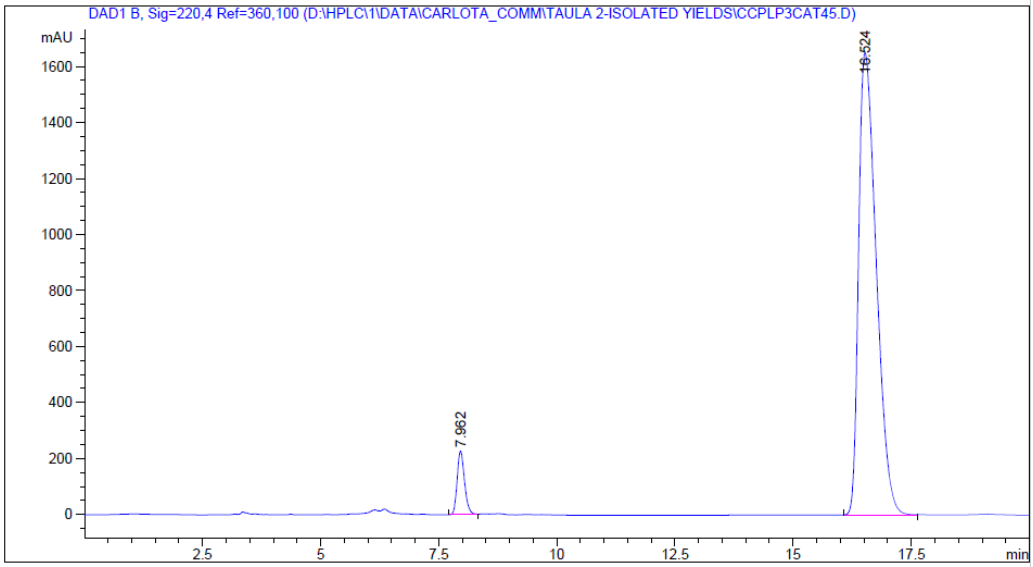


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.947	1	VV	2.24112e4	1882.68323	48.9026
2	16.626	1	VV	2.34170e4	967.02008	51.0974

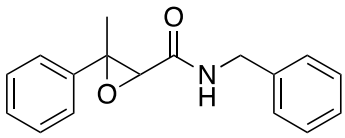
Table 2 entry 8



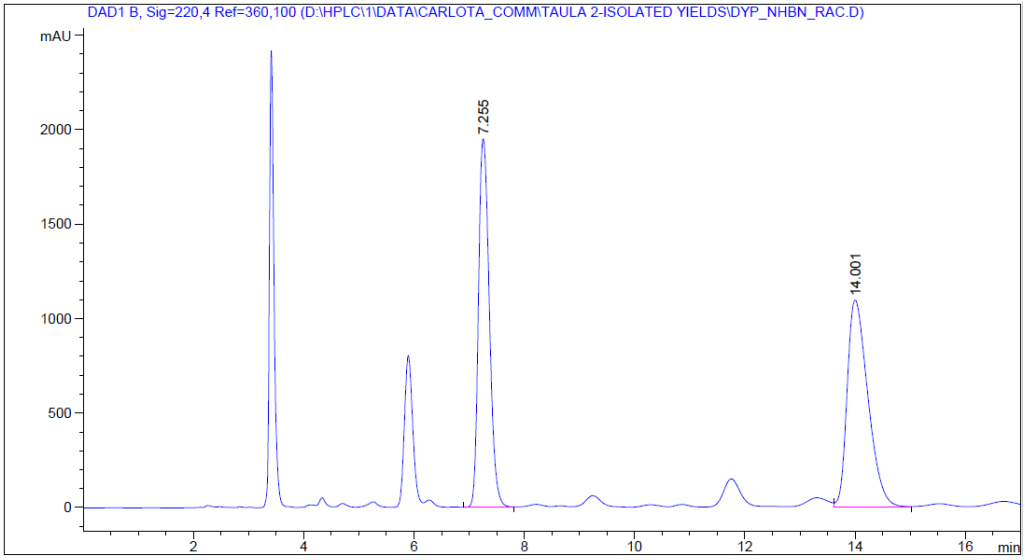
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.962	1	BV	2492.84595	227.69083	5.5035
2	16.524	1	BB	4.28026e4	1650.22705	94.4965

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 7.3 min, t_R(epoxide 2) = 14.0 min

E11

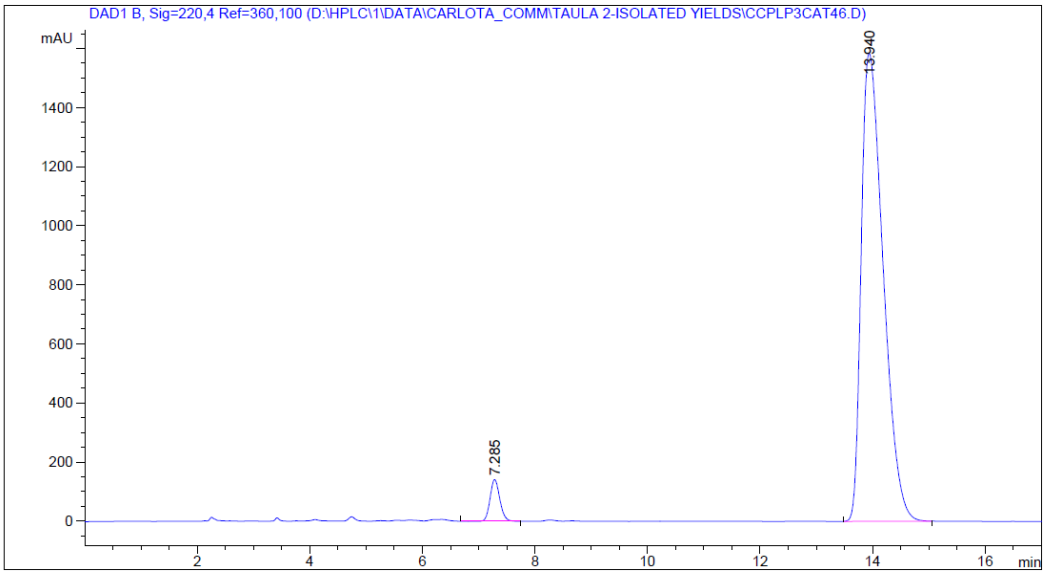


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.255	1	VV	2.66704e4	1950.68091	48.3623
2	14.001	1	VB	2.84767e4	1093.61707	51.6377

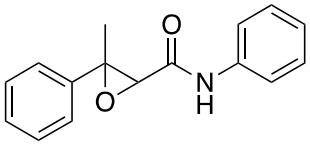
Table 2 entry 9



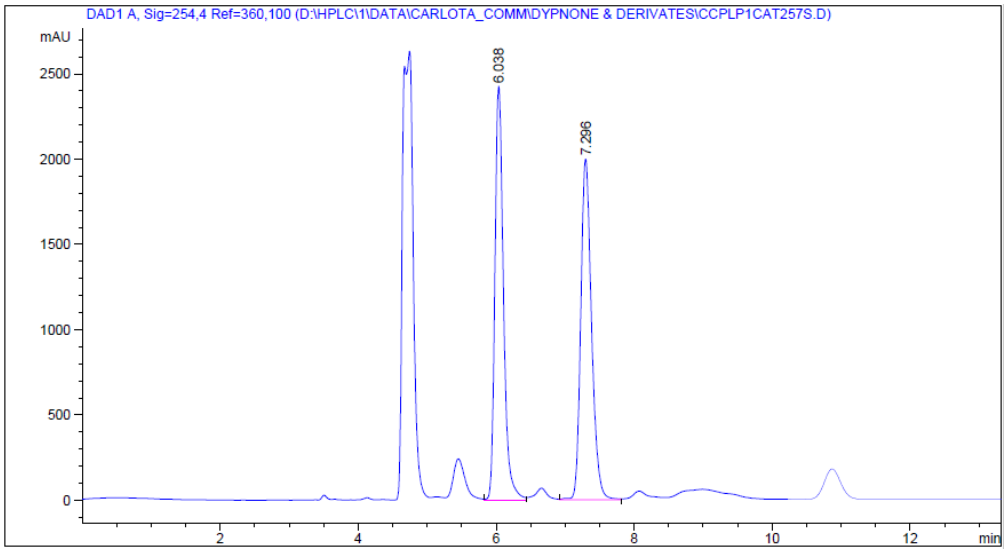
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.285	1	VB	1693.10364	141.02760	3.7981
2	13.940	1	BB	4.28841e4	1584.41846	96.2019

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 70/30, 25°C, flow rate = 1 mL/min, λ = 254 nm, t_R(epoxide 1) = 6.0 min, t_R(epoxide 2) = 7.3 min

E12

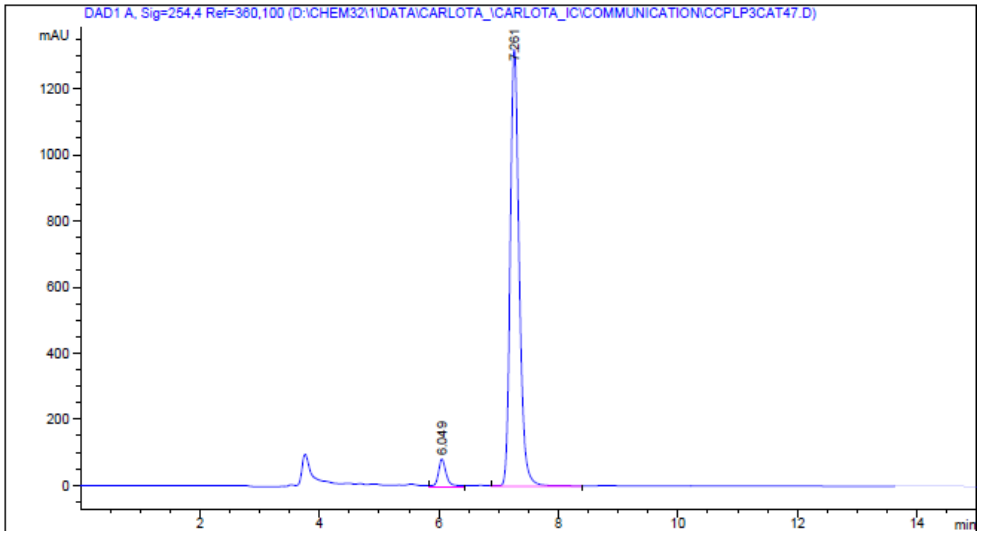


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.038	1	VV	2.09889e4	2424.59424	49.1642
2	7.296	1	VV	2.17025e4	1996.19141	50.8358

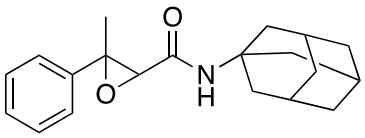
Table 2 entry 10



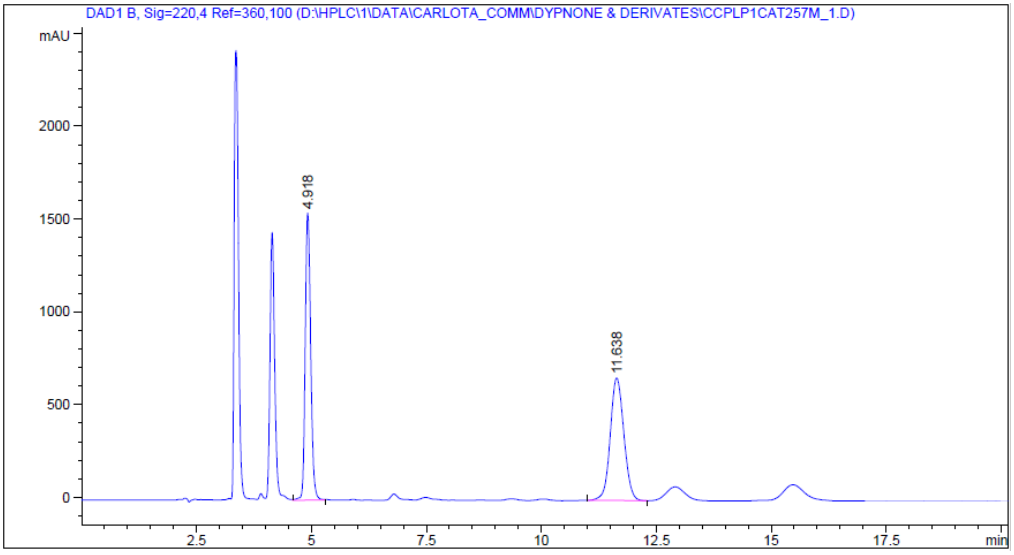
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.049	1	VV	760.36749	82.95781	5.1814
2	7.261	1	VB	1.39144e4	1319.57092	94.8186

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25°C, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 4.9 min, t_R(epoxide 2) = 11.6 min

E13

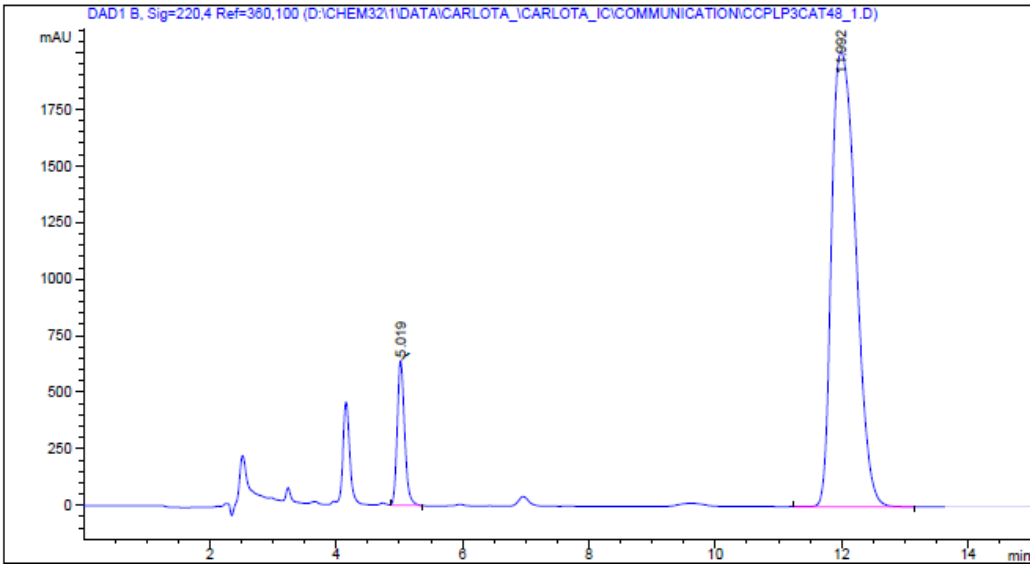


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	4.918	1	VB	1.28114e4	1546.19604	48.5114
2	11.638	1	BB	1.35977e4	660.31378	51.4886

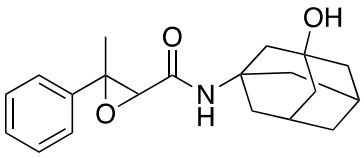
Table 2 entry 11



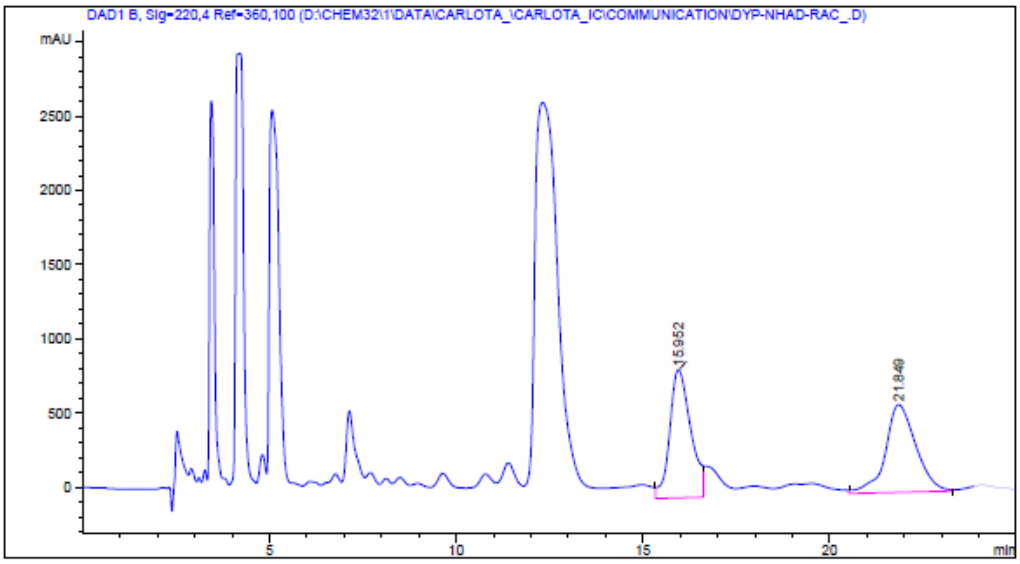
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.019	1	MM	5186.63135	638.75879	8.8273
2	11.992	1	BB	5.35701e4	2009.85632	91.1727

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25°C, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 15.9 min, t_R(epoxide 2) = 21.8 min

EO13

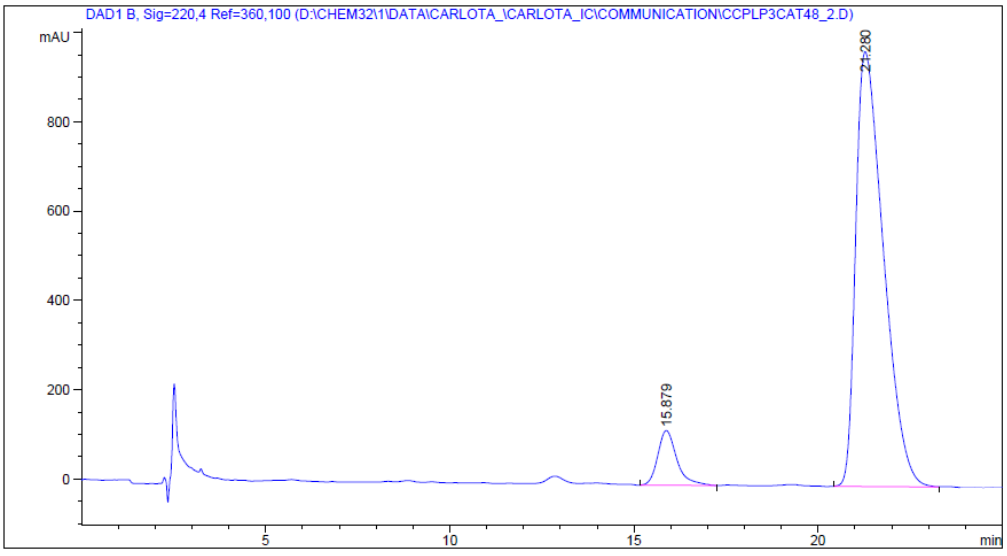


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	15.952	1	MF	3.38154e4	864.04572	50.2509
2	21.849	1	VV	3.34778e4	590.49371	49.7491

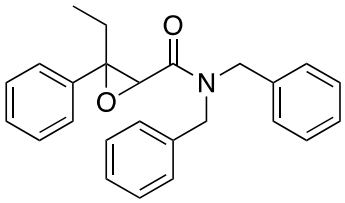
Table 2 entry 11



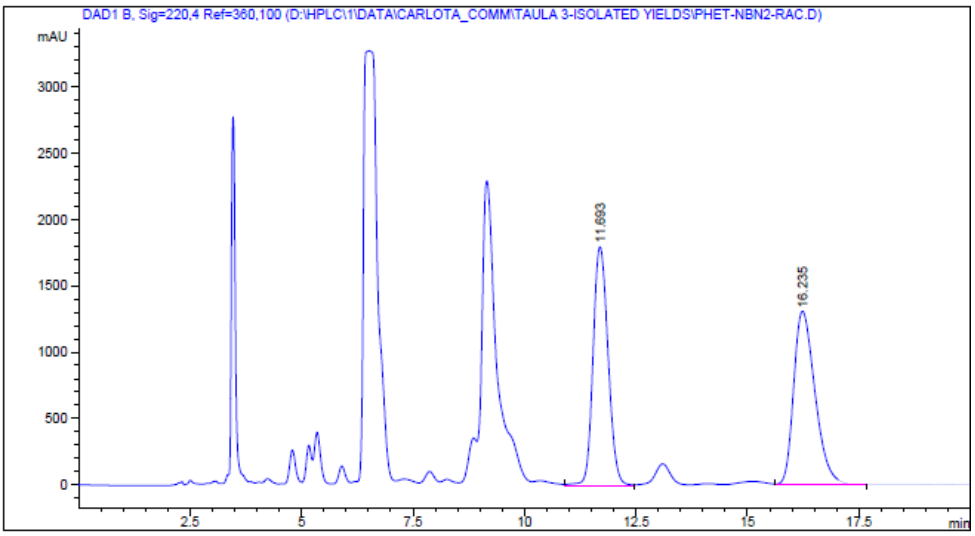
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	15.879	1	BB	4388.79004	122.38078	7.9041
2	21.280	1	BB	5.11366e4	974.14526	92.0959

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 11.7 min, t_R(epoxide 2) = 16.2 min

E14

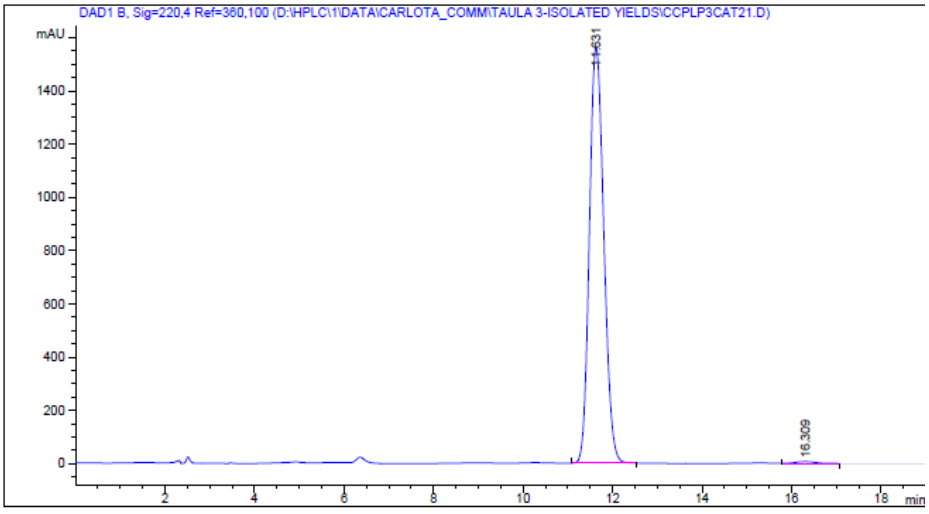


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	11.693	1	VV	4.19461e4	1797.18799	48.8658
2	16.235	1	VB	4.38932e4	1311.67285	51.1342

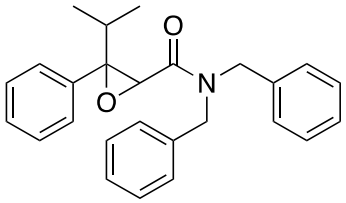
Table 3 entry 1



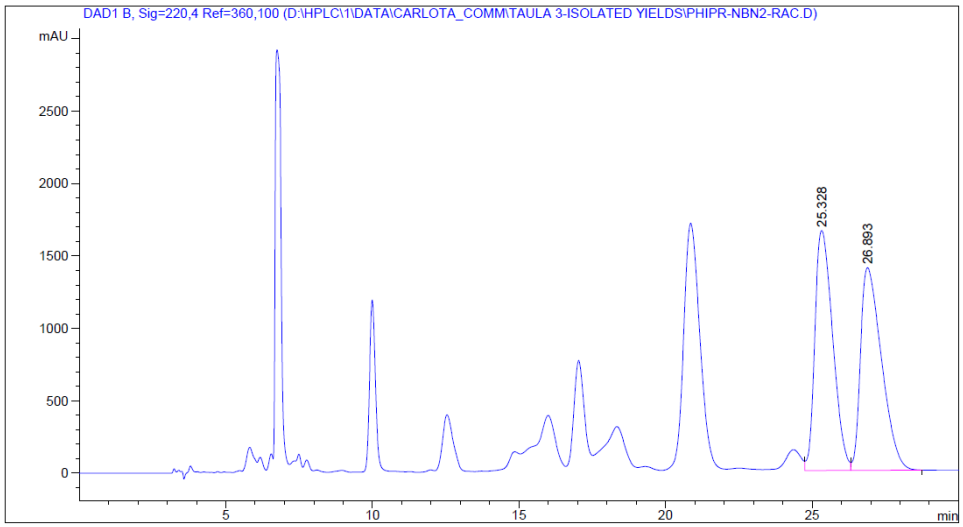
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	11.631	1	BB	3.49396e4	1562.86584	99.4574
2	16.309	1	BB	190.62032	6.33166	0.5426

HPLC analysis: Chiralpack IA, *n*-Hex:^{i}PrOH = 90/10, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 25.3 min, t_R(epoxide 2) = 26.9 min

E15

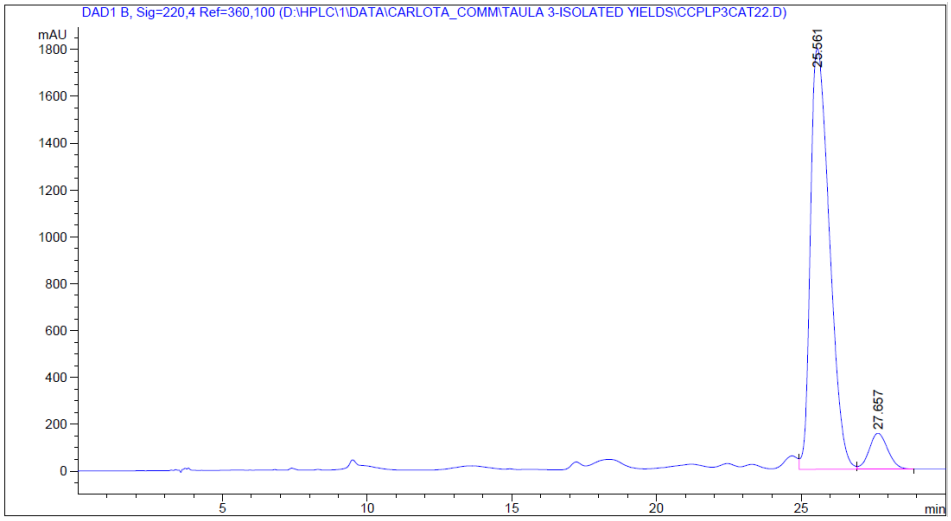


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	25.328	1	VV	7.00775e4	1655.96509	50.0621
2	26.893	1	VB	6.99036e4	1398.50403	49.9379

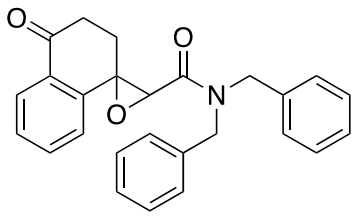
Table 3 entry 2



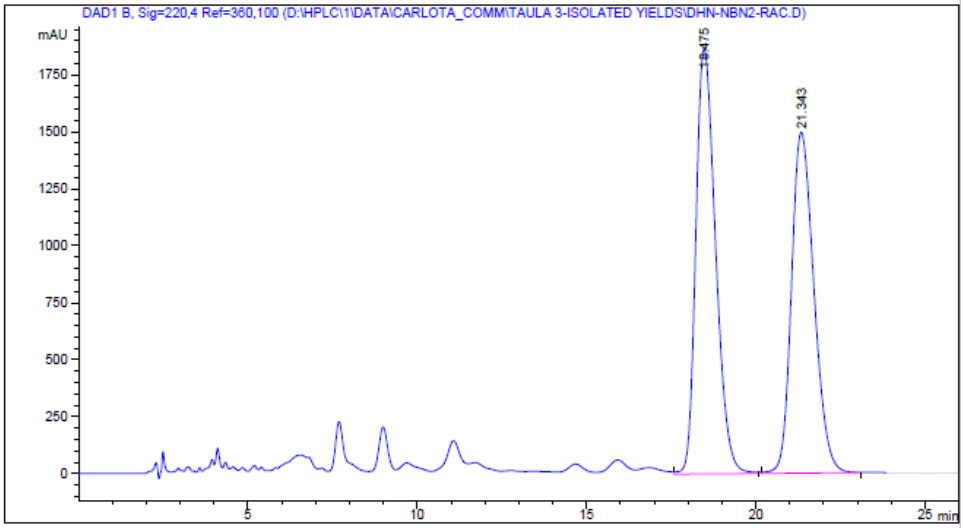
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	25.561	1	VV	8.22709e4	1797.31079	92.2980
2	27.657	1	VB	6865.26611	153.87462	7.7020

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 70/30, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 18.5 min, t_R(epoxide 2) = 21.3 min

EK16

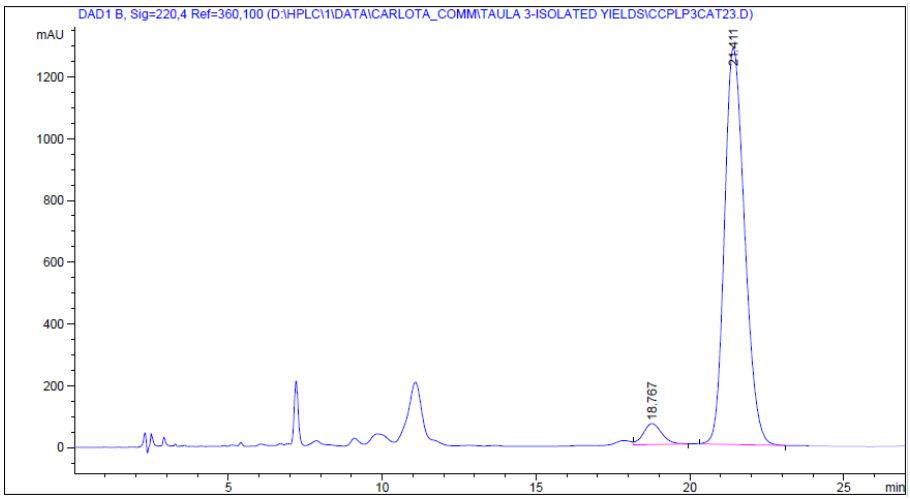


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	18.475	1	VB	7.55551e4	1866.57214	52.3135
2	21.343	1	BB	6.88725e4	1496.13428	47.6865

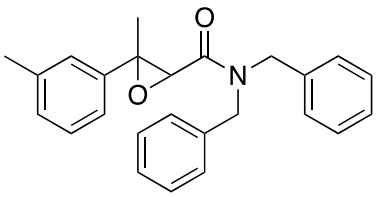
Table 3 entry 3



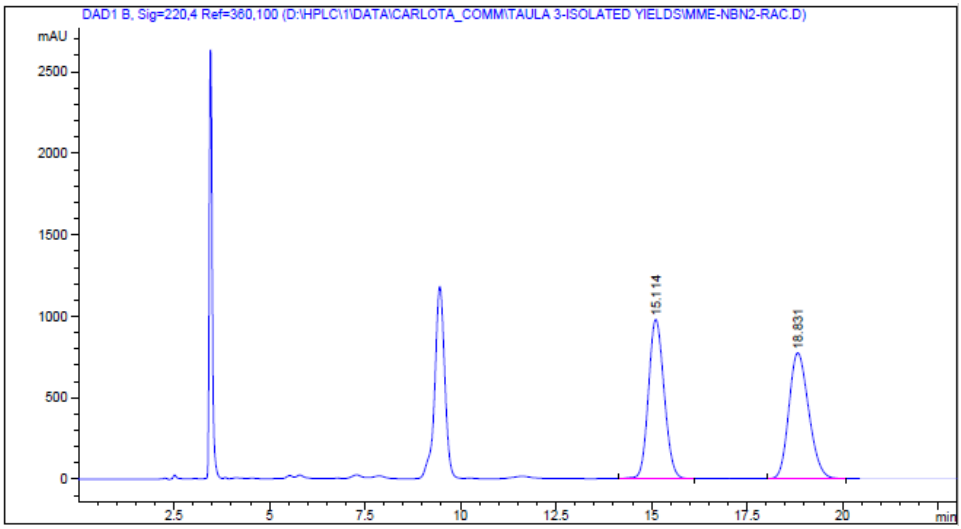
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	18.767	1	VB	2842.10303	67.73098	4.6414
2	21.411	1	BB	5.83923e4	1283.93262	95.3586

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 15.1 min, t_R(epoxide 2) = 18.8 min

E18

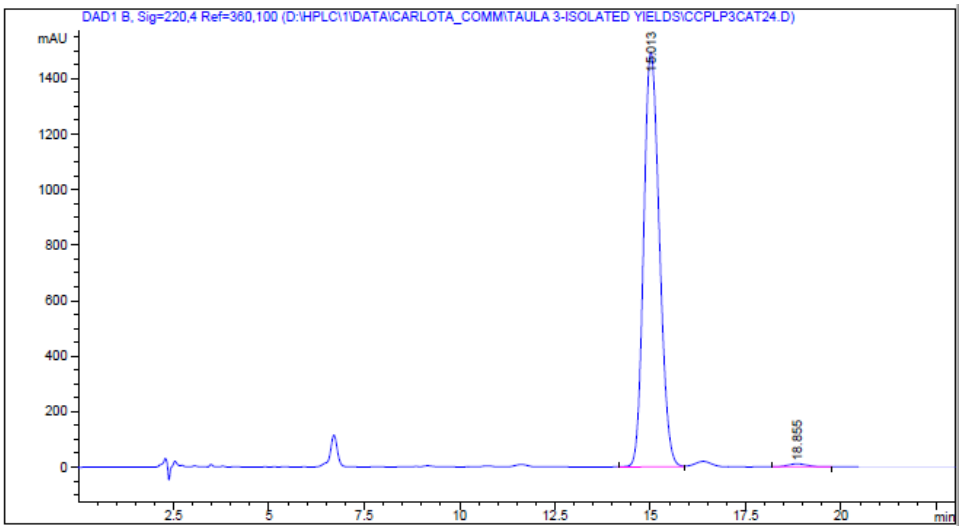


Racemic



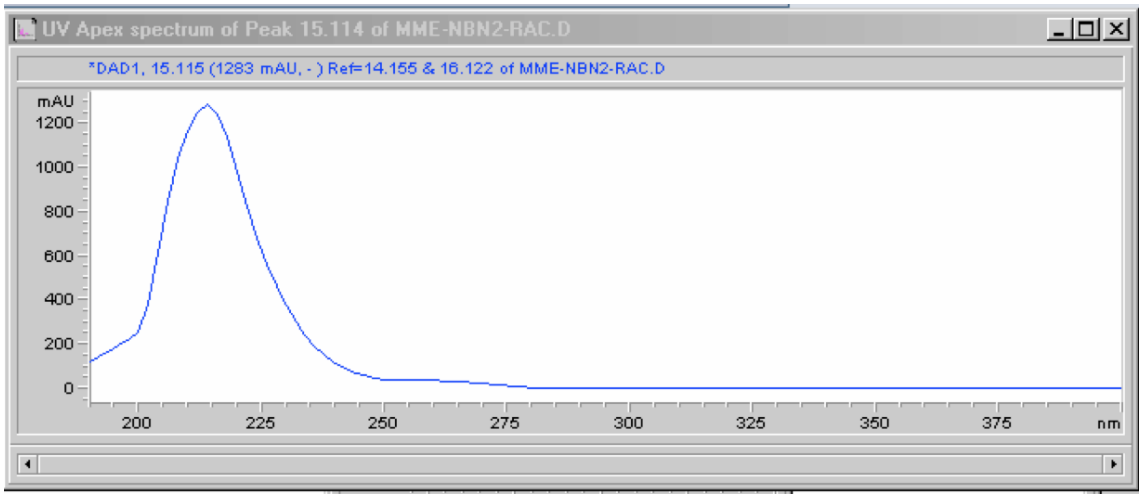
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	15.114	1	BB	2.78229e4	976.66205	50.0215
2	18.831	1	VB	2.77990e4	771.61194	49.9785

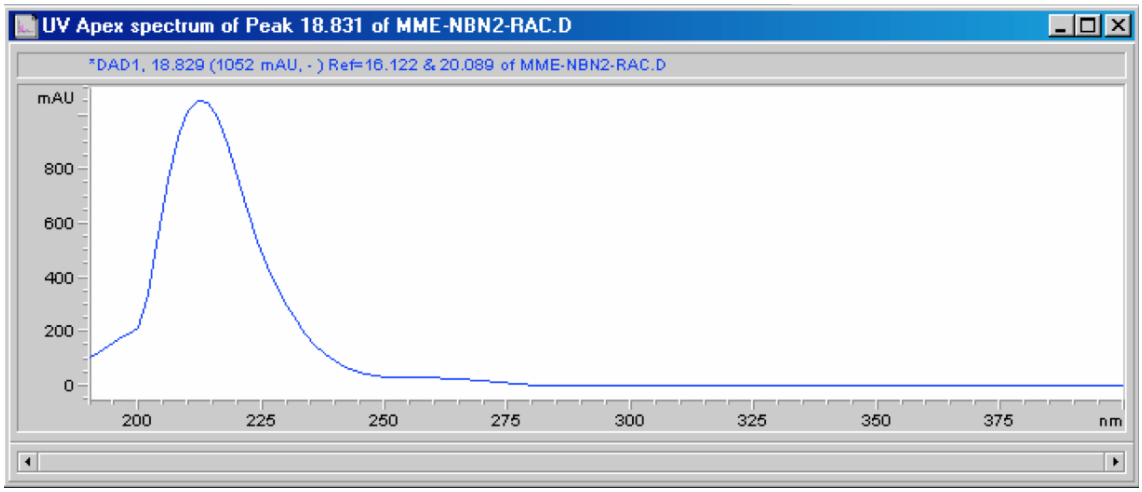
Table 3 entry 5



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	15.013	1	BV	4.28163e4	1493.05298	99.2228
2	18.855	1	BB	335.36014	10.41287	0.7772

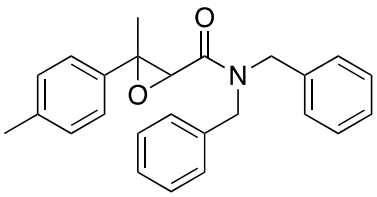
UV-VIS spectra of the enantiomers

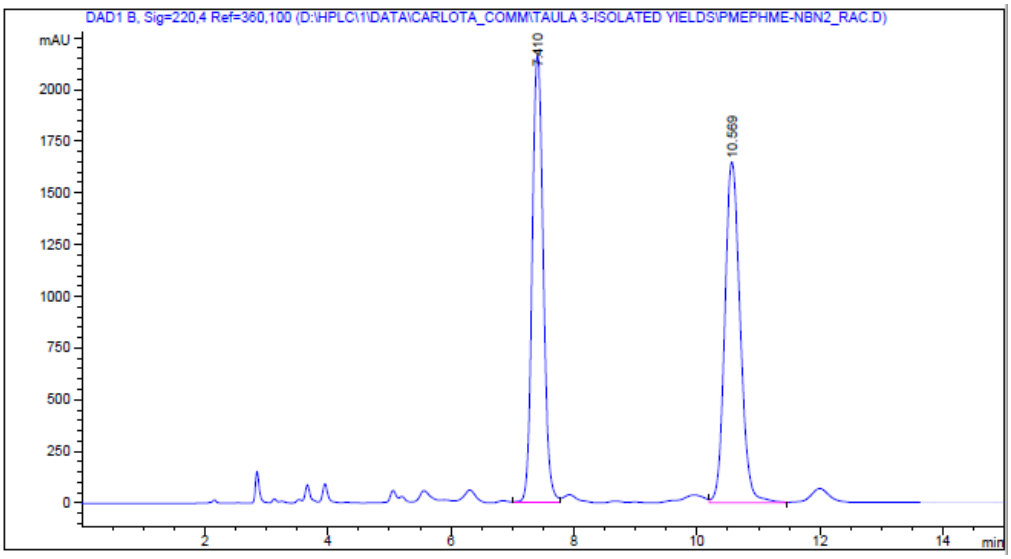




HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25°C, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 7.4 min, t_R(epoxide 2) = 10.6 min

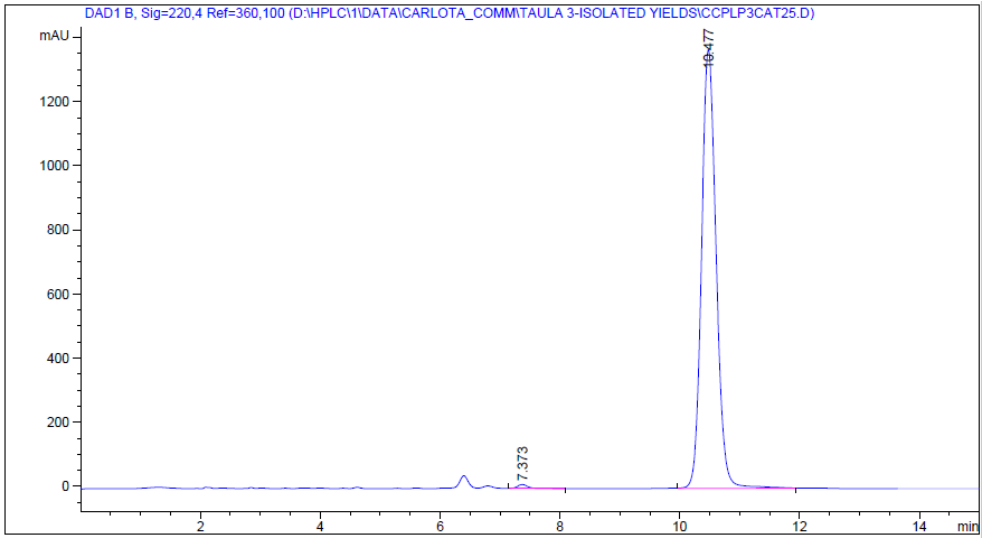
E19





Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.410	1	VV	2.71706e4	2167.49390	48.6957
2	10.569	1	VV	2.86261e4	1648.69360	51.3043

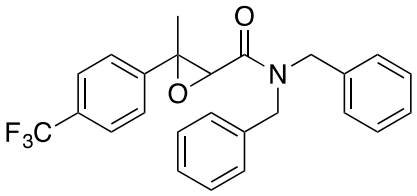
Table 3 entry 6



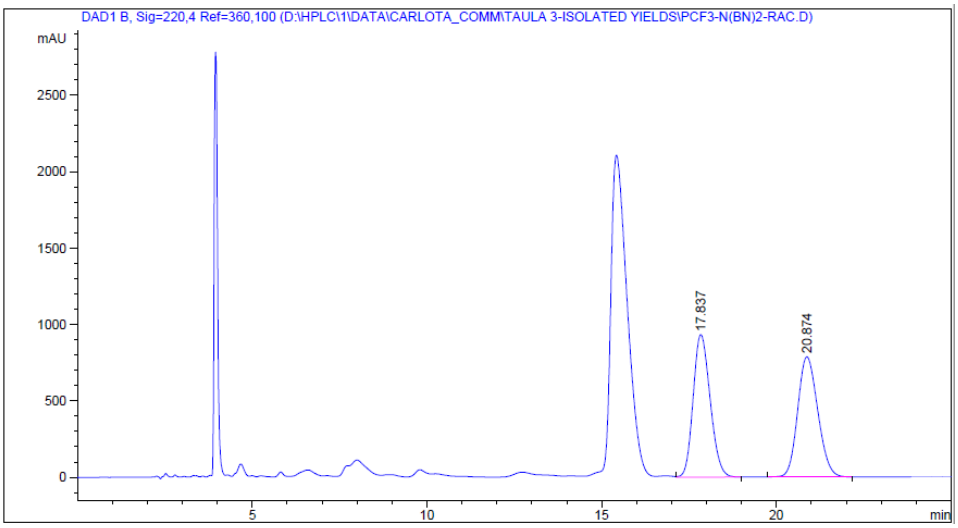
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.373	1	VB	173.99872	12.86082	0.7455
2	10.477	1	BB	2.31660e4	1368.26013	99.2545

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 90/10, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 17.8 min, t_R(epoxide 2) = 20.9 min

E20

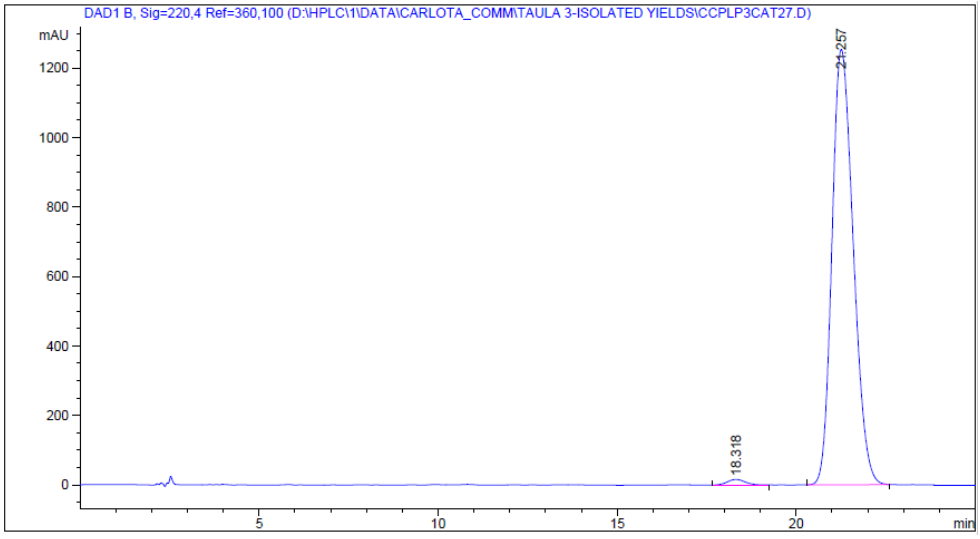


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	17.837	1	VB	3.15441e4	932.99780	50.0498
2	20.874	1	BB	3.14813e4	786.32996	49.9502

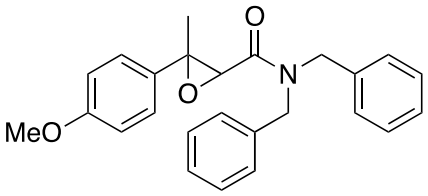
Table 3 entry 7



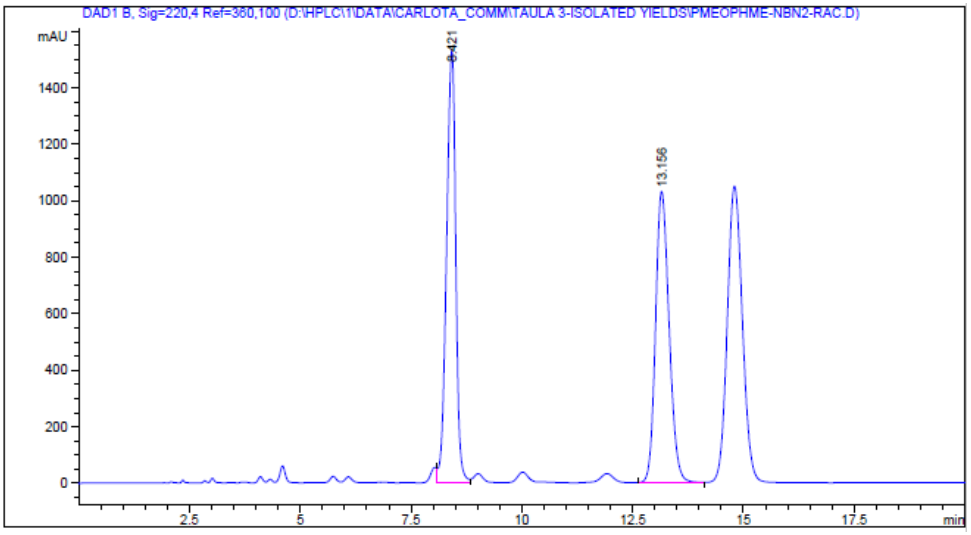
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	18.318	1	BB	552.63336	15.94539	1.0541
2	21.257	1	BB	5.18726e4	1254.39453	98.9459

HPLC analysis: Chiralpack IA, *n*-Hex:^{i}PrOH = 80/20, 25°C, flow rate = 1 mL/min, λ = 220 nm, t_R(epoxide 1) = 8.4 min, t_R(epoxide 2) = 13.2 min

E21

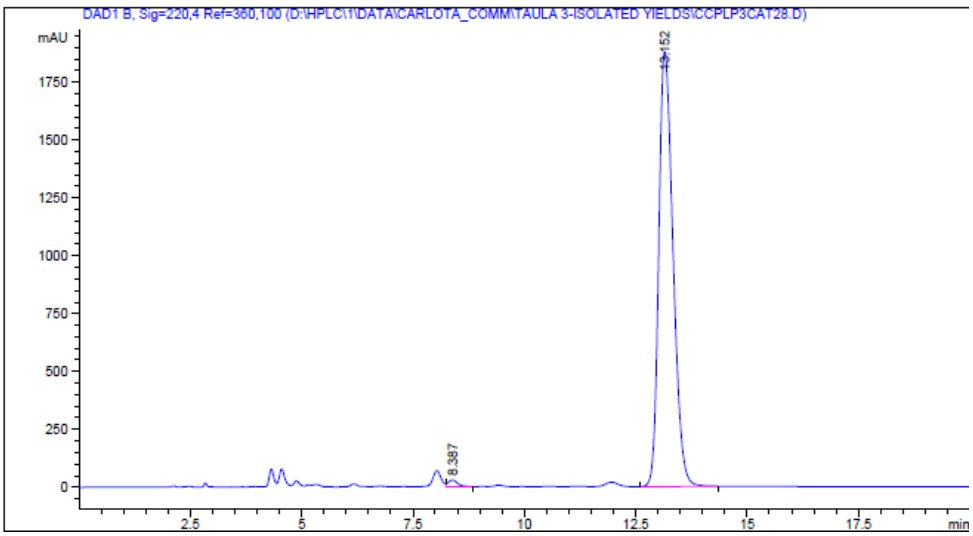


Racemic



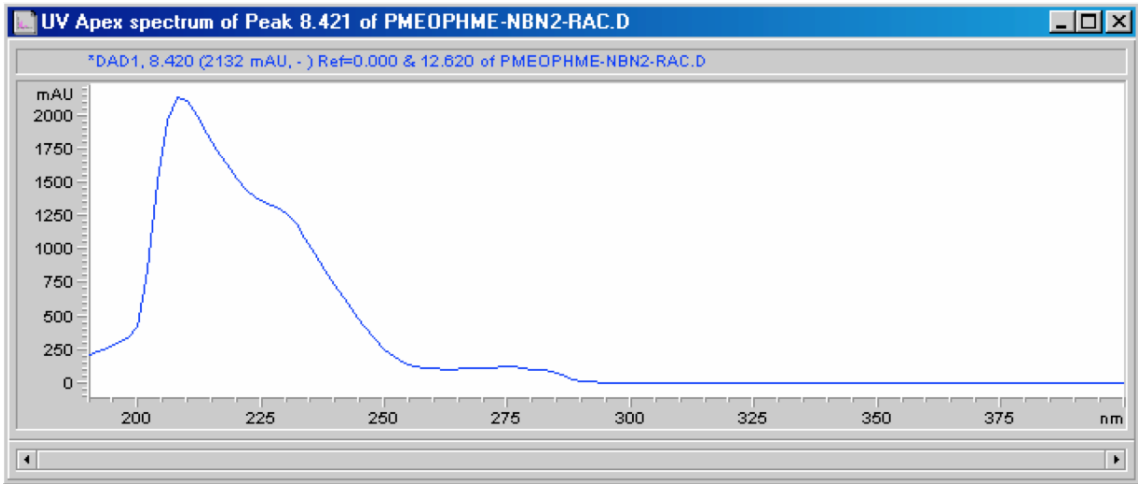
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	8.421	1	VV	2.21207e4	1532.08618	50.1642
2	13.156	1	BB	2.19758e4	1032.05066	49.8358

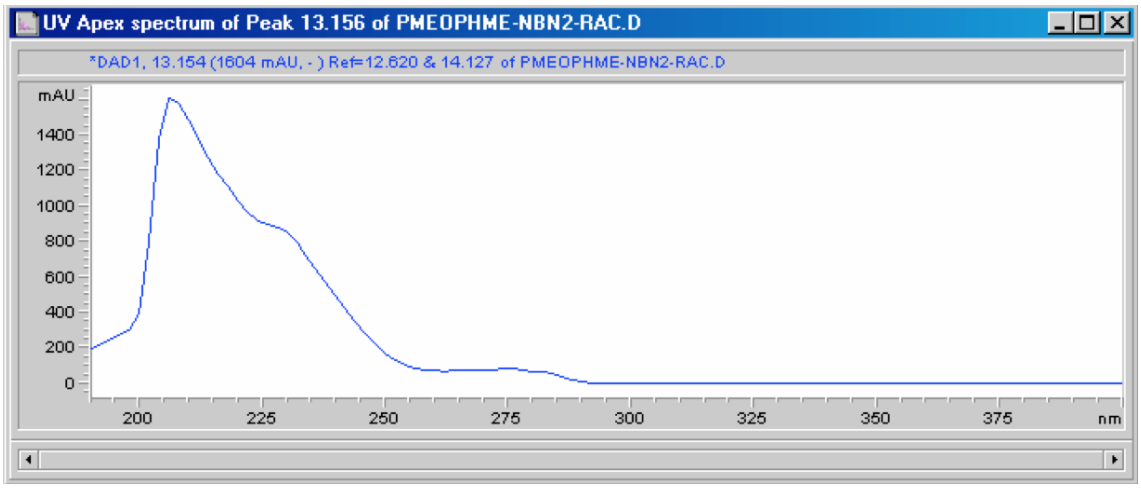
Table 3 entry 8



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	8.387	1	VB	439.49020	29.37983	1.0403
2	13.152	1	BB	4.18078e4	1879.75378	98.9597

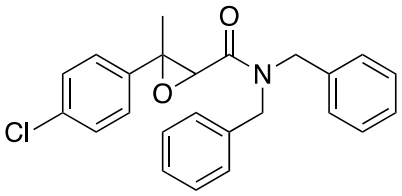
UV-VIS spectra of the enantiomers



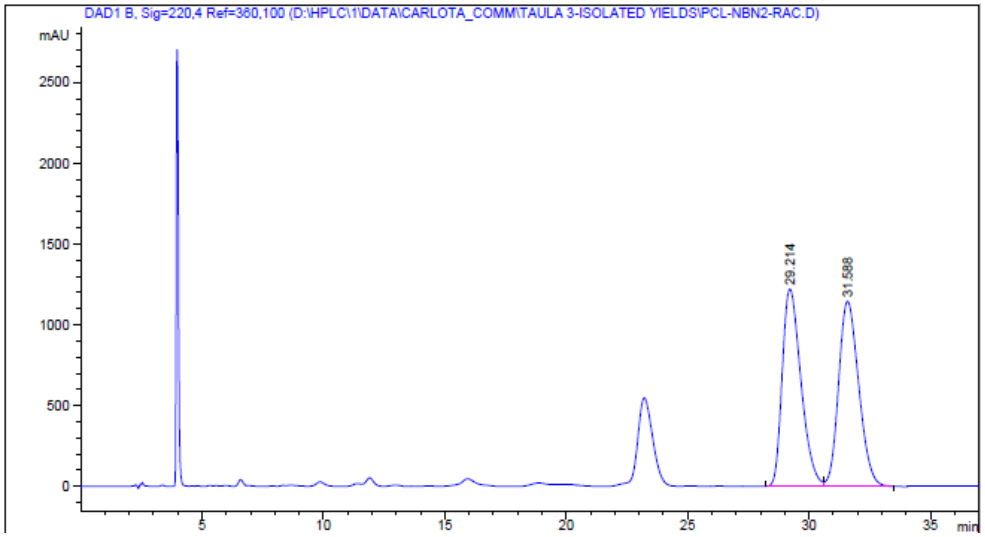


HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 90/10, 25ºC, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 29.2 min, t_R(epoxide 2) = 31.6 min

E22

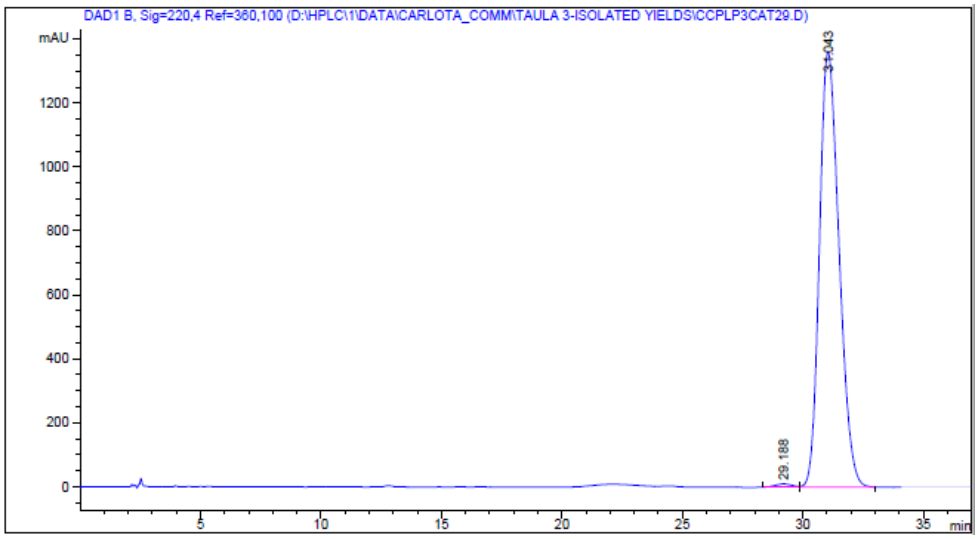


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	29.214	1	BV	6.57155e4	1222.97876	49.7979
2	31.588	1	VB	6.62488e4	1146.67346	50.2021

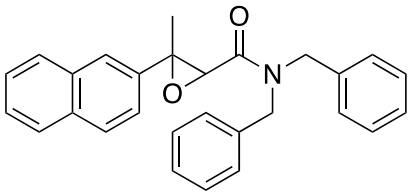
Table 3 entry 9



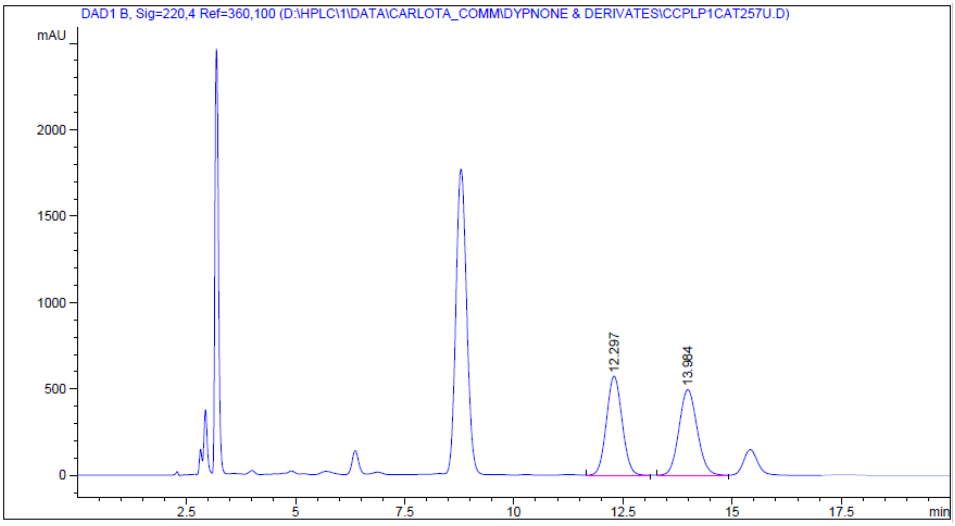
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	29.188	1	BV	482.96341	9.95271	0.6221
2	31.043	1	VB	7.71511e4	1361.76770	99.3779

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 70/30, 25°C, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 12.2 min, t_R(epoxide 2) = 14.0 min

E23

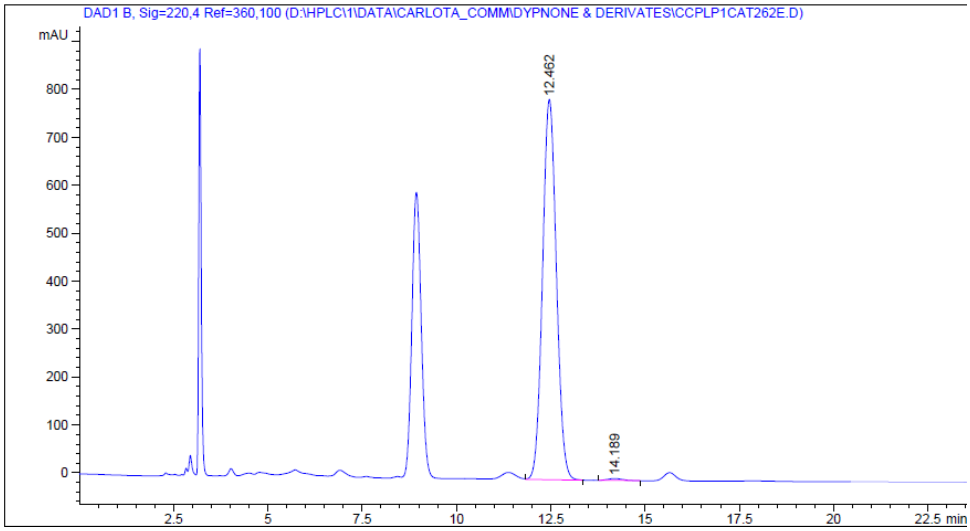


Racemic



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.297	1	VB	1.44287e4	575.23767	49.9437
2	13.984	1	BB	1.44613e4	496.92017	50.0563

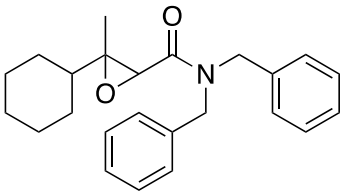
Table 3 entry 10



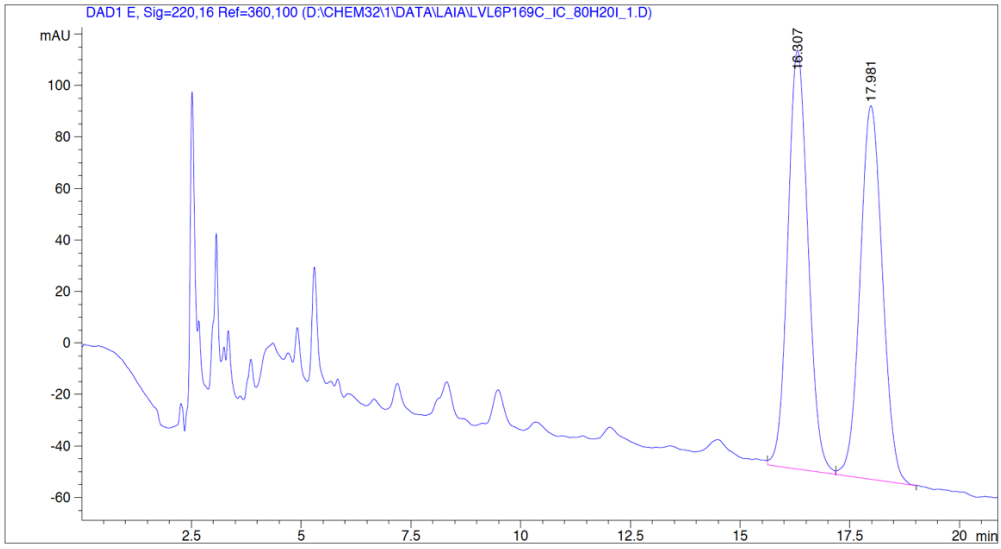
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.462	1	VB	2.02480e4	793.72601	99.4953
2	14.189	1	BB	102.70363	3.76235	0.5047

HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 80/20, 25°C, flow rate = 1.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 16.6 min, t_R(epoxide 2) = 18.7 min

E24

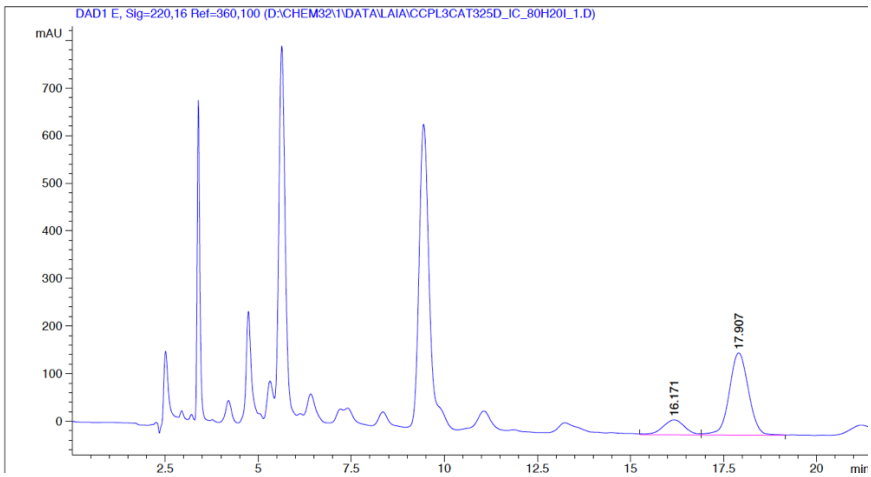


Racemic



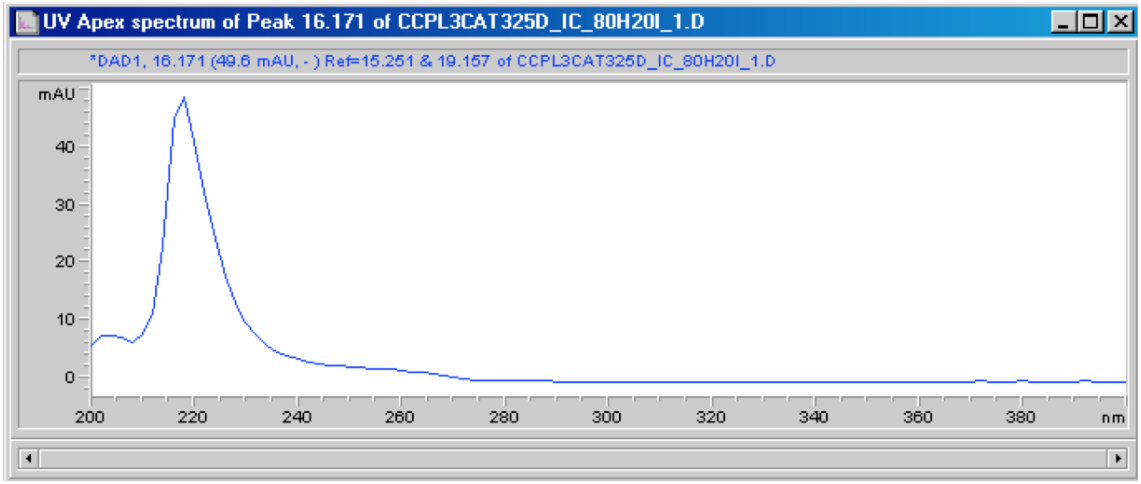
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.307	BV	0.4999	5215.23242	162.72824	50.3526
2	17.981	VB	0.5394	5142.18164	145.11638	49.6474

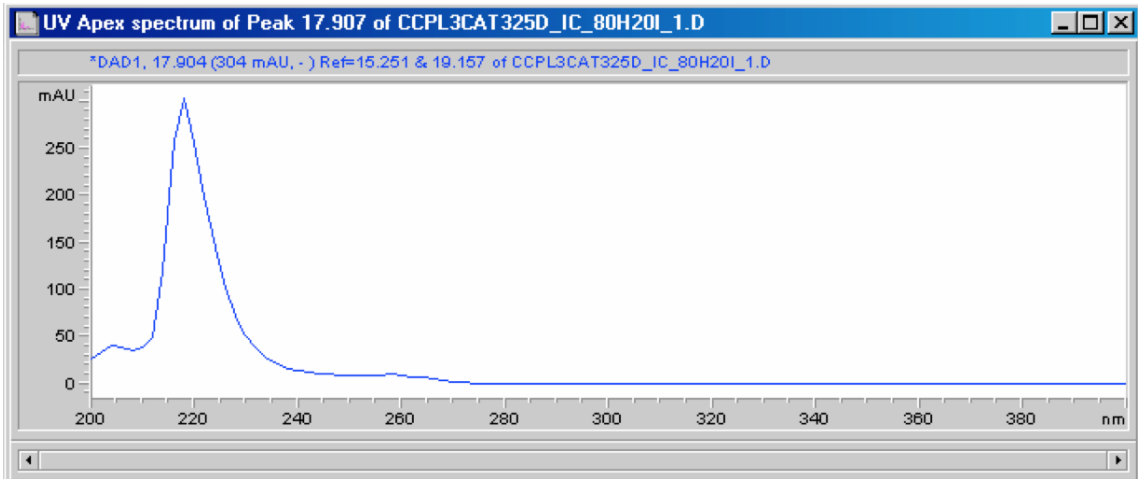
Table 3 entry 11



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.171	BV	0.5517	1297.28491	31.54834	17.3078
2	17.907	VB	0.5585	6198.08105	172.78435	82.6922

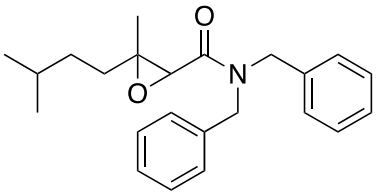
UV-VIS spectra of the enantiomers



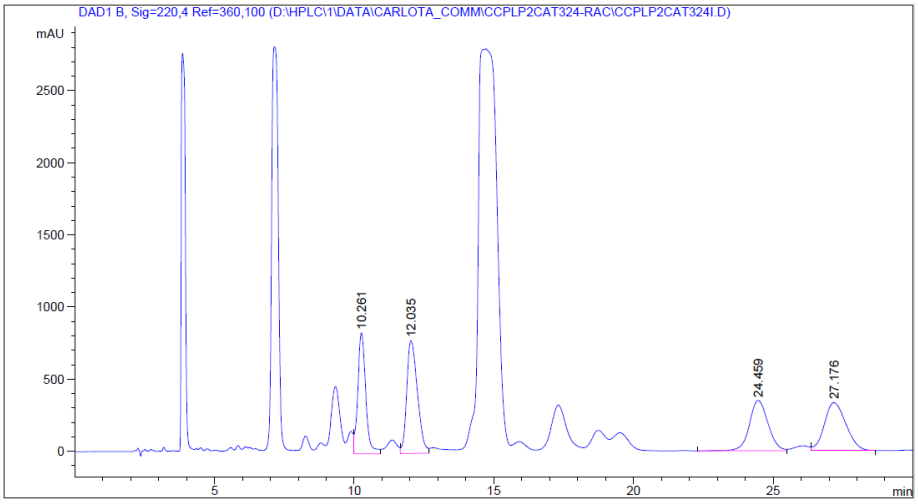


HPLC analysis: Chiralpack IC, *n*-Hex:^{i}PrOH = 90/10, 25°C, flow rate = 1.5 mL/min, λ = 220 nm, *Z* isomer: t_R(epoxide 1) = 10.3 min, t_R(epoxide 2) = 12.0 min; *E* isomer: t_R(epoxide 1) = 24.5 min, t_R(epoxide 2) = 27.2 min

E25

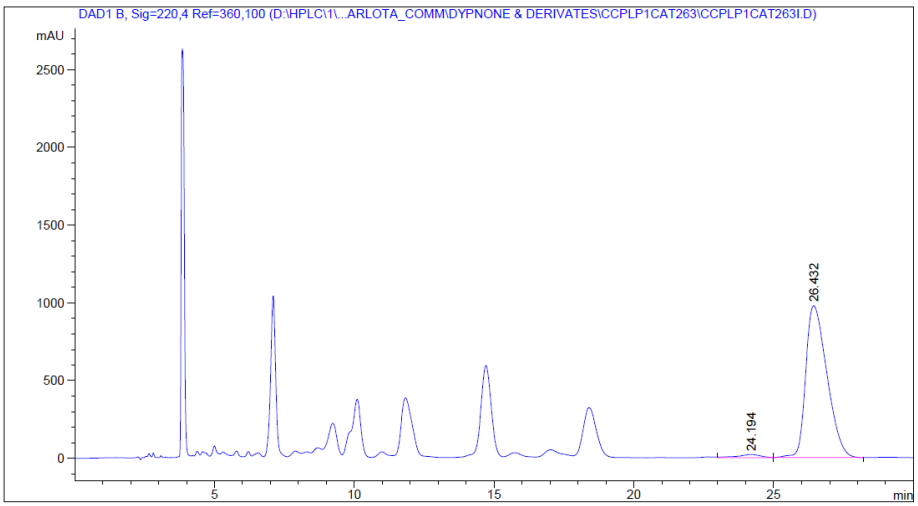


Racemic



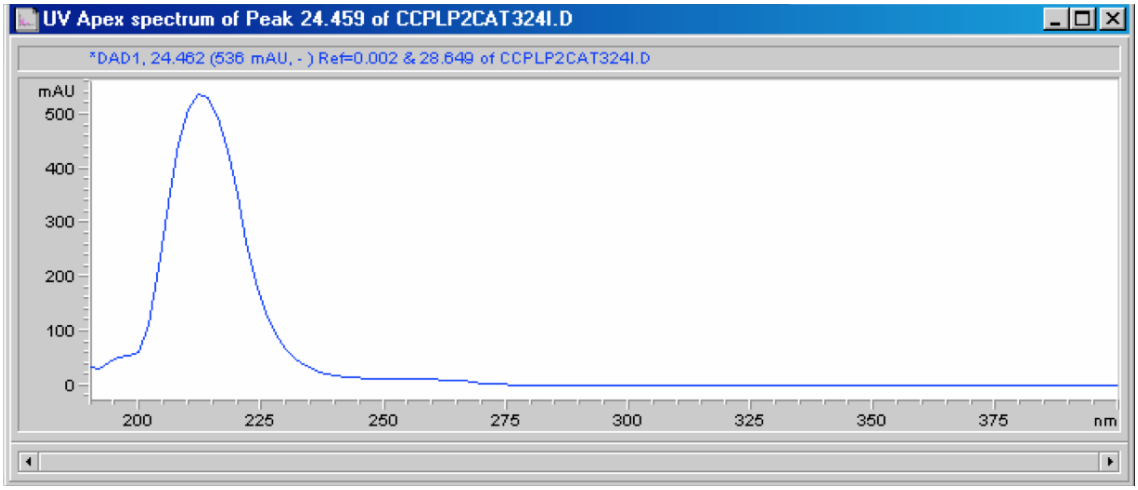
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	10.261	1	VV	1.66112e4	838.82520	23.2910
2	12.035	1	VV	2.08040e4	781.31110	29.1697
3	24.459	1	VV	1.61131e4	348.75607	22.5926
4	27.176	1	VB	1.77921e4	332.53174	24.9467

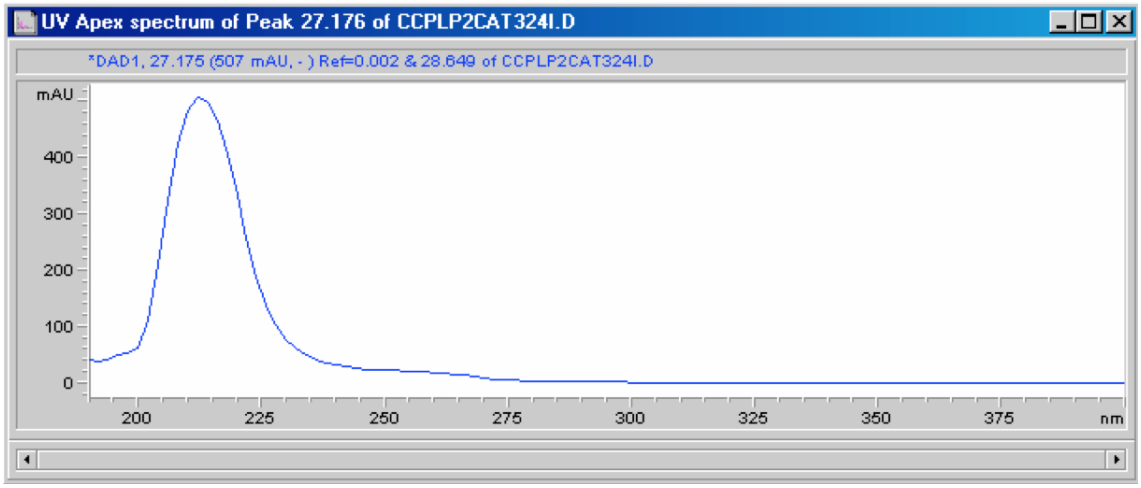
Table 3 entry 12



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	24.194	1	VV	1216.56104	20.95632	2.3052
2	26.432	1	VB	5.15577e4	977.36768	97.6948

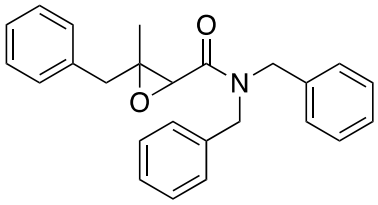
UV-VIS spectra of the enantiomers



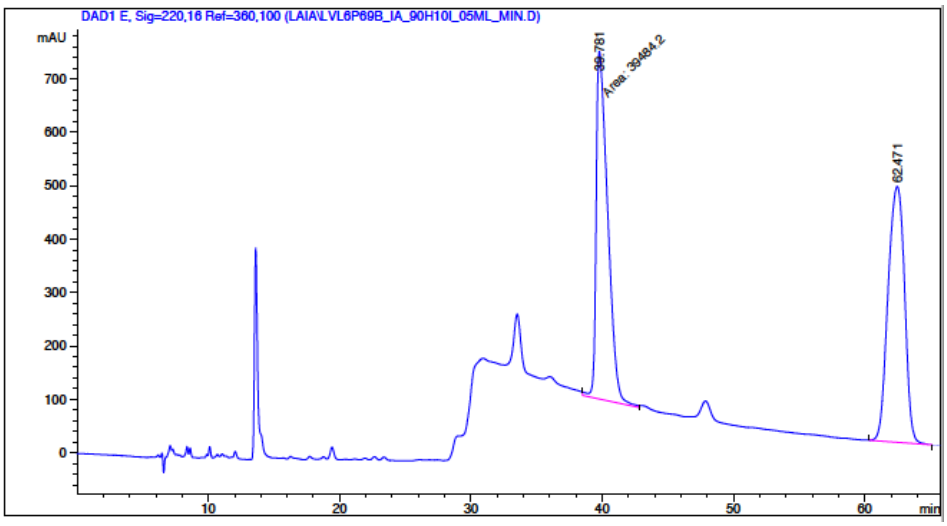


HPLC analysis: Chiralpack IA, *n*-Hex:^{i}PrOH = 90/10, 25°C, flow rate = 0.5 mL/min, λ = 220 nm, t_R(epoxide 1) = 37.0 min, t_R(epoxide 2) = 56.8 min

E26

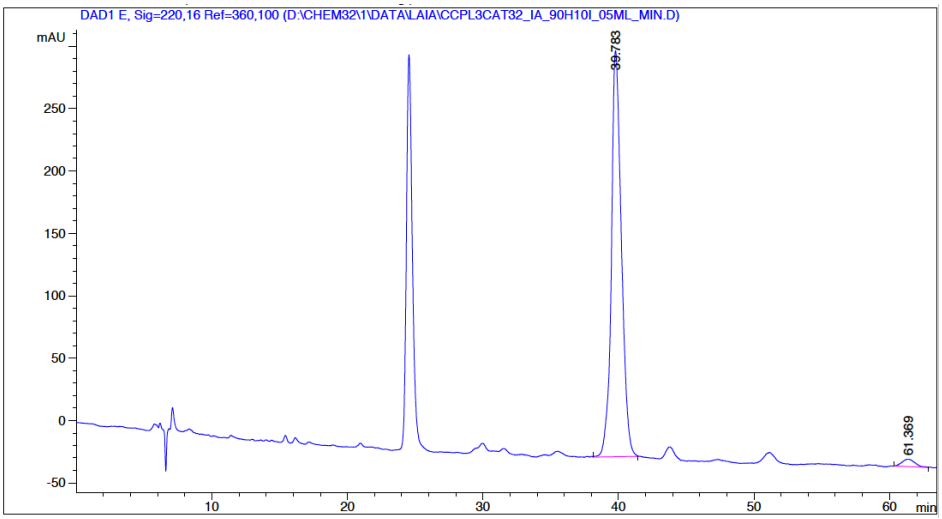


Racemic



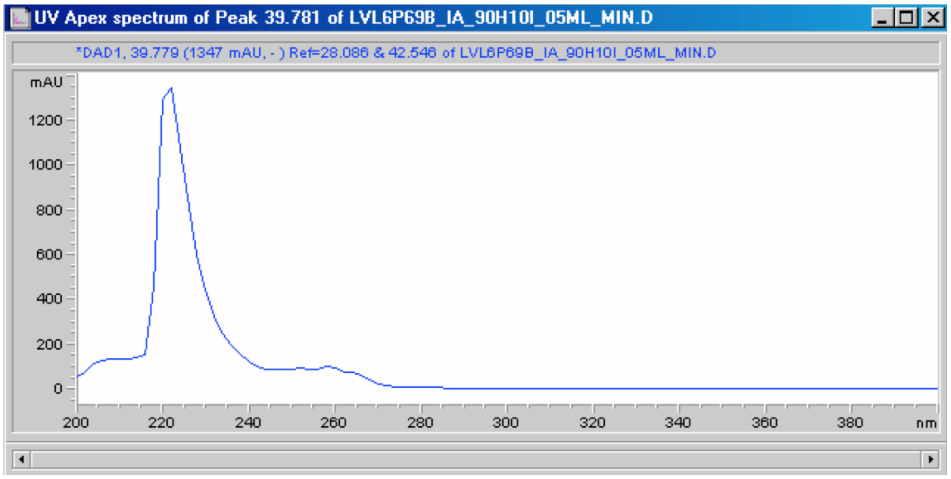
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.781	MM	1.0118	3.94842e4	650.40948	48.5529
2	62.471	BB	1.4170	4.18379e4	478.99362	51.4471

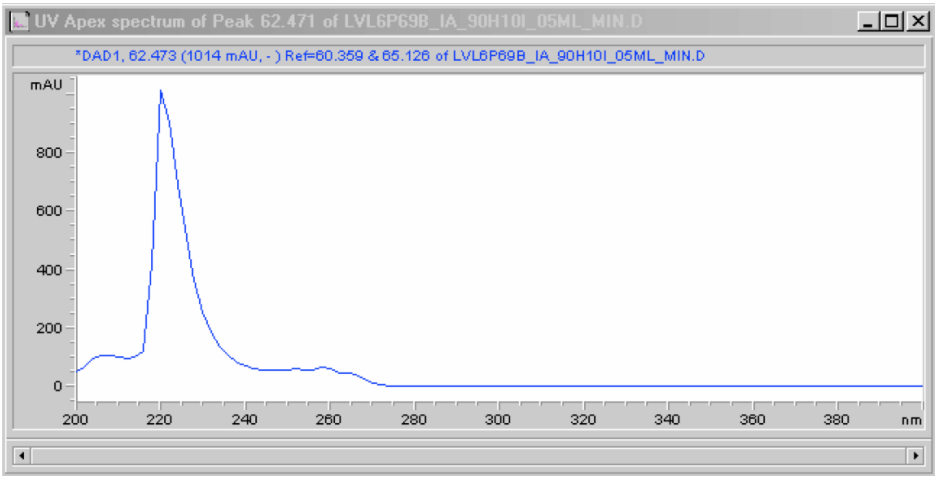
Table 3 entry 13



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.783	VB	0.7656	1.67232e4	325.37418	97.6622
2	61.369	BB	0.7737	400.31412	6.13173	2.3378

UV-VIS spectra of the enantiomers





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