Supplementary Materials for

Thioamide-directed enantioselective *α*-C–H arylation of amines using palladium catalysts

Pankaj Jain, PrithaVerma, Guoqin Xia, Jin-Quan Yu†

Corresponding author. Email: yu200@scripps.edu

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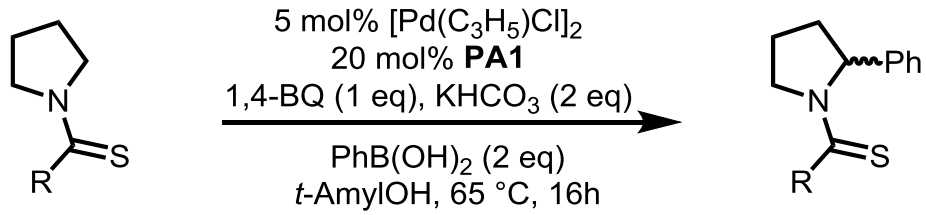
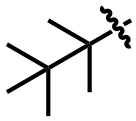
General Information: Solvents were obtained from Sigma-Aldrich, Alfa-Aesar and Acros and used directly without further purification. Anhydrous *t*-Amyl alcohol was obtained from sigma. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light and Vogel's permanganate. ^{1}H NMR spectra were recorded on Bruker DRX-600instrument (600 MHz). When the ^{1}H NMR solvent was $CDCl_3$, chemical shifts were quoted in parts per million (ppm) referenced to 0.00 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker DRX-600 instrument (150 MHz), and were fully decoupled by broad band proton decoupling. When the ^{13}C NMR solvent was $CDCl_{3,}$ chemical shifts were reported in ppm referenced to 77.00 ppm for chloroform-d. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Enantiomeric ratios (er) were determined on a Hitachi LaChrom Elite HPLC system using commercially available chiral columns.

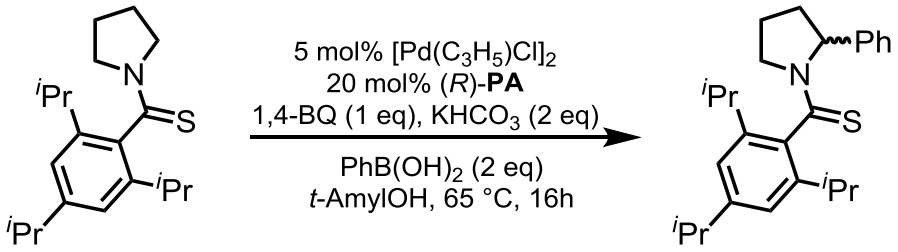
Table 1: Screening of different directing groups with pyrrolidine substrate

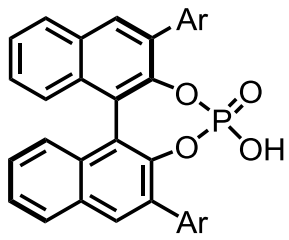


		% Conversion	er
DG1	R = R'_3C R' = Me	36	55:45
DG2	R = R'_3C R' = Et	38	67:33
DG3	R = 	24	53:47
DG4	R = 2,6-F_2-C_6H_3	NR	ND
DG5	R = 2,4,6-Me_3-C_6H_2	13	ND
DG6	R = 2,4,6-$^{i}Pr_3$-C_6H_2	40	74:26

The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard. Enantiomeric ratios (er) were determined by chiral high-performance liquid chromatography. N.R., no reaction. N.D., not determined.

Table 2: Initial screening of different BINOL-derived phosphoric acids with pyrrolidine substrate

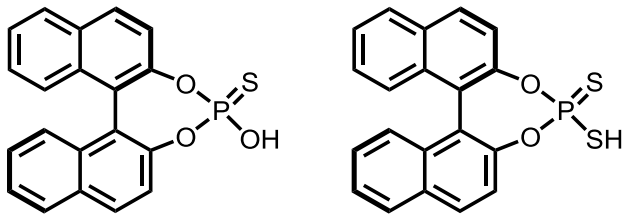




(*R*)-**PA**

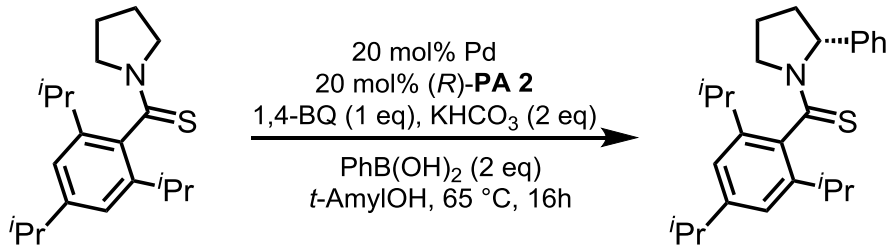
PA1: Ar = 2,4,6-$^{i}Pr_3$-C_6H_2
40% yield, 26:74 er (*R:S*)
PA2: Ar = 9-anthrycenyl
52% yield, 83:17 er (*R:S*)
PA3: Ar = 3,5-CF_3-C_6H_2
16% yield, 80:20 er (*R:S*)

The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard. Enantiomeric ratios (er) were determined by chiral high-performance liquid chromatography.



The use of thiophosphoric acid and dithiophoshoric acid as ligands under the reaction conditions show no product formation.

Table 3: Screening of different palladium sources with pyrrolidine substrate:

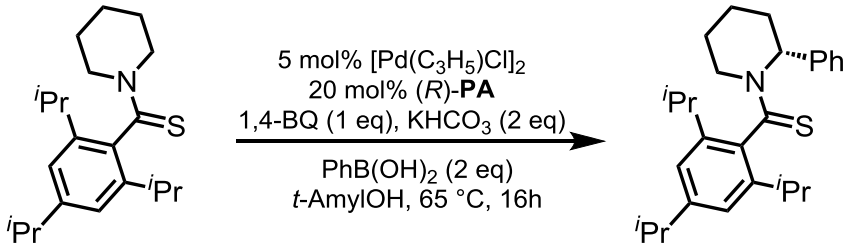


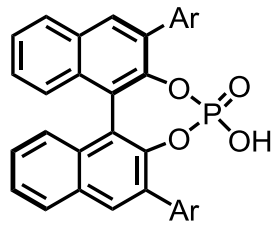
Palladium source	Yield	er (R:S)
$Pd(TFA)_2$	83	50:50
$[Pd(C_3H_5)Cl]_2$	52	83:17
$PdCl_2(CH_3CN)_2$	53	70:30
$PdCl_2(PhCN)_2$	60	81:19
$Pd(OAc)_2$	92	90:10
$Pd_2(dba)_3$	87	98:2
$PdCl_2$	53	83:17
Pd/C	NR	--

The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard. Enantiomeric ratios (er) were determined by chiral high-performance liquid chromatography.

Note: When the palladium loading was reduced to 10 mol % (with $Pd_2(dba)_3$) the er dropped from 98:2 to 96:4. However, carrying out the reaction under nitrogen and increasing the reaction concentration from 0.05 M to 0.2 M enabled the formation of product with 98:2 er.

Table 4: Initial screening of different Binol-derived phosphoric acids with piperidine substrate

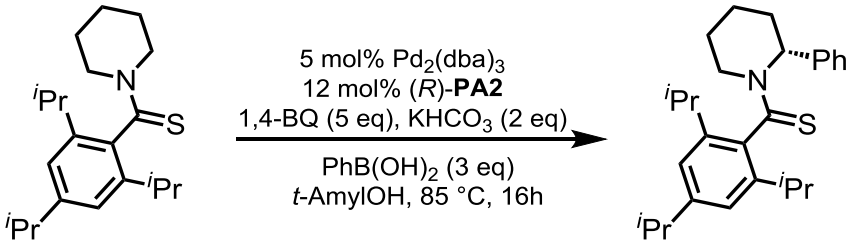




(*R*)-**PA**

PA1: Ar = 2,4,6-^{i}Pr$_3$-C$_6$H$_2$
14% yield, 17:83 er (*R:S*)
With $Pd_2(dba)_3$ 24% yield, 17:83 er (*R:S*)
PA2: Ar = 9-anthrycenyl
17% yield, 82:18 er (*R:S*)
With $Pd_2(dba)_3$ 24% yield, 92:8 er (*R:S*)
PA3: Ar = 3,5-(CF$_3$)$_2$-C$_6$H$_2$
9% yield, 63:37 er (*R:S*)
PA4: Ar = α-napthyl
With $Pd_2(dba)_3$ 25% yield, 85:15 er
PA5: Ar = 3,5-*t*-Bu$_2$-C$_2$H$_6$
With $Pd_2(dba)_3$ 15% yield, 85:15 er

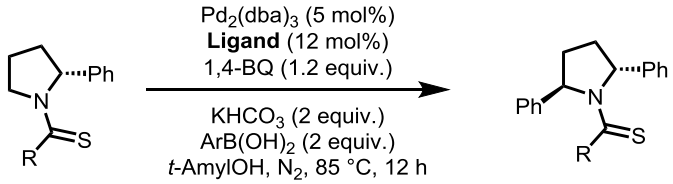
The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as an internal standard. Enantiomeric ratios (er) were determined by chiral high-performance liquid chromatography.



63%, 93:7 er

Increasing the reaction concentration from 0.05 M to 0.2 M enabled the formation of product with 95.5:4.5 er with similar yields.

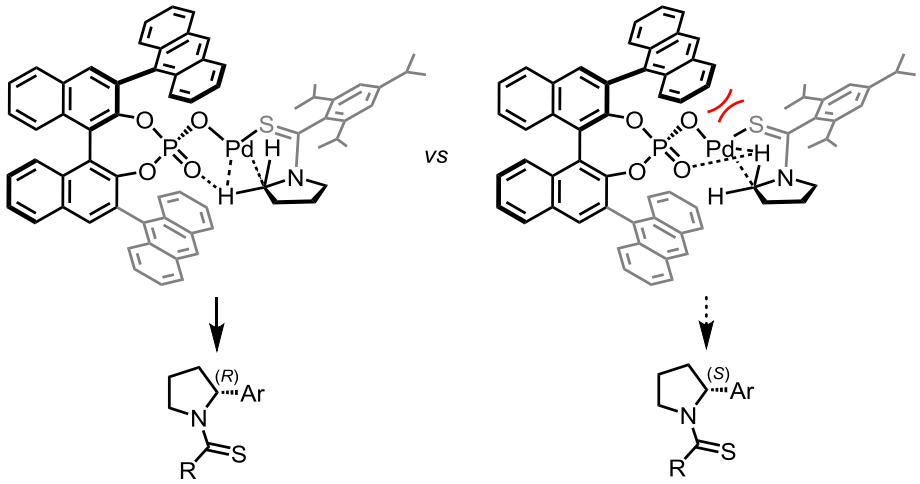
Table 5: Diarylation of Pyrrolidine



LIgand	Conversion %
(*R*)-PA2	35
(*S*)-PA2	<5
BINOL-PA	85

To test if the diarylation reaction is substrate-controlled or catalyst-controlled, we used (*R*)-phenylpyrrolidine as the substrate and tested three different ligand systems: (*R*)-PA2, (*S*)-PA2 and the racemic BINOL phosphoric acid. The less hindered BINOL-PA shows high conversion, where as the (*R*)-PA2 gave 35% conversion. Interesting the (S)-PA2 gave less than 5% conversion. In all the cases only trans-product was obtained. Based on these results the stereochemistry of the second arylation is controlled by the substrate, however the catalyst geometry needs to match the substrate for it to be able to carry out the transformation. These results also show that kinetic resolution of racemic amines could be possible with chiral phosphoric acids.

Proposed stereo-models for enantioselective induction



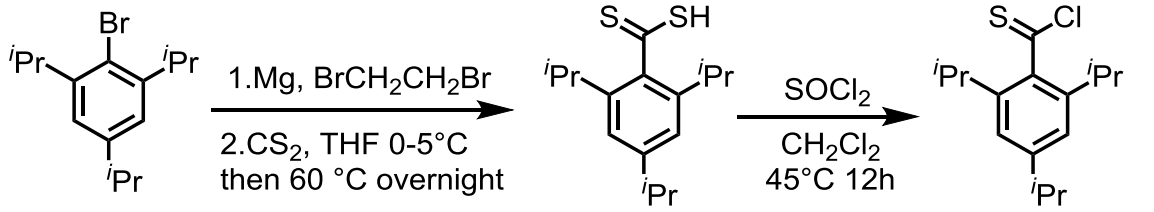
Experimental Section

Ligand Synthesis**:**

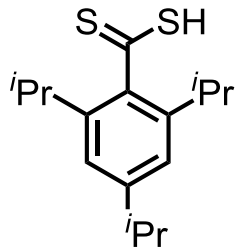
Chiral phosphoric acids were synthesized from known literature procedures[1-3] or obtained from commercial sources. The final step involving phosphorylation in all cases was carried out following Akiyama's procedure[2]. (*S*)-**PA2** was obtained from Sigma Aldrich (CAS-361342-52-1).

Directing group:

Synthesis of 2,4,6-triisopropylbenzothioyl chloride.



69% overall yield

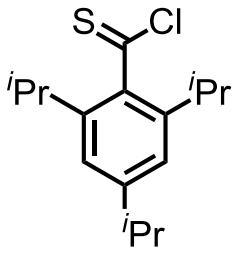


Synthesis of 2,4,6-triisopropylbenzodithioic acid.

The Grignard was synthesized using literature procedure[4]: 4.5 g (185 mmol) of Magnesium was added to a three neck round-bottom flask (flask 1) equipped with a addition funnel and reflux condenser. Then in a different flask (flask 2) 30 g of 2,4,6-triisopropylphenyl bromide (106 mmol) and 70 ml of ether were added. 10-15 ml of this solution from flask 2 was added to the flask 1. Then 0.2 ml of 1,2-dibromoethane was added to flask 1 and was heated to 40-45 ˚C. In about 10 min the magnesium was observed to be reacting, at this point remaining solution from flask 2 was added dropwise via the addition funnel. Once the addition was complete the reaction mixture was refluxed for 16 hrs.

Next day, 20 ml carbon disulfide and 20 ml of THF were taken in a round bottom flask under a nitrogen balloon and cooled to -5 to -10 ˚C. Then, the Grignard solution was added drop wise to the flask. After the addition was complete the solution was warmed to

room temperature and refluxed at 60 ˚C for 16 hrs. The resulting solution was quenched with 1M HCl and the organic layer separated. The aqueous layer was washed with ethyl acetate and the organic layers were combined. Then the solvent was removed on high vacuum and the residue was washed with cold hexanes giving the pure product in 76% yield (22.6 g) as pink solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 2H), 6.74 (s, 1H), 3.27 (hept, *J* = 6.8 Hz, 2H), 2.88 (hept, *J* = 6.8 Hz, 1H), 1.38-1.10 (m, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.43, 143.76, 142.19, 121.38, 34.24, 30.42, 24.75, 24.32, 23.92. HRMS (ESI-TOF) Calcd for $C_{16}H_{24}ClS$ $[M+H]^+$: 281.1392; found: 281.1394.



Synthesis of 2,4,6-triisopropylbenzothioyl chloride

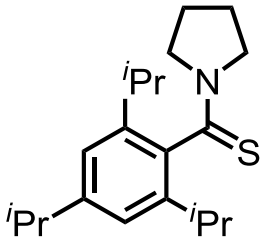
In a round bottom flask containing 10 ml of thionyl chloride and 30 ml of dichloromethane, 2,4,6-triisopropylbenzodithioic acid (10 g, 35 mmol) was added at once and the resulting solution was heated at 45 ˚C for 12 hrs. Then the solvent was removed on high vacuum and the residue was washed with cold hexanes giving the pure product in 91 % yield (9.1 g) as red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 2H), 3.20 (hept, *J* = 6.8 Hz, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.24 (s, 6H), 1.19 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.69, 149.94, 143.94, 142.48, 121.26, 34.30, 30.77, 24.31, 23.87.

Substrate Preparation: Installation of the directing group

General procedure for the preparation of thioamides: The amine (4 mmol) and triethylamine (12 mmol, 1.67 ml) were added to 50-ml dichloromethane in a round bottom flask and stirred for 5 min. Then the temperature was reduced to 0 ˚C and the 2,4,6-triisopropylbenzothioyl chloride (4 mmol, 1.13 g) was added in portions over 1 min. After the addition was complete the mixture was stirred at room temperature for 1-4 hours. Then the organic layer was washed with saturated $NaHCO_3$ solution. The organic

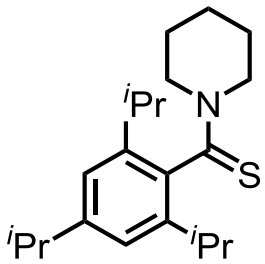
solvent was evaporated and the residue was purified on silica gel choromatography with ethyl acetate and hexanes (1:100 to 1:20) as the solvent.

Note: For non-symmetric amines the product sometimes appear as two spots on TLC due the restricted C-N thioamide bond rotation.



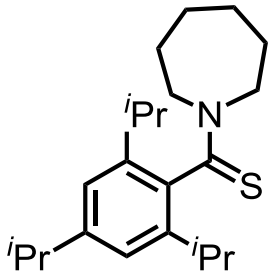
Pyrrolidin-1-yl(2,4,6-triisopropylphenyl)methanethione (1a)

Following the general procedure for the preparation of thioamides, the title compound was obtained in 92% yield (1.16 g) as a colorless solid.^{1}H NMR (600 MHz, $CDCl_3$): δ 6.97 (s, 2H), 4.00 (t, *J* = 7.3 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H), 2.90-2.79 (m, 3H), 2.09 (m, 2H), 1.94 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.20 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.52, 148.53, 141.84, 138.63, 121.46, 52.90, 51.86, 34.20, 30.66, 26.10, 25.04, 24.63, 23.99, 23.57. HRMS (ESI-TOF) Calcd for $C_{20}H_{32}NS$ $[M+H]^+$: 318.2250; found:318.2246.



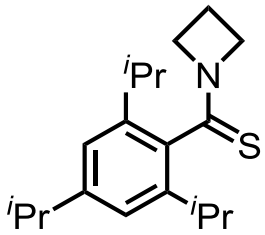
Piperdin-1-yl(2,4,6-triisopropylphenyl)methanethione (1b)

Following the general procedure for the preparation of thioamides, the title compound was obtained in 83% yield (1.1 g) as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.95 (s, 2H), 4.45-4.39 (m, 2H), 3.43-3.39 (m, 2H), 2.84 (hept, *J* = 6.9 Hz, 3H), 1.83-1.77 (m, 2H), 1.74-1.68 (m, 2H), 1.57-1.51 (m, 2H), 1.26 (d, *J* = 6.7 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.19 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.32, 148.27, 141.99, 137.28, 121.44, 51.99, 48.93, 34.15, 30.66, 26.25, 25.52, 25.11, 24.09, 23.99, 23.66. HRMS (ESI-TOF) Calcd for $C_{21}H_{34}NS$ $[M+H]^+$: 332.2406; found: 332.2400.



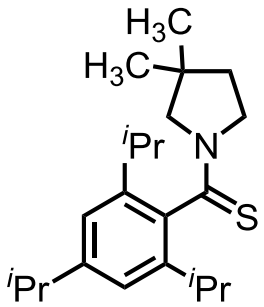
Azepan-1-yl(2,4,6-triisopropylphenyl)methanethione (1c)

Following the general procedure for the preparation of thioamides, the title compound was obtained in 86% (1.18 g) yield as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (s, 2H), 4.30-4.25 (m, 2H), 3.49-3.45 (m, 2H), 2.89-2.76 (m, 3H), 2.02-1.95 (m, 2H), 1.74-1.64 (m, 4H), 1.62-1.57 (m, 2H), 1.26 (d, *J* = 6.7 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.39, 148.26, 141.90, 137.77, 121.48, 53.62, 51.90, 34.14, 30.73, 28.64, 28.34, 26.28, 26.11, 25.26, 23.98, 23.51. HRMS (ESI-TOF) Calcd for $C_{22}H_{36}NS$ $[M+H]^+$: 346.2563; found: 346.2564.



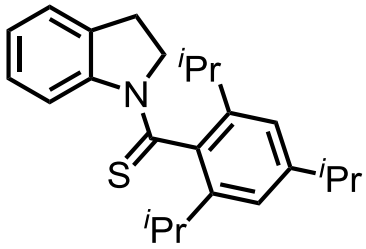
Azetidin-1-yl(2,4,6-triisopropylphenyl)methanethione (1d)

Following the general procedure for the preparation of thioamides, the title compound was obtained in 90% yield (1.09 g) as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 (s, 2H), 4.41 (t, *J* = 8.0 Hz, 2H), 3.84 (t, *J* = 7.7 Hz, 2H), 2.94 (hept, *J* = 6.8 Hz, 2H), 2.86 (hept, *J* = 6.9 Hz, 1H), 2.36-2.26 (m, 2H), 1.26-1.20 (m, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.70, 148.99, 143.00, 134.53, 121.34, 54.10, 52.85, 34.22, 30.68, 25.13, 23.95, 23.86, 14.08. HRMS (ESI-TOF) Calcd for $C_{19}H_{30}NS$ $[M+H]^+$: 304.2093; found: 304.2097.



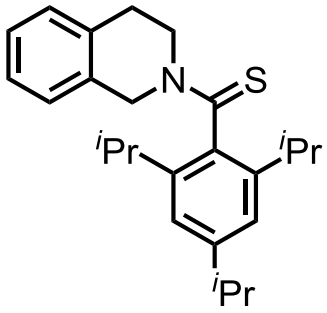
(3,3-dimethylpyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (1e)

Following the general procedure for the preparation of thioamides, the title compound was obtained in 88% yield (1.20 g) as a colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$) (57:43 mixture of rotamers, peaks corresponding to minor rotamer starred): δ 6.98-6.96 (m, 2H), 4.05 (t, *J* = 7.4 Hz, 1.14H), 3.80 (s, 0.86H)*, 3.29 (t, *J* = 7.2 Hz, 0.86H)*, 2.99 (s, 1.14H), 2.90-2.76 (m, 3H), 1.87 (t, *J* = 7.4 Hz, 1.14H), 1.77 (t, *J* = 7.2 Hz, 0.86H)*, 1.32-1.19 (m, 18H), 1.17 (s, 2.58H)*, 1.07 (s, 3.42H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.95*, 197.75, 148.48*, 148.46, 141.79, 141.72*, 138.35, 138.18*, 121.36, 64.82, 64.37*, 51.69*, 51.11, 39.42, 38.99, 38.13, 37.40, 34.11*, 34.07, 30.67, 30.63*, 26.19, 25.53, 25.21, 25.08, 23.92, 23.90, 23.41. HRMS (ESI-TOF) Calcd for $C_{22}H_{36}NS$ $[M+H]^+$: 346.2563; found: 346.2563.



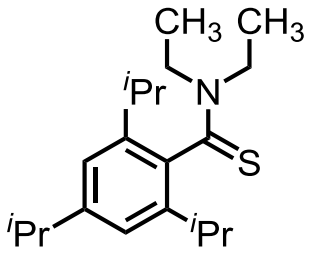
Indolin-1-yl(2,4,6-triisopropylphenyl)methanethione (1f)

Following the general procedure for the preparation of thioamides, the title compound was obtained in 82% yield (1.19 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.5 Hz, 1H), 7.00 (s, 2H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 7.9 Hz, 1H), 5.58 (d, *J* = 6 Hz, 1H), 4.75-4.68 (m, 2H), 3.21 (t, 2H), 2.98-2.85 (m, 3H), 1.32-1.18 (m, 12H), 0.93 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.55, 149.33, 142.39, 142.13, 138.06, 135.03, 127.03, 125.73, 124.68, 121.80, 116.73, 54.39, 34.21, 30.65, 26.04, 24.67, 24.02, 23.27. HRMS (ESI-TOF) Calcd for $C_{24}H_{32}NS$ $[M+H]^+$: 366.2250; found: 366.2250.

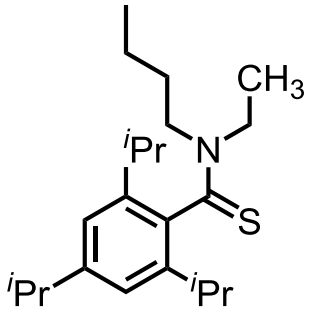


(3,4-dihydroisoquinolin-2(1*H*)-yl)(2,4,6-triisopropylphenyl)methanethione (1g)

Following the general procedure for the preparation of thioamides, the title compound was obtained in 85% yield (1.28 g). ^{1}H NMR (600 MHz, $CDCl_3$) (93:7 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.35-7.29 (m, 0.14H)*, 7.28-7.22 (m, 1.86H), 7.20-7.14 (m, 1H), 7.04 (s, 0.14H)*, 7.01 (s, 1.86), 6.94-6.89 (m, 0.93H), 4.64-4.59 (m, 1.86H), 4.56 (s, 1.86H), 3.77-3.67 (m, 0.14H)*, 3.15 (t, *J* = 6.1 Hz, 1.86H), 2.95-2.77 (m, 3.14H), 1.31-1.21 (m, 12.42H), 1.04 (d, *J* = 6.9 Hz, 5.58H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.27, 199.83, 148.63, 142.41, 142.20, 137.22, 137.20, 134.67, 133.42, 132.27, 132.07, 128.50, 128.11, 127.35, 126.52, 125.87, 121.54, 52.84, 51.01, 48.74, 47.13, 34.16, 30.77, 30.55, 29.38, 28.02, 25.00, 24.84, 23.96, 23.60, 23.47. HRMS (ESI-TOF) Calcd for $C_{25}H_{34}NS$ $[M+H]^+$: 380.2406; found: 380.2399.



***N,N*-diethyl-2,4,6-triisopropylbenzothioamide (1h)** Following the general procedure for the preparation of thioamides, the title compound was obtained in 82% yield (1.04 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.40 (q, *J* = 7.2 Hz, 2H), 2.89-2.78 (m, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.26 (d, *J* = 6.7 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.87, 148.28, 142.01, 137.41, 121.41, 46.97, 44.26, 34.15, 30.50, 25.25, 23.99, 23.35, 12.99, 10.76. HRMS (ESI-TOF) Calcd for $C_{20}H_{34}NS$ $[M+H]^+$: 320.2406; found: 320.2406.

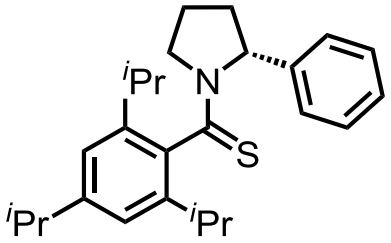


***N*-Butyl-*N*-ethyl-2,4,6-triisopropylbenzothioamide (1i)**

Following the general procedure for the preparation of thioamides, the title compound was obtained in 79% yield (1.09 g). ^{1}H NMR (600 MHz, $CDCl_3$) (84:16 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 6.95-6.93 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 1.84H), 4.13-4.09 (m, 0.16H)*, 3.43-3.37 (m, 0.16H)*, 3.27-3.21 (m, 1.84H), 2.89-2.76 (m, 3H),1.88-1.82 (m 0.16H)*, 1.54-1.47 (m, 2.08H), 1.47-1.42 (m, 0.16H)*, 1.39 (t, *J* = 7.1 Hz, 2.76H), 1.28-1.18 (m, 18H), 1.16-1.08 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 0.24H)*, 0.77 (t, *J* = 7.4 Hz, 2.76H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.90, 148.34, 141.99, 137.32, (121.42), 121.33, 77.21, 77.00, 76.79, 52.39, 49.46*, 47.45*, 45.19, 34.18, 30.53, 29.76, 27.35*, 25.38, 25.25*, 24.00, 23.37*, 23.22, 20.44, 20.10, 13.79*, 13.44, 12.97*, 10.75. HRMS (ESI-TOF) Calcd for $C_{22}H_{38}NS$ $[M+H]^+$: 348.2719; found: 348.2719.

General Procedure for enantioselective arylation: To a reaction vial with a magnetic stir bar was added the thioamide (0.2 mmol, 1.0 eq), potassium bicarbonate (40 mg, 0.4 mmol, 2.0 eq), arylboronic acid (0.4 mmol, 2.0 equiv. unless otherwise noted), 1,4-benzoquinone (23.8 mg, 0.2 mmol, 1.1 equiv., unless otherwise noted), chiral phosphoric acid (0.024 mmol, 0.12 eq) Tris(dibenzylideneacetone)dipalladium(0) (9.15 mg, 0.01 mmol, 0.05 eq). Then the reaction tube was connected to vacuum and backfilled with nitrogen three times. Then 1 ml of anhydrous 2-methyl-2-butanol was added and stirred rapidly at 65 ˚C for 16 hours. The reaction was then cooled to room temperature and the mixture was passed through a pad of celite. After the celite was washed with ethyl acetate, the combined organic layers were concentrated under vacuum. The crude residue was purified by preparative TLC with ethyl acetate and hexanes (1:20) as eluent.

Note: The products usually appear as two spots due to the restricted C-N thioamide bond rotation.

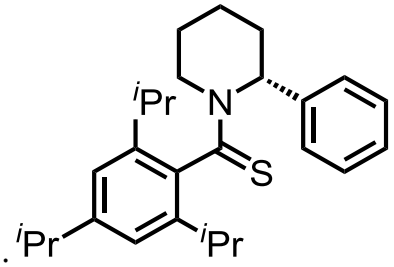


(*R*)-(2-phenylpyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (2a)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 84% yield (66 mg). The er value was determined by HPLC analysis on a Chiralcel OD-H column (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 7.87 min (minor), 8.63 min (major): 98:2 er.

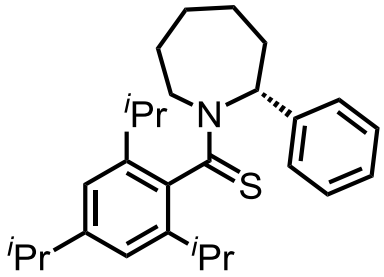
^{1}H NMR (600 MHz, $CDCl_3$) (60:40 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.38-7.34 (m, 0.8H)*, 7.29-7.25 (m, 1.2H), 7.23-7.16 (m, 1.8H), 6.99-6.97 (m, 0.8H)*, 6.96 (d, *J* = 1.7 Hz, 0.6H), 6.87-6.83 (m, 1.2H), 6.68 (d, *J* = 1.7 Hz, 0.6H), 5.90 (dd, *J* = 8.4, 3.5 Hz, 0.4H)*, 4.86 (d, *J* = 6.7 Hz, 0.6H), 4.33-4.22 (m, 1.2H), 3.57-3.46 (m, 0.8H)*, 2.96 (hept, *J* = 6.8 Hz, 0.4H)*, 2.92-2.83 (m, 0.8H)*, 2.79 (h, *J* = 6.9 Hz, 0.6H), 2.65 (hept, *J* = 6.8 Hz, 0.6H), 2.53-2.44 (m, 1H), 2.28-2.01 (m, 2.6H), 1.97-1.89 (m, 0.4H)*, 1.85-1.78 (m, 0.6H), 1.33 (d, *J* = 6.9 Hz, 1.8H), 1.30 (d, *J* = 7.0 Hz, 1.2H)*, 1.28-1.25 (m, 2.6H), 1.25-1.22 (m, 4H), 1.20-1.17 (m, 3.6H), 1.14 (d, *J* = 6.7 Hz, 1.2H)*, 1.10 (d, *J* = 6.7 Hz, 1.8H), 0.10 (d, *J* = 6.8 Hz, 1.8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.74, 199.17*, 148.55*, 148.51, 143.61, 142.57, 142.01, 141.33, 141.27*, 141.08, 138.53*, 137.96, 128.54, 128.45*, 127.27, 127.02*, 126.08*, 125.58, 121.66*, 121.41, 120.77, 66.79, 66.03*, 53.98*, 53.20, 34.82, 34.56*, 34.19*, 34.12, 31.32, 30.82*, 30.57, 30.13*, 25.71, 25.62, 25.26, 24.62, 24.01*, 23.98, 23.92, 23.78*, 23.29*, 23.19, 21.45, 21.36. HRMS (ESI-TOF) Calcd for $C_{26}H_{36}NS$ $[M+H]^+$: 394.2563; found: 394.2556.

The absolute stereochemistry was assigned by comparison of the HPLC data with the commercially available (*R*)-2-phenyl pyrrolidine (CAS: 56523-47-8 from Astatech) after installation of the directing group. The HPLC data was also compared after removal of the directing group from **2a** followed by Boc protection with the commercial material.



(*R*)-(2-phenylpiperidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (2b)

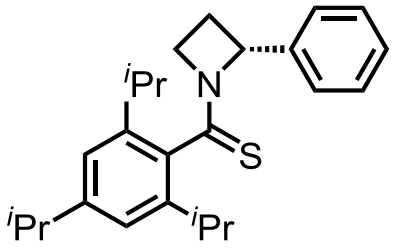
Following the general procedure for the enantioselective arylation with 3 equiv. of phenyl boronic acid, 5 equiv. of 1,4-BQ at 85˚C, the title compound was obtained in 62% yield (50.4 mg). The er value was determined by HPLC analysis on a Chiralcel AD-H column (5% isopropanol in hexanes, 0.5 mL/min) with t_r= 11.52 min (major), 18.613 min (minor): 95.5:4.5 er. ^{1}H MR (600 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 7.44-7.37 (m, 3H), 7.32-7.28 (m, 1H), 6.99 (dd, *J* = 15.5, 1.6 Hz, 2H), 3.74 (d, *J* = 12.9 Hz, 1H), 3.14-2.98 (m, 3H), 2.87 (p, *J* = 6.9 Hz, 1H), 2.57 (dd, *J* = 14.6, 2.8 Hz, 1H), 1.85-1.71 (m, 2H), 1.57-1.50 (m, 2H), 1.37-1.17 (m, 16H), 1.14 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.04, 148.39, 142.26, 141.96, 137.98, 137.10, 128.72, 127.10, 126.94, 121.62, 57.23, 47.71, 34.14, 30.83, 30.62, 27.36, 26.08, 25.80, 24.55, 23.98, 23.64, 23.49, 19.24. HRMS (ESI-TOF) Calcd for $C_{27}H_{38}NS$ $[M+H]^+$: 408.2719; found: 408.2719.



(*R*)-(2-phenylazepan-1-yl)(2,4,6-triisopropylphenyl)methanethione (2c)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 54% yield (45.4 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 17.58 min (minor), 18.63 min and 19.62 min(major): 98.5:1.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (88:12 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.46-7.43 (m, 1.76H), 7.37-7.33 (m, 1.76H), 7.29-7.25 (m, 0.88H), 7.22-7.14 (m, 0.36H)*, 6.97 (dd, *J* = 1.8, 0.5 Hz, 0.88H), 6.96 (d, *J* = 1.4 Hz, 0.12H)*, 6.89 (dd, *J* = 1.8, 0.5 Hz, 0.88H), 6.82-6.79 (m, 0.24H)*,

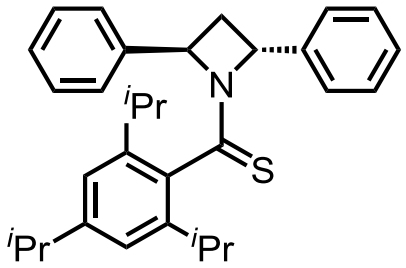
6.68 (d, *J* = 1.7 Hz, 0.12H)*, 6.65 (dd, *J* = 11.5, 5.6 Hz, 0.88H), 5.57 (dd, *J* = 13.0, 5.2 Hz, 0.12H)*, 4.83 (dd, *J* = 11.6, 6.0 Hz, 0.12H)*, 3.92 (ddd, *J* = 14.1, 5.1, 3.1 Hz, 0.88H), 3.72-3.65 (m, 0.12H)*, 3.58 (ddd, *J* = 14.1, 11.1, 2.2 Hz, 0.88H), 3.04 (hept, *J* = 6.7 Hz, 0.88H), 2.93 (hept, *J* = 7.0 Hz, 0.12H)*, 2.89-2.79 (m, 1.00H), 2.45 (hept, *J* = 6.8 Hz, 0.88H), 2.41-2.31 (m, 1.00H), 2.18-2.10 (m, 0.12H)*, 2.06-1.90 (m, 2.12H), 1.87-1.80 (m, 0.88H), 1.62-1.48 (m, 3.12H), 1.46-1.37 (m, 1.00H), 1.36 (d, *J* = 6.9 Hz, 0.36H)*, 1.31 (dd, *J* = 6.8, 1.5 Hz, 5.28H), 1.29 (d, *J* = 6.7 Hz, 0.36H)*, 1.23 (d, *J* = 6.9 Hz, 5.28H), 1.21 (dd, *J* = 6.9, 1.6 Hz, 0.72H)*, 1.13 (d, *J* = 6.9 Hz, 2.64H), 1.05 (d, *J* = 6.7 Hz, 0.36H)*, 0.95 (d, *J* = 6.7 Hz, 2.64H), 0.02 (d, *J* = 6.7 Hz, 0.36H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 202.5*, 202.4, 148.4*, 148.2, 143.1*, 142.3, 142.1*, 141.8, 141.5, 141.2*, 137.6, 136.9*, 128.7*, 128.1, 127.1*, 127.1, 125.5*, 121.7, 121.5*, 121.3, 120.7*,66.6*, 64.4, 50.2, 50.2*, 39.3*, 35.8, 34.1*, 34.1, 31.6, 31.3*, 30.5*, 29.7, 29.6*, 28.6, 27.0*, 26.0, 25.9*, 25.9, 25.7*, 25.4*, 24.8, 24.1*, 24.0, 23.9, 23.3*, 22.9, 22.8, 20.8*. HRMS (ESI-TOF) Calcd for $C_{28}H_{40}NS$ $[M+H]^+$: 422.2876; found: 422.2882.



***(R)-(*2-phenylazetidin-1-yl)(2,4,6-triisopropylphenyl)methanethione ($2d_{mono}$)**

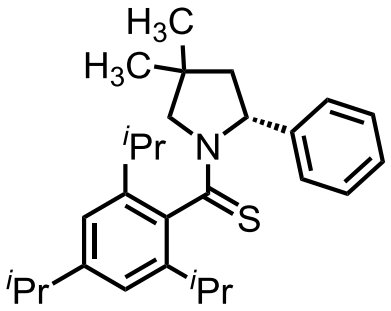
Following the general procedure for the enantioselective arylation, the title compound was obtained in 40% yield (30.3 mg). The er value was determined by HPLC analysis on a Chiralcel OD-H column (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 8.813 min (minor), 9.253 min (major): 98:2 er. ^{1}H NMR (600 MHz, $CDCl_3$) (69:31 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.47-7.39 (m, 1.31H), 7.35-7.31 (m, 0.31H)*, 7.19-7.10 (m, 2.07H), 7.00-6.97 (m, 1.31H), 6.80-6.77 (m, 1.31H), 6.59 (d, *J* = 1.6 Hz, 0.69H), 5.78-5.71 (m, 0.31H)*, 4.96-4.90 (m, 0.69H), 4.58-4.48 (m, 1.31H), 4.10-4.03 (m, 0.31H)*, 3.95-3.87 (m, 0.31H)*, 3.11-2.95 (m, 0.62H), 2.90-2.70 (m, 2.71H), 2.50-2.36 (m, 1.38H), 2.27-2.19 (m, 0.31H)*, 1.46 (d, *J* = 6.9 Hz, 2.07H),

1.34-1.16 (m, 11.79H), 1.07 (d, J = 6.7 Hz, 2.07H), 0.18 (d, J = 6.8 Hz, 2.07H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.38, 199.93*, 149.20, 148.99, 144.41, 143.16*, 142.85*, 141.86, 139.74*, 138.18, 134.91*, 134.49, 128.67*, 128.56, 128.40, 127.88*, 127.41, 126.51, 121.45*, 121.32*, 120.98, 120.41, 69.31, 68.49*, 53.34*, 51.65, 34.32, 34.23*, 31.06, 30.94*, 30.70, 30.30*, 30.17*, 29.68*, 26.04, 25.43*, 24.79*, 24.54*, 24.51*, 24.23, 23.98, 23.96, 23.51, 23.45*, 23.10, 21.13. HRMS (ESI-TOF) Calcd for $C_{25}H_{34}NS$ $[M+H]^+$: 380.2406; found: 380.2398.



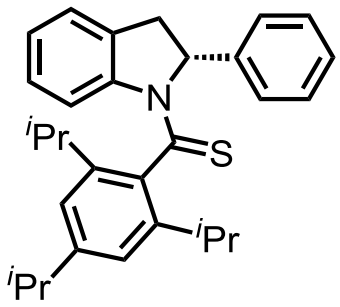
((2*R*,4*R*)-2,4-diphenylazetidin-1-yl)(2,4,6-triisopropylphenyl)methanethione ($2d_{di}$)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 13% yield (11.8 mg). The er value was determined by HPLC analysis on a Chiralcel OD-H column (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 10.63 min (minor), 12.31 min (major): 98:2 er. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2H), 7.47-7.42 (m, 2H), 7.38-7.33 (m, 1H), 7.20-7.12 (m, 3H), 6.95 (d, J = 1.6 Hz, 1H), 6.90-6.86 (m, 2H), 6.53 (d, J = 1.6 Hz, 1H), 3.07 (hept, J = 6.8 Hz, 1H), 3.00-2.93 (m, 1H), 2.84-2.74 (m, 2H), 2.46 (hept, J = 6.8 Hz, 1H).1.56 (d, J = 7.0 Hz, 6H), 1.22-1.15 (m, 6H), 1.07 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.7 Hz, 3H), 0.22 (d, J = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.05, 149.13, 144.94, 142.05, 138.87, 138.44, 134.63, 128.62, 128.48, 128.40, 128.23, 128.12, 127.82, 121.05, 120.35, 68.85, 67.32, 34.32, 33.91, 30.83, 29.85, 26.56, 25.63, 24.25, 23.99, 23.22, 21.40. HRMS (ESI-TOF) Calcd for $C_{31}H_{38}NS$ $[M+H]^+$: 456.2719; found: 456.2710.



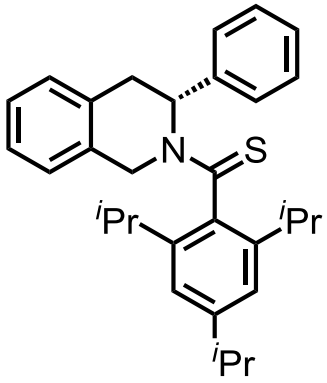
(*R*)-(4,4-dimethyl-2-phenylpyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (2e)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 78% yield (65.6 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 25.10 min (minor), 49.86 min (major): 95.5:4.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (77:23 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.37-7.30 (m, 3.08H), 7.27-7.23 (m, 0.77H), 7.11-7.06 (m, 0.69H), 6.98-6.96 (m, 1H), 6.95-6.91 (m, 0.77H), 6.66-6.63 (m, 0.46H)*, 6.55 (d, *J* = 1.7 Hz, 0.23H)*, 5.61 (t, *J* = 9.0 Hz, 0.77H), 5.07 (dd, *J* = 13.3, 1.6 Hz, 0.23H)*, 4.70 (t, *J* = 8.3 Hz, 0.23H)*, 3.73 (d, *J* = 13.3 Hz, 0.23H)*, 3.47 (dd, *J* = 11.8, 1.8 Hz, 0.77H), 3.34 (d, *J* = 11.9 Hz, 0.77H), 3.04-2.73 (m, 2.77H), 2.44-2.30 (m, 1H), 2.29-2.21 (m, 0.23H)*, 2.01-1.92 (m, 1H), 1.43 (d, *J* = 6.9 Hz, 0.69H)*, 1.31-1.18 (m, 15H), 1.17 (s, 2.31H), 1.12-1.08 (m, 3H) 1.01 (d, *J* = 6.7 Hz, 2.31H), 0.17 (d, *J* = 6.7 Hz, 0.69H)*. ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.36*, 199.08, 148.74*, 148.45, 144.46*, 142.76, 142.64, 142.37*, 141.75, 140.50*, 138.63, 137.23*, 128.51*, 128.18, 127.20*, 127.15, 126.91, 126.60*, 121.52, 121.12*, 120.43*, 67.04, 66.60*, 66.52*, 66.08, 52.17*, 50.81, 37.83, 36.68*, 34.25*, 34.13, 31.06, 30.79*, 29.63, 27.58*, 27.27*, 26.32*, 25.88, 25.78, 25.68, 24.56, 24.20*, 23.97, 23.45, 22.99*, 21.39*. HRMS (ESI-TOF) Calcd for $C_{28}H_{40}NS$ $[M+H]^+$: 422.2876; found: 422.2872.



(*R*)-(2-phenylindolin-1-yl)(2,4,6-triisopropylphenyl)methanethione (2f)

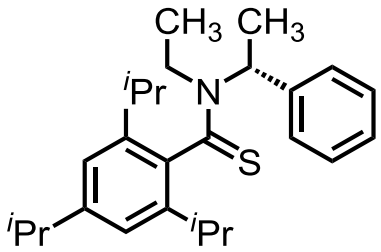
Following the general procedure for the enantioselective arylation, the title compound was obtained in 86% yield (75.8 mg). The er value was determined by HPLC analysis with two columns, onChiralcelOD-H column and chiralcel IC column attached one after the other (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 19.33 min (minor), 19.98 min (major): er. ^{1}H NMR (400 MHz, $CDCl_3$) (92:8 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.33-7.15 (m, 6H), 7.08-6.92 (m, 3H), 6.81 (t, *J* = 7.9 Hz, 0.92H), 6.74 (dd, *J* = 9.8, 1.8 Hz, 1H), 6.62-6.57 (m, 0.08H)*, 5.64 (d, *J* = 8.4 Hz, 0.92H), 5.58 (d, *J* = 8.4 Hz, 0.08H)*, 4.76-4.69 (m, 0.16H)*, 3.78 (dd, *J* = 16.2, 9.7 Hz, 0.92H), 3.25-3.18 (m, 0.16H)*, 3.04-2.70 (m, 4H), 1.31-1.06 (m, 15.24H), 0.68 (d, *J* = 6.9 Hz, 2.76H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.95, 149.47, 143.90, 143.03, 141.58, 141.35, 137.83, 133.40, 128.70*, 128.47, 127.52, 127.24, 125.95, 125.93, 125.14, 121.87, 117.18, 67.74, 36.44, 34.31, 30.77, 30.02, 25.02, 24.76*, 24.33, 24.14, 24.10*, 24.07, 23.68, 23.37*, 22.62. HRMS (ESI-TOF) Calcd for $C_{30}H_{36}NS$ $[M+H]^+$: 442.2563; found: 442.2559.



(*R*)-(3-phenyl-3,4-dihydroisoquinolin-2(1H)-yl)(2,4,6-triisopropylphenyl) methanethione (2g)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 77% yield (70 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 20.70 min (minor), 24.30 min(major): 94:6 er. ^{1}H NMR (400 MHz, $CDCl_3$) (87:13 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.66 (d, *J* = 6.1 Hz, 0.87H), 7.37-6.88 (m, 9.74H), 6.80 (m, 0.39H)*, 6.71 (d, *J* = 7.7 Hz,

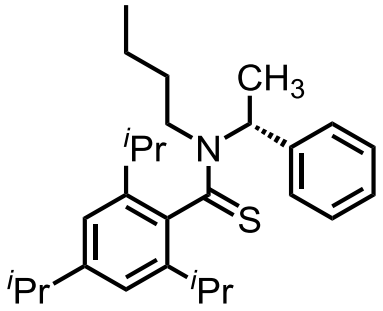
0.87H), 5.74 (d, *J* = 19.0 Hz, 0.13H)*, 5.51 (dd, *J* = 5.1, 2.5 Hz, 0.13H)*, 5.35 (d, *J* = 19.0 Hz, 0.13H)*, 4.55 (d, *J* = 16.7 Hz, 0.87H), 3.98 (d, *J* = 16.6 Hz, 0.87H), 3.64 (dd, *J* = 17.1, 6.3 Hz, 0.87H), 3.49-3.29 (m, 1H), 3.15-2.95 (m, 1H), 2.94-2.49 (m, 2.13H), 1.37-1.06 (m, 15H), 0.68 (d, *J* = 6.9 Hz, 2.61H), 0.21 (d, *J* = 6.8 Hz, 0.39H)*. ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.97*, 200.68, 148.63, 148.53*, 143.86*, 142.24, 142.07, 141.54*, 139.61*, 138.16, 137.15*, 136.87, 132.59, 132.54*, 131.42, 131.00*, 128.74, 128.51, 128.36*, 128.20*, 127.76, 127.38, 127.19, 127.11*, 127.04*, 126.37, 126.30*, 125.90, 125.58, 121.79*, 121.51, 121.00, 60.83*, 55.58, 52.07*, 49.06, 36.72*, 34.13, 34.09*, 31.37*, 30.64*, 30.45, 30.16, 25.58*, 25.52*, 24.88, 24.43, 23.96, 23.92, 23.26*, 22.86, 21.61*. HRMS (ESI-TOF) Calcd for $C_{31}H_{38}NS$ $[M+H]^+$: 456.2719; found: 456.2710.



(*R*)-N-ethyl-2,4,6-triisopropyl-N-(1-phenylethyl)benzothioamide (2h)

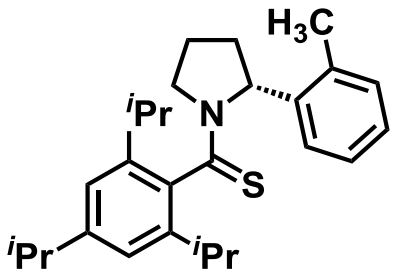
Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 49% yield (38.7 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 16.22 min (minor), 17.05 (major): 98:2 er. ^{1}H NMR (400 MHz, $CDCl_3$) (85:15 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.56-7.21 (m, 5.7H), 7.14 (d, *J* = 7.6 Hz, 0.3H)*, 6.95 (d, *J* = 6.1 Hz, 1.7H), 5.26 (q, *J* = 7.2 Hz, 0.15H)*, 4.81-4.67 (m, 0.15H)*, 3.73-3.61 (m, 0.15H)*, 3.35-3.22 (m, 0.85H), 3.17-3.04 (m, 0.85H), 2.98-2.75 (m, 3H), 1.76 (d, *J* = 7.1 Hz, 2.53H), 1.62 (d, *J* = 7.0 Hz, 0.47H)*, 1.44 (t, *J* = 7.0 Hz, 0.47H)*, 1.37-1.08 (m, 17.53H), 0.70-0.57 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.54, 201.48*, 148.37, 148.24*, 143.19*, 142.26*, 142.00, 141.69, 140.10*, 139.34, 137.33, 137.11*, 128.57, 128.00, 127.94, 127.3*2, 126.42*, 121.87*, 121.36, 121.21*, 61.69*, 57.46, 43.82*, 43.56, 34.13, 34.07*, 31.07, 30.77, 30.73, 30.21*, 25.69*, 25.62, 25.48, 23.98, 23.93, 23.17*, 22.99,

22.87, 22.75*, 19.65*, 15.44, 14.73, 12.34*. HRMS (ESI-TOF) Calcd for $C_{26}H_{38}NS$ $[M+H]^+$: 396.2719; found: 396.2713.



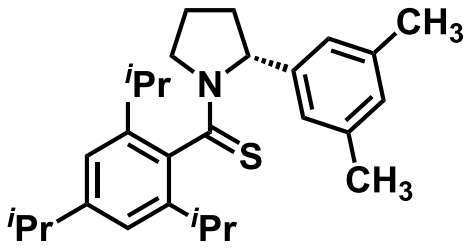
(*R*)-*N*-butyl-2,4,6-triisopropyl-*N*-(1-phenylethyl)benzothioamide (2i)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 53% yield (44.8 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (2% isopropanol in hexanes, 0.5 mL/min) with t_r = 16.48 min (minor), 18.28 (major): 92:8 er. ^{1}H NMR (600 MHz, $CDCl_3$) (65:35 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.52-7.49 (m, 1.35H), 7.46-7.37 (m, 2H), 7.35-7.29 (m, 1.35H), 7.27-7.23 (m, 0.35H)*, 7.16-7.12 (m, 0.65H), 6.97-6.92 (m, 1.65H), 6.85 (d, *J* = 1.7 Hz, 0.35H)*, 5.25 (q, *J* = 7.0 Hz, 0.35H)*, 4.62-4.53 (m, 0.35H)*, 3.56-3.49 (m, 0.35H)*, 3.08-3.00 (m, 0.65H), 2.98-2.76 (m, 3.65H), 1.73 (d, *J* = 7.1 Hz, 1.95H), 1.61 (d, *J* = 7.0 Hz, 1.05H), 1.34-1.11 (m, 17H), 1.14 (d, *J* = 6.9 Hz, 1.95H), 0.95 (t, *J* = 7.4 Hz, 1.05H), 0.80-0.62 (m, 2H), 0.60 (d, *J* = 6.8 Hz, 1.05H). 0.40 (t, *J* = 7.3 Hz, 1.95H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.60*, 201.38, 148.52, 148.22*, 143.18*, 142.23*, 141.99, 141.75, 140.15*, 139.36, 137.22, 137.19, 128.54, 128.02*, 127.99, 127.32*, 126.46, 121.89*, 121.25, 121.21, 61.62*, 57.46, 49.32*, 48.53, 34.22, 34.08*, 31.09*, 30.84, 30.75*, 30.56*, 30.27, 29.70, 28.26, 25.75*, 25.64, 24.01, 23.94, 23.20*, 22.81, 22.75, 22.71, 20.58*, 20.06, 19.78*, 15.27, 13.66*, 12.70. HRMS (ESI-TOF) Calcd for $C_{28}H_{42}NS$ $[M+H]^+$: 424.3032; found: 424.3027.



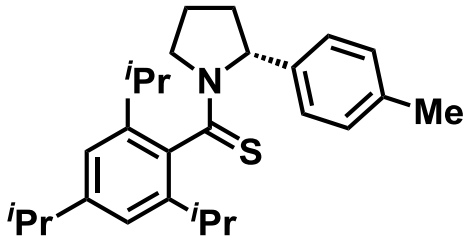
(*R*)-(2-(*o*-tolyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3a)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 71% yield (57.8 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 26.55 min and 33.33 min (minor), 34.98 (major): 97:3 er. ^{1}H NMR (600 MHz, $CDCl_3$) (64:36 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.22-7.13 (m, 2.28H), 7.10-7.06 (m, 0.36H)*, 7.03-6.96 (m, 2.64H), 6.96-6.93 (m, 0.36H)*, 6.68 (d, *J* = 1.7 Hz, 0.36H)*, 6.00 (dd, *J* = 8.3, 3.7 Hz, 0.64H), 5.13-5.09 (m, 0.36H)*, 4.34-4.18 (m, 0.72H)*, 3.58-3.52 (m, 1.28H), 3.00 (hept, *J* = 6.8 Hz, 0.64H), 2.87 (heptd, *J* = 6.7, 2.0 Hz, 1.28H), 2.79 (hept, *J* = 7.0 Hz, 0.36H)*, 2.68 (hept, *J* = 6.8 Hz, 0.36H)*, 2.53-2.44 (m, 2.56H), 2.43-2.36 (m, 0.36H)*, 2.36-2.26 (m, 0.36H)*, 2.26-2.08 (m, 1.36H), 1.99-1.88 (m, 1.28H), 1.69 (dd, *J* = 11.4, 6.3 Hz, 0.36H)*, 1.62 (s, 1.08H)*, 1.33 (dd, *J* = 6.9, 5.6 Hz, 3.00H), 1.30-1.22 (m, 8.76H), 1.18 (dd, *J* = 6.9, 1.0 Hz, 2.16H)*, 1.13 (d, *J* = 6.8 Hz, 1.92H), 1.08 (d, *J* = 6.7 Hz, 1.08H)*, 0.03 (d, *J* = 6.8 Hz, 1.08H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 199.4*, 198.8, 148.6*, 148.6, 143.6*, 142.8, 141.4, 141.3*, 140.2, 139.6*, 138.4, 138.3*, 135.2, 133.9*, 130.8, 130.3*, 127.2*, 127.0, 126.4*, 125.7, 125.4*, 123.8, 121.8, 121.4, 120.8*, 63.4*, 63.3, 54.3, 53.4*, 34.3*, 34.2, 33.1, 33.0*, 31.5*, 30.9, 30.6*, 30.1, 25.8*, 25.6*, 25.4, 24.7, 24.1, 24.1*, 24.1, 24.0, 24.0*, 23.9, 23.3, 23.1*, 21.5*, 21.2*, 19.6, 18.5*. HRMS (ESI-TOF) Calcd for $C_{27}H_{38}NS$ $[M+H]^+$: 408.2719; found: 408.2715.



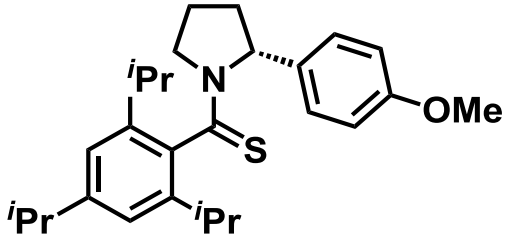
(*R*)-(2-(3,5-dimethylphenyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3b)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 88 % yield (74 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 39.77 min (minor), 55.86 (major): 97:3 er. ^{1}H NMR (600 MHz, $CDCl_3$) (65:35 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.00-6.97 (m, 1.30H), 6.96 (d, *J* = 1.7 Hz, 0.35H)*, 6.92-6.90 (m, 0.65H), 6.86 (dd, *J* = 1.6, 0.8 Hz, 1.30H), 6.82-6.79 (m, 0.35H)*, 6.68 (d, *J* = 1.7 Hz, 0.35H)*, 6.41-6.39 (m, 0.70H)*, 5.83 (dd, *J* = 8.2, 3.6 Hz, 0.65H), 4.77 (d, *J* = 6.5 Hz, 0.35H)*, 4.32-4.26 (m, 0.35H)*, 4.25-4.20 (m, 0.35H)*, 3.54-3.46 (m, 1.30H), 3.07 (hept, *J* = 6.9 Hz, 0.65H), 2.91-2.83 (m, 1.30H), 2.81 (hept, *J* = 7.0 Hz, 0.35H)*, 2.64 (hept, *J* = 6.8 Hz, 0.35H)*, 2.52 (hept, *J* = 6.7 Hz, 0.35H)*, 2.48-2.41 (m, 0.65H), 2.33 (s, 3.90H), 2.26-2.17 (m, 0.65H), 2.20 (s, 2.10H)*, 2.15-2.05 (m, 1.00H), 2.04-1.98 (m, 0.70H)*, 1.94-1.87 (m, 0.65H), 1.86-1.79 (m, 0.35H)*, 1.33 (dd, *J* = 6.9, 4.1 Hz, 3.00H), 1.27 (d, *J* = 4.0 Hz, 1.95H), 1.25 (d, *J* = 3.7 Hz, 1.95H), 1.23 (dd, *J* = 6.9, 1.9 Hz, 4.95H), 1.20 (d, *J* = 2.1 Hz, 1.05H)*, 1.19 (d, *J* = 2.1 Hz, 1.05H)*, 1.17 (d, *J* = 6.7 Hz, 1.95H), 1.12 (d, *J* = 6.7 Hz, 1.05H)*, 0.16 (d, *J* = 6.8 Hz, 1.05H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 199.6*, 198.9, 148.5, 148.5*, 143.8*, 142.5, 141.9, 141.3, 141.2*, 141.0*, 138.6, 138.0*, 138.0, 128.8*, 128.7, 123.6, 123.4*, 121.7, 121.5, 121.3*, 120.8*, 66.9*, 66.1, 54.0, 53.2*, 34.9*, 34.7, 34.2, 34.2*, 31.4*, 30.8, 30.6*, 30.2, 25.8*, 25.7*, 25.3, 24.8, 24.3, 24.1*, 24.0, 24.0, 23.9*, 23.8, 23.3, 23.1*, 21.7*, 21.5, 21.3, 21.1*. HRMS (ESI-TOF) Calcd for $C_{28}H_{40}NS$ $[M+H]^+$: 422.2876; found: 422.2870.



(*R*)-(2-(*p*-tolyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3c)

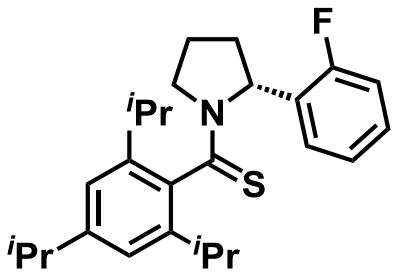
Following the general procedure for the enantioselective arylation, the title compound was obtained in 61% yield (49.6 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 40.49 min (major), 43.21 (minor): 93:7 er. ^{1}H NMR (600 MHz, $CDCl_3$) (75:25 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.20-7.15 (m, 3.00H), 7.03-7.01 (m, 0.50H)*, 6.99 (d, *J* = 0.8 Hz, 1.50H), 6.96 (d, *J* = 1.7 Hz, 0.25H)*, 6.74 (d, *J* = 8.1 Hz, 0.50H)*, 6.69 (d, *J* = 1.7 Hz, 0.25H)*, 5.88 (dd, *J* = 8.2, 3.6 Hz, 0.75H), 4.83 (d, *J* = 6.5 Hz, 0.25H)*, 4.32-4.22 (m, 0.50H)*, 3.55-3.46 (m, 1.50H), 2.98 (hept, *J* = 6.8 Hz, 0.75H), 2.88 (dhept, *J* = 10.8, 6.8 Hz, 1.50H), 2.80 (hept, *J* = 7.0 Hz, 0.25H)*, 2.66 (hept, *J* = 6.8 Hz, 0.25H)*, 2.53-2.43 (m, 1.00H), 2.36 (s, 2.25H), 2.28 (s, 0.75H)*, 2.26-2.19 (m, 0.50H)*, 2.19-2.06 (m, 1.00H), 2.06-2.00 (m, 0.75H), 1.96-1.89 (m, 0.75H), 1.84-1.77 (m, 0.25H)*, 1.33 (d, *J* = 6.9 Hz, 0.75H)*, 1.30 (d, *J* = 7.0 Hz, 2.25H), 1.27 (dd, *J* = 6.9, 2.0 Hz, 4.50H), 1.25-1.23 (m, 5.25H), 1.20 (dd, *J* = 6.9, 3.4 Hz, 1.50H)*, 1.16 (d, *J* = 6.7 Hz, 2.25H), 1.11 (d, *J* = 6.7 Hz, 0.75H)*, 0.13 (d, *J* = 6.7 Hz, 0.75H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 199.5*, 199.0, 148.5, 148.4*, 143.6*, 142.5, 141.3, 141.0*, 139.0, 138.6, 138.3*, 138.0*, 136.9*, 136.5, 129.2, 129.1*, 125.9, 125.5*, 121.6, 121.4, 121.4*, 120.7*, 66.6*, 65.8, 53.9, 53.1*, 34.9*, 34.6, 34.2, 34.1*, 31.3*, 30.8, 30.5*, 30.1, 25.7*, 25.6*, 25.3, 24.6, 24.0, 24.0, 23.9*, 23.7, 23.3, 23.2*, 21.5*, 21.3*, 21.1, 20.9*. HRMS (ESI-TOF) Calcd for $C_{27}H_{38}NS$ $[M+H]^+$: 408.2719; found: 408.2724.



(*R*)-(2-(4-methoxyphenyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3d)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 84% yield (71.2 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 39.90 min and 64.08 min (minor), 43.05 min and 46.93 min (major):

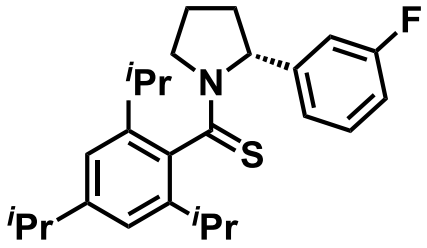
98.5:1.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (67:33 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.23-7.17 (m, 1.37H), 6.99-6.94 (m, 1.67H), 6.78-6.68 (m, 1.34H), 6.92-6.87 (m, 1.67H), 5.86 (dd, *J* = 8.2, 3.6 Hz, 0.67H), 4.82 (d, *J* = 6.3 Hz, 0.33H), 4.32-4.19 (m, 0.67H), 3.81 (s, 2H), 3.75 (s, 1H), 3.54-3.43 (m, 1H), 2.95-2.77 (m, 2.34H), 2.64 (hept, *J* = 6.8 Hz, 0.33H), 2.53-2.40 (m, 1H), 2.25-2.00 (m, 2.34H), 1.96-1.88 (m, 0.66H), 1.81-1.77 (m, 0.33H), 1.32 (d, *J* = 6.9 Hz, 1H), 1.30-1.17 (m, 13H), 1.14 (d, *J* = 6.7 Hz, 2H), 1.11 (d, *J* = 6.7 Hz, 1H), 0.18 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.56*, 198.95, 158.84*, 158.49, 148.52, 148.46*, 143.63*, 142.51, 141.27, 141.07*, 138.57, 137.98*, 134.07, 133.58*, 127.30, 126.72*, 121.63, 121.41, 121.38*, 120.76*, 113.93*, 113.82, 66.30*, 65.43, 55.33*, 55.20, 53.86, 53.09*, 34.93*, 34.55, 34.19, 34.13*, 31.32*, 30.81, 30.56, 30.10, 25.71*, 25.62*, 25.24, 24.64, 24.01, 23.98*, 23.94*, 23.76, 23.29, 23.19, 21.49*. HRMS (ESI-TOF) Calcd for $C_{27}H_{38}NOS$ $[M+H]^+$: 424.2669; found: 424.2662.



(*R*)-(2-(2-fluorophenyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3e)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 78% yield (64 mg). The er value was determined by HPLC analysis on two columns attached one after the other with Chiralcel ADH followed by Chiralcel IC column (0.5% isopropanol in hexanes, 0.5 mL/min) with t_r = 32.45 min (minor), 41.02 (major): 98.5:1.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (66:34 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.29-7.24 (m, 0.66H), 7.24-7.20 (m, 0.66H), 7.20-7.16 (m, 0.34H)*, 7.14-7.04 (m, 1.66H), 7.02-6.97 (m, 1.66H), 6.96 (d, *J* = 1.7 Hz, 0.34H)*, 6.91-6.86 (m, 0.34H)*, 6.69 (d, *J* = 1.6 Hz, 0.34H)*, 5.99 (dd, *J* = 8.3, 4.5 Hz, 0.66H), 5.17 (d, *J* = 7.3 Hz, 0.34H)*, 4.34-4.27 (m, 0.34H)*, 4.26-4.20 (m, 0.34H)*, 3.59-3.49 (m, 1.32H), 2.95 (hept, *J* = 6.8 Hz, 0.66H), 2.90-2.83 (m, 1.32H), 2.80 (hept, *J* = 6.9 Hz, 0.34H)*, 2.63 (hept, *J* = 6.8 Hz, 0.34H)*,

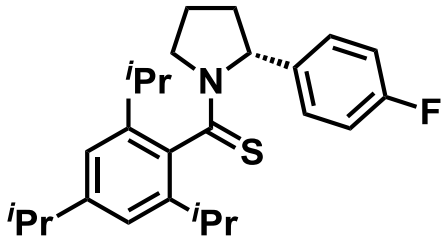
2.57-2.49 (m, 1.00H), 2.28-2.19 (m, 0.34H)*, 2.19-2.13 (m, 0.66H), 2.13-2.03 (m, 1.34H), 1.97-1.89 (m, 0.66H), 1.89-1.85 (m, 0.34H)*, 1.33 (d, *J* = 7.0 Hz, 1.02H)*, 1.29 (d, *J* = 7.0 Hz, 1.98H), 1.26 (dd, *J* = 6.8, 3.7 Hz, 3.96H), 1.24-1.22 (m, 4.98H), 1.19 (dd, *J* = 6.9, 3.7 Hz, 2.04H)*, 1.15-1.11 (m, 3.00H), 0.19 (d, *J* = 6.8 Hz, 1.02H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.3*, 199.3, 160.04 (d, *J* = 246.1 Hz), 159.01 (d, *J* = 246.8 Hz)*, 148.7*, 148.6, 143.4*, 142.6, 141.4, 141.2*, 138.6, 137.7*, 130.9*, 128.7, 128.4*, 128.3*,128.95 (d, *J* = 9.0 Hz)*, 128.76 (d, *J* = 8.6 Hz), 127.97 (d, *J* = 4.4 Hz), 127.37 (d, *J* = 3.4 Hz)*, 124.17 (d, *J* = 3.4 Hz)*, 123.74 (d, *J* = 3.3 Hz), 121.7, 121.4, 121.4*, 121.0*,115.80 (d, *J* = 21.9 Hz), 115.46 (d, *J* = 21.1 Hz)* , 61.3, 61.3, 60.8*, 60.8*, 54.0, 53.2*, 34.2, 34.2*, 33.6*, 33.6, 31.3*, 30.8, 30.6*, 30.2, 25.7*, 25.6*, 25.3, 24.7, 24.3, 24.0, 24.0, 24.0, 23.9, 23.3, 23.1*, 21.8*, 21.7*. HRMS (ESI-TOF) Calcd for $C_{26}H_{35}FNS$ $[M+H]^+$: 412.2469; found: 412.2461.



(*R*)-(2-(3-fluorophenyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3f)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 80% yield (65.6 mg). The er value was determined by HPLC analysis on two columns attached one after the other with Chiralcel ADH followed by Chiralcel IC column (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 28.64 min (minor), 32.05 (major): 99:1 er. ^{1}H NMR (600 MHz, $CDCl_3$) (64:36 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.35-7.30 (m, 0.56H), 7.21-7.16 (m, 0.44H)*, 7.08-7.05 (m, 0.56H), 7.00-6.93 (m, 2.7H), 6.89 (tdd, *J* = 8.4, 2.6, 0.8 Hz, 0.44H)*, 6.70 (d, *J* = 1.6 Hz, 0.44H)*, 6.65 (ddt, *J* = 7.6, 1.5, 0.7 Hz, 0.44H)*, 6.56 (dt, *J* = 9.7, 2.1 Hz, 0.44H)*, 5.88 (dd, *J* = 8.5, 3.7 Hz, 0.56H), 4.85 (d, *J* = 7.1 Hz, 0.44H)*, 4.33-4.19 (m, 0.88H)*, 3.58-3.45 (m, 1.12H), 3.01-2.76 (m, 2.2H), 2.63 (hept, *J* = 6.8 Hz, 0.44H), 2.56-2.44 (m, 1.12H), 2.31-2.12 (m, 1.12H), 2.12-1.99 (m, 1.12H), 1.99-1.90 (m, 0.56H), 1.88-1.78 (m, 0.44H), 1.37-1.11 (m, 16.68H), 0.21 (d, *J* = 6.8 Hz,

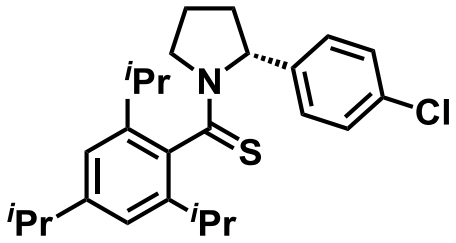
1.32H)*. ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.17*, 199.66, 163.03 (d, *J* = 245.9 Hz)*, 162.88 (d, *J* = 247.2 Hz), 148.73*, 148.71, 144.69 (d, *J* = 6.7 Hz), 143.90 (d, *J* = 6.5 Hz)*, 143.61*, 142.60, 141.28, 141.09*, 138.36, 137.81*, 130.15 (d, *J* = 8.3 Hz)*, 130.04 (d, *J* = 8.4 Hz), 121.88 (d, *J* = 2.4 Hz), 121.72, 121.50*, 121.45, 121.26 (d, *J* = 2.5 Hz), 120.87*, 114.27 (d, *J* = 21.1 Hz)*, 113.95 (d, *J* = 21.0 Hz), 112.95 (d, *J* = 22.2 Hz). 112.84 (d, *J* = 22.1 Hz)*, 66.23*, 65.61, 53.96, 53.12*, 34.77*, 34.50, 34.21, 34.14*, 31.35*, 30.87, 30.62*, 30.26, 25.72, 25.63*, 25.26, 24.58*, 24.06, 24.01, 23.99, 23.91*, 23.84*, 23.27, 23.15*, 21.53*, 21.38. HRMS (ESI-TOF) Calcd for $C_{26}H_{35}FNS$ $[M+H]^+$: 412.2469; found: 412.2464.



(*R*)-(2-(4-fluorophenyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3g)

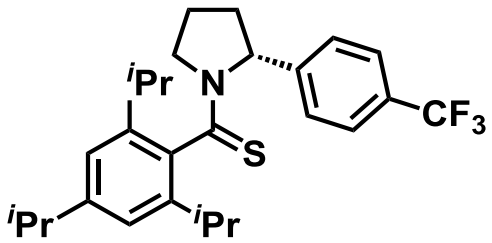
Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 87% yield (71.4 mg). The er value was determined by HPLC analysis on two columns attached one after the other with Chiralcel ADH followed by Chiralcel IC column (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 25.76 min (major), 35.29 min (minor): 95.5:4.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (63:37 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.27-7.23 (m, 1.26H), 7.07-7.03 (m, 1.26H), 6.99-6.97 (m, 1.26H), 6.96 (d, *J* = 1.7 Hz, 0.37H)*, 6.94-6.89 (m, 0.74H)*, 6.84-6.80 (m, 0.74H)*, 6.70 (d, *J* = 1.8 Hz, 0.37H)*, 5.87 (dd, *J* = 8.3, 3.8 Hz, 0.63H), 4.85 (d, *J* = 6.9 Hz, 0.37H)*, 4.32-4.18 (m, 0.74H)*, 3.57-3.51 (m, 0.63H), 3.51-3.45 (m, 0.63H), 2.92-2.76 (m, 2.38H), 2.63 (hept, *J* = 6.8 Hz, 0.37H)*, 2.54-2.43 (m, 1.00H), 2.28-2.12 (m, 1.05H)*, 2.12-1.99 (m, 1.26H), 1.98-1.90 (m, 0.63H), 1.82-1.76 (m, 0.37H)*, 1.32 (d, *J* = 6.9 Hz, 1.11H)*, 1.28-1.25 (m, 5.67H), 1.23 (dd, *J* = 6.8, 2.1 Hz, 4.89H), 1.19 (dd, *J* = 6.9, 3.5 Hz, 2.22H)*, 1.14 (d, *J* = 6.7 Hz, 1.89H), 1.11 (d, *J* = 6.7 Hz, 1.11H)*, 0.19 (d, *J* = 6.8 Hz, 1.11H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.0*, 199.4, 161.76 (d, *J* = 245.2 Hz), 162.02 (d, *J* = 245.6 Hz)*, 148.7, 143.6*, 142.5, 141.3,

141.1*, 138.4, 137.9*, 137.80 (d, *J* = 4.1 Hz), 137.26 (d, *J* = 3.3 Hz)*, 127.79 (d, *J* = 7.7 Hz), 127.23 (d, *J* = 7.9 Hz), 121.7, 121.5, 121.4*, 120.9*, 115.35 (d, *J* = 21.4 Hz). 115.45 (d, *J* = 21.6 Hz)*, 66.1*, 65.3, 53.9, 53.1*, 34.9*, 34.6, 34.2, 34.2*, 31.3*, 30.9, 30.6*, 30.2, 25.7*, 25.6*, 25.3, 24.6, 24.0, 24.0*, 23.9*, 23.8, 23.3, 23.2*, 21.5. HRMS (ESI-TOF) Calcd for $C_{26}H_{35}FNS$ $[M+H]^+$: 412.2469; found: 412.2468.



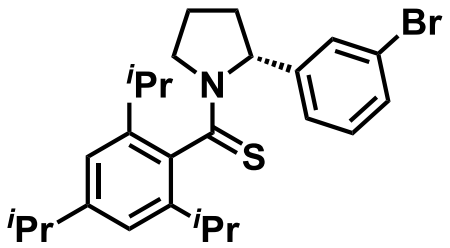
(*R*)-(2-(4-chlorophenyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3h)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 77% yield (65.2 mg). The er value was determined by HPLC analysis on two columns attached one after the other with Chiralcel ADH followed by Chiralcel IC column (0.5% isopropanol in hexanes, 0.5 mL/min) with t_r = 22.57 min (major),39.39 min (minor): 96:4 er. ^{1}H NMR (600 MHz, $CDCl_3$) (57:43 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.36-7.31 (m, 1.14H), 7.23-7.17 (m, 2.00H), 6.99-6.97 (m, 1.14H), 6.96 (d, *J* = 1.7 Hz, 0.43H)*, 6.82-6.78 (m, 0.86H)*, 6.70 (d, *J* = 1.7 Hz, 0.43H)*, 5.85 (dd, *J*= 8.3, 3.9 Hz, 0.57H), 4.83 (d, *J* = 7.4 Hz, 0.43H)*, 4.32-4.20 (m, 0.86H)*, 3.57-3.51 (m, 0.57H), 3.50-3.45 (m, 0.57H), 2.94-2.76 (m, 2.14H), 2.63 (hept, *J* = 6.8 Hz, 0.43H)*, 2.53-2.41 (m, 1.00H), 2.29-2.12 (m, 1.29H)*, 2.12-1.98 (m, 1.14H), 1.98-1.89 (m, 0.57H), 1.82-1.76 (m, 0.43H)*, 1.32 (d, *J* = 6.9 Hz, 1.29H)*, 1.30-1.21 (m, 9.84H), 1.19 (dd, *J* = 6.9, 3.1 Hz, 2.58H)*, 1.15 (d, *J* = 6.7 Hz, 1.71H), 1.11 (d, *J* = 6.7 Hz, 1.29H)*, 0.20 (d, *J* = 6.7 Hz, 1.29H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.1*, 199.5, 148.7, 143.6*, 142.5, 141.3, 141.1*, 140.6, 139.9*, 138.4, 137.8*, 133.2*, 132.7, 128.7*, 128.7, 127.5, 127.0*, 121.7*, 121.5, 120.9*, 66.1*, 65.5, 54.0, 53.1*, 34.8*, 34.6, 34.2, 34.2*, 31.3*, 30.9, 30.6*, 30.2, 25.7*, 25.6*, 25.3, 24.6, 24.0*, 24.0, 24.0*, 23.9*, 23.9, 23.3, 23.2*, 21.5*, 21.4*. HRMS (ESI-TOF) Calcd for $C_{26}H_{35}ClNS$ $[M+H]^+$: 428.2173; found: 428.2175.



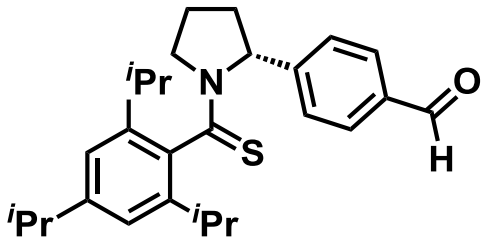
(*R*)-(2-(4-(trifluoromethyl)phenyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3i)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 71% yield (65.4 mg). The er value was determined by HPLC analysis on two columns attached one after the other with Chiralcel ADH followed by Chiralcel IC column (0.5% isopropanol in hexanes, 0.5 mL/min) with t_r = 29.97 min (minor), 31.46 min (major): 96:4 er. ^{1}H NMR (600 MHz, $CDCl_3$) (94:6 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.65-7.60 (m, 1.88H), 7.51-7.48 (m, 0.12H)*, 7.41-7.36 (m, 1.88H), 7.02-6.98 (m, 2.00H), 6.98 (d, *J* = 1.7 Hz, 0.06H)*, 6.68 (d, *J* = 1.7 Hz, 0.06H)*, 5.93 (dd, *J* = 8.5, 3.8 Hz, 0.94H), 4.92 (d, *J* = 7.6 Hz, 0.06H)*, 4.33-4.27 (m, 0.12H)*, 3.61-3.54 (m, 0.94H), 3.54-3.48 (m, 0.94H), 2.94 (hept, *J* = 6.9 Hz, 0.94H), 2.90-2.78 (m, 1.94H), 2.65 (hept, *J* = 6.8 Hz, 0.06H)*, 2.58-2.49 (m, 0.94H), 2.43 (hept, *J* = 6.7 Hz, 0.06H)*, 2.34-2.25 (m, 0.06H), 2.22-2.15 (m, 0.12H)*, 2.12-1.93 (m, 2.82H), 1.86-1.80 (m, 0.06H)*, 1.34 (d, *J* = 6.9 Hz, 0.18H)*, 1.32 (d, *J* = 7.0 Hz, 2.82H), 1.29-1.22 (m, 11.46H), 1.19 (dd, *J* = 6.9, 3.9 Hz, 0.36H)*, 1.16 (d, *J* = 6.7 Hz, 2.82H), 1.10 (d, *J* = 6.7 Hz, 0.18H)*, 0.10 (d, *J* = 6.8 Hz, 0.18H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.2*, 199.8, 148.8, 146.2, 145.4*, 143.4*, 142.5, 141.3, 141.2*, 138.2, 137.8*,129.25 (q, *J* = 32.8 Hz), 126.4, 126.0*, 125.53 (q, *J* = 3.6 Hz), 124.11 (d, *J* = 271.8 Hz), 121.7, 121.5, 120.9*, 66.2*, 65.7, 54.1, 53.2*, 34.7*, 34.6, 34.2, 34.1*, 31.3*, 30.9, 30.6*, 30.3, 25.7*, 25.6*, 25.2, 24.6, 24.0, 24.0, 24.0, 23.9, 23.3, 23.2*, 21.5*, 21.2*. HRMS (ESI-TOF) Calcd for $C_{27}H_{35}F_3NS$ $[M+H]^+$: 462.2437; found: 462.2443.



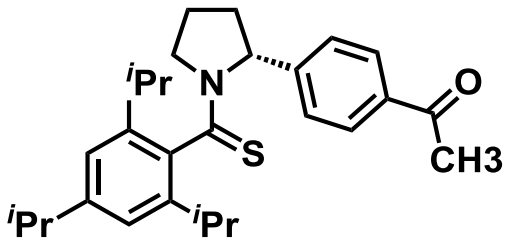
(*R*)-(2-(3-bromophenyl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3j)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 50% yield (47 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 21.59 min (minor), 27.316 min (major): 93:7 er.^{1}H NMR (600 MHz, $CDCl_3$) (84:16 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.42-7.39 (m, 0.84H), 7.39-7.37 (m, 0.84H), 7.33 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 0.16H)*, 7.25-7.22 (m, 1.68H), 7.09 (t, *J* = 7.8 Hz, 0.16H)*, 7.01-6.98 (m, 1.68H), 6.98 – 6.96 (m, 0.32H)*, 6.80-6.77 (m, 0.16H)*, 6.71 (d, *J* = 1.7 Hz, 0.16H)*, 5.83 (dd, *J* = 8.4, 3.8 Hz, 0.84H), 4.82 (d, *J* = 7.2 Hz, 0.16H)*, 4.33-4.27 (m, 0.16H)*, 4.26-4.21 (m, 0.16H)*, 3.57-3.46 (m, 1.68H), 2.96 (hept, *J* = 6.8 Hz, 0.84H), 2.91-2.79 (m, 1.84H), 2.63 (hept, *J* = 6.8 Hz, 0.16H)*, 2.55-2.46 (m, 1.00H), 2.30-2.13 (m, 0.48H)*, 2.12-2.00 (m, 1.68H), 1.98-1.89 (m, 0.84H), 1.83 (dd, *J* = 11.7, 5.6 Hz, 0.16H)*, 1.35 (d, *J* = 6.9 Hz, 2.52H), 1.33 (d, *J* = 6.9 Hz, 0.48H)*, 1.29-1.22 (m, 10.56H), 1.20 (dd, *J* = 6.9, 3.0 Hz, 0.96H)*, 1.18 (d, *J* = 6.8 Hz, 2.52H), 1.13 (d, *J* = 6.7 Hz, 0.48H)*, 0.23 (d, *J* = 6.8 Hz, 0.48H)*.^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.2*, 199.6, 148.8*, 148.7, 144.4, 143.6*, 143.6*, 142.6, 141.3, 141.0*, 138.3, 137.8*, 130.5*, 130.2*, 130.1, 130.1, 128.7*, 128.6, 125.3, 124.3*, 122.8*, 122.7, 121.7, 121.5*, 121.4, 120.9*, 66.1*, 65.5, 54.0, 53.1*, 34.8*, 34.6, 34.2, 34.1*, 31.4*, 30.9, 30.6*, 30.3, 25.8*, 25.6*, 25.2, 24.6, 24.2, 24.0, 24.0, 23.9,* 23.9, 23.3, 23.1*, 21.6*, 21.3*. HRMS (ESI-TOF) Calcd for $C_{26}H_{35}BrNS$ $[M+H]^+$: 472.1668; found: 472.1674.



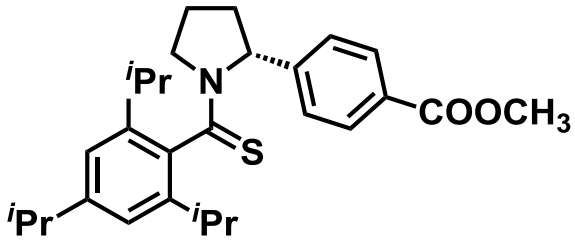
(*R*)-4-(1-(2,4,6-triisopropylphenylcarbonothioyl)pyrrolidin-2-yl)benzaldehyde (3k)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 71% yield (59.8 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 86.21 min (minor), 93.86 min (major): 97:3 er. ^{1}H NMR (600 MHz, $CDCl_3$) (70:30 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 10.02 (s, 0.70H), 9.96 (s, 0.30H)*, 7.91-7.88 (m, 1.40H), 7.77-7.74 (m, 0.60H)*, 7.45-7.42 (m, 1.40H), 7.06-7.03 (m, 0.60H)*, 7.00-6.98 (m, 1.40H), 6.97 (d, *J* = 1.7 Hz, 0.30H)*, 6.66 (d, *J* = 1.6 Hz, 0.30H)*, 5.90 (dd, *J* = 8.5, 4.3 Hz, 0.70H), 4.93 (d, *J* = 7.7 Hz, 0.30H)*, 4.36-4.26 (m, 0.60H)*, 3.62-3.56 (m, 0.70H), 3.56-3.50 (m, 0.70H), 2.94 (hept, *J* = 6.9 Hz, 0.70H), 2.90-2.76 (m, 1.70H), 2.64 (hept, *J* = 6.8 Hz, 0.30H)*, 2.60-2.53 (m, 0.70H), 2.46 (hept, *J* = 6.8 Hz, 0.30H)*, 2.35-2.27 (m, 0.30H)*, 2.22-2.15 (m, 0.60H)*, 2.14-1.94 (m, 2.10H), 1.86-1.81 (m, 0.30H)*, 1.34 (d, *J* = 6.9 Hz, 0.90H)*, 1.32 (d, *J* = 7.0 Hz, 2.10H), 1.27 (d, *J* = 6.9 Hz, 2.10H), 1.26-1.22 (m, 7.20H), 1.18 (dd, *J* = 6.9, 4.1 Hz, 1.80H)*, 1.14 (d, *J* = 6.8 Hz, 2.10H), 1.09 (d, *J* = 6.7 Hz, 0.90H)*, 0.08-0.06 (m, 0.90H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.4*, 199.8, 191.7, 191.5*, 149.3, 148.9, 148.8*, 148.2*, 143.4*, 142.5, 141.4, 141.2*, 138.2, 137.8*, 135.6*, 135.3, 130.1, 130.1*, 126.7, 126.4*, 121.7, 121.5, 121.5*, 121.0*, 66.5*, 66.0, 54.2, 53.2*,34.7*, 34.7, 34.2, 34.1*, 31.3*, 30.9, 30.7*, 30.3, 25.7*, 25.6*, 25.3, 24.6, 24.1, 24.0, 24.0, 23.9*, 23.3, 23.2*, 21.6*, 21.4*. HRMS (ESI-TOF) Calcd for $C_{27}H_{36}NOS$ $[M+H]^+$: 422.2512; found: 422.2516.



(*R*)-1-(4-(1-(2,4,6-triisopropylphenylcarbonothioyl)pyrrolidin-2-yl)phenyl)ethan-1-one (3l)

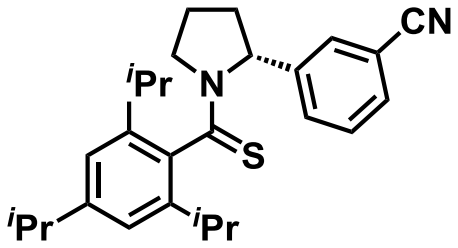
Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 79% yield (69 mg). The er value was determined by HPLC analysis on two columns attached one after the other with Chiralcel ADH followed by Chiralcel IC column (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 52.00 min and 92.01 min (minor), 54.39 min (major): 97:3 er. ^{1}H NMR (600 MHz, $CDCl_3$) (66:34 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 8.02-7.93 (m, 1.32H), 7.86-7.80 (m, 0.68H), 7.40-7.34 (m, 1.32H), 7.02-6.95 (m, 2.34H), 6.69-6.62 (m, 0.34H), 5.90 (dd, *J* = 8.4, 4.1 Hz, 0.66H), 4.92 (d, *J* = 7.6 Hz, 0.34H), 4.37-4.24 (m, 0.66H), 3.62-3.48 (m, 1.34H), 2.95 (p, *J* = 6.8 Hz, 0.66H), 2.92-2.75 (m, 1.65H), 2.69-2.42 (m, 4.4H), 2.34-2.24 (m, 0.34H), 2.45-2.13 (m, 0.66H), 2.15-1.91 (m, 1.95H), 1.84-1.80 (m, 0.34H), 1.35-1.31 (m, 3H), 1.31-1.22 (m, 9H), 1.22-1.17 (m, 2H), 1.15 (d, *J* = 6.7 Hz, 2H), 1.10 (d, *J* = 6.7 Hz, 1H), 0.08 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.21*, 199.75, 197.58, 197.38*, 148.79, 147.68, 146.62*, 143.45*, 142.56, 141.34, 141.17*, 138.28, 137.81*, 136.25*, 135.96, 128.79, 128.67*, 126.25, 125.91*, 121.74, 121.50, 120.95*, 66.44*, 65.98, 54.18, 53.19*, 34.72*, 34.66, 34.22, 34.14*, 31.29, 30.89, 30.63, 30.29, 26.61, 25.71*, 25.63*, 25.26, 24.59, 24.08*, 24.02, 23.99, 23.94*, 23.29, 23.19*, 21.54*, 21.44. HRMS (ESI-TOF) Calcd for $C_{28}H_{38}NOS$ $[M+H]^+$: 436.2669; found:436.2664.



Methyl (*R*)-4-(1-(2,4,6-triisopropylphenylcarbonothioyl)pyrrolidin-2-yl)benzoate (3m)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 72% yield (65 mg). The er value was determined by HPLC analysis on two Chiralcel ADH columns attached one after the other (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 16.15 min (minor),18.43 min (major): 94.5:5.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (32:68 mixture of rotamers, peaks

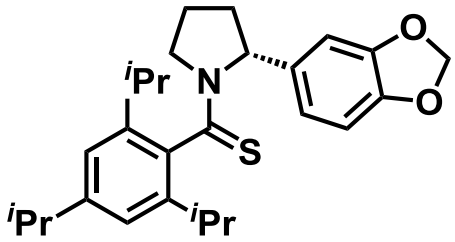
corresponding to minor rotamer starred) δ 8.07-8.02 (m, 0.64H)*, 7.92-7.87 (m, 1.36H), 7.37-7.31 (m, 0.64H)*, 6.99 (s, 0.64H)*, 6.96 (d, *J* = 1.6 Hz, 0.68H), 6.96-6.93 (m, 1.36H), 6.66 (d, *J*= 1.8 Hz, 0.68H), 5.90 (dd, *J* = 8.4, 4.0 Hz, 0.32H)*, 4.91 (d, *J* = 7.5 Hz, 0.68H), 4.35-4.23 (m, 1.36H), 3.92 (s, 0.96H)*, 3.90 (s, 2.04H), 3.60-3.54 (m, 0.32H)*, 3.54-3.48 (m, 0.32H)*, 2.94 (hept, *J* = 6.9 Hz, 0.32H)*, 2.90-2.75 (m, 1.32H), 2.64 (hept, *J* = 6.9 Hz, 0.68H), 2.58-2.42 (m, 1.00H), 2.32-2.23 (m, 0.68H), 2.23-2.13 (m, 1.36H), 2.13-1.99 (m, 0.64H)*, 2.00-1.91 (m, 0.32H)*, 1.84-1.78 (m, 0.68H), 1.35-1.30 (m, 3.00H), 1.28-1.22 (m, 5.88H), 1.18 (dd, *J* = 6.9, 4.0 Hz, 4.08H), 1.14 (d, *J* = 6.7 Hz, 0.96H)*, 1.09 (d, *J* = 6.7 Hz, 2.04H), 0.09 (d, *J* = 6.8 Hz, 2.04H). ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.2, 199.7*, 166.8*, 166.6, 148.8, 148.7*, 147.4*, 146.4, 143.5, 142.6*, 141.3*, 141.1, 138.3*, 137.8, 130.0*, 129.9, 129.3, 128.9*, 126.1*, 125.7, 121.7*, 121.5, 121.5*, 120.9,66.5, 66.0*, 54.1*, 53.2, 52.2, 52.1*, 34.7, 34.6*, 34.2*, 34.1, 31.3, 30.9*, 30.6, 30.3*, 25.7, 25.6, 25.3*, 24.6*, 24.1*, 24.0, 23.9, 23.3*, 23.2, 21.5, 21.5. HRMS (ESI-TOF) Calcd for $C_{28}H_{38}NO_2S$ $[M+H]^+$: 452.2618; found: 452.2616.



(*R*)-3-(1-(2,4,6-triisopropylphenylcarbonothioyl)pyrrolidin-2-yl)benzonitrile (3n)

Following the general procedure for the enantioselective arylation with 2 equiv. of 1,4-BQ, the title compound was obtained in 68% yield (57 mg). The er value was determined by HPLC analysis on two columns attached one after the other with Chiralcel ADH followed by Chiralcel IC column (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 39.68 min (major), 43.77 min and 55.29 min (minor): 87.5:12.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (72:28 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.58 (dt, *J* = 7.5, 1.4 Hz, 0.72H), 7.56-7.54 (m, 0.72H), 7.53-7.50 (m, 1.00H), 7.48 (td, *J* = 7.7, 0.6 Hz, 0.72H), 7.36 (td, *J* = 7.7, 0.7 Hz, 0.28H)*, 7.14-7.10 (m, 0.56H)*, 6.99 (d, *J* = 0.5 Hz, 1.44H), 6.98 (d, *J* = 1.7 Hz, 0.28H)*, 6.68 (d, *J* = 1.7 Hz, 0.28H)*, 5.86 (dd, *J* = 8.4, 4.1 Hz, 0.72H), 4.88 (d, *J* = 7.7 Hz, 0.28H)*, 4.36-4.22 (m, 0.56H)*, 3.61-3.54 (m, 0.72H), 3.54-3.48 (m, 0.72H), 2.92-2.77 (m, 2.44H), 2.66-2.51 (m, 1.00H), 2.43 (hept, *J*

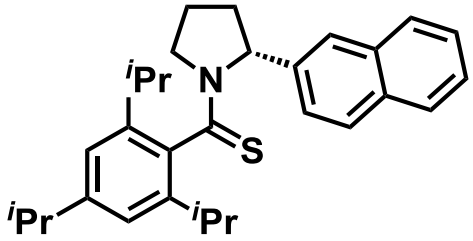
= 6.8 Hz, 0.28H)*, 2.35-2.25 (m, 0.28H)*, 2.24-2.12 (m, 0.56H)*, 2.12-1.94 (m, 2.16H), 1.82 (dd, *J* = 12.5, 6.1 Hz, 0.28H)*, 1.34 (dd, *J* = 7.0, 3.9 Hz, 3.00H), 1.27 (d, *J* = 6.9 Hz, 2.16H), 1.25-1.21 (m, 7.32H), 1.20 (dd, *J* = 6.9, 3.9 Hz, 1.68H)*, 1.16 (d, *J* = 6.7 Hz, 2.16H), 1.11 (d, *J* = 6.7 Hz, 0.84H)*, 0.15 (d, *J* = 6.8 Hz, 0.84H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.6*, 200.0, 149.0*, 148.9, 143.7, 143.4*, 143.1*, 142.6, 141.3, 141.2*, 138.1, 137.6*, 131.2, 131.1*, 130.8, 130.0*, 129.5*, 129.4, 129.4, 129.3*, 121.8, 121.5, 121.5*, 121.1*, 118.7, 118.3*, 112.9*, 112.6, 65.9*, 65.4, 54.1, 53.1*, 34.8*, 34.6, 34.2, 34.1*, 31.3*, 30.9, 30.7*, 30.4, 25.7*, 25.6*, 25.2, 24.5, 24.1, 24.0, 24.0, 23.9*, 23.3, 23.1*, 21.6*, 21.4*. HRMS (ESI-TOF) Calcd for $C_{27}H_{35}N_2S$ $[M+H]^+$: 419.2515; found: 419.2524.



(*R*)-(2-(1,3-dihydroisobenzofuran-5-yl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3o)

Following the general procedure for the enantioselective arylation, the title compound was obtained in 78% yield (68 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (5% isopropanol in hexanes, 0.5 mL/min) with t_r = 25.66 min 41.48 min (minor), 27.13 min and 39.19 min (major): 93.5:6.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (60:40 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 6.98 (s, 1.20H), 6.95 (d, *J* = 1.6 Hz, 0.40H)*, 6.79 (dd, *J* = 7.9, 0.5 Hz, 0.60H), 6.76-6.73 (m, 1.00H), 6.73-6.71 (m, 0.60H), 6.63 (d, *J* = 8.0 Hz, 0.40H)*, 6.36 (d, *J* = 1.8 Hz, 0.40H)*, 6.26 (ddd, *J* = 8.1, 1.9, 0.6 Hz, 0.40H)*, 5.98-5.95 (m, 1.20H), 5.90 (dd, *J* = 10.0, 1.4 Hz, 0.80H)*, 5.81 (dd, *J* = 8.2, 3.7 Hz, 0.60H), 4.77 (d, *J* = 6.5 Hz, 0.40H)*, 4.29-4.18 (m, 0.80H)*, 3.54-3.43 (m, 1.20H), 2.95 (hept, *J* = 6.9 Hz, 0.60H), 2.90-2.76 (m, 1.60H), 2.62 (hept, *J* = 6.8 Hz, 0.40H)*, 2.54 (hept, *J* = 6.7 Hz, 0.40H)*, 2.49-2.40 (m, 0.60H), 2.26-2.15 (m, 1.00H), 2.15-2.04 (m, 0.80H)*, 2.03-1.97 (m, 0.60H), 1.95-1.87 (m, 0.60H), 1.84-1.76 (m, 0.40H)*, 1.31 (d, *J* = 6.9 Hz, 1.20H)*, 1.29 (d, *J* = 6.9 Hz, 1.80H), 1.25 (dd, *J* = 6.8, 0.9 Hz, 3.60H), 1.24-1.21

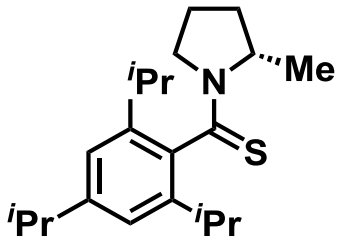
(m, 4.80H), 1.20 (dd, *J* = 6.9, 3.4 Hz, 2.40H)*, 1.16 (d, *J* = 6.7 Hz, 1.80H), 1.13 (d, *J* = 6.7 Hz, 1.20H)*, 0.31 (d, *J* = 6.7 Hz, 1.20H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.1*, 199.5, 148.8, 148.8*, 148.1, 148.1*, 147.0*, 146.7, 143.9*, 142.8, 141.5, 141.3*, 138.7, 138.1*, 136.2, 135.6*, 121.9, 121.7, 121.0*, 119.3, 119.1*, 108.5, 108.4*, 107.0, 106.5*, 101.3, 101.3*, 66.7*, 66.0, 54.1, 53.4*, 35.2*, 34.9, 34.4, 34.4*, 31.6*, 31.1, 30.8*, 30.4, 25.9*, 25.9*, 25.5, 24.9, 24.3*, 24.2, 24.2, 24.2*, 24.0, 23.5, 23.4*, 21.8*, 21.8*. HRMS (ESI-TOF) Calcd for $C_{27}H_{36}NO_2S$ $[M+H]^+$: 438.2461; found: 438.2466.



(*R*)-(2-(naphthalen-2-yl)pyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3p)

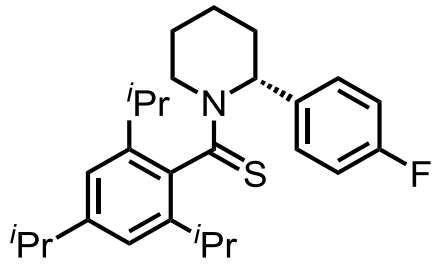
Following the general procedure for the enantioselective arylation, the title compound was obtained in 78% yield (69 mg). The er value was determined by HPLC analysis on two Chiralcel IC columns attached one after the other (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 32.43 min and 57.35 min (minor), 33.75 min and 40.76 min (major): 98:2 er. ^{1}H NMR (600 MHz, $CDCl_3$) (83:17 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.88-7.86 (m, 0.83H), 7.86-7.83 (m, 0.83H), 7.80-7.75 (m, 1.00H), 7.73-7.69 (m, 0.34H)*, 7.68 (dd, *J* = 1.8, 0.8 Hz, 0.83H), 7.51-7.44 (m, 2.00H), 7.42 (dd, *J* = 8.4, 1.9 Hz, 0.83H), 7.27 (s, 0.17H)*, 7.01 (q, *J* = 1.7 Hz, 1.66H), 6.98 (dd, *J* = 8.0, 1.8 Hz, 0.34H)*, 6.58 (d, *J* = 1.7 Hz, 0.17H)*, 6.07 (dd, *J* = 8.3, 3.3 Hz, 0.83H), 5.03 (d, *J* = 7.0 Hz, 0.17H)*, 4.36 (dd, *J* = 9.3, 5.1 Hz, 0.34H)*, 3.64-3.55 (m, 1.66H), 3.11 (hept, *J* = 6.8 Hz, 0.83H), 2.90 (dhept, *J* = 24.0, 6.9 Hz, 1.66H), 2.78 (hept, *J* = 6.9 Hz, 0.17H)*, 2.71 (hept, *J* = 6.8 Hz, 0.17H)*, 2.59-2.49 (m, 1.00H), 2.36-2.22 (m, 0.34H)*, 2.21-2.07 (m, 1.83H), 2.01-1.89 (m, 1.00H), 1.42 (d, *J* = 7.0 Hz, 2.49H), 1.38 (d, *J* = 6.9 Hz, 0.51H)*, 1.28 (dd, *J* = 11.3, 6.8 Hz, 4.98H), 1.26-1.23 (m, 5.49H), 1.18 (dd, *J* = 6.9, 5.1 Hz, 1.02H)*, 1.14 (d, *J* = 6.7 Hz, 2.49H), 1.06 (d, *J* = 6.7 Hz, 0.51H)*, -0.25 (d, *J* = 6.8 Hz, 0.51H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 200.0*, 199.3, 148.6, 148.6*, 143.7*, 142.6,

141.4, 141.1*, 139.4, 138.6*, 138.5, 137.9*, 133.4, 133.2*, 132.6, 132.5*, 128.5, 128.4*, 127.8, 127.7, 127.5*, 126.4*, 126.2, 126.0*, 125.7, 124.7, 124.4*, 124.2, 123.7*, 121.7, 121.5, 121.4*, 120.8*, 66.9*, 66.2, 54.1, 53.3*, 34.7*, 34.5, 34.2, 34.1*, 31.2*, 30.9, 30.6*, 30.3, 25.7*, 25.7*, 25.3, 24.7, 24.3, 24.0, 24.0, 23.9*, 23.9, 23.3, 23.2*, 21.6*, 21.2*. HRMS (ESI-TOF) Calcd for $C_{30}H_{38}NS$ $[M+H]^+$: 444.2719; found: 444.2710.



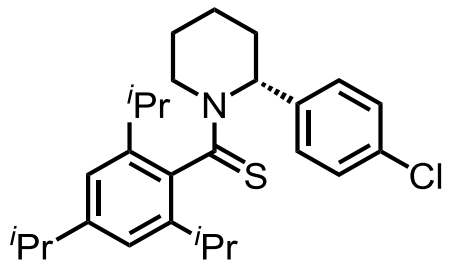
(*S*)-(2-methylpyrrolidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (3q)

Following the general procedure for the enantioselective arylation with Na_2CO_3 as the base (instead of $KHCO_3$), 12 equiv. of $MeB(OH)_2$ at 0.05M concentration at 80 ˚C under air, the title compound was obtained in 47% yield (31.2 mg). The er value was determined by HPLC analysis on Chiralcel IC column (1% isopropanol in hexanes, 0.5 mL/min) with t_r = 12.30 min (major), 13.26 min (minor): 87.5:12.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (75:25 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 6.98-6.95 (m, 2.00H), 5.05-4.97 (m, 0.75H), 4.15-4.07 (m, 0.25H)*, 4.00-3.94 (m, 0.25H)*, 3.91 (p, *J* = 6.8 Hz, 0.25H)*, 3.28-3.19 (m, 1.50H), 2.93-2.81 (m, 2.75H), 2.58 (hept, *J* = 6.8 Hz, 0.25H)*, 2.24-2.08 (m, 1.25H), 2.06-1.95 (m, 1.00H), 1.90-1.83 (m, 0.75H), 1.83-1.77 (m, 0.75H), 1.73-1.67 (m, 0.25H)*, 1.49 (d, *J* = 6.4 Hz, 2.25H), 1.31 (d, *J* = 6.6 Hz, 0.75H)*, 1.28-1.21 (m, 9.75H), 1.19 (dd, *J* = 7.0, 5.3 Hz, 4.50H), 0.97 (d, *J* = 6.6 Hz, 0.75H)*. ^{13}C NMR (150 MHz, $CDCl_3$) (mixture of rotamers, peaks corresponding to minor rotamer starred) δ 197.2, 197.2*, 148.5*, 148.4, 143.3*, 142.0, 141.3*, 141.2, 138.7, 137.8*, 121.5, 121.4, 121.4*, 121.2*, 58.7*, 57.7, 52.4, 51.6*, 34.2, 34.2*, 32.7*, 32.0, 31.2*, 30.7, 30.6*, 30.1, 26.2*, 25.6*, 25.2, 24.8, 24.0, 24.0, 24.0*, 23.7, 23.6, 23.4, 22.9*, 22.6*, 22.0*, 19.1*, 17.2. HRMS (ESI-TOF) Calcd for $C_{21}H_{34}NS$ $[M+H]^+$: 332.2406; found: 332.2409.



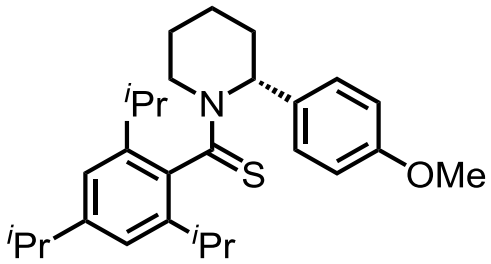
(*R*)-(2-(4-fluorophenyl)piperidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (4a)

Following the general procedure for the enantioselective arylation with 3 equiv. of arylboronic acid, 5 equiv. of 1,4-BQ at 85 ˚C, the title compound was obtained in 48% yield (40.7 mg). The er value was determined by HPLC analysis on a Chiralcel ADH column (5% isopropanol in hexanes, 0.5 mL/min) with t_r= 9.37 min (major), 14.85 min (minor): 94.5:5.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (82:18 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.49-7.41 (m, 1.64H), 7.38 (d, *J* = 4.7 Hz, 0.18H)*, 7.16-7.12 (m, 2H), 7.04-6.95 (m, 2.18H), 6.82-6.81 (m, 0.18H)*, 5.25-5.22 (m, 0.18H)*, 3.74 (d, *J* = 14.4 Hz, 0.82H), 3.42-3.36 (m, 0.18H)*, 3.05-2.95 (m, 2.46H), 2.91-2.76 (m, 1.18H), 2.51 (d, *J* = 18.0 Hz, 0.82H), 2.19 (d, *J* = 18.0 Hz, 0.18H)*, 2.15-2.06 (m, 1H), 1.85-1.71 (m, 2H), 1.69-1.65 (m 0.36H)*, 1.61-1.46 (m, 2H), 1.36-1.15 (m, 16H), 1.12 (d, *J* = 7.0 Hz, 2.31H),0.55 (d, *J* = 6.8 Hz, 0.54H)*.^{13}C NMR (150 MHz, $CDCl_3$) δ 202.62*, 201.18, 161.88 (d, *J* = 246.2 Hz),161.59* (d, *J* = 246.7 Hz),, 148.49, 148.28*, 142.99*, 142.25, 142.09*, 141.88, 136.97, 136.61*, 134.00*, 133.82, 128.72* (d, *J* = 7.8 Hz), 128.32 (d, *J* = 7.9 Hz), 125.50*, 121.90*, 121.66, 121.50, 121.31*, 115.54 (d, *J* = 21.3 Hz)., 115.52* (d, *J* = 20.9 Hz).*, 60.99*, 56.53, 47.56, 45.47*, 34.14, 31.92*, 31.15*, 30.85, 30.61, 30.31, 29.70, 29.66*, 27.40, 26.02, 25.94*, 25.77, 25.60*, 25.51*, 24.52, 23.98, 23.89*, 23.59, 23.49, 23.39*, 23.01*, 22.69*, 19.20, 19.12*. HRMS (ESI-TOF) Calcd for $C_{27}H_{37}FNS$ $[M+H]^+$: 426.2625; found: 426.2628.



(*R*)-(2-(4-chlorophenyl)piperidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (4b)

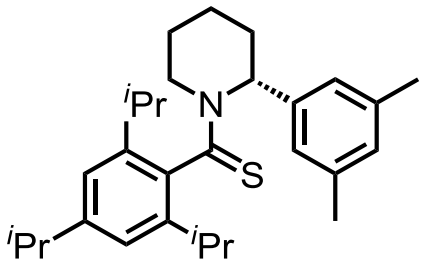
Following the general procedure for the enantioselective arylation with 3 equiv. of aryl boronic acid, 5 equiv. of 1,4-BQ at 85 ˚C, the title compound was obtained in 53% yield (46.8 mg). The er value was determined by HPLC analysis on a Chiralcel ADH column (2% isopropanol in hexanes, 0.5 mL/min) with t_r= 12.25 min (major), 24.05 min (minor): 94.5:5.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (70:30 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.42-7.35 (m, 3.3H), 7.32-7.29 (m, 0.7H), 7.13-7.10 (m, 0.7H), 7.01-6.95 (m, 1.7H), 6.82 (d, *J* = 1.7 Hz, 0.3H)*, 6.03 (d, *J*= 13.8 Hz, 0.3H)*, 5.23 (brs, 0.3H)*, 4.32-4.24 (m, 0.3H)*, 4.17-4.09 (m, 0.3H)*, 3.75 (d, *J* = 13.3 Hz, 0.7H), 3.41-3.33 (m, 0.3H)*, 3.04-2.95 (m, 2.1H), 2.91-2.78 (m, 1.3H), 2.50 (d, *J* = 14.6 Hz, 0.7H), 2.32-2.29 (m, 0.3H)*, 2.19 (d, *J* = 14.0 Hz, 0.3H)*, 2.14-1.44 (m, 5H), 1.37-1.11 (16H) 0.88-0.89 (m, 0.9H)*,0.56 (d, *J* = 6.8 Hz, 0.9H)*. ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.72*, 201.39, 148.53, 148.33*, 142.99*, 142.25, 142.11*, 141.90, 136.91, 136.87*, 136.63, 136.55*, 133.95*, 133.02, 132.83*, 128.86, 128.77*, 128.44, 128.12*, 121.92*, 121.67, 121.52, 121.33*, 61.02*, 56.67, 47.66, 45.51*, 34.23*, 34.15, 34.06*, 34.03*, 31.93, 31.15*, 30.85, 30.68, 30.46*, 29.71, 29.66, 27.35, 25.97, 25.94*, 25.77, 25.60*, 25.47*, 24.52, 23.98, 23.92*, 23.88*, 23.64, 23.48, 23.39*, 23.0*9, 22.69*, 19.18, 14.12*. HRMS (ESI-TOF) Calcd for $C_{27}H_{37}ClNS$ $[M+H]^+$: 442.2330; found: 442.2333.



(*R*)-(2-(4-methoxyphenyl)piperidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (4c)

Following the general procedure for the enantioselective arylation with 3 equiv. of aryl boronic acid, 5 equiv. of 1,4-BQ at 85 ˚C, the title compound was obtained in 66% yield (58 mg). The er value was determined by HPLC analysis on a Chiralcel ADH column (5% isopropanol in hexanes, 0.5 mL/min) with t_r= 17.40 min (major), 26.05 min (minor): 96:4 er. ^{1}H NMR (600 MHz, $CDCl_3$) (89:11 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.40 (d, *J* = 8.6 Hz, 1.78H), 7.36 (d, *J* = 4.5 Hz, 0.89H), 7.08 (d,

J = 8.6 Hz, 0.22H)*, 6.99 (s, 0.89H), 6.97-6.95 (m, 1H), 6.92 (d, *J* = 8.7 Hz, 0.89H), 6.87-6.81 (m, 0.33H)*, 6.03-5.98 (m, 0.11H)*, 5.23-5.20 (m, 0.11)*,3.83 (s, 2.67H), 3.79 (s, 0.33H)*, 3.71 (d, *J* = 12.5 Hz, 0.89H), 3.10-2.97 (m, 2.67H), 2.93-2.78 (m, 1H), 2.51 (d, *J* = 14.2 Hz, 0.89H), 2.34-2.38 (m, 0.11H)*, 2.13-2.00 (m, 1.11H), 1.88-1.47 (m, 3.33H), 1.37-1.17 (m, 17H), 1.12 (d, *J* = 6.9 Hz, 2.67H), 0.59 (d, *J* = 6.8 Hz, 0.33H)*. ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.72, 158.63, 158.35*, 148.35, 148.33*, 143.03*, 142.26, 142.10*, 141.90, 137.16, 136.74, 130.01, 128.21, 127.79*, 121.88*, 121.62, 121.46, 121.23*, 114.03, 56.64, 55.29, 47.51, 34.14, 31.92, 31.15, 30.83, 30.56, 29.70, 27.38, 26.13, 25.96*, 25.78*, 25.64, 24.55, 23.99, 23.64, 23.52, 19.26, 19.16*. HRMS (ESI-TOF) Calcd for $C_{28}H_{40}NOS$ $[M+H]^+$: 438.2825; found: 438.2832.

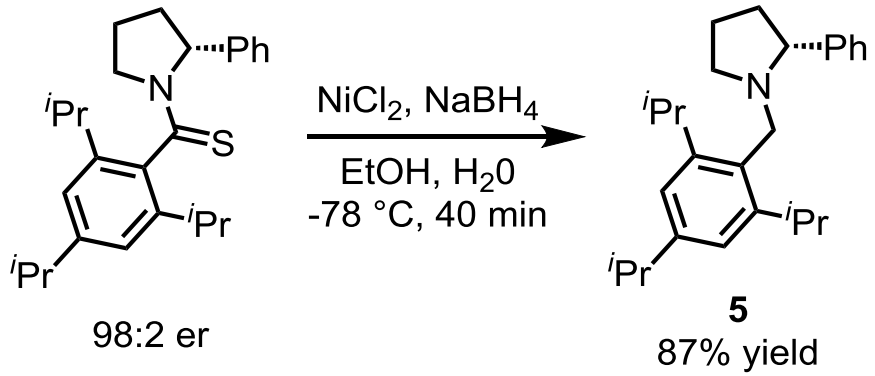


(*R*)-(2-(3,5-dimethylphenyl)piperidin-1-yl)(2,4,6-triisopropylphenyl)methanethione (4d)

Following the general procedure for the enantioselective arylation with 3 equiv. of aryl boronic acid, 5 equiv. of 1,4-BQ at 85˚C, the title compound was obtained in 76% yield (66 mg). The er value was determined by HPLC analysis on a Chiralcel ADH column (0.5% isopropanol in hexanes, 0.5 mL/min) with t_r= 9.41 min (minor), 12.07 min (major): 92.5:7.5 er. ^{1}H NMR (600 MHz, $CDCl_3$) (73:27 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.35 (d, *J* = 4.1 Hz, 0.73H), 7.05 (s, 1.46H), 7.00 (d, *J* = 1.6 Hz, 0.73 H), 6.98 (d, *J* = 1.6 Hz, 0.73H), 6.95 (d, *J* = 1.6 Hz, 0.27H)*, 6.93 (s, 0.73H), 6.84 (s, 0.27H)*, 6.81 (d, *J* = 1.6 Hz, 0.27H)*, 6.74 (s, 0.54H)*, 6.02 (d, *J* = 12.8 Hz, 0.27H)*, 5.18 (s, 0.27H)*, 3.74 (d, *J* = 12.9 Hz, 0.73H), 3.49-3.42 (m, 0.27H)*, 3.16 (hept, *J* = 6.9 Hz, 0.73H), 3.11-2.91 (m, 2H), 2.90-2.76 (m 1H), 2.59-2.50 (m, 0.73H), 2.34 (s, 4.38H), 2.28 (s, 1.62H), 2.10-2.01 (m, 0.73H), 1.97-1.89 (m, 0.27H)*, 1.84-1.48 (m, 4.16H), 1.36-1.16 (m, 17.19), 0.58 (d, *J* = 6.8 Hz, 0.81H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.02*, 200.72, 148.35, 148.09*, 142.93*, 142.28, 142.07*,

141.85, 138.22, 138.09*, 137.94*, 137.72, 137.18, 136.70*, 128.64, 128.43*, 124.61, 124.37*, 121.88*, 121.66, 121.46, 121.17*, 61.64*, 57.27, 47.73, 45.62*, 34.14, 34.03*, 31.15*, 30.81, 30.68*, 30.64, 30.36*, 27.39, 26.11, 25.94*, 25.80, 25.76*, 25.51*, 24.67, 23.99, 23.92*, 23.71, 23.52, 23.38*, 22.74*, 21.55, 21.50*, 19.35*, 19.28. HRMS (ESI-TOF) Calcd for $C_{29}H_{42}NS$ $[M+H]^+$: 436.3032; found: 436.3032.

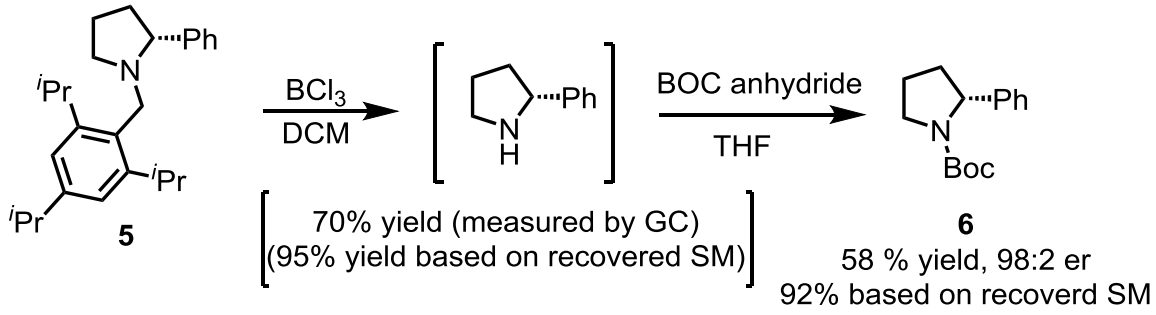
Removal of the directing group:



(*R*)-2-phenyl-1-(2,4,6-triisopropylbenzyl)pyrrolidine (5)

The thioamide (0.1mmol, 39.3 mg) and $NiCl_2.6H_20$ (0.8mmol, 190 mg) were taken in a reaction vial with a stir bar and 2 ml of ethanol was added. Then the vial was cooled to -78 ˚C . $NaBH_4$ (2.5 mmol, 94.6 mg) was dissolved in 0.4ml of water and immediately added drop wise (over 10 sec) to the solution, at this stage the solution turns black and was kept at -78˚C for 40 min. Then ethyl acetate was added (at low temp) and the reaction mixture was quickly filtered through pad of Celite. The solvent was then removed under reduced pressure and the residue was purified on a preparative TLC with ethyl acetate and hexanes (1:20) as the eluent. The dethiolated product was obtained as an oil in 87% yield (31.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28-7.23 (m, 1H), 6.91 (s, 2H), 3.50 (d, *J* = 12.7 Hz, 1H), 3.37-3.25 (m, 4H), 2.91-2.78 (m, 2H), 2.30 (q, *J* = 8.4, 7.5 Hz, 1H), 2.25-2.16 (m, 1H), 1.85-1.66 (m, 3H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.05 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.15, 146.94, 144.03, 130.29, 128.24, 127.96, 127.06, 120.63, 70.64, 52.94, 49.12, 34.76, 34.04, 28.49, 25.03, 24.04, 23.95, 23.50, 23.04. HRMS (ESI-TOF) Calcd for $C_{26}H_{38}N$ $[M+H]^+$: 364.2999; found: 364.2990.

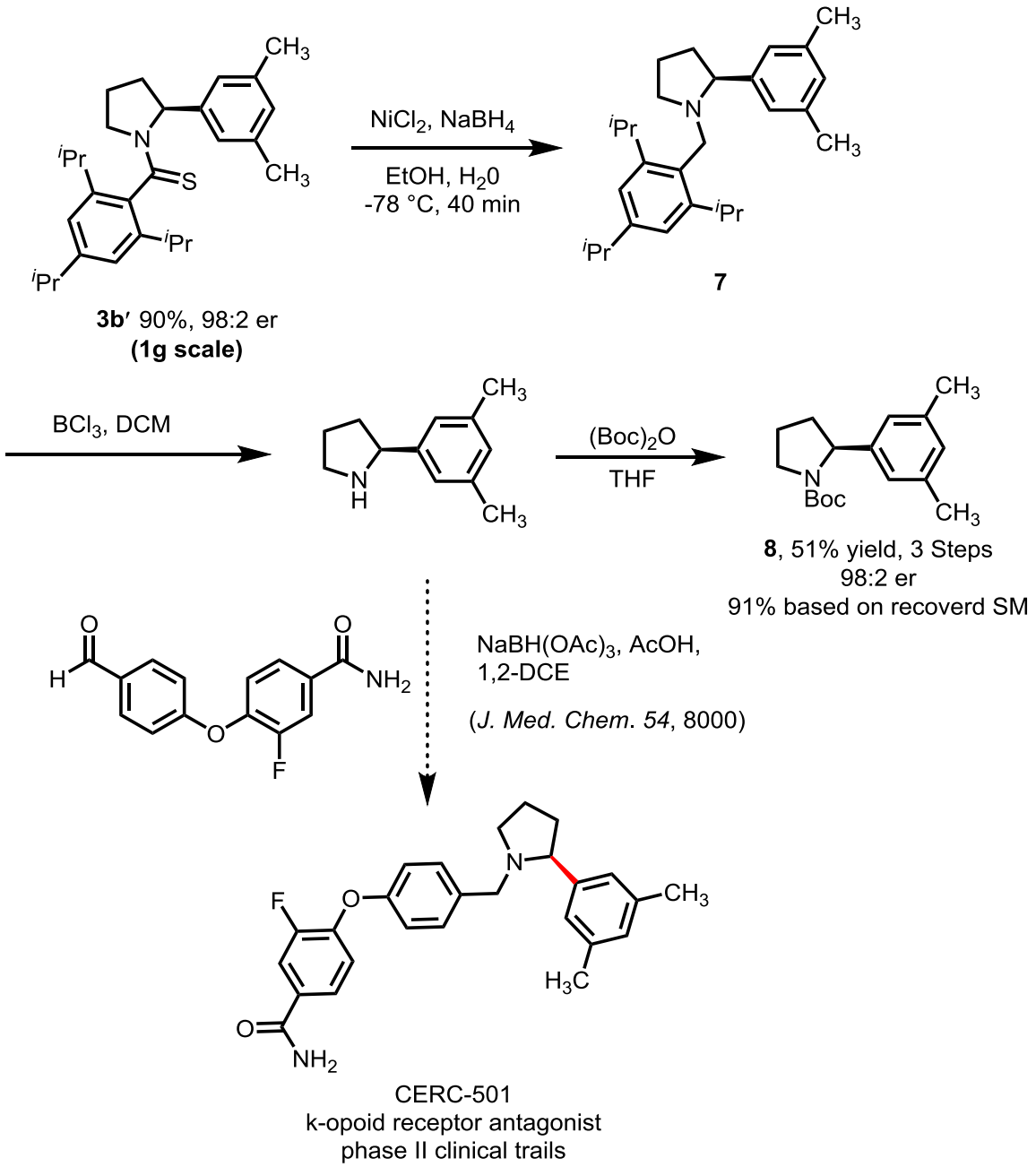
Note: When the dethiolation was done at room temperature partial racemizaton of the final product was observed.

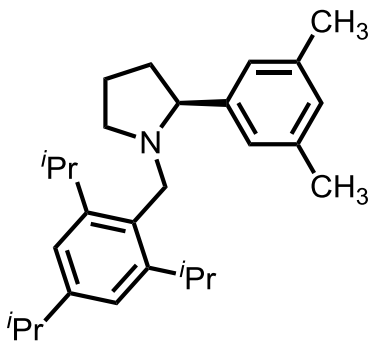


_t_-butyl (_R_)-2-phenylpyrrolidine-1-carboxylate (6)

The benzyl amine (0.1 mmol, 36 mg) and 2 ml dichloromethane were taken in a reaction vial equipped with a stir bar. Then boron trichloride, 0.2 mmol, 0.19 ml of 1 M soultion (from a fresh bottle of 1M solution of boron trichloride in dichloromethane) was added at room temperature and the solution was stirred at this temperature for 24 hrs. (The reaction was monitored on GC after base workup). Then 1 ml of 1M HCl was added carefully and stirred for 2 min, followed by addition of saturated $NaHCO_3$ solution to make the pH >10. Then the organic layer was separated and the aqueous layer was extracted with more dichloromethane. The organic layers were combined, dried over Na_2SO_4, and the solvent was removed under reduced pressure. Then 1ml of THF was added along with 2 equiv of Boc anhydride and the reaction was stirred for 8 hours. Then the solvent was removed and the residue was purified over preparative TLC with ethyl acetate and hexanes (1:10) as eluent to obtain the title compound in 58% yield (14.2 mg) as colorless oil. The er value was determined by HPLC analysis on a Chiralcel IC column (5% isopropanol in hexanes, 0.5 mL/min) with t_r= 17.92 min (major), 21.72 min (minor): 98:2 er. ^{1}H NMR (600 MHz, $CDCl_3$) (70:30 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.23-7.14 (m, 3H), 4.96 (s, 0.3H), 4.76 (s, 0.7H), 3.71-3.44 (m, 2H), 2.38-2.20 (m, 1H), 1.96-1.77 (m, 3H), 1.46 (s, 3H), 1.18 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.55, 145.11, 144.02*, 128.06, 126.43, 125.47, 79.12, 61.31, 60.60*, 47.06, 35.99, 34.78*, 28.49*, 28.10, 23.41*, 23.16. HRMS (ESI-TOF) Calcd for $C_{15}H_{22}NO_2$ $[M+H]^+$: 248.1645; found: 248.1648.

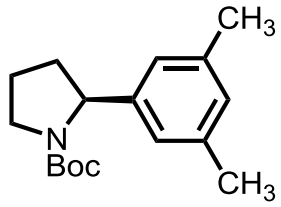
Application towards synthesis of CERC-501





(*S*)-2-(3,5-dimethylphenyl)-1-(2,4,6-triisopropylbenzyl)pyrrolidine (7)

The title compound was obtained by following the method used to synthesize compound **5.** The dethiolated product was obtained as an oil in 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (s, 2H), 6.95-6.89 (m, 3H), 3.54 (d, *J* = 12.7 Hz, 1H), 3.40 (m, 2H), 3.32 (d, *J* = 12.7 Hz, 1H), 3.21 (t, *J* = 8.0 Hz, 1H), 2.92 – 2.80 (m, 2H), 2.36 (s, 6H), 2.32 – 2.14 (m, 2H), 1.85 – 1.65 (m, 3H), 1.22 (m, 12H), 1.10 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.16, 146.87, 143.96, 137.41, 130.42, 128.60, 125.91, 120.60, 70.78, 52.80, 49.21, 34.85, 34.03, 28.57, 25.20, 23.95, 23.56, 22.84, 21.33.

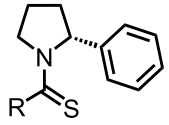


***t*-butyl (*S*)-2-(3,5-dimethylphenyl)pyrrolidine-1-carboxylate (8)**

The title compound was obtained by following the method used to synthesize compound **6.** The BOC protected product **8** was obtained as an yellow oil in 59 % yield (2 steps). The er value was determined by HPLC analysis on a Chiralcel IC column (5% isopropanol in hexanes, 0.5 mL/min) with t_r= 27.36 min (minor), 38.87 min (major): 98:2 er. ^{1}H NMR (600 MHz, $CDCl_3$) (2:1 mixture of rotamers, peaks corresponding to minor rotamer starred) δ 6.83 (s, 1H), 6.76 (s, 2H), 4.87 (brs, 0.33H)*, 4.69 (s, 0.66H), 3.67-3.43 (m, 2H), 2.36-2.18 (m, 7H), 1.98 – 1.73 (m, 3H), 1.46 (s, 3H)*, 1.19 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.66, 154.48*, 144.99, 144.06*, 137.66*, 137.44, 128.27*, 127.95, 123.37, 123.12*, 79.05, 61.19, 60.63*, 47.35*, 47.01, 35.90, 34.87*, 28.51*, 28.13, 23.49*, 23.22, 21.29.

HPLC data:

Please note: Due to restricted C-N thioamide bond rotation the HPLC spectum can show four peaks.



2a

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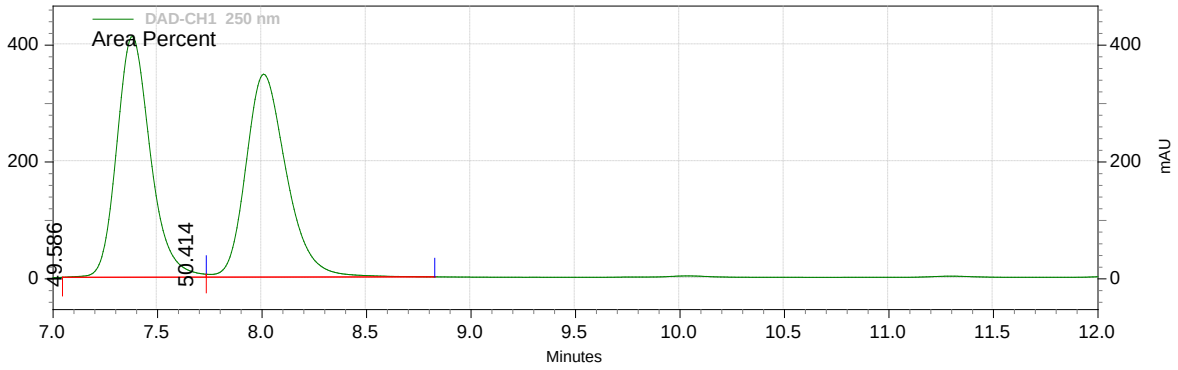

DAD-CH1 250 nm Results

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8.007	18714453	50.41
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Area % Report

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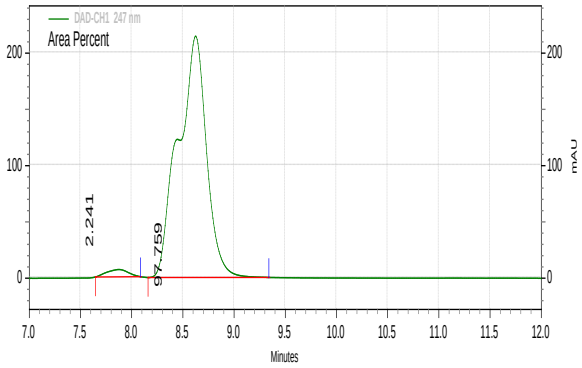
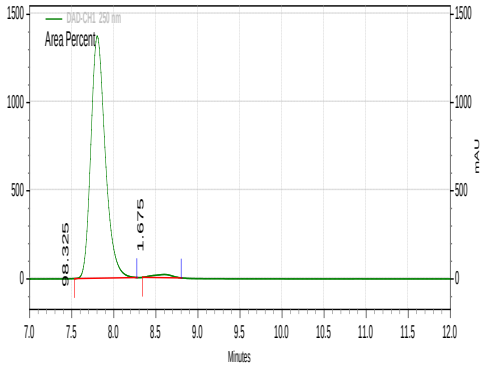


R-isomer



S-isomer

Retention Time	Area	Area %	Retention Time	Area	Area %
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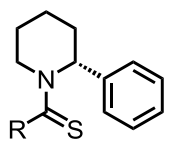
8.627	16467183	97.76	8.600	1109477	1.67
Totals	16844732	100.00	Totals	66238990	100.00



2b

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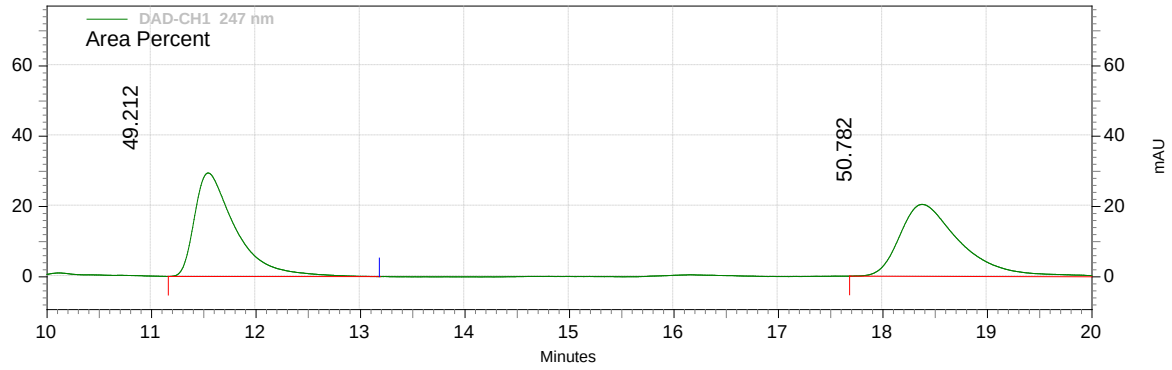

DAD-CH1 247 nm Results

Retention Time	Area	Area %
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18.373	3308053	50.78
Totals	6514185	100.00

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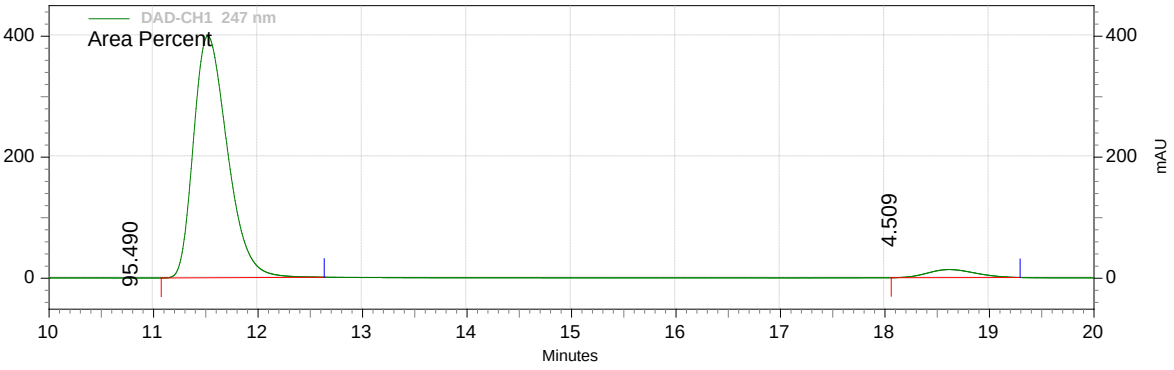

DAD-CH1 247 nm Results

Retention Time	Area	Area %
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18.613	1697228	4.51
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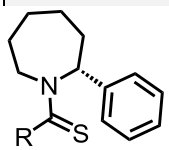

2c

Area % Report
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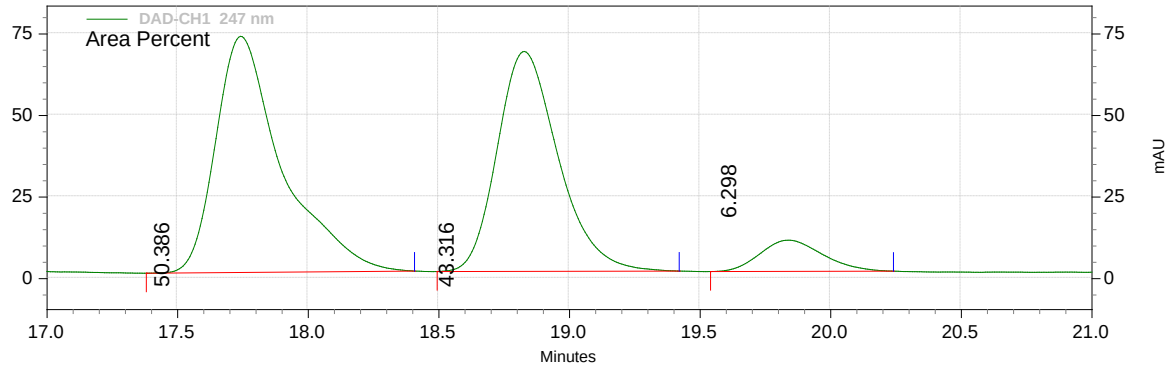

DAD-CH1 247 nm Results

Retention Time	Area	Area %
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19.840	636588	6.30
Totals	10107536	100.00

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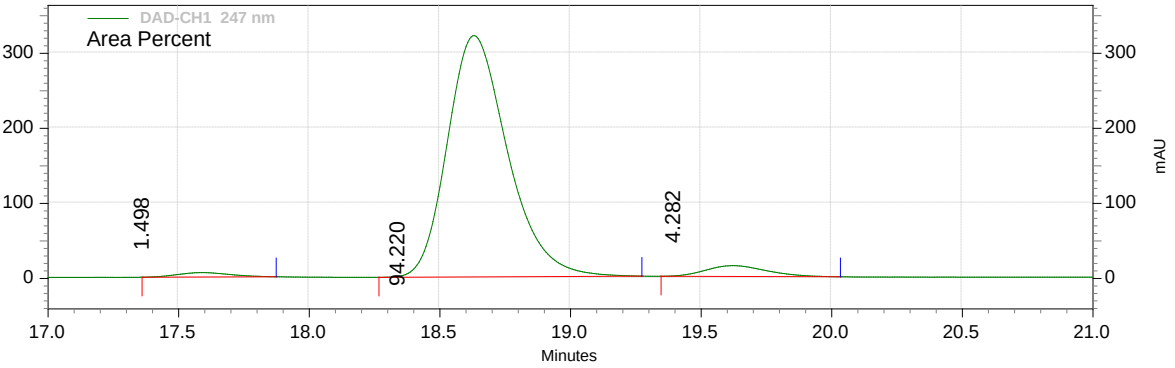

DAD-CH1 247 nm Results

Retention Time	Area	Area %
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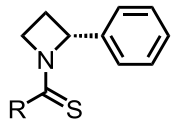
Totals	21882274	100.00



2d$_{mono}$

Area % Report

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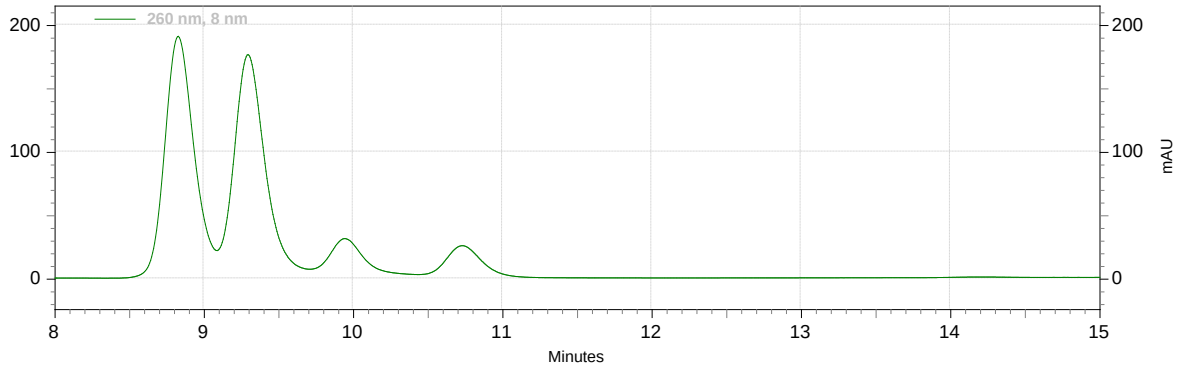

8.827	33369517	35.97
9.293	32295605	34.82
9.947	10161730	10.95
10.727	7708026	8.31

Area % Report

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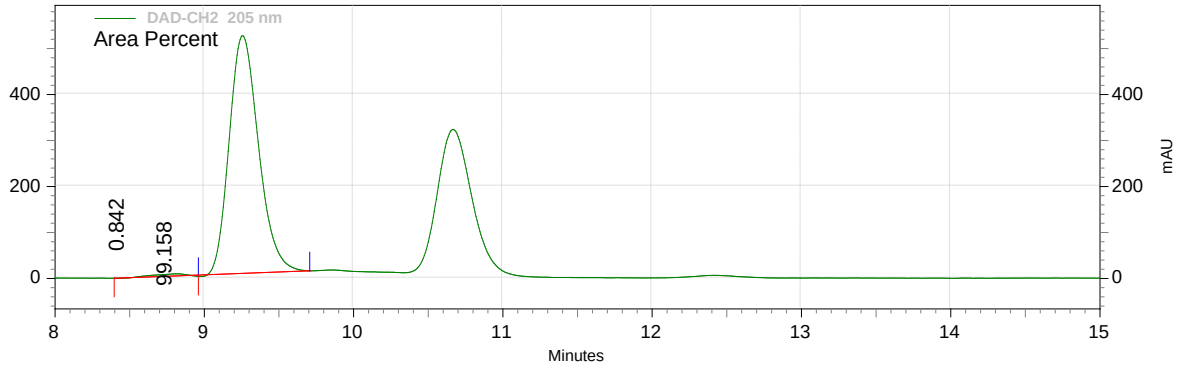
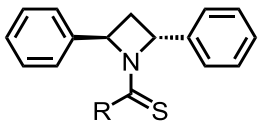


DAD-CH2 205 nm Results

Retention Time	Area	Area %
8.813	239650	0.84
9.253	28236062	99.16
Totals	28475712	100.00



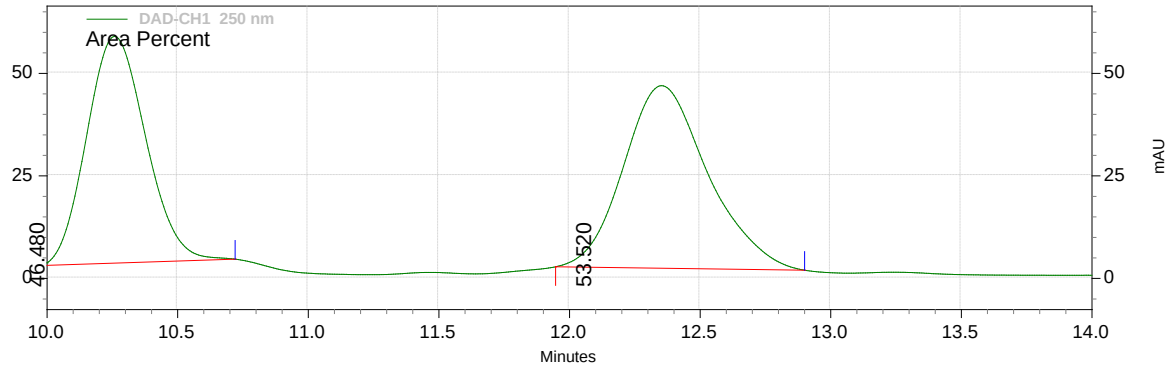
2d$_{di}$

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\145C-higher-ODH

Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 45 min without fc 0.5 ml per min.met

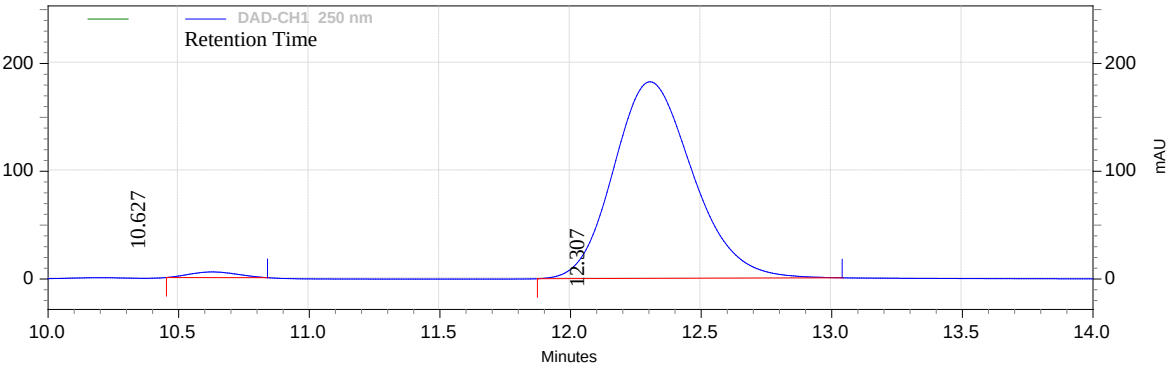
Acquired: 7/1/2015 5:09:12 PM



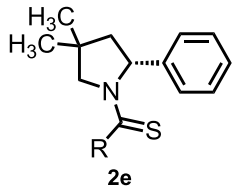
DAD-CH1 250 nm Results

Retention Time	Area	Area %
10.260	3470420	46.48
12.353	3996080	53.52
Totals	7466500	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\145B-higher-ODH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 45 min without fc 0.5 ml per min.met
Acquired: 7/1/2015 5:38:01 PM



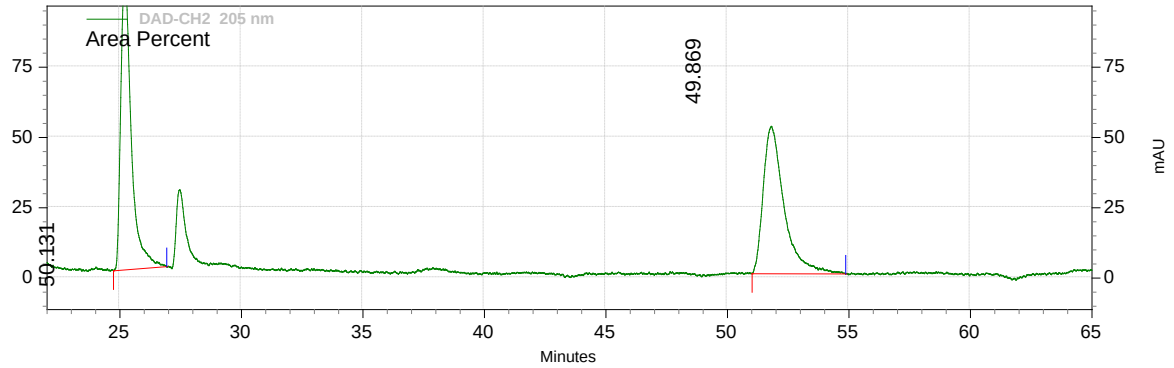
Retention Time	Area	Area %	Height	Height %
10.627	262966	1.68	20964	2.79
12.307	15361317	98.32	729785	97.21
Totals	15624283	100.00	750749	100.00



2e

Area % Report

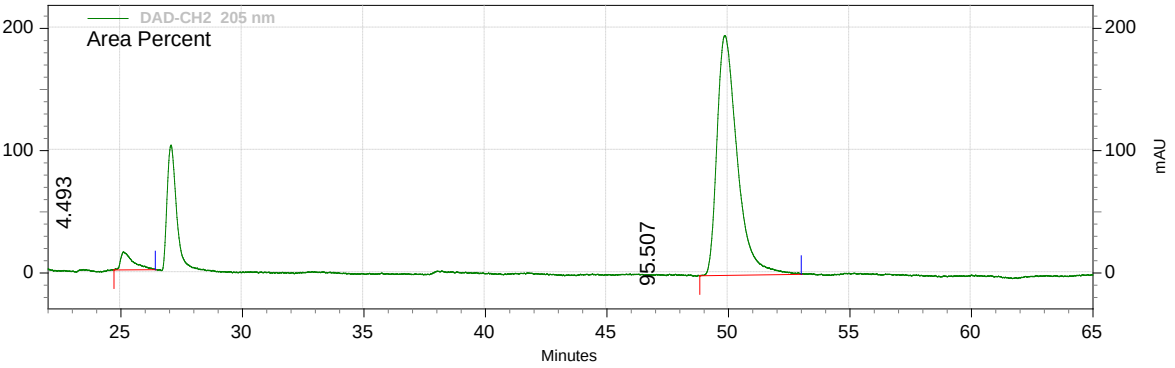
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\X-1-48-1re2-IC-IC-1-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met



DAD-CH2 205 nm Results

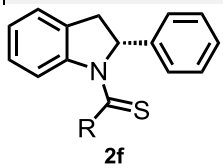
Retention Time	Area	Area %
25.200	12616586	50.13
51.800	12550729	49.87
Totals	25167315	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\X-1-48-2-IC-IC-1-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 12/15/2015 7:49:03 PM
Printed: 2/3/2016 3:00:24 PM



DAD-CH2 205 nm Results

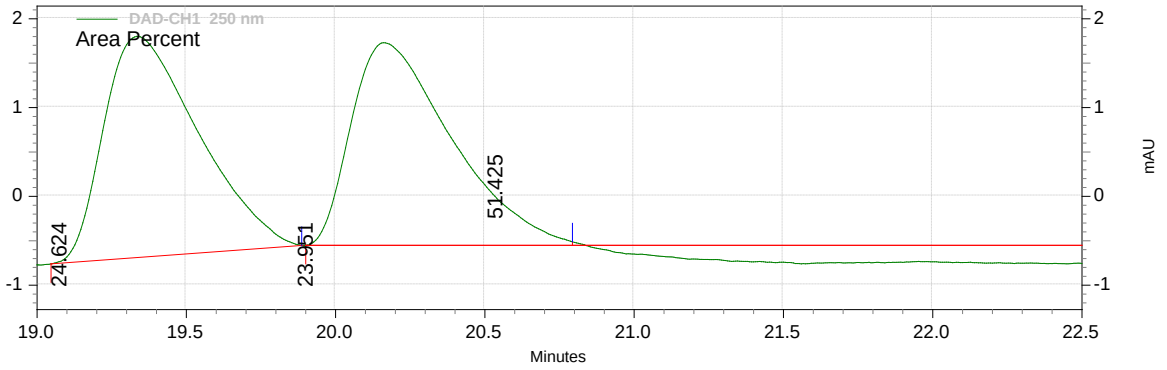
Retention Time	Area	Area %
25.100	2134294	4.49
49.860	45366926	95.51
Totals	47501220	100.00



2f

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\XG-1-29-2-ODH-IC-1-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 40 min without fc 0.5 ml per min.met

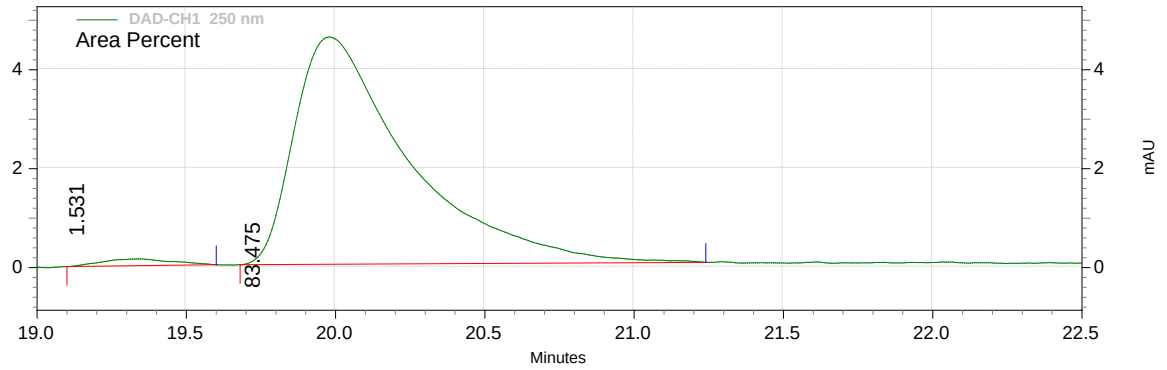


DAD-CH1 250 nm Results

Retention Time	Area	Area %
19.333	219287	24.62
20.160	213298	23.95
20.793	457962	51.42
Totals	890547	100.00

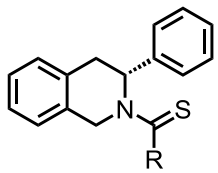
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\XG-1-38-ODH-IC-1-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 40 min without fc 0.5 ml per min.met



DAD-CH1 250 nm Results

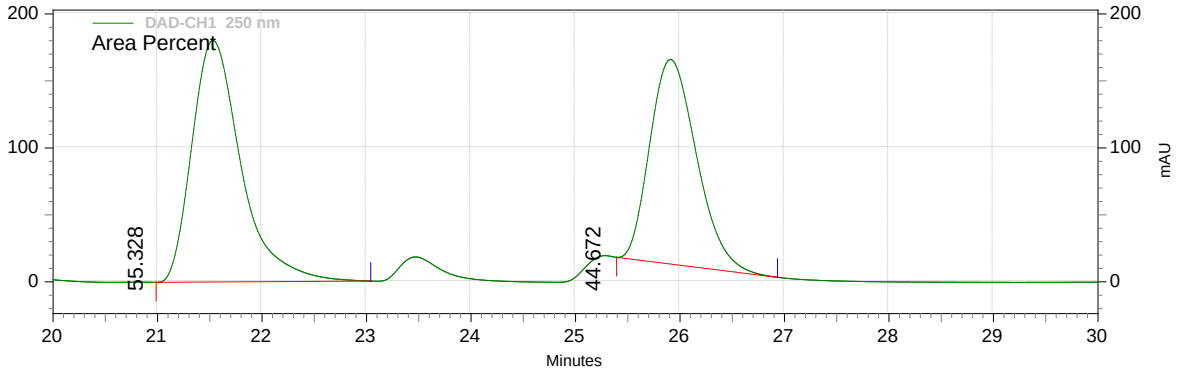
Retention Time	Area	Area %
19.333	8968	1.53
19.980	489047	83.47
Totals	585862	100.00



2g

Area % Report

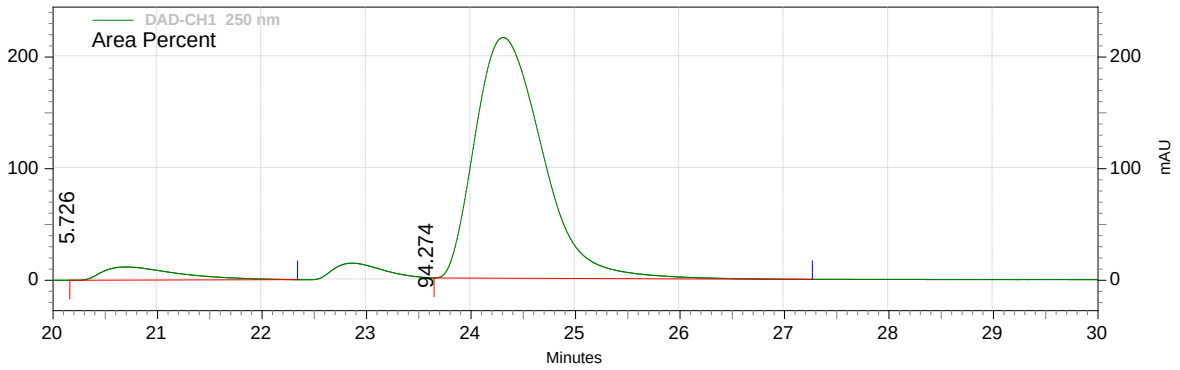
Data File:C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\x-1-51-2-IC-IC-1-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 60 min without fc 0.5 ml per min.met



DAD-CH1 250 nm Results

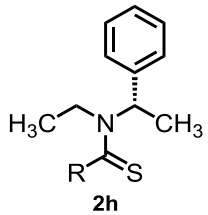
Retention Time	Area	Area %
21.533	23542079	55.33
25.907	19007697	44.67
Totals	42549776	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\x-1-57-2(1)-IC-IC-1-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met



DAD-CH1 250 nm Results

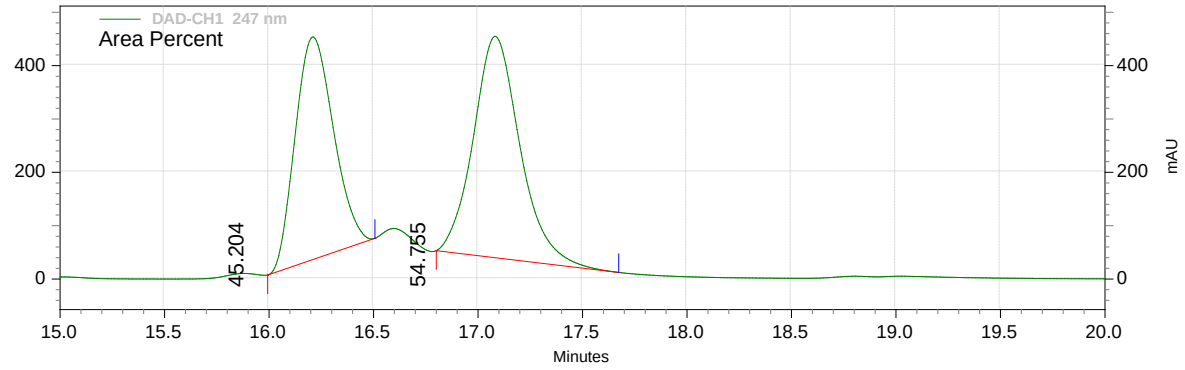
Retention Time	Area	Area %
20.700	2344156	5.73
24.307	38591343	94.27
Totals	40935499	100.00



2h

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-70Bre-rac-5-0.5-IC-IC
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met

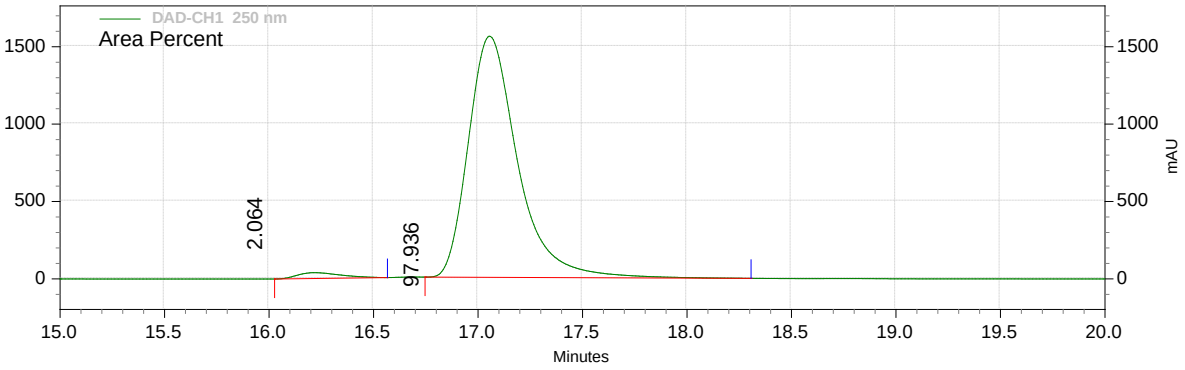


DAD-CH2 205 nm Results

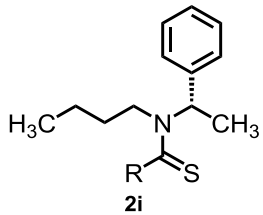
Retention Time	Area	Area %
16.213	30654718	44.43
17.080	38345249	55.57
Totals	68999967	100.00

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-76C-chiral-5-0.5-IC-IC
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met



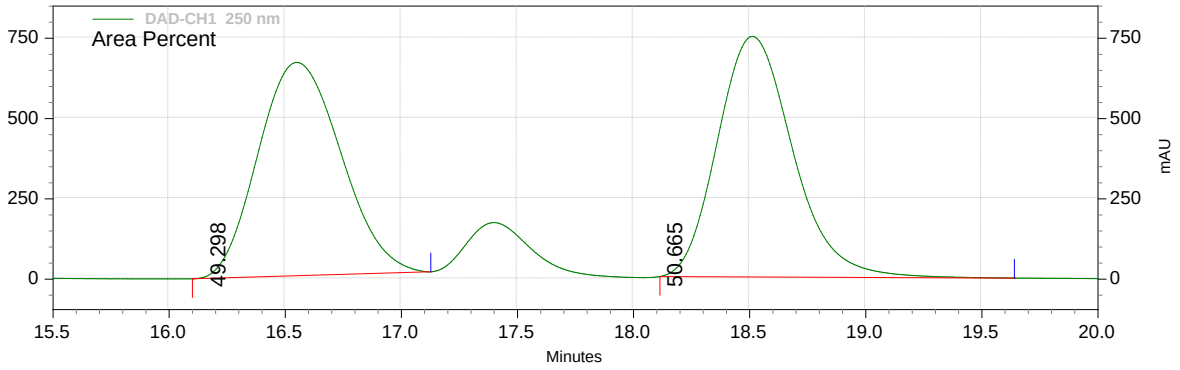
Retention Time	Area	Area %
16.220	2152338	2.06
17.053	102137556	97.94
Totals	104289894	100.00



2i

Area % Report

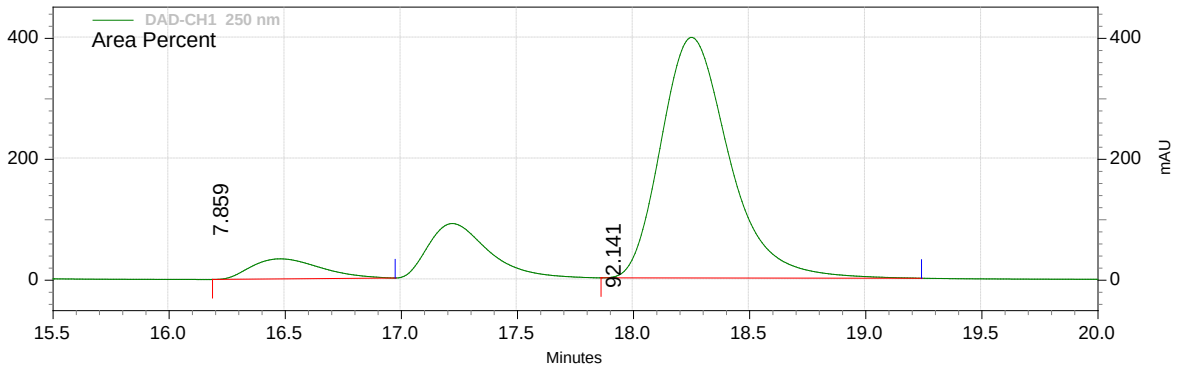
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-81A-IC-IC-2-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met



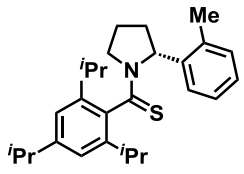
DAD-CH2 205 nm Results

Retention Time	Area	Area %
16.553	94715396	49.30
18.513	97422812	50.70
Totals	192138208	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-81B-IC-IC-2-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met

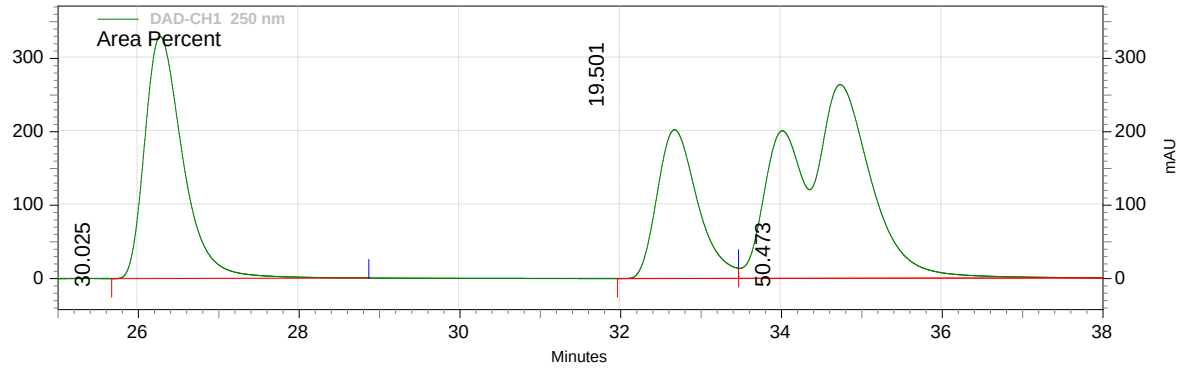


Retention Time	Area	Area %
16.480	2763811	7.86
18.247	32403059	92.14
Totals	35166870	100.00



3a

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-673-rac-670-3-1%IPA-0.5ml.min-75min-IC-IC

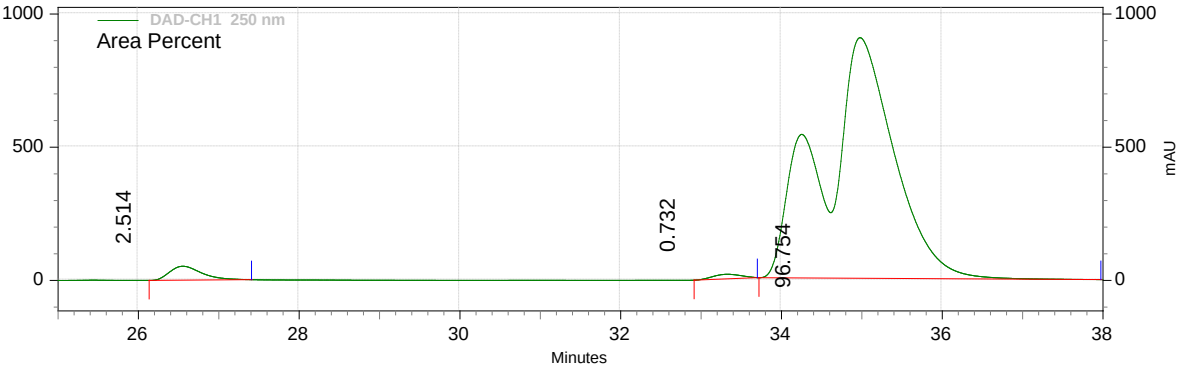


DAD-CH1 250 nm Results

Retention Time	Area	Area %
26.273	43479896	30.03
32.667	28240403	19.50
34.733	73091564	50.47
Totals	144811863	100.00

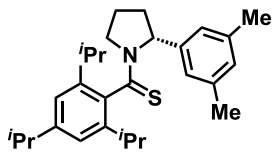
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-673-3-1%IPA-0.5ml.min-75min-IC-IC



DAD-CH1 250 nm Results

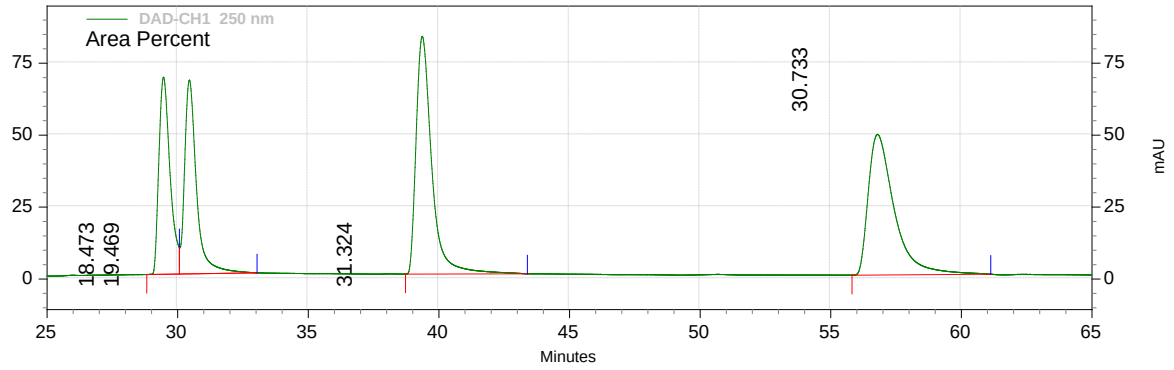
Retention Time	Area	Area %
26.553	5783370	2.51
33.327	1683241	0.73
34.980	222536525	96.75
Totals	230003136	100.00



3b

Area % Report

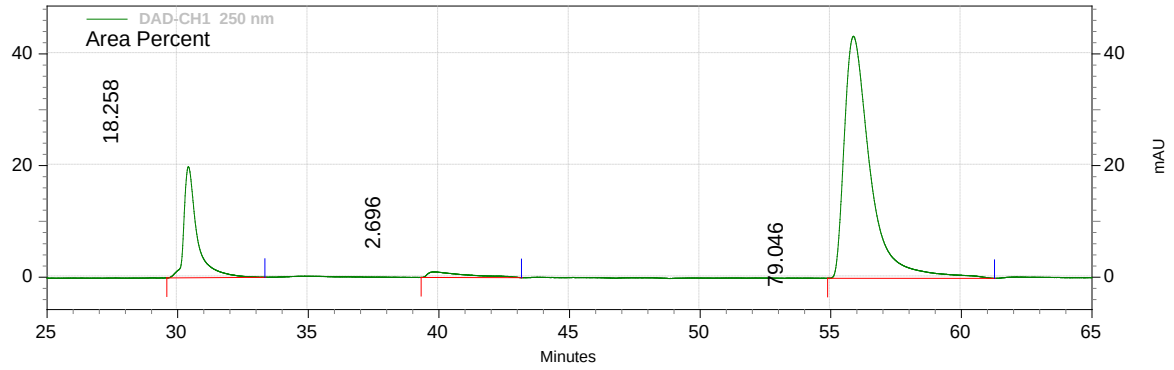
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-671-1-1%IPA-0.5ml.min-90min-IC-IC



DAD-CH1 250 nm Results

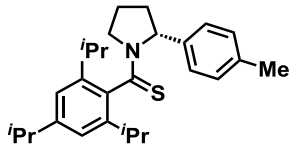
Retention Time	Area	Area %
29.460	8122943	18.47
30.447	8561302	19.47
39.367	13774311	31.32
56.793	13514423	30.73
Totals	43972979	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-676-1-1%IPA-0.5ml.min-90min-IC-IC



DAD-CH1 250 nm Results

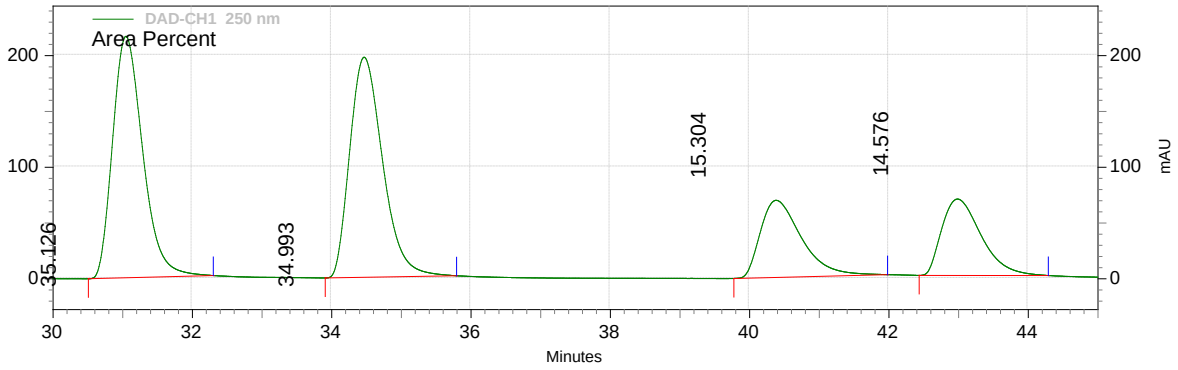
Retention Time	Area	Area %
30.413	2768633	18.26
39.767	408841	2.70
55.867	11986692	79.05
Totals	15164166	100.00



3c

Area % Report

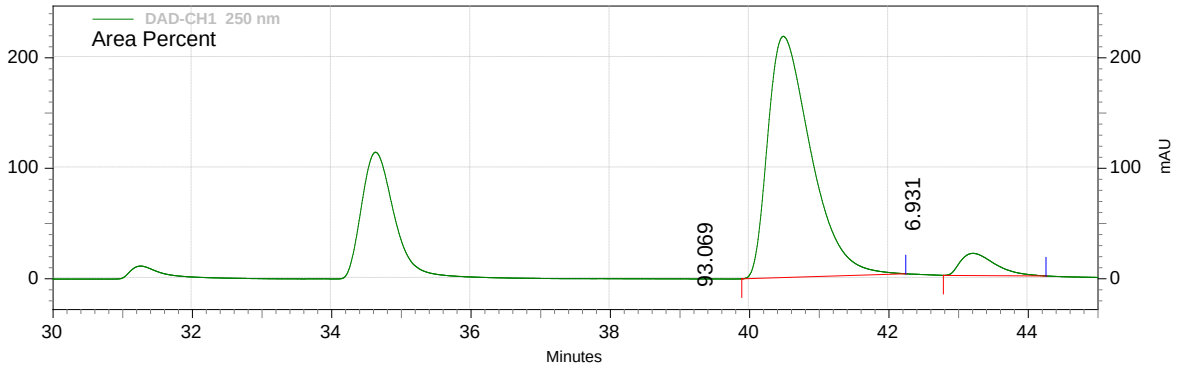
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-672-rac-569-1-1%IPA-0.5ml.min-60min-IC-IC



DAD-CH1 250 nm Results

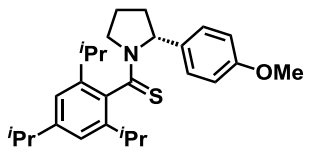
Retention Time	Area	Area %
31.047	25984462	35.13
34.467	25886243	34.99
40.380	11321337	15.30
42.987	10782455	14.58
Totals	73974497	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-672-1-1%IPA-0.5ml.min-60min-IC-IC



DAD-CH1 250 nm Results

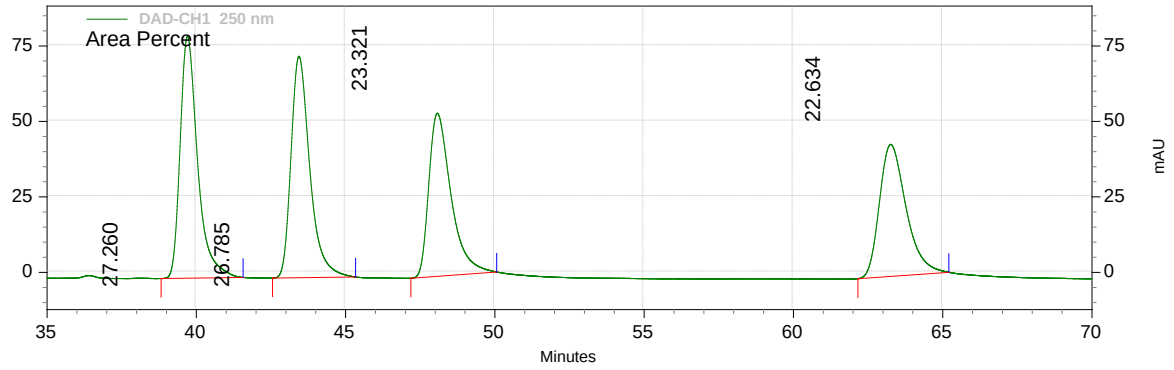
Retention Time	Area	Area %
40.487	37552590	93.07
43.207	2796590	6.93
Totals	40349180	100.00



3d

Area % Report

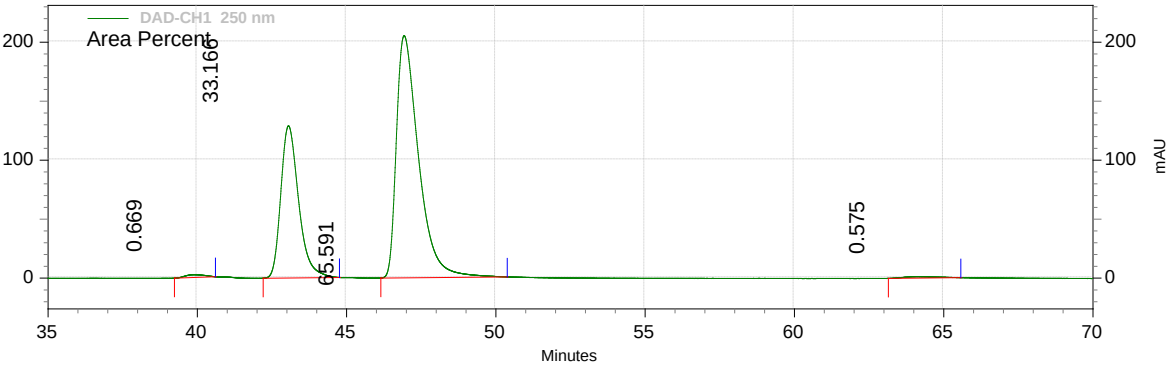
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-581-rac-570-3-1%IPA-0.5ml.min-90min-IC-IC



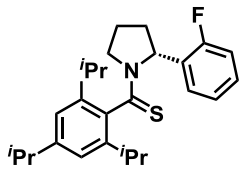
DAD-CH1 250 nm Results

Retention Time	Area	Area %
39.700	13040534	27.26
43.440	12813209	26.79
48.073	11155982	23.32
63.260	10827253	22.63
Totals	47836978	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-581-3-1%IPA-0.5ml.min-90min-IC-IC



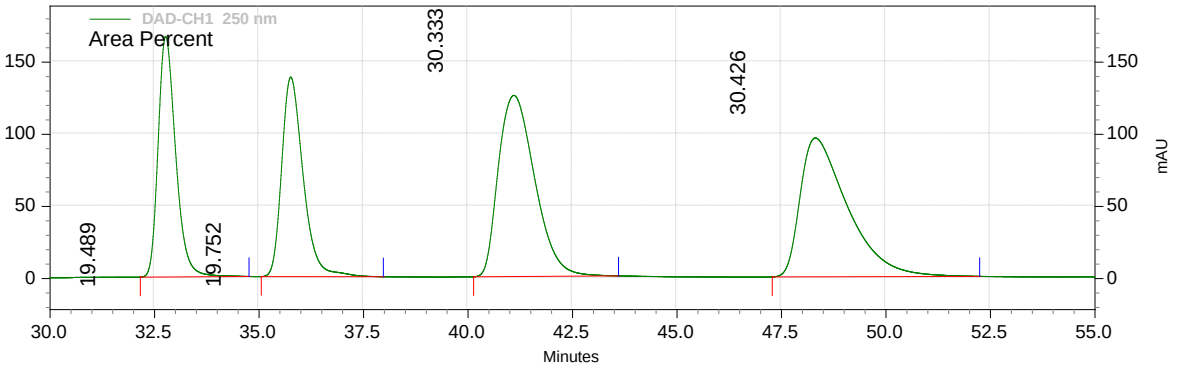
Retention Time	Area	Area %
39.900	431654	0.67
43.053	21411535	33.17
46.927	42345338	65.59
64.080	v371071	0.57
Totals	64559598	100.00



3e

Area % Report

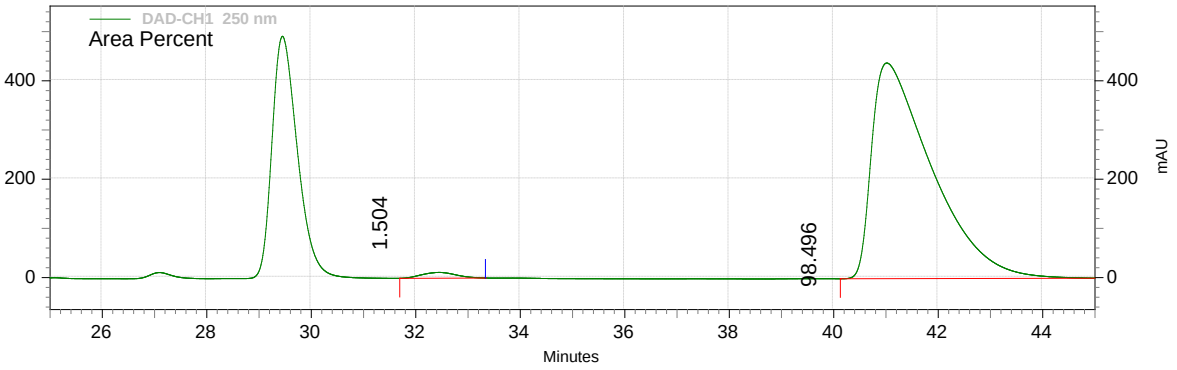
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-660-rac-656-0.5%IPA-0.5ml.min-75min-ADH-IC



DAD-CH1 250 nm Results

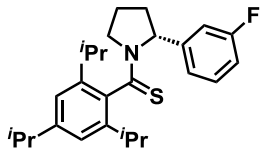
Retention Time	Area	Area %
32.767	19470143	19.49
35.760	19732825	19.75
41.100	30304428	30.33
48.313	30396973	30.43
Totals	99904369	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-660-1-0.5%IPA-0.5ml.min-75min-ADH-IC



DAD-CH1 250 nm Results

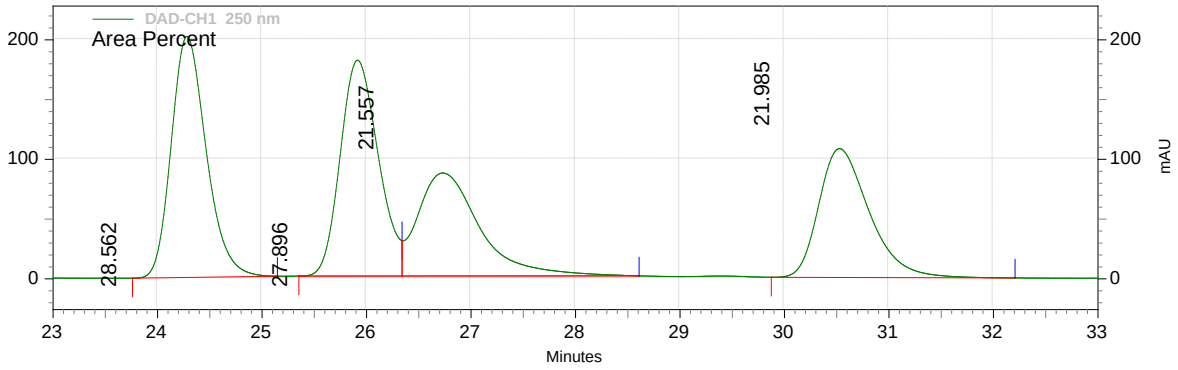
Retention Time	Area	Area %
32.453	2138274	1.50
41.020	140064803	98.50
Totals	142203077	100.00



3f

Area % Report

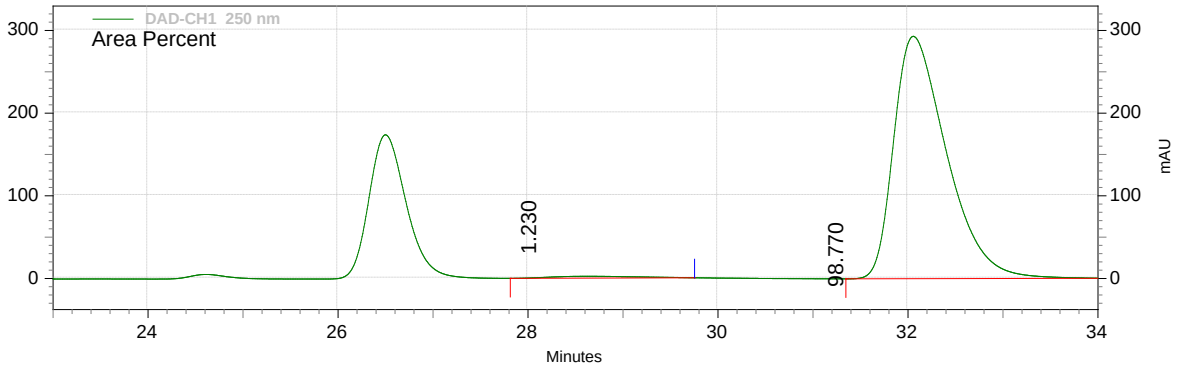
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-661-1-rac-572-n-0.5%IPA-0.5ml.min-120min-ADH-IC



DAD-CH1 250 nm Results

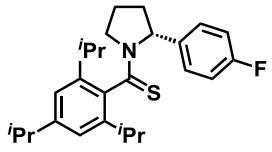
Retention Time	Area	Area %
24.280	18746537	28.56
25.913	18309077	27.90
26.733	14148859	21.56
30.527	14429503	21.98
Totals	65633976	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-661-1-0.5%IPA-0.5ml.min-120min-ADH-IC



DAD-CH1 250 nm Results

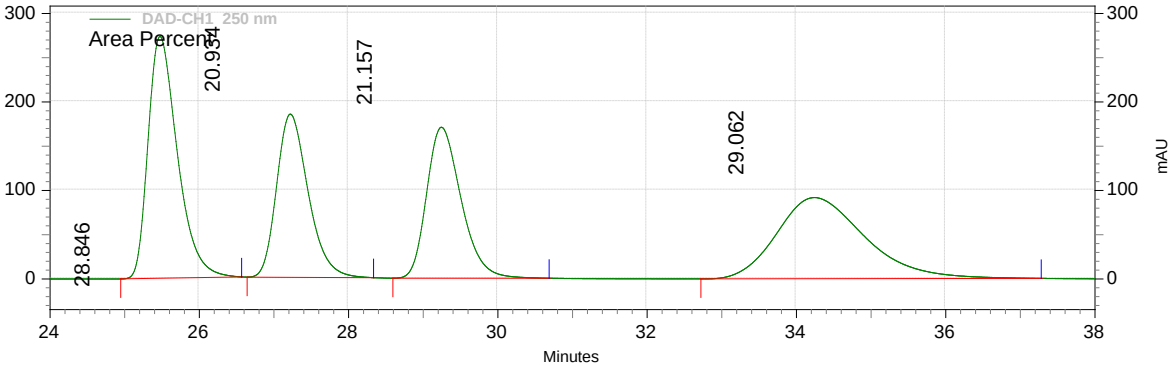
Retention Time	Area	Area %
28.640	564453	1.23
32.053	45321782	98.77
Totals	45886235	100.00



3g

Area % Report

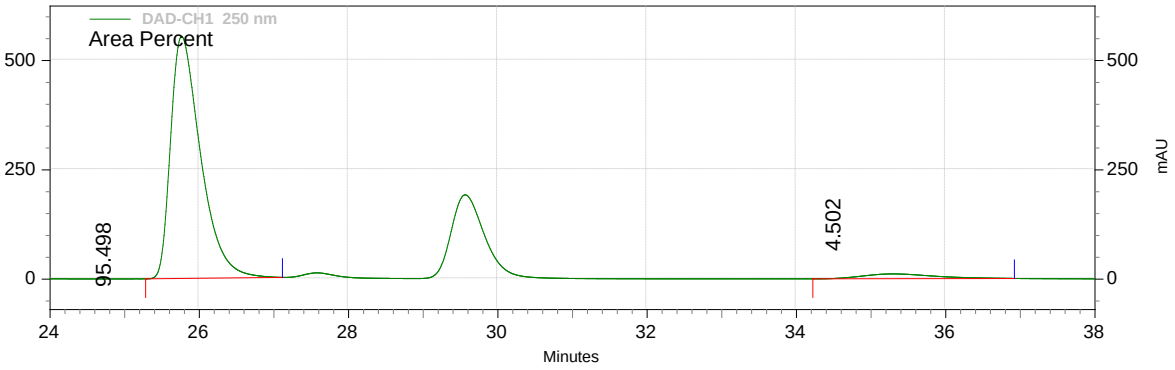
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-662-1-rac-655-0.5%IPA-0.5ml.min-120min-ADH-IC



DAD-CH1 250 nm Results

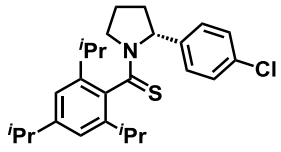
Retention Time	Area	Area %
25.473	29826477	28.85
27.220	21645613	20.93
29.247	21876573	21.16
34.240	30050324	29.06
Totals	103398987	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-662-1-0.5%IPA-0.5ml.min-120min-ADH-IC



DAD-CH1 250 nm Results

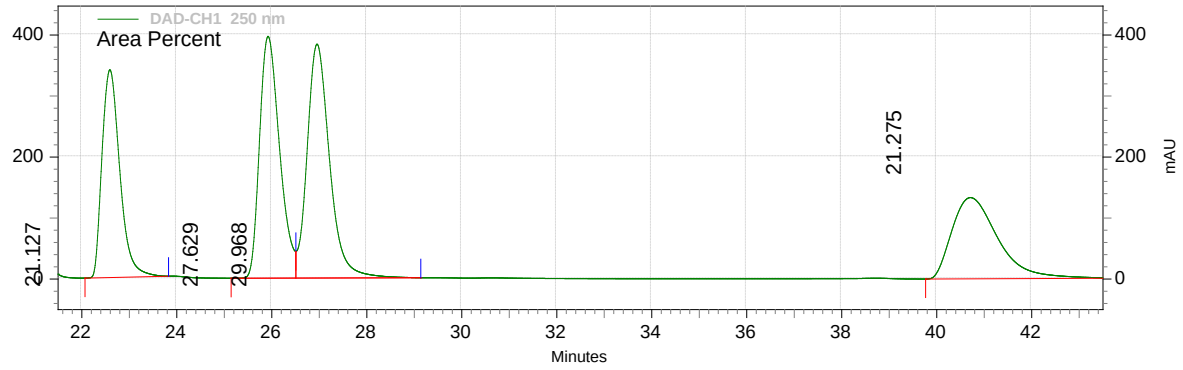
Retention Time	Area	Area %
25.760	61874506	95.50
35.293	2917242	4.50
Totals	64791748	100.00



3h

Area % Report

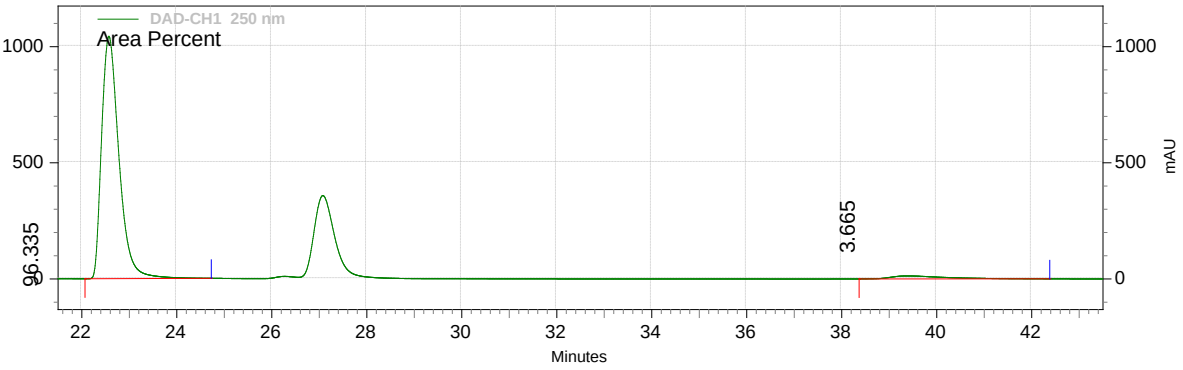
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-609-571-rac-1-0.5%IPA-0.5ml.min-120min-ADH-IC



DAD-CH1 250 nm Results

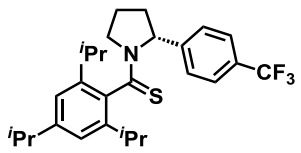
Retention Time	Area	Area %
22.593	35479071	21.13
25.920	46397797	27.63
26.953	50325587	29.97
40.713	35727575	21.28
Totals	167930030	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-609-1-0.5%IPA-0.5ml.min-120min-ADH-IC



DAD-CH1 250 nm Results

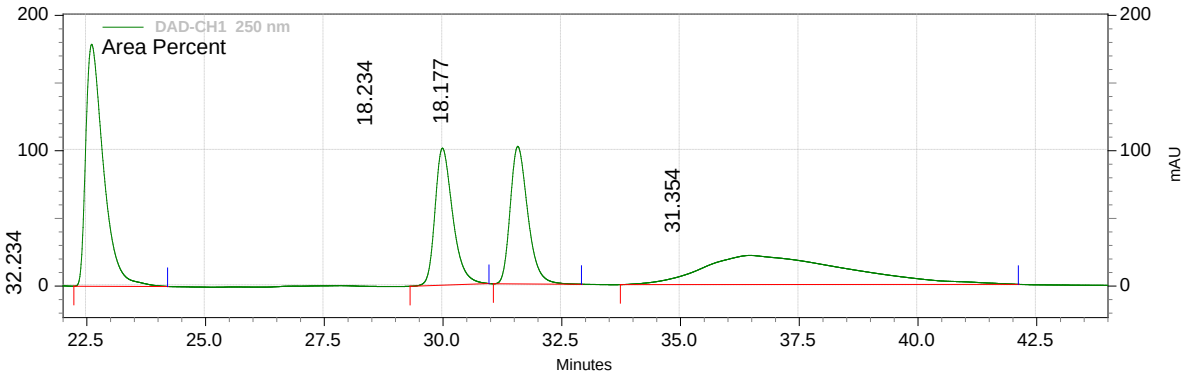
Retention Time	Area	Area %
22.573	105762029	96.33
39.387	4023694	3.67
Totals	109785723	100.00



3i

Area % Report

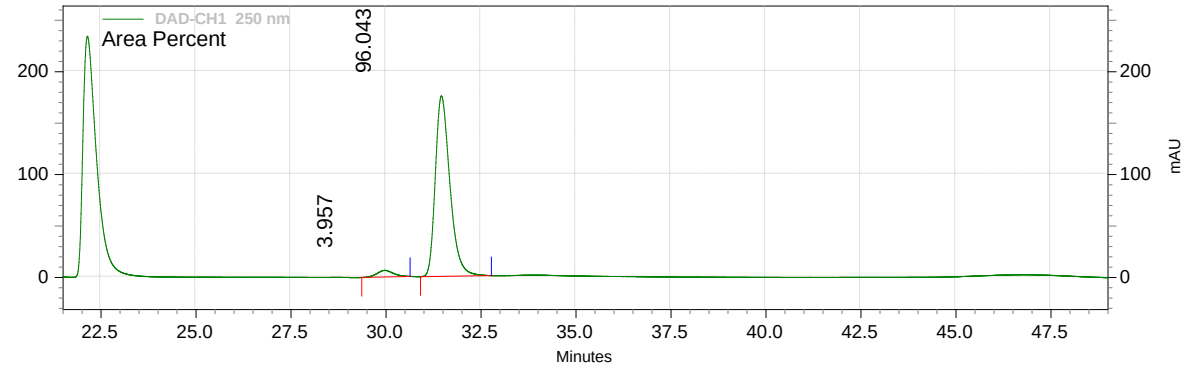
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-645-2-rac-448-0.5%IPA-0.5ml.min-120min-ADH-IC



DAD-CH1 250 nm Results

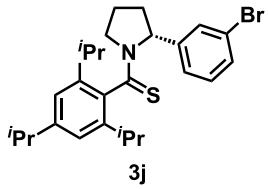
Retention Time	Area	Area %
22.600	18566076	32.23
29.987	10502587	18.23
31.573	10469571	18.18
36.467	18059364	31.35
Totals	57597598	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-645-2-0.5%IPA-0.5ml.min-120min-ADH-IC



DAD-CH1 250 nm Results

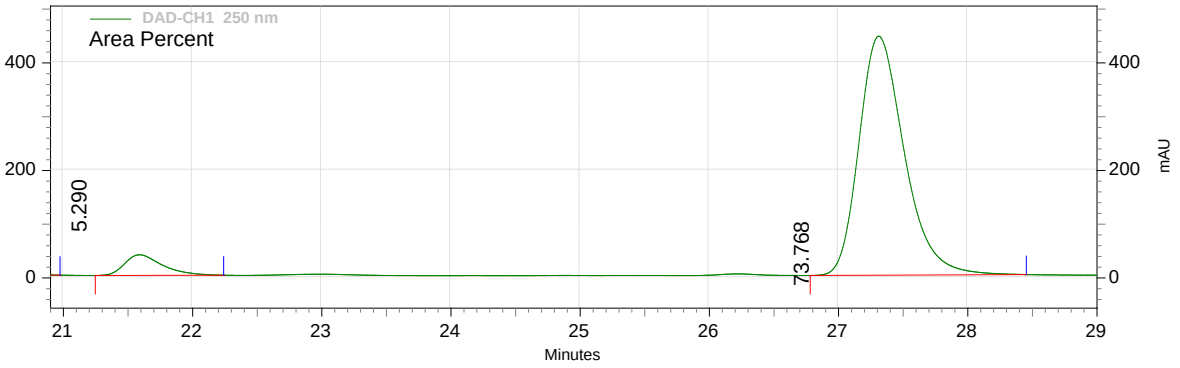
Retention Time	Area	Area %
29.967	770805	3.96
31.460	18709828	96.04
Totals	19480633	100.00



3j

Area % Report

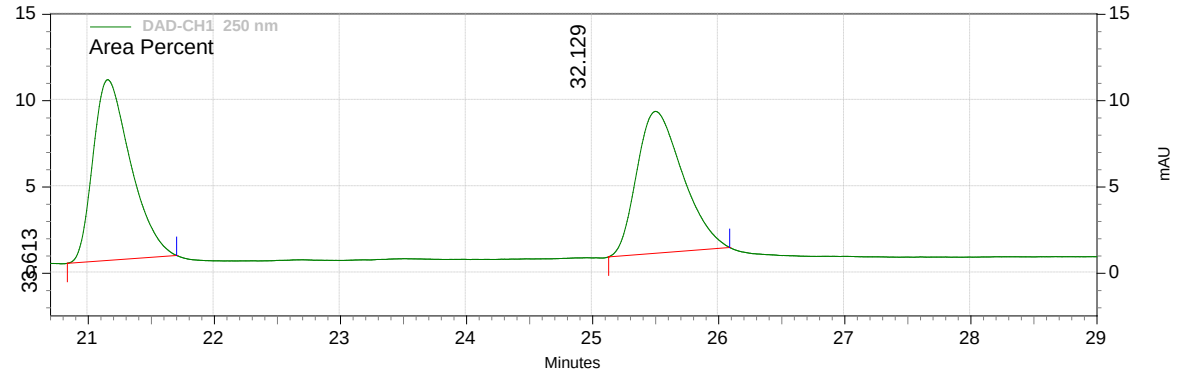
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-610-1-5%IPA-0.5ml.min-40min-IC-IC



DAD-CH1 250 nm Results

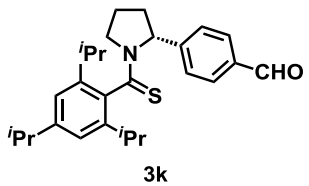
Retention Time	Area	Area %
21.587	3101923	5.29
27.313	43256034	73.77
Totals	58637811	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-591-1-5%IPA-0.5ml.min-150min-IC-IC



DAD-CH1 250 nm Results

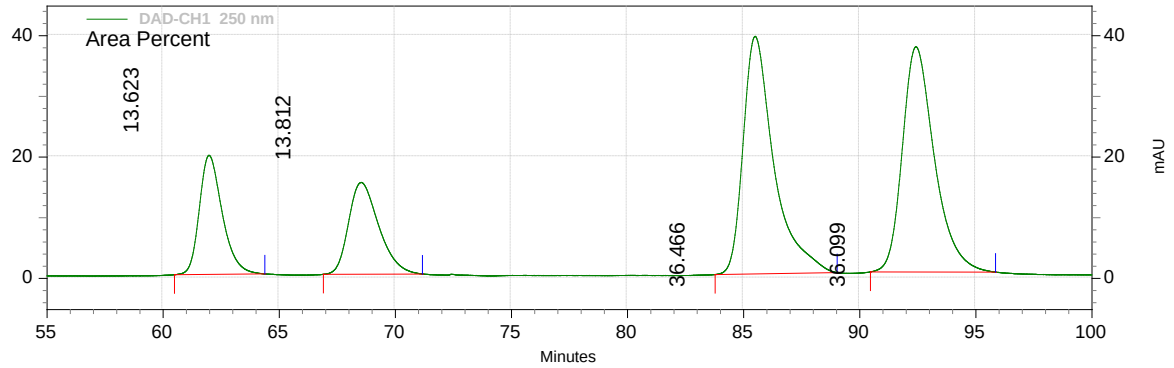
Retention Time	Area	Area %
21.153	868721	33.61
25.500	830376	32.13
Totals	2584511	100.00



3k

Area % Report

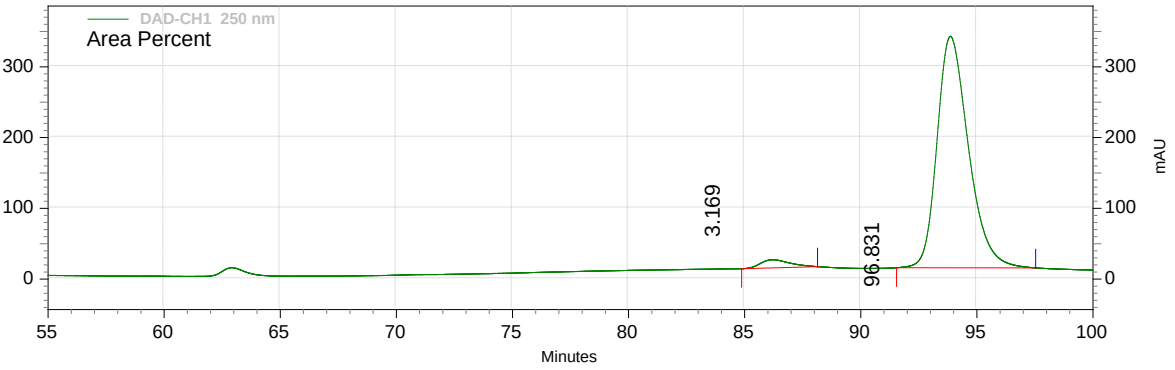
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-612-1-5%IPA-0.5ml.min-120min-IC-IC



DAD-CH1 250 nm Results

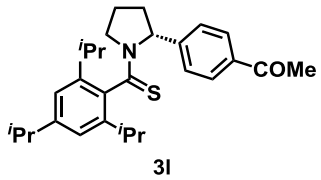
Retention Time	Area	Area %
61.973	5382274	13.62
68.527	5456785	13.81
85.493	14406892	36.47
92.420	14262209	36.10
Totals	39508160	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-621-1-5%IPA-0.5ml.min-120min-IC-IC



DAD-CH1 250 nm Results

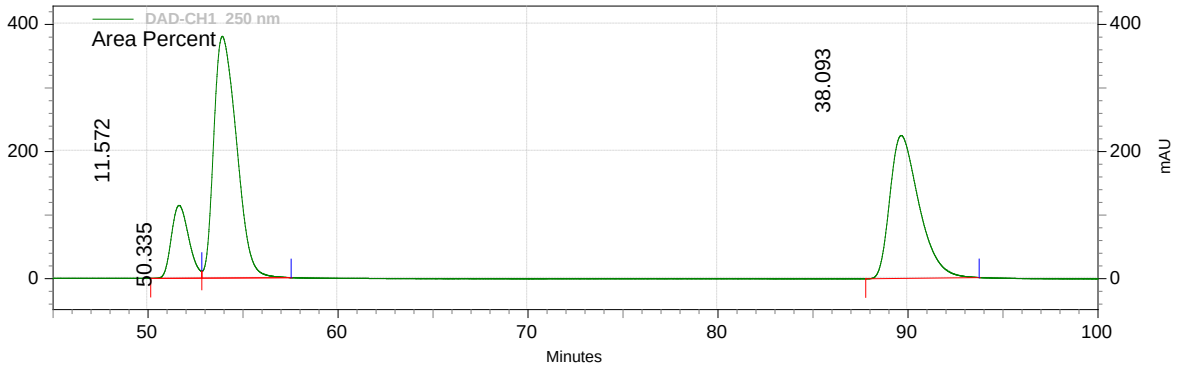
Retention Time	Area	Area %
86.207	4023522	3.17
93.860	122959007	96.83
Totals	126982529	100.00



3l

Area % Report

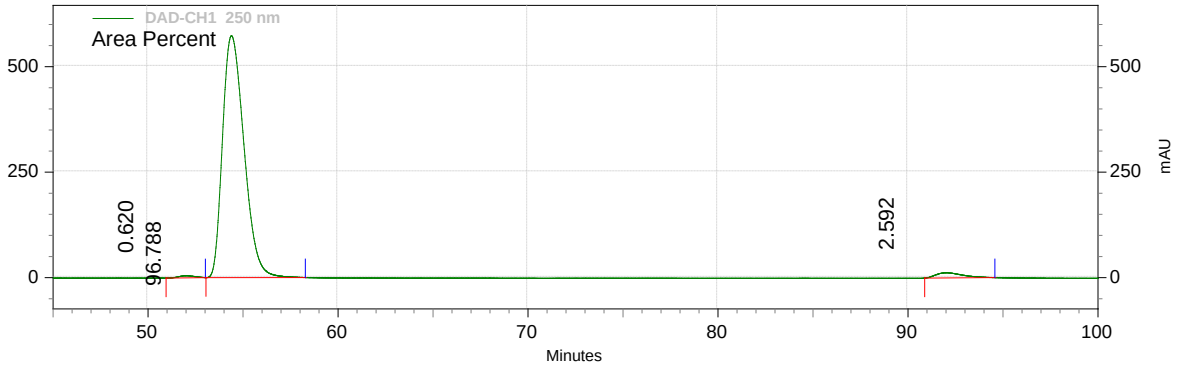
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-646-4-rac-590-5%IPA-0.5ml.min-150min-ADH-IC



DAD-CH1 250 nm Results

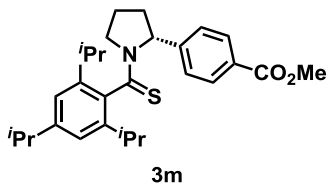
Retention Time	Area	Area %
51.633	29083244	11.57
53.907	126503815	50.34
89.640	95735506	38.09
Totals	251322565	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-646-3-5%IPA-0.5ml.min-150min-ADH-IC



DAD-CH1 250 nm Results

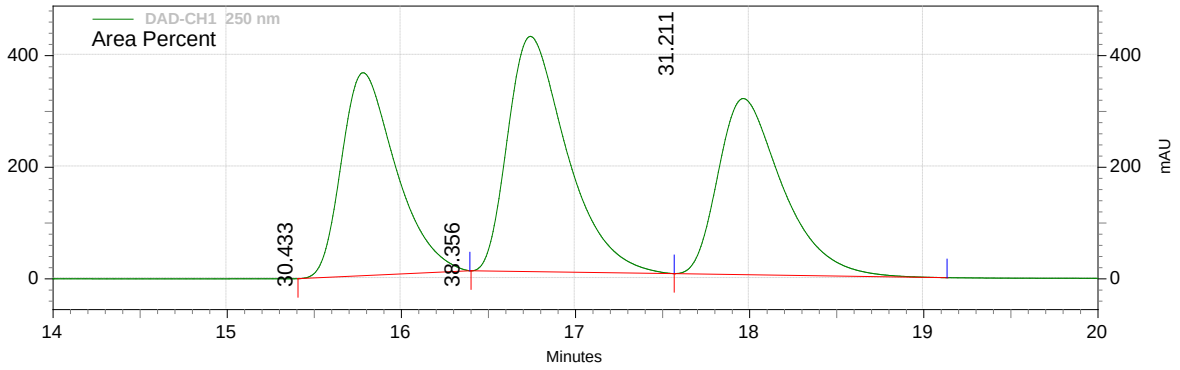
Retention Time	Area	Area %
52.000	1154839	0.62
54.393	180164566	96.79
92.013	4824093	2.59
Totals	186143498	100.00



3m

Area % Report

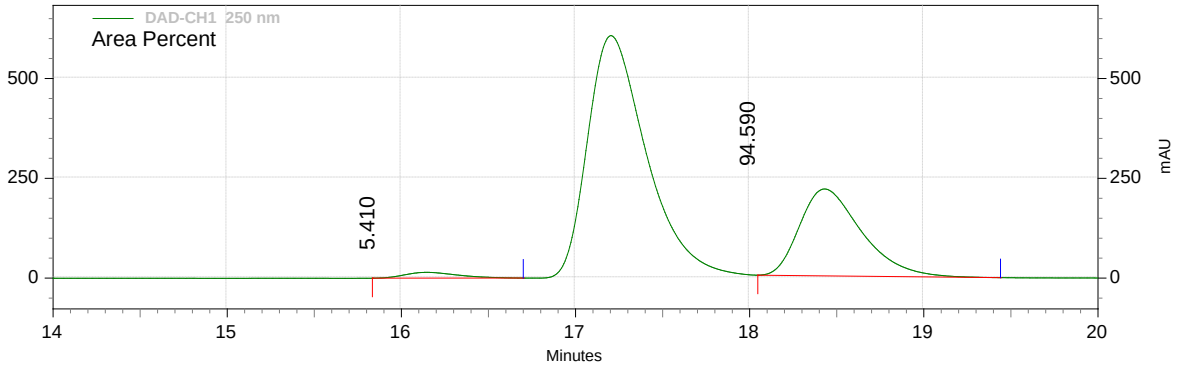
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-657-1-5%IPA-0.5ml.min-90min-ADH-ADH



DAD-CH1 250 nm Results

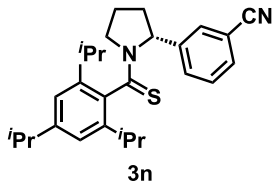
Retention Time	Area	Area %
15.780	31572650	30.43
16.740	39792203	38.36
17.967	32380145	31.21
Totals	103744998	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-667-2-5%IPA-0.5ml.min-90min-ADH-ADH



DAD-CH1 250 nm Results

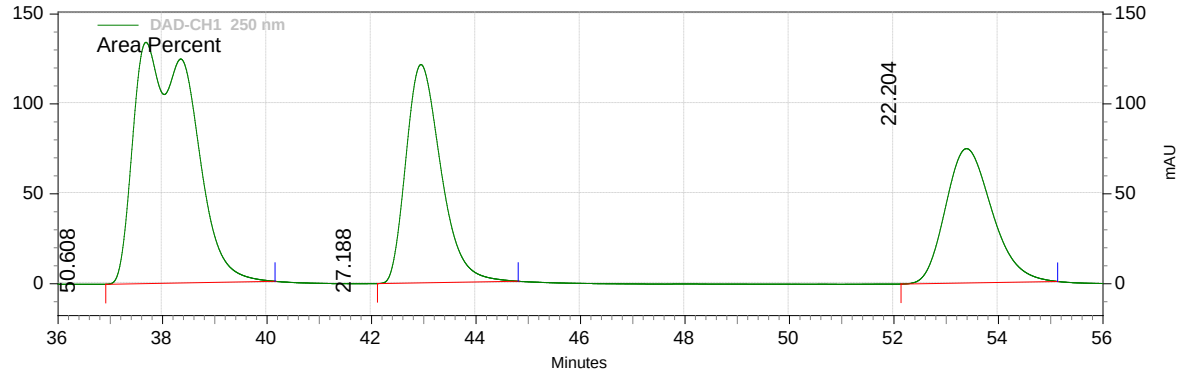
Retention Time	Area	Area %
16.147	1229846	5.41
18.433	21501226	94.59
Totals	22731072	100.00



3n

Area % Report

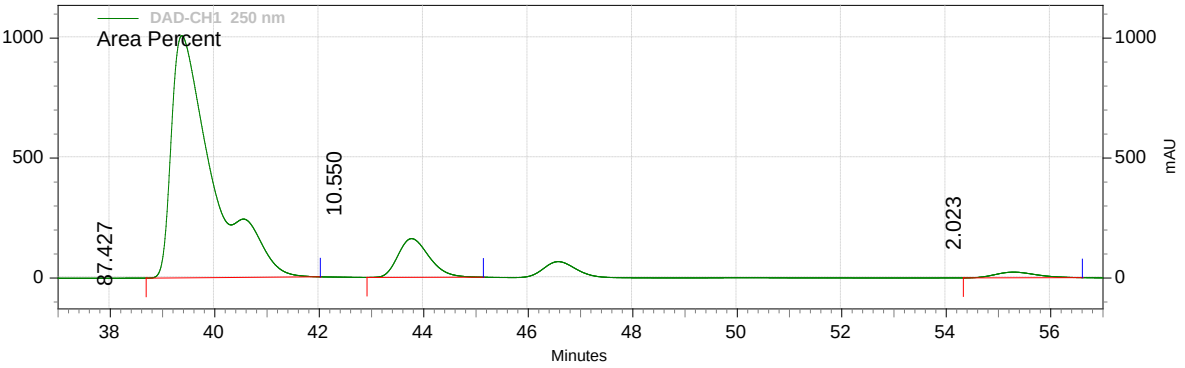
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-664-1-rac-615-5%IPA-0.5ml.min-75min-ADH-IC



DAD-CH1 250 nm Results

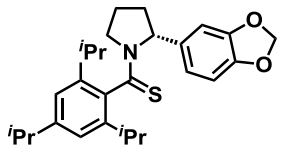
Retention Time	Area	Area %
37.680	42106719	50.61
42.947	22621055	27.19
53.387	18474257	22.20
Totals	83202031	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-664-1-5%IPA-0.5ml.min-75min-ADH-IC



DAD-CH1 250 nm Results

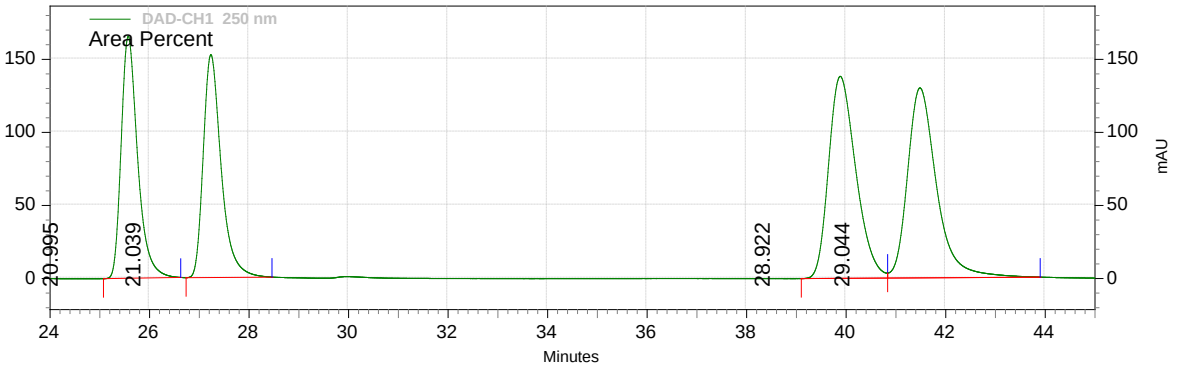
Retention Time	Area	Area %
39.367	221294207	87.43
43.767	26704346	10.55
55.287	5120296	2.02
Totals	253118849	100.00



3o

Area % Report

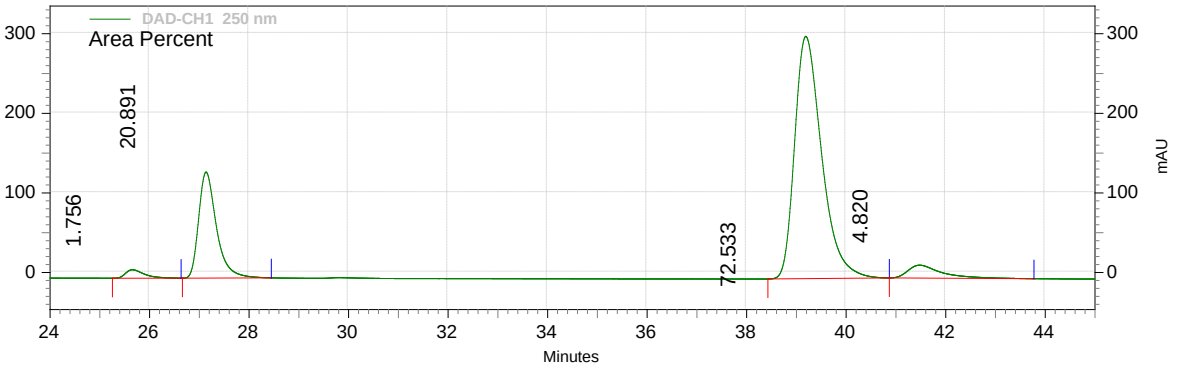
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-614-2-5%IPA-0.5ml.min-120min-IC-IC



DAD-CH1 250 nm Results

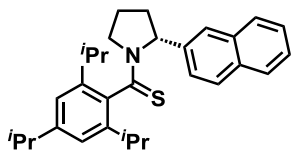
Retention Time	Area	Area %
25.573	15233920	20.99
27.233	15266057	21.04
39.880	20986174	28.92
41.480	21074387	29.04
Totals	72560538	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-622-1-5%IPA-0.5ml.min-120min-IC-IC



DAD-CH1 250 nm Results

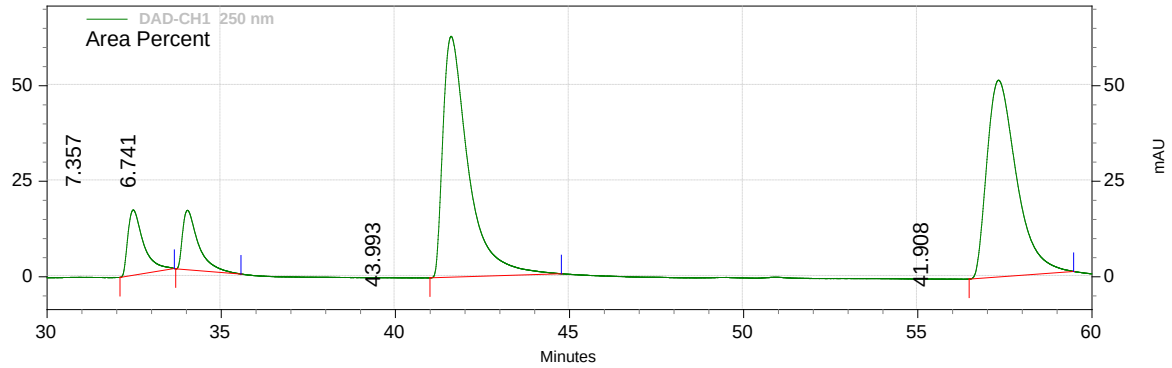
Retention Time	Area	Area %
25.660	1111742	1.76
27.133	13228584	20.89
39.187	45929882	72.53
41.480	3052269	4.82
Totals	63322477	100.00



3p

Area % Report

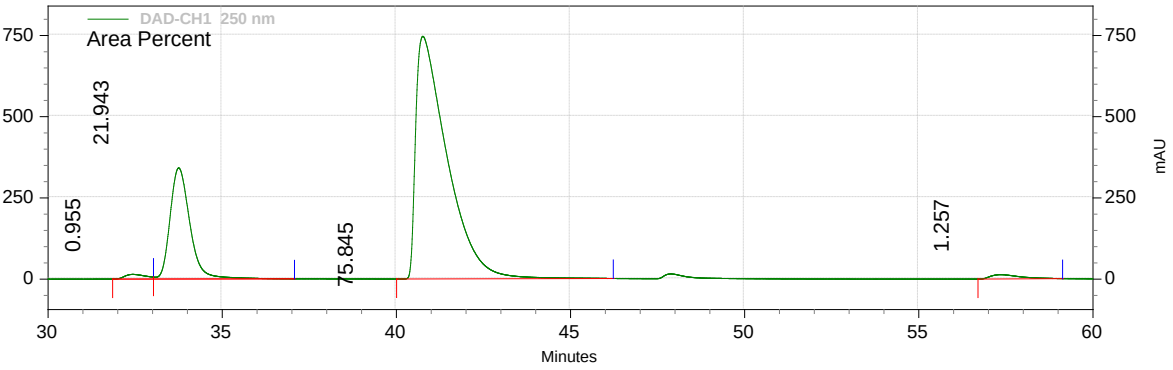
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-675-rac-669-1-1%IPA-0.5ml.min-60min-IC-IC



DAD-CH1 250 nm Results

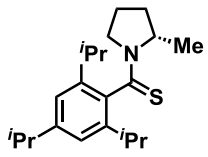
Retention Time	Area	Area %
32.473	2136277	7.36
34.033	1957312	6.74
41.600	12773658	43.99
57.320	12168351	41.91
Totals	29035598	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-675-1-1%IPA-0.5ml.min-60min-IC-IC



DAD-CH1 250 nm Results

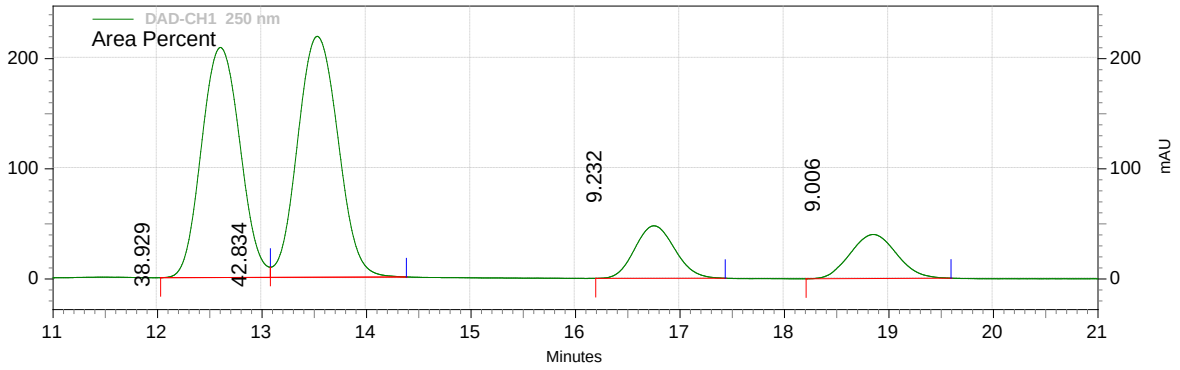
Retention Time	Area	Area %
32.433	2349216	0.96
33.753	53961097	21.94
40.760	186514787	75.84
57.353	3090692	1.26
Totals	245915792	100.00



3q

Area % Report

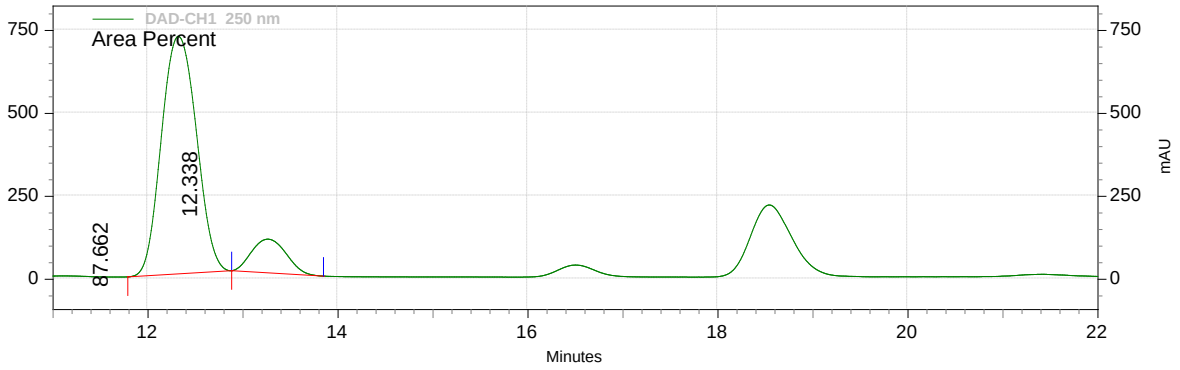
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-05-681-recent-1%IPA-0.5ml.min-40min-IC



DAD-CH1 250 nm Results

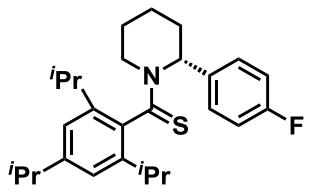
Retention Time	Area	Area %
12.600	21400445	38.93
13.527	23547316	42.83
16.753	5074922	9.23
18.847	4950849	9.01
Totals	54973532	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-05-754-1-1%IPA-0.5ml.min-40min-IC



DAD-CH1 250 nm Results

Retention Time	Area	Area %
12.320	73337621	87.66
13.260	10321513	12.34
Totals	83659134	100.00

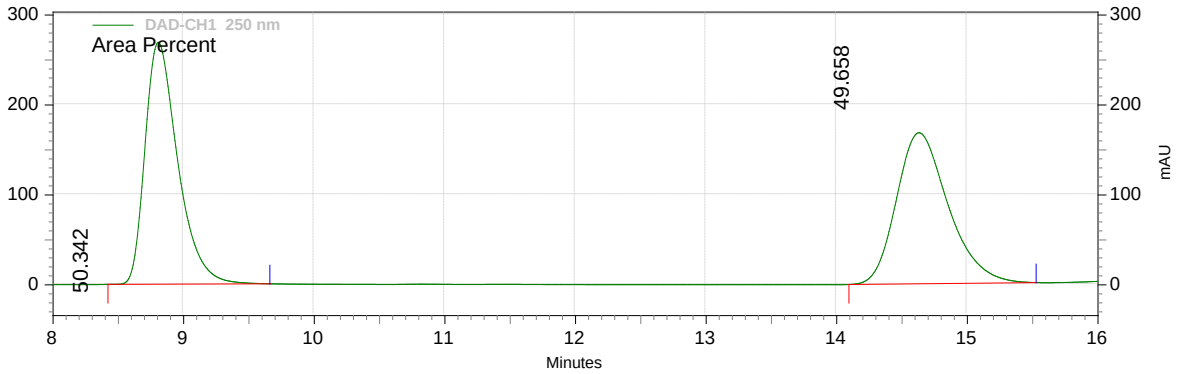


4a

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-03-543-1-5%IPA-0.5ml.min-60min-ADH

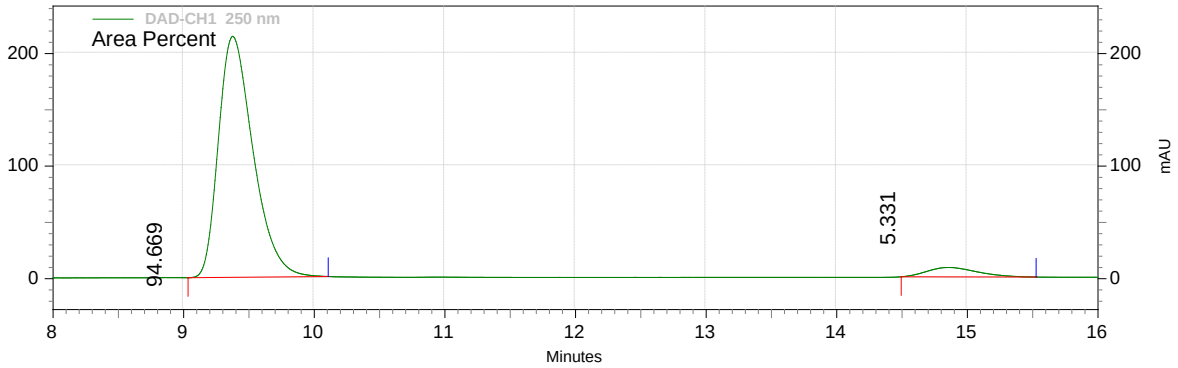
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 60 min without fc 0.5 ml per min.met



DAD-CH1 250 nm Results

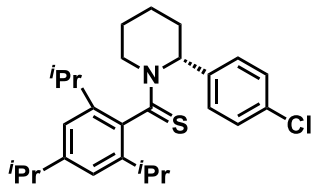
Retention Time	Area	Area %
8.807	18720025	50.34
14.633	18465987	49.66
Totals	37186012	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pritha\pv-04-559-1-5%IPA-0.5ml.min-60min-ADH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 60 min without fc 0.5 ml per min.met



DAD-CH1 250 nm Results

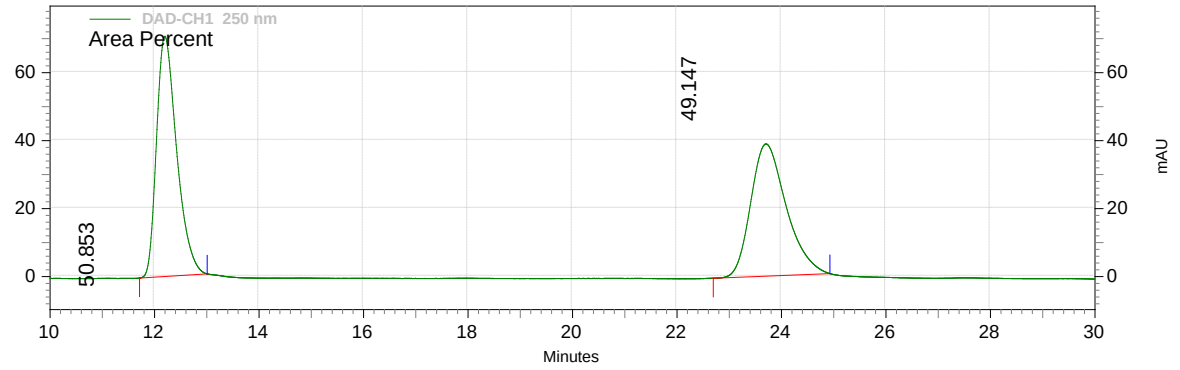
Retention Time	Area	Area %
9.373	15781094	94.67
14.853	888740	5.33
Totals	16669834	100.00



4b

Area % Report

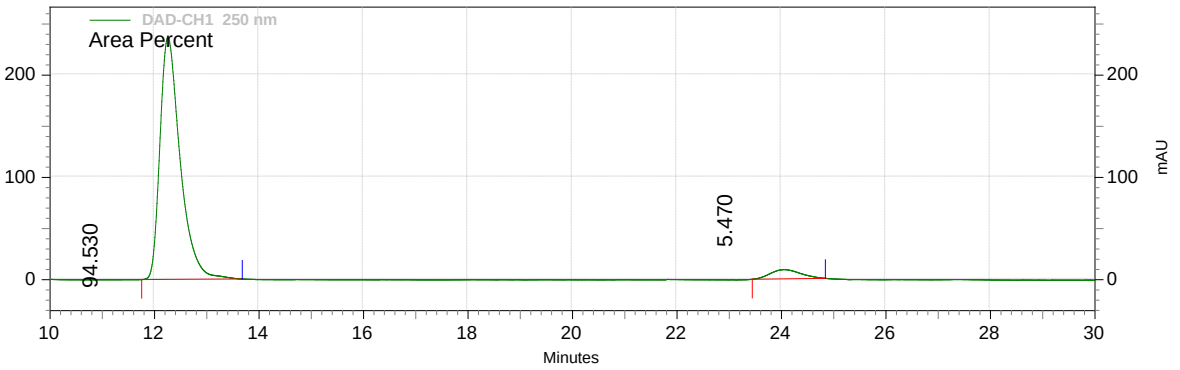
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-84AArac-CORR--ADH-2-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 50 min without fc 0.5 ml per min.met



DAD-CH1 250 nm Results

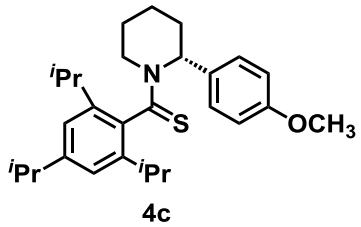
Retention Time	Area	Area %
12.193	7573190	50.85
23.707	7319151	49.15
Totals	14892341	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-84Dchiral--ADH-2-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 50 min without fc 0.5 ml per min.met



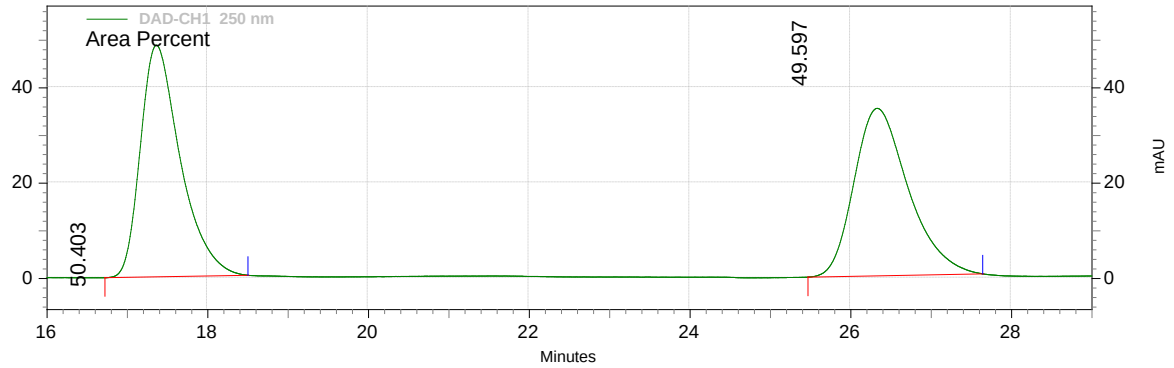
DAD-CH1 250 nm Results

Retention Time	Area	Area %
12.253	25452983	94.53
24.053	1472813	5.47
Totals	26925796	100.00



4c

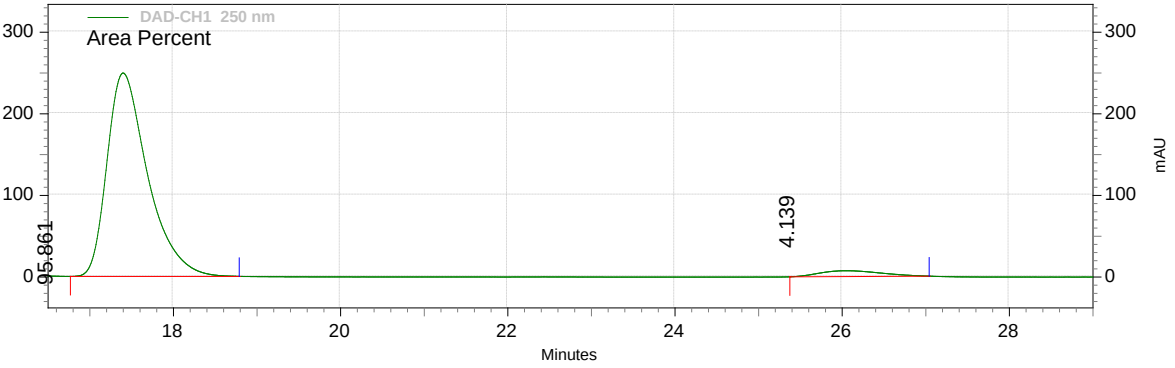
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-38A-racemic-ADH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 40 min without fc 0.5 ml per min.met



DAD-CH1 250 nm Results

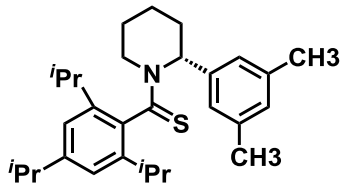
Retention Time	Area	Area %
17.360	6698812	50.40
26.327	6591598	49.60
Totals	13290410	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-38A-ADH
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 40 min without fc 0.5 ml per min.met



DAD-CH1 250 nm Results

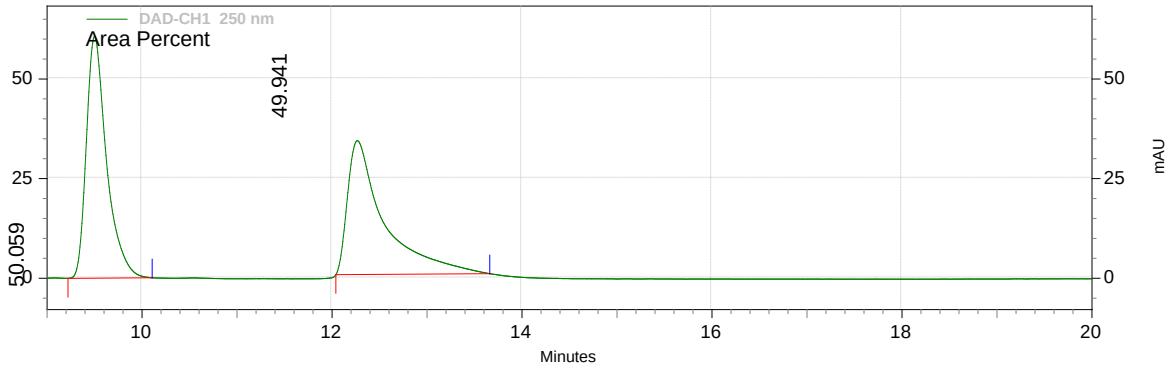
Retention Time	Area	Area %
17.400	33593865	95.86
26.053	1450632	4.14
Totals	35044497	100.00



4d

Area % Report

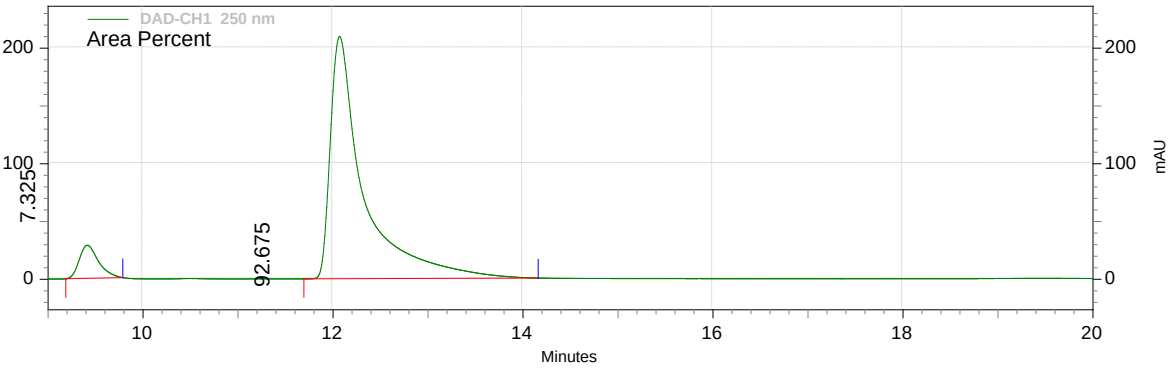
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-84BArac-COR--ADH-0.5-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 50 min without fc 0.5 ml per min.met



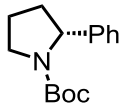
DAD-CH1 250 nm Results

Retention Time	Area	Area %
9.500	3593412	50.06
12.267	3584970	49.94
Totals	7178382	100.00

Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\pj3-84Echiral--ADH-0.5-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 50 min without fc 0.5 ml per min.met



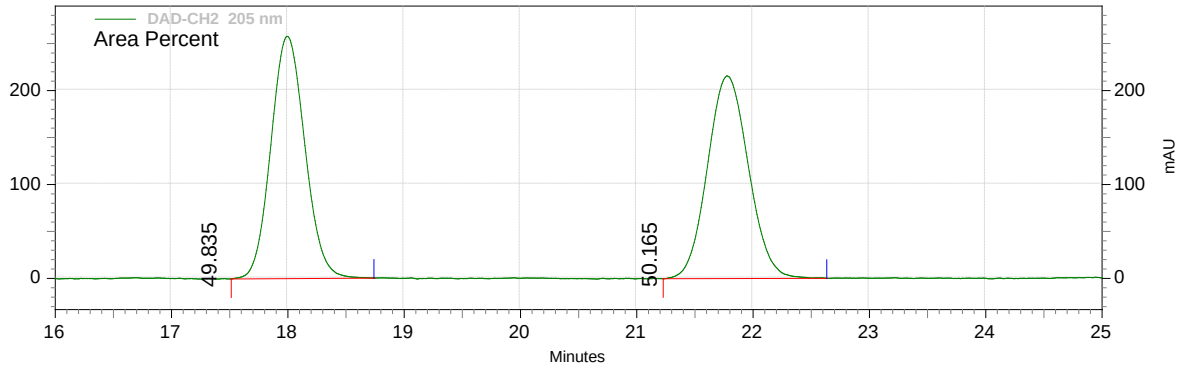
Retention Time	Area	Area %
9.413	1608020	7.33
12.067	20343985	92.67
Totals	21952005	100.00



6

Area % Report

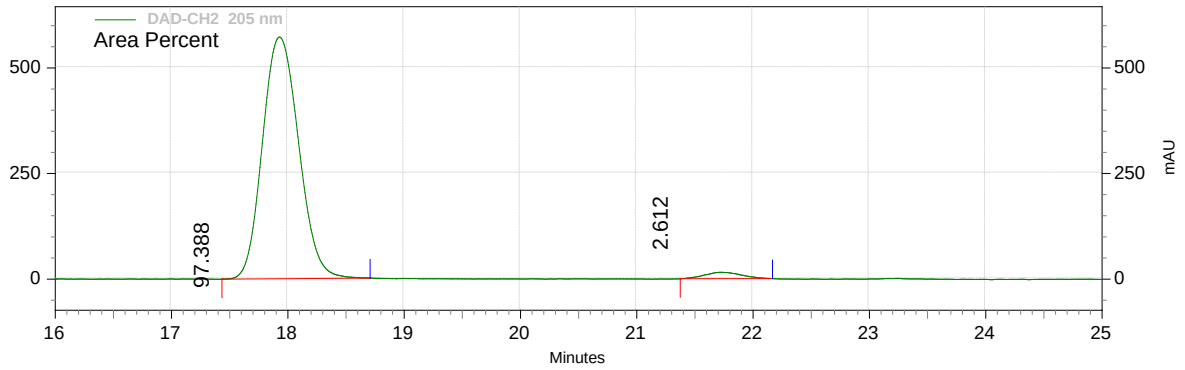
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\PPBoc-pure-IC-5-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met



DAD-CH2 205 nm Results

Retention Time	Area	Area %
17.993	20986575	49.83
21.780	21125754	50.17
Totals	42112329	100.00

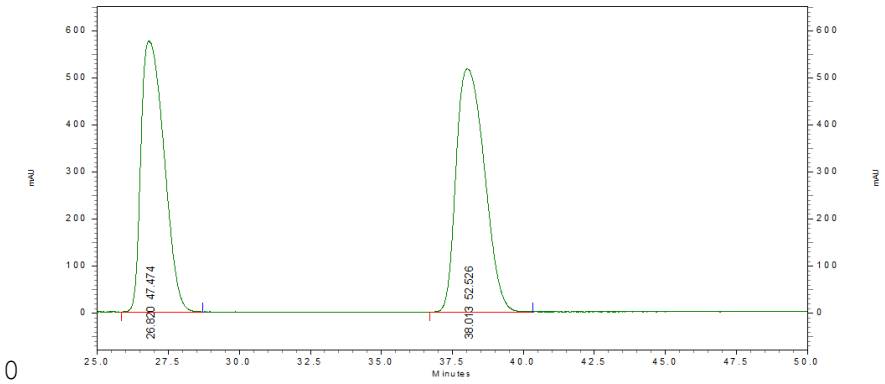
Data File: C:\EZChrom Elite\Enterprise\Projects\Default\Data\Pankaj\52B-IC-5-0.5
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met



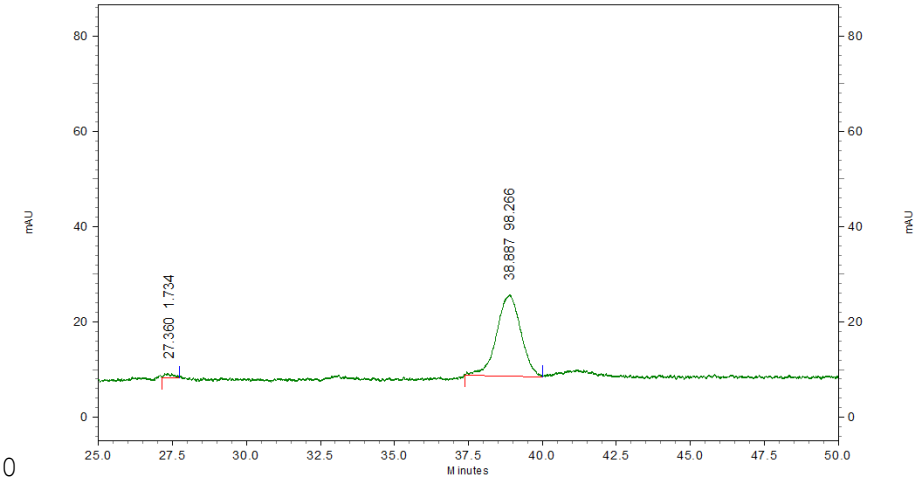
DAD-CH2 205 nm Results

Retention Time	Area	Area %
17.927	49458439	97.39
21.720	1326334	2.61
Totals	50784773	100.00

Datafile: C:\YuLabData\GangChen\Pankaj112Chiral-3.dat Method:
C:\YuLabData\wqf\method\2% 0.5 90 min.met



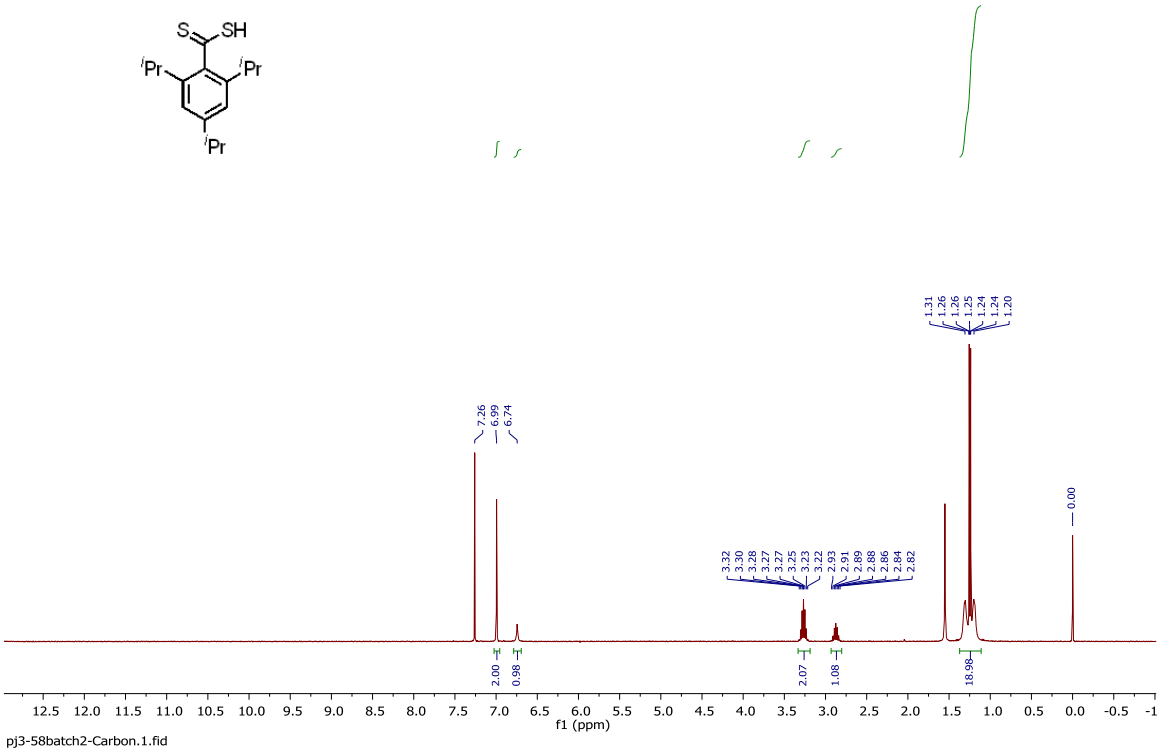
Name	RT (min)	Area Percent
Sample Data	26.820	47.474
	38.013	52.526



Name	RT (min)	Conc (ng)
Sample Data	27.360	1.734
	38.887	98.266

^{1}H and ^{13}CNMR Spectra

pj3-58 batch2.1.fid



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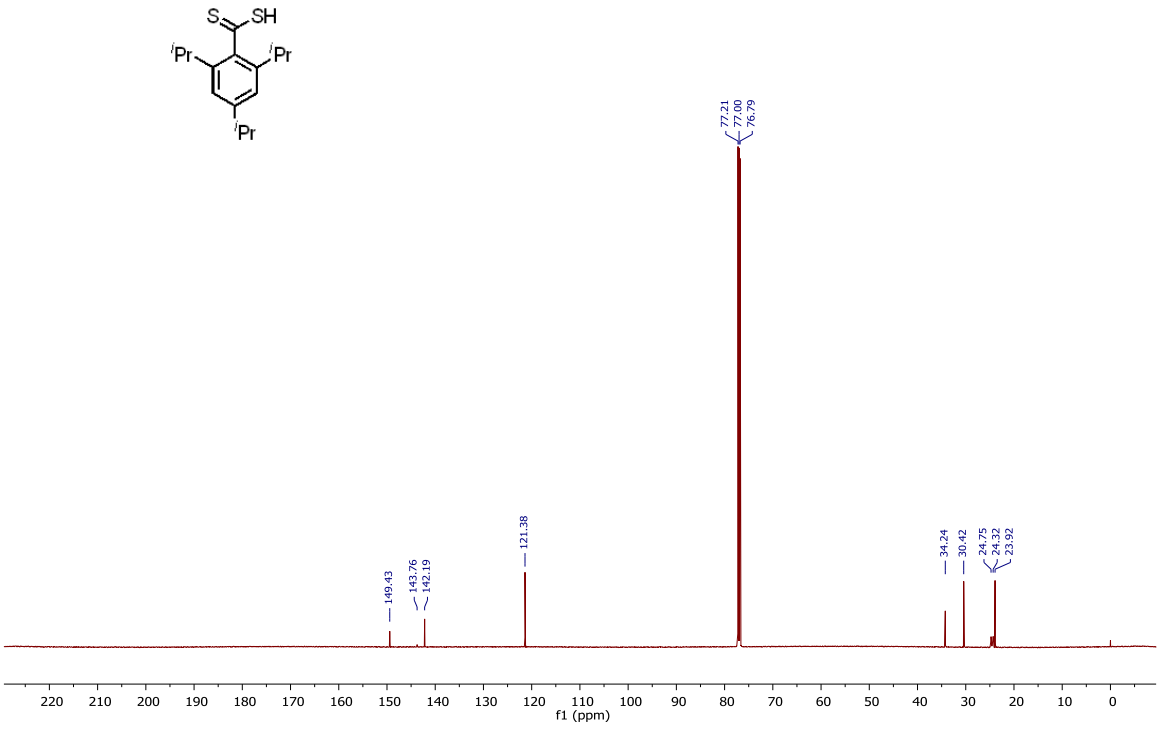

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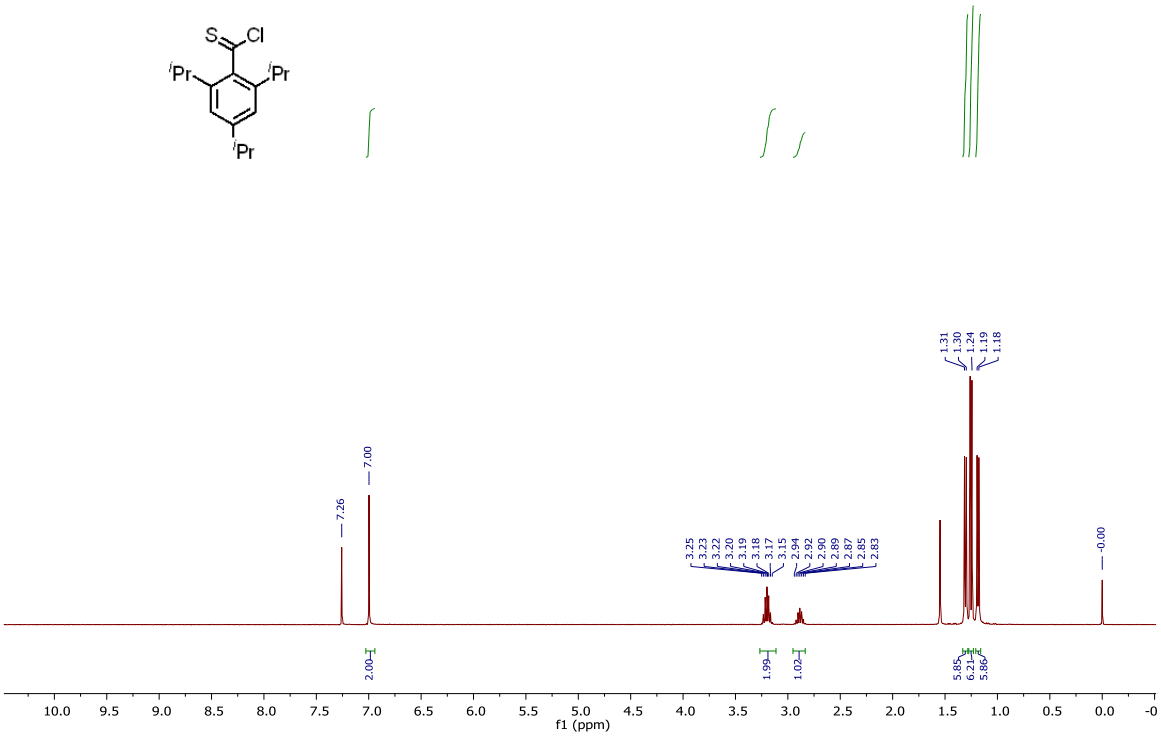

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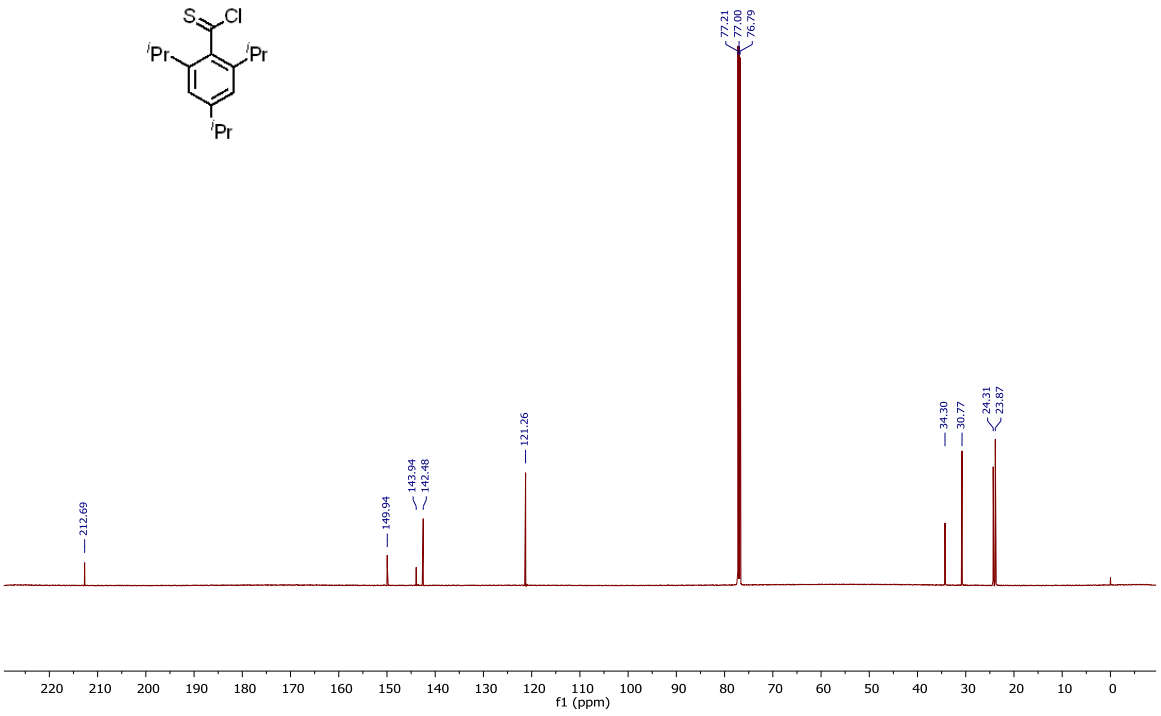
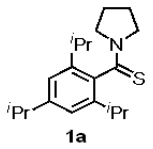


pj-pyrrolidine-SM-paper.1.fid



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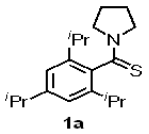

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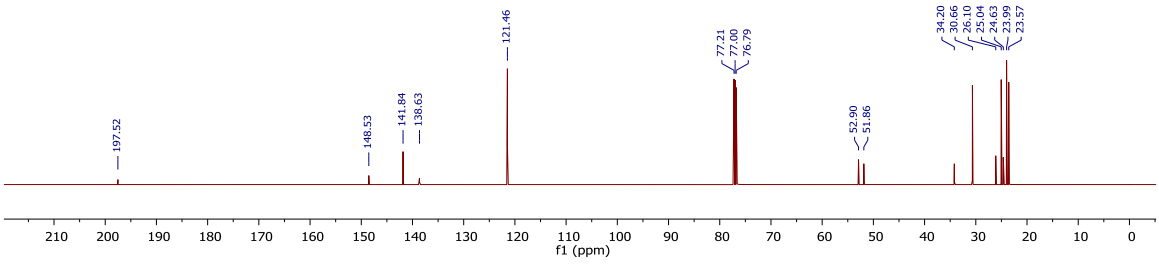

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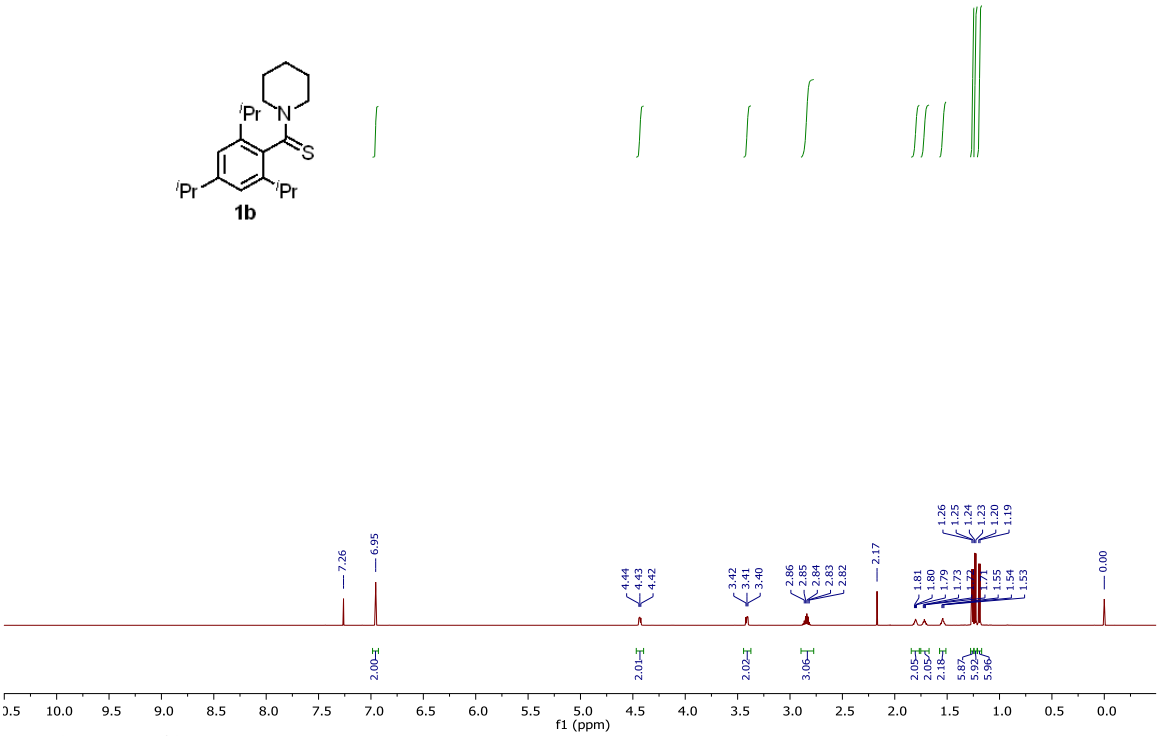

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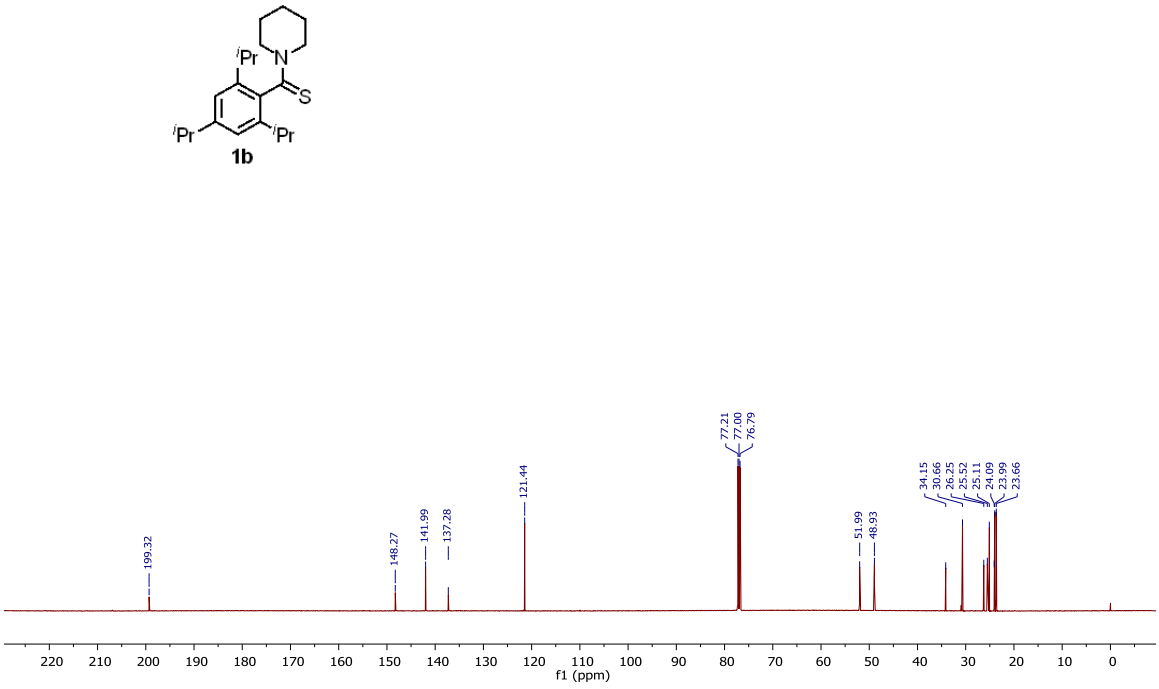

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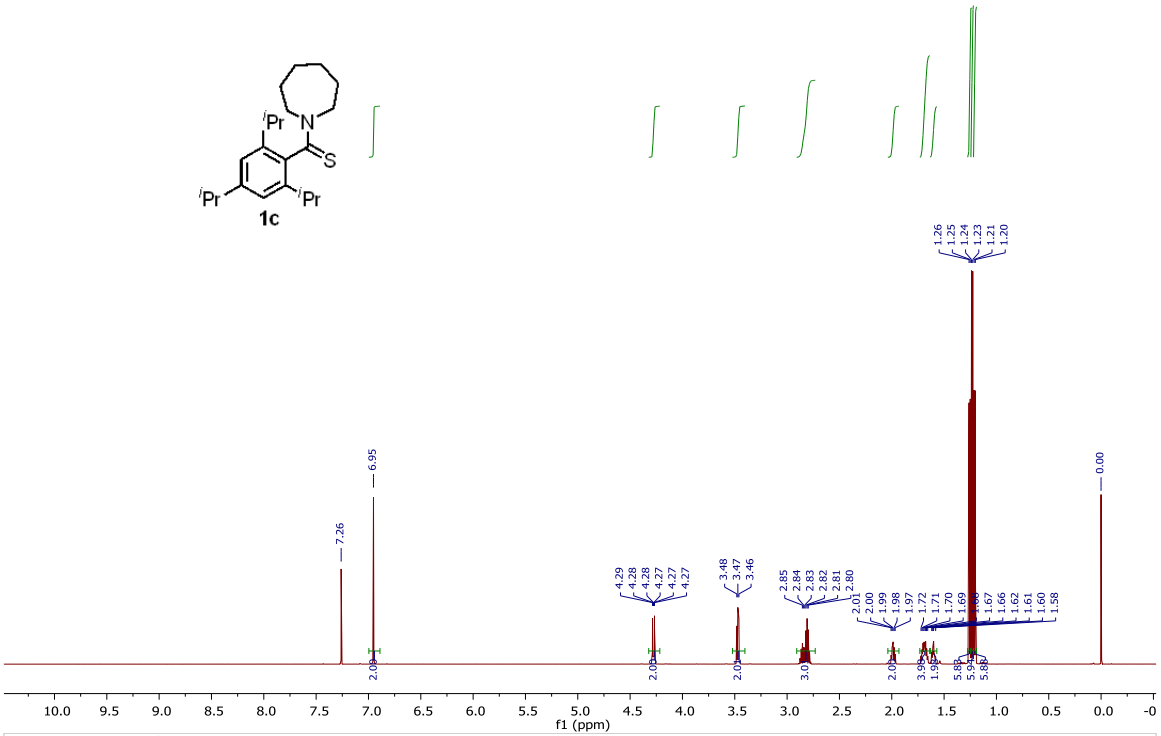

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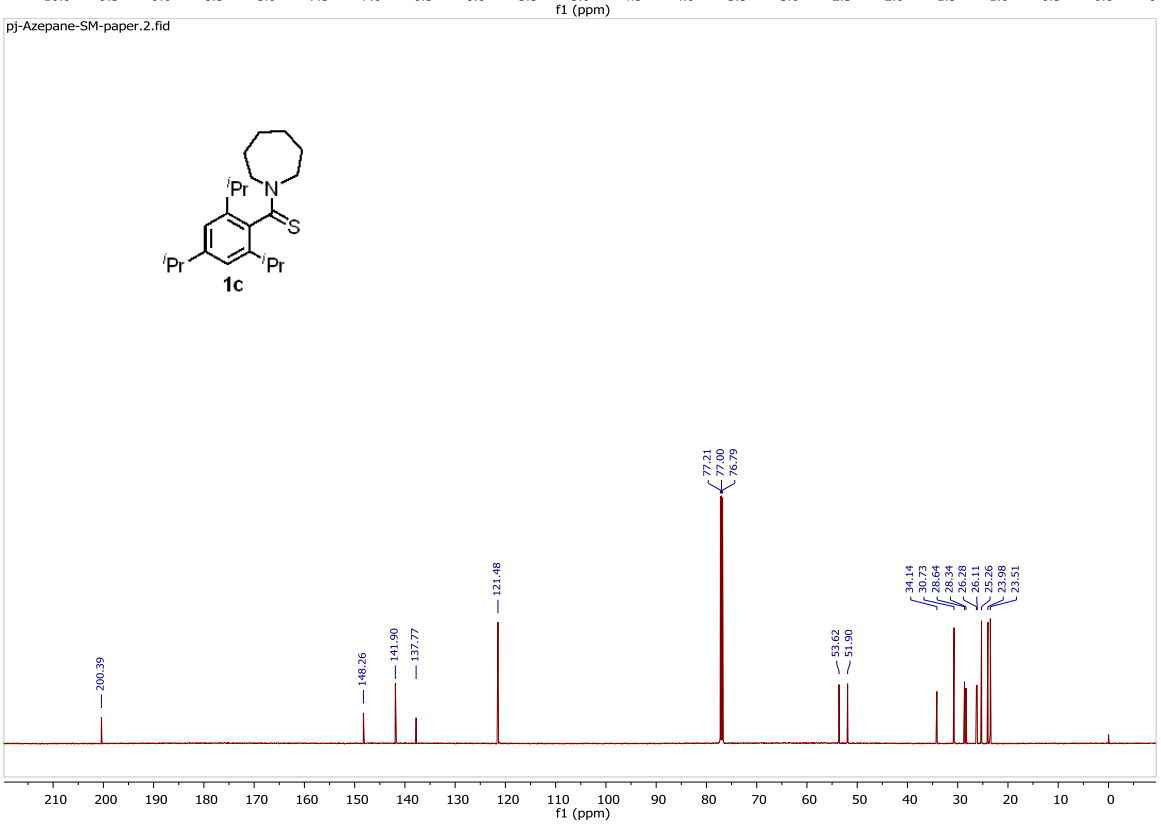

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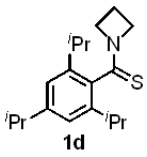

1d

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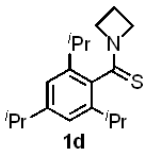

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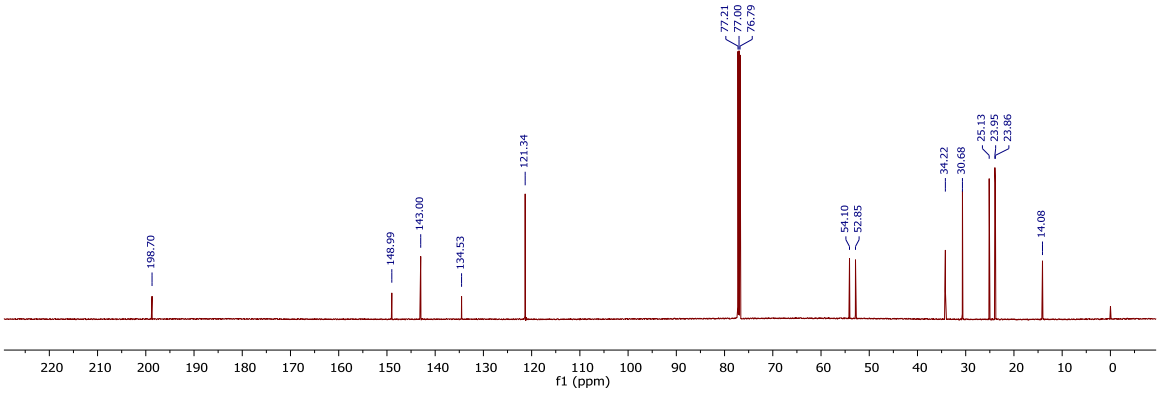
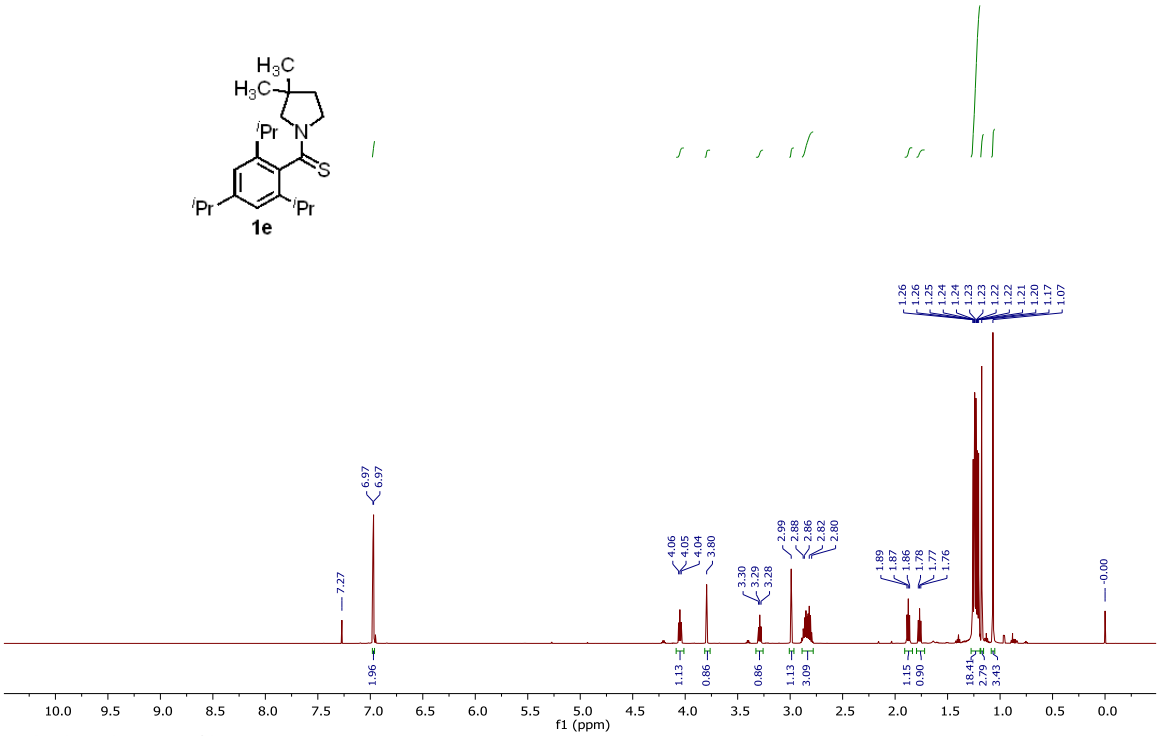


pj3-dimethypyrroli-SM-paper.1.fid



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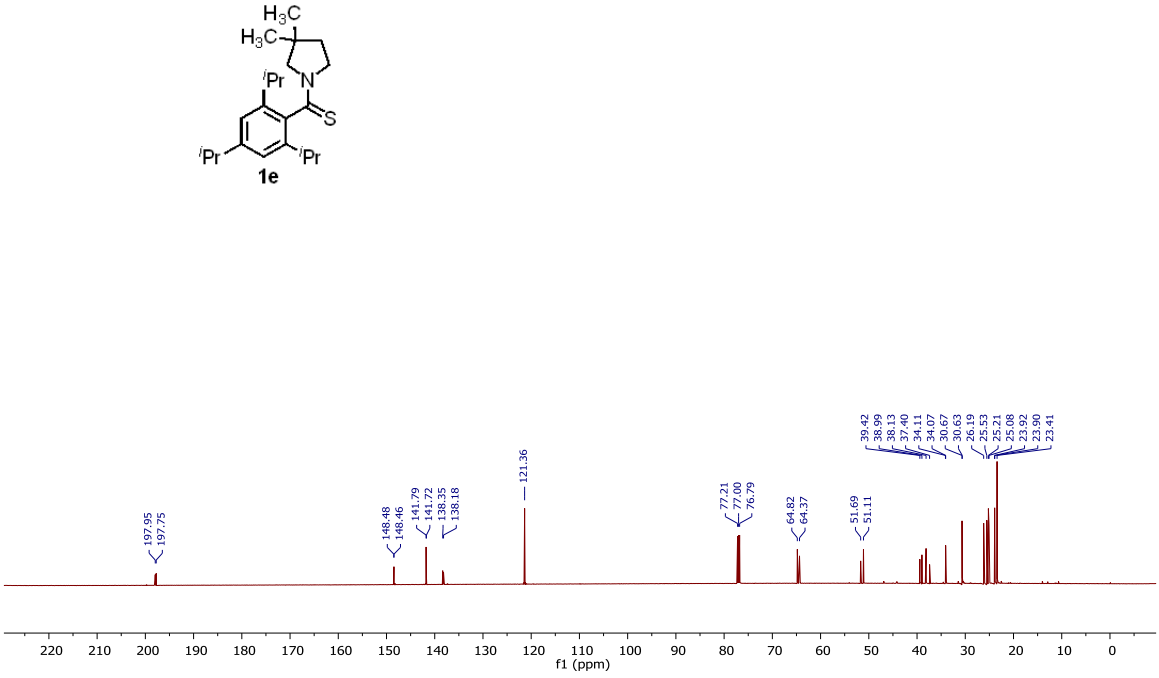

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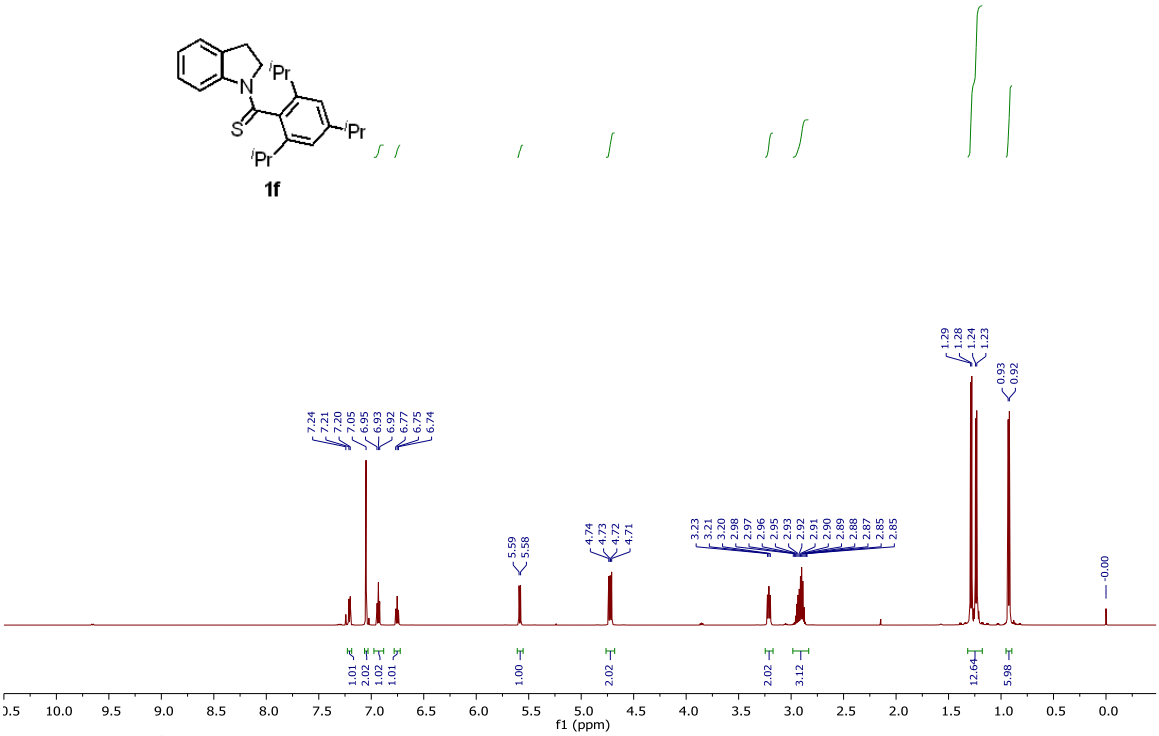

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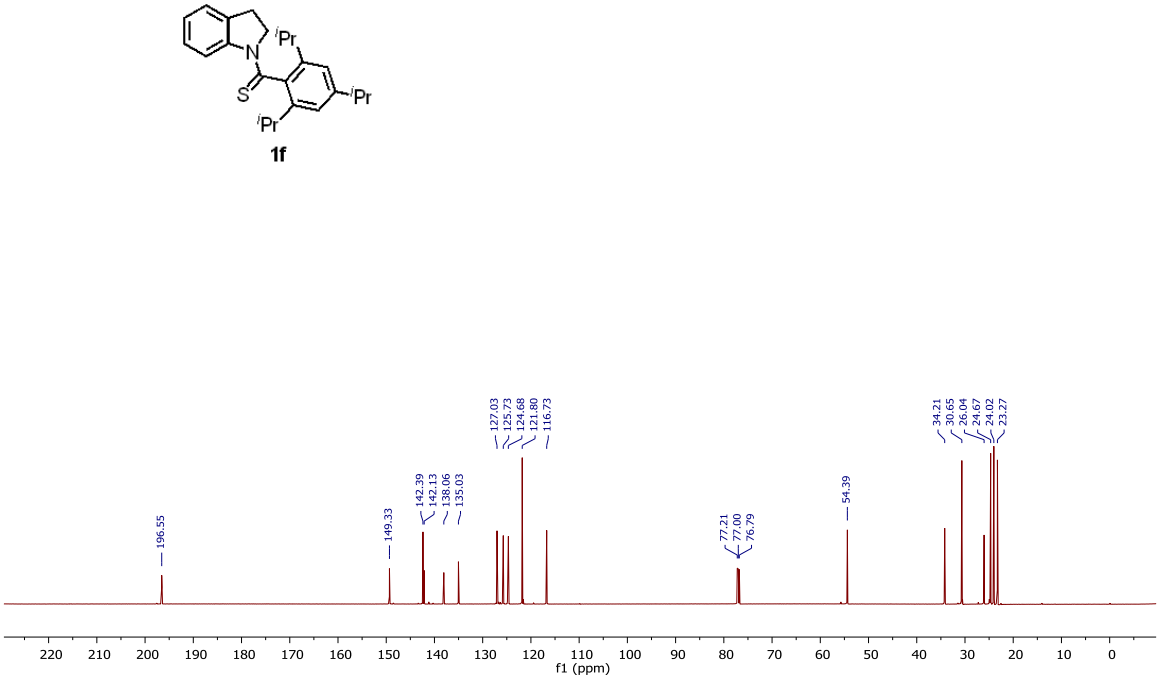

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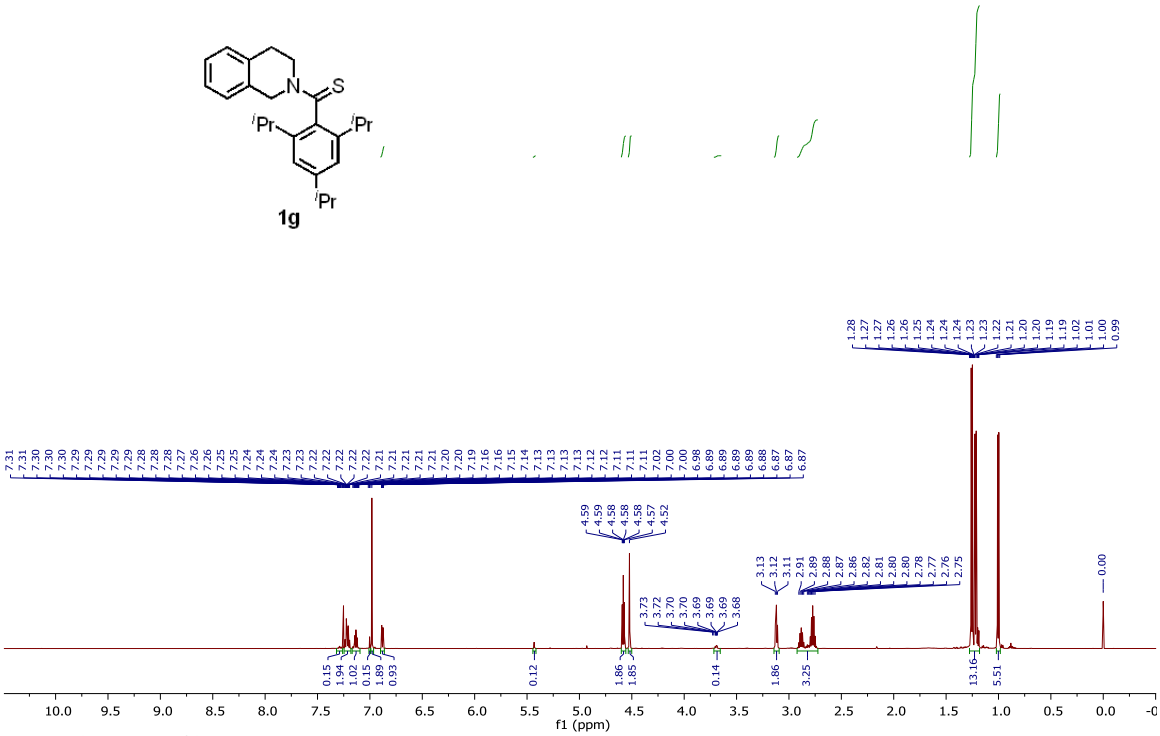

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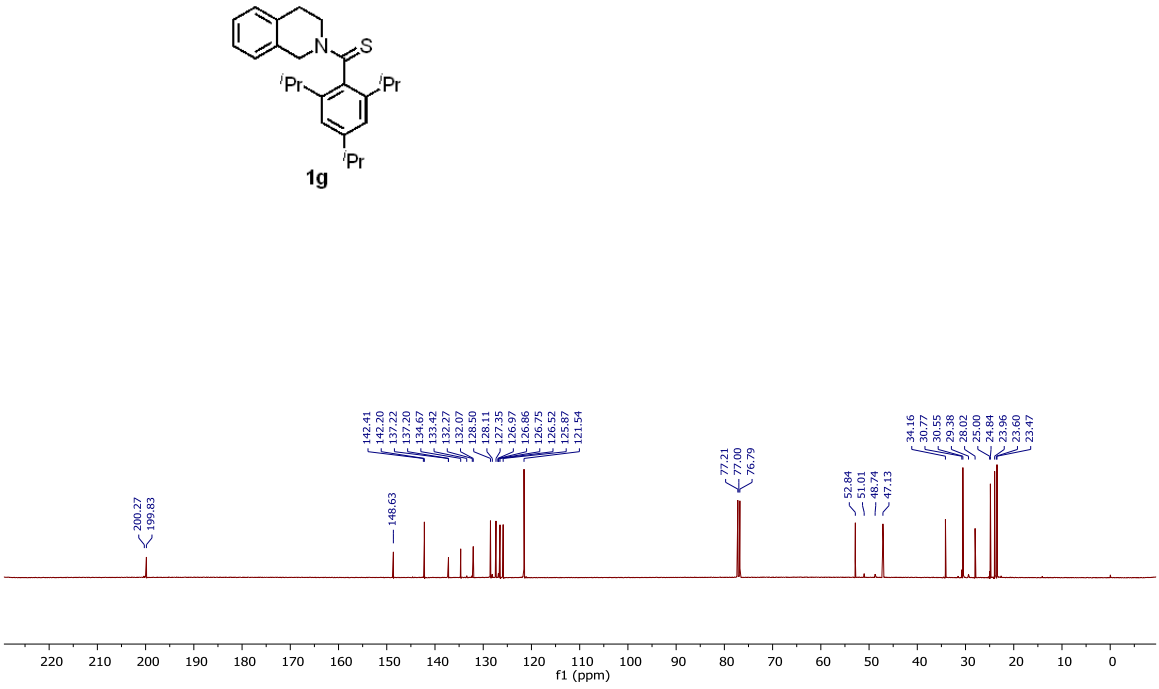
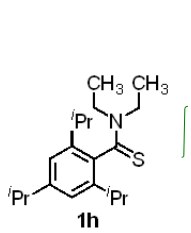
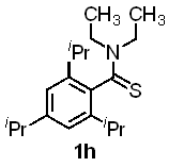


pj-diethylcorrect-SM-paper.1.fid



1h

pj-diethylcorrect-SM-paper.2.fid



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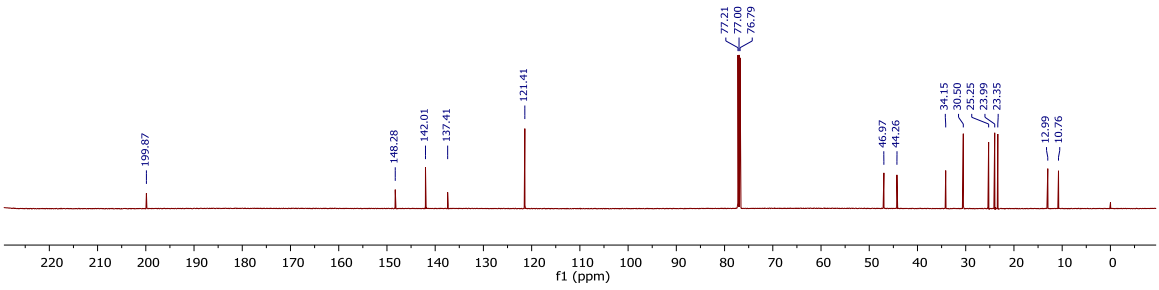
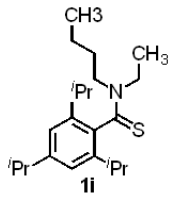


pj-ethylButyl-SM-paper.1.fid



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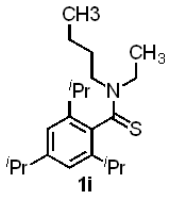

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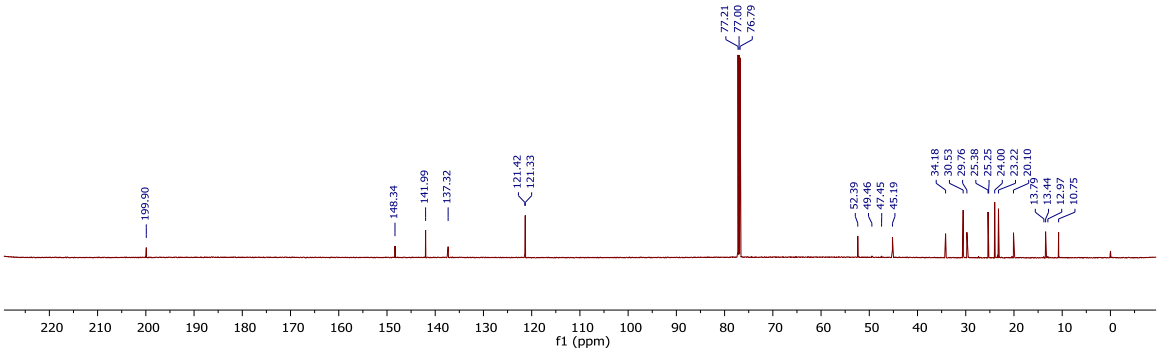
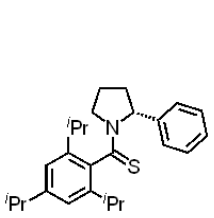
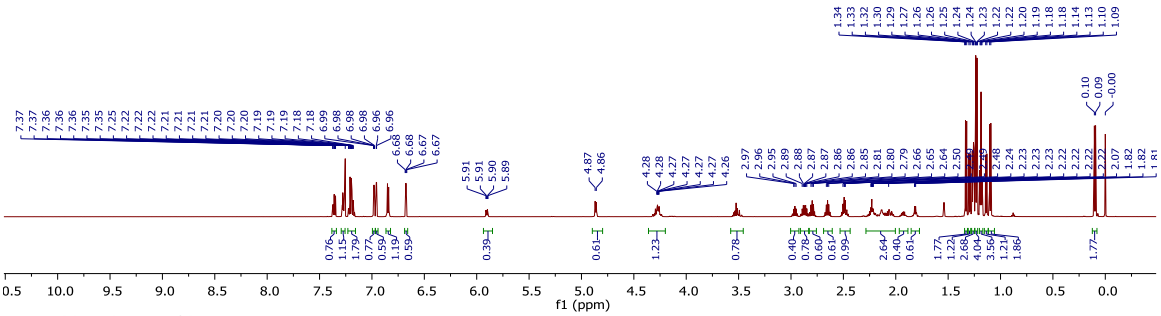


pj3-pyrrolidine-pdt-paper.1.fid



2a



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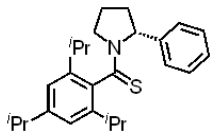
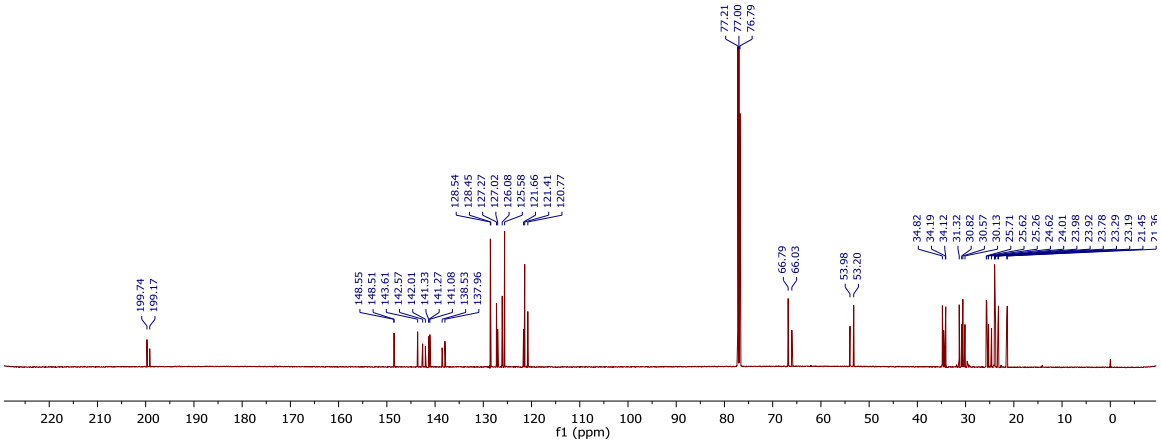


2a



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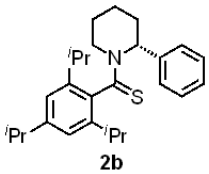
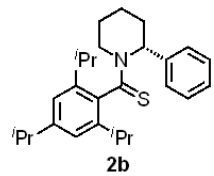
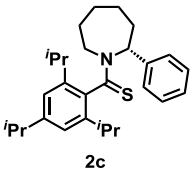


2b

pj3-piperidine-pdtnew-paper.2.fid



2b



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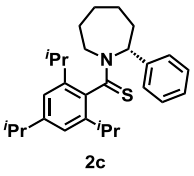

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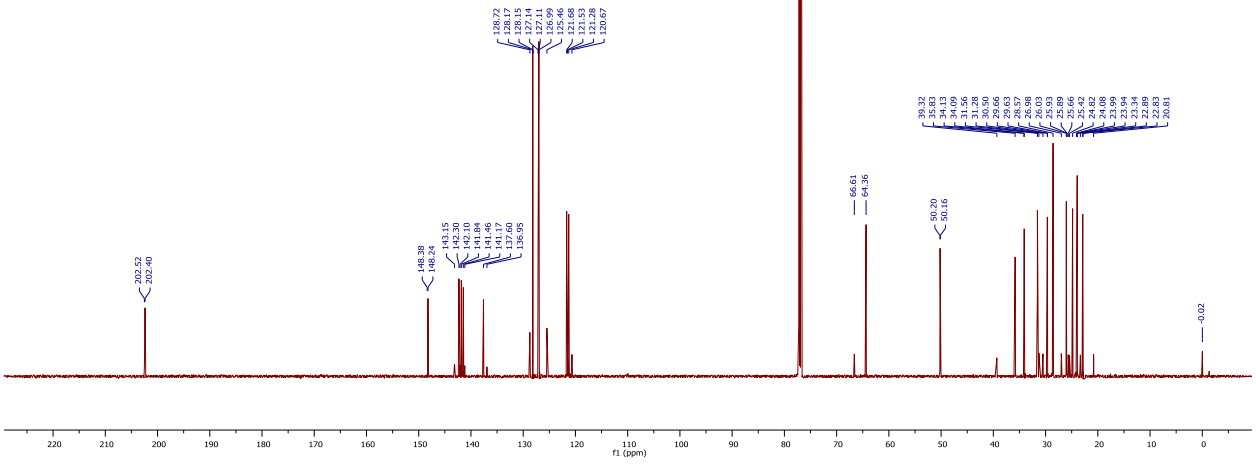

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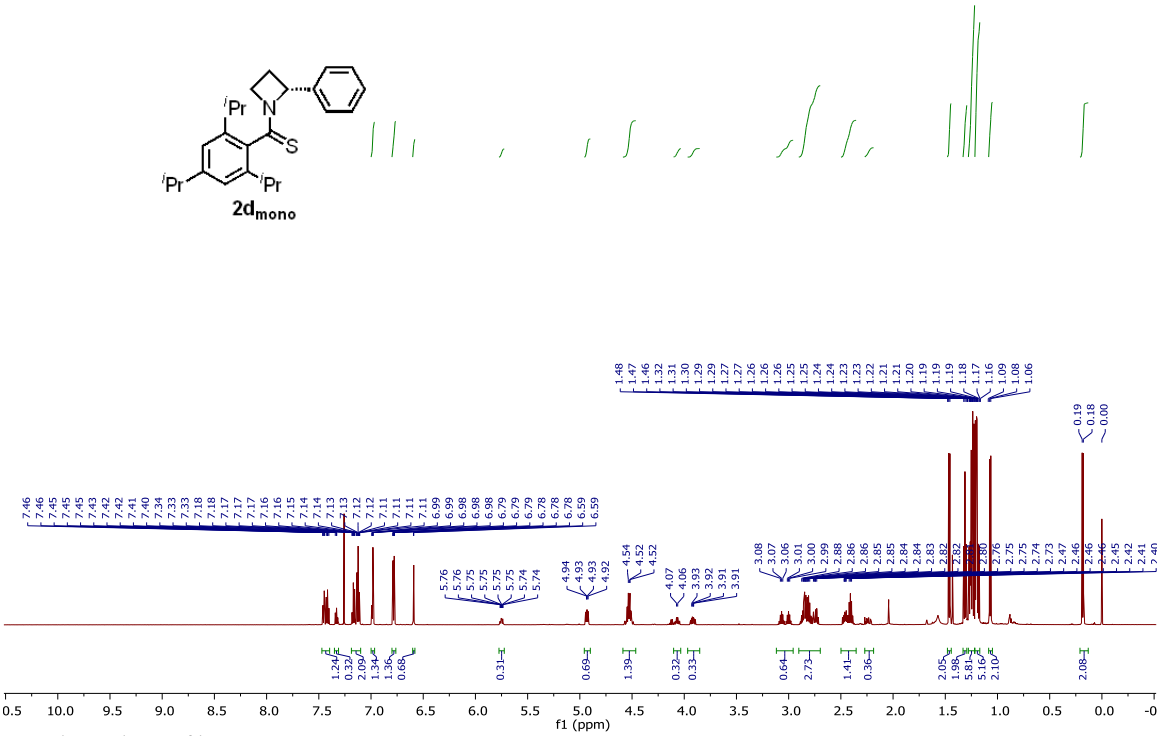

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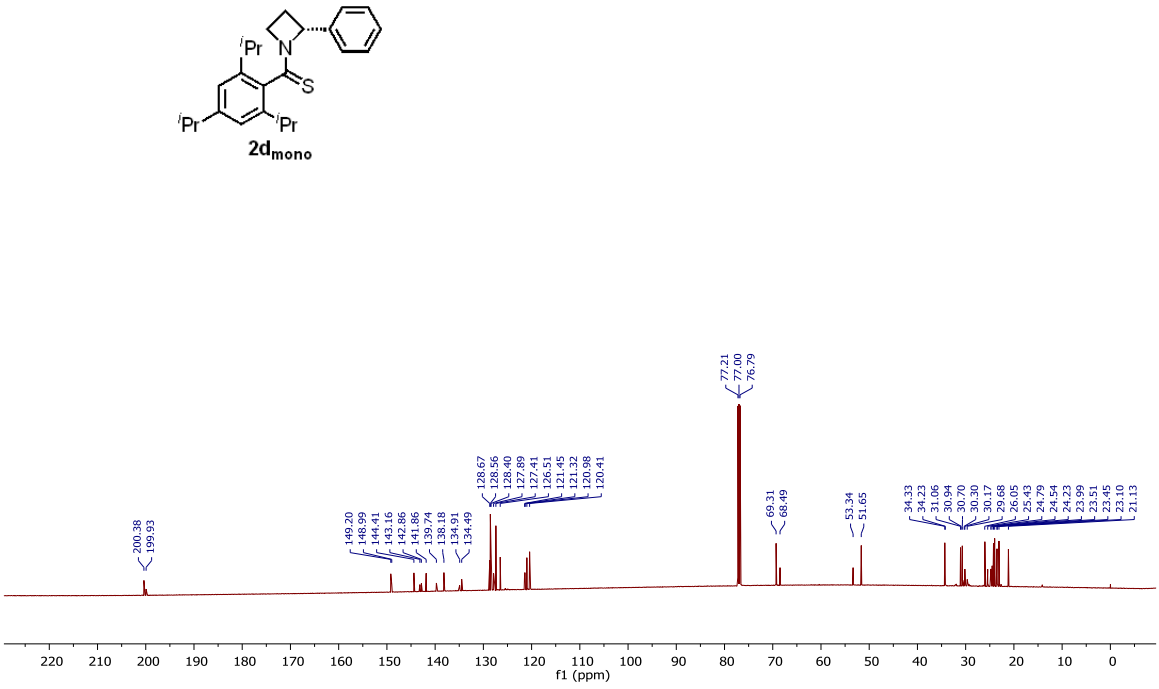

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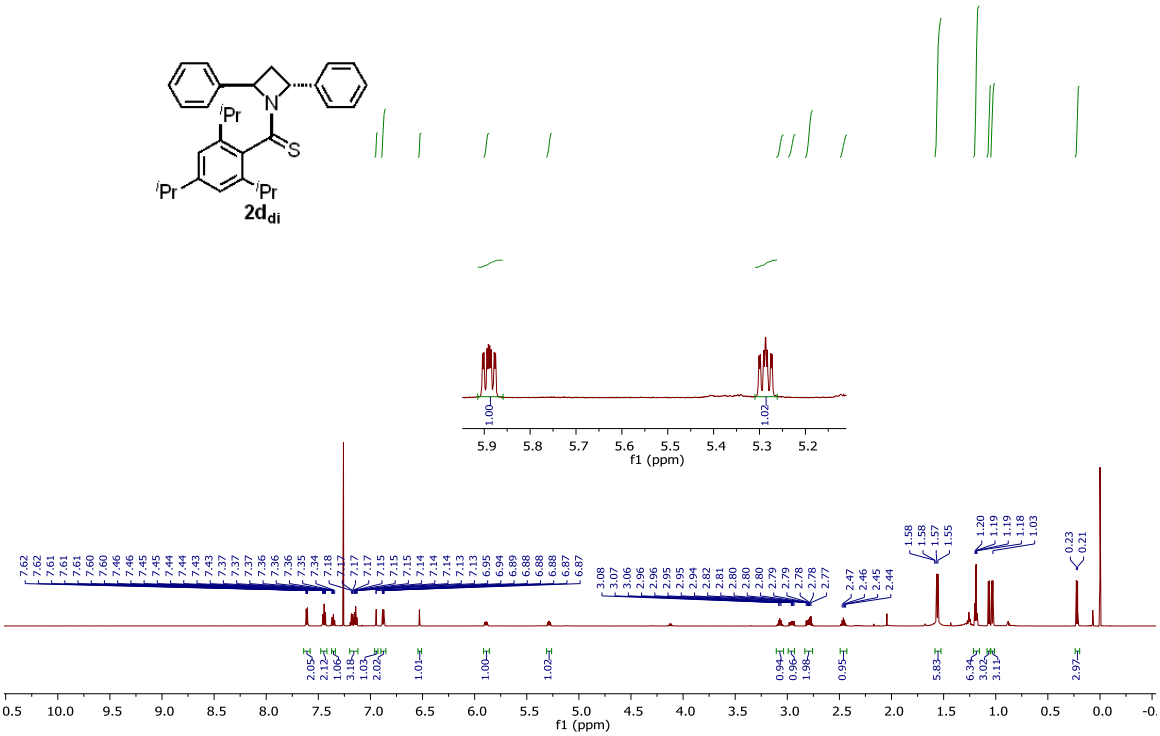

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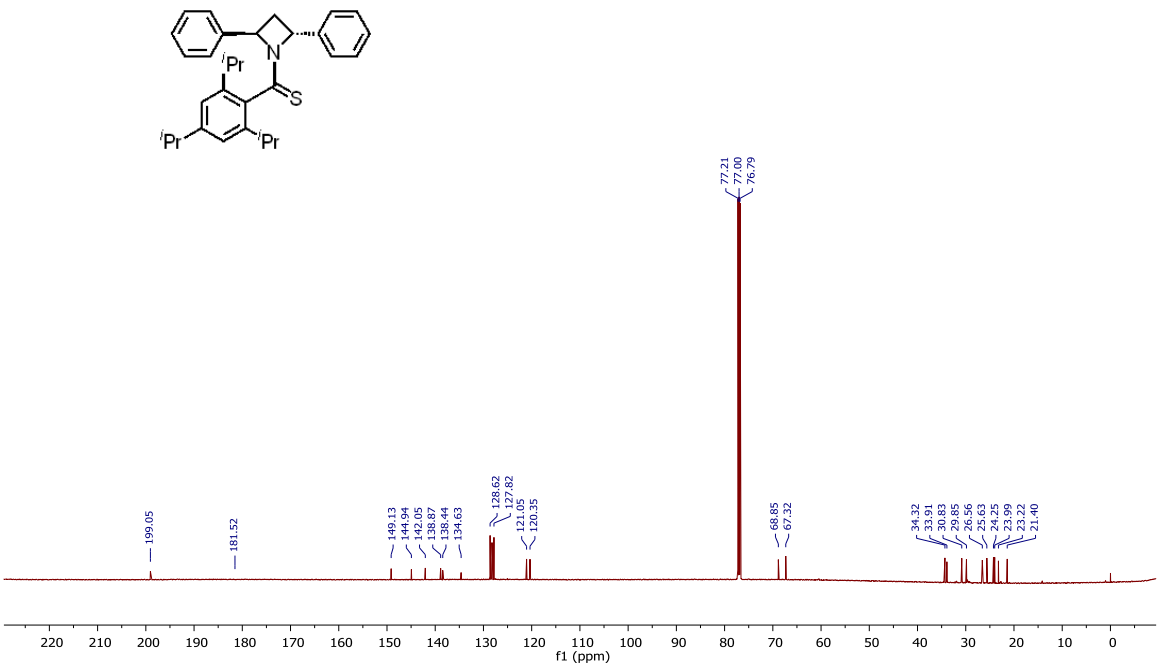

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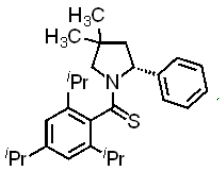

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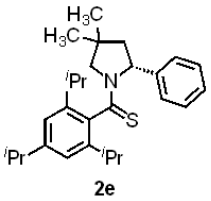
pj3-X1-48-1.2.fid



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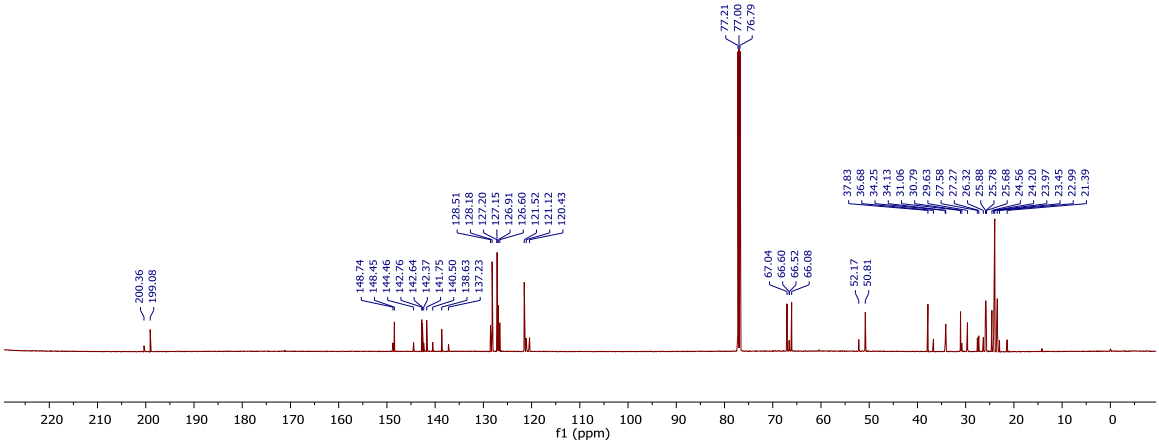

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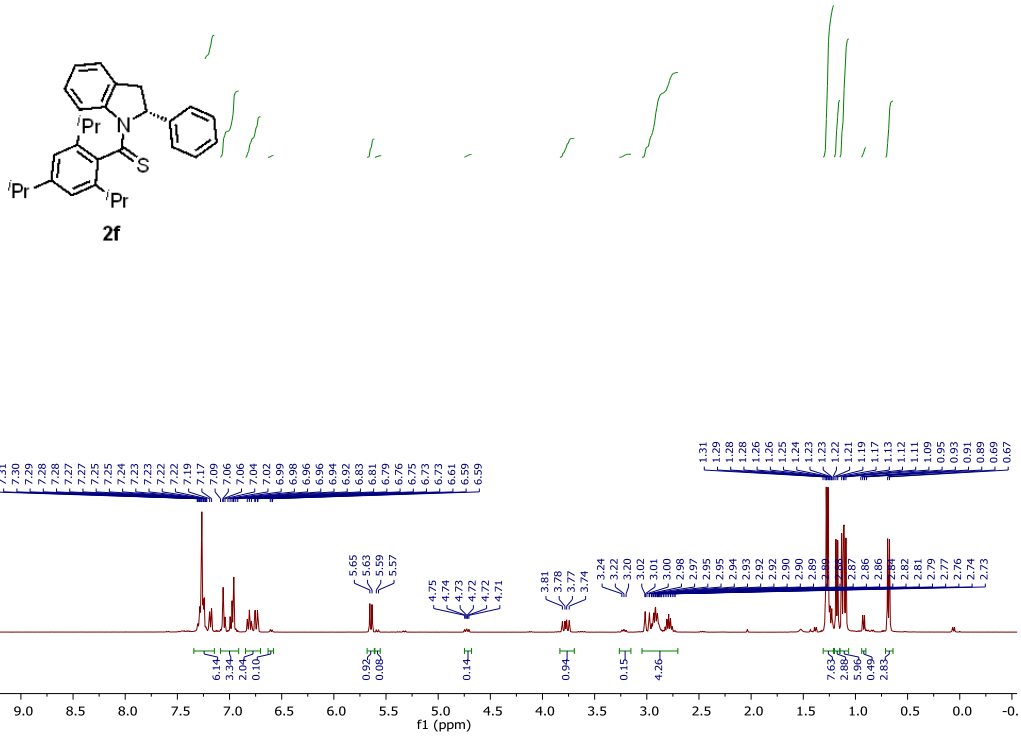

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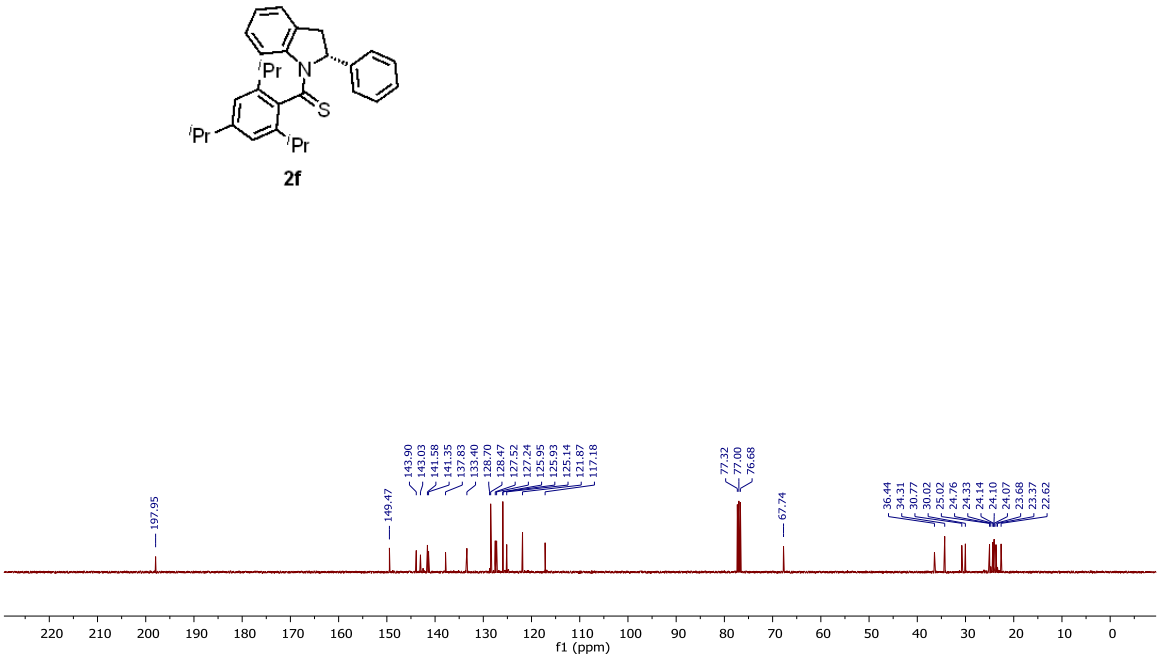

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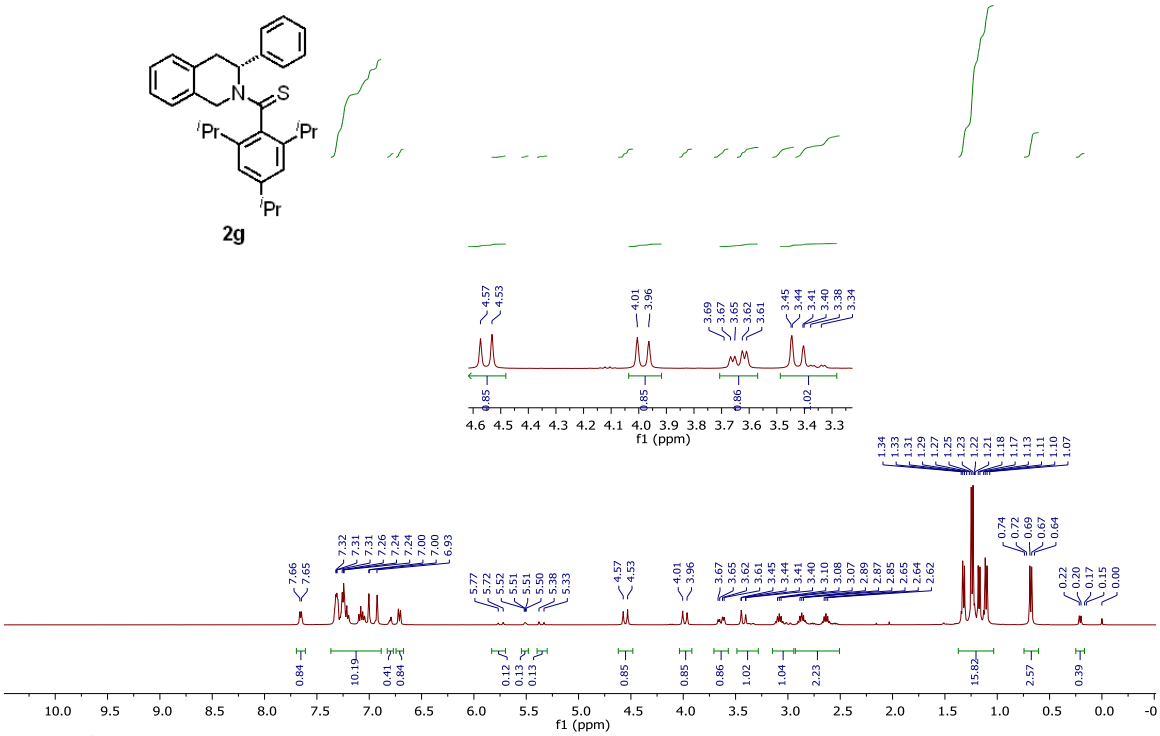

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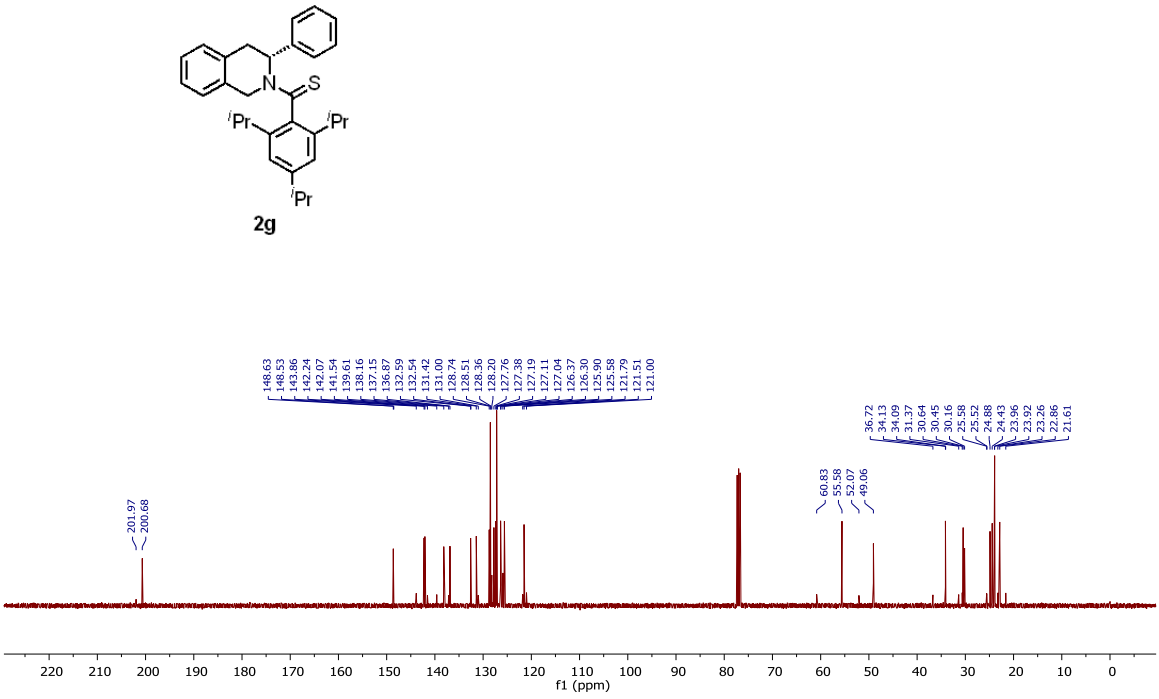

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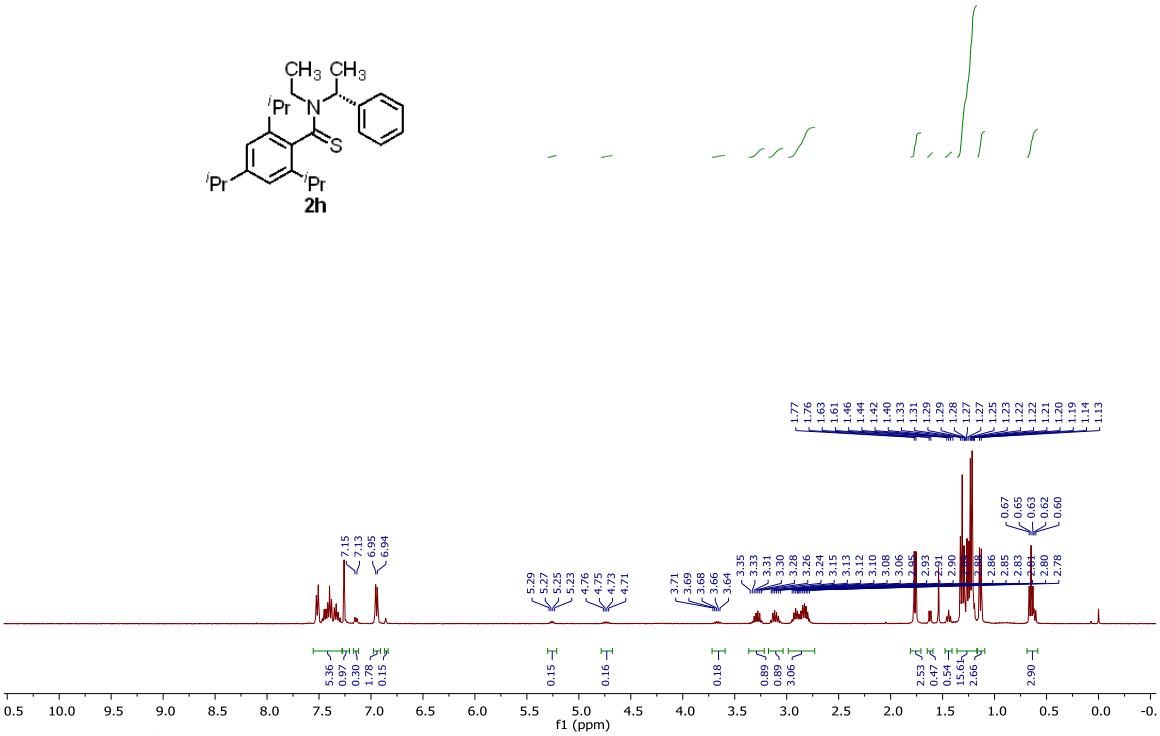
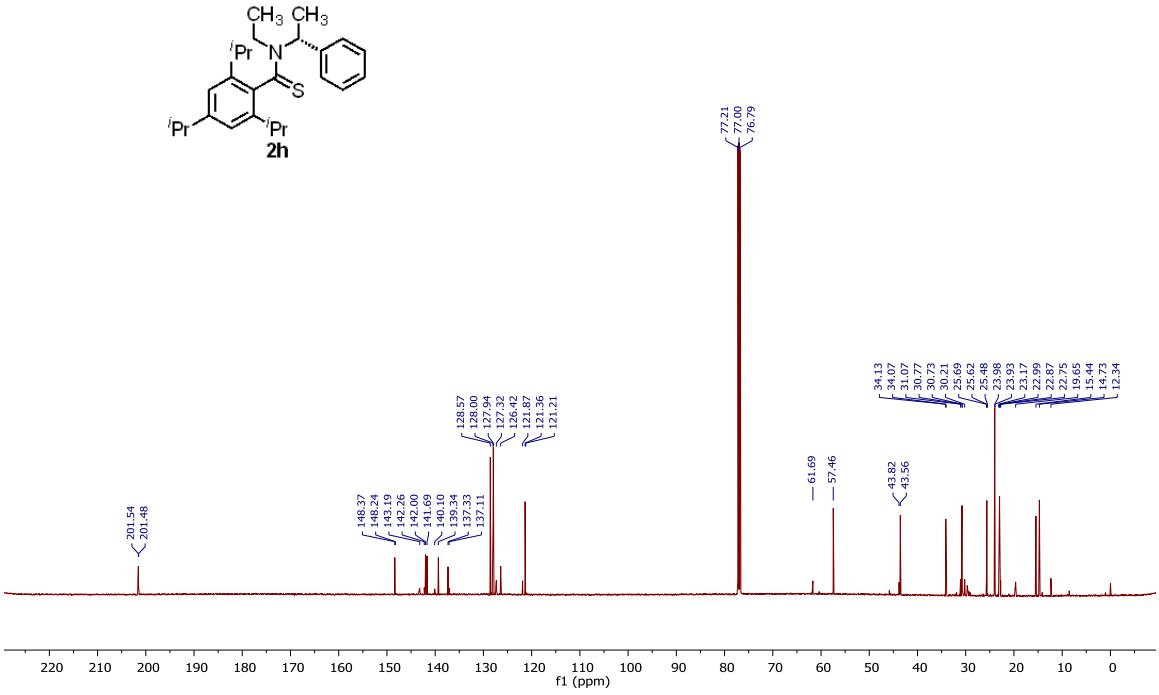
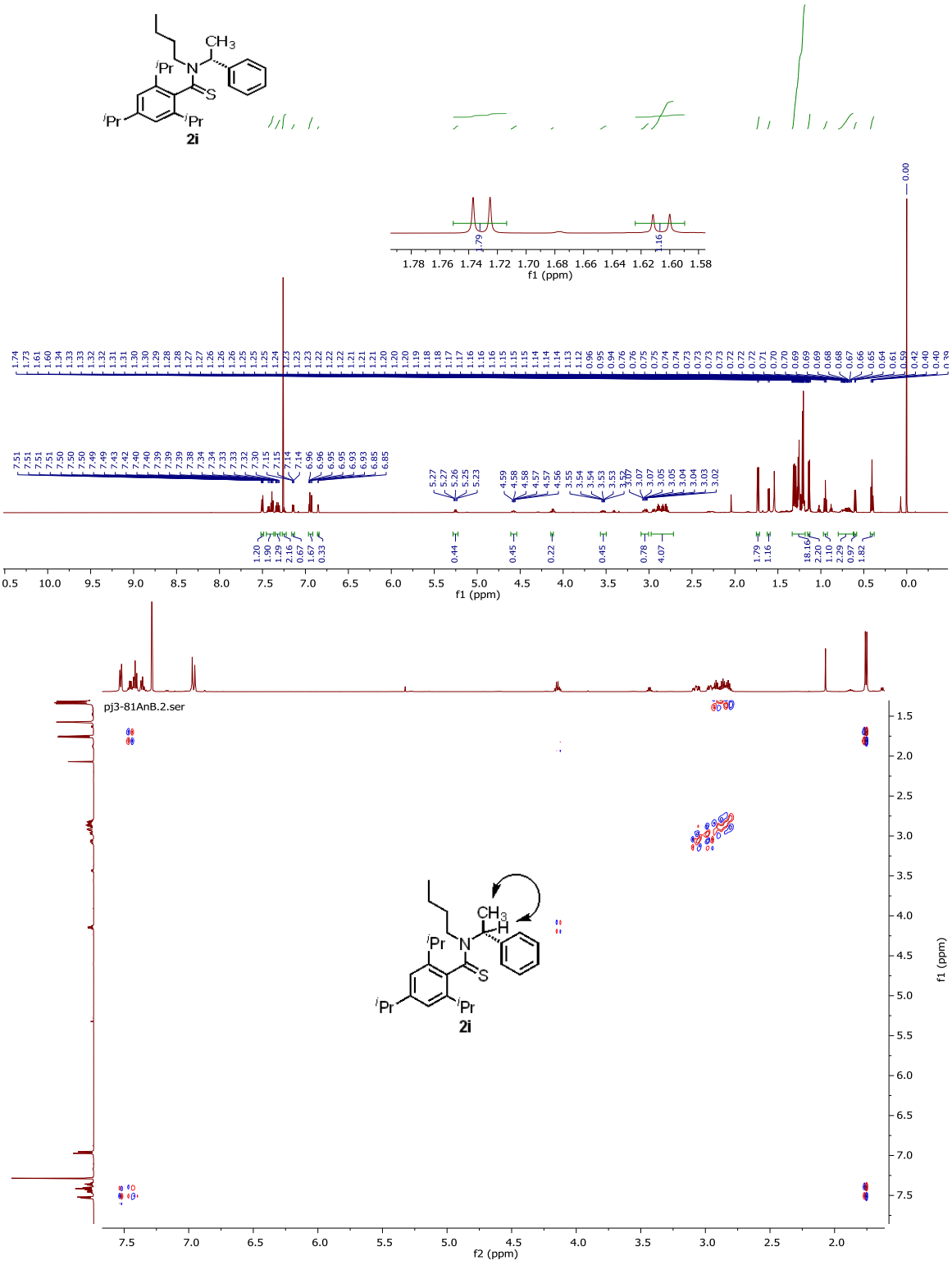


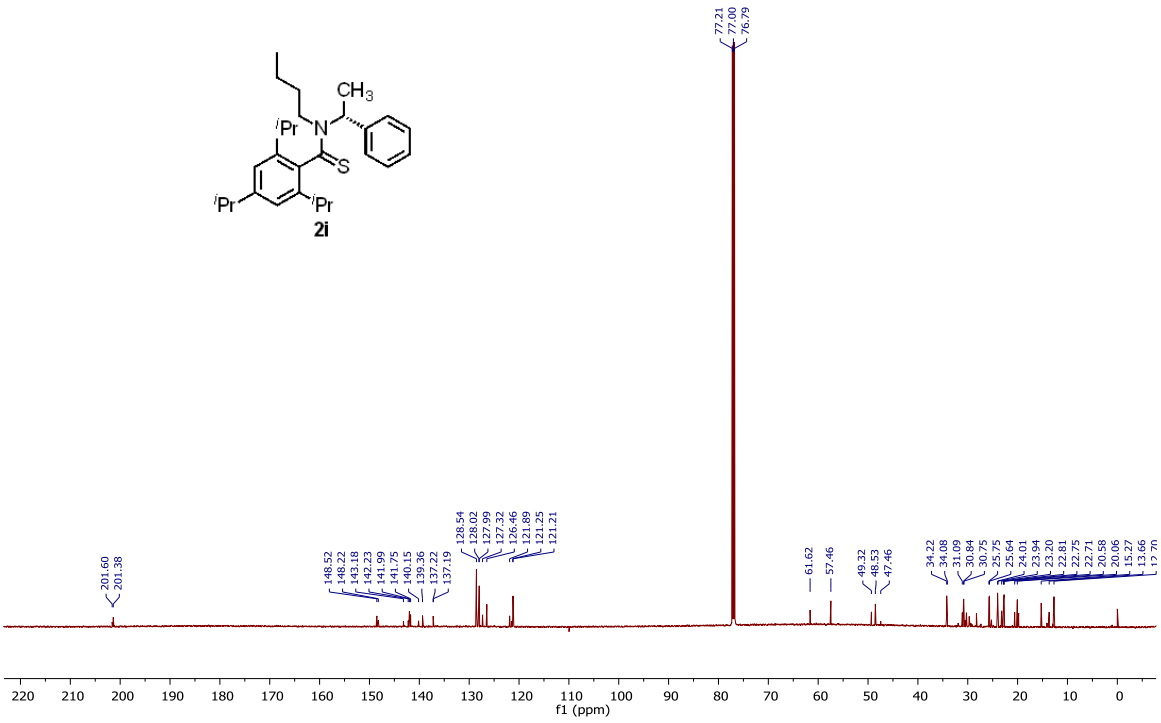
pj3-diethyl-pdt-paper.2.fid

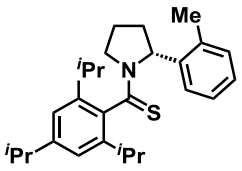


pj3-ethylbutyl-pdt-paper.1.fid



pj3-ethylbutyl-pdt-paper.2.fid





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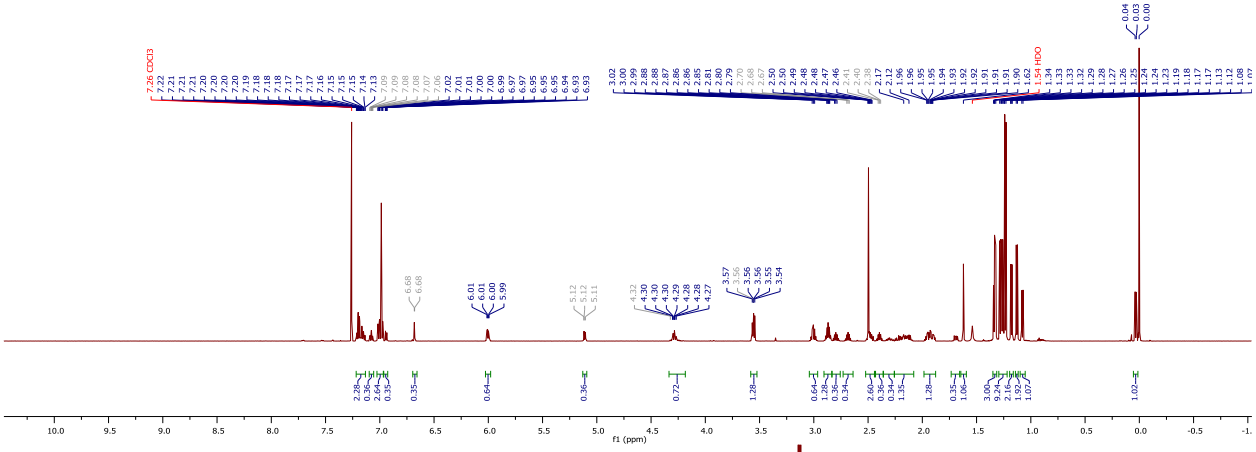

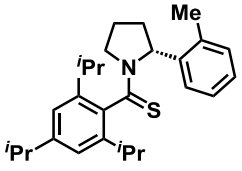

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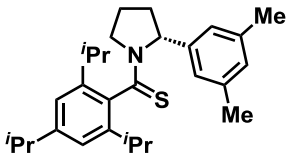
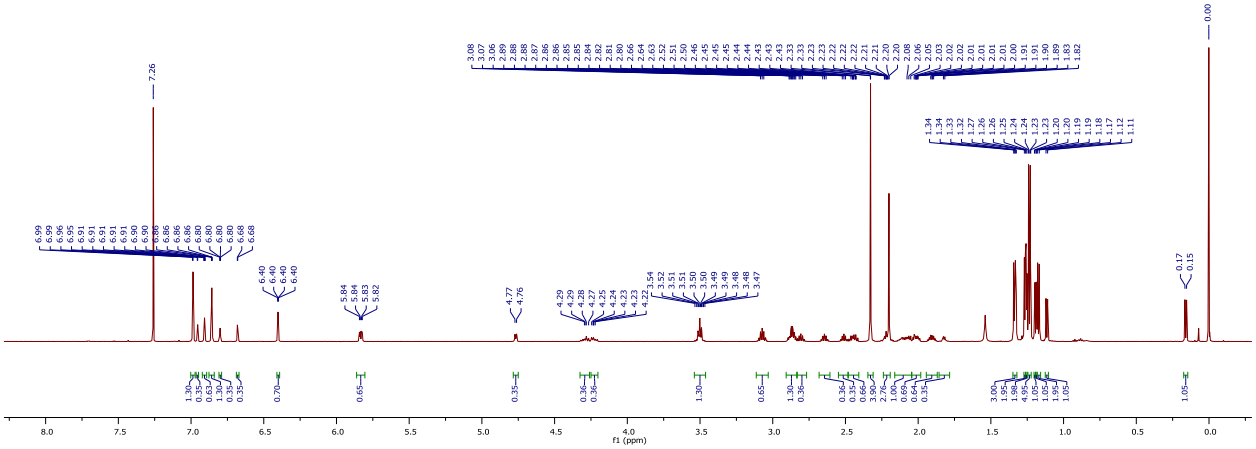
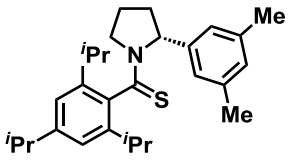

Me
iPr
N
S
Me
iPr
iPr

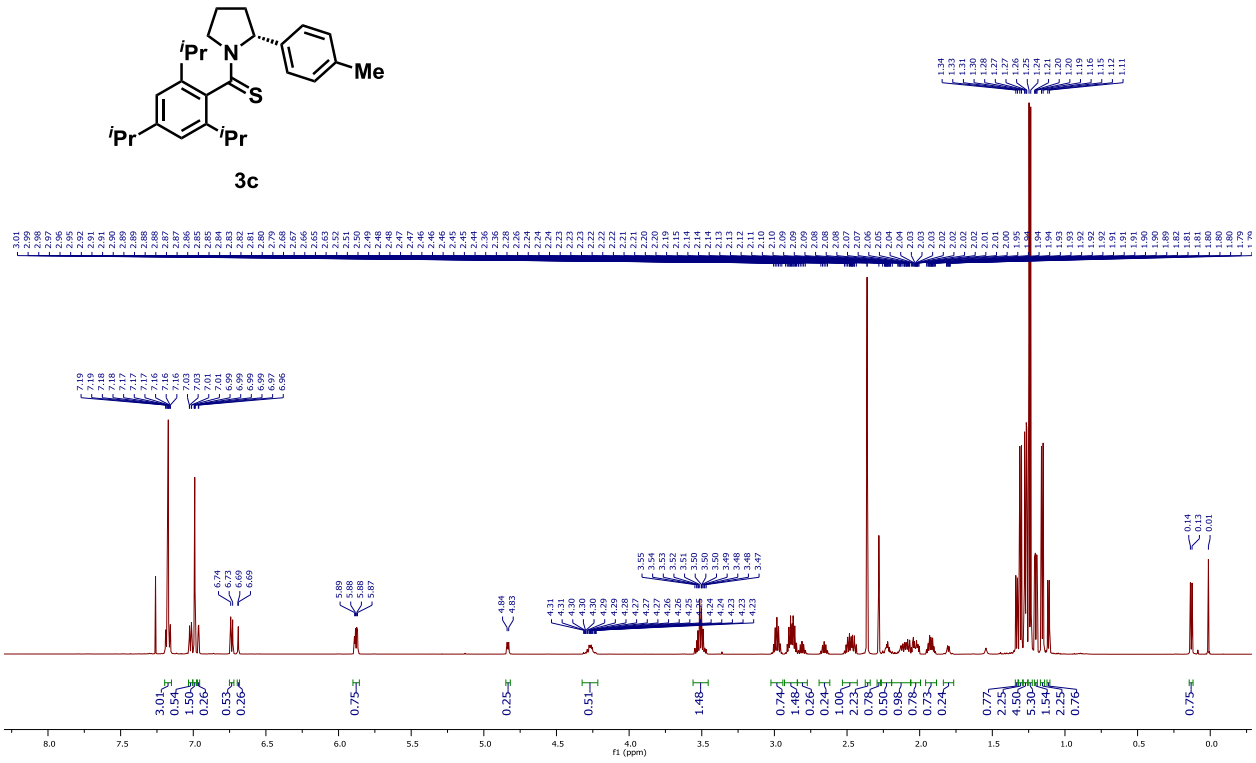
3b

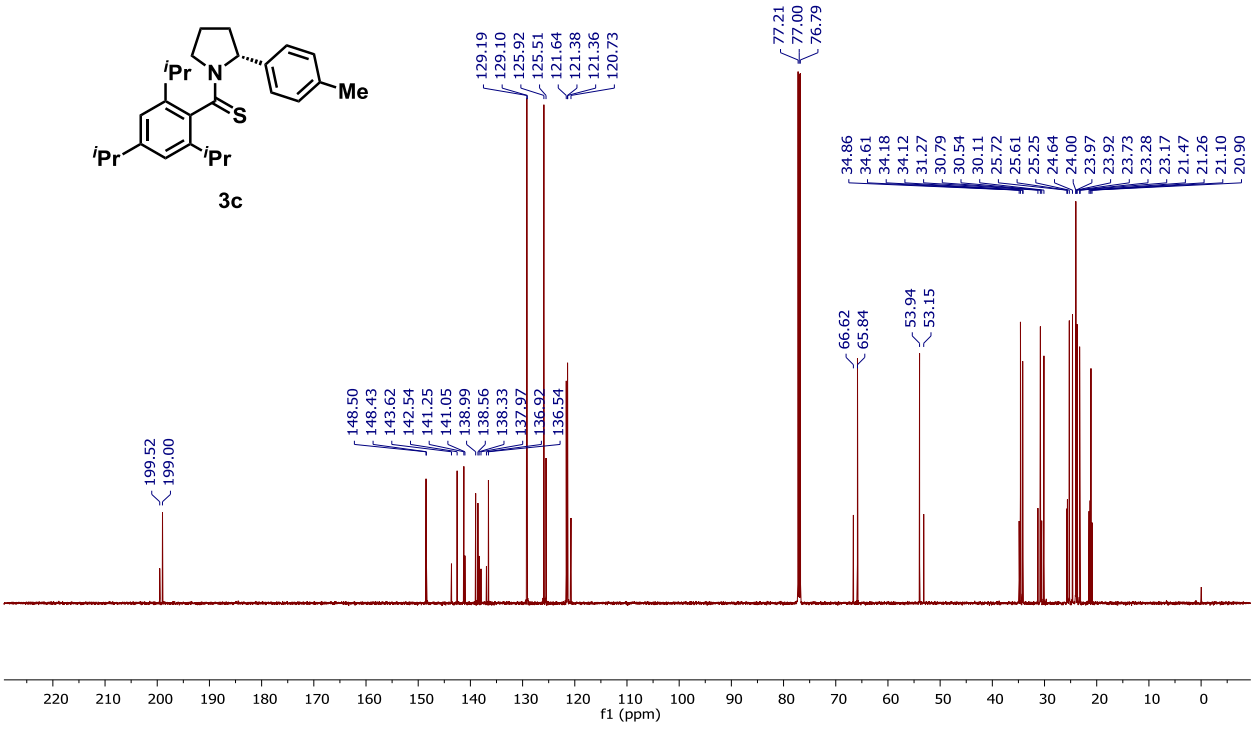

7.26
0.00
f1 (ppm)

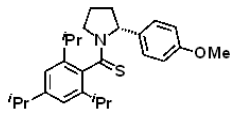

Me
iPr
N
S
Me
iPr
iPr

3b

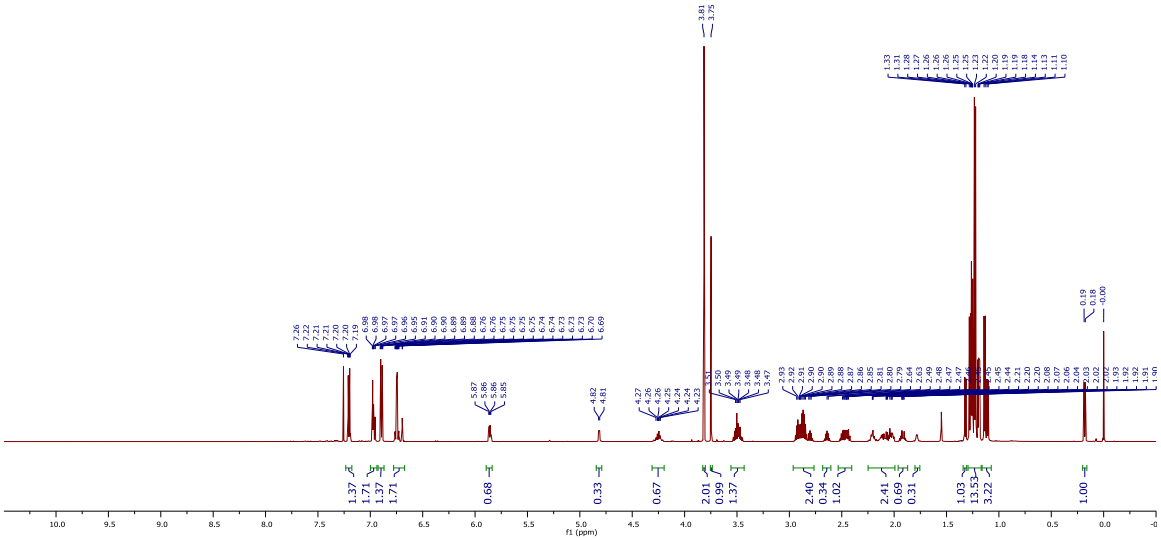
77.21
77.00
76.79
f1 (ppm)
f1 (ppm)

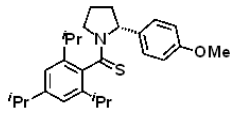

iPr
N
S
Me
iPr
iPr
3c
f1 (ppm)


iPr
N
S
Me
iPr
iPr
3c
f1 (ppm)



3d





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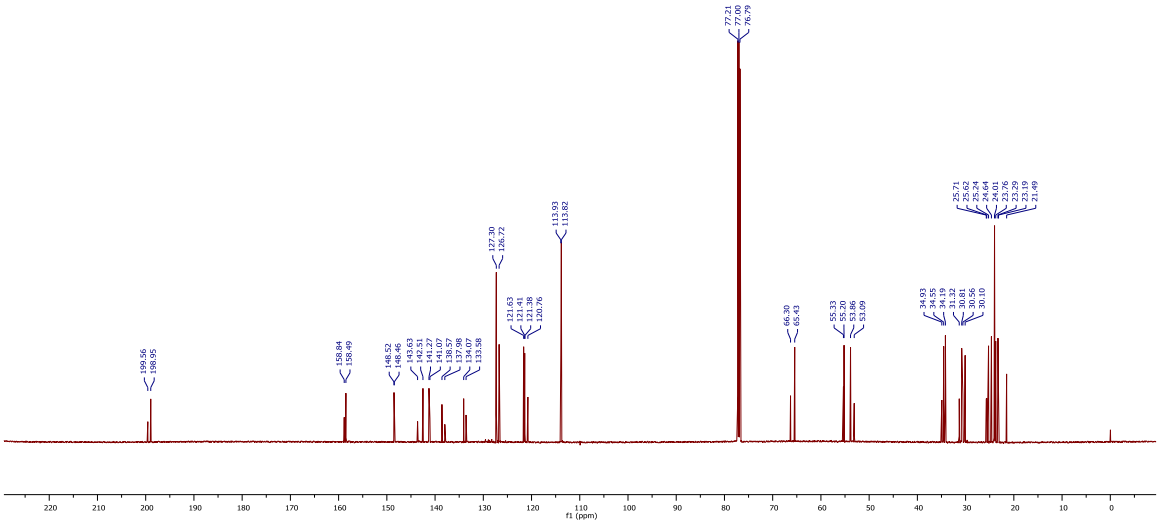
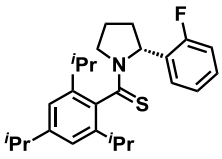
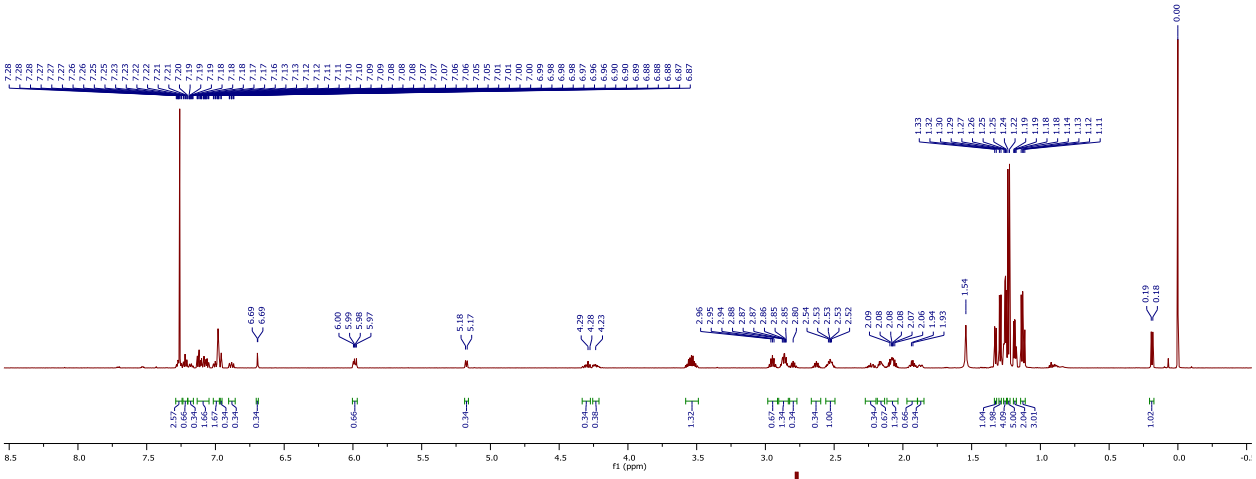
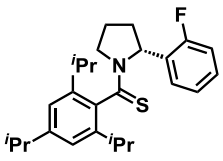




3e





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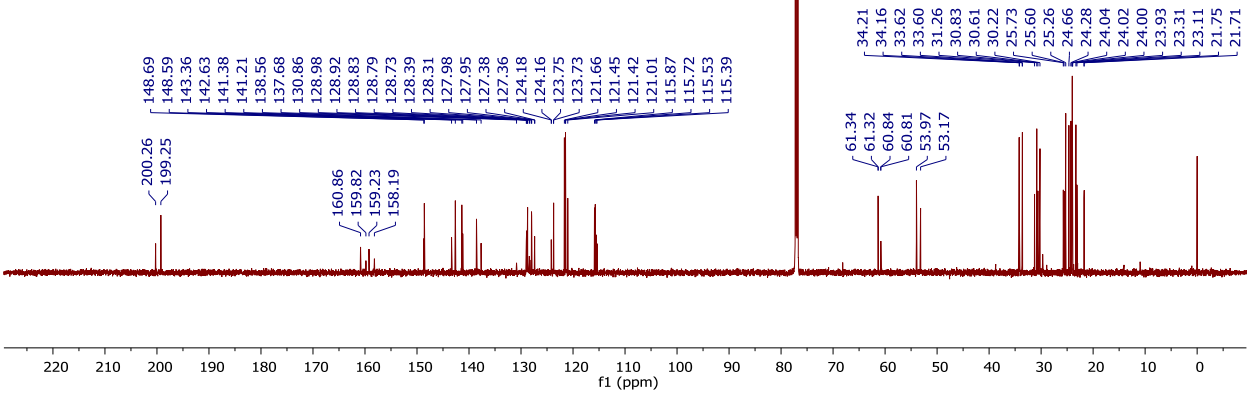
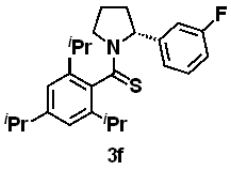


572-proton.1.fid



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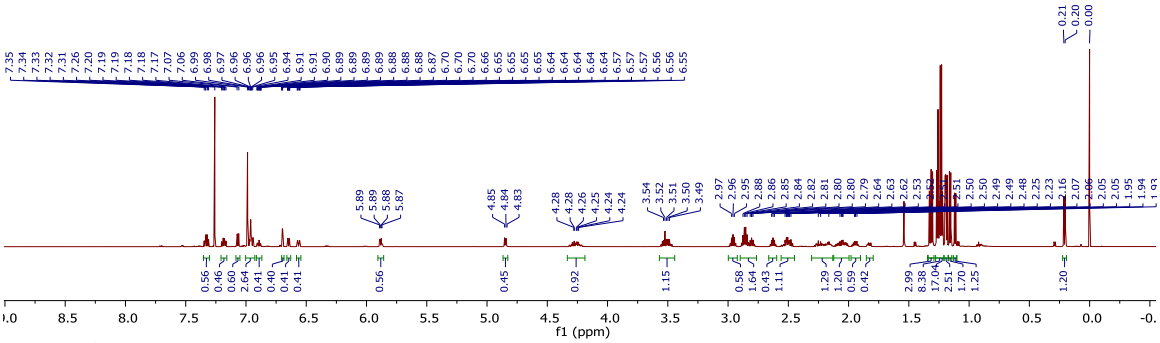
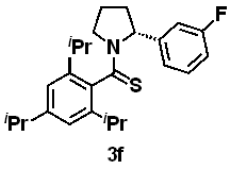


572-carbon.1.fid



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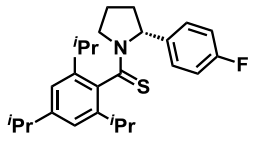
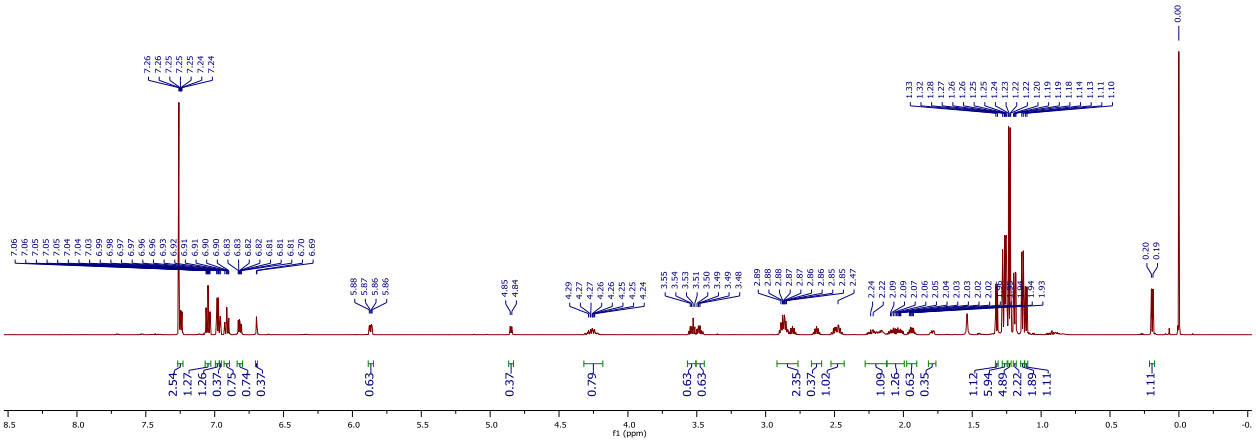
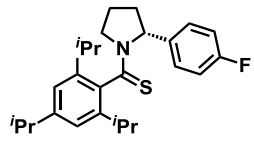


3g





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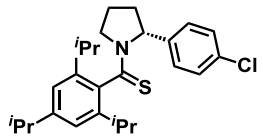
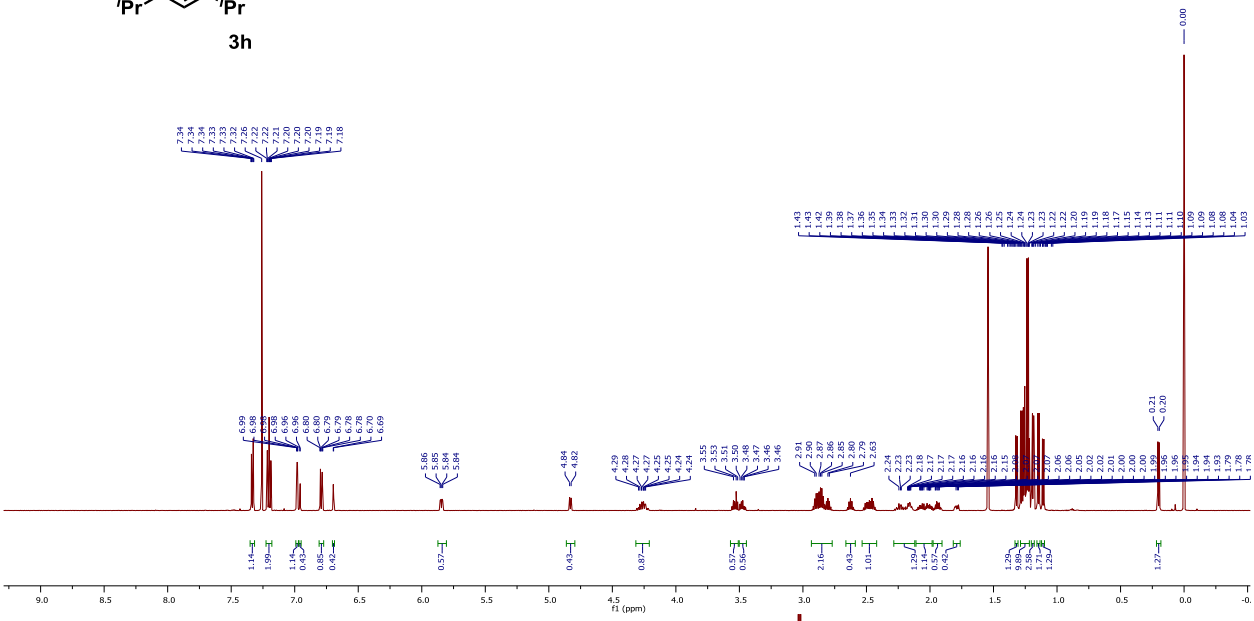
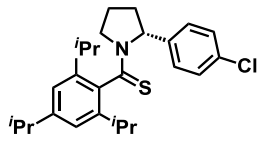
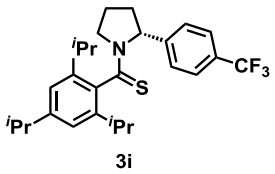


3h



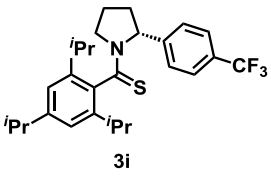


3h

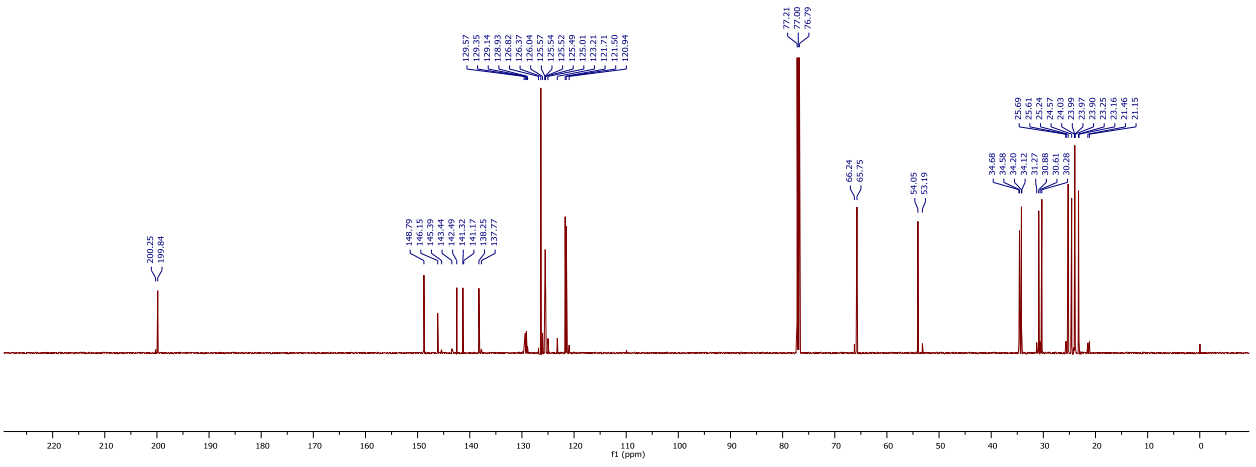

iPr
N
S
CF3
iPr
iPr

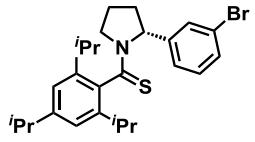
3i

1.88
0.13
1.88
2.00
0.06
0.06
0.94
0.06
0.12
0.94
0.94
0.94
1.95
0.07
0.94
0.07
0.06
0.12
2.82
0.06
0.19
2.79
11.46
0.39
2.82
0.18
0.18
f1 (ppm)

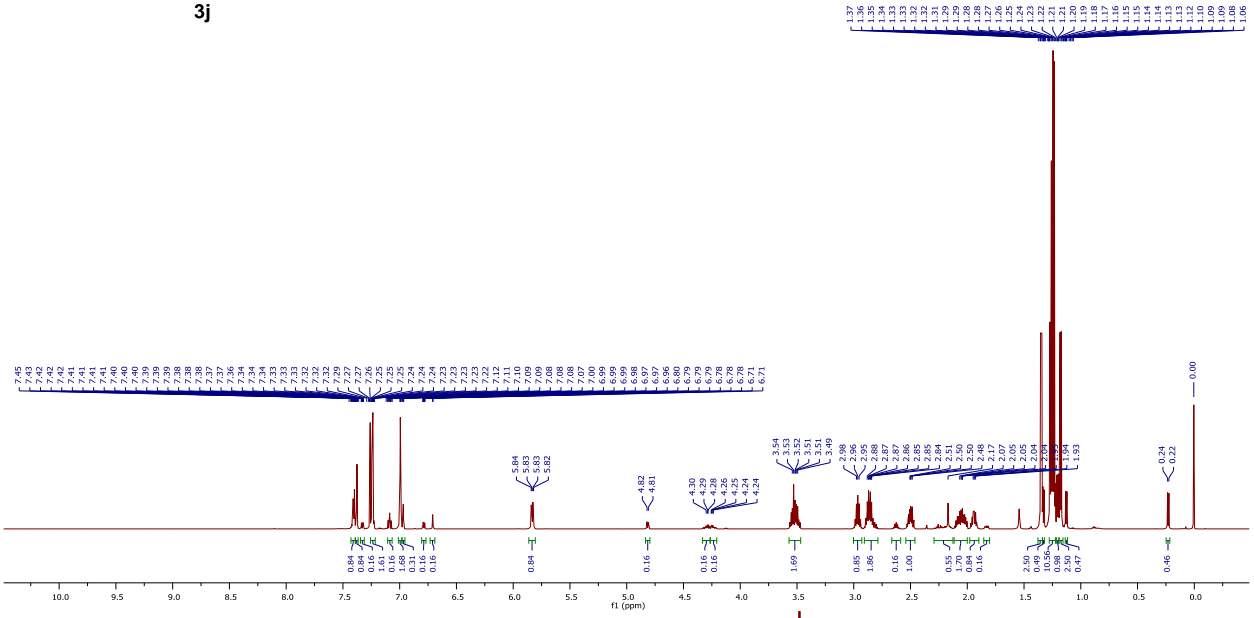

iPr
N
S
CF3
iPr
iPr

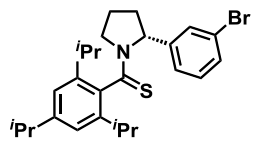
3i


200.25
199.84
148.79
146.15
145.39
143.44
142.49
141.32
141.17
138.25
137.77
129.57
129.35
129.14
128.93
126.82
126.77
126.04
125.57
125.54
125.53
125.49
125.01
123.21
121.71
121.50
120.94
77.21
77.00
76.79
66.24
65.75
54.05
53.19
34.68
34.58
34.20
34.12
31.27
30.88
30.61
30.28
25.69
25.61
25.24
25.17
24.03
23.99
23.97
23.90
23.25
23.16
21.46
21.15
f1 (ppm)

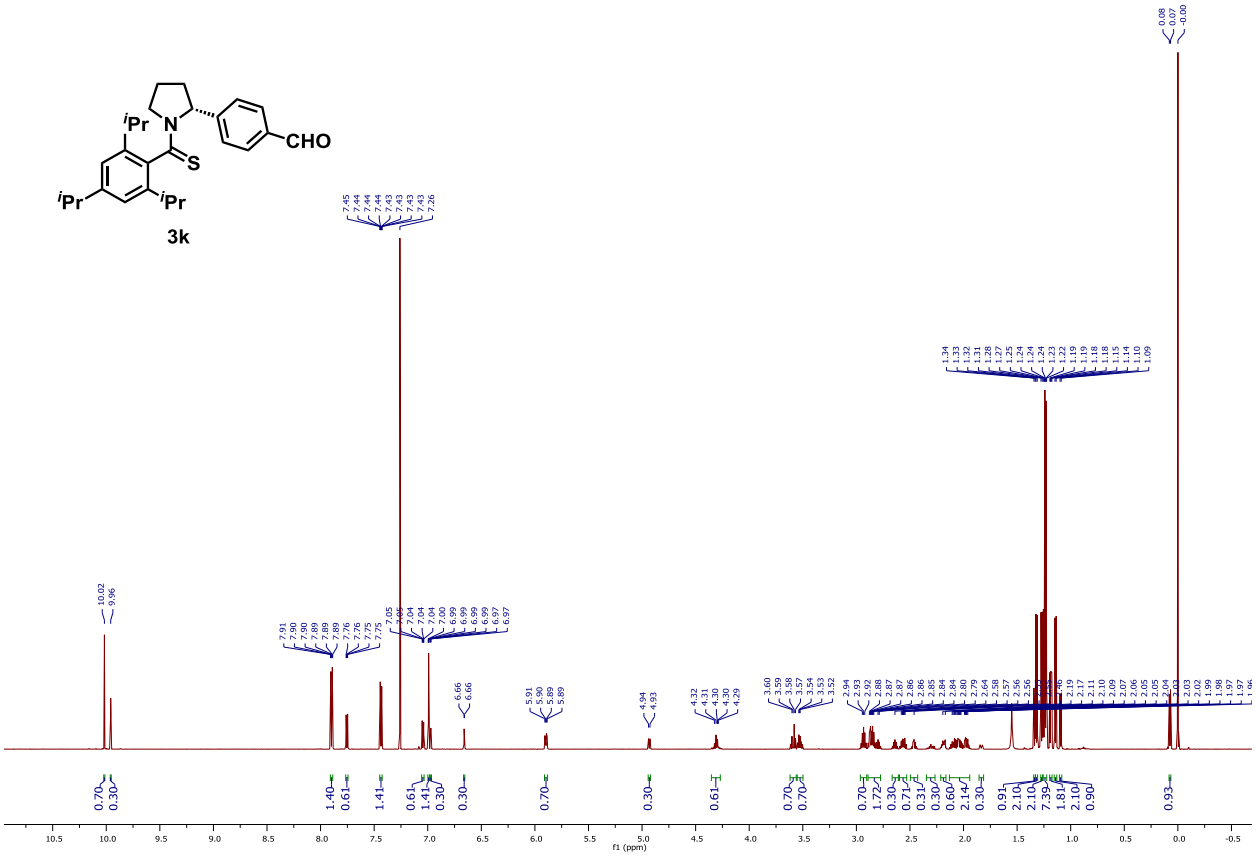


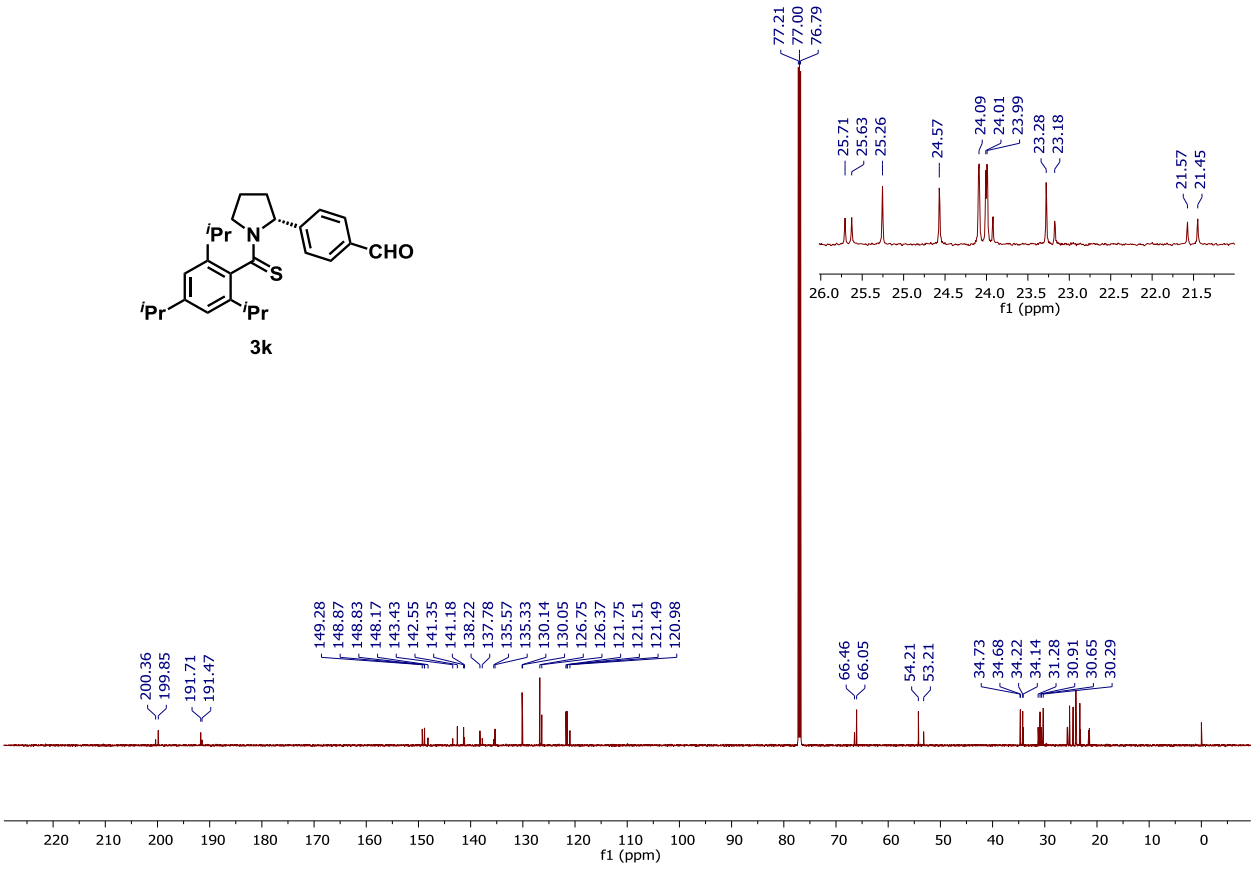
3j

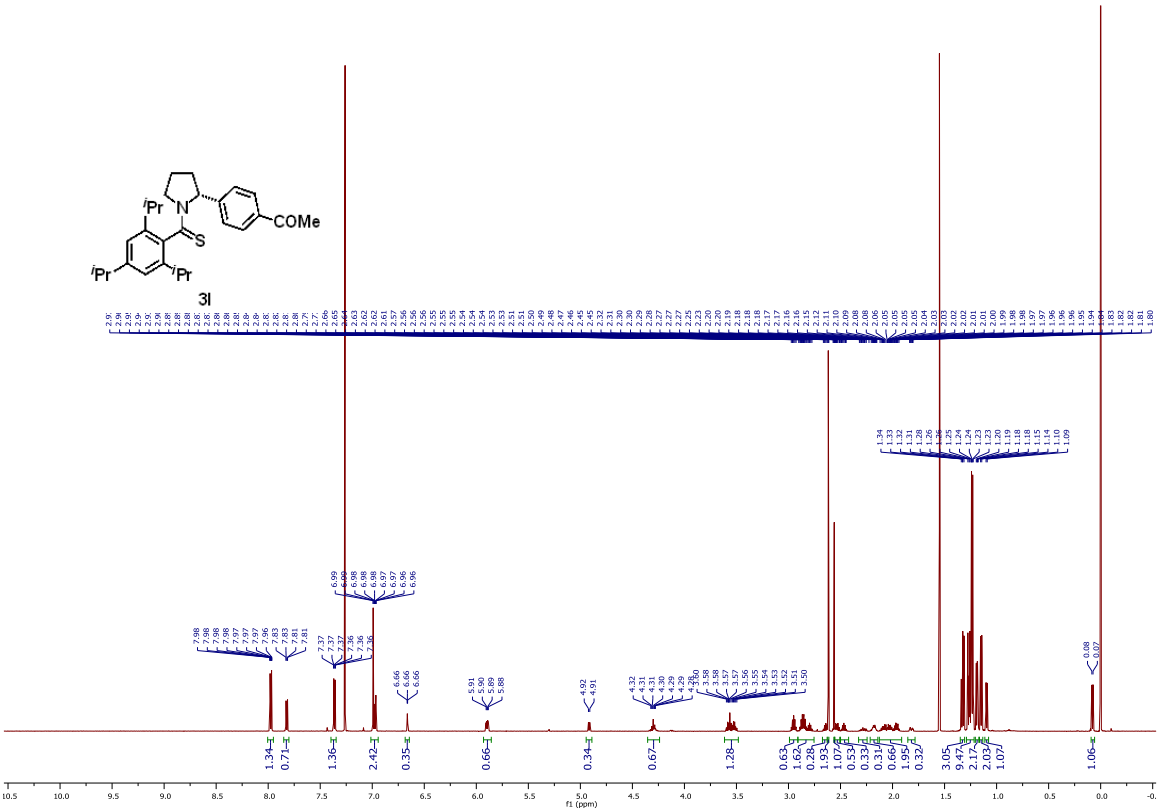


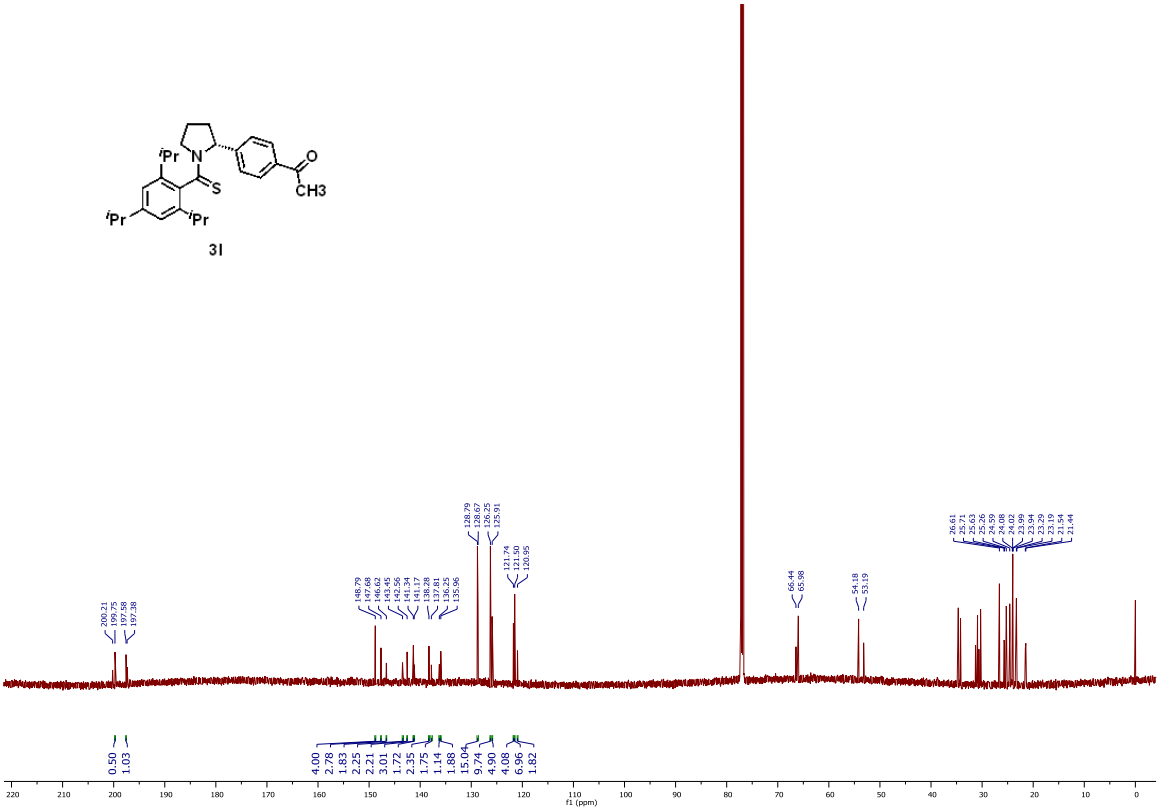


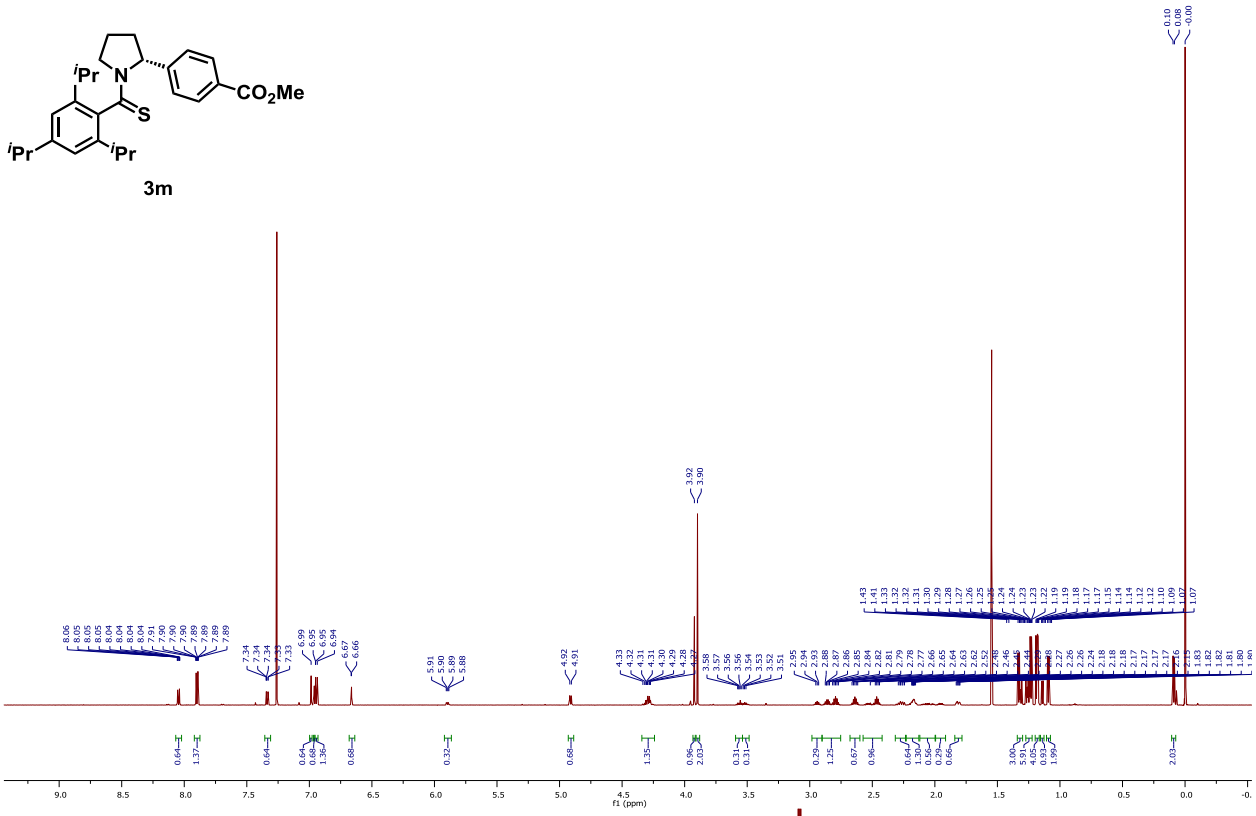
3j

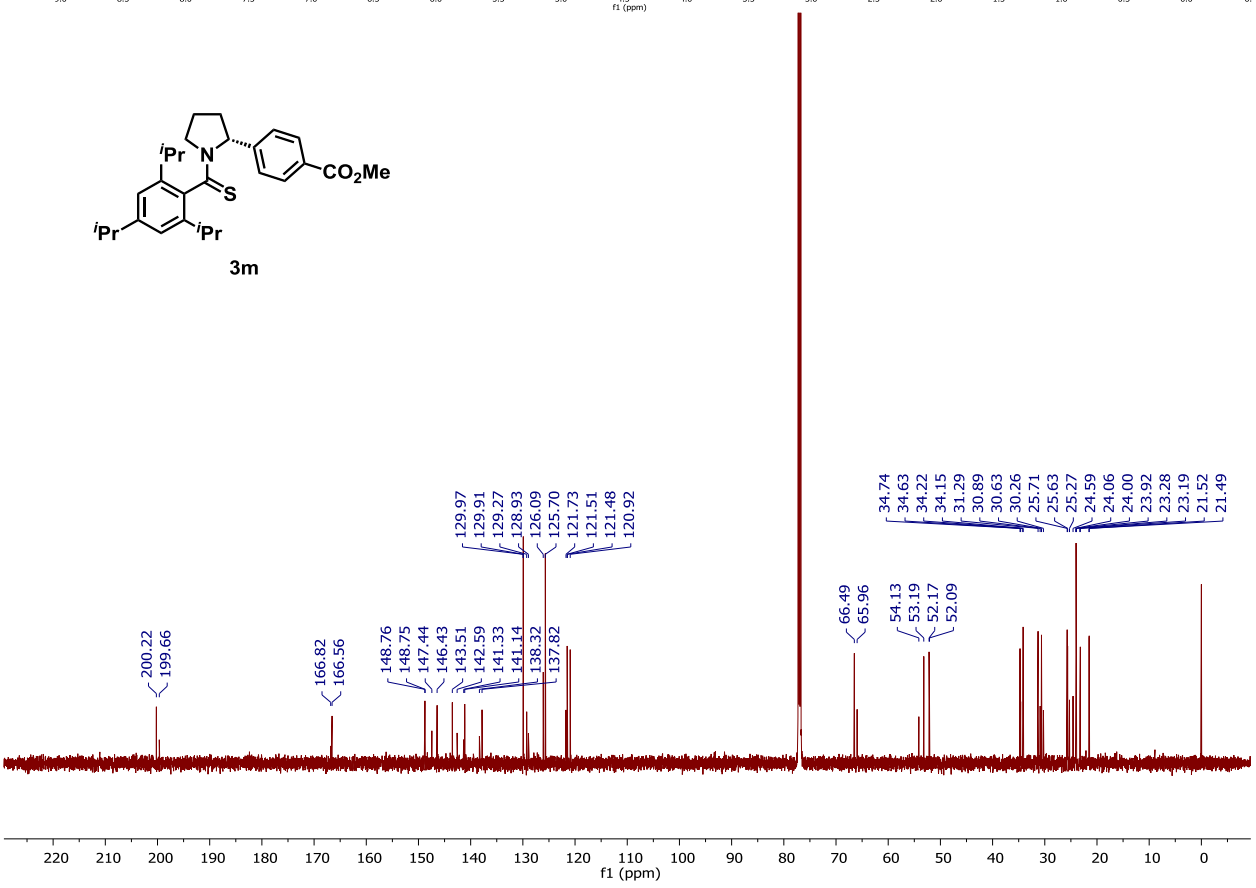

iPr
N
S
CHO
iPr
iPr
3k
f1 (ppm)

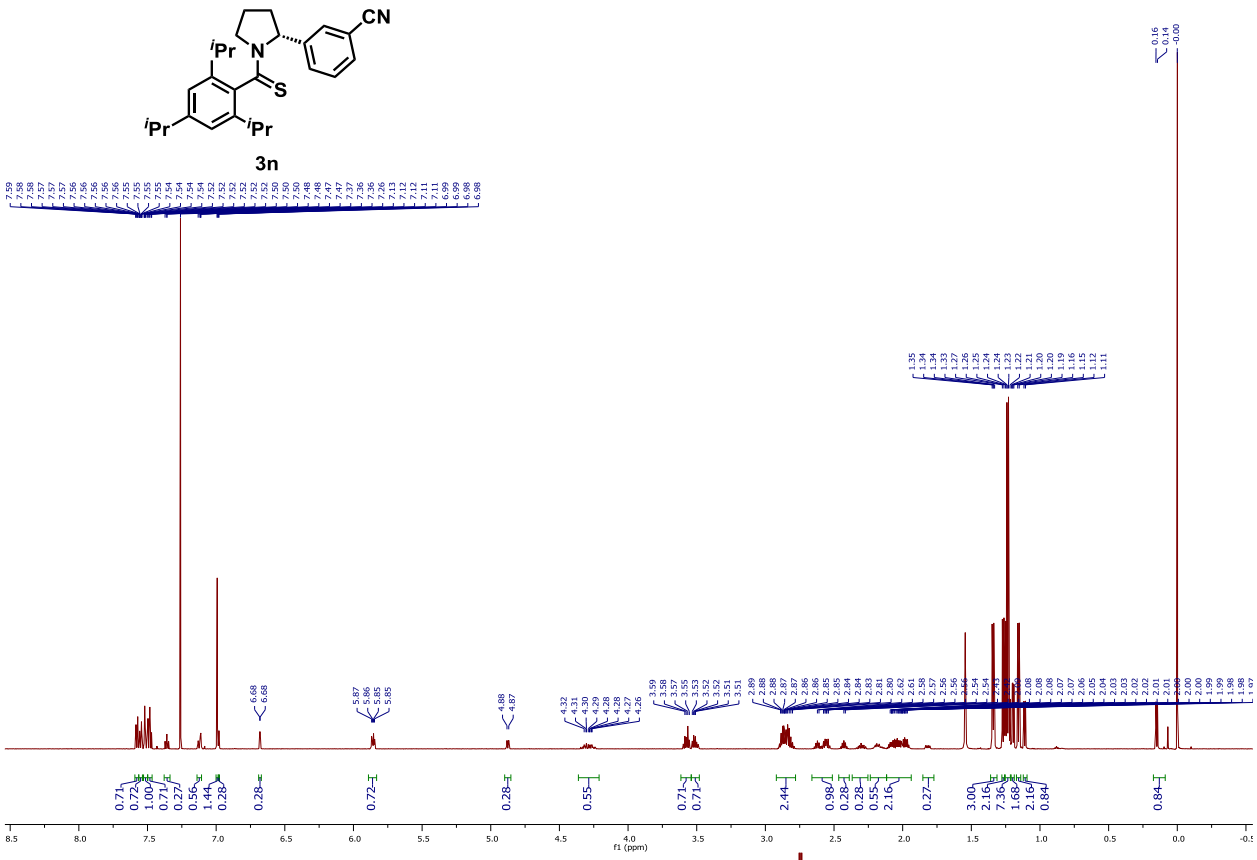

iPr
N
S
CHO
iPr
iPr
3k
f1 (ppm)

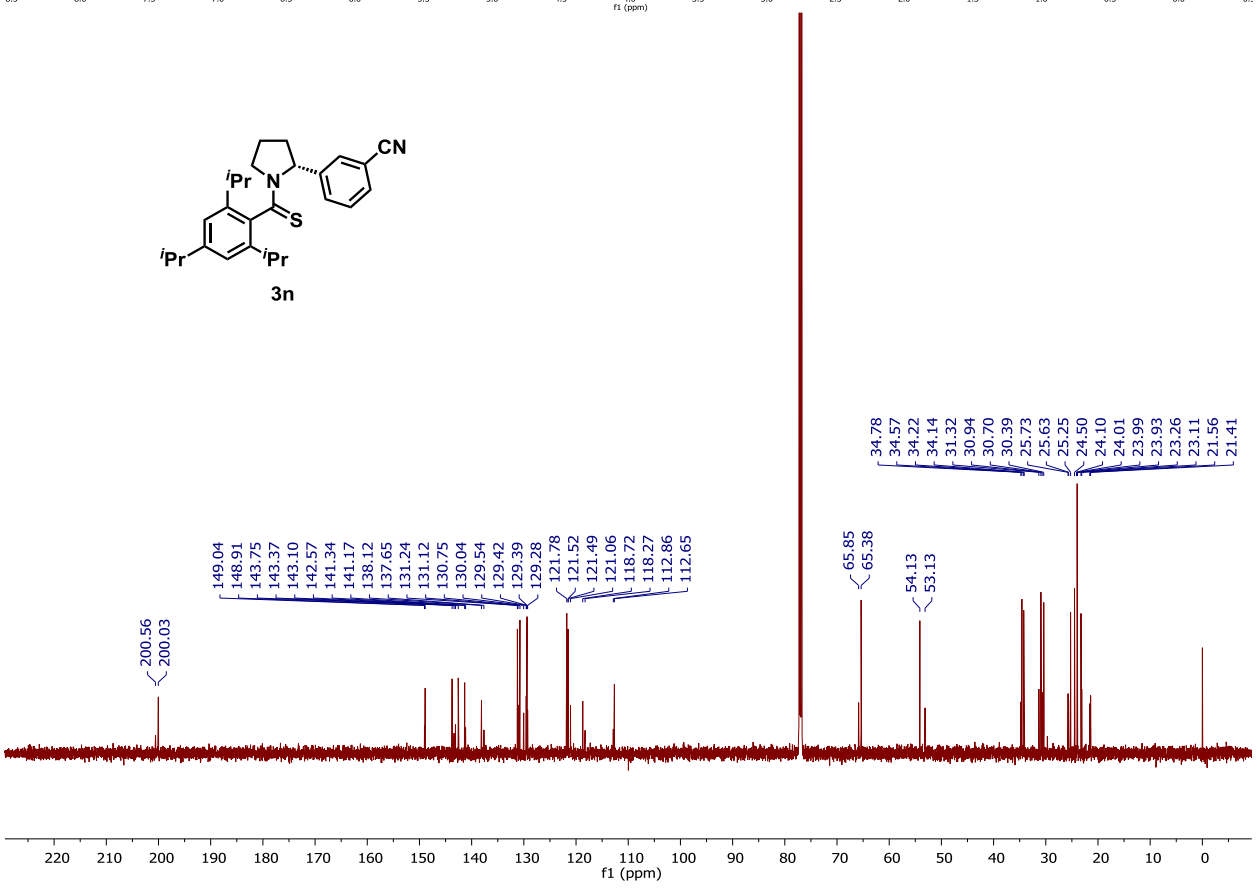

iPr
N
S
COMe
iPr
iPr
3l

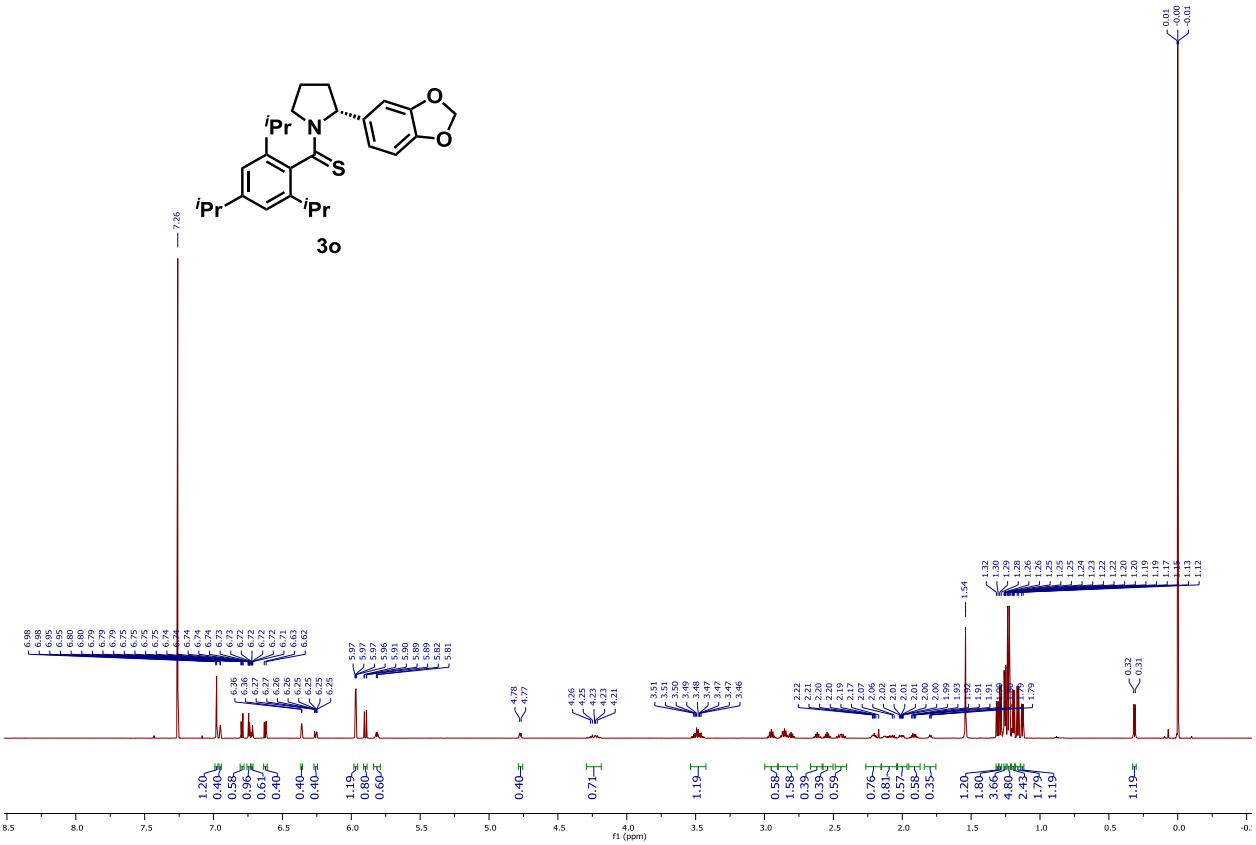

iPr
N
S
O
CH3
iPr
iPr
3l

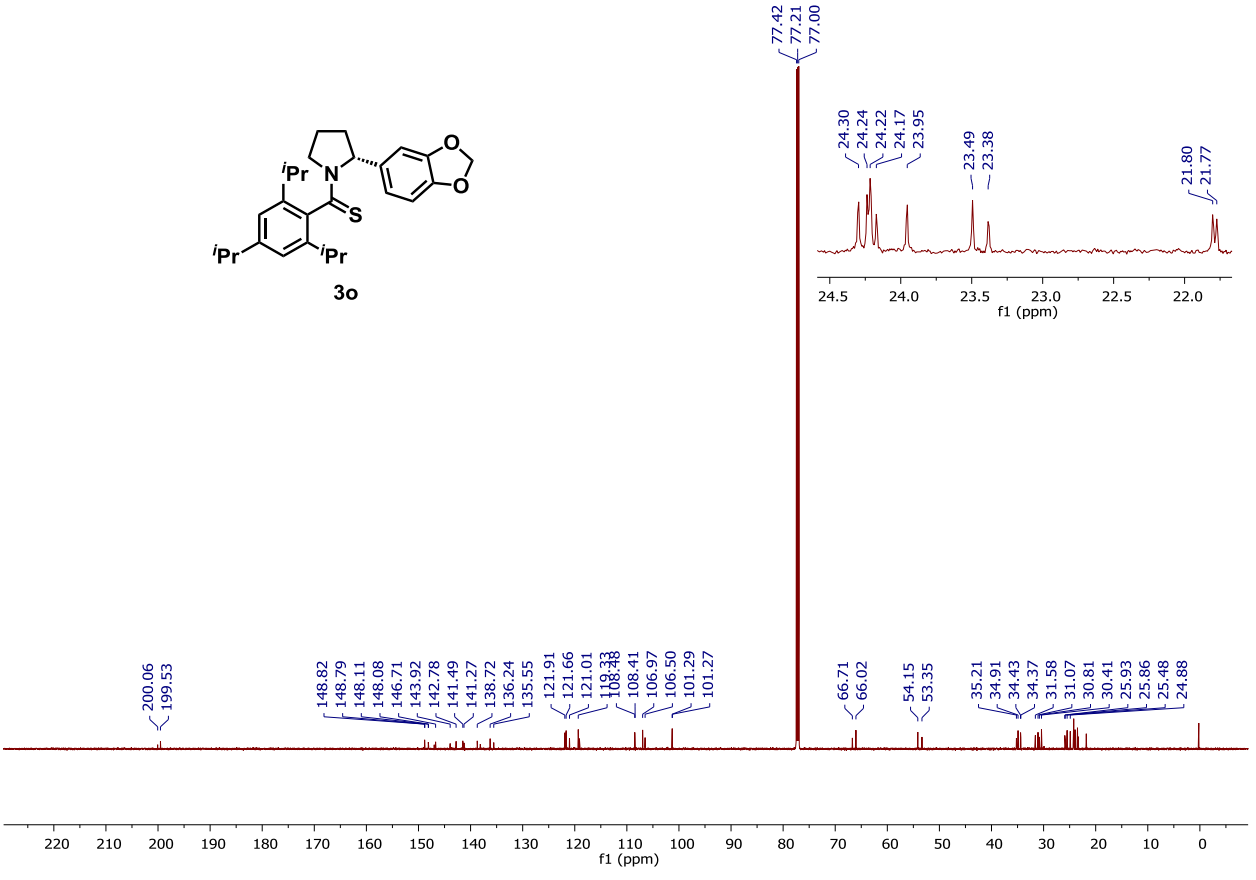

3m
f1 (ppm)

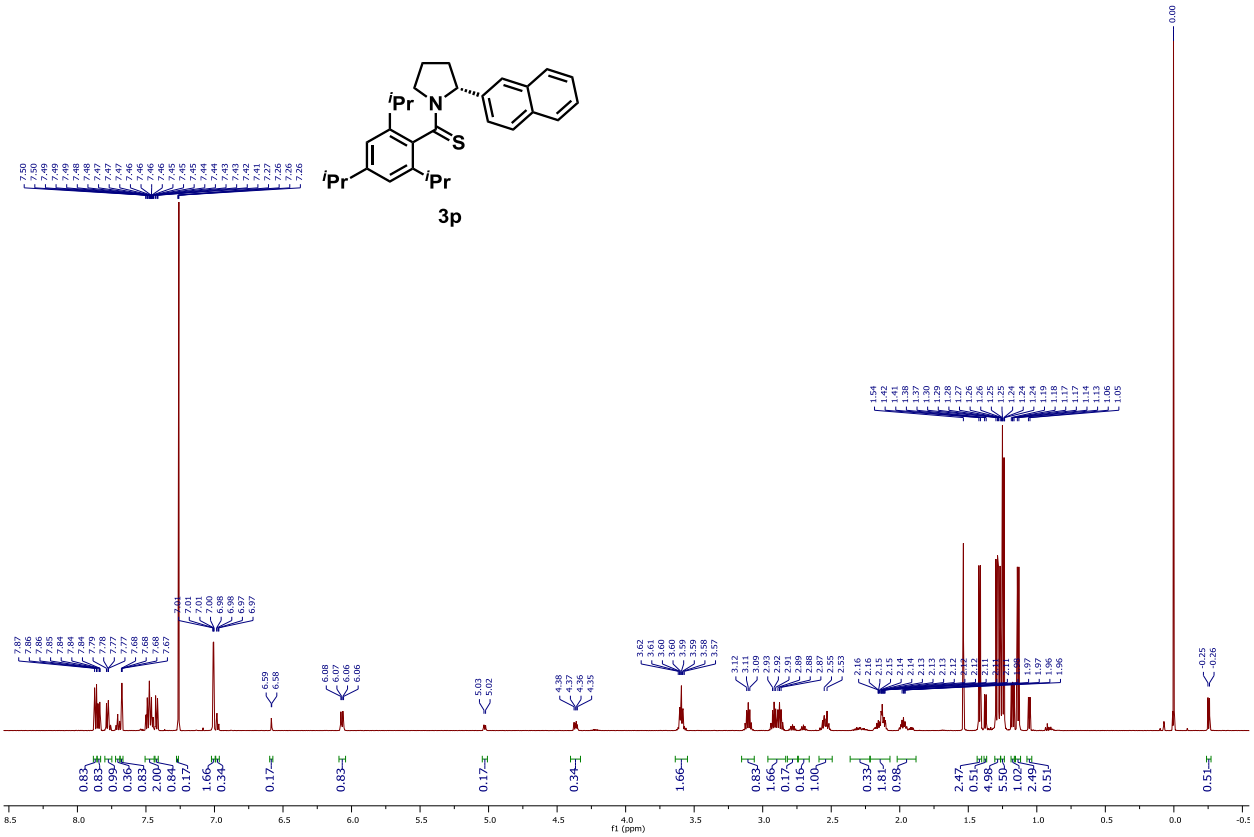

3m
f1 (ppm)

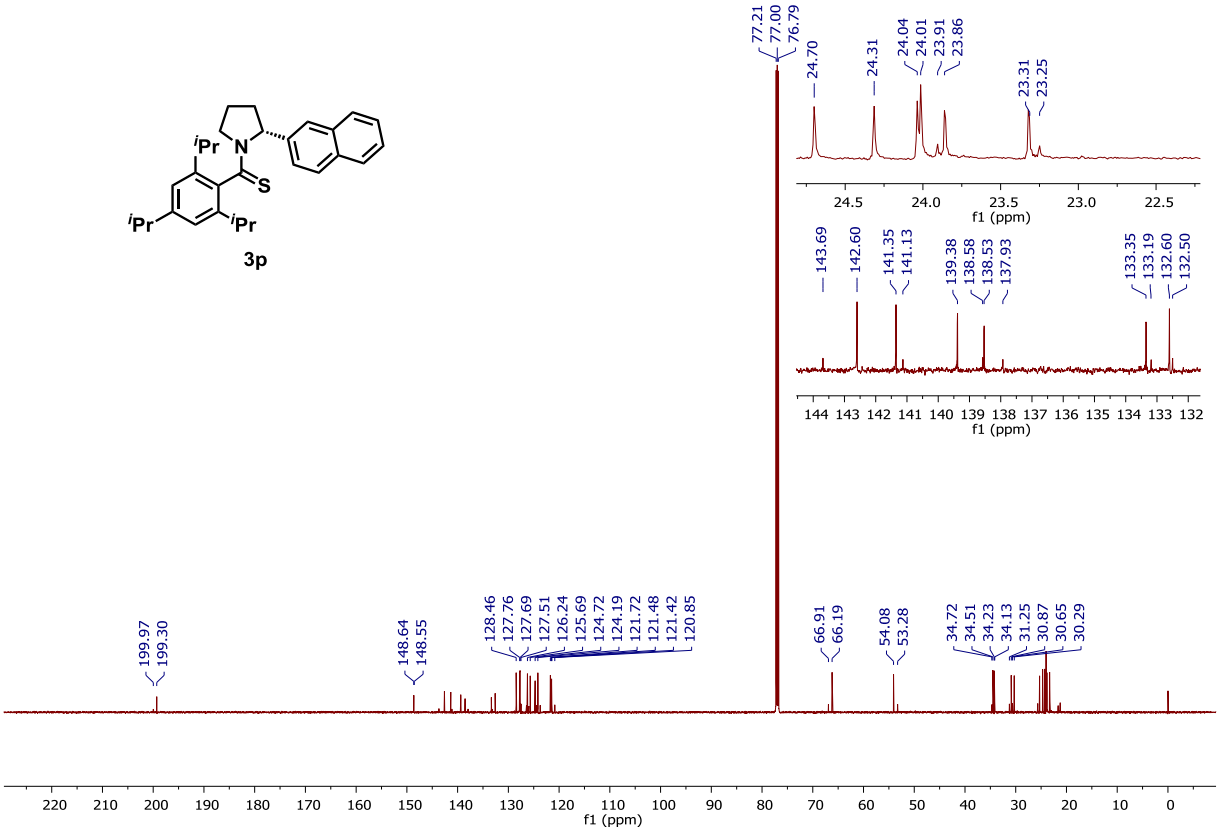

CN
iPr
N
S
iPr
iPr
3n
f1 (ppm)

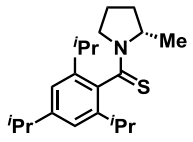

CN
iPr
N
S
iPr
iPr
3n
f1 (ppm)


3o
f1 (ppm)

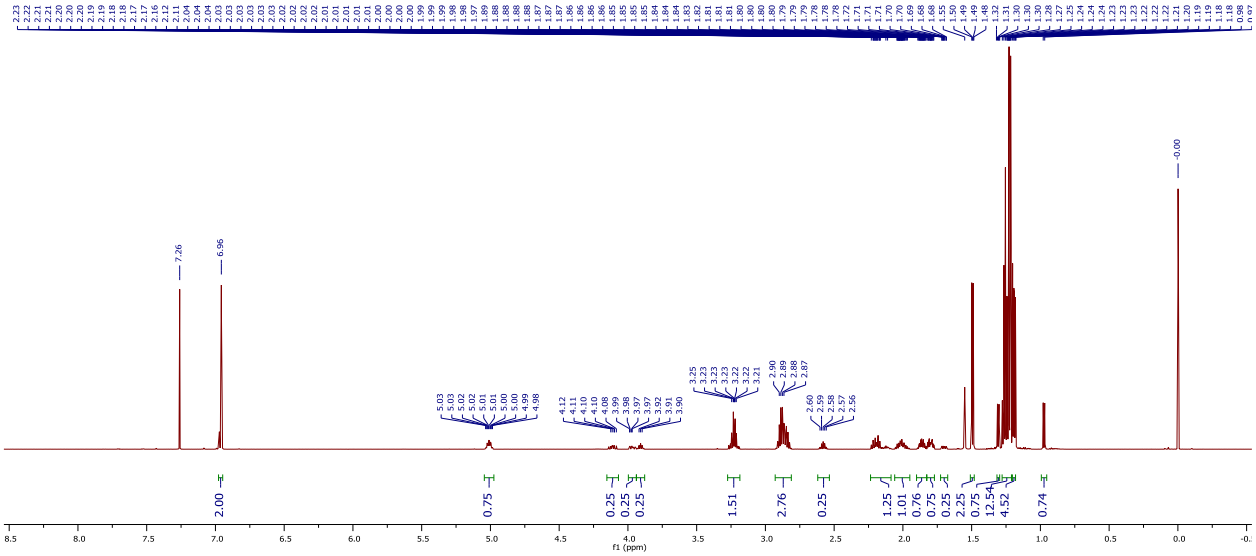

3o
f1 (ppm)


3p
f1 (ppm)


3p
f1 (ppm)


iPr
N
Me
S
iPr
iPr

3q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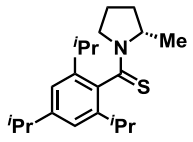
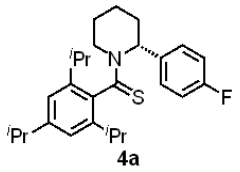
6.96
-0.00
2.00
0.75
0.25
0.25
0.25
1.51
2.76
0.25
1.25
1.01
0.76
0.75
0.25
2.25
0.75
12.54
4.52
0.74
f1 (ppm)


iPr
N
Me
S
iPr
iPr

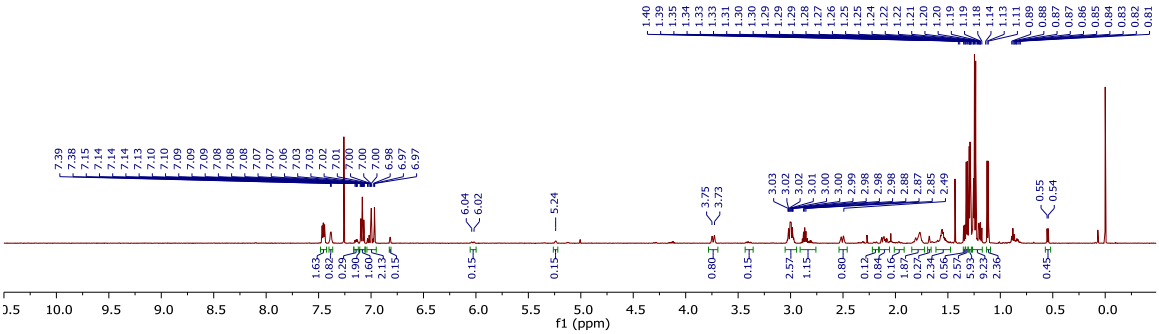
3q

77.21
77.00
76.79
26.18
25.61
25.18
24.85
24.02
24.00
23.98
23.74
23.65
23.44
22.94
22.03
f1 (ppm)
197.22
197.19
148.54
148.40
143.26
141.97
141.34
141.22
138.72
137.80
121.49
121.44
121.38
121.16
58.70
57.72
52.39
51.63
34.20
34.18
31.95
30.69
30.09
19.13
17.22
f1 (ppm)

pj-6mem-pFlouro-paper.1.fid



4a



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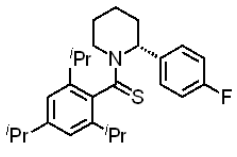
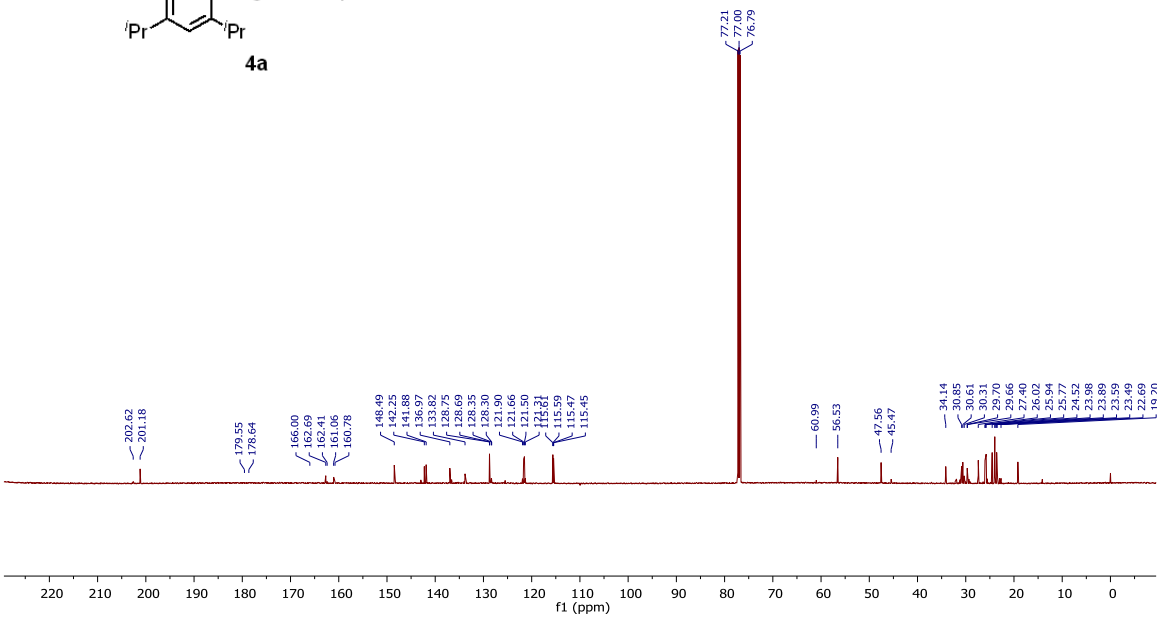


4a



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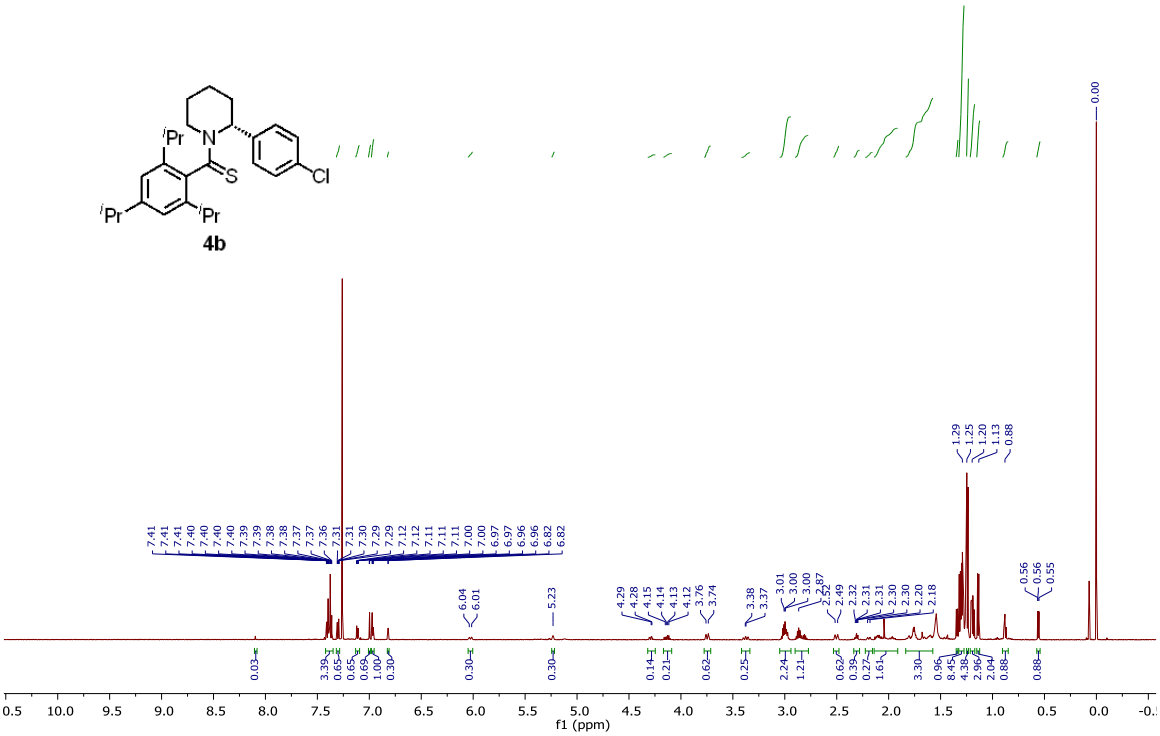

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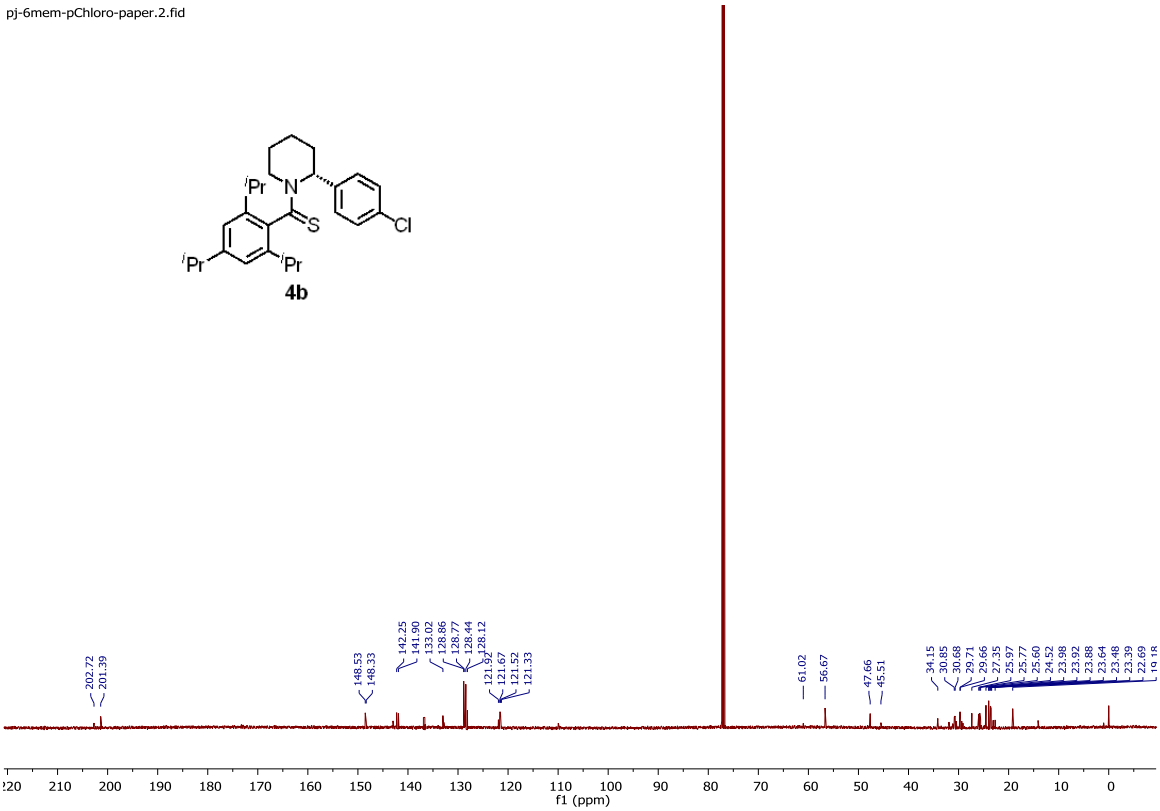

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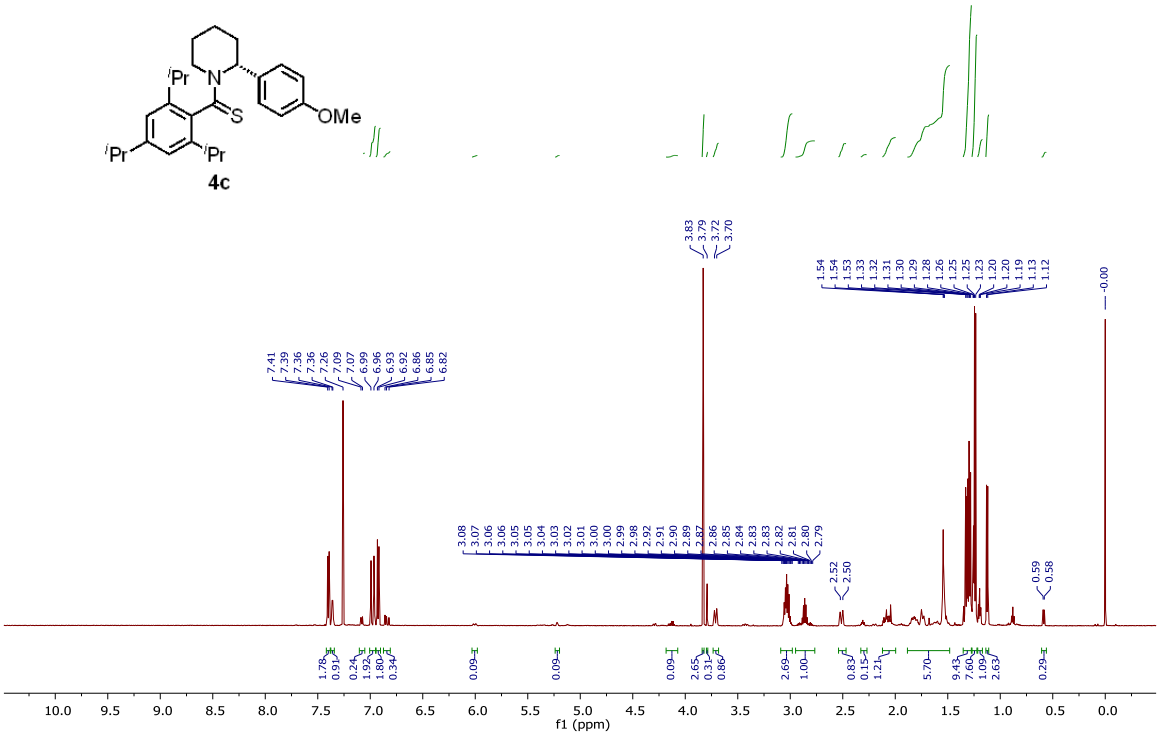

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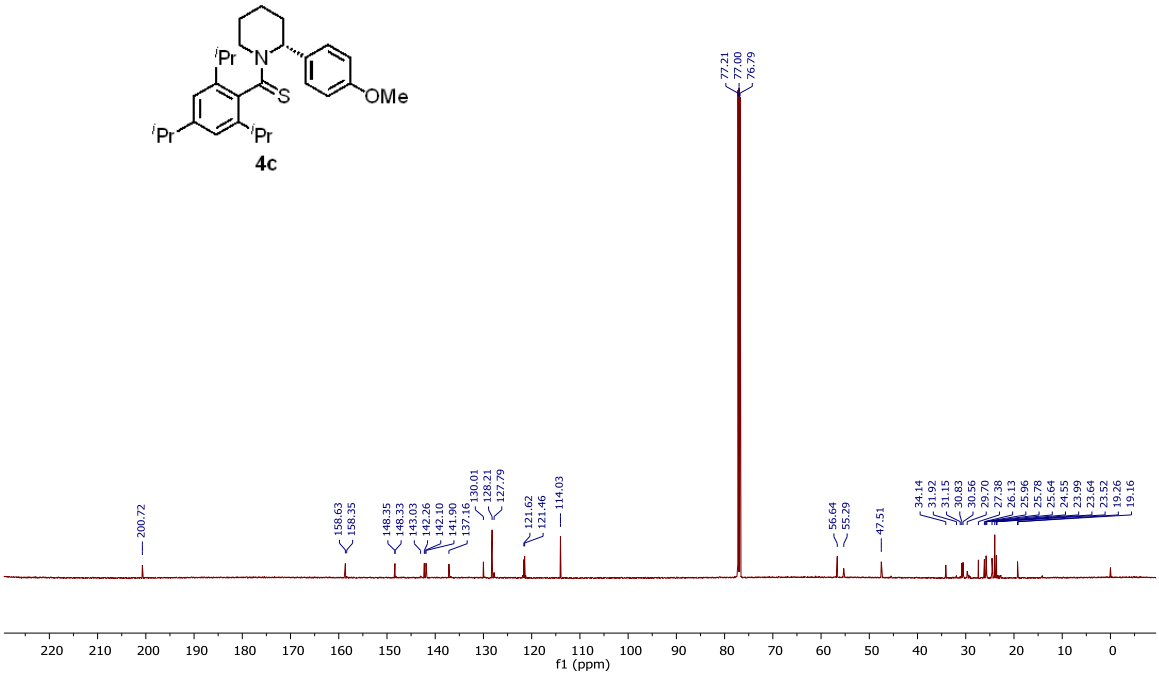

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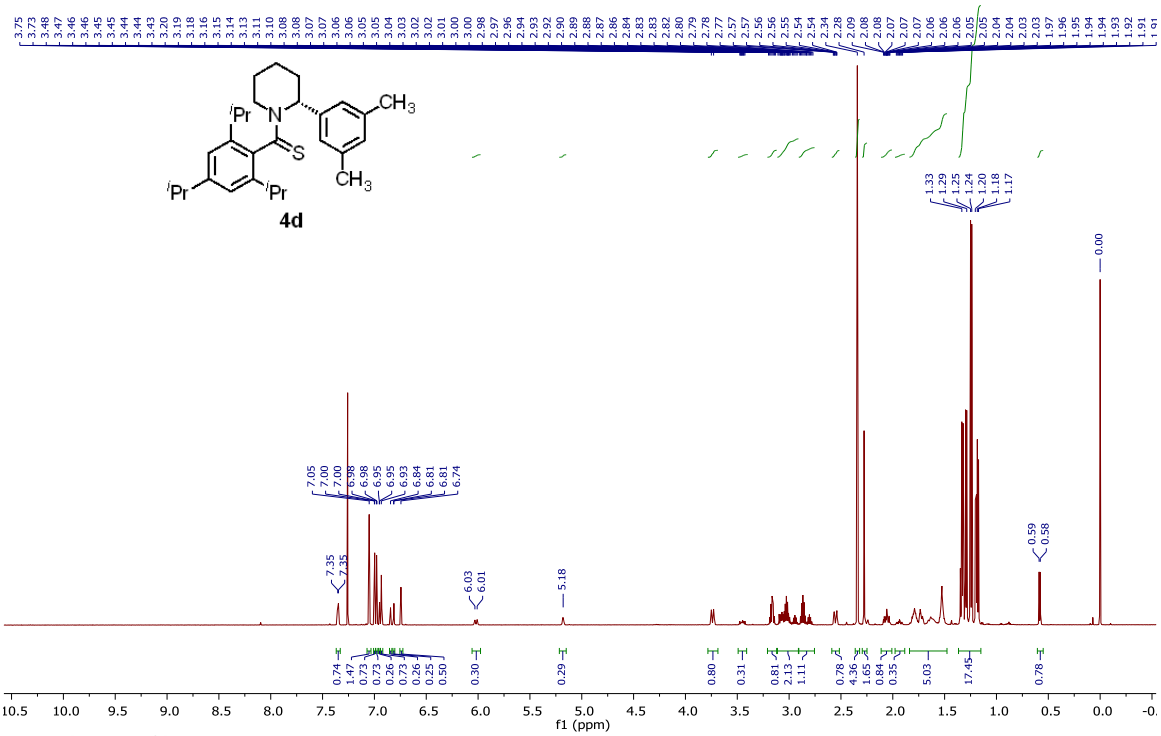

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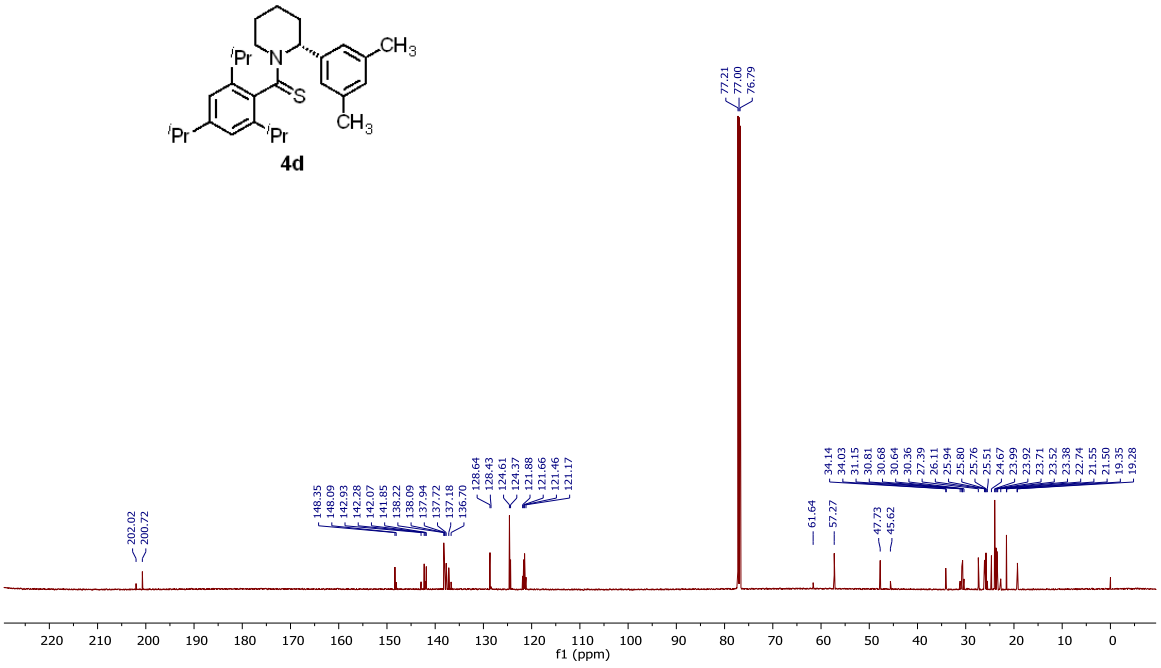

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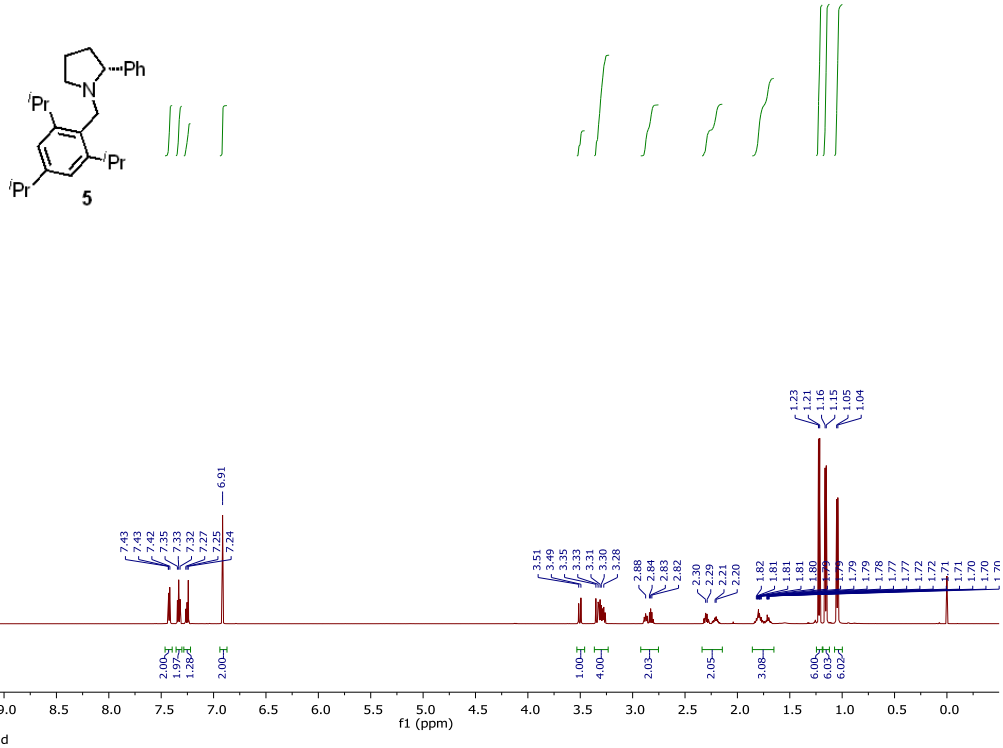

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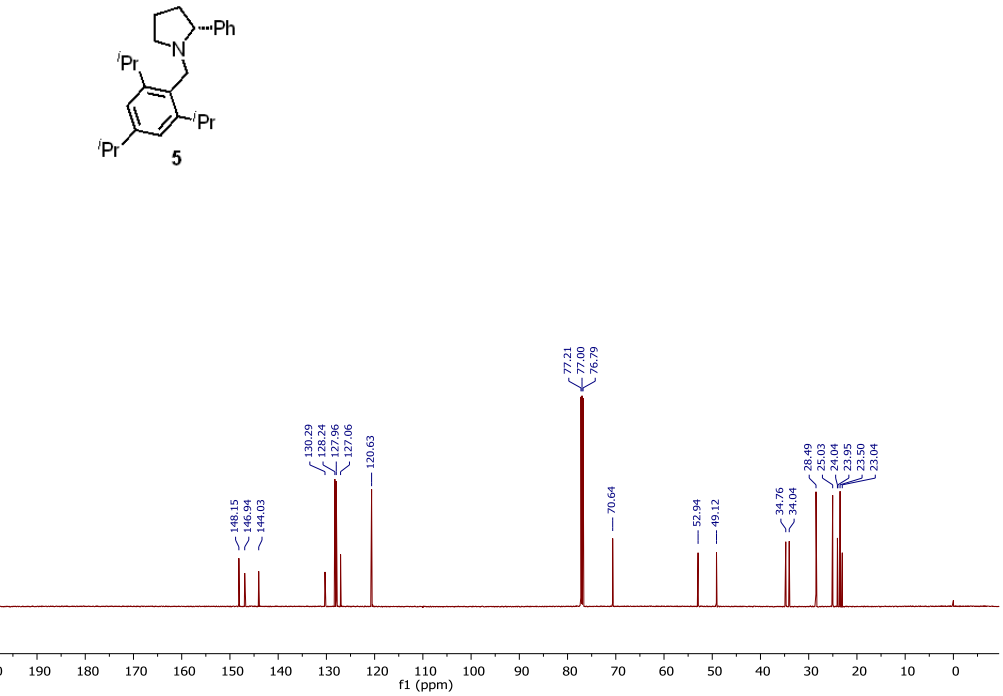

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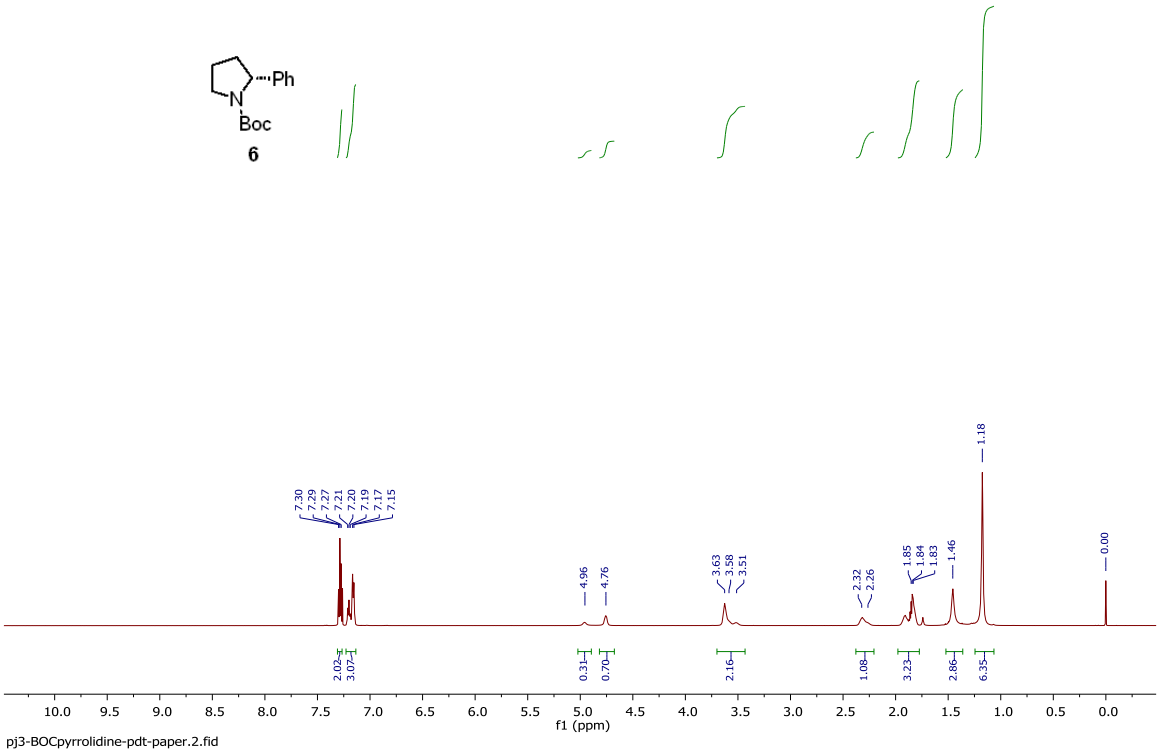

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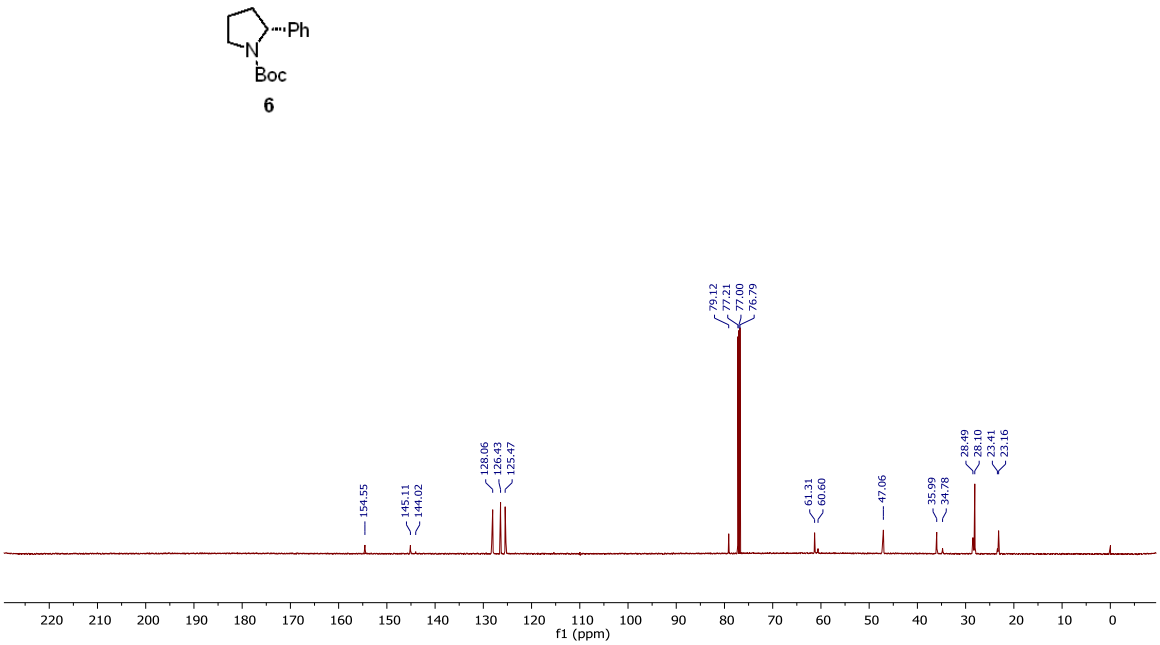

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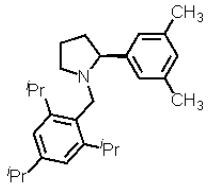

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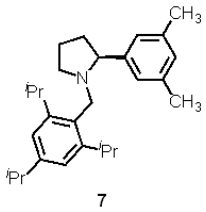

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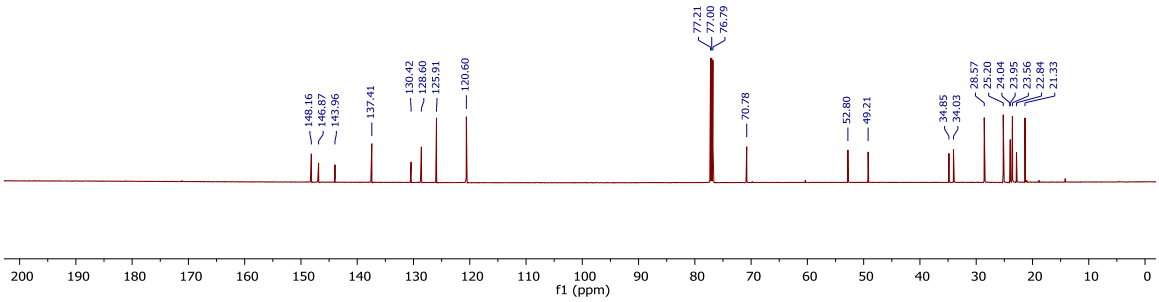

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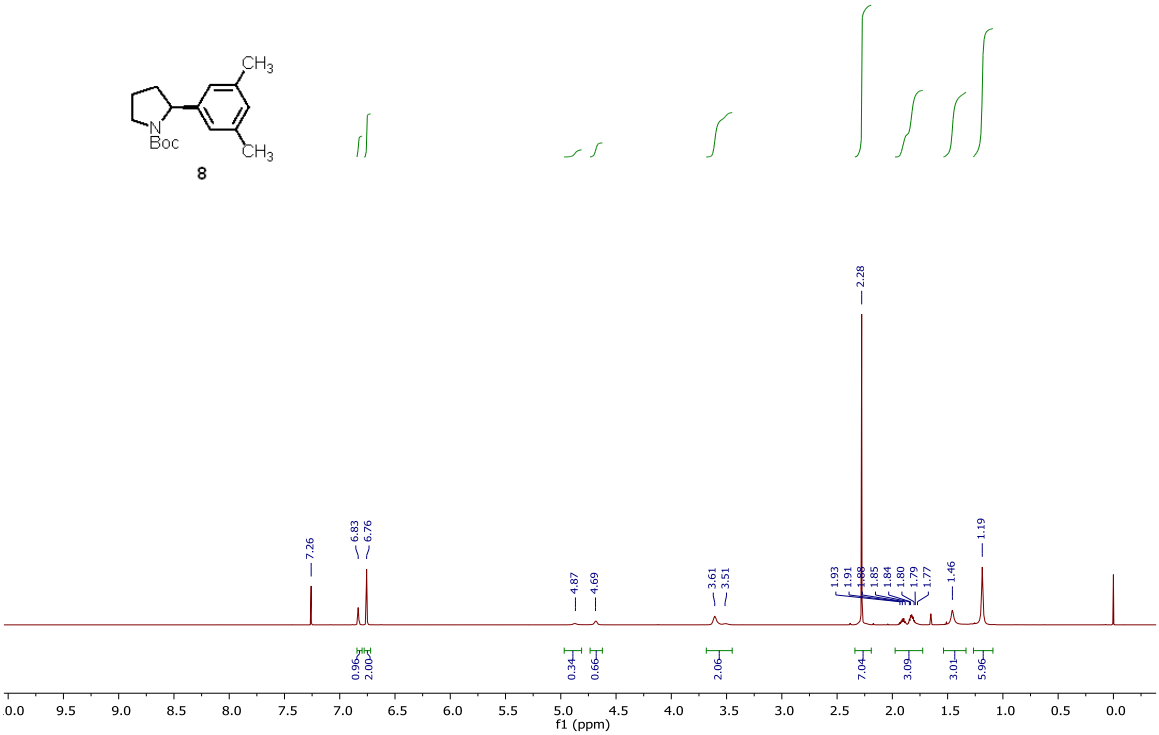

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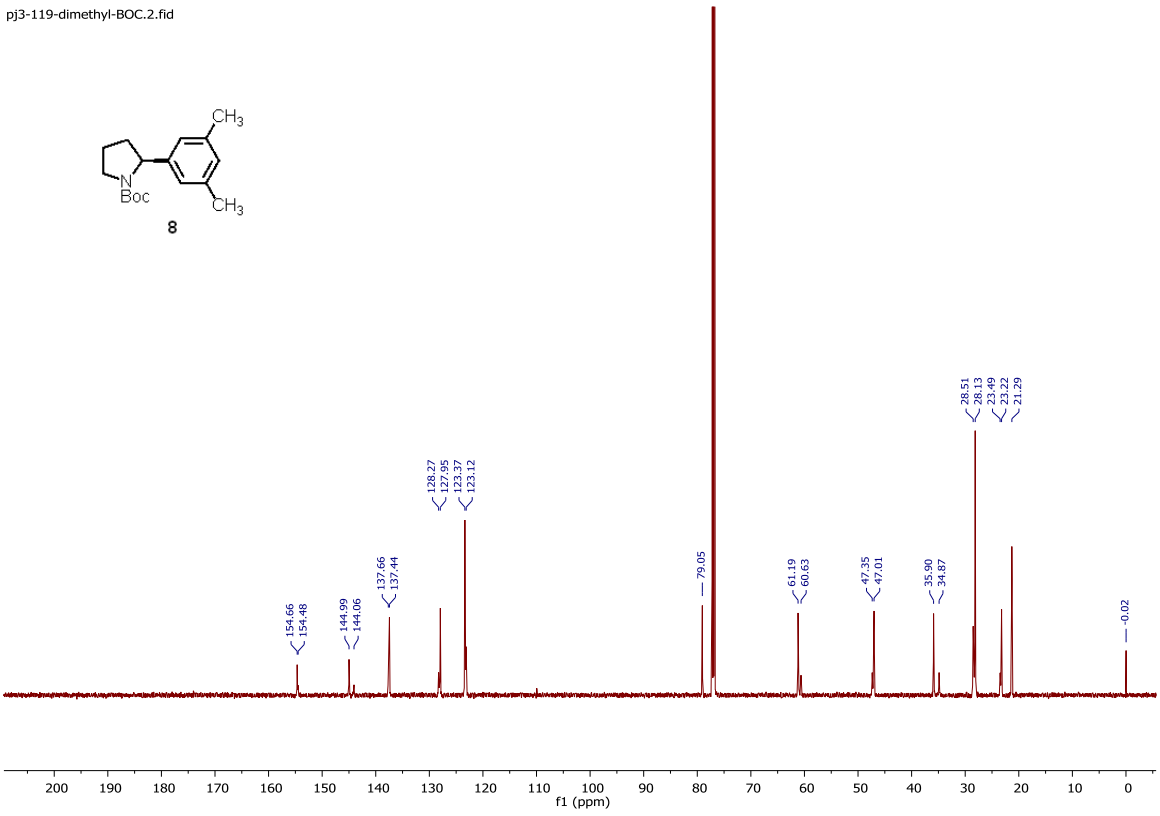

References and Notes:

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