Electronic Supplementary Material (ESI) for RSC Advances.

One-pot synthesis of various 2-amino-4H-chromene derivatives using highly active supported ionic liquid catalyst

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Supplementary Information

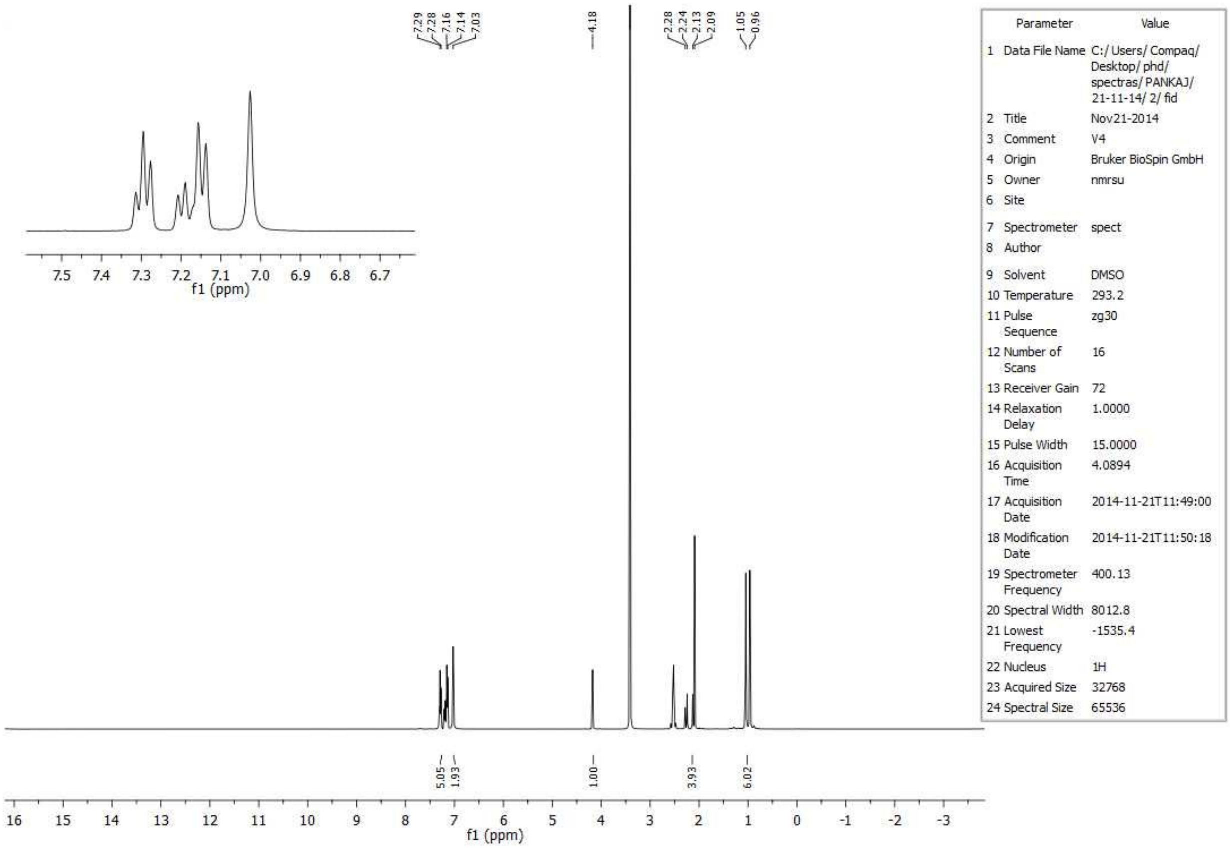
Spectral data of some products

2-amino-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4*H*-chromene-3-carbonitrile (entry 1, table 3)

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.96 (s, 3H, CH$_3$), 1.06 (s, 3H, CH$_3$), 2.09-2.28 (m, 4H, 2 X CH$_2$), 4.17 (s, 1H, CH), 7.03 (s, 2H, NH$_2$) 7.14-7.29 (m, 5H, ArH).

^{13}C NMR (100 MHz, DMSO-d$_6$): δ 27.2, 28.9, 32.2, 36.0, 40.3, 50.8, 58.8, 113.2, 120.2, 127.1, 127.7, 128.9, 145.2, 159.0, 163.0, 196.2.

MS: *m/z* 295 (M$^+$).



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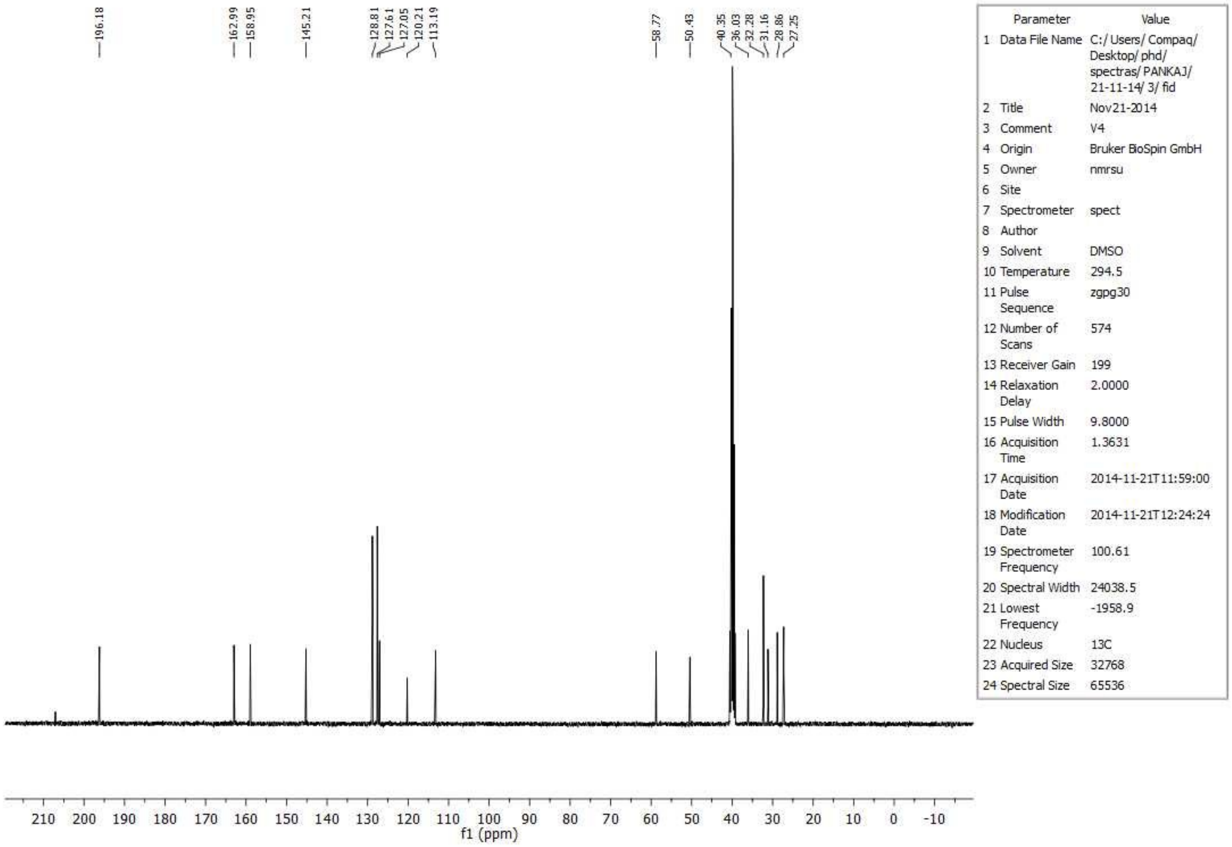
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Fig. S1 ^{1}H NMR of 2-amino-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4*H*-chromene-3-carbonitrile



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11	Pulse Sequence	zgpg30
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19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

Fig. S2 ^{13}C NMR of 2-amino-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4*H*-chromene-3-carbonitrile

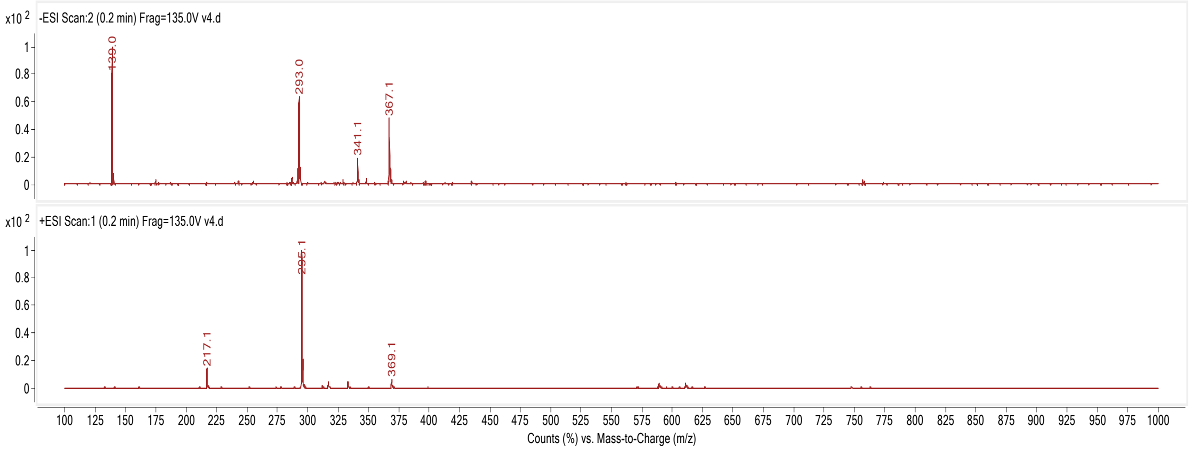


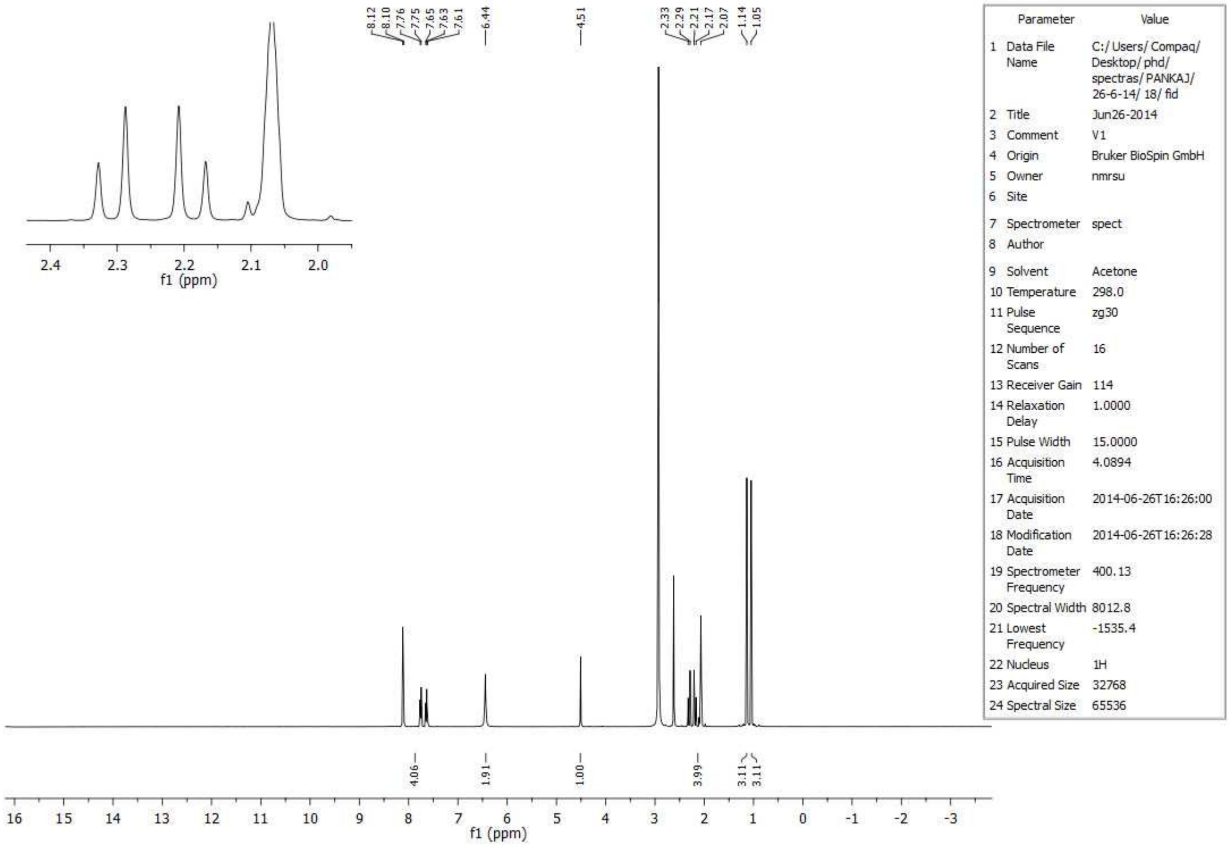
Fig. S3 Mass spectra of 2-amino-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4*H*-chromene-3-carbonitrile

2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile (entry 3, table 3)

^{1}H NMR (400 MHz, DMSO-d_6): δ 1.06 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 2.06-2.28 (m, 4H, 2 X CH_2), 4.51 (s, 1H, CH), 6.44 (s, 2H, NH_2), 7.61-8.11 (m, 4H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ 26.6, 27.9, 31.8, 36.0, 40.0, 50.1, 59.5, 112.5, 118.2, 121.7, 122.2, 129.7, 134.3, 147.1, 148.4, 158.9, 162.8, 195.3.

MS: *m/z* 340 (M^+).



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7	Spectrometer	spect
8	Author	
9	Solvent	Acetone
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12	Number of Scans	16
13	Receiver Gain	114
14	Relaxation Delay	1.0000
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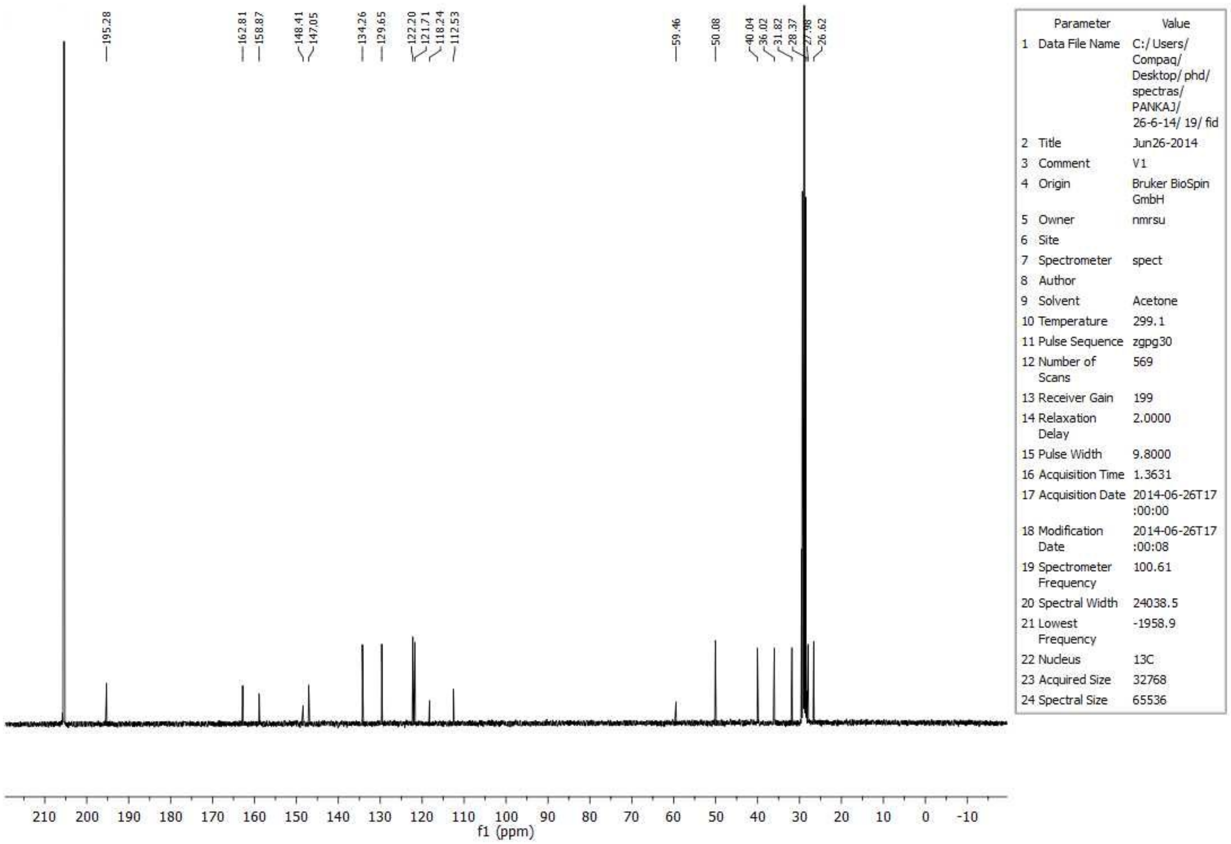
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Fig. S4 ^{1}H NMR of 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile



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7	Spectrometer	spect
8	Author	
9	Solvent	Acetone
10	Temperature	299.1
11	Pulse Sequence	zgpg30
12	Number of Scans	569
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
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19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

Fig. S5 ^{13}C NMR of 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

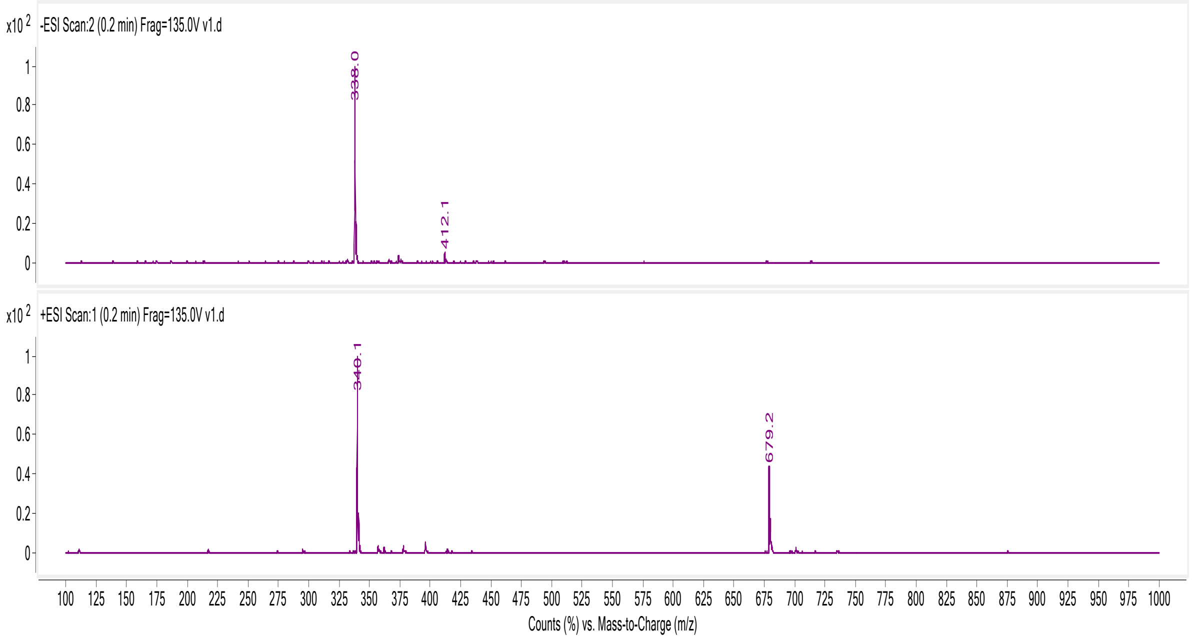


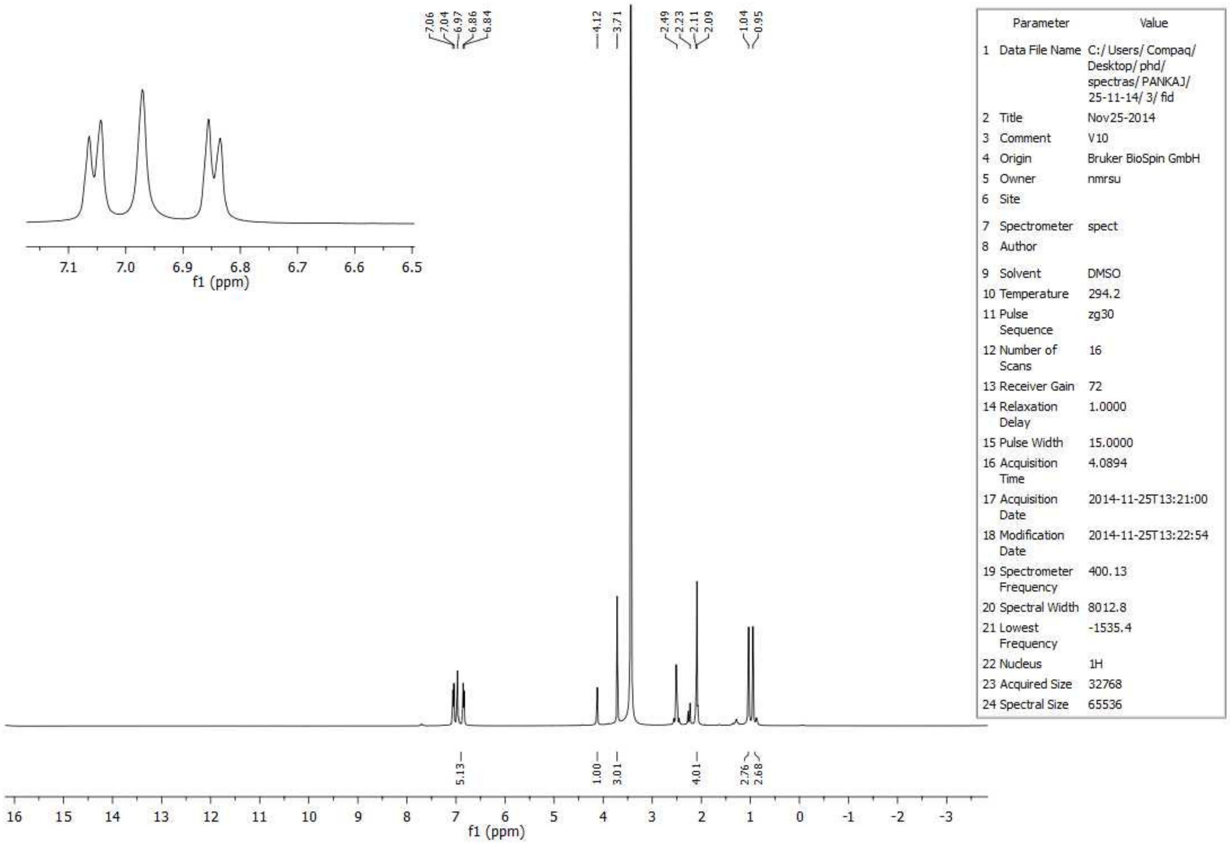
Fig. S6 Mass spectra of 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

2-amino-4-(4-methoxyphenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile (entry 10, table 3)

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.94 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.09-2.23 (m, 4H, 2 X CH_2), 3.71 (s, 3H, OCH_3), 4.12 (s, 1H, CH), 6.84 (d, 2H, ArH), 6.97 (s, 2H, NH_2), 7.04 (d, 2H, ArH).

^{13}C NMR (100 MHz, DMSO-d$_6$): δ 27.2, 28.9, 32.3, 35.2, 40.6, 50.5, 55.5, 59.0, 113.4, 114.1, 120.3, 128.7, 137.3, 158.4, 158.9, 162.7, 196.2.

MS: *m/z* 325 (M^+).



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8	Author	
9	Solvent	DMSO
10	Temperature	294.2
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	72
14	Relaxation Delay	1.0000
15	Pulse Width	15.0000
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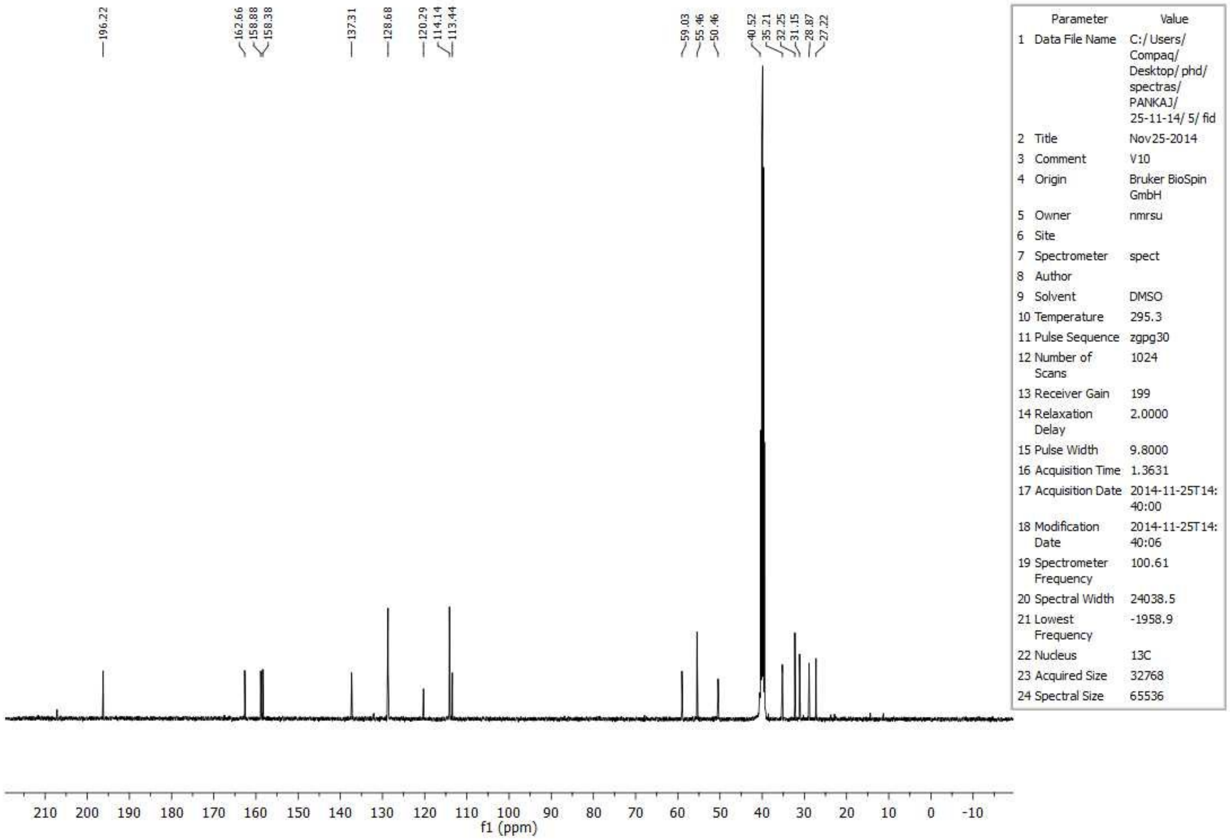
18	Modification Date	2014-11-25T13:22:54
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1535.4
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

Fig. S7 ^{1}H NMR of 2-amino-4-(4-methoxyphenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile



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5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	DMSO
10	Temperature	295.3
11	Pulse Sequence	zgpg30
12	Number of Scans	1024
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2014-11-25T14:40:00
18	Modification Date	2014-11-25T14:40:06
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

Fig. S8 ^{13}C NMR of 2-amino-4-(4-methoxyphenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile

Crystallography data collection and refinement

X-ray data of complexes were collected on an X'calibur- Oxford Diffraction single crystal diffractometer (Department of Physics and Electronics, University of Jammu, Jammu) with CCD area-detector (graphite-monochromator, Mo-Kα radiations, λ = 0.71073 Å). Data were corrected for Lorentz, polarization and absorption factors. The structures were solved by direct methods using SHELXS97.[1] All non-H atoms of the molecule were located in the best E-map. Full-matrix least-squares refinement was carried out using SHELXL97.[1] The geometry of the molecule was calculated using WinGX,[2] PARST[3] and PLATON.[4] Atomic scattering factors were taken from

International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). Molecular drawings were obtained using DIAMOND version 2.1.[5] Crystallographic data, details of the data collection, structure solution and refinements are listed in **Table S1**.

1. G. M. Sheldrick, Acta Crystallogr, 2008, A64, 112.
2. L.J. Farrugia, J Appl Crystallogr, 1999, 32, 837.
3. M. Nardelli, J Appl Crystallogr, 1995, 28, 659.
4. A. L. Spek, Acta Crystallogr, 2009, D65, 148.
5. K. Brandenburg, DIAMOND, Version 2.1. Crystal Impact GbR, 1998, Bonn, Germany.

Table S1: Experimental details

Crystal data	
Chemical formula	$C_{144}H_{136}N_{24}O_{32}$
M_r	2714.77
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, *b*, *c* (Å)	12.0002 (5), 12.0002 (5), 24.7801 (14)
α, β, γ (°)	93.670 (3), 93.670 (3), 103.706 (4)
V (Å^3)	3448.2 (3)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.30 × 0.20 × 0.20
Data collection	
Diffractometer	Xcalibur, Sapphire3 diffractometer
Absorption	Multi-scan

correction	*CrysAlis PRO*, Agilent Technologies, Version 1.171.36.28 (release 01-02-2013 CrysAlis171 .NET) (compiled Feb 1 2013,16:14:44) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{\min}$, $T_{\max}$	0.934, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13673, 10570, 6910
R_{int}	0.022
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.168, 0.462, 1.08
No. of reflections	10570
No. of parameters	910
No. of restraints	0
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.1305P)^2 + 41.3017P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.63, −0.43

Table S2: Selected geometric parameters (Å, º)

O1—C10	1.395 (10)	C21—H21	0.9300
O1—C2	1.408 (12)	C22—H22	0.9300
O13—C5	1.236 (11)	C17—C22—C21	121.3 (9)
O24—N23	1.231 (12)	C17—C22—H22	119.4

O26—N23	1.217 (13)	C21—C22—H22	119.3
N14—C2	1.325 (12)	H12A—C12—H12C	109.5
N14—H14A	0.8600	H12B—C12—H12C	109.5
N14—H14B	0.8600	N16—C15—C3	177.1 (12)
N16—C15	1.118 (14)	C18—C17—C22	117.6 (9)
N23—C19	1.461 (12)	C18—C17—C4	121.1 (8)
C2—C3	1.326 (12)	C22—C17—C4	121.2 (8)
C3—C15	1.425 (15)	C17—C18—C19	120.1 (10)
C3—C4	1.525 (12)	C17—C18—H18	120.0
C4—C17	1.543 (12)	C19—C18—H18	120.0
C4—C9	1.555 (13)	C20—C19—C18	122.7 (9)
C4—H4	0.9800	C20—C19—N23	119.1 (9)
C5—C9	1.463 (12)	C18—C19—N23	118.2 (9)
C5—C6	1.493 (13)	C19—C20—C21	118.2 (9)
C6—C7	1.532 (13)	C19—C20—H20	120.9
C6—H6A	0.9700	C21—C20—H20	120.9
C6—H6B	0.9700	C20—C21—C22	120.0 (11)
C7—C12	1.496 (16)	C20—C21—H21	120.0
C7—C8	1.510 (14)	C22—C21—H21	120.0
C7—C11	1.529 (14)	C10—C8—H8A	109.0
C8—C10	1.482 (14)	C7—C8—H8A	109.0

C8—H8A	0.9700	C10—C8—H8B	109.0
C8—H8B	0.9700	C7—C8—H8B	109.0
C9—C10	1.323 (11)	H8A—C8—H8B	107.8
C11—H11A	0.9600	C10—C9—C5	118.4 (8)
C11—H11B	0.9600	C10—C9—C4	124.2 (8)
C11—H11C	0.9600	C5—C9—C4	117.4 (7)
C12—H12A	0.9600	C9—C10—O1	121.5 (8)
C12—H12B	0.9600	C9—C10—C8	126.4 (8)
C12—H12C	0.9600	O1—C10—C8	112.2 (7)
C17—C18	1.358 (12)	C7—C11—H11A	109.5
C17—C22	1.386 (15)	C7—C11—H11B	109.5
C18—C19	1.383 (13)	H11A—C11—H11B	109.5
C18—H18	0.9300	C7—C11—H11C	109.5
C19—C20	1.348 (15)	H11A—C11—H11C	109.5
C20—C21	1.363 (15)	H11B—C11—H11C	109.5
C20—H20	0.9300	C7—C12—H12A	109.5
C21—C22	1.389 (15)	C7—C12—H12B	109.5
C10—O1—C2	118.1 (7)	H12A—C12—H12B	109.5
C2—N14—H14A	120.0	C7—C12—H12C	109.5
C2—N14—H14B	120.0	C7—C6—H6A	108.7
H14A—N14—H14B	120.0	C5—C6—H6B	108.8

O26—N23—O24	120.9 (10)	C7—C6—H6B	108.8
O26—N23—C19	120.3 (10)	H6A—C6—H6B	107.6
C17—C4—H4	109.5	C12—C7—C8	110.7 (9)
C9—C4—H4	109.5	C12—C7—C6	111.2 (9)
O13—C5—C9	121.5 (9)	C8—C7—C6	108.4 (9)
O13—C5—C6	120.6 (9)	C12—C7—C11	107.1 (11)
C9—C5—C6	117.8 (8)	C8—C7—C11	110.4 (8)
C5—C6—C7	114.0 (8)	C6—C7—C11	109.0 (8)
C5—C6—H6A	108.7	C10—C8—C7	113.1 (7)

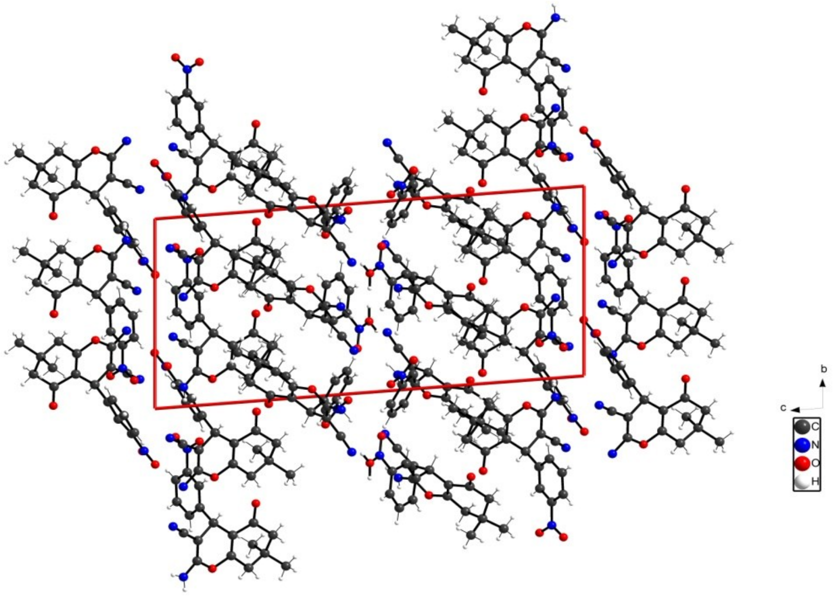

Fig. S9 The packing arrangement of the molecules viewed down the a-axis

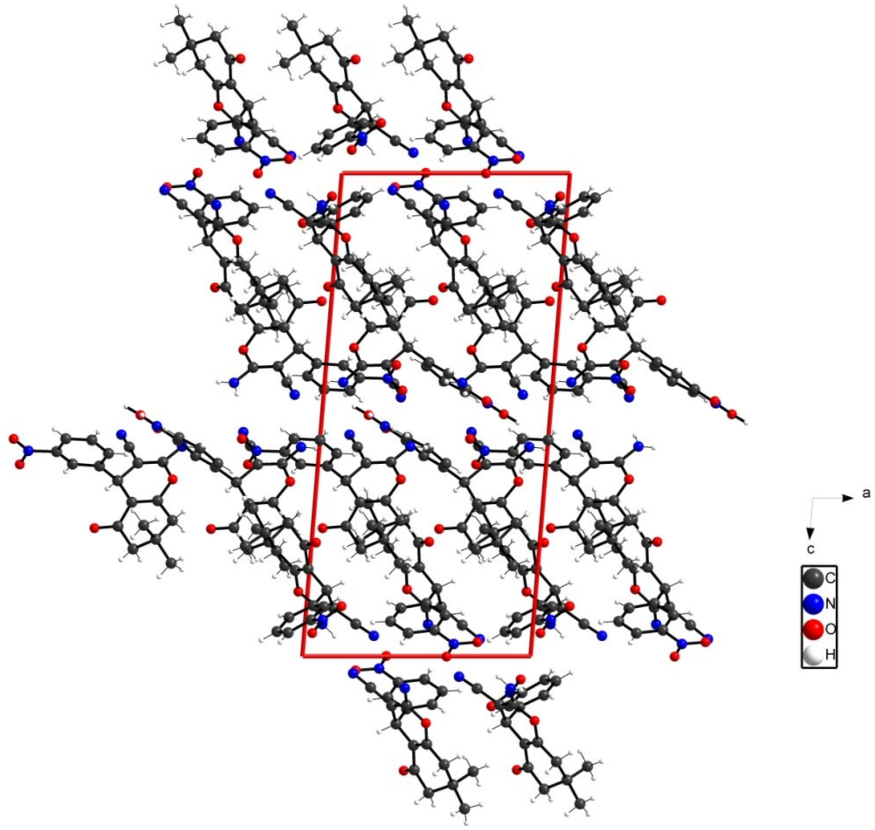

Fig. S10 Packing arrangement of 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile along *b* axis

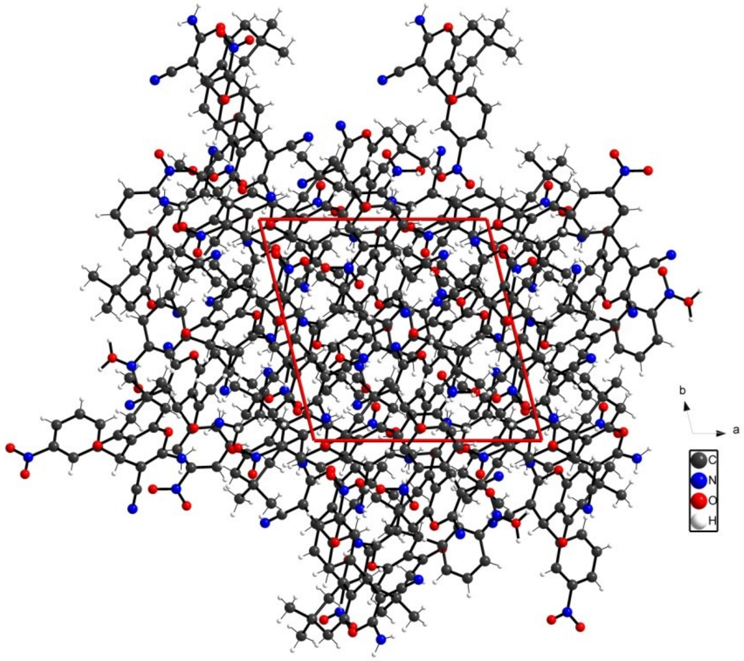

Fig. S11 Packing arrangement of 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile along *c* axis