

Supplementary Information for

## Prolinamides containing 2-(2-aminocyclohexyl)phenols as highly enantioselective organocatalysts for aldol reactions

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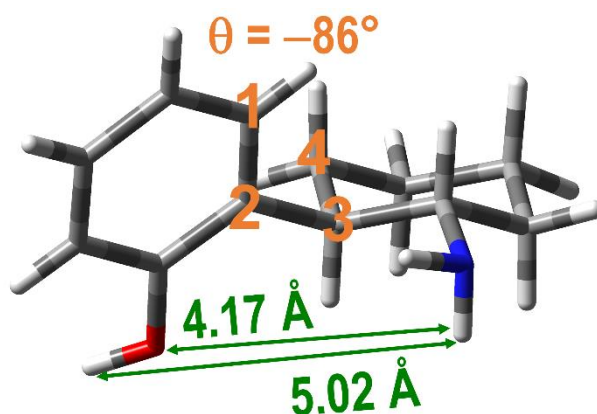
<sup>d</sup> TÜBİTAK SAGE, 06261 Mamak, Ankara, Türkiye

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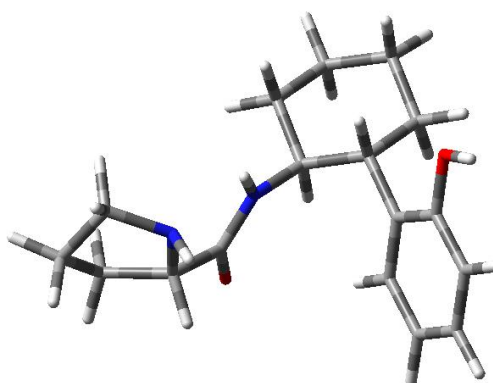
**Figure S1.** X-ray crystal structure of 2-((1R,2S)-2-aminocyclohexyl)phenol ((1R,2S)-**18**). CCDC1848757.  $\theta$ : The C1—C2—C3—C4 dihedral angle.

### Calculations:

Transition state geometries for the aldol reactions and geometry optimizations were performed using the Gaussian 16 Program. Structures of (*S*,1*S*,2*R*)-**31** and (*S*,1*R*,2*S*)-**32** geometries were optimized by the B3LYP with the 6-311+G(d,p) basis set. Frequency calculations of the transition structures **TS1**, **TS2**, **TS3** and **TS4** were performed at B3LYP with 6-31 G(d,p) basis set.

The resulting Z-matrix for the considered structures (*S*,1*S*,2*R*)-**31**, (*S*,1*R*,2*S*)-**32**, **TS1**, **TS2**, **TS3** and **TS4**, as well as the corresponding computed energies are the follows:

#### Structure of (*S*,1*S*,2*R*)-**31**



Electronic Energy (a.u)	-922.498683
EE + Zero-point Energy (a.u)	-922.106881
EE + Thermal Energy Correction (a.u)	-922.087433
EE + Thermal Enthalpy Correction (a.u)	-922.086489
EE + Thermal Free Energy Correction (a.u)	-922.157346

C	0.11647300	2.83612800	0.06269800
C	1.32929600	3.70339000	-0.29522400
C	2.61566300	3.13415000	0.31360100
C	2.81657300	1.66702200	-0.08335700
C	1.59752500	0.78443500	0.28416000
C	0.31317900	1.36532900	-0.35072200
H	3.48124600	3.72695700	-0.00003400

H	1.43222500	3.74744800	-1.38695600
H	1.16578700	4.73177400	0.04282000
H	-0.05996900	2.87940400	1.14589300
H	-0.78756900	3.21724800	-0.42124000
H	2.98635400	1.59651500	-1.16523200
H	3.70810400	1.26018300	0.40124000
H	1.47494600	0.84503800	1.37239100
H	0.38507200	1.32703100	-1.44055700
H	2.56540600	3.20950100	1.40750500
H	-1.06908200	0.34043300	0.96069900
C	-1.71918600	0.05799700	-0.91260600
O	-1.62183600	0.19774900	-2.12818600
N	-0.85899600	0.57150400	-0.00506800
C	-2.88036300	-0.74865400	-0.31608800
C	-4.25241700	-0.11205300	-0.66739600
H	-2.80746500	-1.74218200	-0.77032200
C	-4.12599100	-0.34544100	1.70414300
C	-5.12882500	-0.44756000	0.54684300
H	-4.64164100	-0.48858700	-1.61278100
H	-4.14462300	0.97194600	-0.76932700
H	-4.41493400	-0.90984100	2.59339100
H	-4.00440700	0.70146400	2.00572200
H	-5.51489800	-1.47009400	0.47139700
H	-5.98174100	0.22673500	0.65629600
N	-2.84465500	-0.85377600	1.16449600
H	-2.70143500	-1.81607700	1.44223600
C	1.87069800	-0.67117900	-0.05905400
C	2.53961200	-1.48698500	0.86905300
C	1.53008600	-1.24503300	-1.28738000
C	2.84672600	-2.81613700	0.57915300
C	1.83463200	-2.57202500	-1.59086800
H	0.99535400	-0.65391300	-2.02133100
C	2.49508600	-3.36020200	-0.65354000
H	3.36367900	-3.42218200	1.31851700
H	1.55064800	-2.98370800	-2.55215100
H	2.73775700	-4.39362900	-0.87381100
O	2.88438400	-0.92263600	2.07716900
H	3.31375100	-1.58556400	2.62729200

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3 4 1.0 7 1.0 16 1.0

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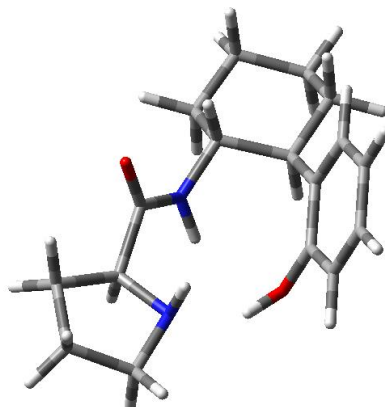
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44 45 1.0  
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## Structure of (S,1R,2S)-32



Electronic Energy (a.u)	-922.496598
EE + Zero-point Energy (a.u)	-922.103749
EE + Thermal Energy Correction (a.u)	-922.084848
EE + Thermal Enthalpy Correction (a.u)	-922.083904
EE + Thermal Free Energy Correction (a.u)	-922.151833

C	-2.20696800	-2.47863300	-0.12171400
C	-3.70767000	-2.34732700	0.15224800
C	-4.28553500	-1.12963900	-0.57526500
C	-3.53795700	0.14481100	-0.16955100
C	-2.02310100	0.06140600	-0.45496300
C	-1.41329700	-1.20360400	0.22365700
H	-5.35167300	-1.01990300	-0.35217600
H	-3.87824800	-2.24069100	1.23119200
H	-4.22232100	-3.26336100	-0.15465100
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H	-1.77736100	-3.31523500	0.43714500
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H	-3.94933300	1.01593600	-0.68839900
H	-1.90589600	-0.07933300	-1.53666400
H	-1.39611400	-1.06112400	1.30746700
H	-4.20612600	-1.27813900	-1.65988400
H	0.15186300	-1.20869400	-1.17574500
C	1.05777300	-1.35729900	0.62395900
O	1.00504900	-1.36290800	1.84534000
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H	5.15350000	-0.27477700	1.07667800
H	5.62761600	-1.38283000	-0.20360000
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C	-1.27842300	1.34305600	-0.08874400
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H	1.27510300	0.79510400	-1.66234600
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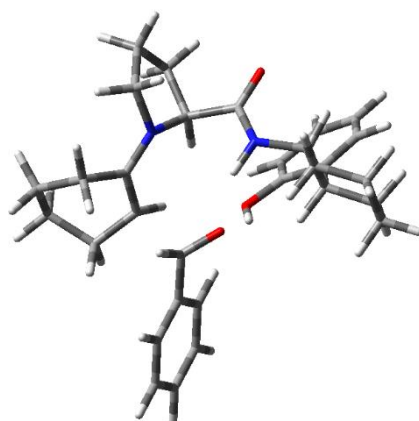
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 43 44 1.0  
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**Structure of TS1**



Electronic Energy (a.u)	-1501.273887
EE + Zero-point Energy (a.u)	-1500.644190
EE + Thermal Energy Correction (a.u)	-1500.614712
EE + Thermal Enthalpy Correction (a.u)	-1500.613768
EE + Thermal Free Energy Correction (a.u)	-1500.702996

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 C      -3.75002500   -1.17274700   -3.32371900  
 C      -3.64911500   -2.45146000   -2.48300700  
 C      -3.75862700   -2.12171300   -0.99117100  
 C      -2.67740900   -1.12017400   -0.54058600  
 C      -2.68478000   0.15860900   -1.43824400  
 H      -4.44502900   -3.16251500   -2.77161300  
 H      -4.74201900   -0.70238800   -3.18154700  
 H      -3.67891600   -1.41699800   -4.39998300  
 H      -1.65433400   -0.62668200   -3.19876100



H	-2.72788000	0.73946900	-3.53478200
H	-4.76708700	-1.71498800	-0.77699500
H	-3.67025200	-3.04545700	-0.38776100
H	-1.67090500	-1.61682100	-0.66391500
H	-3.58954700	0.77695600	-1.20531000
H	-2.68981400	-2.96494500	-2.68906700
H	-0.56435800	0.48018800	-1.38270000
C	-1.46614000	1.91924800	-0.14597200
O	-2.47645000	2.49843200	0.21965600
N	-1.45870600	0.95927000	-1.14287100
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C	-0.15987900	3.64082800	1.17045700
H	0.13345600	1.41972400	1.23470500
C	0.89059200	3.78975000	-1.05799400
C	0.33057900	4.63911200	0.10248000
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C	2.16285600	1.68303700	-0.48326900
C	2.35135600	0.48475600	0.23387300
H	1.63569100	0.22524500	1.02585400
C	3.79935400	0.17223300	0.55478300
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C	2.52300800	-3.81630300	1.51604900
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C	2.39042400	-2.19783700	-0.28423200
C	3.42131500	-2.87268300	-0.95821700
C	3.99593500	-4.01474000	-0.39575300
C	3.54823700	-4.48709800	0.84324200
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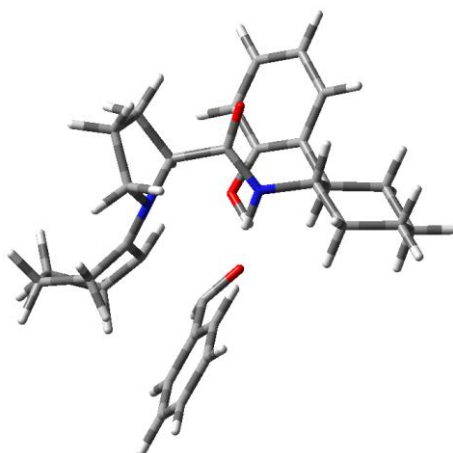
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## Structure of TS2



Electronic Energy (a.u)	-1501.274542
EE + Zero-point Energy (a.u)	-1500.644540
EE + Thermal Energy Correction (a.u)	-1500.615165
EE + Thermal Enthalpy Correction (a.u)	-1500.614221
EE + Thermal Free Energy Correction (a.u)	-1500.703009

C	-1.85810400	2.76663600	1.36726100
C	-3.00329700	3.75723600	1.13521200
C	-3.48362500	3.69791400	-0.32050400
C	-3.94383800	2.28153000	-0.68129500
C	-2.82771700	1.24325600	-0.45510500
C	-2.28131300	1.32857000	1.00607900
H	-4.31053200	4.41456700	-0.47862700
H	-3.84346900	3.53470000	1.82082100
H	-2.66858700	4.78156100	1.38391100
H	-0.97978200	3.06688600	0.75922300
H	-1.52804900	2.80045600	2.42235100
H	-4.83688500	2.01829500	-0.08108500
H	-4.26770700	2.24233300	-1.73891400
H	-1.97520600	1.49185800	-1.15248200
H	-3.05715100	0.95675300	1.72363300
H	-2.66840700	4.01565000	-0.99948900
H	-0.28071600	0.75744000	0.48355300
C	-1.18438300	-0.86212200	1.47964500
O	-2.08915600	-1.28550600	2.18105600
N	-1.06529000	0.46780000	1.11411000
C	-0.08831300	-1.82618500	0.94016600
C	-0.11500400	-3.14265300	1.74606900
H	-0.30007700	-1.98161100	-0.15602100
C	1.68616200	-1.66681200	2.55922700
C	0.92214200	-2.96936800	2.87304900
H	0.12454400	-4.00375800	1.10158800
H	-1.13177500	-3.32611500	2.15772600
H	2.78411400	-1.78002700	2.67412200

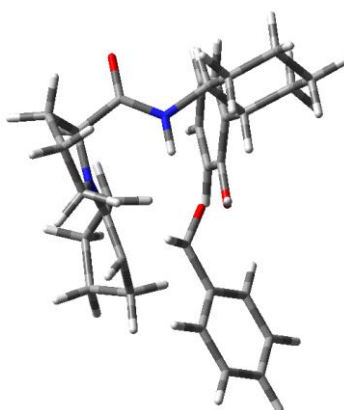
H	1.36024400	-0.83639300	3.22504500
H	1.60195100	-3.83538900	2.92411200
H	0.42155500	-2.90060300	3.85625900
N	1.29931100	-1.30616900	1.15527100
C	-3.31745900	-0.15078300	-0.76469300
C	-2.54799300	-1.04364700	-1.54511100
C	-4.54694200	-0.61765000	-0.28090500
C	-3.00529200	-2.33594800	-1.86683300
C	-5.01182300	-1.89975300	-0.58517300
H	-5.15215000	0.03323700	0.35222100
C	-4.24220900	-2.75372800	-1.38362100
H	-2.38700600	-2.97705500	-2.48750400
H	-5.96808500	-2.23565600	-0.19466500
H	-4.60902100	-3.75020700	-1.62445900
O	-1.30465300	-0.75636700	-2.02135500
C	2.20298300	-1.14745100	0.13918500
C	1.83457100	-0.96804500	-1.20969900
H	0.81969100	-1.27375600	-1.51603600
C	2.91398100	-1.31519300	-2.21462500
H	3.56370600	-0.44252700	-2.42613500
H	2.44741200	-1.59502600	-3.17943700
C	3.78716400	-2.47296300	-1.70095600
H	4.55787100	-2.72682900	-2.45163100
H	3.16081500	-3.37988200	-1.59194900
C	4.45439900	-2.13620500	-0.35816000
H	5.47826100	-1.75203000	-0.53304100
H	4.57364500	-3.06325100	0.23438400
H	-0.98430000	0.21755100	-1.79371800
C	3.67554100	-1.09354200	0.46844700
H	3.89240500	-1.23503600	1.54740500
H	4.05379000	-0.07101700	0.22850000
O	0.25320600	1.09605400	-1.16154100
C	1.44709100	0.94676700	-1.55206800
H	1.62199800	0.82730200	-2.63450900
C	4.47925400	3.11249200	0.60865900
C	3.24640100	2.84156900	1.21320500
C	2.26843500	2.12983200	0.51586100
C	2.51913600	1.67985500	-0.78940300
C	3.75077100	1.96228300	-1.39605600
C	4.72934400	2.67455900	-0.69545000
H	5.24005000	3.67169200	1.15080500
H	3.04595200	3.19444400	2.22344600
H	1.29500400	1.92585700	0.97131400
H	3.94843400	1.63269900	-2.41596200
H	5.68376500	2.89531400	-1.17016400

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### Structure of TS3



Electronic Energy (a.u)	-1501.285707
EE + Zero-point Energy (a.u)	-1500.656332
EE + Thermal Energy Correction (a.u)	-1500.626622
EE + Thermal Enthalpy Correction (a.u)	-1500.625678
EE + Thermal Free Energy Correction (a.u)	-1500.715901

C	-2.76014400	-0.04434300	-2.69145200
C	-3.60747900	-1.18259000	-3.26709500
C	-3.04007400	-2.54408900	-2.84744500
C	-2.98444400	-2.65802200	-1.32115000
C	-2.15162500	-1.52362500	-0.68634200
C	-2.66908200	-0.13279600	-1.15143800
H	-3.65970000	-3.36012900	-3.26358500
H	-4.65597400	-1.08682100	-2.92424100
H	-3.63931100	-1.10614000	-4.36998600
H	-1.74473900	-0.07599200	-3.13350000
H	-3.19010100	0.93404200	-2.97777100
H	-4.01191700	-2.65056100	-0.90867400
H	-2.55011100	-3.63295700	-1.02648900
H	-1.08521500	-1.63143500	-1.04130900
H	-3.67360300	0.07935400	-0.69960800
H	-2.02796700	-2.68025400	-3.27544800
H	-0.69795300	0.68372500	-0.87416500
C	-2.10333000	2.04431500	-0.04596400
O	-3.27558600	2.30260100	0.20102900
N	-1.69983300	0.90990400	-0.70020200
C	-1.03194900	3.08553200	0.39012700
C	-1.24199900	4.38883100	-0.40739900
H	-1.17658800	3.25317400	1.49005300
C	0.91113200	3.41360200	-1.09065800
C	-0.20975500	4.36243100	-1.54632800
H	-1.09320300	5.26803300	0.24544200
H	-2.28018300	4.46403500	-0.78801700
H	1.83427800	3.96754100	-0.81488100
H	1.17769300	2.67711500	-1.88150000
H	0.17741200	5.37295000	-1.76152600
H	-0.67421200	3.99982000	-2.48271900
N	0.38109900	2.70067400	0.11469000
C	-2.18529200	-1.66753100	0.81534200
C	-1.01501200	-1.97351900	1.54520700
C	-3.38465900	-1.56042400	1.53181700
C	-1.04941400	-2.22219300	2.93131100
C	-3.43014600	-1.78388400	2.91038600
H	-4.30207600	-1.29769100	1.00288500
C	-2.26449500	-2.13035000	3.60404700
H	-0.12803900	-2.48296100	3.44414700
H	-4.37275500	-1.69231600	3.44272400
H	-2.30635300	-2.32306200	4.67499100
O	0.22836500	-2.04179100	0.99261300
C	2.37283900	1.32663600	0.39757900
C	1.09983200	1.77697500	0.81269400
H	3.01849300	1.97789200	-0.18534600
C	0.49880300	1.14152500	2.03324900



H	0.34816600	0.05088200	1.79434600
H	-0.50349800	1.51646700	2.30746300
C	1.45559800	1.25834600	3.23441200
H	1.19177200	0.46820100	3.96533000
H	1.28761600	2.22153100	3.75094700
C	2.93701400	1.13303800	2.83878400
H	3.47576500	0.52182200	3.58579700
H	3.41616600	2.12959200	2.85753000
C	3.10523400	0.51039000	1.44152100
H	2.71255400	-0.53004900	1.46158500
H	4.17672800	0.42791000	1.18324200
C	1.92631600	0.10404200	-1.14530600
O	0.77304700	-0.36955700	-0.93557400
H	0.28835600	-1.60738200	0.03750900
H	1.98235500	0.96208500	-1.84119200
C	5.32275300	-2.53025200	-1.22699200
C	4.11329100	-2.96924400	-0.68020700
C	3.01179700	-2.10988200	-0.63809900
C	3.11666400	-0.80714300	-1.14530700
C	4.33299400	-0.36807800	-1.69121600
C	5.43183000	-1.22924800	-1.73197300
H	6.18049100	-3.19998400	-1.26044300
H	4.02638700	-3.98042000	-0.28533200
H	2.06189500	-2.44662900	-0.20691500
H	4.42468500	0.64297000	-2.08292500
H	6.37401500	-0.88914100	-2.15700900

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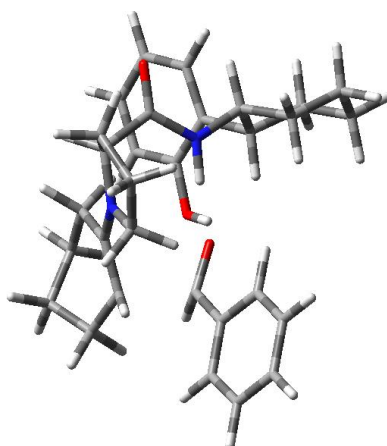
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**Structure of TS4**



Electronic Energy (a.u)	-1501.288463
EE + Zero-point Energy (a.u)	-1500.659006
EE + Thermal Energy Correction (a.u)	-1500.629617
EE + Thermal Enthalpy Correction (a.u)	-1500.628673
EE + Thermal Free Energy Correction (a.u)	-1500.717311

C	-1.25366700	3.25965400	0.43010000
C	-2.19198600	4.23053500	-0.29337600
C	-2.53752100	3.70802600	-1.69331400
C	-3.18356400	2.32166300	-1.61026300
C	-2.28116800	1.30833200	-0.87484300
C	-1.87538300	1.84891600	0.52475700
H	-3.22081500	4.41151500	-2.20449900
H	-3.11811100	4.37422400	0.29631000
H	-1.71827400	5.22735300	-0.36483100
H	-0.28411200	3.21283300	-0.10395600
H	-1.02795200	3.63232600	1.44681800
H	-4.16406200	2.39515500	-1.10150700
H	-3.40091100	1.94019100	-2.62689100
H	-1.33602600	1.17560000	-1.47934200
H	-2.76845300	1.87163400	1.20389300
H	-1.62329900	3.66320100	-2.31654800
H	-0.02350200	0.75064700	0.49473700
C	-1.05172700	0.27537800	2.28803200
O	-2.04842400	0.42678300	2.98376800
N	-0.84139500	0.94394700	1.10871600

C	0.05229200	-0.68636400	2.81087100
C	0.70014000	-0.06626400	4.06638100
H	-0.45286000	-1.65718800	3.05490800
C	2.36927200	-0.07115900	2.25678300
C	1.99552400	0.60660500	3.58530000
H	0.91184100	-0.84876100	4.81738800
H	0.01562900	0.65229900	4.55912200
H	3.26883800	-0.71557500	2.35985500
H	2.57711600	0.67397400	1.45650000
H	2.80217400	0.50581900	4.33137600
H	1.83931800	1.69216300	3.43992700
N	1.19114600	-0.91588300	1.87709700
C	-2.99367400	-0.01874300	-0.78619000
C	-2.50521800	-1.14639100	-1.48601500
C	-4.18728300	-0.16681200	-0.06964800
C	-3.21994200	-2.35872000	-1.52614100
C	-4.89346800	-1.37334900	-0.07916300
H	-4.57433000	0.67438000	0.50740500
C	-4.41757000	-2.45934000	-0.82257100
H	-2.82717500	-3.18661400	-2.10844700
H	-5.81549900	-1.46443400	0.48805000
H	-4.98222300	-3.39016700	-0.84676200
O	-1.32451300	-1.14993900	-2.16257900
C	2.25852200	-1.77669700	-0.11105600
C	1.17096700	-1.74189500	0.79028300
H	3.21159400	-1.35967800	0.22572300
C	-0.07865900	-2.55288600	0.58117900
H	-0.94616100	-1.86874200	0.40360400
H	-0.32568100	-3.12744100	1.49894700
C	0.02973600	-3.51109200	-0.61311300
H	-0.20709600	-2.95293600	-1.55026200
H	-0.74008200	-4.29970700	-0.52919700
C	1.43020200	-4.11796400	-0.70113500
H	1.46962200	-4.87165700	-1.50960700
H	1.67155700	-4.66049300	0.23221900
C	2.46806300	-3.01651500	-0.95875600
H	2.44170900	-2.74177900	-2.03707200
H	3.48443000	-3.41741500	-0.77501600
C	1.79130100	-0.35237400	-1.42920900
H	1.78575900	-1.07830400	-2.26363500
O	0.68665600	0.17931900	-1.10215100
H	-0.67974300	-0.37630300	-1.85169800
C	4.03815400	2.63825300	-0.74375200
C	2.91373900	1.81184300	-0.81134500
C	3.02504100	0.50935900	-1.31827000
C	4.26722800	0.04517000	-1.77399100
C	5.39085300	0.87316400	-1.70574400

C	5.27825300	2.16840600	-1.18850300
H	3.94713200	3.65039300	-0.35393100
H	1.93331100	2.17253700	-0.48973800
H	4.35859800	-0.96124500	-2.18113800
H	6.35437400	0.51154100	-2.06047700
H	6.15460100	2.81246800	-1.13895500

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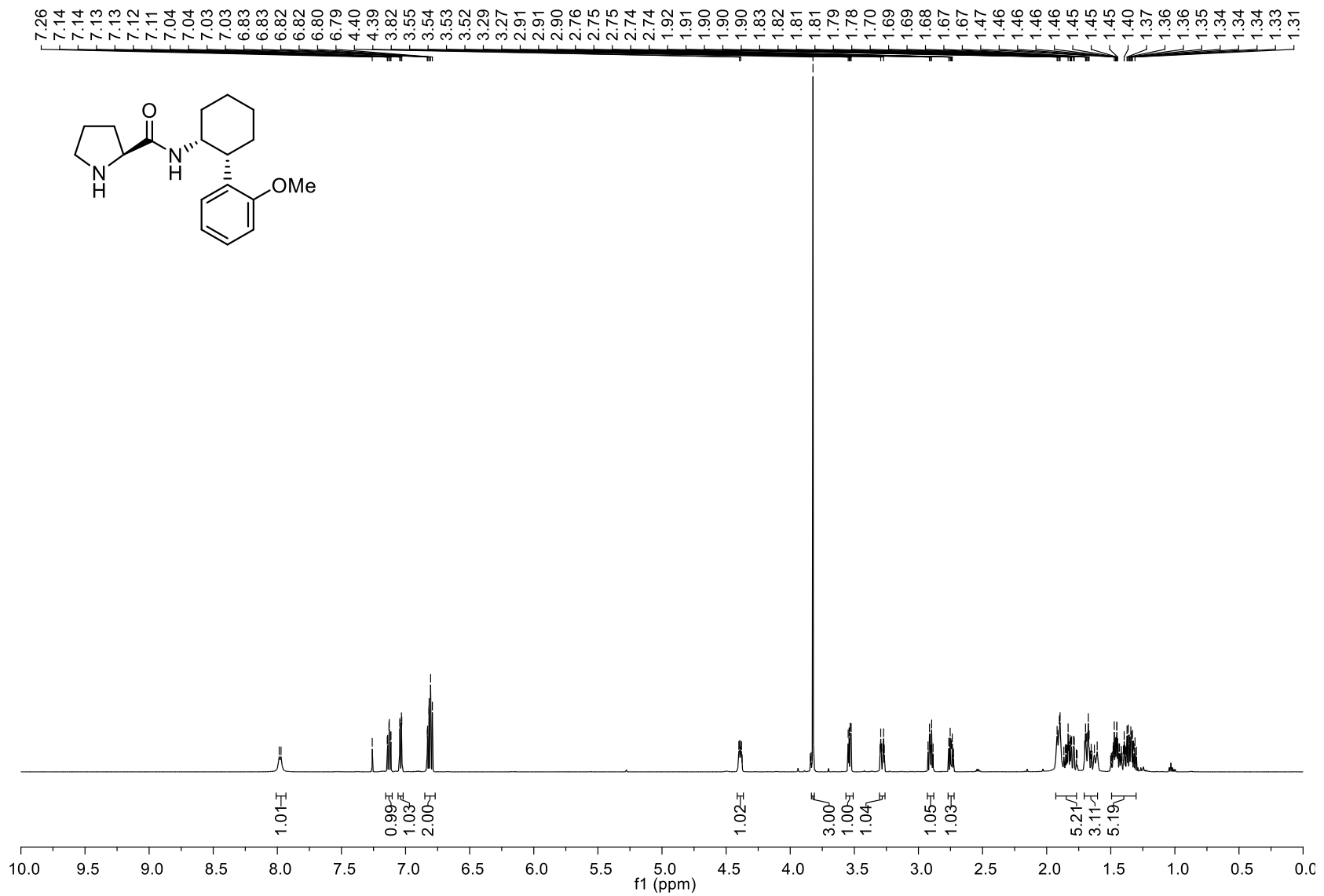
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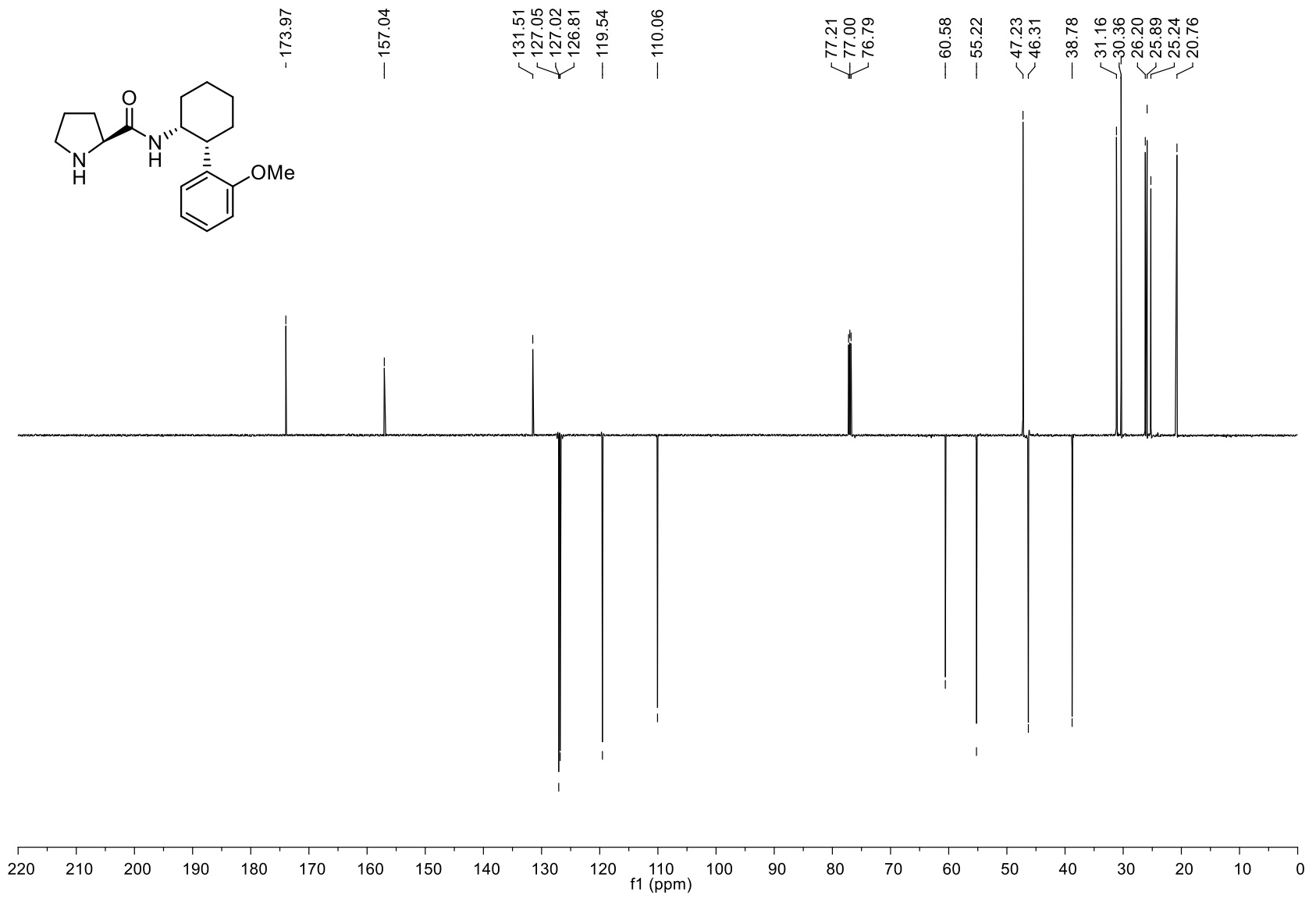
**Table S1.**  $R_f$  Values of the related diastereomers determined by thin layer chromatography.

entry	structure	$R_f$	structure	$R_f$	mobile phase
1	 (±)-20	0.67	 (±)-37	0.56	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3.5:1:0.25:0.25, v/v
2	 (±)-17	0.53	 (±)-18	0.49	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3:1:0.5:0.5, v/v
3	 (S,1R,2S)-21	0.93	 (S,1S,2R)-22	0.88	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3:1:0.5:0.5, v/v
4	 (S,1R,2R)-23	0.73	 (S,1S,2S)-24	0.68	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3:1:0.5:0.5, v/v
5	 (S,1S,2R)-25	0.35	 (S,1R,2S)-26	0.47	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 6.5:3:0.25:0.25, v/v
6	 (S,1R,2R)-27	0.68	 (S,1S,2S)-28	0.54	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3:1:0.5:0.5, v/v
7	 (S,1R,2R)-29	0.52	 (S,1S,2S)-30	0.42	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3:1:0.5:0.5, v/v
8	 (S,1S,2R)-31	0.30	 (S,1R,2S)-32	0.39	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3:1:0.5:0.5, v/v
9	 (S,1S,2R)-39	0.29	 (S,1R,2S)-40	0.36	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 6.5:3:0.25:0.25, v/v
10	 (S,1S,2R)-41	0.49	 (S,1R,2S)-42	0.52	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3.5:1:0.25:0.25, v/v
11	 (S,1S,2R)-43	0.16	 (S,1R,2S)-44	0.24	Hexane/EtOAc/NEt <sub>3</sub> /MeOH 3.5:1:0.25:0.25, v/v

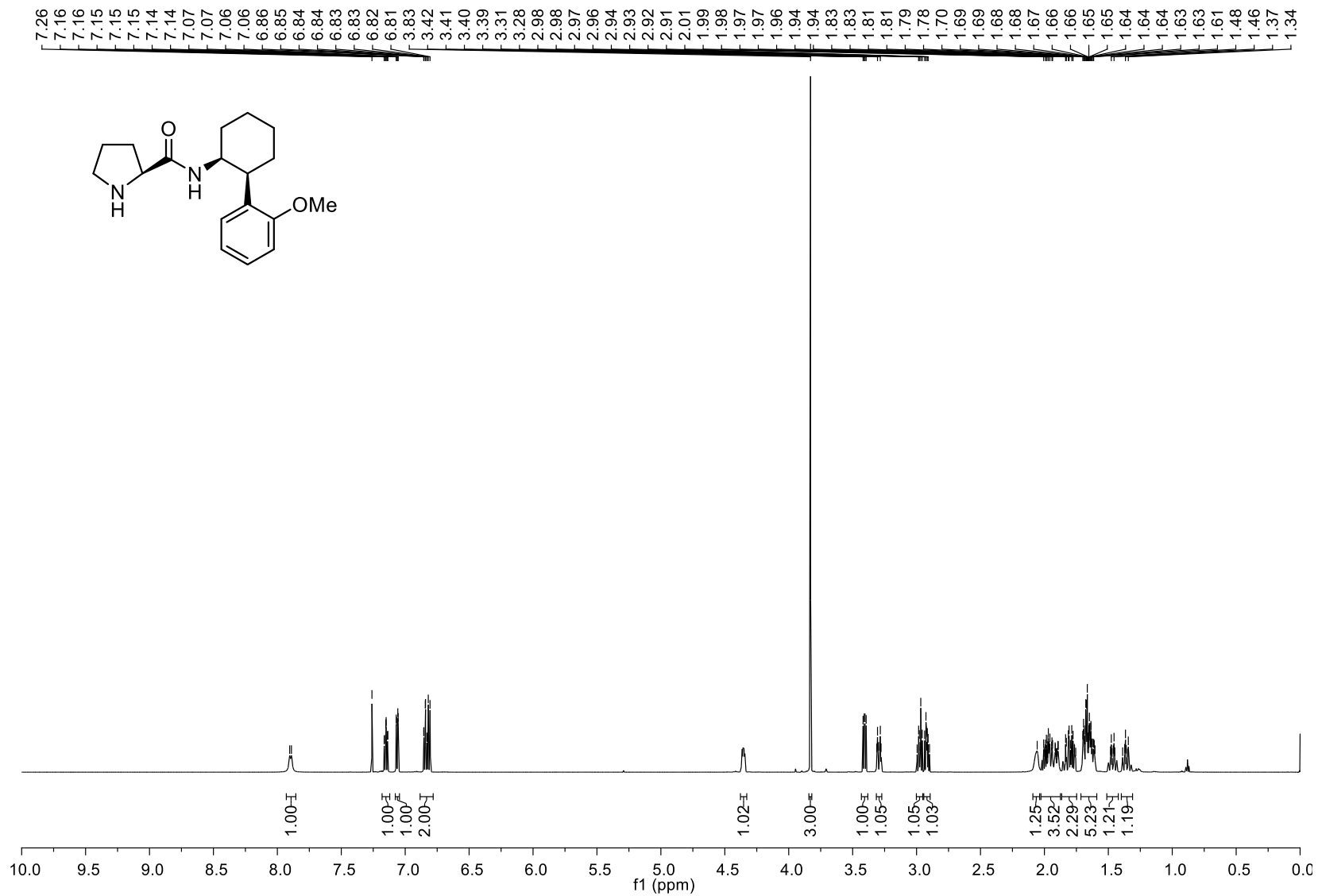


**<sup>1</sup>H NMR Spectrum of (S,1R,2R)-27 (600 MHz, CDCl<sub>3</sub>)**

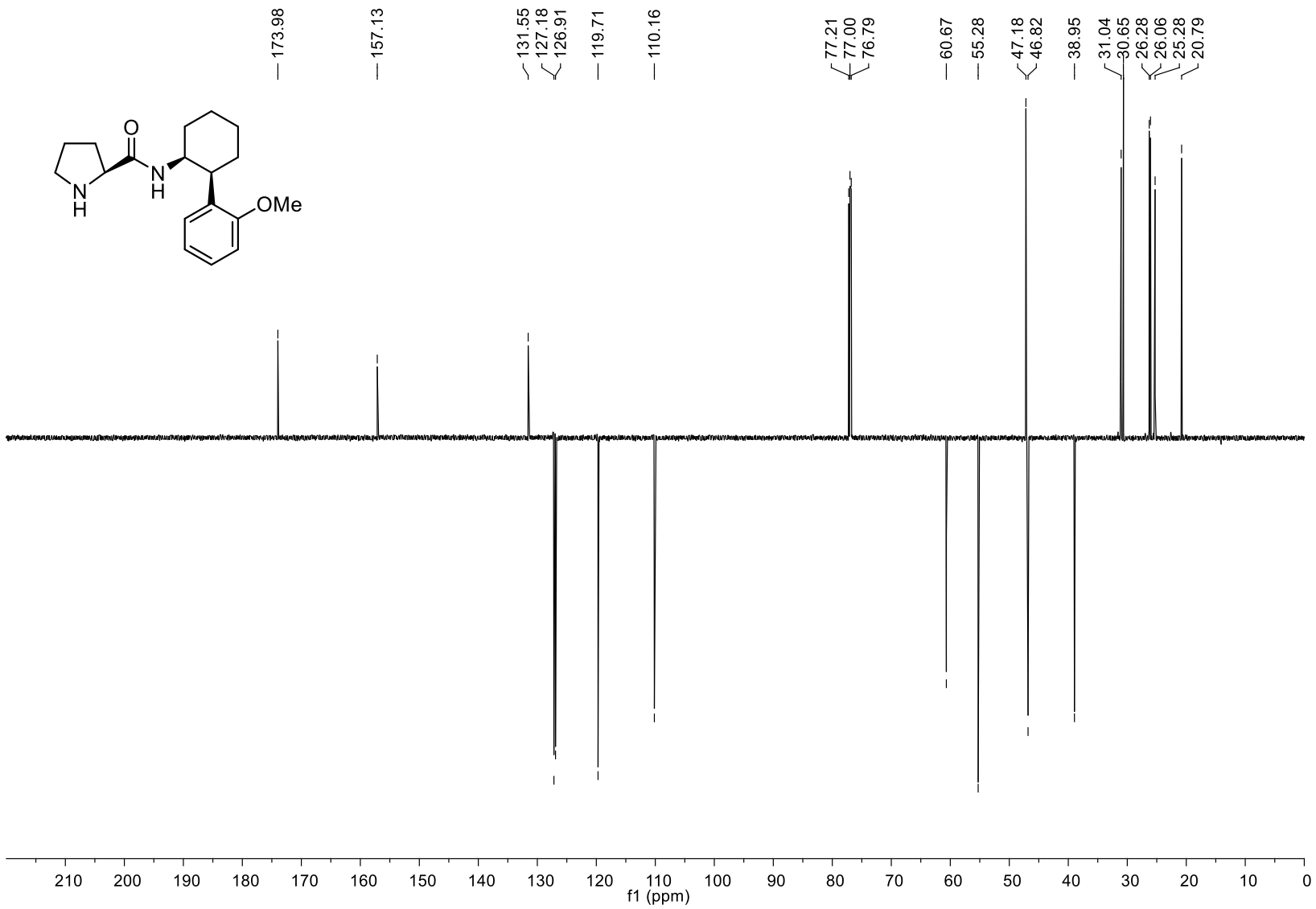




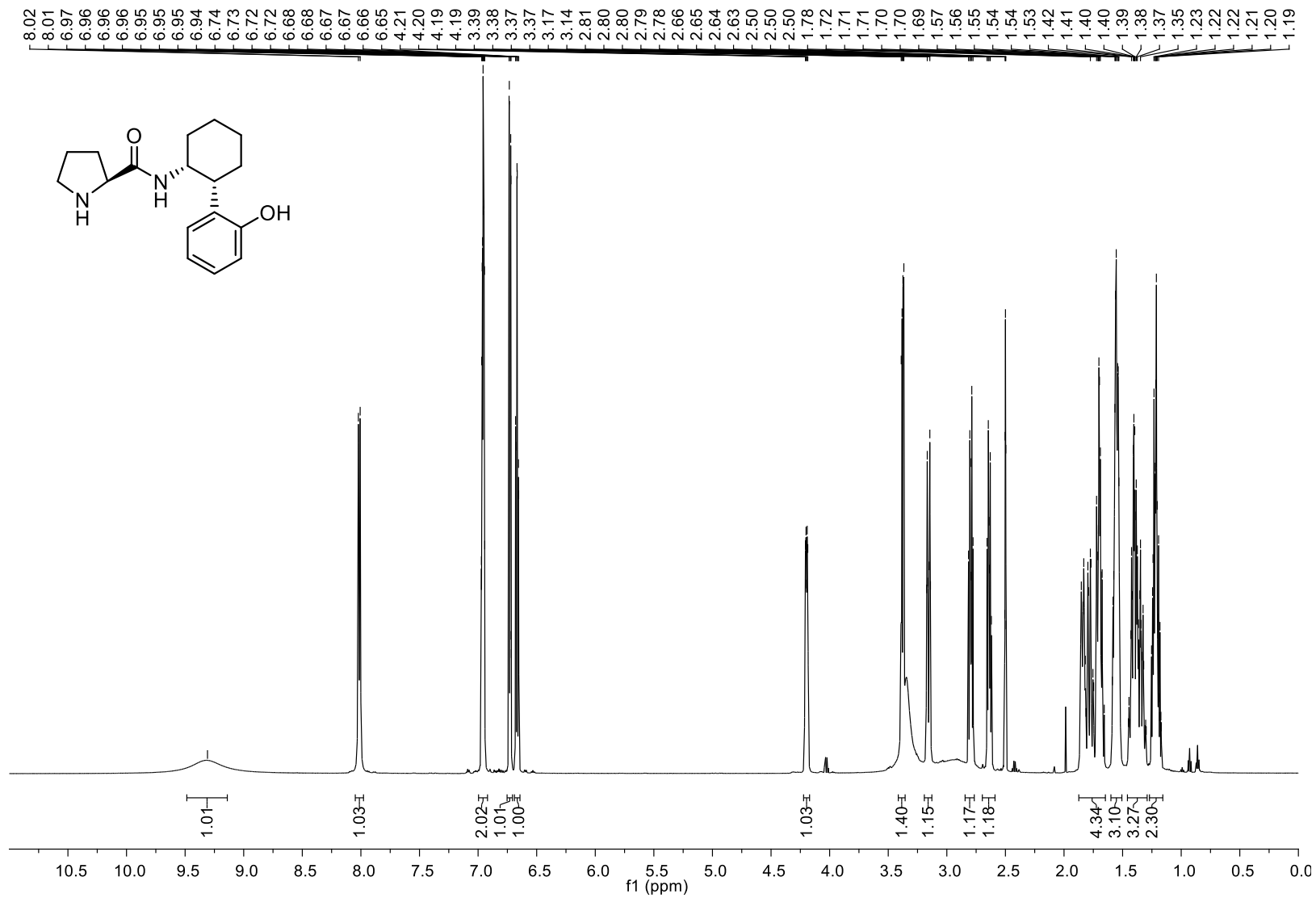
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (S,1R,2R)-27 (APT, 150 MHz, CDCl<sub>3</sub>)



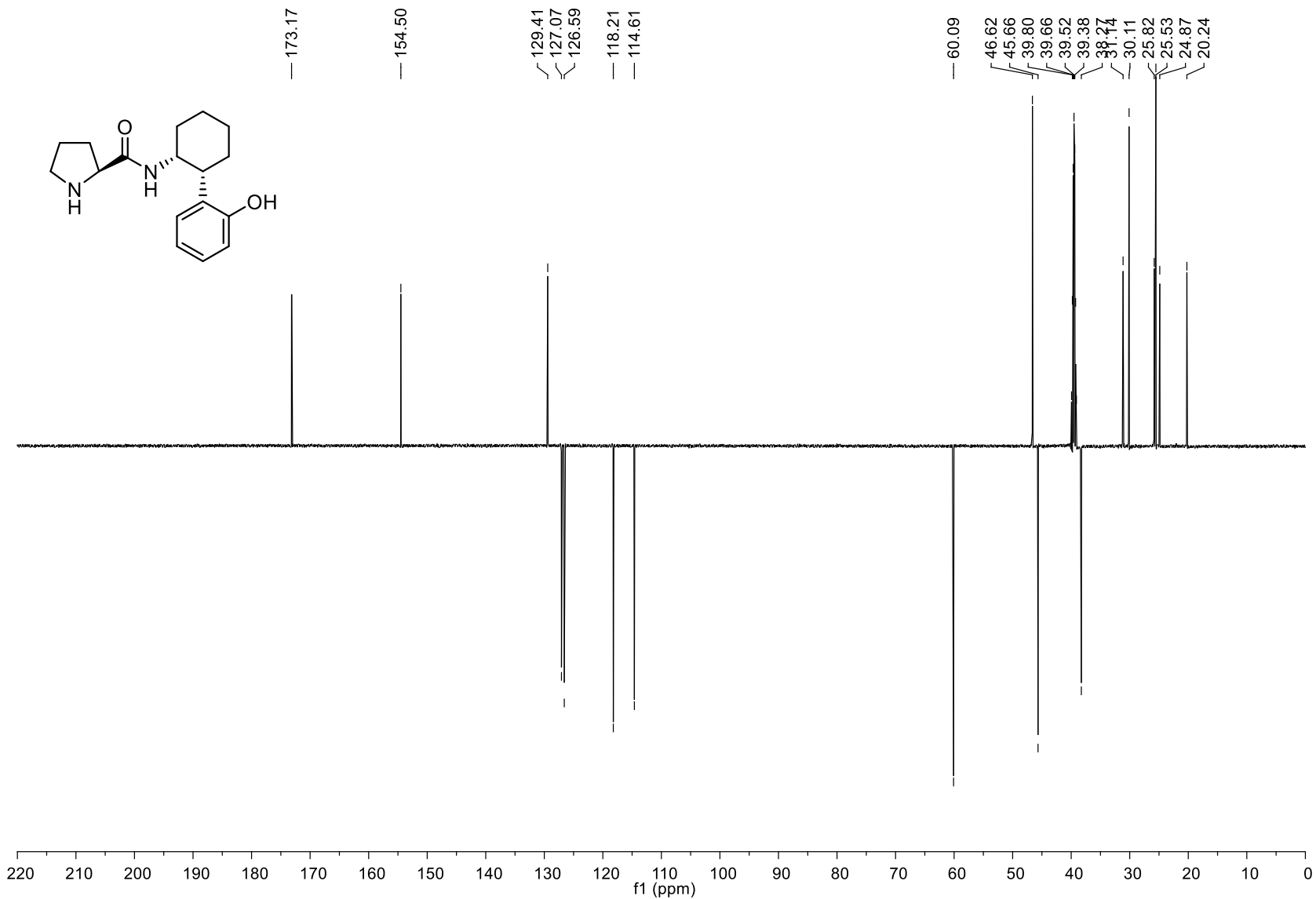
**<sup>1</sup>H NMR Spectrum of (S,1S,2S)-28 (600 MHz, CDCl<sub>3</sub>)**



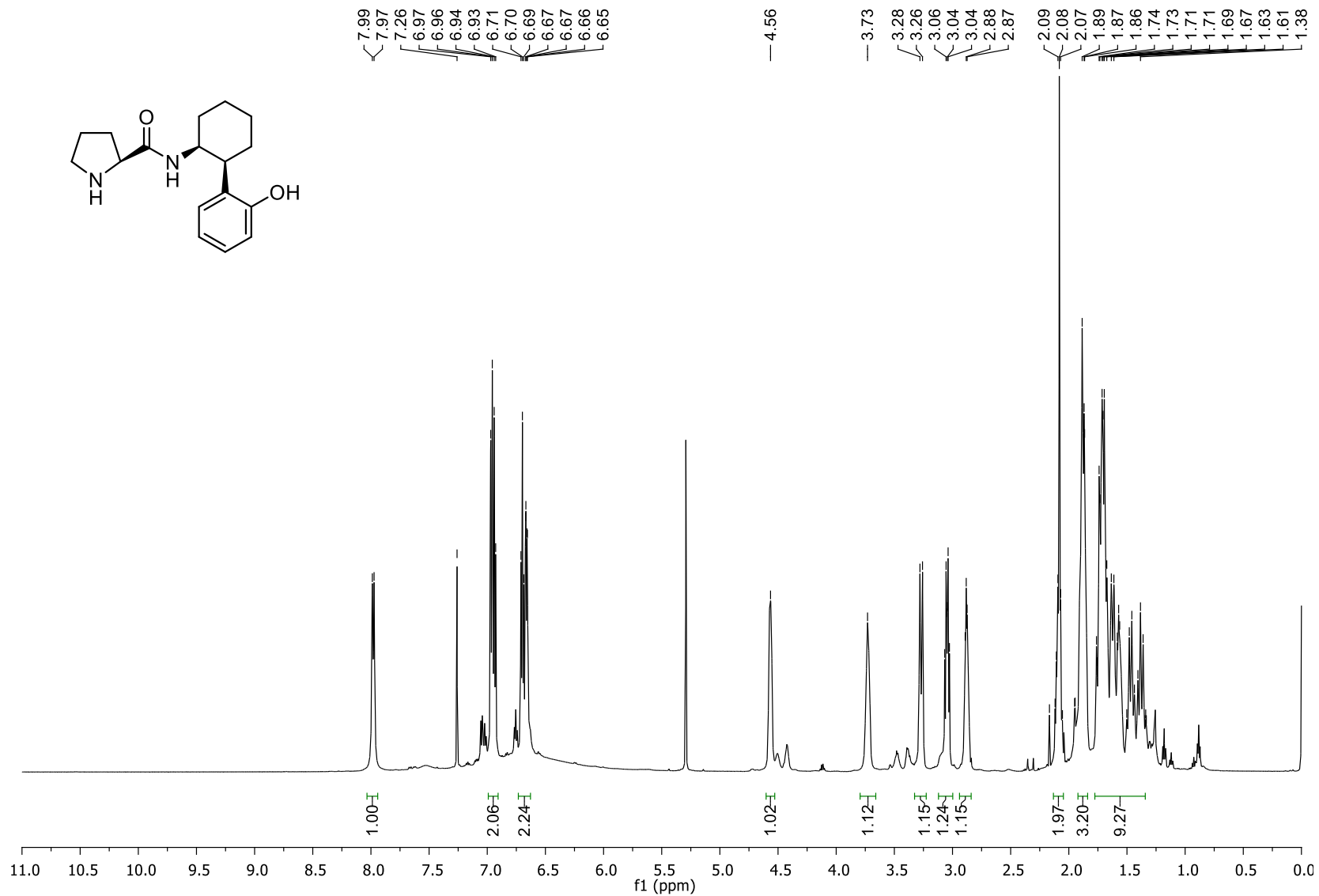
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (S,1S,2S)-28 (APT, 150 MHz,  $\text{CDCl}_3$ )



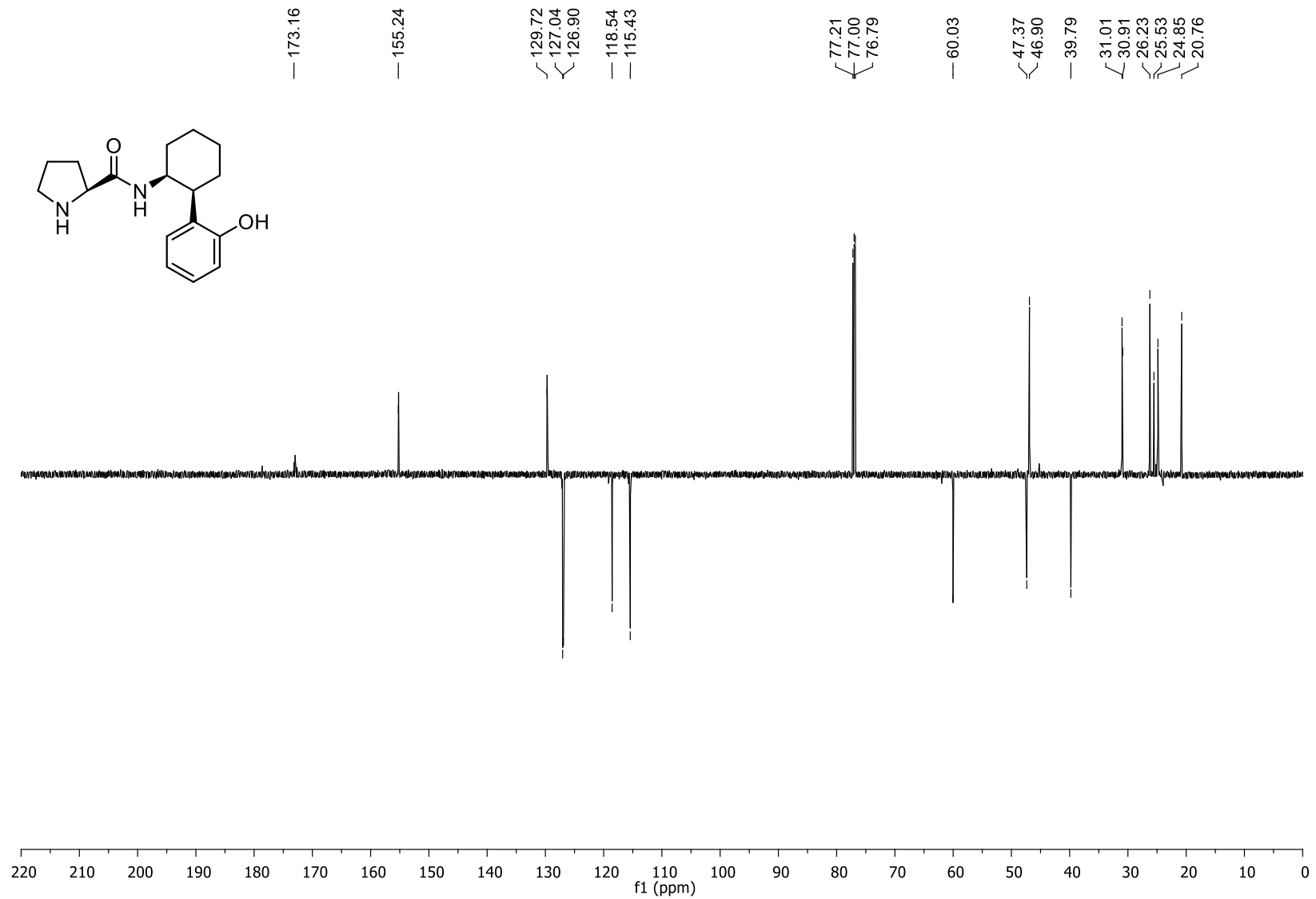
**<sup>1</sup>H NMR Spectrum of (S,1R,2R)-29 (600 MHz, DMSO-d<sub>6</sub>)**



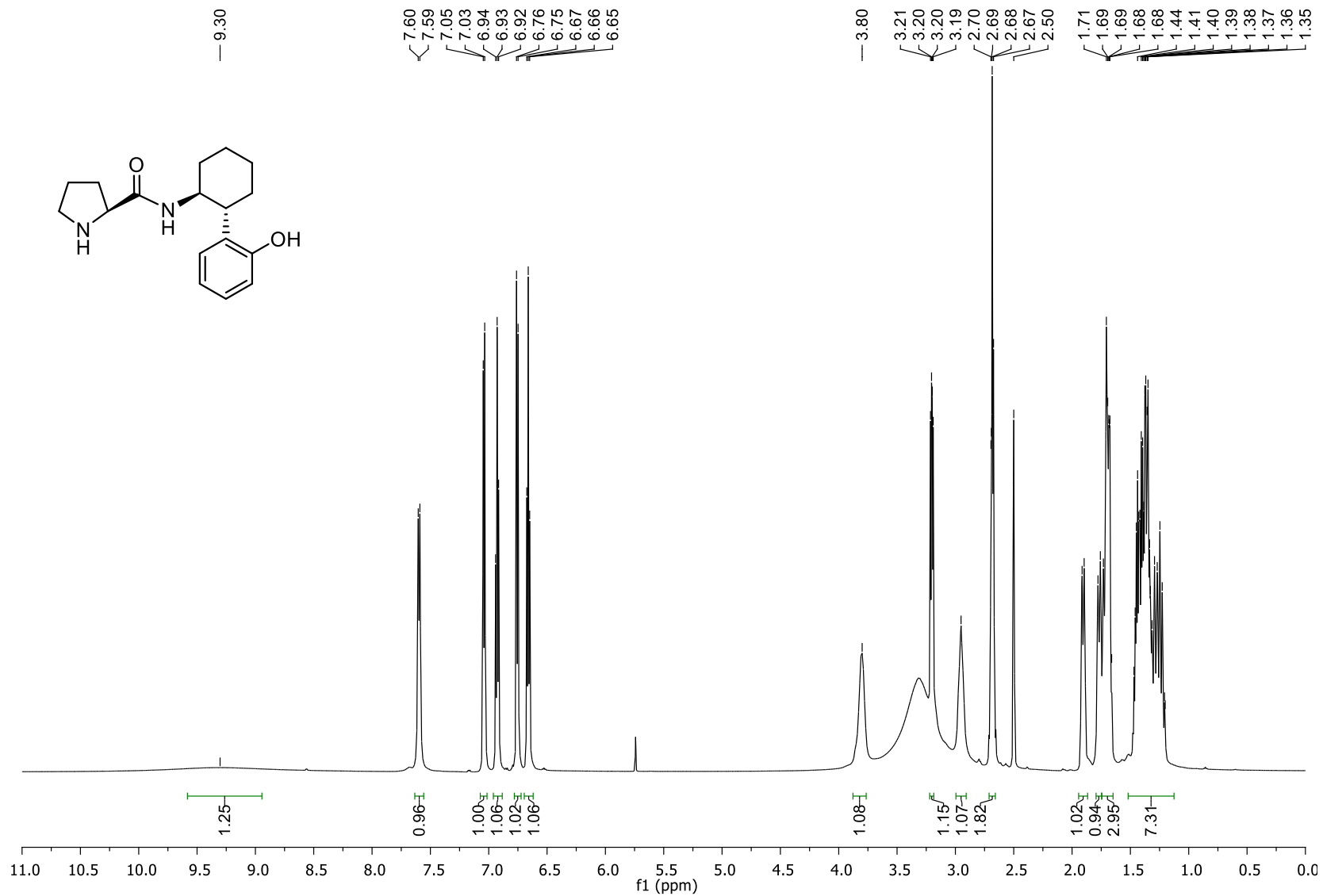
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (S,1R,2R)-29 (APT, 150 MHz, DMSO- $d_6$ )



<sup>1</sup>H NMR Spectrum of (S,1S,2S)-30 (600 MHz, CDCl<sub>3</sub>)

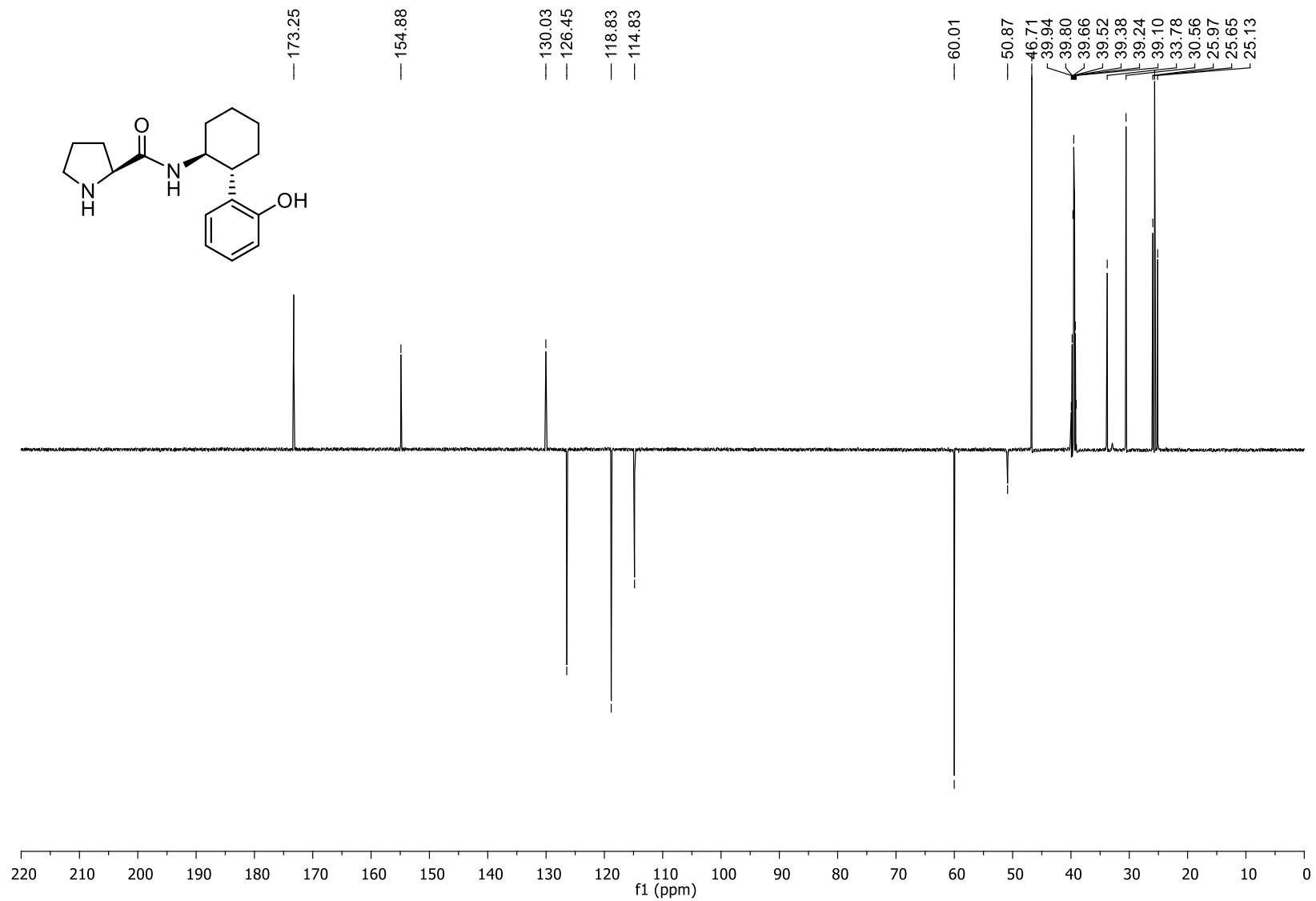


$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (S,1S,2S)-30 (APT, 150 MHz,  $\text{CDCl}_3$ )

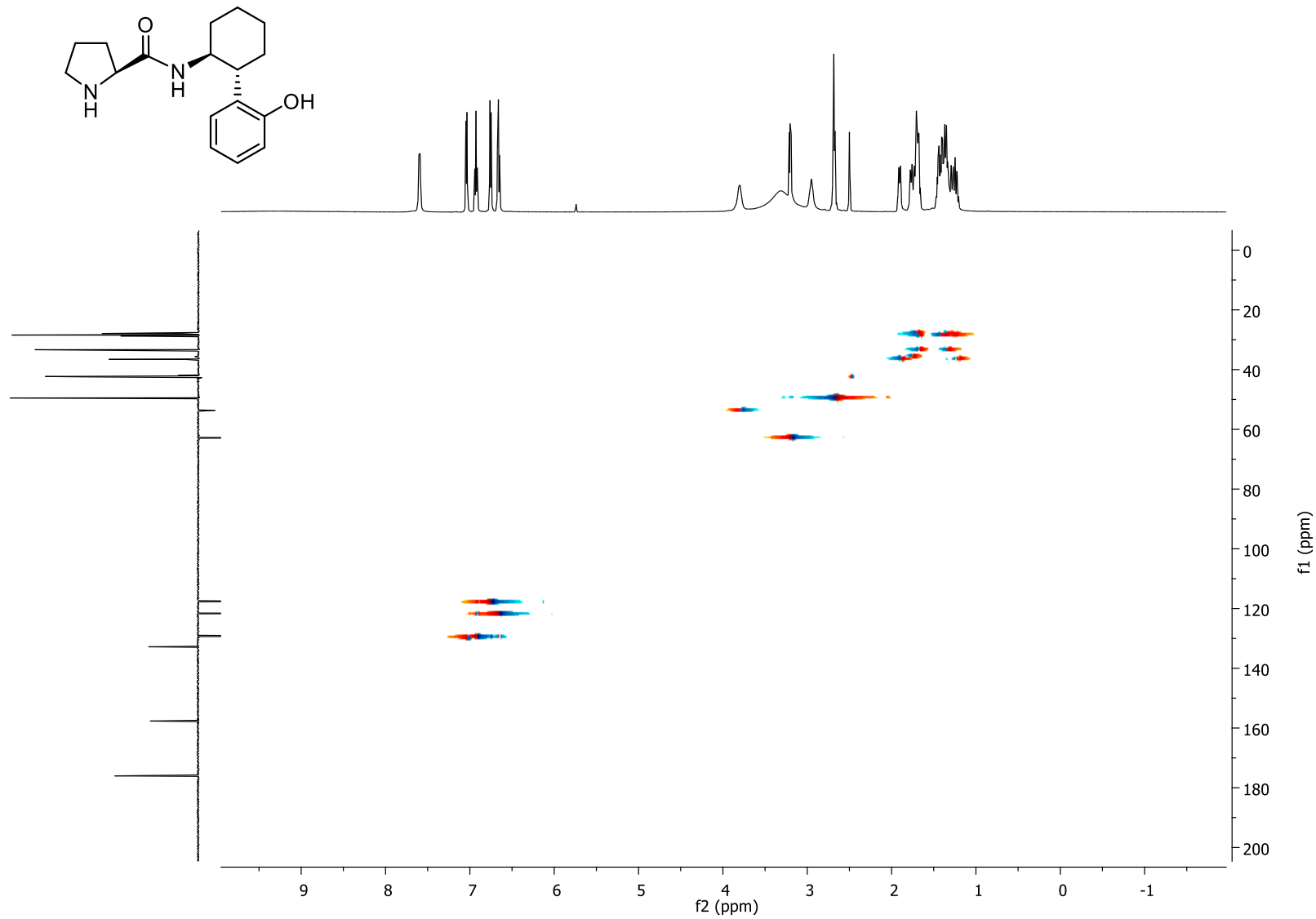


<sup>1</sup>H NMR Spectrum of (S,1S,2R)-31 (600 MHz, DMSO-d<sub>6</sub>)

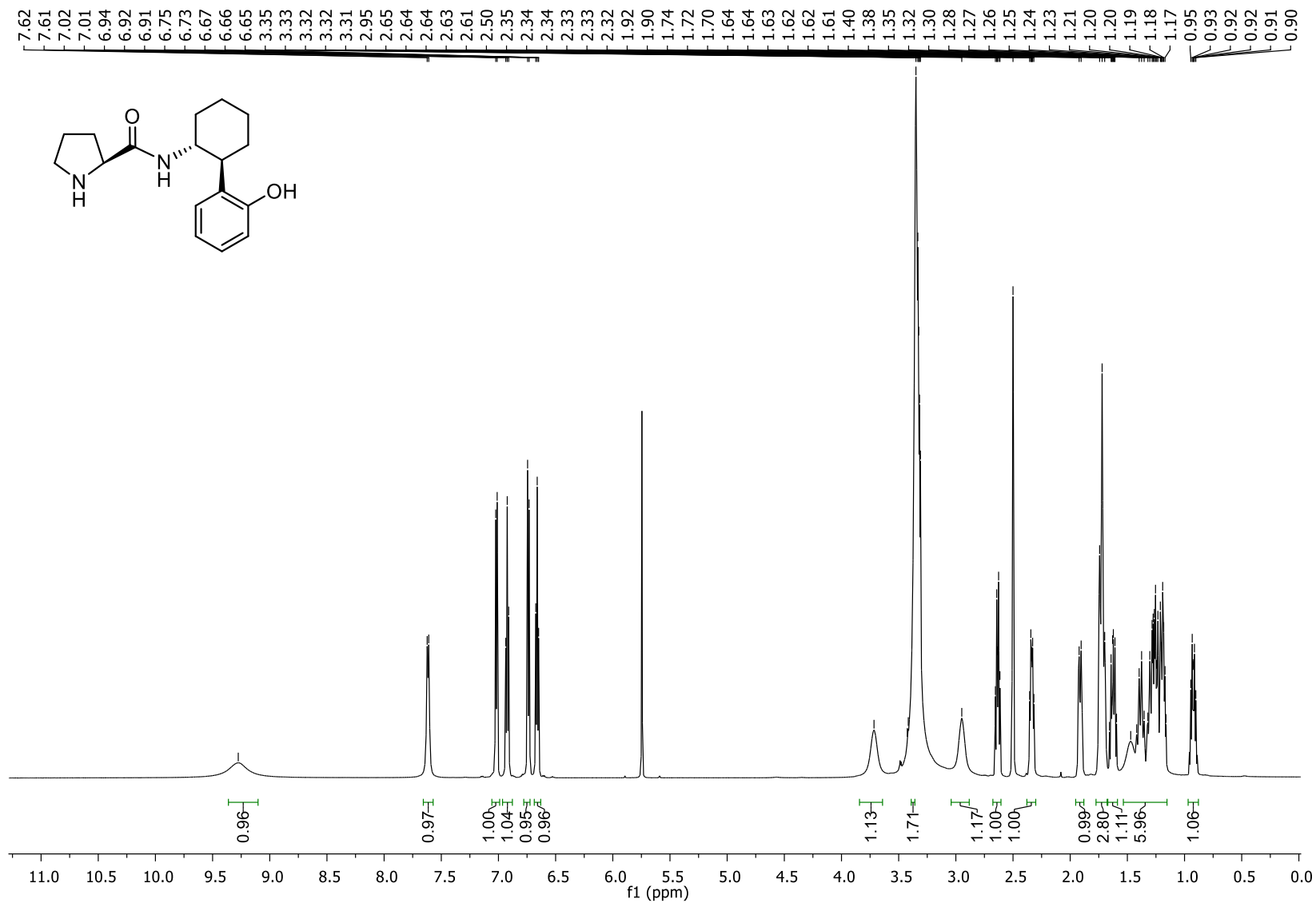




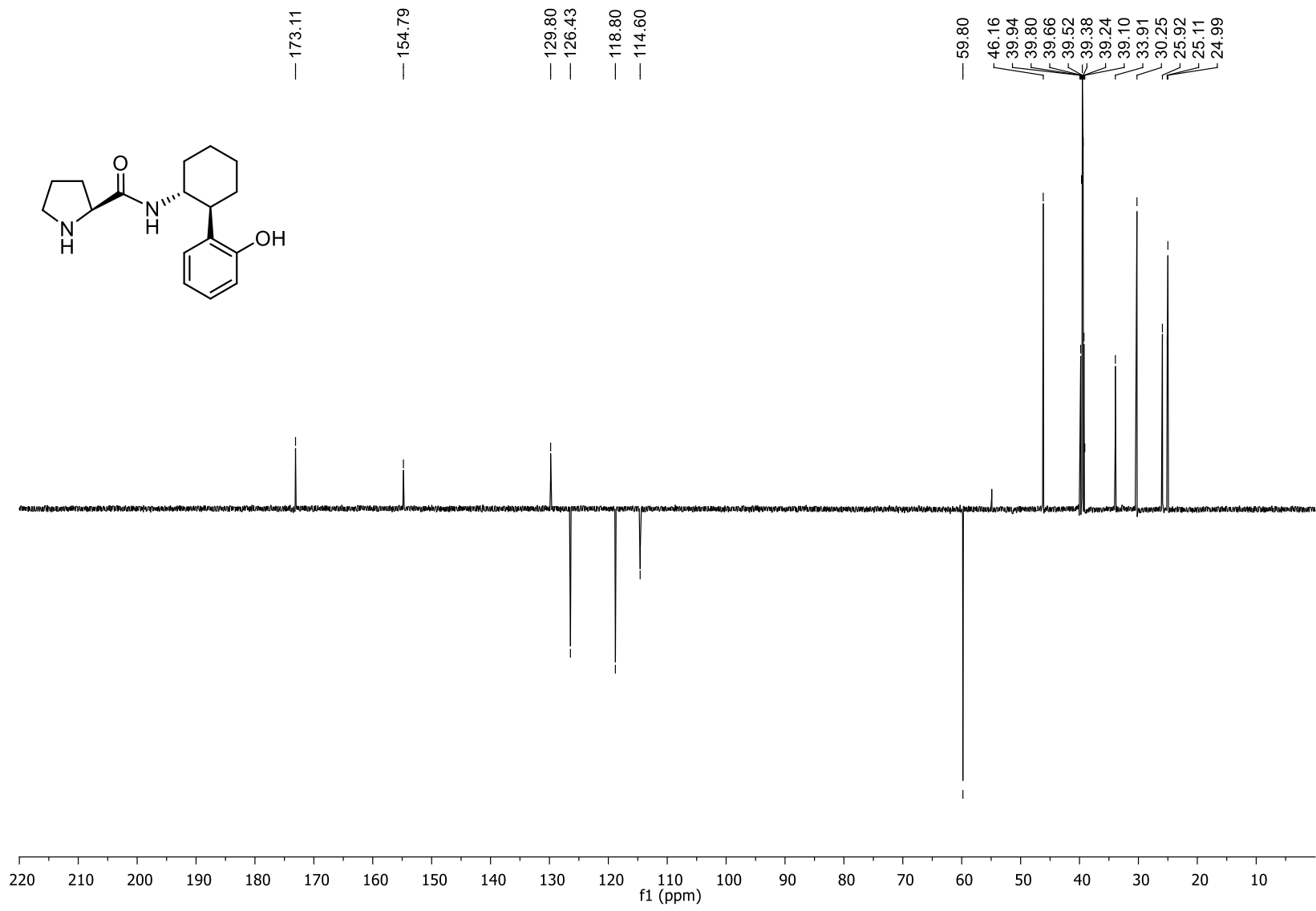
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (S,1S,2R)-31 (APT, 150 MHz, DMSO- $d_6$ )



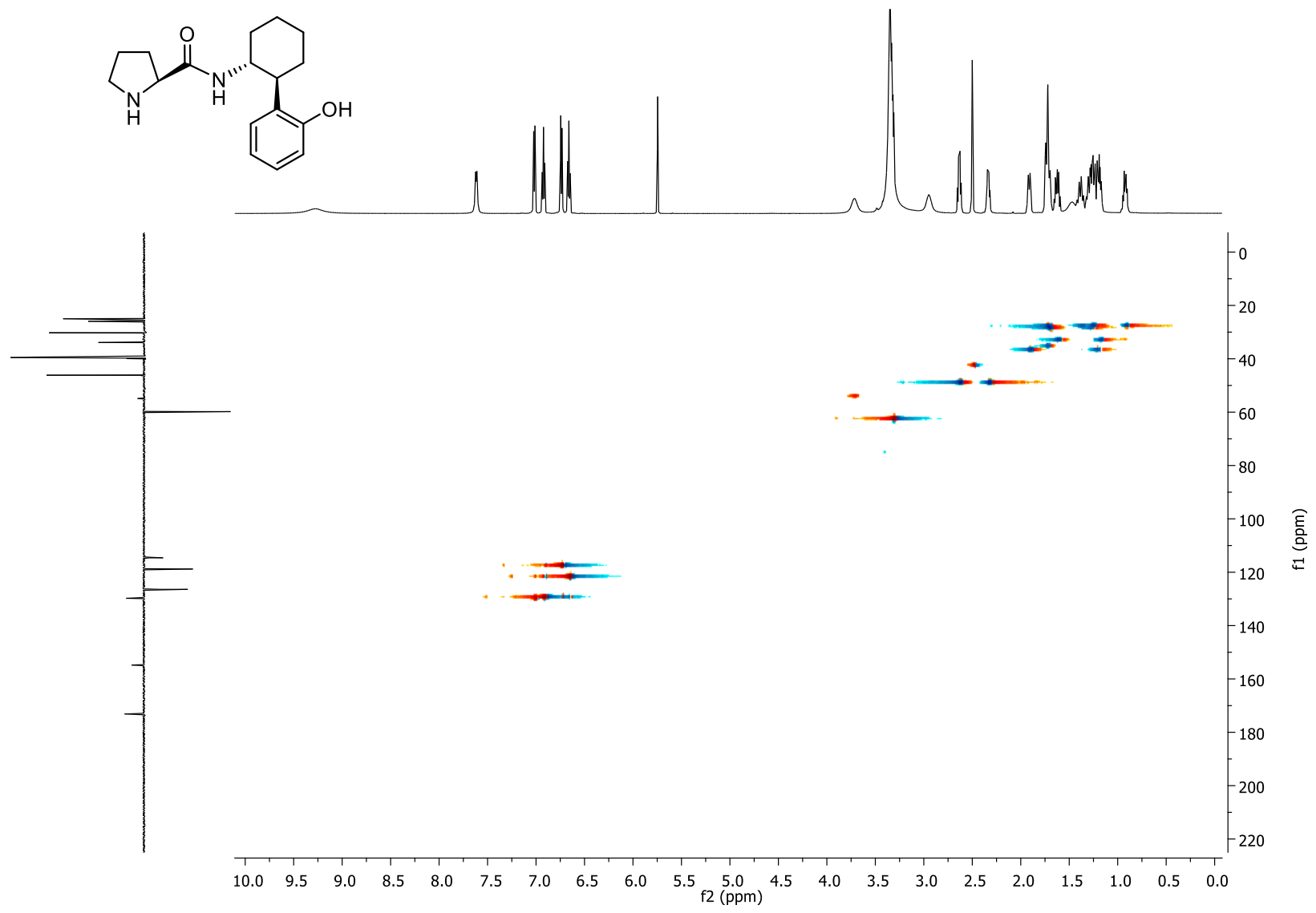
HSQC NMR Spectrum of (S,1S,2R)-31 (DMSO-*d*<sub>6</sub>)



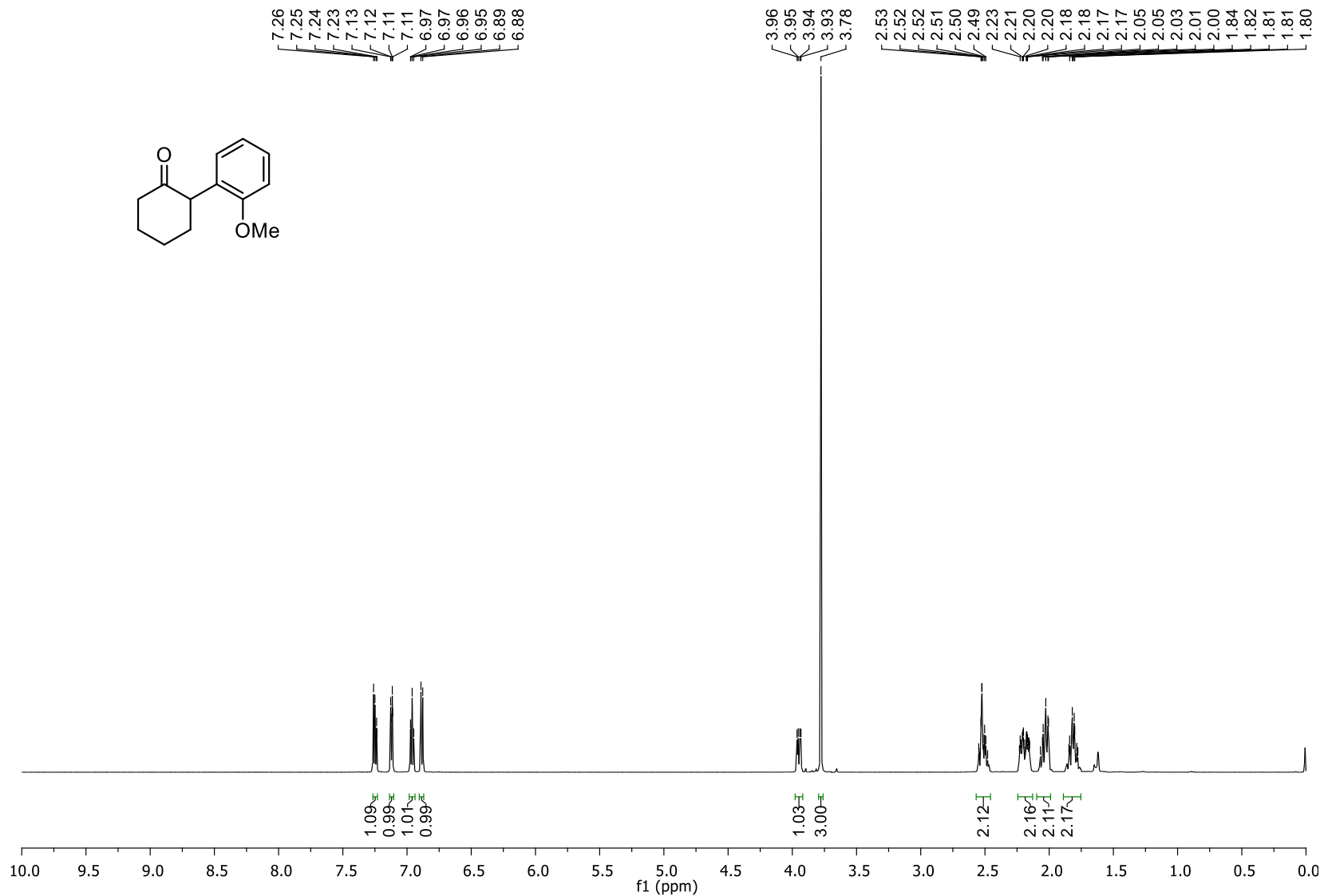
<sup>1</sup>H NMR Spectrum of (S,1R,2S)-32 (600 MHz, DMSO-d<sub>6</sub>)



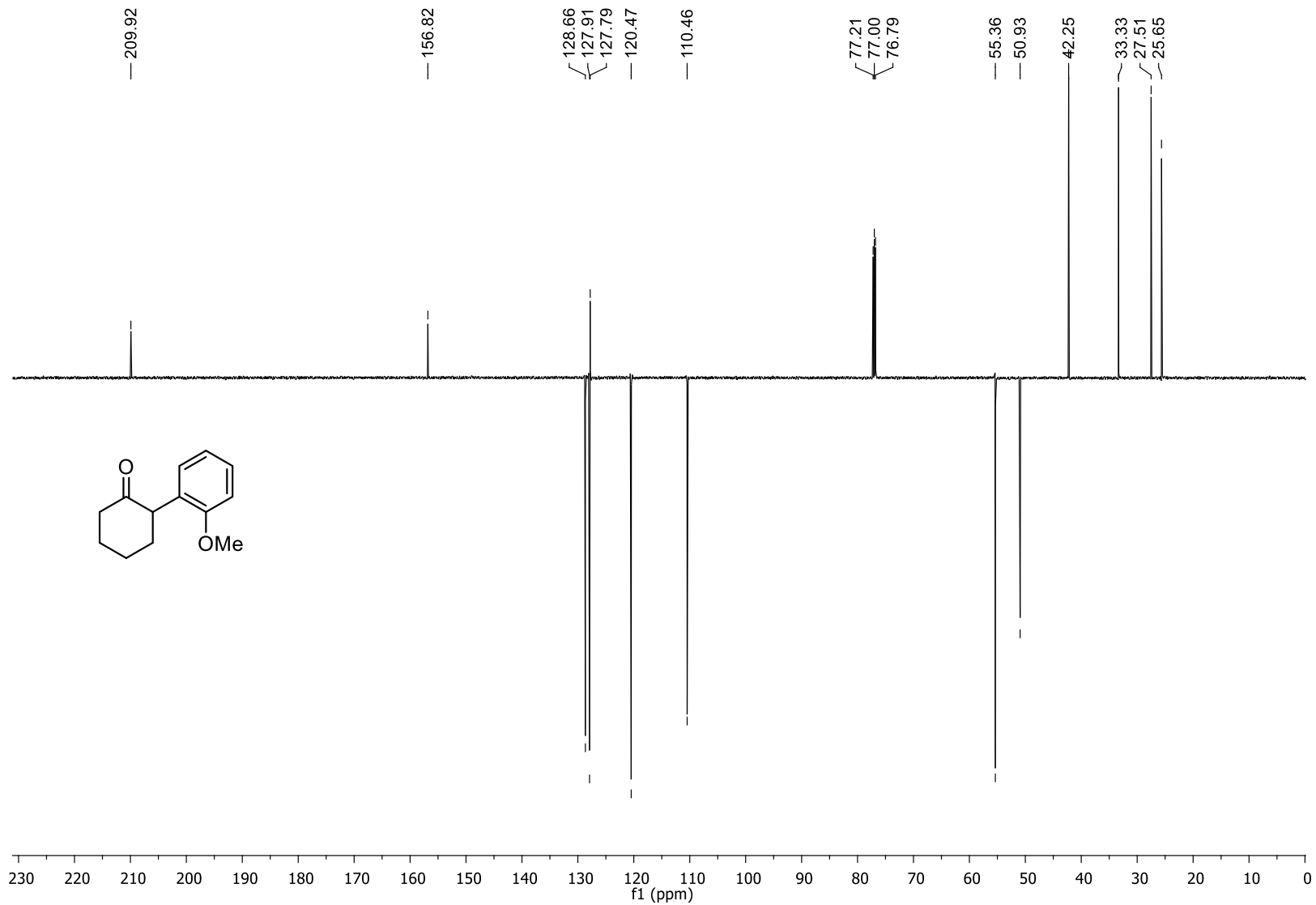
**$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (S,1R,2S)-32 (APT, 150 MHz, DMSO- $d_6$ )**



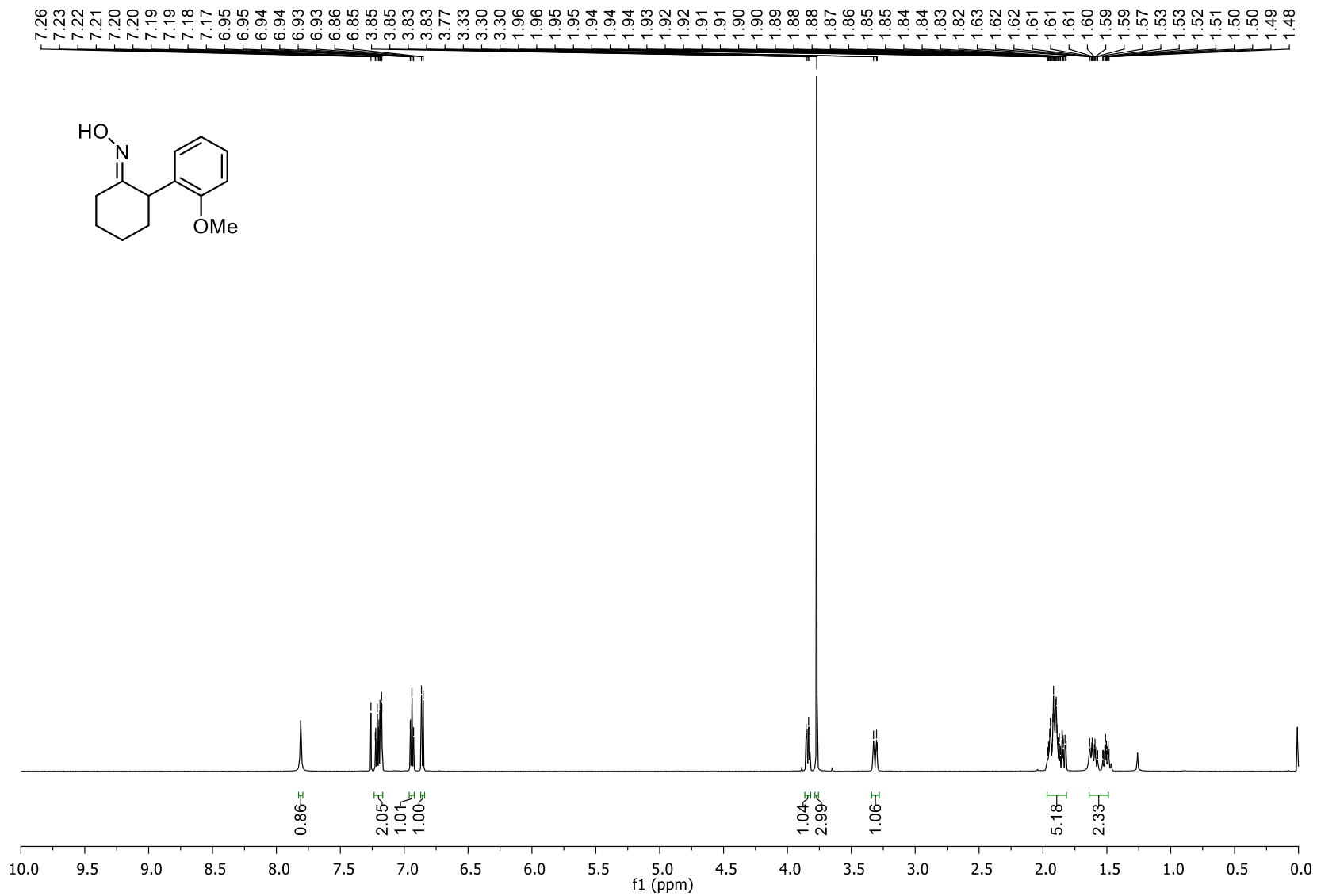
HSQC NMR Spectrum of (*S*,1*R*,2*S*)-32 (DMSO-*d*<sub>6</sub>)



**<sup>1</sup>H NMR Spectrum of (±)-35 (600 MHz, CDCl<sub>3</sub>)**

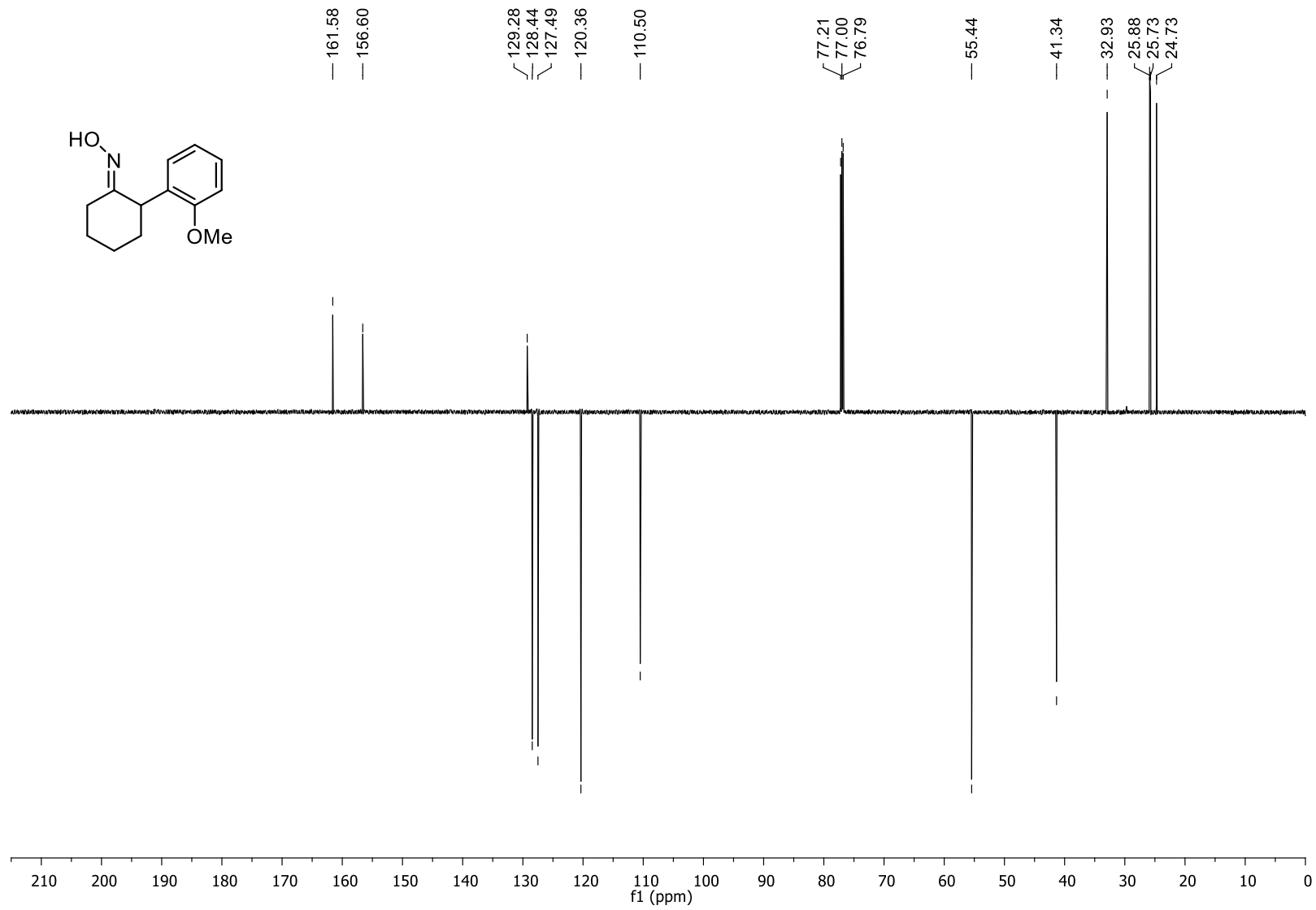


$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (±)-35 (APT, 150 MHz,  $\text{CDCl}_3$ )

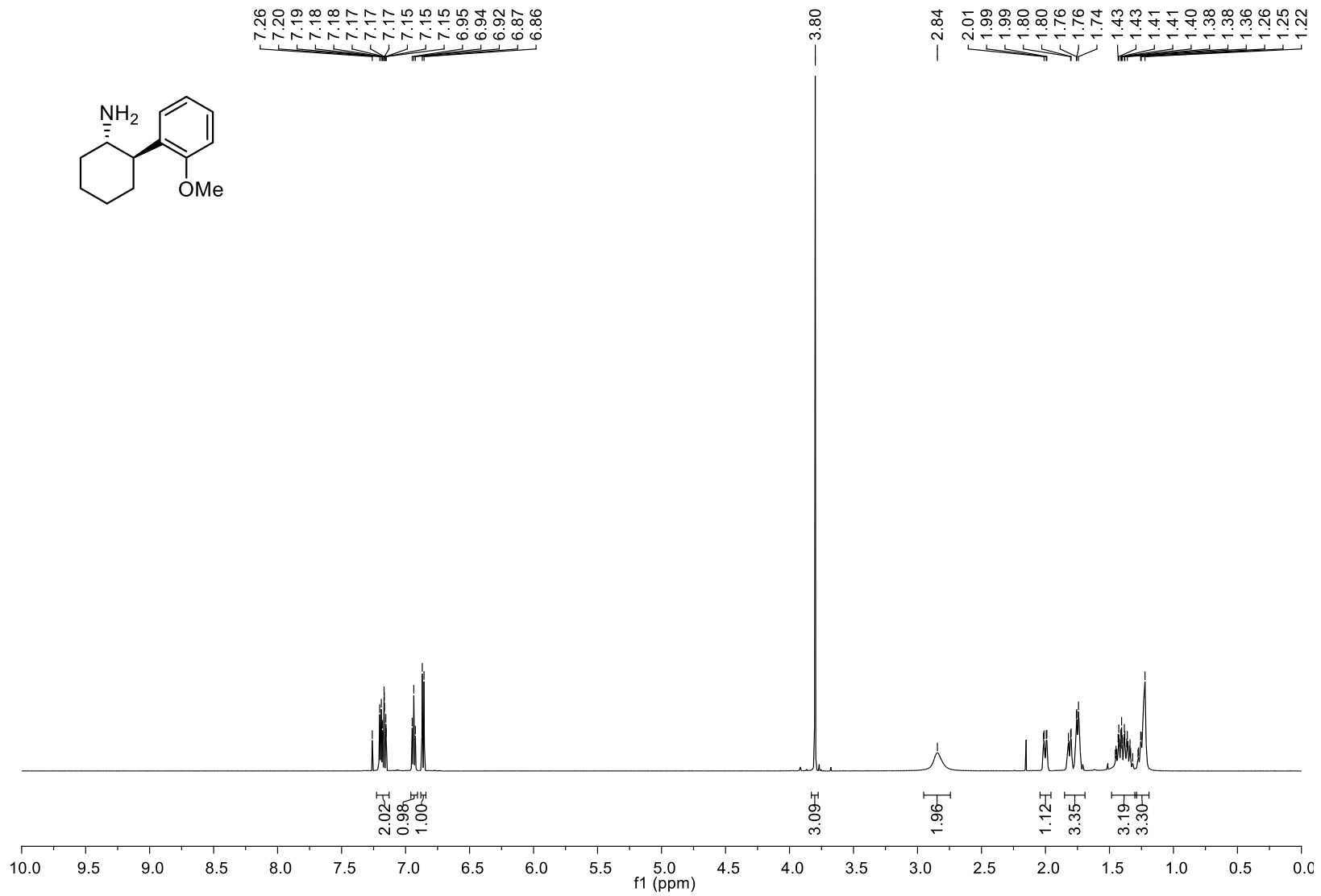


<sup>1</sup>H NMR Spectrum of (±)-36 (600 MHz, CDCl<sub>3</sub>)

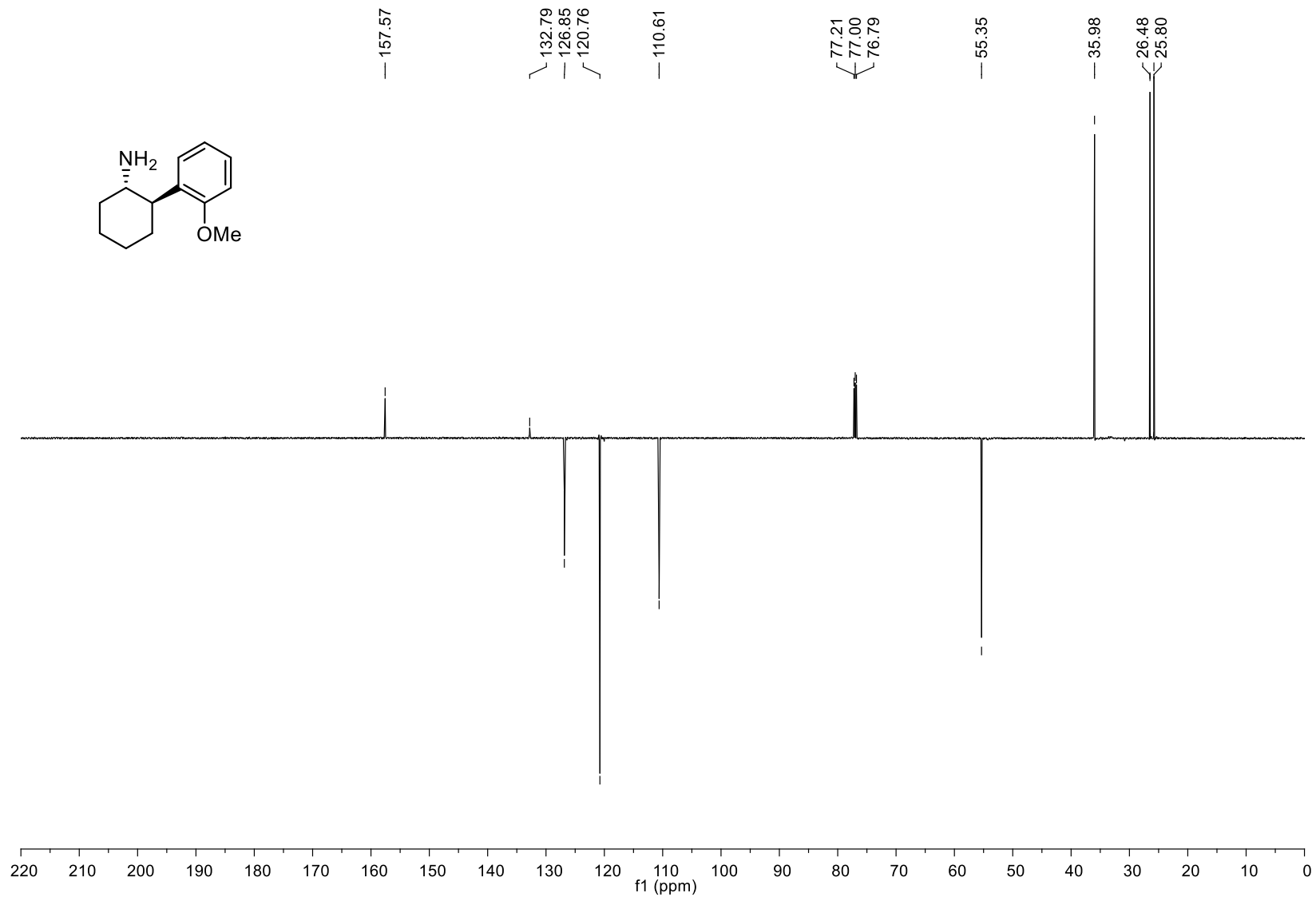




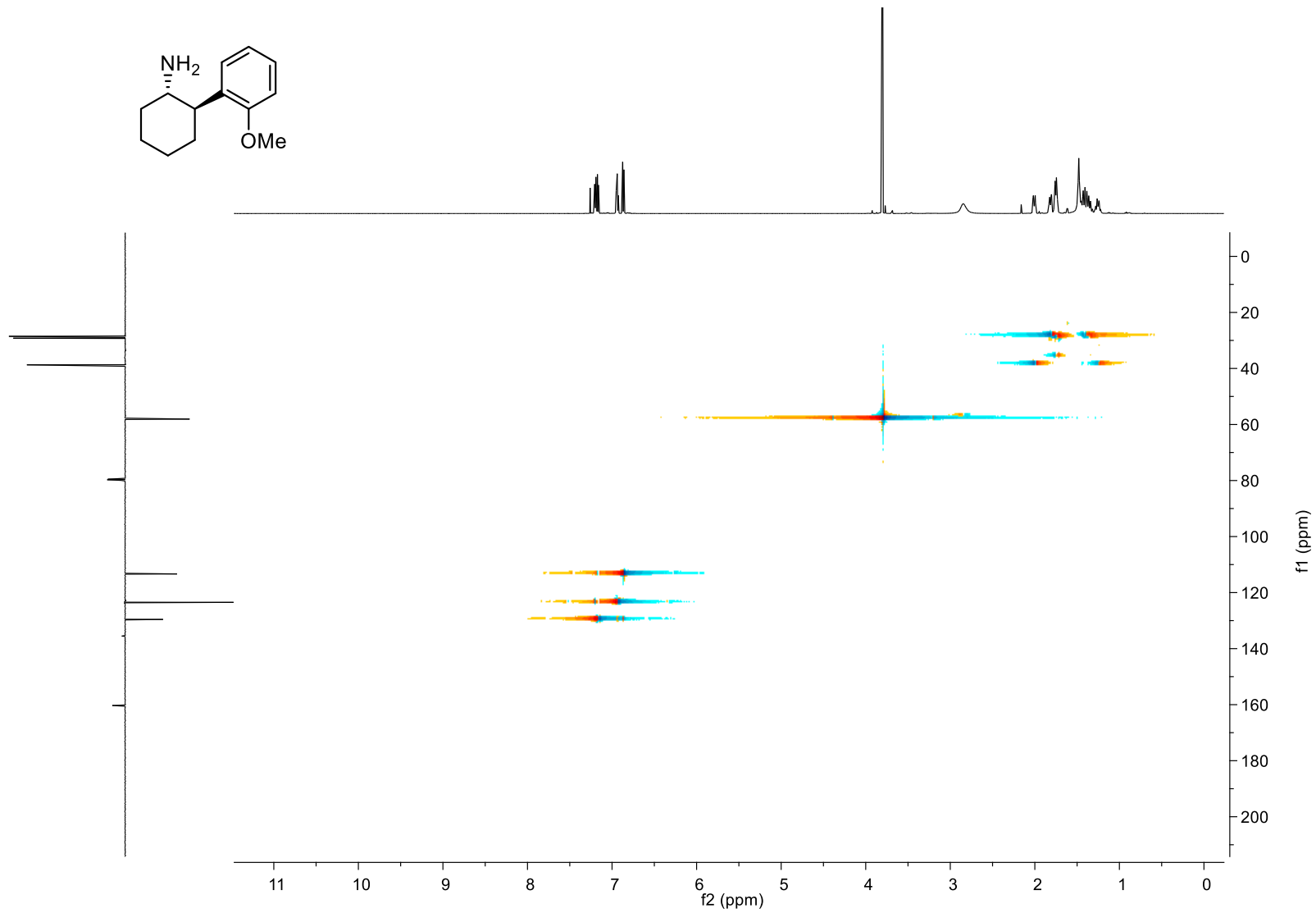
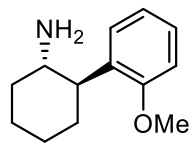
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (±)-36 (APT, 150 MHz,  $\text{CDCl}_3$ )

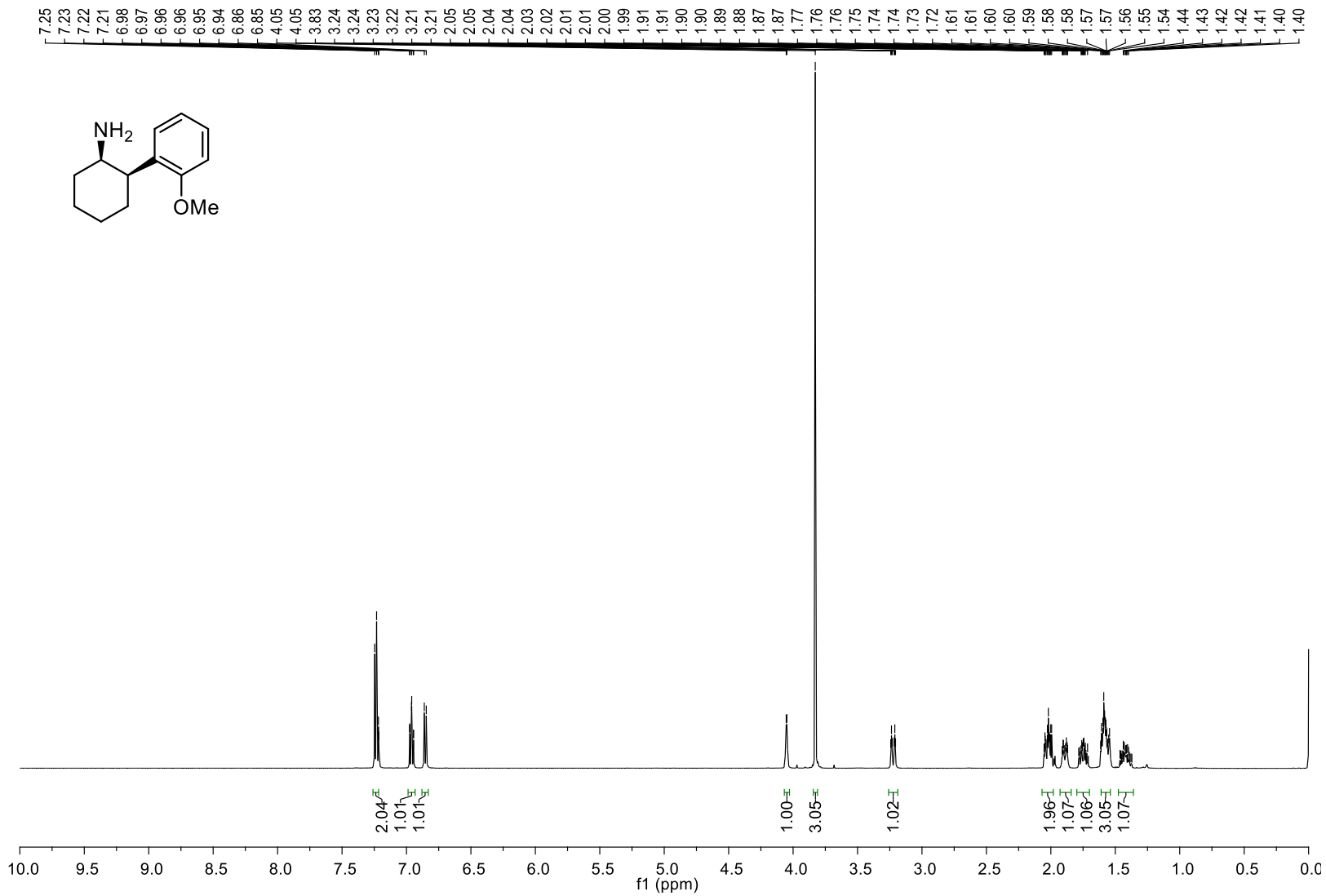


**<sup>1</sup>H NMR Spectrum of (±)-37 (600 MHz, CDCl<sub>3</sub>)**

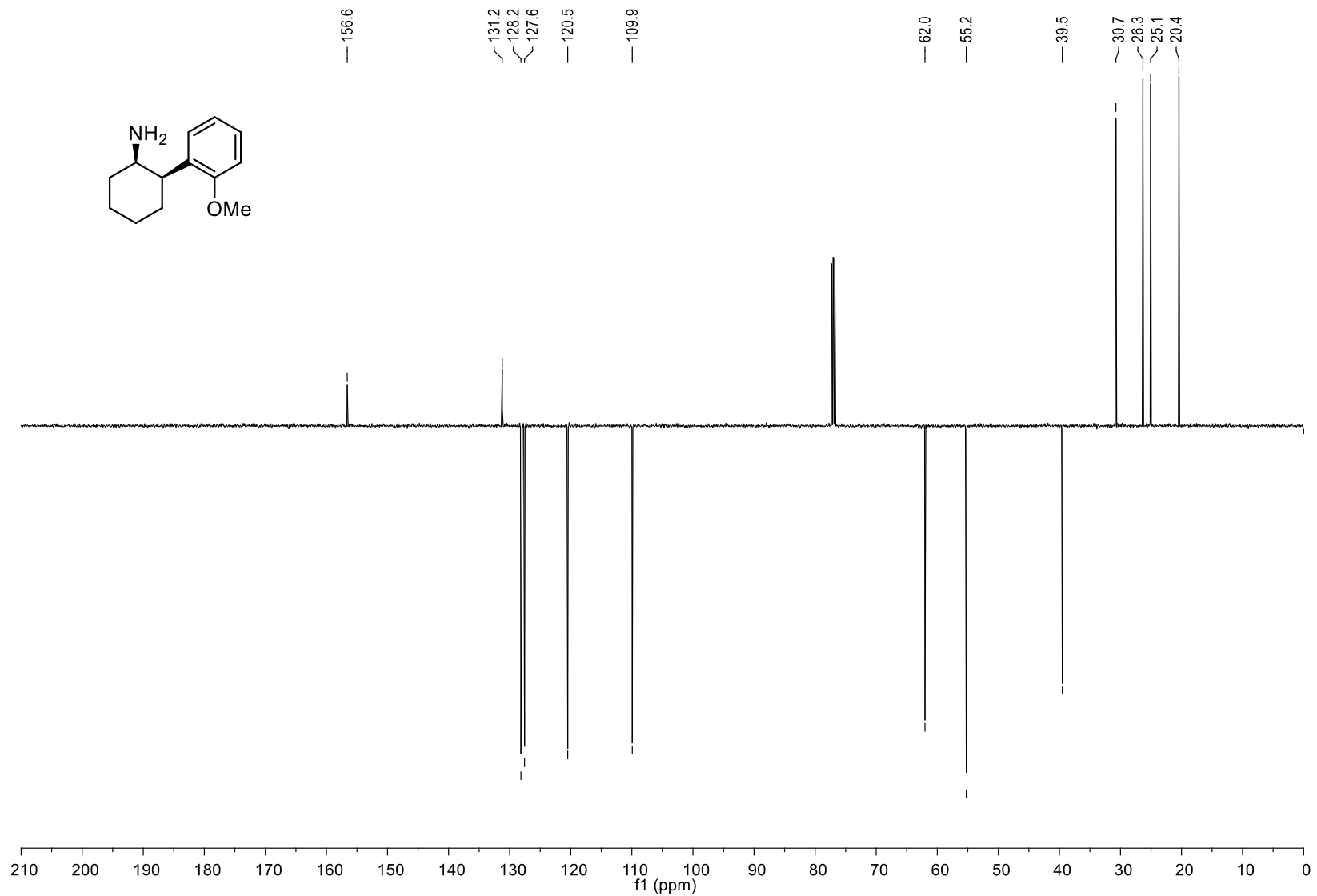


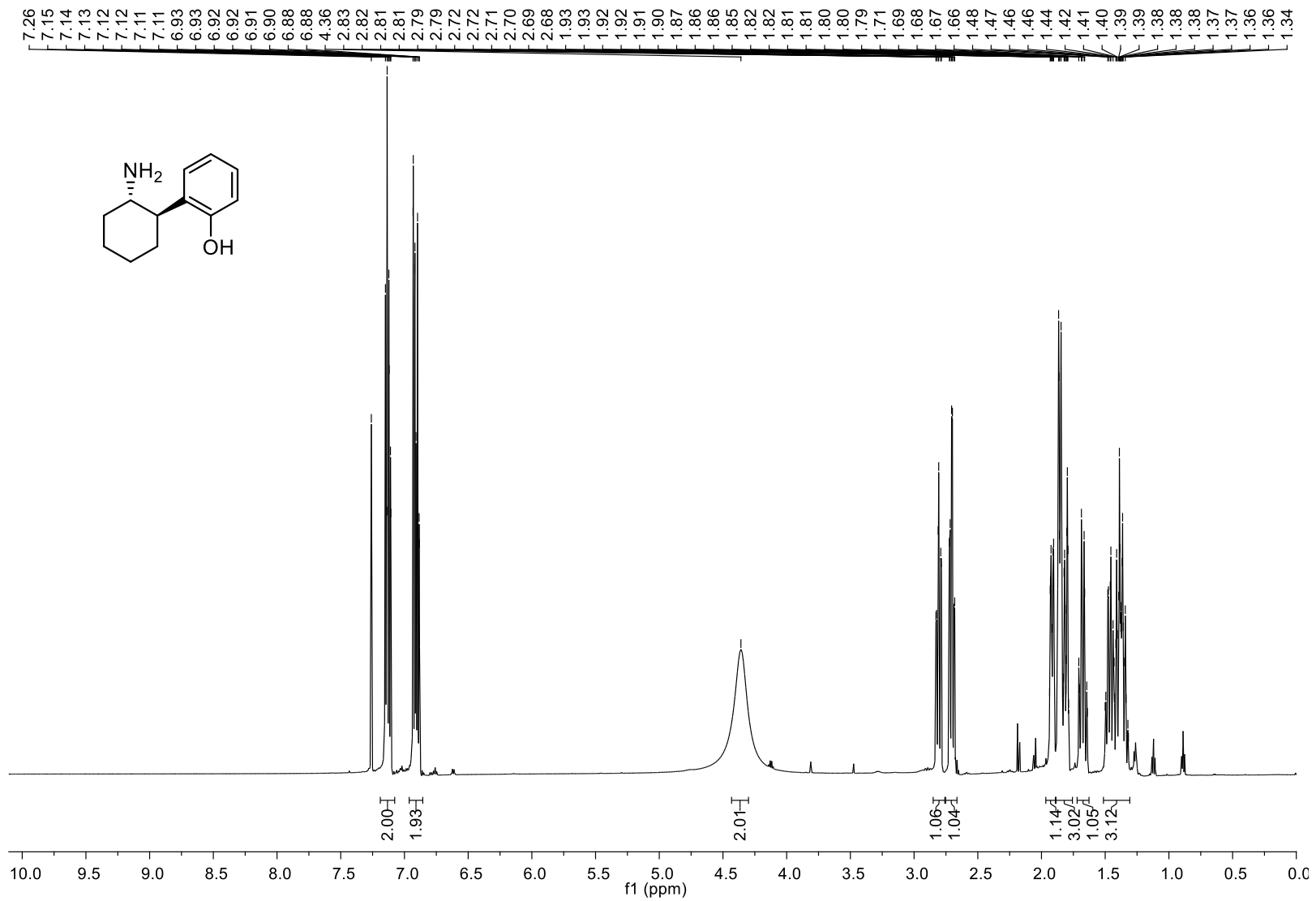
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (±)-37 (APT, 150 MHz,  $\text{CDCl}_3$ )



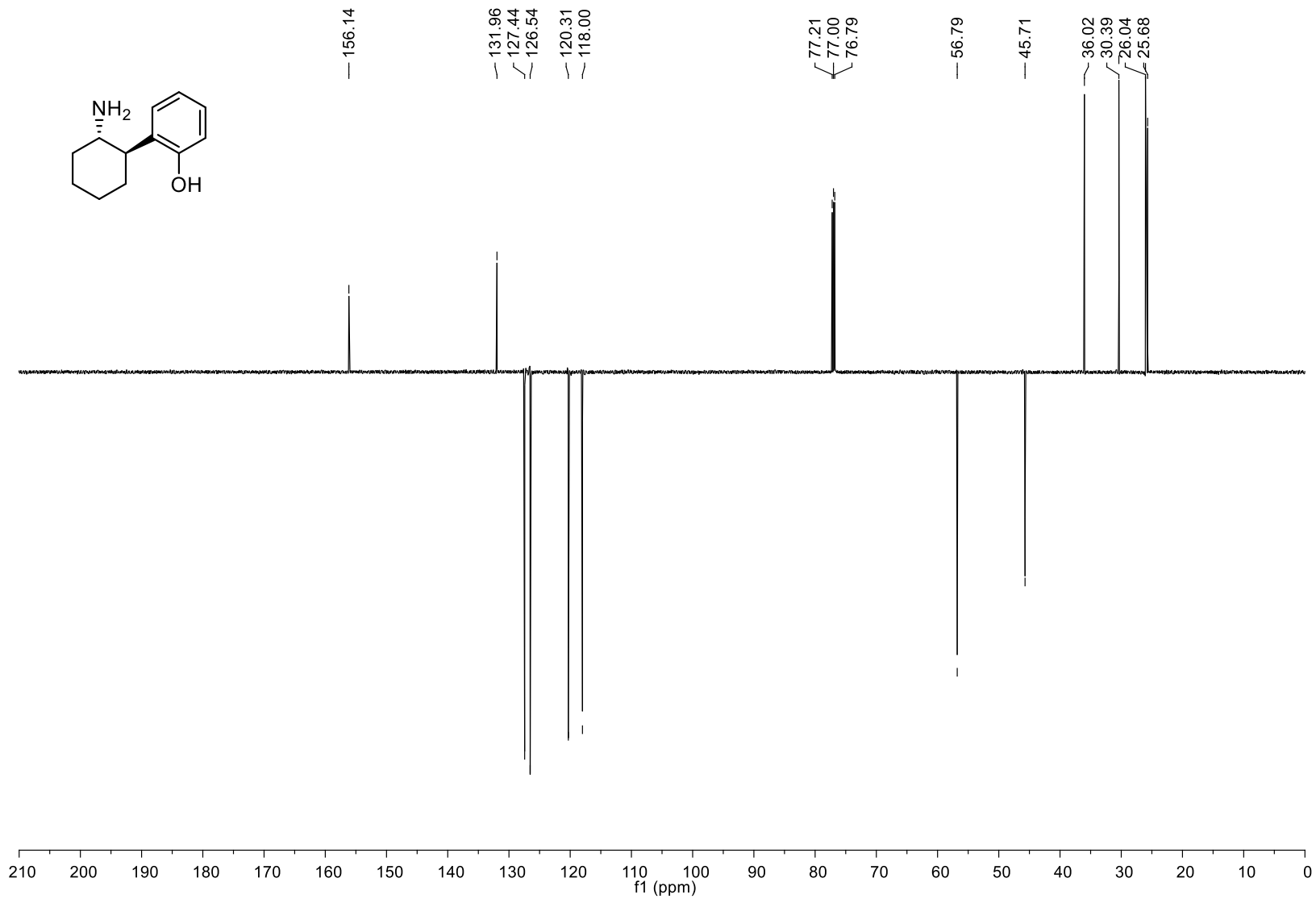


**<sup>1</sup>H NMR Spectrum of (±)-20 (500 MHz, CDCl<sub>3</sub>)**

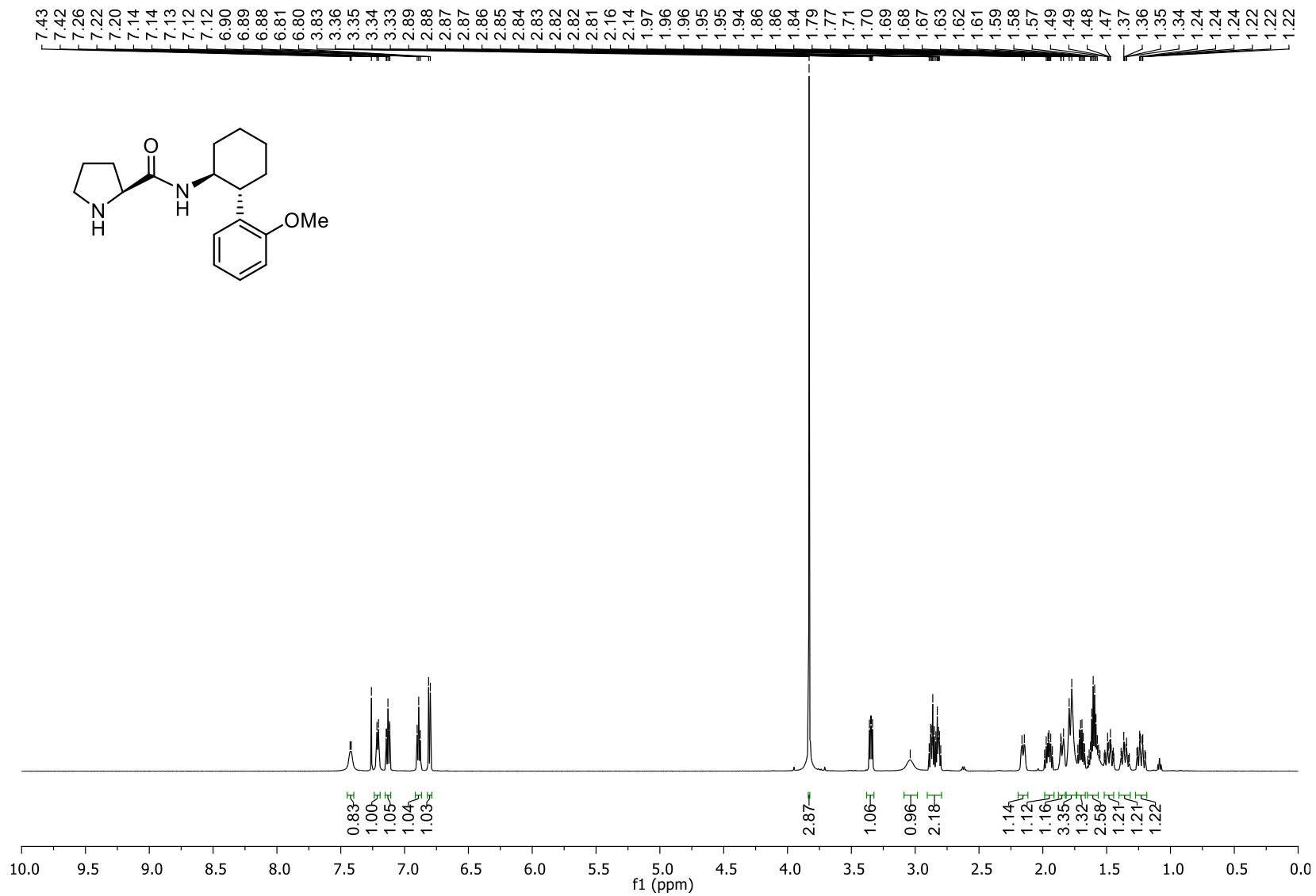




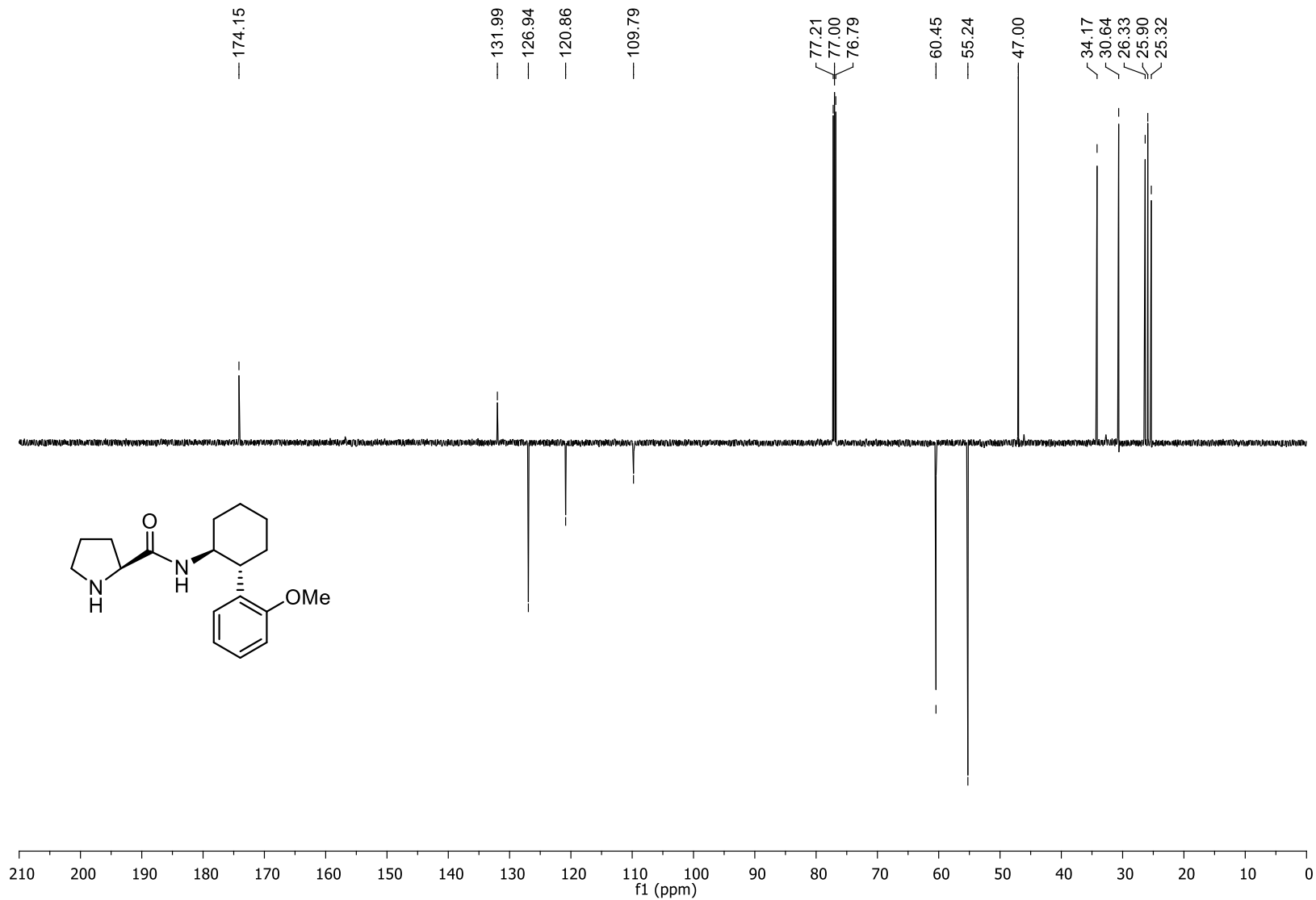
<sup>1</sup>H NMR Spectrum of (±)-18 (600 MHz, CDCl<sub>3</sub>)



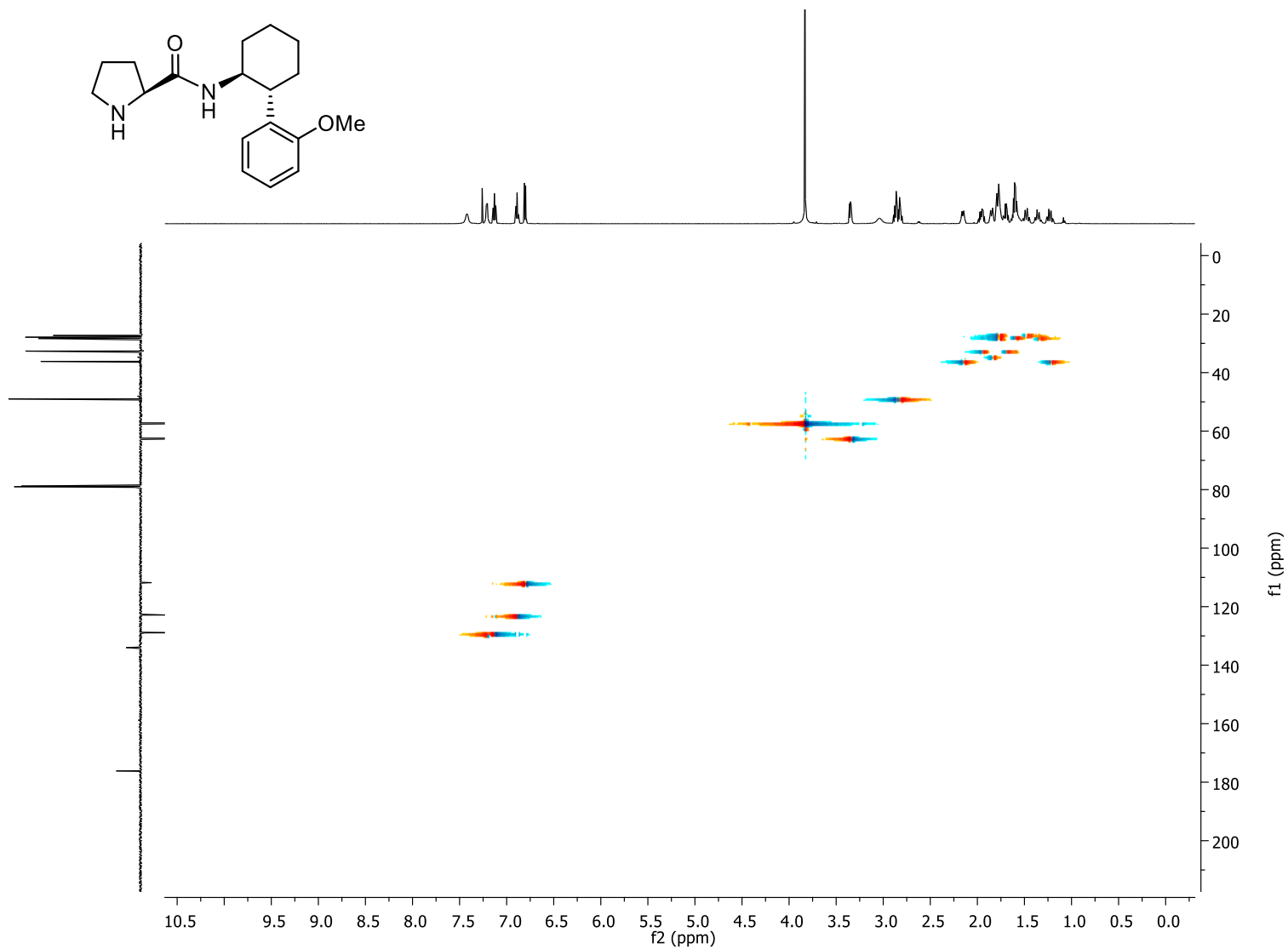
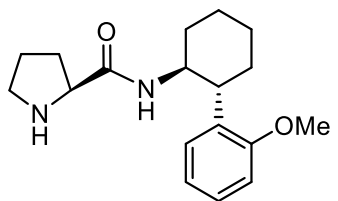




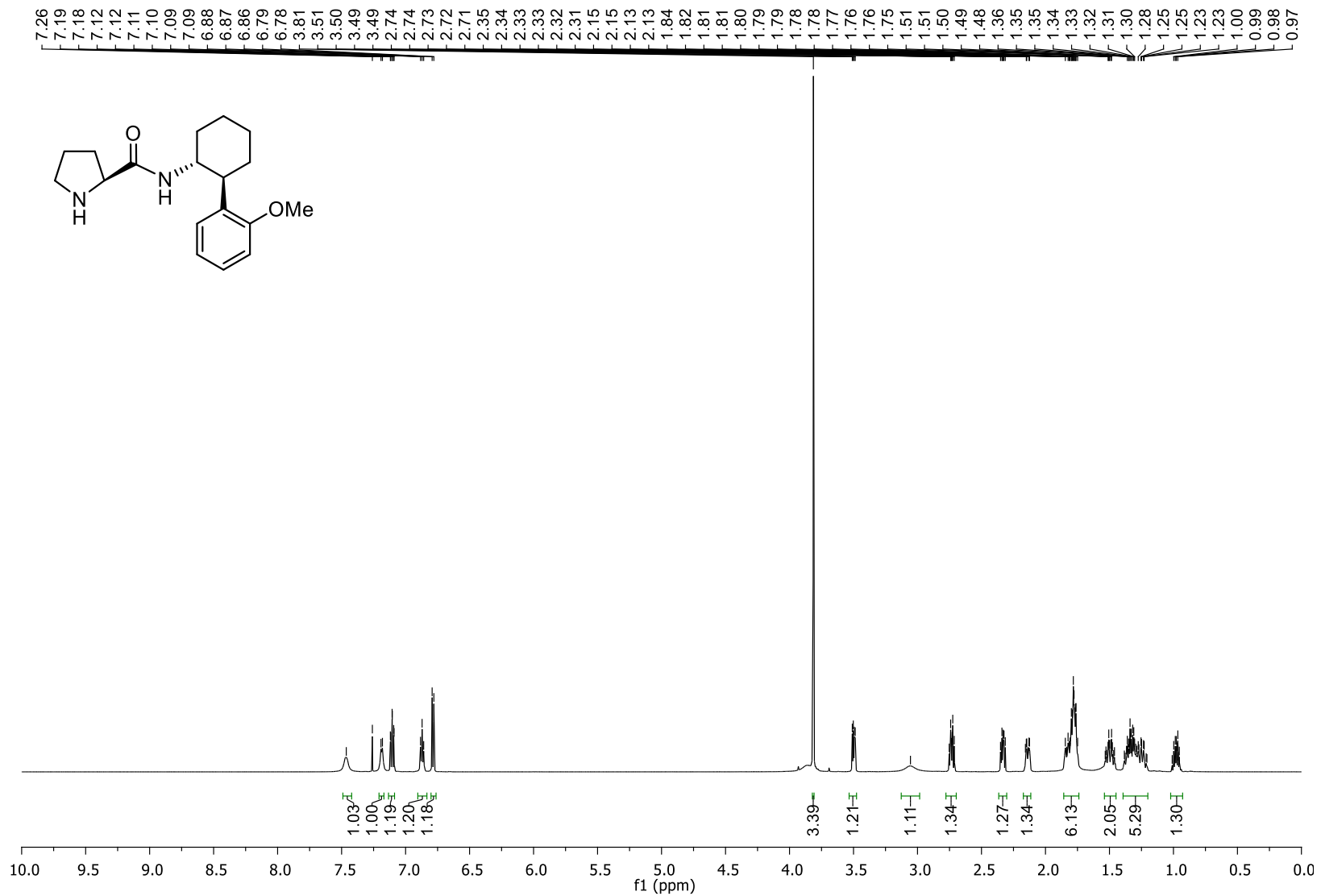
**<sup>1</sup>H NMR Spectrum of (S,1S,2R)-43 (600 MHz, CDCl<sub>3</sub>)**

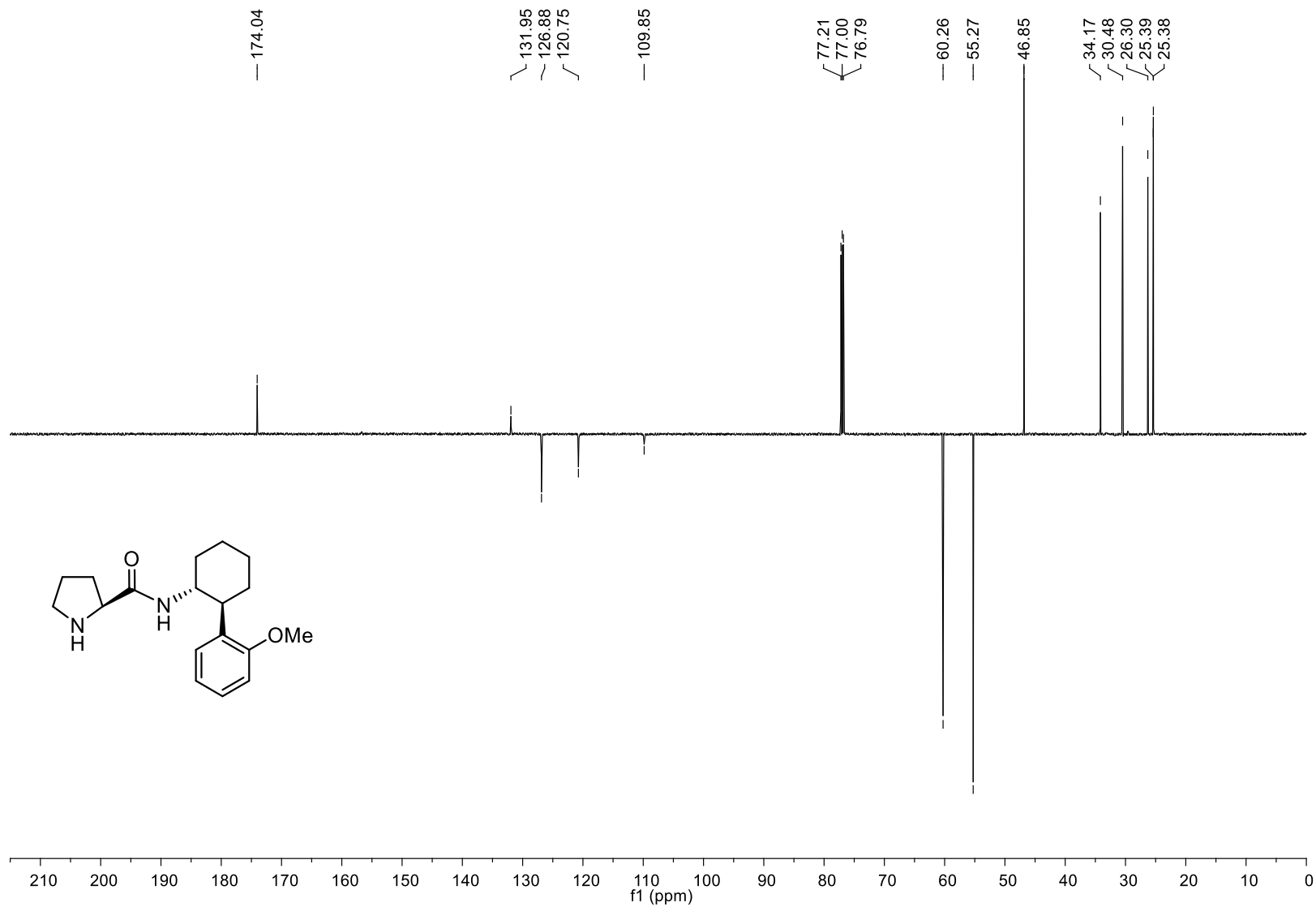


$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (S,1S,2R)-43 (APT, 150 MHz,  $\text{CDCl}_3$ )

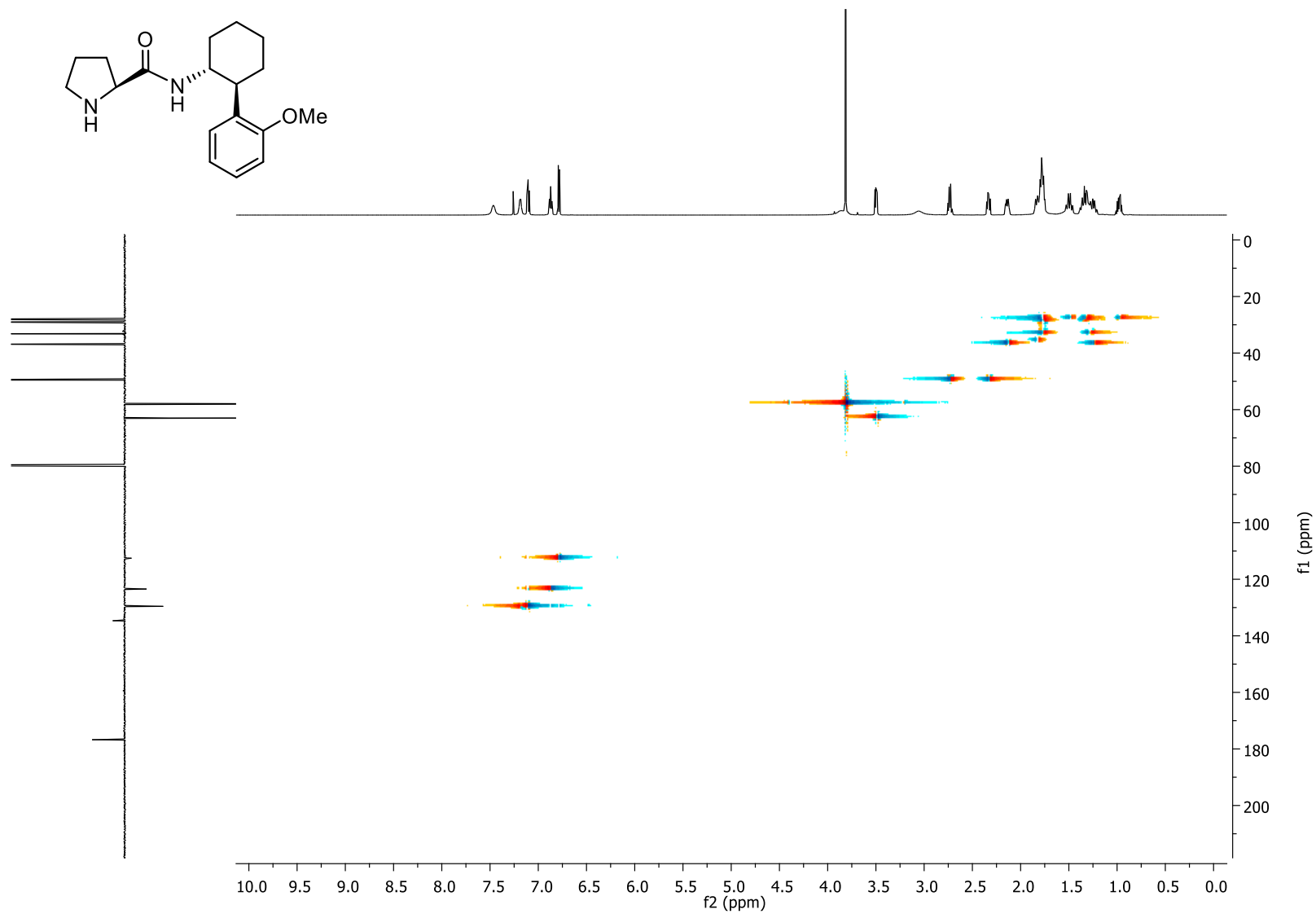
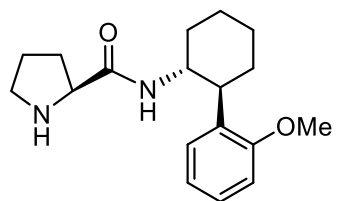


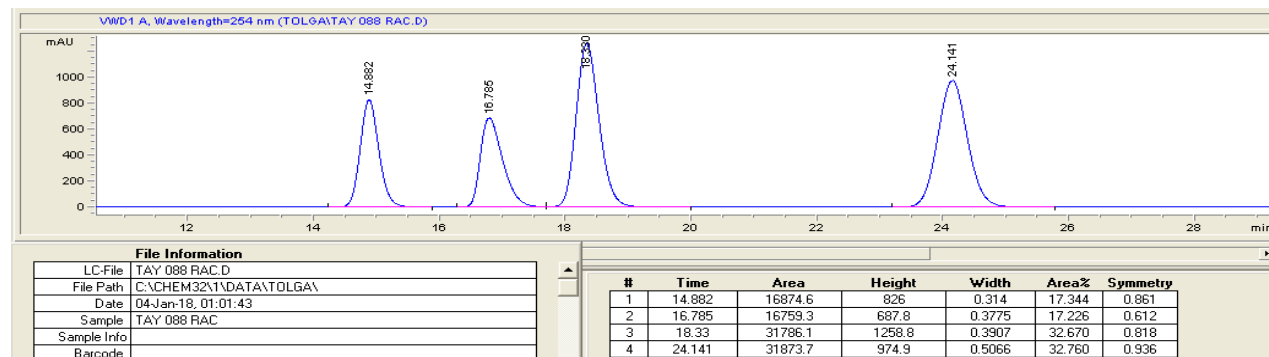
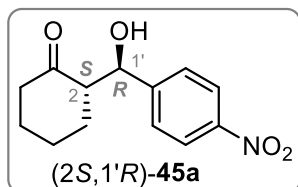
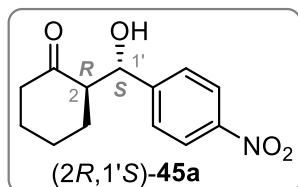
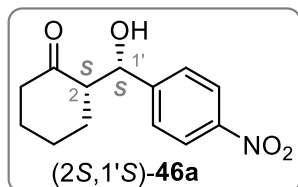
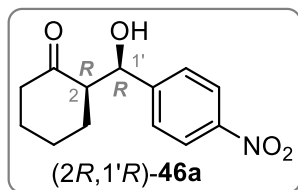
HSQC NMR Spectrum of (S,1S,2R)-43 (CDCl<sub>3</sub>)



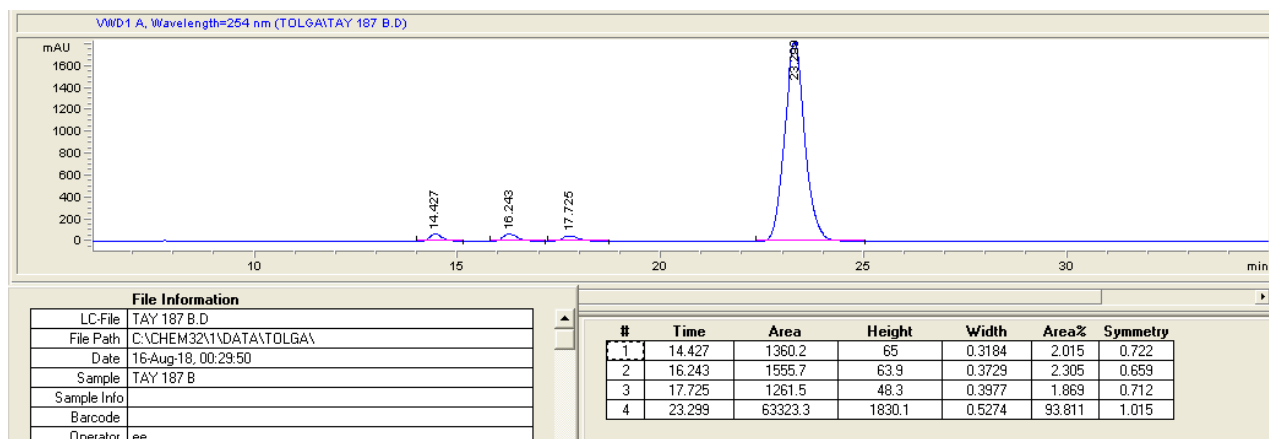


$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (S,1R,2S)-44 (APT, 150 MHz,  $\text{CDCl}_3$ )





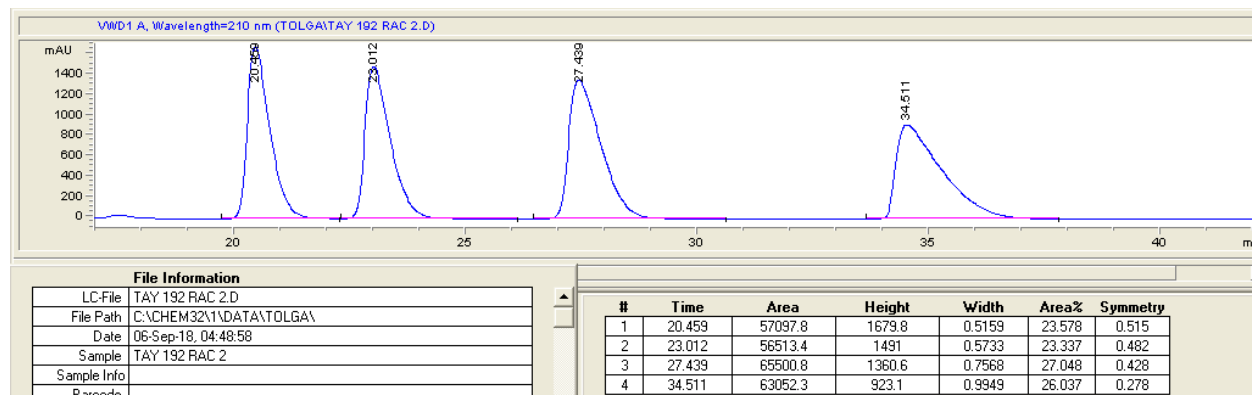
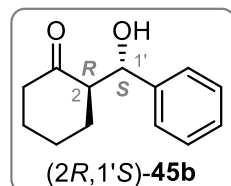
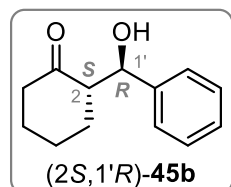
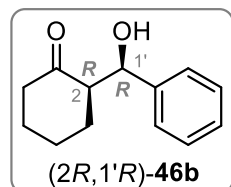
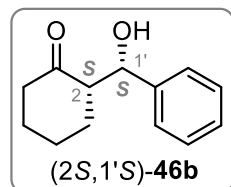
**(±)-45a and (±)-46a**



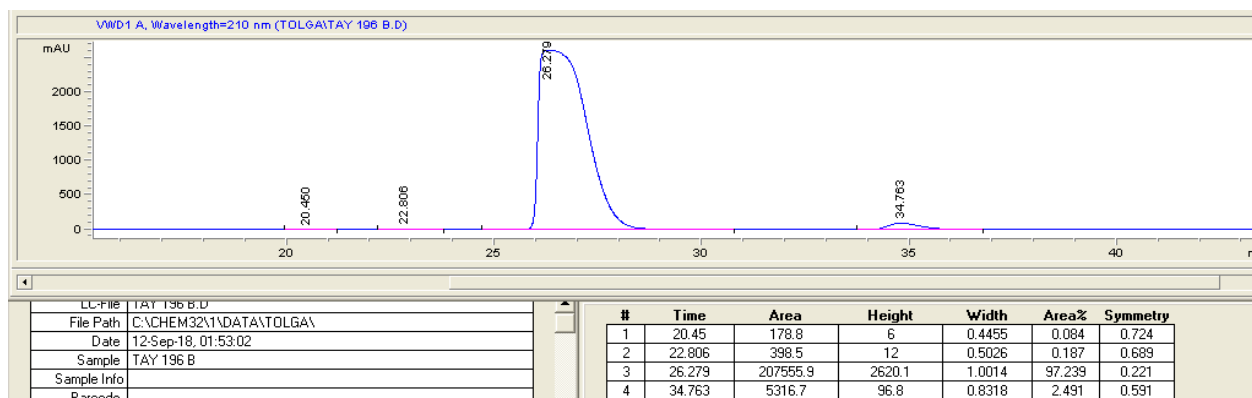
**(2S,1'R)-45a and (2R,1'R)-46a**

**HPLC:** Daicel Chiralpak AD-H (4.60 mm ID × 250 mm column length); *n*-hexane/<sup>i</sup>PrOH (85:15), 1.0 mL/min; 254 nm (UV/Vis);  $t_R$ =14.8 min ((2R,1'R)-46a),  $t_R$ =16.8 min ((2S,1'S)-46a),  $t_R$ =18.3 min ((2R,1'S)-45a),  $t_R$ =24.1 min ((2S,1'R)-45a).

**HPLC Chromatograms of (±)-45a, (±)-46a, and (2S,1'R)-45a**



(±)-45b and (±)-46b

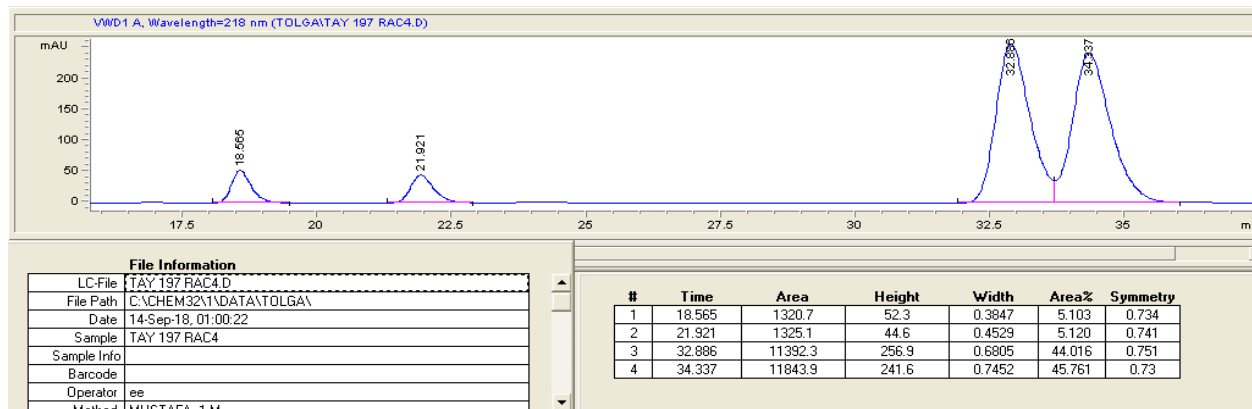
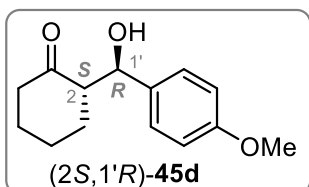
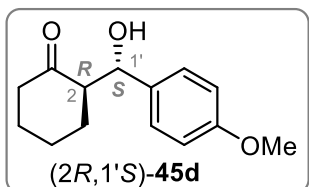
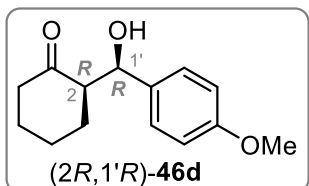
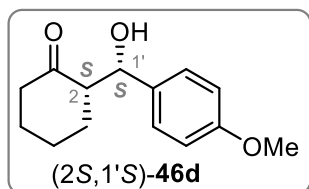


(2S,1'R)-45b and (2R,1'R)-46b

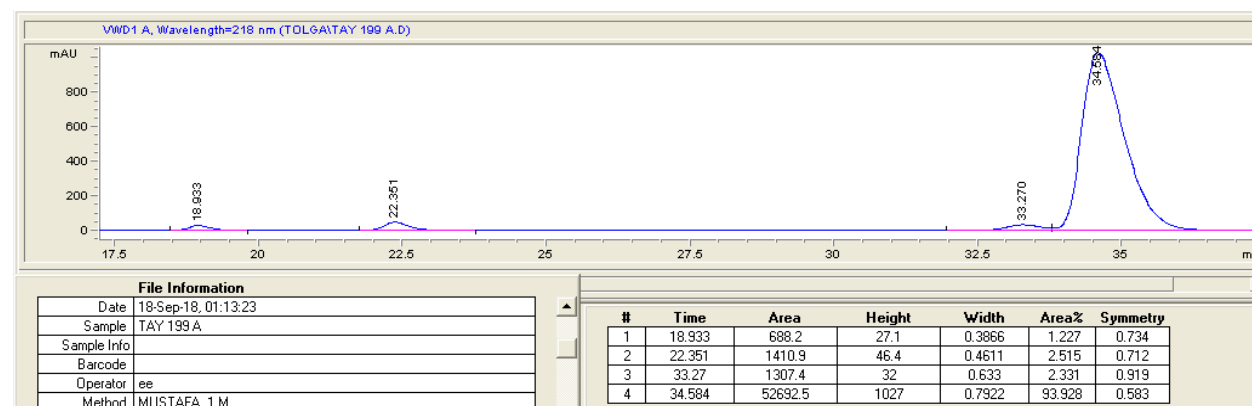
**HPLC:** Daicel Chiralpak OD-H (4.60 mm ID × 250 mm column length); *n*-hexane/*i*PrOH (95:5), 0.5 mL/min; 254 nm (UV/Vis);  $t_R=20.5$  min ((2S,1'S)-46b),  $t_R=23.0$  min ((2R,1'R)-46b),  $t_R=27.4$  min ((2S,1'R)-45b),  $t_R=34.5$  min ((2R,1'S)-45b).

### HPLC Chromatograms of (±)-45b, (±)-46b, and (2S,1'R)-45b





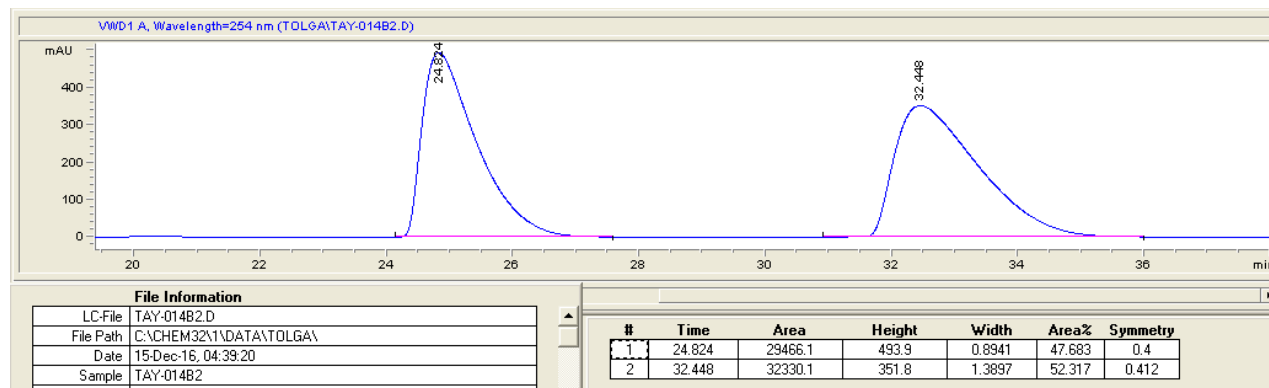
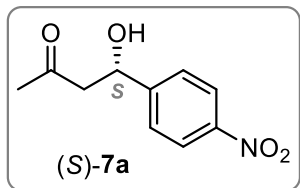
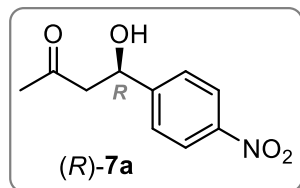
(±)-**45d** and (±)-**46d**



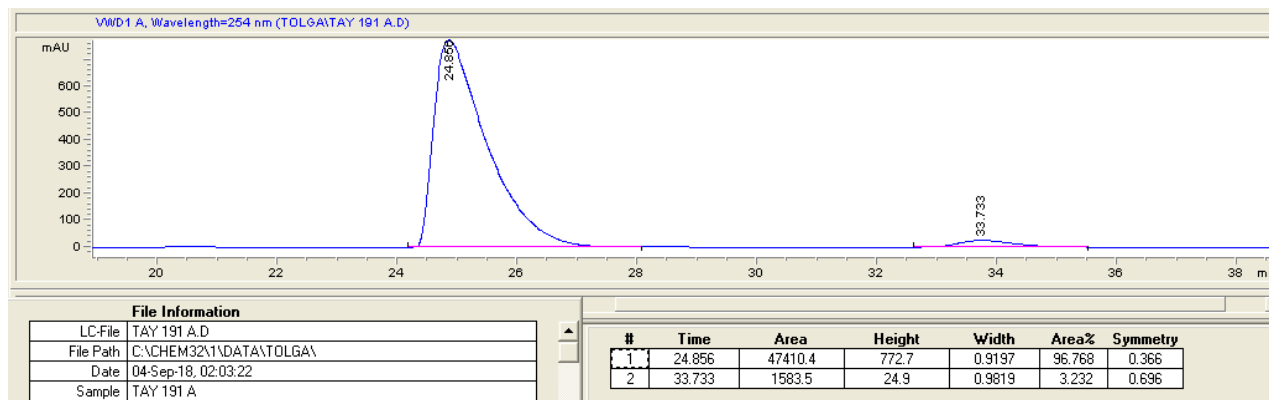
(2*S*,1'*R*)-**45d** and (2*R*,1'*R*)-**46d**

**HPLC:** Daicel Chiralpak AD-H (4.60 mm ID × 250 mm column length); *n*-hexane/*i*PrOH (94:6), 1.0 mL/min; 218 nm (UV/Vis);  $t_R$ =18.6 min ((2*S*,1'*S*)-**46d**),  $t_R$ =21.9 min ((2*R*,1'*R*)-**46d**),  $t_R$ =32.8 min ((2*R*,1'*S*)-**45d**),  $t_R$ =34.3 min ((2*S*,1'*R*)-**45d**).

**HPLC Chromatograms of (±)-45d, (±)-46d, and (2*S*,1'*R*)-45d**



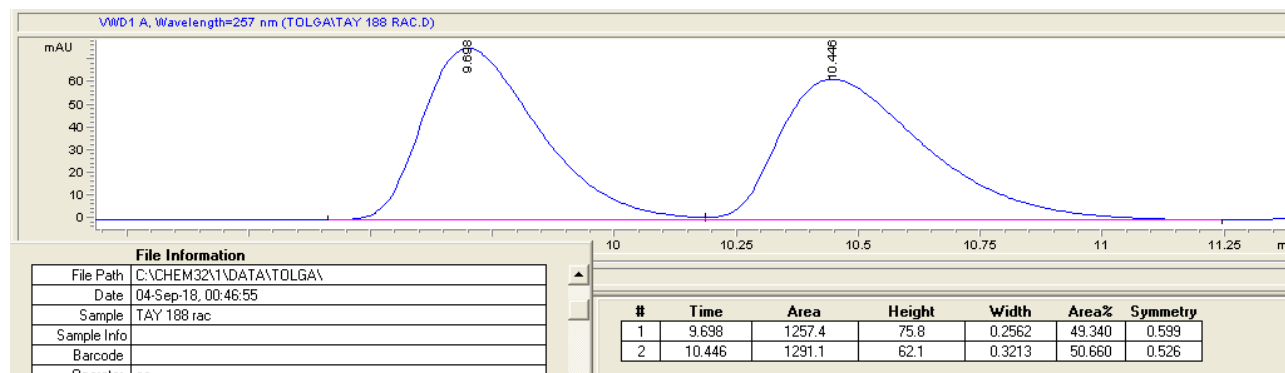
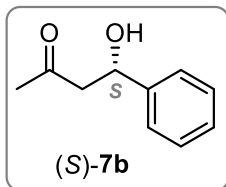
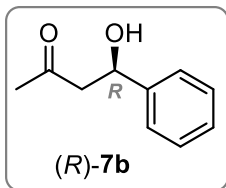
(±)-7a



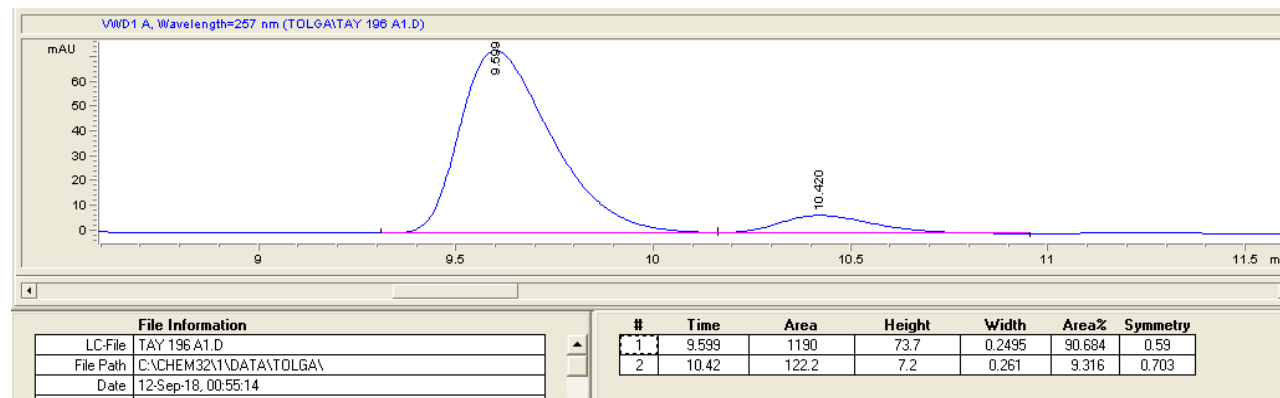
(R)-7a (94% ee)

**HPLC:** Daicel Chiralpak AS-H (4.60 mm ID × 250 mm column length); *n*-hexane/*i*PrOH (85:15), 1.0 mL/min; 254 nm (UV/Vis);  $t_R$ =25.1 min ((R)-7a),  $t_R$ =32.4 min ((S)-7a).

**HPLC Chromatograms of (±)-7a and (R)-7a**



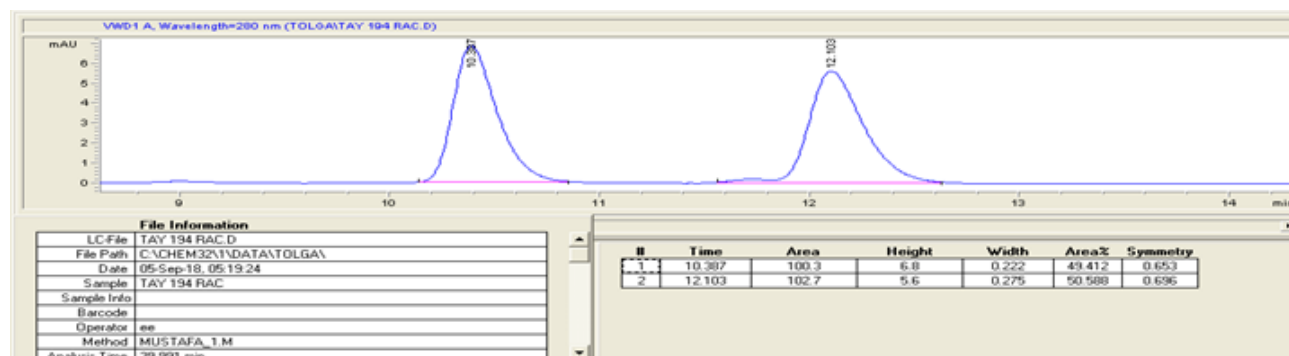
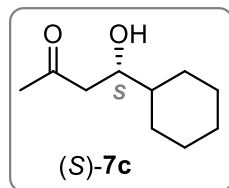
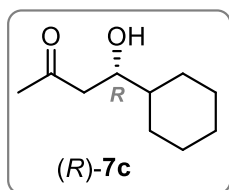
**(±)-7b**



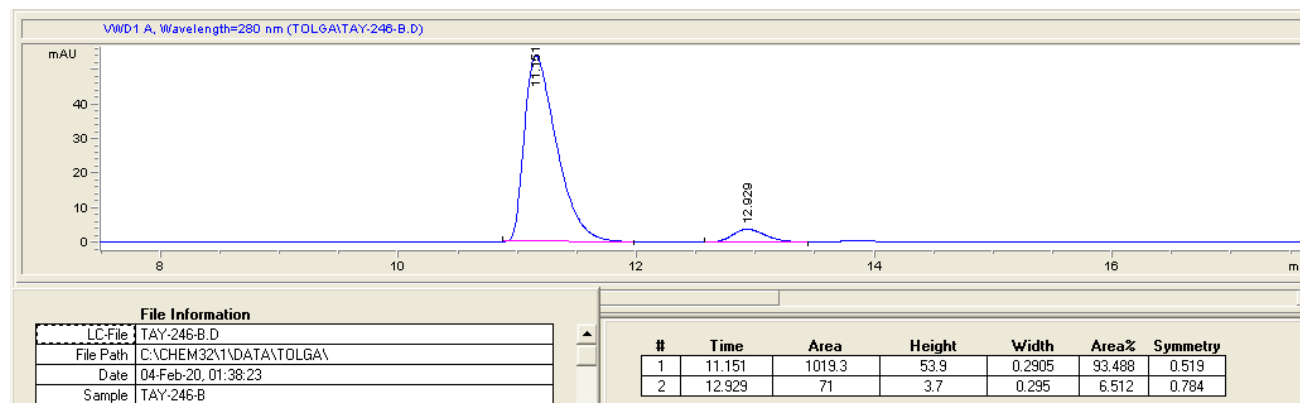
**(R)-7b (81% ee)**

**HPLC:** Daicel Chiralpak AS-H (4.60 mm ID × 250 mm column length); *n*-hexane/*i*PrOH (85:15), 1.0 mL/min; 257 nm (UV/Vis);  $t_R$ =9.7 min ((*R*)-7b),  $t_R$ =10.5 min ((*S*)-7b).

**HPLC Chromatograms of (±)-7b and (R)-7b**



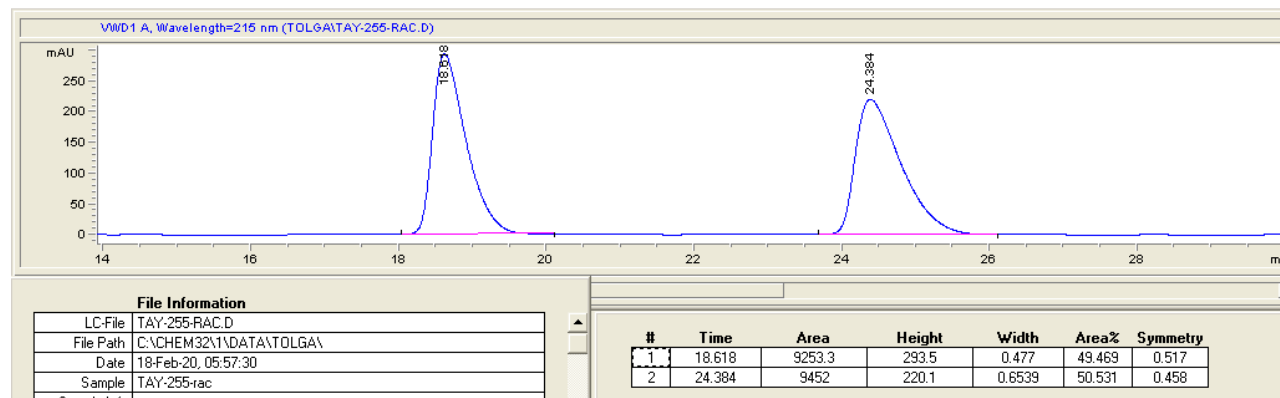
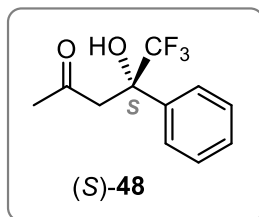
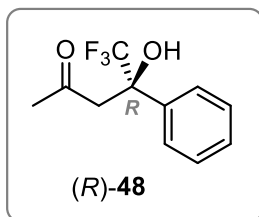
(±)-7c



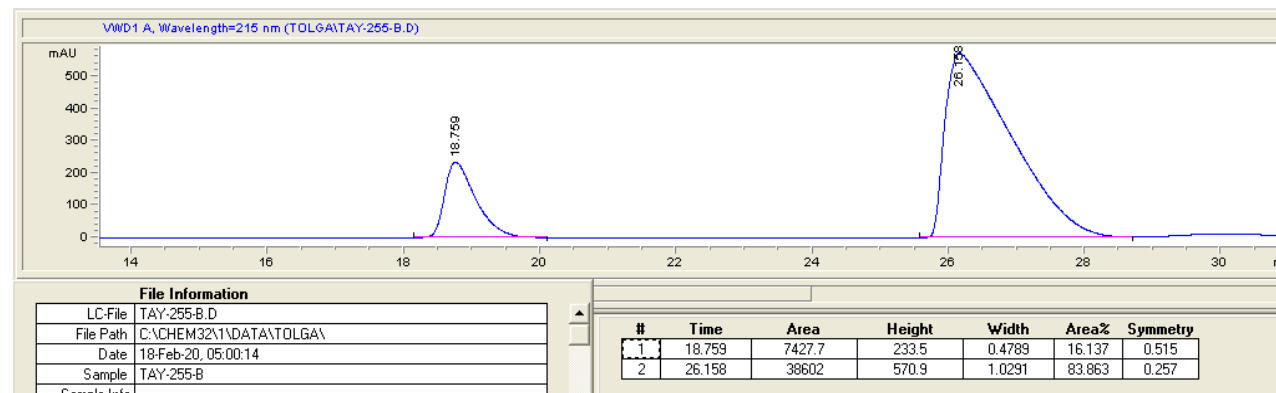
(R)-7c (87% ee)

**HPLC:** Daicel Chiralpak AD-H (4.60 mm ID × 250 mm column length); *n*-hexane/*i*-PrOH (95:5), 1.0 mL/min; 280 nm (UV/Vis);  $t_R$ =10.4 min ((R)-7c),  $t_R$ =12.1 min ((S)-7c).

HPLC Chromatograms of (±)-7c and (R)-7c



(±)-48



(S)-48 (68% ee)

**HPLC:** Daicel Chiralpak OD-H (4.60 mm ID × 250 mm column length); *n*-hexane/*i*PrOH (99:1), 1.0 mL/min; 215 nm (UV/Vis);  $t_R$ =18.6 min ((R)-48),  $t_R$ =24.4 min ((S)-48).

HPLC Chromatograms of (±)-48 and (S)-48