Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Immobilized piperazine on the surface of graphene oxide as a heterogeneous bifunctional acid-base catalyst for the multicomponent synthesis of 2-amino-3-cyano-4*H*-chromenes

Asma Khazaee,[a] Roya Jahanshahi,[a] Sara Sobhani,*[a] Jørgen Skibsted [b] and José Miguel Sansano[c]

[a]Department of Chemistry, College of Sciences, University of Birjand, Birjand, Iran, email: ssobhani@birjand.ac.ir, sobhanisara@yahoo.com.

[b]Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark.

[c]Departamento de Química Orgánica, Facultad de Ciencias, Centro de Innovación en Química Avanzada (ORFEO-CINQA) and Instituto de Sı´ntesis Orga´nica (ISO), Universidad de Alicante, Apdo. 99, 03080-Alicante, Spain.

Spectral data of some of the products:

2-Amino-4-(phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S1, Table 2, entry 1): IR (KBr) V_{max}/cm^{-1}: 3389, 3323 (NH_2), 2192 (CN), 1679 (CO),^{1}H NMR (300 MHz, DMSO); δ 0.98 (s, 3 H), 1.06 (s, 3 H), 2.13 (d, *J* = 16.0 Hz, 1 H), 2.28 (d, *J* = 16.1 Hz, 1 H), 2.54 (s, 2 H), 4.22 (s, 1 H), 7.03 (s, 2 H), 7.17-7.23 (m, 3 H), 7.29-7.33 (m, 2 H) ppm.

2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S2, Table 2, entry 2): ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.09 (s, 3 H), 1.13 (s, 3 H), 2.20 (d, *J* = 16.2 Hz, 1 H,), 2.27 (d, *J* = 16.2 Hz, 1 H), 2.48 (s, 2 H), 4.79 (s, 2 H), 4.88 (s, 1 H), 7.13-7.18 (m , 1 H), 7.20-7.23 (m, 2 H), 7.33-7.36 (m, 1 H) ppm.

2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S3, Table 2, entry 3): IR (KBr) V_{max}/cm^{-1}: 3393, 3321 (NH_2), 2192 (CN), 1714 (CO), ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.06 (s, 3 H), 1.15 (s, 3 H), 2.22 (d, *J* = 16.2 Hz, 1 H), 2.29 (d, *J* = 16.2 Hz, 1 H), 2.48 (s, 2 H), 4.42 (s, 1 H), 4.63 (s, 2 H), 7.19-7.22 (m, 2 H), 7.28- 7.31 (m, 2 H) ppm.

2-Amino-4-(2,6-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S4, Table 2, entry 4): ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.08 (s, 3 H), 1.11 (s , 3 H), 2.19 (d, *J* = 16.2 Hz, 1 H), 2.25 (d, *J* = 16.2 Hz, 1 H), 2.41 (s, 2 H), 4.93 (s, 2 H), 5.45 (s, 1 H), 7.10 (t, *J* = 7.9 Hz, 1 H), 7.21 (d, *J* = 7.5 Hz, 1 H), 7.36 (d, *J* = 7.8 Hz, 1 H) ppm.

2-Amino-4-(3-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S5, Table 2, entry 7): IR (KBr) V_{max}/cm^{-1}: 3438, 3332 (NH_2), 2179 (CN), 1664 (CO), ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.08 (s, 3 H), 1.16 (s, 3 H), 2.23 (d, *J* = 16.2 Hz, 1 H), 2.30 (d, *J* = 16.3 Hz, 1 H), 2.49 (d, *J* = 17.2 Hz, 1 H), 2.57 (d, *J* = 17.7 Hz, 1 H), 4.56 (s, 1 H), 4.76 (s, 2 H), 7.52 (t, *J* = 7.8 Hz, 1 H), 7.69-7.73 (m, 1 H), 8.06-8.08 (m, 1 H), 8.10-8.14 (m, 1 H) ppm.

2-Amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S6, Table 2, entry 9): IR (KBr) V_{max}/cm^{-1}: 3359, 3255 (NH_2), 2187 (CN), 1683 (CO),^{1}H NMR (300 MHz, $CDCl_3$); δ 1.06 (s, 3 H), 1.16 (s, 3 H), 2.23 (d, *J* = 16.3 Hz, 1 H), 2.30 (d, *J* = 16.3 Hz, 1 H), 2.51 (s, 2 H), 4.50 (s, 1 H), 4.66 (s, 2 H), 7.40 (d, *J* = 8.2 Hz, 2 H), 7.64 (d, *J* = 8.2 Hz, 2 H) ppm.

2-Amino-4-(p-tolyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S7, Table 2, entry 10)**:** IR (KBr) V_{max}/cm^{-1}: 3403, 3314 (NH_2), 2192 (CN), 1642 (CO),^{1}H NMR (300 MHz, DMSO); δ 0.97 (s, 3 H), 1.06 (s, 3 H), 2.12 (d, *J* = 16.1 Hz, 1 H), 2.27 (s, 3 H H), 2.28 (d, *J* = 16.1 Hz, 1 H), 2.50 (d, *J* = 17.4 Hz, 1 H), 2.57 (d, *J* = 17.7 Hz, 1 H), 4.18 (s, 1 H), 6.99 (s, 2 H), 7.05-7.13 (m, 4 H) ppm.

2-Amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S8, Table 2, entry 11): IR (KBr) V_{max}/cm^{-1}: 3256, 3212 (NH_2), 2194 (CN), 1682 (CO),^{1}H NMR (300 MHz, $CDCl_3$); δ 1.06 (s, 3 H), 1.14 (s, 3 H), 2.22 (d, *J* = 16.2 Hz, 1 H), 2.28 (d, *J* = 16.2 Hz, 1 H), 2.47 (s, 2 H), 3.79 (s, 3 H), 4.39 (s, 1 H), 4.58 (s, 2 H), 6.83-6.86 (m, 2 H), 7.17-7.20 (m, 2 H) ppm.

2-Amino-4-(2,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S9, Table 2, entry 12): IR (KBr) V_{max}/cm^{-1}: 3296, 3161 (NH_2), 2192 (CN), 1679 (CO),^{1}H NMR (300 MHz, $CDCl_3$); δ 1.06 (s, 3 H), 1.13 (s, 3 H), 2.19 (d, *J* = 16.5 Hz, 1 H), 2.26 (d, *J* = 16.3 Hz, 1 H), 2.40 (d, *J* = 17.5 Hz, 1 H), 2.48 (d, *J* = 18.1 Hz, 1 H), 3.78 (s, 3 H), 3.81 (s, 3 H), 4.58 (s, 1 H), 4.61 (s, 2 H), 6.41-6.44 (m, 2 H), 7.03-7.06 (m, 1 H) ppm.

2-Amino-4-(3,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S10, Table 2, entry 13): IR (KBr) V_{max}/cm^{-1}: 3390, 3324 (NH_2), 2183 (CN), 1679 (CO), ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.05 (s, 3 H), 1.11 (s, 3 H), 2.19 (d, *J* = 16.3 Hz, 1 H), 2.26 (d, *J* = 16.3 Hz, 1 H), 2.44 (s, 2 H), 3.83 (s, 3 H), 3.86 (s, 3H), 4.34 (s, 1 H), 4.8 (s, 2 H), 6.73-6.81 (m, 3 H) ppm.

N-(4-(2-amino-3-cyano-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromen-4yl)phenyl) acetamide (Figure S11, Table 2, entry 15): IR (KBr) V_{max}/cm^{-1}: 3319, 3168 (NH_2), 2197 (CN), 1647 (CO), ^{1}H NMR (300 MHz, DMSO); δ 0.97 (s, 3 H), 1.05 (s, 3 H), 2.03 (s, 3

H), 2.11 (d, *J* = 16.0 Hz, 1 H), 2.26 (d, *J* = 16.0 Hz, 1 H), 4.14 (s, 1 H), 6.99 (s, 2 H), 7.07 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 9.90 (s, 1 H) ppm.

2-Amino-4-(3-pyridyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S12, Table 2, entry 18): ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.05 (s, 3 H), 1.14 (s, 3 H), 2.21 (d, *J* = 16.3 Hz, 1 H), 2.30 (d, *J* = 16.3 Hz, 1 H), 2.50 (s, 2 H), 4.46 (s, 1 H), 4.91 (s, 2 H), 7.24-7.28 (m, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 8.47-8.52 (m, 2 H) ppm.

2-Amino-4-(naphthalen-1-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S13, Table 2, entry 19): ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.09 (s, 3 H), 1.16 (s, 3 H), 2.19 (d, *J* = 16.2 Hz, 1 H), 2.27 (d, *J* = 16.2 Hz, 1 H), 2.51 (d, *J* = 17.6 Hz, 1 H), 2.58 (d, *J* = 17.7 Hz, 1 H), 4.55 (s, 2 H), 5.30 (s, 1 H), 7.26-7.28 (m , 1 H), 7.43 (t, *J* = 8.0 Hz, 1 H), 7.48-7.54 (m, 1 H), 7.58-7.63 (m, 1 H), 7.75 (d, *J* = 8.1 Hz, 1 H), 7.86 (d, *J* = 8.2 Hz, 1 H), 8.42 (d, *J* = 8.4 Hz, 1 H) ppm.

2-Amino-7,7-dimethyl-5-oxo-4-styryl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S14, Table 2, entry 20): ^{1}H NMR (300 MHz, DMSO); δ 1.02 (s, 3 H), 1.05 (s, 3 H), 2.23 (d, *J* = 16.0 Hz, 1 H), 2.31 (d, *J* = 16.0 Hz, 1 H), 2.45-2.52 (m, 2 H), 3.83 (d, *J* = 7.3 Hz, 1 H), 6.09 (dd, *J* = 7.4 Hz, *J* = 15.8 Hz, 1 H), 6.38 (d, *J* = 15.7 Hz, 1 H), 7.08 (s, 2 H), 7.21-7.41 (m, 5 H) ppm.

2-Amino-4,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S15, Table 2, entry 22): ^{1}H NMR (300 MHz, $CDCl_3$); δ 1.11 (s, 3 H), 1.12 (s, 3 H), 1.25 (d, *J* = 6.5 Hz, 3 H), 2.30 (bs, 2 H), 2.36 (bs, 2 H), 3.36 (q, *J* = 6.5 Hz, 1 H), 4.55 (s, 2 H).

2-Amino-4-(iso-propyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S16, Table 2, entry 23): IR (KBr) V_{max}/cm^{-1}: 3385, 3212 (NH_2), 2194 (CN), 1677 (CO),^{1}H NMR (300 MHz, $CDCl_3$); δ 0.75 (d, *J* = 6.6 Hz, 3 H), 1.04 (d, *J* = 6.9 Hz, 3 H), 1.10 (s, 3 H), 1.12 (s, 3 H), 1.86-1.92 (m, 1 H), 2.29 (s, 2 H) , 2.39 (s, 2 H), 3.34 (s, 1 H), 4.80 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.8, 20.2, 27.2, 29.3, 32.0, 33.3, 35.2, 40.6, 50.8, 57.4, 114.4, 120.3, 160.2, 163.2, 196.6 ppm.

2-Amino-4-(iso-butyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S17, Table 2, entry 24): IR (KBr) V_{max}/cm^{-1}: 3385, 3327 (NH_2), 2193 (CN), 1677 (CO),^{1}H NMR (300 MHz, $CDCl_3$); δ 0.88 (d, *J* = 6.3 Hz, 3 H), 1.01 (d, *J* = 6.6 Hz, 3 H), 1.09 (s, 3 H), 1.11 (s, 3 H), 1.36 (t, *J* = 6.3 Hz, 2 H), 1.79-1.92 (m, 1 H), 2.29 (s , 2 H), 2.37 (s, 2 H), 3.39 (t , *J* = 6.3 Hz, 1 H), 4.71 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 23.9, 24.7, 27.2, 27.3, 29.0, 32.1, 40.6, 46.5, 50.8, 61.2, 115.6, 119.9, 159.1, 162.4, 196.5 ppm.

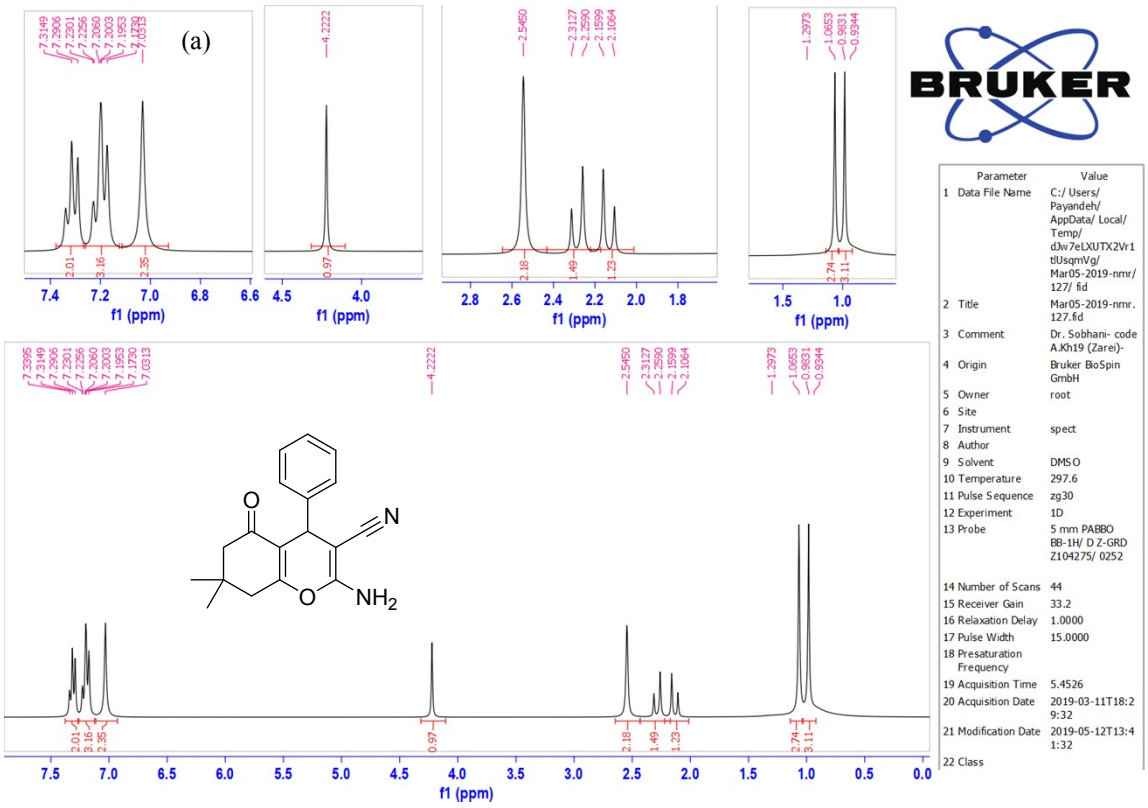
2-Amino-4-(butyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S18, Table 2, entry 26): IR (KBr) V_{max}/cm^{-1}: 3337, 3275 (NH_2), 2180 (CN), 1678 (CO),^{1}H NMR (300 MHz, $CDCl_3$); δ 0.89 (t, *J* = 6.7 Hz, 3 H), 1.12 (s, 3 H), 1.13 (s, 3 H), 1.17-1.38 (m, 4 H), 1.51-1.72 (m, 2 H), 2.30 (bs, 2 H), 2.38 (s, 2 H), 3.42-3.45 (m, 1 H), 4.58 (s, 2 H) ppm.

2-Amino-4-(heptyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S19, Table 2, entry 28): IR (KBr) V_{max}/cm^{-1}: 3387, 3322 (NH_2), 2187 (CN), 1682 (CO), ^{1}H NMR (300 MHz, $CDCl_3$); δ .87 (t, *J* = 6.4 Hz, 3 H), 1.10 (s, 3 H), 1.12 (s, 3 H), 1.25 (bs, 10 H), 1.45-1.68 (m, 2 H), 2.29 (s, 2 H), 2.37 (s, 2 H), 3.40-3.43 (m, 1 H), 4.67 (s, 2 H) ppm.

2-Amino-5-oxo-4-(phenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Figure S20, Scheme 3): IR (KBr) V_{max}/cm^{-1}: 3328, 3173 (NH_2), 2192 (CN), 1652 (CO), ^{1}H NMR (300 MHz, DMSO); δ 1.84-2.02 (m, 2 H), 2.21-2.39 (m, 2 H), 2.50-2.69 (m, 2 H), 4.22 (s, 1 H), 7.02 (s, 2 H), 7.17-7.23 (m, 3 H), 7.28-7.33 (m, 2 H) ppm.

Methyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-chromene-3-carboxylate (Figure S21, Scheme 3): IR (KBr) V_{max}/cm^{-1}: 3407, 3332 (NH_2), 2192 (CN), 1691(CO), ^{1}H NMR (300 MHz, DMSO); δ 1.04 (s, 3H), 2.34 (s, 3 H), 4.33 (s, 1 H), 6.93 (s, 2H), 7.18 (d, *J* = 6.7 Hz, 2 H), 7.24 (d, *J* = 7.0 Hz, 1 H), 7.33 (t, *J* = 7.3 Hz, 2 H) ppm.

3-Amino-1-phenyl-1H-benzo[f]chromene-2-carbonitrile (Figure S22, Scheme 3): IR (KBr) V_{max}/cm^{-1}: 3430, 3328 (NH_2), 2184 (CN), 1633 (CO), ^{1}H NMR (300 MHz, DMSO); δ 5.31 (s, 1 H), 6.99 (s, 2 H), 7.16-7.28 (m, 5 H), 7.36 (d, *J* = 8.9 Hz, 1 H), 7.42-7.46 (m, 2 H), 7.84-7.97 (m, 3 H) ppm.



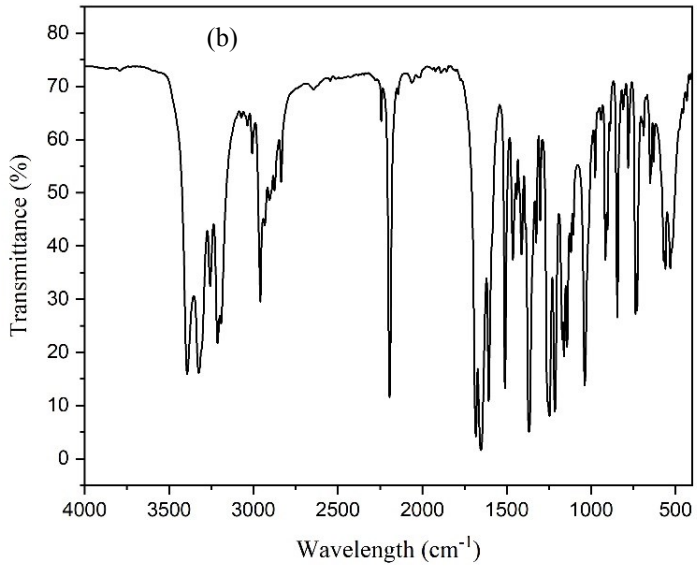


Figure S1: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

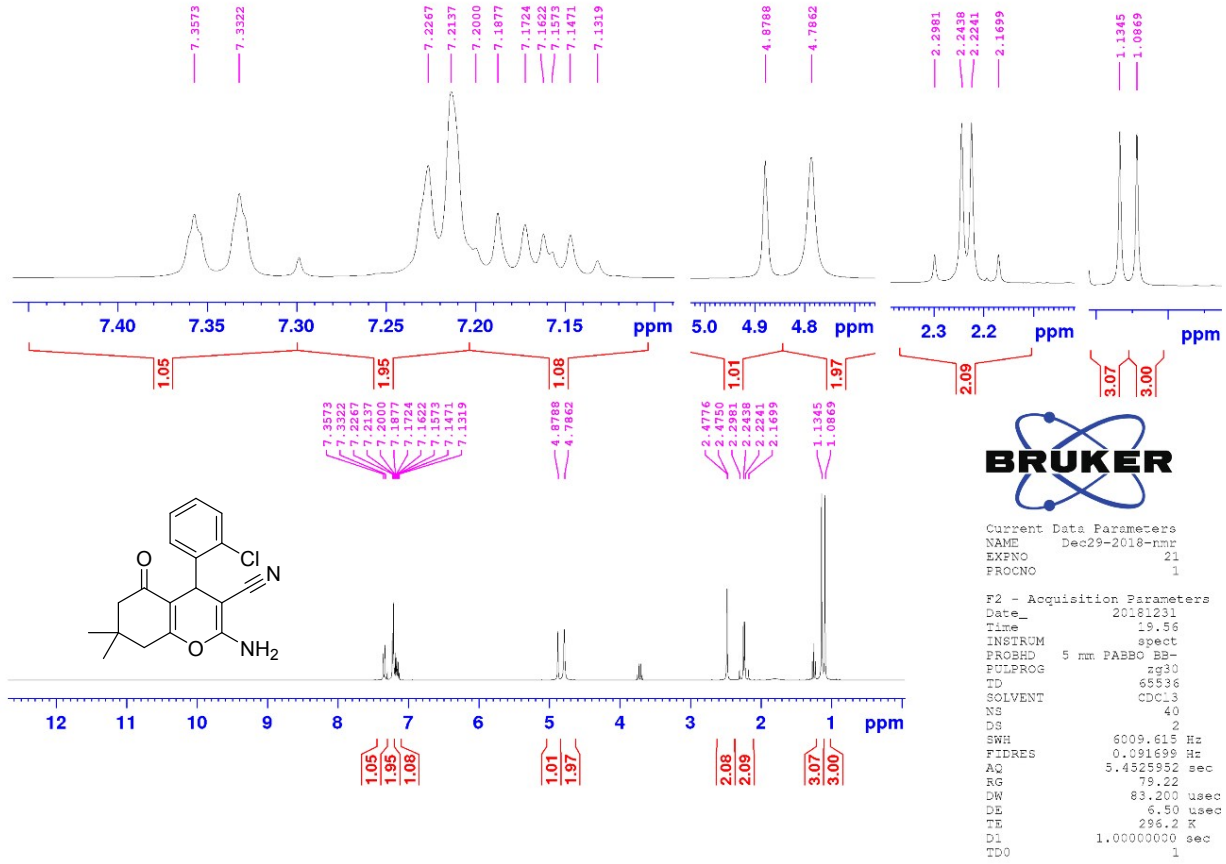


Figure S2: 1H NMR spectrum of 2-amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

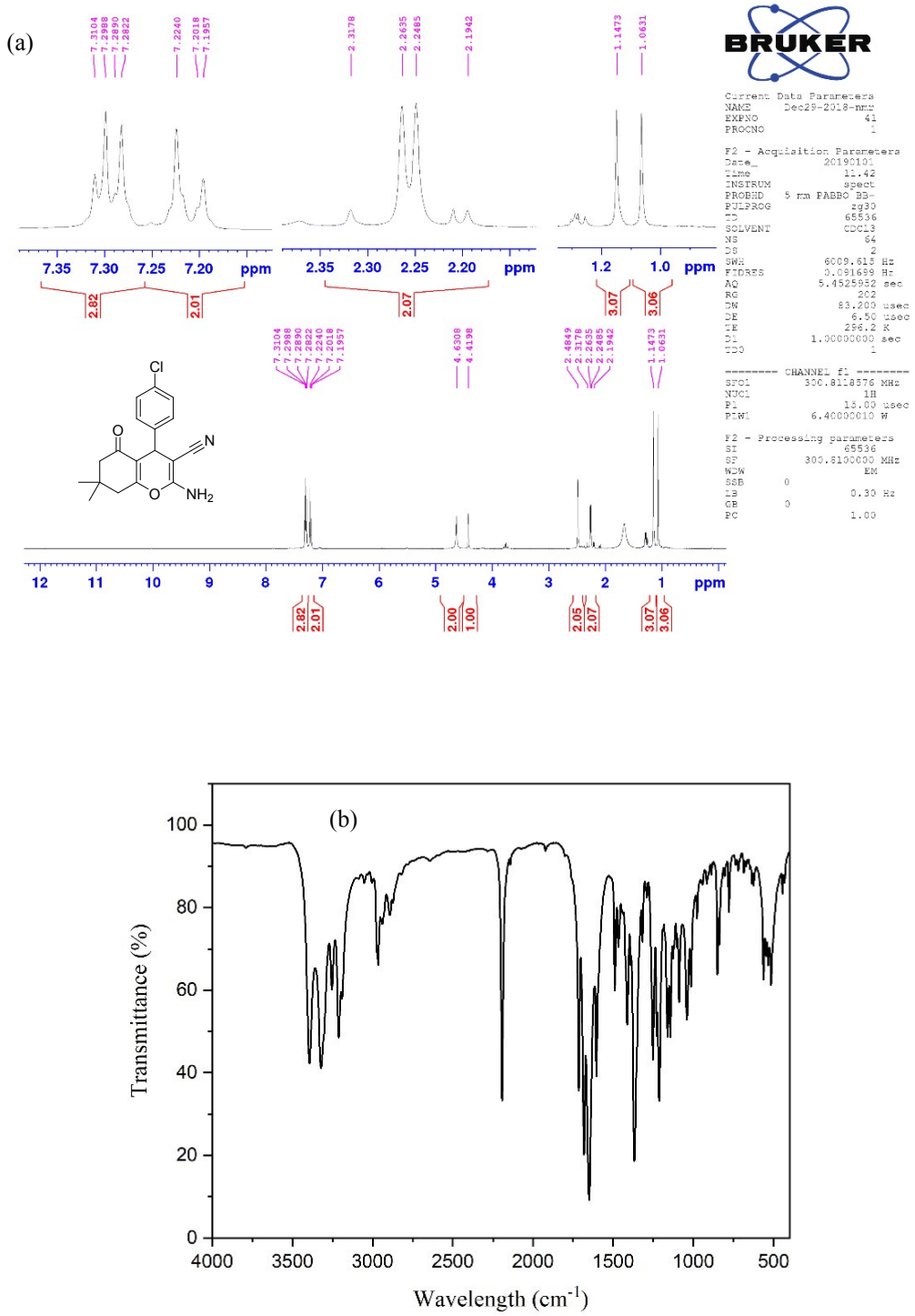


Figure S3: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

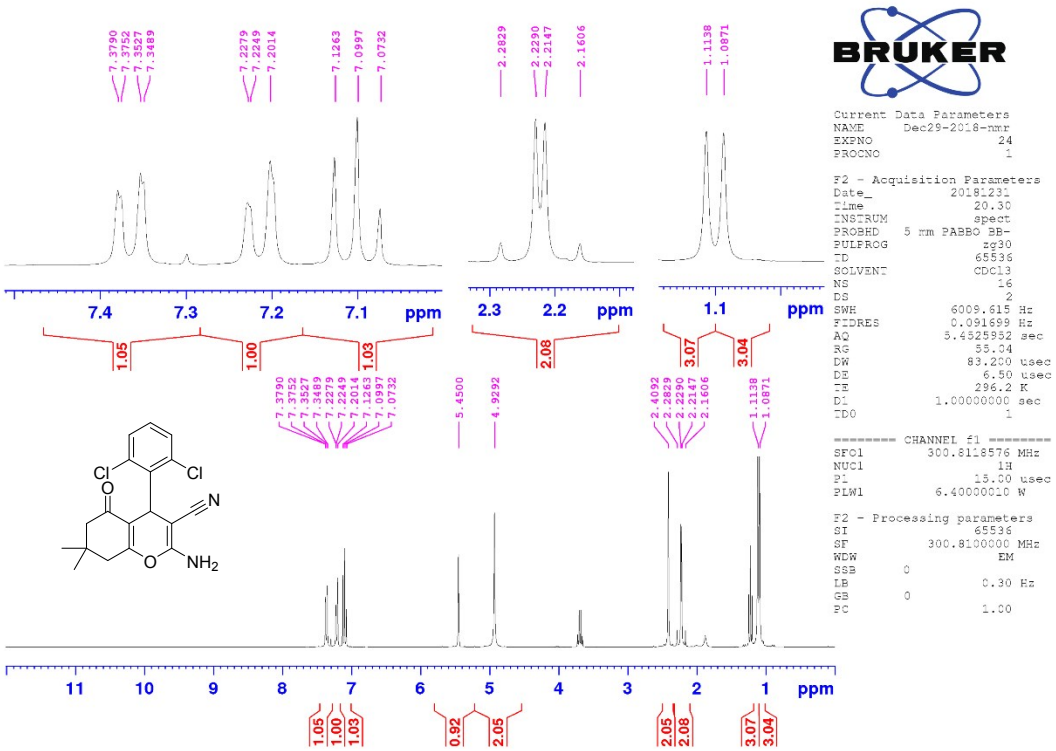
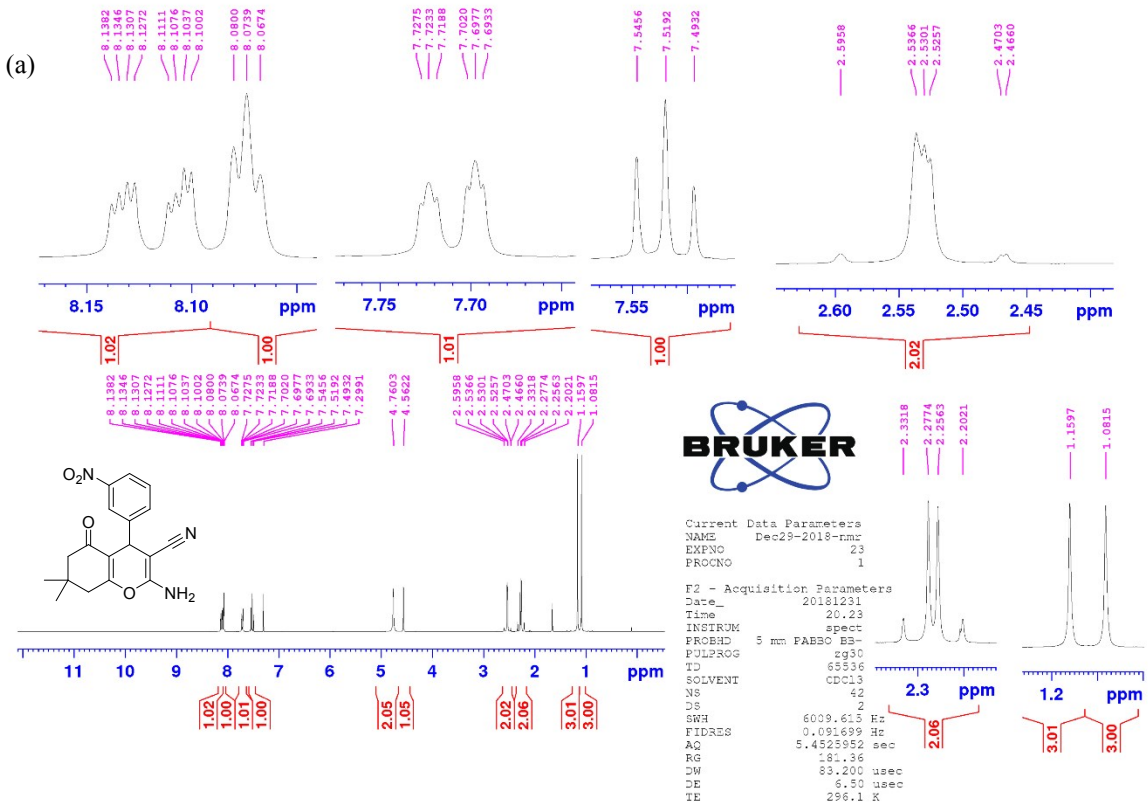


Figure S4: ^{1}H NMR spectrum of 2-amino-4-(2,6-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.



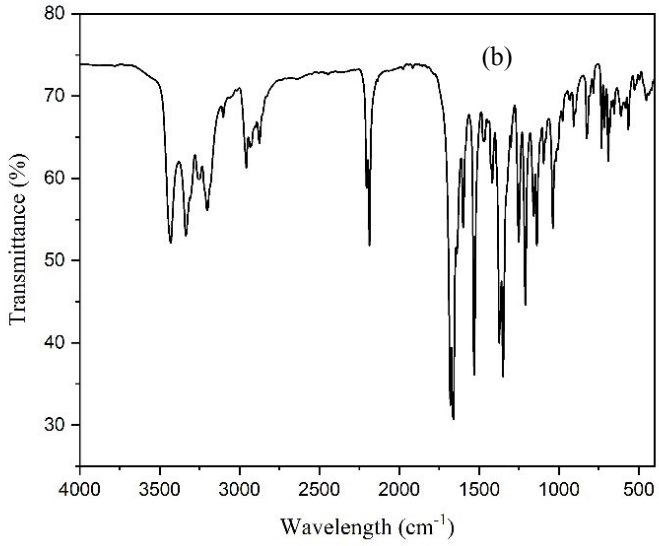
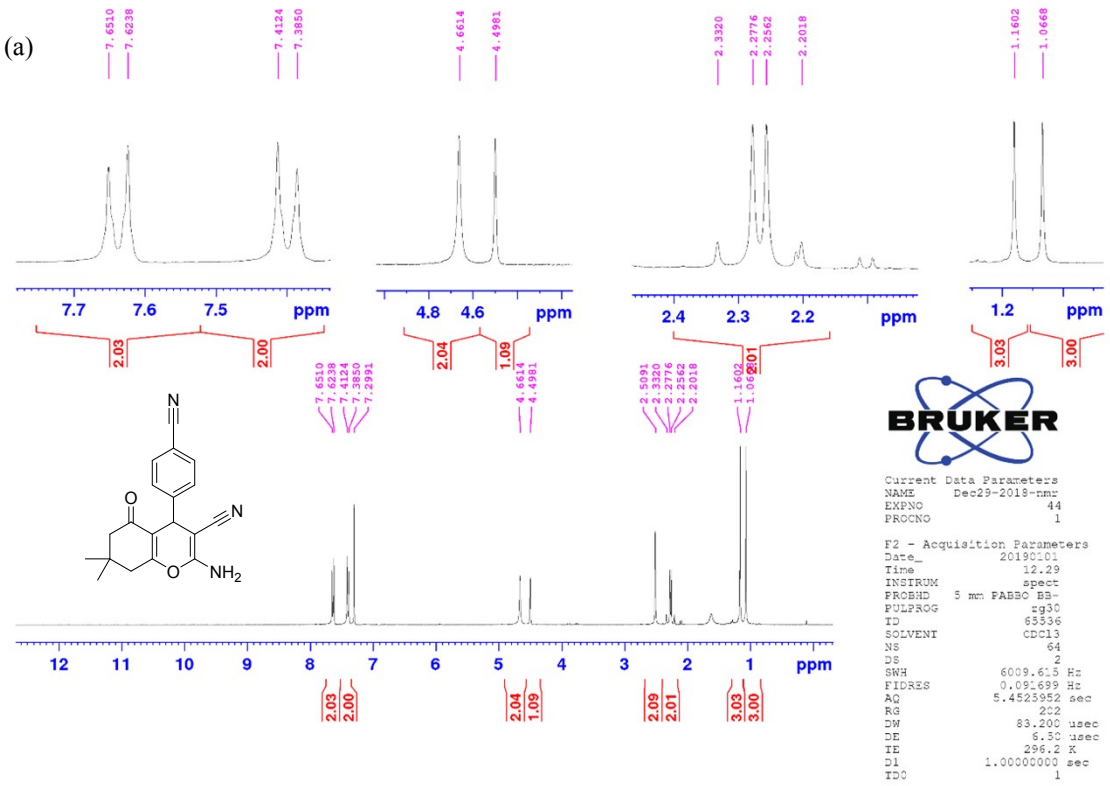


Figure S5: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(3-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.



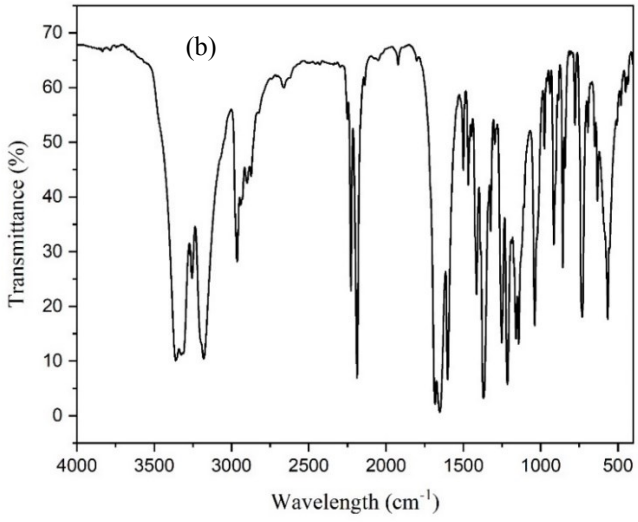
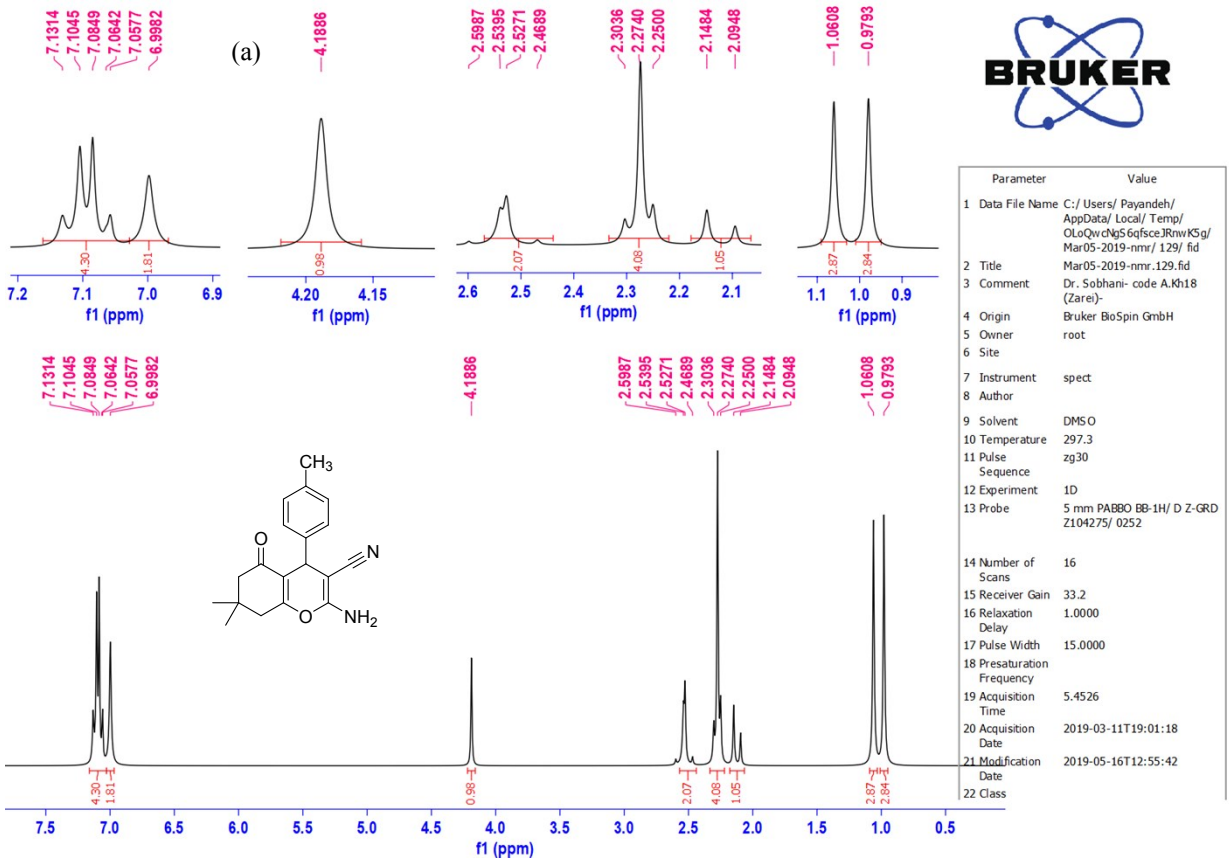


Figure S6: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.



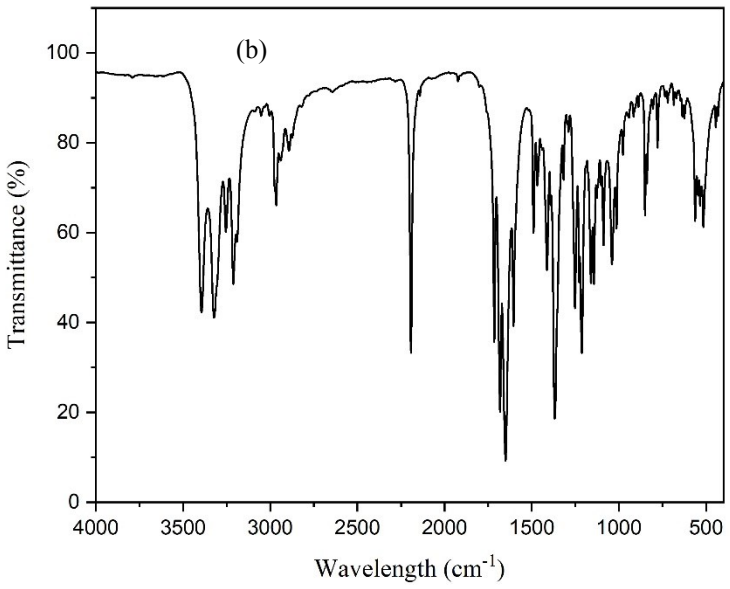
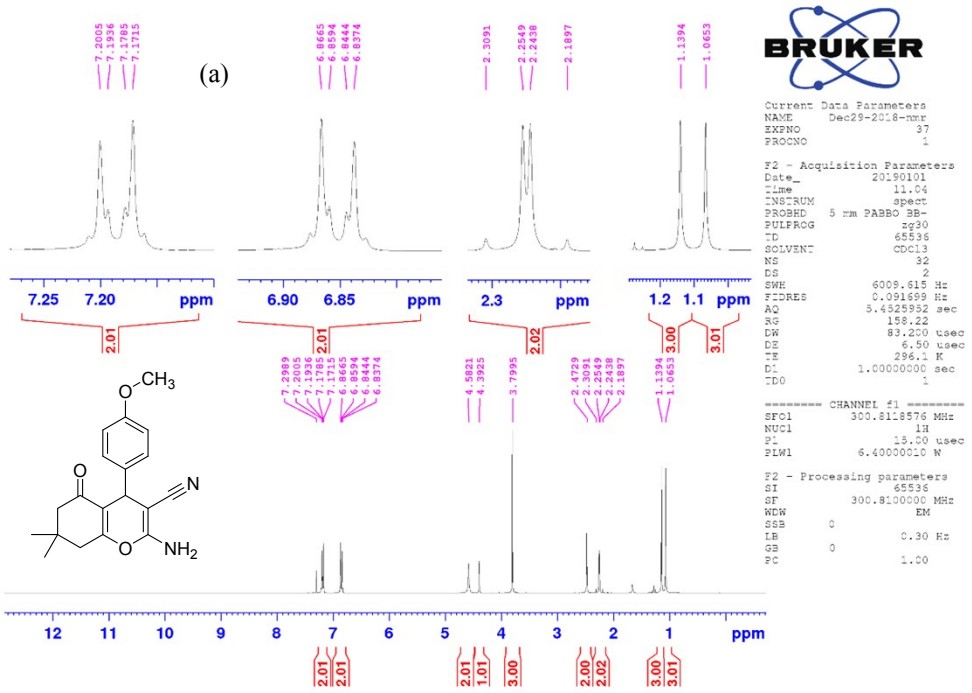


Figure S7: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(*p*-tolyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.



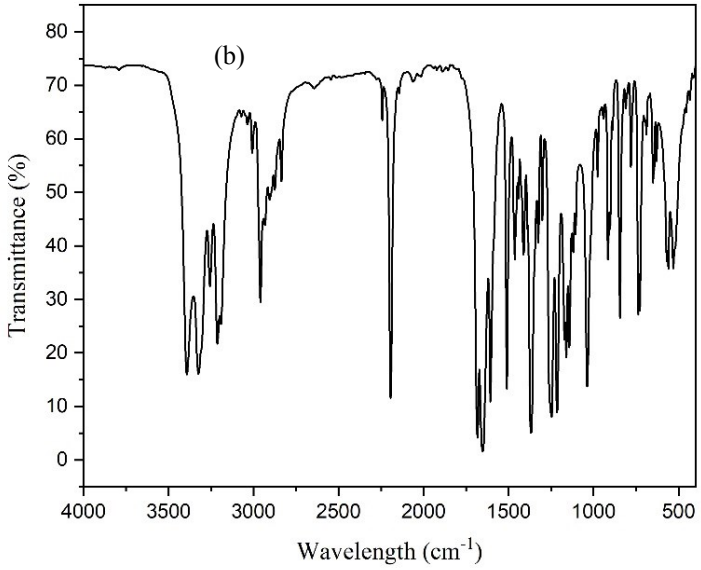


Figure S8: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

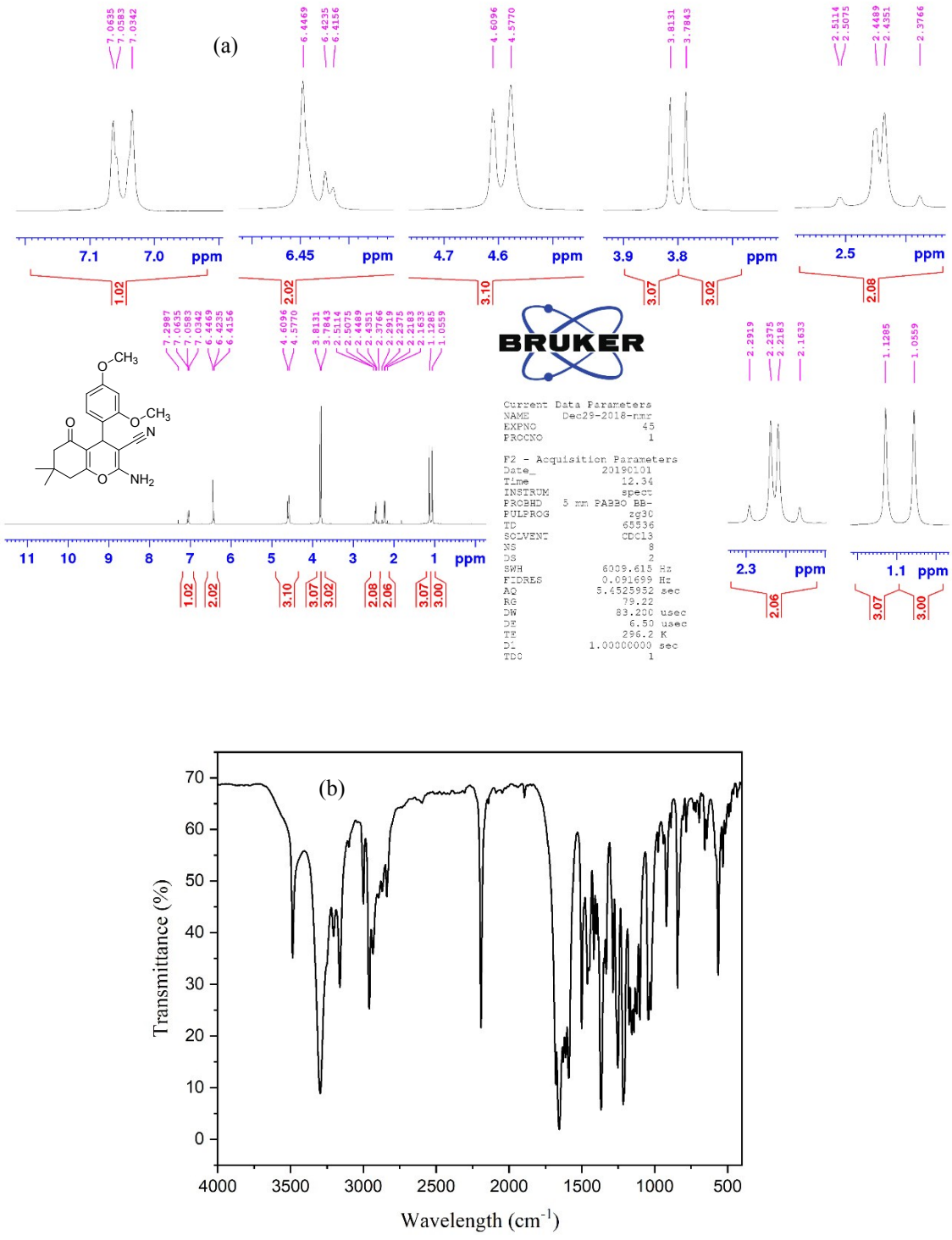
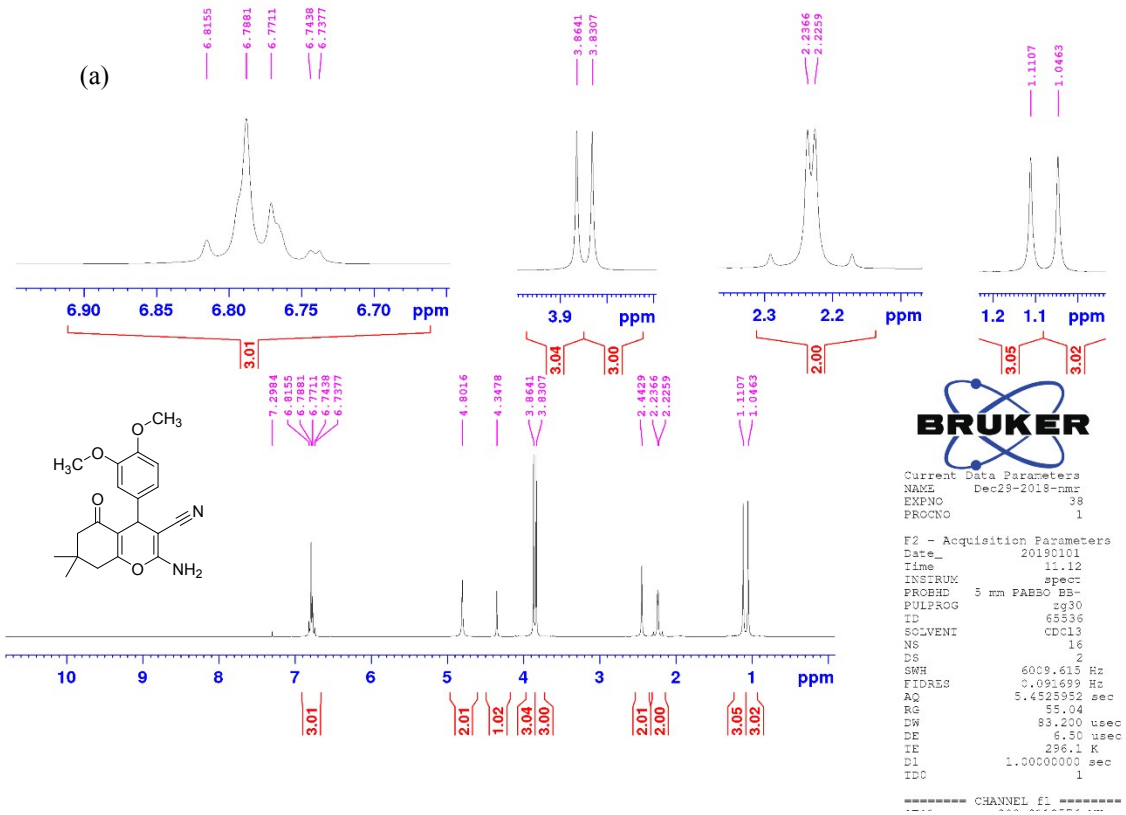


Figure S9: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(2,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.



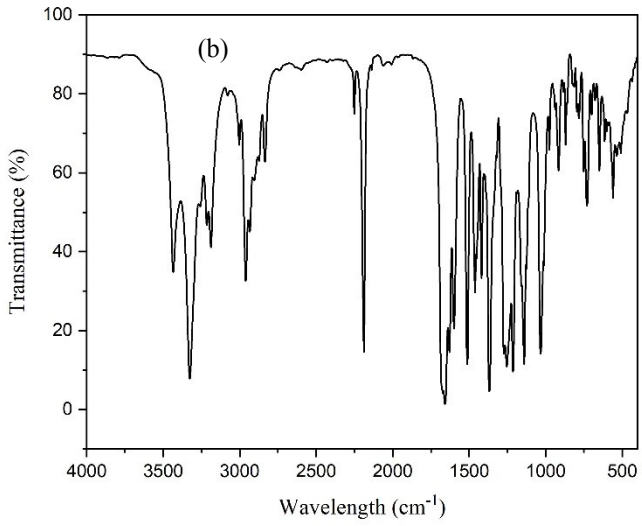
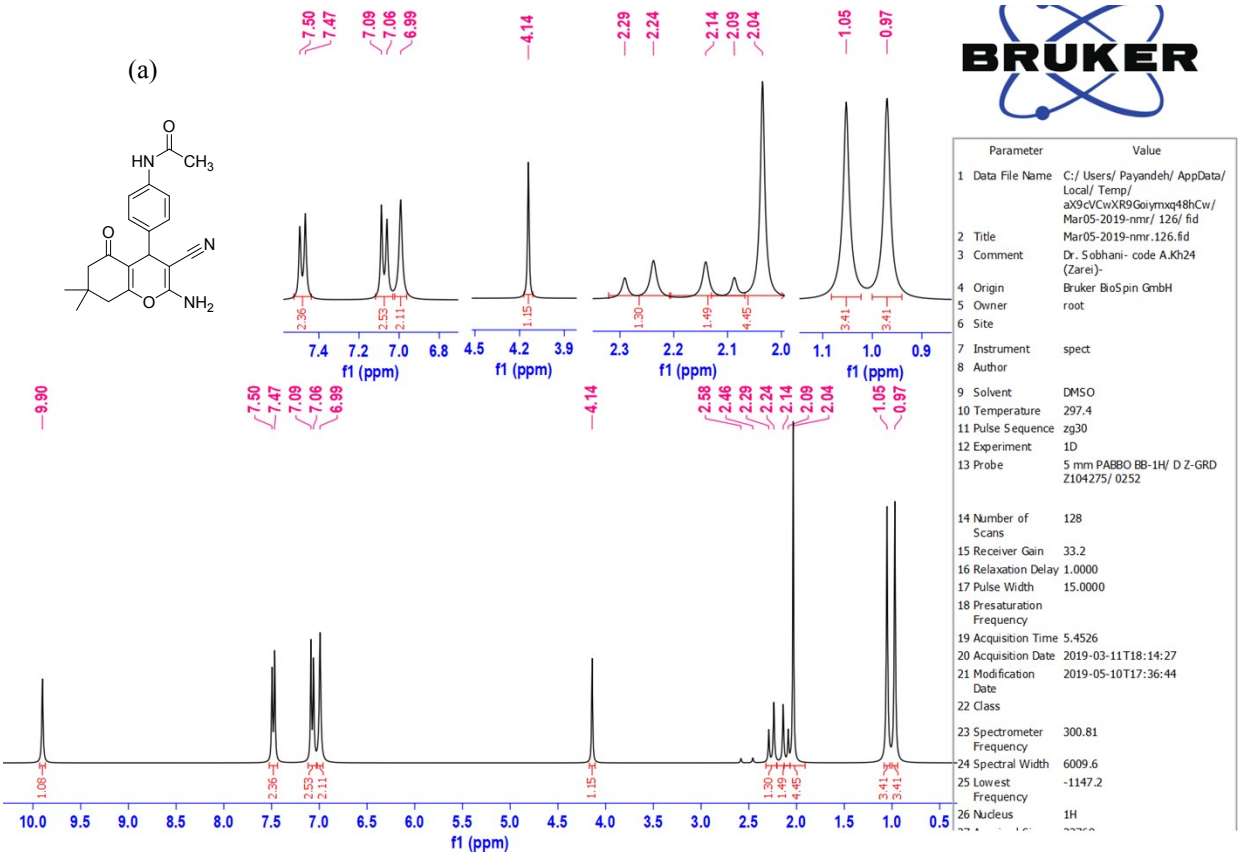


Figure S10: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(3,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.



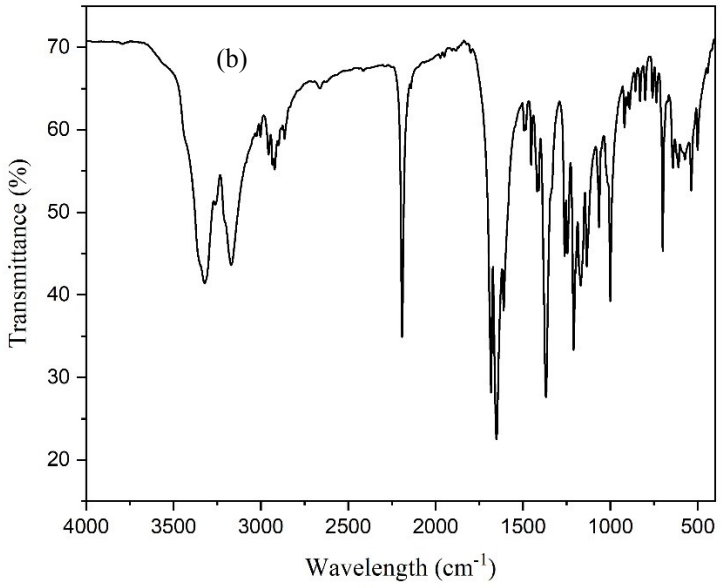


Figure S11: a) ^{1}H NMR and b) FT-IR spectra of *N*-(4-(2-amino-3-cyano-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromen-4yl)phenyl) acetamide.

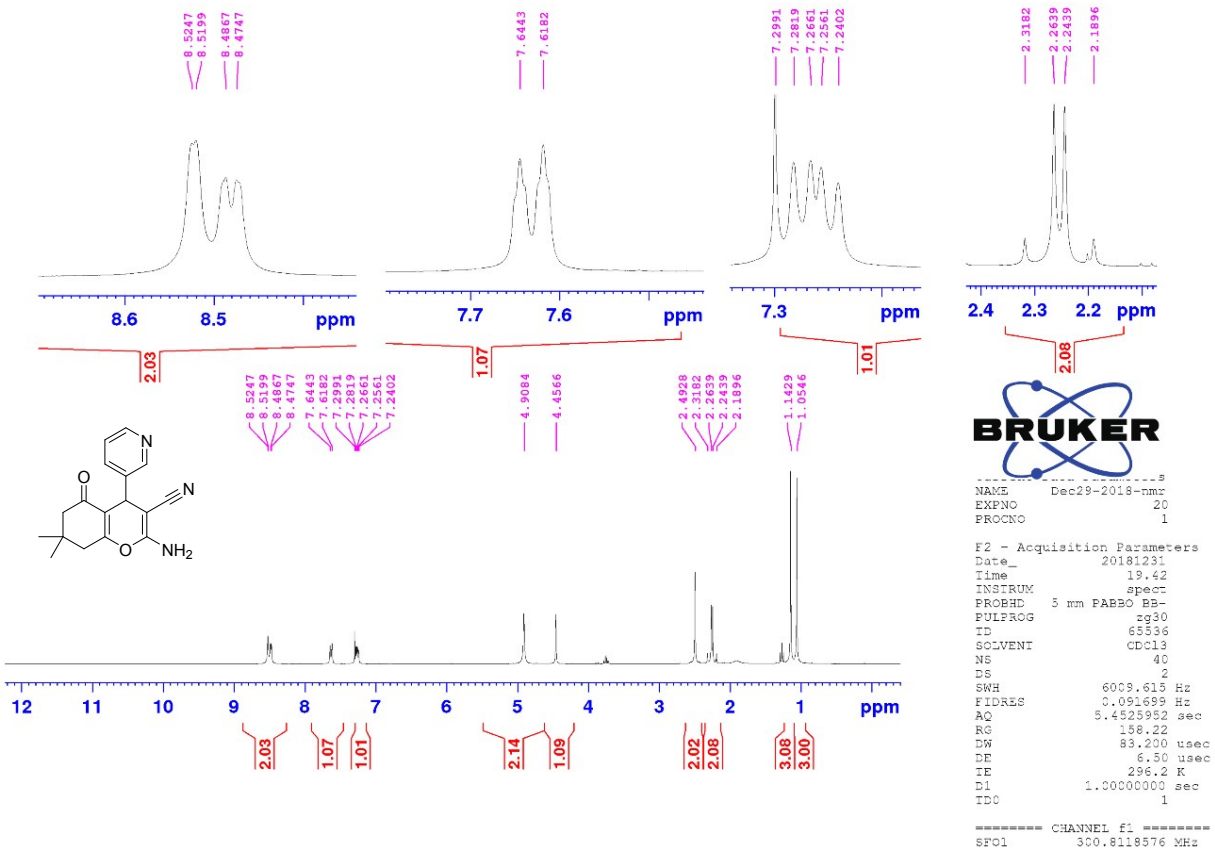


Figure S12: ^{1}H NMR spectrum of 2-amino-4-(3-pyridyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

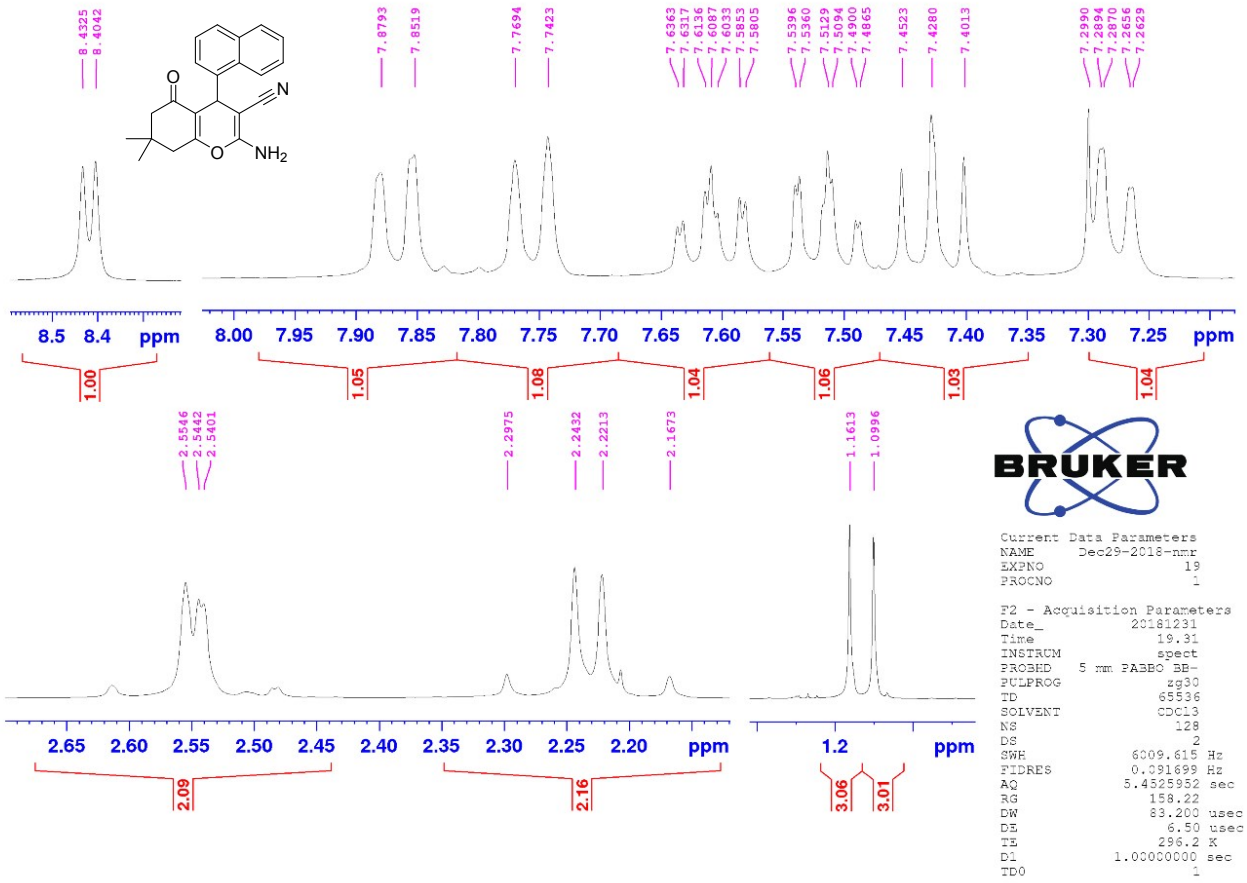


Figure S13: ^{1}H NMR spectrum of 2-amino-4-(naphthalen-1-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

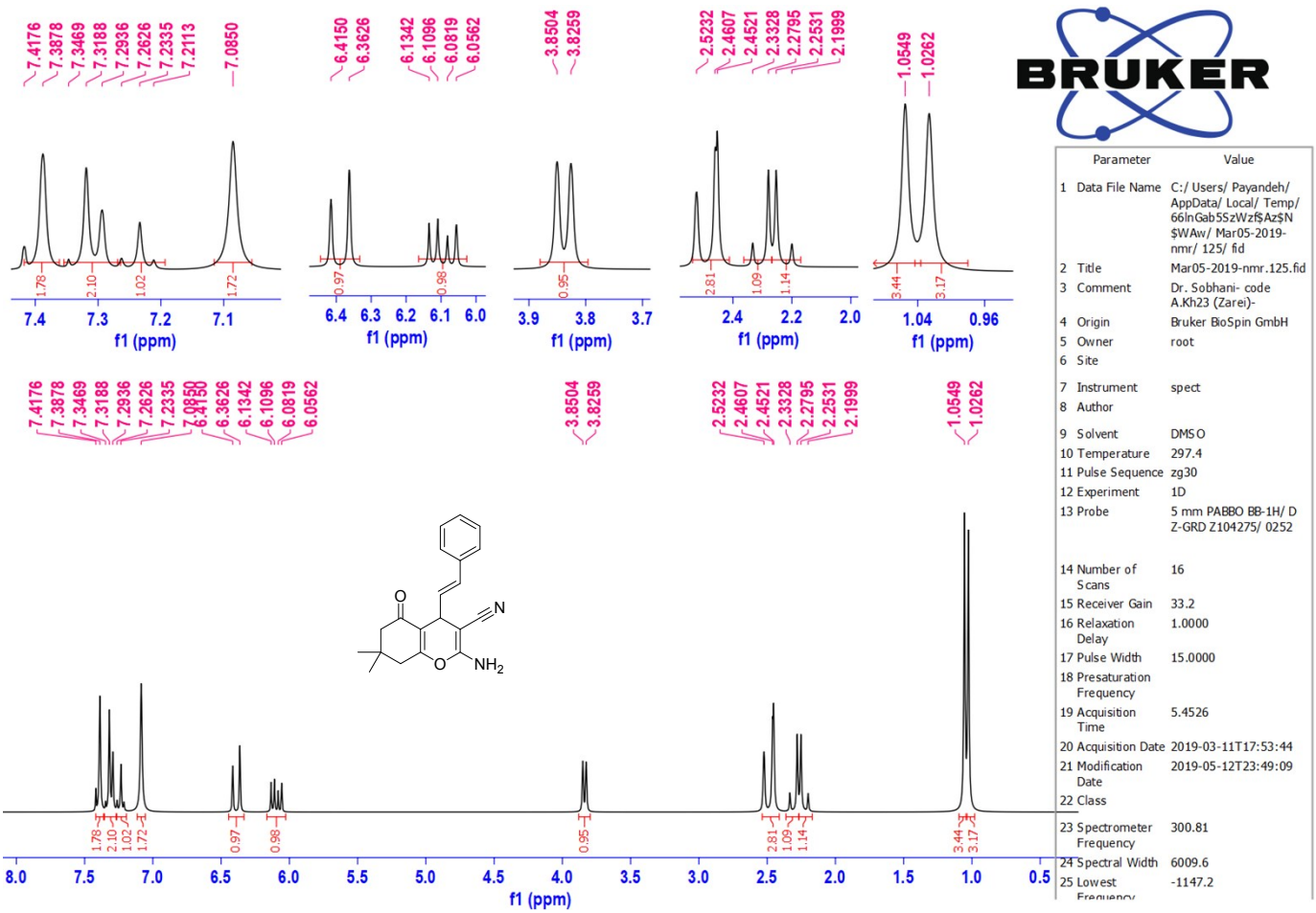


Figure S14: ^{1}H NMR spectrum of 2-amino-7,7-dimethyl-5-oxo-4-styryl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

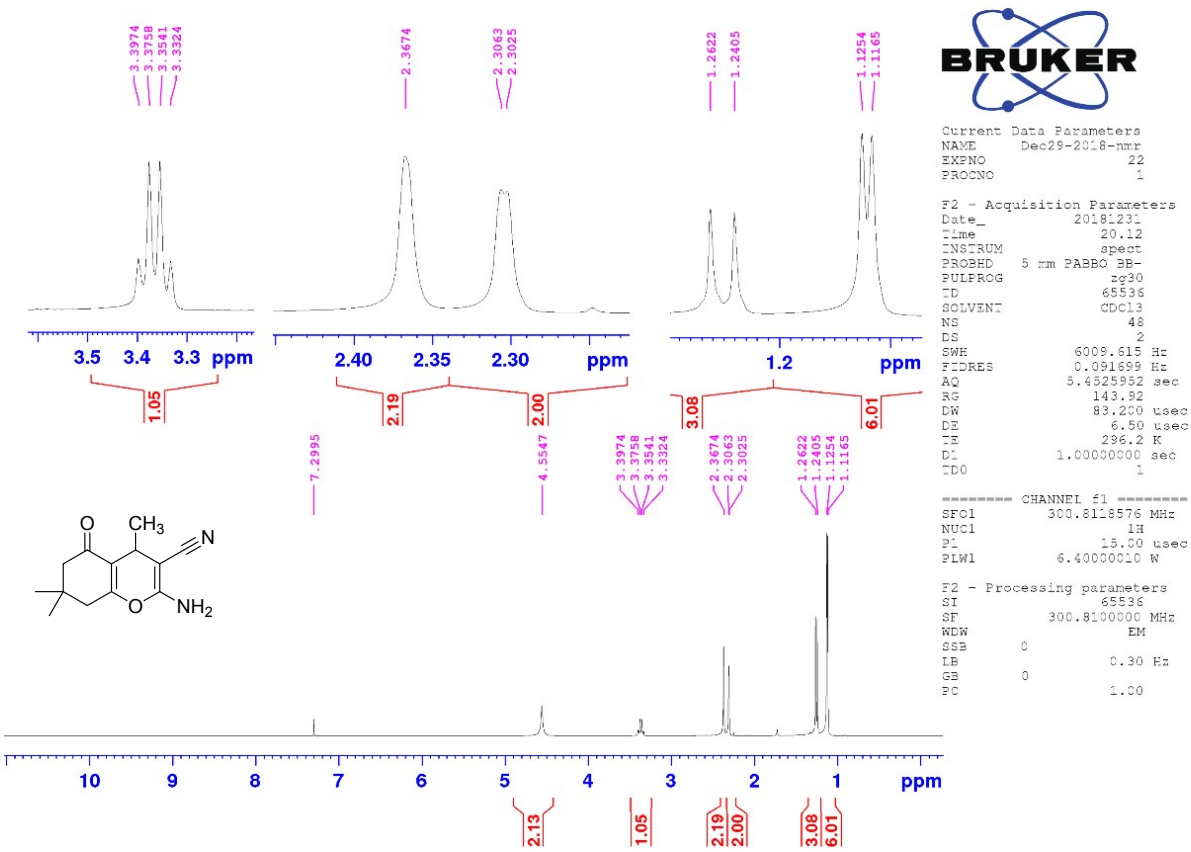
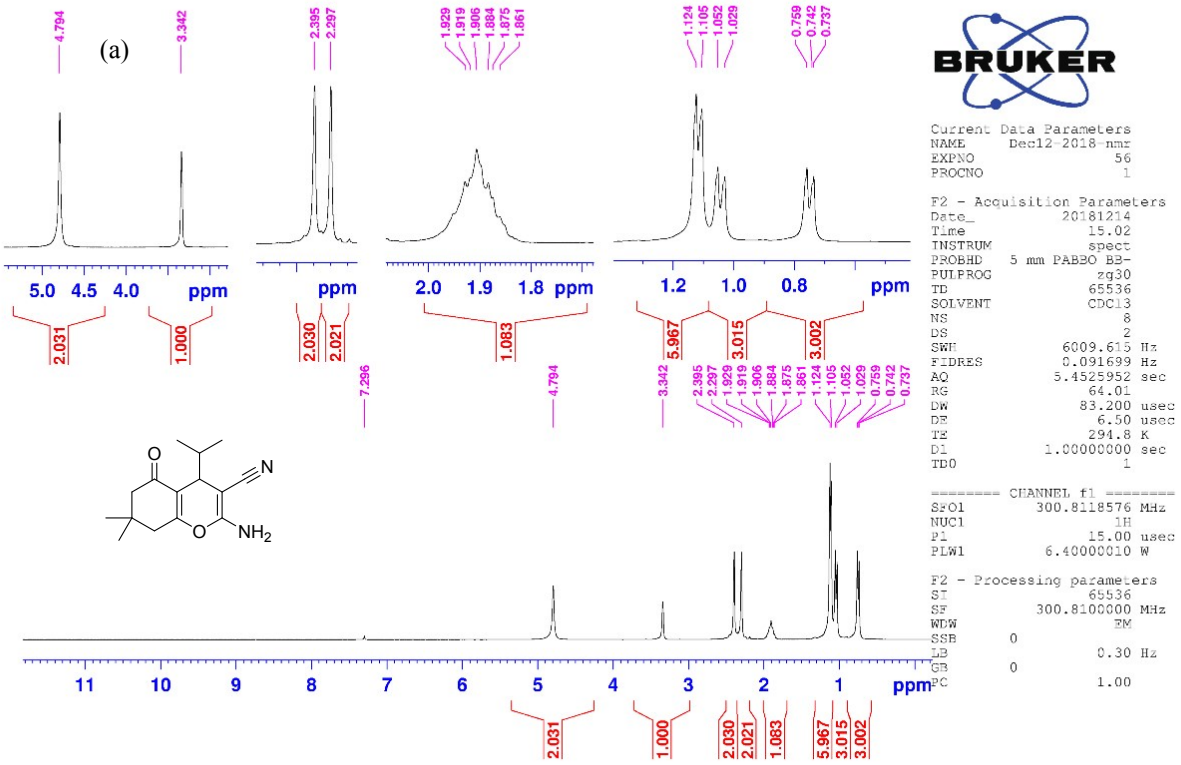


Figure S15: ^{1}H NMR spectrum of 2-Amino-4,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

(a)



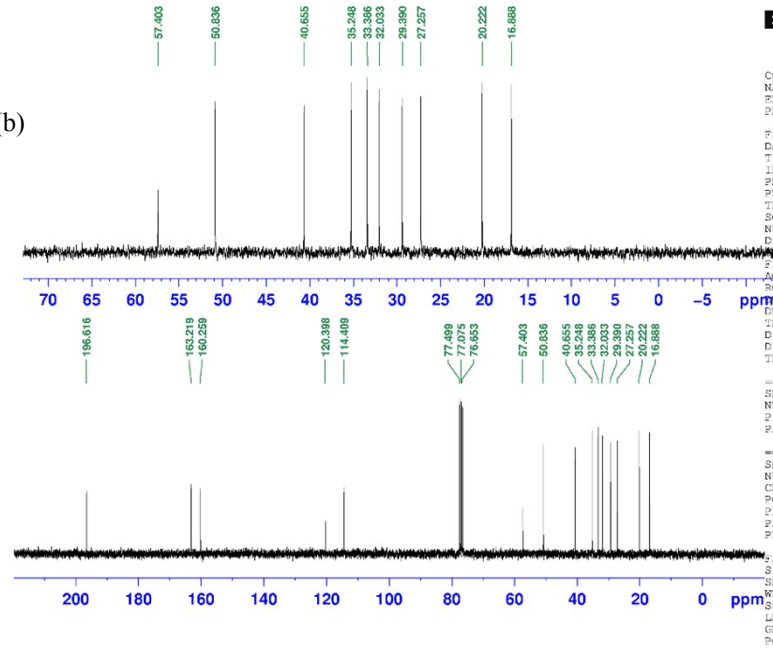

```
Current Data Parameters
NAME      Dec12-2018-nmr
EXPNO                56
PROCNO                1

F2 - Acquisition Parameters
Date_          20181214
Time              15.02
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6009.615 Hz
FIDRES        0.091699 Hz
AQ            5.4525952 sec
RG                64.01
DW               83.200 usec
DE                6.50 usec
TE                294.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         300.8118576 MHz
NUC1                 1H
P1                15.00 usec
PLW1          6.40000010 W

F2 - Processing parameters
SI                65536
SF           300.8100000 MHz
WDW                  EM
SSB          0
LB                0.30 Hz
GB           0
PC                1.00
```

(b)




```
Current Data Parameters
NAME      Dec15-2018-nmr
EXPNO                24
PROCNO                1

F2 - Acquisition Parameters
Date_          20181216
Time               8.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   80
DS                    4
SWH           18115.941 Hz
FIDRES        0.276427 Hz
AQ            1.8087935 sec
RG                  202
DW               27.600 usec
DE                6.50 usec
TE                297.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         75.6462982 MHz
NUC1                 13C
P1                10.00 usec
PLW1         30.00000000 W

======== CHANNEL f2 ========
SFO2         300.8112032 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2          6.40000010 W
PLW12         0.17778000 W
PLW13         0.14399999 W

F2 - Processing parameters
SI                32768
SF           75.6387350 MHz
WDW                  EM
SSB          0
LB                1.00 Hz
GB           0
PC                1.40
```

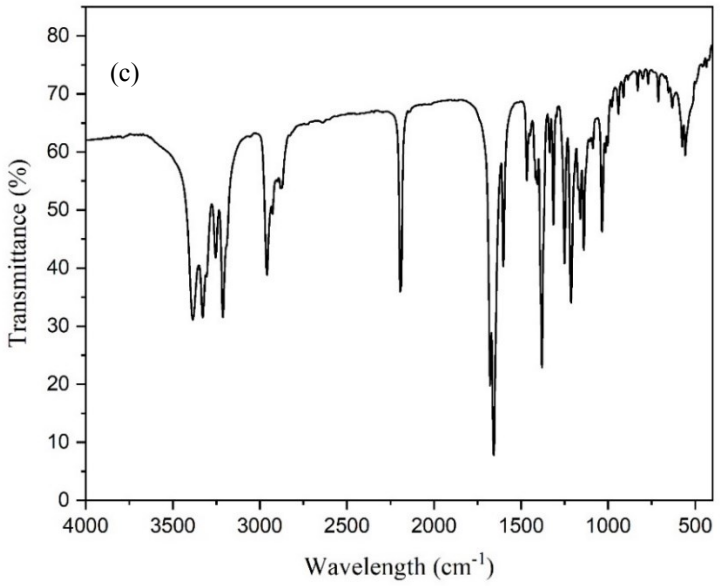
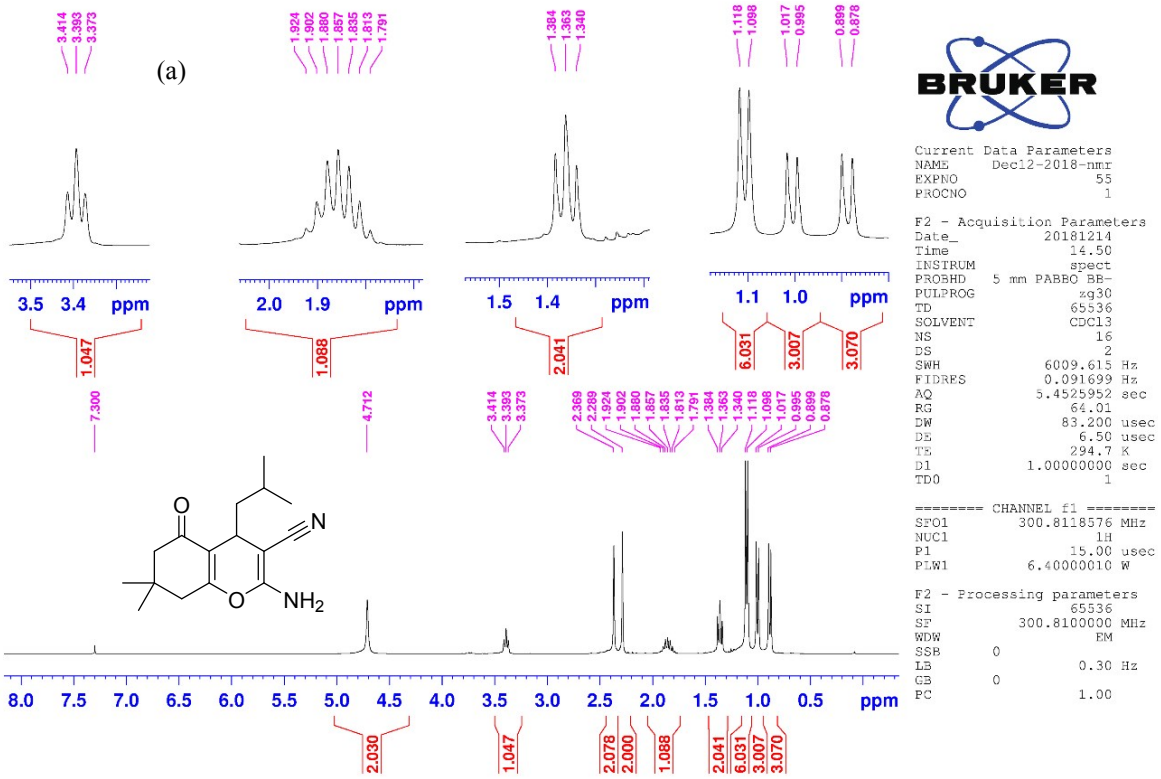
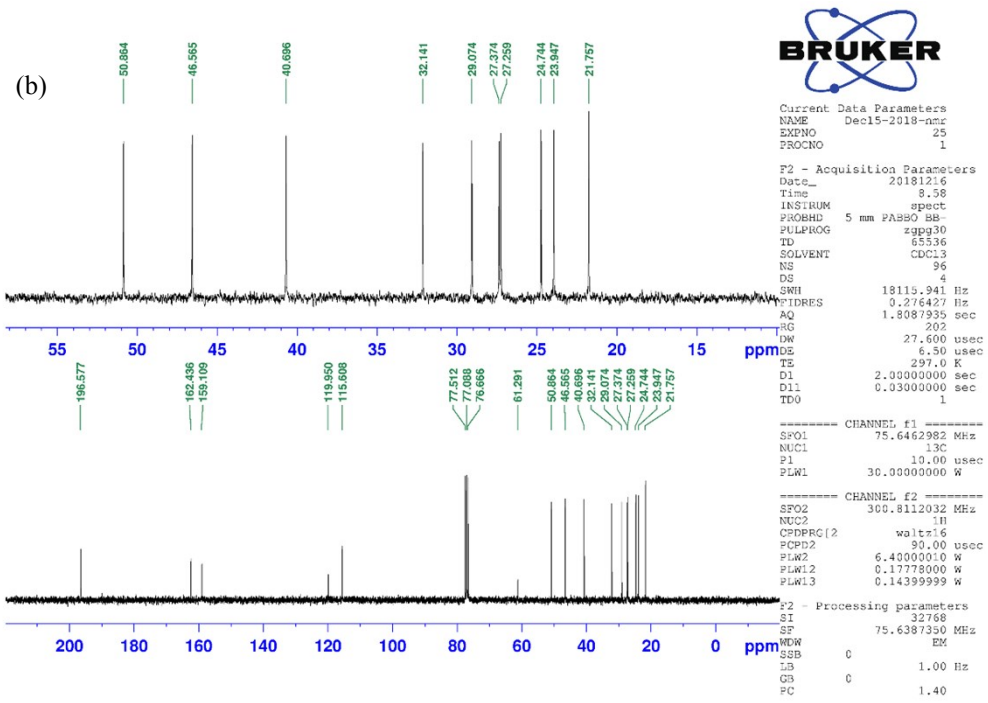


Figure S16: a) ^{1}H NMR b) ^{13}C NMR and c) FT-IR spectra of 2-amino-4-(*iso*-propyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.





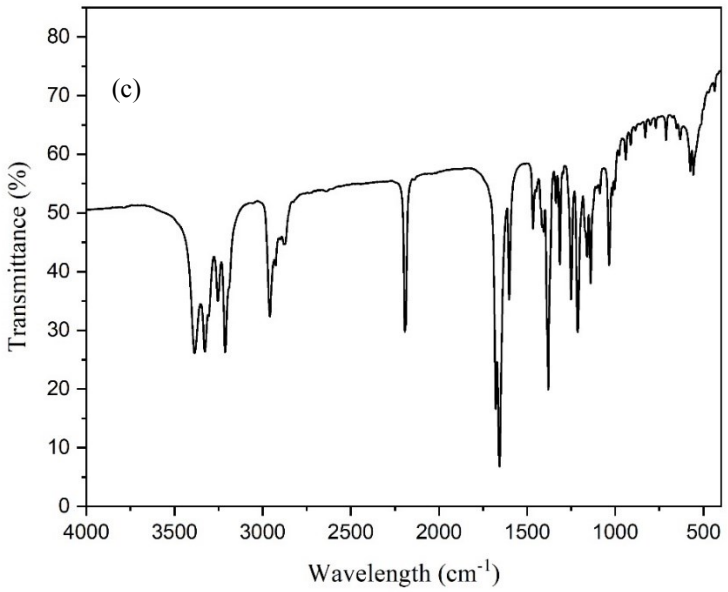


Figure S17: a) ^{1}H NMR b) ^{13}C NMR and c) FT-IR spectra of 2-amino-4-(*iso*-butyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

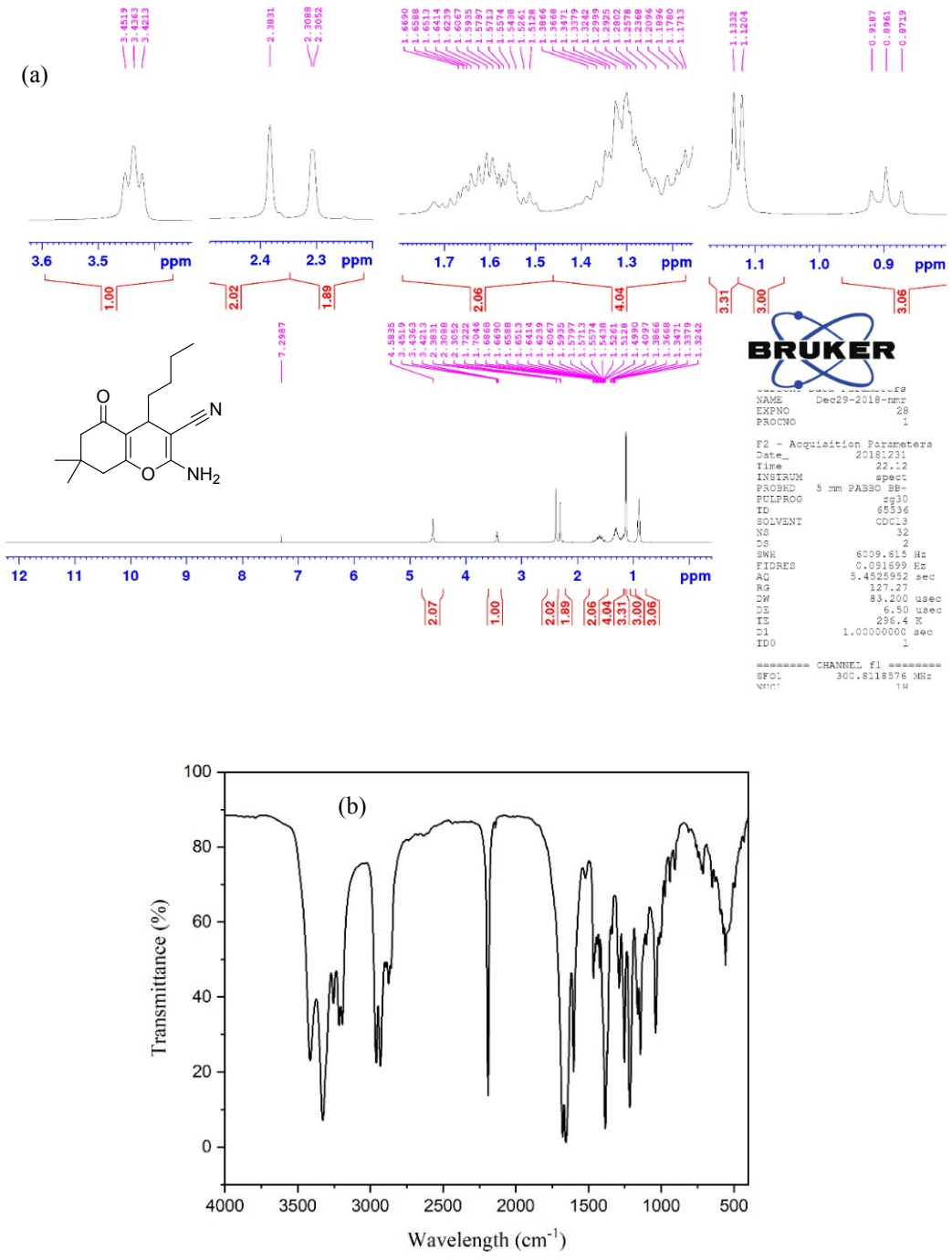


Figure S18: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(butyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

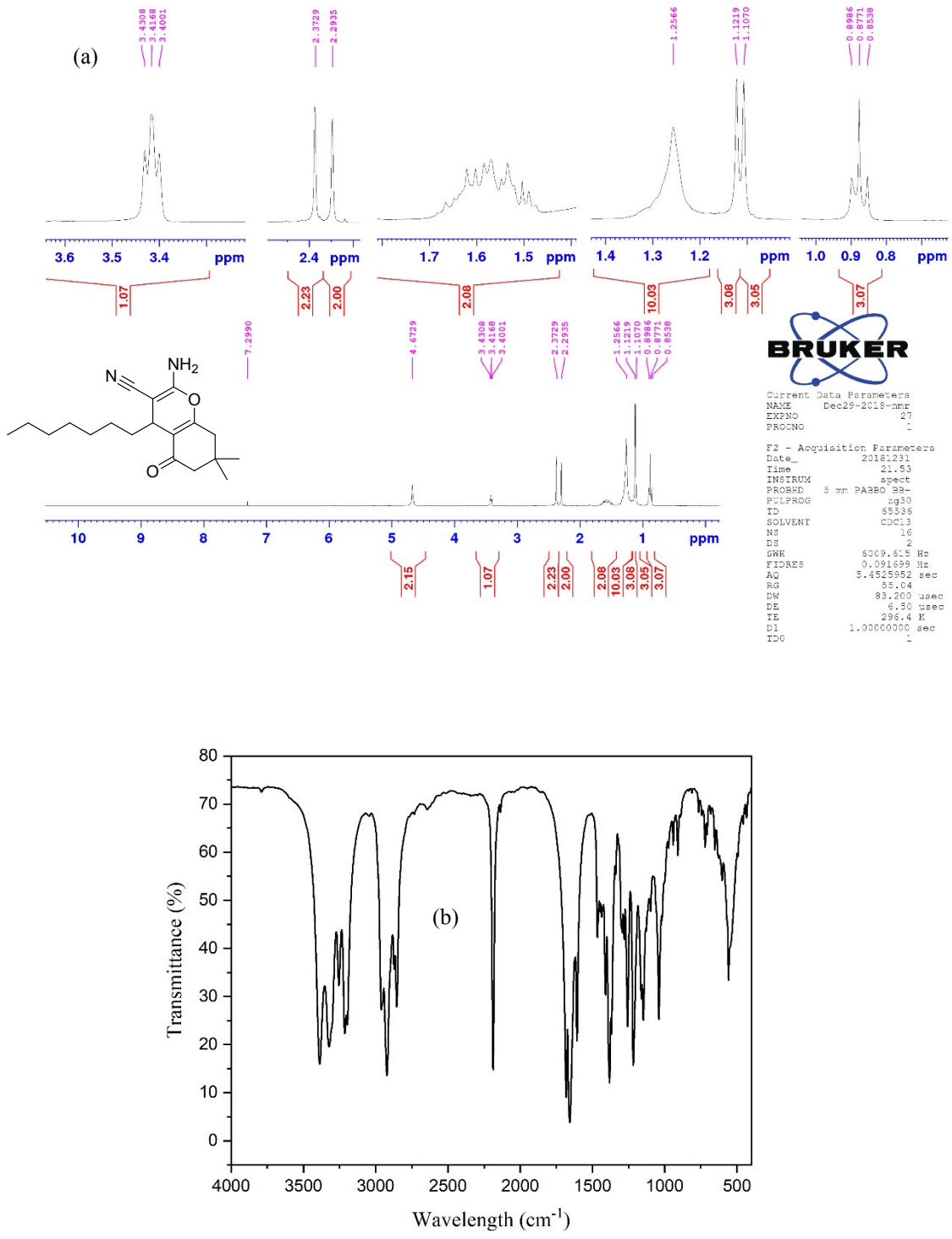
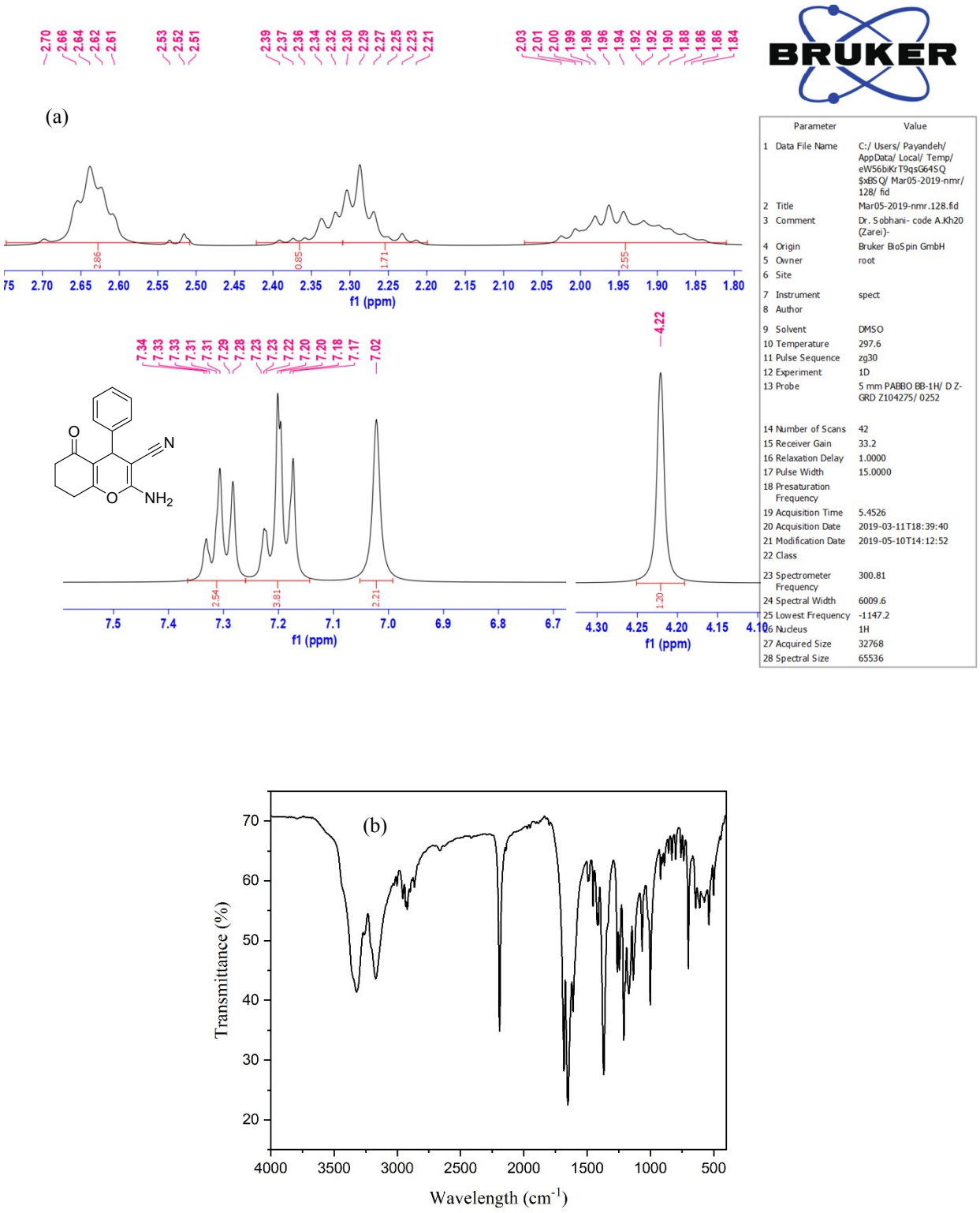


Figure S19: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-4-(heptyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.



	Parameter	Value
1	Data File Name	C:/ Users/ Payandeh/ AppData/ Local/ Temp/ eW56biKrT9qsG64SQ $xBSQ/ Mar05-2019-nmr/ 128/ fid
2	Title	Mar05-2019-nmr.128.fid
3	Comment	Dr. Sobhani- code A.Kh20 (Zarei)-
4	Origin	Bruker BioSpin GmbH
5	Owner	root
6	Site	
7	Instrument	spect
8	Author	
9	Solvent	DMSO
10	Temperature	297.6
11	Pulse Sequence	zg30
12	Experiment	1D
13	Probe	5 mm PABBO BB-1H/ D Z-GRD Z104275/ 0252
14	Number of Scans	42
15	Receiver Gain	33.2
16	Relaxation Delay	1.0000
17	Pulse Width	15.0000
18	Presaturation Frequency	
19	Acquisition Time	5.4526
20	Acquisition Date	2019-03-11T18:39:40
21	Modification Date	2019-05-10T14:12:52
22	Class	
23	Spectrometer Frequency	300.81
24	Spectral Width	6009.6
25	Lowest Frequency	-1147.2
26	Nucleus	1H
27	Acquired Size	32768
28	Spectral Size	65536

Figure S20: a) ^{1}H NMR and b) FT-IR spectra of 2-amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile.

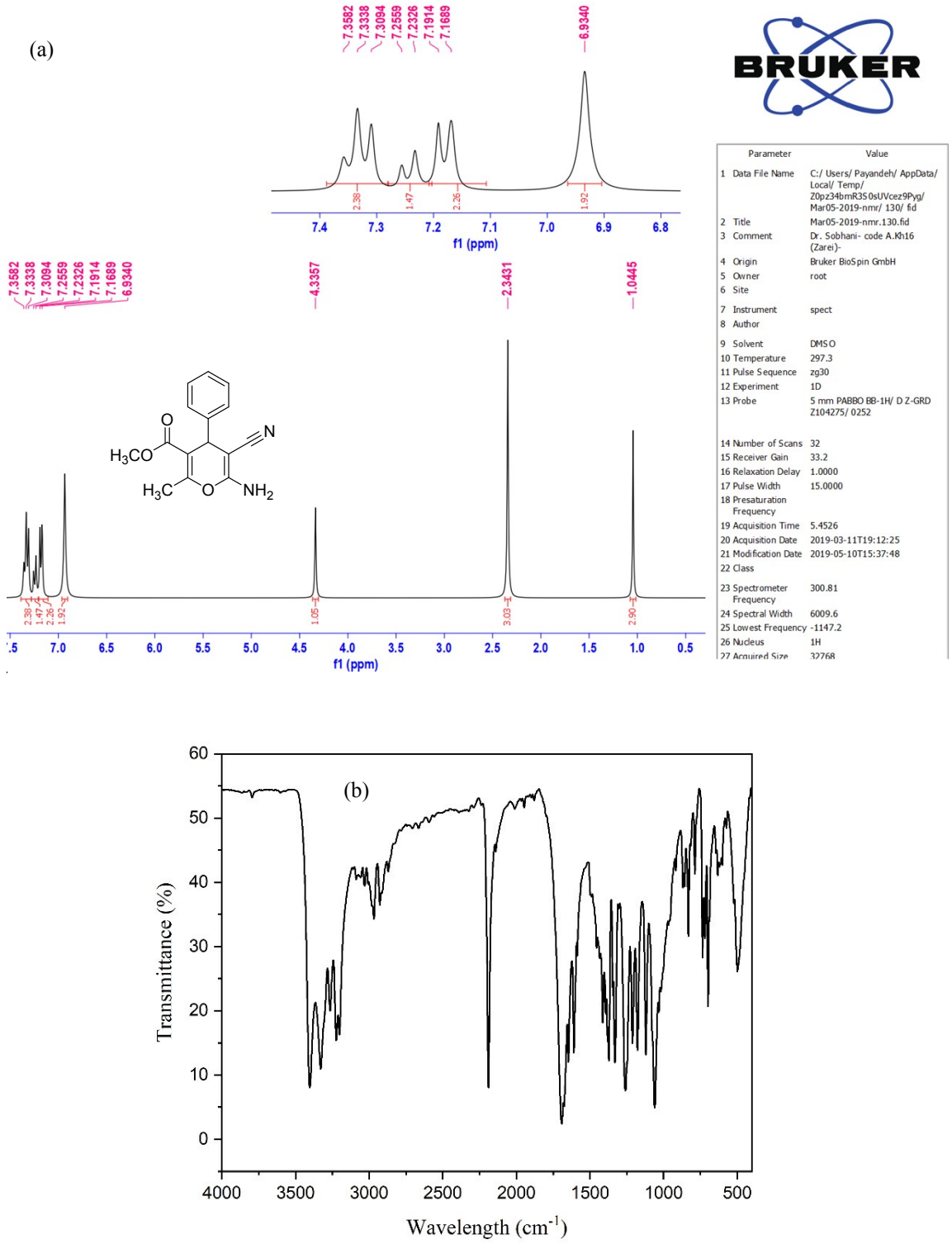
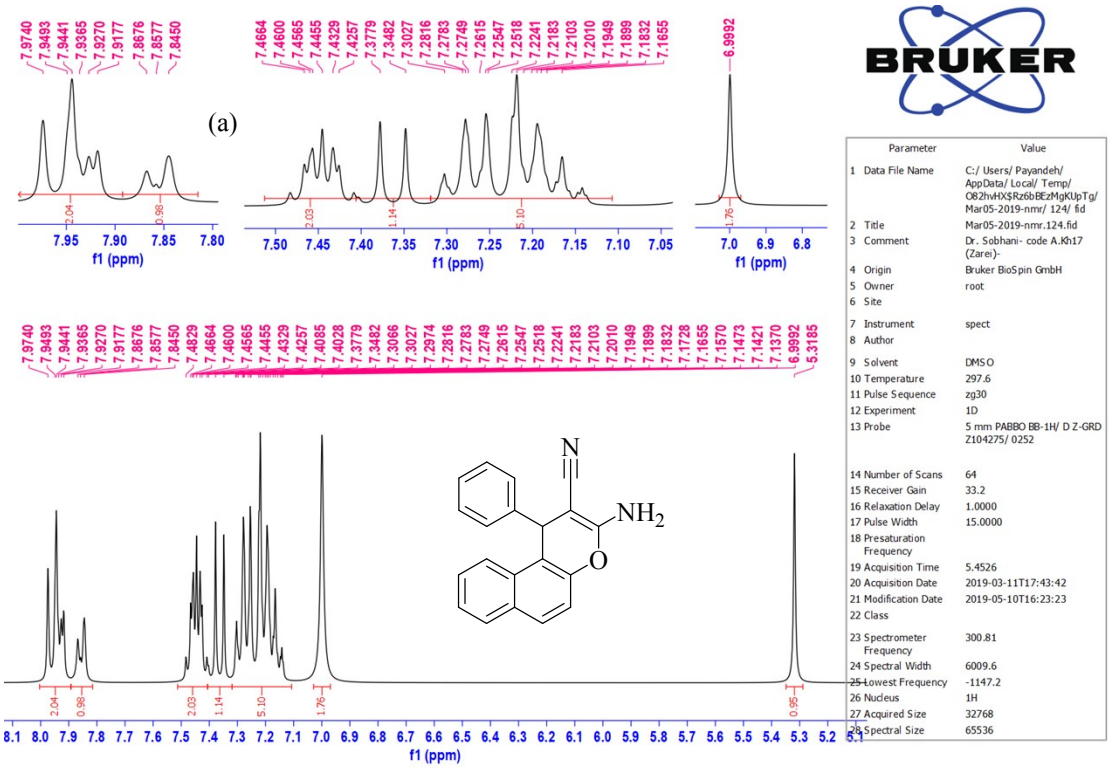


Figure S21: a) ^{1}H NMR and b) FT-IR spectra of methyl 6-amino-5-cyano-2-methyl-4-phenyl-4*H*-chromene-3-carboxylate.



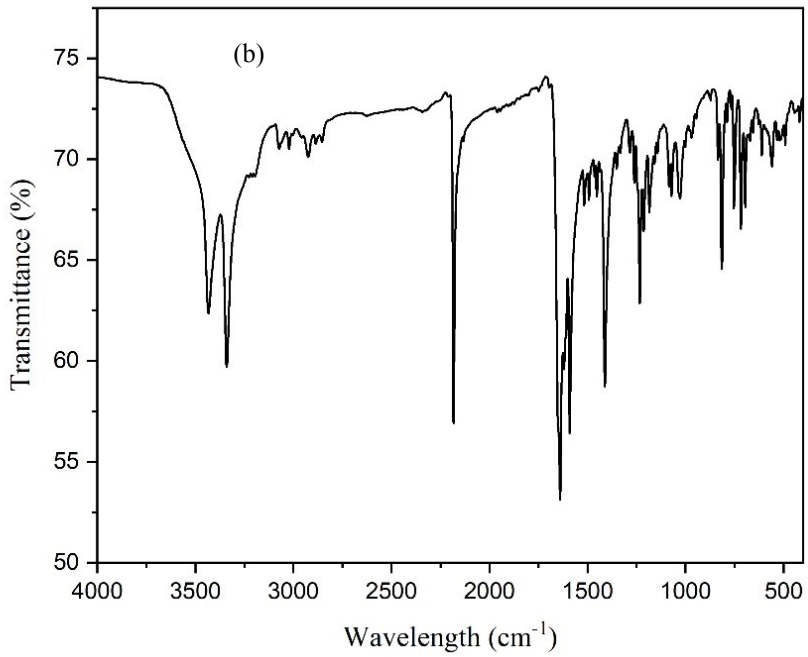
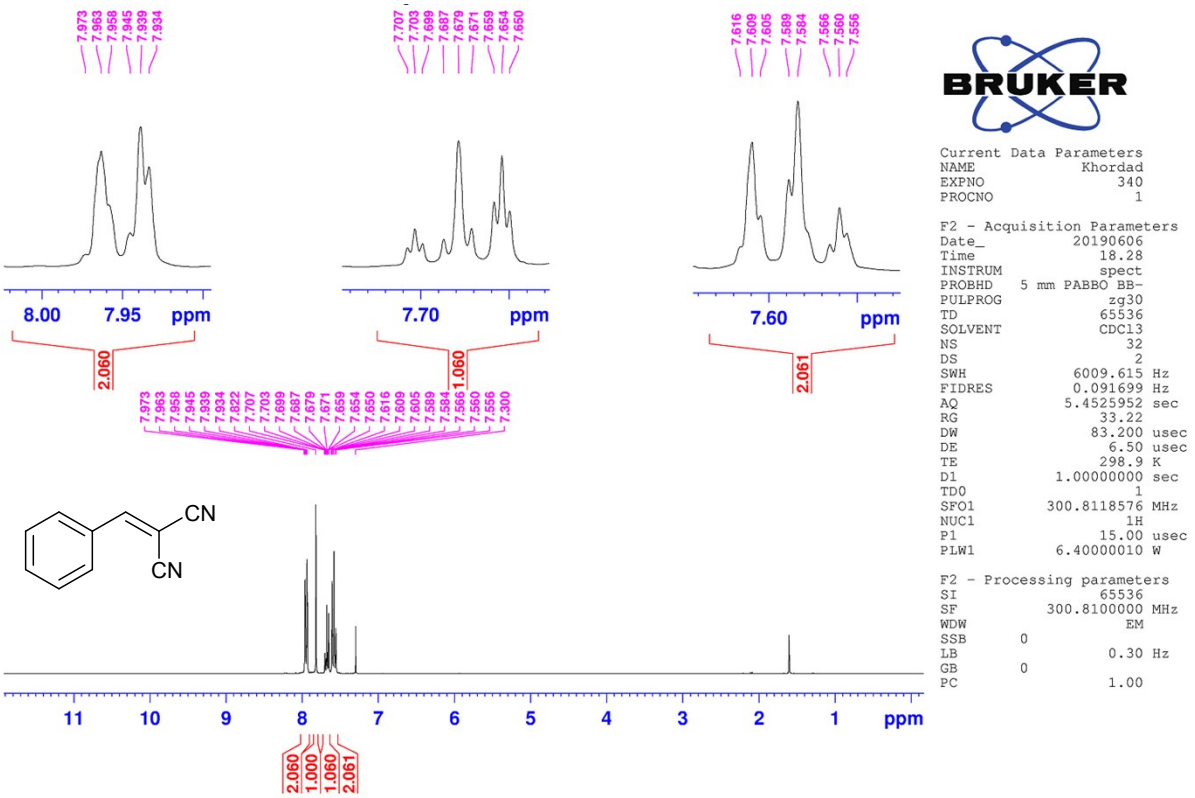


Figure S22: a) ^{1}H NMR and b) FT-IR spectra of 3-amino-1-phenyl-1*H*-benzo[f]chromene-2-carbonitrile.




```
Current Data Parameters
NAME                  Khordad
EXPNO                     340
PROCNO                      1

F2 - Acquisition Parameters
Date_                20190606
Time                    18.28
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        32
DS                         2
SWH                 6009.615 Hz
FIDRES              0.091699 Hz
AQ                  5.4525952 sec
RG                      33.22
DW                     83.200 usec
DE                      6.50 usec
TE                     298.9 K
D1                1.00000000 sec
TD0                        1
SFO1             300.8118576 MHz
NUC1                      1H
P1                     15.00 usec
PLW1               6.40000010 W

F2 - Processing parameters
SI                     65536
SF               300.8100000 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

Figure S23: ^{1}H NMR spectrum of 2-benzylidenemalononitrile.

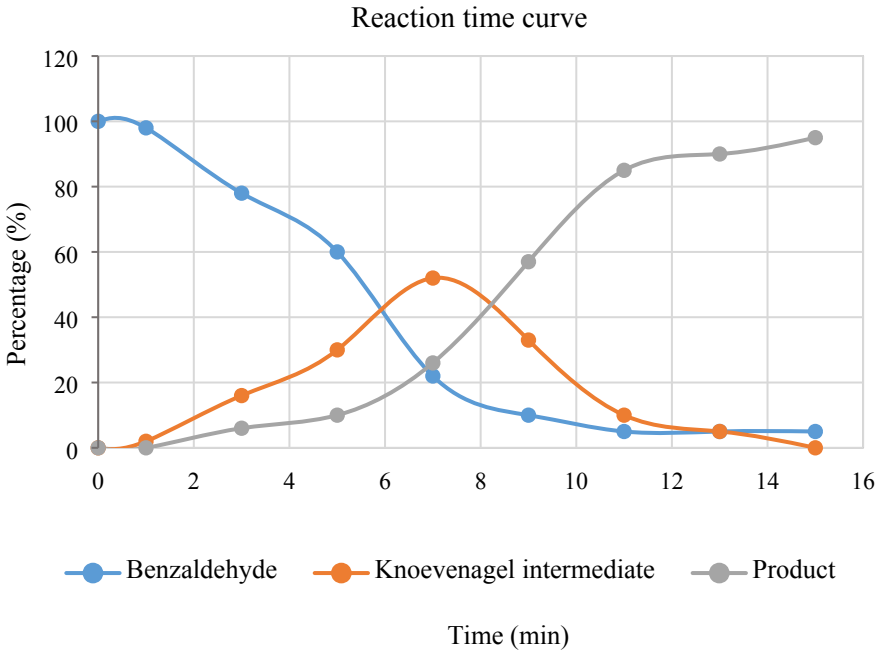


Figure S24. The reaction time curve for the one pot three-component reaction of benzaldehyde, malononitrile and dimedone.

Green chemistry metrics analysis

The following formulae were used for calculating atom economy (AE), atom efficiency (AE_f), carbon efficiency (CE), reaction mass efficiency (RME), optimum efficiency (OE), process mass intensity (PMI), E factor, solvent and water intensity (SI and WI).[1,2]

$$AE = \frac{Molecular\ weight\ of\ the\ product}{Total\ molecular\ weight\ of\ reactants} \cdot 100$$

$$AE_f = AE \cdot Yield(\%)$$

$$CE = \frac{Amount\ of\ carbon\ in\ the\ product}{Total\ carbon\ present\ in\ reactants} \cdot 100$$

$$RME = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} \cdot 100$$

$$OE = \frac{RME}{AE} \cdot 100$$

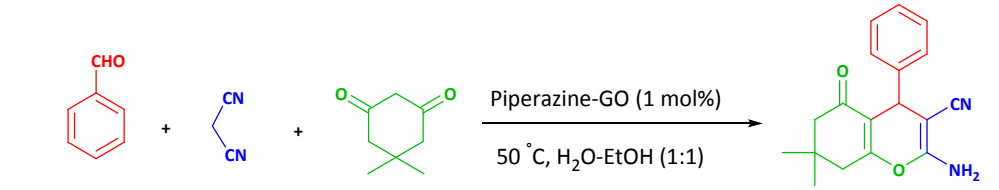
$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process}{Mass\ of\ product}$$

$$E\ factor = PMI - 1$$

$$SI = \frac{Total\ mass\ of\ solvents\ excluding\ water\ in\ the\ whole\ process}{Mass\ of\ product}$$

$$WI = \frac{Total\ mass\ of\ water\ used\ in\ the\ whole\ process}{Mass\ of\ product}$$

Synthesis of 2-amino-4-(phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile catalyzed by piperazine-GO (Table 2, entry 1)



M.W. = 106.12 M.W. = 66.06 M.W.= 140.18 M.W. = 294.35

95%

Experimental procedure: Benzaldehyde (1 mmol), dimedone (0.14 g, 1 mmol) and malononitrile (0.066 g, 1 mmol) were added to a mixture of piperazine-GO (0.004 g) in EtOH:H_2O (1:1, 1 mL). The reaction mixture was heated at 50 °C and stirred until TLC monitoring indicated no further progress in the reaction. Then, the reaction mixture was cooled to room temperature. EtOH (5 mL) was added to the reaction mixture and the catalyst was separated by centrifugation, washed with EtOH (5 mL), dried and re-used for a consecutive run under the same reaction conditions. The solvent of the combined organic layer was evaporated under reduced pressure to obtain a residue, which was recrystallized in EtOH to produce the pure product.

Materials used for metrics calculations: Benzaldehyde (0.106 g, 1 mmol), dimedone (0.14 g, 1 mmol) and malononitrile (0.066 g, 1 mmol), EtOH (15.5 mL, 12.23 g), H_2O (0.5 mL, 0.5 g), product (0.279 g, 0.95 mmol).

$$AE = \frac{294.35}{106.12 + 140.18 + 66.06} \cdot 100 = 94.23$$

$$AE_f = 94.23 \times 95(\%) = 89.52$$

$$CE = \frac{18 \times 0.00095}{7 \times 0.001 + 8 \times 0.001 + 3 \times 0.001} \cdot 100 = 95$$

$$RME = \frac{0.279}{0.106 + 0.140 + 0.066} \cdot 100 = 89.42$$

$$OE = \frac{89.42}{94.23} \cdot 100 = 94.89$$

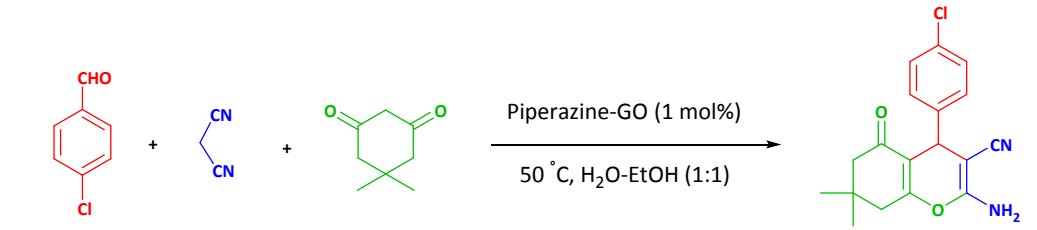
$$PMI = \frac{0.106 + 0.140 + 0.066 + 12.23 + 0.5}{0.279} = 46.74$$

$$E\,factor = 46.74 - 1 = 45.74$$

$$SI = \frac{15.5 \times 0.7893}{0.279} = 43.85$$

$$WI = \frac{0.5}{0.279} = 1.8$$

Synthesis of 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile catalyzed by piperazine-GO (Table 2, entry 3)



M.W. = 140.57 M.W. = 66.06 M.W. = 140.18 M.W. =328.80

98%

Materials used for metrics calculations: 4-Chlorobenzaldehyde (0.14 g, 1 mmol), dimedone (0.14 g, 1 mmol) and malononitrile (0.066 g, 1 mmol), EtOH (15.5 mL, 12.23 g), H_2O (0.5 mL, 0.5 g), product (0.322 g, 0.98 mmol).

$$AE = \frac{328.80}{140.57 + 140.18 + 66.06} \cdot 100 = 94.80$$

$$AE_f = 94.80 \times 98(\%) = 92.90$$

$$CE = \frac{18 \times 0.00098}{7 \times 0.001 + 8 \times 0.001 + 3 \times 0.001} \cdot 100 = 98$$

$$RME = \frac{0.322}{0.140 + 0.140 + 0.066} \cdot 100 = 93.06$$

$$OE = \frac{93.06}{94.80} \cdot 100 = 98.16$$

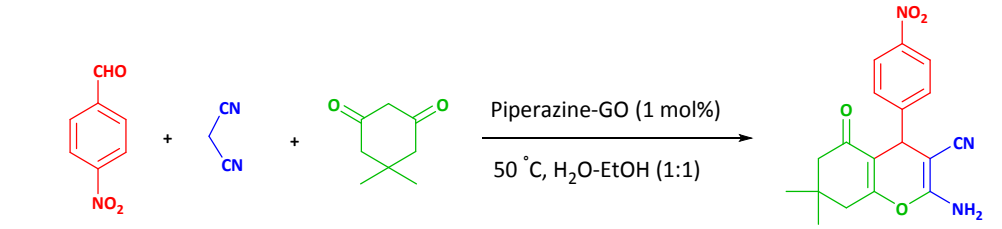
$$PMI = \frac{0.140 + 0.140 + 0.066 + 12.23 + 0.5}{0.322} = 40.60$$

$$E\,factor = 40.60 - 1 = 39.60$$

$$SI = \frac{15.5 \times 0.7893}{0.322} = 38$$

$$WI = \frac{0.5}{0.322} = 1.55$$

Synthesis of 2-amino-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile catalyzed by piperazine-GO (Table 2, entry 8)



M.W. = 151.12 M.W.= 66.06 M.W. = 140.18 M.W. = 339.35

90%

Materials used for metrics calculations: 4-Nitrobenzaldehyde (0.15 g, 1 mmol), dimedone (0.14 g, 1 mmol) and malononitrile (0.066 g, 1 mmol), EtOH (15.5 mL, 12.23 g), H_2O (0.5 mL, 0.5 g), product (0.305 g, 0.90 mmol).

$$AE = \frac{339.35}{151.12 + 140.18 + 66.06} \cdot 100 = 95$$

$$AE_f = 95 \times 90(\%) = 85.50$$

$$CE = \frac{18 \times 0.0009}{7 \times 0.001 + 8 \times 0.001 + 3 \times 0.001} \cdot 100 = 90$$

$$RME = \frac{0.305}{0.151 + 0.140 + 0.066} \cdot 100 = 85.43$$

$$OE = \frac{85.43}{95} \cdot 100 = 89.92$$

$$PMI = \frac{0.151 + 0.140 + 0.066 + 12.23 + 0.5}{0.305} = 42.90$$

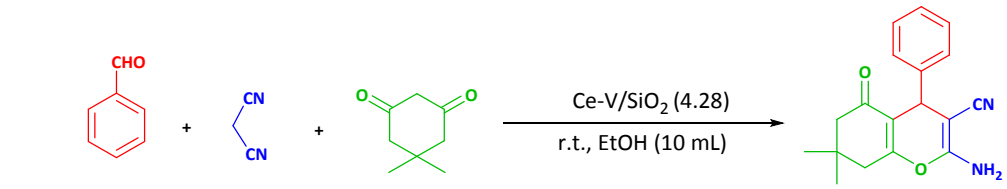
$$E\,factor = 42.90 - 1 = 41.90$$

$$SI = \frac{15.5 \times 0.7893}{0.305} = 40.11$$

$$WI = \frac{0.5}{0.305} = 1.64$$

Synthesis of 2-amino-4-(phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile catalyzed by Ce-V/SiO_2 (Table 3, entry 8)[3]

Materials used for metrics calculations: Benzaldehyde (0.106 g, 1 mmol), dimedone (0.140 g, 1 mmol) and malononitrile (0.072 g, 1.1 mmol), EtOH (10 mL, 7.89 g), acetone (30 mL, 23.53 g), product (0.279 g, 0.95 mmol).



M.W. = 106.12 M.W. = 72.66 M.W.= 140.18 M.W. = 294.35

95%

$$AE = \frac{294.35}{106.12 + 140.18 + 72.66} \cdot 100 = 92.28$$

$$AE_f = 92.28 \times 95(\%) = 87.67$$

$$CE = \frac{18 \times 0.00095}{7 \times 0.001 + 8 \times 0.001 + 3 \times 0.0011} \cdot 100 = 93.44$$

$$RME = \frac{0.279}{0.106 + 0.140 + 0.072} \cdot 100 = 87.73$$

$$OE = \frac{87.73}{92.28} \cdot 100 = 95.06$$

$$PMI = \frac{0.106 + 0.140 + 0.072 + (7.89) + 23.53}{0.279} = 113.75$$

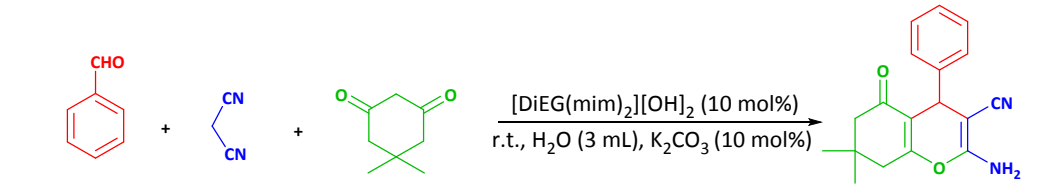
$$E\,factor = 113.75 - 1 = 112.75$$

$$SI = \frac{10 \times 0.7893 + 30 \times 0.7845}{0.279} = 112.62$$

$$WI = \frac{0}{0.279} = 0$$

Synthesis of 2-amino-4-(phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile catalyzed by $[DiEG(mim)_2][OH]_2$ (Table 3, entry 17)[4]

Materials used for metrics calculations: Benzaldehyde (0.106 g, 1 mmol), dimedone (0.140 g, 1 mmol) and malononitrile (0.066 g, 1 mmol), K_2CO_3 (0.013 g, 10 mol%), H_2O (3 mL, 3 g), EtOH (20 mL, 15.78 g), product (0.270 g, 0.92 mmol).



M.W. = 106.12 M.W. = 66.06 M.W.= 140.18 M.W. = 294.35

92%

$$AE = \frac{294.35}{106.12 + 140.18 + 66.06} \cdot 100 = 94.23$$

$$AE_f = 94.23 \times 92(\%) = 86.69$$

$$CE = \frac{18 \times 0.00092}{7 \times 0.001 + 8 \times 0.001 + 3 \times 0.001} \cdot 100 = 92$$

$$RME = \frac{0.270}{0.106 + 0.140 + 0.066} \cdot 100 = 86.53$$

$$OE = \frac{86.53}{94.23} \cdot 100 = 91.82$$

$$PMI = \frac{0.106 + 0.140 + 0.066 + 0.013\ g + 3 + \ 15.78}{0.270} = 70.75$$

$$E\ factor = 70.75 - 1 = 69.75$$

$$SI = \frac{20 \times 0.7893}{0.270} = 58.44$$

$$WI = \frac{3}{0.270} = 11.11$$

References:

1. F. Roschangar, R. A. Sheldon, C. H. Senanayake, *Green Chem.*, 2015, **17**, 752-768.
2. D. J. Constable, A. D. Curzons, V. L. Cunningham, *Green Chem.*, 2002, **4**, 521-527.
3. S. N. Maddila, S. Maddila, W. E. van Zyl and S. B. Jonnalagadda, *Chem. Open*, 2016, **5**, 38-42.
4. K. Niknam, M. Khataminejad and F. Zeyaei, *Tetrahedron Lett.,* 2016, **57**, 361-365.