Electronic Supplementary Material (ESI) for Green Chemistry.


***Supporting Information***

# Development of A Robust, Immobilized Organophosphine Catalyst and Applications in Redox-Neutral Stereospecific Mitsunobu Inversion of Secondary Alcohols

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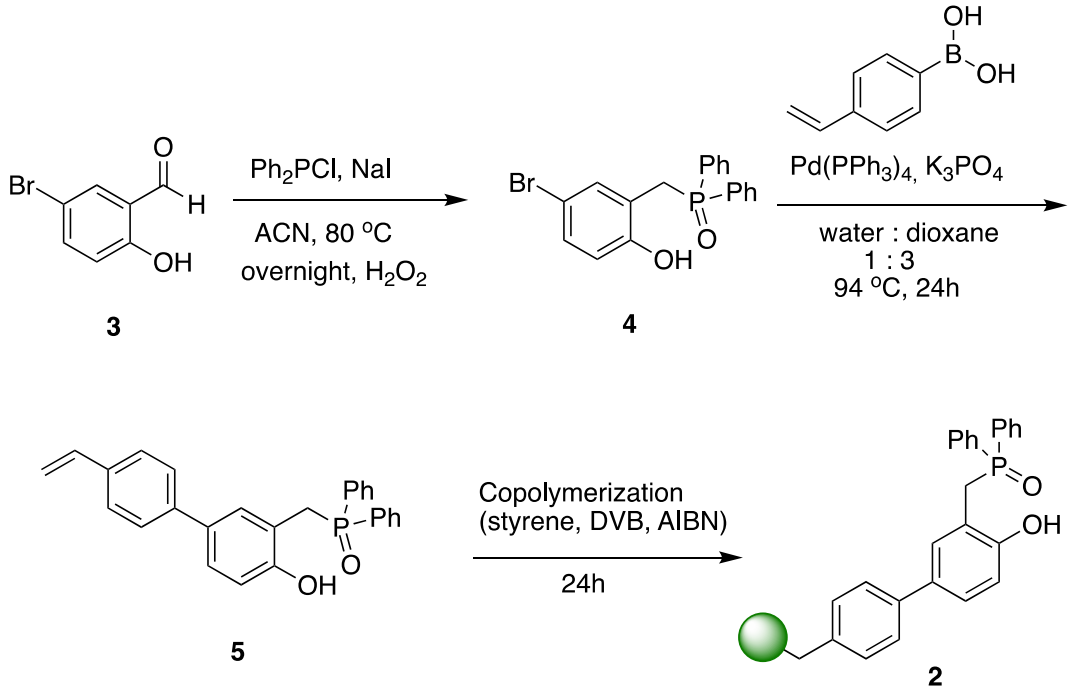
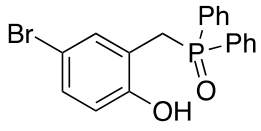
## 1. General information

Unless otherwise stated, all reactions were conducted under air. All commercial reagents were used as received. Flash chromatography was carried out using 60 mesh silica gel and dry-packed columns. The continuous flow experiments were carried out using a syringe pump (Legato 200 from KDSCIENTIFIC). The packed-bed reactor consisted in an Omnifit glass chromatography column (10 mm bore size and up to maximal 70 mm of adjustable bed height). Thin layer chromatography was carried out using Merck TLC Silicagel 60 F254 aluminum sheets. Components were visualized by UV light (λ = 254 nm) and stained with phosphomolybdic dip. NMR spectra were recorded at 298 K on a Fourier 300 MHz Bruker, a Bruker Avance 400 Ultrashield or a Bruker Avance 500 Ultrashield apparatus. $^{1}H$ NMR spectroscopy chemical shifts are quoted in ppm relative to tetramethylsilane (TMS). $CDCl_3$ was used as internal standard for $^{13}C$ NMR spectra. Chemical shifts are given in $\delta$ and coupling constants in Hz. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer and are reported in wavenumbers ($cm^{-1}$). Elemental analyses were performed by MEDAC Ltd. (Surrey, UK) on a LECO CHNS 932 micro-analyzer. High performance liquid chromatography (HPLC) was performed on Agilent Technologies chromatographs (1100 and 1200 Series), using Chiralpak IC, AD-H, OJ-H columns and guard columns. FAB mass spectra were obtained on a Fisons V6-Quattro instrument, ESI mass spectra were obtained on a Waters LCT Premier Instrument and CI and EI spectra were obtained on a Waters GCT spectrometer. Specific optical rotation measurements were carried out on a Jasco P-1030 polarimeter.

## 2. Preparation of the immobilized phosphine oxide catalyst




Scheme S1. Synthetic procedure for the preparation on immobilized catalyst **2**




**4**

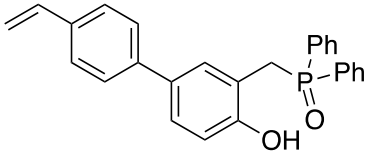
**4** was synthesized following a modification of a literature procedure.[1] Under an argon atmosphere, to a stirred mixture of chlorodiphenylphosphane (11.9 g, 4.5 equiv, 54 mmol), sodium iodide (8.1 g, 4.5 equiv, 54 mmol) in anhydrous ACN (30 mL), 20 mL of an ACN solution of 5-bromo-2-hydroxybenzaldehyde (2.4 g, 1 equiv, 12 mmol) were added at room temperature. The reaction mixture was then stirred at 80°C for 24 hours, then allowed to cool down to room temperature. Afterwards, 30% $H_2O_2$ (3 mL,) was slowly added to the mixture at 0 °C. After 30 minutes, sat. aq. $Na_2S_2O_3$ was added to the reaction mixture which was then extracted with DCM (100mL x 2). The collected organic layers were then washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using cyclohexane/ EtOAc (1.5:1) as the eluent to afford **4** as a pale yellow solid (2.2 g, 56% yield).

**$^1$H NMR** (400 MHz, DMSO-$d_6$): δ 9.96 (s, 1H), 7.83 – 7.76 (m, 4H), 7.67 – 7.46 (m, 6H), 7.26 (t, *J* = 2.4 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 3.85 (d, *J* = 13.7 Hz, 2H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$): δ 155.4, 155.3, 134.0 (x2), 133.9, 132.9, 132.3 (x2), 131.1, 131.0, 130.8, 130.7, 129.1, 129.0, 122.1, 122.0, 118.2 (x2), 110.3 (x2), 30.7, 30.0.

$^{31}$P **NMR** (162 MHz, DMSO-$d_6$): δ 33.6.

**IR** (ATR): ν 2892, 1590, 1497, 1426, 1132, 1093, 690 $cm^{-1}$.




**5**

To a mixture of **4** (1.55 g, 1 equiv, 4 mmol), (4-vinylphenyl) boronic acid (1.18 g, 2 equiv, 8 mmol) and $K_3PO_4$ (2.55 g, 3 equiv, 12 mmol), tetrakis(triphenylphosphine)palladium (347 mg, 0.075 equiv, 0.3 mmol) was added in a glove box. After taken out from the glove box, degassed solvent (12 mL: 36 mL = water: dioxane) was added to the mixture at room temperature, then the reaction was allowed to stir at 95°C. Once complete, about 24 hours later, the reaction flask was put in a ice water bath, then 1M HCl was added and the mixture extracted with DCM The separated organic layers were then washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using cyclohexane/ EtOAc (1.5:1) as the eluent to give compound **5** as a slightly yellow solid (1.6 g, 39% yield).

Pale yellow solid. M.p.: 180.2

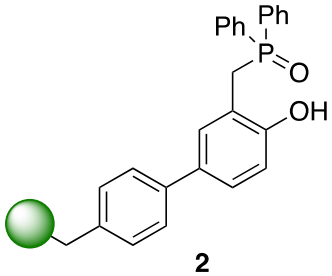
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.79 (dd, *J* = 11.7, 7.4 Hz, 4H), 7.64 – 7.24 (m, 11H), 7.12 – 6.92 (m, 2H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.30 (d, *J* = 14.1 Hz, 1H), 3.79 (d, *J* = 12.8 Hz, 2H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 156.4, 156.3, 140.1, 136.4, 135.9, 133.1 (x2), 132.5 (x2), 131.1, 131.0, 130.2, 130.1, 130.0, 128.9, 128.8, 127.6, 127.5, 126.6, 126.5, 119.8 (x2), 119.7, 119.6, 113.6, 35.7, 35.0.

$^{31}$P **NMR** (162 MHz, $CDCl_3$): δ 41.2.

**IR** (ATR): ν 3054, 1494, 1436, 1119, 822, 692 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{27}H_{24}O_2P$ $[M+H]^+$: 411.1508, found: 411.1505.




**2**

**2** was synthesized following a modification of a literature procedure.[2] A degassed solution of divinylbenzene (DVB), filtered on a short pad of silica immediately before use, (80%, 33.9 mg, 0.21 mmol, 0.14 equiv), **5** (616 mg, 1.50 mmol), styrene (0.75 mL, 6.56 mmol, 4.37 equiv) and AIBN (10 mg, 0.06 mmol, 0.04 equiv) in toluene (2 mL) was prepared in a 50 mL reactor. In another 50 mL flask, a suspension of polyvinyl alcohol (PV-OH) (31 mg, 0.30 µmol, 0.0002 equiv) in 18 mL of degassed Mili-Q water was heated at 100 °C until PV-OH was dissolved. Then, it was cooled to RT and a solution of boric acid (139 mg, 2.25 mmol) in 6 mL of degassed Mili-Q water was transferred to the flask, and subsequently transferred together

to the 50 mL reactor. Then, the system was heated at 90 °C and magnetically stirred at 440 rpm overnight. Afterwards the aqueous solution was decanted off and the resin was washed with water (50 °C) several times, followed by MeOH and $CH_2Cl_2$. Finally, it was dried overnight in a vacuum oven at 40°C to furnish **2** as a pale yellow solid (0.9 g)

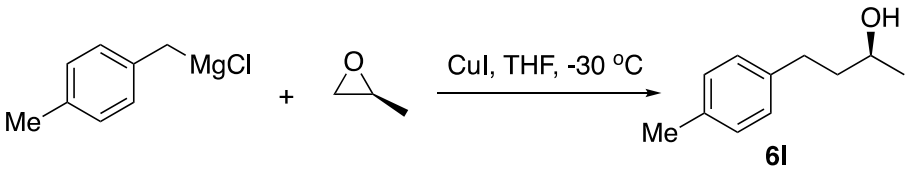
P elemental analysis (%): 2.97

$f_{(P)}$: 0.96 mmol/g resin

## **3.** Preparation of the alcohol starting materials

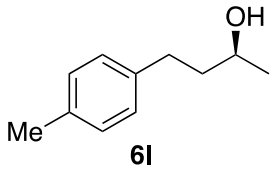
Alcohols **6a**-**6g**, **6j**, **6k** and **6s**-**6u** were used as received; **6h**, **6i** and **6p**-**6r** were prepared according to same procedure described in literature.[3]

**6l**-**6n** were prepared following a modification of a literature procedure.[4]




Scheme S2. Synthetic procedure for the preparation of **6l**

Under an argon atmosphere, 4-methyl-benzylmagnesium chloride (6.5 mL, 13 mmol, 2.0 M THF) was added dropwise to a -30 °C suspension of CuI (2.45 g, 13 mmol) in THF (19 mL) and stirred for 5 minutes. (*S*)-Proplylene oxide (0.6 mL, 8.5 mmol) was added and the reaction was warmed to 0 °C and stirred for an additional 2.5 hours. The reaction was then quenched with a saturated solution of $NH_4Cl$ and warmed to room temperature. Ether was added and the organic layer was washed with a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using cyclohexane/ EtOAc (4:1) as the eluent to give compound **6l** as a yellow oil (1.25 g, 90% yield).




**6l**. Yellow oil. Reported compound.[4]

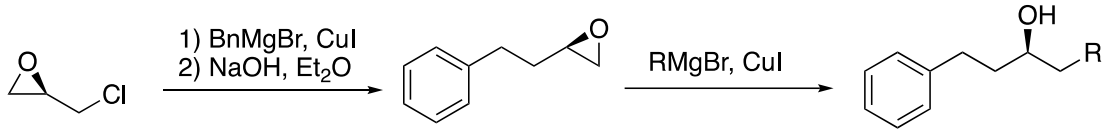
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.19 (dd, J = 2.6, 1.3 Hz, 4H), 4.12 – 3.69 (m, 1H), 2.95 – 2.67 (m, 2H), 2.62 – 2.47 (m, 1H), 2.42 (dd, J = 2.7, 1.3 Hz, 3H), 2.05 – 1.71 (m, 2H), 1.32 (ddd, J = 6.3, 2.7, 1.4 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 139.2, 135.2, 129.2 (x2), 128.4 (x2), 67.4, 41.1, 31.8, 23.6, 21.1.

**[α]$_D$**: –16.9 (*c* 0.99, $CH_2Cl_2$).

**IR** (ATR): ν 3348, 2923, 1515, 1453, 1126, 1067, 806, 546 $cm^{-1}$.

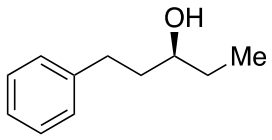
**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (98:2), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 15.686 min; $t_{minor}$ = 14.089 min. 99% ee.




Scheme S3. Synthetic procedure for the preparation of **6m** and **6n**

To a -78 °C suspension of CuI (4.6 g, 24 mmol) in THF (15 mL) was added benzylmagnesium bromide (12 mL, 2.0 M in THF, 24 mmol) and stirred for 5 minutes. (*R*)-epichlorohydrin (1.3 mL, 16 mmol) was added and the reaction was warmed to 0 °C and then stirred for 3 hours. The reaction was then quenched with a saturated solution of $NH_4Cl$ and warmed to room temperature. Ether was added and the organic layer was washed then with a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using cyclohexane/EtOAc (4:1) as the eluent to give intermediate alcohol as a colorless oil. Then it was dissolved in 80 mL diethyl ether, NaOH (1.28 g, 32 mmol) added, and the reaction mixture stirred at rt overnight. Then purified by column chromatography on silica gel using cyclohexane/ EtOAc (4:1) as the eluent to give the oxirane intermediate as a colorless oil.

To a -78 °C suspension of CuI (1.15 g, 6 mmol), in THF (4 mL) was added alkylmagnesium bromide (2.5 mL, 2.0 M in $Et_2O$, 5 mmol) and stirred for 5 minutes. A solution of oxirane intermediate (0.6 g, 4 mmol) in THF (3 mL) was then added and the reaction was warmed to 0 °C for 3 hours with stirring. The reaction was then quenched with a saturated solution of $NH_4Cl$ and warmed to room temperature. Ether was added and the organic layer was washed with a saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using cyclohexane/ EtOAc (4:1) as the eluent to give corresponding alcohol.




**6m**

**6m** was prepared according to above-described procedure using methylmagnesium bromide in 74 % yield (0.49 g). Colorless oil. Reported compound.[4]

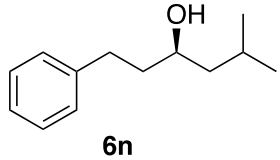
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.40 – 7.16 (m, 5H), 3.60 (tt, *J* = 8.2, 4.6 Hz, 1H), 2.90 – 2.65 (m, 2H), 1.94 – 1.68 (m, 3H), 1.67 – 1.43 (m, 2H), 1.11 – 0.93 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 142.3, 128.5 (x2), 128.4 (x2), 125.8, 72.7, 38.6, 32.1, 30.3, 9.9.

**[α]$_D$**: +16.2 (*c* 1.15, $CH_2Cl_2$).

**IR** (ATR): ν 3330, 2939, 1453, 1122, 749, 698 $cm^{-1}$.

**HPLC** (Daicel Chiralpak OD-H column, hexane/*i*-PrOH (95:5), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 14.525 min; $t_{minor}$ = 9.883 min. 71% ee.




**6n**

**6n** was prepared according to above-described procedure using *iso*-propylmagnesium bromide in 70 % yield (0.54 g). Colorless oil. Reported compound.[4]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.47 – 7.10 (m, 5H), 3.77 (tt, *J* = 8.5, 4.3 Hz, 1H), 2.91 – 2.70 (m, 2H), 1.96 – 1.66 (m, 4H), 1.59 – 1.27 (m, 2H), 0.99 (ddd, *J* = 6.6, 5.6, 1.0 Hz, 6H).

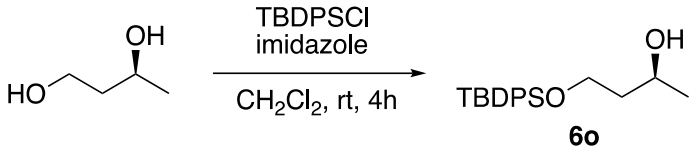
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 142.3, 128.5 (x2), 128.4 (x2), 125.8, 69.4, 46.9, 39.8, 32.1, 24.7, 23.5, 22.2.

**$[\alpha]_D$**: +3.0 (*c* 0.72, $CH_2Cl_2$).

**IR** (ATR): ν 3340, 2953, 1495, 1454, 1031, 697 $cm^{-1}$.

**HPLC** (Daicel Chiralpak OD-H column, hexane/*i*-PrOH (95:5), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 11.289 min; $t_{minor}$ = 8.115 min. 71% ee.

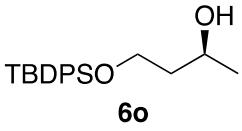
**6o** was prepared by mono-protection of a chiral diol.




**6o**

Scheme S4. Synthetic procedure for the preparation of **6o**

To a solution of (*R*)-1,3-butanediol (0.36 g, 4.0 mmol) and imidazole (0.30 g, 4.4 mmol) in $CH_2Cl_2$ (3.0 mL) was added TBDPSCl (1.14 mL, 4.4 mmol) dropwise. The reaction was stirred for four hours, before the reaction mixture was diluted with $Et_2O$ (10 mL) and washed with $H_2O$ (2 × 10 mL), then brine (10 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude residue was purified by column chromatography on silica gel using cyclohexane/ EtOAc (4:1) as the eluent to give desired alcohol. (1.2 g, 90 % yield)




**6o**

**6o.** Colorless oil. Reported compound.[6]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.76 – 7.68 (m, 4H), 7.54 – 7.36 (m, 6H), 4.13 (ddd, *J* = 8.8, 5.9, 2.8 Hz, 1H), 4.01 – 3.77 (m, 2H), 3.30 (d, *J* = 2.5 Hz, 1H), 1.87 – 1.56 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.09 (s, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 135.6 (x2), 133.1, 133.0, 129.9 (x2), 127.8, 67.9, 63.5, 40.1, 26.8, 23.4, 19.1.

**$[\alpha]_D$**: –0.9 (*c* 0.72, $CH_2Cl_2$).

**IR** (ATR): ν 3372, 2930, 1427, 1107, 700, 504 $cm^{-1}$.

**HPLC** (Daicel Chiralpak OD-H column, hexane/*i*-PrOH (95:5), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 4.765 min; $t_{minor}$ = 5.884 min. 95% ee.

## 4. General Procedure for the heterogeneous Mitsunobu coupling reaction

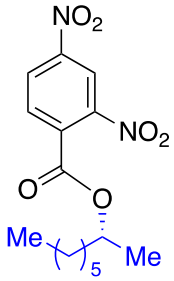
Figure S1. Set up used for the heterogeneous Mitsunobu coupling reaction

To a solution of benzoic acid **7** (1.0 mmol, 1.0 equiv.) in toluene (12.5 mL), alcohol **6** (1.5 mmol, 1.5 equiv.) and catalyst **2** (0.5 mmol, 521 mg, 50 mol %) were added. The reaction mixture was heated to reflux and shaked using the setup shown in the above picture, with a Dean-Stark apparatus to separate water and a long glass tube as air condenser. After 72 hours, the solvent was removed with a syringe, and the resin was washed twice with 6 mL of hot toluene. The mixture was then concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using cyclohexane/EtOAc (12:1) as the eluent to give the desired ester product.

(Retention products were obtained from direct condensation of acid and alcohol by use of DCC and catalytic amount of DMAP)

## 5. Characterization Data for Compounds 8aa-8ua

**(*R*)-oct-2-yl 2,4-dinitrobenzoate**




**8aa**

**8aa**. Pale yellow solid. 243 mg, 75% yield. Reported compound.[3]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 2.2 Hz, 1H), 8.54 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 5.32 – 5.10 (m, 1H), 1.86 – 1.59 (m, 2H), 1.40 – 1.29 (m, 11H), 0.97 – 0.85 (m, 3H).

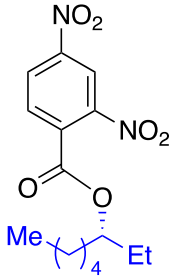
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.3, 148.8, 133.6, 131.2, 127.4, 119.5, 75.3, 35.5, 31.7, 29.0, 25.2, 22.6, 19.3, 14.0.

**[α]$_D$**: –53.5 (*c* 1.00, $CH_2Cl_2$).

**IR** (ATR): ν 3101, 2919, 1730, 1527, 1374, 731 $cm^{-1}$.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (98:2), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 11.950 min; $t_{minor}$ = 13.838 min. 97% ee.

**(*R*)-oct-3-yl 2,4-dinitrobenzoate**




**8ba**

**8ba**. Pale yellow oil. 172 mg, 53% yield. New compound.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.73 (d, *J* = 2.2 Hz, 1H), 8.52 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 5.21 – 4.91 (m, 1H), 1.79 – 1.54 (m, 4H), 1.41 – 1.23 (m, 6H), 1.09 – 0.74 (m, 6H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 163.4, 148.8, 148.1, 133.4, 131.2, 127.4, 119.5, 79.7, 32.8, 31.5, 26.3, 24.7, 22.4, 13.9, 9.3.

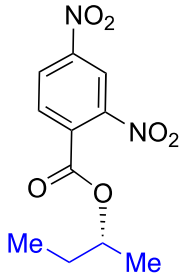
**[α]$_D$**: –16.8 (*c* 1.00, $CH_2Cl_2$).

**IR** (ATR): ν 2931, 1729, 1537, 1346, 1282, 1107, 731 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{15}H_{20}N_2NaO_6$ $[M+Na]^+$: 347.1214, found: 347.1216.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (98.5:1.5), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 13.318 min; $t_{minor}$ = 14.108 min. 95% ee

**(*R*)-*sec*-butyl 2,4-dinitrobenzoate**




**8ca**

**8ca**. Colorless oil. 155 mg, 58% yield. New compound.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.75 (d, *J* = 2.2 Hz, 1H), 8.52 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 5.13 (q, *J* = 6.3 Hz, 1H), 1.89 – 1.52 (m, 2H), 1.35 (d, J = 6.3 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 163.3, 148.7, 148.0, 133.4, 131.4, 127.4, 119.5, 76.2, 28.4, 18.7, 9.4.

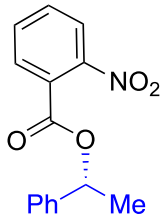
**[α]$_D$**: –39.6 (*c* 0.94, $CH_2Cl_2$).

**IR** (ATR): ν 3107, 2976, 1729, 1536, 1346, 1057, 730 $cm^{-1}$.

**HRMS** (ESI+): *m*/*z* calcd. for $C_{11}H_{12}N_2NaO_6$ $[M+Na]^+$: 291.0588, found: 291.0592.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (95:5), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 25.583 min; $t_{minor}$ = 27.241 min. 90% ee.

**(*R*)-1-phenylethyl 2,4-dinitrobenzoate**



**8db**

**8db**. Pale yellow oil. 206 mg, 76% yield. Reported compound.[3]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.97 – 7.85 (m, 1H), 7.84 – 7.71 (m, 1H), 7.71 – 7.57 (m, 2H), 7.49 – 7.30 (m, 5H), 6.16 (q, *J* = 6.6 Hz, 1H), 1.70 (d, *J* = 6.6 Hz, 3H).

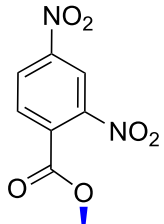
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 164.5, 148.3, 140.5, 132.7, 131.7, 130.0, 128.6 (x2), 128.2 (x2), 127.7, 126.3, 123.8, 74.9, 21.5.

**[α]$_D$**: –35.4 (*c* 0.84, $CH_2Cl_2$).

**IR** (ATR): ν 2983, 1725, 1531, 1280, 1129, 697 $cm^{-1}$.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (85:15), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 7.275 min; $t_{minor}$ = 8.963 min. 79% ee.

**(*S*)-1-phenylpropyl 2,4-dinitrobenzoate**



**8ea**

**8ea**. Pale yellow oil. 320 mg, 97% yield. New compound.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 2.2 Hz, 1H), 8.50 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.16 (m, 5H), 5.46 (dt, *J* = 7.2, 6.3 Hz, 1H), 2.99 (ddd, *J* = 60.4, 13.8, 6.8 Hz, 2H), 1.42 (d, *J* = 6.3 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.2, 148.7, 147.8, 136.8, 133.4, 131.0, 129.4 (x2), 128.5 (x2), 127.5, 126.8, 119.5, 75.2, 41.9, 19.0.

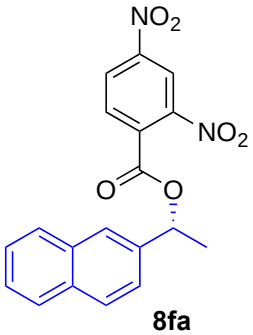
**[α]$_D$**: +66.9 (*c* 0.97, $CH_2Cl_2$).

**IR** (ATR): ν 3107, 1730, 1535, 1346, 1281, 1055, 731 $cm^{-1}$.

**HRMS** (ESI+): *m*/*z* calcd. for $C_{16}H_{14}N_2NaO_6$ $[M+Na]^+$: 353.0744, found: 353.0743.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (85:15), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 12.132 min; $t_{minor}$ = 10.535 min. 71% ee.

**(*R*)-1-(naphth-2-yl)ethyl 2,4-dinitrobenzoate**




**8fa**

**8fa**. Pale yellow solid. 326 mg, 89% yield. New compound. M.p.: 153.3 °C

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.50 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.99 – 7.77 (m, 5H), 7.52 (ddd, *J* = 7.1, 3.7, 2.1 Hz, 3H), 6.36 (q, *J* = 6.6 Hz, 1H), 1.81 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 162.9, 148.9, 137.1, 133.3, 133.1, 133.0, 131.3, 128.7, 128.1, 127.7, 127.3, 126.5, 125.7, 123.9, 119.5, 76.3, 21.3.

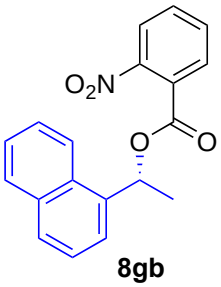
**[α]$_D$**: –136.4 (*c* 1.09, $CH_2Cl_2$).

**IR** (ATR): ν 3078, 2987, 1739, 1530, 1248, 1056, 828, 478 $cm^{-1}$.

**HRMS** (ESI+): *m*/*z* calcd. for $C_{19}H_{14}N_2NaO_6$ $[M+Na]^+$: 389.0744, found: 389.0742.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (85:15), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 17.936 min; $t_{minor}$ = 23.316 min. 29% ee. 90% ee. (After simple recrystallization)

**(*R*)-1-(naphth-1-yl)ethyl 2-nitrobenzoate**




**8gb**

**8gb**. Pale yellow oil. 215 mg, 67% yield. New compound.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.00 – 7.84 (m, 3H), 7.77 – 7.71 (m, 1H), 7.69 – 7.46 (m, 6H), 6.98 (q, *J* = 6.6 Hz, 1H), 1.90 (d, *J* = 6.6 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 164.6, 148.2, 136.4, 133.8, 132.8, 131.7, 130.2, 129.9, 129.0, 128.8, 127.7, 126.5, 125.8, 125.4, 123.9, 123.6, 123.0, 72.0, 21.1.

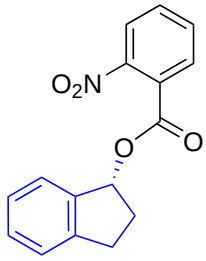
**[α]$_D$**: –67.5 (*c* 1.13, $CH_2Cl_2$).

**IR** (ATR): ν 2984, 1725, 1530, 1281, 1069, 776 $cm^{-1}$.

**HRMS** (ESI+): *m*/*z* calcd. for $C_{19}H_{15}NNaO_4$ $[M+Na]^+$: 344.0893, found: 344.0890.

**HPLC** (Daicel Chiralpak OJ-H column, hexane/*i*-PrOH (80:20), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 34.845 min; $t_{minor}$ = 24.558 min. 65% ee.

**(*R*)-2,3-dihydro-1*H*-inden-1-yl 2-nitrobenzoate**



**8hb**

**8hb**. Pale yellow oil. 241mg, 85% yield. Reported compound.[3]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.82 – 7.71 (m, 1H), 7.71 – 7.51 (m, 3H), 7.40 – 7.24 (m, 3H), 6.49 (dd, *J* = 6.9, 3.4 Hz, 1H), 3.18 (ddd, *J* = 16.2, 8.3, 6.6 Hz, 1H), 2.96 (ddd, *J* = 16.2, 8.6, 4.5 Hz, 1H), 2.62 (ddt, *J* = 14.2, 8.6, 6.7 Hz, 1H), 2.34 (dddd, *J* = 14.2, 8.1, 4.5, 3.4 Hz, 1H).

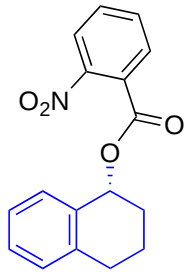
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 165.4, 148.1, 144.7, 140.0, 132.9, 131.7, 129.9, 129.3, 127.9, 126.8, 125.8, 124.9, 123.8, 80.8, 31.9, 30.3.

**[α]$_D$**: –7.0 (*c* 0.74, $CH_2Cl_2$).

**IR** (ATR): ν 2943, 1724, 1530, 1284, 1124, 735 $cm^{-1}$.

**HPLC** (Daicel Chiralpak OJ-H column, hexane/*i*-PrOH (90:10), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 21.792 min; $t_{minor}$ = 15.491 min. 38% ee.

**(*R*)-1,2,3,4-tetrahydronaphth-1-yl 2-nitrobenzoate**



**8ib**

**8ib**. Pale yellow oil. 208 mg, 70% yield. New compound.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.79 – 7.58 (m, 3H), 7.43 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.35 – 7.11 (m, 3H), 6.31 (t, *J* = 4.3 Hz, 1H), 3.01 – 2.74 (m, 2H), 2.40 – 2.23 (m, 1H), 2.22 – 2.06 (m, 1H), 2.06 – 1.83 (m, 2H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 165.2, 147.9, 138.2, 133.4, 132.9, 131.4, 129.9, 129.7, 129.1, 128.5, 128.4, 126.2, 123.9, 72.5, 28.9, 28.5, 18.6.

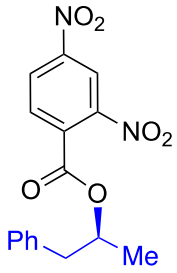
**[α]$_D$**: –28.0 (*c* 1.02, $CH_2Cl_2$).

**IR** (ATR): ν 2940, 1722, 1530, 1349, 1252, 739 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{17}H_{15}NNaO_4$ $[M+Na]^+$: 320.0893, found: 320.0880.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (85:15), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 9.625 min; $t_{minor}$ = 8.313 min. 57% ee.

**(*S*)-1-phenylprop-2-yl 2,4-dinitrobenzoate**




**8ja**

**8ja**. Yellow oil. 142 mg, 43% yield. Reported compound.[3]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.49 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.21 (m, 5H), 5.46 (dt, *J* = 7.2, 6.3 Hz, 1H), 2.99 (ddd, *J* = 60.2, 13.8, 6.8 Hz, 2H), 1.42 (d, *J* = 6.3 Hz, 3H).

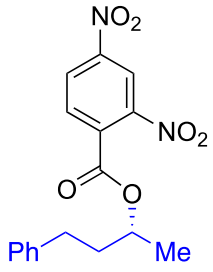
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.2, 148.7, 136.8, 133.4, 131.0, 129.4, 128.5 (x2), 128.3, 127.5, 126.8, 119.6, 119.5, 75.2, 41.9, 19.0.

**[α]$_D$**: +52.4 (*c* 0.90, $CH_2Cl_2$).

**IR** (ATR): ν 3106, 1730, 1534, 1280, 1111, 833, 700 $cm^{-1}$.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (90:10), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 14.955 min; $t_{minor}$ = 16.412 min. 92% ee.

**(*R*)-4-phenylbut-2-yl 2,4-dinitrobenzoate**




**8ka**

**8ka.** Pale yellow oil. 248 mg, 72% yield. Reported compound.[3]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.75 (d, *J* = 2.2 Hz, 1H), 8.51 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.09 (m, 5H), 5.28 (dqd, *J* = 7.4, 6.2, 4.8 Hz, 1H), 2.86 – 2.53 (m, 2H), 2.33 – 1.84 (m, 2H), 1.45 (d, *J* = 6.3 Hz, 3H).

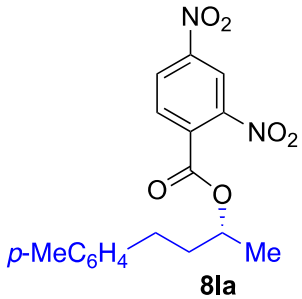
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 163.3, 148.8, 148.0, 141.1, 133.2, 131.3, 128.5 (x2), 128.3 (x2), 127.4, 126.1, 119.5, 74.6, 37.1, 31.6, 19.4.

**[α]$_D$**: –64.9 (*c* 0.98, $CH_2Cl_2$).

**IR** (ATR): ν 2936, 1730, 1535, 1346, 1282, 1047, 833, 731 $cm^{-1}$.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (90:10), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 25.089 min; $t_{minor}$ = 30.748 min. 95% ee.

**(*R*)-4-(*p*-tolyl)but-2-yl 2,4-dinitrobenzoate**




**8la**

**8la**. Pale yellow oil. 290 mg, 81% yield. New compound.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 2.2 Hz, 1H), 8.51 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.12 (s, 4H), 5.44 – 5.22 (m, 1H), 2.88 – 2.64 (m, 2H), 2.34 (s, 3H), 2.21 – 1.86 (m, 2H), 1.46 (d, *J* = 6.3 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.2, 148.8, 148.0, 138.0, 135.5, 133.2, 131.2, 129.2 (x2), 128.2 (x2), 127.4, 119.4, 74.6, 37.2, 31.1, 20.9, 19.4.

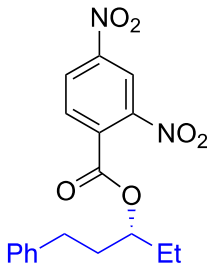
**[α]$_D$**: +74.7 (*c* 1.08, $CH_2Cl_2$).

**IR** (ATR): ν 2925, 1728, 1536, 1352, 1054, 833, 731 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. $C_{18}H_{18}N_2NaO_6$ $[M+Na]^+$: 381.1057, found: 381.1041.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (80:20), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 17.634 min; $t_{minor}$ = 15.782 min. 98% ee.

**(*R*)-1-phenylpent-3-yl 2,4-dinitrobenzoate**




**8ma**

**8ma**. Pale yellow oil. 261 mg, 73% yield. New compound.

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 8.75 (d, *J* = 2.2 Hz, 1H), 8.51 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 5.22 (dtd, *J* = 7.5, 6.1, 4.5 Hz, 1H), 2.84 – 2.61 (m, 2H), 2.15 – 1.93 (m, 2H), 1.91 – 1.77 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 163.4, 148.8, 148.1, 141.3, 133.1, 131.3, 128.5, 128.3, 127.3, 126.0, 119.5, 79.1, 34.7, 31.5, 26.5, 9.4.

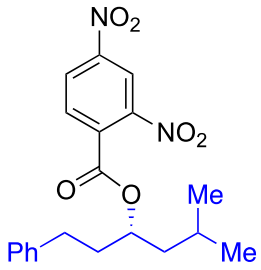
**[α]$_D$**: –20.8 (*c* 0.95, $CH_2Cl_2$).

**IR** (ATR): ν 2969, 1729, 1535, 1346, 1280, 1055, 833, 699 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{18}H_{18}N_2NaO_6$ $[M+Na]^+$: 381.1057, found: 381.1042.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (80:20), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 15.866 min; $t_{minor}$ = 18.440 min. 71% ee.

**(*S*)-5-methyl-1-phenylhex-3-yl 2,4-dinitrobenzoate**




**8na**

**8na**. Pale yellow oil. 178 mg, 46% yield. New compound.

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 8.78 (d, *J* = 2.1 Hz, 1H), 8.52 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.11 (m, 5H), 5.53 – 5.28 (m, 1H), 2.74 (qdd, *J* = 13.8, 9.1, 6.9 Hz, 2H), 2.04 (dtd, *J* = 9.7, 6.7, 4.3 Hz, 2H), 1.73 (ddt, *J* = 18.9, 13.0, 6.2 Hz, 2H), 1.56 – 1.42 (m, 1H), 0.98 (dd, *J* = 11.6, 6.3 Hz, 6H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 163.3, 148.9, 148.1, 141.2, 133.2, 131.2, 128.5, 128.4, 128.3, 127.3, 126.0, 119.5, 42.7, 35.7, 31.5 (x2), 24.7, 22.9, 22.3.

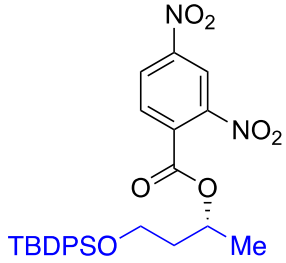
**[α]$_D$**: –3.5 (*c* 1.00, $CH_2Cl_2$).

**IR** (ATR): ν 2958, 1730, 1536, 1346,1280, 1057, 833, 732, 699 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{20}H_{22}N_2NaO_6$ $[M+Na]^+$: 409.1370, found: 409.1359.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (80:20), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 12.321 min; $t_{minor}$ = 14.799 min. 70% ee.

**(*R*)-4-((*tert*-butyldiphenylsilyl)oxy)but-2-yl 2,4-dinitrobenzoate**




**8oa**

**8oa**. Pale yellow oil. 214 mg, 41% yield. New compound.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.46 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.91 – 7.68 (m, 6H), 7.45 (dddd, *J* = 10.8, 6.9, 5.1, 1.9 Hz, 8H), 5.63 – 5.46 (m, 1H), 3.82 (dd, *J* = 6.7, 5.4 Hz, 2H), 2.10 – 1.88 (m, 2H), 1.47 (d, *J* = 6.3 Hz, 3H), 1.13 (d, *J* = 3.7 Hz, 10H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.2, 148.7, 147.9, 135.6 (x2), 134.8, 133.6 (x2), 133.3, 131.2, 129.7, 129.6, 127.8, 127.7, 127.3, 119.5, 72.5, 60.0, 38.3, 26.8, 26.5, 19.5, 19.2.

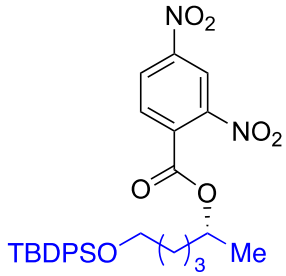
**[α]$_D$**: +22.5 (*c* 1.00, $CH_2Cl_2$).

**IR** (ATR): ν 2931, 2857, 1734, 1537, 1346, 1105, 822, 700 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{27}H_{30}N_2NaO_7Si$ $[M+Na]^+$: 545.1714, found: 545.1709.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (95:5), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 12.589 min; $t_{minor}$ = 15.906 min. 90% ee.

**(*R*)-6-[(*tert*-butyldiphenylsilyl)oxy]hex-2-yl 2,4-dinitrobenzoate**




**8pa**

**8pa**. Pale yellow oil. 281 mg, 51% yield. Reported compound. [3]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.80 (d, J = 2.1 Hz, 1H), 8.47 (dd, J = 8.4, 2.2 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.83 – 7.66 (m, 4H), 7.53 – 7.36 (m, 6H), 5.34 – 5.17 (m, 1H), 3.73 (t, J = 6.1 Hz, 2H), 1.86 – 1.45 (m, 6H), 1.40 (d, J = 6.2 Hz, 3H), 1.08 (s, 9H).

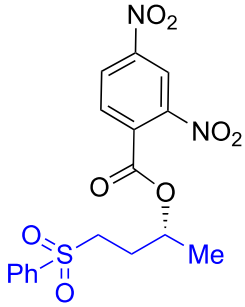
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 163.3, 148.7, 148.0, 135.5 (x2), 134.0, 133.5, 131.17, 129.6, 127.6 (x2), 127.4, 119.5, 75.0, 63.5, 35.2, 32.2, 26.9, 21.6, 19.3, 19.2.

**[α]$_D$**: +29.8 (*c* 1.04, $CH_2Cl_2$).

**IR** (ATR): ν 2931, 2857, 1732, 1538, 1346, 1105, 702 $cm^{-1}$.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (98:2), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 15.043 min; $t_{minor}$ = 16.402 min. 96% ee.

**(*R*)-4-(phenylsulfonyl)but-2-yl 2,4-dinitrobenzoate**



**8qa**

**8qa**. Pale yellow oil. 139 mg, 34% yield. Reported compound.[3]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.74 (d, *J* = 2.2 Hz, 1H), 8.51 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.93 – 7.86 (m, 3H), 7.69 – 7.63 (m, 1H), 7.61 – 7.54 (m, 2H), 5.43 – 5.05 (m, 1H), 3.26 – 3.12 (m, 2H), 2.09 (td, *J* = 7.6, 4.7 Hz, 2H), 1.37 (d, *J* = 6.3 Hz, 3H).

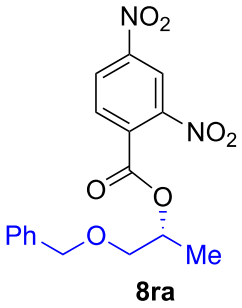
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 163.1, 148.9, 138.6, 134.0, 132.8, 131.3, 129.4, 129.3, 128.0, 127.7, 119.5, 72.6, 66.0, 53.1, 52.2, 31.5, 28.6, 23.5, 19.3.

**[α]$_D$**: +36.4 (*c* 1.12, $CH_2Cl_2$).

**IR** (ATR): ν 2924, 1732, 1536, 1279, 1050, 687 $cm^{-1}$.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (75:25), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 26.948 min; $t_{minor}$ = 51.617 min. 93% ee.

**(*R*)-1-(benzyloxy)prop-2-yl 2,4-dinitrobenzoate**



**8ra**

**8ra**. Pale yellow oil. 76 mg, 21% yield. Reported compound.[3]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.81 (d, *J* = 2.2 Hz, 1H), 8.52 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.29 (m, 5H), 5.57 – 5.39 (m, 1H), 4.68 – 4.46 (m, 2H), 3.63 (d, *J* = 5.1 Hz, 2H), 1.42 (d, *J* = 6.5 Hz, 3H).

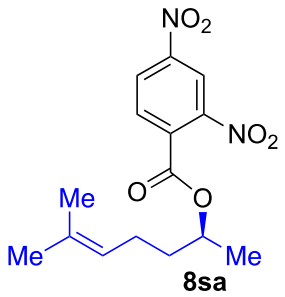
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.3, 148.8, 147.9, 137.8, 133.3, 131.3, 128.4 (x2), 127.8 (x2), 127.6, 127.4, 119.5, 73.2, 73.0, 71.9, 16.0.

**[α]$_D$**: +30.8 (*c* 0.74, $CH_2Cl_2$).

**IR** (ATR): ν 2070, 1733, 1535, 1348, 1056, 732 $cm^{-1}$.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (80:20), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 13.440 min; $t_{minor}$ = 12.138 min. 78% ee.

**(*S*)-6-methylhept-5-en-2-yl 2,4-dinitrobenzoate**



**8sa**

**8sa**. Yellow oil. 126 mg, 39% yield. Reported compound.[3]

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.76 (d, *J* = 2.2 Hz, 1H), 8.53 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 5.20 (dt, *J* = 7.1, 5.8 Hz, 1H), 5.10 (ddt, *J* = 8.6, 7.2, 1.5 Hz, 1H), 2.06 (q, *J* = 7.4 Hz, 2H), 1.81 – 1.58 (m, 8H), 1.37 (d, *J* = 6.3 Hz, 3H).

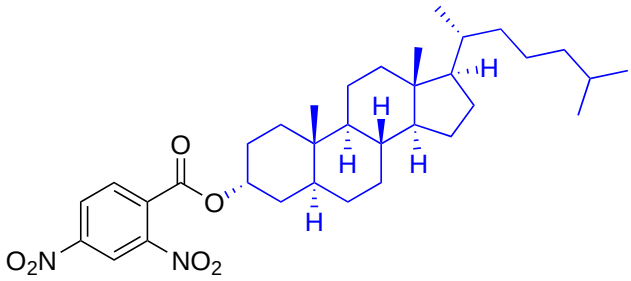
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 163.2, 148.8, 148.1, 133.4, 132.5, 131.2, 127.3, 123.0, 119.5, 74.8, 35.5, 25.6, 23.8, 19.3, 17.6.

**[α]$_D$**: +71.9 (*c* 1.02, $CH_2Cl_2$).

**IR** (ATR): ν 2931, 1731, 1536, 1282, 1054, 833, 730 $cm^{-1}$.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (95:5), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 17.786 min; $t_{minor}$ = 16.154 min. 96% ee.

**5α-Cholestan-3α-yl 2,4-dinitrobenzoate**




**8ta**

**8ta**. Pale yellow solid. 111 mg, 19% yield. Reported compound. [3]

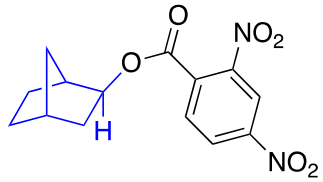
**$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.76 (d, *J* = 2.2 Hz, 1H), 8.54 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 5.37 (t, *J* = 2.8 Hz, 1H), 2.01 – 1.54 (m, 12H), 1.35 – 1.02 (m, 19H), 0.88 (d, *J* = 1.4 Hz, 3H), 0.86 (d, *J* = 1.4 Hz, 3H), 0.82 (s, 3H), 0.66 (d, *J* = 2.1 Hz, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ 163.0, 148.8, 148.7, 133.4, 131.4, 127.2, 119.4, 74.5, 56.4, 56.2, 54.1, 42.5, 40.1, 39.9, 39.5, 36.1, 35.8, 35.6, 35.4, 32.9, 32.5, 31.8, 28.3, 28.2, 28.0, 25.8, 24.1, 23.8, 22.8, 22.5, 20.7, 18.6, 12.0, 11.3.

**[α]$_D$**: +13.0 (*c* 1.05, $CH_2Cl_2$).

**IR** (ATR): ν 3107, 2928, 1714, 1538, 1351, 1298, 1134, 730 $cm^{-1}$.

***exo*-norbornyl 2,4-dinitrobenzoate**




**8ua**

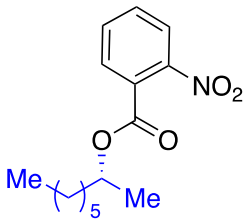
**8ua**. Retention product. Pale yellow oil. 125 mg, 41% yield. Reported compound. [3]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 2.2 Hz, 1H), 8.53 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 5.00 – 4.87 (m, 1H), 2.53 – 2.44 (m, 1H), 2.35 (td, *J* = 4.3, 2.0 Hz, 1H), 1.83 (ddd, *J* = 13.8, 7.1, 2.5 Hz, 1H), 1.68 – 1.42 (m, 4H), 1.29 – 1.07 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 163.0, 148.8, 148.3, 133.1, 131.4, 127.2, 119.4, 81.1, 41.2, 38.8, 35.3, 28.0, 24.1.

**IR** (ATR): ν 3102, 2959, 2872, 1727, 1528, 1349,1060, 728 $cm^{-1}$.

**(*R*)-oct-2-yl 2-nitrobenzoate**



**8ab**

**8ab**. Pale yellow oil. 98 mg, 35% yield. New compound.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.06 – 7.83 (m, 1H), 7.81 – 7.54 (m, 3H), 5.17 (dt, *J* = 7.0, 6.0 Hz, 1H), 1.82 – 1.64 (m, 1H), 1.64 – 1.49 (m, 1H), 1.42 – 1.27 (m, 11H), 1.01 – 0.68 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 164.9, 132.7, 131.4, 129.7, 128.2, 123.7, 73.8, 35.6, 31.7, 29.0, 25.2, 22.5, 19.3, 14.0.

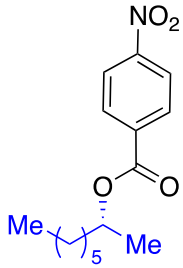
**[α]$_D$**: -47. 5 (*c* 0.85, $CH_2Cl_2$).

**IR** (ATR): ν 2929, 2858, 1726, 1534, 1287, 1073, 733 cm$^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{15}H_{21}NNaO_4$ [M+Na]$^+$: 302.1363, found: 302.1365.

**HPLC** (Daicel Chiralpak AD-H column, hexane/*i*-PrOH (98:2), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 6.290 min; $t_{minor}$ = 6.988 min. 90% ee.

**(*R*)-oct-2-yl 4-nitrobenzoate**



**8ac**

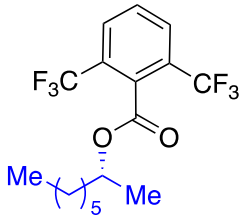
**8ac**. Pale yellow oil. 17 mg, 6% yield. Reported compound.[7]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.33 – 8.27 (m, 2H), 8.25 – 8.19 (m, 2H), 5.27 – 5.14 (m, 1H), 1.86 – 1.73 (m, 1H), 1.71 – 1.60 (m, 1H), 1.41 – 1.27 (m, 11H), 0.96 – 0.86 (m, 3H).

**[α]$_D$**: -21.0 (*c* 0.47, $CH_2Cl_2$).

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (95:5), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 10.192 min; $t_{minor}$ = 11.338 min. 60% ee.

**(*R*)-oct-2-yl 2,6-bis(trifluoromethyl)benzoate**



**8ad**

**8ad**. Pale yellow oil. 122 mg, 33% yield. New compound.[8]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.69 (ddt, *J* = 8.4, 7.5, 0.9 Hz, 1H), 5.21 (h, *J* = 6.3 Hz, 1H), 1.90 – 1.69 (m, 1H), 1.70 – 1.53 (m, 1H), 1.43 – 1.26 (m, 11H), 1.03 – 0.81 (m, 3H).

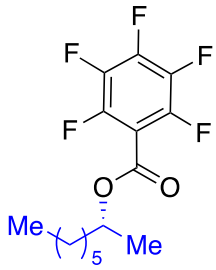
**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 164.5, 131.4, 129.7 (t, $^3J_{C\text{-}F}$ = 2.3 Hz, 2 signals), 128.8 (q, $^2J_{C\text{-}F}$ = 32.6 Hz, 2 signals), 122.9 (q, $^1J_{C\text{-}F}$ = 274.3 Hz, 2 signals), 74.7, 35.4, 31.6, 29.0, 24.8, 22.5, 18.8, 13.9.

**[α]$_D$**: -17.4 (*c* 1.30, $CH_2Cl_2$).

**HRMS** (ESI+): *m/z* calcd. for $C_{17}H_{20}F_6NaO_2$ [M+Na]$^+$: 393.1260, found: 393.1264.

**IR** (ATR): ν 2932, 2861, 1738, 1341, 1274, 1139, 677 cm$^{-1}$.

**(*R*)-oct-2-yl 2,3,4,5,6-pentafluorobenzoate**



**8ae**

**8ae**. Pale yellow oil. 100 mg, 31% yield. New compound.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 5.35 – 5.07 (m, 1H), 1.85 – 1.68 (m, 1H), 1.62 (ddt, *J* = 13.9, 11.5, 4.9 Hz, 1H), 1.44 – 1.28 (m, 11H), 0.96 – 0.84 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 158.6, 146.3 (dd, *J* = 11.8, 7.1 Hz, 1 signal), 145.28– 142.9 (m, 1 signal), 139.9 – 138.3 (m, 1 signal), 136.4 (dd, *J* = 12.9, 5.7 Hz, 1 signal), 109.0, 74.6, 35.7, 31.6, 29.0, 25.1, 22.5, 19.8, 13.9.

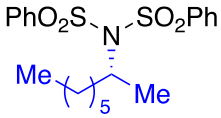
**[α]$_D$**: -18.0 (*c* 0.70, $CH_2Cl_2$).

**IR** (ATR): ν 2932, 2860, 1735, 1496, 1325, 1234, 995 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{15}H_{17}F_5NaO_2$ $[M+Na]^+$: 347.1041, found: 347.1053.

**HPLC** (Daicel Chiralpak IA column, hexane/*i*-PrOH (99.5:0.5), flow rate 1.0 mL/min, λ = 240 nm): $t_{minor}$ = 6.400 min; $t_{major}$ = 7.193 min. 98% ee.

**(*R*)-*N*-(oct-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide**



**8af**

**8af**. Pale yellow oil. 102 mg, 25% yield. Reported compound.[3]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 4H), 7.72 – 7.46 (m, 6H), 4.14 (dt, *J* = 7.8, 6.7 Hz, 1H), 2.01 – 1.69 (m, 2H), 1.40 (d, *J* = 6.9 Hz, 3H), 1.33 – 1.02 (m, 9H), 0.87 (t, *J* = 7.2 Hz, 3H).

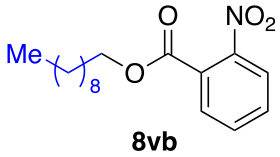
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 133.6 (X2), 128.9 (X4), 128.3 (X6), 61.1, 35.6, 31.5, 28.8, 27.2, 22.4, 19.7, 14.0.

**[α]$_D$**: -0.7 (*c* 0.96, $CH_2Cl_2$).

**IR** (ATR): ν 2928, 2857, 1448, 1365, 1166, 1084, 551 $cm^{-1}$.

**HPLC** (Daicel Chiralpak IC column, hexane/*i*-PrOH (88:12), flow rate 1.0 mL/min, λ = 254 nm): $t_{major}$ = 8.546 min; $t_{minor}$ = 9.564 min. 89% ee.

**1-decyl 2-nitrobenzoate**



**8vb**

**8vb**. Colorless oil. 230 mg, 75% yield. New compound.

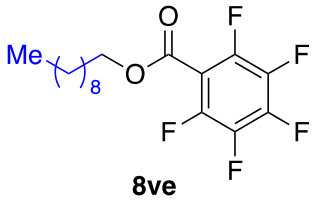
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.14 – 7.88 (m, 1H), 7.86 – 7.76 (m, 1H), 7.74 – 7.59 (m, 2H), 4.34 (t, *J* = 6.7 Hz, 2H), 1.74 (dq, *J* = 8.1, 6.7 Hz, 2H), 1.56 – 1.16 (m, 14H), 1.05 – 0.77 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 165.4, 132.7, 131.6, 129.9, 127.8, 123.8, 66.7, 31.8, 29.5, 29.4, 29.2, 29.1, 28.2, 25.8, 22.6, 14.1.

**IR** (ATR): ν 2924, 2854, 1731,1534, 1466, 1288, 1125, 733$cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{17}H_{25}NNaO_4$ $[M+Na]^+$: 330.1676, found: 330.1671.

**1-decyl 2,3,4,5,6-pentafluorobenzoate**



**8ve**

**8ve**. Pale yellow oil. 151 mg, 43% yield. New compound.

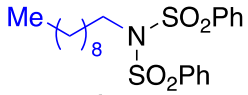
**$^1$H NMR** (400 MHz, $CDCl_3$): δ 4.39 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.70 (m, 2H), 1.50 – 1.21 (m, 14H), 0.99 – 0.83 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 159.0, 147.2 – 145.9 (m, *1 signal*), 144.9 – 143.4 (m, *1 signal*), 142.1 – 141.1 (m, *1 signal*), 139.1 – 138.4 (m, *1 signal*), 137.3 – 135.3 (m, *1 signal*), 108.5 (t, *J* = 16.1 Hz, *1 signal*), 67.0, 31.8, 29.5, 29.4, 29.2, 29.1, 28.4, 25.7, 22.6, 14.0.

**IR** (ATR): ν 26, 2856, 1740, 1651, 1497, 1327, 1223, 998 $cm^{-1}$.

**HRMS** (ESI+): *m/z* calcd. for $C_{17}H_{21}F_5NaO_2$ $[M+Na]^+$: 375.1354, found: 375.1351.

***N*-(1-decyl)-*N*-(phenylsulfonyl)benzenesulfonamide**



**8vf**

**8vf**. White solid. 253 mg, 58% yield. Reported compound.[3]

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.19 – 7.91 (m, 4H), 7.78 – 7.62 (m, 2H), 7.64 – 7.47 (m, 4H), 3.82 – 3.59 (m, 2H), 1.68 (t, *J* = 7.3 Hz, 2H), 1.32 – 1.21 (m, 14H), 0.98 – 0.79 (m, 3H).

## 6. General procedure for recycling experiments.

To a solution of benzoic acid **7a** (1.0 mmol, 1.0 equiv) in toluene (12.5 mL) were added alcohol **8a** (1.5 mmol, 1.5 equiv) and catalyst **2** (0.5 mmol, 521 mg, 50 mol %). The reaction mixture was heated to reflux and shaked, with a Dean-Stark apparatus to separate water and a long glass tube as air condenser. After 72 hours, the solvent was removed with a syringe, and the resin washed twice with 6 mL of hot toluene. The combined solution was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using cyclohexane/EtOAc (12:1) as the eluent to give the desired ester product. (The resin was reused for the next cycle without further treatment). Results are shown in the manuscript.

## 7. General procedure for the reactivation of catalyst

At 70 $^{o}$C, to a mixture of 10 cycles used resin catalyst (1 mmol) and 10 mL of toluene, was added 0.5 mL of *n*BuNH$_2$. And the system was allowed to be shaken for 1 hour. Then, the brown liquid was taken out via a syringe, and the remaining solid was washed with hot toluene. The washed resin was then dried under vacuum at 40 $^{o}$C and used in further reactions or analyzed by $^{31}$P NMR.

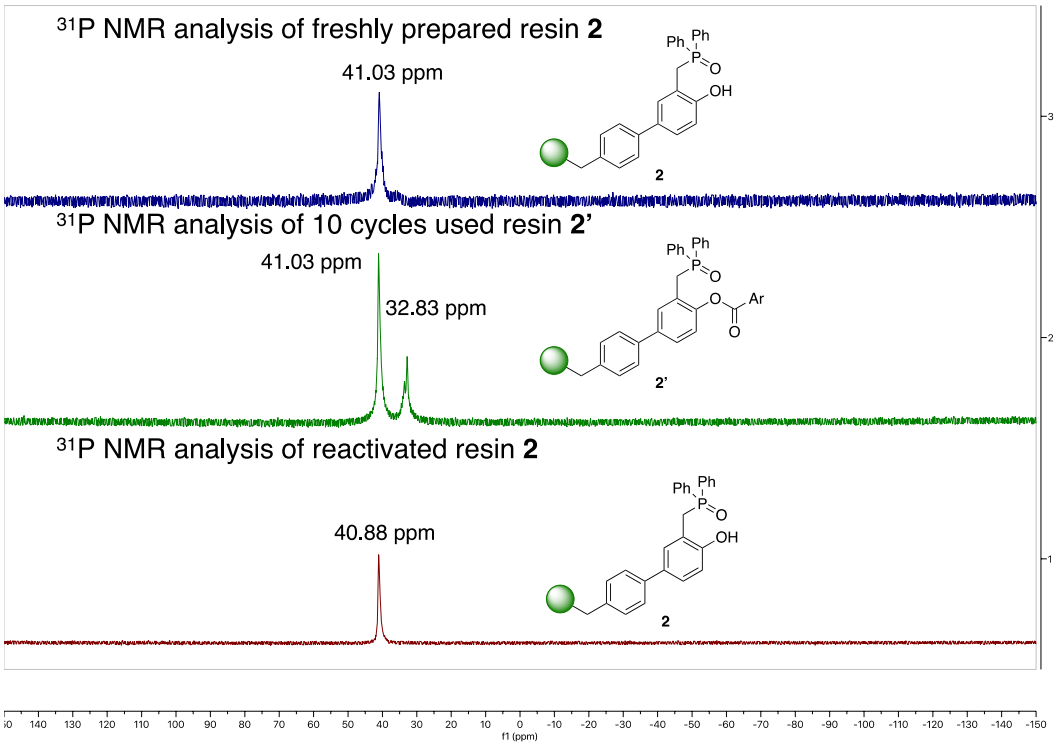
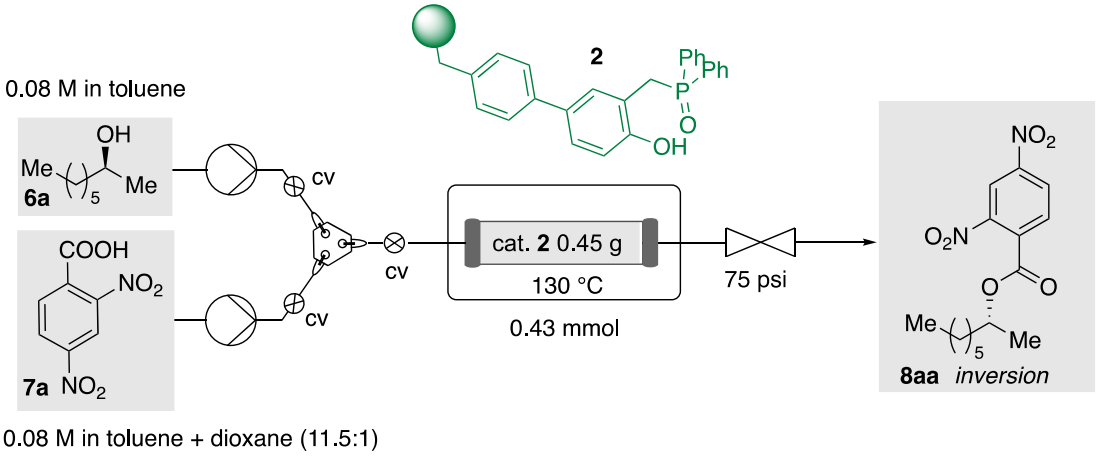



Figure S2. $^{31}$P NMR analysis of freshly prepared, 10 cycles used and reactivated resin **2**

## 8. Process for the attempted preparation of ester and ether products in continuous flow[5]

### A. Attempted preparation of 8aa in continuous flow.



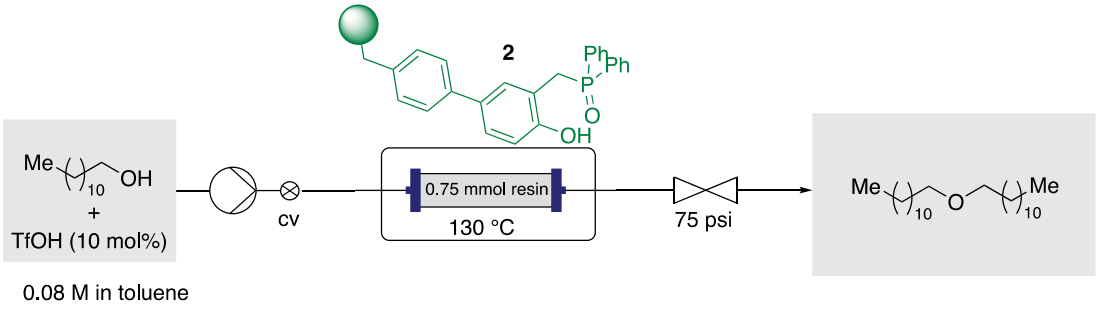

Scheme S5. Continuous flow process for the preparation of ester product **8aa**

In order to perform the continuous flow experiment, a solution of (*S*)-octanol (0.08 M in toluene) and a solution of 2,4-dinitrobenzoic acid (0.08 M in 11.5:1 mixture of toluene and dioxane) were prepared. An Omnifit glass column (1 cm internal diameter) was loaded with catalyst **2** (450 mg, 0.43 mmol, $f$ = 0.96 mmol $g^{-1}$). The column was assembled to a flow system as shown in scheme S5.

Firstly, toluene was circulated for 1 hour at 0.1 mL $min^{-1}$ flow rate at 130 °C to swell the resin. After that, the solution of (*S*)-octanol (0.08 M in toluene), and the solution of 2,4-dinitrobenzoic acid was pumped through the reactor at a flow rate of 0.025 mL $min^{-1}$. The produced solution was collected in a receiving flask, and was checked by $^1$H NMR analysis every hour. After continuous flow of 6 hours, no desired product was detected.

Further adjustment of flow parameters failed to produce the desired products

**B. Attempted preparation of didodecyl ether in continuous flow.**




Scheme S6. Continuous flow process for the preparation of didodecyl ether

For the continuous flow set up of etherification, a mixed solution of 2.0 mmol dodecanol and 0.2 mmol triflate acid in 25 mL toluene was prepared. An Omnifit glass column (1 cm internal diameter) was loaded with catalyst **2** (780 mg, 0.75 mmol, $f$ = 0.96 mmol $g^{-1}$). The column was assembled to a flow system as shown in scheme S6.

Firstly, toluene was circulated for 1 hour at 0.1 mL $min^{-1}$ flow rate at 130 °C to swell the resin. After that, the solution of dodecanol and triflate acid was pumped through the reactor at a flow rate of 0.02 mL $min^{-1}$. The produced solution was collected in a receiving flask, and was detected by $^1$H NMR analysis every hour. After continuous flow of 6 hours, no desired product was detected.

Further adjustment of flow parameters failed to produce the desired products.

## 9. References

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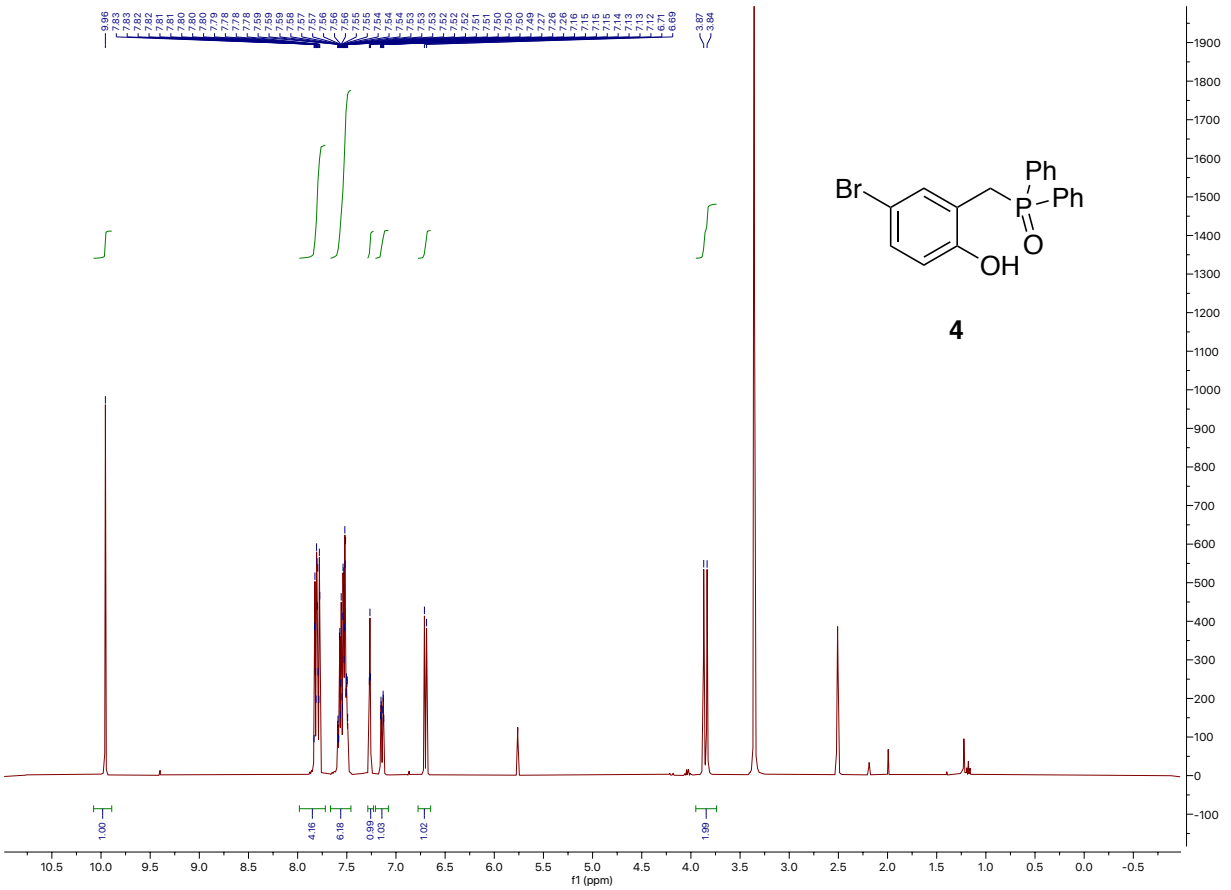
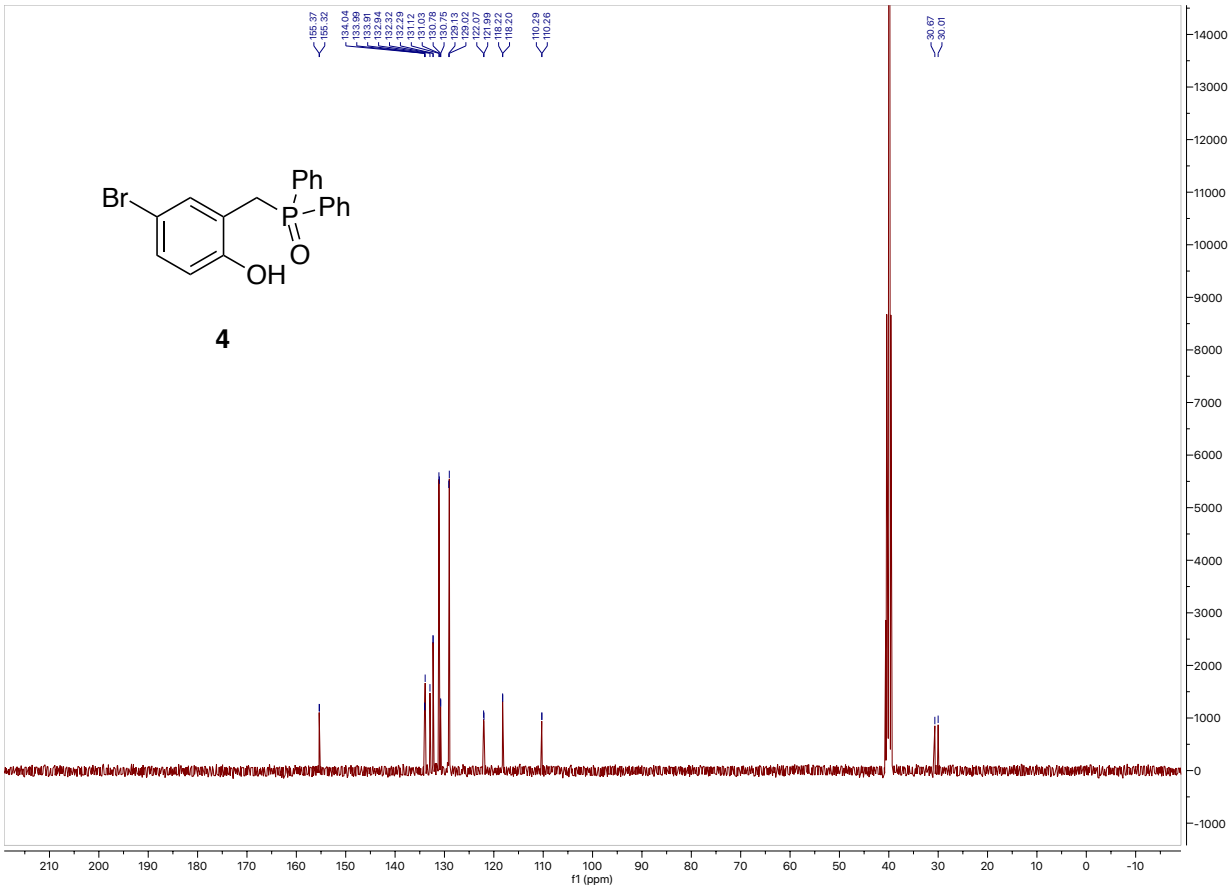
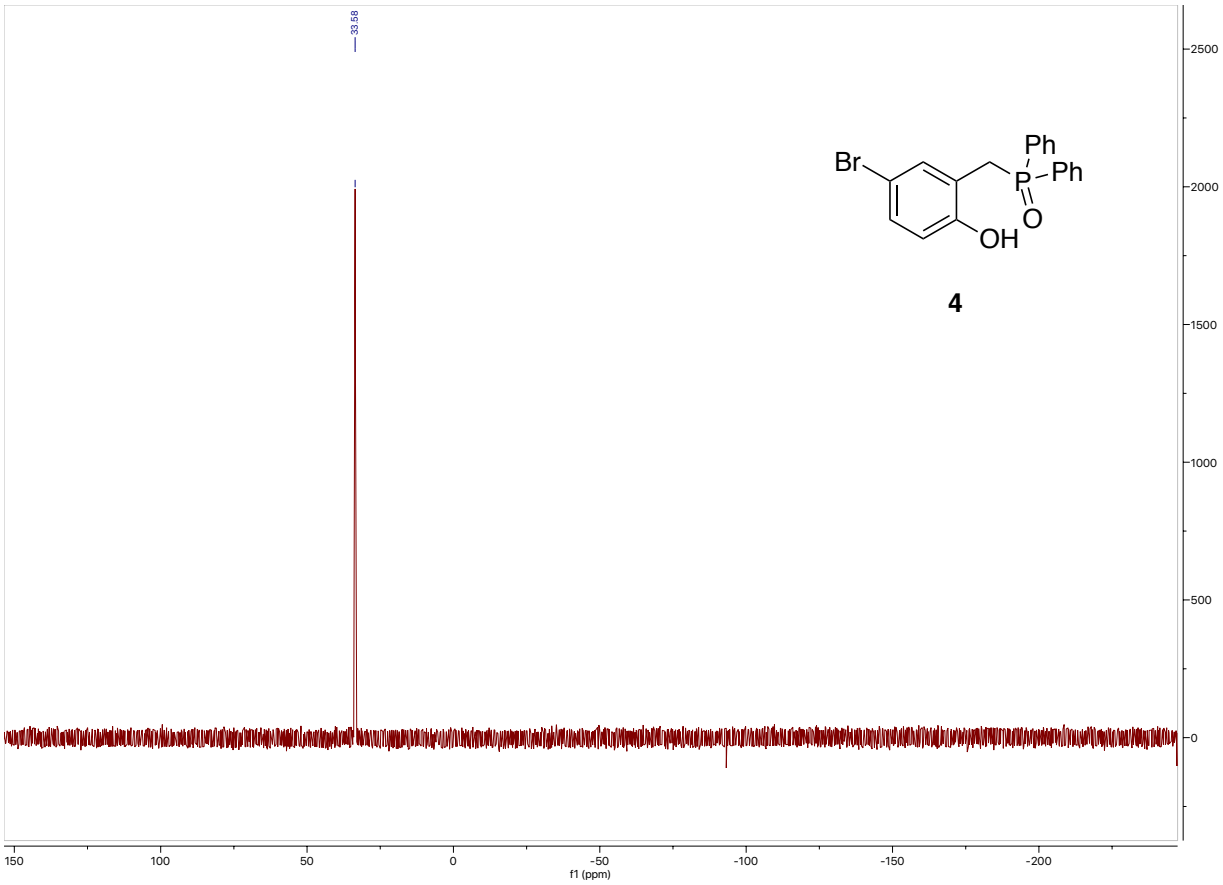
8) The racemic mixture could not be resolved by chiral HPLC.

## 10. $^{1}H$ , $^{13}C$ and $^{31}P$NMR Spectra

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Ph
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500
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100
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0
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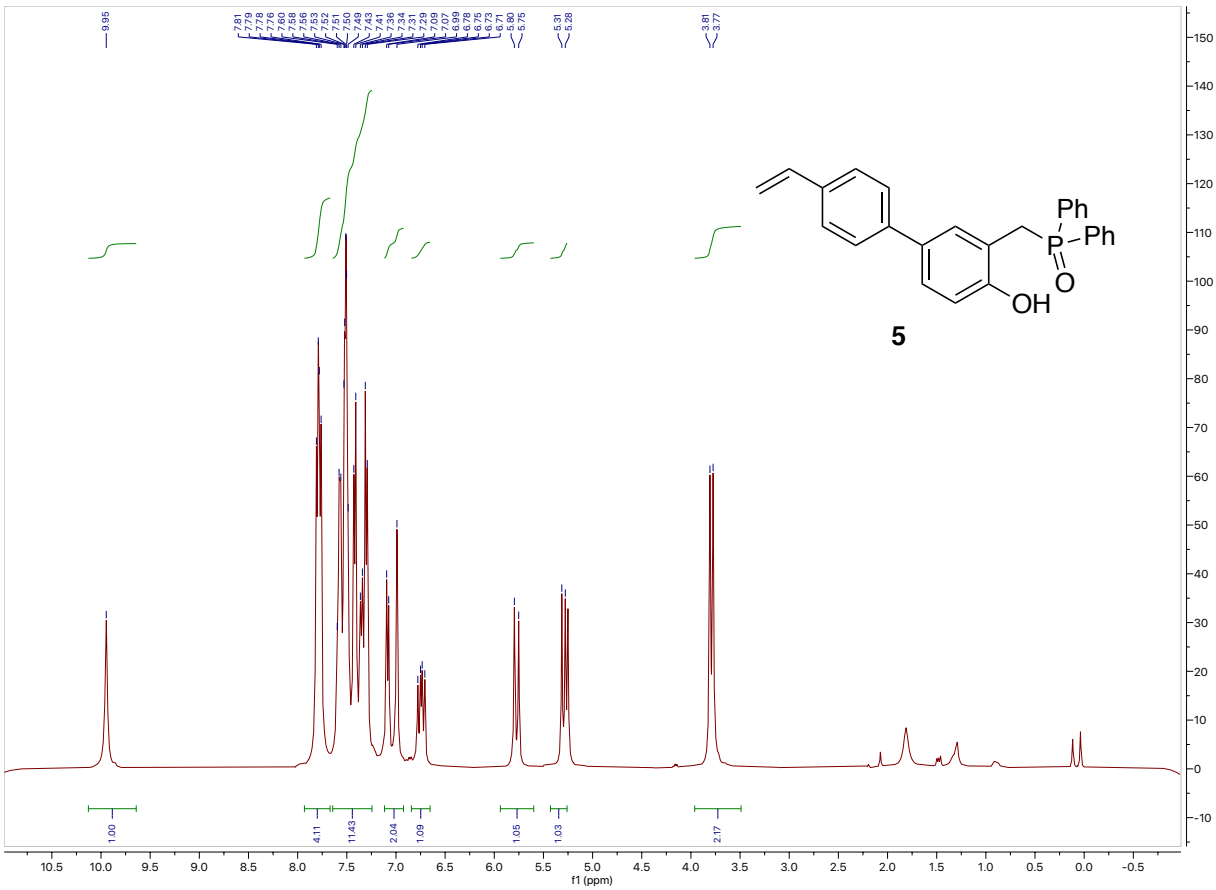
-100
-150
-200
f1 (ppm)

**4**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5.31
5.28
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3.77
Ph
P
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O
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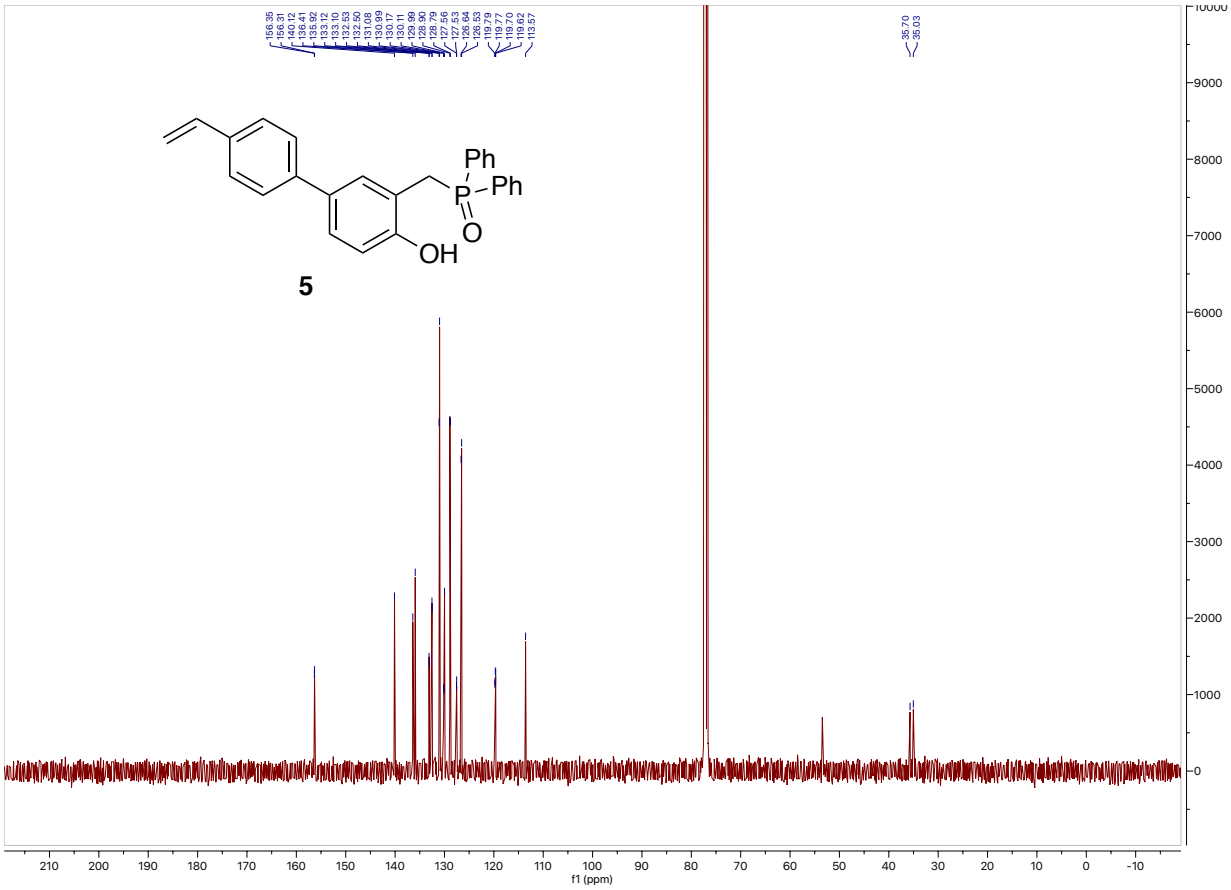
f1 (ppm)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Ph
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OH
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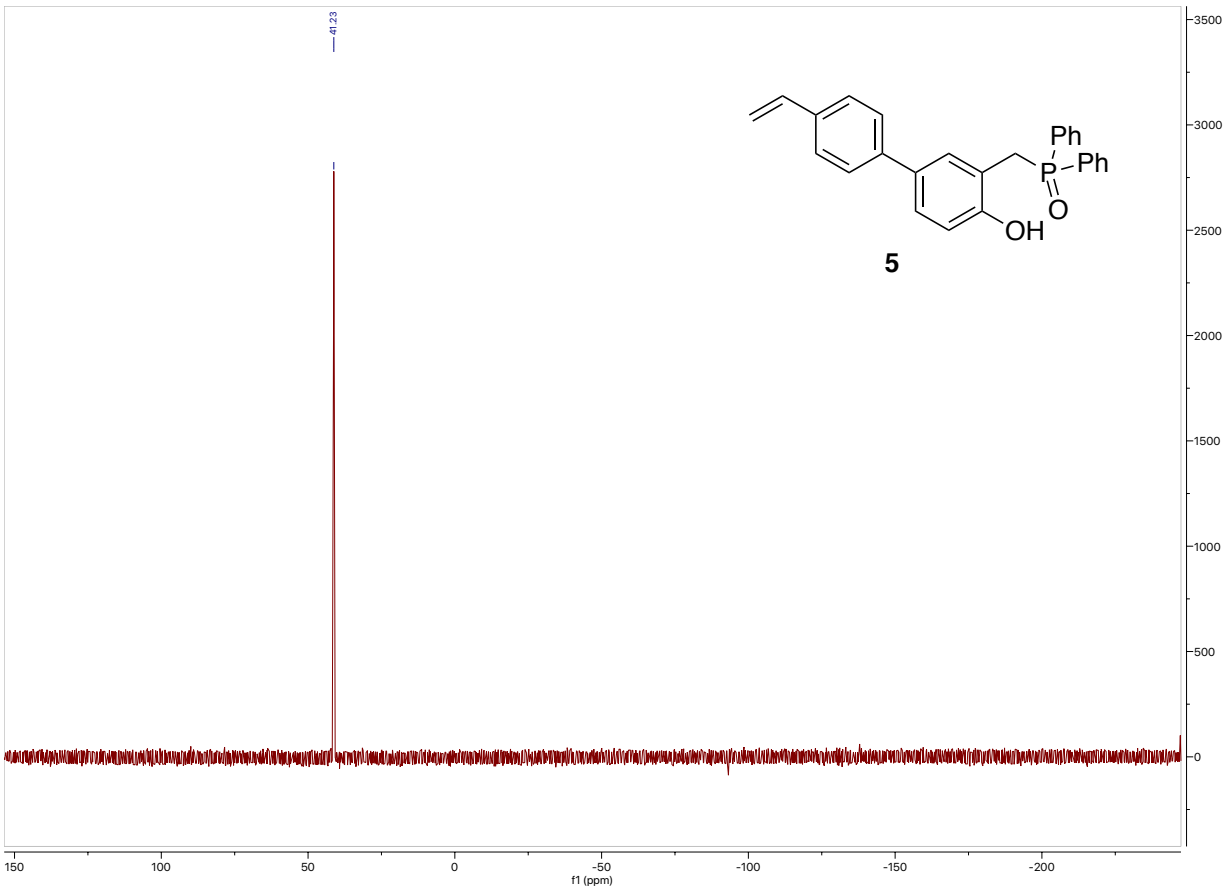
f1 (ppm)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P
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50
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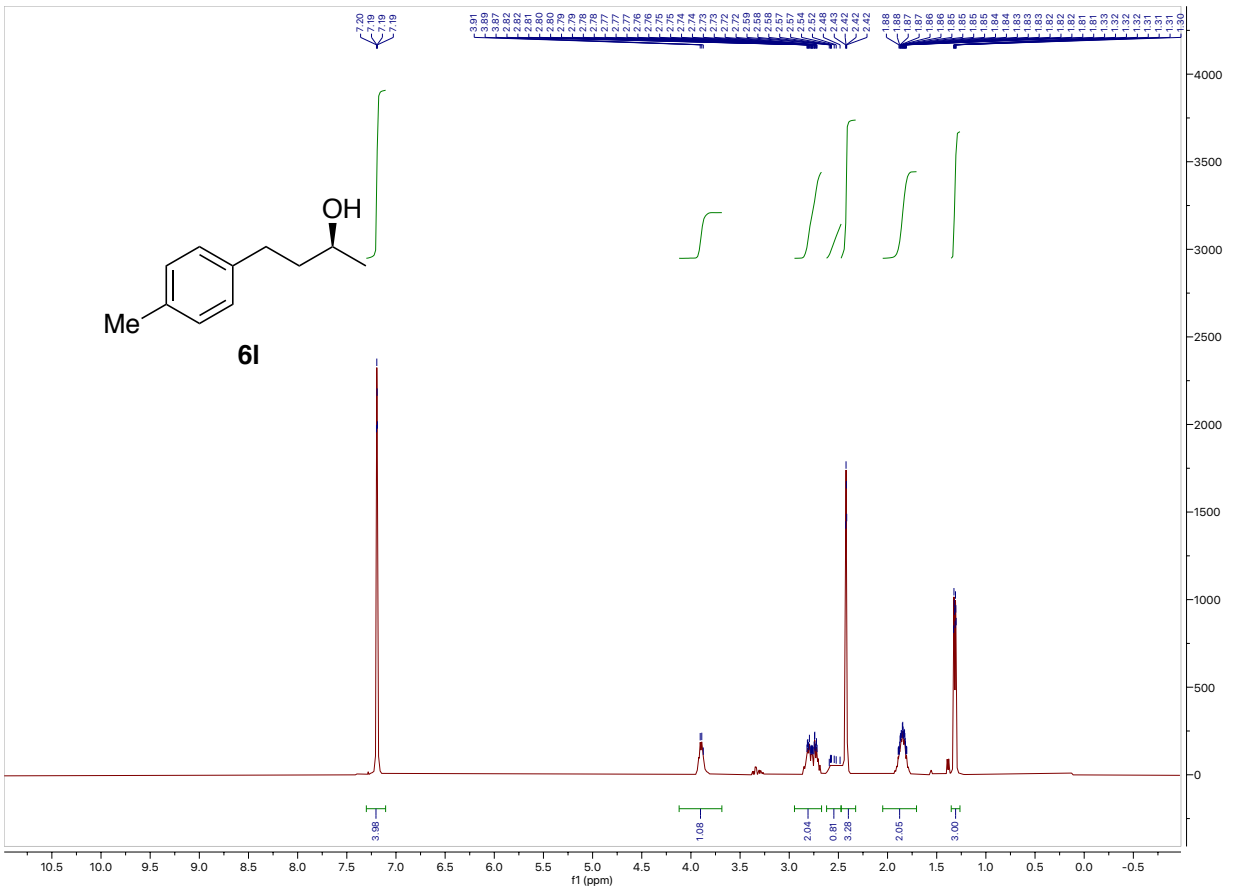
-100
-150
-200
f1 (ppm)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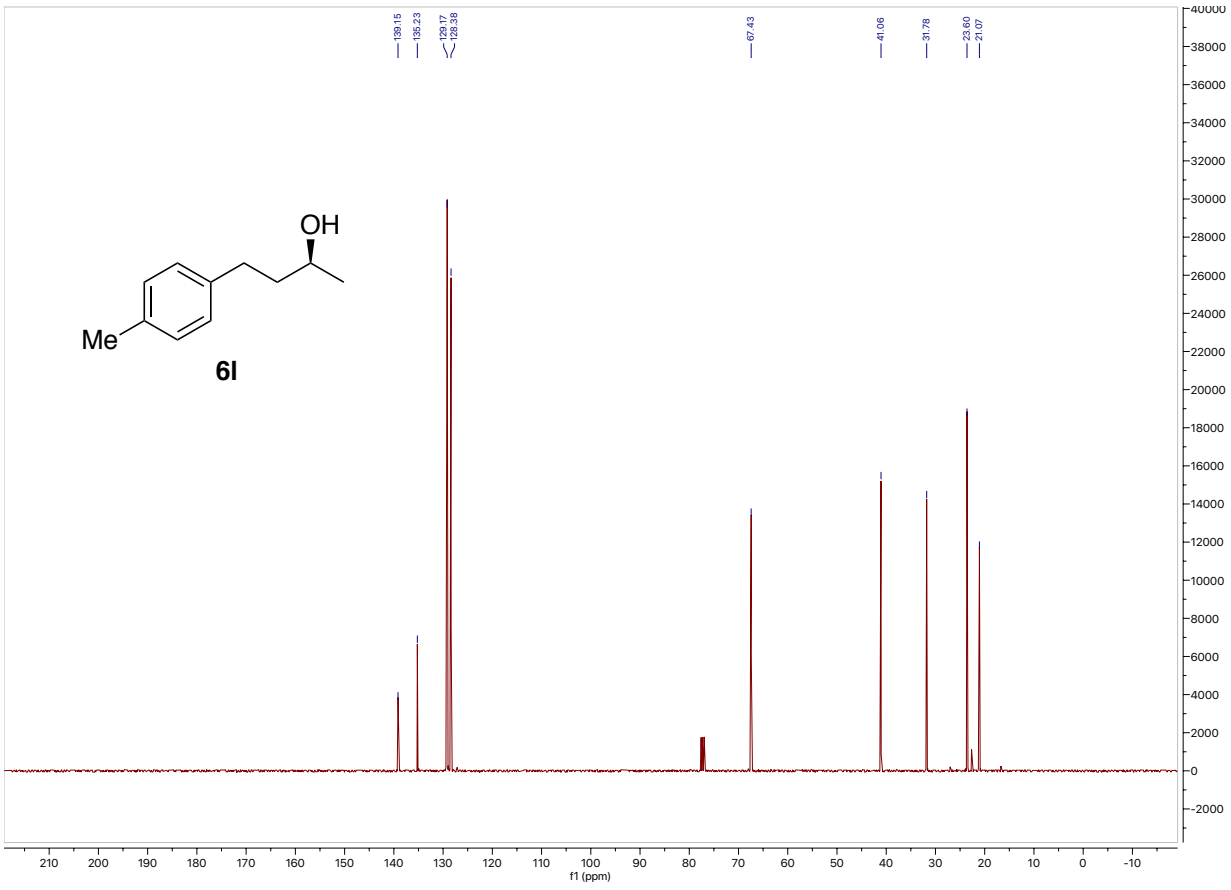
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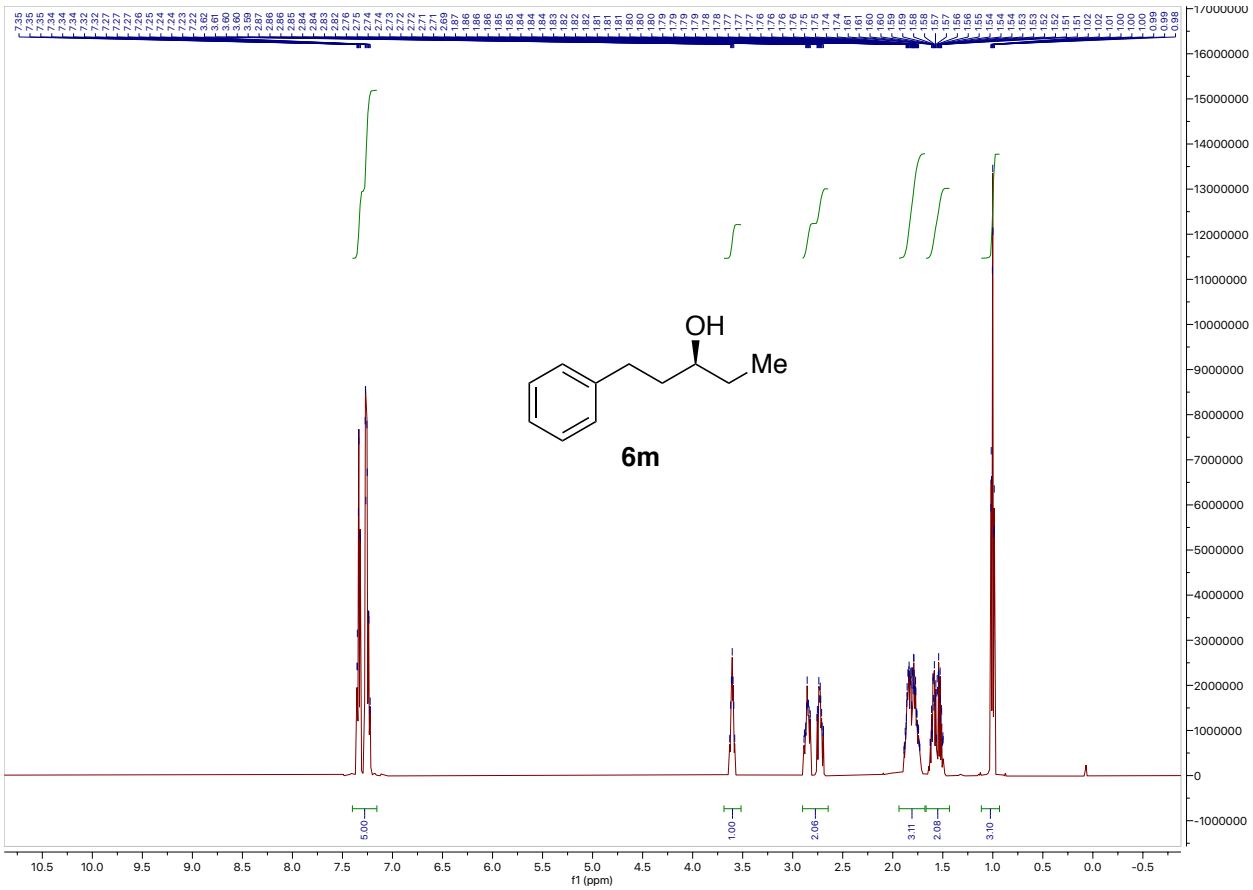
Me
6l
f1 (ppm)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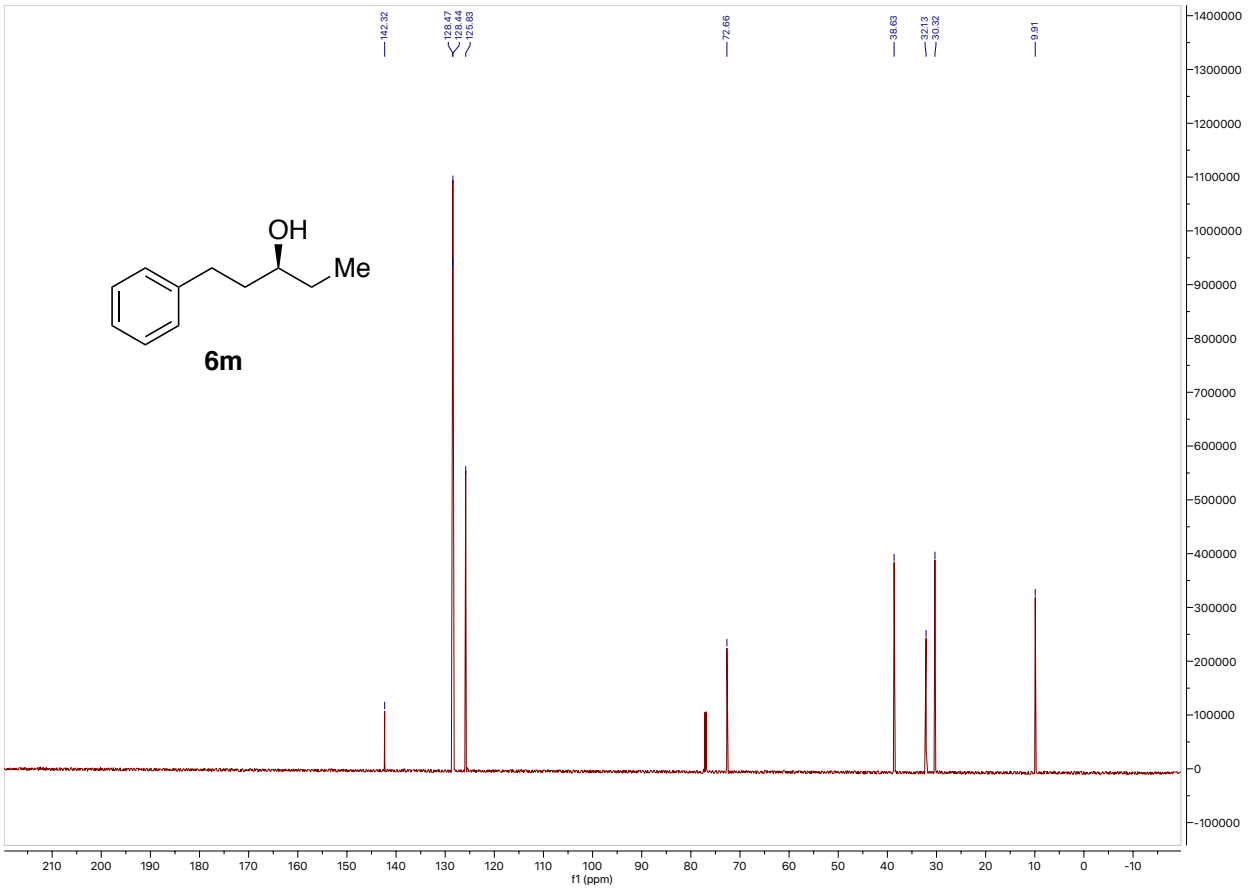
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Me
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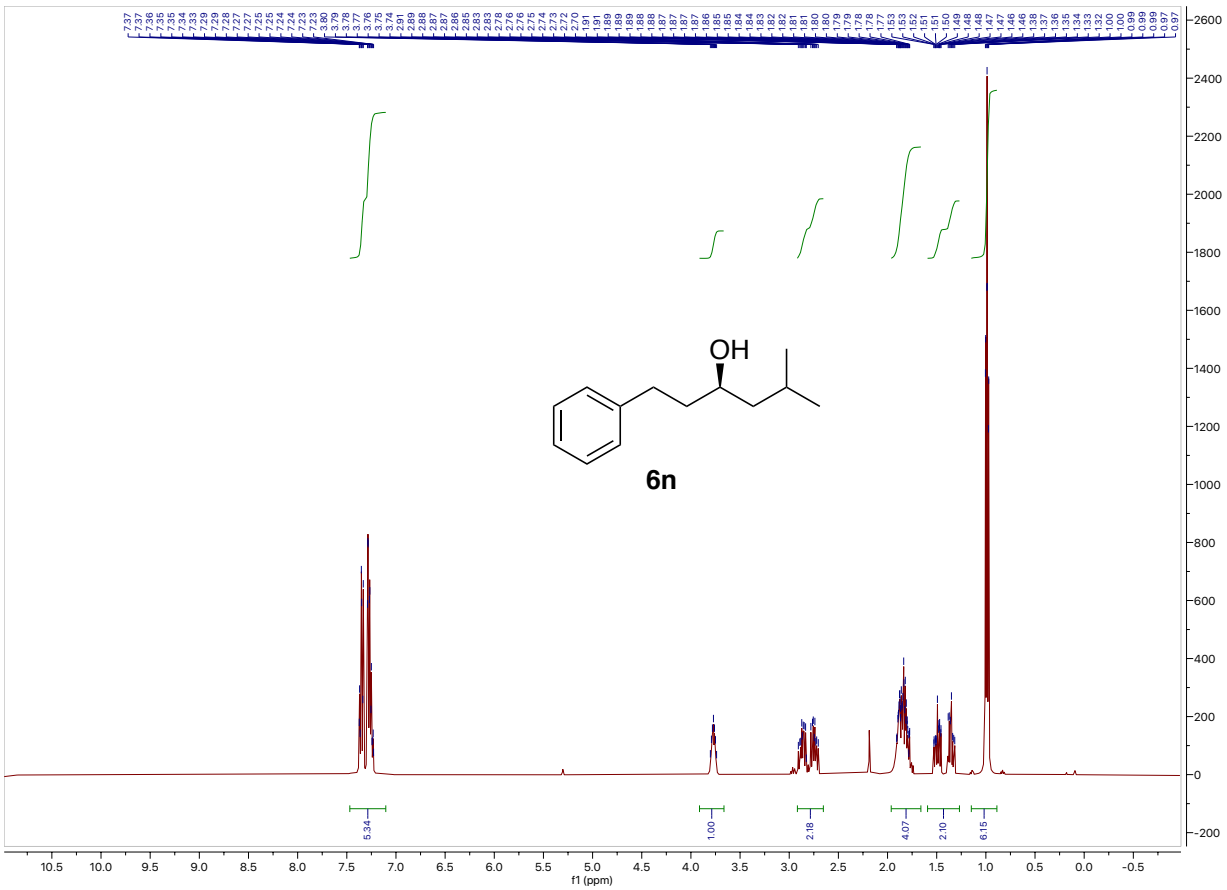
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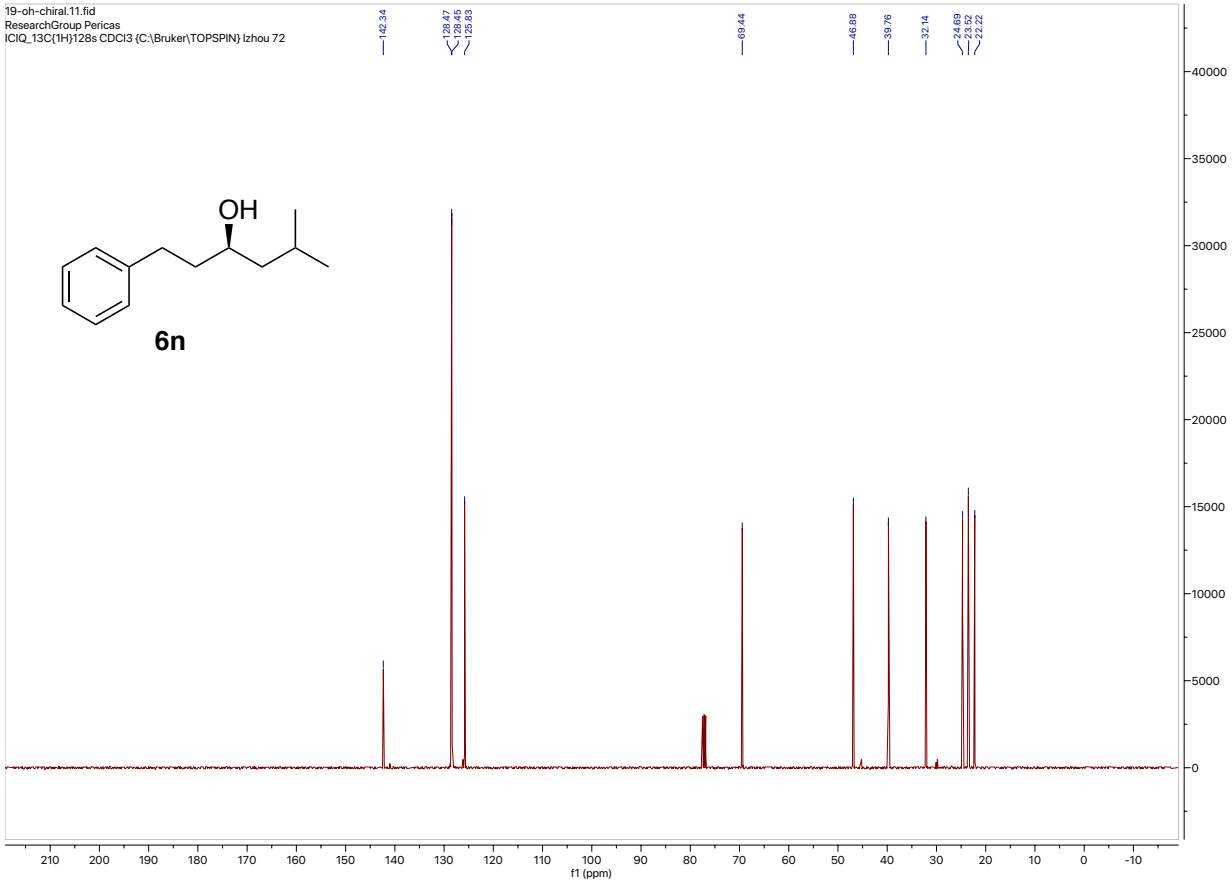
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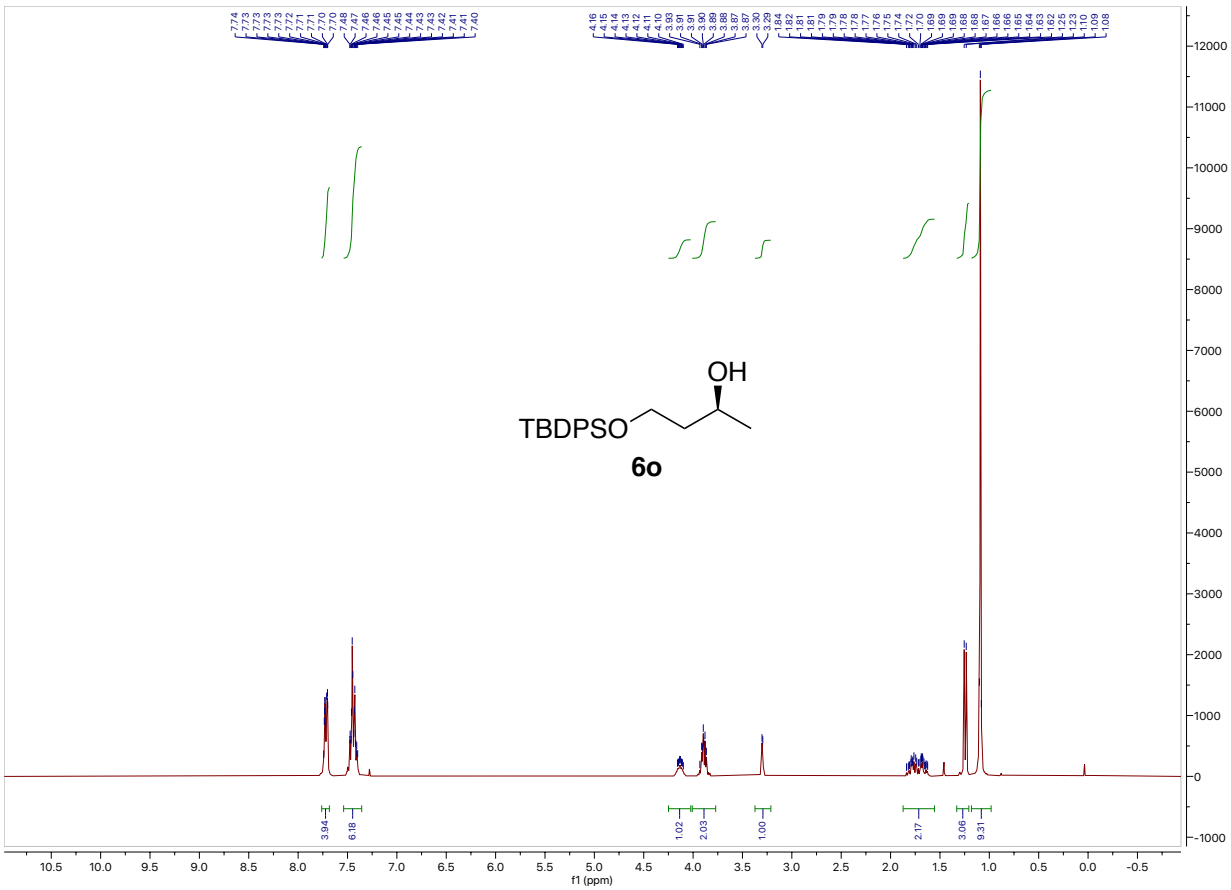
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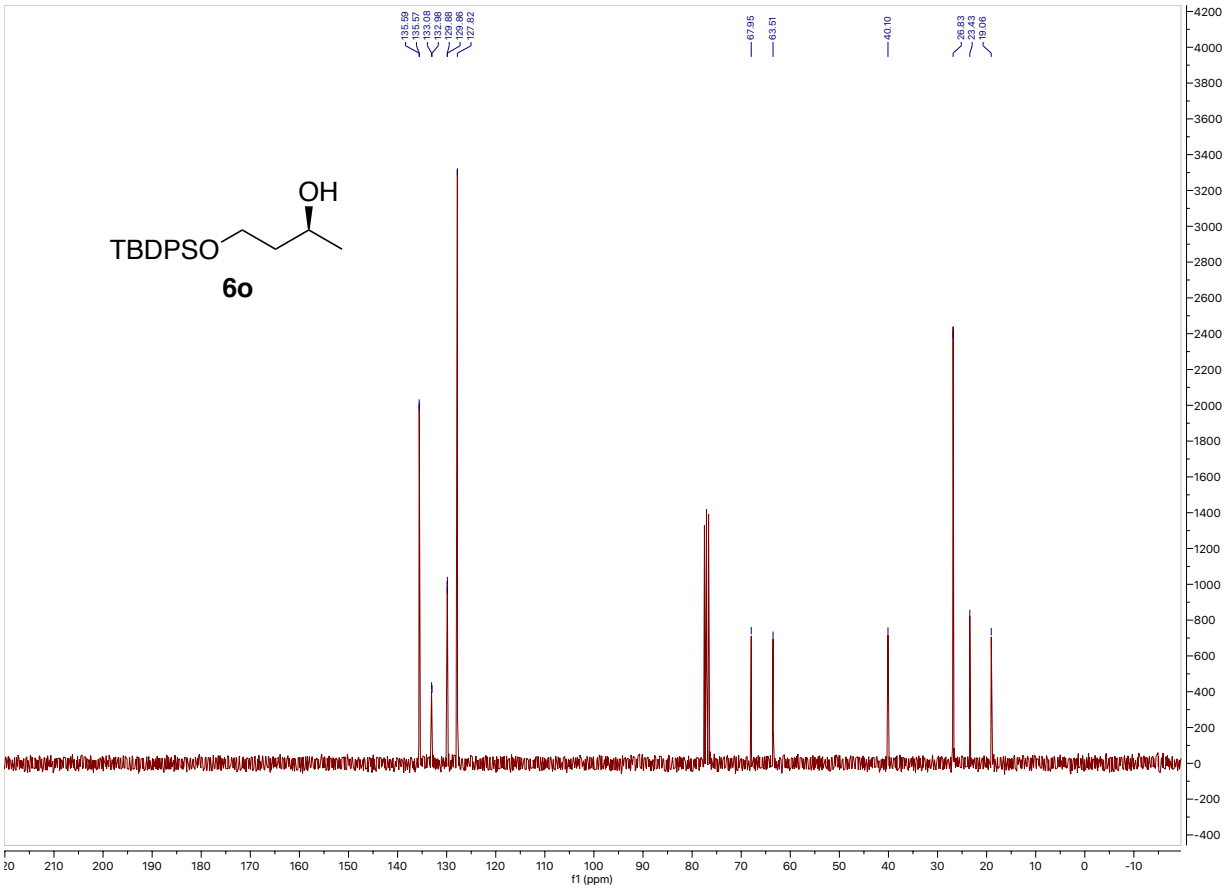
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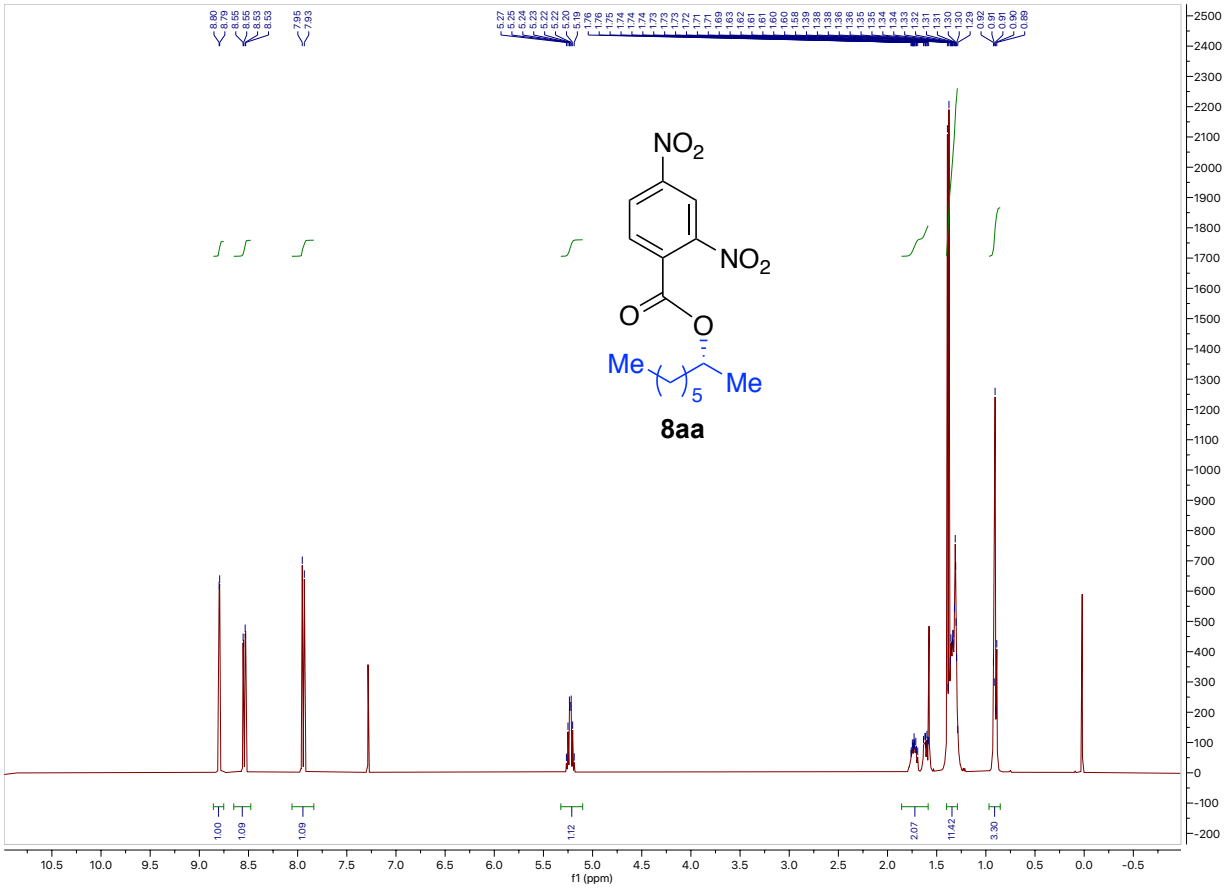
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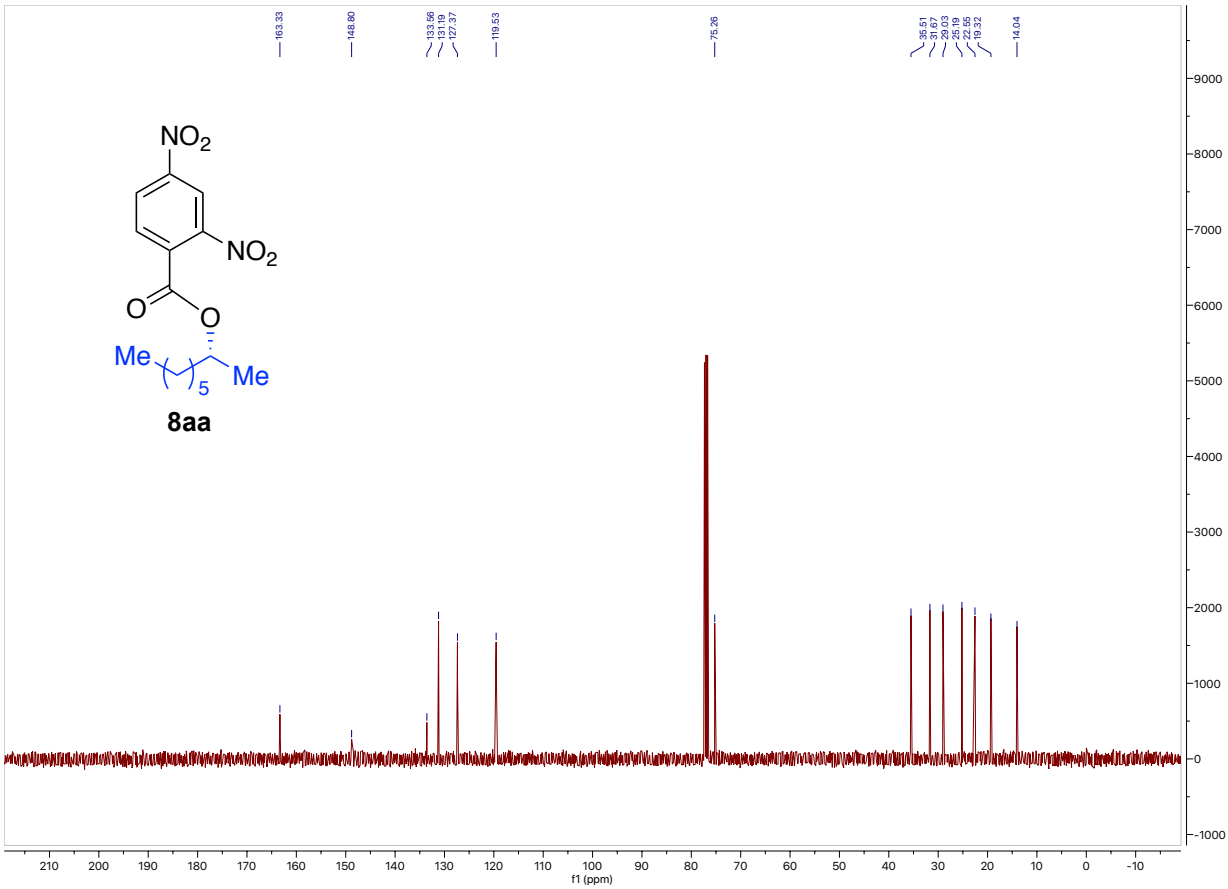
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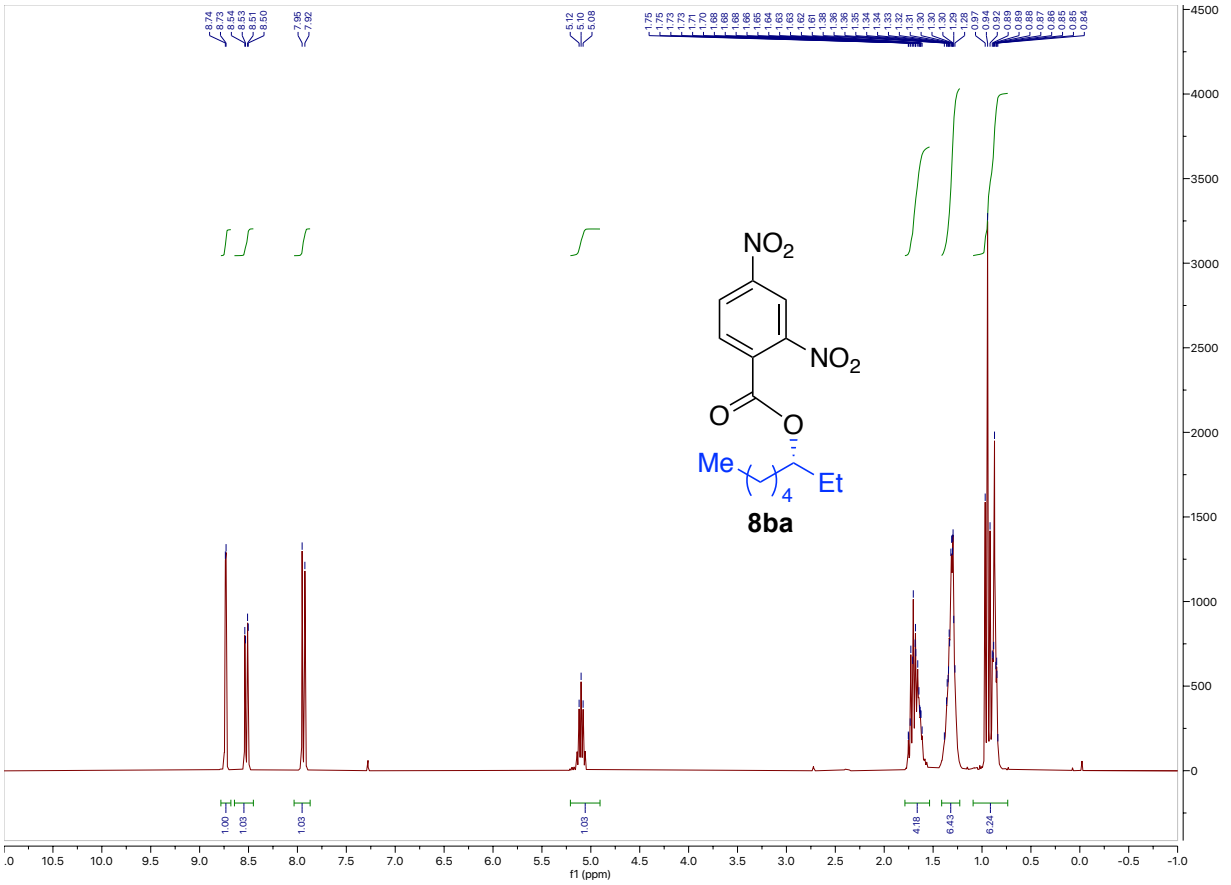
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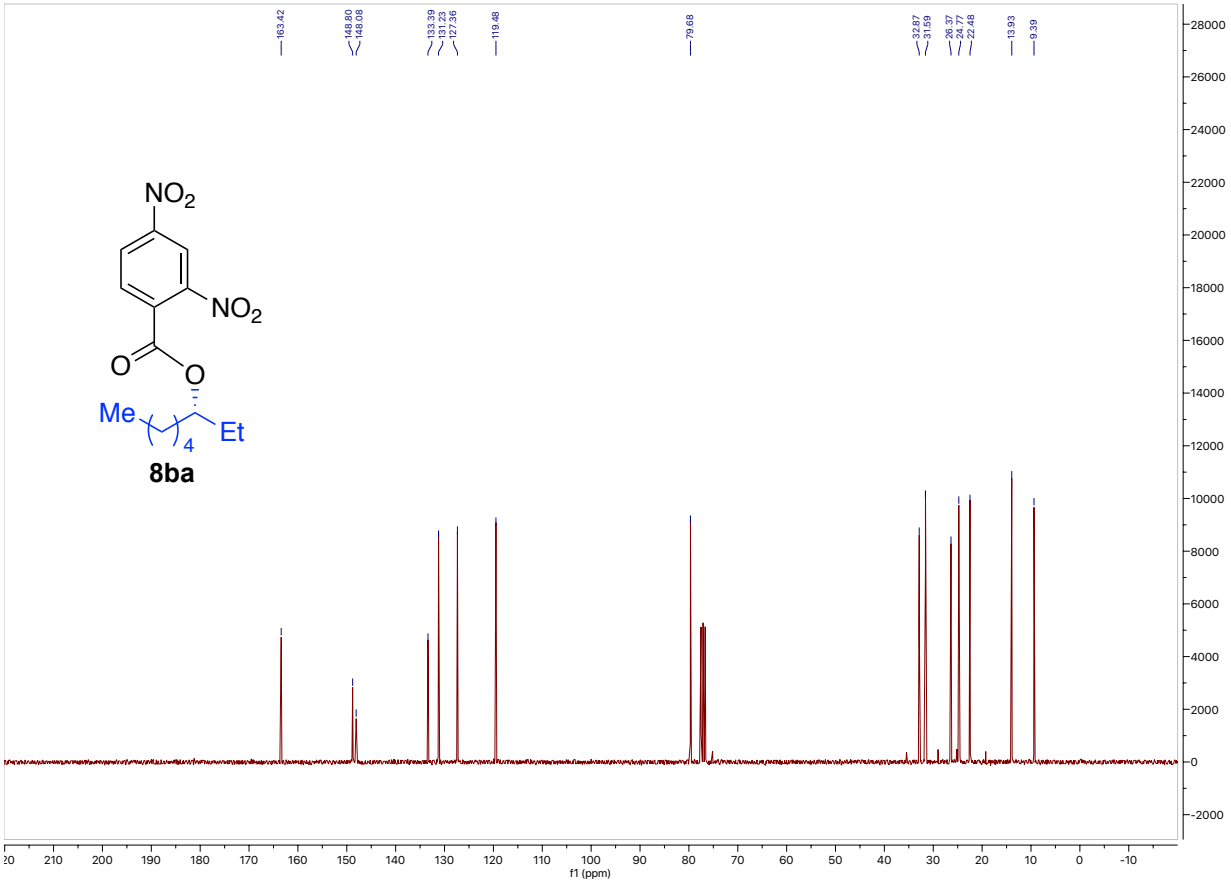
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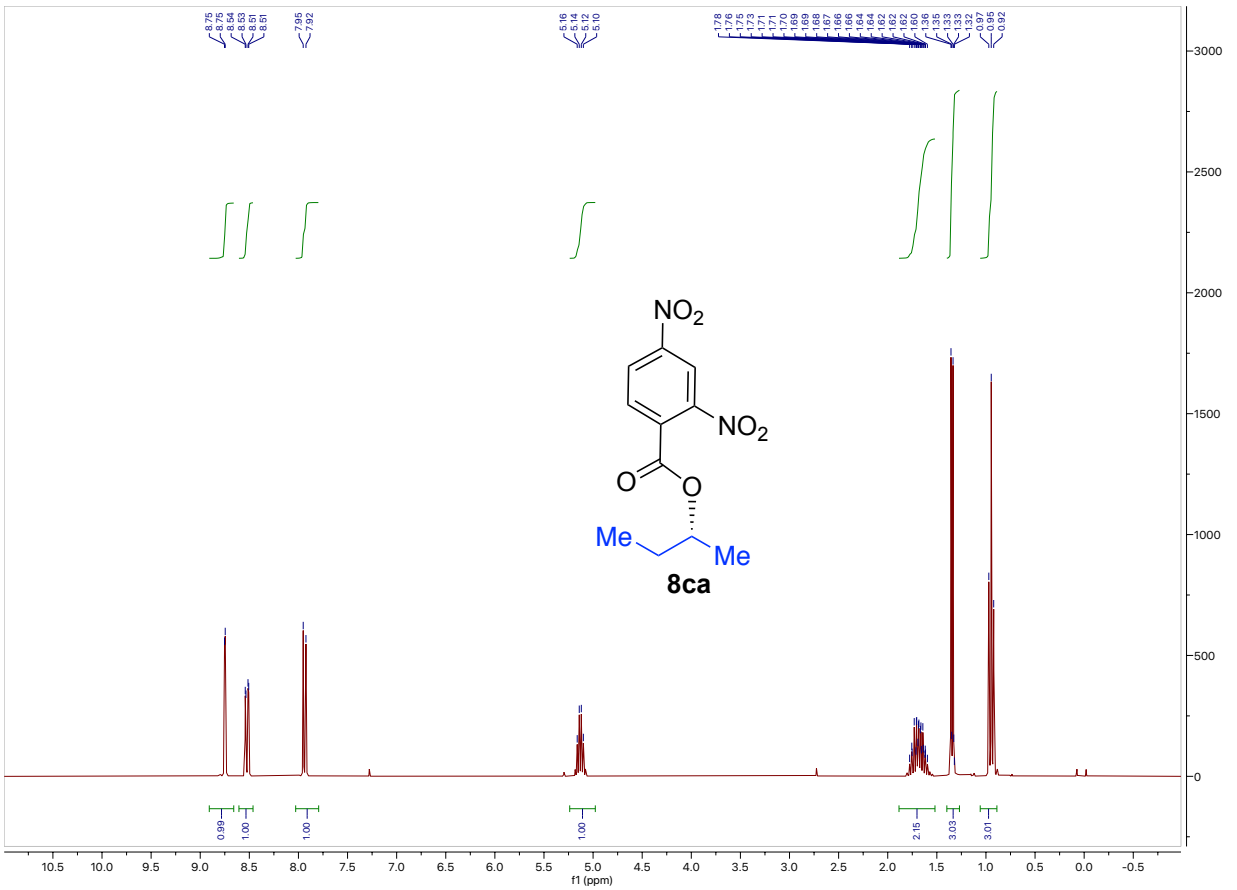
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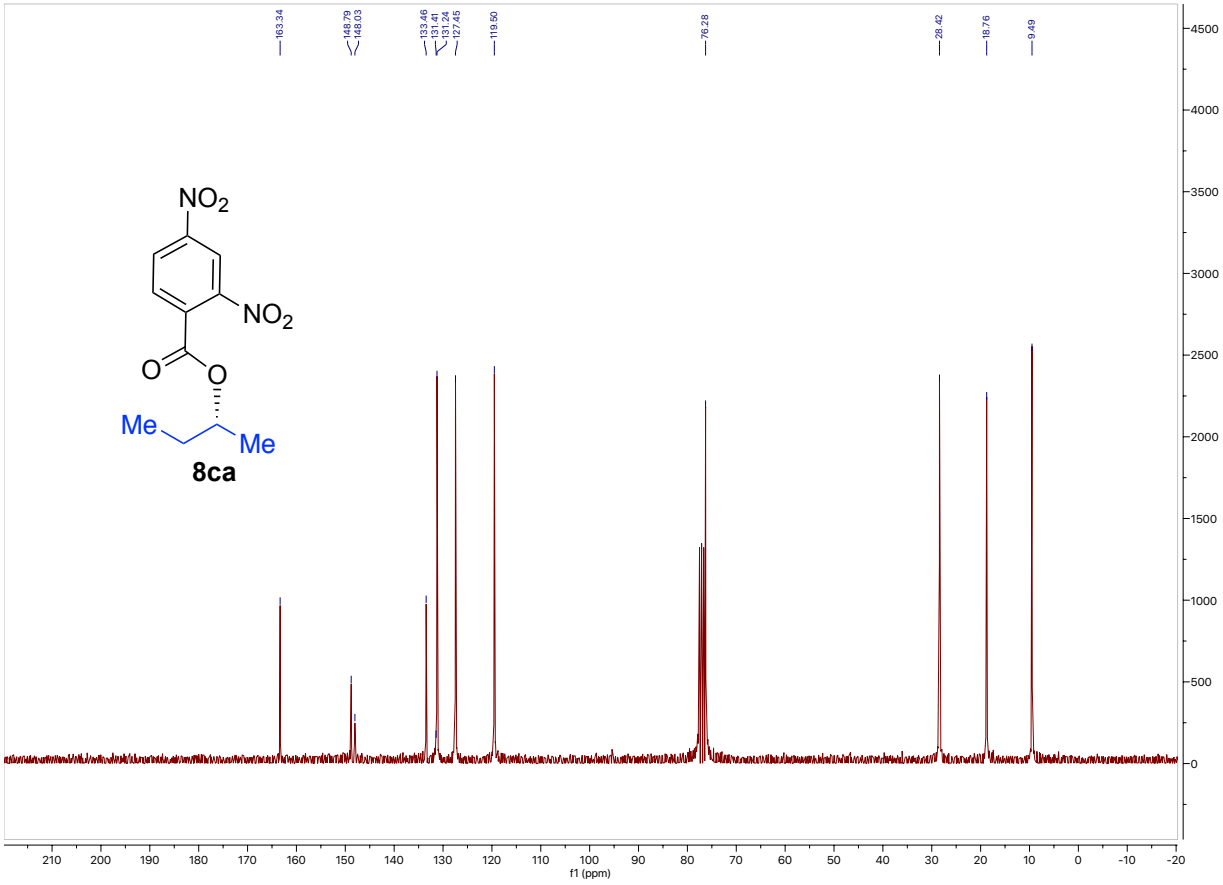
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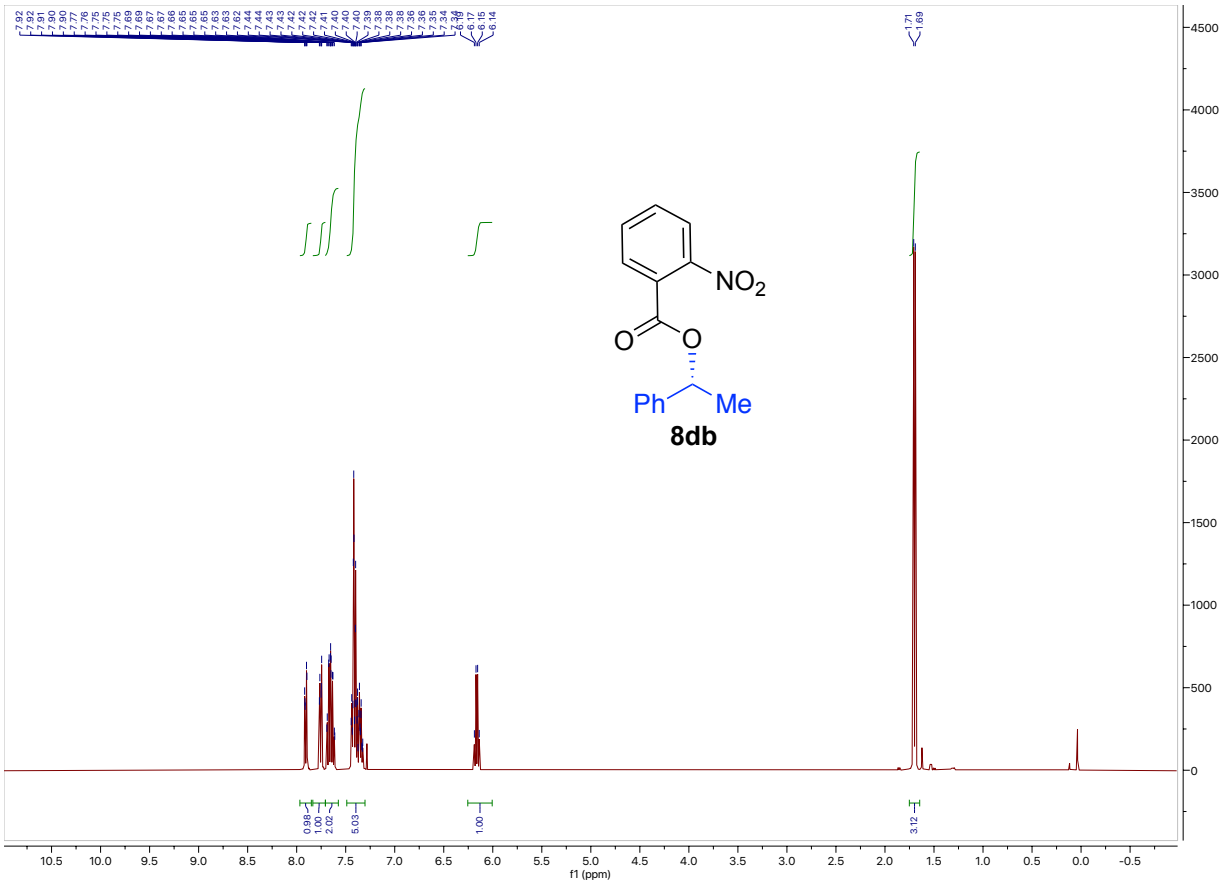
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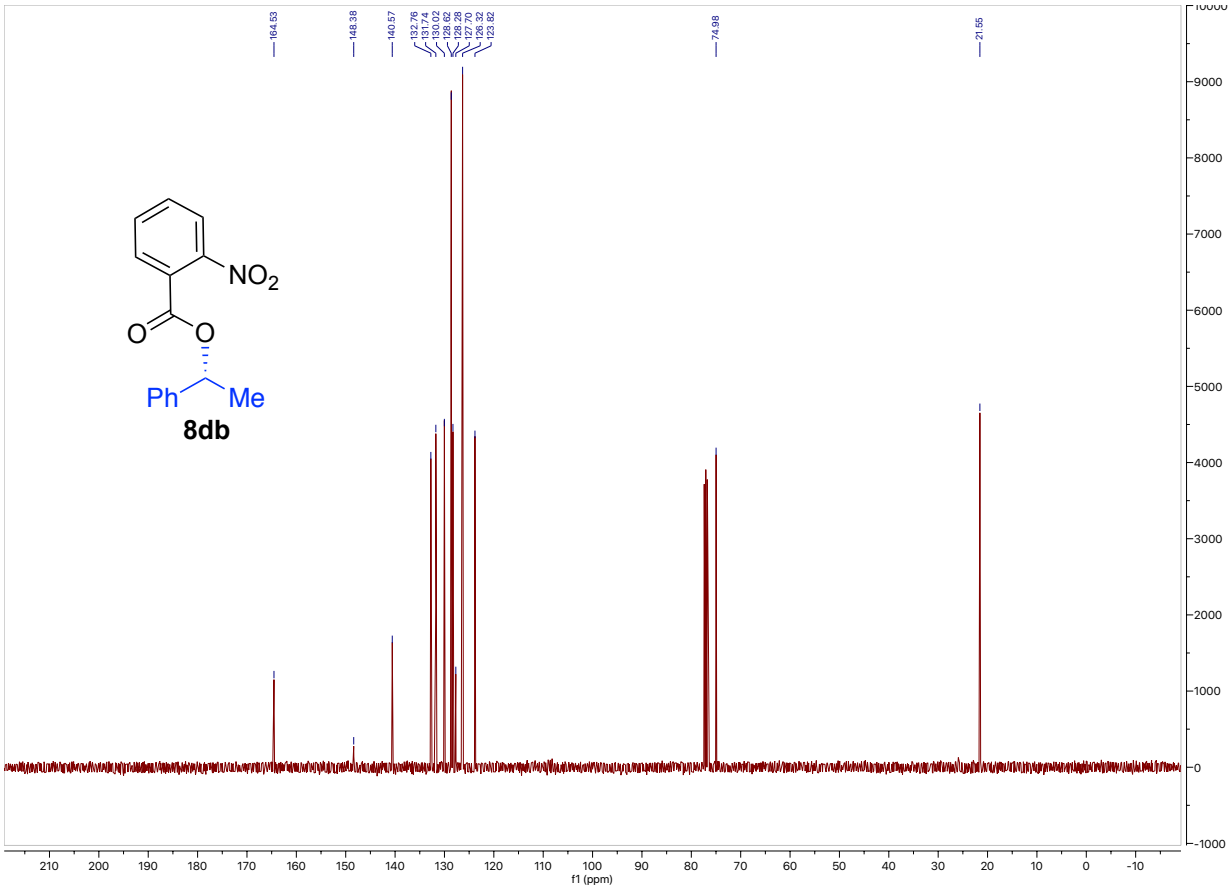
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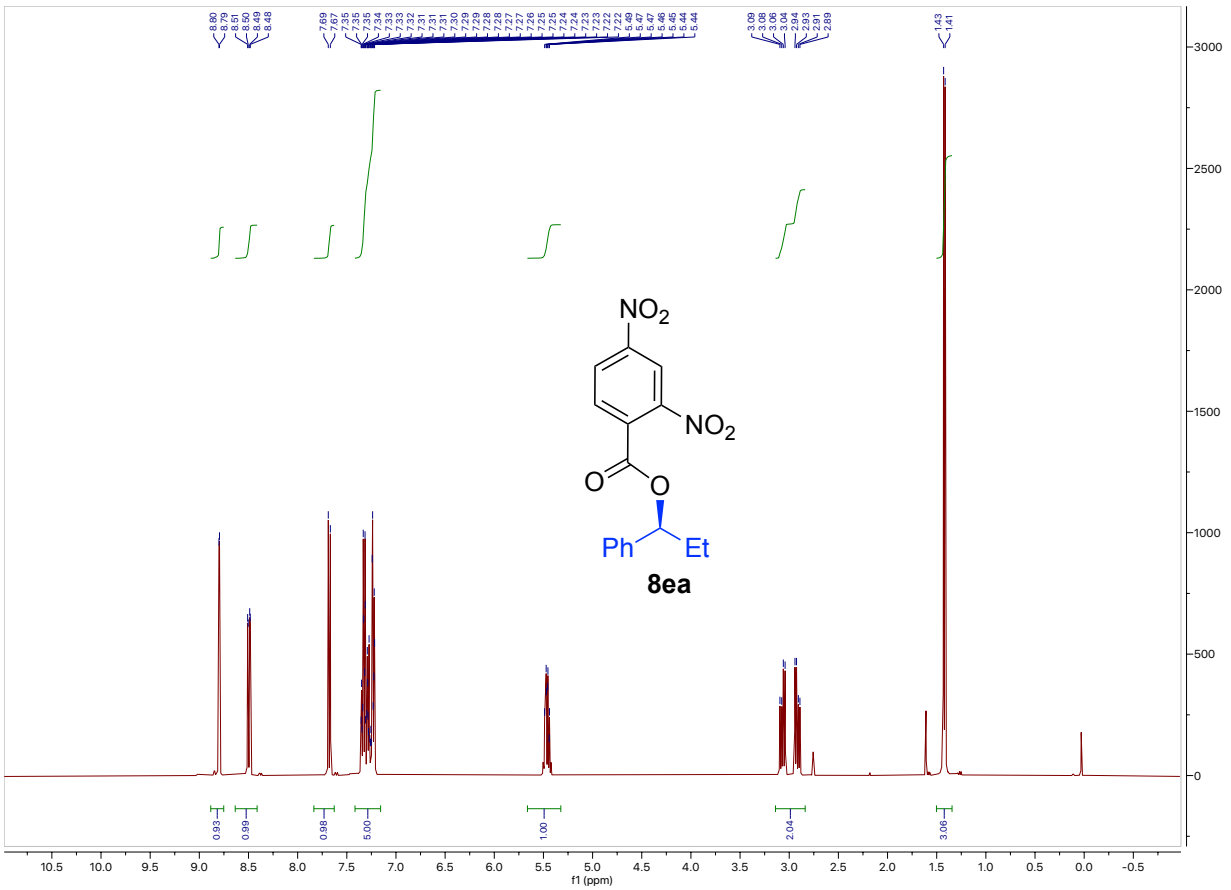
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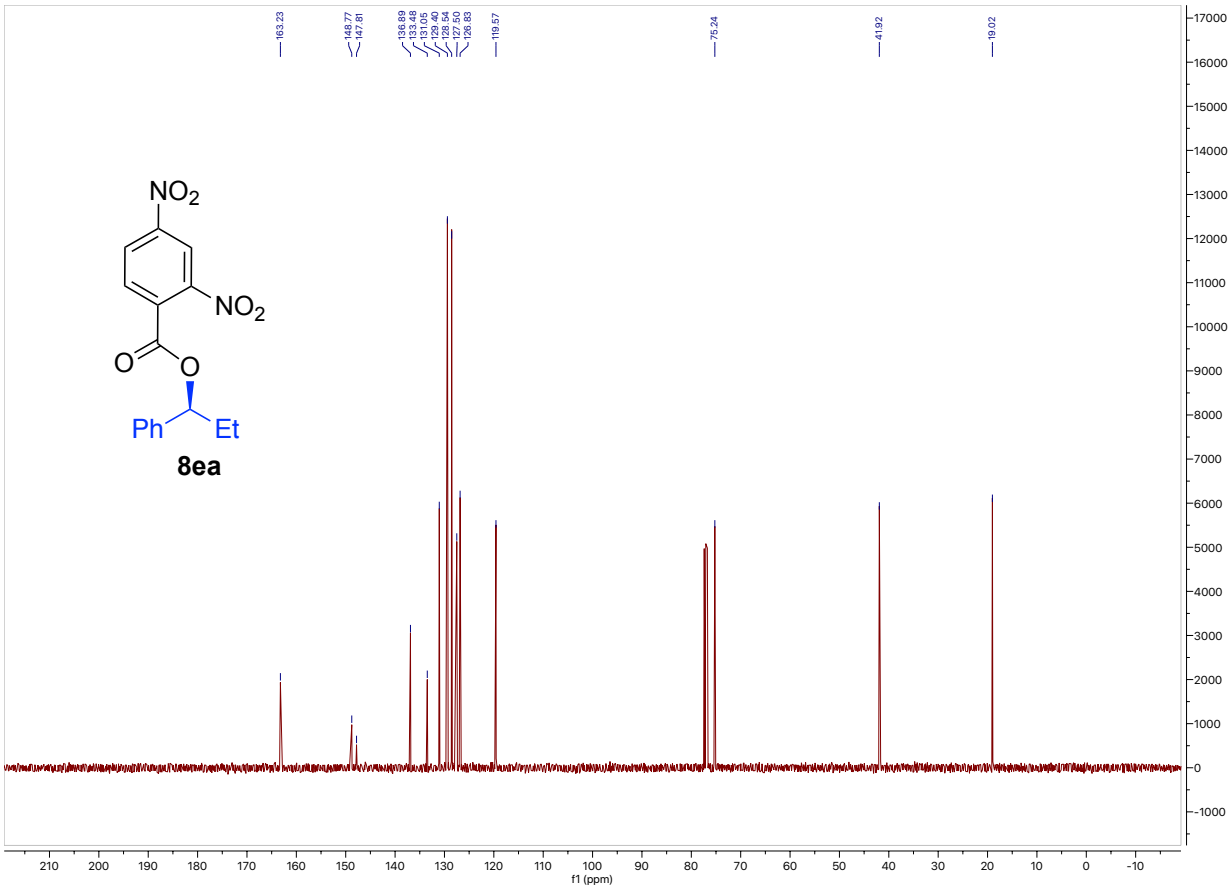
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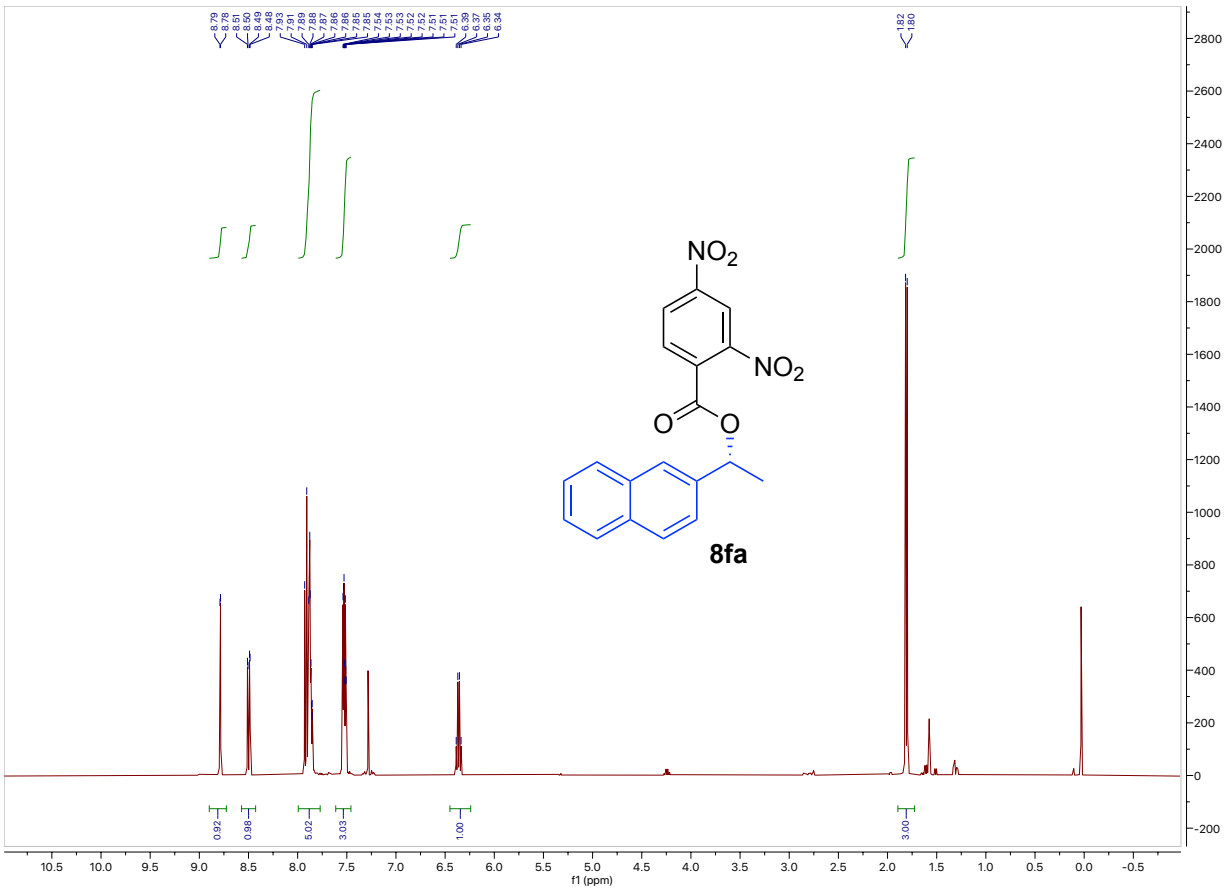
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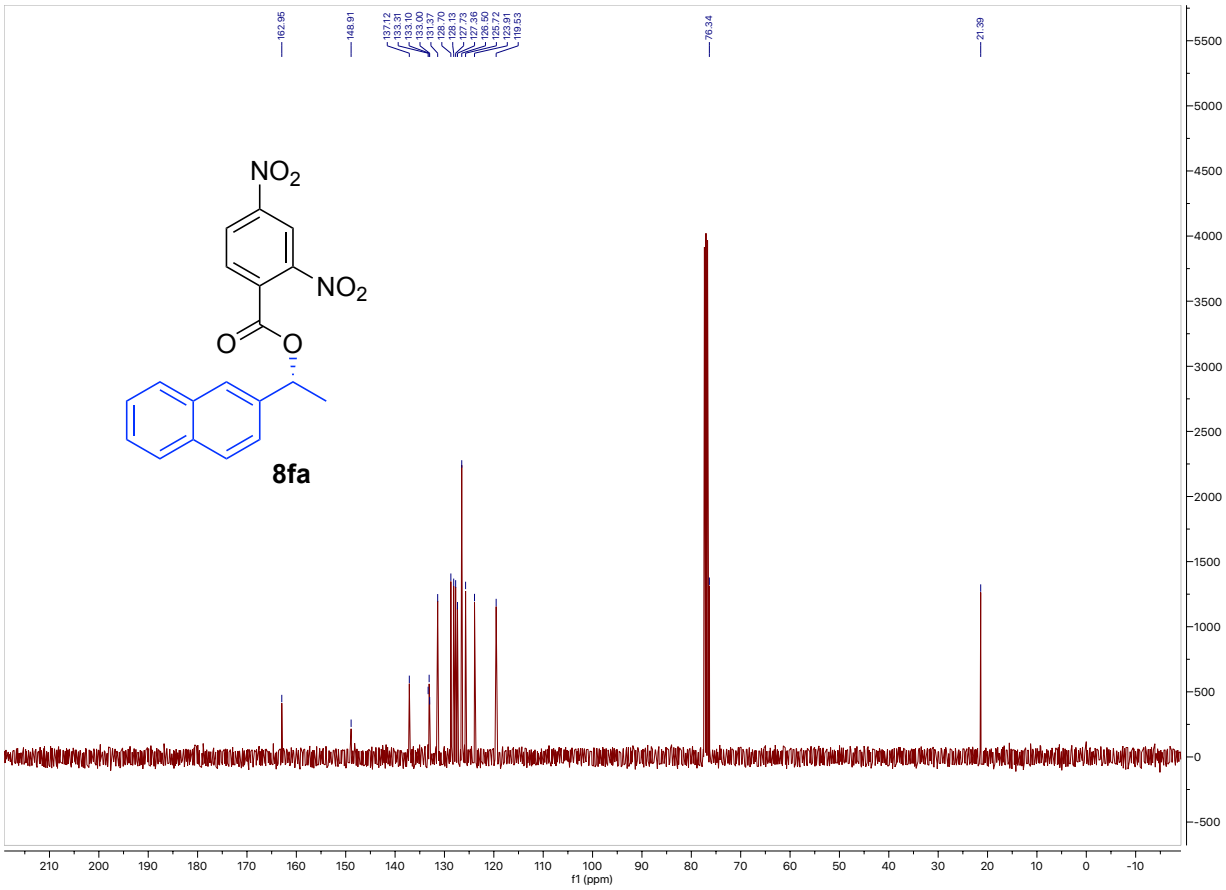
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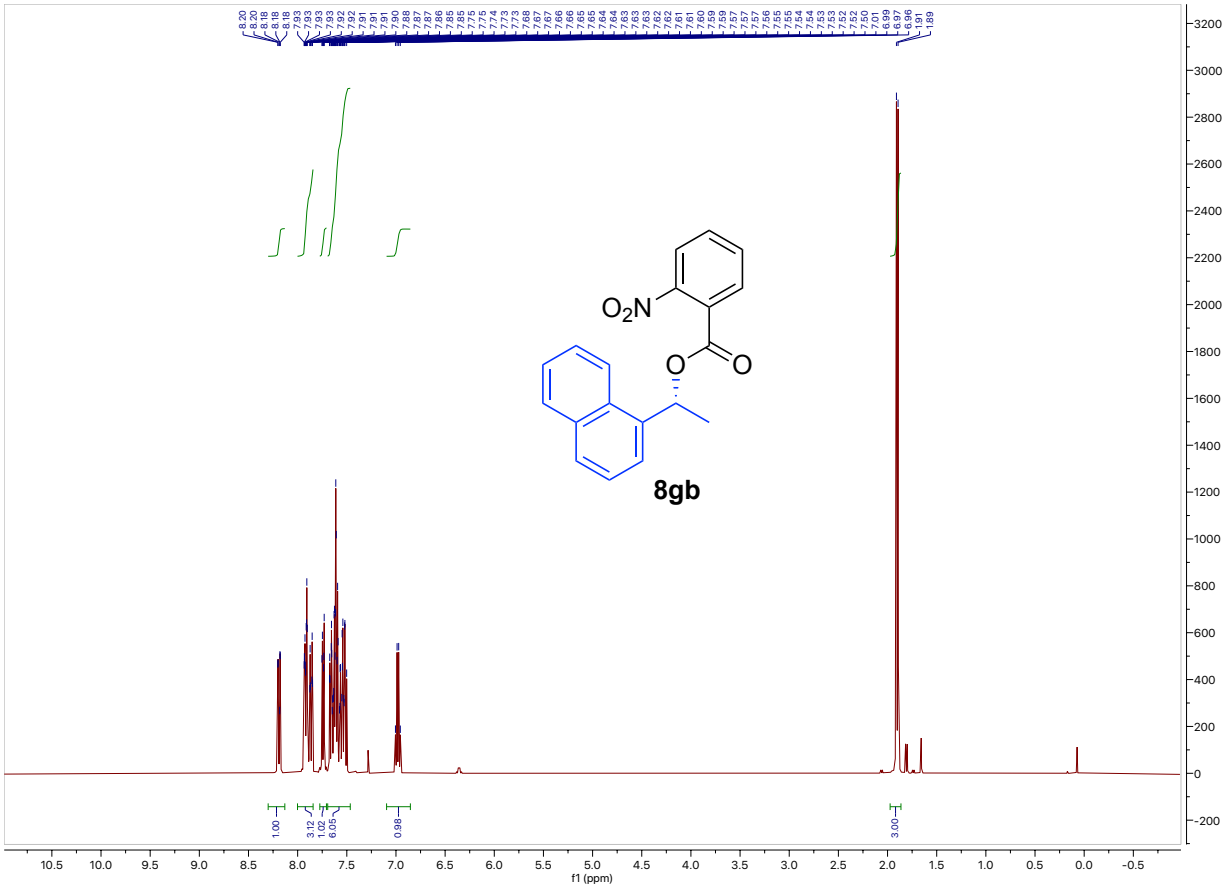
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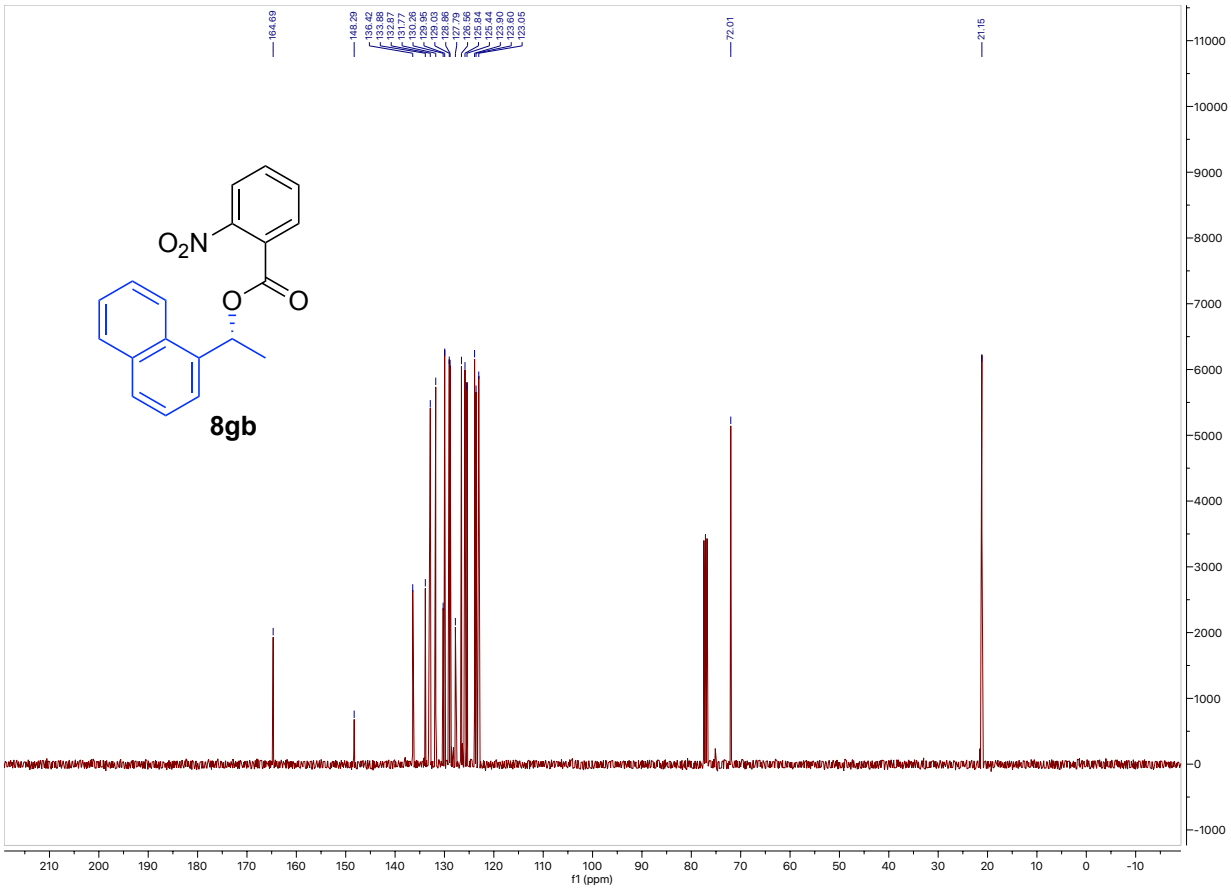
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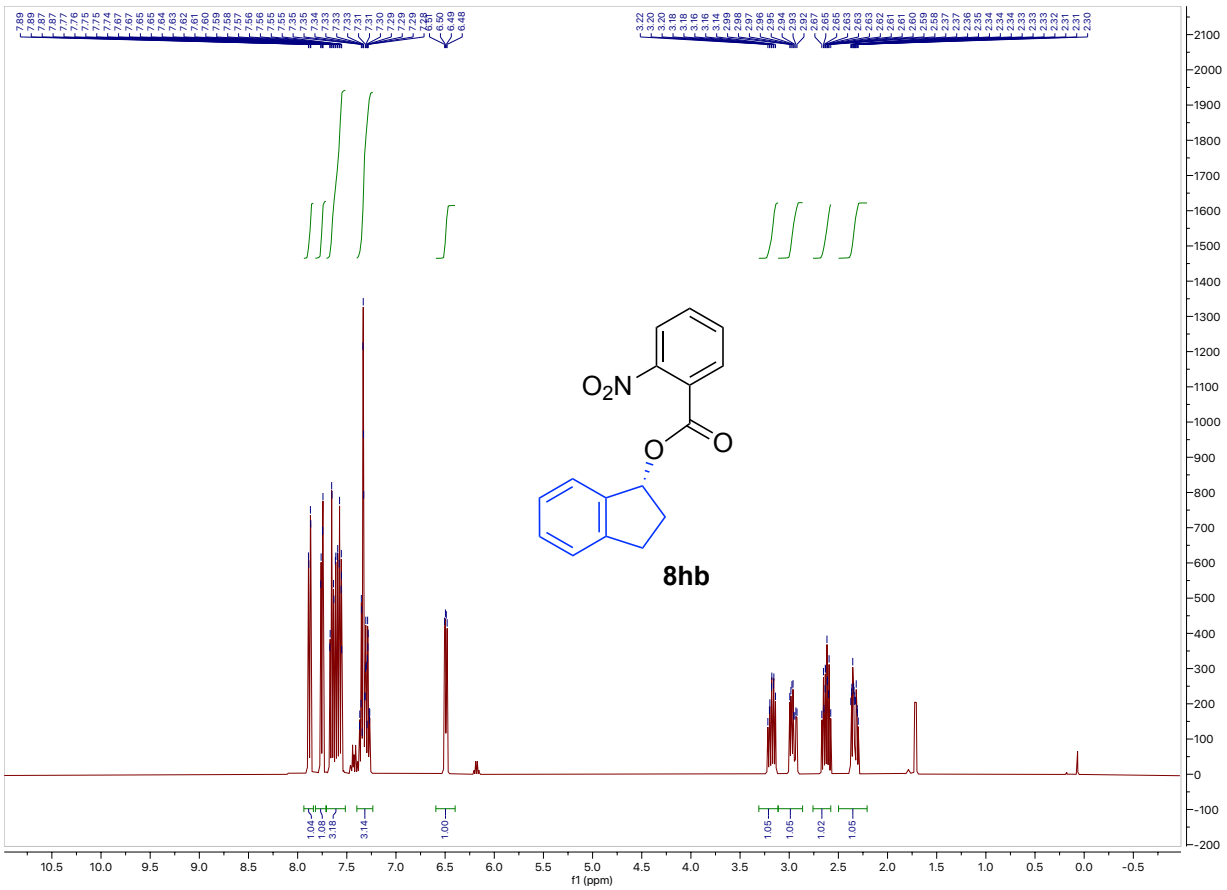
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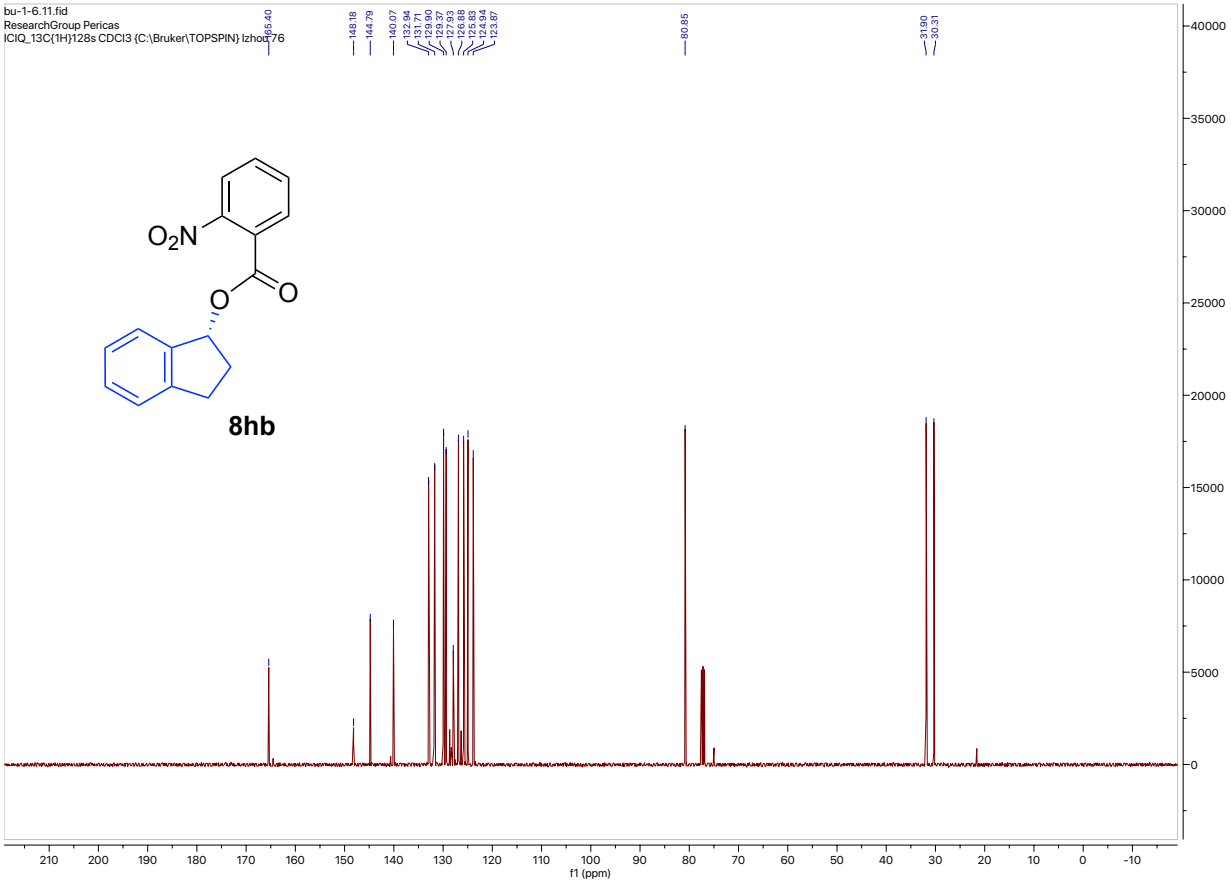
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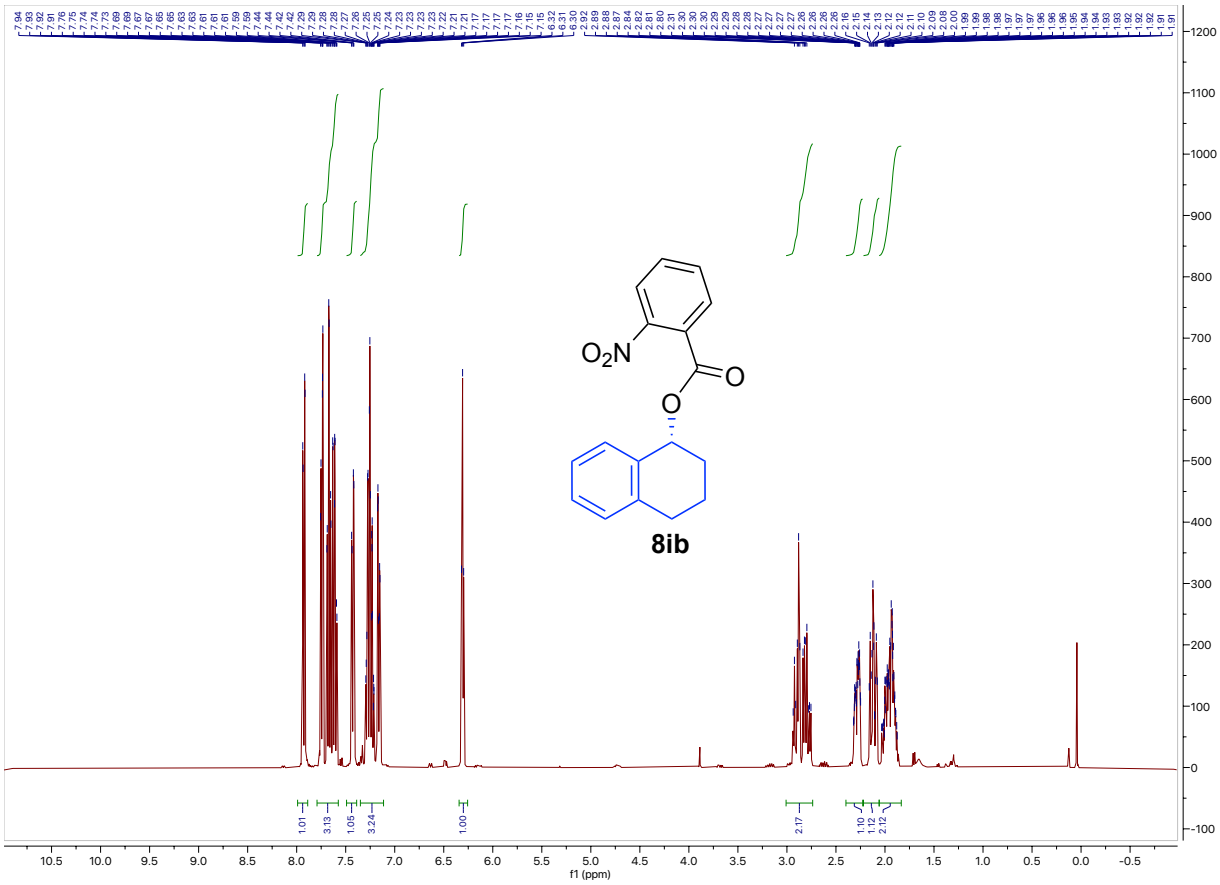
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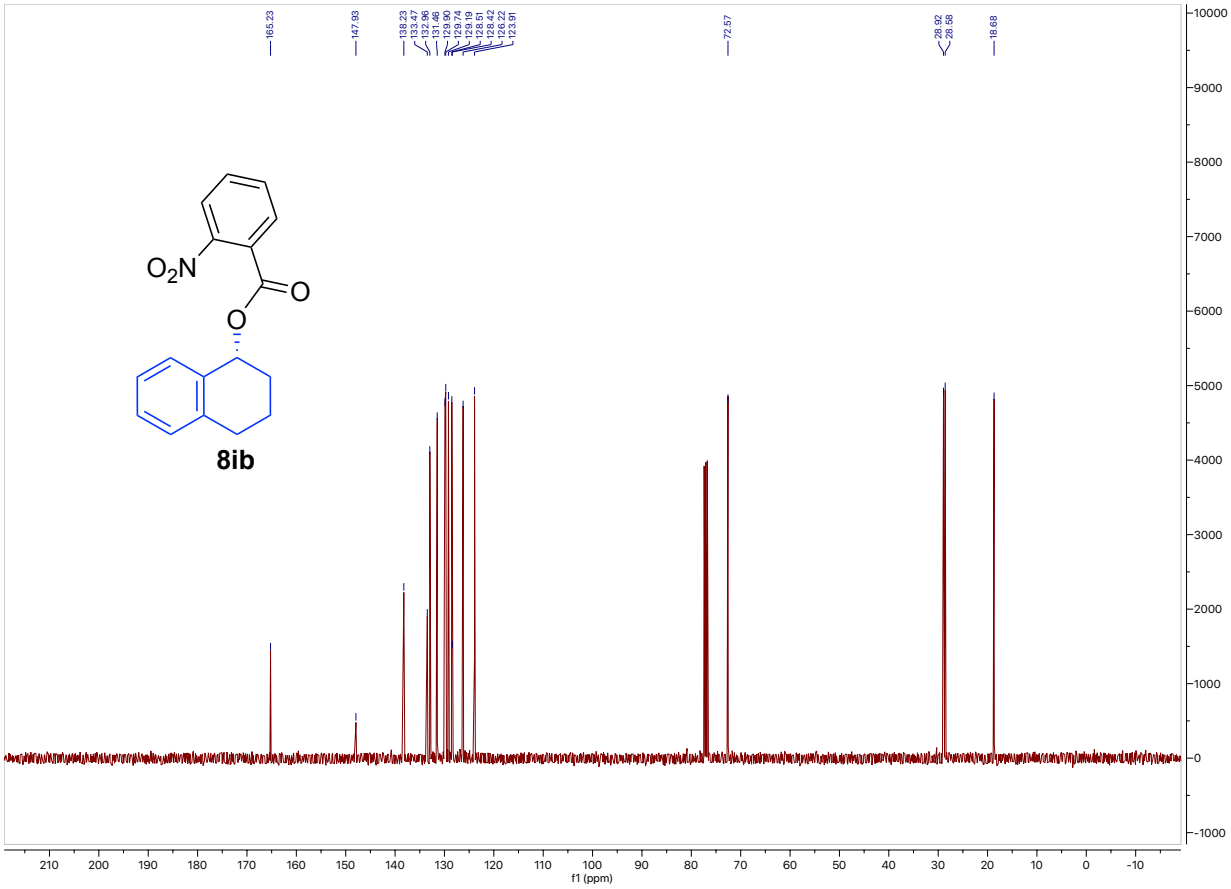
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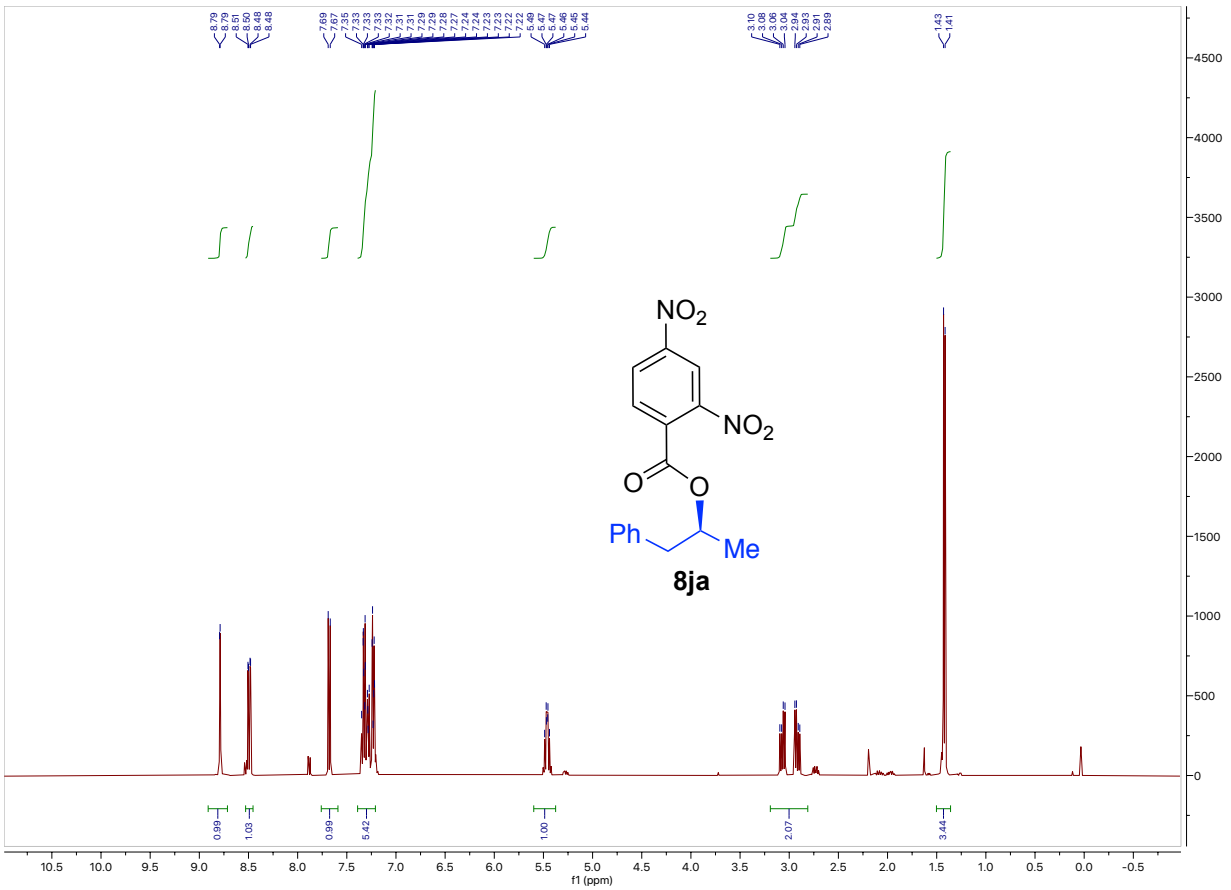
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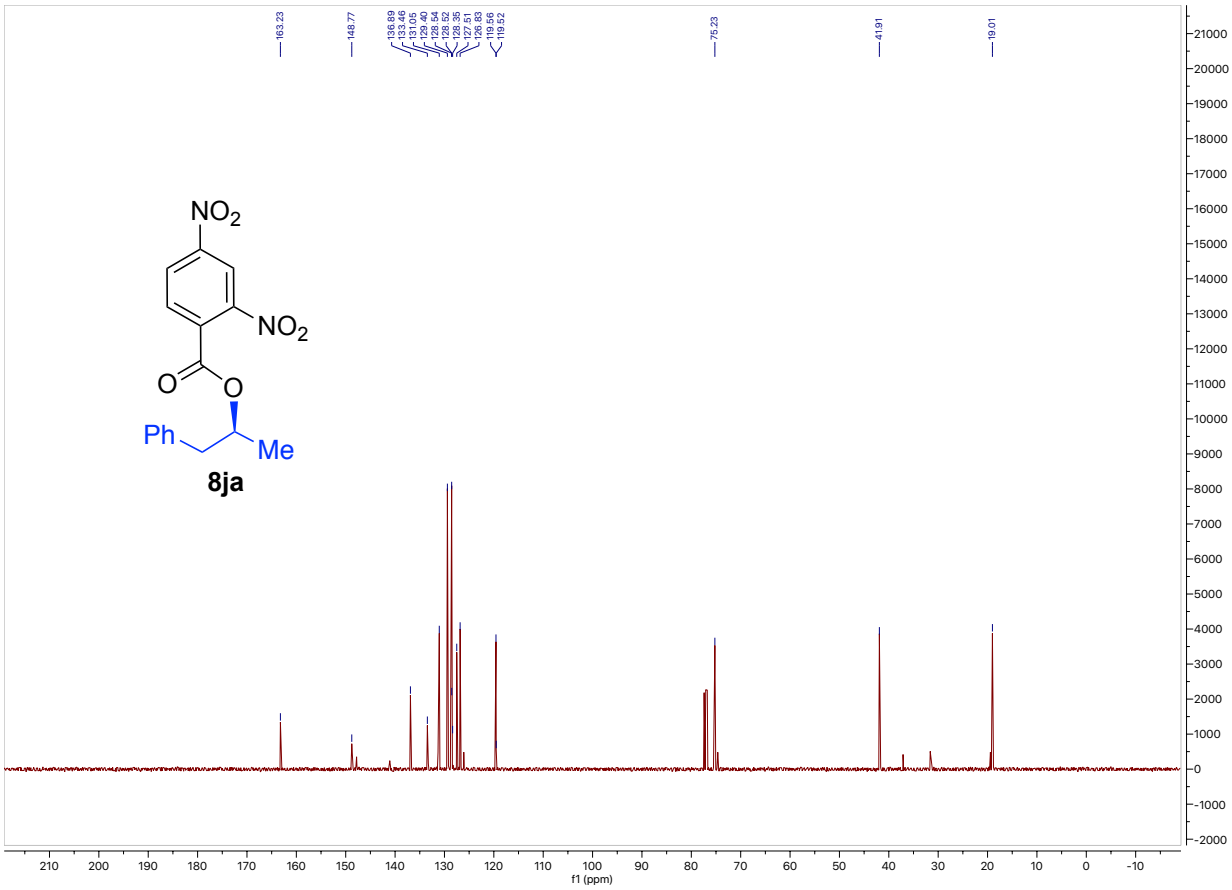
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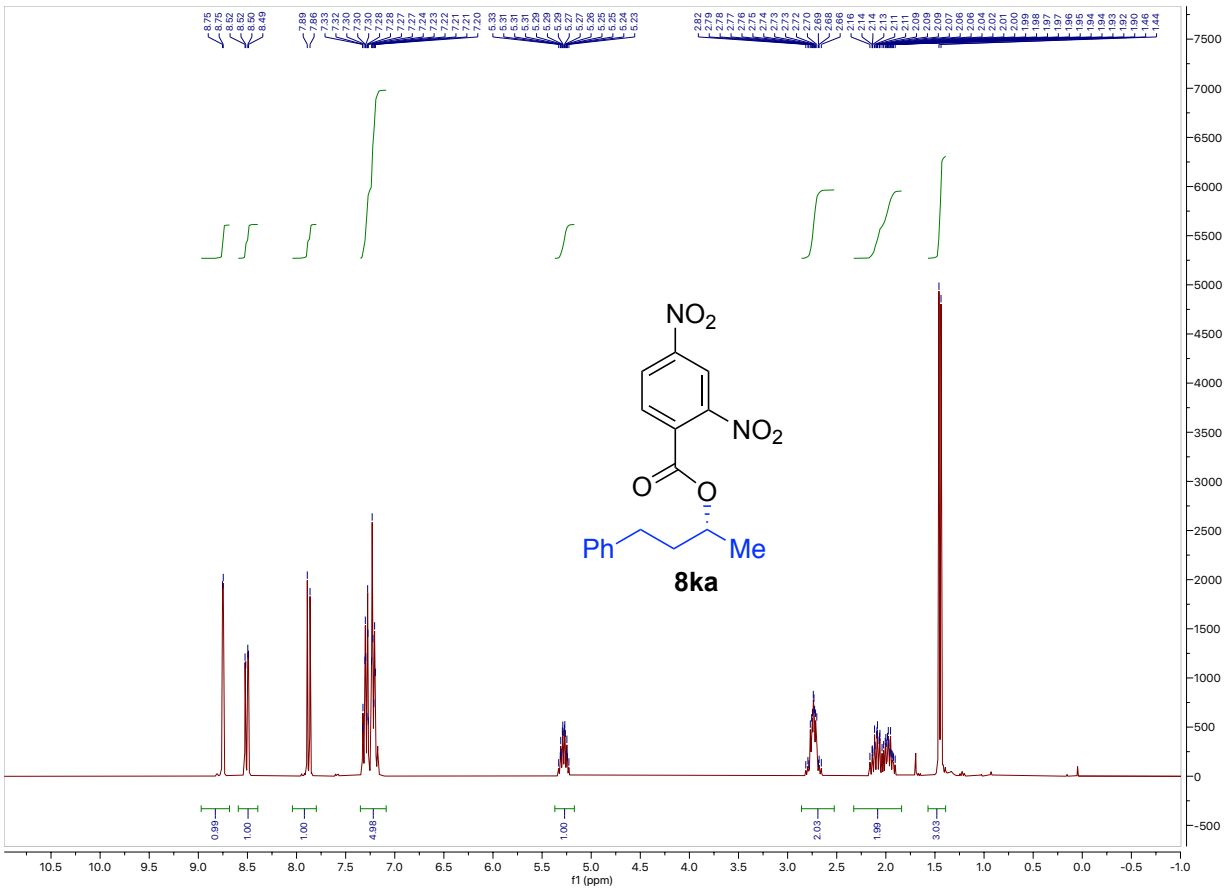
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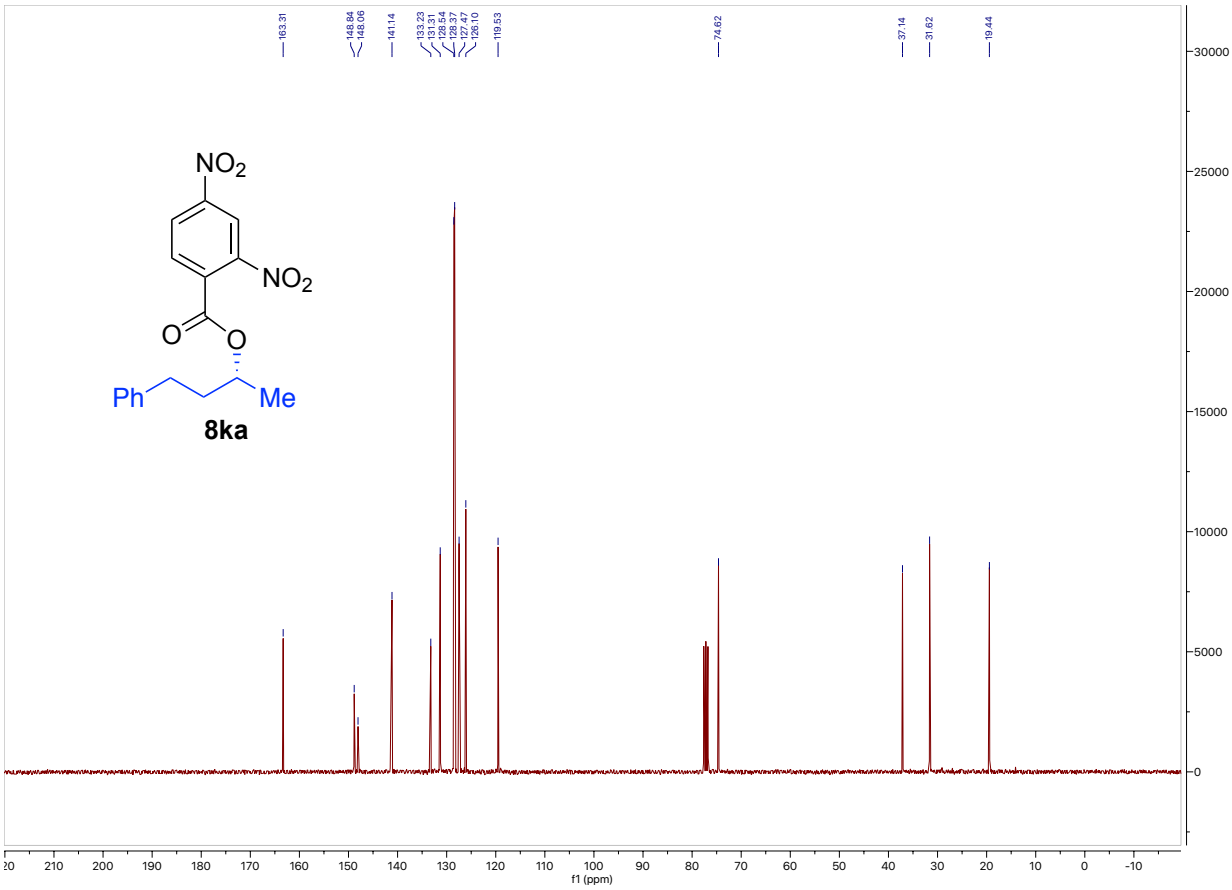
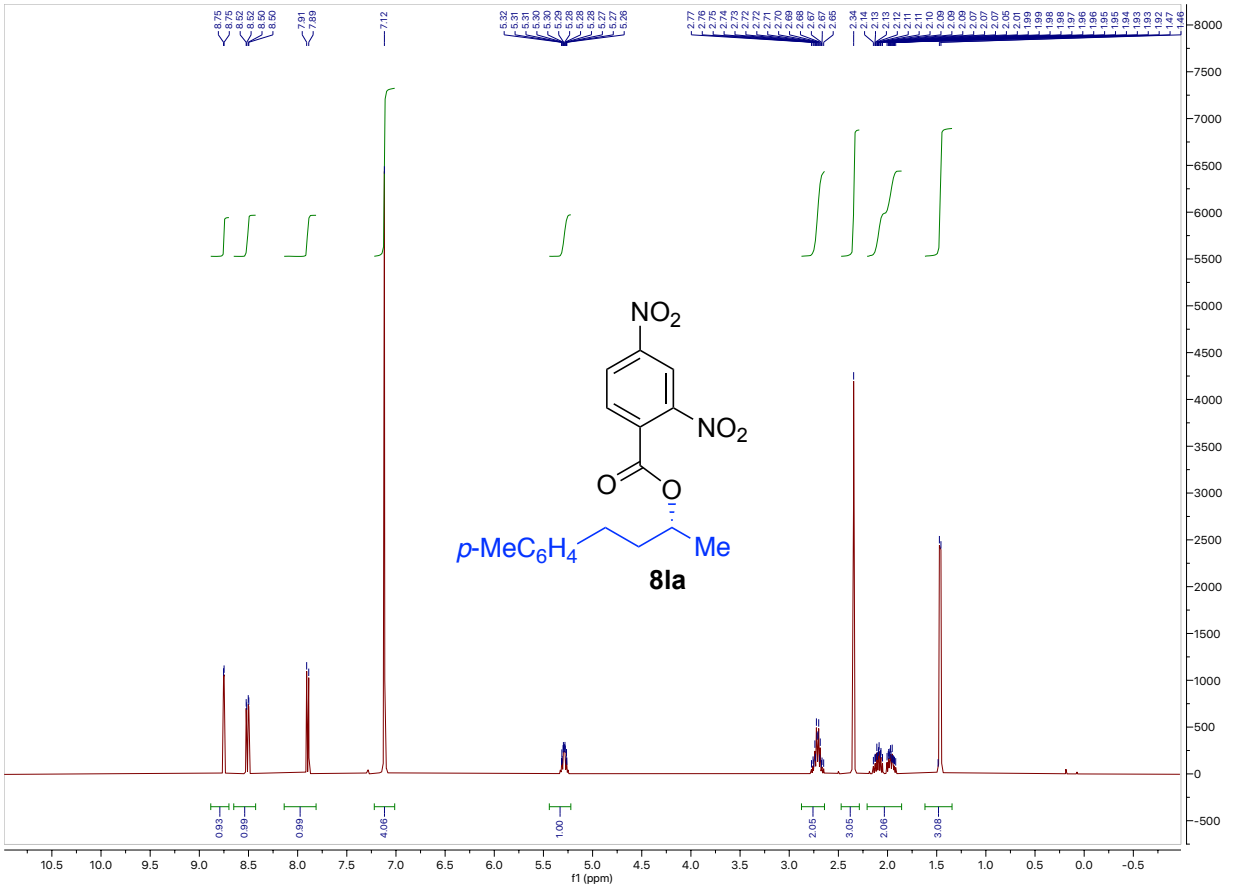
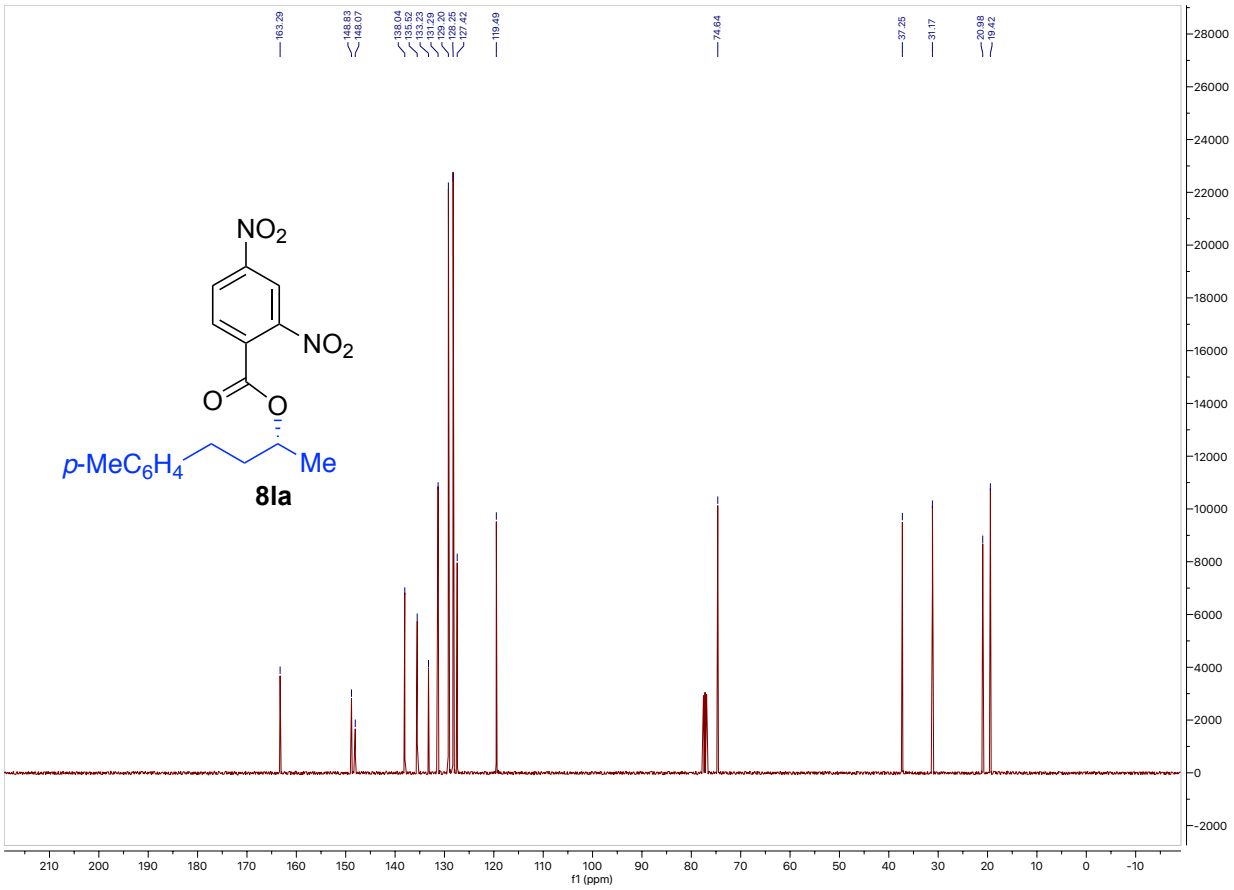
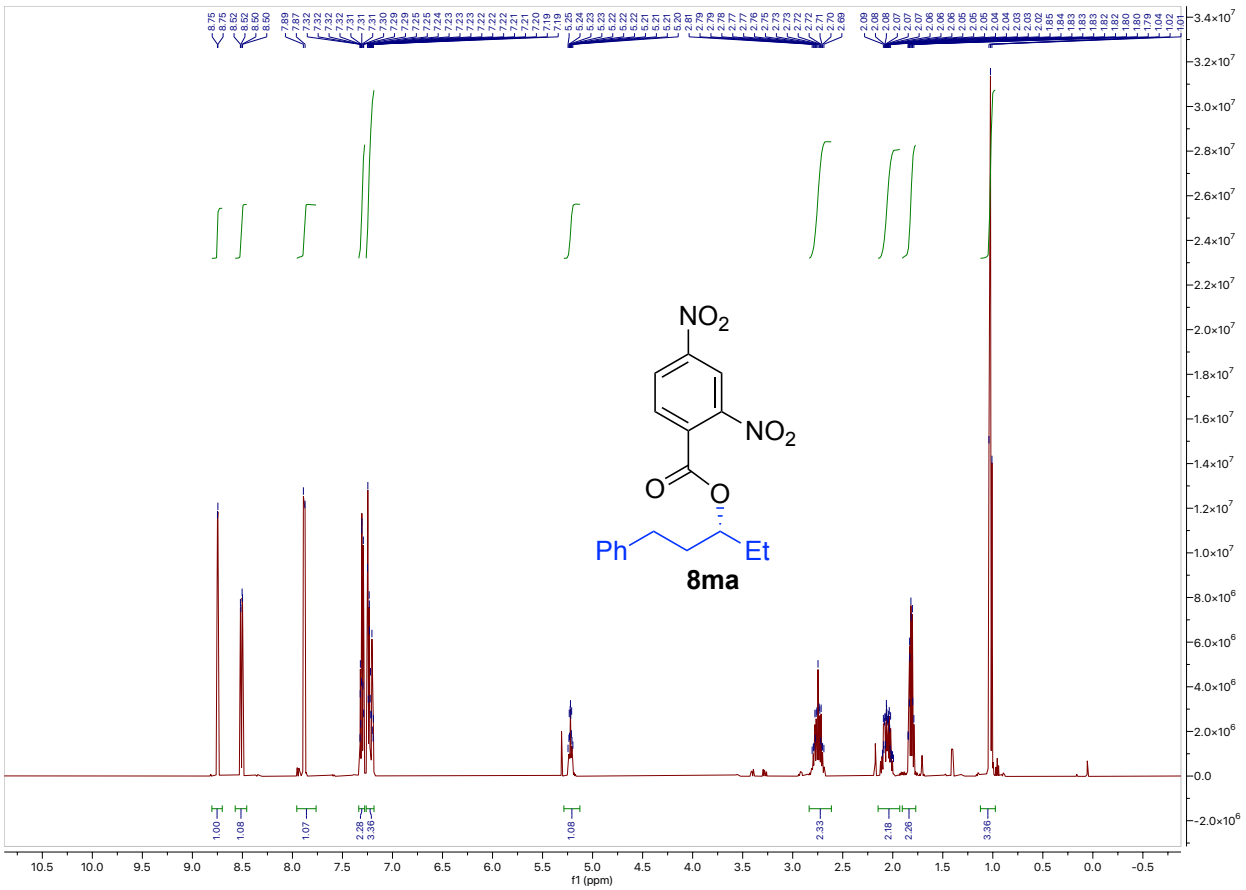
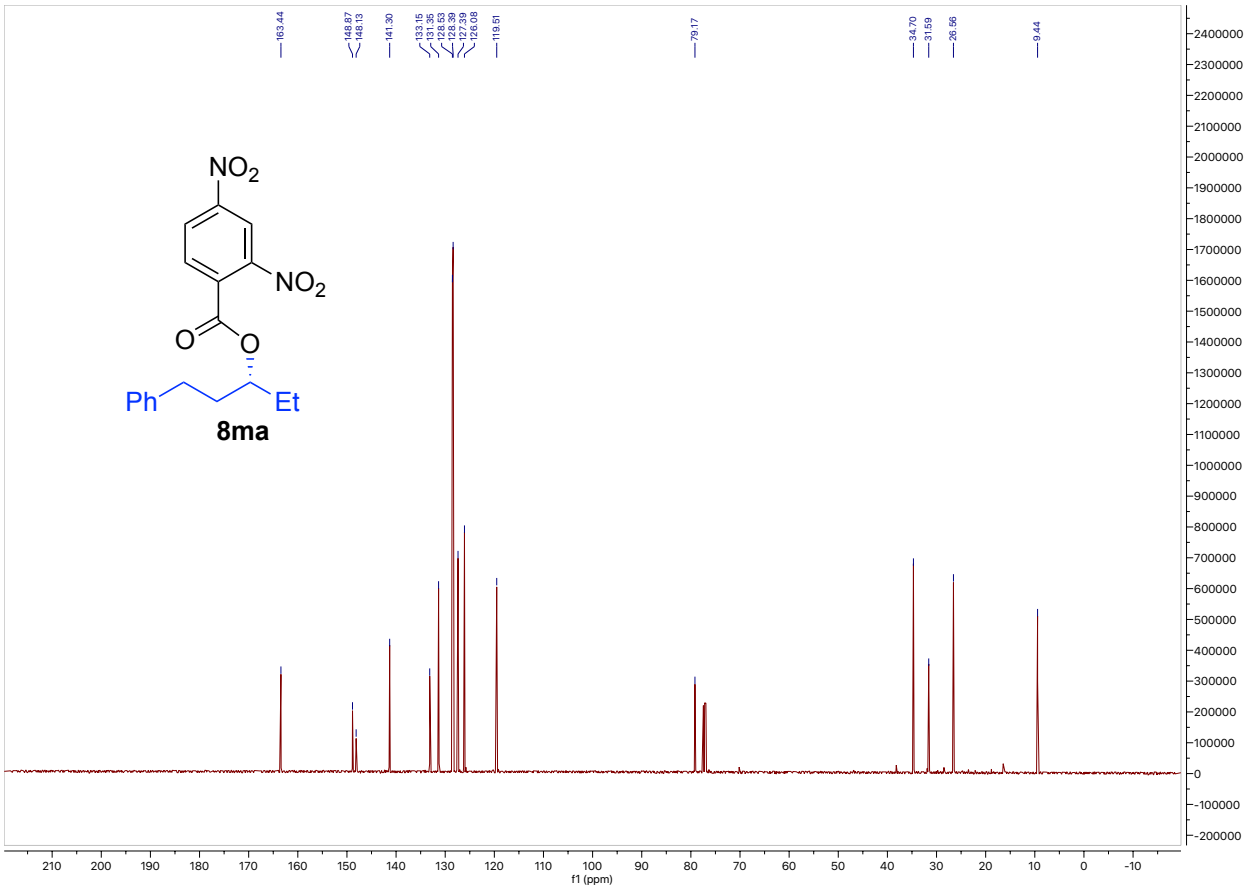
8ka
f1 (ppm)

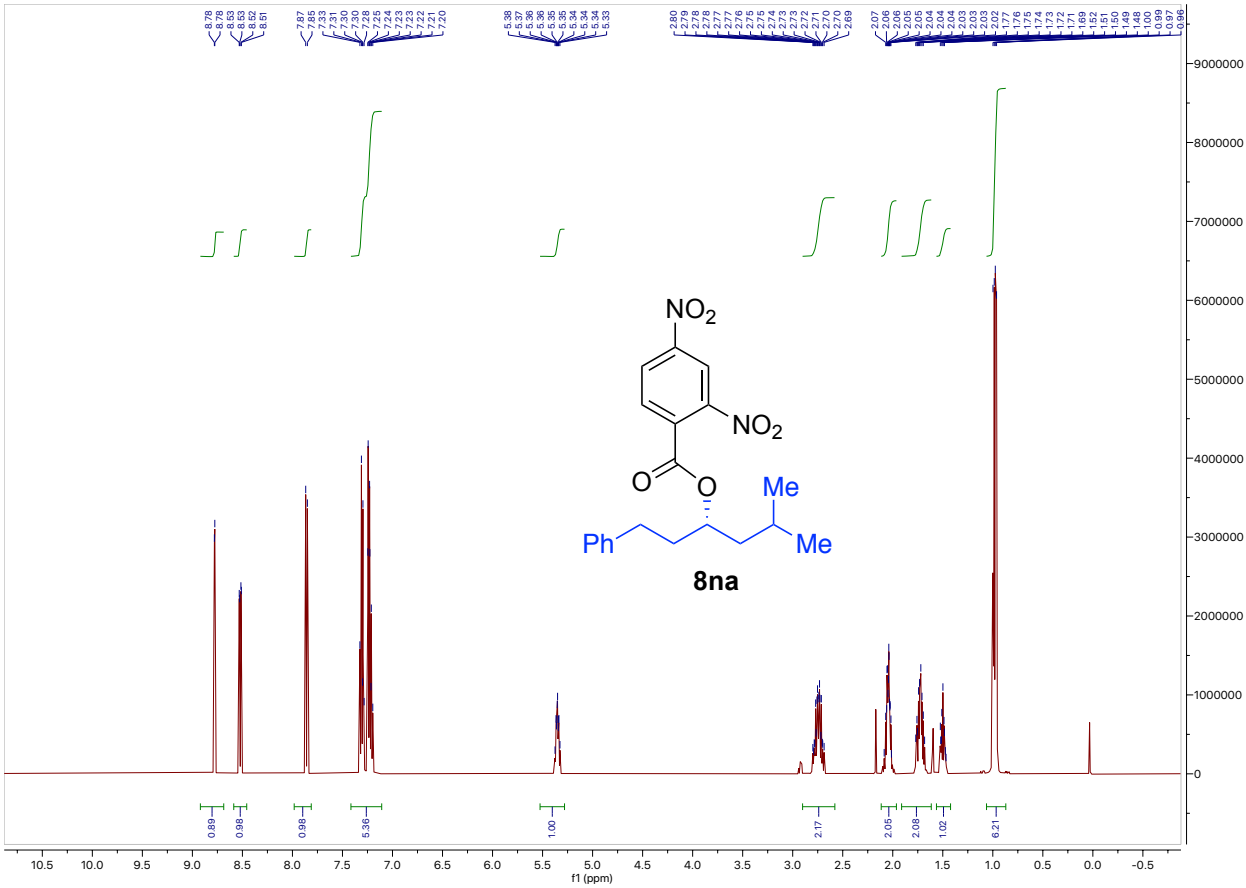

NO2
NO2
O
O
Ph
Me
8ka
f1 (ppm)

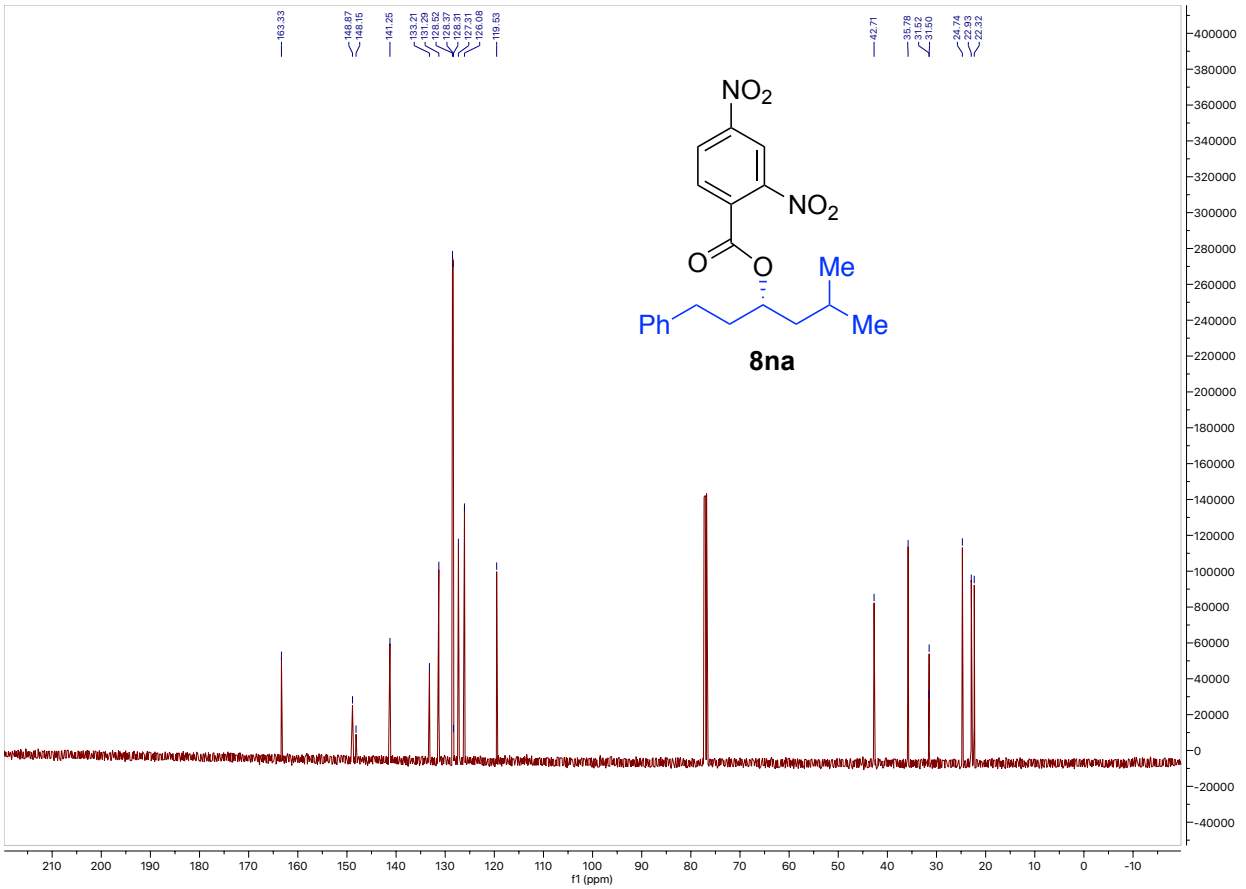

NO2
NO2
O
O
p-MeC6H4
Me
8la

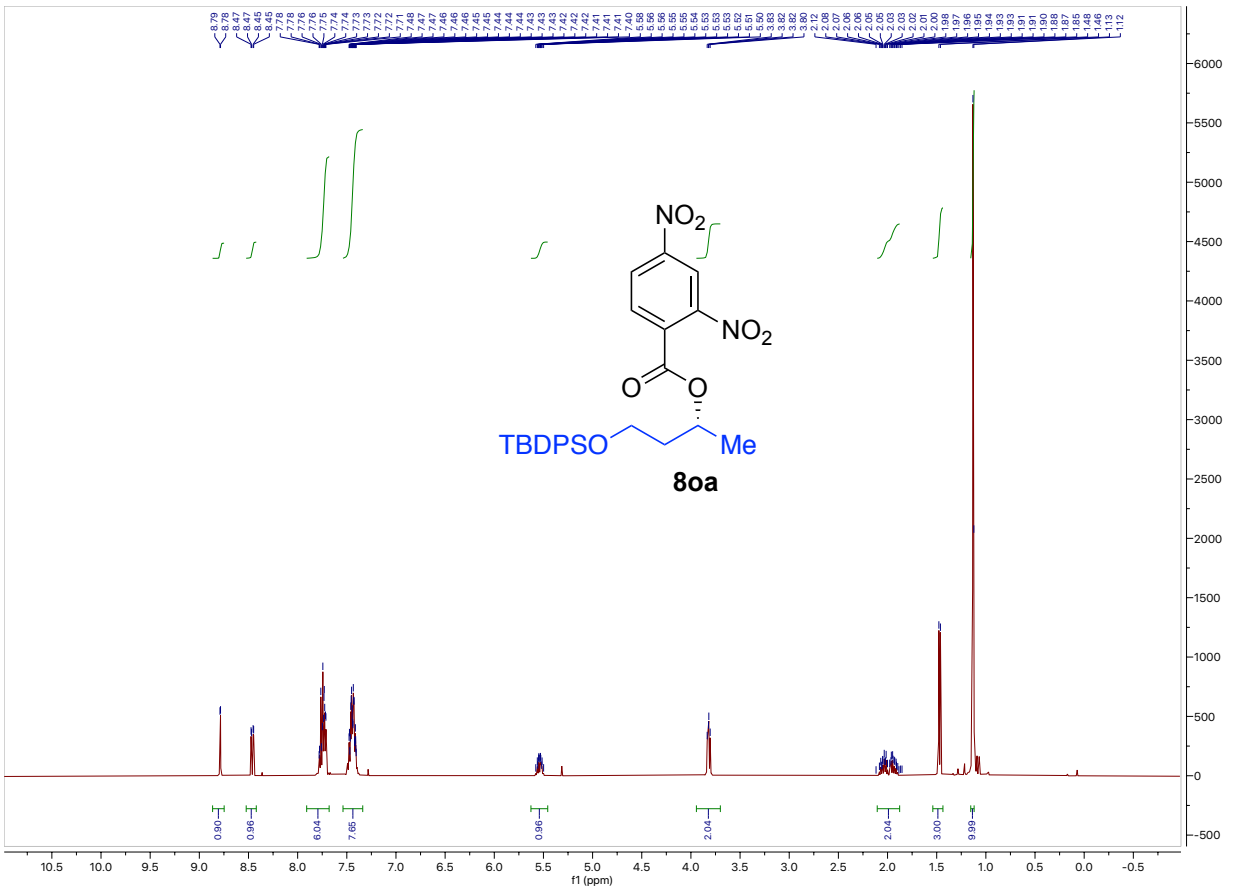

NO2
NO2
O
O
p-MeC6H4
Me
8la

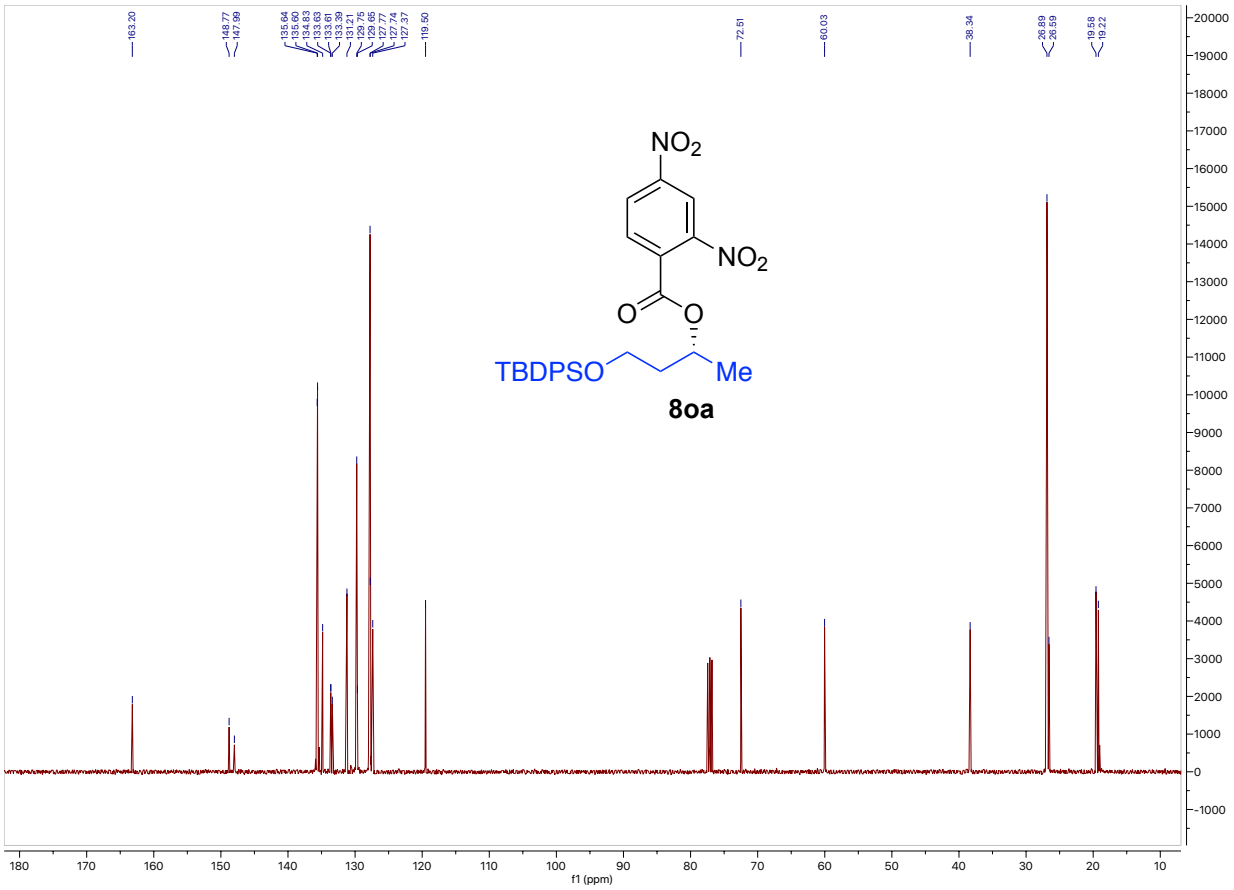

NO2
NO2
O
O
Ph
Et
8ma
f1 (ppm)

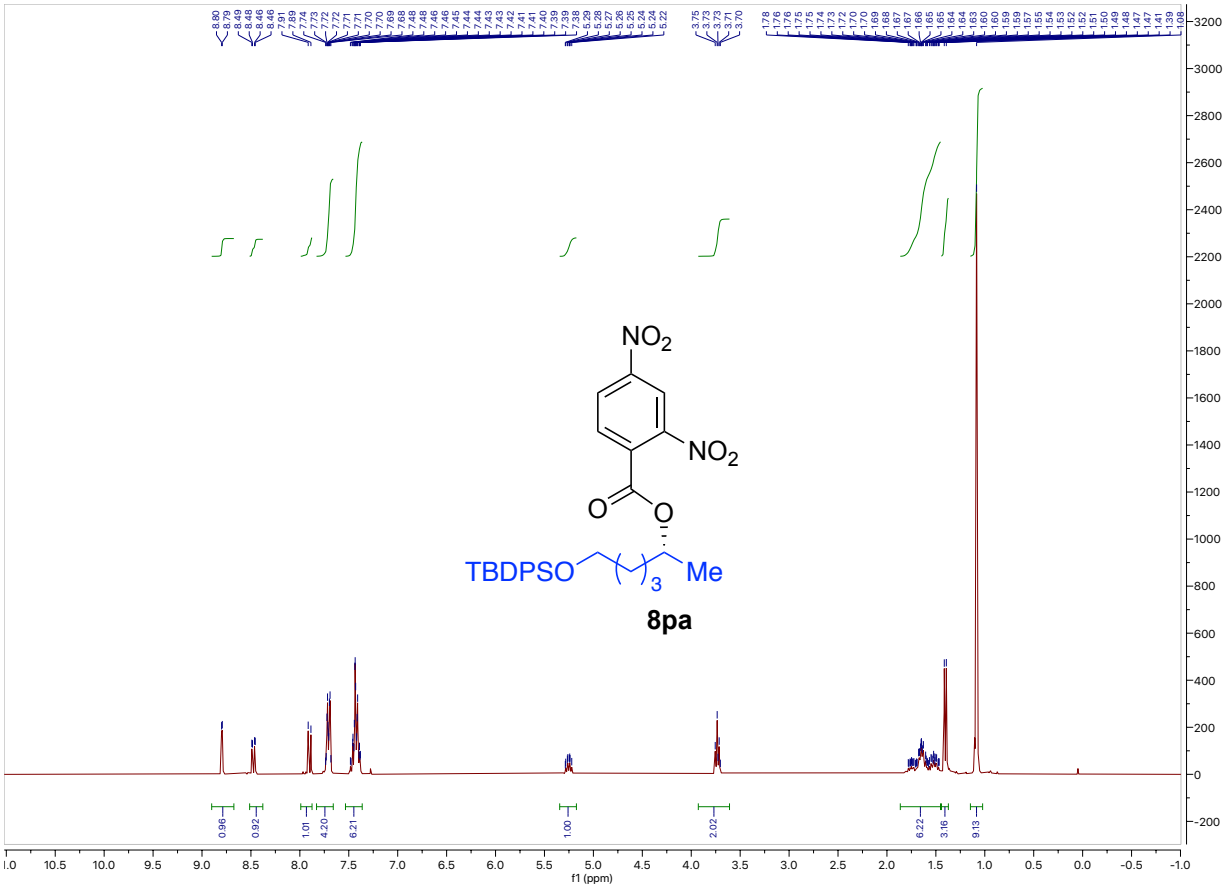

NO2
NO2
O
O
Ph
Et
8ma
f1 (ppm)

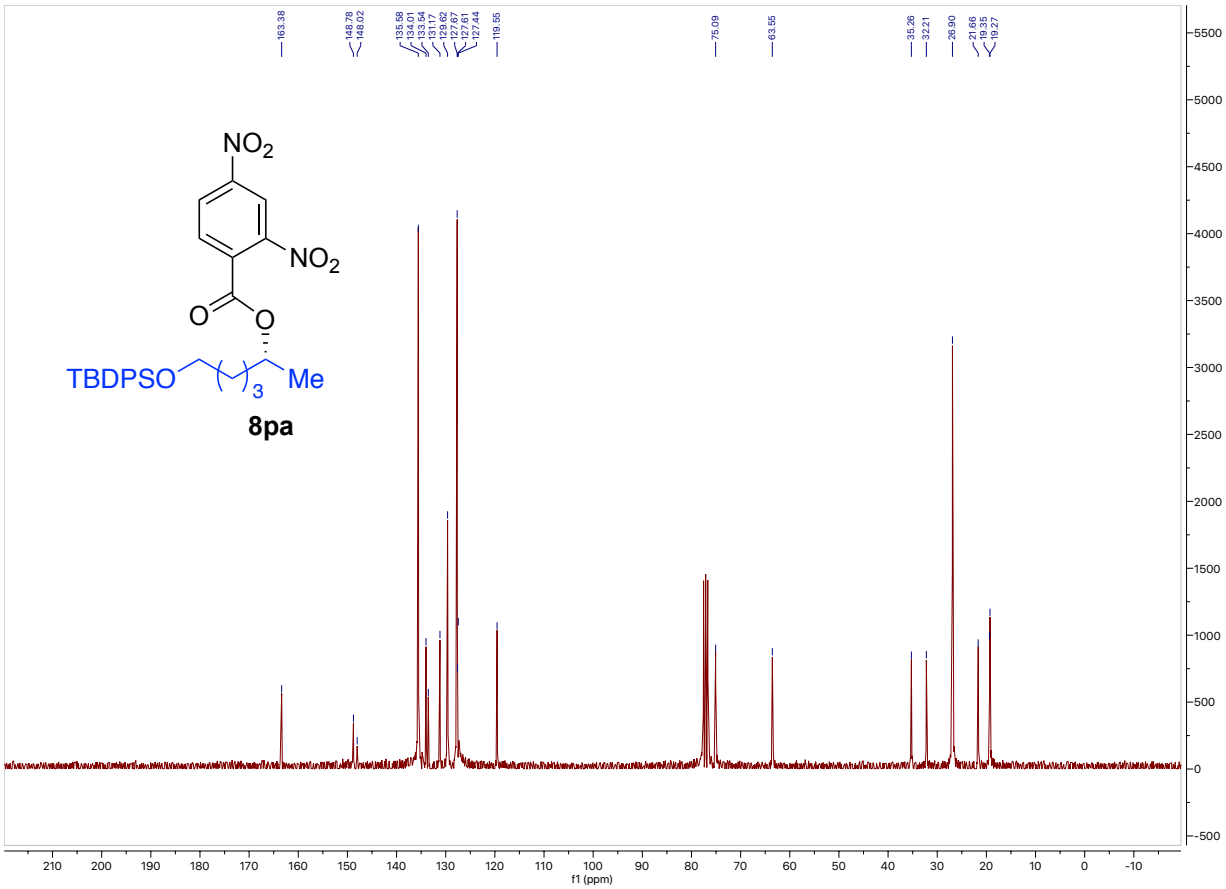

NO2
NO2
O
O
Me
Ph
Me
8na
f1 (ppm)

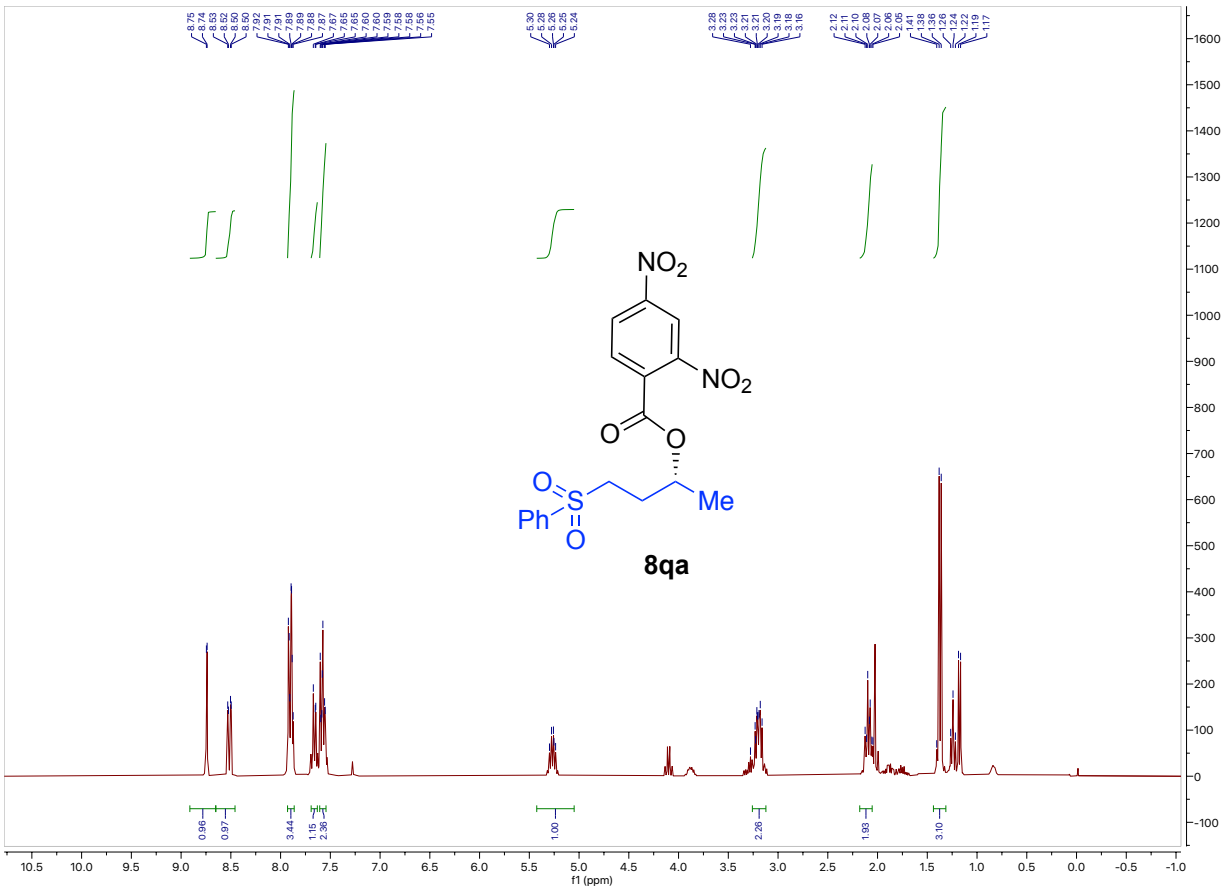

NO2
NO2
O
O
Me
Ph
Me
8na
f1 (ppm)

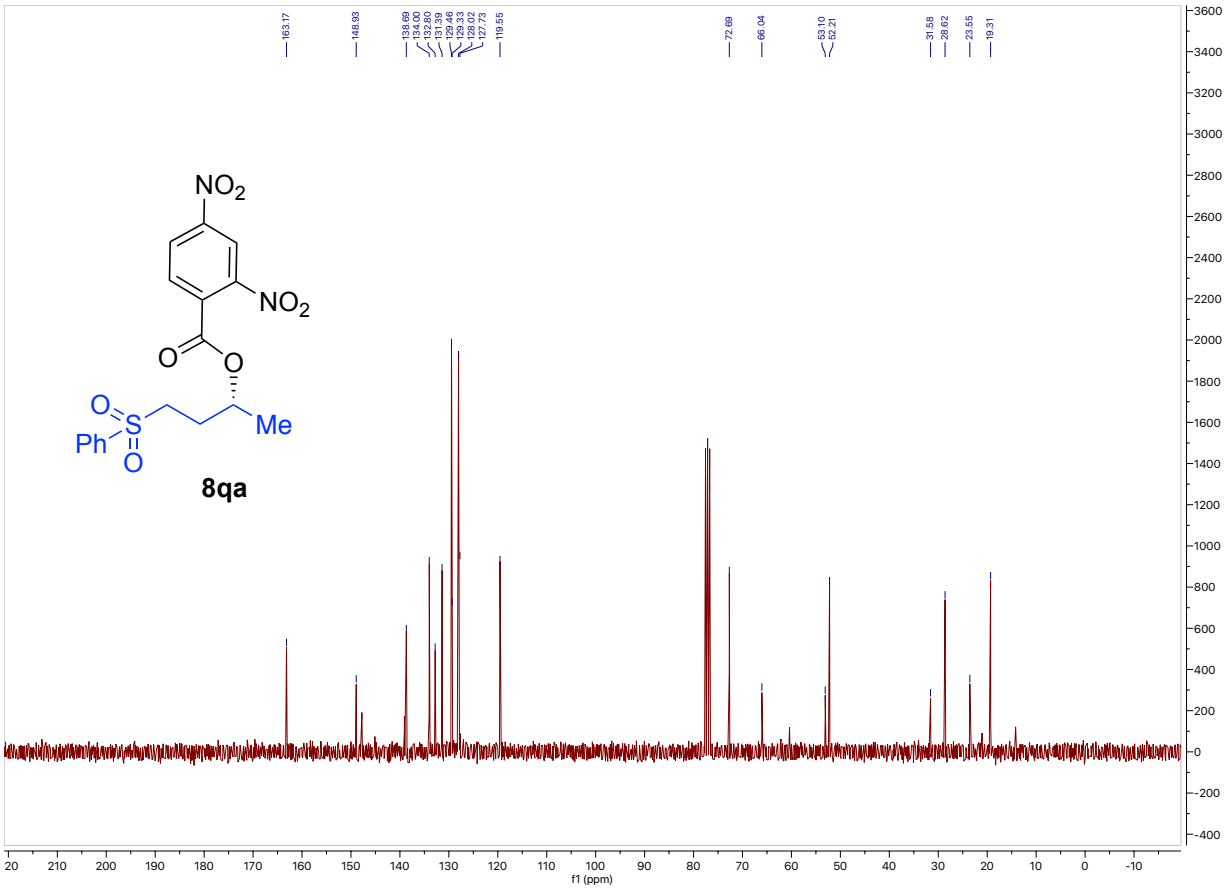

NO2
NO2
O
O
TBDPSO
Me
8oa
f1 (ppm)

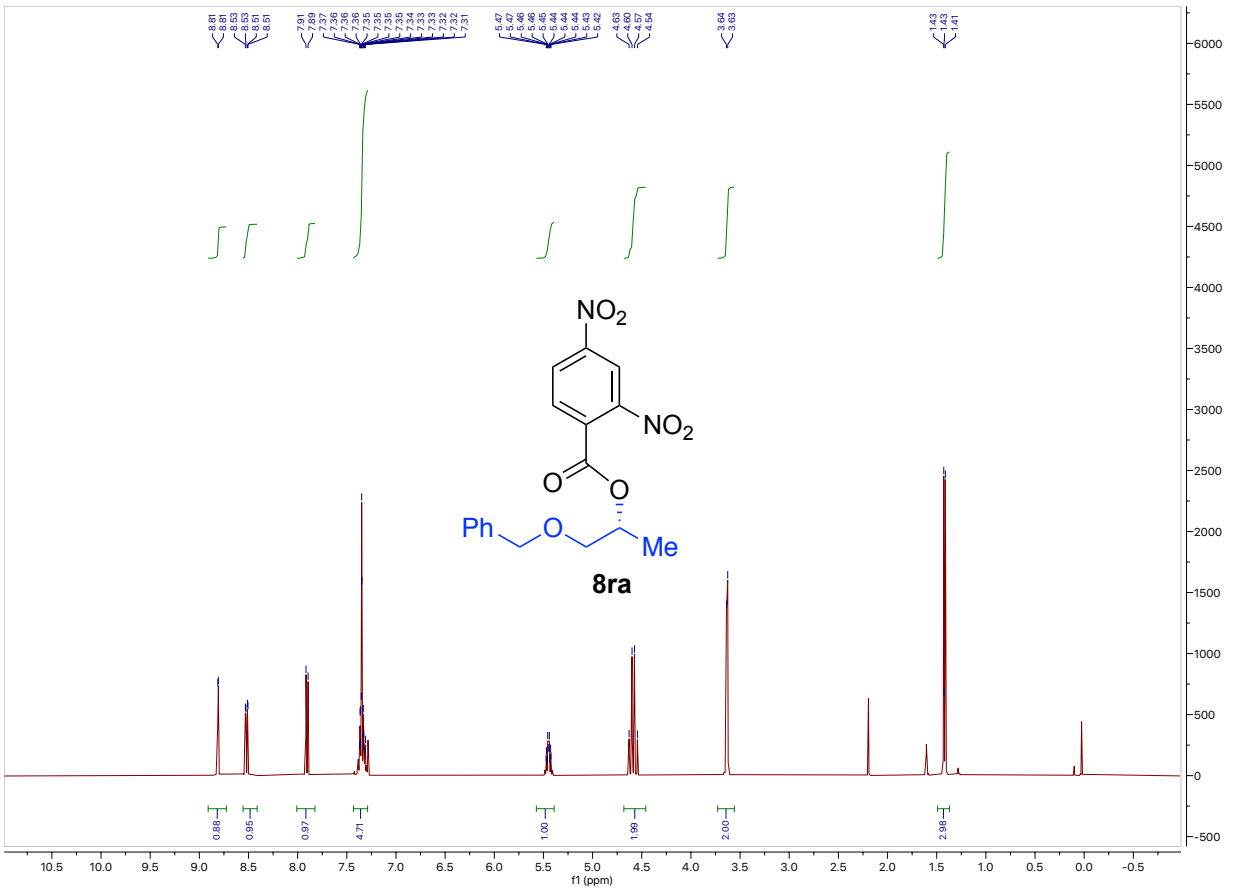

NO2
NO2
O
O
TBDPSO
Me
8oa
f1 (ppm)

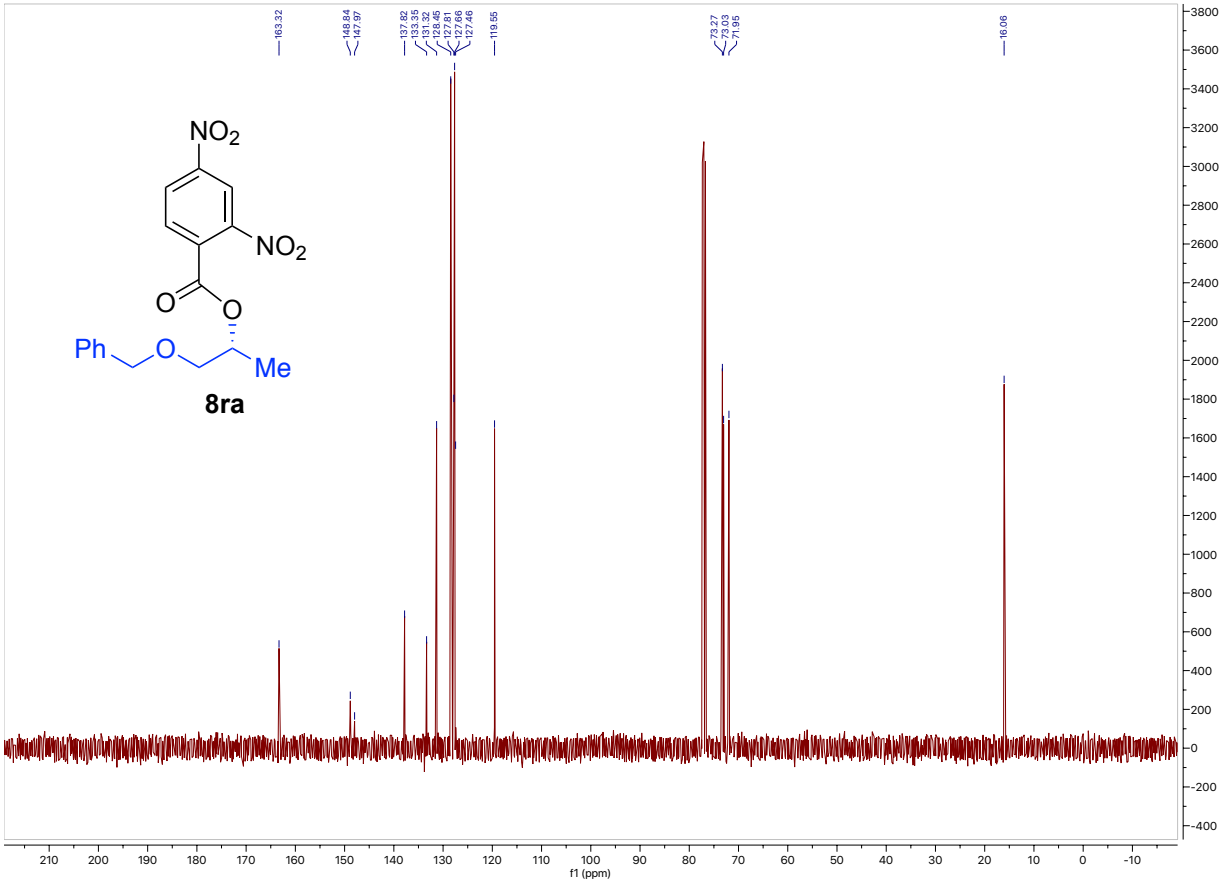

NO2
NO2
O
O
TBDPSO
3
Me
8pa
f1 (ppm)

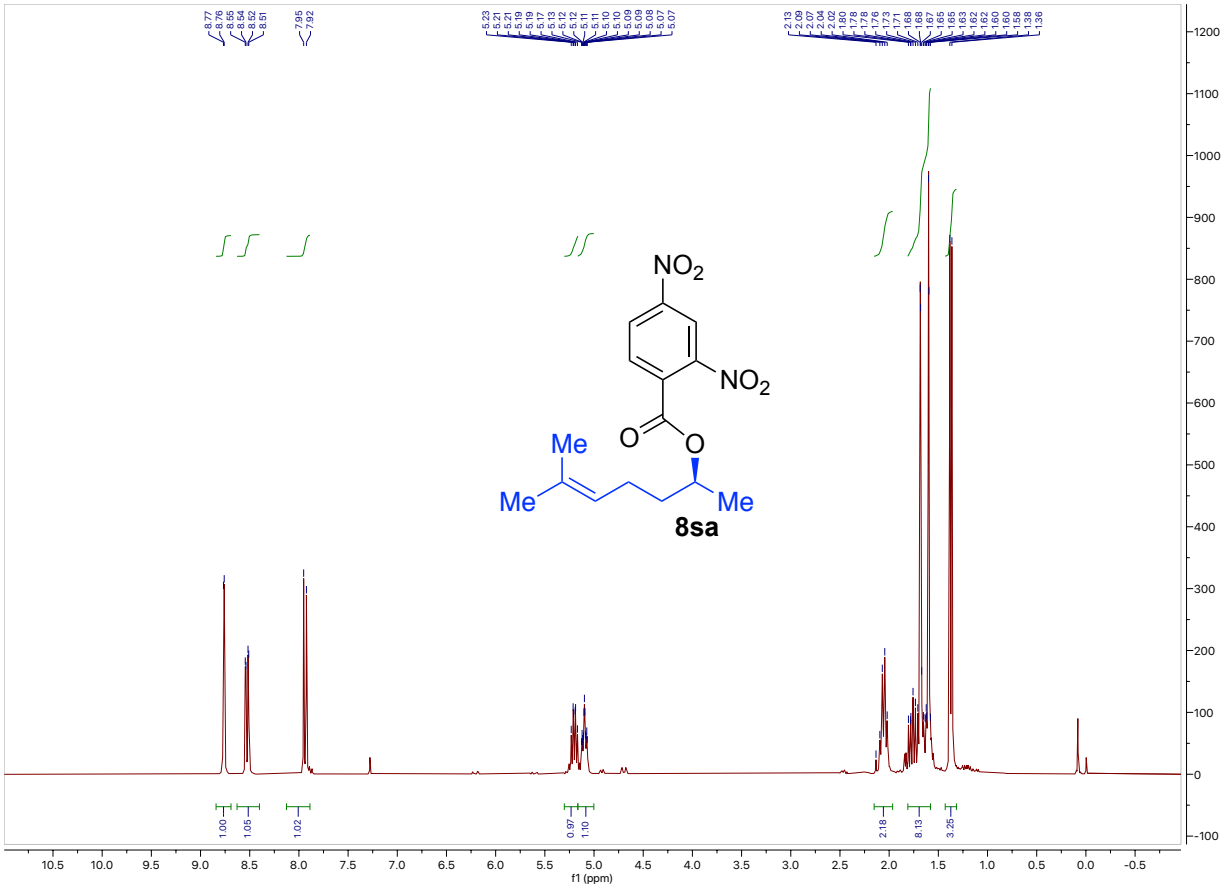

NO2
NO2
O
O
TBDPSO
3
Me
8pa
f1 (ppm)

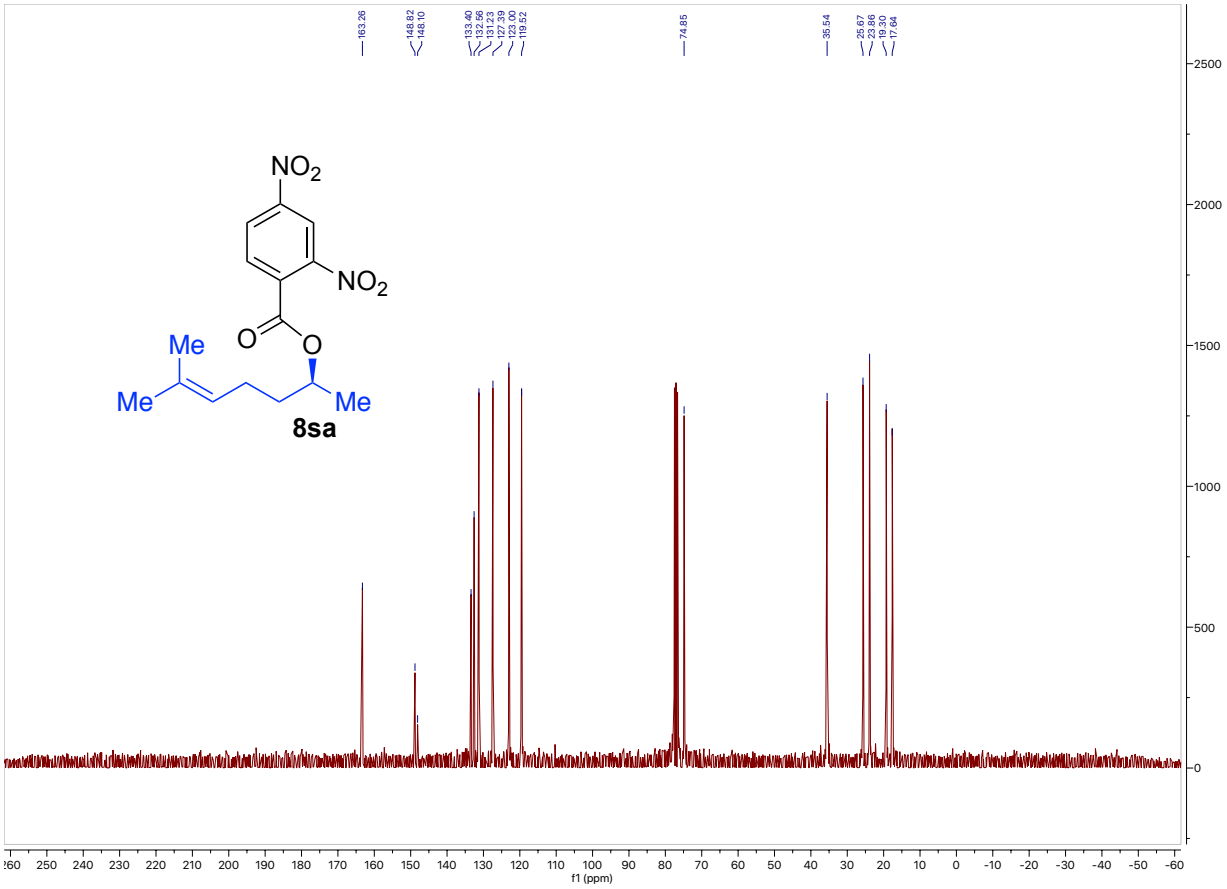

8qa

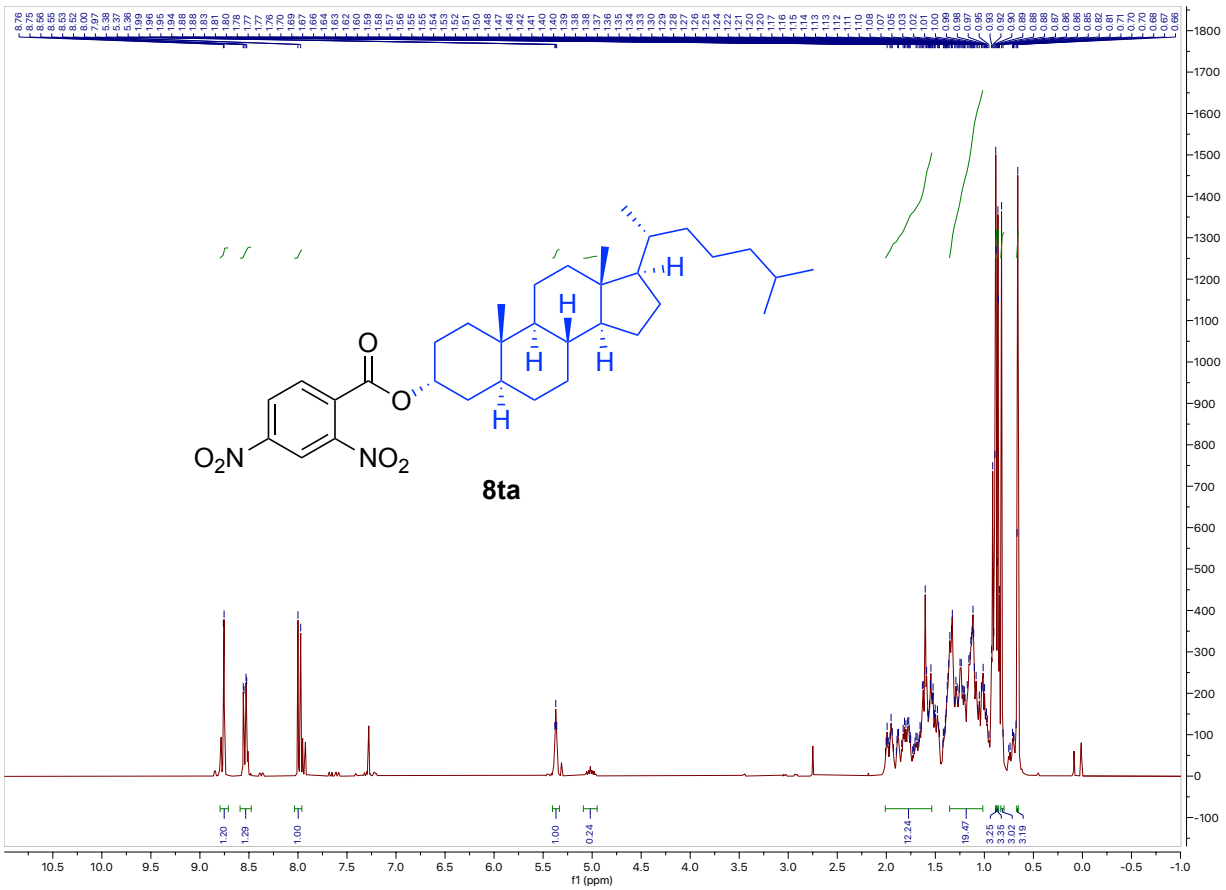

8qa

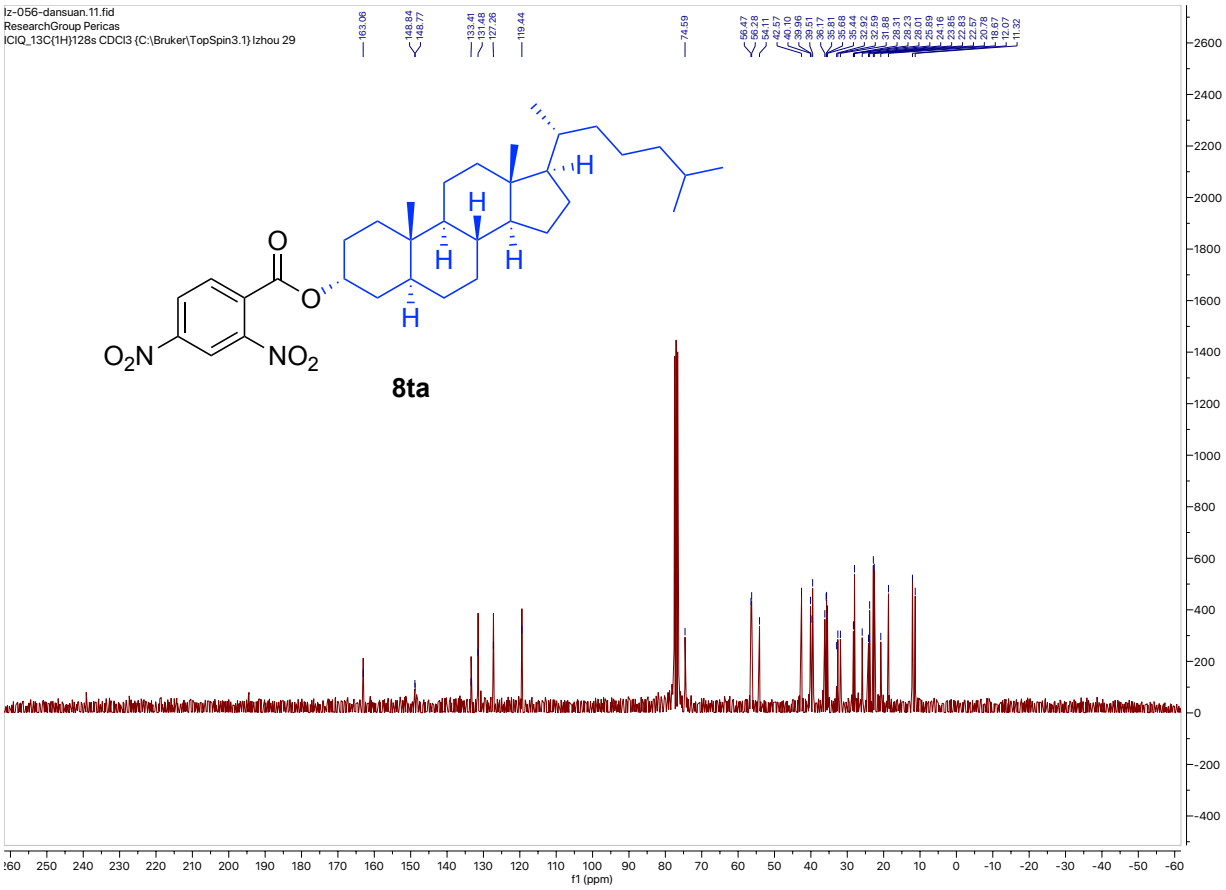

NO2
NO2
O
O
Ph
O
Me
8ra
f1 (ppm)

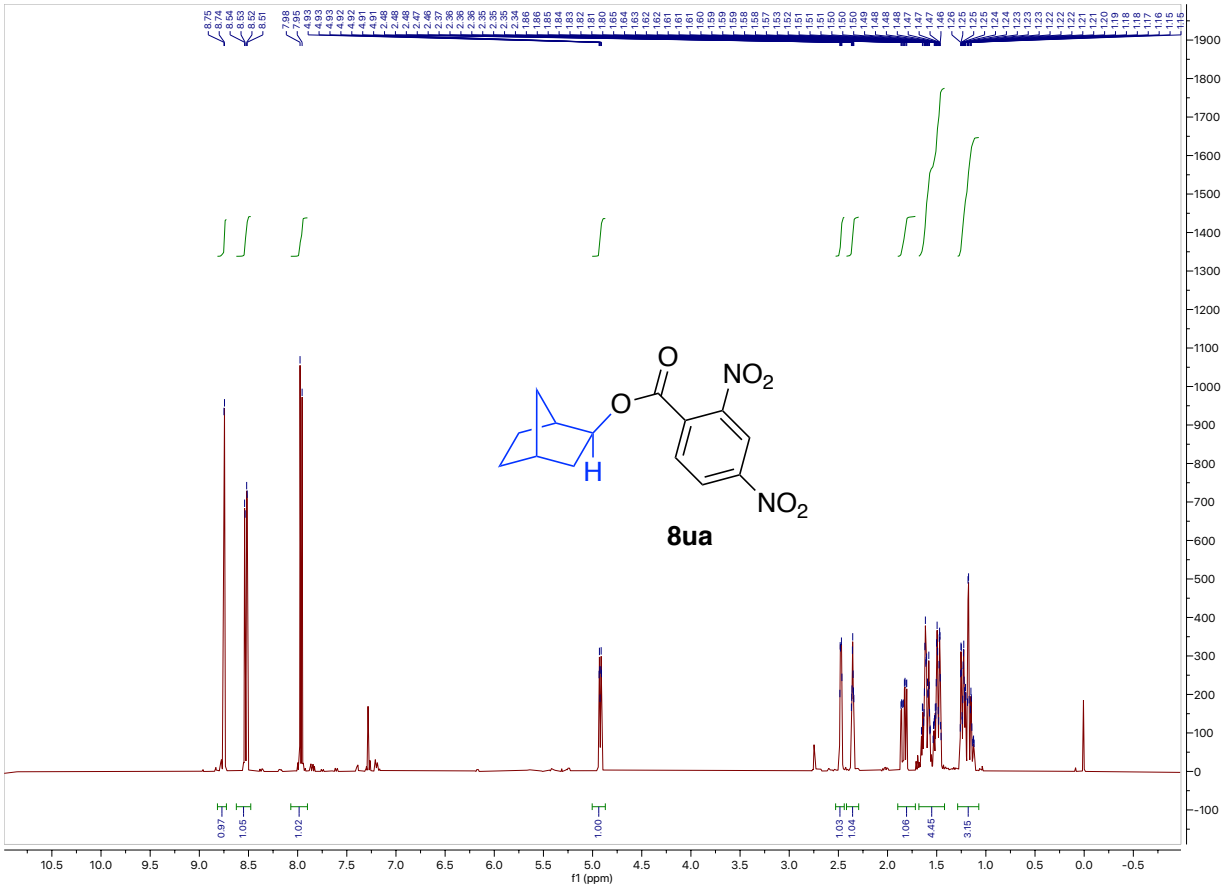

NO2
NO2
O
O
Ph
O
Me
8ra
f1 (ppm)

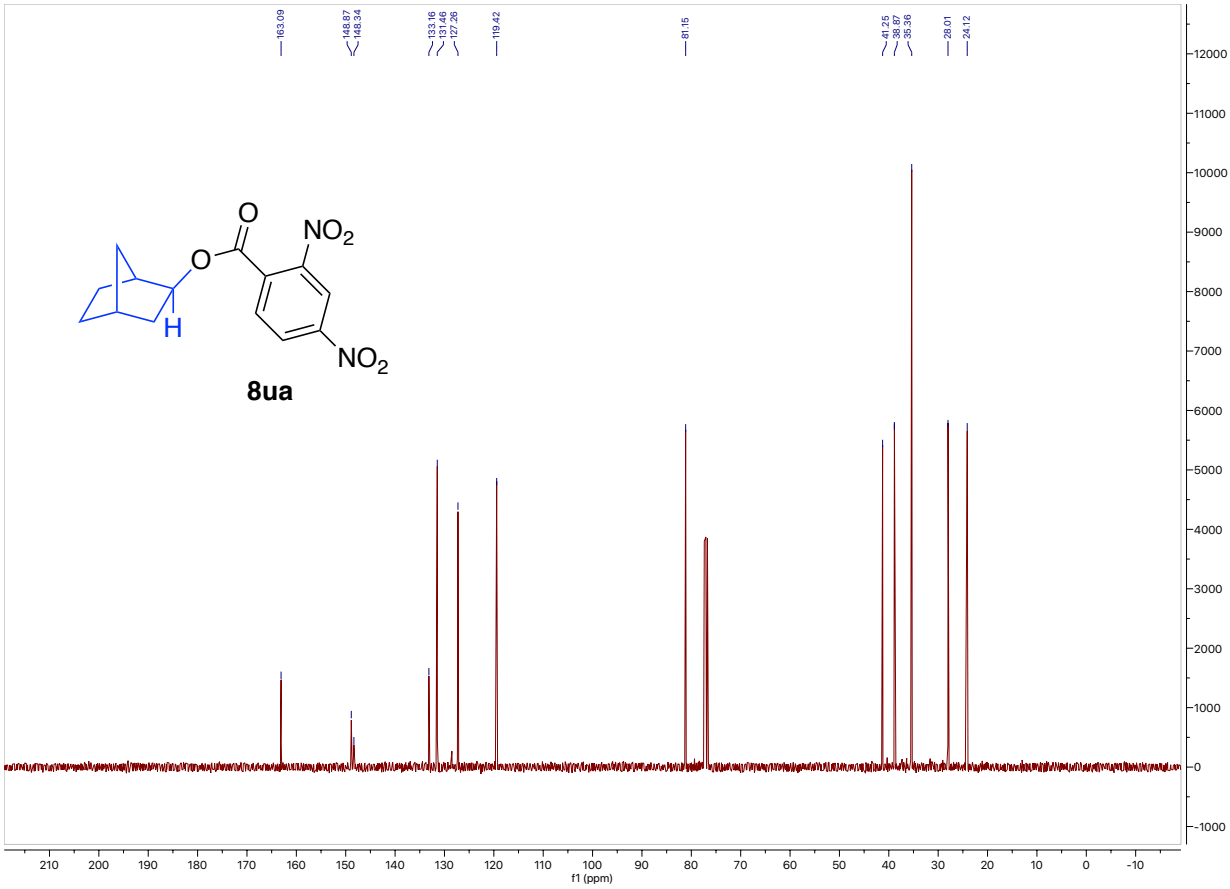

NO2
NO2
O
O
Me
Me
Me
8sa
f1 (ppm)

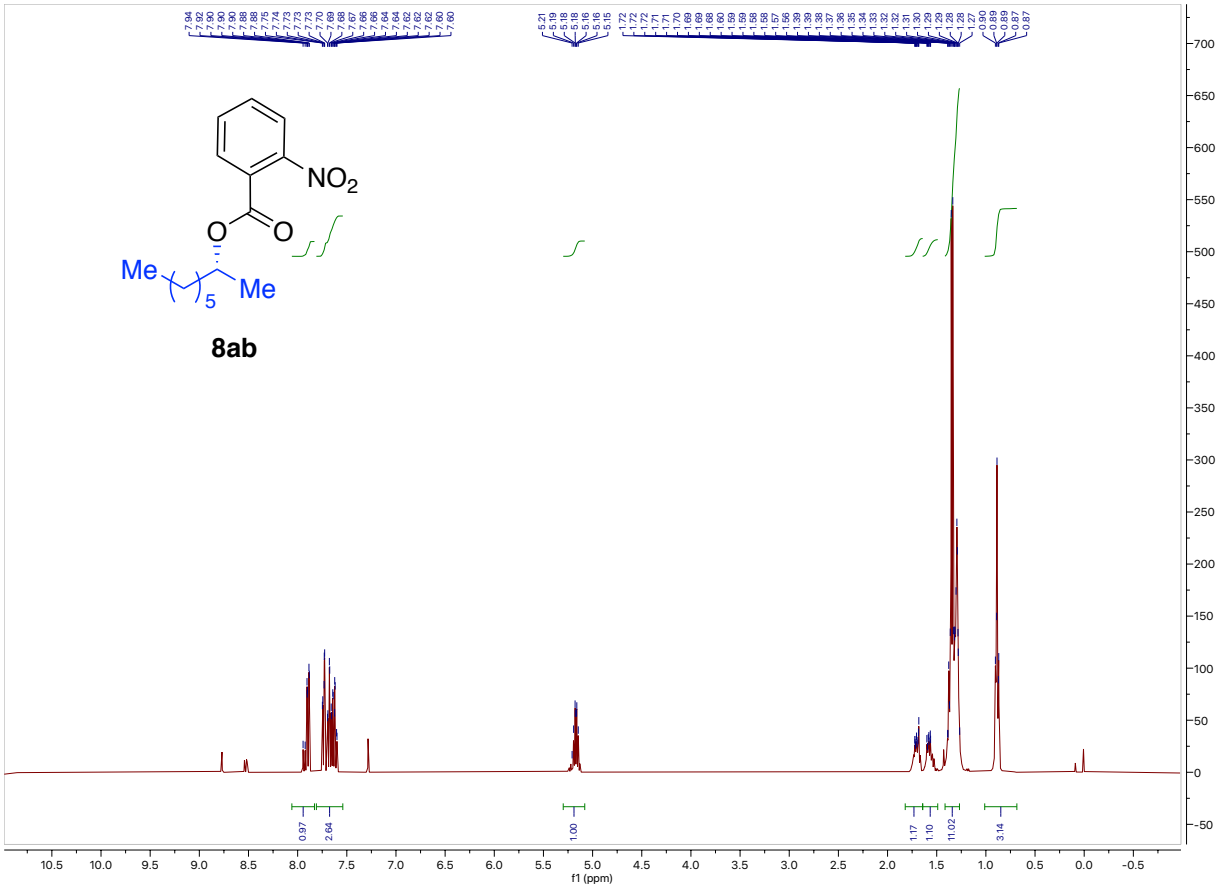

NO2
NO2
O
O
Me
Me
Me
8sa
f1 (ppm)

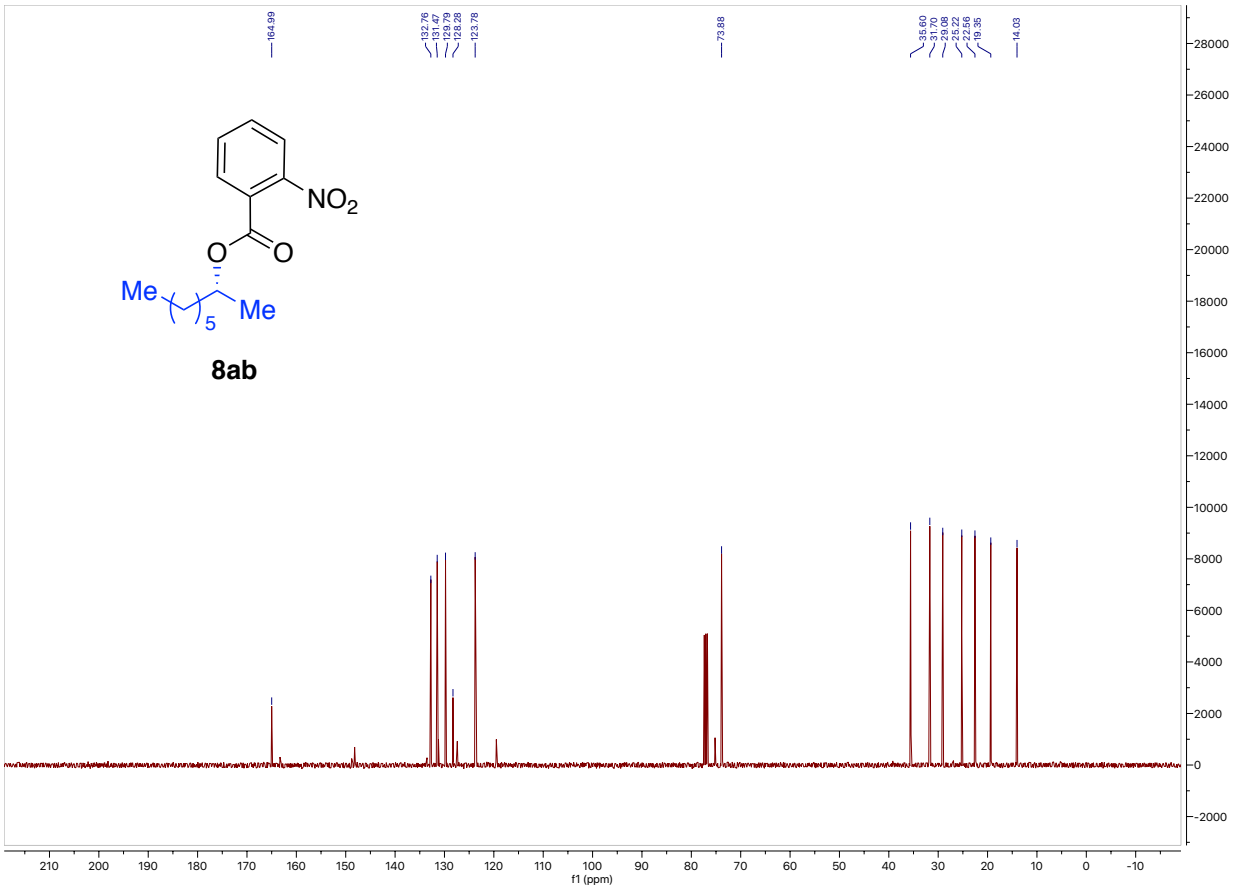

8ta
f1 (ppm)

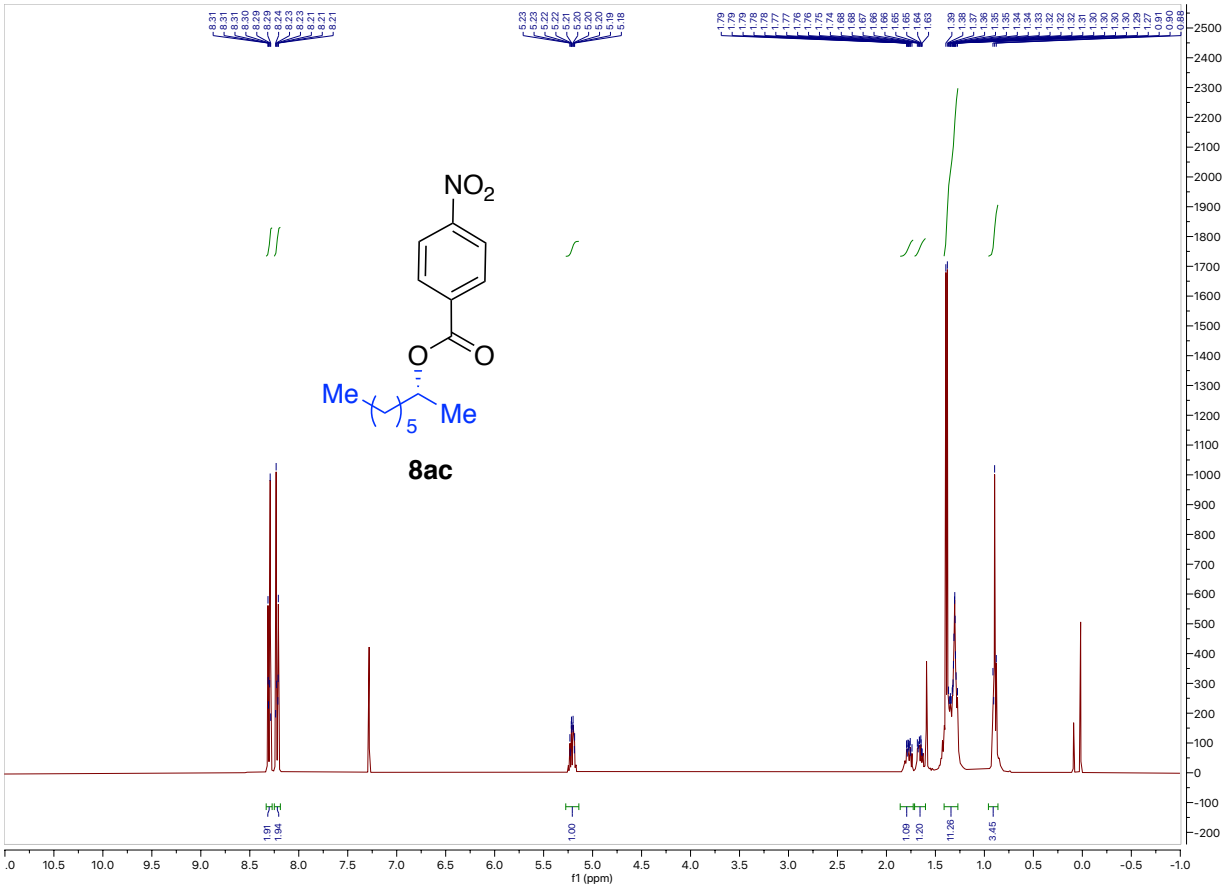

lz-056-dansuan.11.fid
ResearchGroup Pericas
ICIQ_13C{1H}128s CDCl3 {C:\Bruker\TopSpin3.1} lzhou 29
8ta
f1 (ppm)

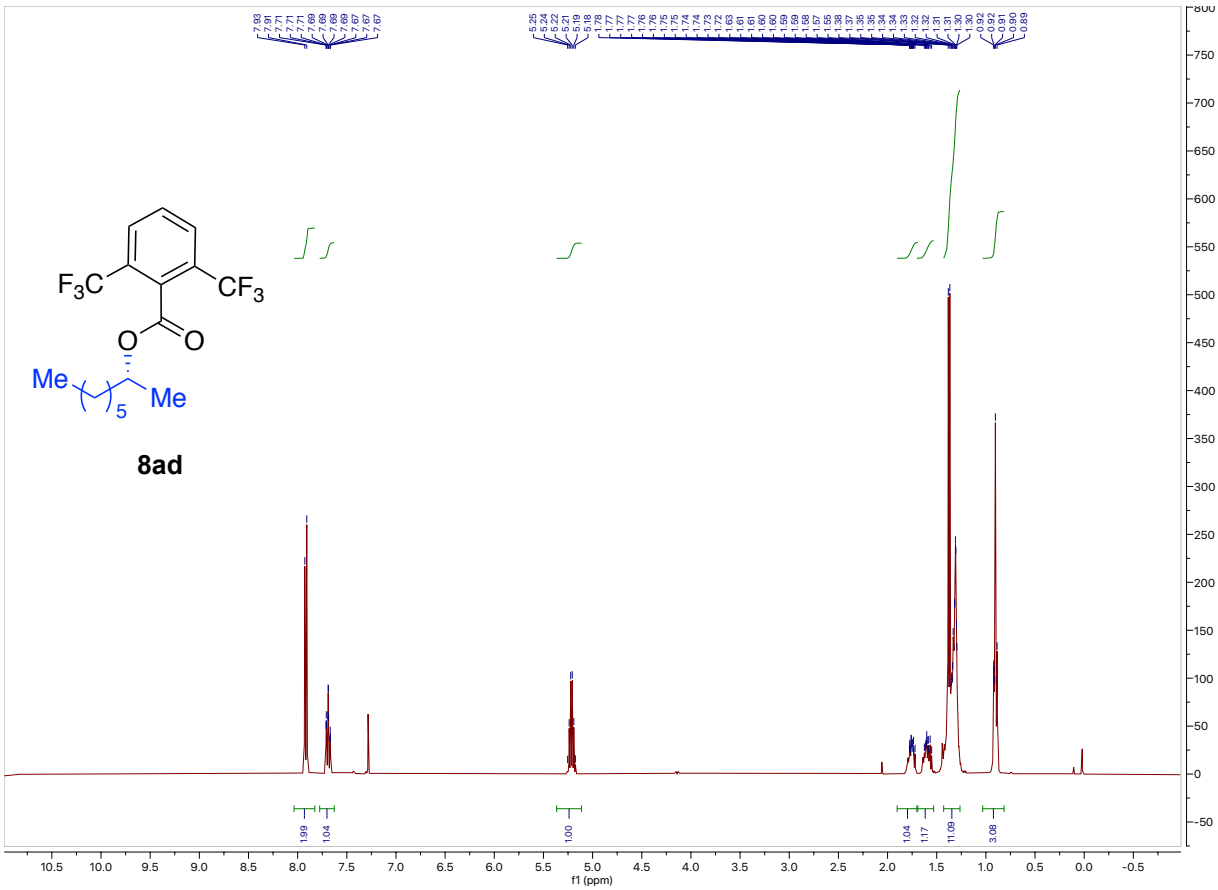

O
O
NO2
NO2
H
8ua
f1 (ppm)

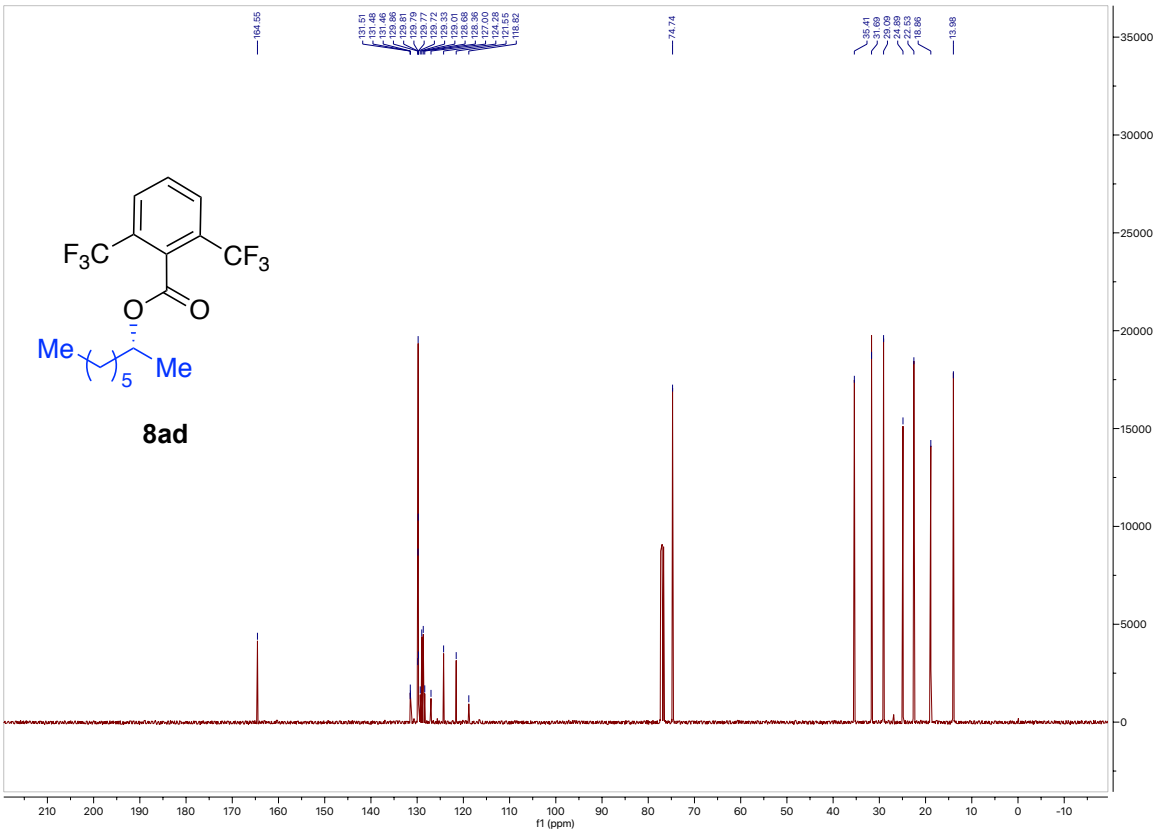

O
O
NO2
NO2
H
8ua
f1 (ppm)

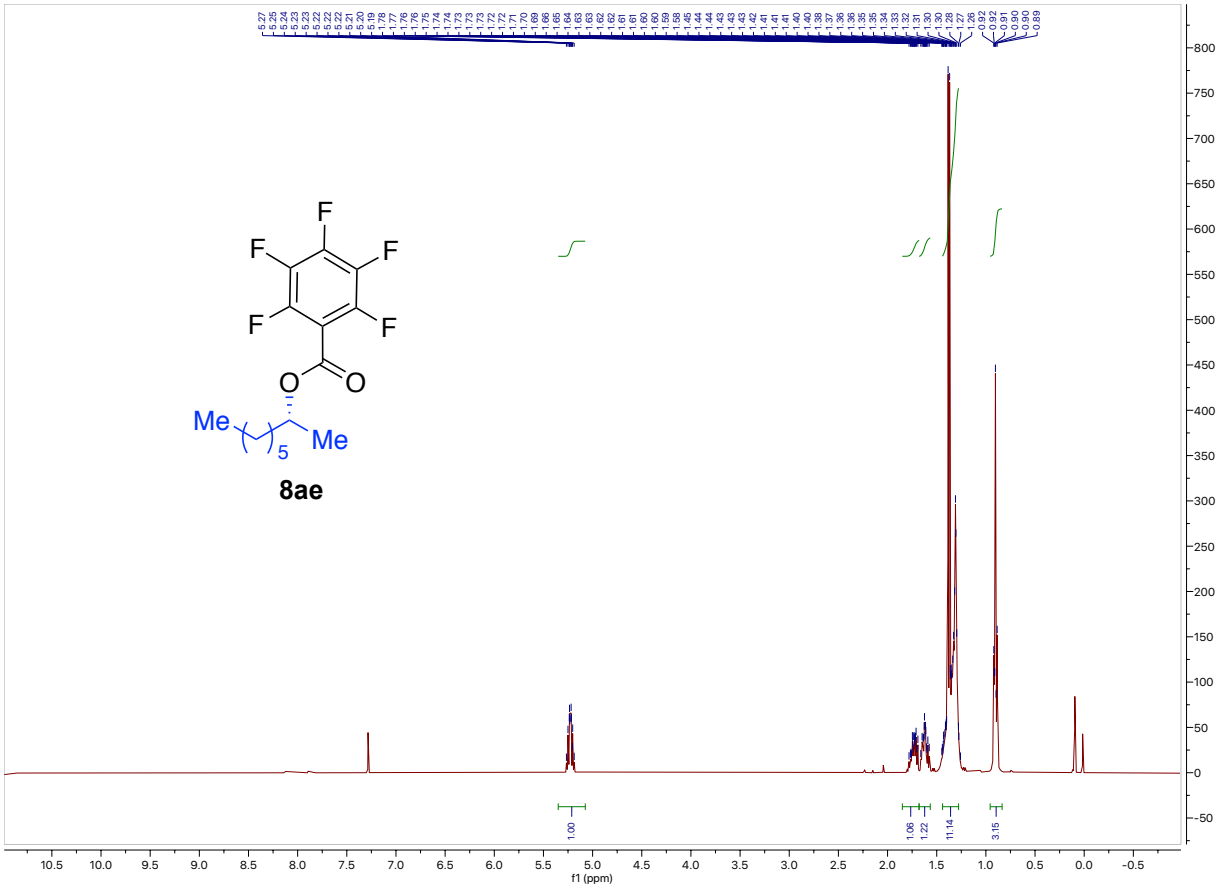

NO2
O
O
Me
5
Me
8ab
f1 (ppm)

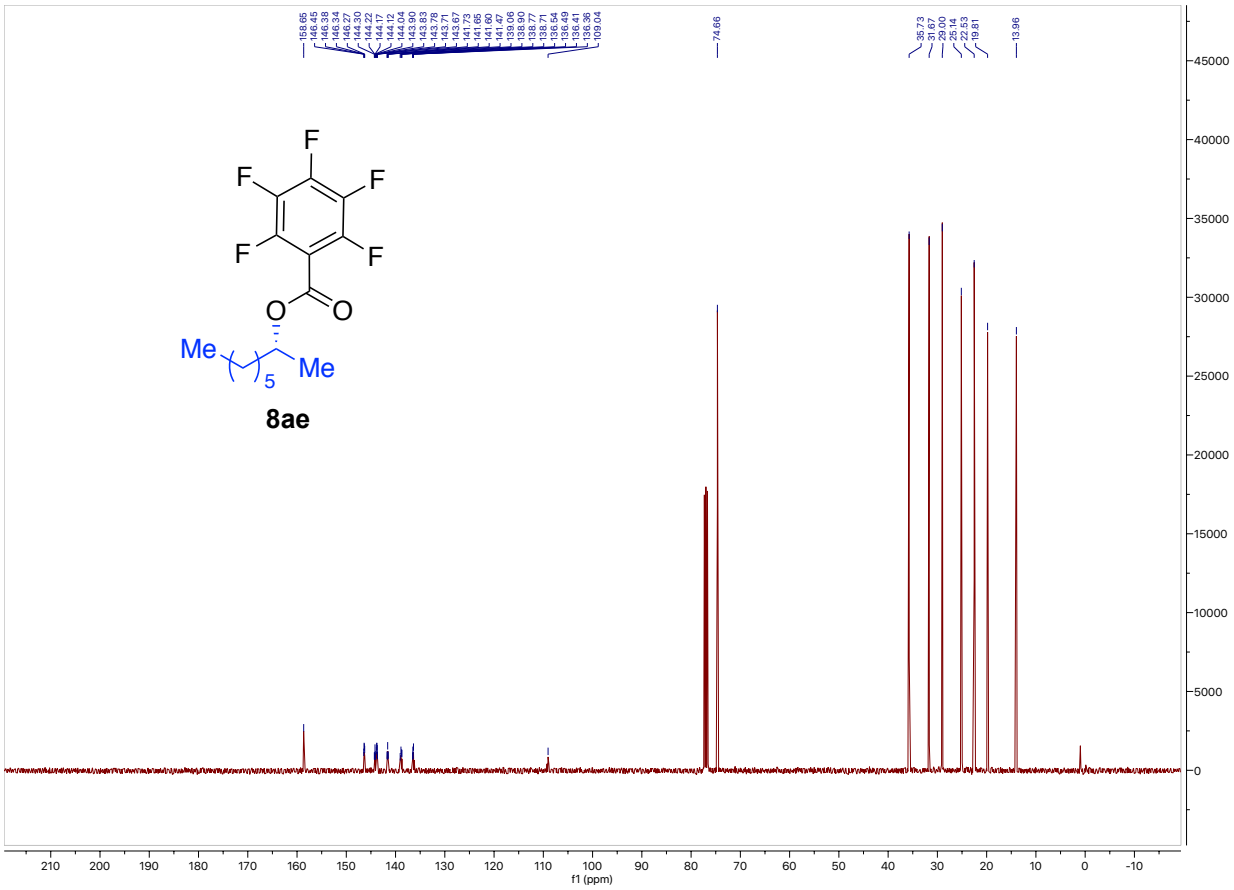

NO2
O
O
Me
5
Me
8ab
f1 (ppm)

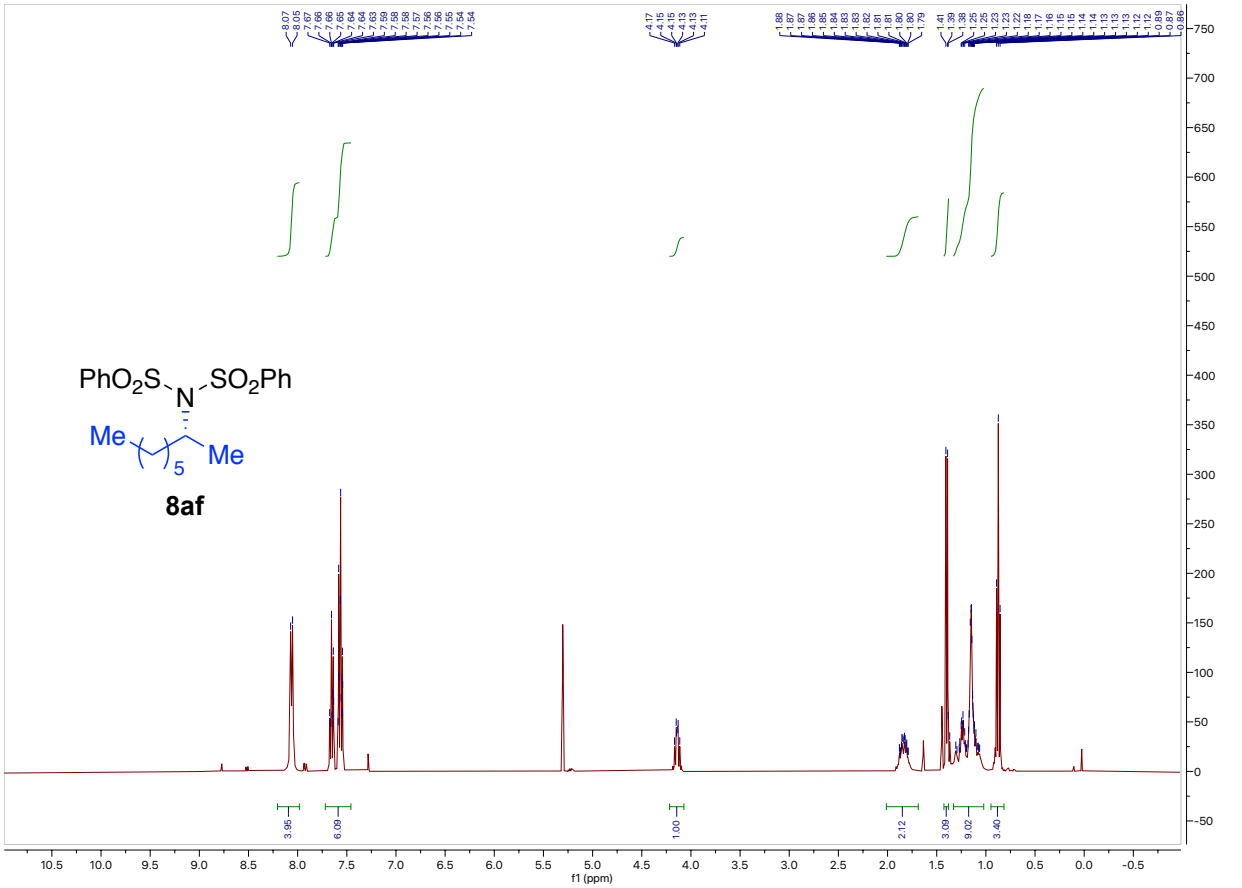

NO2
O
O
Me
5
Me
8ac
f1 (ppm)

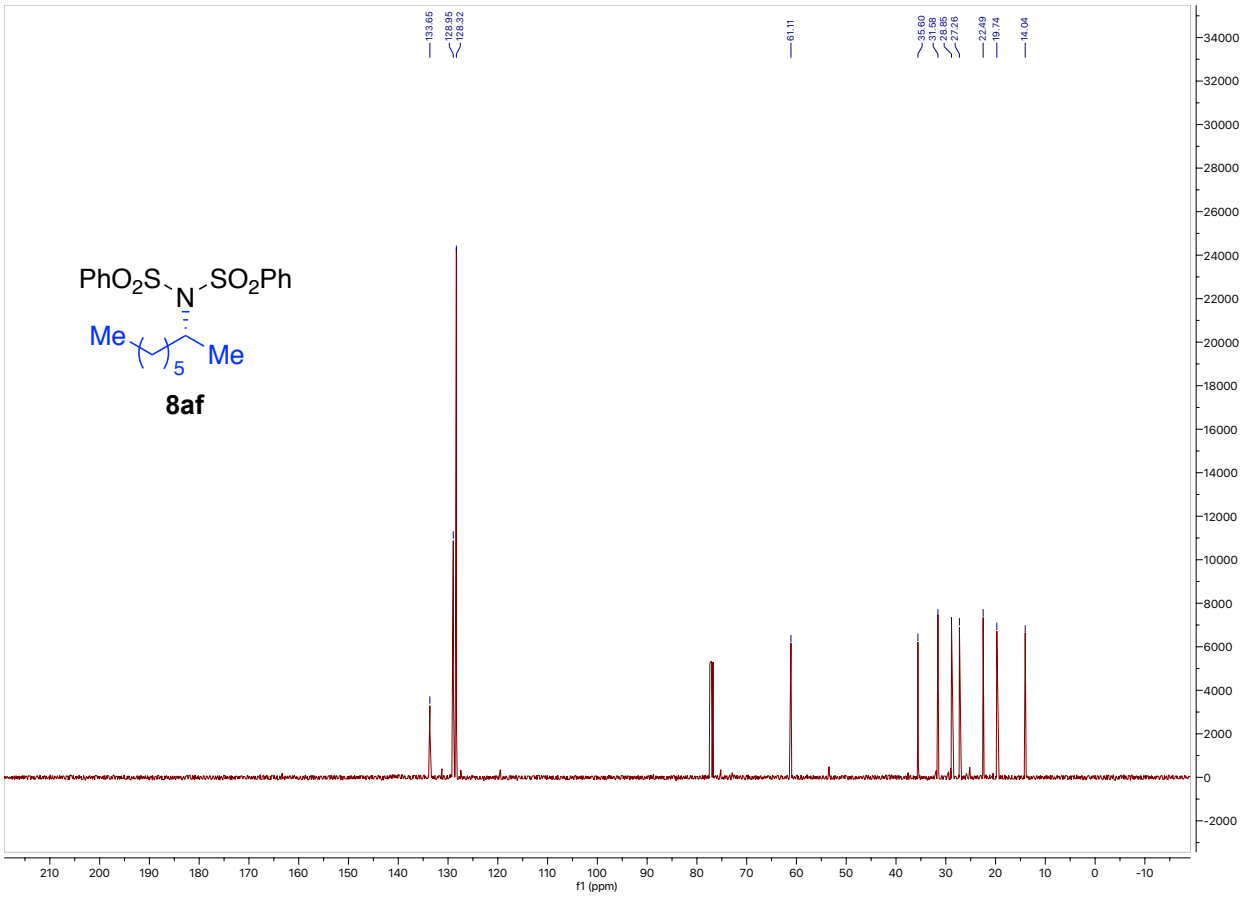

F3C
CF3
O
O
Me
5
Me
8ad
f1 (ppm)

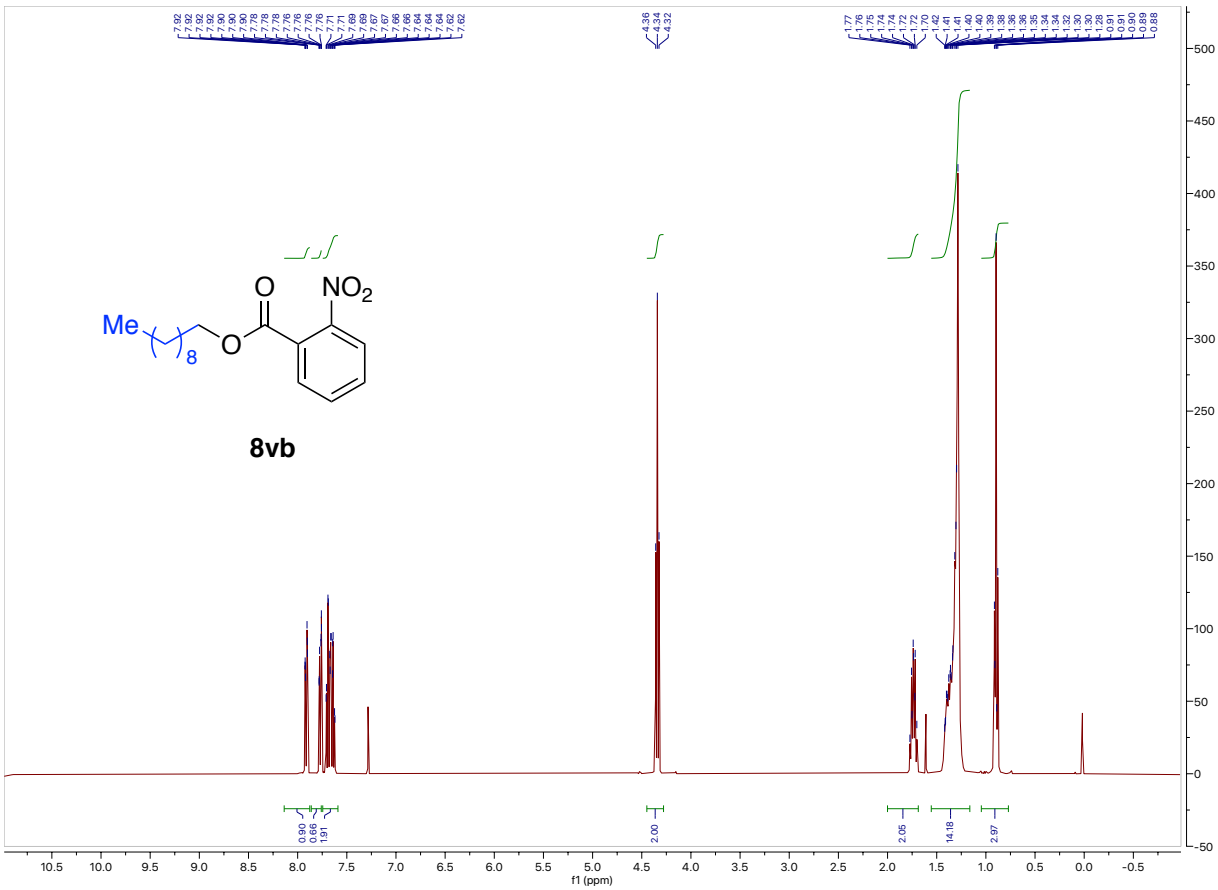

F3C
CF3
O
O
Me
5
Me
8ad
f1 (ppm)

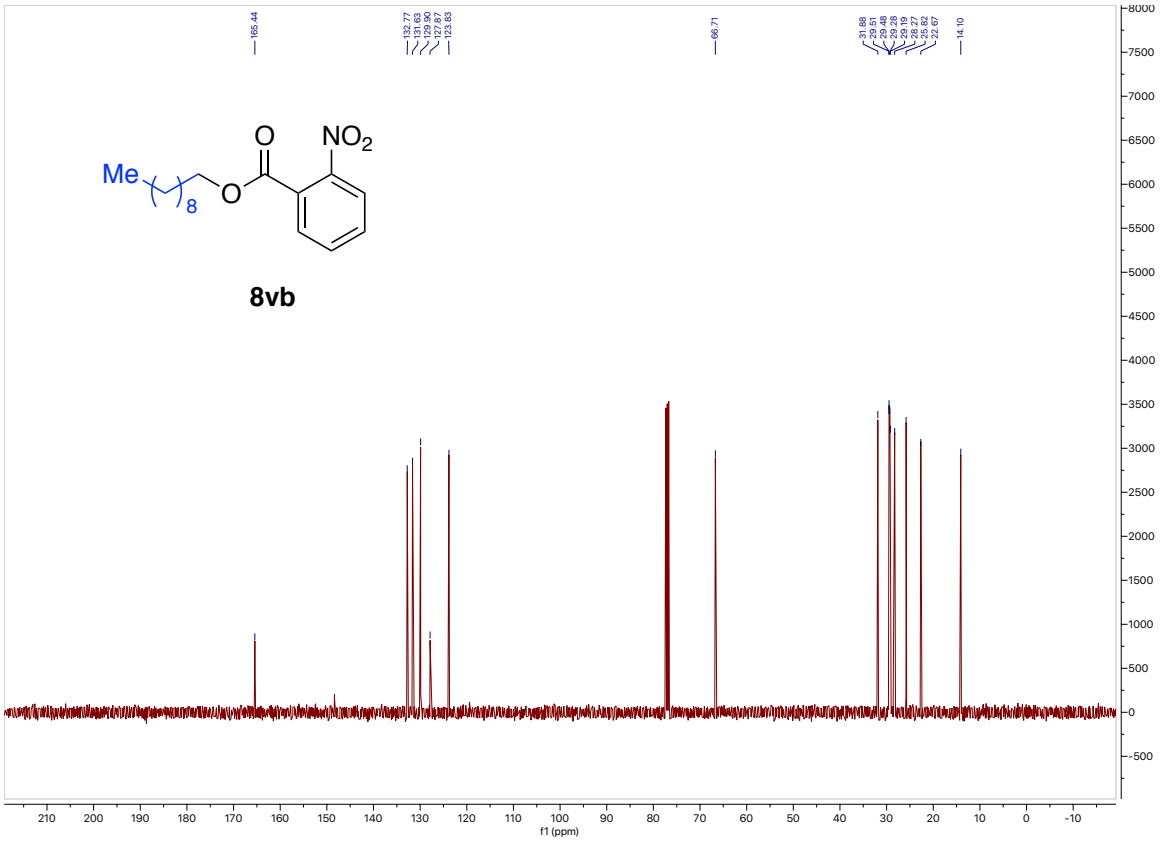

F
F
F
F
F
O
O
Me
5
Me
8ae
f1 (ppm)

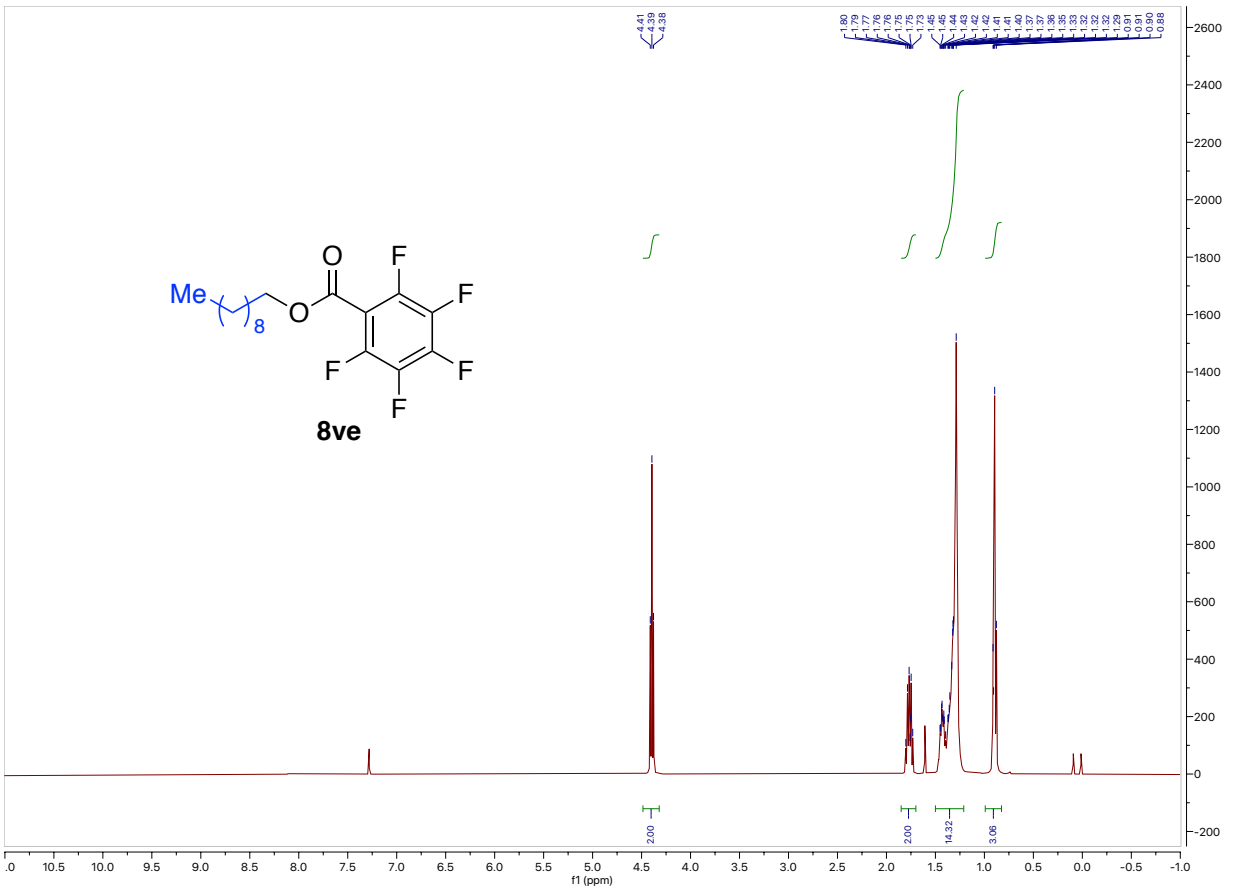

F
F
F
F
F
O
O
Me
5
Me
8ae
f1 (ppm)

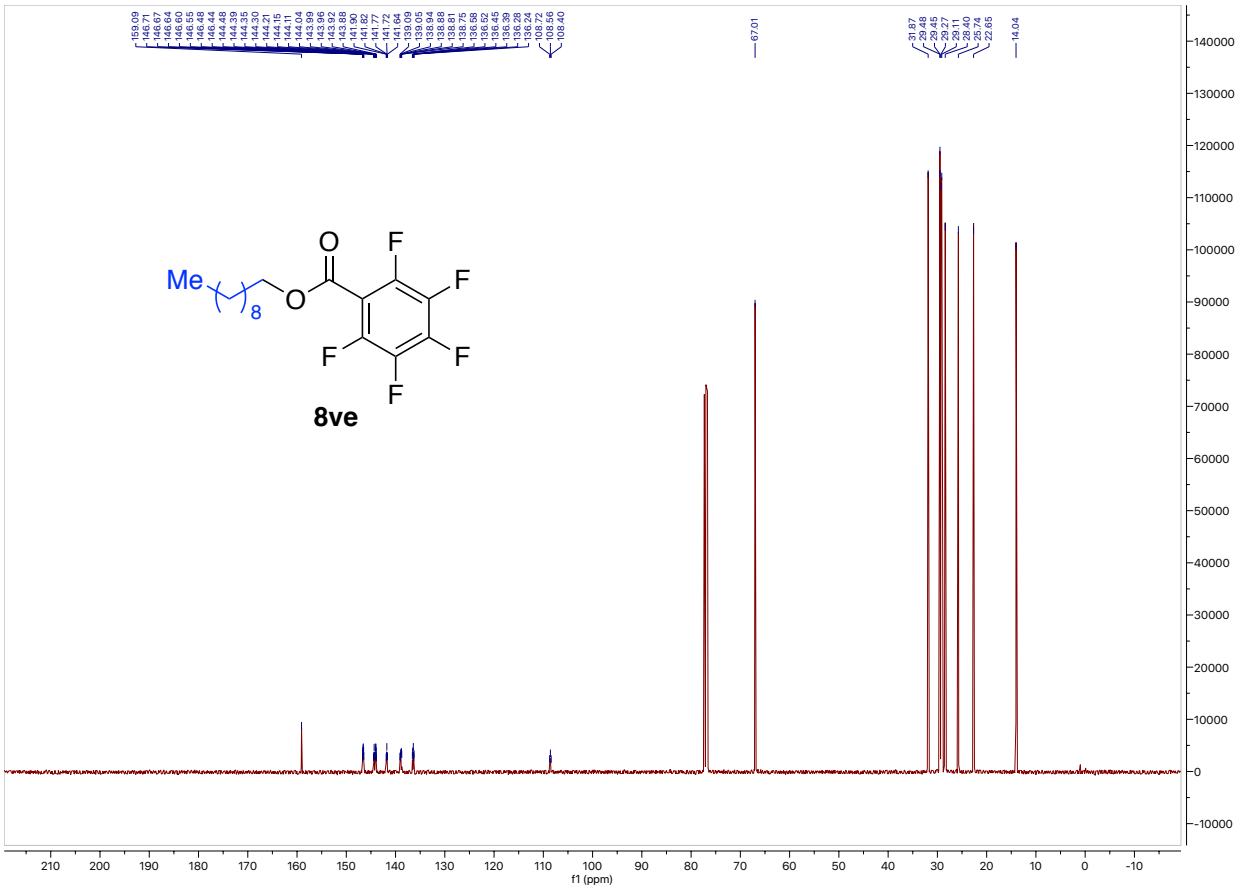

PhO2S
N
SO2Ph
Me
5
Me
8af
f1 (ppm)

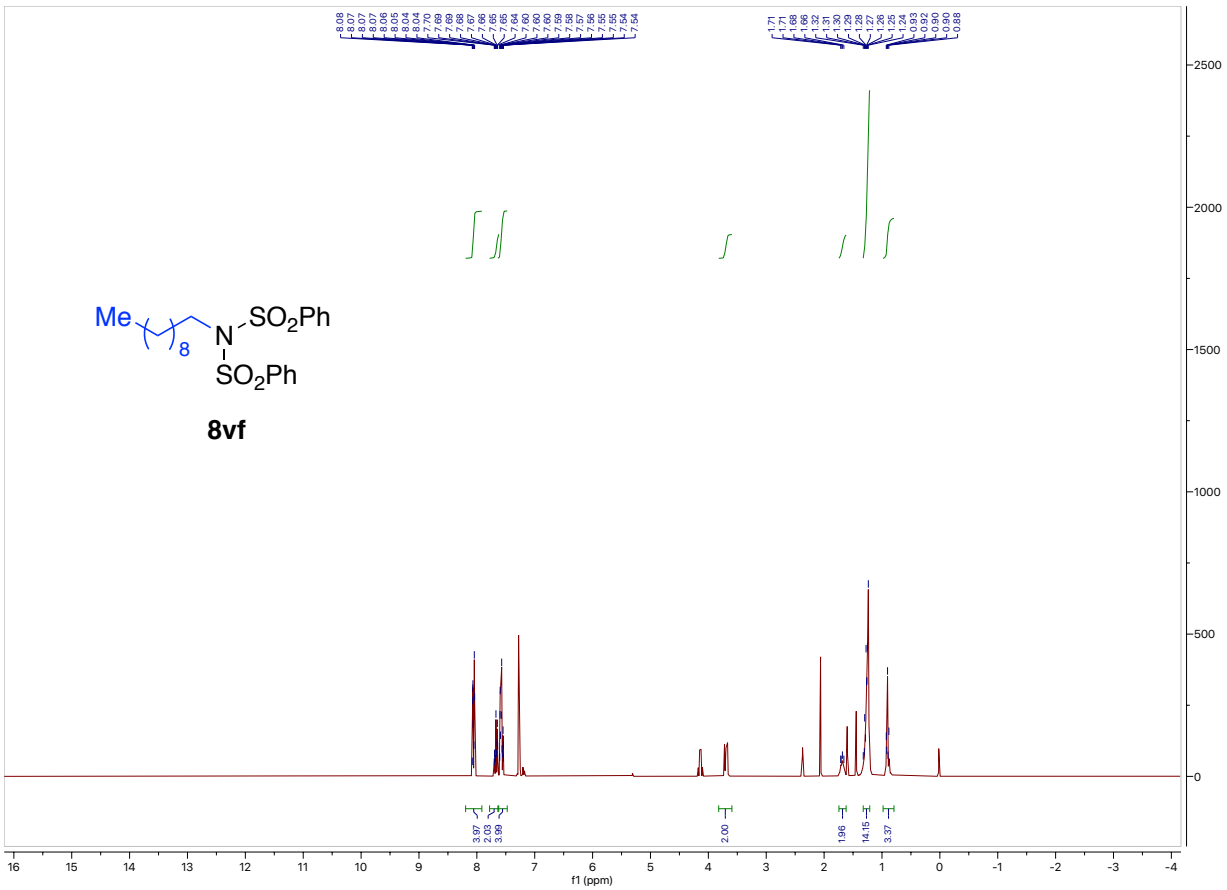

PhO2S
N
SO2Ph
Me
5
Me
8af
f1 (ppm)


Me
8
O
O
NO2
8vb
f1 (ppm)


Me
8
O
O
NO2
8vb
f1 (ppm)

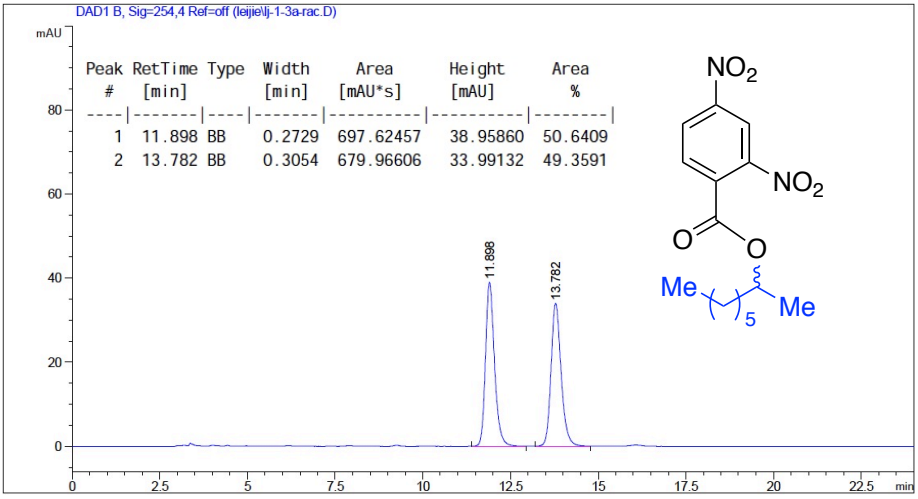

Me
O
O
F
F
F
F
F
8
8ve
f1 (ppm)


Me
O
O
F
F
F
F
F
8
8ve
f1 (ppm)

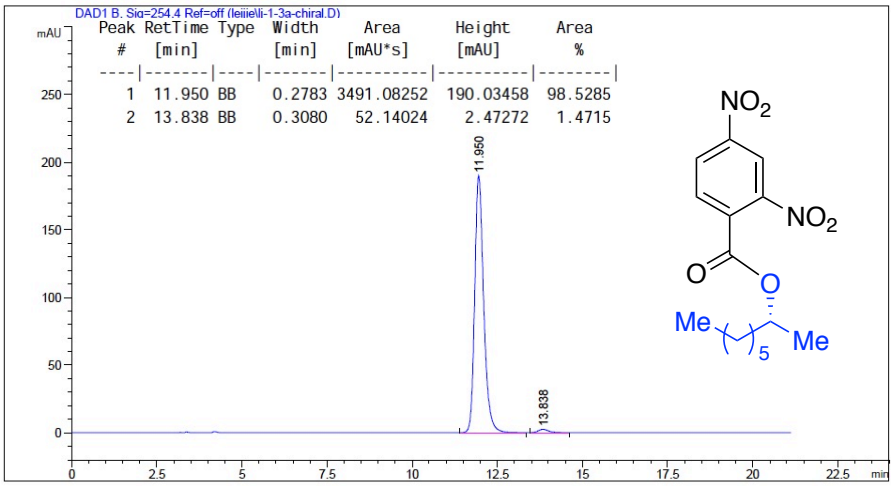

Me
8
N
SO2Ph
SO2Ph
8vf
f1 (ppm)

## 11. HPLC Chromatograms

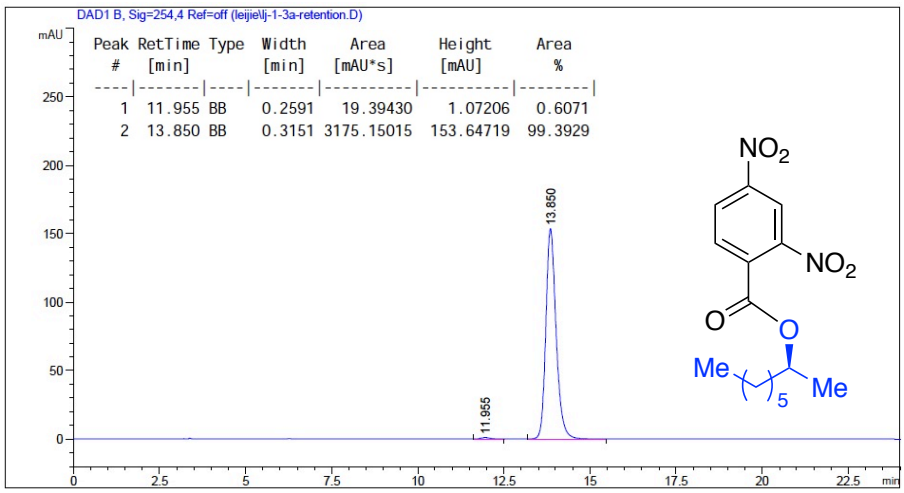
### HPLC Chromatogram of compound 8aa *(racemic product)*



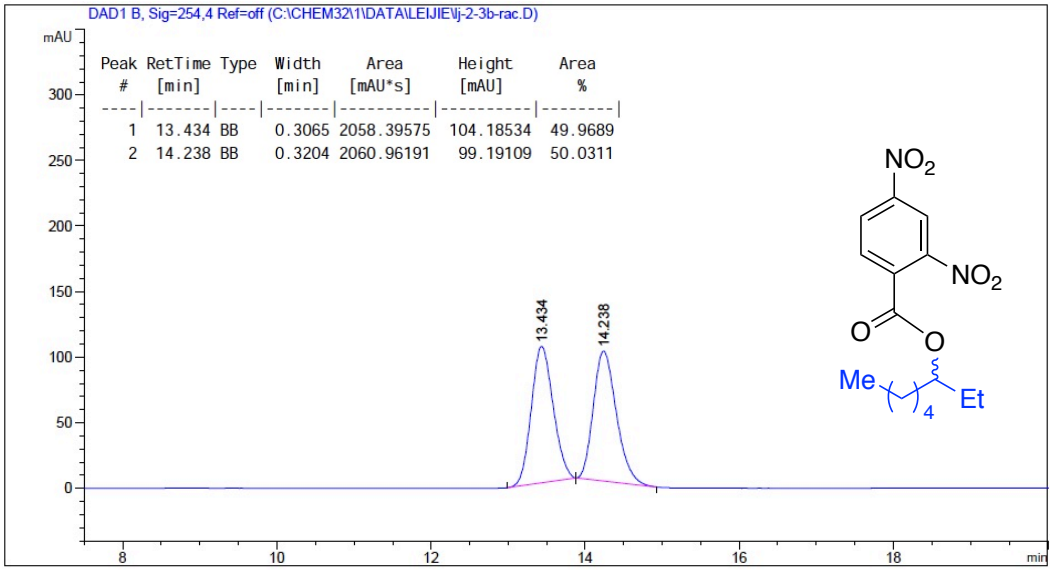

### HPLC Chromatogram of compound 8aa *(inversion product)*



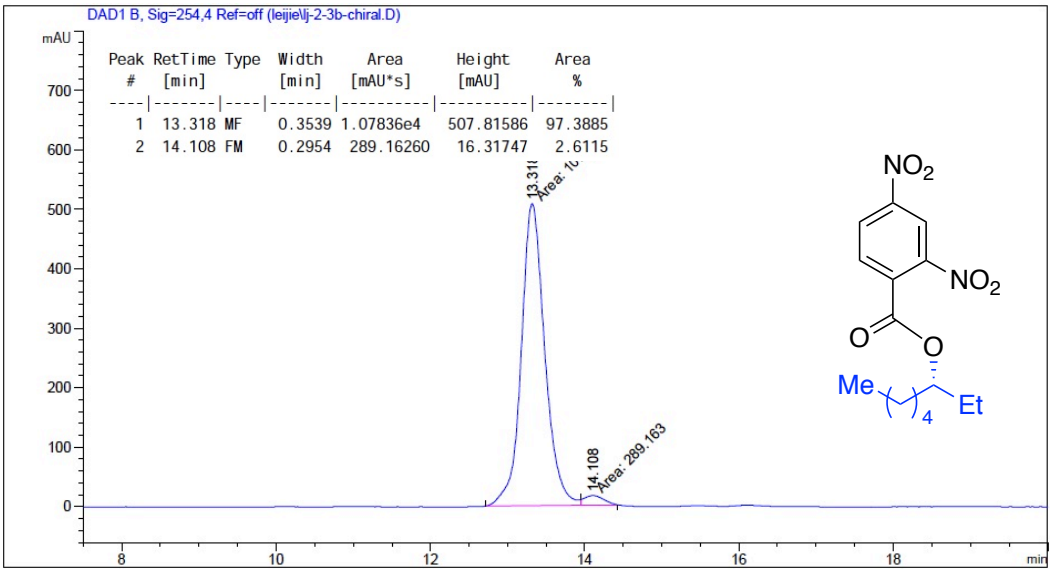

### HPLC Chromatogram of compound 8aa *(retention product)*



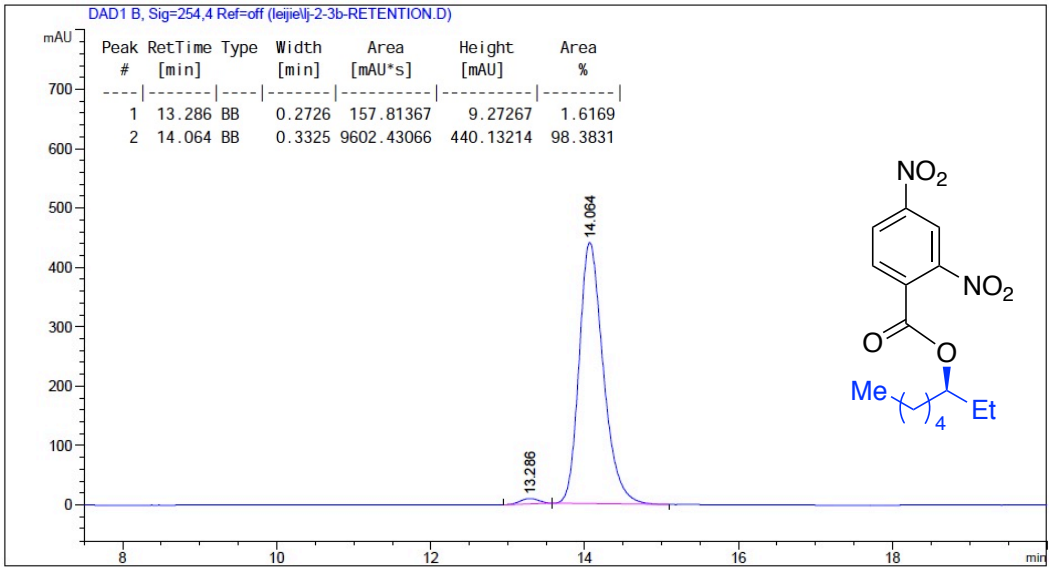
## HPLC Chromatogram of compound 8ba *(racemic product)*



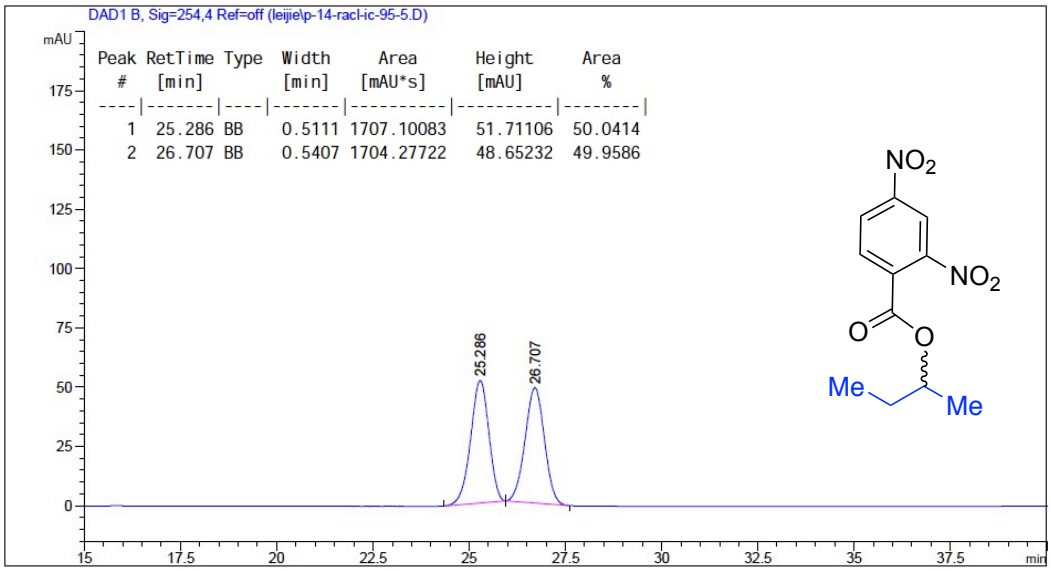

## HPLC Chromatogram of compound 8ba *((inversion product)*



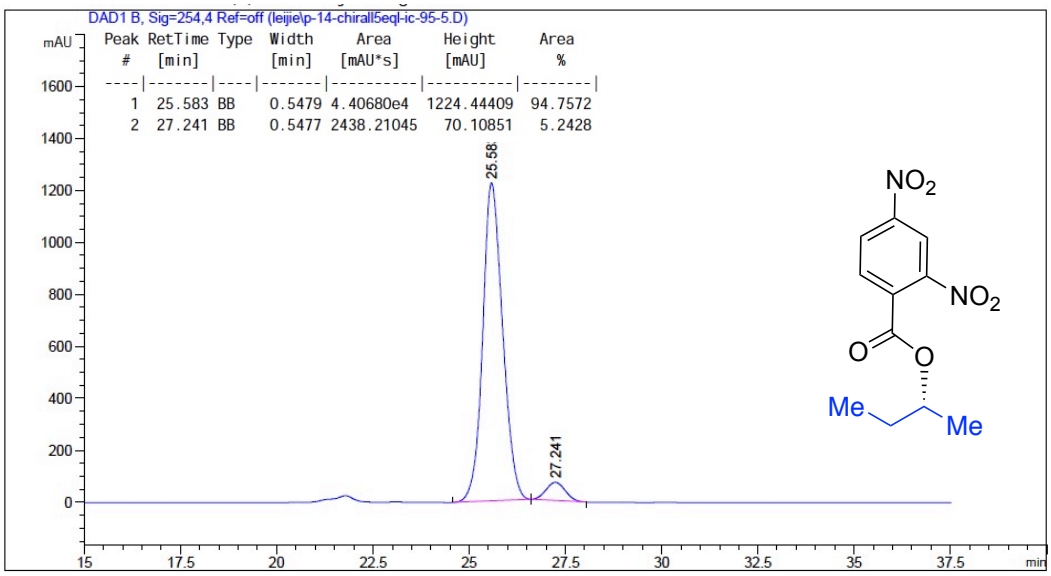

## HPLC Chromatogram of compound 8ba *(retention product)*



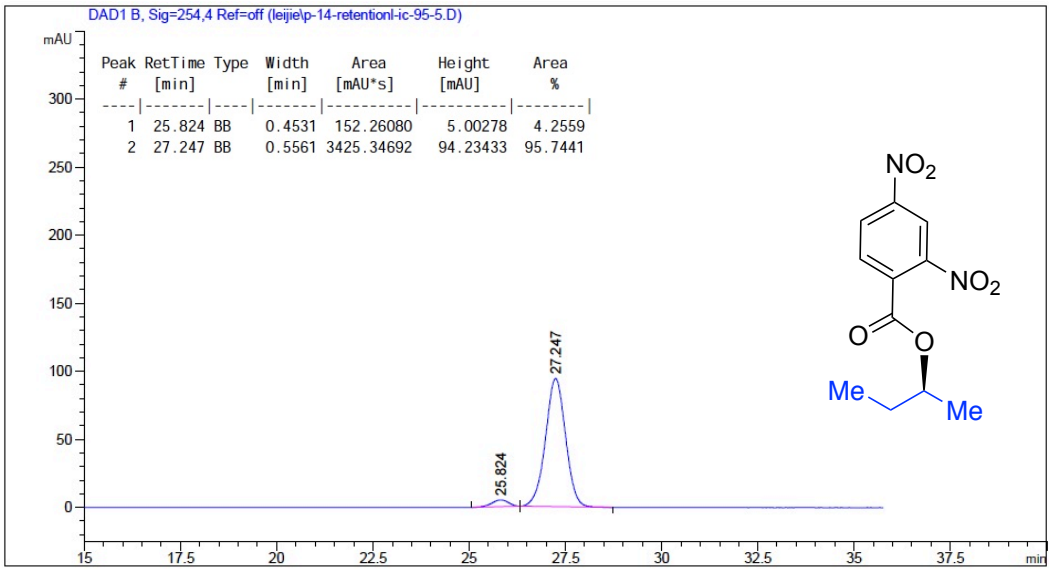
## HPLC Chromatogram of compound 8ca *(racemic product)*



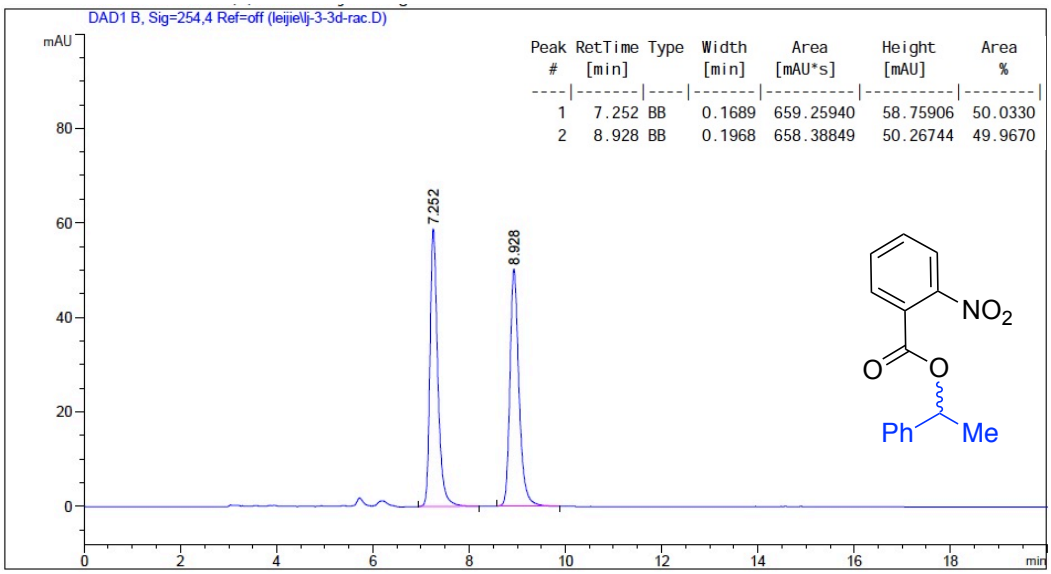

## HPLC Chromatogram of compound 8ca *((inversion product)*




## HPLC Chromatogram of compound 8ca *(retention product)*

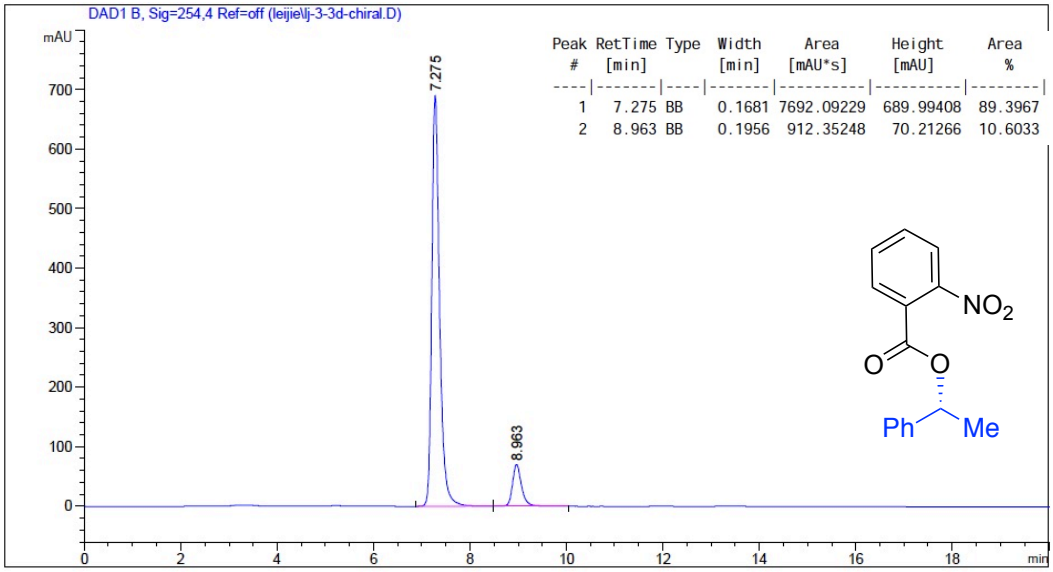


## HPLC Chromatogram of compound 8db *(racemic product)*



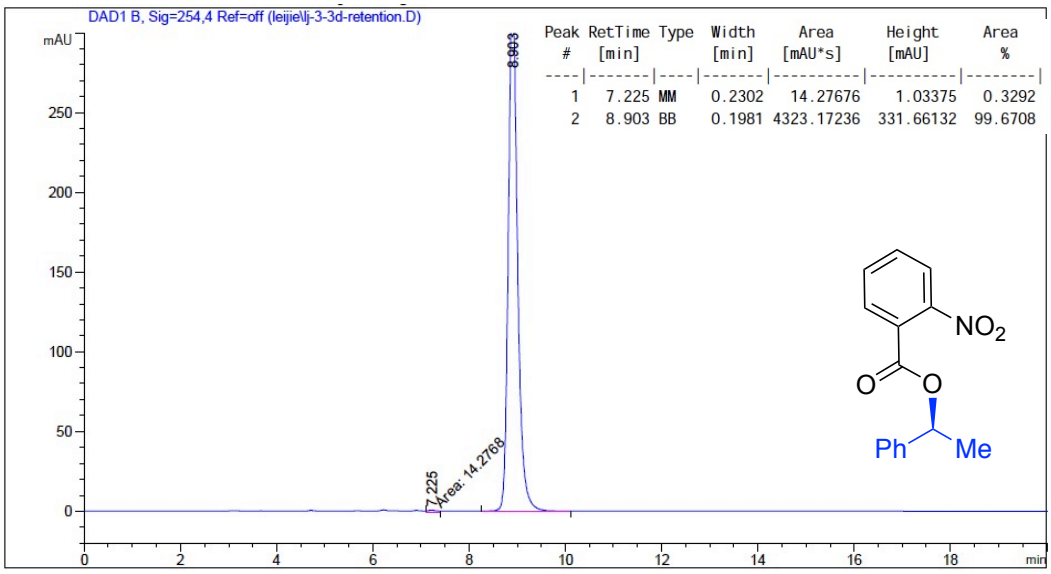

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.252 | BB | 0.1689 | 659.25940 | 58.75906 | 50.0330 |
| 2 | 8.928 | BB | 0.1968 | 658.38849 | 50.26744 | 49.9670 |

## HPLC Chromatogram of compound 8db *((inversion product)*



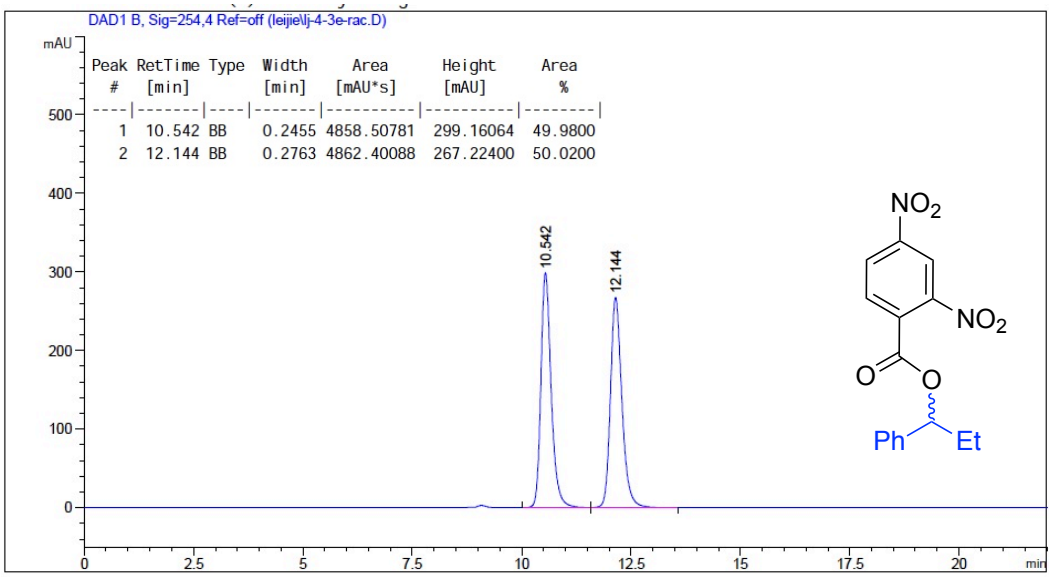

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.275 | BB | 0.1681 | 7692.09229 | 689.99408 | 89.3967 |
| 2 | 8.963 | BB | 0.1956 | 912.35248 | 70.21266 | 10.6033 |

## HPLC Chromatogram of compound 8db *(retention product)*

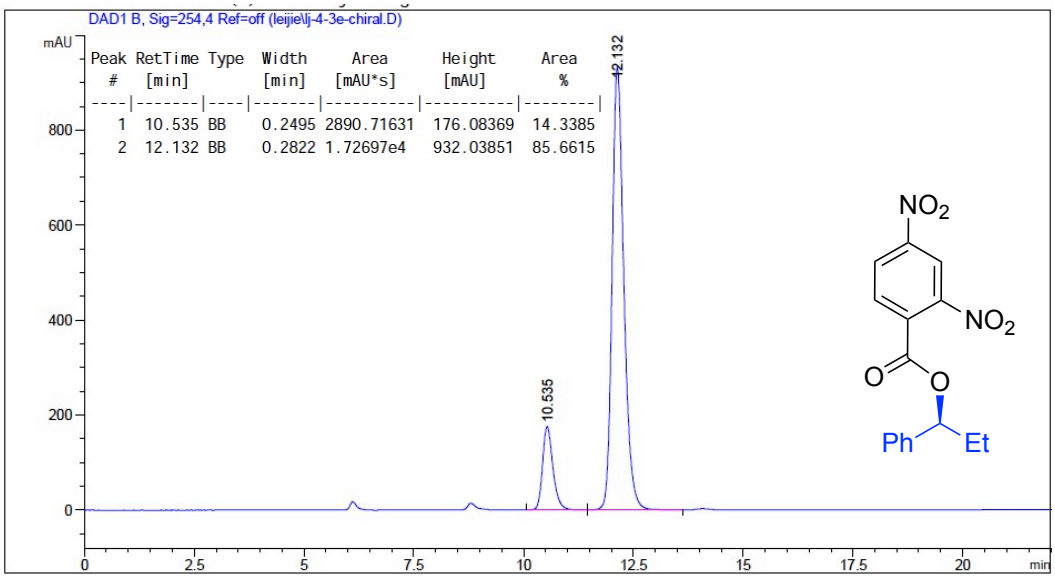



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.225 | MM | 0.2302 | 14.27676 | 1.03375 | 0.3292 |
| 2 | 8.903 | BB | 0.1981 | 4323.17236 | 331.66132 | 99.6708 |

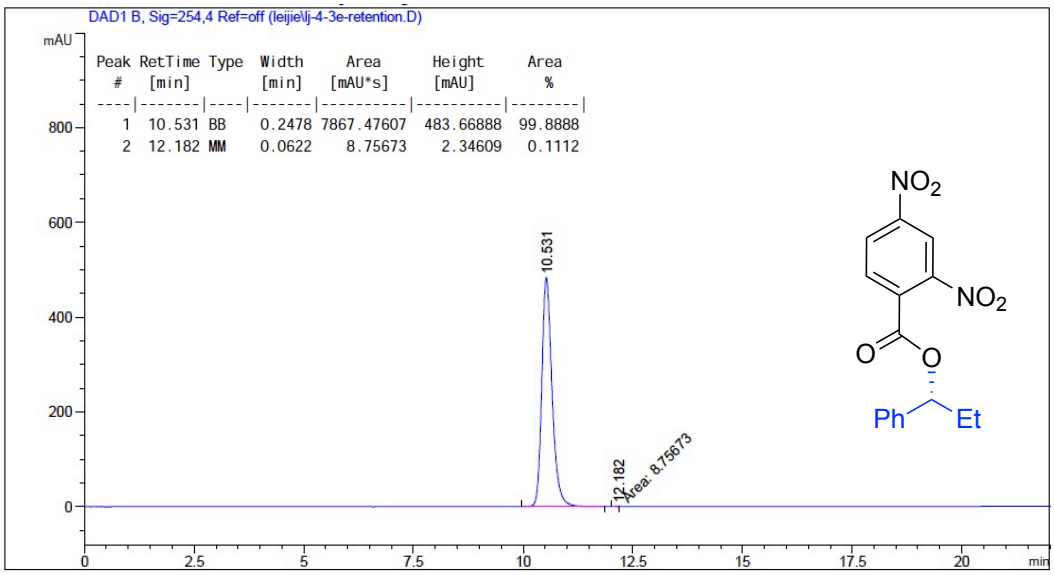
## HPLC Chromatogram of compound 8ea *(racemic product)*



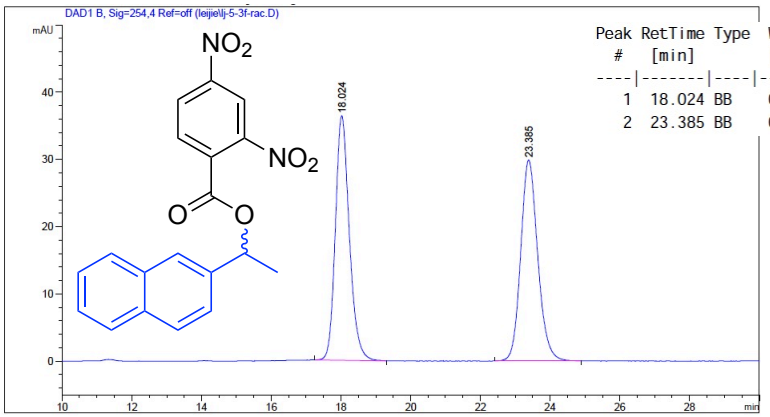

## HPLC Chromatogram of compound 8ea *((inversion product)*




## HPLC Chromatogram of compound 8ea *(retention product)*

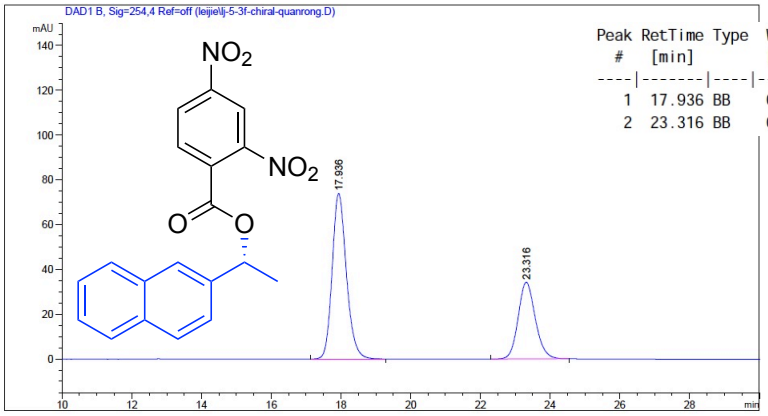


## HPLC Chromatogram of compound 8fa *(racemic product)*



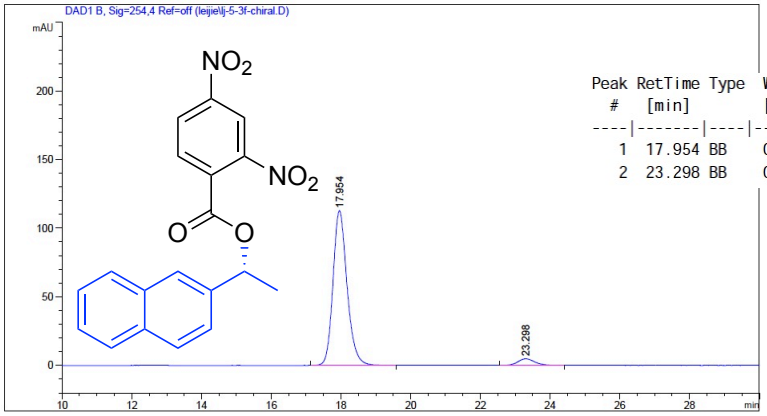

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.024 | BB | 0.4254 | 1014.19305 | 36.35941 | 49.9996 |
| 2 | 23.385 | BB | 0.5223 | 1014.20850 | 29.86014 | 50.0004 |

## HPLC Chromatogram of compound 8fa *((inversion product)*



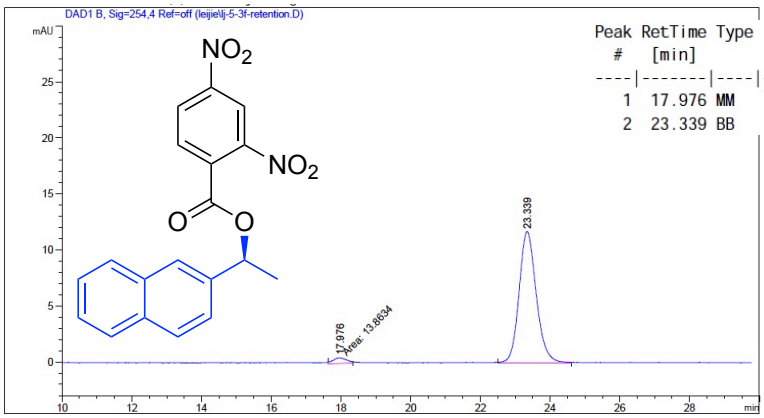

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.936 | BB | 0.4338 | 2103.90918 | 73.98361 | 64.1785 |
| 2 | 23.316 | BB | 0.5275 | 1174.30359 | 34.29103 | 35.8215 |

## HPLC Chromatogram of compound 8fa *((inversion product after recrystallization)*



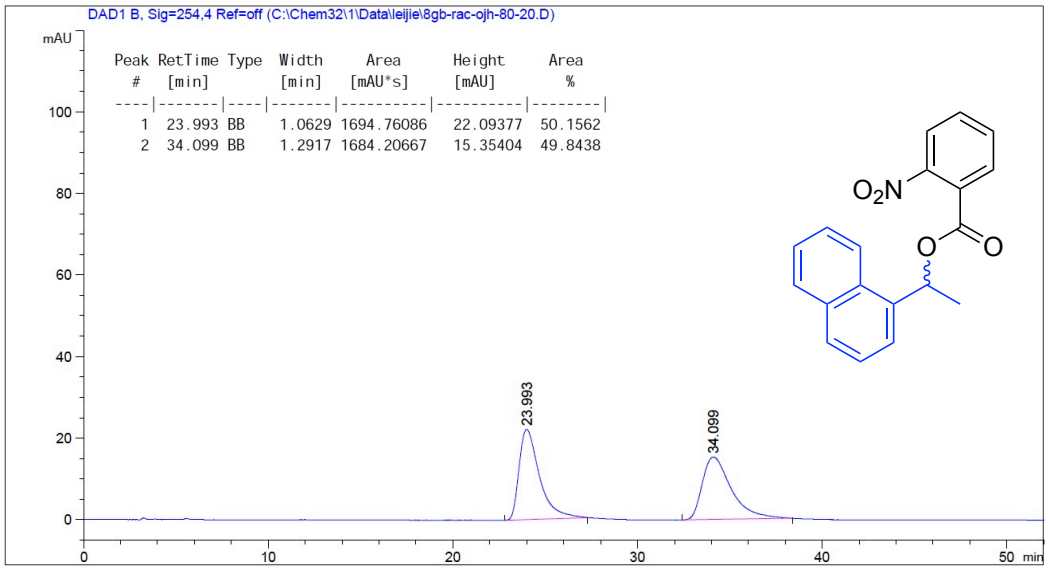

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.954 | BB | 0.4284 | 3156.10156 | 112.79724 | 95.2234 |
| 2 | 23.298 | BB | 0.4989 | 158.31490 | 4.72539 | 4.7766 |

## HPLC Chromatogram of compound 8fa *(retention product)*

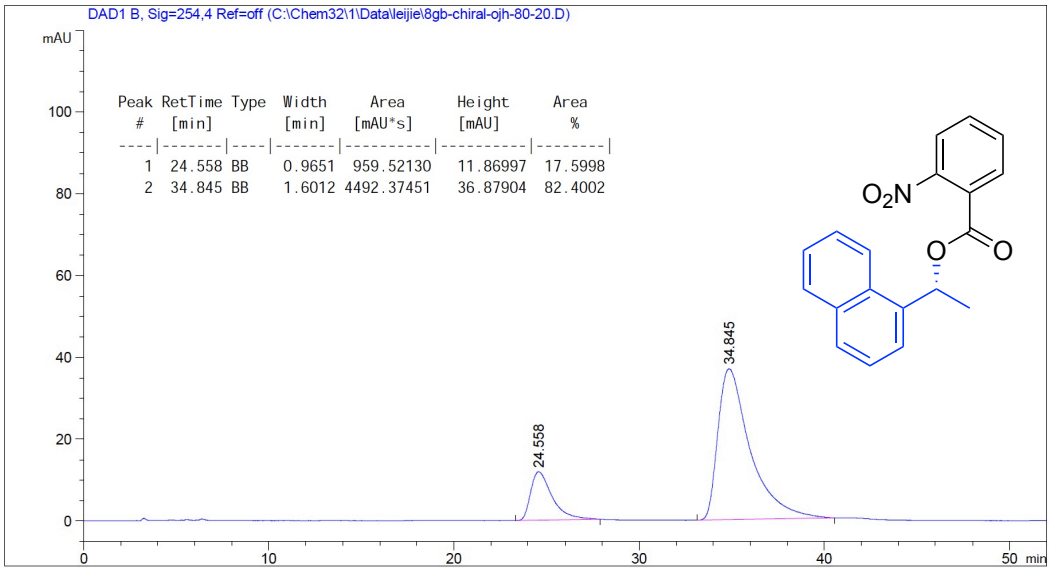



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.976 | MM | 0.4639 | 13.86339 | 4.98083e-1 | 3.3677 |
| 2 | 23.339 | BB | 0.5152 | 397.79587 | 11.68415 | 96.6323 |

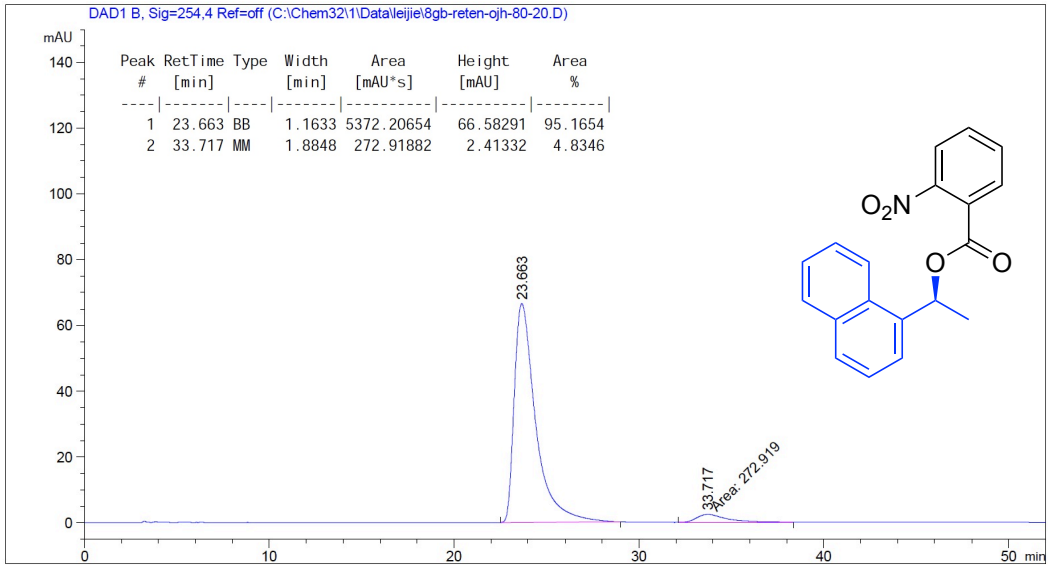
## HPLC Chromatogram of compound 8gb *(racemic product)*



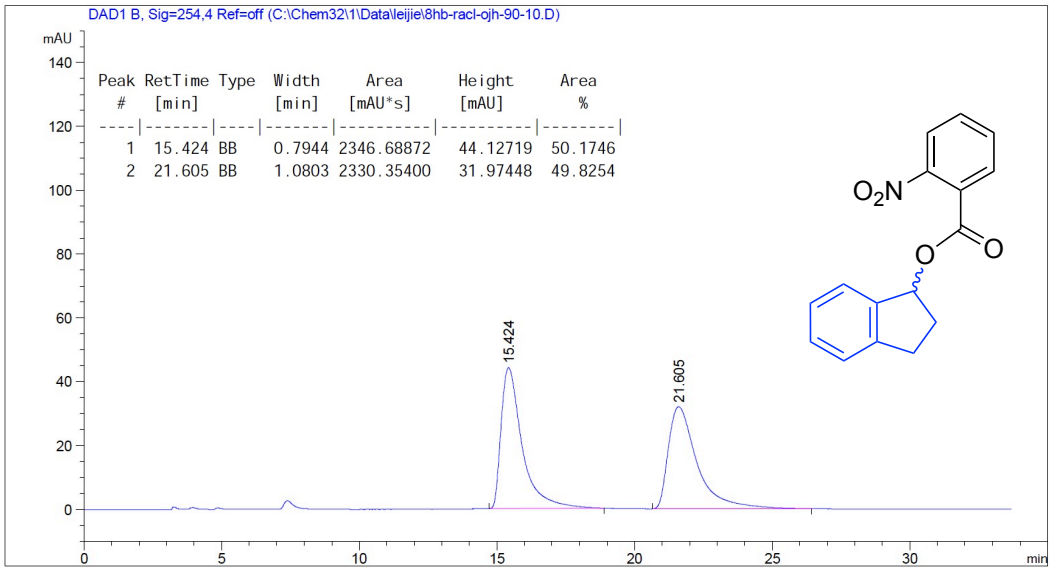

## HPLC Chromatogram of compound 8gb *((inversion product)*



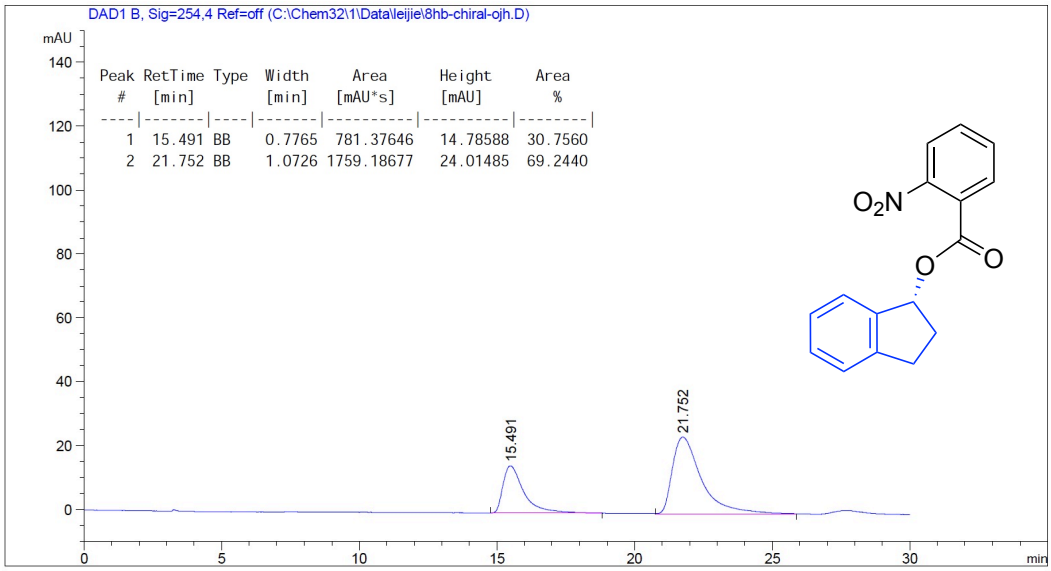

## HPLC Chromatogram of compound 8gb *(retention product)*



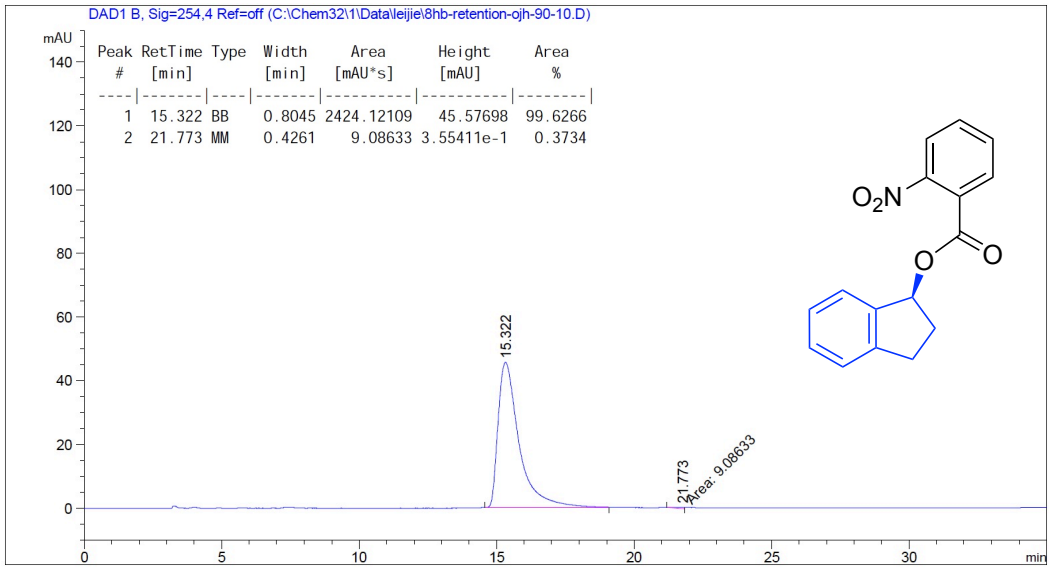
## HPLC Chromatogram of compound 8hb *(racemic product)*



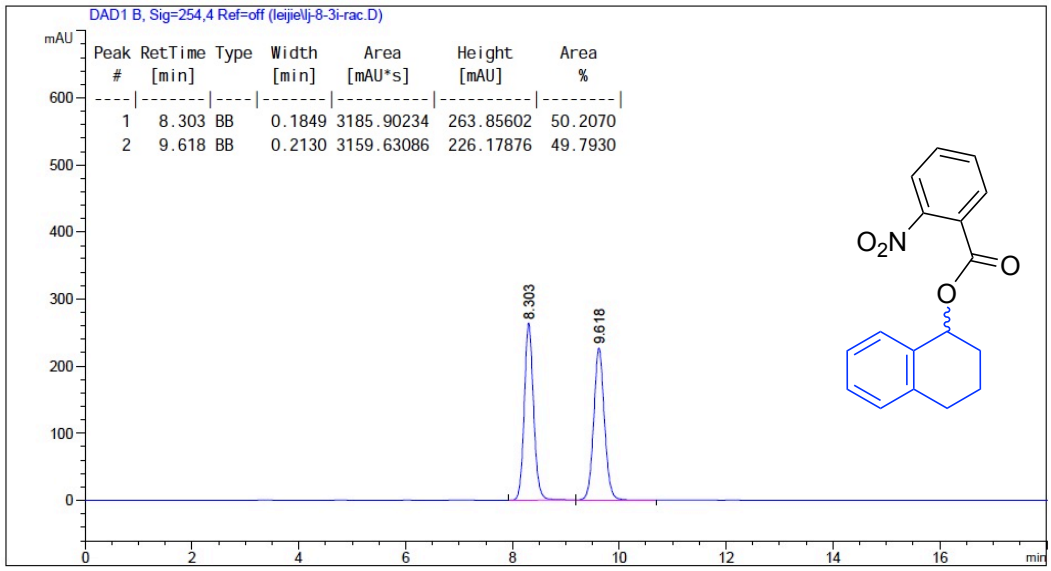

## HPLC Chromatogram of compound 8hb *((inversion product)*



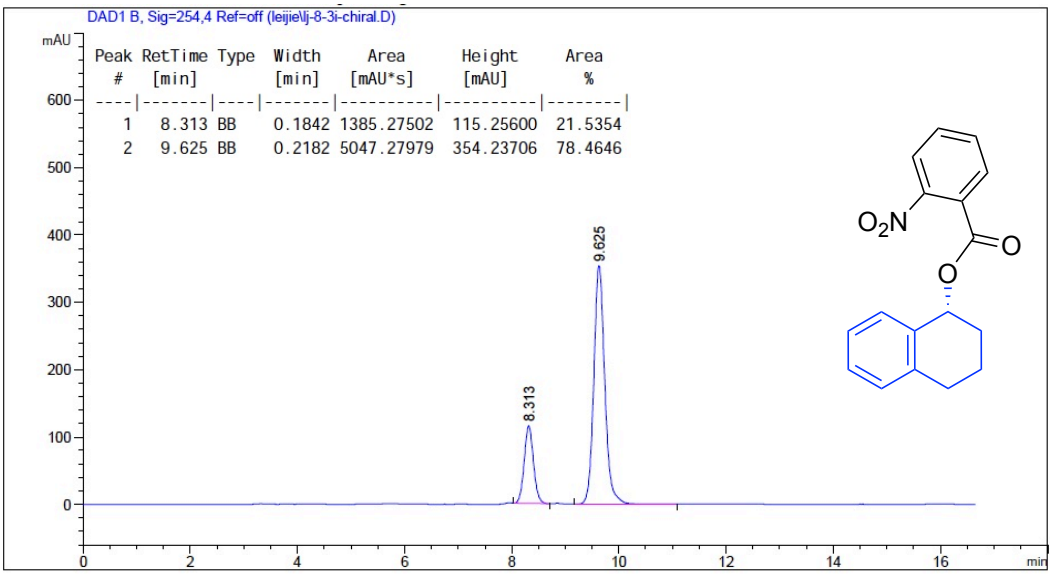

## HPLC Chromatogram of compound 8hb *(retention product)*



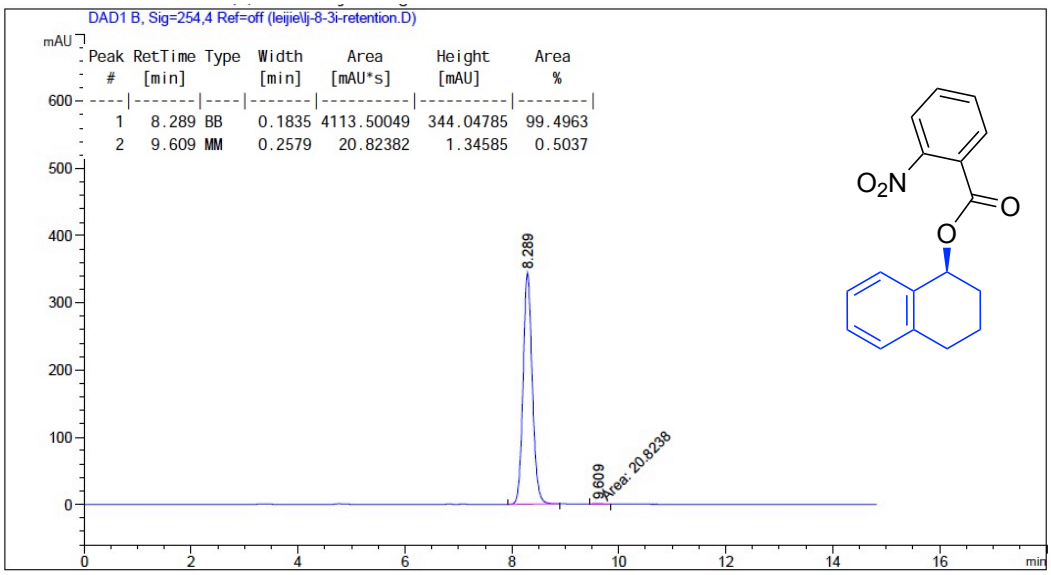
## HPLC Chromatogram of compound 8ib *(racemic product)*



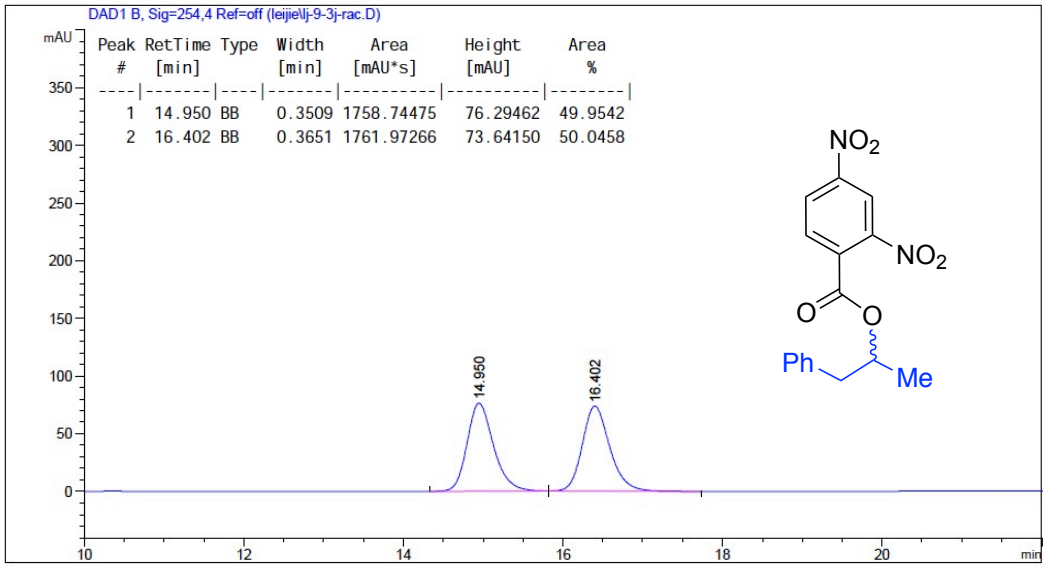

## HPLC Chromatogram of compound 8ib *((inversion product)*



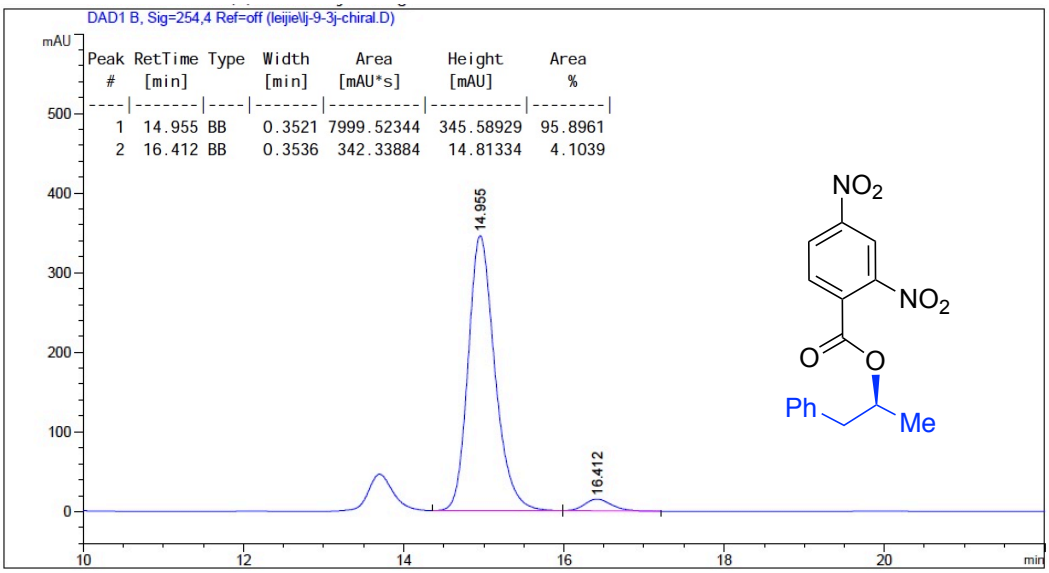

## HPLC Chromatogram of compound 8ib *(retention product)*



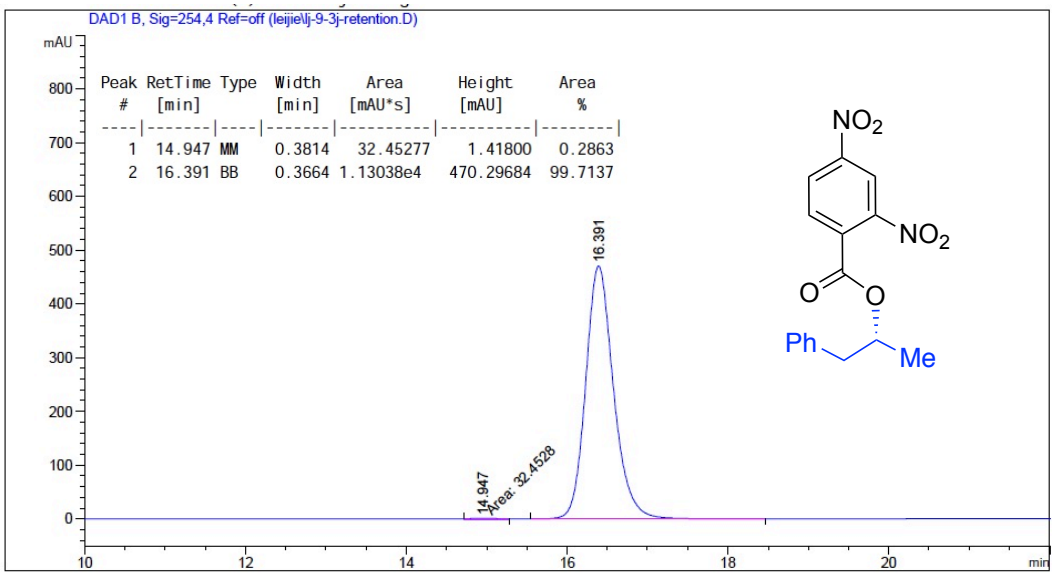
## HPLC Chromatogram of compound 8ja *(racemic product)*



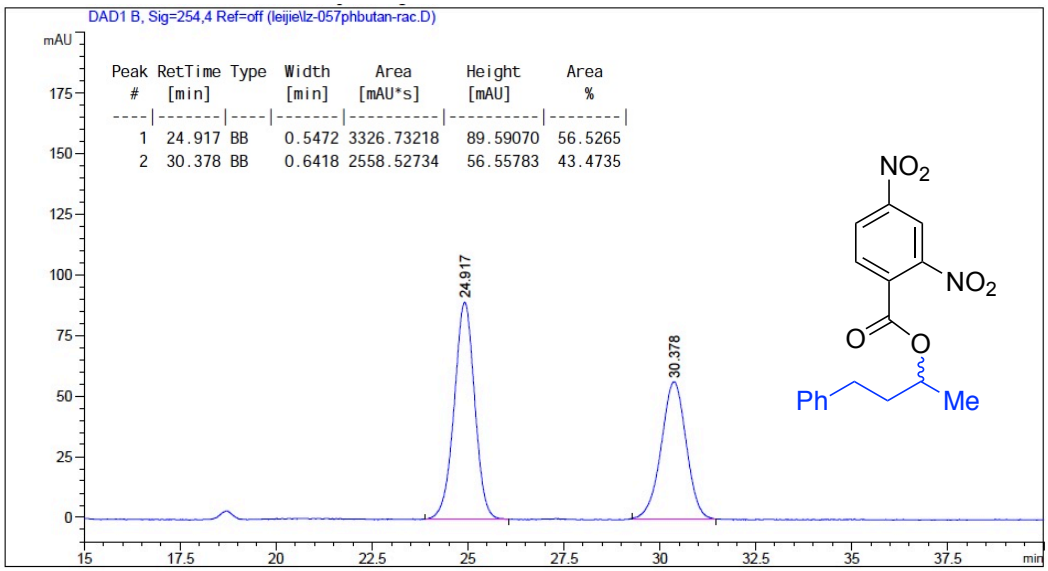

## HPLC Chromatogram of compound 8ja *((inversion product)*



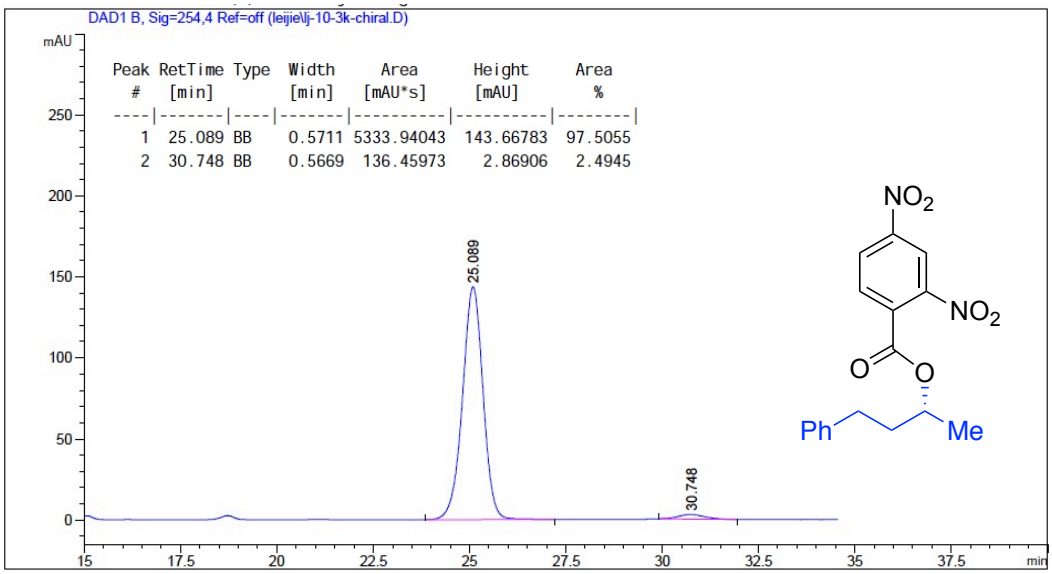

## HPLC Chromatogram of compound 8ja *(retention product)*



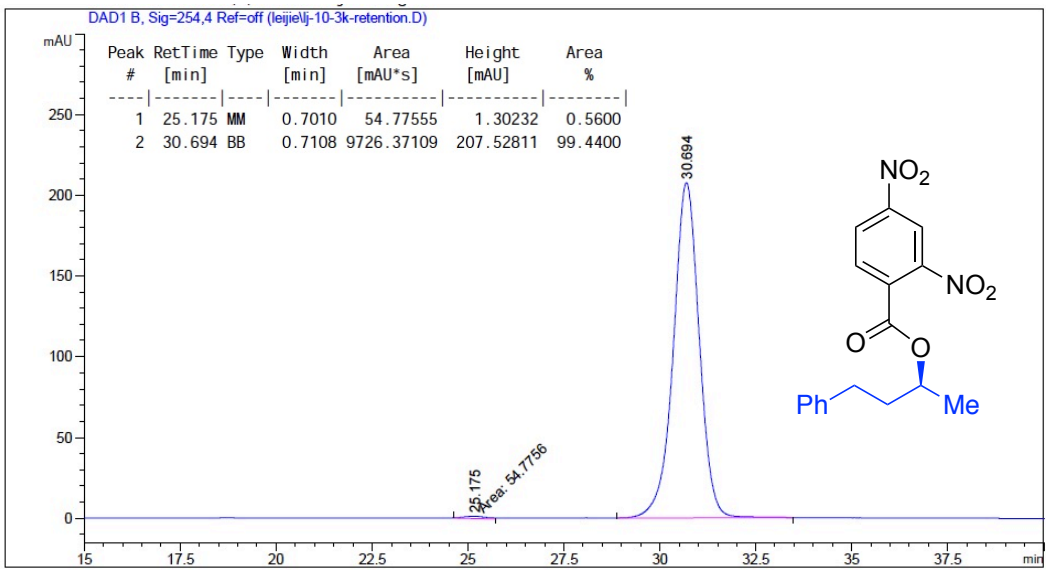
## HPLC Chromatogram of compound 8ka *(racemic product)*



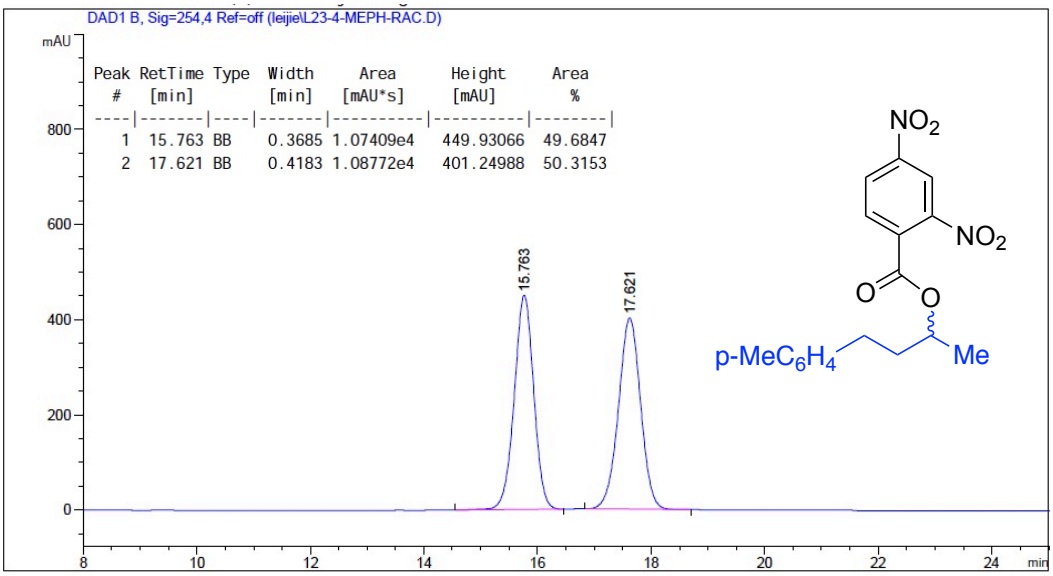

## HPLC Chromatogram of compound 8ka *((inversion product)*



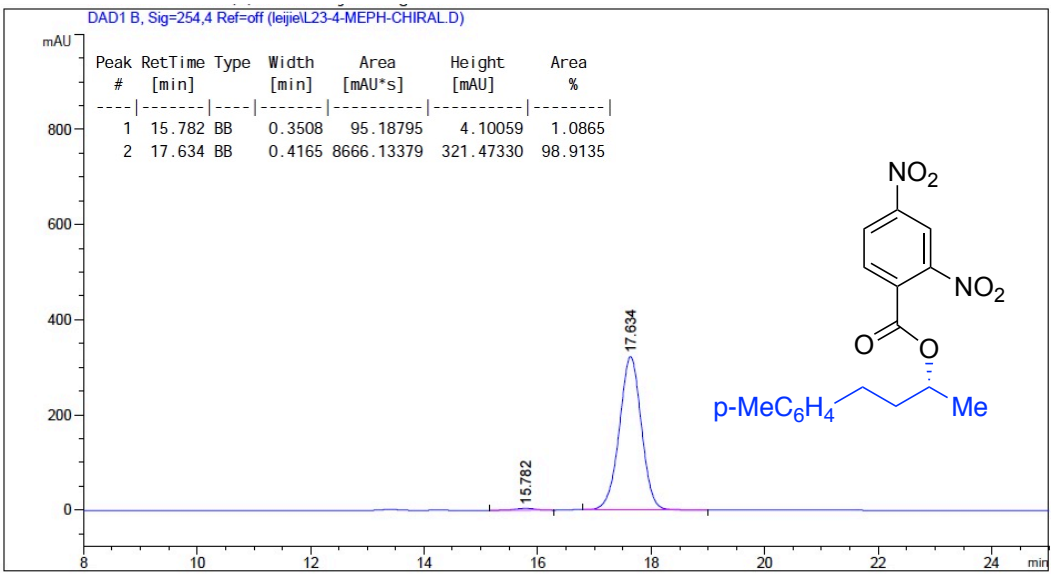

## HPLC Chromatogram of compound 8ka *(retention product)*



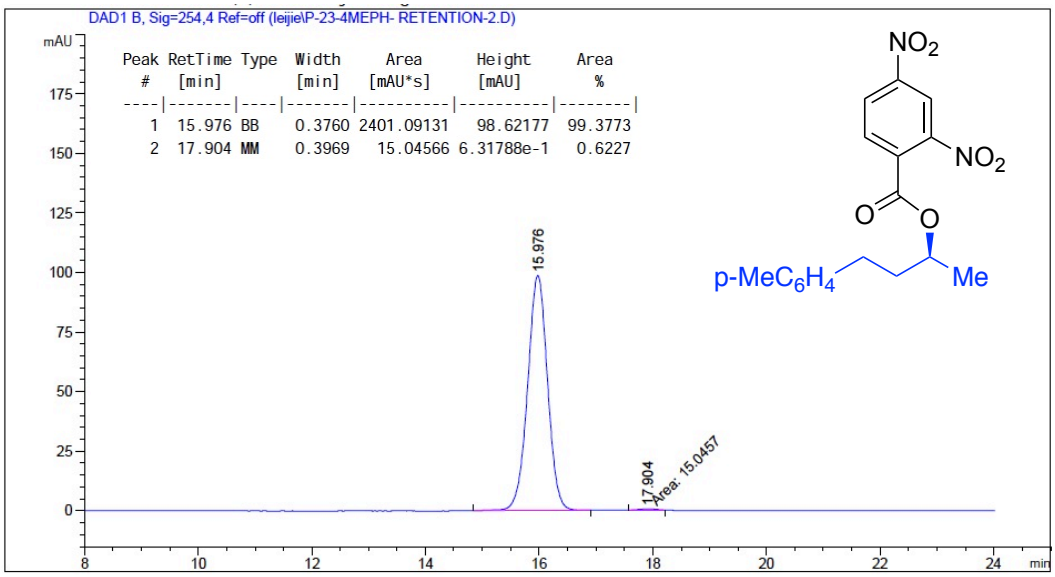
## HPLC Chromatogram of compound 8la *(racemic product)*



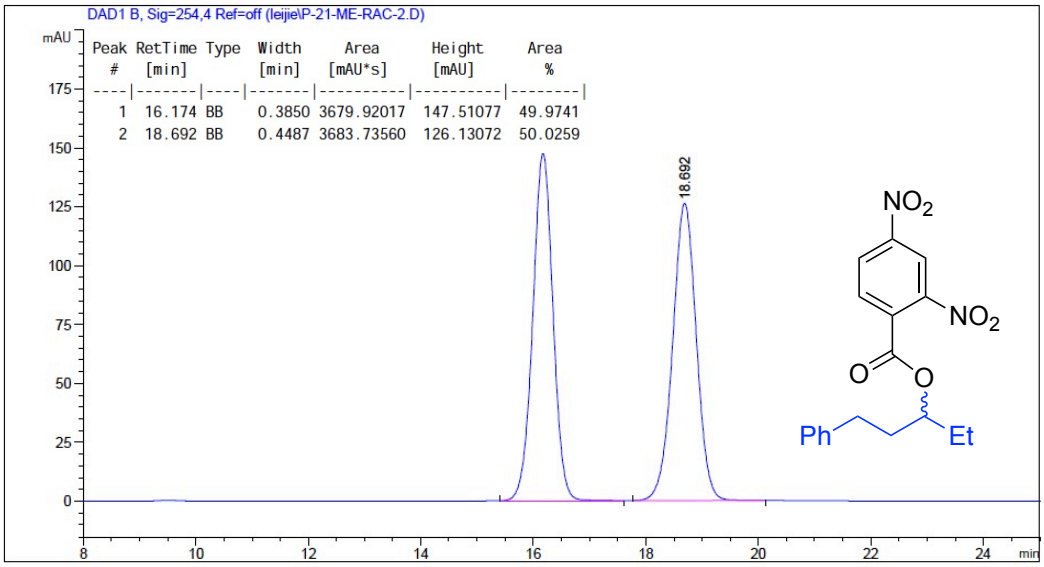

## HPLC Chromatogram of compound 8la *((inversion product)*



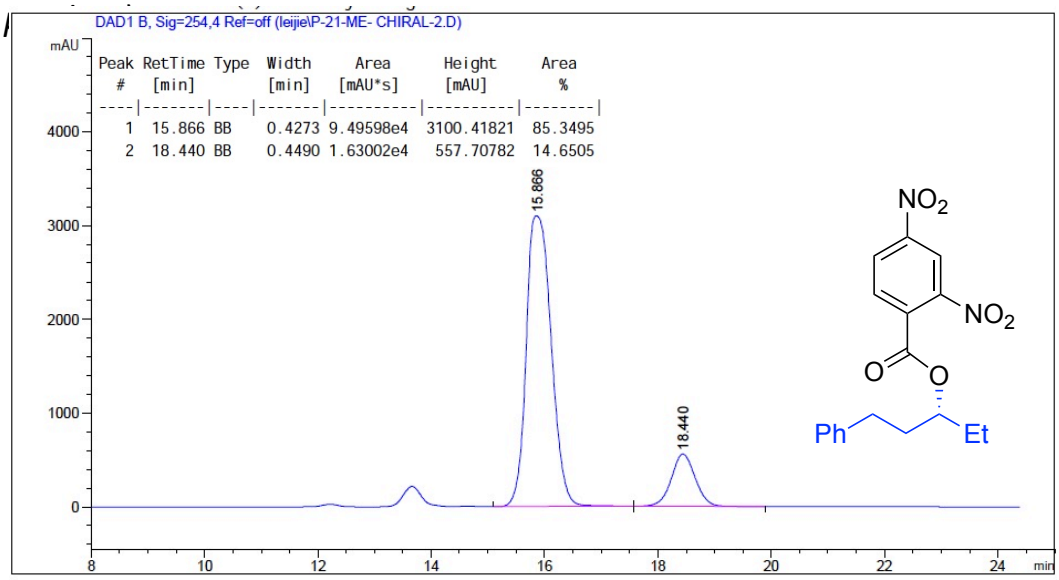

## HPLC Chromatogram of compound 8la *(retention product)*



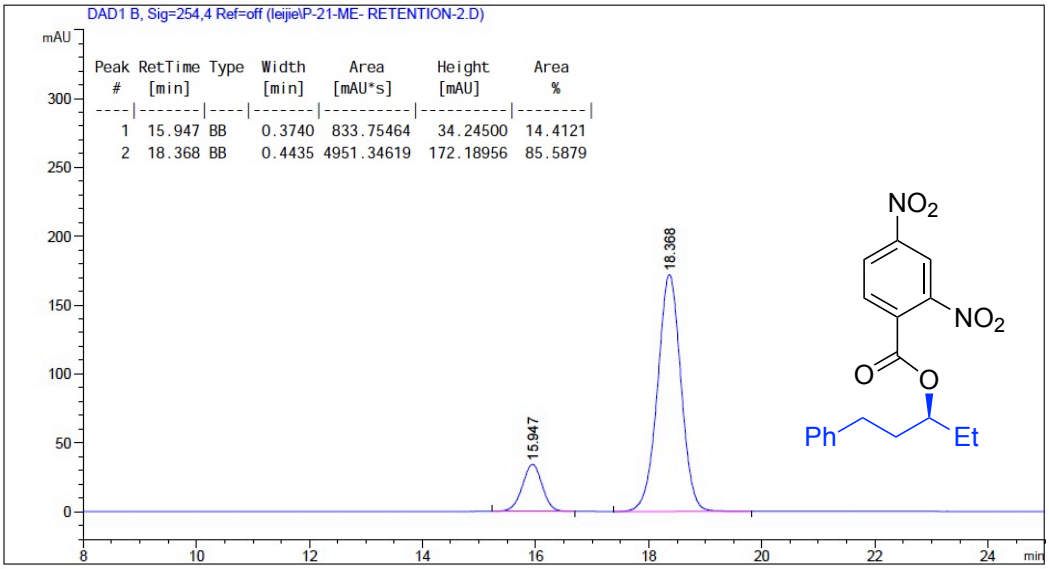
## HPLC Chromatogram of compound 8ma *(racemic product)*



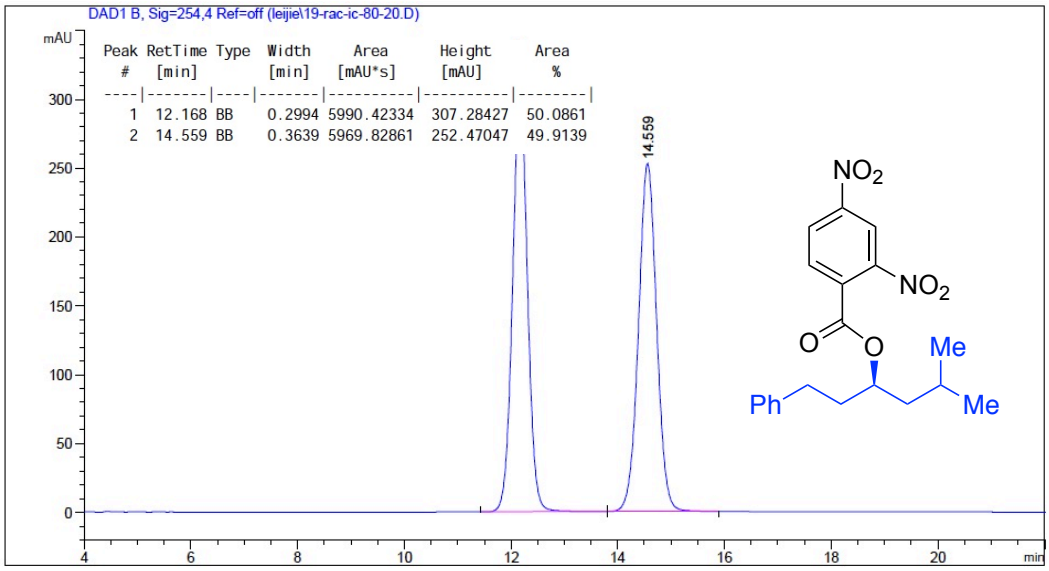

## HPLC Chromatogram of compound 8ma *((inversion*



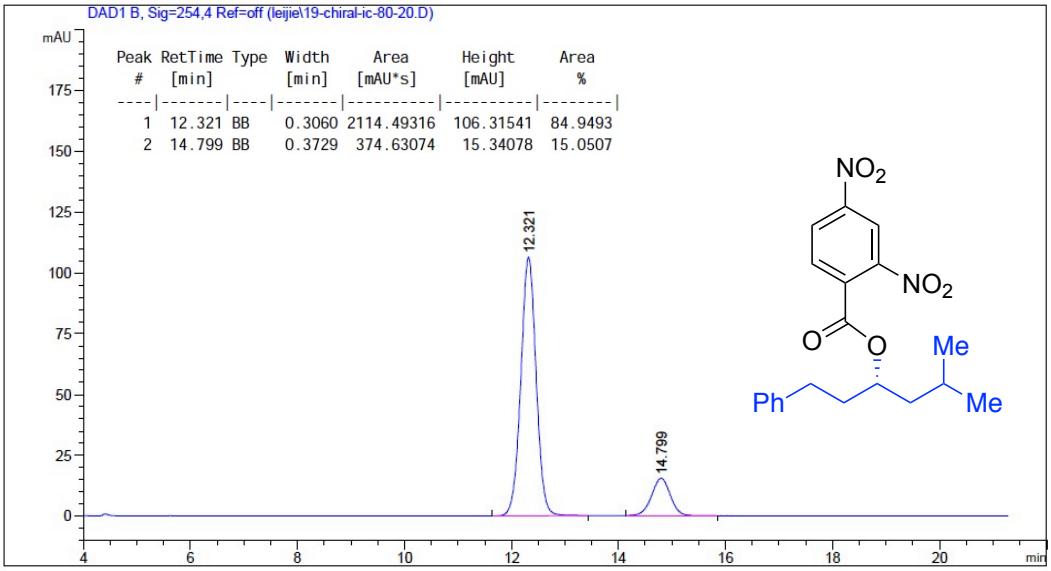

## HPLC Chromatogram of compound 8ma *(retention product)*



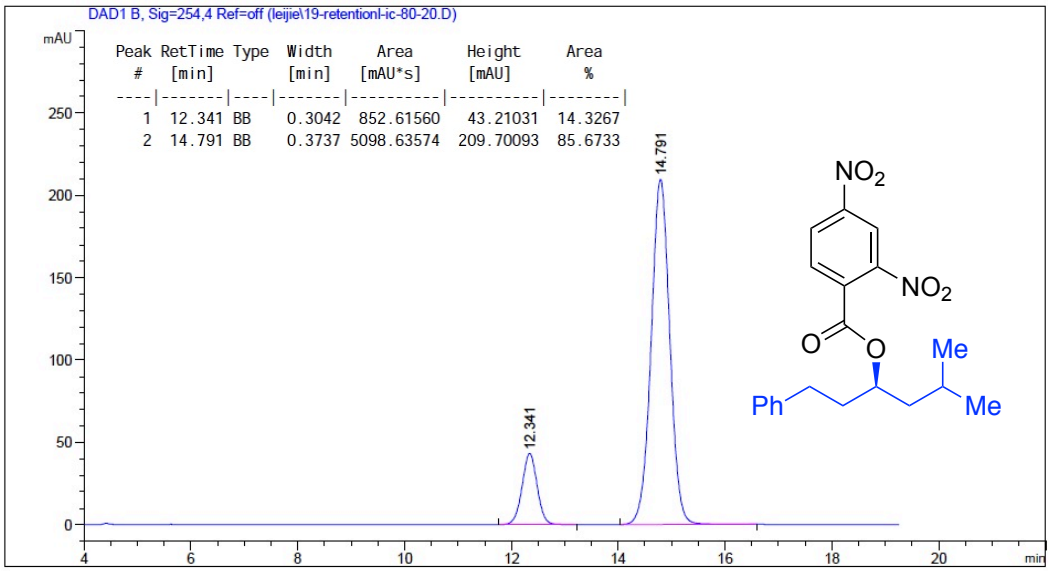
## HPLC Chromatogram of compound 8na *(racemic product)*



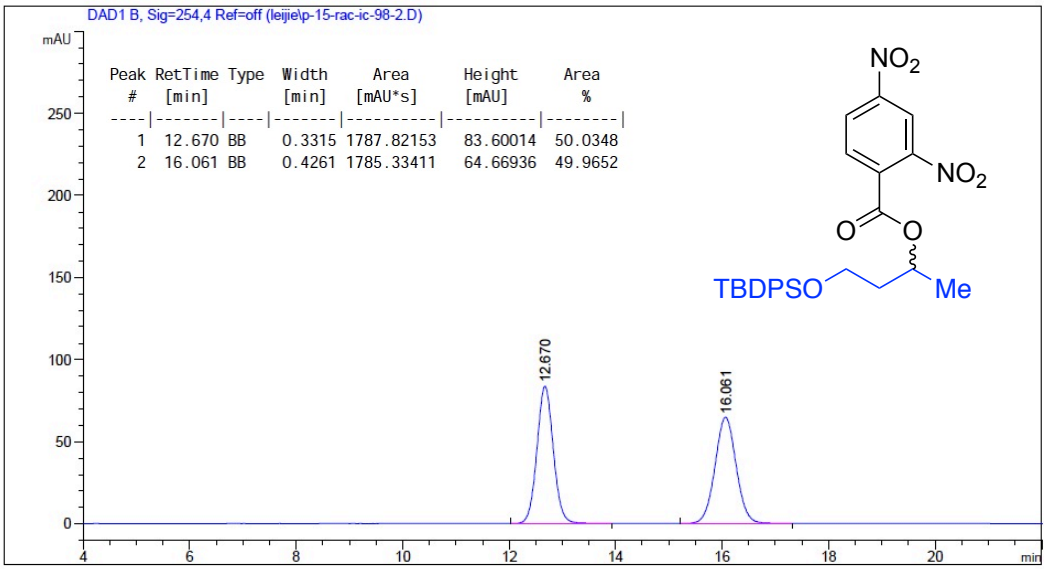

## HPLC Chromatogram of compound 8na *((inversion product)*



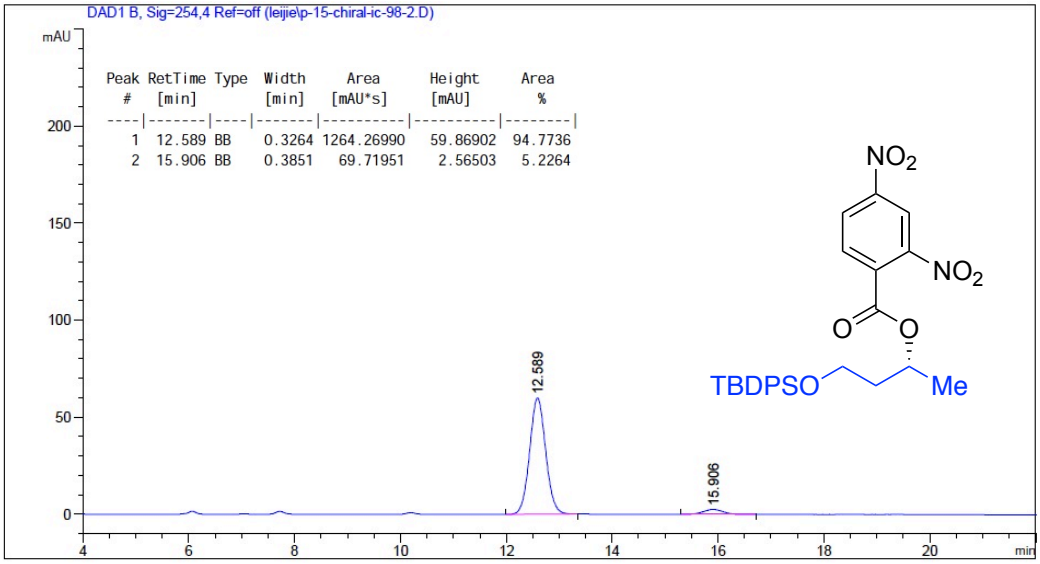

## HPLC Chromatogram of compound 8na *(retention product)*



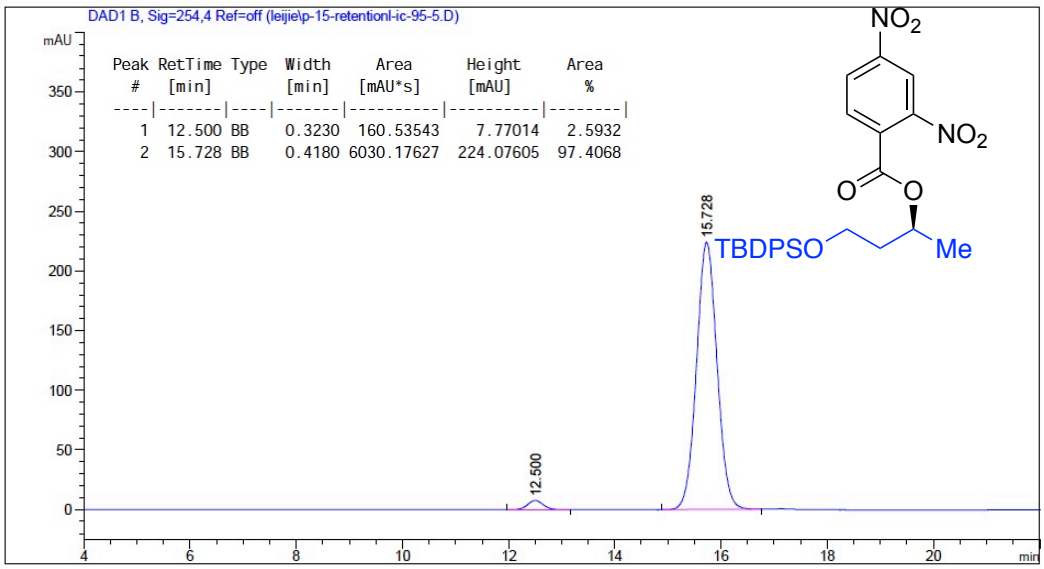
## HPLC Chromatogram of compound 8oa *(racemic product)*



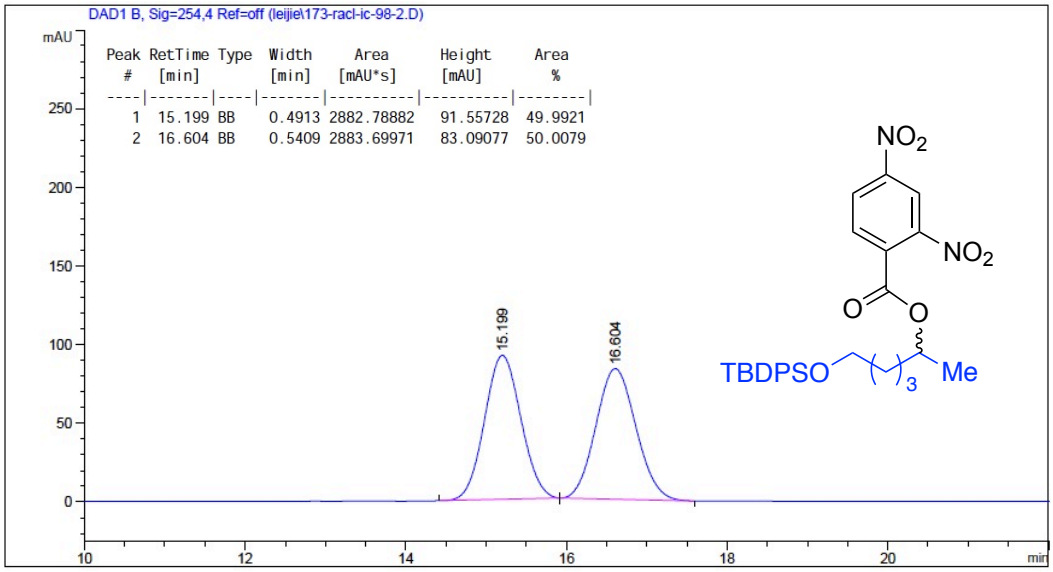

## HPLC Chromatogram of compound 8oa *((inversion product)*



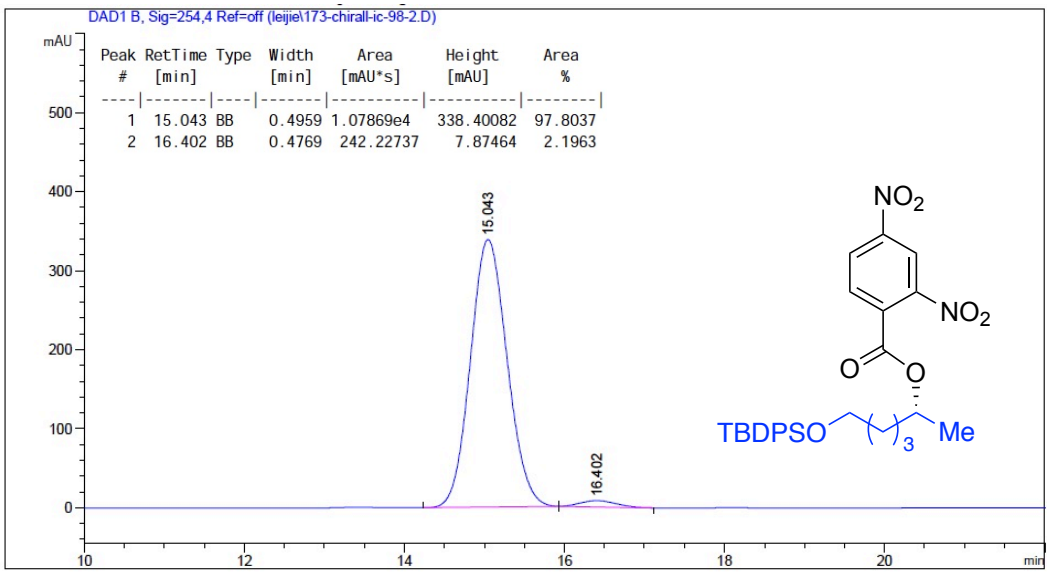

## HPLC Chromatogram of compound 8oa *(retention product)*



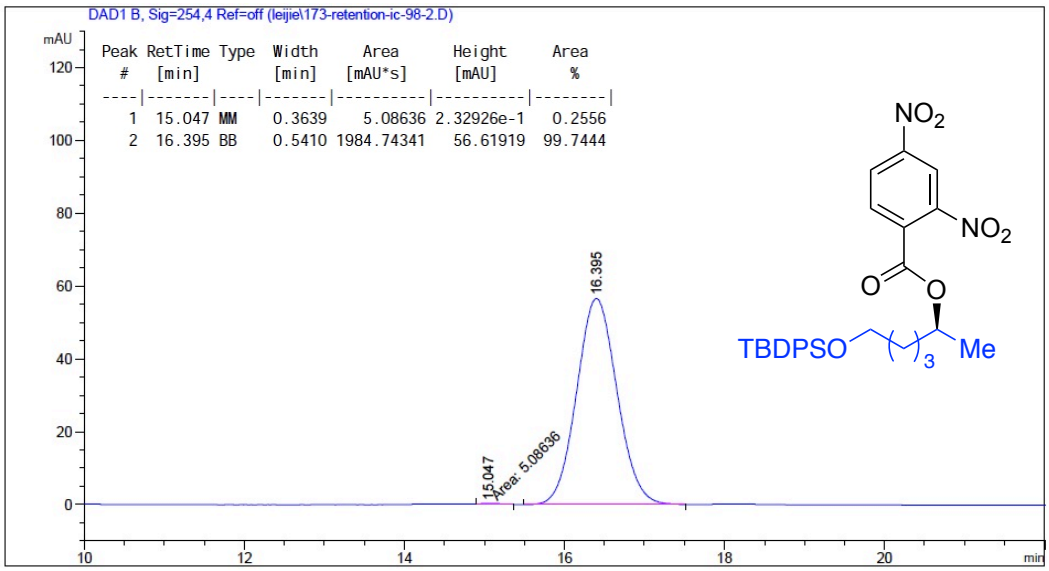
## HPLC Chromatogram of compound 8pa *(racemic product)*



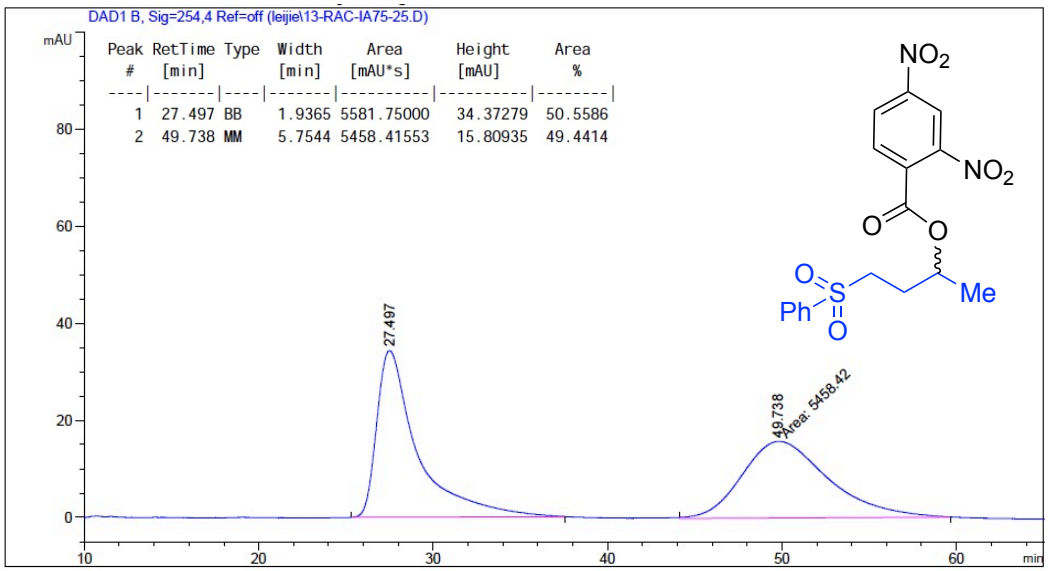

## HPLC Chromatogram of compound 8pa *((inversion product)*



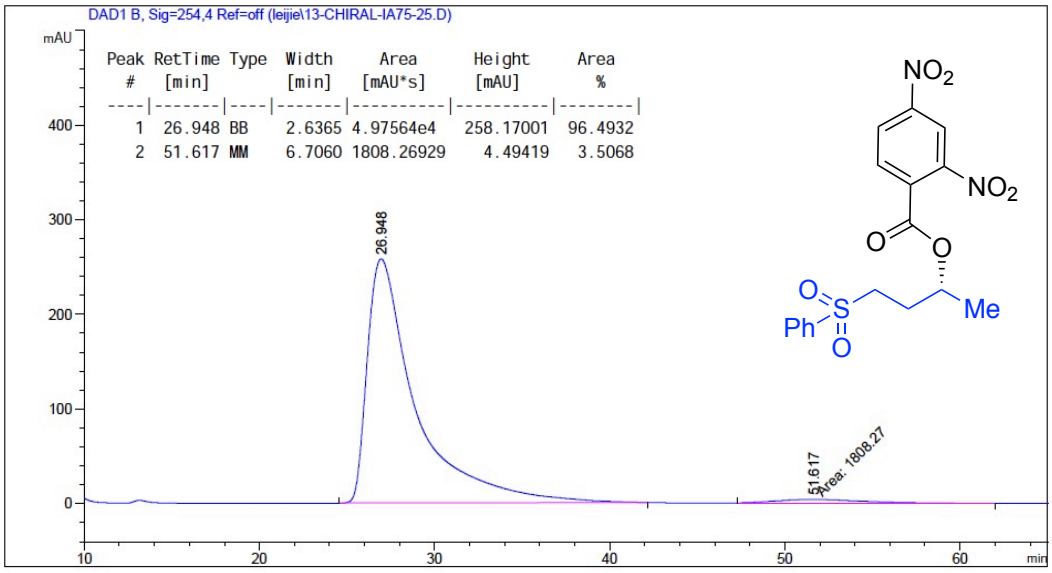

## HPLC Chromatogram of compound 8pa *(retention product)*



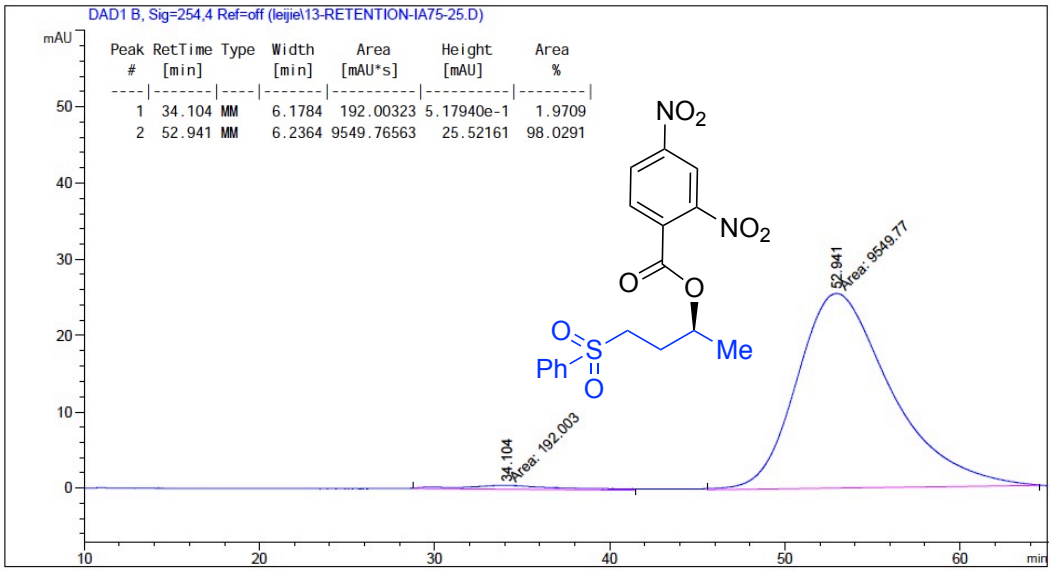
## HPLC Chromatogram of compound 8qa *(racemic product)*



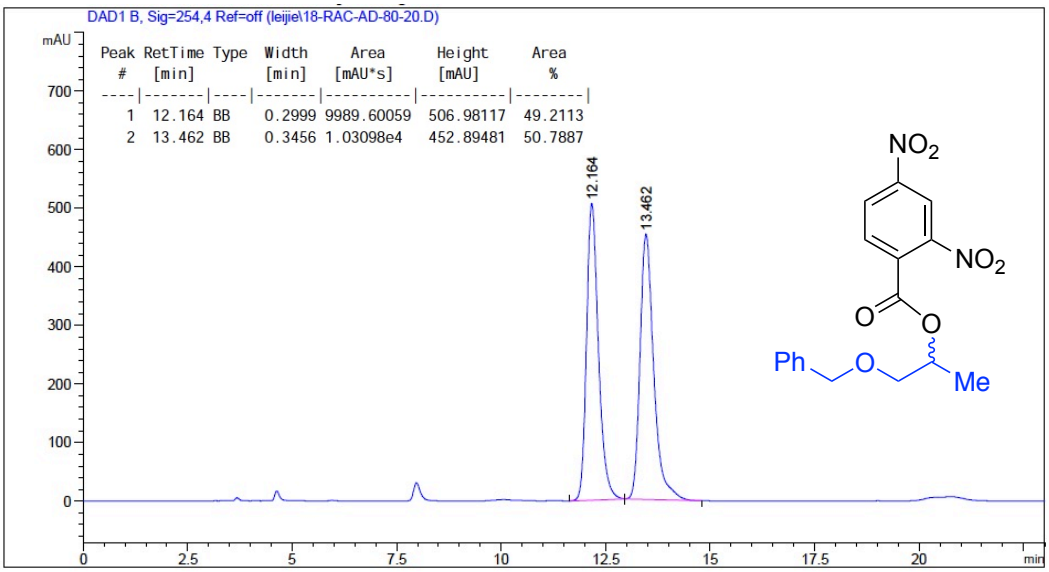

## HPLC Chromatogram of compound 8qa *((inversion product)*



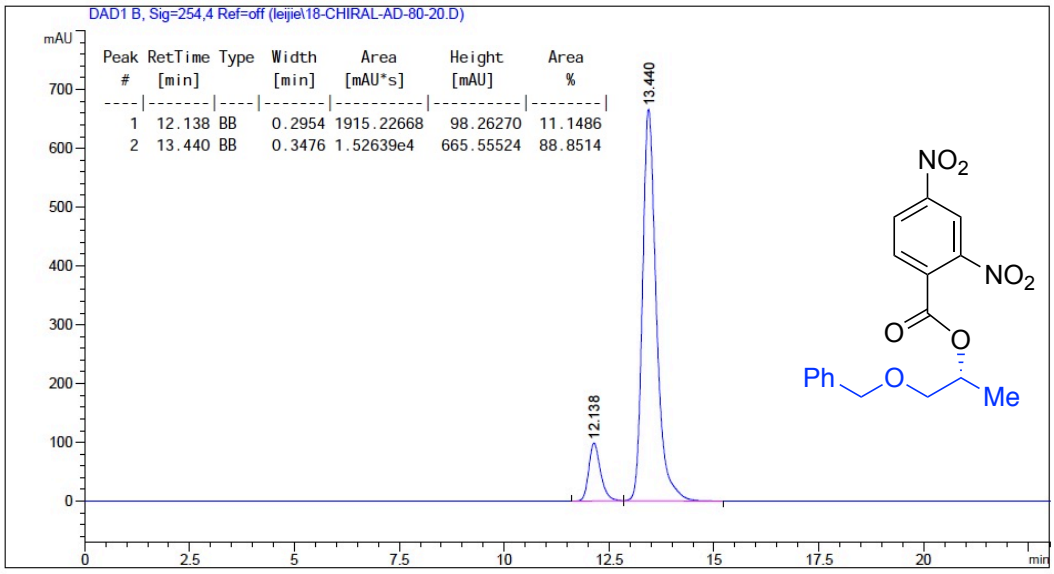

## HPLC Chromatogram of compound 8qa *(retention product)*



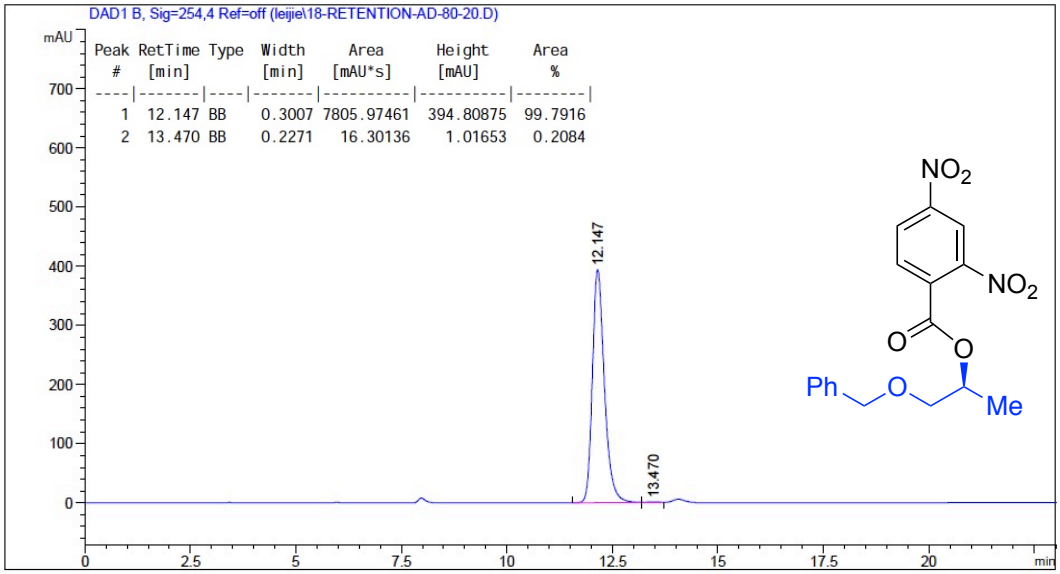
## HPLC Chromatogram of compound 8ra *(racemic product)*



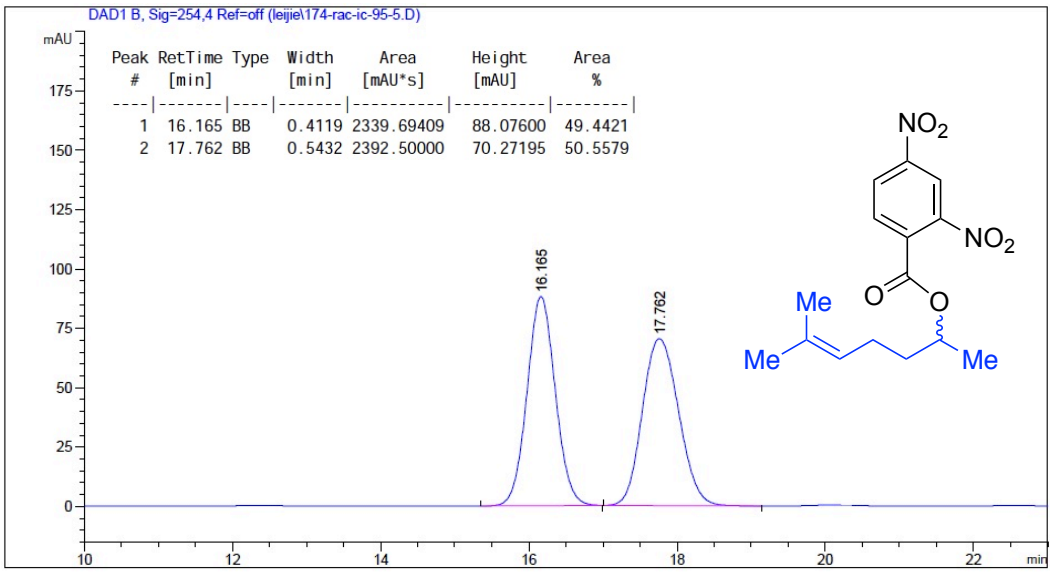

## HPLC Chromatogram of compound 8ra *((inversion product)*



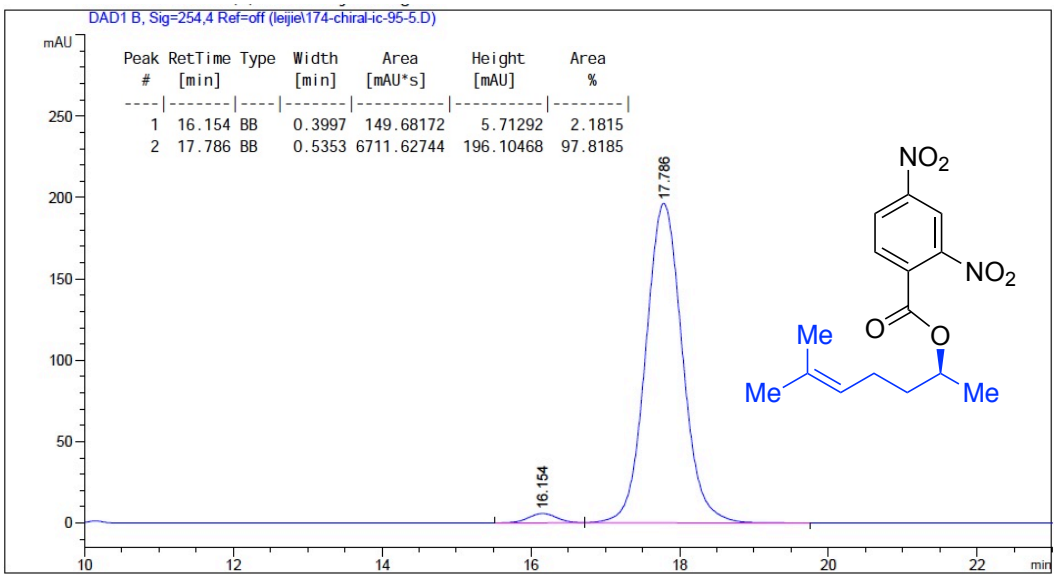

## HPLC Chromatogram of compound 8ra *(retention product)*



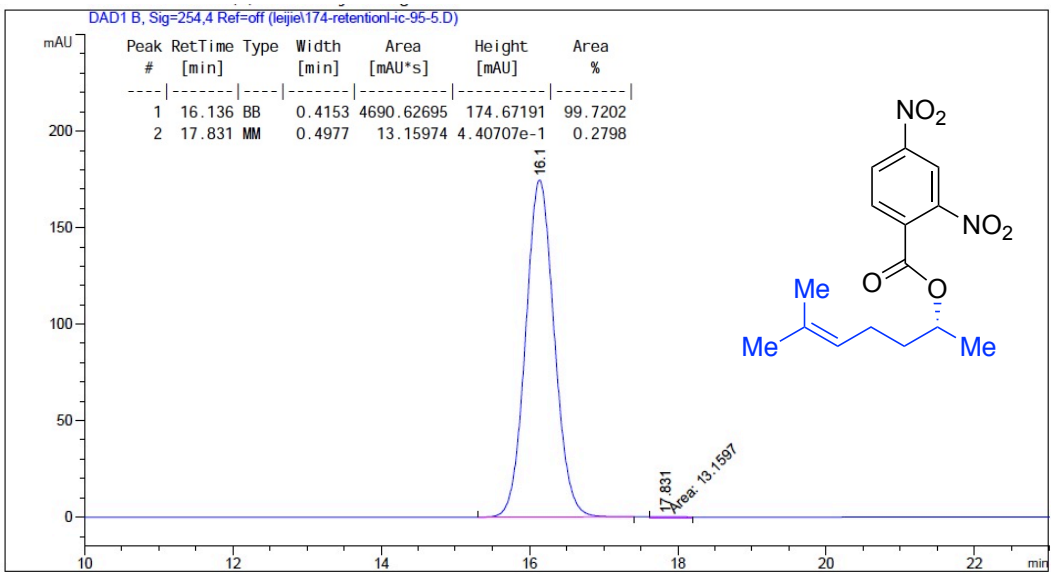
## HPLC Chromatogram of compound 8sa *(racemic product)*



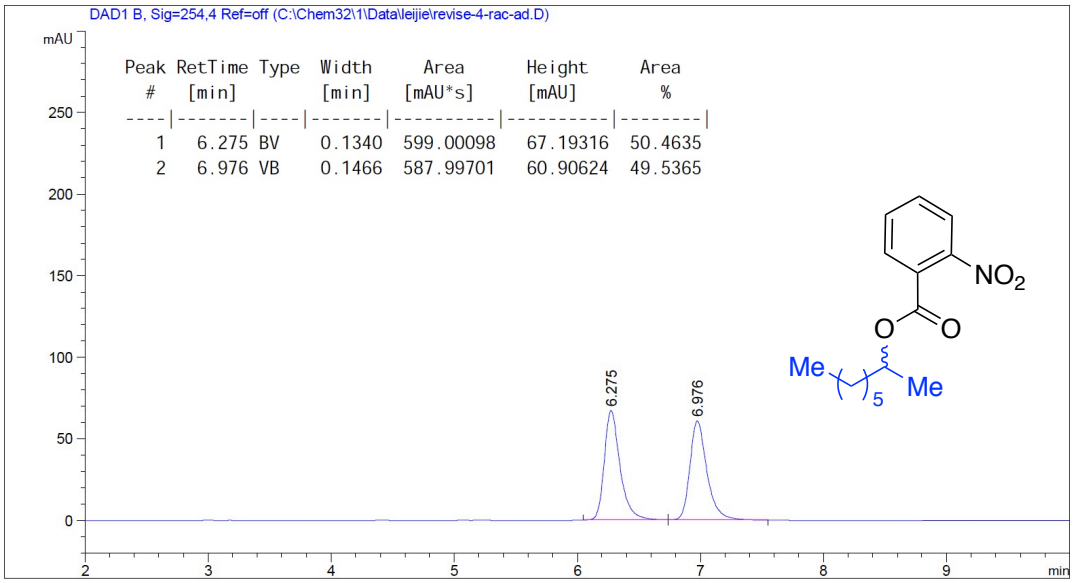

## HPLC Chromatogram of compound 8sa *((inversion product)*



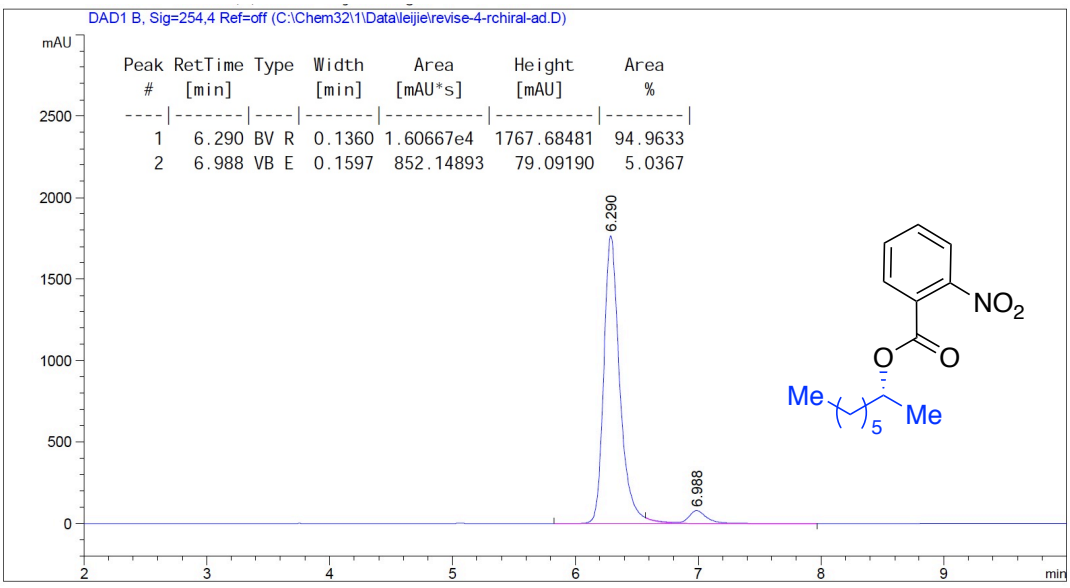

## HPLC Chromatogram of compound 8sa *(retention product)*



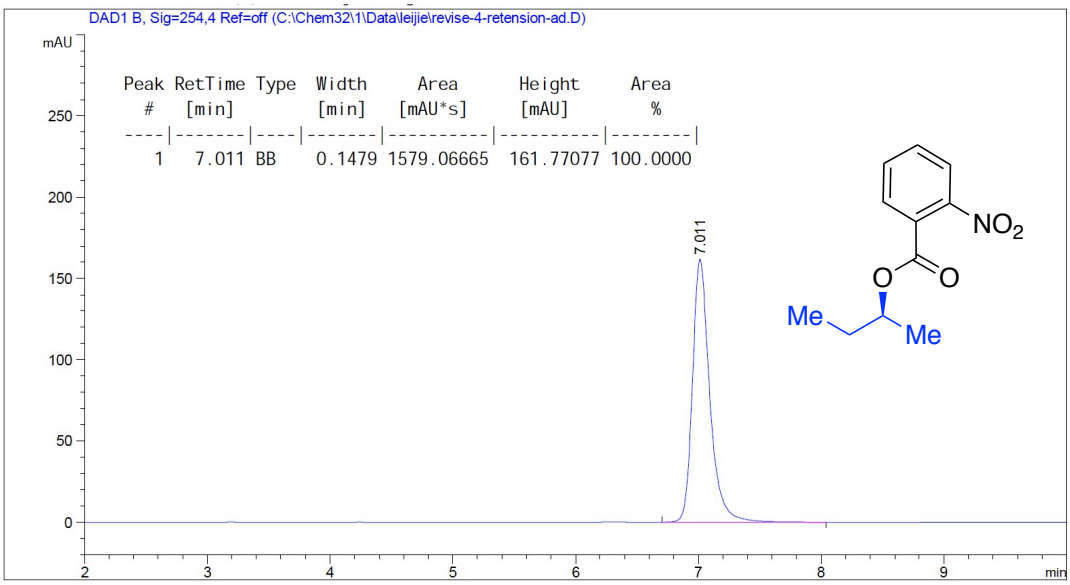
## HPLC Chromatogram of compound 8ab *(racemic product)*



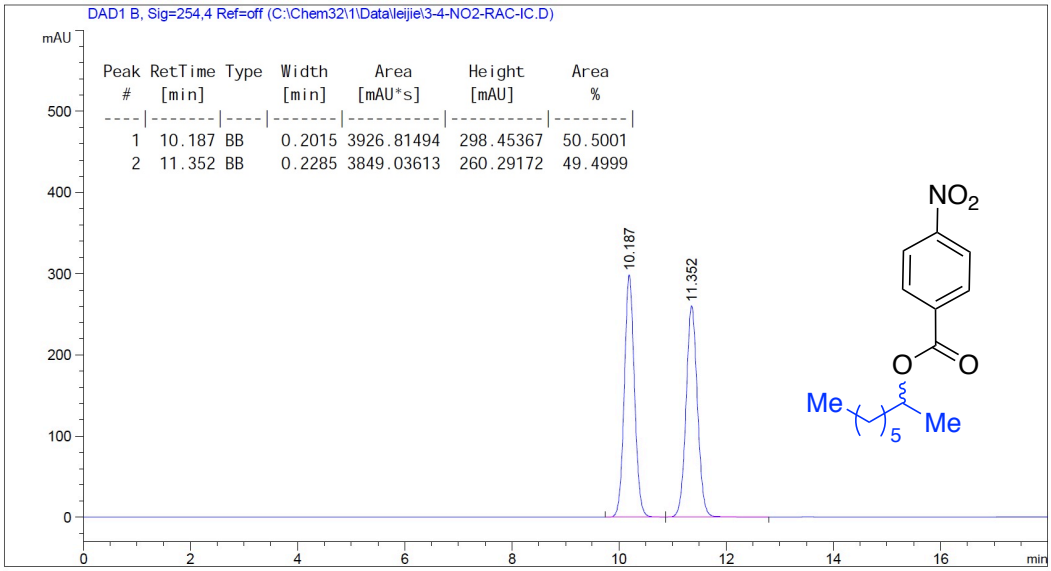

## HPLC Chromatogram of compound 8ab *((inversion product)*



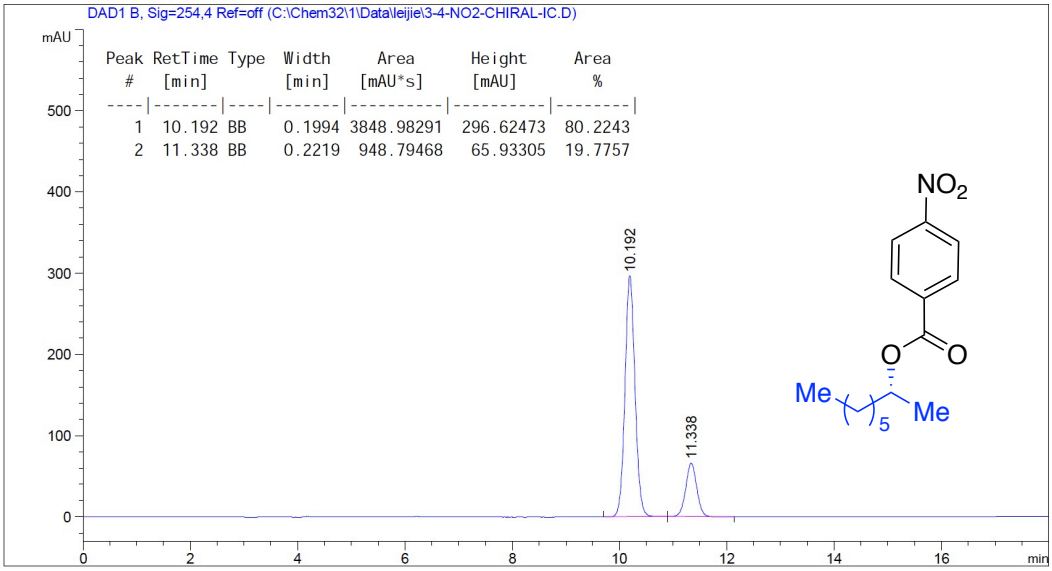

## HPLC Chromatogram of compound 8ab *(retention product)*



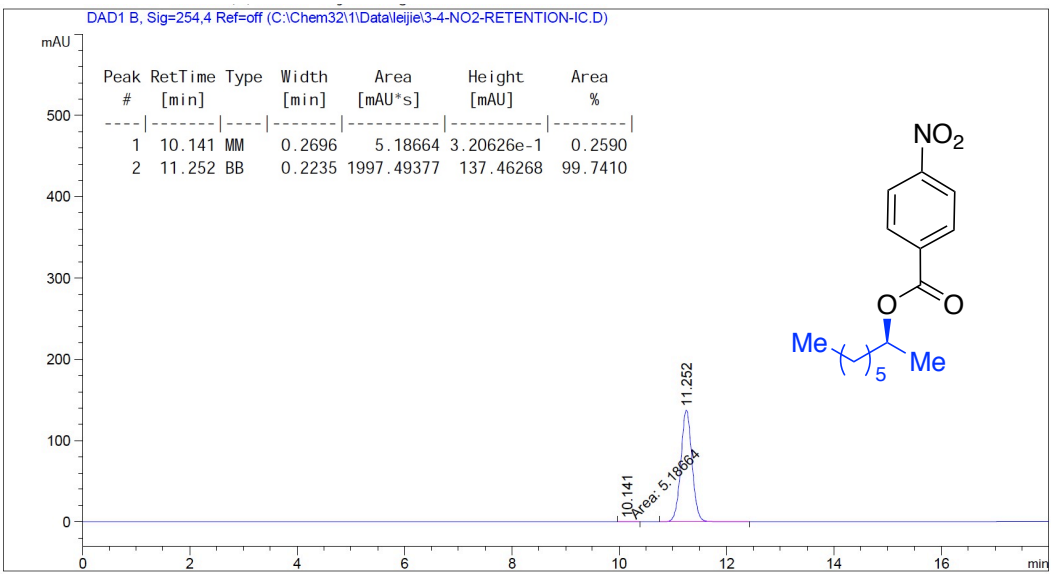
## HPLC Chromatogram of compound 8ac *(racemic product)*



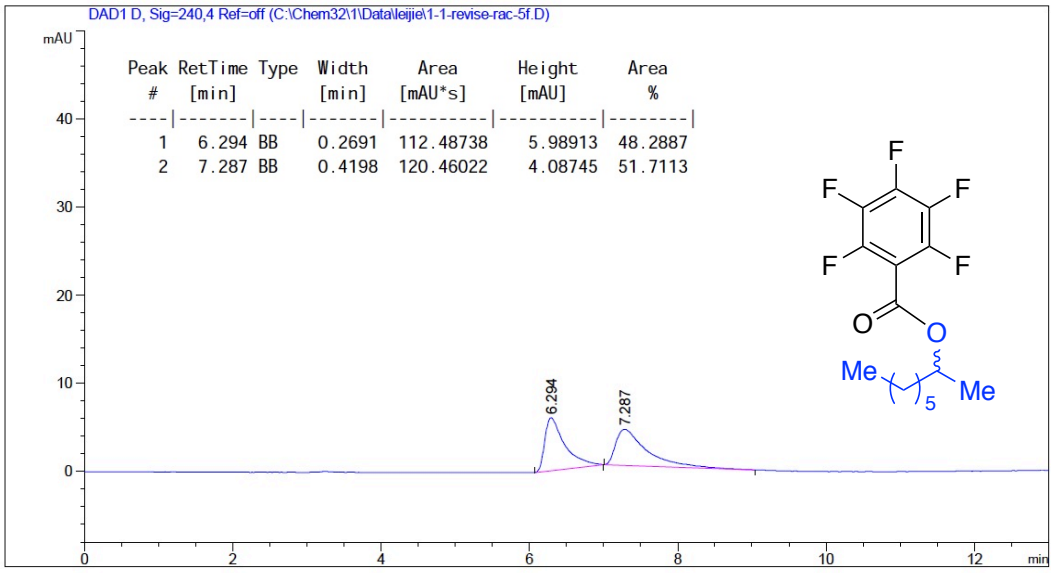

## HPLC Chromatogram of compound 8ac *((inversion product)*



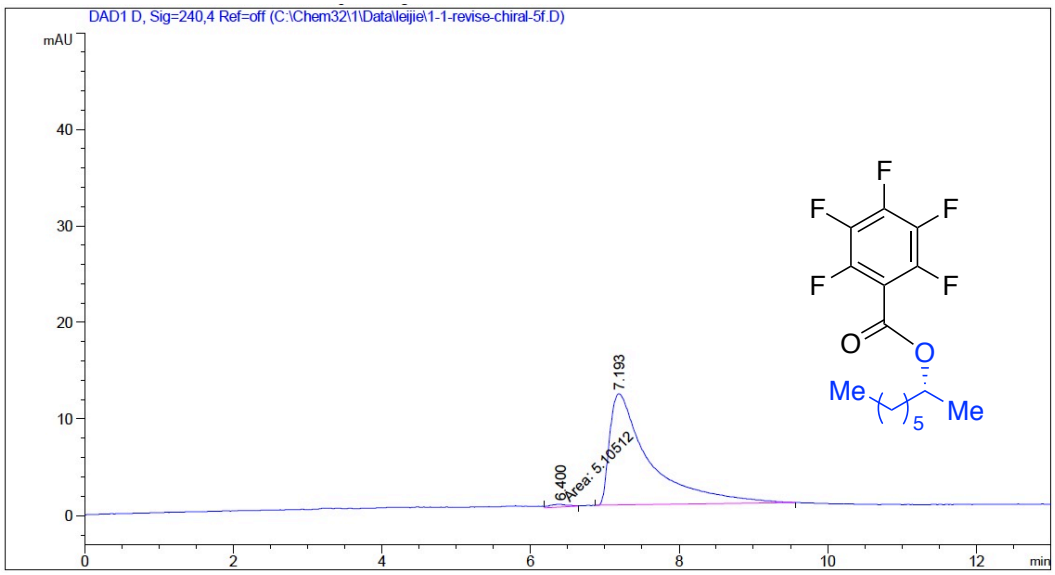

## HPLC Chromatogram of compound 8ac *(retention product)*



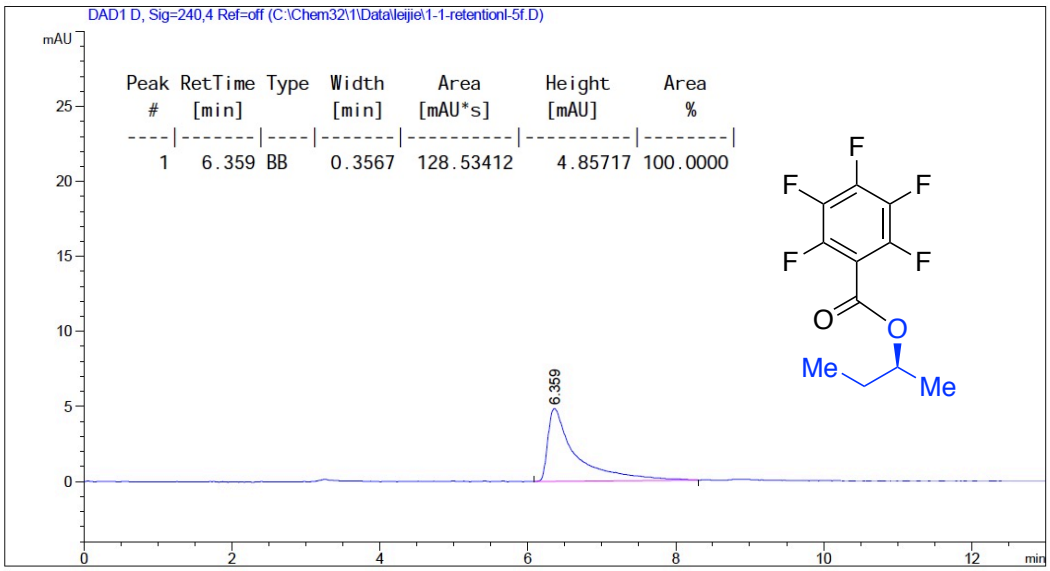
## HPLC Chromatogram of compound 8ae *(racemic product)*



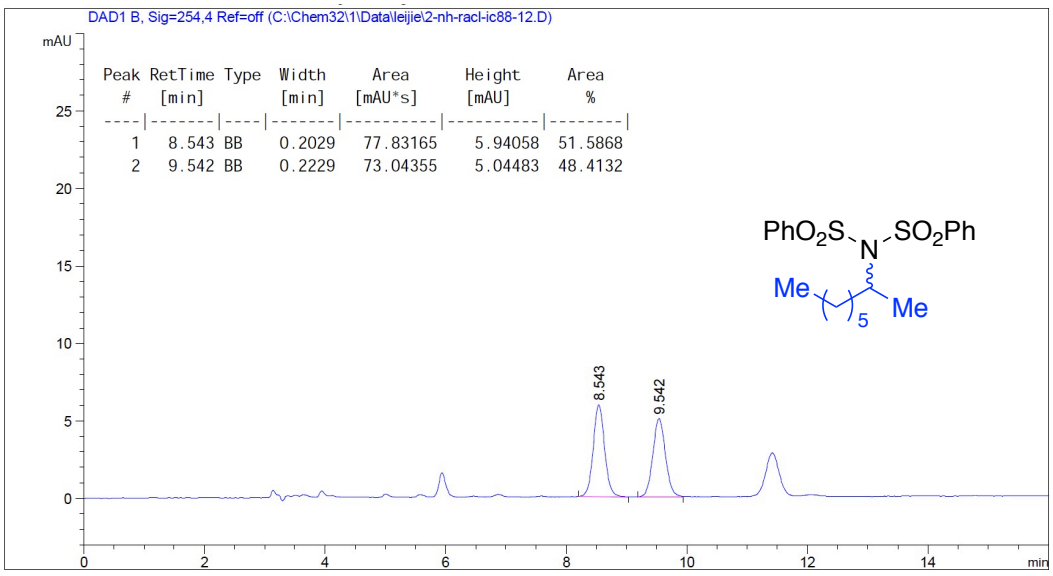

## HPLC Chromatogram of compound 8ae *((inversion product)*



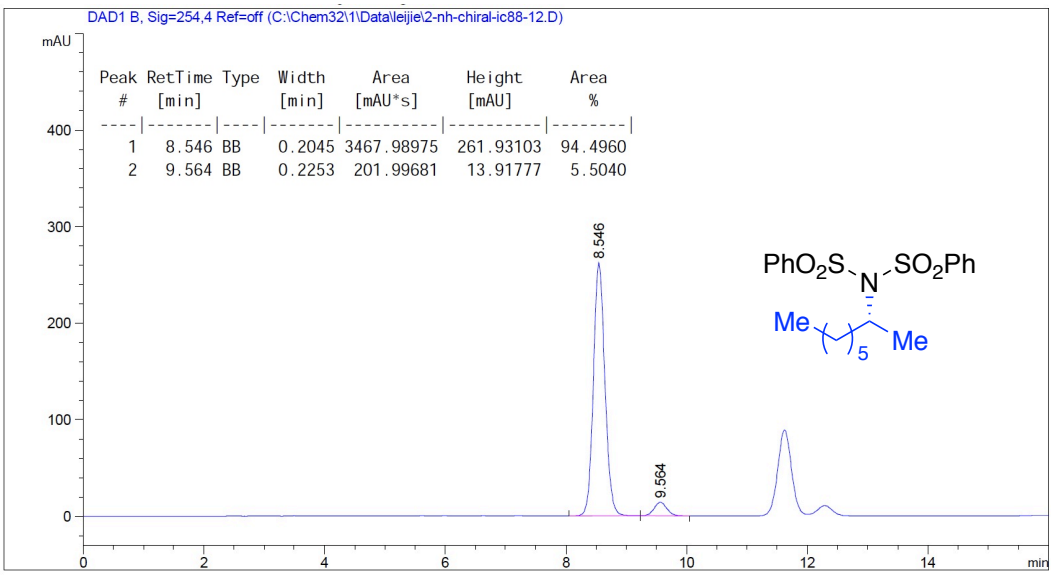

## HPLC Chromatogram of compound 8ae *(retention product)*



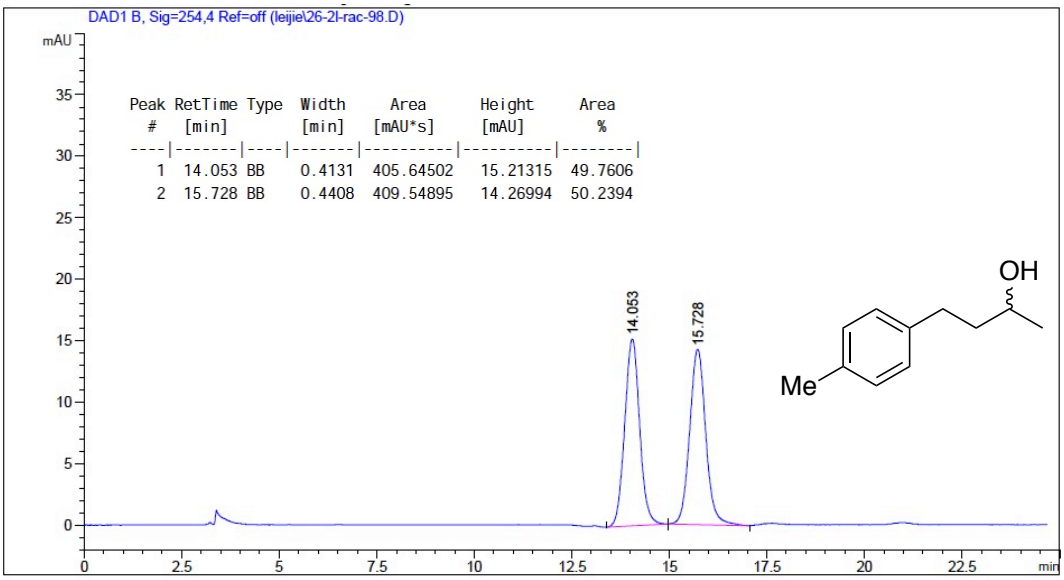
## HPLC Chromatogram of compound 8af *(racemic product)*



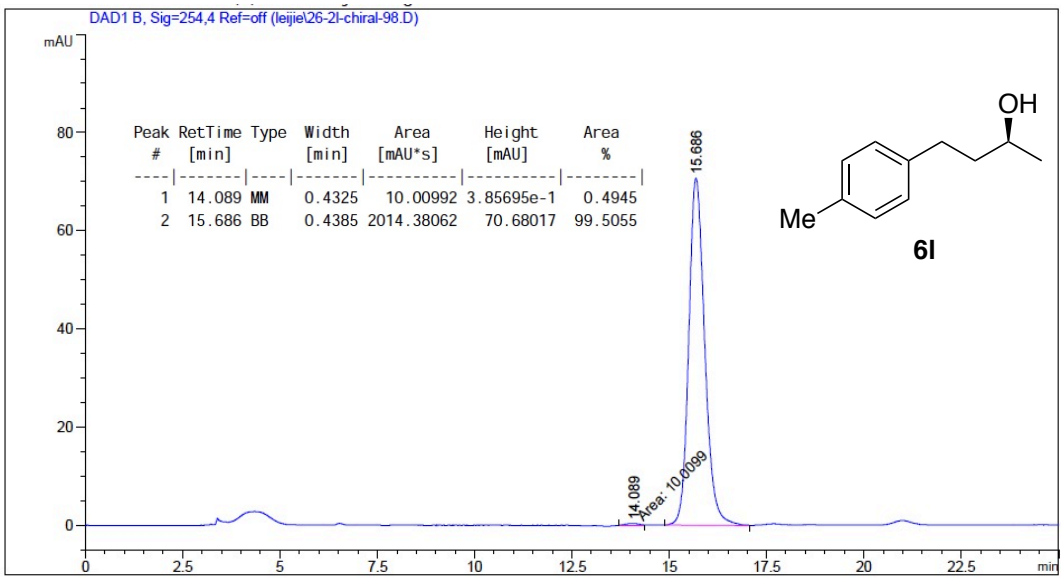

## HPLC Chromatogram of compound 8af *((inversion product)*



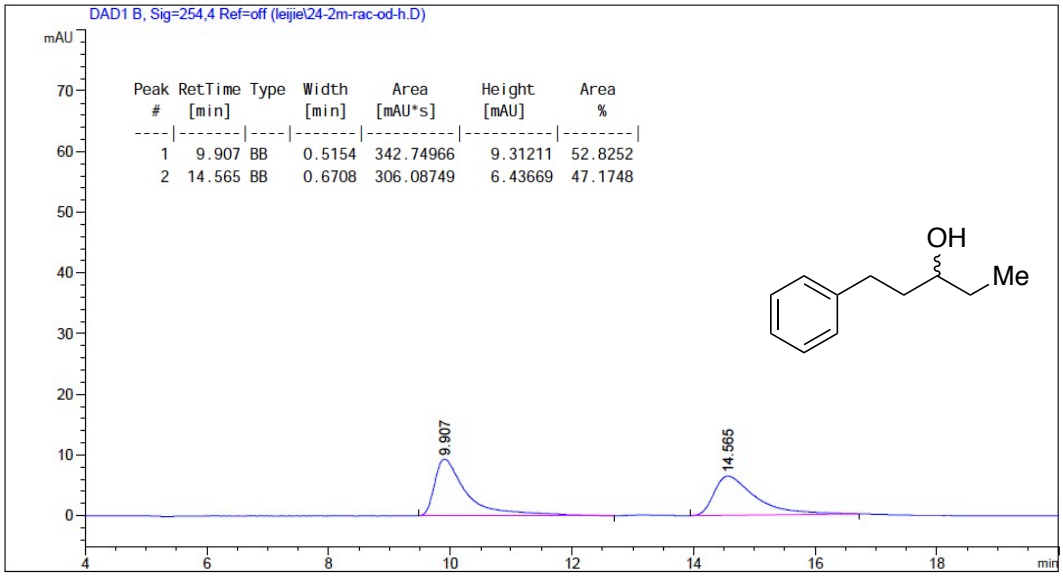
## HPLC Chromatogram of compound 6l *(racemic product)*



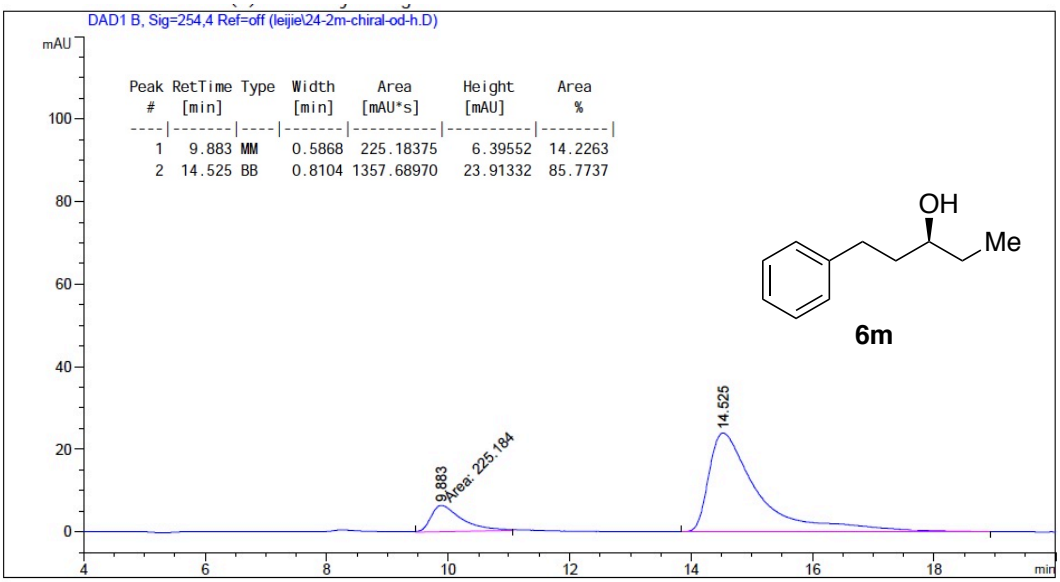

## HPLC Chromatogram of compound 6l *(chiral product)*



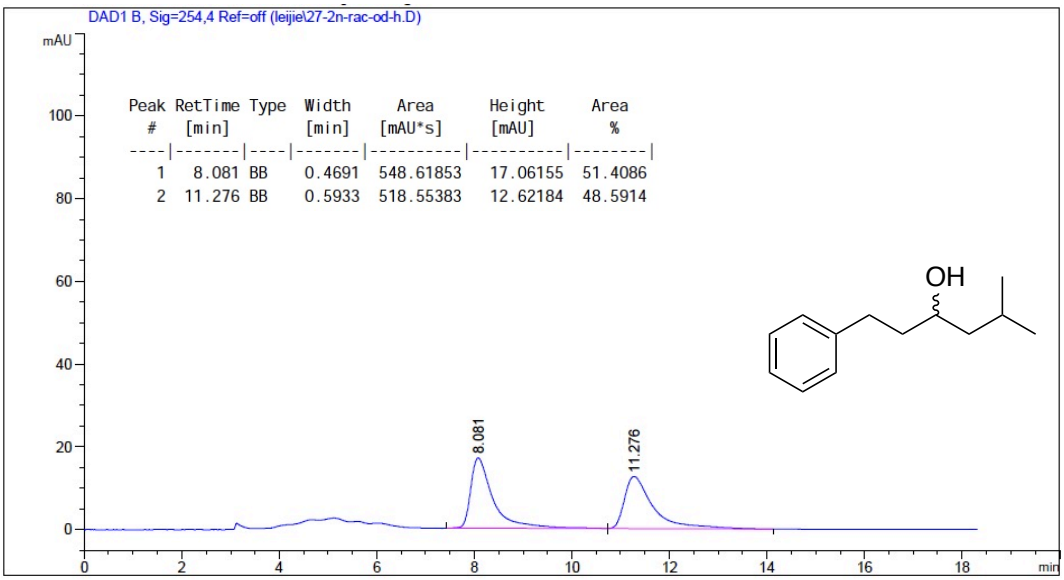
## HPLC Chromatogram of compound 6m *(racemic product)*



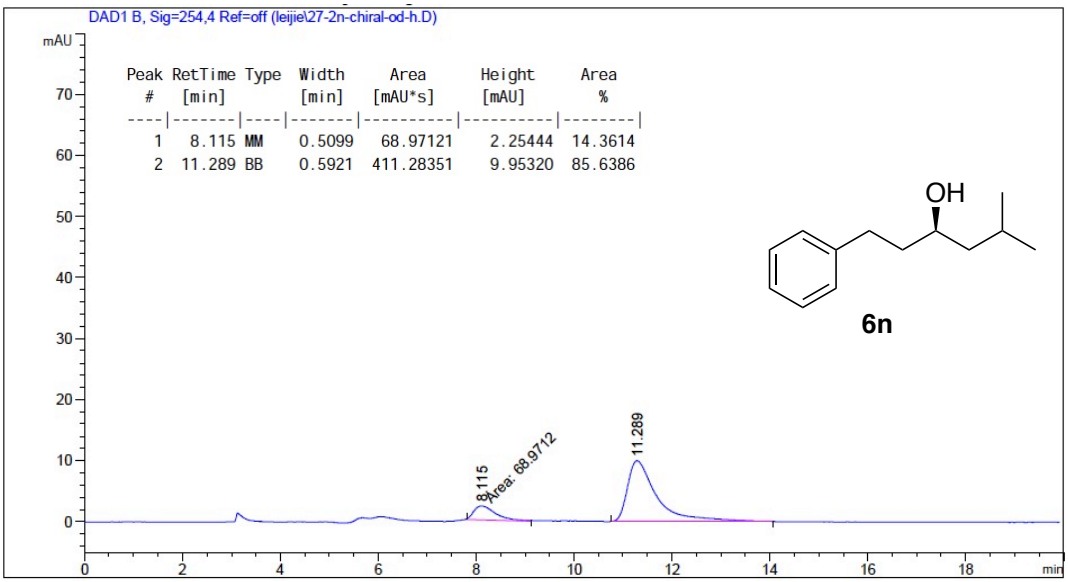

## HPLC Chromatogram of compound 6m *(chiral product)*



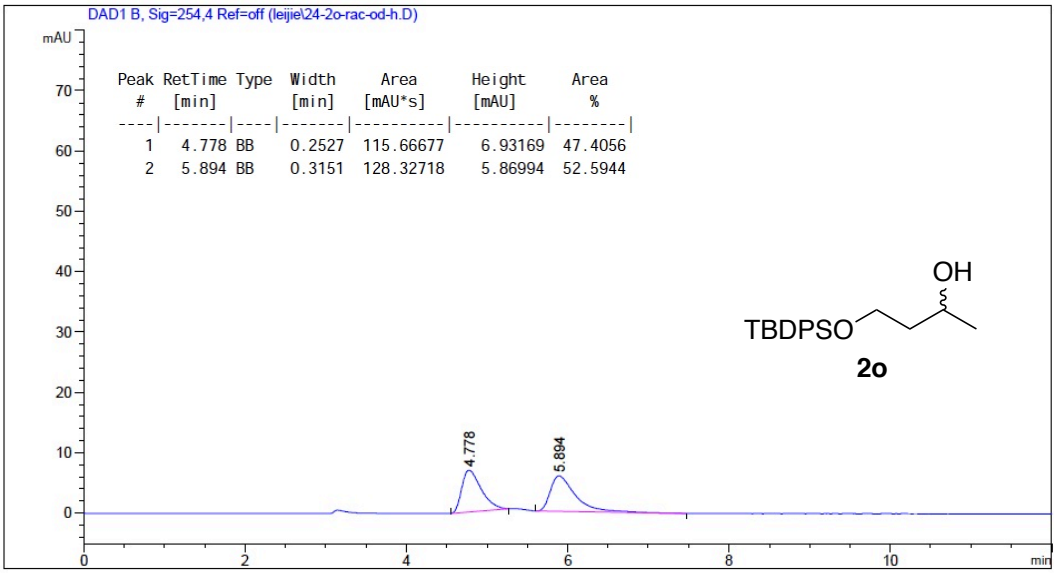
## HPLC Chromatogram of compound 6n *(racemic product)*




## HPLC Chromatogram of compound 6n *(chiral product)*



## HPLC Chromatogram of compound 6o *(racemic product)*




## HPLC Chromatogram of compound 6o *(chiral product)*