

Synthesis and Characterization of Novel Methyl (3)5-(*N*-Boc-piperidinyl)- 1*H*-pyrazole-4-carboxylates

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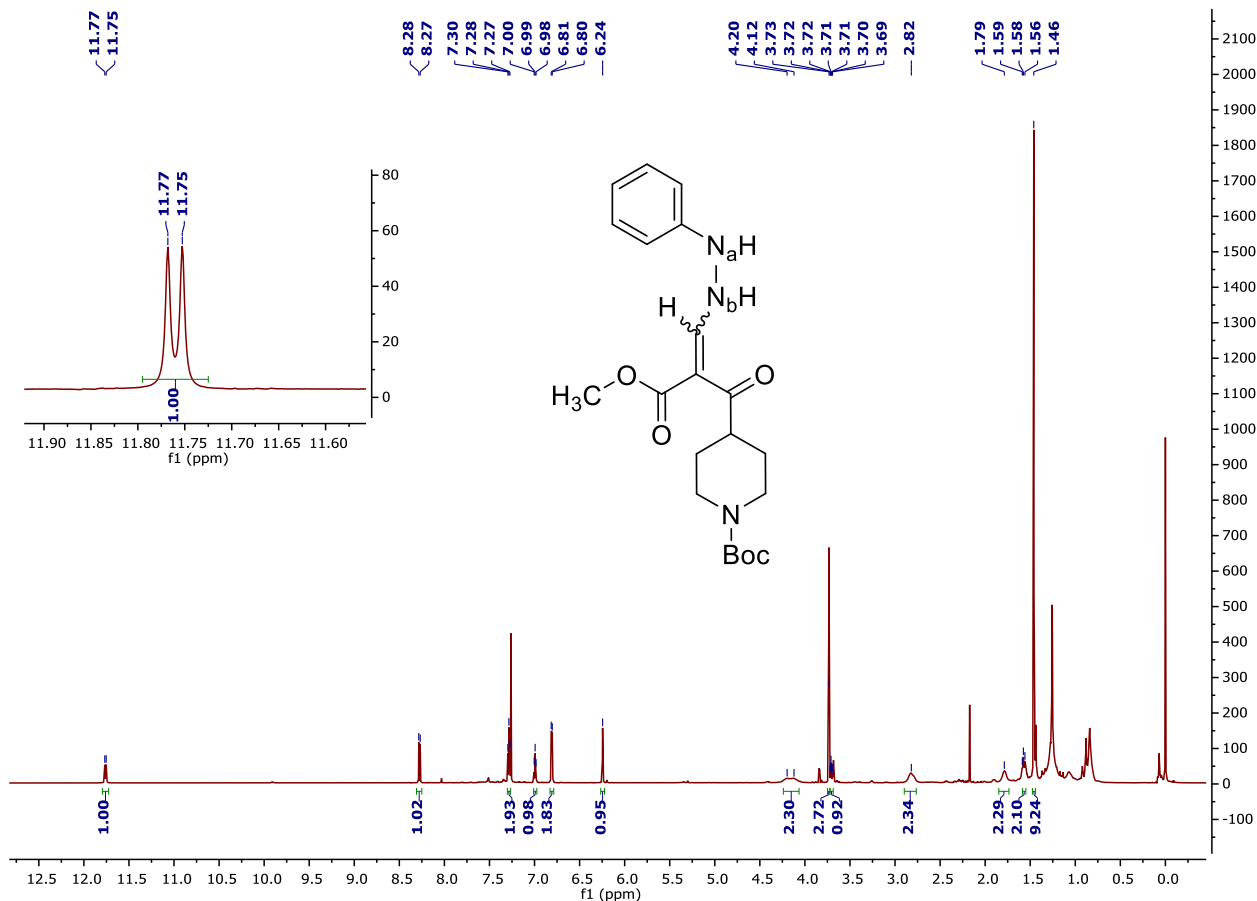


Figure S1. *tert*-Butyl 4-[(*E*(*Z*))-2-(methoxycarbonyl)-3-(2-phenylhydrazinyl)prop-2-enoyl]piperidine-1-carboxylate (**4a**). ¹H NMR spectrum (700 MHz, CDCl₃).

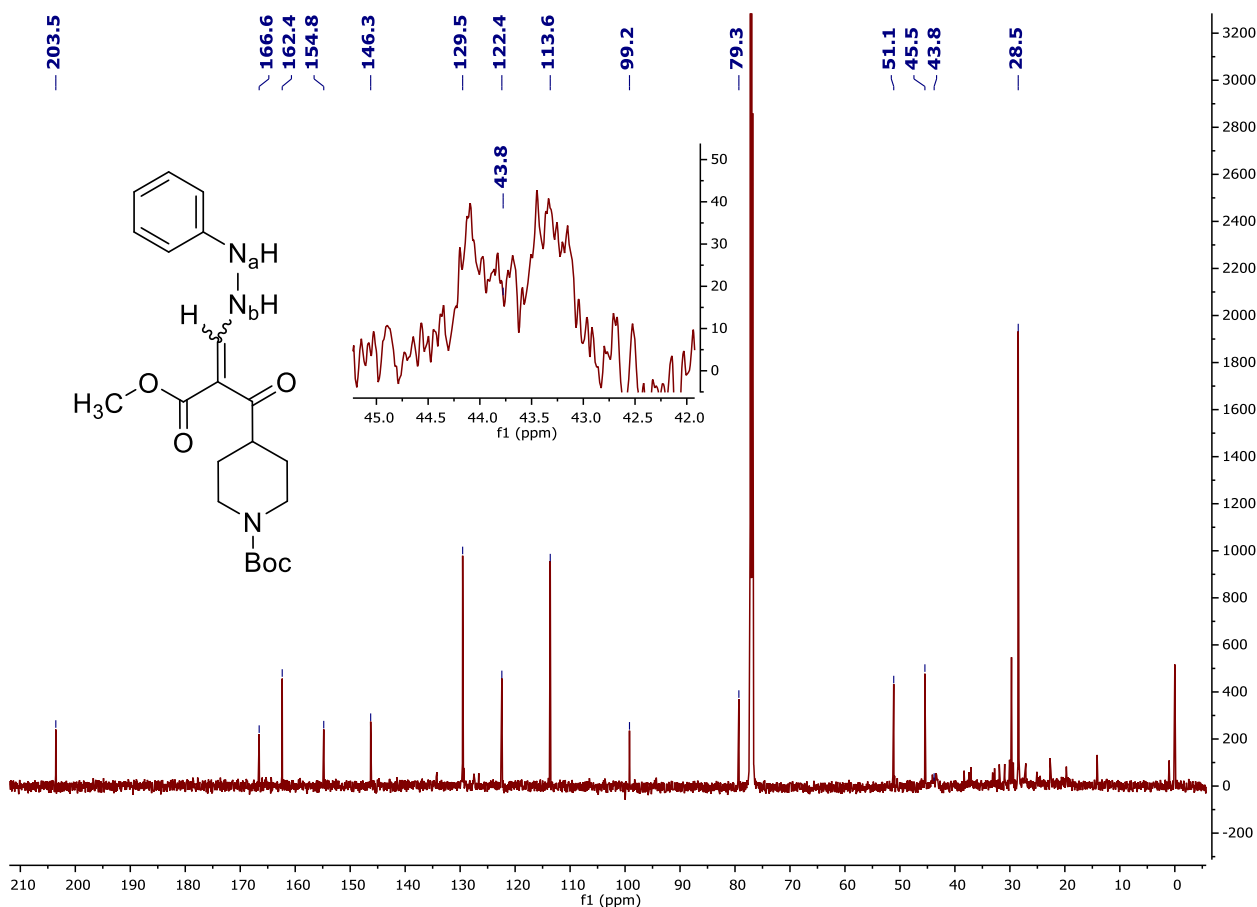


Figure S2. *tert*-Butyl 4-[(*E*(*Z*))-2-(methoxycarbonyl)-3-(2-phenylhydrazinyl)prop-2-enoyl]piperidine-1-carboxylate (**4a**). ¹³C NMR spectrum (176 MHz, CDCl₃).

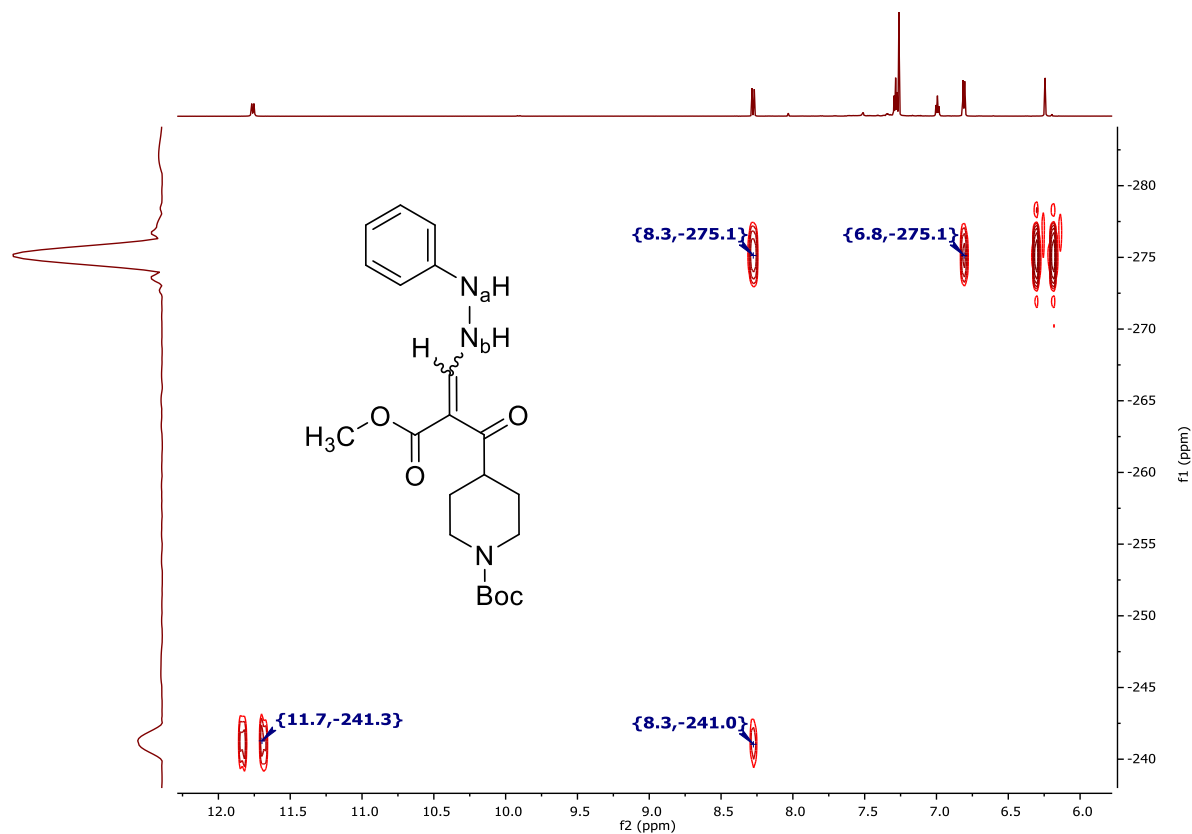


Figure S3. *tert*-Butyl 4-[(2*E*(*Z*))-2-(methoxycarbonyl)-3-(2-phenylhydrazinyl)prop-2-enoyl]piperidine-1-carboxylate (4a). ^1H - ^{15}N HMBC spectrum (71 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

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 Sample Name GMP-601-E_tarpinis
 Comment AB

Acquisition Date 12/5/2020 1:48:04 AM
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 Instrument micrOTOF-Q III 8228888.20448

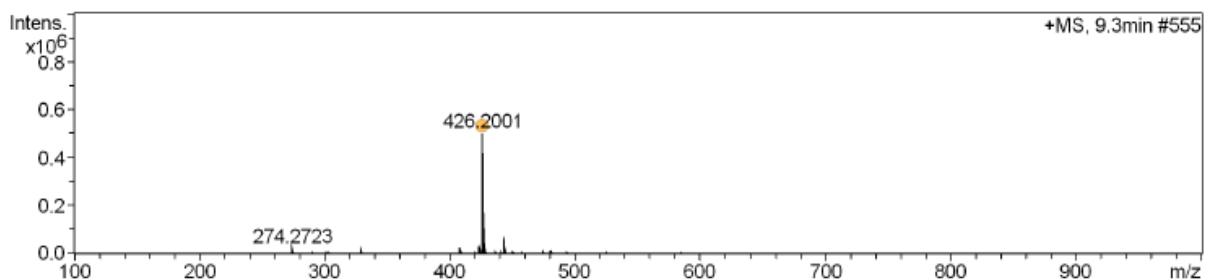
Acquisition Parameter

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Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



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+MS, 9.3min #555



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
426.2001	1	C ₂₁ H ₂₉ N ₃ NaO ₅	426.1999	-0.5	7.3	1	100.00	8.5	even	ok

Figure S4. *tert*-Butyl 4-[(2*E*(*Z*))-2-(methoxycarbonyl)-3-(2-phenylhydrazinyl)prop-2-enoyl]piperidine-1-carboxylate (4a). HRMS (ESI-TOF).

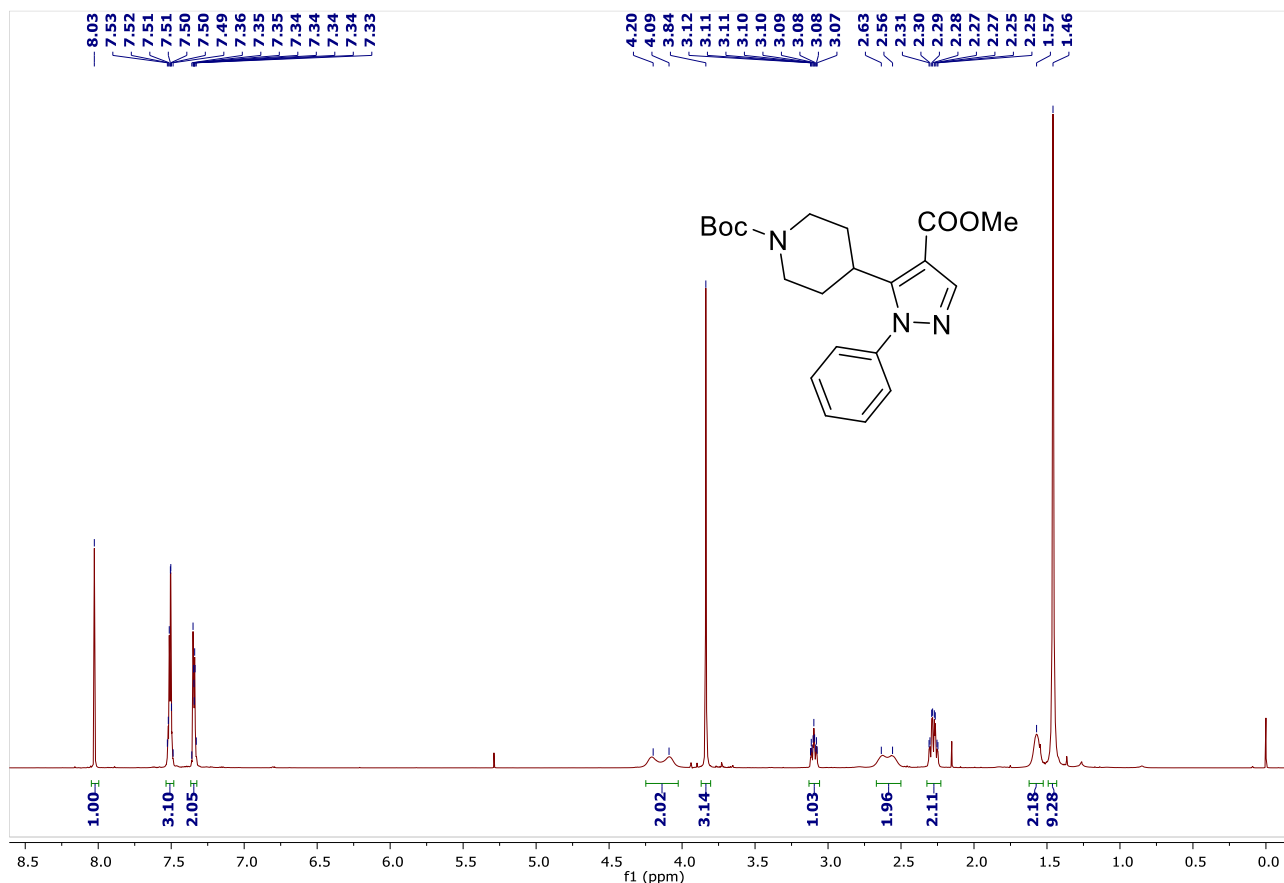


Figure S5. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5a). ¹H NMR spectrum (700 MHz, CDCl₃).

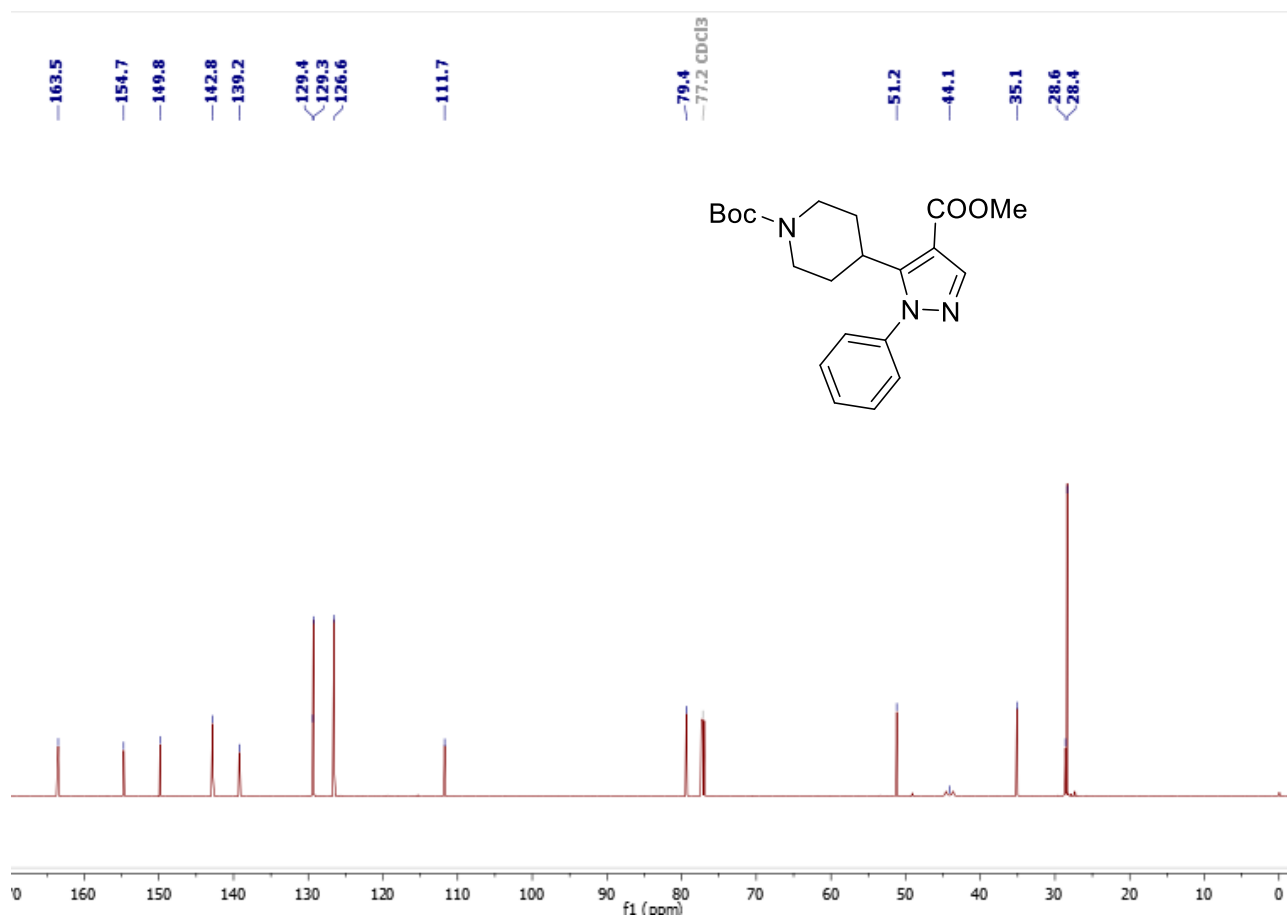


Figure S6. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5a). ¹³C NMR spectrum (176 MHz, CDCl₃).

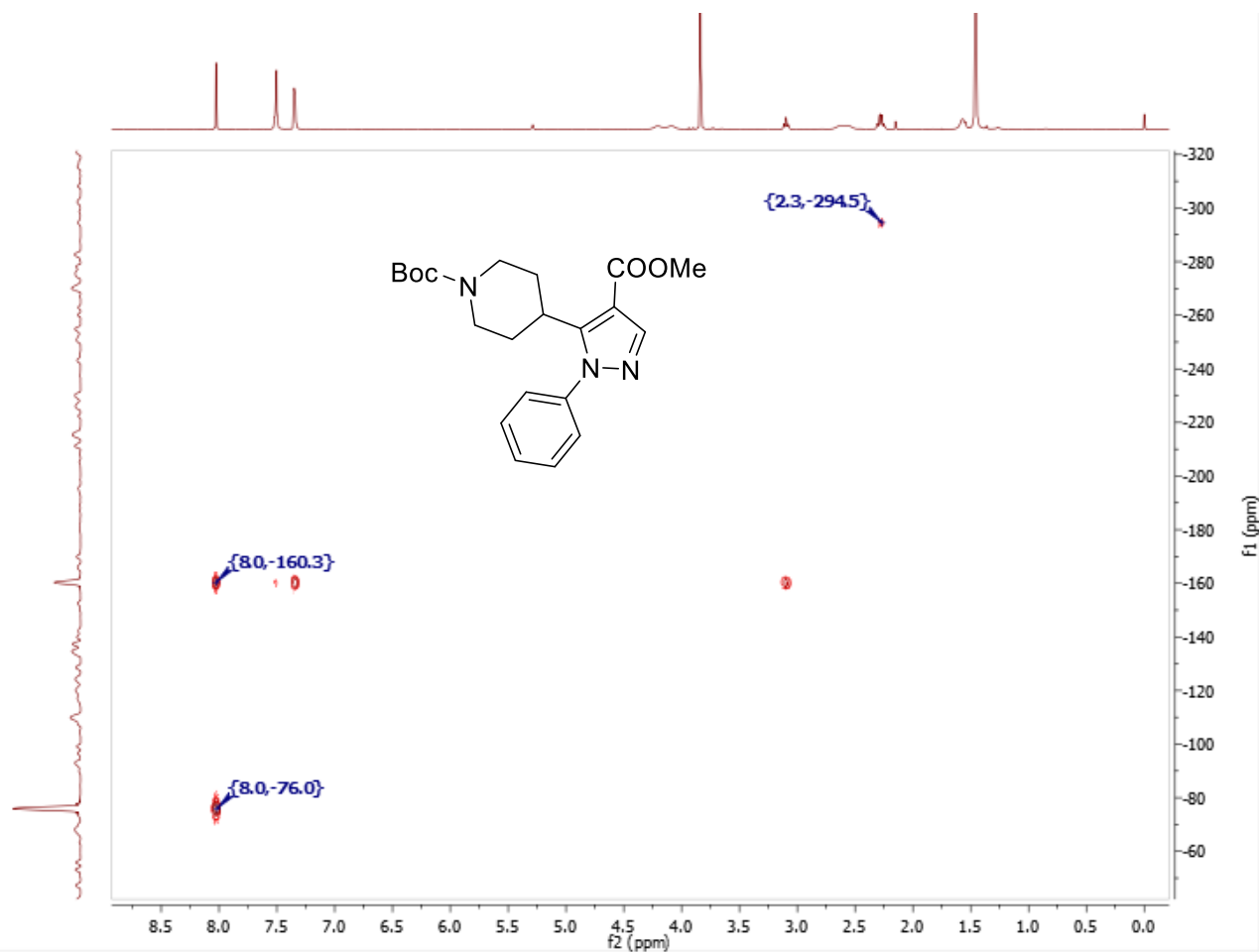


Figure S7. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5a). ^1H - ^{15}N HMBC spectrum (71 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

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Sample Name GMA-021
Comment SB

Acquisition Date 11/27/2018 11:59:44 AM

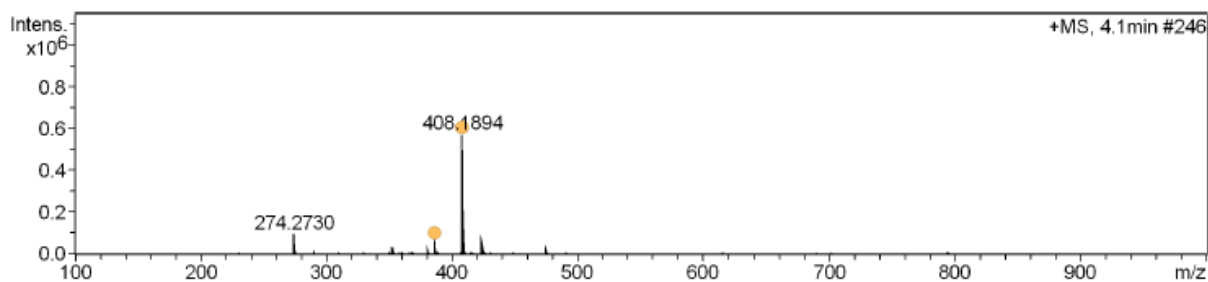
Operator hplc
Instrument micrOTOF-Q III 8228888.20448

Acquisition Parameter

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n.a.	0.2	n.a.	Single spectrum	n.a.	n.a.	n.a.	304.2632	n.a.
n.a.	4.1	n.a.	Single spectrum	n.a.	n.a.	n.a.	408.1894	n.a.

+MS, 4.1min #246



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
386.2075	1	C21H28N3O4	386.2074	-0.2	5.8	1	100.00	9.5	even	ok
408.1894	1	C21H27N3NaO4	408.1894	0.1	1.4	1	100.00	9.5	even	ok

Figure S8. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5a). HRMS (ESI-TOF).

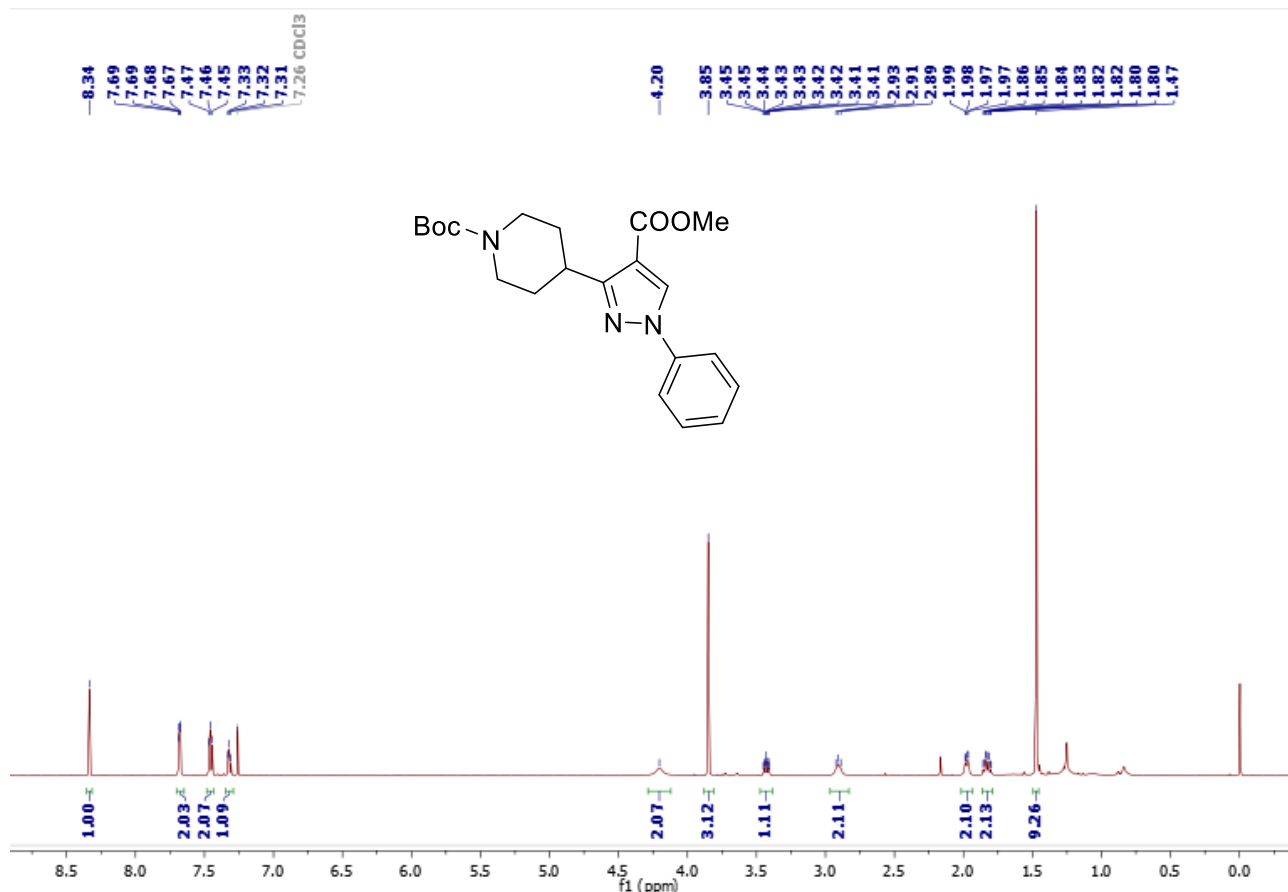


Figure S9. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (6a). ¹H NMR spectrum (700 MHz, CDCl₃).

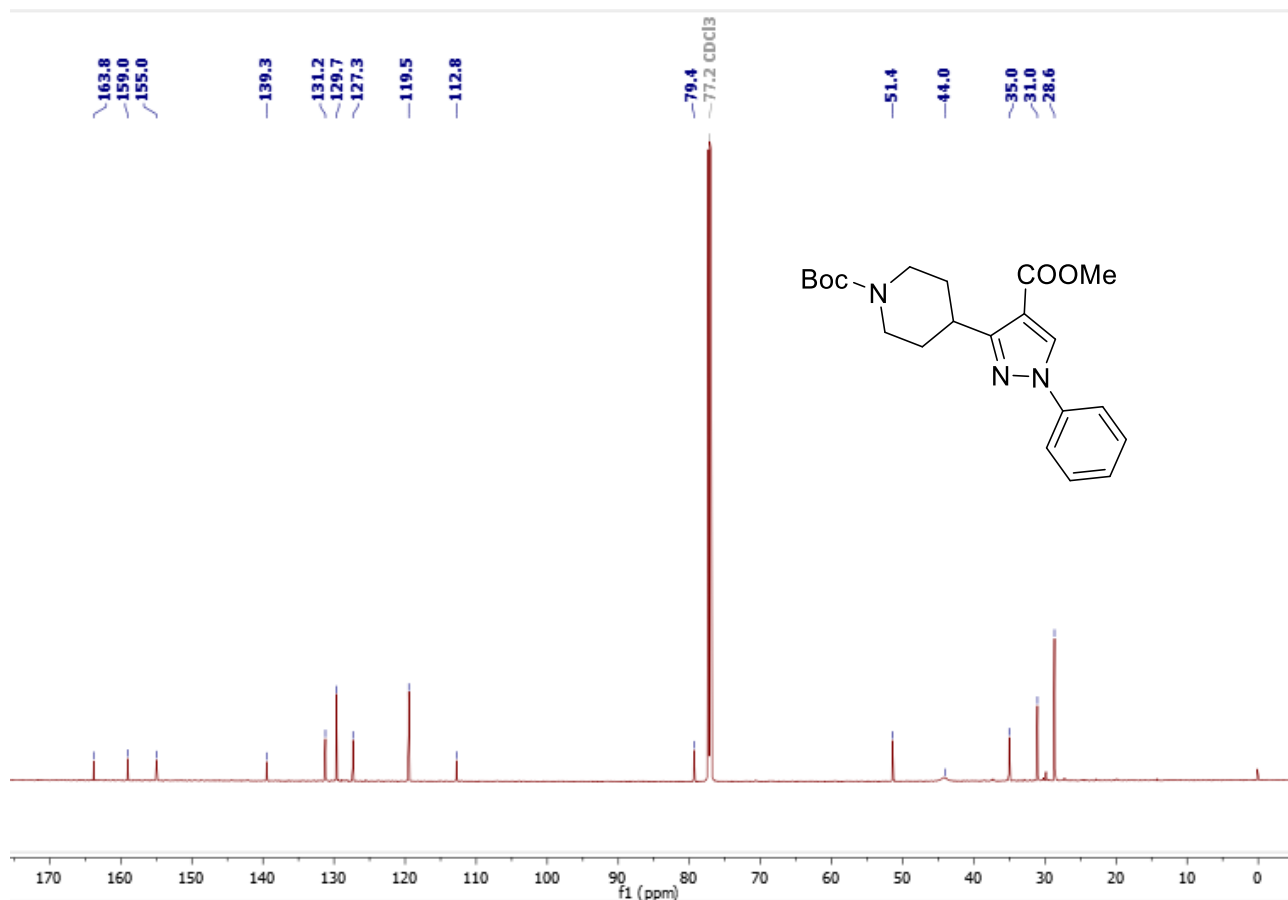


Figure S10. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (6a). ¹³C NMR spectrum (176 MHz, CDCl₃).

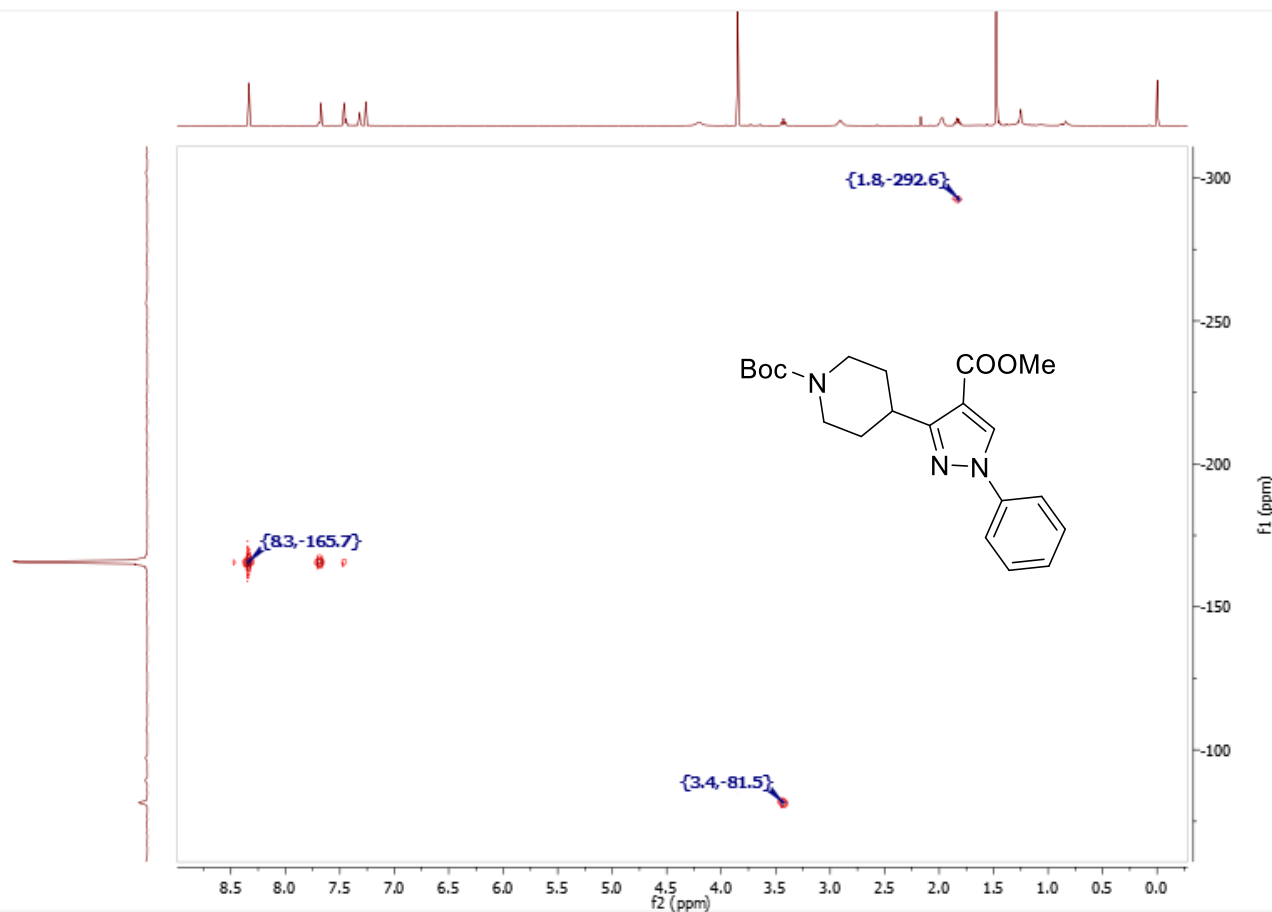


Figure S11. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (6a). ^1H - ^{15}N HMBC spectrum (71 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

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 Sample Name GMP-601-E1
 Comment AB

Acquisition Date 2/4/2021 11:29:42 PM

Operator hplc
 Instrument micrOTOF-Q III 8228888.20448

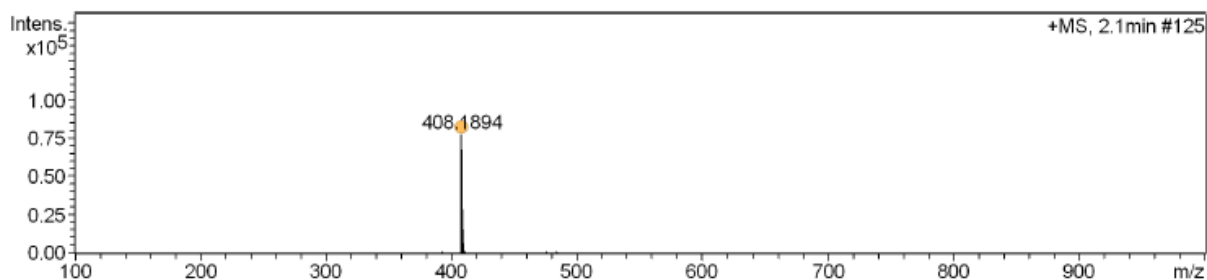
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Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



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n.a.	2.1	n.a.	Single spectrum	n.a.	n.a.	n.a.	408.1894	n.a.

+MS, 2.1min #125



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
408.1894	1	C ₂₁ H ₂₇ N ₃ NaO ₄	408.1894	-0.1	5.8	1	100.00	9.5	even	ok

Figure S12. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (6a). HRMS (ESI-TOF).

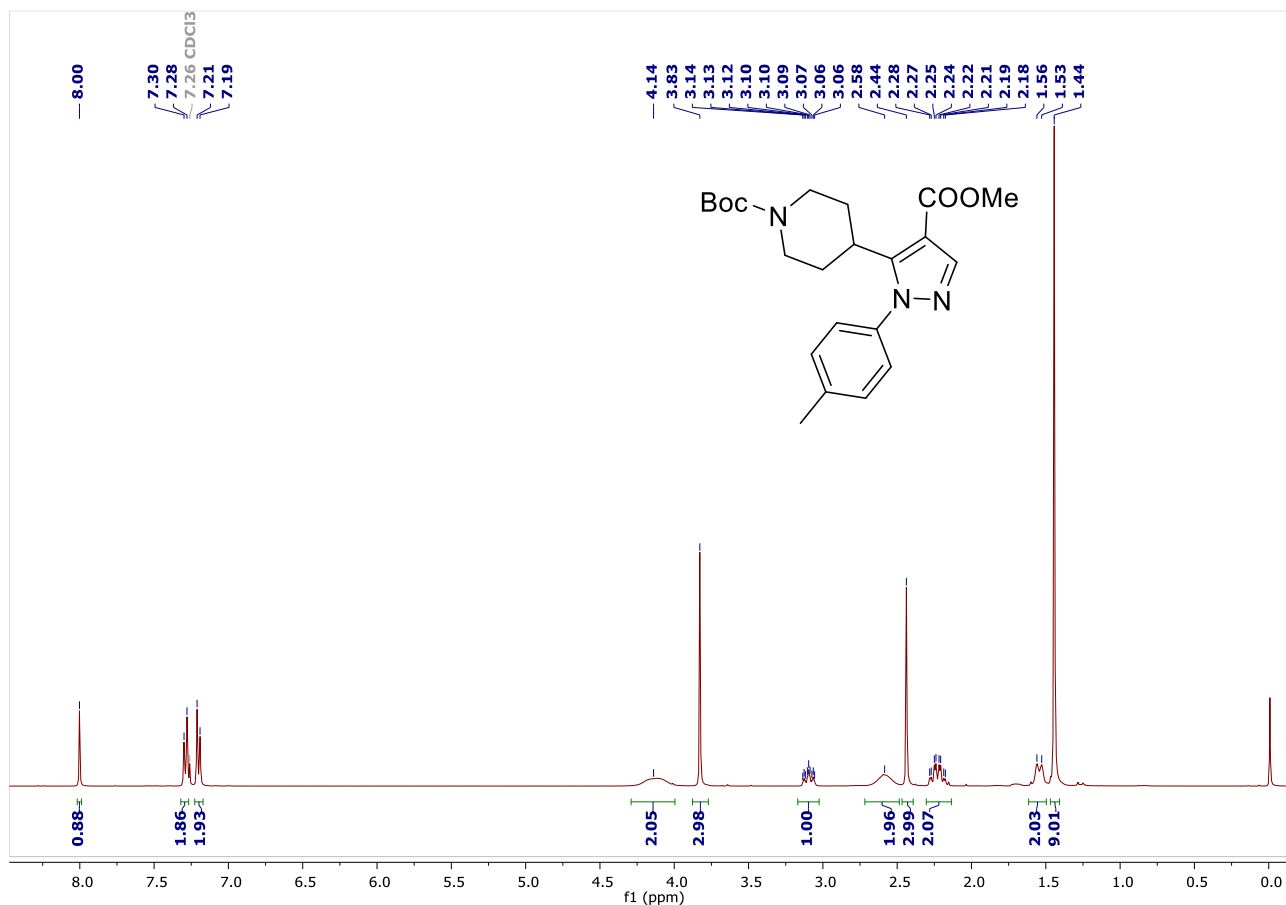


Figure S13. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5b). ¹H NMR spectrum (400 MHz, CDCl₃).

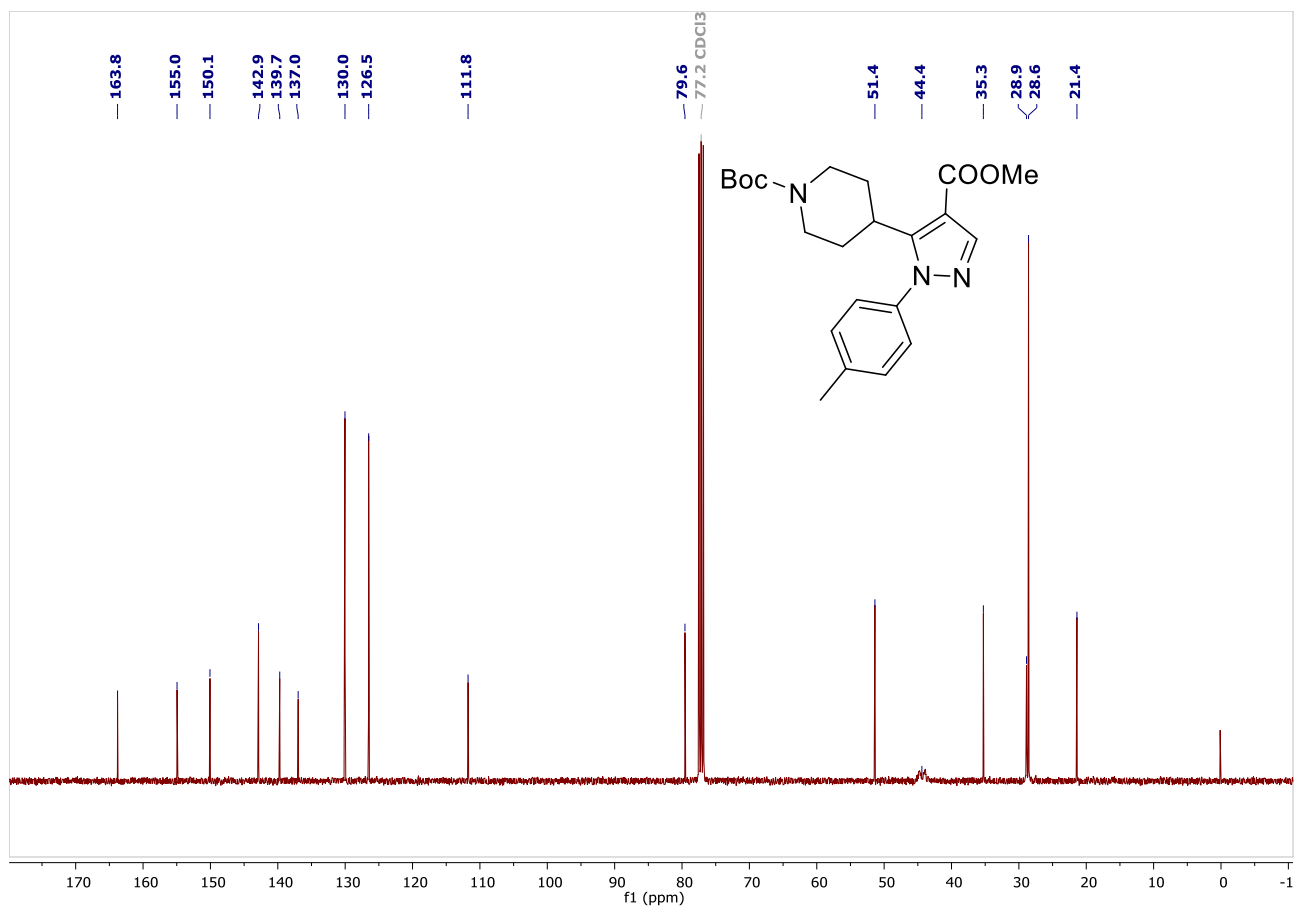


Figure S14. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5b). ¹³C NMR spectrum (101 MHz, CDCl₃).

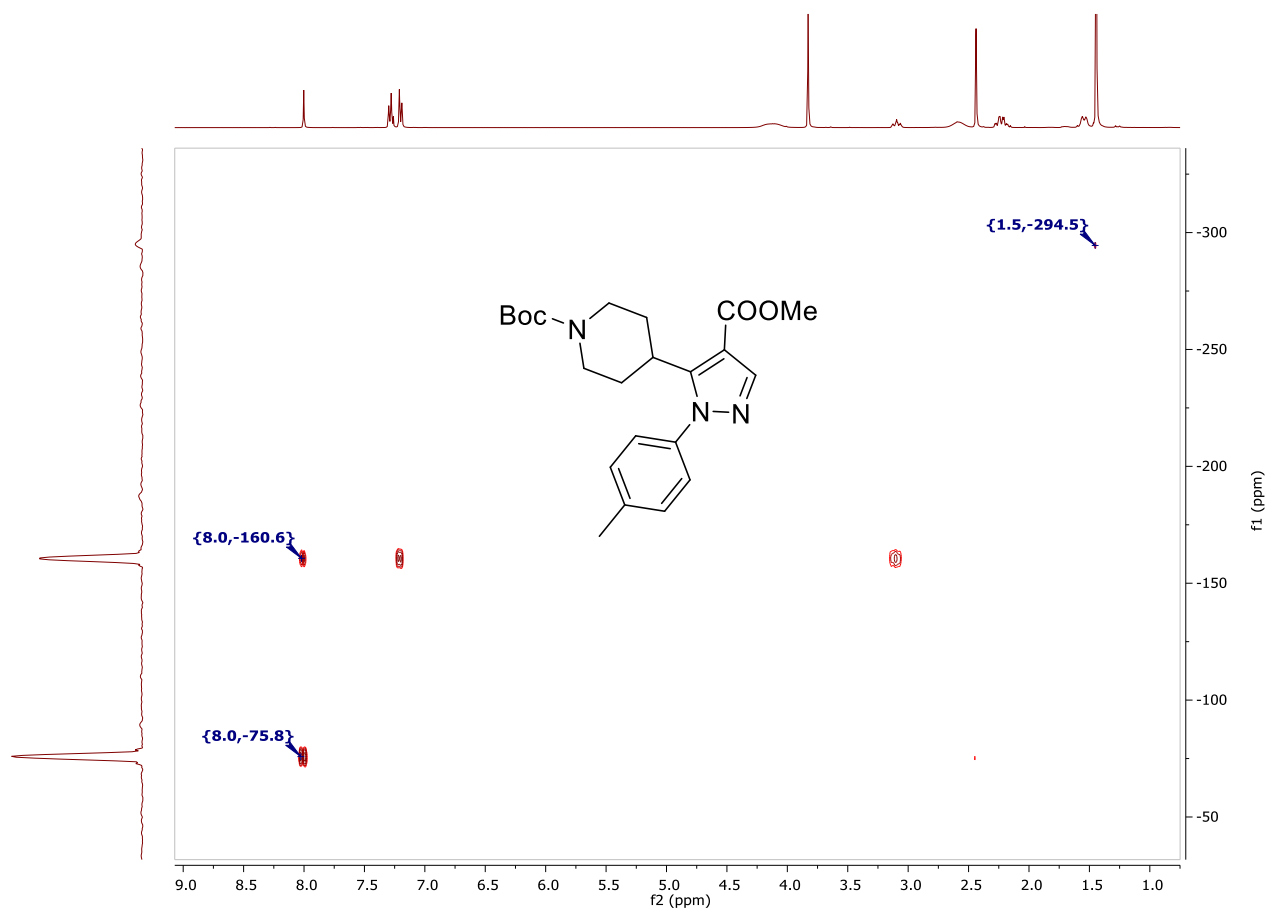


Figure S15. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5b). ¹H-¹⁵N HMBC spectrum (41 MHz, CDCl₃).

Compound Spectrum SmartFormula Report

Analysis Info

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 Comment SB

Acquisition Date 11/27/2018 11:44:50 AM

Operator hplc
 Instrument micrOTOF-Q III 8228888.20448

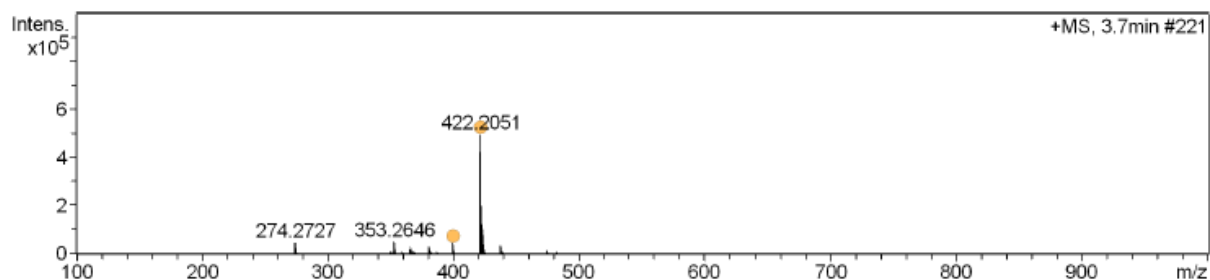
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Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



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n.a.	0.2	n.a.	Single spectrum	n.a.	n.a.	n.a.	304.2634	n.a.
n.a.	3.7	n.a.	Single spectrum	n.a.	n.a.	n.a.	422.2051	n.a.

+MS, 3.7min #221



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422.2051	1	C22H29N3NaO4	422.2050	-0.2	2.1	1	100.00	9.5	even	ok

Figure S16. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5b). HRMS (ESI-TOF).

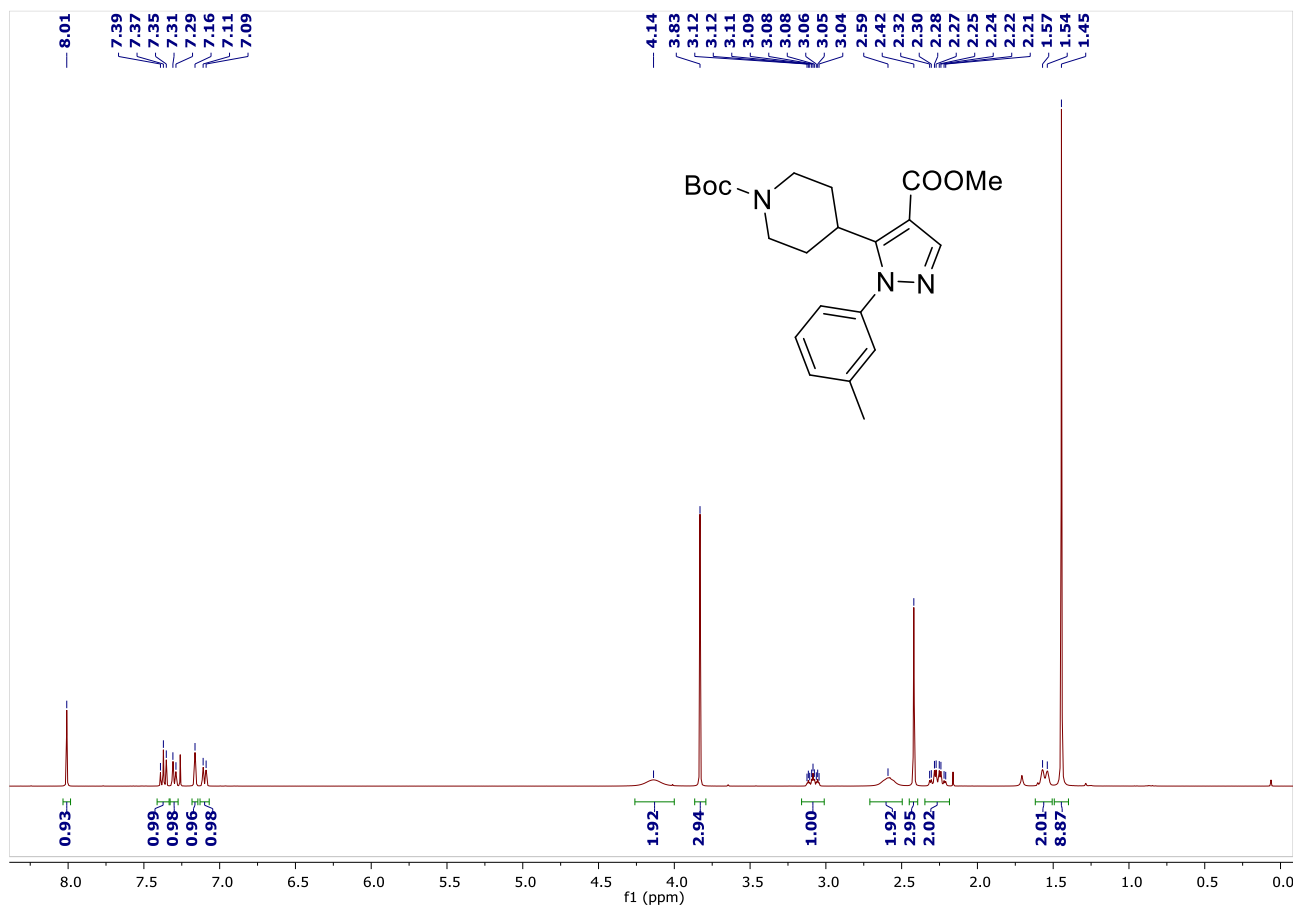


Figure S17. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(3-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5c). ¹H NMR spectrum (400 MHz, CDCl₃).

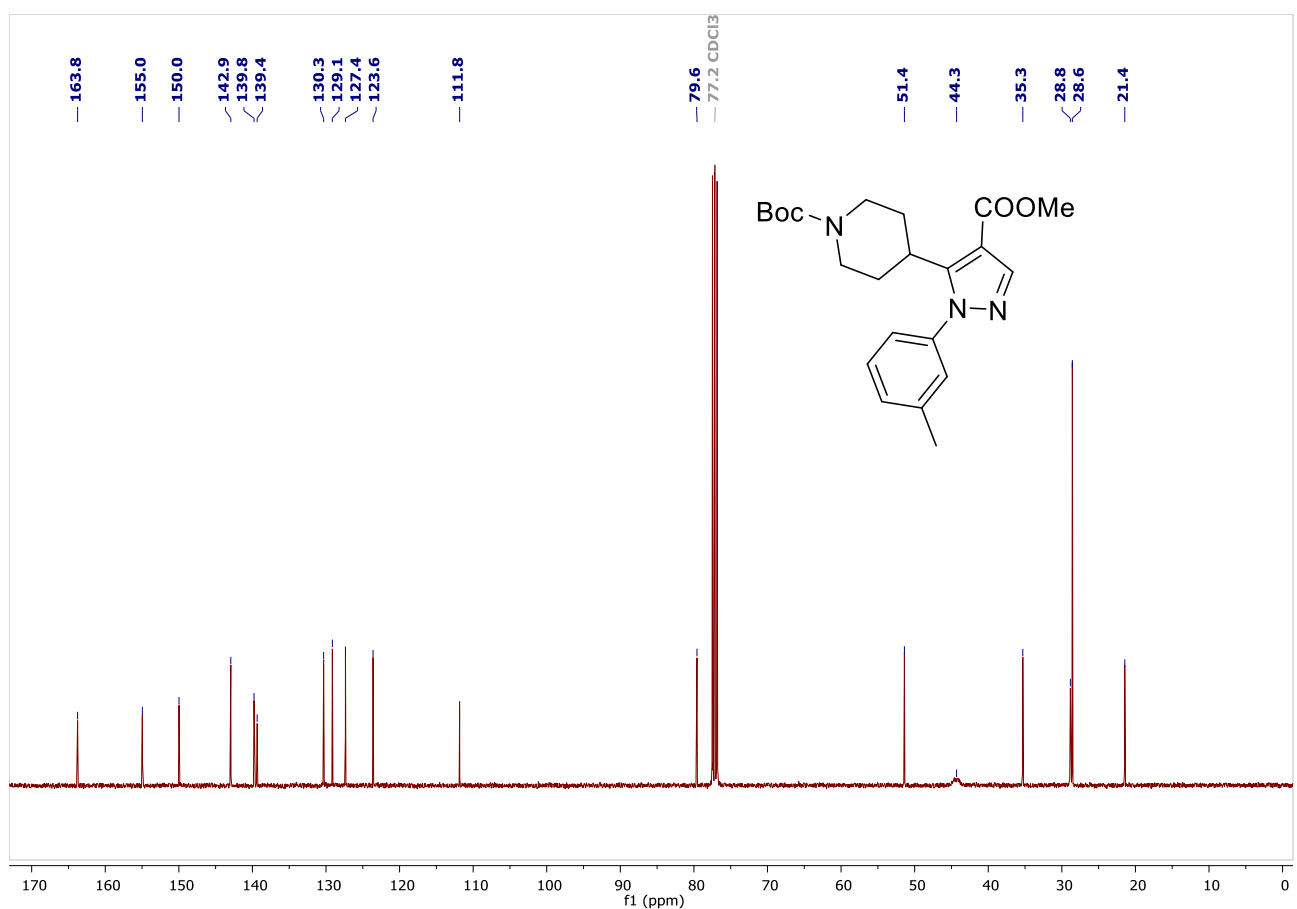


Figure S18. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(3-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5c). ¹³C NMR spectrum (176 MHz, CDCl₃).

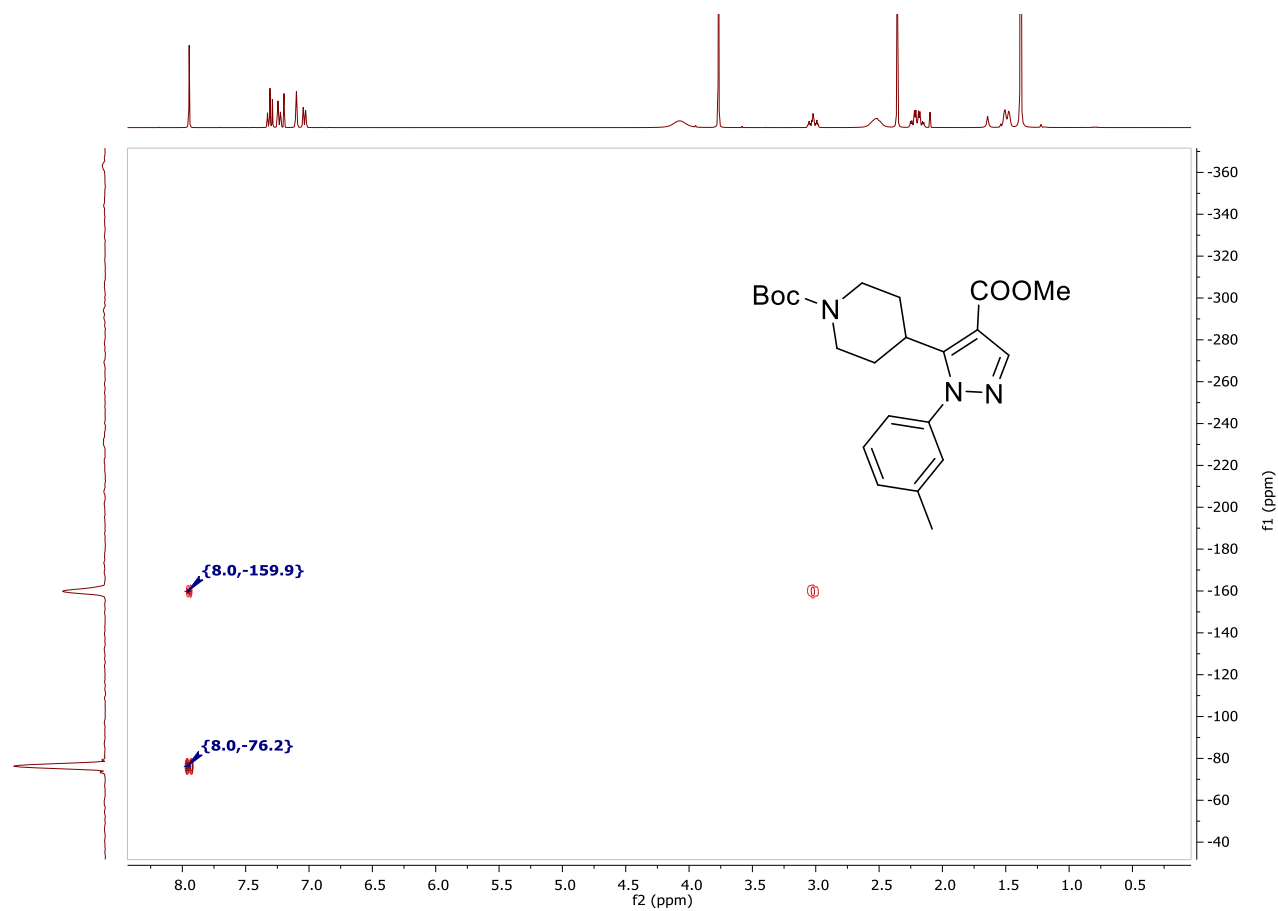


Figure S19. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(3-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5c). ^{15}N NMR spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

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Operator hplc
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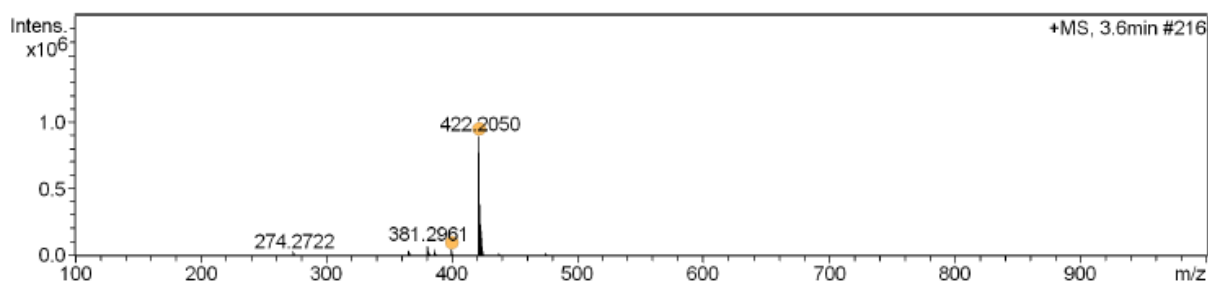
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n.a.	3.6	n.a.	Single spectrum	n.a.	n.a.	n.a.	422.2050	n.a.

+MS, 3.6min #216



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400.2223	1	C22H30N3O4	400.2231	-2.0	41.0	1	100.00	9.5	even	ok
422.2050	1	C22H29N3NaO4	422.2050	-0.0	11.7	1	100.00	9.5	even	ok

Figure S20. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(3-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5c). HRMS (ESI-TOF).

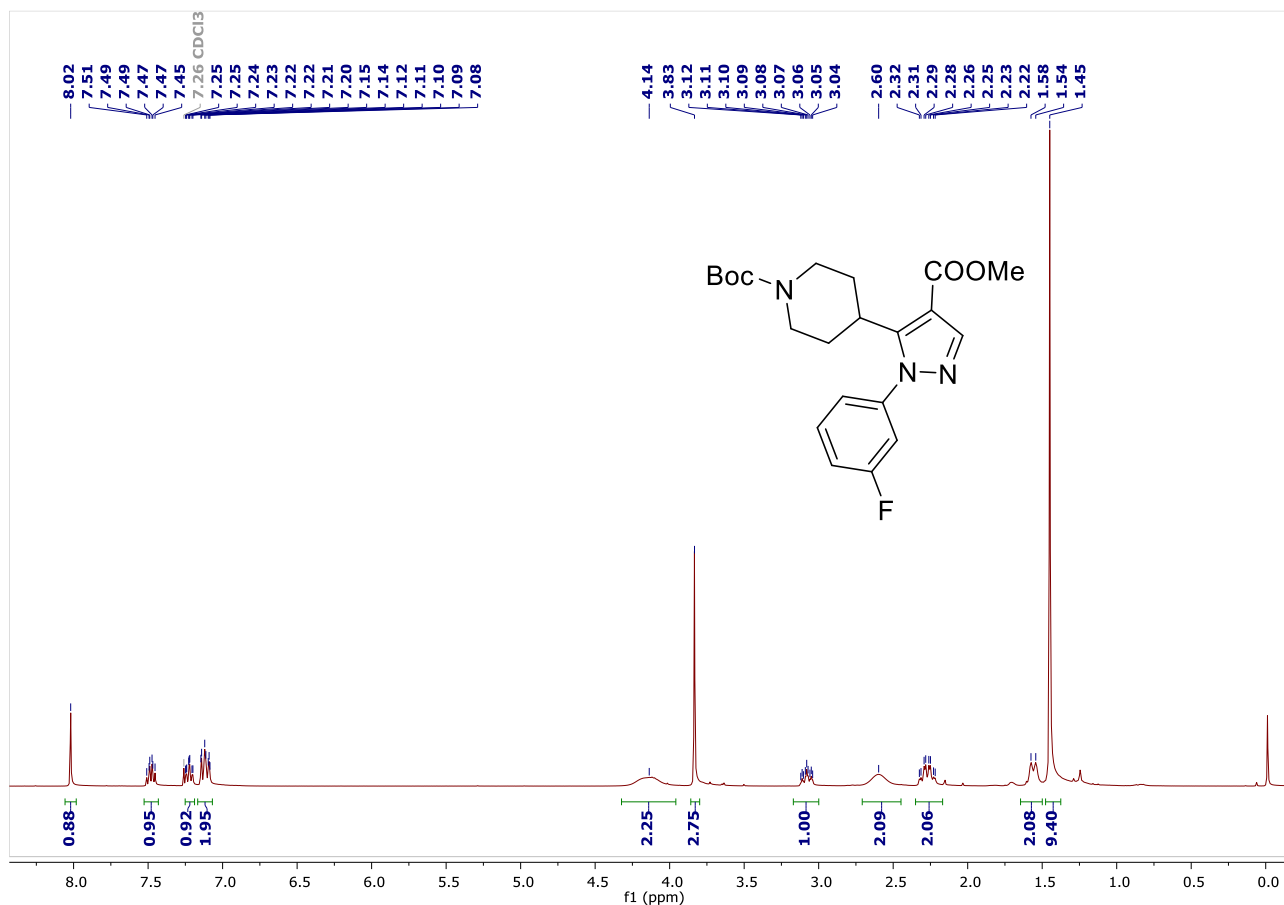


Figure S21. *tert*-Butyl 4-[1-(3-fluorophenyl)-4-(methoxycarbonyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5d). ¹H NMR spectrum (400 MHz, CDCl₃).

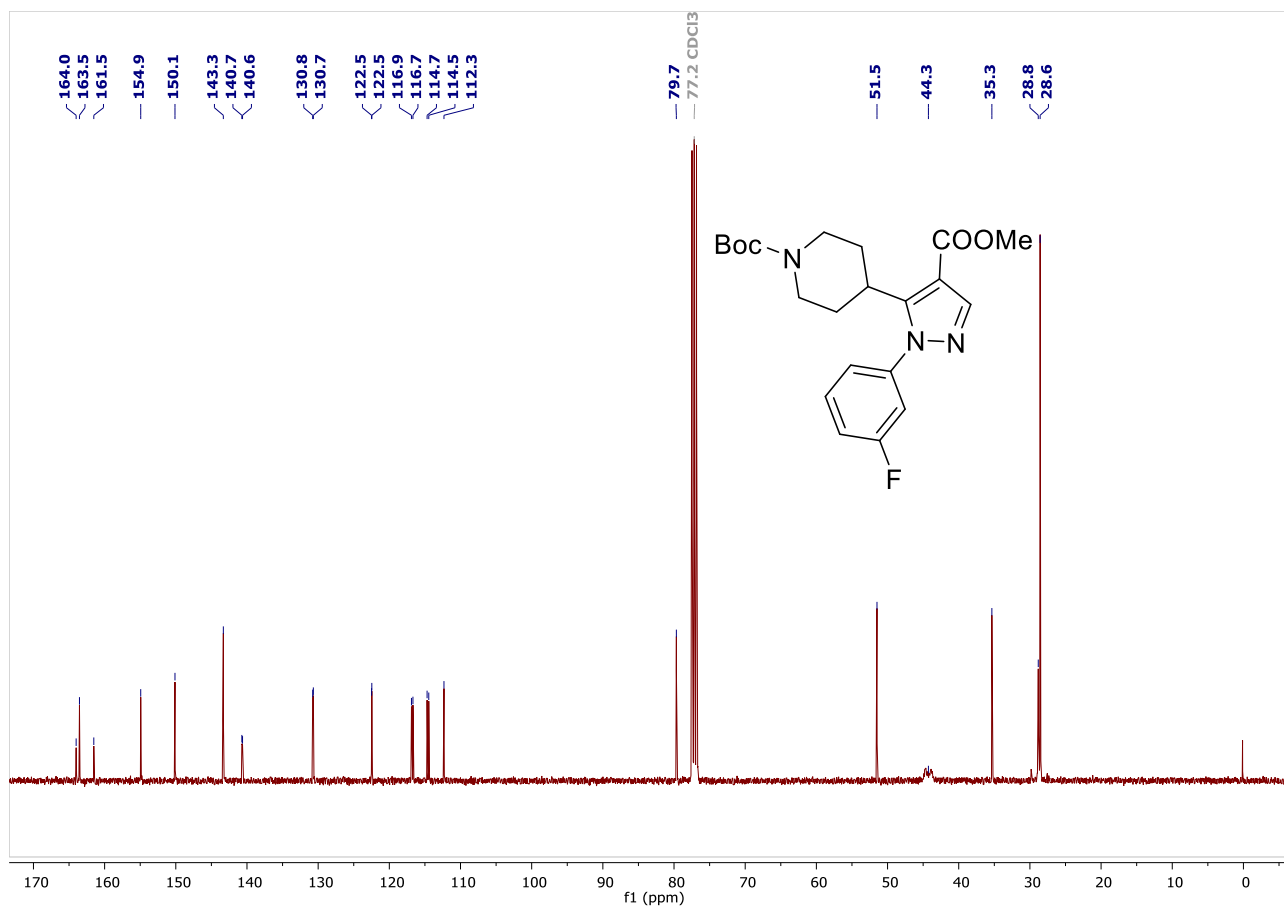


Figure S22. *tert*-Butyl 4-[1-(3-fluorophenyl)-4-(methoxycarbonyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5d). ¹³C NMR spectrum (101 MHz, CDCl₃).

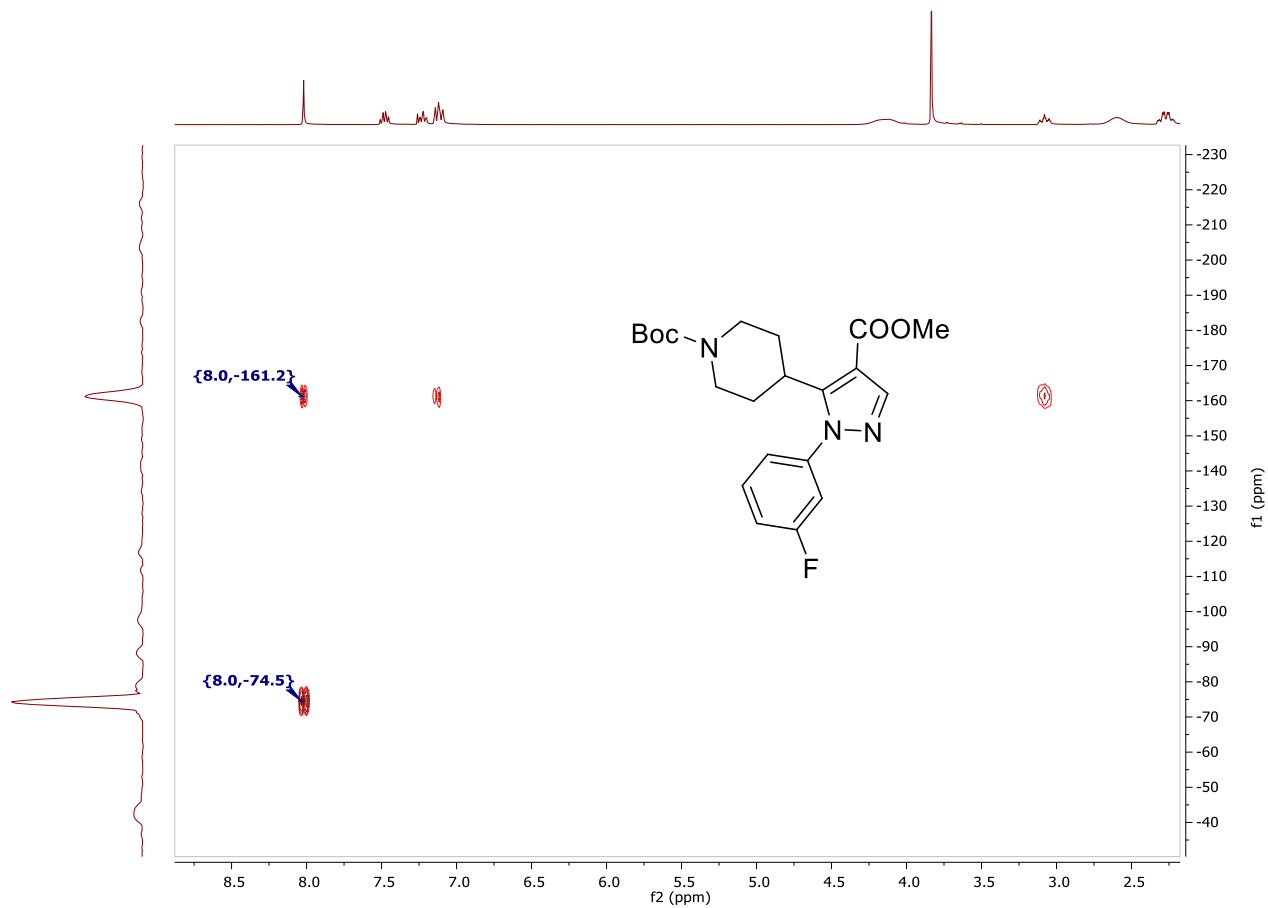


Figure S23. *tert*-Butyl 4-[1-(3-fluorophenyl)-4-(methoxycarbonyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5d). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

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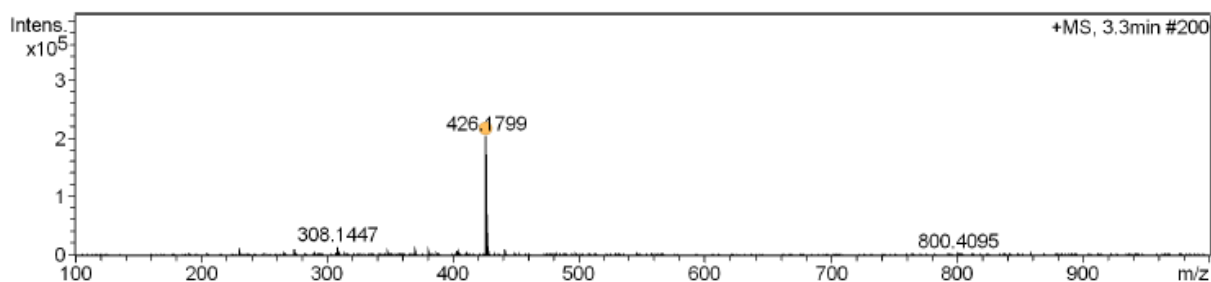
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n.a.	0.3	n.a.	Single spectrum	n.a.	n.a.	n.a.	304.2632	n.a.
n.a.	3.3	n.a.	Single spectrum	n.a.	n.a.	n.a.	426.1799	n.a.

+MS, 3.3min #200



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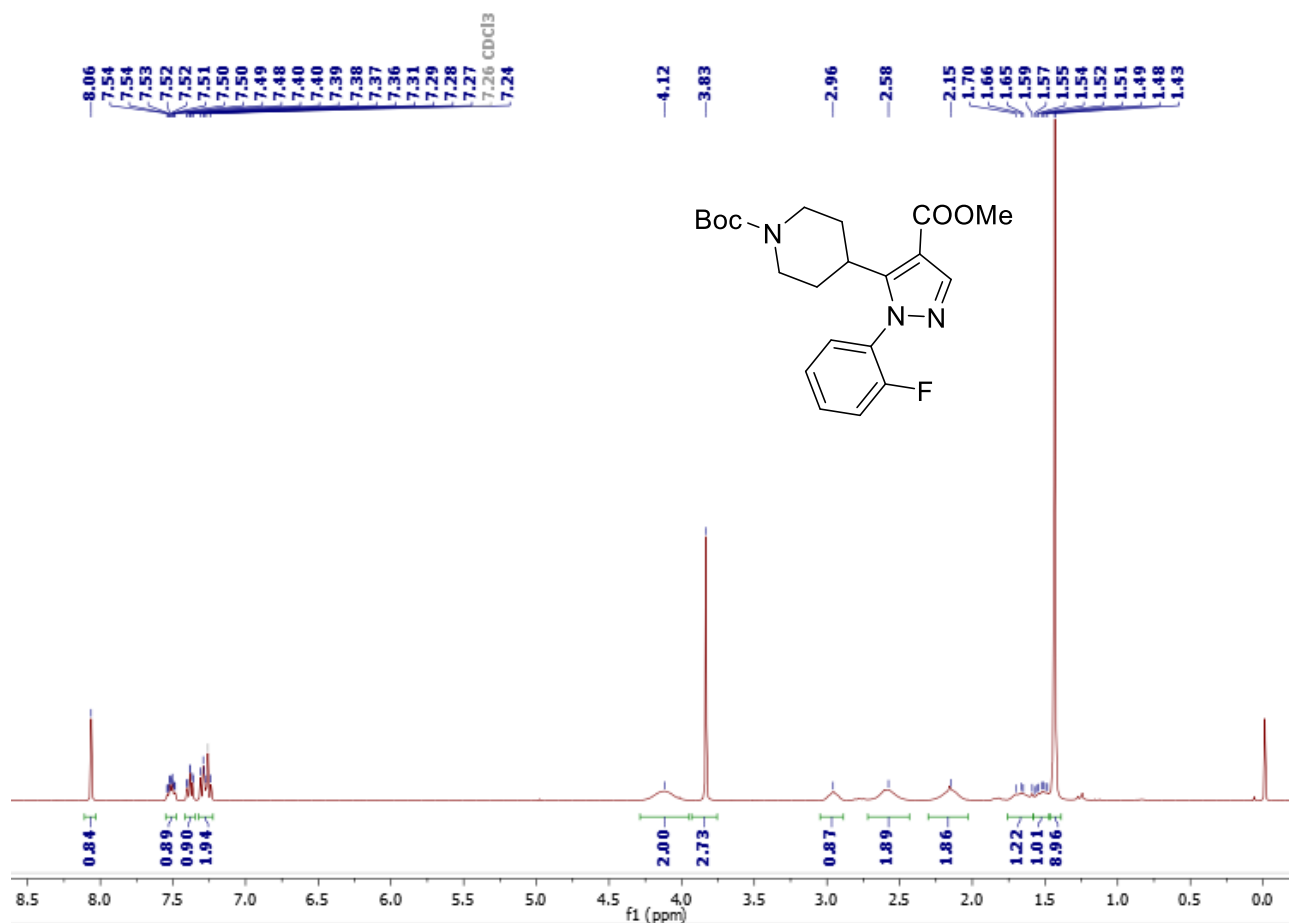


Figure S25. *tert*-Butyl 4-[1-(2-fluorophenyl)-4-(methoxycarbonyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5e). ¹H NMR spectrum (400 MHz, CDCl₃).

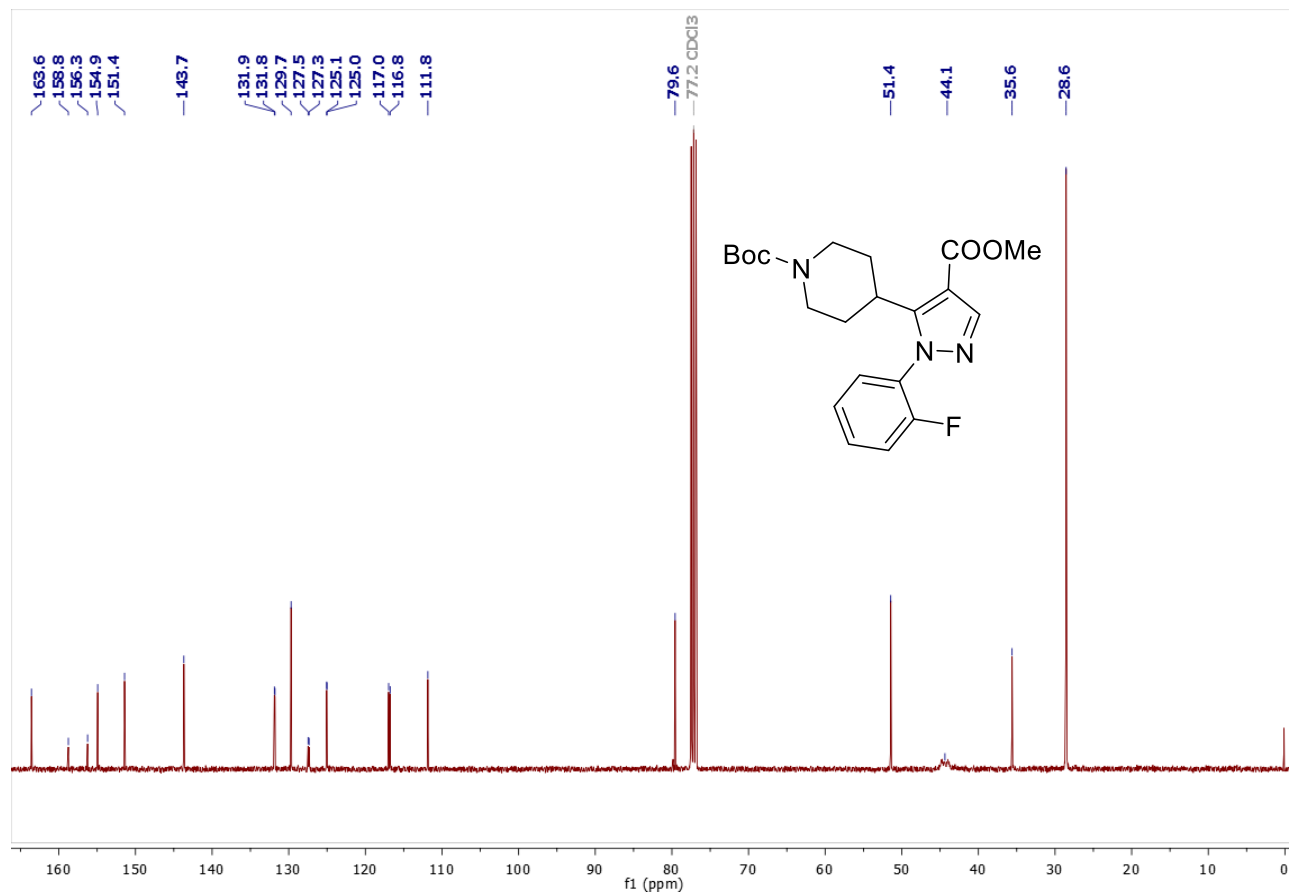


Figure S26. *tert*-Butyl 4-[1-(2-fluorophenyl)-4-(methoxycarbonyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5e). ¹³C NMR spectrum (101 MHz, CDCl₃).

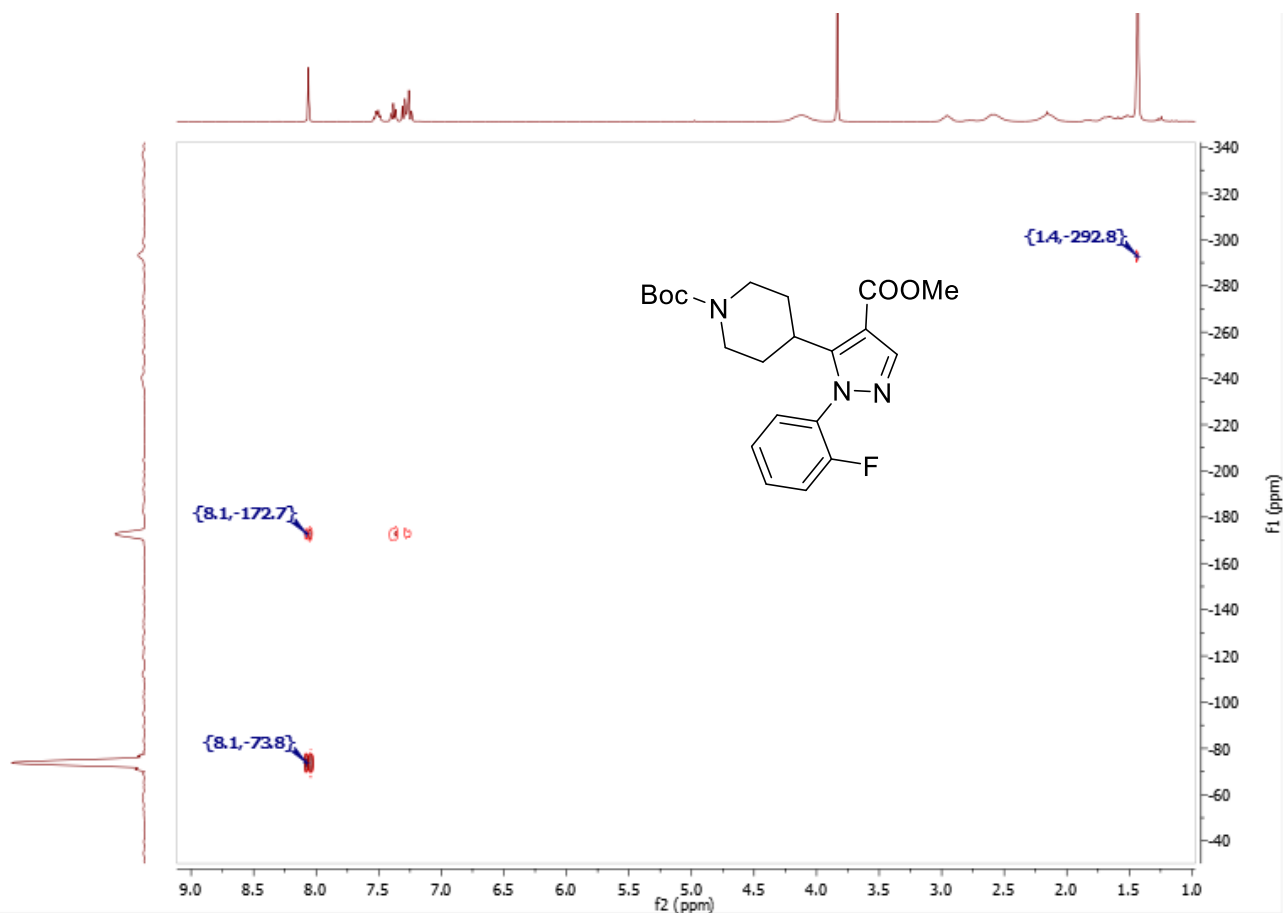


Figure S27. *tert*-Butyl 4-[1-(2-fluorophenyl)-4-(methoxycarbonyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5e). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

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Sample Name GMP-013
Comment SB

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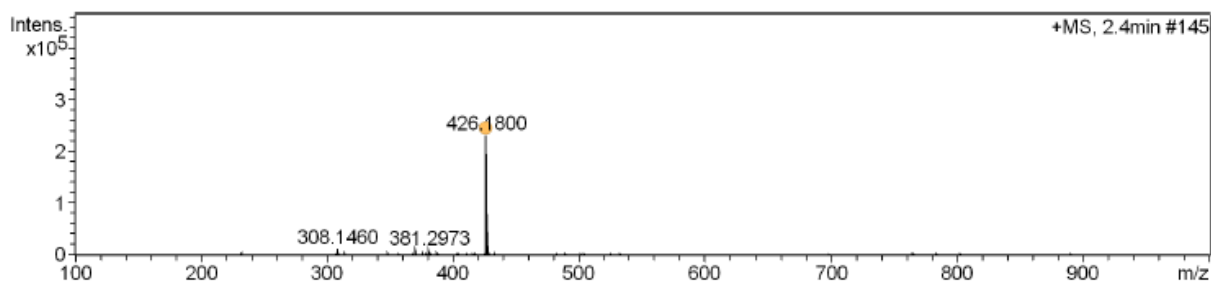
Operator hplc
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n.a.	2.4	n.a.	Single spectrum	n.a.	n.a.	n.a.	426.1800	n.a.

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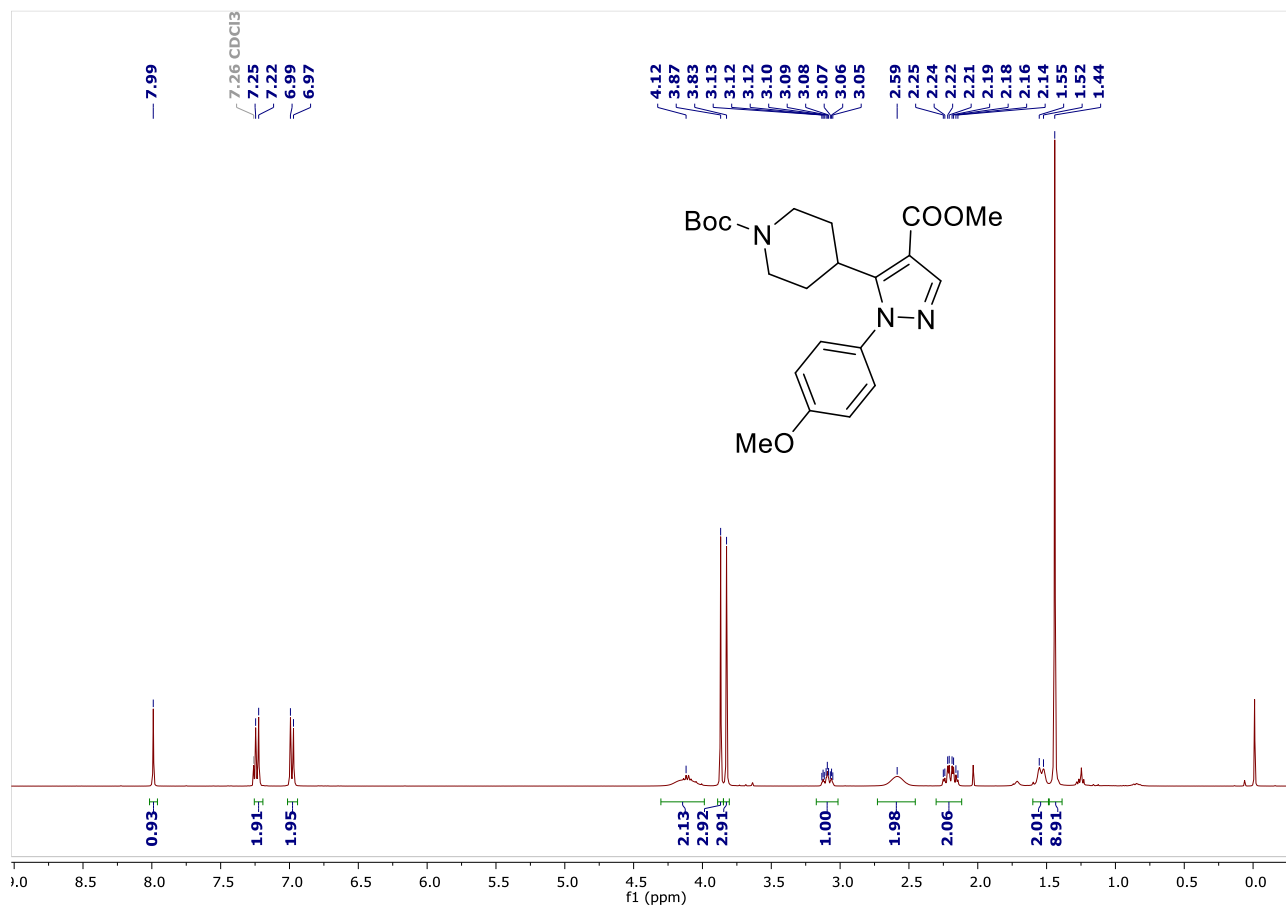


Figure S29. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(4-methoxyphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5f). ¹H NMR spectrum (400 MHz, CDCl₃).

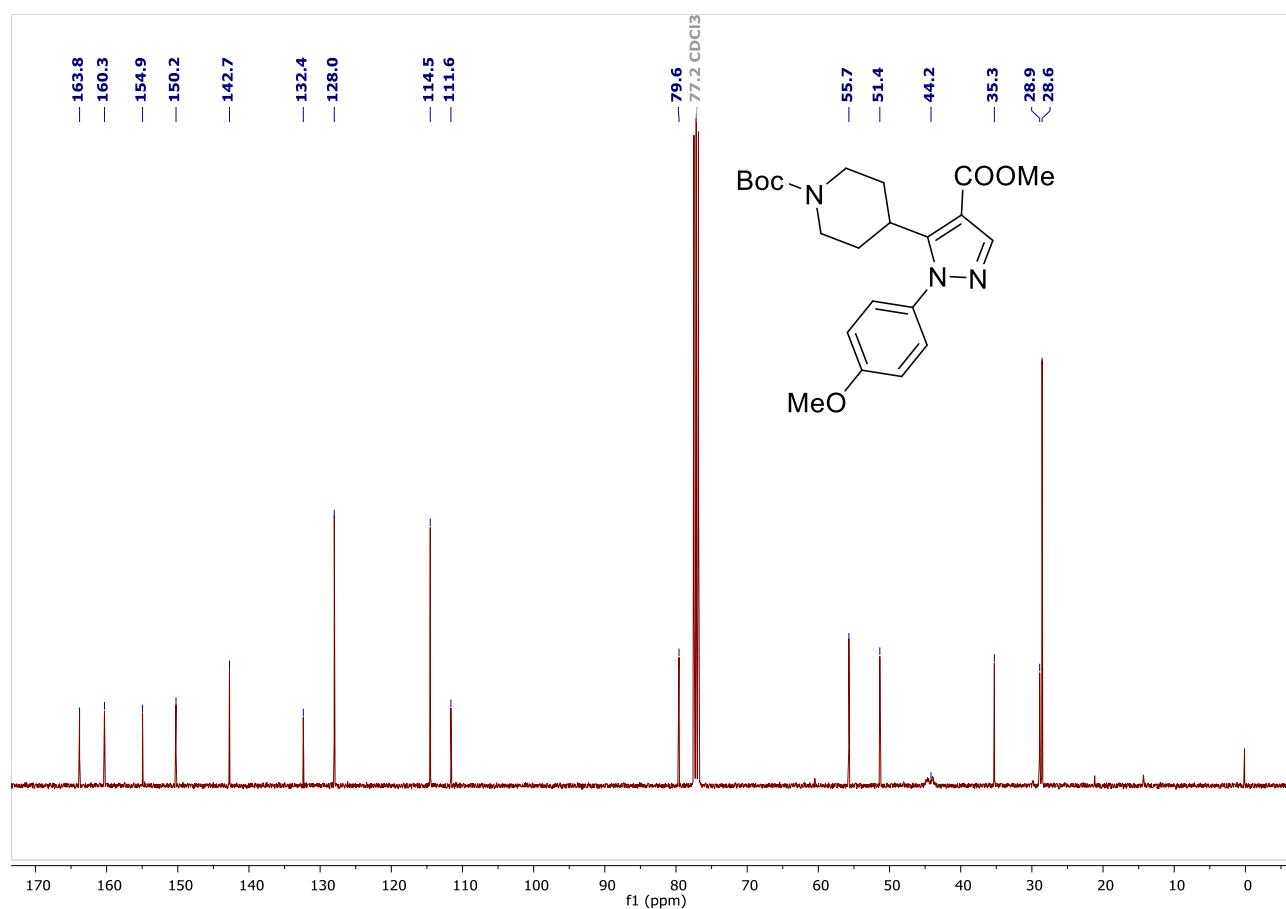


Figure S30. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(4-methoxyphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5f). ¹³C NMR spectrum (176 MHz, CDCl₃).

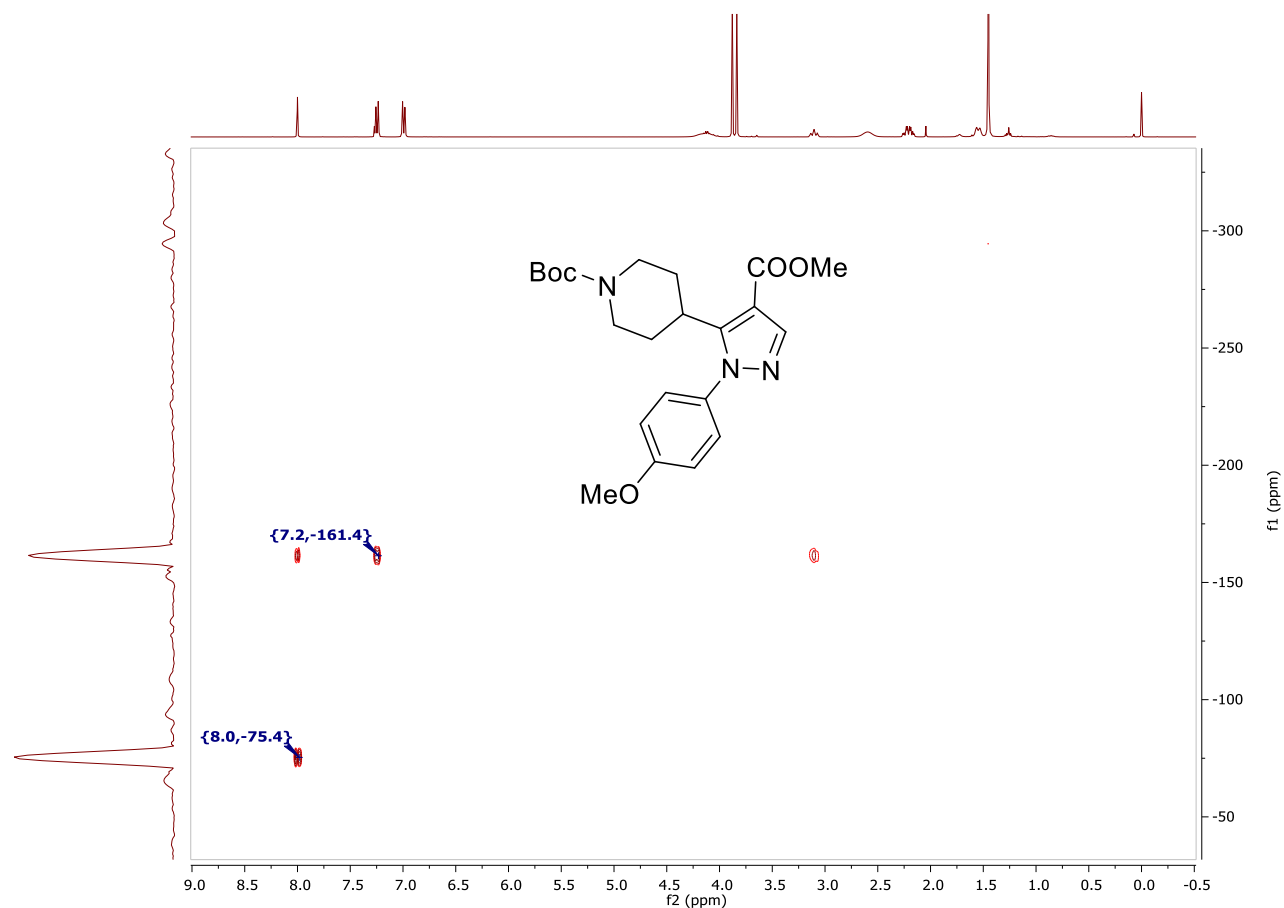


Figure S31. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(4-methoxyphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5f). ^{15}N NMR spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

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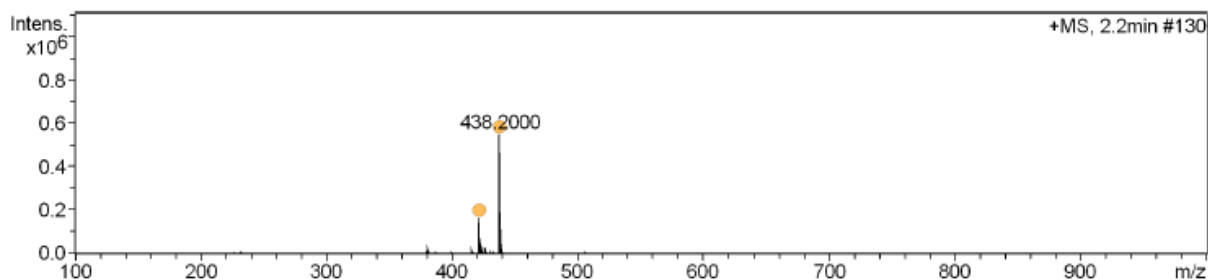
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Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



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n.a.	0.2	n.a.	Single spectrum	n.a.	n.a.	n.a.	304.2631	n.a.
n.a.	2.2	n.a.	Single spectrum	n.a.	n.a.	n.a.	438.2000	n.a.

+MS, 2.2min #130



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
422.2046	1	C22H29N3NaO4	422.2050	1.0	4.5	1	100.00	9.5	even	ok
438.2000	1	C22H29N3NaO5	438.1999	0.0	4.4	1	100.00	9.5	even	ok

Figure S32. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(4-methoxyphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5f). HRMS (ESI-TOF).

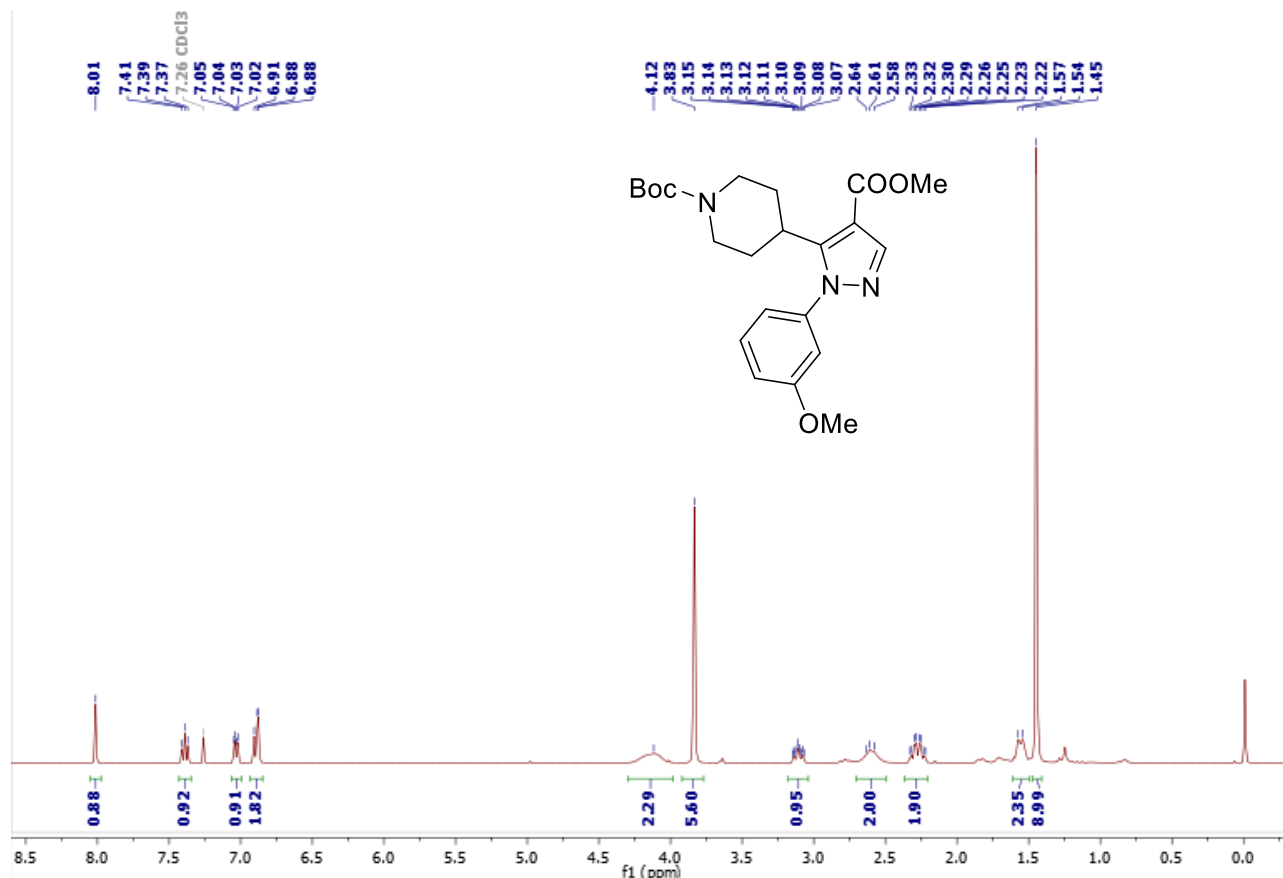


Figure S33. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(3-methoxyphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5g). ¹H NMR spectrum (400 MHz, CDCl₃).

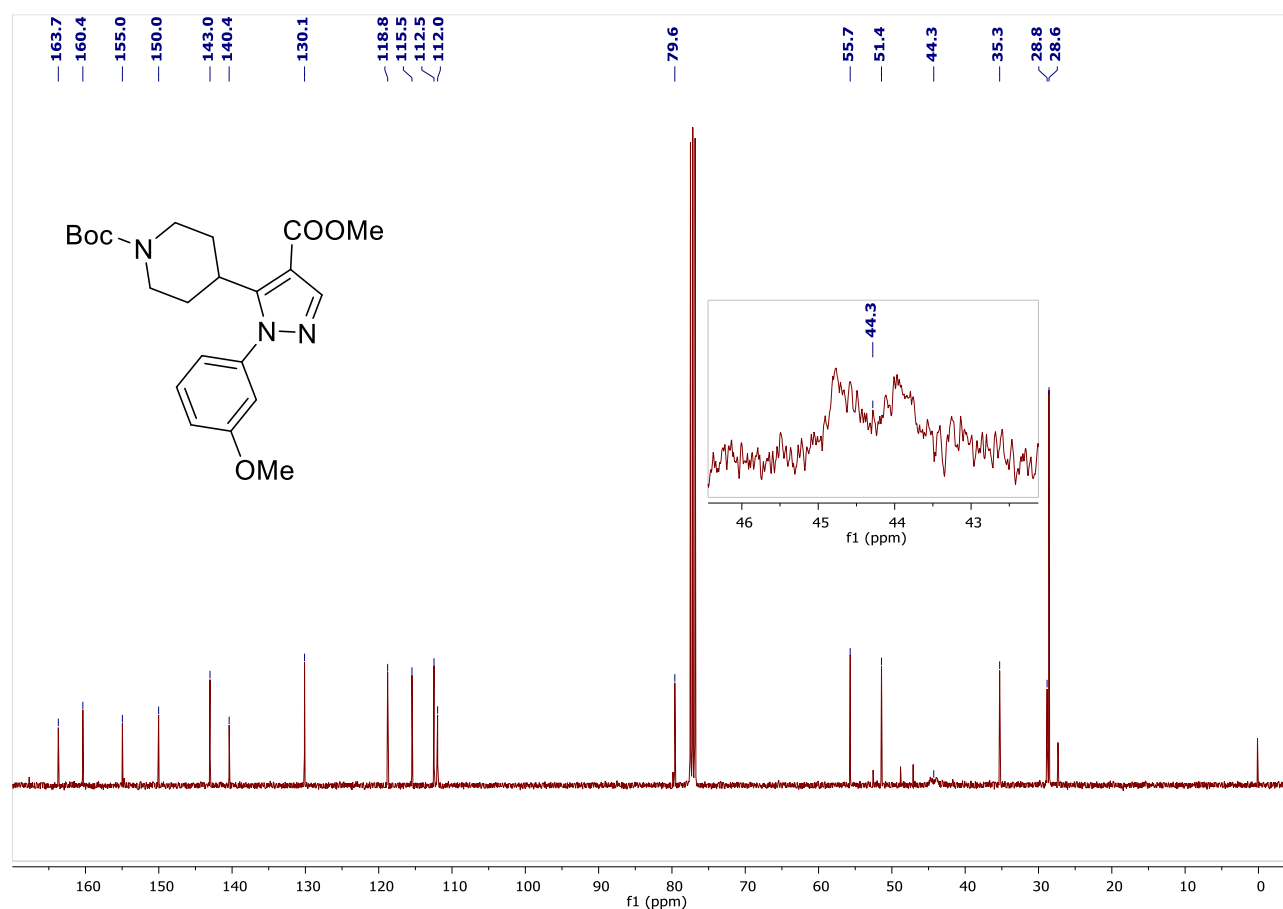


Figure S34. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(3-methoxyphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5g). ¹³C NMR spectrum (101 MHz, CDCl₃).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-16.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-16
Comment AB

Acquisition Date 2/4/2021 11:39:59 PM

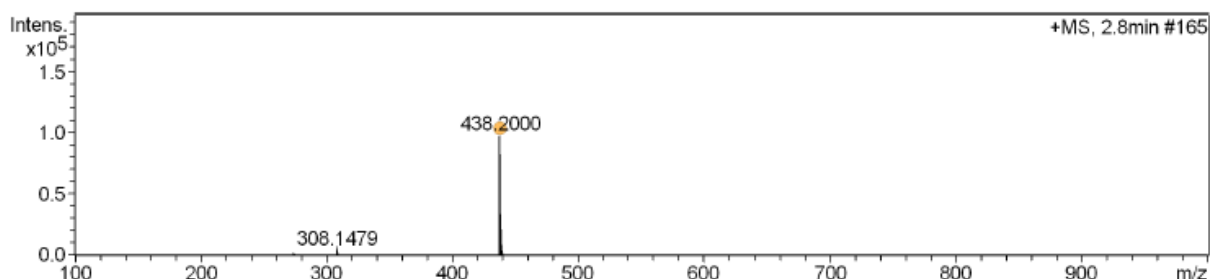
Operator hplc
Instrument micrOTOF-Q III 8228888.20448

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste

#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	2.8	n.a.	Single spectrum	n.a.	n.a.	n.a.	438.2000	n.a.

+MS, 2.8min #165



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
438.2000	1	C22H29N3NaO5	438.1999	-0.0	2.3	1	100.00	9.5	even	ok

Figure S35. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-(3-methoxyphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5g). HRMS (ESI-TOF).

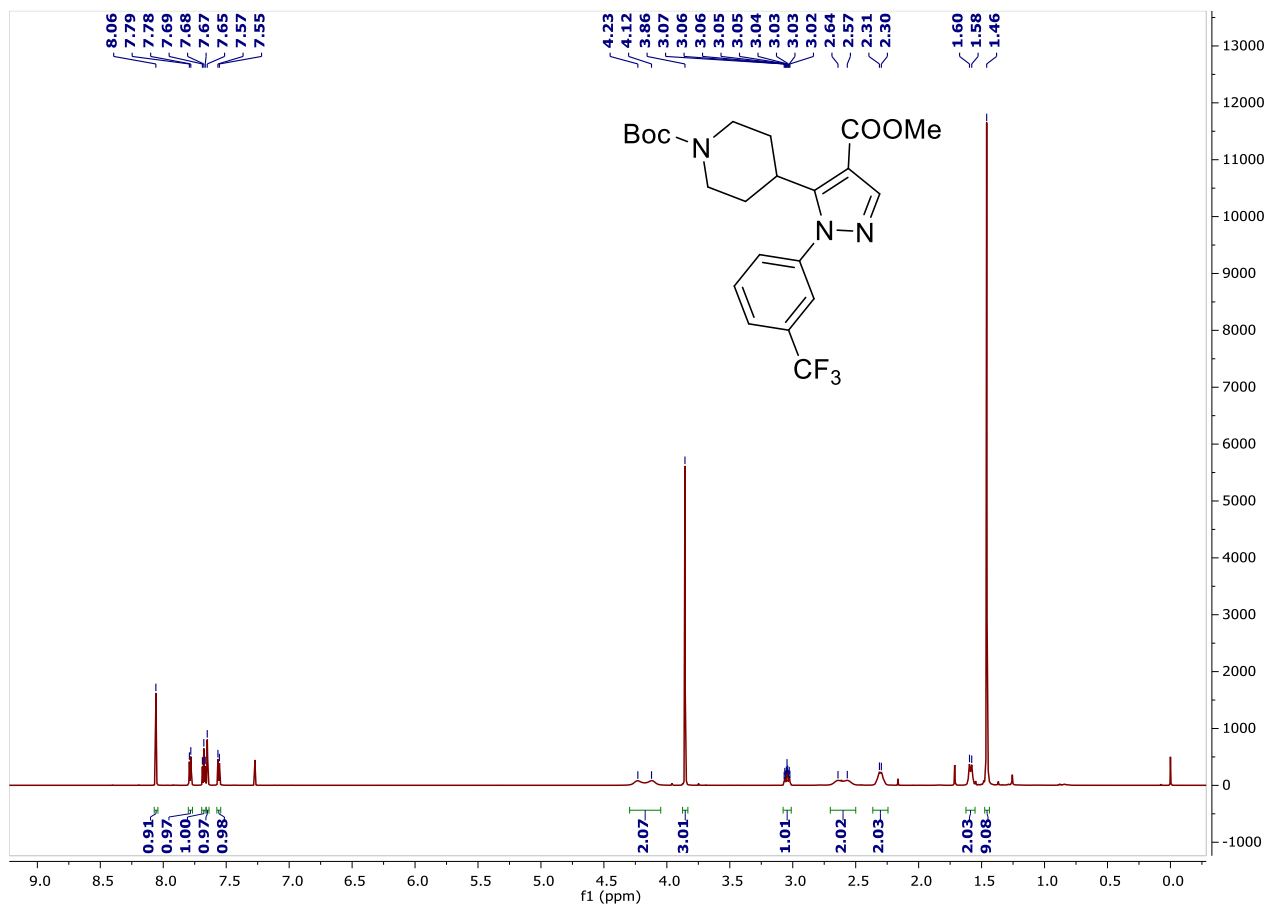


Figure S36. *tert*-Butyl 4-{4-(methoxycarbonyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazol-5-yl}piperidine-1-carboxylate (5h). ¹H NMR spectrum (700 MHz, CDCl₃).

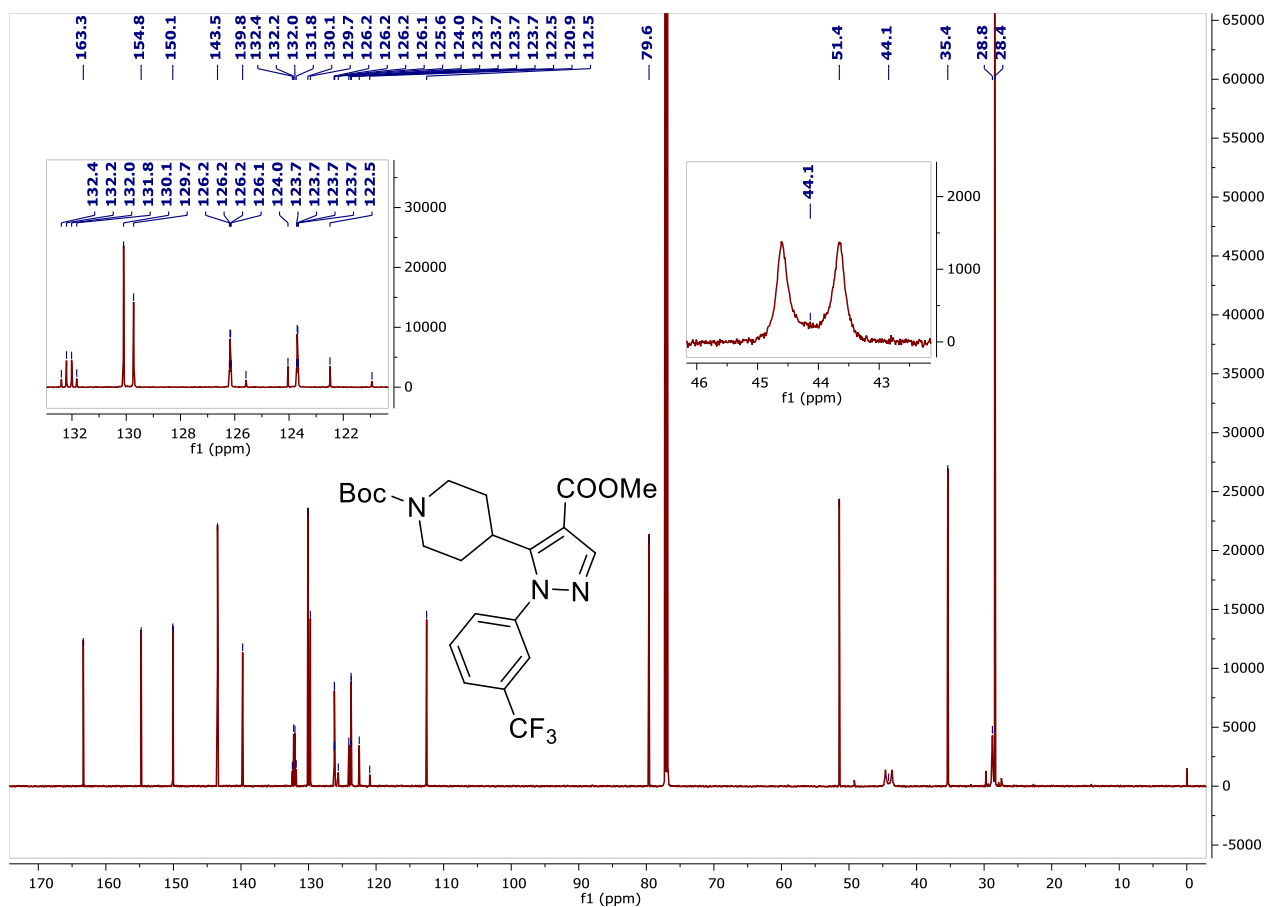


Figure S37. *tert*-Butyl 4-{4-(methoxycarbonyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazol-5-yl}piperidine-1-carboxylate (5h). ¹³C NMR spectrum (176 MHz, CDCl₃).

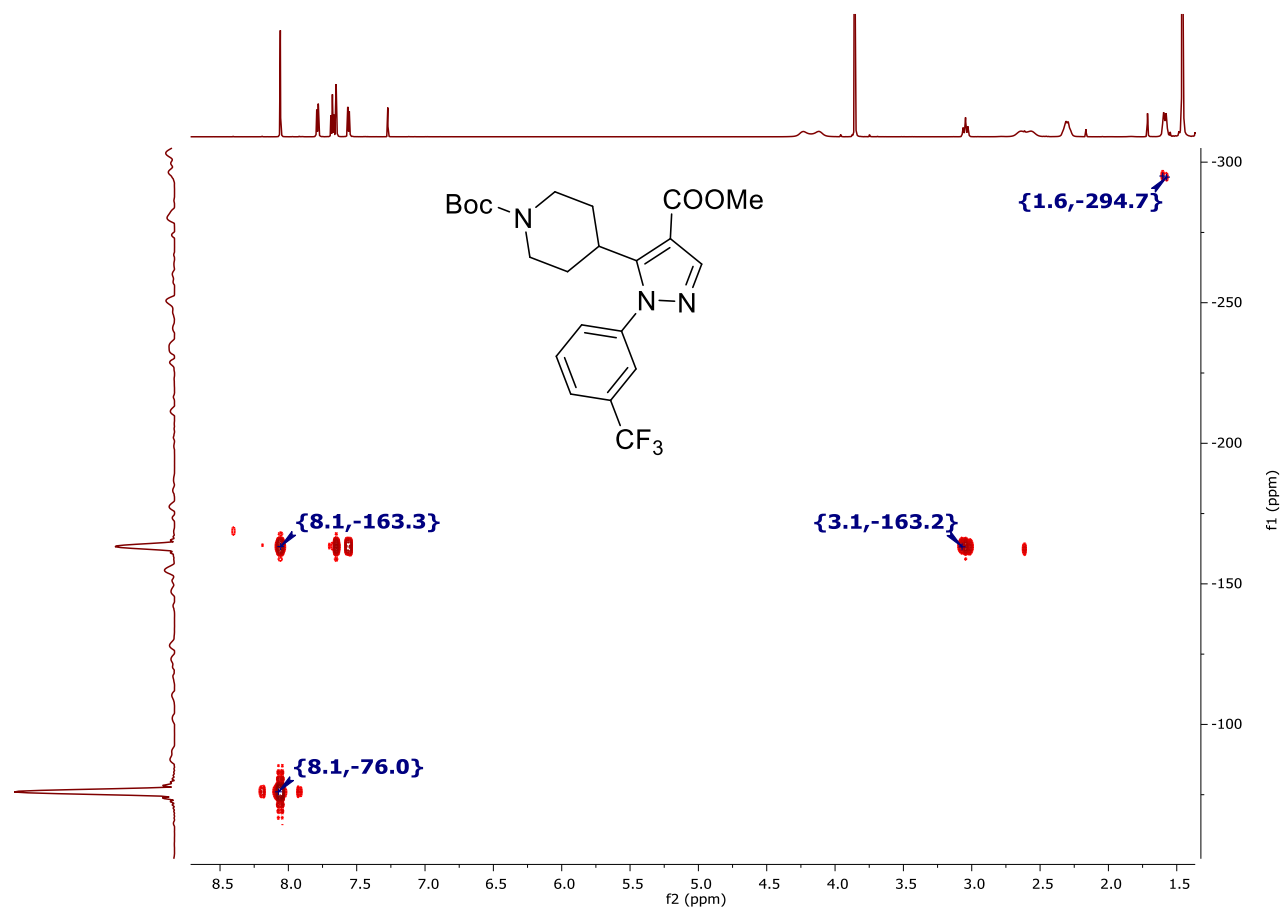


Figure S38. *tert*-Butyl 4-{4-(methoxycarbonyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazol-5-yl}piperidine-1-carboxylate (5h). ¹H-¹⁵N HMBC spectrum (71 MHz, CDCl₃).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-035.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-035
Comment SB

Acquisition Date 11/29/2018 11:19:05 AM

Operator hplc
Instrument micrOTOF-Q III 8228888.20448

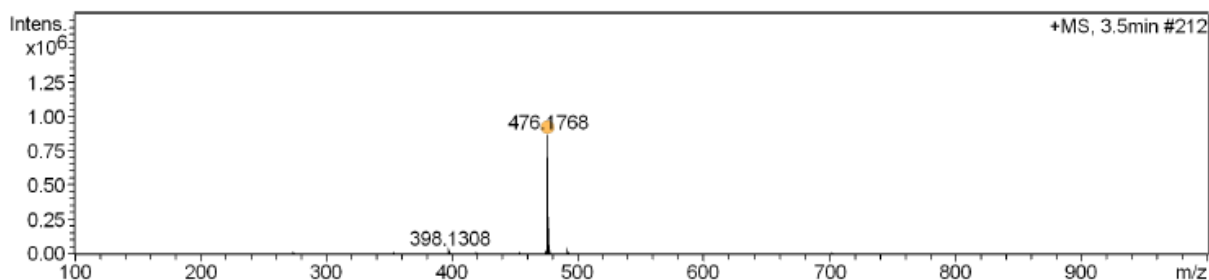
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.5	n.a.	Single spectrum	n.a.	n.a.	n.a.	226.9518	n.a.
n.a.	3.5	n.a.	Single spectrum	n.a.	n.a.	n.a.	476.1768	n.a.

+MS, 3.5min #212



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
476.1768	1	C22H26F3N3NaO4	476.1768	-0.1	7.6	1	100.00	9.5	even	ok

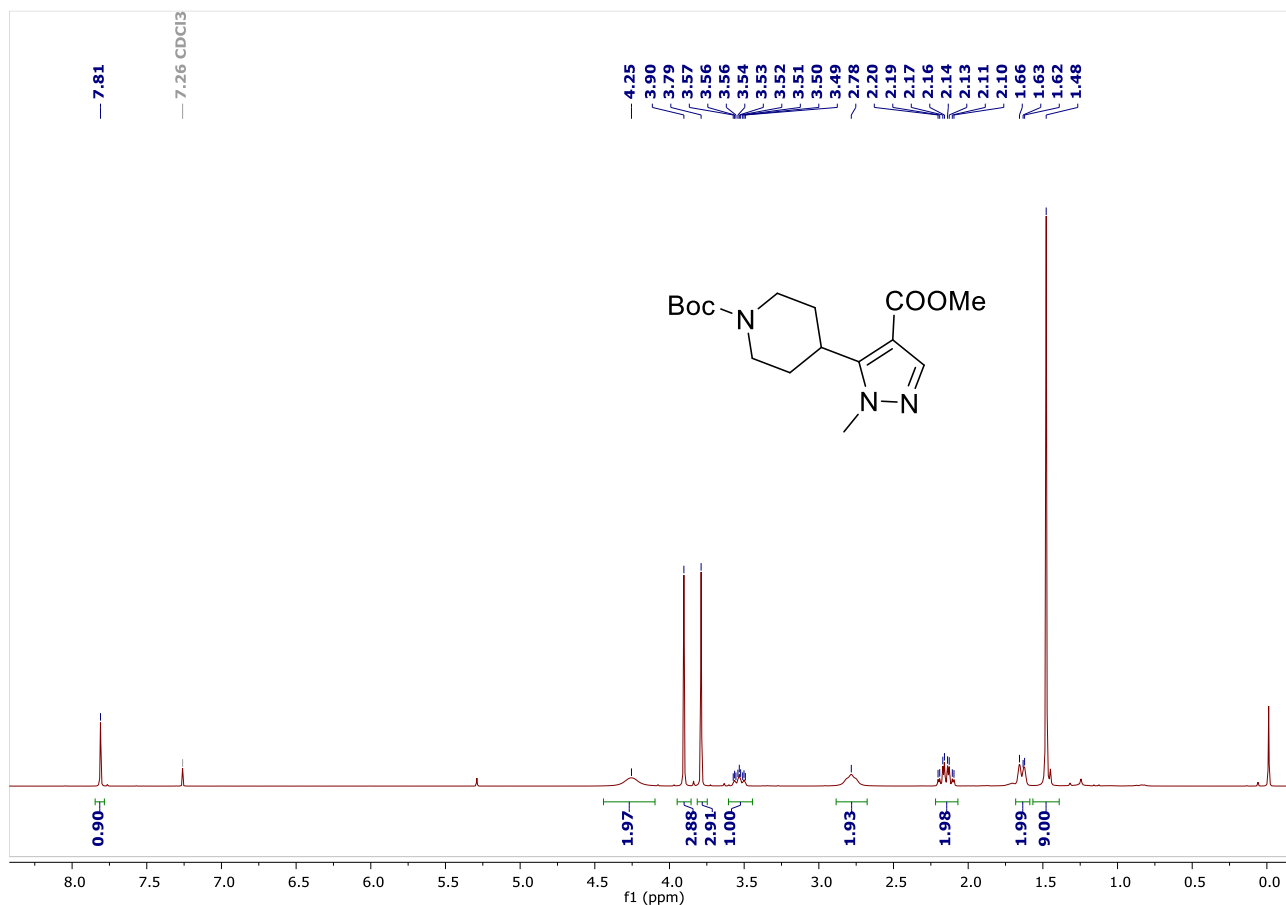


Figure S40. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (**5i**). ¹H NMR spectrum (400 MHz, CDCl₃).

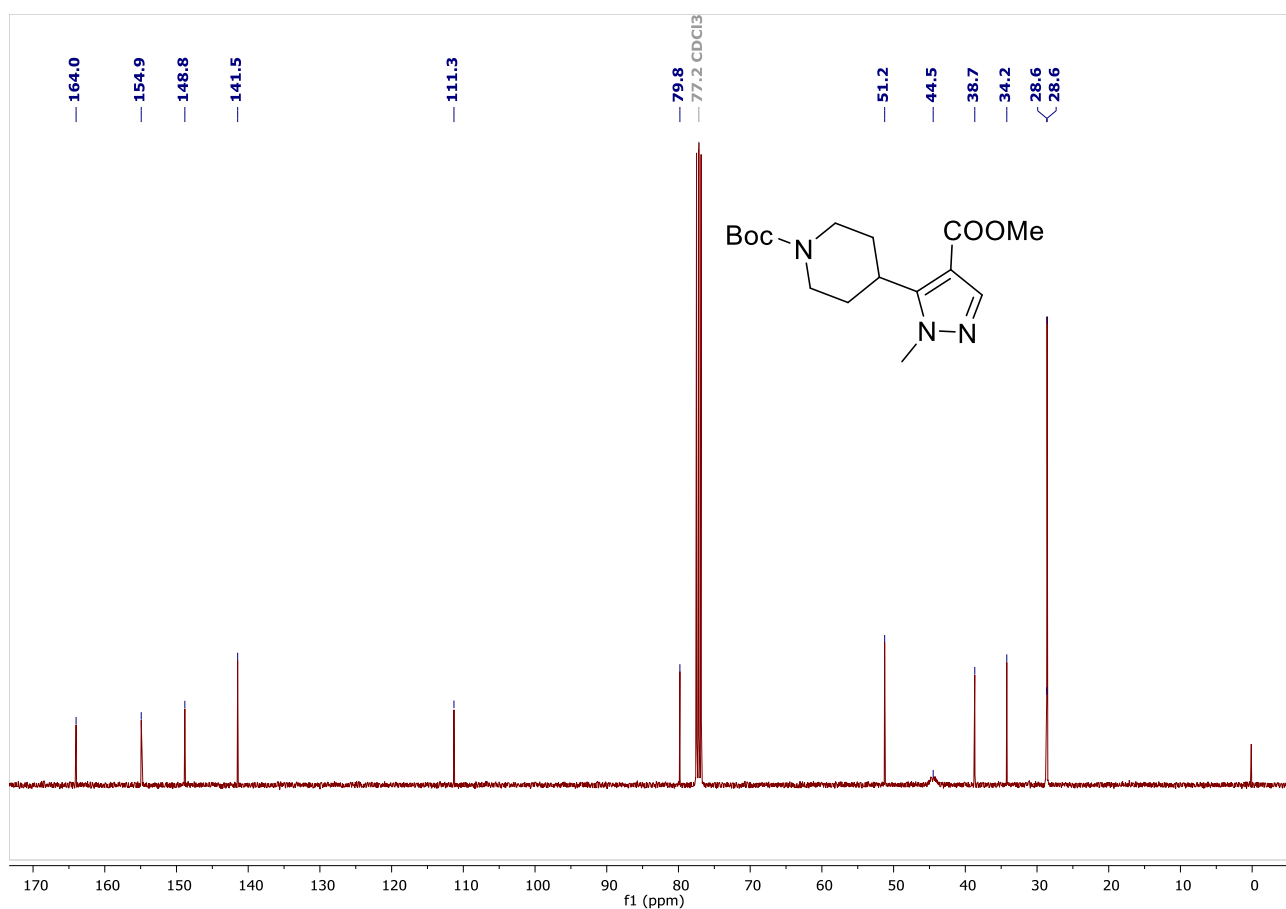


Figure S41. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (**5i**). ¹³C NMR spectrum (101 MHz, CDCl₃).

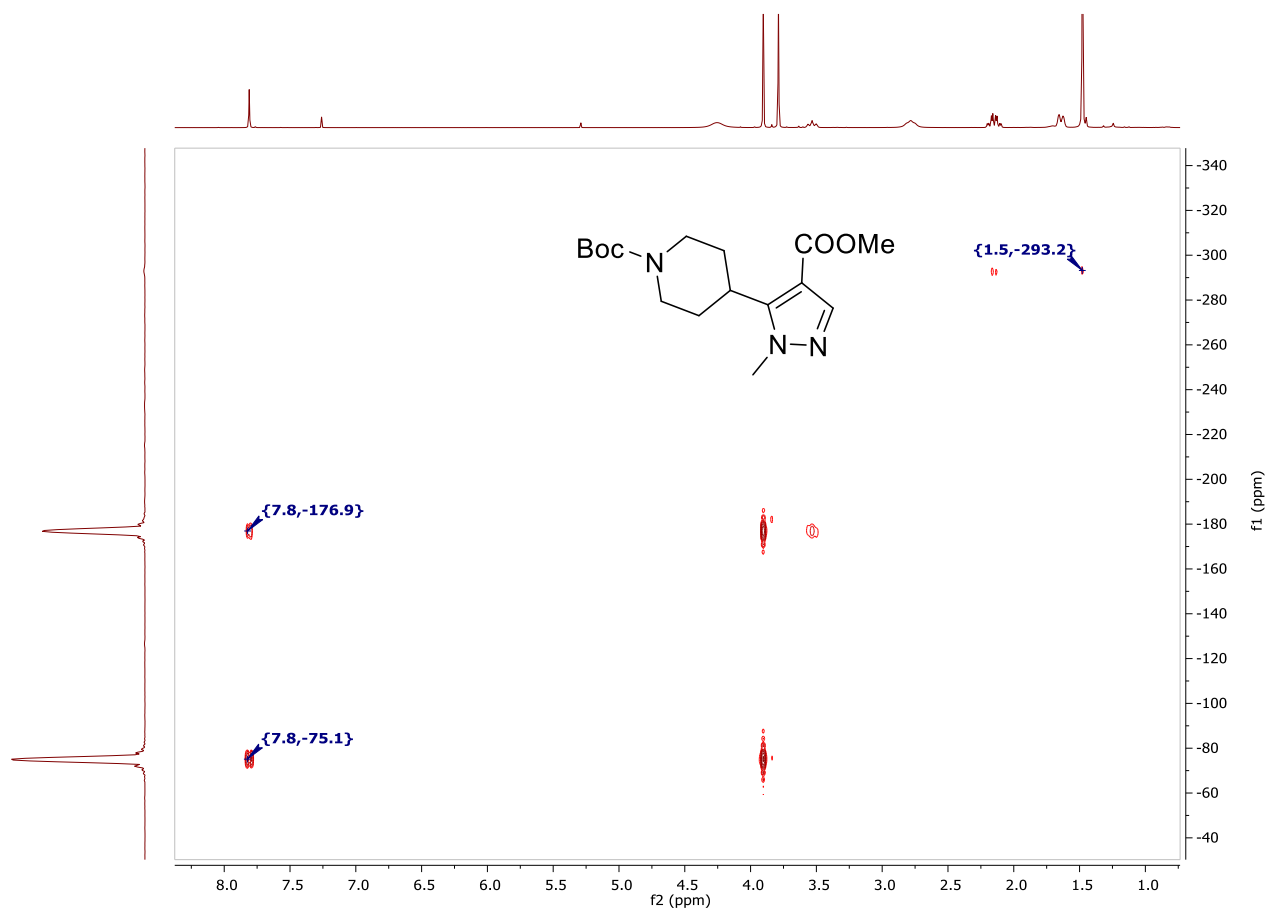


Figure S42. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5i). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-012.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-012
Comment SB

Acquisition Date 11/27/2018 11:31:36 AM

Operator hplc
Instrument micrOTOF-Q III 8228888.20448

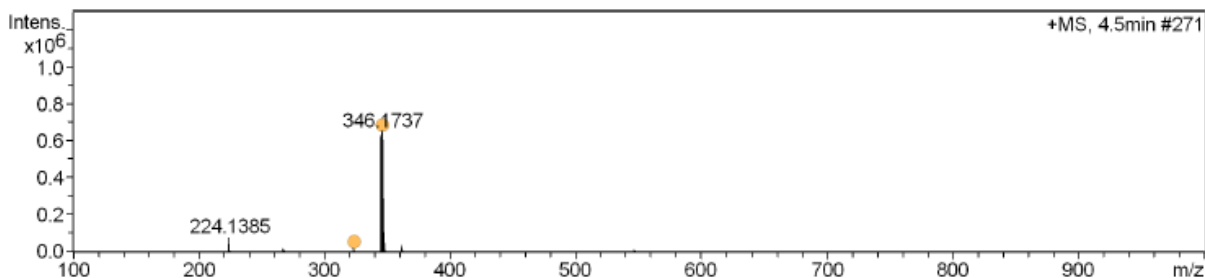
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.2	n.a.	Single spectrum	n.a.	n.a.	n.a.	304.2632	n.a.
n.a.	4.5	n.a.	Single spectrum	n.a.	n.a.	n.a.	346.1737	n.a.

+MS, 4.5min #271



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
324.1906	1	C16H26N3O4	324.1918	-3.5	21.5	1	100.00	5.5	even	ok
346.1737	1	C16H25N3NaO4	346.1737	0.1	2.4	1	100.00	5.5	even	ok

Figure S43. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (**5i**). HRMS (ESI-TOF).

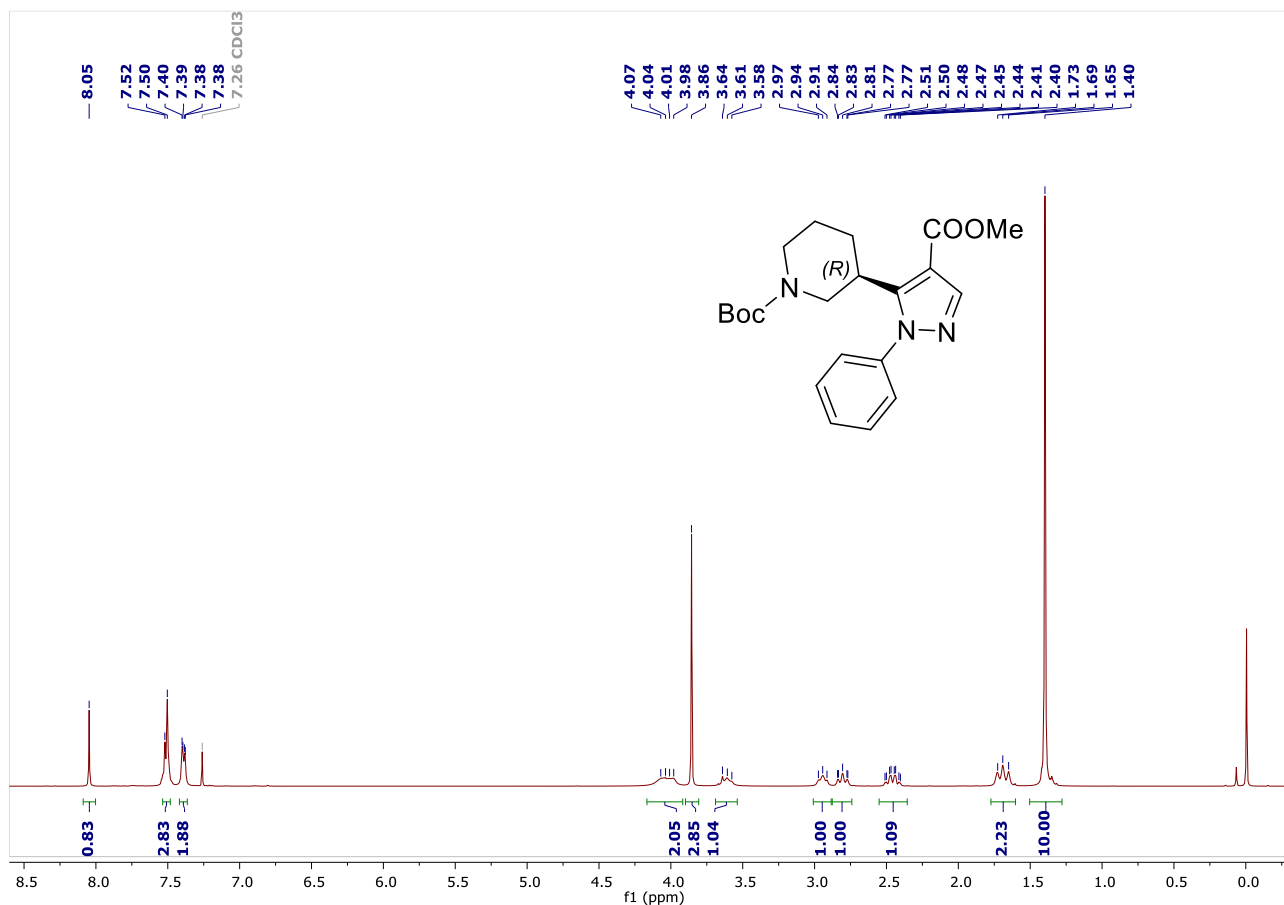


Figure S44. *tert*-Butyl (3*R*)-3-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5j). ¹H NMR spectrum (400 MHz, CDCl₃).

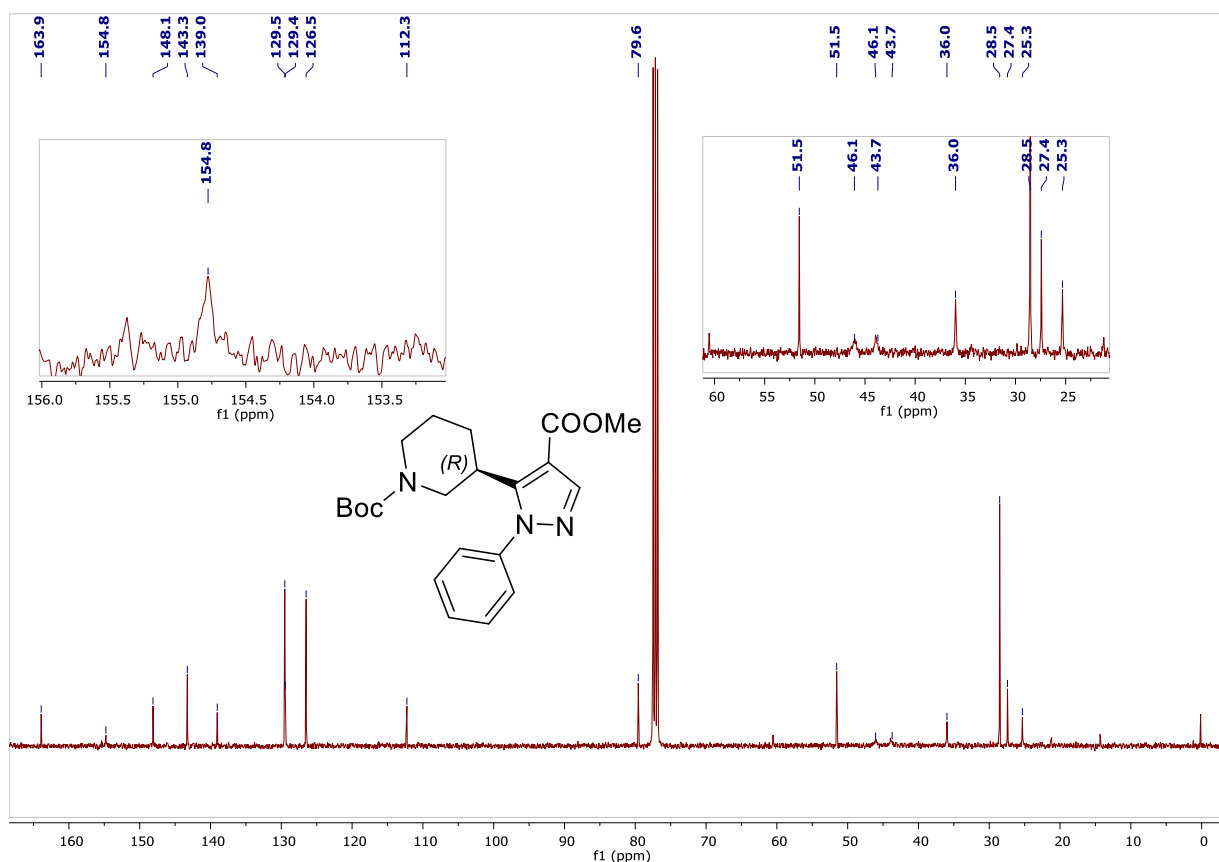


Figure S45. *tert*-Butyl (3*R*)-3-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5j). ¹³C NMR spectrum (101 MHz, CDCl₃).

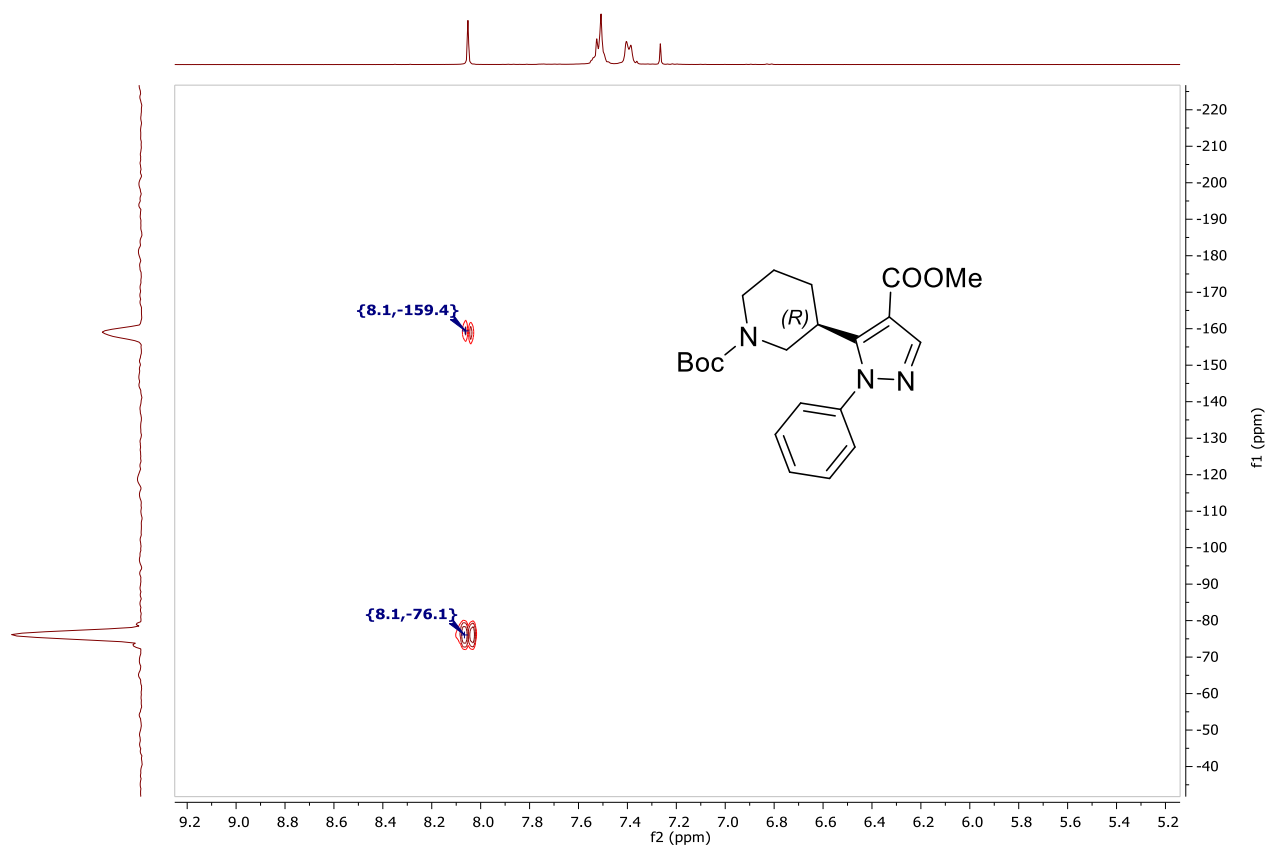


Figure S46. *tert*-Butyl (3*R*)-3-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5j). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-117.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-117
Comment AB

Acquisition Date 2/5/2021 12:32:27 AM

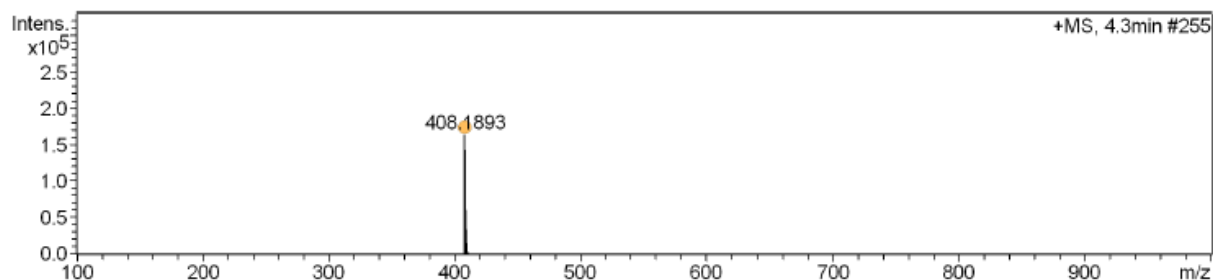
Operator hplc
Instrument micrOTOF-Q III 8228888.20448

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste

#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	4.3	n.a.	Single spectrum	n.a.	n.a.	n.a.	408.1893	n.a.

+MS, 4.3min #255



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
408.1893	1	C ₂₁ H ₂₇ N ₃ NaO ₄	408.1894	-0.1	2.9	1	100.00	9.5	even	ok

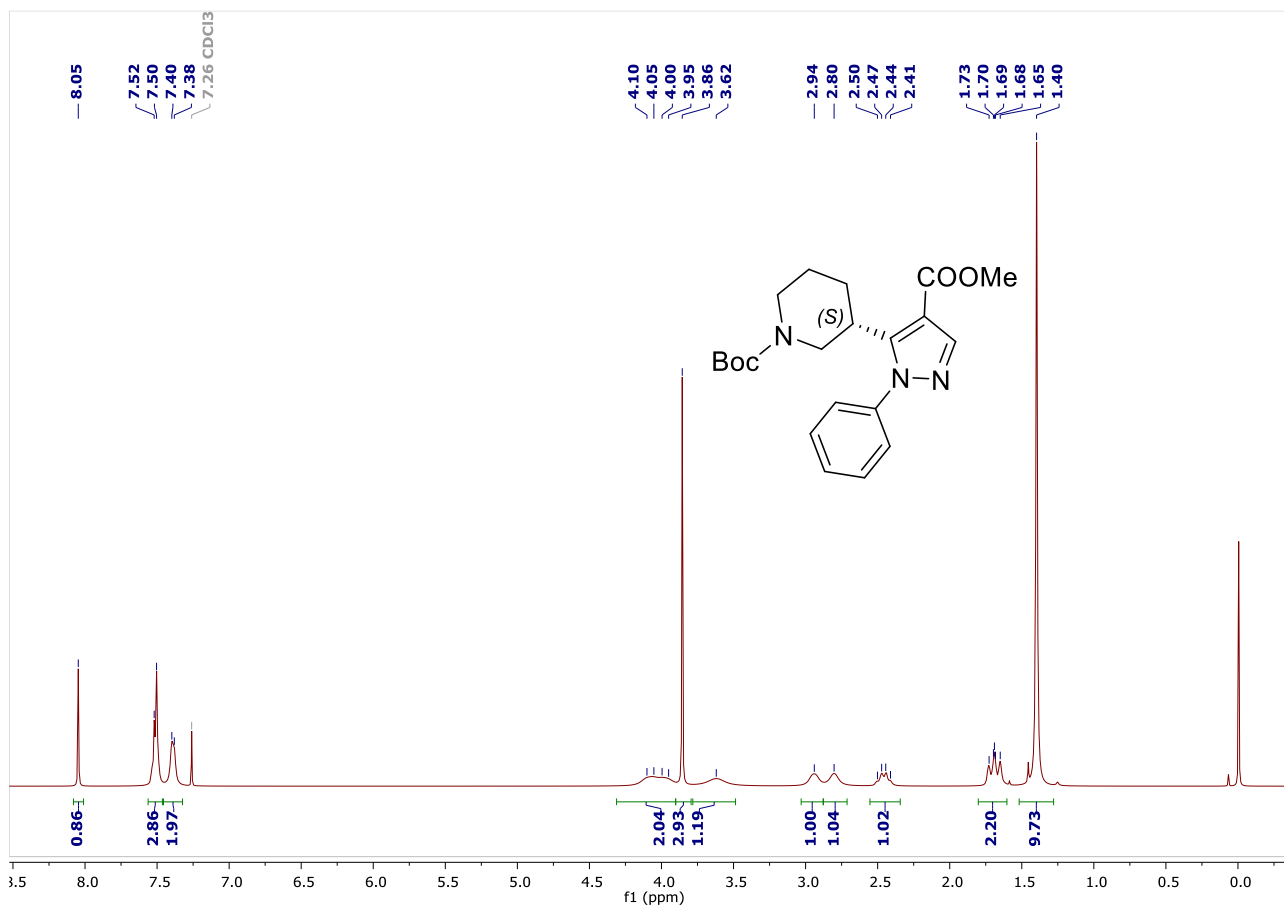


Figure S48. *tert*-Butyl (3*S*)-3-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5k). ¹H NMR spectrum (400 MHz, CDCl₃).

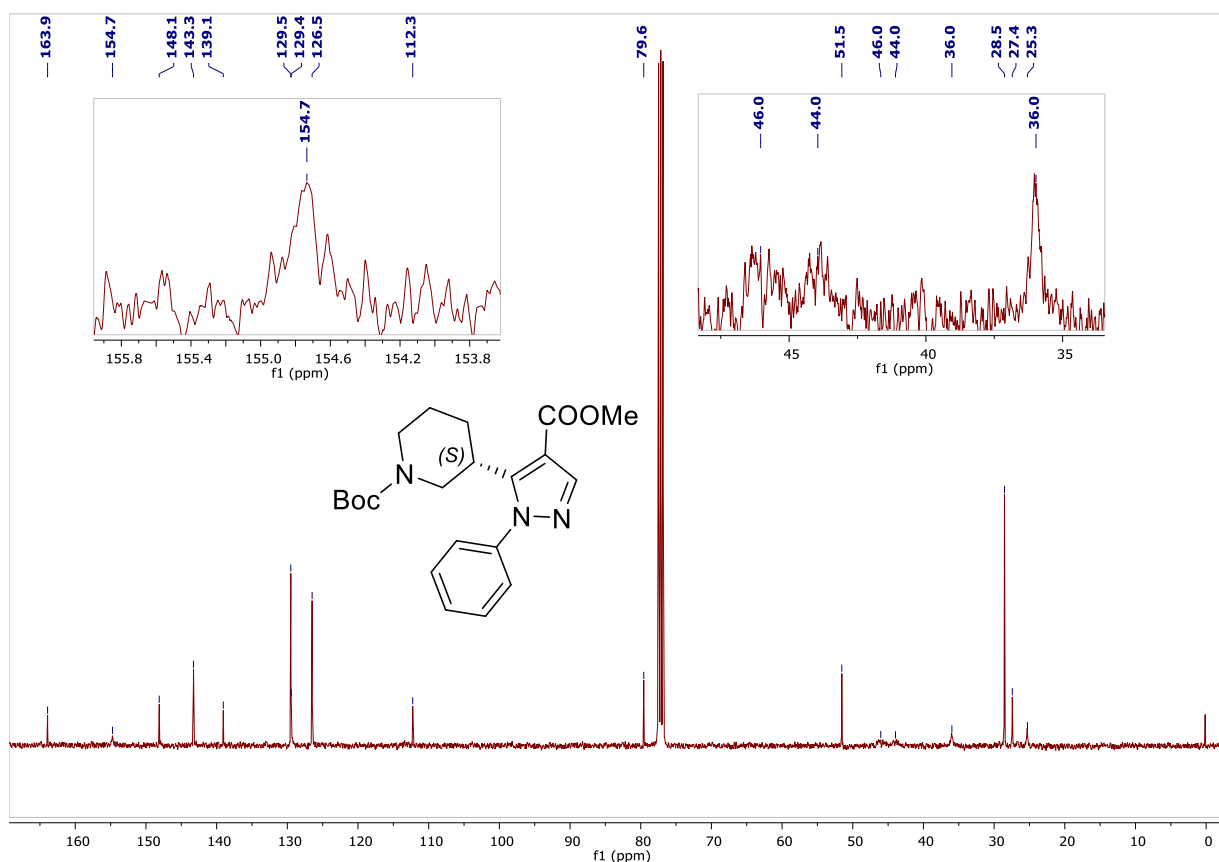


Figure S49. *tert*-Butyl (3*S*)-3-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5k). ¹³C NMR spectrum (101 MHz, CDCl₃).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-146.d
 Method DirectInfusion_TuneLow_pos.m
 Sample Name GMP-146
 Comment AB

Acquisition Date 2/5/2021 12:21:40 AM

Operator hplc
 Instrument micrOTOF-Q III 8228888.20448

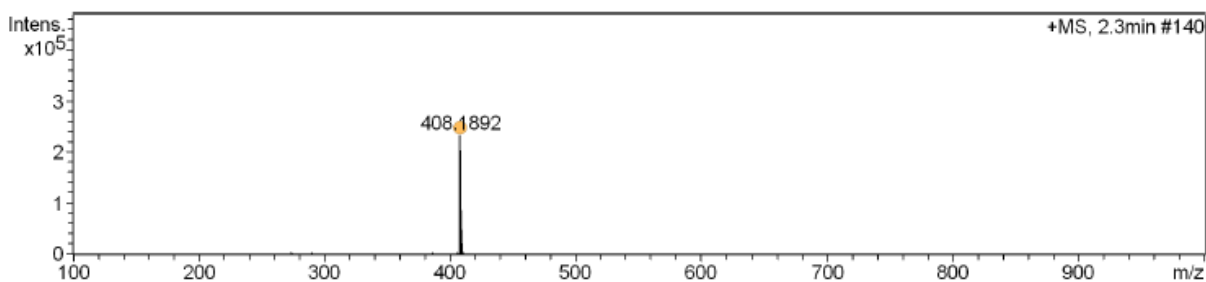
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	2.3	n.a.	Single spectrum	n.a.	n.a.	n.a.	408.1892	n.a.

+MS, 2.3min #140



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
408.1892	1	C ₂₁ H ₂₇ N ₃ NaO ₄	408.1894	0.4	1.8	1	100.00	9.5	even	ok

Figure S50. *tert*-Butyl (3*S*)-3-[4-(methoxycarbonyl)-1-phenyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5k). HRMS (ESI-TOF).

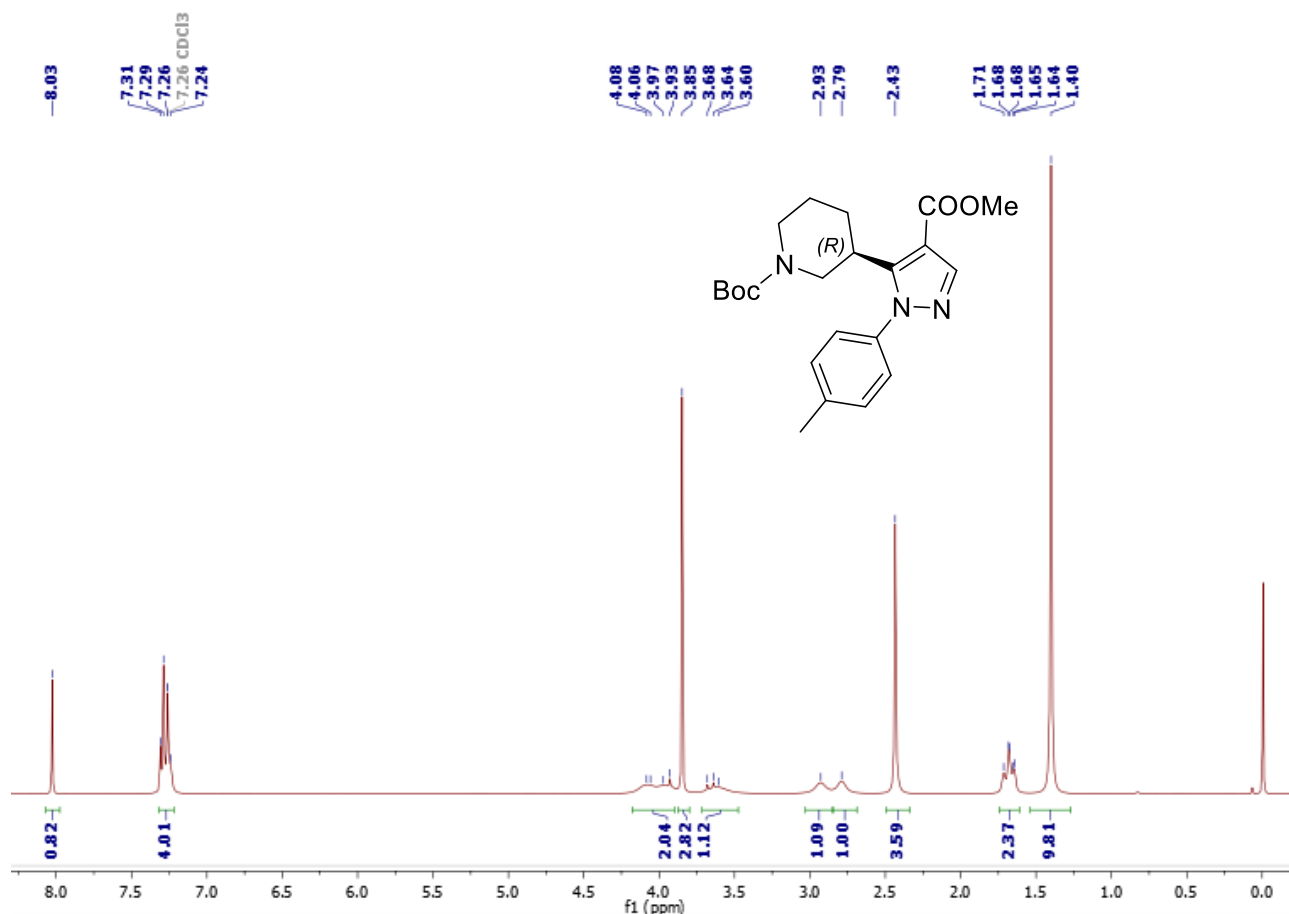


Figure S51. *tert*-Butyl (3*R*)-3-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5l). ¹H NMR spectrum (400 MHz, CDCl₃).

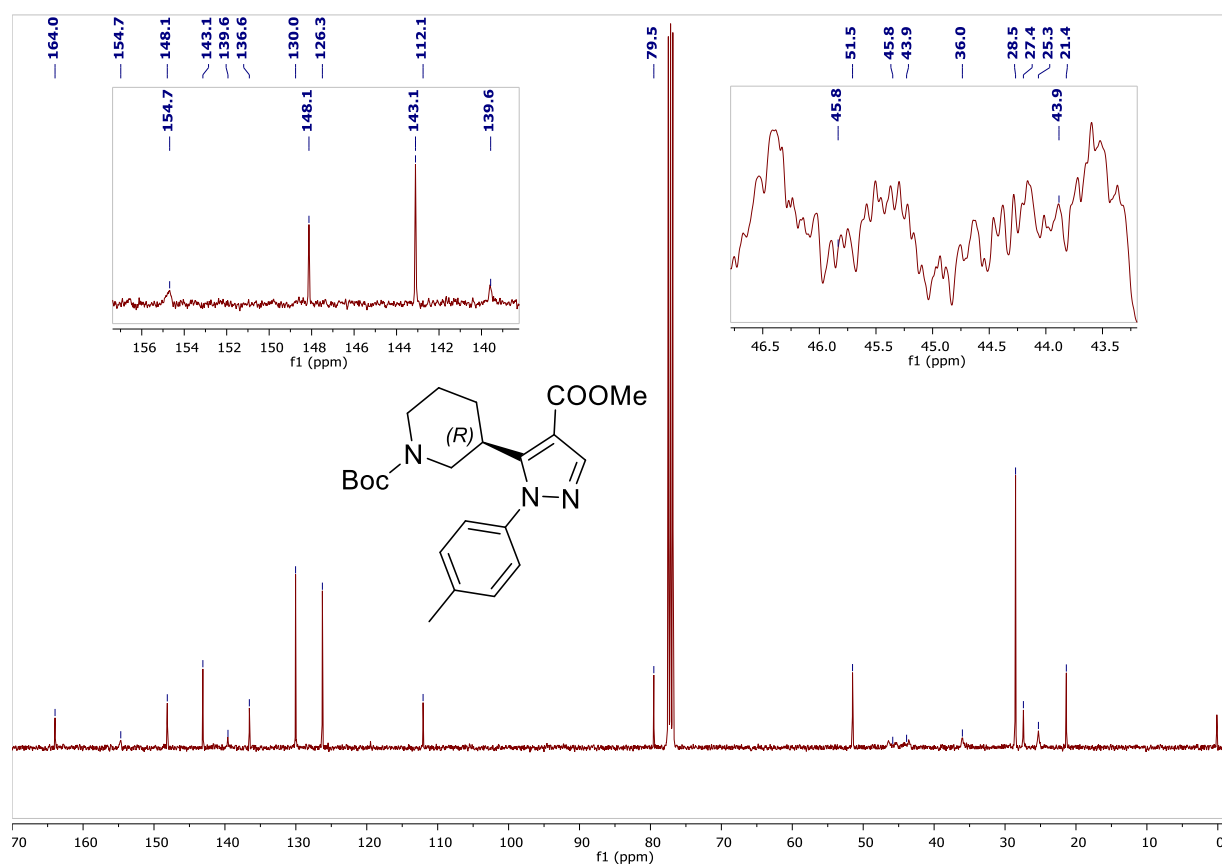


Figure S52. *tert*-Butyl (3*R*)-3-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5l). ¹³C NMR spectrum (101 MHz, CDCl₃).

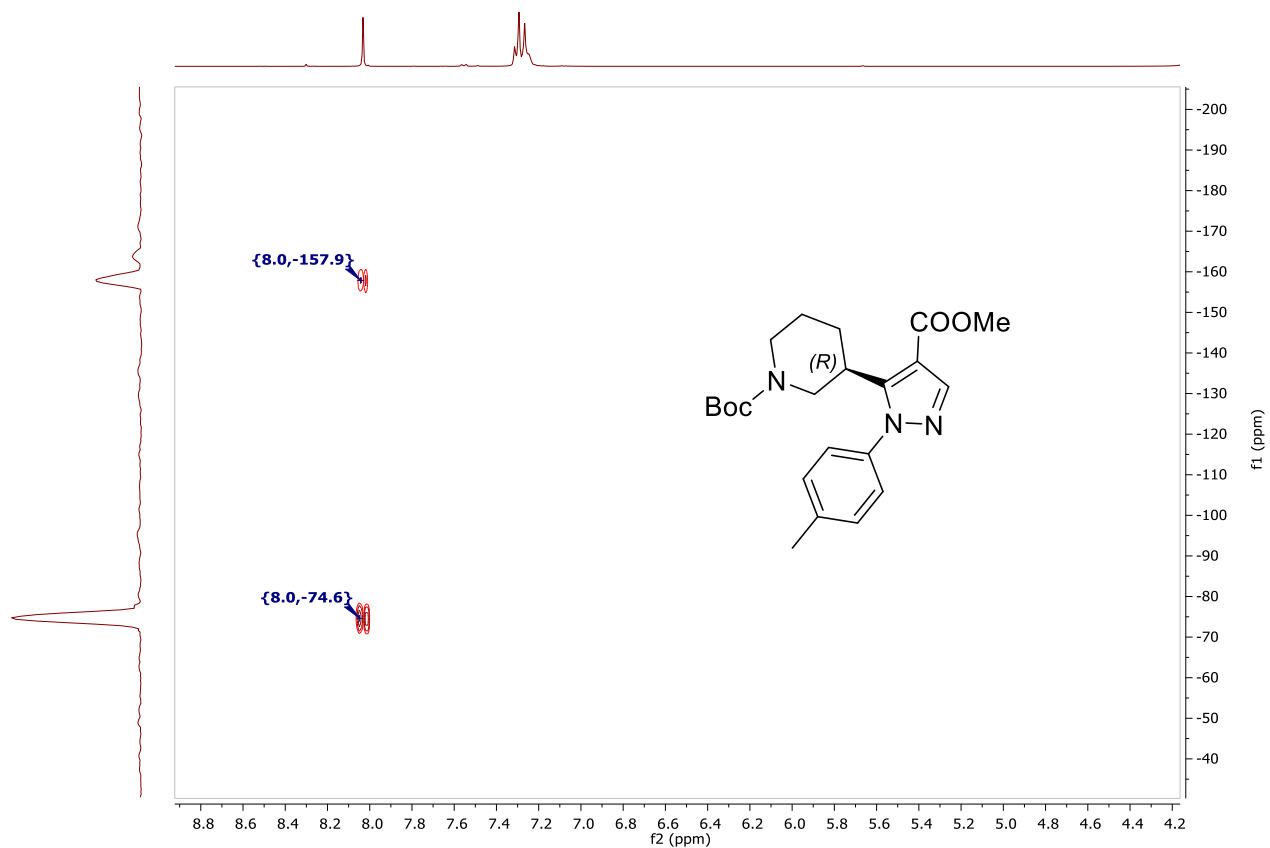


Figure S53. *tert*-Butyl (3*R*)-3-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (51). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-116.d
 Method DirectInfusion_TuneLow_pos.m
 Sample Name GMP-116
 Comment AB

Acquisition Date 2/5/2021 12:09:00 AM

Operator hplc
 Instrument micrOTOF-Q III 8228888.20448

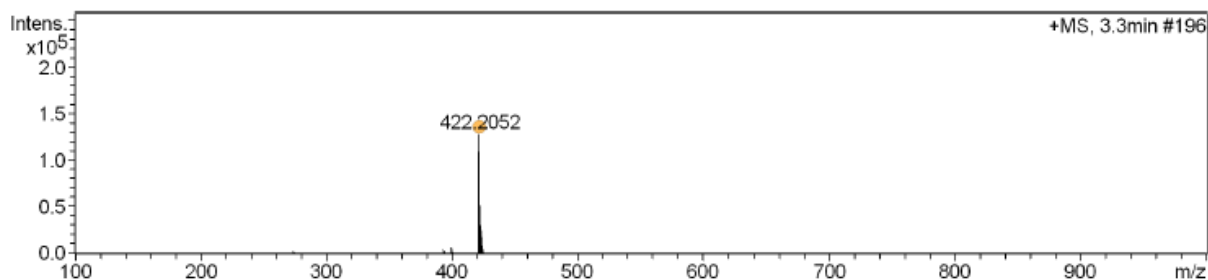
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	3.3	n.a.	Single spectrum	n.a.	n.a.	n.a.	422.2052	n.a.

+MS, 3.3min #196



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
422.2052	1	C22H29N3NaO4	422.2050	-0.3	3.3	1	100.00	9.5	even	ok

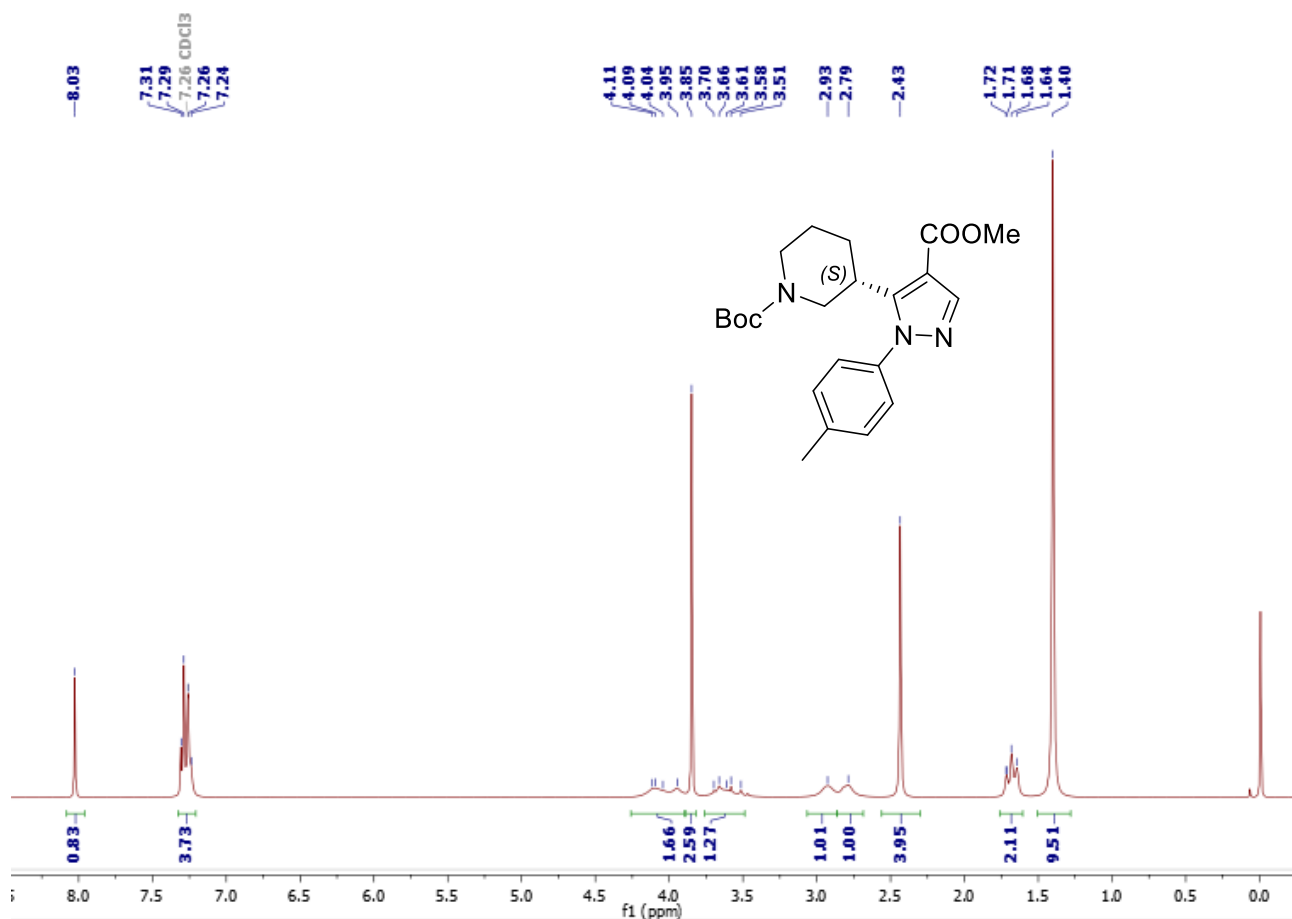


Figure S55. *tert*-Butyl (3*S*)-3-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5m). ¹H NMR spectrum (400 MHz, CDCl₃).

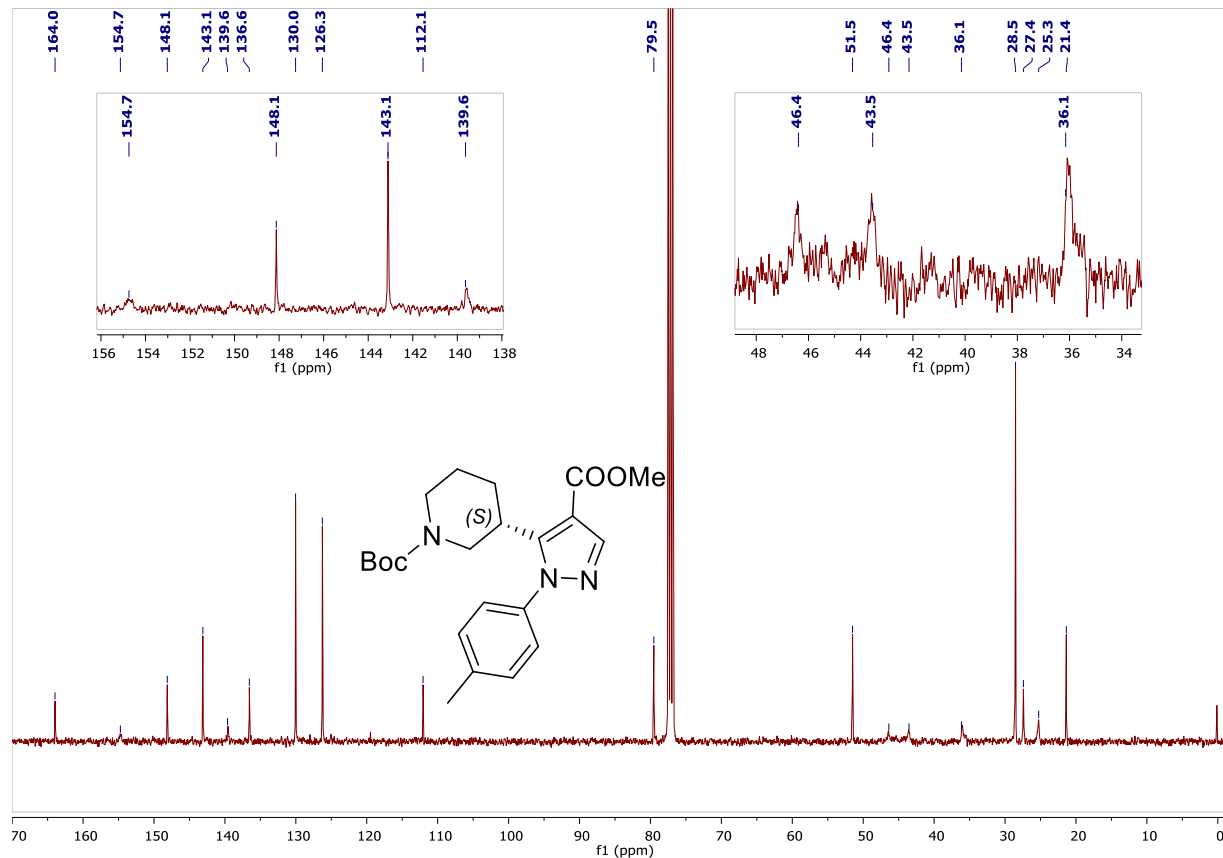


Figure S56. *tert*-Butyl (3*S*)-3-[4-(methoxycarbonyl)-1-(4-methylphenyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5m). ¹³C NMR spectrum (101 MHz, CDCl₃).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-147.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-147
Comment AB

Acquisition Date 2/4/2021 11:52:08 PM

Operator hplc
Instrument micrOTOF-Q III 8228888.20448

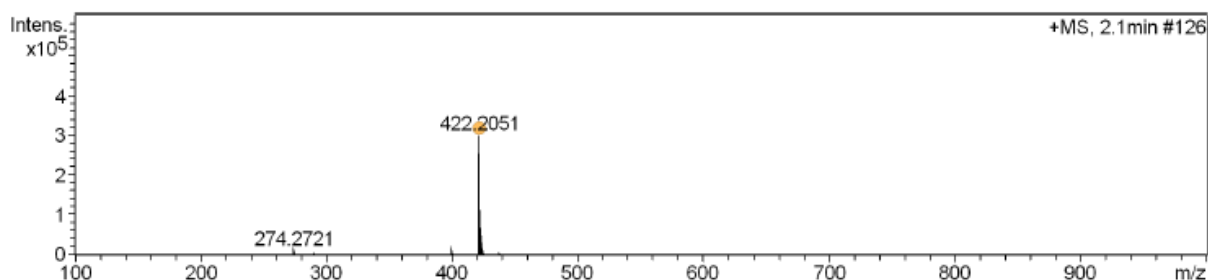
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	2.1	n.a.	Single spectrum	n.a.	n.a.	n.a.	422.2051	n.a.

+MS, 2.1min #126



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
422.2051	1	C22H29N3NaO4	422.2050	-0.3	4.4	1	100.00	9.5	even	ok

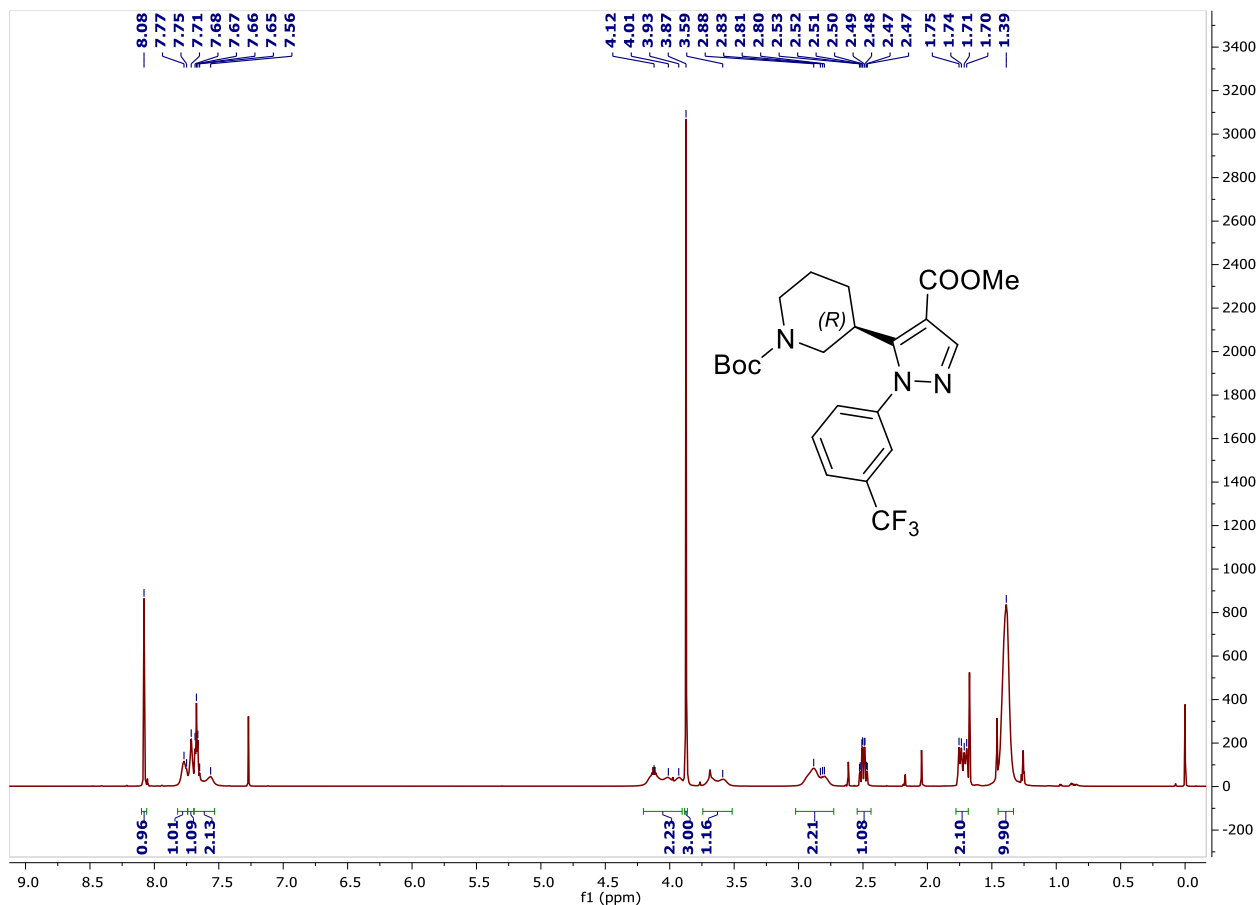


Figure S58. *tert*-Butyl (3*R*)-3-{4-(methoxycarbonyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazol-5-yl}piperidine-1-carboxylate (5n). ¹H NMR spectrum (700 MHz, CDCl₃).

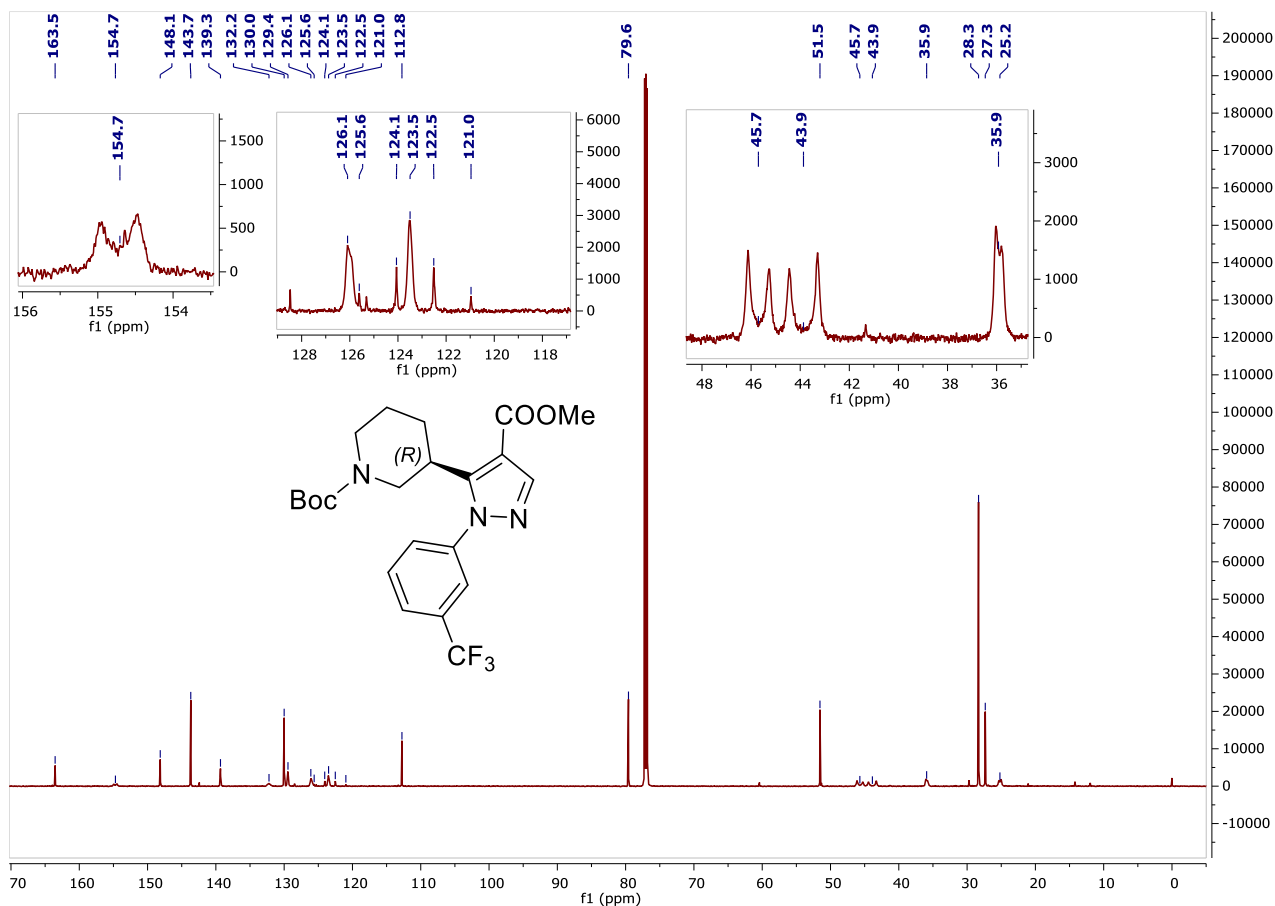


Figure S59. *tert*-Butyl (3*R*)-3-{4-(methoxycarbonyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazol-5-yl}piperidine-1-carboxylate (5n). ¹³C NMR spectrum (176 MHz, CDCl₃).

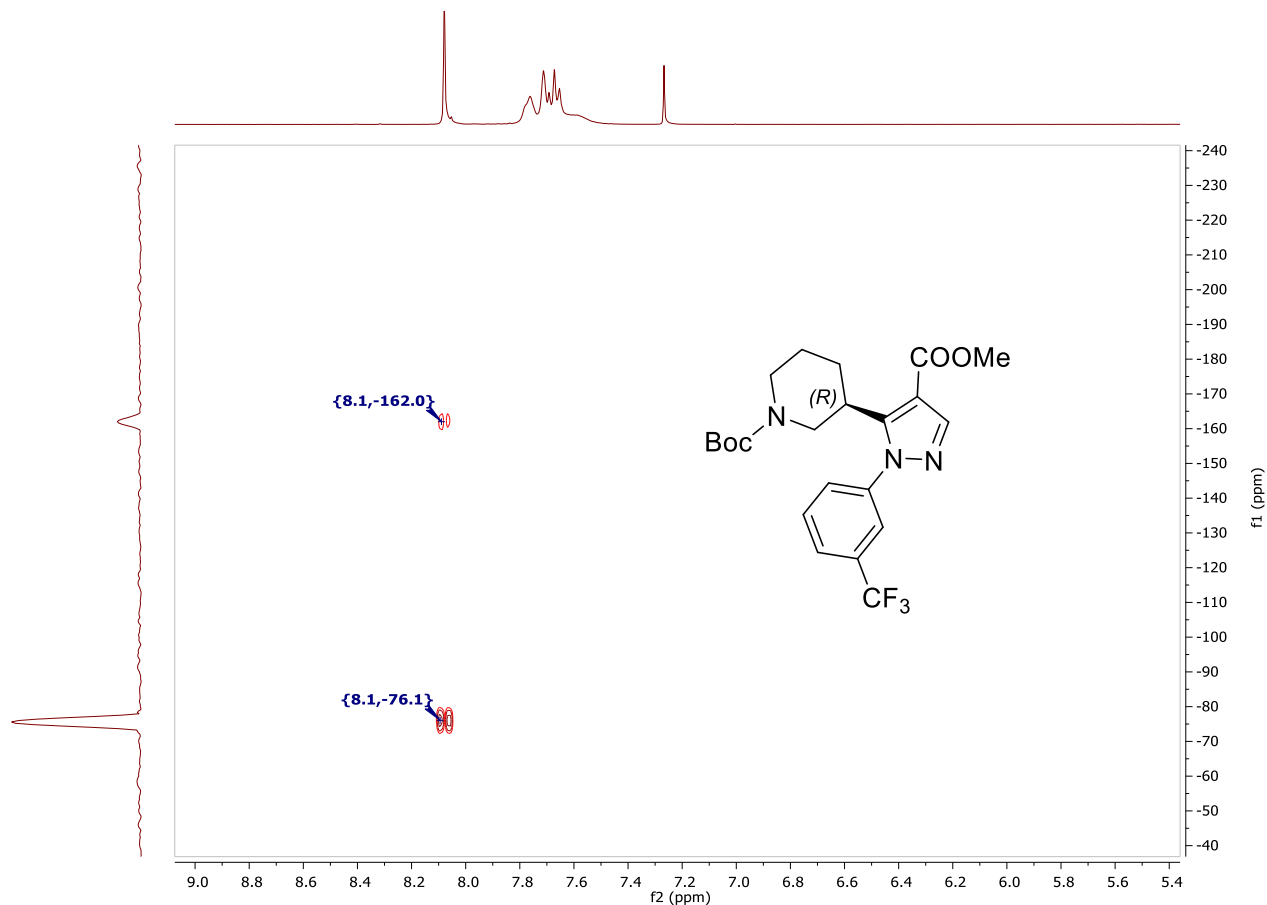


Figure S60. *tert*-Butyl (3*R*)-3-{4-(methoxycarbonyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazol-5-yl}piperidine-1-carboxylate (5n). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-115.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-115
Comment AB

Acquisition Date 2/5/2021 1:01:16 AM

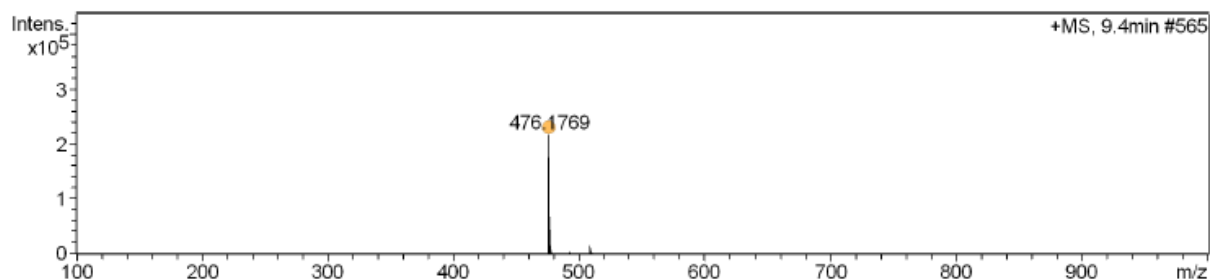
Operator hplc
Instrument micrOTOF-Q III 8228888.20448

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste

#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	9.4	n.a.	Single spectrum	n.a.	n.a.	n.a.	476.1769	n.a.

+MS, 9.4min #565



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
476.1769	1	C22H26F3N3NaO4	476.1768	-0.3	3.4	3	100.00	9.5	even	ok

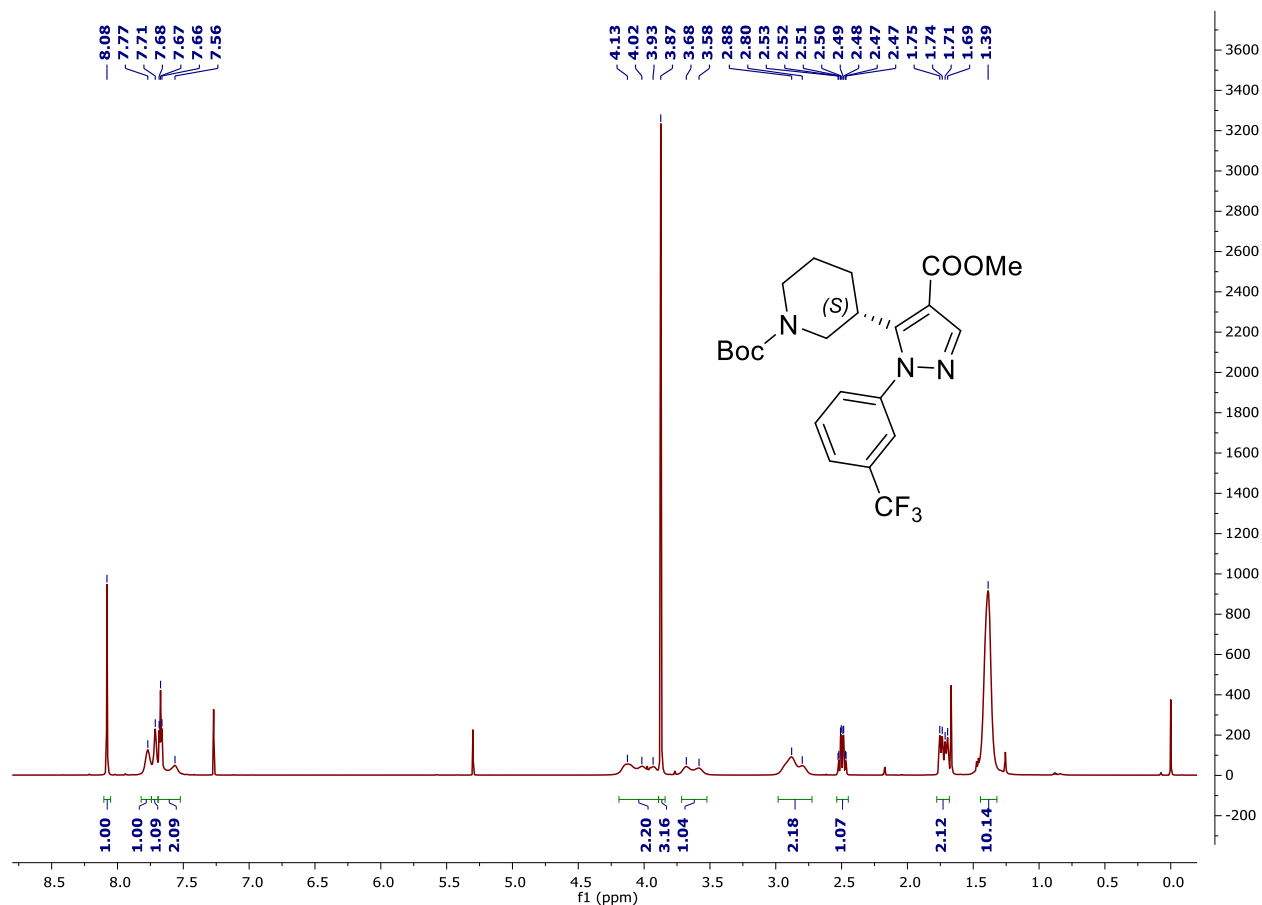


Figure S62. *tert*-Butyl (3*S*)-3-{4-(methoxycarbonyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazol-5-yl}piperidine-1-carboxylate (5o). ¹H NMR spectrum (700 MHz, CDCl₃).

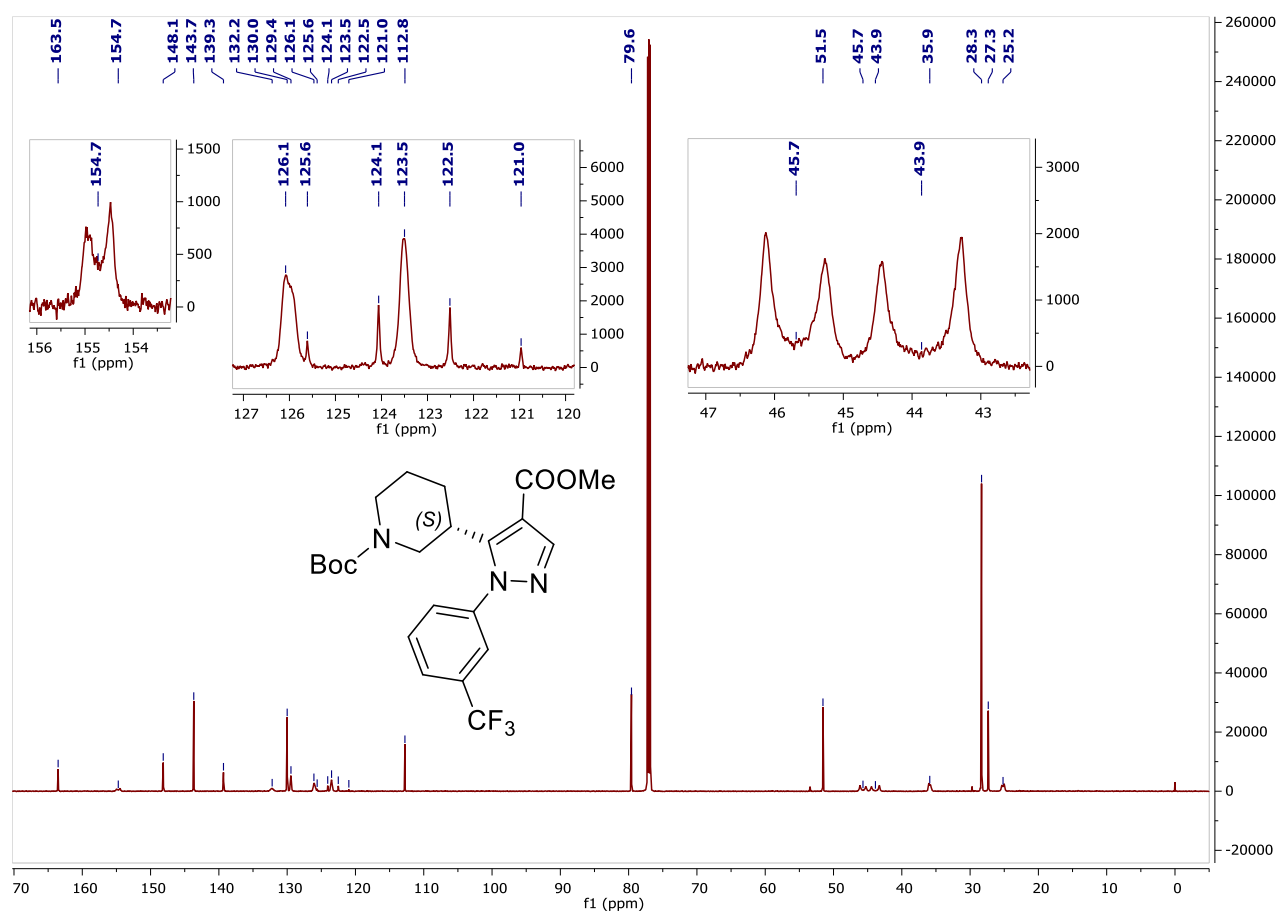


Figure S63. *tert*-Butyl (3*S*)-3-{4-(methoxycarbonyl)-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrazol-5-yl}piperidine-1-carboxylate (5o). ¹³C NMR spectrum (176 MHz, CDCl₃).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-148.d
 Method DirectInfusion_TuneLow_pos.m
 Sample Name GMP-148
 Comment AB

Acquisition Date 2/4/2021 8:10:28 PM
 Operator hplc
 Instrument micrOTOF-Q III 8228888.20448

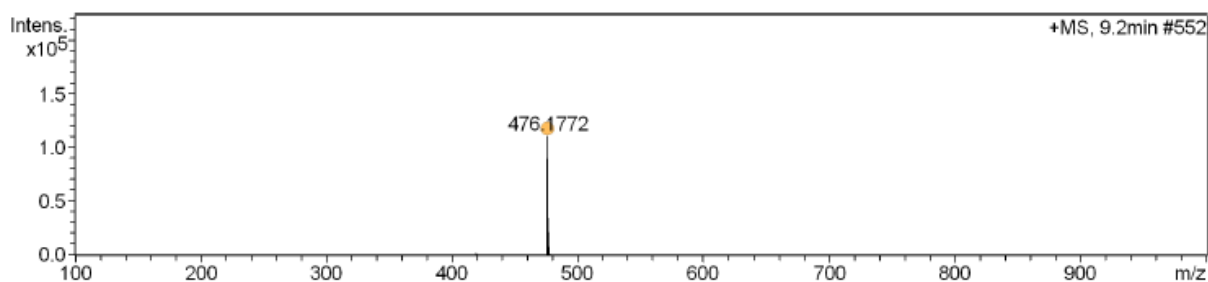
Acquisition Parameter

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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	9.2	n.a.	Single spectrum	n.a.	n.a.	n.a.	476.1772	n.a.

+MS, 9.2min #552



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
476.1772	1	C22H26F3N3NaO4	476.1768	-1.0	8.8	2	100.00	9.5	even	ok

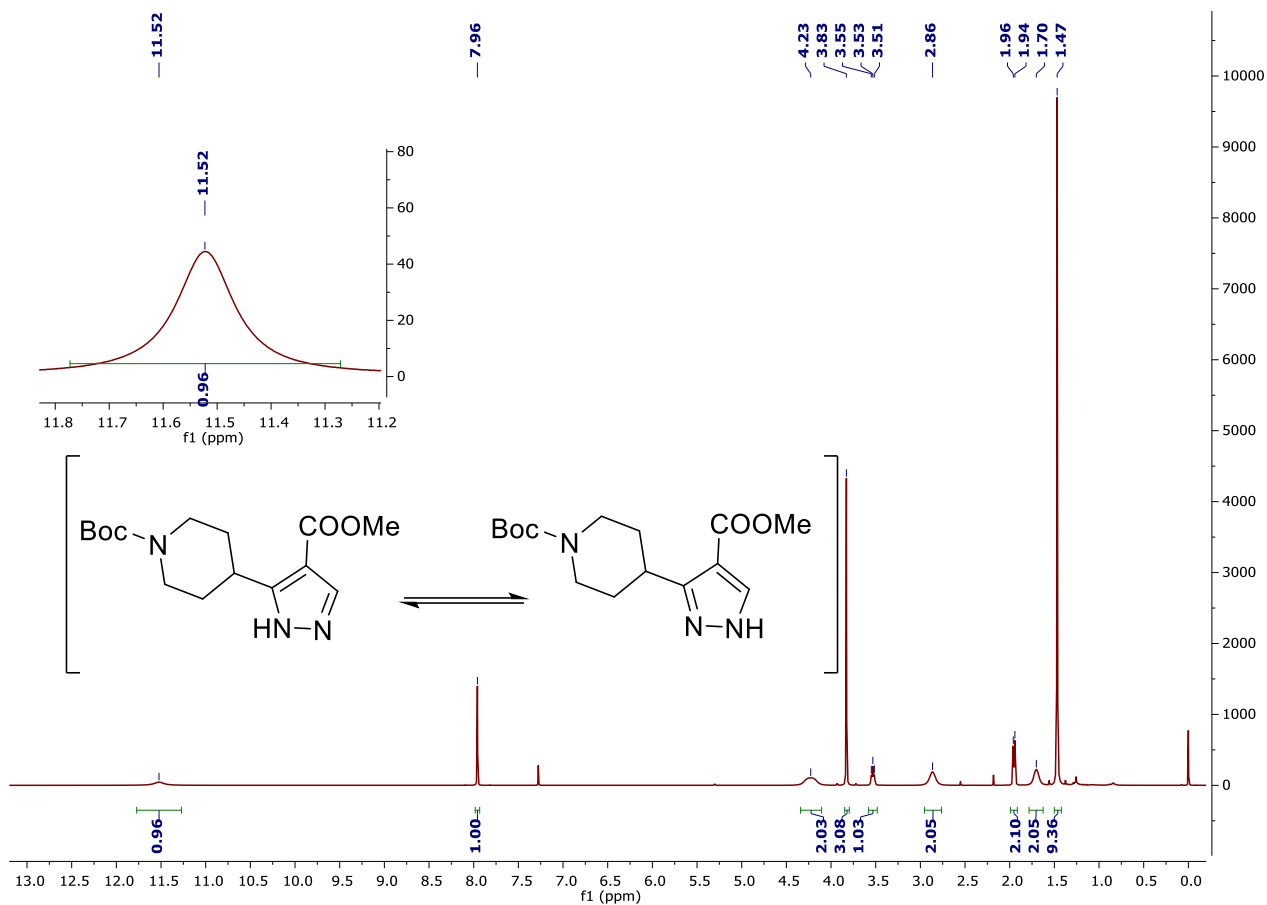


Figure S65. *tert*-Butyl 4-[4-(methoxycarbonyl)-1*H*-pyrazolyl]piperidine-1-carboxylate (**7**).
¹H NMR spectrum (700 MHz, CDCl₃).

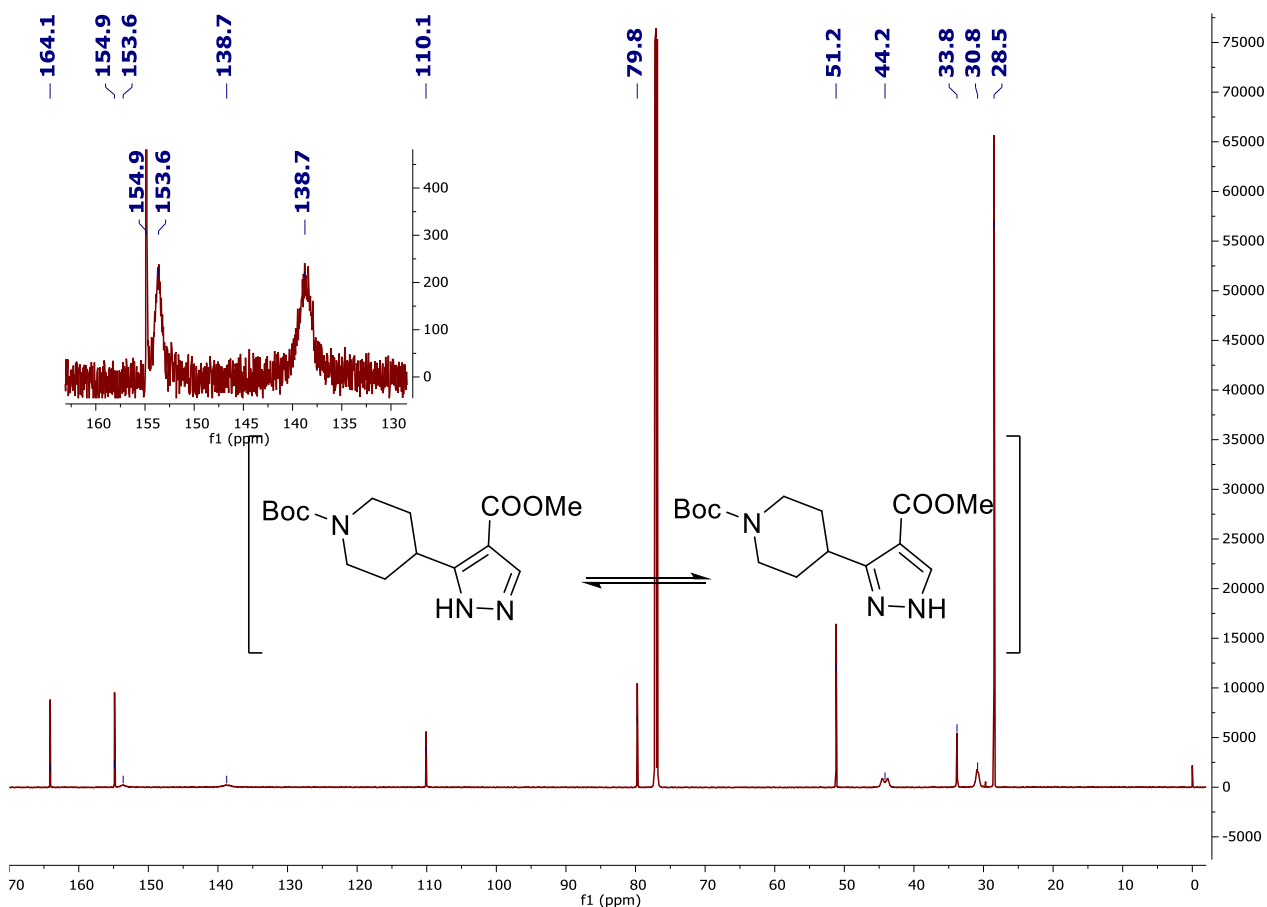


Figure S66. *tert*-Butyl 4-[4-(methoxycarbonyl)-1*H*-pyrazolyl]piperidine-1-carboxylate (**7**).
¹³C NMR spectrum (176 MHz, CDCl₃).

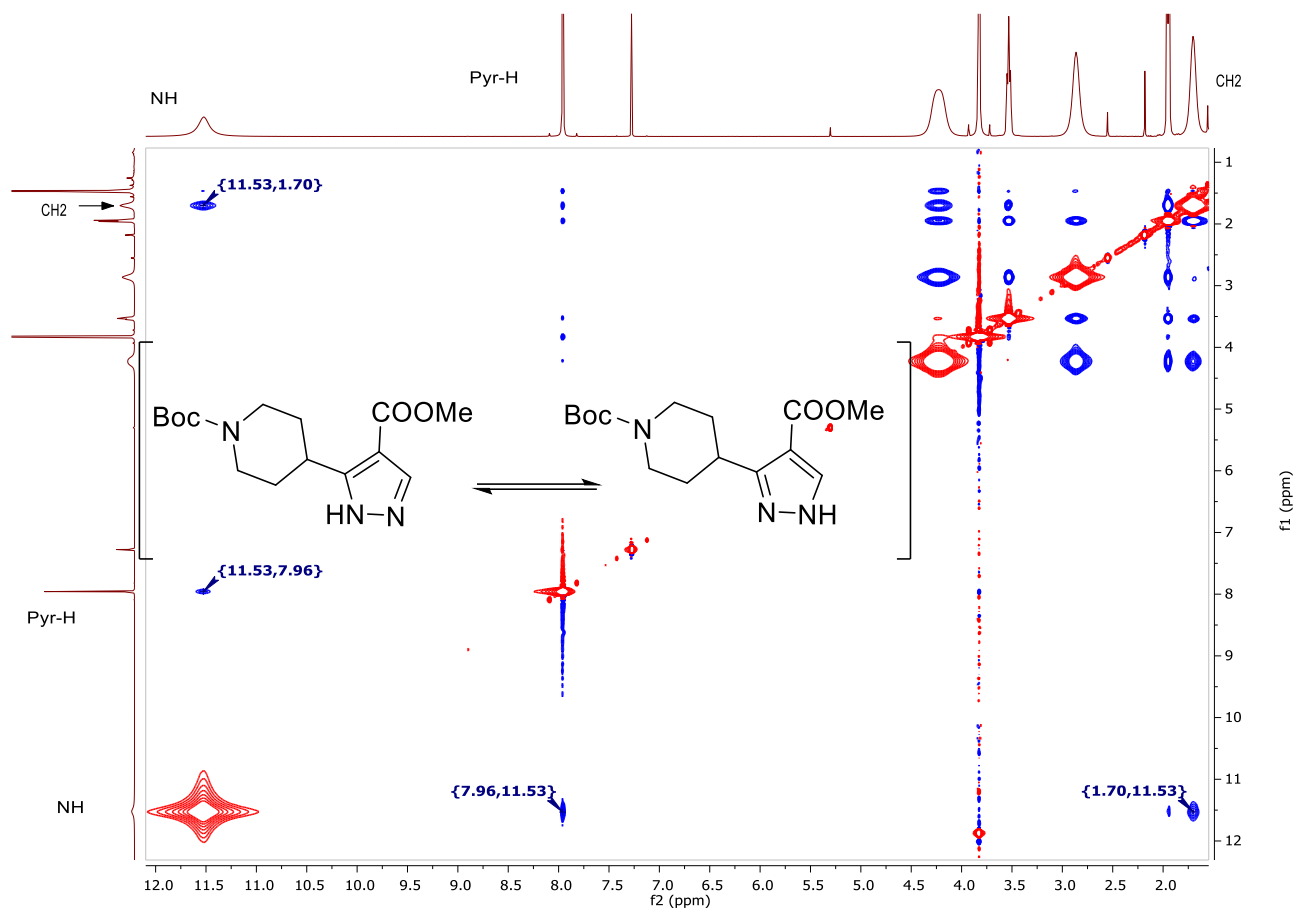


Figure S67. *tert*-Butyl 4-[4-(methoxycarbonyl)-1*H*-pyrazolyl]piperidine-1-carboxylate (7). ^1H - ^1H NOESY spectrum (CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-018.d
 Method DirectInfusion_TuneLow_pos.m
 Sample Name GMP-018
 Comment SB

Acquisition Date 11/27/2018 2:33:41 PM

Operator hplc
 Instrument micrOTOF-Q III 8228888.20448

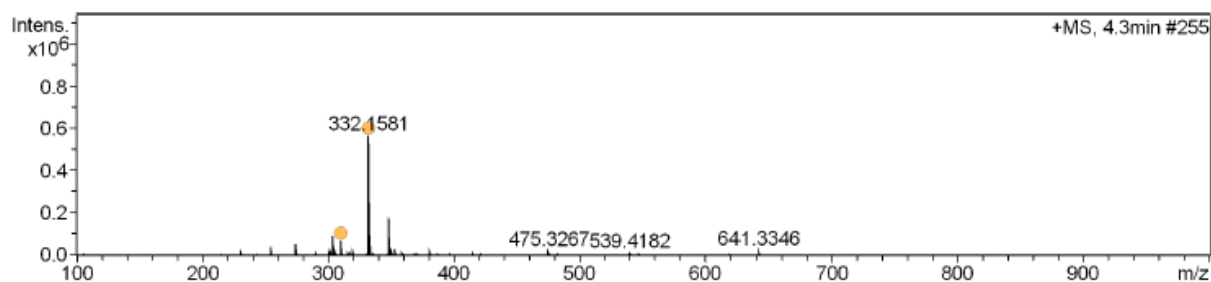
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.2	n.a.	Single spectrum	n.a.	n.a.	n.a.	304.2632	n.a.
n.a.	4.3	n.a.	Single spectrum	n.a.	n.a.	n.a.	332.1581	n.a.

+MS, 4.3min #255



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
310.1759	1	C15H24N3O4	310.1761	-0.8	4.2	1	100.00	5.5	even	ok
332.1581	1	C15H23N3NaO4	332.1581	0.1	1.0	1	100.00	5.5	even	ok

Figure S68. *tert*-Butyl 4-[4-(methoxycarbonyl)-1*H*-pyrazolyl]piperidine-1-carboxylate (7). HRMS (ESI-TOF).

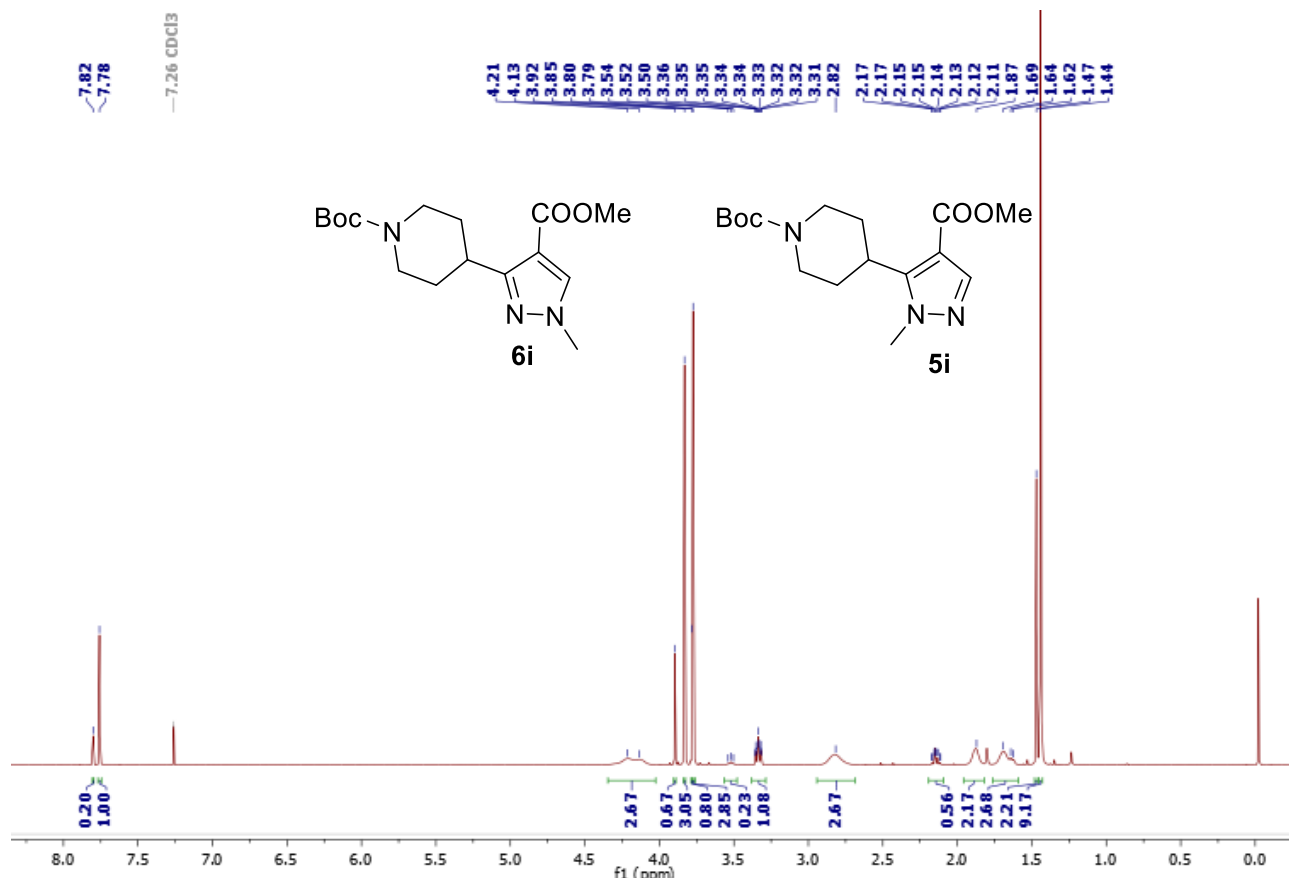


Figure S69. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (6i) and *tert*-butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5i). ¹H NMR spectrum (700 MHz, CDCl₃).

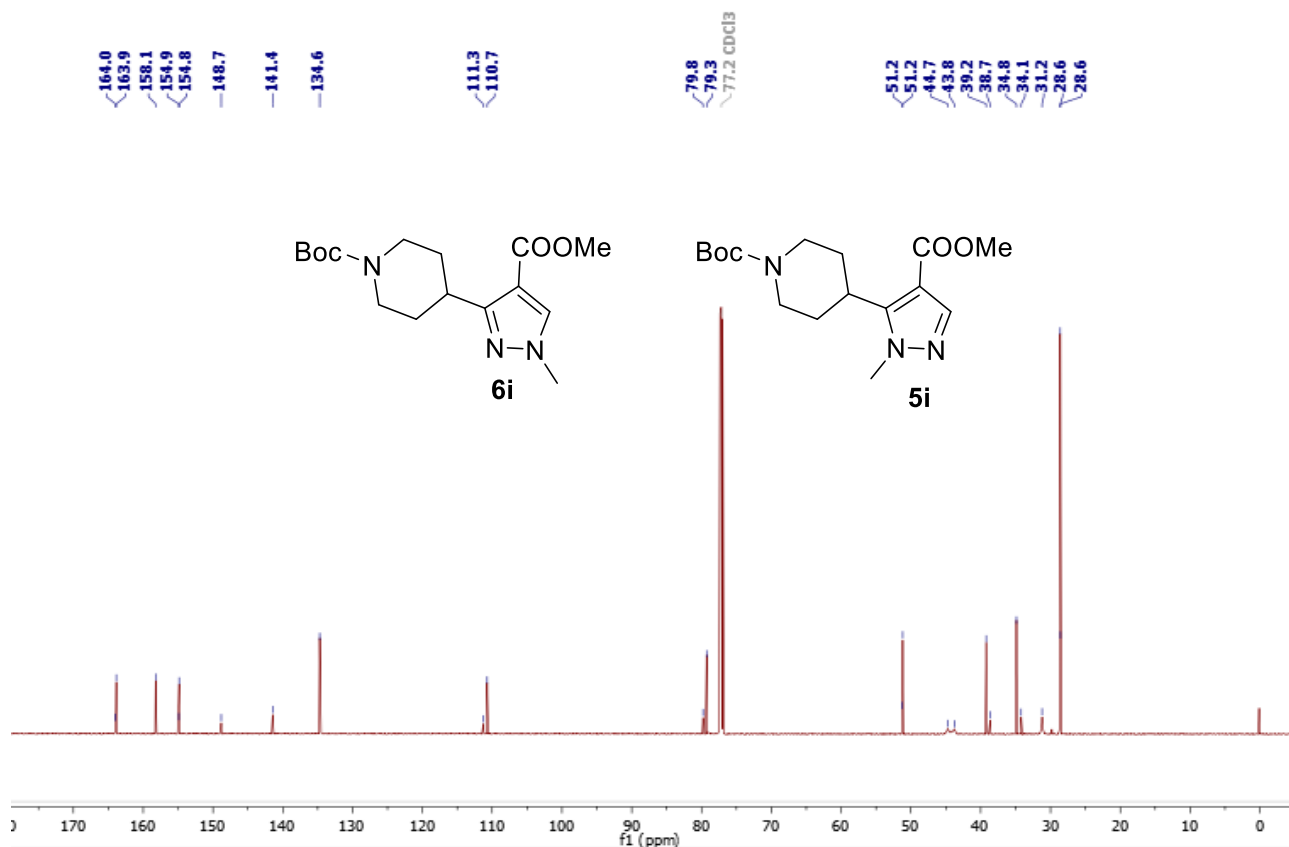


Figure S70. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (6i) and *tert*-butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5i). ¹³C NMR spectrum (176 MHz, CDCl₃).

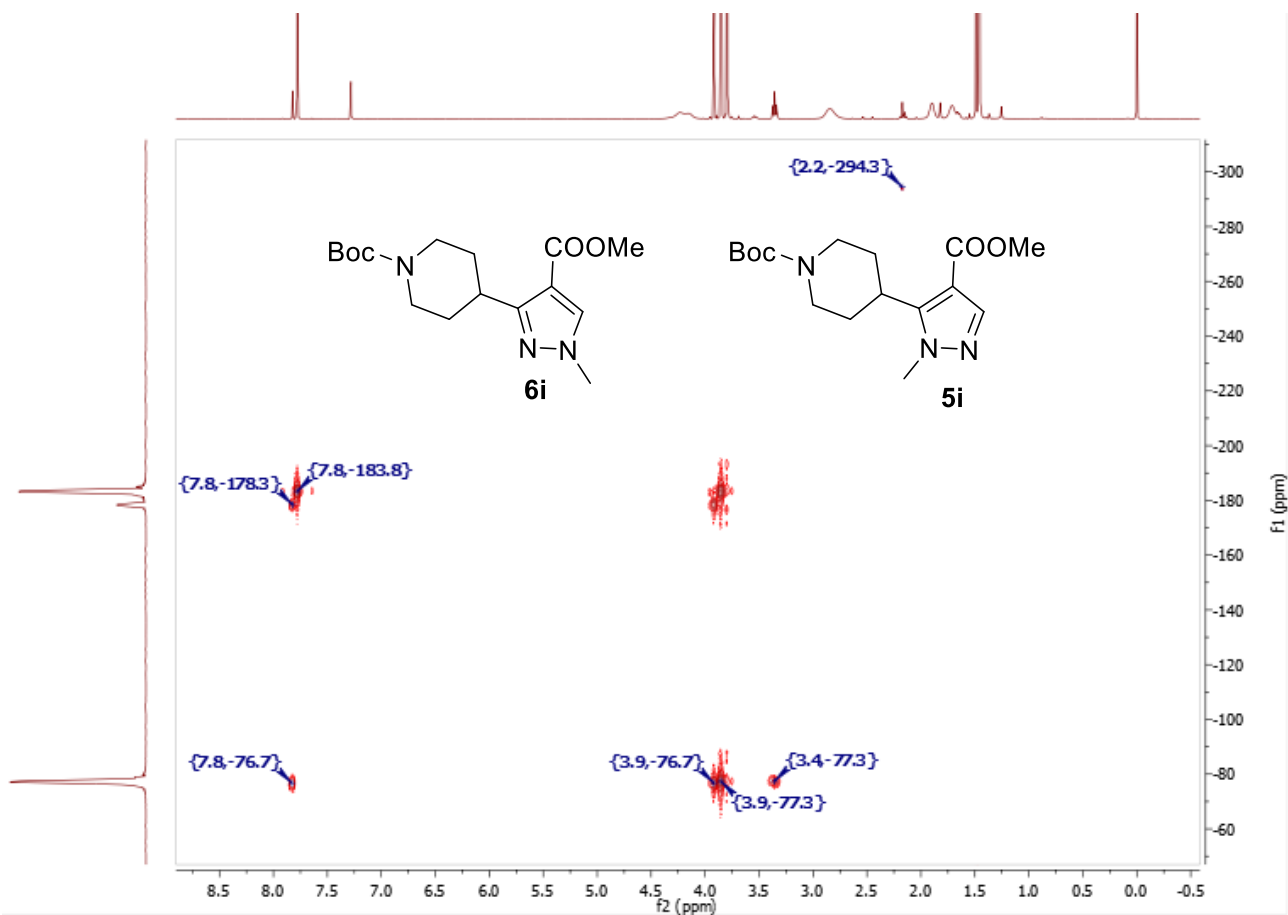


Figure S71. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (**6i**) and *tert*-butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (**5i**). ^1H - ^{15}N HMBC spectrum (71 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-517.d
 Method DirectInfusion_TuneLow_pos.m
 Sample Name GMP-517
 Comment AB

Acquisition Date 2/4/2021 11:12:05 PM

Operator hplc
 Instrument micrOTOF-Q III 8228888.20448

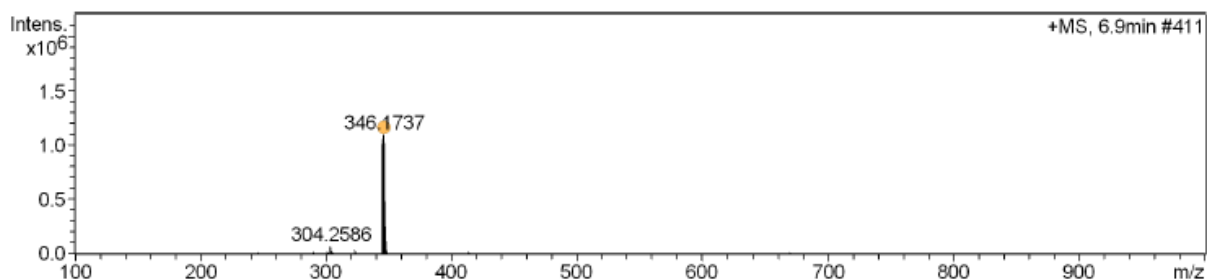
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	6.9	n.a.	Single spectrum	n.a.	n.a.	n.a.	346.1737	n.a.

+MS, 6.9min #411



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
346.1737	1	C ₁₆ H ₂₅ N ₃ NaO ₄	346.1737	-0.1	37.5	1	100.00	5.5	even	ok

Figure S72. *tert*-Butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (6i) and *tert*-butyl 4-[4-(methoxycarbonyl)-1-methyl-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (5i). HRMS (ESI-TOF).

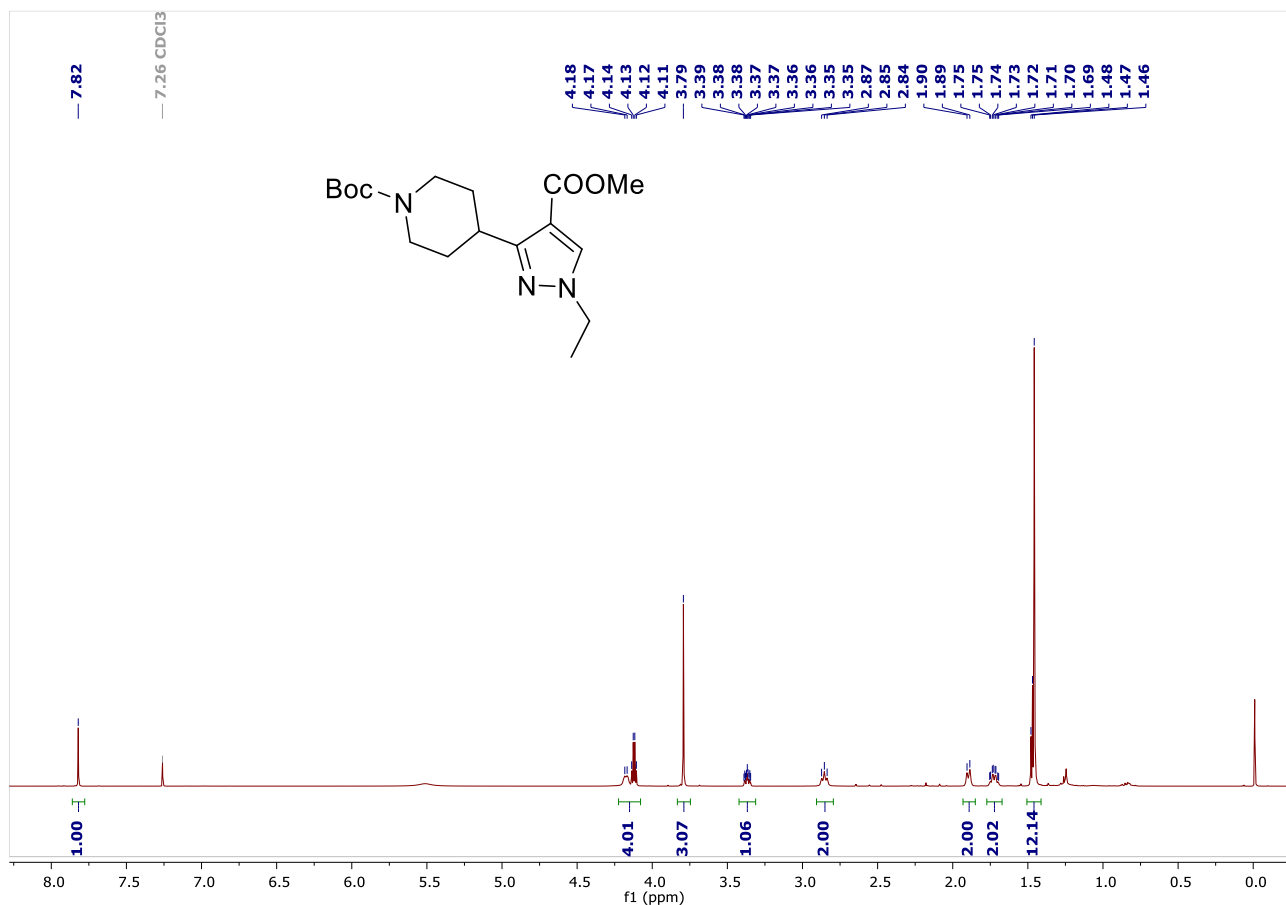


Figure S73. *tert*-Butyl 4-[1-ethyl-4-(methoxycarbonyl)-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (8). ¹H NMR spectrum (700 MHz, CDCl₃).

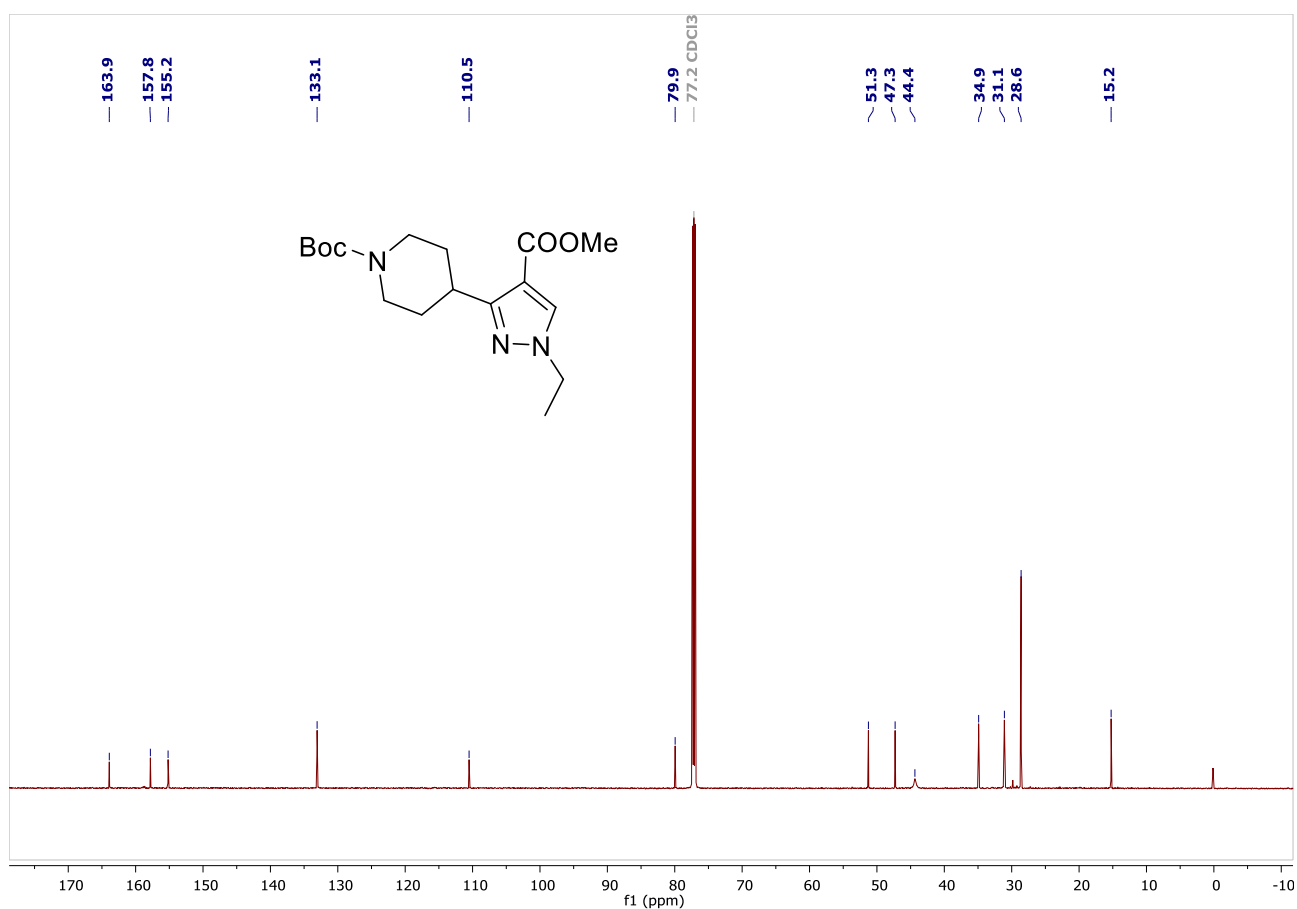


Figure S74. *tert*-Butyl 4-[1-ethyl-4-(methoxycarbonyl)-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (8). ¹³C NMR spectrum (176 MHz, CDCl₃).

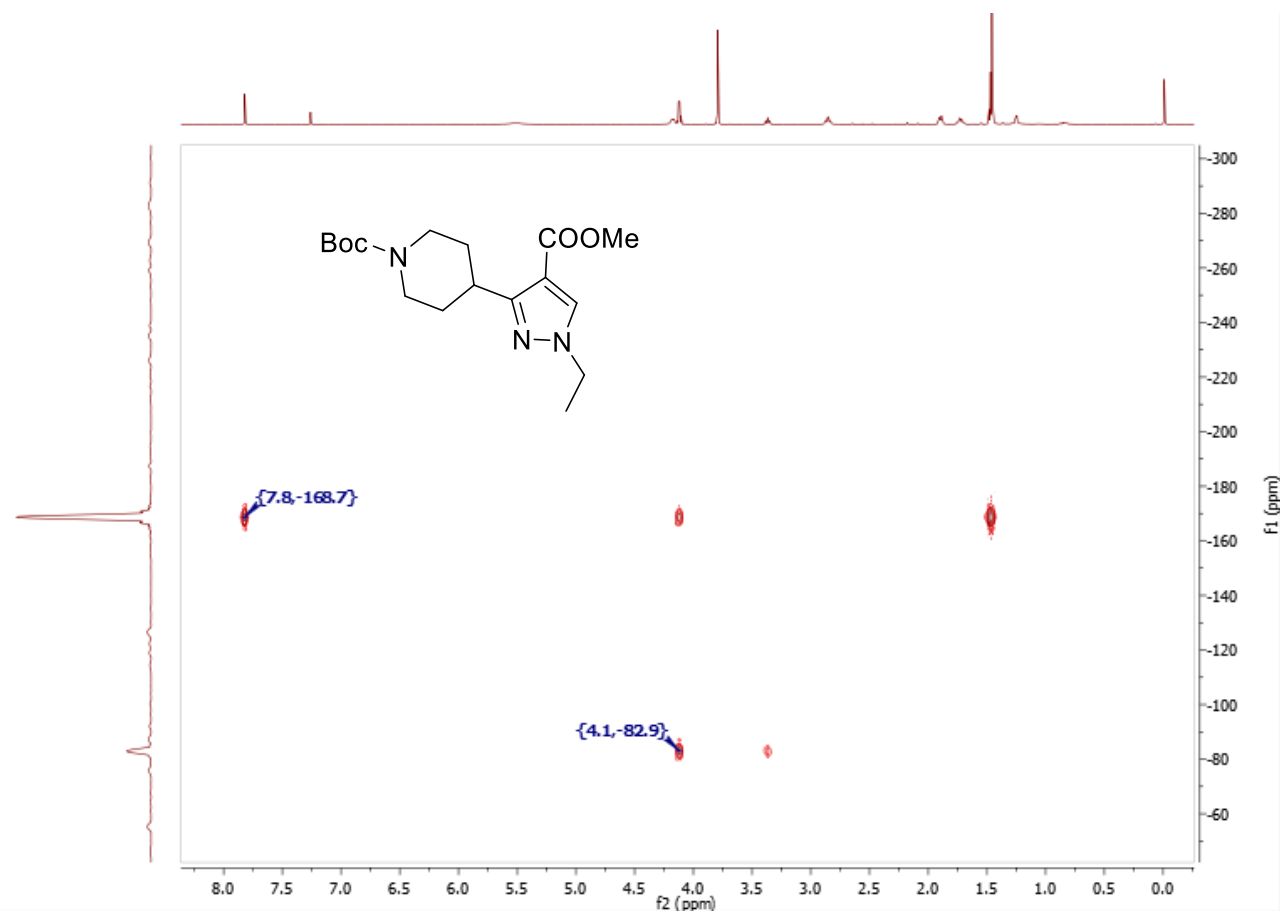


Figure S75. *tert*-Butyl 4-[1-ethyl-4-(methoxycarbonyl)-1*H*-pyrazol-3-yl]piperidine-1-carboxylate (8). ^1H - ^{15}N HMBC spectrum (71 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-019.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-019
Comment SB

Acquisition Date 11/27/2018 2:44:43 PM

Operator hplc
Instrument micrOTOF-Q III 8228888.20448

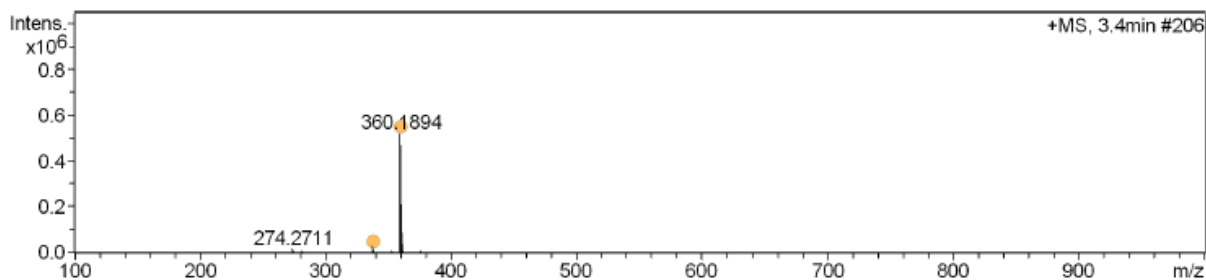
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.3	n.a.	Single spectrum	n.a.	n.a.	n.a.	304.2634	n.a.
n.a.	3.4	n.a.	Single spectrum	n.a.	n.a.	n.a.	360.1894	n.a.

+MS, 3.4min #206



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
338.2064	1	C17H28N3O4	338.2074	-3.1	16.8	1	100.00	5.5	even	ok
360.1894	1	C17H27N3NaO4	360.1894	-0.1	3.5	1	100.00	5.5	even	ok

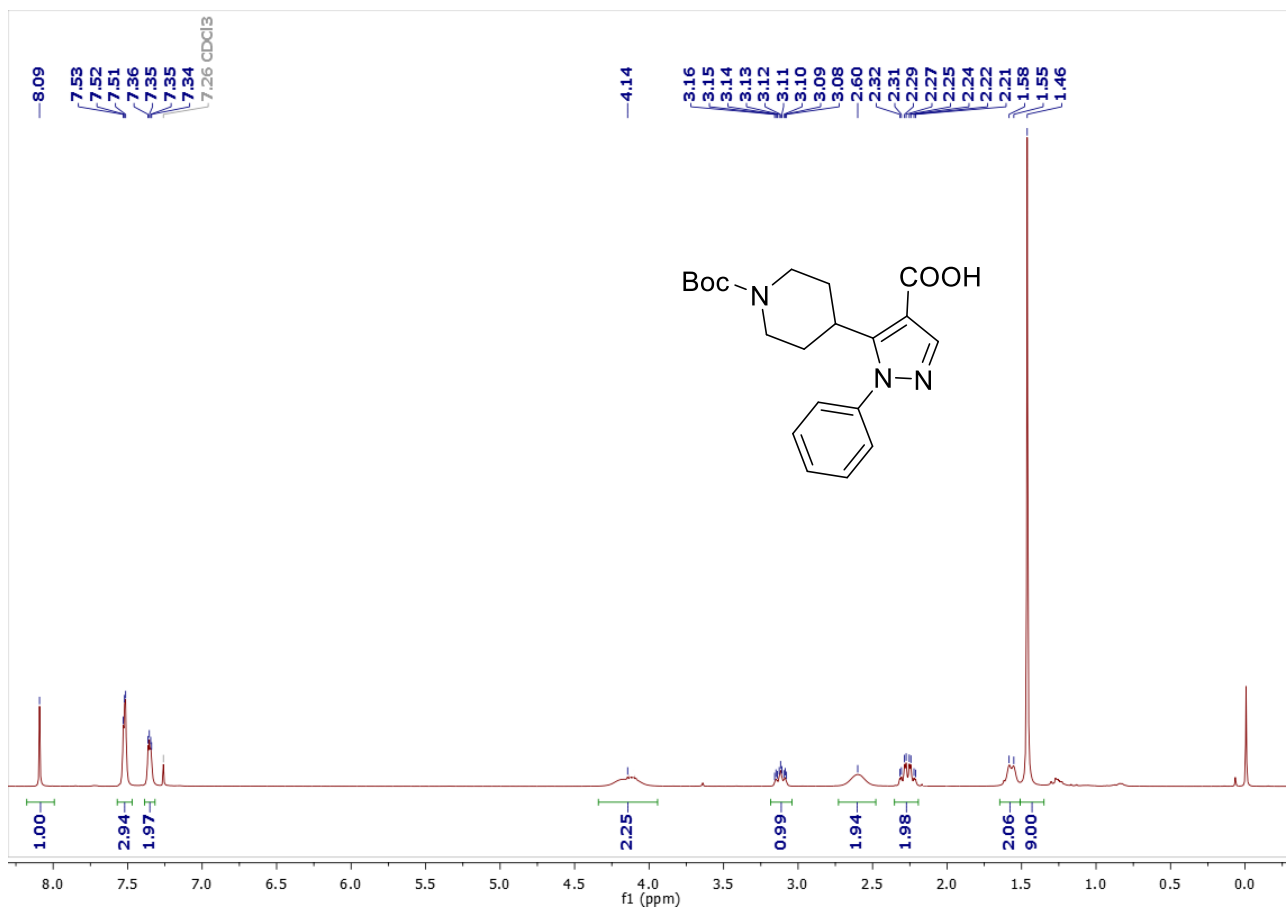


Figure S77. 5-[1-(*tert*-Butoxycarbonyl)piperidin-4-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9a). ¹H NMR spectrum (400 MHz, CDCl₃).

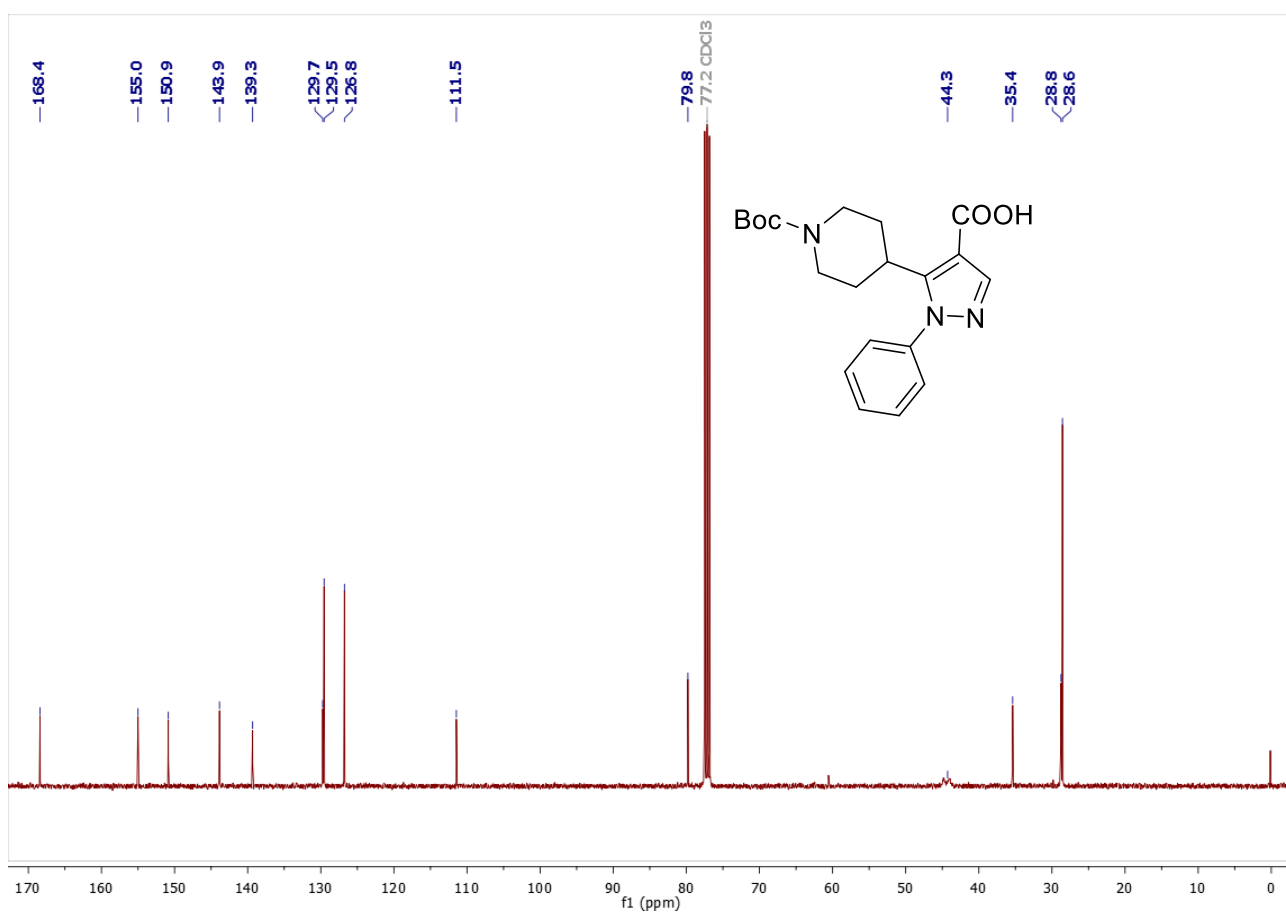


Figure S78. 5-[1-(*tert*-Butoxycarbonyl)piperidin-4-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9a). ¹³C NMR spectrum (101 MHz, CDCl₃).

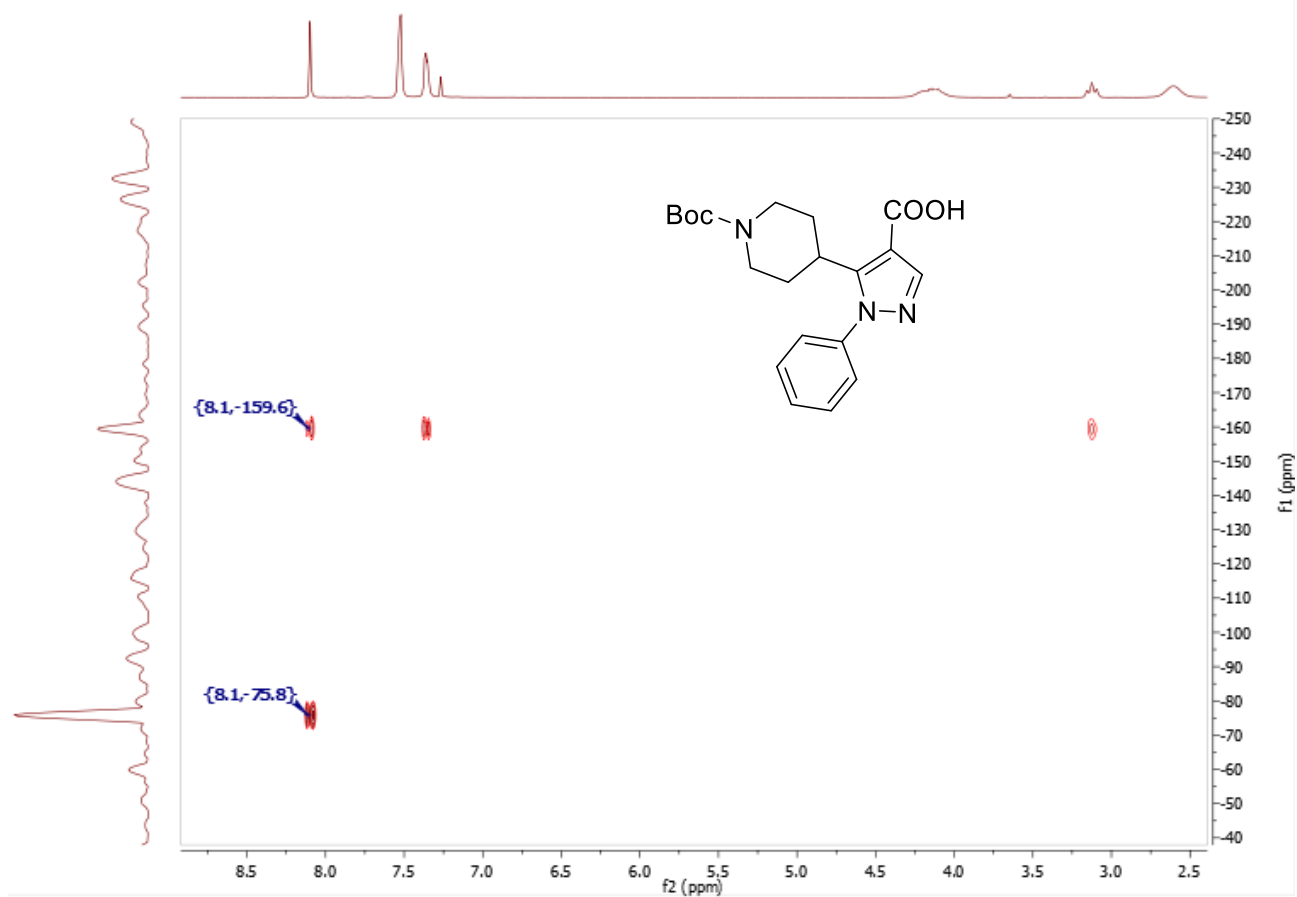


Figure S79. 5-[1-(*tert*-Butoxycarbonyl)piperidin-4-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9a). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-121.d
 Method DirectInfusion_TuneLow_pos.m
 Sample Name GMP-121
 Comment AB

Acquisition Date 2/4/2021 9:41:19 PM
 Operator hplc
 Instrument microTOF-Q III 8228888.20448

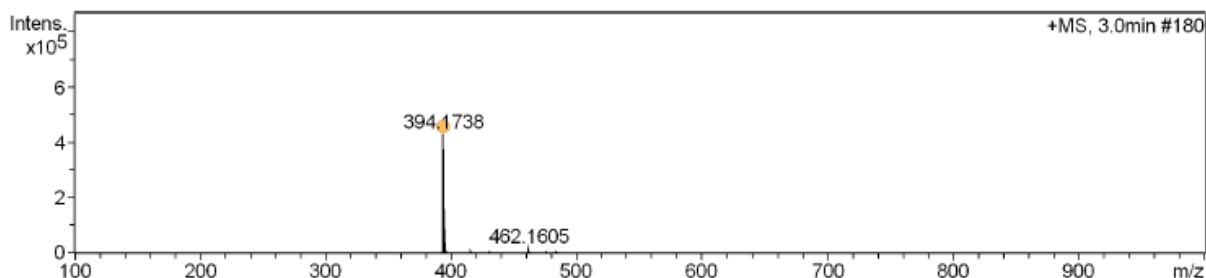
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	3.0	n.a.	Single spectrum	n.a.	n.a.	n.a.	394.1738	n.a.

+MS, 3.0min #180



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
394.1738	1	C20H25N3NaO4	394.1737	-0.2	1.2	1	100.00	9.5	even	ok

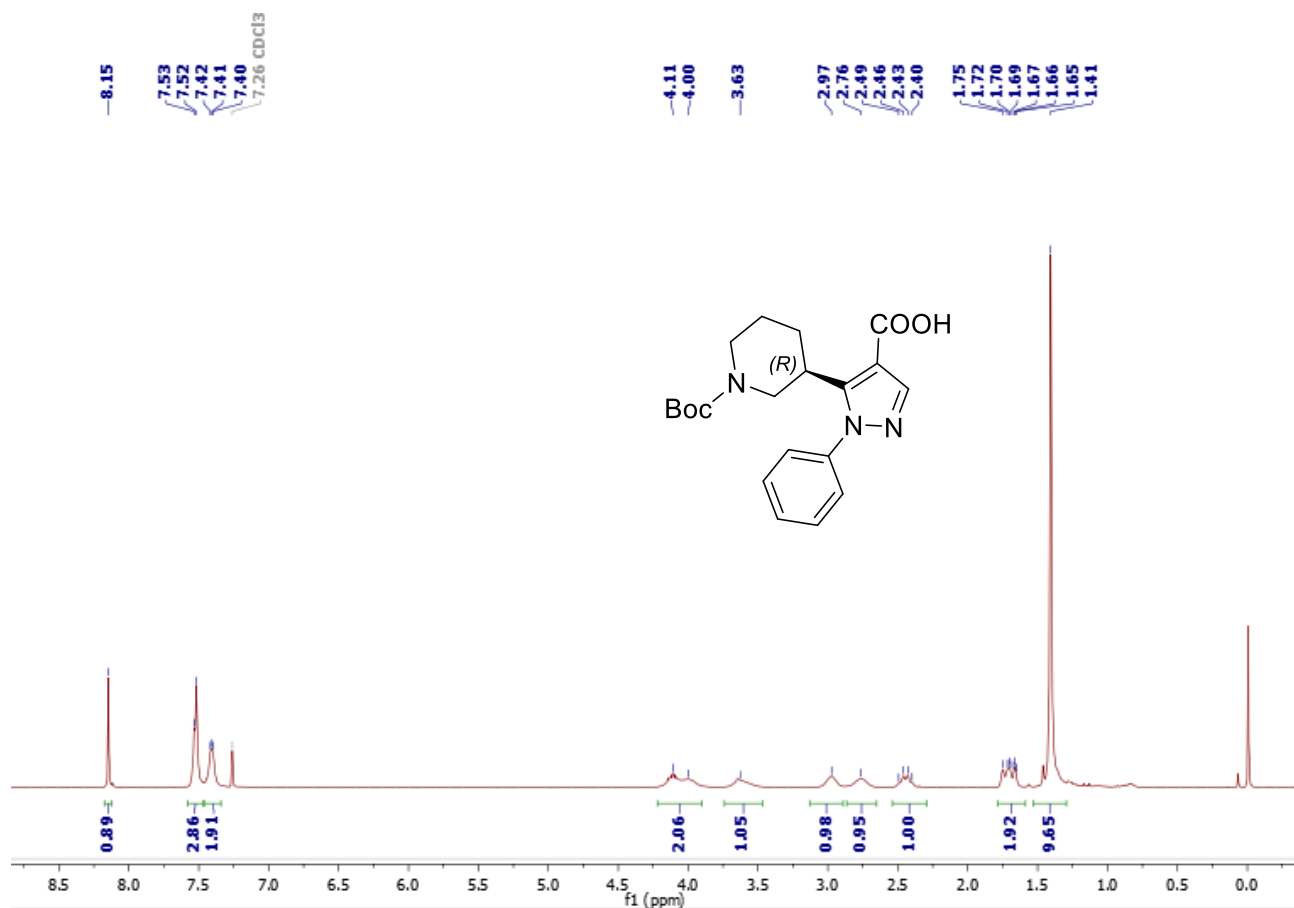


Figure S81. 5-[(3*R*)-1-(*tert*-Butoxycarbonyl)piperidin-3-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9b). ¹H NMR spectrum (400 MHz, CDCl₃).

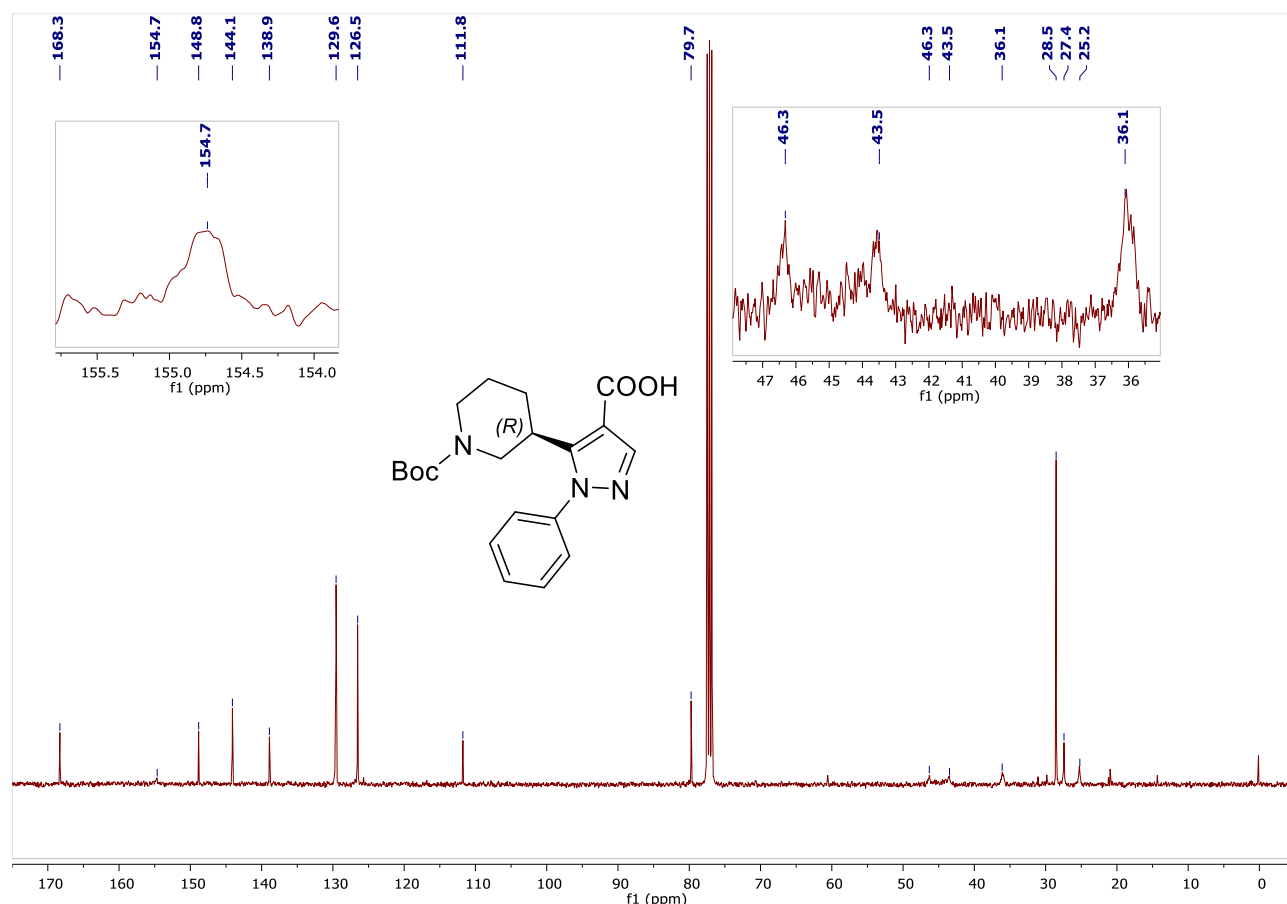


Figure S82. 5-[(3*R*)-1-(*tert*-Butoxycarbonyl)piperidin-3-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9b). ¹³C NMR spectrum (101 MHz, CDCl₃).

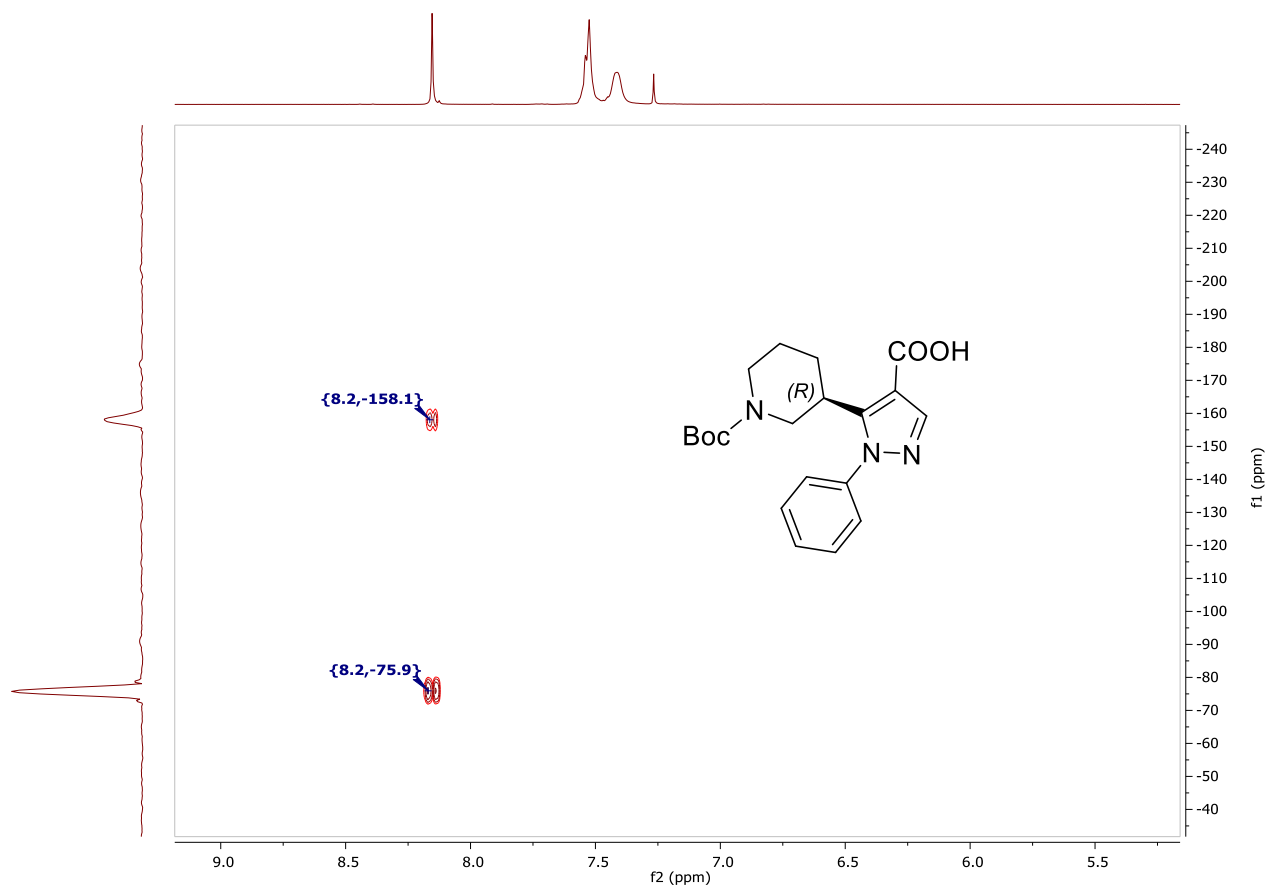


Figure S83. 5-[(3R)-1-(*tert*-Butoxycarbonyl)piperidin-3-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9b). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-124.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-124
Comment AB

Acquisition Date 2/4/2021 9:18:32 PM

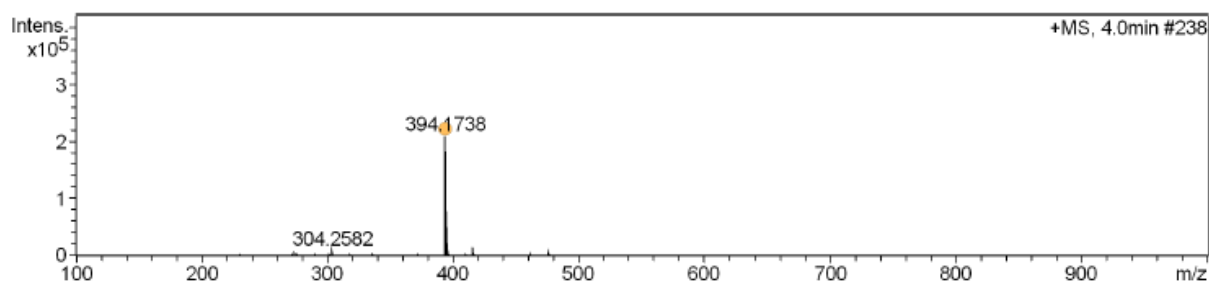
Operator hplc
Instrument micrOTOF-Q III 8228888.20448

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste

#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	4.0	n.a.	Single spectrum	n.a.	n.a.	n.a.	394.1738	n.a.

+MS, 4.0min #238



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
394.1738	1	C20H25N3NaO4	394.1737	0.1	21.6	3	100.00	9.5	even	ok

Figure S84. 5-[(3*R*)-1-(*tert*-Butoxycarbonyl)piperidin-3-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9b). HRMS (ESI-TOF).

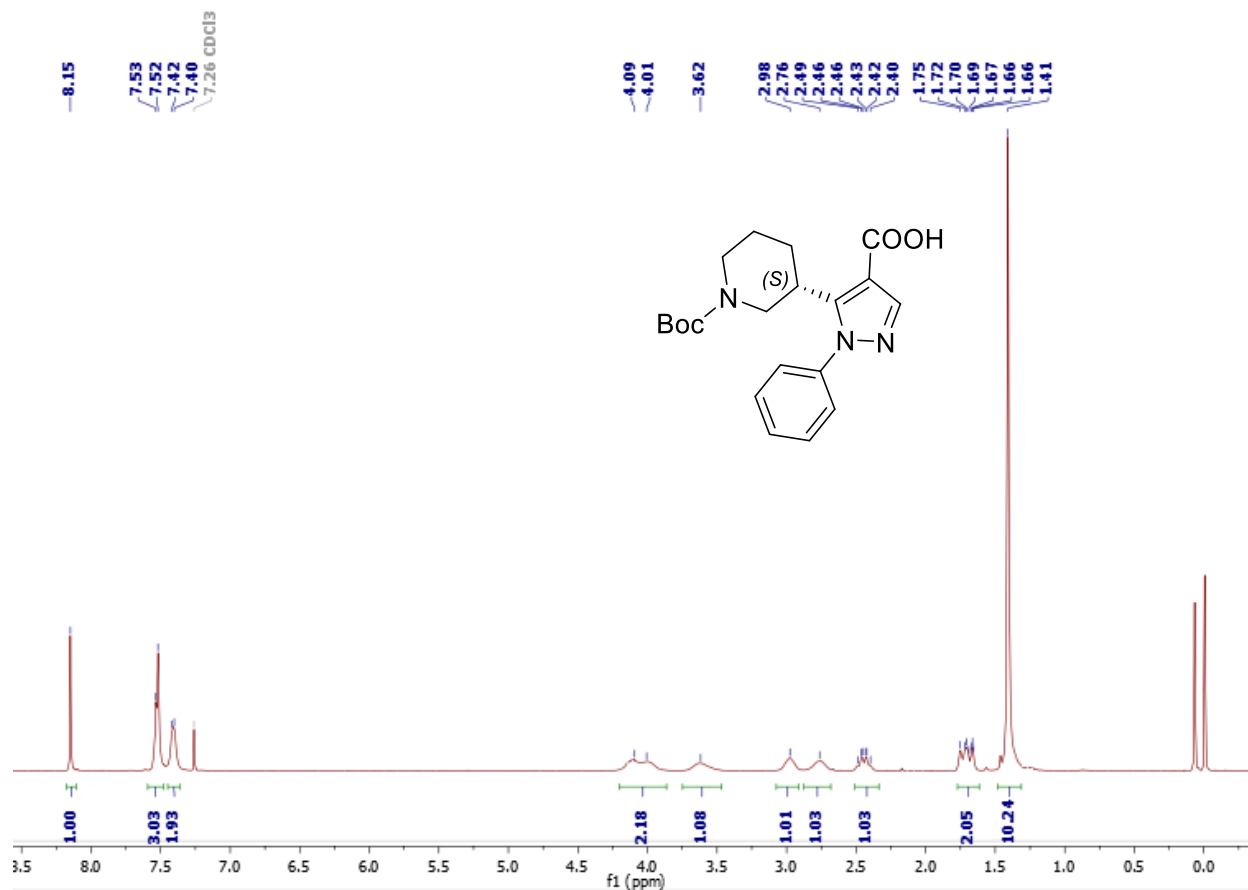


Figure S85. 5-[(3*S*)-1-(*tert*-Butoxycarbonyl)piperidin-3-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9c). ¹H NMR spectrum (400 MHz, CDCl₃).

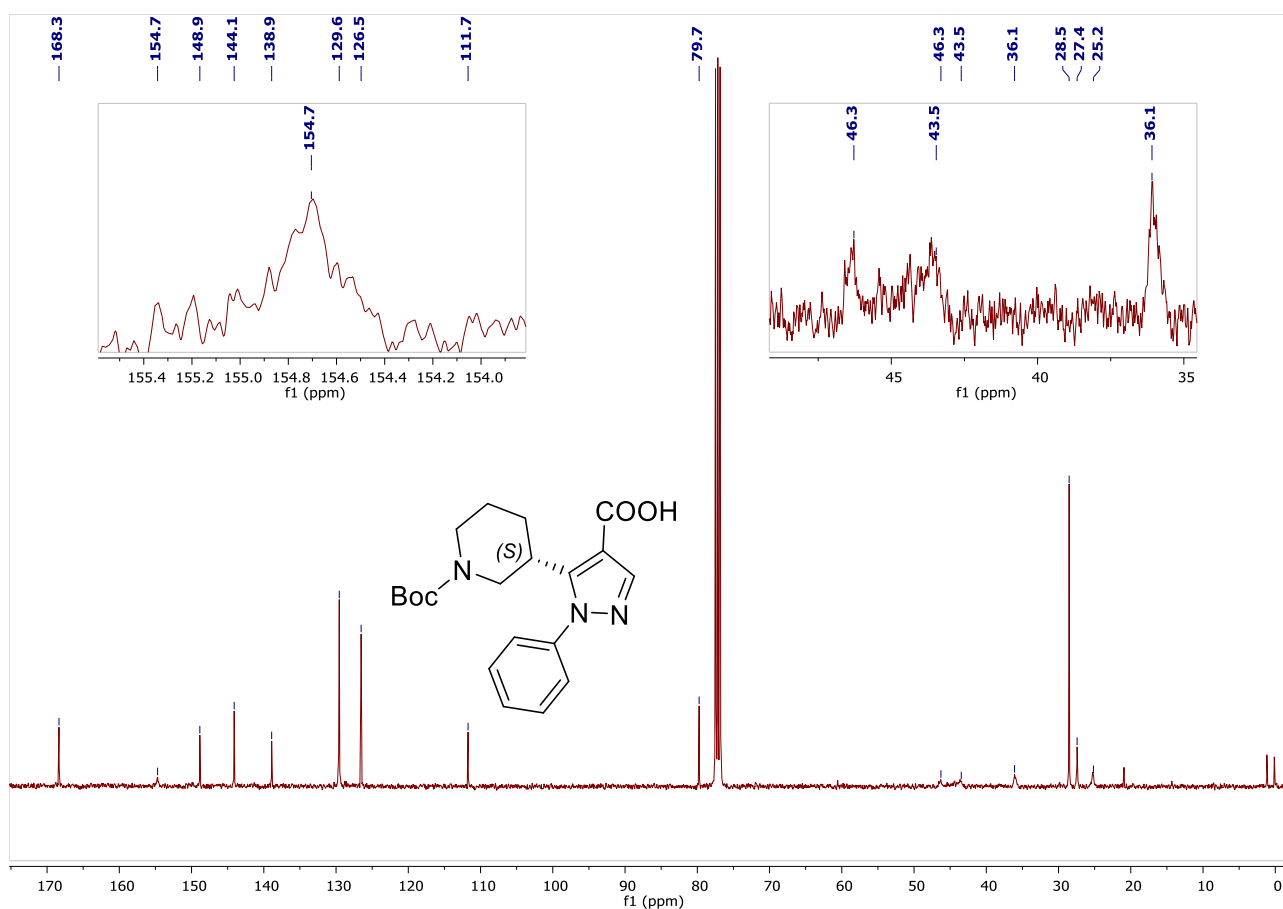


Figure S86. 5-[(3*S*)-1-(*tert*-Butoxycarbonyl)piperidin-3-yl]-1-phenyl-1*H*-pyrazole-4-carboxylic acid (9c). ¹³C NMR spectrum (101 MHz, CDCl₃).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-152.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-152
Comment AB

Acquisition Date 2/4/2021 2:07:00 PM

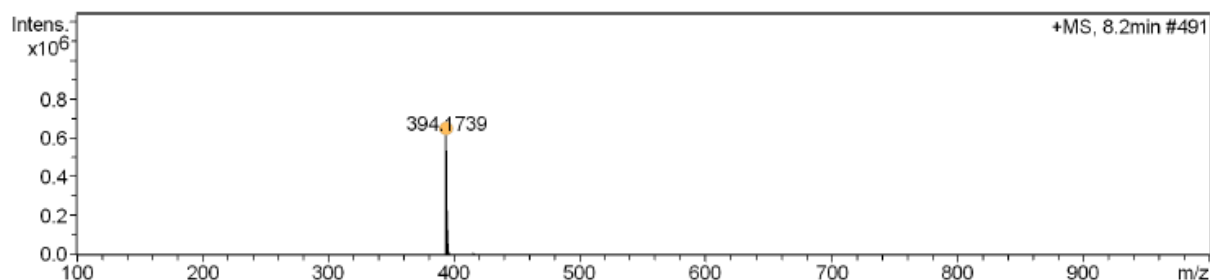
Operator hplc
Instrument micrOTOF-Q III 8228888.20448

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste

#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	8.2	n.a.	Single spectrum	n.a.	n.a.	n.a.	394.1739	n.a.

+MS, 8.2min #491



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
394.1739	1	C20H25N3NaO4	394.1737	-0.3	7.5	1	100.00	9.5	even	ok

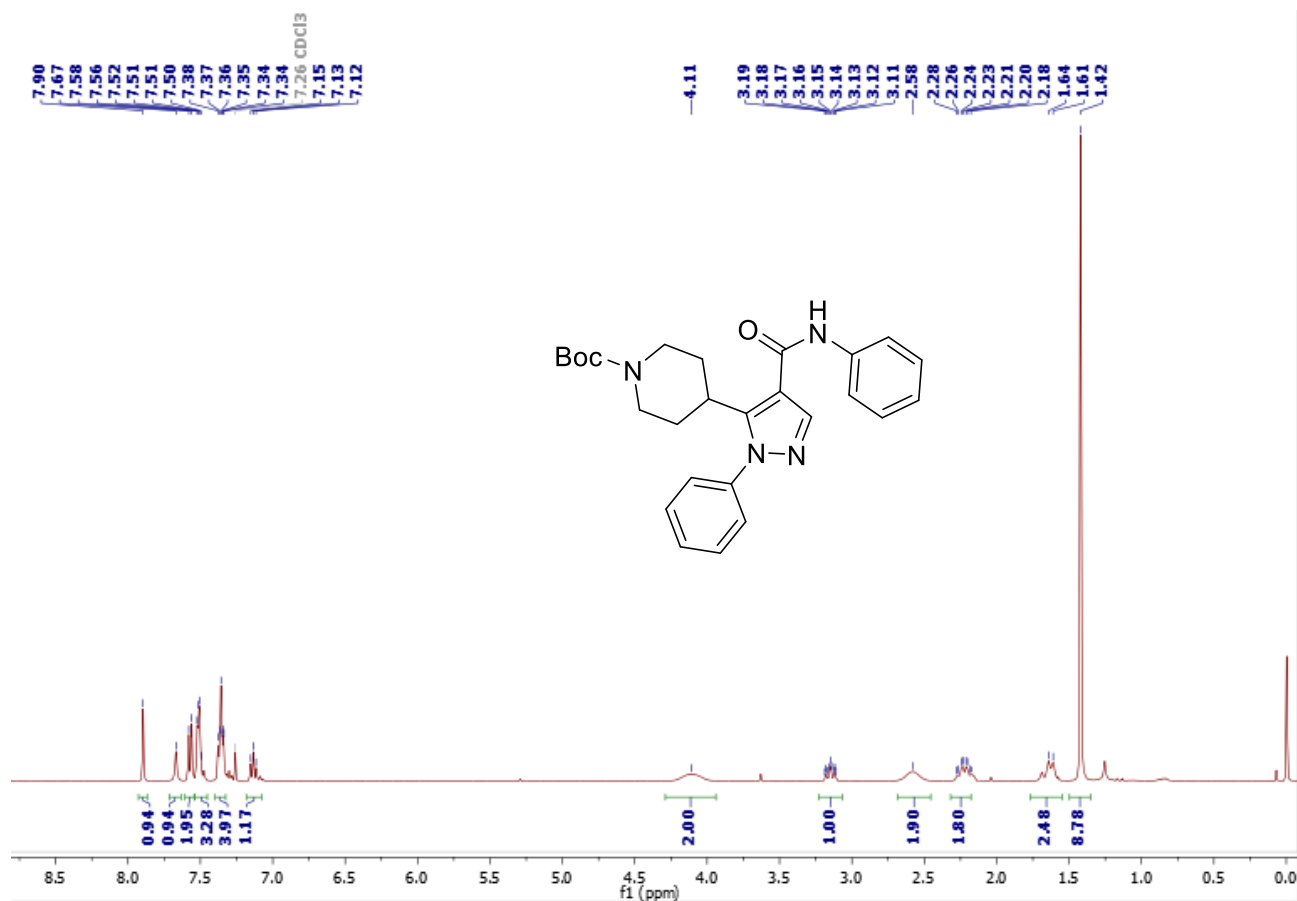


Figure S88. *tert*-Butyl 4-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10a). ¹H NMR spectrum (400 MHz, CDCl₃).

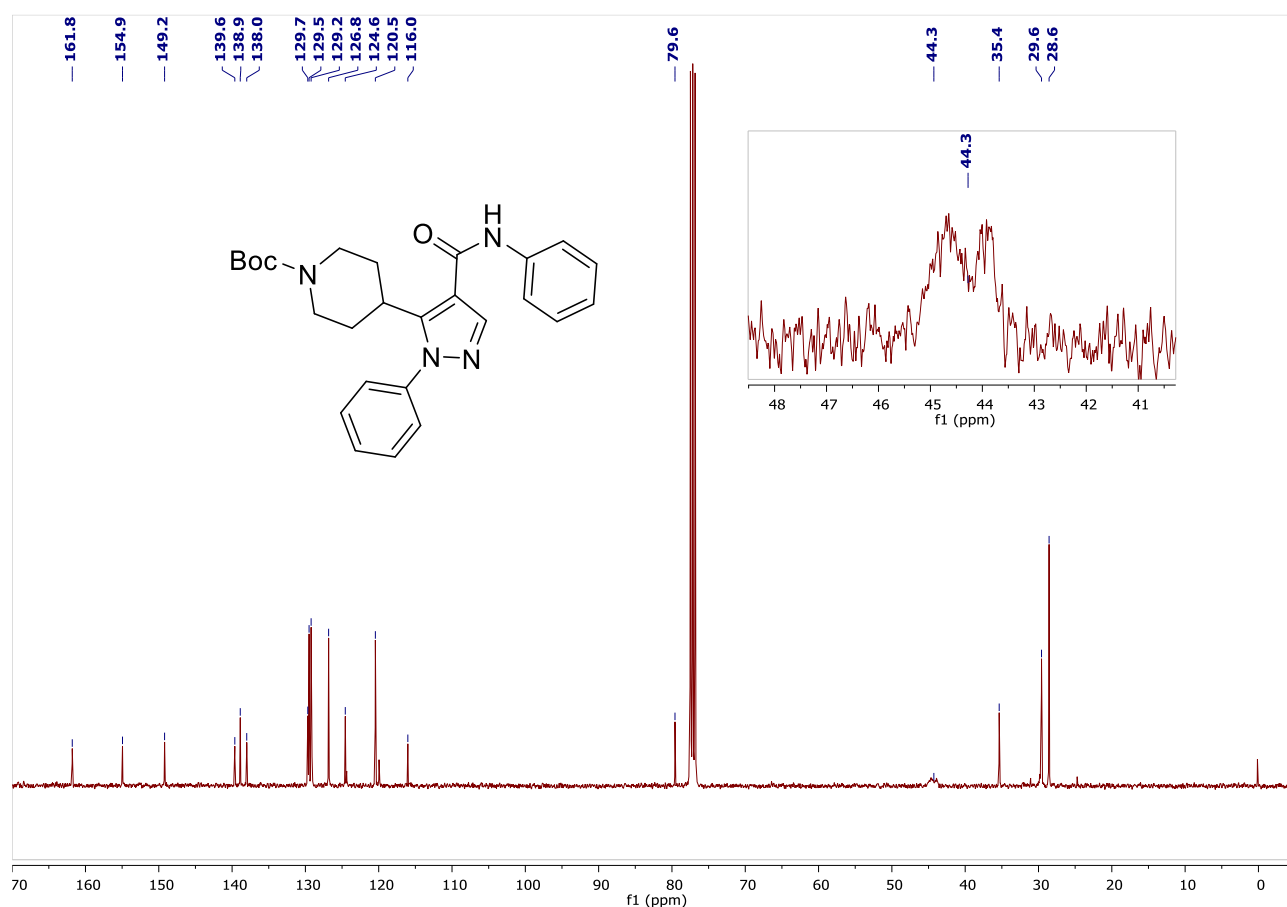


Figure S89. *tert*-Butyl 4-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10a). ¹³C NMR spectrum (101 MHz, CDCl₃).

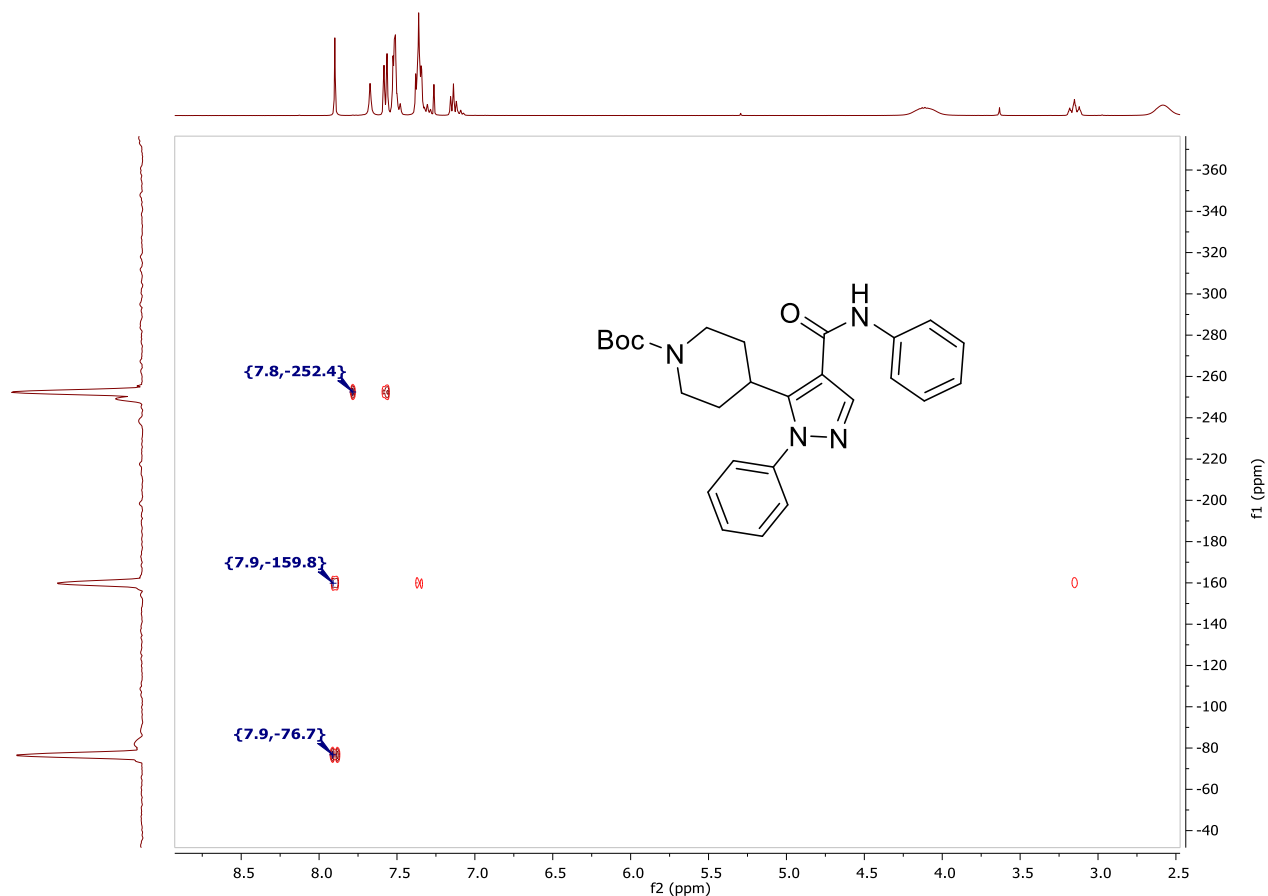


Figure S90. *tert*-Butyl 4-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10a). ¹H-¹⁵N HMBC spectrum (41 MHz, CDCl₃).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-126.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-126
Comment AB

Acquisition Date 2/4/2021 9:31:08 PM

Operator hplc
Instrument micrOTOF-Q III 8228888.20448

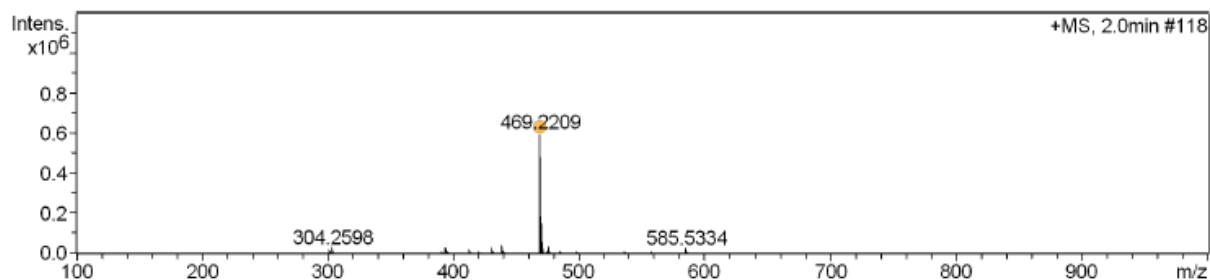
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	2.0	n.a.	Single spectrum	n.a.	n.a.	n.a.	469.2209	n.a.

+MS, 2.0min #118



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
469.2209	1	C ₂₆ H ₃₀ N ₄ NaO ₃	469.2210	-0.2	3.0	1	100.00	13.5	even	ok

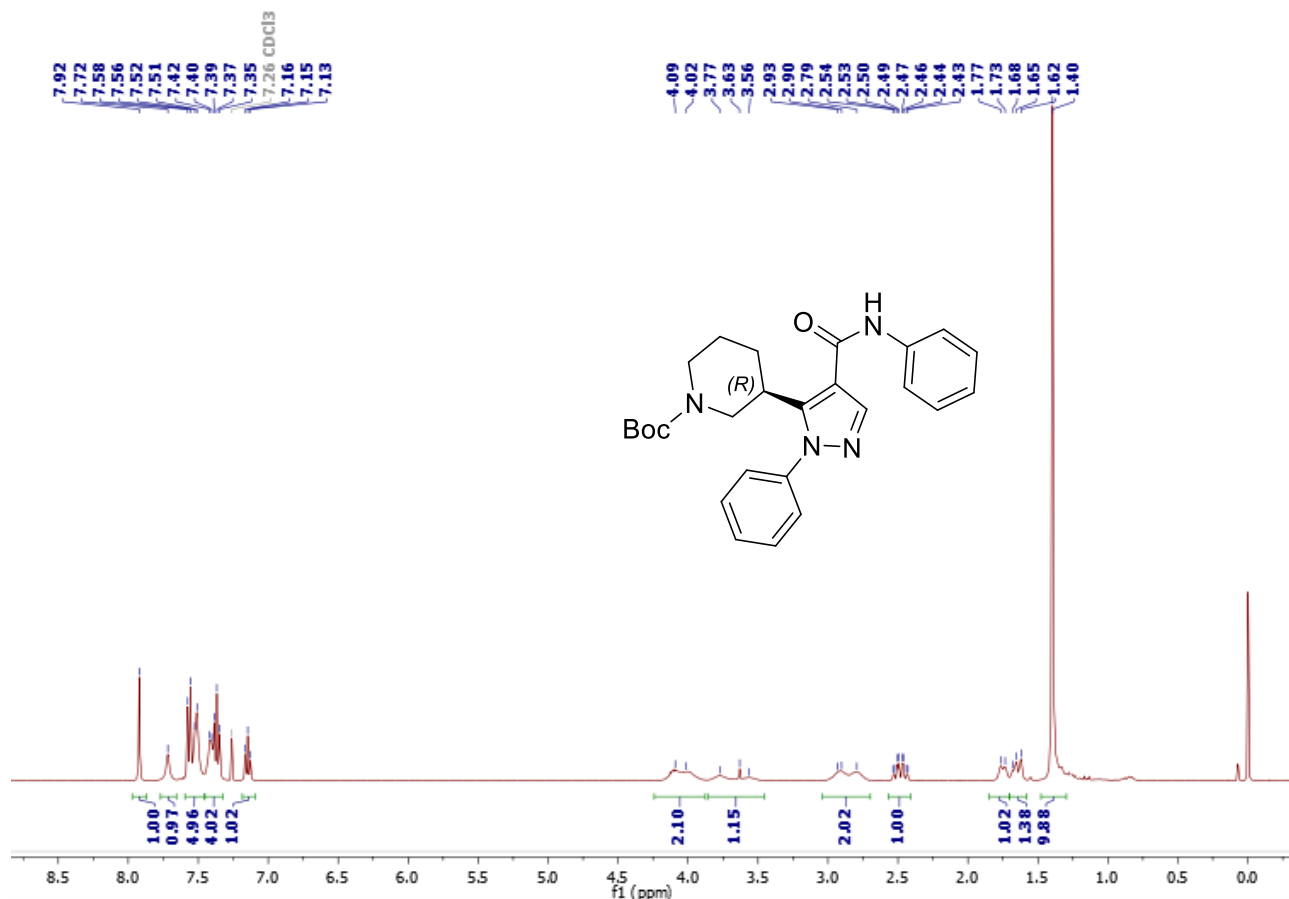


Figure S92. *tert*-Butyl (3*R*)-3-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10b). ¹H NMR spectrum (400 MHz, CDCl₃).

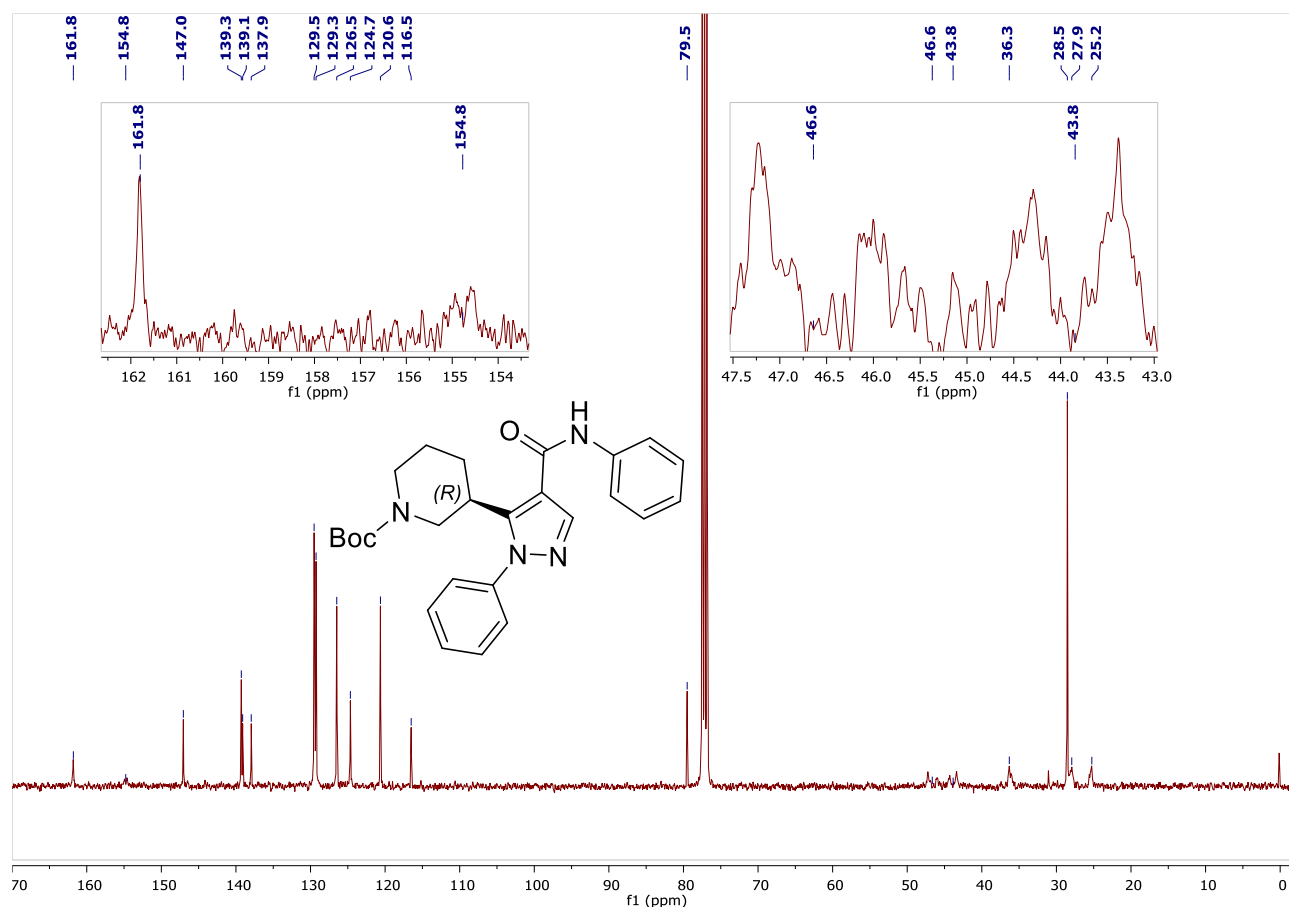


Figure S93. *tert*-Butyl (3*R*)-3-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10b). ¹³C NMR spectrum (101 MHz, CDCl₃).

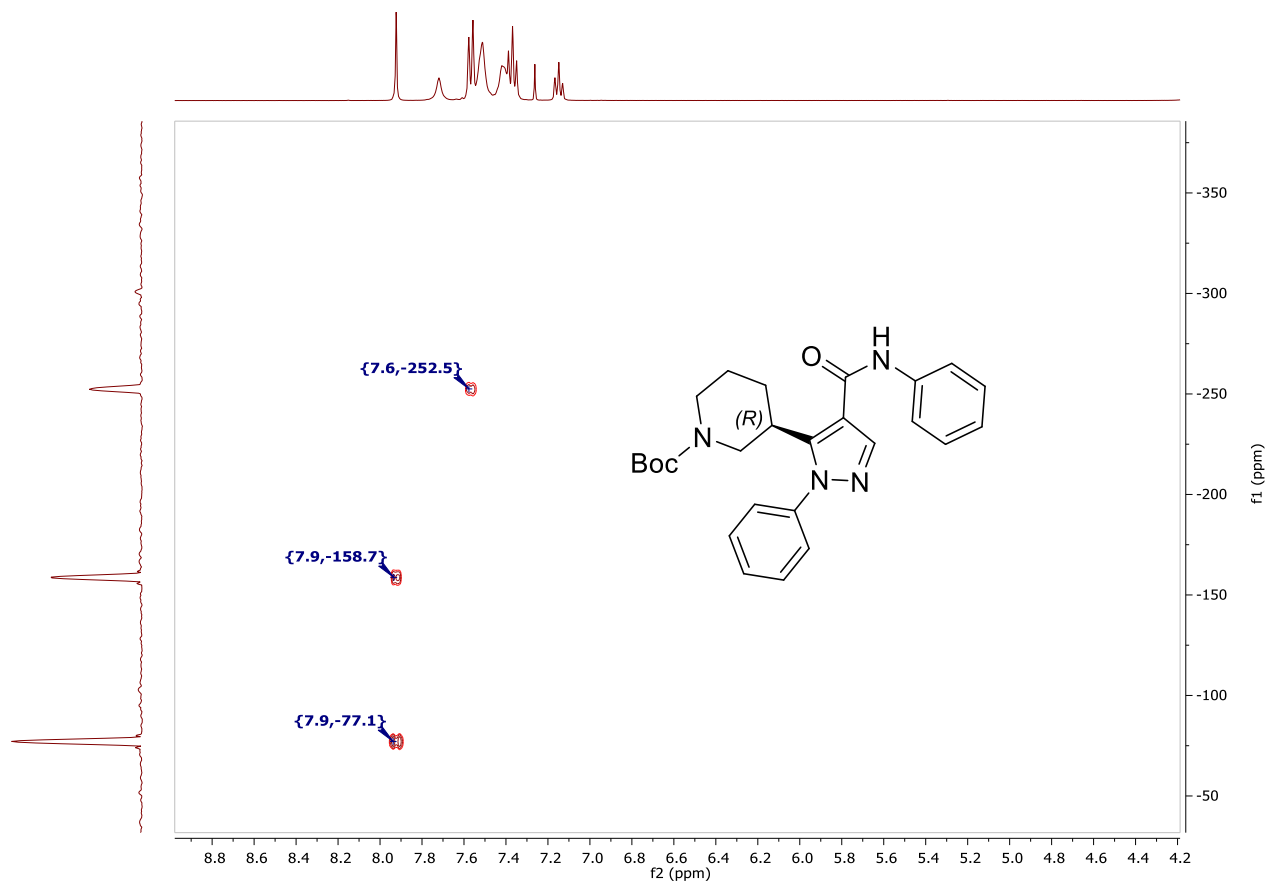


Figure S94. *tert*-Butyl (3*R*)-3-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10b). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-129.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-129
Comment AB

Acquisition Date 2/4/2021 9:00:51 PM

Operator hplc
Instrument micrOTOF-Q III 8228888.20448

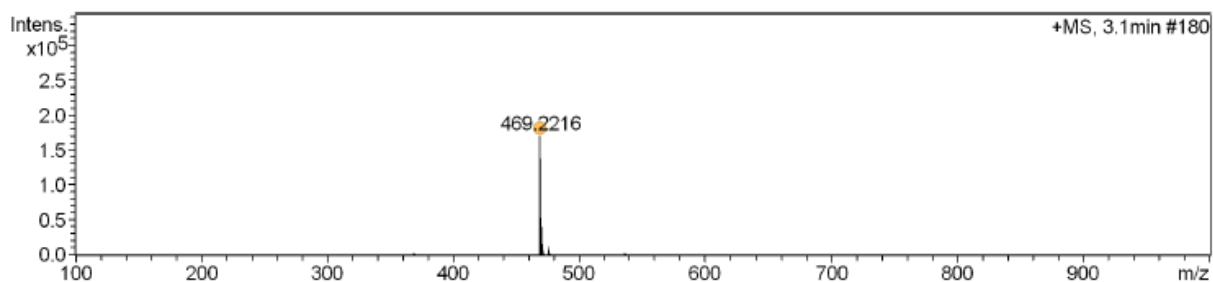
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	3.1	n.a.	Single spectrum	n.a.	n.a.	n.a.	469.2216	n.a.

+MS, 3.1min #180



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
469.2216	1	C26H30N4NaO3	469.2210	1.3	4.9	1	100.00	13.5	even	ok

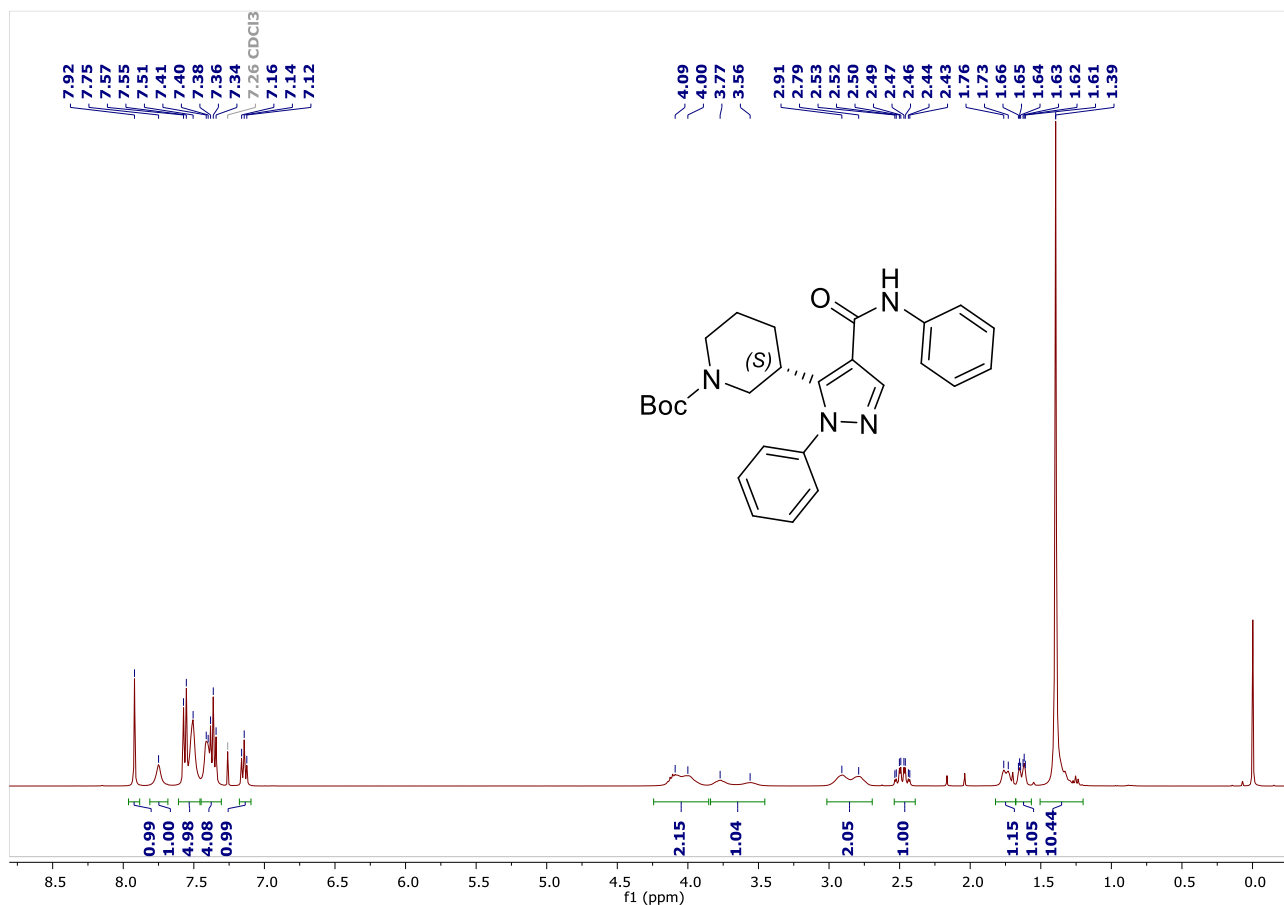


Figure S96. *tert*-Butyl (3*S*)-3-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10c). ¹H NMR spectrum (400 MHz, CDCl₃).

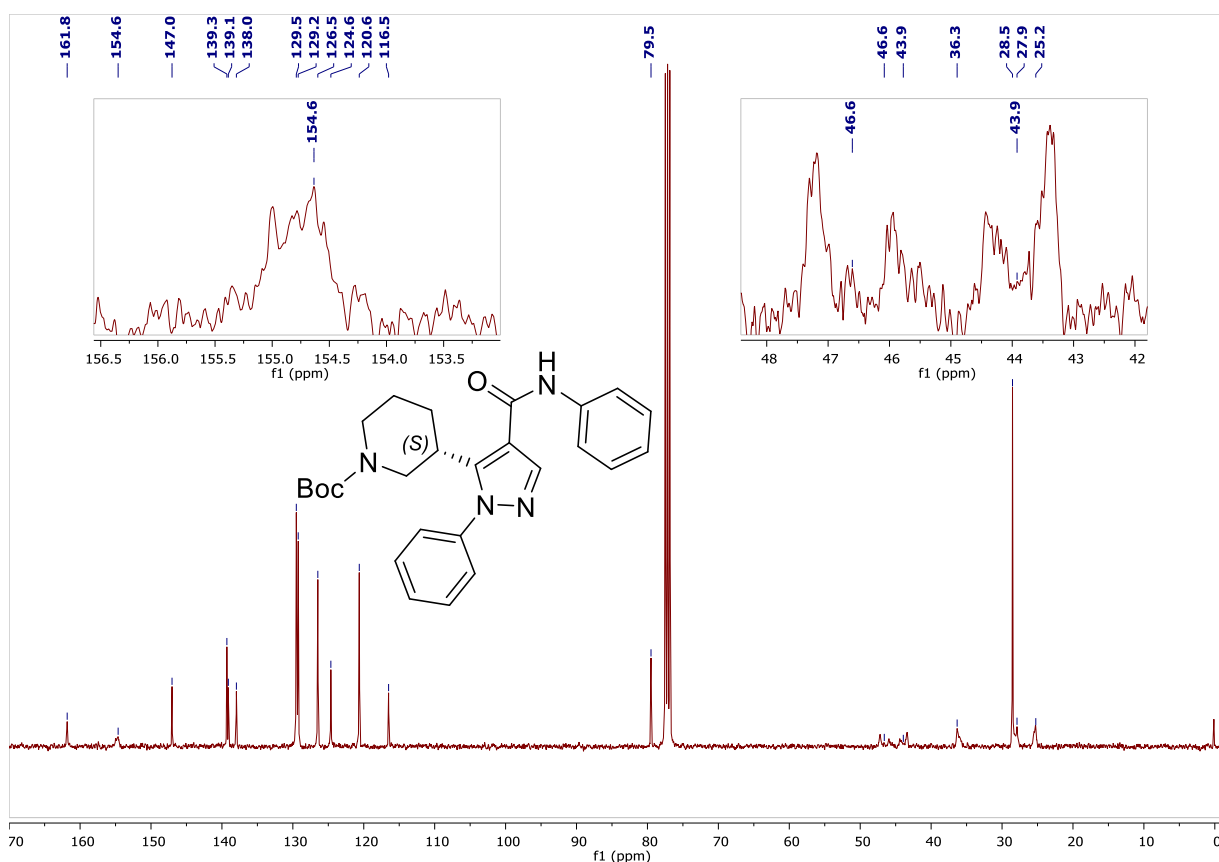


Figure S97. *tert*-Butyl (3*S*)-3-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10c). ¹³C NMR spectrum (101 MHz, CDCl₃).

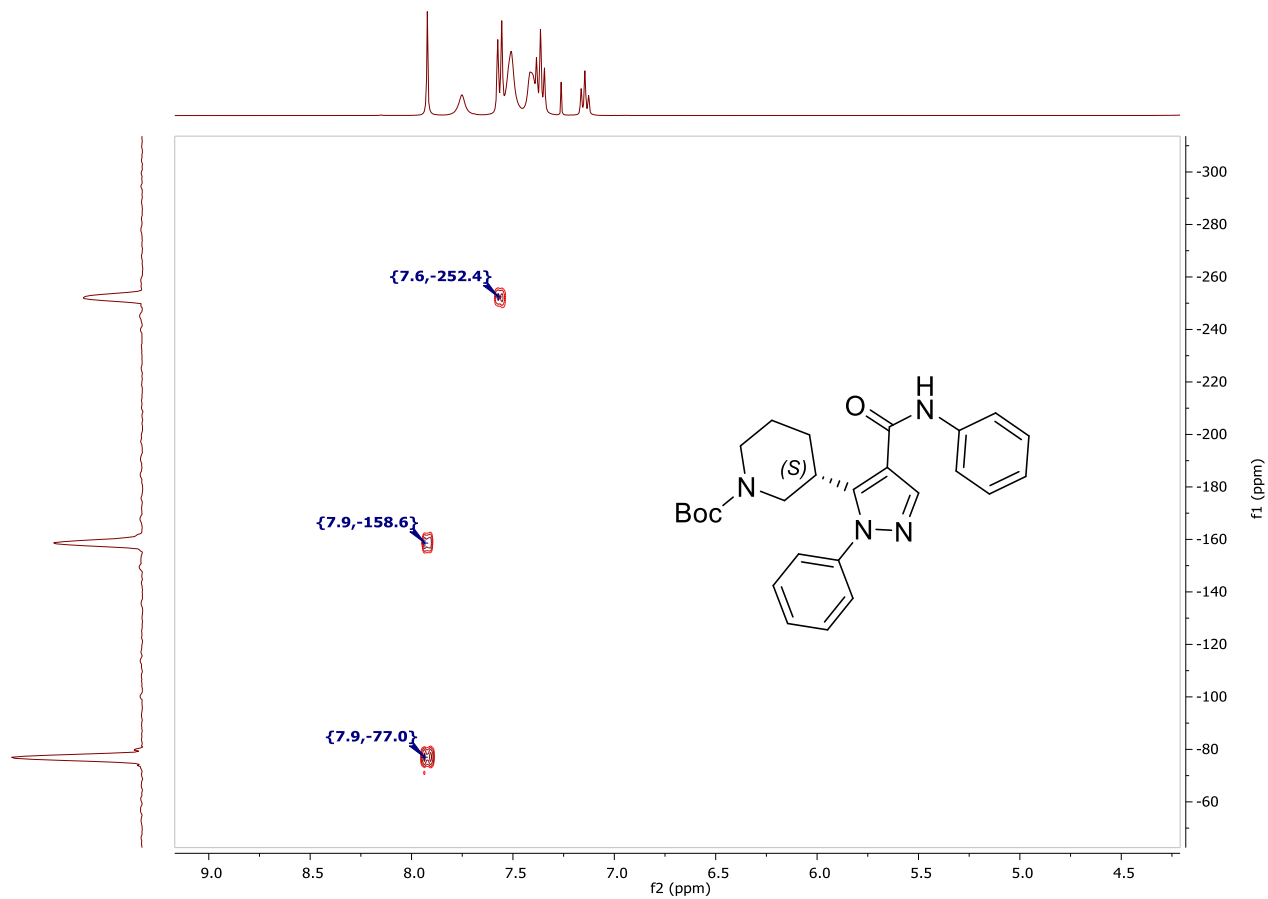


Figure S98. *tert*-Butyl (3*S*)-3-[1-phenyl-4-(phenylcarbamoyl)-1*H*-pyrazol-5-yl]piperidine-1-carboxylate (10c). ^1H - ^{15}N HMBC spectrum (41 MHz, CDCl_3).

Compound Spectrum SmartFormula Report

Analysis Info

Analysis Name D:\Data\GMP-155.d
Method DirectInfusion_TuneLow_pos.m
Sample Name GMP-155
Comment AB

Acquisition Date 2/4/2021 1:42:18 PM

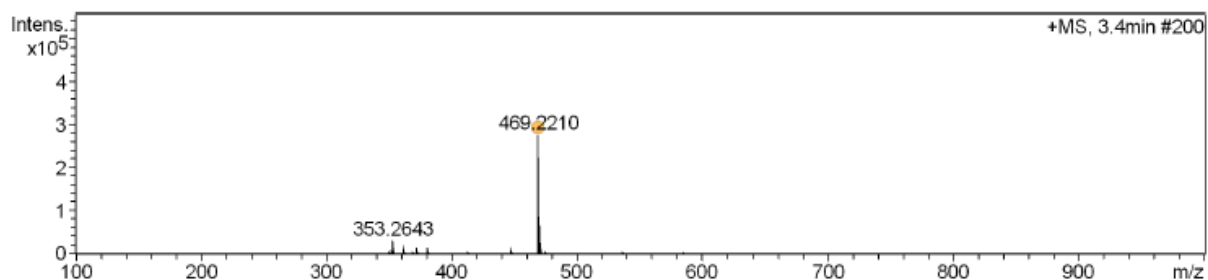
Operator hplc
Instrument microTOF-Q III 8228888.20448

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	140.0 Vpp	Set Divert Valve	Waste

#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	3.4	n.a.	Single spectrum	n.a.	n.a.	n.a.	469.2210	n.a.

+MS, 3.4min #200



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdB	e ⁻ Conf	N-Rule
469.2210	1	C ₂₆ H ₃₀ N ₄ NaO ₃	469.2210	-0.1	5.0	1	100.00	13.5	even	ok