Enantioselective one-carbon ring expansion of aromatic rings by simultaneous formation and chromoselective irradiation of a transient coloured enolate

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Experimental

1 Experimental

1.1 General Information: Reactions requiring anhydrous conditions (where specified) were executed under dry nitrogen or argon atmospheres in glassware that was dried using either a combination of vacuum and heat-gun, oven, or flame drying. Reaction mixtures were stirred magnetically. Air- and moisture-sensitive liquids and solutions were transferred via syringe into the reaction vessels through rubber septa. All reagents were purchased (unless specified) at highest commercial quality and used as received. Non-anhydrous solvents were purchased (unless specified) at the highest commercial quality and used as received. Anhydrous CH_2Cl_2 and THF were obtained from the University of Bristol's dry solvent system and were purified by filtration over a column of activated alumina. All temperatures described below −10 °C were achieved using a Julabo cryostat.

1.2 Analytical Information:

Rf: TLC was performed on aluminium-backed silica plates (0.2 mm, 60 F254) which were developed using standard visualising agents: UV fluorescence (254 & 366 nm), phosphomolybdic acid / Δ, vanillin / Δ, potassium permanganate / Δ and Seebach / Δ. Chromatography: Flash chromatography was performed on an automated Biotage Isolera TM Spectra Four using gradient elution on pre-packed silica gel Biotage® Sfar Silica D Duo columns.

MP: Melting points were measured on a Kofler hotstage melting point apparatus and are uncorrected.

IR: IR spectra were recorded on neat compounds using a Perkin Elmer (Spectrum One) FT-IR spectrometer (ATR sampling accessory). Only strong and selected absorbance's (ν_{max} expressed in cm^{-1}) are reported.

^{1}H NMR: Spectra were recorded on Jeol ECS (400 MHz) or Bruker NMR (400 MHz or 500 MHz) instruments. Chemical shifts (δ H) are quoted in parts per million (ppm) was used. Spin-spin coupling constants (J) are reported in Hertz (Hz). 2D NMR experiments NOSY, HSQC and HMBC where necessary.

13C NMR: Spectra were recorded on Jeol ECS (101 MHz) or Bruker NMR (101 MHz or 125 MHz) instruments. Chemical shifts (δ C) are quoted in parts per million (ppm) and referenced to the appropriate solvent peak(s). Spin-spin coupling constants (J) are reported in Hertz (Hz).

HRMS: High resolution mass spectra were recorded on a Bruker Daltronics MicrOTOF 2 mass spectrometer (ESI).

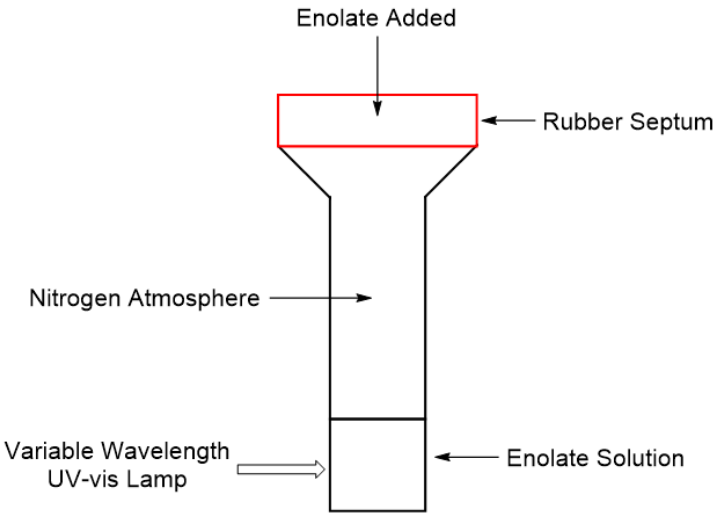
High Performance Liquid Chromatography: Enantiomeric ratios were determined by HPLC on Agilent 1100 series or Agilent Technologies 1260 Infinity with UV detection at 280 and 254. Chiral Regis Whelk O1 and CHIRALPAK® IA with hexane:2-propanol (IPA) as the eluent for all separations, unless otherwise stated. If the temperature could be set the separation was performed at 25 °C otherwise room temperature.

UV-Vis: UV-visible spectra were recorded on an Agilent Cary Series 300 UV-Vis Spectrophotometer.

1.3 UV-visible Spectroscopy Measurements

To an oven-dried 1 mm cuvette was attached a septum and secured with Parafilm®. The cuvette was swing-purged using a Schlenk line before being washed with *n*-butyl lithium (0.1 mL) and dry THF (0.1 mL) to remove any excess water. The cuvette was then placed in an ice bath before addition of a solution of enolate (~$4x10^{-4}$ mmol/mL formed from the corresponding amide and deprotonation with 1 equivalent of *n*-butyl lithium) in dry THF by syringe. The cuvette was kept in an ice bath until running the spectrum.

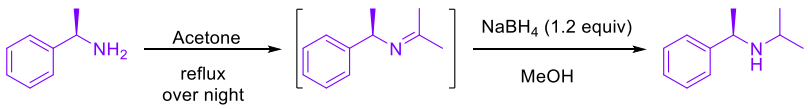
A blank sample containing *n*-butyl lithium and dry THF was ran before UV-vis measurements.



1.4 Known Starting Materials

Starting material amines[1] and *N*-benzyl-*N*-(alkyl)benzamides were prepared according to the procedures reported. Spectroscopic data for the materials prepared as described above were consistent with those reported in the literature.

Synthesis of N-(1-Phenylethyl)-1-methylethylamine



[1] S. Leleu, C. Papamicael, F. Marsais, G. Dupas, V. Levacher *Tetrahedron:Asymmetry* **2004**, 15 3919–3928

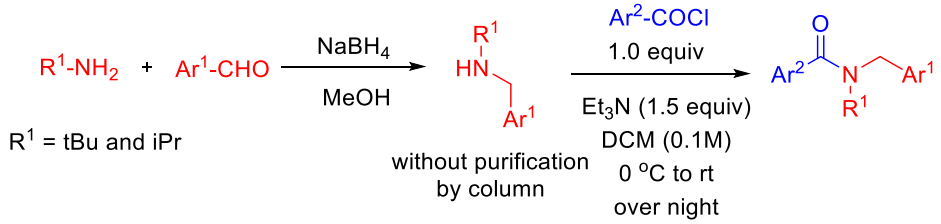
1.5 General Procedure 1: Synthesis of *rec-N*-(1-Phenylethyl)-1-methylethylamine. A solution of α-methylbenzylamine (10 g) in acetone (300 mL) was refluxed for 16 h. After evaporation of the solvent *in vacuo*, the residue was dissolved in methanol (350 mL) and sodium tetrahydroborate (3.2 g) was slowly added at 0 °C. The solution was stirred for 2.5 h at 20 °C. After evaporation of the solvent *in vacuo*, water (30 mL) was added, and the resulting aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash silica chromatography (20% EtOAC/Hexane) afforded the title amine in 80% yield.

1.6 General Procedure 2: Synthesis of *(R)-N*-(1-Phenylethyl)-1-methylethylamine. A solution of *(R)*-α-methylbenzylamine in acetone (400 mL) was refluxed for 12 h. After evaporation of the solvent under vacuum, the residue was dissolved in methanol (300 mL) and sodium tetrahydroborate (1.5 g, 39.7 mmol) was slowly added at 0 °C. The solution was stirred for 2 h at 20 °C. After evaporation of the solvent *in vacuo*, water (30 mL) was added, and the resulting aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash silica chromatography (20% EtOAC/Hexane) afforded the title amine in 80% yield.

1.7 General Procedure 3: Synthesis of *(S)-N*-(1-Phenylethyl)-1-methylethylamine.[2] A solution of *(S)*-α-methylbenzylamine in acetone (400 mL) was refluxed 12 h. After evaporation of the solvent under vacuum, the residue was dissolved in methanol (300 mL) and sodium tetrahydroborate (1.5 g, 39.7 mmol) was slowly added at 0 °C. The solution was stirred for 2 h at 20 °C. After evaporation of the solvent *in vacuo*, water (30 mL) was added and the resulting aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash silica chromatography (20% EtOAC/Hexane) afforded the title amine in 80% yield.

[2] D. M. Mercea, M. G. Howlett, A. D. Piascik, D J. Scott, A Steven, A E. Ashley, M. J. Fuchter *Chem. Commun*., **2019**, 55, 7077

1.8 General Procedure 4: Starting material 2 synthesis[3].



tert-Butylamine (20 mmol, 1.0 equiv.) and aldehyde (20 mmol, 1.0 equiv) were dissolved in MeOH (50 mL). The resulting mixture was stirred for 3 h at RT, and then $NaBH_4$ (1.2 equiv) was added portion-wise at 0 °C and warmed to room temperature. After 2 h, water (30 mL) was added to the solution and then extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure to give the secondary amine. The product was used in the next step without further purification.

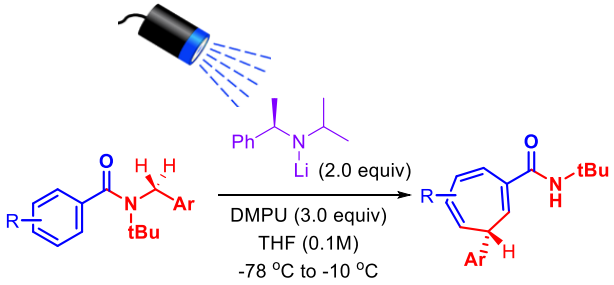
The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-alkyl benzylamine (3.59 mmol, 1.0 equiv) and triethyl amine (1.5 equiv) in CH_2Cl_2 (0.1M) at 0 °C. The mixture was allowed to warm to room temperature overnight. The reaction was quenched with water and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (5% to 20% EtOAC/Hexane) afforded the title compound.

1.9 General Procedure 5: General procedure for the synthesis of amides 10.

The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine (2.31 mmol to 3.61 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10% to 20% EtOAC/Hexane) afforded the title compound.

[3] Y. Nakagawa, S. Chanthamath, Y. Liang, K. Shibatomi, S. Iwasa *J. Org. Chem*. **2019**, 84, 2607−2618,

1.10 General Procedure 6: Enantioselective Photochemical Ring Expansion

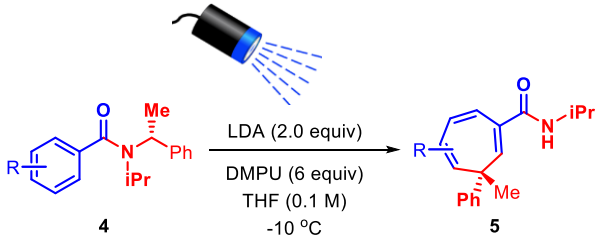


To a suspension of chiral amine (2.0 equiv.) in dry THF (0.1 M) at –78 °C was added *n*-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C before a solution of amide (0.28 mmol to 0.39 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil Tuna Blue lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added, and further irradiation was continued until consumption of the amide was observed by TLC. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with EtOAc/petrol to afford the title compound.

1.10 General Procedure 7: *rec*-Photochemical Ring Expansion

Freshly prepared LDA (2.0 equiv) in dry THF (0.1M) was cooled to –10 °C and a solution of amide (0.30 mmol) in THF (0.5 mL) and DMPU (3.0 equiv.) were sequentially added dropwise, and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil Tuna Blue lamp until consumption of the amide was observed by TLC. Saturated ammonium chloride solution was added, the layers separated, and the aqueous layer was extracted with ethyl acetate. The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with EtOAc/petrol, affording the title compound.

1.11 General Procedure 8: Stereospecific Photochemical Ring Expansion

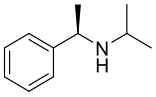


The chiral amide (0.33 mmol to 0.37 mmol) was dissolved in dry THF (0.1 M) under a nitrogen atmosphere. After cooling down to -10 °C, freshly prepared LDA (2.0 equiv) and DMPU (6.0 equiv) were sequentially added dropwise, and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil Tuna Blue lamp until consumption of the amide was observed by TLC. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10 to 15% EtOAC/Hexane) afforded the title compound.

1.12 General Procedure 9: rec-Stereospecific Photochemical Ring Expansion

The chiral amide (0.3 mmol) was dissolved in dry THF (0.1 M) under a nitrogen atmosphere. After cooling down to -10 °C, freshly prepared LDA (2.0 equiv) and DMPU (6.0 equiv) were sequentially added dropwise, and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil Tuna Blue lamp until consumption of the amide was observed by TLC. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10 to 15% EtOAC/Hexane) afforded the title compound.

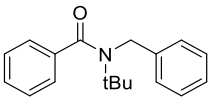
1.13 Analytical data of amine



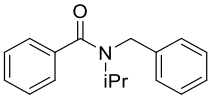
IR (neat, cm^{-1}) 3315, 2962, 1451, 1169, 759, 698, 585, 554, 517

***(R)-N*-(1-Phenylethyl)-1-methylethylamine**[1] **(1c).** The crude product was purified by flash silica chromatography (hexane/EtOAc = 80/20) to afford **1c** as colorless oil; $[\alpha]_D^{23}$ = 68 (c = 1.00 in $CHCl_3$); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 – 7.22 (m, 5H), 3.92 (q, *J* = 6.6 Hz, 1H), 2.66 (hept, *J* = 6.3 Hz, 1H), 1.38 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.2 Hz, 3H), 1.03 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.09, 128.41, 126.75, 126.46, 55.09, 45.55, 24.88, 24.06, 22.19. **HRMS** (ESI^+) m/z calcd for $C_{11}H_{17}NNa$ $[M+Na]^+$ 186.1259, found 186.1262.

1.14 Analytical data of amides



***N*-benzyl-*N*-(tert-butyl)benzamide**[4] (**2a**); By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **2a** as colorless needles (720 mg, 75%); **MP**: 121-123 ° C: ν_{max} /cm^{-1}(neat): 2971, 1636, 1391, 1361, 1203, 704; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 2H), 7.31 – 7.23 (m, 5H), 7.22 – 7.15 (m, 3H), 4.57 (s, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.95, 140.11, 139.39, 129.03, 128.59, 128.43, 127.06, 126.40, 126.29, 58.12, 51.68, 28.82. **HRMS** (ESI) calcd for $[C_{18}H_{21}NONa]$ requires $[M+Na]^+$ 290.1521, found 290.1524.

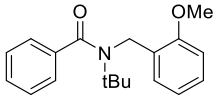


***N*-benzyl-*N*-isopropylbenzamide**[5] (**2a'**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **2a'** as pale-yellow needles (750 mg, 83%); **MP**: 68-70 °C; ν_{max} /cm^{-1}(neat): 2976, 1626, 1411, 1341, 1175, 1060, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 – 7.11 (m, 10H), 4.67 (s, 2H), 1.33 – 0.96 (m, 6H). **^{13}C**

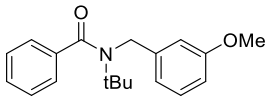
[4] P.-L. Lagueux-Tremblay, A. Fabrikant, B. A. Arndtsen ACS Catal. **2018**, 8, 5350−5354

[5] D. Lu, H.-X. Wei, J. Zhang, Y. Gu, P. Osenkowski, W. Ye, D. J. Selkoe, M. S. Wolfe, C. E. Augelli-Szafran *Bioorg. Med. Chem. Lett.* **2016**, *26*, 2129–2132

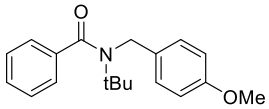
NMR (101 MHz, Chloroform-*d*) δ 172.33, 139.52, 137.48, 129.31, 128.61, 128.52, 127.12, 126.91, 126.33, 50.84, 43.39, 21.49. **HRMS** (ESI) calcd for [$C_{17}H_{19}NONa$] requires [M+Na]+ 276.1359, found 276.1364.



***N*-(tert-butyl)-*N*-(2-methoxybenzyl)benzamide** (**2b**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 85/15) to afford **2b** as colorless needles (700 mg, 66%); **MP**: 122-124 ° C; ν_{max} /cm^{-1}(neat): 2976, 1628, 1490, 1461, 1391, 1239, 1198, 1025, 752, 705; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 – 7.36 (m, 3H), 7.32 – 7.21 (m, 4H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 4.59 (s, 2H), 3.74 (s, 3H), 1.53 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.14, 155.96, 139.51, 128.80, 128.18, 128.11, 127.88, 127.70, 126.06, 120.25, 110.10, 57.88, 55.13, 46.57, 28.54. **HRMS** (ESI) calcd for [$C_{19}H_{23}NO_2Na$] requires [M+Na]+ 320.1621, found 320.1623.

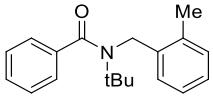


***N*-(*tert*-butyl)-*N*-(3-methoxybenzyl)benzamide** (**2c**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 85/15) to afford **2c** as colorless needles (740 mg, 69%); **MP**: 82-84 ° C; ν_{max} /cm^{-1}(neat): 2971, 1632, 1488, 1388, 1252, 1198, 1047, 971, 750, 698, 655; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 2H), 7.30 (q, *J* = 3.7 Hz, 3H), 7.24 (dd, *J* = 8.9, 7.6 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.80 – 6.75 (m, 2H), 4.59 (s, 2H), 3.79 (s, 3H), 1.54 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.80, 159.81, 141.79, 139.29, 129.59, 128.97, 128.38, 126.17, 118.59, 112.26, 112.05, 58.10, 55.18, 51.56, 28.74. **HRMS** (ESI) calcd for [$C_{19}H_{23}NO_2Na$] requires [M+Na]+ 320.1621, found 320.1628.

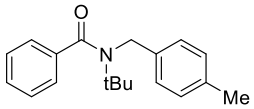


***N*-(*tert*-butyl)-*N*-(4-methoxybenzyl)benzamide** (**2d**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 85/15) to afford **2d** as colorless needles (780 mg, 73%); **MP**: 122-124 ° C; ν_{max} /cm^{-1}(neat): 2971, 1630, 1511, 1388, 1243, 1032, 750, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 2H), 7.31 – 7.26 (m, 3H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.54 (s, 2H), 3.78 (s, 3H), 1.49 (s, 9H). **^{13}C**

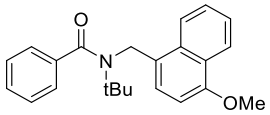
NMR (101 MHz, $CDCl_3$) δ 173.86, 158.61, 139.33, 131.84, 128.96, 128.35, 127.45, 126.28, 113.92, 57.97, 55.28, 51.01, 28.74. **HRMS** (ESI) calcd for [$C_{19}H_{23}NO_2Na$] requires [M+Na]+ 320.1626, found 320.1632.



***N*-(*tert*-butyl)-*N*-(2-methylbenzyl)benzamide** (**2e**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **2e** as colorless needles (630 mg, 62%); **MP**: 96-98 ° C; ν_{max} /cm^{-1}(neat): 2971, 1631, 1393, 1197, 1066, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.29 – 7.17 (m, 4H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 4.46 (s, 2H), 2.05 (s, 3H), 1.53 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 174.04, 139.32, 137.96, 133.86, 130.38, 128.94, 128.29, 126.75, 126.37, 126.05, 125.87, 58.15, 49.12, 28.62, 19.00. **HRMS** (ESI) calcd for [$C_{19}H_{23}NONa$] requires [M+Na]+ 304.1672, found 304.1665.

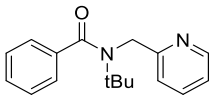


***N*-(*tert*-butyl)-*N*-(4-methylbenzyl)benzamide** (**2f**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **2f** as colorless needles (780 mg, 77%); **MP**: 72-74 ° C; ν_{max} /cm^{-1}(neat): 2971, 1631, 1385, 1199, 1066, 790, 654, 698; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.29 – 7.23 (m, 3H), 7.13 – 7.05 (m, 4H), 4.55 (s, 2H), 2.31 (s, 3H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 173.93, 139.45, 137.02, 136.66, 129.27, 128.99, 128.42, 126.32, 58.08, 51.46, 28.82, 21.11. **HRMS** (ESI) calcd for [$C_{19}H_{24}NO$] requires [M+ H]+ 282.1852, found 282.1862.

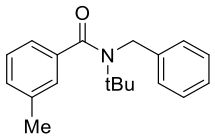


N-(tert-butyl)-N-((4-methoxynaphthalen-1-yl)methyl)benzamide (**2g**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 80/20) to afford **2g** as colorless needles (805 mg, 64%); **MP**: 160-162 ° C; ν_{max} /cm^{-1}(neat): 2971, 1621, 1586, 1384, 1265, 1195, 1089, 697, 749; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35 – 8.27 (m, 1H), 7.67 – 7.62 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.40 (dd, *J* = 7.9, 1.6

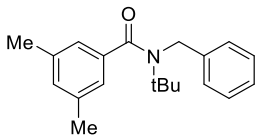
Hz, 2H), 7.24 – 7.13 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.91 (s, 2H), 4.03 (s, 3H), 1.58 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.07, 154.73, 139.25, 130.60, 128.87, 128.17, 126.90, 126.68, 125.72, 125.63, 125.13, 124.25, 122.91, 121.61, 103.04, 58.25, 55.52, 48.56, 28.59. **HRMS** (ESI) calcd for [$C_{23}H_{25}NO_2Na$] requires [M+Na]+ 370.1777, found 370.1781.



***N*-(tert-butyl)-*N*-(pyridin-2-ylmethyl)benzamide** (**2h**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 80/20) to afford **2h** as colorless needles (630 mg, 65%); **MP**: 94-96 ° C; ν_{max} /cm^{-1}(neat): 2971, 1633, 1388, 1197, 974, 749, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.30 – 7.21 (m, 4H), 7.14 – 7.09 (m, 1H), 4.66 (s, 2H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 174.04, 159.66, 149.37, 139.37, 136.53, 129.03, 128.41, 126.24, 122.08, 121.11, 58.07, 53.46, 28.80. **HRMS** (ESI) calcd for [$C_{17}H_{20}N_2ONa$] requires [M+Na]+ 291.1473, found 291.1475.

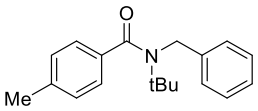


***N*-benzyl-*N*-(tert-butyl)-3-methylbenzamide** (**2i**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **2i** as colorless needles (650 mg, 71%); **MP**: 93-95° C; ν_{max} /cm^{-1}(neat): 2967, 1633, 1386, 1358, 1195, 973, 739, 701; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.15 (m, 5H), 7.15 – 7.06 (m, 2H), 4.59 (s, 2H), 2.26 (s, 3H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.16, 140.20, 139.33, 138.20, 129.74, 128.54, 128.27, 127.05, 127.02, 126.44, 123.19, 58.06, 51.72, 28.82, 21.39. **HRMS** (ESI) calcd for [$C_{19}H_{24}NO$] requires [M+H] $^+$ 282.1858, found 282.1864.

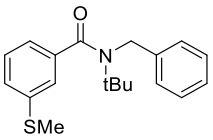


***N*-benzyl-*N*-(tert-butyl)-3,5-dimethylbenzamide** (**2j**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **2j** as colorless needles (520 mg, 59%); **MP**: 92-94 ° C; ν_{max} /cm^{-1}(neat): 2969, 1633, 1390, 1358, 1196, 855, 746; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.22 (t, *J* = 7.3 Hz,

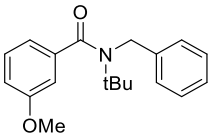
3H), 6.99 (s, 2H), 6.93 – 6.89 (m, 1H), 4.60 (s, 2H), 2.24 – 2.21 (m, 6H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.34, 140.29, 139.31, 138.00, 130.55, 128.49, 126.97, 126.49, 123.99, 57.98, 51.76, 28.82, 21.26. **HRMS** (ESI) calcd for [$C_{20}H_{25}NONa$] requires $[M+Na]^+$ 318.1828, found 318.1843.



***N*-benzyl-*N*-(tert-butyl)-4-methylbenzamide** (**2k**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **2k** as colorless needles (690 mg, 75%); **MP**: 123-125 ° C; ν_{max} /cm^{-1}(neat): 2971, 1631, 1384, 1358, 1199, 1074, 958. 829, 744, 701; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 4H), 7.25 – 7.19 (m, 3H), 7.10 – 7.05 (m, 2H), 4.61 (s, 2H), 2.29 (s, 3H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.18, 140.26, 139.04, 136.50, 129.02, 128.56, 127.00, 126.42, 126.39, 58.03, 51.75, 28.83, 21.34. **HRMS** (ESI) calcd for [$C_{19}H_{23}NONa$] requires $[M + Na]^+$ 304.1672, found 304.1686.

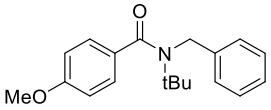


***N*-benzyl-*N*-(*tert*-butyl)-3-(methylthio)benzamide** (**2l**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 85/15) to afford **2l** as pale yellow needles (500 mg, 59%); **MP**: 101-103 ° C; ν_{max} /cm^{-1}(neat): 2971, 1633, 1384, 1358, 1253, 1198, 977, 746; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.26 – 7.19 (m, 4H), 7.19 – 7.13 (m, 3H), 4.58 (s, 2H), 2.30 (s, 3H), 1.51 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.29, 140.03, 138.93, 128.70, 128.56, 127.22, 127.01, 126.22, 123.60, 122.79, 58.20, 51.56, 28.67, 15.46. **HRMS** (ESI) calcd for [$C_{19}H_{23}NOSNa$] requires [M+Na]+ 336.1393, found 336.1395.

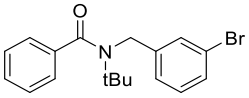


***N*-benzyl-*N*-(tert-butyl)-3-methoxybenzamide**[5] (**2m**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 85/15) to afford **2m** as colorless needles (750 mg, 85%); **MP**: 92-93 ° C; ν_{max} /cm^{-1}(neat): 2971, 1633, 1452, 1391, 1358, 1197, 1046, 699, 744; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.25 –

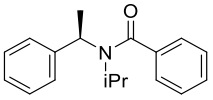
7.16 (m, 4H), 6.98 (dt, *J* = 7.5, 1.1 Hz, 1H), 6.91 – 6.87 (m, 1H), 6.85 – 6.80 (m, 1H), 4.60 (s, 2H), 3.65 (s, 3H), 1.51 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.58, 159.36, 140.47, 140.18, 129.50, 128.51, 126.93, 126.27, 118.43, 115.31, 111.18, 58.10, 55.17, 51.58, 28.69. **HRMS** (ESI) calcd for [$C_{19}H_{23}NO_2Na$] requires [M+Na]+ 297.1721, found 320.1625.



***N*-benzyl-*N*-(tert-butyl)-4-methoxybenzamide**[6] (**2n**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 85/15) to afford **2n**as colorless needles (710 mg, 81%); **MP**: 130-132 ° C; ν_{max} /cm^{-1}(neat): 2970, 1630, 1382, 1246, 1027, 838, 745, 702; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 3H), 6.80 – 6.75 (m, 2H), 4.62 (s, 2H), 3.75 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.96, 160.31, 140.37, 131.68, 128.57, 128.32, 127.01, 126.46, 113.66, 58.01, 55.34, 51.85, 28.83. **HRMS** (ESI) calcd for [$C_{19}H_{23}NO_2Na$] requires [M+Na]+ 320.1621, found 320.1609.



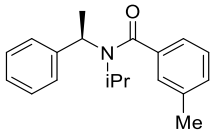
***N*-(3-bromobenzyl)-*N*-(*tert*-butyl)benzamide** (**2o**), By following general Procedure 4: The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **2o** as colorless needles (600 mg, 48%); **MP**: 116-118 ° C; ν_{max} /cm^{-1}(neat): 2971, 1632, 1383, 1195, 1069, 968, 774; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 3H), 7.33 – 7.26 (m, 4H), 7.22 – 7.12 (m, 2H), 4.56 (s, 2H), 1.50 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 173.93, 142.58, 139.06, 130.24, 130.19, 129.43, 129.21, 128.54, 126.11, 124.95, 122.81, 58.28, 51.10, 28.86. **HRMS** (ESI) calcd for [$C_{18}H_{20}BrNONa$] requires [M+Na]+ 368.0620, found 368.0615.



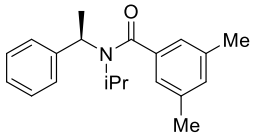
***(R)*-*N*-isopropyl-*N*-(1-phenylethyl)benzamide** (**10a**), By following general procedure 5: The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine

[6] J. Clayden, K. Tchabanenko, S. A. Yasin, M. D. Turnbull. *Synlett* **2001** (2), 302-304.

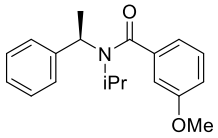
(3.61 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **10a** as colorless oil (705 mg, 73%); ν_{max} /cm^{-1}(neat): 2976, 1630, 1439, 1333, 854, 756; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.47 – 7.37 (m, 5H), 7.35 (dd, J = 7.2, 3.2 Hz, 4H), 7.27 (d, J = 4.3 Hz, 1H), 4.91 (d, J = 6.2 Hz, 1H), 3.38 (brs s, 1H), 1.65 (brs s, 3H), 1.45 (brs s, 3H), 1.14 (s, 3H). **13C NMR** (101 MHz, Chloroform-d) δ 171.45, 138.81, 134.63, 130.67, 128.98, 128.89, 128.70, 128.38, 127.30, 125.88, 59.93 (br), 39.12 (br), 21.15 (br), 20.33 (br), 17.70 (br). **HRMS** (ESI) calcd for [$C_{18}H_{21}NONa$] requires [M+Na]+ 290.1521, found 290.1520.



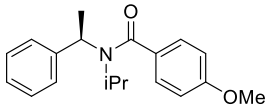
***(R)*-*N*-isopropyl-3-methyl-*N*-(1-phenylethyl)benzamide** (**10b**), By following general procedure 5: The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine (3.26 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **10b** as colorless oil (690 mg, 75%); ν_{max} /cm^{-1}(neat): 2971, 1632, 1435, 1353, 756, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 4.7 Hz, 4H), 7.28 – 7.19 (m, 4H), 7.19 – 7.15 (m, 1H), 4.90 (br s, 1H), 3.36 (br s, 1H), 2.37 (s, 3H), 1.64 (br s, 3H), 1.44 (br s, 3H), 1.14 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.65, 138.80, 138.54, 129.60, 128.53, 128.36, 127.32, 126.53, 122.77, 56.07 (br), 48.55 (br), 21.53, 21.14 (br), 20.33 (br), 17.69 (br). **HRMS** (ESI) calcd for [$C_{19}H_{23}NONa$] requires [M+Na]+ 304.1677, found 304.1683.



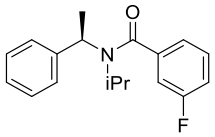
***(R)*-*N*-isopropyl-3,5-dimethyl-*N*-(1-phenylethyl)benzamide** (**10c**), By following general procedure 5: The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine (3.00 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **4c** as colorless needles (630 mg, 71%); **MP:** 81-83 °C; ν_{max} /cm^{-1}(neat): 2976, 1629, 1435, 1333, 854, 756, 698; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 4.5 Hz, 4H), 7.29 – 7.22 (m, 1H), 7.02 (d, *J* = 11.7 Hz, 3H), 4.93 (br s, 1H), 3.39 (br s, 1H), 2.33 (s, 6H), 1.65 (br s, 3H), 1.45 (br s, 3H), 1.14 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.74, 138.75, 138.23, 130.31, 128.25, 127.26, 123.36, 60.40 (br), 49.88 (br), 21.33, 21.05 (br), 20.27 (br), 14.21. **HRMS** (ESI) calcd for [$C_{20}H_{25}NONa$] requires [M+Na]$^+$ 318.1824, found 318.1828.



***(R)*-*N*-isopropyl-3-methoxy-*N*-(1-phenylethyl)benzamide** (**10d**), By following general procedure 5: The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine (2.95 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **10d** as colorless needles (685 mg, 78%); **MP:** 78-80 °C; ν_{max} /cm^{-1}(neat): 2971, 1629, 1433, 1351, 1236, 749; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.29 (m, 5H), 7.27 – 7.20 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.90 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 4.89 (br s, 1H), 3.81 (s, 3H), 3.37 (br s, 1H), 1.63 (br s, 3H), 1.44 (br s, 3H), 1.14 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.14, 159.81, 140.03, 129.87, 128.38, 127.31, 118.02, 114.72, 111.45, 56.97 (br), 55.45, 48.08 (br), 21.13 (br), 20.25 (br), 17.64 (br). **HRMS** (ESI) calcd for [$C_{19}H_{23}NO_2Na$] requires [M+Na]+ 320.1621, found 320.1626.

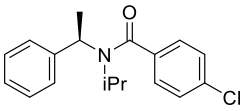


***(R)*-*N*-isopropyl-4-methoxy-*N*-(1-phenylethyl)benzamide** (**10e**), By following general procedure 5: The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine (2.95 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **10e** as colorless needles (640 mg, 73%); **MP:** 84-86 °C; ν_{max} /cm^{-1}(neat): 2976, 1625, 1511, 1432, 1360, 1246, 1174, 1024; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 4.4 Hz, 4H), 7.24 (q, *J* = 4.6 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.96 (q, *J* = 6.7 Hz, 1H), 3.80 (s, 3H), 3.46 (s, 1H), 1.65 (d, *J* = 6.8 Hz, 3H), 1.42 (d, *J* = 6.6 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.45, 160.12, 131.13, 128.36, 127.73, 127.36, 127.26, 113.96, 60.48 (br), 55.39, 48.51 (br), 21.21 (br), 20.48 (br), 17.88 (br). **HRMS** (ESI) calcd for [$C_{19}H_{23}NO_2Na$] requires [M+Na]+ 320.1621, found 320.1619.

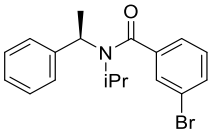


***(R)*-3-fluoro-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10f)** By following general procedure 5: The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine (3.20 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **10f** as colorless oil (540 mg, 59%); ν_{max} /cm^{-1}(neat): 2972, 1629, 1583, 1441, 1327, 1055, 785, 749, 697; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.33 (m, 5H), 7.33 – 7.27 (m, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.11 (tdd, *J* = 8.6, 2.6, 1.0 Hz, 1H), 4.90 (d, *J* = 6.3 Hz, 1H), 3.44 (br s, 1H), 1.69 (br s, 3H), 1.48 (br s, 3H), 1.16 (s, 3H). **^{13}C NMR** (101 MHz,

Chloroform-*d*) δ 169.76, 162.69(d $^{1}J_{CF}$ = 248.46 Hz), 140.67 (d, $^{3}J_{CF}$ = 7.49 Hz), 130.50 (d, $^{3}J_{CF}$ = 7.07 Hz), 128.39, 127.50, 127.18, 121.50 (d, $^{4}J_{CF}$ = 3.03 Hz), 115.85 (d, $^{2}J_{CF}$ = 21.21 Hz), 113.33 (d, $^{2}J_{CF}$ = 23.23 Hz), 56.27 (br), 48.79 (br), 21.02 (br), 20.17 (br), 17.69 (br). **HRMS** (ESI) calcd for [$C_{18}H_{20}FNONa$] requires [M+Na]+ 308.1427, found 308.1431.



***(R)*-4-chloro-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10g)** By following general procedure 5: The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine (2.92 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **10g** as colorless oil (590 mg, 67%); ν_{max} /cm^{-1}(neat): 2971, 1630, 1565, 1443, 784, 749, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.71 – 8.61 (m, 2H), 7.37 – 7.20 (m, 7H), 4.77 (q, *J* = 6.9 Hz, 1H), 3.31 (s, 1H), 1.78 – 1.26 (m, 6H), 1.13 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.72, 150.46, 145.99, 128.55, 127.22, 120.38, 57.15 (br), 48.34 (br), 21.01 (br), 19.87 (br), 17.48 (br). **HRMS** (ESI) calcd for [$C_{18}H_{20}ClNONa$] requires [M+Na]+ 324.1131, found 324.1136.

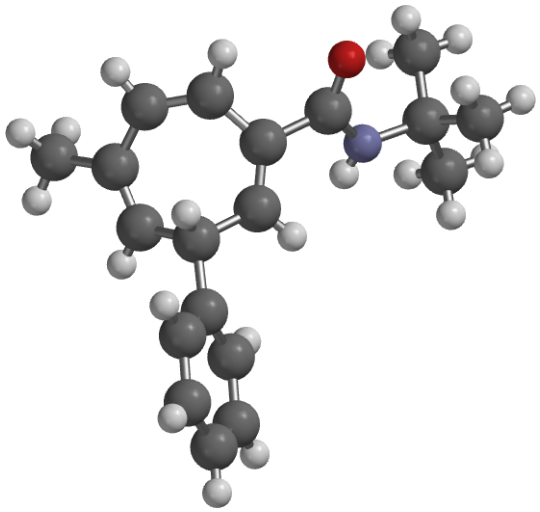


***(R)*-3-bromo-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10h)** By following general procedure 5: The acid chloride (1.0 equiv) was added dropwise to a solution of *N*-(1-phenylethyl)propan-2-amine (2.31 mmol) and triethyl amine (2.0 equiv) in CH_2Cl_2 (0.2M) at 0 °C. The mixture was allowed to warm to room temperature for 12 h. The reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. The crude product was purified by flash silica chromatography (hexane/EtOAc = 90/10) to afford **10h** as colorless oil (554 mg, 69%); ν_{max} /cm^{-1}(neat): 2972, 1628, 1435, 1361, 1322,

1065, 796, 723, 695, 657; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.54 (ddd, *J* = 7.9, 2.0, 1.2 Hz, 1H), 7.43 – 7.26 (m, 7H), 4.95 – 4.78 (m, 1H), 3.45 (br s, 1H), 1.69 (br s, 3H), 1.47 (br s, 3H), 1.17 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.52, 140.54, 131.96, 130.27, 128.97, 128.40, 127.18, 124.35, 122.79, 65.86 (br), 48.48 (br), 20.99 (br), 20.23 (br), 17.78 (br). **HRMS** (ESI) calcd for [$C_{18}H_{20}BrNONa$] requires $[M+Na]^+$ 368.0626, found 368.0629.

1.15 X-ray crystallography Data

X-ray Structure of 4k

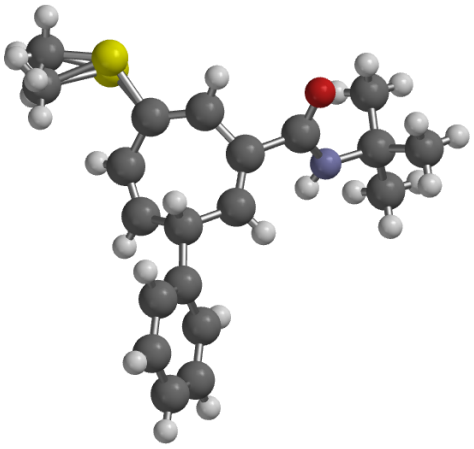


Colorless crystals of **4k** were grown from a hexanes/Aectone solution by slow volatilization. CCDC: 2083306

Bond precision:	C-C = 0.0020 A		Wavelength=1.54178
Cell:	a=5.8270(3)	b=16.2460(7)	c=16.8144(8)
	alpha=90	beta=90	gamma=90
Temperature:	100 K		
	Calculated		Reported
Volume	1591.74(13)		1591.74(13)
Space group	P 21 21 21		P 21 21 21
Hall group	P 2ac 2ab		P 2ac 2ab
Moiety formula	C19 H23 N O		C19 H23 N O
Sum formula	C19 H23 N O		C19 H23 N O
Mr	281.38		281.38
Dx,g cm-3	1.174		1.174

Z	4	4
Mu (mm-1)	0.553	0.553
F000	608.0	608.0
F000’	609.61	
h,k,lmax	7,19,20	7,19,20
Nref	2907[1707]	2906
Tmin,Tmax	0.923,0.967	0.511,0.754
Tmin’	0.802	
Correction method= # Reported T Limits:		Tmin=0.511 Tmax=0.754
AbsCorr =	MULTI-SCAN	
Data completeness=	1.70/1.00	
heta(max)=	68.236	
R(reflections)= 0.0261(2895)	wR2(reflections)= 0.0656(2906)	
S = 1.098	Npar= 198	

X-ray Structure of 4l



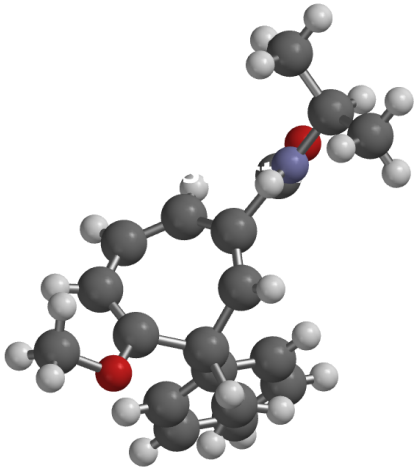
Colorless crystals of **4l** were grown from a hexanes/EtOAc solution by slow volatilization. CCDC: 2083307

Bond precision:	C-C = 0.0022 A		Wavelength=1.54178
Cell:	a=5.8465(1)	b=16.2467(4)	c=17.6742(4)
	alpha=90	beta=90	gamma=90
Temperature:	100 K		

	Calculated	Reported
Volume	1678.81(6)	1678.81(6)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C19 H23 N O S	C19 H23 N O S
Sum formula	C19 H23 N O S	C19 H23 N O S
Mr	313.44	313.44
Dx,g cm-3	1.240	1.240
Z	4	4
Mu (mm-1)	1.708	1.708
F000	672.0	672.0
F000’	674.95	674.95
h,k,lmax	7,19,21	7,19,21
Nref	3180 [1862]	3179
Tmin,Tmax	0.782,0.872	0.284,0.754
Tmin’	0.537	
Correction method= # Reported T Limits:		Tmin=0.284 Tmax=0.754
AbsCorr =	MULTI-SCAN	
Data completeness=1.71/1.00	Theta(max)= 70.060	

R(reflections)= 0.0242(3167)	wR2(reflections)= 0.0624(3179)
S = 1.084	Npar= 227

X-ray Structure of 11d

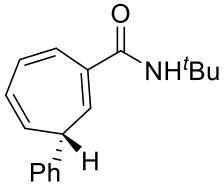


Colorless crystals of **11d** were grown from a hexanes/Aectone solution by slow volatilization. CCDC: 2083305

Bond precision:	C-C = 0.0022 A		Wavelength=1.54178
Cell:	a=9.4746(3)	b=12.0701(4)	c=30.0751(11)
	alpha=90	beta=90	gamma=90
Temperature:	100 K		
	Calculated		Reported
Volume	3439.4(2)		3439.4(2)
Space group	P 21 21 21		P 21 21 21
Hall group	P 2ac 2ab		P 2ac 2ab
Moiety formula	C19 H23 N O2		C19 H23 N O2
Sum formula	C19 H23 N O2		C19 H23 N O2
Mr	297.38		297.38
Dx,g cm-3	1.149		1.149
Z	8		8
Mu (mm-1)	0.582		0.582
F000	1280.0		1280.0
F000’	1283.61		
h,k,lmax	11,14,36		11,14,36
Nref	6342[3593]		6333
Tmin,Tmax	0.876,0.933		0.434,0.753
Tmin’	0.711		

Correction method= # Reported T Limits:	Tmin=0.434 Tmax=0.753
AbsCorr = MULTI-SCAN	
Data completeness=1.76/1.00	Theta(max)= 68.552
R(reflections)= 0.0266(6290)	wR2(reflections)= 0.0674(6333)
S = 1.051	Npar= 452

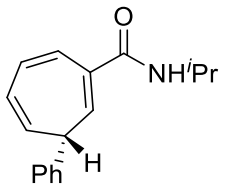
1.16 Analytical data of enantioselective photochemical ring expansion



***(R)-N*-(tert-butyl)-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4a):**

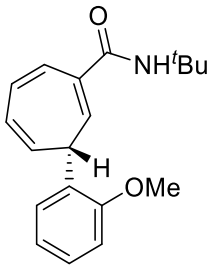
General Procedure 6: To a suspension of chiral amine (2.0 equiv) in dry THF (0.1 M) at –78 °C was added *n*-butyl lithium (3.0 equiv, 2.5 M in hexanes) dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C and a solution of amide **2a** (100 mg, 0.37 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil Tuna Blue lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 2.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 10:90 EtOAc:Petrol (Rf = 0.4), afforded the title compound (71 mg, 71%) as a colourless oil. R_f = 0.40; $[\alpha]_D^{23}$ = 16 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3322, 2970, 1642, 1452, 1392, 1218, 1075, 753, 698; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.36 (m, 4H), 7.31 – 7.28 (m, 1H), 7.07 (d, *J* = 11.2 Hz, 1H), 6.83 (dd, *J* = 11.2, 5.6 Hz, 1H), 6.26 (ddd, *J* = 9.2, 5.6, 1.5 Hz, 1H), 5.93 (d, *J* = 6.1 Hz, 1H), 5.55 (s, 1H), 5.49 (ddq, *J* = 9.2, 5.4, 0.9 Hz, 1H), 2.72 (td, *J* = 5.9, 1.5 Hz, 1H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.10, 142.91, 133.64, 132.32, 128.93, 128.19, 127.70, 127.06, 126.47, 125.32, 51.61, 44.65, 28.86. **HRMS** (ESI+): m/z calcd for $C_{18}H_{21}NONa$ [M+Na]+ 290.1515, found 290.1517. **HPLC**: *er* 3.798: 96.202; Chiral Regis Whelk O1,

Hexane:IPA = 85:15 flow = 1.0 mL/min, λ = 280 nm, tR = 20.10 mins (minor), and 25.99 mins (major).

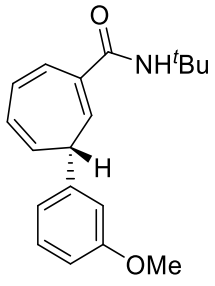


***(R)-N*-isopropyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4a'):**

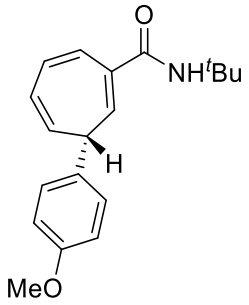
General Procedure 6: To a suspension of chiral amine (2.0 equiv) in dry THF (0.1 M) at –78 °C, was added *n*-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C and a solution of amide **2a'** (100 mg, 0.39 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil Tuna Blue lamp. The mixture was stirred at –78 °C for 30 minutes before the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 2.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 85:15 petrol-EtOAc (Rf = 0.40), afforded the title compound (72 mg, 72%) as a pale-yellow oil. R_f = 0.40; $[\alpha]_D^{23}$ = 8 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3295, 2976, 1632, 1531, 1447, 697; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 4H), 7.22 – 7.19 (m, 1H), 7.00 (d, *J* = 11.2 Hz, 1H), 6.74 (dd, *J* = 11.2, 5.6 Hz, 1H), 6.16 (ddd, *J* = 9.2, 5.6, 1.5 Hz, 1H), 5.89 (d, *J* = 6.0 Hz, 1H), 5.58 (d, *J* = 6.5 Hz, 1H), 5.41 – 5.33 (m, 1H), 4.10 – 3.94 (m, 1H), 2.64 (td, *J* = 6.0, 1.4 Hz, 1H), 1.07 (d, *J* = 1.4 Hz, 3H), 1.05 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.73, 142.78, 132.66, 132.30, 128.85, 128.43, 128.03, 127.61, 127.52, 126.98, 126.23, 125.28, 44.61, 41.83, 22.77, 22.75. **HRMS** (ESI+): m/z calcd for $C_{17}H_{20}NO$ [M+H]+ 254.1539, found 254.1547; **HPLC**: *er* 42:58; CHIRALPAK® IA column, Hexane: PA = 98:02 flow = 1.0 mL/min, λ = 280 nm, tR = 18.22 mins (minor) and 24.32 mins (major) respectively.



***(R)-N*-(tert-butyl)-3-(2-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide (4b): General Procedure 6:** To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 ºC (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2b** (100 mg, 0.33 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 ºC for 30 minutes, then the temperature of the Cryostat was set to -10 ºC and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 6.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 85:15 petrol-EtOAc (Rf = 0.35), afforded the title compound (63 mg, 63%) as a colorless needles (**MP**: 120-122 ºC). R_f = 0.38; $[\alpha]_D^{23}$ = 16 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3327, 2967, 1644, 1494, 1454, 1242, 1027, 751, 716; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.03 (d, *J* = 11.2 Hz, 1H), 6.97 (td, *J* = 7.5, 1.1 Hz, 1H), 6.94 – 6.90 (m, 1H), 6.82 – 6.75 (m, 1H), 6.21 (ddd, *J* = 9.2, 5.6, 1.5 Hz, 1H), 5.90 (d, *J* = 6.0 Hz, 1H), 5.56 (s, 1H), 5.49 – 5.41 (m, 1H), 3.79 (s, 3H), 3.07 (td, *J* = 5.8, 1.5 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.28, 157.43, 133.36, 132.08, 130.71, 129.18, 128.61, 128.27, 128.04, 127.93, 127.34, 126.80, 124.89, 120.89, 111.01, 55.45, 51.50, 40.01, 28.87. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NO_2Na$ [M+Na]+ 320.1621, found 320.1622; **HPLC**: er 8:92; CHIRALPAK® IA column, Hexane:IPA = 97:3 flow = 1.0 mL/min, λ = 280 nm, tR = 8.9 mins (minor) and 10.11 mins (major).

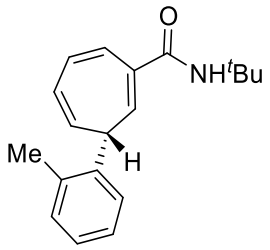


***(R)-N*-(tert-butyl)-3-(3-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide (4c): General Procedure 6:** To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 ºC (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2c** (100 mg, 0.33 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 ºC for 30 minutes, then the temperature of the Cryostat was set to -10 ºC and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 22.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 85:15 petrol-EtOAc (Rf = 0.35), afforded the title compound (56 mg, 56%) as a colorless needles (**MP**: 107-109 ºC). R_f = 0.40; $[\alpha]_D^{24}$ = 20 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3327, 2968, 1642, 1453, 1391, 1220, 1156, 1049, 752, 716, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 1H), 7.08 (d, *J* = 11.2 Hz, 1H), 6.98 – 6.93 (m, 1H), 6.91 – 6.89 (m, 1H), 6.87 – 6.81 (m, 2H), 6.26 (ddd, *J* = 9.2, 5.6, 1.5 Hz, 1H), 5.93 (d, *J* = 5.3 Hz, 1H), 5.58 (s, 1H), 5.53 – 5.47 (m, 1H), 2.71 (td, *J* = 5.9, 1.4 Hz, 1H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.11, 160.06, 144.56, 133.68, 132.30, 129.95, 128.24, 127.25, 126.35, 125.31, 119.99, 113.55, 112.33, 55.35, 51.60, 44.72, 28.86. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NO_2Na$ [M+Na]+ 320.1621, found 320.1626; **HPLC**: er 9:91; CHIRALPAK® IA column, Hexane:IPA = 99:1 flow = 1.0 mL/min, λ = 280 nm, tR = 14.11 mins (minor) and 19.42 mins (major).

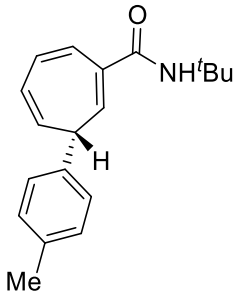


***(R)-N*-(tert-butyl)-3-(4-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide (4d):**

To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2d** (100 mg, 0.33 mmol) in THF (0.5 mL) and 3.0 equiv DMPU were sequentially added dropwise. The mixture was stirred at –78 °C for 30 minutes before being slowly warmed to room temperature over 5 hours. After 5h reaction mixture was re-cool to -10 °C and placed under kessil LED. Irradiation was continued at -10 °C for 10 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 85:15 petrol-EtOAc, afforded the title compound (30 mg, 30%) as a colorless needles (**MP**: 99-101 °C). R_f = 0.40; $[\alpha]_D^{23.2}$ = 8 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3295, 2971, 1633, 1512, 1392, 1247; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.27 (m, 2H), 7.07 (d, *J* = 11.2 Hz, 1H), 6.94 – 6.91 (m, 2H), 6.84 (dd, *J* = 11.4, 5.5 Hz, 1H), 6.25 (ddd, *J* = 9.2, 5.6, 1.5 Hz, 1H), 5.93 (d, *J* = 6.0 Hz, 1H), 5.54 (s, 1H), 5.52 – 5.45 (m, 1H), 3.83 (s, 3H), 2.71 – 2.66 (m, 1H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.06, 158.59, 132.27, 128.82, 128.57, 128.11, 127.42, 127.16, 125.05, 114.21, 55.35, 51.51, 43.86, 28.79. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NO_2Na$ [M+Na]+ 320.1621, found 320.1621; **HPLC**: er 23:77; Chiral Regis Whelk O1, Hexane:IPA = 80:20 flow = 1.0 mL/min, λ = 280 nm, tR = 31.285 mins(minor) and 40:568 mins (major).

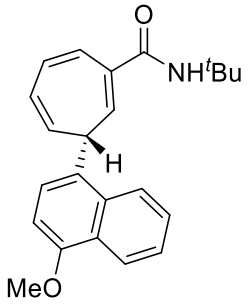


***(R)-N*-(tert-butyl)-3-(o-tolyl)cyclohepta-1,4,6-triene-1-carboxamide (4e): General Procedure 6:** To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2e** (100 mg, 0.35 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 3.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 90:10 petrol-EtOAc (Rf = 0.35), afforded the title compound (85 mg, 85%) as a pale-yellow oil. R_f = 0.40; $[\alpha]_D^{23.2}$ = 20 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3322, 2970, 1640, 1525, 1452, 1392, 1219, 1065, 752; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.20 – 7.17 (m, 2H), 7.06 (d, *J* = 11.1 Hz, 1H), 6.81 (dd, *J* = 11.3, 5.5 Hz, 1H), 6.27 (ddd, *J* = 9.1, 5.7, 1.5 Hz, 1H), 5.86 – 5.78 (m, 1H), 5.54 (s, 1H), 5.42 – 5.32 (m, 1H), 2.90 (td, *J* = 5.8, 1.5 Hz, 1H), 2.19 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.13, 140.90, 136.34, 133.88, 131.95, 130.70, 128.05, 126.86, 126.79, 126.61, 125.61, 125.36, 124.57, 51.59, 40.57, 28.86, 19.64; **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NONa$ [M+Na]+ 304.1675, found 304.1672; **HPLC**: *er* 4:96; Chiral Regis Whelk O1, Hexane:IPA = 90:10, flow = 1.0 mL/min, λ = 280 nm, tR = 30.722 mins(minor) and 44.404 mins (major).

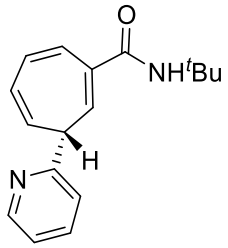


***(R)-N*-(tert-butyl)-3-(*p*-tolyl)cyclohepta-1,4,6-triene-1-carboxamide (4f):**

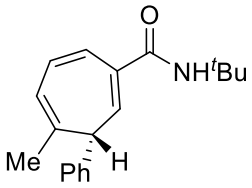
General Procedure 6: To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2f** (100 mg, 0.35 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 8.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 90:10 petrol-EtOAc (Rf = 0.35), afforded the title compound (40 mg, 40%) as a pale-yellow oil. R_f = 0.40; $[\alpha]_D^{23.2}$ = 12 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3327, 2959, 1644, 1512, 1451, 1363, 1217, 750, 697; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.23 (t, *J* = 6.2 Hz, 2H), 7.11 (d, *J* = 11.2 Hz, 1H), 6.87 (dd, *J* = 11.2, 5.6 Hz, 1H), 6.31 – 6.25 (m, 1H), 5.94 (d, *J* = 6.0 Hz, 1H), 5.57 (s, 1H), 5.52 (dd, *J* = 9.1, 5.4 Hz, 1H), 2.73 (t, *J* = 5.5 Hz, 1H), 2.39 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (126 MHz Chloroform-*d*) δ 167.09, 139.84, 136.58, 133.51, 132.24, 129.51, 128.16, 127.75, 126.86, 125.13, 51.51, 44.24, 28.78, 21.07. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NONa$ [M+Na]+ 304.1675, found 304.1671; **HPLC**: *er* 4:96; CHIRALPAK® IA column, Hexane:IPA = 99:01, flow = 1.0 mL/min, λ = 280 nm, tR = 10.271 mins(minor) and 12.86 mins (major).



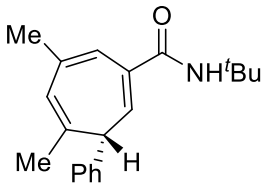
***(R)-N*-(tert-butyl)-3-(4-methoxynaphthalen-1-yl)cyclohepta-1,4,6-triene-1-carboxamide (4g): General Procedure 6:** To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2g** (100 mg, 0.28 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 14.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 80:20 petrol-EtOAc (Rf = 0.35), afforded the title compound (40 mg, 40%) as a yellow oil. R_f = 0.40; $[\alpha]_D^{22.6}$ = 12 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3327, 2970, 1649, 1586, 1518, 1392, 1225, 1055, 759; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.37 – 8.31 (m, 1H), 7.89 – 7.81 (m, 1H), 7.52 – 7.45 (m, 3H), 7.11 (d, *J* = 11.0 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.30 (ddd, *J* = 9.0, 5.7, 1.4 Hz, 1H), 5.95 (d, *J* = 6.0 Hz, 1H), 5.60 – 5.47 (m, 2H), 4.01 (s, 3H), 3.28 (t, *J* = 5.7 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.19, 154.98, 133.63, 132.39, 131.90, 129.84, 128.20, 126.62, 126.40, 125.42, 125.18, 124.72, 124.02, 123.58, 122.97, 103.29, 55.64, 51.59, 40.63, 28.86. **HRMS** (ESI+): m/z calcd for $C_{23}H_{25}NO_2Na$ [M+Na]+ 370.1777, found 370.1788; **HPLC**: er 6:94 Chiral Regis Whelk O1, Hexane:IPA = 70:30 flow = 1.0 mL/min, λ = 280 nm, tR = 33.68 (minor), and 41.3 (major).



***(R)-N*-(tert-butyl)-3-(pyridin-2-yl)cyclohepta-1,4,6-triene-1-carboxamide (4h): General Procedure 6:** To a suspension of chiral *(R)*-amine (2.0 equiv) in dry THF (0.1) at –78 ºC (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2h** (100 mg, 0.28 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 ºC for 30 minutes, then the temperature of the Cryostat was set to -10 ºC and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 5.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 80:20 petrol-EtOAc (Rf = 0.35), afforded the title compound (60 mg, 60%) as a yellow oil. R_f = 0.35 $[\alpha]_D^{23.2}$ = 12 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3313, 2970, 1650, 1543, 1363, 1223, 1052, 749; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.65 (ddd, *J* = 7.5, 1.9 Hz, 1H), 7.51 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.16 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.73 (dd, *J* = 10.4, 6.3 Hz, 1H), 6.32 (dd, *J* = 8.4, 6.3 Hz, 1H), 5.59 – 5.51 (m, 1H), 5.48 (s, 1H), 5.01 (ddt, *J* = 7.8, 5.3, 2.5 Hz, 1H), 2.11 – 2.06 (m, 1H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.86, 157.47, 149.29, 136.84, 136.57, 130.12, 128.80, 126.57, 122.00, 121.08, 103.02, 101.69, 51.62, 41.91, 28.96. **HRMS** (ESI+): m/z calcd for $C_{17}H_{20}N_2ONa$ [M+Na]+ 291.1467, found 291.1472; **HPLC**: er 39:61 Chiral Regis Whelk O1, Hexane:IPA = 85:15 flow = 1.0 mL/min, λ = 280 nm, tR = 20.987 mins(minor) and 22.505 mins (major).

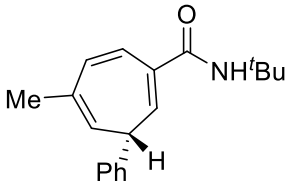


***(S)-N*-(tert-butyl)-4-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4i): General Procedure 6:** To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooling down to -78 °C, a solution of amide **4i** (100 mg, 0.35 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 4.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 90:10 petrol-EtOAc (Rf = 0.40), afforded the title compound (68 mg, 68%) as a colorless oil. R_f = 0.40; $[\alpha]_D^{23}$ = 20 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3354, 2971, 1644, 1532, 1451, 1393, 1055; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 – 7.18 (m, 3H), 7.17 – 7.14 (m, 2H), 6.70 (d, *J* = 11.2 Hz, 1H), 6.55 (dd, *J* = 11.2, 5.7 Hz, 1H), 6.27 (d, *J* = 7.4 Hz, 1H), 6.00 (d, *J* = 6.6 Hz, 1H), 5.52 (s, 1H), 3.04 (d, *J* = 7.4 Hz, 1H), 1.61 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.02, 139.94, 137.31, 133.88, 132.12, 128.67, 128.28, 127.39, 126.77, 125.56, 122.28, 51.48, 48.29, 28.81, 22.11. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NONa$ [M+Na]+ 304.1672, found 304.1674; **HPLC**: *er* 5.3: 94:6; Chiral Regis Whelk O1, Hexane:IPA = 70:30 flow = 1.0 mL/min, λ = 280 nm, tR = 21.53 mins (minor) and 29.20 mins (major) respectively.



***(S)-N*-(tert-butyl)-4,6-dimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4j): General Procedure 6:** To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear

yellow solution. This was then cooled down to -78 °C, a solution of amide **2j** (100 mg, 0.33 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -5 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 8.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 90:10 petrol-EtOAc (Rf = 0.40), afforded the title compound (50 mg, 50%) as a colorless oil. R_f = 0.39; $[\alpha]_D^{22.8}$ = 16 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3320, 2971, 1662, 1529, 1455, 1398, 1065; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.17 (m, 5H), 6.53 (s, 1H), 6.25 (d, *J* = 7.2 Hz, 1H), 5.87 (s, 1H), 5.55 (s, 1H), 3.13 (d, *J* = 7.2 Hz, 1H), 2.01 (s, 3H), 1.61 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.46, 141.46, 140.22, 136.06, 134.16, 128.66, 128.26, 126.69, 126.09, 125.40, 122.98, 51.41, 48.19, 28.82, 24.69, 21.95. **HRMS** (ESI+): m/z calcd for $C_{20}H_{25}NONa$ $[M+Na]^+$ 318.1834, found 318.1831; **HPLC**: *er* 29:71; Chiral Regis Whelk O1, Hexane:IPA = 70:30 flow = 1.0 mL/min, λ = 280 nm, tR = 10.41 mins (minor) and 11.99 mins (major).

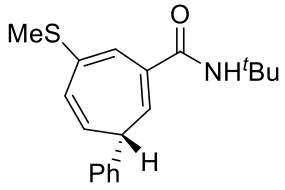


***(R)-N*-(tert-butyl)-5-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4k):**

Condition 1: General Procedure 6: To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added *n*-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2k** (100 mg, 0.35 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 8.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with

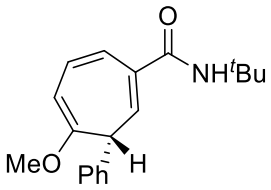
EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 9:1 petrol-EtOAc (Rf = 0.40), afforded the title compound (84 mg, 84%) as a colorless oil. **HPLC**: Chiral Regis Whelk O1, eluting with hexane-IPA (70:30), showed it to consist of a 20:80 mixture of two enantiomers with retention times 9.88 mins (minor) and 16.17 min (major) respectively.

Condition 2: General Procedure 6: To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2k** (100 mg, 0.35 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -20 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 14.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 90:10 petrol-EtOAc (Rf = 0.40), afforded the title compound (86 mg, 86%) as a colorless needles (**MP**: 97-99 °C). R_f = 0.40; $[\alpha]_D^{22.5}$ = 48 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3327, 2967, 1641, 1529, 1451, 1218, 753, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 2H), 7.29 (dt, *J* = 7.7, 1.7 Hz, 3H), 7.27 – 7.23 (m, 1H), 6.90 (d, *J* = 10.7 Hz, 1H), 6.58 (d, *J* = 10.7 Hz, 1H), 5.58 (s, 1H), 5.52 (dt, *J* = 5.8, 1.3 Hz, 1H), 4.81 – 4.74 (m, 1H), 2.52 (t, *J* = 5.5 Hz, 1H), 1.94 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.01, 143.20, 134.79, 132.66, 132.48, 128.81, 127.40, 126.76, 114.33, 110.58, 51.51, 41.40, 28.88, 21.56. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NONa$ [M+Na]+ 304.1677, found 304.1674; **HPLC**: *er* 12:88; Chiral Regis Whelk O1, Hexane:IPA = 70:30 flow = 1.0 mL/min, λ = 280 nm, tR = 10.41 mins (minor) and 16.29 mins (major).



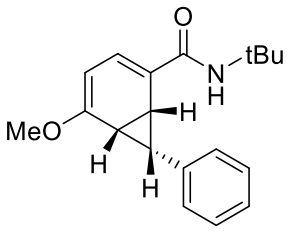
***(R)*-*N*-(tert-butyl)-6-(methylthio)-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4l): General Procedure 6:** To a suspension of chiral amine (2.0 equiv) in dry THF

(0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2l** (100 mg, 0.31 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 4.5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 90:10 petrol-EtOAc (Rf = 0.35), afforded the title compound (30 mg, 30%) as a yellow needle (**MP**: 110-112 °C). R_f = 0.42; $[\alpha]_D^{23.2}$ = 16 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3322, 2962, 1638, 1523, 752, 700; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 – 7.34 (m, 4H), 7.33 – 7.28 (m, 1H), 6.92 (s, 1H), 6.19 (dt, *J* = 9.5, 1.4 Hz, 1H), 5.90 (d, *J* = 5.8 Hz, 1H), 5.61 (ddt, *J* = 9.6, 5.9, 0.7 Hz, 1H), 5.54 (s, 1H), 2.98 (td, *J* = 5.8, 1.4 Hz, 1H), 2.43 (s, 3H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.05, 142.95, 142.47, 133.88, 128.97, 128.52, 127.68, 127.53, 127.15, 125.75, 121.77, 100.01, 51.65, 44.84, 28.86, 15.88. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NOSNa$ [M+Na]+ 336.1396, found 336.1397; **HPLC**: er 1:99; CHIRALPAK® IA column, Hexane:IPA = 99:05, flow = 1.0 mL/min, λ = 280 nm, tR = 7.68 mins(minor) and 8.982 mins (major).



***(R)-N*-(tert-butyl)-4-methoxy-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4m):** To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2m** (100 mg, 0.33 mmol) in THF (0.5 mL) and 3.0 equiv DMPU were sequentially added dropwise. The mixture was stirred at –78 °C for 30 minutes before being slowly warmed to room temperature over 5 hours. After 5h reaction mixture was re-cool to -10 °C and placed under kessil LED. Irradiation was continued at -10 °C for 4 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer

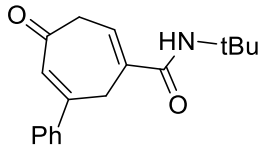
was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 85:15 petrol-EtOAc, afforded the title compound (65 mg, 65%) as a colorless needles (**MP**: 123-125 °C); R_f = 0.40; $[\alpha]_D^{22.8}$ = 8 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3322, 2969, 1649, 1532, 1410, 1229, 700; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 – 7.12 (m, 6H), 6.48 – 6.43 (m, 2H), 6.17 (d, *J* = 8.1 Hz, 1H), 5.57 (s, 1H), 5.41 (dd, *J* = 4.5, 2.5 Hz, 1H), 3.60 (d, *J* = 8.1 Hz, 1H), 3.56 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.25, 155.14, 137.97, 135.57, 130.06, 128.50, 127.89, 126.75, 125.53, 121.08, 97.05, 56.65, 51.46, 47.81, 28.81. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NO_2Na$ [M+Na]+ 320.1621, found 320.1633; **HPLC**: er 39:61; CHIRALPAK® IA column, Hexane:IPA = 90:10 flow = 1.0 mL/min, λ = 280 nm, tR = 6.025 mins (minor) and 7.58 mins (major).



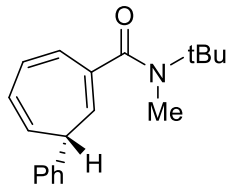
(1*R*,6*S*,7*S*)-*N*-(tert-butyl)-5-methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (5n): General Procedure 6: To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooled down to -78 °C, a solution of amide **2n** (100 mg, 0.33 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 4.5 h. Saturated aq. NH_4Cl was added, the layers separated, and the aqueous layer was extracted with ethyl acetate (10 x 3). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 85:15 petrol-EtOAc (Rf = 0.35), afforded the title compound (78 mg, 78%) as a yellow oil. R_f = 0.40; $[\alpha]_D^{22}$ = 41 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3327, 2969, 1646, 1553, 1452, 1231, 749, 697; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.20 – 7.11 (m, 2H), 7.11 – 7.03 (m, 1H), 7.02 – 6.94 (m, 2H), 6.61 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.45 (s, 1H), 5.26 (dd, *J* = 8.3,

1.4 Hz, 1H), 3.52 (s, 3H), 3.32 (t, *J* = 5.9 Hz, 1H), 2.71 (ddd, *J* = 6.7, 4.8, 1.4 Hz, 1H), 1.57 (t, *J* = 4.9 Hz, 1H), 1.24 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.65, 161.35, 141.55, 128.58, 126.73, 126.23, 126.16, 113.59, 98.82, 55.84, 51.27, 28.92, 28.76, 25.79. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NO_2Na$ [M+Na]+ 320.1621, found 320.1617; **HPLC**: *er* 6:94 CHIRALPAK® IA column, Hexane:IPA = 95:5 flow = 1.0 mL/min, λ = 280 nm, tR = 18.05 mins (minor), and 23.82 mins (major).

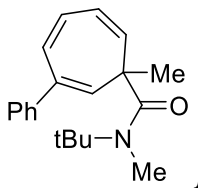
1.17 Analytical data of Product modifications



tert-butyl 4-oxo-6-phenylcyclohepta-1,5-diene-1-carboxylate (6n): To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 ºC (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooling down to -78 °C, a solution of amide **2f** (100 mg, 0.33 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 ºC for 30 minutes, then the temperature of the Cryostat was set to -10 ºC and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 4.5 h. Saturated aq. NH_4Cl was added, the layers separated, and the aqueous layer was extracted with ethyl acetate (10 x 3). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, and conc HCl (1 ml) was added to a solution of the crude cycoheptadiene in THF (10 ml) at 0 ºC and warm to room temperature for 4h, water was added to the reaction, and the layers were separated. The standard work-up gave a crude product which was purified by flash chromatography, eluting with 1:1 petrol-EtOAc to afford the title product as a yellow oil (60 mg, 60%); R_f = 0.35; ν_{max} /cm^{-1}(neat): 3330, 2977, 1643, 1525, 1216, 752, 697; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.40 – 7.29 (m, 3H), 6.77 (t, *J* = 6.2 Hz, 1H), 6.73 (s, 1H), 5.63 (s, 1H), 3.52 (s, 2H), 3.17 (d, *J* = 6.2 Hz, 2H), 1.41 (s, 9H).. **^{13}C NMR** (101 MHz, Chloroform-*D*) δ 209.71, 165.86, 140.85, 139.11, 138.24, 129.19, 128.78, 128.45, 126.36, 122.78, 51.79, 49.07, 44.41, 28.87. **HRMS** (ESI+): m/z calcd for $C_{18}H_{21}NO_2Na$ [M+Na]+ 306.1464, found 306.1473.



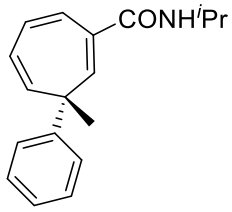
(R)-N-(tert-butyl)-N-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (8): To a suspension of chiral amine (2.0 equiv) in dry THF (0.1) at –78 °C (Cryostat), was added n-butyl lithium (3.0 equiv, 2.5 M in hexanes), dropwise. The resulting mixture was allowed to warm to room temperature over 15 minutes, resulting in a clear yellow solution. This was then cooling down to -78 °C, a solution of amide **2a** (100 mg, 0.37 mmol) in THF (0.5 mL) was added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp. The mixture was stirred at –78 °C for 30 minutes, then the temperature of the Cryostat was set to -10 °C and the reaction mixture was slowly allowed to warm. After a further 1 h, DMPU (3.0 equiv.) was added and further irradiation was continued for 2.5 h. Stop the irradiation and 5.0 equiv iodomethane was added to reaction mixture and reaction further run for 2 h at -10 °C. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated to yield a crude product, which was purified by flash chromatography, eluting with 90:10 petrol-EtOAc afforded the title compound (71 mg, 68%) as a colorless needles (**MP**: 107-109 °C). R_f = 0.40; $[\alpha]_D^{22.6}$ = 92 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 2972, 1636, 1365, 1066, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.34 (m, 4H), 7.27 (d, *J* = 1.4 Hz, 1H), 6.91 – 6.85 (m, 1H), 6.80 (dd, *J* = 11.1, 5.6 Hz, 1H), 6.29 – 6.23 (m, 1H), 5.51 (ddq, *J* = 9.2, 5.6, 0.8 Hz, 1H), 5.43 – 5.38 (m, 1H), 2.71 (td, *J* = 5.7, 1.5 Hz, 1H), 2.66 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.65, 143.19, 136.00, 131.73, 129.67, 128.84, 127.70, 126.91, 126.38, 124.87, 124.13, 56.48, 44.62, 34.38, 27.78. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NONa$ [M+Na]+ 304.1671, found 304.1671; **HPLC**: *er* 9:91; CHIRALPAK® IA, Hexane:IPA = 95:5 flow = 1.0 mL/min, λ = 280 nm, tR = 5.79 mins (minor), and 6.65 mins (major).



***N*-(tert-butyl)-N,1-dimethyl-3-phenylcyclohepta-2,4,6-triene-1-carboxamide (9):** The *(R)*-*N*-(*tert*-butyl)-*N*-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (**8**, 100 mg,

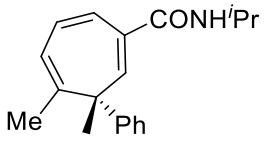
0.35 mmol) was dissolved in dry THF (0.1 M) under a nitrogen atmosphere. After cooling down to -10 °C (Cryostat), freshly prepared LDA (1.5 equiv) was sequentially added dropwise and the reaction mixture was stirred at 700 rpm. After 15 mins, iodomethane (4.0 equiv.) was added and the reaction was continued for 2 h. The reaction was quenched with sat. aq. NH_4Cl (5 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10:90 EtOAC/Hexane) afforded the title compound as yellow oil. R_f = 0.40; ν_{max} /cm^{-1}(neat): 2971, 1634, 1363, 1217, 1143, 1074, 752, 698; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.22 – 7.17 (m, 2H), 7.17 – 7.11 (m, 2H), 7.10 – 7.05 (m, 1H), 6.38 – 6.35 (m, 2H), 6.29 (ddd, *J* = 8.9, 5.1, 2.1 Hz, 1H), 5.33 – 5.27 (m, 2H), 2.69 (s, 3H), 1.53 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.07, 146.63, 136.76, 130.12, 128.91, 128.12, 127.39, 126.77, 125.88, 125.73, 123.41, 120.59, 56.45, 40.74, 34.16, 30.83, 27.87. **HRMS** (ESI+): m/z calcd for $C_{20}H_{25}NONa$ [M+Na]+ 318.1834, found 318.1834. **HPLC**: *er* 53:47; CHIRALPAK® IA, Hexane:IPA = 99:1 flow = 1.0 mL/min, λ = 280 nm, tR = 6.70 mins, and 7.39 mins.

1.18 Analytical data of stereospecific photochemical ring expansion

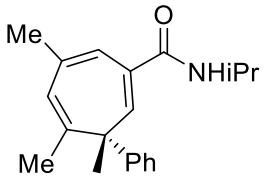


(*R*)-*N*-isopropyl-3-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11a): The *(R)-N*-isopropyl-*N*-(1-phenylethyl)benzamide **10a** (100 mg, 0.37 mmol) was dissolved in dry THF (0.1 M) under a nitrogen atmosphere. After cooling down to -10 °C (Cryostat), freshly prepared LDA (2.0 equiv) and DMPU (6.0 equiv) were sequentially added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp for 8 h at -10 °C. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAC/Hexane) afforded the title compound (90 mg, 90%) as pale yellow needles (**MP**: 104-106 °C); R_f = 0.17; $[\alpha]_D^{23}$ = -92 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1} (neat): 3304, 2971, 1634, 1527, 1445, 1055, 749, 698; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.20 – 7.13 (m,

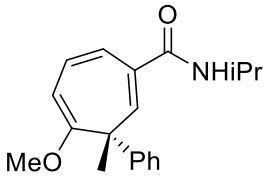
4H), 7.13 – 7.08 (m, 1H), 6.63 – 6.56 (m, 1H), 6.36 – 6.27 (m, 2H), 5.63 (d, *J* = 7.8 Hz, 1H), 5.18 (dd, *J* = 3.4, 1.2 Hz, 1H), 4.71 – 4.64 (m, 1H), 4.18 (dp, *J* = 7.8, 6.5 Hz, 1H), 1.48 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.05, 145.39, 131.69, 128.84, 127.30, 126.99, 126.88, 125.95, 125.77, 104.70, 41.63, 35.21, 28.40, 22.63. **HRMS** (ESI+): m/z calcd for $C_{18}H_{21}NONa$ [M+Na]+ 290.1515, found 290.1525; **HPLC**: er 0.42:99.57, Chiral Whelk O1, Hexane-IPA (80:20), flow = 1.0 mL/min, λ = 280 nm tR = 15.472 mins(minor) and 20.112 mins (major).



(R)-N-isopropyl-3,4-dimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide **(11b)**: The *(R)-N*-isopropyl-3-methyl-*N*-(1-phenylethyl)benzamide **10b** (100 mg, 0.35 mmol) was dissolved in dry THF (0.1 M) under a nitrogen atmosphere. After cooling down to -10 °C (Cryostat), freshly prepared LDA (2.0 equiv) and DMPU (6.0 equiv) were sequentially added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp for 4 h at -10 °C. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (25% EtOAC/Hexane) afforded the title compound (80 mg, 80%) as pale-yellow oil. R_f = 0 40; $[\alpha]_D^{22.7}$ = -80 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3318, 2971, 1635, 1527, 1445, 1066, 749, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.41 – 4.32 (m, 5H), 3.73 (dq, *J* = 7.8, 3.4 Hz, 1H), 3.56 – 3.46 (m, 2H), 3.08 (s, 1H), 2.96 – 2.80 (m, 1H), 1.47 (dp, *J* = 13.5, 6.8 Hz, 1H), -0.62 (s, 3H), -1.11 (s, 3H), -1.49 (d, *J* = 2.5 Hz, 3H), -1.50 (d, *J* = 2.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.21, 146.00, 132.08, 130.59, 127.08, 126.78, 125.70, 125.36, 124.31, 122.73, 43.83, 41.88, 29.84, 22.87. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NONa$ [M+Na]+ 304.1672, found 304.1682; **HPLC**: er 2: 98 Chiral Whelk O1, Hexane:IPA = 85:15, flow = 1.0 mL/min, λ = 280 nm, tR = 25.838 mins (major) and 28.485 mins (minor).

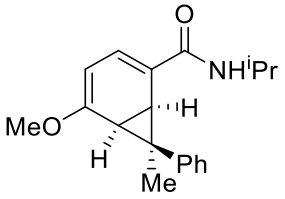


***(S)-N*-isopropyl-3,4,6-trimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11c):** The *(R)-N*-isopropyl-3,5-dimethyl-*N*-(1-phenylethyl)benzamide **10c** (100 mg, 0.33 mmol) was dissolved in dry THF (0.1 M) under a nitrogen atmosphere. After cooling down to -10 °C (Cryostat), freshly prepared LDA (2.0 eq.) and DMPU (6.0 equiv) were sequentially added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp for 4 h at -10 °C (Cryostat). The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (25% EtOAC/Hexane) afforded the title compound (57 mg, 57%) as colorless oil. R_f = 0.30; $[\alpha]_D^{21}$ = -124 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1} (neat): 3294, 2971, 1638, 1533, 1450,; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.08 – 7.01 (m, 5H), 6.16 (s, 1H), 6.00 (s, 1H), 5.76 (s, 1H), 5.57 (d, *J* = 9.4 Hz, 1H), 4.16 (dq, *J* = 13.1, 6.5 Hz, 1H), 2.02 (s, 3H), 1.69 (s, 3H), 1.54 (s, 3H), 1.20 (d, *J* = 2.6 Hz, 3H), 1.18 (d, *J* = 2.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.55, 146.90, 140.13, 132.17, 127.16, 126.59, 125.69, 122.65, 43.84, 41.87, 29.62, 23.53, 22.96, 22.91, 22.58. **HRMS** (ESI+): m/z calcd for $C_{20}H_{25}NONa$ [M+Na]+ 318.34, found 318.48; **HPLC**: er 90:10 Chiral Whelk O1, Hexane:IPA = 85:15 flow = 1.0 mL/min, λ = 280 nm, tR = 14.81 (major), and 16.01 (minor).



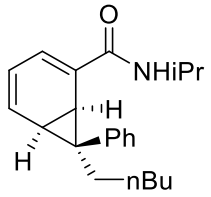
***(R)-N*-isopropyl-4-methoxy-3-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11d):** The *(R)-N*-isopropyl-3-methoxy-*N*-(1-phenylethyl)benzamide **10d** (100 mg, 0.33 mmol) was dissolved in dry THF (0.1 M) under a nitrogen atmosphere. After cooling down to -10 °C (Cryostat), freshly prepared LDA (2.0 eq.) and DMPU (6.0 equiv) were sequentially added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp for 8 h at -10 °C. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAC/Hexane) afforded the title compound (76 mg, 76%) as colorless needles. R_f = 0.40; **MP:** 192-194 °C; $[\alpha]_D^{21}$ = -124 (c = 1.00 in $CHCl_3$);

ν_{max} /cm^{-1}(neat): 3333, 2971, 1637, 1542, 1415, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 – 6.93 (m, 5H), 6.17 (d, *J* = 6.6 Hz, 2H), 6.10 (s, 1H), 5.56 (d, *J* = 7.1 Hz, 1H), 5.48 (d, *J* = 6.0 Hz, 1H), 4.16 – 4.05 (m, 1H), 3.69 (s, 3H), 1.57 (s, 3H), 1.14 (dd, *J* = 6.6, 3.3 Hz, 7H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.27, 158.86, 145.02, 133.66, 131.79, 129.57, 128.27, 126.97, 126.07, 125.83, 120.06, 98.05, 56.94, 48.43, 41.88, 29.53, 22.82. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NO_2Na$ [M+Na]+ 320.1621, found 320.1632; **HPLC**: er 100:00 Chiral Whelk O1, Hexane:IPA = 85:15, flow = 1.0 mL/min, λ = 280 nm, tR = 17.575.



(1*R*,6*S*,7*R*)-*N*-isopropyl-5-methoxy-7-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (11e): The *(R)*-*N*-isopropyl-4-methoxy-*N*-(1-phenylethyl)benzamide **10e** (100 mg, 0.33 mmol) was dissolved in dry THF (0.1 M) under a nitrogen atmosphere. After cooling down to -10 °C (Cryostat), freshly prepared LDA (2.0 equiv) and DMPU (6.0 equiv) were sequentially added dropwise and the reaction mixture was stirred at 700 rpm and irradiated with a 40 W Kessil lamp for 5 h at -10 °C (Cryostat). The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAC/Hexane) afforded the title compound (85 mg, 85%) as colorless needles (**MP**: 114-116 °C). R_f = 0.17; $[\alpha]_D^{21}$ = -36 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3336, 2971, 1555, 1219, 1174, 1027, 748, 699; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 – 7.16 (m, 4H), 7.11 (ddd, *J* = 8.6, 5.4, 2.6 Hz, 1H), 6.57 (d, *J* = 7.1 Hz, 1H), 5.49 (d, *J* = 6.3 Hz, 1H), 4.97 (d, *J* = 7.1 Hz, 1H), 4.14 (dq, *J* = 13.3, 6.6 Hz, 1H), 3.63 (s, 3H), 2.58 (dd, *J* = 9.1, 0.9 Hz, 1H), 2.31 (dd, *J* = 9.1, 1.2 Hz, 1H), 1.17 – 1.11 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.84, 161.24, 128.52, 128.36, 128.01, 126.29, 121.22, 93.11, 55.77, 41.52, 34.03, 33.31, 23.02, 16.14. **HRMS** (ESI+): m/z calcd for $C_{19}H_{23}NO_2Na$ [M+Na]+ 320.1621, found 320.1632; **HPLC**: *er* 2:98; Chiral Whelk O1, Hexane:IPA = 70:30, flow = 1.0 mL/min, λ = 280 nm, tR = 14.25 (minor), and 22.63 (major).

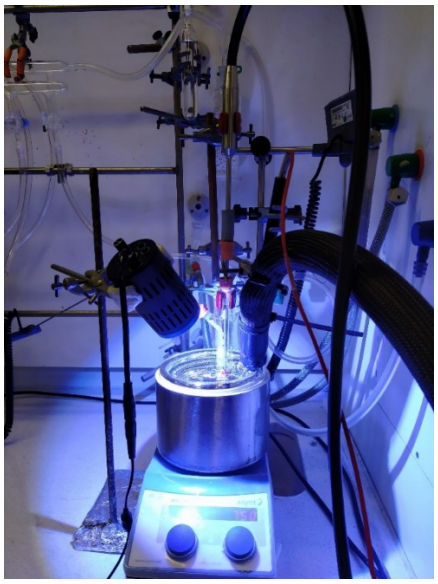
1.19 Analytical data of carbolithiation and photochemical rearrangements



(1*R*,6*S*,7*S*)-*N*-isopropyl-7-pentyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (14): To a stirred solution of freshly distilled (−)-sparteine (2 equiv.) in dry diethyl ether (3.7 mL) at −78 °C, RLi (2 equiv.) was added resulting in a pale-yellow solution. The reaction was left to stir at the same temperature for 15 min. before the *N*-isopropyl-*N*-(1-phenylvinyl)benzamide (0.37 mmol, 1 equiv.) in solution in dry diethyl ether (1 mL) was slowly added dropwise resulting in a red-orange solution and irradiated with a 40 W Kessil lamp. The reaction was warm up to -10 ºC and stirred for 5 h. The reaction was quenched with sat. aq. NH_4Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10% EtOAC/Hexane) afforded the title compound (50 mg, 41%) as yellow oil. R_f = 0.17; $[\alpha]_D^{25}$ = -68 (c = 1.00 in $CHCl_3$); ν_{max} /cm^{-1}(neat): 3334, 2971, 1560, 1230, 1174,; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 – 7.05 (m, 5H), 6.47 (d, *J* = 8.6 Hz, 1H), 6.29 (t, *J* = 7.4 Hz, 1H), 6.16 – 6.07 (m, 1H), 5.61 (d, *J* = 7.7 Hz, 1H), 4.32 (d, *J* = 5.6 Hz, 1H), 4.25 – 4.14 (m, 1H), 3.89 (dd, *J* = 7.4, 5.0 Hz, 1H), 1.67 – 1.59 (m, 2H), 1.19 (dqd, *J* = 13.5, 7.5, 6.7, 2.8 Hz, 12H), 0.82 – 0.75 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.36, 142.45, 131.09, 129.34, 128.08, 127.37, 126.87, 126.08, 125.50, 80.21, 79.76, 41.83, 39.89, 33.97, 32.15, 25.52, 22.99, 22.60, 14.09. **HRMS** (ESI+): m/z calcd for $C_{22}H_{29}NONa$ $[M+Na]^+$ 346.2141, found 346.2137; **HPLC**: er 27:73, Chiral Whelk O1, Hexane:IPA = 92:08, flow = 1.0 mL/min, λ = 254 nm, tR = 28.04 (minor) and 29.3 (major) min.

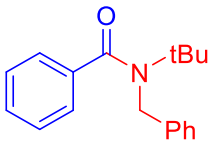
2 Mechanistic Study

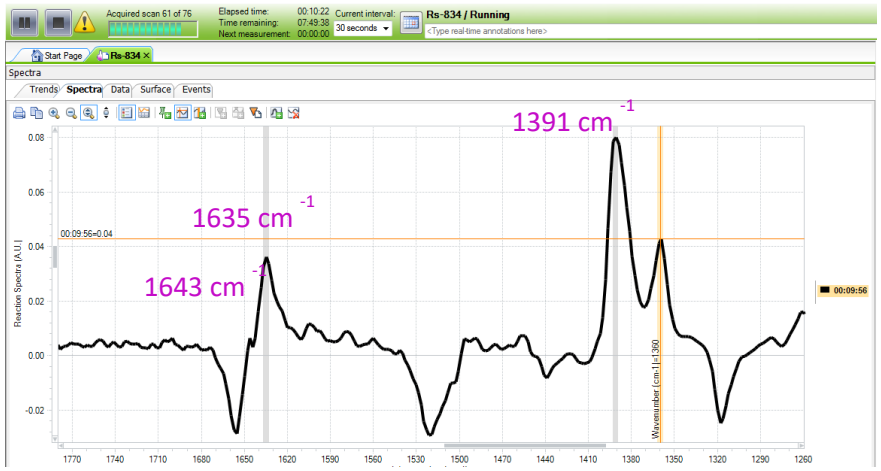
2.1 experimental setup of ReactIR



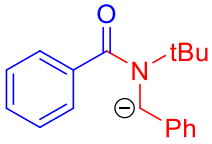
2.1.1 React-IR study

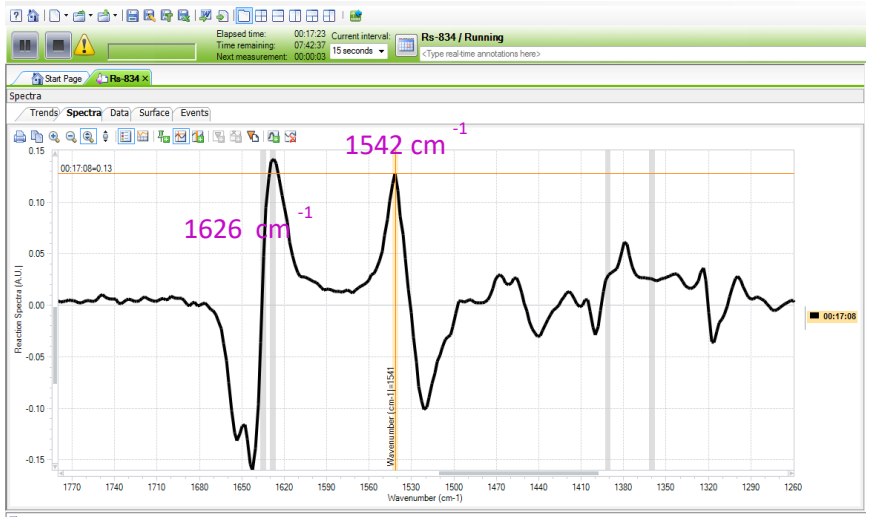
Starting material peaks with THF+DMPU in background

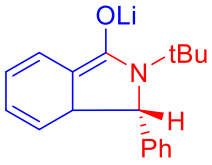


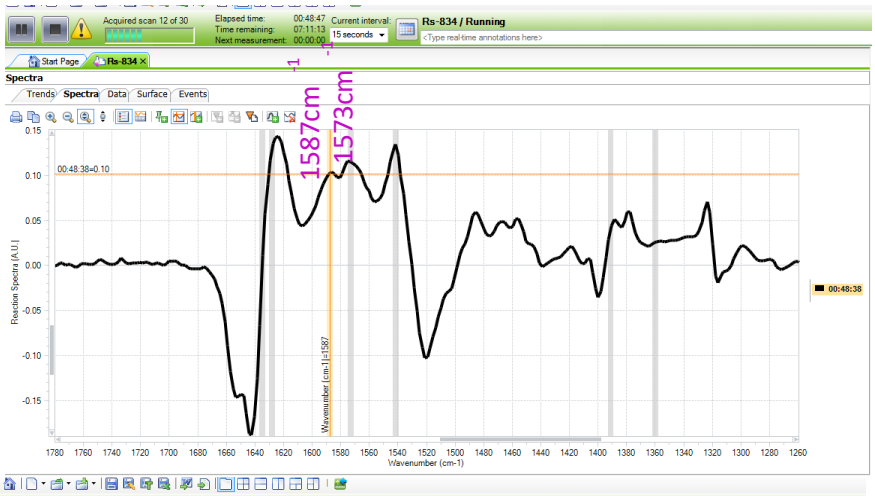


LDA addition

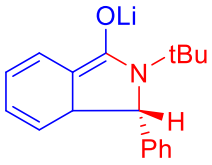


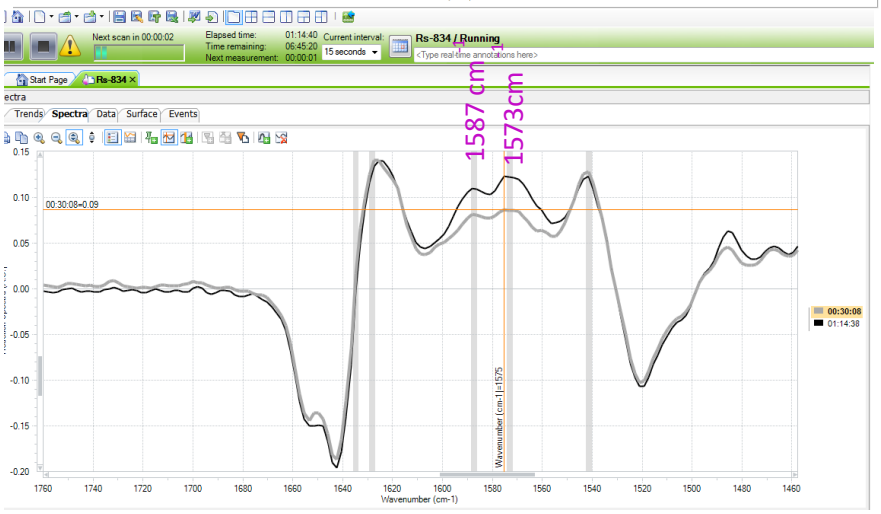




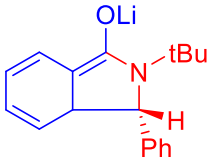


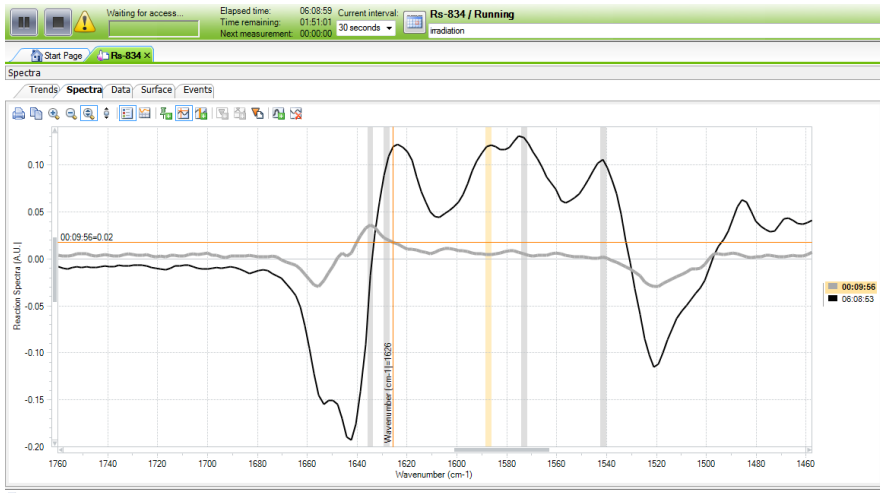
After (1.14 h)



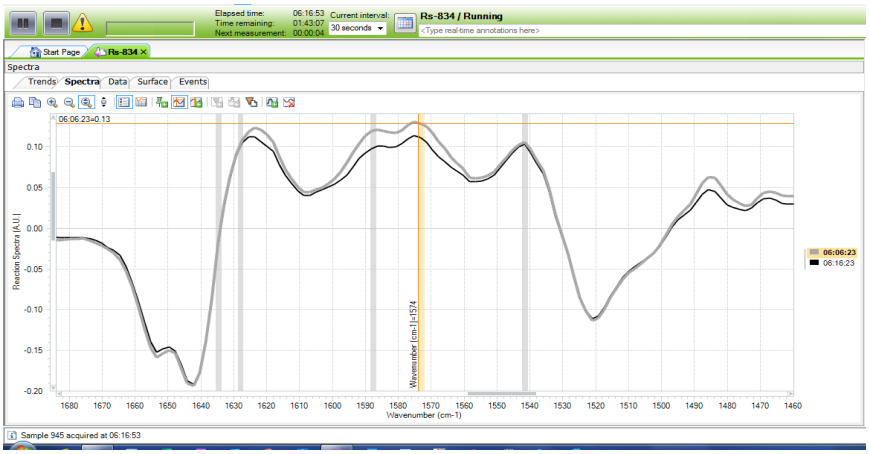


dearomatizing cyclization done Confirmed by TLC

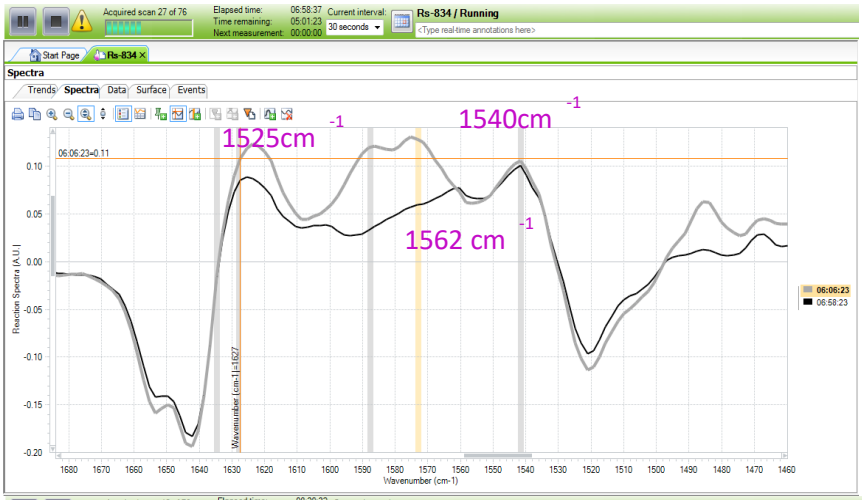


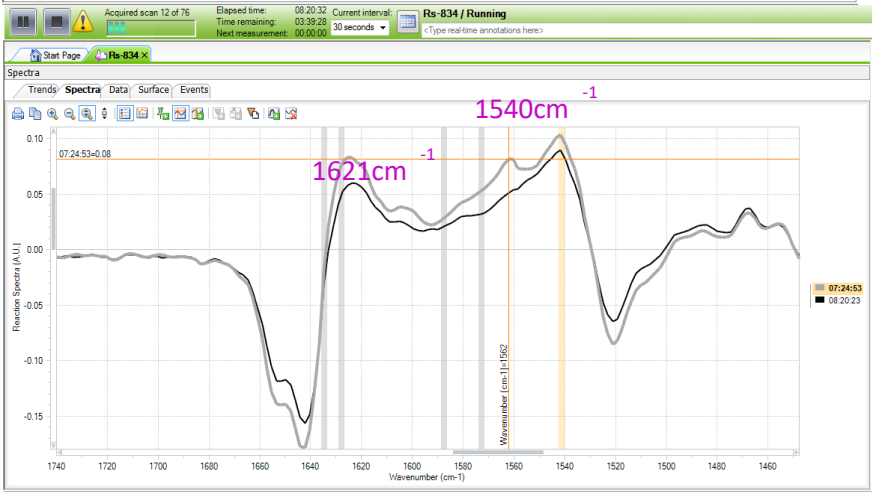


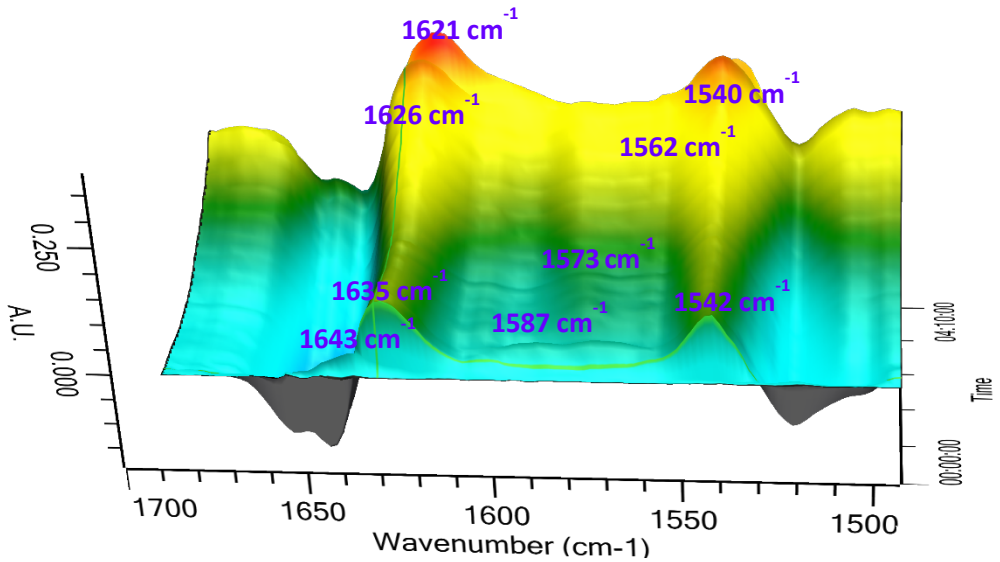
Irradiation start (after 10 mins of irradiation)



After 50 mins of Irradiation



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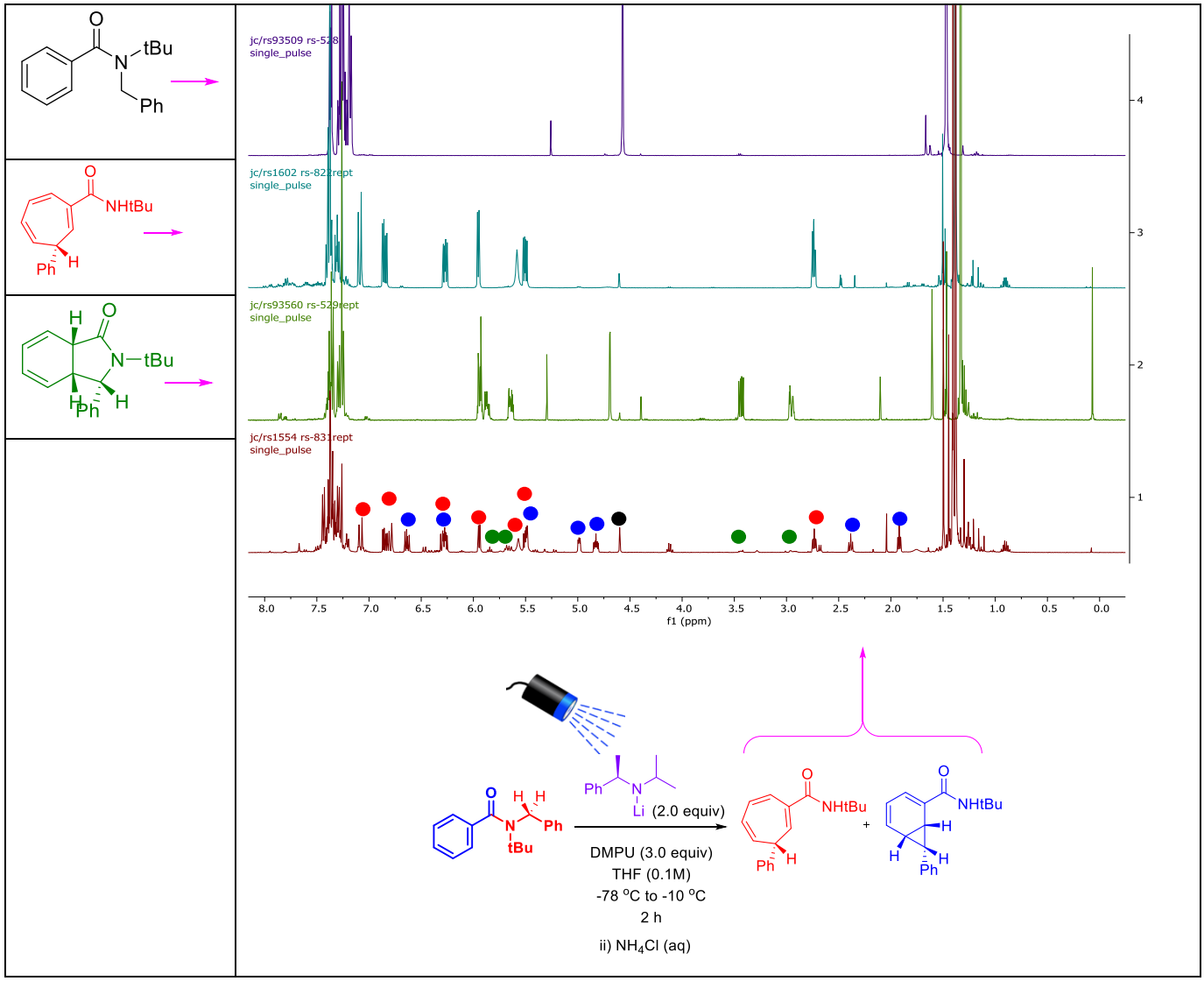
1540 cm-1
1562 cm-1
1573 cm-1
1635 cm-1
1643 cm-1
1587 cm-1
1542 cm-1
0.250
0.000
A.U.
1700
1650
1600
1550
1500
Wavenumber (cm-1)
04:10:00
00:00:00
Time

2.2 NMR Study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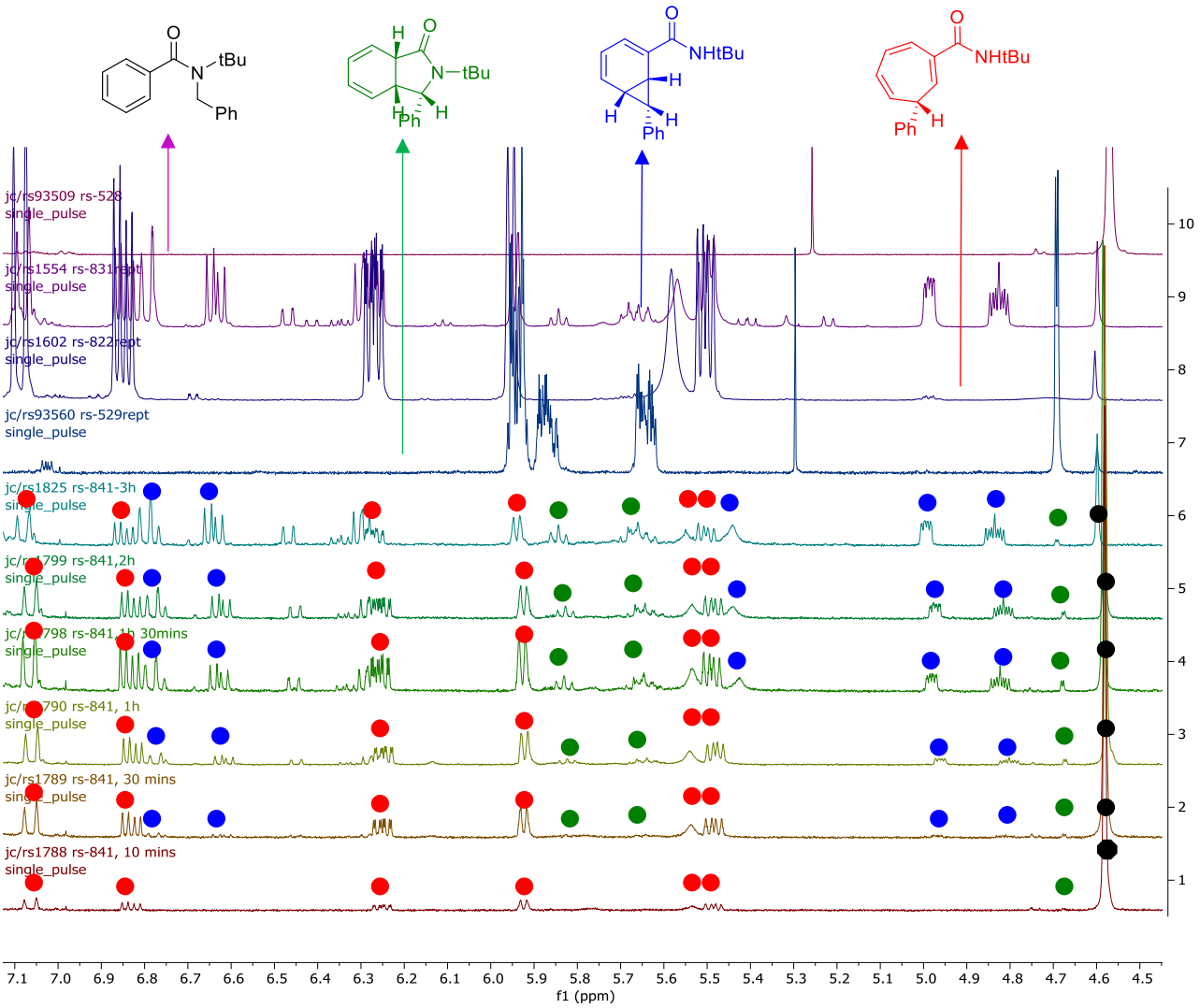
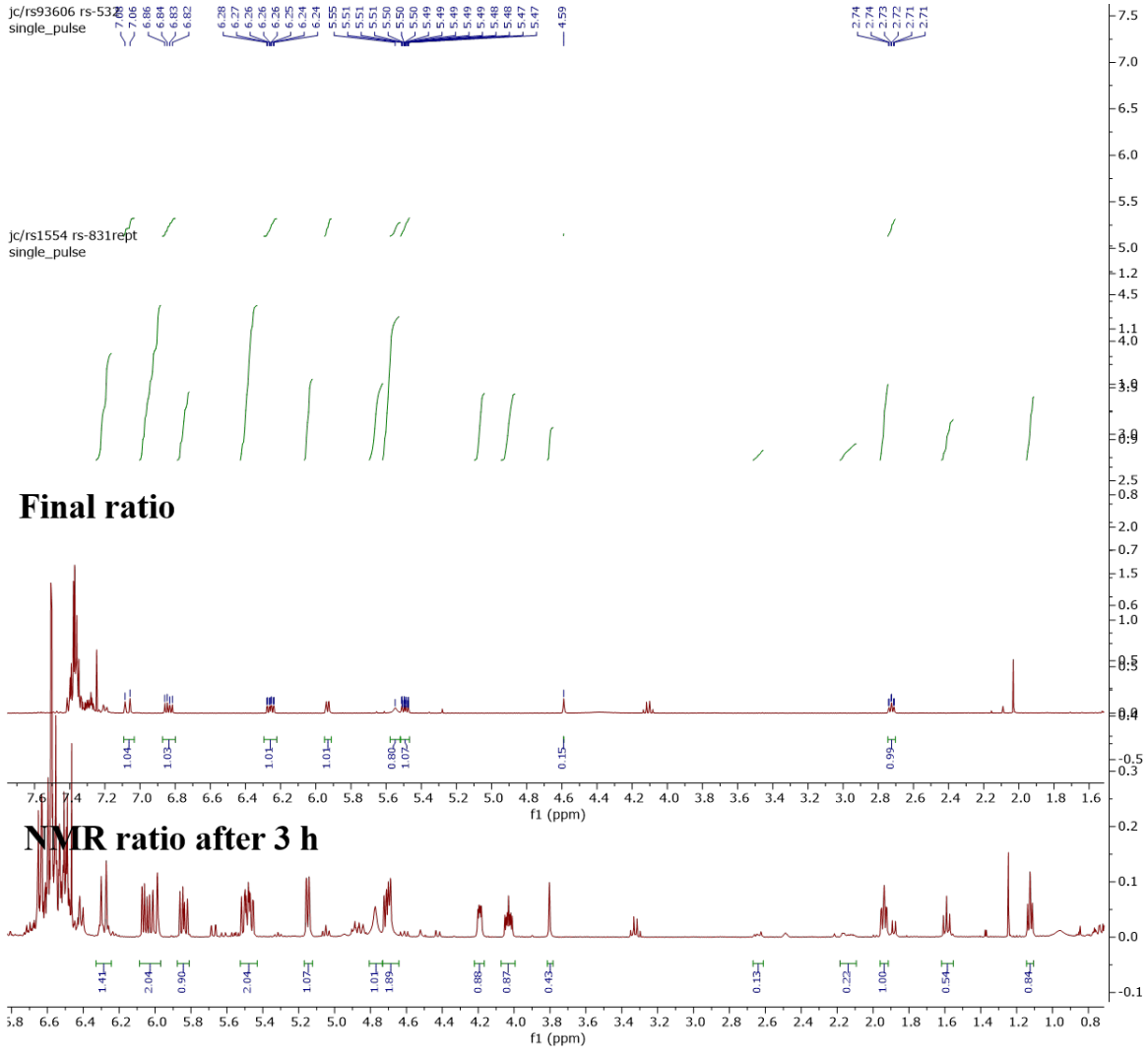
single_pulse
jc/rs1602 rs-82
single_pulse
jc/rs93560 rs-529rept
single_pulse
jc/rs1554 rs-83
single_pulse
f1 (ppm)
(2.0 equiv)
DMPU (3.0 equiv)
THF (0.1M)
-78 °C to -10 °C
2 h
ii) NH4Cl (aq)

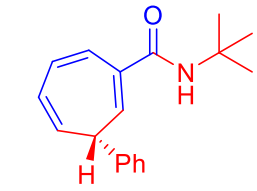
Reaction monitoring by NMR

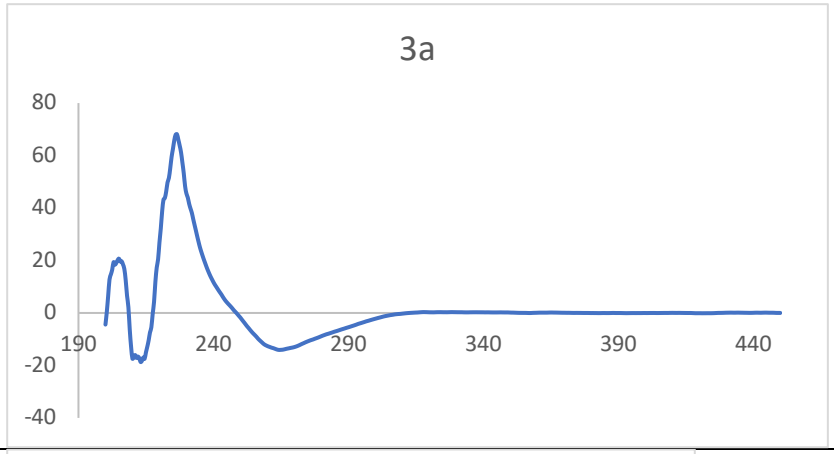


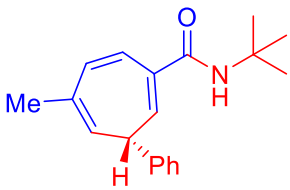
NMR ratio after 3 h and Final ratio

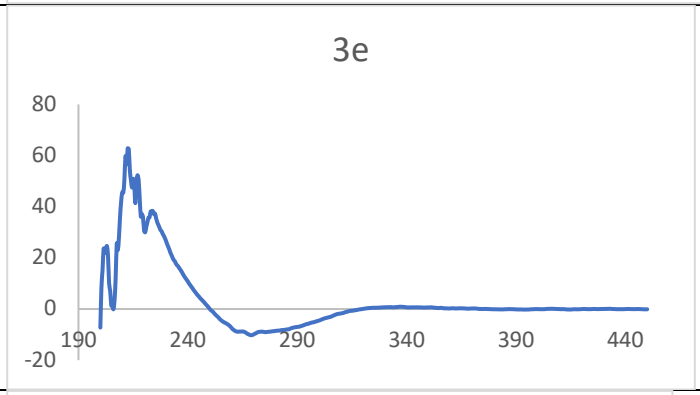


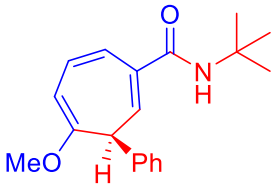
2.2 VCD spectra

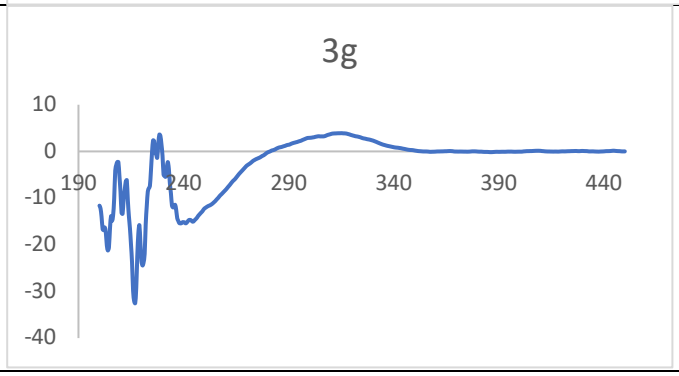


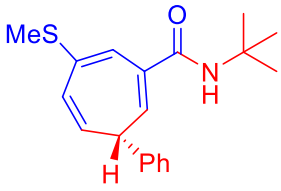








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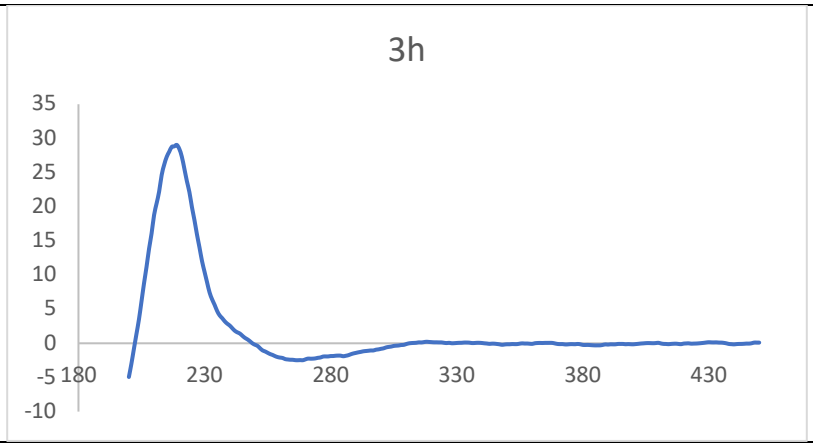
N
H
H
Ph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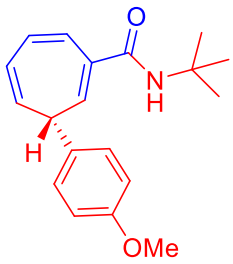
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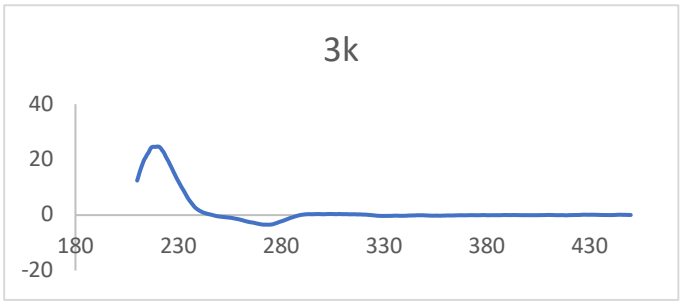
N
H
H
OMe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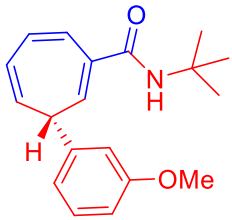
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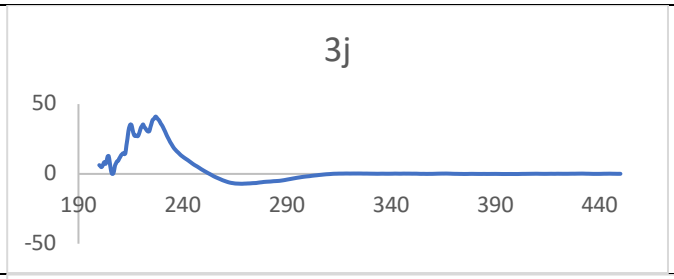
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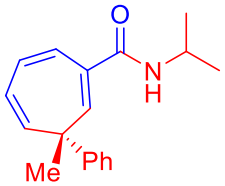
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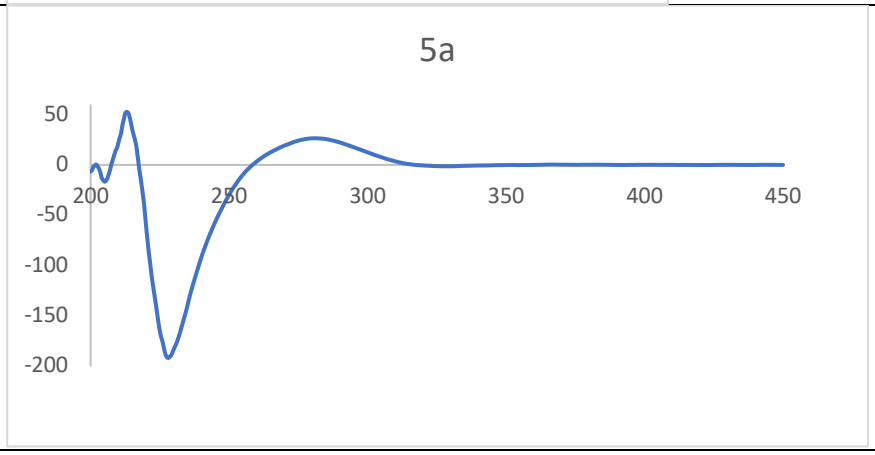
H
Me
Ph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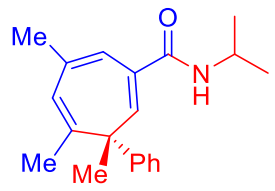
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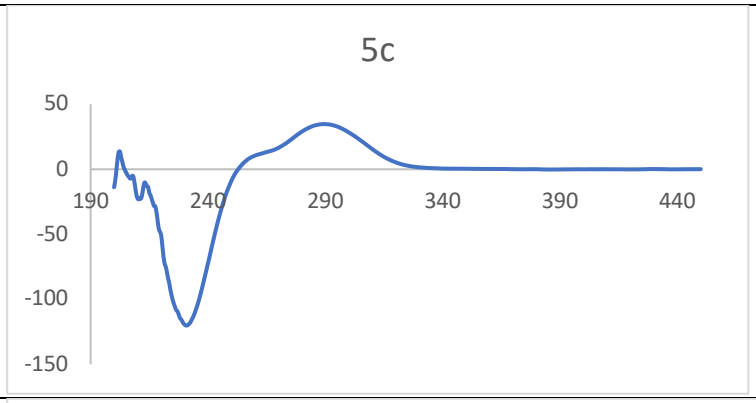
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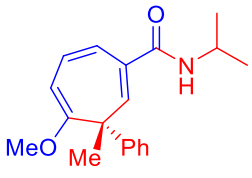
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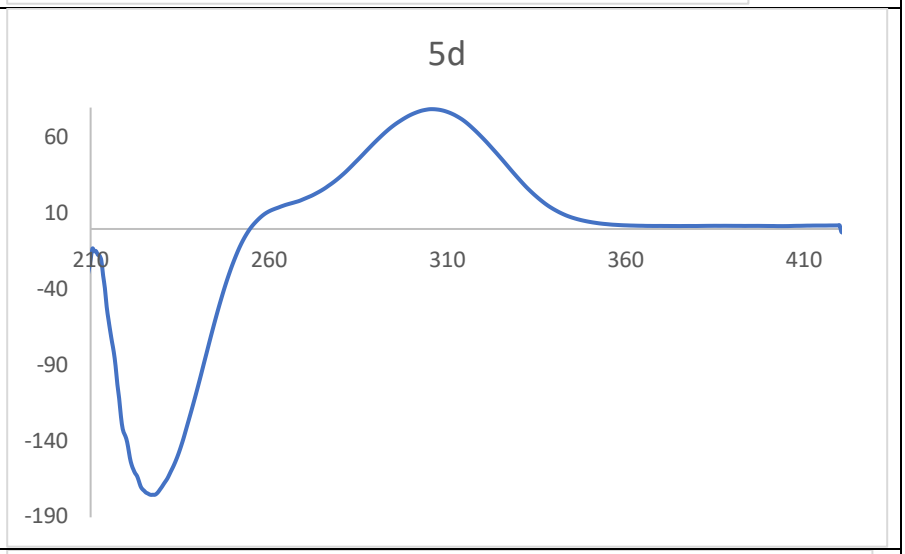
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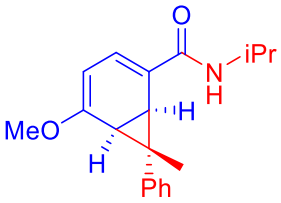
360
410


O
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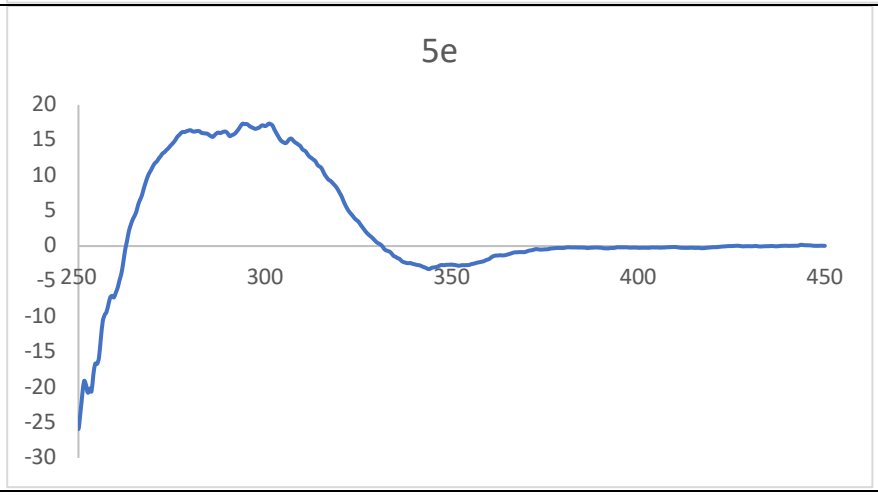
H
iPr
MeO
H
H
Ph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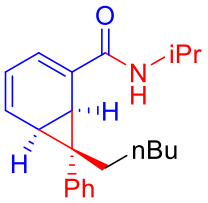
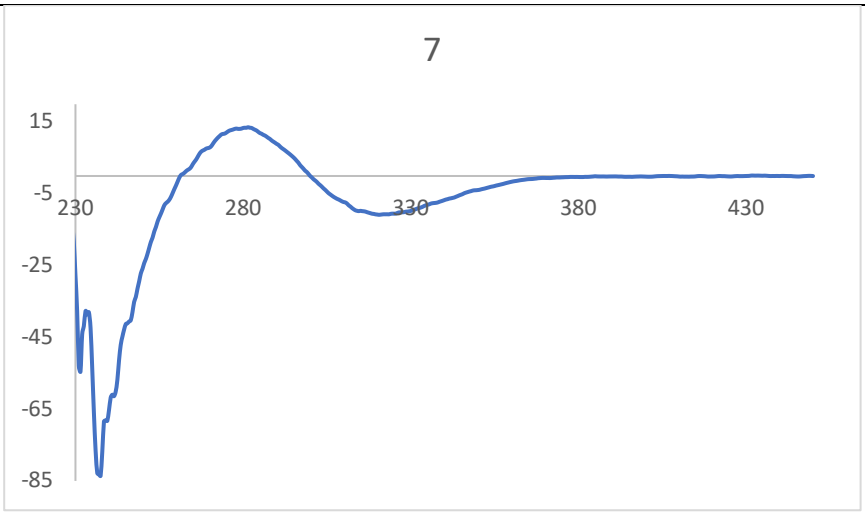
15
10
5
0
-5
-10
-15
-20
-25
-30
250
300
350
400
450

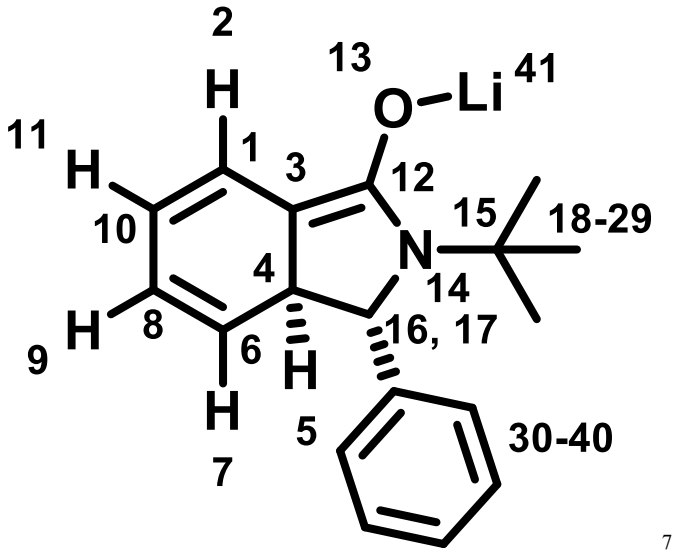

O
N
H
iPr
H
H
nBu
Ph


7
15
-5
-25
-45
-65
-85
230
280
330
380
430

Time-Dependent DFT Calculations

Computational characterizations of the ground- and excited-state properties of the enolate were performed using Gaussian 16 software[7]. The ground electronic state geometry of the enolate was computed using density functional theory (DFT). The B3LYP functional was used with the 6-31+G(d,p) basis set. Solvent effects for THF were included by implicit simulation of solvation as a conductor-like polarizable continuum medium. Vertical transition energies, oscillator strengths and excitation amplitudes were computed using time-dependent density functional theory (TD-DFT) using the Coulomb attenuated variant of the B3LYP functional (CAM-B3LYP). CAM-B3LYP was used with the 6-31+G(d,p) basis set and conductor-like continuum simulation of THF as solvent.

Cartesian Coordinates of Optimised Structure



7

Tag	Symbol	X	Y	Z
1	C	-3.1034110	-1.5153440	-0.5790170
2	H	-4.0000200	-1.0658490	-1.0067870
3	C	-1.9312920	-0.7477870	-0.4228190
4	C	-0.6286430	-1.4240440	-0.0889220
5	H	-0.1441670	-1.7987030	-1.0162150
6	C	-0.8702700	-2.5858350	0.8455920

[7]Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

7	H	-0.0838380	-2.9158470	1.5220180
8	C	-2.0437770	-3.2703660	0.7399130
9	H	-2.1958230	-4.1656800	1.3419480
10	C	-3.1416040	-2.8111160	-0.0885310
11	H	-4.0427030	-3.4120360	-0.1685380
12	C	-1.7318110	0.6348070	-0.5121380
13	O	-2.5684210	1.5307190	-0.8866810
14	N	-0.4061030	0.9681140	-0.1299630
15	C	-0.1430150	2.3175950	0.4874950
16	C	0.2496590	-0.2435130	0.4315210
17	H	0.1798910	-0.2230750	1.5318700
18	C	-1.1216400	2.5745380	1.6560800
19	H	-0.9014510	3.5385080	2.1278760
20	H	-2.1561920	2.5889470	1.3067590
21	H	-1.0225560	1.7971530	2.4223970
22	C	-0.2826450	3.4120140	-0.5910410
23	H	-1.2906710	3.4341030	-1.0031190
24	H	-0.0532330	4.3903720	-0.1531590
25	H	0.4255930	3.2299410	-1.4068880
26	C	1.2930380	2.4040470	1.0380430
27	H	1.4397010	3.4094540	1.4454500
28	H	1.4791910	1.6927900	1.8467380
29	H	2.0397360	2.2433700	0.2571560
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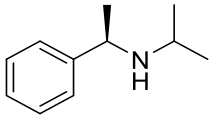
31	C	2.6159170	-0.9560080	0.9721610
32	C	2.1525170	-0.2015160	-1.2683780
33	C	3.9402070	-1.2284650	0.6115060
34	H	2.2893300	-1.1405580	1.9930570
35	C	3.4748430	-0.4666820	-1.6326300
36	H	1.4598100	0.2050160	-1.9992900
37	C	4.3760140	-0.9825440	-0.6935730
38	H	4.6293460	-1.6269960	1.3510510
39	H	3.8030410	-0.2700330	-2.6497990
40	H	5.4046990	-1.1874560	-0.9760870
41	Li	-4.2423990	1.8094970	-1.4791560

TDDFT UV-Vis Prediction Data

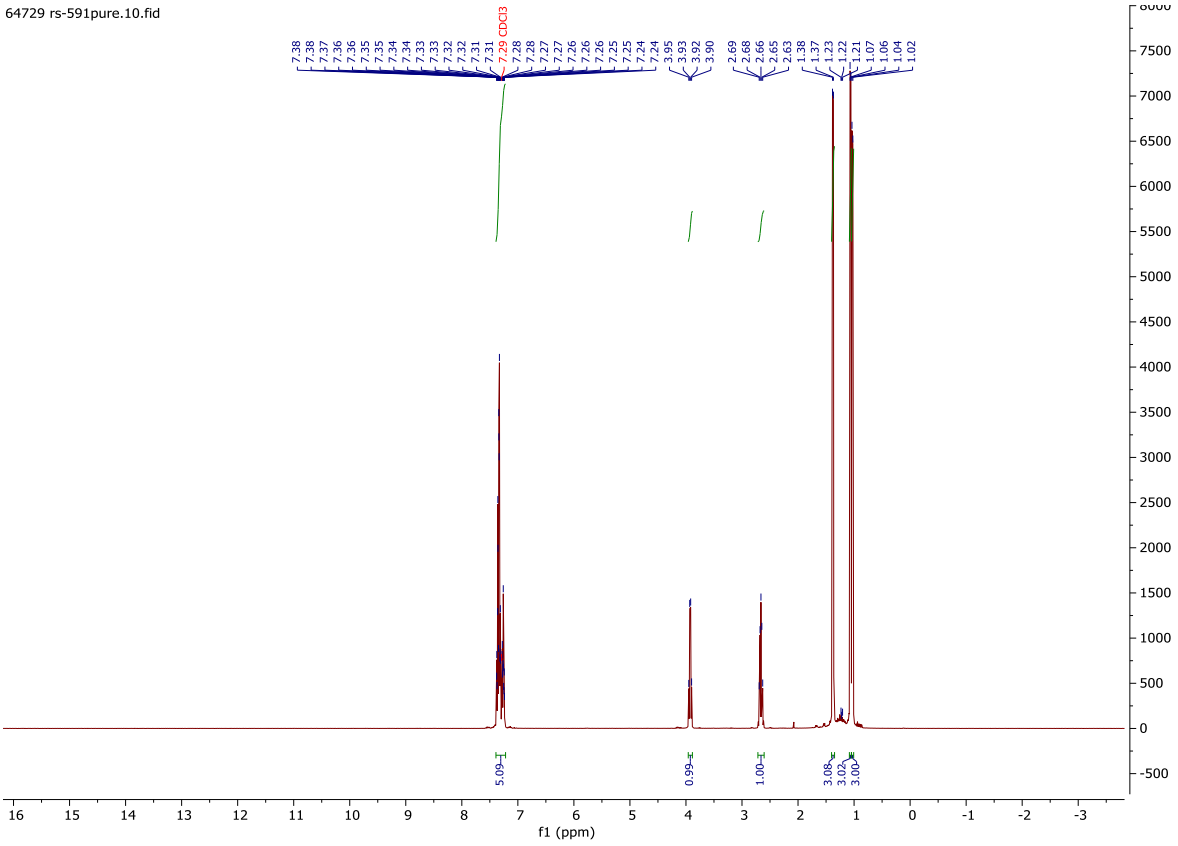
Transition	Wavelength (nm)	Energy (eV)	Oscillator Strength
$S_0 \rightarrow S_1$	415.00	2.9875	0.2465
$S_0 \rightarrow S_2$	357.99	3.4634	0.0048
$S_0 \rightarrow S_3$	315.33	3.9319	0.0160
$S_0 \rightarrow S_4$	306.60	4.0438	0.0045

Copies of ^{1}H, ^{13}C NMR spectra (all in $CDCl_3$) and HPLC traces

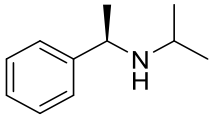
^{1}H NMR



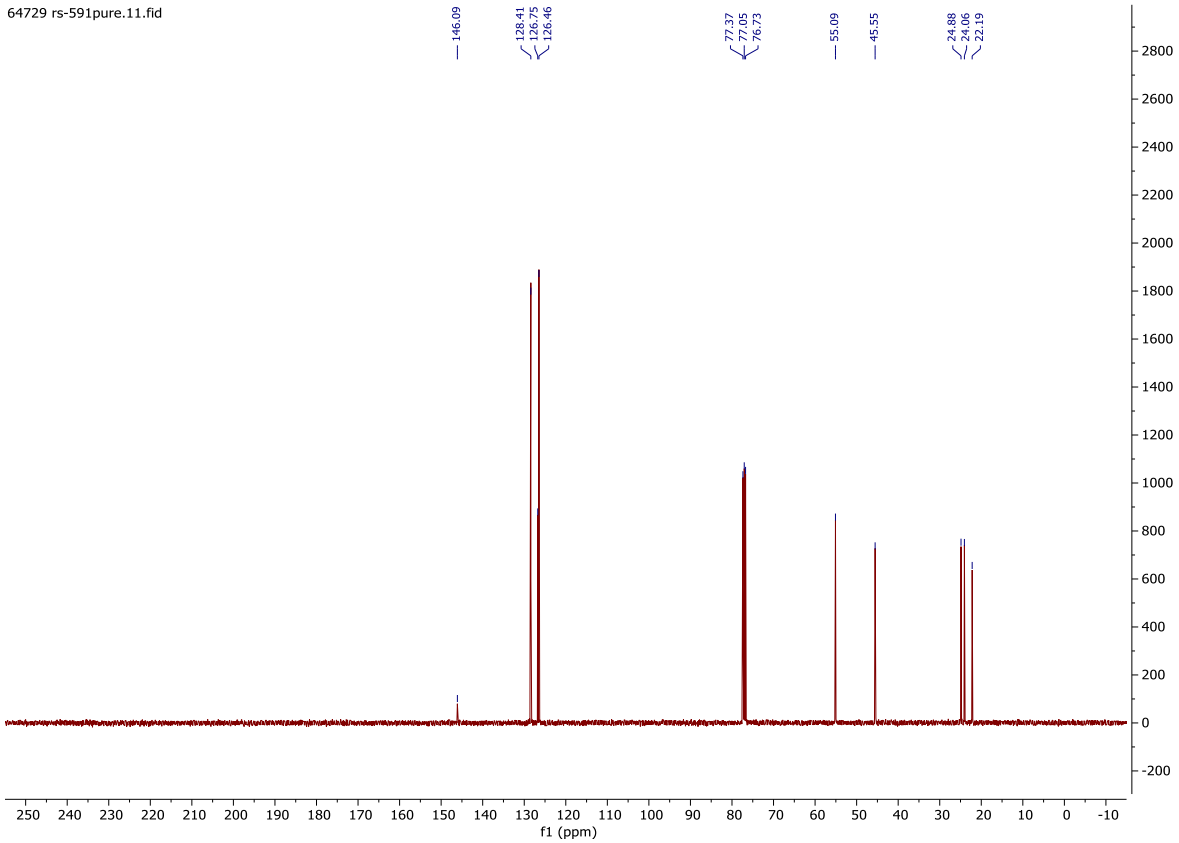
(R)-N-(1-Phenylethyl)-1-methylethylamine (1c)



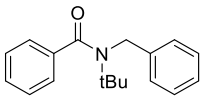
^{13}C NMR



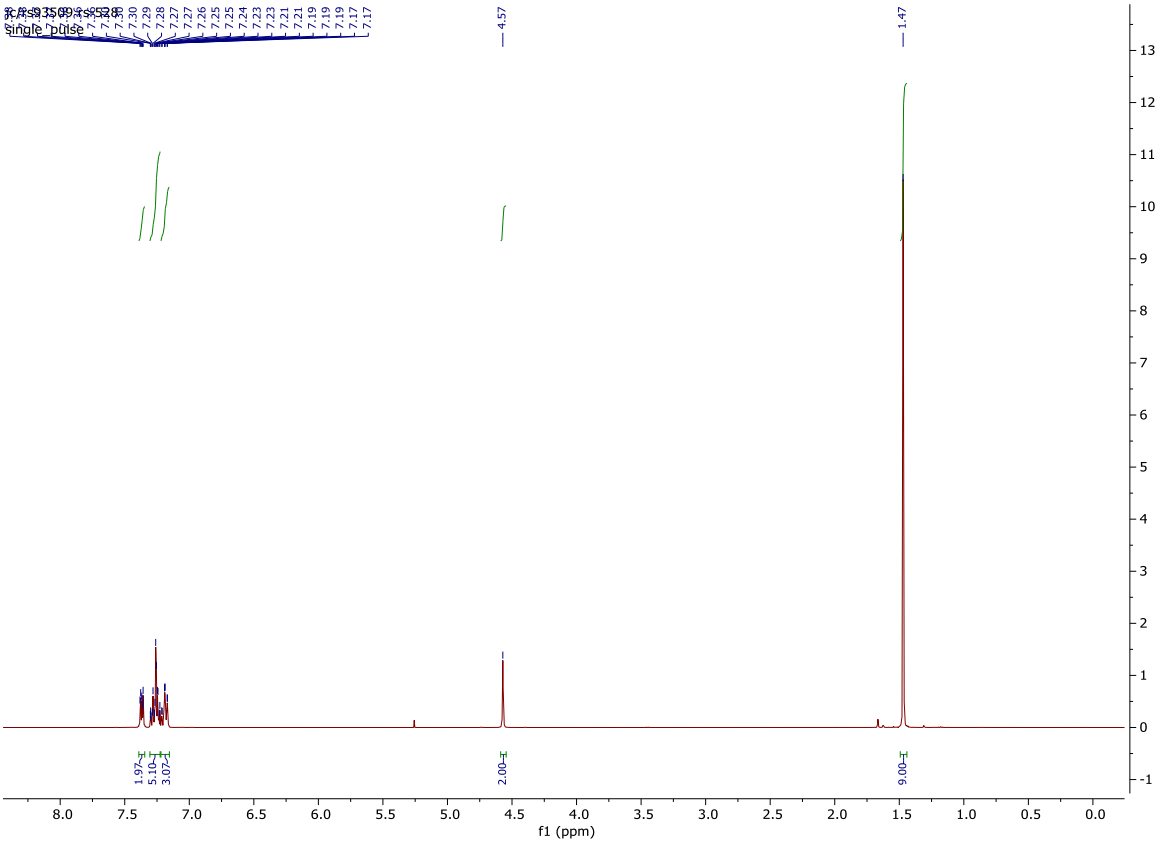
(R)-N-(1-Phenylethyl)-1-methylethylamine (1c)



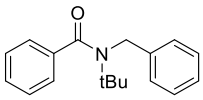
^{1}H NMR



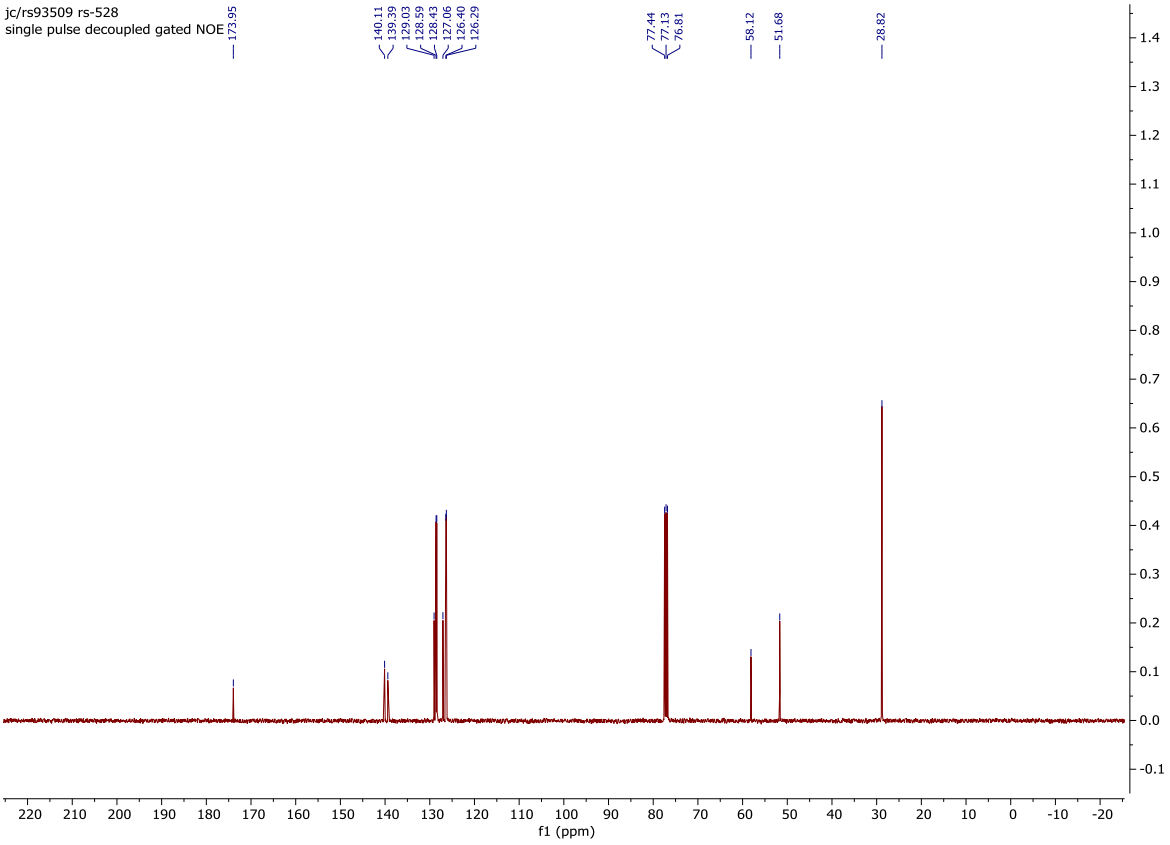
N-benzyl-*N*-(tert-butyl)benzamide (2a)



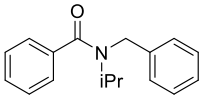
^{13}C NMR



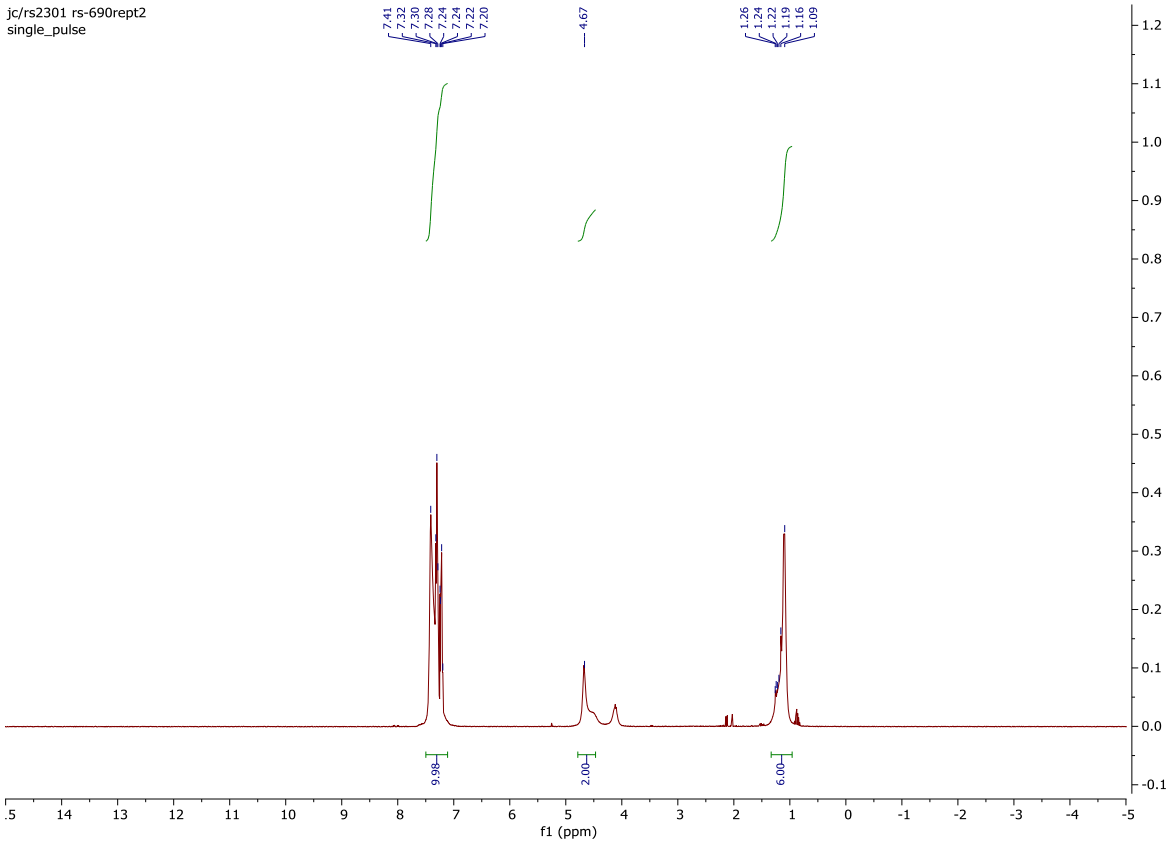
N-benzyl-*N*-(tert-butyl)benzamide (2a)



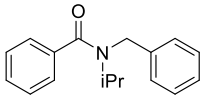
^{1}H NMR



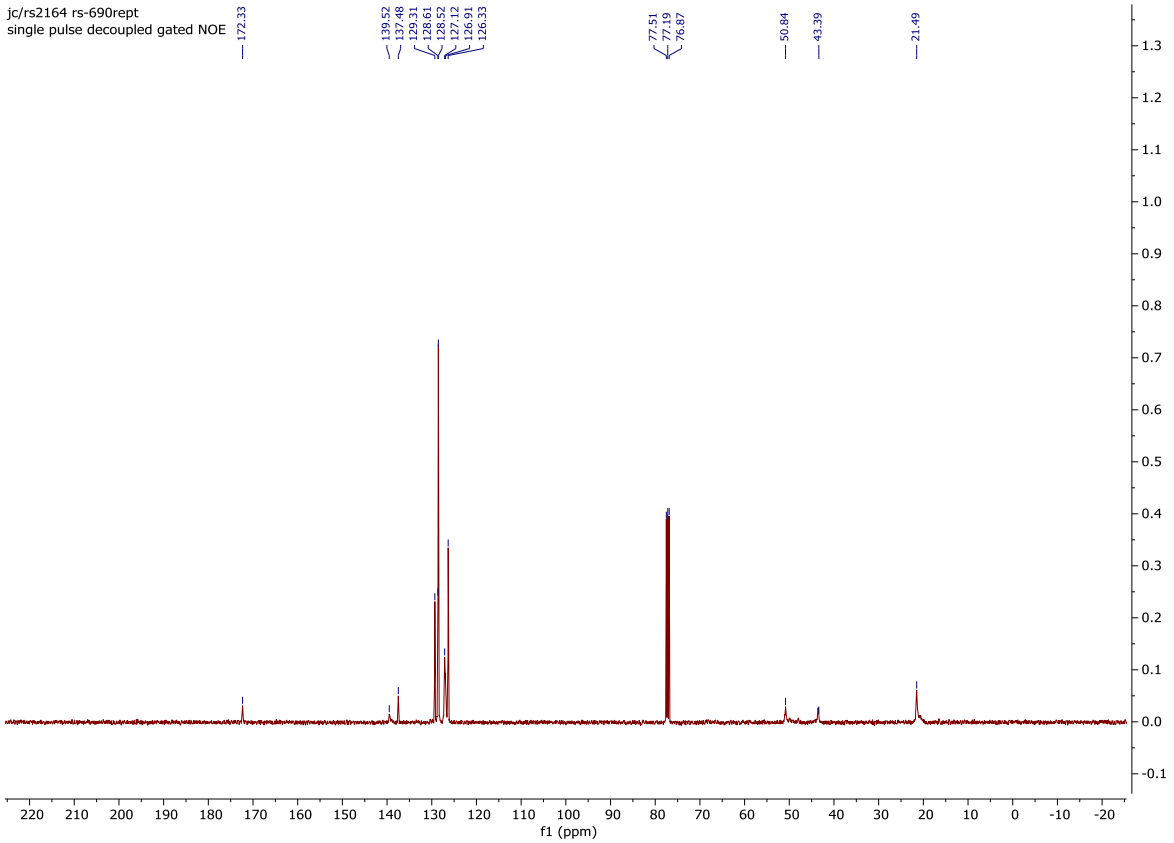
N-benzyl-*N*-isopropylbenzamide (2a')



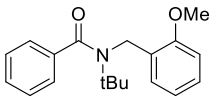
^{13}C NMR



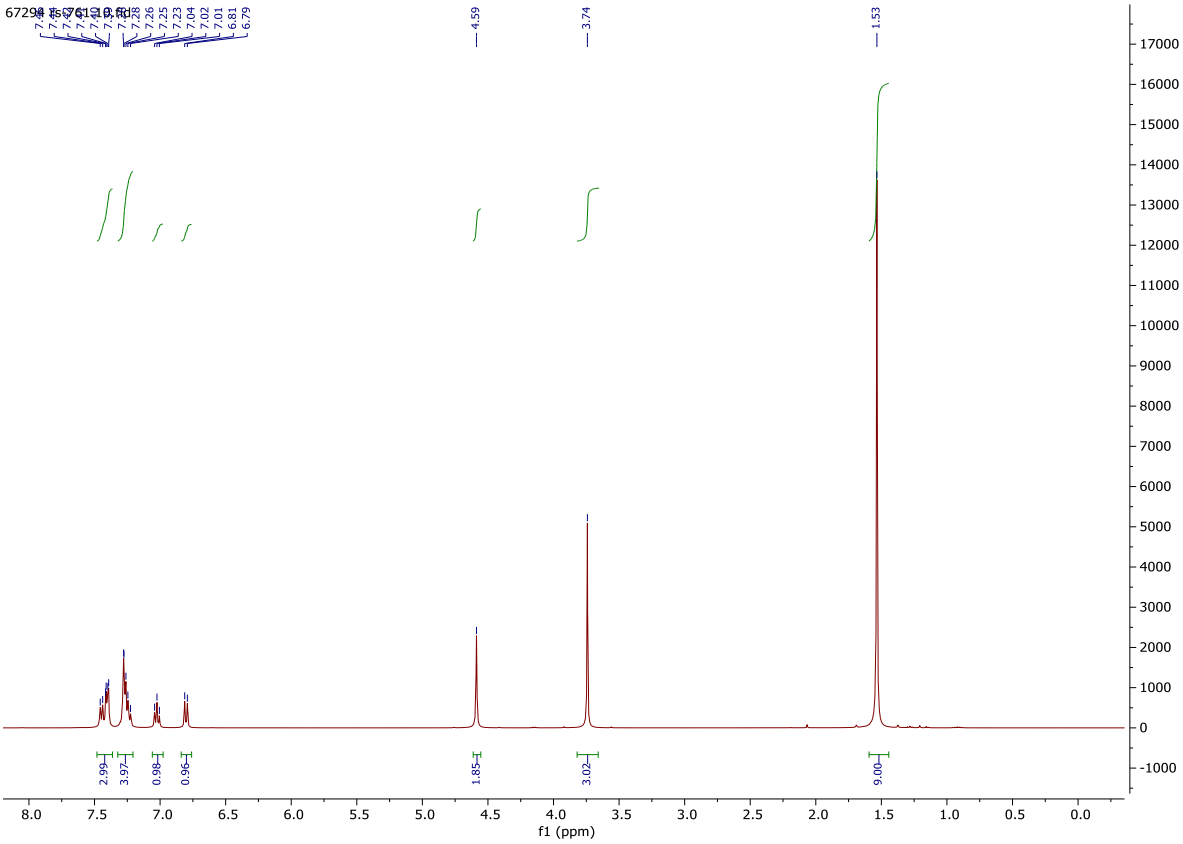
N-benzyl-*N*-isopropylbenzamide (2a')



^{1}H NMR



***N*-(tert-butyl)-*N*-(2-methoxybenzyl)benzamide (2b)**



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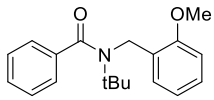
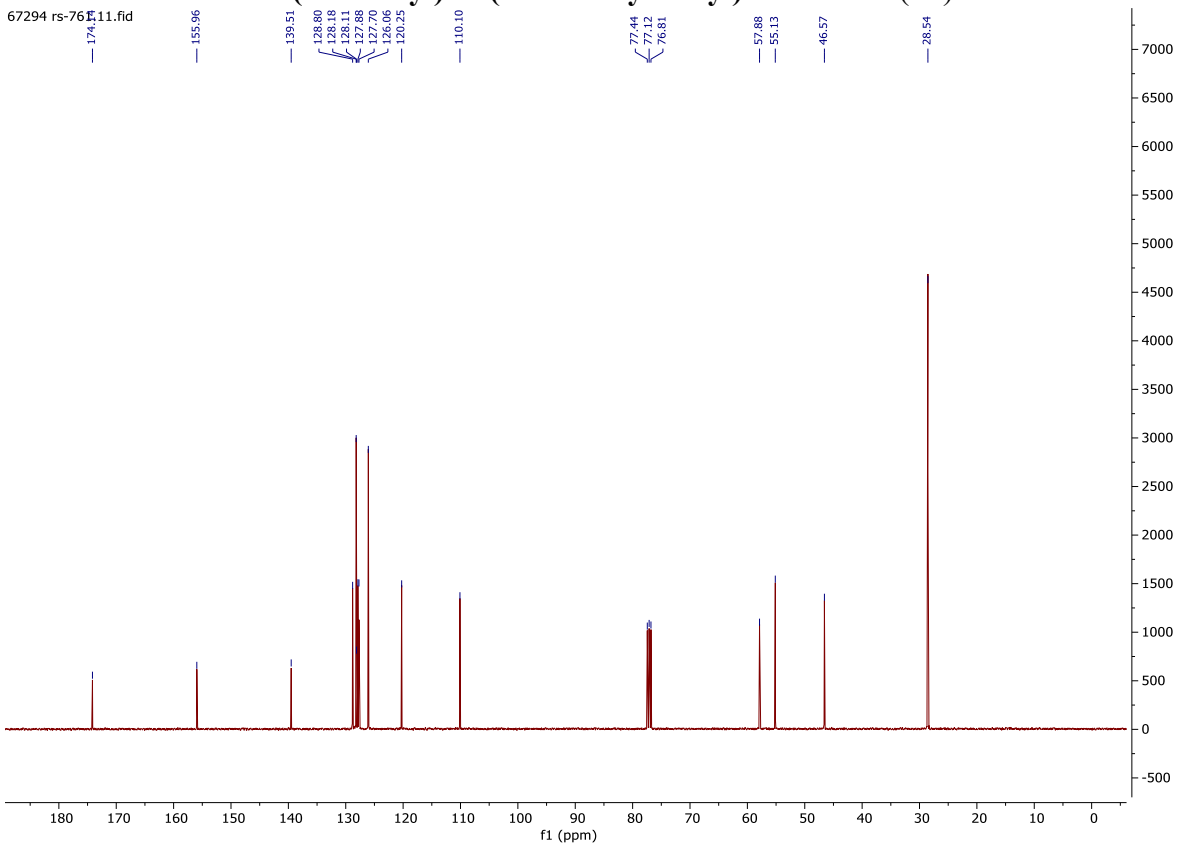


***N*-(tert-butyl)-*N*-(2-methoxybenzyl)benzamide (2b)**



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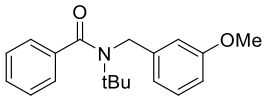
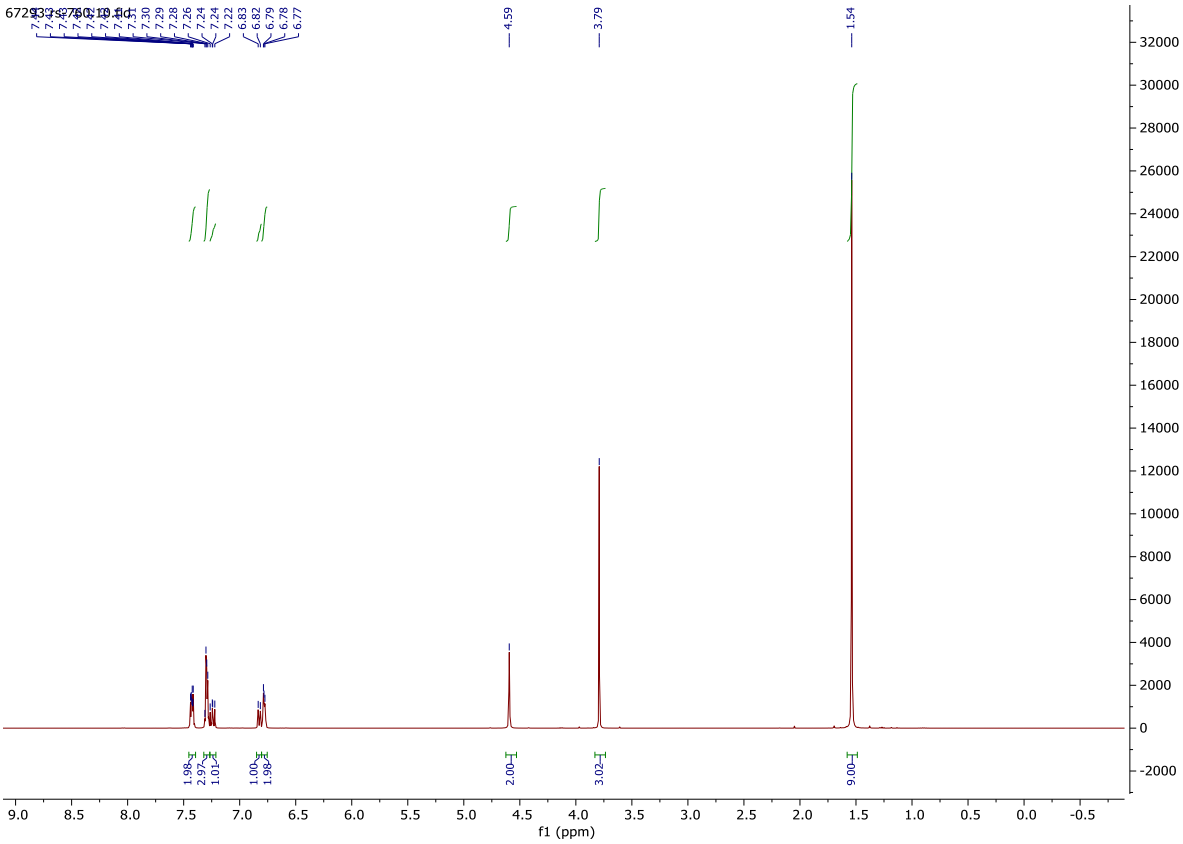


***N*-(tert-butyl)-*N*-(3-methoxybenzyl)benzamide (2c)**



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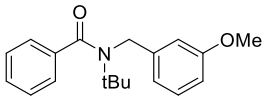
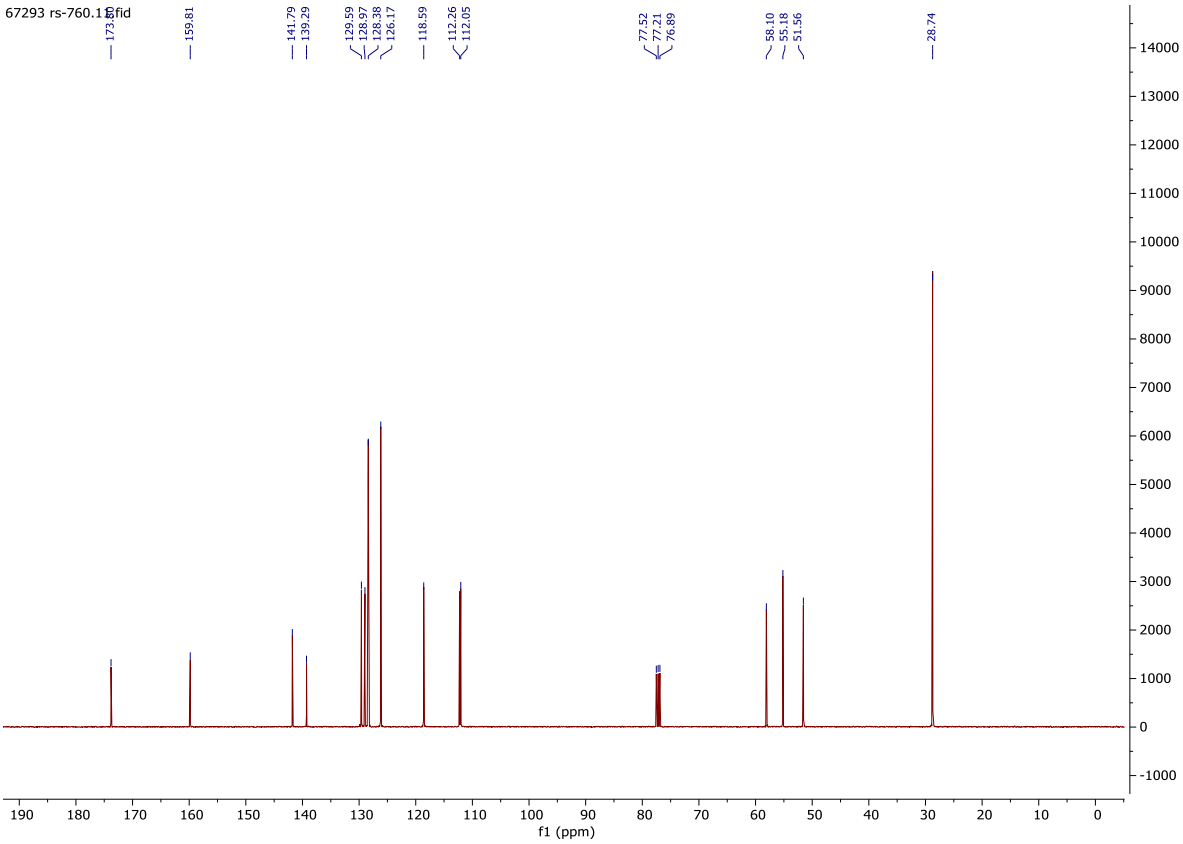


***N*-(tert-butyl)-*N*-(3-methoxybenzyl)benzamide (2c)**



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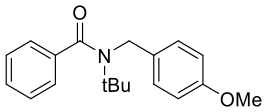
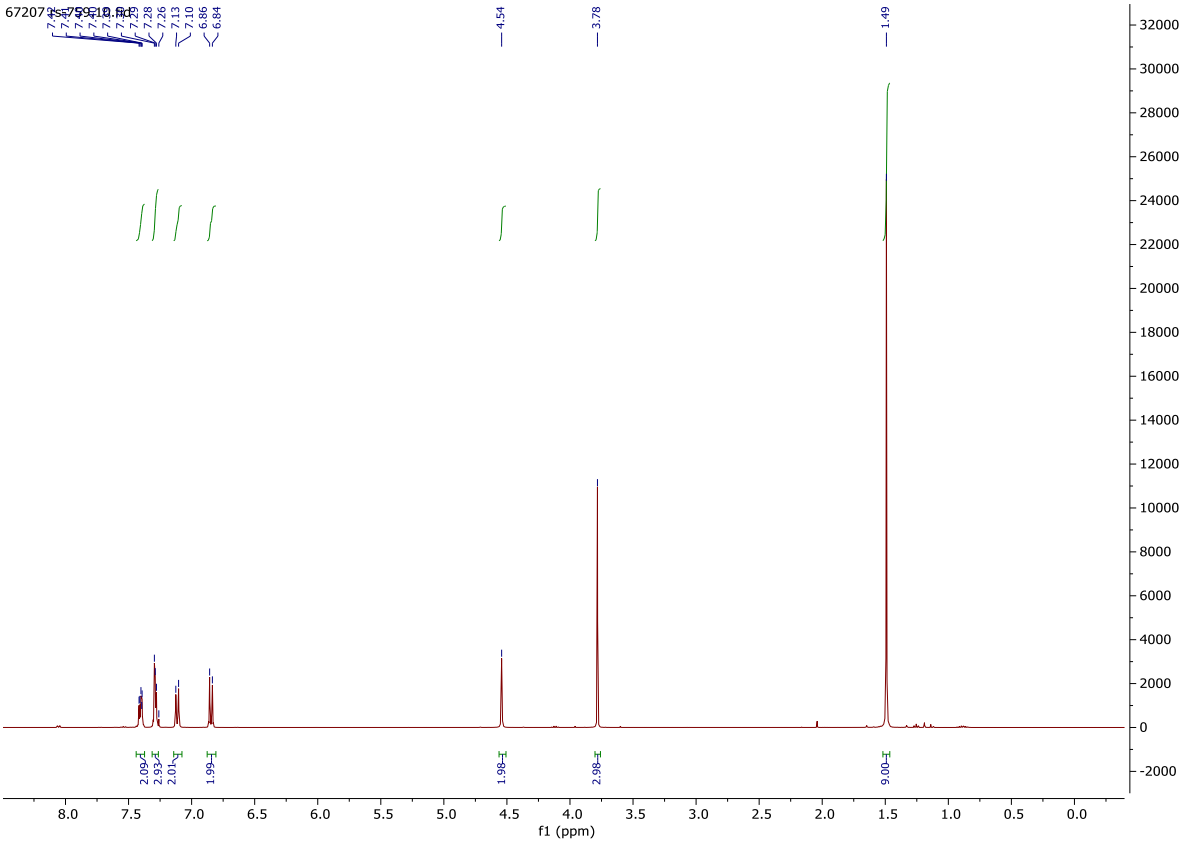
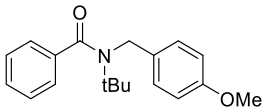


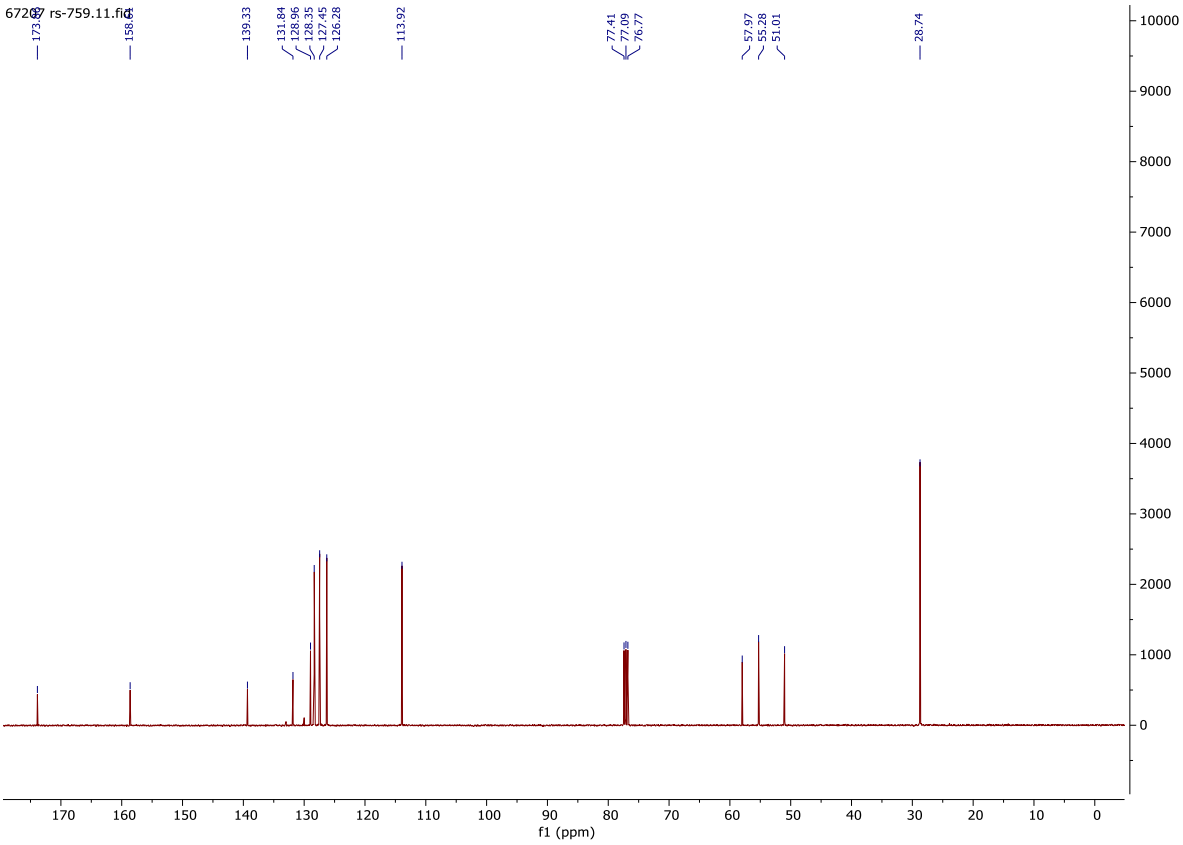
***N*-(*tert*-butyl)-*N*-(4-methoxybenzyl)benzamide (2d)**



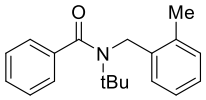
^{13}C NMR



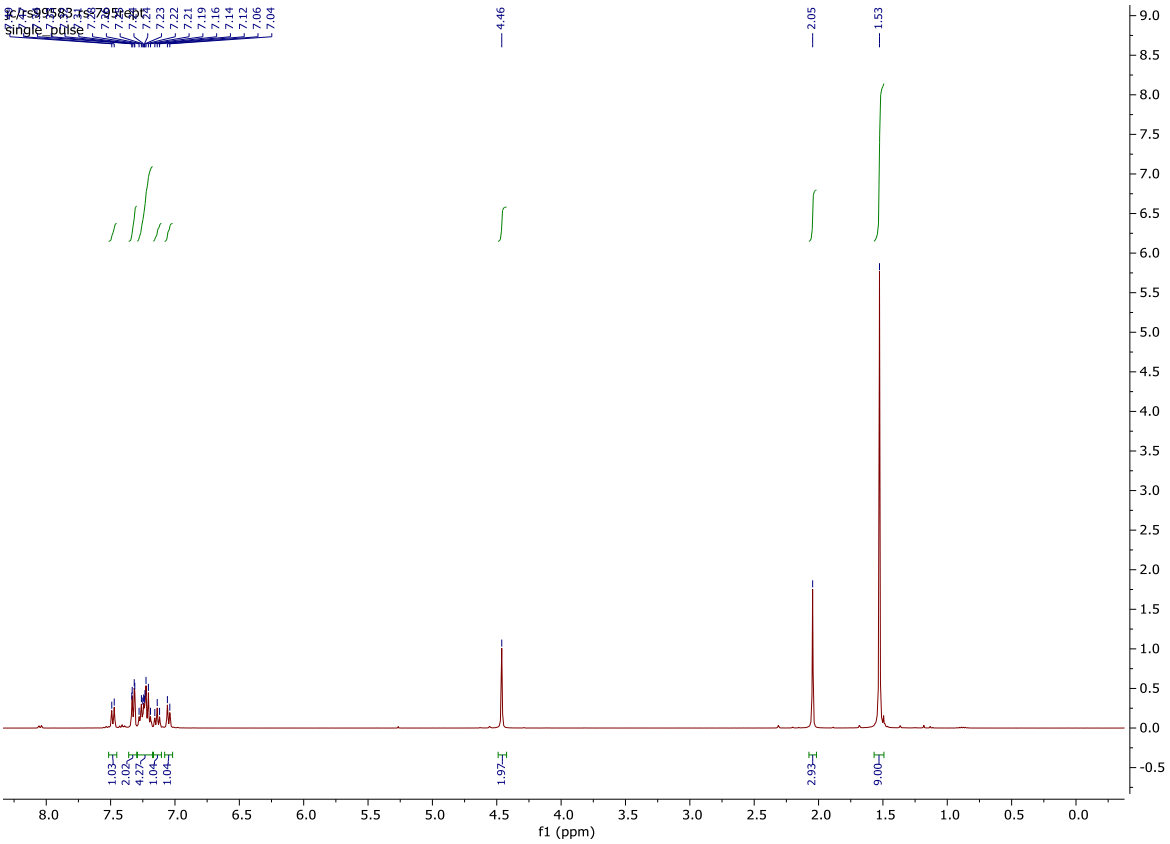
***N*-(*tert*-butyl)-*N*-(4-methoxybenzyl)benzamide (2d)**



^{1}H NMR



***N*-(*tert*-butyl)-*N*-(2-methylbenzyl)benzamide (2e)**



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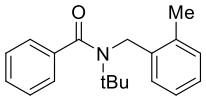
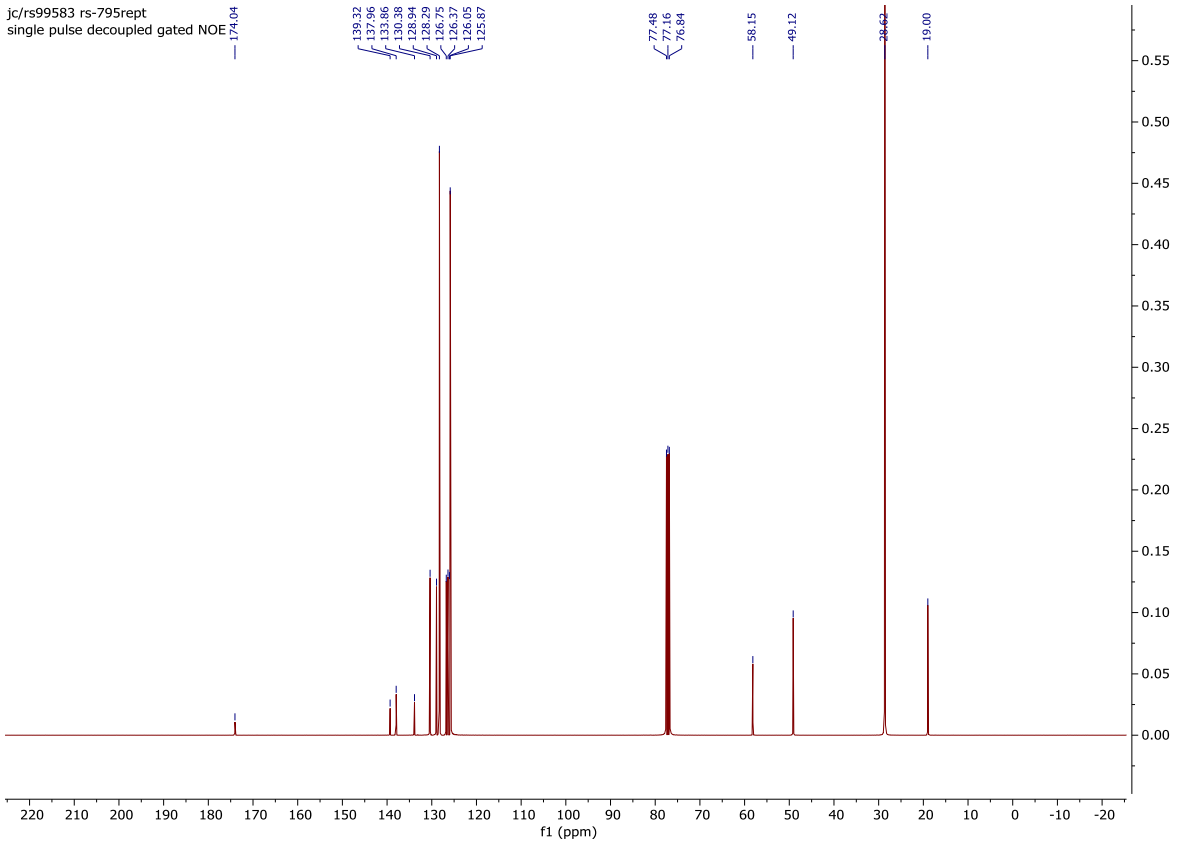
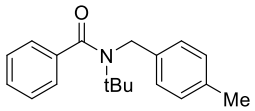


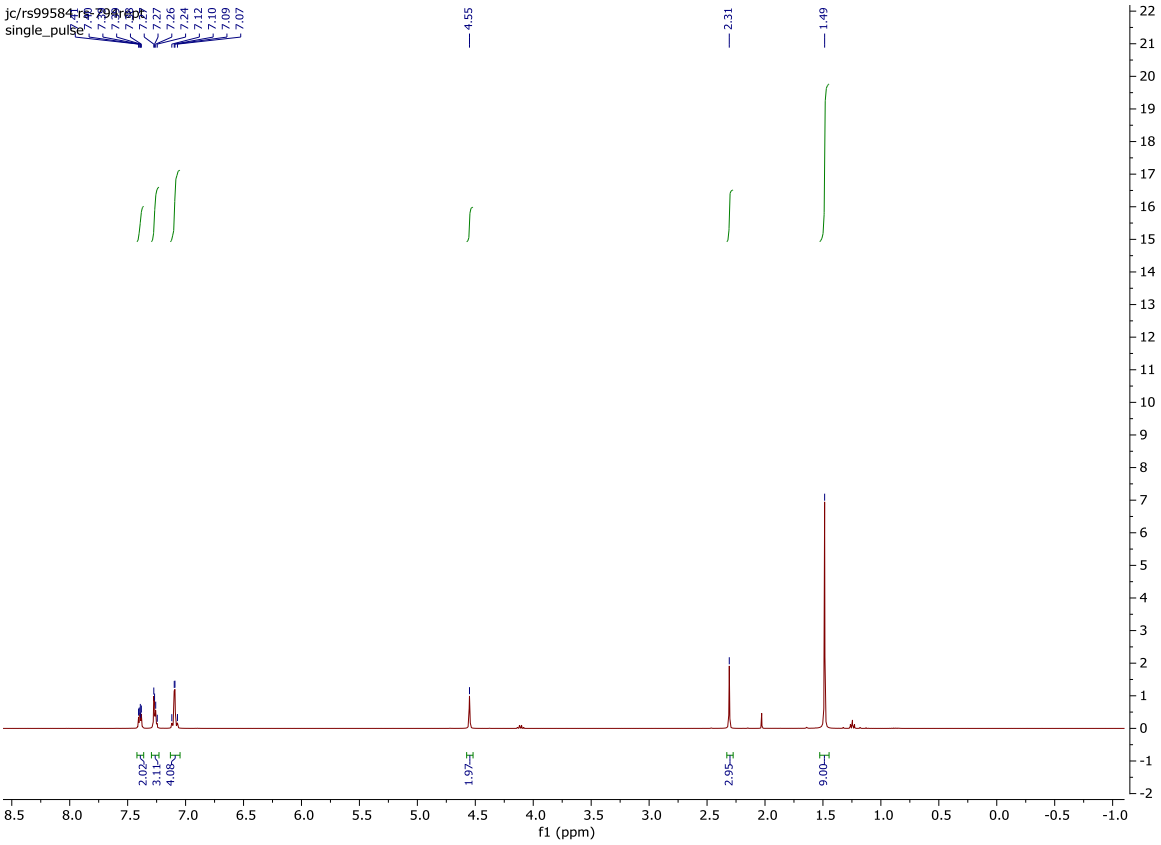
_N_-(_tert_-butyl)-_N_-(2-methylbenzyl)benzamide (2e)



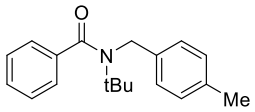
^{1}H NMR



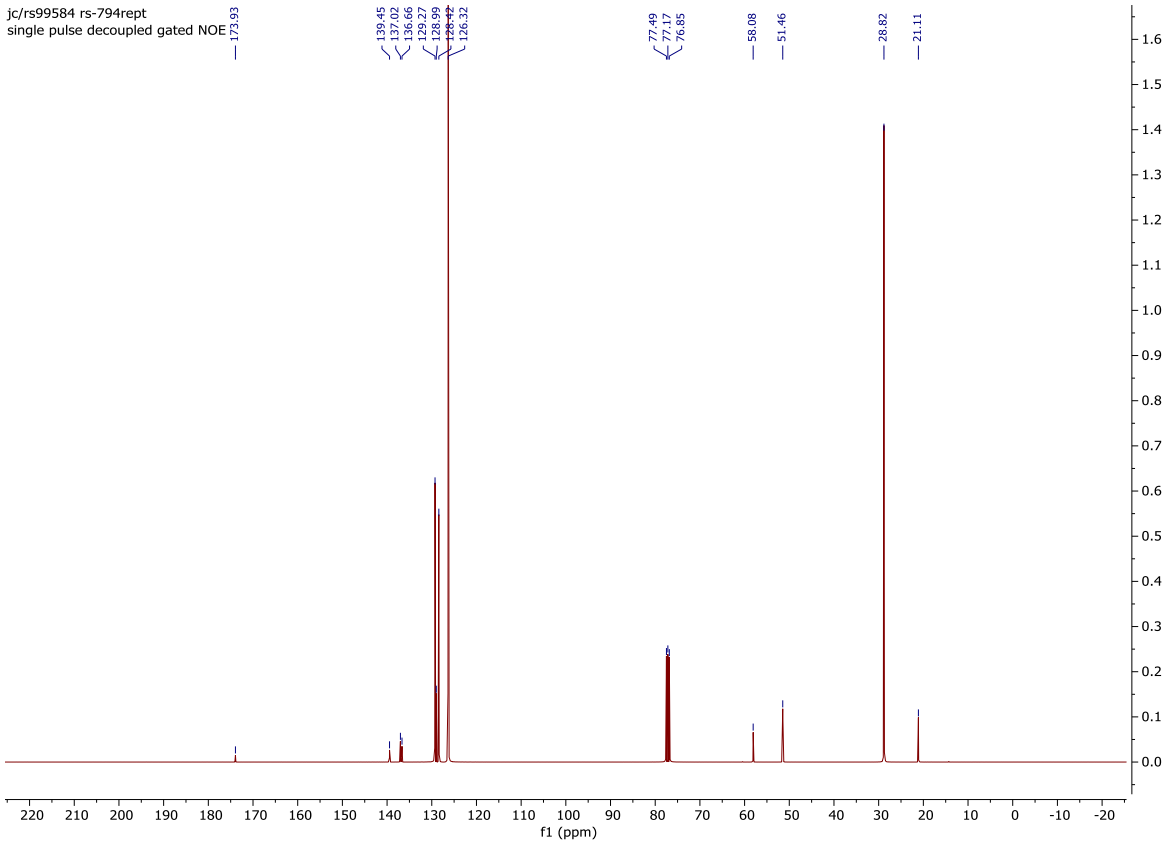
***N*-(tert-butyl)-*N*-(4-methylbenzyl)benzamide (2f)**



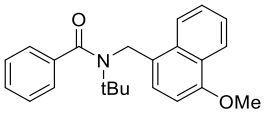
^{13}C NMR



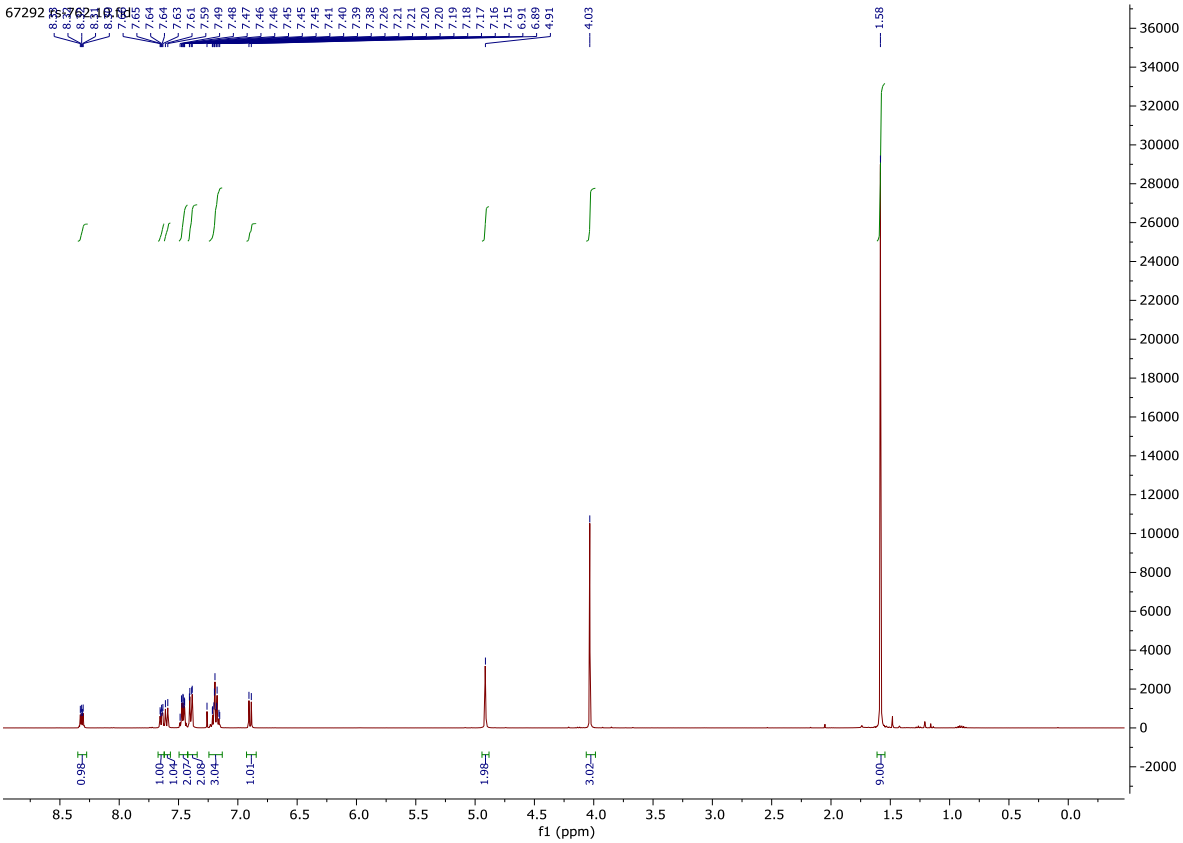
_N_-(tert-butyl)-_N_-(4-methylbenzyl)benzamide (2f)



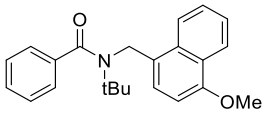
^{1}H NMR



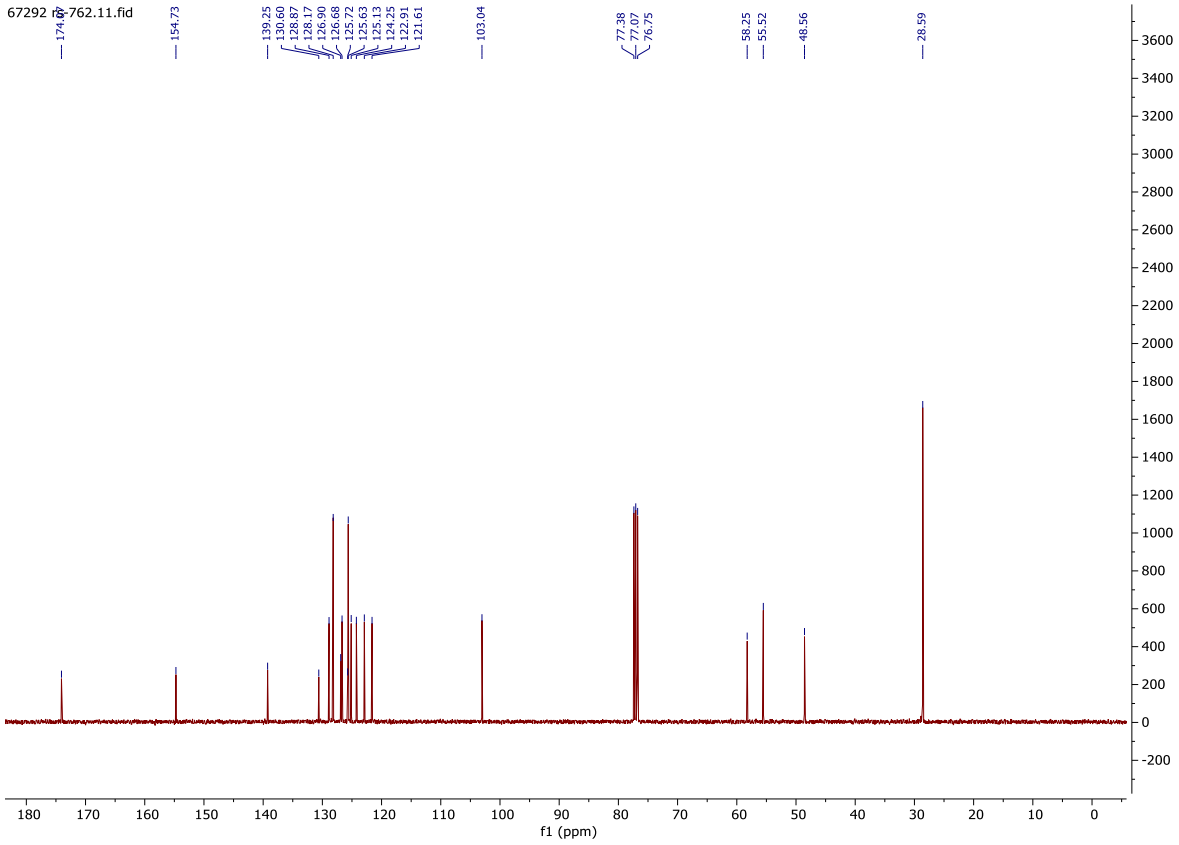
***N*-(tert-butyl)-*N*-((4-methoxynaphthalen-1-yl)methyl)benzamide (2g)**



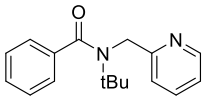
^{13}C NMR



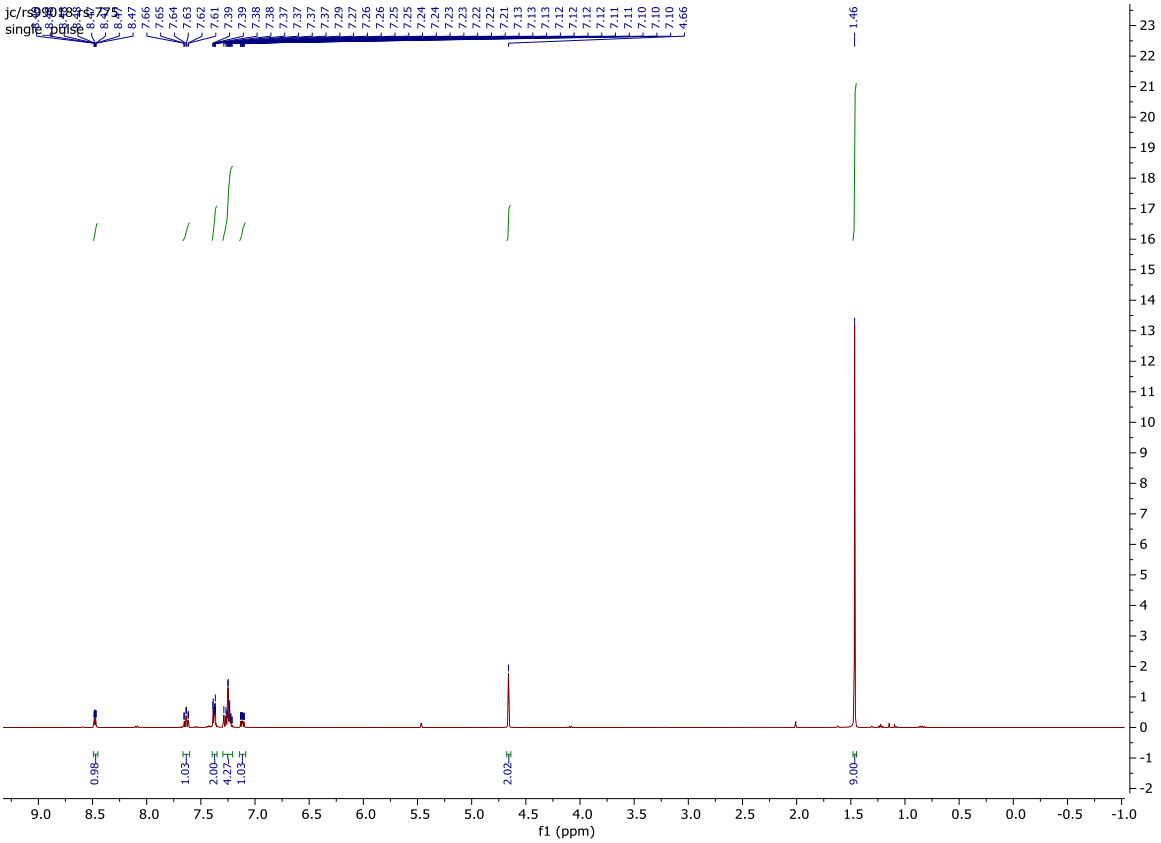
_N_-(tert-butyl)-_N_-((4-methoxynaphthalen-1-yl)methyl)benzamide (2g)



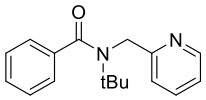
^{1}H NMR



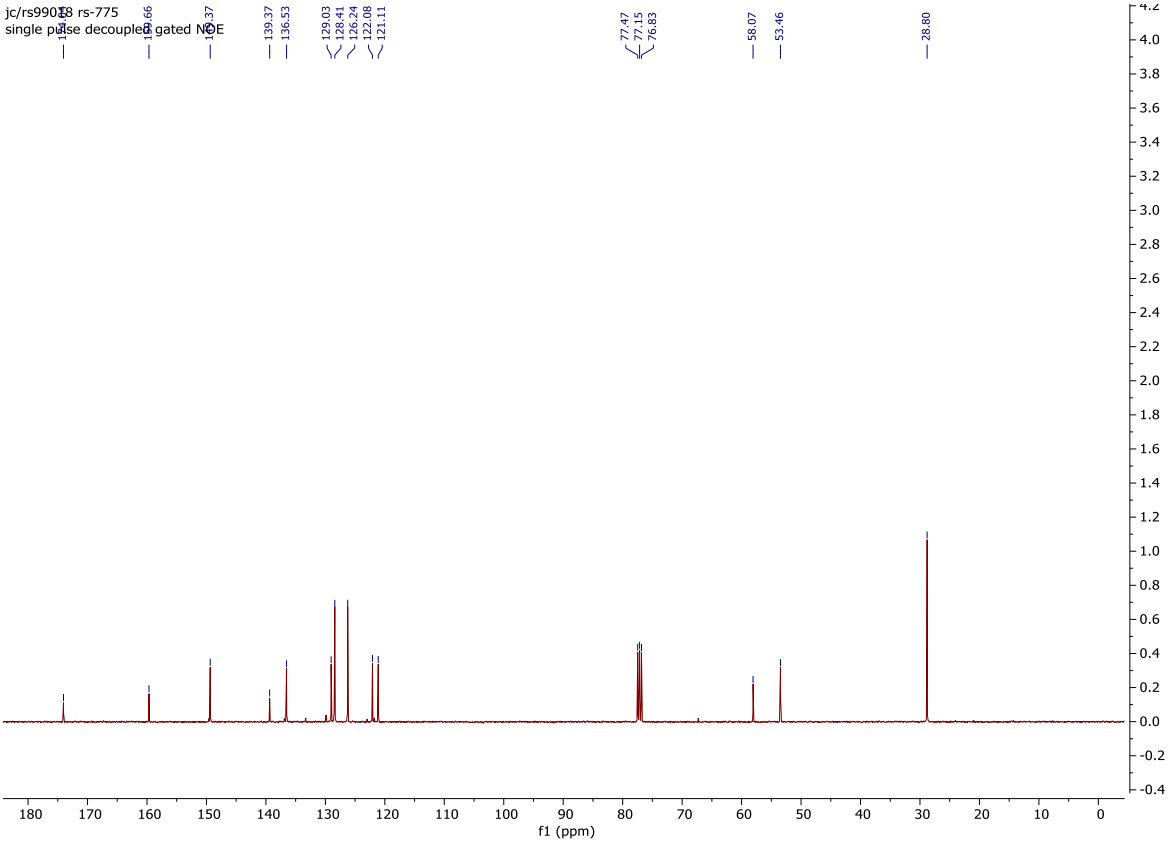
***N*-(tert-butyl)-*N*-(pyridin-2-ylmethyl)benzamide (2h)**



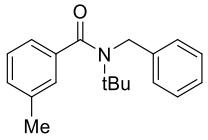
^{13}C NMR



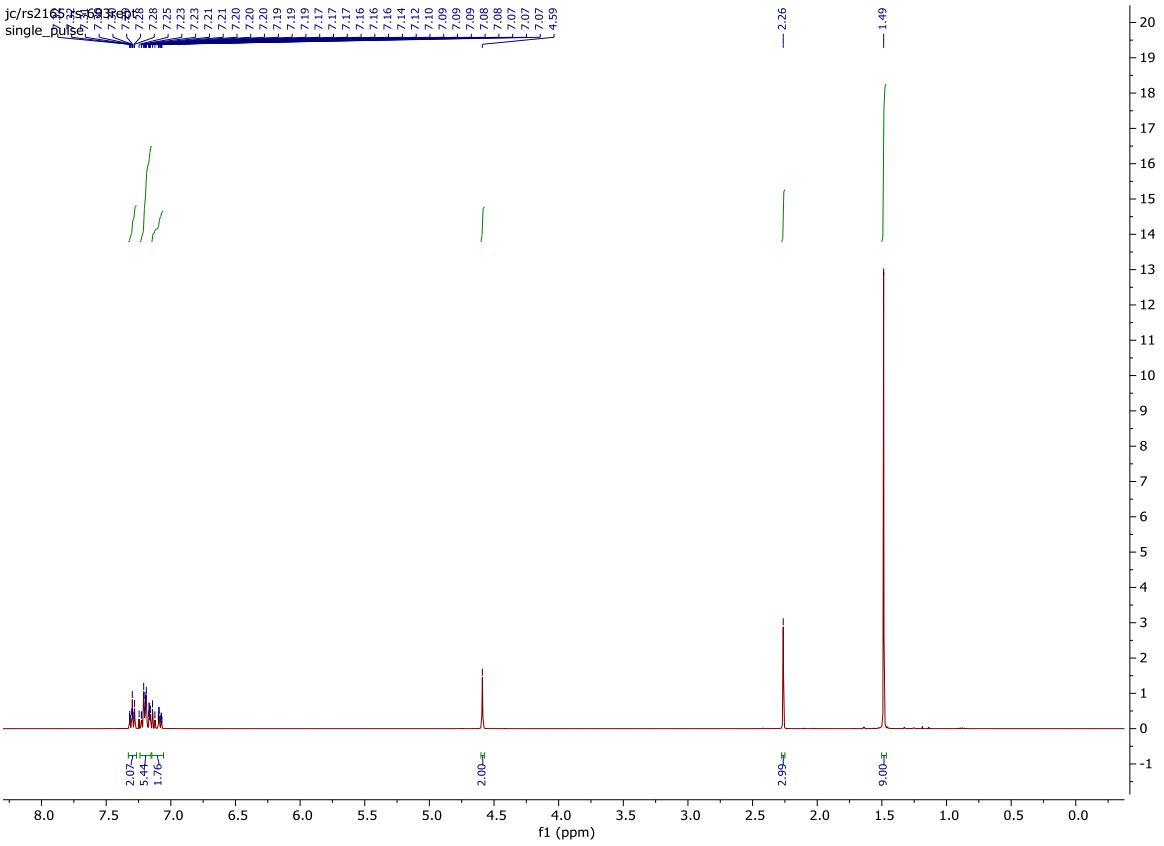
N-(tert-butyl)-*N*-(pyridin-2-ylmethyl)benzamide (2h)



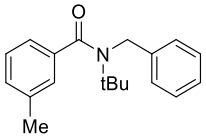
^{1}H NMR



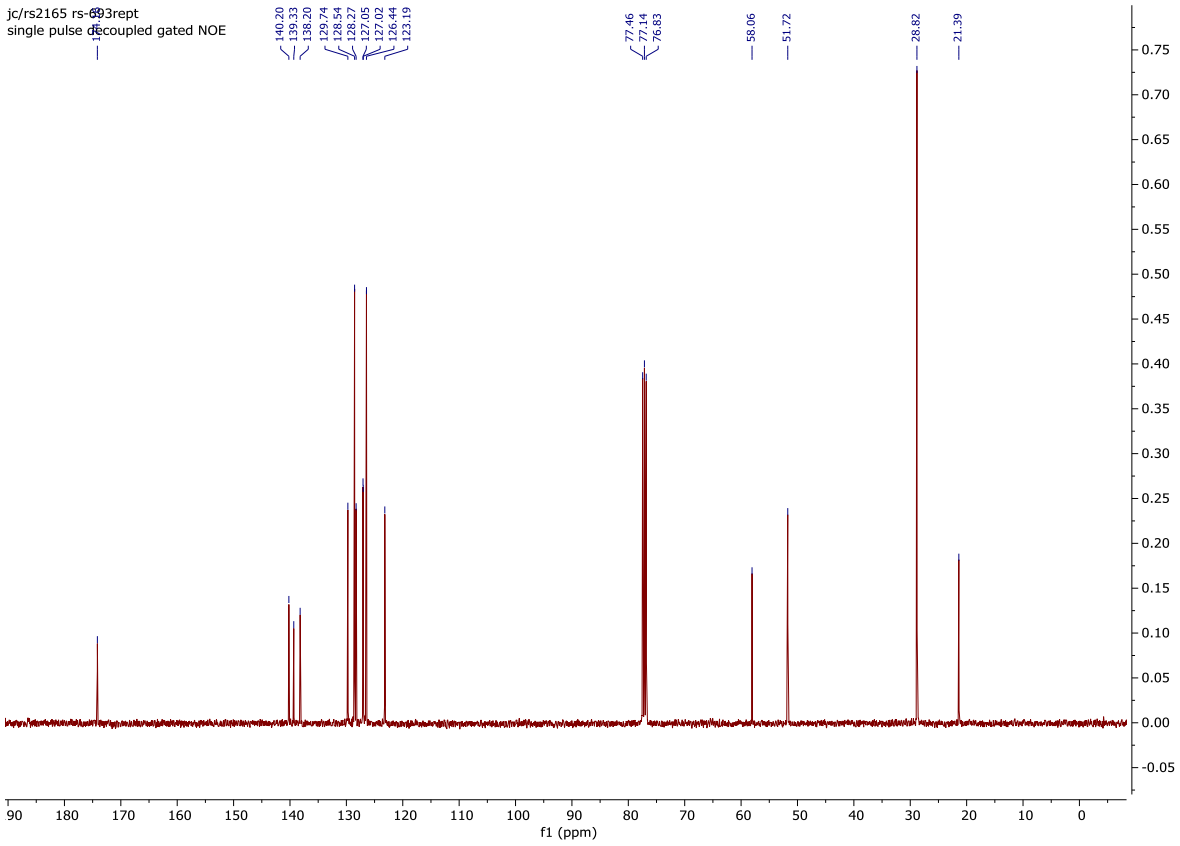
N-benzyl-*N*-(tert-butyl)-3-methylbenzamide (2i)



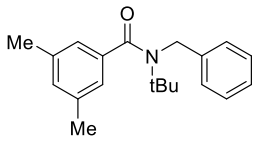
^{13}C NMR



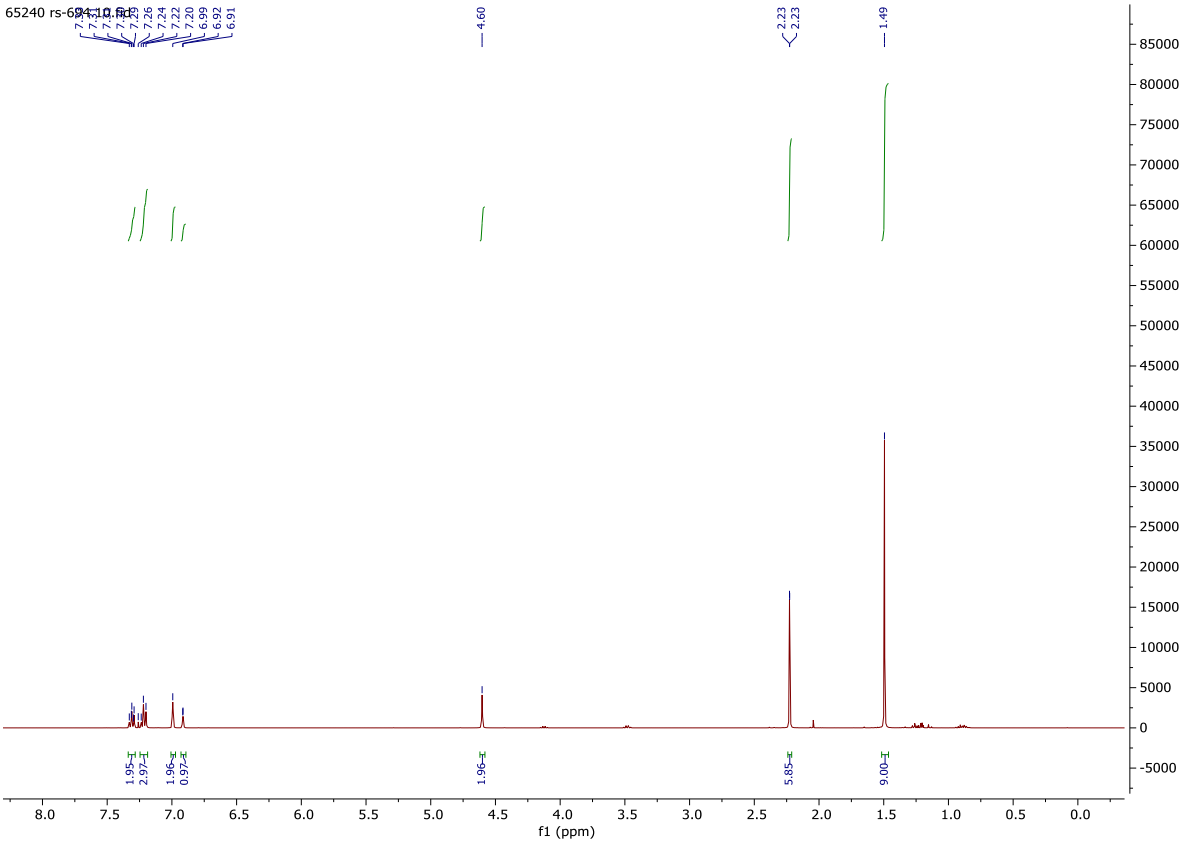
N-benzyl-*N*-(tert-butyl)-3-methylbenzamide (2i)



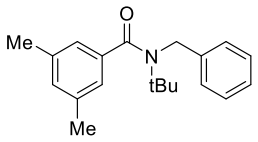
^{1}H NMR



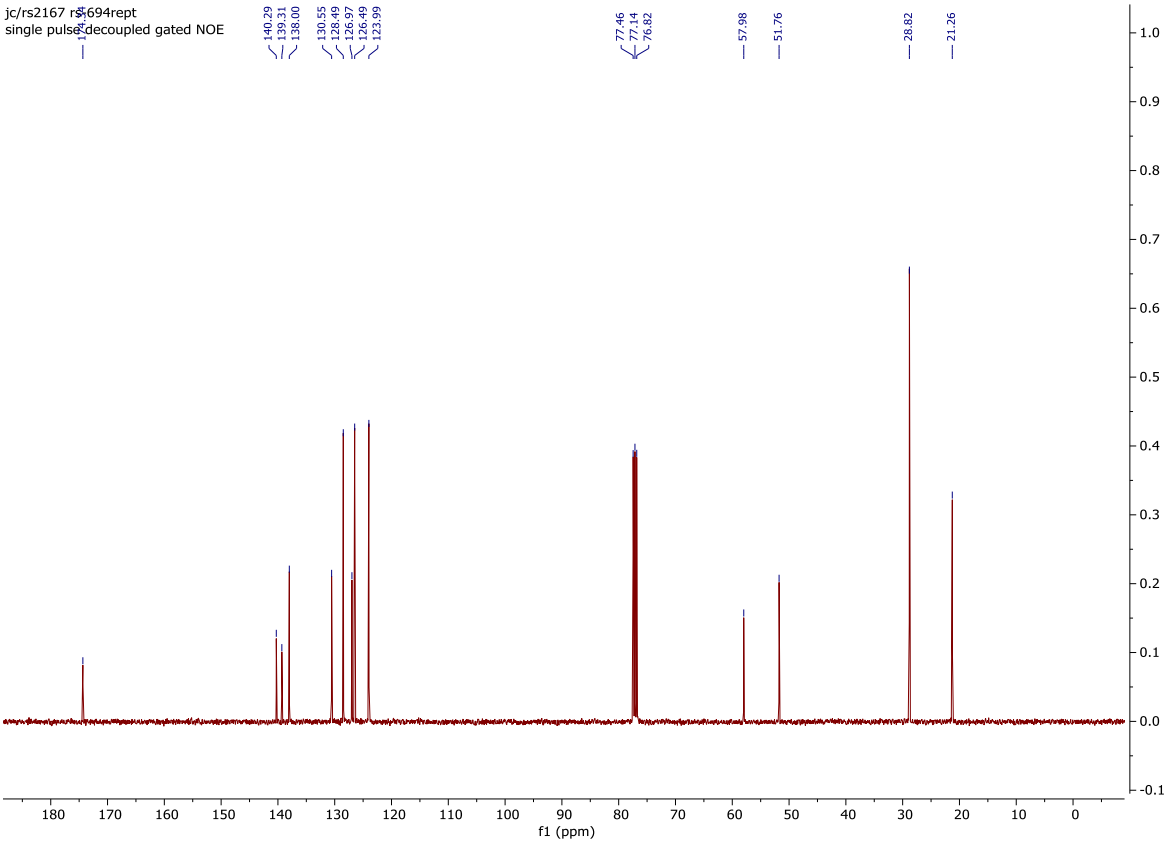
***N*-benzyl-*N*-(tert-butyl)-3,5-dimethylbenzamide (2j)**



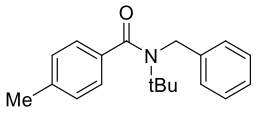
^{13}C NMR



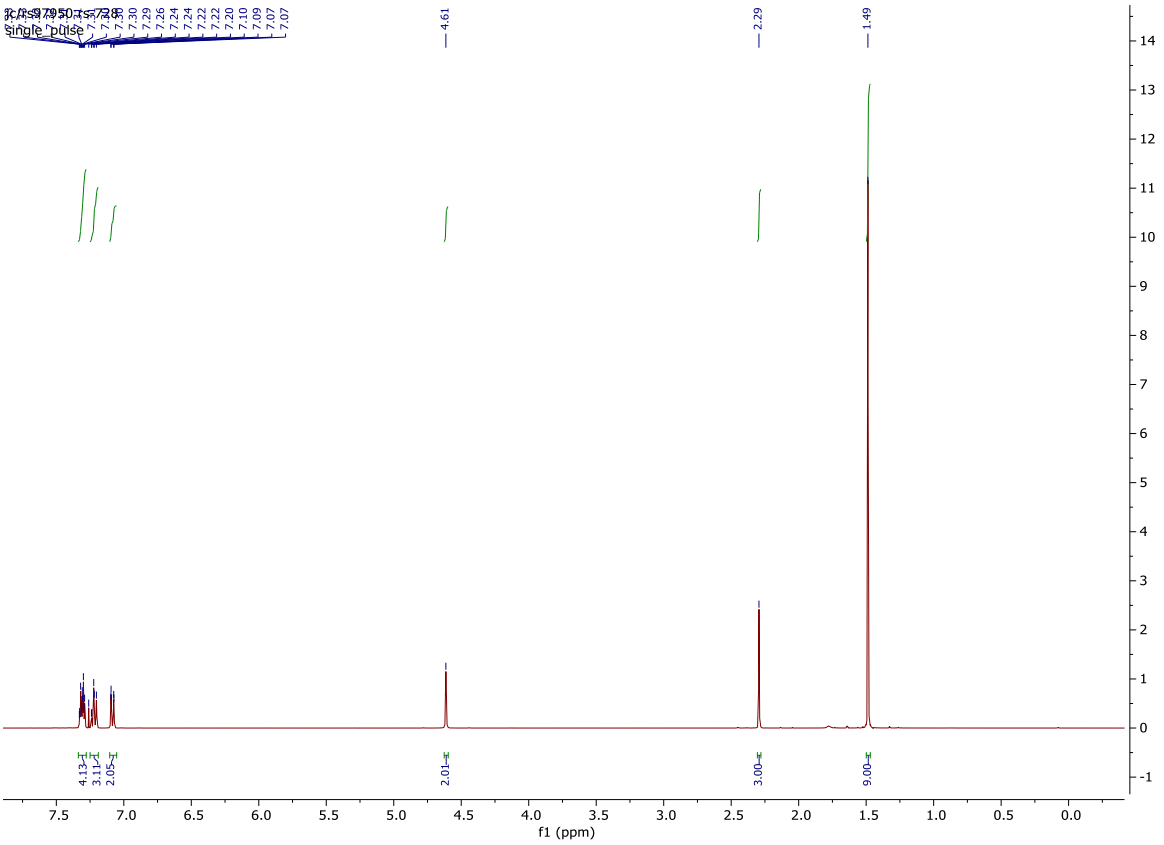
***N*-benzyl-*N*-(tert-butyl)-3,5-dimethylbenzamide (2j)**



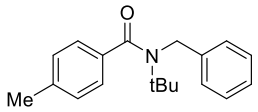
^{1}H NMR



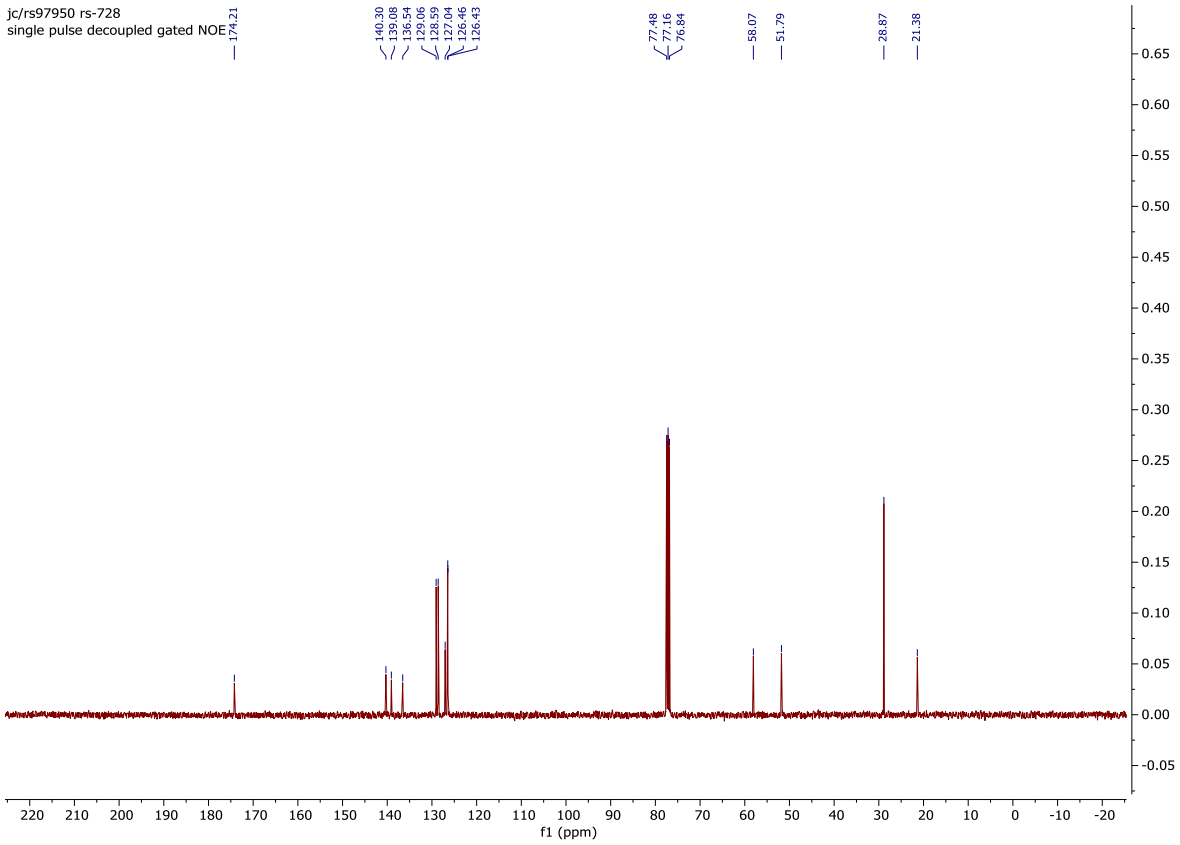
***N*-benzyl-*N*-(tert-butyl)-4-methylbenzamide (2k)**



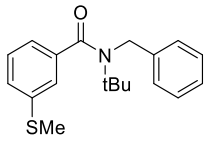
^{13}C NMR



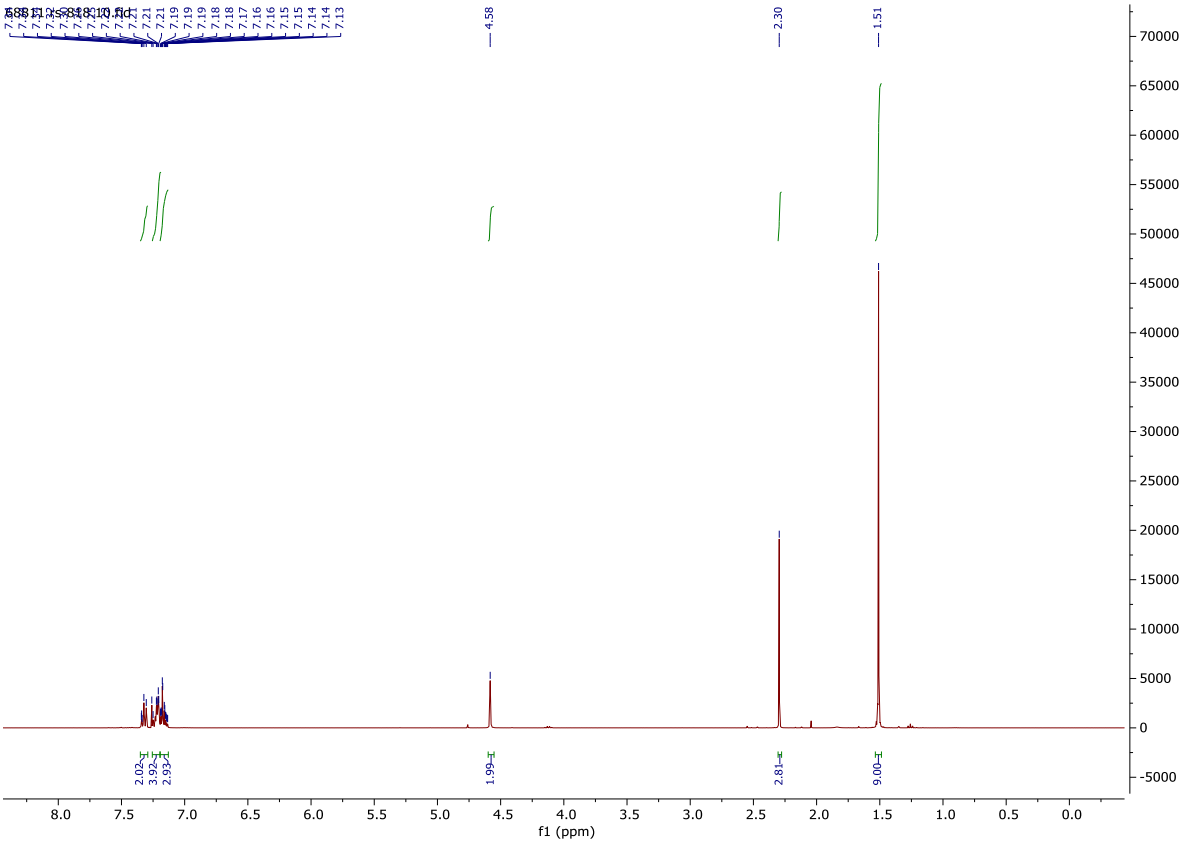
_N_-benzyl-_N_-(tert-butyl)-4-methylbenzamide (2k)



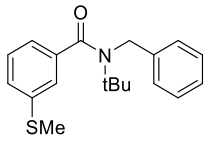
^{1}H NMR



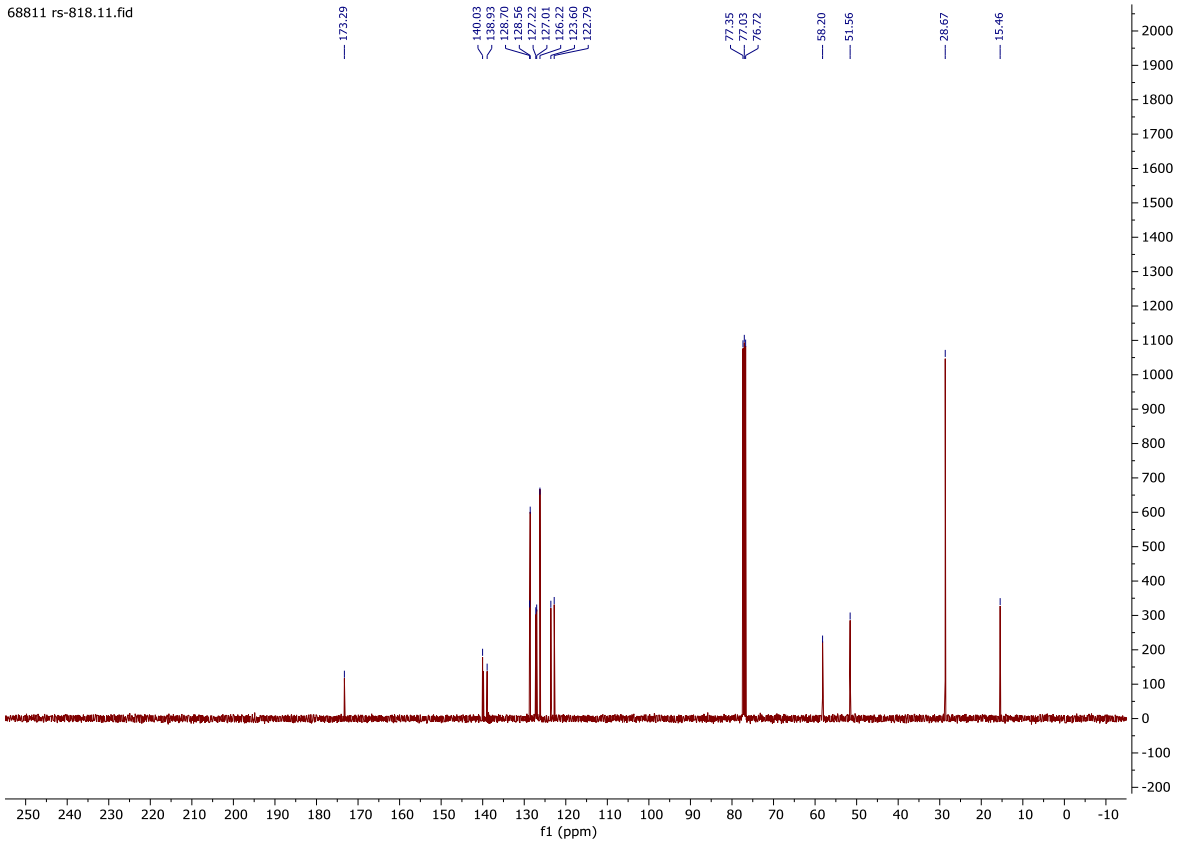
***N*-benzyl-*N*-(*tert*-butyl)-3-(methylthio)benzamide (2l)**



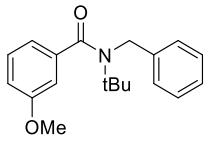
^{13}C NMR



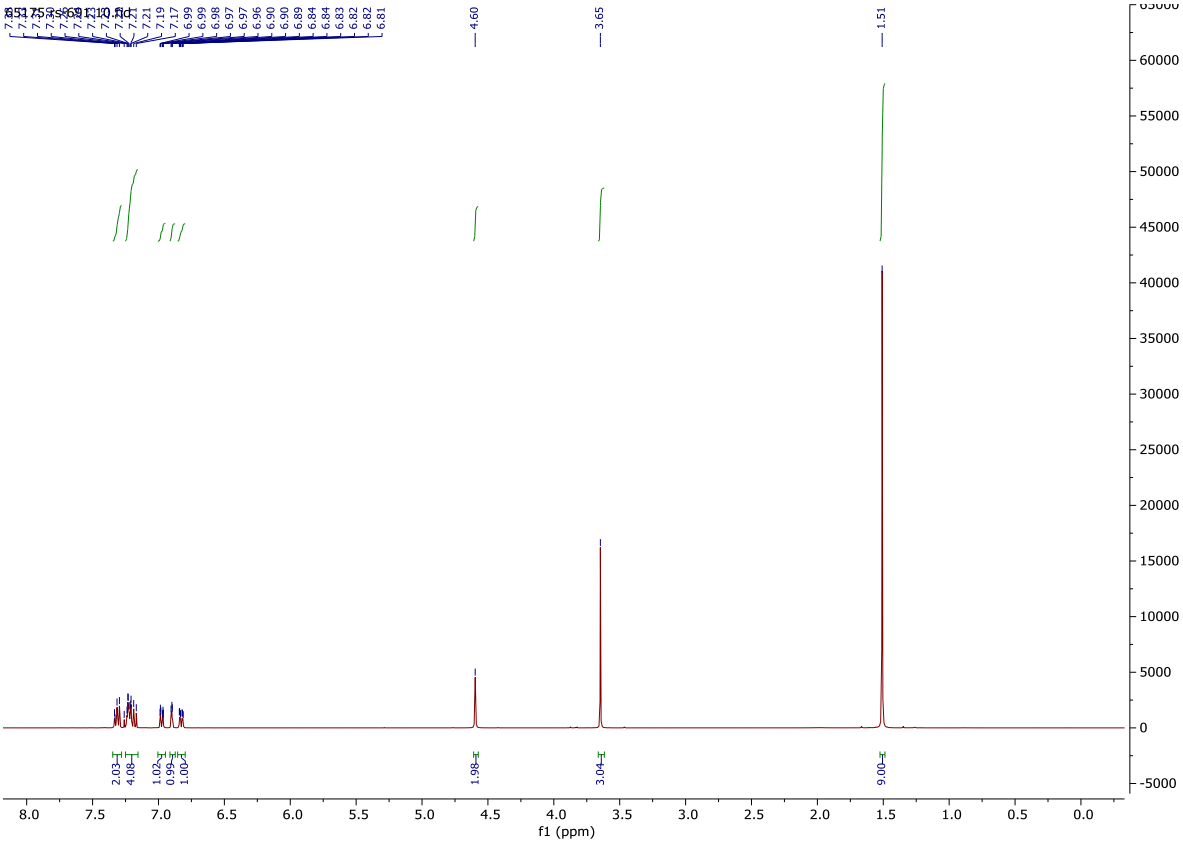
***N*-benzyl-*N*-(*tert*-butyl)-3-(methylthio)benzamide (2l)**



^{1}H NMR



***N*-benzyl-*N*-(tert-butyl)-3-methoxybenzamide (2m)**



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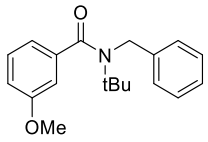
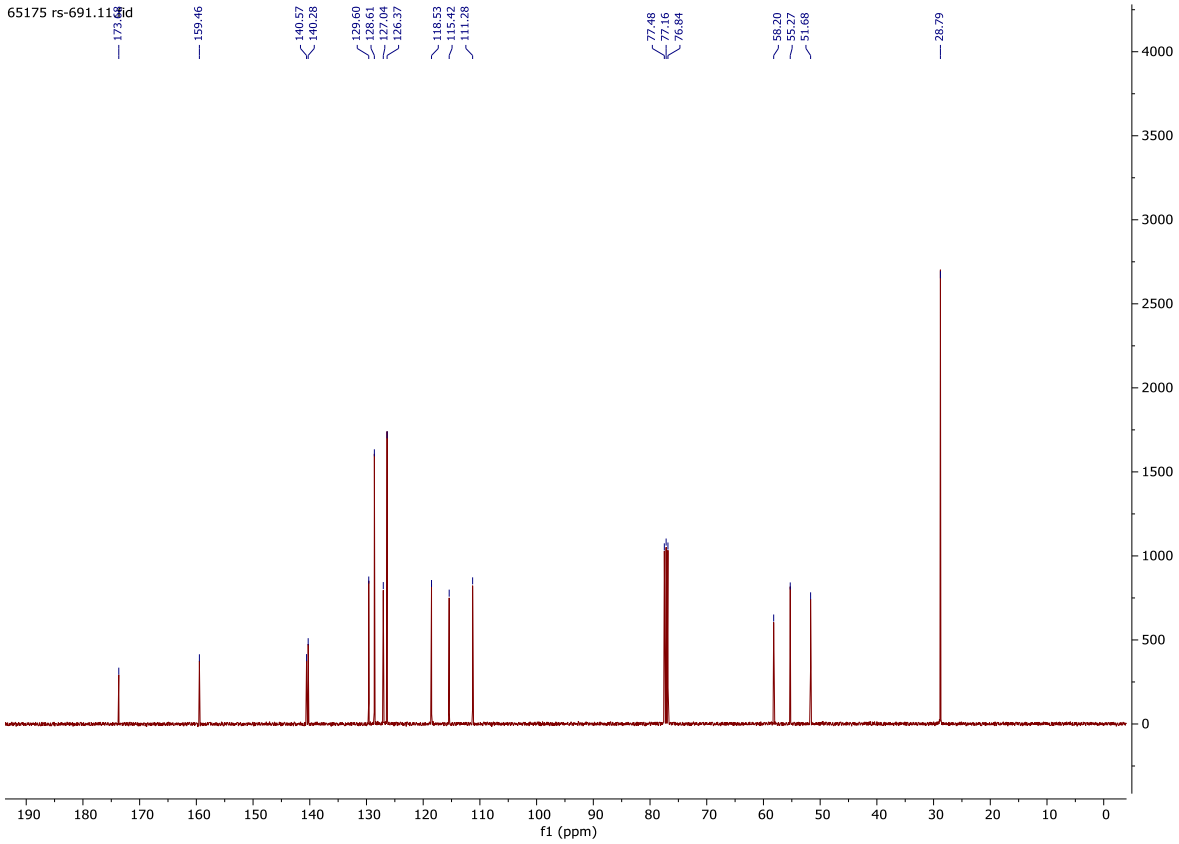
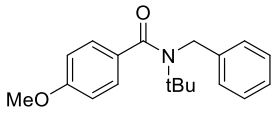


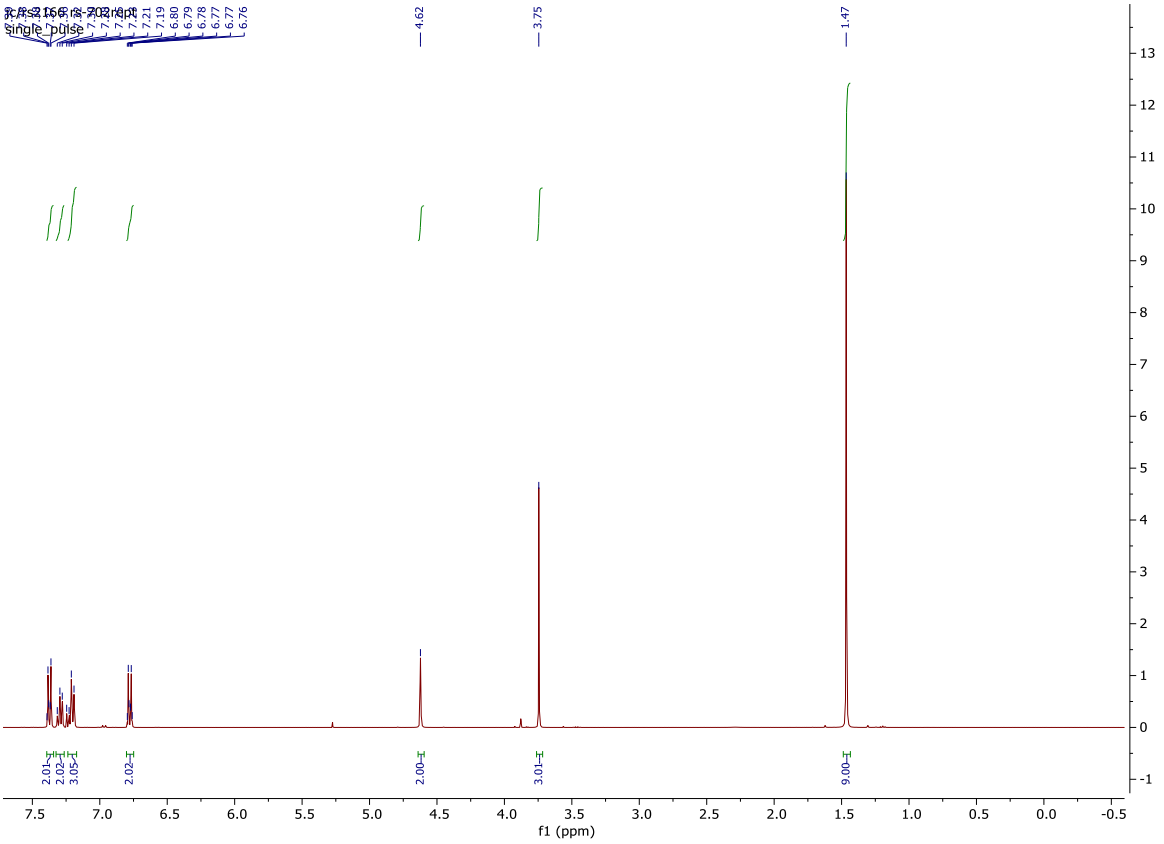
***N*-benzyl-*N*-(tert-butyl)-3-methoxybenzamide (2m)**



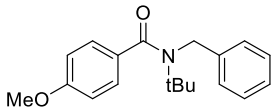
^{1}H NMR



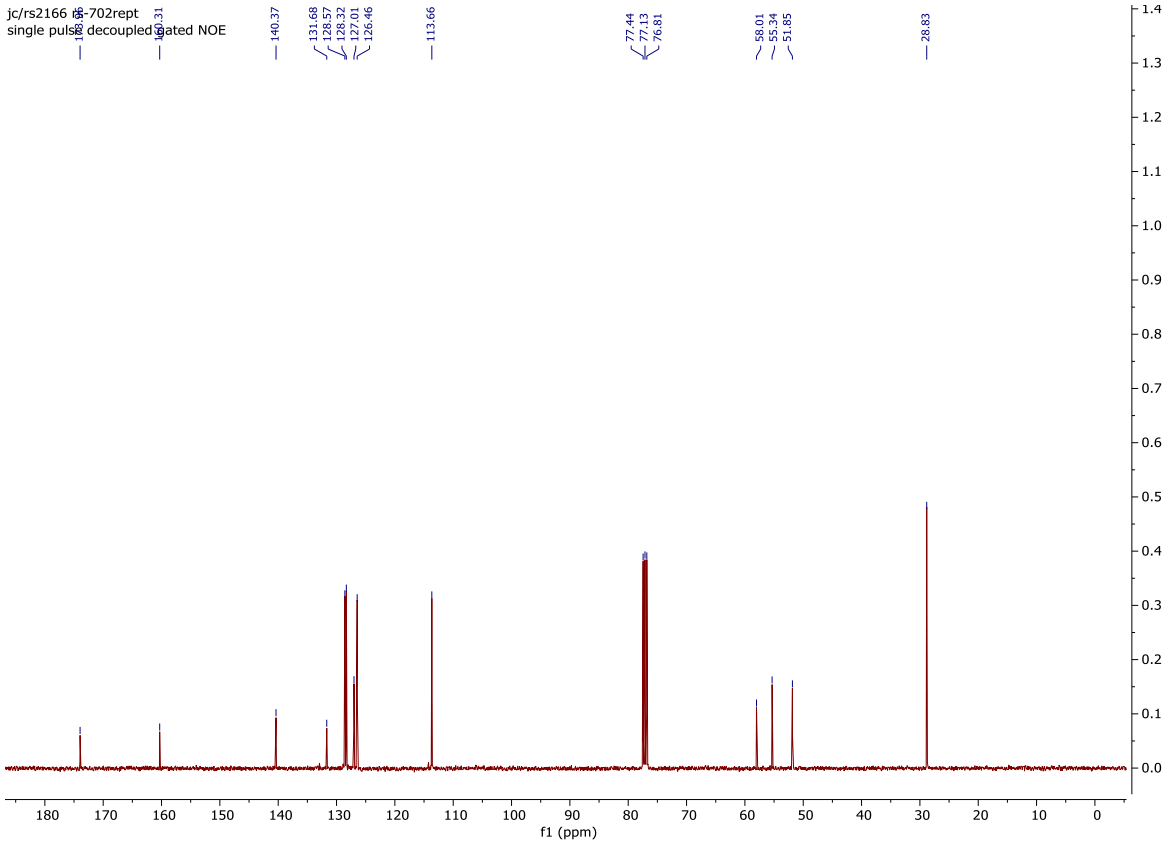
***N*-benzyl-*N*-(tert-butyl)-4-methoxybenzamide (2n)**



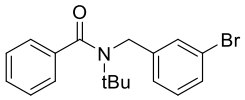
^{13}C NMR



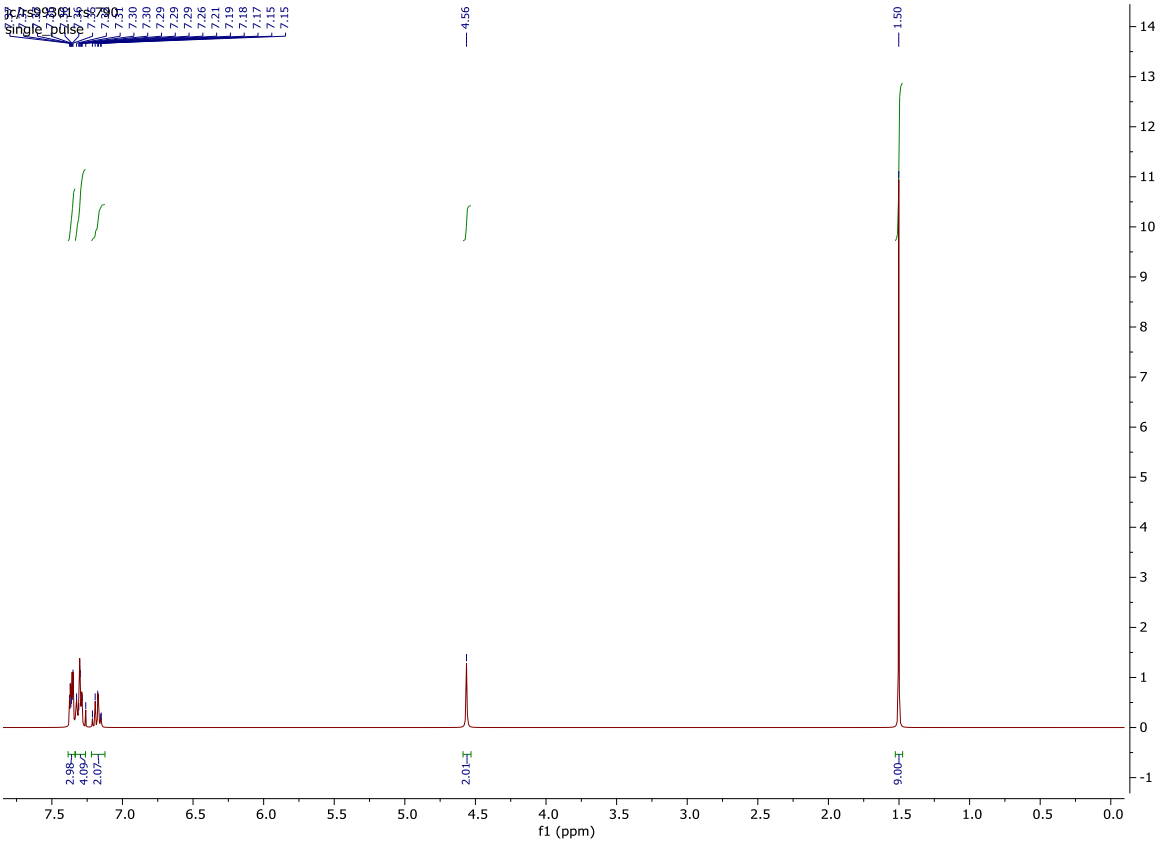
_N_-benzyl-_N_-(tert-butyl)-4-methoxybenzamide (2n)



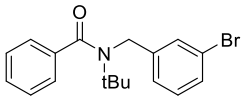
^{1}H NMR



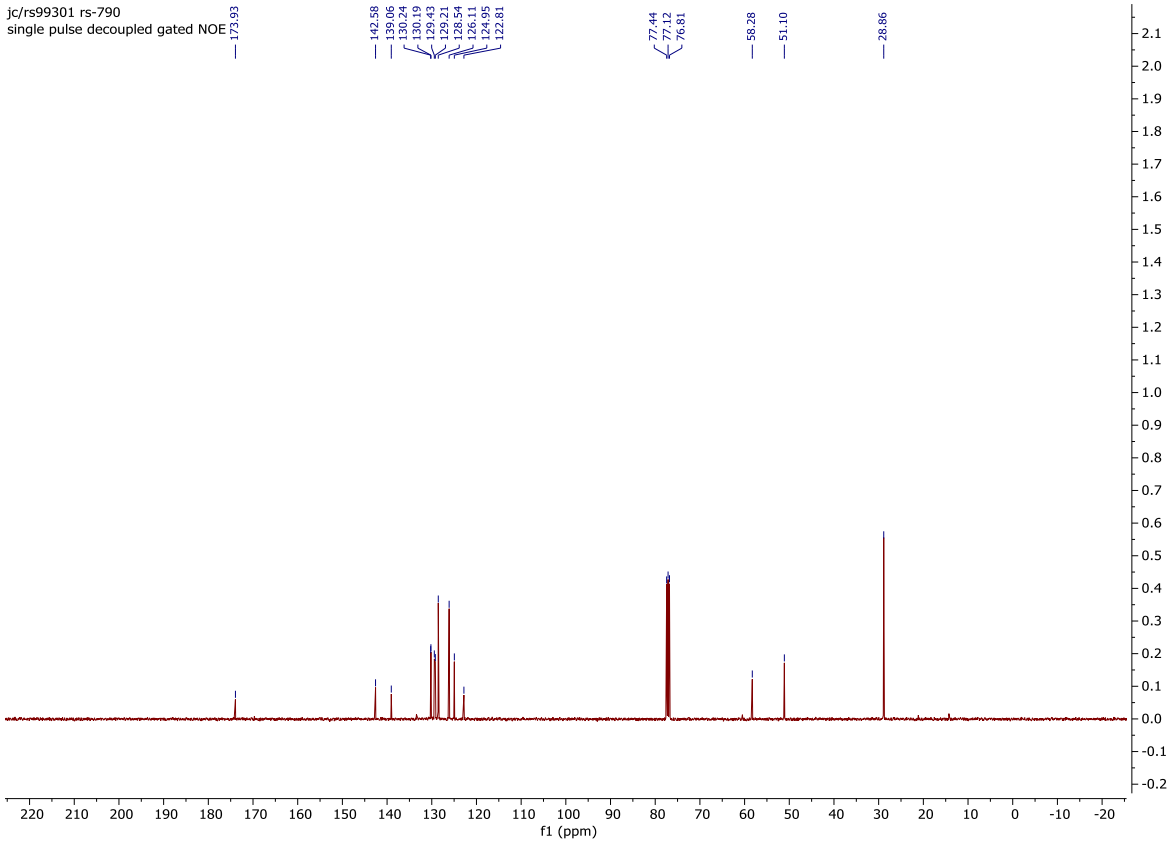
_N_-(3-bromobenzyl)-_N_-(tert-butyl)benzamide (2o)



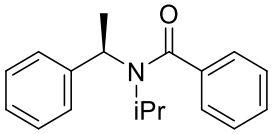
^{13}C NMR



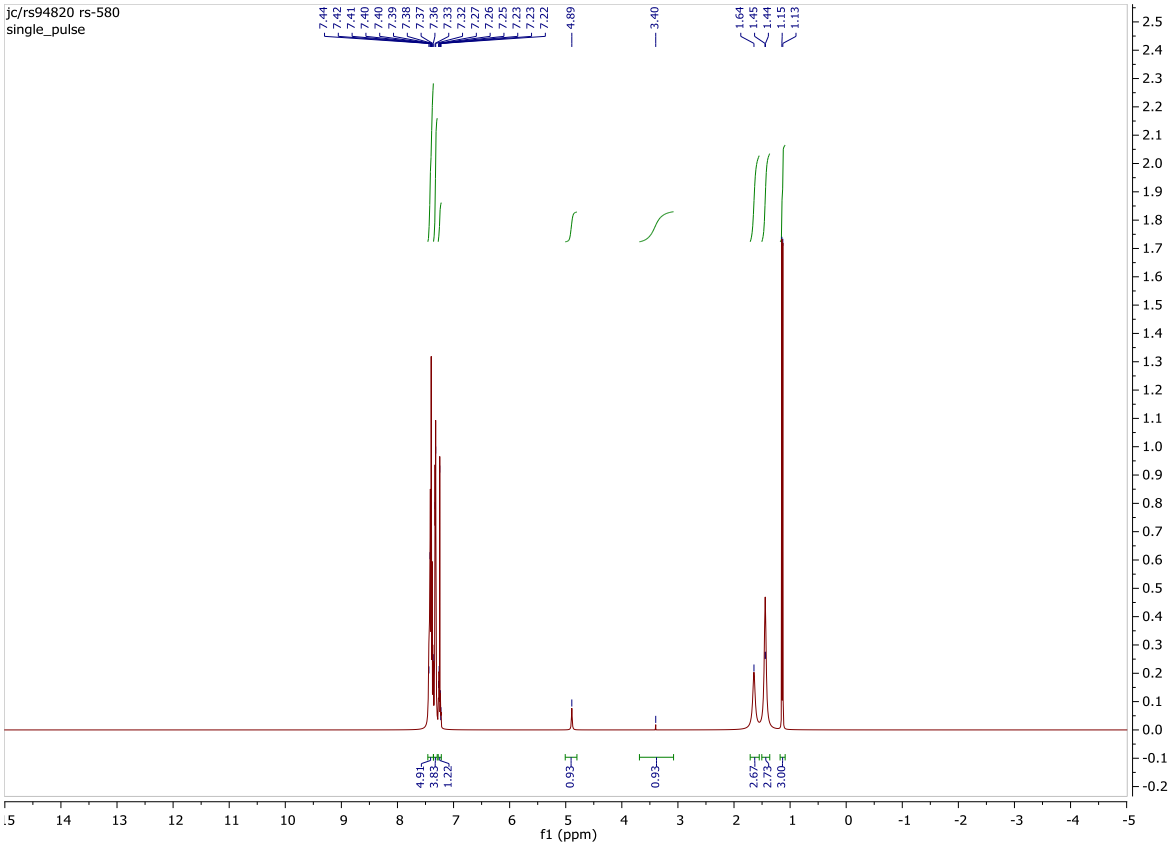
N-(3-bromobenzyl)-*N*-(tert-butyl)benzamide (2o)



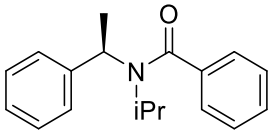
^{1}H NMR



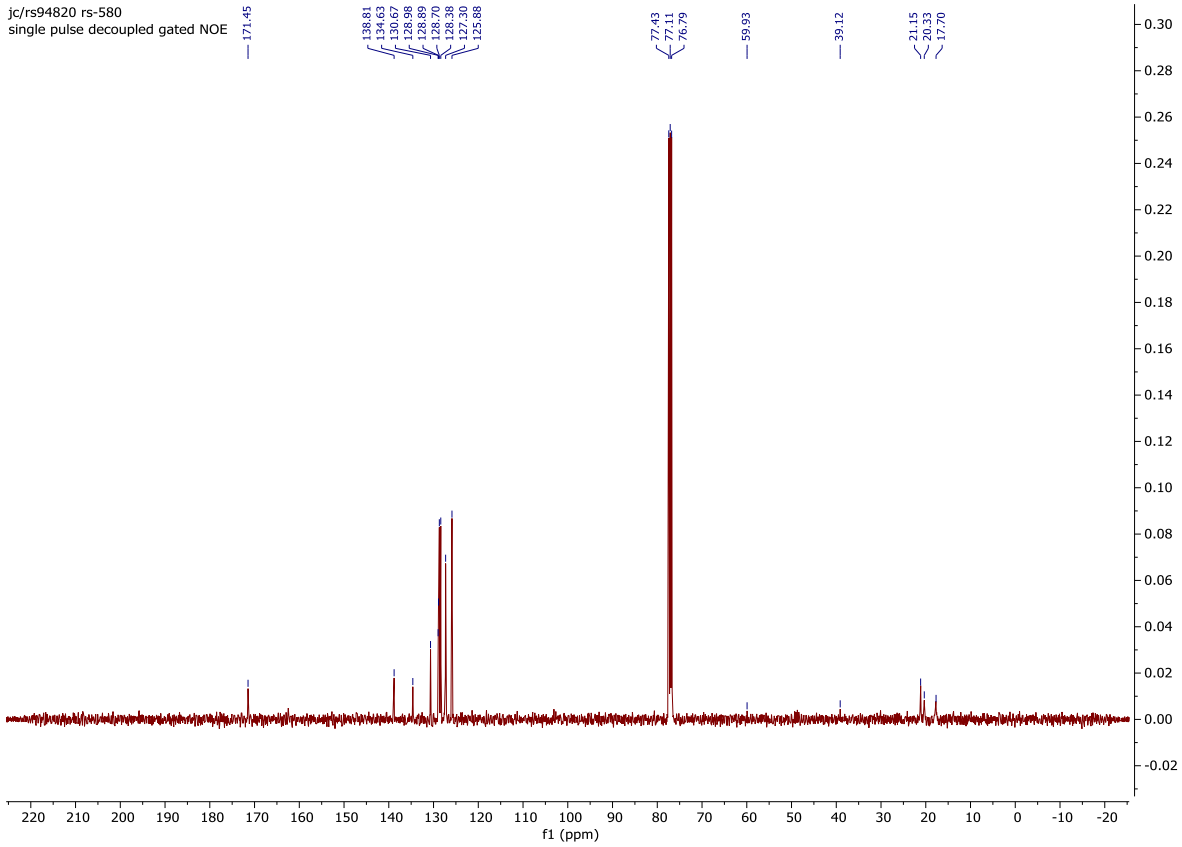
(R)-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10a)



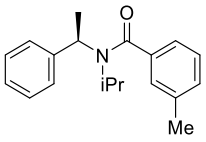
^{13}C NMR



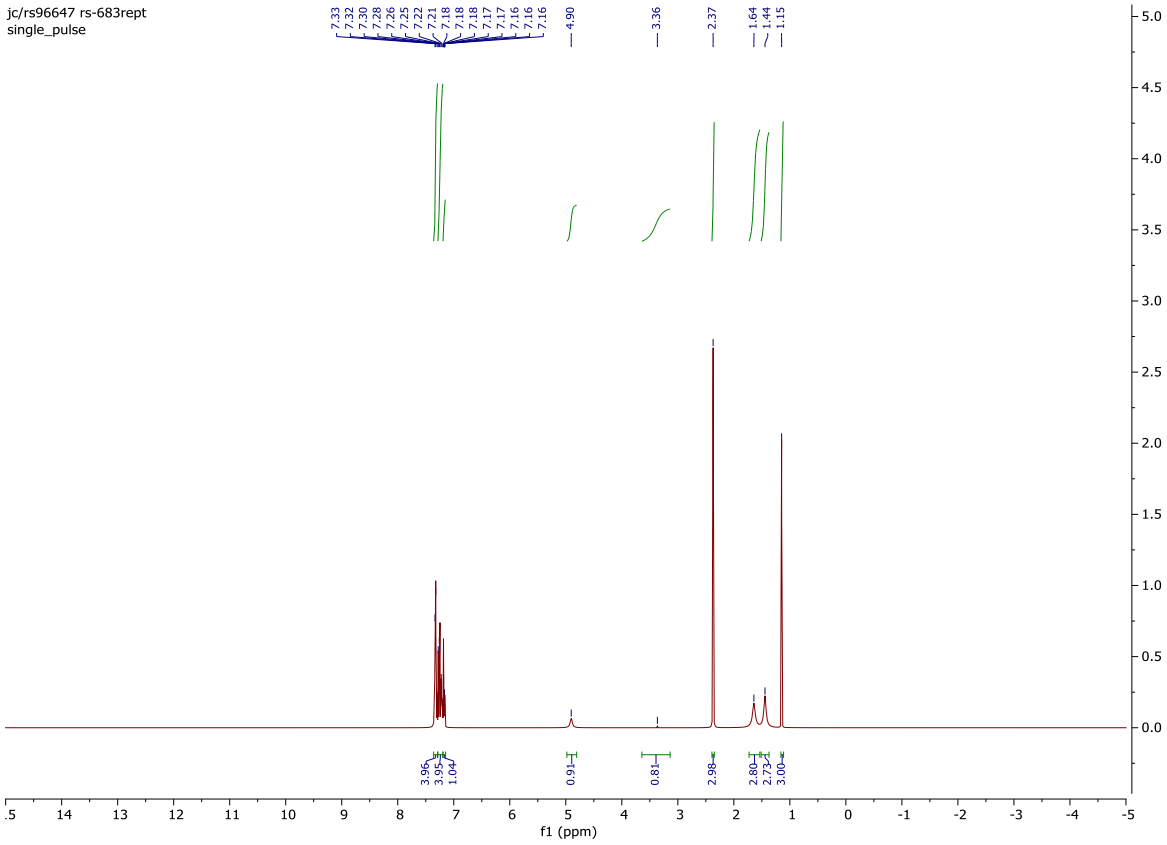
(R)-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10a)



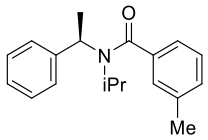
^{1}H NMR



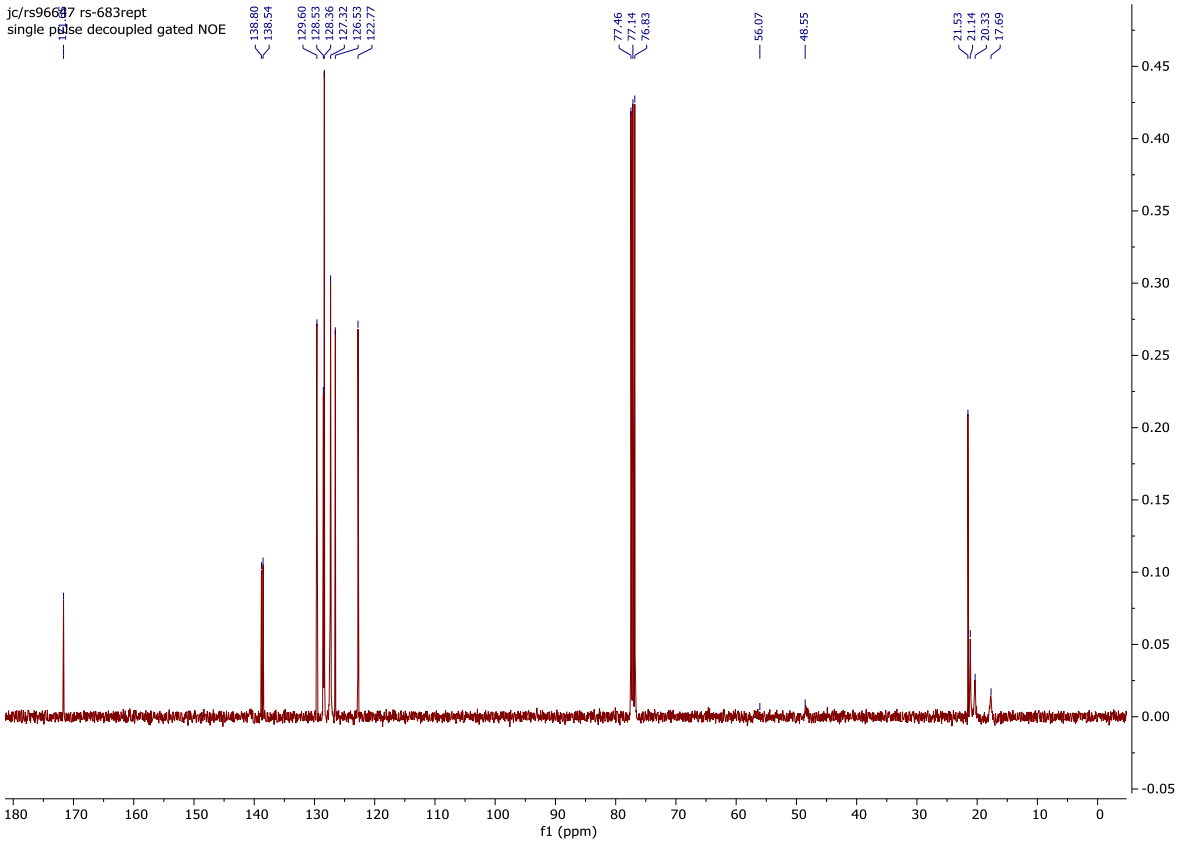
***(R)*-*N*-isopropyl-3-methyl-*N*-(1-phenylethyl)benzamide (10b)**



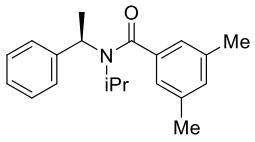
^{13}C NMR



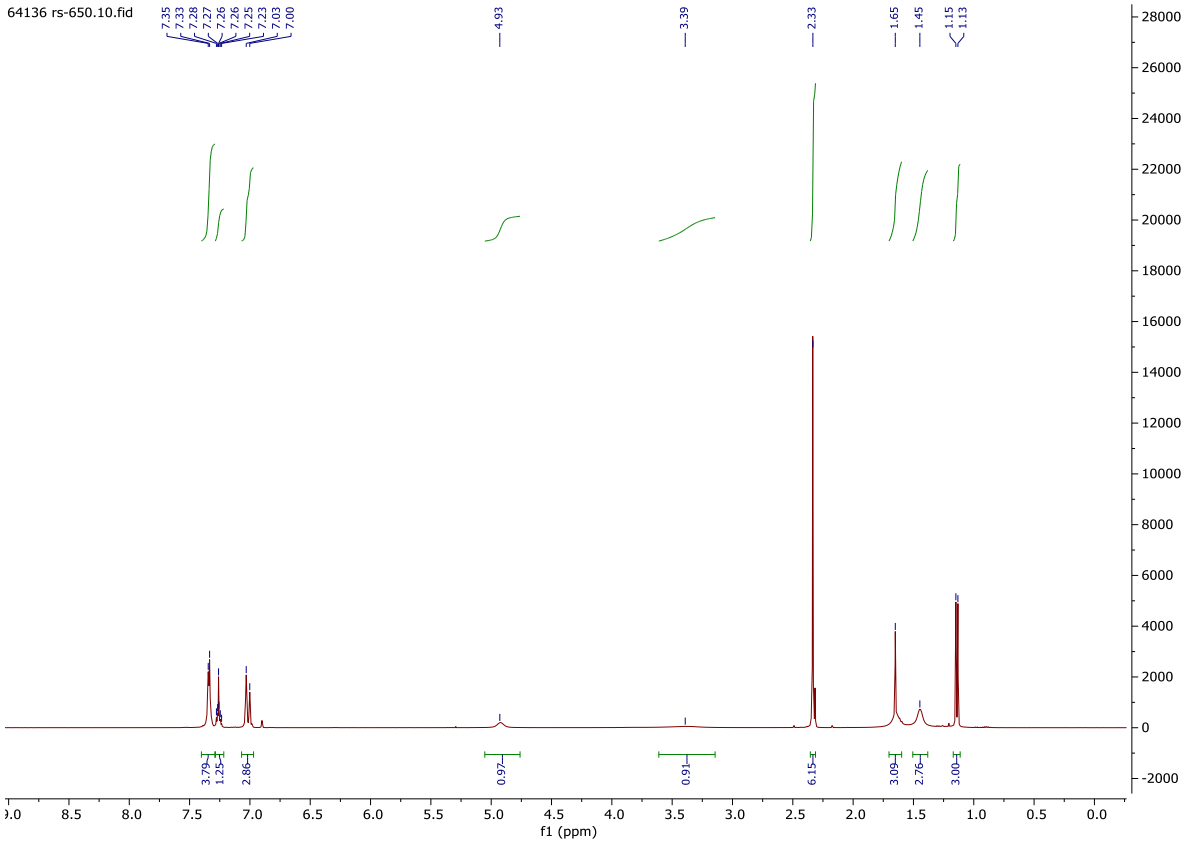
***(R)*-*N*-isopropyl-3-methyl-*N*-(1-phenylethyl)benzamide (10b)**



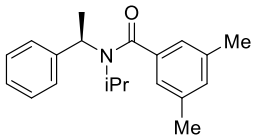
^{1}H NMR



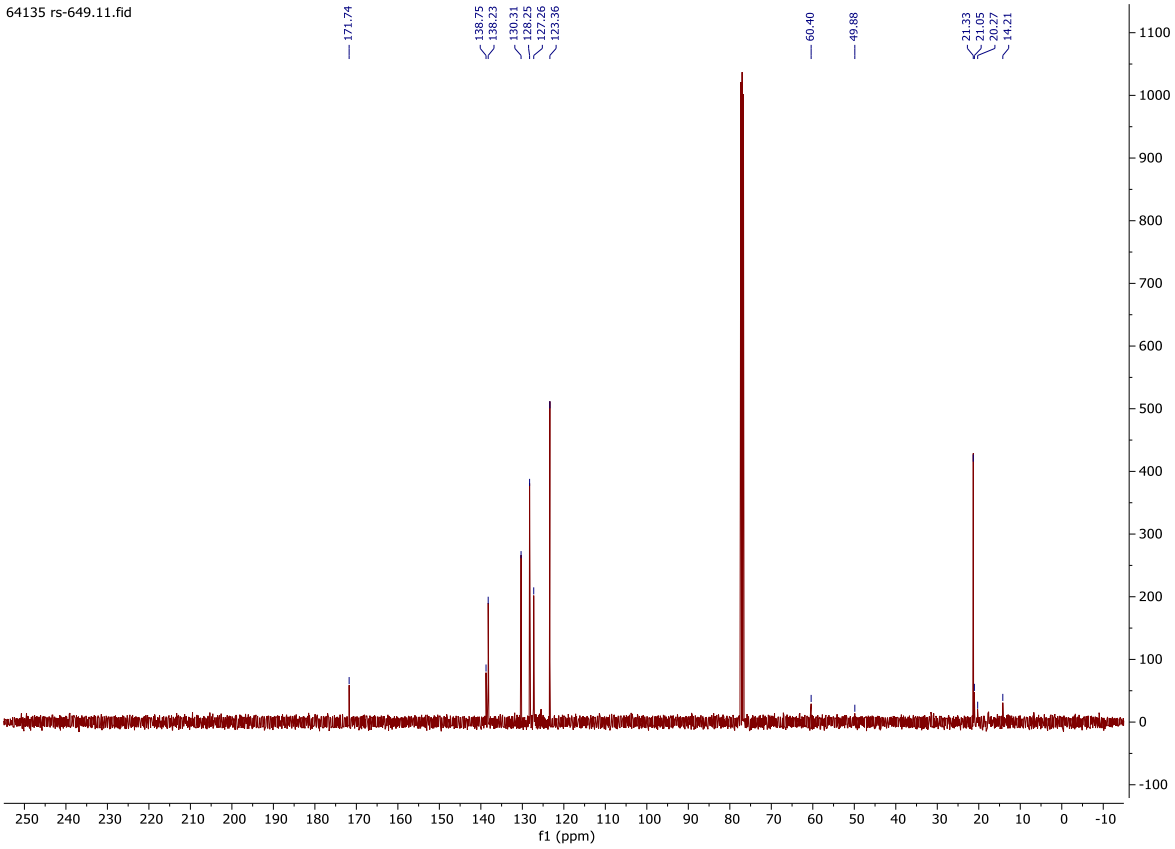
***(R)*-*N*-isopropyl-3,5-dimethyl-*N*-(1-phenylethyl)benzamide (10c)**



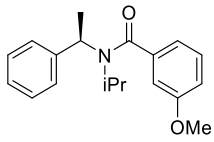
^{13}C NMR



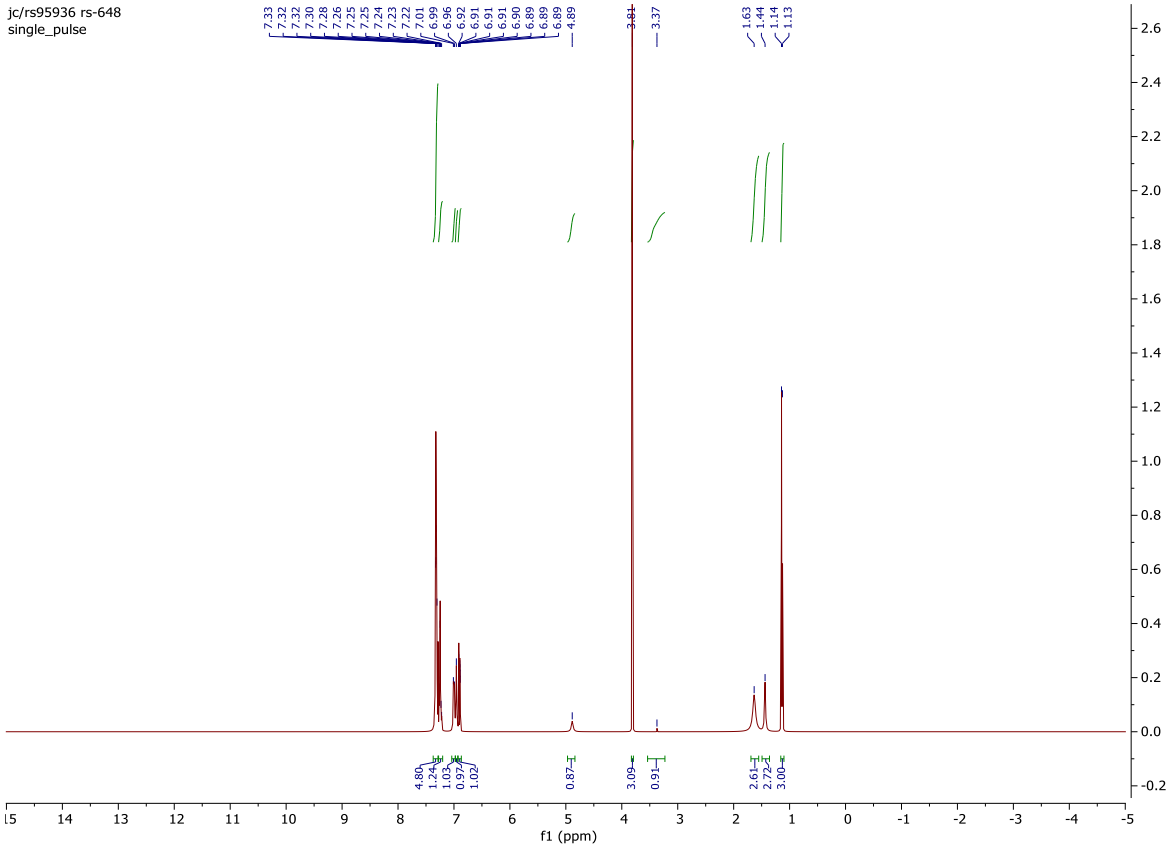
***(R)*-*N*-isopropyl-3,5-dimethyl-*N*-(1-phenylethyl)benzamide (10c)**



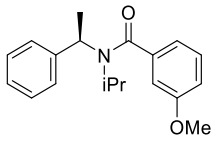
^{1}H NMR



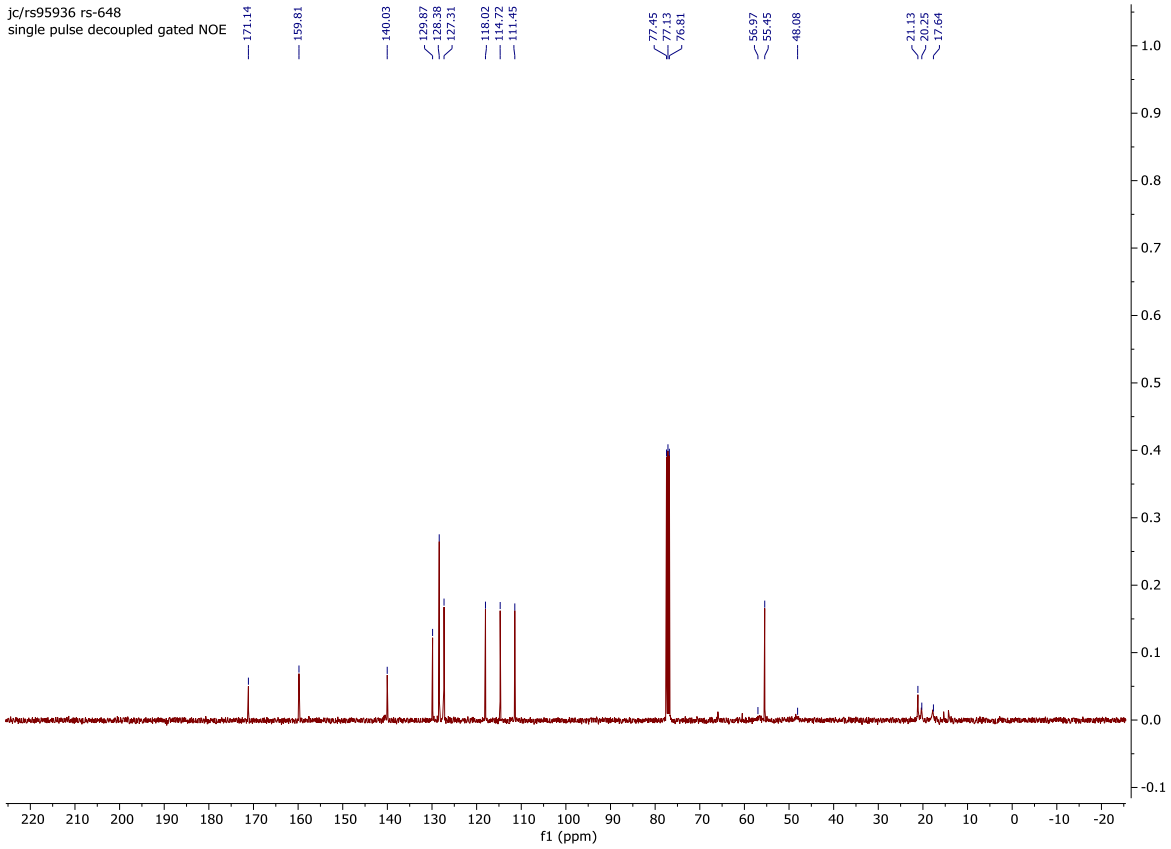
***(R)*-*N*-isopropyl-3-methoxy-*N*-(1-phenylethyl)benzamide (10d)**



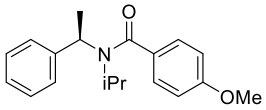
^{13}C NMR



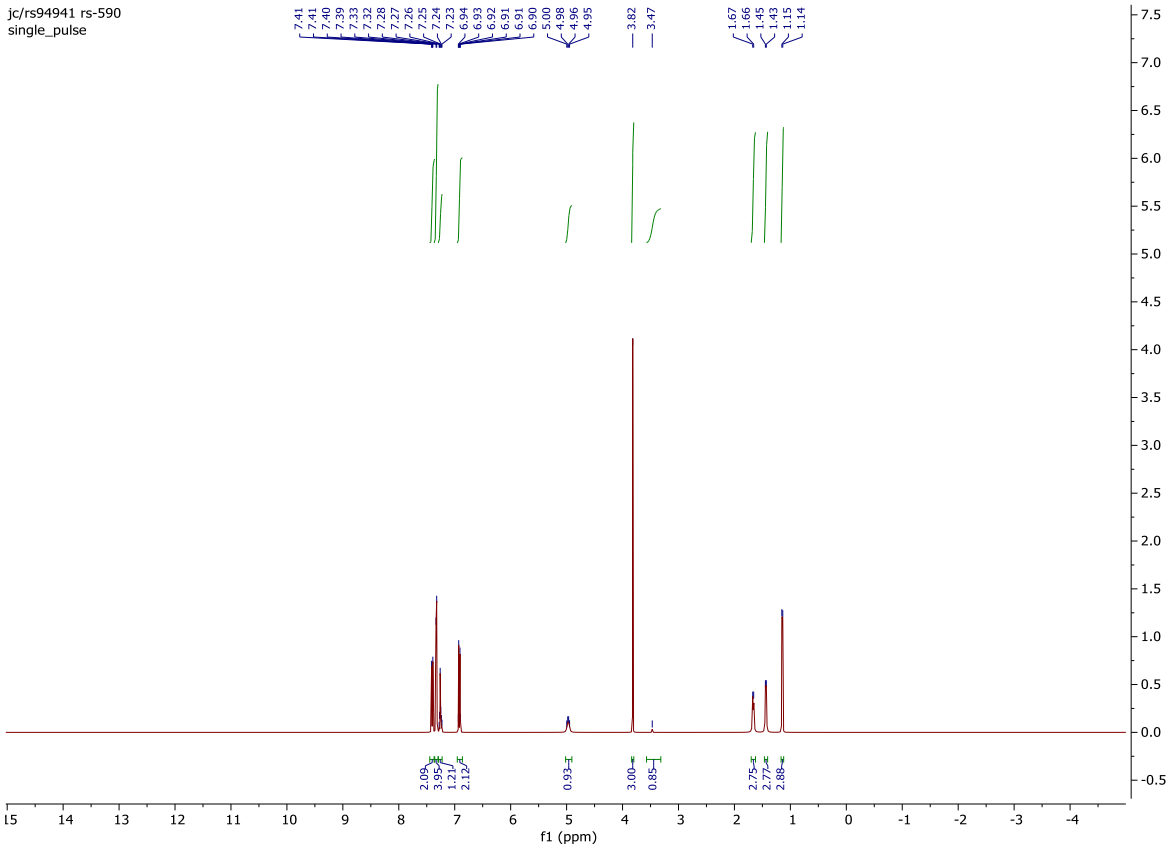
(R)-*N*-isopropyl-3-methoxy-*N*-(1-phenylethyl)benzamide (10d)



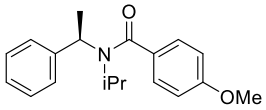
^{1}H NMR



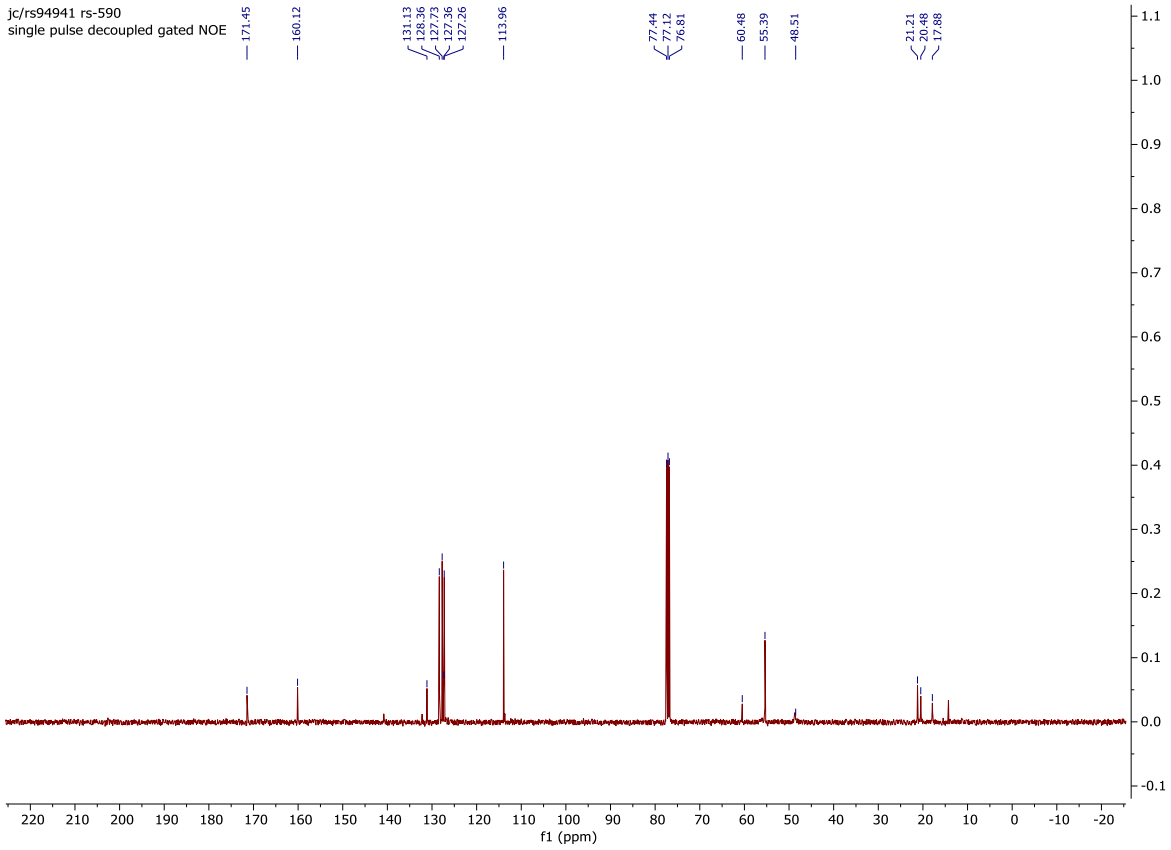
***(R)*-*N*-isopropyl-4-methoxy-*N*-(1-phenylethyl)benzamide (10e)**



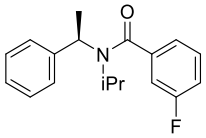
^{13}CNMR



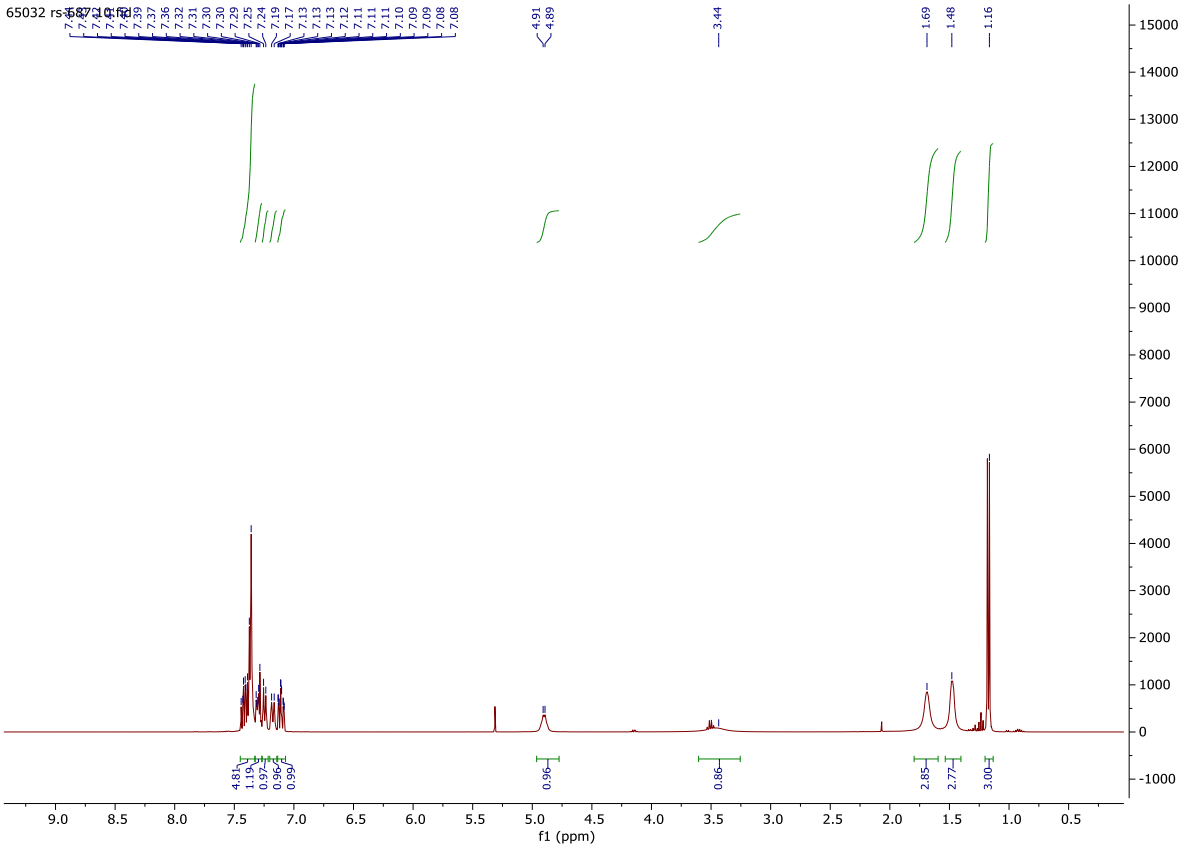
(R)-N-isopropyl-4-methoxy-*N*-(1-phenylethyl)benzamide (10e)



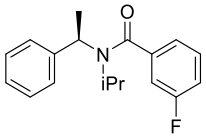
^{1}H NMR



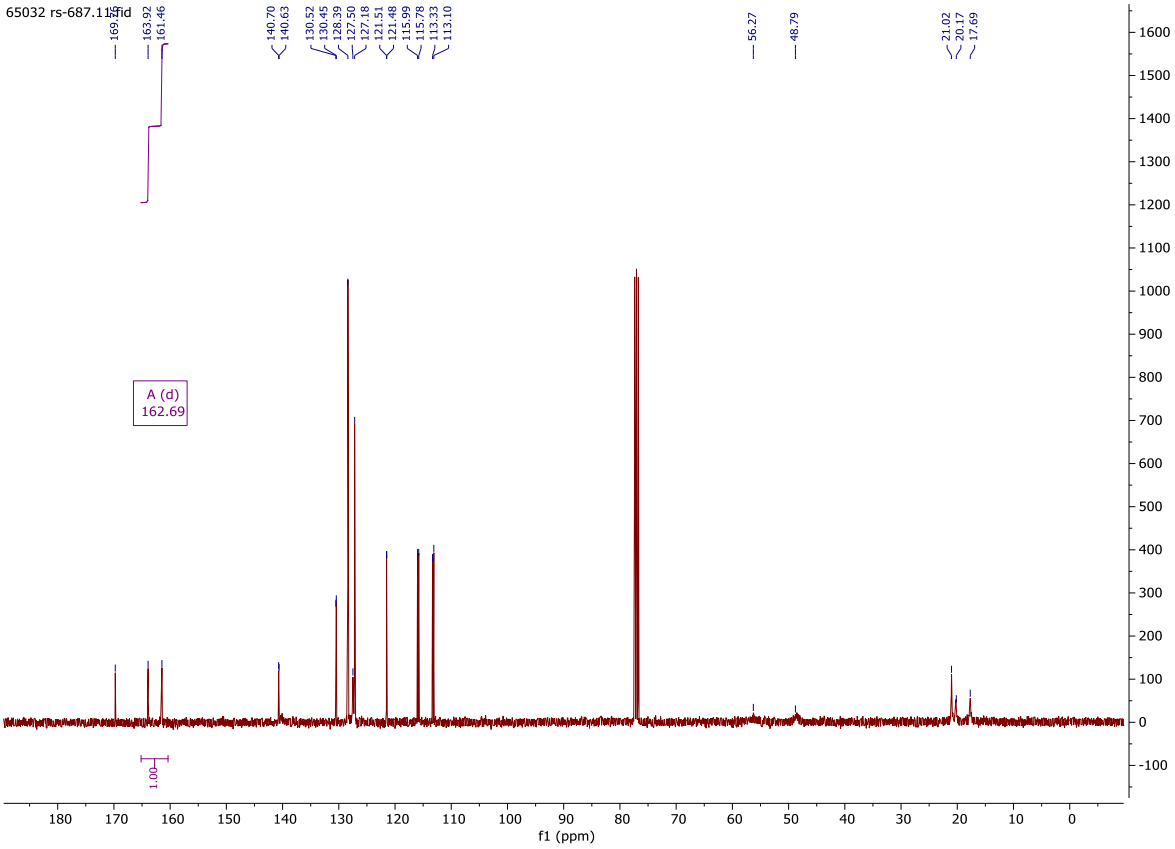
***(R)*-3-fluoro-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10f)**



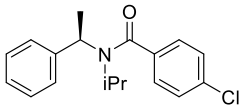
^{13}C NMR



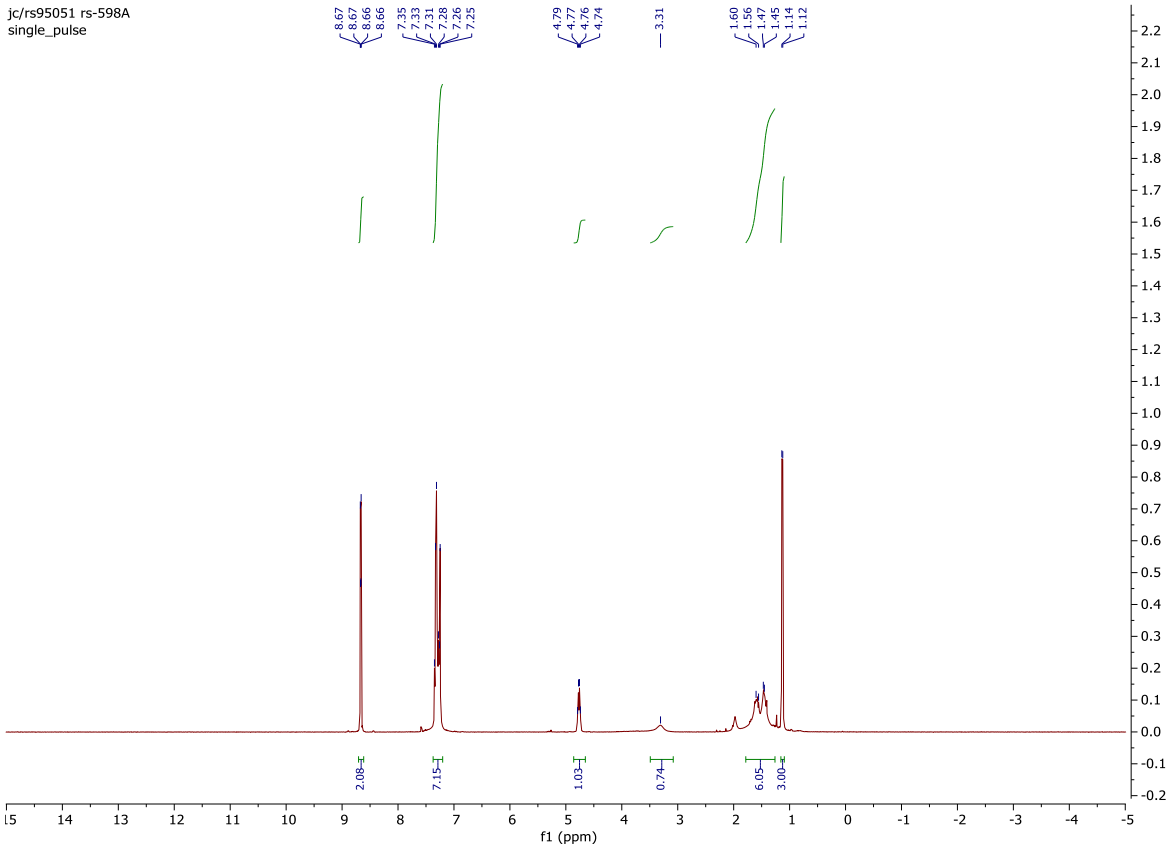
***(R)*-3-fluoro-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10f)**



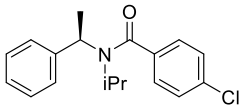
^{1}H NMR



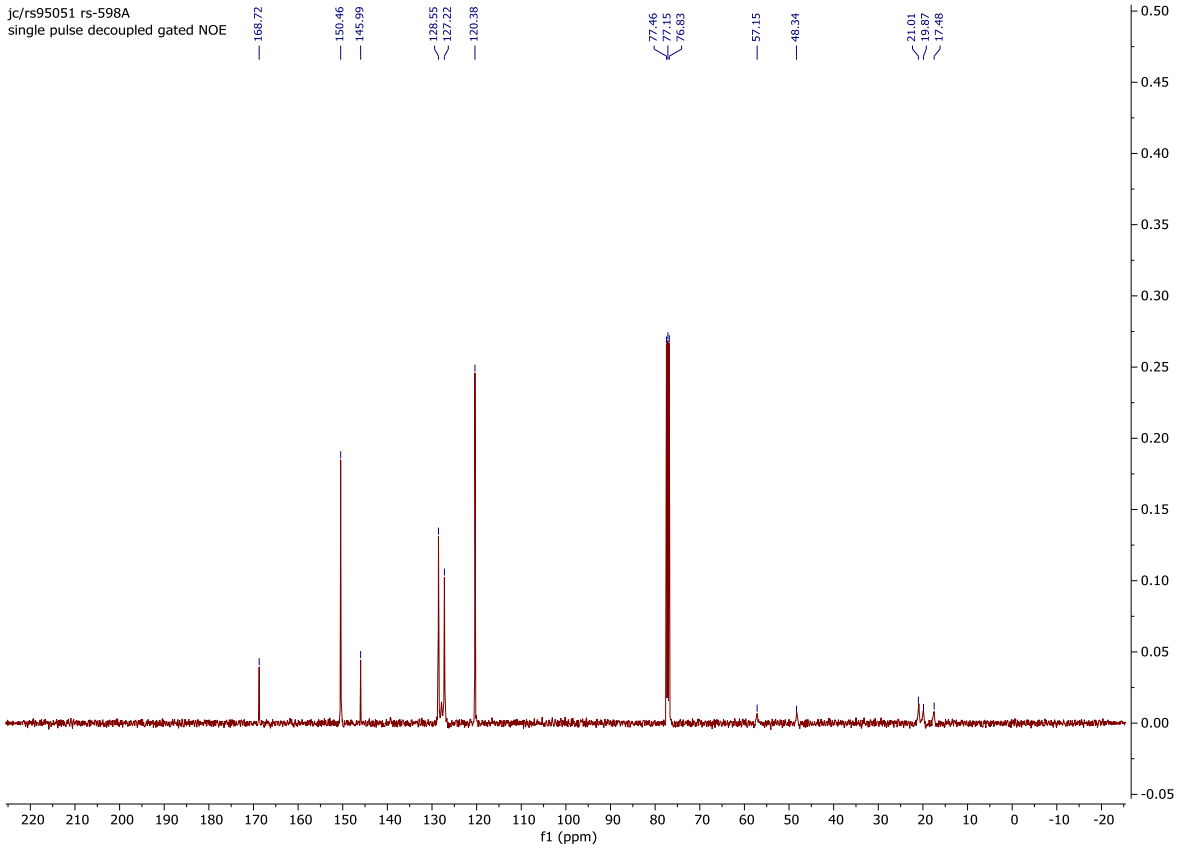
(R)-4-chloro-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10g)



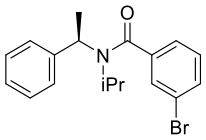
^{13}C NMR



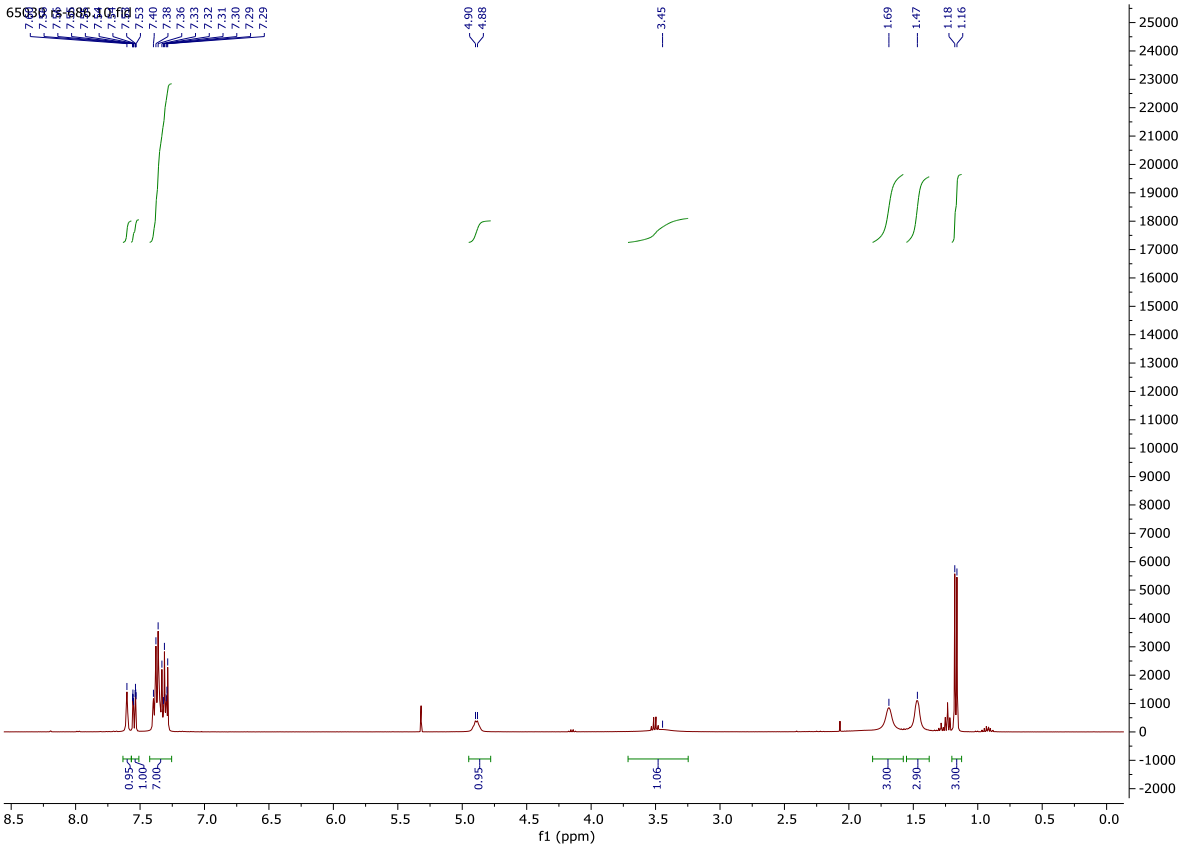
(R)-4-chloro-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10g)



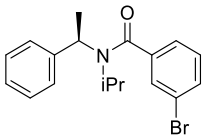
^{1}H NMR



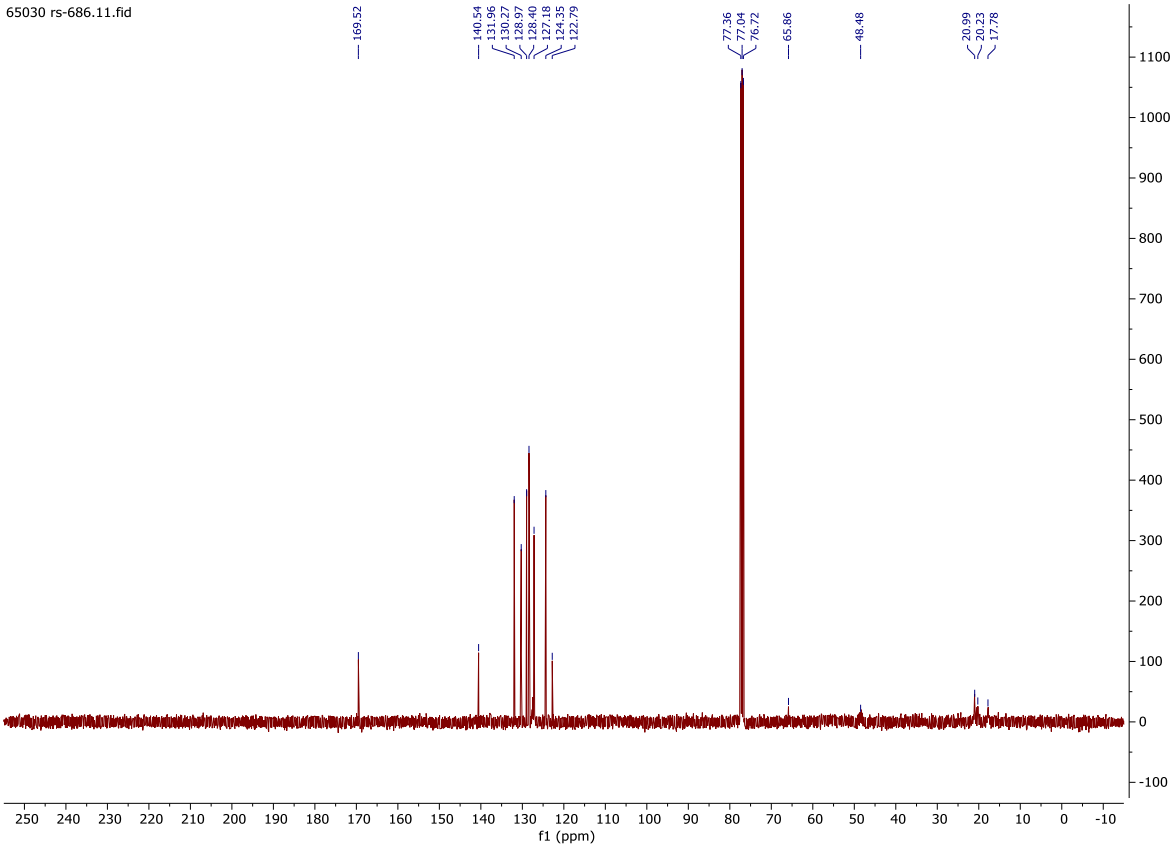
***(R)*-3-bromo-*N*-isopropyl-*N*-(1-phenylethyl)benzamide (10h)**



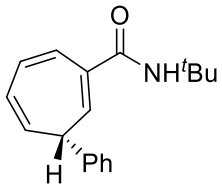
^{13}C NMR



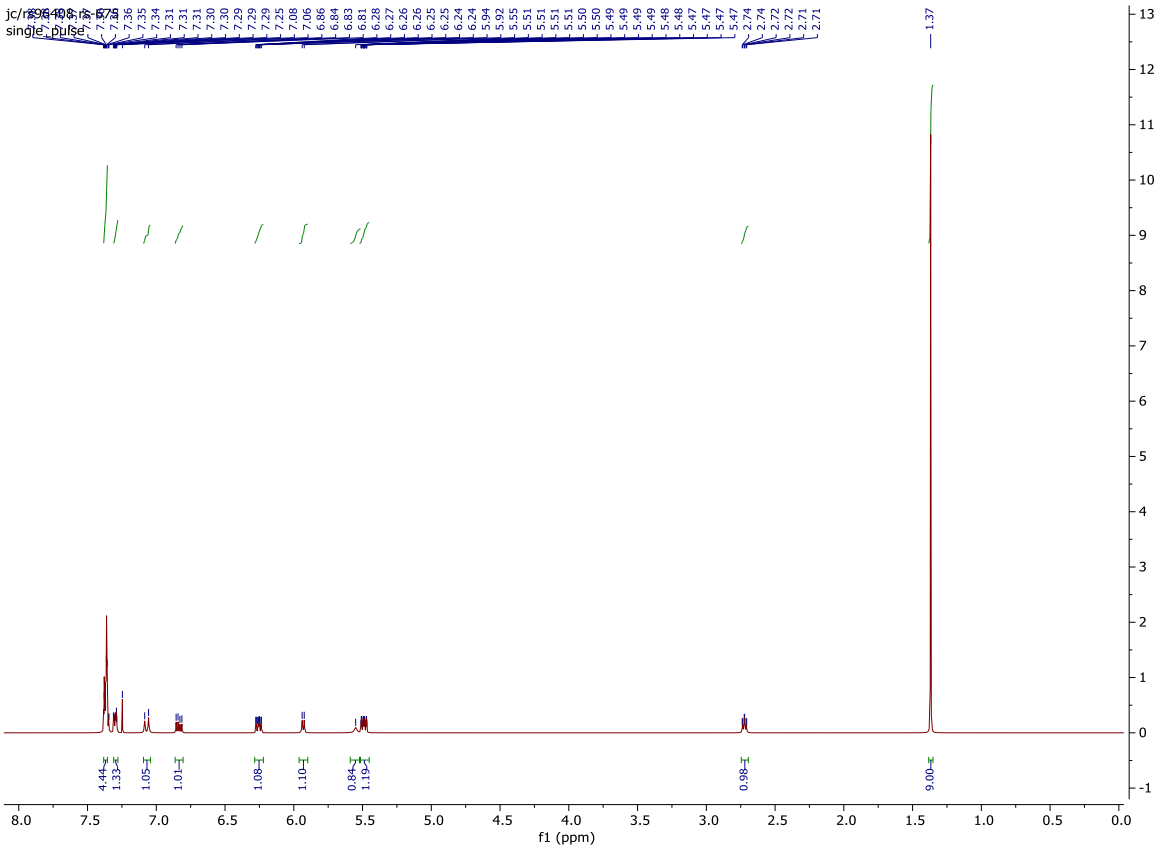
_(R)_-3-bromo-_N_-isopropyl-_N_-(1-phenylethyl)benzamide (10h)



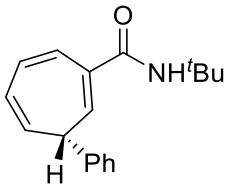
^{1}H NMR



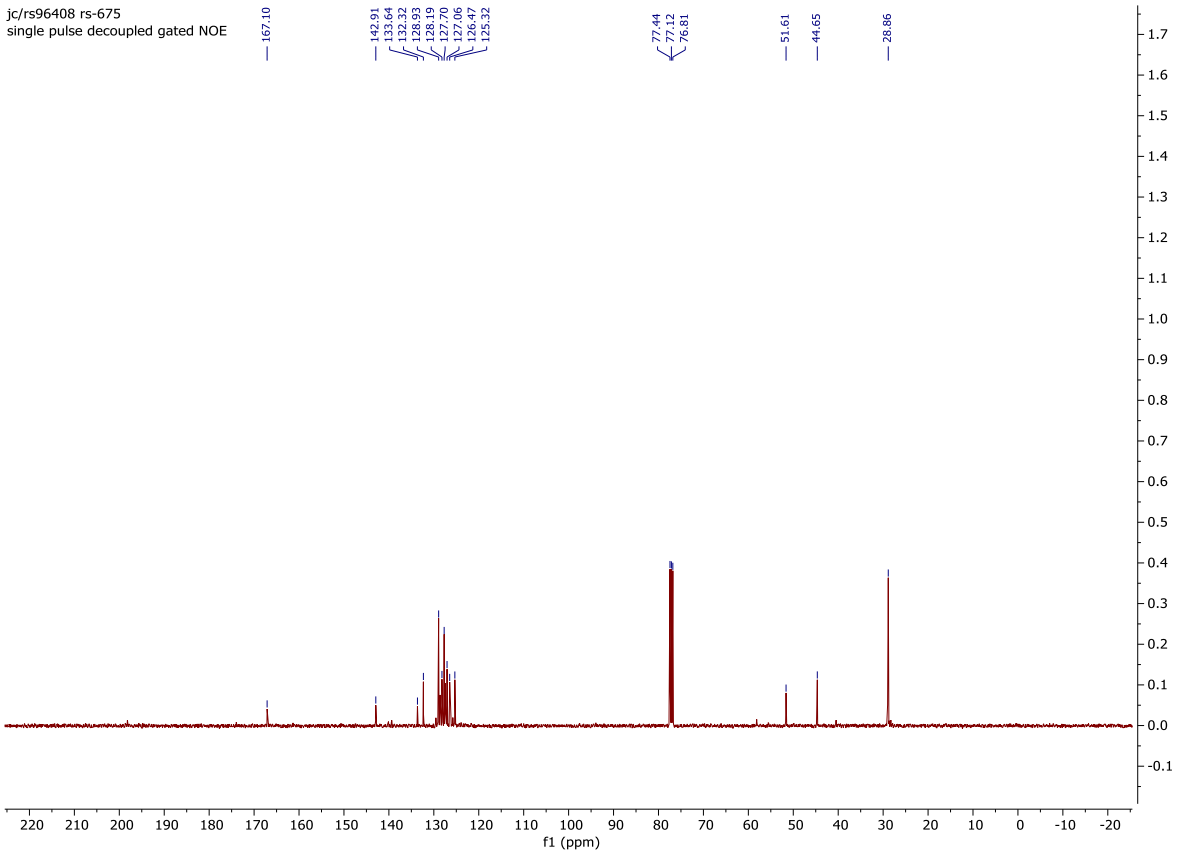
***(R)-N*-(tert-butyl)-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4a)**



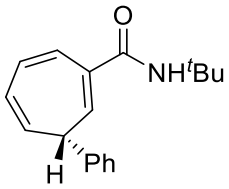
^{13}C NMR



***(R)*-*N*-(tert-butyl)-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4a)**

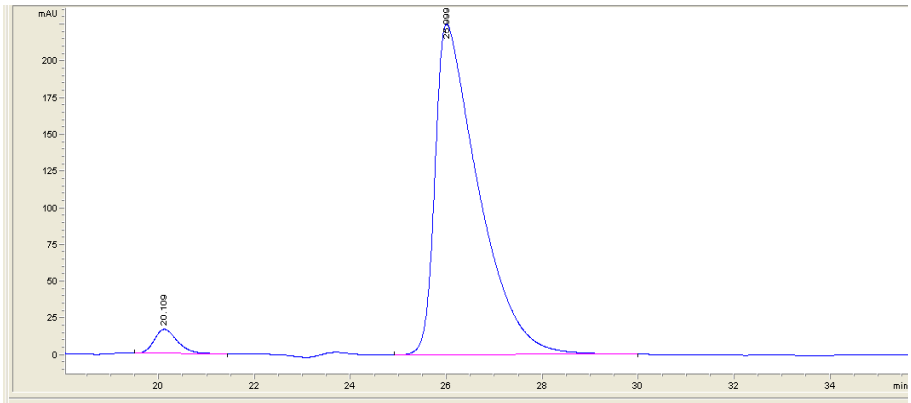


HPLC



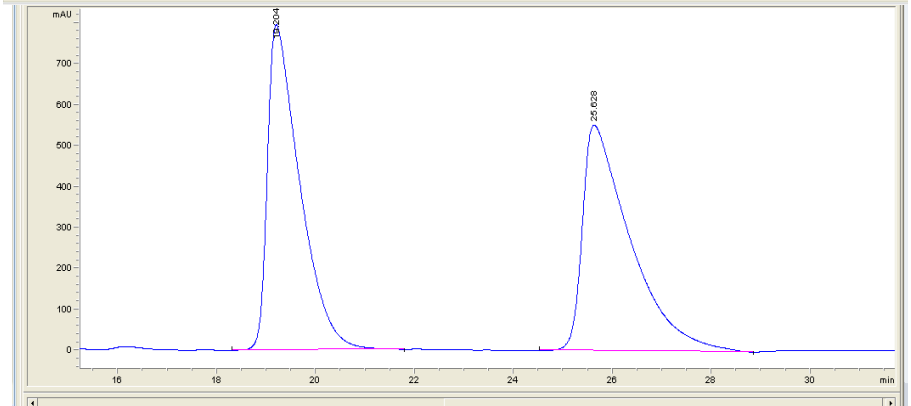
***(R)-N*-(tert-butyl)-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4a)**

Analytical HPLC (Chiral Regis Whelk O1), eluting with IPA–hexane (15:85), showed it to consist of a 3.798:96.202 mixture of two enantiomers with retention times 20.100 and 25.999 min respectively (ee = 92 %).



File Information	
LC-File	RS-703.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-09-29 16-17-39\
Date	29-Sep-20, 16:18:20
Sample	RS-703
Sample Info	85:15 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 85-15 HEXANE-IPA1ML.M
Analysis Time	42.247 min
Sampling Rate	0.0067 min (0.402 sec), 6338 datapoints

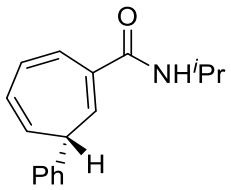
#	Time	Area	Height	Width	Area%	Symmetry
1	20.109	559.9	16.5	0.5142	3.798	0.699
2	25.999	14182.4	225.1	0.9051	96.202	0.341



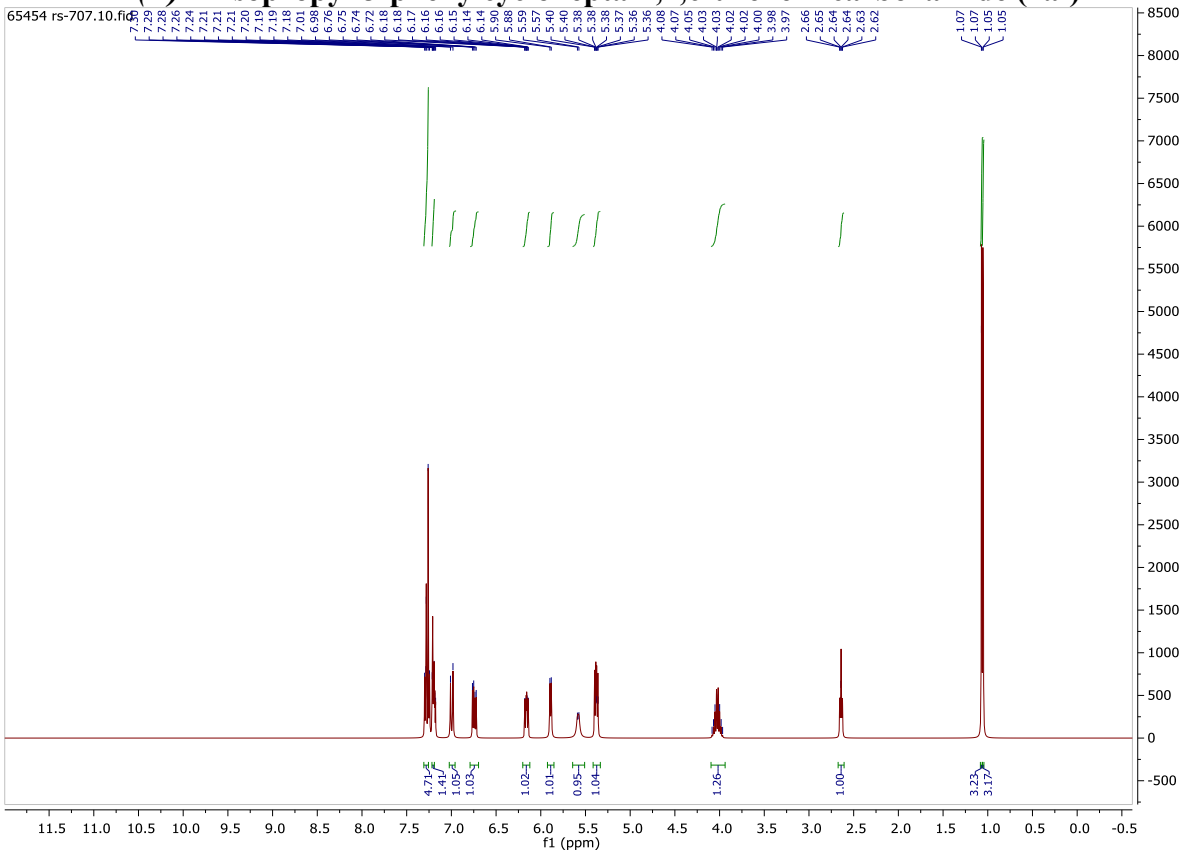
File Information	
LC-File	RS-688.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-09-23 10-46-48\
Date	23-Sep-20, 10:47:29
Sample	RS-688
Sample Info	85:15 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 85-15 HEXANE-IPA1ML.M
Analysis Time	31.813 min
Sampling Rate	0.0067 min (0.402 sec), 4773 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	19.204	36107.8	794.2	0.6584	49.289	0.36
2	25.628	37149.4	551.7	0.9435	50.711	0.304

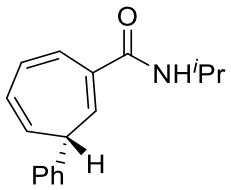
^{1}H NMR



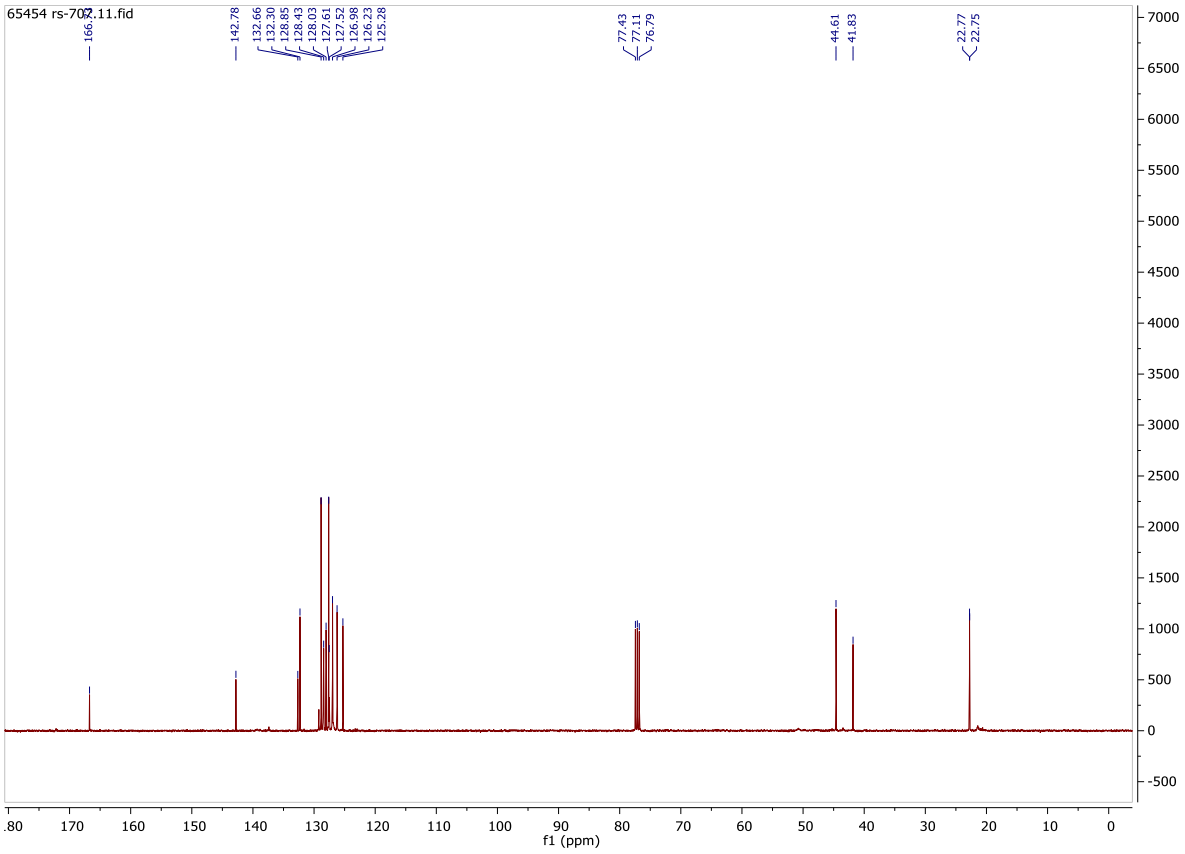
***(R)-N*-isopropyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4a')**



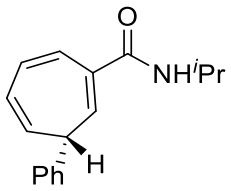
^{13}C NMR



***(R)-N*-isopropyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4a')**

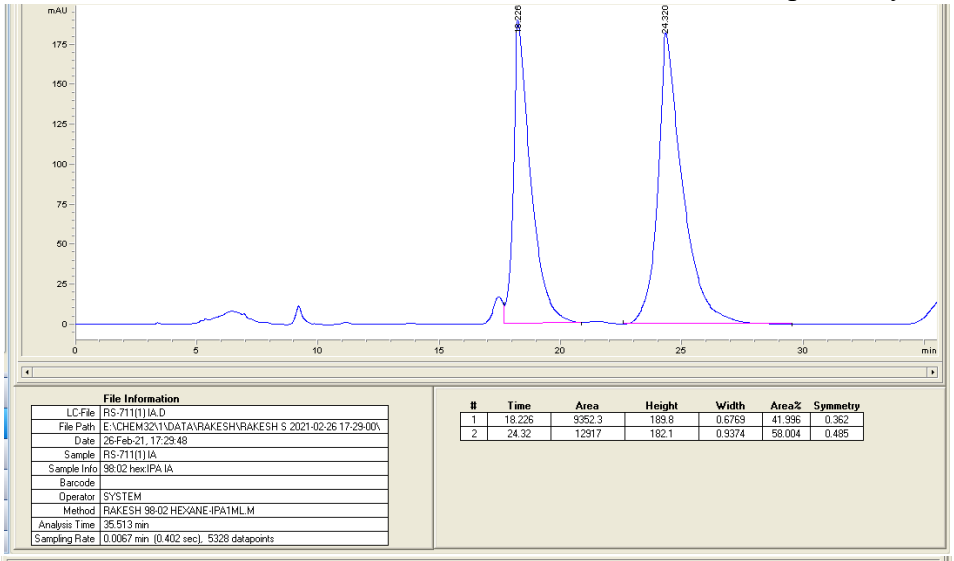


HPLC



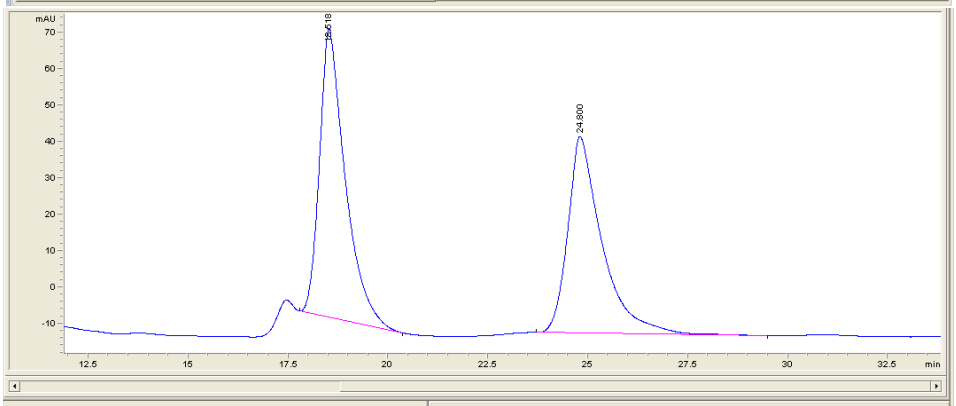
***(R)-N*-isopropyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4a')**

Analytical HPLC (IA column), eluting with IPA–hexane (02:98), showed it to consist of a 42:58 mixture of two enantiomers with retention times 18.22 and 24.32 min respectively.



File Information	
LC-File	RS-711(1) IA.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2021-02-26 17-29-00\
Date	26-Feb-21, 17:29:48
Sample	RS-711(1) IA
Sample Info	98:02 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 98-02 HEXANE-IPA1ML.M
Analysis Time	35.513 min
Sampling Rate	0.0067 min (0.402 sec), 5328 datapoints

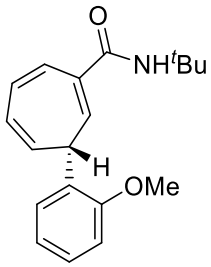
#	Time	Area	Height	Width	Area%	Symmetry
1	18.226	9352.3	189.8	0.6769	41.996	0.362
2	24.32	12917	182.1	0.9374	58.004	0.485



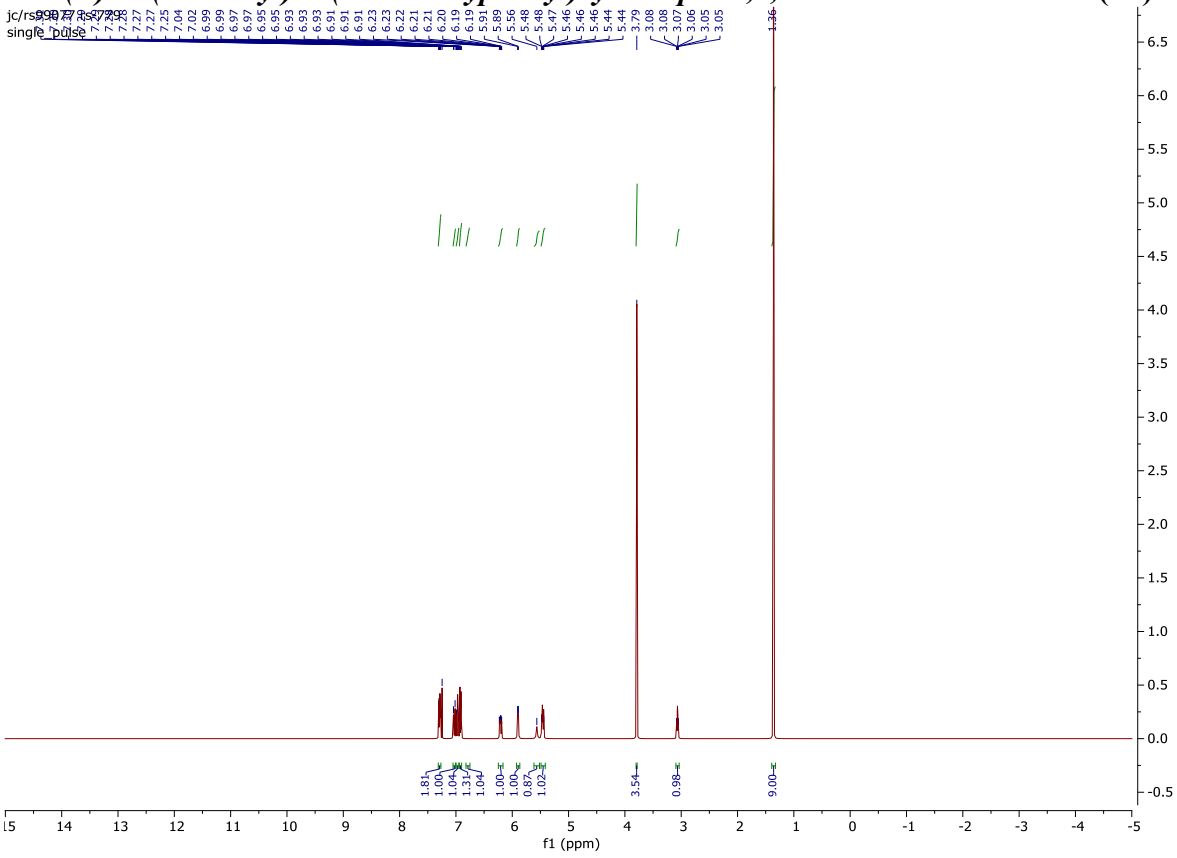
File Information	
LC-File	RS-707 IA.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2021-02-26 18-42-28\
Date	26-Feb-21, 18:43:15
Sample	RS-707 IA
Sample Info	98:02 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 98-02 HEXANE-IPA1ML.M
Analysis Time	33.833 min
Sampling Rate	0.0067 min (0.402 sec), 5076 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	18.518	3536.5	79.3	0.6466	52.424	0.545
2	24.8	3209.5	54	0.8176	47.576	0.521

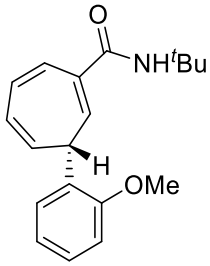
^{1}H NMR



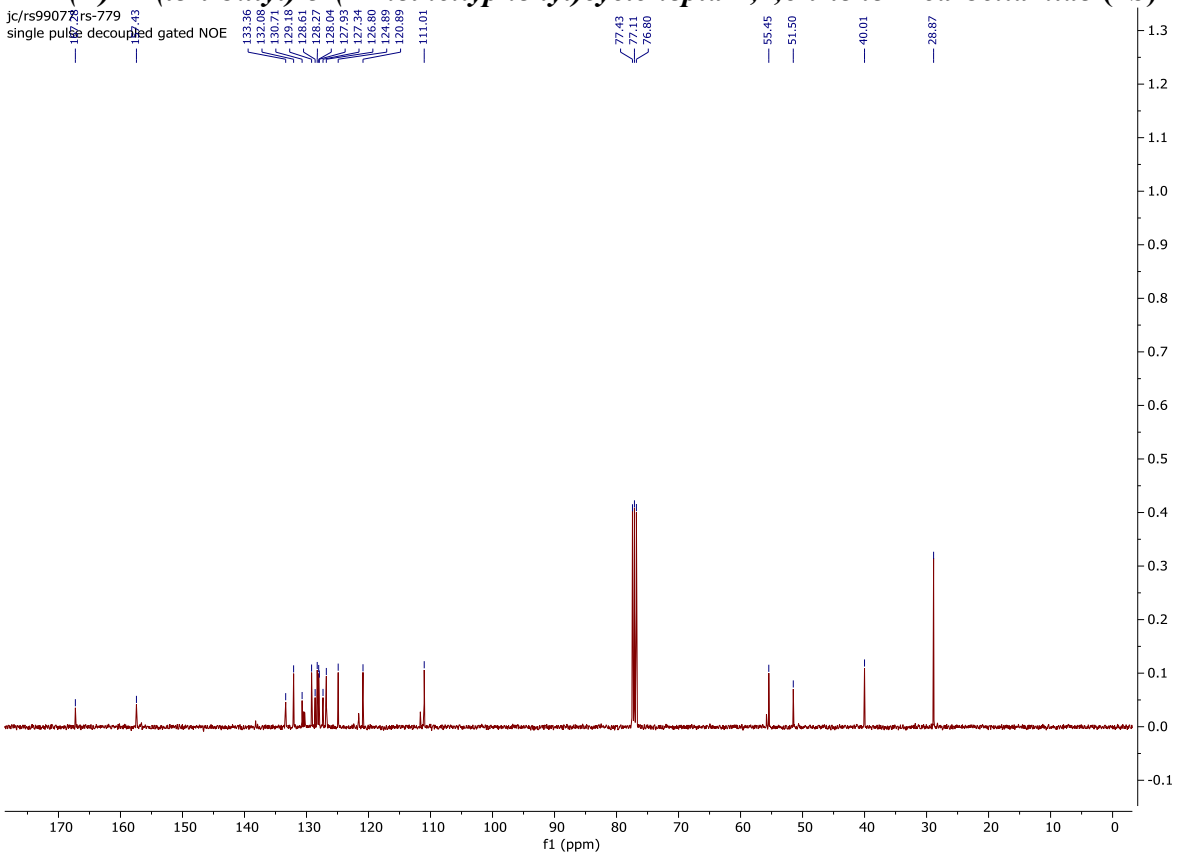
(R)-N-(tert-butyl)-3-(2-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide **(4b)**



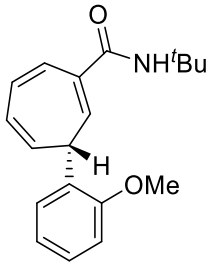
^{13}C NMR



(R)-N-(tert-butyl)-3-(2-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide **(4b)**

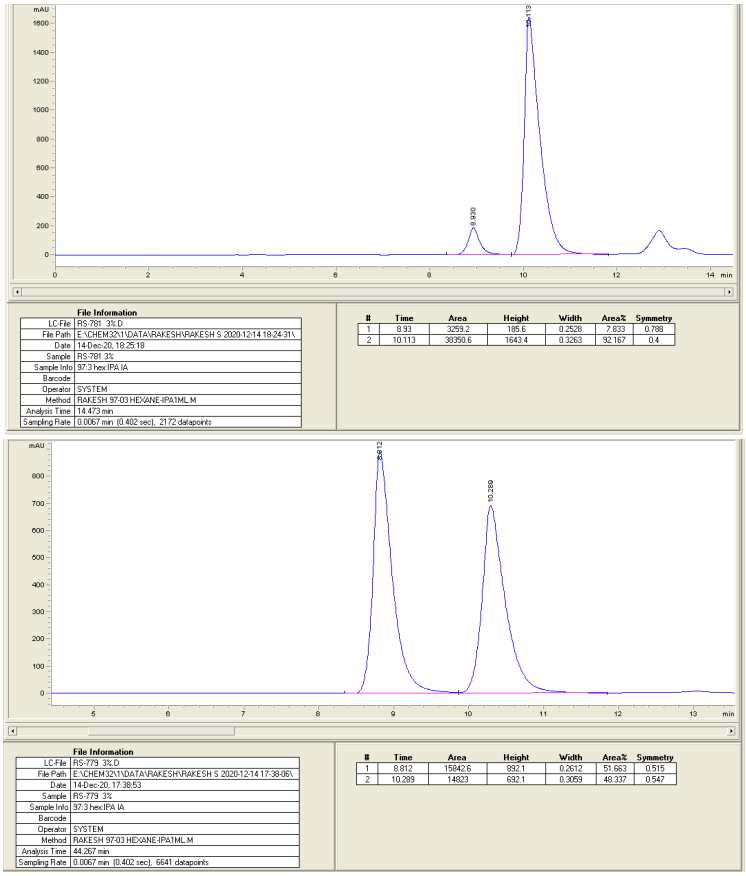


HPLC

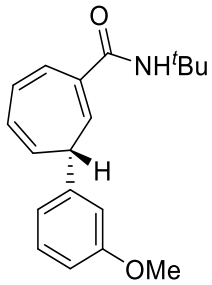


(R)-N-(tert-butyl)-3-(2-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide **(4b)**

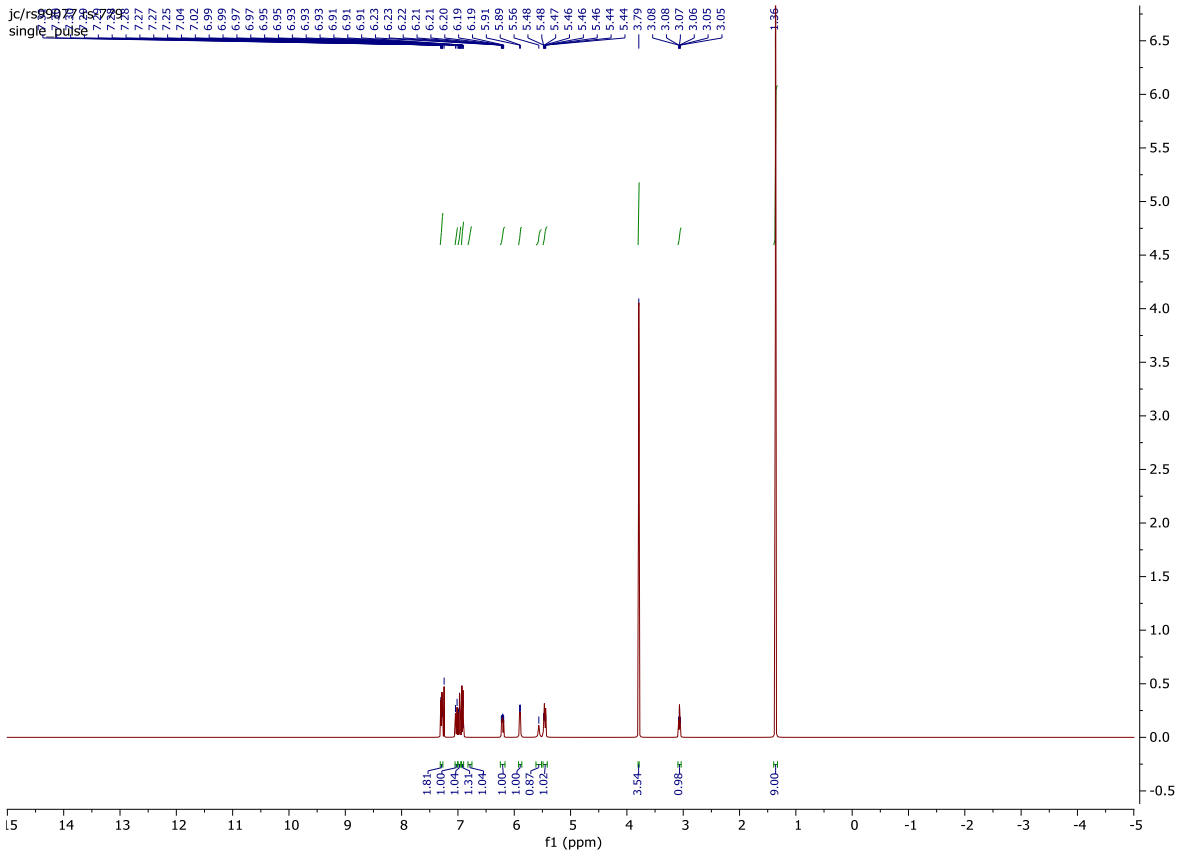
Analytical HPLC (IA Column), eluting with hexane-IPA–(3:97), showed it to consist of 8:92 mixture of two enantiomers with retention times 8.93 mins (minor) and 10.11 mins (major), respectively.



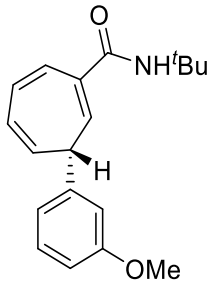
^{1}H NMR



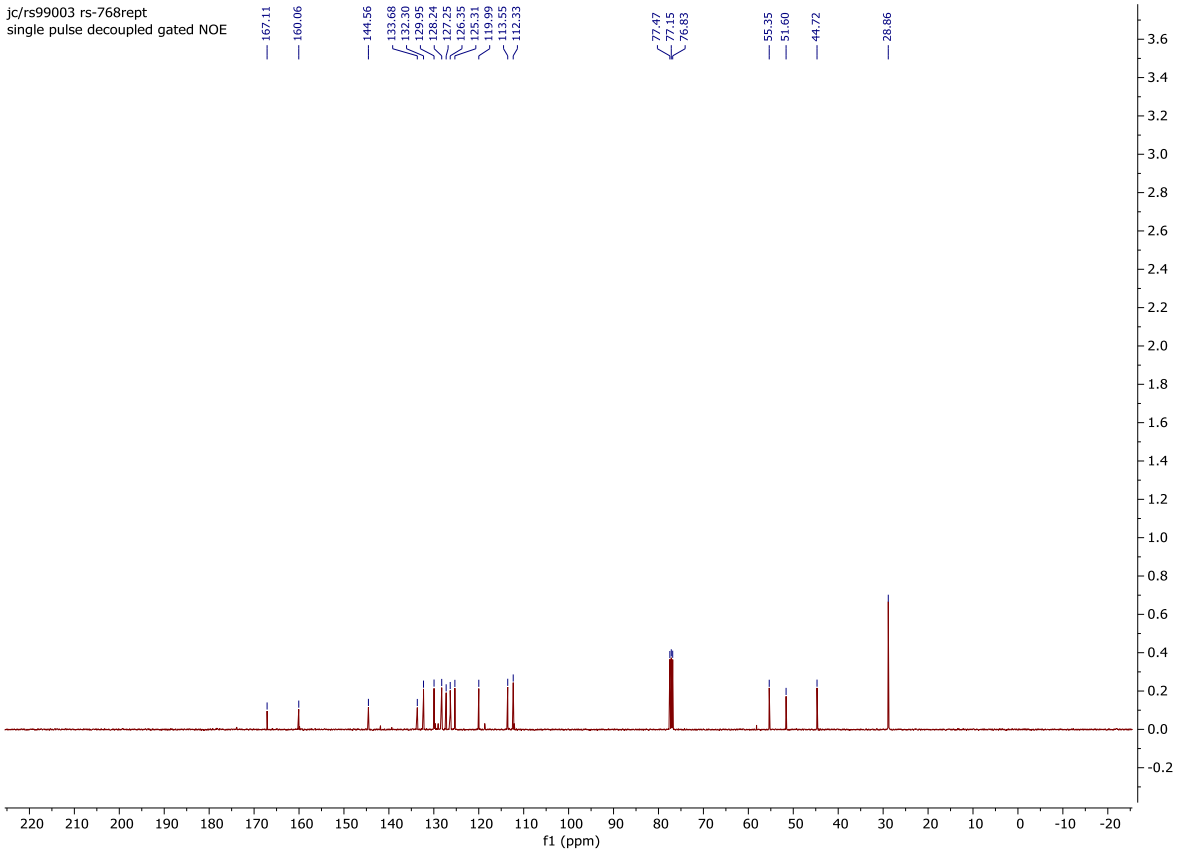
***(R)-N*-(tert-butyl)-3-(3-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide (4c)**



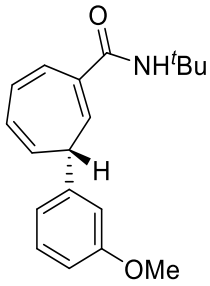
^{13}C NMR



***(R)-N*-(tert-butyl)-3-(3-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide (4c)**

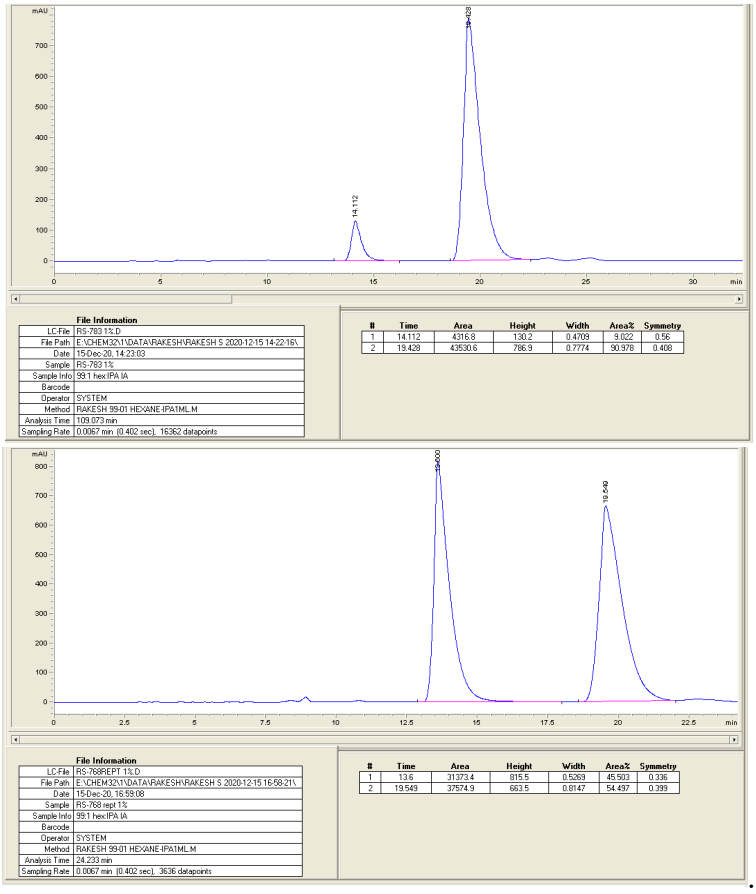


HPLC

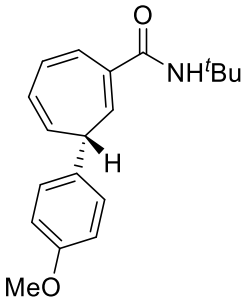


***(R)-N*-(tert-butyl)-3-(3-methoxyphenyl)cycloheptа-1,4,6-triene-1-carboxamide (4c)**

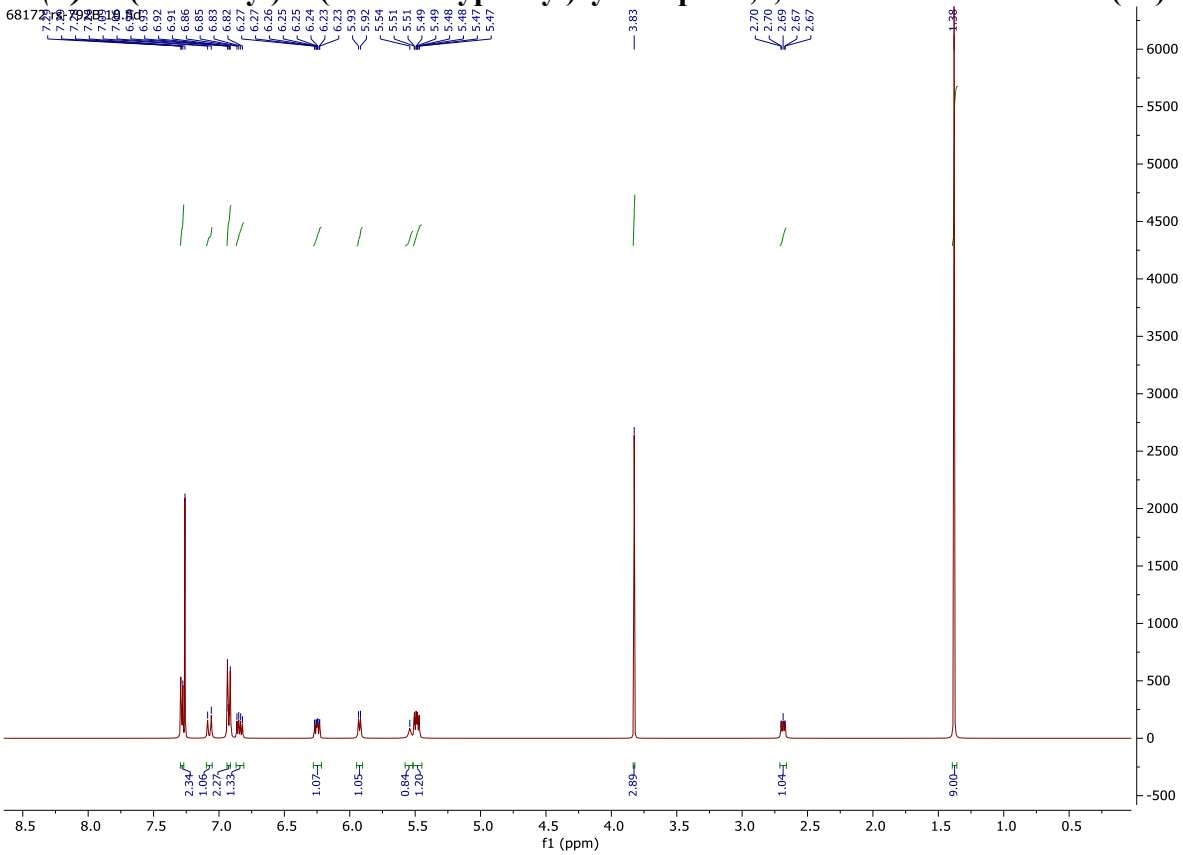
Analytical HPLC (IA Column), eluting with hexane-IPA (99:1), showed it to consist of a 9:91 mixture of two enantiomers with retention times 14.11 mins(minor) and 19.42 mins (major), respectively



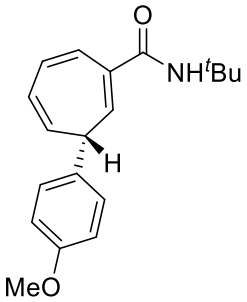
^{1}H NMR



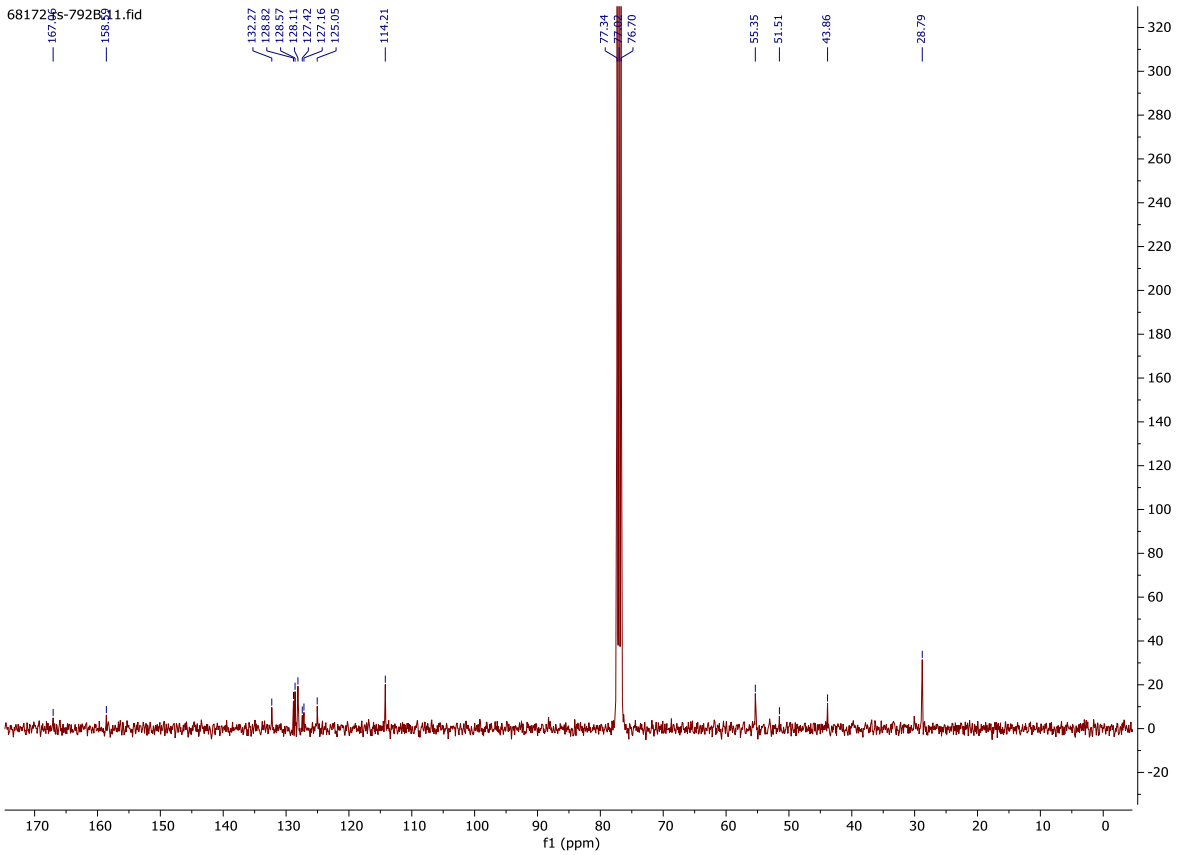
***(R)*-*N*-(tert-butyl)-3-(4-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide (4d)**



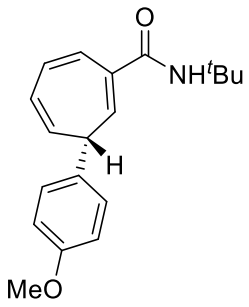
^{13}C NMR



***(R)-N*-(tert-butyl)-3-(4-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide (4d)**

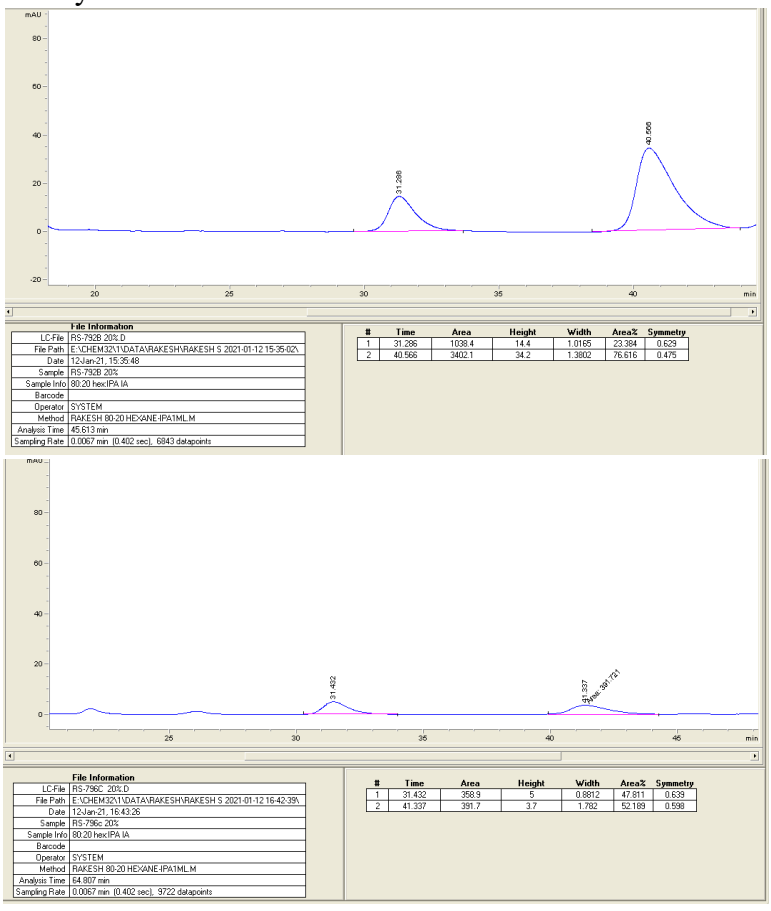


HPLC

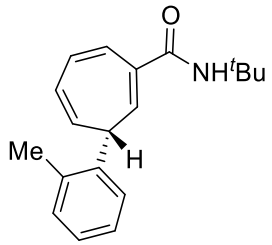


***(R)-N*-(tert-butyl)-3-(4-methoxyphenyl)cyclohepta-1,4,6-triene-1-carboxamide (4d)**

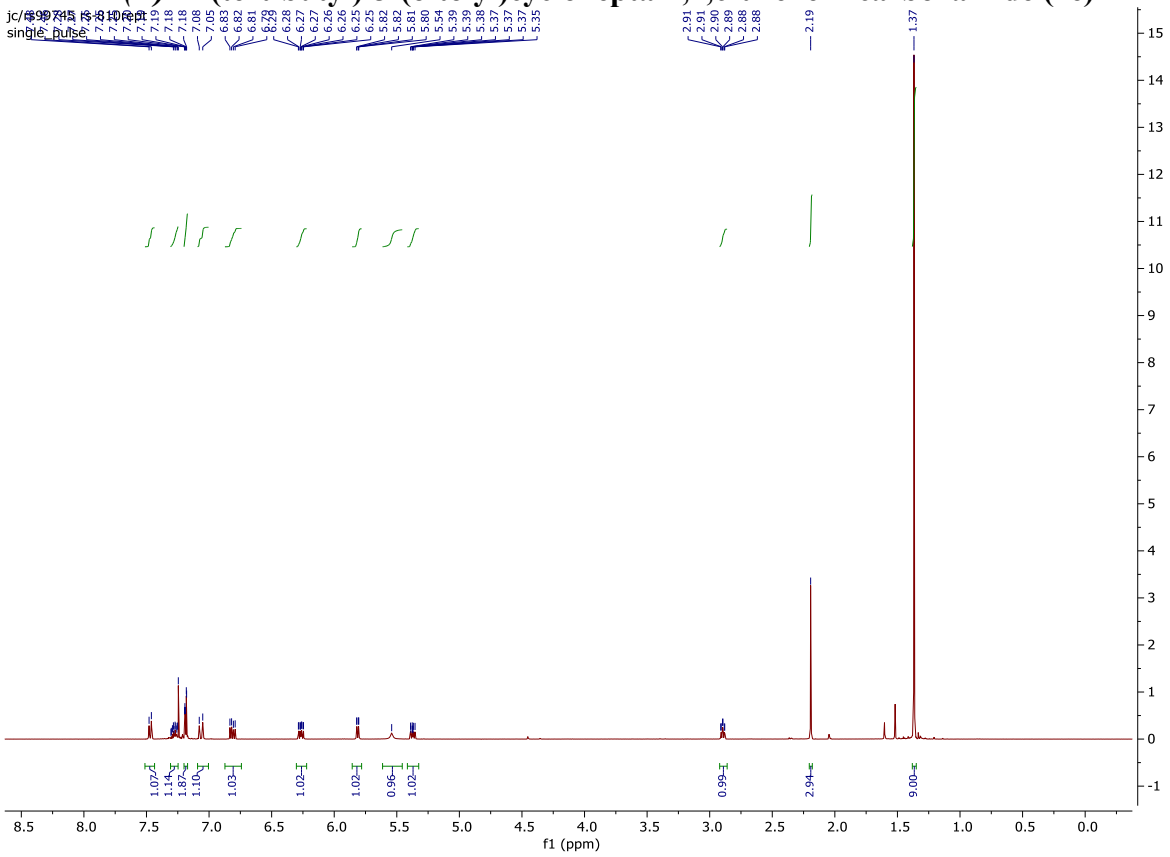
Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (80:20), showed it to consist of a mixture of 23:77 two enantiomers with retention times tR = 31.285 mins(minor) and 40:568 mins (major) respectively.



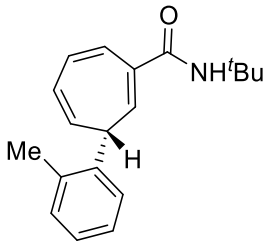
1H NMR



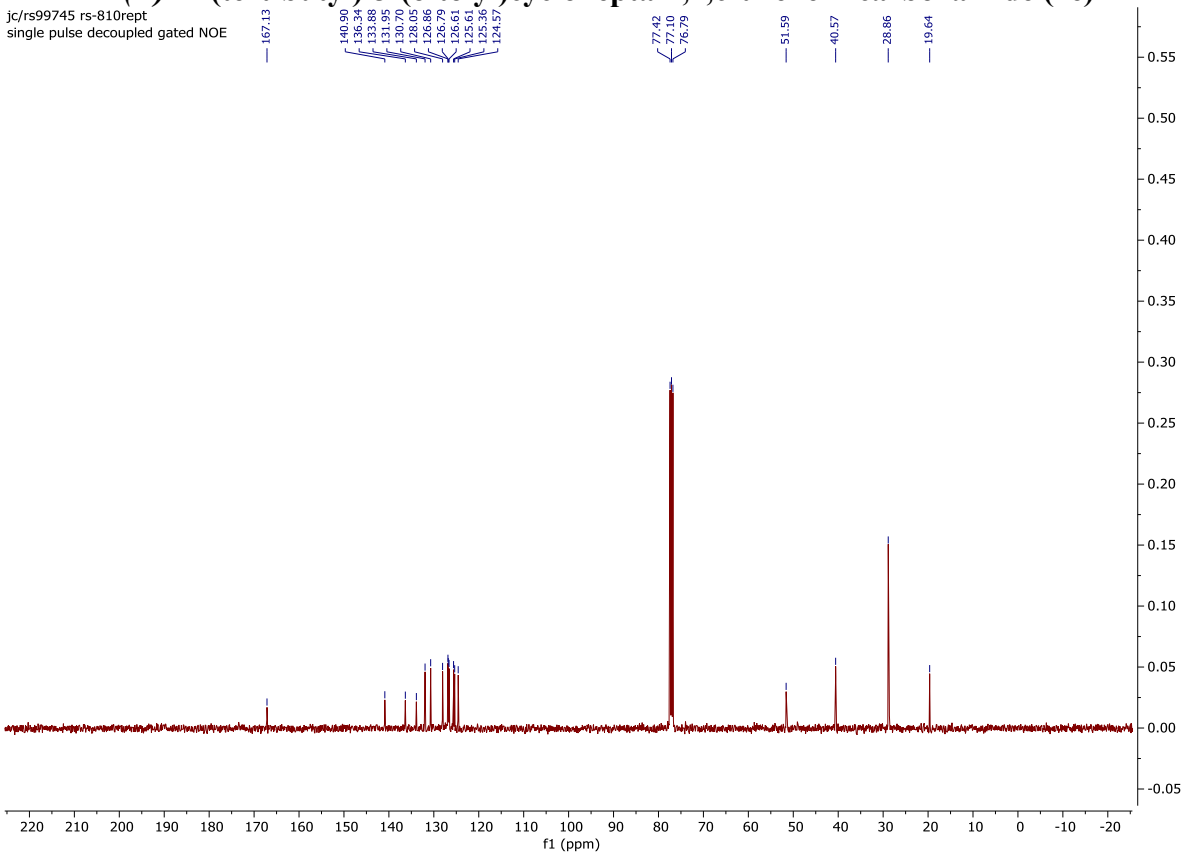
(*R*)-*N*-(tert-butyl)-3-(o-tolyl)cycloheptа-1,4,6-triene-1-carboxamide (4e)



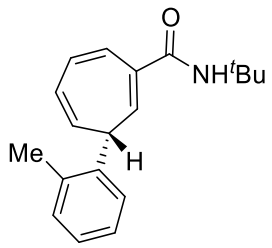
^{13}C NMR



(*R*)-*N*-(tert-butyl)-3-(o-tolyl)cyclohepta-1,4,6-triene-1-carboxamide (4e)

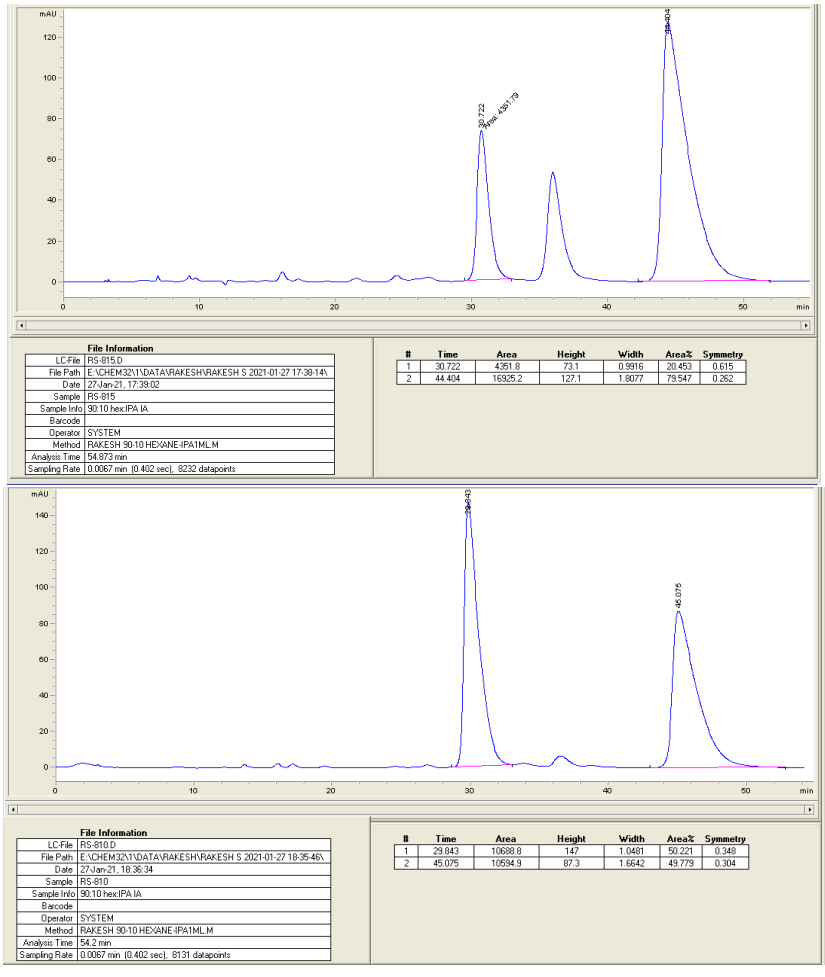


HPLC

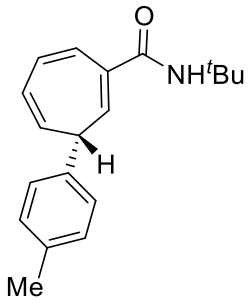


***(R)-N*-(tert-butyl)-3-(o-tolyl)cyclohepta-1,4,6-triene-1-carboxamide (4e)**

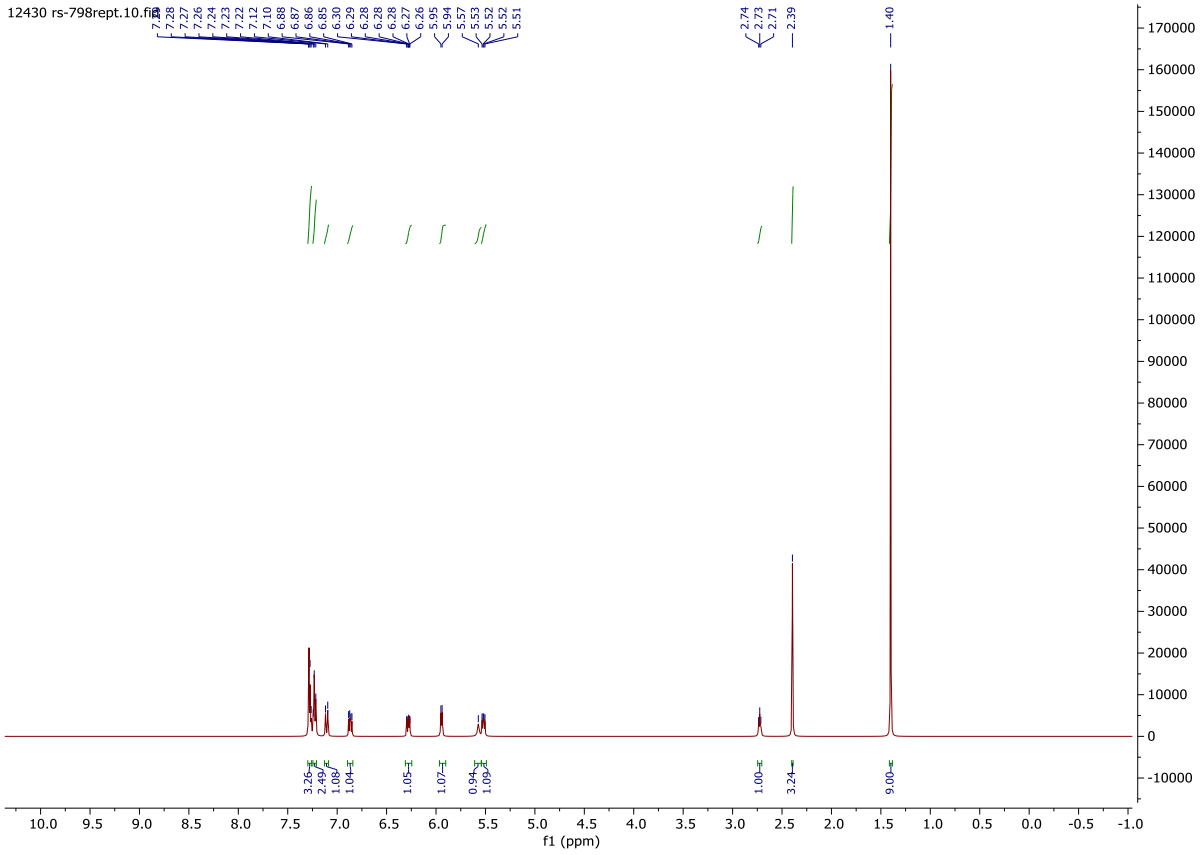
Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane- IPA (90:10), showed it to consist of a 20:80 mixture of two enantiomers with retention times 30.722 mins(minor) and 44.404 mins(major), respectively.



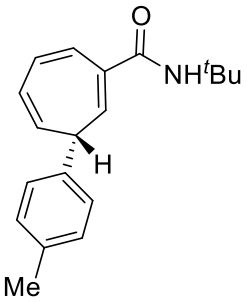
1H NMR



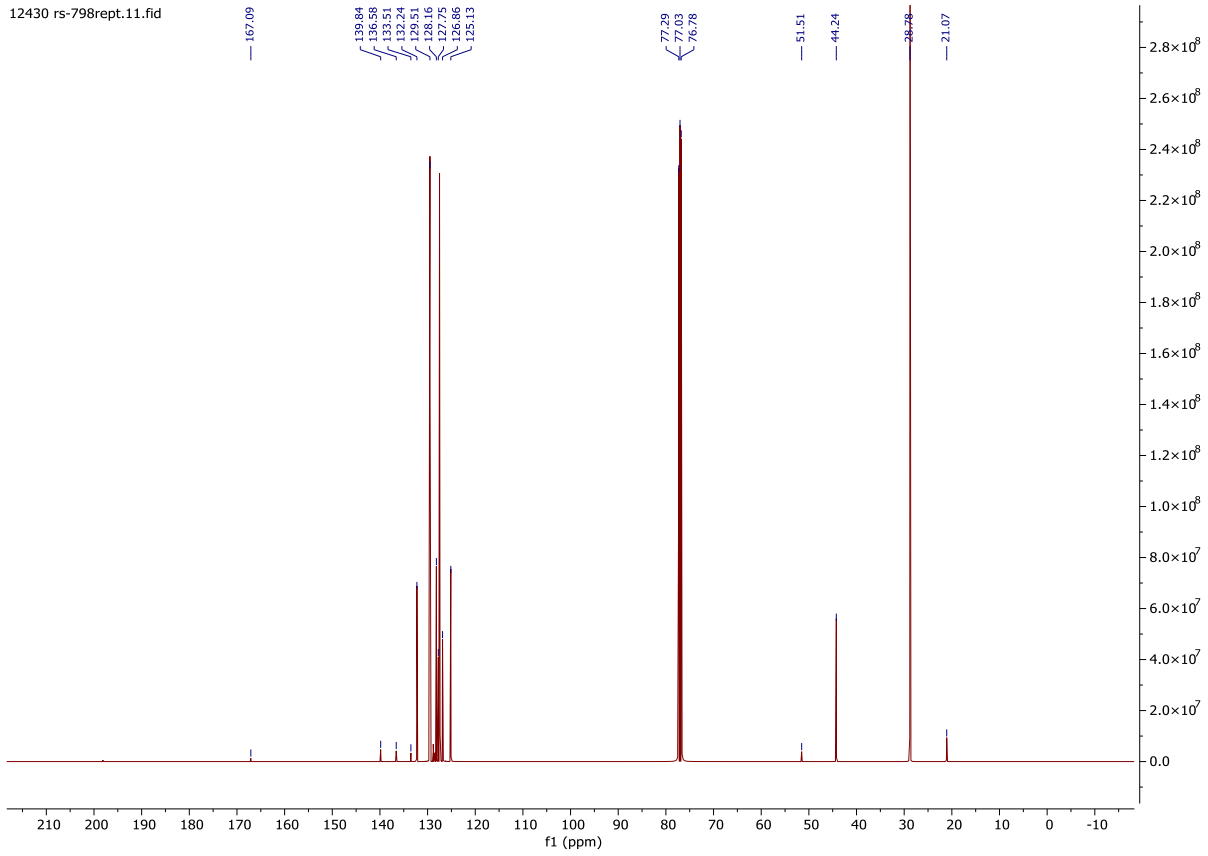
***(R)-N*-(tert-butyl)-3-(p-tolyl)cyclohepta-1,4,6-triene-1-carboxamide (4f)**



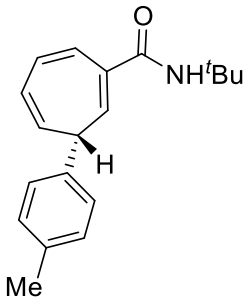
^{13}C NMR



***(R)*-*N*-(tert-butyl)-3-(p-tolyl)cyclohepta-1,4,6-triene-1-carboxamide (4f)**

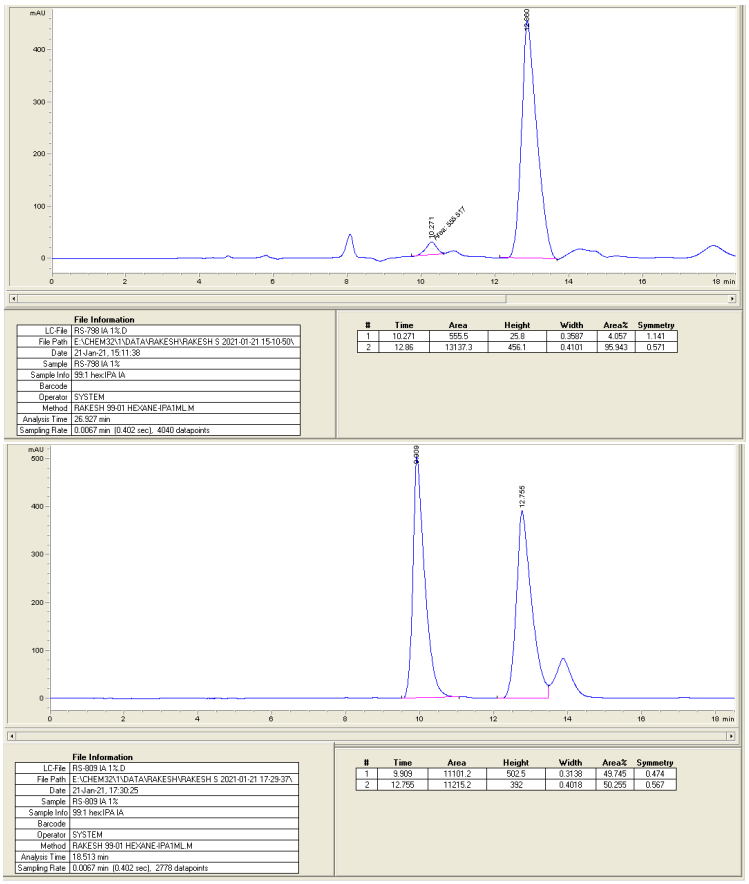


HPLC

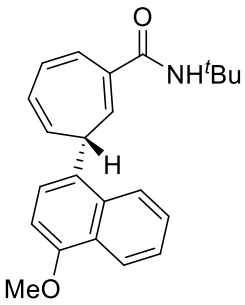


***(R)-N*-(tert-butyl)-3-(p-tolyl)cycloheptа-1,4,6-triene-1-carboxamide (4f)**

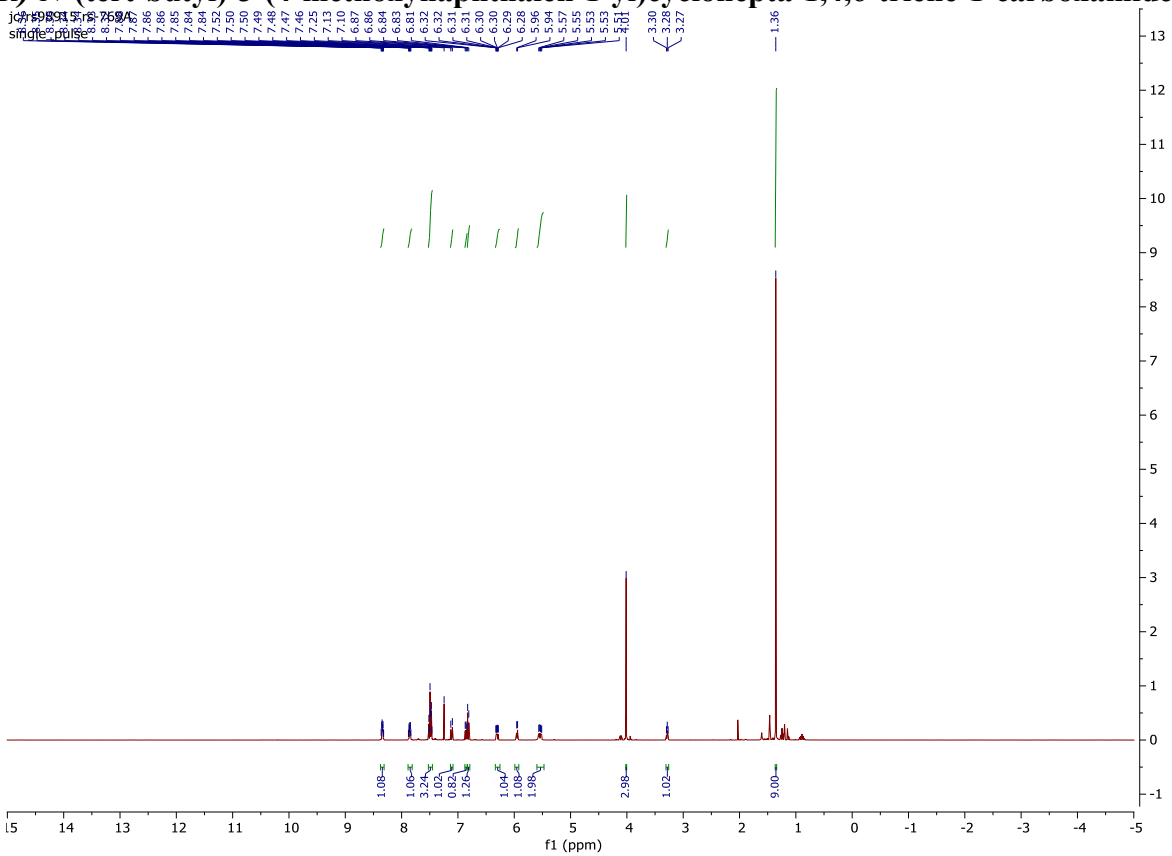
Analytical HPLC (IA Column), eluting with hexane- IPA (99:1), showed it to consist of a 4:96 mixture of two enantiomers with retention times 10.271 mins(minor) and 12.86 mins (major), respectively.



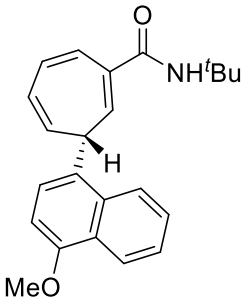
^{1}H NMR



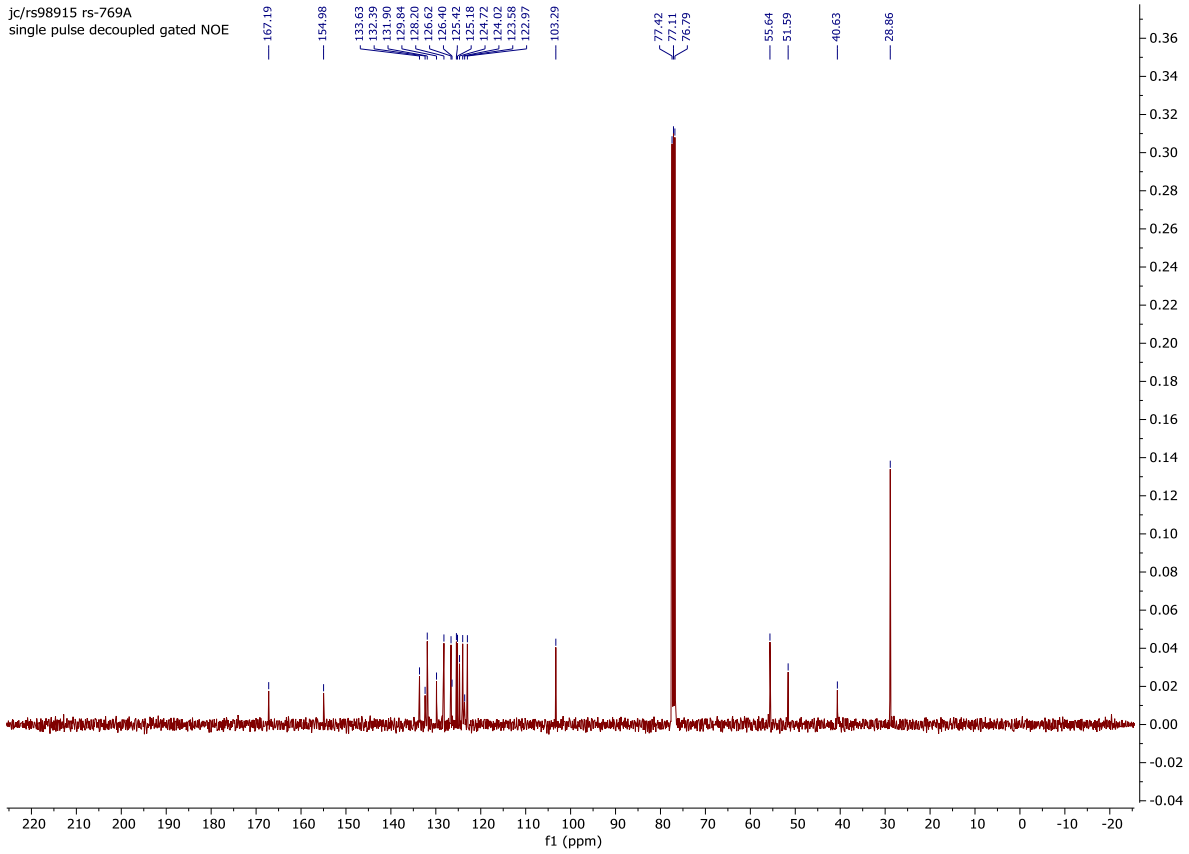
***(R)-N*-(tert-butyl)-3-(4-methoxynaphthalen-1-yl)cyclohepta-1,4,6-triene-1-carboxamide (4g)**



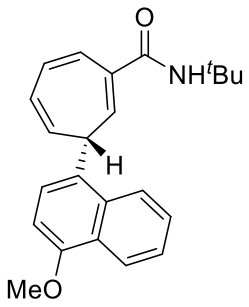
^{13}C NMR



***(R)-N*-(tert-butyl)-3-(4-methoxynaphthalen-1-yl)cyclohepta-1,4,6-triene-1-carboxamide (4g)**

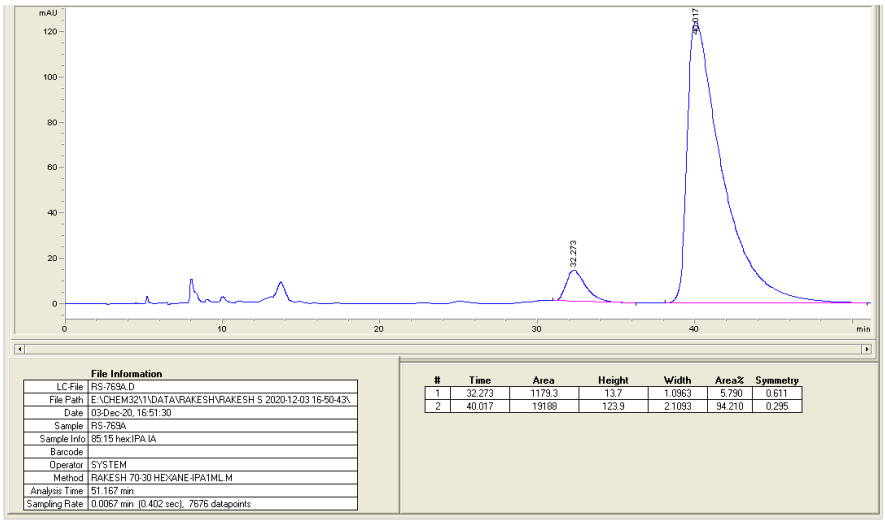


HPLC



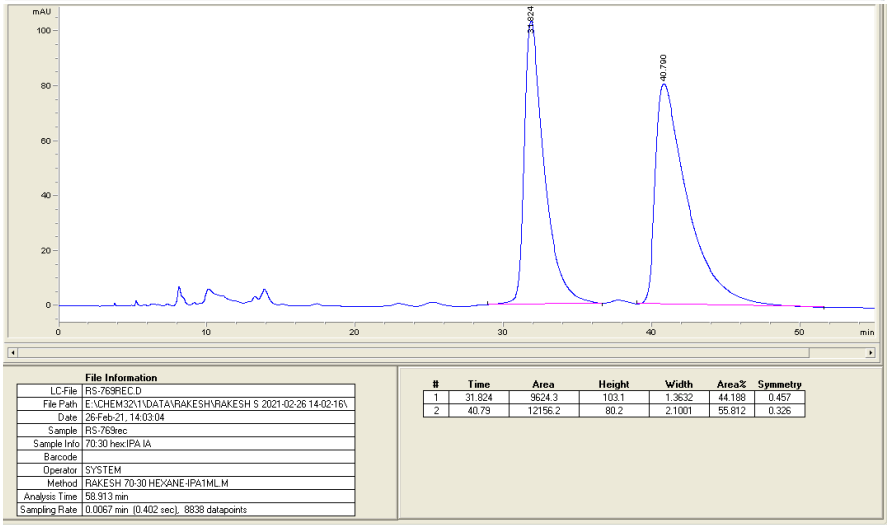
***(R)-N*-(tert-butyl)-3-(4-methoxynaphthalen-1-yl)cyclohepta-1,4,6-triene-1-carboxamide (4g)**

Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (15:85), showed it to consist of a 5.79:94.210 mixture of two enantiomers with retention times 32.273 mins (minor) and 40.017 mins (major).



File Information	
LC-File	RS-769A.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-12-03 16-50-43\
Date	03-Dec-20, 16:51:30
Sample	RS-769A
Sample Info	85:15 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 70-30 HEXANE-IPA1ML.M
Analysis Time	51.167 min
Sampling Rate	0.0067 min (0.402 sec), 7676 datapoints

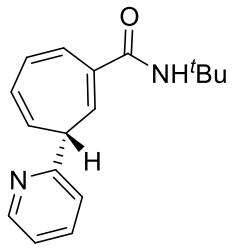
#	Time	Area	Height	Width	Area%	Symmetry
1	32.273	1179.3	13.7	1.0963	5.790	0.611
2	40.017	19188	123.9	2.1093	94.210	0.295



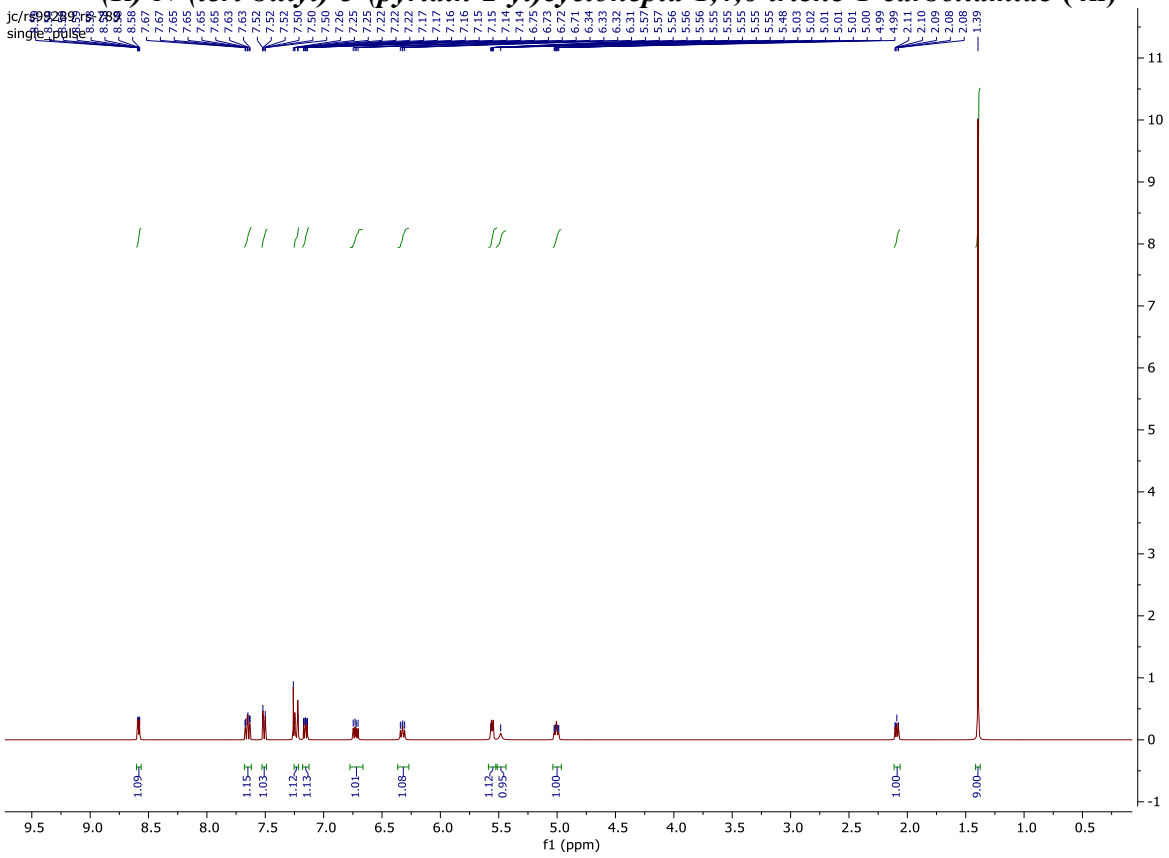
File Information	
LC-File	RS-769REC.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2021-02-26 14-02-16\
Date	26-Feb-21, 14:03:04
Sample	RS-769rec
Sample Info	70:30 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 70-30 HEXANE-IPA1ML.M
Analysis Time	58.913 min
Sampling Rate	0.0067 min (0.402 sec), 8838 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	31.824	9624.3	103.1	1.3632	44.188	0.457
2	40.79	12156.2	80.2	2.1001	55.812	0.326

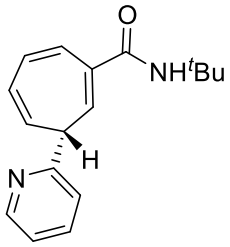
^{1}H NMR



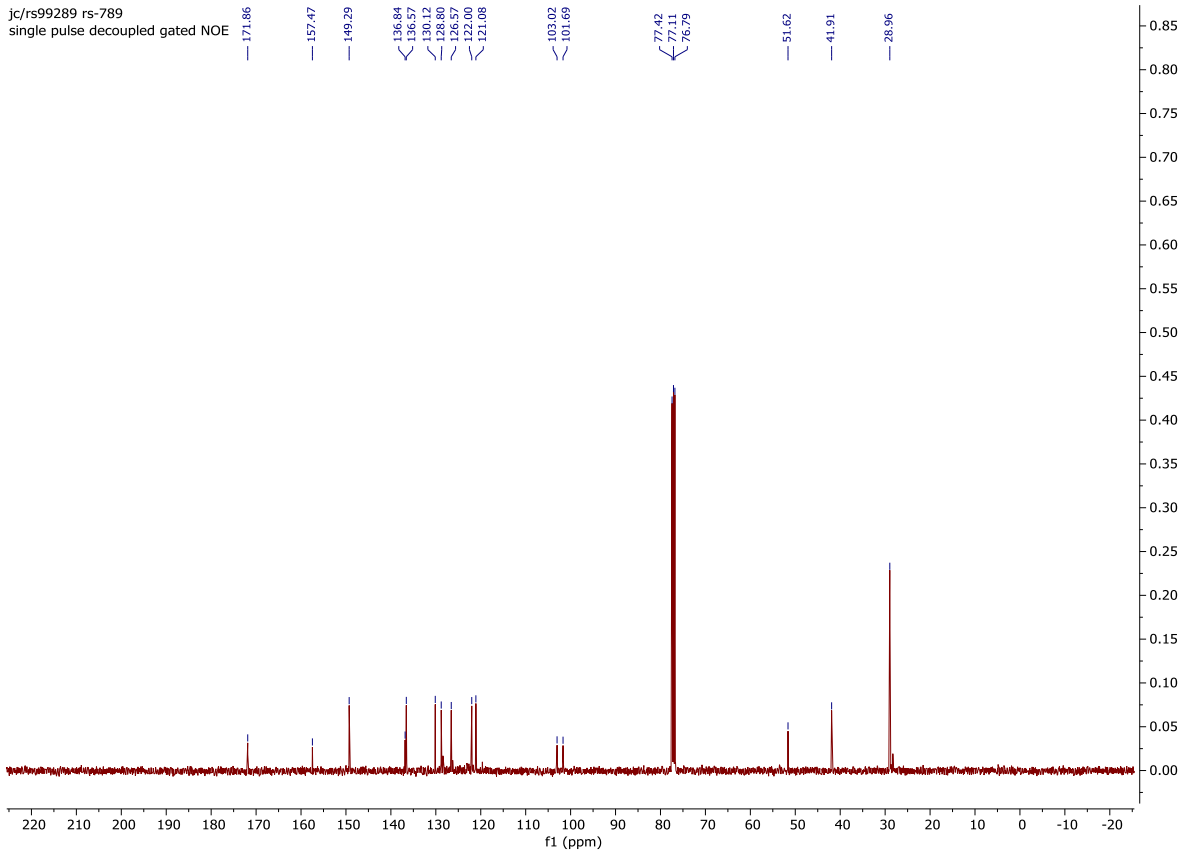
***(R)-N-(tert-butyl)-3-(pyridin-2-yl)cyclohepta-1,4,6-triene-1-carboxamide* (4h)**



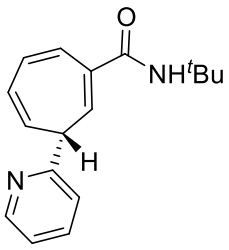
^{13}C NMR



***(R)-N-(tert-butyl)-3-(pyridin-2-yl)cyclohepta-1,4,6-triene-1-carboxamide* (4h)**

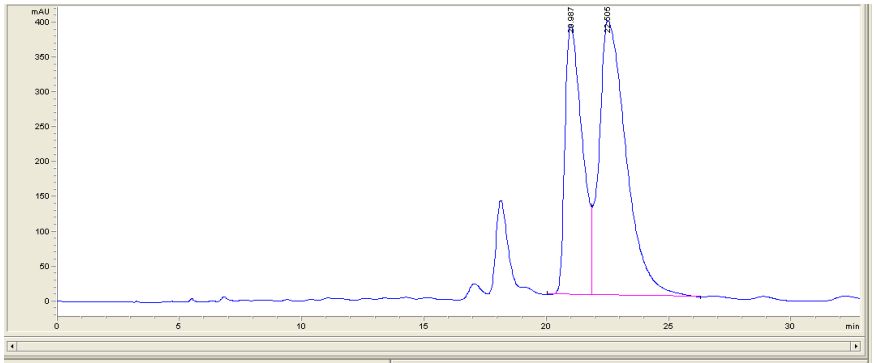


HPLC



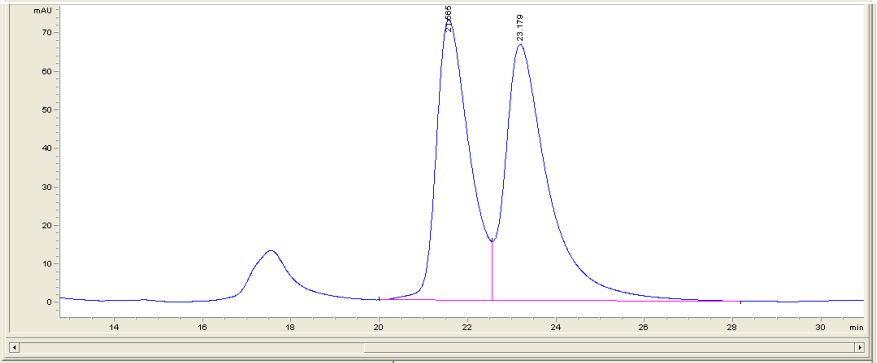
***(R)-N-(tert-butyl)-3-(pyridin-2-yl)cyclohepta-1,4,6-triene-1-carboxamide* (4h)**

Analytical HPLC (Chiral Regis Whelk O1), eluting with IPA–hexane (85:15), showed it to consist of a 39:61 mixture of two enantiomers with retention times 20.987 mins(minor) and 22.505 mins (major), respectively.



File Information	
LC-File	RS-789.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2021-01-11 17-41-22\
Date	11-Jan-21, 17:42:09
Sample	RS-789
Sample Info	85:15 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 85-15 HEXANE-IPA1ML.M
Analysis Time	32.82 min
Sampling Rate	0.0067 min (0.402 sec), 4924 datapoints

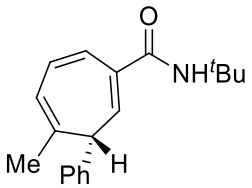
#	Time	Area	Height	Width	Area%	Symmetry
1	20.987	19095.3	387.6	0.7407	38.597	0.48
2	22.505	30378.1	394	1.1695	61.403	0.458



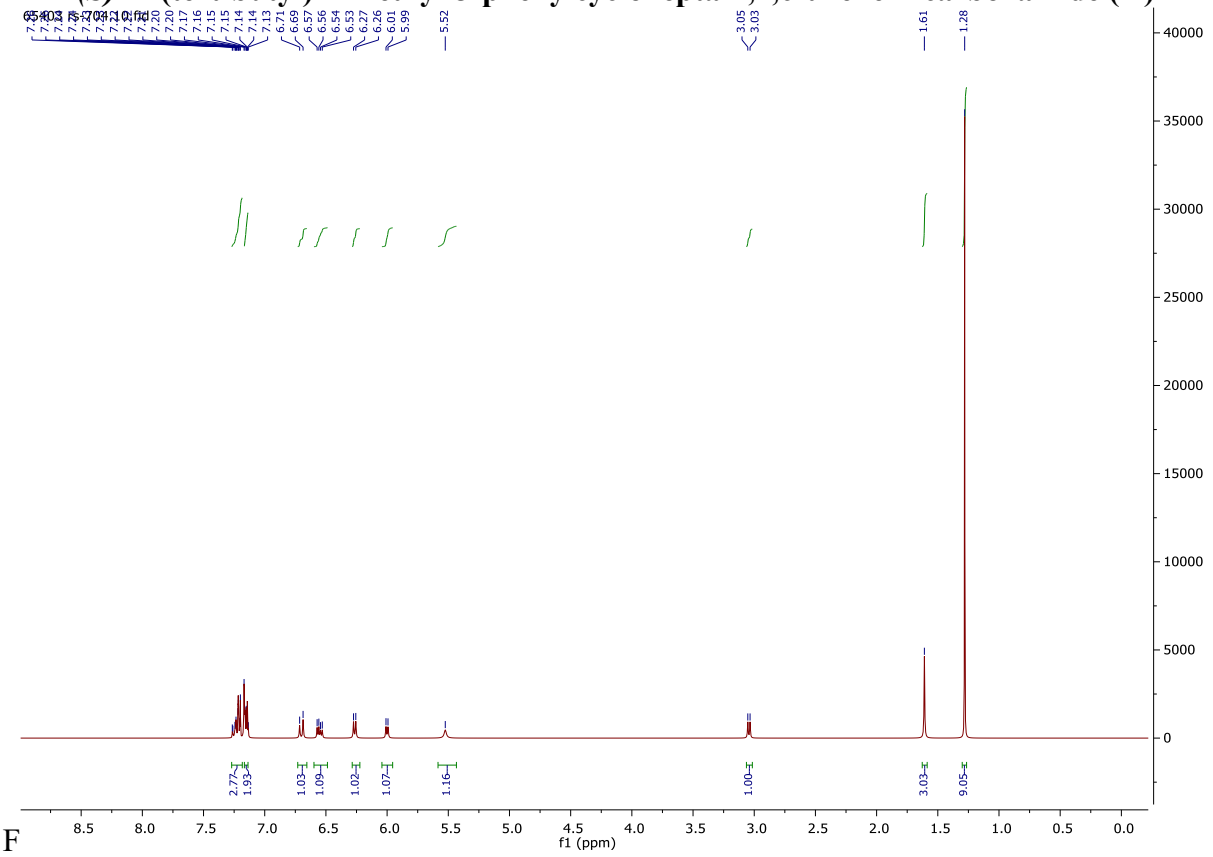
File Information	
LC-File	RS-782 15%.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-12-18 14-35-35\
Date	18-Dec-20, 14:36:23
Sample	RS-782 15%
Sample Info	70:30 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 85-15 HEXANE-IPA1ML.M
Analysis Time	30.967 min
Sampling Rate	0.0067 min (0.402 sec), 4646 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	21.565	3802.6	72.8	0.785	45.755	0.585
2	23.179	4508.1	66.5	0.9768	54.245	0.48

^{1}H NMR

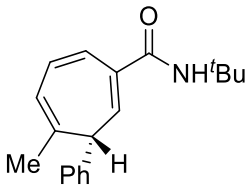


***(S)*-*N*-(tert-butyl)-4-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4i)**

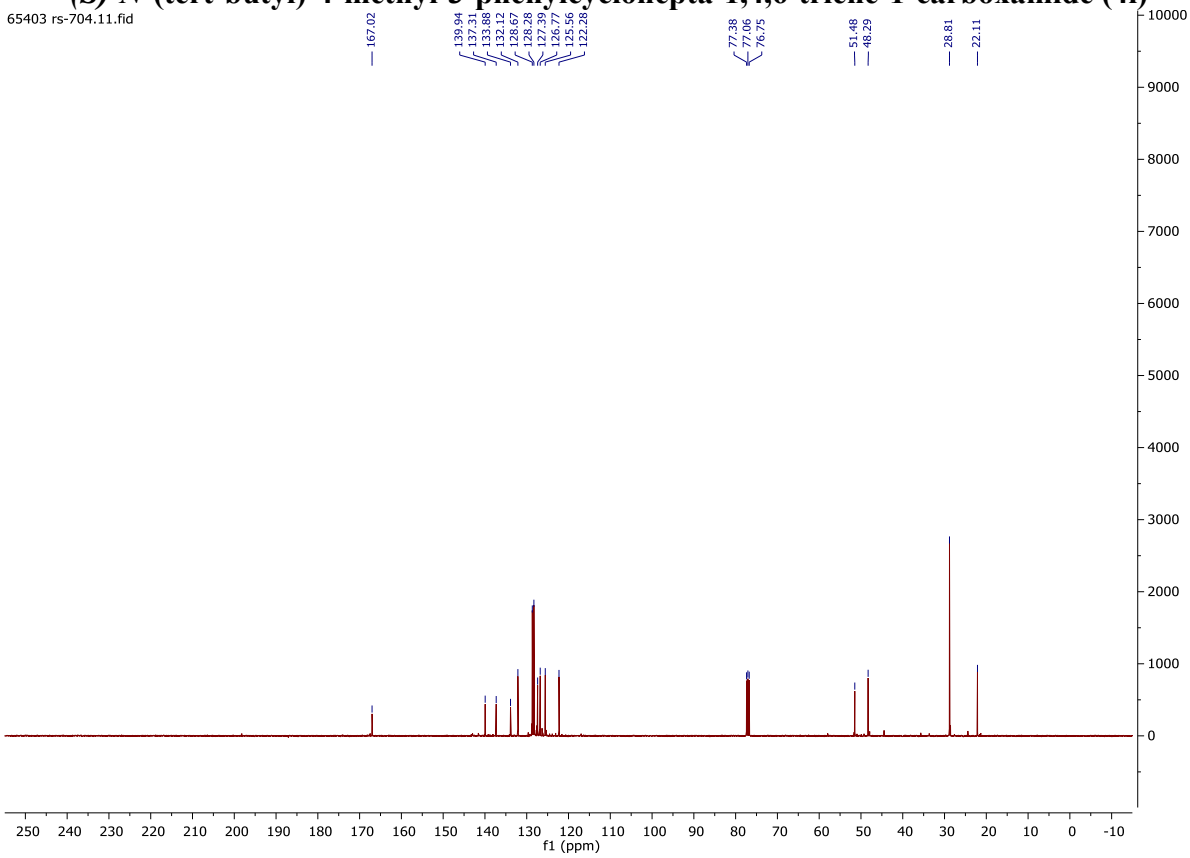


F

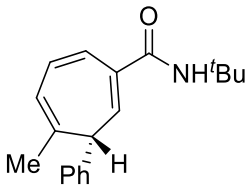
^{13}C NMR



(*S*)-*N*-(tert-butyl)-4-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4i)

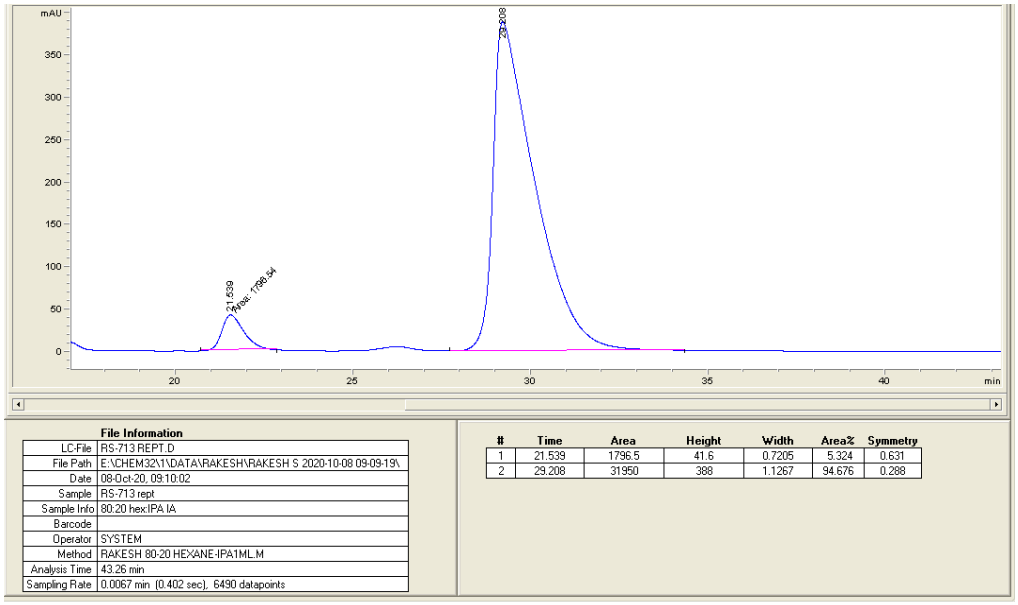


HPLC



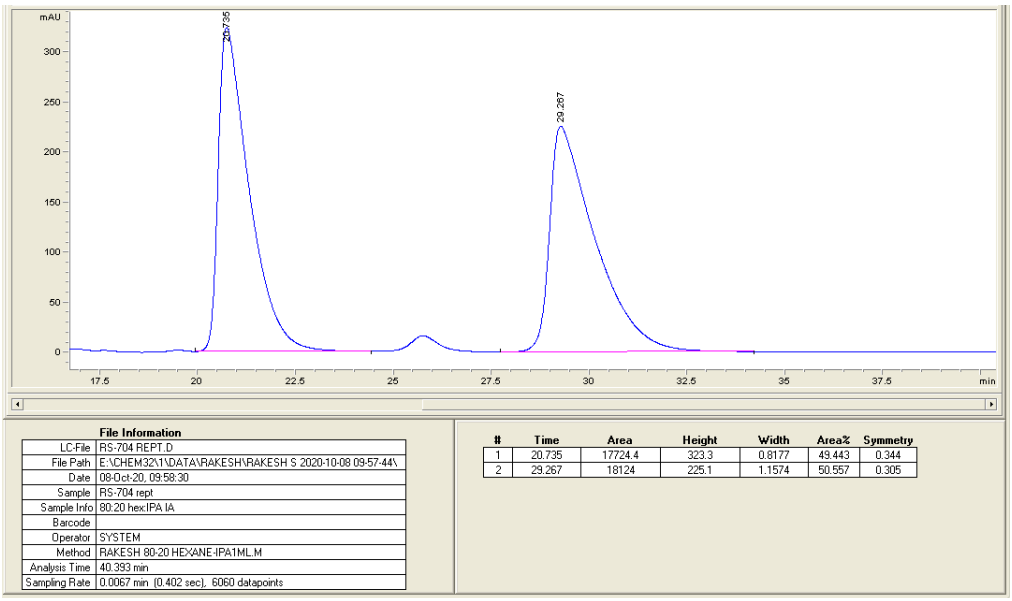
***(S)-N*-(tert-butyl)-4-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4i)**

Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane- IPA (70:30), showed it to consist of a 5.3: 94:6 mixture of two enantiomers with retention times 21.53 mins (minor) and 29.20 mins (major) respectively.



File Information	
LC-File	RS-713 REPT.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-10-08 09-09-19\
Date	08-Oct-20, 09:10:02
Sample	RS-713 rept
Sample Info	80:20 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 80-20 HEXANE-IPA1ML.M
Analysis Time	43.26 min
Sampling Rate	0.0067 min (0.402 sec), 6490 datapoints

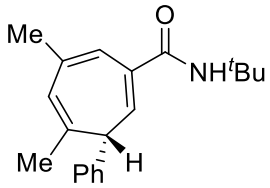
#	Time	Area	Height	Width	Area%	Symmetry
1	21.539	1796.5	41.6	0.7205	5.324	0.631
2	29.208	31950	388	1.1267	94.676	0.288



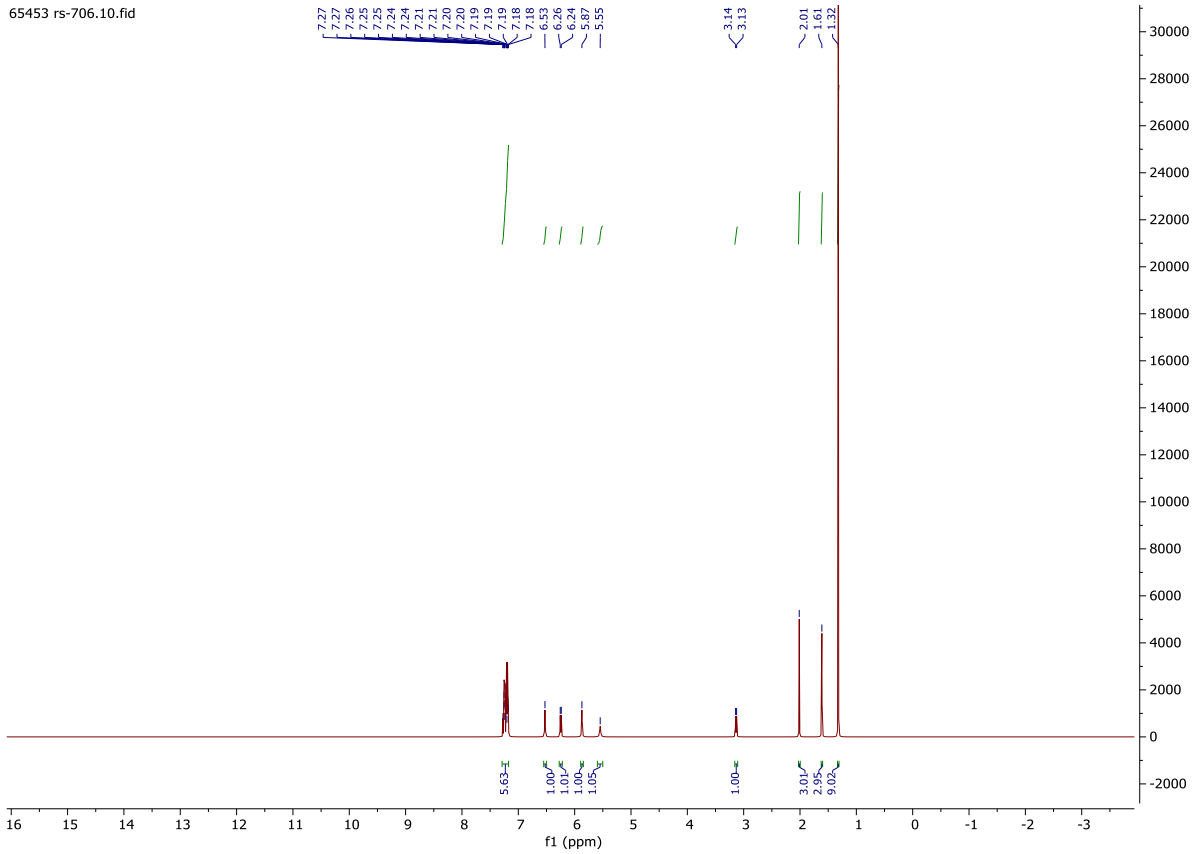
File Information	
LC-File	RS-704 REPT.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-10-08 09-57-44\
Date	08-Oct-20, 09:58:30
Sample	RS-704 rept
Sample Info	80:20 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 80-20 HEXANE-IPA1ML.M
Analysis Time	40.393 min
Sampling Rate	0.0067 min (0.402 sec), 6060 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	20.735	17724.4	323.3	0.8177	49.443	0.344
2	29.267	18124	225.1	1.1574	50.557	0.305

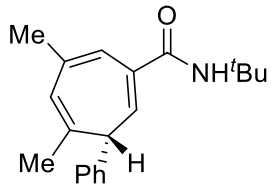
^{1}H NMR



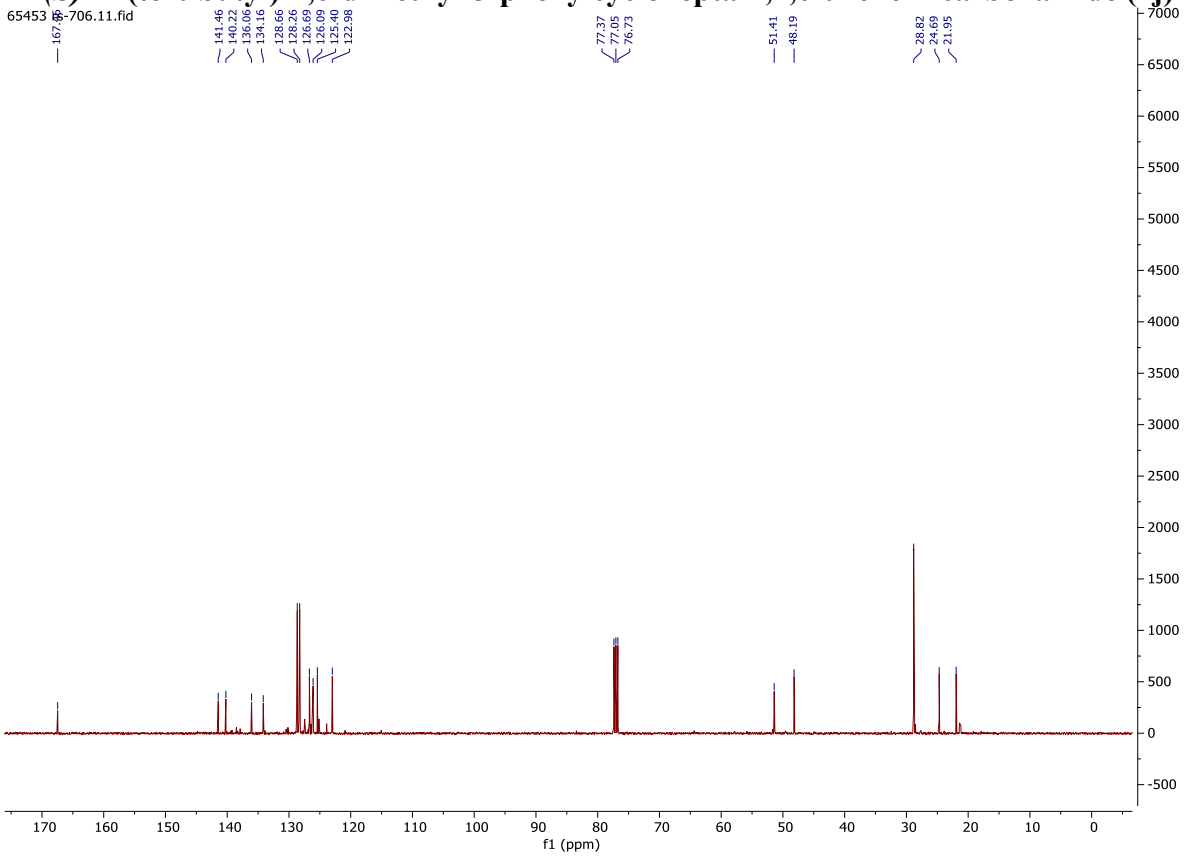
***(S)*-*N*-(tert-butyl)-4,6-dimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4j)**


65453 rs-706.10.fid
7.27
7.27
7.26
7.25
7.25
7.24
7.24
7.21
7.21
7.20
7.20
7.19
7.19
7.19
7.18
7.18
6.53
6.26
6.24
5.87
5.55
3.14
3.13
2.01
1.61
1.32
5.63
1.00
1.01
1.00
1.05
1.00
3.01
2.95
9.02
f1 (ppm)

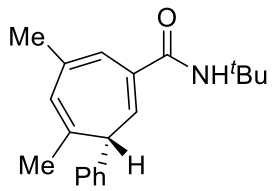
^{13}C NMR



***(S)-N*-(tert-butyl)-4,6-dimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4j)**

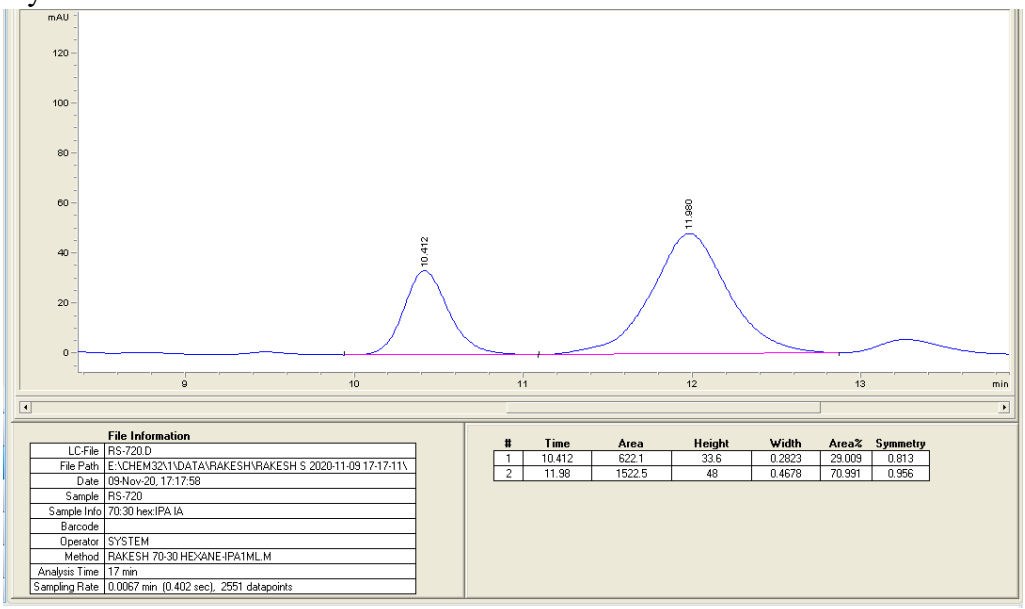


HPLC



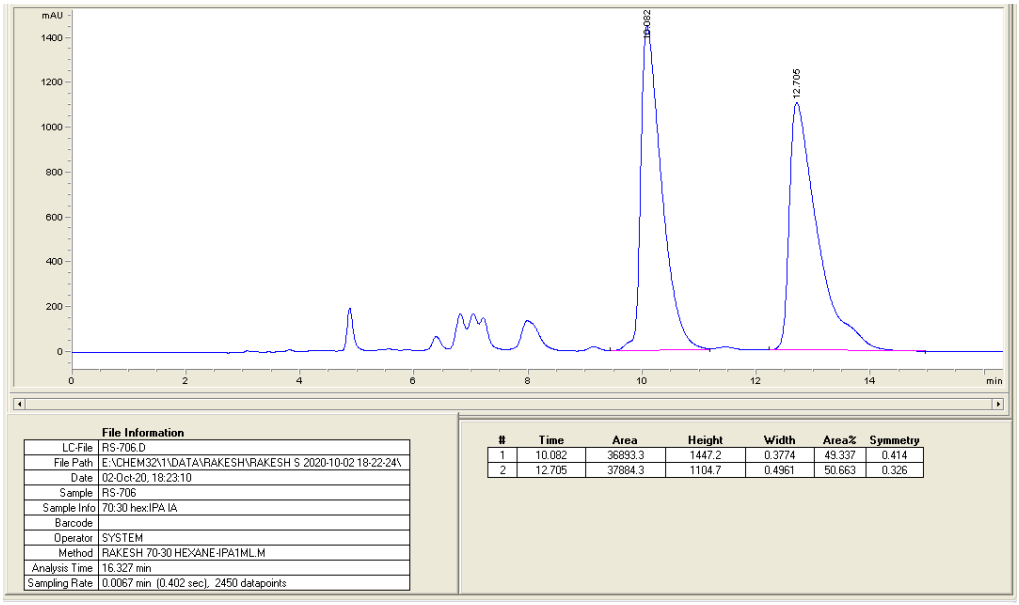
***(S)-N*-(tert-butyl)-4,6-dimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4j)**

Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (70:30), showed it to consist of a 29.00: 70.99 mixture of two enantiomers with retention times tR = 10.41 and 11.99 respectively.



File Information	
LC-File	RS-720.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-11-09 17-17-11\
Date	09-Nov-20, 17:17:58
Sample	RS-720
Sample Info	70:30 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 70-30 HEXANE-IPA1ML.M
Analysis Time	17 min
Sampling Rate	0.0067 min (0.402 sec), 2551 datapoints

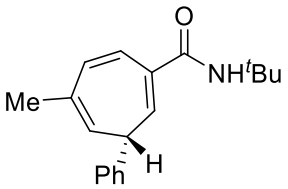
#	Time	Area	Height	Width	Area%	Symmetry
1	10.412	622.1	33.6	0.2823	29.009	0.813
2	11.98	1522.5	48	0.4678	70.991	0.956



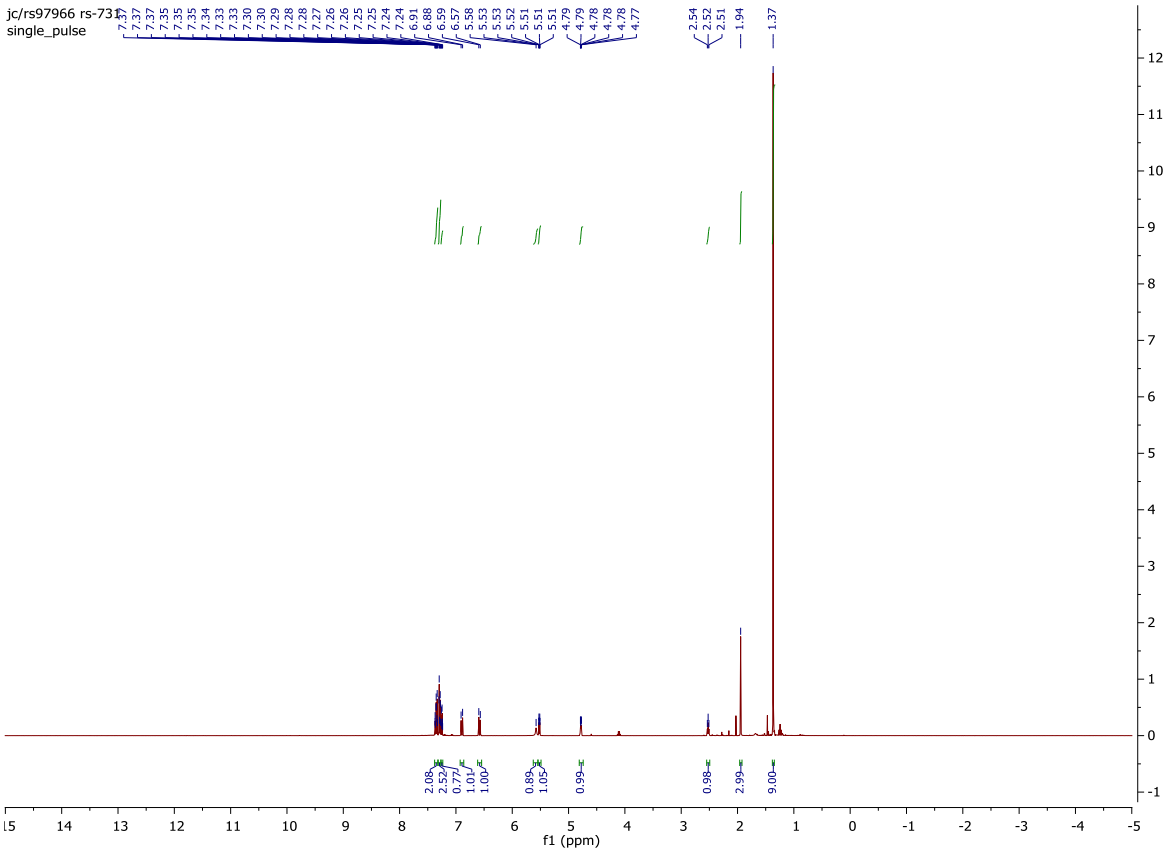
File Information	
LC-File	RS-706.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-10-02 18-22-24\
Date	02-Oct-20, 18:23:10
Sample	RS-706
Sample Info	70:30 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 70-30 HEXANE-IPA1ML.M
Analysis Time	16.327 min
Sampling Rate	0.0067 min (0.402 sec), 2450 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	10.082	36893.3	1447.2	0.3774	49.337	0.414
2	12.705	37884.3	1104.7	0.4961	50.663	0.326

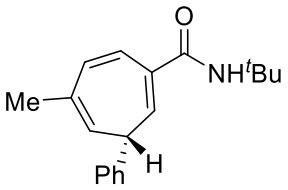
^{1}H NMR



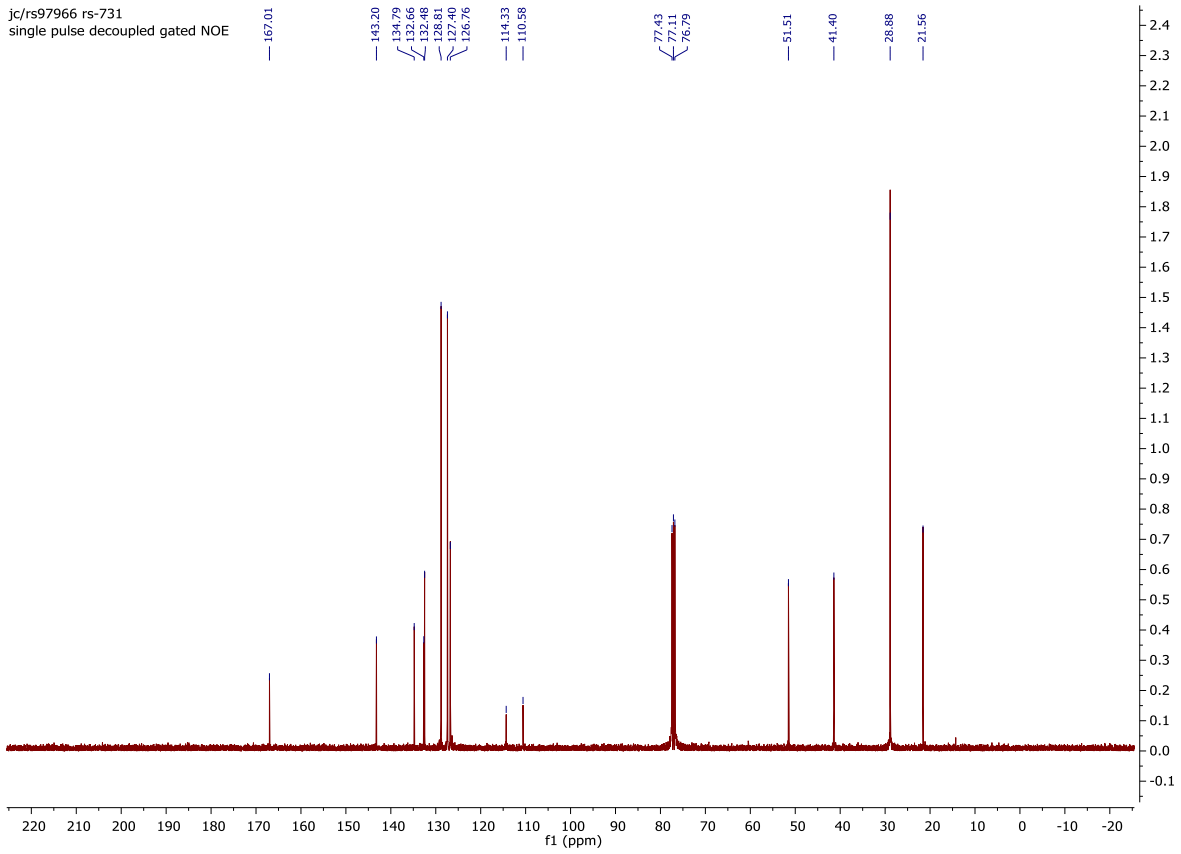
***(R)-N*-(tert-butyl)-5-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4k)**



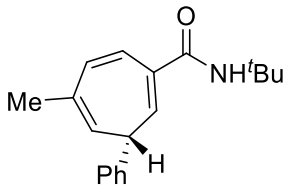
^{13}C NMR



***(R)-N*-(tert-butyl)-5-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4k)**



HPLC

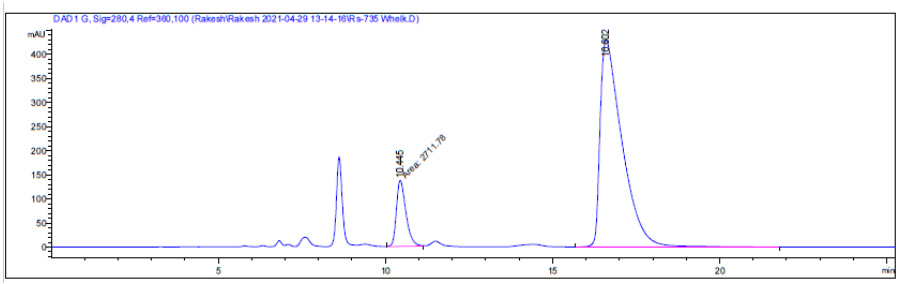


***(R)-N*-(tert-butyl)-5-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4k)**

Condition 1: Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (70:30), showed it to consist of a 12:88 mixture of two enantiomers with retention times 10.44 mins (minor) and 16.60 min (major) respectively.

Condition 2: Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (70:30), showed it to consist of a 20:80 mixture of two enantiomers with retention times 9.88 mins (minor) and 16.17 min (major) respectively.

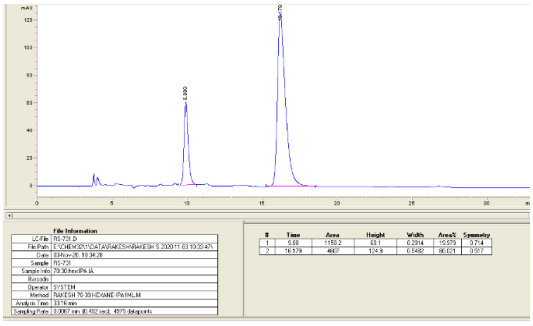
Condition 1:



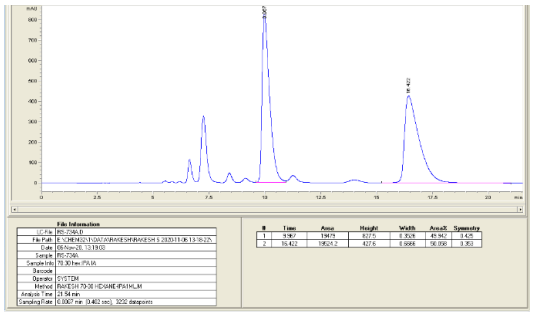
Signal 1: DAD1 G, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.445	MM	0.3299	2711.78003	137.00198	12.1189
2	16.602	BB	0.6740	1.96646e4	429.59396	87.8811
Totals :				2.23764e4	566.59595	

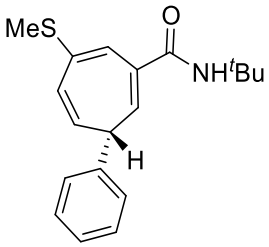
Condition 2:



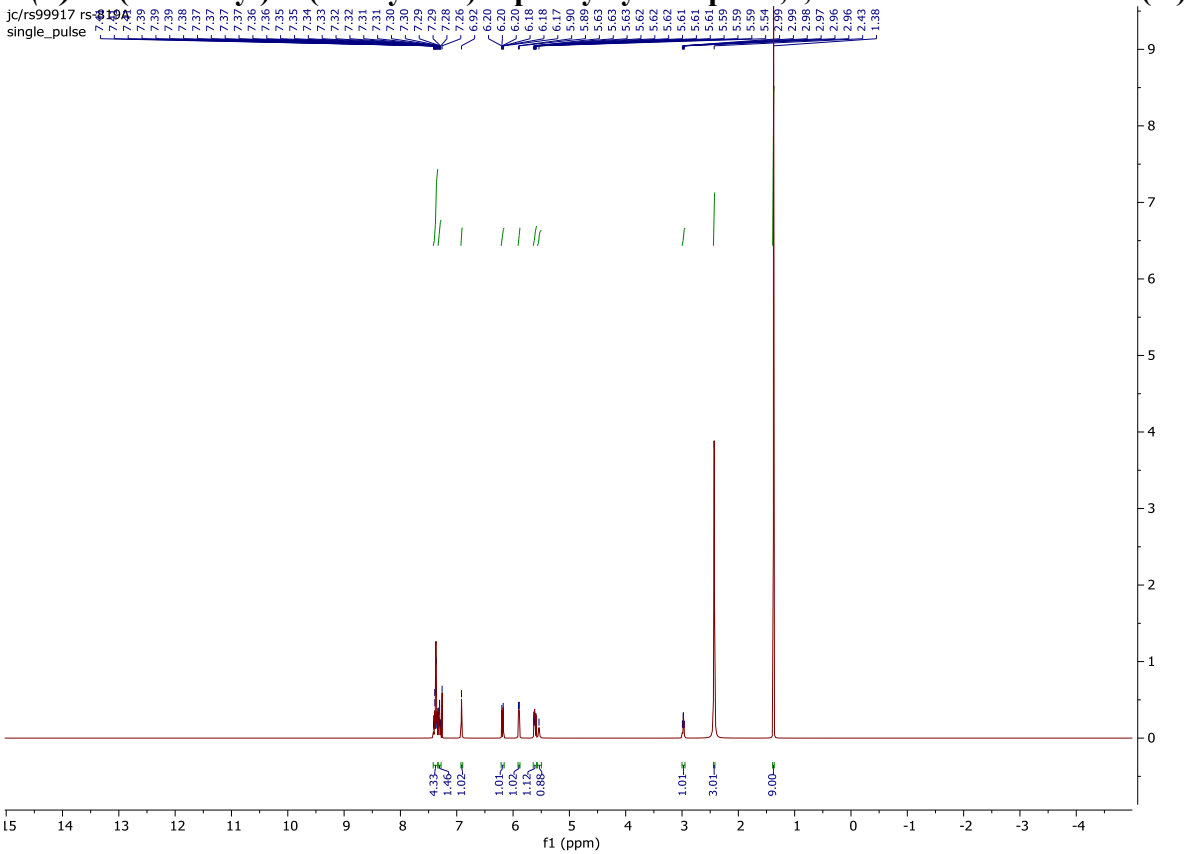
rec-



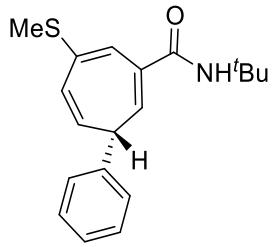
1H NMR



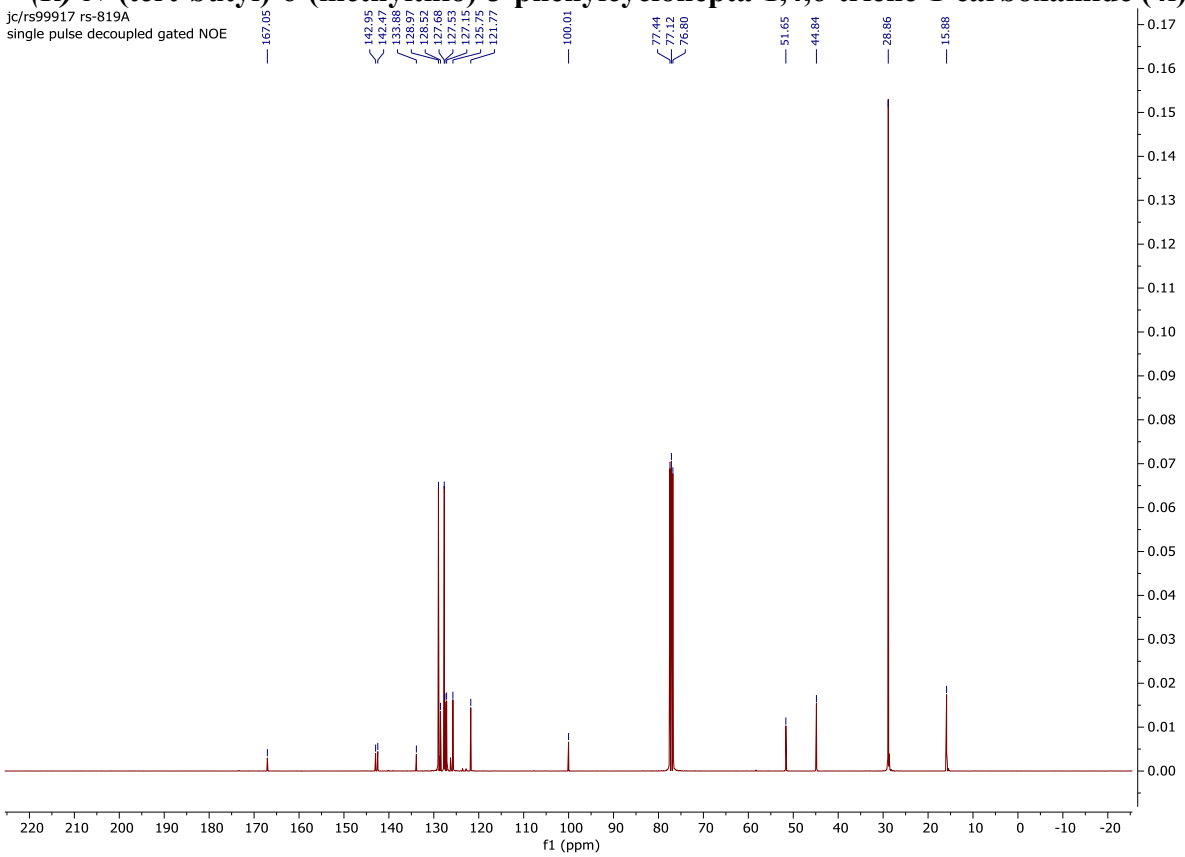
(*R*)-*N*-(tert-butyl)-6-(methylthio)-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4l)



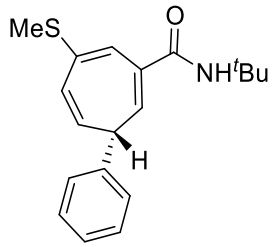
^{13}C NMR



***(R)-N*-(tert-butyl)-6-(methylthio)-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4l)**

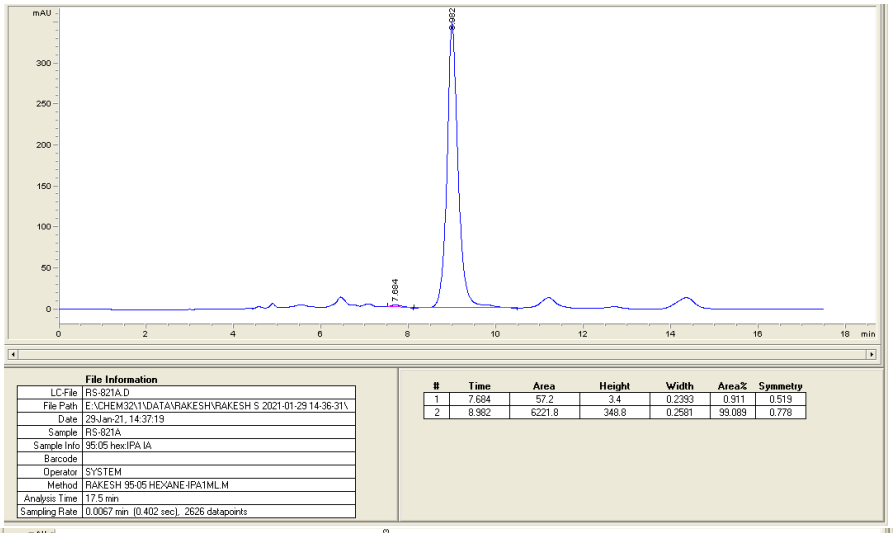


HPLC



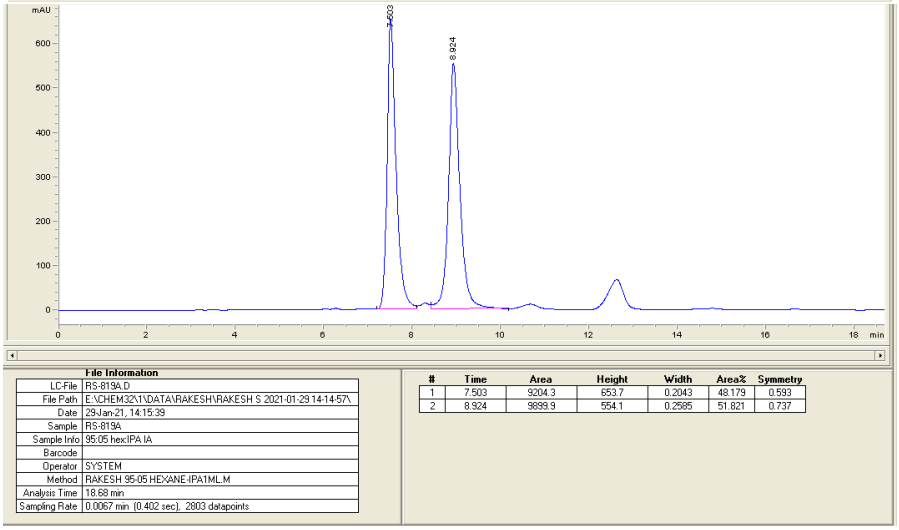
***(R)-N*-(tert-butyl)-6-(methylthio)-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4l)**

Analytical HPLC (IA Column), eluting with hexane- IPA (99:5), showed it to consist of a 1:99 mixture of two enantiomers with retention times 7.68 mins(minor) and 8.982 mins (major), flow rate 1mL/min.



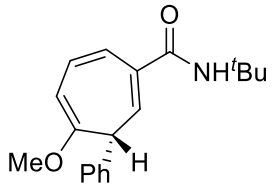
File Information	
LC-File	RS-821A.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2021-01-29 14-36-31\
Date	29-Jan-21, 14:37:19
Sample	RS-821A
Sample Info	95:05 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 95-05 HEXANE-IPA1ML.M
Analysis Time	17.5 min
Sampling Rate	0.0067 min (0.402 sec), 2626 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.684	57.2	3.4	0.2393	0.911	0.519
2	8.982	6221.8	348.8	0.2581	99.089	0.778

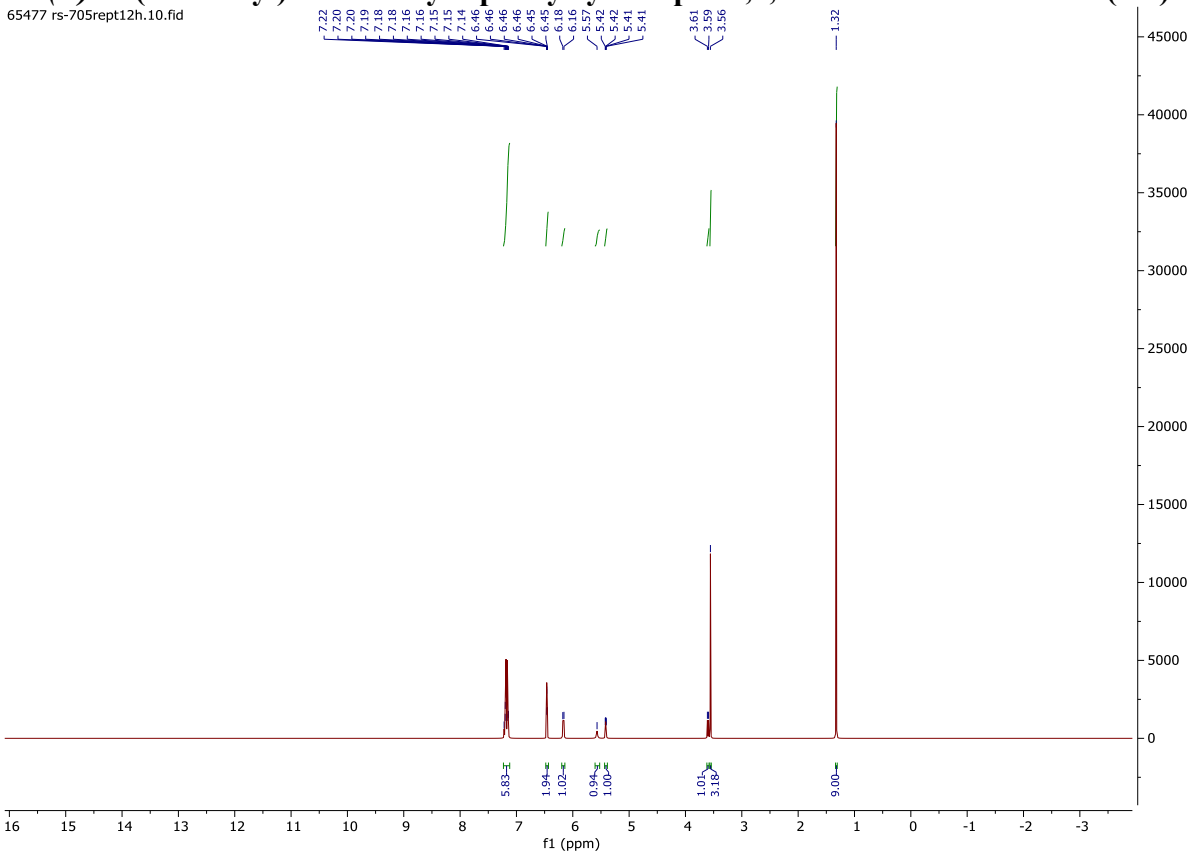


File Information	
LC-File	RS-819A.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2021-01-29 14-14-57\
Date	29-Jan-21, 14:15:39
Sample	RS-819A
Sample Info	95:05 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 95-05 HEXANE-IPA1ML.M
Analysis Time	18.68 min
Sampling Rate	0.0067 min (0.402 sec), 2803 datapoints

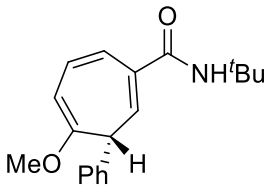
#	Time	Area	Height	Width	Area%	Symmetry
1	7.503	9204.3	653.7	0.2043	48.179	0.593
2	8.924	9899.9	554.1	0.2585	51.821	0.737



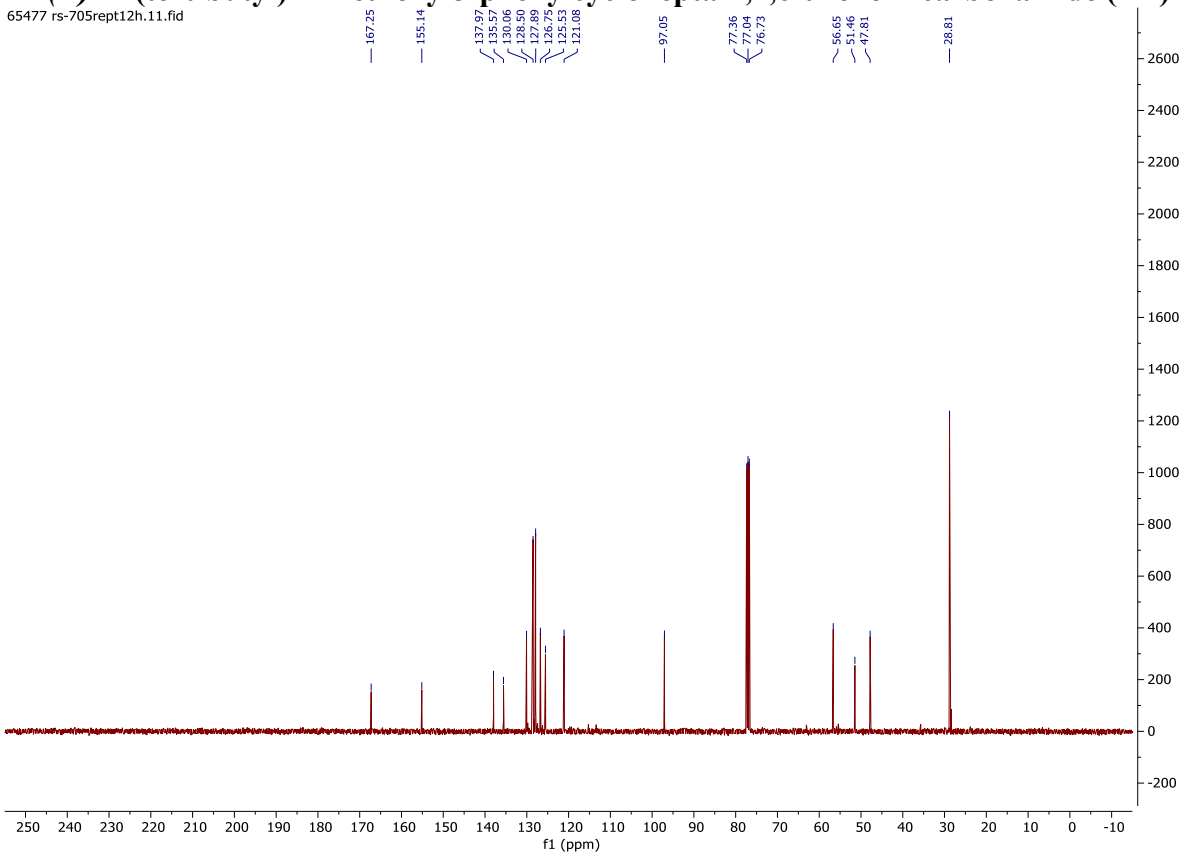
(*R*)-*N*-(tert-butyl)-4-methoxy-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4m)



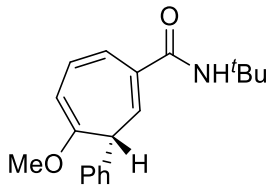
^{13}C NMR



***(R)-N*-(tert-butyl)-4-methoxy-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4m)**

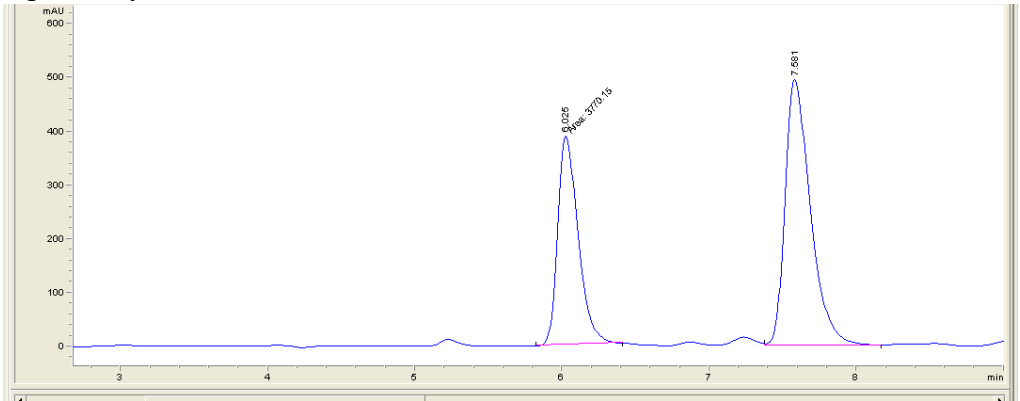


HPLC



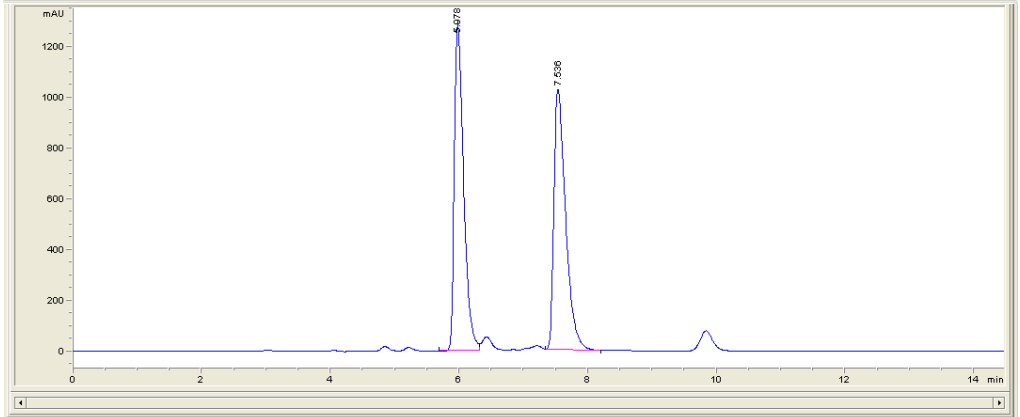
***(R)-N*-(tert-butyl)-4-methoxy-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (4m)**

Analytical HPLC (IA Column), eluting with hexane-IPA–(10:90), showed it to consist of a mixture of 39:61 two enantiomers with retention times tR = 6.025 mins (minor) and 7.58 mins (major) respectively.



File Information	
LC-File	RS-726 PREP.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-11-05 09-52-08\
Date	05-Nov-20, 09:52:55
Sample	RS-726 prep
Sample Info	90:10 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 90-10 HEXANE-IPA1ML.M
Analysis Time	21.88 min
Sampling Rate	0.0067 min (0.402 sec), 3283 datapoints

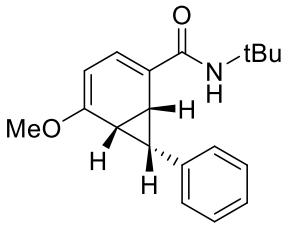
#	Time	Area	Height	Width	Area%	Symmetry
1	6.025	3770.2	388.7	0.1616	38.847	0.667
2	7.581	5935	494	0.1842	61.153	0.587



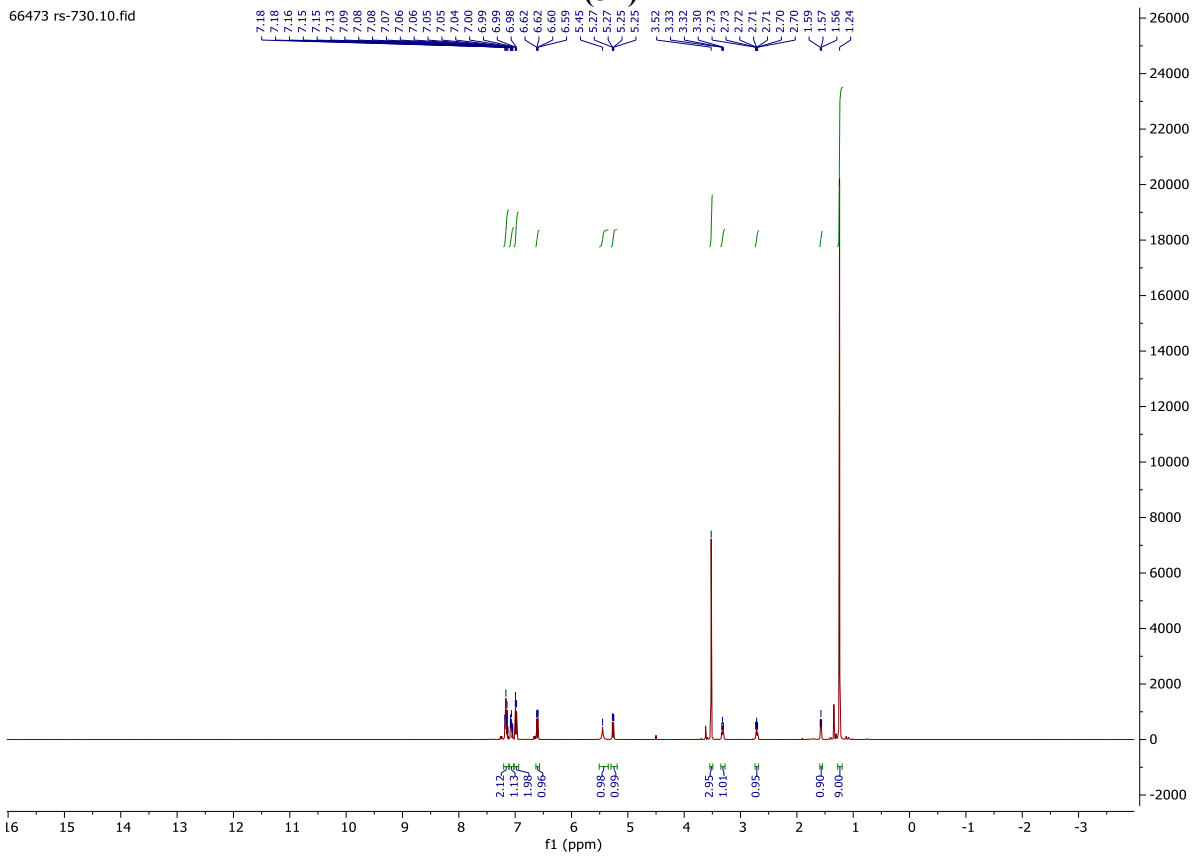
File Information	
LC-File	RS-705A PREP.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-11-05 09-32-20\
Date	05-Nov-20, 09:33:12
Sample	RS-705A prep
Sample Info	90:10 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 90-10 HEXANE-IPA1ML.M
Analysis Time	14.473 min
Sampling Rate	0.0067 min (0.402 sec), 2172 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	5.978	12965.2	1286.9	0.1535	49.941	0.533
2	7.536	12996	1027.2	0.1916	50.059	0.494

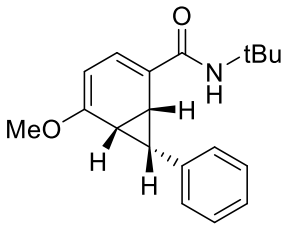
^{1}H NMR



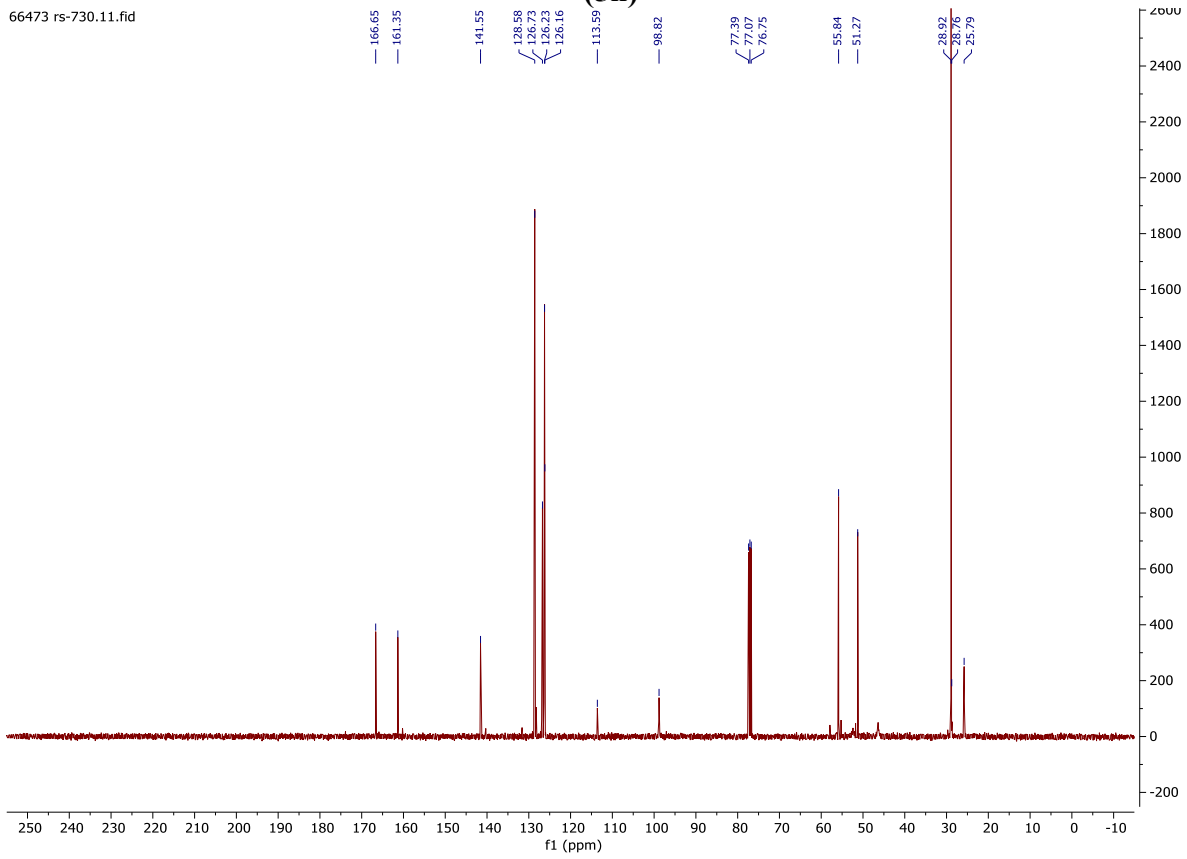
(1*R*,6*S*,7*S*)-*N*-(tert-butyl)-5-methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (5n)



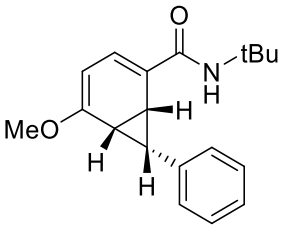
^{13}C NMR



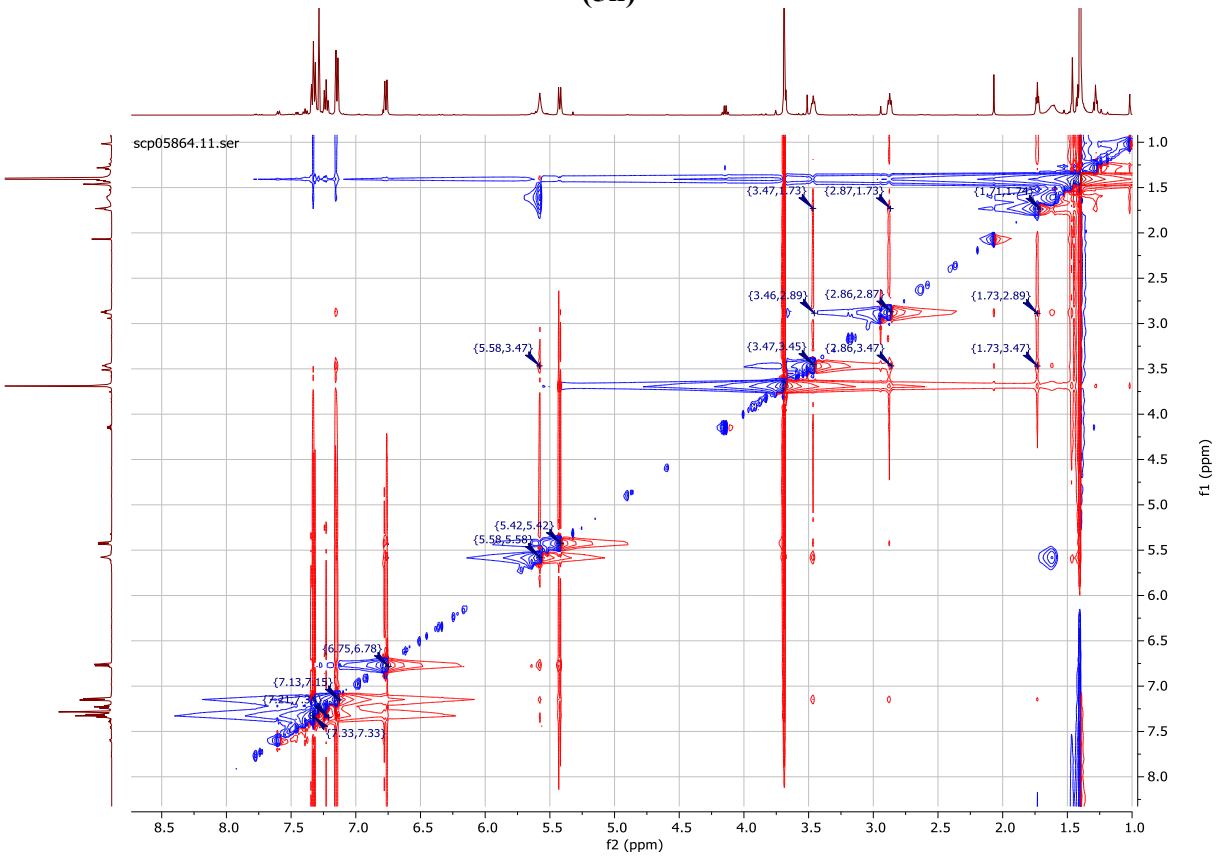
(1*R*,6*S*,7*S*)-*N*-(tert-butyl)-5-methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (5n)



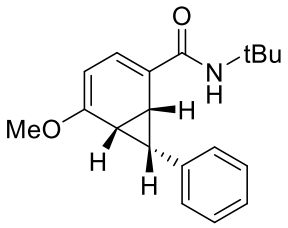
NOSY



(1*R*,6*S*,7*S*)-*N*-(tert-butyl)-5-methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (5n)

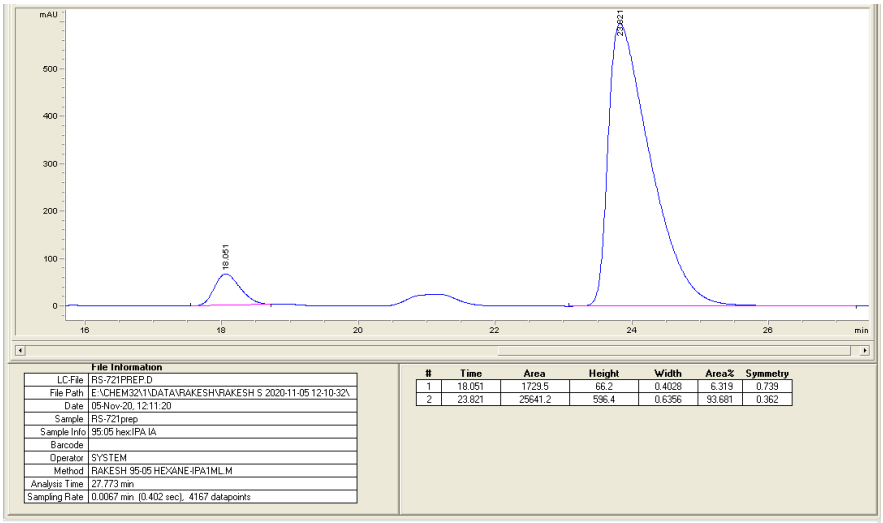


HPLC



(1*R*,6*S*,7*S*)-*N*-(tert-butyl)-5-methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide 5n)

Analytical HPLC (IA Column), eluting with hexane-IPA (95:5), showed it to consist of a 6:94 mixture of two enantiomers with retention times 18.05 mins (minor) and 23.82 mins (major) respectively.



File Information

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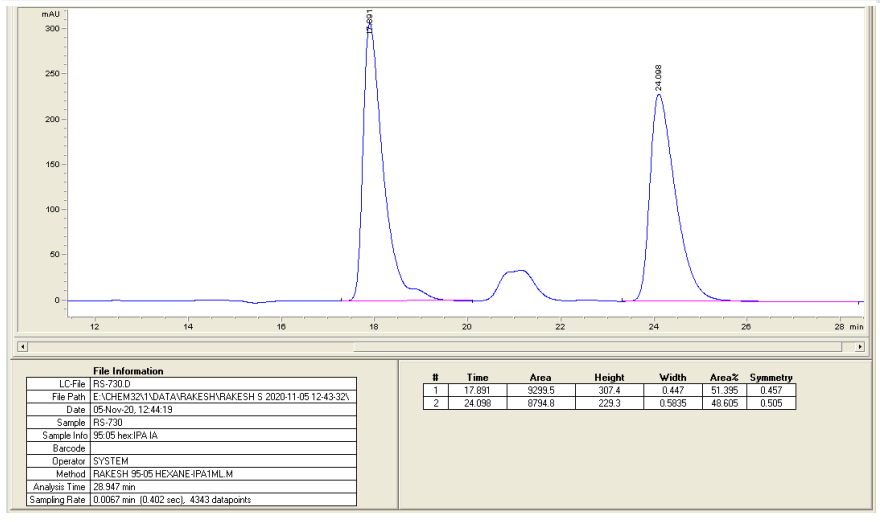
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-11-05 12-10-32\
Date	05-Nov-20, 12:11:20
Sample	RS-721prep
Sample Info	95:05 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 95-05 HEXANE-IPA1ML.M
Analysis Time	27.773 min
Sampling Rate	0.0067 min (0.402 sec), 4167 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	18.051	1729.5	66.2	0.4028	6.319	0.739
2	23.821	25641.2	596.4	0.6356	93.681	0.362

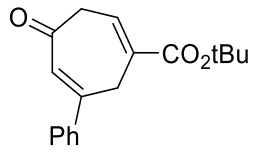


File Information

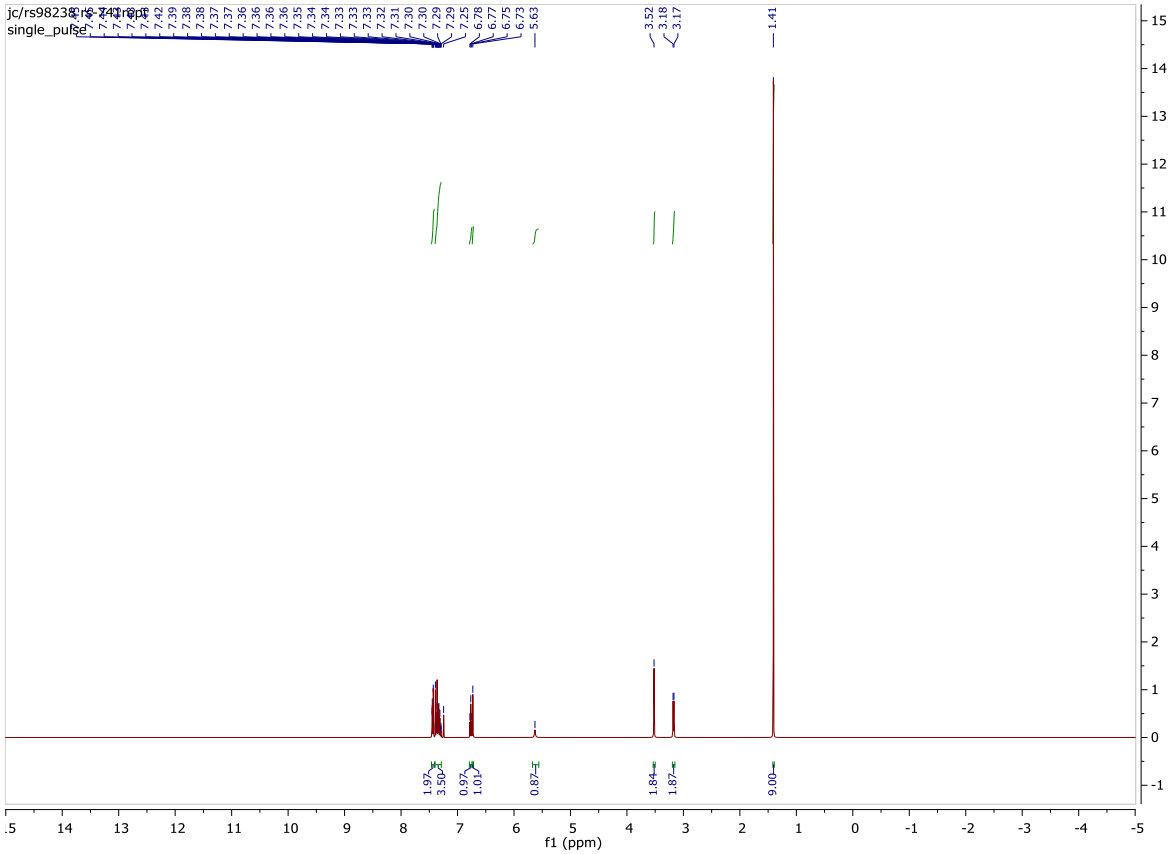
LC-File	RS-730.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-11-05 12-43-32\
Date	05-Nov-20, 12:44:19
Sample	RS-730
Sample Info	95:05 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 95-05 HEXANE-IPA1ML.M
Analysis Time	28.947 min
Sampling Rate	0.0067 min (0.402 sec), 4343 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	17.891	9299.5	307.4	0.447	51.395	0.457
2	24.098	8794.8	229.3	0.5835	48.605	0.505

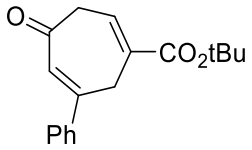
^{1}H NMR



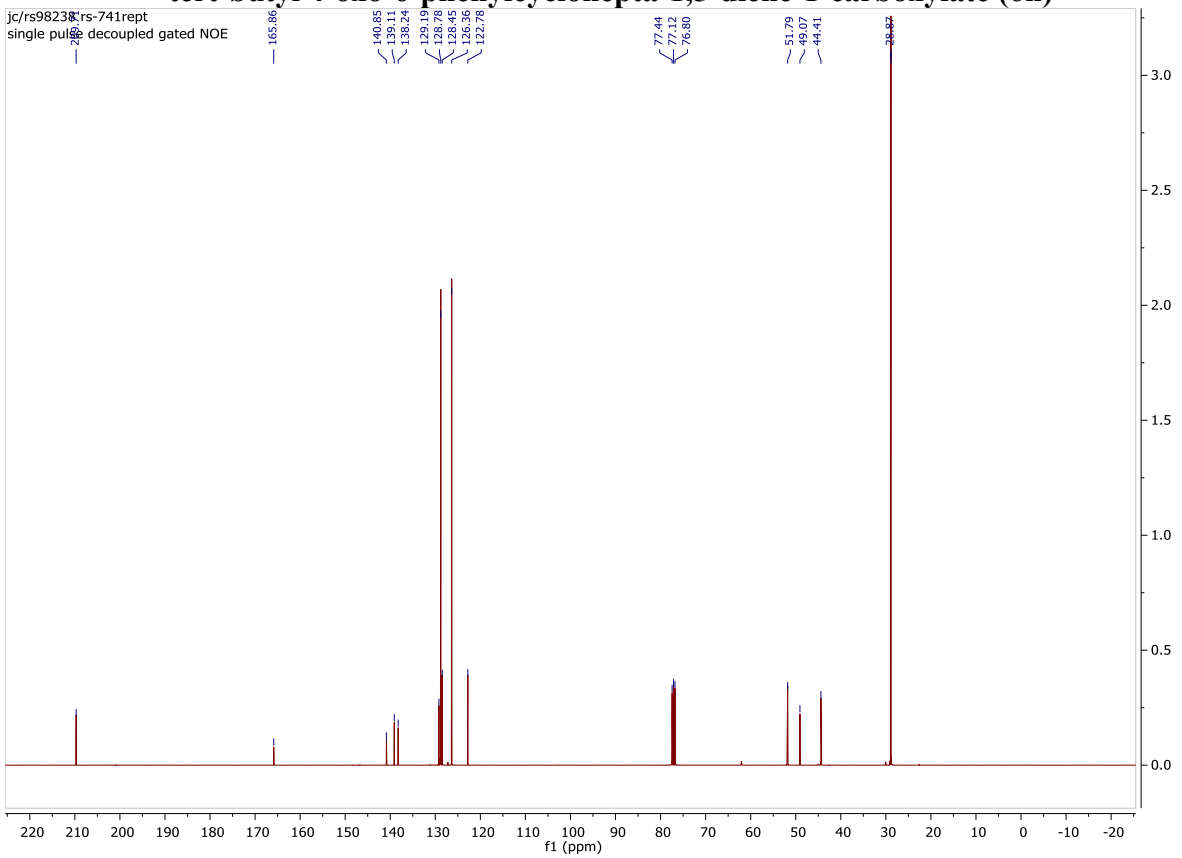
tert-butyl 4-oxo-6-phenylcyclohepta-1,5-diene-1-carboxylate (6n)



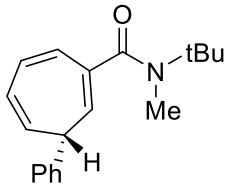
^{13}C NMR



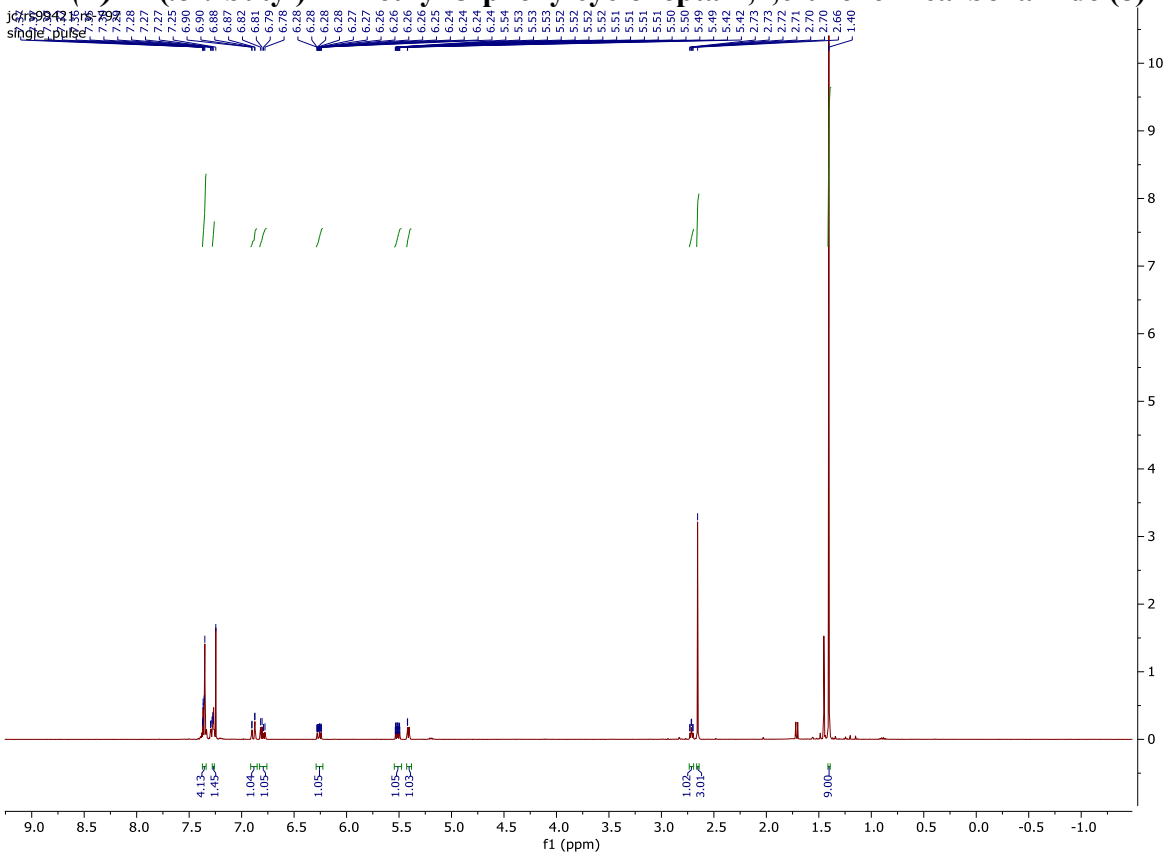
tert-butyl 4-oxo-6-phenylcyclohepta-1,5-diene-1-carboxylate (6n)



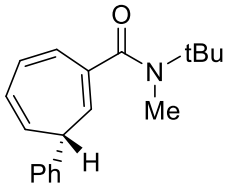
^{1}H NMR



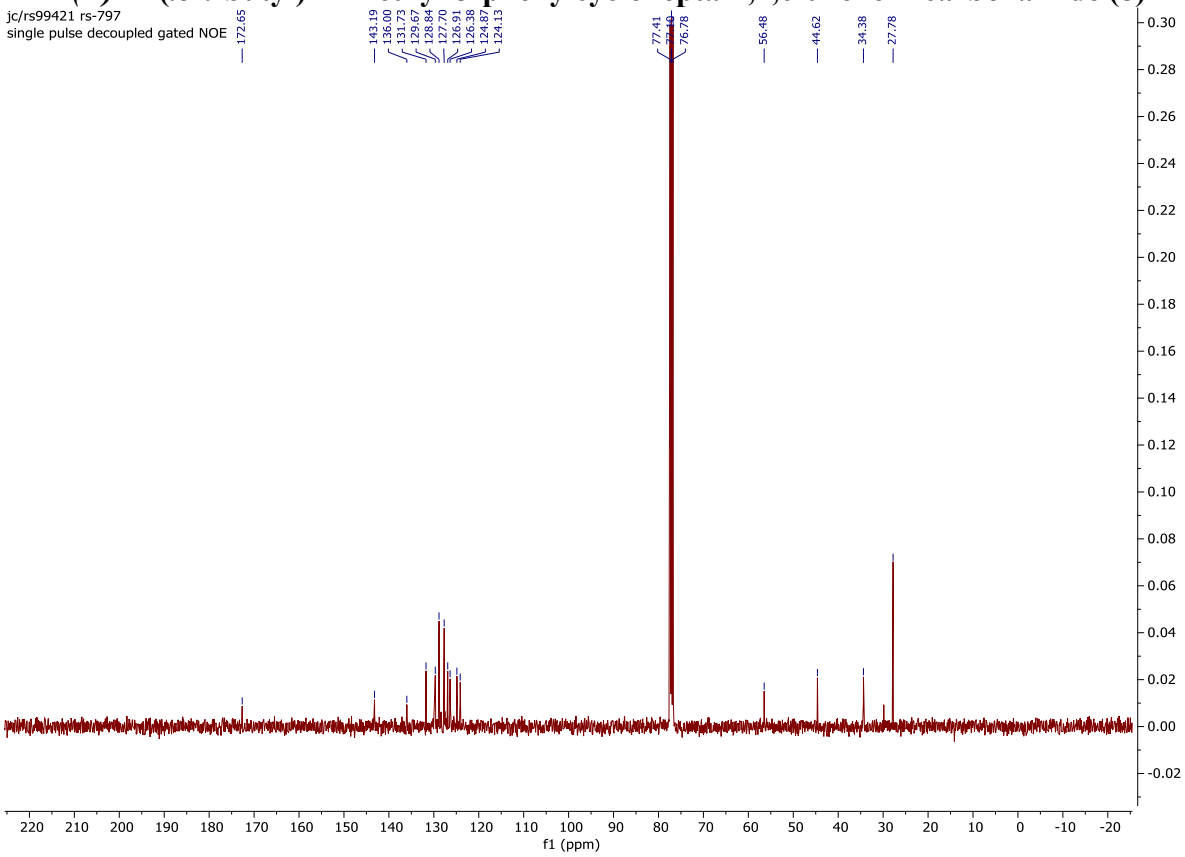
***(R)*-*N*-(*tert*-butyl)-*N*-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (8)**



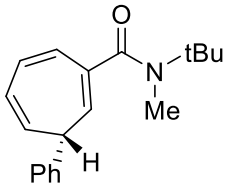
^{13}C NMR



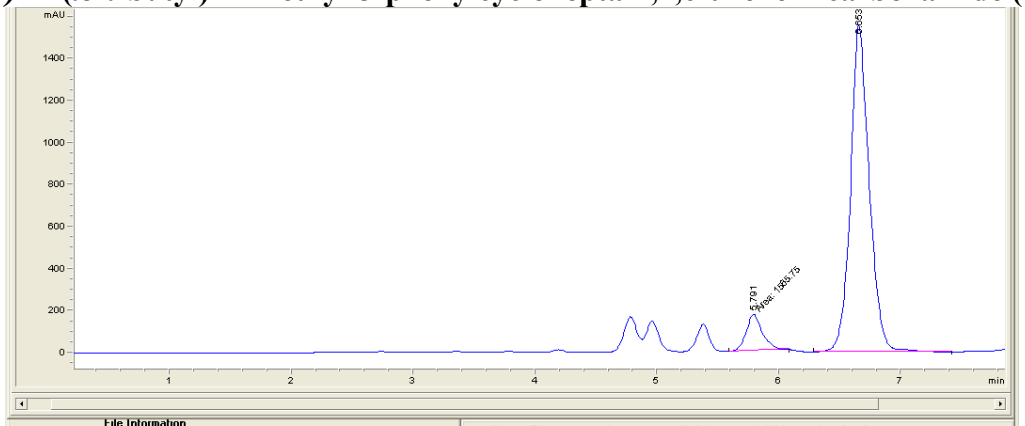
***(R)*-*N*-(*tert*-butyl)-*N*-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (8)**



HPLC



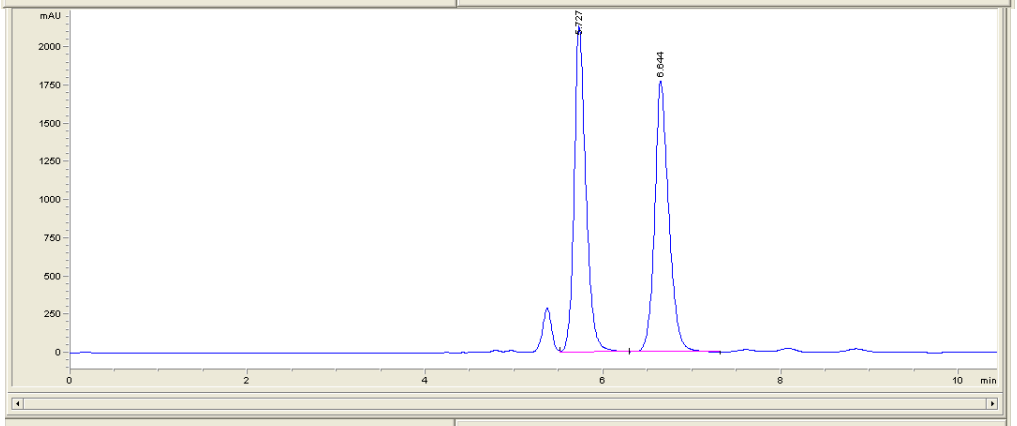
***(R)*-*N*-(*tert*-butyl)-*N*-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (8)**



File Information

LC-File	RS-842.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2021-02-24 16-51-33\
Date	24-Feb-21, 16:52:20
Sample	RS-842
Sample Info	95:05 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 95-05 HEXANE-IPA1ML.M
Analysis Time	8.92 min
Sampling Rate	0.0067 min (0.402 sec), 1339 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	5.791	1565.7	171.8	0.1519	8.590	0.807
2	6.653	16662.5	1554.9	0.157	91.410	0.759

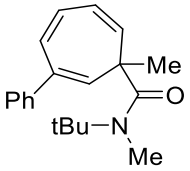


File Information

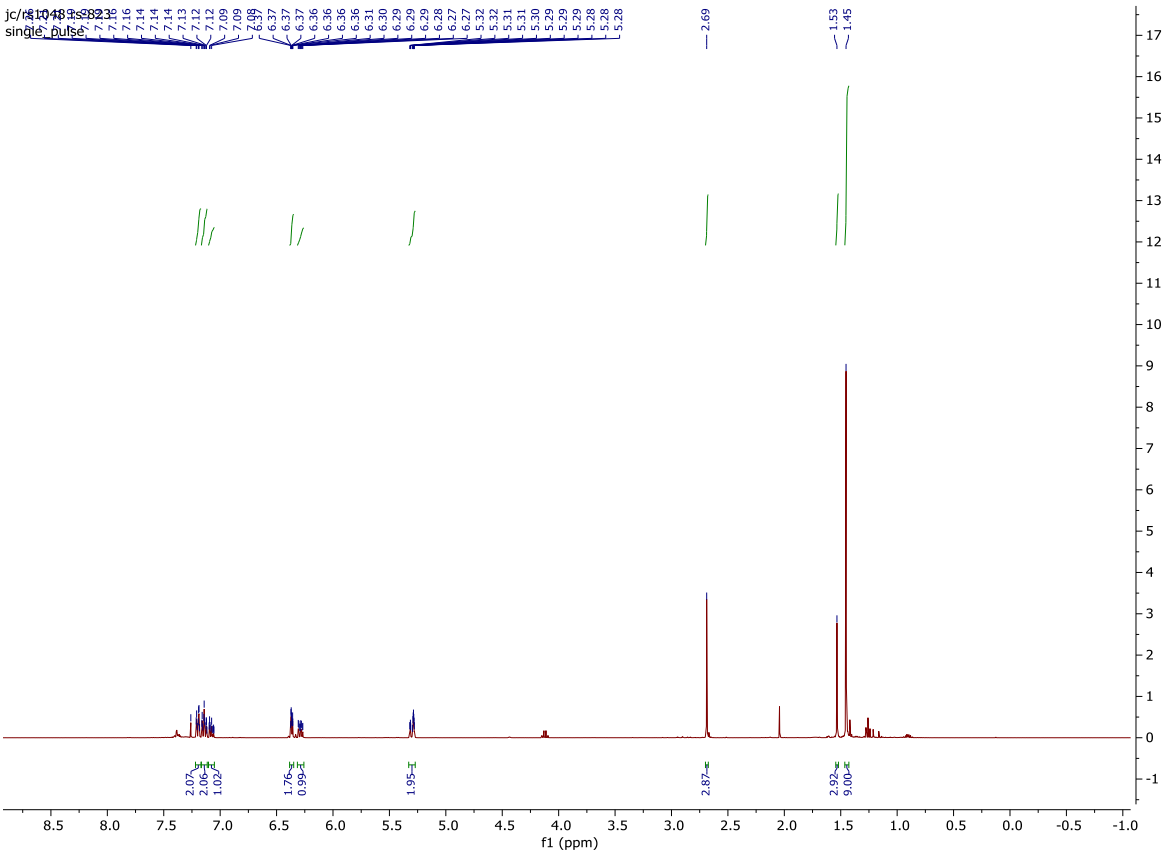
LC-File	RS-797.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2021-02-24 16-38-23\
Date	24-Feb-21, 16:39:10
Sample	RS-797
Sample Info	95:05 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 95-05 HEXANE-IPA1ML.M
Analysis Time	10.433 min
Sampling Rate	0.0067 min (0.402 sec), 1566 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	5.727	19489.3	2133.8	0.1366	49.975	0.678
2	6.644	19509.2	1774.9	0.1602	50.025	0.698

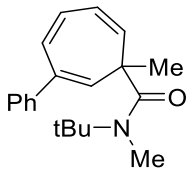
^{1}H NMR



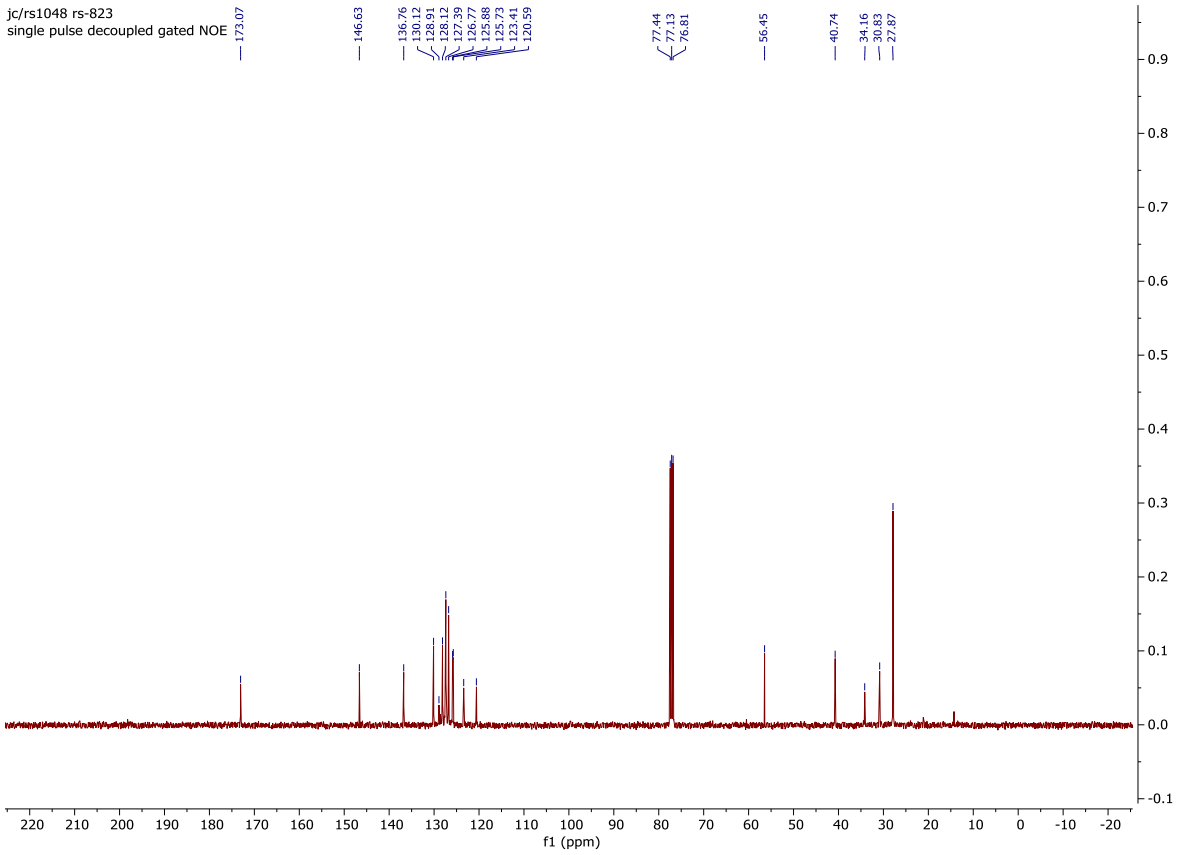
***N*-(tert-butyl)-N,1-dimethyl-3-phenylcyclohepta-2,4,6-triene-1-carboxamide (9)**



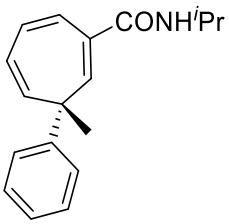
^{13}C NMR



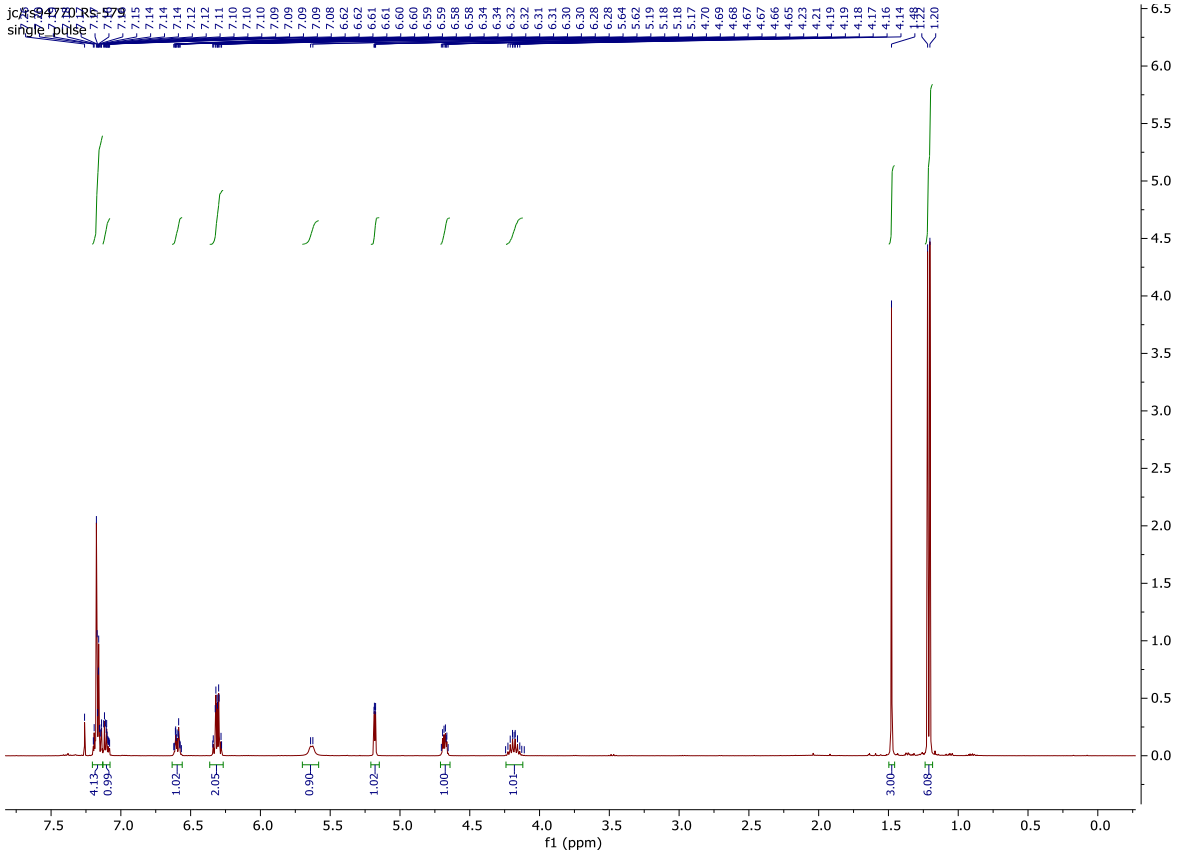
_N_-(tert-butyl)-N,1-dimethyl-3-phenylcyclohepta-2,4,6-triene-1-carboxamide (9)



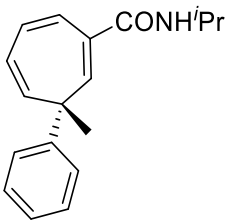
^{1}H NMR



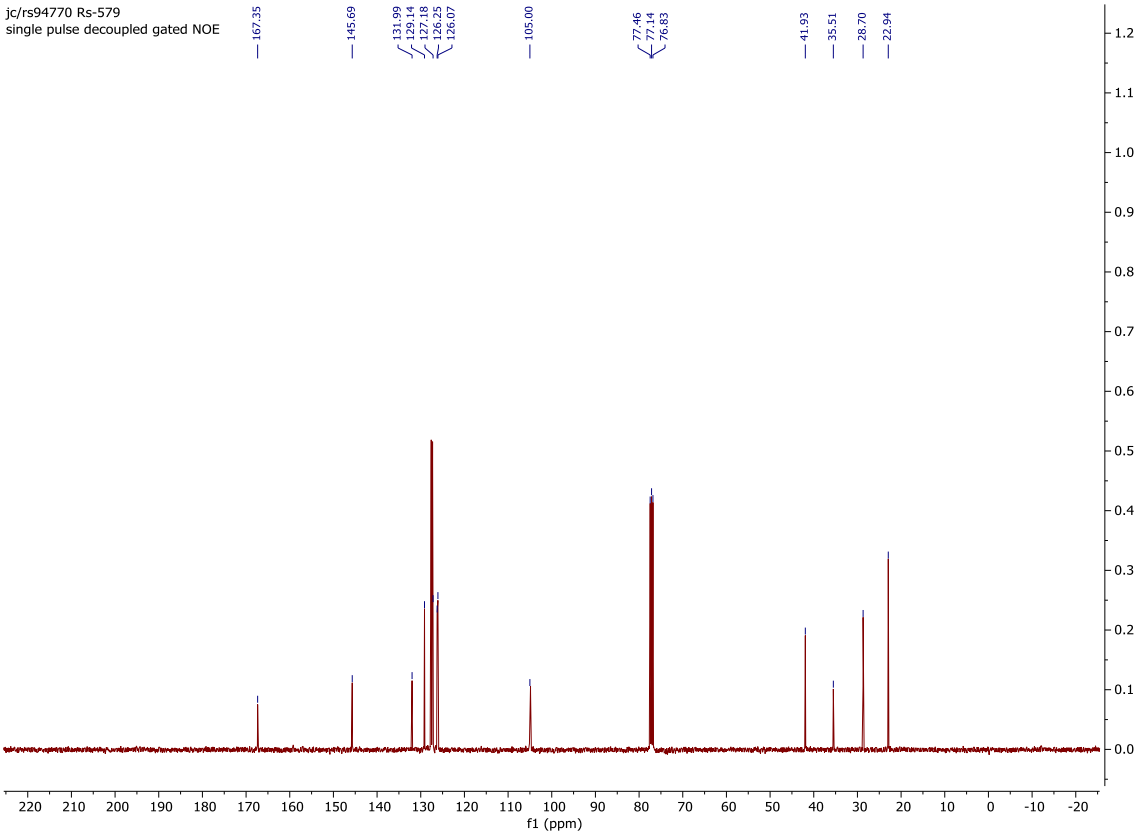
(*R*)-*N*-isopropyl-3-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11a)



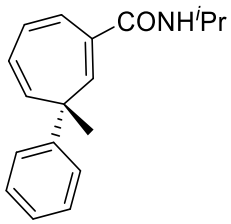
^{13}C NMR



(*R*)-*N*-isopropyl-3-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11a)

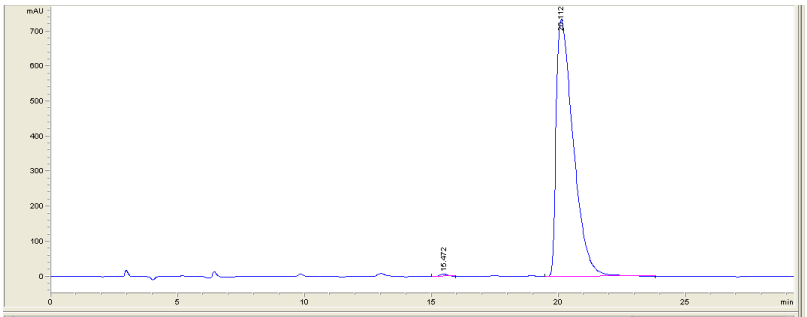


HPLC



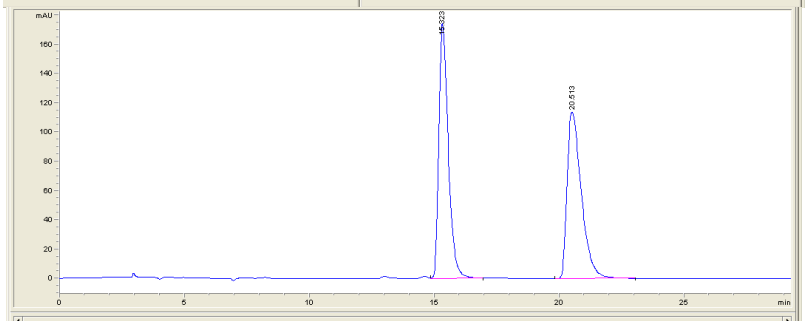
***(R)-N*-isopropyl-3-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11a)**

Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (80:20), showed it to consist of a 0.42:99.57 mixture of two enantiomers with retention times 15.472 mins(minor) and 20.112 mins (major), respectively.



File Information	
LC-File	RS-579.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-03-18 11-25-48\
Date	18-Mar-20, 11:26:34
Sample	RS-579
Sample Info	80:20 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 85-15 HEXANE-IPA1ML.M
Analysis Time	36.527 min
Sampling Rate	0.0067 min (0.402 sec), 5480 datapoints

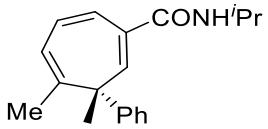
#	Time	Area	Height	Width	Area%	Symmetry
1	15.472	148	6.6	0.3535	0.428	0.937
2	20.112	34396.5	733.7	0.7089	99.572	0.389



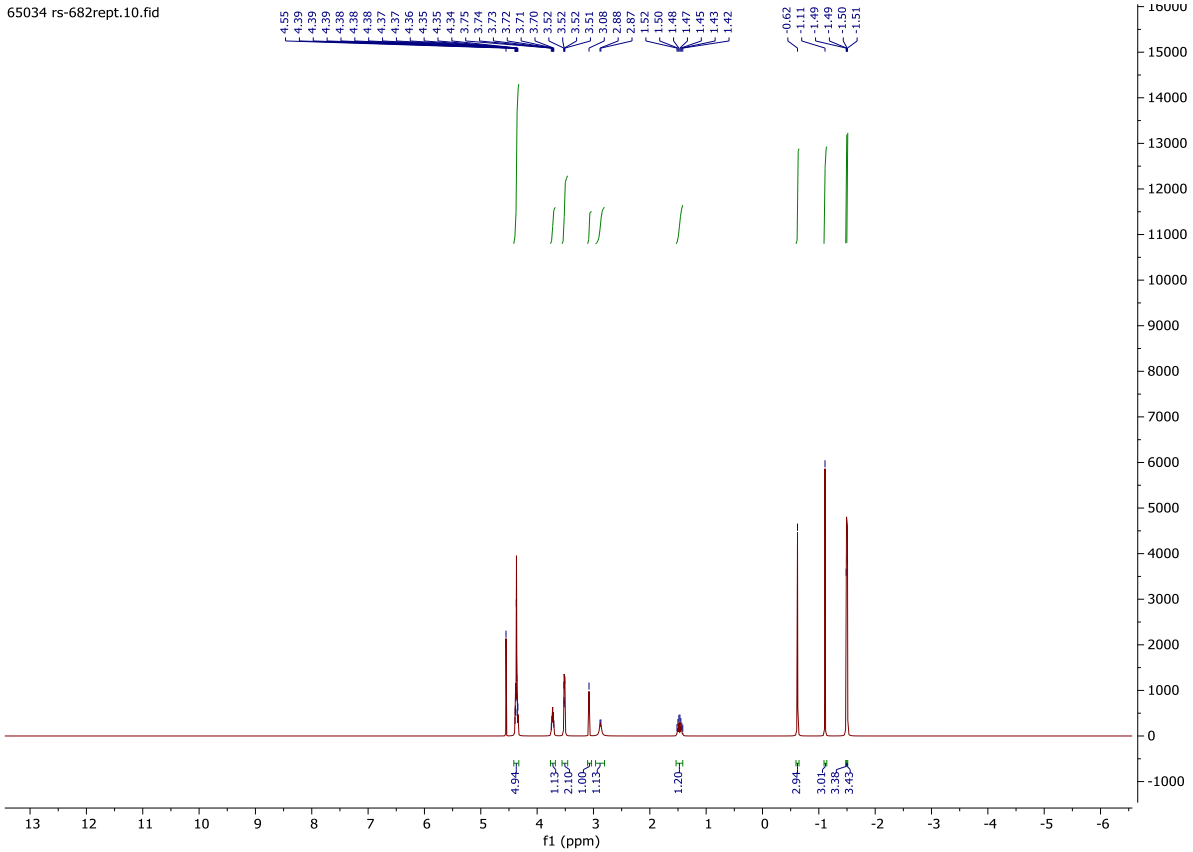
File Information	
LC-File	RS-581.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-03-20 17-49-30\
Date	20-Mar-20, 17:50:10
Sample	RS-581
Sample Info	80:20 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 85-15 HEXANE-IPA1ML.M
Analysis Time	29.287 min
Sampling Rate	0.0067 min (0.402 sec), 4394 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	15.323	4565.8	174	0.4021	50.338	0.592
2	20.513	4504.4	113.7	0.6063	49.662	0.501

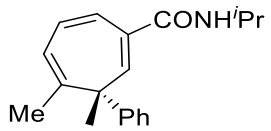
^{1}H NMR



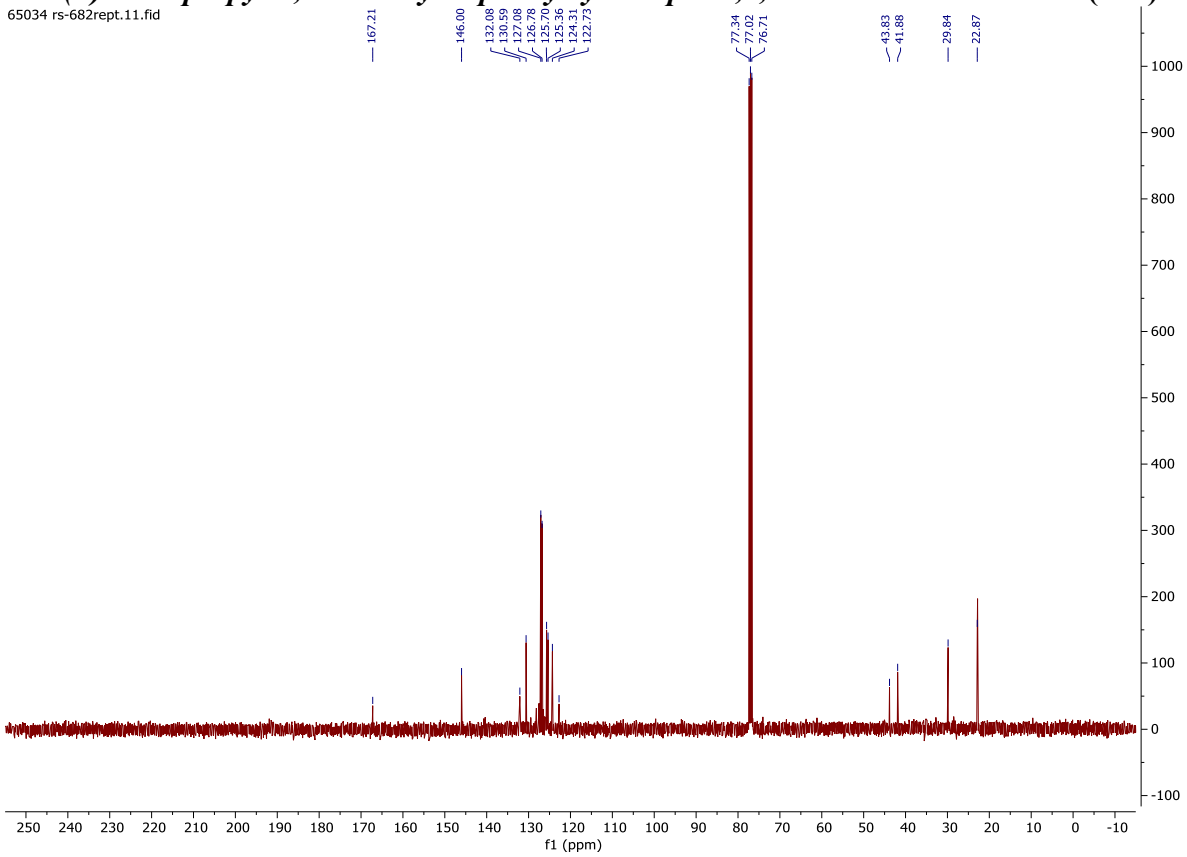
(S)-N-isopropyl-3,4-dimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11b)



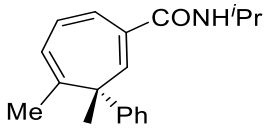
^{13}C NMR



(S)-N-isopropyl-3,4-dimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide **(11b)**

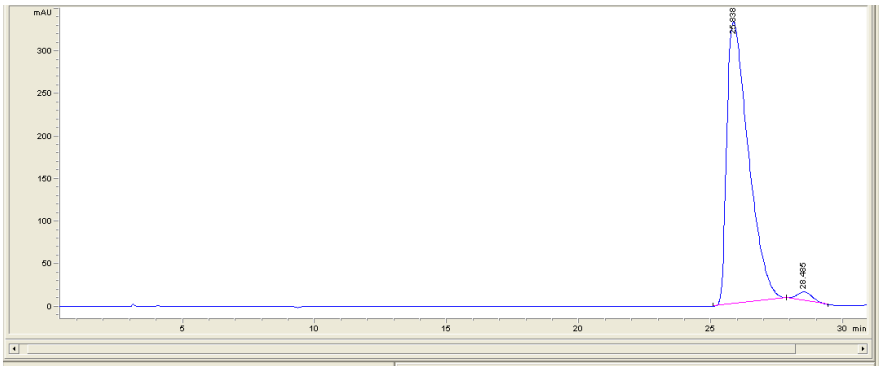


HPLC



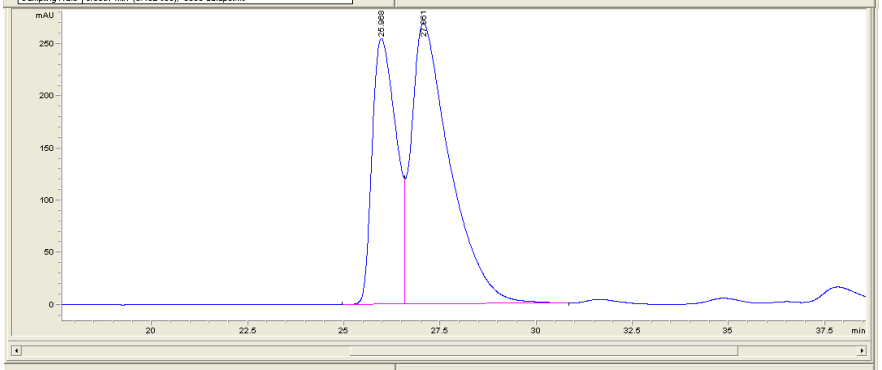
***(S)-N*-isopropyl-3,4-dimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11b)**

Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (85:15), showed it to consist of a 2:98 mixture of two enantiomers with retention times 25.838 mins(minor) and 28.485 mins (major), respectively.



File Information	
LC-File	RS-689PREP.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-09-25 17-26-01\
Date	25-Sep-20, 17:26:47
Sample	RS-689 prep
Sample Info	85:15 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 90-10 HEXANE-IPA1ML.M
Analysis Time	33.327 min
Sampling Rate	0.0067 min (0.402 sec), 5000 datapoints

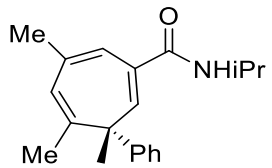
#	Time	Area	Height	Width	Area%	Symmetry
1	25.838	18850	331.4	0.8655	97.870	0.411
2	28.485	410.2	10	0.6343	2.130	0.704



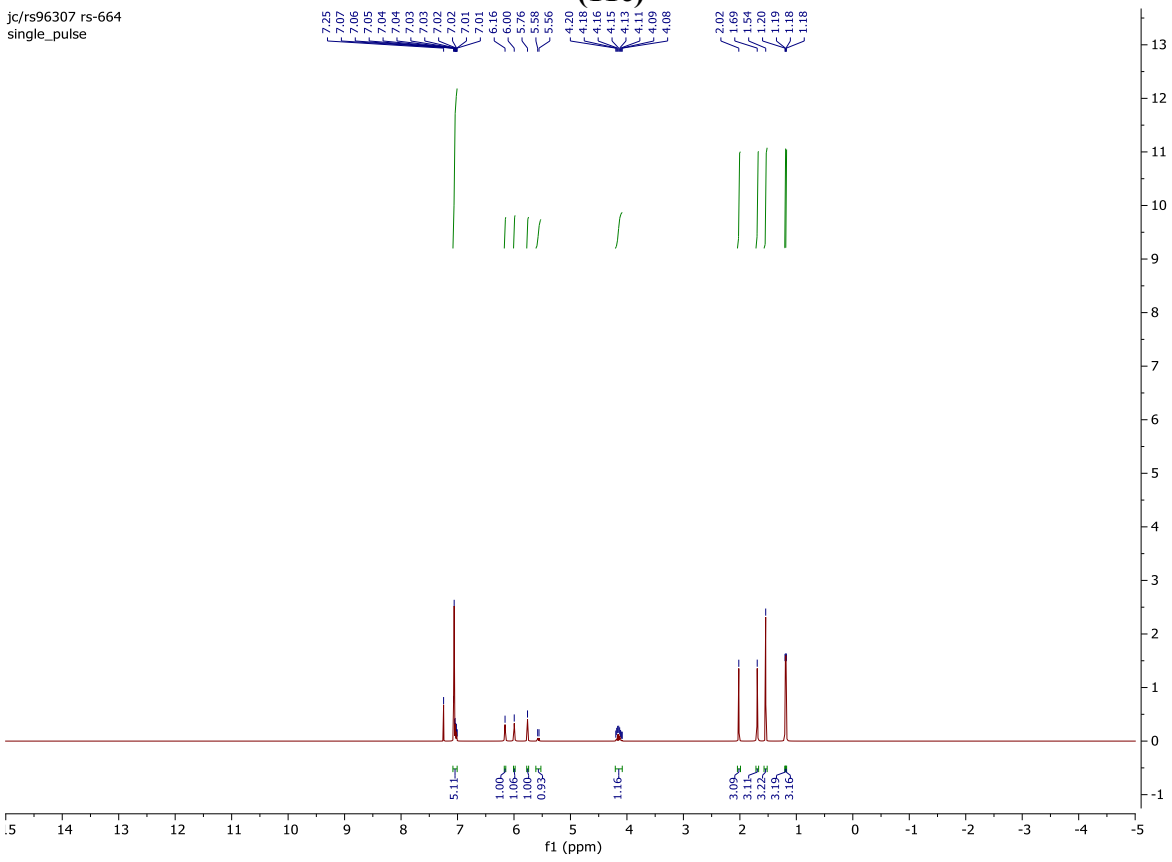
File Information	
LC-File	RS-682.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-09-23 12-43-28\
Date	23-Sep-20, 12:44:14
Sample	RS-682
Sample Info	90:10 hex:IPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 90-10 HEXANE-IPA1ML.M
Analysis Time	44.94 min
Sampling Rate	0.0067 min (0.402 sec), 6742 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	25.968	11132.5	254.9	0.6755	37.206	0.601
2	27.061	18789.1	269.7	1.0028	62.794	0.408

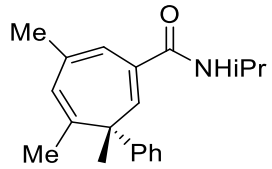
^{1}H NMR



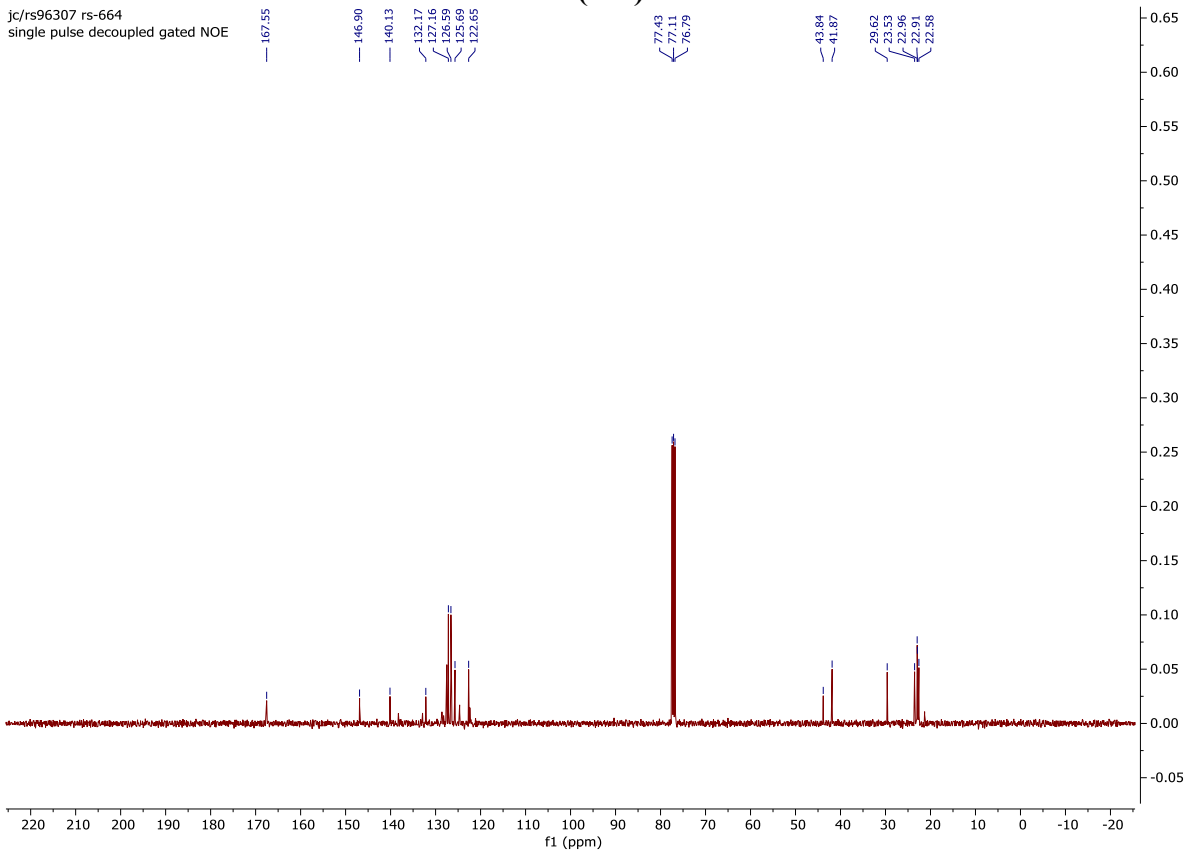
***(S)-N*-isopropyl-3,4,6-trimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11c)**



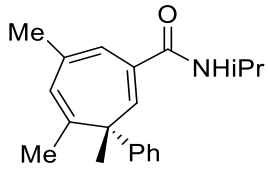
^{13}C NMR



***(S)-N*-isopropyl-3,4,6-trimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11c)**

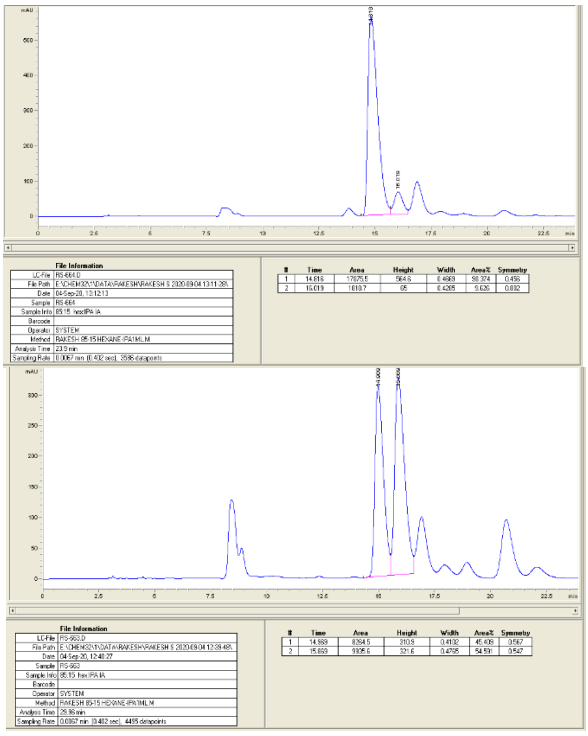


HPLC

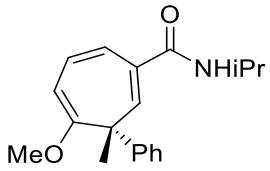


***(S)-N*-isopropyl-3,4,6-trimethyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11c)**

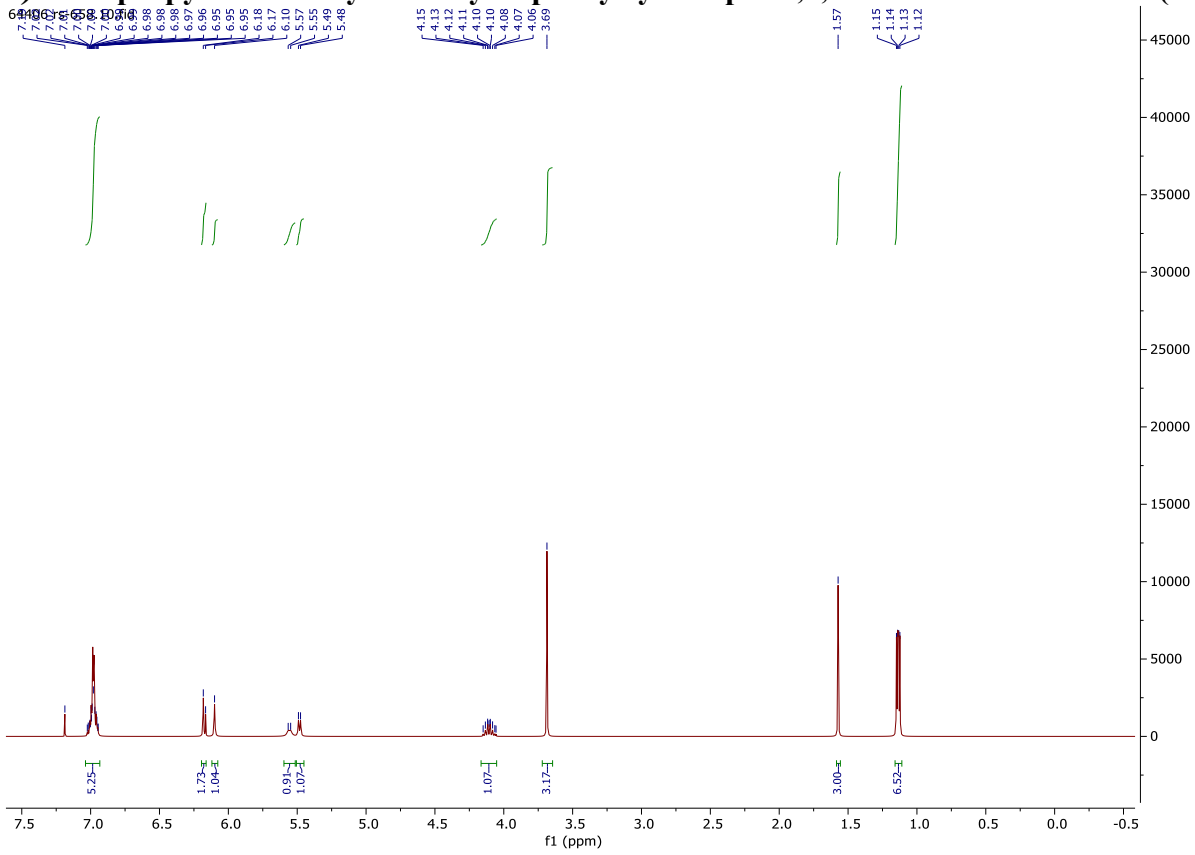
Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (85:15), showed it to consist of a 90:10 mixture of two enantiomers with retention times 14.816 mins(major) and 16.019 mins (minor), respectively.



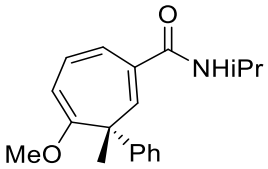
^{1}H NMR



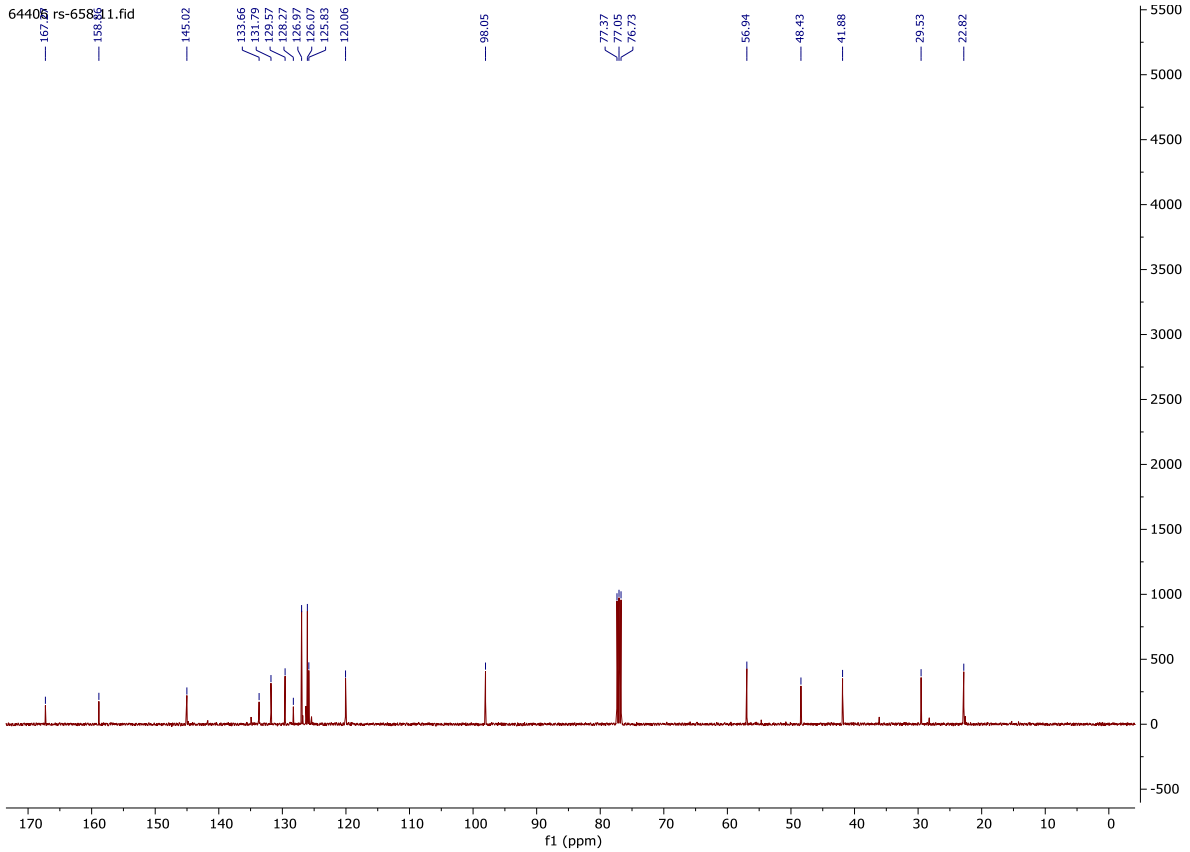
***(R)-N*-isopropyl-4-methoxy-3-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11d)**



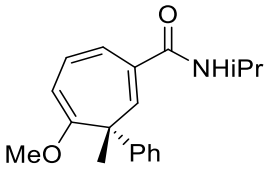
^{13}C NMR



***(R)-N*-isopropyl-4-methoxy-3-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11d)**

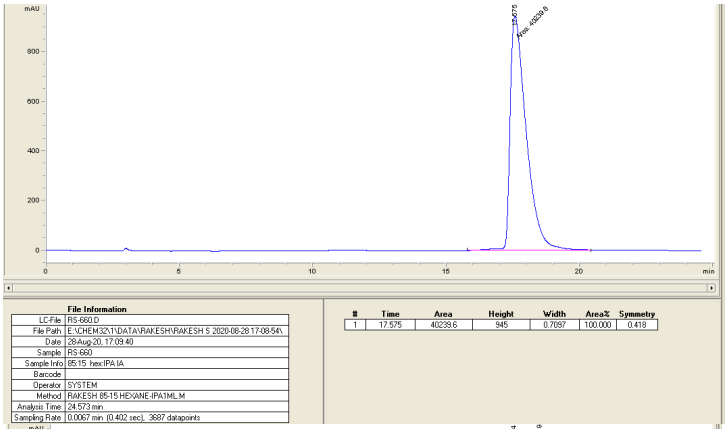


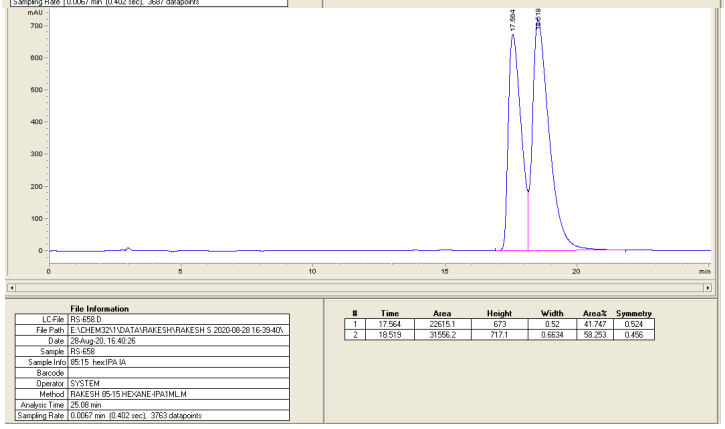
HPLC



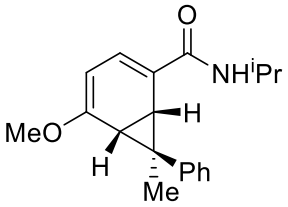
***(R)-N*-isopropyl-4-methoxy-3-methyl-3-phenylcyclohepta-1,4,6-triene-1-carboxamide (11d)**

Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (85:15), showed it to consist of a 100:00 mixture of one enantiomer with retention times 17.575 mins.

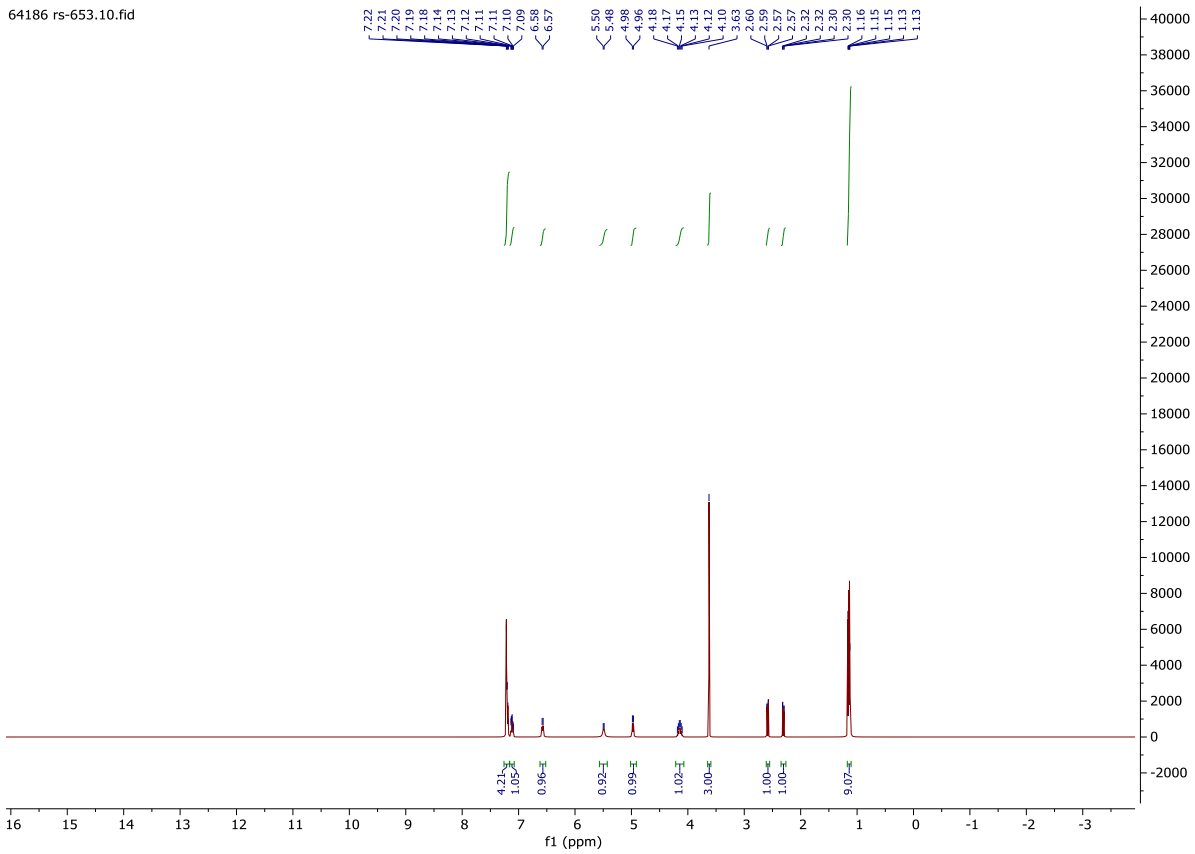




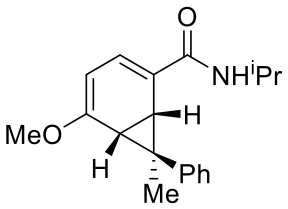
^{1}H NMR



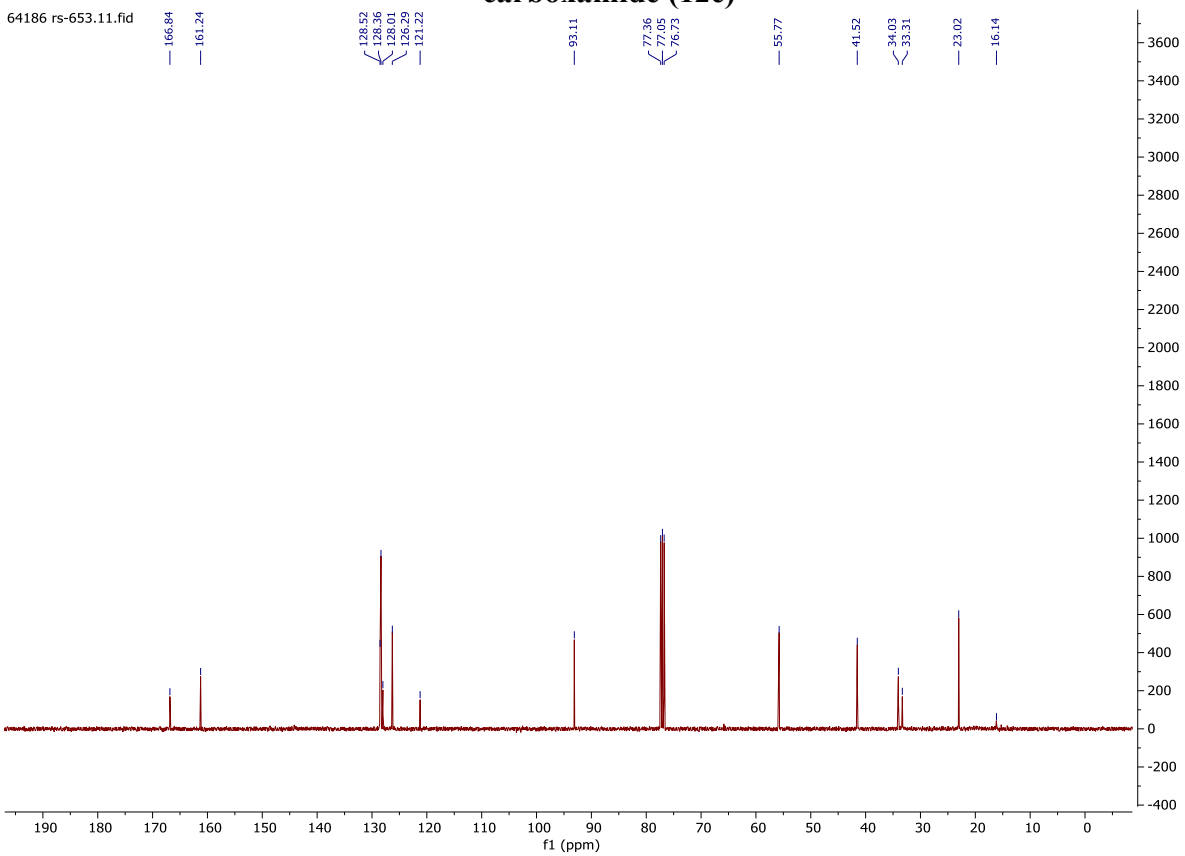
(1*S*,6*R*,7*R*)-*N*-isopropyl-5-methoxy-7-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (12e)



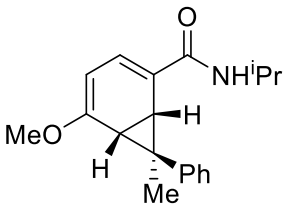
^{13}C NMR



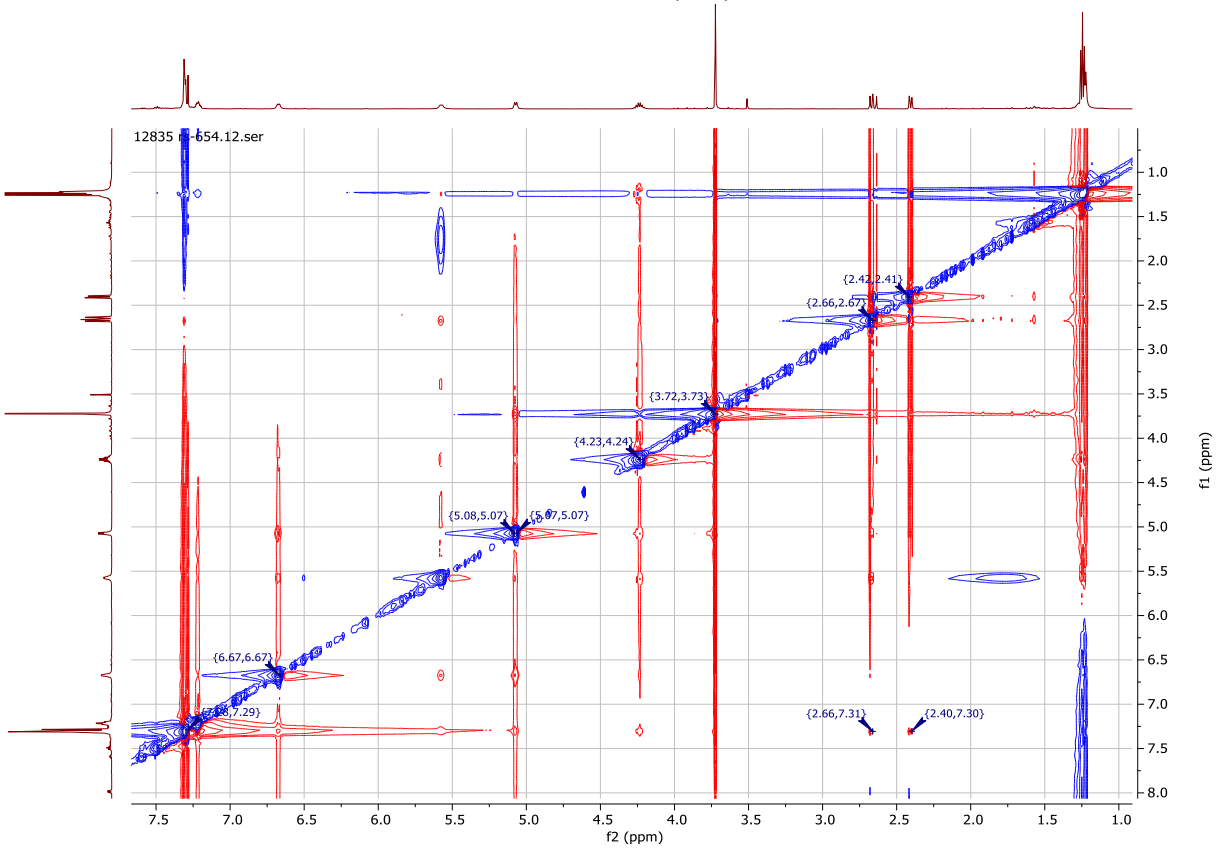
(1*S*,6*R*,7*R*)-*N*-isopropyl-5-methoxy-7-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (12e)



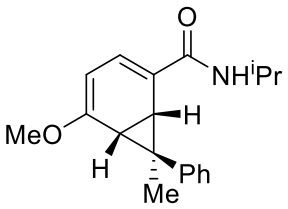
NOSY



(1*S*,6*R*,7*R*)-*N*-isopropyl-5-methoxy-7-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (12e)

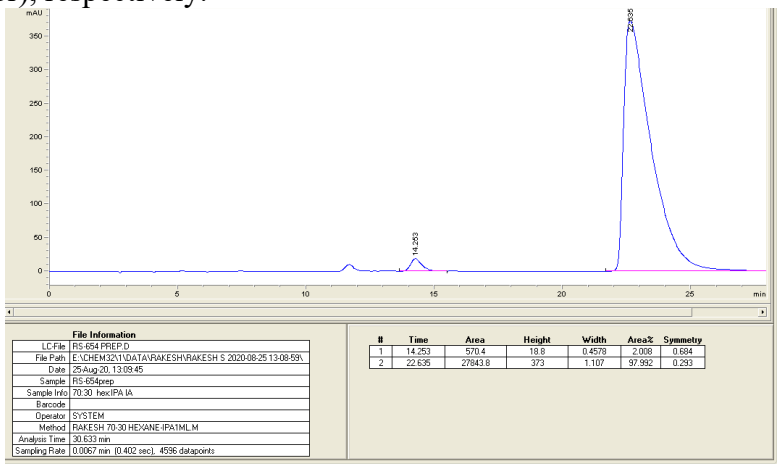


HPLC



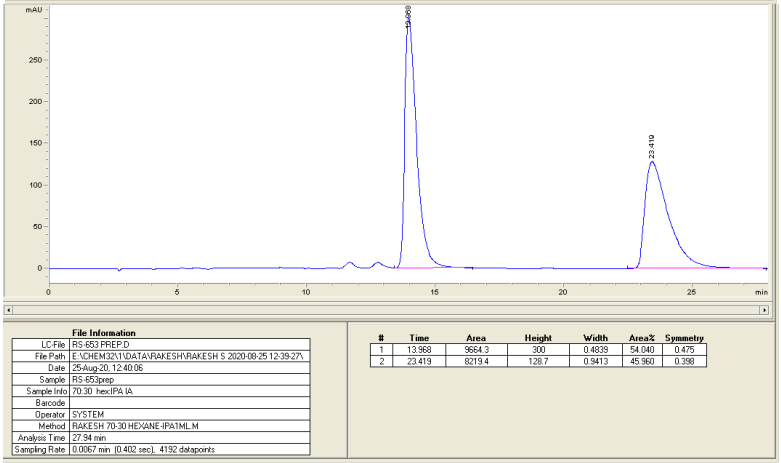
(1*S*,6*R*,7*R*)-*N*-isopropyl-5-methoxy-7-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (12e)

Analytical HPLC (Chiral Regis Whelk O1), eluting with hexane-IPA (70:30), showed it to consist of a 2:98 mixture of two enantiomers with retention times 14.253 mins (minor) and 22.635 mins (major), respectively.



File Information	
LC-File	RS-654 PREP.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-08-25 13-08-59\
Date	25-Aug-20, 13:09:45
Sample	RS-654prep
Sample Info	70:30 hexIPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 70-30 HEXANE-IPA1ML.M
Analysis Time	30.633 min
Sampling Rate	0.0067 min (0.402 sec), 4596 datapoints

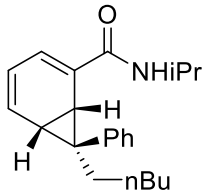
#	Time	Area	Height	Width	Area%	Symmetry
1	14.253	570.4	18.8	0.4578	2.008	0.684
2	22.635	27843.8	373	1.107	97.992	0.293



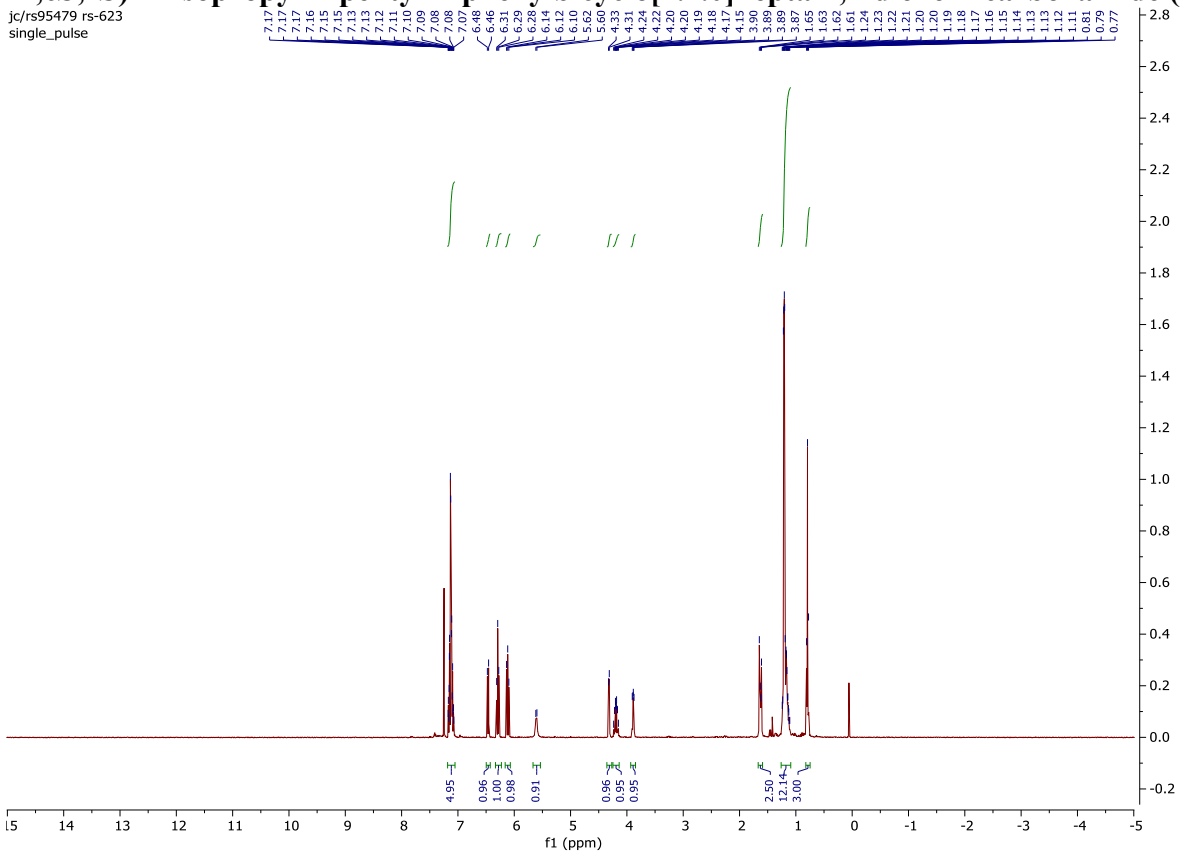
File Information	
LC-File	RS-653 PREP.D
File Path	E:\CHEM32\1\DATA\RAKESH\RAKESH S 2020-08-25 12-39-27\
Date	25-Aug-20, 12:40:06
Sample	RS-653prep
Sample Info	70:30 hexIPA IA
Barcode	
Operator	SYSTEM
Method	RAKESH 70-30 HEXANE-IPA1ML.M
Analysis Time	27.94 min
Sampling Rate	0.0067 min (0.402 sec), 4192 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	13.968	9664.3	300	0.4839	54.040	0.475
2	23.419	8219.4	128.7	0.9413	45.960	0.398

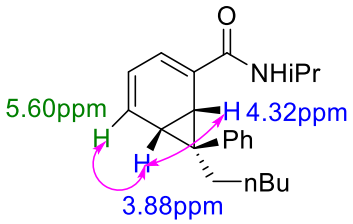
^{1}H NMR



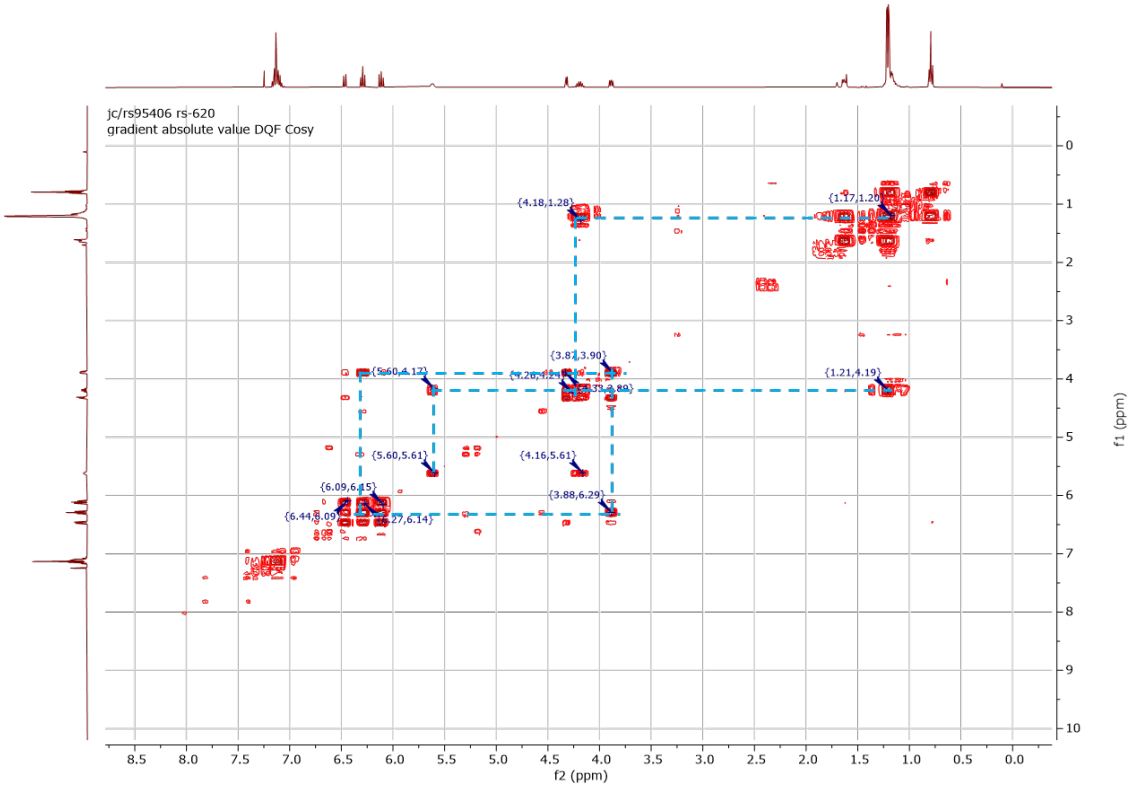
(1*R*,6*S*,7*S*)-*N*-isopropyl-7-pentyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (14)



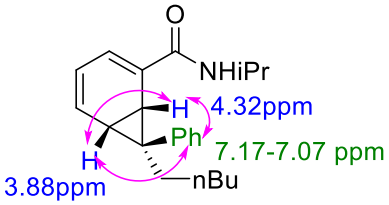
COSY



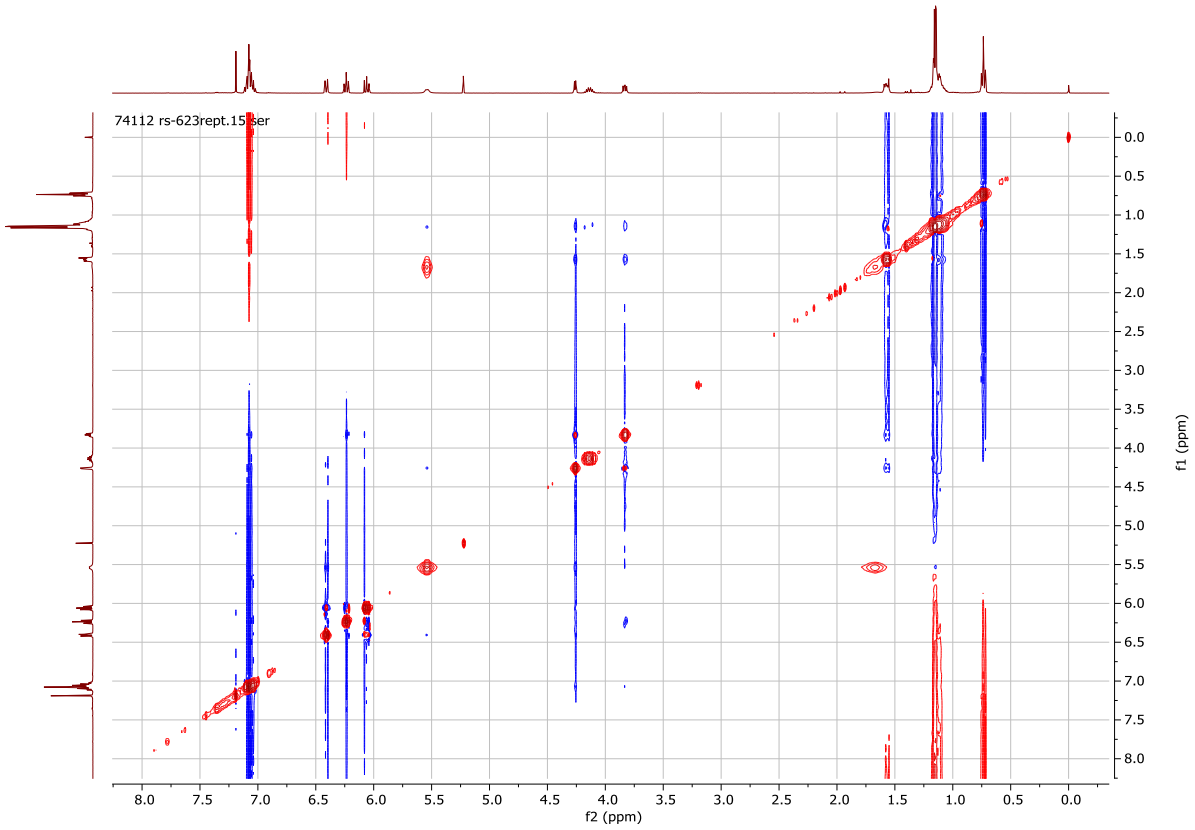
(1*R*,6*S*,7*S*)-*N*-isopropyl-7-pentyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (14)



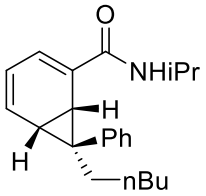
NOSY



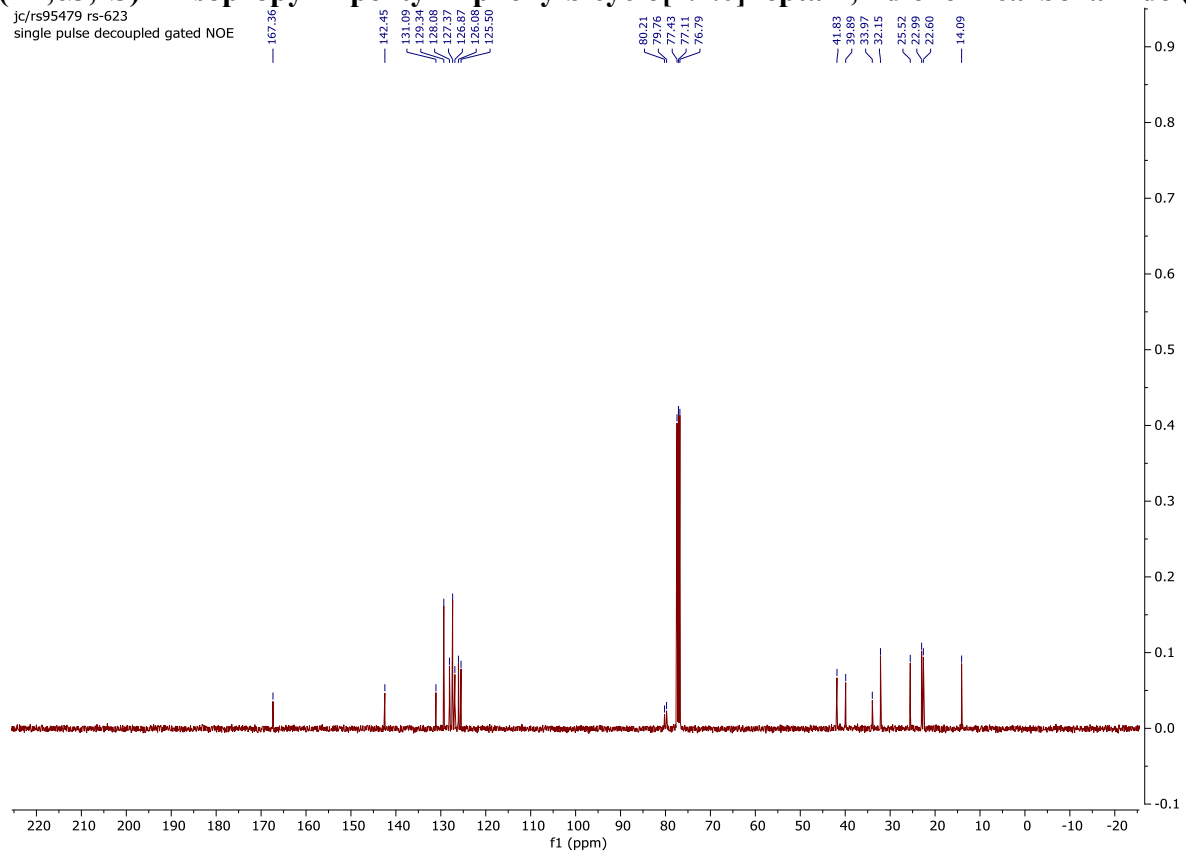
(1*R*,6*S*,7*S*)-*N*-isopropyl-7-pentyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (14)



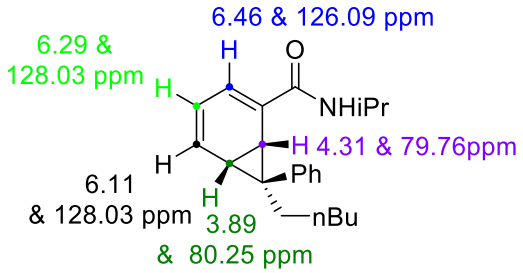
^{13}C NMR



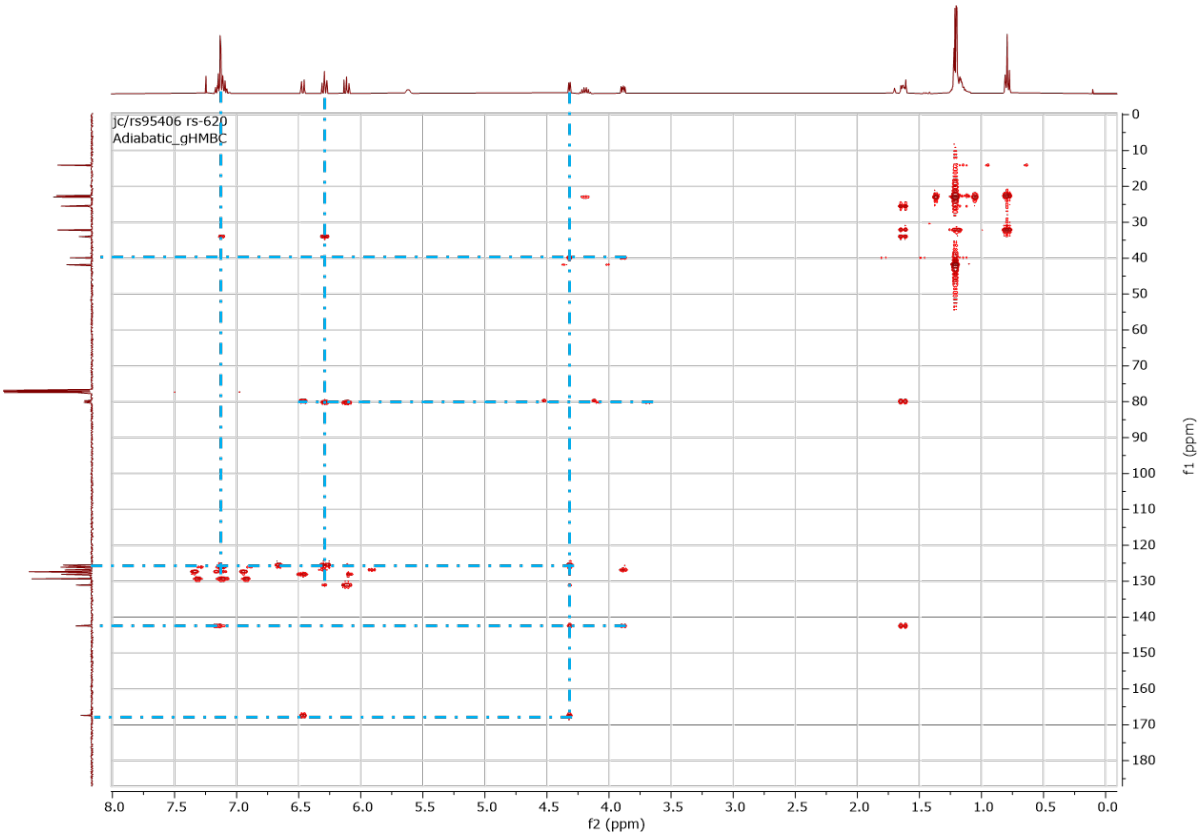
(1*R*,6*S*,7*S*)-*N*-isopropyl-7-pentyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (14)



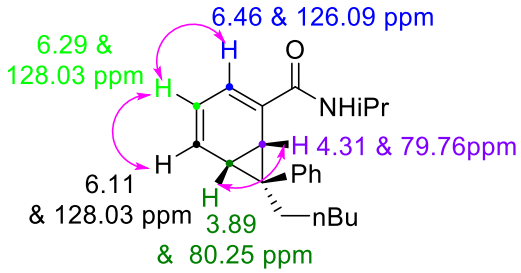
HMBC



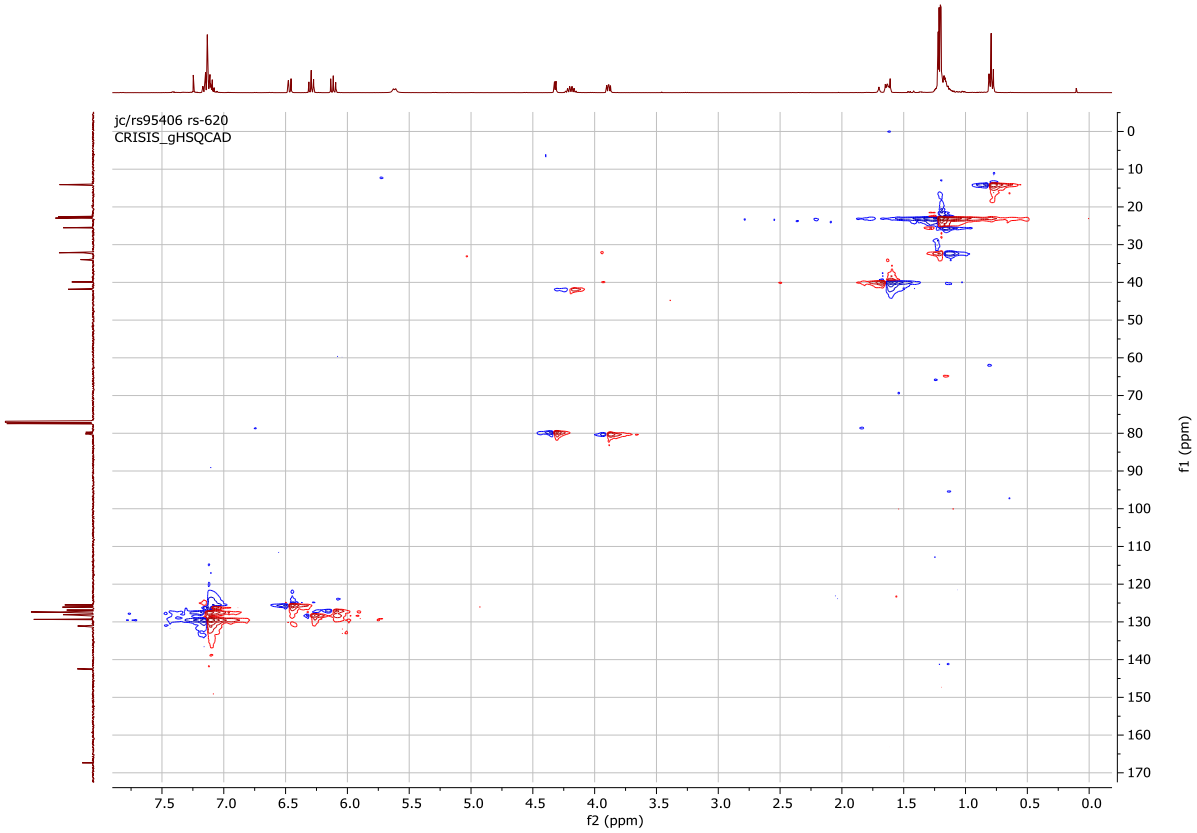
(1*R*,6*S*,7*S*)-*N*-isopropyl-7-pentyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (14)



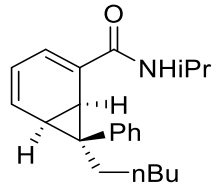
HSQC



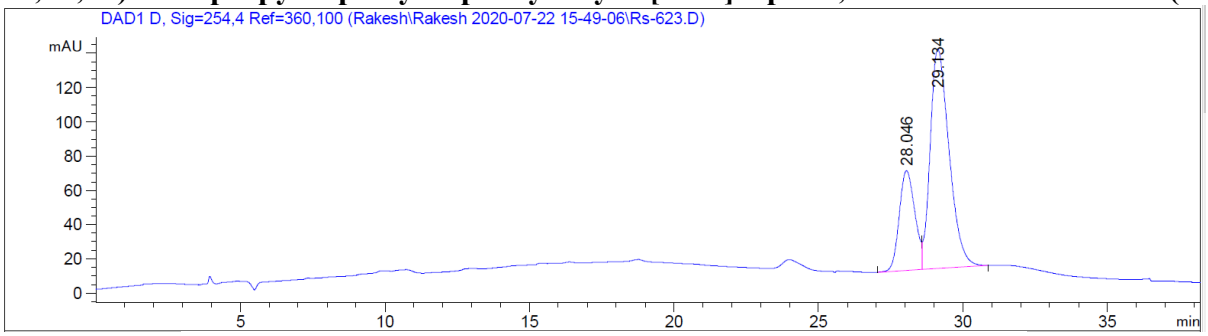
(1*R*,6*S*,7*S*)-*N*-isopropyl-7-pentyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (14)



HPLC

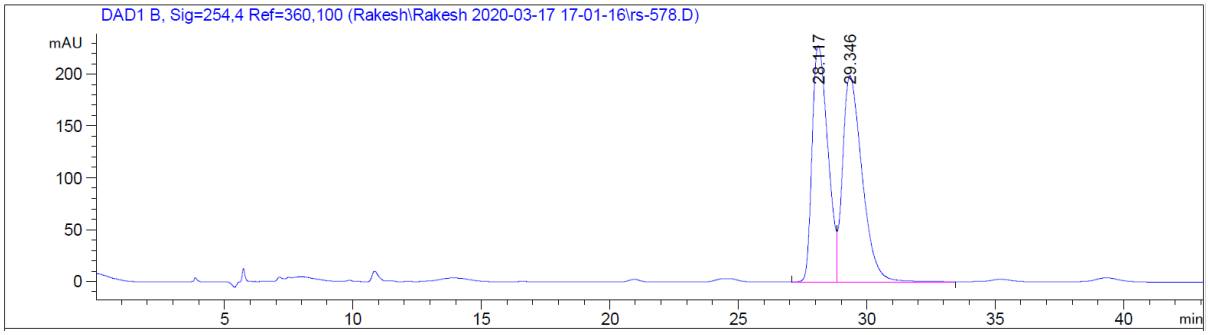


(1*R*,6*S*,7*S*)-*N*-isopropyl-7-pentyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-2-carboxamide (14)



Signal 1: DAD1 D, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.046	BV	0.5827	2180.86279	58.26950	27.1906
2	29.134	VB	0.6485	5839.78369	127.94576	72.8094
Totals :				8020.64648	186.21527	



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.117	BV	0.6686	9653.18652	227.72067	47.8699
2	29.346	VB	0.8067	1.05123e4	198.88542	52.1301
Totals :				2.01654e4	426.60609	