Supporting Information

Expedient iron-catalyzed stereospecific synthesis of triazines *via* cycloaddition of aziridines with diaziridines

Table of Contents

General Information. Alkenes, amines, (*S*)-(+)-2-phenylglycinol (99%), $FeCl_3$•$6H_2O$ (>98%), $FeCl_2$•$4H_2O$ (98%), $Fe(acac)_3$ (97%), $Pd(dppf)Cl_2$•CH_2Cl_2 (>99%), $Pd(PPh_3)_4$ (99%) and 2,6-bis[(4*S*)-(-)-isopropyl-2-oxazolin-2-yl]pyridine (99%) were purchased from Aldrich and used as received. $Fe(NO_3)_3$•$9H_2O$ (98%) was purchased from Mereck and $FeCl_3$ (96%) was purchased from Rankem. Diaziridines[1] and aziridines[2,3] were prepared according to reported procedure. (*R*,*R*)-(-)-N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine[4] and (1*R*,2*S*)-1-[(3,5-di-tert-butyl-2-hydroxybenzylidene)amino]-2-indanol[5] were prepared according to reported procedure. SRL silica gel G/GF 254 plates were used for analytical TLC and SRL silica gel (100-200 mesh) was used for column chromatography. NMR (^1H, ^{13}C and ^{19}F) spectra were recorded with Bruker Ascend 400 MHz spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in ppm and in Hz, respectively, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. FT-IR spectra were collected on Perkin Elmer IR spectrometer. Q-Tof ESI-MS instrument (model HAB 273) was used for recording mass spectra. Optical rotation was determined by using Rudolph autopol I automatic polarimeter. HPLC analysis was carried out using Waters-2489 with Daicel Chiralcel AD column using *iso*-propanol and hexane as eluent. Single crystal X-ray data of **3ai** was determined using Bruker SMART APEX-II CCD diffractometer, which is equipped with 1.75 kW sealed-tube Mo-Kα irradiation and the crystal structure was solved by direct method using SHELXL-14 (Göttingen, Germany) and refined with full-matrix least squares on F^2 using SHELXL-14, while single crystal X-ray data of **3ik** was collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/Kα radiation and the structure was solved by direct method using *SHELXL-16* (Göttingen, Germany).

Crystal Structure and Data of 3ai

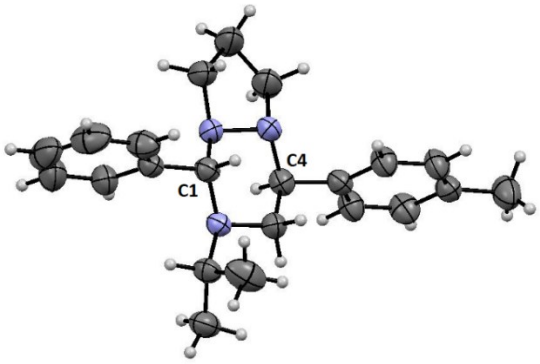


Figure S1. ORTEP diagram of 2-isopropyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine **3ai** (CCDC 1972128).

Identification code	**3ai**
Empirical formula	'C22 H29 N3'
Formula weight	335.48
Crystal habit, colour	block/Colorless
Temperature, *T*/K	293 K
Wavelength, λ/Å	0.71073
Crystal system	'monoclinic'
Space group	'P 21/n'
Unit cell dimensions	a = 16.2354(8) Å b = 5.8866(4) Å c = 20.5287(11) Å α = 90 β = 93.513(4) γ = 90
Volume, *V*/Å^3	1958.3(2)
Z	4
Calculated density, Mg·m^{-3}	1.138
Absorption coefficient, μ/mm^{-1}	0.067
F(000)	428
θ range for data collection	2.51 to 25°
Limiting indices	-19 ≤ h ≤ 19, –3 ≤ k ≤ 7, –24 ≤ l ≤ 21
Reflection collected / unique	3450/2277
Completeness to θ	99.9%
Absorption correction	Multi-scan

Max. and min. transmission	1.000 and 0.839
Refinement method	'SHELXL-2014/7 (Sheldrick, 2014)'
Data / restraints / parameters	3450/0/ 229
Goodness–of–fit on F^2	1.024
Final *R* indices [*I*>2sigma(*I*)]	R1 = 0.0532, wR2 = 0.1448
R indices (all data)	R1 = 0.0846, wR2 = 0.1764

Crystal Structure and Data of 3ik

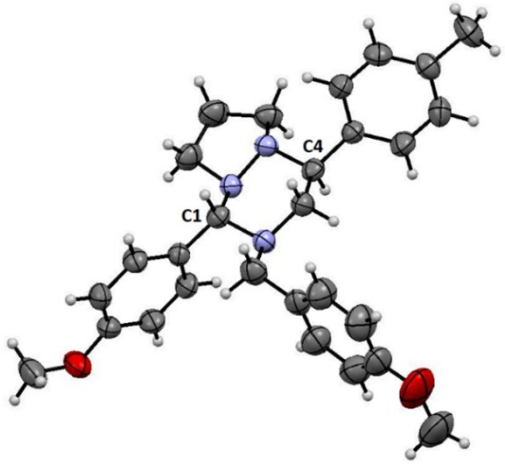
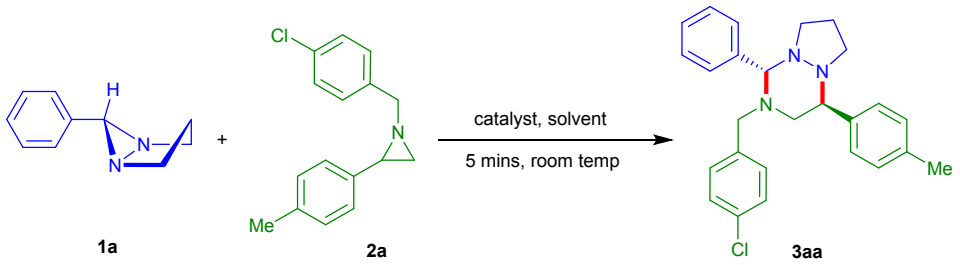


Figure S2. ORTEP diagram of 2-(4-methoxybenzyl)-1-(4-methoxyphenyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine **3ik** (CCDC 1972182).

Identification code	**3ik**
Empirical formula	'C28 H33 N3 O2'
Formula weight	443.57
Crystal habit, colour	block/Colorless
Temperature, *T*/K	298 K
Wavelength, λ/Å	0.71073
Crystal system	'triclinic'
Space group	'P -1'
Unit cell dimensions	a = 6.1688(8) Å b = 10.0037(13) Å c = 20.560(3) Å α = 103.548(5) β = 91.180(5) γ = 95.599(5)

Volume, V/Å^3	1226.4(3)
Z	2
Calculated density, Mg·m^{-3}	1.201
Absorption coefficient, μ/mm^{-1}	0.076
F(000)	476
θ range for data collection	2.23 to 25°
Limiting indices	-7 ≤ h ≤ 7, –11 ≤ k ≤ 11, –23 ≤ l ≤ 23
Reflection collected / unique	3951/2297
Completeness to θ	100%
Absorption correction	Multi-scan
Max. and min. transmission	0.989 and 0.977
Refinement method	'SHELXL-2016/6 (Sheldrick, 2016)'
Data / restraints / parameters	3951/0/ 301
Goodness–of–fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0668, wR2 = 0.1608
R indices (all data)	R1 = 0.1299, wR2 = 0.2092

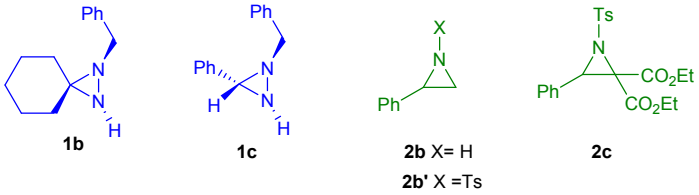
Table S1. Optimization of the reaction conditions[a]



Entry	Catalyst (10 mol %)	Solvent	Yield (**3aa**, %)[b]
1	**$FeCl_3$**	**CH_2Cl_2**	**95**
2	$FeCl_3$•$6H_2O$	CH_2Cl_2	79
3	$Fe(NO_3)_3$•$9H_2O$	CH_2Cl_2	32
4	$FeCl_2$•$4H_2O$	CH_2Cl_2	n.r.
5	$Fe(acac)_3$	CH_2Cl_2	n.r.
6	$FeCl_3$	$(CH_2Cl)_2$	86
7	$FeCl_3$	MeOH	54
8	$FeCl_3$	DMSO	n.r.
9	$FeCl_3$	THF	72

10	$FeCl_3$	Toluene	81
11	$FeCl_3$	H_2O	n.r.
12	-	CH_2Cl_2	n.r.

unsuccessful substrates



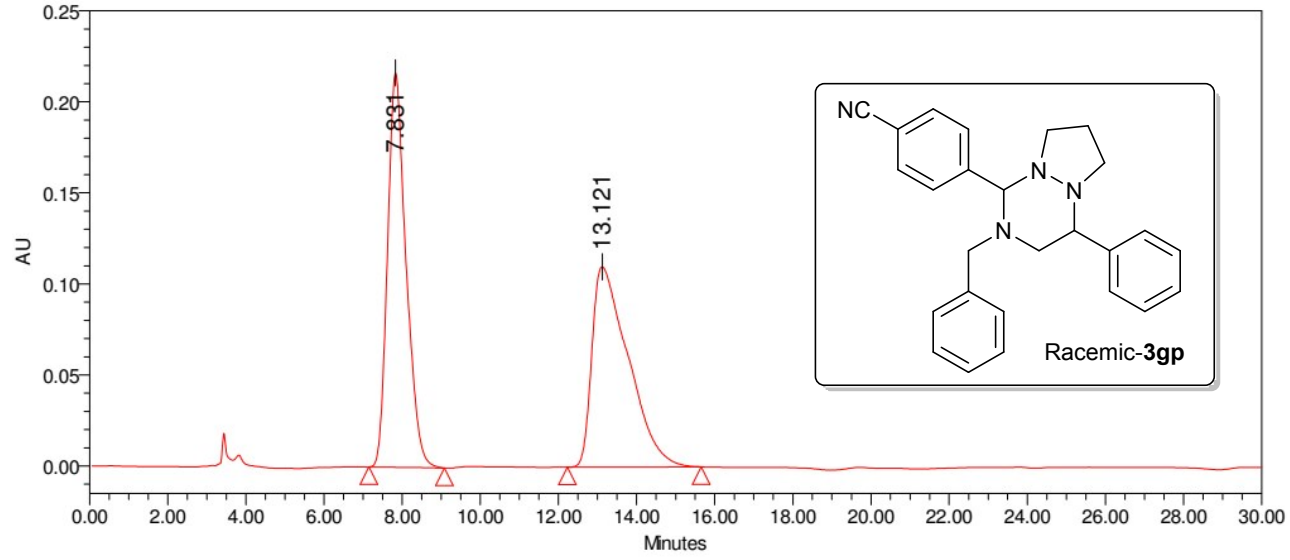
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (10 mol %), solvent (2 mL), 5 minutes, room temperature. [b]Isolated yield. n.r. = no reaction.

General Procedure for the Synthesis of [1,2,4]-Triazines. Diaziridine **1** (0.2 mmol), *N*-substituted aziridine **2** (0.2 mmol) and $FeCl_3$ (3 mg, 0.02 mmol) were stirred in dichloromethane (2.0 mL) at room temperature (25 °C) for 5 minutes. The reaction mixture was then diluted using dichloromethane (5 mL) and passed through a short pad of celite using dichloromethane (10 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to afford [1,2,4]-triazine motifs.

General Procedure for the Synthesis of [1,2,4]-Triazines from cyclodimer 1i′. A mixture of cyclo-dimer **1i′** (0.1 mmol), *N*-alkyl aziridine **2** (0.2 mmol) and $FeCl_3$ (3 mg, 0.02 mmol) was stirred in dichloromethane (2.0 mL) at room temperature (25 °C) for 5 minutes. The purification was carried as above described in general procedure.

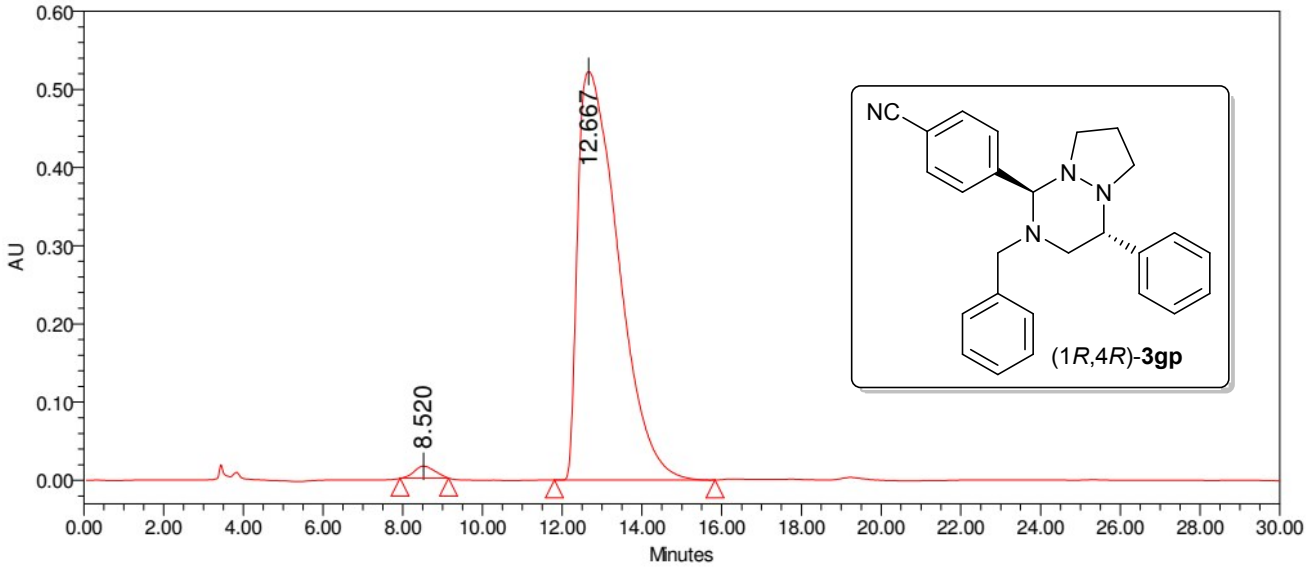
General Procedure for the Enantiospecific Synthesis of [1,2,4]-Triazines. A mixture of diaziridine **1** (0.2 mmol), (*S*)-1-benzyl-2-phenylaziridine **2p** (0.2 mmol) and $FeCl_3$ (3 mg, 0.02 mmol) was stirred in dichloromethane (2.0 mL) at room temperature (25 °C) for 5 minutes. The purification was performed as above presented in general procedure. The enantiomeric excess was determined using chiral HPLC.

HPLC chromatograms



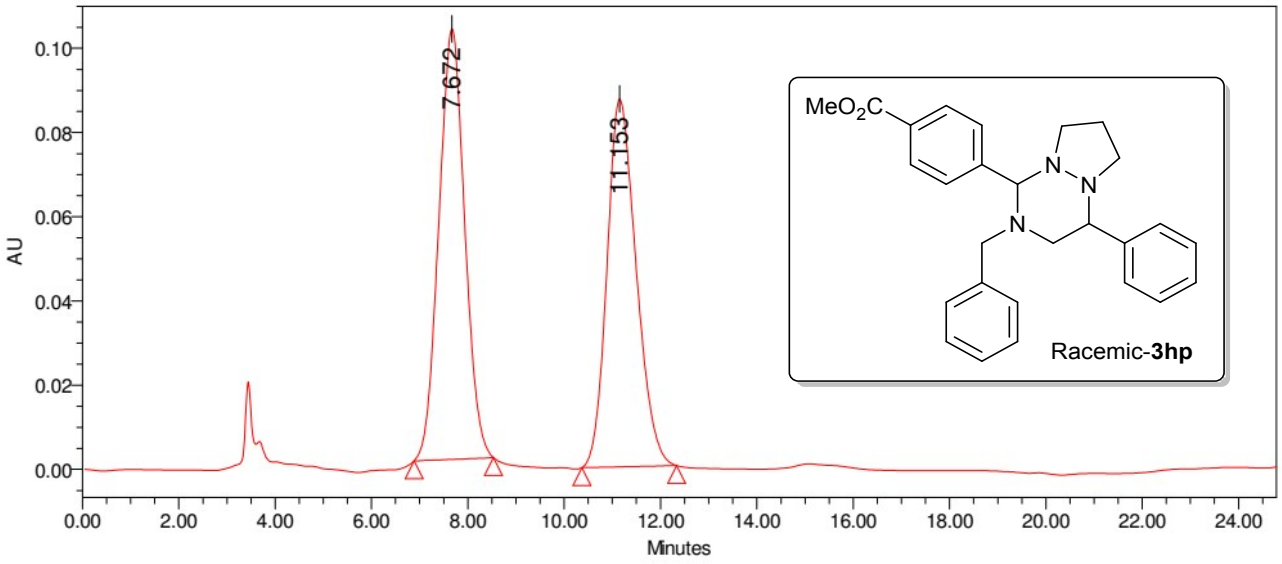
Peak Results

	RT	% Area
1	7.831	50.09
2	13.121	49.91



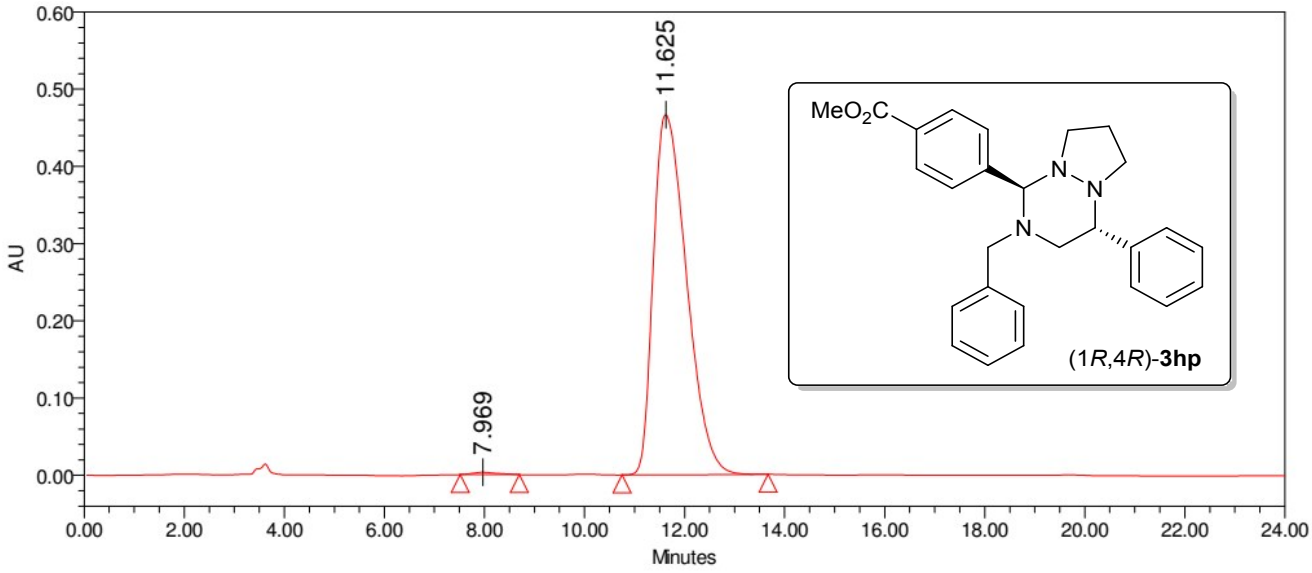
Peak Results

	RT	% Area
1	8.520	1.49
2	12.667	98.51



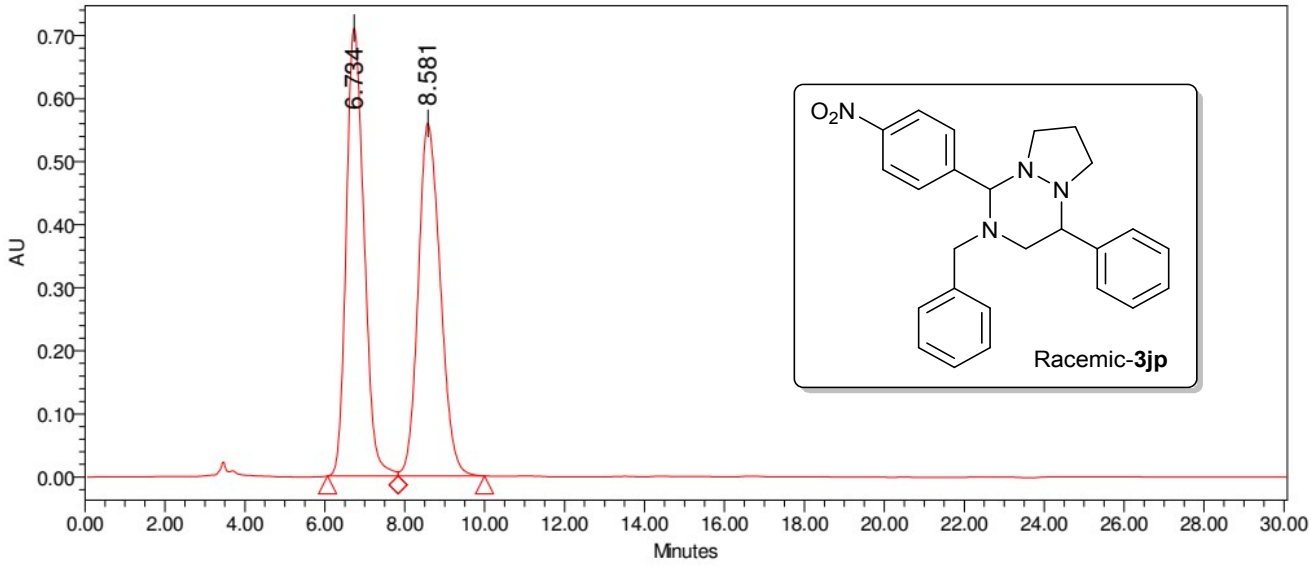
Peak Results

	RT	% Area
1	7.672	50.89
2	11.153	49.11



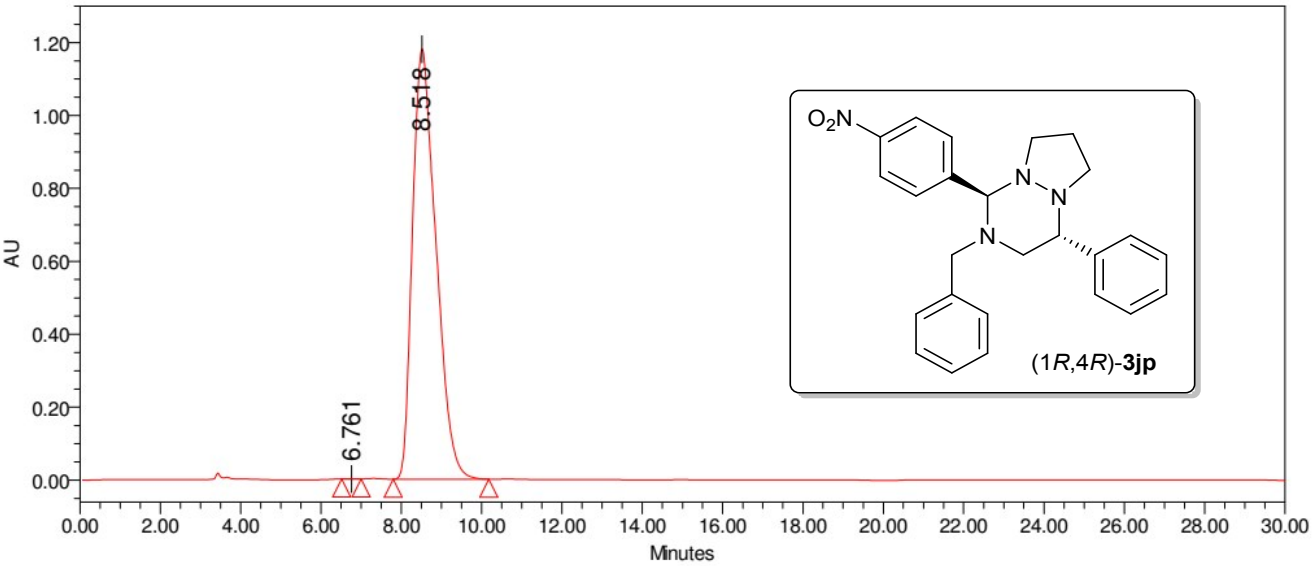
Peak Results

	RT	% Area
1	7.969	0.48
2	11.625	99.52



Peak Results

	RT	% Area
1	6.734	50.57
2	8.581	49.43

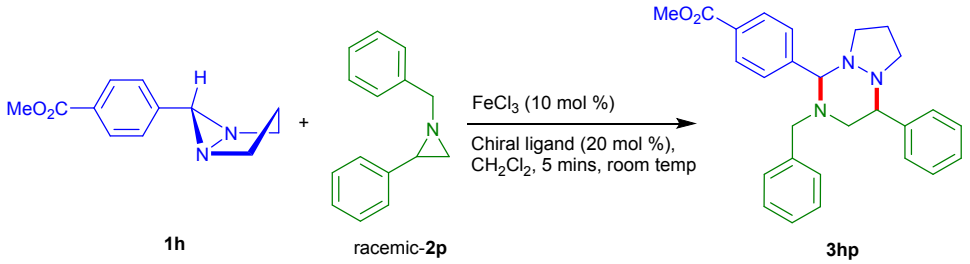


Peak Results

	RT	% Area
1	6.761	0.01
2	8.518	99.99

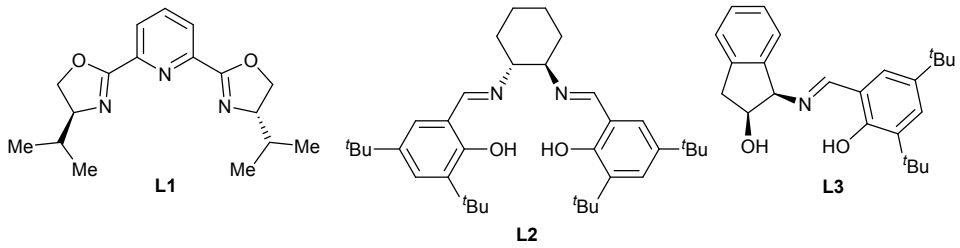
General Procedure for the Asymmetric Synthesis of [1,2,4]-Triazines. Chiral ligand **L1-3** (0.04 mmol) and $FeCl_3$ (3 mg, 0.02 mmol) were stirred in dichloromethane (2.0 mL) at room temperature (25 °C) for 1 h. Methyl-4-(1,5-diazabicyclo[3.1.0]hexan-6-yl)benzoate **1h** (44 mg, 0.2 mmol) and racemic 1-benzyl-2-phenylaziridine **2p** (42 mg, 0.2 mmol) were added and the resultant mixture was stirred at room temperature (25 °C) for 5 min. The workup and purification were performed as presented in the general procedure. The enantiomeric excess was determined using chiral HPLC analysis with Daicel Chiralcel AD column using *iso*-propanol and hexane as an eluent.

Table S2. Asymmetric reaction conditions[a]



1h racemic-**2p** **3hp**

Entry	Ligand (20 mol %)	Yield (**3hp**, %)[b]	*ee* (%)[c]
1	**L1**	73	4.5
11	**L2**	81	3.0
12	**L3**	79	0



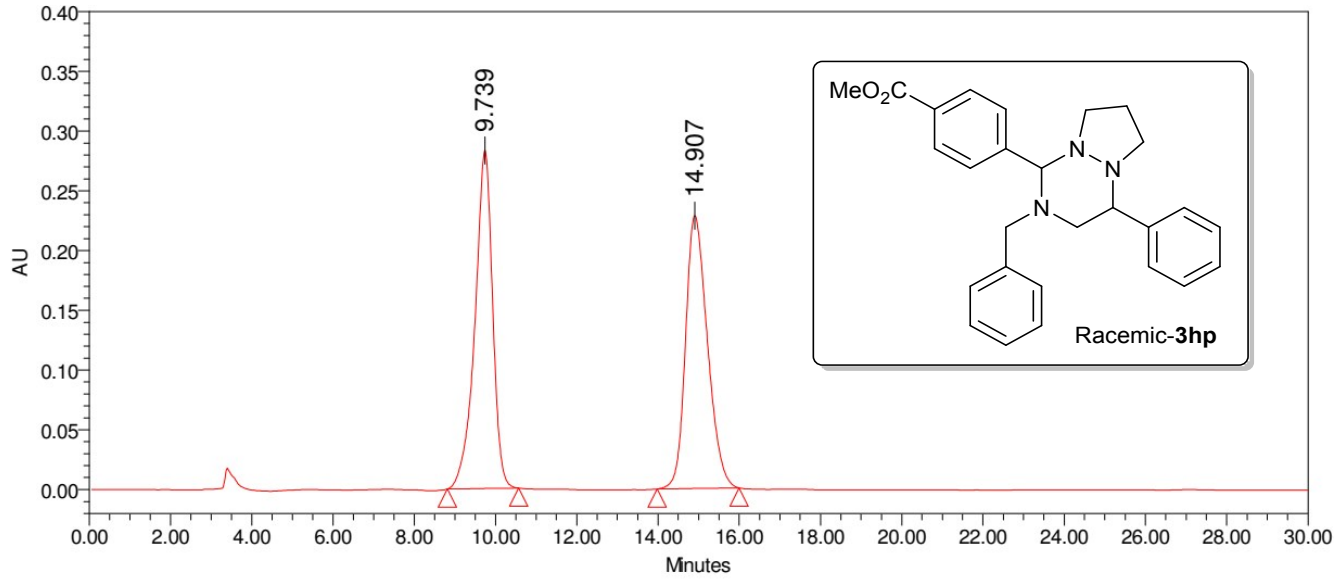
L1

L2

L3

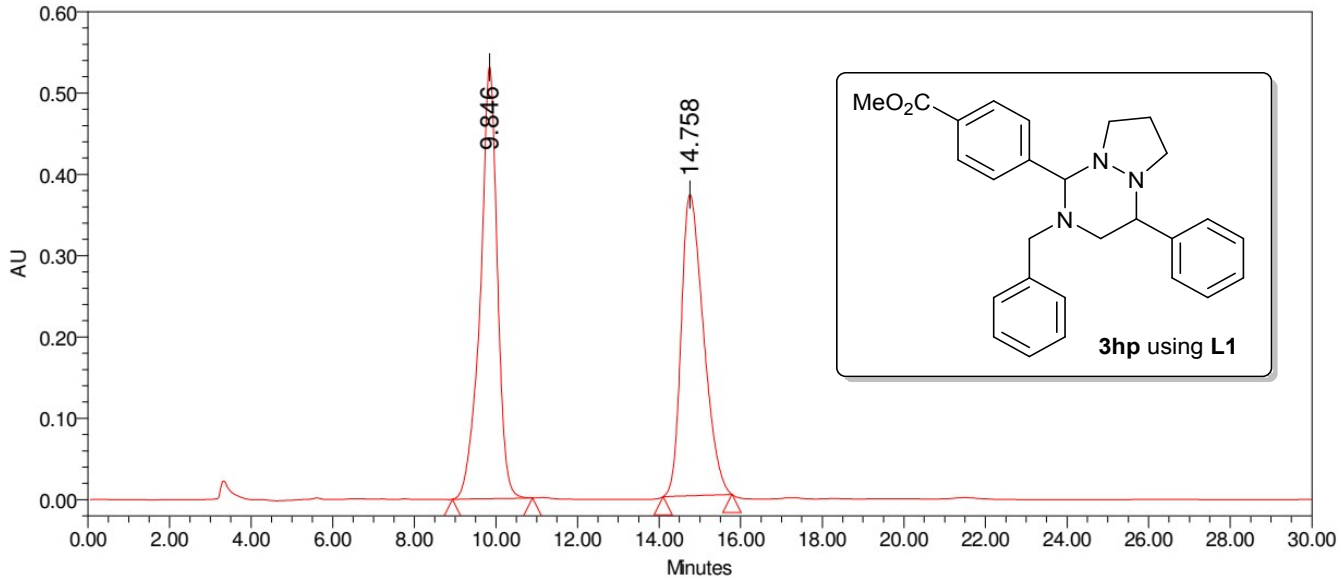
[a]Reaction conditions: **1h** (0.2 mmol), racemic **2p** (0.2 mmol), $FeCl_3$ (10 mol %), Chiral ligand **L** (20 mol %), CH_2Cl_2 (2 mL), 5 minutes, room temperature. [b]Isolated yield. [c]Chiral HPLC analysis.

HPLC chromatograms



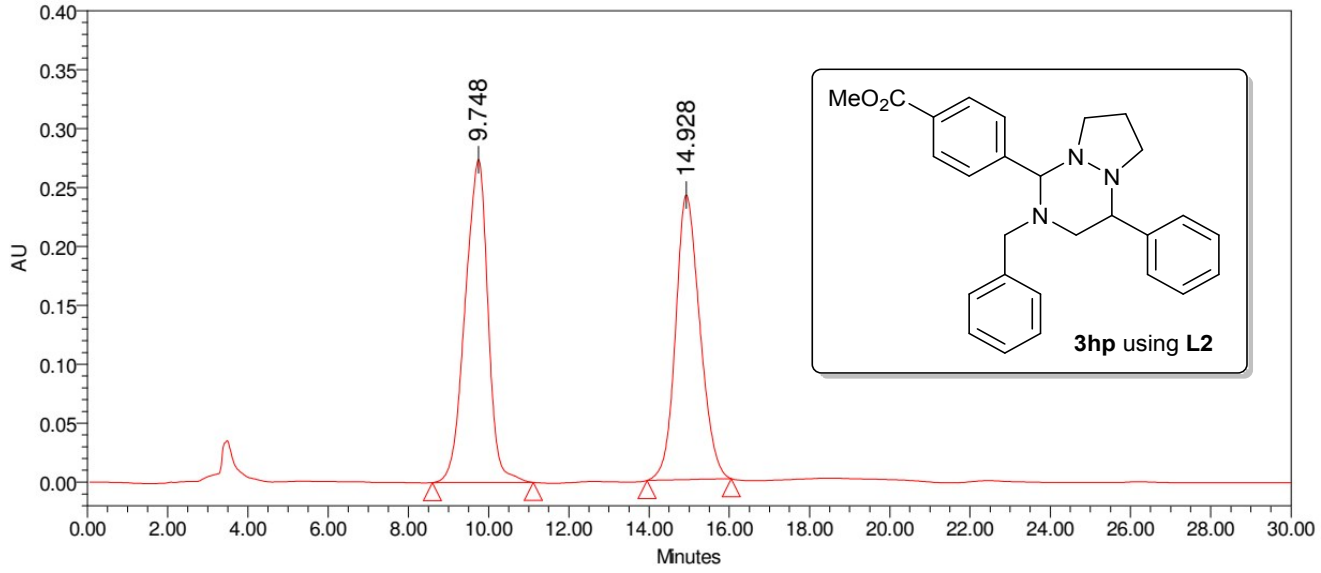
Peak Results

	RT	% Area
1	9.739	50.01
2	14.907	49.99



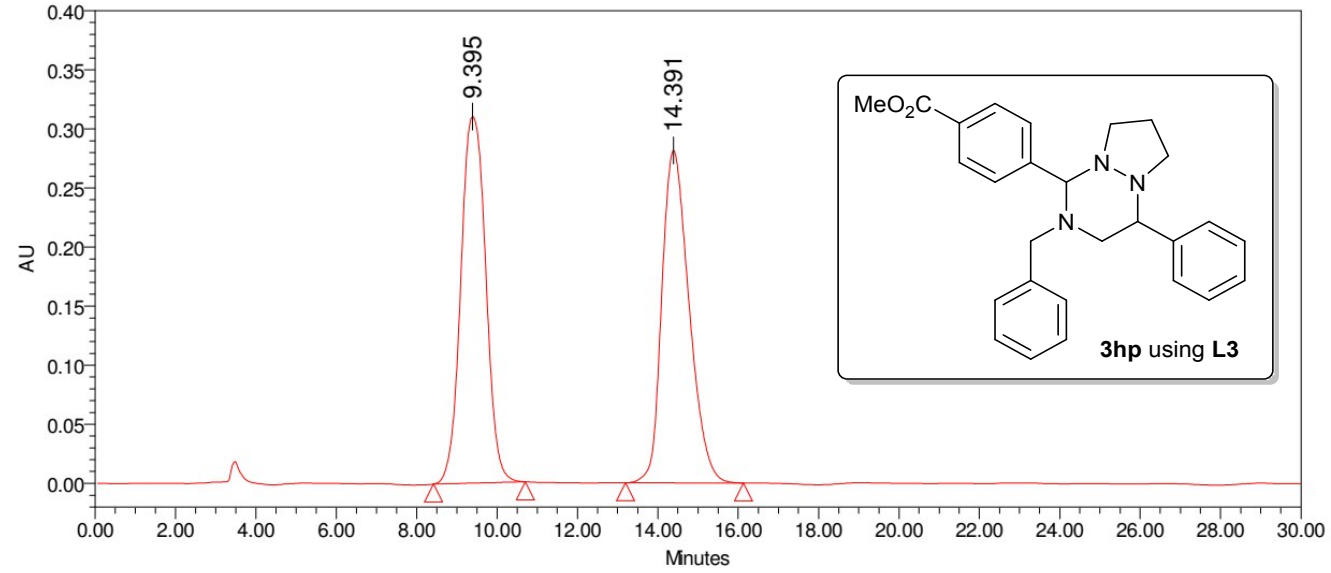
Peak Results

	RT	% Area
1	9.846	52.26
2	14.758	47.74



Peak Results

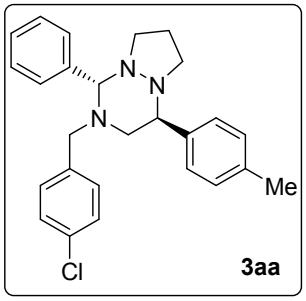
	RT	% Area
1	9.748	51.53
2	14.928	48.47



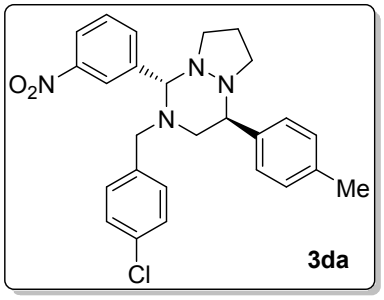
Peak Results

	RT	% Area
1	9.395	50.22
2	14.391	49.78

Characterization Data

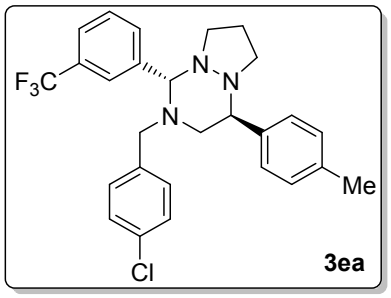


2-(4-Chlorobenzyl)-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3aa. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 138-139 °C; yield 95% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.53 (m, 2H), 7.32-7.24 (m, 3H), 7.19-7.17 (m, 2H), 7.10-7.05 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 2H), 3.72 (s, 1H), 3.55-3.51 (m, 2H), 2.83-2.77 (m, 3H), 2.44-2.38 (m, 1H), 2.37-2.32 (m, 1H), 2.30-2.23 (m, 5H), 1.71-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 137.59, 137.54, 137.1, 132.4, 130.0, 129.19, 129.15, 128.9, 128.6, 128.3, 127.9, 89.7, 68.0, 59.1, 56.6, 51.9, 50.8, 22.0, 21.2; FT-IR (KBr) 2824, 2768, 1514, 1451, 1355, 1127, 1017 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{29}ClN_3$: 418.2045, found: 418.2044.

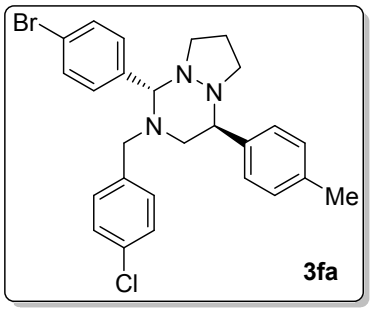


2-(4-Chlorobenzyl)-1-(3-nitrophenyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3da. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.50; thick liquid; yield 83% (76 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.15-8.12 (m, 1H), 7.93-7.91 (m, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.19-7.17 (m, 2H), 7.11-7.09 (m, 2H), 7.04-7.02 (m, 4H), 3.84 (s, 1H), 3.55-3.51 (m, 1H), 3.44 (d, *J* = 13.2 Hz, 1H), 2.89-2.79 (m, 3H), 2.41-2.20 (m, 7H), 1.73-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 142.1, 137.7, 136.8, 135.3, 132.8, 129.8, 129.6, 129.2, 128.5, 127.9, 124.3, 124.0, 88.5, 67.8, 58.9, 56.7, 51.9, 50.8, 22.0, 21.2; FT-IR (neat) 2830, 1633,

1530, 1352, 1129, 1092, 1014 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{28}ClN_4O_2$: 463.1895, found: 463.1896.

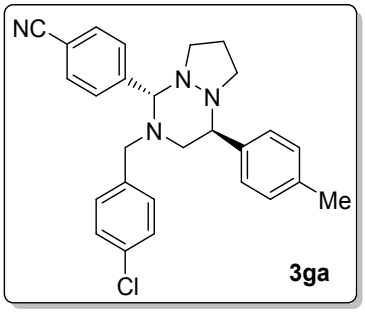


2-(4-Chlorobenzyl)-4-(*p*-tolyl)-1-(3-(trifluoromethyl)phenyl)hexahydro-6H-pyrazolo[1,2-a]-[1,2,4]triazine 3ea. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.48; thick liquid; yield 85% (82 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.19-7.17 (m, 2H), 7.11-7.08 (m, 2H), 7.04-7.02 (m, 4H), 3.78 (s, 1H), 3.54-3.51 (m, 1H), 3.45 (d, *J* = 13.2 Hz, 1H), 2.84-2.78 (m, 3H), 2.42-2.36 (m, 1H), 2.35-2.28 (m, 2H), 2.26-2.21 (m, 4H), 1.72-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 137.7, 137.1, 136.9, 132.7, 132.6, 131.5 (J_{C-F} = 32.3 Hz), 129.9, 129.2, 129.1, 128.4, 128.2 (J_{C-F} = 270.6 Hz), 127.9, 126.1 (J_{C-F} = 3.0 Hz), 125.9 (J_{C-F} = 3.7 Hz), 89.0, 67.9, 59.0, 56.7, 51.9, 50.8, 22.0, 21.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.3; FT-IR (neat) 2829, 1638, 1514, 1490, 1324, 1165, 1128, 1071 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{28}ClF_3N_3$: 486.1918, found: 486.1912.

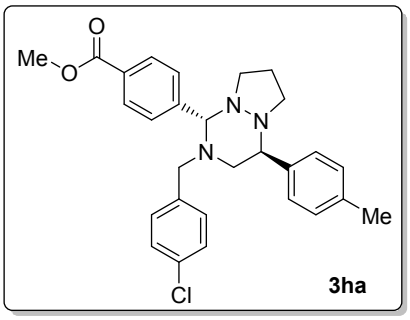


1-(4-Bromophenyl)-2-(4-chlorobenzyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]tria-zine 3fa. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 162-163^{o}C; yield 91% (90 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 4H), 7.18-7.16 (m, 2H), 7.11-7.09 (m, 2H), 7.05-7.01 (m, 4H), 3.68 (s, 1H), 3.50-3.47 (m, 2H), 2.81-2.76 (m, 3H), 2.44-2.39 (m, 1H), 2.33-2.20 (m, 6H), 1.71-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 137.6,

137.2, 137.0, 132.6, 131.8, 130.8, 129.9, 129.1, 128.4, 127.9, 122.8, 88.9, 68.0, 59.0, 56.6, 51.9, 50.8, 22.0, 21.2; FT-IR (KBr) 2827, 1638, 1591, 1488, 1314, 1128, 1012 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{28}BrClN_3$: 496.1150, found: 496.1157.

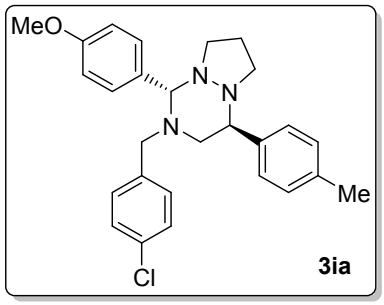


4-(2-(4-Chlorobenzyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazin-1-yl)benzonitrile 3ga. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 180-181 °C; yield 77% (68 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.70 – 7.67 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 2H), 7.11-7.09 (m, 4H), 3.84 (s, 1H), 3.59-3.56 (m, 1H), 3.49 (d, *J* = 13.2 Hz, 1H), 2.93-2.84 (m, 3H), 2.46-2.40 (m, 1H), 2.38-2.26 (m, 6H), 1.80-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 137.7, 136.7, 132.8, 132.4, 130.0, 129.8, 129.2, 128.5, 127.9, 118.6, 112.8, 88.8, 67.9, 58.8, 56.6, 51.8, 50.7, 22.0, 21.2; FT-IR (KBr) 2830, 2228, 1609, 1543, 1489, 1300, 1128, 1015 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{28}ClN_4$: 443.1997, found: 443.1998.

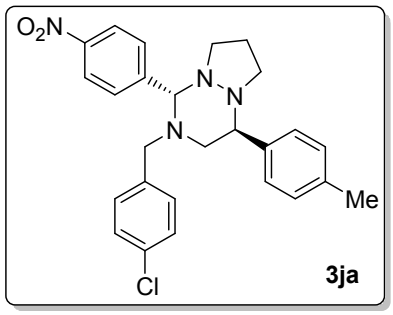


Methyl 4-(2-(4-chlorobenzyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazin-1-yl)-benzoate 3ha. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 184-185 °C; yield 82% (78 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.65-7.63 (m, 2H), 7.19-7.17 (m, 2H), 7.10-7.08 (m, 2H), 7.05-7.01 (m, 4H), 3.84 (s, 3H), 3.77 (s, 1H), 3.54-3.50 (m, 1H), 3.46 (d, *J* = 13.6 Hz, 1H), 2.83-2.77 (m, 3H), 2.41-2.35 (m, 1H), 2.33-2.21 (m, 6H),

1.71-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 144.6, 137.6, 137.1, 136.9, 132.6, 130.8, 130.0, 129.9, 129.3, 129.1, 128.4, 127.9, 89.1, 68.0, 58.9, 56.6, 52.3, 51.8, 50.7, 22.0, 21.2; FT-IR (KBr) 2822, 1722, 1611, 1432, 1276, 1102, 1014 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{31}ClN_3O_2$: 476.2099, found: 476.2116.

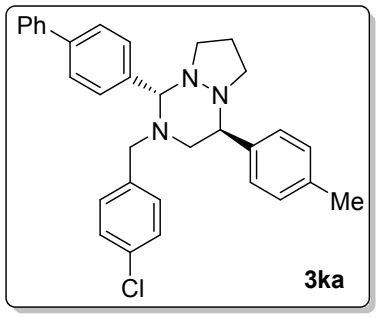


2-(4-Chlorobenzyl)-1-(4-methoxyphenyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ia. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 169-170 °C; yield 94% (84 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.45 (m, 2H), 7.19-7.17 (m, 2H), 7.10-7.05 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.68 (s, 1H), 3.58-3.50 (m, 2H), 2.83-2.77 (m, 3H), 2.47-2.42 (m, 1H), 2.36-2.23 (m, 6H), 1.71-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 137.67, 137.60, 137.1, 132.4, 131.5, 130.2, 130.0, 129.1, 128.3, 127.9, 113.9, 89.1, 68.1, 59.1, 56.5, 55.3, 52.0, 50.8, 21.9, 21.2; FT-IR (KBr) 2825, 1611, 1510, 1239, 1126 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{31}ClN_3O$: 448.2150, found: 448.2164.

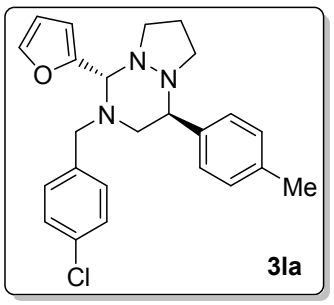


2-(4-Chlorobenzyl)-1-(4-nitrophenyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ja. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.42; yellow solid; mp 122-123 °C; yield 79% (73 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.17 (m, 2H), 7.77-7.75 (m, 2H), 7.19-7.16 (m, 2H), 7.12-7.09 (m, 2H), 7.04-7.02 (m, 4H), 3.82 (s, 1H), 3.53-3.50 (m, 1H), 3.41 (d, *J* = 13.6 Hz, 1H), 2.87-2.78 (m, 3H), 2.39-2.19 (m, 7H), 1.73-1.65 (m, 2H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 148.4, 147.0, 137.8, 136.78, 136.71, 132.9, 130.2, 129.8, 129.2, 128.5, 127.9, 123.8, 88.5, 67.9, 58.8, 56.6, 51.8, 50.7, 22.0, 21.2; FT-IR (KBr) 2964, 2828, 1607, 1519, 1489, 1342, 1127, 1014 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{28}ClN_4O_2$: 463.1895, found: 463.1892.

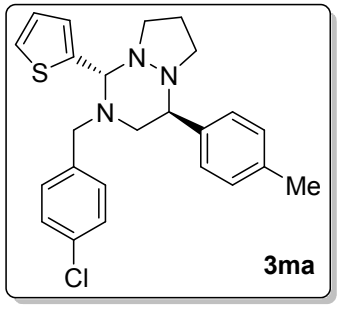


1-([1,1'-Biphenyl]-4-yl)-2-(4-chlorobenzyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]-triazine 3ka. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 158-159 °C; yield 92% (90 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.54-7.51 (m, 4H), 7.37-7.33 (m, 2H), 7.27-7.23 (m, 1H), 7.20-7.16 (m, 2H), 7.09 (s, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.76 (s, 1H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.56-3.52 (m, 1H), 2.85-2.79 (m, 3H), 2.52-2.47 (m, 1H), 2.40-2.33 (m, 1H), 2.30-2.25 (m, 2H), 2.23 (s, 3H), 1.72-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.8, 138.5, 137.6, 137.5, 137.1, 132.5, 130.0, 129.5, 129.1, 128.9, 128.3, 127.9, 127.5, 127.3, 127.2, 89.4, 68.1, 59.1, 56.7, 51.9, 50.8, 22.0, 21.2; FT-IR (KBr) 2824, 1511, 1487,1314, 1129, 1014 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{32}H_{33}ClN_3$: 494.2358, found: 494.2368.

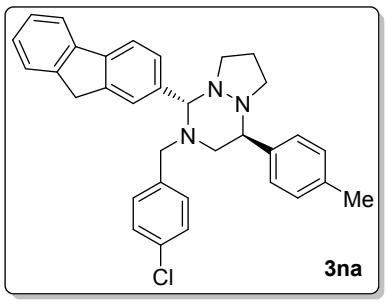


2-(4-Chlorobenzyl)-1-(furan-2-yl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3la. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 123-124 °C; yield 91% (74 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.388-7.383 (m, 1H), 7.18-7.09 (m, 6H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.44-6.43 (m, 1H), 6.29-6.28 (m, 1H), 3.90 (s, 1H), 3.60-3.53 (m, 2H),

2.96 (d, J = 13.2 Hz, 1H), 2.82-2.74 (m, 2H), 2.65-2.59 (m, 1H), 2.40-2.33 (m, 1H), 2.31-2.21 (m, 5H), 1.77-1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 142.8, 137.6, 137.2, 136.9, 132.5, 130.2, 129.1, 128.3, 127.9, 110.4, 110.1, 82.2, 67.6, 58.9, 56.5, 51.9, 50.4, 21.9, 21.2; FT-IR (KBr) 2846, 2823, 2736, 1491, 1336, 1151, 1128, 1077 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{27}ClN_3O$: 408.1837, found: 408.1856.

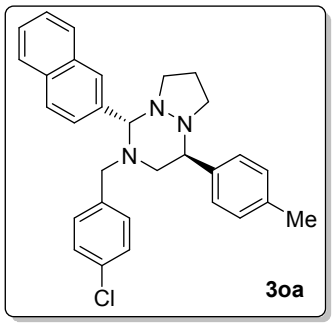


2-(4-Chlorobenzyl)-1-(thiophen-2-yl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ma. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.46; thick liquid; yield 93% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 4.8 Hz, 1H), 7.18-7.15 (m, 2H), 7.14-7.08 (m, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.90-6.88 (m, 1H), 4.03 (s, 1H), 3.71 (d, J = 13.2 Hz, 1H), 3.55-3.51 (m, 1H), 2.84-2.786 (m, 2H), 2.781-2.74 (m, 1H), 2.62-2.57 (m, 1H), 2.40-2.32 (m, 1H), 2.30-2.23 (m, 5H), 1.74-1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.6, 137.3, 136.9, 132.6, 130.1, 129.1, 128.3, 127.9, 127.2, 126.9, 125.8, 84.5, 67.8, 59.0, 56.6, 52.1, 51.0, 21.8, 21.2; FT-IR (neat) 2973, 2826, 1591, 1488, 1291, 1127, 1012 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{27}ClN_3S$: 424.1609, found: 424.1608.

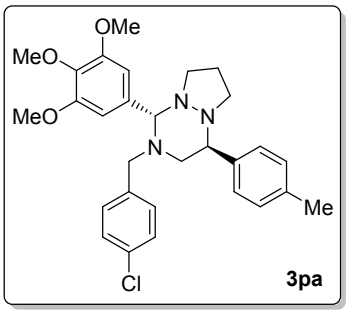


2-(4-Chlorobenzyl)-1-(9H-fluoren-2-yl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3na. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 189-190 ^{o}C; yield 89% (90 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.68 (m, 3H), 7.50-7.44 (m, 2H), 7.29-7.25 (m, 1H), 7.22-7.18 (m, 3H), 7.09-7.07 (m, 4H), 7.03 (d, J = 7.6 Hz, 2H), 3.84 (s,

2H), 3.78 (s, 1H), 3.62 (d, J = 13.2 Hz, 1H), 3.56-3.53 (m, 1H), 2.84-2.79 (m, 3H), 2.49-2.44 (m, 1H), 2.41-2.34 (m, 1H), 2.31-2.26 (m, 2H), 2.22 (s, 3H), 1.70-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.6, 142.5, 141.3, 138.0, 137.59, 137.56, 137.1, 132.4, 130.0, 129.1, 128.3, 127.9, 126.9, 126.8, 125.4, 125.1, 120.0, 119.8, 89.8, 68.2, 59.1, 56.7, 51.9, 50.9, 36.9, 22.0, 21.2; FT-IR (KBr) 2852, 2819, 1723, 1613, 1513, 1123 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{33}H_{33}ClN_3$: 506.2358, found: 506.2376.

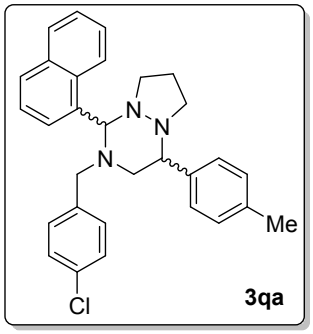


2-(4-Chlorobenzyl)-1-(naphthalen-2-yl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3oa. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 177-178 ^{o}C; yield 88% (82 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.91-7.84 (m, 4H), 7.53-7.48 (m, 2H), 7.31 (d, J = 7.6 Hz, 2H), 7.18-7.11 (m, 6H), 3.97 (s, 1H), 3.71-3.62 (m, 2H), 2.94 – 2.89 (m, 3H), 2.54-2.44 (m, 2H), 2.43-2.36 (m, 2H), 2.33 (s, 3H), 1.80-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 137.4, 137.1, 137.0, 133.9, 133.2, 132.5, 130.0, 129.1, 128.65, 128.62, 128.3, 128.1, 128.0, 127.8, 126.3, 126.2, 89.8, 68.1, 59.1, 56.7, 52.0, 50.9, 22.0, 21.2; FT-IR (KBr) 2823, 2800, 1489, 1289, 1139, 1092, 1014 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{30}H_{31}ClN_3$: 468.2201, found: 468.2204.

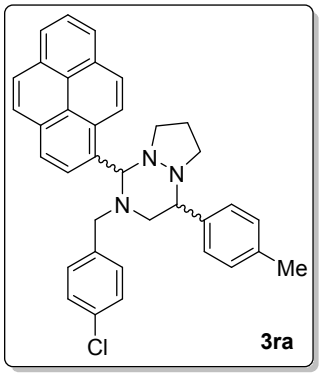


2-(4-Chlorobenzyl)-4-(*p*-tolyl)-1-(3,4,5-trimethoxyphenyl)hexahydro-6H-pyrazolo[1,2-a]-[1,2,4]triazine 3pa. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.44; colorless

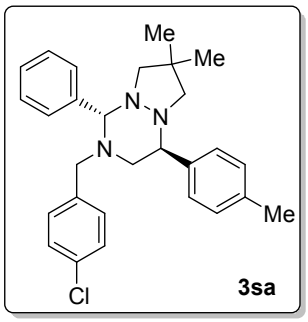
solid; mp 159-160 °C; yield 92% (93 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.17 (m, 2H), 7.12-7.07 (m, 4H), 7.05-7.01 (m, 2H), 6.77 (s, 2H), 3.82 (s, 6H), 3.77 (s, 3H), 3.62-3.51 (m, 3H), 2.83-2.77 (m, 3H), 2.54-2.49 (m, 1H), 2.36-2.32 (m, 1H), 2.30-2.23 (m, 5H), 1.73-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 138.2, 137.6, 137.5, 137.0, 134.9, 132.5, 129.8, 129.1, 128.3, 127.9, 106.8, 105.9, 90.0, 67.8, 60.9, 59.3, 56.6, 56.3, 51.9, 50.7, 22.0, 21.2; FT-IR (KBr) 2829, 1592, 1504, 1490, 1462, 1356, 1230, 1127, 1013 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{29}H_{35}ClN_3O_3$: 508.2361, found: 508.2369.



2-(4-Chlorobenzyl)-1-(naphthalen-1-yl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3qa. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.48; thick liquid; yield 82% (76 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 8.4 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 0.57H), 8.18-8.16 (m, 0.57H), 7.82-7.73 (m, 3.23H), 7.52-7.40 (m, 5H), 7.32-7.15 (m, 5.01H), 7.11-6.97 (m, 8H), 6.88 (d, *J* = 8.4 Hz, 2.01H), 4.80 (s, 0.59H), 4.06 (s, 1H), 3.68-3.65 (m, 1.02H), 3.63-3.59 (m, 0.58H), 3.55 – 3.43 (m, 0.97H), 3.36 (d, *J* = 13.2 Hz, 1H), 2.90-2.73 (m, 5H), 2.46-2.19 (m, 12.02H), 1.69-1.56 (m, 4.01H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.64, 137.62, 137.5, 137.3, 137.1, 135.1, 134.9, 134.5, 133.6, 132.7, 132.4, 132.3, 131.6, 130.3, 129.9, 129.6, 129.2, 129.1, 128.8, 128.7, 128.5, 128.2, 128.1, 128.0, 127.8, 127.0, 126.2, 126.07, 126.02, 125.5, 125.0, 124.7, 122.7, 93.1, 81.9, 68.6, 67.8, 59.4, 57.2, 56.0, 52.3, 51.9, 50.7, 50.1, 29.8, 22.2, 21.9, 21.28, 21.25; FT-IR (KBr) 2853, 2828, 1634, 1512, 1489, 1128, 1014 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{30}H_{31}ClN_3$: 468.2201, found: 468.2209.

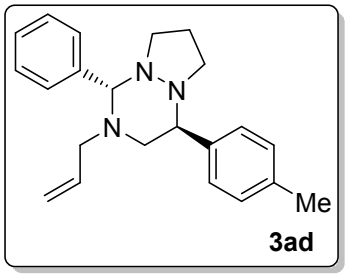


2-(4-Chlorobenzyl)-1-(pyren-1-yl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ra. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.46; colorless solid; mp >200 ^{o}C; yield 78% (84 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (d, *J* = 9.42 Hz, 1H), 8.80-8.72 (m, 1.71H), 8.33-8.01 (m, 14.53H), 7.40-7.38 (m, 3.66H), 7.18-7.09 (m, 7.24H), 7.06-6.98 (m, 4H), 5.16 (s, 0.81H), 4.43 (s, 1H), 3.90-3.87 (m, 1.02H), 3.81-3.78 (m, 0.86H), 3.58 (d, *J* = 13.6 Hz, 0.89H), 3.47 (d, *J* = 13.2 Hz, 1.03H), 3.06-2.89 (m, 5.79H), 2.63 (t, *J* = 10.8 Hz, 0.92H), 2.57-2.36 (m, 11.52H), 2.29-2.24 (m, 120H), 1.78-1.65 (m, 4.72H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.67, 137.62, 137.4, 137.3, 137.2, 133.0, 132.9, 132.4, 132.36, 132.34, 131.9, 131.4, 131.36, 131.30, 130.6, 130.3, 130.28, 130.25, 130.0, 129.9, 129.24, 129.21, 129.1, 128.2, 128.1, 128.0, 127.99, 127.95, 127.8, 127.7, 127.6, 127.3, 126.7, 126.2, 126.1, 126.0, 125.728, 125.721, 125.6, 125.3, 125.2, 125.0, 124.9, 124.7, 124.6, 124.2, 122.3, 93.2, 82.5, 68.6, 68.1, 59.6, 59.4, 57.4, 56.2, 52.3, 52.0, 50.9, 50.2, 22.2, 22.0, 21.2; FT-IR (KBr) 2834, 1512, 1489, 1313, 1126, 1014 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{36}H_{33}ClN_3$: 542.2358, found: 542.2379.

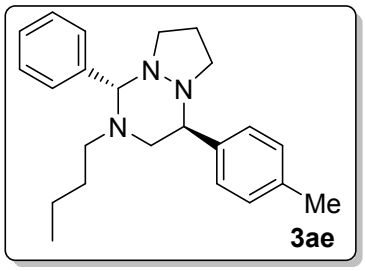


2-(4-Chlorobenzyl)-7,7-dimethyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]-triazine 3sa. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.52; colorless solid; mp 139-140 ^{o}C; yield 92% (82 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.31-7.23 (m,

3H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.09-7.00 (m, 6H), 3.67 (s, 1H), 3.52-3.48 (m, 2H), 2.78-2.74 (m, 2H), 2.54 (d, *J* = 8.8 Hz, 1H), 2.24-2.07 (m, 7H), 0.94 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.5, 137.44, 137.40, 132.4, 130.1, 129.2, 129.1, 128.8, 128.5, 128.2, 127.8, 89.7, 67.9, 67.2, 66.2, 59.3, 56.6, 36.2, 29.1, 28.9, 21.2; FT-IR (KBr) 2959, 2823, 1642, 1514, 1490, 1450, 1130, 1015 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{33}ClN_3$: 446.2358, found: 446.2360.

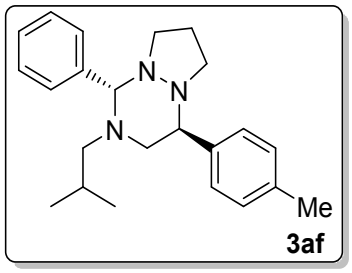


2-Allyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ad. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 110-111 ^oC; yield 92% (61 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.37-7.32 (m, 5H), 7.15 (d, *J* = 7.6 Hz, 2H), 5.78-5.67 (m, 1H), 5.02-4.97 (m, 2H), 3.71 (s, 1H), 3.68-3.65 (m, 1H), 3.13-3.05 (m, 2H), 2.92-2.86 (m, 1H), 2.57- 2.28 (m, 8H), 1.77-1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 137.5, 137.4, 135.1, 129.2, 129.1, 128.7, 128.4, 128.0, 117.5, 89.2, 68.1, 59.1, 56.1, 51.9, 50.7, 22.0, 21.2; FT-IR (KBr) 2828, 1641, 1512, 1128, 1021 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{28}N_3$: 334.2278, found: 334.2287.



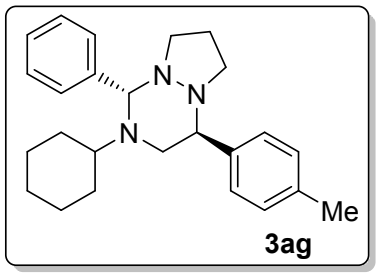
2-Butyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ae. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.56; thick liquid; yield 87% (61 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44- 7.43 (m, 2H), 7.28-7.25 (m, 5H), 7.09 (d, *J* = 7.6 Hz, 2H), 3.61-3.58 (m, 2H), 3.10-3.06 (m, 1H), 2.84-2.79 (m, 1H), 2.40-2.36 (m, 1H), 2.35-2.29 (m, 2H), 2.27 (s, 3H), 2.26-2.21 (m, 2H), 1.90-1.83 (m, 1H), 1.69-1.61 (m, 2H), 1.28-1.19 (m, 2H), 1.13-1.05 (m, 1H),

1.03 – 0.92 (m, 1H), 0.64 (t, J = 7.6 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.57, 137.54, 129.2, 129.1, 128.5, 128.3, 128.0, 89.8, 68.2, 59.1, 52.5, 52.0, 50.7, 28.7, 22.0, 21.3, 20.4, 14.0; FT-IR (neat) 2827, 1636, 1513, 1315, 1129, 1021 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{32}N_3$: 350.2591, found: 350.2605.



3af

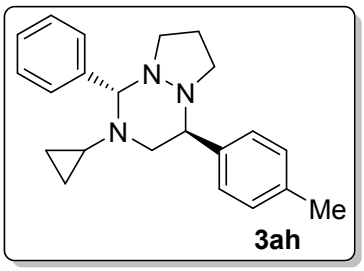
2-Isobutyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3af. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.52; thick liquid; yield 89% (62 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H), 7.28-7.24 (m, 5H), 7.09 (d, J = 8.0 Hz, 2H), 3.61-3.57 (m, 1H), 3.54 (s, 1H), 3.08-3.05 (m, 1H), 2.84-2.79 (m, 1H), 2.38-2.33 (m, 1H), 2.30-2.21 (m, 6H), 1.88-1.82 (m, 1H), 1.75-1.71 (m, 1H), 1.69-1.61 (m, 2H), 1.60-1.52 (m, 1H), 0.71 (d, J = 6.4 Hz, 3H), 0.57 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.58, 137.55, 129.5, 129.1, 128.5, 128.2, 128.0, 90.3, 68.2, 60.9, 59.7, 51.9, 50.8, 25.7, 21.9, 21.29, 21.20, 20.3; FT-IR (neat) 2954, 2826, 1638, 1514, 1451, 1127, 1022 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{32}N_3$: 350.2591, found: 350.2608.



3ag

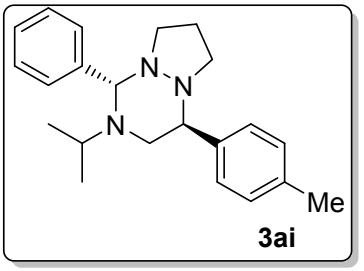
2-Cyclohexyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ag. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.54; thick liquid; yield 76% (57 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.35-7.33 (m, 5H), 7.16 (d, J = 7.6 Hz, 2H), 4.05 (s, 1H), 3.62 (d, J = 10.4 Hz, 1H), 3.01-2.98 (m, 1H), 2.90-2.85 (m, 1H), 2.71 (t, J = 10.8 Hz, 1H), 2.43-2.38 (m, 1H), 2.34-2.33 (m, 3H), 2.31-2.21 (m, 2H), 1.76-1.53 (m, 8H), 1.44-1.39 (m, 1H), 1.36-1.29 (m, 1H), 1.25-1.14 (m, 1H), 1.01-0.88 (m, 1H), 0.86-0.73 (m, 1H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 139.5, 137.9, 137.4, 129.1, 129.0, 128.5, 128.4, 128.0, 87.0, 68.6, 57.3, 52.5, 51.9, 50.8, 31.9, 26.6, 26.4, 25.9, 24.9, 22.0, 21.2; FT-IR (neat) 2928, 2852, 2826, 1514, 1450, 1125, 1020 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{25}H_{34}N_3$: 376.2747, found: 376.2746.



3ah

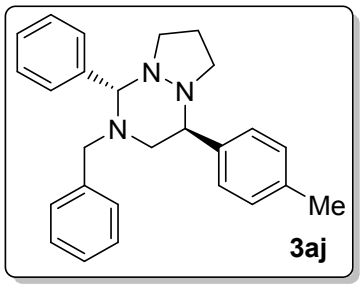
2-Cyclopropyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ah. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.52; thick liquid; yield 73% (49 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.34-7.30 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 1H), 3.65-3.62 (m, 1H), 3.15-3.12 (m, 1H), 2.93-2.88 (m, 1H), 2.70-2.60 (m, 2H), 2.34 (s, 3H), 2.32-2.23 (m, 2H), 1.78-1.71 (m, 2H), 1.61-1.56 (m, 1H), 0.23-0.12 (m, 2H), -0.05- -0.12 (m, 1H), -0.22--0.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.5, 137.3, 129.6, 129.2, 128.3, 127.9, 127.8, 90.6, 67.8, 61.2, 51.9, 50.5, 35.0, 22.1, 21.2, 8.8, 4.8; FT-IR (neat) 2827, 1633, 1513, 1315, 1133, 1021 cm^{-1}; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{28}N_3$: 334.2278, found: 334.2280.



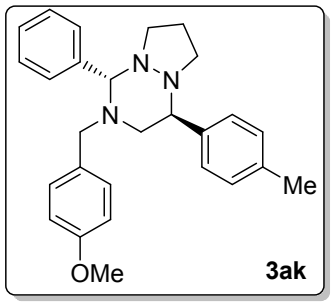
3ai

2-Isopropyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ai. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.54; colorless solid; mp 130-131 ^oC; yield 79% (53 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.29-7.27 (m, 5H), 7.10 (d, *J* = 7.6 Hz, 2H), 3.87 (s, 1H), 3.57-3.54 (m, 1H), 2.89-2.85 (m, 1H), 2.84-2.79 (m, 1H), 2.70-2.63 (m, 1H), 2.55 (t, *J* = 10.8 Hz, 1H), 2.36-2.31 (m, 1H), 2.30-2.20 (m, 5H), 1.67-1.62 (m, 2H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.8, 137.5, 129.18, 129.12, 128.6, 128.5, 128.0, 87.4, 68.5, 51.9, 50.8, 50.4, 47.7, 22.0, 21.7, 21.2, 13.2; FT-IR (KBr) 2966,

2822, 1629, 1511, 1361, 1309, 1127, 1009 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{30}N_3$: 336.2434, found: 336.2445.

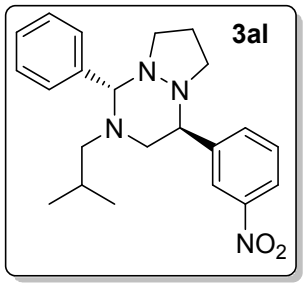


2-Benzyl-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3aj. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.50; colorless solid; mp 147-148 °C; yield 91% (70 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.32-7.23 (m, 3H), 7.20-7.10 (m, 6H), 7.08-7.04 (m, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 3.73 (s, 1H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.56-3.52 (m, 1H), 2.87-2.77 (m, 3H), 2.46-2.40 (m, 1H), 2.38-2.31 (m, 1H), 2.30 – 2.25 (m, 2H), 2.22 (s, 3H), 1.71-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 139.0, 137.5, 137.2, 129.2, 129.1, 128.8, 128.7, 128.5, 128.2, 128.0, 126.8, 89.8, 68.1, 59.0, 57.3, 51.9, 50.8, 22.0, 21.2; FT-IR (KBr) 2826, 1631, 1491, 1314, 1126, 1066 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{30}N_3$: 384.2434, found: 384.2439.

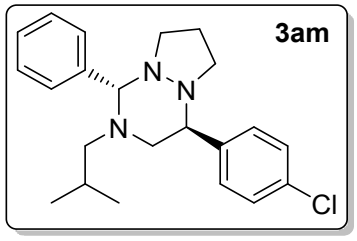


2-(4-Methoxybenzyl)-1-phenyl-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ak. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 153-154 °C; yield 93% (77 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.32-7.23 (m, 3H), 7.20-7.17 (m, 2H), 7.02 (t, *J* = 8.4 Hz, 4H), 6.68 – 6.65 (m, 2H), 3.70 (s, 1H), 3.65 (s, 3H), 3.55-3.51 (m, 2H), 2.86-2.82 (m, 1H), 2.80-2.74 (m, 2H), 2.45-2.39 (m, 1H), 2.37-2.30 (m, 1H), 2.29-2.21 (m, 5H), 1.70-1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 139.7, 137.4, 137.3, 130.9, 129.9, 129.2, 129.1, 128.7, 128.5, 128.0, 113.5, 89.8, 68.1, 58.9, 56.7, 55.3, 51.9, 50.8, 22.0, 21.2; FT-IR (KBr)

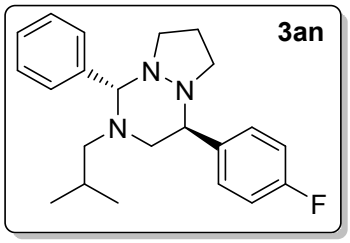
2824, 1611, 1512, 1251, 1125, 1035 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{32}N_3O$: 414.2540, found: 414.2549.



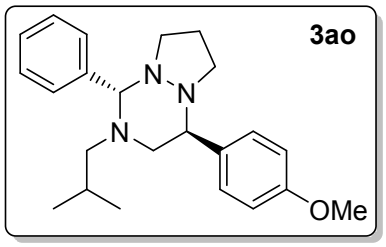
2-Isobutyl-4-(3-nitrophenyl)-1-phenylhexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3al. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.48; thick liquid; yield 92% (70 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.34-8.33 (m, 1H), 8.16-8.13 (m, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.53-7.49 (m, 3H), 7.35-7.32 (m, 3H), 3.82-3.78 (m, 1H), 3.63 (s, 1H), 3.16-3.13 (m, 1H), 2.88-2.83 (m, 1H), 2.46-2.41 (m, 1H), 2.39-2.24 (m, 3H), 1.97-1.91 (m, 1H), 1.83-1.70 (m, 3H), 1.67-1.57 (m, 1H), 0.78 (d, *J* = 6.4 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 142.8, 139.4, 134.3, 129.4, 128.7, 128.3, 123.0, 122.9, 90.0, 67.7, 60.7, 59.6, 51.9, 50.7, 25.7, 21.9, 21.1, 20.3; FT-IR (neat) 2958, 2832, 1628, 1530, 1352, 1127, 1024 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{29}N_4O_2$: 381.2285, found: 381.2286.



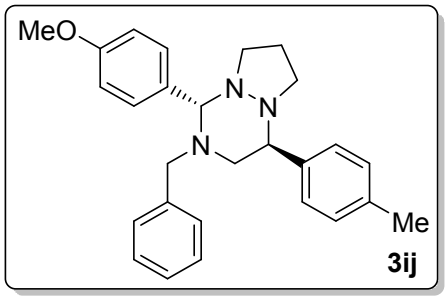
4-(4-Chlorophenyl)-2-isobutyl-1-phenylhexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3am. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.54; thick liquid; yield 89% (66 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.48 (m, 2H), 7.40-7.37 (m, 2H), 7.34-7.26 (m, 5H), 3.68-3.65 (m, 1H), 3.60 (s, 1H), 3.13-3.09 (m, 1H), 2.88-2.83 (m, 1H), 2.45-2.22 (m, 4H), 1.95-1.90 (m, 1H), 1.82-1.78 (m, 1H), 1.76-1.68 (m, 2H), 1.67-1.57 (m, 1H), 0.77 (d, *J* = 6.4 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 139.0, 133.4, 129.4, 128.68, 128.61, 128.2, 90.2, 67.8, 60.8, 59.6, 51.9, 50.7, 25.7, 21.9, 21.1, 20.3; FT-IR (neat) 2956, 2829, 1491, 1292, 1127, 1090, 1015 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{29}ClN_3$: 370.2045, found: 370.2057.



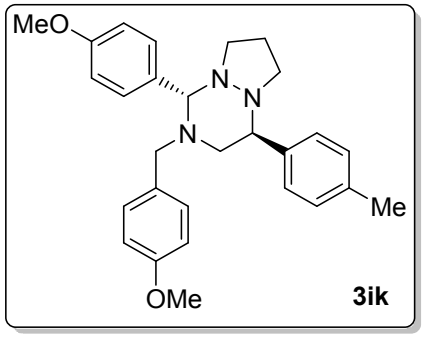
4-(4-Fluorophenyl)-2-isobutyl-1-phenylhexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3an. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.52; thick liquid; yield 94% (66 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.44-7.40 (m, 2H), 7.34-7.31 (m, 3H), 7.01 (t, *J* = 8.8 Hz, 2H), 3.69-3.65 (m, 1H), 3.60 (s, 1H), 3.14-3.10 (m, 1H), 2.87-2.81 (m, 1H), 2.45-2.24 (m, 4H), 1.96-1.90 (m, 1H), 1.82-1.78 (m, 1H), 1.75-1.58 (m, 3H), 0.78 (d, *J* = 6.4 Hz, 3H), 0.65 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 ($J_{C\text{-}F}$ = 244.2 Hz), 139.7, 136.3 ($J_{C\text{-}F}$ = 3.1 Hz), 129.6 ($J_{C\text{-}F}$ = 7.8 Hz), 129.5, 128.5, 128.2, 115.4 ($J_{C\text{-}F}$ = 21.0 Hz), 90.3, 67.7, 60.9, 59.7, 51.9, 50.8, 25.7, 21.9, 21.1, 20.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.7; FT-IR (neat) 2957, 2827, 1607, 1510, 1223, 1127, 1105 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{29}FN_3$: 354.2340, found: 354.2348.



2-Isobutyl-4-(4-methoxyphenyl)-1-phenylhexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ao. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.48; thick liquid; yield 87% (63 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.39-7.30 (m, 5H), 6.89-6.85 (m, 2H), 3.80 (s, 3H), 3.66-3.62 (m, 1H), 3.61 (s, 1H), 3.15-3.11 (m, 1H), 2.88-2.83 (m, 1H), 2.45-2.39 (m, 1H), 2.37-2.27 (m, 3H), 1.95-1.89 (m, 1H), 1.82-1.78 (m, 1H), 1.75-1.68 (m, 2H), 1.66-1.59 (m, 1H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 139.8, 132.7, 129.5, 129.1, 128.5, 128.2, 113.8, 90.3, 67.8, 60.9, 59.6, 55.3, 51.9, 50.8, 25.7, 21.9, 21.1, 20.3; FT-IR (neat) 2955, 2830, 1611, 1513, 1248, 1172, 1128, 1036 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{23}H_{32}N_3O$: 366.2540, found: 366.2542.

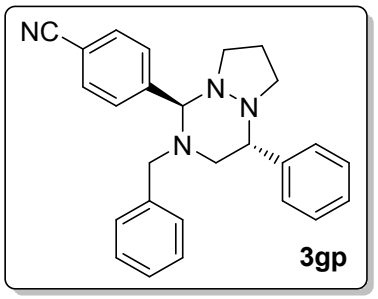


2-Benzyl-1-(4-methoxyphenyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3ij. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.44; colorless solid; mp 160-161 °C; yield 92% (76 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.19-7.17 (m, 2H), 7.15-7.10 (m, 4H), 7.08-7.03 (m, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.84-6.82 (m, 2H), 3.73 (s, 3H), 3.68-3.61 (m, 2H), 3.54-3.51 (m, 1H), 2.86-2.77 (m, 3H), 2.48-2.43 (m, 1H), 2.36-2.22 (m, 6H), 1.70-1.63 (m, 2H); 13C NMR (100 MHz, $CDCl_3$) δ 159.9, 139.1, 137.4, 137.3, 131.8, 130.2, 129.1, 128.7, 128.1, 128.0, 126.8, 113.9, 89.2, 68.1, 59.1, 57.3, 55.3, 52.0, 50.8, 22.0, 21.2; FT-IR (KBr) 2831, 1610, 1585, 1512, 1300, 1248, 1128, 1037 cm^{-1}; HRMS (ESI) m/z [M+H]+ calcd for $C_{27}H_{32}N_3O$: 414.2540, found: 414.2541.

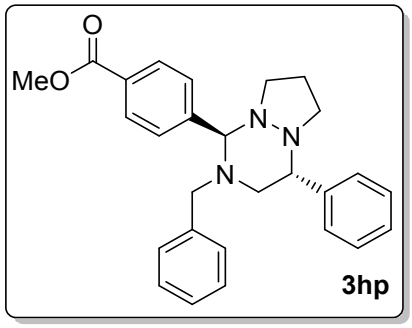


2-(4-Methoxybenzyl)-1-(4-methoxyphenyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]-triazine 3ik. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.42; colorless solid; mp 161-162 °C; yield 89% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.19-7.17 (m, 2H), 7.04-7.00 (m, 4H), 6.85-6.82 (m, 2H), 6.68-6.65 (m, 2H), 3.74 (s, 3H), 3.65 (s, 4H), 3.57-3.49 (m, 2H), 2.85-2.73 (m, 3H), 2.47-2.42 (m, 1H), 2.35-2.21 (m, 6H), 1.70-1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 158.5, 137.45, 137.40, 131.9, 131.1, 130.2, 129.9, 129.0, 128.0, 113.8, 113.6, 89.2, 68.1, 59.0, 56.6, 55.38, 55.33, 52.0, 50.8, 22.0, 21.2; FT-IR (KBr) 2953, 2831, 1510,

1585, 1510, 1300, 1245, 1127, 1036 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{34}N_3O_2$: 444.2646, found: 444.2650.

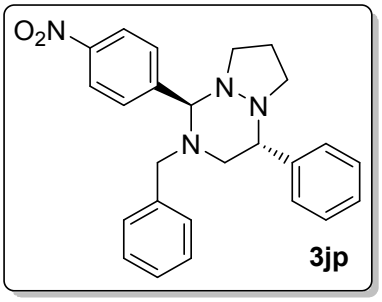


4-((1R,4R)-2-Benzyl-4-phenylhexahydro-6H-pyrazolo[1,2-a][1,2,4]triazin-1-yl)benzonitrile 3gp. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.52; colorless solid; mp >200 ^oC; yield 79% (62 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.30-7.28 (m, 2H), 7.23-7.07 (m, 8H), 3.79 (s, 1H), 3.57-3.53 (m, 1H), 3.48 (d, *J* = 13.2 Hz, 1H), 2.89-2.85 (m, 2H), 2.83-2.77 (m, 1H), 2.40-2.20 (m, 4H), 1.73-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ145.2, 139.9, 138.2, 132.4, 130.1, 128.56, 128.50, 128.3, 128.1, 127.9, 127.1, 118.7, 112.7, 89.0, 68.2, 58.8, 57.4, 51.8, 50.7, 22.0; FT-IR (KBr) 2830, 2227, 1607, 1494, 1452, 1301, 1128, 1027 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{26}H_{27}N_4$: 395.2230, found: 395.2234; $[\alpha]_D^{20.8}$ = -24.00 (c = 0.02, $CHCl_3$); HPLC: >97% *ee* [CHIRALCEL AD, hexane/^{i}PrOH = 98:2, flow rate: 1 mL /min, λ = 254 nm, t_R = 8.52 min (minor), 12.66 min (major)].



Methyl 4-((1R,4R)-2-benzyl-4-phenylhexahydro-6H-pyrazolo[1,2-a][1,2,4]triazin-1-yl)benzoate 3hp. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 182-183 ^oC; yield 85% (72 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.78-7.76 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.15 (m, 8H), 3.94 (s, 3H), 3.89 (s, 1H), 3.68-3.60 (m, 2H), 2.99-2.87 (m, 3H), 2.53-2.32 (m, 4H), 1.82-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 144.8,

140.1, 138.5, 130.7, 129.9, 129.3, 128.6, 128.4, 128.2, 128.1, 127.9, 127.0, 89.2, 68.3, 58.9, 57.3, 52.2, 51.9, 50.7, 22.0; FT-IR (KBr) 2831, 1724, 1636, 1276, 1127, 1018 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{27}H_{30}N_3O_2$: 428.2333, found: 428.2334; $[\alpha]_D^{21.5}$ = -70.00 (c = 0.02, $CHCl_3$); HPLC: >99% *ee* [CHIRALCEL AD, hexane/^{i}PrOH = 98:2, flow rate: 1 mL /min, λ = 254 nm, t_R = 7.96 min (minor), 11.62 min (major)].

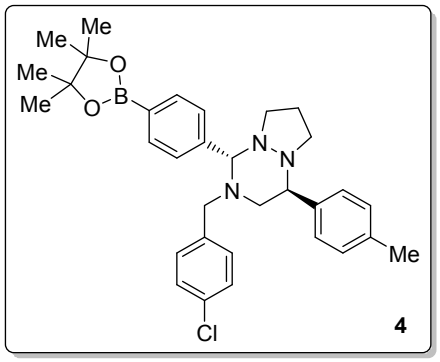


(1R,4R)-2-Benzyl-1-(4-nitrophenyl)-4-phenylhexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 3jp. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.46; yellow solid; mp 193-194 °C; yield 81% (67 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.17 (m, 2H), 7.79-7.77 (m, 2H), 7.30-7.28 (m, 2H), 7.23-7.06 (m, 8H), 3.85 (s, 1H), 3.58-3.55 (m, 1H), 3.48 (d, *J* = 13.2 Hz, 1H), 2.90-2.87 (m, 2H), 2.83-2.78 (m, 1H), 2.40-2.20 (m, 4H), 1.74-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 147.1, 139.8, 138.1, 130.2, 128.56, 128.51, 128.3, 128.1, 128.0, 127.1, 123.8, 88.6, 68.2, 58.8, 57.4, 51.8, 50.7, 22.0; FT-IR (KBr) 2830, 1606, 1522, 1493, 1346, 1314, 1128, 1026 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{25}H_{27}N_4O_2$: 415.2129, found: 415.2129; $[\alpha]_D^{21.4}$ = -25.00 (c = 0.02, $CHCl_3$); HPLC: >99% *ee* [CHIRALCEL AD, hexane/*i*PrOH = 98:2, flow rate: 1 mL /min, λ = 254 nm, t_R = 6.76 min (minor), 8.51 min (major)].

Intermolecular Competitive Experiment Using 1i and 1j. 1-(4-Chlorobenzyl)-2-(*p*-tolyl)aziridine **2a** (52 mg, 0.2 mmol), **1i** (38 mg, 0.2 mmol), **1j** (42 mg, 0.2 mmol) and $FeCl_3$ (3 mg, 0.02 mmol) were stirred in dichloromethane (2.0 mL) at room temperature (25 °C) for 1 minute. Next, the reaction mixture was diluted with dichloromethane (5 mL) and passed through a short pad of celite using dichloromethane (10 mL) as solvent. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to give **3ia** and **3ja** in 50 and 42% yields, respectively.

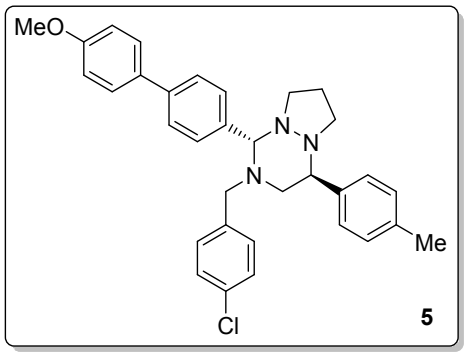
Intermolecular Competitive Experiment Using 2n and 2o. 6-Phenyl-1,5-diazabicyclo[3.1.0]-hexane **1a** (32 mg, 0.2 mmol), **2n** (38 mg, 0.2 mmol), **2o** (42 mg, 0.2 mmol) and $FeCl_3$ (3 mg, 0.02 mmol) were stirred in dichloromethane (2.0 mL) at room temperature (25 ^oC) for 1 minute. Next, the reaction mixture was diluted with dichloromethane (5 mL) and passed through a short pad of celite using dichloromethane (10 mL) as solvent. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to give **3an** and **3ao** in 47 and 42% yields, respectively.

Epimerization Reaction of 3aa.[6] Acetic acid (6 μL, 0.1 mmol) was added to a stirring solution of **3aa** (42 mg, 0.1 mmol) in dichloromethane (2 mL) and the reaction mixture was stirred at room temperature (25 ^oC) for 6 h. Next, the reaction mixture was quenched by using saturated aq. $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3×10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to give **3aa** as a sole product in 96% yield (40 mg).

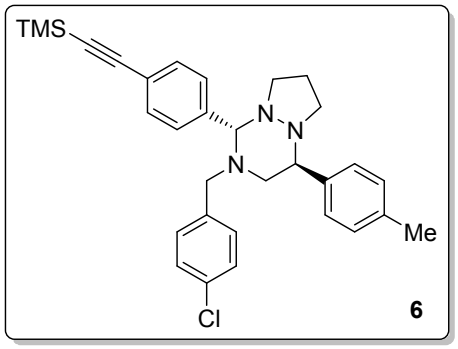


2-(4-Chlorobenzyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4-(*p*-tolyl)he-xahydro-6H-pyrazolo[1,2-a][1,2,4]triazine 4.[7] The cyclo-adduct **3fa** (100 mg, 0.2 mmol), bis(pinacolato)diboron (50 mg, 0.2 mmol), KOAc (40 mg, 0.4 mmol), $Pd(dppf)Cl_2$•CH_2Cl_2 (8 mg, 0.01 mmol) and dry THF (3 mL) were heated to reflux at 100 ^oC for 4 h under nitrogen atmosphere. After completion, the reaction mixture was cooled to room temperature and passed through a short pad of celite with CH_2Cl_2 (15 ml). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as an eluent to give **4**. Analytical TLC on silica gel, 1:16 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 194-195 ^oC; yield 75% (81 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.6 Hz, 2H), 7.56 (s, 2H), 7.19-7.17 (m, 2H),

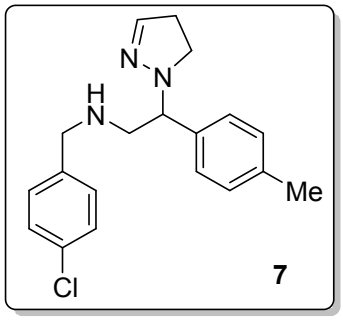
7.09-7.01 (m, 6H), 3.72 (s, 1H), 3.54-3.47 (m, 2H), 2.83-2.76 (m, 3H), 2.45-2.39 (m, 1H), 2.35-2.22 (m, 6H), 1.70-1.63 (m, 2H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 137.6, 137.4, 137.1, 135.1, 132.5, 130.1, 129.1, 128.6, 128.3, 128.0, 89.7, 84.0, 68.1, 59.1, 56.6, 51.9, 50.7, 25.05, 25.02, 22.0, 21.2; FT-IR (KBr) 2977, 2827, 1612, 1489, 1360, 1143, 1016 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{32}H_{40}BClN_3O_2$: 544.2897, found: 544.2893.



2-(4-Chlorobenzyl)-1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo-[1,2-a][1,2,4]triazine 5.[7] The coupled adduct **4** (54 mg, 0.1 mmol), 4-bromoanisole (19 mg, 0.1 mmol), $Pd(PPh_3)_4$ (2.3 mg, 0.002), Na_2CO_3 (22 mg, 0.2 mmol), H_2O (50 μL) and toluene:EtOH (1:1, 2 mL) were heated to reflux at 100 ^oC for 3 h under nitrogen atmosphere. After completion, the reaction mixture was cooled to room temperature and passed through a short pad of celite with CH_2Cl_2 (10 ml). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as an eluent to give **5**. Analytical TLC on silica gel, 1:12 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 173-174 ^oC; yield 82% (43 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.55 (t, *J* = 8.4 Hz, 4H), 7.28-7.26 (m, 2H), 7.17 (s, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.99-6.96 (m, 2H), 3.85-3.83 (m, 4H), 3.70 (d, *J* = 13.6 Hz, 1H), 3.63-3.60 (m, 1H), 2.93-2.87 (m, 3H), 2.61-2.56 (m, 1H), 2.48-2.41 (m, 1H), 2.38-2.31 (m, 5H), 1.80-1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 141.3, 137.8, 137.6, 137.1, 133.3, 132.5, 130.0, 129.5, 129.1, 128.3, 128.2, 128.0, 126.8, 114.3, 89.4, 68.1, 59.1, 56.7, 55.4, 52.0, 50.9, 22.0, 21.2; FT-IR (KBr) 3831, 1610, 1496, 1248, 1180, 1128, 1015 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{33}H_{35}ClN_3O$: 524.2463, found: 524.2463.



2-(4-Chlorobenzyl)-4-(*p*-tolyl)-1-(4-((trimethylsilyl)ethynyl)phenyl)hexahydro-6H-pyrazolo-[1,2-a][1,2,4]triazine 6.[7] The cyclo-adduct **3fa** (50 mg, 0.1 mmol), trimethylsilylacetylene (12 mg, 0.12 mmol), CuI (2 mg, 0.01 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005) and dry THF/Et_3N (1:1, 2 mL) were heated to reflux at 100 ^oC for 12 h under nitrogen atmosphere. After completion, the reaction mixture was cooled to room temperature and passed through a short pad of celite with CH_2Cl_2 (10 ml). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as an eluent to give **5**. Analytical TLC on silica gel, 1:24 ethyl acetate/hexane R_f = 0.46; thick liquid; yield 71% (36 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 2H), 7.50-7.48 (m, 2H), 7.26-7.23 (m, 2H), 7.17-7.15 (m, 2H), 7.11-7.08 (m, 4H), 3.76 (s, 1H), 3.58-3.52 (m, 2H), 2.89-2.83 (m, 3H), 2.50-2.45 (m, 1H), 2.40-2.27 (m, 6H), 1.78-1.70 (m, 2H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 137.6, 137.2, 137.0, 132.6, 132.3, 130.0, 129.19, 129.13, 128.4, 127.9, 123.7, 104.8, 94.9, 89.2, 68.0, 59.0, 56.6, 51.9, 50.7, 22.0, 21.2, 0.09; FT-IR (neat) 2828, 2157, 1634, 1490, 1249, 1128, 1015 cm-1; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{37}ClN_3Si$: 514.2440, found: 514.2444.



***N*-(4-Chlorobenzyl)-2-(4,5-dihydro-1H-pyrazol-1-yl)-2-(*p*-tolyl)ethan-1-amine 7**.

1-(4-Bromophenyl)-2-(4-chlorobenzyl)-4-(*p*-tolyl)hexahydro-6H-pyrazolo[1,2-a][1,2,4]triazine **3fa** (50 mg, 0.1 mmol) and TFA (2 mL) were stirred at 70 ^oC for 2 h under air. The reaction mixture

was then cooled to room temperature and diluted with ethyl acetate (5 mL). The resultant solution was treated with saturated aq. $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (3×10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to give **7**. Analytical TLC on silica gel, 1:1 ethyl acetate/hexane R_f = 0.42; thick liquid; yield 63% (21 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.11 (m, 6H), 7.06-7.04 (m, 2H), 6.699-6.690 (m, 1H), 3.94-3.91 (m, 1H), 3.75-3.68 (m, 2H), 3.37-3.32 (m, 1H), 2.91-2.87 (m, 1H), 2.78-2.73 (m, 2H), 2.52-2.37 (m, 2H), 2.25 (s, 3H), 1.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 139.0, 137.4, 136.2, 132.5, 129.5, 129.1, 128.57, 128.54, 68.0, 53.7, 53.2, 50.7, 33.3, 21.2; FT-IR (neat) 3320, 2919, 2839, 1490, 1407, 1286, 1088, 1014 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{23}ClN_3$: 328.1575, found: 328.1593.

Large-scale Preparation of 3aa. 6-Phenyl-1,5-diazabicyclo[3.1.0]hexane **1a** (800 mg, 5 mmol), 1-(4-chlorobenzyl)-2-(*p*-tolyl)aziridine **2a** (1288 mg, 5 mmol) and $FeCl_3$ (81 mg, 0.5 mmol) were stirred in dichloromethane (50 mL) at room temperature (25 ^{o}C) for 5 minutes. Next, the reaction mixture was diluted with dichloromethane (20 mL) and passed through a short pad of celite using dichloromethane (100 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and hexane as an eluent to yield **3aa** in 86% yield (1.8 g).

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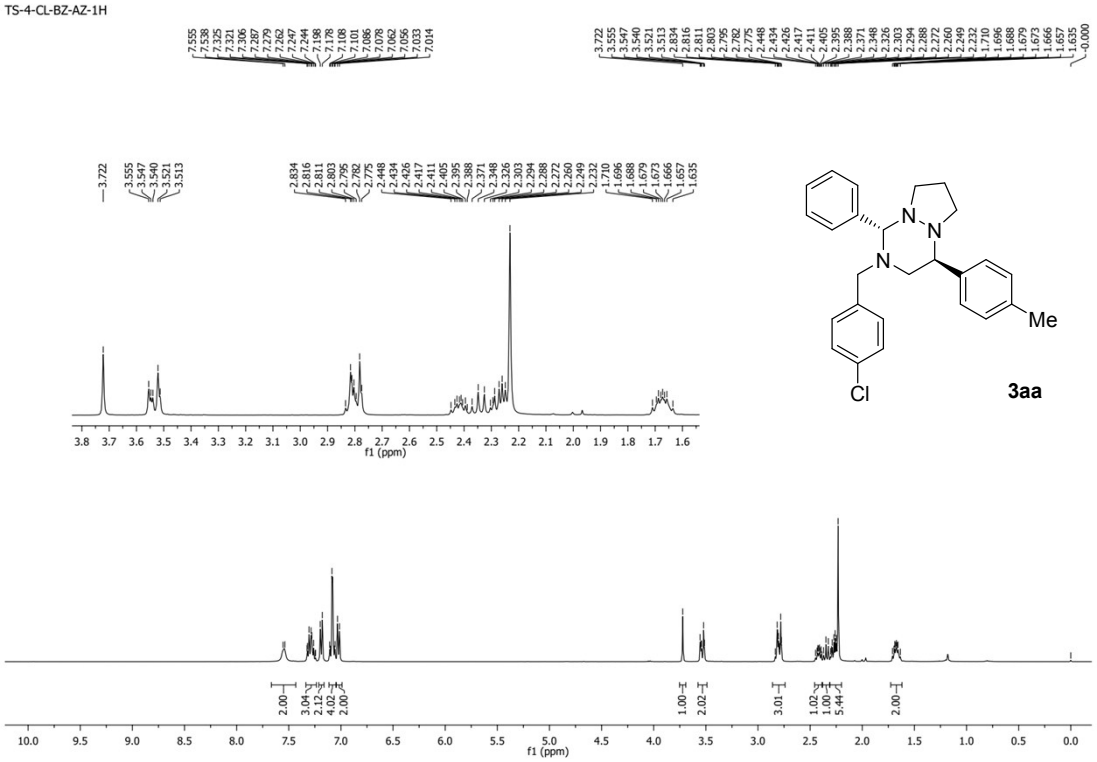
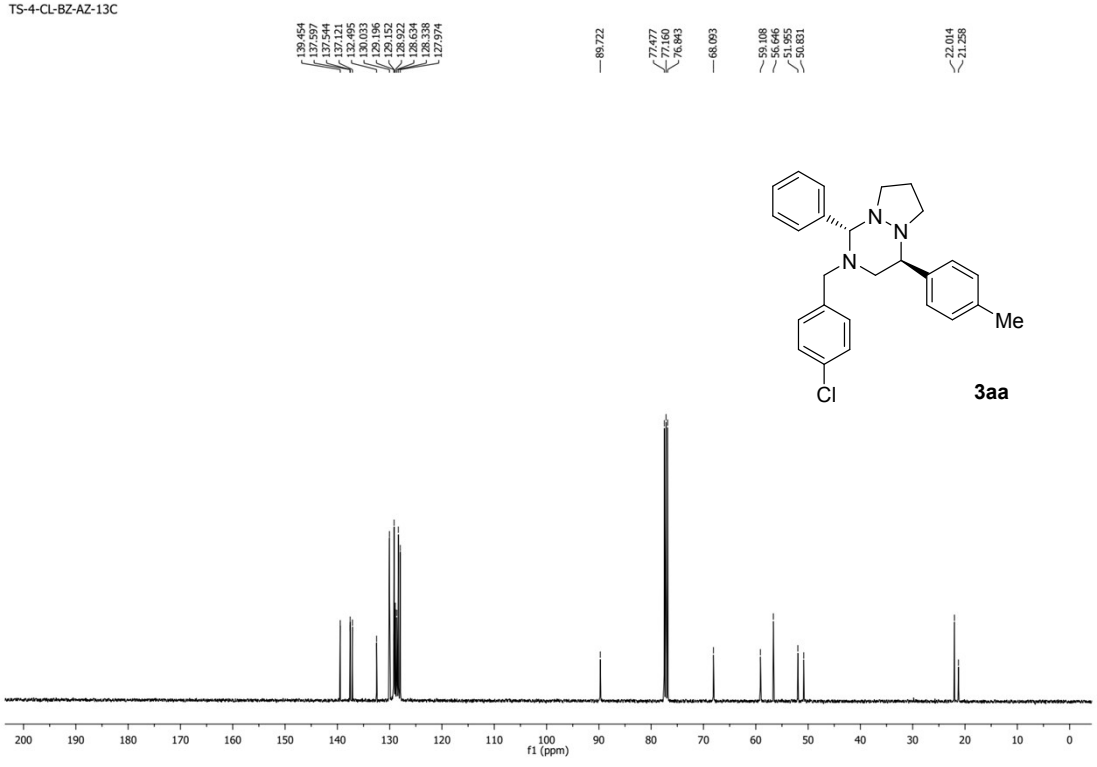
NMR Spectra

TS-4-CL-BZ-AZ-1H



TS-4-CL-BZ-AZ-13C



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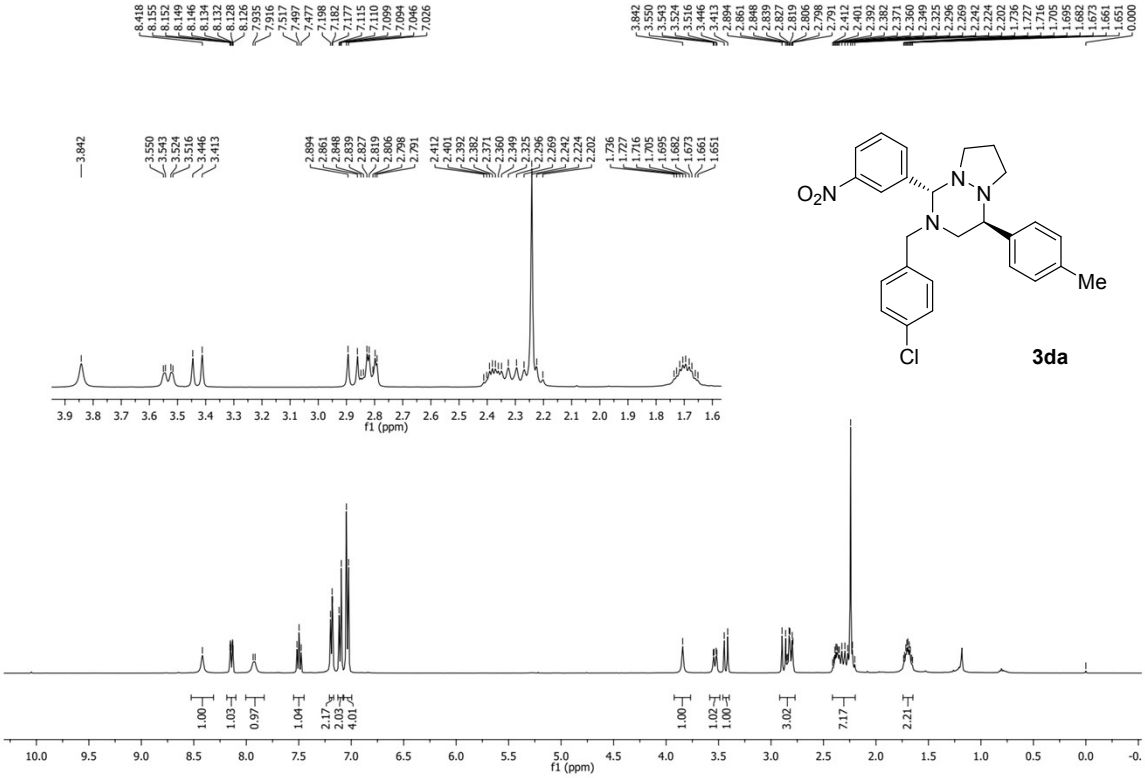

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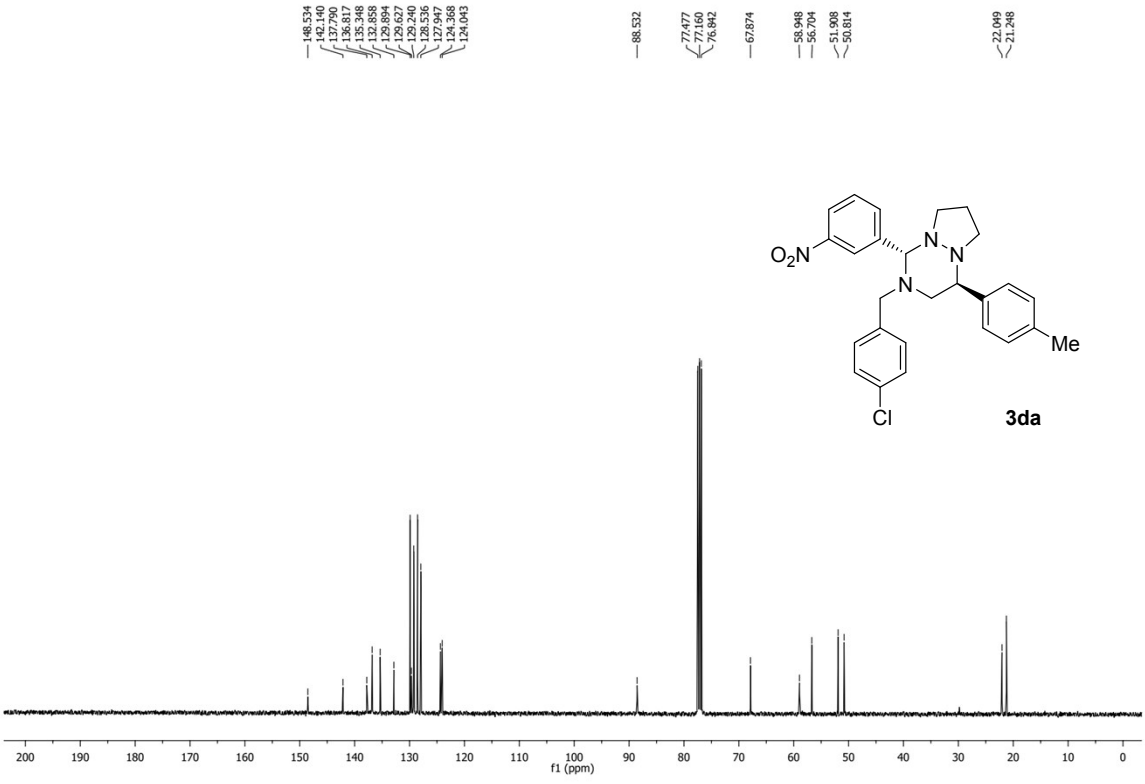

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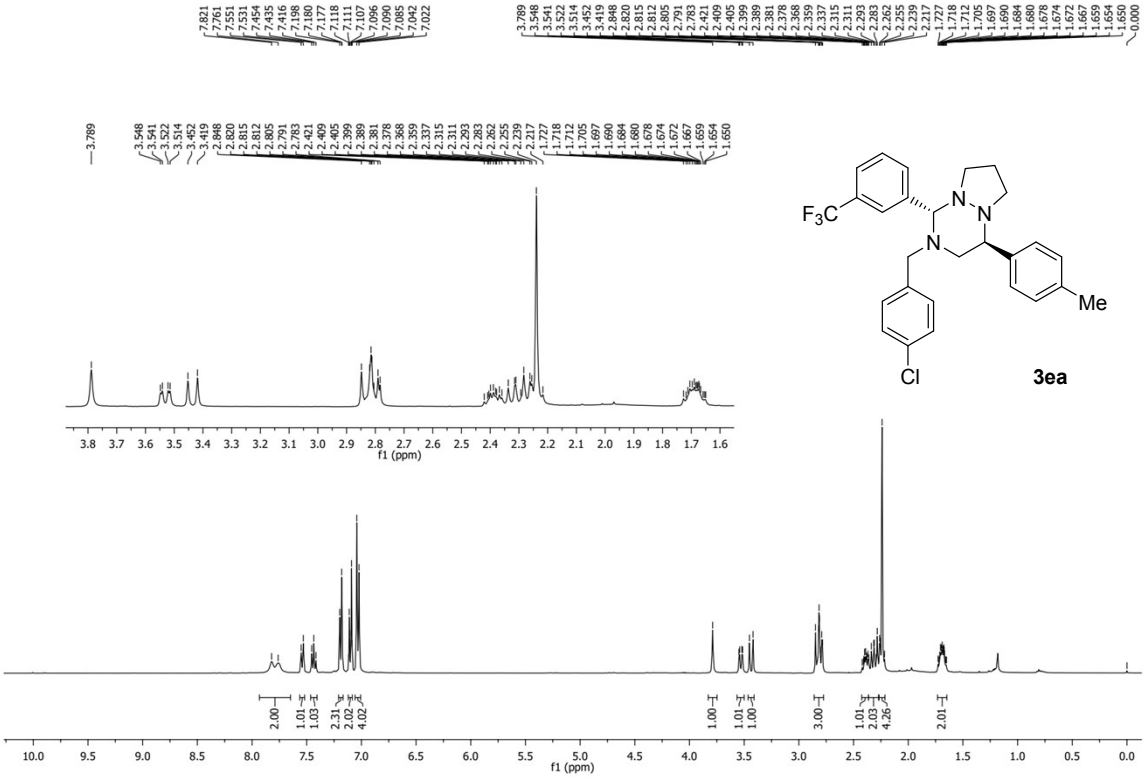

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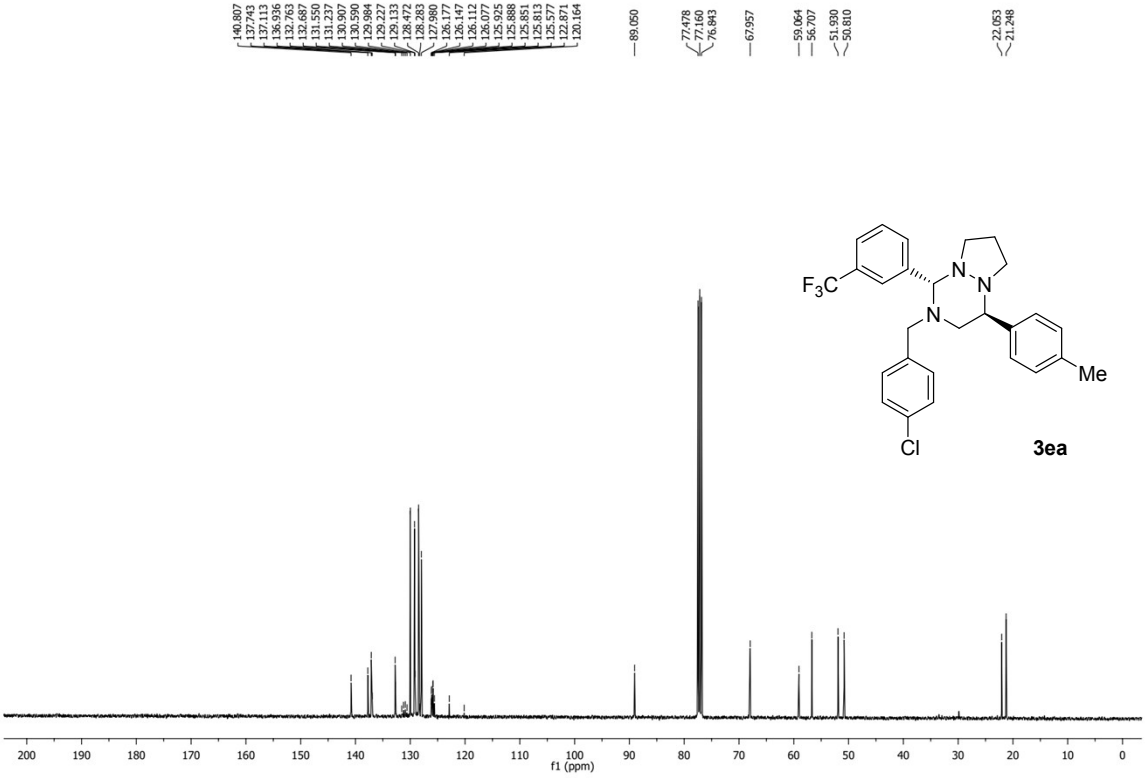

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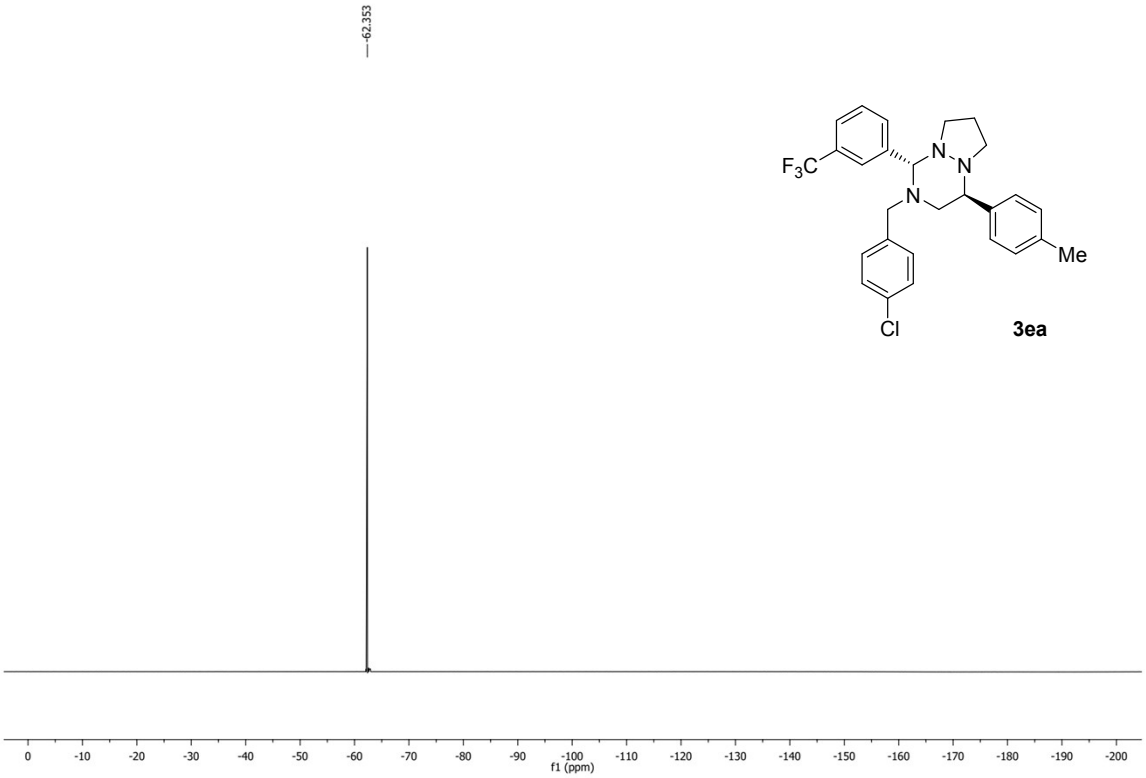

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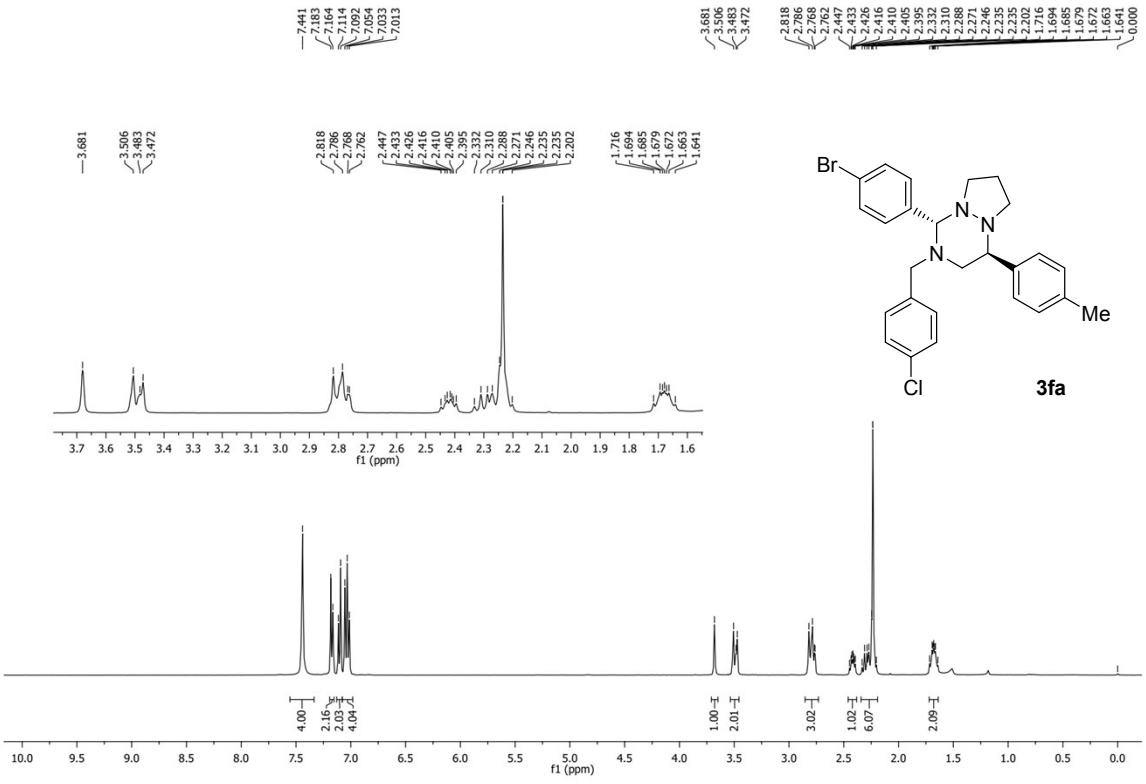

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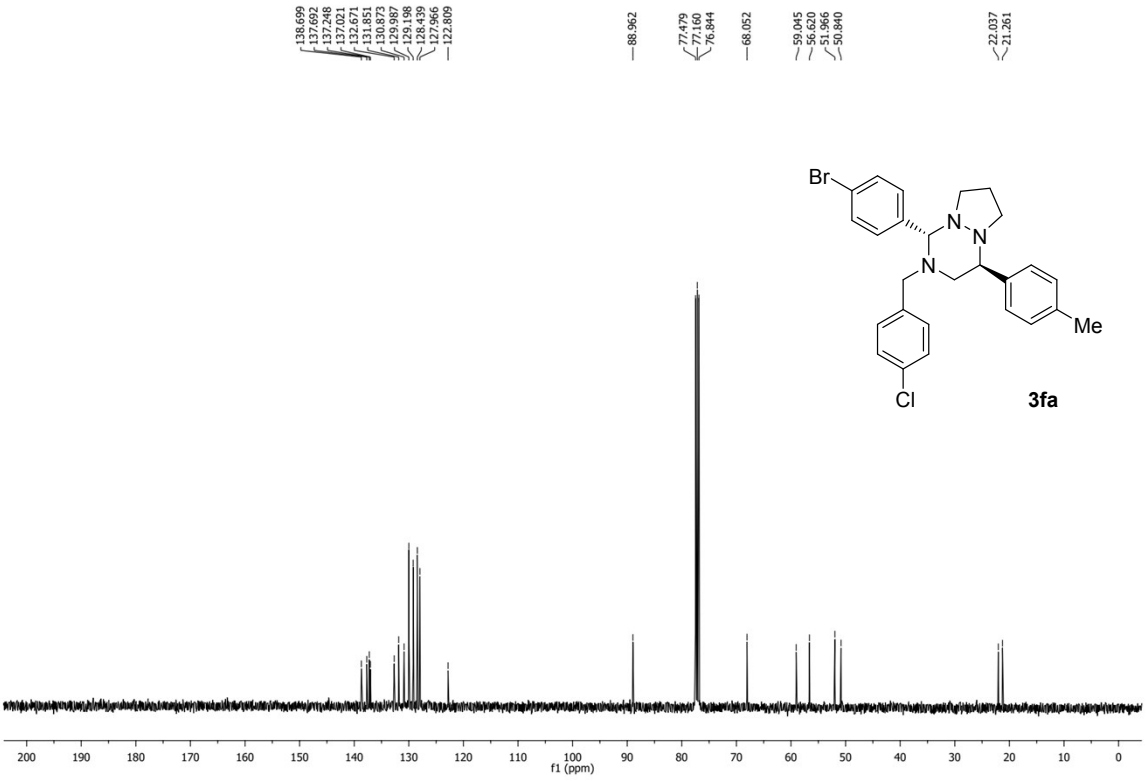

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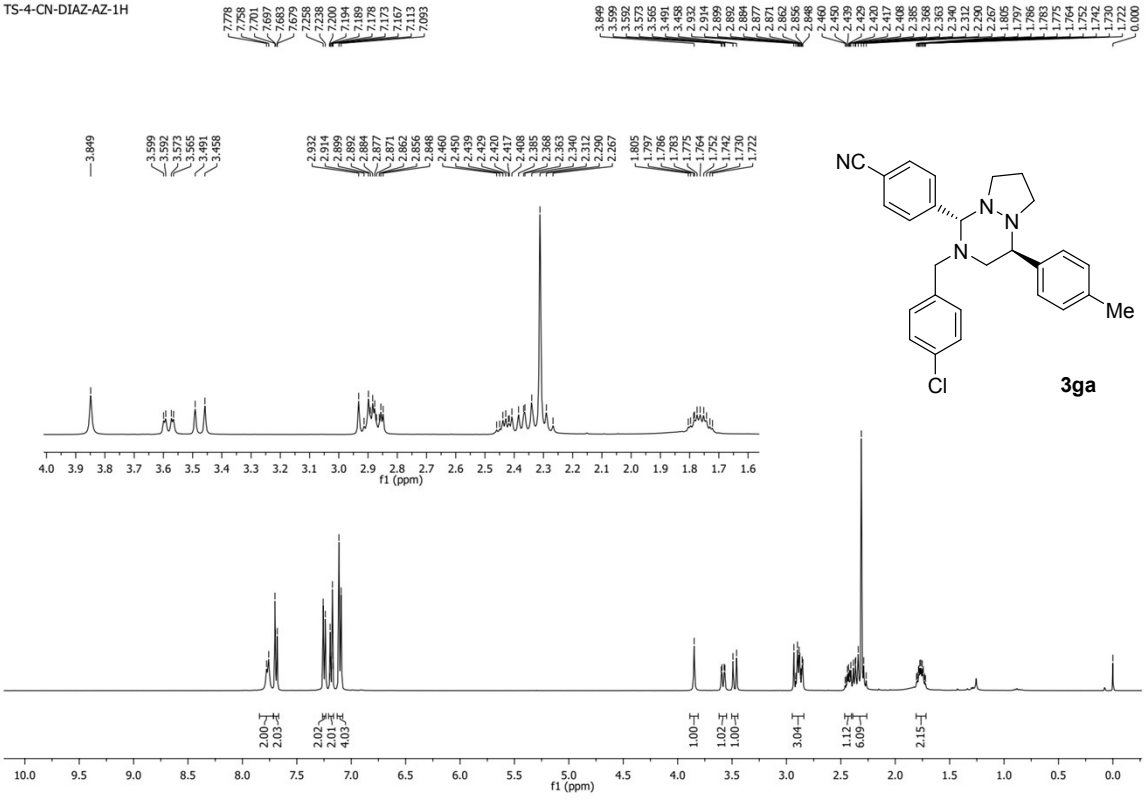

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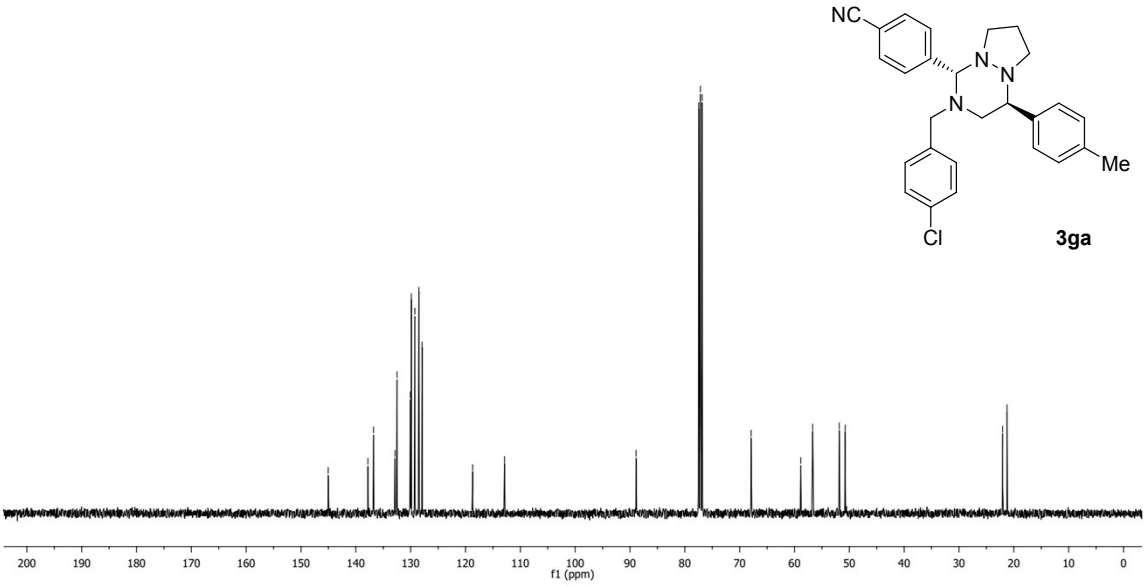

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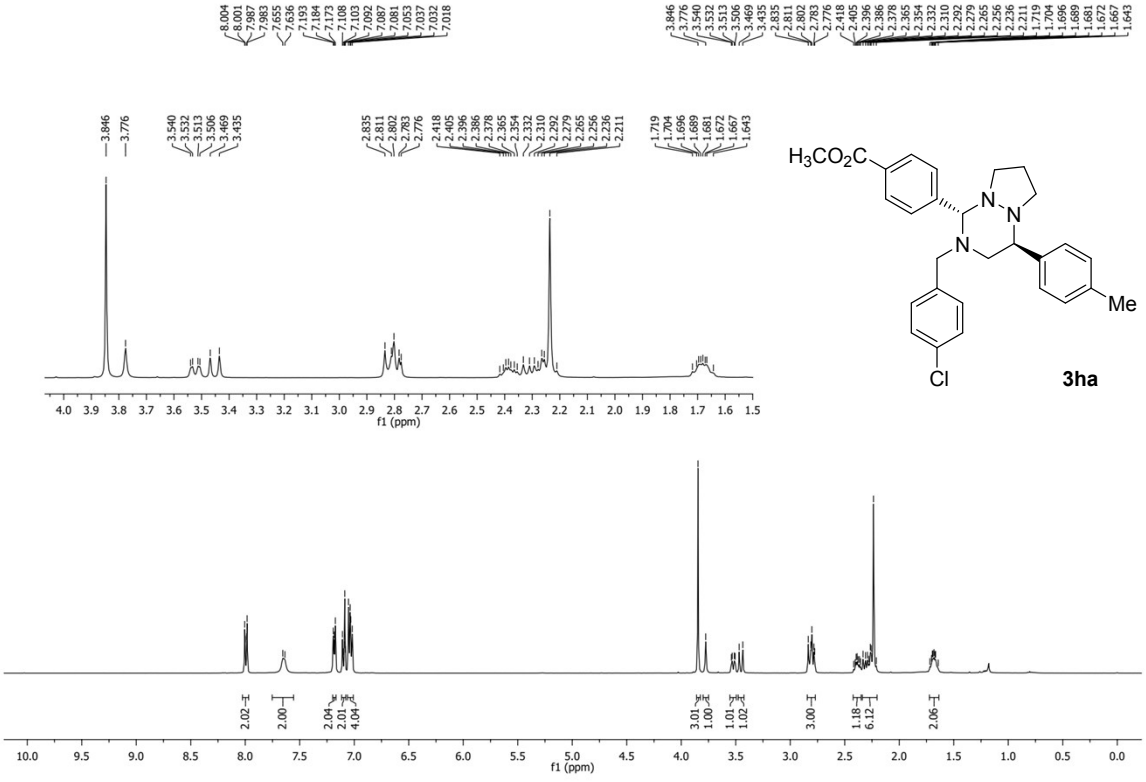

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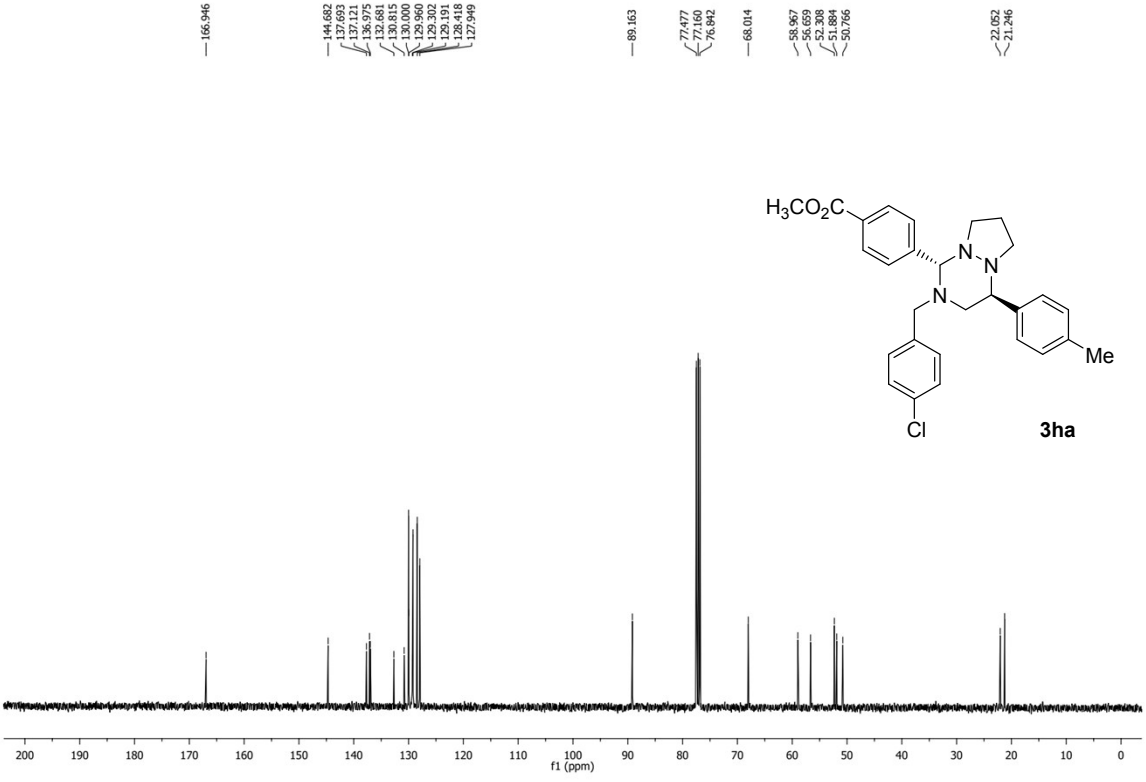

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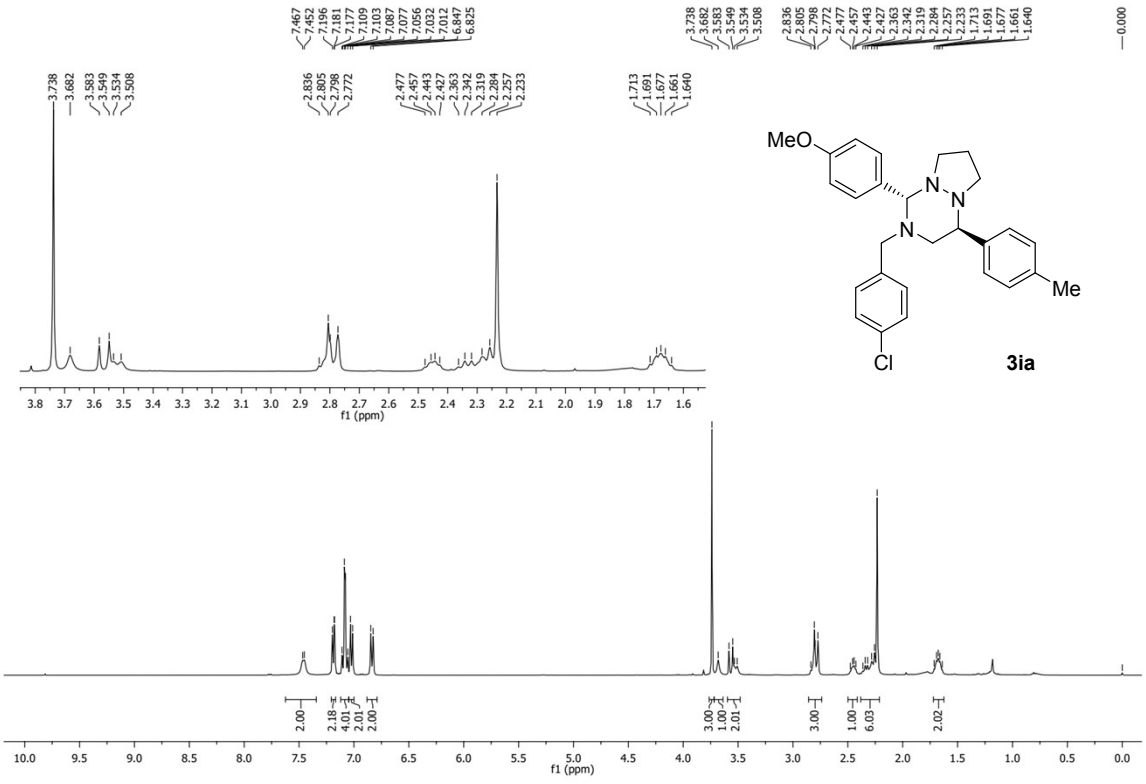

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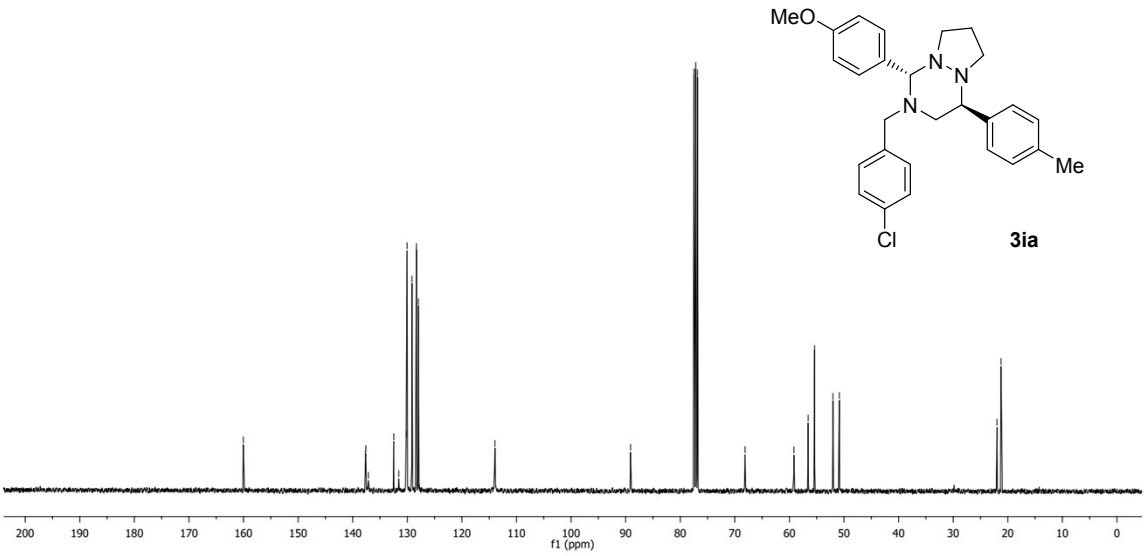

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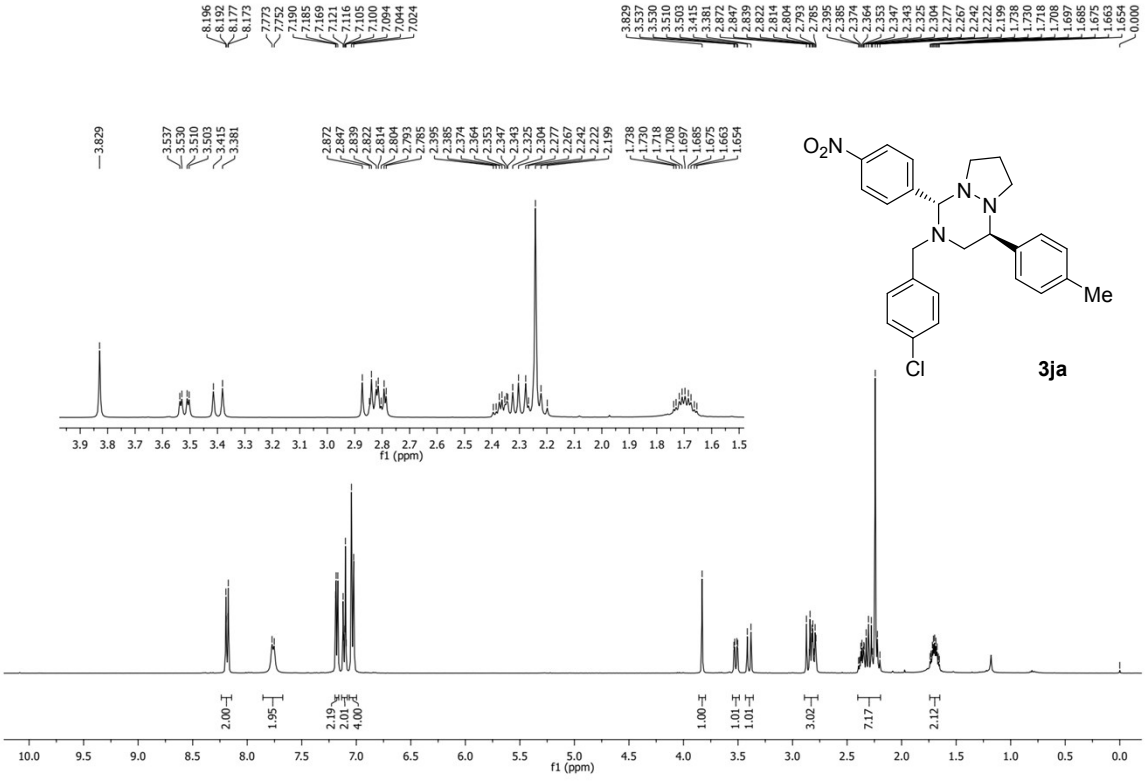

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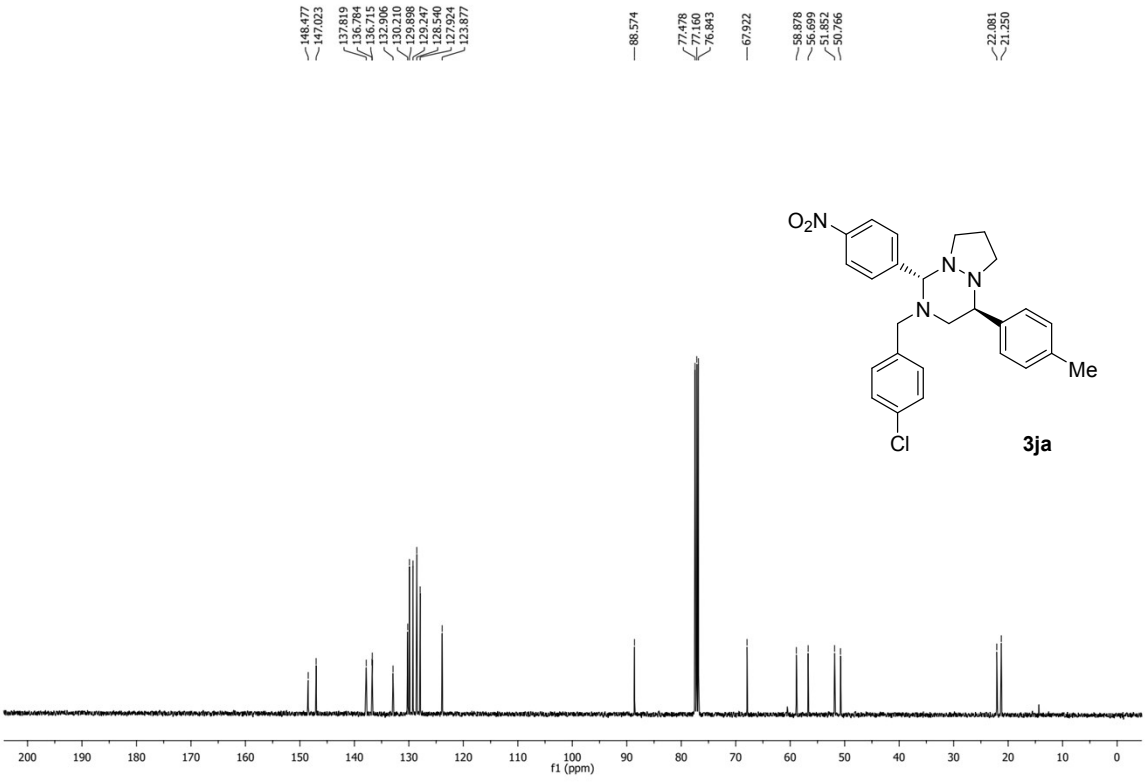

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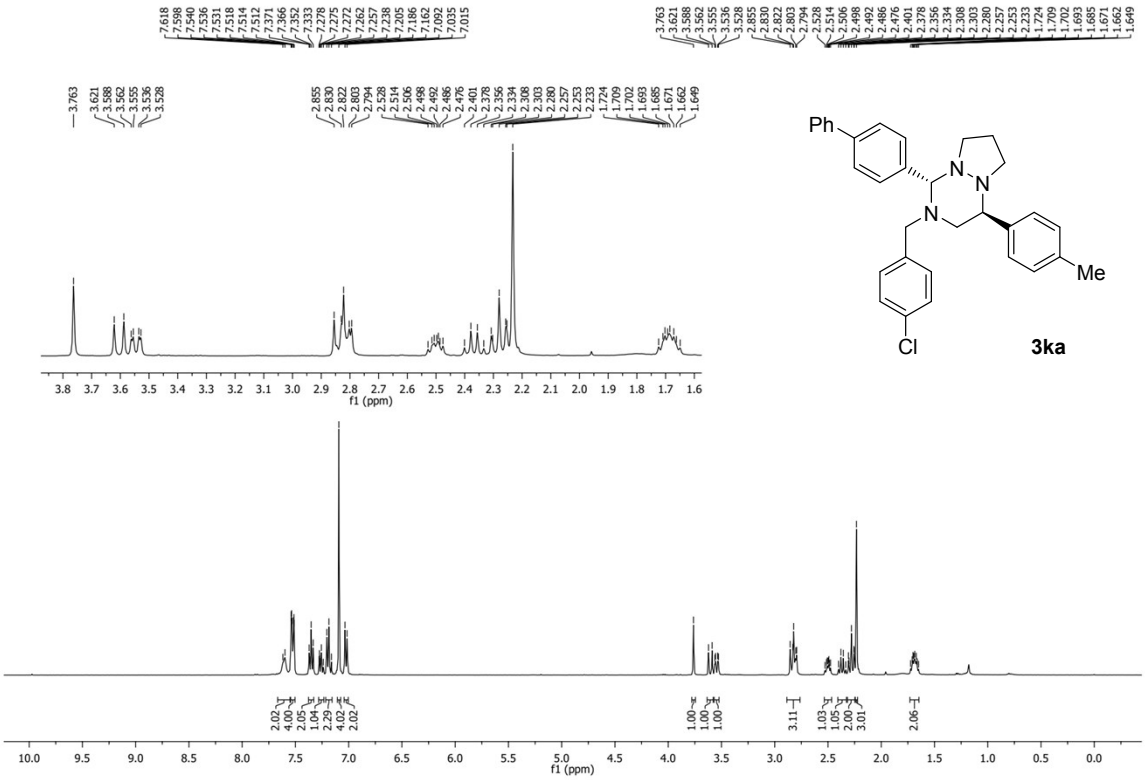

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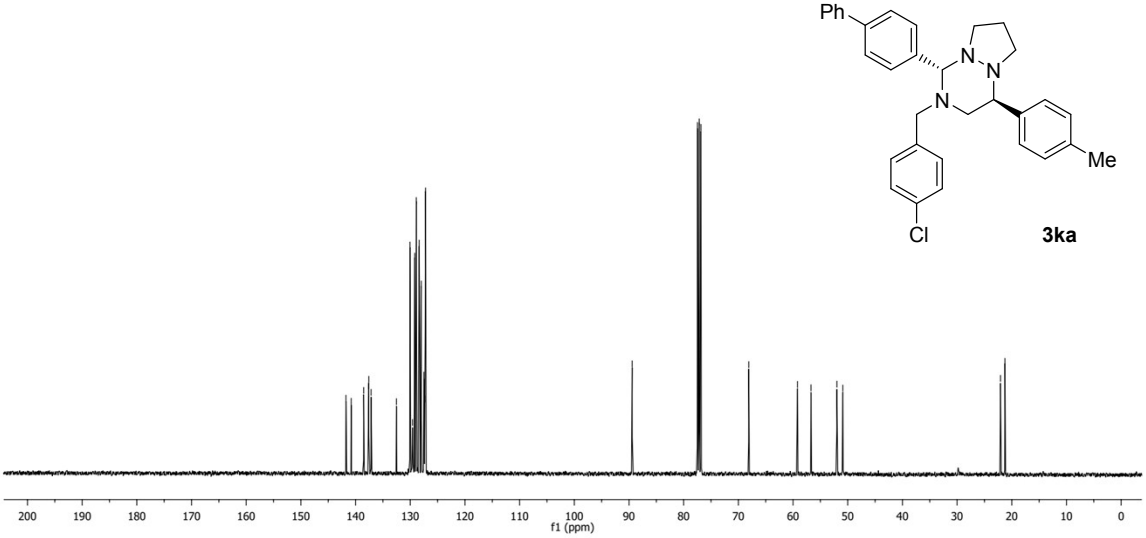

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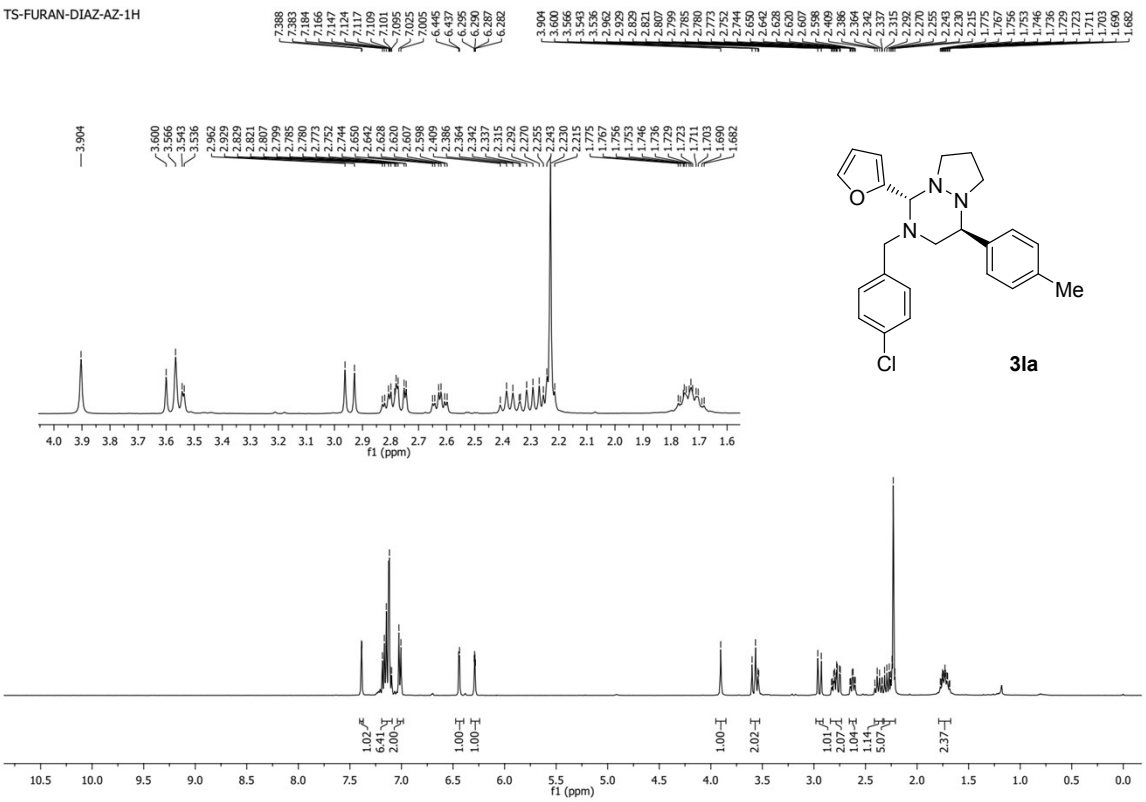

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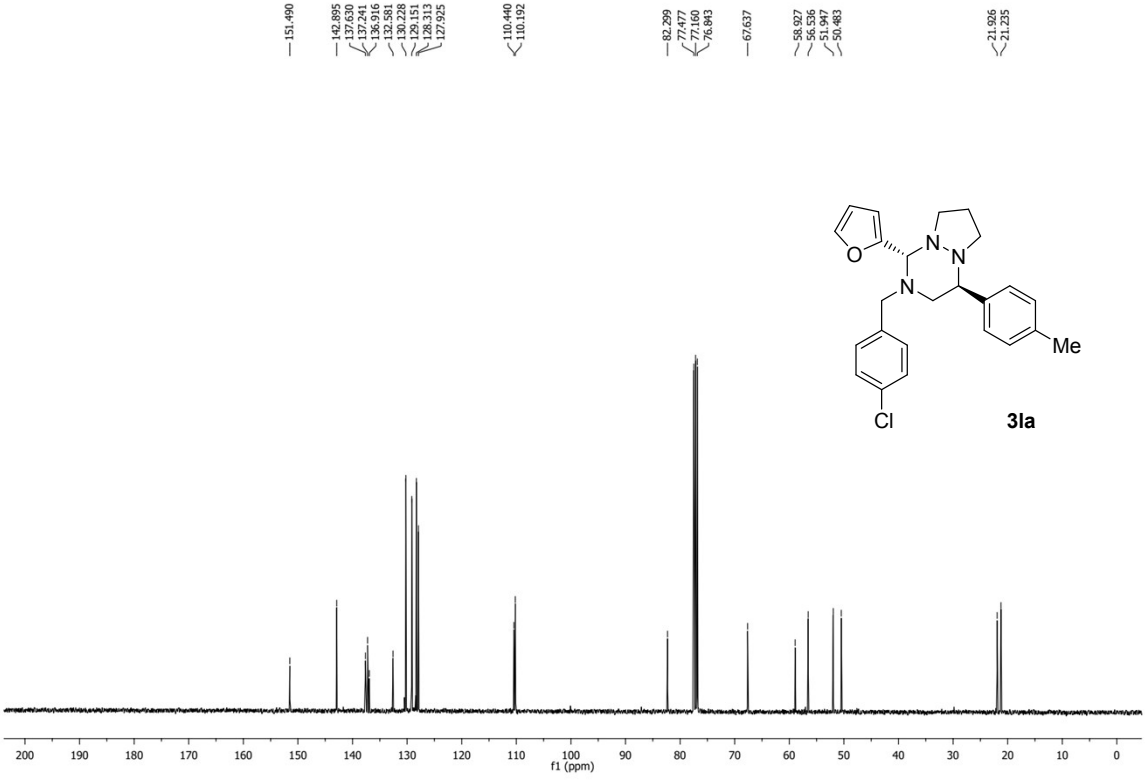

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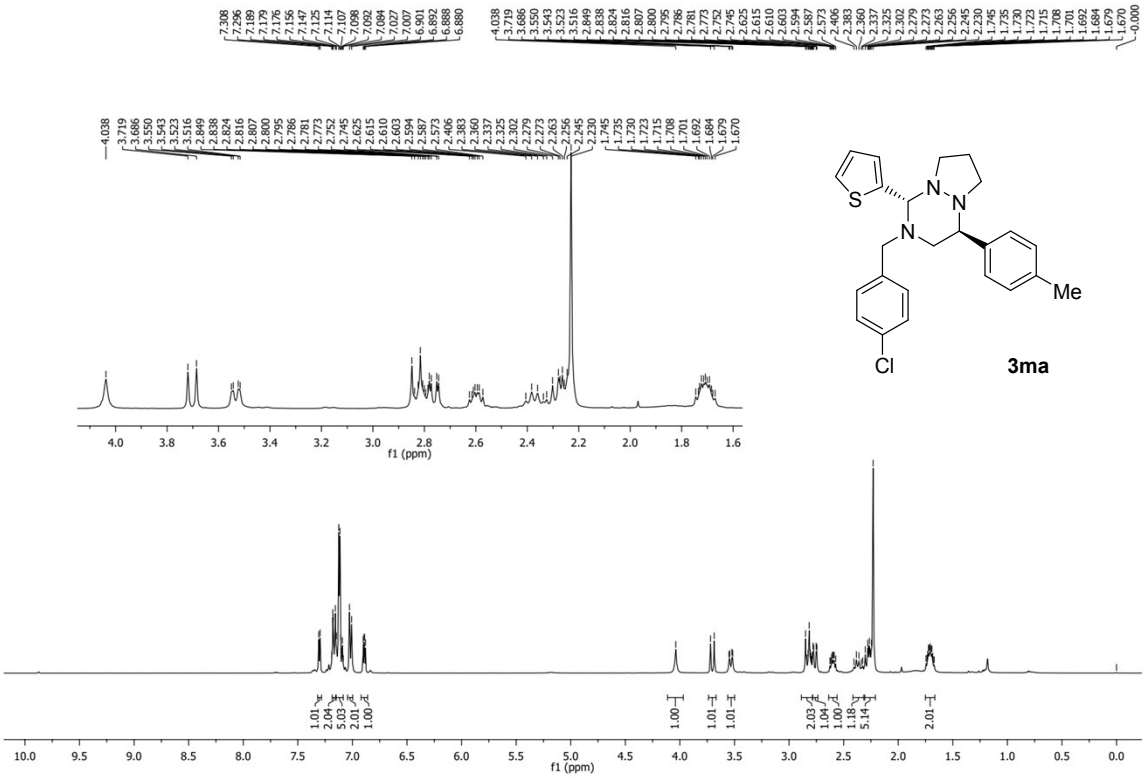
TS-2-THIO-DIAZ-AZ-1H



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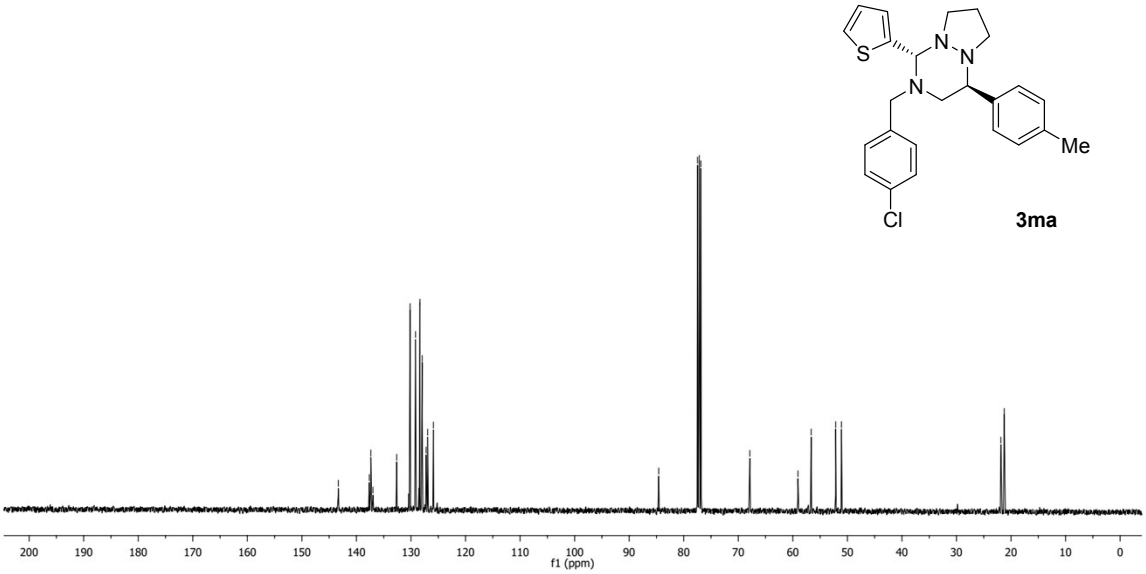
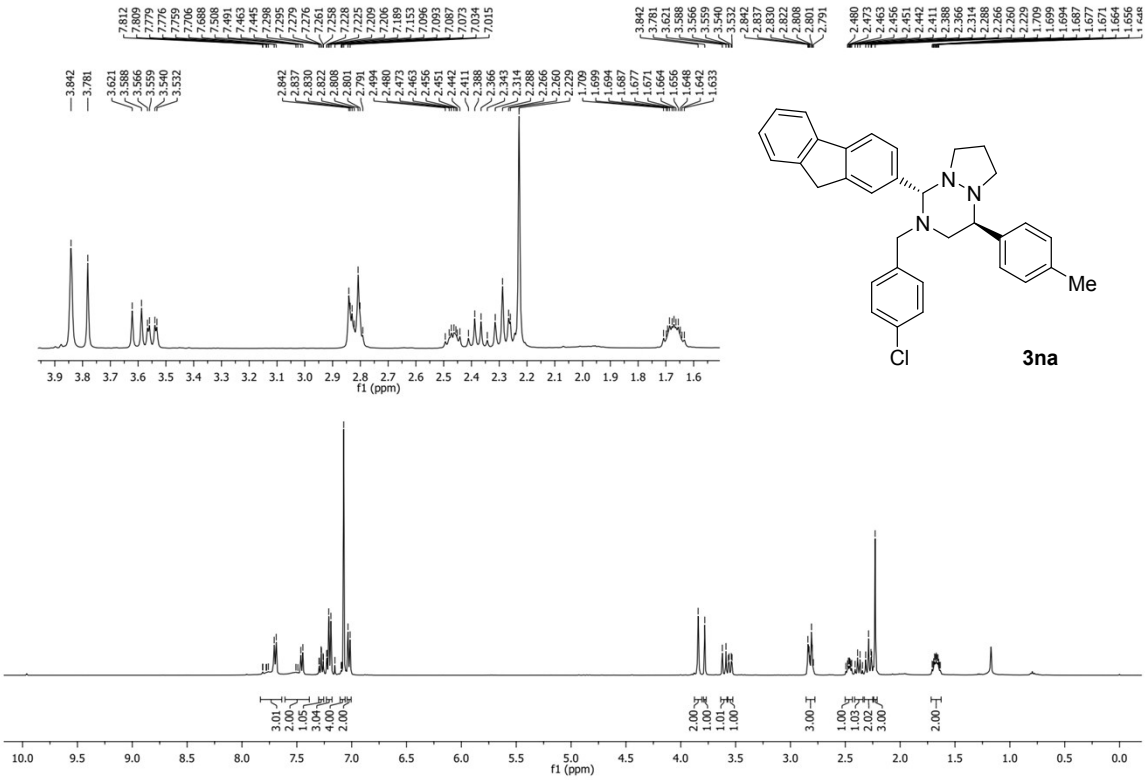


TS-FLUORENE-DIAZ-AZ



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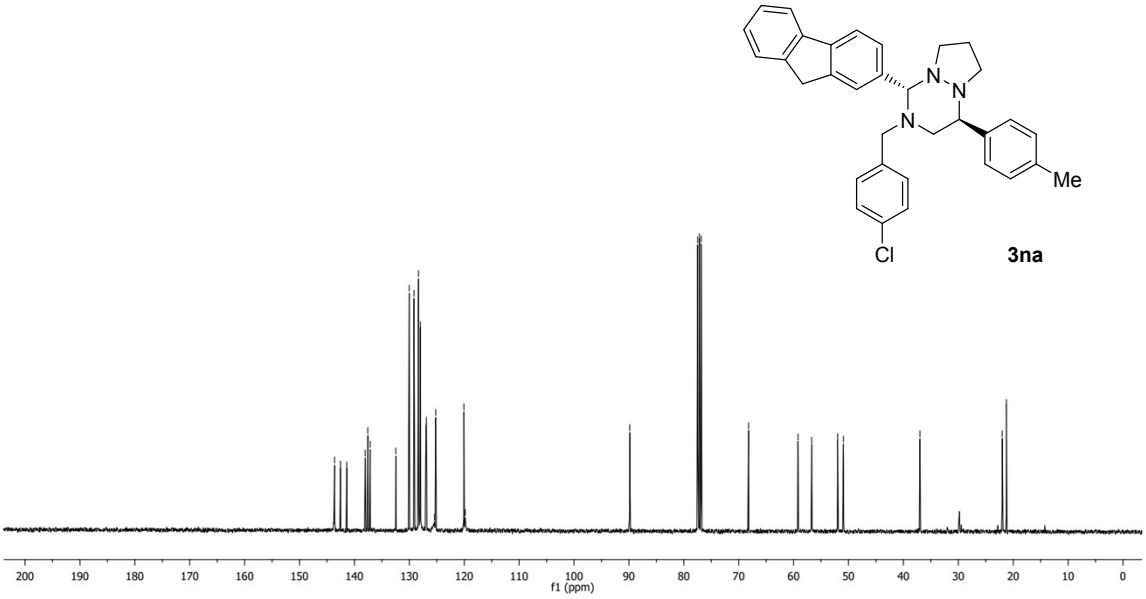

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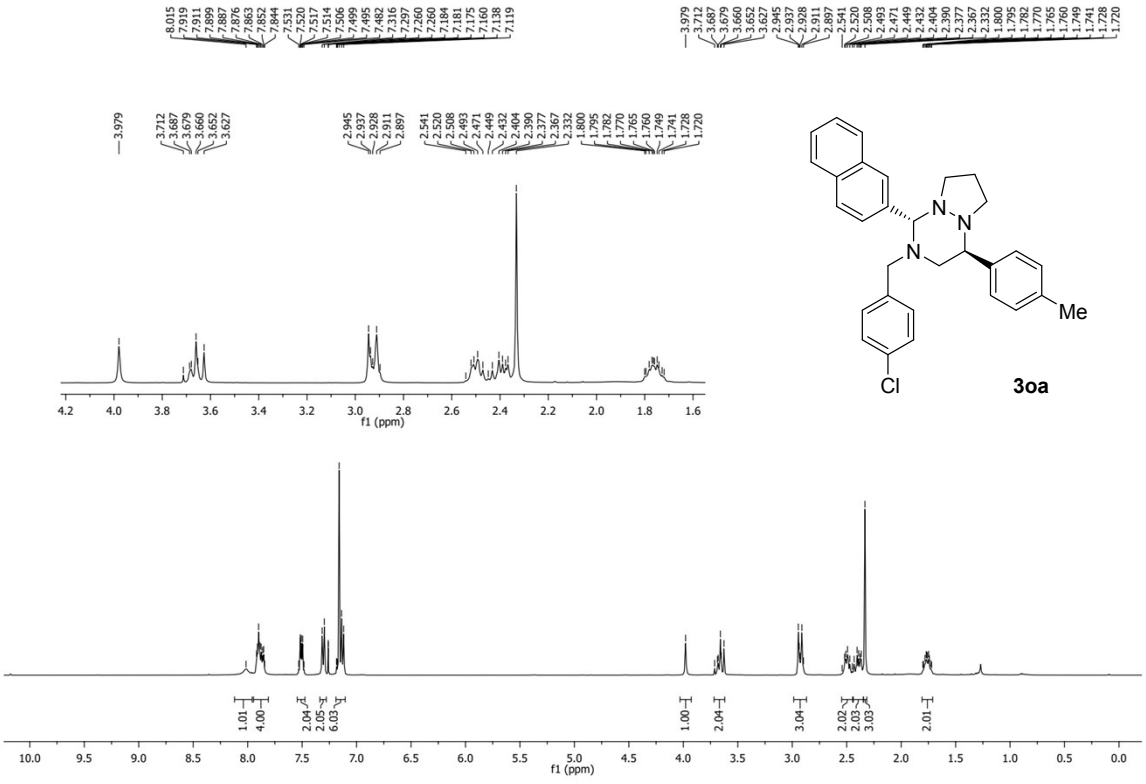

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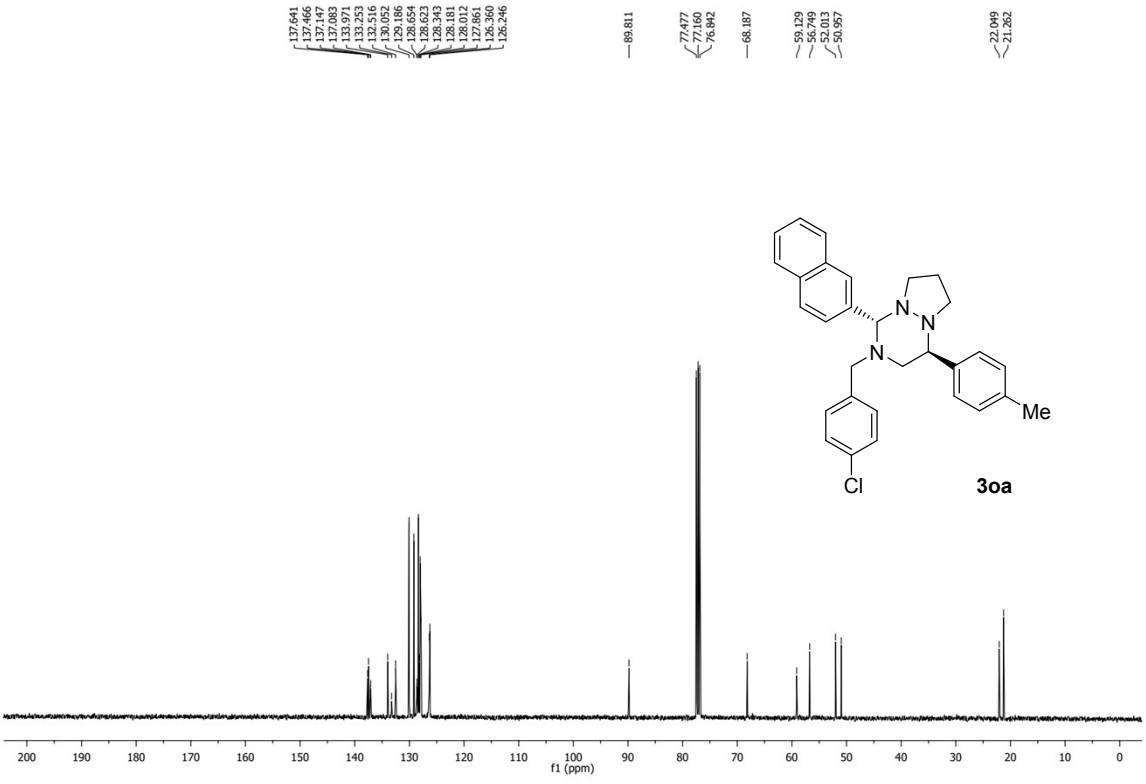

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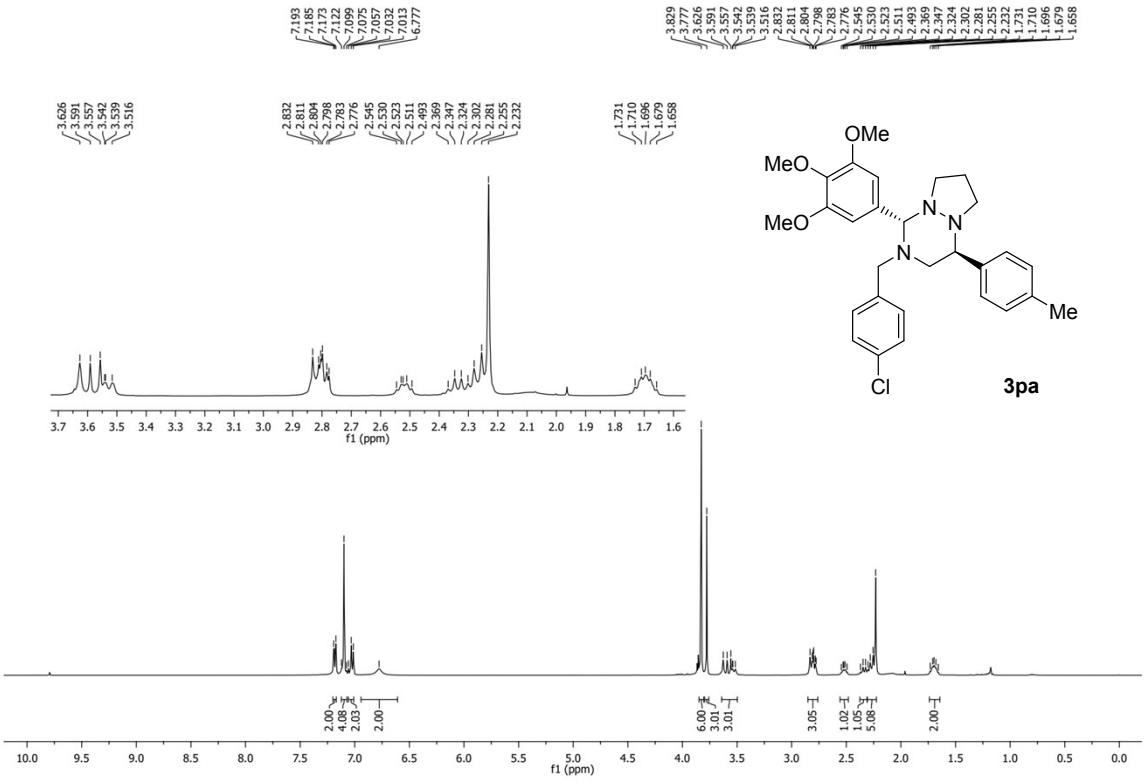

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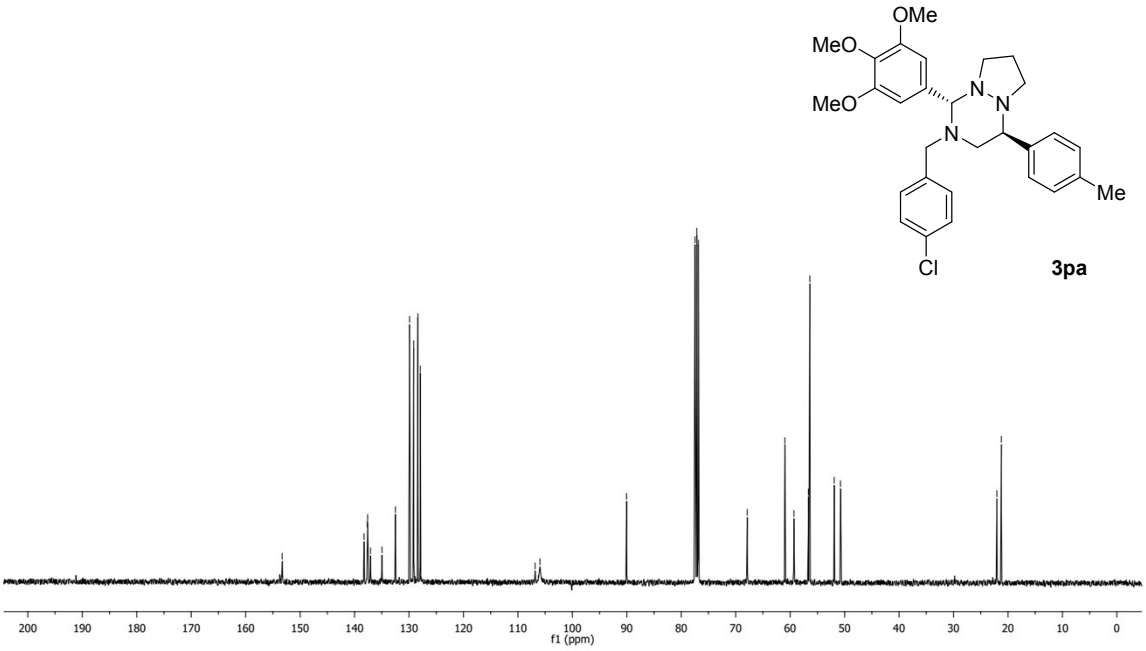

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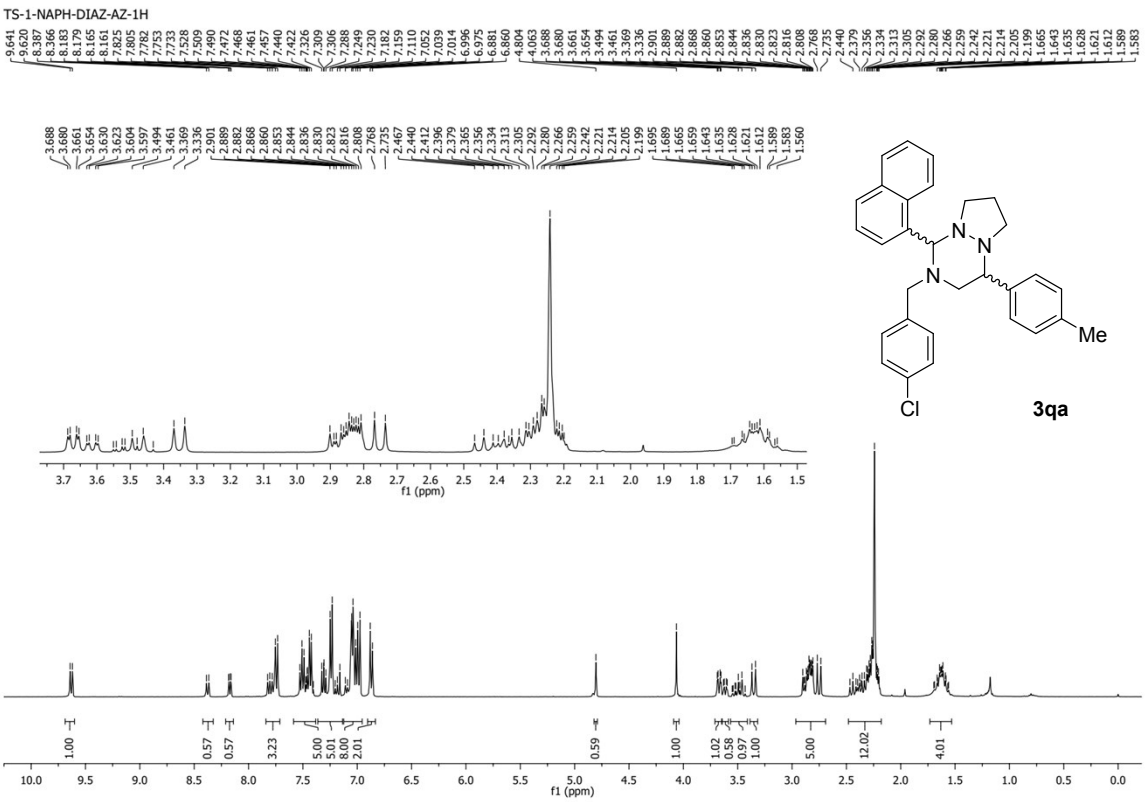

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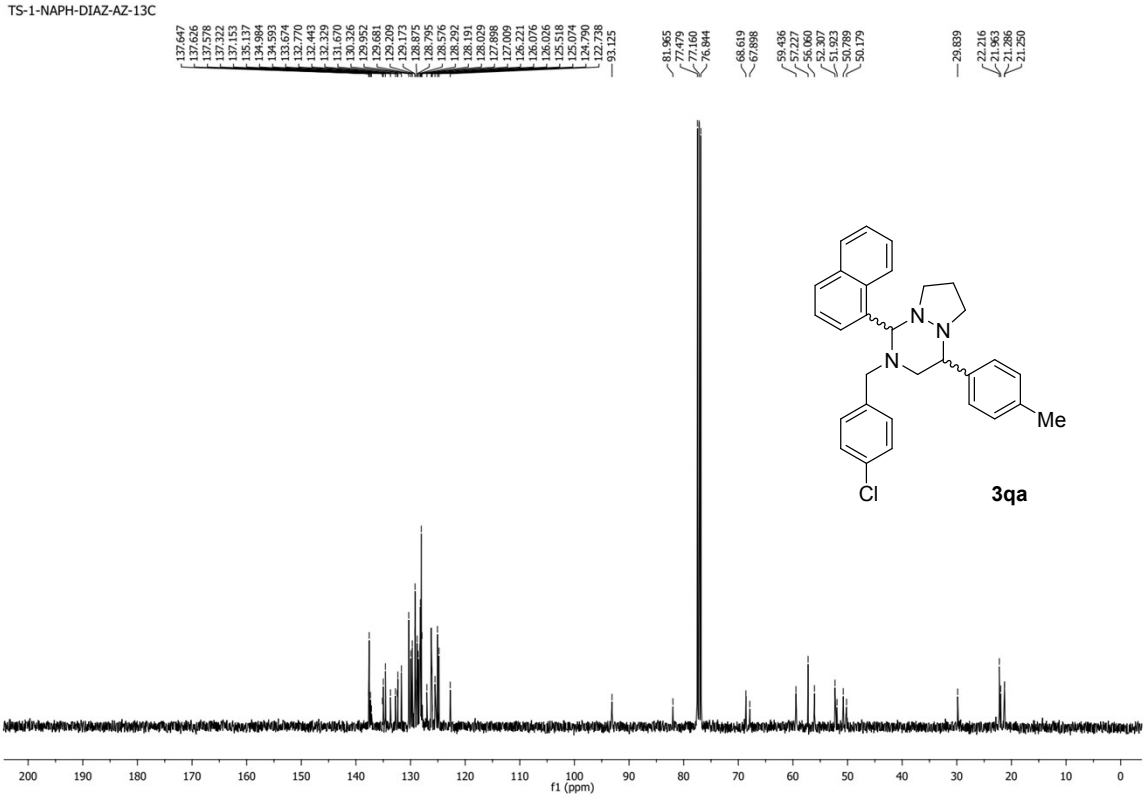

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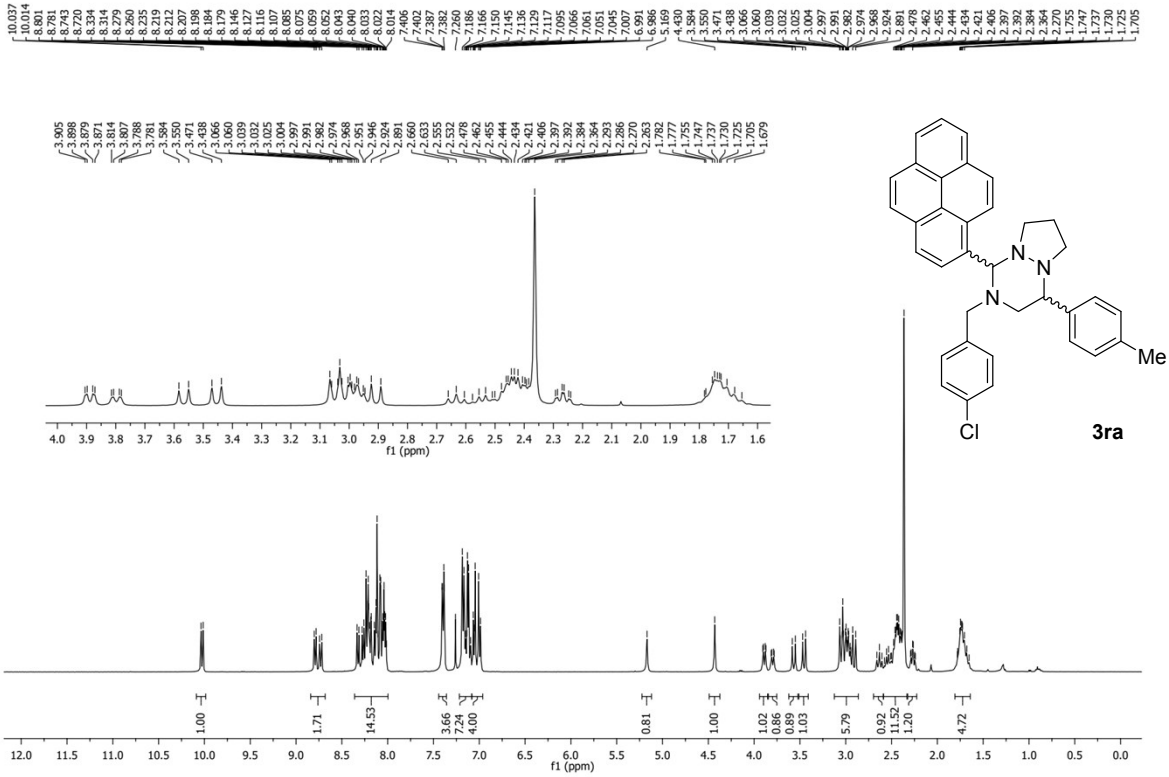

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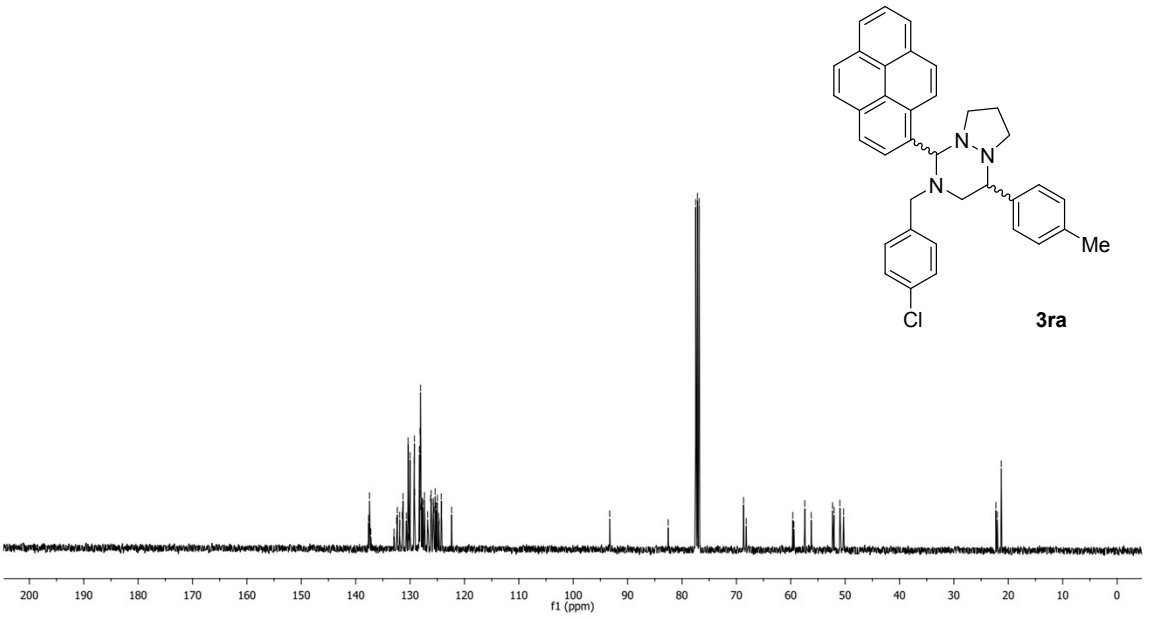

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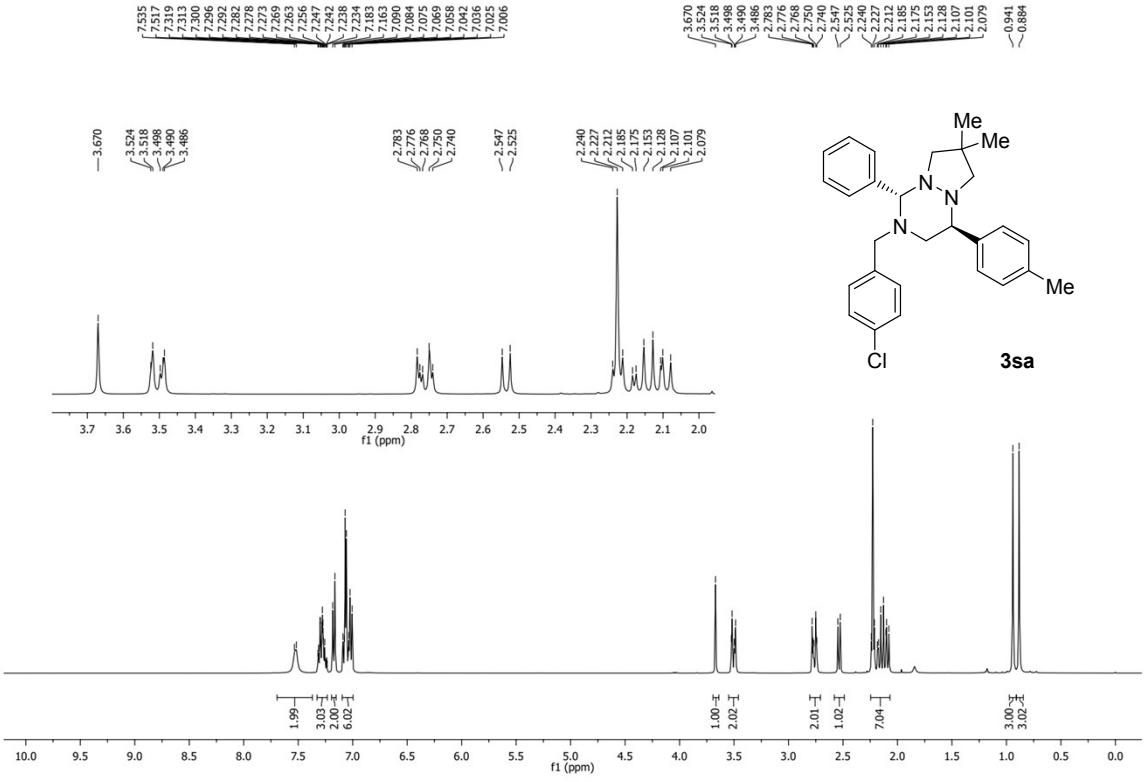

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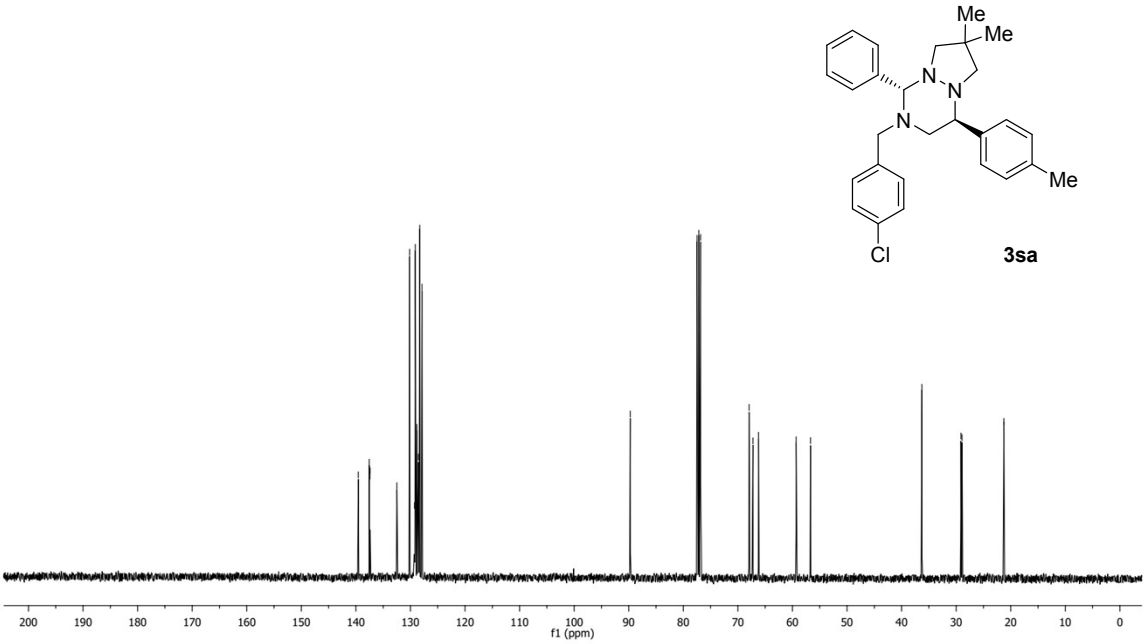

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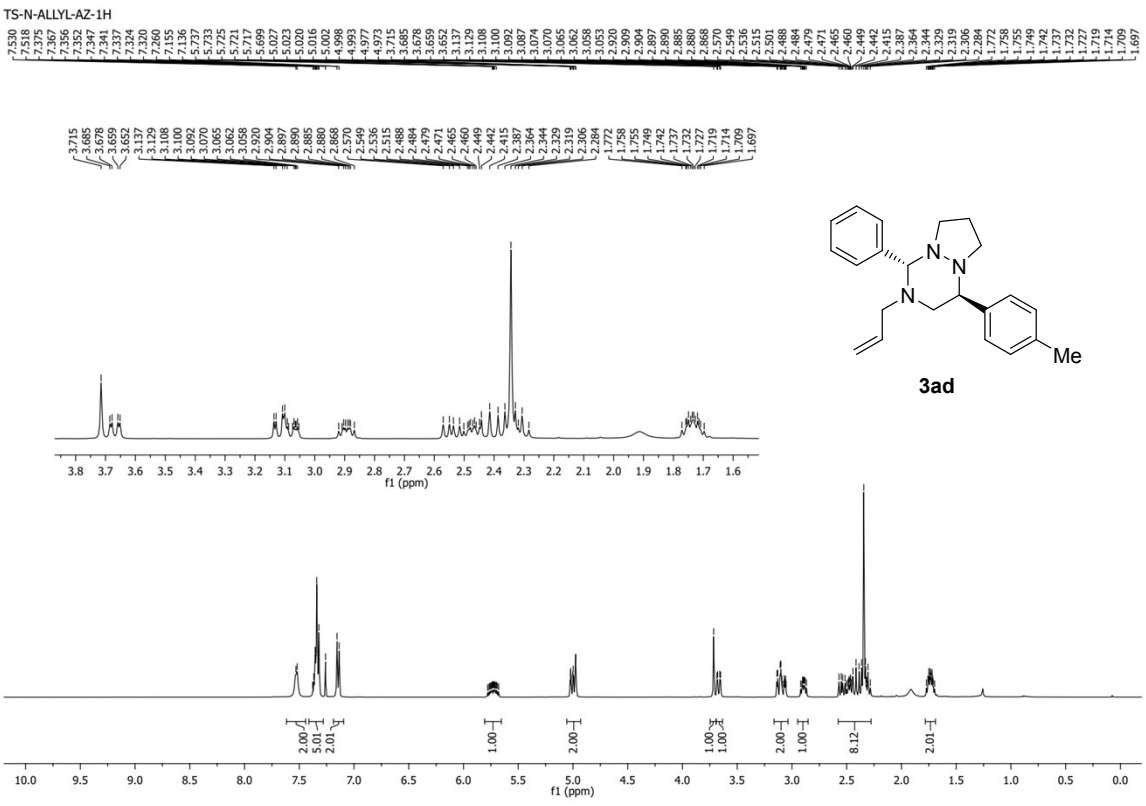

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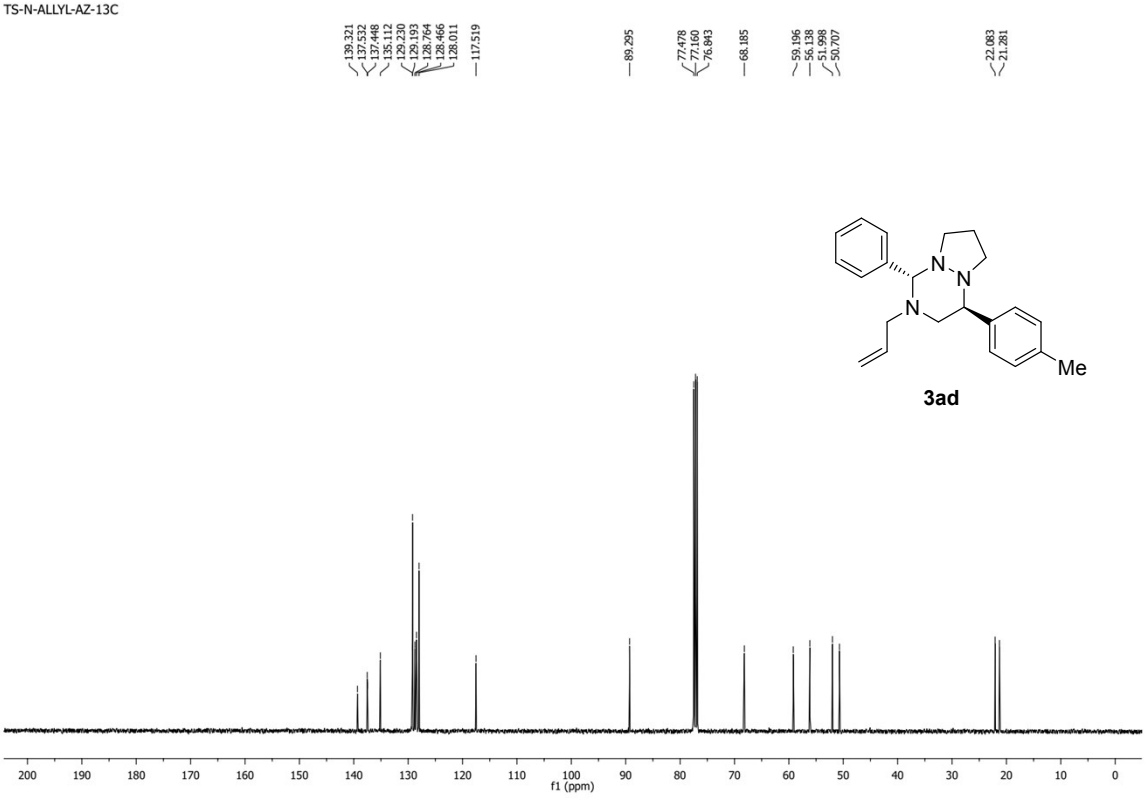

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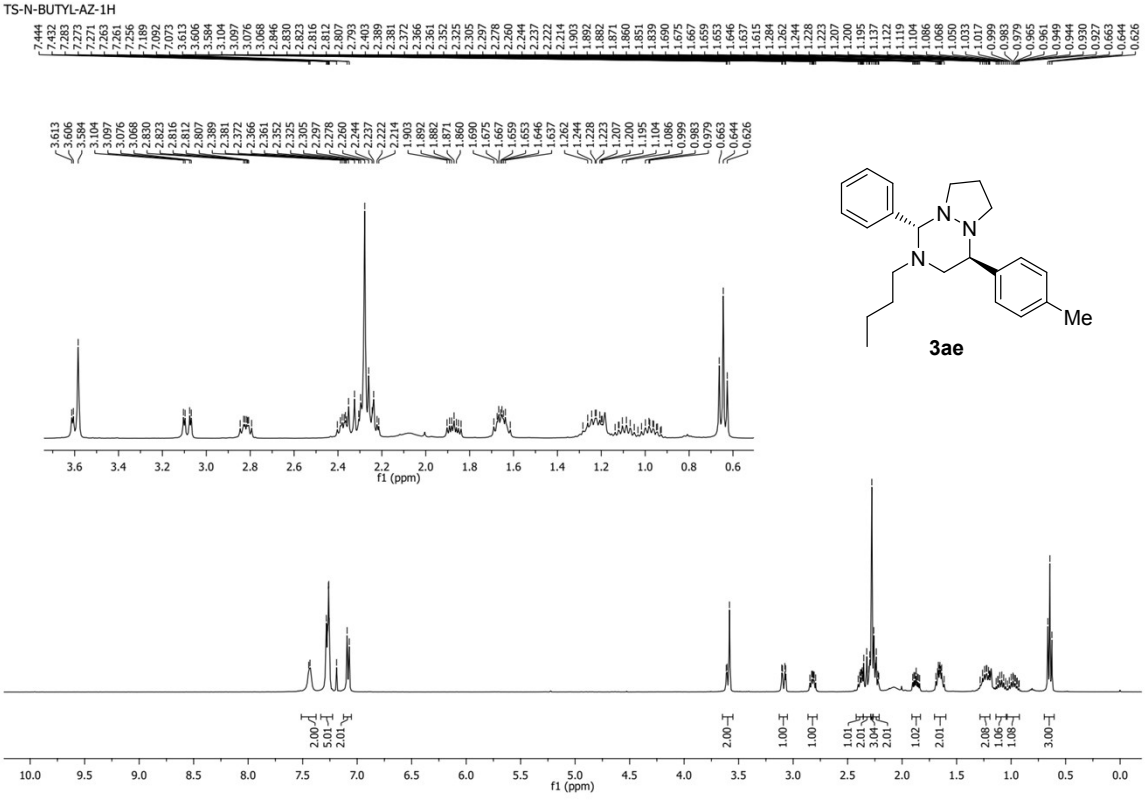

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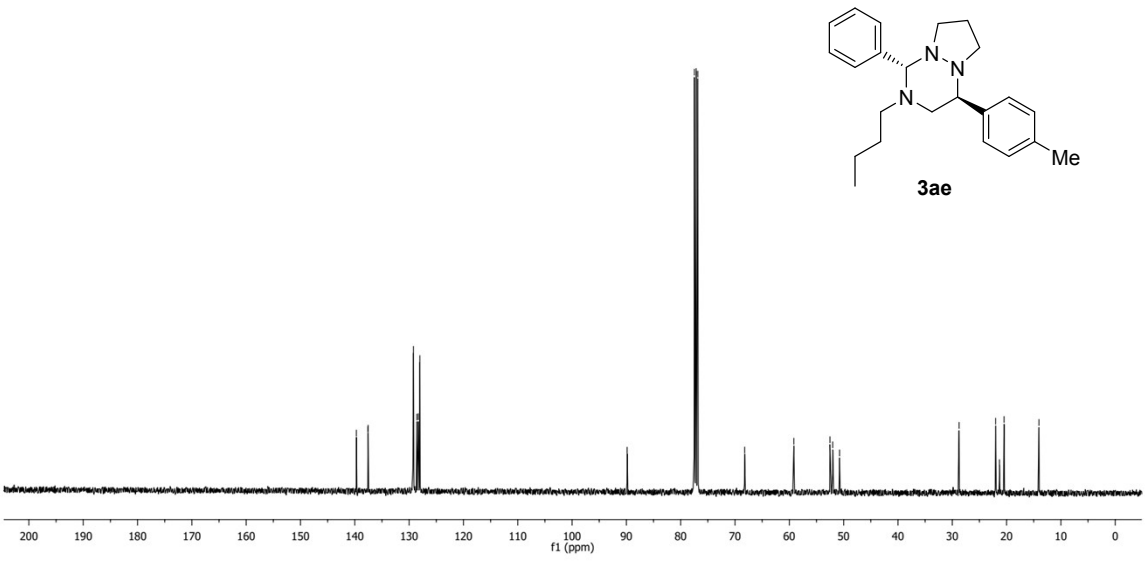

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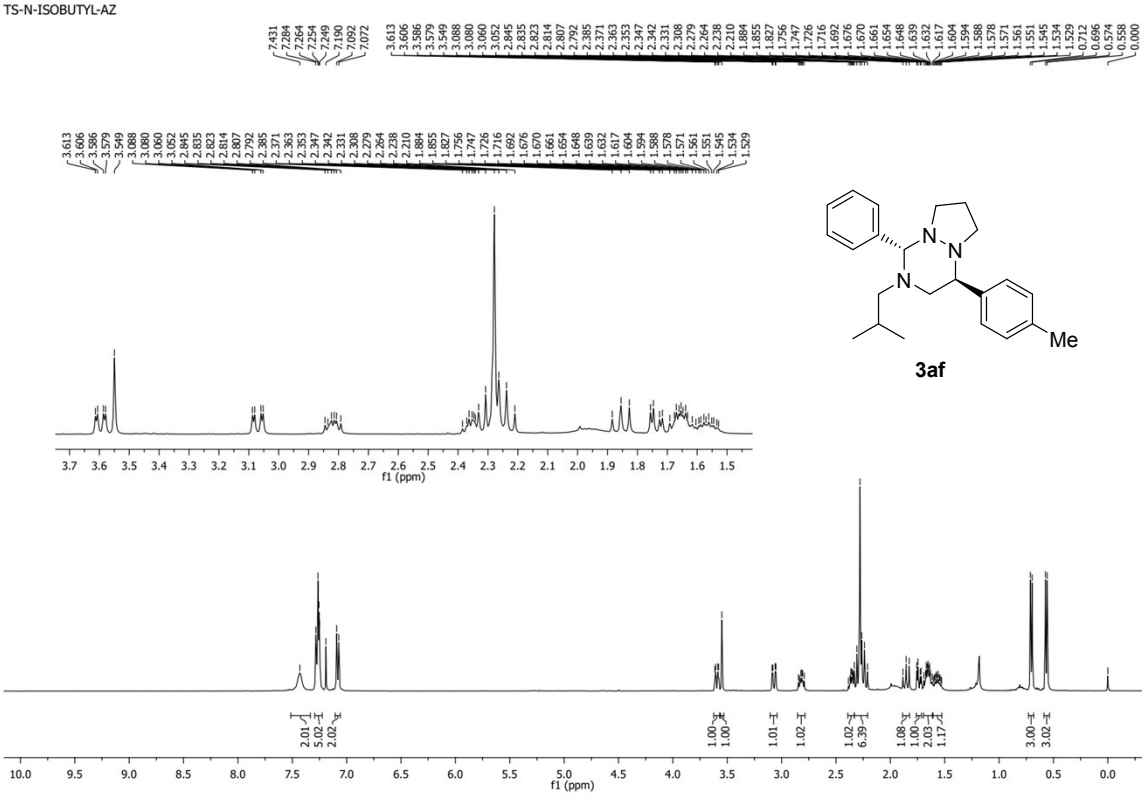

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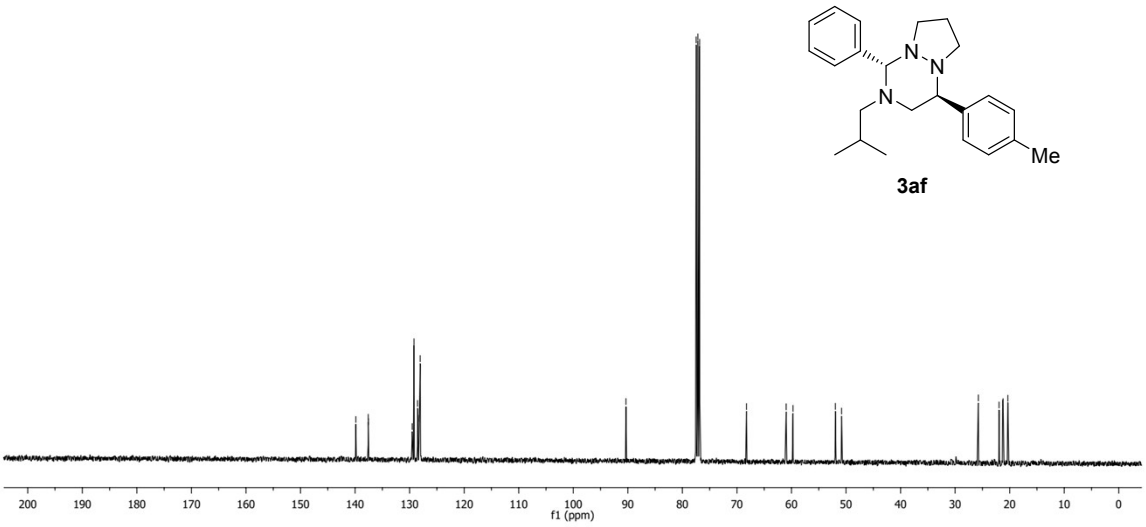

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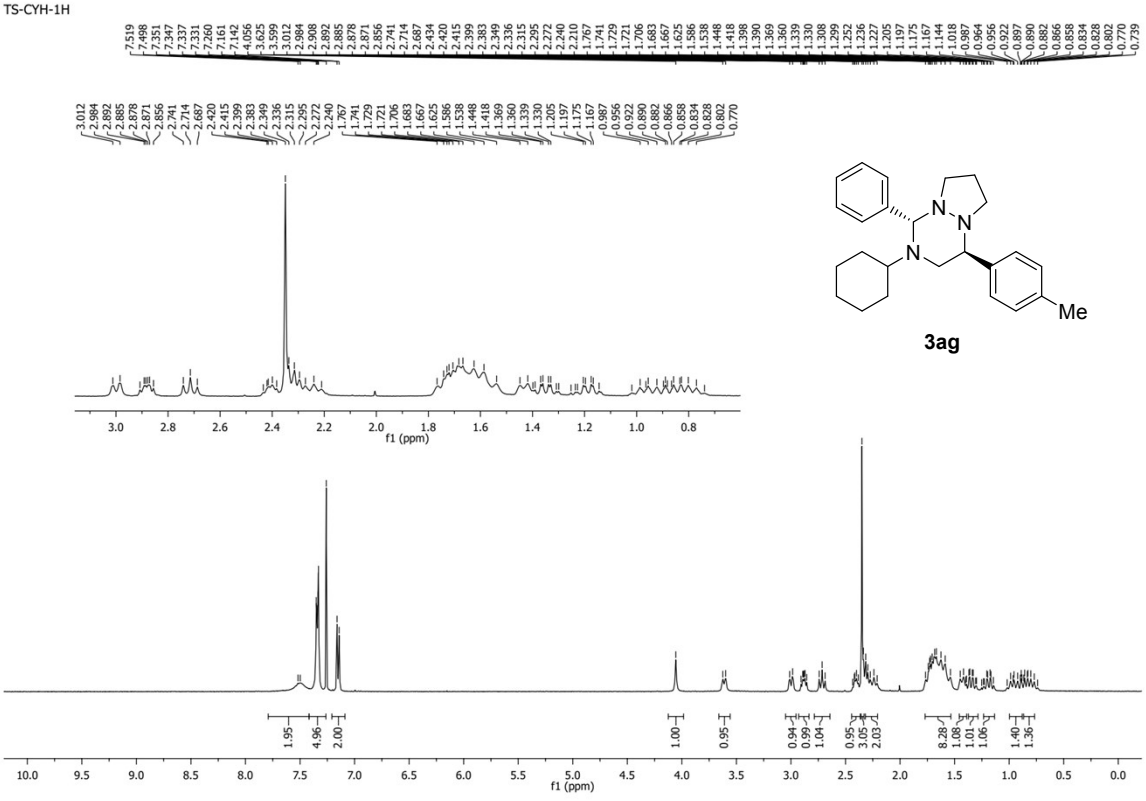

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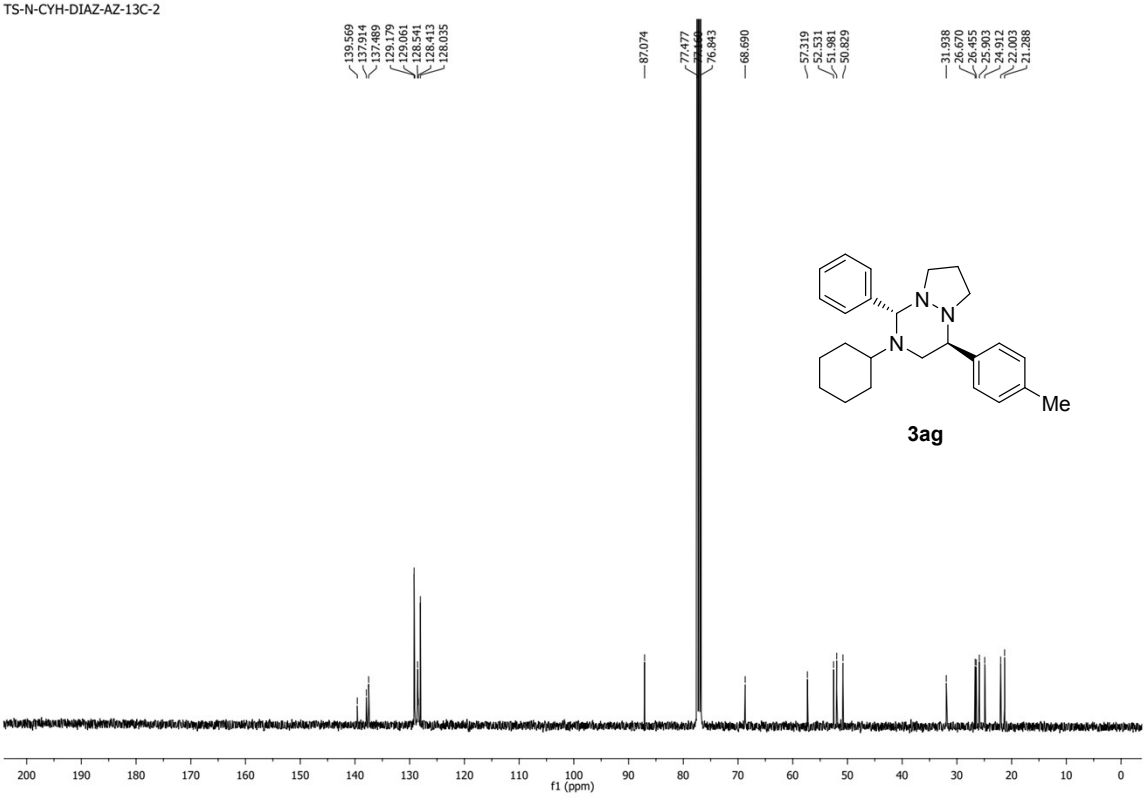

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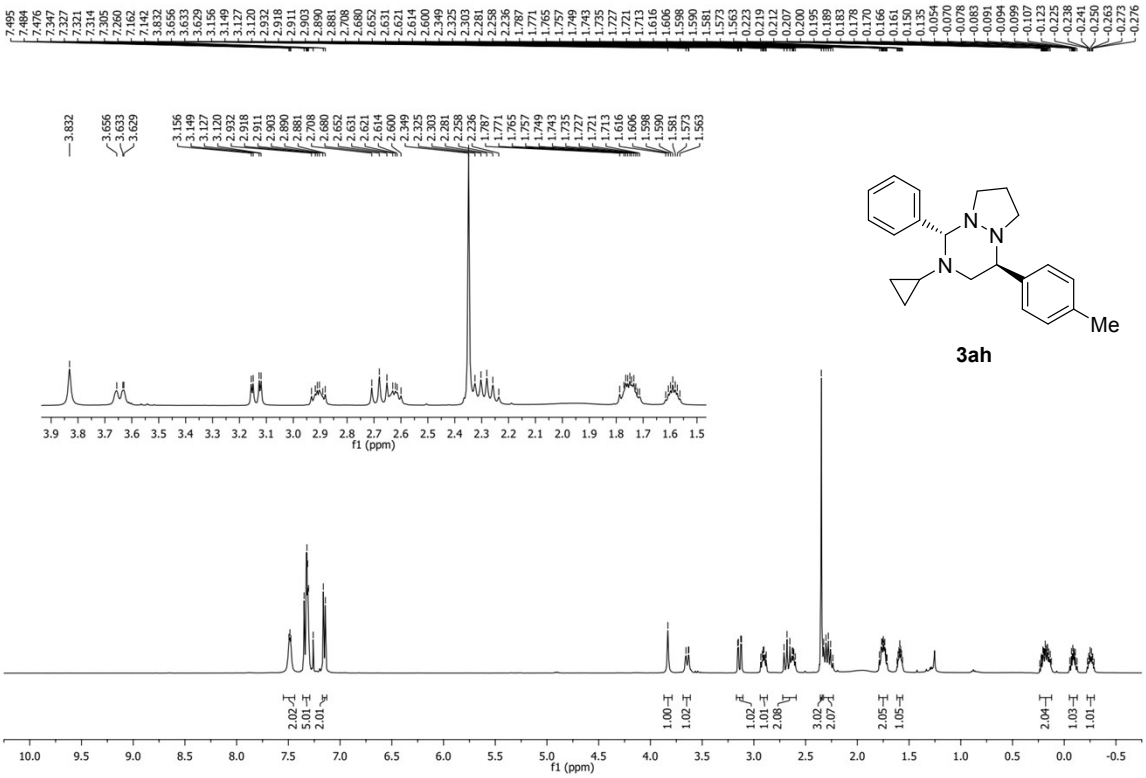

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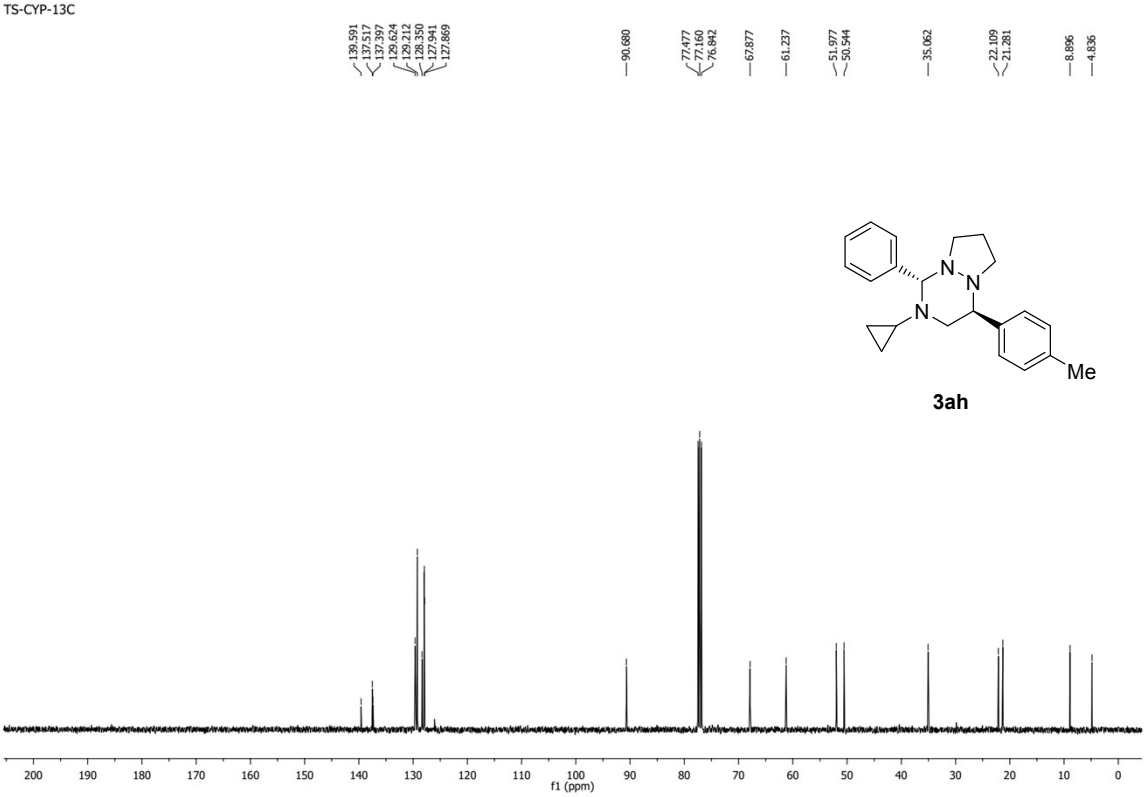

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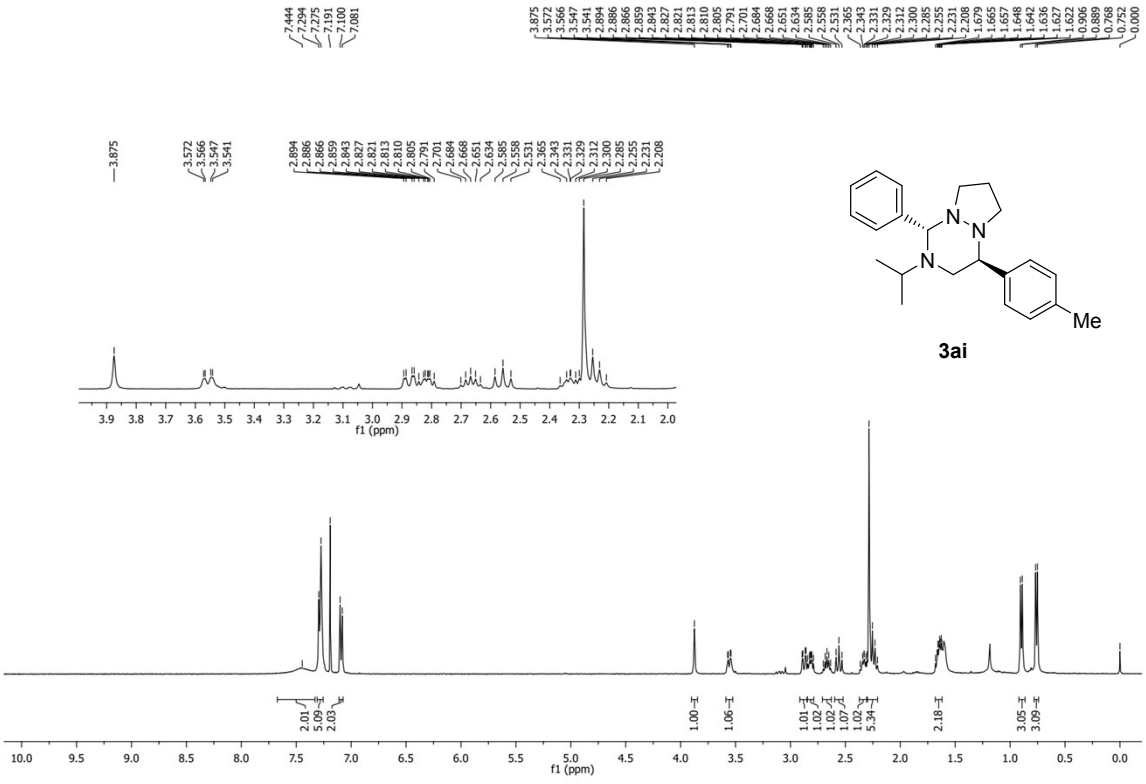

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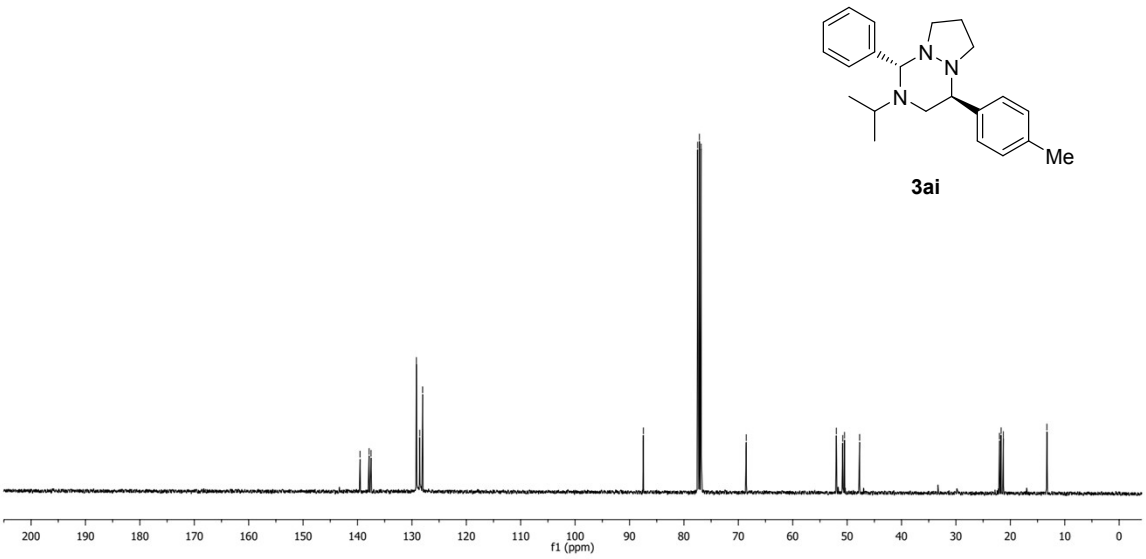

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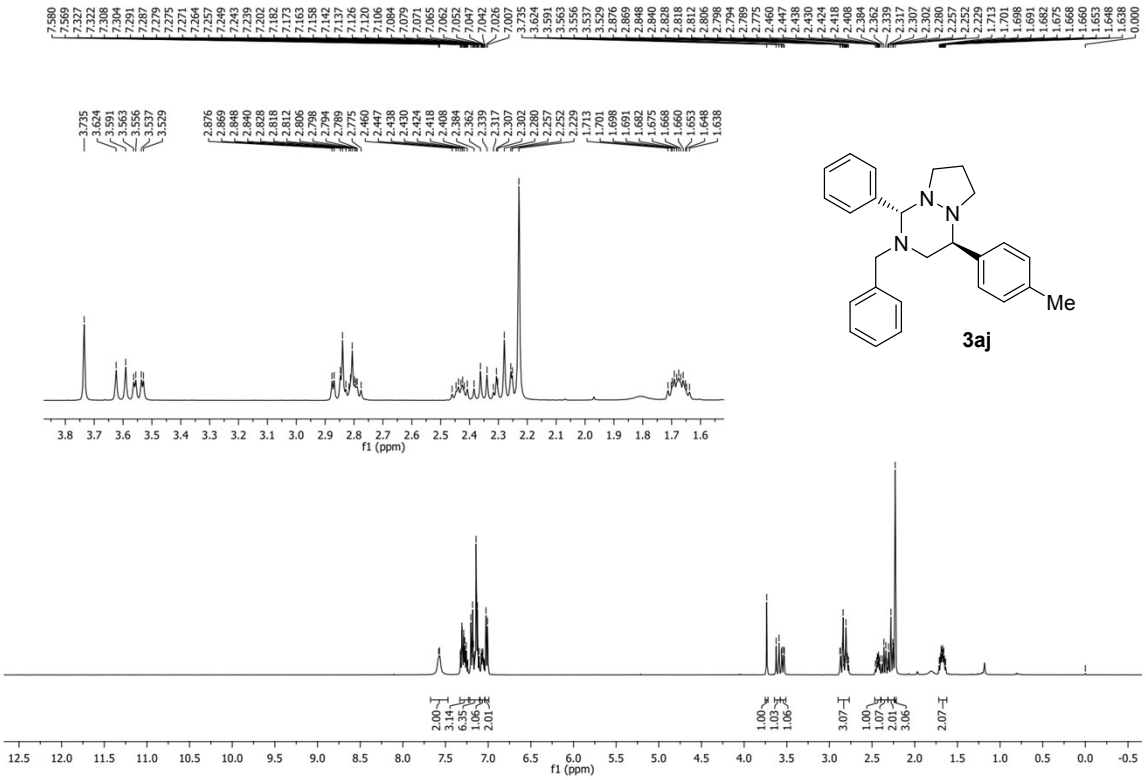

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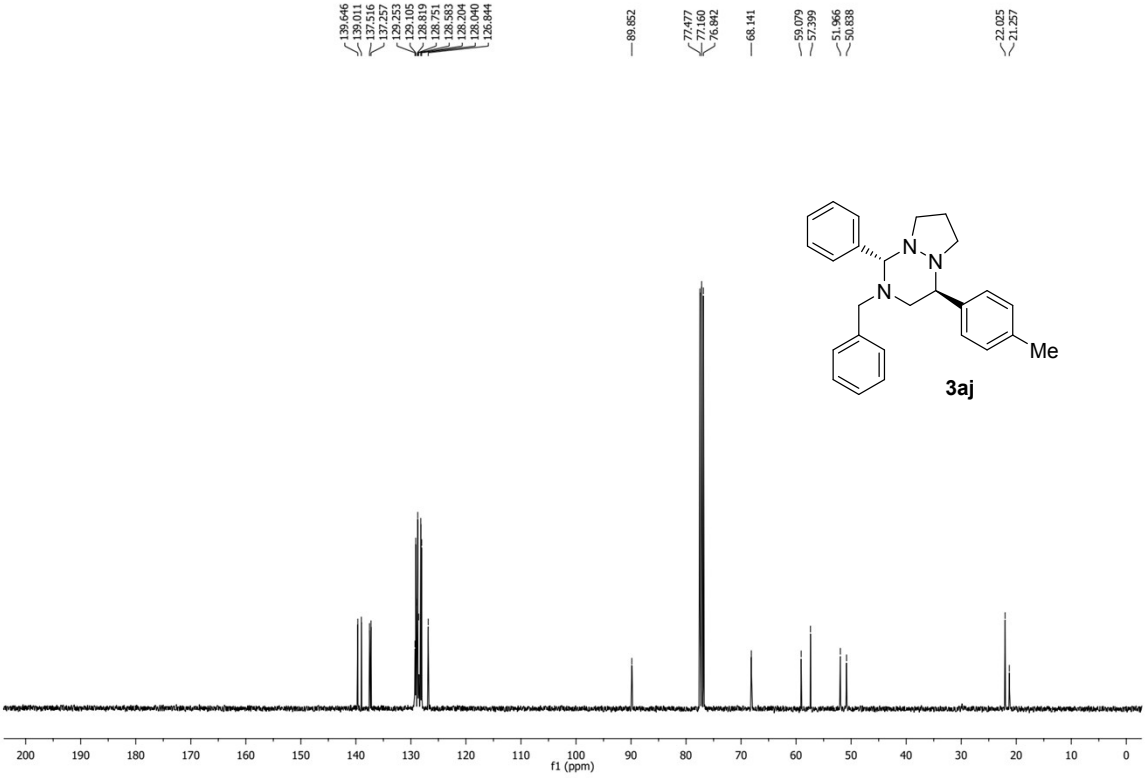

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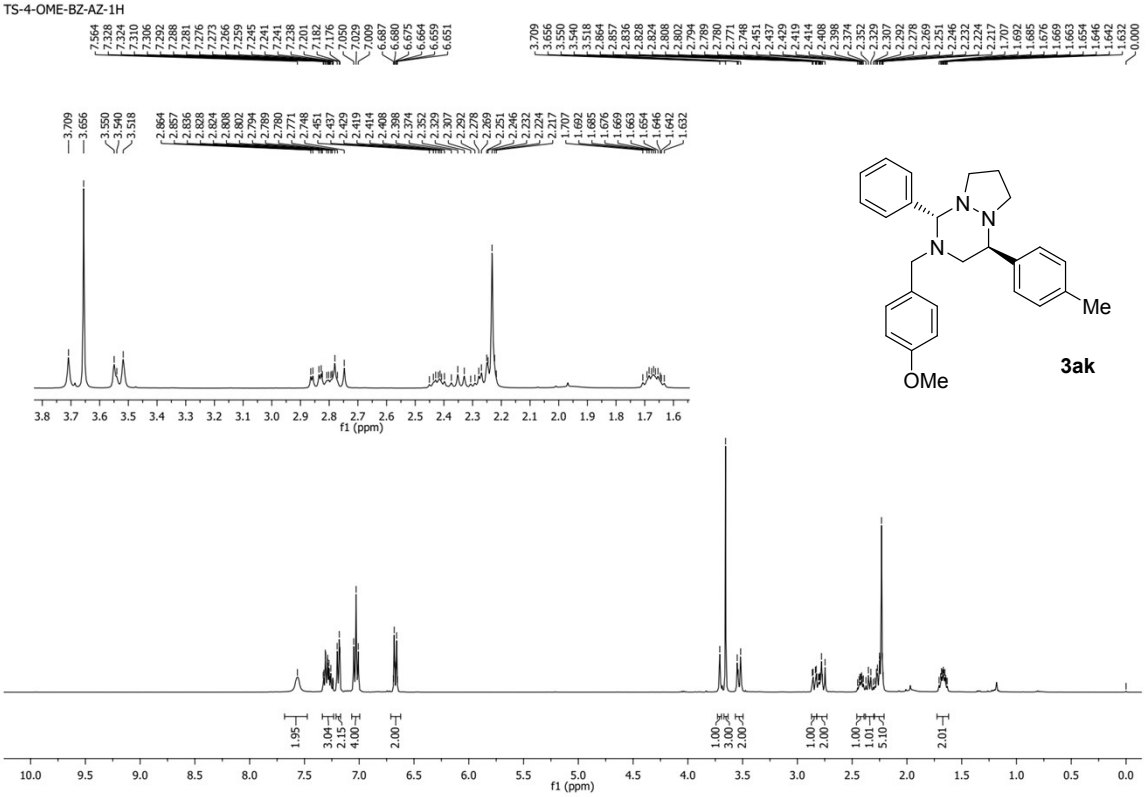

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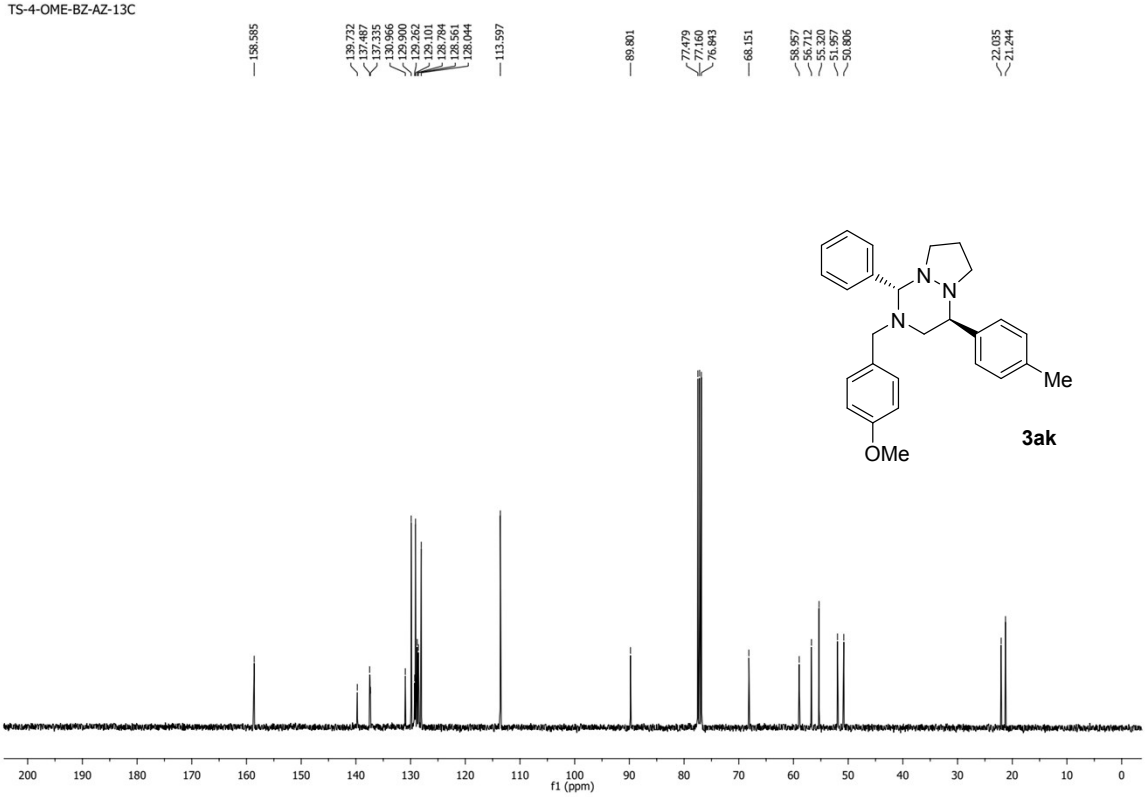

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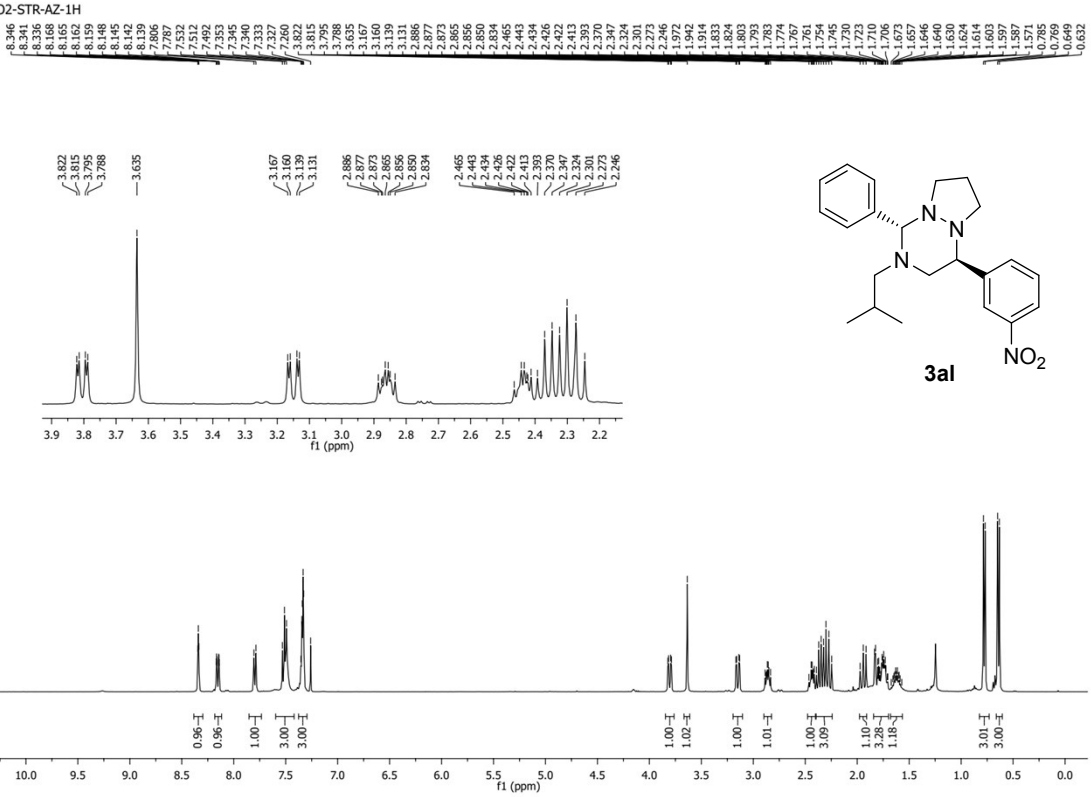

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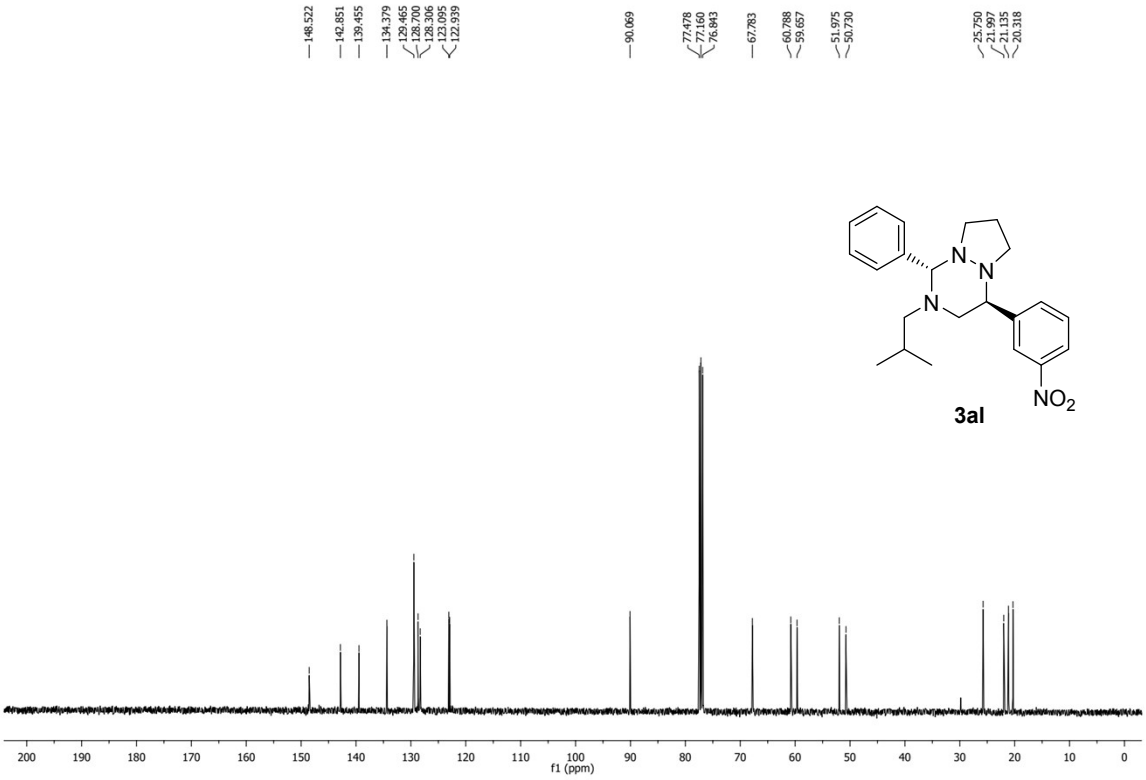

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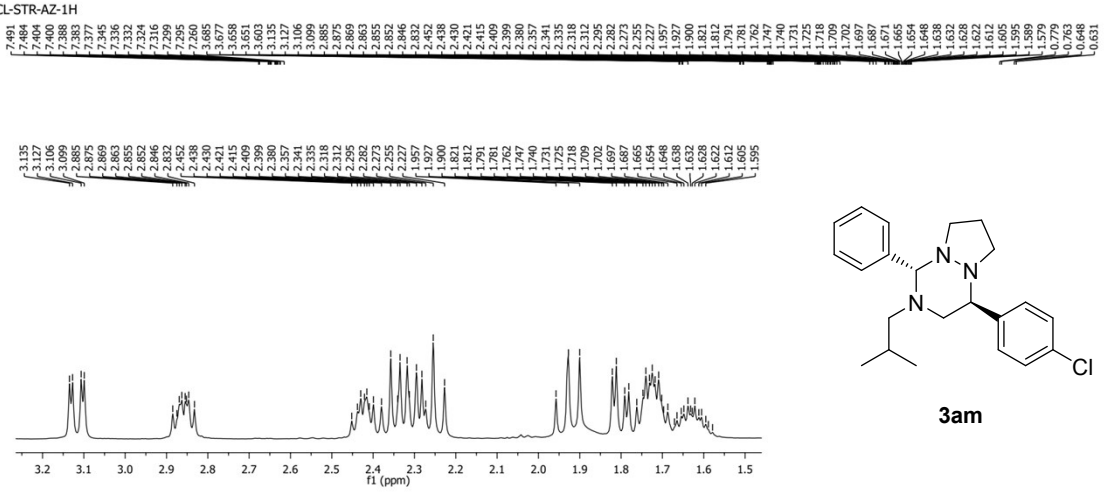

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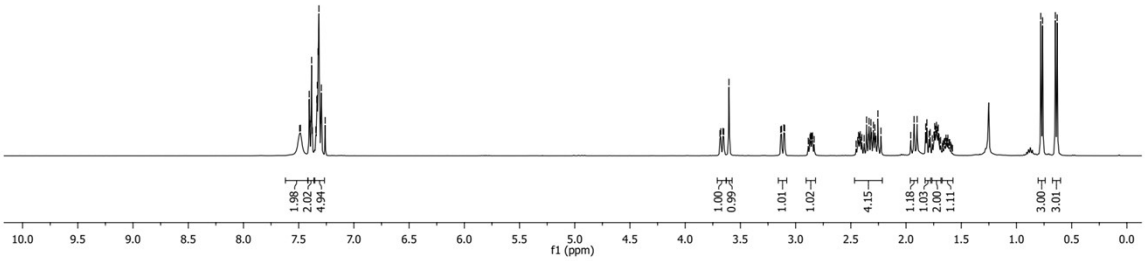

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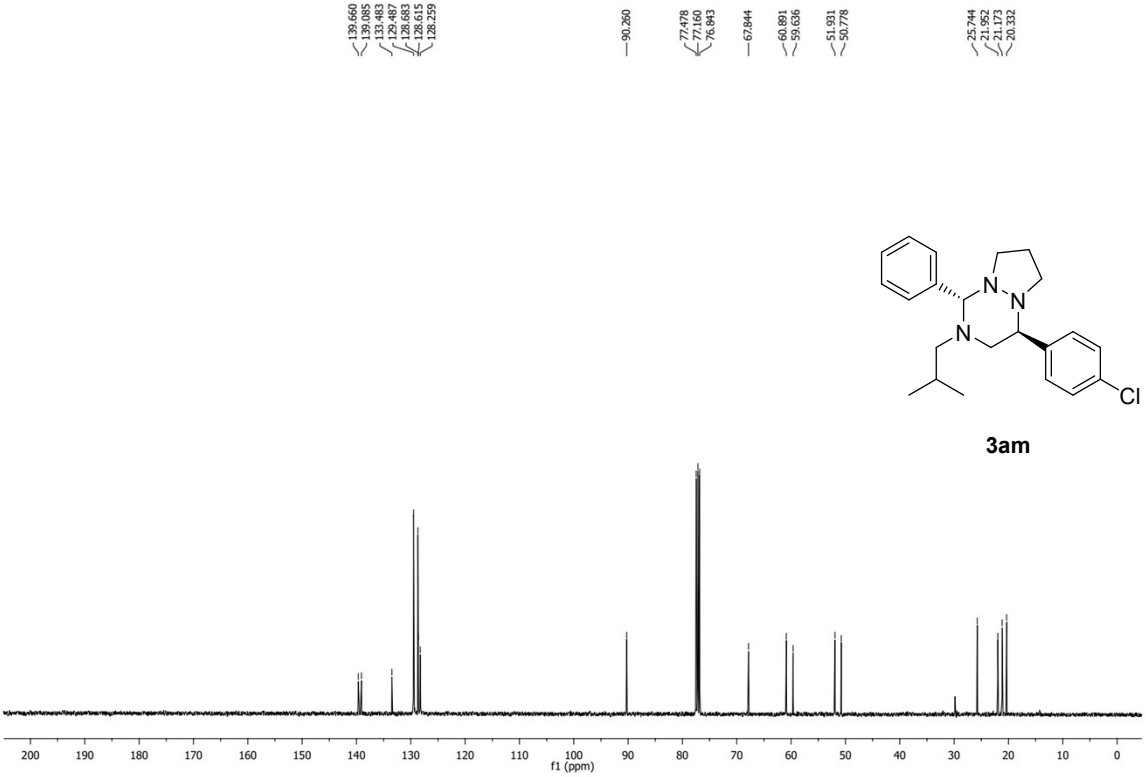

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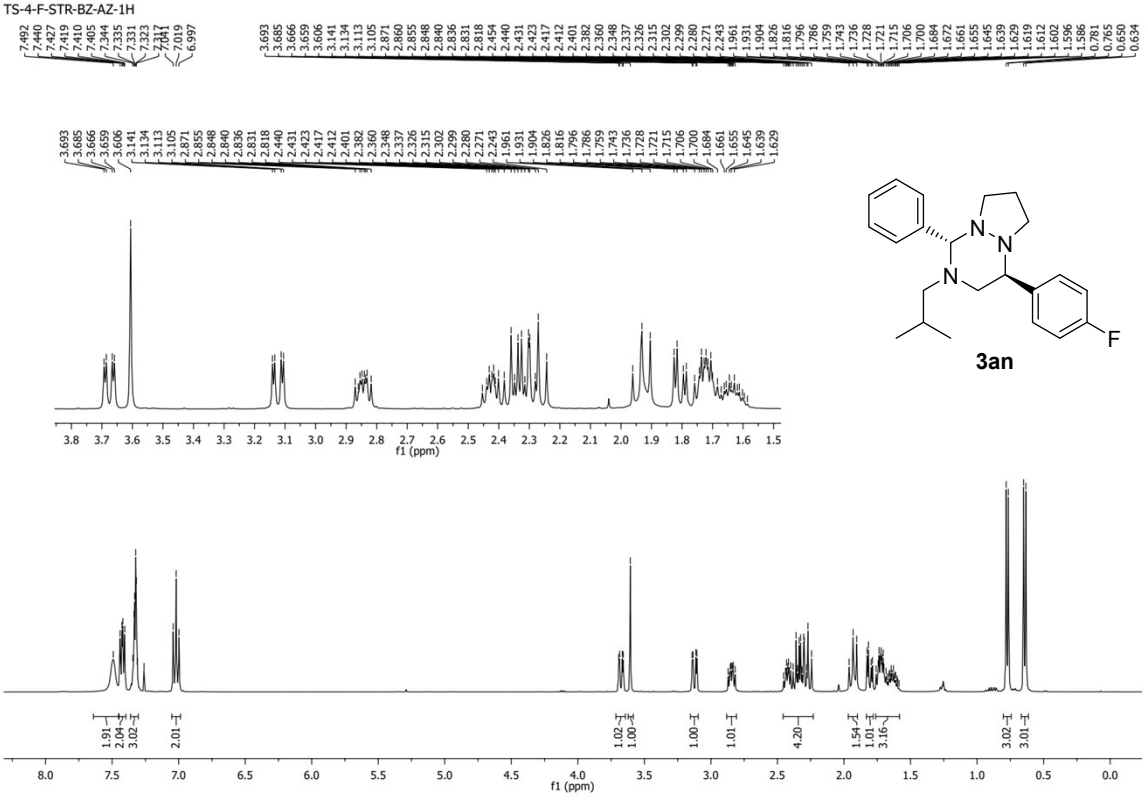

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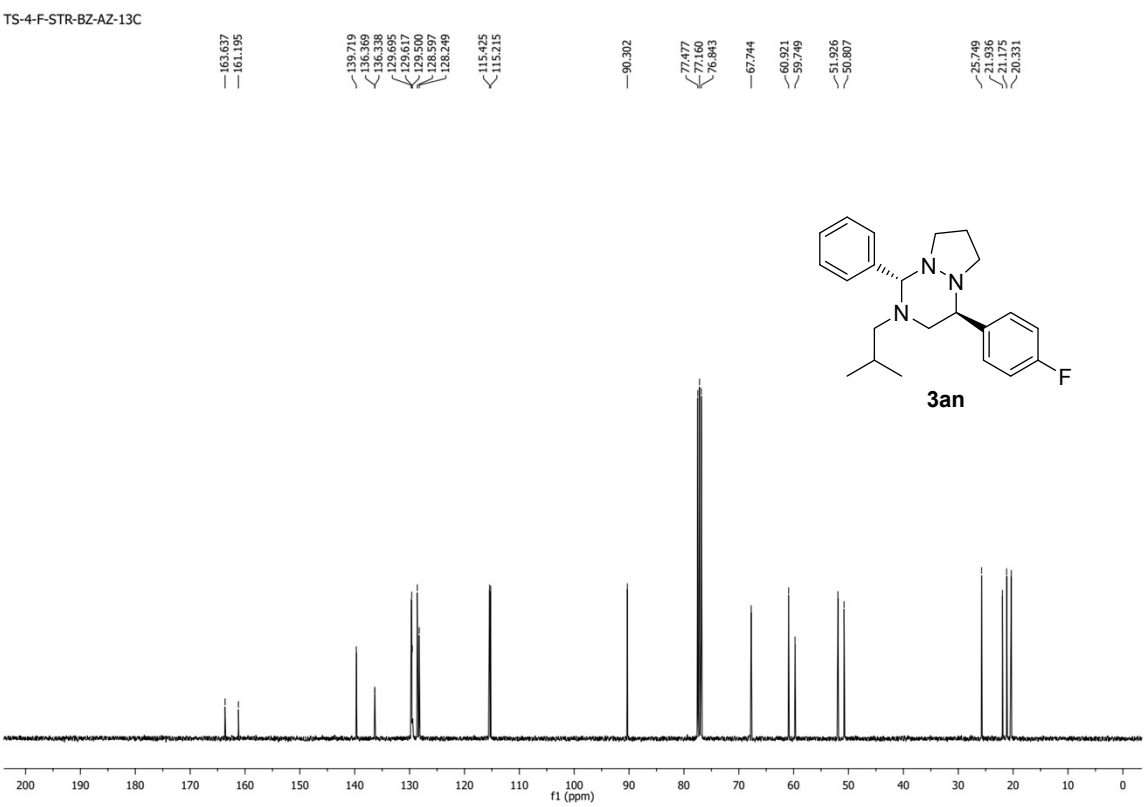

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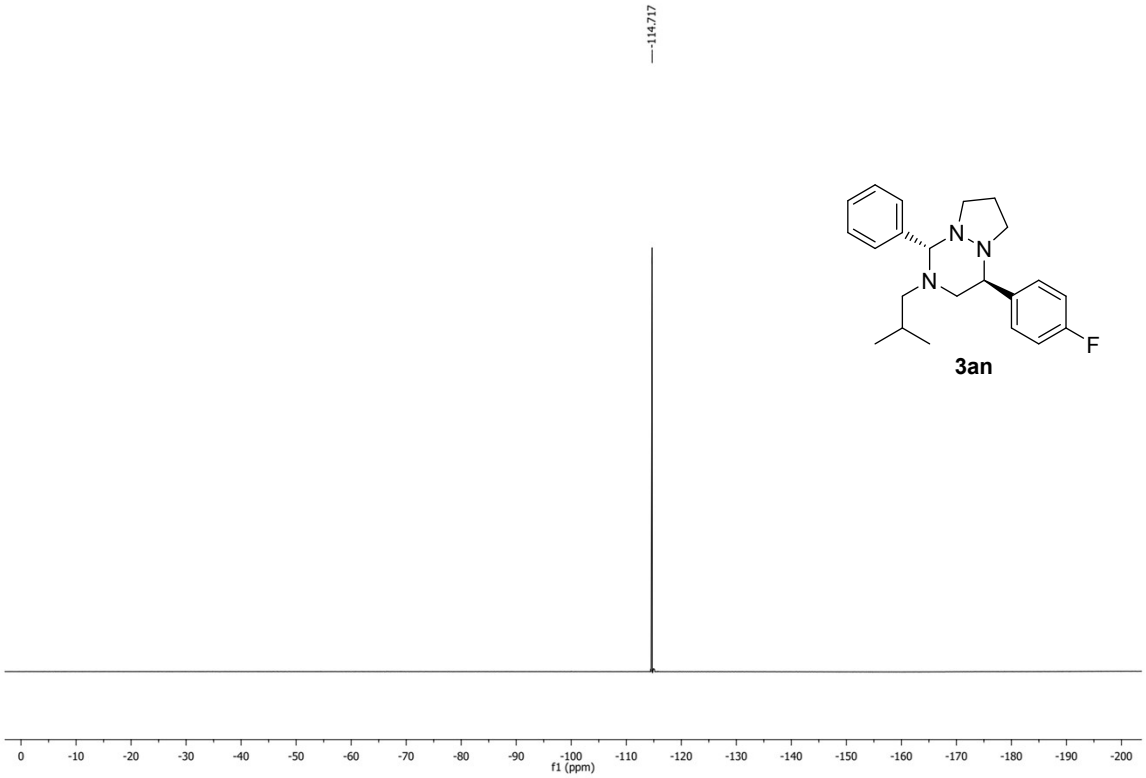

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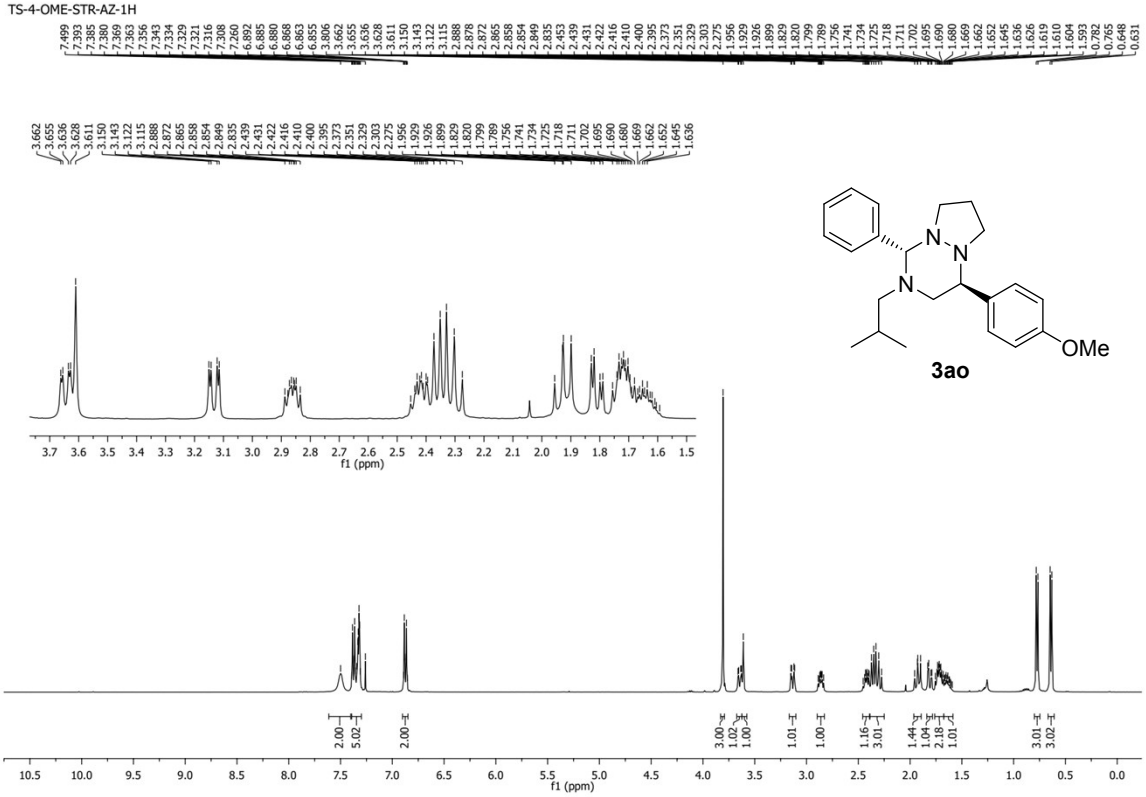

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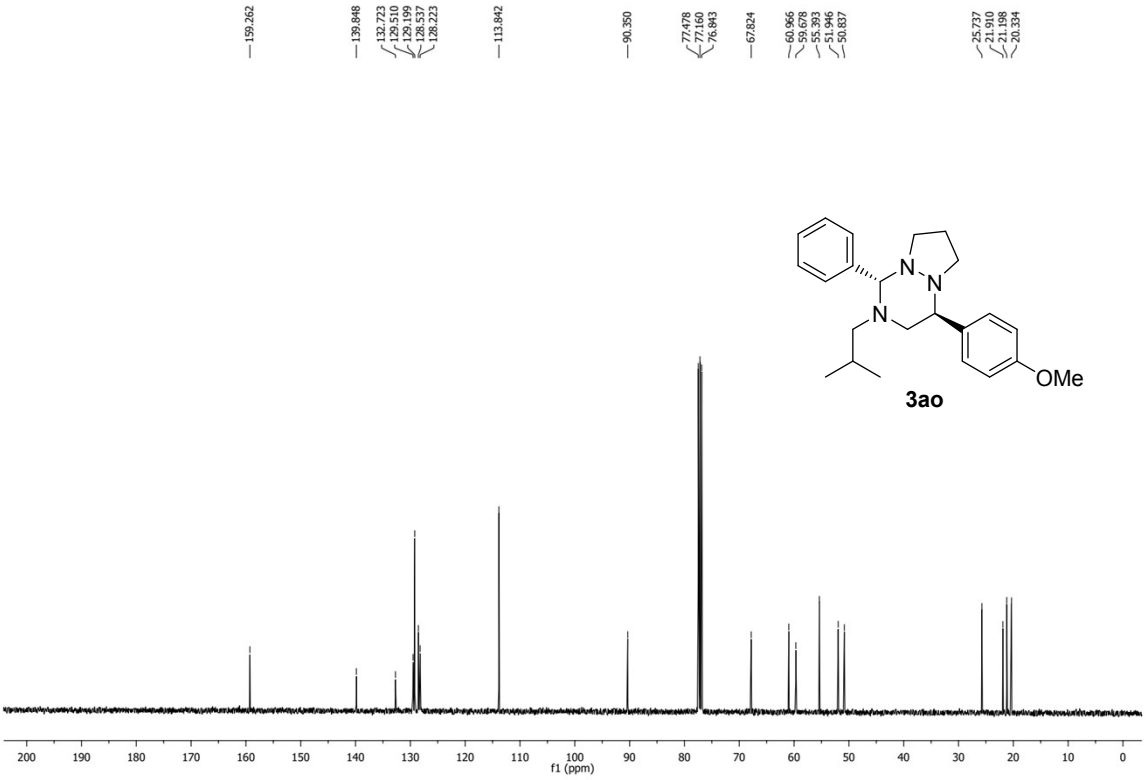

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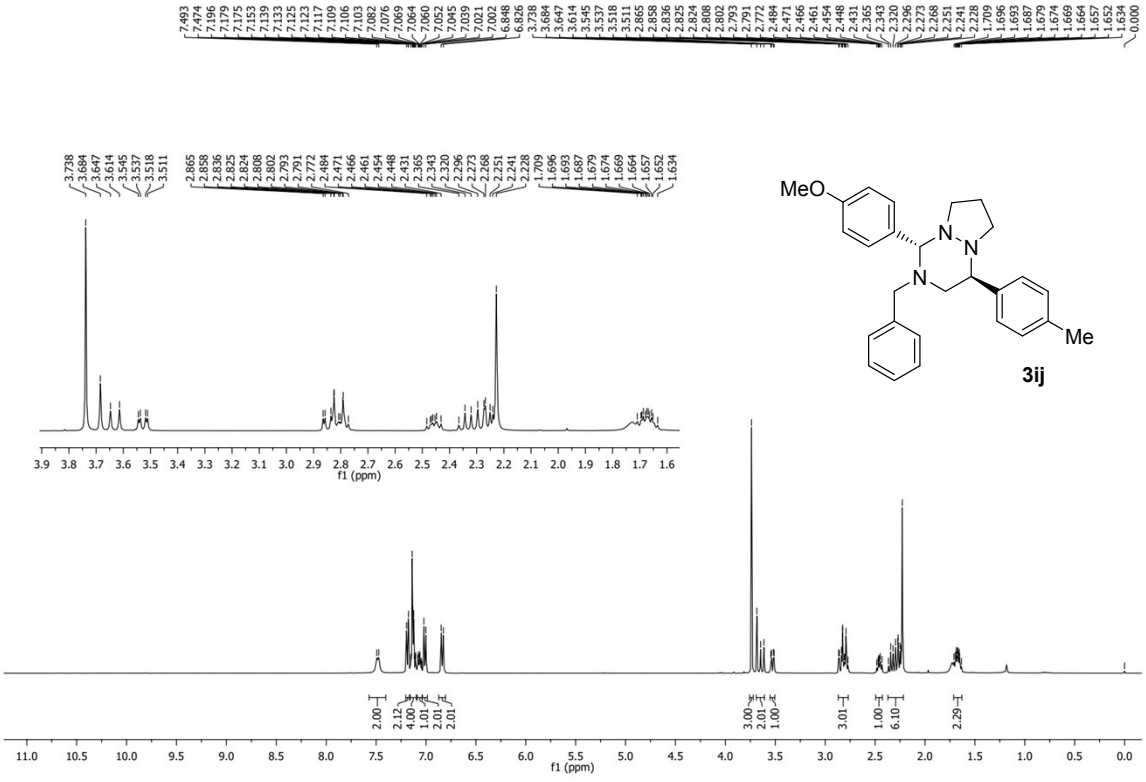

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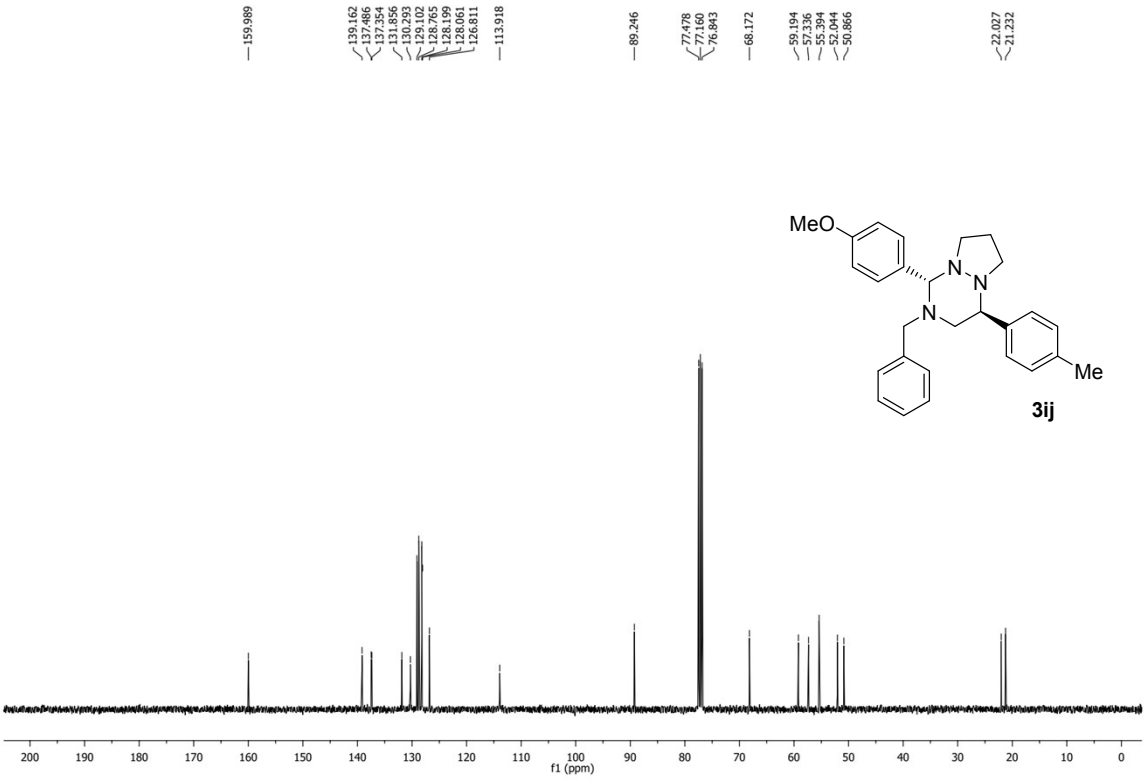

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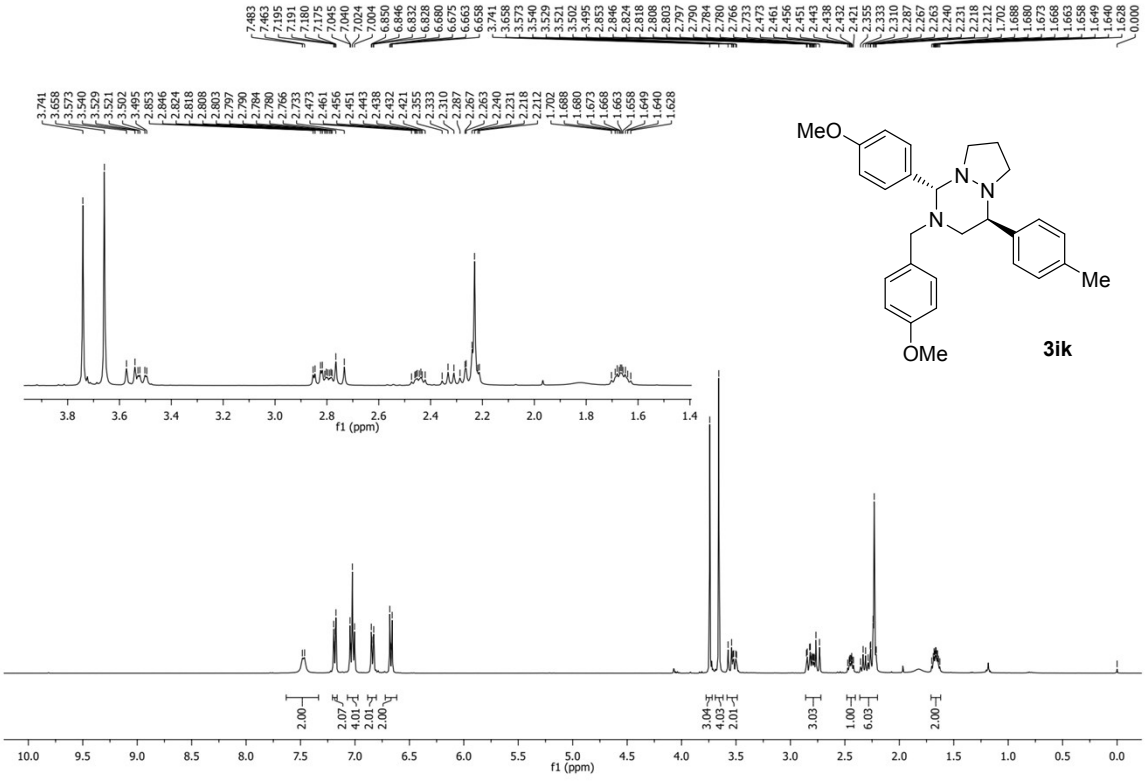

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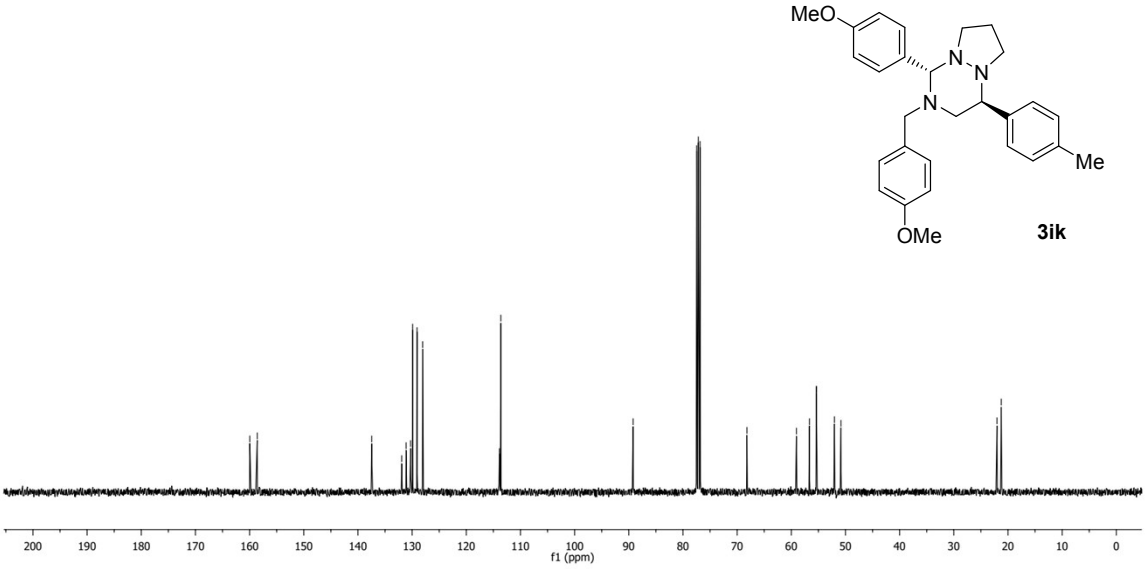

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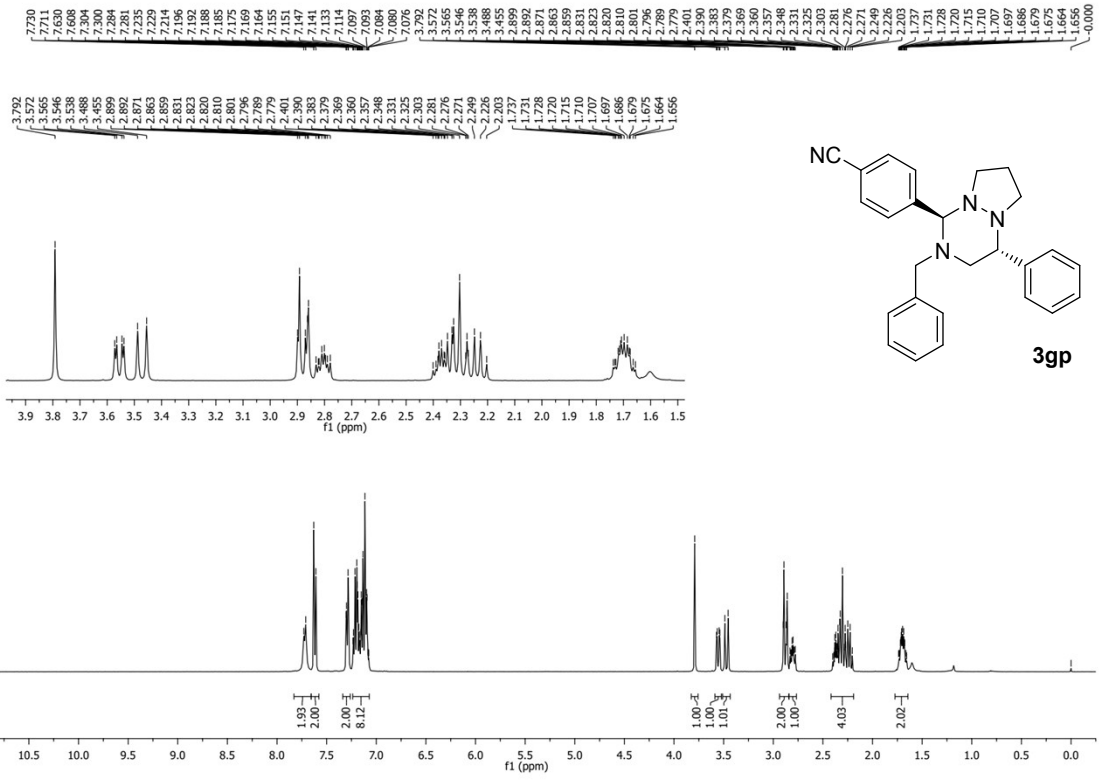

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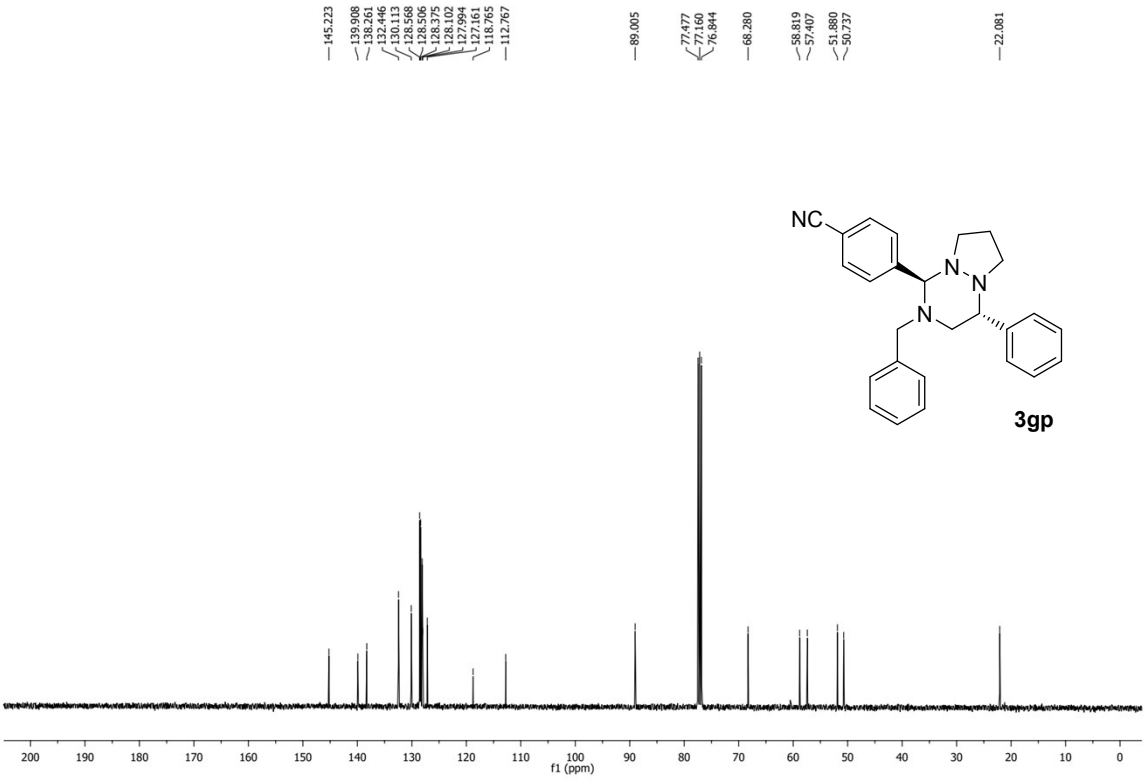

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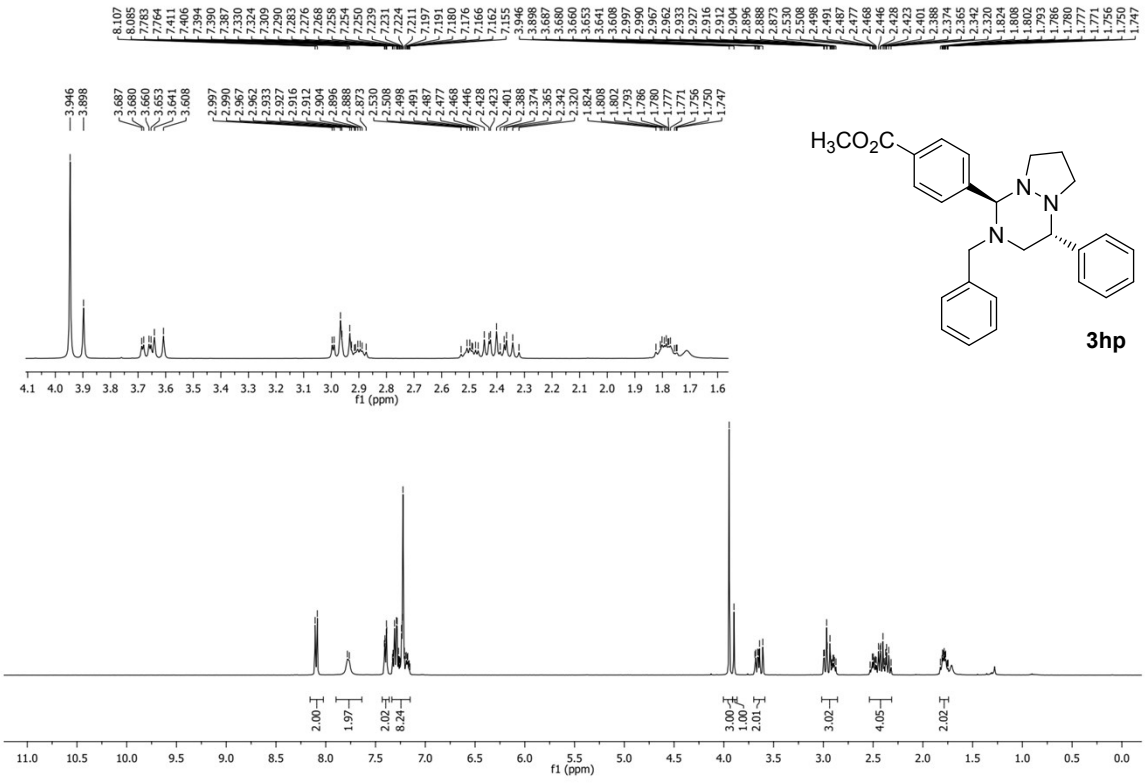

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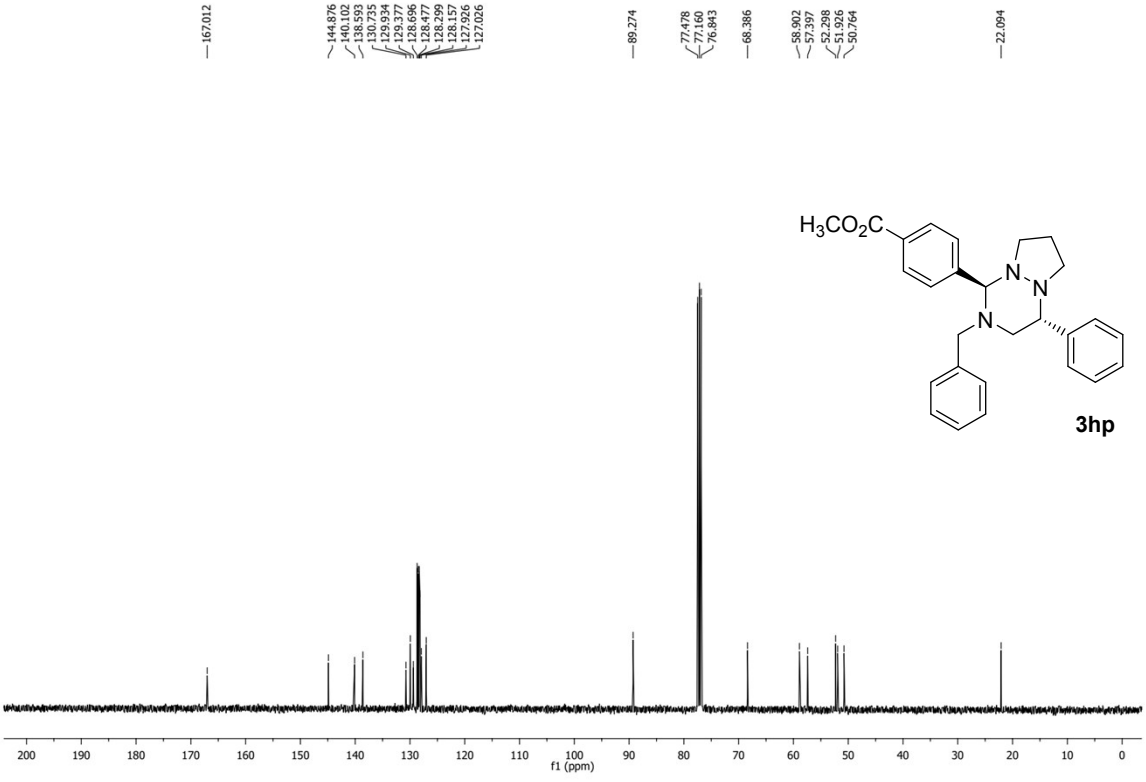

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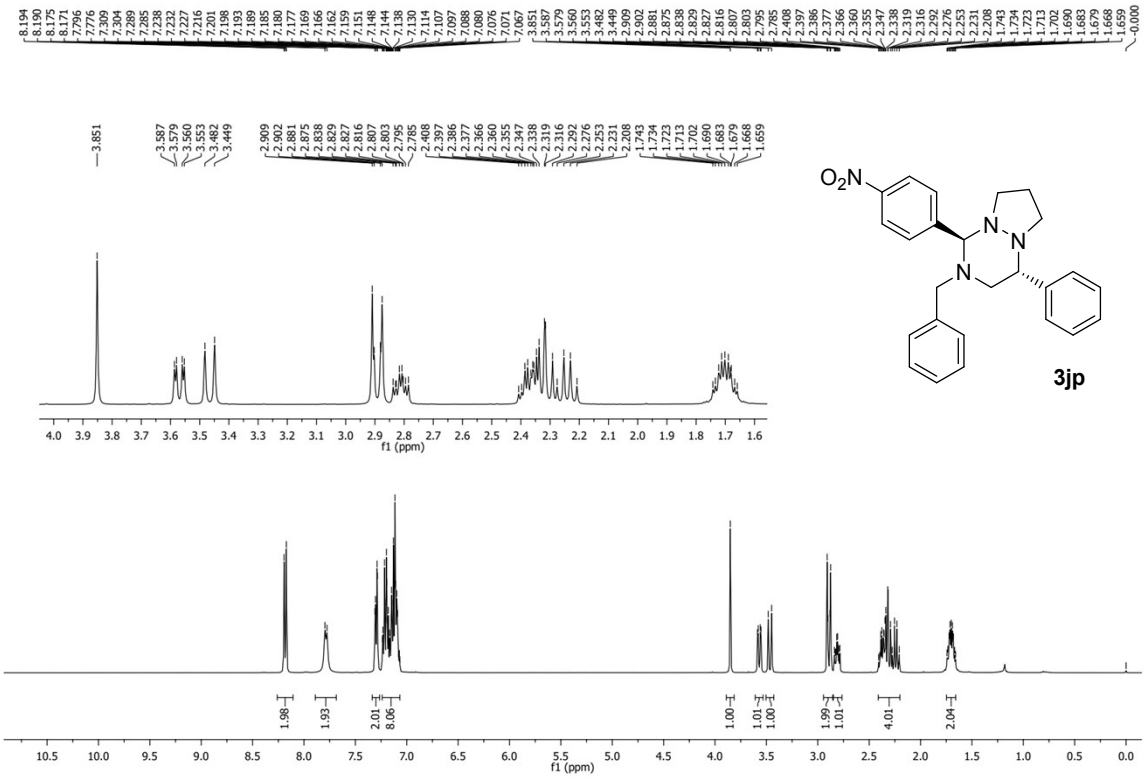

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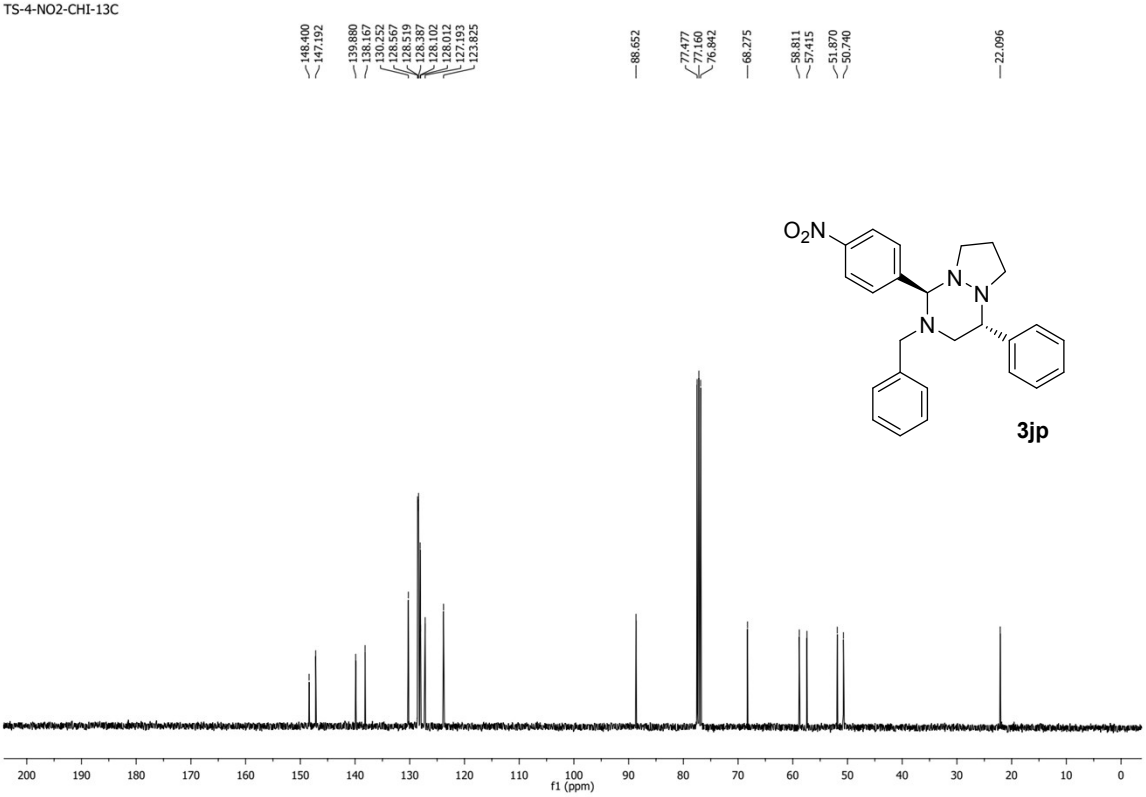

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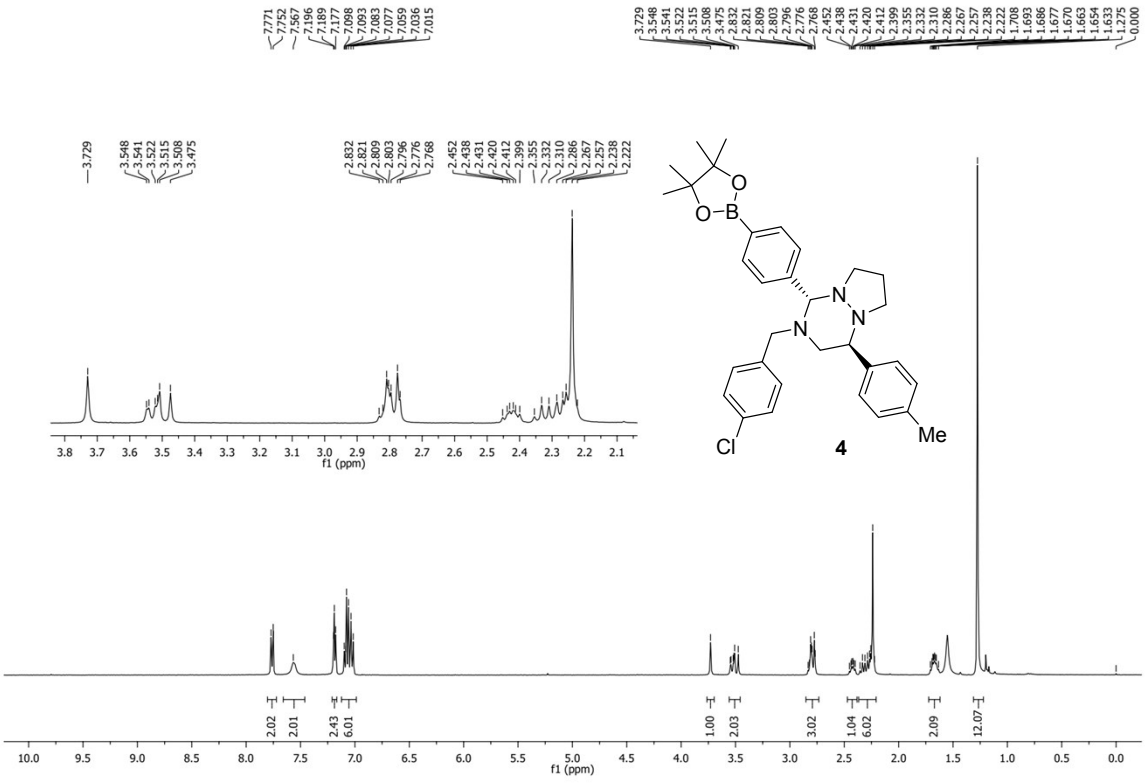

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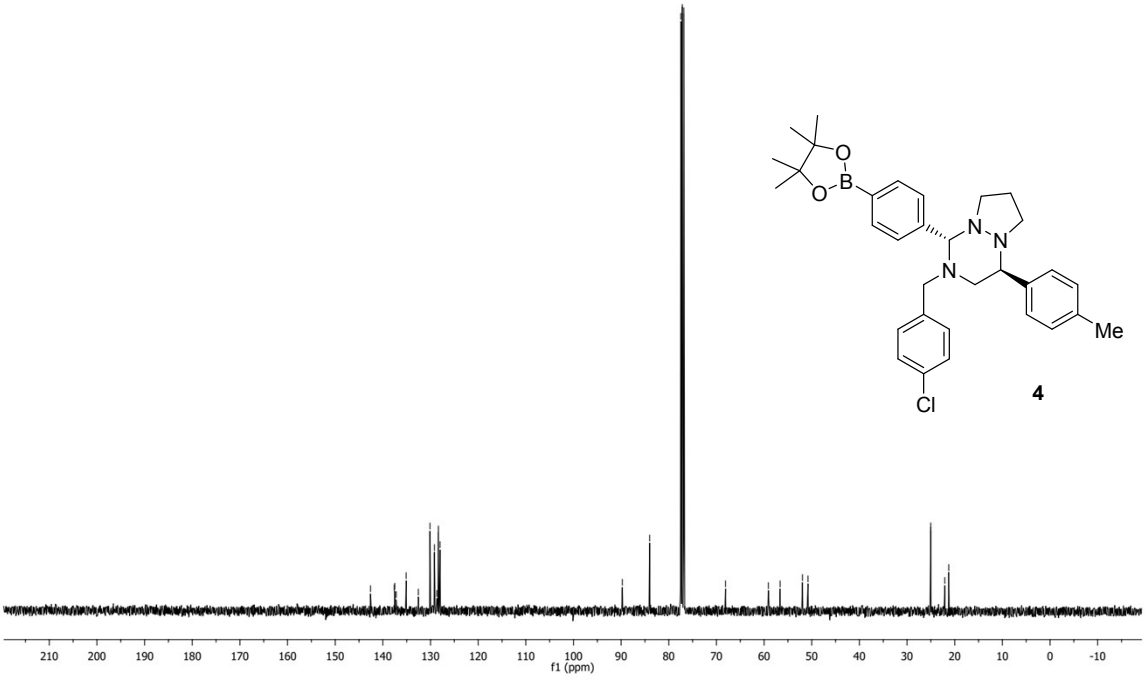

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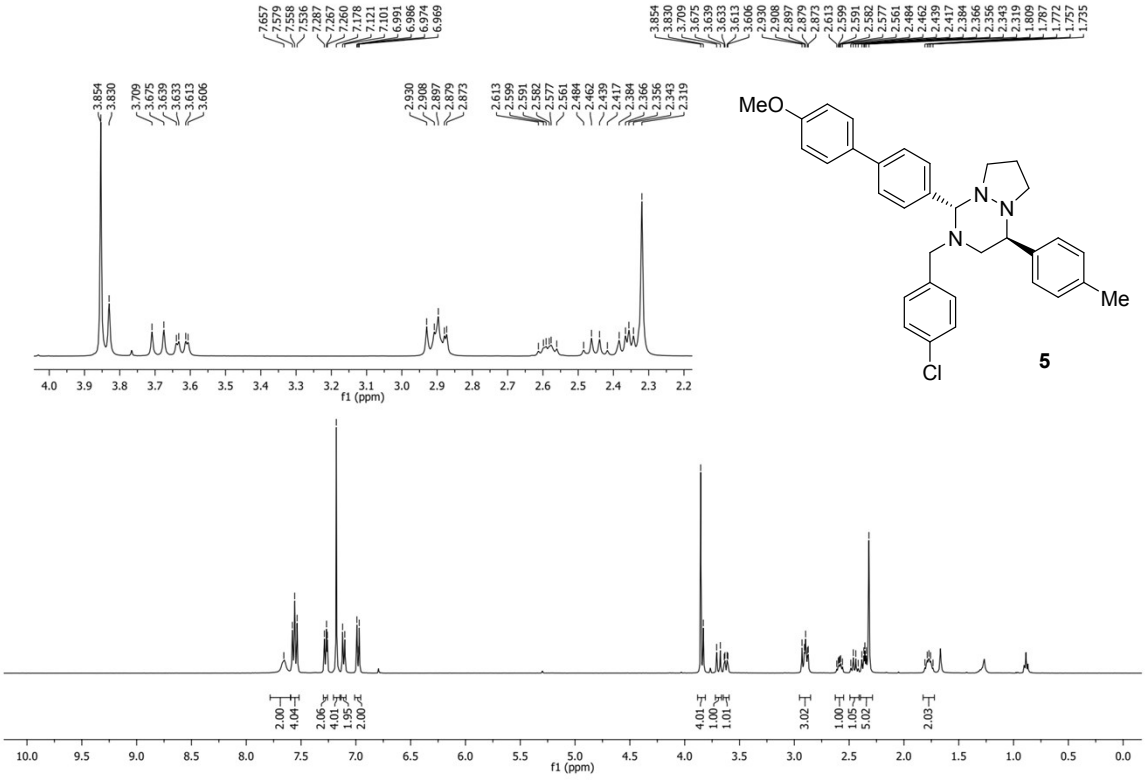

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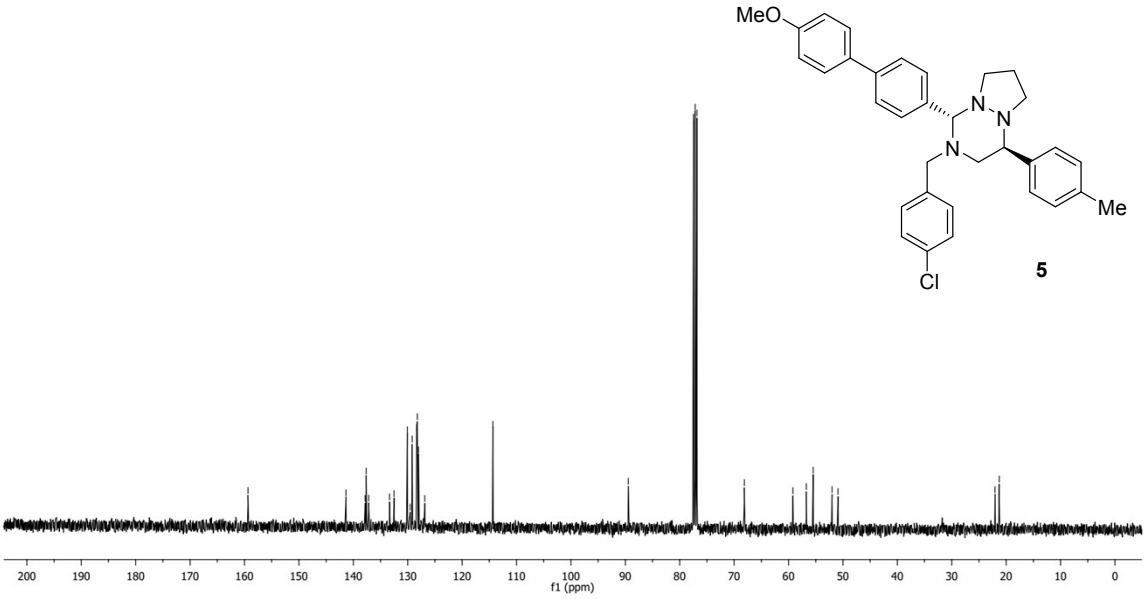

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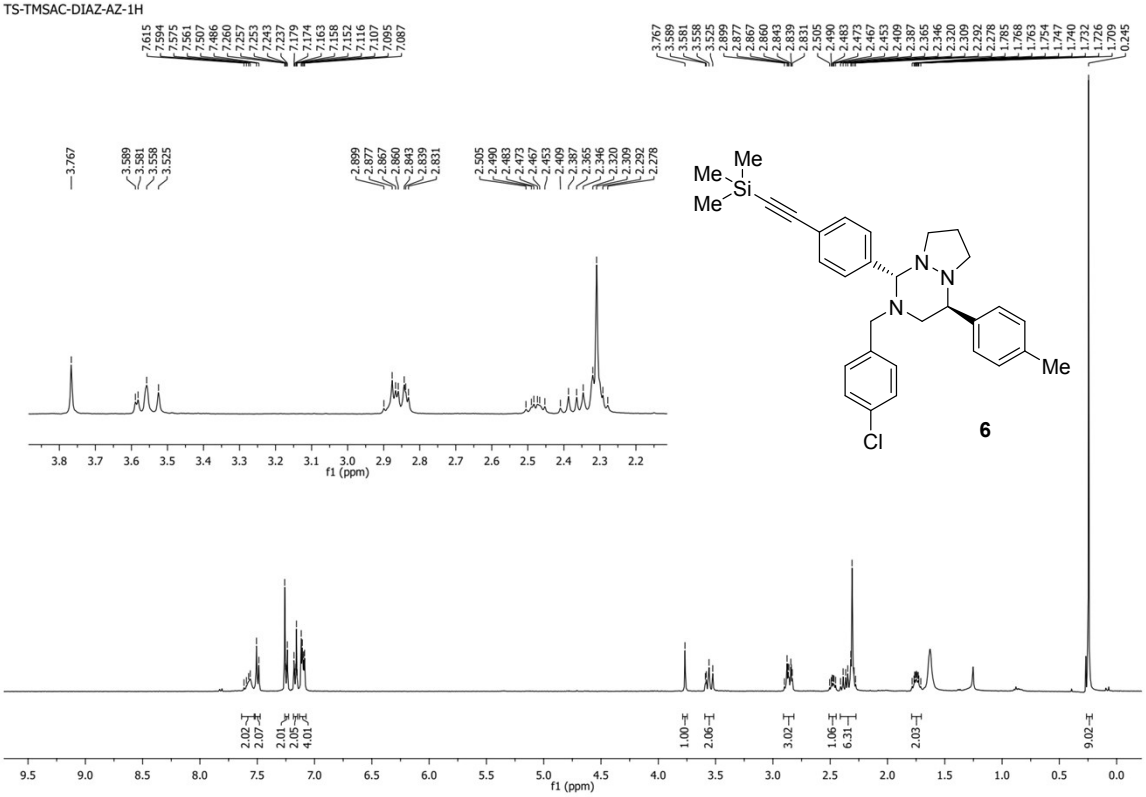

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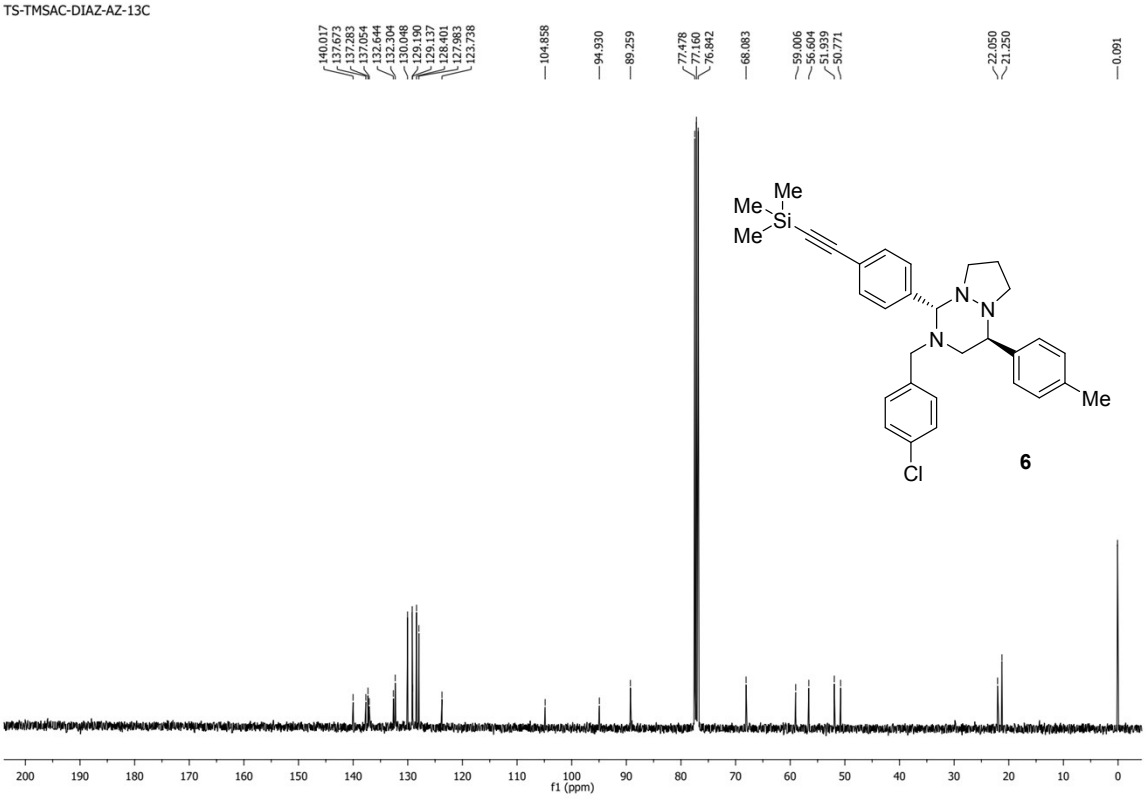

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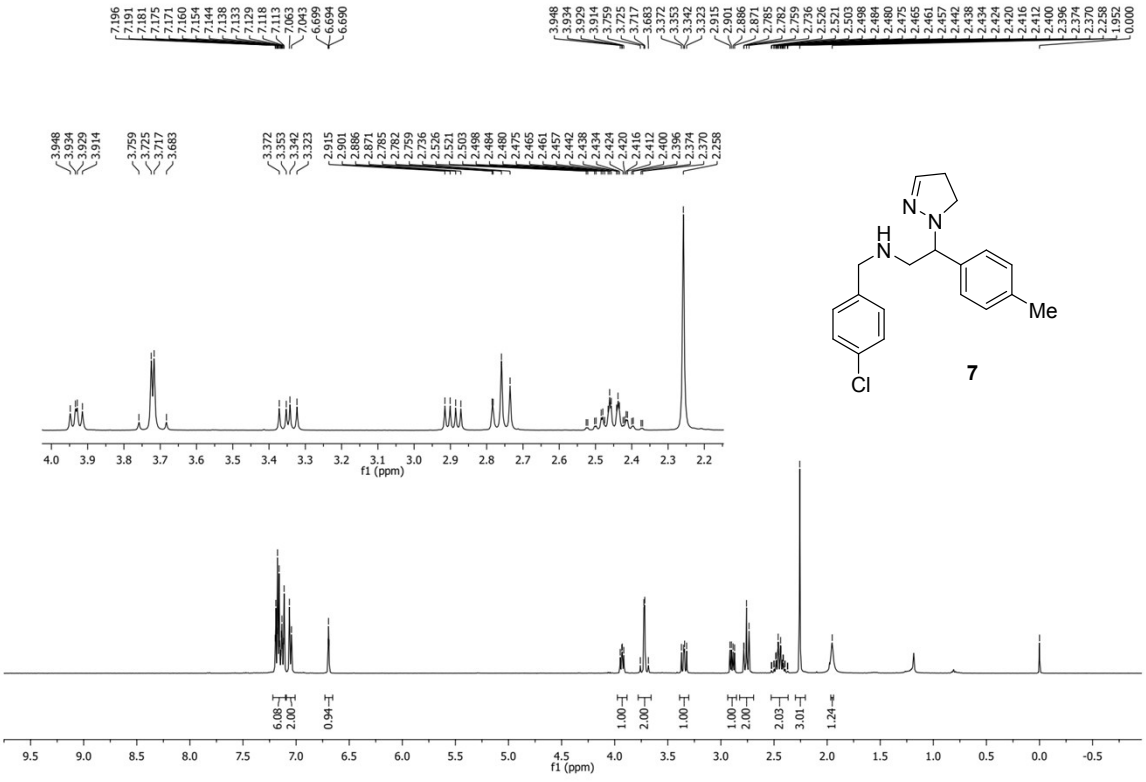

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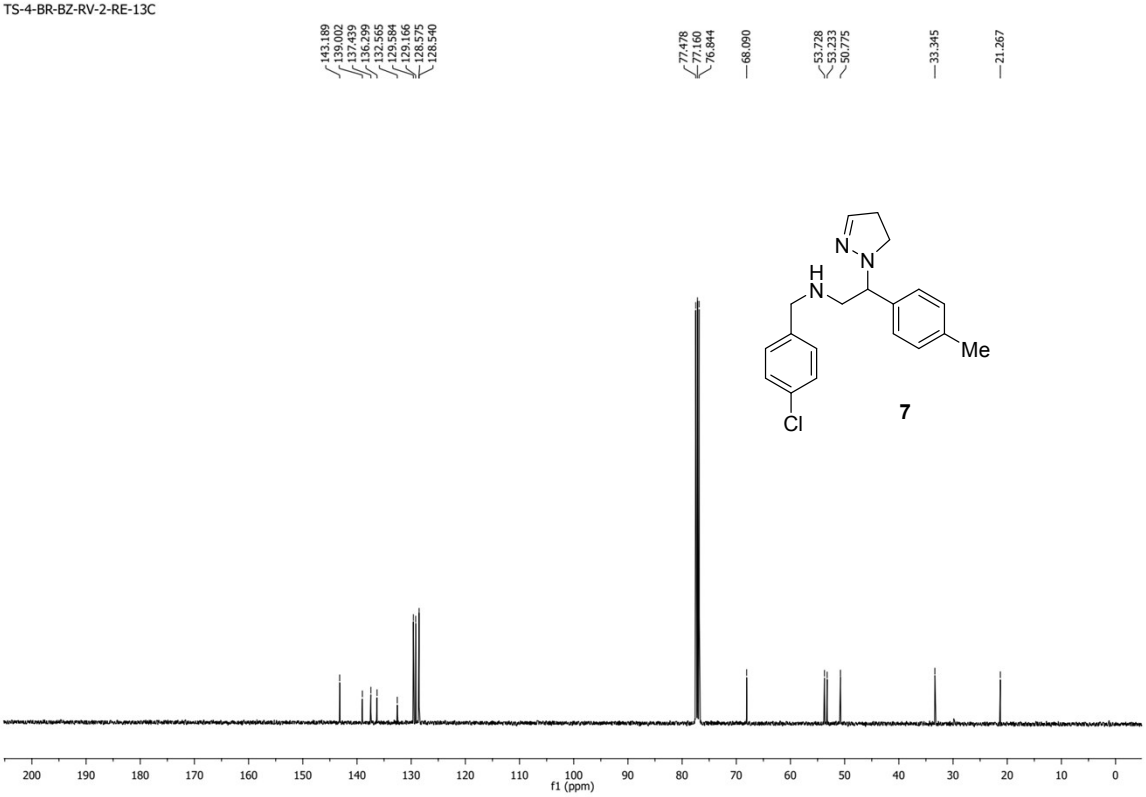

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