Supporting Information

Diastereo- and Enantioselective Synthesis of Trisubstituted Benzopyrans by Cascade Reactions Catalyzed by Monomeric and Polymeric Recoverable Bifunctional Thioureas and Squaramides.

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Table S1 Crystal data and structure refinement for 3ac **S37**

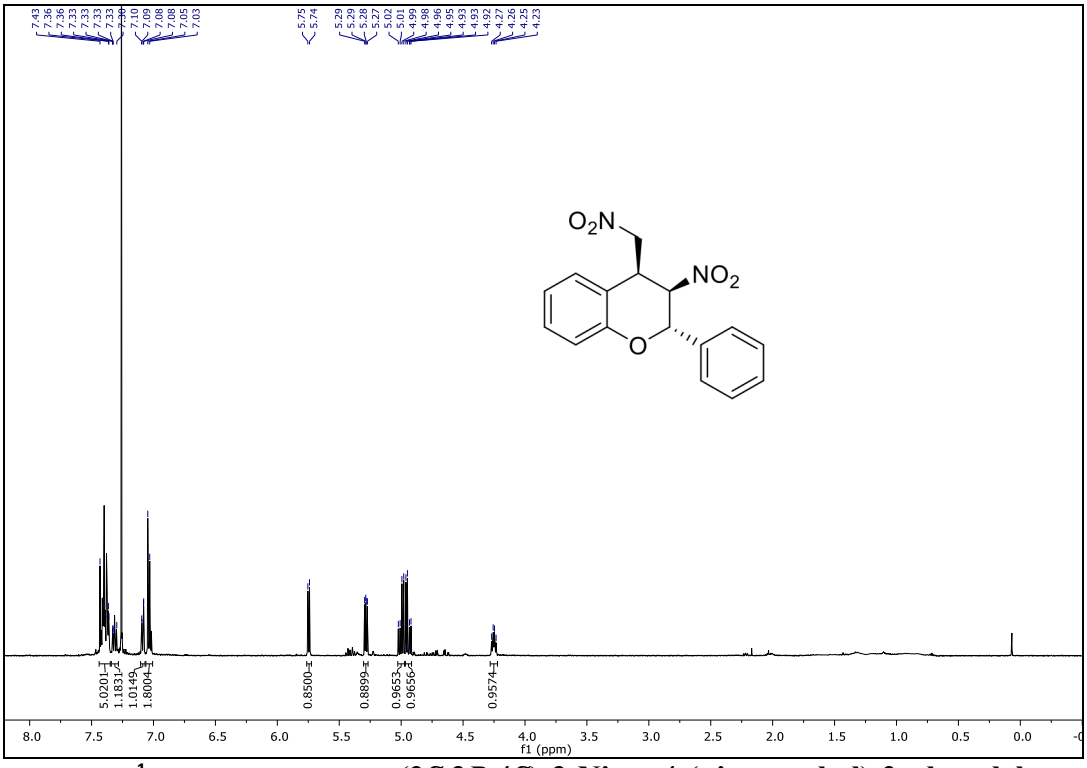


Figure S1. ^{1}HNMR spectrum of (2*S*,3*R*,4*S*)-3-Nitro-4-(nitromethyl)-2-phenylchromane (*epi*-3aa).

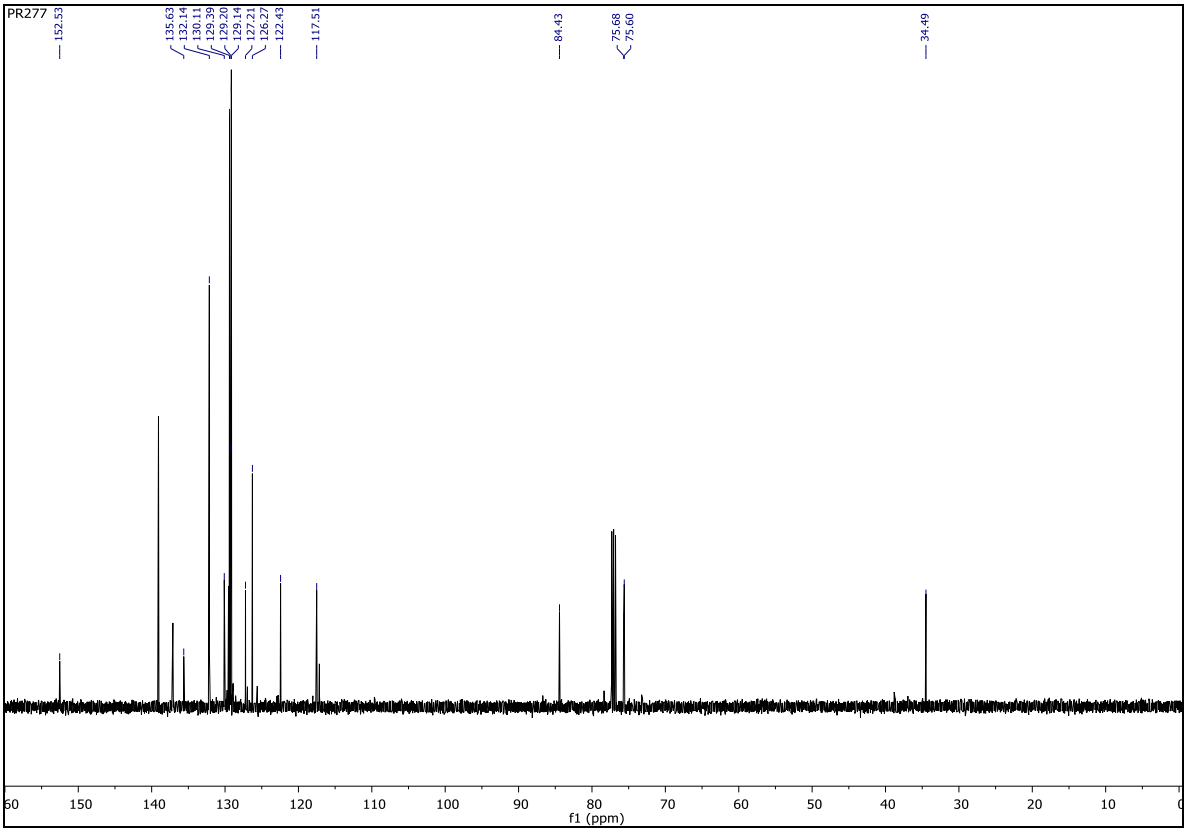


Figure S2. ^{13}CNMR spectrum of (2*S*,3*R*,4*S*)-3-Nitro-4-(nitromethyl)-2-phenylchromane (*epi*-3aa).

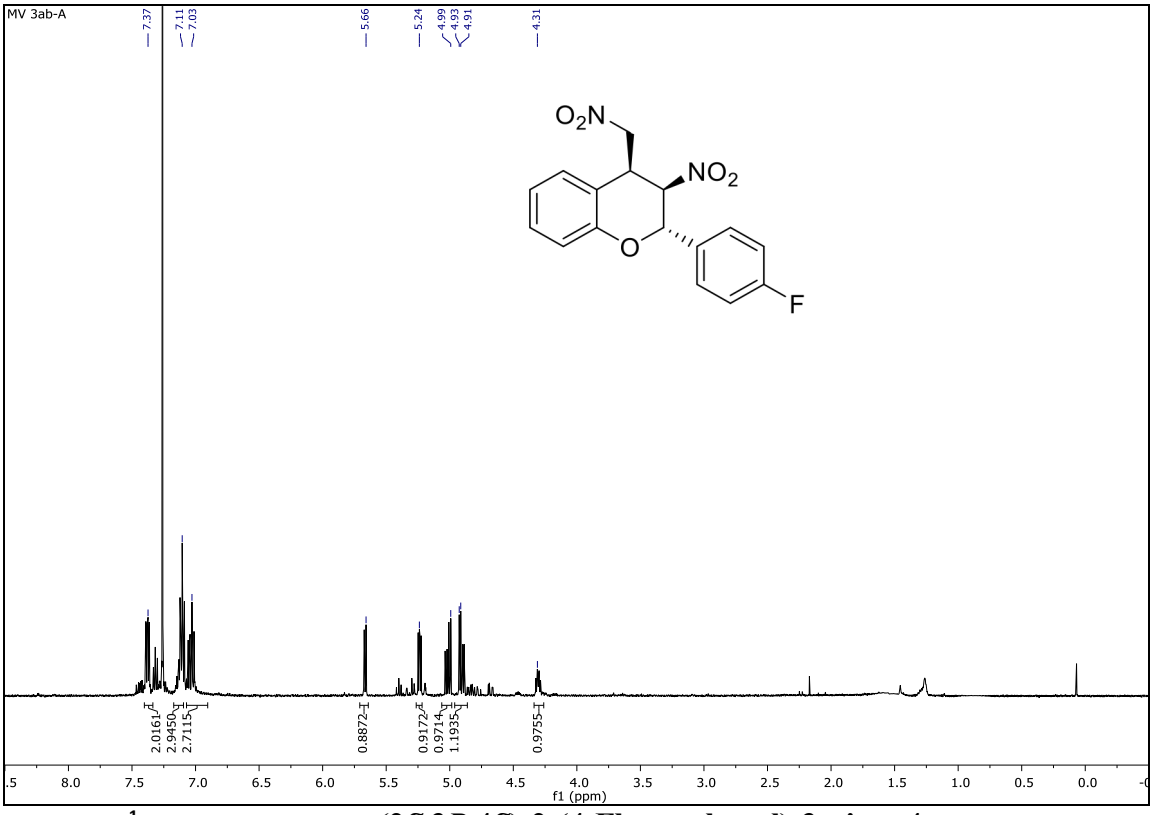


Figure S3. ^{1}**HNMR spectrum of (2*S*,3*R*,4*S*)-2-(4-Fluorophenyl)-3-nitro-4-(nitromethyl)chromane (*epi*-3ab).**

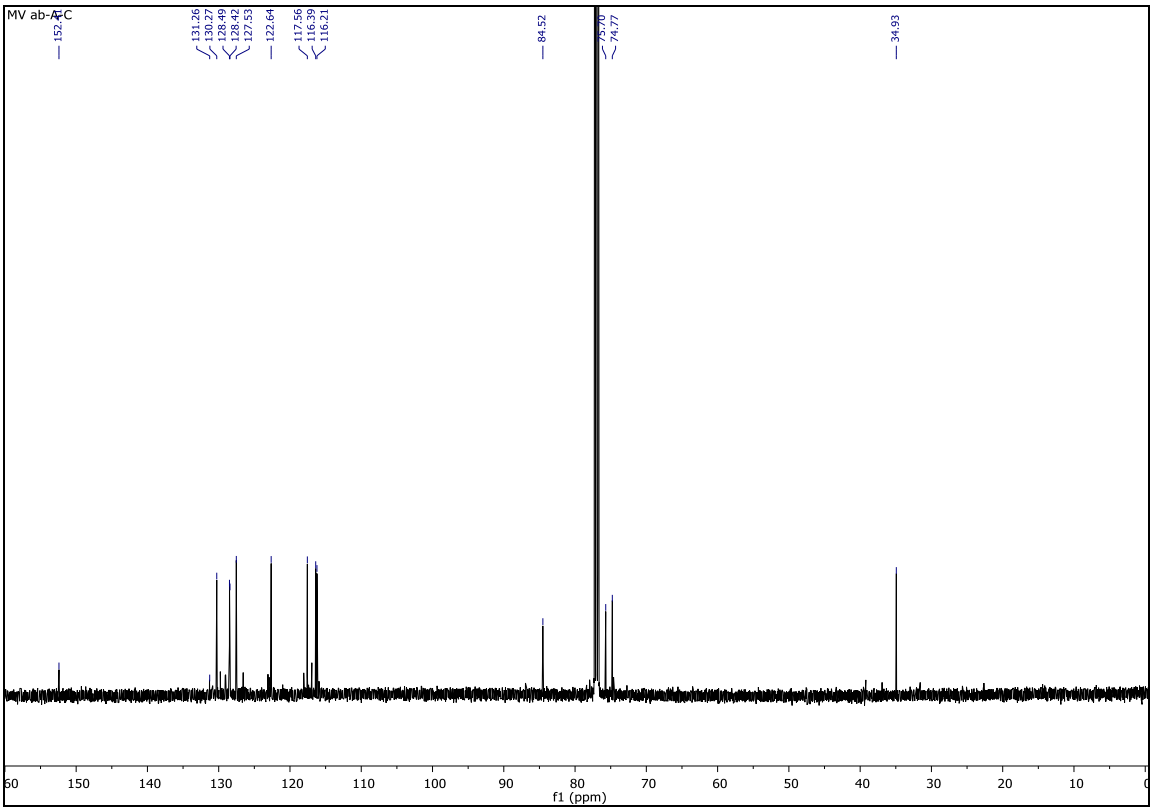


Figure S4. ^{13}**CNMR spectrum of (2*S*,3*R*,4*S*)-2-(4-Fluorophenyl)-3-nitro-4-(nitromethyl)chromane (*epi*-3ab).**

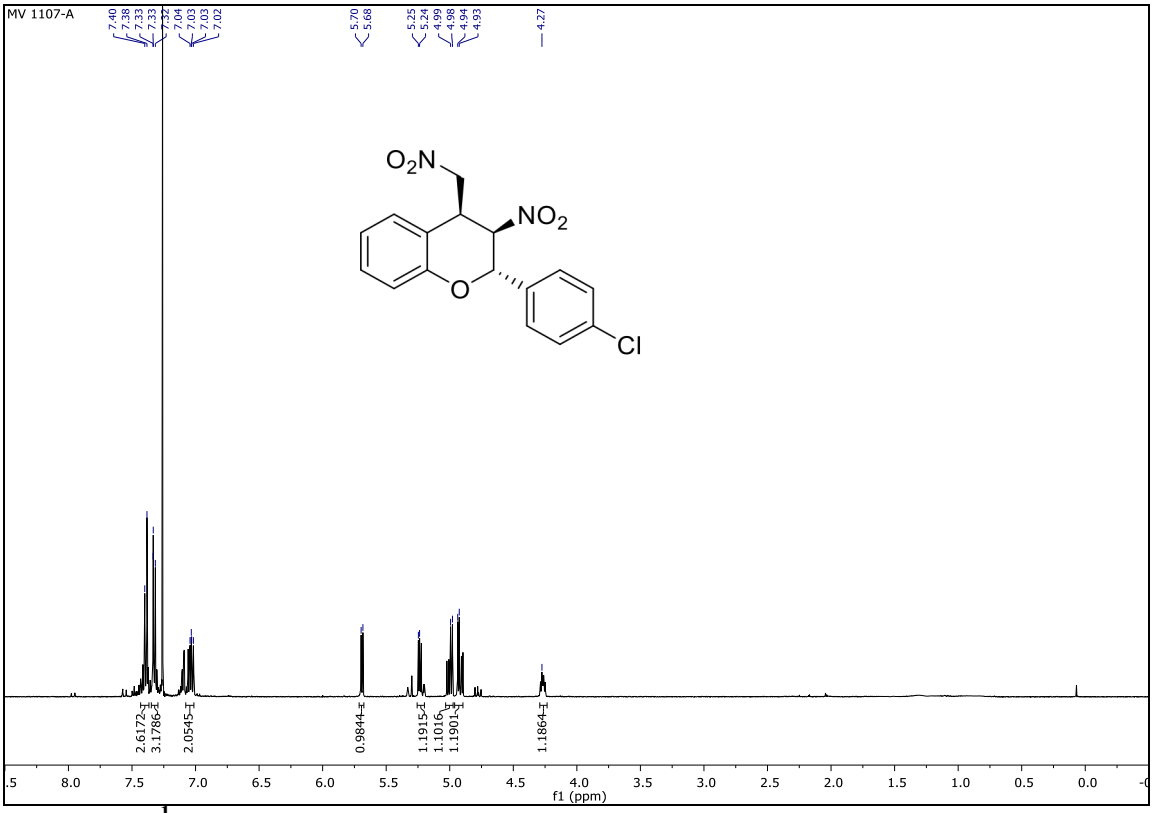


Figure S5. ^{1}NMR spectrum of (2*S*,3*R*,4*S*)-2-(4-Chlorophenyl)-3-nitro-4-(nitromethyl)chromane (*epi*-3ac).

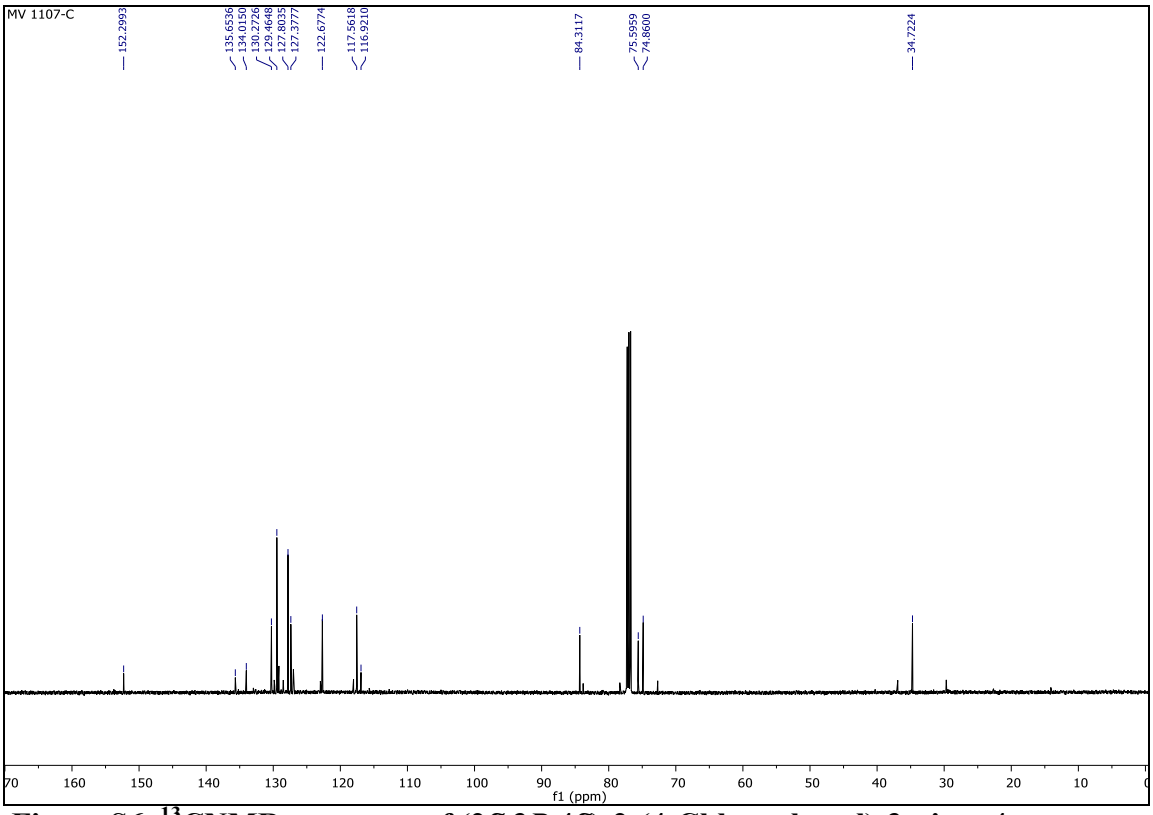


Figure S6. ^{13}CNMR spectrum of (2*S*,3*R*,4*S*)-2-(4-Chlorophenyl)-3-nitro-4-(nitromethyl)chromane (*epi*-3ac).

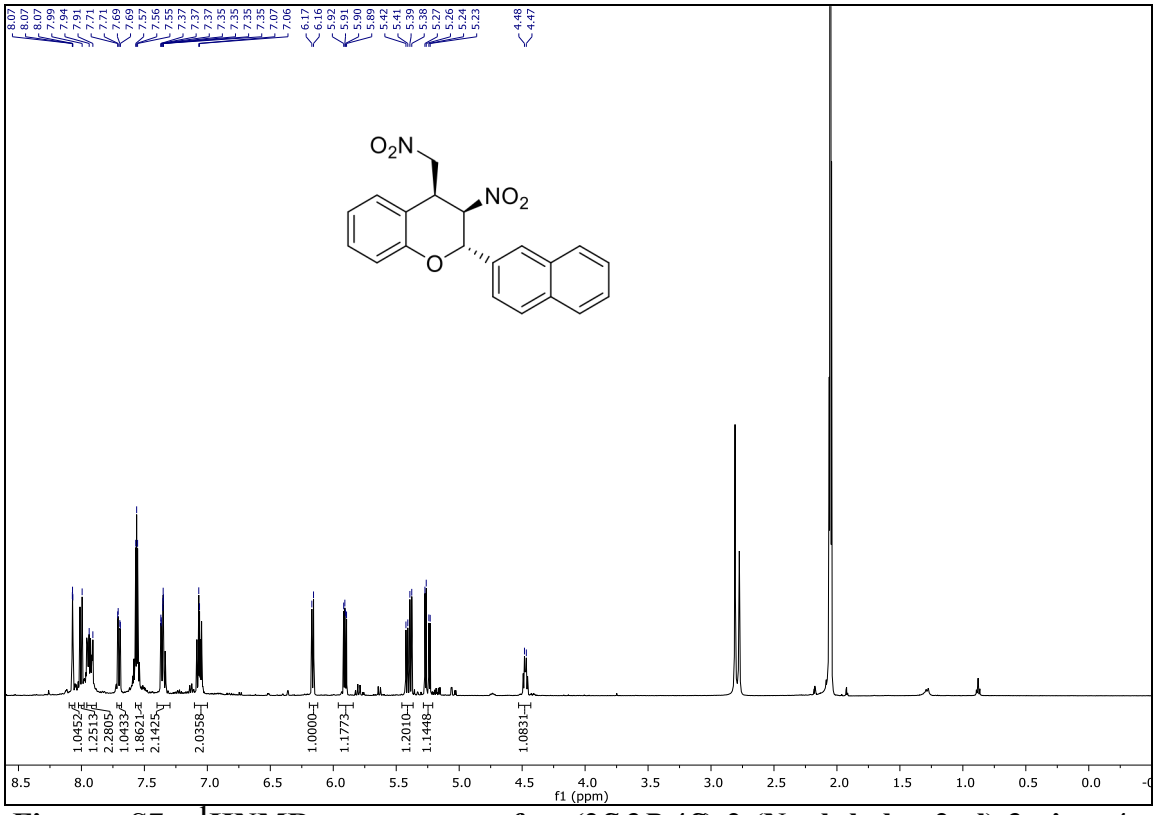


Figure S7. ^{1}HNMR specrrum of (2*S*,3*R*,4*S*)-2-(Naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (*epi*-3ae)

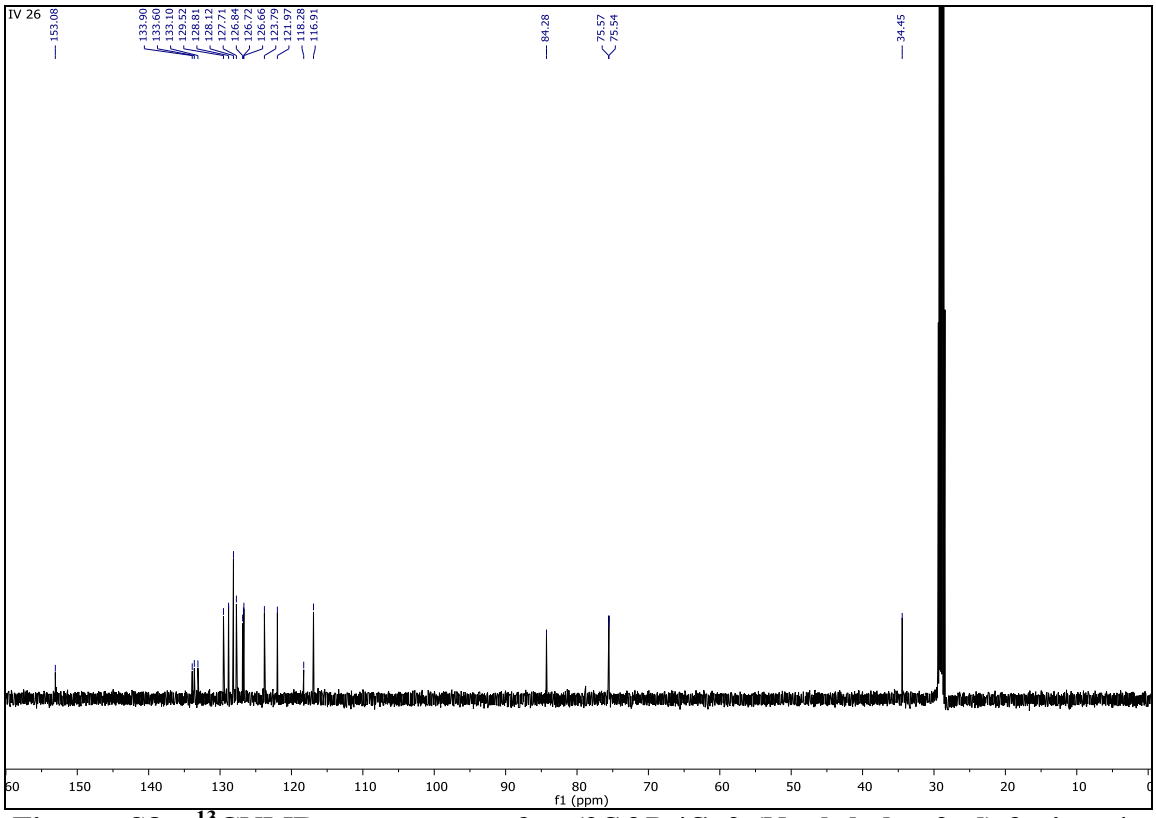


Figure S8. ^{13}CNMR specrrum of (2*S*,3*R*,4*S*)-2-(Naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (*epi*-3ae)

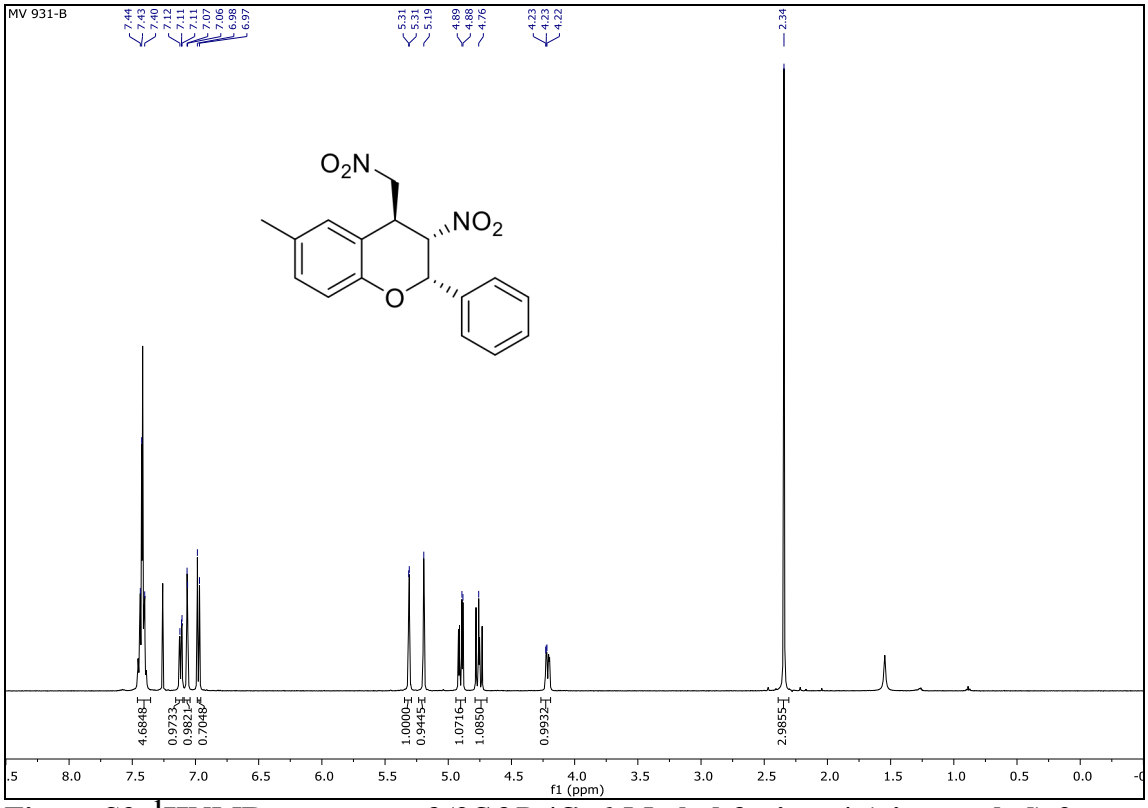


Figure S9. ^{1}HNMR spectrum of (2*S*,3*R*,4*S*)-6-Methyl-3-nitro-4-(nitromethyl)-2-phenylchromane (3ba)

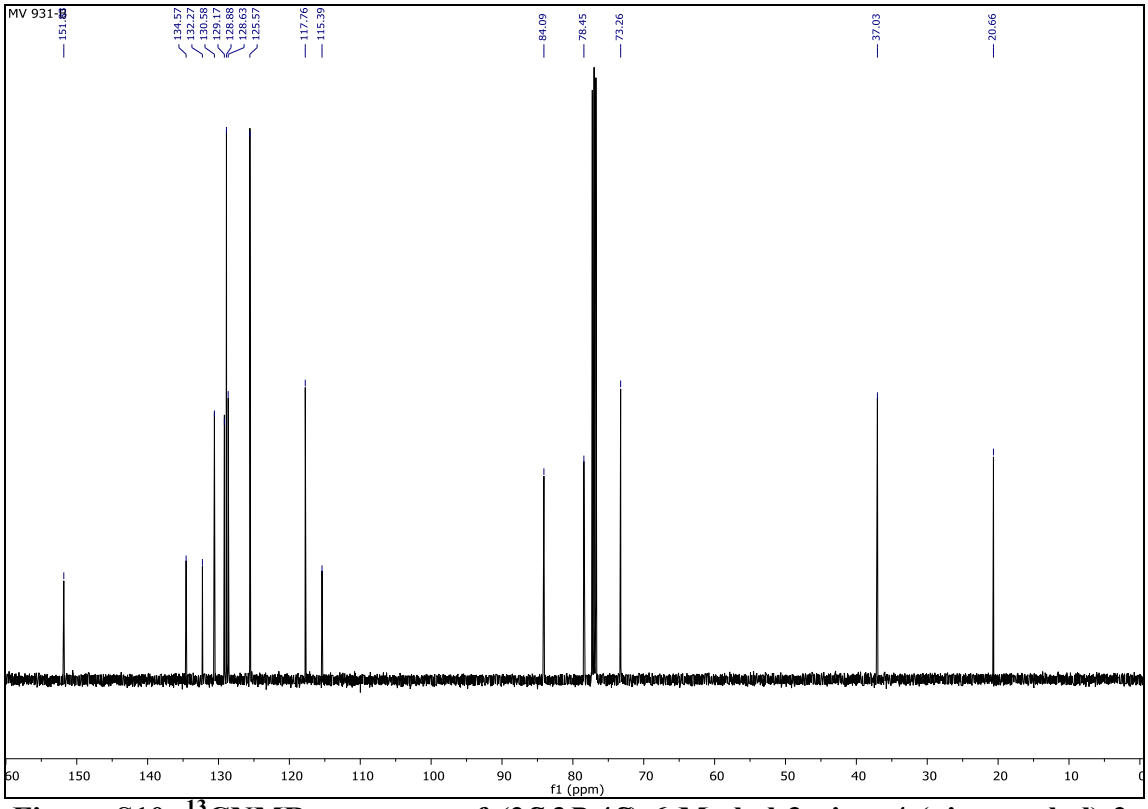


Figure S10. ^{13}CNMR spectrum of (2*S*,3*R*,4*S*)-6-Methyl-3-nitro-4-(nitromethyl)-2-phenylchromane (3ba)

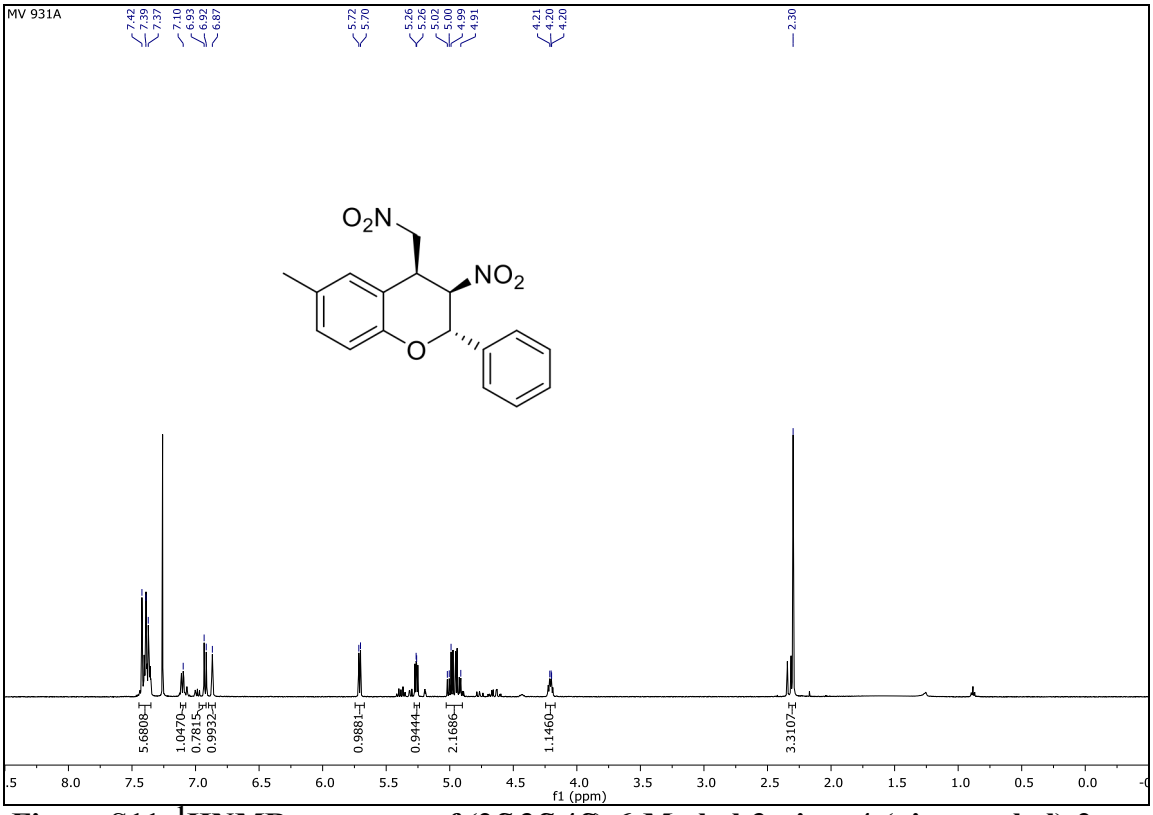


Figure S11. ^{1}HNMR spectrum of (2*S*,3*S*,4*S*)-6-Methyl-3-nitro-4-(nitromethyl)-2-phenylchromane (*epi*-3ba).

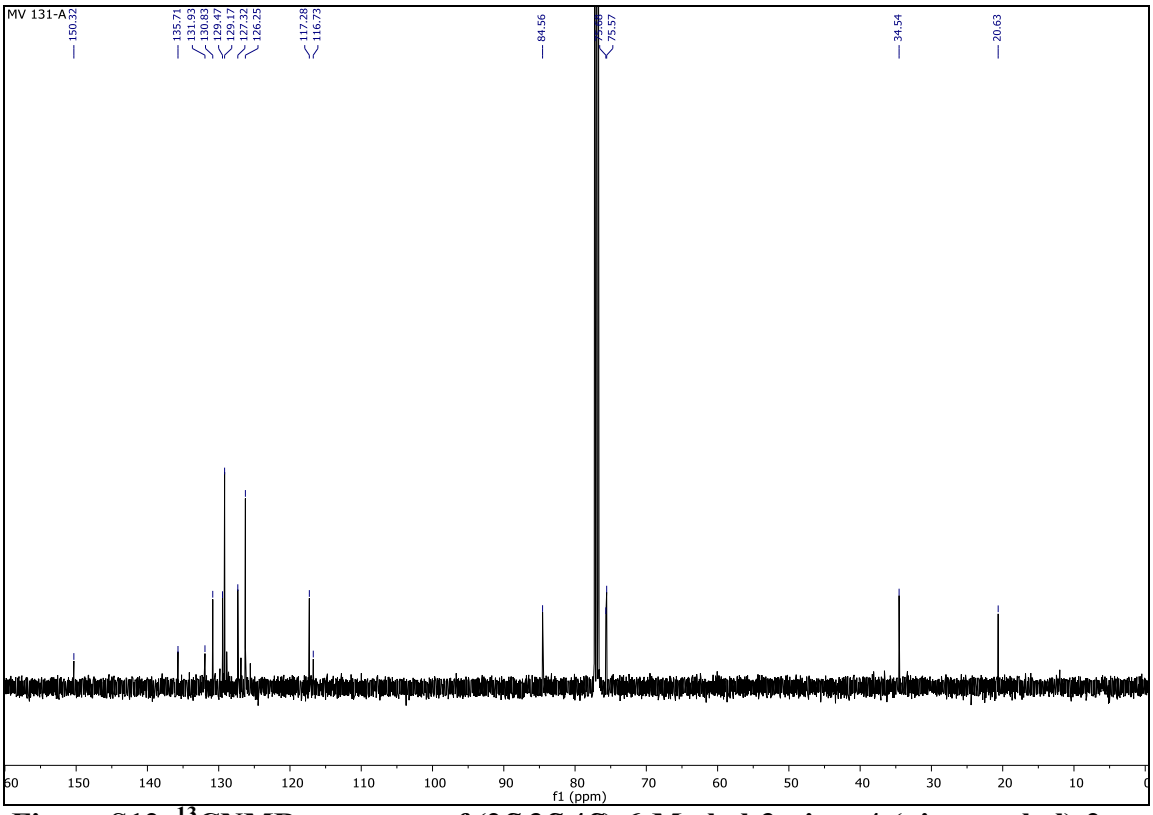


Figure S12. ^{13}CNMR spectrum of (2*S*,3*S*,4*S*)-6-Methyl-3-nitro-4-(nitromethyl)-2-phenylchromane (*epi*-3ba).

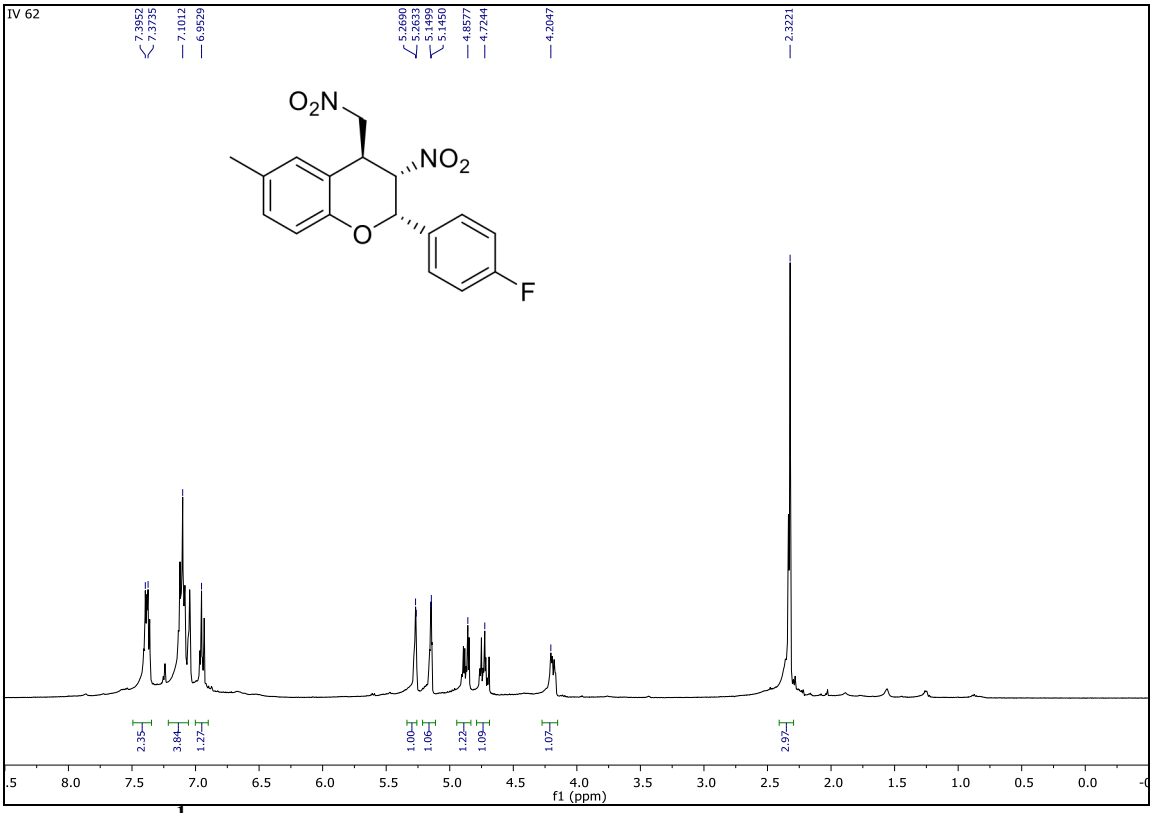


Figure S13. ^{1}HNMR spectrum of(2*S*,3*S*,4*S*)-2-(4-Fluorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (3bb).

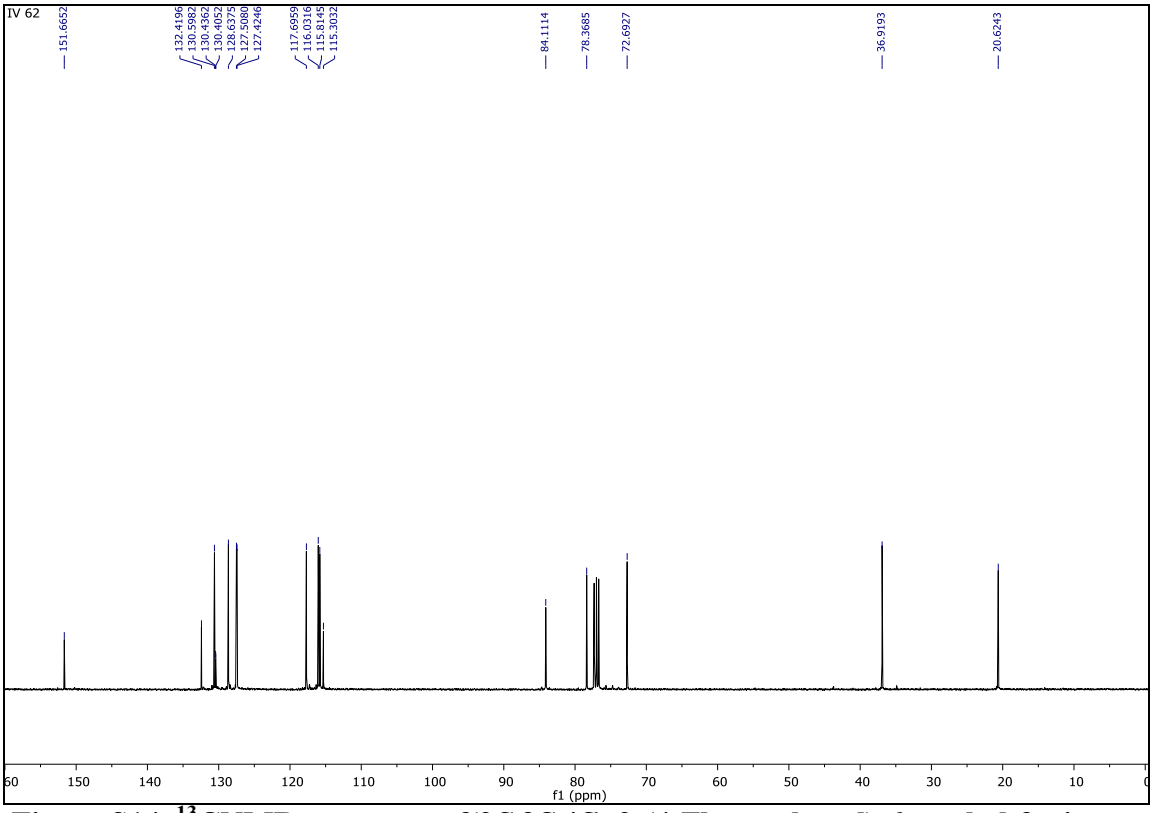


Figure S14. ^{13}CNMR spectrum of(2*S*,3*S*,4*S*)-2-(4-Fluorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (3bb).

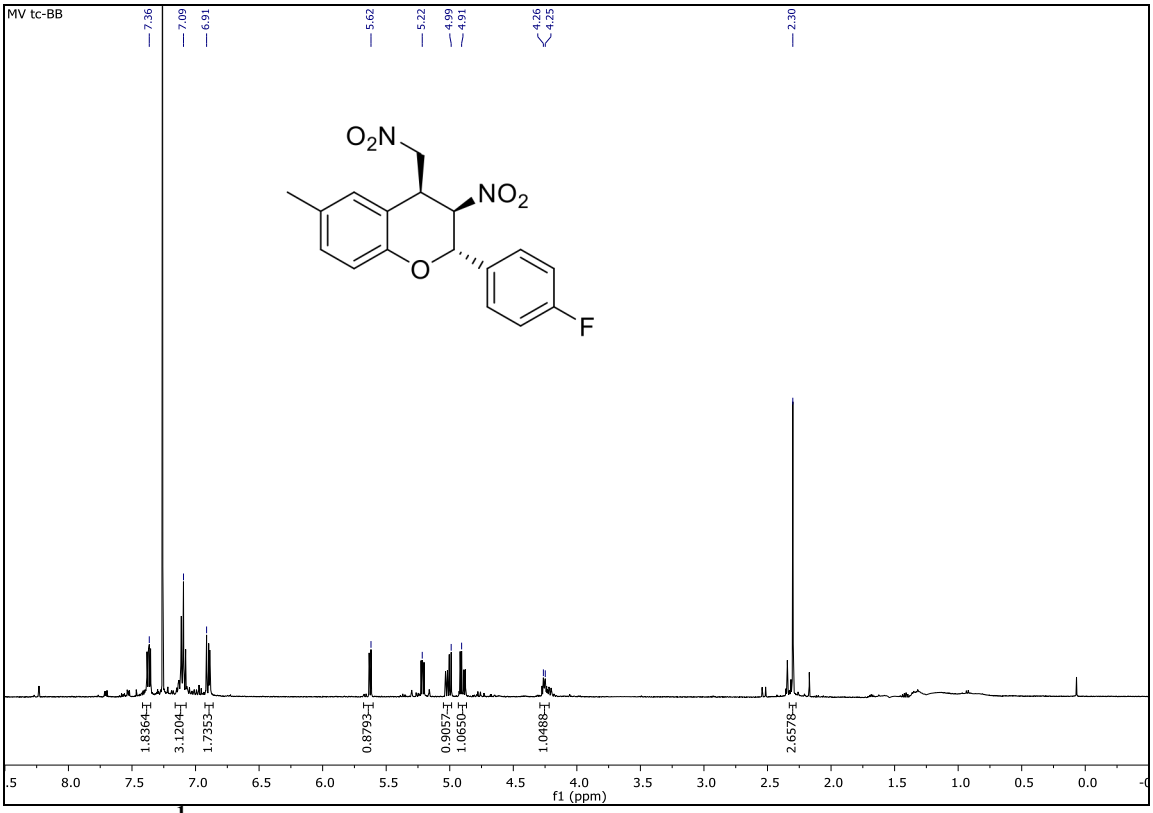


Figure S15. ^{1}HNMR spectrum of (2*S*,3*R*,4*S*)-2-(4-Fluorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (*epi*-3bb).

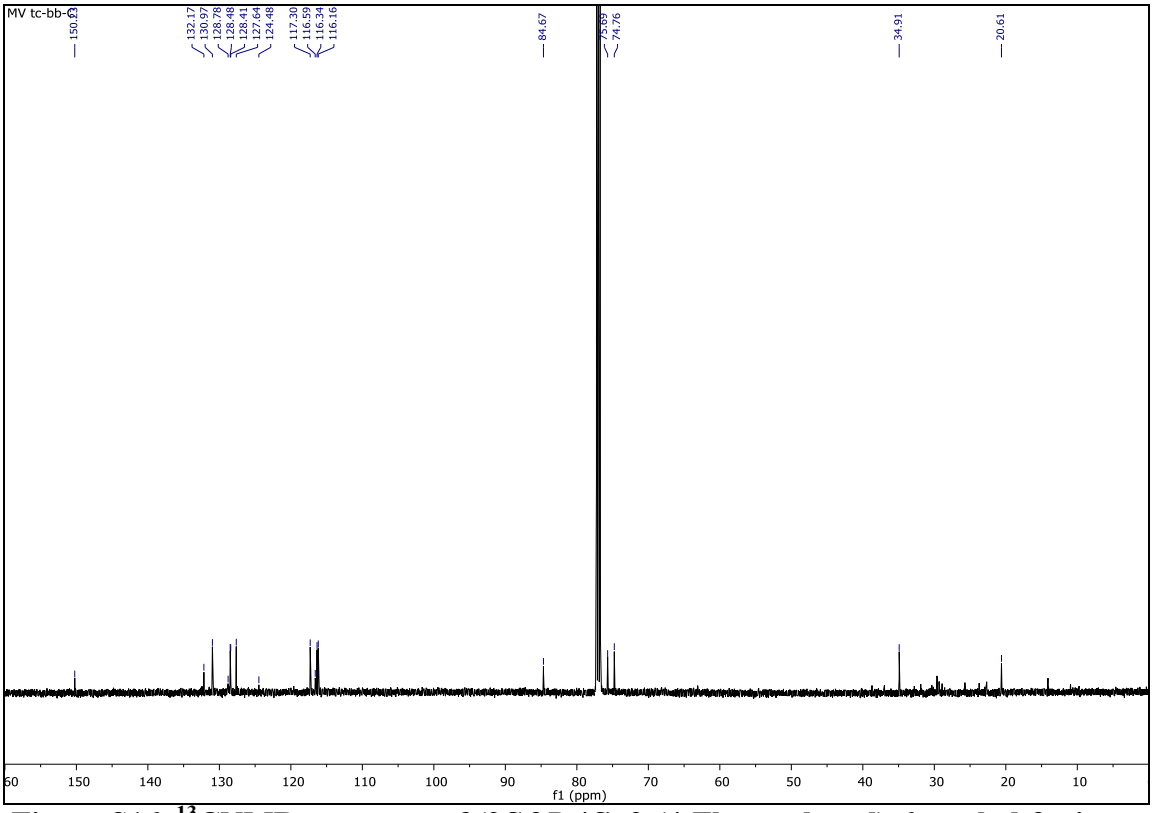


Figure S16. ^{13}CNMR spectrum of (2*S*,3*R*,4*S*)-2-(4-Fluorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (*epi*-3bb).

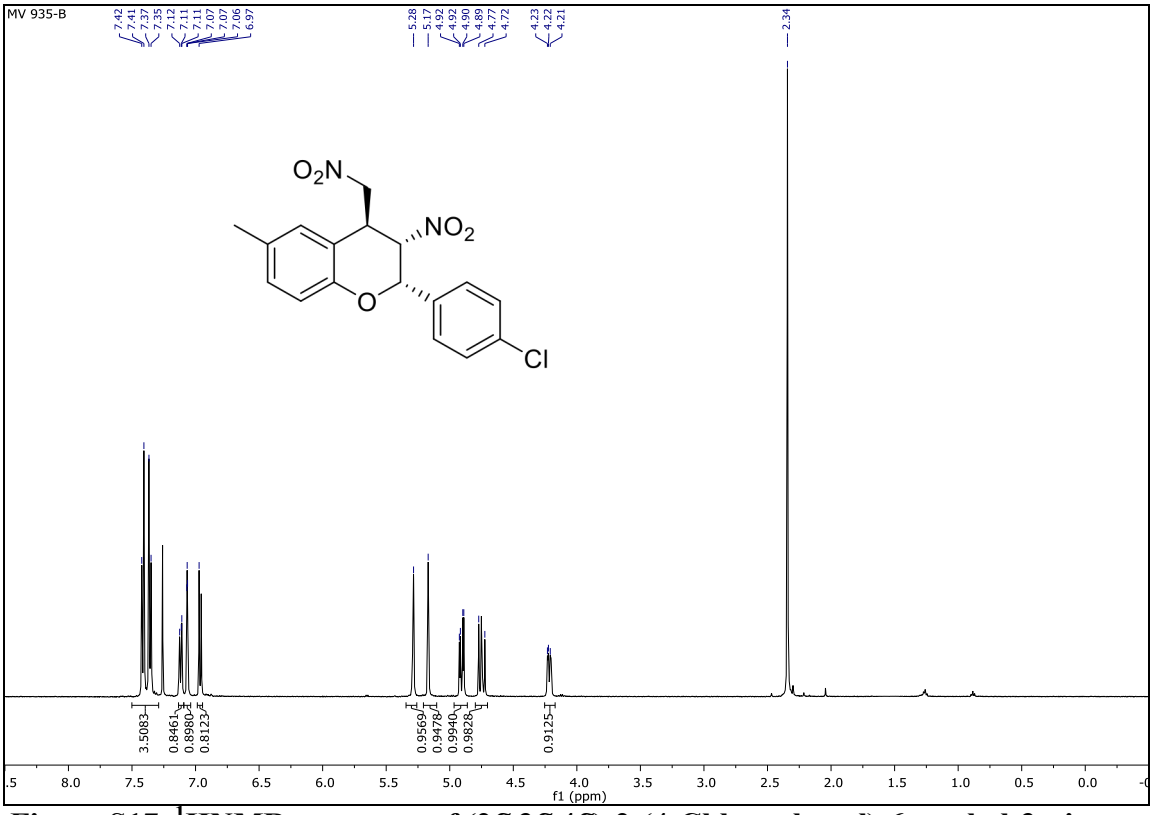


Figure S17. ^{1}HNMR spectrum of (2*S*,3*S*,4*S*)-2-(4-Chlorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (3bc).

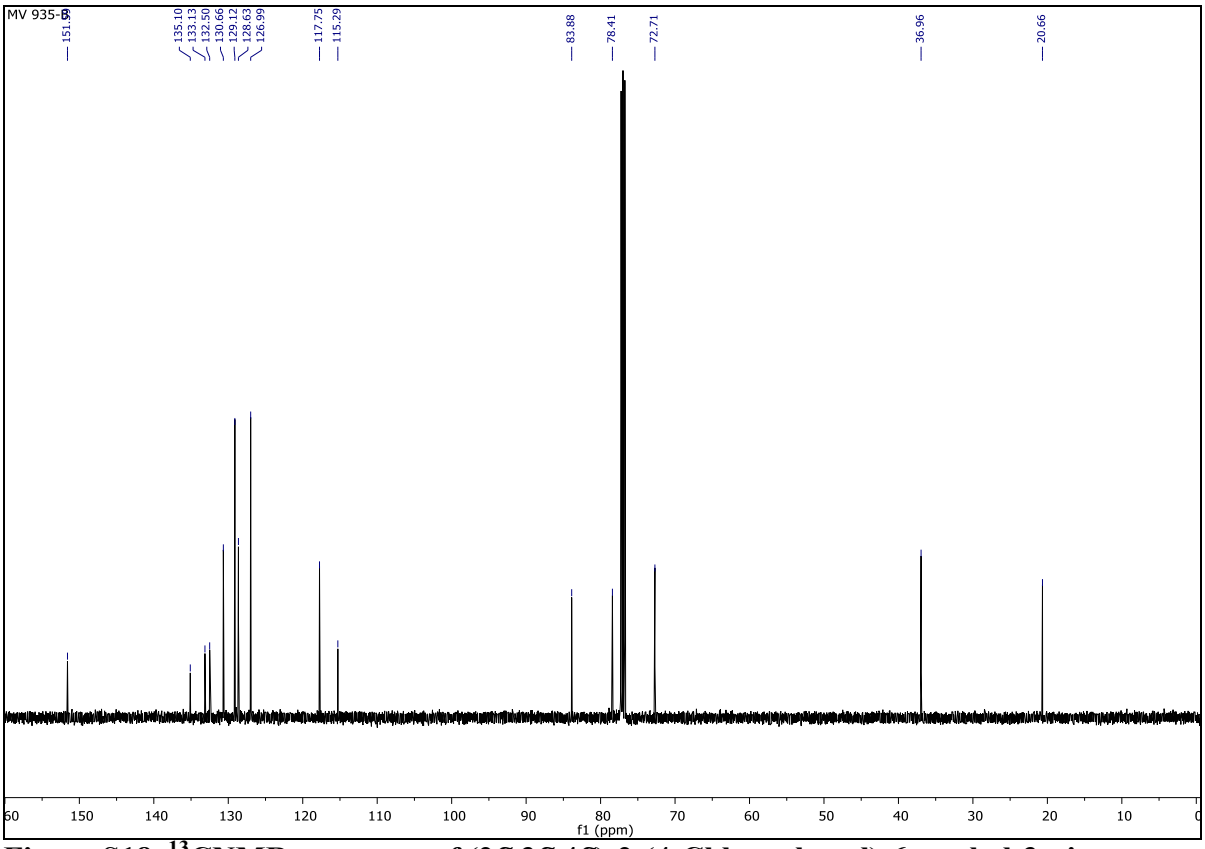


Figure S18. ^{13}CNMR spectrum of (2*S*,3*S*,4*S*)-2-(4-Chlorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (3bc).

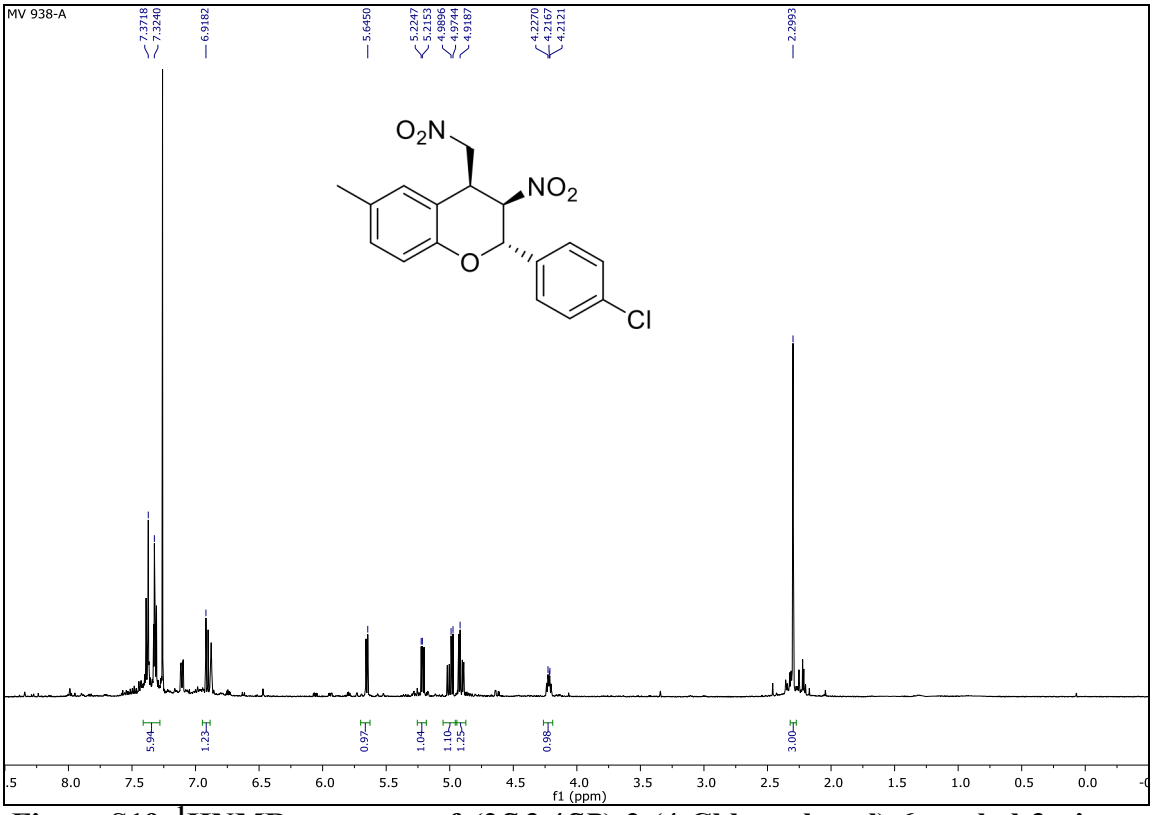


Figure S19. ^{1}HNMR spectrum of (2*S*,3,4*SR*)-2-(4-Chlorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (*epi*-3bc).

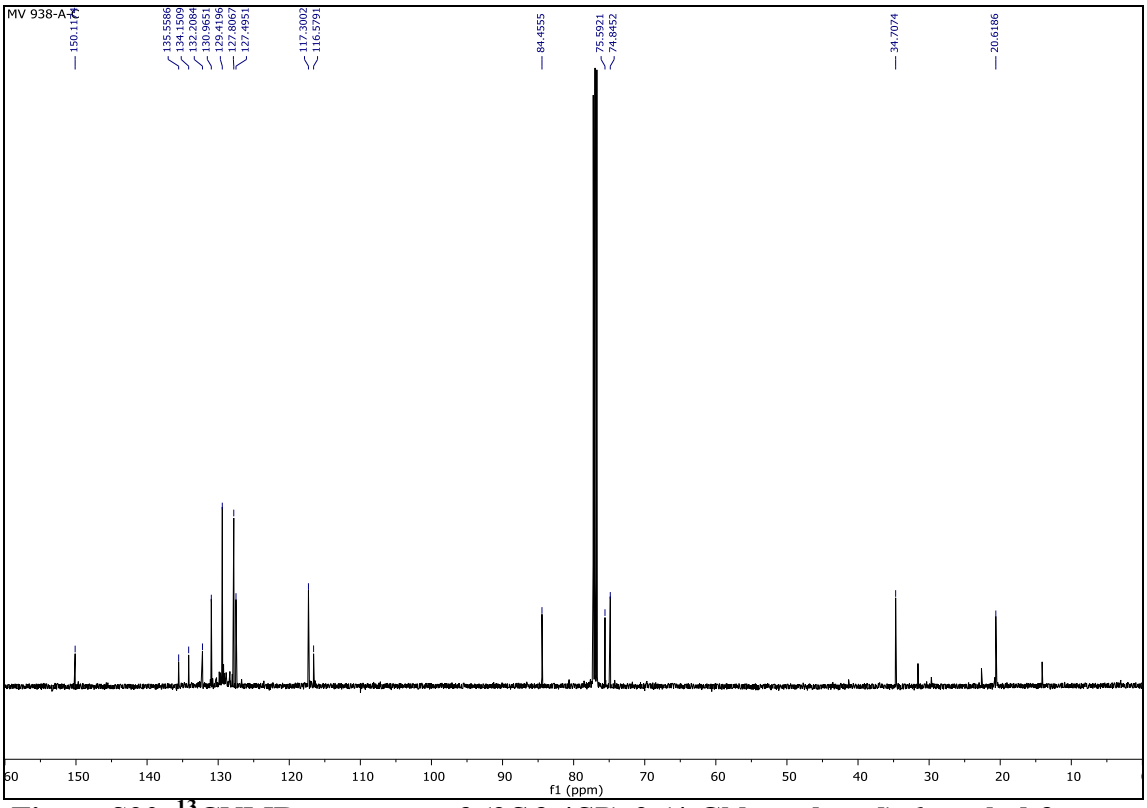


Figure S20. ^{13}CNMR spectrum of (2*S*,3,4*SR*)-2-(4-Chlorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (*epi*-3bc).

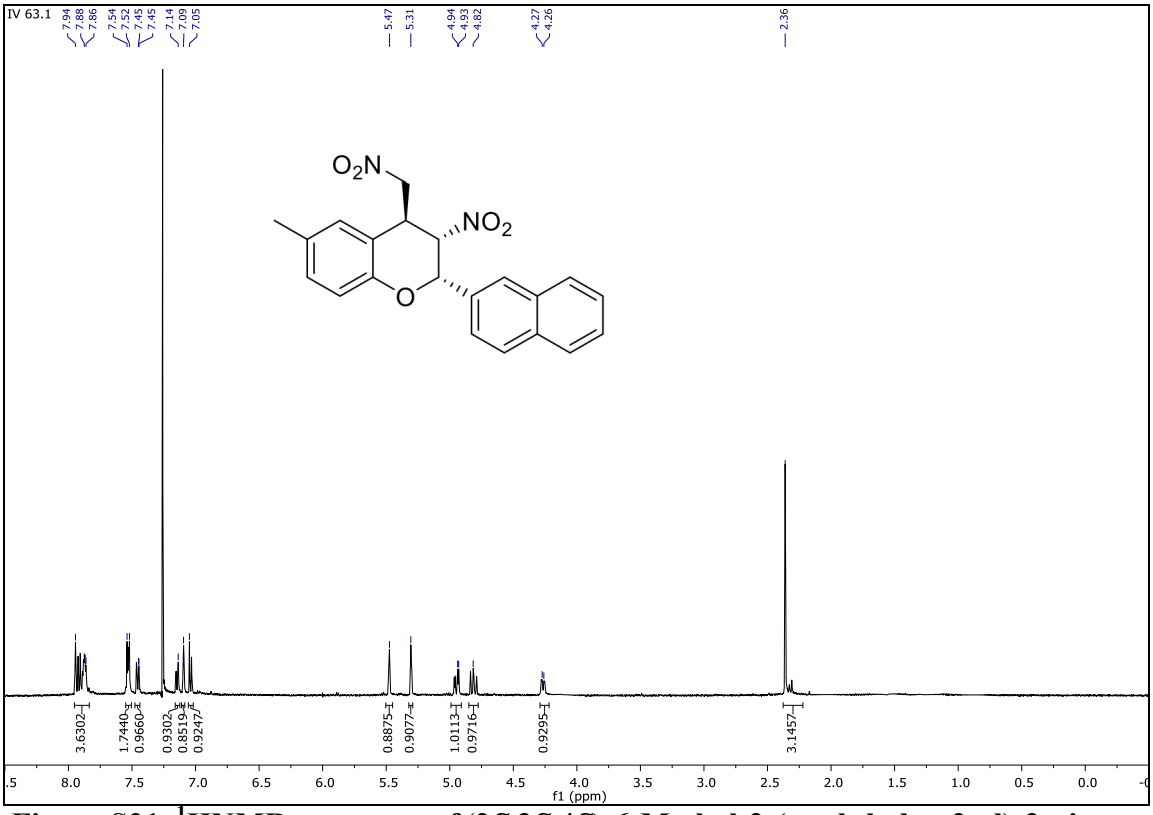


Figure S21. ^{1}HNMR spectrum of (2*S*,3*S*,4*S*)-6-Methyl-2-(naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (3be).

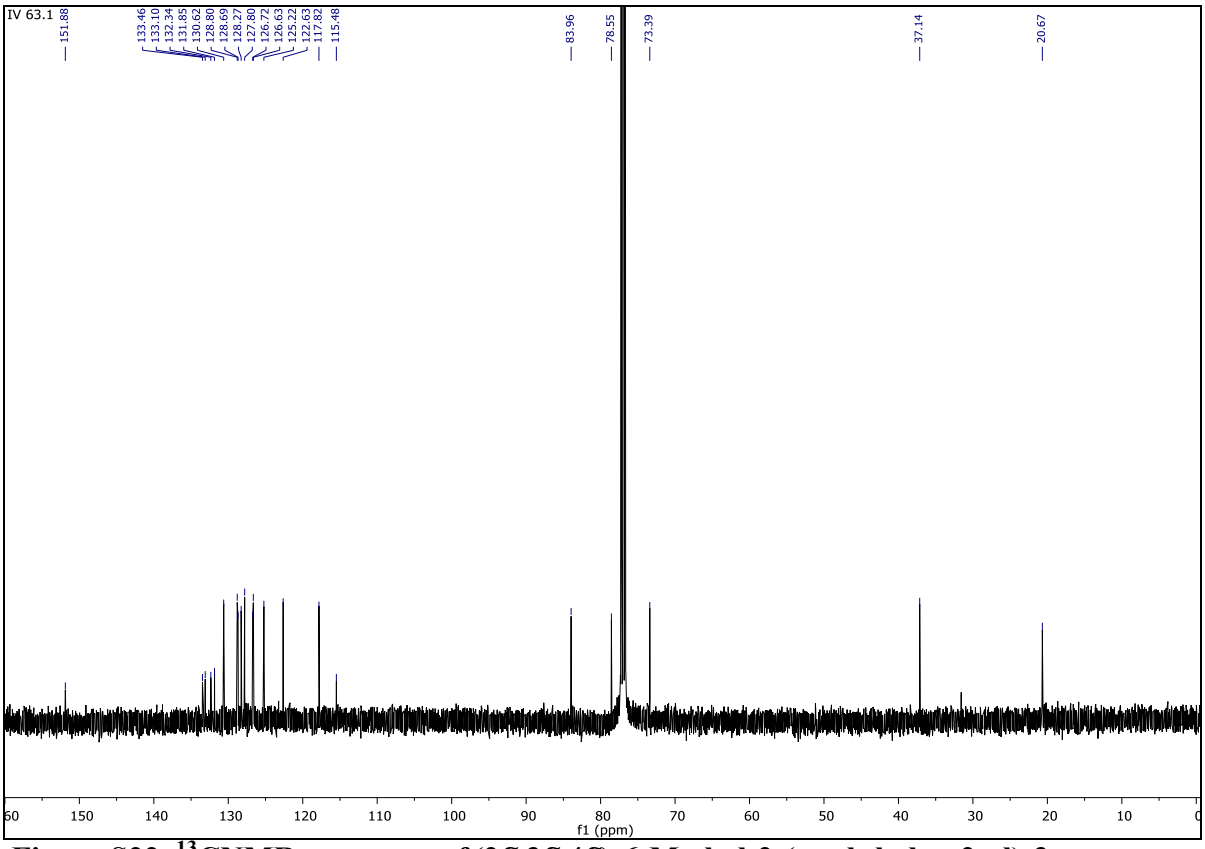


Figure S22. ^{13}CNMR spectrum of (2*S*,3*S*,4*S*)-6-Methyl-2-(naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (3be).

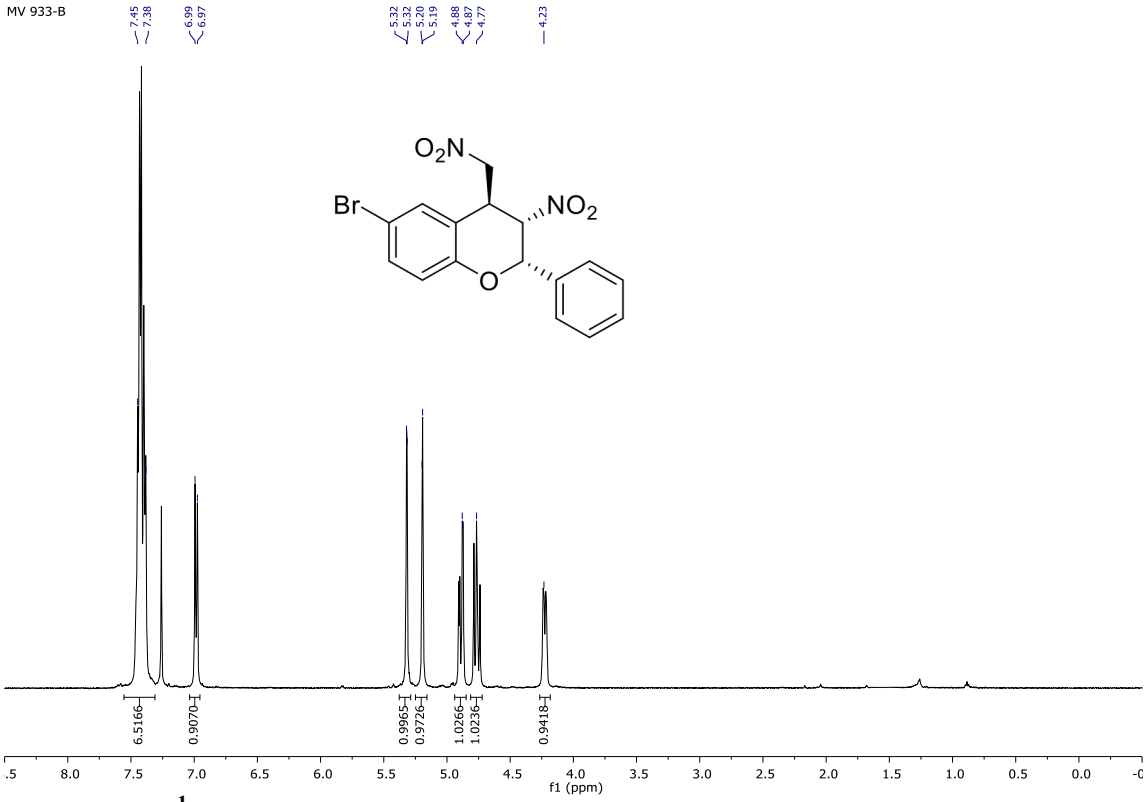


Figure S23. ^{1}HNMR spectrum of (2*S*,3*S*,4*S*)-6-Bromo-3-nitro-4-(nitromethyl)-2-phenylchromane (3ca).

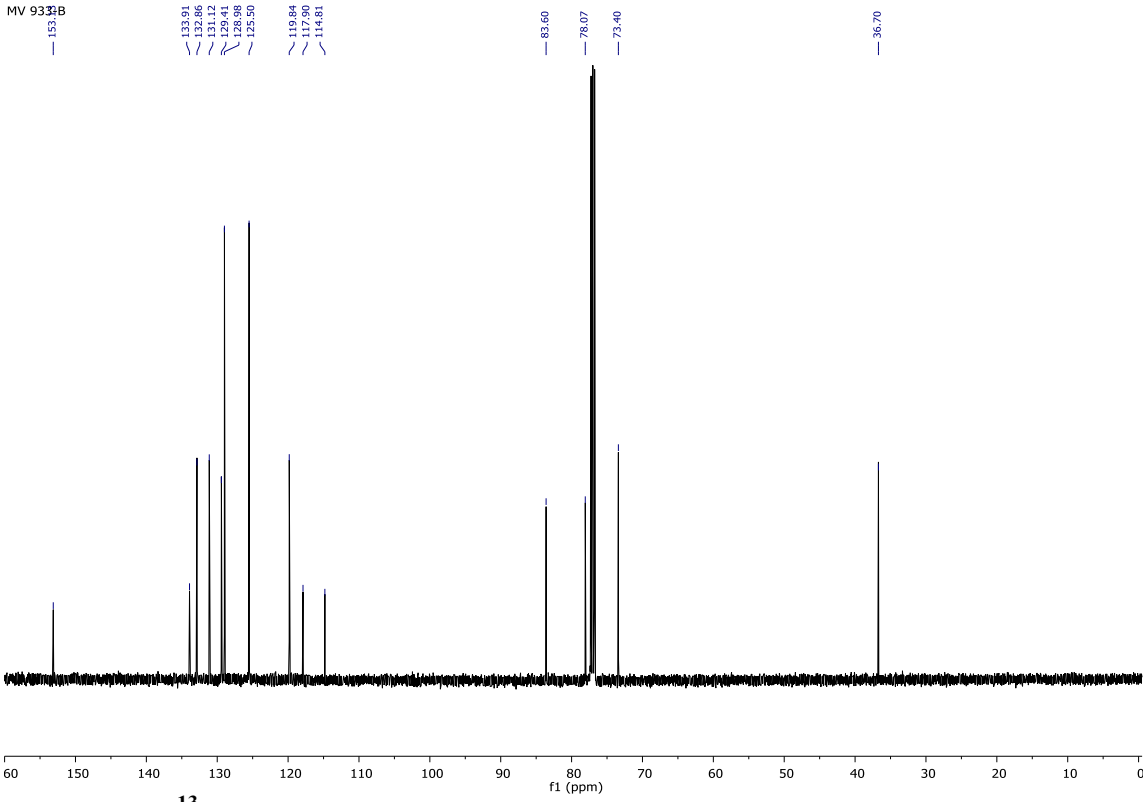


Figure S24. ^{13}CNMR spectrum of (2*S*,3*S*,4*S*)-6-Bromo-3-nitro-4-(nitromethyl)-2-phenylchromane (3ca).

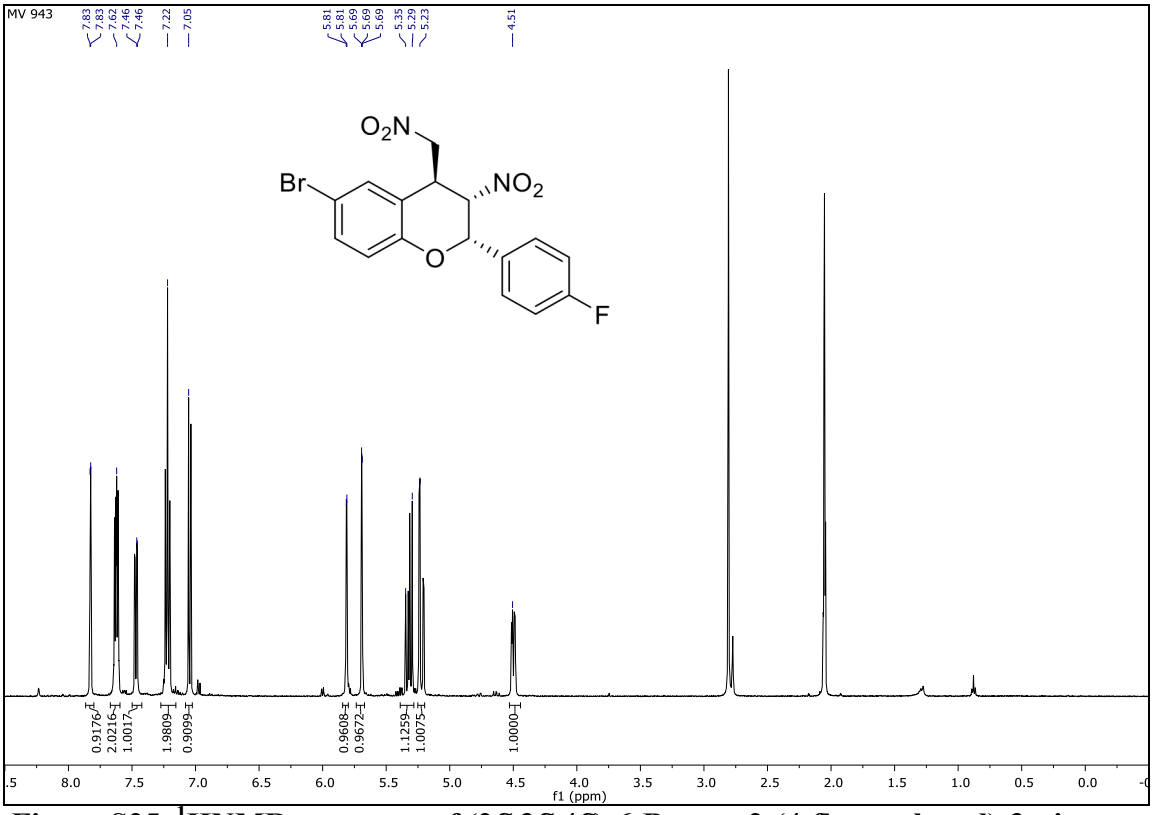


Figure S25. ^{1}HNMR spectrum of (2*S*,3*S*,4*S*)-6-Bromo-2-(4-fluorophenyl)-3-nitro-4-(nitromethyl)chromane (3cb).

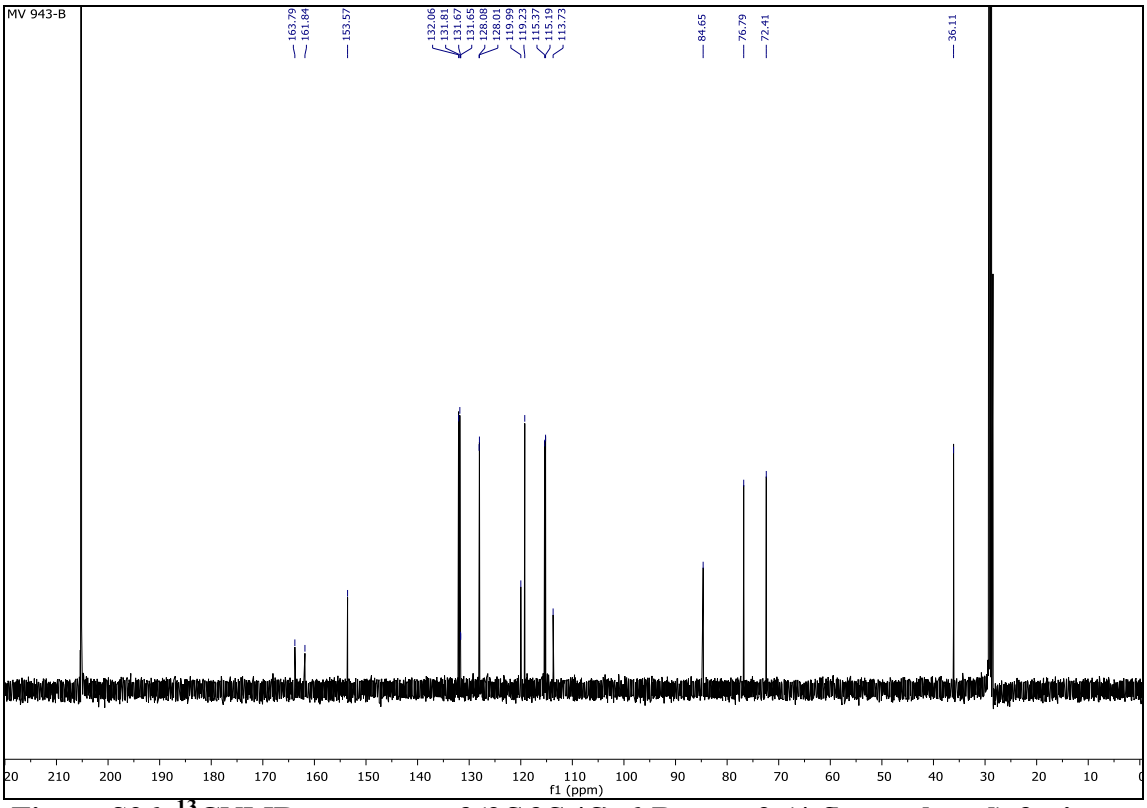


Figure S26. ^{13}CNMR spectrum of (2*S*,3*S*,4*S*)-6-Bromo-2-(4-fluorophenyl)-3-nitro-4-(nitromethyl)chromane (3cb).

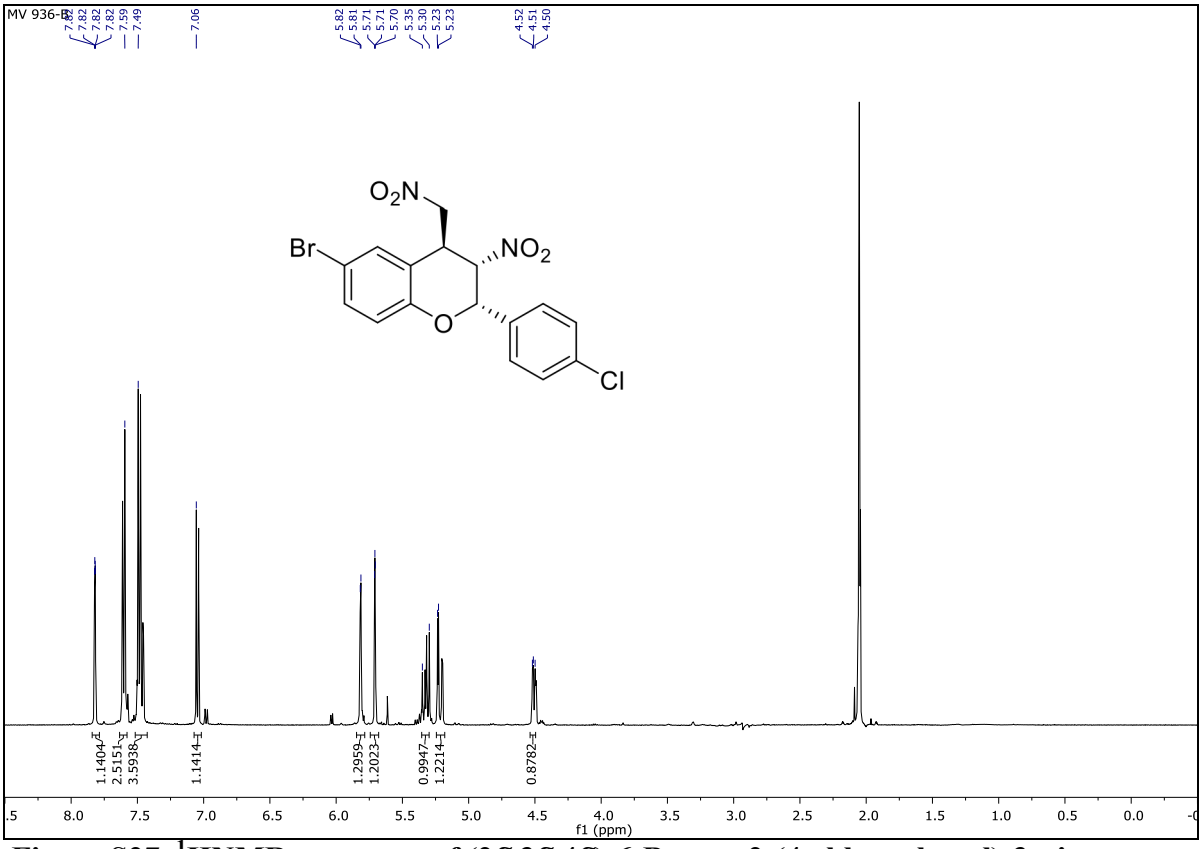


Figure S27. ^{1}HNMR spectrum of (2*S*,3*S*,4*S*)-6-Bromo-2-(4-chlorophenyl)-3-nitro-4-(nitromethyl)chromane (3cc).

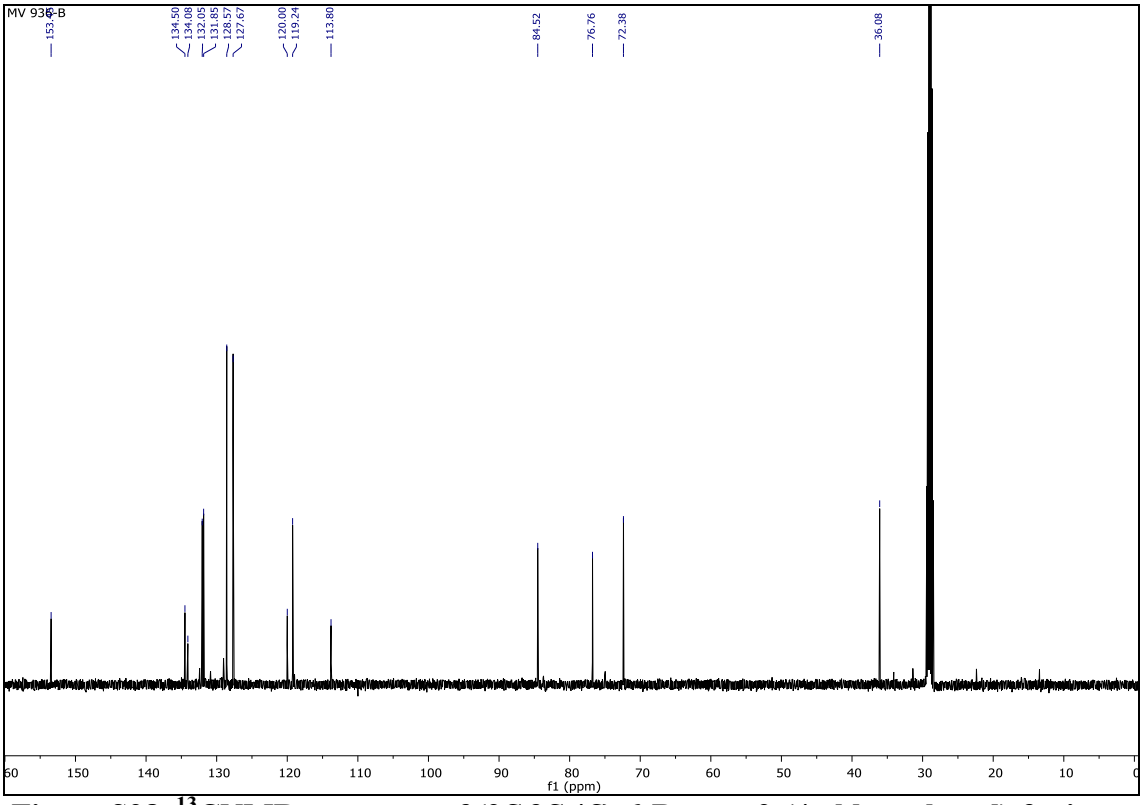


Figure S28. ^{13}CNMR spectrum of (2*S*,3*S*,4*S*)-6-Bromo-2-(4-chlorophenyl)-3-nitro-4-(nitromethyl)chromane (3cc).

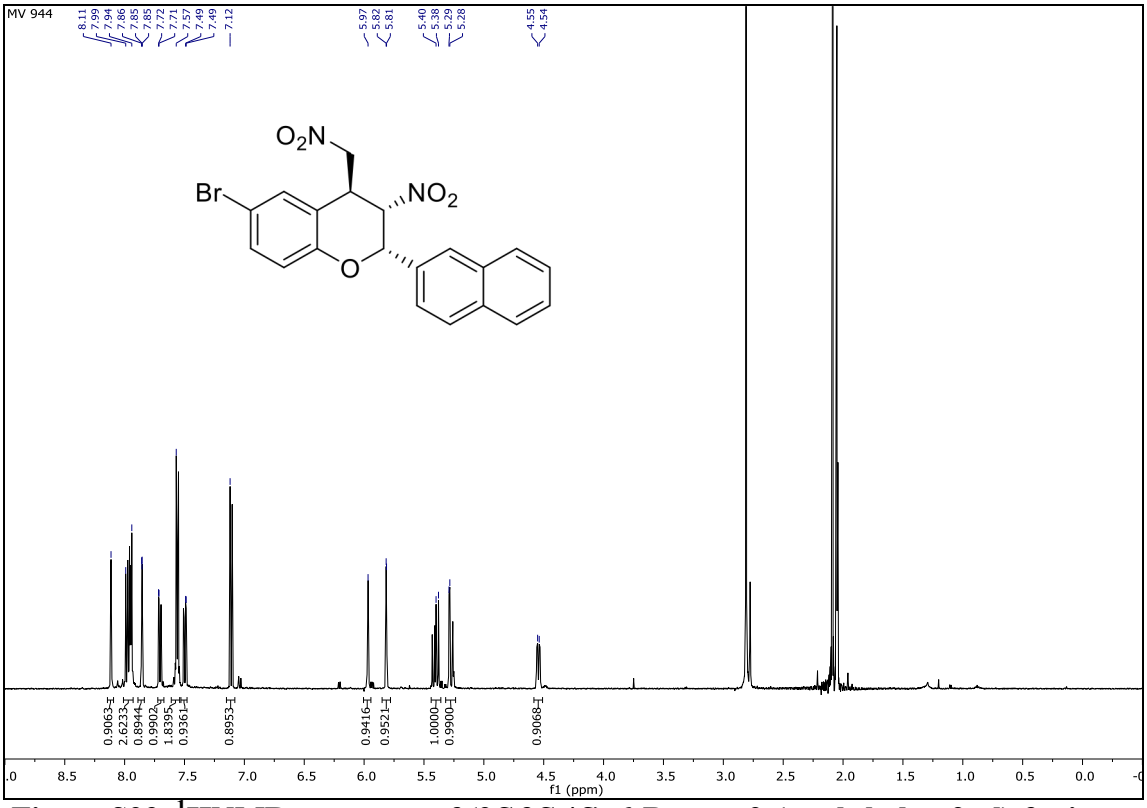


Figure S29. ^{1}HNMR spectrum of (2*S*,3*S*,4*S*)-6-Bromo-2-(naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (3ce).

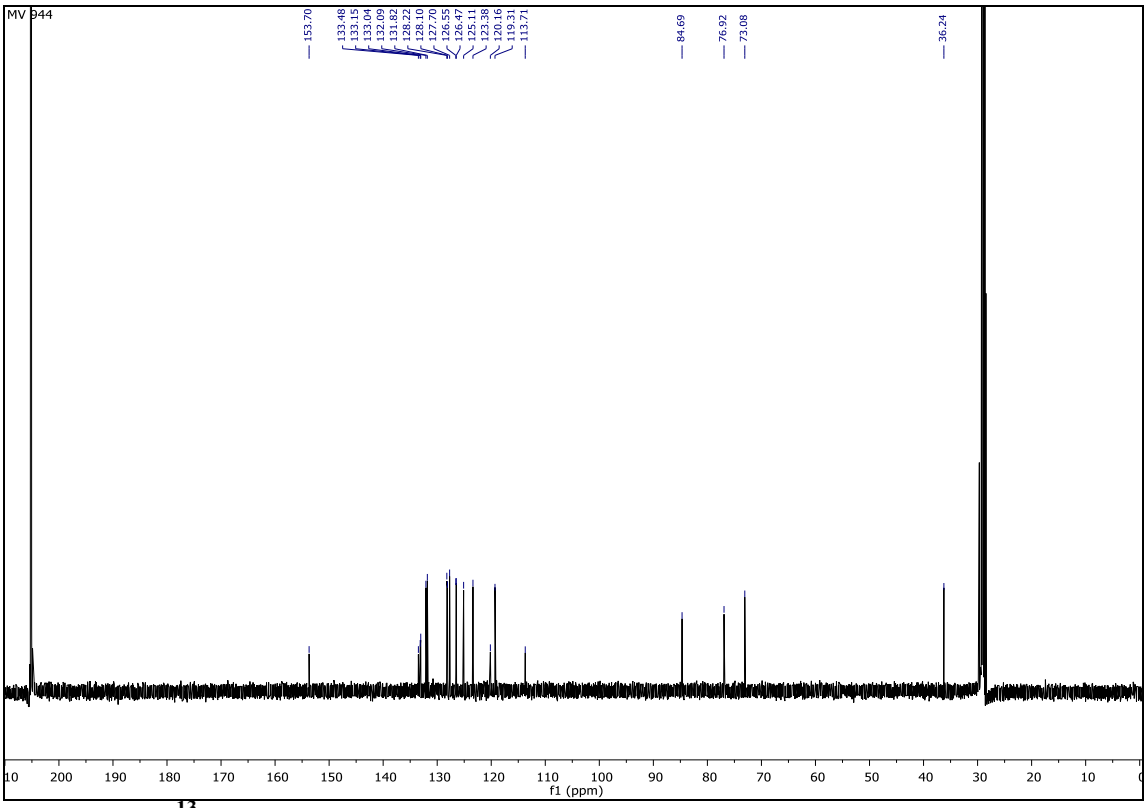


Figure S30. ^{13}CNMR spectrum of (2*S*,3*S*,4*S*)-6-Bromo-2-(naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (3ce).

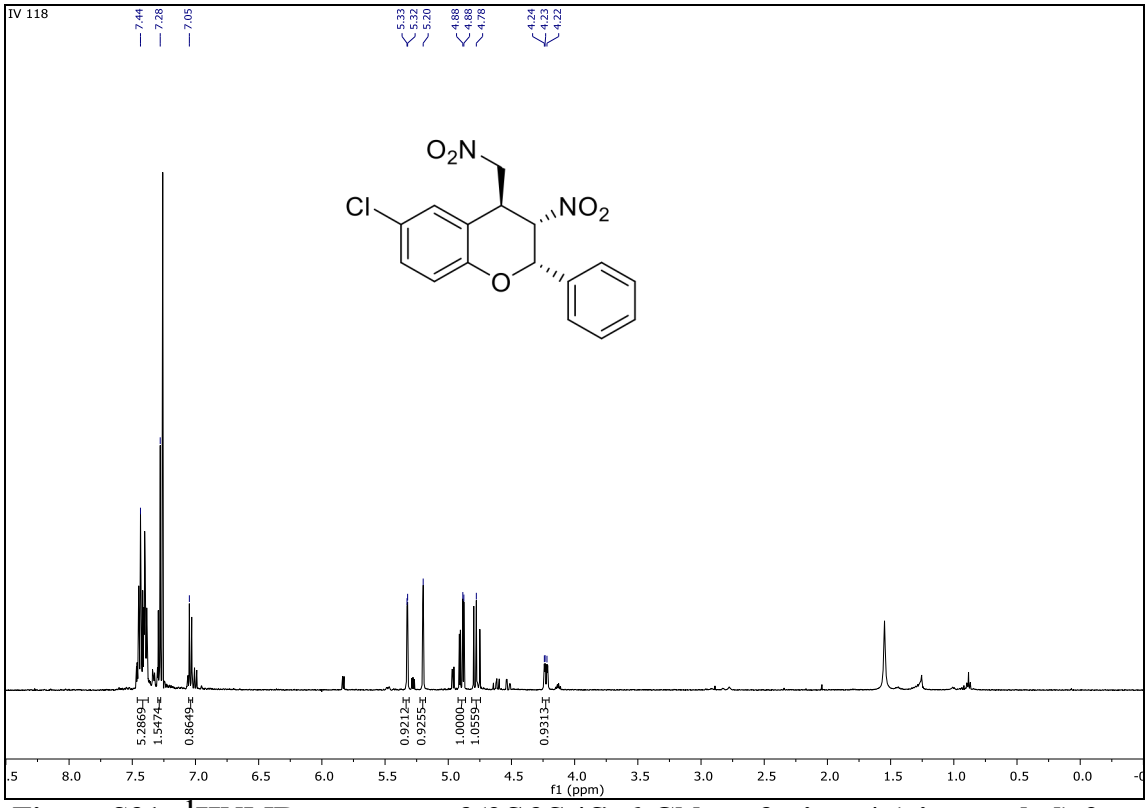


Figure S31. ^{1}**HNMR spectrum of (2*S*,3*S*,4*S*)-6-Chloro-3-nitro-4-(nitromethyl)-2-phenylchromane (3da).**

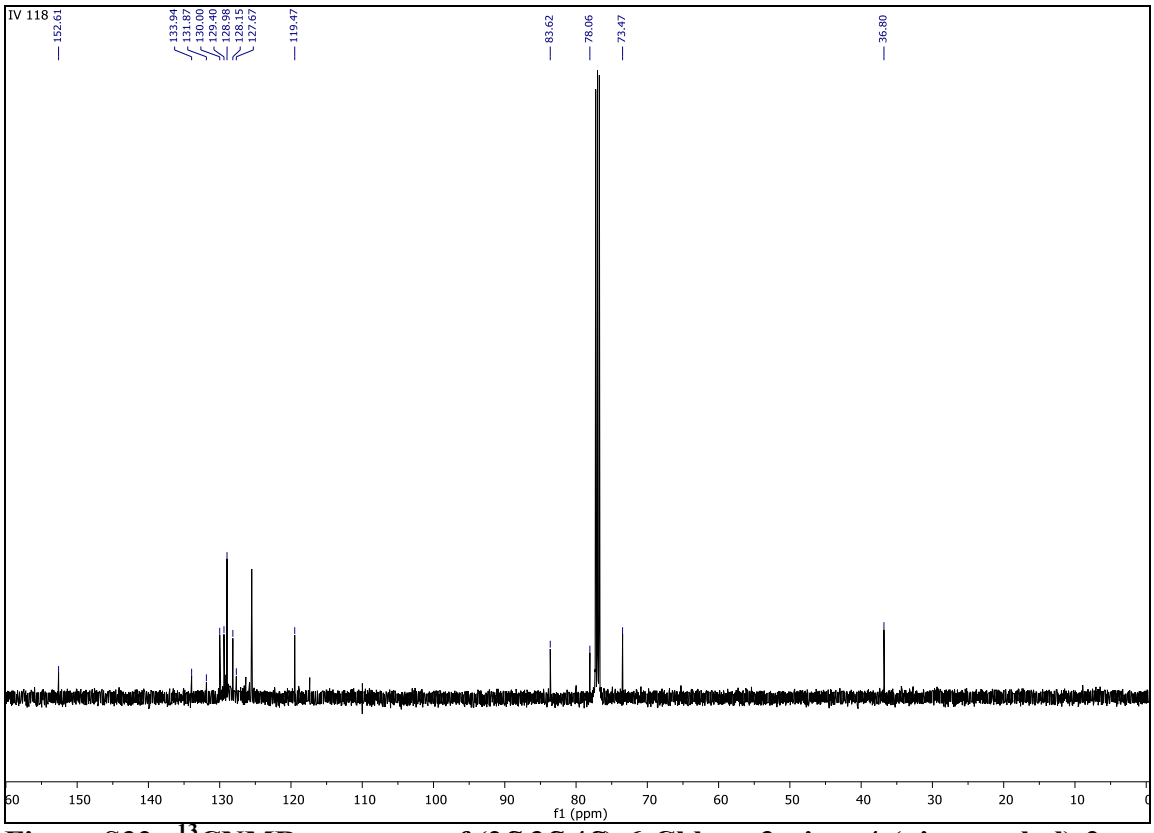


Figure S32. ^{13}**CNMR spectrum of (2*S*,3*S*,4*S*)-6-Chloro-3-nitro-4-(nitromethyl)-2-phenylchromane (3da).**

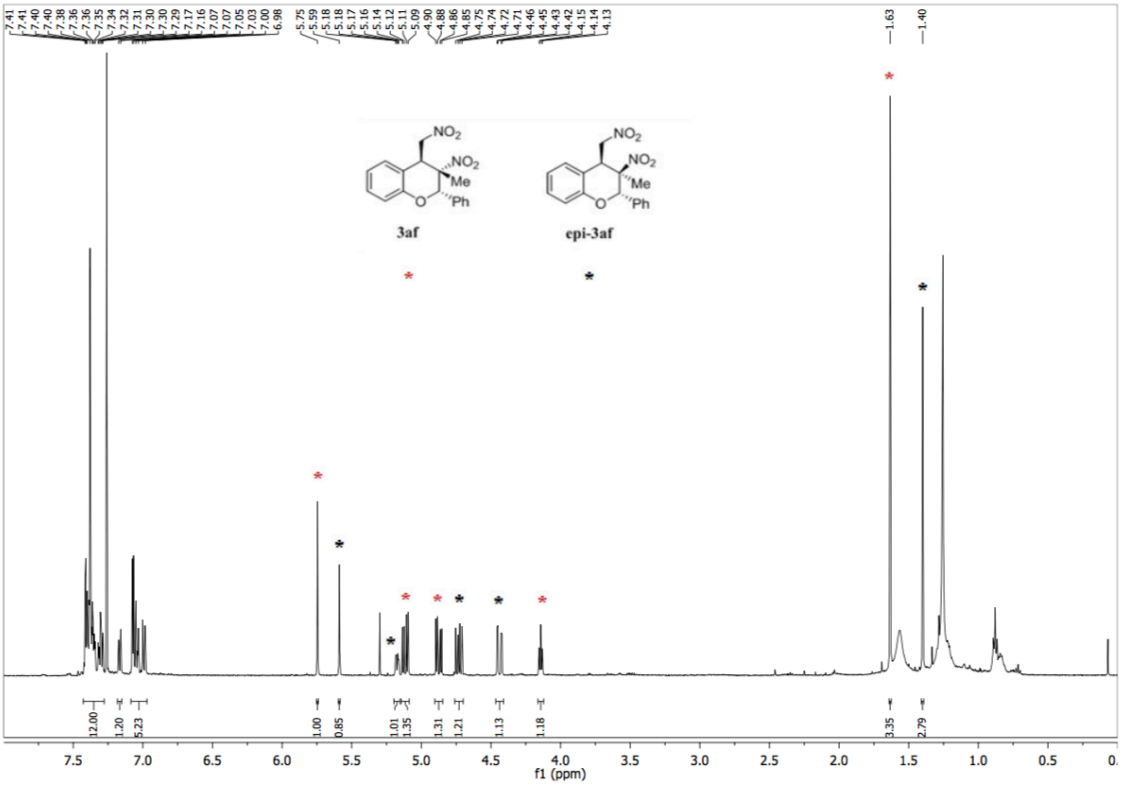


Figure S33. ^{1}**HNMR spectrum of the mixture of (2S,3S,4S)-3-methyl-3-nitro-4-(nitromethyl)-2-phenylchromane (3af) and (2S,3R,4S)-3-methyl-3-nitro-4-(nitromethyl)-2-phenylchroman (epi-3af).**

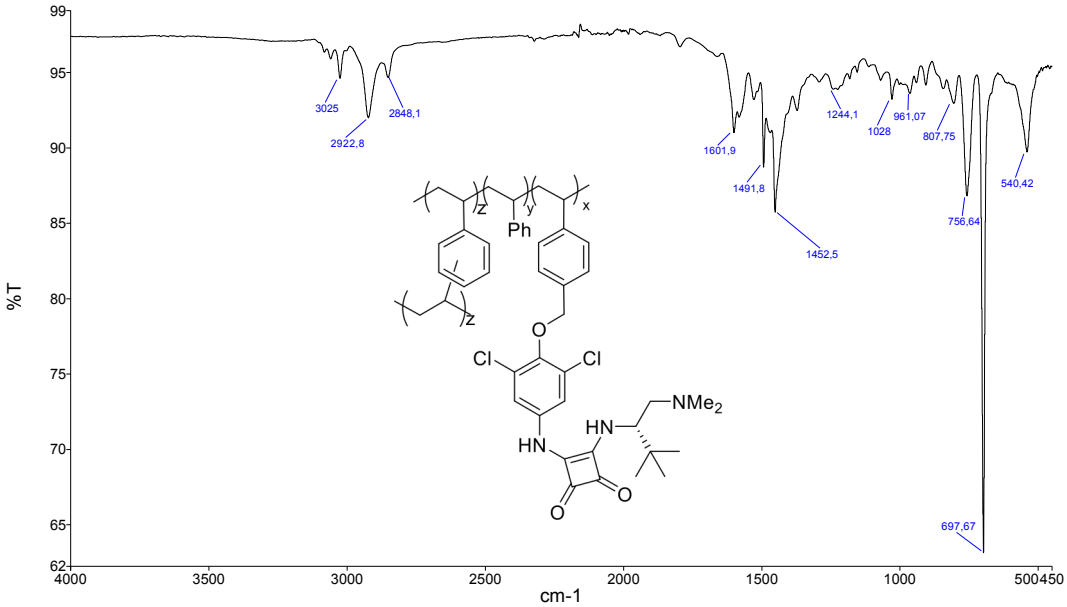
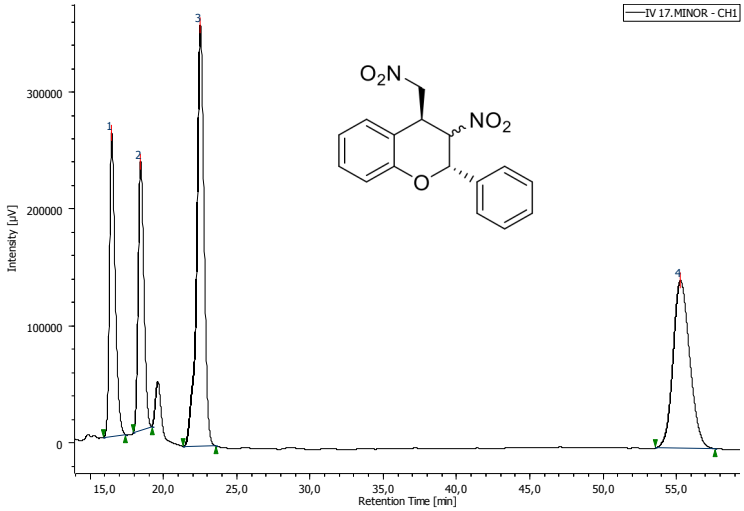


Figure 34. IR (ATR) for squaramide *sq*-9.

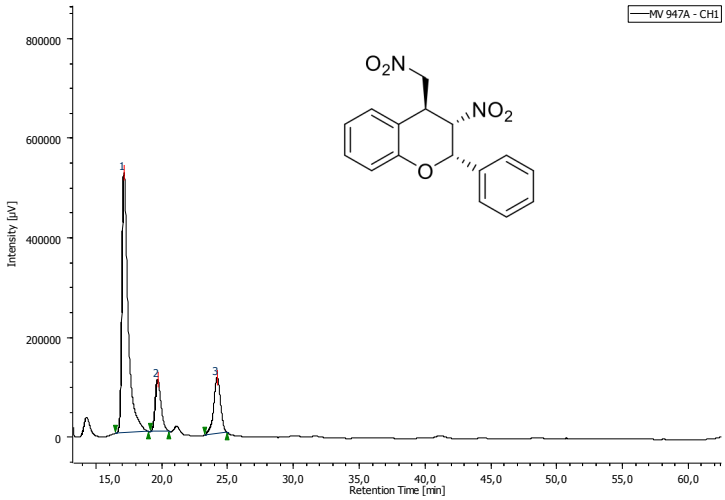
3. HPLC Profile of the oxa-Michael-nitro-Michael products.

Figure S35. HPLC Profile of (2*S*,3*S*,4*S*)-3-Nitro-4-(nitromethyl)-2-phenylchromane (3aa). (Racemic mixture of two diastereoisomers):



Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**16,467**	6887383	258778	**16,875**	26,148	1,405
2	**18,442**	7171369	229277	**17,568**	23,167	1,187
3	22,517	13417335	358572	32,869	36,231	0,868
4	55,233	13343450	143043	32,688	14,454	1,148

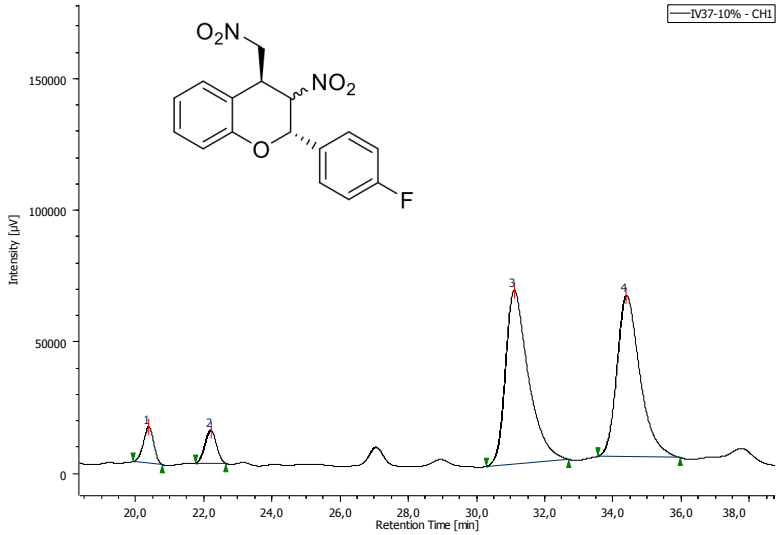
Figure S36 HPLC profile for **3aa**. Entry 3, table 1**. 83:17** dr, **84:16** er.



Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**17,133**	16788355	521708	**70,121**	70,337	2,056
2	**19,683**	3201760	104689	**13,373**	14,114	1,333
3	24,192	3951863	110546	16,506	14,904	1,000

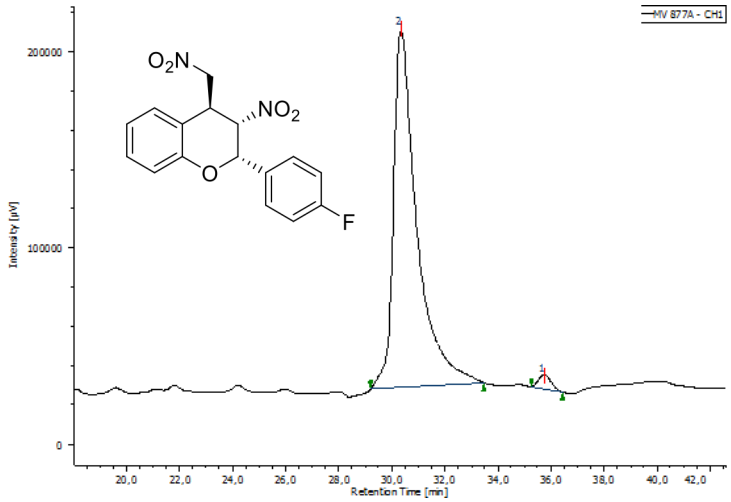
Figure S37. HPLC Profile of (2*S*,3*S*,4*S*)-2-(4-Fluorophenyl)-3-nitro-4-(nitromethyl)chromane (3ab).

Racemic mixture of two diastereoisomers:



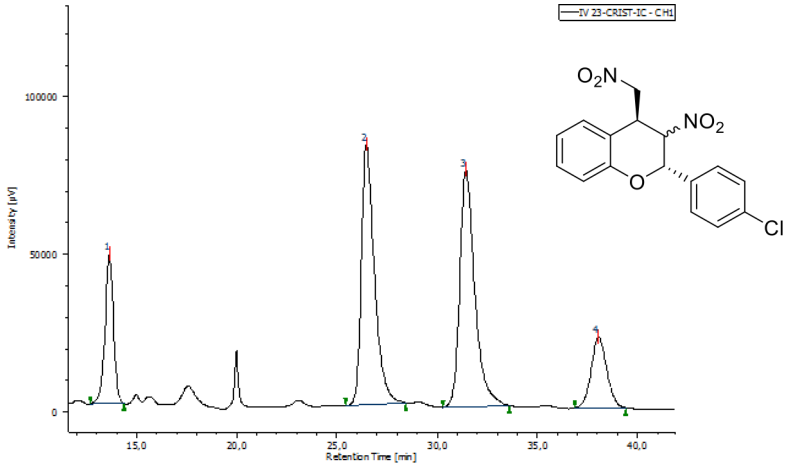
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	20,383	292404	13855	3,472	9,032	0,940
2	22,200	289540	12424	3,438	8,098	0,991
3	**31,092**	3912250	65964	**46,454**	42,999	1,512
4	**34,375**	3927578	61166	**46,636**	39,871	1,390

Figure S38. HPLC profile for **3ab**. Entry 3, table 2**. >99:<1** dr, **98:2** er.



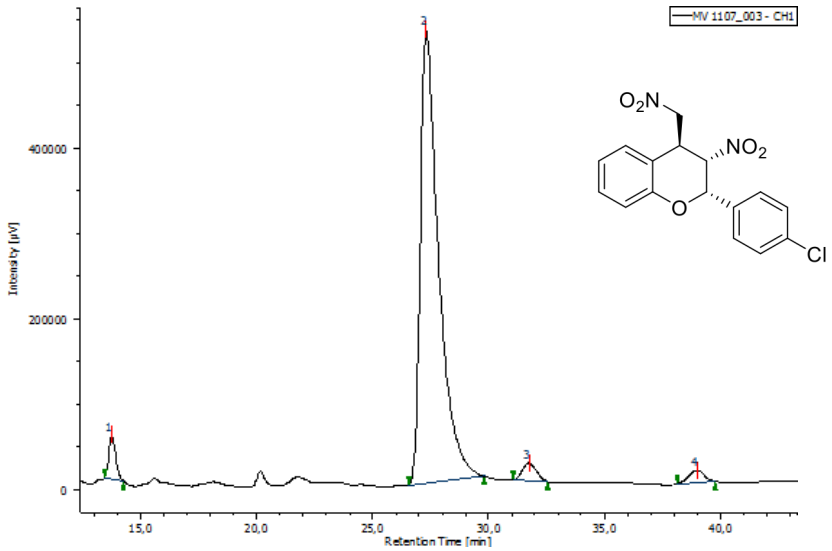
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**31,925**	11144680	181955	**97,916**	96,185	1,131
2	**35,930**	237198	7216	**2,084**	3,815	1,859

Figure S39. HPLC Profile of (2*S*,3*S*,4*S*)-2-(4-Chlorophenyl)-3-nitro-4-(nitromethyl)chromane (3ac). Racemic mixture of two diastereoisomers:



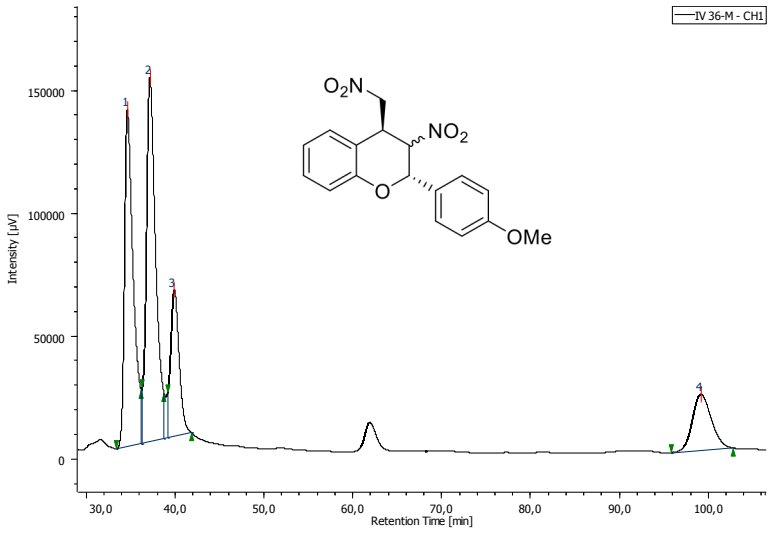
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	13,633	1322536	47527	13,178	20,943	0,815
2	**26,442**	3715507	82198	**37,022**	36,221	1,522
3	**31,408**	3687004	74750	**36,738**	32,939	1,447
4	38,017	1310894	22459	13,062	9,897	1,079

Figure S40. HPLC profile for **3ac**. Entry 6, table 2**. 95:5** dr, **97:3** er.



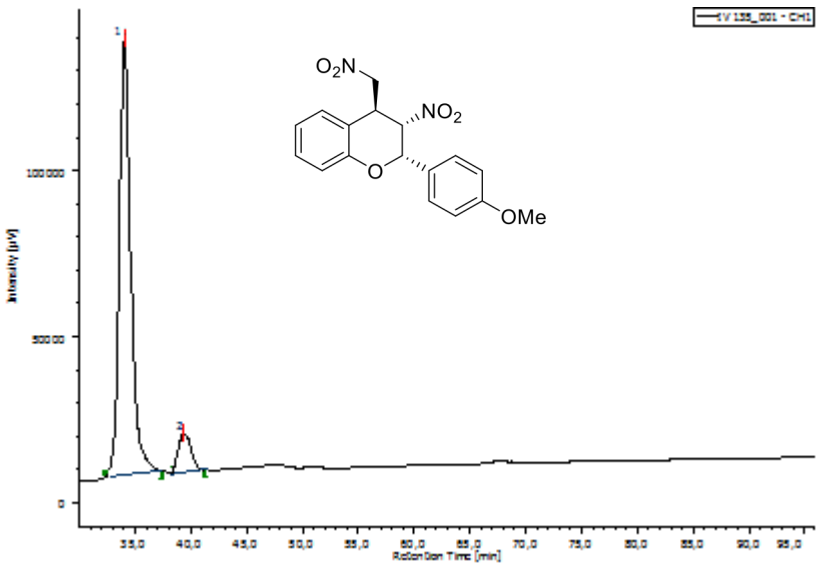
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	13,750	1286589	51749	4,079	8,399	1,234
2	**27,283**	28944325	529983	**91,765**	86,019	2,015
3	**31,717**	850997	20169	**2,698**	3,273	1,065
4	38,933	459879	14220	1,458	2,308	0,972

Figure S41. HPLC Profile of (2*S*,3*S*,4*S*)-2-(4-Methoxyphenyl)-3-nitro-4-(nitromethyl)chromane (3ad). Racemic mixture of two diastereoisomers:



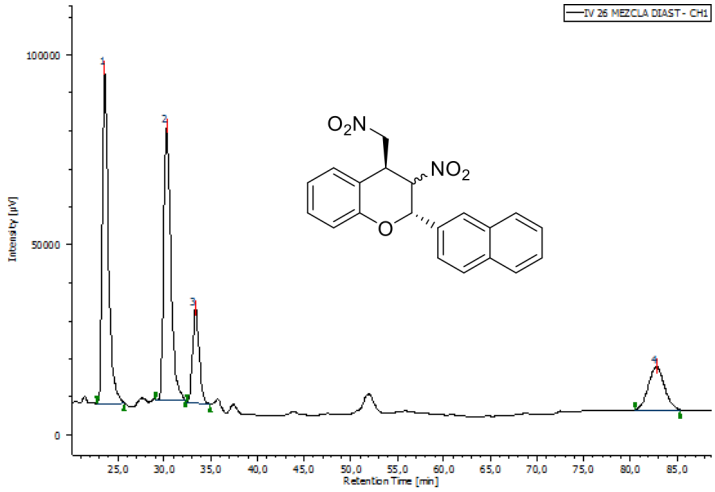
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**34,633**	9415218	136948	**37,223**	37,263	N/A
2	**37,175**	9568500	148125	**37,829**	40,304	N/A
3	39,925	3198943	59655	12,647	16,232	N/A
4	99,092	3111425	22788	12,301	6,201	1,157

Figure S42. HPLC profile for **3ad**. Entry 10, table 2**. 91:9** dr, **>99:<1** er.



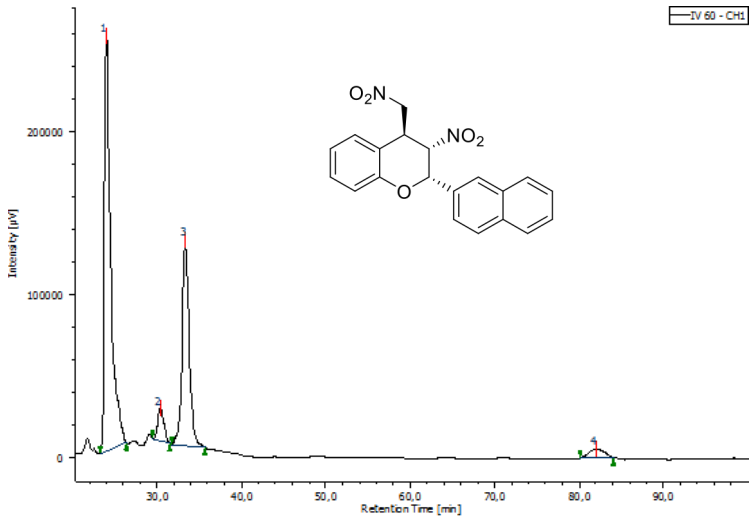
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**34,992**	9253837	130931	**90,838**	91,718	1,157
2	39,927	933350	11822	9,162	8,282	1,246

Figure 43. HPLC Profile of (2*S*,3*S*,4*S*)-2-(Naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (3ae). Racemic mixture of two diastereoisomers:



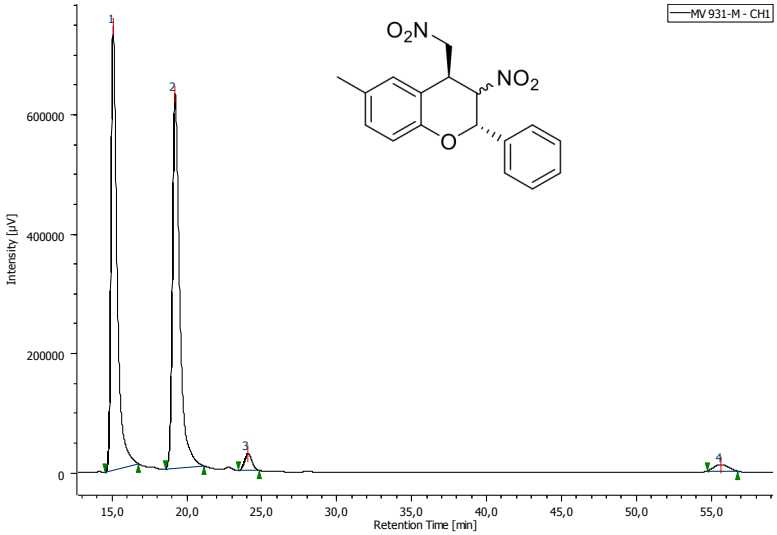
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**23,600**	3951694	88309	**38,027**	44,967	1,576
2	**30,258**	3933508	71996	**37,852**	36,660	1,369
3	33,350	1248160	24821	12,011	12,639	1,166
4	82,750	1258448	11260	12,110	5,734	1,041

Figure 44. HPLC profile for **3ae**. Entry 12, table 2**. 64:36** dr, **93:7** er.



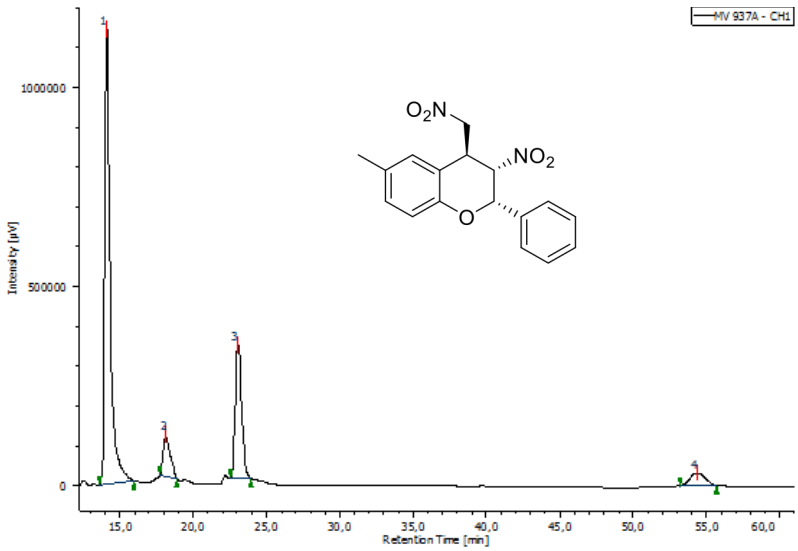
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**24,658**	13245990	253840	**59,116**	62,700	2,285
2	**31,367**	1005616	19530	**4,488**	4,824	1,246
3	34,008	7508510	126044	33,351	31,134	1,079
4	82,575	685539	5435	3,045	1,343	1,049

Figure 45. HPLC Profile of (2*S*,3*S*,4*S*)-6-Methyl-3-nitro-4-(nitromethyl)-2-phenylchromane (3ba). Racemic mixture of two diastereoisomers:



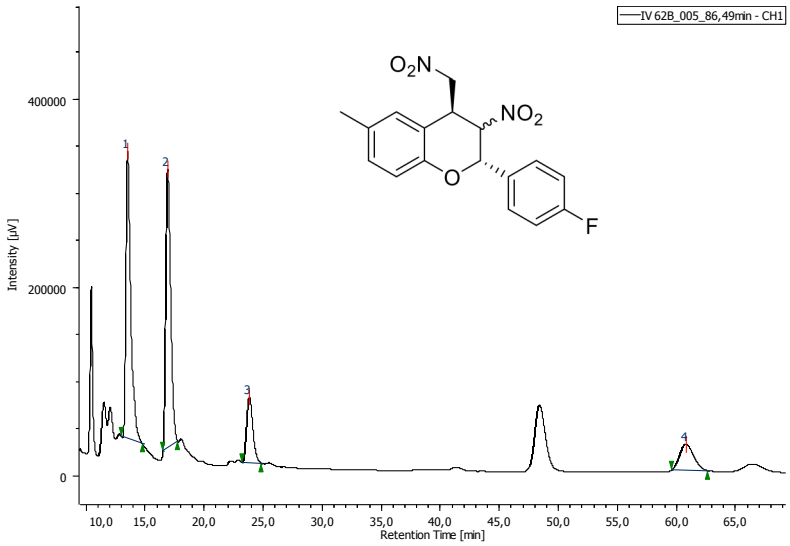
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**15,075**	20497681	741566	**48,351**	52,712	1,852
2	**19,200**	20141151	626562	**47,510**	44,538	1,686
3	24,067	936472	28063	2,209	1,995	1,079
4	55,583	818194	10626	1,930	0,755	1,091

Figure 46. HPLC profile for **3ba**. Entry 15, table 2**. 73:27** dr, **90:10** er.



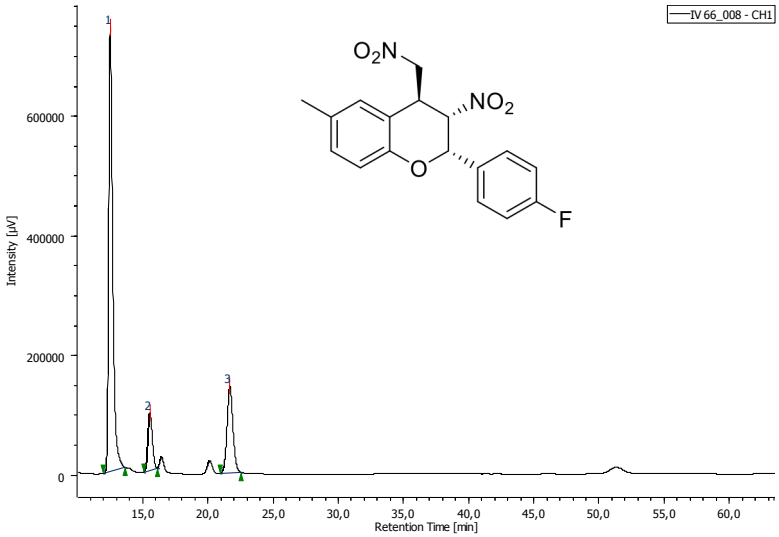
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**14,092**	29926191	1137267	**65,346**	70,757	1,922
2	**18,108**	3402681	103647	**7,430**	6,449	1,506
3	23,883	10192014	334433	22,255	20,807	1,178
4	54,725	2275628	31927	4,969	1,986	1,039

Figure 47. HPLC Profile of (2*S*,3*S*,4*S*)-2-(4-Fluorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (3bb). Racemic mixture of two diastereoisomers:



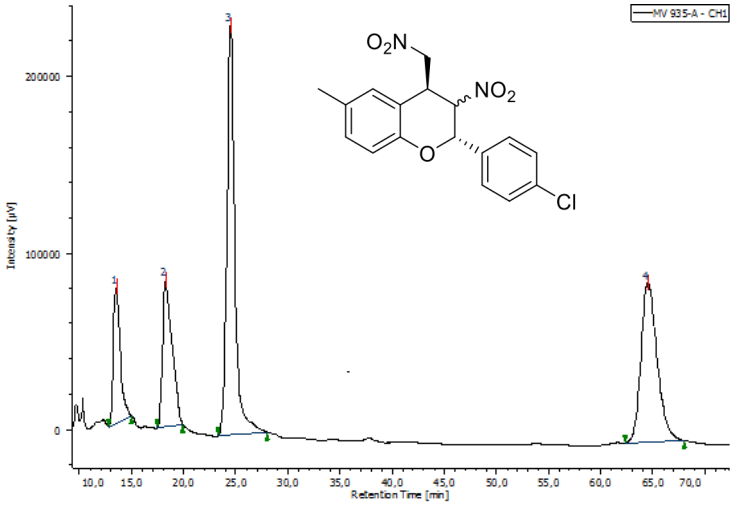
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**13,508**	8726629	303802	**39,268**	43,646	1,798
2	**16,900**	8717295	295080	**39,226**	42,393	1,400
3	23,817	2389666	69626	10,753	10,003	1,262
4	60,733	2389666	27549	10,753	3,958	1,174

Figure 48. HPLC profile for **3bb**. Entry 17, table 2. **80:20** dr, **88:12** er.



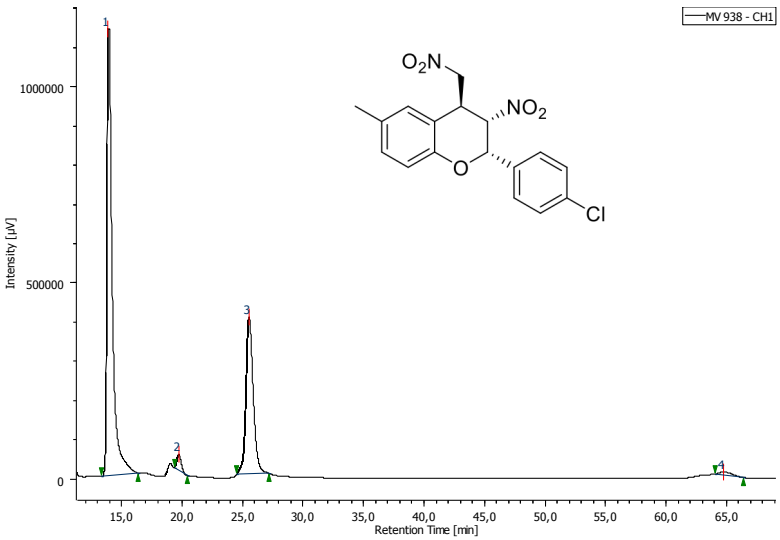
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**12,500**	15692505	741024	**69,885**	75,055	1,600
2	**15,550**	2218529	94248	**9,880**	9,546	1,099
3	21,658	4543719	143069	20,235	14,491	1,110

Figure 49. HPLC Profile of (2*S*,3*S*,4*S*)-2-(4-Chlorophenyl)-6-methyl-3-nitro-4-(nitromethyl)chromane (3bc). Racemic mixture of two diastereoisomers:



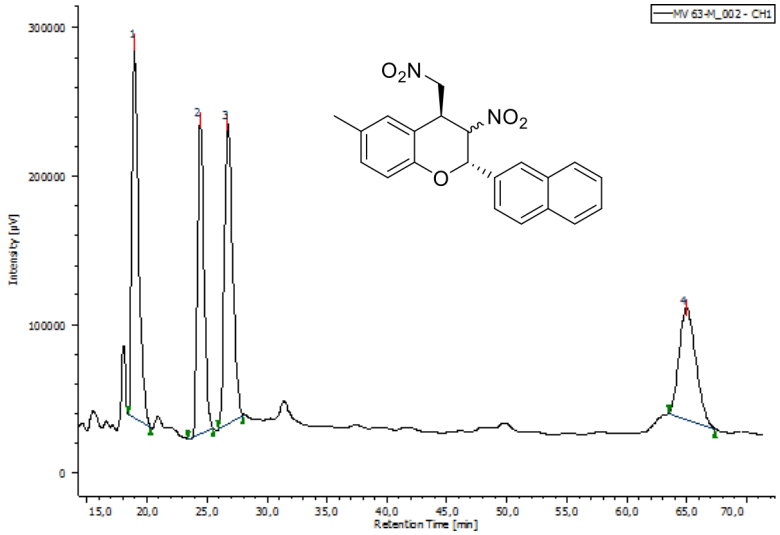
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**13,517**	3577190	76688	**14,421**	15,983	1,525
2	**18,250**	3720565	82331	**14,999**	17,159	1,563
3	24,442	8818327	230742	35,550	48,091	1,288
4	64,442	8689339	90038	35,030	18,766	1,259

Figure 50. HPLC profile for **3bc**. Entry 18, table 2**. 68:32** dr, **95:5** er.



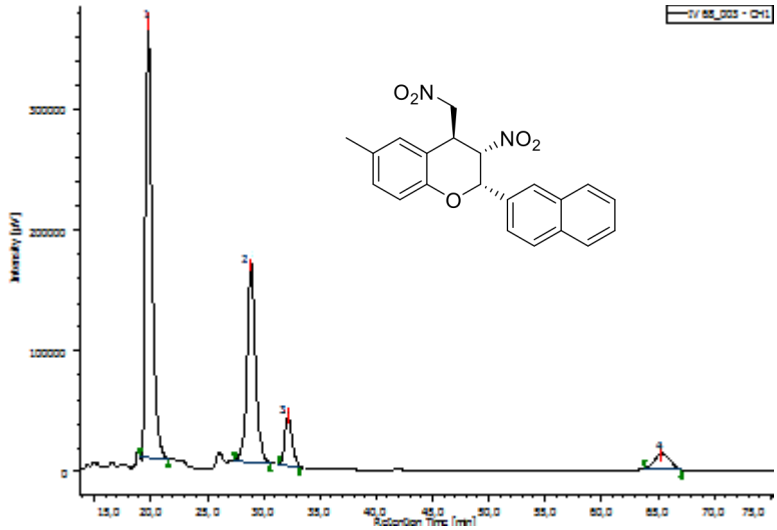
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**13,875**	35822456	1134573	**64,681**	71,707	1,672
2	**19,717**	1800510	40105	**3,251**	2,535	1,175
3	25,525	17160507	399734	30,985	25,264	1,140
4	64,717	599800	7817	1,083	0,494	1,431

Figure 51. HPLC Profile of (2*S*,3*S*,4*S*)-6-Methyl-2-(naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (3be). Racemic mixture of two diastereoisomers:



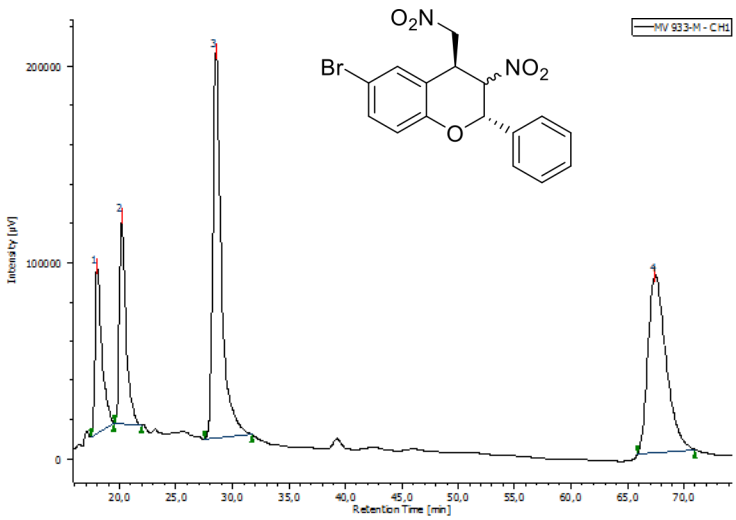
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**18,942**	9727964	253305	**28,213**	34,188	1,743
2	24,442	7617761	210565	22,093	28,420	1,237
3	**26,733**	9576250	202337	**27,773**	27,309	1,319
4	65,933	7558455	74704	21,921	10,083	1,207

Figure 52. HPLC profile for **3be**. Entry 19, table 2**. 62:38** dr, **88:12** er.



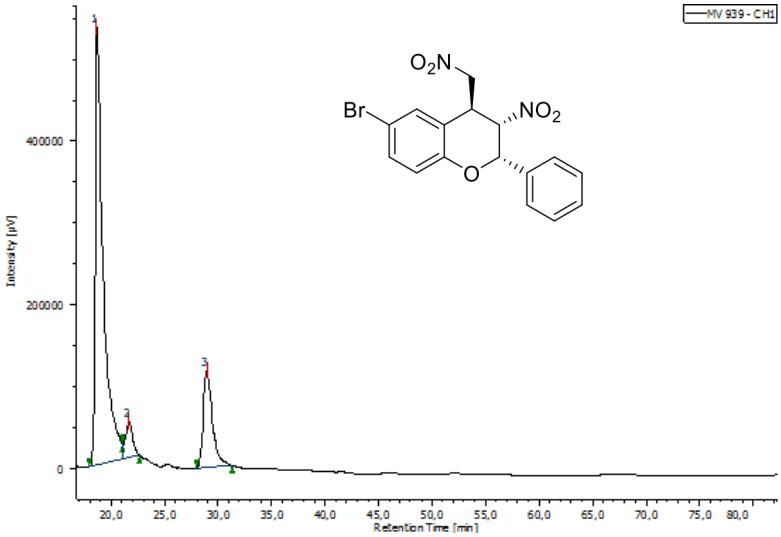
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**18,742**	13847236	362034	**54,343**	62,566	1,754
2	24,550	8549444	40590	33,552	7,015	1,296
3	**28,383**	1914400	163511	**7,513**	28,257	1,020
4	68,500	1170350	12512	4,593	2,162	1,037

Figure 53. HPLC Profile of (2*S*,3*S*,4*S*)-6-Bromo-3-nitro-4-(nitromethyl)-2-phenylchromane (3ca). Racemic mixture of two diastereoisomers:



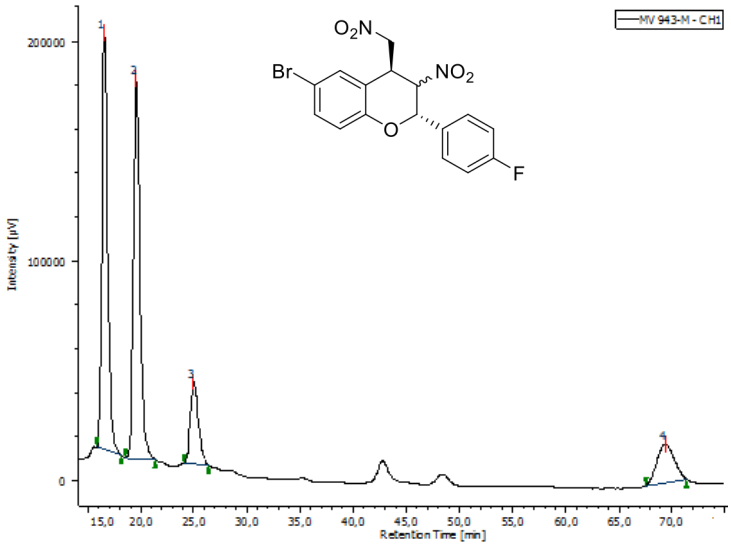
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**17,992**	3633083	84786	**13,626**	17,775	2,057
2	**20,183**	3581357	105714	**13,432**	22,162	1,720
3	28,525	9749545	196406	36,566	41,175	1,877
4	67,417	9698886	90101	36,376	18,889	1,448

Figure 54. HPLC profile for **3ca**. Entry 20, table 2**. 79:21** dr, **96:4** er.



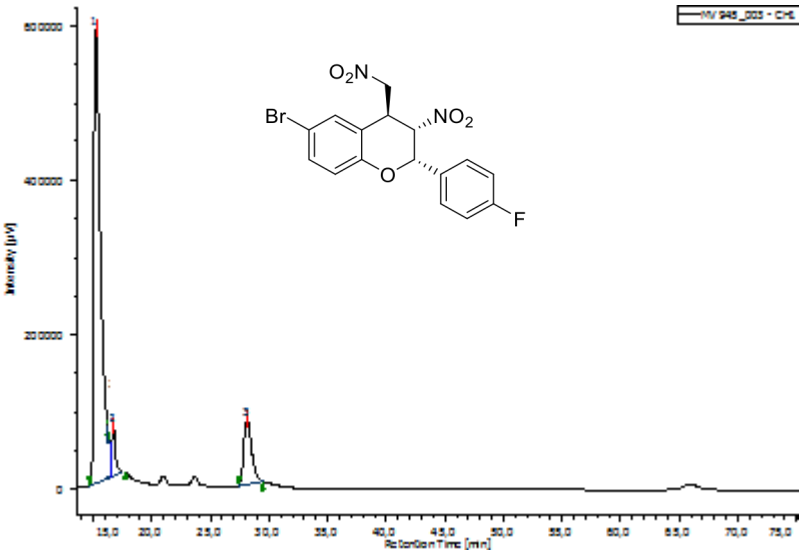
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**18,675**	26092141	528319	**75,075**	77,824	3,030
2	**21,658**	1223020	32103	**3,519**	4,729	1,361
3	29,833	7439605	118439	21,406	17,447	1,612

Figure 55. HPLC Profile of (2*S*,3*S*,4*S*)-6-Bromo-2-(4-fluorophenyl)-3-nitro-4-(nitromethyl)chromane (3cb). Racemic mixture of two diastereoisomers:



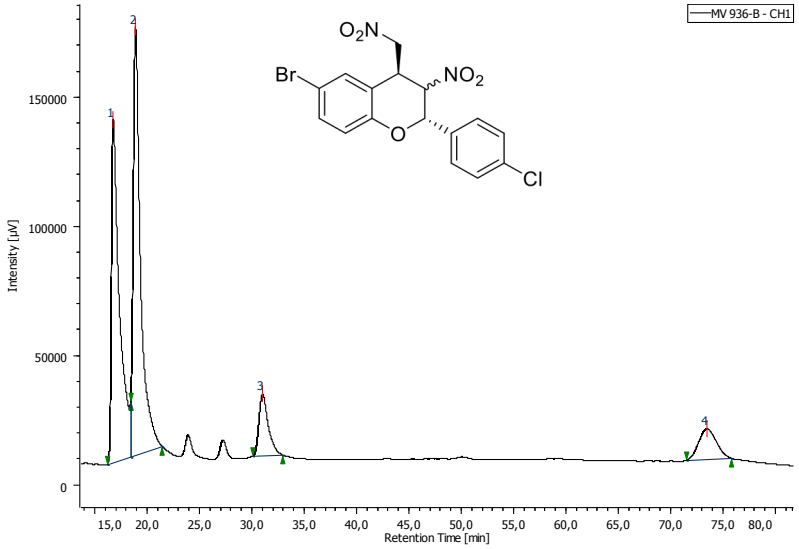
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**17,758**	7095204	189387	**38,616**	45,423	1,346
2	**20,067**	7347842	172871	**39,991**	41,461	1,277
3	25,183	1959743	37188	10,666	8,919	1,272
4	70,017	1970951	17497	10,727	4,197	1,063

Figure 56. HPLC profile for **3cb**. Entry 22, table 2**. 86:14** dr, **97:3** er.



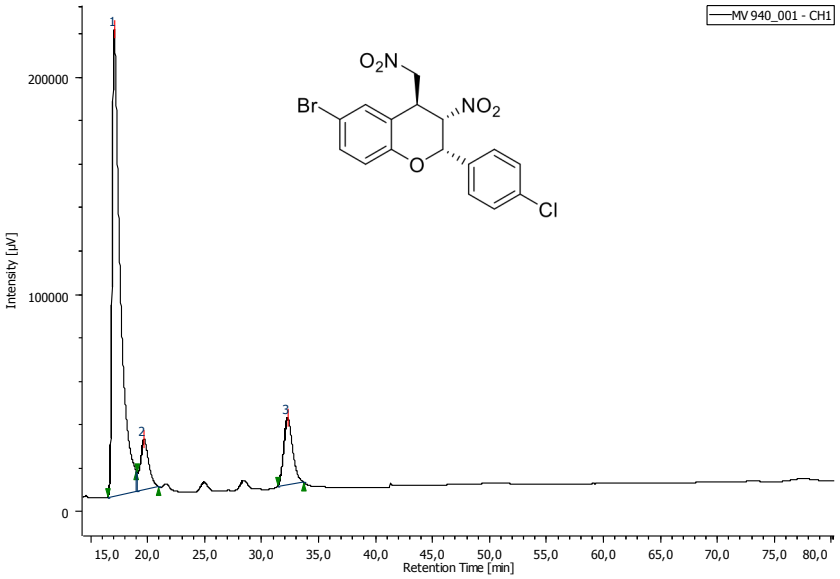
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**15,233**	22751886	588129	**82,893**	72,943	N/A
2	**16,733**	448686	131706	**2,615**	16,335	N/A
3	28,133	4026233	82484	14,492	10,230	1,316

Figure 57. HPLC Profile of (2*S*,3*S*,4*S*)-6-Bromo-2-(4-chlorophenyl)-3-nitro-4-(nitromethyl)chromane (3cc). Racemic mixture of two diastereoisomers:



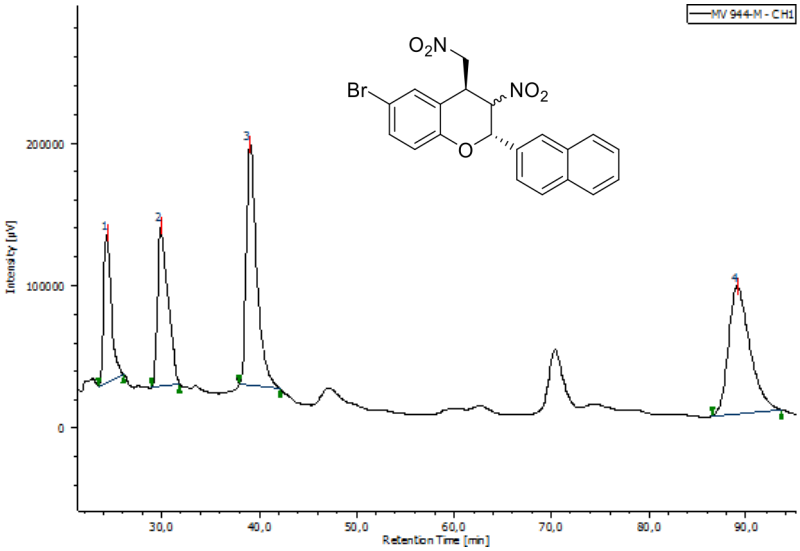
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**16,758**	7103709	132434	**41,512**	39,715	N/A
2	**18,900**	7325143	165255	**42,806**	49,557	N/A
3	31,008	1387304	24007	8,107	7,199	1,493
4	73,375	1296266	11770	7,575	3,530	1,110

Figure 58. HPLC profile for **3cc**. Entry 23, table 2**. 88:12** dr, **93:7** er.



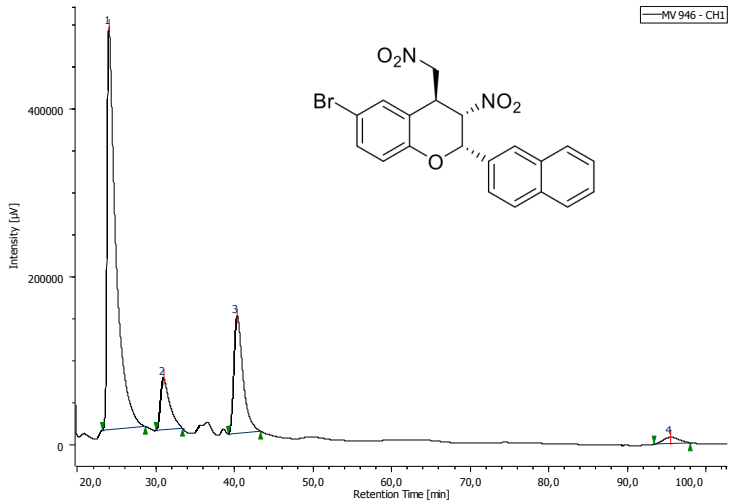
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**17,075**	10518546	214314	**81,426**	79,892	3,030
2	**19,683**	795873	23294	**6,161**	8,684	N/A
3	32,258	1603501	30647	12,413	11,425	1,262

Figure 59. HPLC Profile of (2*S*,3*S*,4*S*)-6-Bromo-2-(naphthalen-2-yl)-3-nitro-4-(nitromethyl)chromane (3ce). Racemic mixture of two diastereoisomers:



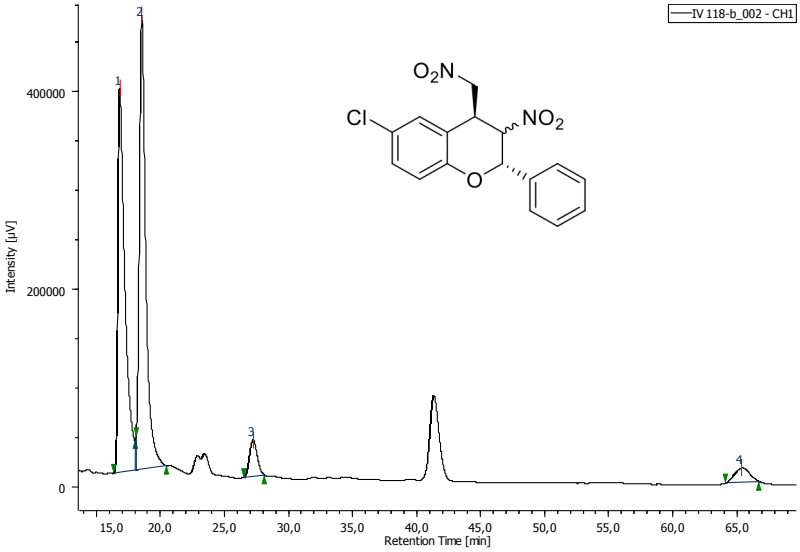
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**24,092**	8066402	120905	**21,145**	22,904	2,308
2	**30,083**	8407445	149076	**22,039**	28,241	2,216
3	39,042	10838619	168519	28,412	31,924	1,720
4	88,967	10835567	89371	28,404	16,930	1,409

Figure 60. HPLC profile for **3ce**. Entry 24, table 2**. 78:22** dr, **88:12** er.



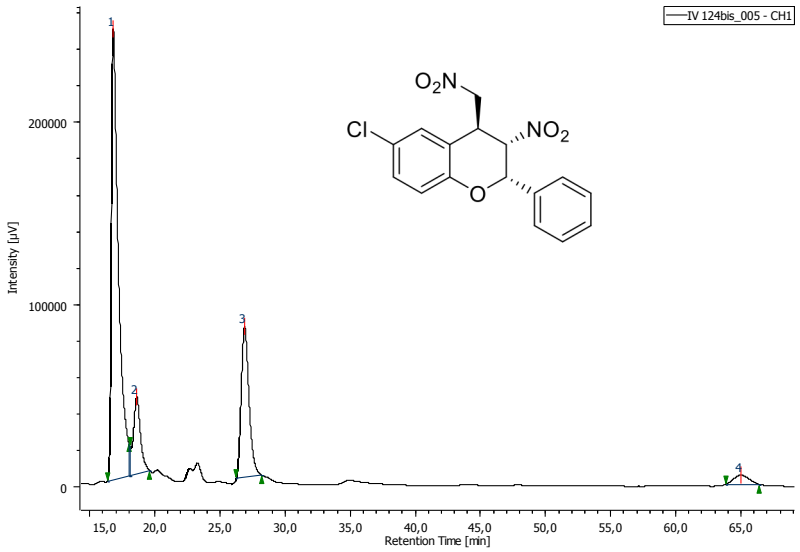
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**24,017**	37102726	479175	**68,349**	69,626	3,446
2	**30,942**	4988177	61946	**9,189**	9,001	1,854
3	40,325	11309575	139666	20,834	20,294	1,714
4	95,467	884290	7424	1,629	1,079	1,057

Figure 61. HPLC Profile of (2*S*,3*S*,4*S*)-6-Chloro-3-nitro-4-(nitromethyl)-2-phenylchromane (3da). Racemic mixture of two diastereoisomers:



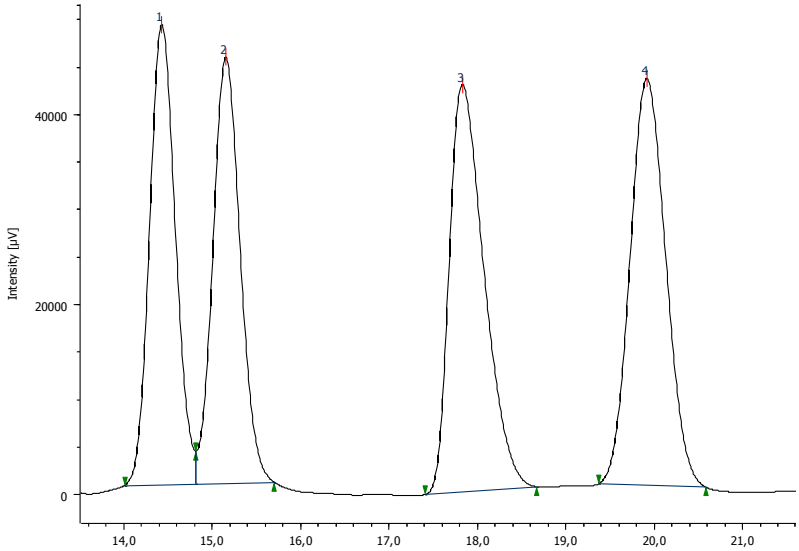
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**16,825**	14725745	387586	**45,805**	43,251	N/A
2	**18,533**	14866556	457390	**46,243**	51,041	N/A
3	27,217	1273734	36794	3,962	4,106	1,130
4	65,333	1282414	14354	3,989	1,602	1,030

Figure 62. HPLC profile for **3da**. Entry 25, table 2**. 74:26** dr, **85:15** er.



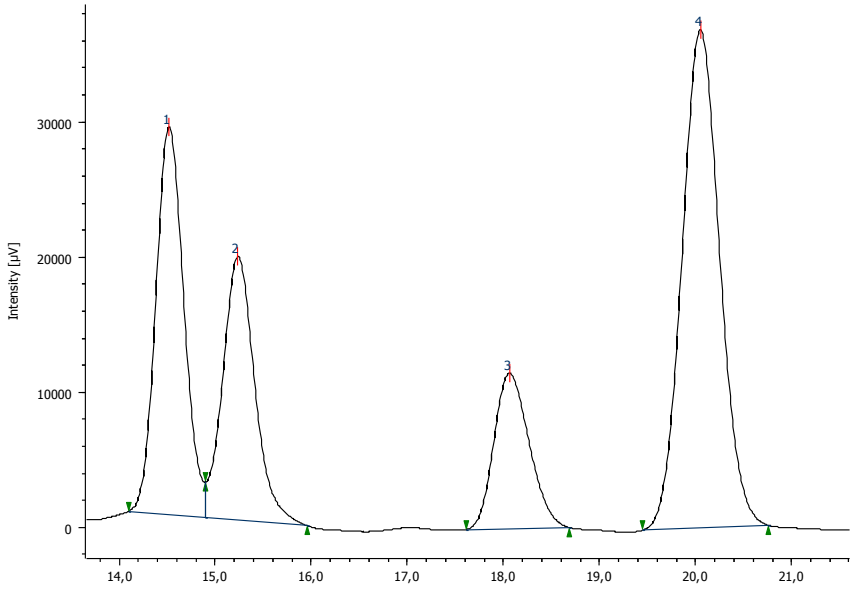
Peak Name	t_R	Area	Height	Area%	Height%	Symmetry Factor
1	**16,808**	9266912	246197	**62,955**	65,486	N/A
2	**18,608**	1648481	42356	**11,199**	11,266	N/A
3	26,875	3395291	82333	23,066	21,900	1,346
4	64,908	409360	5066	2,781	1,347	1,096

Figure 63. HPLC Profile of (2S,3S,4S)-3-methyl-3-nitro-4-(nitromethyl)-2-phenylchromane (3af). Racemic mixture of diastereoisomers



Peak Number	**tR**	Area	Height	**Area%**	Height%
1	**14,425**	984314	48345	**22,845**	27,051
2	**15,150**	960451	44812	**22,291**	25,074
3	**17,825**	1166288	42809	**27,068**	23,953
4	**19,908**	1197661	42753	**27,796**	23,922

Figure 64. HPLC Profile for (3af). Entry 27, table 2**. 56:44** dr, **77:23** er.



Peak Number	**tR**	Area	Height	**Area%**	Height%
1	**14,517**	580473	28640	**24,962**	29,720
2	**15,233**	450717	19485	**19,382**	20,220
3	**18,058**	291232	11453	**12,524**	11,885
4	**20,042**	1003007	36787	**43,132**	38,175

Figure 65. ORTEP Single Crystal X-Ray Diffraction of 3ac. The ellipsoids are shown at 50% probability

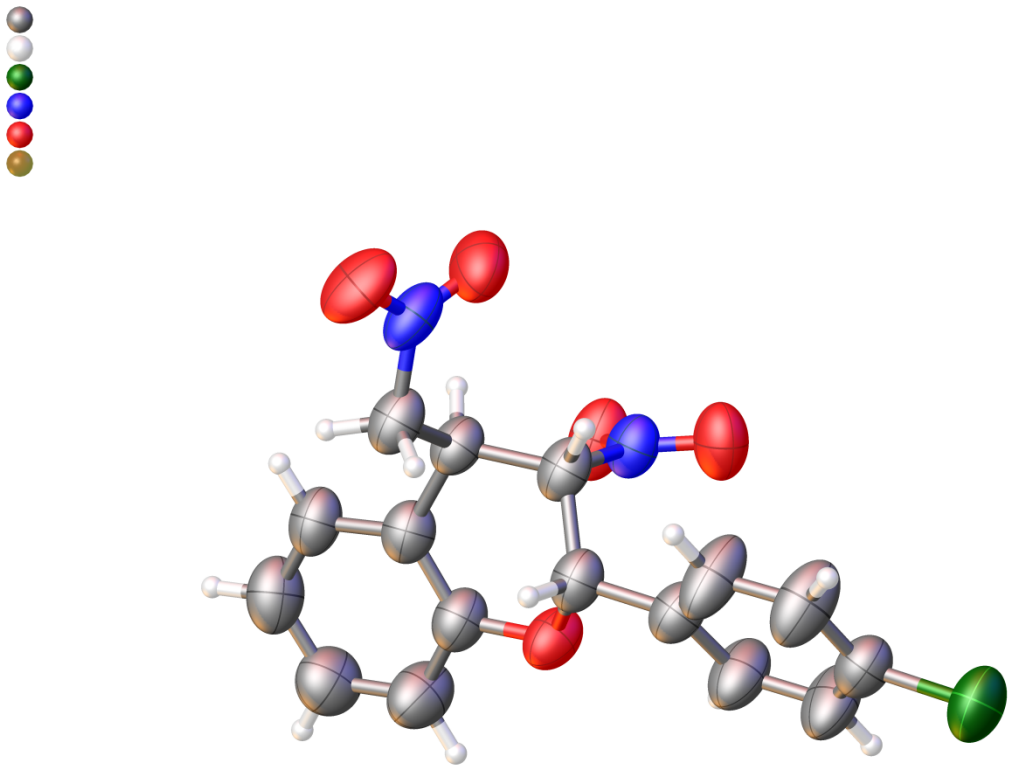


Table S-1. Crystal data and structure refinement for **3ac**.

Identification code	**3ac**
Empirical formula	$C_{16}H_{13}ClN_2O_5$
Formula weight	348.73
Temperature/K	293
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.7832(3)
b/Å	9.2550(11)
c/Å	30.117(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1612.0(2)
Z	4
ρ_{calc}g/cm^3	1.437
μ/mm^{-1}	2.370
F(000)	720.0
Crystal size/mm^3	0.34 × 0.07 × 0.034
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.998 to 150.282
Index ranges	$-7 \leq h \leq 7$, $-11 \leq k \leq 11$, $-36 \leq l \leq 37$
Reflections collected	14747
Independent reflections	3281 [R_{int} = 0.0730, R_{sigma} = 0.0434]
Data/restraints/parameters	3281/0/217
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0663, wR_2 = 0.1856
Final R indexes [all data]	R_1 = 0.0863, wR_2 = 0.2241
Largest diff. peak/hole / e Å^{-3}	0.22/-0.39
Flack parameter	-0.03(3)