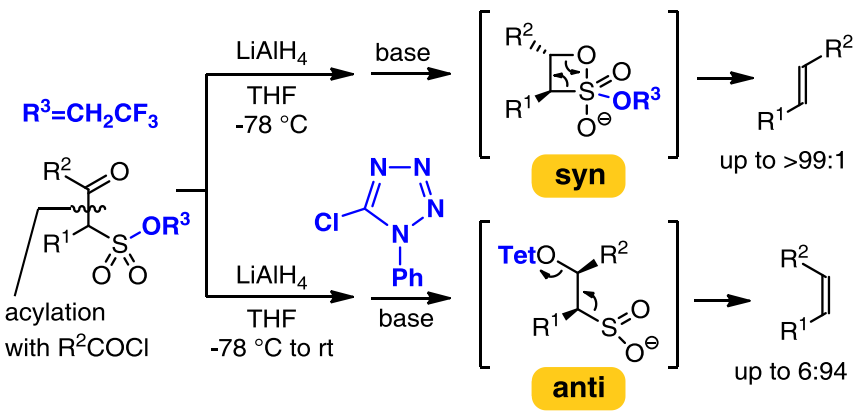
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Stereodivergent synthesis of alkenes by controllable *syn*-/*anti*-fragmentation of β-hydroxysulfonyl intermediates

by Bartosz Górski, Dariusz Basiak, Łukasz Grzesiński and Michał Barbasiewicz*



Supporting Information

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1. General informations

Synthetic manipulations with organometallic reagents were performed under argon (oxygen-free) using Schlenk technique unless stated otherwise. Anhydrous THF (inhibitor-free) and DMF, LiHMDS (1M solution in THF), LiHMDS (1M solution in toluene), *t*-BuOLi (1M solution in THF), $LiAlH_4$ (1M solution in THF), benzoyl chloride, 1-naphthoyl chloride, 4-chlorobenzoyl chloride, *p*-toluoyl chloride, 4-methoxybenzoyl chloride, phenylacetyl chloride, hydrocinnamoyl chloride, cinnamoyl chloride, octanoyl chloride, 4-pentenoyl chloride, cyclohexanecarbonyl chloride, pivaloyl chloride, ethyl chloroformate, 5-chloro-1-phenyl-1*H*-tetrazole, thiourea, benzenesulfinic acid sodium salt, and *n*-octyl bromide were purchased from Sigma-Aldrich (presently Merck). Tetrabutylammonium borohydride, bromomethylcyclohexane, and 2,2,2-trifluoroethanol were purchased from Fluorochem. *t*-BuOK (1M solution in THF) was purchased from TCI. *N*-Chlorosuccinimide and *N,N'*-dicyclohexylcarbodiimide were purchased from Fluka. Commercially available solvents (for chromatography, extraction, etc.) and materials were used without further purification.

Column chromatography was performed on silica gel (high purity grade, pore size 60 Å, 230-400 mesh particle size, 40-63 μm, 60737), and thin layer chromatography (TLC) was performed on Supelco silica gel on TLC Al foils with fluorescent UV_{254} indicator (56524), both purchased from Sigma-Aldrich. Visualization of spots on TLC was performed using ultraviolet light (254 nm), or potassium permanganate ($KMnO_4$) in a basic water solution.

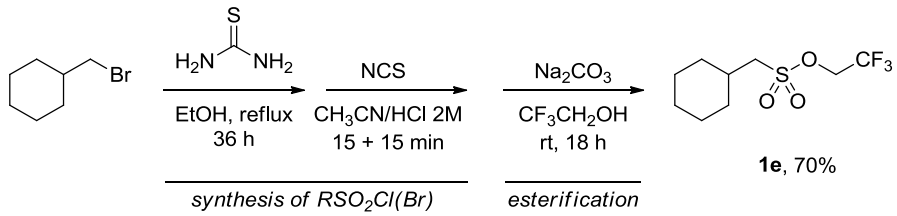
Analytical gas-liquid chromatography (GLC) was performed on a Perkin Elmer Clarus 580 chromatograph equipped with a flame ionization detector, and a GL Sciences InertCap® 5MS/Sil column with helium as a carrier gas (column 0.25 mm × 30 m, carrier flow 1.5 mL/min, method parameters 50°C, +10 °C/min to 300 °C, then 15 min at 300 °C).

^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Agilent 400 MHz NMR spectrometer. Chemical shifts (δ) are given in parts per million (ppm) with the solvent resonance as the internal standard (for $CDCl_3$: 7.24 ppm, and 77.0 ppm), or with $CFCl_3$ in $CDCl_3$ (0.0 ppm for ^{19}F NMR). Spin multiplicity was abbreviated as follows: s – singlet, d – doublet, t – triplet, q – quartet, pent – pentet, hept – heptet.

2. Synthesis of carbanion precursors

Syntheses of sulfonates: 2,2,2-trifluoroethyl 1-octanesulfonate (**1a**), 2,2,2-trifluoroethyl ethanesulfonate (**1b**), 2,2,2-trifluoroethyl 1-propanesulfonate (**1c**), 2,2,2-trifluoroethyl 2-methylpropanesulfonate (**1d**), and *neo*-pentyl 1-octanesulfonate were described in our previous report: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.

2.1. Synthesis of 2,2,2-trifluoroethyl cyclohexylmethanesulfonate 1e

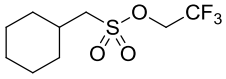


Synthesis of 2,2,2-trifluoroethyl cyclohexylmethanesulfonate (**1e**) was based on procedures described in: Z. Yang, J. Xu, *Synthesis* **2013**, *45,* 1675-1682, and B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.

A 100 mL round-bottom flask was charged with bromomethylcyclohexane (4.92 g; 27.8 mmol), thiourea (2.13 g; 28.0 mmol) and EtOH (28.0 mL) and placed in an oil bath. The mixture was refluxed for 36 h and then evaporated and dried *in vacuo* to obtain white solid (7.75 g). The solid was slowly added during 15 min to a 250 ml round-bottom flask containing a mixture of *N*-chlorosuccinimide (NCS; 18.58 g; 139.2 mmol), HCl_{aq} (9.0 mL; 2 M aqueous solution) and CH_3CN (45 mL) cooled in a water bath (ca. 10 °C). After the addition was finished, water bath was removed. The mixture was stirred for another 15 min and then H_2O (100 mL) was added. Resulted mixture was extracted with Et_2O (100 mL) and dried over anhydrous Na_2SO_4. The mixture was filtered, evaporated, and residue was purified with column chromatography (d=9 cm; ø 6 cm; SiO_2) on cyclohexane : ethyl acetate (1:0→2:1) to elute off a pale-yellow oil (4.372 g).

The crude product after the first step contained two similar components, ca. 1:2 according to ^{1}H NMR δ 3.72 (d, *J*=6.3 Hz, 2H), 3.60 (d, *J*=6.2 Hz, 2H), and ^{13}C NMR δ 76.97, 72.5. We assigned them as sulfonyl bromide and chloride, respectively (compare analytical data in: M. Jereb, L. Hribernik, *Green Chem.* **2017**, *19*, 2286-2295). In the following step both of them transformed into **1e**.

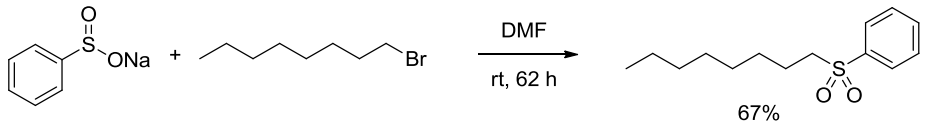
A 25 mL round-bottom flask was charged with crude product from a previous step, trifluoroethanol (9.0 mL), placed in a water bath (rt), and to the resulted solution Na_2CO_3 (3.54 g; 33.42 mmol) was added. The mixture was stirred at rt for 18 h and quenched with aqueous solution of NH_4Cl (50 mL; 10% *w*/*v*). Resulted mixture was extracted with ethyl acetate (3×50 mL), and combined organic phases were washed with H_2O (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then the mixture was filtered, evaporated, and residue was separated with column chromatography (d=9 cm; ø 6 cm; SiO_2) on cyclohexane : ethyl acetate (1:0→4:1) to obtain **1e** (5.05 g; 19.40 mmol; 70%) as a white solid.



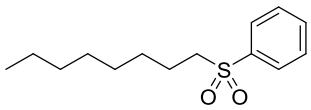
1e, white solid, mp. 32.5-33.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (q, $^3J_{F\text{-}H}$=8.0 Hz, 2H), 3.07 (d, *J*=6.5 Hz, 2H), 2.05-1.95 (m, 1H), 1.94-1.86 (m, 2H), 1.75-1.58 (m, 3H), 1.34-1.22 (m, 2H), 1.19-1.01 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.1 (q,

$^{1}J_{C\text{-}F}$=278 Hz), 63.4 (q, $^{2}J_{C\text{-}F}$=38.0 Hz), 57.8, 33.5, 32.4, 25.54, 25.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.5 (t, $^{3}J_{F\text{-}H}$=7.9 Hz). HRMS (EI, *m/z*), calcd for $C_9H_{16}F_3O_3S$: 261.0772; found: 261.0769 ($M+H^+$). MS (EI, *m/z*, relative intensity): 178 (2), 163 (1), 96 (81), 81 (100), 67 (84), 56 (88), 42 (49).

2.2. Synthesis of octyl phenyl sulfone



A 100 mL round-bottom flask was charged with sodium benzenesulfinate (4.107 g; 25.018 mmol) and argonated. Then DMF (10 mL) and *n*-octyl bromide (4.829 g, 25.004 mmol) were added. The mixture was vigorously stirred for 62 h at rt. Then the mixture was transferred to the separatory funnel, followed by addition of H_2O (100 mL), and extracted with ethyl acetate (3×100 mL). Combined organic phases were washed with water (100 mL), brine (100 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered, evaporated and residue was separated with column chromatography (d=18 cm; ø 5 cm; SiO_2) on cyclohexane : ethyl acetate (10:1) to obtain **octyl phenyl sulfone** (4.229 g; 16.624 mmol; 66%) as a colorless oil.

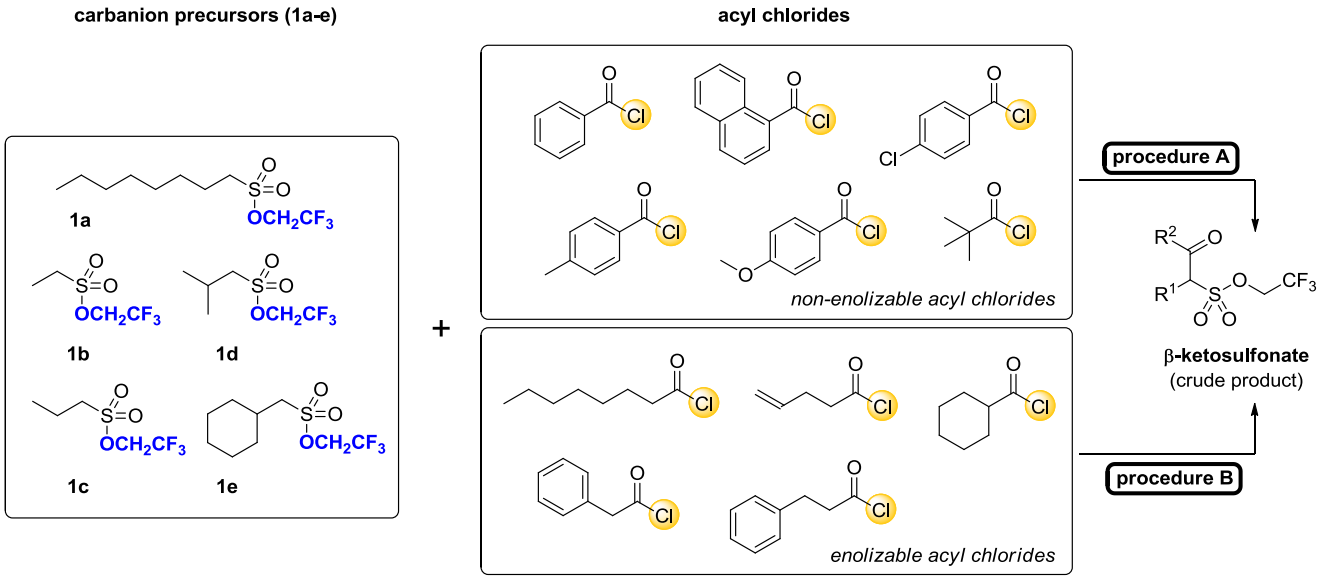


octyl phenyl sulfone, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.79 (m, 2H), 7.60-7.53 (m, 1H), 7.52-7.44 (m, 2H), 3.00 (dd, *J*=9.6, 6.8 Hz, 2H), 1.67-1.56 (m, 2H), 1.31-1.21 (m, 2H), 1.21-1.08 (m, 8H), 0.80-0.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 133.4, 129.0, 127.8, 56.0, 31.4, 28.7, 28.6, 28.0, 22.4, 22.3, 13.8.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: P.K. Shyam, H.-Y. Jang, *J. Org. Chem.* **2017**, *82*, 1761-1767.

3. Synthesis and characterization of alkenes and ketones

3.1. General procedures - acylation of sulfonates 1a-e



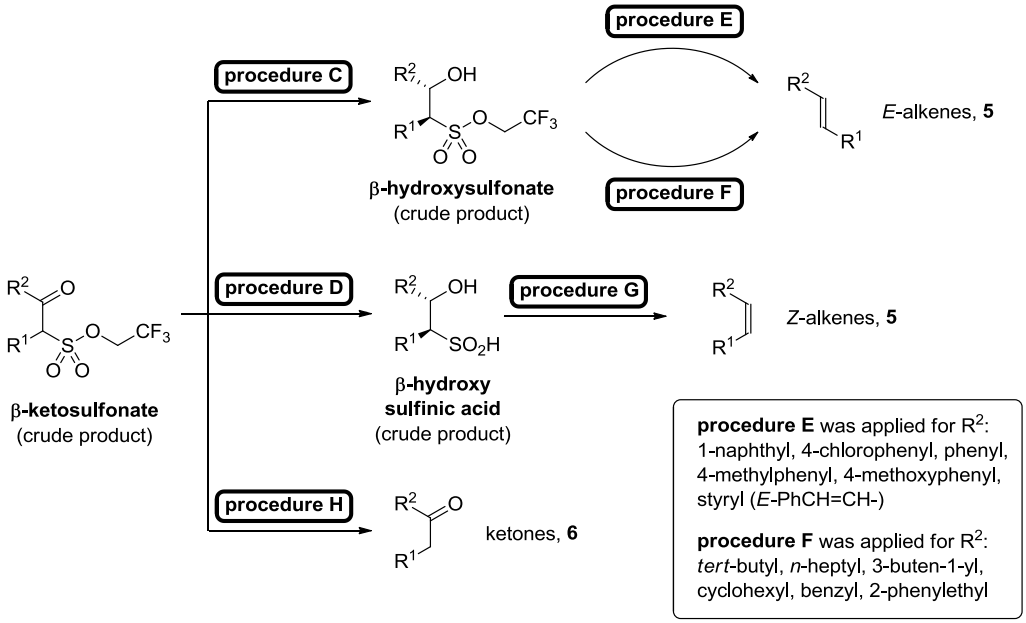
Procedure A (acylation of sulfonyl esters with <u>non-enolizable</u> acyl chlorides)

A 30 mL Schlenk flask was charged with sulfonyl ester (**1a-e**; 2.0 mmol), acyl chloride (2.0 mmol; non-enolizable, see structures shown above) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution LiHMDS (lithium bis(trimethylsilyl)amide; 4.4 mL; 4.4 mmol; 1.0 M solution in THF) was added over ca. 1 min with stirring. After 1 h the cooling bath was removed and aqueous solution of $NaHCO_3$ (10 mL; 5%) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of $NaHCO_3$ (50 mL; 5% *w*/*v*), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a silica pad, rinsed with ethyl acetate, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt.

Procedure B (acylation of sulfonyl esters with <u>enolizable</u> acyl chlorides)

A 30 mL Schlenk flask was charged with sulfonyl ester (**1a-e**; 2.0 mmol) and argonated. Then THF (4 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution LiHMDS (lithium bis(trimethylsilyl)amide; 4.4 mL; 4.4 mmol; 1.0 M solution in THF) was added over ca. 1 min with stirring. After 5 min a solution of acyl chloride (2.4 mmol; enolizable, see structures shown above) in THF (4 mL) was added over ca. 1 min. After 1 h the mixture was slowly warmed to −40°C (for next ~80-90 min) and then aqueous solution of $NaHCO_3$ (10 mL; 5% *w*/*v*) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of $NaHCO_3$ (50 mL; 5%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a silica pad, rinsed with ethyl acetate, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt.

3.2. General procedures - reduction-fragmentation



Two **alternative procedures**: **E** (*tert*-BuOLi, THF, rt, 1 h) and **F** (LiHMDS, toluene, 115 °C, 1 h) were applied for fragmentation of crude β-hydroxysulfonates to the *E*-alkenes. The more harsh conditions (F) were required for substrates with aliphatic substituents R^2, which poorly reacted under conditions E. Most likely the difference in reactivity correlates with the ability of the R^2 substituent to stabilize positive charge on the course of the *syn*-fragmentation process. Similar observations were reported by us in: B. Górski, D. Basiak, A. Talko, T. Basak, T. Mazurek, M. Barbasiewicz, *Eur. J. Org. Chem.* **2018**, *15*, 1774-1784.

Procedure C (reduction of crude β-ketosulfonates to β-hydroxysulfonates)

A 30 mL Schlenk flask was charged with crude β-ketosulfonate obtained using procedure A or B, lithium chloride (4.0 mmol) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution $LiAlH_4$ (2.2 mL; 2.2 mmol; 1.0 M solution in THF) was added over ca. 1 min with stirring. After 1 h the cooling bath was removed and aqueous solution of HCl (10 mL; 3.5% *w*/*v*) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10% *w*/*v*), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a silica pad, rinsed with ethyl acetate, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt.

Procedure D (reduction of crude β-ketosulfonates to β-hydroxysulfinic acids)

A 30 mL Schlenk flask was charged with crude β-ketosulfonate obtained using procedure A or B and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution $LiAlH_4$ (2.0 mL; 2.0 mmol; 1.0 M solution in THF) was added over ca. 1 min with

stirring. After 1 h the flask was transferred to a water bath (rt) and stirred for another 1 h. Then aqueous solution of HCl (10 mL; 3.5% *w*/*v*) was added. The mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10% *w*/*v*), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt.

Procedure E (fragmentation of crude β-hydroxysulfonates to the *E*-alkenes, *t*-BuOLi)

A 30 mL Schlenk flask was charged with crude β-hydroxysulfonate obtained using procedure C and argonated. Then THF (8 mL) was added. To the resulted solution *t*-BuOLi (4.0 mL; 4.0 mmol; 1.0 M solution in THF) was added over ca. 1 min with stirring. The mixture was stirred for 1 h at rt and then aqueous solution of NH_4Cl (10 mL; 10% *w*/*v*) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10% *w*/*v*), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and residue was separated using column chromatography (d=20 cm; ø 3 cm; SiO_2) on cyclohexane to elute off the olefinic product. Then solution of the product was evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar or 10 mbar in case of more volatile compounds) with vigorous stirring for 1 h at rt.

Procedure F (fragmentation of crude β-hydroxysulfonates to the *E*-alkenes, LiHMDS)

A 30 mL Schlenk flask was charged with crude β-hydroxysulfonate obtained using procedure C and argonated. Then toluene (8 mL) was added, and the flask was placed in a heating bath at 115°C. To the resulted solution LiHMDS (lithium bis(trimethylsilyl)amide; 2.0 mL; 2.0 mmol; 1.0 M solution in toluene) was added dropwise over ca 1 min with stirring. After 1 h the flask was transferred to a water bath (rt), stirred for 2 min to cool down, and then aqueous solution of NH_4Cl (10 mL; 10% *w*/*v*) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10% *w*/*v*), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and residue was separated using column chromatography (d=20 cm; ø 3 cm; SiO_2) on cyclohexane to elute off the olefinic product. Then solution of the product was evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar or 10 mbar in case of more volatile compounds) with vigorous stirring for 1 h at rt.

Procedure G (fragmentation of crude β-hydroxysulfinic acids to the *Z*-alkenes)

A 30 mL Schlenk flask was charged with crude β-hydroxysulfinic acid obtained using procedure D and argonated. Then THF (4 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution *t*-BuOK (4.0 mL; 4.0 mmol; 1.0 M solution in THF) was added dropwise over ca. 1 min with stirring. After 5 min a solution of 5-chloro-1-phenyl-1*H*-tetrazole (0.362 g; 2.0 mmol) in THF (4 mL) was added over ca. 1 min. After another 5 min the cooling bath was removed and stirring was continued for 18 h at rt. Then aqueous solution of NH_4Cl (10 mL; 10% *w*/*v*) was added and the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10%

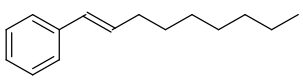
w/*v*), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and residue was separated using column chromatography (d=20-35 cm; ø 3 cm; SiO_2) on cyclohexane to elute off the olefinic product. Then solution of the product was evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar or 10 mbar in case of more volatile compounds) with vigorous stirring for 1 h at rt.

Procedure H (transformation of crude β-ketosulfonates to the ketones)

A 30 mL Schlenk flask was charged with crude β-ketosulfonate obtained using procedure A or B and argonated. Then DMF (4 mL) was added, and the flask was placed in a heating bath at 85°C. To the resulted mixture a freshly prepared solution of NBu_4BH_4 (2.0 mmol) in DMF (4 mL) was added dropwise over ca 3 min with stirring. After next 2 min (total reaction time: 5 min) the flask was transferred to a water bath (rt), stirred for another 2 min to cool down (total reaction time: 7 min), and then aqueous solution of NH_4Cl (10 mL; 10% *w*/*v*) was added. Then, the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10% *w*/*v*), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and residue was separated using column chromatography (d=20 cm; ø 3 cm; SiO_2) on cyclohexane : ethyl acetate mixture (20:1) to elute off the product. Then solution of the product was evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar or 10 mbar in case of more volatile compounds) with vigorous stirring for 1 h at rt.

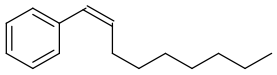
Use of excess of NBu_4BH_4 should be avoided, as it causes reduction of the ketone to the corresponding alcohol. The presented conditions ensure optimal conversion of the substrates (β-ketosulfonates) with only little formation of the over-reduction products (alcohols).

3.3. Characterization data of alkenes



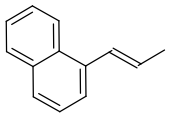
5a was obtained from **1a** and benzoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.341 g; 1.685 mmol; 85%, colorless oil, mixture of *E*/*Z* isomers (98:2 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 7.44-7.41 (m, 2H), 7.39-7.34 (m, 2H), 7.29-7.24 (m, 1H), 6.46 (d, *J*=15.8 Hz, 1H), 6.31 (dt, *J*=15.8, 6.9 Hz, 1H), 2.29 (qd, *J*=6.9, 1.4 Hz, 2H), 1.60-1.51 (m, 2H), 1.48-1.32 (m, 8H), 1.02-0.95 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 137.9, 131.1, 129.7, 128.4, 126.7, 125.9, 33.1, 31.9, 29.4, 29.2 (ovl), 22.7, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, D. Basiak, A. Talko, T. Basak, T. Mazurek, M. Barbasiewicz, *Eur. J. Org. Chem.* **2018**, *15*, 1774-1784.



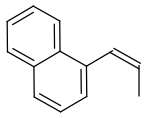
5a was obtained from **1a** and benzoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.112 g; 0.554 mmol; 55% (1.0 mmol scale), colorless oil, mixture of *E*/*Z* isomers (6:94 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) 7.39-7.29 (m, 4H), 7.26-7.21 (m, 1H), 6.44 (dt, *J*=11.7, 1.7 Hz, 1H), 5.70 (dt, *J*=11.6, 7.3 Hz, 1H), 2.36 (qd, *J*=7.3, 1.8 Hz, 2H), 1.53-1.43 (m, 2H), 1.41-1.24 (m, 8H), 0.96-0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 137.8, 133.2, 128.72, 128.65, 128.1, 126.4, 31.8, 30.0, 29.3, 29.2, 28.7, 22.7, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, D. Basiak, A. Talko, T. Basak, T. Mazurek, M. Barbasiewicz, *Eur. J. Org. Chem.* **2018**, *15*, 1774-1784.



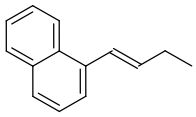
5b was obtained from **1b** and 1-naphthoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.276 g; 1.640 mmol; 82%, colorless oil, mixture of *E*/*Z* isomers (97:3 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 8.18-8.13 (m, 1H), 7.89-7.84 (m, 1H), 7.77 (d, *J*=8.1 Hz, 1H), 7.57 (d, *J*=7.1 Hz, 1H), 7.55-7.42 (m, 3H), 7.17 (d, *J*=15.5 Hz, 1H), 6.28 (dqd, *J*=15.5, 6.6, 0.8 Hz, 1H), 2.03 (dd, *J*=6.6, 1.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 135.7, 133.6, 131.1, 128.9, 128.4, 128.2, 127.2, 125.74, 125.65, 125.59, 123.9, 123.4, 19.0.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: W. Huang, S.-H. Zhao, N. Xu; *Synthesis* **2015**, *47*, 359-366.



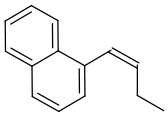
5b was obtained from **1b** and 1-naphthoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.179 g; 1.064 mmol; 53%, colorless oil, mixture of *E*/*Z* isomers (8:92 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) 8.06-7.98 (m, 1H), 7.91-7.85 (m, 1H), 7.82-7.76 (m, 1H), 7.54-7.48 (m, 2H), 7.48-7.44 (m, 1H), 7.41-7.36 (m, 1H), 6.93 (d, *J*=11.4 Hz, 1H), 6.06 (dq, *J*=11.4, 7.0 Hz, 1H), 1.76 (dd, *J*=7.0, 1.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 134.5, 133.5, 131.9, 128.5, 128.3, 127.9, 127.1, 126.5, 125.7, 125.6, 125.2, 125.0, 14.6.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: W. Huang, S.-H. Zhao, N. Xu, *Synthesis* **2015**, *47*, 359-366.

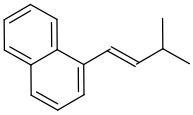


5c was obtained from **1c** and 1-naphthoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.265 g; 1.454 mmol; 73%, colorless oil, mixture of *E*/*Z* isomers (94:6 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 8.13 (d, *J*=7.8 Hz, 1H), 7.82 (d, *J*=7.7 Hz, 1H), 7.73 (d, *J*=8.2 Hz, 1H), 7.55 (d, *J*=7.1 Hz, 1H), 7.53-7.39 (m, 3H), 7.11 (d, *J*=15.4 Hz, 1H), 6.28 (dt, *J*=15.6, 6.5 Hz, 1H), 2.40-2.30 (m, 2H), 1.17 (t, *J*=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 136.0, 135.7, 133.6, 131.1, 128.4, 127.2, 125.9, 125.72, 125.66, 125.59, 123.9, 123.5, 26.5, 13.7.

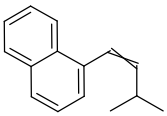
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: S. Zhang, Y. Wang, X. Feng, M. Bao, *J. Am. Chem. Soc.* **2012**, *134*, 5492-5495.



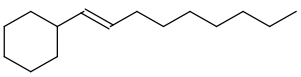
5c obtained from **1c** and 1-naphthoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.186 g; 1.020 mmol; 51%, colorless oil, mixture of *E*/*Z* isomers (8:92 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) 8.05-7.99 (m, 1H), 7.88-7.82 (m, 1H), 7.81-7.75 (m, 1H), 7.54-7.43 (m, 3H), 7.37 (dd, *J* = 7.0, 1.2 Hz, 1H), 6.87 (d, *J*=11.4 Hz, 1H), 5.95 (dt, *J*=11.4, 7.4 Hz, 1H), 2.23-2.14 (m, 2H), 1.02 (td, *J*=7.4, 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 136.1, 134.9, 133.5, 131.9, 128.3, 127.1, 126.30, 126.28, 125.72, 125.65, 125.2, 125.1, 22.1, 14.4. HRMS (EI, *m*/*z*): calcd for $C_{14}H_{14}$: 182.1096; found: 182.1102 ($M^{+\bullet}$). MS (EI, *m*/*z*, relative intensity): 182 (80), 167 (100), 165 (76), 153 (86), 128 (22).



5d was obtained from **1d** and 1-naphthoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.299 g; 1.523 mmol; 76%, colorless oil, mixture of *E*/*Z* isomers (>99:<1 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 8.16 (d, *J*=8.3 Hz, 1H), 7.86 (d, *J*=7.7 Hz, 1H), 7.76 (d, *J*=8.0 Hz, 1H), 7.59 (d, *J*=7.2 Hz, 1H), 7.56-7.41 (m, 3H), 7.11 (d, *J*=15.6 Hz, 1H), 6.24 (dd, *J*=15.6, 6.8 Hz, 1H), 2.69-2.55 (m, 1H), 1.21 (d, *J*=6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 141.3, 135.7, 133.6, 131.2, 128.4, 127.1, 125.7, 125.63, 125.57, 123.91, 123.90, 123.4, 31.9, 22.5. HRMS (EI, *m*/*z*): calcd for $C_{15}H_{16}$: 196.1252; found: 196.1255 ($M^{+\bullet}$). MS (EI, *m*/*z*, relative intensity): 196 (58), 181 (100), 165 (63), 153 (39), 128 (17).



5d obtained from **1d** and 1-naphthoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.155 g; 0.790 mmol; 39%, colorless oil, mixture of *E*/*Z* isomers (48:52 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.16 (m, 1H, isom *E*), 8.10-8.04 (m, 1H, isom *Z*), 7.92-7.86 (m, 1H+1H), 7.83-7.76 (m, 1H+1H), 7.61 (d, *J*=7.2Hz, 1H, isom *E*), 7.58-7.44 (m, 3H+3H), 7.39 (dt, *J*=6.9, 1.2 Hz, 1H, isom *Z*), 7.11 (d, *J*=15.6 Hz, 1H, isom *E*), 6.79 (d, *J*=11.4, 1H, isom *Z*), 6.26 (dd, *J*=15.6, 6.8 Hz, 1H, isom *E*), 5.78 (dd, *J*=11.4, 10.2 Hz, 1H, isom *Z*), 2.75-2.56 (m, 1H+1H), 1.23 (d, *J*=6.8 Hz, 6H, isom *E*), 1.01 (d, *J*=6.6 Hz, 6H, isom *Z*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (*Z*), 141.4 (*E*), 135.8 (*E*), 135.3 (*Z*), 133.6 (*E*) 133.5 (*Z*), 132.0 (*Z*), 131.2 (*E*), 128.4 (*E*) 128.3 (*Z*), 127.2 (*E*) 127.0 (*Z*), 126.1 (*Z*), 125.71 (*E*+*Z*), 125.68 (*Z*), 125.64 (*E*), 125.57 (*E*), 125.3 (*Z*), 125.1 (*Z*), 124.5 (*Z*), 123.93 (*E*), 123.91 (*E*), 123.5 (*E*), 31.9 (*E*), 27.5 (*Z*), 23.2 (*Z*) 22.5 (*E*). HRMS (EI, *m*/*z*): calcd for $C_{15}H_{16}$: 196.1252; found: 196.1258 ($M^{+\bullet}$). MS (EI, *m*/*z*, relative intensity): 196 (48), 181 (100), 165 (51), 153 (40), 128 (18).



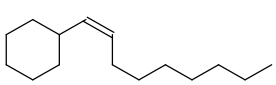
5e was obtained using two different set of procedures (B→C→F and B→D→G) and two different combination of substrates (**1e** and octanoyl chloride - entry 4, and **1a** and cyclohexanecarbonyl chloride - entry 9). Data for all four combinations are given below.

► obtained from **1e** and octanoyl chloride, using procedures B→C→F toward ***E*-isomer**: 0.272 g; 1.305 mmol; 65%, colorless oil, mixture of *E*/*Z* isomers (87:13 according to GC).

► obtained from **1a** and cyclohexanecarbonyl chloride, using procedures B→C→F toward ***E*-isomer**: 0.297 g; 1.425 mmol; 74%, colorless oil, mixture of *E*/*Z* isomers (97:3 according to GC).

^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 5.41-5.29 (m, 2H), 1.99-1.92 (m, 2H), 1.92-1.83 (m, 1H), 1.75-1.58 (m, 5H), 1.40-0.97 (m, 15H), 0.92-0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 136.4, 127.8, 40.8, 33.3, 32.7, 31.9, 29.8, 29.3, 29.2, 26.3, 26.2, 22.7, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: A. G. M. Barrett, J. M. Hill, E. M. Wallace, *J. Org. Chem.* **1992**, *57*, 386-389.

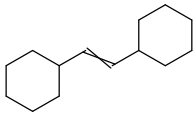


► obtained from **1e** and octanoyl chloride, using procedures B→D→G toward **Z-isomer**: 0.139 g; 0.667 mmol; 34%, colorless oil, mixture of *E*/*Z* isomers (26:74 according to GC).

► obtained from **1a** and cyclohexanecarbonyl chloride, using procedures B→D→G toward **Z-isomer**: 0.103 g; 0.494 mmol; 25%, colorless oil, mixture of *E*/*Z* isomers (7:93 according to GC).

^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) 5.27-5.13 (m, 2H), 2.29-2.17 (m, 1H), 2.05-1.97 (m, 2H), 1.73-1.53 (m, 5H), 1.37-0.95 (m, 15H), 0.91-0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 136.0, 128.1, 36.3, 33.4, 31.9, 30.0, 29.3, 29.2, 27.4, 26.09, 26.01, 22.7, 14.1.

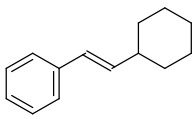
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: A. G. M. Barrett, J. M. Hill, E. M. Wallace, *J. Org. Chem.* **1992**, *57*, 386-389.



5f was obtained from **1e** and cyclohexanecarbonyl chloride, using procedures B→C→F toward ***E*-isomer**: 0.255 g; 1.326 mmol; 66%, colorless oil, mixture of *E*/*Z* isomers (97:3 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 5.29 (dd, *J*=3.7, 1.7 Hz, 2H), 1.92-1.79 (m, 2H), 1.74-1.56 (m, 10H), 1.31-0.95 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.8, 40.7, 33.4, 26.3, 26.2.

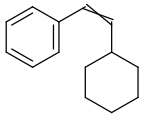
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: L. R. Collazo, F. S. Guziec Jr., *J. Org. Chem.* **1993**, *58*, 43-46.

5f was obtained from **1e** and cyclohexanecarbonyl chloride, using procedures B→D→G toward **Z-isomer**: 0.012 g; 0.062 mmol; 3%, colorless oil, mixture of *E*/*Z* isomers (37:63 according to GC).



5g was obtained from **1e** and benzoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.295 g; 1.583 mmol; 79%, colorless oil, mixture of *E*/*Z* isomers (>99:<1 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 7.44-7.40 (m, 2H), 7.38-7.32 (m, 2H), 7.28-7.22 (m, 1H), 6.42 (dd, *J*=16.0, 1.2 Hz, 1H), 6.25 (dd, *J*=16.0, 6.9 Hz, 1H), 2.26-2.14 (m, 1H), 1.93-1.81 (m, 4H), 1.80-1.72 (m, 1H), 1.47-1.34 (m, 2H), 1.34-1.20 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 138.0, 136.7, 128.4, 127.2, 126.7, 125.9, 41.1, 32.9, 26.1, 26.0.

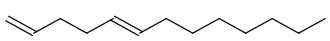
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, D. Basiak, A. Talko, T. Basak, T. Mazurek, M. Barbasiewicz, *Eur. J. Org. Chem.* **2018**, *15*, 1774-1784.



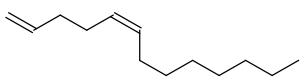
5g was obtained from **1e** and benzoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.148 g; 0.794 mmol; 40%, colorless oil, mixture of *E*/*Z* isomers (62:38 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.18 (m, 5H+5H), 6.41-6.31 (m,

1H+1H), 6.20 (dd, *J*=16.0, 6.9 Hz, 1H, isom *E*), 5.52 (dd, *J*=11.7, 10.2 Hz, 1H, isom *Z*), 2.69-2.54 (m, 1H, isom *Z*), 2.24-2.08 (m, 1H, isom *E*), 1.89-1.63 (m, 5H+5H), 1.42-1.12 (m, 5H+5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0 (*Z*), 138.0 (*E*), 137.9 (*Z*), 136.8 (*E*), 128.6 (*Z*), 128.4 (*E*), 128.1 (*Z*), 127.2 (*E*), 126.8 (*Z*), 126.7 (*E*), 126.4 (*Z*), 125.9 (*E*), 41.1 (*E*), 36.9 (*Z*), 33.2 (*Z*), 32.9 (*E*), 26.1 (*E*), 26.03 (*E*), 26.01 (*Z*), 25.7 (*Z*).

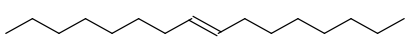
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, D. Basiak, A. Talko, T. Basak, T. Mazurek, M. Barbasiewicz, *Eur. J. Org. Chem.* **2018**, *15*, 1774-1784.



5h was obtained from **1a** and 4-pentenoyl chloride, using procedures B→C→F toward ***E*-isomer**: 0.188 g; 1.042 mmol; 55%, colorless oil, mixture of *E*/*Z* isomers (90:10 according to ^{13}C NMR, the isomers were inseparable on GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 5.82-5.69 (m, 1H), 5.42-5.27 (m, 2H), 4.98 (ddt, *J*=17.2, 2.1, 1.4 Hz, 1H), 4.96-4.90 (m, 1H), 2.11-2.00 (m, 4H), 1.98-1.90 (m, 2H), 1.34-1.13 (m, 10H), 0.86 (t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 138.6, 131.0, 129.3, 114.4, 33.9, 32.6, 32.0, 31.9, 29.6, 29.19, 29.11, 22.7, 14.1. HRMS (EI, *m*/*z*): calcd for $C_{13}H_{24}$: 180.1878; found: 180.1882 ($M^{+\bullet}$). MS (EI, *m*/*z*, relative intensity): 180 (3), 109 (11), 97 (48), 83 (92), 69 (61), 67 (55), 55 (100).

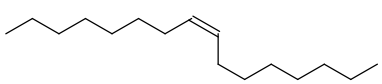


5h was obtained from **1a** and 4-pentenoyl chloride, using procedures B→D→G toward **Z-isomer**: 0.126 g; 0.699 mmol; 35%, colorless oil, mixture of *E*/*Z* isomers (8:92 according to ^{13}C NMR, the isomers were inseparable on GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) 5.87-5.75 (m, 1H), 5.42-5.30 (m, 2H), 5.01 (ddt, *J*=17.1, 2.0, 1.5 Hz, 1H), 4.94 (ddt, *J*=10.2, 2.1, 1.1 Hz, 1H), 2.13-2.04 (m, 4H), 2.04-1.96 (m, 2H), 1.37-1.18 (m, 10H), 0.87 (t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 138.5, 130.5, 128.8, 114.5, 33.9, 31.9, 29.7, 29.3, 29.2, 27.3, 26.7, 22.7, 14.1. HRMS (EI, *m*/*z*): calcd for $C_{13}H_{24}$: 180.1878; found: 180.1876 ($M^{+\bullet}$). MS (EI, *m*/*z*, relative intensity): 180 (4), 109 (12), 97 (51), 83 (85), 69 (64), 67 (90), 55 (100).



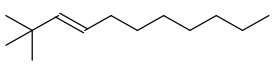
5i obtained from **1a** and octanoyl chloride, using procedures B→C→F toward ***E*-isomer**: 0.309 g; 1.377 mmol; 69% (1.0 mmol scale), colorless oil, mixture of *E*/*Z* isomers (90:10 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 5.37 (ddd, *J*=5.3, 3.7, 1.6 Hz, 2H), 2.00-1.90 (m, 4H), 1.39-1.20 (m, 20H), 0.91-0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 130.4, 32.6, 31.9, 29.7, 29.25, 29.16, 22.7, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: S. C. Söderman, A. L. Schwan, *J. Org. Chem.* **2012**, *77*, 10978-10984.



5i was obtained from **1a** and octanoyl chloride, using procedures B→D→G toward **Z-isomer**: 0.118 g; 0.526 mmol; 53%, colorless oil, mixture of *E*/*Z* isomers (7:93 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) 5.34 (ddd, *J*=5.6, 4.4, 1.1 Hz, 2H), 2.03-1.97 (m, 4H), 1.37-1.20 (m, 20H), 0.91-0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 129.9, 31.9, 29.8, 29.31, 29.26, 27.2, 22.7, 14.1.

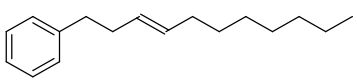
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: S. C. Söderman, A. L. Schwan, *J. Org. Chem.* **2012**, *77*, 10978-10984.



5j was obtained from **1a** and pivaloyl chloride, using procedures A→C→F toward ***E*-isomer**: 0.143 g; 0.784 mmol; 39%, colorless oil, mixture of *E*/*Z* isomers (>99:<1 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 5.42 (dt, *J*=15.6, 1.3 Hz, 1H), 5.29 (dt, *J*=15.6, 6.6 Hz, 1H), 2.00-1.91 (m, 2H), 1.38-1.20 (m, 10H), 0.97 (s, 9H), 0.90-0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 141.4, 124.8, 32.72, 32.70, 31.9, 29.85, 29.79, 29.2, 29.1, 22.7, 14.1.

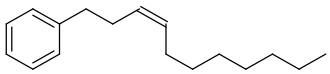
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.

5j was obtained from **1a** and pivaloyl chloride, using procedures A→D→G toward ***Z*-isomer**: 0.024 g; 0.132 mmol; 7%, colorless oil, mixture of *E*/*Z* isomers (23:77 according to GC).



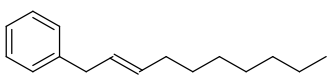
5k was obtained from **1a** and hydrocinnamoyl chloride, using procedures B→C→F toward ***E*-isomer**: 0.304 g; 1.319 mmol; 66%, colorless oil, mixture of *E*/*Z* isomers (89:11 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 7.35-7.30 (m, 2H), 7.26-7.20 (m, 3H), 5.52-5.47 (m, 2H), 2.75-2.69 (m, 2H), 2.40-2.32 (m, 2H), 2.07-1.99 (m, 2H), 1.44-1.27 (m, 10H), 0.97 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 142.2, 131.2, 129.3, 128.4, 128.2, 125.7, 36.2, 34.5, 32.6, 31.9, 29.6, 29.2, 29.1, 22.7, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, D. Basiak, A. Talko, T. Basak, T. Mazurek, M. Barbasiewicz, *Eur. J. Org. Chem.* **2018**, *2018*, 1774-1784.



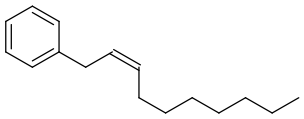
5k was obtained from **1a** and hydrocinnamoyl chloride, using procedures B→D→G toward ***Z*-isomer**: 0.188 g; 0.816 mmol; 41%, colorless oil, mixture of *E*/*Z* isomers (10:90 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) 7.30-7.24 (m, 2H), 7.21-7.13 (m, 3H), 5.41-5.36 (m, 2H), 2.69-2.60 (m, 2H), 2.38-2.31 (m, 2H), 2.01-1.92 (m, 2H), 1.35-1.19 (m, 10H), 0.91-0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 142.2, 130.8, 128.6, 128.4, 128.2, 125.7, 36.0, 31.9, 29.6, 29.3, 29.21, 29.18, 27.2, 22.7, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, D. Basiak, A. Talko, T. Basak, T. Mazurek, M. Barbasiewicz, *Eur. J. Org. Chem.* **2018**, *2018*, 1774-1784.



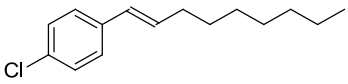
5l was obtained from **1a** and phenylacetyl chloride, using procedures B→C→F toward ***E*-isomer**: 0.226 g; 1.045 mmol; 52% (yield based on β-ketosulfonate purified by distilling off unreacted sulfonyl ester *in vacuo*, overall yield starting from **1a**: 46%), colorless oil, mixture of *E*/*Z* isomers (91:9 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 7.32-7.27 (m, 2H), 7.22-7.17 (m, 3H), 5.62-5.48 (m, 2H), 3.34 (d, *J*=5.9 Hz, 2H), 2.07-1.99 (m, 2H), 1.44-1.24 (m, 10H), 0.93-0.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 141.1, 132.2, 128.7, 128.5, 128.3, 125.8, 39.1, 32.5, 31.9, 29.5, 29.17, 29.16, 22.7, 14.1.

The ^{1}H NMR spectrum was moderately consistent with those described in literature: X.-L. Tang, Z. Wu, M.-B. Li, Y. Gu, S.-K. Tian, *Eur. J. Org. Chem.* **2012**, *2012*, 4107-4109.



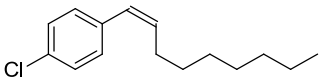
5l was obtained from **1a** and phenylacetyl chloride, using procedures B→D→G toward **Z-isomer**: 0.131 g; 0.605 mmol; 30% (yield based on β-ketosulfonate purified by distilling off unreacted sulfonyl ester *in vacuo*, overall yield based on **1a**: 26%), colorless oil, mixture of *E*/*Z* isomers (12:88 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) 7.30-7.24 (m, 2H), 7.20-7.14 (m, 3H), 5.59-5.45 (m, 2H), 3.39 (d, *J*=6.1 Hz, 2H), 2.18-2.08 (m, 2H), 1.44-1.19 (m, 10H), 0.90-0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 141.3, 131.1, 128.37, 128.34, 127.9, 125.8, 33.5, 31.9, 29.7, 29.3, 29.2, 27.3, 22.7, 14.1.

The ^{1}H NMR spectrum was consistent with those described in literature: X.-L. Tang, Z. Wu, M.-B. Li, Y. Gu, S.-K. Tian, *Eur. J. Org. Chem.* **2012**, *2012*, 4107-4109.



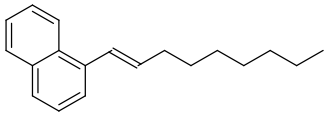
5m was obtained from **1a** and 4-chlorobenzoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.413 g; 1.744 mmol; 87%, colorless oil, mixture of *E*/*Z* isomers (98:2 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) δ 7.26-7.25 (m, 4H), 6.33 (dt, *J*=15.8, 1.3 Hz, 1H), 6.21 (dt, *J*=15.8, 6.7 Hz, 1H), 2.25-2.16 (m, 2H), 1.54-1.42 (m, 2H), 1.40-1.25 (m, 8H), 0.95-0.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 136.4, 132.2, 131.9, 128.52, 128.48, 127.0, 33.0, 31.8, 29.3, 29.21, 29.19, 22.7, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: Z.-Y. Peng, F.-F. Ma, L.-F. Zhu, X.-M. Xie, Z. Zhang, *J. Org. Chem.* **2009**, *74,* 6855-6858.



5m was obtained from **1a** and 4-chlorobenzoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.249 g; 1.052 mmol; 53%, colorless oil, mixture of *E*/*Z* isomers (8:92 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) δ 7.33-7.26 (m, 2H), 7.23-7.18 (m, 2H), 6.35 (d, *J*=11.7 Hz, 1H), 5.69 (dt, *J*=11.6, 7.3 Hz, 1H), 2.34-2.26 (m, 2H), 1.50-1.41 (m, 2H), 1.37-1.21 (m, 8H), 0.95-0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 136.2, 133.9, 132.1, 130.0, 128.2, 127.5, 31.8, 29.9, 29.3, 29.2, 28.6, 22.7, 14.1.

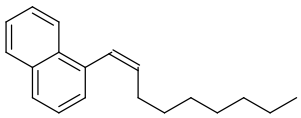
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: A. Pelter, D. Buss, E. Colclough, B. Singaram, *Tetrahedron* **1993**, *49*, 7077-7103.



5n was obtained from **1a** and 1-naphthoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.412 g; 1.632 mmol; 81%, colorless oil, mixture of *E*/*Z* isomers (95:5 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 8.25-8.17 (m, 1H), 7.93-7.86 (m, 1H), 7.80 (dt, *J*=8.0, 1.1 Hz, 1H), 7.63 (dt, *J*=7.1, 1.0 Hz, 1H), 7.60-7.45 (m, 3H), 7.19 (d, *J*=15.6 Hz, 1H), 6.31 (dt, *J*=15.5, 6.9 Hz, 1H), 2.39 (qd, *J*=7.0, 1.6 Hz, 2H), 1.68-1.55 (m, 2H), 1.53-1.33 (m, 8H), 1.03-0.97 (m, 3H). ^{13}C NMR

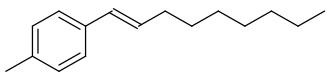
(100 MHz, $CDCl_3$) δ (isom *E*) 135.8, 134.5, 133.6, 131.1, 128.4, 127.1, 126.8, 125.7, 125.63, 125.56, 123.9, 123.4, 33.5, 31.9, 29.4, 29.2 (ovl), 22.7, 14.1.

The ^1H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.



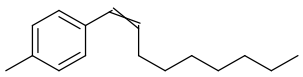
5n was obtained from **1a** and 1-naphthoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.254 g; 1.006 mmol; 50%, colorless oil, mixture of *E*/*Z* isomers (16:84 according to GC). ^1H NMR (400 MHz, $CDCl_3$) δ (isom *Z*) δ 8.11-8.04 (m, 1H), 7.94-7.86 (m, 1H), 7.84-7.79 (m, 1H), 7.58-7.38 (m, 4H), 6.94 (d, *J*=11.5 Hz, 1H), 5.99 (dt, *J*=11.5, 7.4 Hz, 1H), 2.22 (qd, *J*=7.4, 1.6 Hz, 2H), 1.53-1.19 (m, 10H), 0.94-0.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *Z*) 134.9, 134.6, 133.5, 131.9, 128.3, 127.0, 126.8, 126.3, 125.67, 125.62, 125.2, 125.1, 31.8, 29.8, 29.19, 29.12, 28.6, 22.6, 14.1.

The ^1H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.



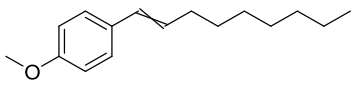
5o was obtained from **1a** and *p*-toluoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.357 g; 1.650 mmol; 82%, colorless oil, mixture of *E*/*Z* isomers (98:2 according to GC). ^1H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 7.33-7.28 (m, 2H), 7.19-7.14 (m, 2H), 6.42 (dt, *J*=15.8, 1.5 Hz, 1H), 6.24 (dt, *J*=15.8, 6.9 Hz, 1H), 2.39 (s, 3H), 2.31-2.22 (m, 2H), 1.59-1.47 (m, 2H), 1.46-1.30 (m, 8H), 1.01-0.93 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 136.3, 135.1, 130.1, 129.5, 129.1, 125.8, 33.1, 31.9, 29.5, 29.2 (ovl), 22.7, 21.1, 14.1.

^1H NMR and ^{13}C NMR spectra were consistent with those described in literature: Z.-Y. Peng, F.-F. Ma, L.-F. Zhu, X.-M. Xie, Z. Zhang, *J. Org. Chem.* **2009**, *74,* 6855-6858.



5o obtained from **1a** and *p*-toluoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.244 g; 1.128 mmol; 57%, colorless oil, mixture of *E*/*Z* isomers (37:63 according to GC). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.11 (m, 4H+4H), 6.44-6.35 (m, 1H+1H), 6.21 (dt, *J*=16.1, 6.9 Hz, 1H, isom *E*), 5.66 (dt, *J*=11.9, 7.2 Hz, 1H, isom *Z*), 2.42-2.33 (m, 2H, isom *Z*), 2.39 (s, 3H, isom *Z*), 2.37 (s, 3H, isom *E*), 2.27-2.19 (m, 2H, isom *E*), 1.56-1.44 (m, 2H+2H), 1.42-1.25 (m, 8H+8H), 0.99-0.88 (m, 3H+3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3 (*E*), 136.0 (*Z*), 135.1 (*E*), 134.9 (*Z*), 132.5 (*Z*), 130.1 (*E*), 129.5 (*E*), 129.1 (*E*), 128.8 (*Z*), 128.6 (*Z*), 128.5 (*Z*), 125.8 (*E*), 33.0 (*E*), 31.86 (*E*), 31.84 (*Z*), 30.0 (*Z*), 29.5 (*E*), 29.3 (*Z*), 29.20 (*E*(ovl)+*Z*), 28.7 (*Z*), 22.68 (*E*), 22.66 (*Z*), 21.12 (*Z*), 21.09 (*E*), 14.1 (*E*+*Z*).

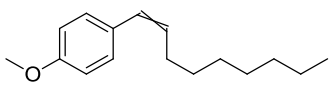
The ^1H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.



5p obtained from **1a** and 4-methoxybenzoyl chloride, using procedures A→C→E toward ***E*-isomer**: 0.330 g; 1.420 mmol; 71%, pale-yellow oil,

mixture of *E*/*Z* isomers (98:2 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ (isom *E*) 7.32-7.25 (m, 2H), 6.87-6.81 (m, 2H), 6.33 (dt, *J*=15.7, 1.5 Hz, 1H), 6.10 (dt, *J*=15.7, 6.9 Hz, 1H), 3.80 (s, 3H), 2.19 (qd, *J*=7.0, 1.5 Hz, 2H), 1.52-1.42 (m, 2H), 1.39-1.25 (m, 8H), 0.94-0.88 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *E*) 158.6, 130.8, 129.01, 128.97, 126.9, 113.8, 55.2, 33.0, 31.9, 29.5, 29.2 (ovl), 22.7, 14.1.

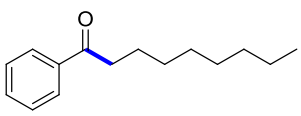
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.



5p obtained from **1a** and 4-methoxybenzoyl chloride, using procedures A→D→G toward **Z-isomer**: 0.278 g; 1.196 mmol; 59%, colorless oil, mixture of *E*/*Z* isomers (90:10 according to GC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 2H+2H), 6.91-6.82 (m, 2H+2H), 6.40-6.29 (m, 1H+1H), 6.10 (dt, *J*=15.7, 6.9 Hz, 1H, isom *E*), 5.59 (dt, *J*=11.6, 7.2 Hz, 1H, isom *Z*), 3.81 (s, 3H, isom *Z*), 3.80 (s, 3H, isom *E*), 2.34 (qd, *J*=7.3, 1.9 Hz, 2H, isom *Z*), 2.20 (qd, *J*=7.0, 1.5 Hz, 2H, isom *E*), 1.52-1.43 (m, 2H+2H), 1.40-1.19 (m, 8H+8H), 0.96-0.86 (m, 3H+3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5 (*E*), 158.1 (*Z*), 131.6 (*Z*), 130.7 (*E*), 130.5 (*Z*), 129.9 (*Z*), 128.99 (*E*), 128.95 (*E*), 128.0 (*Z*), 126.9 (*E*), 113.8 (*E*), 113.4 (*Z*), 55.15 (*E*), 55.12 (*Z*), 33.0 (*E*), 31.83 (*E*), 31.82 (*Z*), 30.0 (*Z*), 29.5 (*E*), 29.3 (*Z*), 29.21 (*E*+*Z*), 29.19 (*E*), 28.6 (*Z*), 22.66 (*E*), 22.63 (*Z*) 14.1 (*E*+*Z*).

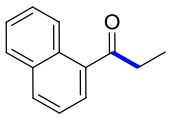
The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.

3.4. Characterization data of ketones



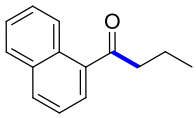
6a, was obtained from **1a** and benzoyl chloride, using procedures A→H: 0.374 g; 1.713 mmol; 86%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.89 (m, 2H), 7.55-7.47 (m, 1H), 7.44-7.36 (m, 2H), 2.96-2.88 (m, 2H), 1.75-1.65 (m, 2H), 1.41-1.17 (m, 10H), 0.90-0.81 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 137.0, 132.7, 128.4, 127.9, 38.5, 31.7, 29.4, 29.3, 29.1, 24.3, 22.6, 14.0.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: M. Iinuma, K. Moriyama, H. Togo, *Eur. J. Org. Chem.* **2014**, *4*, 772-780.



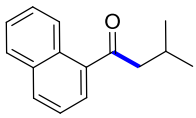
6b was obtained from **1b** and 1-naphthoyl chloride, using procedures A→H: 0.268 g; 1.455 mmol; 73%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61-8.55 (m, 1H), 7.97-7.92 (m, 1H), 7.89-7.77 (m, 2H), 7.61-7.41 (m, 3H), 3.05 (qd, *J*=7.3, 0.7 Hz, 2H), 1.28 (t, *J*=7.3 Hz, 3H). ^{13}C NMR (100 MHz $CDCl_3$) δ 205.1, 136.1, 133.8, 132.2, 130.0, 128.3, 127.7, 127.0, 126.3, 125.7, 124.3, 35.2, 8.6.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: B. Suchand, G. Satyanarayana, *Eur. J. Org. Chem.* **2017**, *2017*, 3886-3895.



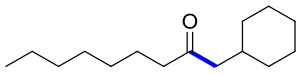
6c was obtained from **1c** and 1-naphthoyl chloride using procedures A→H: 0.269 g; 1.357 mmol; 68%, pale yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58-8.52 (m, 1H), 7.97 (d, *J*=8.2 Hz, 1H), 7.87 (d, *J*=8.1 Hz, 1H), 7.83 (dd, *J*=7.2, 1.3 Hz, 1H), 7.60-7.44 (m, 3H), 3.01 (t, *J*=7.3 Hz, 2H), 1.90-1.77 (m, 2H), 1.02 (t, *J*=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 136.4, 133.9, 132.2, 130.1, 128.3, 127.7, 127.1, 126.3, 125.7, 124.3, 44.1, 18.1, 13.8.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: J.-B. Peng, B. Chen, X. Qi, J. Ying, X.-F. Wu, *Adv. Synth. Catal.* **2018**, *360*, 4153-4160.

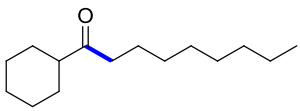


6d was obtained from **1d** and 1-naphthoyl chloride, using procedures A→H: 0.261 g; 1.229 mmol; 61%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59-8.53 (m, 1H), 7.97 (d, *J*=8.2 Hz, 1H), 7.89-7.85 (m, 1H), 7.82 (dd, *J*=7.2, 1.2 Hz, 1H), 7.62-7.46 (m, 3H), 2.91 (d, *J*=7.0 Hz, 2H), 2.40-2.28 (m, 1H), 1.01 (d, *J*=6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 136.7, 133.9, 132.2, 130.0, 128.4, 127.7, 127.2, 126.3, 125.7, 124.3, 51.2, 25.6, 22.7.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: A. Kišić, M. Stephan, B. Mohar, *Org. Lett.* **2013**, *15*, 1614-1617.

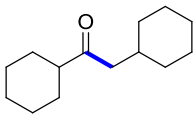


6e was obtained from **1e** and octanoyl chloride, using procedures B→H: 0.300 g; 1.337 mmol; 66%, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34-2.27 (m, 2H), 2.20 (d, *J*=6.9 Hz, 2H), 1.85-1.69 (m, 1H), 1.67-1.54 (m, 5H), 1.54-1.44 (m, 2H), 1.31-1.14 (m, 10H), 1.14-1.00 (m, 1H), 0.93-0.75 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 50.5, 43.5, 33.9, 33.2, 31.6, 29.2, 29.1, 26.2, 26.1, 23.8, 22.6, 14.0. HRMS (EI, *m/z*): calcd for $C_{15}H_{28}O$: 224.2140; found: 224.2140 ($M^{+\bullet}$). MS (EI, *m/z*, relative intensity): 224 (15), 143 (64), 142 (30), 140 (13), 127 (39), 125 (51), 97 (75), 55 (100).



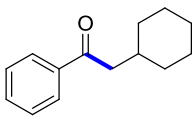
6e' was obtained from **1a** and cyclohexanecarbonyl chloride, using procedures A→H: 0.302 g; 1.1 mmol; 67%, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40-2.32 (m, 2H), 2.31-2.21 (m, 1H), 1.81-1.66 (m, 4H), 1.64-1.56 (m, 1H), 1.53-1.42 (m, 2H), 1.32-1.07 (m, 15H), 0.85-0.78 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.2, 50.7, 40.5, 31.7, 29.33, 29.25, 29.1, 28.4, 25.8, 25.6, 23.6, 22.5, 14.0.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: S. Dohi, K. Moriyama, H. Togo, *Tetrahedron* **2012**, *68*, 6557-6564.



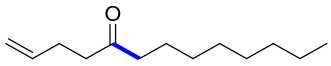
6f was obtained from **1e** and cyclohexanecarbonyl chloride, using procedures B→H: 0.257 g; 1.234 mmol; 62%, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28-2.17 (m, 3H), 1.84-1.65 (m, 5H), 1.65-1.51 (m, 6H), 1.31-0.98 (m, 8H), 0.90-0.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.8, 51.1, 48.3, 33.6, 33.2, 28.2, 26.2, 26.0, 25.8, 25.6.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: Y. Wei, B. Rao, X. Cong, X. Zeng, *J. Am. Chem. Soc.* **2015**, *125*, 9250-9253.



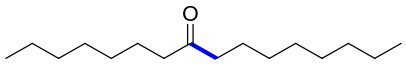
6g was obtained from **1e** and benzoyl chloride, using procedures A→H: 0.288 g; 1.424 mmol; 70%, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.54-7.48 (m, 1H), 7.45-7.39 (m, 2H), 2.80 (d, *J*=6.8 Hz, 2H), 2.02-1.88 (m, 1H), 1.78-1.57 (m, 5H), 1.33-1.06 (m, 3H), 1.05-0.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 137.3, 132.7, 128.4, 128.0, 46.1, 34.4, 33.3, 26.2, 26.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: W. Kong, C. Yu, H. An, Q. Song, *Org. Lett.* **2018**, *20*, 349-352.



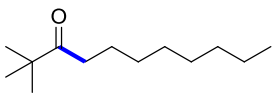
6h was obtained from **1a** and 4-pentenoyl chloride, using procedures B→H: 0.275 g; 1.400 mmol; 70%, pale yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddt, *J*=16.8, 10.2, 6.5 Hz, 1H), 5.00 (dq, *J*=17.1, 1.7 Hz, 1H), 4.96 (ddt, *J*=10.2, 1.8, 1.3 Hz, 1H), 2.47 (t, *J*=7.5 Hz, 2H), 2.37 (t, *J*=7.5 Hz, 2H), 2.34-2.27 (m, 2H), 1.60-1.50 (m, 2H), 1.34-1.19 (m, 10H), 0.85 (t, *J*=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 137.2, 115.1, 42.9, 41.7, 31.8, 29.3, 29.2, 29.1, 27.8, 23.8, 22.6, 14.1.

The ^{1}H NMR spectrum was consistent with that described in the literature: Y. Naoshima, M. Kawakubo, S. Wakabayashi, S. Hayashi, *Agric. Biol. Chem.* **1981**, *45*, 439-442.



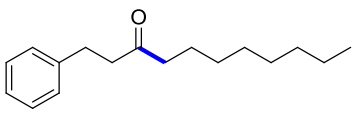
6i was obtained from **1a** and octanoyl chloride, using procedures B→H: 0.347 g; 1.443 mmol; 73%, pale-yellow solid, mp. 35-36 °C (Lit. 36-37 °C; S. Dohi, K. Moriyama, H. Togo, *Tetrahedron* **2012**, *68*, 6557-6564). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (t, *J*=7.4 Hz, 4H), 1.56-1.45 (m, 4H), 1.32-1.14 (m, 18H), 0.86-0.80 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 42.7 (ovl), 31.7, 31.6, 29.3, 29.20, 29.16, 29.07, 29.02, 23.8 (ovl), 22.57, 22.53, 13.98, 13.96.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: S. Dohi, K. Moriyama, H. Togo, *Tetrahedron* **2012**, *68*, 6557-6564.



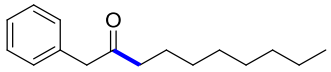
6j was obtained from **1a** and pivaloyl chloride, using procedures A→H: 0.212 g; 1.069 mmol; 53%, pale yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (dd, *J*=7.6, 7.1 Hz, 2H), 1.55-1.45 (m, 2H), 1.31-1.15 (m, 10H), 1.09 (s, 9H), 0.84 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.1, 44.0, 36.4, 31.8, 29.5, 29.3, 29.2, 26.4, 23.9, 22.6, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in the literature: K. Moriyama, M. Takemura, H. Togo, *J. Org. Chem.* **2014**, *79*, 6094-6104.



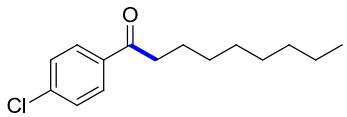
6k was obtained from **1a** and hydrocinnamoyl chloride, using procedures B→H: 0.388 g; 1.575 mmol; 79%, pale yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 2.91 (t, *J*=7.6 Hz, 2H), 2.73 (t, *J*=7.4 Hz, 2H), 2.38 (t, *J*=7.4 Hz, 2H), 1.60-1.49 (m, 2H), 1.35-1.18 (m, 10H), 0.90 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 141.1, 128.3, 128.2, 125.9, 44.1, 42.9, 31.7, 29.7, 29.2, 29.1, 29.0, 23.7, 22.5, 14.0.

The ^{1}H NMR spectrum was consistent with that described in the literature: S. Nimgirawath, E. Ritchie, W.C. Taylor, *Aust. J. Chem.* **1973**, *26*, 183-193.



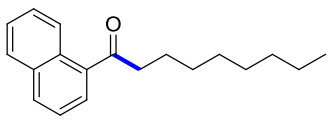
6l was obtained from **1a** and phenylacetyl chloride, using procedures B→H: 0.156 g; 0.671 mmol; 67% (at 1.0 mmol scale, yield based on β-ketosulfonate purified by distilling off unreacted sulfonyl ester *in vacuo*, overall yield based on **1a**: 59%), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 2H), 7.29-7.23 (m, 1H), 7.22-7.18 (m, 2H), 3.66 (s, 2H), 2.42 (t, *J*=7.4 Hz, 2H), 1.61-1.44 (m, 2H), 1.36-1.14 (m, 10H), 0.85 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 134.4, 129.4, 128.7, 126.9, 50.1, 42.0, 31.8, 29.3, 29.1 (ovl), 23.7, 22.6, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: M. Arisawa, M. Kuwajima, F. Toriyama, G. Li, M. Yamaguchi; *Org. Lett.* **2012**, 14, 3804-3807.

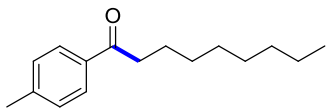


6m was obtained from **1a** and 4-chlorobenzoyl chloride, using procedures A→H: 0.420 g; 1.662 mmol; 83%, pale-yellow solid, mp. 57.5-58.5 °C (Lit. 58-58.5 °C; S. Dohi, K. Moriyama, H. Togo, Tetrahedron, **2012**, *68*, 6557-6564). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.81 (m, 2H), 7.39-7.33 (m, 2H), 2.91-2.84 (m, 2H), 1.71-1.62 (m, 2H), 1.37-1.16 (m, 10H), 0.87-0.79 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 139.1, 135.2, 129.4, 128.7, 38.5, 31.7, 29.4, 29.2, 29.1, 24.1, 22.6, 14.0.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: S. Dohi, K. Moriyama, H. Togo, *Tetrahedron* **2012**, *68*, 6557-6564.

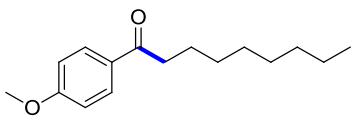


6n obtained from **1a** and 1-naphthoyl chloride, using procedures A→H: 0.355 g; 1.323 mmol; 66%, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61-8.56 (m, 1H), 7.94 (d, *J*=8.3 Hz, 1H), 7.87-7.78 (m, 2H), 7.61-7.41 (m, 3H), 3.06-2.97 (m, 2H), 1.85-1.72 (m, 2H), 1.47-1.20 (m, 10H), 0.94-0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 136.3, 133.8, 132.1, 130.0, 128.3, 127.6, 127.1, 126.2, 125.7, 124.2, 42.1, 31.7, 29.4, 29.3, 29.1, 24.6, 22.6, 14.0. HRMS (EI+, *m/z*), calcd for $C_{19}H_{24}O$: 268.1827; found: 268.1826 ($M^{+\bullet}$). MS (EI, *m/z*, relative intensity): 268 (22), 170 (48), 155 (100), 127 (53).



6o was obtained from **1a** and *p*-toluyl chloride, using procedures A→H: 0.409 g; 1.760 mmol; 88%, white solid, mp. 36.5-37 °C (Lit. 36-37 °C; S. Dohi, K. Moriyama, H. Togo, *Tetrahedron* **2012**, *68*, 6557-6564). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 2H), 7.23-7.19 (m, 2H), 2.93-2.85 (m, 2H), 2.37 (s, 3H), 1.76-1.63 (m, 2H), 1.40-1.18 (m, 10H), 0.89-0.81 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 200.1, 143.4, 134.5, 129.1, 128.1, 38.4, 31.8, 29.4, 29.3, 29.1, 24.4, 22.6, 21.5, 14.0.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: S. Dohi, K. Moriyama, H. Togo, *Tetrahedron* **2012**, *68*, 6557-6564.



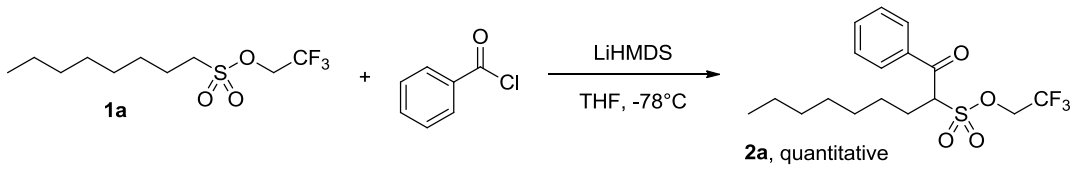
6p was obtained from **1a** and 4-methoxybenzoyl chloride, using procedures A→H: 0.359 g; 1.445 mmol; 72%, pale-yellow solid, mp. 43.5-44.5 °C (Lit. 43-44 °C; S. Dohi, K. Moriyama, H. Togo, *Tetrahedron* **2012**, *68*, 6557-6564). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.85 (m, 2H), 6.91-6.83 (m, 2H), 3.83 (s, 3H), 2.89-2.82 (m, 2H), 1.73-1.61 (m, 2H), 1.38-1.17 (m, 10H), 0.87-0.79 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 163.2, 130.2, 130.1, 113.6, 55.4, 38.3, 31.8, 29.42, 29.40, 29.1, 24.6, 22.6, 14.1.

The ^{1}H NMR and ^{13}C NMR spectra were consistent with those described in literature: S. Dohi, K. Moriyama, H. Togo, *Tetrahedron* **2012**, *68*, 6557-6564.

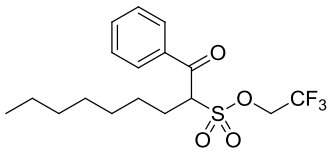
4. Mechanistic studies, intermediates, and other findings

4.1. Synthesis of β-ketosulfonate 2a

Warning! Procedure of acylation described below is applicable only for non-enolizable acyl chlorides. For general procedures of acylation, see section 3.1, page S-6.

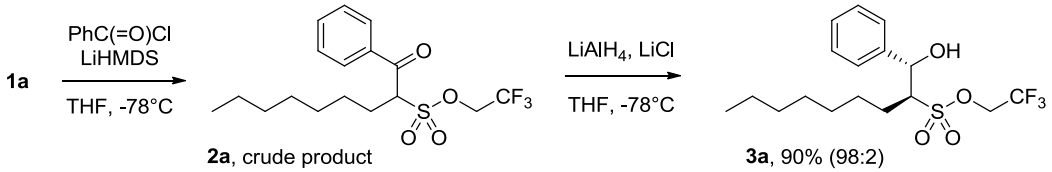


A 30 mL Schlenk flask was charged with **1a** (0.554 g, 2.005 mmol), benzoyl chloride (0.284 g, 2.020 mmol) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78 °C. To the resulted solution LiHMDS (lithium bis(trimethylsilyl)amide; 4.4 mL; 4.4 mmol; 1.0 M solution in THF) was added over ca 1 min with stirring. After 1 h the cooling bath was removed and aqueous solution of $NaHCO_3$ (10 mL; 5%) was added. The mixture was transferred to the separatory funnel, followed by addition of aqueous solution of $NaHCO_3$ (50 mL; 5%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a silica pad, rinsed with ethyl acetate, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt, yielding yellowish oil (0.763 g). NMR analysis revealed that the crude β-ketosulfonate **2a** was obtained in a nearly quantitative yield, and may be used for next step without further purification.



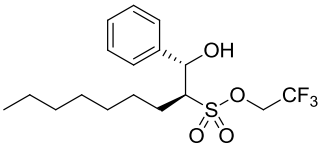
2a, yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.94 (m, 2H), 7.68-7.62 (m, 1H), 7.56-7.49 (m, 2H), 5.21 (dd, *J*=9.7, 4.4 Hz, 1H), 4.61-4.38 (m, 2H), 2.42-2.17 (m, 2H), 1.43-1.12 (m, 10H), 0.82 (t, *J*=6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 135.9, 134.7, 129.1, 128.8, 121.8 (q, $^1J_{C-F}$=277.7 Hz), 66.2, 65.8 (q, $^2J_{C-F}$=38.2 Hz), 31.4, 29.0, 28.9, 28.6, 26.6, 22.4, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.74. MS (ES+, *m/z*) calcd for $C_{17}H_{24}F_3O_4S$: 381.42; found: 381.13 ($M+H^+$). Elem anal, calcd for $C_{17}H_{23}F_3O_4S$: C, 53.67; H, 6.09; found: C, 53.67; H, 6.14.

4.2. Synthesis of β-hydroxysulfonate 3a



A 30 mL Schlenk flask was charged with **1a** (0.554 g, 2.005 mmol), benzoyl chloride (0.284 g, 2.020 mmol) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution LiHMDS (lithium bis(trimethylsilyl)amide; 4.4 mL; 4.4 mmol; 1.0 M solution in THF) was added over ca 1 min with stirring. After 1 h the cooling bath was removed and aqueous solution of $NaHCO_3$ (10 mL; 5%) was added. Then the mixture was transferred to the separatory

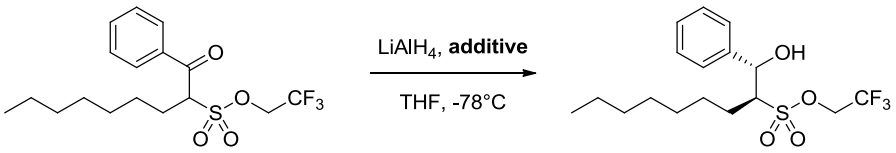
funnel, followed by addition of aqueous solution of $NaHCO_3$ (50 mL; 5%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a silica pad, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt. The resulting oil was placed in a 30 mL Schlenk flask together with lithium chloride (4.0 mmol) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution $LiAlH_4$ (2.2 mL; 2.2 mmol; 1.0 M solution in THF) was added over ca 1 min with stirring. After 1 h the cooling bath was removed and aqueous solution of HCl (10 mL; 3.5%) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and residue was separated with column chromatography (d=20 cm; ø 2 cm; SiO_2) on cyclohexane : ethyl acetate (50:1→4:1) to obtain β-ketosulfonate **2a** (0.046 g, 0.121 mmol, 6% of recovery) and β-hydroxysulfonate **3a** (0.687 g, 1.797 mmol, 90%).



3a, colorless oil, mixture of *S*,S** and *R*,S** diastereoisomers (98:2 according to ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.26 (m, 5H+5H), 5.52 (s, 1H, isom *R*,S**), 4.98 (d, *J*=8.5 Hz, 1H, isom *S*,S**), 4.61-4.32 (m, 2H+2H), 3.48 (dt, *J*=8.4, 5.2 Hz, 1H, isom *S*,S**), 3.34 (m, 1H, isom *R*,S**), 3.23 (br s, 1H+1H), 1.96-1.74 (m, 2H, isom *R*,S**), 1.71-1.49 (m, 2H, isom *S*,S**), 1.36-0.94 (m, 10H+10H), 0.82 (t, *J*=7.2 Hz, 3H+3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (isom *S*,S**) 139.4, 128.9, 128.8, 126.8, 122.1 (q, $^1J_{C\text{-}F}$=277.7 Hz), 73.3, 69.1, 64.0 (q, $^2J_{C\text{-}F}$=38.1 Hz), 31.4, 28.9, 28.5, 27.2, 26.3, 22.4, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.3 (t, $^3J_{F\text{-}H}$=8.2 Hz, isom *R*,S**), -74.4 (t, $^3J_{F\text{-}H}$=8.2 Hz, isom *S*,S**).

The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were consistent with those described in literature: B. Górski, A. Talko, T.Basak, M. Barbasiewicz, *Org. Lett.* **2017**, 19, 1756-1759.

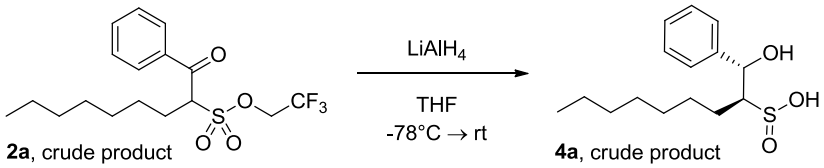
Performing of the above reduction without addition of LiCl resulted in lower yield of β-hydroxysulfonate **3a** (0.601 g, 1.571 mmol, 79%) and higher recovery of β-ketosulfonate **2a** (0.120 g, 0.315 mmol, 16%).



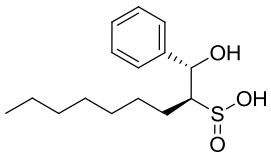
2a, crude product **3a**

Additive	Yield of **3a**	*S*,S**: *R*,S**
-	79%	97:3
LiCl (2.0 eq)	90%	98:2
LiBr (1.0 eq)	86%	97:3
LiBr (2.0 eq)	90%	97:3
$ZnCl_2$ (1.0 eq)	88%	96:4

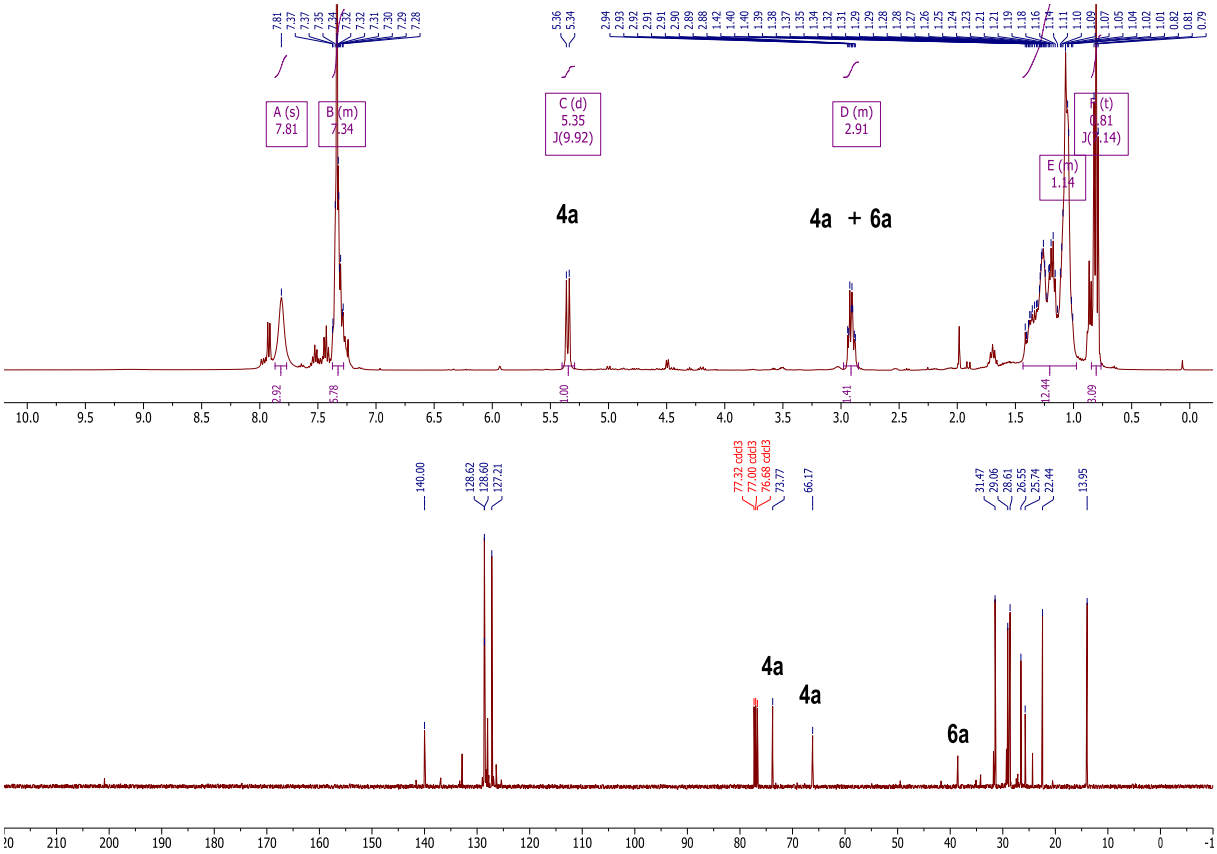
4.3. Synthesis of β-hydroxysulfinic acid 4a



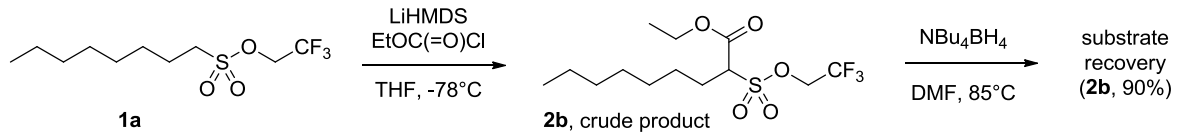
A 30 mL Schlenk flask was charged with crude β-ketosulfonate **2a** (766 mg, 2.014 mmol) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution $LiAlH_4$ (2.0 mL; 2.0 mmol; 1.0 M solution in THF) was added over ca 1 min with stirring. After 1 h the cooling bath was removed and the mixture was stirred for another 2 h at rt. Then aqueous solution of HCl (10 mL; 3.5%) was added. The mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt resulting in a cloudy, yellow oil (0.547 g). NMR spectroscopy (^1H, ^{13}C, gCOSY and gHSQCAD) revealed it is a mixture of β-hydroxysulfinic acid (**4a**) and ketone (**6a**) in a proportion of ca 5:1 (see the spectra below). Attempts to purify compound **4a** by chromatography have failed.



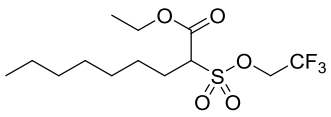
4a, crude product. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (broad s, 2H), 7.37-7.28 (m, 5H), 5.35 (d, *J*=9.9 Hz, 1H), 2.98-2.85 (m, 1H), 1.43-0.97 (m, 12H), 0.81 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 128.62, 128.60, 127.2, 73.8, 66.2, 31.5, 29.1, 28.6, 26.6, 25.7, 22.4, 14.0. HRMS (EI+, *m/z*), calcd for $C_{15}H_{23}O_3S$: 283.1368; found: 283.1378 ($M-H^+$).



4.4. Synthesis and reduction of ester derivative 2b



A 30 mL Schlenk flask was charged with **1a** (0.553 g, 2.001 mmol), ethyl chloroformate (0.221 g, 2.040 mmol) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution LiHMDS (lithium bis(trimethylsilyl)amide; 4.4 mL; 4.4 mmol; 1.0 M solution in THF) was added over ca 1 min with stirring. After 1 h the cooling bath was removed and aqueous solution of $NaHCO_3$ (10 mL; 5%) was added. The mixture was transferred to the separatory funnel, followed by addition of aqueous solution of $NaHCO_3$ (50 mL; 5%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a silica pad, rinsed with ethyl acetate, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt, to obtain **2b** as a yellowish oil (0.707 g).

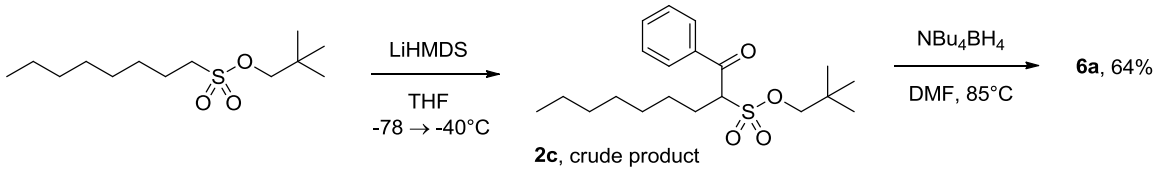


2b, yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60-4.45 (m, 2H), 4.25 (q, J=7.1 Hz, 2H), 4.02 (dd, J=9.9, 4.9 Hz, 1H), 2.19-2.01 (m, 2H), 1.41-1.15 (m, 10H), 1.28 (t, J=7.2 Hz, 3H), 0.87-0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 121.8 (d, $^1J_{C\text{-}F}$=278 Hz), 67.0, 65.8 (q, $^2J_{C\text{-}F}$=38.3 Hz), 62.8, 31.5, 28.73, 28.68, 27.9, 26.5, 22.5, 13.9, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.7 (t, $^3J_{F\text{-}H}$=7.8 Hz). HRMS (EI+, *m/z*) calcd for $C_{13}H_{24}O_5SF_3$: 349.1297; found: 349.1292 ($M+H^+$, 7), 263 (40), 250 (64), 204 (33), 185 (21), 101 (33), 97 (35), 73 (47), 55 (100).

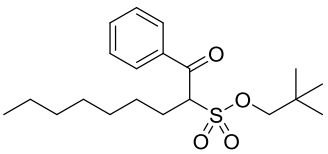
So obtained crude ester **2b** was dissolved in DMF (4 mL) and transferred to a 30 mL Schlenk flask, and the flask was placed in a heating bath at 85°C. To the stirred mixture a freshly prepared solution of NBu_4BH_4 (0.514 g, 2.001 mmol) in DMF (4 mL) was added dropwise over ca 3 min with stirring. After next 2 min the flask was transferred to a water bath (rt), stirred for 2 min to cool down, and then aqueous solution of NH_4Cl (10 mL; 10%) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and the residue was separated using column chromatography (d=23 cm; ø 3 cm; SiO_2) on cyclohexane : ethyl acetate mixture (20:1→4:1) to obtain recovered substrate **2b** (0.647 g; 1.801 mmol, 90%).

4.5. Synthesis and reduction of *neo*-pentyl β-ketosulfonate 2c

Synthesis of *neo*-pentyl 1-octanesulfonate was described in our previous report: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759.



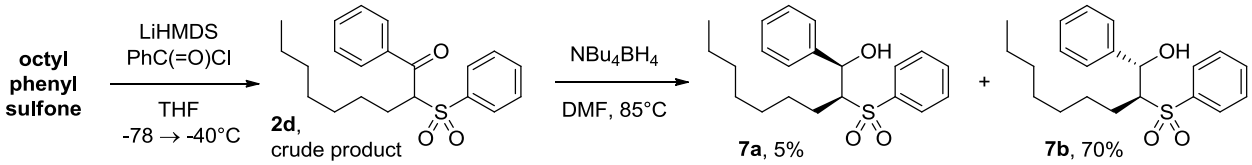
A 30 mL Schlenk flask was charged with *neo*-pentyl 1-octylsulfonate (0.527 g; 1.99 mmol), benzoyl chloride (0.285 g; 2.03 mmol) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution LiHMDS (lithium bis(trimethylsilyl)amide; 4.4 mL; 4.4 mmol; 1.0 M solution in THF) was added over ca 1 min with stirring. After 1 h the mixture was slowly warmed to −40°C (~80 min) and then aqueous solution of $NaHCO_3$ (10 mL; 5%) was added Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of $NaHCO_3$ (50 mL; 5%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a silica pad, rinsed with ethyl acetate, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt. The resulted yellowish oil (0.720 g) contained 94%$_{mol}$ of β-ketosulfonate **2c** and 6%$_{mol}$ of unreacted *neo*-pentyl 1-octylsulfonate (according to ^{1}H NMR).



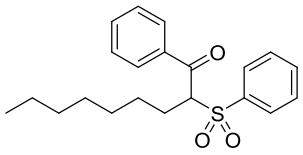
2c, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.96 (m, 2H), 7.67-7.56 (m, 1H), 7.55-7.44 (m, 2H), 5.07 (dd, *J*=10.3, 3.9 Hz, 1H), 3.89 (d, *J*=9.2 Hz, 1H), 3.81 (d, *J*=9.2 Hz, 1H), 2.44-2.29 (m, 1H), 2.27-2.09 (m, 1H), 1.37-1.08 (m, 10H), 0.85 (s, 9H), 0.82 (t, *J*=8.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 136.6, 134.2, 128.9 (*ovl*), 80.2, 65.3, 31.8, 31.5, 29.2, 28.7, 28.4, 26.9, 25.8, 22.5, 14.0. HRMS (ESI+, *m/z*) calcd for $C_{20}H_{32}O_4SNa$: 391.1914; found: 391.1913.

So obtained crude β-ketosulfonate **2c** was dissolved in DMF (8 mL) and transferred to a 30 mL Schlenk flask. The flask was placed in a heating bath at 85°C. To the stirred mixture a freshly prepared solution of NBu_4BH_4 (0.516 g, 2.005 mmol) in DMF (8 mL) was added dropwise over ca 10 min. After 30 min the heating was removed and aqueous solution of NH_4Cl (16 mL; 10%) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and the residue was separated using column chromatography (d=20 cm; ø 3 cm; SiO_2) on cyclohexane : ethyl acetate mixture (30:1→1:1) to obtain ketone **6a** (0.276 g; 1.264 mmol; 64%).

4.6. Synthesis and reduction of β-ketosulfone 2d

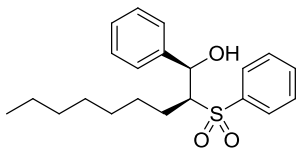


A 30 mL Schlenk flask was charged with octyl phenyl sulfone (0.508 g; 2.00 mmol), benzoyl chloride (0.286 g; 2.03 mmol) and argonated. Then THF (8 mL) was added, and the flask was placed in a cooling bath at -78°C. To the resulted solution LiHMDS (lithium bis(trimethylsilyl)amide; 4.4 mL; 4.4 mmol; 1.0 M solution in THF) was added over ca 1 min with stirring. After 1 h the mixture was slowly warmed to −40°C (~80 min) and then aqueous solution of $NaHCO_3$ (10 mL; 5%) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of $NaHCO_3$ (50 mL; 5%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a silica pad, rinsed with ethyl acetate, evaporated, transferred into a small round-bottom flask and dried *in vacuo* (~2.0×10^{-2} mbar) with vigorous stirring for 1 h at rt to obtain **2d** (0.706 g, 98% according to ^{1}H NMR).

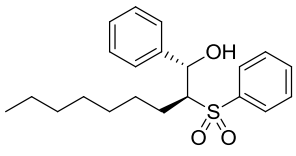


2d, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.88 (m, 2H), 7.80-7.72 (m, 2H), 7.66-7.53 (m, 2H), 7.52-7.40 (m, 4H), 5.05 (dd, *J*=10.5, 3.9 Hz, 1H), 2.18-1.95 (m, 2H), 1.30-1.05 (m, 10H), 0.79 (t, *J*=7.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 137.2, 136.5, 134.1, 134.0, 129.7, 128.9, 128.8, 128.7, 69.9, 31.5, 29.2, 28.7, 28.3, 26.9, 22.4, 13.9. HRMS (ESI+, *m/z*) calcd for $C_{21}H_{27}O_3SNa$: 381.1495; found: 381.1496 ($M+Na^+$).

So obtained crude β-ketosulfone **2d** was dissolved in DMF (8 mL) and transferred to a 30 mL Schlenk flask. The flask was placed in a heating bath at 85°C. To the stirred mixture a freshly prepared solution of NBu_4BH_4 (0.517 g, 2.009 mmol) in DMF (8 mL) was added dropwise over ca 10 min. After 30 min the heating was removed and aqueous solution of NH_4Cl (16 mL; 10%) was added. Then the mixture was transferred to the separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and the residue was separated using column chromatography (d=20 cm; ø 3 cm; SiO_2) on cyclohexane : ethyl acetate mixture (30:1→1:1) to obtain β-hydroxysulfones **7a** (0.037 g; 0.103 mmol; 5%) and **7b** (0.504 g; 1.398 mmol; 70%).



7a, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.93 (m, 2H), 7.73-7.65 (m, 1H), 7.65-7.56 (m, 2H), 7.32-7.18 (m, 5H), 5.39 (s, 1H), 3.42 (d, *J*=2.1 Hz, 1H), 3.09 (ddd, *J*=6.2, 4.8, 1.4 Hz, 1H), 1.90-1.76 (m, 2H), 1.18-1.05 (m, 2H), 1.04-0.82 (m, 8H), 0.78 (t, *J*=7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.8, 134.1, 129.4, 128.7, 128.4, 127.6, 125.3, 70.3, 69.4, 31.5, 28.8, 28.5, 28.4, 22.4, 21.0, 14.0. MS (ESI+, *m/z*) calcd for $C_{21}H_{28}O_3SNa$: 383.1651; found: 383.17 ($M+Na^+$). Elem anal, calcd for $C_{21}H_{28}O_3S$: C, 69.96; H, 7.83; found: C, 70.18; H, 7.70.

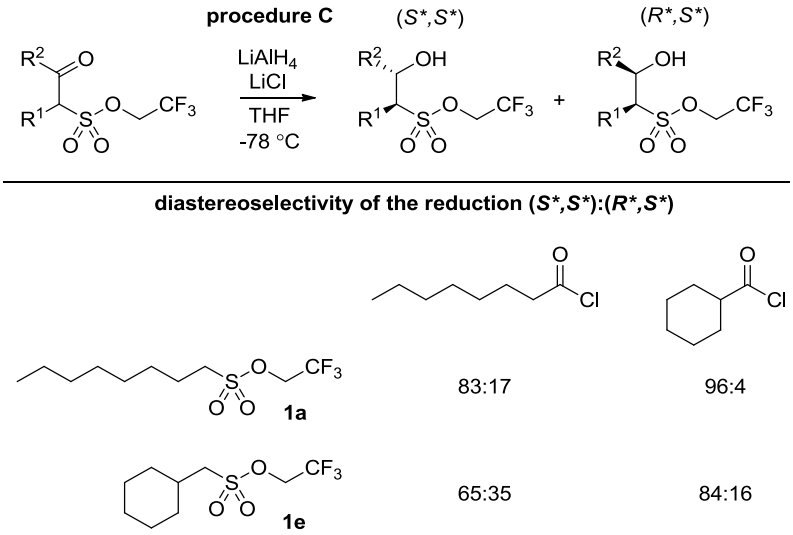


7b, white waxy solid, mp.: 51.0-52.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.86 (m, 2H), 7.67-7.60 (m, 1H), 7.58-7.50 (m, 2H), 7.31-7.25 (m, 5H), 4.98 (dd, *J*=8.7, 2.5 Hz, 1H), 4.42 (d, *J*=2.5 Hz, 1H), 3.28 (ddd, *J*=8.7, 6.0, 4.4 Hz, 1H), 1.62-1.44 (m, 1H), 1.31-1.15 (m, 1H), 1.14-1.03 (m, 2H), 1.00-0.90 (m,

2H), 0.90-0.60 (m, 6H), 0.77 (t, *J*=7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 138.2, 133.8, 129.1, 128.6, 128.44, 128.42, 127.2, 73.4, 70.4, 31.3, 28.7, 28.3, 26.9, 26.4, 22.3, 13.9. MS (ESI+, *m/z*) calcd for $C_{21}H_{28}O_3SNa$: 383.51; found: 383.17 ($M+Na^+$). Elem anal, calcd for $C_{21}H_{28}O_3S$: C, 69.96; H, 7.83; found: C, 69.95; H, 7.75.

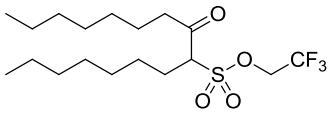
4.7. Stereoselectivity of reduction of the β-ketosulfonates (procedure C)

Four β-ketosulfonates were selected to study the effect of structure of the R^1 and R^2 substituents (linear or branched) on the stereoselectivity of the carbonyl group reduction under conditions of the procedure C ($LiAlH_4$, -78 °C). The results are presented at Table below. NMR characterization of the four crude β-ketosulfonates and four crude β-hydroxysulfonates is presented in chapters 4.8 and 4.9, respectively.

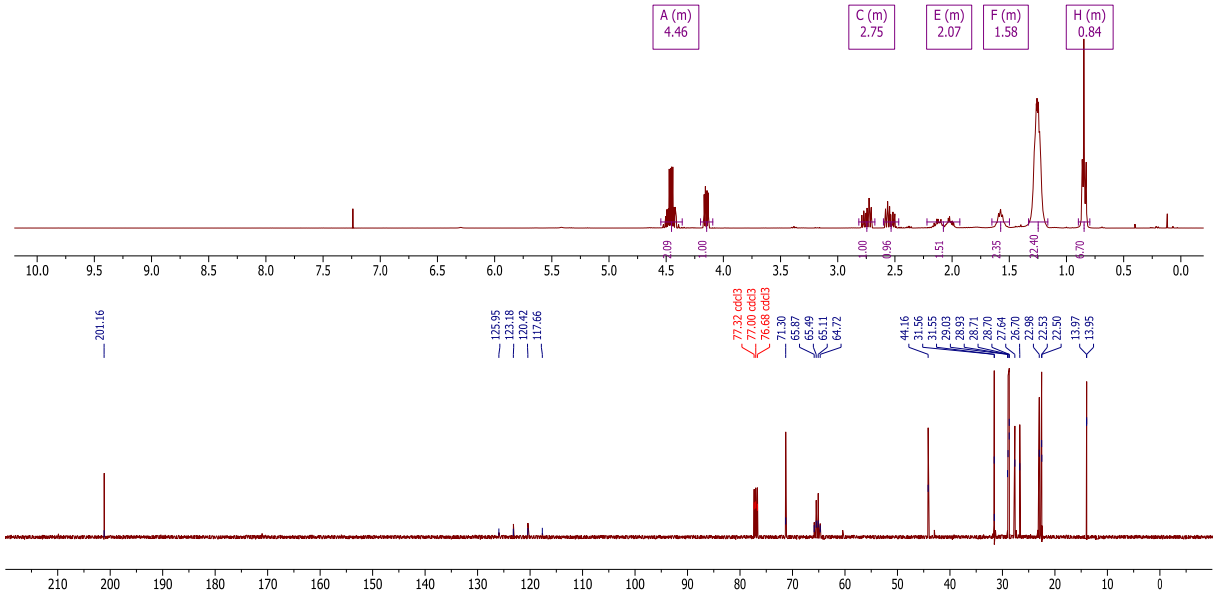


4.8. NMR characterization of crude intermediates: β-ketosulfonates

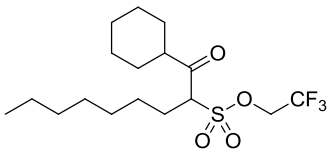
crude mixture containing mainly



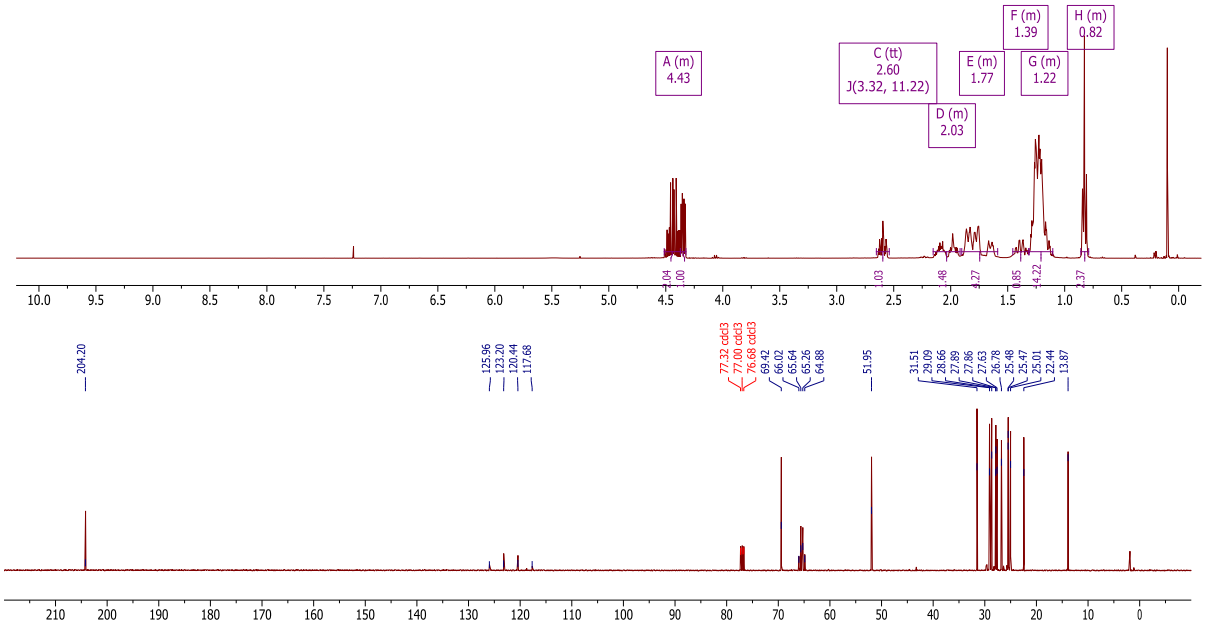
Pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53-4.38 (m, 2H), 4.15 (dd, *J*=10.0, 4.4 Hz, 1H), 2.79-2.70 (m, 1H), 2.59-2.48 (m, 1H), 2.18-2.06 (m, 1H), 2.06-1.96 (m, 1H), 1.64-1.52 (m, 2H), 1.33-1.16 (m, 18H), 0.88-0.82 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 121.8 (q, $^{1}J_{C\text{-}F}$= 278 Hz), 71.3, 65.3 (q, $^{2}J_{C\text{-}F}$= 38.3 Hz), 44.2, 31.56, 31.55, 29.0, 28.9, 28.71, 28.70, 27.6, 26.7, 23.0, 22.53, 22.50, 13.97, 13.95. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.7 (t, $^{3}J_{F\text{-}H}$=7.9 Hz).



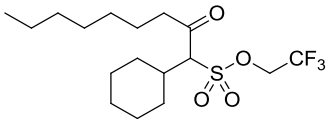
crude mixture containing mainly



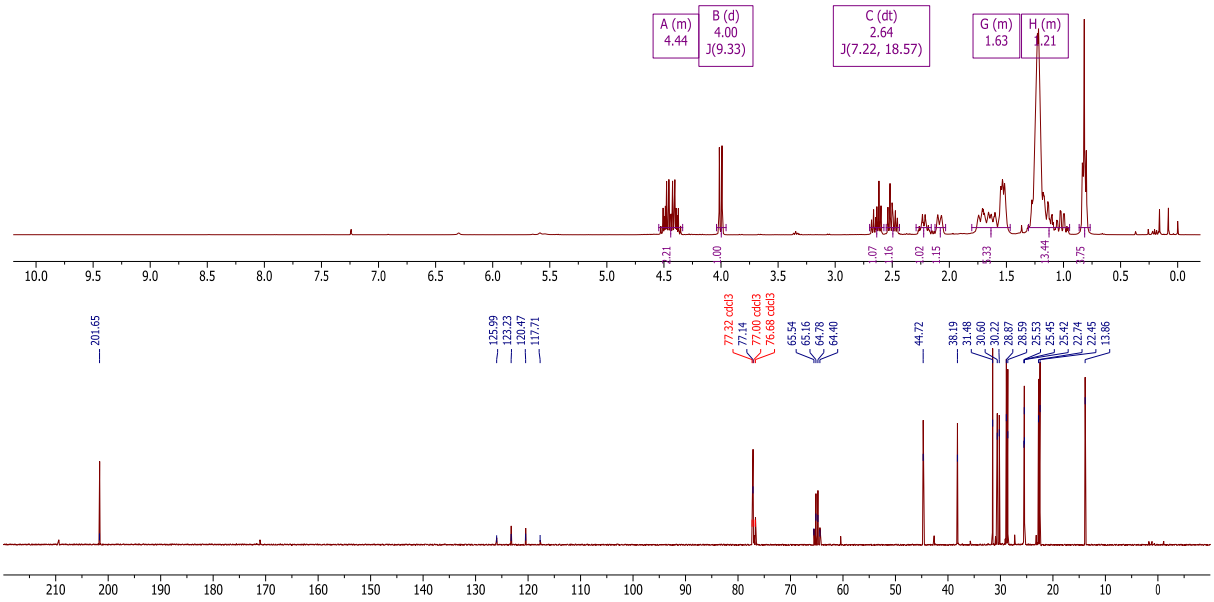
Pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51-4.37 (m, 2H), 4.35 (dd, *J*=9.9, 4.3 Hz, 1H), 2.60 (tt, *J*=11.2, 3.3 Hz, 1H), 2.15-1.92 (m, 2H), 1.90-1.59 (m, 4H), 1.45-1.33 (m, 2H), 1.32-1.10 (m, 14H), 0.85-0.80 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 121.8 (q, $^{1}J_{C\text{-}F}$=278 Hz), 69.4, 65.5 (q, $^{2}J_{C\text{-}F}$=38.2 Hz), 52.0, 31.5, 29.1, 28.7, 27.89, 27.86, 27.6, 26.8, 25.48, 25.47, 25.0, 22.4, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.7 (t, $^{3}J_{F\text{-}H}$=7.9 Hz).



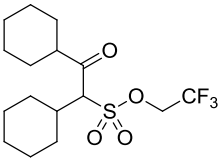
crude mixture containing mainly



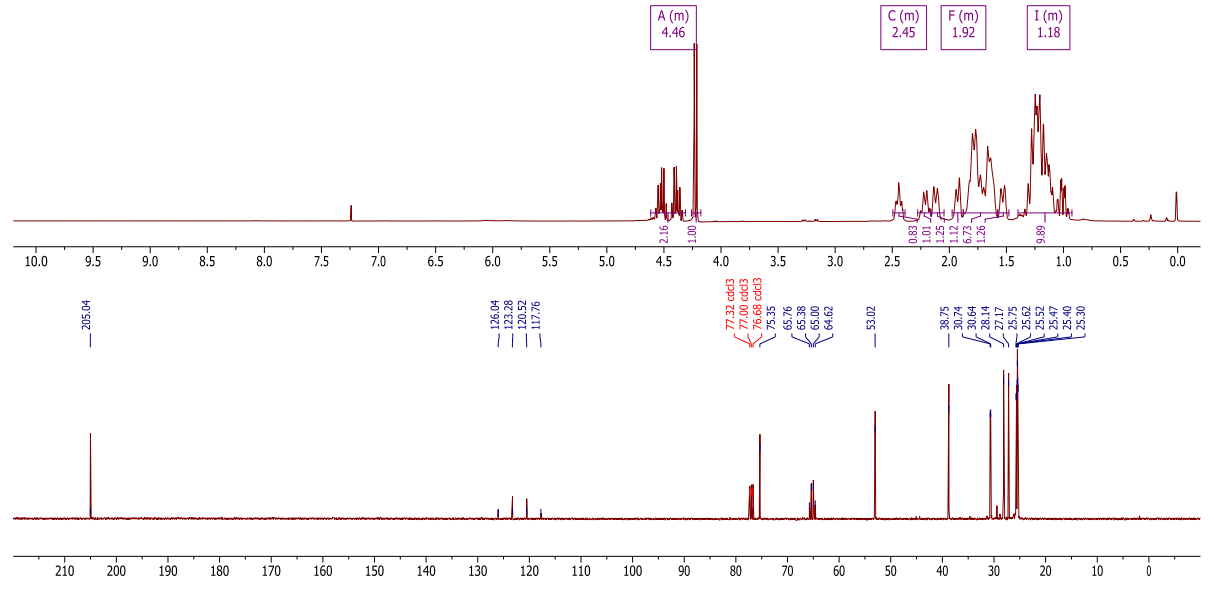
Pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54-4.38 (m, 2H), 4.00 (d, J=9.3 Hz, 1H), 2.64 (dt, J=18.6, 7.2 Hz, 1H), 2.50 (dt, J=18.5, 7.2 Hz, 1H), 2.29-2.16 (m, 1H), 2.13-2.03 (m, 1H), 1.79-1.47 (m, 6H), 1.32-0.94 (m, 13H), 0.86-0.77 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 121.8 (q, $^{1}J_{C\text{-}F}$=278 Hz), 77.1, 65.0 (q, $^{2}J_{C\text{-}F}$=38.2 Hz), 44.7, 38.2, 31.5, 30.6, 30.2, 28.9, 28.6, 25.53, 25.45, 25.42, 22.7, 22.5, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.6 (t, $^{3}J_{F\text{-}H}$=8.0 Hz).



crude mixture containing mainly

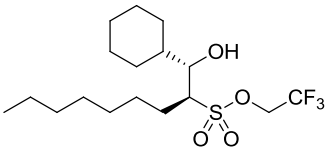


Pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58-4.33 (m, 2H), 4.22 (d, J=9.1 Hz, 1H), 2.49-2.39 (m, 1H), 2.28-2.16 (m, 1H), 2.16-2.08 (m, 1H), 1.98-1.89 (m, 1H), 1.87-1.58 (m, 7H), 1.57-1.49 (m, 1H), 1.40-0.93 (m, 10H).^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 121.9 (q, $^{1}J_{C\text{-}F}$=278 Hz), 75.4, 65.2 (q, $^{2}J_{C\text{-}F}$=38.2 Hz), 53.0, 38.8, 30.7, 30.6, 28.1, 27.2, 25.8, 25.6, 25.52, 25.47, 25.40, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.5 (t, $^{3}J_{F\text{-}H}$=8.1 Hz).

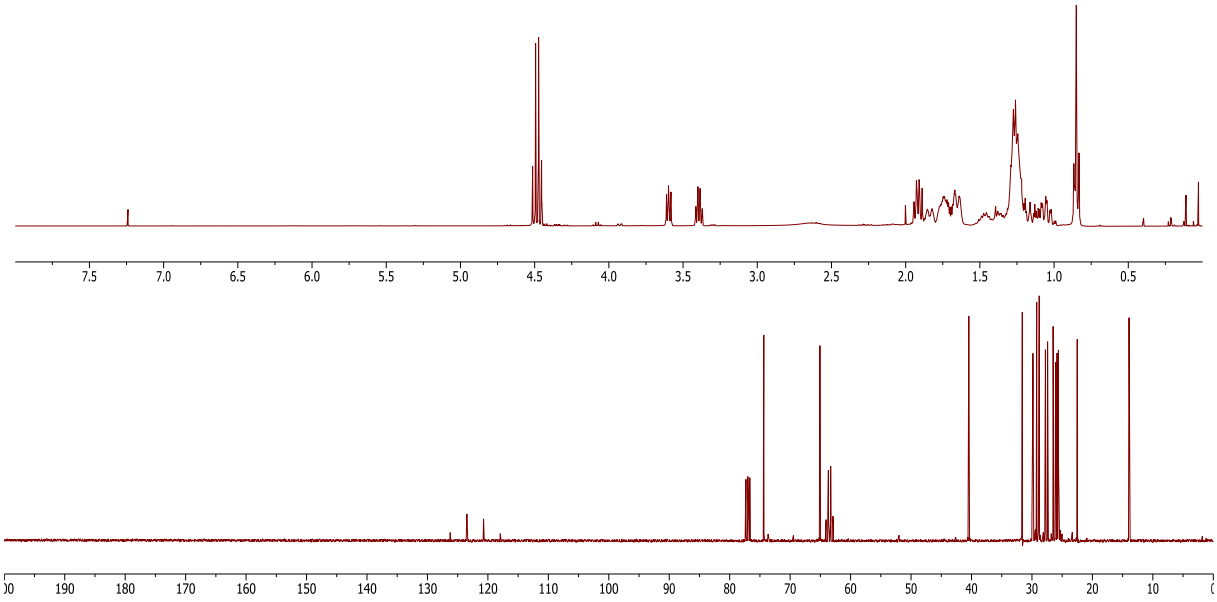


4.9. NMR characterization of crude intermediates: β-hydroxysulfonates

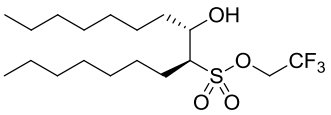
crude mixture containing mainly



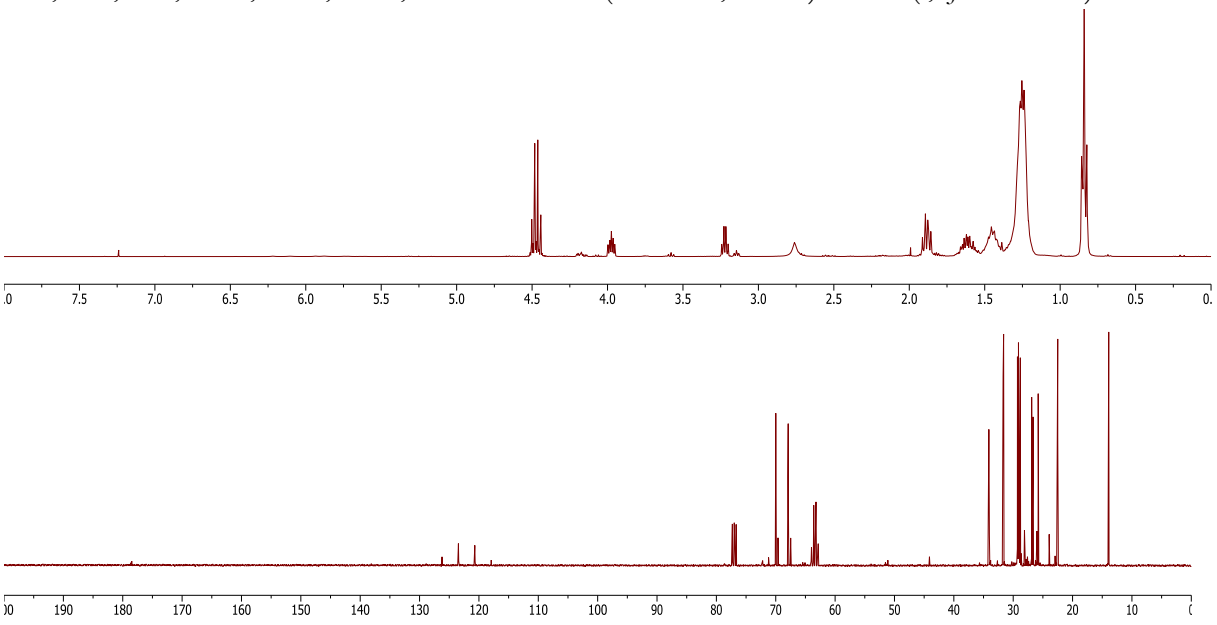
Pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (q, $^{3}J_{F\text{-}H}$=8.1 Hz, 2H), 3.93 (dd, *J*=9.2, 1.3 Hz, 1H, minor isom), 3.60 (dd, *J*=6.8, 5.1 Hz, 1H), 3.39 (ddd, *J*=6.6, 5.7, 5.2 Hz, 1H), 3.30 (ddd, *J*=7.5, 4.0, 1.3 Hz, 1H, minor isom), 2.65 (s br, 1H), 1.96-1.88 (m, 2H), 1.87-1.81 (m, 1H), 1.80-1.61 (m, 4H), 1.54-0.97 (m, 16H), 0.89-0.81 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.1 (q, $^{1}J_{C\text{-}F}$=278 Hz), 74.4, 65.1, 63.5 (q, $^{2}J_{C\text{-}F}$=38.1 Hz), 40.5, 31.6, 29.9, 29.2, 28.8, 27.8, 27.4, 26.5, 26.1, 25.9, 25.6, 22.5, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.4 (t, $^{3}J_{F\text{-}H}$=8.1 Hz).



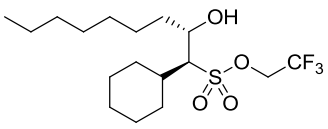
crude mixture containing mainly



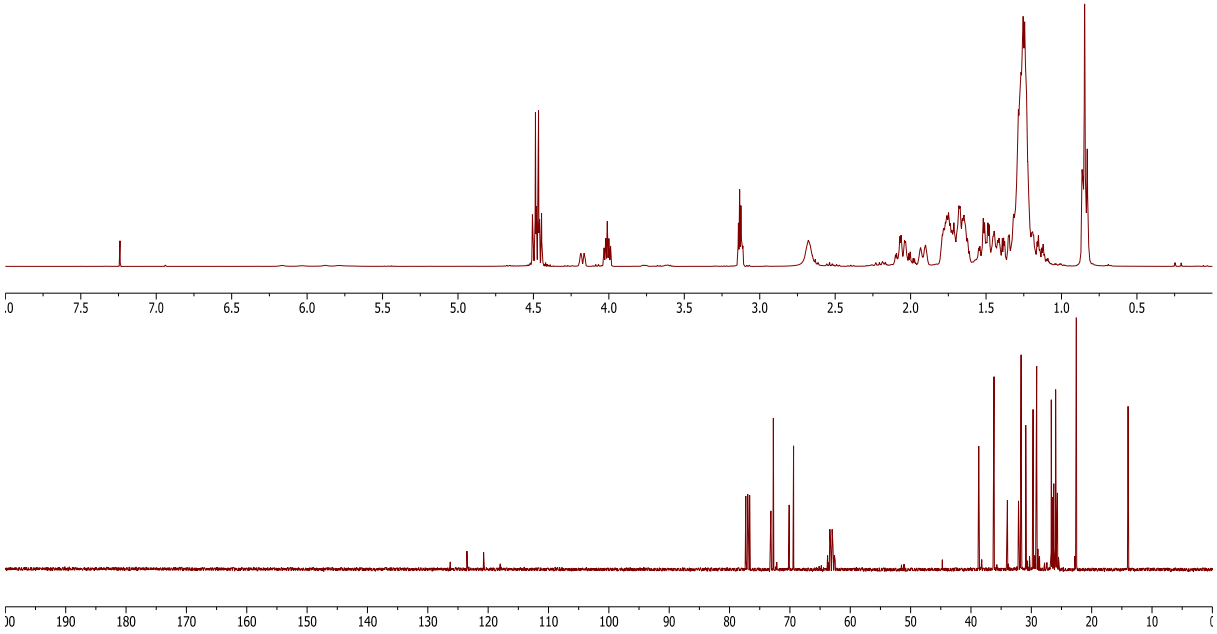
Pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (q, $^{3}J_{F\text{-}H}$=8.0 Hz, 2H), 4.19 (ddd, *J*=8.9, 4.3, 1.7 Hz, 1H, minor isom), 3.97 (ddd, *J*=8.9, 5.0, 4.0 Hz, 1H), 3.22 (td, *J*=6.1, 4.9 Hz, 1H), 3.15 (ddd, *J*=6.8, 4.8, 1.6 Hz, 1H, minor isom), 2.76 (s br, 1H), 1.93-1.83 (m, 2H), 1.70-1.54 (m, 2H), 1.51-1.38 (m, 2H), 1.35-1.17 (m, 18H), 0.90-0.80 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.1 (q, $^{1}J_{C\text{-}F}$=278 Hz), 70.0, 67.9, 63.4 (q, $^{2}J_{C\text{-}F}$=38.1 Hz), 34.1, 31.7, 31.6, 29.3, 29.2, 29.1, 28.8, 26.9, 26.7, 25.8, 22.54, 22.50, 13.93, 13.91. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.4 (t, $^{3}J_{F\text{-}H}$=7.9 Hz).



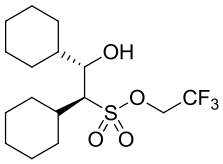
crude mixture containing mainly



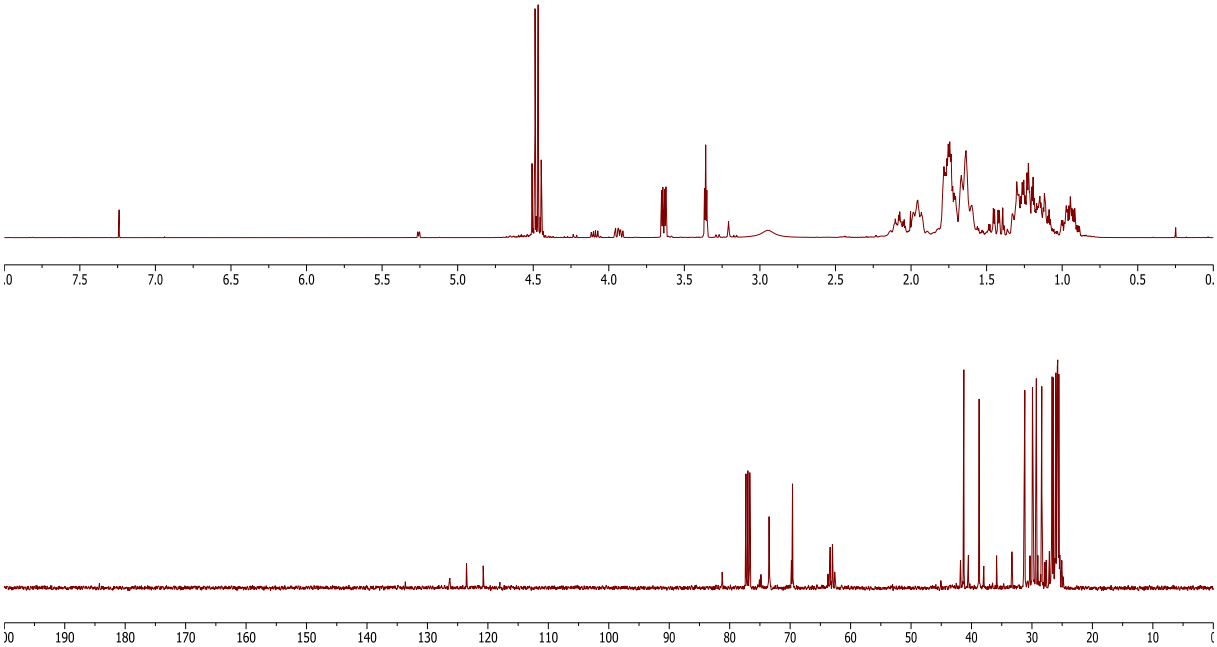
Pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (q, $^{3}J_{F-H}$=8.1 Hz, 2H), 4.17 (dt, *J*=9.5, 2.8 Hz, 1H, minor isom), 4.01 (dt, *J*=8.8, 4.3 Hz, 1H), 3.15-3.11 (m, 1H), 2.68 (s br, 1H), 2.13-1.95 (m, 1H), 1.95-1.87 (m, 1H), 1.82-1.60 (m, 5H), 1.57-1.09 (m, 16H), 0.88-0.81 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.2 (q, $^{1}J_{C-F}$=278 Hz), 72.8, 69.4, 63.1 (q, $^{2}J_{C-F}$=38.0 Hz), 38.7, 36.2, 31.7, 30.9, 29.7, 29.2, 29.1, 26.7, 26.6, 26.0, 25.8, 22.6, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ (-74.15)-(-74.29) (m).



crude mixture containing mainly

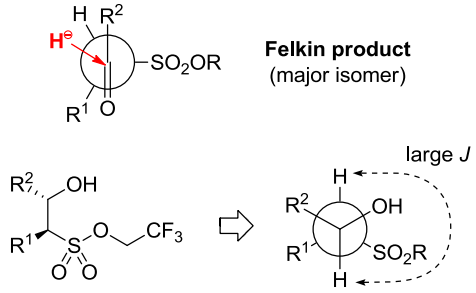


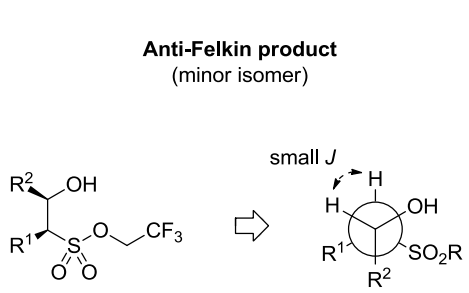
Pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (q, $^{3}J_{F-H}$=8.1 Hz, 2H), 3.95 (dd, *J*=8.9, 1.4 Hz, 1H, minor isom), 3.64 (dd, *J*=8.2, 3.2 Hz, 1H), 3.36 (t, *J*=3.1 Hz, 1H), 3.21 (t, *J*=1.6 Hz, 1H, minor isom), 2.95 (s br, 1H), 2.18-2.02 (m, 1H), 2.02-1.90 (m, 2H), 1.82-1.69 (m, 4H), 1.69-1.58 (m, 4H), 1.50-1.36 (m, 1H), 1.35-1.02 (m, 8H), 1.01-0.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.2 (q, $^{1}J_{C-F}$=278 Hz), 73.5, 69.6, 63.2 (q, $^{2}J_{C-F}$=37.9 Hz), 41.3, 38.8, 31.2, 29.9, 29.3, 28.4, 26.7, 26.5, 26.1, 25.8, 25.7, 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.3 (t, $^{3}J_{F-H}$=8.0 Hz).

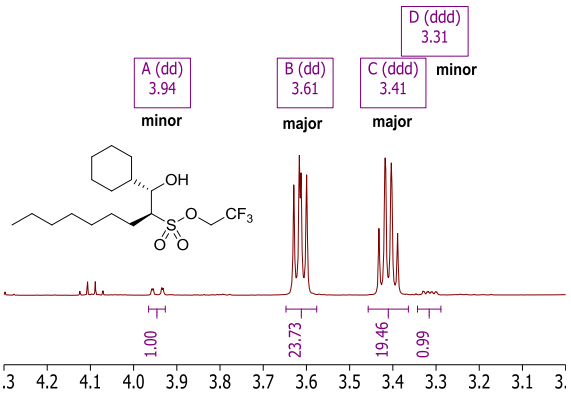


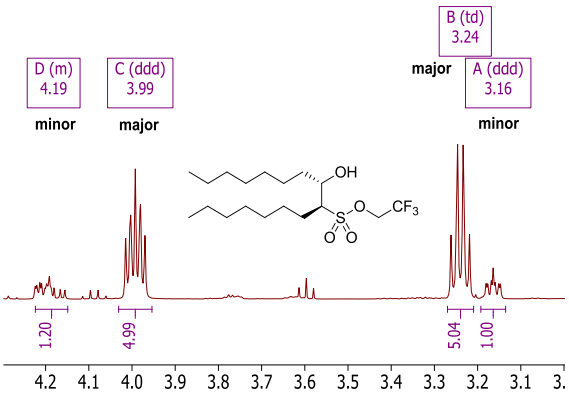
4.10. Structure assignment of β-hydroxysulfonates

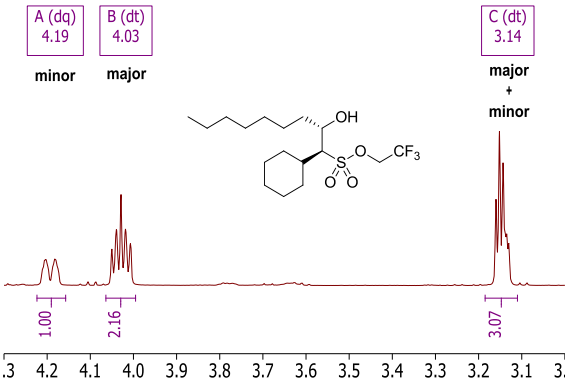
Assignment of stereochemistry of **3a**, based on X-ray studies, was presented in: B. Górski, A. Talko, T. Basak, M. Barbasiewicz, *Org. Lett.* **2017**, *19*, 1756-1759. Similar trends were observed for β-hydroxysulfonates in the present studies (this work).

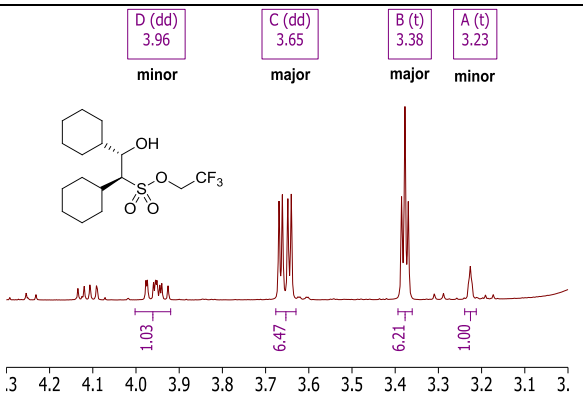




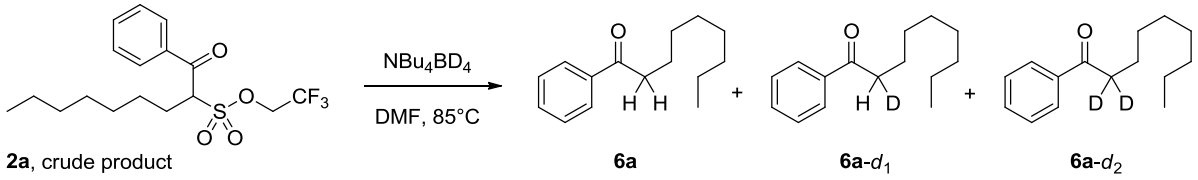








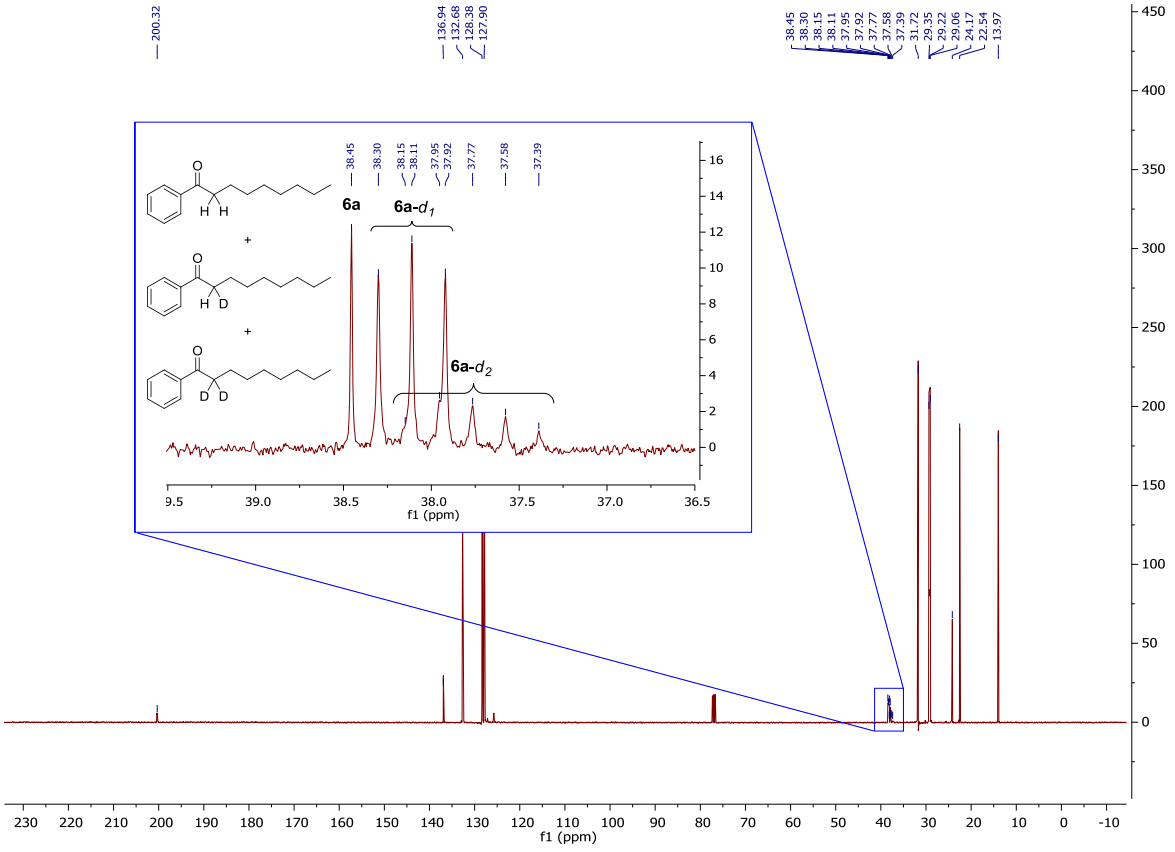
4.11. Reduction of β-ketosulfonate 2a with NBu_4BD_4



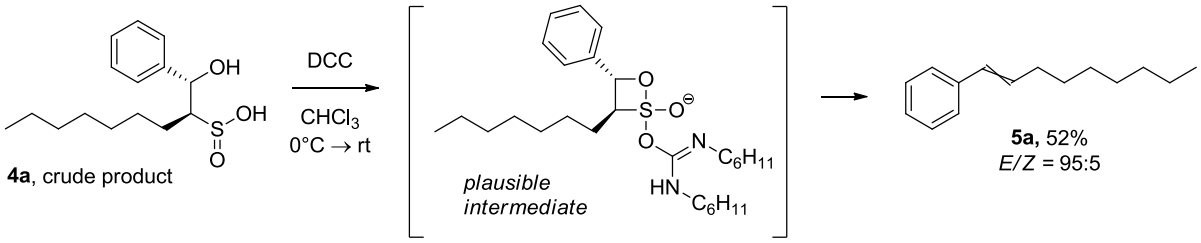
Tetrabutylammonium borodeuteride (NBu_4BD_4) was obtained from $NaBD_4$ (purchased from Aldrich) according to the literature procedure for synthesis of NBu_4BH_4 (Z. Rapi, P. Bakó, G. Keglevich, Á. Szöllősy, L. Drahos, L. Hegedűs, *Carbohydr. Res.* **2013**, *365*, 61-68).

A 50 mL round-bottom flask was charged with tetrabutylammonium hydrogensulphate (3.530 g, 10.397 mmol) and water (12 mL). Then 5 M aqueous NaOH solution (10 mL) was added. The mixture was cooled to rt and $NaBD_4$ (0.514 g, 12.280 mmol) was added portionwise during vigorous stirring. After 4 h at rt the mixture was extracted with CH_2Cl_2 (3×10 mL). The organic layer was dried over K_2CO_3, then evaporated, and the residue was crystallized from ethyl acetate to give NBu_4BD_4 (2.420 g, 9.272 mmol, 89%) as white crystals. Mp: 128.0-128.5 °C.

Crude β-ketosulfonate **2a** (2 mmol) was dissolved in DMF (4 mL) and transferred to a 30 mL Schlenk flask. The flask was placed in a heating bath at 85°C. To the stirred mixture a freshly prepared solution of NBu_4BD_4 (0.524 g, 2.008 mmol) in DMF (4 mL) was added dropwise over ca 10 min. After 30 min the heating was removed and aqueous solution of NH_4Cl (10 mL; 10%) was added. Then the mixture was transferred to a separatory funnel, followed by addition of aqueous solution of NH_4Cl (50 mL; 10%), and extracted with ethyl acetate (3×50 mL). Combined organic phases were washed with water (50 mL), brine (50 mL), and dried over anhydrous $MgSO_4$. Then, the mixture was filtered through a cotton wool, evaporated, and the residue was separated using column chromatography (d=20 cm; ø 3 cm; SiO_2) on cyclohexane : ethyl acetate mixture (50:1→10:1) to obtain a colorless oil (0.381 g). NMR analysis revealed that it is a mixture of non-deuterated, mono-deuterated and di-deuterated ketone **6a**, observed in the ^{13}C NMR as singlet, triplet and pentet respectively (pictured below).


200.32
136.94
132.68
128.38
127.90
38.45
38.30
38.15
38.11
37.95
37.92
37.77
37.58
37.39
31.72
29.35
29.22
29.06
24.17
22.54
13.97
6a
6a-d_1
6a-d_2
f1 (ppm)

4.12. Fragmentation of β-hydroxysulfinic acid 4a with DCC



A 10 mL round bottom flask was charged with β-hydroxysulfinic acid (obtained from 0.969 mmol of sulfonate), 2.5 mL of chloroform and placed in ice-water bath (0°C). To the resulted solution DCC (*N*,*N*'-dicyclohexylcarbodiimide; 0.210 g; 1.02 mmol) was added portionwise with stirring. After 15 minutes water bath was removed. The stirring was continued for 18 h, then the mixture was evaporated, and residue was filtered through a Schott filter in chilled ethyl acetate. Then, the mixture was evaporated, and residue was separated with column chromatography (d=26 cm; ø 3 cm; SiO_2) on cyclohexane to elute off the olefinic product. Then, solution of the product was evaporated, transferred into a small round-bottom flask and dried *in vacuo* (<2.0x10^{-2} mbar) with vigorous stirring for 1 h at rt to obtain **5a** (0.101 g; 0.499 mmol; 52%; *E*/*Z* 95:5) as a colorless oil.

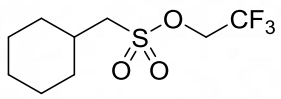
Analogous attempt of fragmentation of another β-hydroxysulfinic acid (obtained by acylation of **1a** with hydrocinnamyl chloride followed by reduction) failed to give alkene.

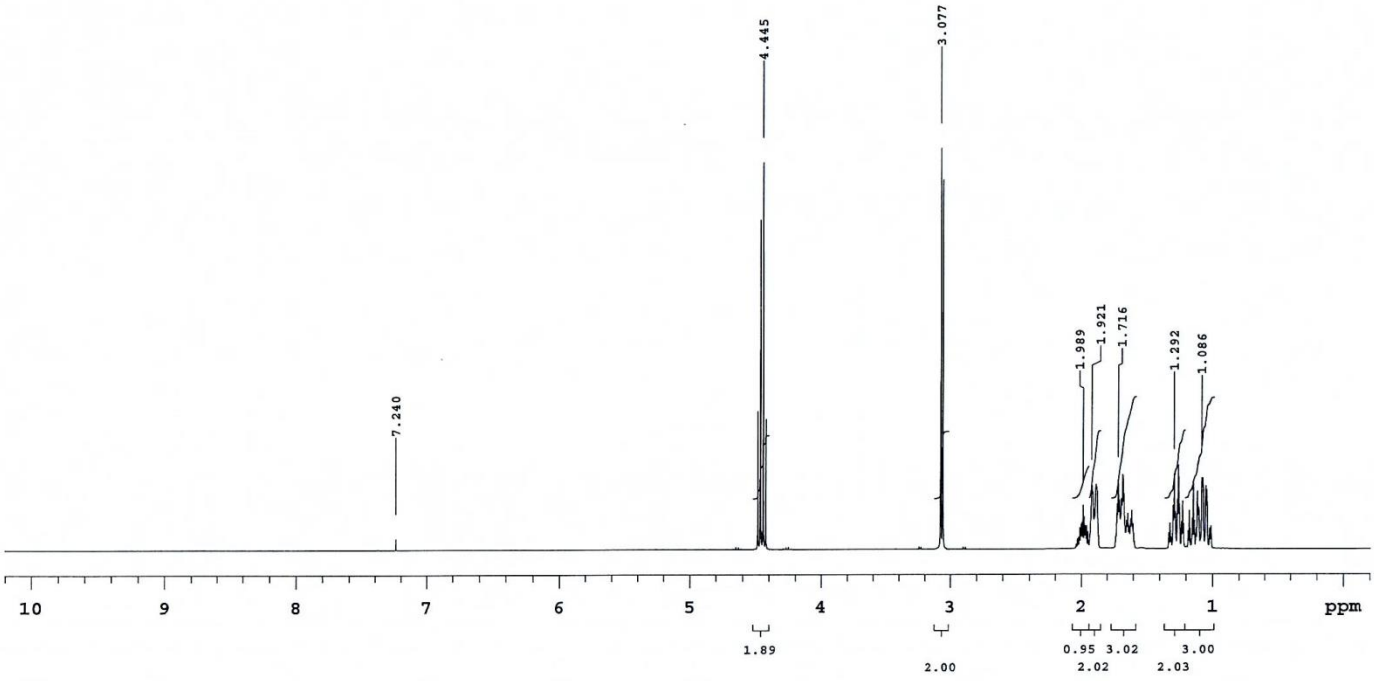
4.13. Other findings concerning substrates and reagents

- use of 2-chlorobenzothiazole, instead of 5-chloro-1-phenyl-1*H*-tetrazole, gave similar results,
- attempts at acylation of 2,2,2-trifluoroethyl 2-propanesulfonate (2° carbanion precursor) with benzoyl chloride gave low yield of the product (≤ 30%),
- acylation of 2,2,2-trifluoroethyl phenylmethanesulfonate with octanoyl chloride was successful and the product was reduced to ketone (1-phenyl-2-nonanone) in 81% of yield; however $LiAlH_4$ reduction of the β-ketosulfonate led to a mixture of diastereoisomers, most likely with a reversed selectivity (27:73),
- acylation of 1,1,1,3,3,3-hexafluoroisopropyl 1-octanesulfonate with benzyl chloride run unselectively,
- attempts to perform acylation-reduction steps or reduction-fragmentation steps in a one-pot version (without isolation) were poorly successful,
- acylation of 2,2,2-trifluoroethyl octanesulfonate with cinnamoyl chloride was successful, but only *E*-alkene was formed in good yield (55%, 91:9); attempts of reduction to ketone or β-hydroxysulfinic acid caused partial reduction of the C=C bond, giving mixtures of products,
- carbanion precursor **1a** was mainly recovered, when subjected to $LiAlH_4$, THF, rt, and to NBu_4BH_4, DMF, 85 °C.

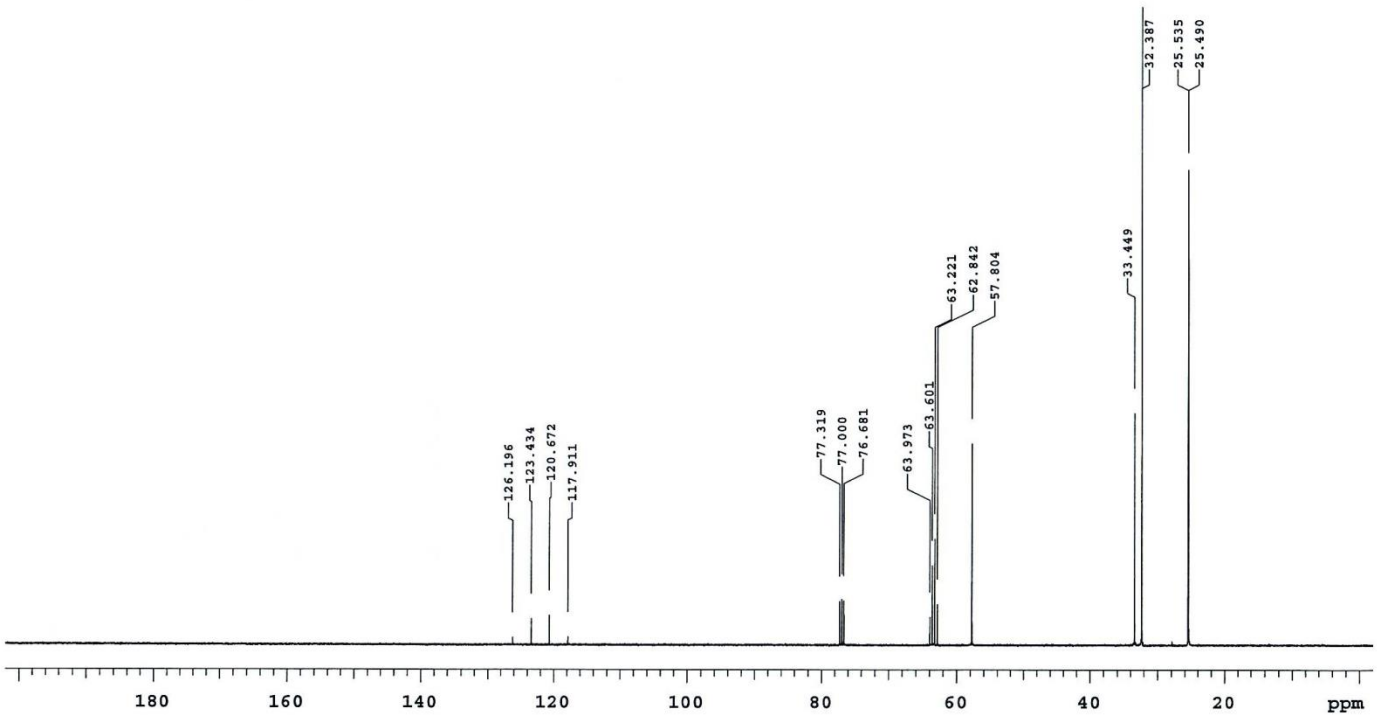
5. Reproductions of ^{1}H and ^{13}C NMR spectra

Sample Name: BG-318
Solvent: cdcl3

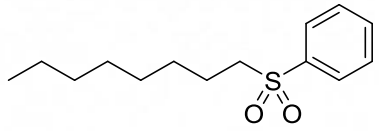


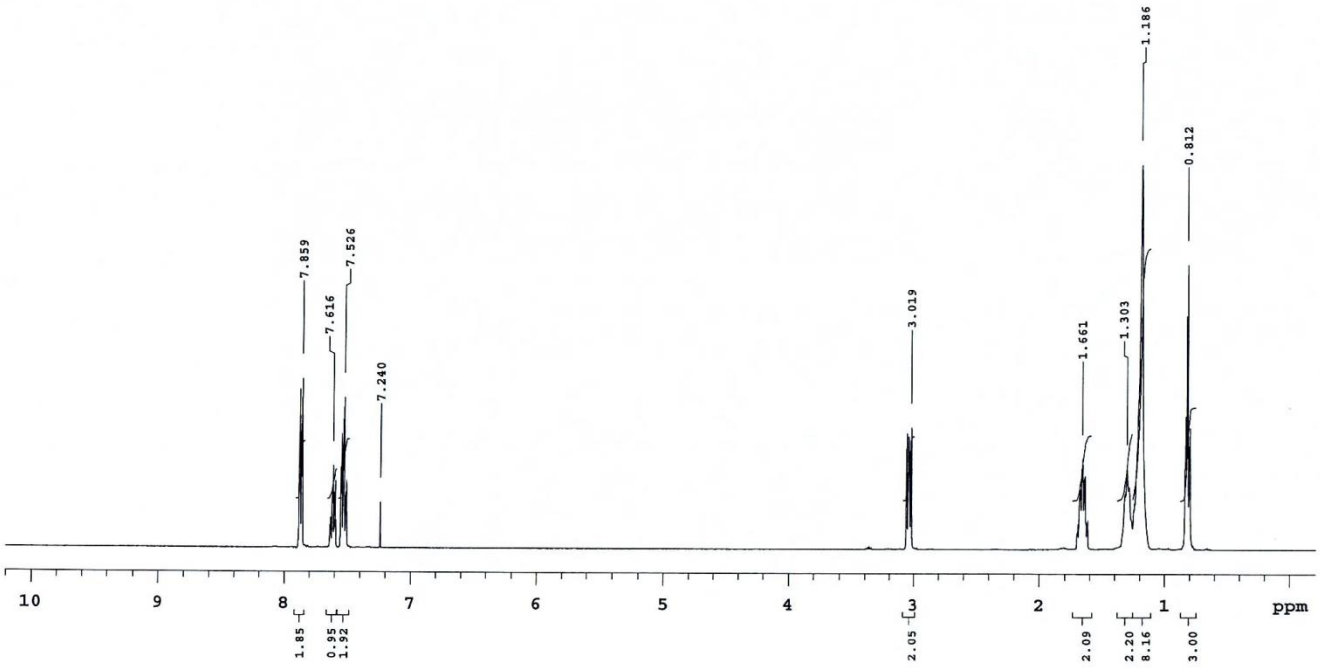


Sample Name: BG-318
Solvent: cdcl3

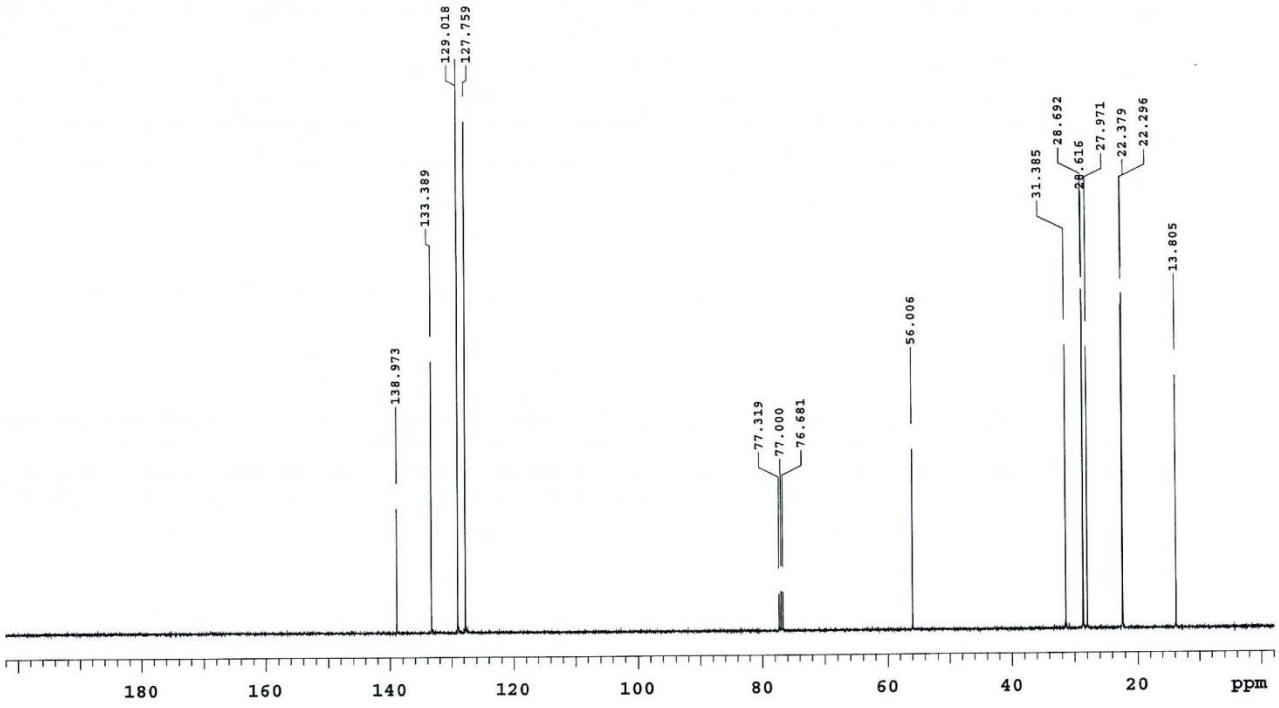


Sample Name: TB-043C
Solvent: cdcl3

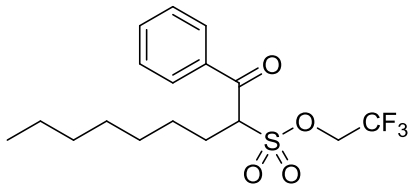


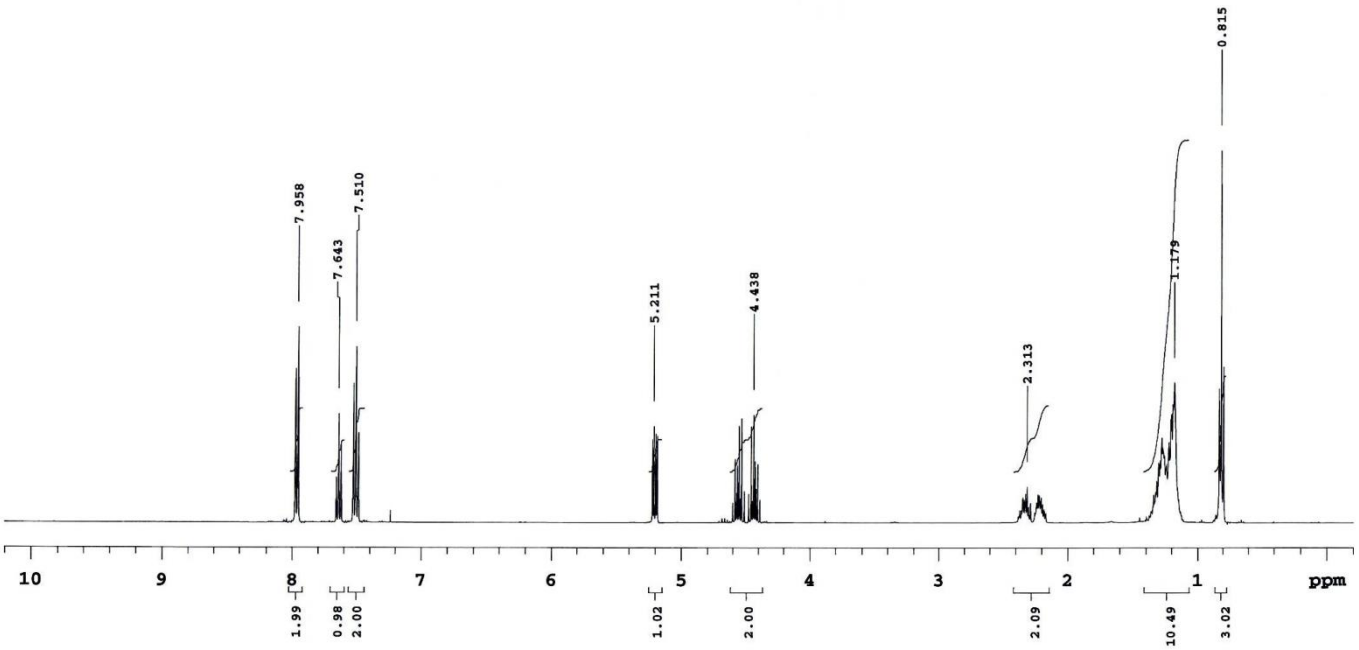


Sample Name: TB-043C_anal
Solvent: cdcl3

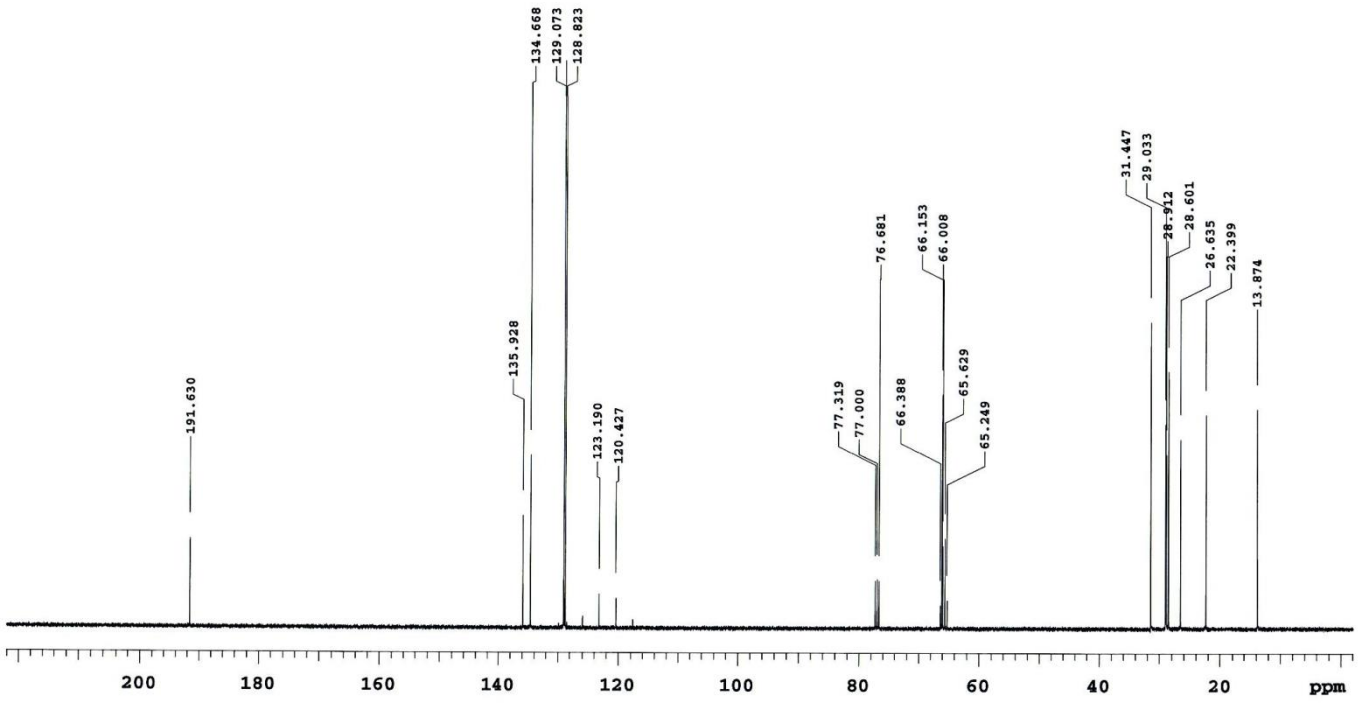


Sample Name: DB-087A_a
Solvent: cdcl3

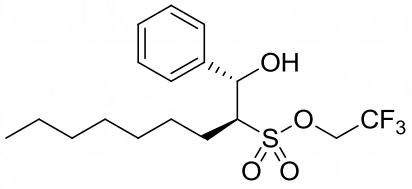


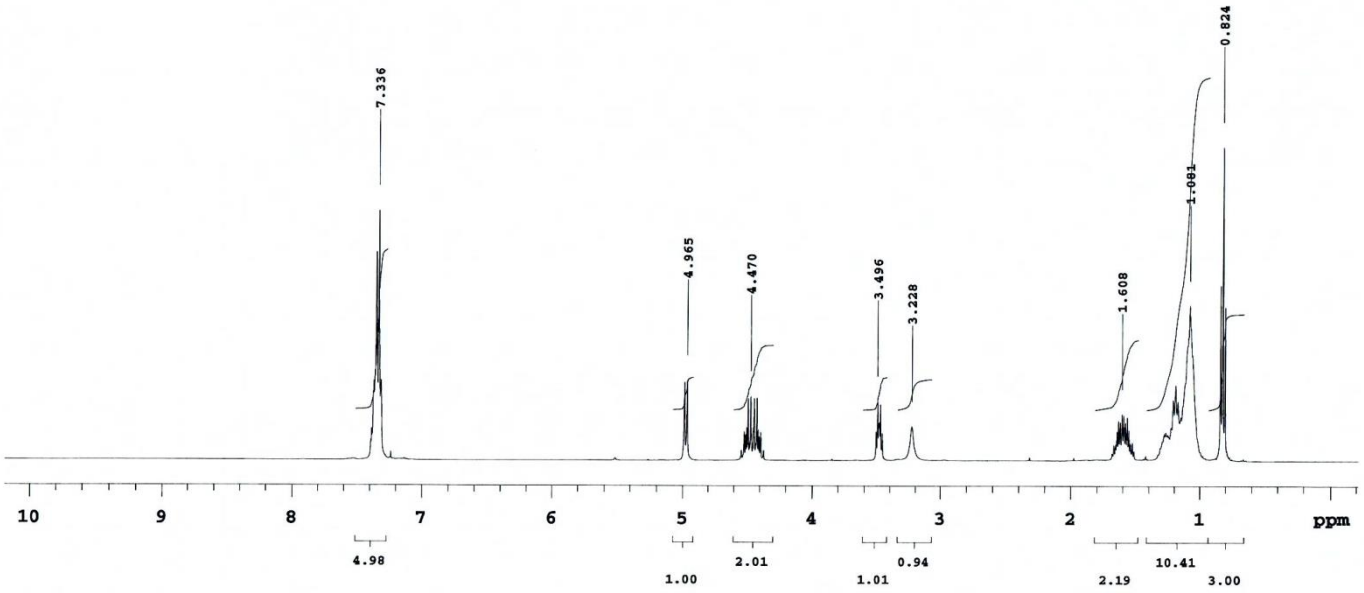


Sample Name: DB-087A_a
Solvent: cdcl3

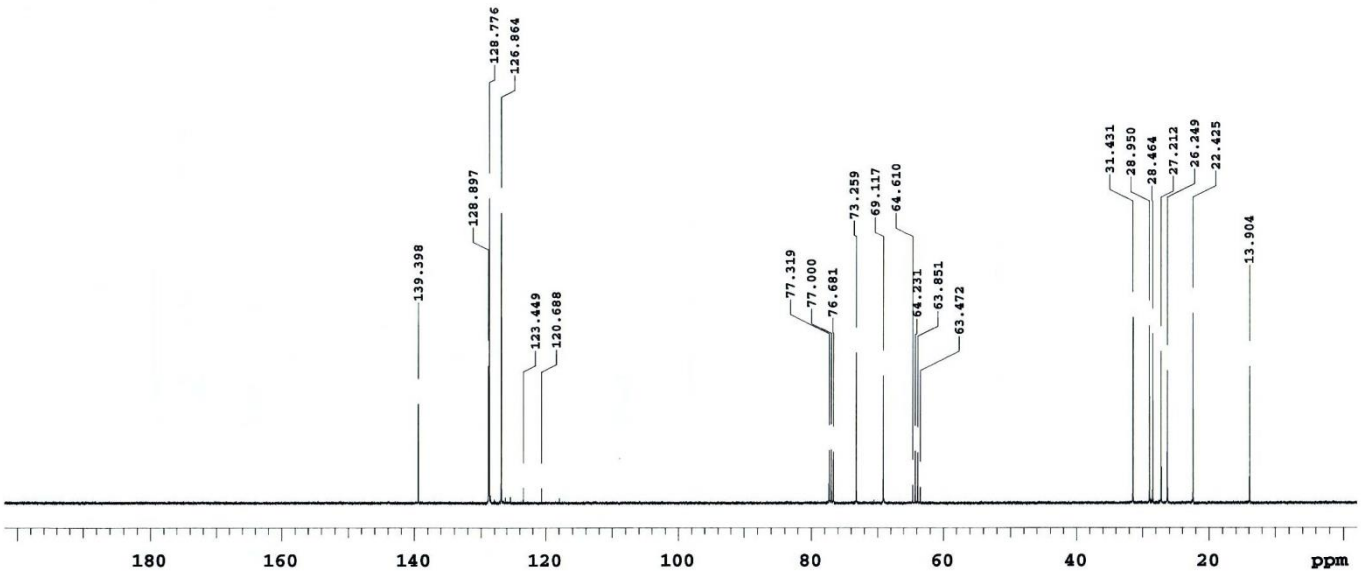


Sample Name: LG-034-B
Solvent: cdcl3

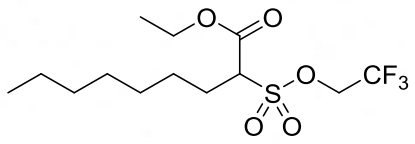


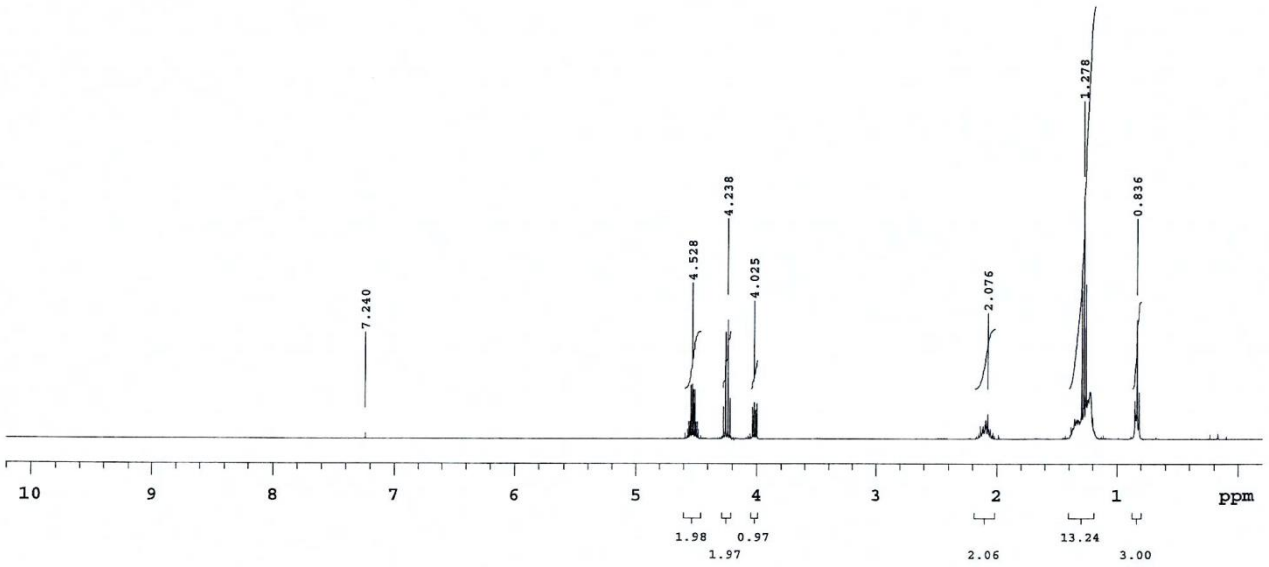


Sample Name: LG-034-B
Solvent: cdcl3

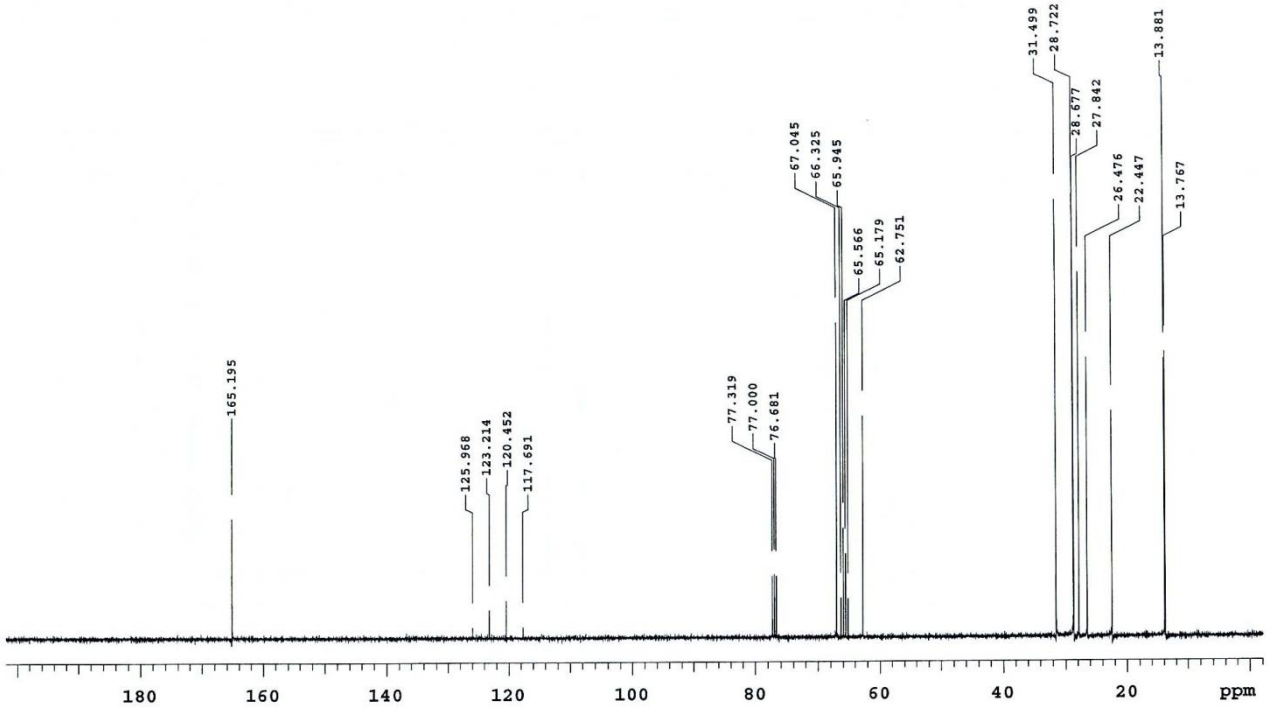


Sample Name: BG-426_sur
Solvent: cdcl3

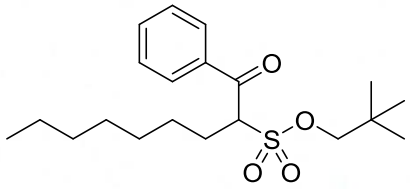




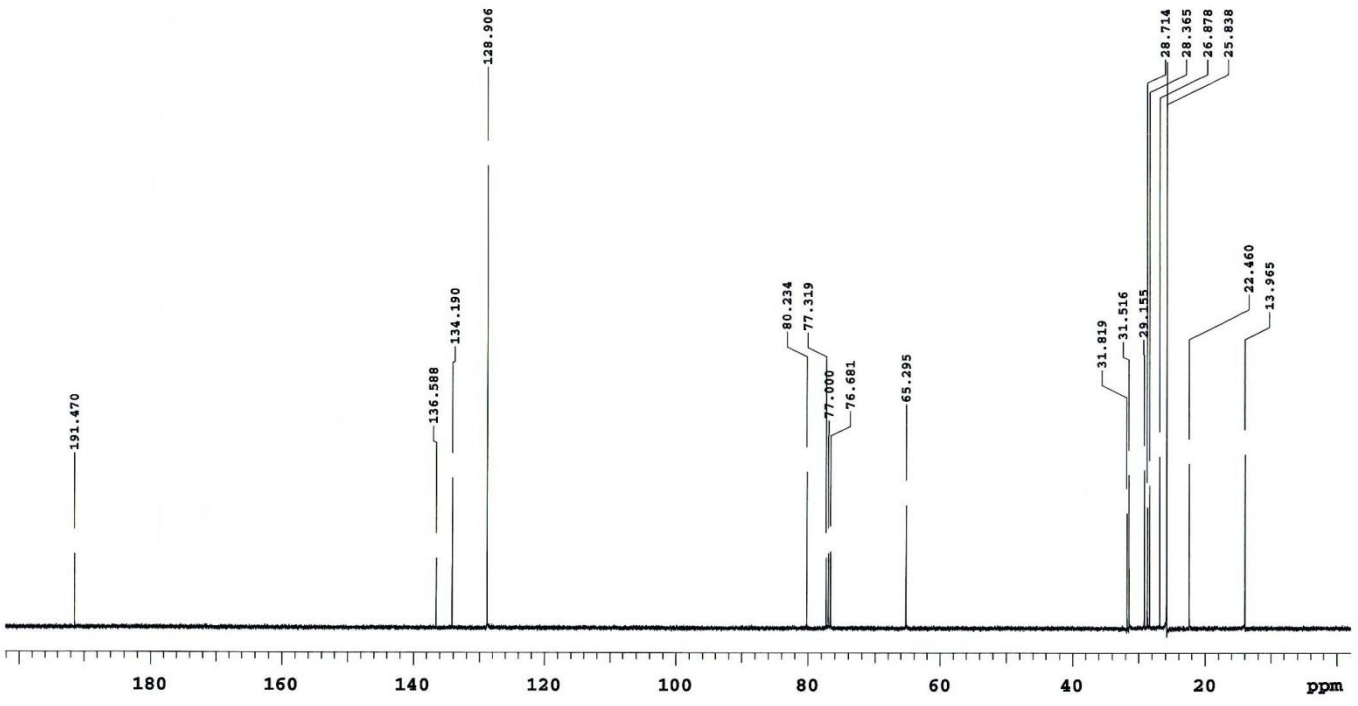
Sample Name: BG-426_sur
Solvent: cdcl3



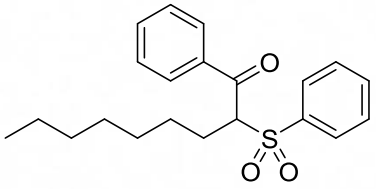
Sample Name: DB-112B_a
Solvent: cdcl3

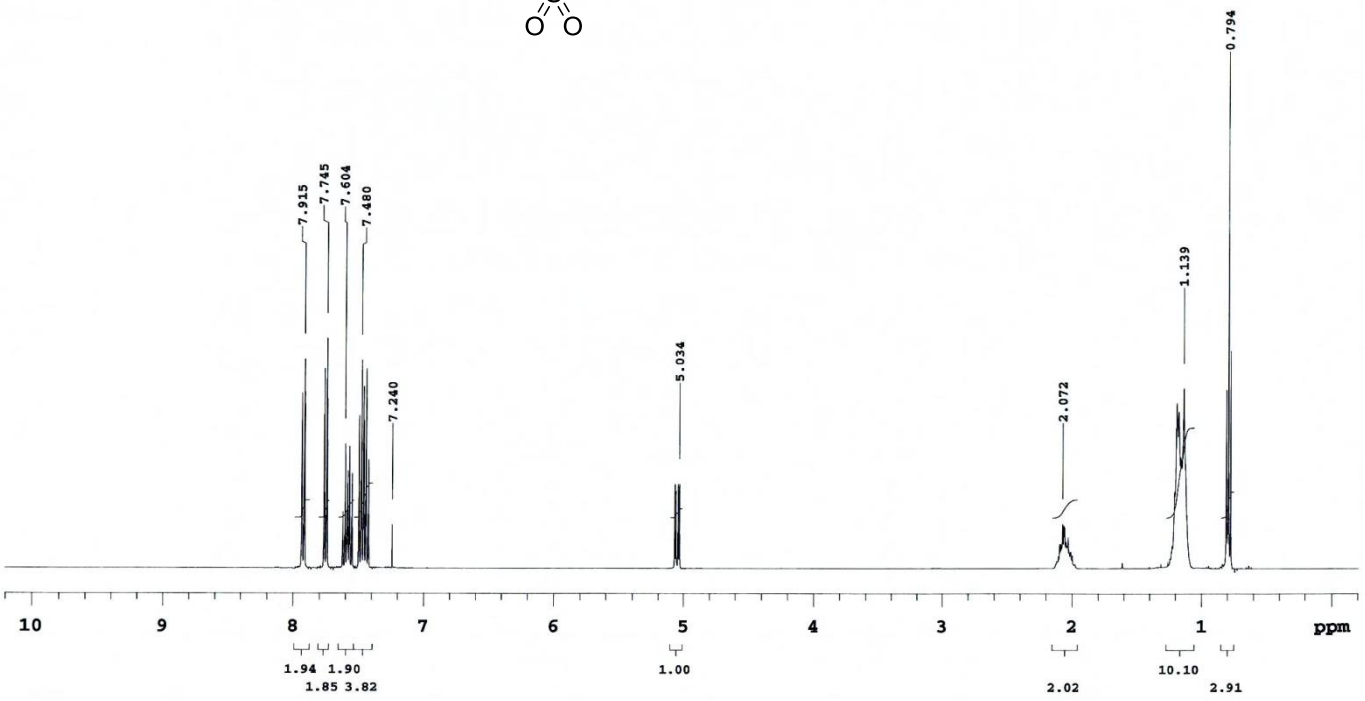


Sample Name: DB-112B_a
Solvent: cdcl3

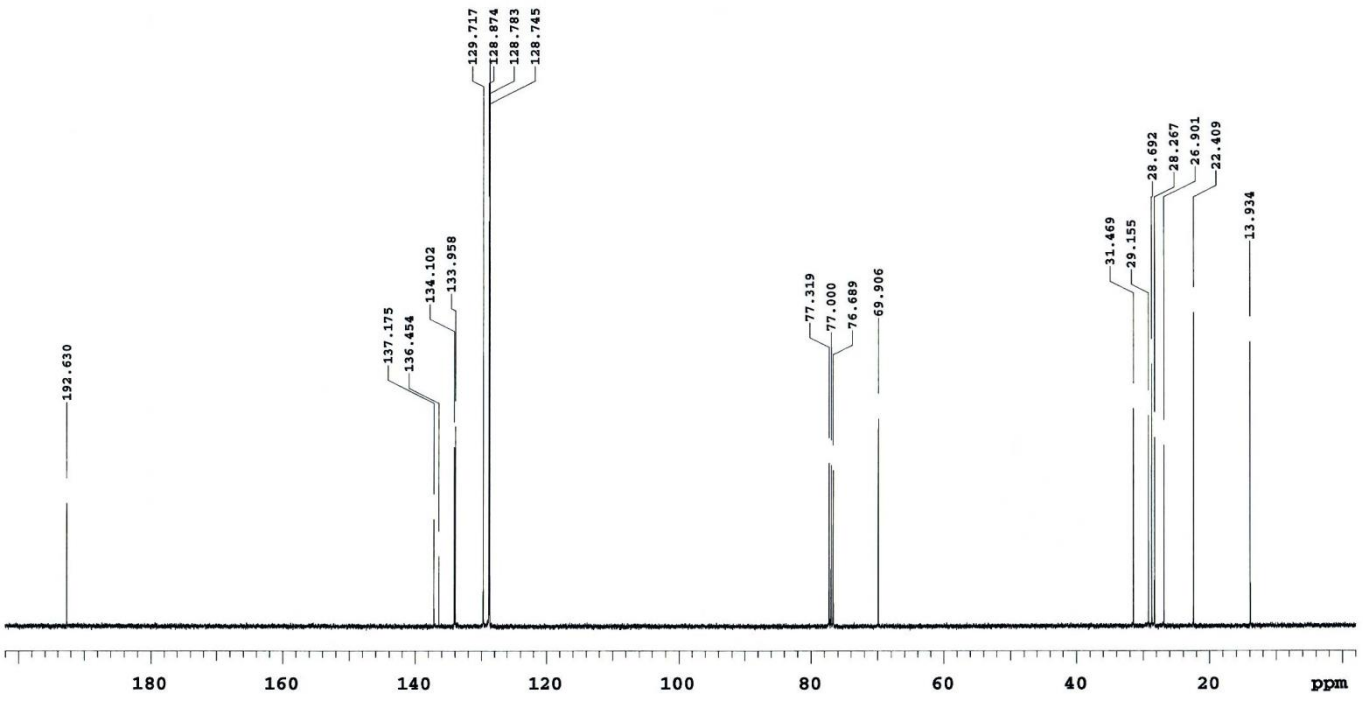


Sample Name: DB-112A_a
Solvent: cdcl3

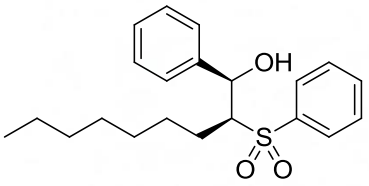


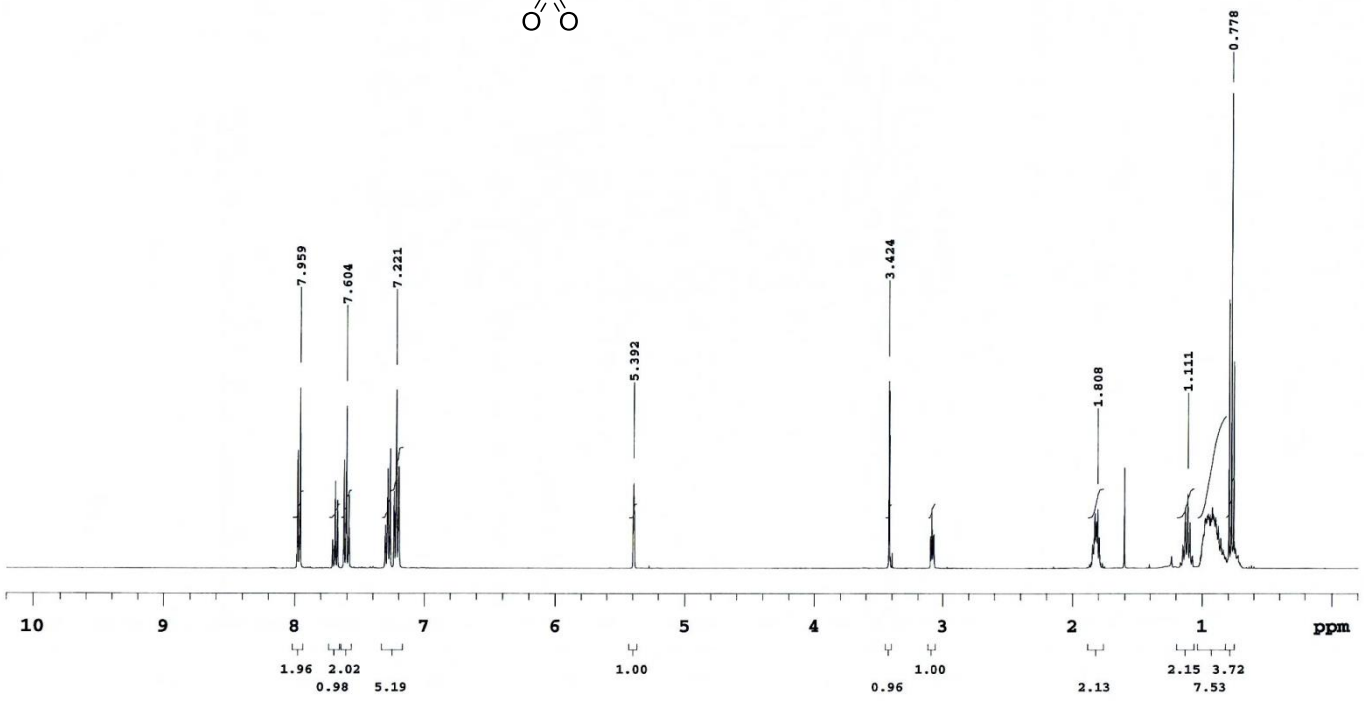


Sample Name: DB-112A_a
Solvent: cdcl3

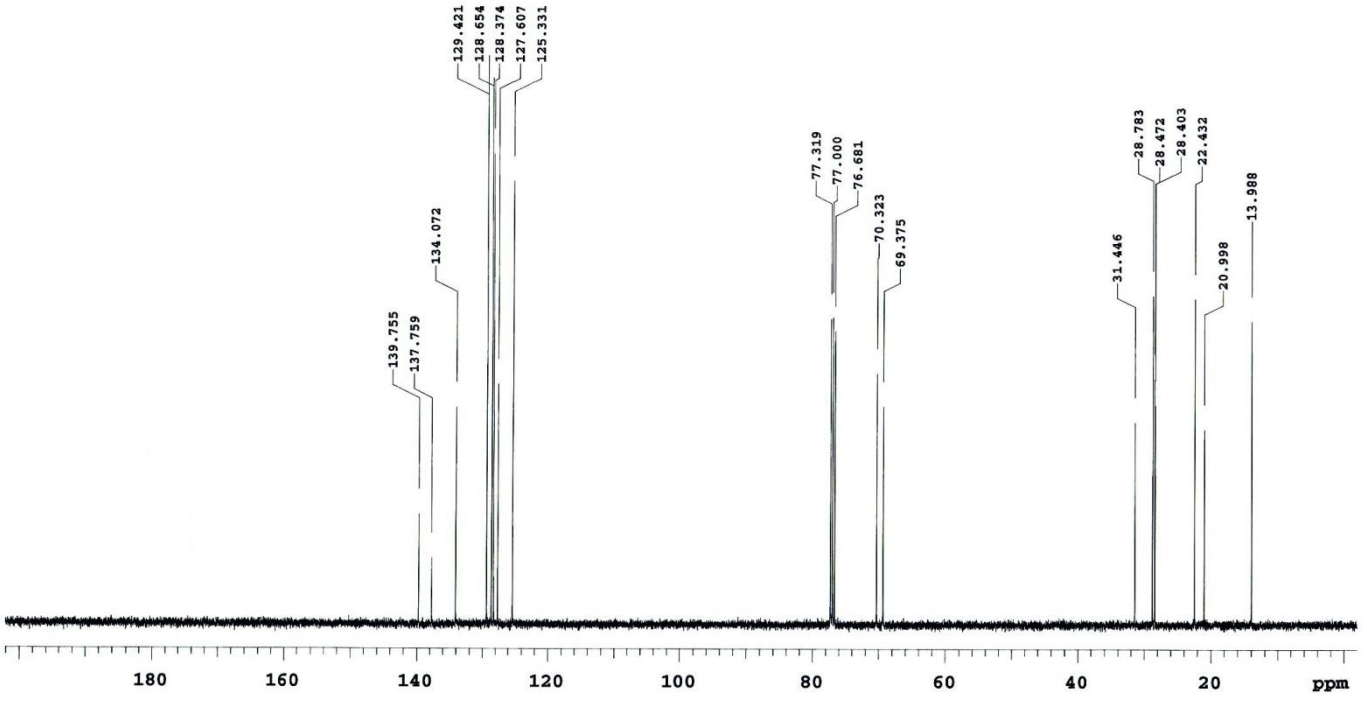


Sample Name: DB-147A_b
Solvent: cdcl3

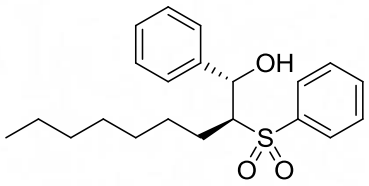


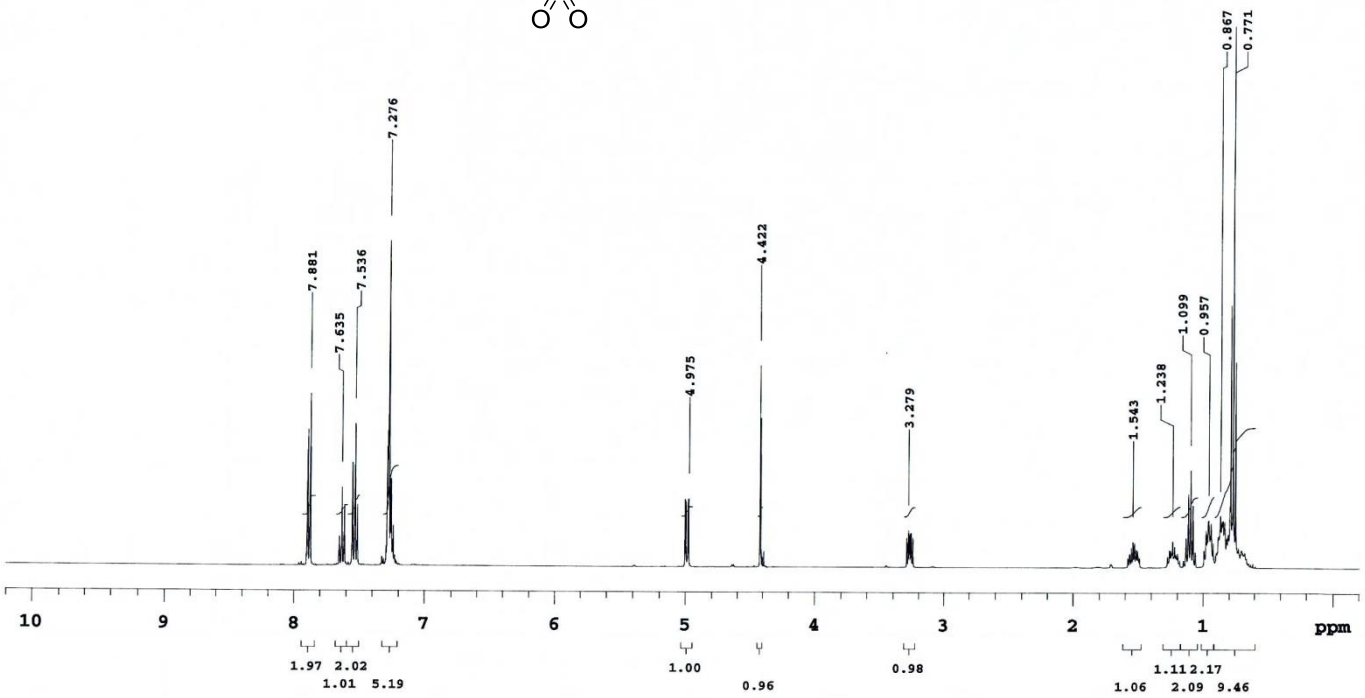


Sample Name: DB-147A_b
Solvent: cdcl3

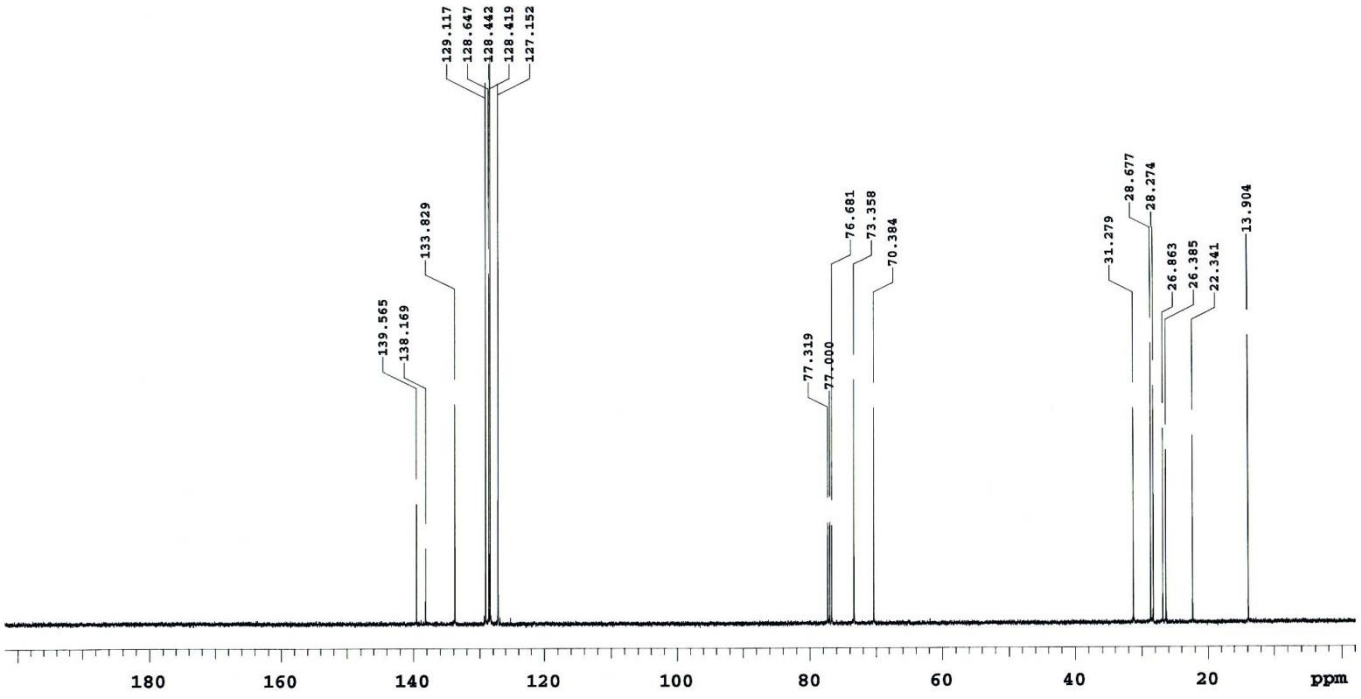


Sample Name: DB-147A_c
Solvent: cdcl3

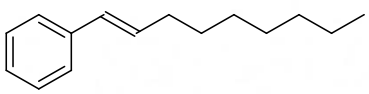


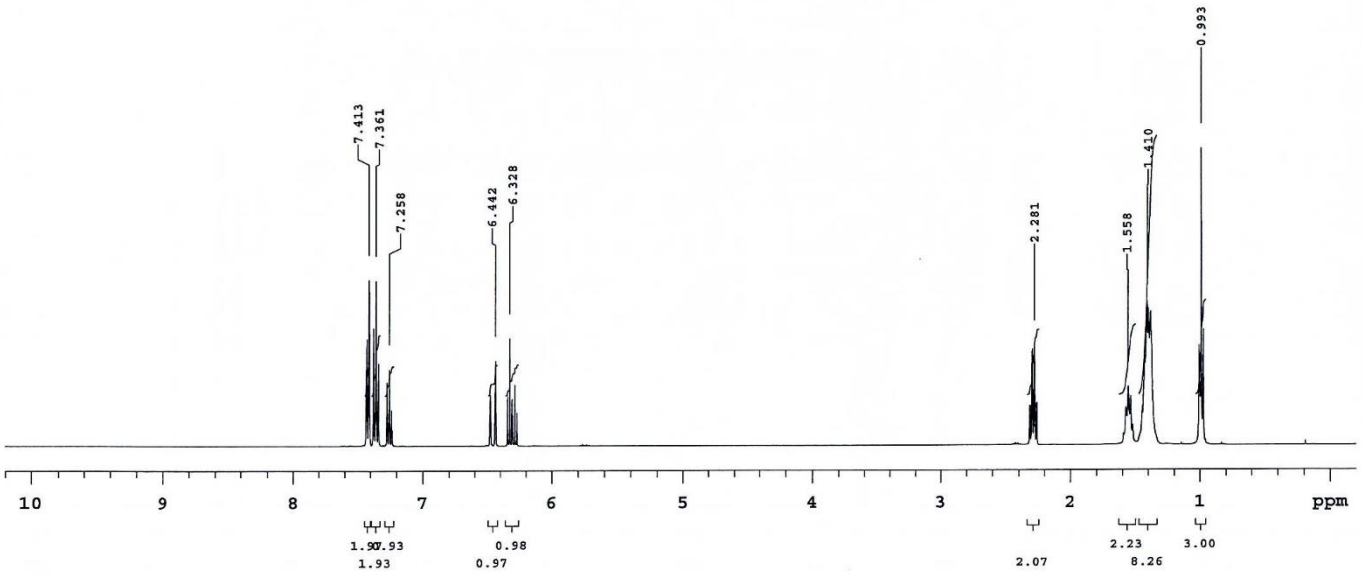


Sample Name: DB-147A_c
Solvent: cdcl3

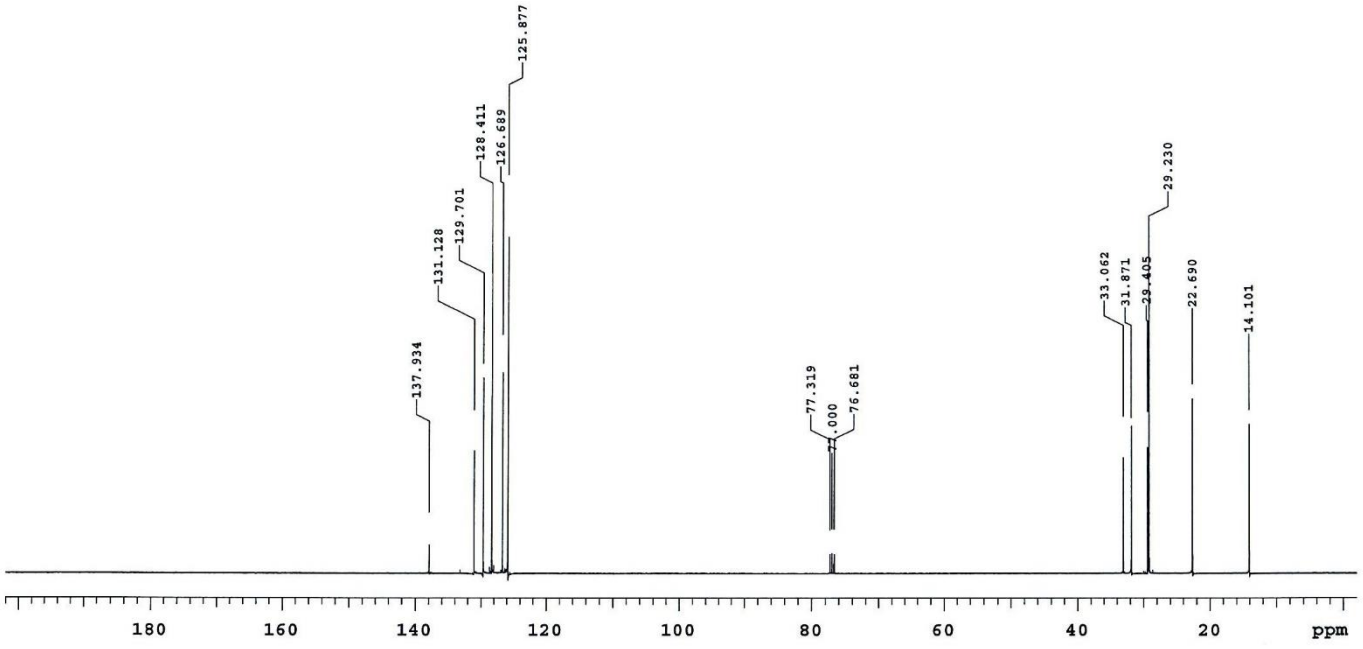


Sample Name: BG-331A
Solvent: cdcl3

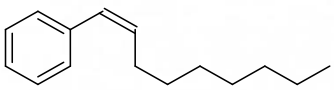


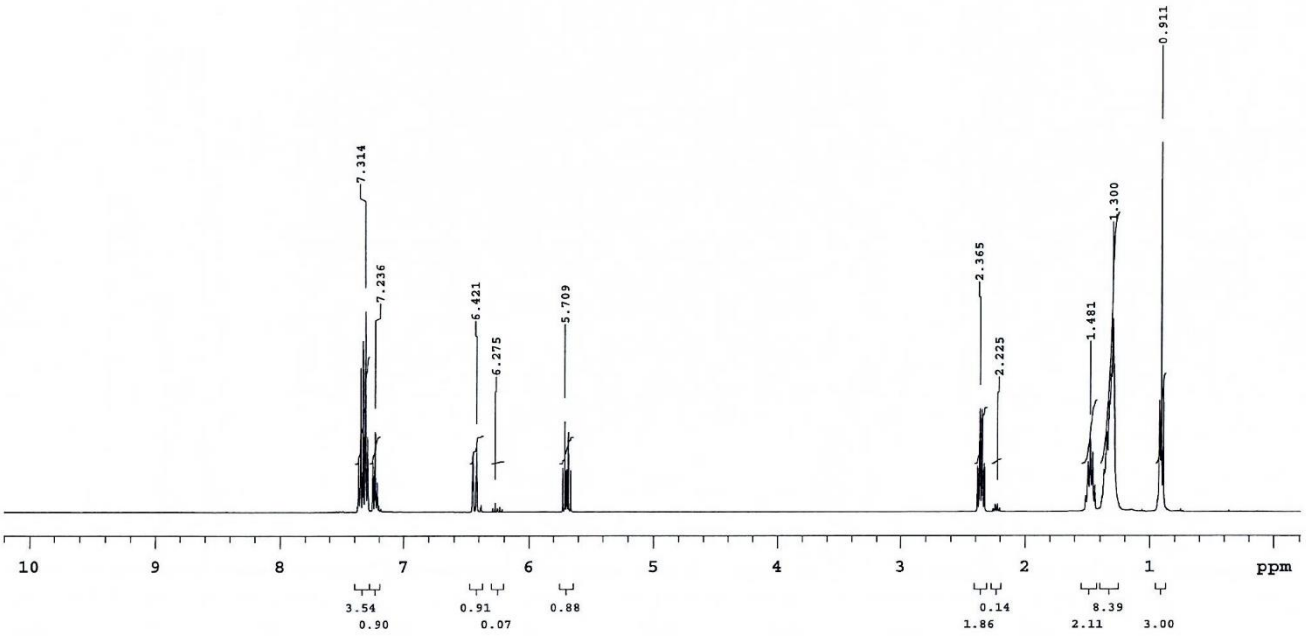


Sample Name: BG-331A
Solvent: cdcl3

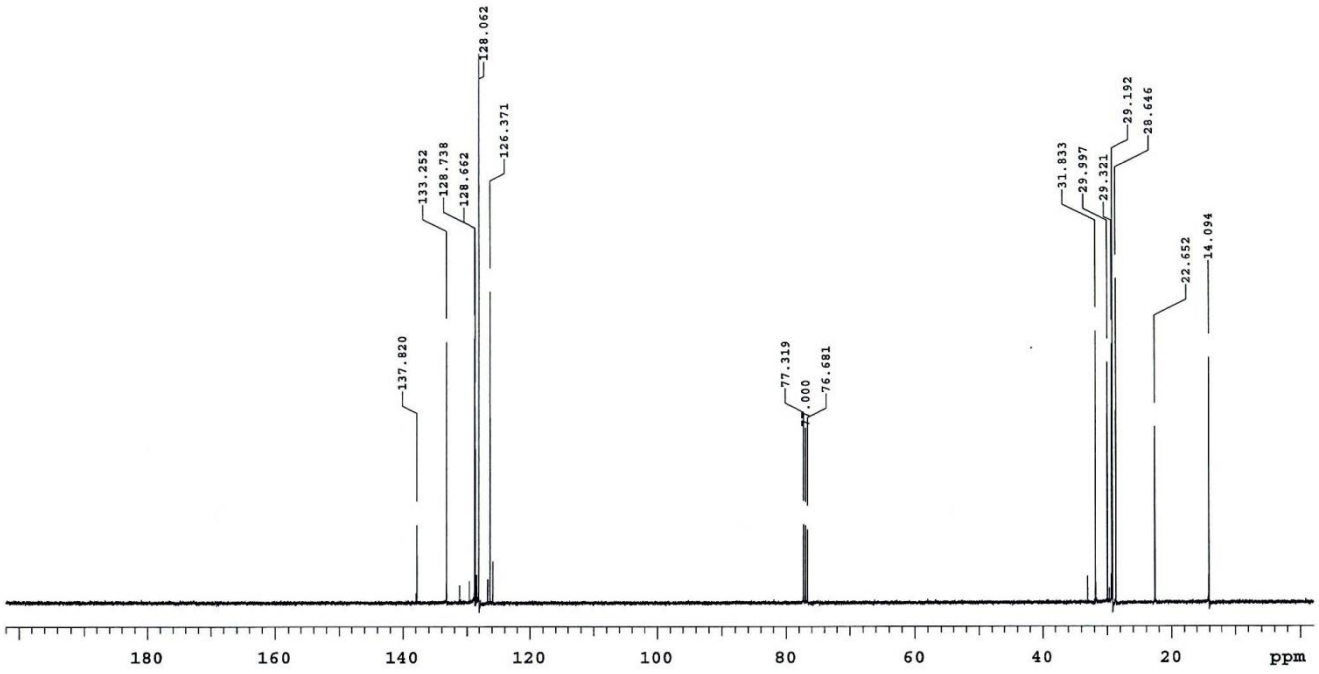


Sample Name: BG-356b_A
Solvent: cdcl3

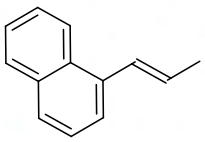


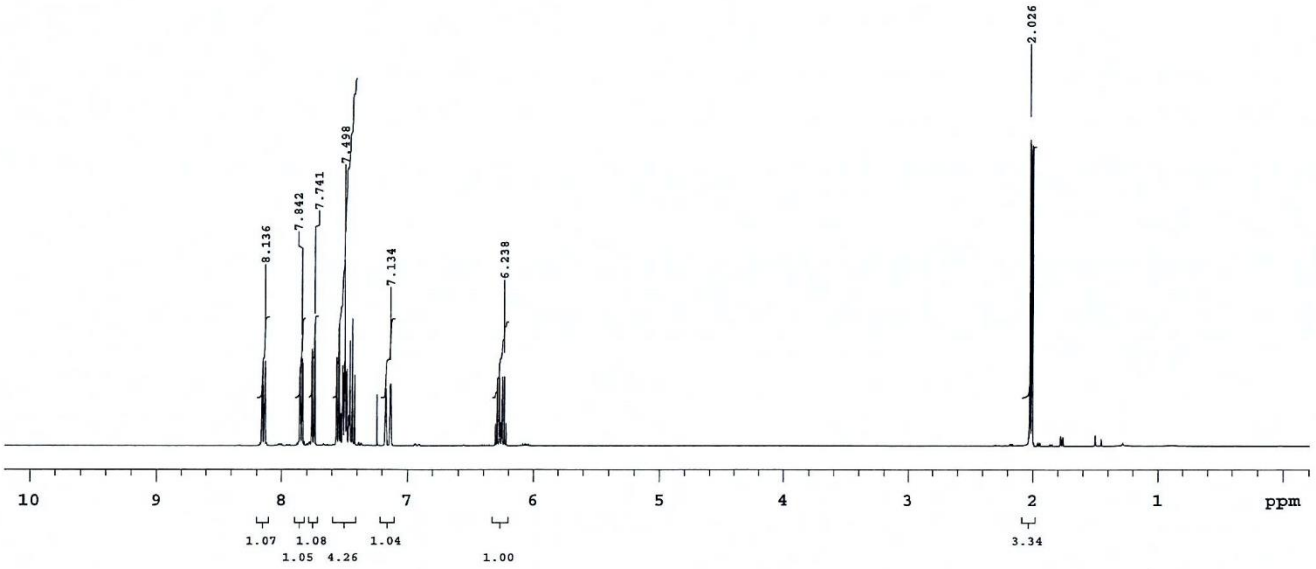


Sample Name: BG-356b_A
Solvent: cdcl3

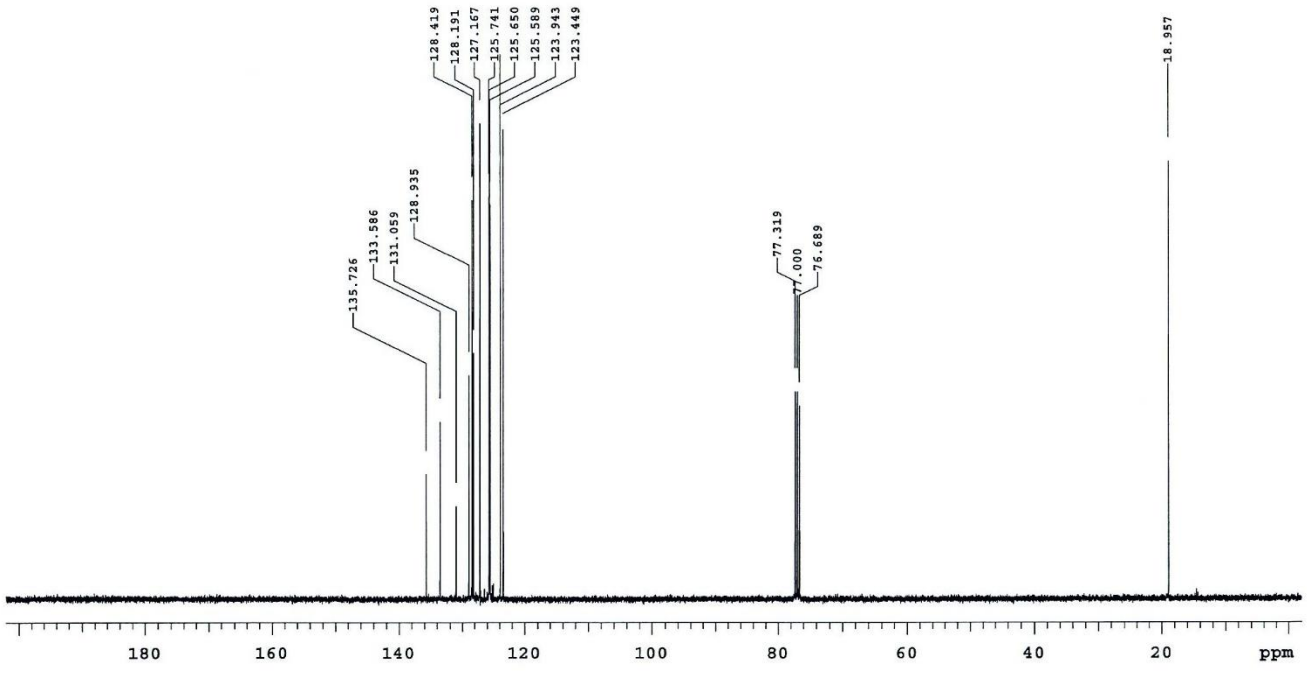


Sample Name: DB-198_a
Solvent: cdcl3

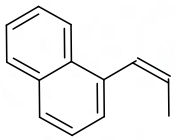


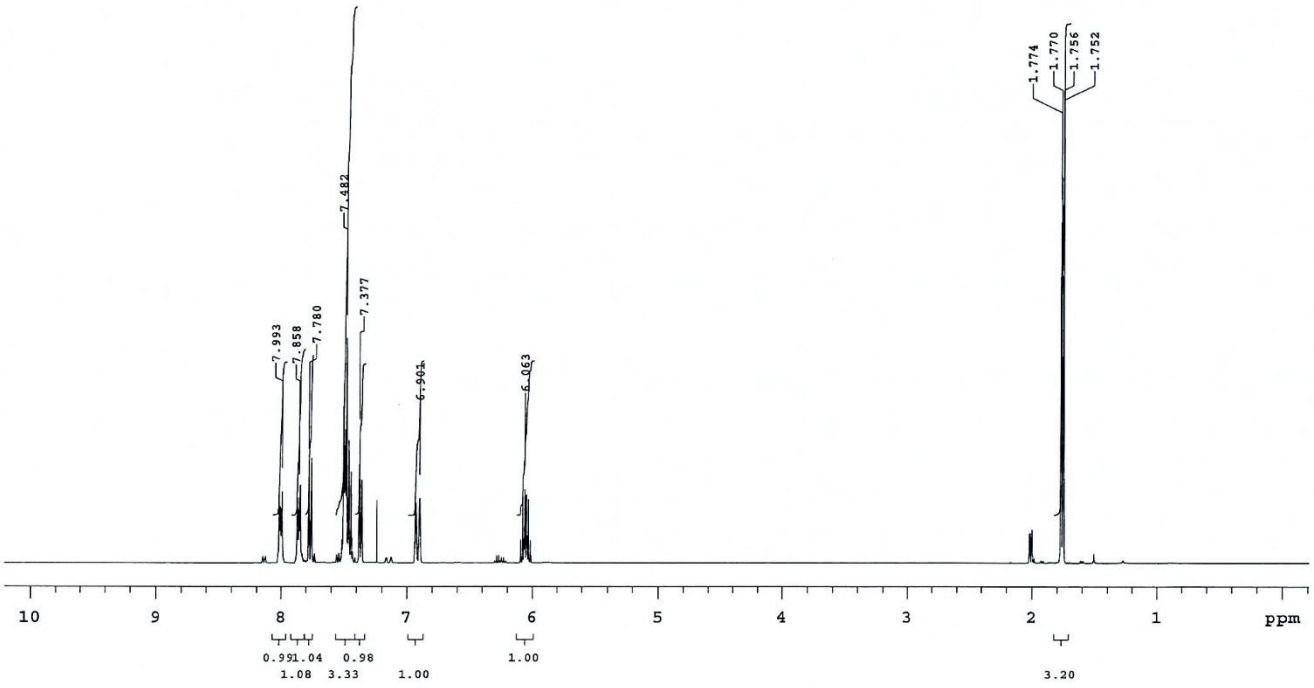


Sample Name: DB-198_a
Solvent: cdcl3

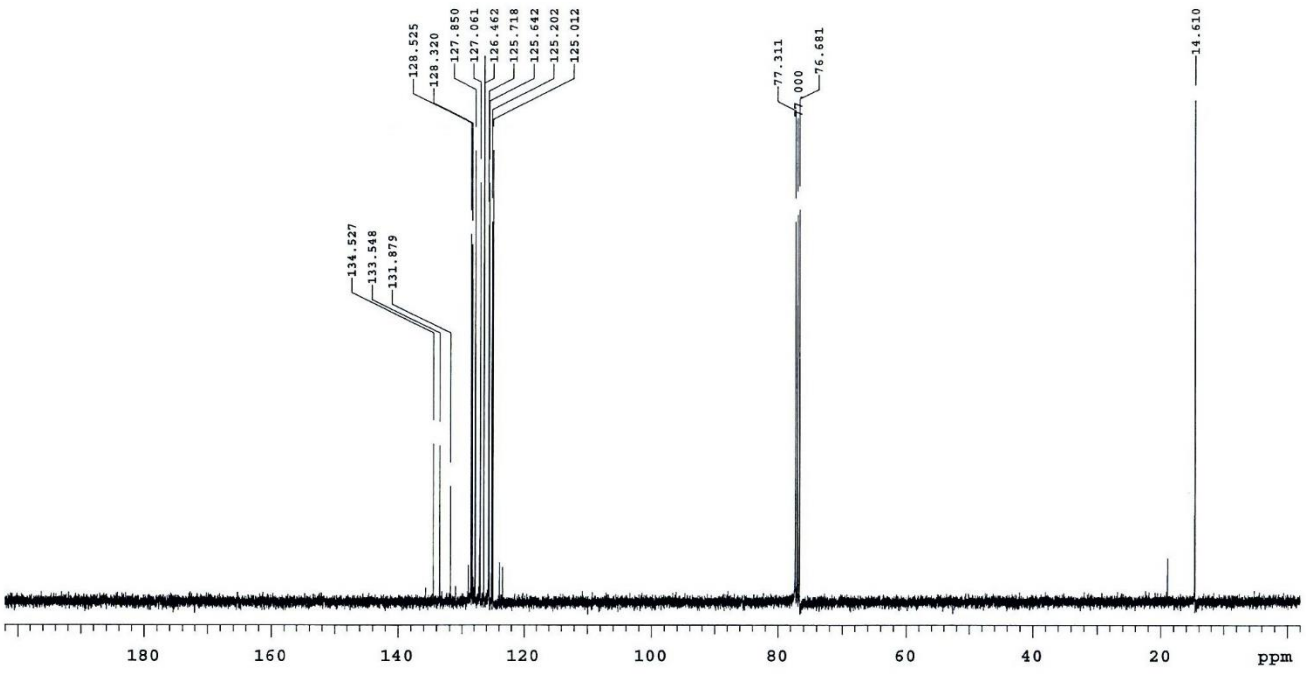


Sample Name: DB-214A_a
Solvent: cdcl3

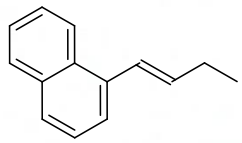


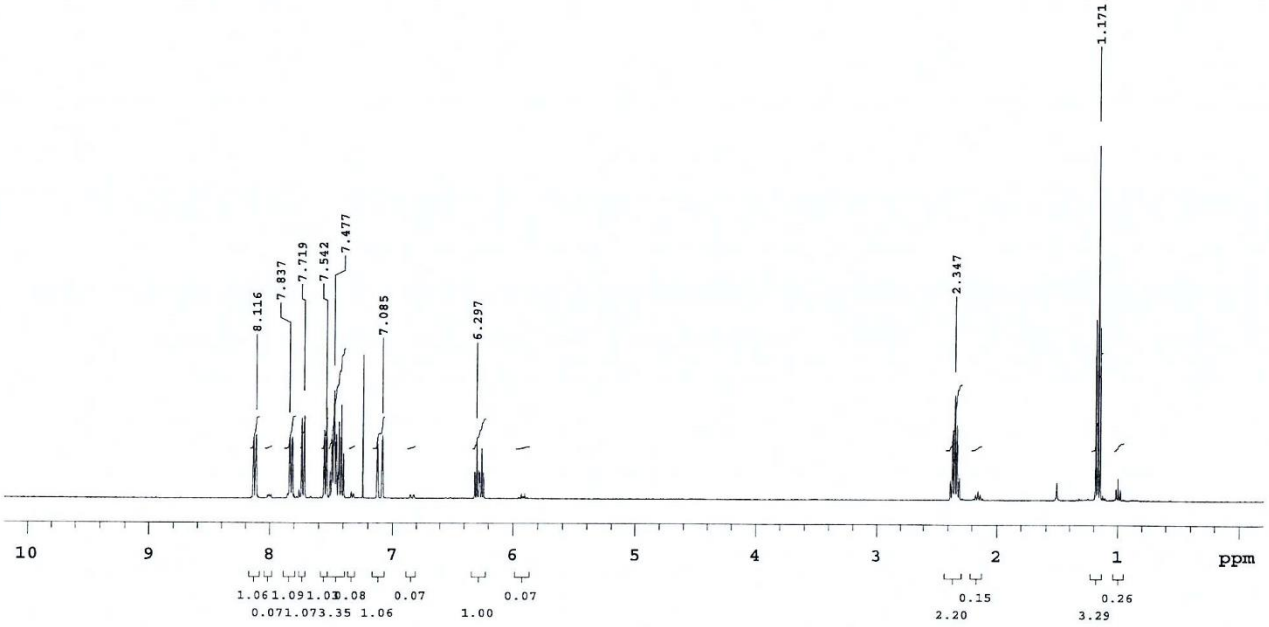


Sample Name: DB-214A_a
Solvent: cdcl3

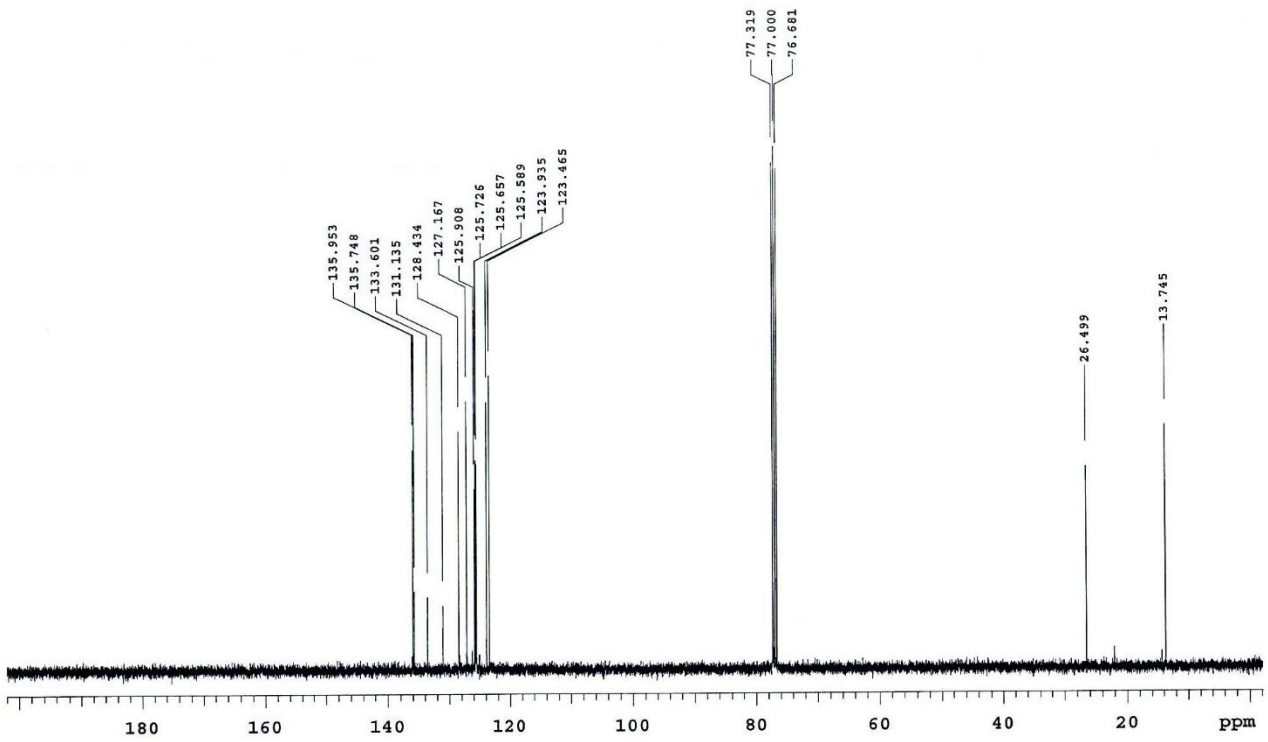


Sample Name: DB-236A_a
Solvent: cdcl3

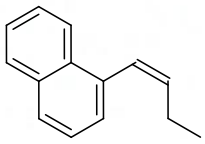


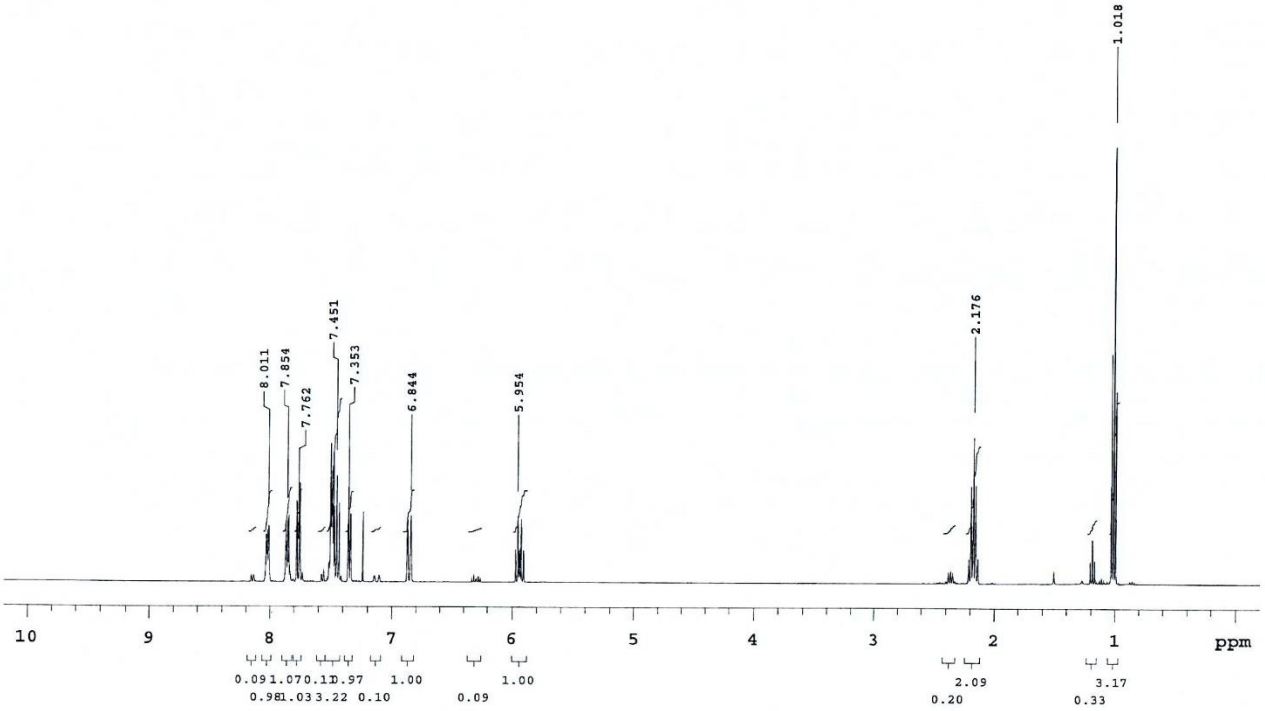


Sample Name: DB-236A_a
Solvent: cdcl3

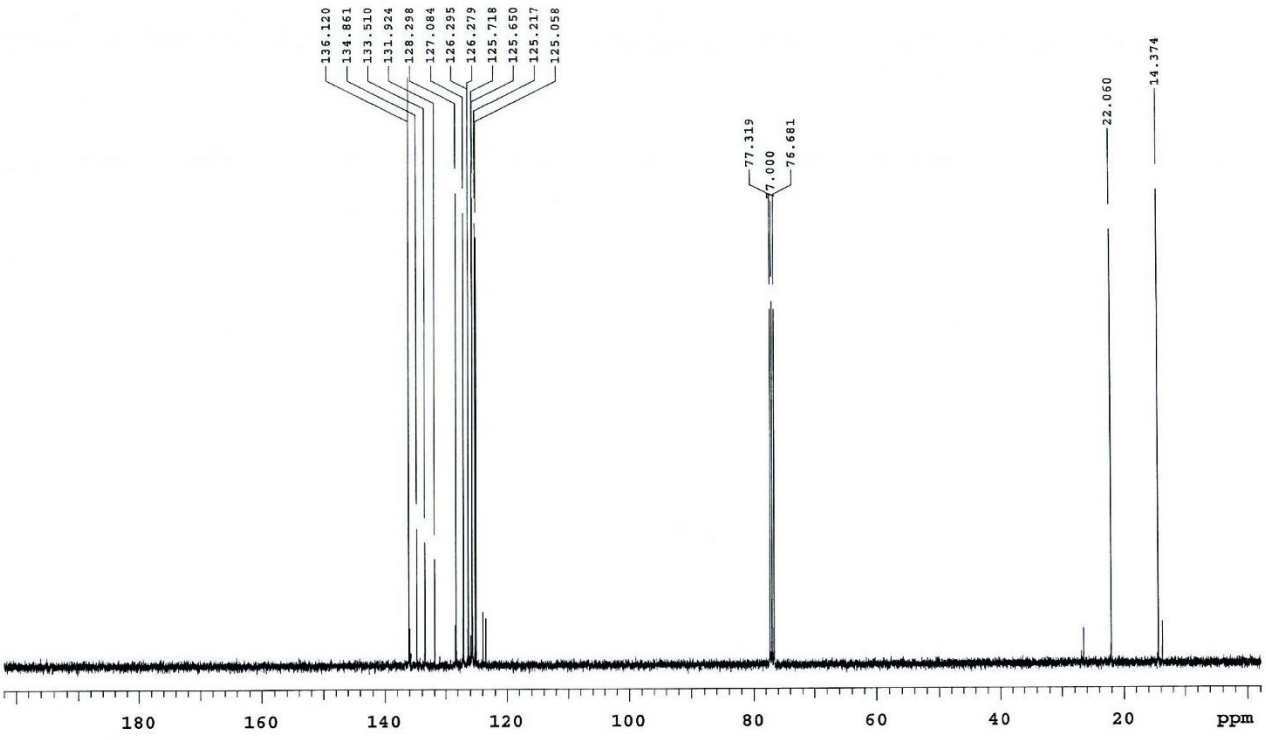


Sample Name: DB-236B_a
Solvent: cdcl3

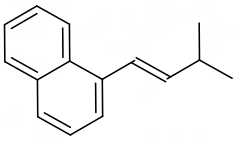


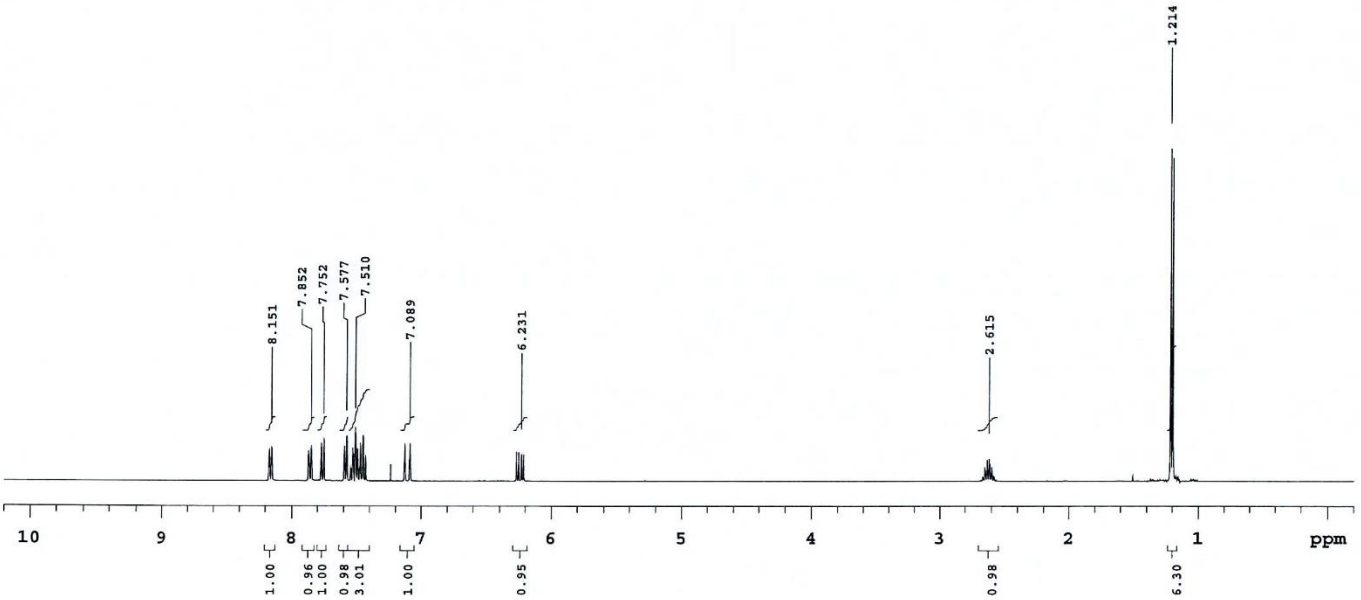


Sample Name: DB-236B_a
Solvent: cdcl3

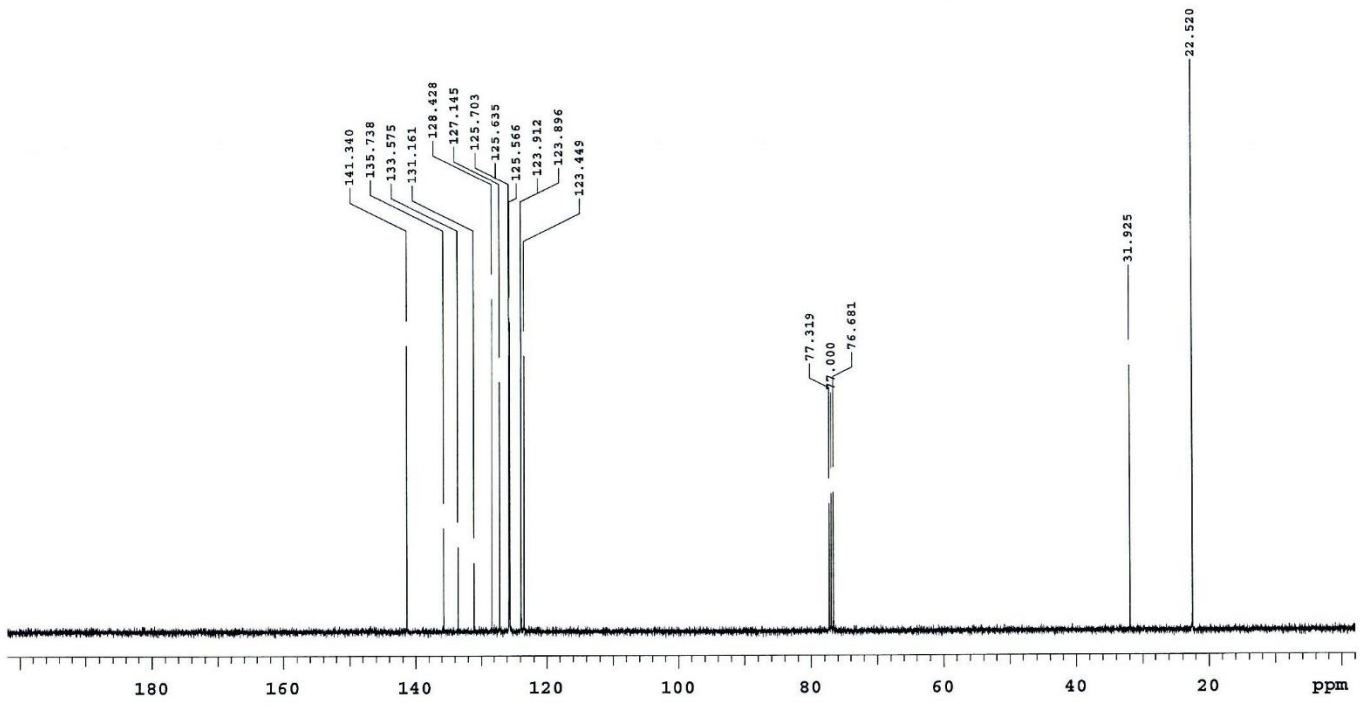


Sample Name: DB-220A_a
Solvent: cdcl3

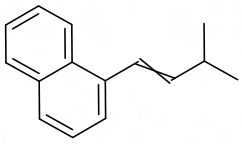




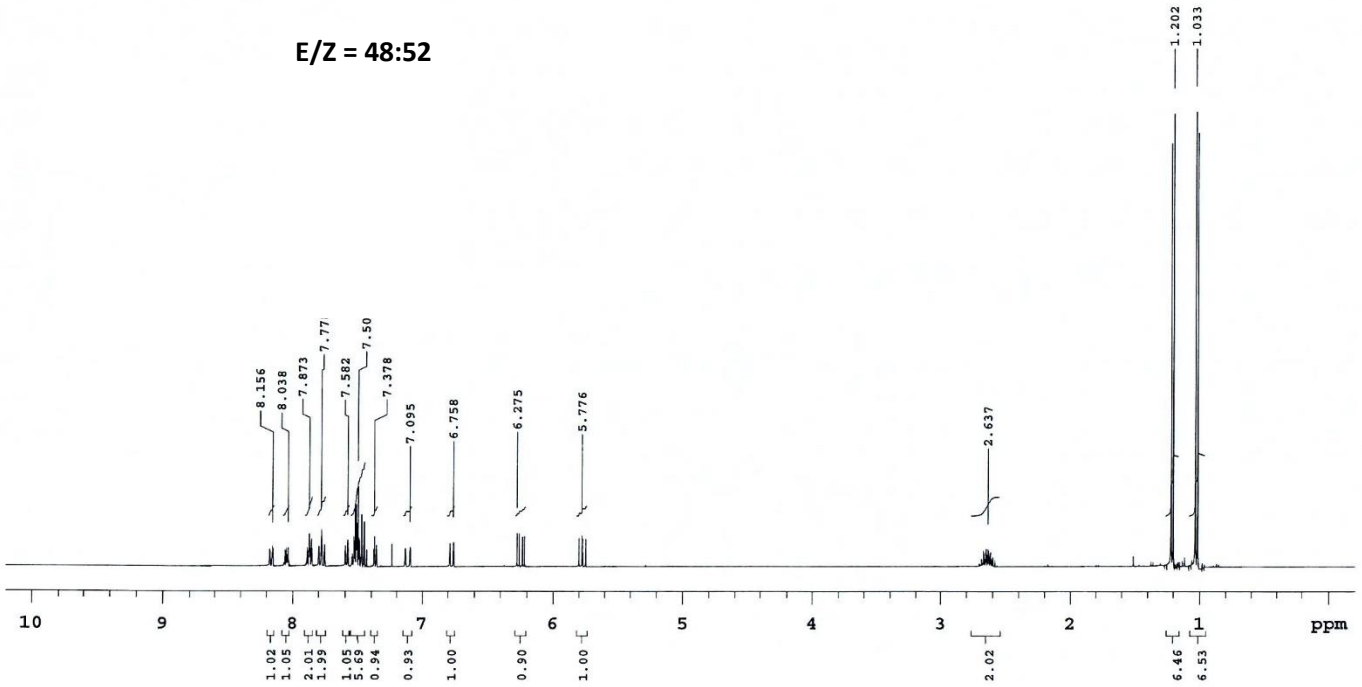
Sample Name: DB-220A_a
Solvent: cdcl3



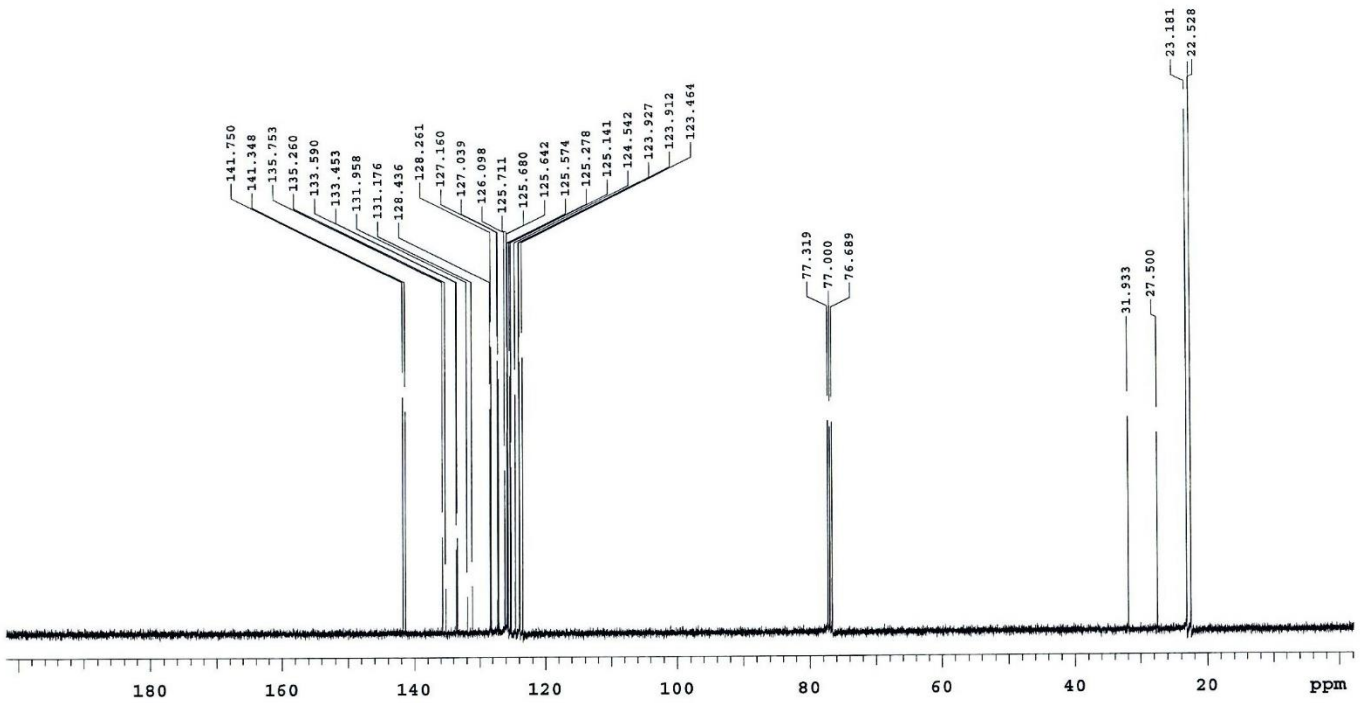
Sample Name: DB-220B_a
Solvent: cdcl3



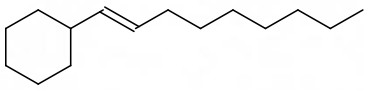
E/Z = 48:52

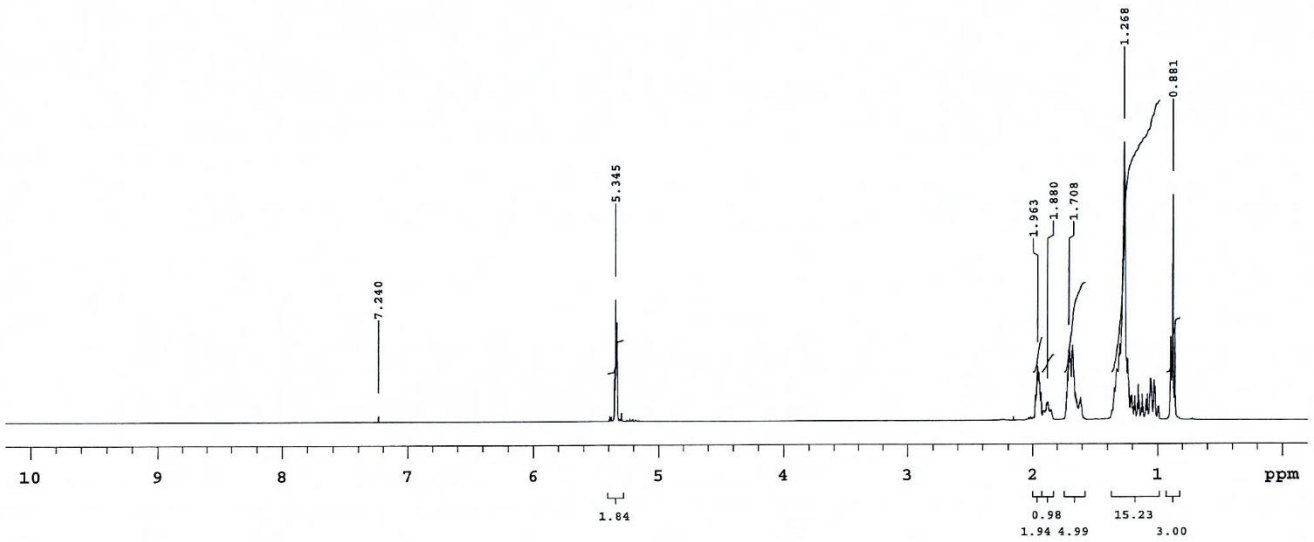


Sample Name: DB-220B_a
Solvent: cdcl3

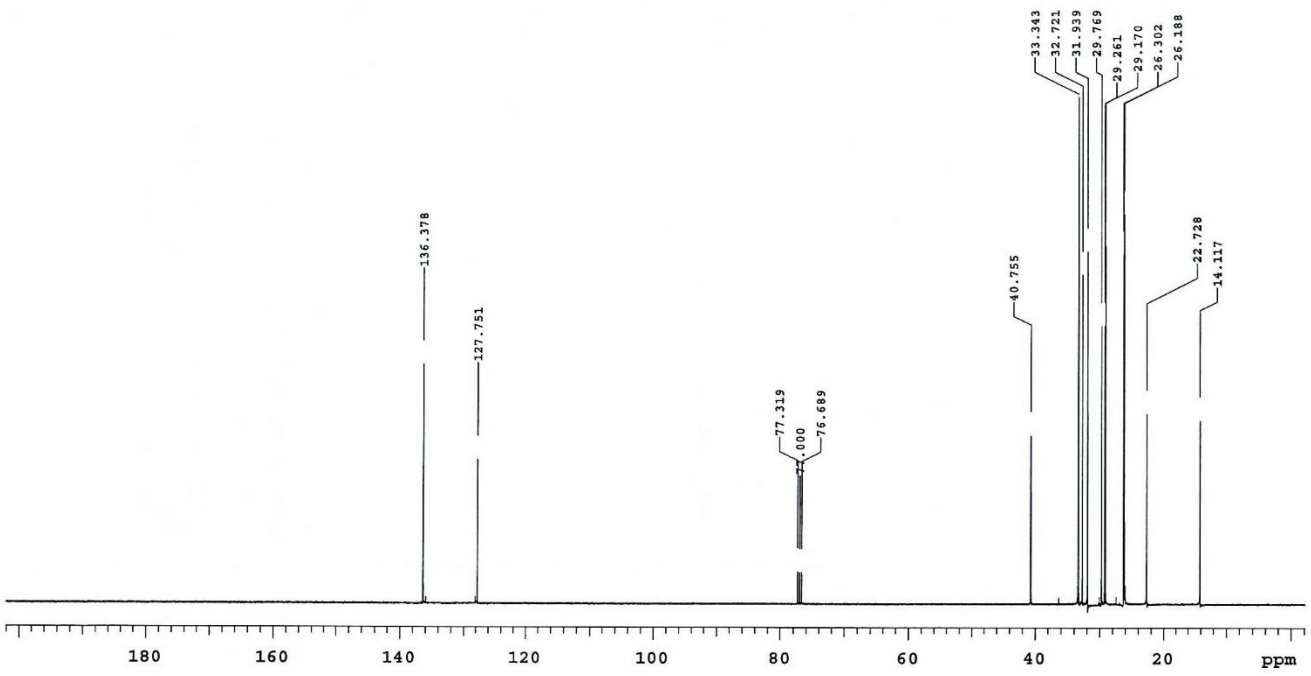


Sample Name: BG-348A
Solvent: cdcl3

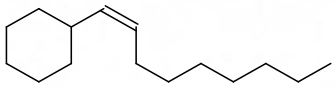


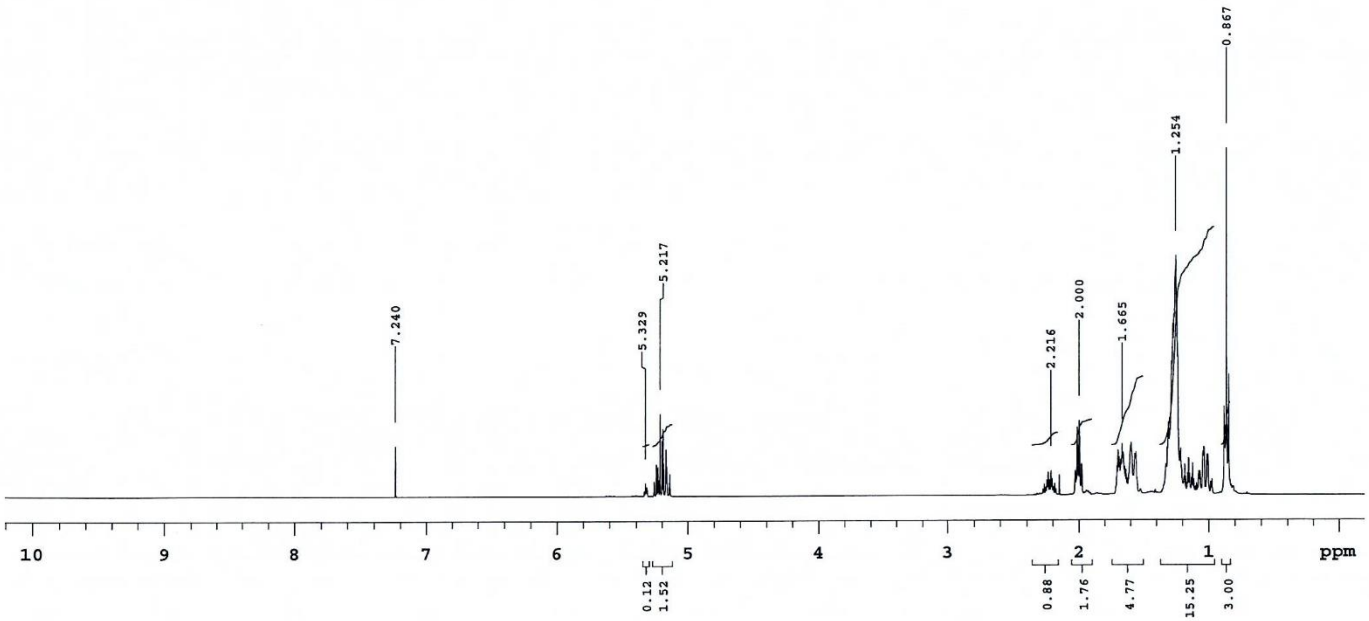


Sample Name: BG-348A
Solvent: cdcl3

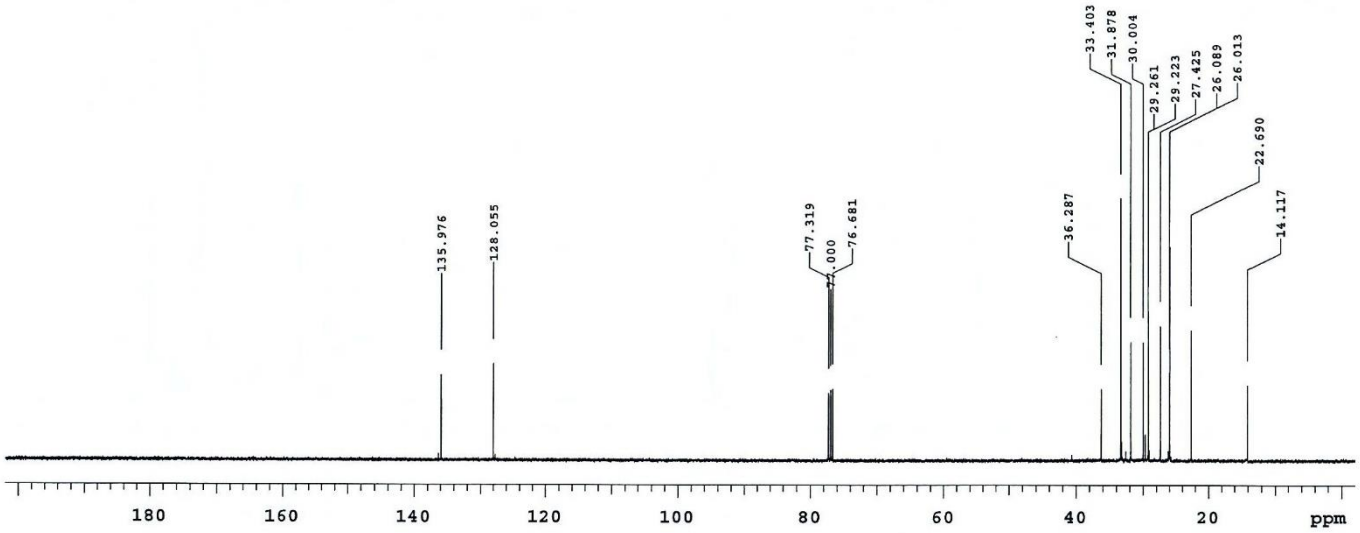


Sample Name: BG-376A
Solvent: cdcl3

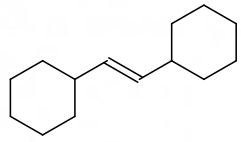


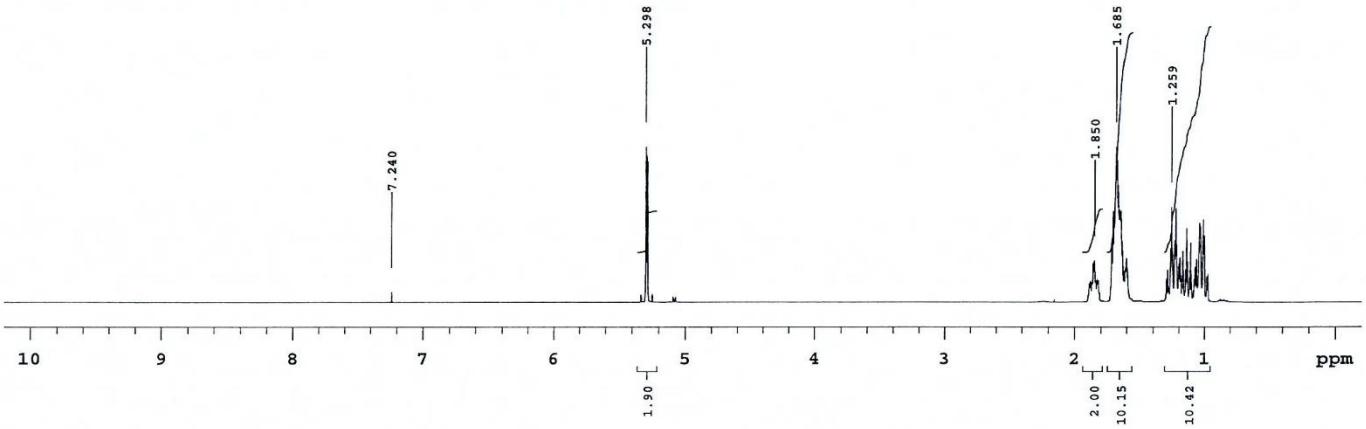


Sample Name: BG-376A
Solvent: cdcl3

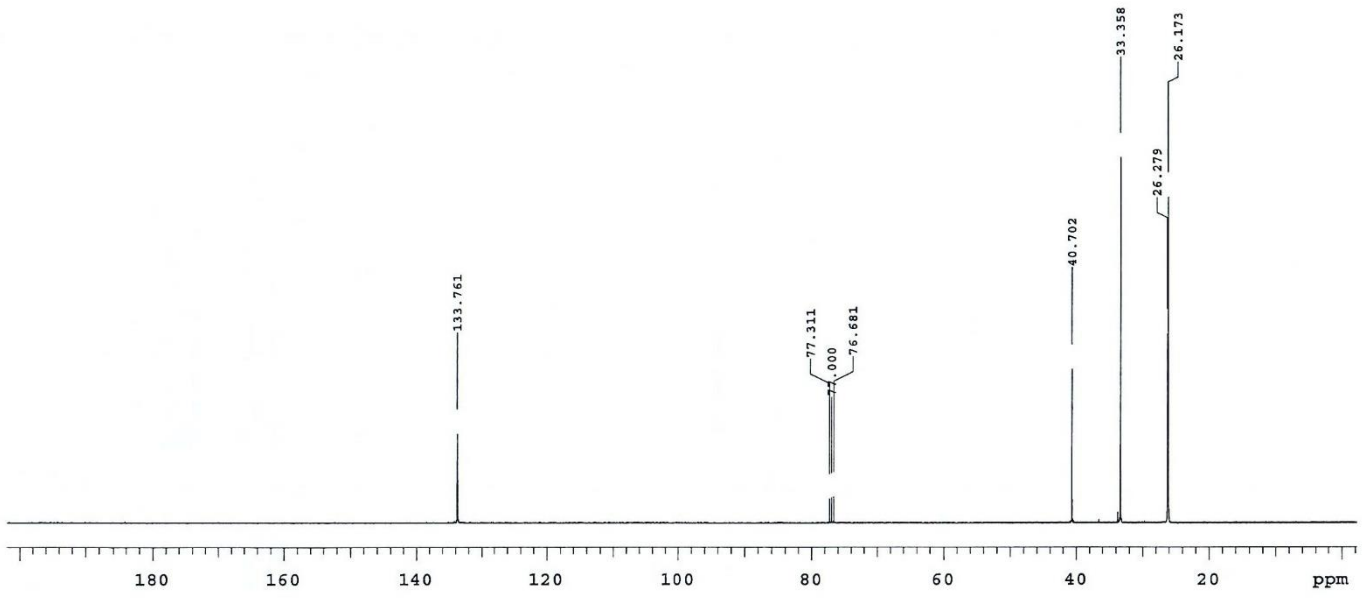


Sample Name: BG-389A
Solvent: cdcl3

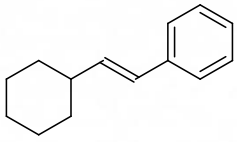


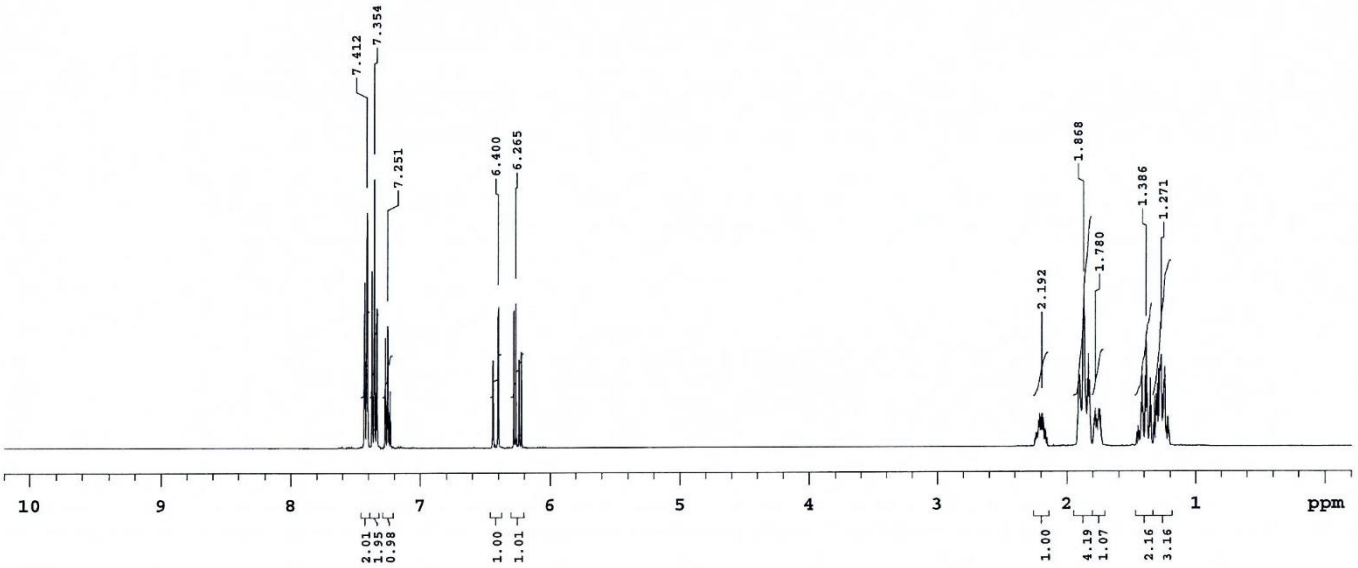


Sample Name: BG-389A
Solvent: cdcl3

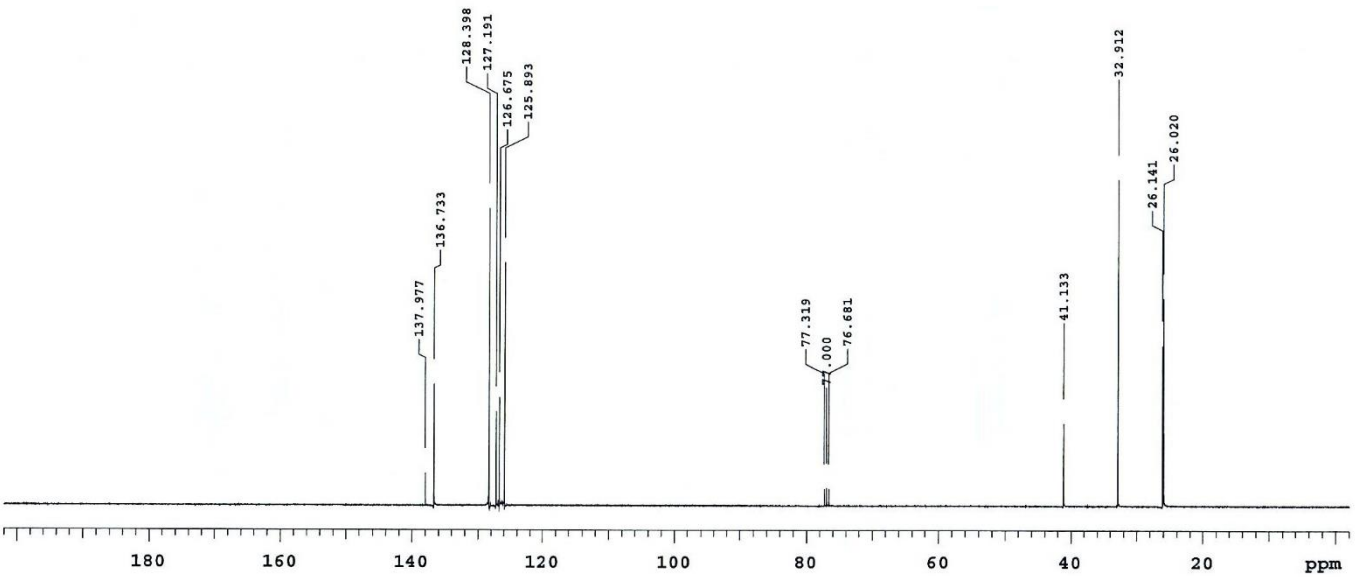


Sample Name: BG-417A
Solvent: cdcl3

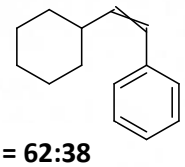




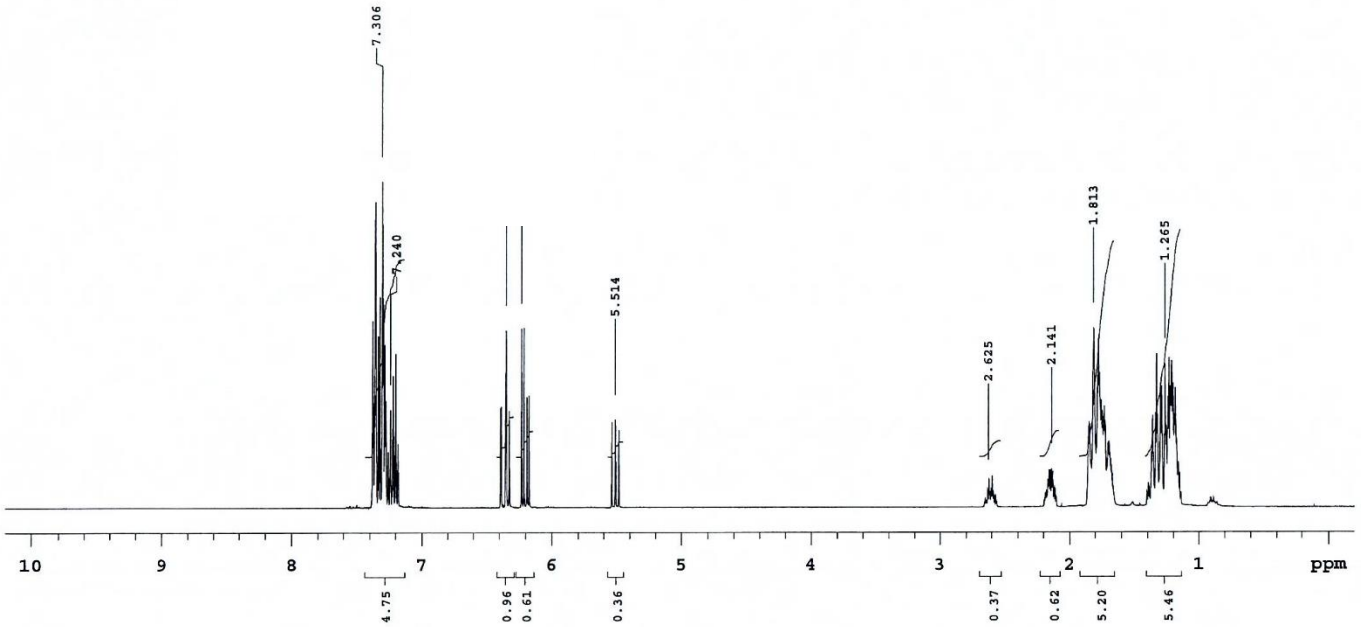
Sample Name: BG-417A
Solvent: cdcl3



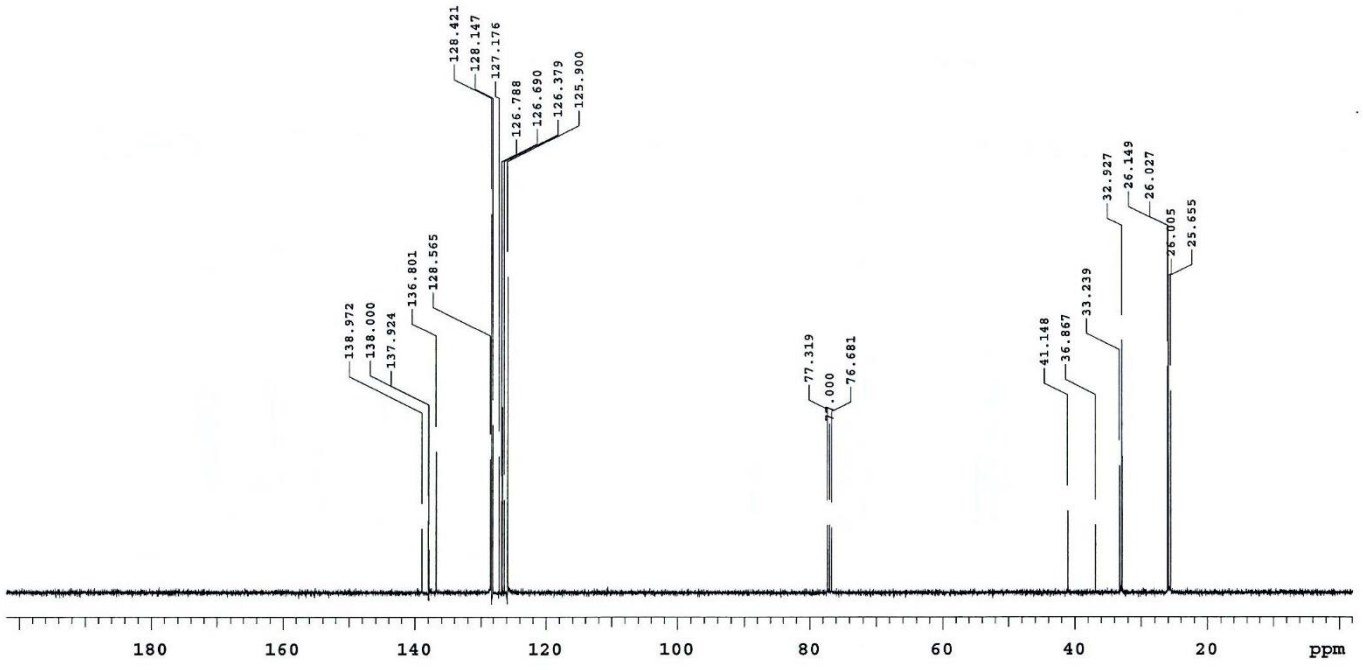
Sample Name: BG-405A
Solvent: cdcl3



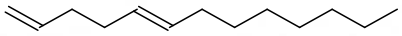
E/Z = 62:38

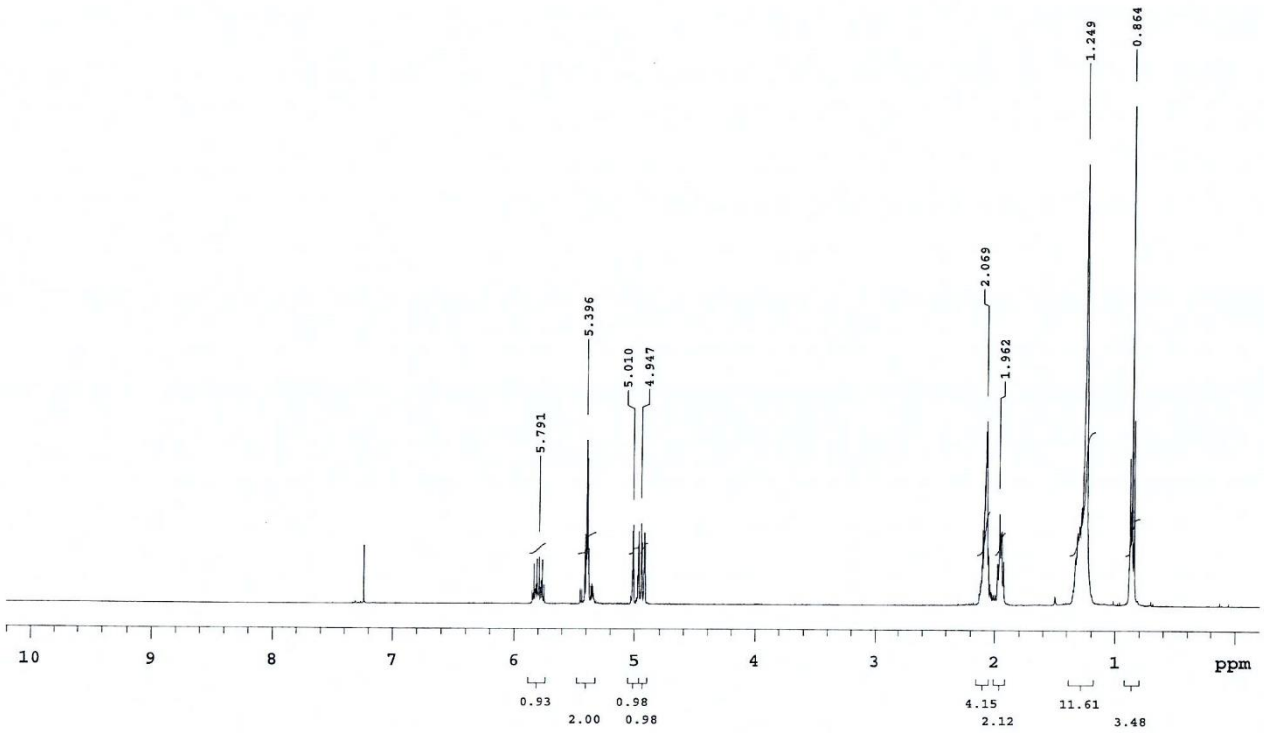


Sample Name: BG-405A
Solvent: cdcl3

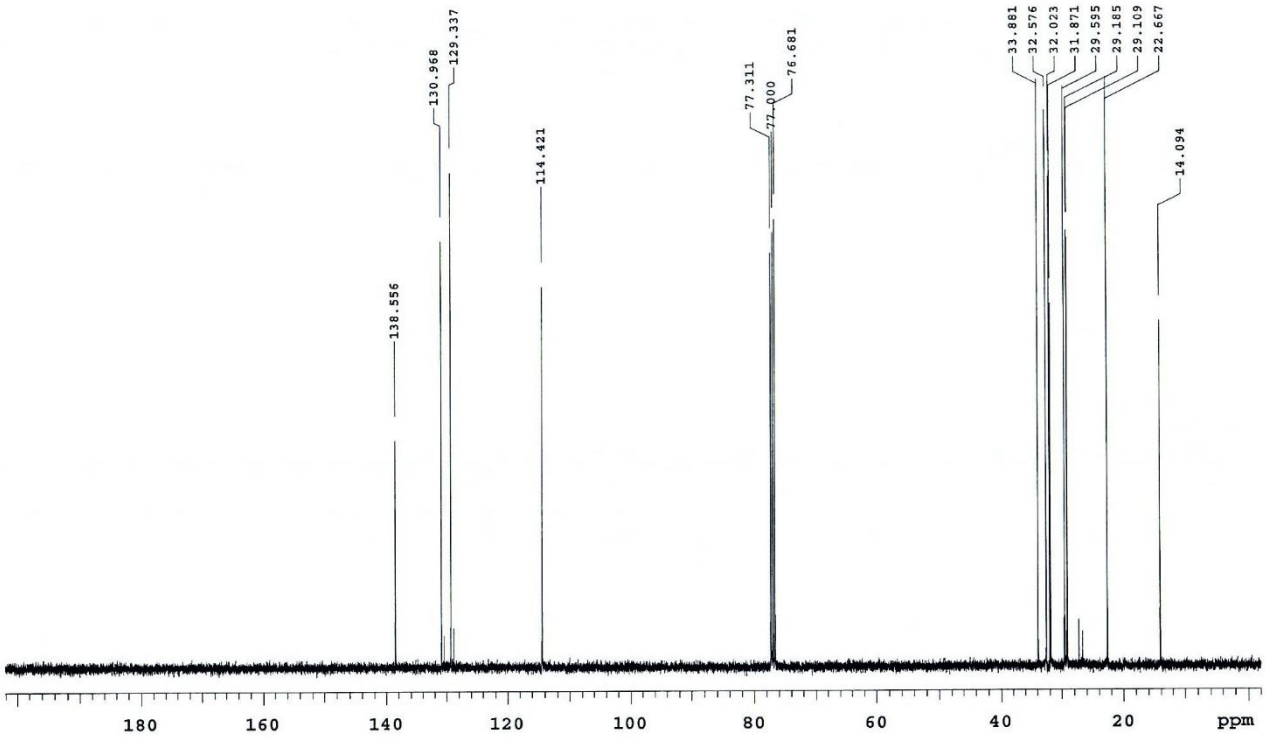


Sample Name: DB-234A-a
Solvent: cdcl3

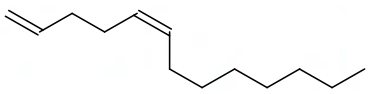


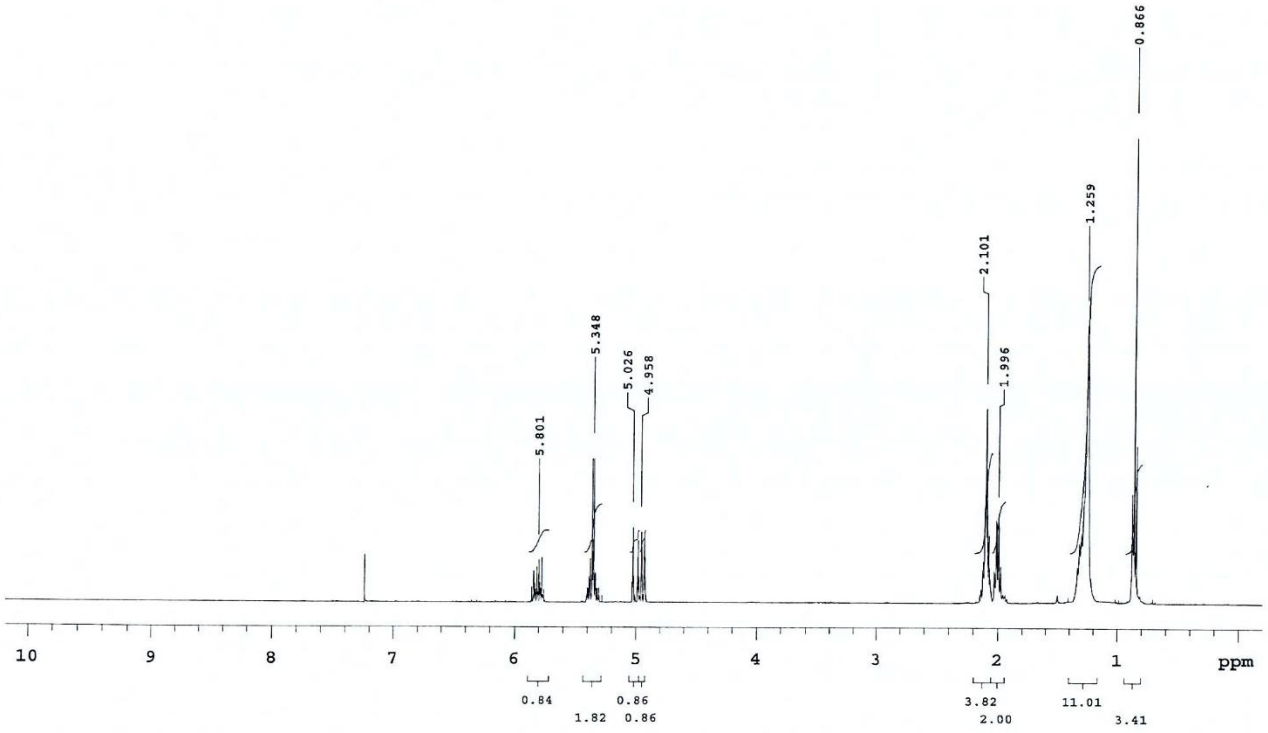


Sample Name: DB-234A-a
Solvent: cdcl3

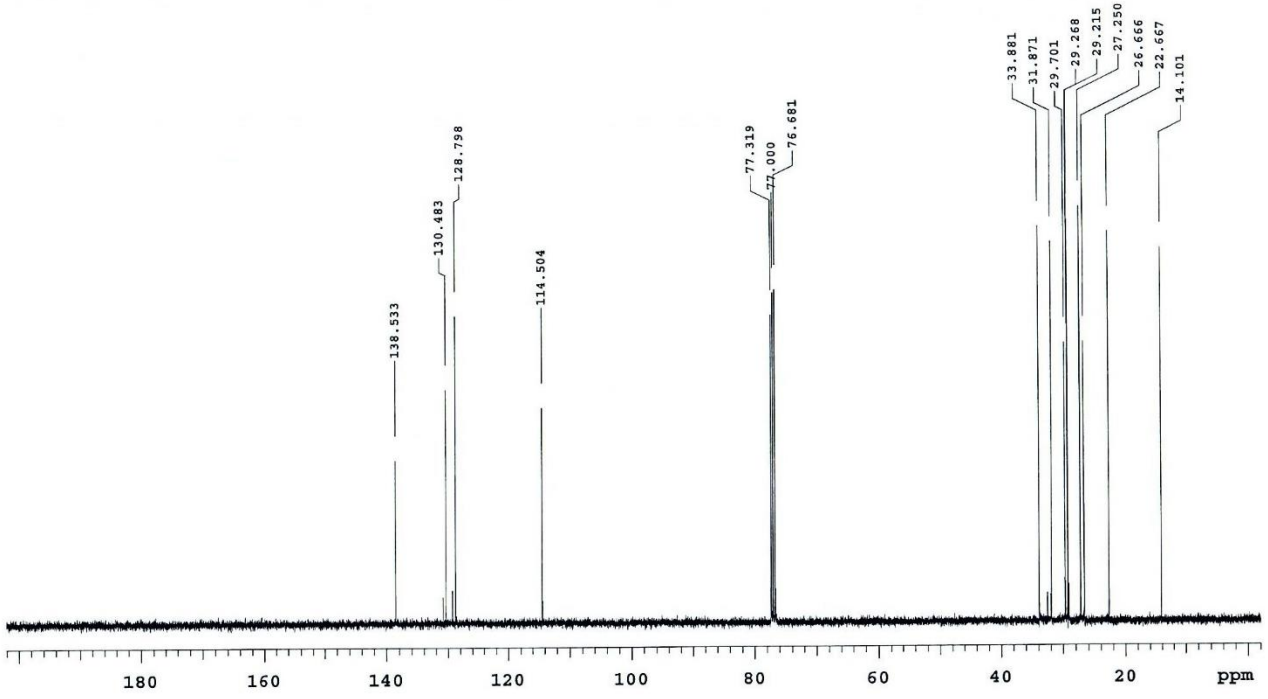


Sample Name: DB-234B_a
Solvent: cdcl3

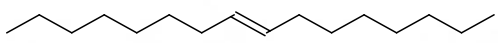


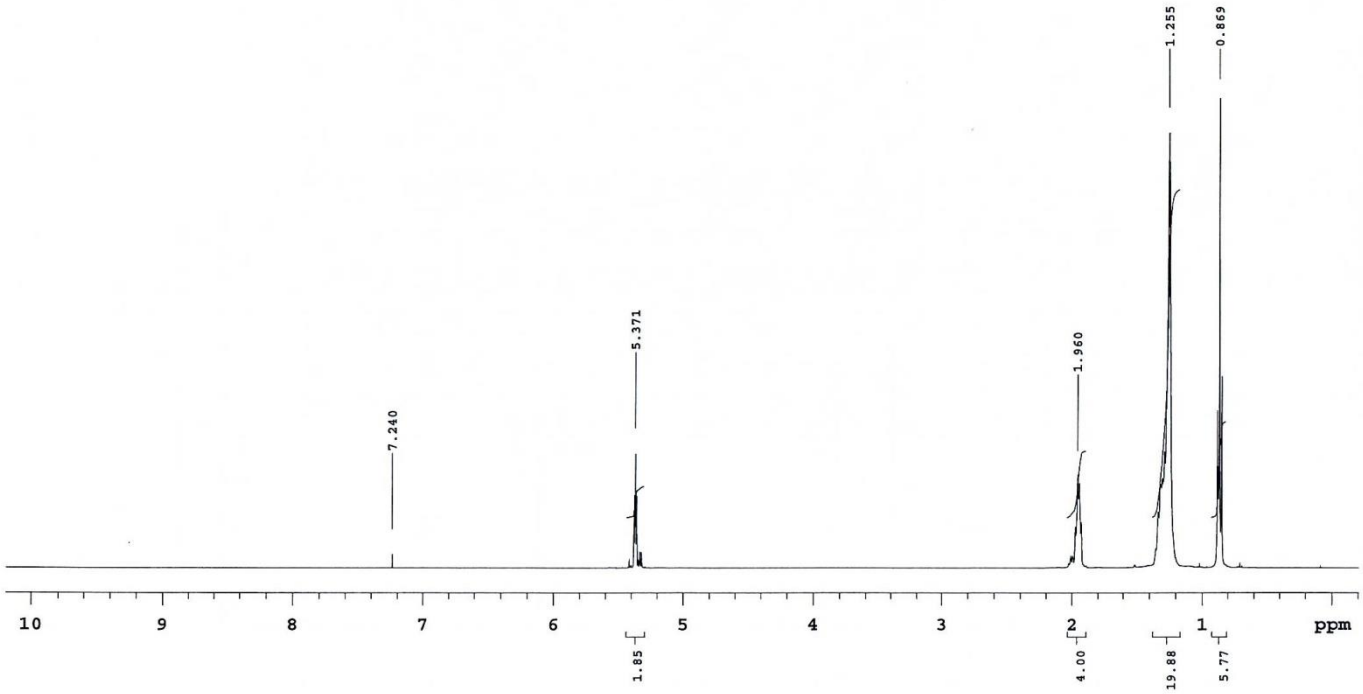


Sample Name: DB-234B_a
Solvent: cdcl3

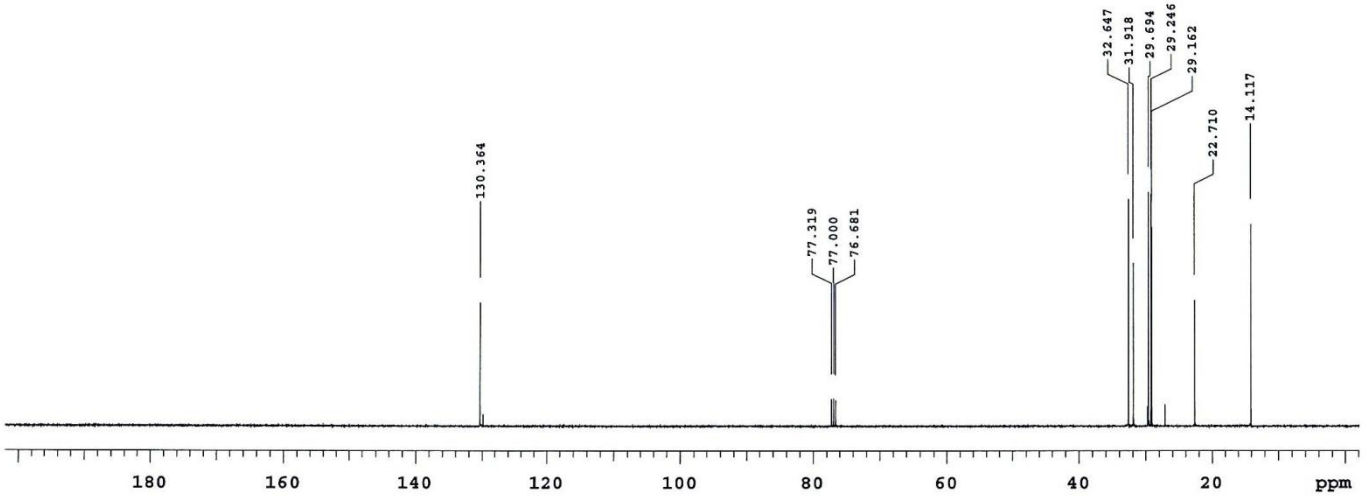


Sample Name: BG-286A
Solvent: cdcl3

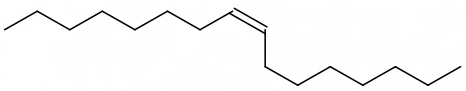


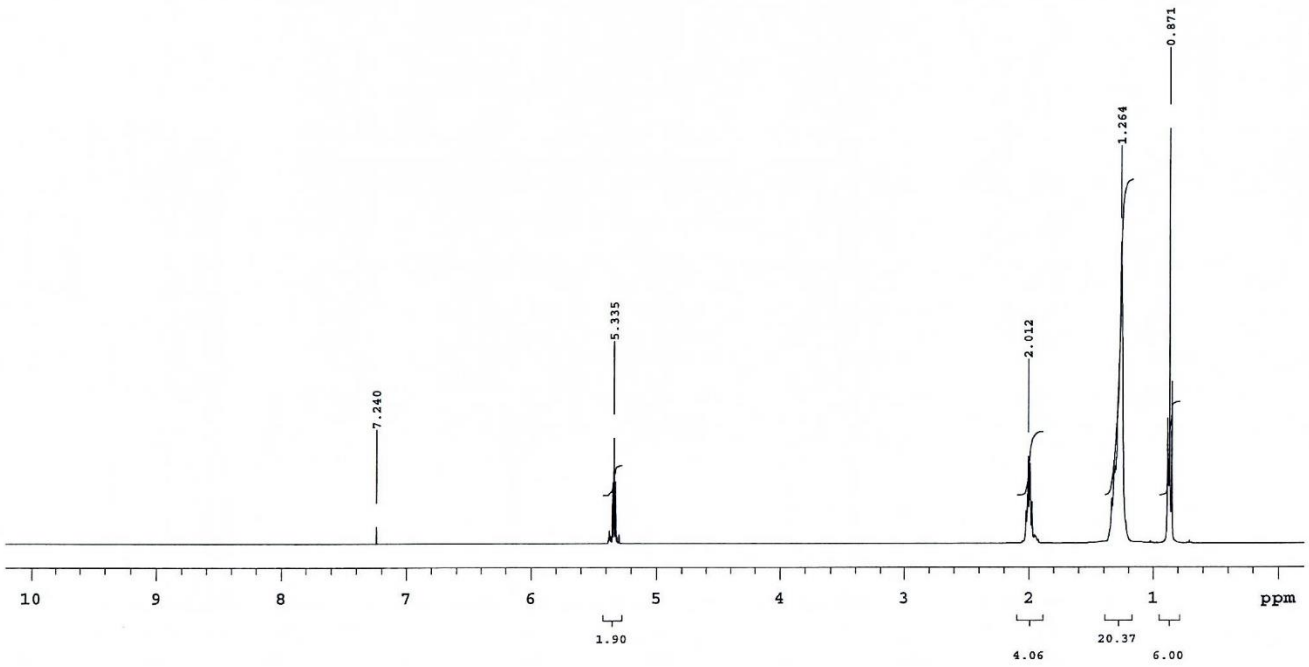


Sample Name: BG-286A
Solvent: cdcl3

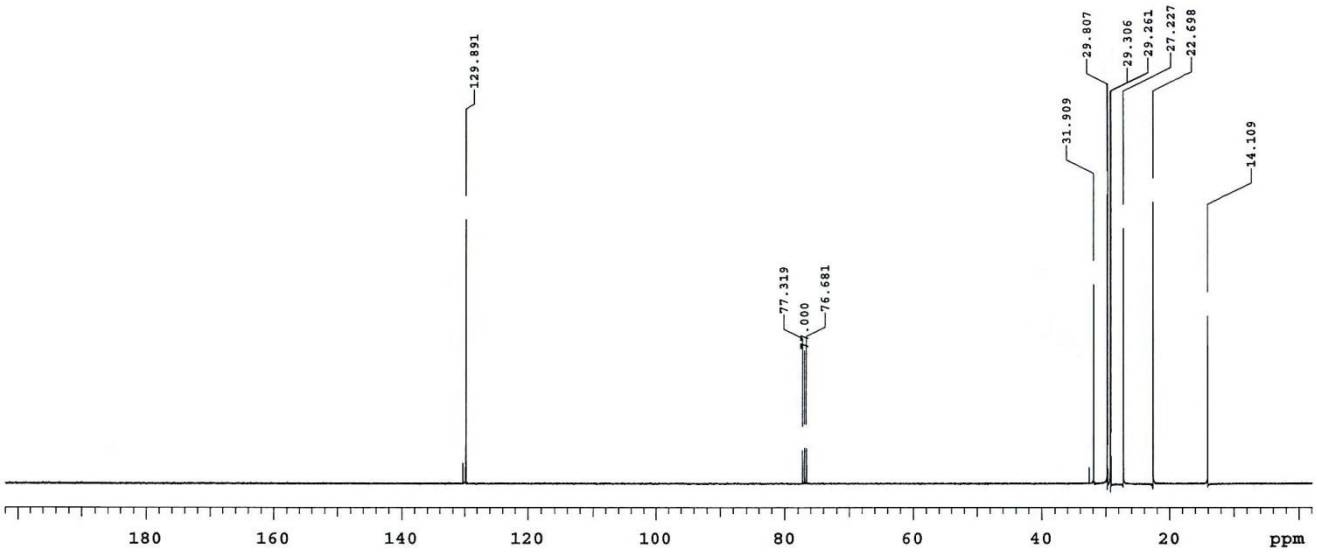


Sample Name: BG-368A
Solvent: cdcl3

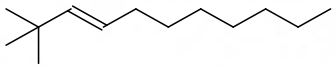


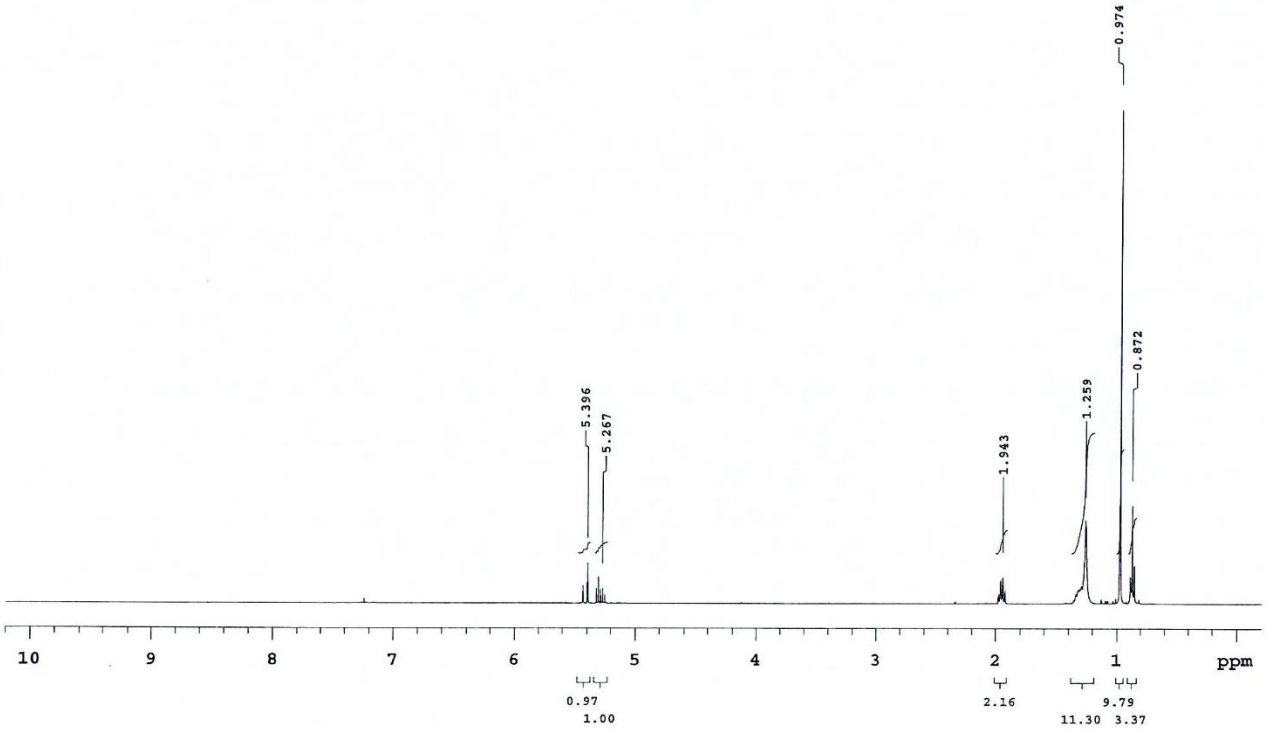


Sample Name: BG-368A
Solvent: cdcl3

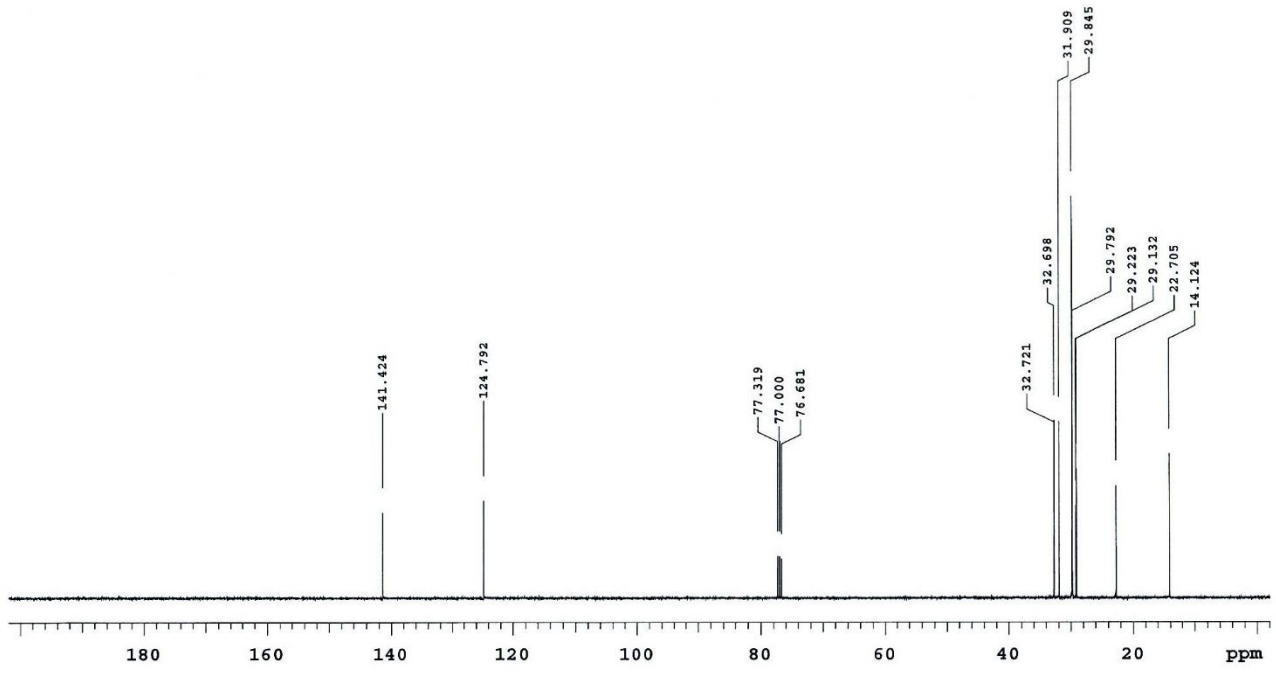


Sample Name: DB-230A_a
Solvent: cdcl3

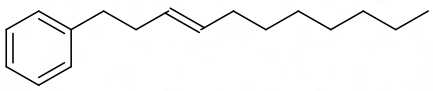


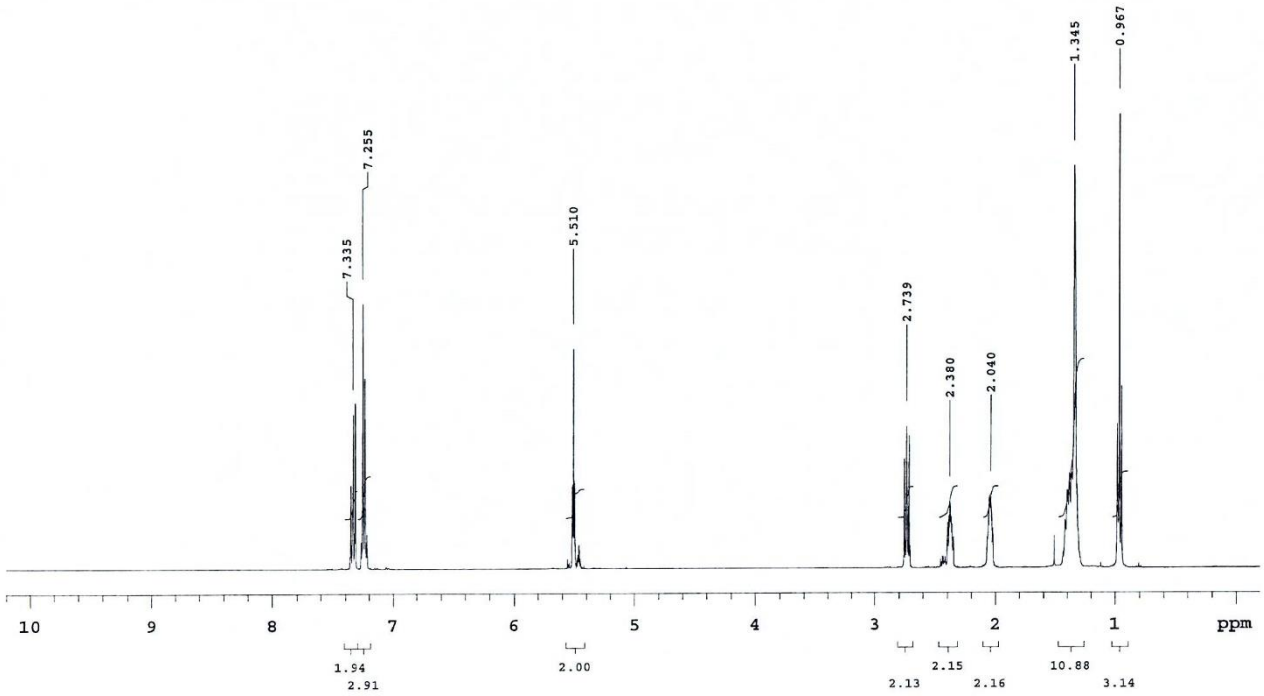


Sample Name: DB-230A_a
Solvent: cdcl3

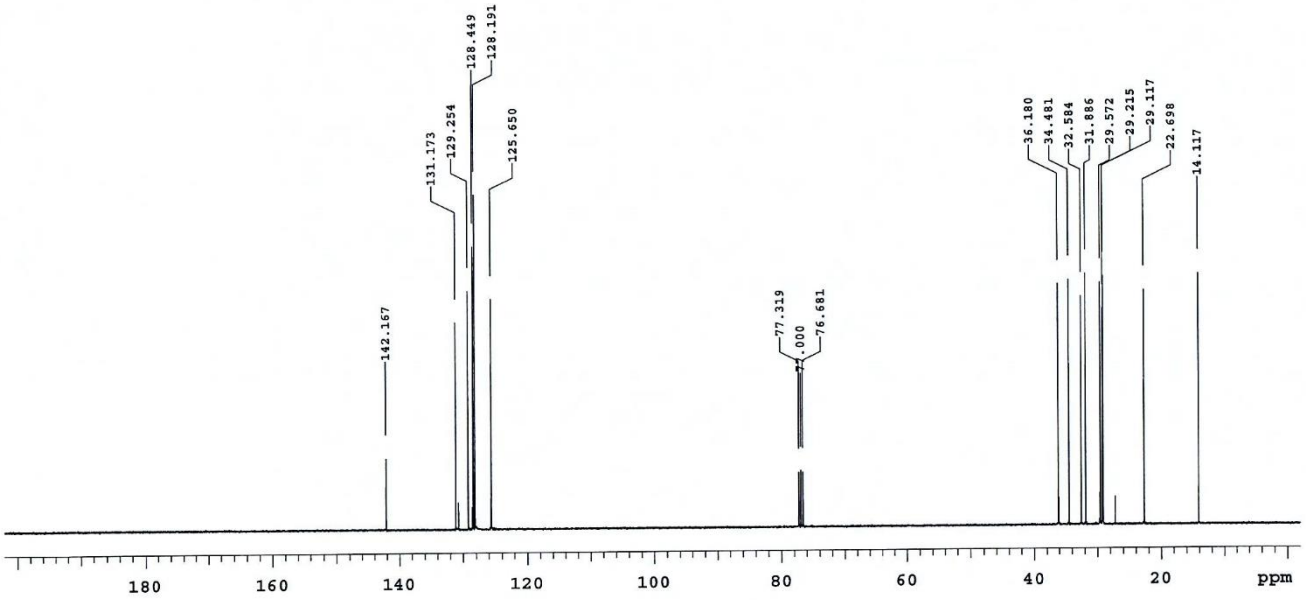


Sample Name: DB-187B_a
Solvent: cdcl3

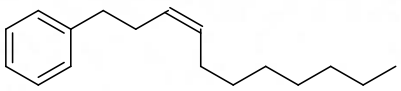


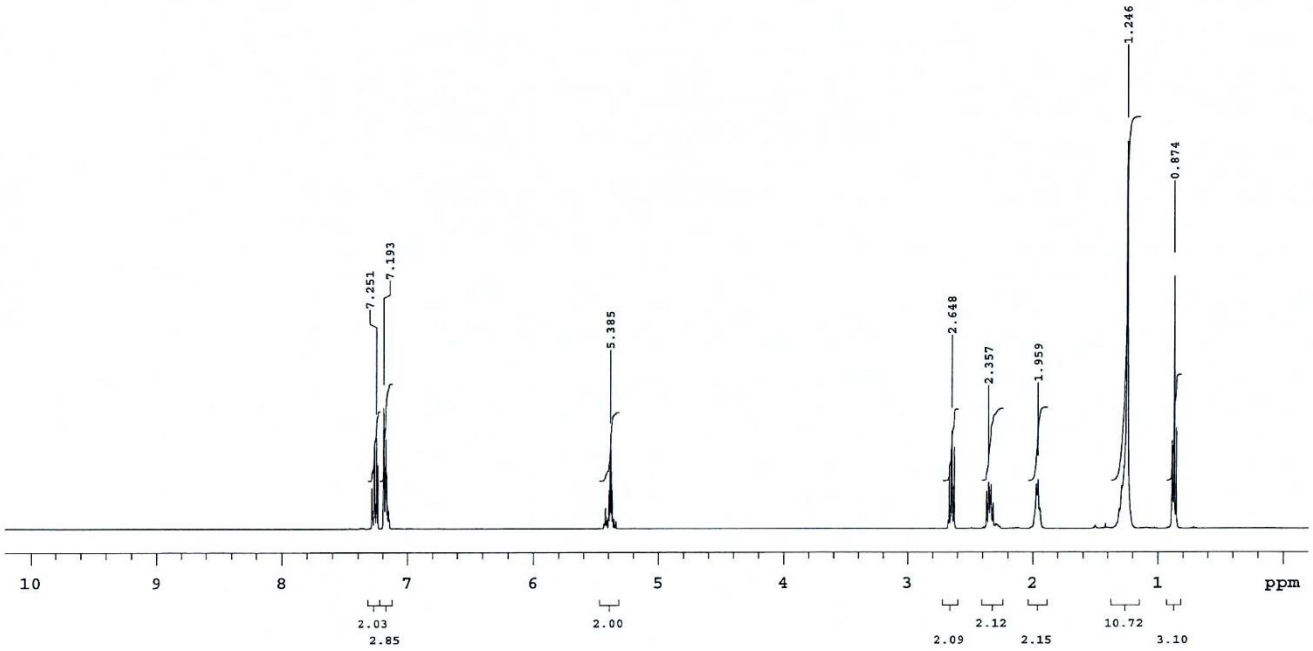


Sample Name: DB-187B_a
Solvent: cdcl3

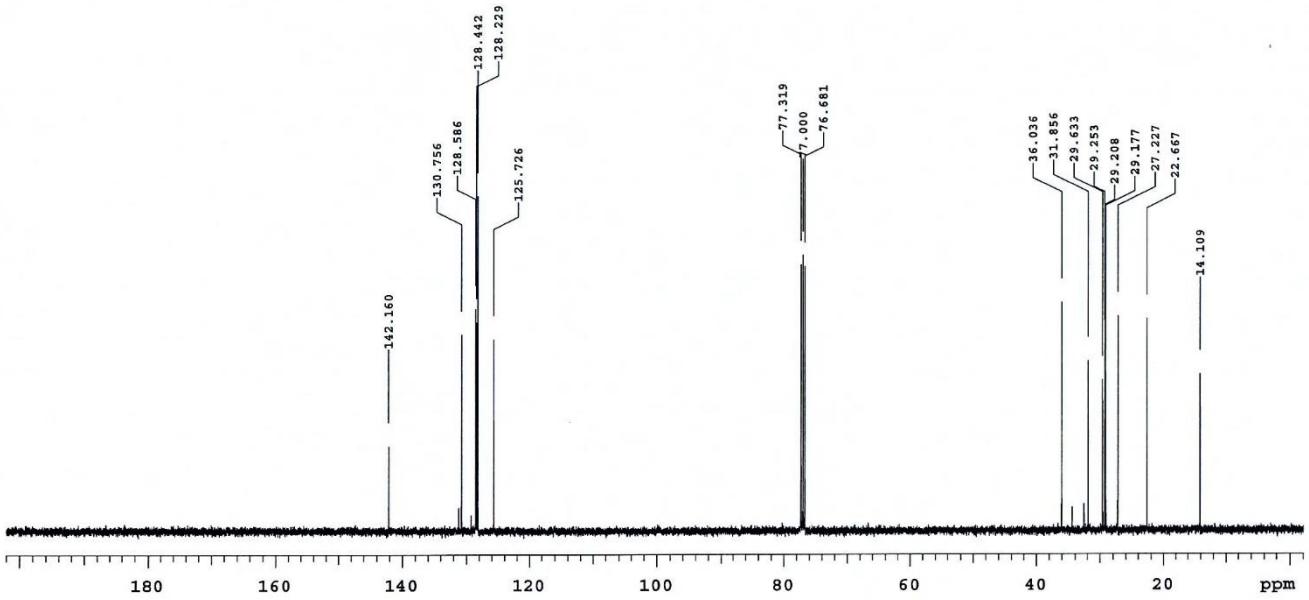


Sample Name: DB-214B_a
Solvent: cdcl3

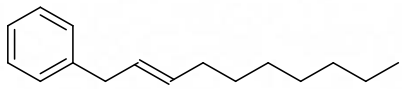


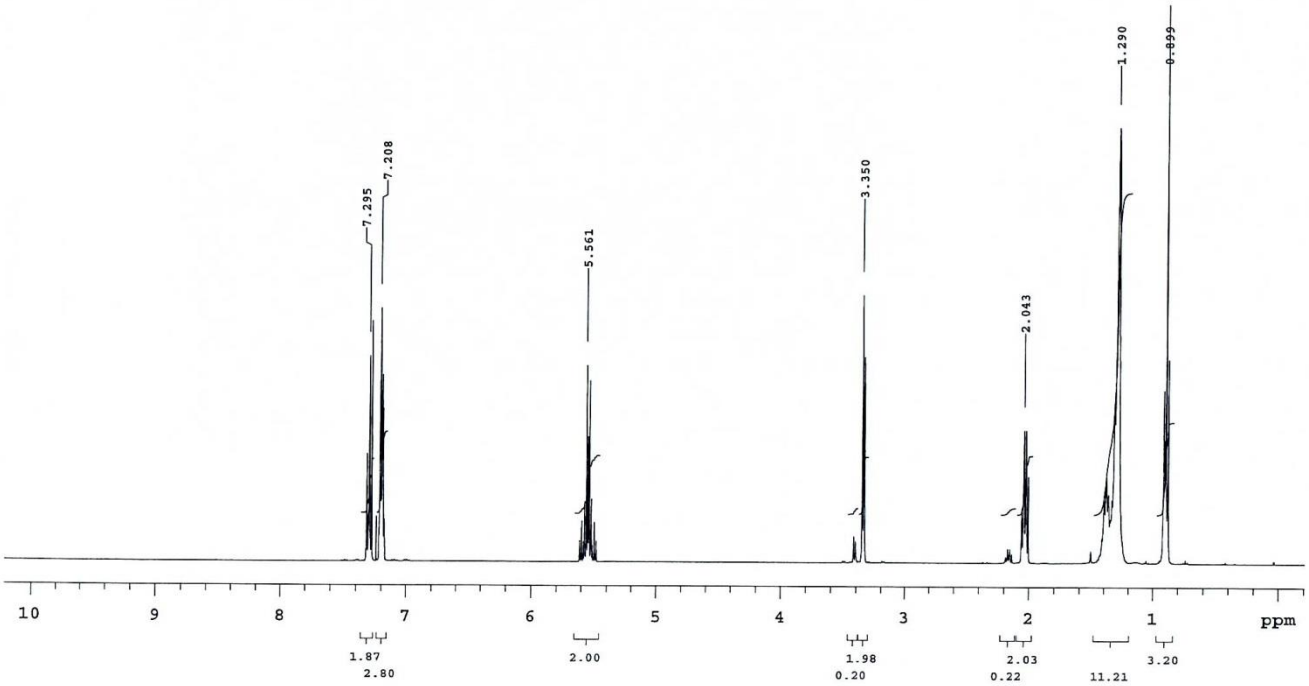


Sample Name: DB-214B_a
Solvent: cdcl3

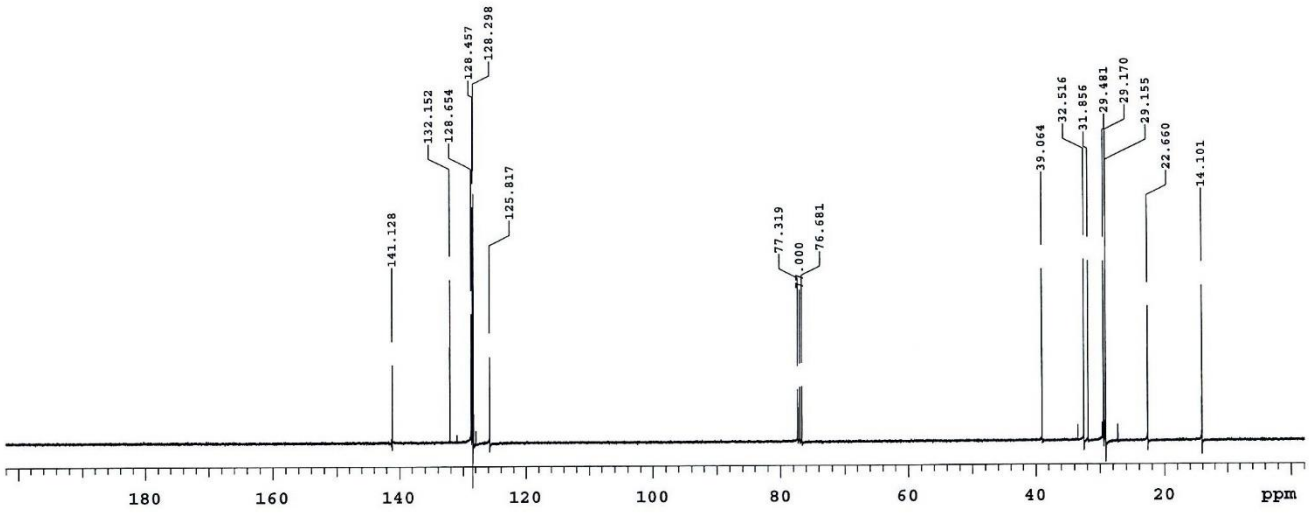


Sample Name: DB-202_a
Solvent: cdcl3

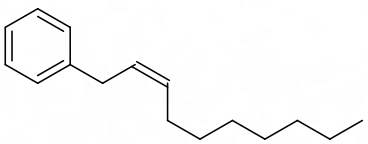


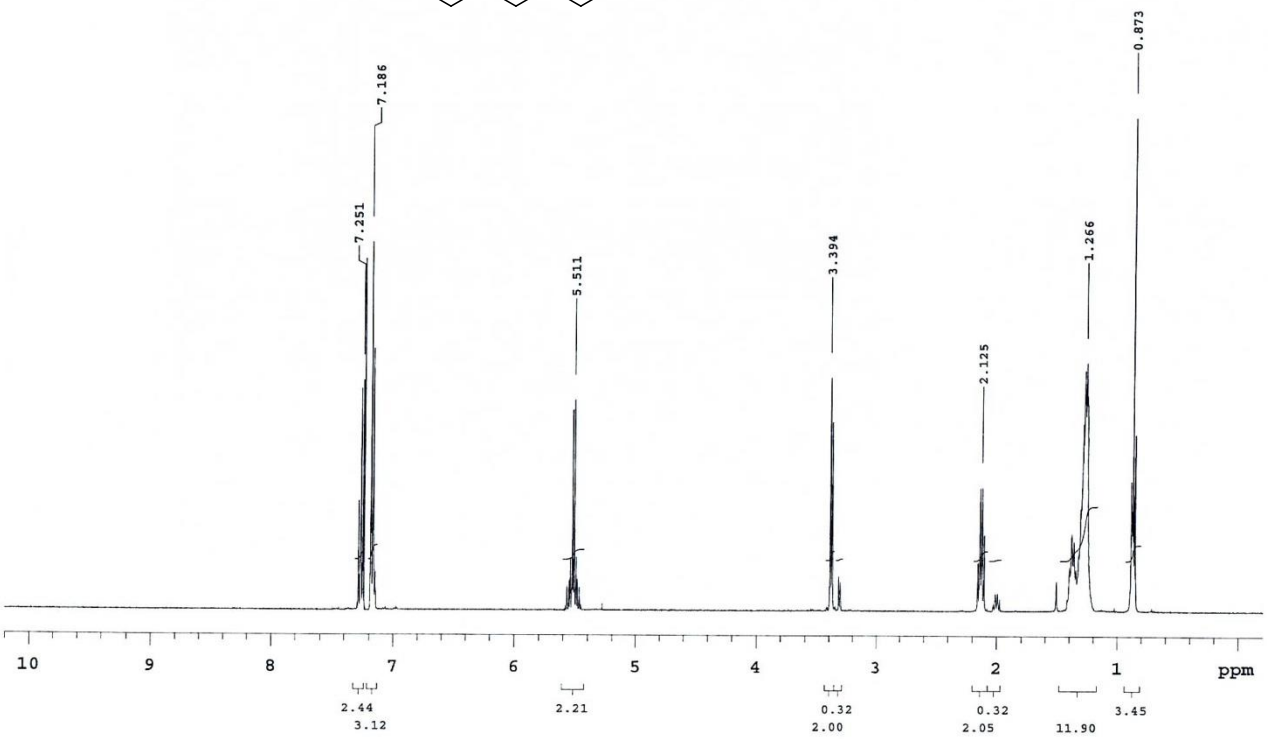


Sample Name: DB-202_a
Solvent: cdcl3

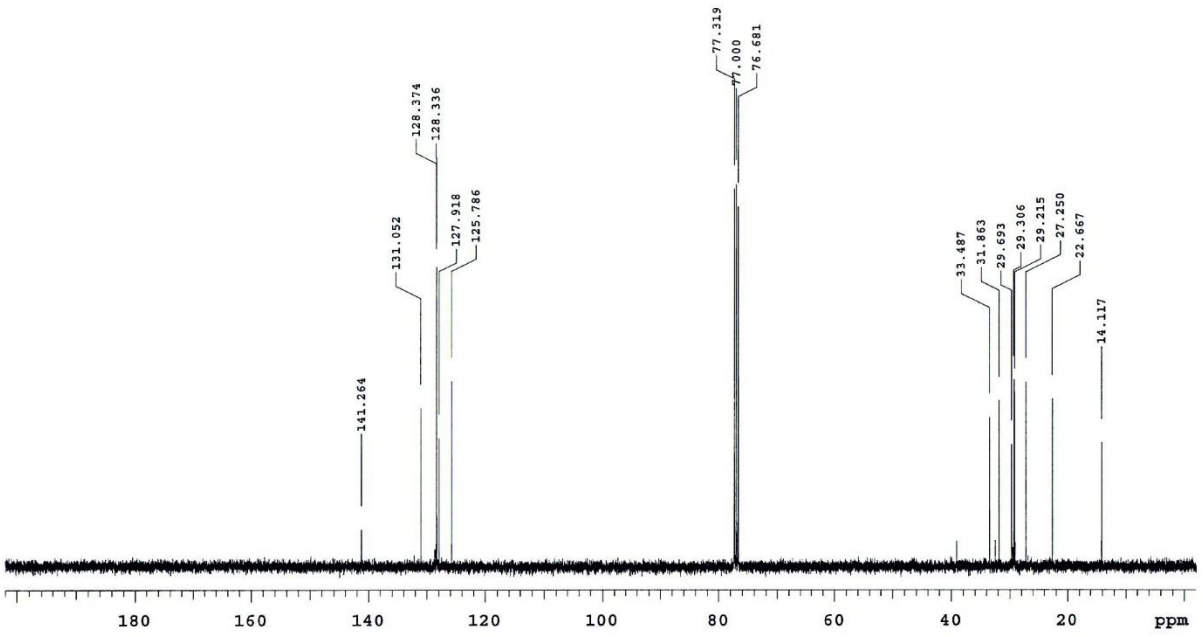


Sample Name: DB-217_a
Solvent: cdcl3

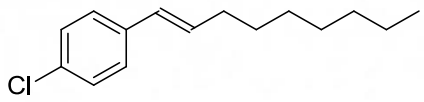


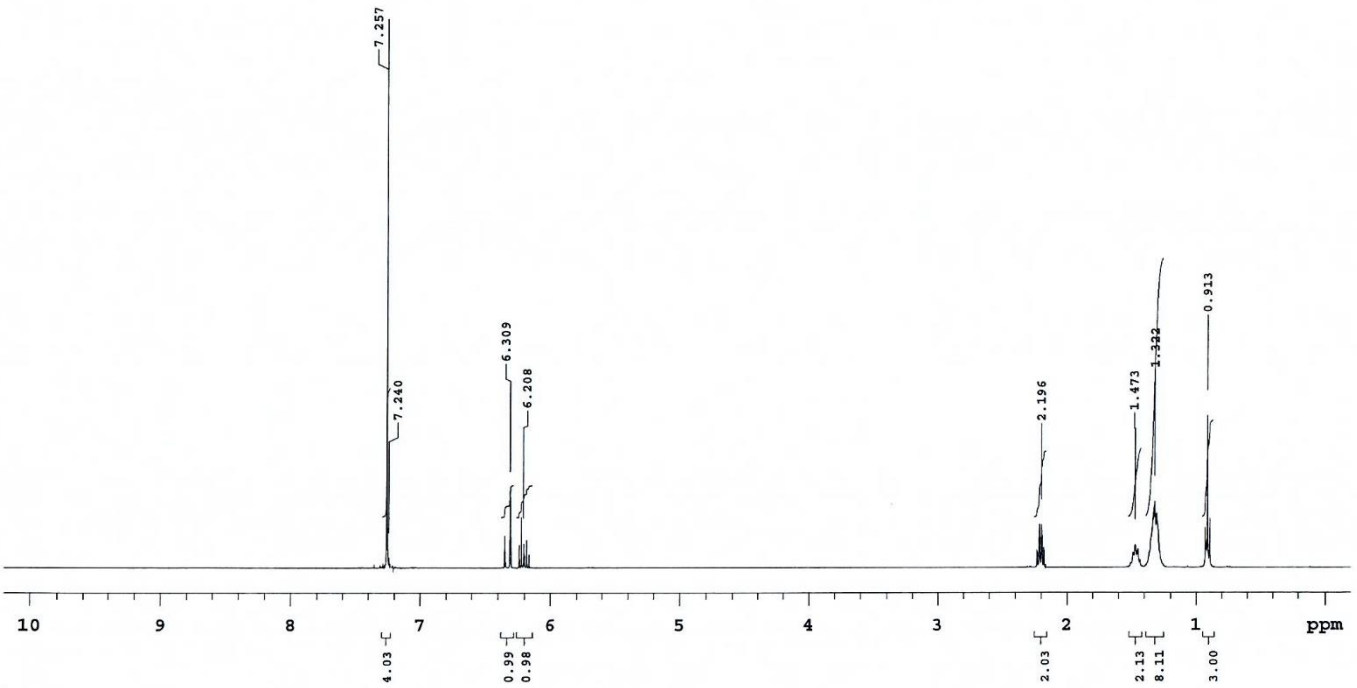


Sample Name: DB-217_a
Solvent: cdcl3

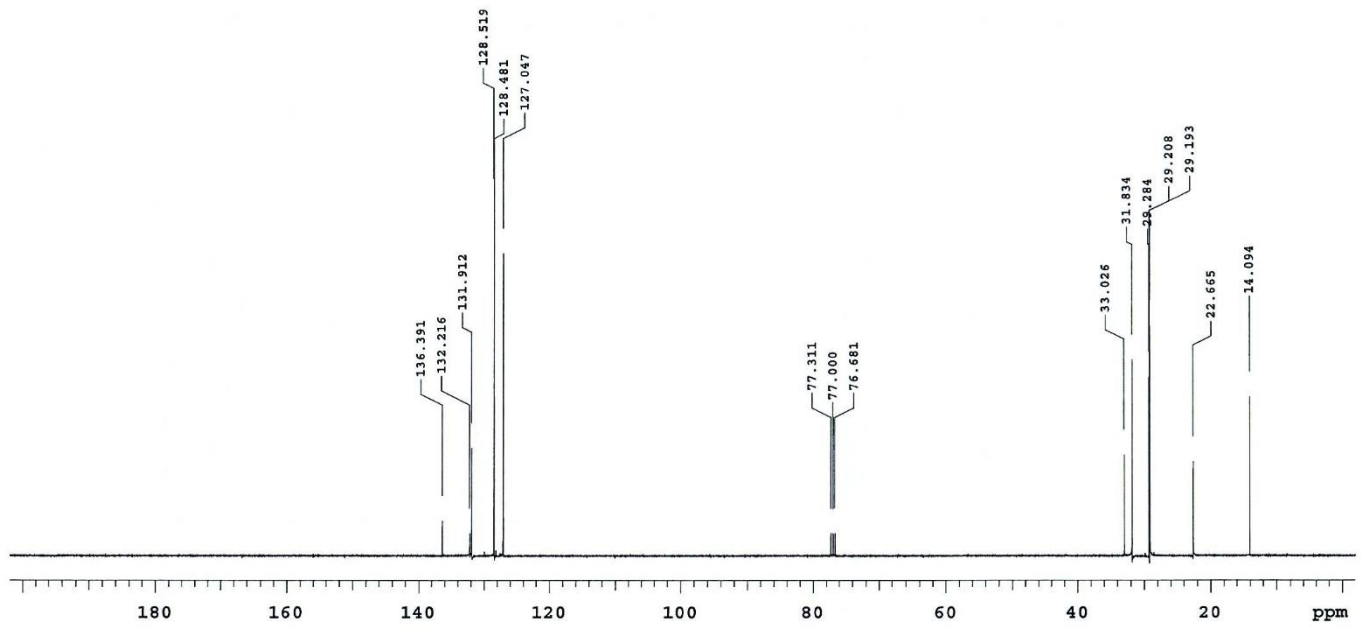


Sample Name: BG-394A
Solvent: cdcl3

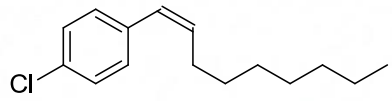


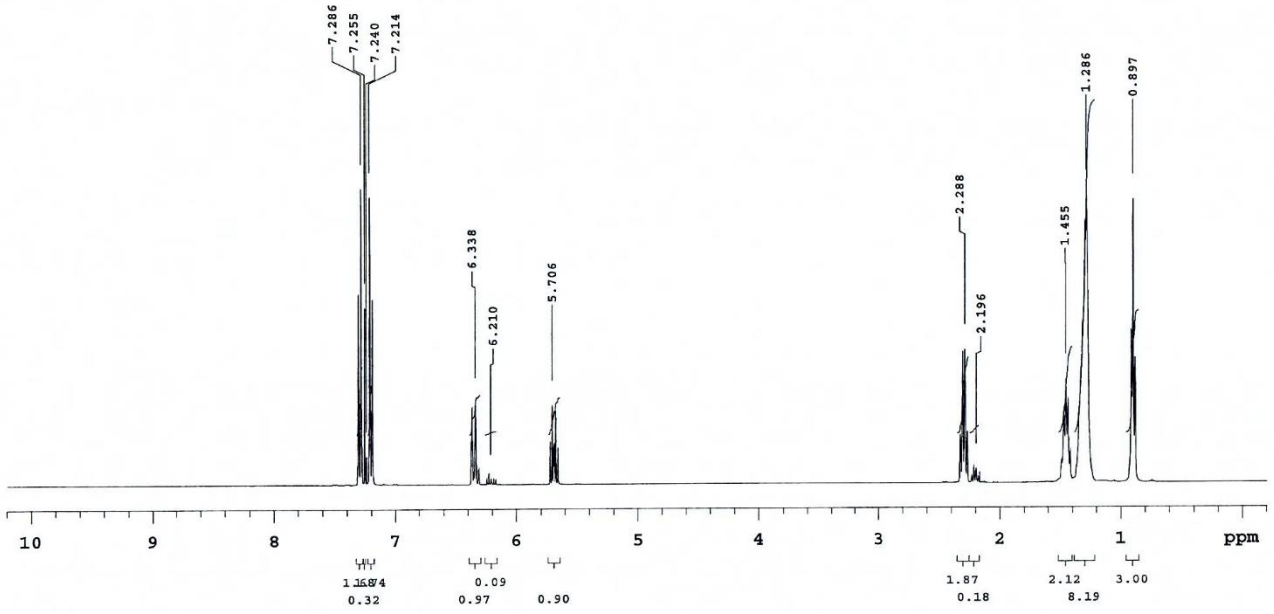


Sample Name: BG-394A
Solvent: cdcl3

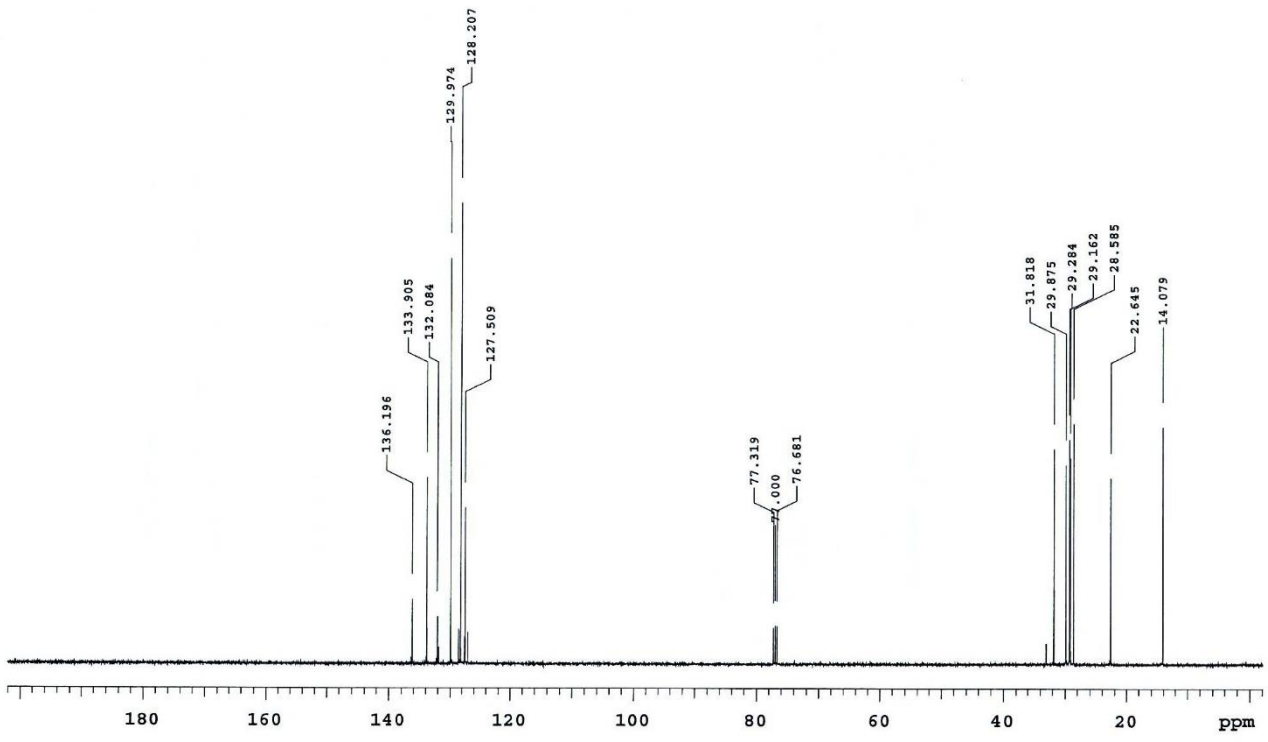


Sample Name: BG-396A
Solvent: cdcl3

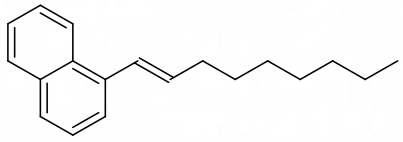


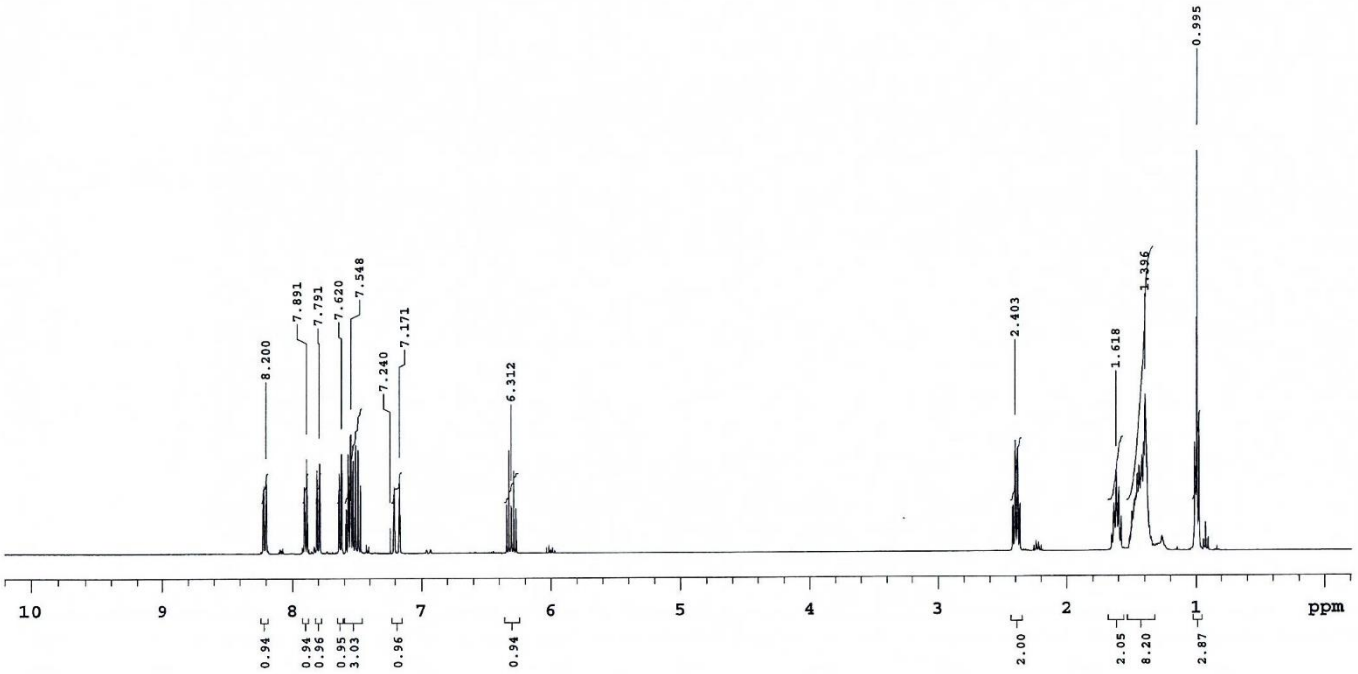


Sample Name: BG-396A
Solvent: cdcl3

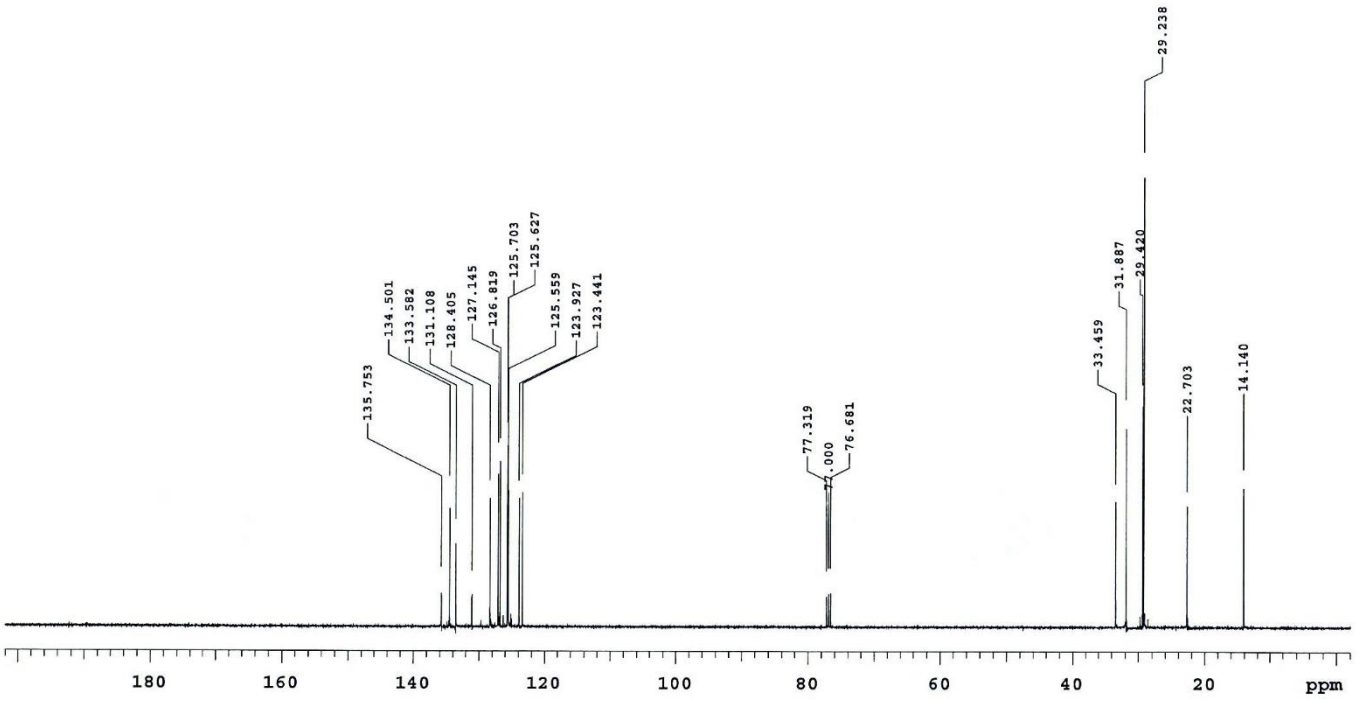


Sample Name: BG-412A
Solvent: cdcl3

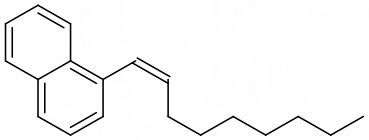


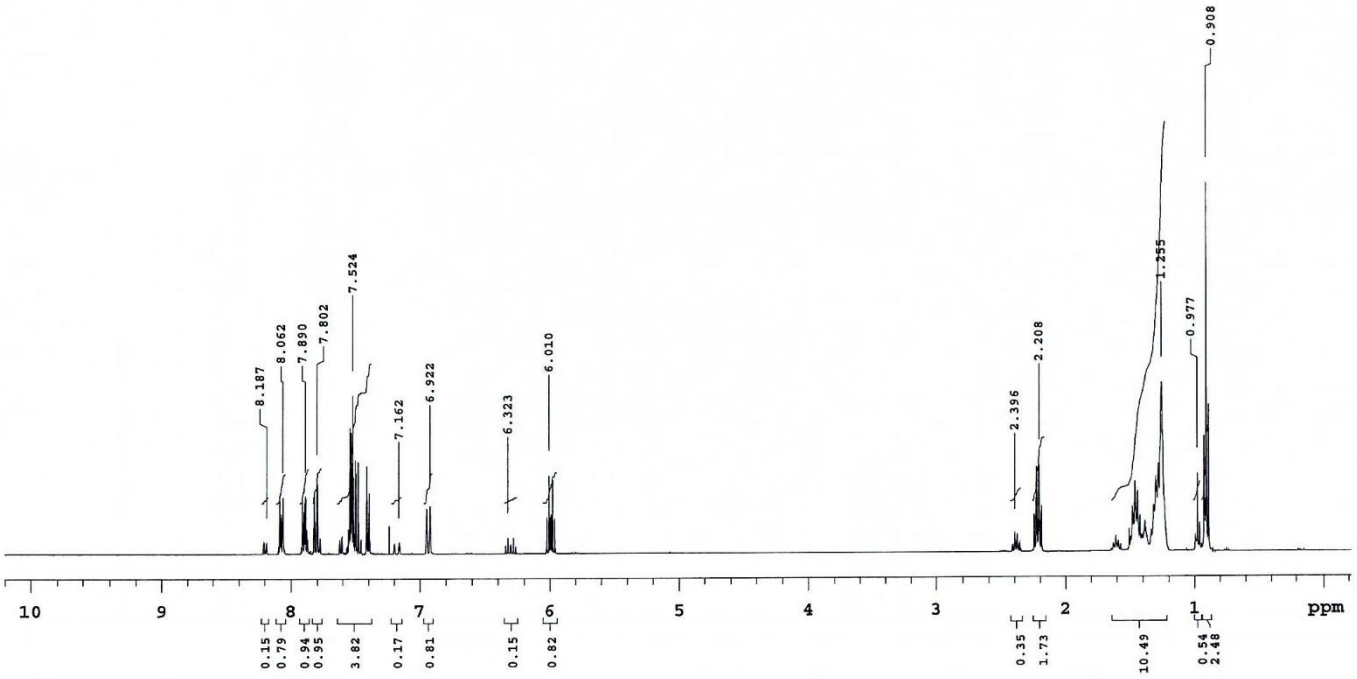


Sample Name: BG-412A
Solvent: cdcl3

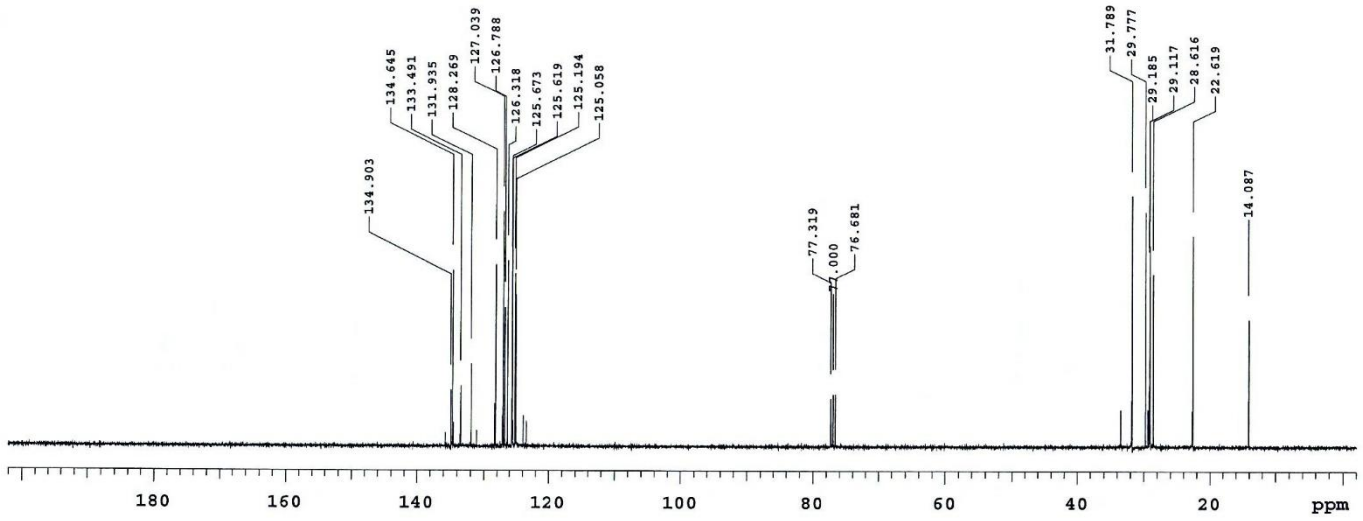


Sample Name: BG-409A
Solvent: cdcl3

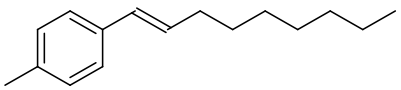


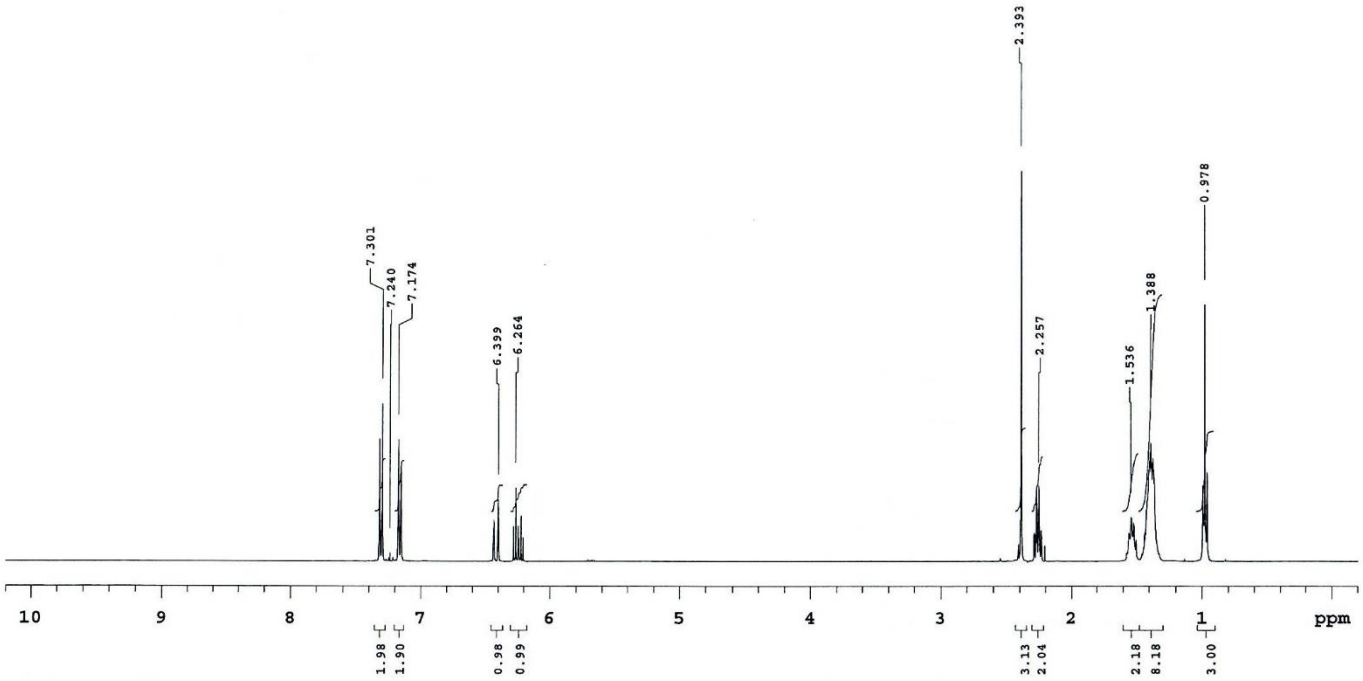


Sample Name: BG-409A
Solvent: cdcl3

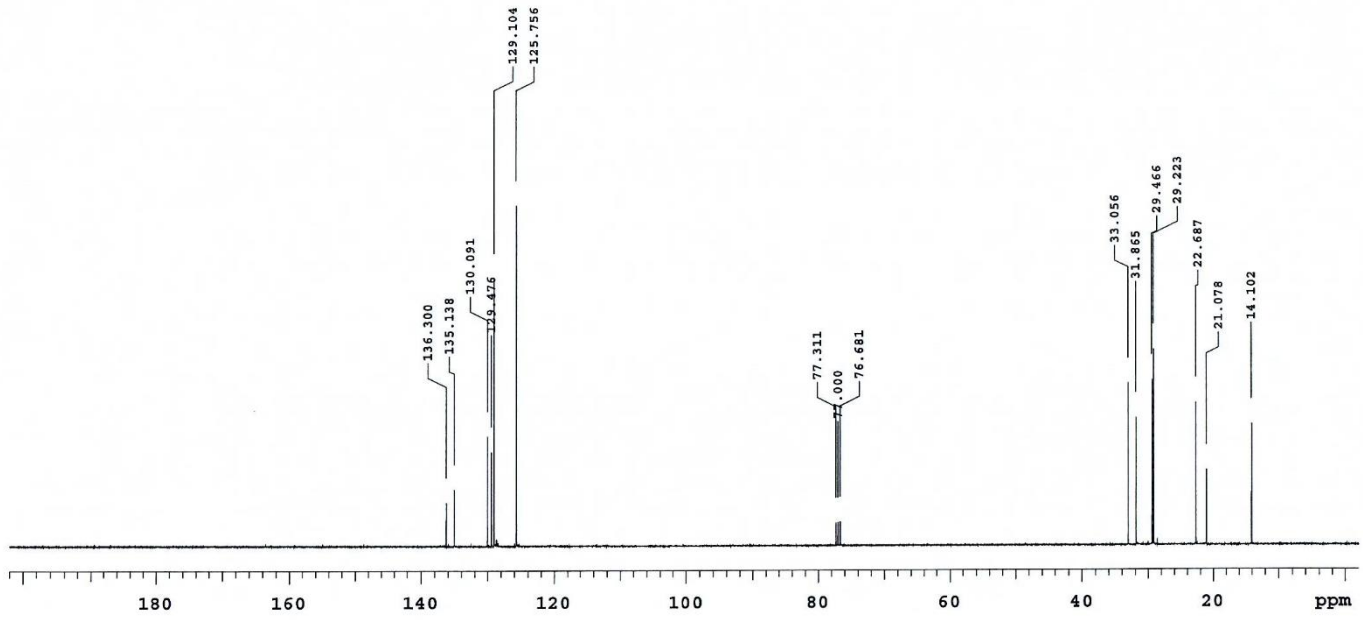


Sample Name: BG-418A
Solvent: cdcl3

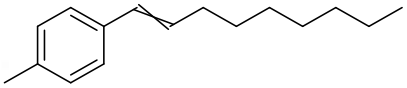




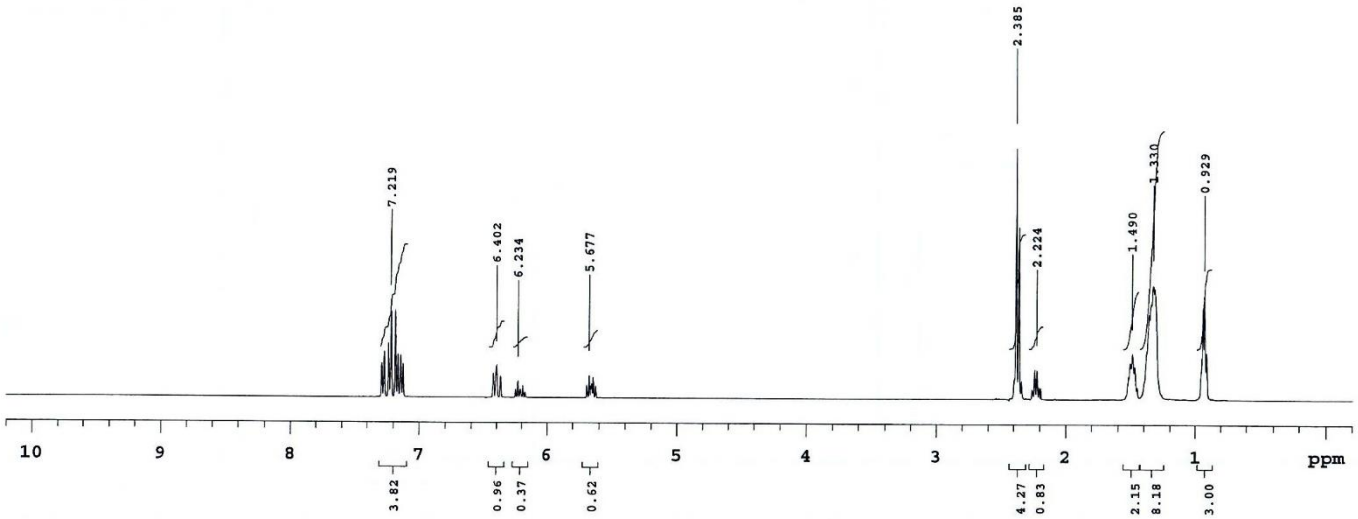
Sample Name: BG-418A
Solvent: cdcl3



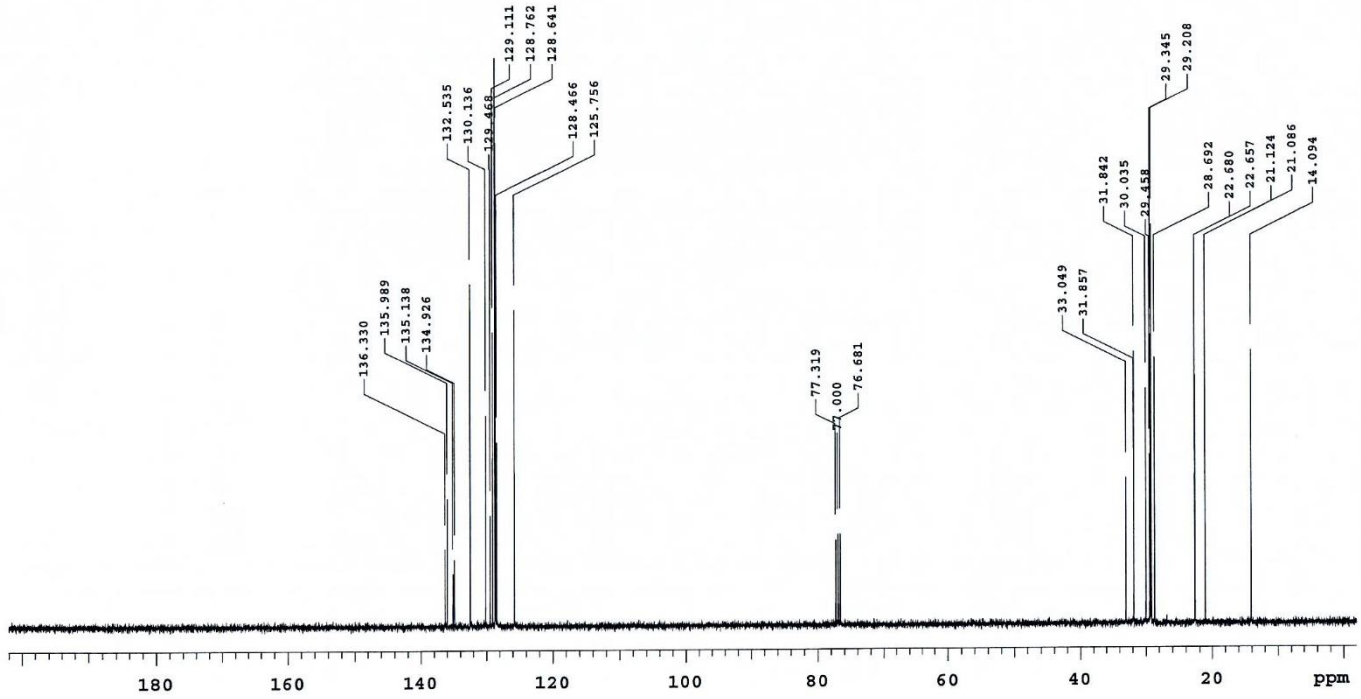
Sample Name: BG-424A
Solvent: cdcl3



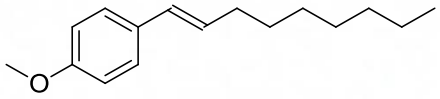
E/Z = 37:63

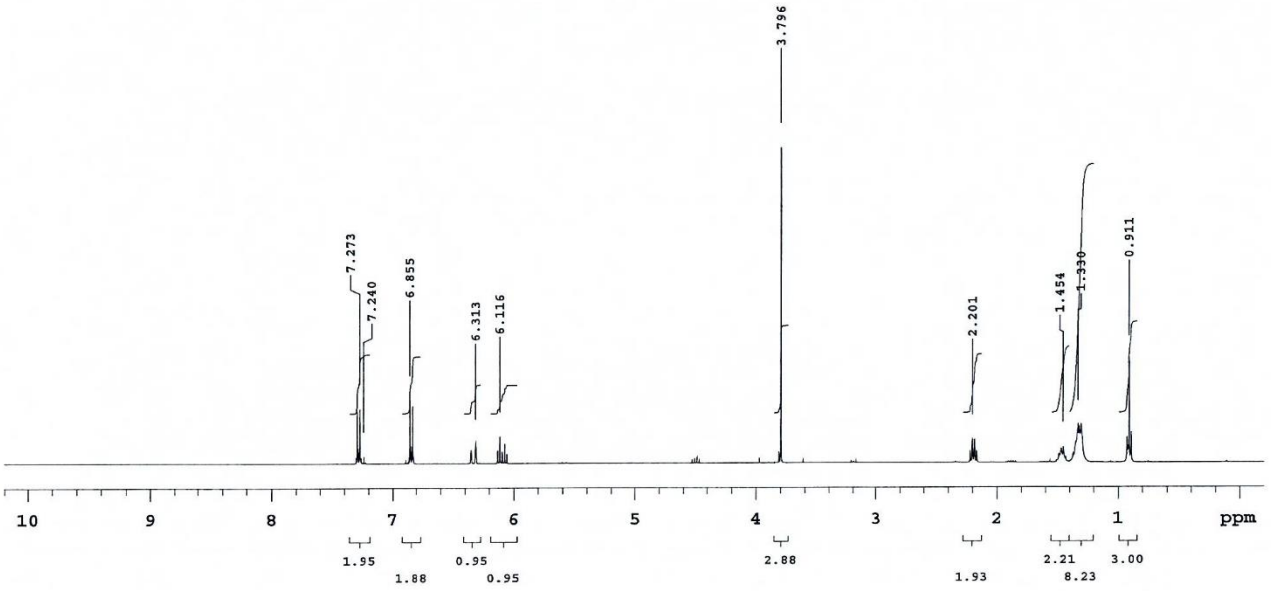


Sample Name: BG-424A
Solvent: cdcl3

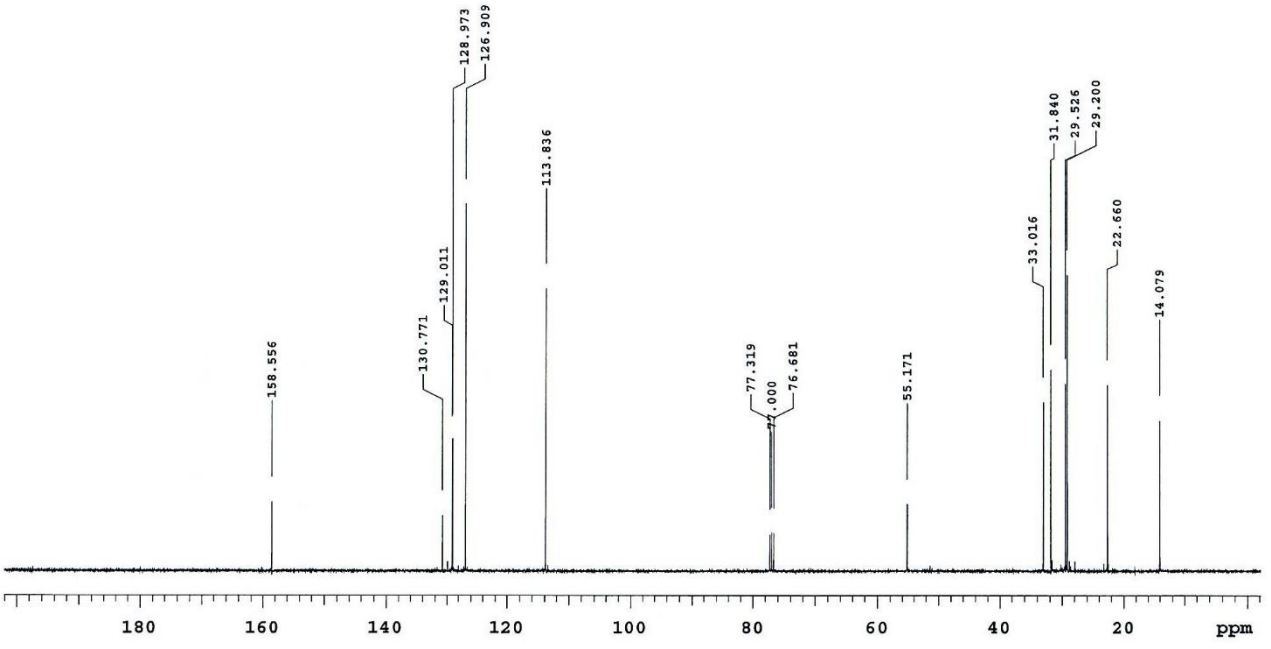


Sample Name: BG-399A
Solvent: cdcl3

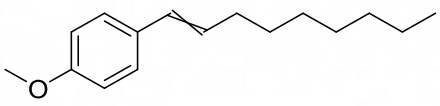




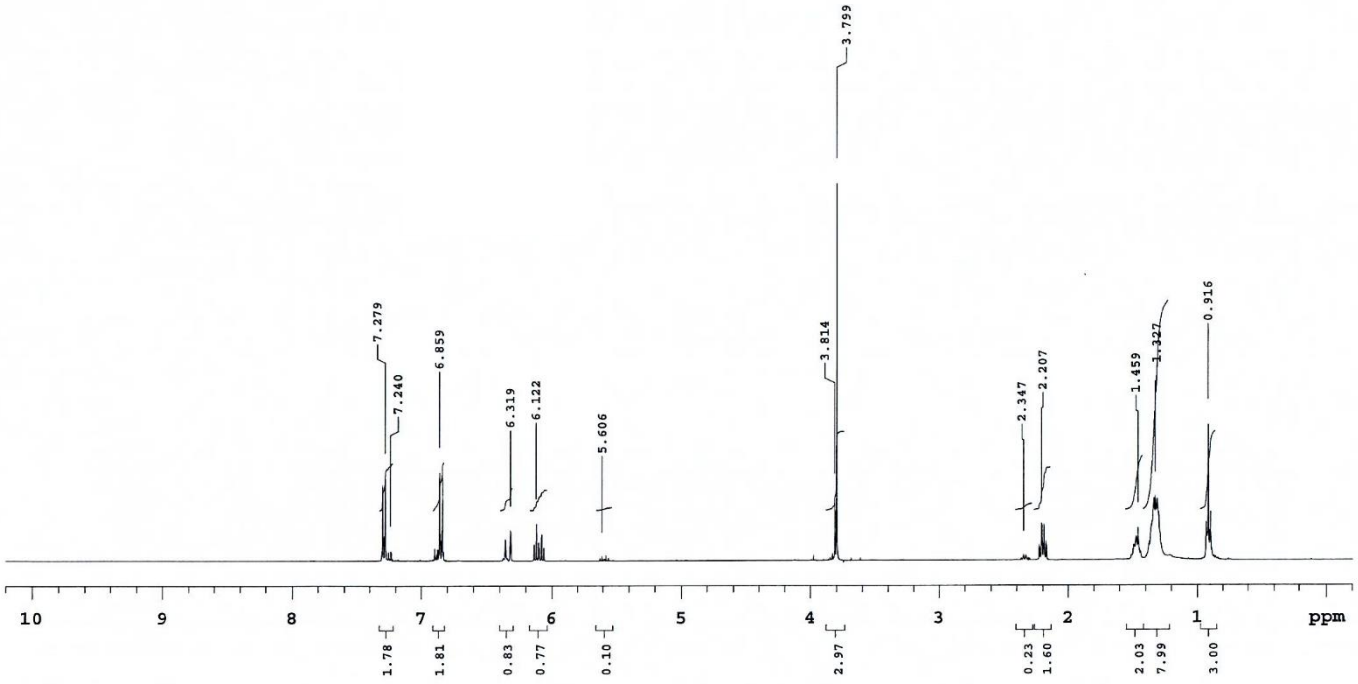
Sample Name: BG-399A
Solvent: cdcl3



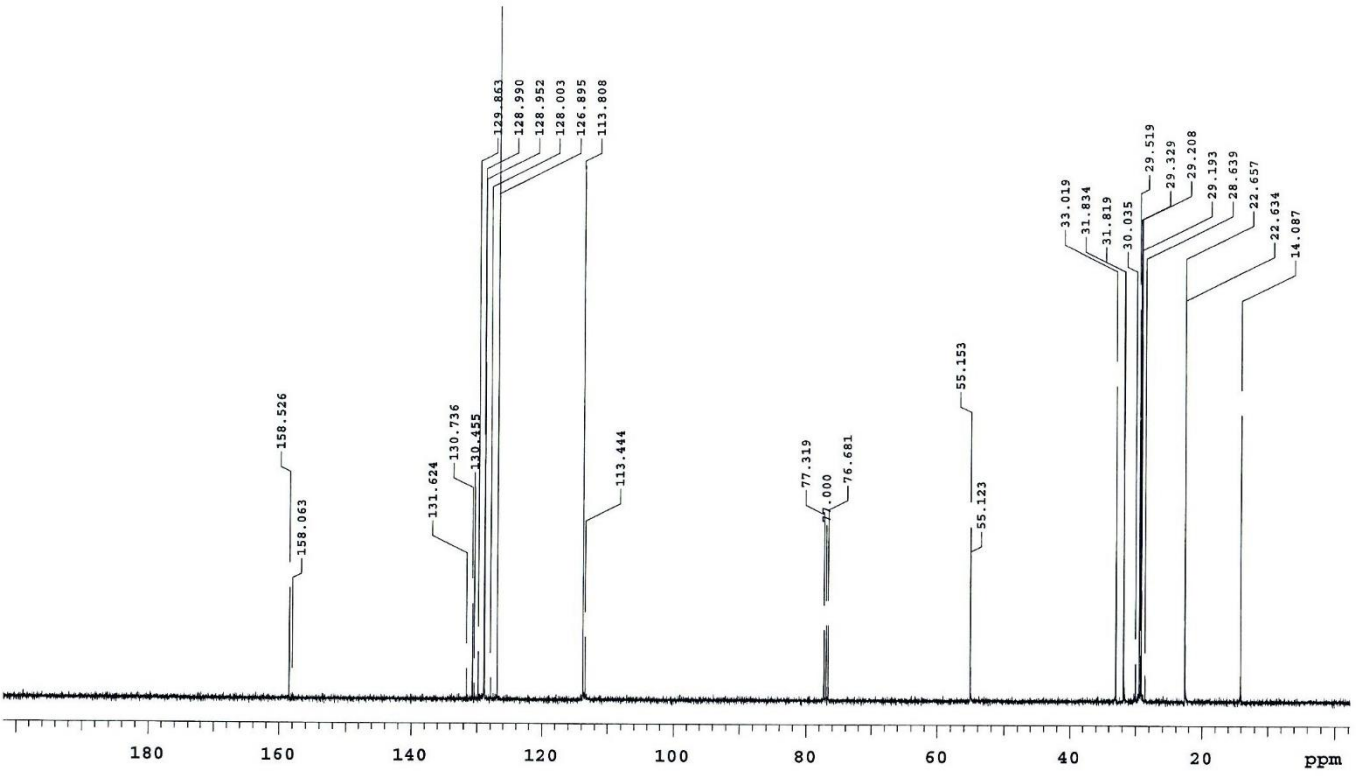
Sample Name: BG-404A
Solvent: cdcl3



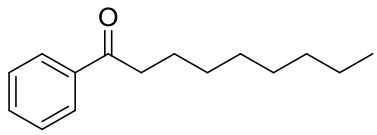
E/Z = 90:10

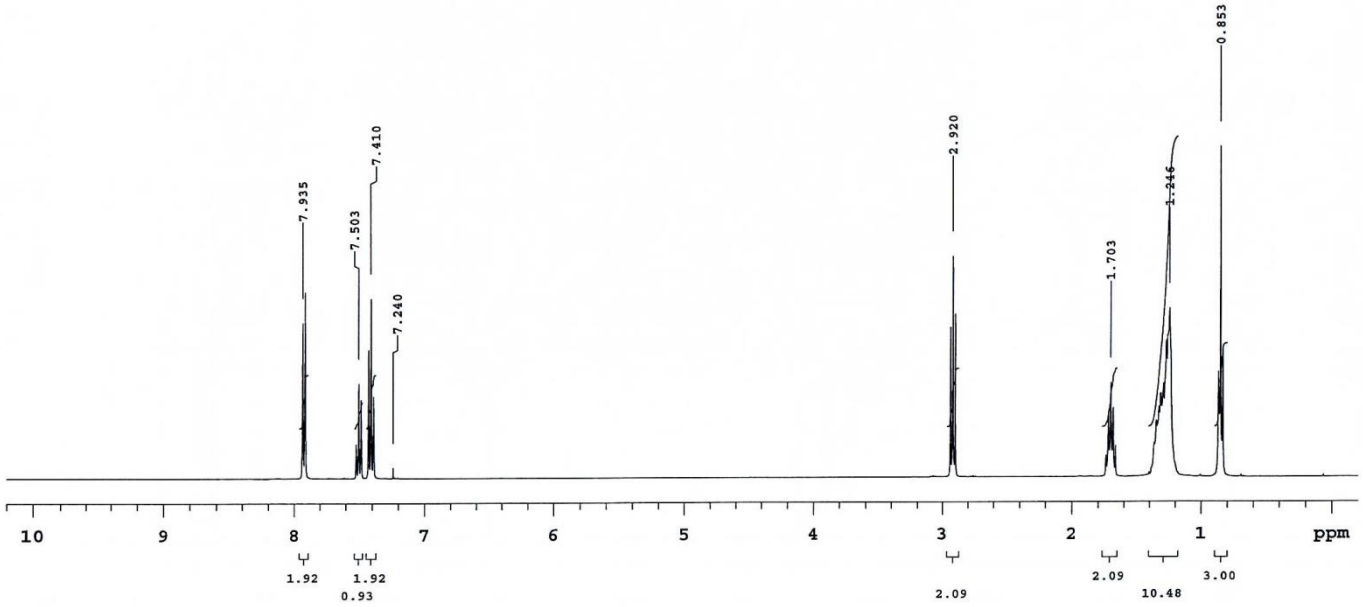


Sample Name: BG-404A
Solvent: cdcl3

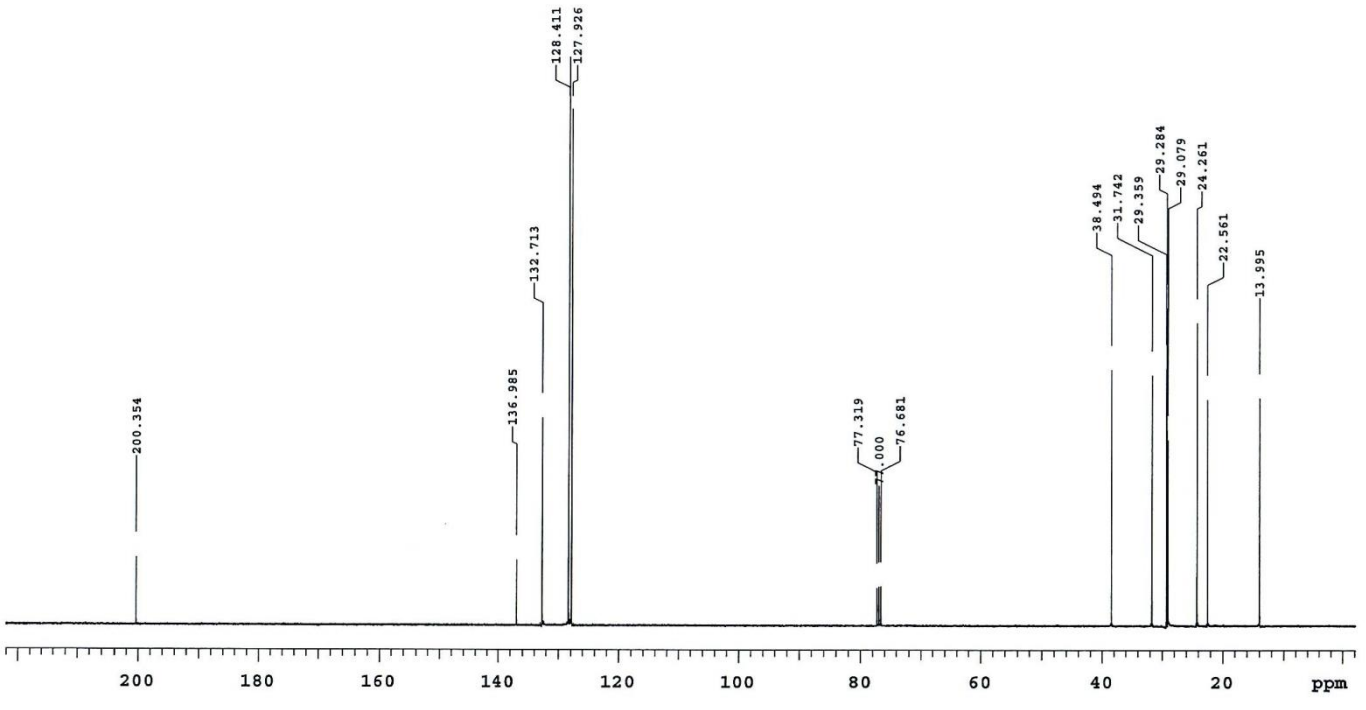


Sample Name: BG-329A
Solvent: cdcl3

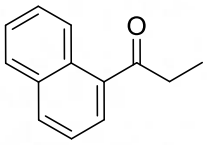


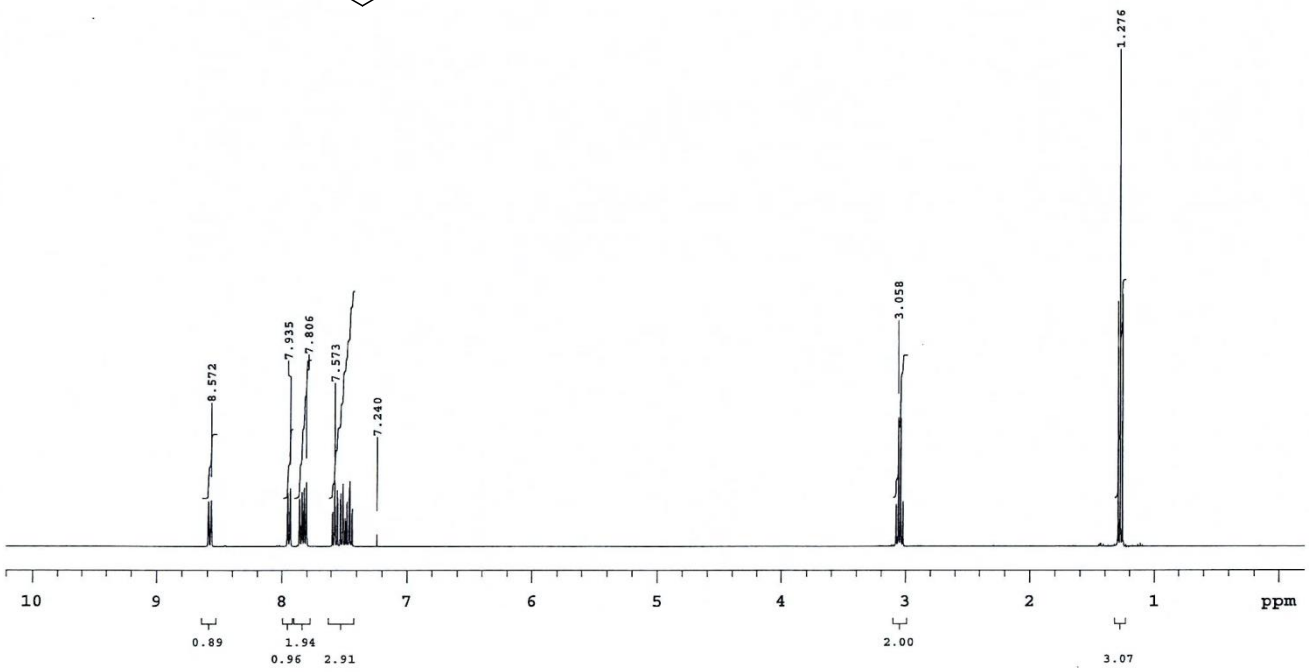


Sample Name: BG-329A
Solvent: cdcl3

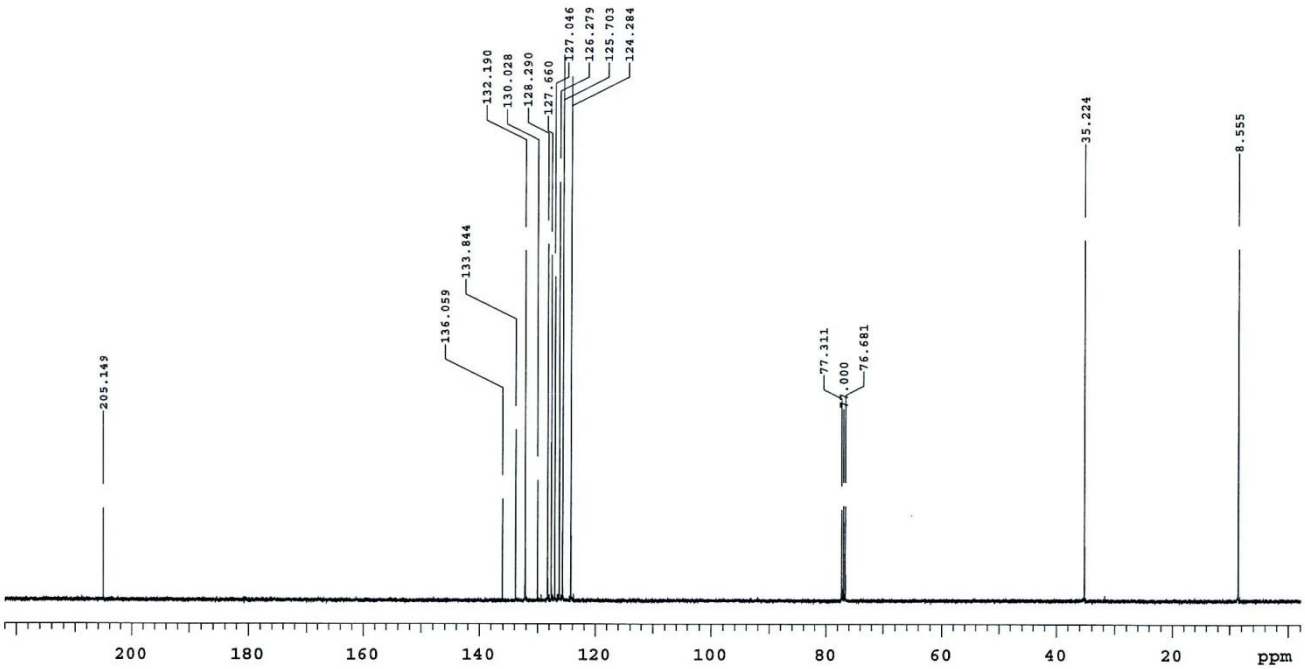


Sample Name: DB-195_a
Solvent: cdcl3

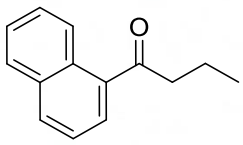


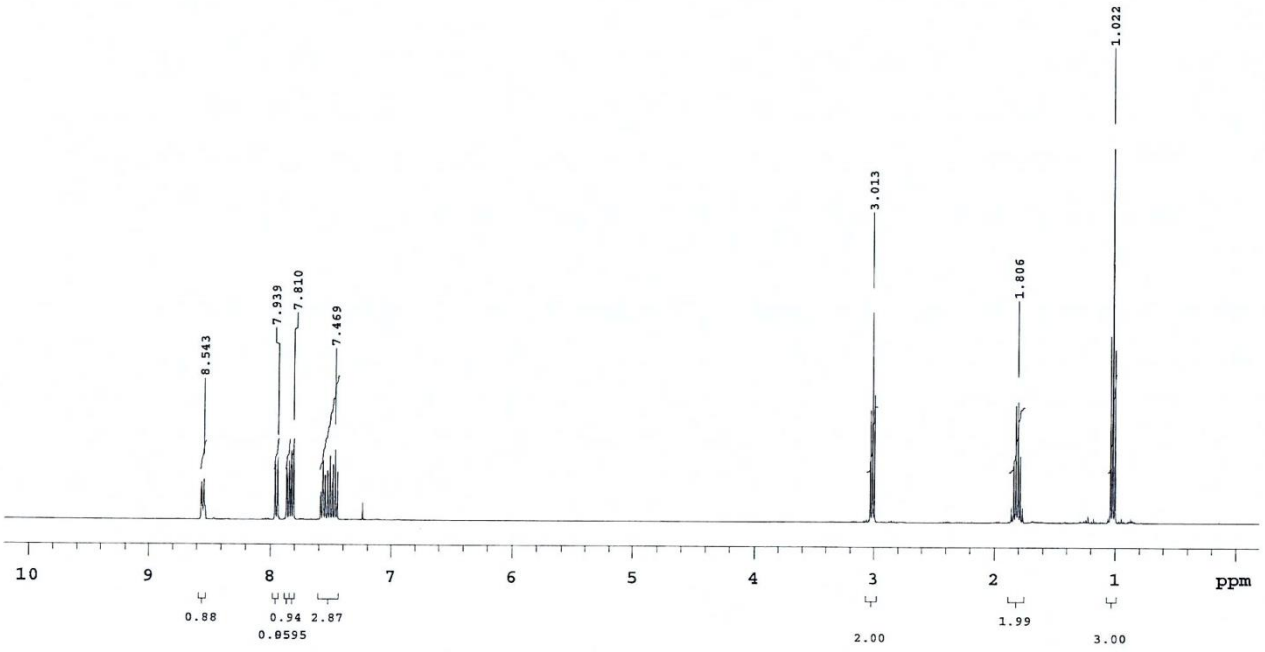


Sample Name: DB-195_a
Solvent: cdcl3

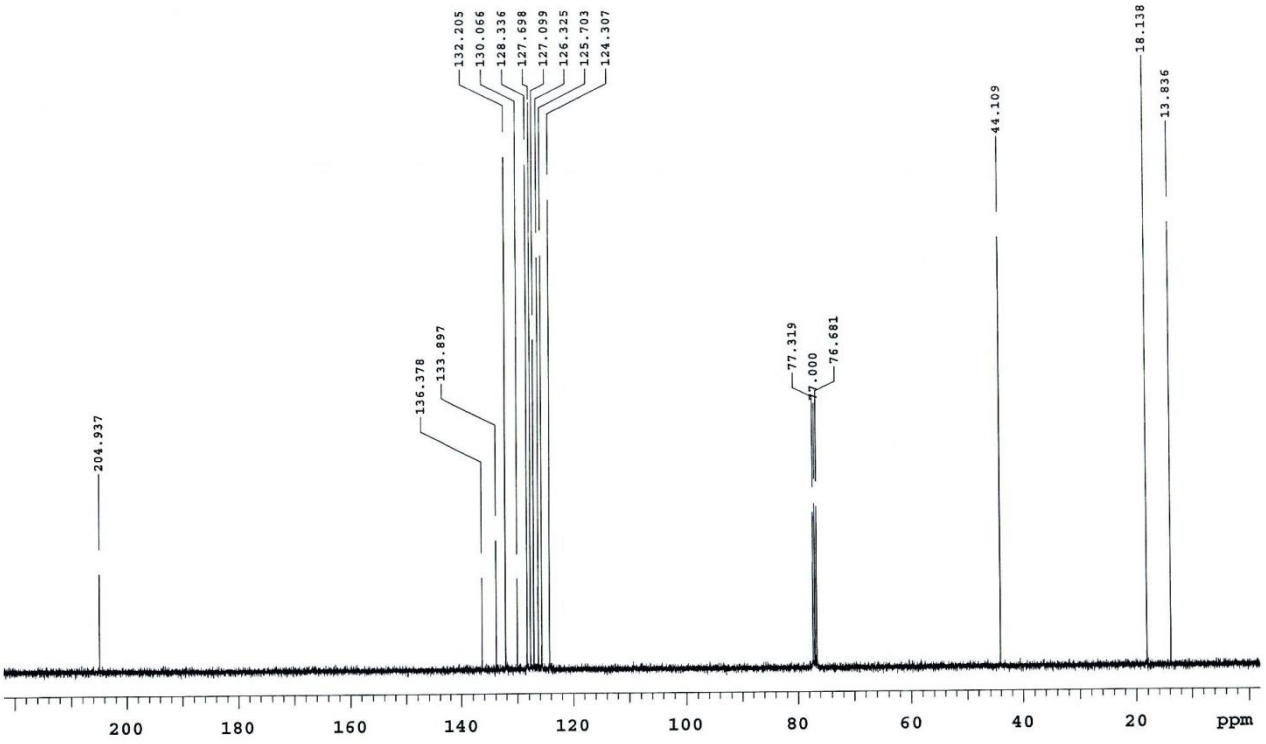


Sample Name: DB-237_a
Solvent: cdcl3

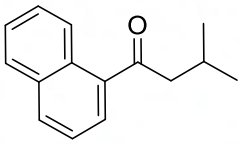


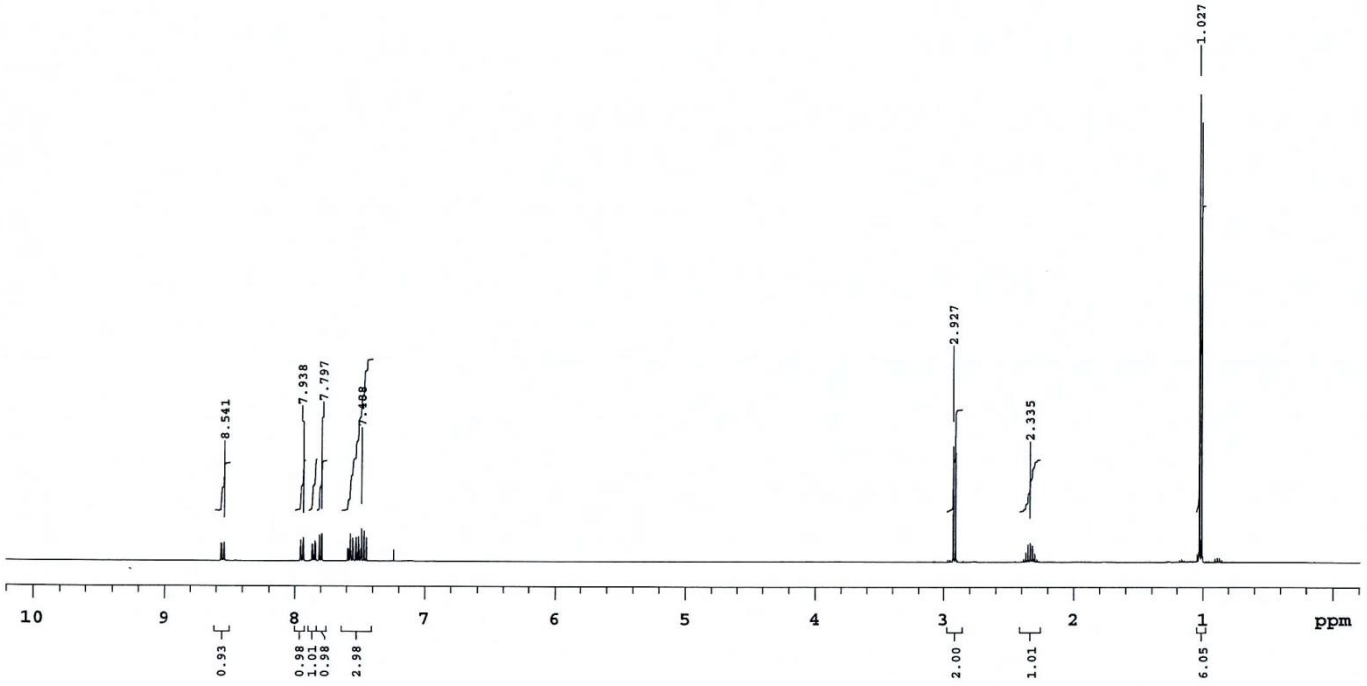


Sample Name: DB-237_a
Solvent: cdcl3

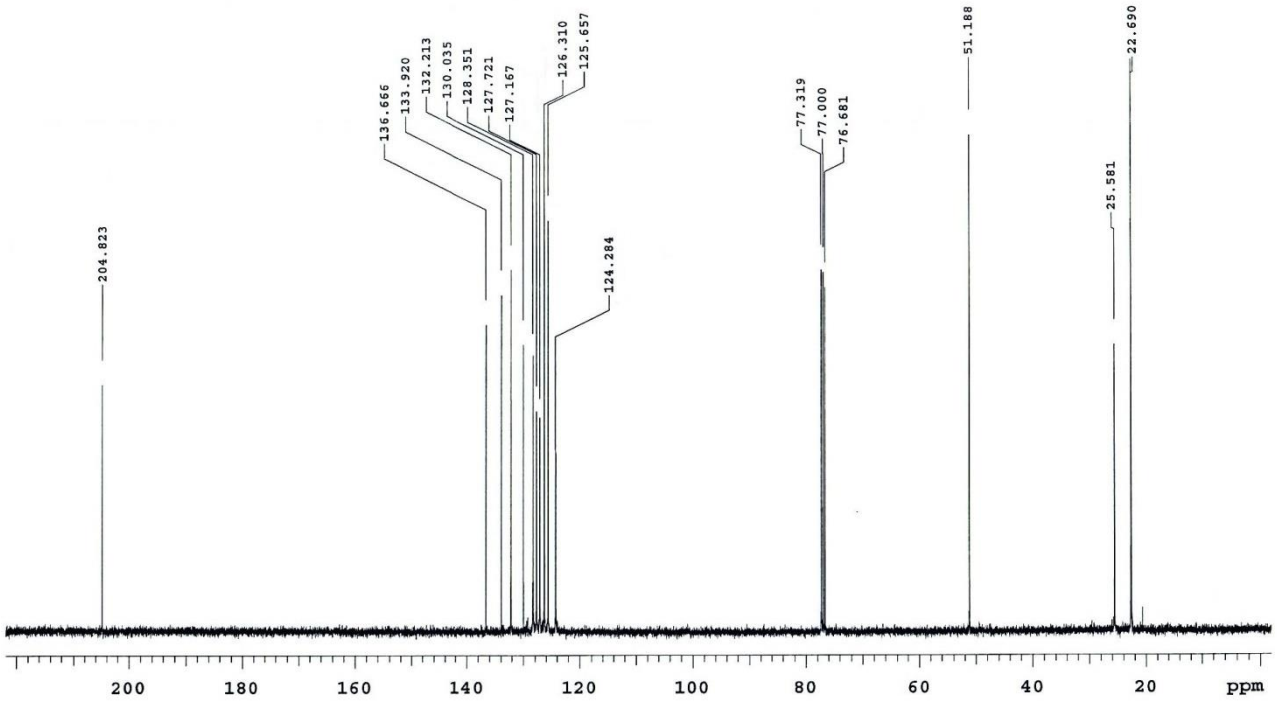


Sample Name: DB-211_a
Solvent: cdcl3

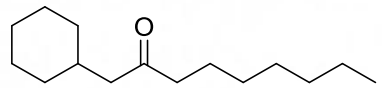


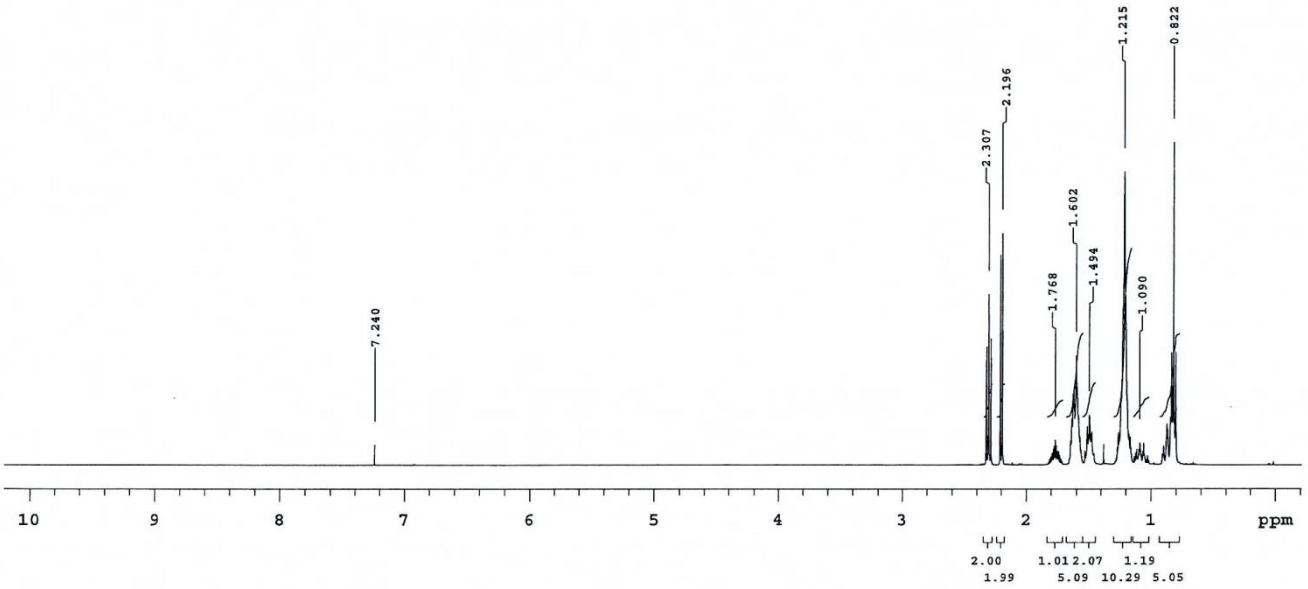


Sample Name: DB-211_a
Solvent: cdcl3

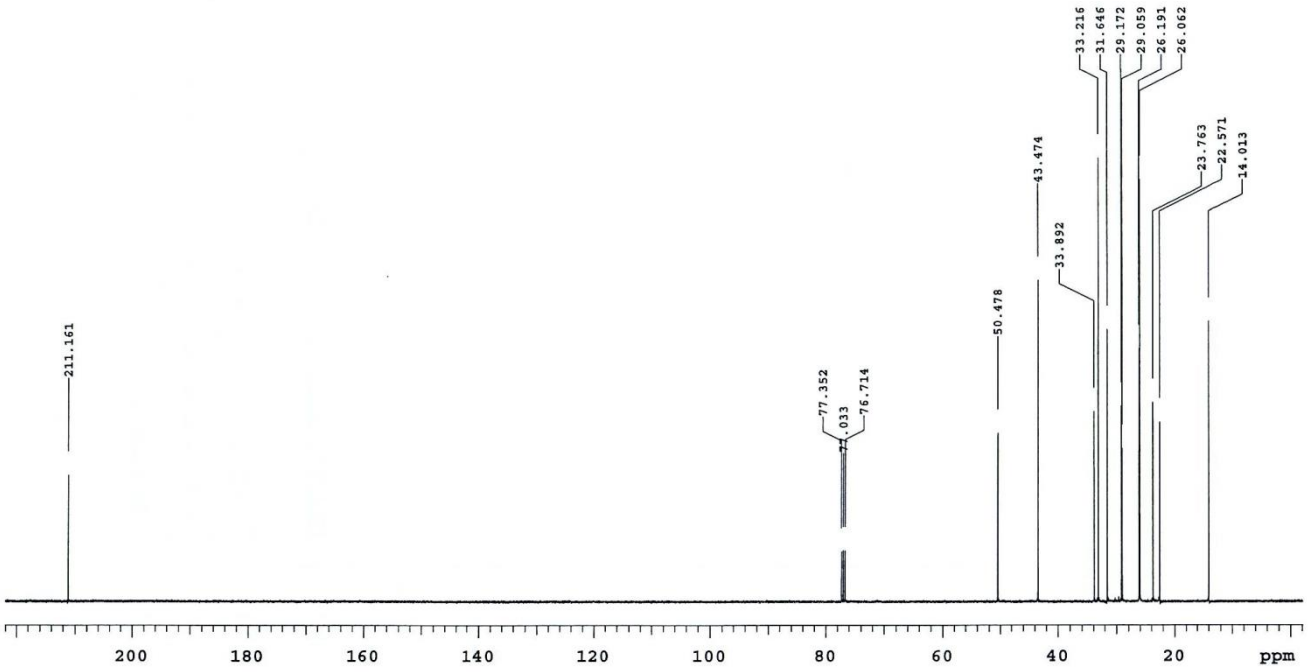


Sample Name: BG-379A
Solvent: cdcl3

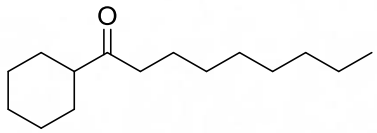


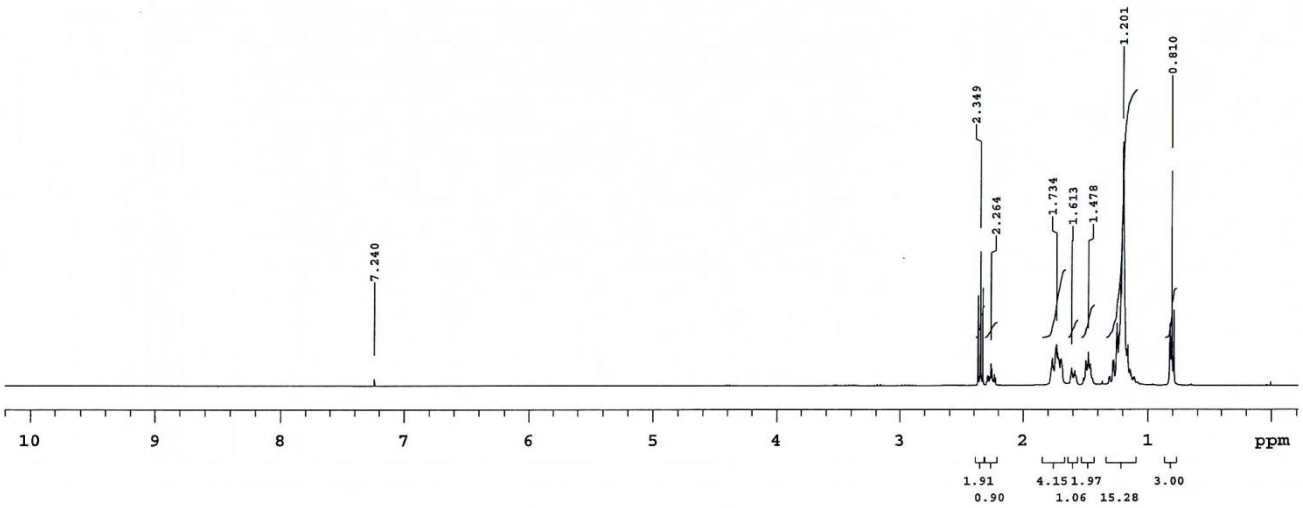


Sample Name: BG-379A
Solvent: cdcl3

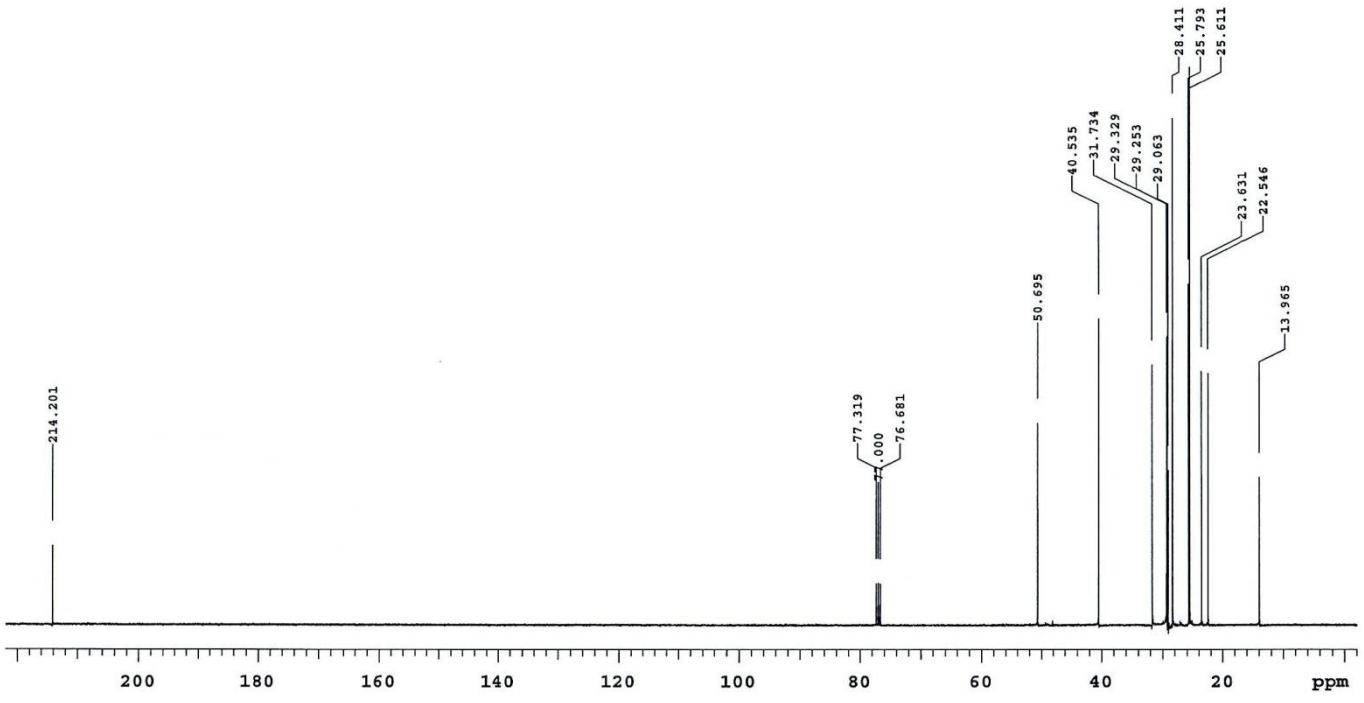


Sample Name: BG-327A
Solvent: cdcl3

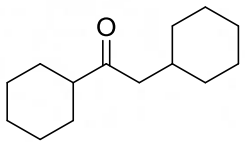


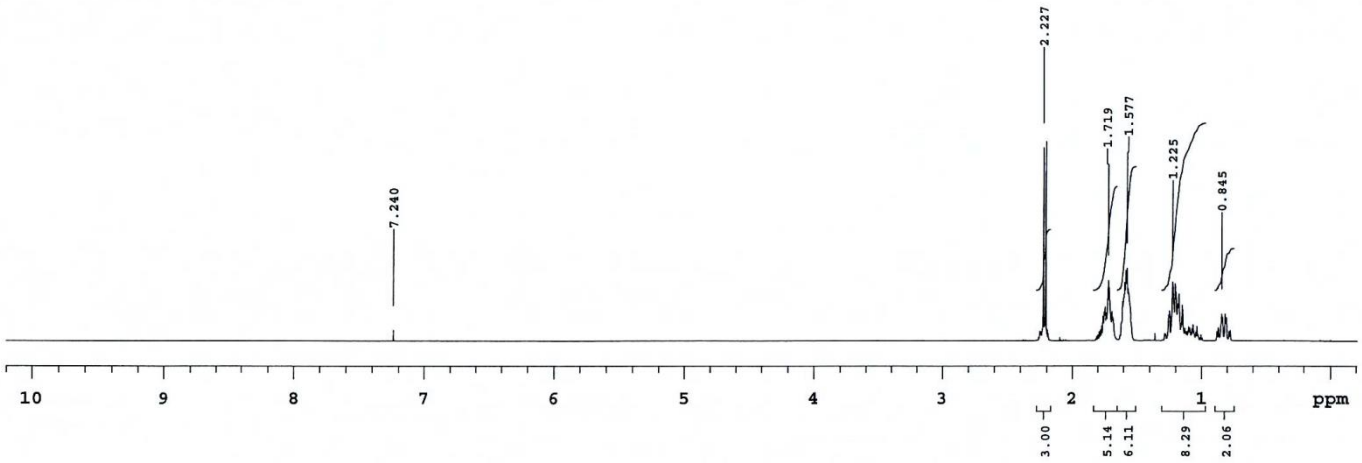


Sample Name: BG-327A
Solvent: cdcl3

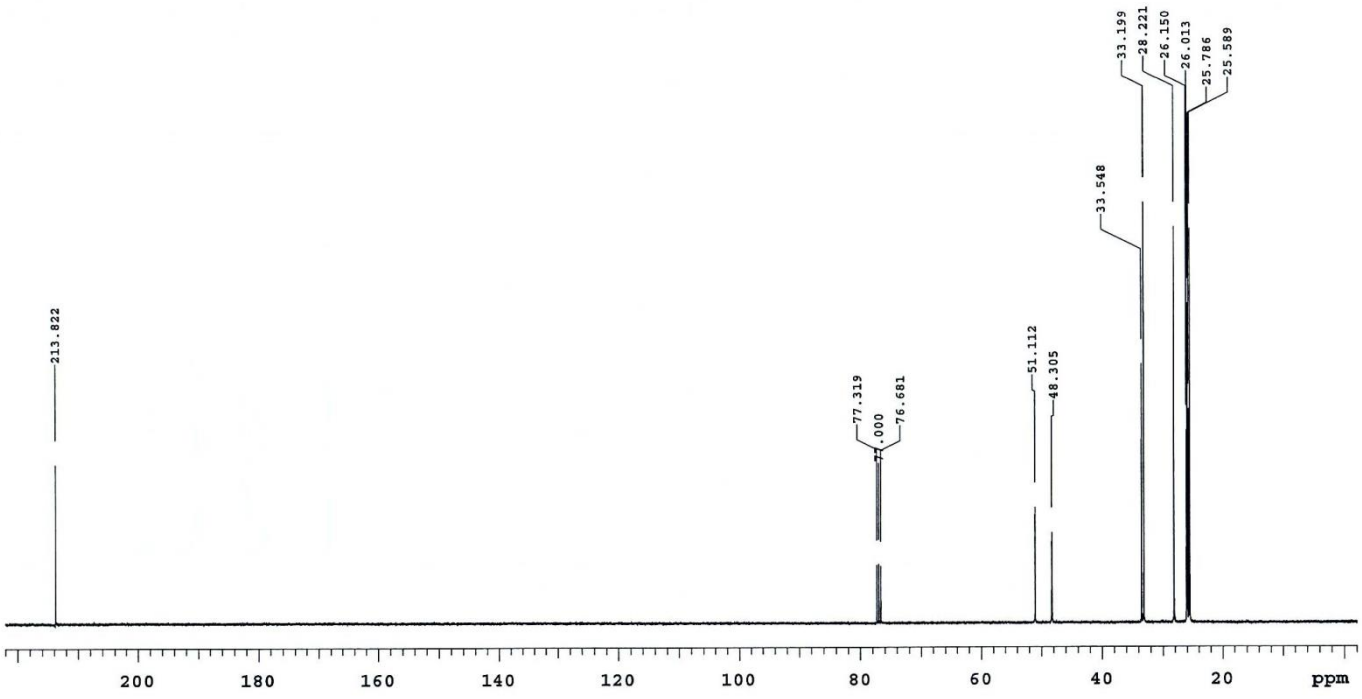


Sample Name: BG-387A
Solvent: cdcl3

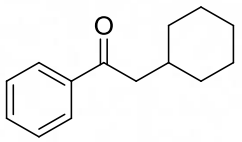


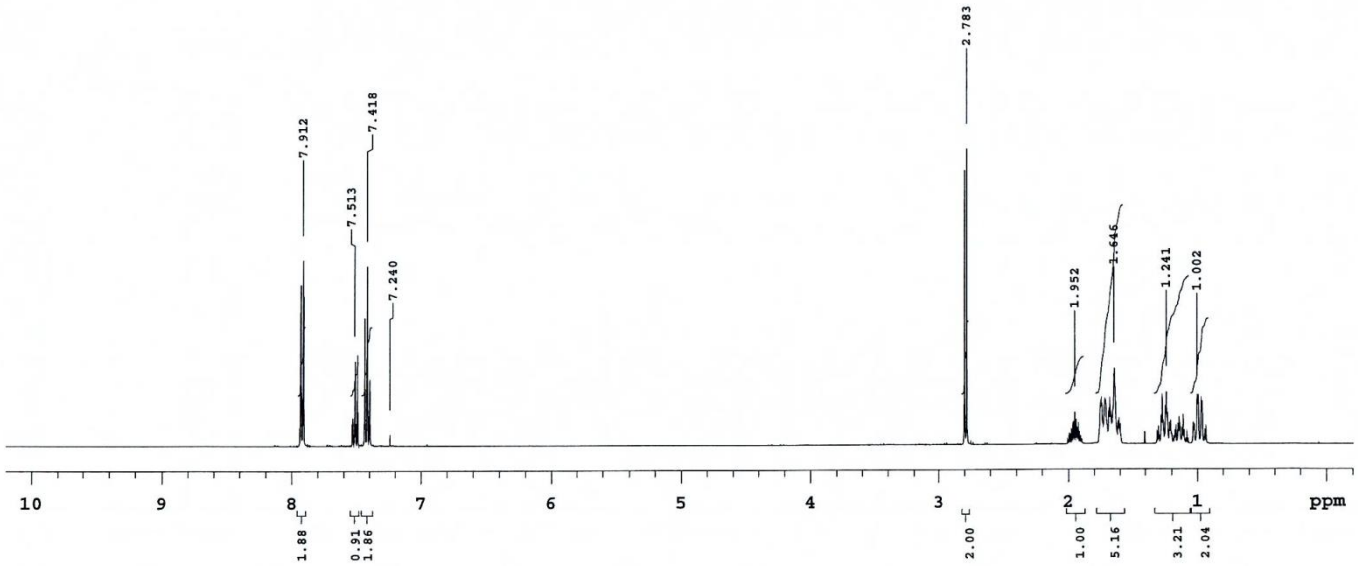


Sample Name: BG-387A
Solvent: cdcl3

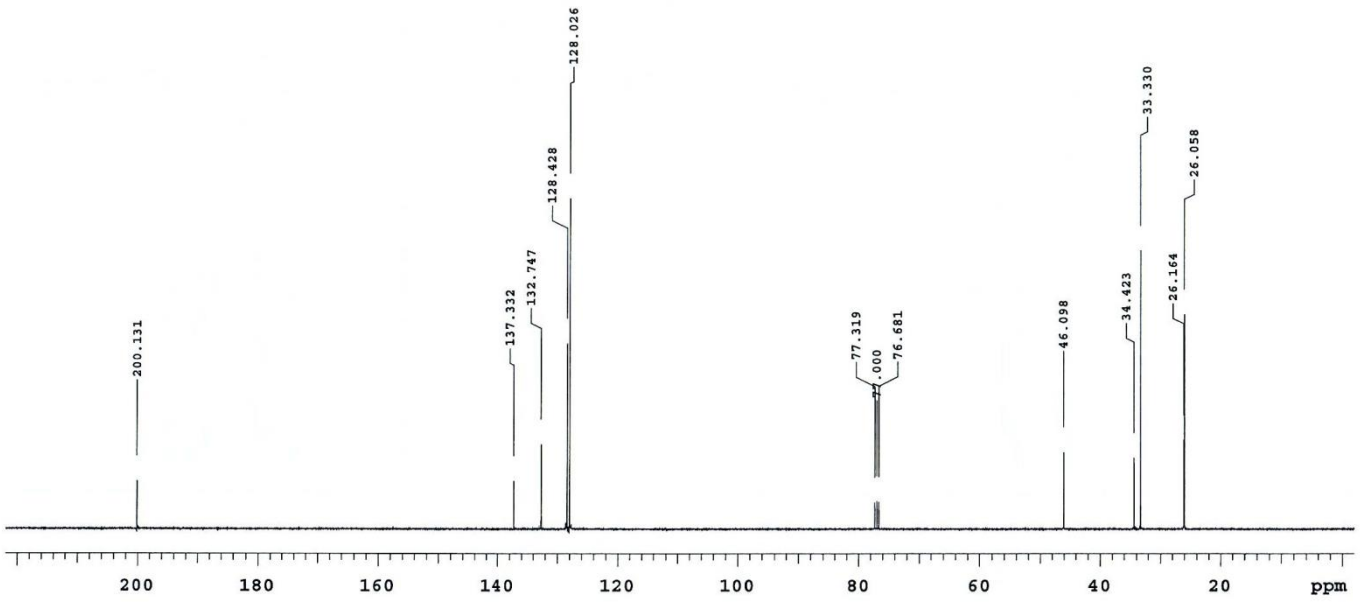


Sample Name: BG-403A
Solvent: cdcl3

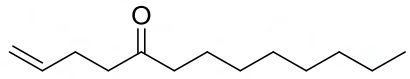


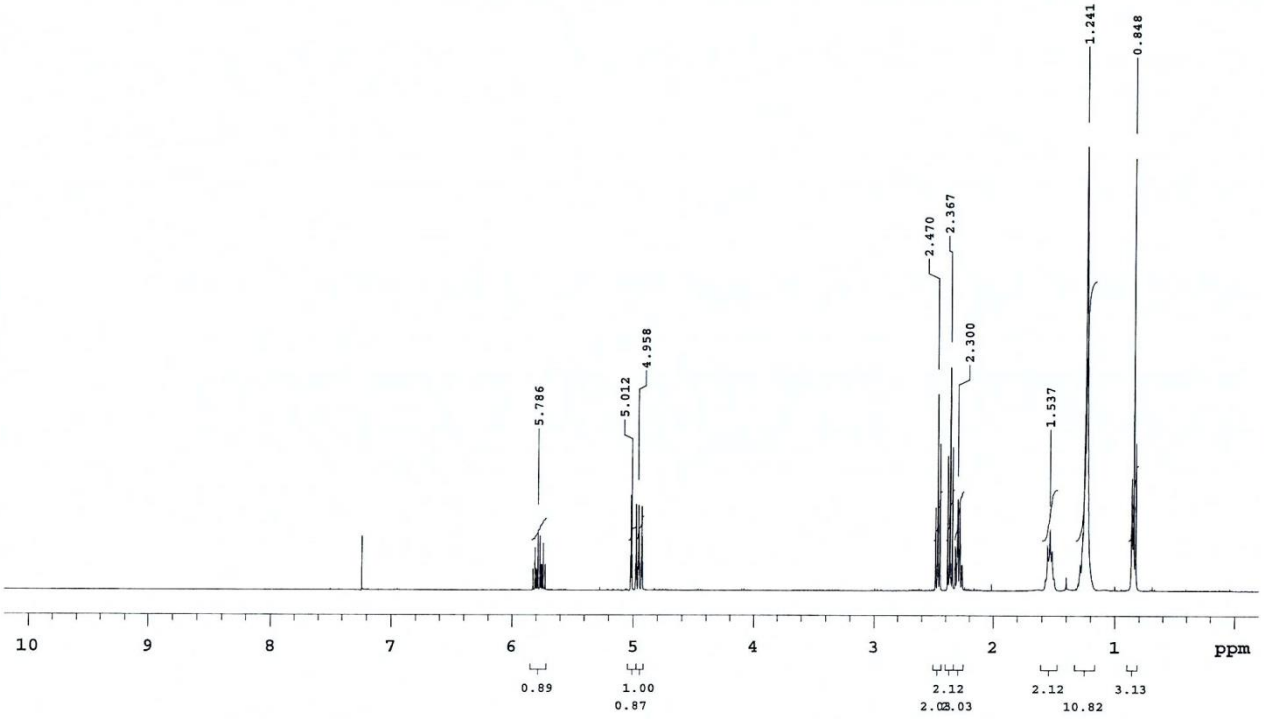


Sample Name: BG-403A
Solvent: cdcl3

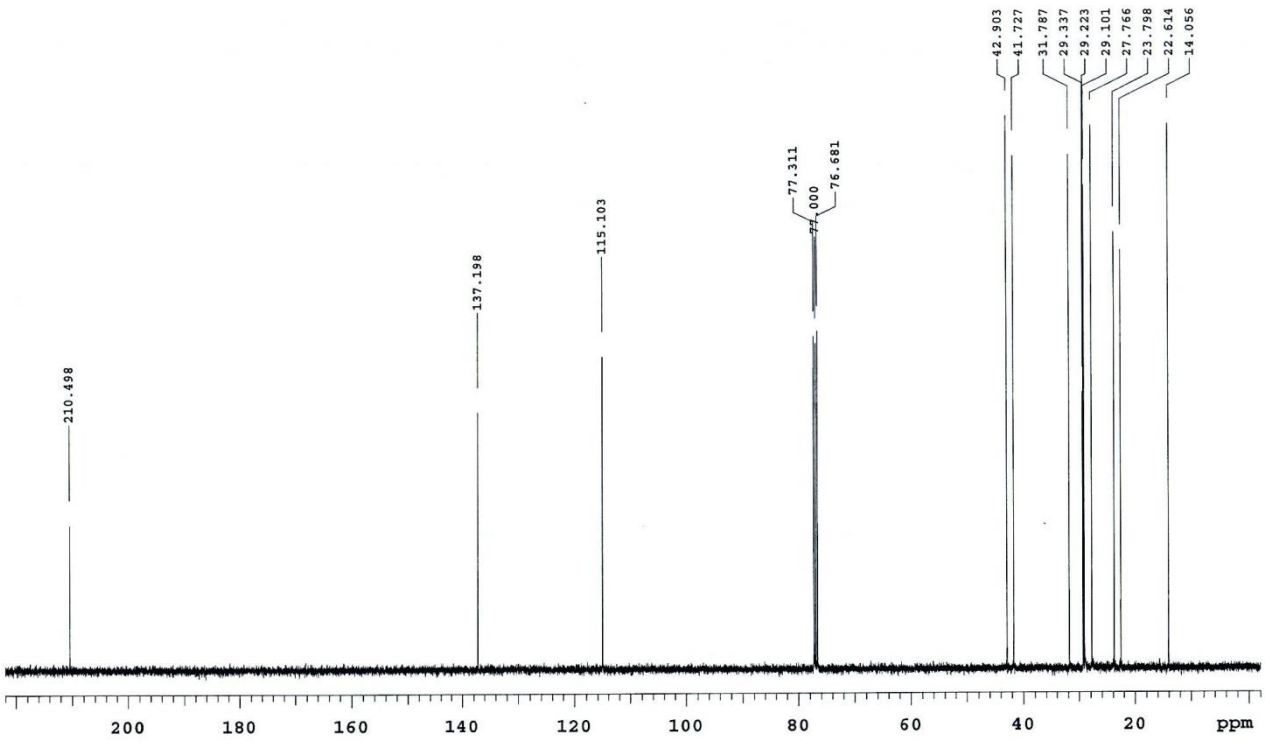


Sample Name: DB-235_a
Solvent: cdcl3

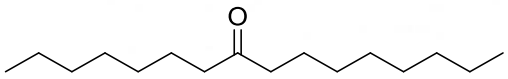


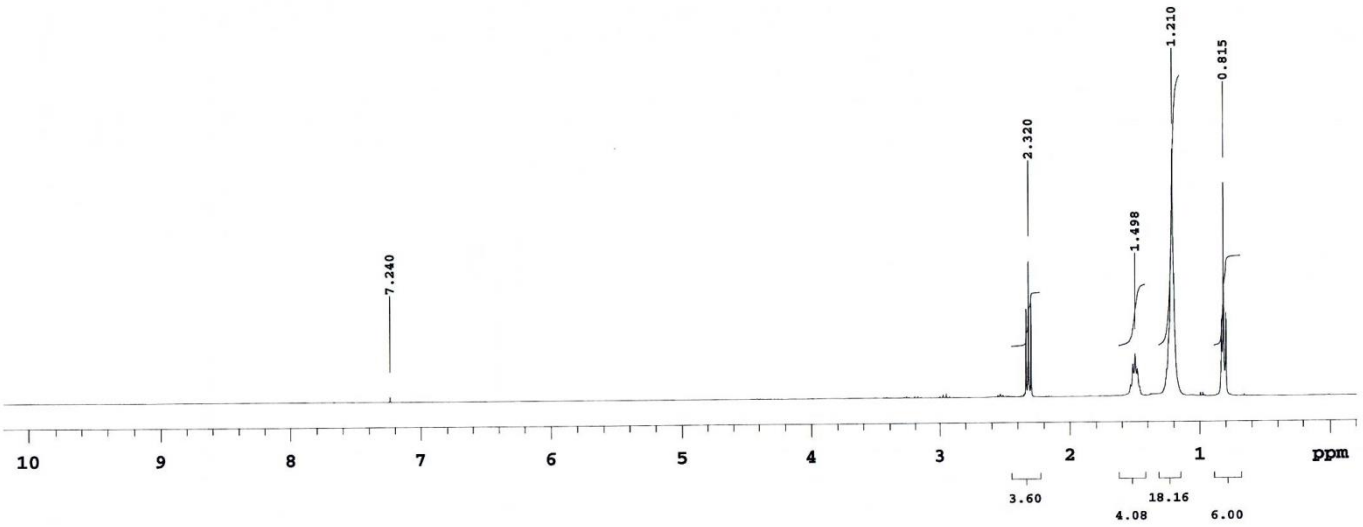


Sample Name: DB-235_a
Solvent: cdcl3

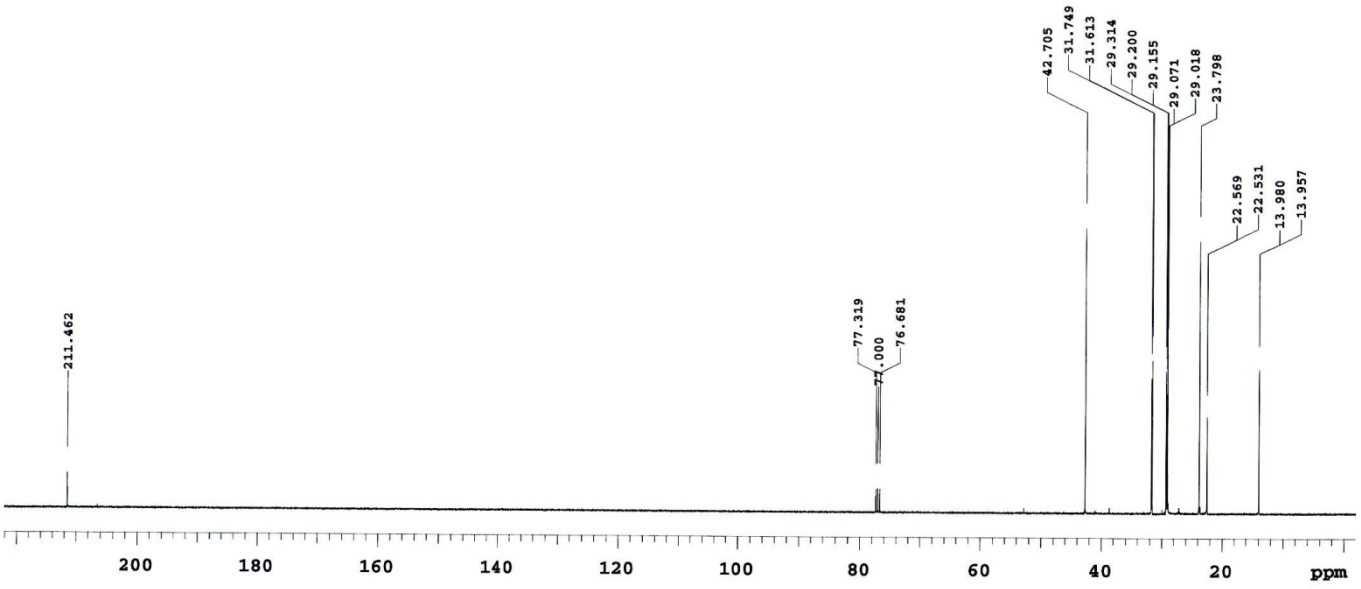


Sample Name: BG-225A
Solvent: cdcl3

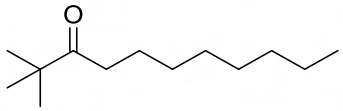




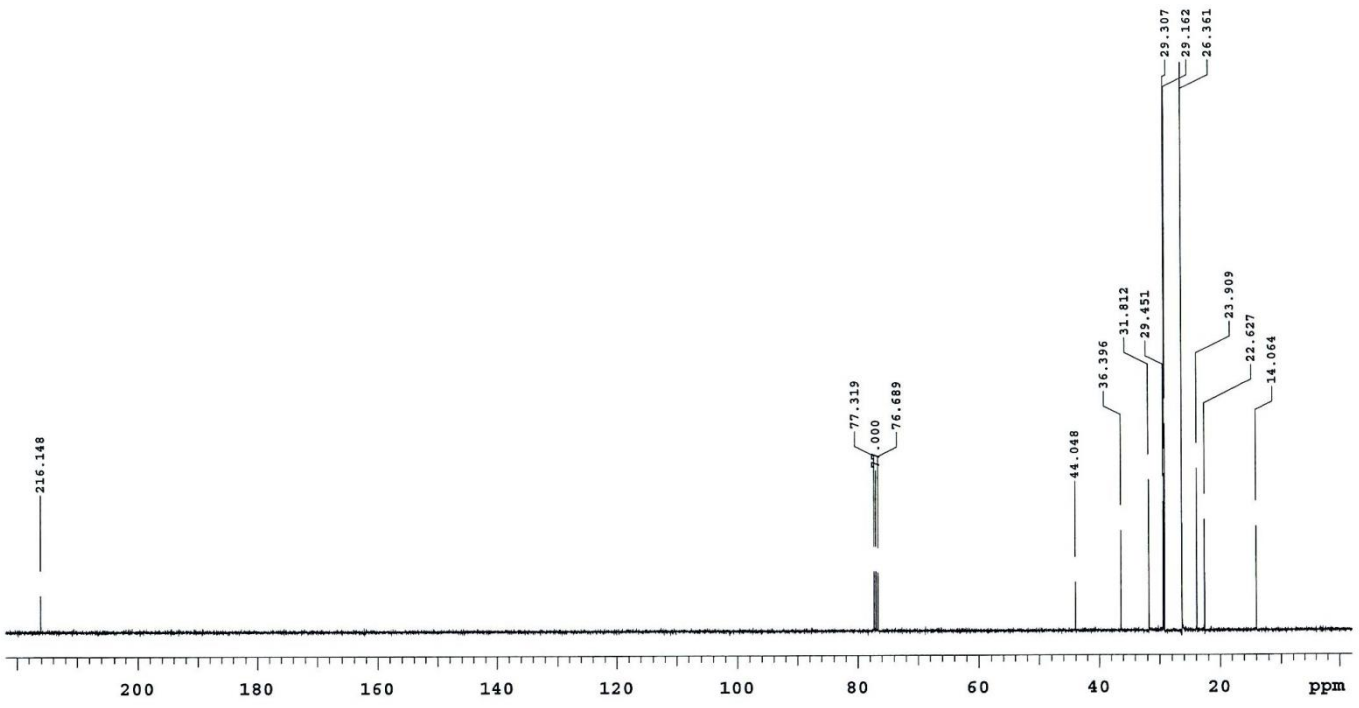
Sample Name: BG-225A
Solvent: cdcl3



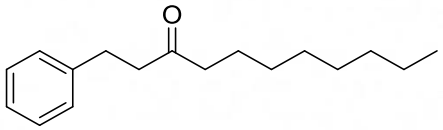
Sample Name: DB-229_a
Solvent: cdcl3

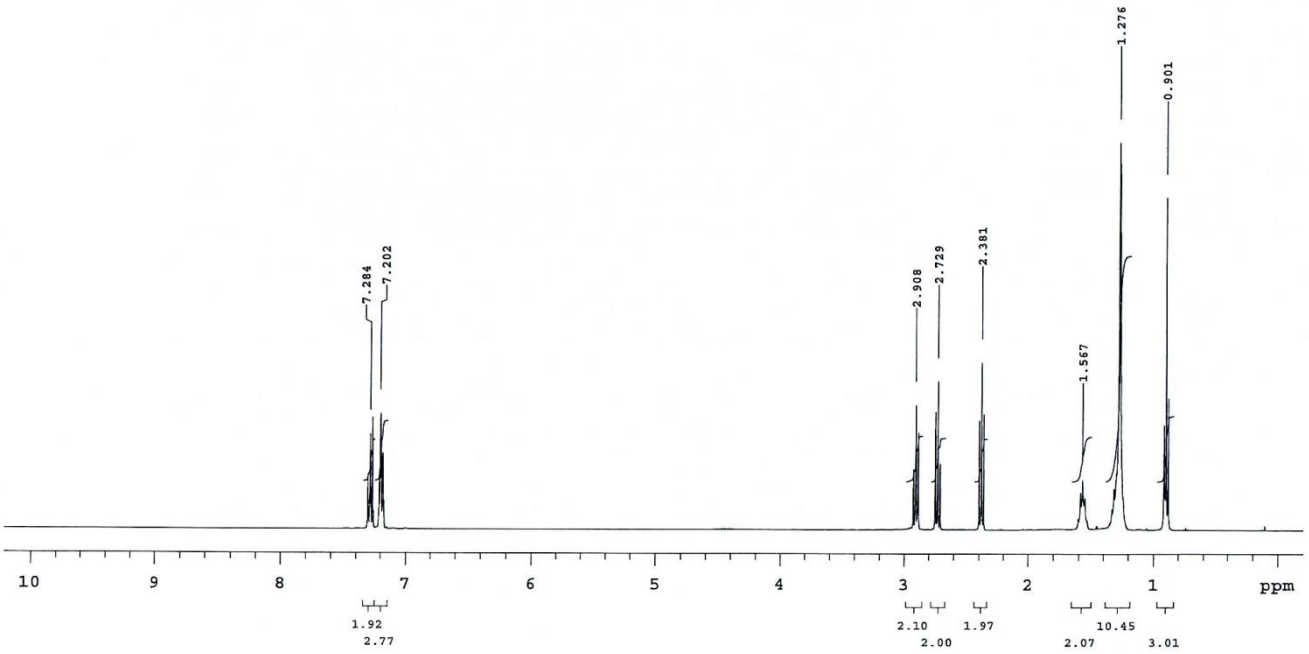


Sample Name: DB-229_a
Solvent: cdcl3

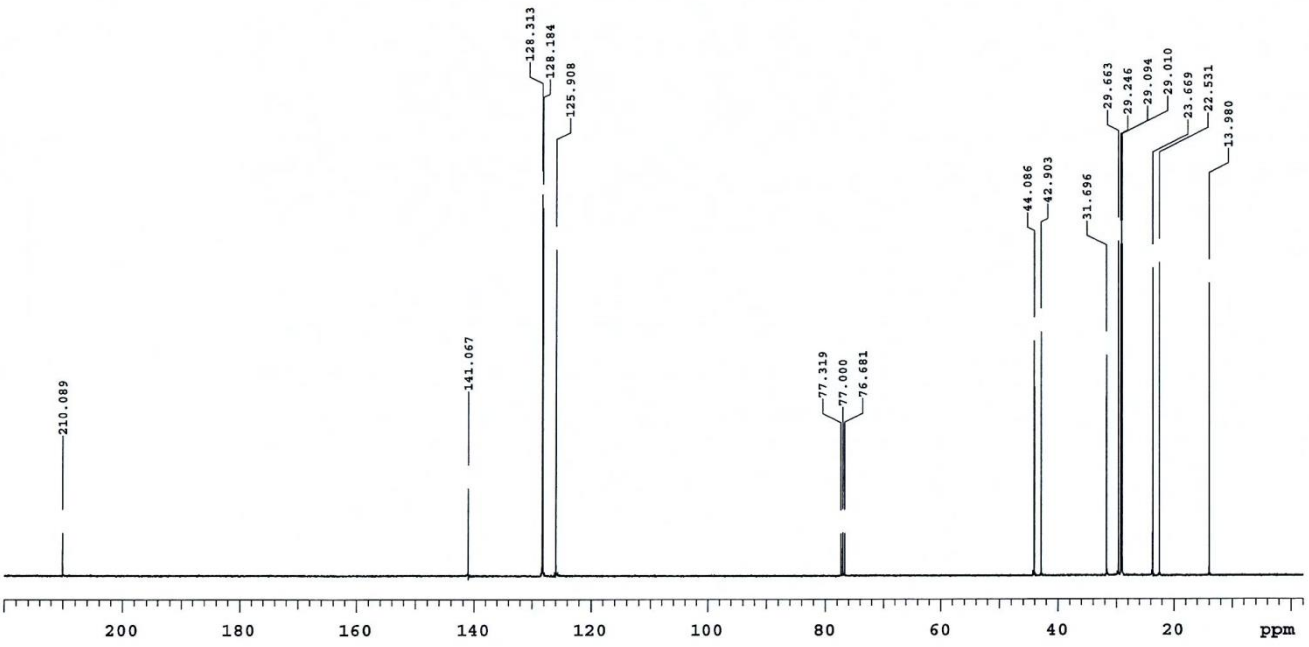


Sample Name: DB-180_a
Solvent: cdcl3

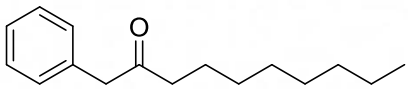


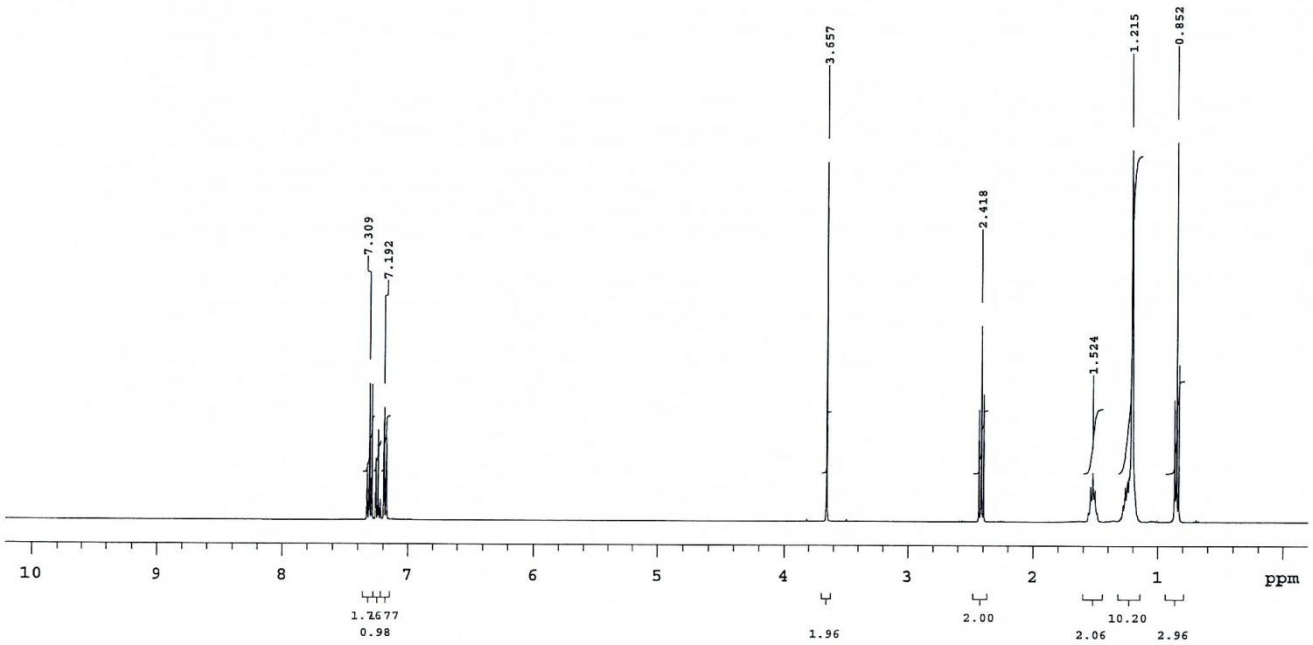


Sample Name: DB-180_a
Solvent: cdcl3

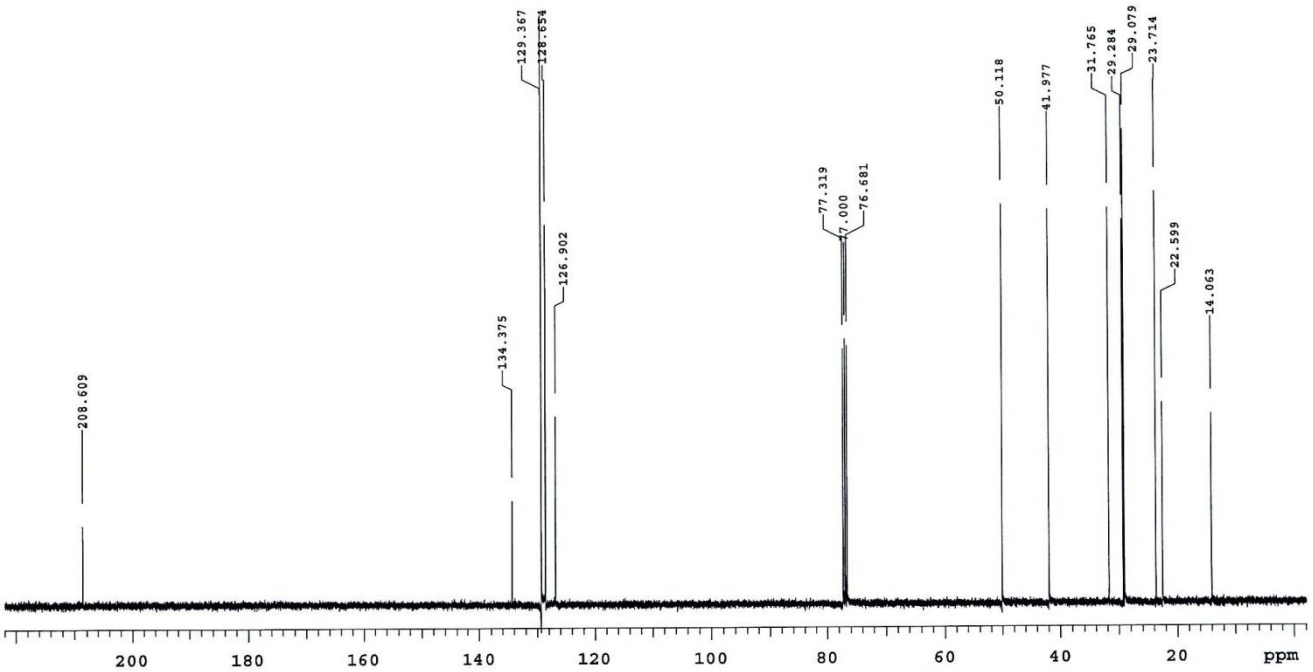


Sample Name: DB-203_a
Solvent: cdcl3

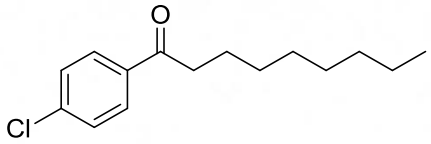


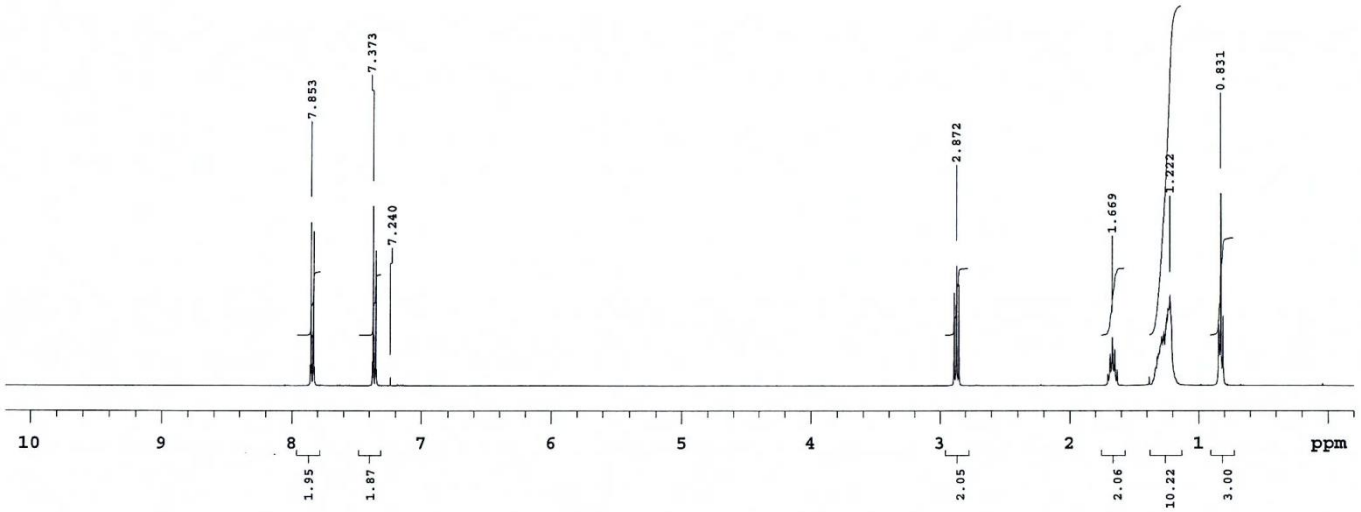


Sample Name: DB-203_a
Solvent: cdcl3

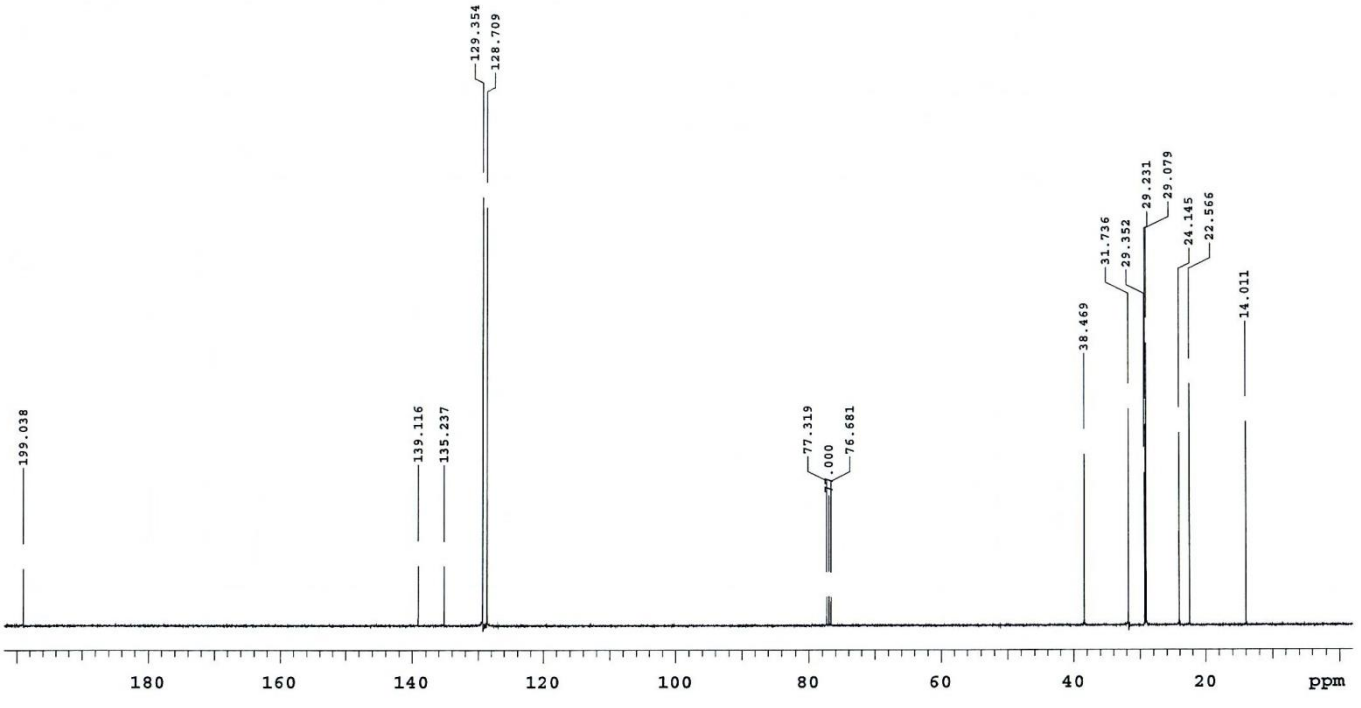


Sample Name: BG-390A
Solvent: cdcl3

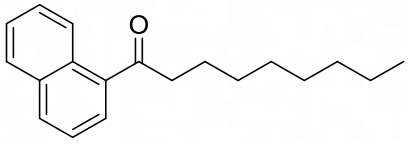


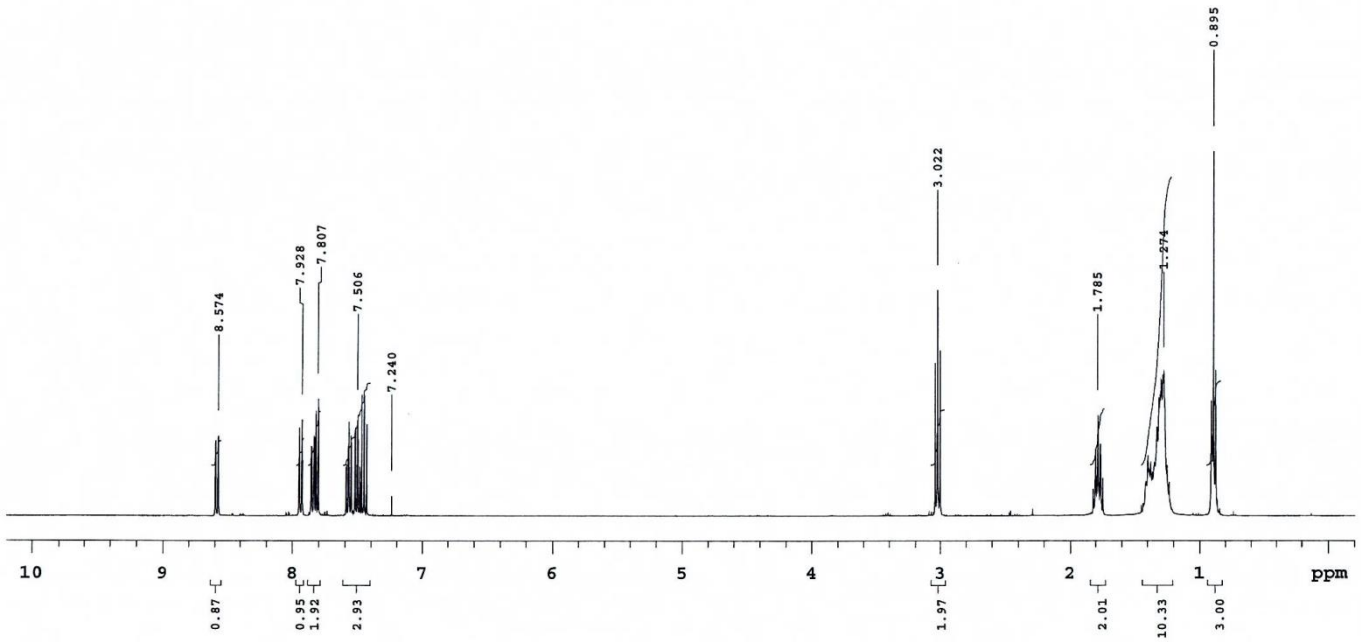


Sample Name: BG-390A
Solvent: cdcl3

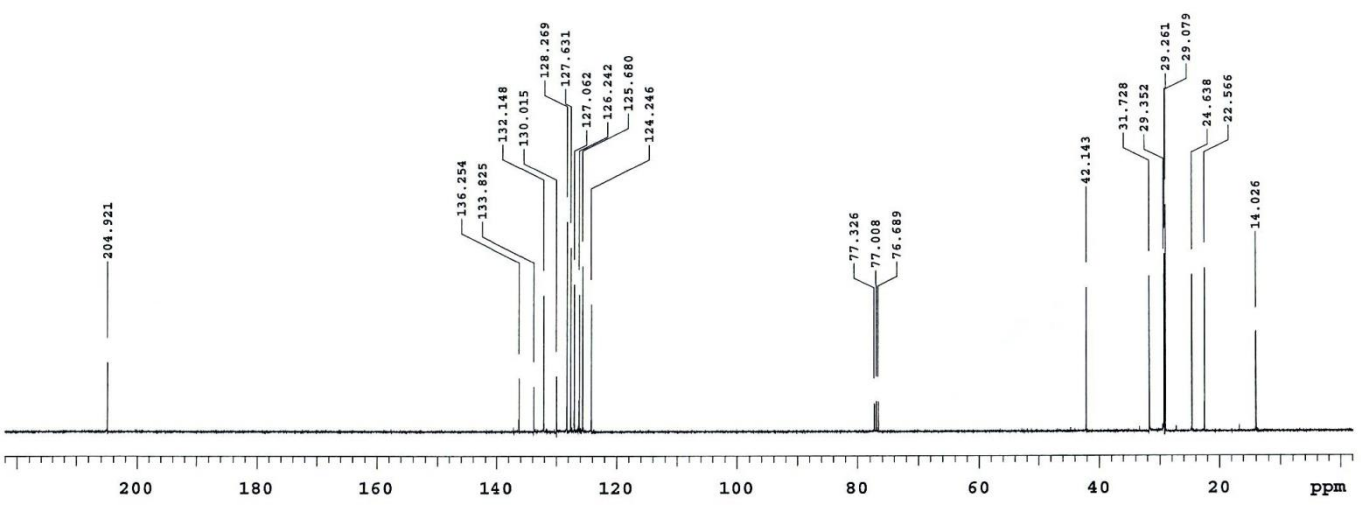


Sample Name: BG-411A
Solvent: cdcl3

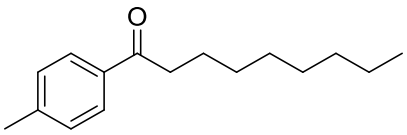


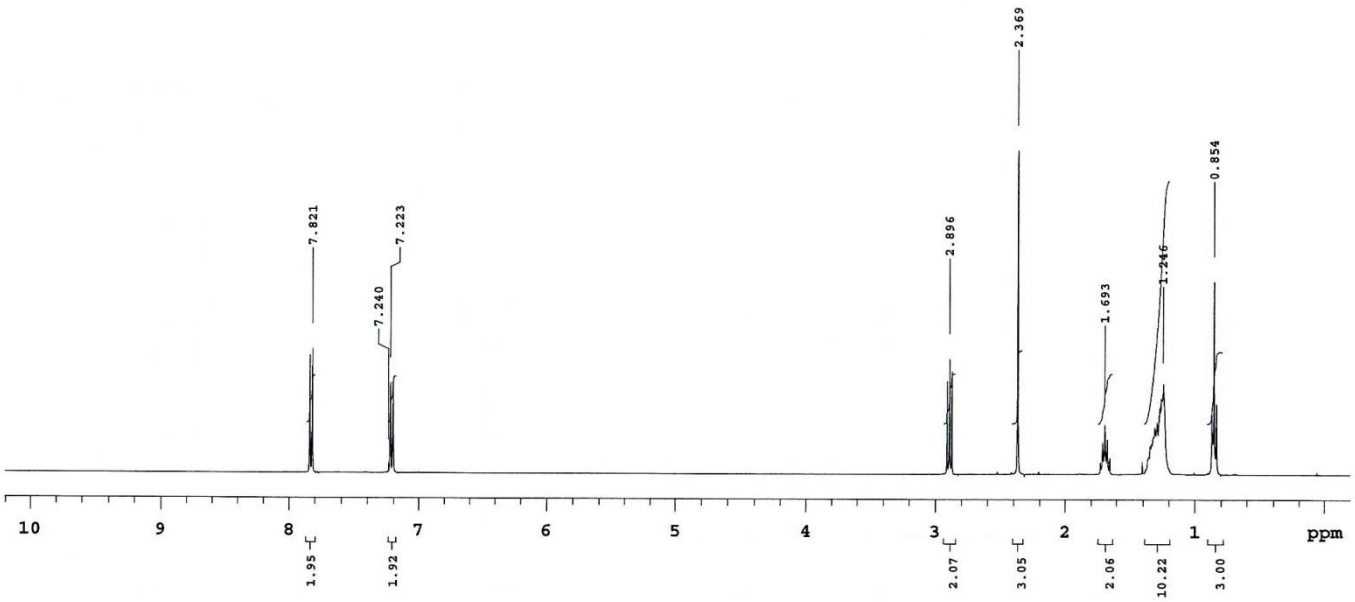


Sample Name: BG-411A
Solvent: cdcl3

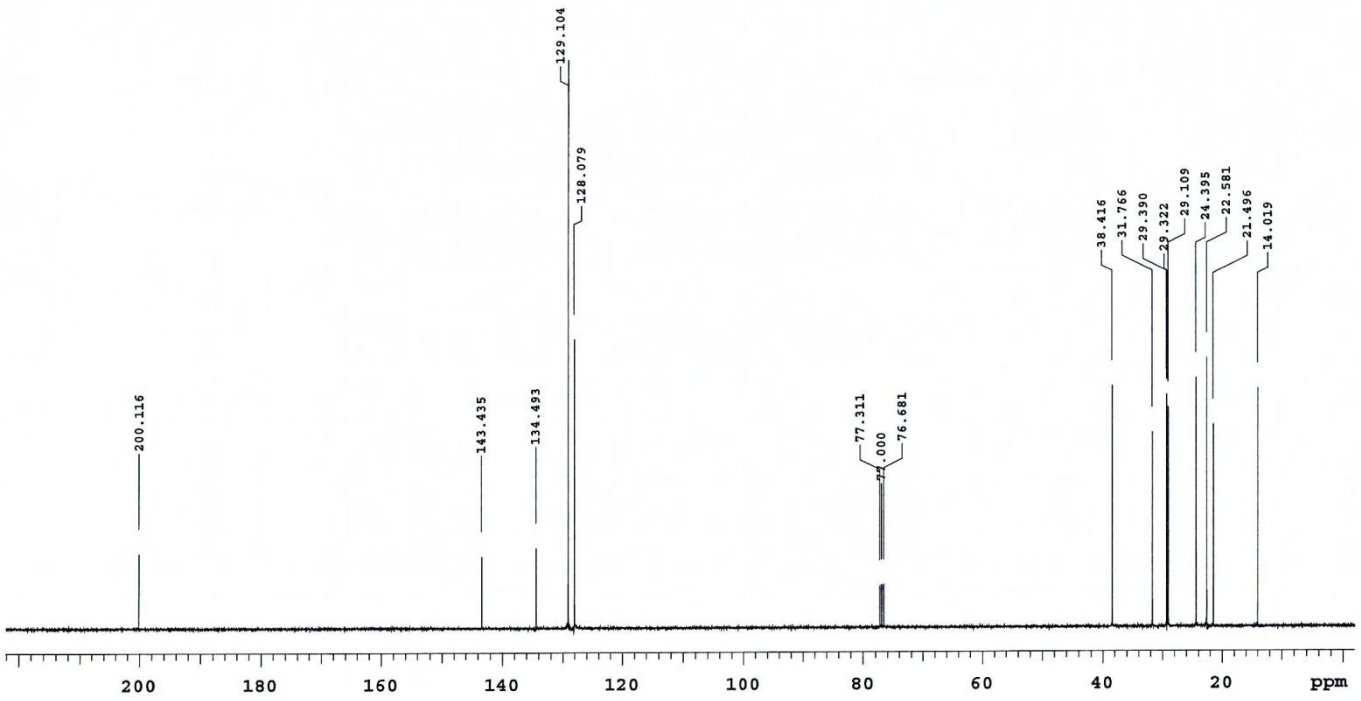


Sample Name: BG-415A
Solvent: cdcl3

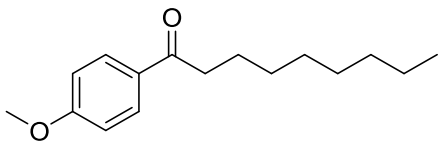


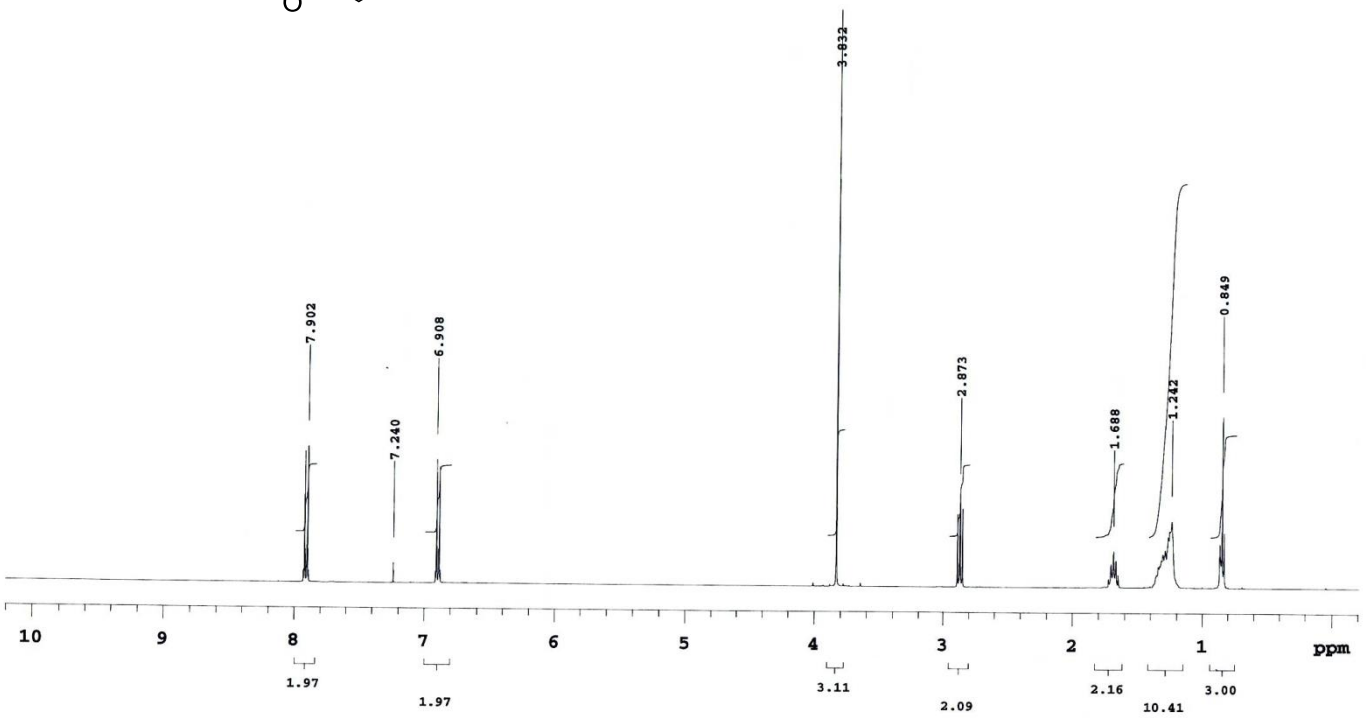


Sample Name: BG-415A
Solvent: cdcl3



Sample Name: BG-224A
Solvent: cdcl3





Sample Name: BG-224A
Solvent: cdcl3