Supporting information for

Cooper-Catalyzed Asymmetric [3+2] Cycloaddition of α-Iminoamides with Activated Olefins

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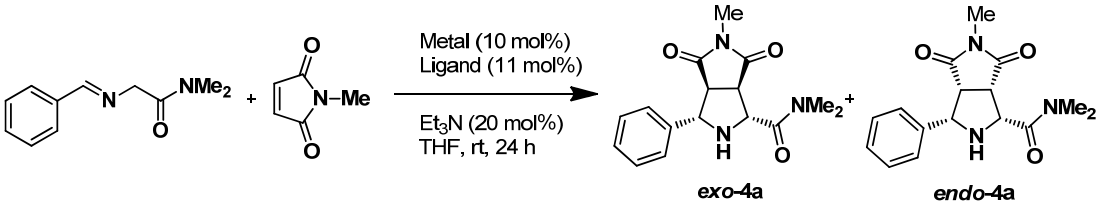
General methods

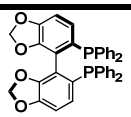
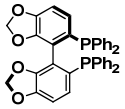
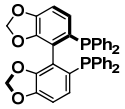
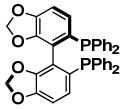
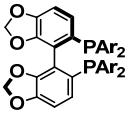
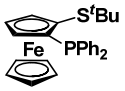
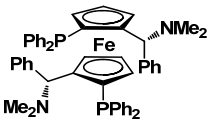
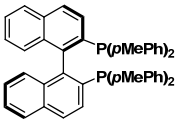
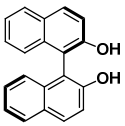
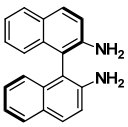
All anaerobic and moisture-sensitive manipulations were carried out in anhydrous solvents and under nitrogen. CH_2Cl_2 and THF were dried and stored over microwave-activated 4Å molecular sieves. Melting points were taken in open-end capillary tubes. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (230-400 mesh). Flash column chromatographies were performed using silica gel (230-400 mesh). NMR spectra were recorded on AC-300 MHz instrument and calibrated using residual undeuterated solvent ($CDCl_3$) as internal reference. MS spectra were recorded on a VG *AutoSpec* mass spectrometer. The HPLC chromatograms of the racemic and enantiomerically enriched cycloadducts are also included.

α-Aminoacetamides [(2-amino- *N*, *N*-dimethylacetamide, 2-amino- *N*-methyl-*N*-methoxyacetamide, 2-amino- *N*-methyl-*N*-(4-fluorophenyl)acetamide)] were prepared in three reaction steps as previously described in the literature.[1] α-Iminoamides **1a-o** were prepared by condensation of α-aminoacetamides and the corresponding aldehydes following a similar procedure to those described for the preparation of α-iminoesters.[2] **Due to their lability, all the α-iminoamides precursors of the azomethine ylides, once isolated were immediately used in the 1,3-dipolar cycloaddition without further purification.**

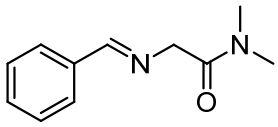
Catalyst optimization studies.

The table below shows other chiral catalyst systems tested in the model [3+2] cycloaddition.



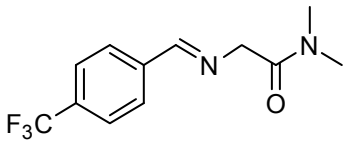
Metal	Ligand	Conversion	*exo: endo*	Yield (%)	*ee* (%) (*exo*-4a)
AgOAc		>98	70:30	74	20 (+)
$Cu(OAc)_2$		>98	92:8	80	48 (+)
$Zn(OAc)_2$		>98	50:50	61	0
$Cu(CH_3CN)_4PF_6$		>98	≥98:<2	91	≥99 (+)
$Cu(CH_3CN)_4PF_6$	 Ar= 4-MeO-3,5(^{t}Bu)$_2$C$_6$H$_2$	>98	≥98:<2	96	≥99 (+)
$Cu(CH_3CN)_4PF_6$		90	86:14	86	93 (-)
$Cu(CH_3CN)_4PF_6$		0	--	--	--
$Cu(CH_3CN)_4PF_6$		>98	90:10	70	24 (+)
$Cu(CH_3CN)_4PF_6$		45	<2:≥98	56	0
$Cu(CH_3CN)_4PF_6$		90	<2:≥98	54	6 (+)

Typical procedures for the synthesis of α-iminoacetamides. **2-Benzylideneamino-*N*,*N*-dimethylacetamide (1a)**



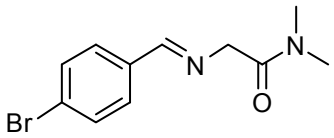
A suspension of 2-amino-*N,N* dimethylacetamide (520 mg, 5.10 mmol), $MgSO_4$ (708 mg, 5.88 mmol) and benzaldehyde (400 µL, 416 mg, 3.92 mmol) in dry CH_2Cl_2 (40 mL) was stirred at 40ºC. After 12h the mixture was filtered over Celite® and the solvent was evaporated under reduced pressure to afford **1a** (596 mg, 80%, colorless oil) which was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.66-7.63 (m, 2H), 7.29-7.27 (m, 3H), 4.33 (s, 2H), 3.10 (s, 3H), 2.85 (s, 3H).

2-[(4-Trifluoromethylbenzylidene)amino]-*N,N*-dimethylacetamide (1b)



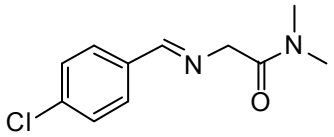
Following the general procedure, the reaction of 4-(trifluoromethyl)benzaldehyde (162 µL, 202 mg, 1.16 mmol) with 2-amino-*N,N*-dimethylacetamide (142 mg, 1.39 mmol) and $MgSO_4$ (209 mg, 1.74 mmol) in CH_2Cl_2 (12 mL) afforded **1b** (296 mg, 99%, colorless solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 4.40 (s, 2H), 3.11 (s, 3H), 2.89 (s, 3H).

2-[(4-Bromobenzylidene)amino]-*N,N*-dimethylacetamide (1c)



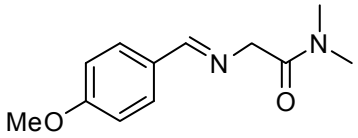
Following the general procedure, the reaction of 4-bromobenzaldehyde (759 mg, 4.10 mmol) with 2-amino-*N,N*-dimethylacetamide (502 mg, 4.92 mmol) and $MgSO_4$ (740 mg, 6.15 mmol) in CH_2Cl_2 (41 mL) afforded **1c** (977 mg, 89%, colorless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 4.29 (s, 2H), 3.03 (s, 3H), 2.82 (s, 3H).

2-[(4-Chlorobenzylidene)amino]-*N,N*-dimethylacetamide (1d)



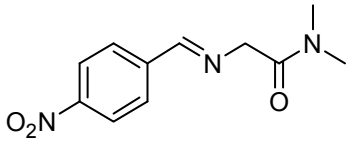
Following the general procedure, the reaction of 4-chlorobenzaldehyde (144 mg, 1.00 mmol) with 2-amino-*N,N*-dimethylacetamide (132 mg, 1.29 mmol) and $MgSO_4$ (181 mg, 1.50 mmol) in CH_2Cl_2 (10 mL) afforded **1d** (218 mg, 97%, colorless solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 4.43 (s, 2H), 3.19 (s, 3H), 2.96 (s, 3H).

2-[(4-Methoxybenzylidene)amino]-*N,N*-dimethylacetamide (1e)



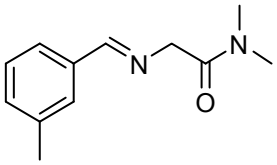
Following the general procedure, the reaction of 4-methoxybenzaldehyde (215 mg, 1.76 mmol) with 2-amino-*N,N*-dimethylacetamide (216 mg, 2.12 mmol) and $MgSO_4$ (318 mg, 2.64 mmol) in CH_2Cl_2 (18 mL) afforded **1e** (380 mg, 98%, orange oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 2H), 3.70 (s, 3H), 3.10 (s, 3H), 2.83 (s, 3H).

2-[(4-Nitrobenzylidene)amino]-*N,N*-dimethylacetamide (1f)



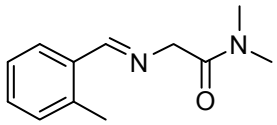
Following the general procedure, the reaction of 4-nitro-benzaldehyde (196 mg, 1.24 mmol) with 2-amino-*N,N*-dimethylacetamide (165 mg, 1.62 mmol) and $MgSO_4$ (225 mg, 1.87 mmol) in CH_2Cl_2 (12 mL) afforded **1f** (287.0 mg, 98%, pale brown solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.10 (d, *J*= 8.8 Hz, 2H), 7.80 (d, *J*= 8.8 Hz, 2H), 4.42 (s, 2H), 3.11 (s, 3H), 2.87 (s, 3H).

2-[(3-Methylbenzylidene)amino]-*N,N*-dimethylacetamide (1g)



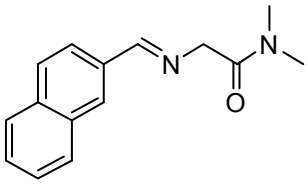
Following the general procedure, the reaction of 3-tolualdehyde (108 µL, 110 mg, 0.89 mmol) with 2-amino-*N,N*-dimethylacetamide (109 mg, 1.07 mmol) and $MgSO_4$ (161 mg, 1.33 mmol) in CH_2Cl_2 (9 mL) afforded **1g** (176.0 mg, 97%, colorless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.61 (s, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.32-7.22 (m, 2H), 4.45 (s, 2H), 3.20 (s, 3H), 2.98 (s, 3H), 2.38 (s, 3H).

2-[(2-Methylbenzylidene)amino]-*N,N*-dimethylacetamide (1h)



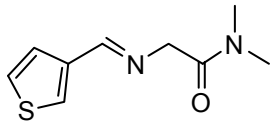
Following the general procedure, the reaction of 2-tolualdehyde (255 µL, 245 mg, 2.14 mmol) with 2-amino-*N,N*-dimethylacetamide (262 mg, 2.57 mmol) and $MgSO_4$ (386 mg, 3.21 mmol) in CH_2Cl_2 (21 mL) afforded **1h** (415 mg, 95%, orange oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.64 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.35-7.17 (m, 3H), 4.49 (s, 2H), 3.22 (s, 3H), 2.99 (s, 3H), 2.52 (s, 3H).

2-[(2-Naphtyl-2-methylidene)amino]-*N,N*-dimethylacetamide (1i)



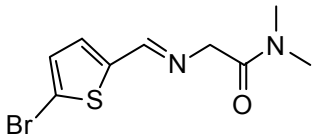
Following the general procedure, the reaction of 2-naphthaldehyde (143 mg, 0.90 mmol) with 2-amino-*N,N*-dimethylacetamide (110 mg, 1.07 mmol) and $MgSO_4$ (163 mg, 1.35 mmol) in CH_2Cl_2 (9 mL) afforded **1i** (205 mg, 95%, yellow solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.07-8.05 (m, 2H), 7.89-7.84 (m, 2H), 7.54-7.51 (m, 3H), 4.51 (s, 2H), 3.22 (s, 3H), 3.00 (s, 3H).

2-[(3-Thienyl-2-methylidene)amino]-*N,N*-dimethylacetamide (1j)



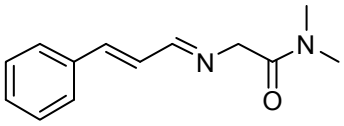
Following the general procedure, the reaction of 3-thiophene-carbaldehyde (123 µL, 157 mg, 1.38 mmol) with 2-amino-*N,N*-dimethylacetamide (183 mg, 1.79 mmol) and $MgSO_4$ (249 mg, 2.07 mmol) in CH_2Cl_2 (14 mL) afforded **1j** (259 mg, 96%, pale brown solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.52 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.41 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.18 (t, *J* = 2.4, 2.4 Hz, 1H), 4.27 (d, *J* = 1.5 Hz, 2H), 3.04 (s, 3H), 2.83 (s, 3H).

2-[(2-(5-Bromo)thienyl-2-methylidene)amino]-*N,N*-dimethylacetamide (1k)



Following the general procedure, the reaction of 5-bromo-2-thiophenecarbaldehyde (187 µL, 300 mg, 1.49 mmol) with 2-amino-*N,N*-dimethylacetamide (198 mg, 1.94 mmol) and $MgSO_4$ (270 mg, 2.24 mmol) in CH_2Cl_2 (15 mL) afforded **1k** (407 mg, 99%, brown oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.13 (s, 1H), 6.93 (d, *J* = 3.9 Hz, 1H), 6.90 – 6.85 (m, 1H), 4.23 (s, 2H), 3.02 (s, 3H), 2.81 (s, 3H).

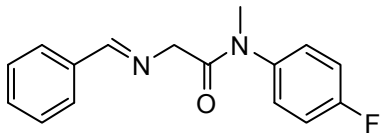
(*E, E*)-2-[3-Phenylprop-2-en-1-ylidene)amino]-*N,N*-dimethylacetamide (1l)



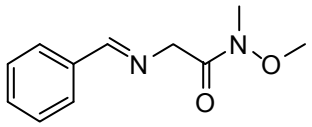
Following the general procedure, the reaction of (2*E*)-3-phenyl-2-propenal (157 µL, 165 mg, 1.24 mmol) with 2-amino-*N,N*-dimethylacetamide (165 mg, 1.62 mmol) and $MgSO_4$ (224 mg, 1.86 mmol) in CH_2Cl_2 (13 mL) afforded **1l** (258 mg, 97%, colorless oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.08 (d, *J* = 5.8 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.37 – 7.30 (m, 3H), 7.01 – 6.92 (m, 2H), 4.36 (s, 2H), 3.14 (s, 3H), 2.97 (s, 3H).

2-Benzylideneamino-*N*-methyl-*N*-(4-fluorophenyl)acetamide (1m)

Following the general procedure, the reaction of of benzaldehyde (109 µL, 114 mg, 1.07 mmol) with 2-amino-*N*-(4-fluorophenyl)-*N*-methyl-acetamide (248 mg, 1.39 mmol) and $MgSO_4$ (193 mg, 1.60 mmol) in CH_2Cl_2 (11 mL) afforded **1m** (283 mg, 98%, colorless solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.72 – 7.63 (m, 2H), 7.40 – 7.29 (m, 3H), 7.25 (dd, *J* = 8.7, 4.8 Hz, 2H), 7.06 (t, *J* = 8.4 Hz, 3H), 4.14 (s, 2H), 3.25 (s, 3H).

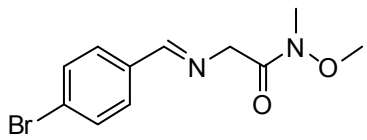


2-Benzylideneamino-*N*-methyl-*N*-methoxyacetamide (1n)[3]



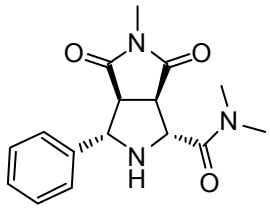
Following the general procedure, the reaction of benzaldehyde (163 µL, 170 mg, 1.60 mmol) with 2-amino-*N*-methoxy-*N*-methyl-acetamide (200 mg, 1.92 mmol) and $MgSO_4$ (289 mg, 2.40 mmol) in CH_2Cl_2 (16 mL) afforded **1n** (294 mg, 89%, yellow solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.80-7.77 (m, 2H), 7.42-7.40 (m, 3H), 4.55 (s, 2H), 3.76 (s, 3H), 3.23 (s, 3H).

2-[(4-Bromobenzylidene)amino]-*N*-methyl-*N*-methoxyacetamide (1o)



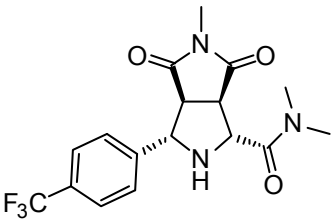
Following the general procedure, the reaction of 4-bromobenzaldehyde (150 mg, 0.80 mmol) with 2-amino-*N*-methoxy-*N*-methyl-acetamide (100 mg, 0.96 mmol) and $MgSO_4$ (144 mg, 1.20 mmol) in CH_2Cl_2 (8 mL) afforded **1o** (216 mg, 95%, colorless solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 4.52 (s, 2H), 3.76 (s, 3H), 3.22 (s, 3H).

General procedure for the 1, 3 dipolar cycloaddition. (1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-phenyl-octahydropyrrolo[3,4-c]pyrrole-1-*N,N*-dimethylcarboxamide (*exo*-4a)



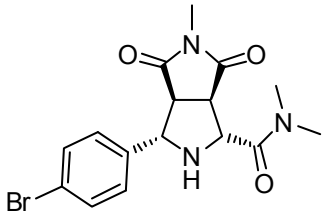
To a solution of (*R*)-DTBM-Segphos (**3c**) (5.8 mg, 4.90 10^{-3} mmol) and $Cu(CH_3CN)_4PF_6$ (1.7 mg, 4.50 10^{-3} mmol) in THF (1.0 mL), under nitrogen atmosphere, at room temperature, a solution of 2-benzylidenamino-*N,N*-dimethylacetamide (**1a**) (128.3 mg, 0.68 mmol) in THF (1.5 mL) and Et_3N (13 µL, 0.090 mmol) were successively added. The resulting solution was added to a suspension of *N*-methylmaleimide (**2**) (50.0 mg, 0.45 mmol) in THF (1.5 mL). The mixture was stirred at room temperature for 48 h, filtered through a plug of Celite® with the aid of CH_2Cl_2 (5.0 mL), and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (hexane-AcOEt 1:1-1:4) to afford the cycloadduct *exo*-**4a** (115.0 mg, 85%, colorless solid). **m.p.**: 180.3-182.2ºC. **$[\alpha]_D^{20}$**:+29.9 (c=1.0, CH_2Cl_2), ≥99% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 23.27 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4a** and 27.21 min (1*S*, 3*R*, 3*aS*, 6*aR*)-*exo*-**4a**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.42-7-30 (m, 3H), 4.32 (d, *J* = 5.9 Hz, 1H), 4.26 (d, *J* = 7.8 Hz, 1H), 3.77-3.72 (m, 1H), 3.47 (t, *J* = 8.9 Hz, 1H), 3.29 (s, 3H), 3.05 (s, 3H), 3.02 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): 177.3, 176.4, 170.4, 139.2, 128.8, 128.0, 126.8, 67.2, 60.1, 54.7, 53.3, 37.2, 36.4, 25.0. **MS** (ESI+): 302.2 ([M+H], 60). **HRMS** (ESI+): Calculated for $C_{16}H_{19}N_3O_3$, 302.1504; found, 302.1502.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(4-trifluromethyl)phenyl-octahydropyrrolo[3,4-c]pyrrole-1- *N,N*-dimethylcarboxamide (*exo*-4b)



Following the general procedure, the reaction of 2-[(4-trifluoromethylbenzylidene)amino]-*N,N*-dimethylacetamide (**1b**) (60.0 mg, 0.23 mmol) with *N*-methylmaleimide (**2**) (17.2 mg, 0.16 mmol), $Cu(CH_3CN)_4PF_6$ (0.6 mg, 1.55 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (2.0 mg, 1.70 10^{-3} mmol) and Et_3N (4 µL, 0.031 mmol), in THF (2.5 mL) at room temperature for 16 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:5), the cycloadduct *exo*-**4b** (58.0 mg, 98%, colorless solid). **m.p.**: 121.8-123.6ºC. **$[\alpha]_D^{20}$**:+33.6 (c=1.1, CH_2Cl_2), 98% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 20.43 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4b** and 23.41 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4b**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 4.34-4.30 (m, 2H), 3.77-3.72 (m, 1H), 3.46-3.41 (m, 1H), 3.26 (s, 3H), 3.01 (s, 6H) **^{19}F RMN** (282 MHz, $CDCl_3$): -62.30. **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.0, 176.2, 170.1, 143.5 (q, $J_{C\text{-}F}$ = 1.3 Hz), 130.2 (q, $J_{C\text{-}F}$ = 32.5 Hz), 127.1 , 125.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.01 (d, $J_{C\text{-}F}$ = 272.1 Hz), 66.5, 60.2, 54.6, 53.1, 37.2, 36.4, 25.1. **MS** (FAB+): 370.1 ([M+H], 100). **HRMS** (FAB+): Calculated for $C_{17}H_{19}N_3O_3F_3$, 370.1379; found, 370.1370.

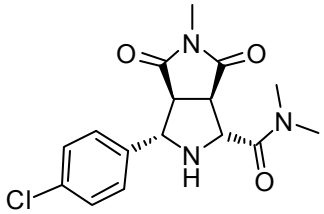
(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(4-bromophenyl)-octahydropyrrolo[3,4-c]pyrrole-1- *N,N*-dimethylcarboxamide (*exo*-4c)



Following the general procedure, the reaction of 2-[(4-bromobenzylidene)amino]-*N,N*-dimethylacetamide (**1c**) (50.0 mg, 0.19

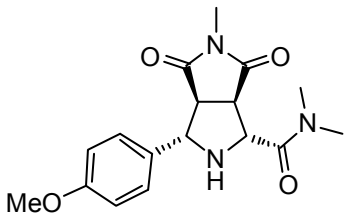
mmol) with *N*-methylmaleimide (**2**) (17.8 mg, 0.16 mmol), $Cu(CH_3CN)_4PF_6$ (0.6 mg, 1.55 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (2.0 mg, 1.70 10^{-3} mmol) and Et_3N (4 µL, 0.031 mmol), in THF (2.5 mL) at room temperature for 48 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:2) the cycloadduct *exo*-**4c** (55.0 mg, 92%, colorless solid). **m.p.**: 172.4-174.8ºC. **$[\alpha]_D^{20}$**:+47.8 (c=1.1, CH_2Cl_2), 99% *ee*. **HPLC:** Daicel Chiralpak OJ, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 26.66 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4c** and 33.48 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4c**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 4.30 (bs, 1H), 4.20 (bs, 1H), 3.75-3.70 (m, 1H), 3.42-3.36 (m, 1H), 3.26 (s, 3H), 3.02 (s, 3H), 3.00 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.1, 176.3, 170.2, 138.5, 131.9, 128.5, 122.1, 66.5, 60.1, 54.7, 53.2, 37.2, 36.5, 25.1. **MS** (ES+): 380.2 ([M+H], 70). **HRMS** (ES+): Calculated for $C_{16}H_{19}N_3O_3Br$, 380.0609; found, 380.0593.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(4-chlorophenyl)-octahydropyrrolo[3,4-c]pyrrole-1- *N,N*-dimethylcarboxamide (*exo*-4d)



Following the general procedure, the reaction of 2-[(4-chlorobenzylidene)amino]-*N,N*-dimethylacetamide (**1d**) (90.9 mg, 0.40 mmol) with *N*-methylmaleimide (**2**) (30.0 mg, 0.27 mmol), $Cu(CH_3CN)_4PF_6$ (1.0 mg, 2.70 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (3.5 mg, 2.97 10^{-3} mmol) and Et_3N (8 µL, 0.031 mmol), in THF (3 mL) at room temperature for 42 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:5) the cycloadduct *exo*-**4d** (85.0 mg, 94%, colorless solid). **m.p.**: 154.0-156.6ºC. **$[\alpha]_D^{20}$**:+48.7 (c=1.1, CH_2Cl_2), ≥ 99% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 21.71 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4d** and 24.37 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4d**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 4.28 (d, *J* = 5.3 Hz, 1H), 4.20 (d, *J* = 7.7 Hz, 1H), 3.71 (dd, *J* = 9.3, 5.3 Hz, 1H), 3.37 (dd, *J* = 9.3, 7.6 Hz, 1H), 3.24 (s, 3H), 3.00 (s, 3H), 2.99 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.1, 176.2, 170.1, 137.9, 133.8, 128.9, 128.1, 66.4, 60.1, 54.6, 53.2, 37.1, 36.4, 25.0. **MS** (ES+): 336.1 ([M+H], 100). **HRMS** (ES+): Calculated for $C_{16}H_{19}N_3O_3Cl$, 336.1104; found, 336.1111.

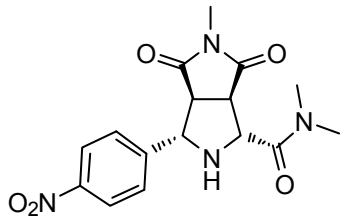
(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(4-methoxyphenyl)-octahydropyrrolo[3,4-c]pyrrole-1- *N,N*-dimethylcarboxamide (*exo*-4e)



Following the general procedure, the reaction of 2-[(4-methoxybenzylidene)amino]-*N,N*-dimethylacetamide (**1e**) (60.0 mg, 0.27 mmol) with *N*-methylmaleimide (**2**) (20.3 mg, 0.18 mmol), $Cu(CH_3CN)_4PF_6$ (0.7 mg, 1.82 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (2.4 mg, 2.00 10^{-3} mmol) and Et_3N (5 µL, 0.031 mmol), in THF (3 mL) at room temperature for 90 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:5) the cycloadduct *exo*-**4e** (40.4 mg, 67%, brown solid). **m.p.**: 137.3-139.5ºC. **$[\alpha]_D^{20}$**:+33.8 (c=0.5, CH_2Cl_2), 96% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 26.15 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4e** and 32.82min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4e**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.7Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.27 (d, *J* = 5.5 Hz, 1H), 4.15 (d, *J* = 7.9 Hz, 1H), 3.78 (s, 3H), 3.71-3.66 (m, 1H), 3.41-3.35 (m, 1H), 3.25 (s, 3H), 3.01 (s, 3H), 2.98 (s, 3H).

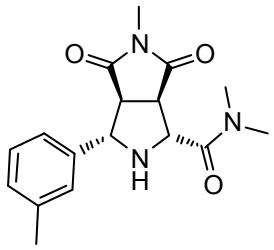
^{13}C NMR (75 MHz, $CDCl_3$): δ 177.2, 176.2, 170.4, 159.4, 131.2, 127.9, 114.2, 66.9, 60.0, 55.3, 54.8, 53.4, 37.1, 36.4, 24.9. **MS** (FAB+): 332.5 ([M+H], 30). **HRMS** (FAB+): Calculated for $C_{17}H_{22}N_3O_4$, 332.1610; found, 332.1617.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(4-nitrophenyl)-octahydropyrrolo[3,4-c]pyrrole-1- *N,N*-dimethylcarboxamide (*exo*-4f)



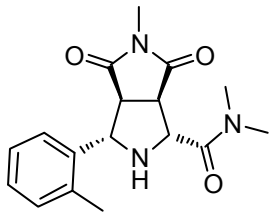
Following the general procedure, the reaction of 2-[(4-nitrobenzylidene)amino]-*N,N*-dimethylacetamide (**1f**) (63.5 mg, 0.40 mmol) with *N*-methylmaleimide (**2**) (30.0 mg, 0.27 mmol), $Cu(CH_3CN)_4PF_6$ (1.0 mg, 2.70 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (3.5 mg, 2.97 10^{-3} mmol) and Et_3N (8 µL, 0.031 mmol), in THF (3 mL) at room temperature for 70 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-0:1) the cycloadduct *exo*-**4f** (80.0 mg, 86%, yellow solid). **m.p.**: 138.3-141.8ºC. **$[\alpha]_D^{20}$**:+60.9 (c=0.32, CH_2Cl_2), ≥ 99% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 42.26 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4f** and 52.42 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4f**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 4.48 – 4.28 (m, 2H), 3.79 (dd, *J* = 9.6, 4.9 Hz, 1H), 3.54 – 3.36 (m, 1H), 3.27 (s, 3H), 3.15 (bs, 1H), 3.02 (s, 3H), 3.00 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.0, 176.3, 169.9, 147.5, 147.1, 127.6, 123.8, 66.1, 60.3, 54.5, 52.8, 37.2, 36.4, 25.2. **MS** (ESI+): 347.3 ([M+H], 100). **HRMS** (ESI+): Calculated for $C_{16}H_{19}N_4O_5$, 347.1349; found, 347.1334.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(3-methylphenyl)-octahydropyrrolo[3,4-c]pyrrole-1- *N,N*-dimethylcarboxamide (*exo*-4g)



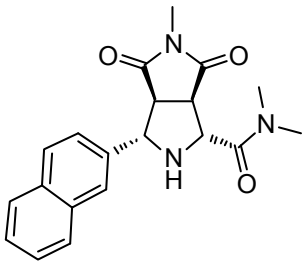
Following the general procedure, the reaction of 2-[(3-methylbenzylidene)amino]-*N,N*-dimethylacetamide (**1g**) (60.0 mg, 0.29 mmol) with *N*-methylmaleimide (**2**) (21.8 mg, 0.20 mmol), $Cu(CH_3CN)_4PF_6$ (0.7 mg, 1.96 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (2.5 mg, 2.16 10^{-3} mmol) and Et_3N (5 µL, 0.031 mmol), in THF (2.5 mL) at room temperature for 45 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:4) the cycloadduct *exo*-**4g** (54.0 mg, 86%, pale yellow oil). **$[\alpha]_D^{20}$**:+25.1 (c=1.1, CH_2Cl_2), 96% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 22.66 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4g** and 26.36 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4g**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.32-7.24 (m, 3H), 7.14-7.11 (m, 1H), 4.28 (d, *J* = 5.6 Hz, 1H), 4.19 (d, *J* = 7.9 Hz, 1H), 3.74-3.69 (m, 1H), 3.47-3.41 (m, 1H), 3.27 (s, 3H), 3.04 (s, 3H), 3.01 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.3, 176.2, 170.4, 139.1, 138.5, 128.9, 128.7, 127.4, 123.9, 67.3, 60.2, 54.8, 53.4, 37.2, 36.4, 25.1, 21.7. **MS** (FAB+): 315.4 ([M+H], 100). **HRMS** (FAB+): Calculated for $C_{17}H_{22}N_3O_3$, 316.1661; found, 316.1658.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(2-methylphenyl)-octahydropyrrolo[3,4-c]pyrrole-1- *N,N*-dimethylcarboxamide (*exo*-4h)



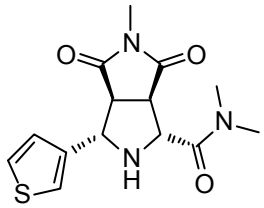
Following the general procedure, the reaction of 2-[(2-methylbenzylidene)amino]-*N,N*-dimethylacetamide (**1h**) (55.1 mg, 0.27 mmol) with *N*-methylmaleimide (**2**) (20.0 mg, 0.18 mmol), $Cu(CH_3CN)_4PF_6$ (3.4 mg, 9.00 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (11.7 mg, 9.90 10^{-3} mmol) and Et_3N (5 µL, 0.036 mmol), in THF (3 mL) at room temperature for 48 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:10) the cycloadduct *exo*-**4h** (47.0 mg, 83%, yellow solid). **m.p.**: 197.4-199.2ºC. $[\alpha]_D^{20}$:-9.1 (c=1.1, CH_2Cl_2), 98% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 10-90, flow rate 0.7 mL/min (λ = 210 nm), t_R: 34.28 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4h** and 41.63 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4h**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.14 (d, *J* = 7.4 Hz, 1H), 7.28-7.17 (m, 3H), 4.42 (d, *J* = 7.9 Hz, 1H), 4.29 (d, *J* = 5.4 Hz, 1H), 3.79-3.74 (m, 1H), 3.57-3.51 (m, 1H), 3.26 (s, 3H), 3.03 (s, 3H), 3.00 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.9, 176.7, 171.0, 137.6, 137.3, 131.5, 128.6, 127.3, 126.2, 64.4, 61.0, 54.9, 53.9, 37.7, 37.0, 25.5, 20.2. **MS** (FAB+): 316.4 ([M+H], 100). **HRMS** (FAB+): Calculated for $C_{17}H_{22}N_3O_3$, 316.1661; found, 316.1662.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(2-napthyl)-octahydropyrrolo[3,4-c]pyrrole-1-*N,N*-dimethylcarboxamide (*exo*-4i)



Following the general procedure, the reaction of 2-[(2-naphtyl-2-methylidene)amino]-*N,N*-dimethylacetamide (**1i**) (80.0 mg, 0.33 mmol) with *N*-methylmaleimide (**2**) (24.7 mg, 0.22 mmol), $Cu(CH_3CN)_4PF_6$ (8.3 mg, 2.22 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (6.4 mg, 0.024 mmol) and Et_3N (6 µL, 0.044 mmol), in THF (3 mL) at room temperature for 13 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-0:1) the cycloadduct *exo*-**4i** (58.8 mg, 76%, colorless solid). **m.p.**: 179.9-180.5ºC. $[\alpha]_D^{20}$:+57.7 (c=1.1, CH_2Cl_2), ≥ 99% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 33.86 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4i** and 39.57 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4i**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.86-7.81 (m, 3H), 7.70-7.67 (m, 1H), 7.49-7.46 (m, 2H), 4.43-4.35 (m, 2H), 3.78 (dd, *J* = 9.3, 5.4 Hz, 1H), 3.55 (dd, *J* = 9.4, 7.6 Hz, 1H), 3.31 (s, 3H), 3.05 (s, 3H), 3.04 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.3, 176.4, 170.4, 136.6, 133.3, 133.1, 128.7, 128.1, 127.7, 126.4, 126.2, 125.7, 124.6, 67.4, 60.3, 54.8, 53.4, 37.2, 36.5, 25.0. **MS** (FAB+): 352.2 ([M+H], 80). **HRMS** (FAB+): Calculated for $C_{20}H_{22}N_3O_3$, 352.1661; found, 352.1665.

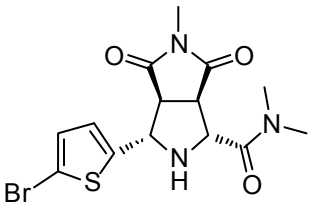
(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(3-thienyl)-octahydropyrrolo[3,4-c]pyrrole-1-*N,N*-dimethylcarboxamide (*exo*-4j)



Following the general procedure, the reaction of 2-[(3-thienyl-2-methylidene)amino]-*N,N*-dimethylacetamide (**1j**) (50.0 mg, 0.26 mmol) with *N*-methylmaleimide (**2**) (18.9 mg, 0.17 mmol), $Cu(CH_3CN)_4PF_6$ (3.17 mg, 8.50 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (11.0 mg, 9.35 10^{-3} mmol) and Et_3N (5 µL, 0.031 mmol), in THF (3 mL) at room temperature for 96 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1) the cycloadduct *exo*-**4j** (50.0 mg, 95%, pale yellow solid). **m.p.**: 166.0-169.0ºC. $[\alpha]_D^{20}$:+58.7 (c=0.31, CH_2Cl_2), ≥ 99% *ee*. **HPLC:** Daicel

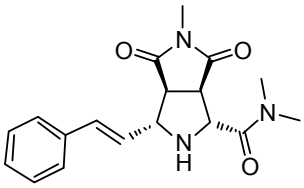
Chiralpak IB, *i*-PrOH-hexane 40-60, flow rate 0.7 mL/min (λ = 210 nm), t_R: 24.93 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4j** and 55.64 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4j**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.42 – 7.25 (m, 3H), 4.36 – 4.17 (m, 2H), 3.70 (dd, *J* = 9.3, 5.5 Hz, 1H), 3.46 – 3.34 (m, 1H), 3.27 (s, 3H), 3.02 (s, 3H), 3.01 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.2, 176.1, 170.2, 140.2, 126.4, 126.4, 121.7, 63.6, 60.0, 54.6, 53.4, 37.2, 36.4, 25.0. **MS** (EI+): 307.4 ([M+H], 100). **HRMS** (EI+): Calculated for $C_{14}H_{18}N_3O_3S$, 307.0991; found, 307.0990.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(2-(5-bromo)thienyl)-octahydropyrrolo[3,4-c]pyrrole-1-*N*,*N*-dimethylcarboxamide (*exo*-4k)



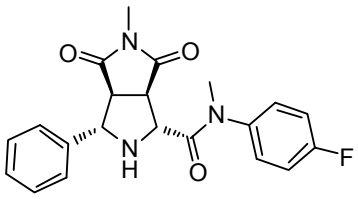
Following the general procedure, the reaction of 2-[(2-(5-bromo)thienyl-2-methylidene)amino]-*N,N*-dimethylacetamide (**1k**) (80.0 mg, 0.29 mmol) with *N*-methylmaleimide (**2**) (16.2 mg, 0.15 mmol), $Cu(CH_3CN)_4PF_6$ (2.7 mg, 7.27 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (9.4 mg, 8.0 10^{-3} mmol) and Et_3N (4 μL, 0.029 mmol), in THF (2 mL) at room temperature for 120 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:5) the cycloadduct *exo*-**4k** (47.3 mg, 82%, pale brown solid). **m.p.**: 128.4-130.0ºC. **$[\alpha]_D^{20}$**:+90.0 (c=0.2, CH_2Cl_2), ≥ 99% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 22.38 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4k** and 30.27 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4k**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.12 – 6.63 (m, 2H), 4.31 (s, 2H), 4.01 – 3.66 (m, 1H), 3.52 (dd, *J* = 9.1, 6.7 Hz, 1H), 3.23 (s, 3H), 2.99 (s, 3H), 2.97 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.3, 175.9, 169.5, 144.7, 129.9, 125.2, 111.9, 63.1, 60.7, 54.6, 52.6, 37.2, 36.4, 25.1. **MS** (EI+): 385.3 ([M+H], 100). **HRMS** (EI+): Calculated for $C_{14}H_{16}BrN_3O_3S$, 385.0096; found, 385.0112.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(styryl)-octahydropyrrolo[3,4-c]pyrrole-1-*N*,*N*-dimethylcarboxamide (*exo*-4l)



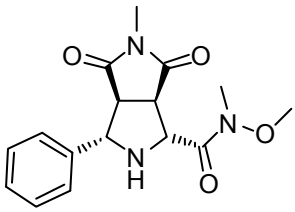
Following the general procedure, the reaction of (*E, E*)-2-[3-phenylprop-2-en-1-ylidene)amino]-*N,N*-dimethylacetamide (**1l**) (87.1 mg, 0.40 mmol) with *N*-methylmaleimide (**2**) (30.0 mg, 0.27 mmol), $Cu(CH_3CN)_4PF_6$ (1.0 mg, 2.70 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (3.5 mg, 2.97 10^{-3} mmol) and Et_3N (8 μL, 0.031 mmol), in THF (3 mL) at room temperature for 62 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:5) the cycloadduct *exo*-**4l** (53.0 mg, 60%, yellow oil). **$[\alpha]_D^{20}$**:+38.6 (c=0.14, CH_2Cl_2), 98% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 250 nm), t_R: 25.19 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4l** and 32.83 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4l**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.46 – 7.18 (m, 5H), 6.69 (d, *J* = 15.6 Hz, 1H), 6.37 (dd, *J* = 15.9, 6.3 Hz, 1H), 4.29 (d, *J* = 4.7 Hz, 1H), 3.90 (t, *J* = 6.5 Hz, 1H), 3.70 (dd, *J* = 9.1, 4.6 Hz, 1H), 3.26 (s, 3H), 3.24-3.21 (m, 1H), 3.03 (s, 3H), 3.01 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.5, 176.4, 170.7, 136.3, 132.3, 129.0, 128.6, 128.3, 127.9, 127.5, 126.6, 65.8, 60.4, 53.5, 52.4, 37.2, 36.5, 25.0. **MS** (EI+): 327.4 ([M+H], 10). **HRMS** (FAB+): Calculated for $C_{18}H_{22}N_3O_3$, 327.1583; found, 327.1590.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-phenyl-octahydropyrrolo[3,4-c]pyrrole-1-[*N*-methyl- *N*-(4-fluorophenyl)]carboxamide (*exo*-4m)



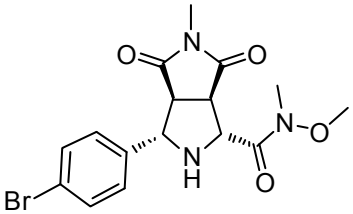
Following the general procedure, the reaction of 2-benzylideneamino-*N*-methyl-*N*-(4-fluorophenyl)acetamide (**1m**) (50.0 mg, 0.19 mmol) with *N*-methylmaleimide (**2**) (13.7 mg, 0.12 mmol), $Cu(CH_3CN)_4PF_6$ (0.5 mg, 1.20 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (1.6 mg, 1.36 10^{-3} mmol) and Et_3N (4 µL, 0.031 mmol), in THF (2 mL) at room temperature for 15 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 3:1-1:1) the cycloadduct *exo*-**4m** (38.0 mg, 83%, colorless solid). **m.p.**: 67.5-68.8ºC. **$[\alpha]_D^{20}$**:-63.1 (c=0.26, CH_2Cl_2), ≥ 99% *ee*. **HPLC:** Daicel Chiralpak IB, *i*PrOH-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 28.94 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4m** and 48.78 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4m**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.53 – 7.46 (m, 2H), 7.42 – 7.28 (m, 5H), 7.12 (dd, *J* = 9.0, 8.0 Hz, 2H), 4.07 (d, *J* = 7.5 Hz, 1H), 3.94 – 3.78 (m, 2H), 3.45 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.33 (s, 3H), 2.90 (s, 3H). **^{19}F NMR** (282 MHz, $CDCl_3$):-112.5. **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.4, 176.3, 170.6, 162.08 (d, $J_{C\text{-}F}$= 248.8 Hz), 139.4, 138.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 129.6 (d, $J_{C\text{-}F}$ = 8.7 Hz), 128.7, 128.0, 126.7, 116.81 (d, $J_{C\text{-}F}$ = 22.7 Hz), 66.8, 60.6, 54.8, 52.7, 38.4, 24.9. **MS** (ESI+): 382.4 ([M+H], 50). **HRMS** (ESI+): Calculated for $C_{21}H_{21}FN_3O_3$, 382.1561; found, 382.1576.

(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-phenyl-octahydropyrrolo[3,4-c]pyrrole-1- (*N*-methyl, *N*-methoxy)carboxamide (*exo*-4n)



Following the general procedure, the reaction of 2-benzylideneamino- *N*-methyl-*N*-methoxyacetamide (**1n**) (50.0 mg, 0.24 mmol) with *N*-methylmaleimide (**2**) (18.0 mg, 0.16 mmol), $Cu(CH_3CN)_4PF_6$ (0.6 mg, 1.62 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (2.1 mg, 1.78 10^{-3} mmol) and Et_3N (5 µL, 0.032 mmol), in THF (2 mL) at room temperature for 17 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1) the cycloadduct *exo*-**4n** (36.0 mg, 71%, colorless solid). **m.p.**: 143.7-145.8ºC. **$[\alpha]_D^{20}$**:-21.4 (c=1.0, CH_2Cl_2), 98% *ee*. **HPLC:** Daicel Chiralpak AS-H, *i*-PrOH-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 27.68 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4n** and 45.69 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4n**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.27 (m, 3H), 4.39 (d, *J* = 5.3 Hz, 1H), 4.32 (d, *J* = 7.2 Hz, 1H), 3.91 (dd, *J* = 9.2, 5.2 Hz, 1H), 3.81 (s, 3H), 3.41 (dd, *J* = 9.2, 7.2 Hz, 1H), 3.25 (s, 3H), 3.02 (s, 3H), 2.92 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 177.2, 176.7, 170.9, 139.9, 128.7, 128.0, 126.7, 66.5, 61.8, 59.9, 53.6, 50.6, 32.7, 25.0. **MS** (ESI+): 318.4 ([M+H], 100). **HRMS** (ESI+): Calculated for $C_{16}H_{19}N_3O_4$, 318.1448; found, 318.1440.

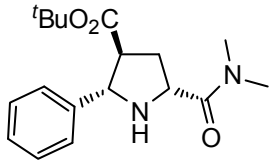
(1*R*, 3*S*, 3*aS*, 6*aR*)-5-methyl-4,6-dioxo-3-(4-bromophenyl)-octahydropyrrolo[3,4-c]pyrrole-1-*N*-methyl, *N*-methoxycarboxamide (*exo*-4o)



Following the general procedure, the reaction of 2-(4-bromo-benzylidene-amino) *N*-methyl-*N*-methoxyacetamide (**1o**) (84.2 mg, 0.30 mmol) with *N*-methylmaleimide (**2**) (21.9 mg, 0.20 mmol),

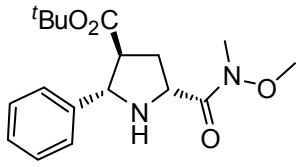
$Cu(CH_3CN)_4PF_6$ (0.7 mg, 1.97 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (2.6 mg, 2.17 10^{-3} mmol) and Et_3N (6 µL, 0.039 mmol), in THF (2 mL) at room temperature for 18 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:2) the cycloadduct *exo*-**4o** (63.0 mg, 79%, colorless oil). **$[\alpha]_D^{20}$**:-7.5 (c=0.03, CH_2Cl_2), 96% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 39.90 min (1*S*, 3*R*, 3*aR*, 6*aS*)-*exo*-**4o** and 55.90 min (1*R*, 3*S*, 3*aS*, 6*aR*)-*exo*-**4o**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 4.38 (d, *J* = 5.2 Hz, 1H), 4.27 (d, *J* = 7.1 Hz, 1H), 3.91 (dd, *J* = 9.2, 5.2 Hz, 1H), 3.80 (s, 3H), 3.33 (dd, *J* = 9.3, 7.1 Hz, 1H), 3.24 (s, 3H), 3.01 (s, 3H), 2.84 (bs, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.1, 176.6, 170.7, 139.2, 131.7, 128.5, 121.7, 65.8, 61.8, 59.8, 53.5, 50.2, 32.6, 25.0. **MS** (ESI+): 396.1 ([M+H], 100). **HRMS** (ESI+): Calculated for $C_{16}H_{18}N_3O_4Br$, 396.0553; found, 396.0538.

(2*R*, 4*S*, 5*R*)- tert-Butyl-2-(dimethylcarbamoyl)-5-phenylpyrrolidine-4- carboxylate (*exo*-11a)



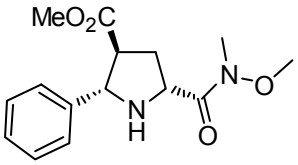
Following the general procedure [using (*R*)-DTBM-Segphos (**3c**) (11 mol%) as ligand] the reaction of 2-benzylidene-amino-*N*,*N*-dimethylacetamide (**1a**) (50.0 mg, 0.26 mmol) with tert-butyl acrylate (**5**) (33 µL, 28.9 mg, 0.22 mmol), $Cu(CH_3CN)_4PF_6$ (8.2 mg, 0.022 mmol), (*R*)-DTBM-Segphos (**3c**) (28.5 mg, 0.024 mmol) and Et_3N (6 µL, 0.04 mmol), in THF (2 mL) at room temperature for 48 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:4), the cycloadduct *exo*-**11a** (57.2 mg, 82%, orange oil). **$[\alpha]_D^{20}$**:+29.9 (c=0.2, CH_2Cl_2), 94% *ee*. **HPLC:** Daicel Chiralpak AD, *i*-PrOH-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R:12.55 min (2*R*, 4*S*, 5*R*)-*exo*-**11a** and 16.43 min (2*S*, 4*R*, 5*S*)-*exo*-**11a**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.36-7.26 (m, 3H), 4.24-4.15 (m, 2H), 3.07 (s, 3H), 3.01 (s, 3H), 2.86-2.78 (m, 1H), 2.57-2.47 (m, 2H), 2.17-2.07 (m, 1H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.0, 169.9, 137.5, 125.5, 124.7, 124.0, 77.8, 65.1, 54.6, 49.9, 33.4, 32.8, 32.4, 24.9. **MS** (ESI+): 388.1 ([M+H], 50). **HRMS** (ESI+): Calculated for $C_{18}H_{26}N_2O_3$, 319.2021; found, 319.2013.

(2*R*, 4*S*, 5*R*)- tert-Butyl-2-(methoxy(methyl)carbamoyl)-5-phenylpyrrolidine-4-carboxylate (*exo*-11n)



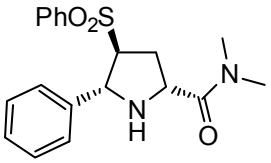
Following the general procedure [using (*R*)-DTBM-Segphos (**3c**) (5.5 mol%) as ligand] the reaction of 2-benzylideneamino- *N*-methyl-*N*-methoxyacetamide (**1n**) (80.0 mg, 0.39 mmol) with *tert*-butyl acrylate (**5**) (28.4 µL, 24.8 mg, 0.19 mmol), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 9.70 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (12.6 mg, 10.5 10^{-3} mmol) and Et_3N (5 µL, 0.040 mmol), in THF (2 mL) at room temperature for 48 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:2), the cycloadduct *exo*-**11n** (32.0 mg, 50%, yellow oil). **$[\alpha]_D^{20}$**:+39.7 (c=0.34, CH_2Cl_2), ≥ 99% *ee*. **HPLC:** Daicel Chiralpak AD, *i*-PrOH-hexane 5-95, flow rate 0.7 mL/min (λ = 210 nm), t_R:32.40 min (2*R*, 4*S*, 5*R*)-*exo*-**11n** and 49.89 min (2*S*, 4*R*, 5*S*)-*exo*-**11n**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.54 – 7.43 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 3H), 4.30 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 3.26 (s, 3H), 3.22 (s, 1H), 2.94 – 2.72 (m, 1H), 2.67 – 2.45 (m, 1H), 2.25 (ddd, *J* = 13.4, 8.8, 5.3 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.4, 172.8, 140.7, 128.5, 127.7, 127.1, 80.7, 67.8, 61.4, 57.4, 52.7, 35.3, 32.6, 28.0. **MS** (ESI+): 335.4 ([M+H], 40). **HRMS** (ESI+): Calculated for $C_{18}H_{27}N_2O_4$, 335.1965; found, 335.1980.

(2*R*, 4*S*, 5*R*)-Methyl 2-(methoxy(methyl)carbamoyl)-5-phenylpyrrolidine-4-carboxylate (*exo*-12)



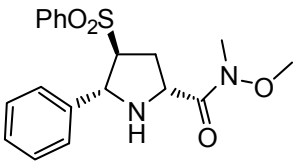
Following the general procedure [using (*R*)-DTBM-Segphos (**3c**) (5.5 mol%) as ligand] the reaction of 2-benzylideneamino-*N*-methyl-*N*-methoxyacetamide (**1n**) (58.8 mg, 0.28 mmol) with methyl acrylate (**6**) (18 µL, 17.2 mg, 0.19 mmol), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 9.70 10^{-3} mmol), (*R*)-DTBM-Segphos (**3c**) (12.6 mg, 10.5 10^{-3} mmol) and Et_3N (5 µL, 0.039 mmol), in THF (2 mL) at room temperature for 48 h afforded, after purification by silica gel flash chromatography (hexane-AcOEt 1:1- 0:1) the cycloadduct *exo*-**12** (33.5 mg, 60%, yellow oil)**.** **$[\alpha]_D^{20}$**:+55.6 (c=0.39, CH_2Cl_2), 98% *ee*. **HPLC:** Daicel Chiralpak AD, *i*-PrOH-hexane 40-60, flow rate 0.7 mL/min (λ = 210 nm), t_R: 14.38 min (2*R*, 4*S*, 5*R*)-*exo*-**12** and 22.11min (2*S*, 4*R*, 5*S*)-*exo*-**12**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.52 – 7.41 (m, 2H), 7.40 – 7.25 (m, 3H), 4.37 (d, *J* = 9.0 Hz, 1H), 4.30 (dd, *J* = 8.6, 5.5 Hz, 1H), 3.74 (s, 3H), 3.63 (s, 3H), 3.25 (s, 3H), 3.04 (bs, 1H), 2.94 (q, *J* = 9.0 Hz, 1H), 2.55 (dt, *J* = 13.1, 9.0 Hz, 1H), 2.41 – 2.21 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.0, 140.4, 128.6, 127.9, 126.97, 67.4, 61.4, 57.4, 51.8, 51.5, 35.5. **MS** (ESI+): 293.3 ([M+H], 100). **HRMS** (ESI+): Calculated for $C_{15}H_{21}N_2O_4$, 293.1495; found, 293.1502.

(2*R*, 4*S*, 5*R*)- 5-phenyl-4-(phenylsulfonyl)pyrrolidine-2- *N*,*N*-dimethylcarboxamide (*exo*-13a)



Following the general procedure [using (*R*)-DTBM-Segphos (**3c**) (11 mol%) as ligand] the reaction of 2-benzylidene-amino-*N*,*N*-dimethylacetamide (**1a**) (84.7 mg, 0.45 mmol) with phenyl vinyl sulfone (**7**) (50 mg, 0.29 mmol), $Cu(CH_3CN)_4PF_6$ (11.1 mg, 0.029 mmol), (*R*)-DTBM-Segphos (**7**) (38.6 mg, 0.033 mmol) and Et_3N (8 µL, 0.06 mmol), in THF (3 mL) at room temperature for 34 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:6), the cycloadduct *exo*-**13a** (89.0 mg, 85%, colorless solid). **m.p.**: 165.3-166.7ºC. **$[\alpha]_D^{20}$**:-5.6 (c=0.49, CH_2Cl_2), ≥ 99% *ee*. **HPLC:** Daicel Chiralpak OJ, *i*-PrOH-hexane 30-70, flow rate 0.7 mL/min (λ = 210 nm), t_R:45.56 min (2*R*, 4*S*, 5*R*)-*exo*-**13a** and 57.91 min (2*S*, 4*R*, 5*S*)-*exo*-**13a**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.79 – 7.66 (m, 2H), 7.59 – 7.31 (m, 3H), 7.14 (m, 5H), 4.50 (d, *J* = 7.0 Hz, 1H), 4.24 (t, *J* = 7.7 Hz, 1H), 3.80 – 3.69 (m, 1H), 3.09 (s, 3H), 2.99 (s, 3H), 2.87 – 2.69 (m, 1H), 2.57 (bs, 1H), 2.31 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.6, 139.8, 138.2, 133.7, 129.1, 128.7, 128.4, 128.0, 126.9, 70.4, 64.78, 57.6, 36.7, 35.9, 32.9.**MS** (ESI+): 359.1 ([M+H], 100). **HRMS** (ESI+): Calculated for $C_{19}H_{23}N_2O_5S$, 359.1423; found, 359.1426.

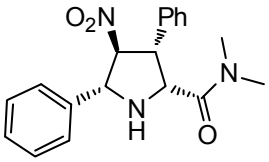
(2*R*, 4*S*, 5*R*)-5-phenyl-4-(phenylsulfonyl)pyrrolidine-2-*N*-methoxy-*N*-methylcarboxamide (*exo*-13n)



Following the general procedure [using (*R*)-DTBM-Segphos (**3c**) (5.5 mol%) as ligand] the reaction of 2-benzylideneamino-*N*-methyl-*N*-methoxyacetamide (**1n**) (110.2 mg, 0.54 mmol) with phenyl vinyl sulfone (**7**) (60.0 mg, 0.36 mmol), $Cu(CH_3CN)_4PF_6$ (6.7 mg, 0.018 mmol), (*R*)-DTBM-Segphos (**3c**) (23.1 mg, 0.020 mmol) and Et_3N (10 µL, 0.071 mmol), in THF (3.5 mL) at room temperature for 40 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 1:1-1:5), the cycloadduct *exo*-**13n** (128.1 mg, 95%, pale yellow solid). **m.p.**: 96.9-99.0ºC (After

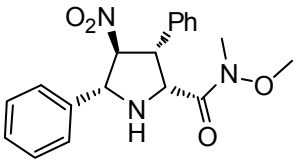
recrystalization: 104.2-105.9ºC) $[\alpha]_D^{20}$:+4.6 (c=0.13, CH_2Cl_2) (After recrystalization:$[\alpha]_D^{20}$:+5.5 (c=0.2, CH_2Cl_2)), 90% *ee* (≥ 99% *ee* after recrystalization, *i*-PrOH). **HPLC:** Daicel Chiralpak AD, *i*-PrOH-hexane 50-50, flow rate 0.7 mL/min (λ = 210 nm), t_R:13.50 min (2*R*, 4*S*, 5*R*)-*exo*-**13n** and 20.34 min (2*S*, 4*R*, 5*S*)-*exo*-**13n**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.51 (s, 1H), 7.38 (s, 2H), 7.15 (s, 5H), 4.57 (d, *J* = 6.7 Hz, 1H), 4.30 (t, *J* = 7.8 Hz, 1H), 3.72 (s, 3H), 3.75 – 3.65 (m, 1H), 3.20 (s, 3H), 3.12 (d, *J* = 7.4 Hz, 1H), 2.76 (ddd, *J* = 13.5, 7.7, 5.5 Hz, 1H), 2.32 (ddd, *J* = 13.9, 9.5, 8.0 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 172.7, 140.2, 138.2, 133.7, 129.1, 128.6, 128.4, 127.9, 127.0, 70.2, 64.0, 61.6, 57.3, 32.5, 32.1. **MS** (FAB+): 375.5 ([M+H], 50). **HRMS** (FAB+): Calculated for $C_{19}H_{23}N_2O_4S$, 375.1373; found, 375.1364.

(2*R*, 3*R*, 4*S*, 5*R*)-4-nitro-3,5-diphenylpyrrolidine-2-*N*,*N*-dimethylcarboxamide (*exo*-14a)



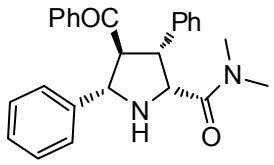
Following the general procedure [using (*R*)-Segphos (**3a**) (5.5 mol%) as ligand] the reaction of 2-benzylidenamino-*N*,*N*-dimethylacetamide (**1a**) (50.0 mg, 0.26 mmol) with trans-*β*-nitrostyrene (**8**) (32.7 mg, 0.22 mmol), $Cu(CH_3CN)_4PF_6$ (8.2 mg, 0.022 mmol), (*R*)-Segphos (**3a**) (14.7 mg, 0.024 mmol) and Et_3N (6 µL, 0.044 mmol) in THF (2.5 mL), at room temperature for 25 h afforded, after purification by silica gel flash chromatography (hexane-AcOEt 2:1-1:1) the cycloadduct *exo*-**14a** (59.3 mg, 80%, pale yellow solid) **m.p.**: 192.0-195.0ºC**.** $[\alpha]_D^{20}$:+98.0 (c=0.15, CH_2Cl_2), 91% *ee*. **HPLC:** Daicel Chiralpak , *i*-PrOH-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 18.64 min (2*S*, 3*S*, 4*R*, 5*S*)-*exo*-**14a** and 24.61 min (2*R*, 3*R*, 4*S*, 5*R*)-*exo*-**14a**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.57 (d, *J* = 6.7 Hz, 2H), 7.45 – 7.29 (m, 3H), 7.28 – 7.23 (m, 5H), 5.21 (dd, *J* = 19.3, 9.2 Hz, 1H), 4.66 (t, *J* = 8.7 Hz, 2H), 4.38 (t, *J* = 10.0 Hz, 1H), 2.60 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.6, 136.9, 134.6, 129.2, 128.7, 128.3, 127.1, 95.9, 68.2, 60.4, 55.5, 36.3, 35.7. **MS** (ESI+): 340.2 ([M+H], 100). **HRMS** (ESI+): Calculated for $C_{19}H_{22}N_3O_3$, 340.1661; found, 340.1665.

(2*R*, 3*R*, 4*S*, 5*R*)-4-nitro-3,5-diphenylpyrrolidine-2-*N*-methoxy-*N*-methylcarboxamide (*exo*-14n)



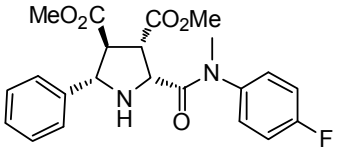
Following the general procedure [using (*R*)-Segphos (**3a**) (11 mol%) as ligand] the reaction of 2-benzylideneamino-*N*-methyl-*N*-methoxyacetamide (**1n**) (50.0 mg, 0.24 mmol) with trans-*β*-nitrostyrene (**8**) (24.1 mg, 0.16 mmol), $Cu(CH_3CN)_4PF_6$ (6.0 mg, 0.016 mmol), (*R*)-Segphos (**3a**) (10.9 mg, 0.017 mmol) and Et_3N (5 µL, 0.032 mmol), in THF (2 mL) at room temperature for 16 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 3:1-2:1), the cycloadduct *exo*-**14n** (49.5 mg, 87%, yellow solid). **m.p.**: 131.5-134.0ºC. $[\alpha]_D^{20}$:+37.1 (c=0.17, CH_2Cl_2), 89% *ee*. **HPLC:** Daicel Chiralpak AD, *i*-PrOH-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R:17.38 min (2*S*, 3*S*, 4*R*, 5*S*)-*exo*-**14n** and 19.68 min (2*R*, 3*R*, 4*S*, 5*R*)-*exo*-**14n**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.42 – 7.29 (m, 3H), 7.27 – 7.09 (m, 5H), 5.15 (t, *J* = 8.3 Hz, 1H), 4.70 (s, 2H), 4.36 (t, *J* = 8.4 Hz, 1H), 3.52 (s, 3H), 3.11 (Bs, 1H), 2.64 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.3, 137.1, 136.1, 129.1, 128.9, 128.4, 128.1, 126.8, 96.8, 68.0, 62.0, 61.2, 55.3, 32.1. **MS** (FAB+): 355.4 ([M+H], 30). **HRMS** (FAB+): Calculated for $C_{19}H_{22}N_3O_4$, 356.1610; found, 356.1618.

(2*R*, 3*S*, 4*S*, 5*S*)-4-benzoyl-3,5-diphenylpyrrolidine-2-*N*,*N*-dimethylcarboxamide (*exo*-15)



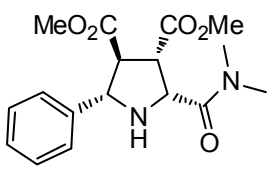
Following the general procedure [using (*R*)-Segphos (**3a**) (11 mol%) as ligand] the reaction of 2-benzylidene-amino-*N*,*N*-dimethylacetamide (**1a**) (50.0 mg, 0.26 mmol) with *trans*-chalcone (**9**) (45.7 mg, 0.22 mmol), $Cu(CH_3CN)_4PF_6$ (8.2 mg, 0.022 mmol), (*R*)-Segphos (**3a**) (14.7 mg, 0.024 mmol) and Et_3N (6 µL, 0.044 mmol), in THF (2 mL) at room temperature for 24 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 2:1-1:5), the cycloadduct *exo*-**15** (50.5 mg, 58%, yellow solid). **m.p.**: 170.5-172.9ºC. $[\alpha]_D^{20}$:+42.9 (c=1.1, CH_2Cl_2), 89% *ee*. **HPLC:** Daicel Chiralpak IB, ethanol-hexane 5-95, flow rate 0.7 mL/min (λ = 210 nm), t_R:38.34 min (2*R*, 3*S*, 4*S*, 5*S*)-*exo*-**15** and 48.56 min (2*S*, 3*R*, 4*R*, 5*R*)-*exo*-**15**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.32-7.10 (m, 11H), 4.70 (bs, 1H), 4.54 (bs, 1H), 4.36-4.22 (m, 2H), 3.34 (bs, 1H), 2.65 (s, 3H), 2.45 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 200.7, 171.7, 139.0, 138.0, 137.4, 132.9, 128.7, 128.4, 128.2, 128.1, 128.1, 128.0, 127.5, 127.0, 69.2, 62.2, 56.4, 36.2, 35.5, 29.7. **MS** (ESI+): 399.2 ([M+H], 100). **HRMS** (ESI+): Calculated for $C_{26}H_{26}N_2O_2$, 399.2072.; found, 399.2066.

(2*R*, 3*S*, 4*S*, 5*S*)-Dimethyl 2-[(4-fluorophenyl)(methyl)carbamoyl]-5-phenylpyrrolidine-3,4-dicarboxylate (*exo*-16m)



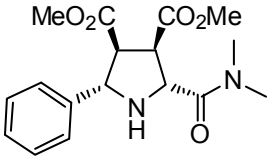
Following the general procedure [using (*R*)-Segphos (**3a**) (11 mol%) as ligand] the reaction of 2-benzylideneamino-*N*-methyl-*N*-(4-fluorophenyl)acetamide (**1m**) (56.3 mg, 0.21 mmol) with dimethyl fumarate (**10**) (21.0 mg, 0.14 mmol), $Cu(CH_3CN)_4PF_6$ (5.2 mg, 13.9 10^{-3} mmol), (*R*)-Segphos (**3a**) (9.3 mg, 0.015 mmol) and Et_3N (4 µL, 0.028 mmol), in THF (2 mL) at room temperature for 40 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 2:1-1:1), the cycloadduct *exo*-**16m** (42.5 mg, 73%, pale brown oil). $[\alpha]_D^{20}$:-8.9 (c=0.3, CH_2Cl_2), 71% *ee*. **HPLC:** Daicel Chiralpak AD, *i*-PrOH-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R:18.88 min (2*S*, 3*R*, 4*R*, 5*R*)-*exo*-**16m** and 26.77 min (2*R*, 3*S*, 4*S*, 5*S*)-*exo*-**16m**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.48 – 7.41 (m, 2H), 7.41 – 7.25 (m, 5H), 7.20 – 7.10 (m, 2H), 4.07 (d, *J* = 8.7 Hz, 1H), 3.97 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 3.66 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.56 (s, 3H), 3.34 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.26 (s, 3H), 2.77 (bs, 1H). **^{19}F NMR** (282 MHz, $CDCl_3$):-112.3. **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.3, 171.8, 169.9, 162.15 (d, $J_{C\text{-}F}$= 249.0 Hz), 139.6, 138.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 129.2 (d, $J_{C\text{-}F}$ = 8.6 Hz), 128.7, 128.1, 127.2, 116.9 (d, $J_{C\text{-}F}$ = 22.7 Hz), 67.7, 61.5, 54.6, 53.2, 52.6, 52.1, 37.7. **MS** (FAB+): 414.4 ([M+H], 80). **HRMS** (FAB+): Calculated for $C_{22}H_{24}N_2O_5F$, 415.1669; found, 415.1661.

(2*R*, 3*S*, 4*S*, 5*S*)-Dimethyl 2-(dimethylcarbamoyl)-5-phenylpyrrolidine-3,4-dicarboxylate (*exo*-16a)



Following the general procedure [using (*R*)-DM-Segphos (**3b**) (11 mol%) as ligand] the reaction of 2-benzylidenamino-*N*,*N*-dimethylacetamide (**1a**) (50.0 mg, 0.26 mmol) with dimethyl fumarate (**10**) (26.6 mg, 0.18 mmol), $Cu(CH_3CN)_4PF_6$ (6.5 mg, 0.018 mmol), (*R*)-DM-Segphos (**3b**) (14.0 mg, 0.019 mmol) and Et_3N (5 µL, 0.035 mmol) in THF (2 mL) at room temperature for 48 h afforded, after purification by silica gel flash chromatography (hexane-AcOEt 1:1-1:2) the cycloadduct *exo*-**16a** (30 mg, 50%, yellow oil) $[\alpha]_D^{20}$:-7.1 (c=0.1, CH_2Cl_2), 70% *ee*. **HPLC:** Daicel Chiralpak AS-H, *i*-PrOH-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R: 17.55 min (2*R*, 3*S*, 4*S*, 5*S*)-*exo*-**16a** and 47.4 min (2*S*, 3*R*,

4*R*, 5*R*)-*exo*-**16a**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.50-7.47 (m, 2H), 7.35-7.28 (m, 3H), 4.42 (d, *J* = 8.0 Hz, 1H), 4.27 (d, *J* = 8.4 Hz, 1H), 3.73-3.58 (m, 2H), 3.67 (s, 3H), 3.64 (s, 3H), 3.12 (s, 3H), 2.96 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): 173.6, 171.8, 169.5, 139.6, 128.7, 128.1, 127.2, 67.9, 61.6, 55.1, 52.7, 52.4, 52.2, 36.9, 35.8. **MS** (ESI+): 335.1 ([M+H], 80). **HRMS** (ESI+): Calculated for $C_{17}H_{22}N_2O_5$, 335.1606; found, 335.1616.



(2*R*, 3*R*, 4*S*, 5*S*)-Dimethyl 2-(dimethylcarbamoyl)-5-phenylpyrrolidine-3,4-dicarboxylate (*exo*-17a)

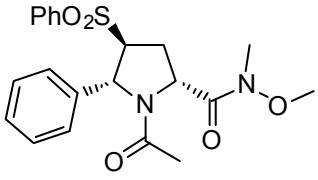
Following the general procedure [using (*R*)-DM-Segphos (**3b**) (11 mol%) as ligand] the reaction of 2-benzylideneamino-*N*,*N*-dimethylacetamide (**1a**) (50.0 mg, 0.26 mmol) with dimethyl maleate (**11**) (26.3 mg, 0.175 mmol), $Cu(CH_3CN)_4PF_6$ (6.5 mg, 0.018 mmol), (*R*)-DM-Segphos (**3b**) (14.0 mg, 0.019 mmol) and Et_3N (5 µL, 0.035 mmol), in THF (2.5 mL) at room temperature for 100 h afforded, after purification by silica gel flash chromatography (hexane-EtOAc 3:1-1:1), the cycloadduct *exo*-**17a** (41 mg, 70%, yellow oil). **$[\alpha]_D^{20}$:**+12.8 (c=3.0, CH_2Cl_2), 94% *ee*. **HPLC:** Daicel Chiralpak AS-H-H, *i*-PrOH-hexane 20-80, flow rate 0.7 mL/min (λ = 210 nm), t_R:16.63 min (2*R*, 3*R*, 4*S*, 5*S*)-*exo*-**17a** and 39.42 min (2*S*, 3*S*, 4*R*, 5*R*)-*exo*-**17a**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.53 – 7.43 (m, 2H), 7.42 – 7.26 (m, 3H), 4.58 (s, 2H), 3.76-3.67 (m, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.36 (t, *J* = 8.7 Hz, 1H), 3.20 (s, 3H), 3.05 (s, 3H), 2.57 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 172.2, 172.0, 171.3, 140.4, 128.8, 128.0, 127.0, 66.2, 60.1, 54.6, 52.4, 52.1, 52.0, 37.1, 36.2. **MS** (ESI+): 335.4 ([M+H], 100). **HRMS** (ESI+): Calculated for $C_{17}H_{23}N_2O_5$, 335.1606; found, 335.1606.

Preparation of racemic products for HPLC determinations

The racemic pyrrolidines were prepared according to the general procedure, but using (±)-BINAP (pyrrolidines **4**, **14**, **16**), PPh_3 (pirrolidine **15**), dppf (pirrolidines **11**, **12**, **13**), and (±)-Segphos (pyrrolidine **17**) instead of (*R*)-DTBM-Segphos, (*R*)-DM-Segphos or (*R*)-Segphos as ligands.

The samples for HPLC analysis were dissolved in methanol or isopropyl alcohol and used as quickly as possible to minimize the formation of decomposition products.

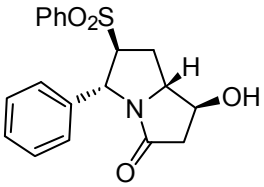
(2*R*, 4*S*, 5*R*)-1-acetyl-5-phenyl-4-(phenylsulfonyl)pyrrolidine-2-*N*-methoxy-*N*-methylcarboxamide (18)



To a solution of (2*R*, 4*S*, 5*R*)- 5-phenyl-4-(phenylsulfonyl)pyrrolidine-2-*N*-methoxy-*N*-methylcarboxamide (*exo*-**13n**) (205.6 mg, 0.55 mmol) in CH_2Cl_2 (5.0 mL), under nitrogen atmosphere, at 0 ºC, Et_3N (0.15 mL, 1.10 mmol) and acetyl chloride (48 µL, 0.66 mmol) were successively added. The reaction mixture was stirred for 10 h at room termperature and water was added, the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic layers dried over $MgSO_4$. The solvent was removed under reduced pressure to afford **18** (222 mg, 97%, colorless solid) which was used in the next step without further purification due to its inestability. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.12 – 7.79 (m, 2H), 7.80 – 7.50 (m, 5H), 7.46 – 7.09 (m, 3H), 5.45 (s, 1H),

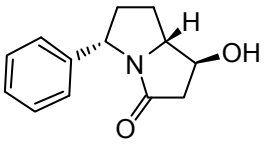
4.98 (t, *J* = 8.8 Hz, 1H), 3.83 (s, 3H), 3.77 – 3.62 (m, 1H), 3.24 (s, 3H), 2.74 – 2.53 (m, 1H), 2.42 – 2.13 (m, 1H), 1.83 (s, 3H).

(1*S*, 5*S*, 6*S*, 7*aR*)-1-hydroxy-5-phenyl-6-(phenylsulfonyl)tetrahydro-1*H*-pyrrolizin-3(2*H*)-one (19)



To a solution of (2*R*, 4*S*, 5*R*)-1-acetyl-*N*-methoxy-*N*-methyl-5-phenyl-4-(phenylsulfonyl)pyrrolidine-2-carboxamide (**18**) (100.0 mg, 0.24 mmol) in THF (3.0 mL) lithium hexamethyldisilazide (360 µL, 1.0M solution in THF, 0.36 mmol) was added. After 14 h the reaction was quenched with NH_4Cl *sat.* solution (3.0 mL). The aqueous phase was extracted with CH_2Cl_2 (2 X 5 mL), the combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to provide the crude pyrrolizidine-1, 3-dione. The residue was diluted with ethanol (12 mL) and sodium borohydride (10.90 mg, 0.29 mmol) was added. After 15 h at room temperature the reaction mixture was quenched with 1M HCl (5 mL). The aqueous pahase was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic phases were washed with brine (10 ml), dried ($MgSO_4$) and concentrated. The residue was purified by silica gel flash chromatography ($CHCl_3$: MeOH 10:0-9:1) to afford **19** (51.5 mg, 60%, orange oil). **$[\alpha]_D^{20}$:**+24.3 (c=0.42, CH_2Cl_2) **^{1}H NMR** (300 MHz, $CDCl_3$): δ7.91 (d, *J* = 7.7 Hz, 2H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.26 – 7.16 (m, 3H), 6.72 (dd, *J* = 5.7, 2.9 Hz, 2H), 4.96 (s, 1H), 4.32 (dt, *J* = 14.6, 7.3 Hz, 2H), 3.63 (dd, *J* = 9.1, 2.0 Hz, 1H), 3.39 (s, 1H), 2.72 (tp, *J* = 15.6, 8.3 Hz, 3H), 2.05 (dt, *J* = 14.2, 9.4 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.2, 137.7, 137.1, 134.6, 129.7, 129.0, 128.9, 128.3, 125.6, 75.8, 73.47, 68.8, 58.0, 45.4, 28.7. **MS** (FAB+): 358.4 ([M+H], 85). **HRMS** (FAB+): Calculated for $C_{19}H_{20}NO_4S$, 358.1113; found, 358.1109

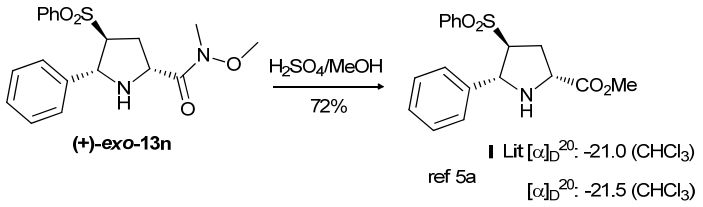
(1*S*, 5*S*, 7*aR*)-1-hydroxy-5-phenyltetrahydro-1*H*-pyrrolizin-3(2*H*)-one (20)

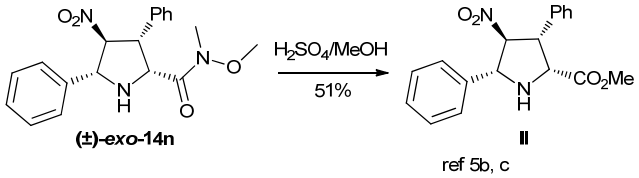


To a solution of (1*S*, 5*R*, 6*S*, 7*aR*)-1-hydroxy-5-phenyl-6-(phenylsulfonyl)tetrahydro-1*H*-pyrrolizin-3(2*H*)-one (**19**) (48.0 mg, 0.13 mmol) in THF: MeOH 1:2 (6 mL) under nitrogen atmosphere, at room temperature, 6% Na(Hg) (480 mg) and Na_2HPO_4 (229 mg, 1.61 mmol) were successively added. The reaction mixture was stirred for 3 h at room temperature. CH_2Cl_2 (30 mL) was added to the reaction mixture and the resulting suspension was filtered and washed with water (2 x 10 mL). The aqueous pahase was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic phases were washed with brine (10 ml), dried ($MgSO_4$) and concentrated. The residue was purified by silica gel flash chromatography (hexane-EtOAc-MeOH 1:1:0-0:9.5:0.5) to afford **20** (19.8 mg, 70%, colorless oil) **$[\alpha]_D^{20}$:**-13.6 (c=0.7, CH_2Cl_2). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.17 – 7.08 (m, 2H), 4.69 (d, *J* = 9.1 Hz, 1H), 4.45 (q, *J* = 8.3 Hz, 1H), 3.93 (ddd, *J* = 10.9, 7.4, 5.2 Hz, 1H), 3.00 – 2.69 (m, 2H), 2.59 (ddd, *J* = 12.8, 8.7, 6.3 Hz, 1H), 2.45 – 2.24 (m, 1H), 2.06 (ddd, *J* = 18.2, 12.3, 6.3 Hz, 2H), 1.88 – 1.63 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.2, 141.0, 128.7, 128.6, 128.4, 127.3, 126.0, 73.2, 70.3, 56.8, 45.9, 38.9, 27.0. **MS** (FAB+): 218.1 ([M+H], 100). **HRMS** (FAB+): Calculated for $C_{13}H_{16}NO_2$, 218.1181; found, 218.1184.

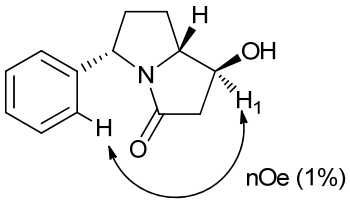
Stereochemical assignment

The absolute and relative configuration of *exo*-**4c** was unequivocally determinated by X-ray crystal structure analysis. The absolute and relative configuration of *exo*-**13n** was unequivocally determined by chemical correlation with the known pyrrolidine 2-carboxylate esters **I**. The relative exo configuration of the 2-amidopyrrolidine **14n** was also established by chemical correlation with the known pyrrolidine carboxylate esters **II**. The configurations of the rest of pyrrolidine adducts have been assigned by chemical analogy.

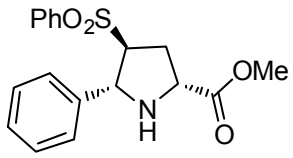




The stereochemistry at C-1 in pyrrolizinone **20** was stablished by the nOe between H1 and the ortho protons of phenyl ring at C-5. This result is in agreement with the reported stereoselectivity in the reduction of pyrrolizin-1,3-diones.[6]



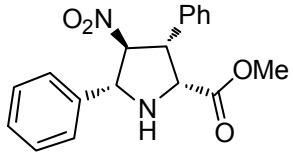
Chemical correlation: (2*R*, 4*S*, 5*R*)-(-)-Methyl-5-phenyl-4-(phenylsulfonyl)pyrrolidine-2-carboxylate (I). [5a]



To a solution of *exo*-**13n** (20.1 mg, 0.054mmol; ≥99% *ee*) in methanol (0.3 mL) at room temperature, H_2SO_4 (54 µL) was added and the resulting solution was refluxed for 4 h. The mixture was poured into a saturated aquous solution of $NaHCO_3$ (5 mL) and extracted with diethyl ether (2 x 5 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum to afford, after purification by silica gel flash chromatography (hexane-EtOAc 1:1), the desired methyl ester (13.3 mg, 72%, colorless solid). **$[\alpha]_D^{20}$: -** 21.5 (c=0.3, $CHCl_3$), ≥ 99% *ee*. **Lit $[\alpha]_D^{20}$: -** 21 (c=0.5, $CHCl_3$), 99% *ee* **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.64 – 7.41 (m, 3H), 7.20 (s, 5H), 4.73 (d, *J* = 5.7 Hz, 1H), 4.18 (t, *J* = 7.8 Hz, 1H), 3.77 (s, 3H), 3.65 (dt, *J* = 9.9, 5.1 Hz, 1H), 2.78 – 2.63 (m, 1H), 2.36 (dt, *J* = 14.0, 8.8 Hz, 1H). Lit **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.85-7.77 (m, 2H), 7.63-7.56 (m, 1H), 7.52-7.44 (m, 2H), 7.21 (bs, 5H), 4.73 (d, *J* = 5.4 Hz, 1H), 4.18 (t, *J* = 7.9

Hz, 1H), 3.77 (s, 3H), 3.66 (m, 1H), 2.70 (ddd, *J* = 14.0, 7.5, 4.4 Hz, 1H), 2.56 (bs, 1H), 2.36 (dt, *J* = 14.0, 8.9 Hz, 1H).

(2*R, 3*R**, 4*S**, 5*R**)-(±)-Methyl-4-nitro-3,5-diphenylpyrrolidine-2-carboxylate (II).**[5b,c]



Following the general procedure, the reaction of (±)-*exo*-**14n** (16.1 mg, 0.045 mmol) with H_2SO_4 (45 μL) in methanol (0.23 mL) at room temperature for 40 h afforded, after purification by flash chromatography (hexane-EtOAc 1:1), the corresponding methyl ester (7.4 mg, 51%, colorless solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.61 – 7.50 (m, 2H), 7.48 – 7.20 (m, 8H), 5.22 (t, *J* = 8.1 Hz, 1H), 4.77 (d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 9.1 Hz, 1H), 4.43 – 4.35 (m, 1H), 3.30 (s, 3H), 2.75 (bs, 1H). Lit **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.56–7.52 (m, 2H), 7.45–7.18 (m, 8H), 5.19 (t, *J* = 8.0 Hz,1H), 4.73 (d, *J* = 7.8 Hz, 1H), 4.48 (d, *J* = 9.1 Hz, 1H), 4.35(t, *J* = 7.8 Hz, 1H), 3.26 (s, 3H), 2.71 (bs, 1H).

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[1]. a) T.V. Goud, A. M. Auberin, J. F. Biellmann *Nucleosides, Nucleotides and Nucleic Acids*, **2008**, *27*, 495; b) R. C. Hider, US Patent nº 20080200520 A1.

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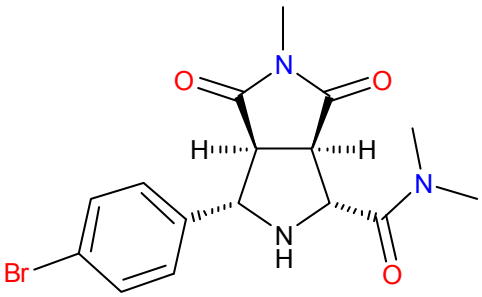
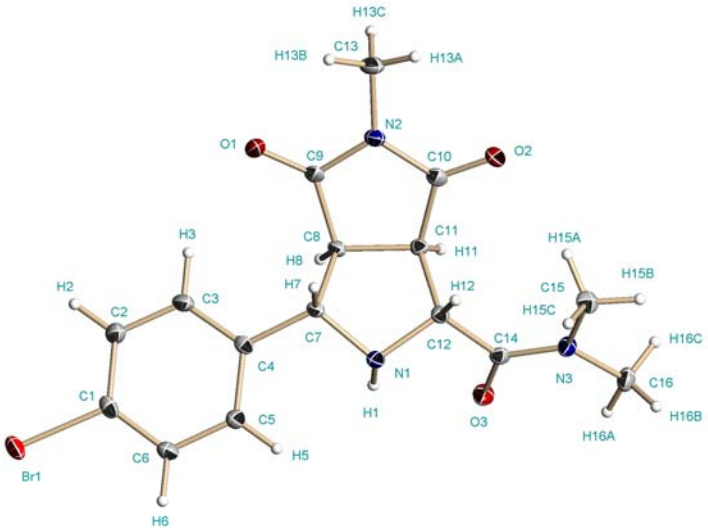
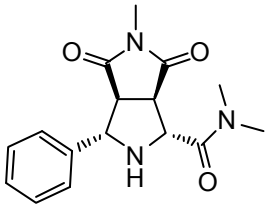
X-Ray diffraction analysis of compound (+)-*exo*-4c.



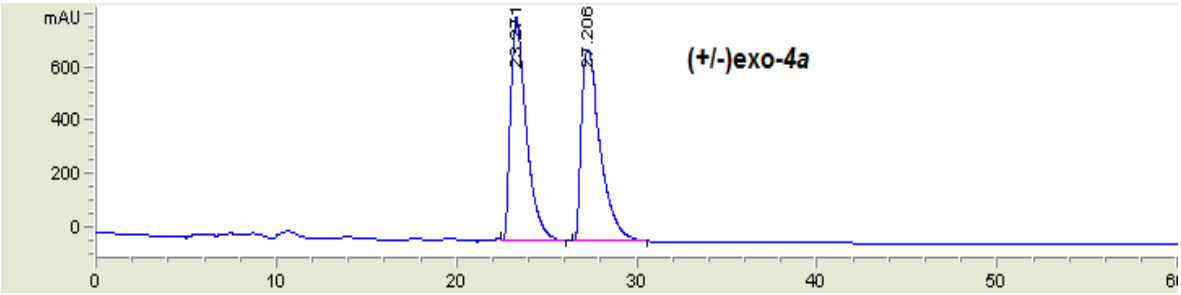
exo-**4c**



HPLC charts.



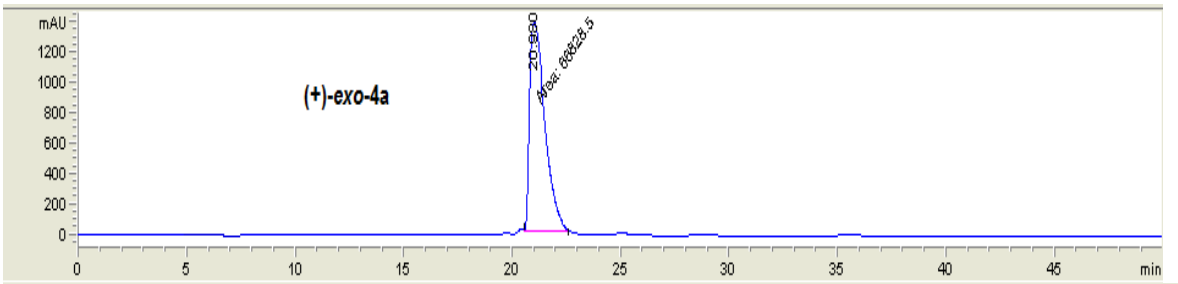
Racemic ***exo*-4a**



#	Time	Area	Height	Width	Area%	Symmetry
1	23.271	53416.2	838.2	0.9995	50.231	0.567
2	27.206	52924.9	719.5	1.1102	49.769	0.43

Table 1, entry 7.

(+)-*exo*-4a; ≥ 99% *ee*



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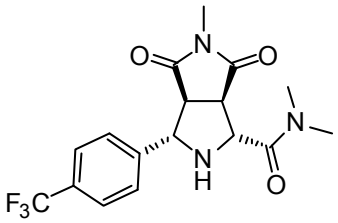
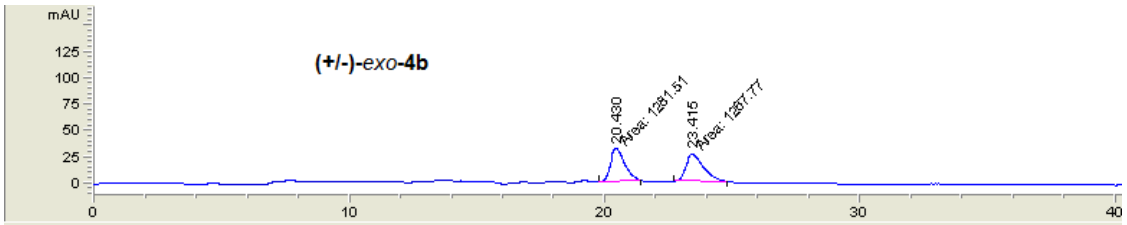
1	20.98	66828.5	1370.4	0.8128	100.000	0.393



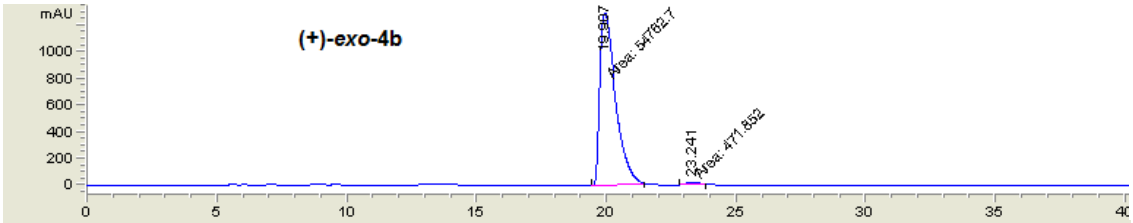
Racemic ***exo*-4b**



#	Time	Area	Height	Width	Area%	Symmetry
1	20.43	1281.5	31.6	0.6759	50.269	0.709
2	23.415	1267.8	26	0.8138	49.731	0.61

Table 2, entry 1.

(+)-*exo*-4b; 98% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	19.907	54762.7	1293.2	0.7058	99.146	0.415
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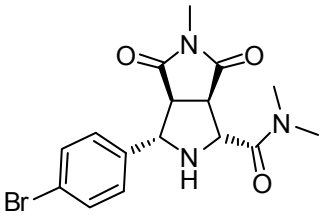
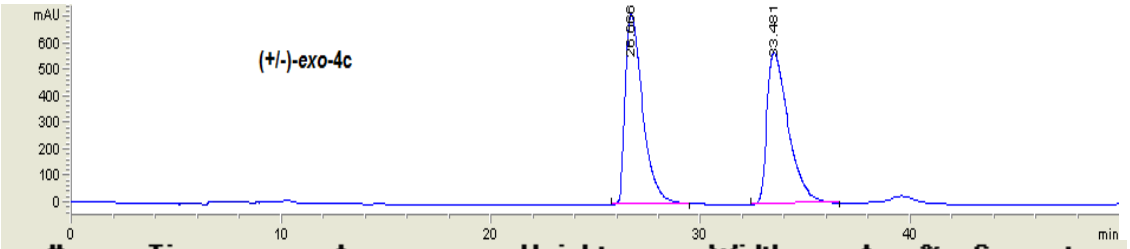


Racemic ***exo*-4c**



#	Time	Area	Height	Width	Area%	Symmetry
1	26.666	41046.4	717.2	0.8637	50.089	0.474
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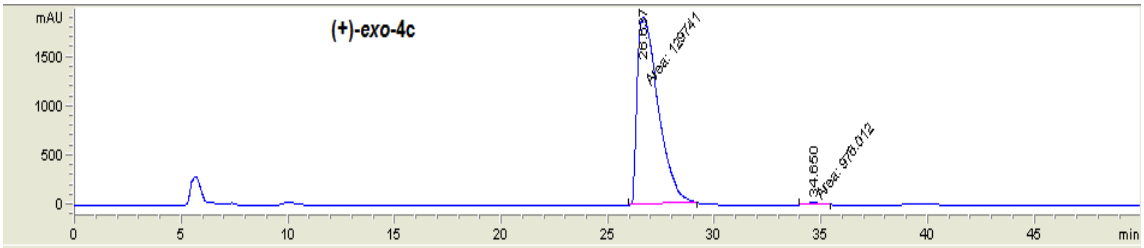
Table 2, entry 2.

(+)-*exo*-4c; 99% *ee*



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1	26.637	129740.5	1905.7	1.1347	99.253	0.371
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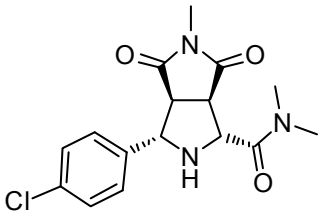
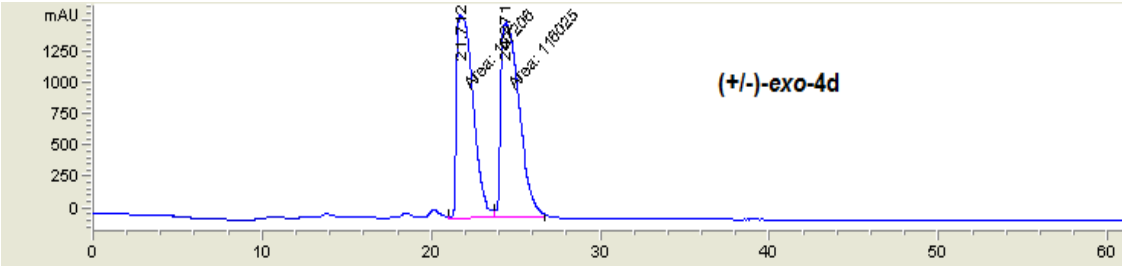


Racemic ***exo*-4d**



#	Time	Area	Height	Width	Area%	Symmetry
1	21.712	107205.9	1623.7	1.1004	48.025	0.338
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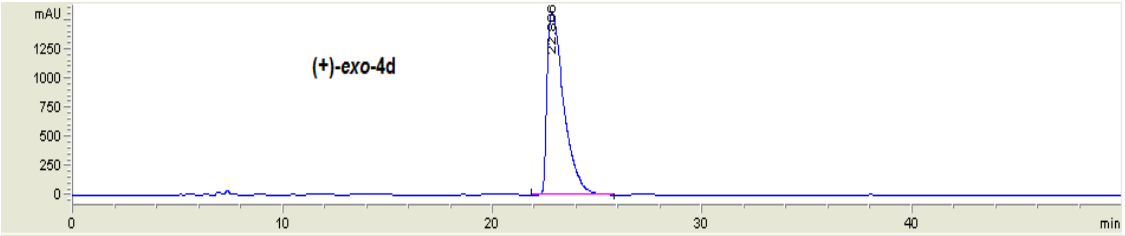
Table 2, entry 3.

(+)-*exo*-4d; ≥ 99% *ee*



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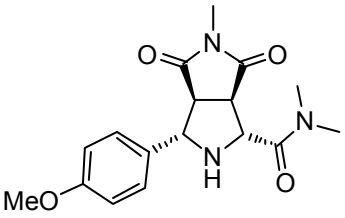
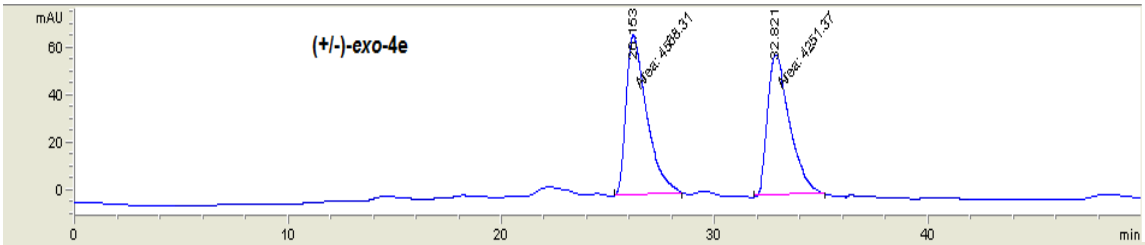


Racemic ***exo*-4e**



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1	26.153	4568.3	67.4	1.1297	51.797	0.52
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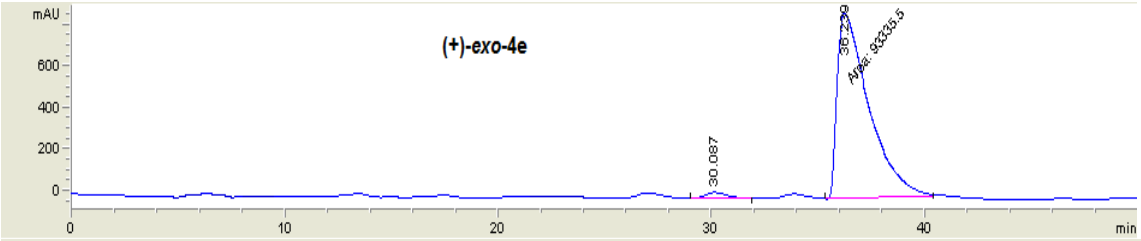
Table 2, entry 4.

(+)-*exo*-4e; 96% *ee*



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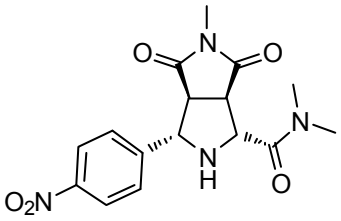
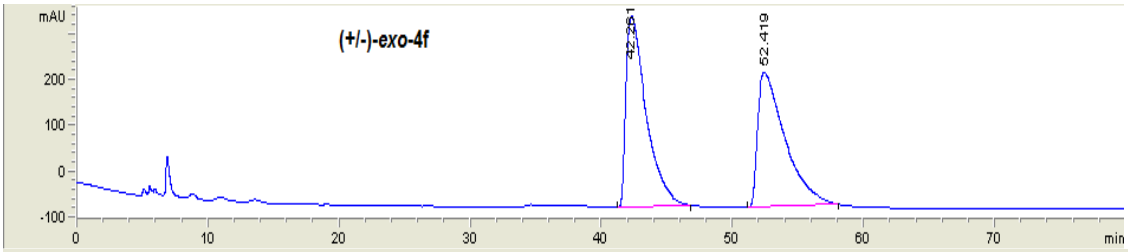


Racemic ***exo*-4f**



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1	42.261	44519.1	416.2	1.5419	50.815	0.34
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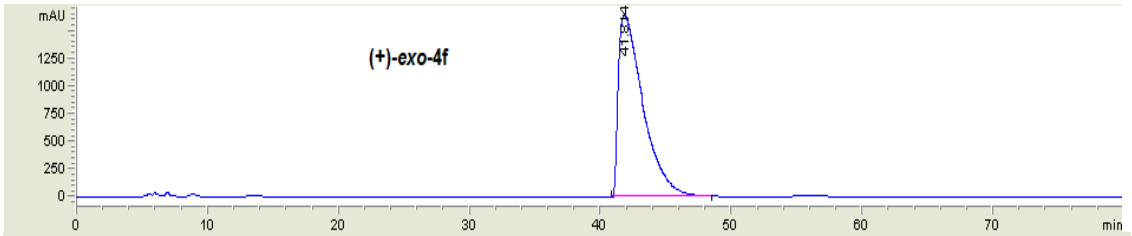
Table 2, entry 5.

(+)-*exo*-4f; ≥ 99% *ee*



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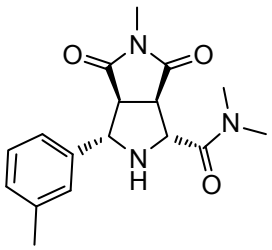
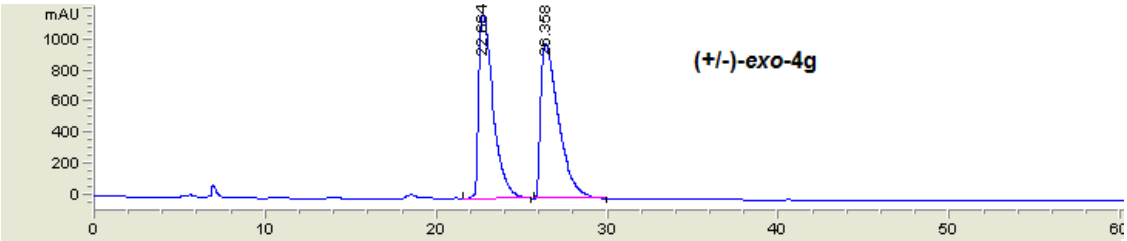


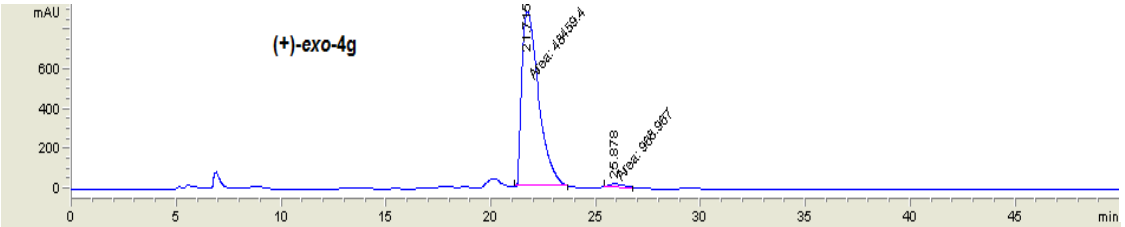
Racemic ***exo*-4g**



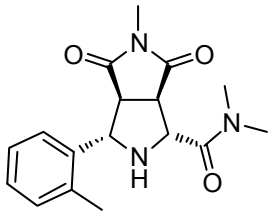
#	Time	Area	Height	Width	Area%	Symmetry
1	22.664	71342.3	1192.9	0.8857	49.855	0.37
2	26.358	71756.2	1002.2	1.0713	50.145	0.349

Table 2, entry 6.

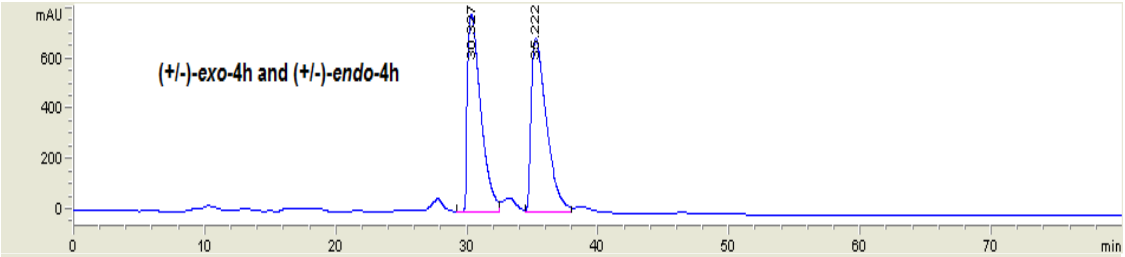
(+)-*exo*-4g; 96% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	21.715	48459.4	876.3	0.9217	98.040	0.46
2	25.878	969	17.9	0.9031	1.960	0.532



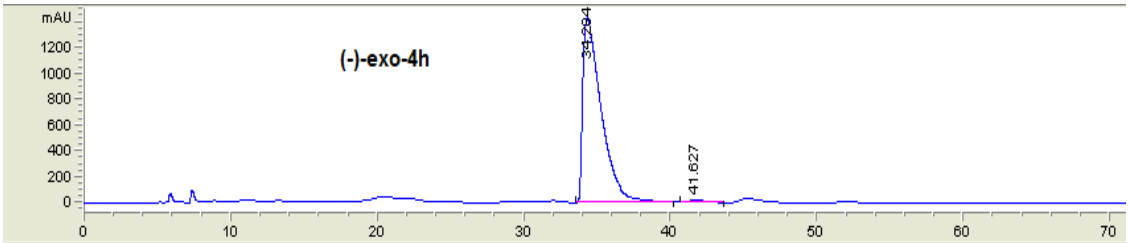
Racemic ***exo*-4h**



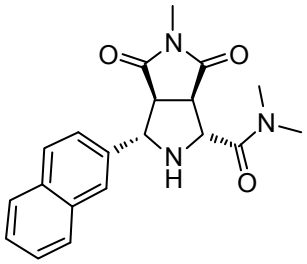
#	Time	Area	Height	Width	Area%	Symmetry
1	30.327	55251.1	787.2	1.0388	49.843	0.41
2	35.222	55599.6	693	1.188	50.157	0.386

Table 2, entry 7.

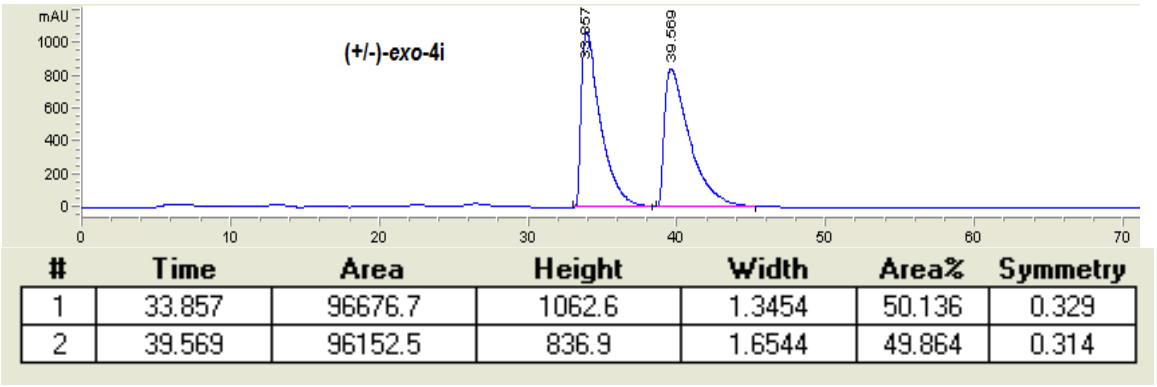
(+)-*exo*-4h; 98% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	34.284	128674.9	1435	1.2761	98.911	0.306
2	41.627	1416.9	17.6	1.0853	1.089	0.522



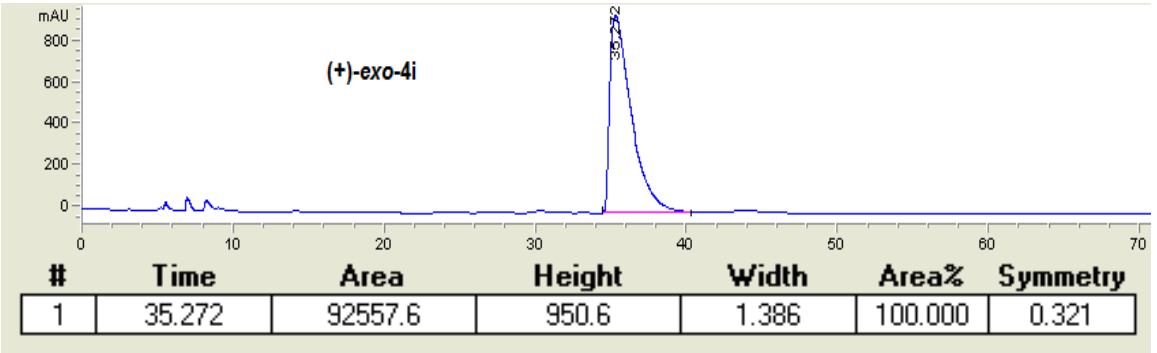
Racemic ***exo*-4i**



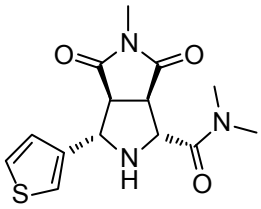
#	Time	Area	Height	Width	Area%	Symmetry
1	33.857	96676.7	1062.6	1.3454	50.136	0.329
2	39.569	96152.5	836.9	1.6544	49.864	0.314

Table 2, entry 8.

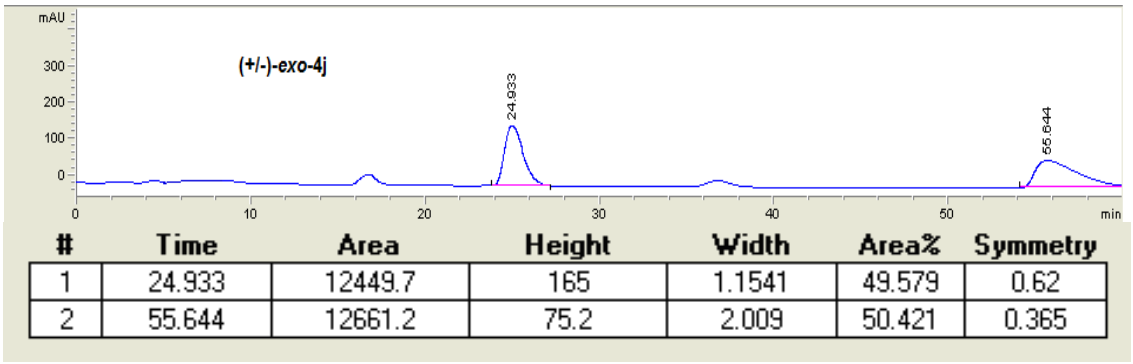
(+)-*exo*-4i; ≥ 99% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	35.272	92557.6	950.6	1.386	100.000	0.321



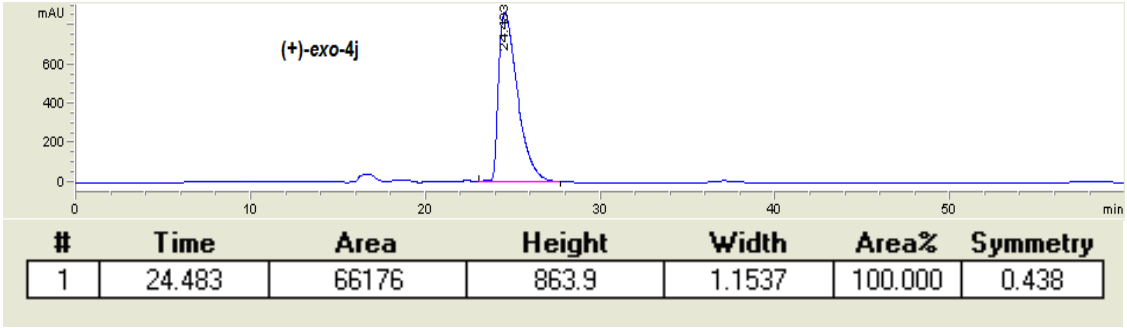
Racemic ***exo*-4j**



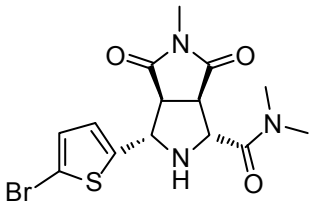
#	Time	Area	Height	Width	Area%	Symmetry
1	24.933	12449.7	165	1.1541	49.579	0.62
2	55.644	12661.2	75.2	2.009	50.421	0.365

Table 2, entry 9.

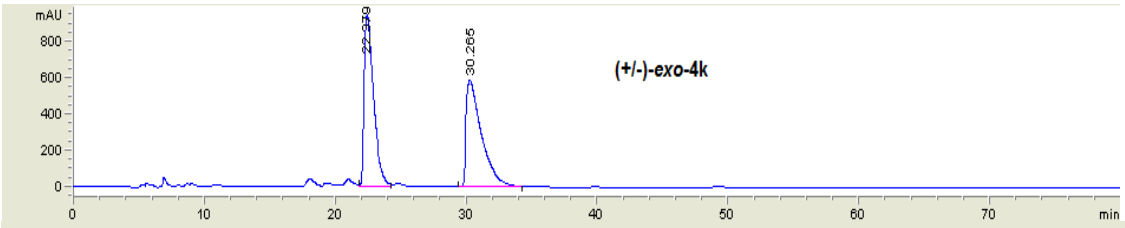
(+)-*exo*-4j; ≥ 99% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	24.483	66176	863.9	1.1537	100.000	0.438



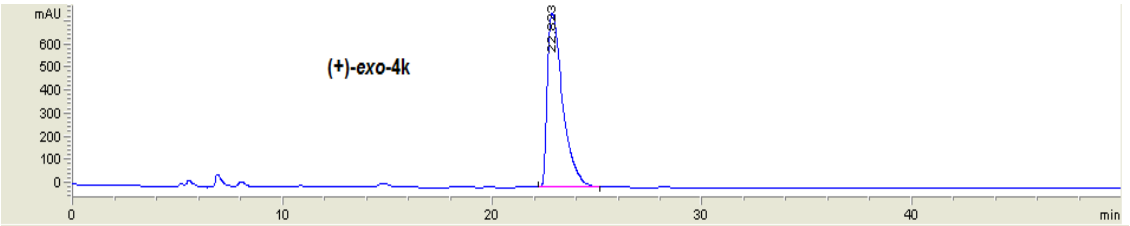
Racemic ***exo*-4k**



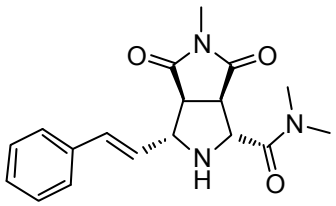
#	Time	Area	Height	Width	Area%	Symmetry
1	22.379	47270.9	949.7	0.7487	49.632	0.4
2	30.265	47971.1	586.7	1.1699	50.368	0.319

Table 2, entry 10.

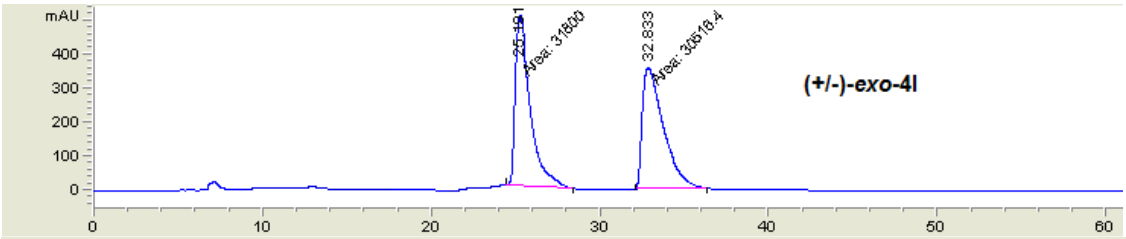
(+)-*exo*-4k; ≥ 99% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	22.823	37828.7	752.8	0.7503	100.000	0.406



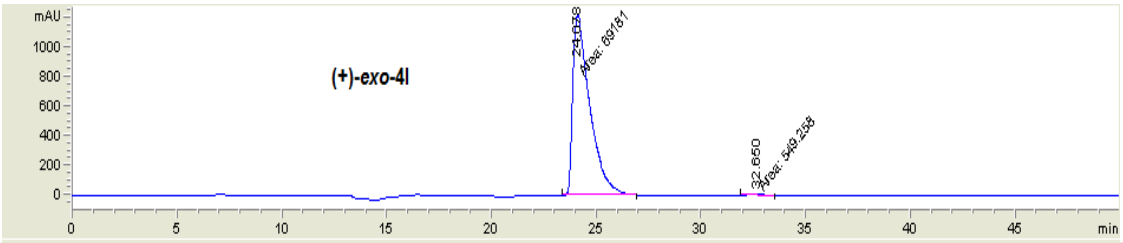
Racemic ***exo*-4l**



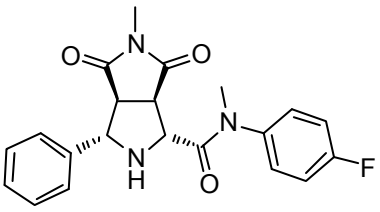
#	Time	Area	Height	Width	Area%	Symmetry
1	25.191	31800	501.8	1.0562	51.030	0.42
2	32.833	30516.4	357.9	1.4211	48.970	0.364

Table 2, entry 11.

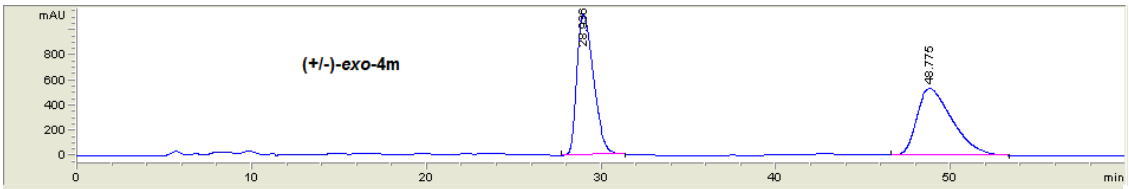
(+)-*exo*-4l; 98% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	24.078	69181	1215.5	0.9486	99.212	0.377
2	32.65	549.3	7.7	1.1896	0.788	0.332



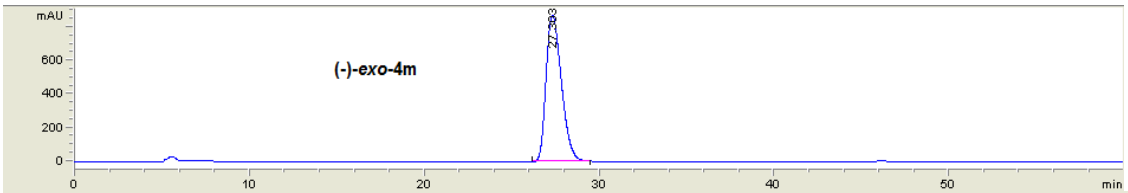
Racemic ***exo*-4m**



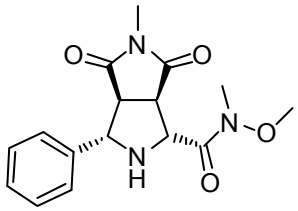
#	Time	Area	Height	Width	Area%	Symmetry
1	28.936	73792.1	1113.2	1.0273	49.689	0.606
2	48.775	74716.7	528.3	1.946	50.311	0.55

Table 2, entry 12.

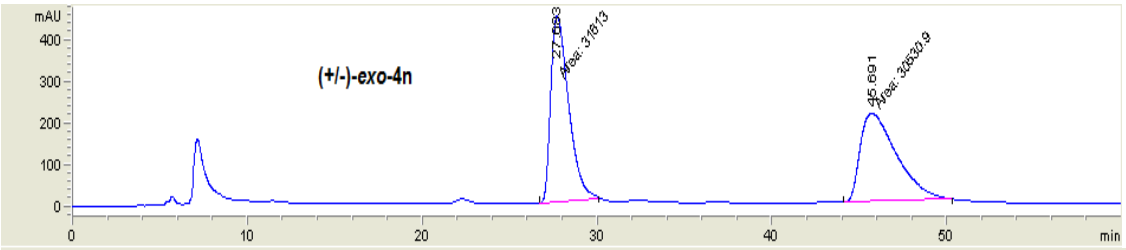
(-)-*exo*-4m; ≥ 99% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	27.303	52678.8	873.8	0.9373	100.000	0.667



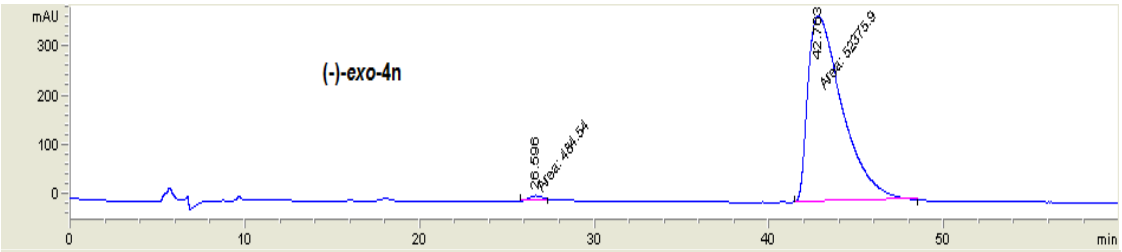
Racemic ***exo*-4n**



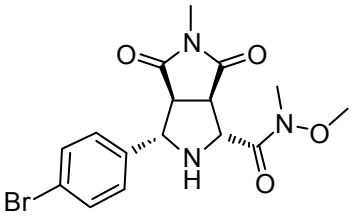
#	Time	Area	Height	Width	Area%	Symmetry
1	27.683	31613	447.9	1.1764	50.871	0.535
2	45.691	30530.9	212.8	2.3907	49.129	0.456

Table 2, entry 13.

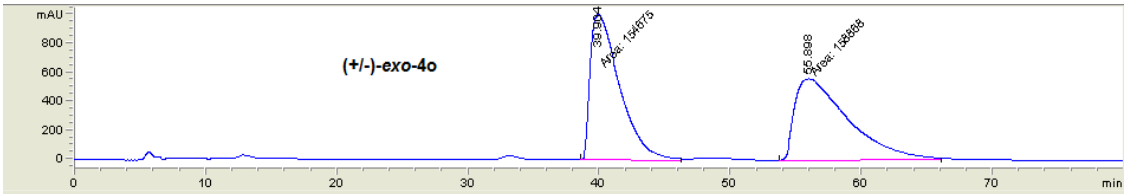
(-)-*exo*-4n; 98% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	26.596	484.5	9.5	0.8485	0.917	0.927
2	42.763	52375.9	378.9	2.3037	99.083	0.406



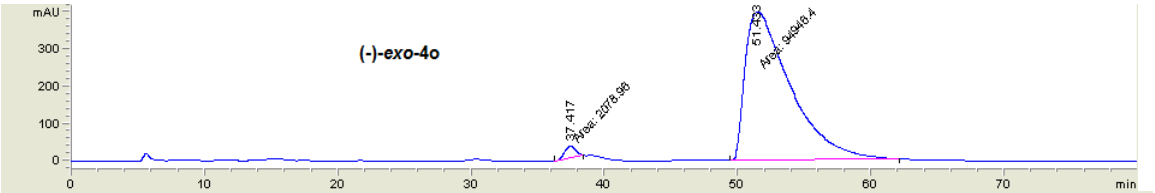
Racemic ***exo*-4o**



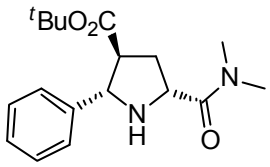
#	Time	Area	Height	Width	Area%	Symmetry
1	39.904	154675.4	1003.6	2.5687	49.331	0.35
2	55.898	158867.7	564.5	4.6908	50.669	0.322

Table 2, entry 14.

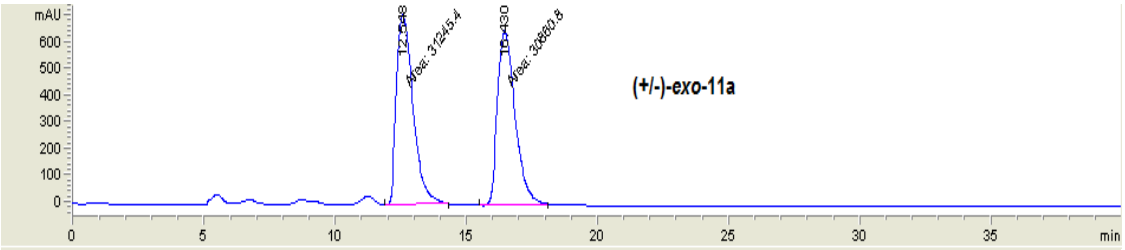
(-)-*exo*-4o; 96% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	37.417	2079	34.1	1.0165	2.143	1.103
2	51.433	94946.4	399.9	3.9574	97.857	0.348



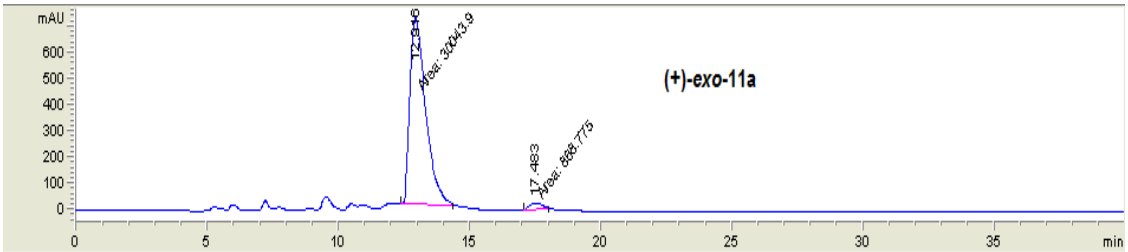
Racemic ***exo*-11a**



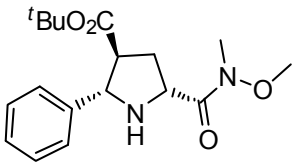
#	Time	Area	Height	Width	Area%	Symmetry
1	12.548	31245.4	712.1	0.7313	50.310	0.598
2	16.43	30860.8	656	0.7841	49.690	0.629

Table 3, entry 1.

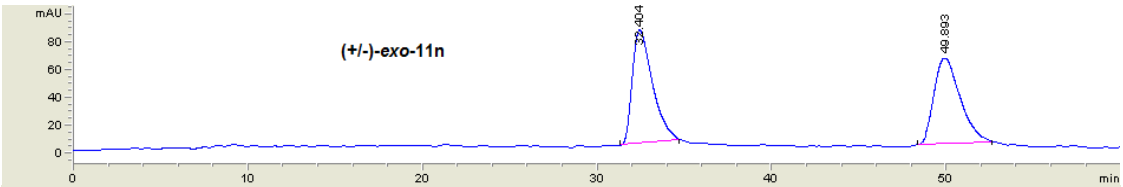
(+)-*exo*-11a; 94% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	12.916	30043.9	714	0.7013	97.190	0.524
2	17.483	868.8	25.4	0.5697	2.810	0.849



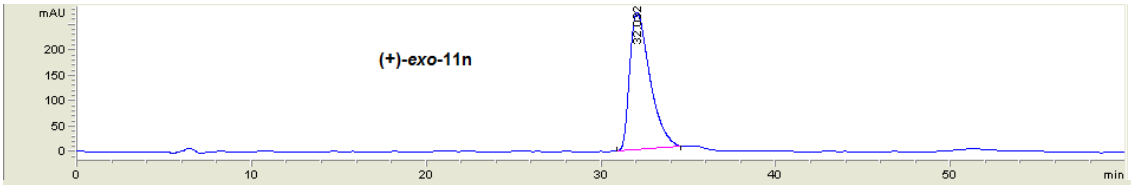
Racemic ***exo*-11n**



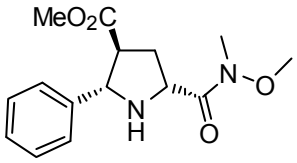
#	Time	Area	Height	Width	Area%	Symmetry
1	32.404	6531	81.8	1.159	50.645	0.535
2	49.893	6364.8	61.5	1.4881	49.355	0.66

Table 3, entry 2.

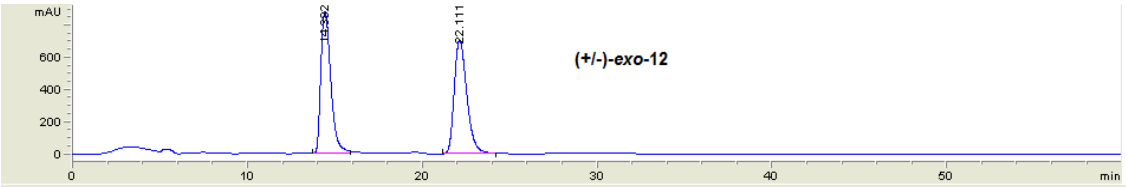
(+)-*exo*-11n; ≥ 99% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	32.032	21551.4	269.5	1.1889	100.000	0.533



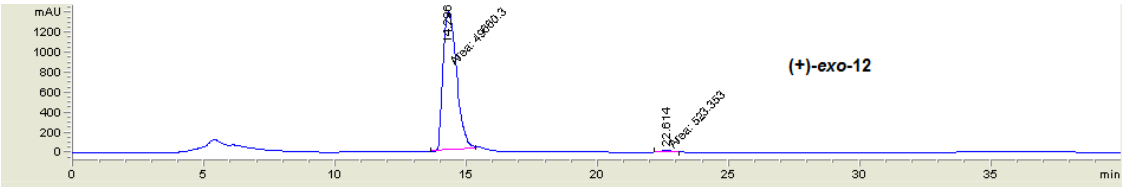
Racemic ***exo*-12**



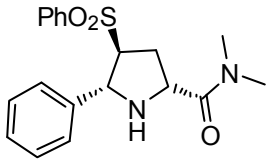
#	Time	Area	Height	Width	Area%	Symmetry
1	14.382	34723.8	881.2	0.6177	50.010	0.627
2	22.111	34710.5	706	0.7636	49.990	0.696

Table 3, entry 3.

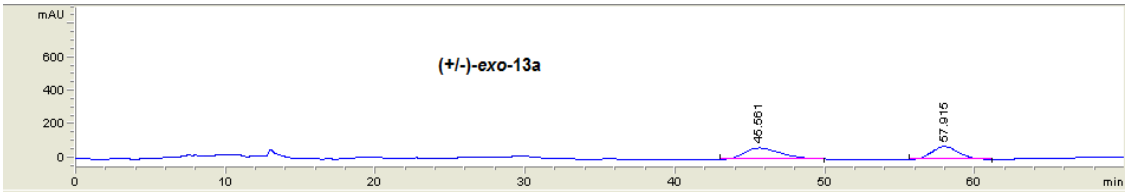
(+)-*exo*-12; 98% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	14.296	49660.3	1386.3	0.597	98.957	0.629
2	22.614	523.4	14.4	0.6046	1.043	0.977



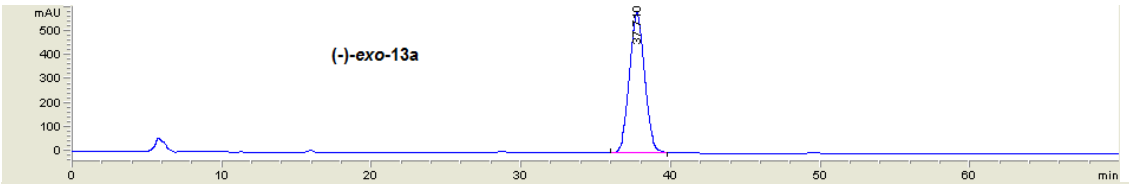
Racemic ***exo*-13a**



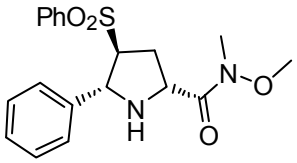
#	Time	Area	Height	Width	Area%	Symmetry
1	45.561	11634.9	67.7	2.0843	54.878	0.662
2	57.915	9566.4	76.7	1.8251	45.122	0.87

Table 3, entry 4.

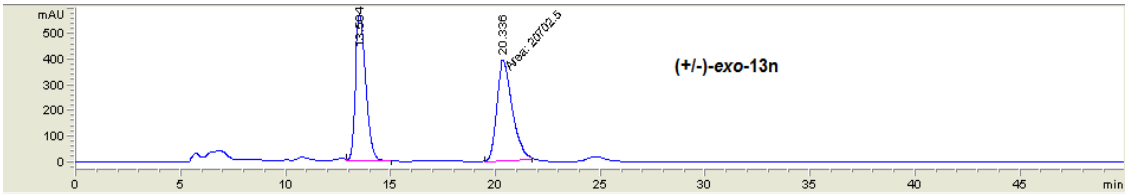
(-)-*exo*-13a; ≥ 99% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	37.71	41776.7	585.4	1.0986	100.000	0.954



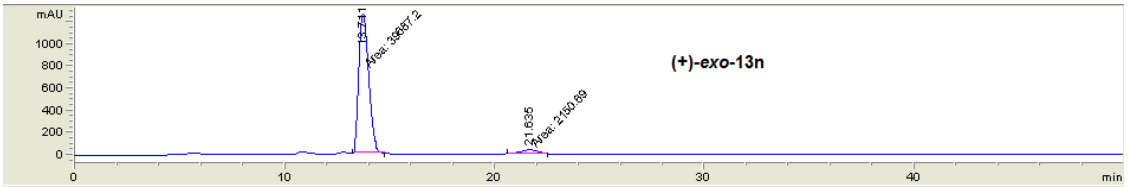
Racemic ***exo*-13n**



#	Time	Area	Height	Width	Area%	Symmetry
1	13.504	19958.8	574.4	0.5434	49.085	0.727
2	20.336	20702.5	396.2	0.8708	50.915	0.681

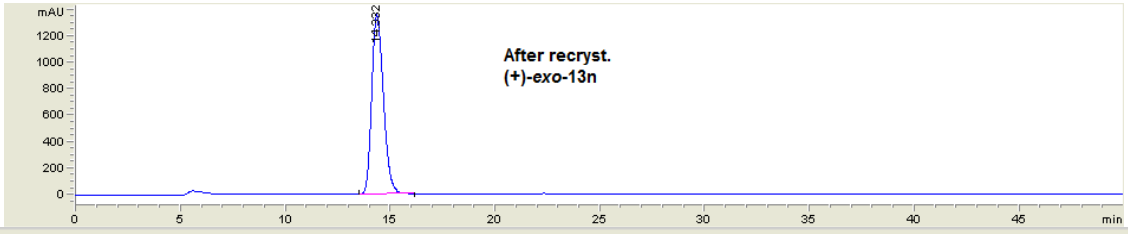
Table 3, entry 5.

(+)-*exo*-13n; 90% *ee*

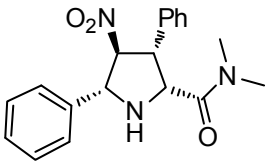


#	Time	Area	Height	Width	Area%	Symmetry
1	13.711	39687.2	1256.4	0.5265	94.859	0.715
2	21.635	2150.7	36.4	0.9861	5.141	1.131

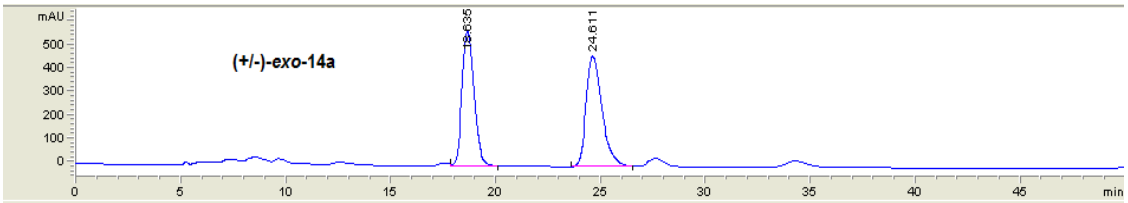
After recrystalitation, ≥ 99% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	14.332	54594.8	1364.1	0.6309	100.000	0.732



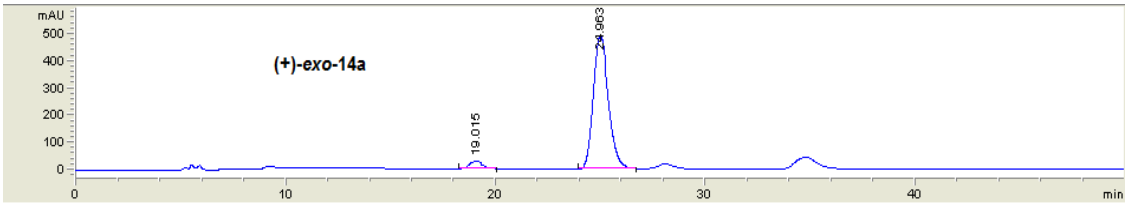
Racemic ***exo*-14a**



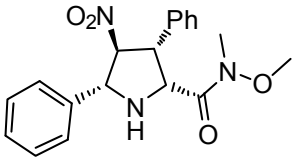
#	Time	Area	Height	Width	Area%	Symmetry
1	18.635	22610.4	572.1	0.6151	47.885	0.81
2	24.611	24607.4	469	0.7802	52.115	0.696

Table 3, entry 7.

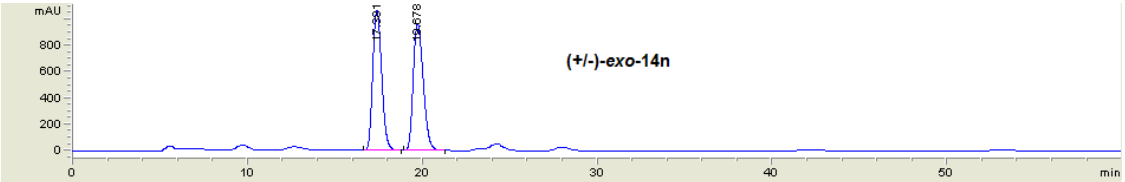
(+)-*exo*-14a; 91% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	19.015	1159.7	28.6	0.5648	4.532	0.838
2	24.963	24429.3	492.5	0.7587	95.468	0.769



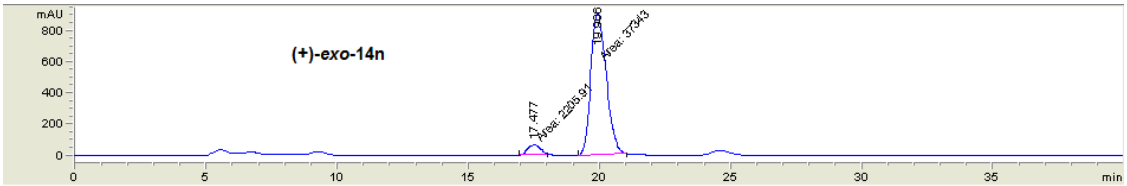
Racemic ***exo*-14n**



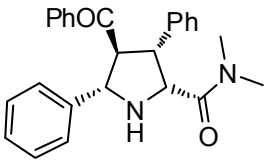
#	Time	Area	Height	Width	Area%	Symmetry
1	17.381	37497.4	1064.4	0.559	49.687	0.801
2	19.678	37969.7	964.9	0.6191	50.313	0.726

Table 3, entry 8.

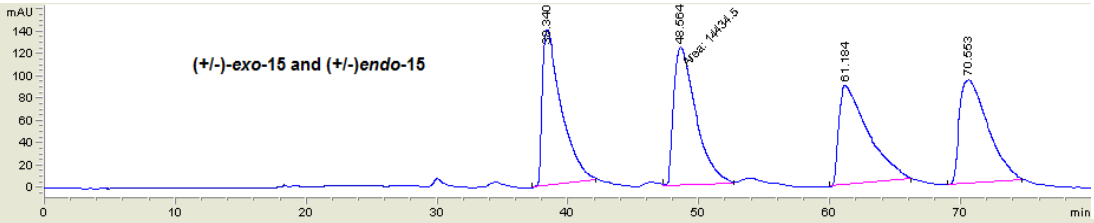
(+)-*exo*-14n; 89% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	17.477	2205.9	66.2	0.555	5.578	0.908
2	19.906	37343	904.4	0.6882	94.422	0.746



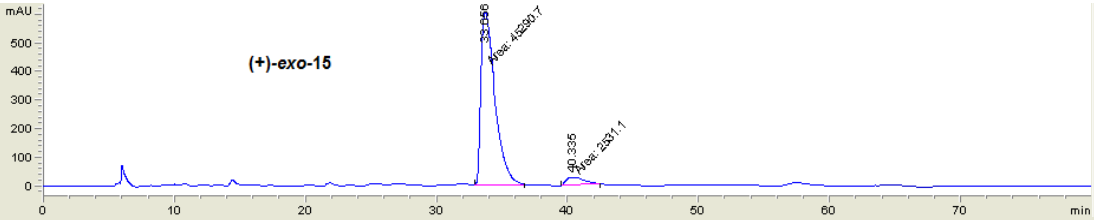
Racemic ***exo*-15**



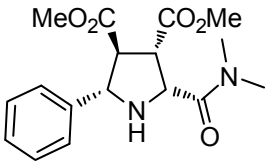
#	Time	Area	Height	Width	Area%	Symmetry
1	38.34	14333.5	139.8	1.3864	25.184	0.298
2	48.564	14434.5	123.5	1.9486	25.361	0.423
3	61.184	14088.3	89.3	1.8496	24.753	0.312
4	70.553	14059.2	92.8	1.7822	24.702	0.441

Table 3, entry 10.

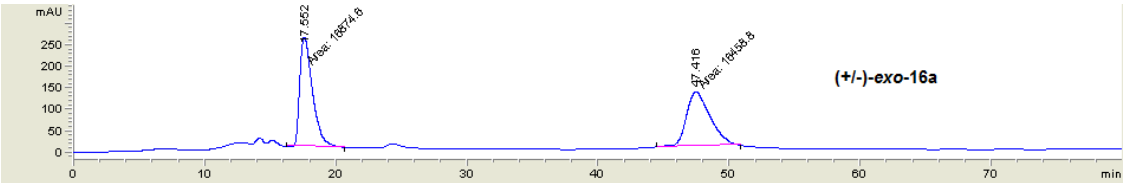
(+)-*exo*-15; 89% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	33.656	45290.7	604.4	1.249	94.707	0.4
2	40.335	2531.1	27	1.5596	5.293	0.493



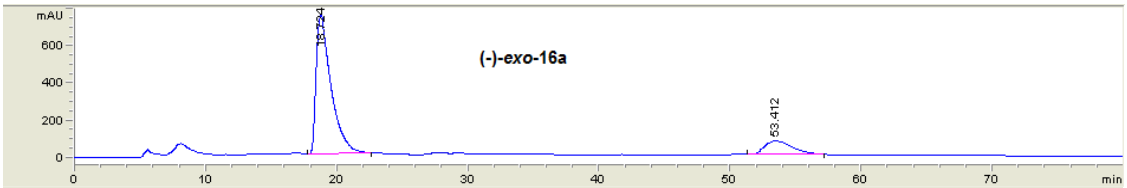
Racemic ***exo*-16a**



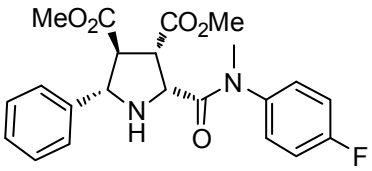
#	Time	Area	Height	Width	Area%	Symmetry
1	17.552	16874.6	255.5	1.1006	50.624	0.526
2	47.416	16458.8	127.2	2.1566	49.376	0.666

Table 3, entry 13.

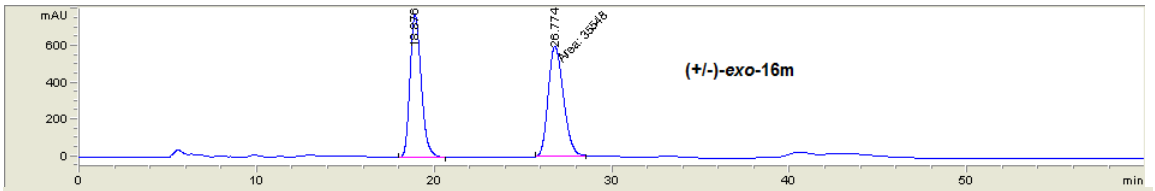
(-)-*exo*-16a; 70% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	18.724	60462	747	1.1843	85.233	0.404
2	53.412	10475.5	71.5	1.7376	14.767	0.608



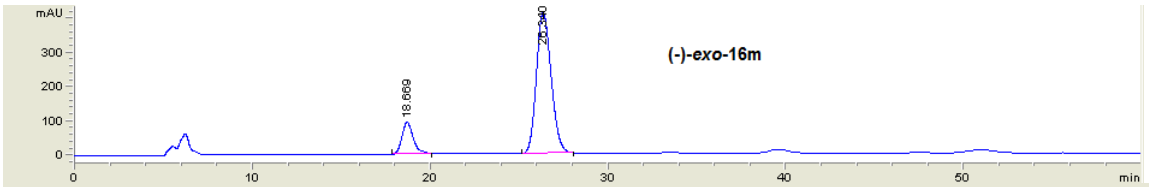
Racemic ***exo*-16m**



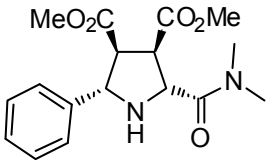
#	Time	Area	Height	Width	Area%	Symmetry
1	18.876	33794.1	774.5	0.6751	48.735	0.77
2	26.774	35548	600.9	0.9859	51.265	0.775

Table 3, entry 15.

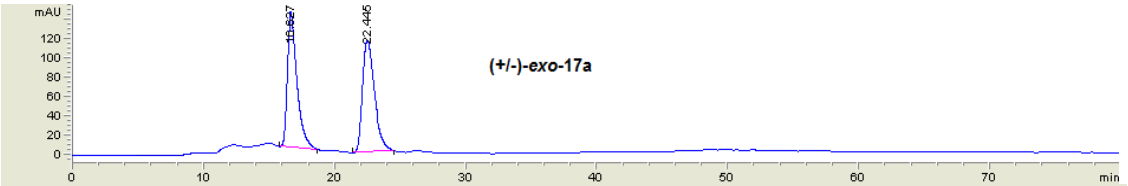
(-)-*exo*-16m; 71% *ee*



#	Time	Area	Height	Width	Area%	Symmetry
1	18.669	4020.6	92.3	0.666	14.641	0.784
2	26.34	23440.4	411.2	0.891	85.359	0.803



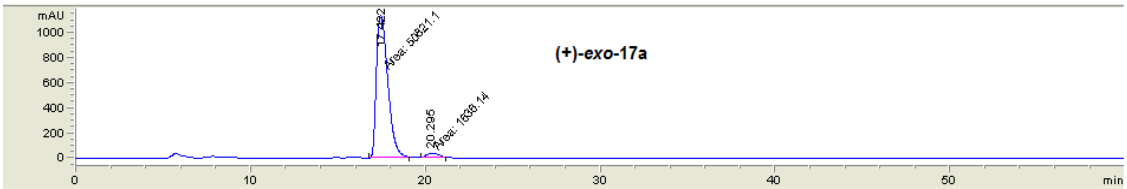
Racemic ***exo*-17a**



#	Time	Area	Height	Width	Area%	Symmetry
1	16.627	7476.7	140.1	0.8047	50.479	0.563
2	22.445	7334.9	115.7	0.9619	49.521	0.606

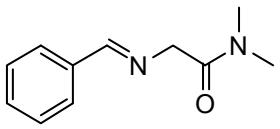
Table 3, entry 18.

(+)-*exo*-17a; 94% *ee*



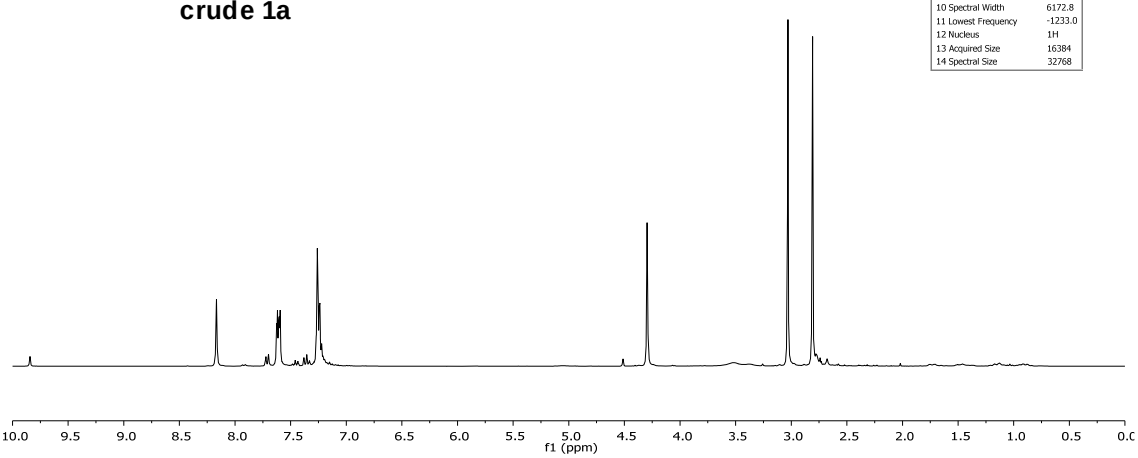
#	Time	Area	Height	Width	Area%	Symmetry
1	17.422	50821.1	1134.7	0.7465	96.881	0.568
2	20.295	1636.1	35.8	0.7609	3.119	0.718

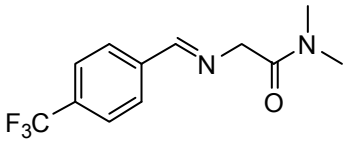
NMR Spectra collection



crude 1a

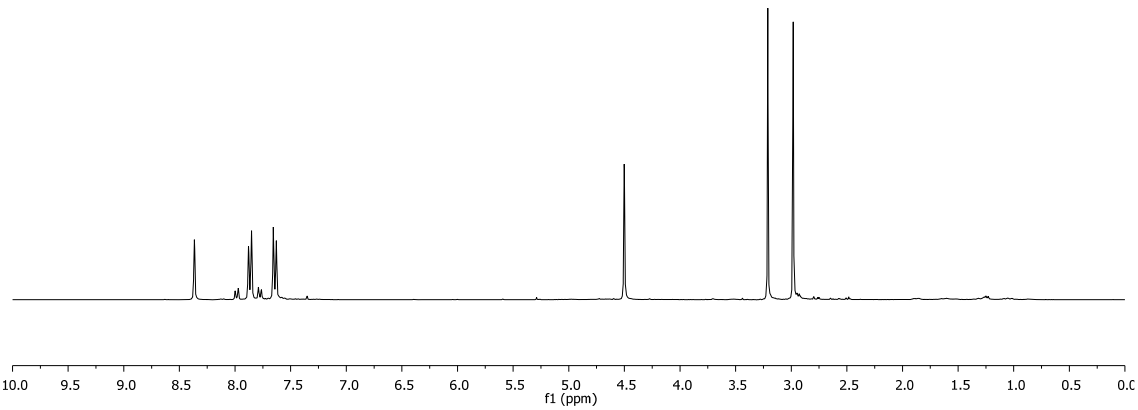
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	298.2
3	Experiment	1D
4	Number of Scans	7
5	Receiver Gain	40
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

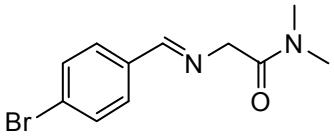




crude 1b

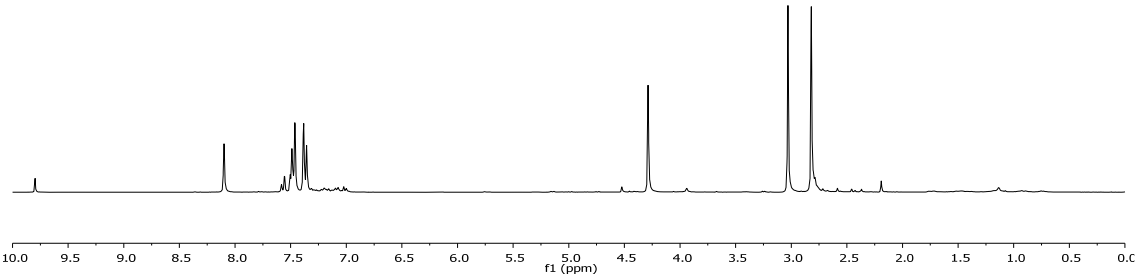
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	14
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

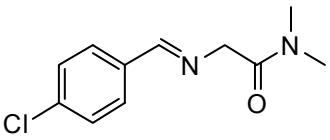




crude 1c

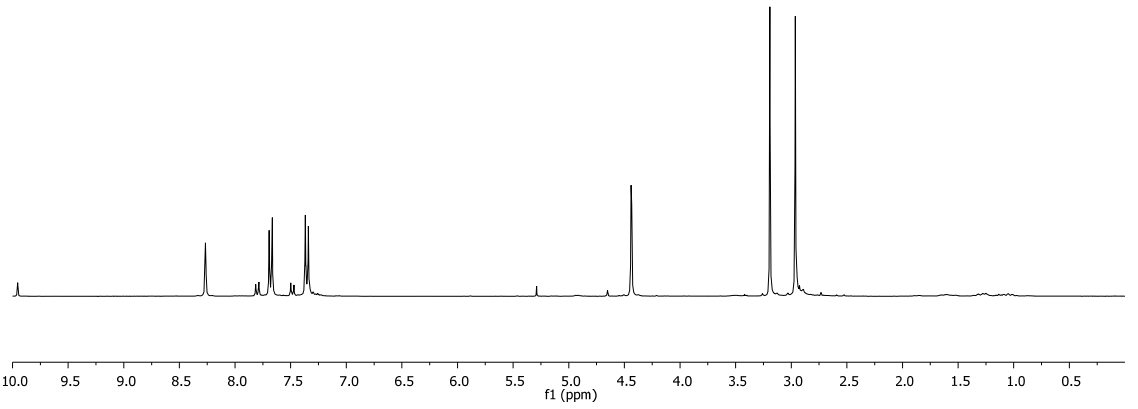
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	14
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

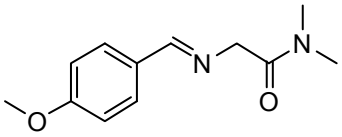




crude 1d

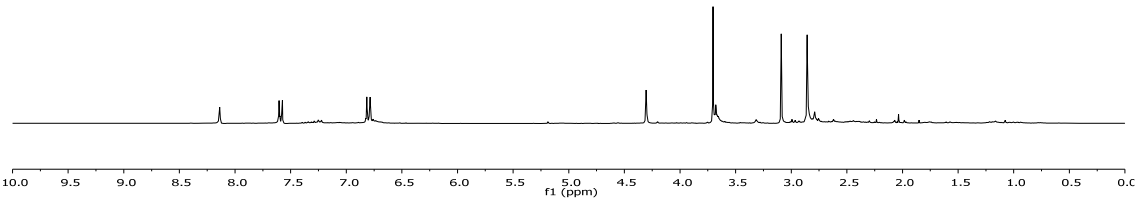
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.1
3	Experiment	1D
4	Number of Scans	8
5	Receiver Gain	51
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1220.6
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

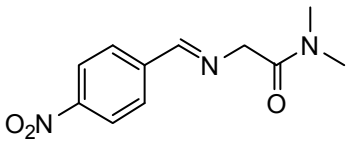




crude 1e

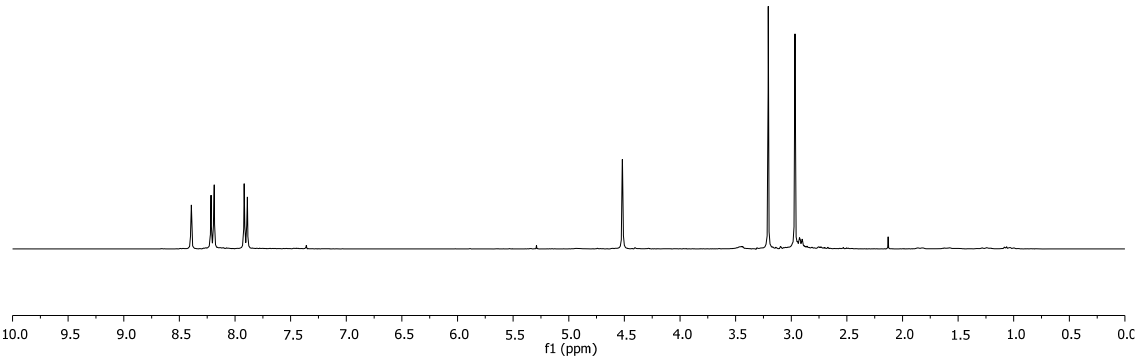
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.1
3	Experiment	1D
4	Number of Scans	9
5	Receiver Gain	36
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1236.8
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

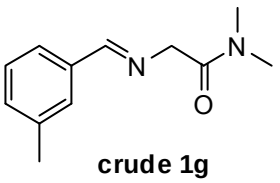




crude 1f

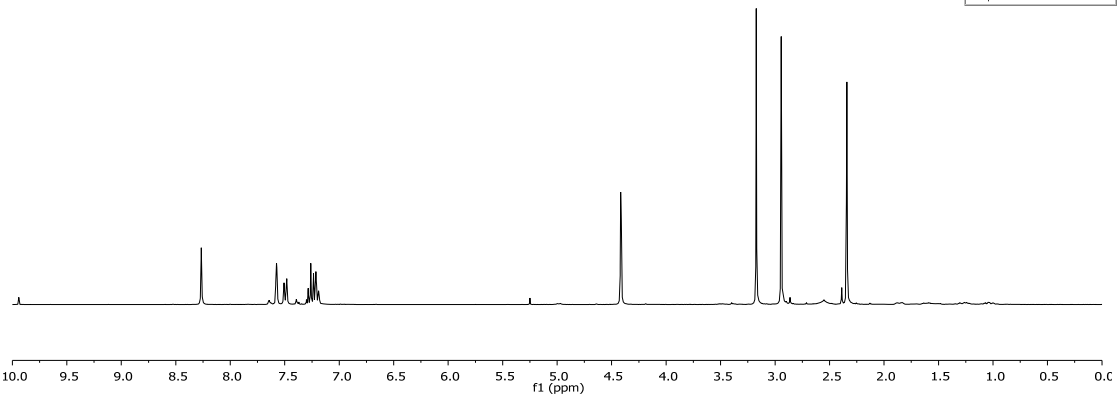
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.1
3	Experiment	1D
4	Number of Scans	6
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1243.6
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

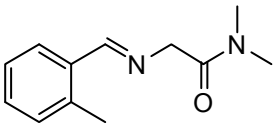




crude 1g

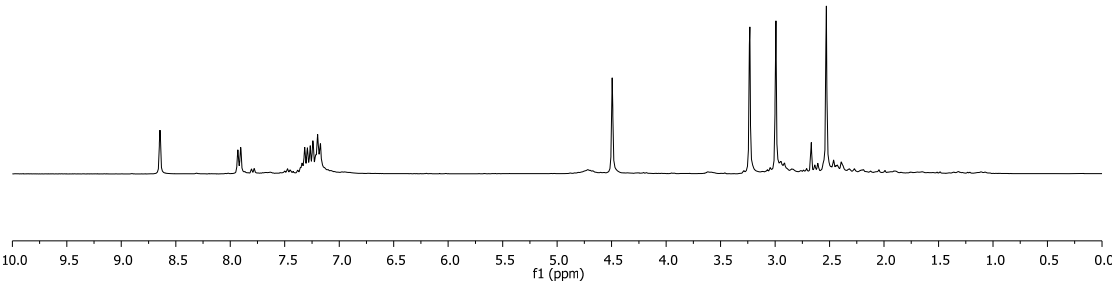
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	7
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

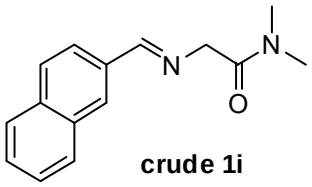




crude 1h

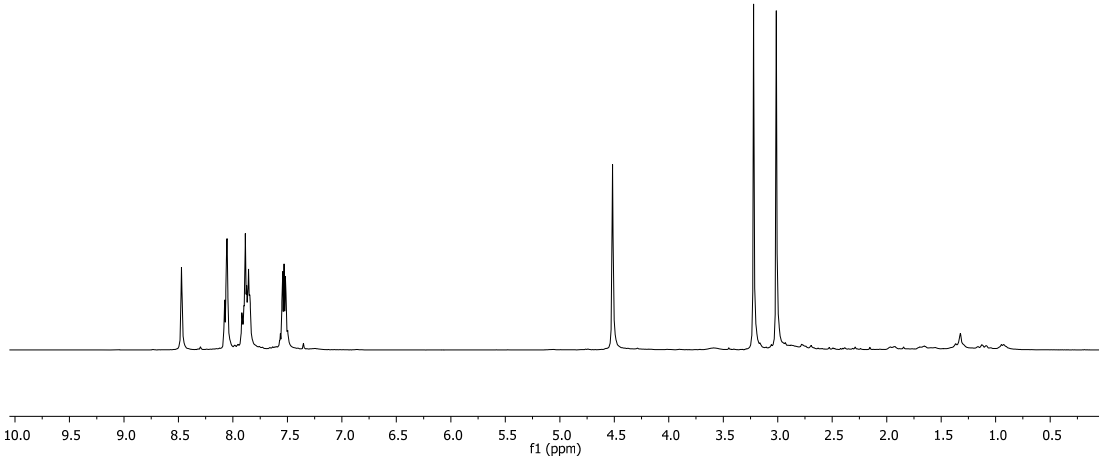
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	10
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

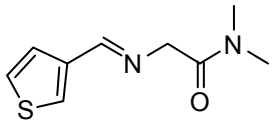




crude 1i

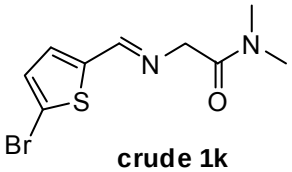
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	7
5	Receiver Gain	40
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768





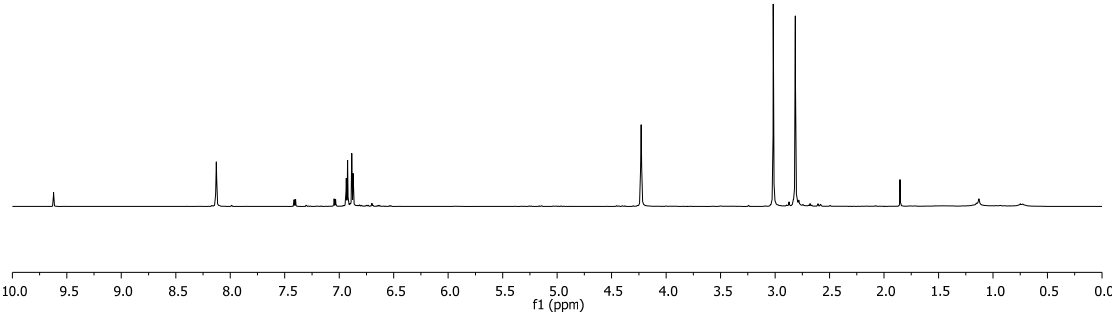
crude 1j

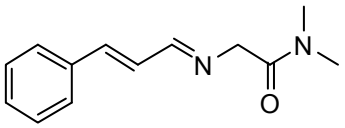
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	6
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1245.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



crude 1k

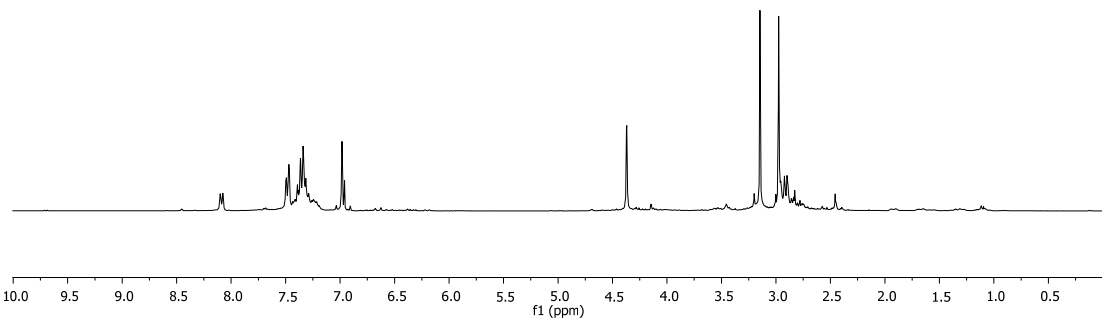
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	8
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

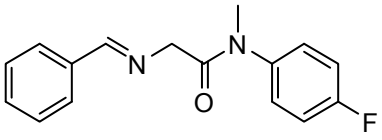




crude 1l

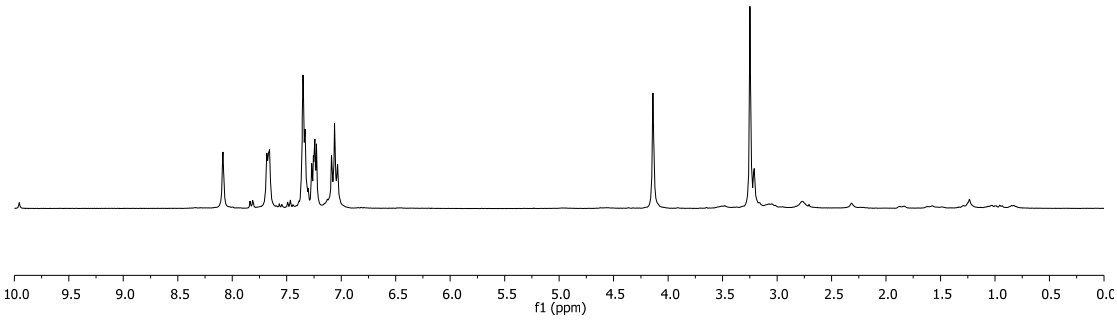
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	11
5	Receiver Gain	36
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1208.4
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

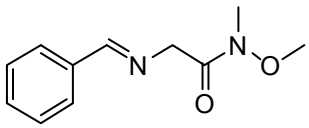




crude 1m

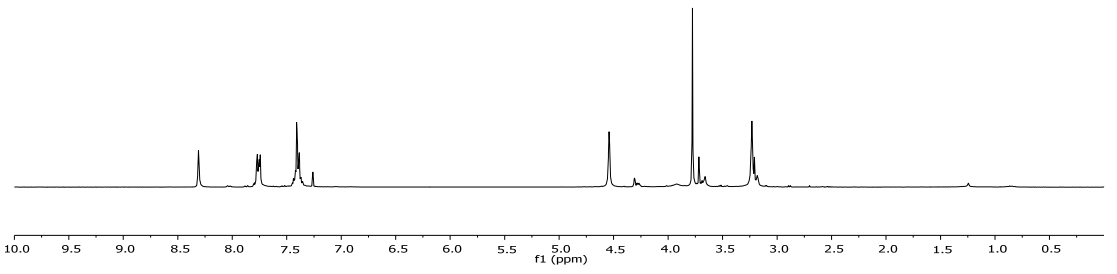
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.1
3	Experiment	1D
4	Number of Scans	5
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

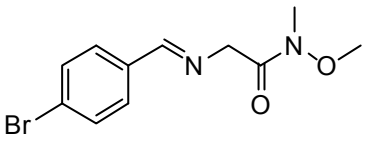




crude 1n

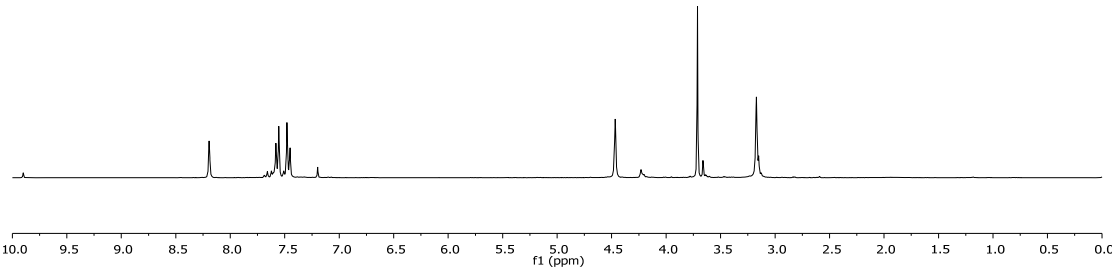
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	15
5	Receiver Gain	18
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

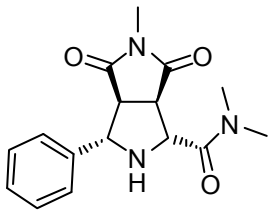




crude 1o

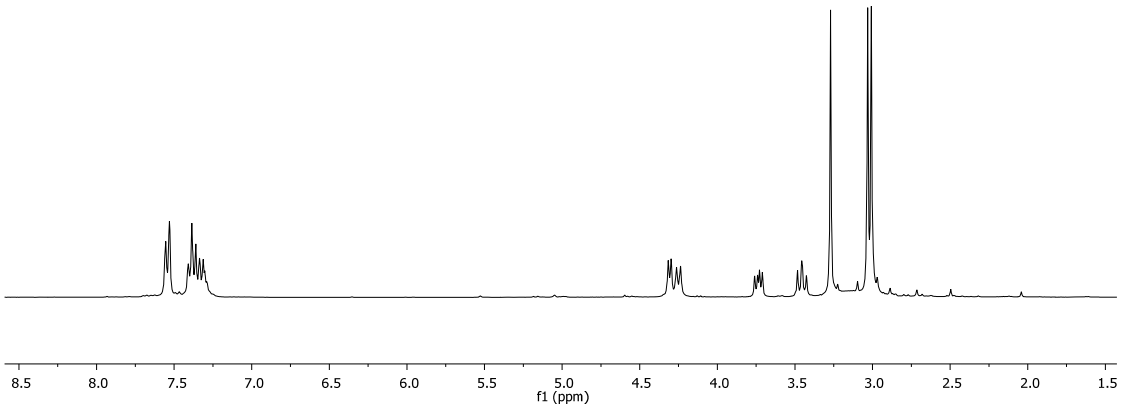
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	298.4
3	Experiment	1D
4	Number of Scans	8
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1244.8
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768





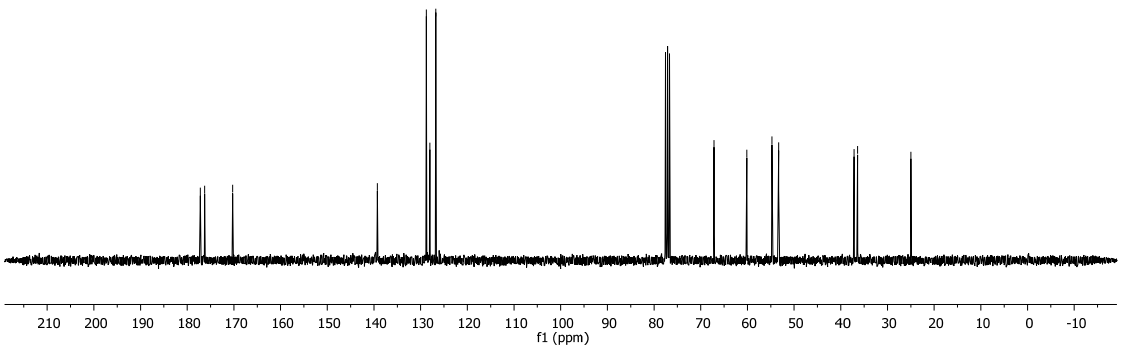
exo-**4a**

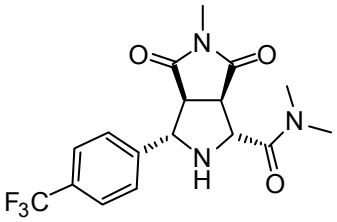
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	16
5	Receiver Gain	90
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	4.5614
9	Spectrometer Frequency	300.13
10	Spectral Width	3592.0
11	Lowest Frequency	-445.4
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



177.2
176.3
170.3
139.3
128.8
128.0
126.7
67.1
60.1
54.7
53.3
37.2
36.4
25.0

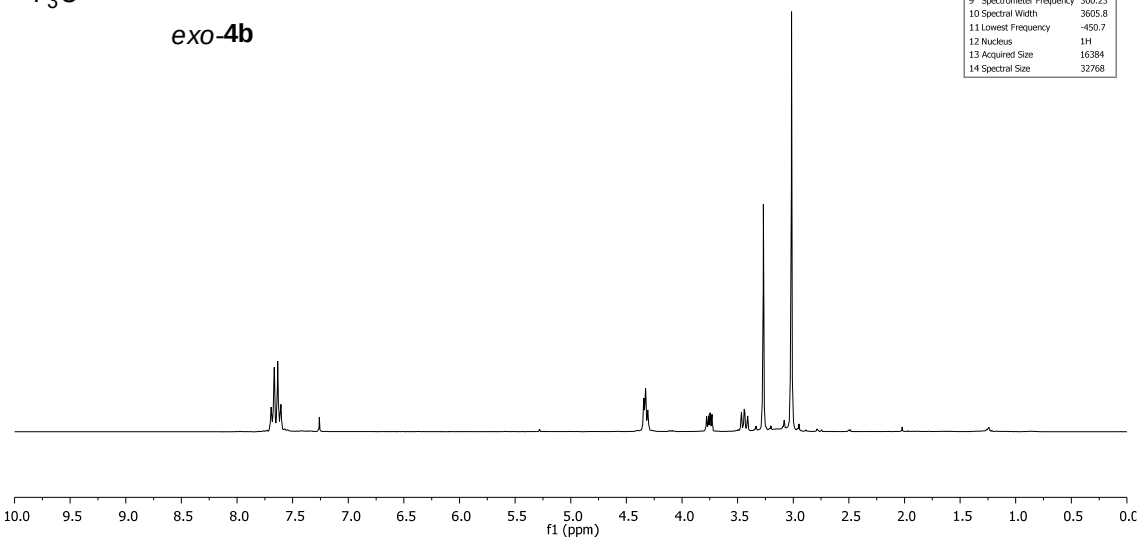
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	299.9
3	Experiment	1D
4	Number of Scans	69
5	Receiver Gain	362
6	Relaxation Delay	2.0000
7	Pulse Width	5.2000
8	Acquisition Time	1.8220
9	Spectrometer Frequency	75.48
10	Spectral Width	17985.6
11	Lowest Frequency	-1446.5
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

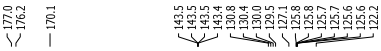




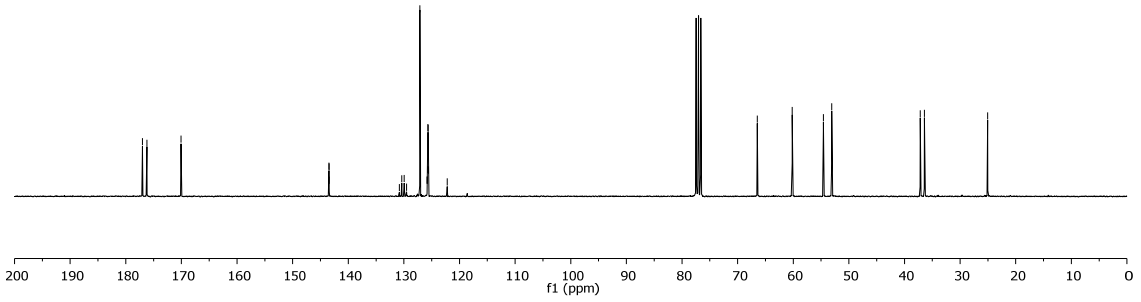
exo-**4b**

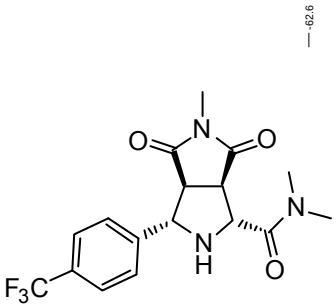
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	16
5 Receiver Gain	181
6 Relaxation Delay	1.0000
7 Pulse Width	10.8000
8 Acquisition Time	4.5439
9 Spectrometer Frequency	300.23
10 Spectral Width	3605.8
11 Lowest Frequency	-450.7
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768





Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	10000
5 Receiver Gain	2050
6 Relaxation Delay	2.0000
7 Pulse Width	8.1000
8 Acquisition Time	1.8176
9 Spectrometer Frequency	75.50
10 Spectral Width	18028.8
11 Lowest Frequency	-1465.6
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

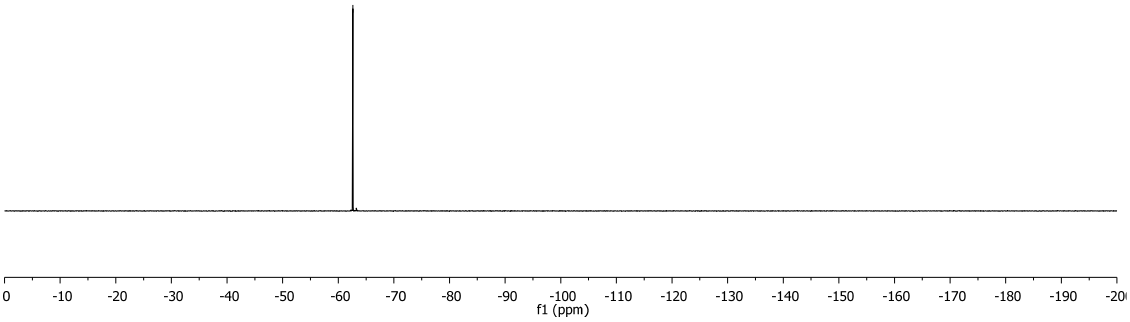


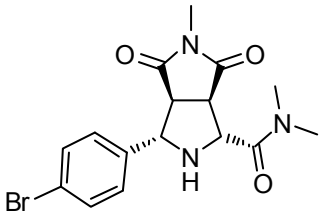


exo-**4b**

^{19}F NMR

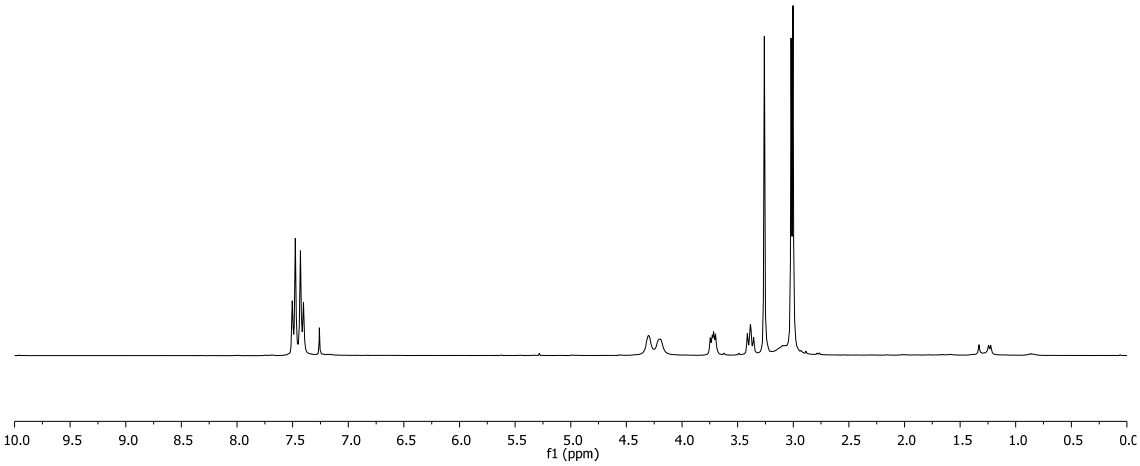
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	32
5	Receiver Gain	8200
6	Relaxation Delay	2.0000
7	Pulse Width	11.5000
8	Acquisition Time	0.9787
9	Spectrometer Frequency	282.47
10	Spectral Width	66964.3
11	Lowest Frequency	-61731.8
12	Nucleus	19F
13	Acquired Size	65536
14	Spectral Size	131072

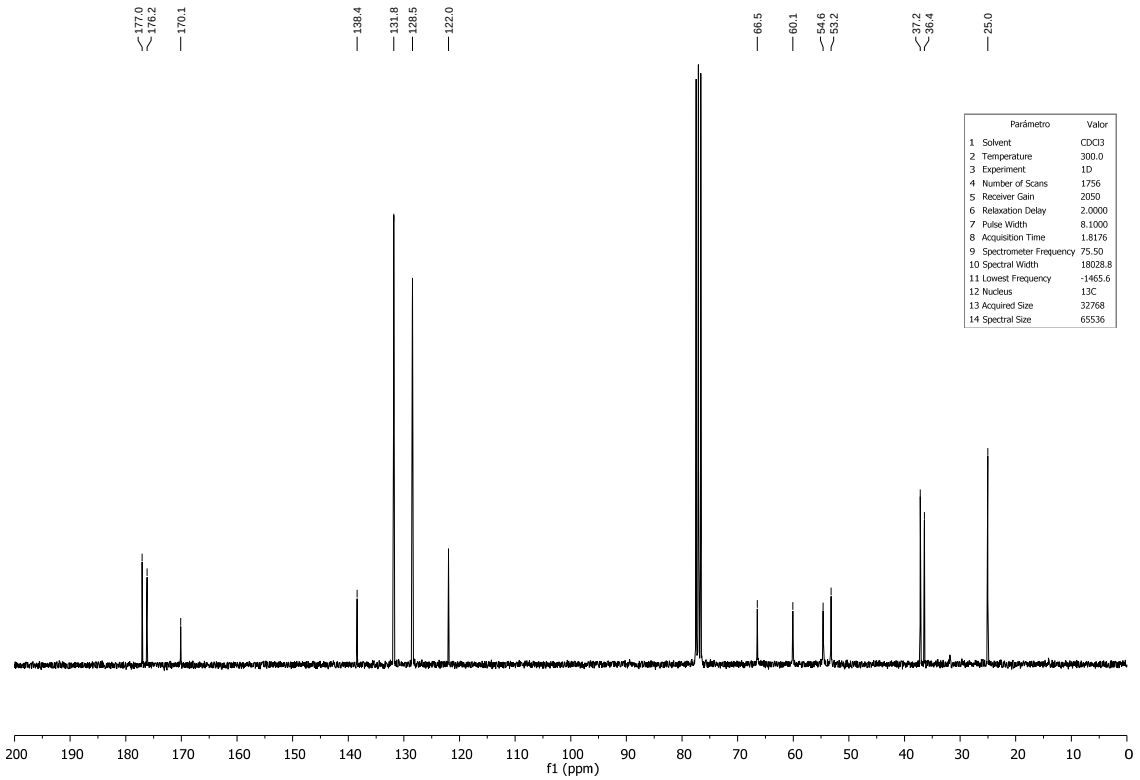




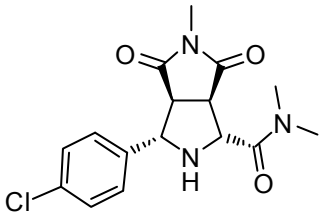
exo-**4c**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	16
5	Receiver Gain	203
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-477.5
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



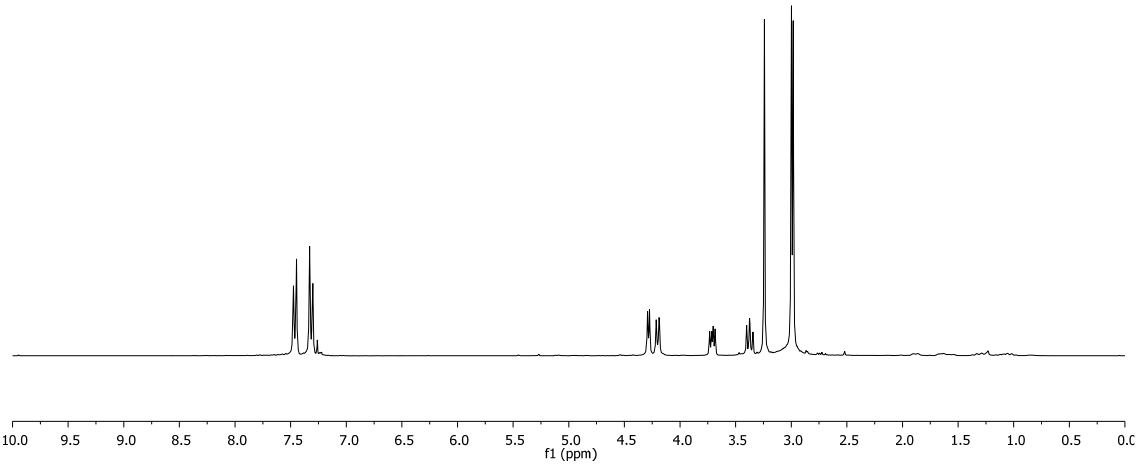


	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	1756
5	Receiver Gain	2050
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



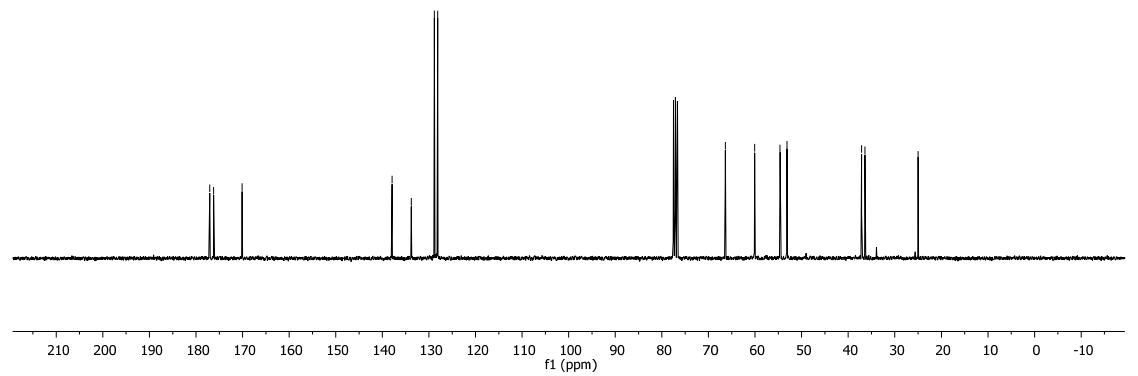
exo-**4d**

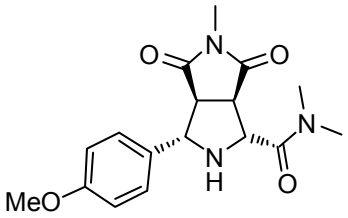
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.1
3	Experiment	1D
4	Number of Scans	6
5	Receiver Gain	128
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	4.5614
9	Spectrometer Frequency	300.13
10	Spectral Width	3592.0
11	Lowest Frequency	-458.3
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



177.1
176.2
170.1
137.9
133.8
128.8
128.1
66.4
60.1
54.6
53.2
37.1
36.4
25.0

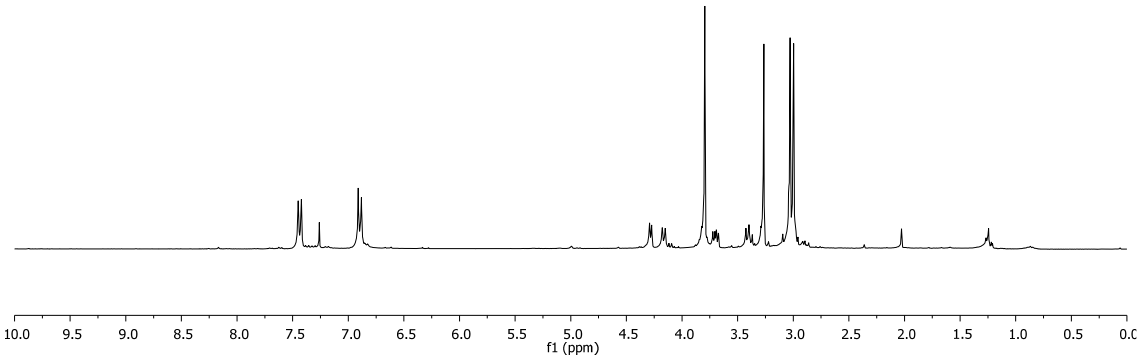
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	209
5	Receiver Gain	2300
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



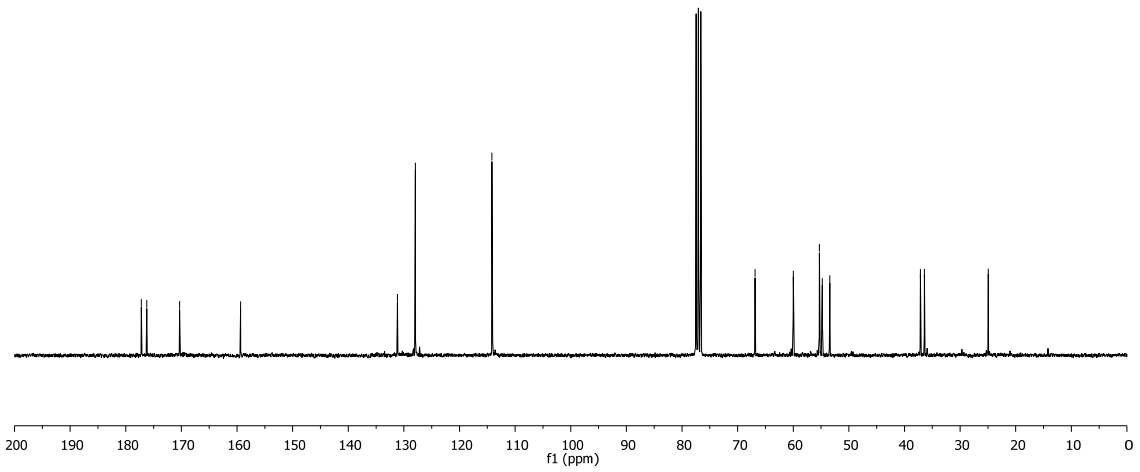


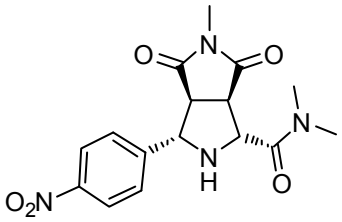
exo-**4e**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	16
5	Receiver Gain	181
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-463.2
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



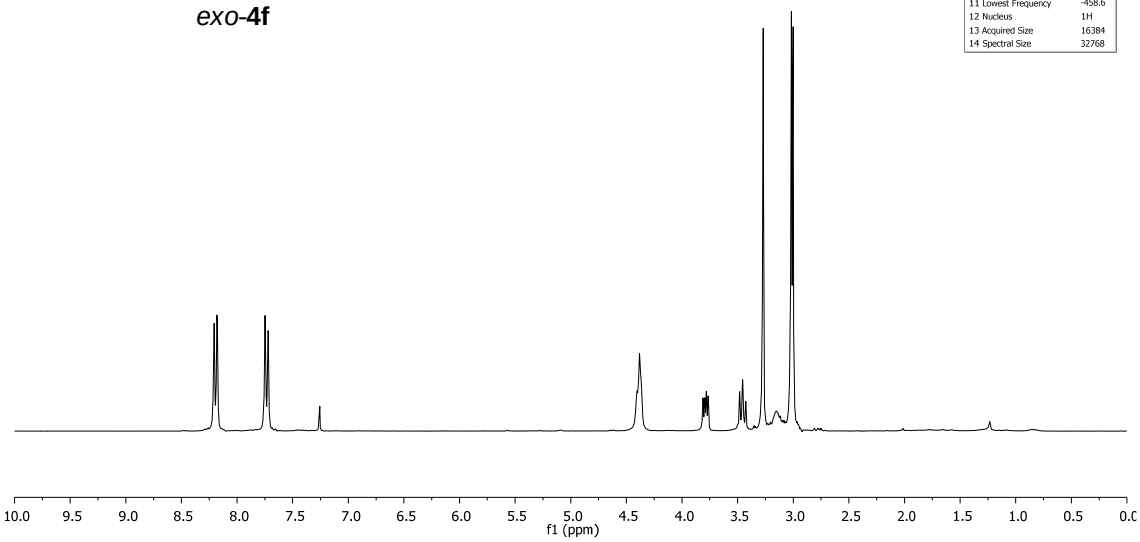
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	2091
5	Receiver Gain	2050
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



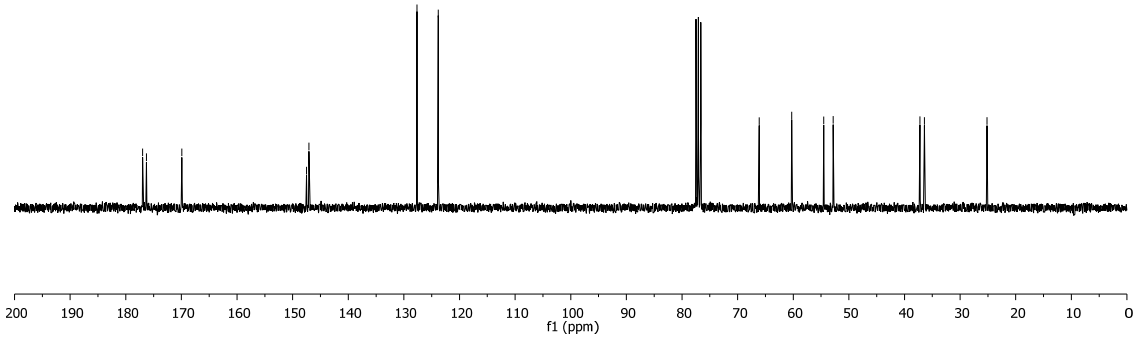


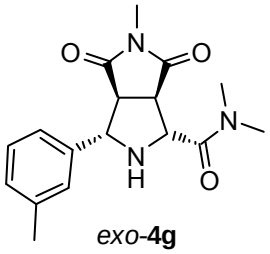
exo-**4f**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	14
5	Receiver Gain	181
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-458.6
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



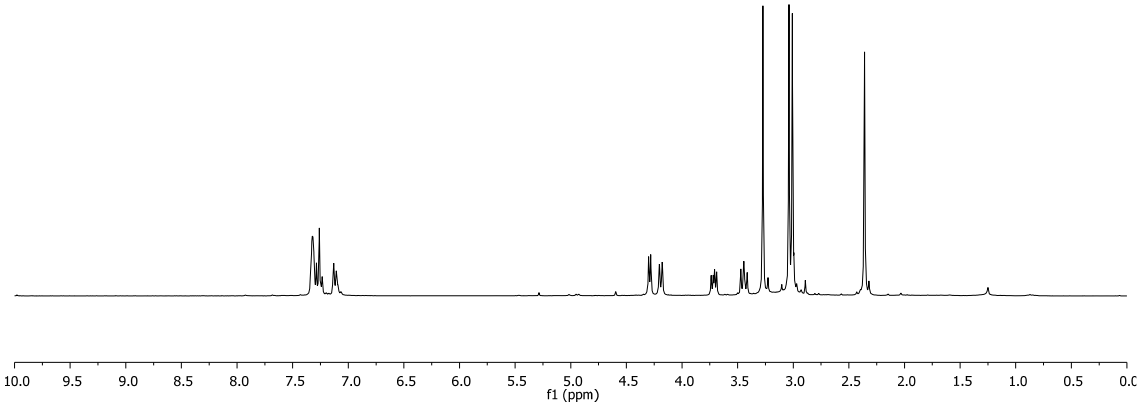
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	103
5	Receiver Gain	1820
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536





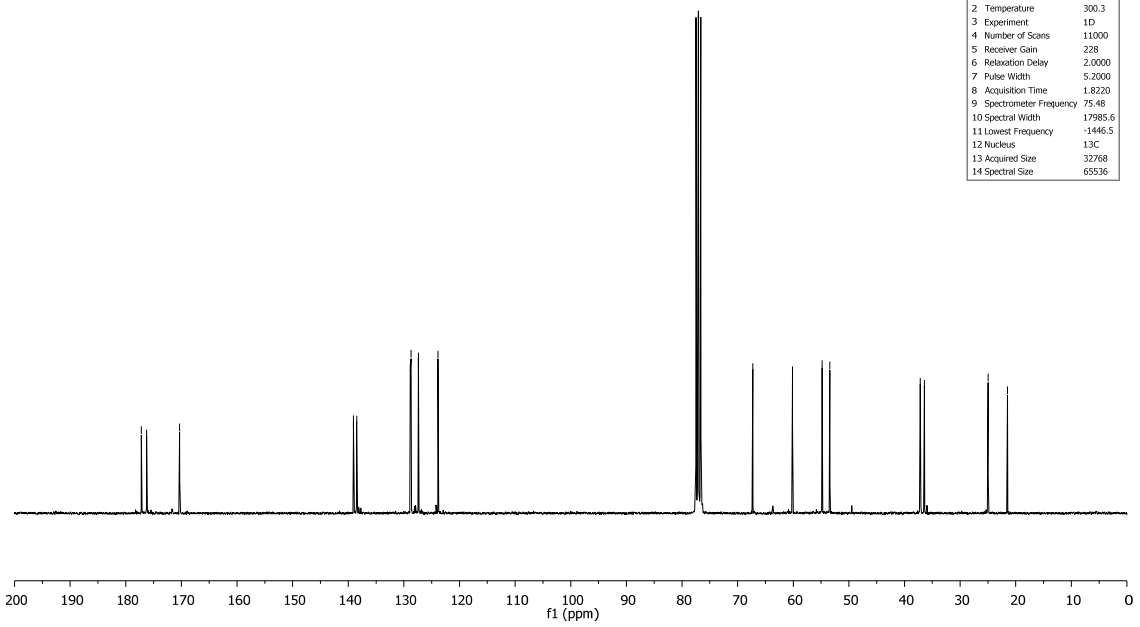
exo-**4g**

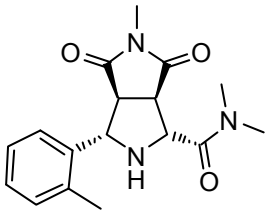
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	13
5	Receiver Gain	228
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	4.5614
9	Spectrometer Frequency	300.13
10	Spectral Width	3592.0
11	Lowest Frequency	-445.4
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



177.2
176.3
170.3
139.1
138.5
128.8
128.7
127.4
123.9
67.3
60.1
54.8
53.4
37.2
36.4
25.0
21.5

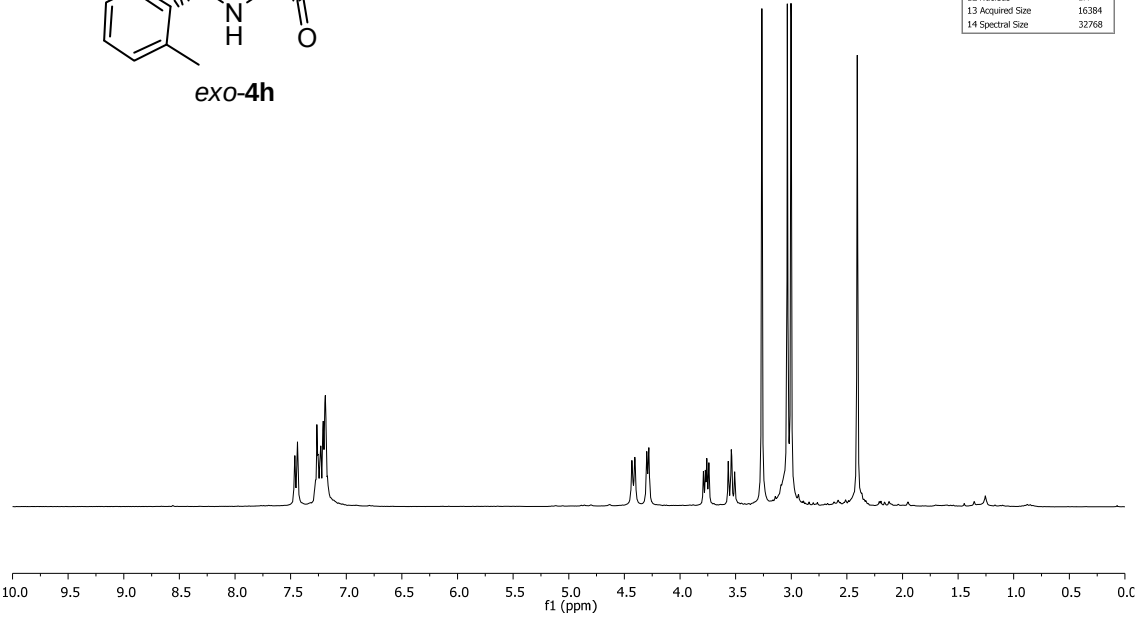
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.3
3	Experiment	1D
4	Number of Scans	11000
5	Receiver Gain	228
6	Relaxation Delay	2.0000
7	Pulse Width	5.2000
8	Acquisition Time	1.8220
9	Spectrometer Frequency	75.48
10	Spectral Width	17985.6
11	Lowest Frequency	-1446.5
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



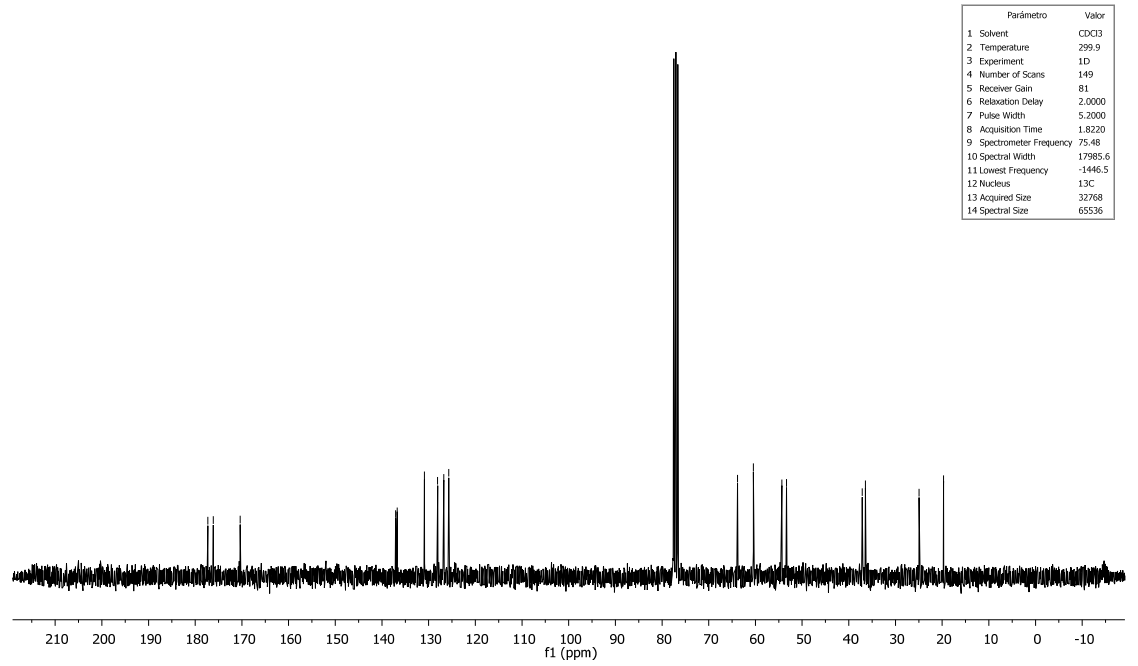


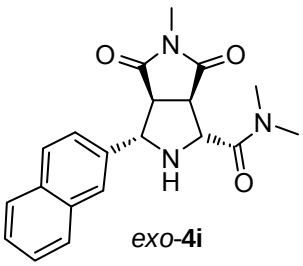
exo-**4h**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.1
3	Experiment	1D
4	Number of Scans	16
5	Receiver Gain	161
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	4.5614
9	Spectrometer Frequency	300.13
10	Spectral Width	3592.0
11	Lowest Frequency	-477.9
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



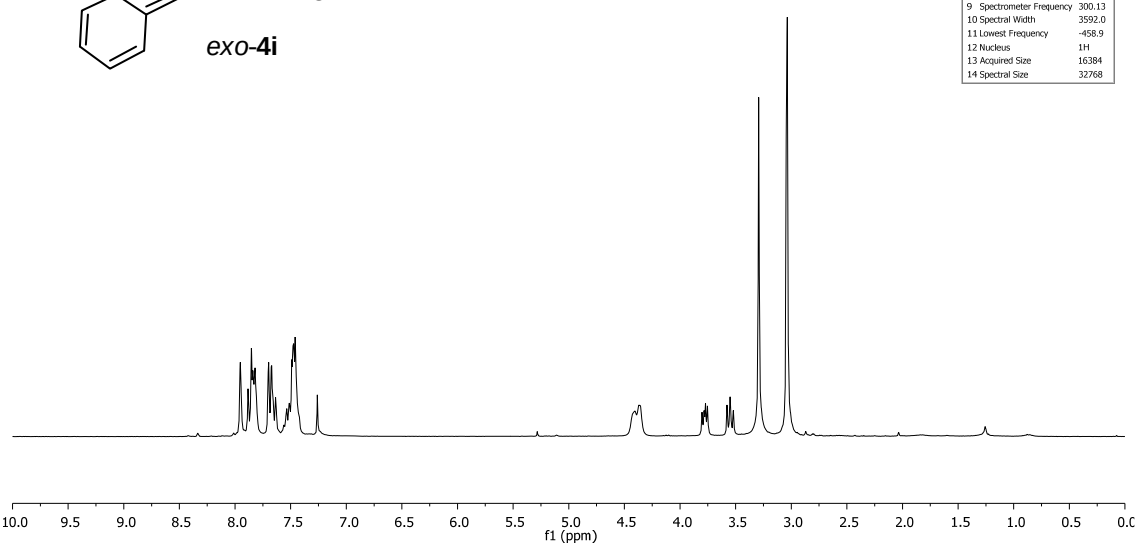
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	299.9
3	Experiment	1D
4	Number of Scans	149
5	Receiver Gain	81
6	Relaxation Delay	2.0000
7	Pulse Width	5.2000
8	Acquisition Time	1.8220
9	Spectrometer Frequency	75.48
10	Spectral Width	17985.6
11	Lowest Frequency	-1446.5
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



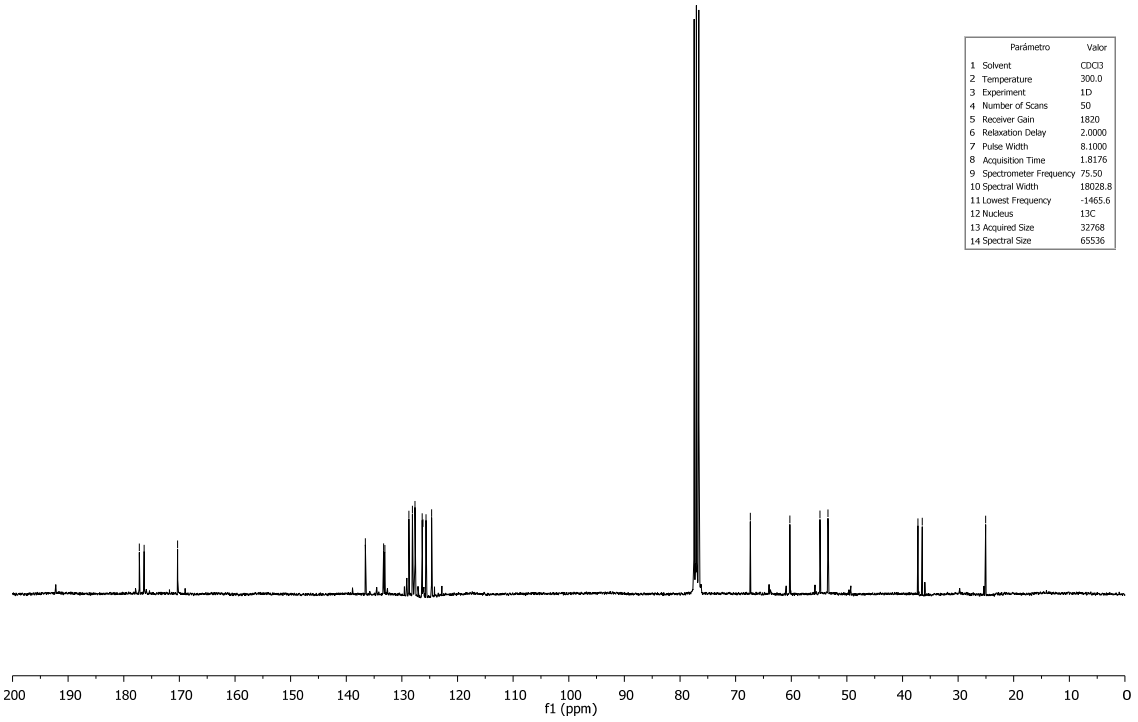


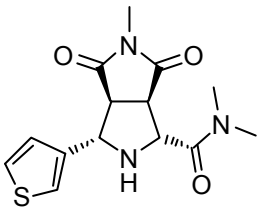
exo-**4i**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.2
3	Experiment	1D
4	Number of Scans	10
5	Receiver Gain	161
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	4.5614
9	Spectrometer Frequency	300.13
10	Spectral Width	3592.0
11	Lowest Frequency	-458.9
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



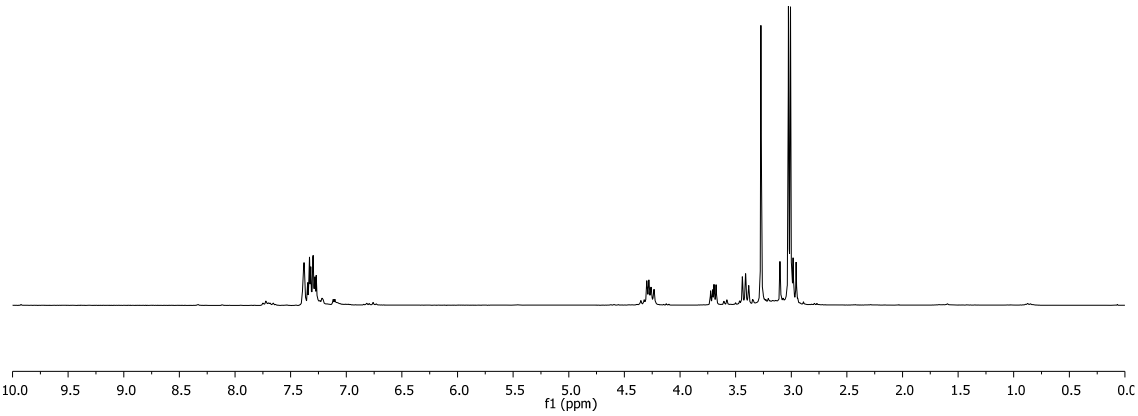
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	50
5	Receiver Gain	1820
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



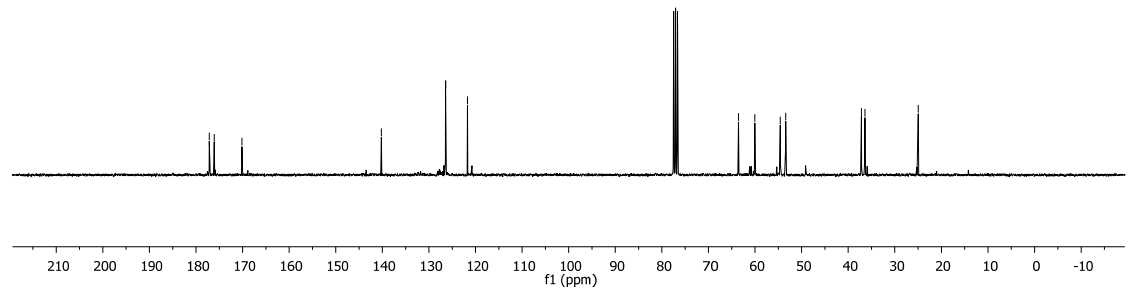


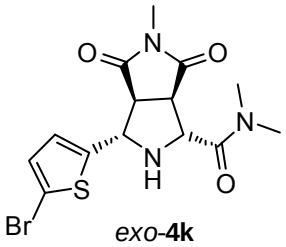
exo-**4j**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	14
5	Receiver Gain	181
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-458.6
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



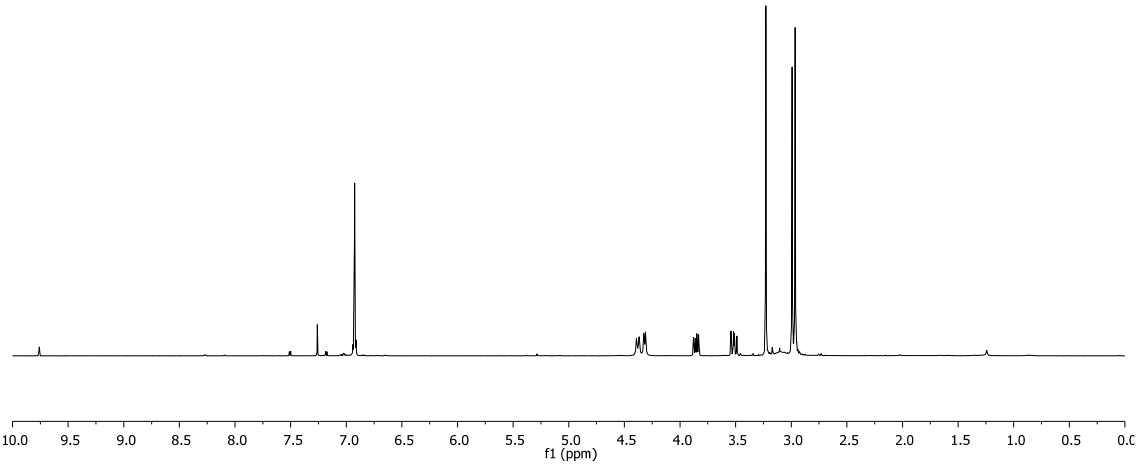
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	103
5	Receiver Gain	1820
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



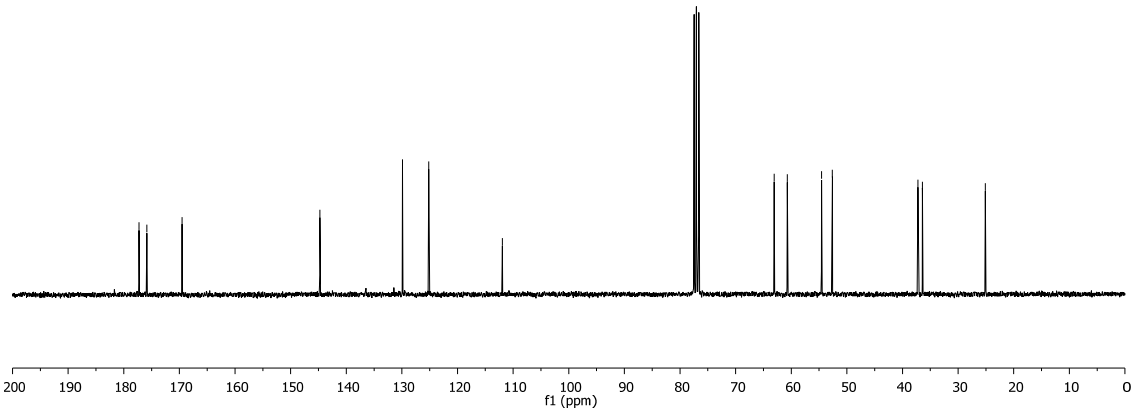


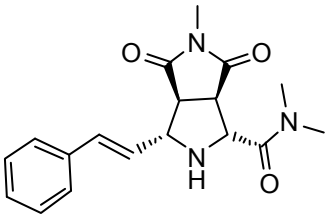
exo-**4k**

Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	8
5 Receiver Gain	256
6 Relaxation Delay	1.0000
7 Pulse Width	10.8000
8 Acquisition Time	4.5439
9 Spectrometer Frequency	300.23
10 Spectral Width	3605.8
11 Lowest Frequency	-459.4
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768



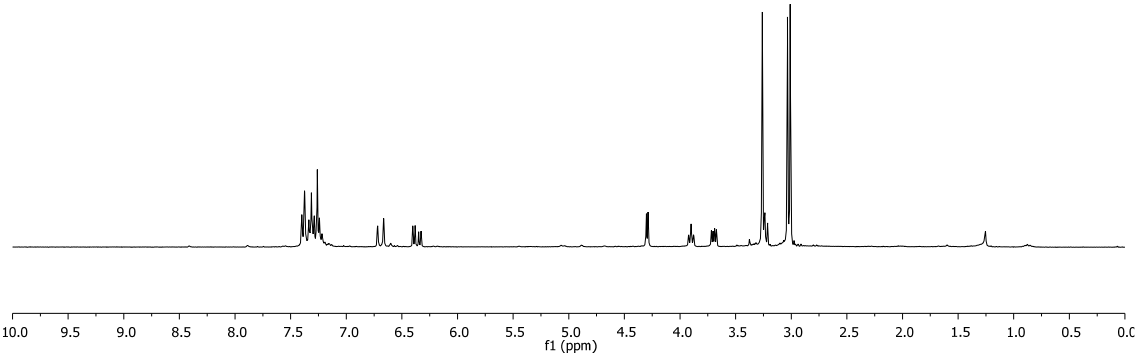
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	702
5 Receiver Gain	2300
6 Relaxation Delay	2.0000
7 Pulse Width	8.1000
8 Acquisition Time	1.8176
9 Spectrometer Frequency	75.50
10 Spectral Width	18028.8
11 Lowest Frequency	-1465.6
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

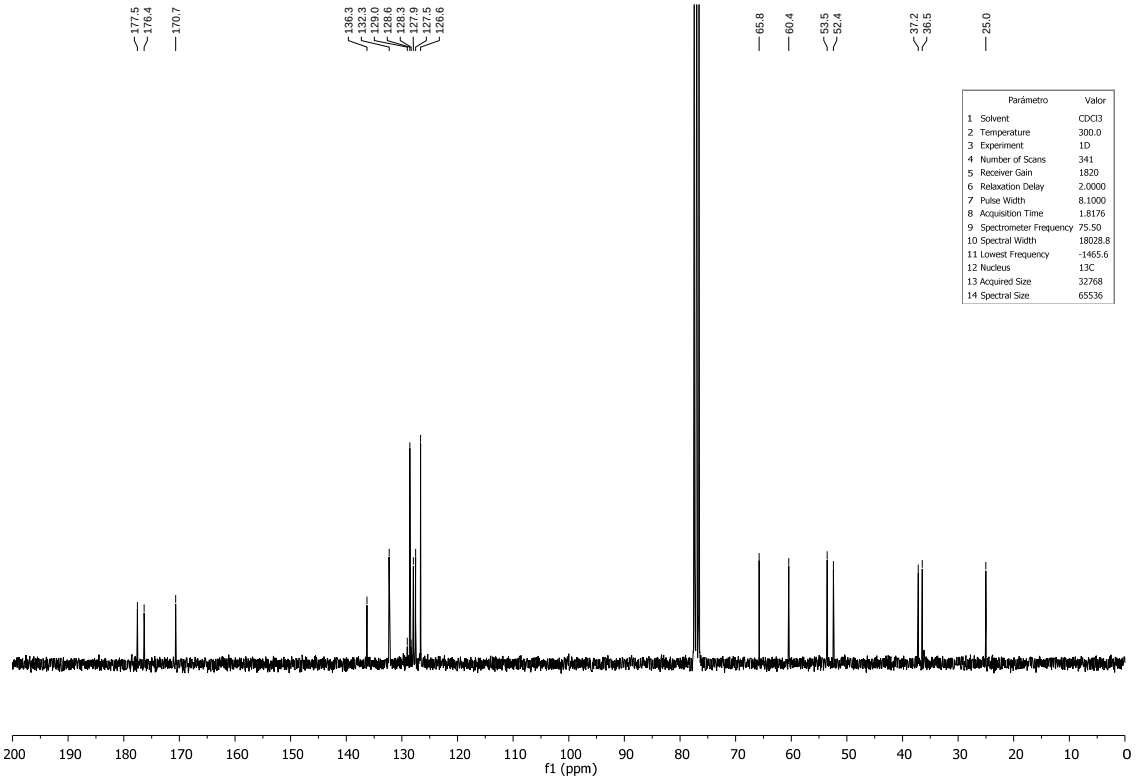




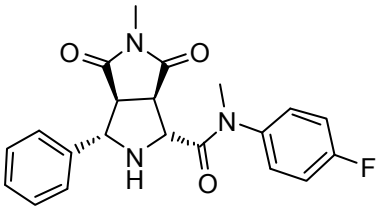
exo-**4l**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	10
5	Receiver Gain	362
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-460.5
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



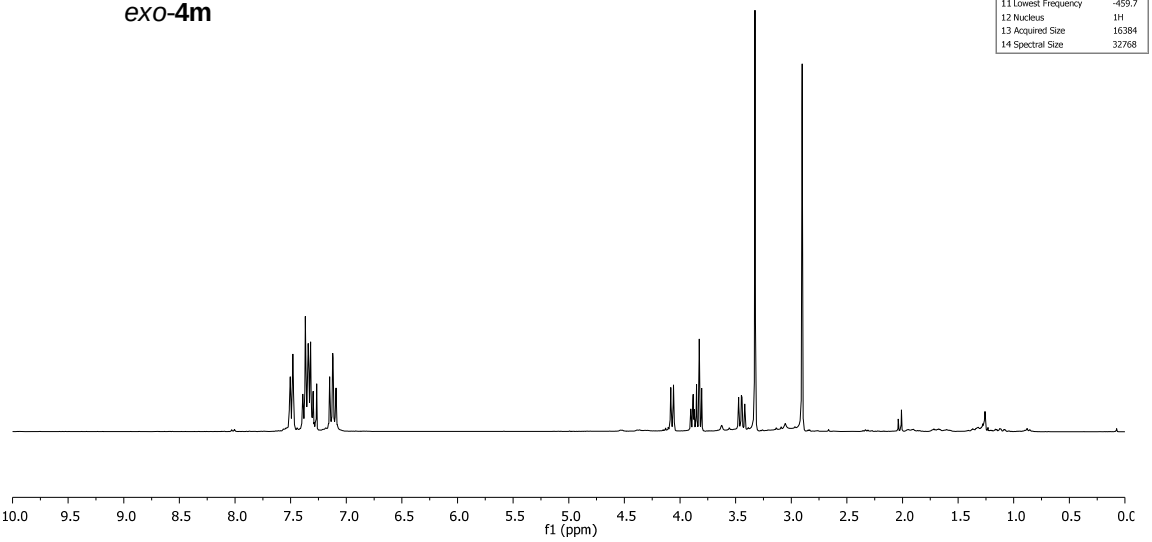


	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	341
5	Receiver Gain	1820
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



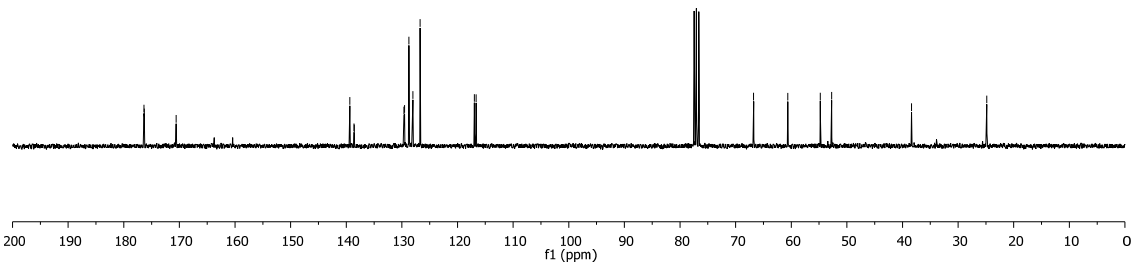
exo-**4m**

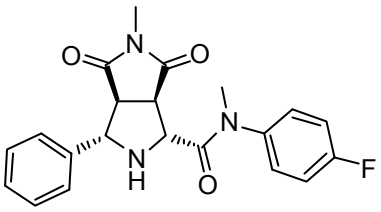
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	16
5	Receiver Gain	181
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-459.7
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



176.4
176.3
170.6
139.4
138.6
138.6
129.6
129.5
128.7
128.0
126.7
117.0
116.7
66.8
60.6
54.8
52.7
38.4
24.9

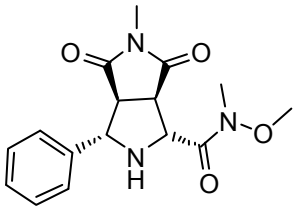
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	195
5	Receiver Gain	2300
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536





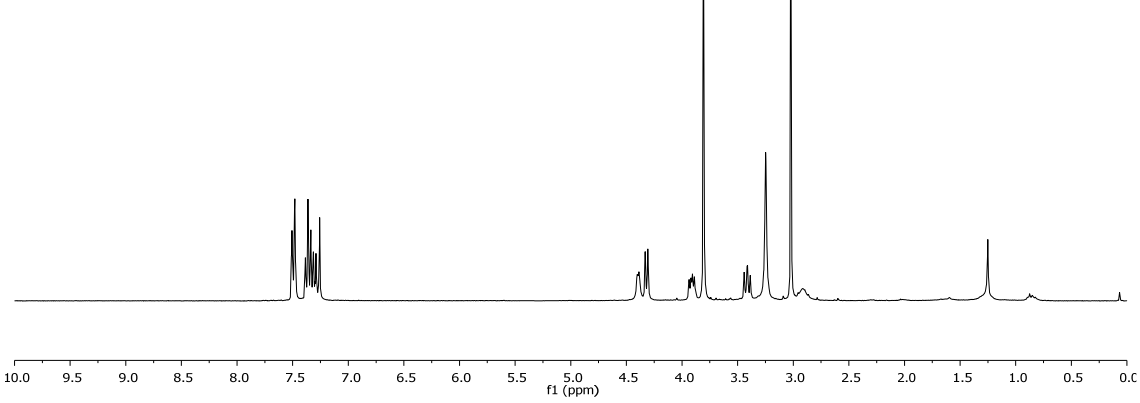
exo-**4m**

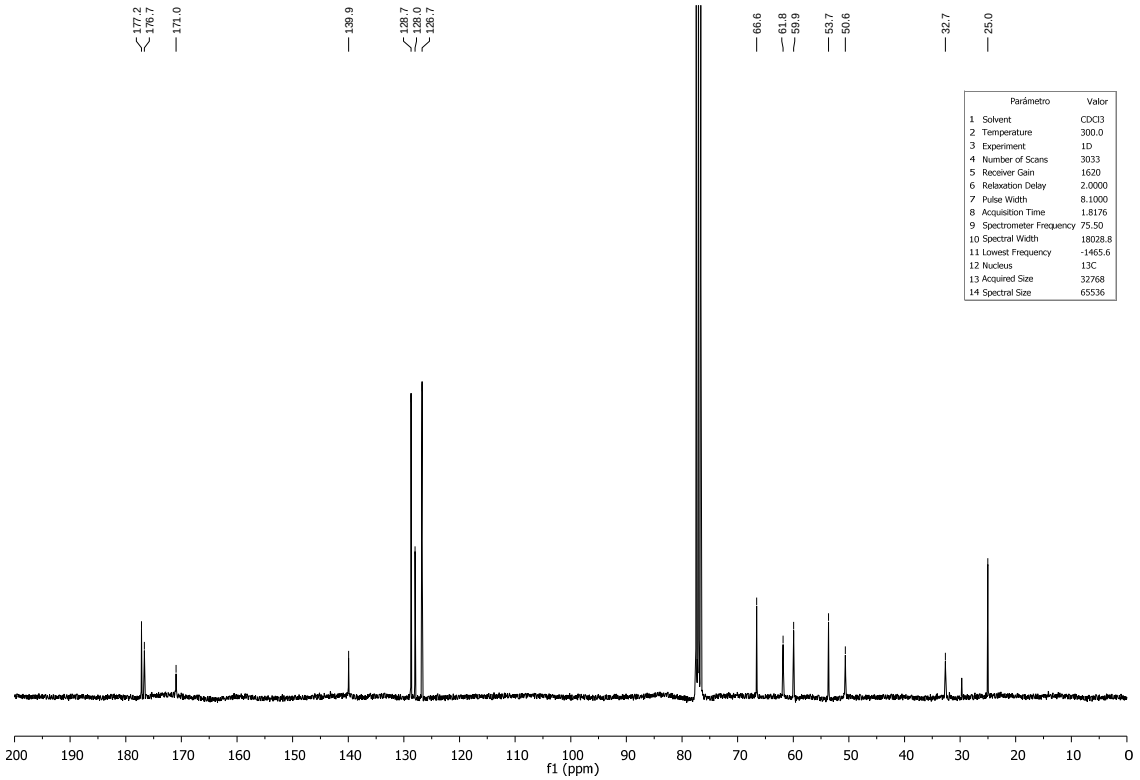
^{19}F NMR



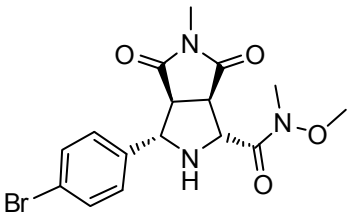
exo-**4n**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	7
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	2.6543
9	Spectrometer Frequency	300.13
10	Spectral Width	6172.8
11	Lowest Frequency	-1233.0
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



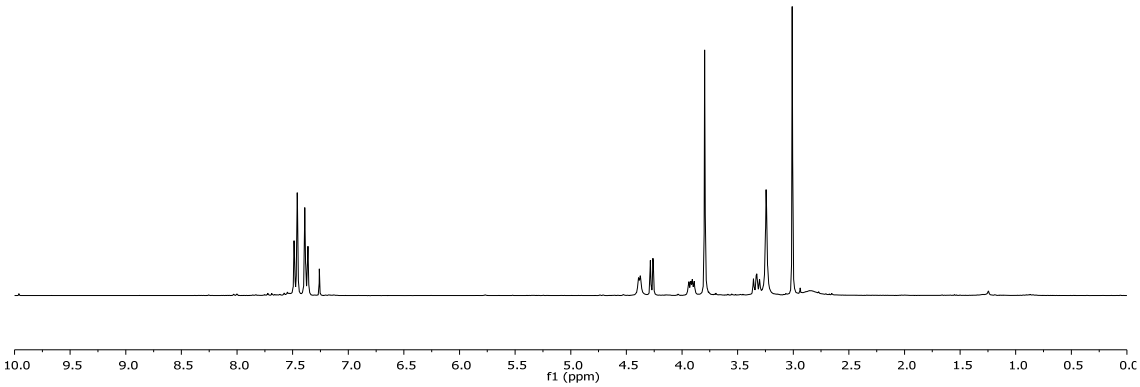


	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	3033
5	Receiver Gain	1620
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

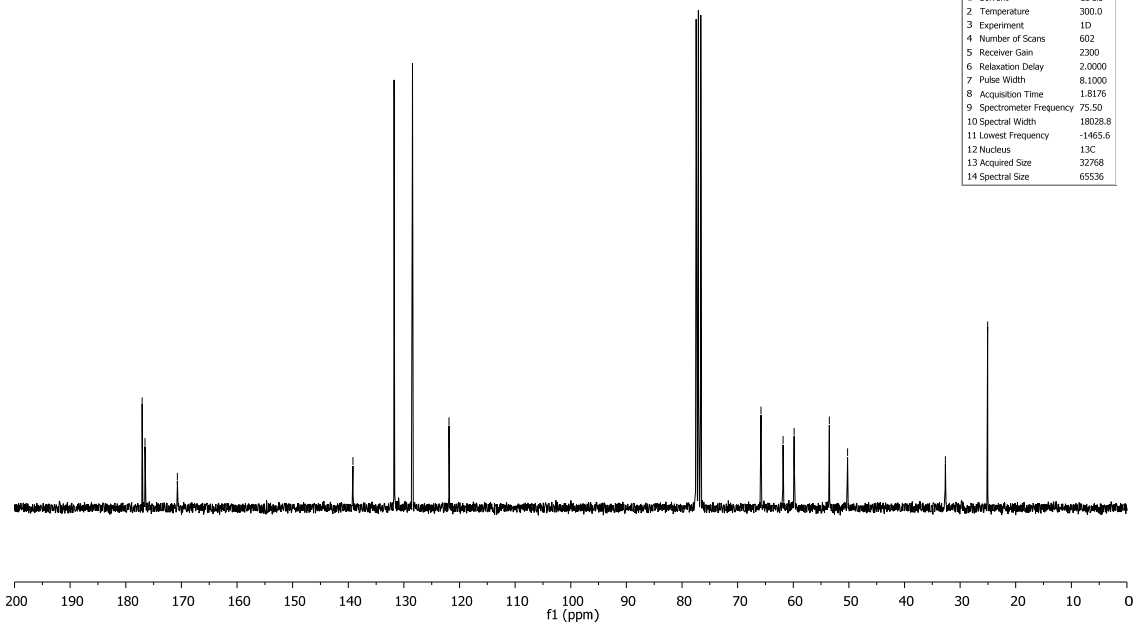


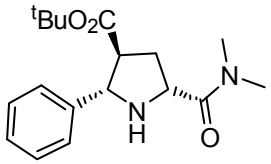
exo-**4o**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	6
5	Receiver Gain	203
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-478.2
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



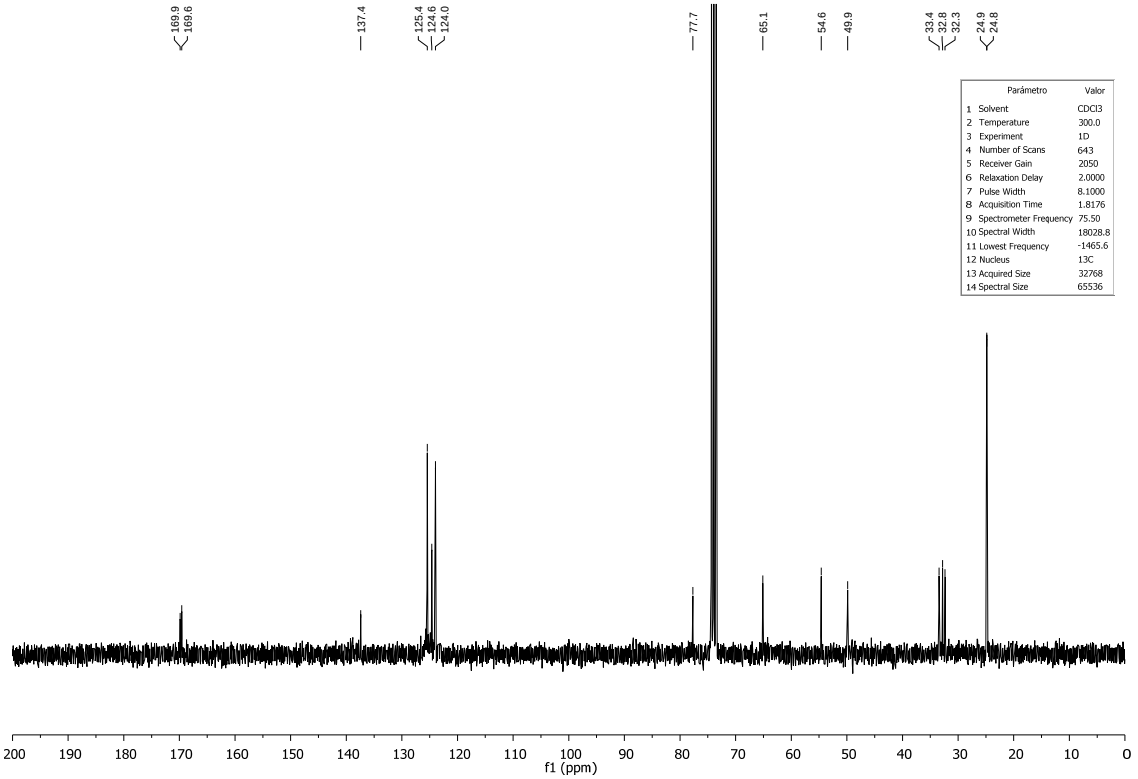
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	602
5	Receiver Gain	2300
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



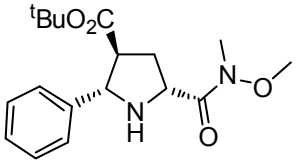


exo-**11a**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.1
3	Experiment	1D
4	Number of Scans	8
5	Receiver Gain	4
6	Relaxation Delay	1.0000
7	Pulse Width	10.4000
8	Acquisition Time	4.5614
9	Spectrometer Frequency	300.13
10	Spectral Width	3592.0
11	Lowest Frequency	-477.3
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



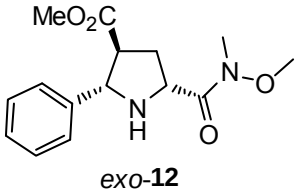
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	643
5	Receiver Gain	2050
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



exo-**11n**

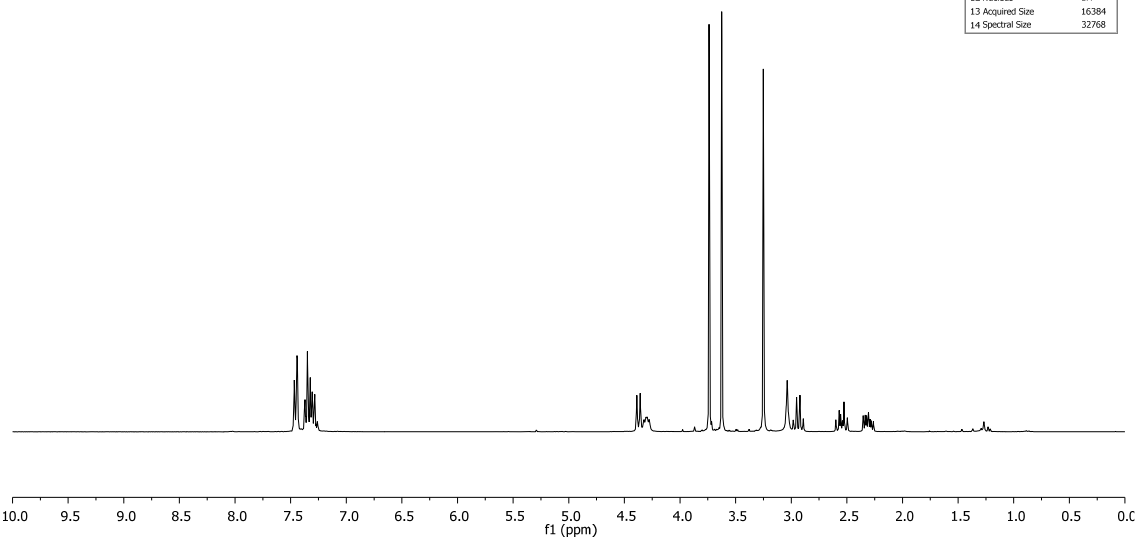
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	9
5	Receiver Gain	256
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-461.1
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	10000
5	Receiver Gain	2050
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

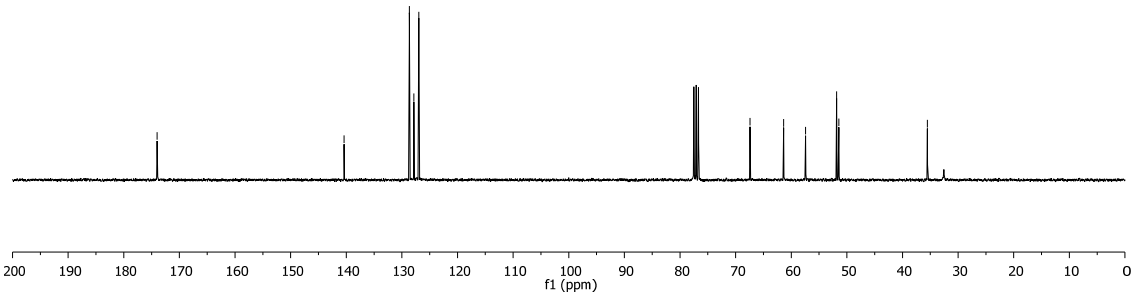


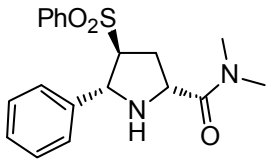
exo-**12**

Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	6
5 Receiver Gain	81
6 Relaxation Delay	1.0000
7 Pulse Width	10.8000
8 Acquisition Time	4.5439
9 Spectrometer Frequency	300.23
10 Spectral Width	3605.8
11 Lowest Frequency	-450.7
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768



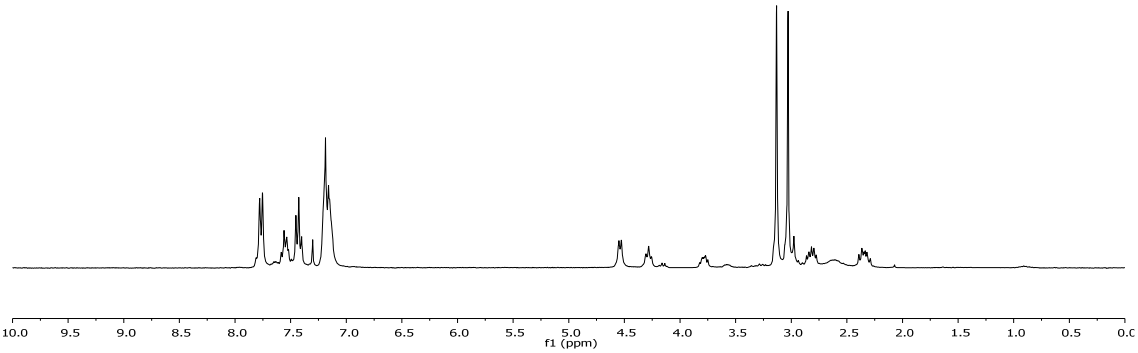
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	252
5 Receiver Gain	2050
6 Relaxation Delay	2.0000
7 Pulse Width	8.1000
8 Acquisition Time	1.8176
9 Spectrometer Frequency	75.50
10 Spectral Width	18028.8
11 Lowest Frequency	-1465.6
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

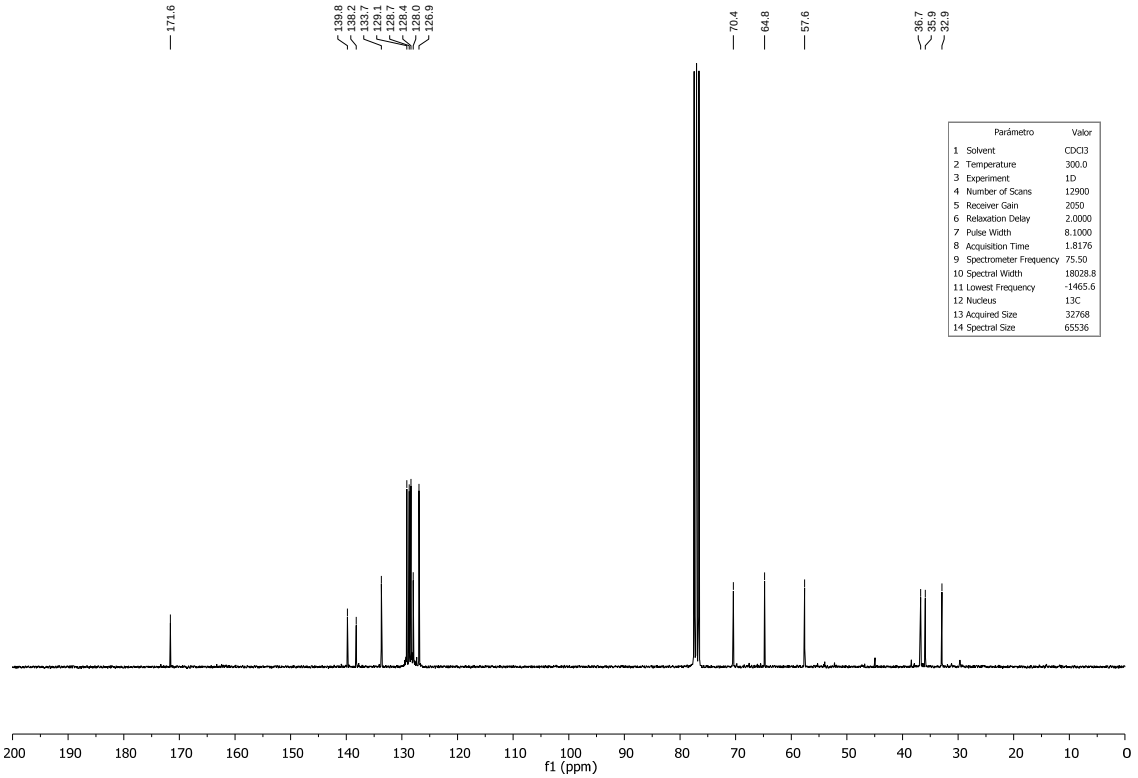




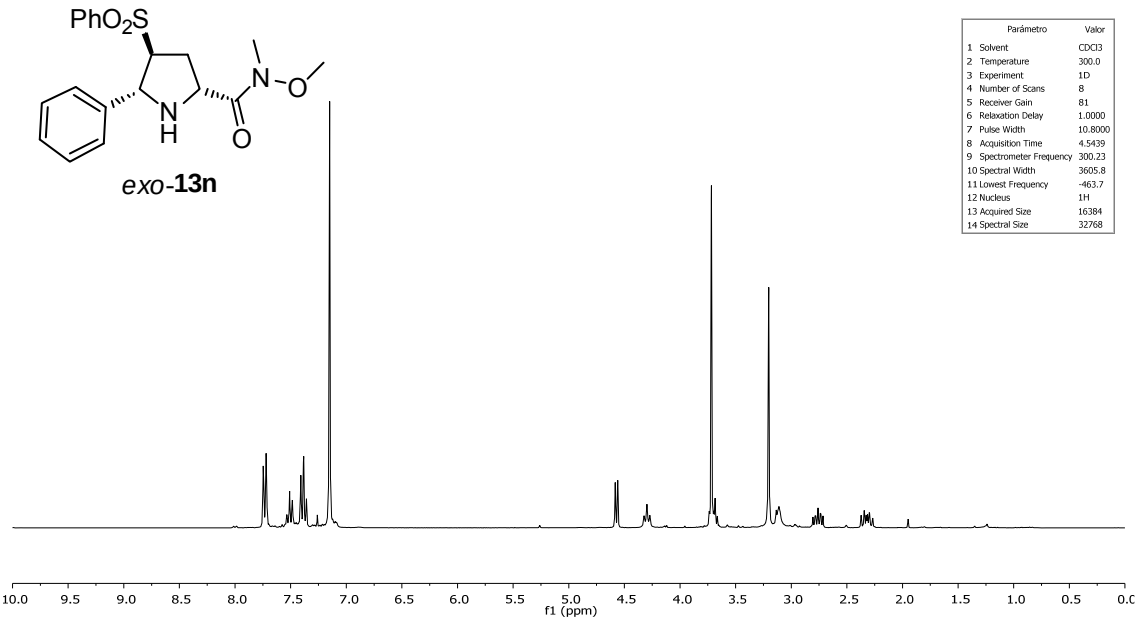
exo-**13a**

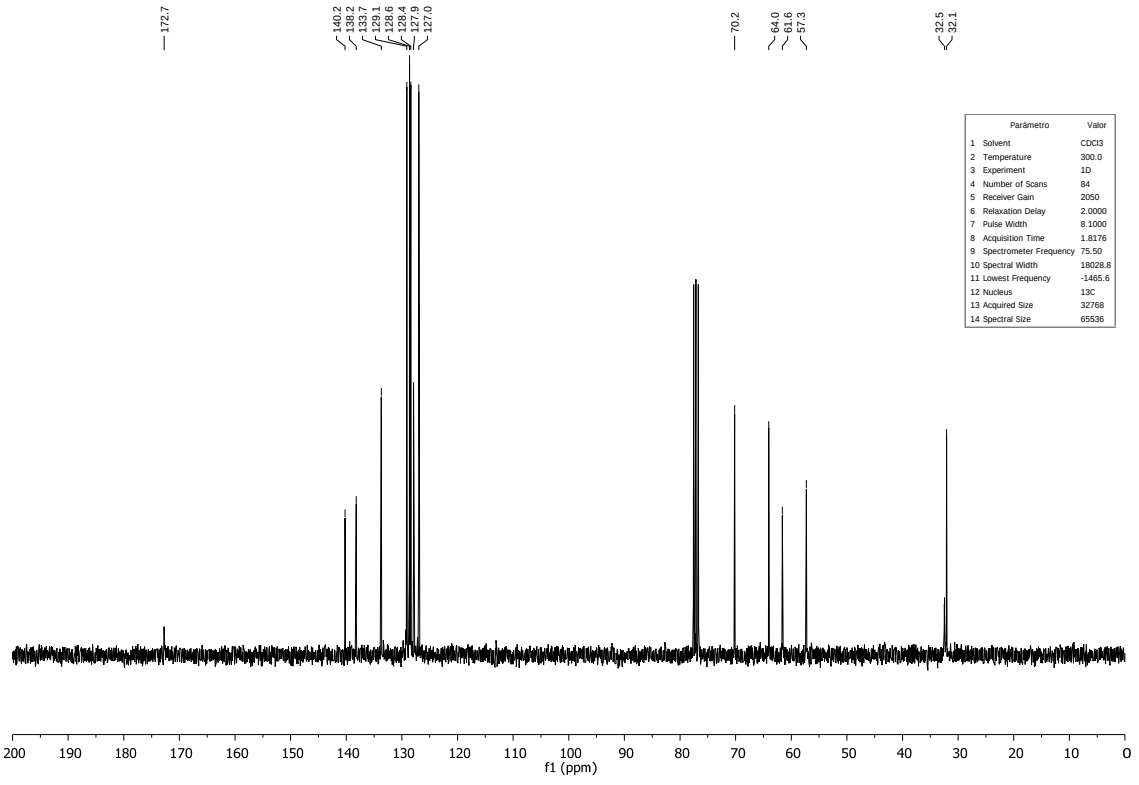
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.3
3 Experiment	1D
4 Number of Scans	8
5 Receiver Gain	4
6 Relaxation Delay	1.0000
7 Pulse Width	10.4000
8 Acquisition Time	4.5614
9 Spectrometer Frequency	300.13
10 Spectral Width	3592.0
11 Lowest Frequency	-445.4
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768

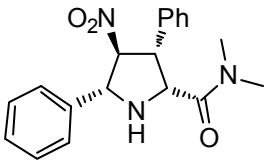




Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	12900
5 Receiver Gain	2050
6 Relaxation Delay	2.0000
7 Pulse Width	8.1000
8 Acquisition Time	1.8176
9 Spectrometer Frequency	75.50
10 Spectral Width	18028.8
11 Lowest Frequency	-1465.6
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

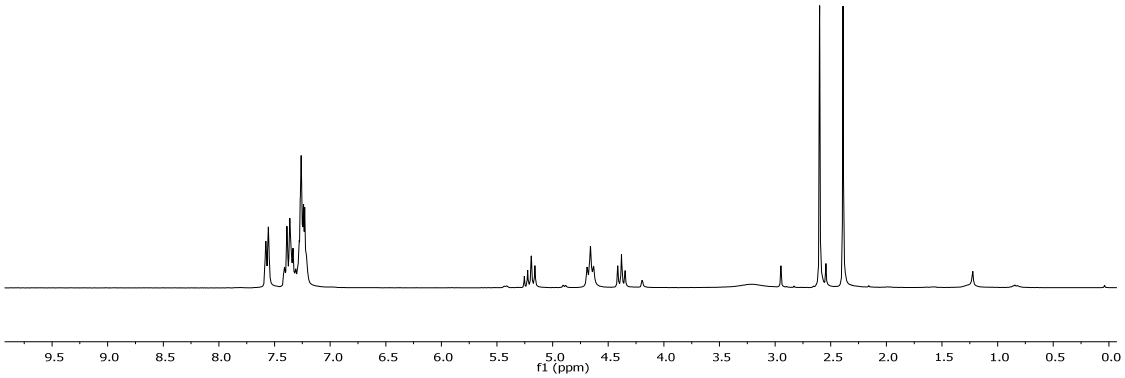

PhO2S
N
O
N
H
O
exo-13n
Parámetro Valor
1 Solvent CDCl3
2 Temperature 300.0
3 Experiment 1D
4 Number of Scans 8
5 Receiver Gain 81
6 Relaxation Delay 1.0000
7 Pulse Width 10.8000
8 Acquisition Time 4.5439
9 Spectrometer Frequency 300.23
10 Spectral Width 3605.8
11 Lowest Frequency -463.7
12 Nucleus 1H
13 Acquired Size 16384
14 Spectral Size 32768
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.7
140.2
138.2
133.7
129.1
128.6
128.4
127.9
127.0
70.2
64.0
61.6
57.3
32.5
32.1
Parámetro Valor
1 Solvent CDCl3
2 Temperature 300.0
3 Experiment 1D
4 Number of Scans 84
5 Receiver Gain 2050
6 Relaxation Delay 2.0000
7 Pulse Width 8.1000
8 Acquisition Time 1.8176
9 Spectrometer Frequency 75.50
10 Spectral Width 18028.8
11 Lowest Frequency -1465.6
12 Nucleus 13C
13 Acquired Size 32768
14 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

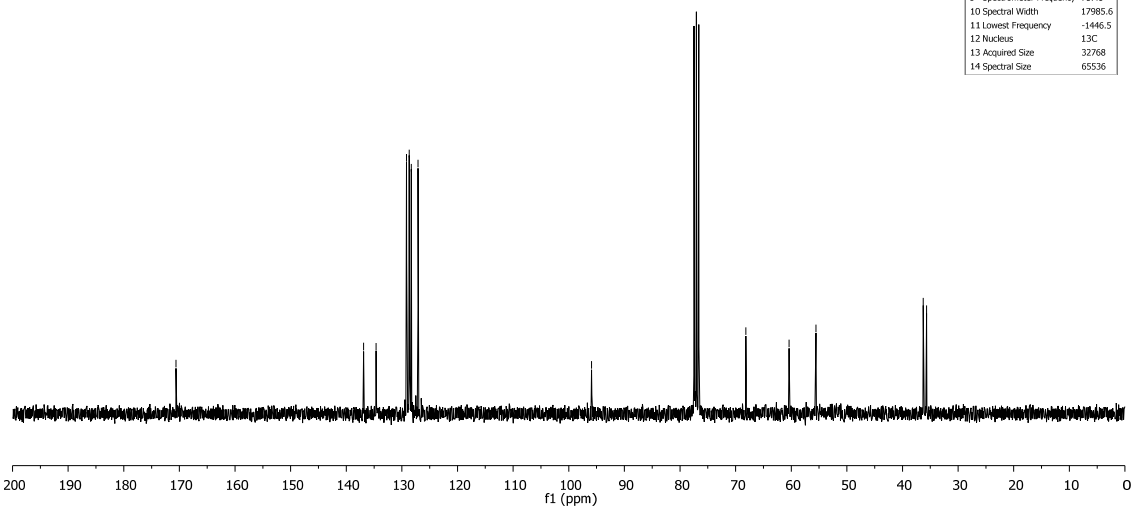


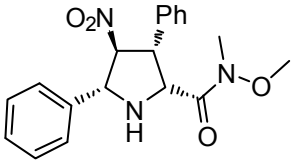
exo-**14a**

Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.3
3 Experiment	1D
4 Number of Scans	14
5 Receiver Gain	228
6 Relaxation Delay	1.0000
7 Pulse Width	10.4000
8 Acquisition Time	4.5614
9 Spectrometer Frequency	300.13
10 Spectral Width	3592.0
11 Lowest Frequency	-445.4
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768



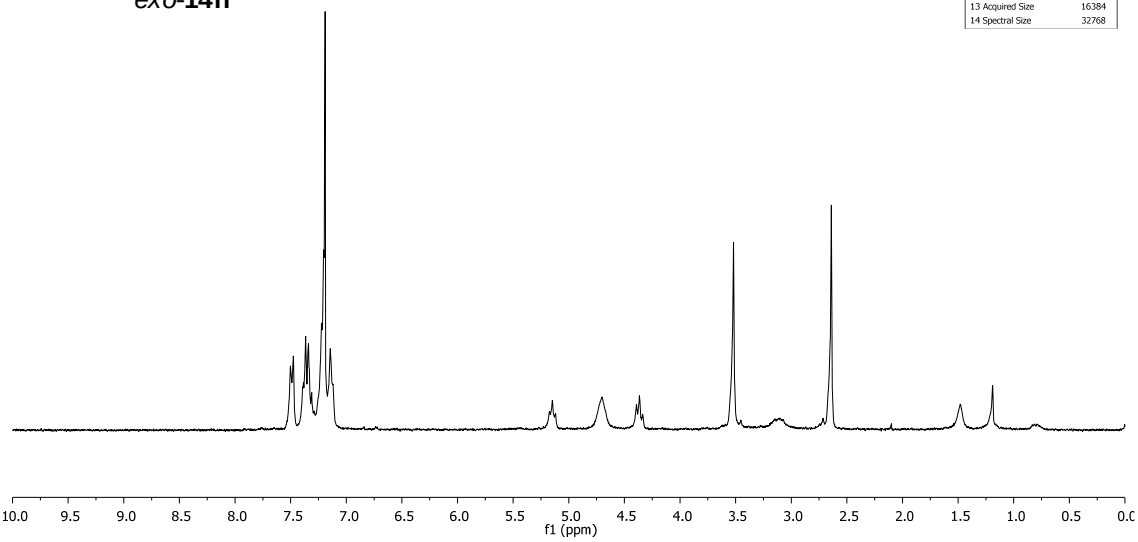
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.5
3 Experiment	1D
4 Number of Scans	212
5 Receiver Gain	256
6 Relaxation Delay	2.0000
7 Pulse Width	5.2000
8 Acquisition Time	1.8220
9 Spectrometer Frequency	75.48
10 Spectral Width	17985.6
11 Lowest Frequency	-1446.5
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

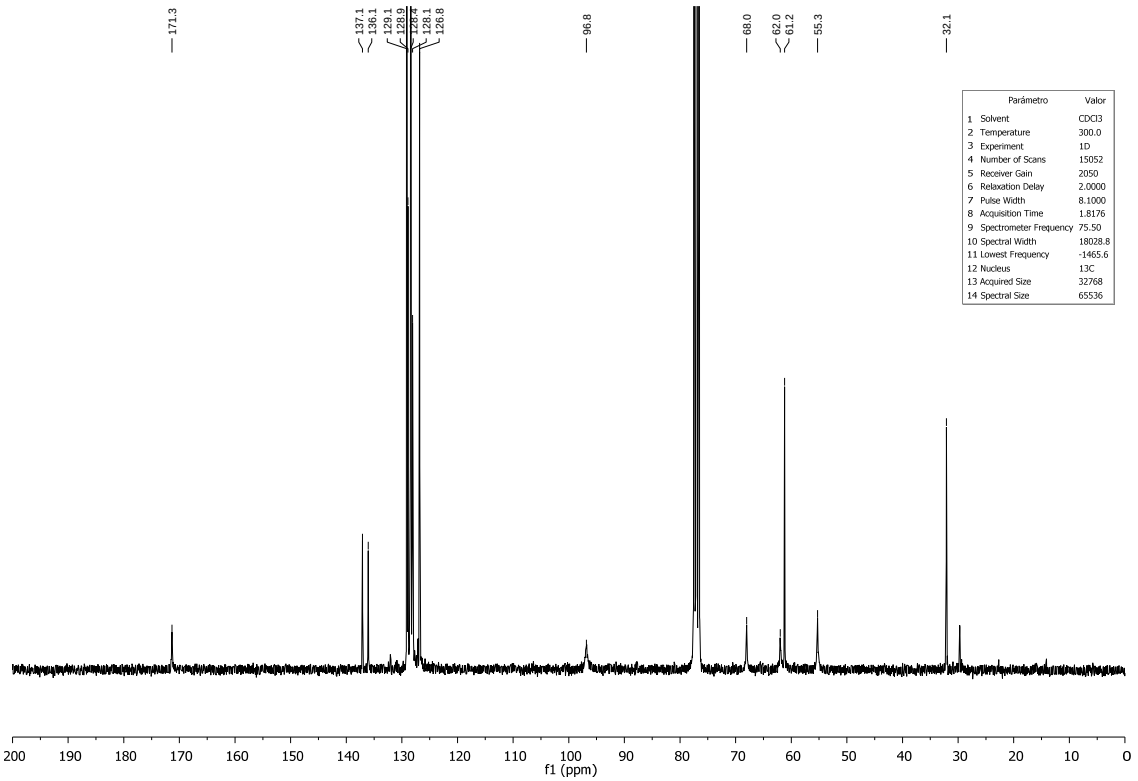




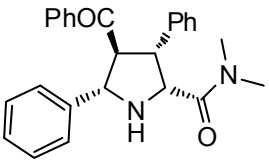
exo-**14n**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	16
5	Receiver Gain	228
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-482.2
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



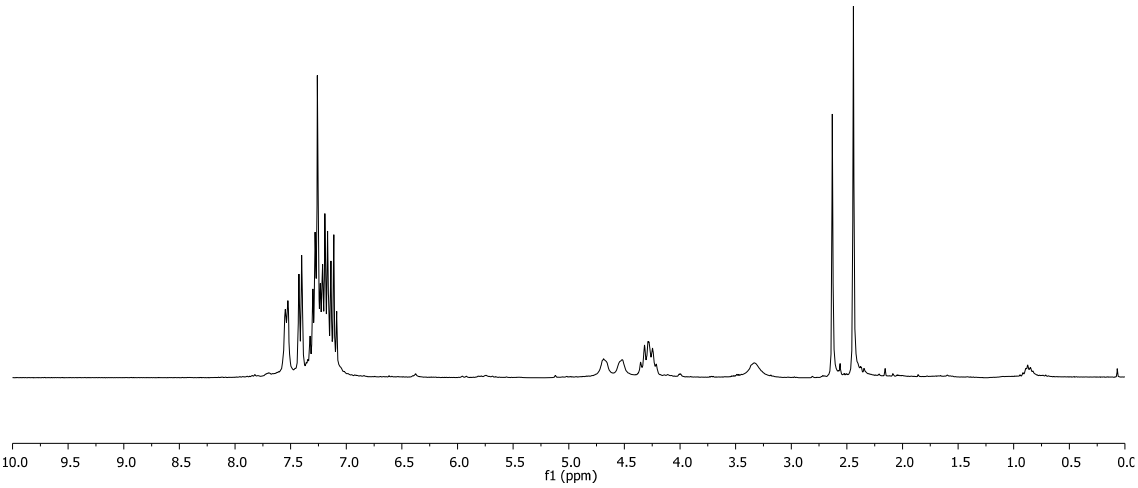


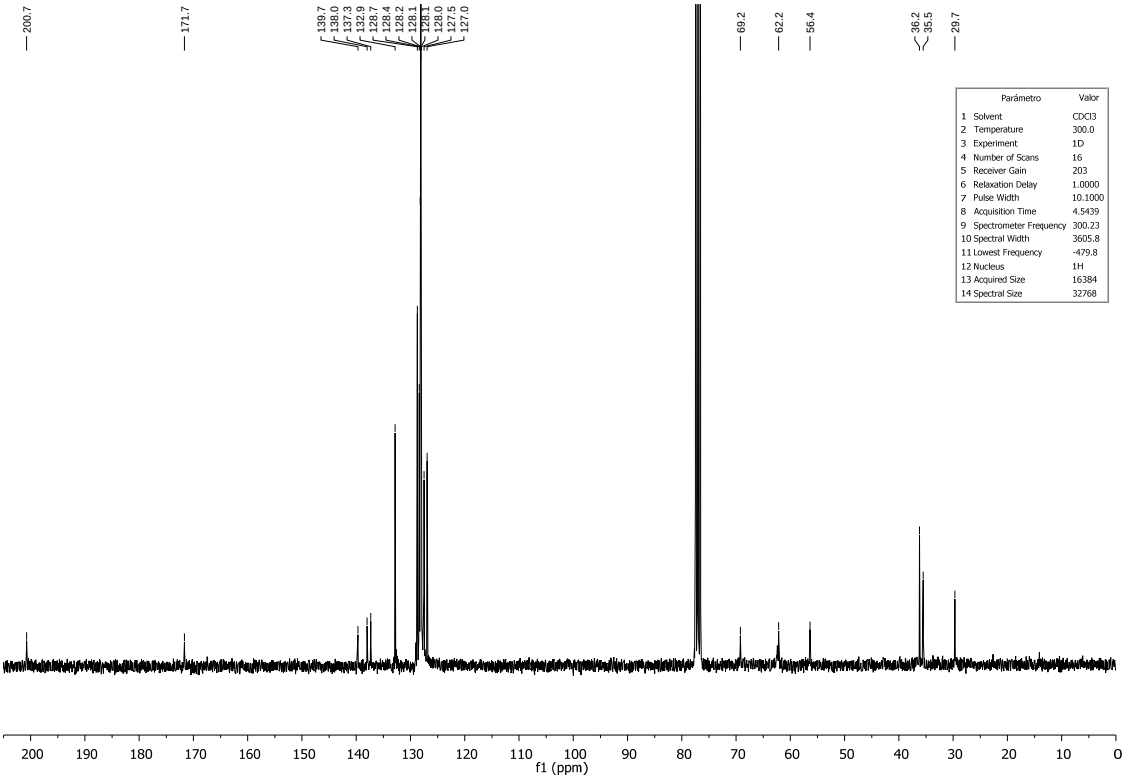
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	15052
5	Receiver Gain	2050
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



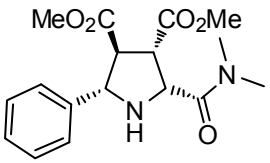
exo-**15**

Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	16
5 Receiver Gain	203
6 Relaxation Delay	1.0000
7 Pulse Width	10.1000
8 Acquisition Time	4.5439
9 Spectrometer Frequency	300.23
10 Spectral Width	3605.8
11 Lowest Frequency	-479.8
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768



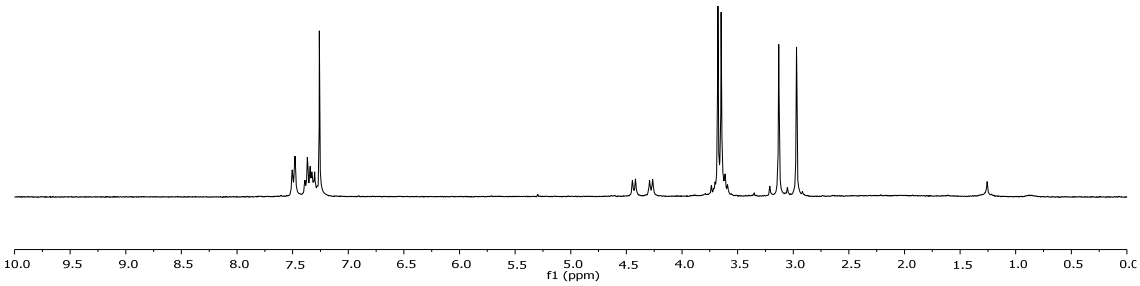


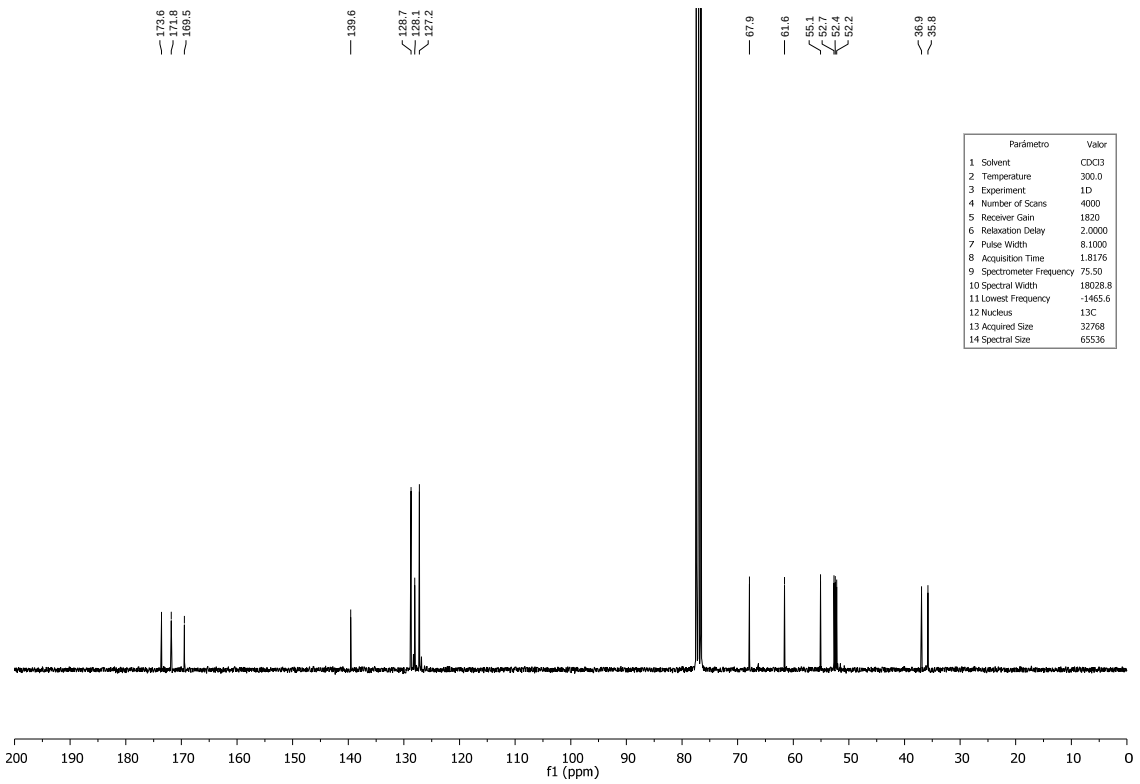
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	16
5 Receiver Gain	203
6 Relaxation Delay	1.0000
7 Pulse Width	10.1000
8 Acquisition Time	4.5439
9 Spectrometer Frequency	300.23
10 Spectral Width	3605.8
11 Lowest Frequency	-479.8
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768



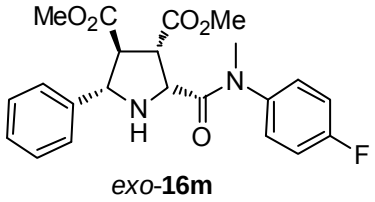
exo-**16a**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	16
5	Receiver Gain	362
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-450.7
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768



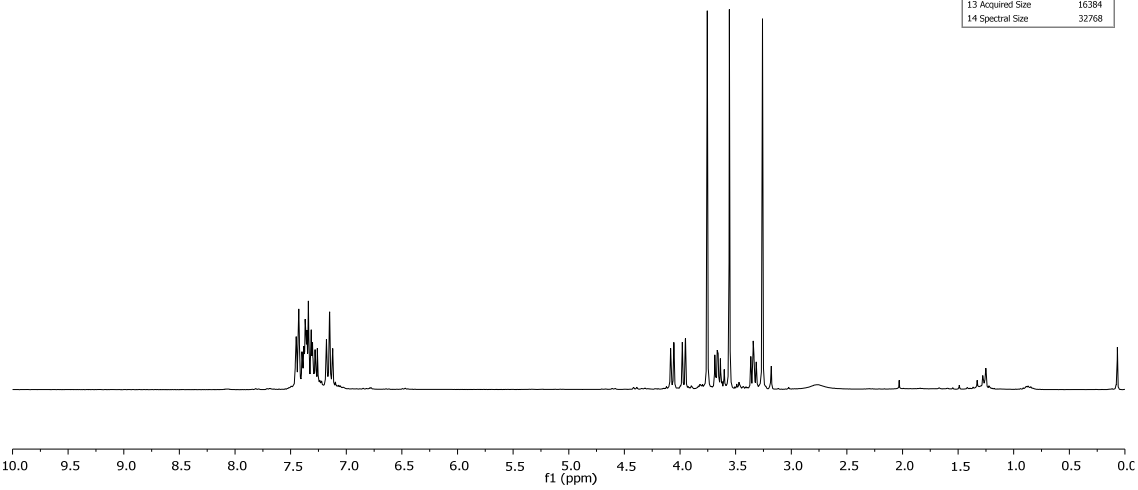


	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	4000
5	Receiver Gain	1820
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536



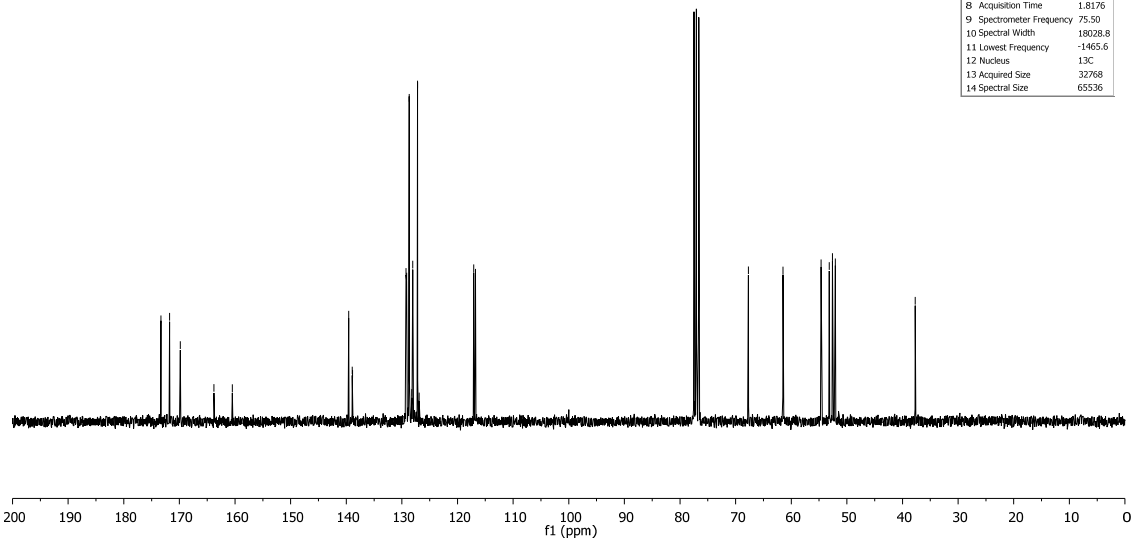
exo-**16m**

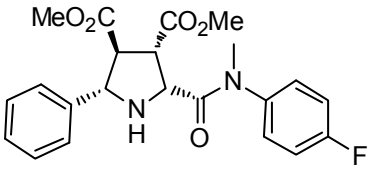
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	16
5 Receiver Gain	181
6 Relaxation Delay	1.0000
7 Pulse Width	10.8000
8 Acquisition Time	4.5439
9 Spectrometer Frequency	300.23
10 Spectral Width	3605.8
11 Lowest Frequency	-459.7
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768



173.3
171.8
169.9
163.8
160.5
139.6
138.9
138.9
129.3
129.2
128.7
128.2
128.1
127.2
126.9
117.1
116.8
67.7
61.5
54.6
53.2
52.6
52.1
37.7

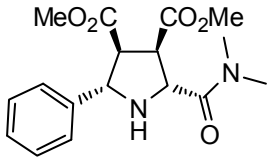
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	300.0
3 Experiment	1D
4 Number of Scans	195
5 Receiver Gain	2300
6 Relaxation Delay	2.0000
7 Pulse Width	8.1000
8 Acquisition Time	1.8176
9 Spectrometer Frequency	75.50
10 Spectral Width	18028.8
11 Lowest Frequency	-1465.6
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536





exo-**16m**

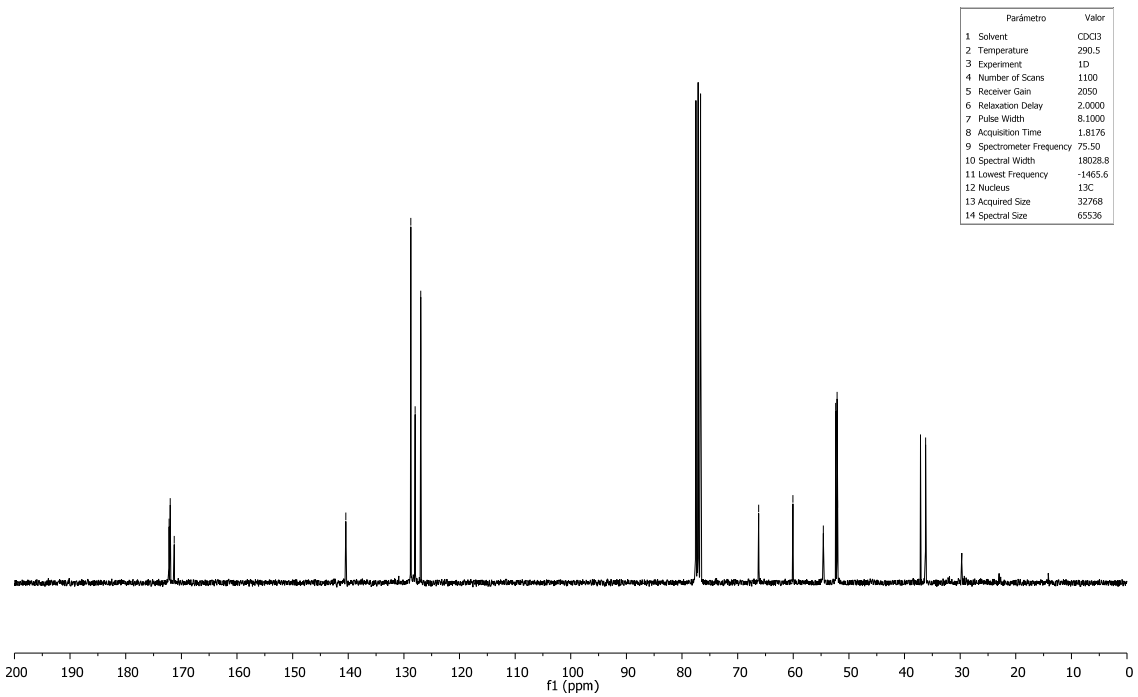
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	32
5	Receiver Gain	8200
6	Relaxation Delay	2.0000
7	Pulse Width	11.5000
8	Acquisition Time	0.9787
9	Spectrometer Frequency	282.47
10	Spectral Width	66964.3
11	Lowest Frequency	-61731.8
12	Nucleus	19F
13	Acquired Size	65536
14	Spectral Size	131072

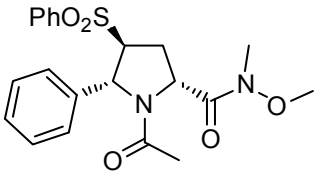


exo-**17a**

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	290.4
3	Experiment	1D
4	Number of Scans	12
5	Receiver Gain	144
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-476.1
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

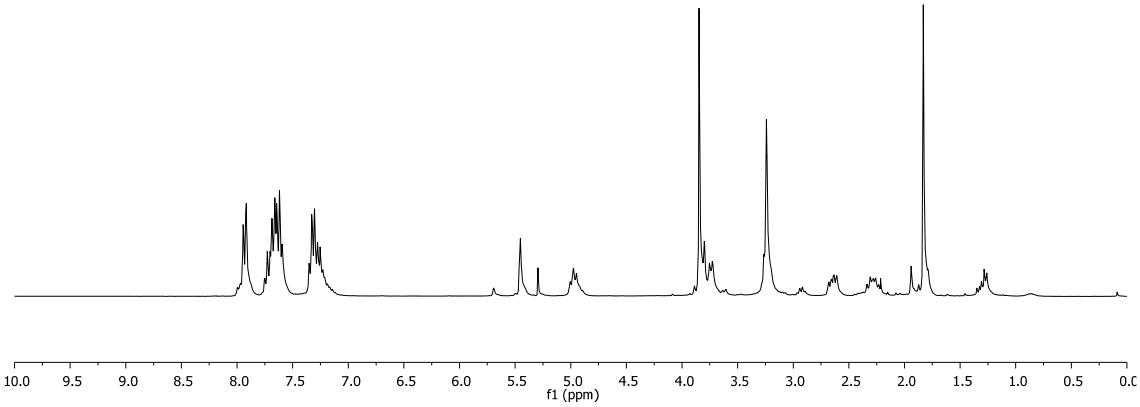
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	290.5
3	Experiment	1D
4	Number of Scans	1100
5	Receiver Gain	2050
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

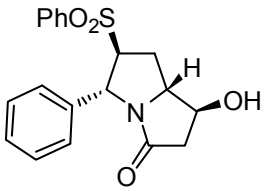




crude 18

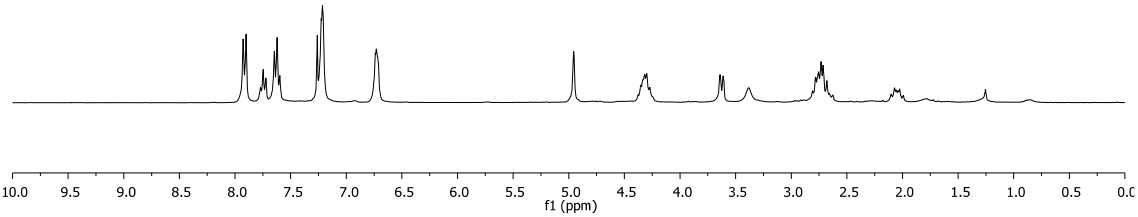
	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	6
5	Receiver Gain	203
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-479.6
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768

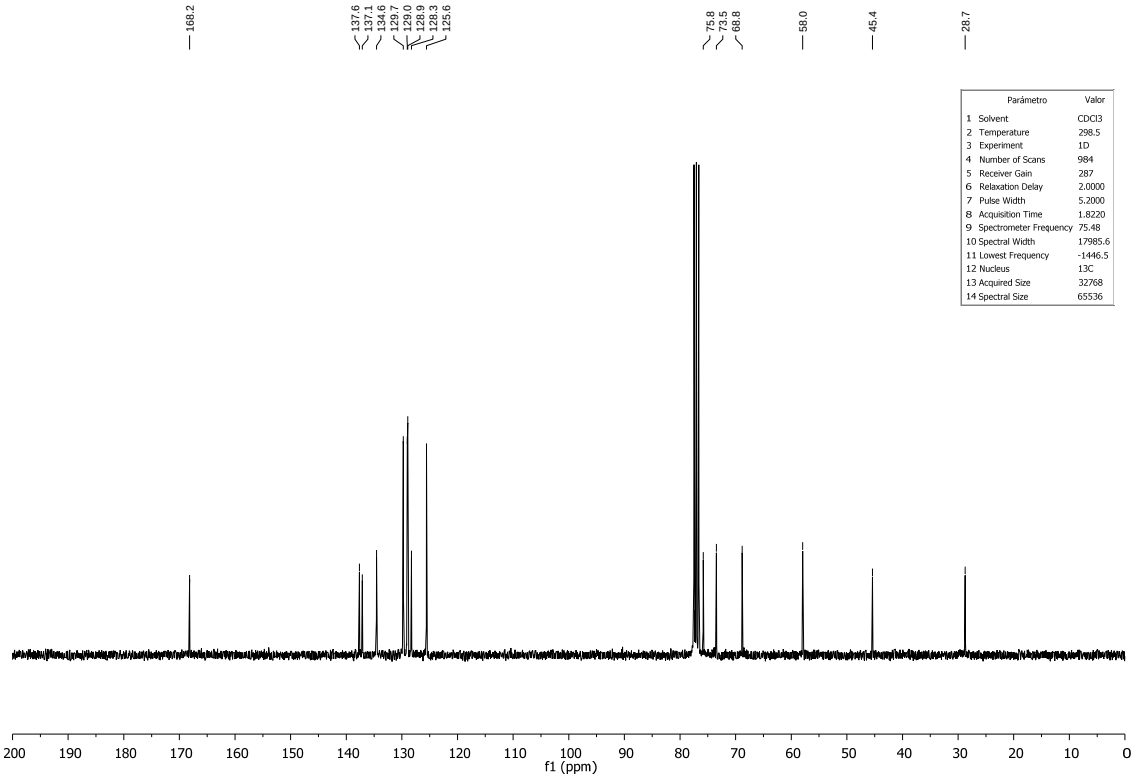




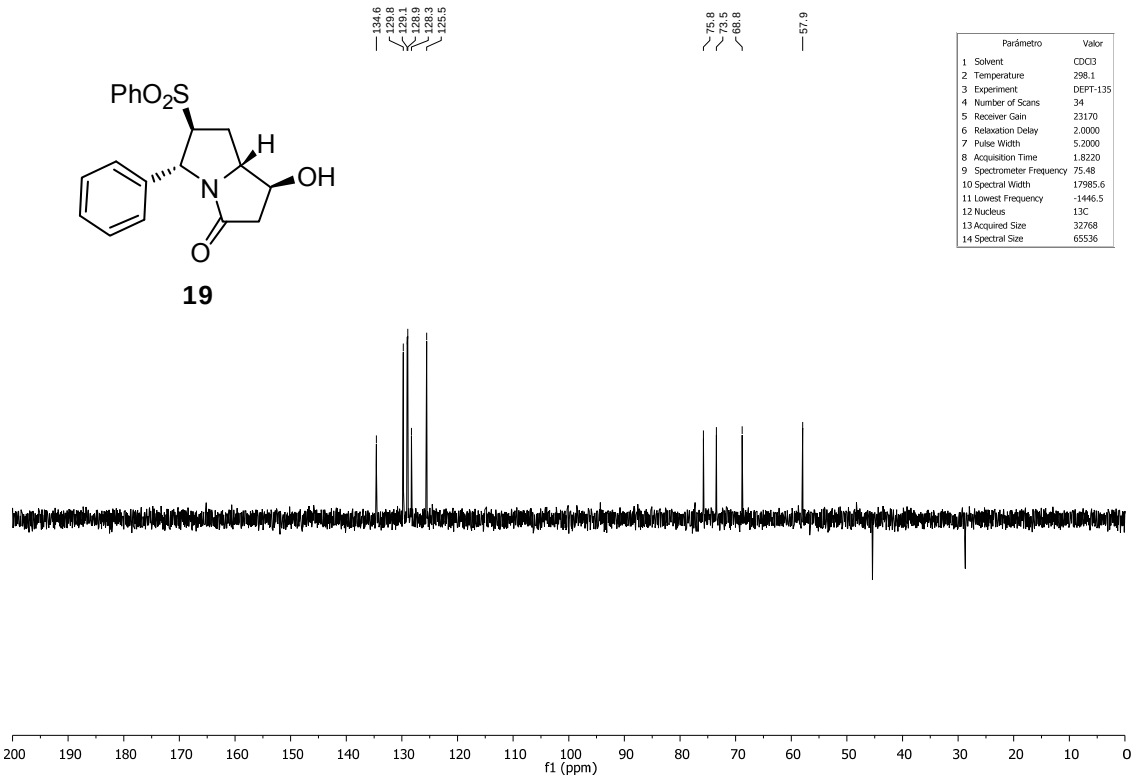
19

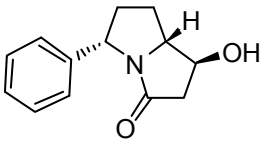
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	298.0
3 Experiment	1D
4 Number of Scans	8
5 Receiver Gain	181
6 Relaxation Delay	1.0000
7 Pulse Width	10.4000
8 Acquisition Time	4.5614
9 Spectrometer Frequency	300.13
10 Spectral Width	3592.0
11 Lowest Frequency	-445.4
12 Nucleus	1H
13 Acquired Size	16384
14 Spectral Size	32768





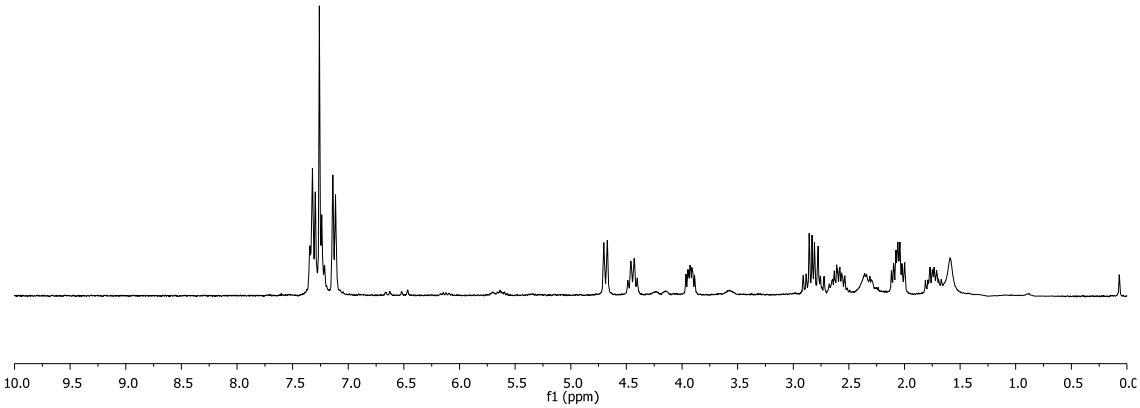
Parámetro	Valor
1 Solvent	CDCl3
2 Temperature	298.5
3 Experiment	1D
4 Number of Scans	984
5 Receiver Gain	287
6 Relaxation Delay	2.0000
7 Pulse Width	5.2000
8 Acquisition Time	1.8220
9 Spectrometer Frequency	75.48
10 Spectral Width	17985.6
11 Lowest Frequency	-1446.5
12 Nucleus	13C
13 Acquired Size	32768
14 Spectral Size	65536

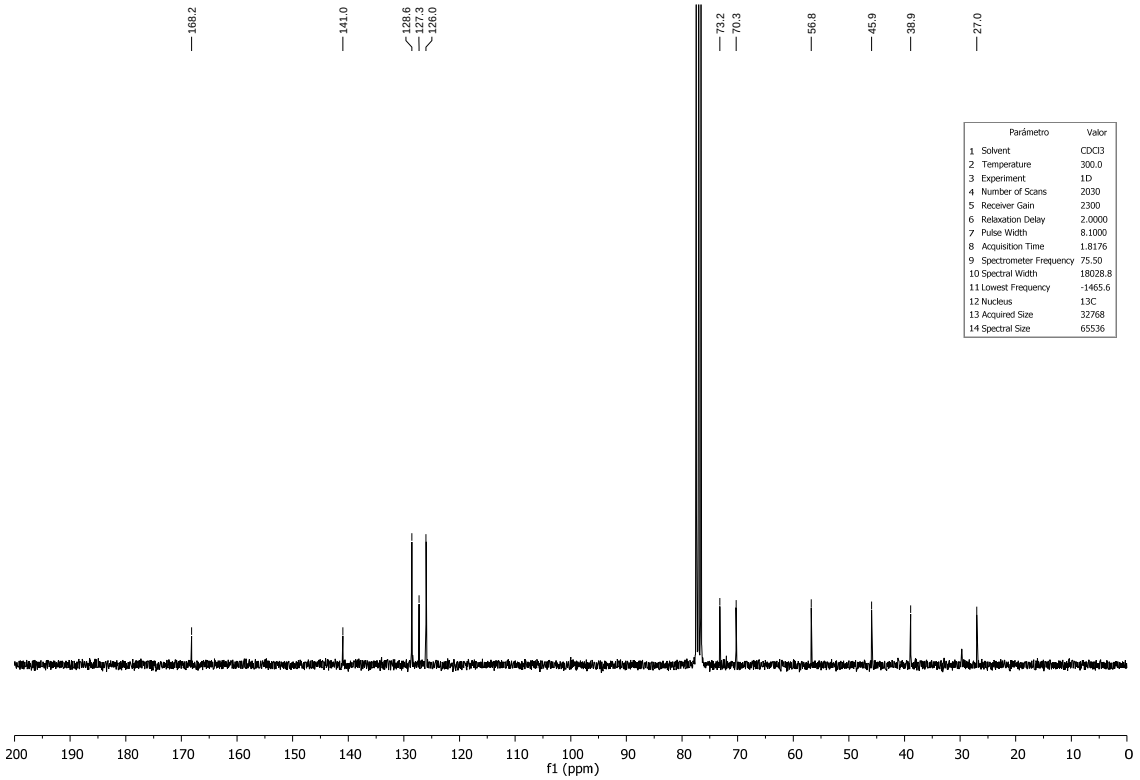

134.6
129.8
129.1
128.9
128.3
125.5
75.8
73.5
68.8
57.9
PhO2S
H
OH
N
O
19
Parámetro Valor
1 Solvent CDCl3
2 Temperature 298.1
3 Experiment DEPT-135
4 Number of Scans 34
5 Receiver Gain 23170
6 Relaxation Delay 2.0000
7 Pulse Width 5.2000
8 Acquisition Time 1.8220
9 Spectrometer Frequency 75.48
10 Spectral Width 17985.6
11 Lowest Frequency -1446.5
12 Nucleus 13C
13 Acquired Size 32768
14 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



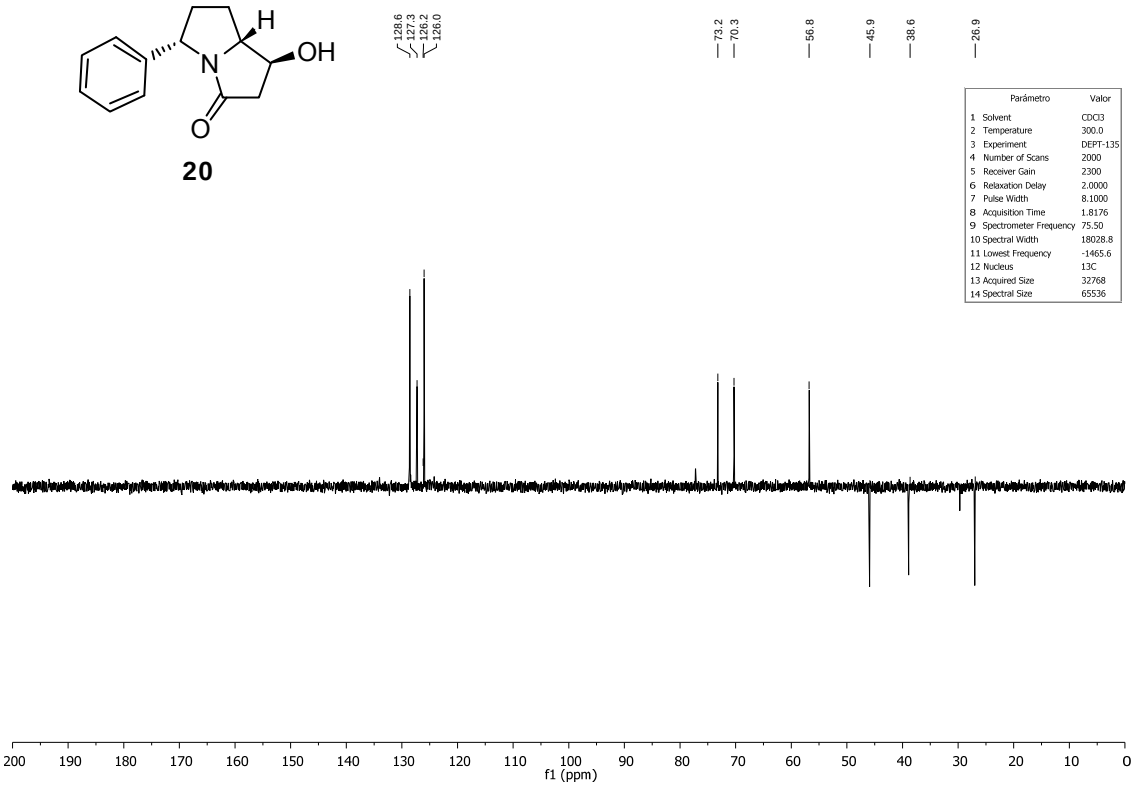
20

	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	10
5	Receiver Gain	512
6	Relaxation Delay	1.0000
7	Pulse Width	10.8000
8	Acquisition Time	4.5439
9	Spectrometer Frequency	300.23
10	Spectral Width	3605.8
11	Lowest Frequency	-461.3
12	Nucleus	1H
13	Acquired Size	16384
14	Spectral Size	32768





	Parámetro	Valor
1	Solvent	CDCl3
2	Temperature	300.0
3	Experiment	1D
4	Number of Scans	2030
5	Receiver Gain	2300
6	Relaxation Delay	2.0000
7	Pulse Width	8.1000
8	Acquisition Time	1.8176
9	Spectrometer Frequency	75.50
10	Spectral Width	18028.8
11	Lowest Frequency	-1465.6
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536


H
N
OH
O
20
128.6
127.3
126.2
126.0
73.2
70.3
56.8
45.9
38.6
26.9
Parámetro Valor
1 Solvent CDCl3
2 Temperature 300.0
3 Experiment DEPT-135
4 Number of Scans 2000
5 Receiver Gain 2300
6 Relaxation Delay 2.0000
7 Pulse Width 8.1000
8 Acquisition Time 1.8176
9 Spectrometer Frequency 75.50
10 Spectral Width 18028.8
11 Lowest Frequency -1465.6
12 Nucleus 13C
13 Acquired Size 32768
14 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)